Development of New Inorganic Luminescent Materials by Organic-Metal Complex Route

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Materials Science & Engineering

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The development of novel inorganic luminescent materials has provided important improvements in lighting, display, and other technologically-important optical devices. The optical characteristics of inorganic luminescent materials (phosphors) depend on their physicochemical characteristics, including the atomic structure, homogeneity in composition, microstructure, defects, and interfaces which are all controlled by thermodynamics and kinetics of synthesis from various raw materials. A large variety of technologically-important phosphors have been produced using conventional high-temperature solid-state methods. For the synthesis of functional ceramic materials with ionic dopants in a host lattice, (such as phosphors), synthesis using organic-metal complex methods and other wet chemistry routes have been found to be excellent techniques. These methods have inherent advantages such as good control of stoichiometry by molecular level of mixing, product homogeneity, simpler synthesis procedures, and use of relatively-low calcination temperatures. Supporting evidence for this claim is accomplished by a comparison of photoluminescence characteristics of a commercially available green phosphor, \( \text{Zn}_2 \text{SiO}_4: \text{Mn} \), with the same material system synthesized by organic-metal synthesis route.
In this study, new inorganic luminescent materials were produced using rare-earth elements (Eu$^{3+}$, Ce$^{3+}$, Tb$^{3+}$) and transition metals (Cu$^+$, Pb$^{2+}$) as dopants within the crystalline host lattices; SrZnO$_2$, Ba$_2$YAlO$_5$, M$_3$Al$_2$O$_6$ (M=Ca,Sr,Ba). These novel phosphors were prepared using the organic-metal complex route. Polyvinyl alcohol, sucrose, and adipic acid were used as the organic component to prepare the ceramic precursors. Materials characterization of the synthesized precursor powders and calcined phosphor samples was performed using X-Ray Diffraction, Scanning Electron Microscopy, Photon-Correlation spectroscopy, and Fourier Transform Infrared Spectroscopy techniques. In addition to the Fluorescence Spectrometer, and Diffuse Reflectance Spectroscopy, the Time Resolved Spectroscopy technique was also used to study the photoluminescence characteristics of the synthesized phosphors. Using these characterization techniques, and through careful comparisons with related studies in the literature, the mechanisms of luminescence for each of the new phosphor materials synthesized here was discussed in a detail.
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Introduction

Inorganic luminescent materials are typically manufactured using conventional solid-state methods. These techniques generally require repeated mixing and grinding steps, and incorporate relatively-high calcination temperatures. At these higher temperatures, long diffusion distances for the reactant atoms and contaminants directly affect the photoluminescence properties of phosphors. Alternatively, chemical synthesis techniques can provide an efficient way to produce the same phosphor materials with improved luminescence. These methods produce phosphors with good homogeneity, have a high chemical purity of phases, produce relatively fine particle sizes with uniform size distributions, and use relatively-low calcination temperatures. More specific to this study, the modified sol-gel techniques used herein are relatively new and their application to the synthesis of phosphors has led to the formation of very efficient phosphors with practical benefits such as reduced process complexity, controllability at molecular level, and low cost.

The organic-metal complex route was used in this study to synthesize the commercial and novel phosphors as an alternative to the more conventional solid-state and wet chemical methods. It is not the scope of this dissertation to extensively investigate the differences between the conventional solid-state and the novel modified sol-gel techniques. The characteristic differences between
these two techniques and their effects on the advanced functional ceramics have been well-defined, since the invention of the Pechini process in 1967.

Section 1 of this dissertation, entitled “Inorganic Luminescent Materials”, acquaints the reader with the principles and the basic aspects of the optical spectroscopy of inorganic luminescent materials by introducing key terms and concepts. The static (crystal field) and dynamic (coordinate configuration model) effects on luminescent centers and how they affect the characteristic optical spectra are also discussed by explaining the energy processes in phosphors. From here, the scope is expanded from the characteristic luminescence properties of transition metal ions (3dⁿ) and trivalent rare-earth ions (4fⁿ5s²5p⁶), to the common techniques and equipment needed to measure the excitation/absorption processes in the phosphors by spectrofluorimeter and time resolved spectroscopy techniques. Additionally, important applications of inorganic phosphors and the outlook for each unique application are discussed.

Section 2 entitled “Synthesis of Inorganic Luminescent Materials” is dedicated to discussion of the advantages and disadvantages of common preparation techniques for phosphors. General characteristics of the conventional solid-state techniques are explained in this chapter. Also, the solid-state processing parameters and their affects on the synthesized compounds and the associated reaction mechanisms are explained. As an alternative route, the modified sol-gel technique and its inherent advantages in synthesis of phosphor materials are
Physicochemical characteristics of the aqueous organic-metal salt solutions are also discussed. Processing details for the metal-organic complex route in aqueous PVA, sucrose, and adipic acid solutions are presented, and the specific instrumentation used for materials and photoluminescence characterization of synthesized phosphors is given with the associated schematic diagrams.

Section 3 entitled “Synthesis of pure Zn$_2$SiO$_4$:Mn green phosphors by the simple PVA-metal complex route (Comparative Study)” presents details of the materials characterization and photoluminescence characteristics of synthesized phosphors and a commercial phosphor product used for comparison. After the experimental details, crystallinity, particle morphology, particle size & distribution, and infrared analysis results for the prepared phosphor powders are reported. The optimum manganese concentration for the Mn$^{2+}$-doped Zn$_2$SiO$_4$ phosphors is reported and the mechanism for the concentration quenching of luminescence in phosphors is explained. The effect of Mn and Mg co-doping on the photoluminescence characteristics, along with a mechanism for the improvement of the brightness of the characteristic green emission are explained using the corresponding energy band diagrams.

Section 4, entitled “Development of New Phosphors by Modified Sol-Gel Routes”, presents the details of the main focus of the work, concerning synthesis of several new phosphors synthesized using the metal-organic complex route.
Transition metals (Pb$^{2+}$, Cu$^{+}$) and rare-earth ions (Eu$^{3+}$, Ce$^{3+}$, Tb$^{3+}$) were introduced into newly-developed host-lattices, viz. SrZnO$_2$, Ba$_2$YAlO$_5$, and M$_3$Al$_2$O$_6$ (M = Ca, Sr, Ba). For each synthesized phosphor, experimental details with the material characterization results are reported. The mechanisms for the characteristic absorption and emission properties of phosphors were identified based on the photoluminescence and time-resolved spectroscopy analysis results. Optimum concentrations and the color coordinates for each phosphor are reported.

Section 5 entitled “Conclusions” presents the significance of this study in phosphor and functional ceramic material synthesis technology. The importance and the necessity of the Organic-Metal-Ion complex synthesis technique is summarized based on the material and photoluminescence characteristics of the commercial and novel phosphors.
SECTION 1

Inorganic Luminescent Materials

1. Background

1.1 Fundamentals of Luminescence

The term “luminescence” originates from the Latin word “lumen”, which means light and the literal translation from Latin is “weak glow”. It was introduced into the scientific literature by Eilhardt Wiedemann, a German physicist, in 1888 [1]. Luminescence, which includes both fluorescence and phosphorescence, in solids is the phenomenon in which the electronic state of a solid is excited by an external energy and the absorbed energy is given off as visible light. Light is comprised of photons, which are quantized waves exhibiting some of the properties of particles, i.e., wave-particle duality [2]. Particles such as electrons also have wave-like properties similar to those of photons. A particle is not entirely localized in space whereas the photon is localized in space, i.e., a point-source. In other words, an electron is attracted or repelled by an electromagnetic field as it moves through space whereas a photon (a localized point source) is only weakly affected [3]. Based on the processes that excite photon absorption and the appearance of secondary photons according to quantum
electrodynamics, luminescence differs from Rayleigh scattering, Raman scattering, and resonance emission by the fact that there are intermediate processes between the absorption and the emission of the light [4]. The intermediate processes, which are strongly influenced by the substance or crystalline matrix, affect the correlation between the optical properties of absorbed and emitted photons. Therefore, the luminescence is a non-equilibrium radiation that is above the thermal radiation background and takes place in the presence of intermediate processes of energy transformation between absorption and emission [4]. These host lattice intermediate processes directly affect the duration of luminescence and the possibility of quenching it.

Luminescence (as a science) is closely related to spectroscopy, which is the study of general laws of the absorption and emission of radiation by matter. Generally, the study of absorption and emission of light at thermodynamic equilibrium assumes that the luminescence is equal to zero and only thermal emission is observed. On the other hand, in luminescence, as a non-equilibrium radiation process, much consideration is given to the radiation that exceeds the thermal emission regarded as the background. The time-resolved radiation intensity, decay, the mechanisms of luminescence excitation, and the dependence of luminescence characteristics on the excitation methods are considered in great detail.

The investigation of luminescence through studies of excitation and emission processes is an inherent part of laser physics and nonlinear optics [5]. Major optical characteristics of the active medium of any laser are the power, the
spectrum, and the quantum yield of luminescence. The characteristic properties of luminescence cannot be explained by classical electrodynamics. Instead, the characteristics of luminescence in solids are explained by quantum mechanics, solid-state physics, and the quantum theory of radiation.

Many different types of energy can be absorbed by inorganic luminescent materials (Table 1.1). Photoluminescence (PL) is excited by electromagnetic radiation with short-wavelengths such as ultraviolet light [6,7]. Cathodoluminescence (CL) is typically excited by a beam of high energy electrons (cathode rays) [8,9]. Ionoluminescence (IL) is light emission (UV, Visible, or IR) generated by the impact of heavy particles on solid surfaces. The excited energy states of sputtered target substrate atoms, ions, and molecules and the backscattered projectiles will subsequently decay by emitting light in the visible and ultraviolet range [10]. The collisional excitation of molecules on the surface of the solid and radiative recombination of electron-hole pairs inside a solid may also contribute to ionoluminescence [11].

**Table 1.1** Luminescence types and the characteristic excitation mechanisms.

<table>
<thead>
<tr>
<th>Luminescence Name</th>
<th>Type of Energy Absorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photoluminescence</td>
<td>Light (UV and Visible)</td>
</tr>
<tr>
<td>Cathodoluminescence</td>
<td>Electron beam</td>
</tr>
<tr>
<td>Electroluminescence</td>
<td>Electric field (Voltage or Current)</td>
</tr>
<tr>
<td>Radioluminescence</td>
<td>X-Rays, α-, β-, γ- rays</td>
</tr>
<tr>
<td>Thermoluminescence</td>
<td>Heat</td>
</tr>
<tr>
<td>Mechanoluminescence</td>
<td>Mechanical energy</td>
</tr>
<tr>
<td>Ionoluminescence</td>
<td>Molecular collision</td>
</tr>
</tbody>
</table>
Electroluminescence (EL) is the direct, non-thermal generation of light resulting from the application of an electric field to a substrate [12,13]. The word “non-thermal” implies that incandescence is excluded. Thermoluminiscence (TL) in solids is the light emission mainly in the visible range during heating of a solid following an earlier absorption of energy from radiation [14]. The release of light from previously absorbed radiation energy makes thermoluminescence distinctly different from incandescence light emission from a substance that is heated to high temperatures. Once TL emission has been observed, the material will not show it again after simply cooling the specimen and reheating it, but has to be re-exposed to radiation to obtain TL again. Heat radiation is only a stimulant and not the exciting agent. Mechanoluminescence (ML) is a type of luminescence induced during any mechanical action on a solid. It can be excited by grinding, rubbing, cutting, cleaving, shaking, scratching, compressing, or crushing of solids [15,16]. ML can also be excited by thermal shocks caused by drastic cooling or heating of materials or by the shocks produced during exposure of samples to powerful laser pulses. Additionally, ML may appear during the deformation caused by phase separation of two dissimilar materials in contact. ML is also known as triboluminescence, piezoluminescence, deformation luminescence, and stress-activated luminescence.

Inorganic luminescent materials can be divided in two classes [3]: i) those that absorb light (pigmented) and ii) those that absorb the energy and emit light (phosphors and solid state lasers). In both cases, certain amounts of transition
and/or lanthanide ion(s) are incorporated to control the absorption and emission characteristics of that solid. In this chapter, the optical characteristics and the nature of the electronic transitions of inorganic luminescent solids (phosphors) will be described and discussed.

1.2 Terms Relating to Phosphors

In scientific literature, the word *phosphor* mainly refers to inorganic phosphors, usually in powder form and synthesized for the purpose of practical applications. In practice, single crystals, thin films, and organic molecules that exhibit luminescence are rarely called phosphors.

*Luminescence*, as defined above, is the general case in which a higher energy photon is absorbed and a lower energy photon is emitted, also known as the Stokes process.

*Fluorescence* involves a process where light emission from a substance occurs during the time it is exposed to exciting radiation. On the other hand, *phosphorescence* is defined as a phenomenon in which photon absorption occurs but the re-emission process is delayed, i.e., after-glow. This delay in light emission depends on the type of activator ion(s), or the presence of solid state defects in the host lattice such as vacancies which trap the energy for a reasonably longer time.

In general, the characteristic decay time of luminescence of phosphors is an exponential process. The decay time is the time for steady state luminescence intensity to decay to $1/e$ (0.3679) of its original value. The range of decay time
for fluorescence is commonly considered to be in the range of $10^{-9}$ sec. to $10^{-3}$ sec, whereas phosphorescence has a decay time range of $10^{-3}$ sec to 100 sec [3]. Note that there are some luminescent materials which glow for hours after being excited. Such a long after-glow is not due to phosphorescence, but to the presence of lattice defects (traps) introduced intentionally during the synthesis of phosphors. For example, CaS activated by Bi$^{3+}$ are sometimes called "daylight" phosphors because they can be excited by visible light and will glow for hours.

1.3 Energy Processes in Phosphors

1.3.1 Electronic Aspects of Phosphors

Phosphors are inorganic solid compounds which convert certain types of energy into electromagnetic radiation (mainly in the visible and ultraviolet range) over and above thermal radiation [18].

In a broader sense, phosphors are known as photon-converters. If a phosphor absorbs a photon of 4.5 eV (275 nm, which is ultraviolet light), then the phosphor might emit a photon of say 2.35 eV (528 nm, which is green light) through the intermediate processes. This energy conversion process, where emitted photons are less energetic than are absorbed, is also called the Stokes process.

In most cases, an inorganic phosphor consists of:

i) a "host matrix" (or inorganic compound) and

ii) the "activator" which is the added transition and/or lanthanide ion(s).
Figure 1.1.a depicts a crystalline host lattice with an ion functioning as an activation or luminescent center within the crystal or grain of the host matrix. The absorption of incoming photon energy may occur in the host or directly in the luminescent ionic impurity (activator center). When the exciting radiation is absorbed by the luminescent ionic impurity, it will be raised to an excited state from the ground state (Figure 1.1.b). The excited state returns to the ground state by emitting the light. For instance, Ce$^{3+}$ doped Y$_3$Al$_5$O$_{12}$ (YAG) is used as a conversion phosphor in white LED’s. The cerium ion, which is an activator, absorbs blue light at 460 nm and produces a yellow colored emission.

Not every doped crystalline host lattice acts as an ideally-efficient phosphor. Some fraction of the absorbed energy is lost to the vibrational states of the host lattice. In other words, non-radiative energy heats the host lattice. Therefore, in order to design efficient phosphors, the non-radiative component of the process has to be minimized. There may be several excited states possible for the luminescent center, but only the lowest excited state is involved in radiative photon emission [3]. The excitation spectrum and the emission spectrum are the optical characteristics to be measured for this crystalline host lattice-activator luminescent system. Also, the ratio of the radiative to non-radiative rates of return to the ground state determines the conversion efficiency of the luminescent material.

The absorption of energy by the host lattice or by another ion co-doped with luminescent ion makes the luminescence mechanism more complex. This
secondary impurity ion may absorb the exciting radiation and then transfer it to the activator.

*Figure 1.1* Schematic representation of a crystal or grain of a phosphor with luminescent impurity (a), and the corresponding energy level scheme of the luminescent ion (I). A: Absorption, E: Emission, H: Heat [18].

In this case the secondary ion is called a “sensitizer”. Figure 1.2.a and Figure 1.2.b shows the energy transfer from a sensitizer (S) to a luminescent ion (I). The lamp phosphor Ca$_5$(PO$_4$)$_3$F co-doped with Sb$^{3+}$ and Mn$^{2+}$ can be excited under ultraviolet radiation because of the Sb$^{3+}$ ion. The emission is partly blue due to the Sb$^{3+}$ and partly yellow because of the Mn$^{2+}$ ion. Although the Mn$^{2+}$ ion is not directly excited, it contributes to the emission spectrum because of the excitation energy transfer from the Sb$^{3+}$ ion to the Mn$^{2+}$ [18]. In this case, Sb$^{3+}$ ion functions as both activator and sensitizer; however, the Mn$^{2+}$ ion is exclusively an activator. Alternatively, the excitation energy absorbed by the host can be transferred to the luminescent ion (activator) so that the host lattice acts as a sensitizer. A typical example is the blue-emitting cathode-ray phosphor, ZnS:Ag$^{+}$, used in
television tubes. Ultraviolet radiation, electron beams, and X-rays are absorbed by the zinc sulfide host lattice which transfers the energy to the luminescent Ag$^+$ ions.

Figure 1.2 The absorption of energy by the Sensitizer (S), and the subsequent energy transfer to luminescent ion (I) in the host lattice (a), and schematic energy level scheme of the energy transfer from sensitizer ion to activator. The level $I_{\text{Excited},1}$ populated during the energy transfer and then decays non-radiatively to the lowest energy level of $I_{\text{Excited},2}$ [18].

In phosphors, the intermediate processes, which are the characteristic electronic transitions, dictate the conversion of the absorbed photon into the emitted light. The next section will give more detailed information about the types of photoluminescence in phosphors with their optical and electronic characteristics.

1.3.2 Absorption of Photon Energy in Phosphors

If an inorganic polycrystalline material is illuminated by light, including ultraviolet, visible, and infra-red radiation, the intensity of this beam will be attenuated after crossing the substrate, i.e., the intensity of the transmitted beam will be lower.
Absorption, reflection, and scattering are the processes that contribute to this attenuation as a result of the interaction of the incoming light with atoms and/or crystallographic defects present in the matter [3]. **Absorption** process will occur if the beam frequency is resonant with a ground-to-excited state transition of the atom in the substrate. A fraction of this intensity is generally emitted at lower frequencies. The other fraction of the absorbed intensity is lost by non-radiative processes, i.e., heat. The second process, **reflection**, occurs at the external and internal surfaces. The last process, **scattering**, will spread in several directions due to elastic (at the same frequency as the incident beam) or inelastic (at lower and higher frequencies than of the incident beam - Raman effect) processes [3].

The first step in luminescence is the absorption of energy by the phosphor and/or activator-- i.e., a small amount of intentionally added transition and/or rare-earth luminescent atoms distributed in crystalline host matrix. When it absorbs energy, the activator changes its electronic energy state from a ground state to an excited state. It is possible to have more than one excited state, depending on the original energy of the exciting photon. The exciting photon energy may be more than the minimum energy required for excitation and this excess energy will cause the upper excitation states to become populated. The host lattice will be excited by the relatively higher energy excitation such as fast electrons, X-rays, or $\gamma$-rays. On the other hand, the activator can also be directly activated only with lower energy photons such as ultraviolet and visible radiation. It is common practice to represent the characteristic energy states of a phosphor by using a configurational – coordinate diagram, which is a potential energy diagram.
containing only the ground state and the lowest excited state, as shown in Figure 1.3. The shape of the ground and the excited state are parabolic because the vibrational motion is assumed to be harmonic. In other words, the restoring force \( F \) is proportional to the displacement

\[
F = -k(r - r_{0G})
\]

which corresponds to a potential energy whose dependence on effective radius is parabolic in character:

\[
E = \frac{1}{2}k(r - r_{0G})^2.
\]

The quantum mechanical solution for this harmonic oscillator gives the energy levels of the oscillator

\[
E_v = (v + \frac{1}{2})\hbar \nu
\]

where \( \nu \) is the frequency of the oscillator (\( \nu = G_0, G_1, G_2, \ldots \)). A simple derivation can be found in reference [19].

All transitions between the ground and excited state parabolas are electronic transitions. The interaction between the electrons and the vibrations of the luminescent center is measured by the value of \( r_{0E} - r_{0G} \). In the configurational – coordinate diagram, after absorption of energy, optical transitions occur as vertical transitions because the transition from the ground state to the excited state is electronic; however, horizontal displacements are nuclear [5]. In a broader sense, the configuration coordinate model represents changes of the nuclear coordinates of all the lattice ions constituting the luminescence center. According to the Franck - Condon principle, a change in electronic state occurs almost instantaneously (\( \sim 10^{-18} \) seconds) as compared to other processes [5].
Compared to the vibrational move of the nuclei, electrons move $10^3$ times or even faster. Therefore, in configuration–coordinate model, it is considered that an electron occupies a stationary energy level corresponding to each position of the nuclei, and nuclei vibrate within the potential determined by the electron.

Figure 1.3 Configurational–coordinate model for the absorption of energy by a single activator center. $G_0$, $G_1$, $G_2$ are the vibrational states for the ground state, and $E_0$, $E_1$, $E_2$, $E_3$ are the vibrational states for the excited state. $r_{0G}$ and $r_{0E}$ are the equilibrium distance in the ground and excited state, respectively [3].

Thus, there are several ground state energies and the lowest is the lowest energy occupied state, i.e., $G_0$. If the vibrational energy of the lattice increases, then the other ground states will become occupied ($G_1$, $G_2$,…). Each of these horizontal lines represents a separate “Stark” state [3]. The luminescent center will become excited when the sufficient energy is absorbed. Wavefunctions of
excited states are generally considered to be more spread out than those of ground states, so that the energy minimum point of the excited state is assumed to be shifted toward the outside.

### 1.3.3 Intermediate Processes in Phosphors

The configurational – coordinate diagram shown in Figure 1.3 is a static one, whereas in reality there are numerous luminescent centers in various energy states which vibrate according to the associated effective values of “r”. This contributes to the density of states whose occupation centers around the original excitation energy transition, as shown in Figure 1.3, but its occupation density will be affected in the excited states due to the presence of vibrational waves (phonon) of the host lattice. This change, \( \Delta r = r_{0E} - r_{0G} \), is a consequence of host lattice vibrations which affect the relative positioning of the luminescent ion center [5]. The variation in effective radius \( (r_{\text{eff.rad.}}) \) arises from a random interaction of phonons with the excited luminescent center. The density of states is expected to have a Gaussian distribution because the interaction perturbation through the vibronic coupling (vibrational + electronic) is totally random process [5].

Absorption and emission processes are dominated by the Franck – Condon principle. The terminal state of the absorption transition is at a higher-energy point than the minimum in the excited state. The lifetime of the excited state is of the order of \( 10^{-8} \) s in the case of allowed transitions and is much longer than the lattice vibration period. Therefore, just after the absorption has completed,
relaxation toward the minimum energy point in the excited state takes place, accompanied by the emission of phonons (non-radiative), and the radiative emission will be produced from the minimum energy level. Therefore, the emission wavelength will always be shifted toward the longer wavelength side of the excitation wavelength. This is known as “Stoke's law”.

It is also important to mention that, in the excited state, the chemical bond is mostly weaker than in the ground state. This is shown in the configurational coordinate diagram as the shift in the parabolas relative to each other, Δr.

1.3.3.1 Time scales for Energy Dissipation Processes

The energy dissipation changes associated with the electronic transitions in the luminescent ion can be written as

\[ E_{\text{original}} = E_{\text{absorbed}} + E_{\text{reflected}}, \]

where

\[ E_{\text{absorbed}} = E_{\text{excitation}} + E_{\text{lattice absorption}}, \]

and

\[ E_{\text{lattice absorption}} = E_{\text{excitation relaxation}} + E_{\text{emission relaxation}} + E_{\text{excited-center quenching relaxation}}. \]

The total energy can then be written as

\[ E_{\text{original}} = E_{\text{reflected}} + E_{\text{excitation}} + E_{\text{lattice absorption}} + E_{\text{emission}}, \]

where the lattice absorption energy includes all the relaxation processes which result in loss of energy during the intermediate processes [5]. The time scales for the energy dissipation processes given above [3] are

Absorption time = 10^{-18} \text{ sec}
Excitation time = $10^{-11}$ sec
Lattice absorption time = $10^{-8}$ sec
Emission time = $10^{-9}$ to $10^{-2}$ sec

Both excitation and emission processes are the characteristic electronic transitions, whereas the lattice absorption is of a vibronic coupling (vibrational + electronic) nature. The time required for the absorption of the energy and then excitation to take place is almost one thousand times faster than the time required for one lattice vibration. Therefore, the luminescent center is not perturbed until it absorbs energy and transforms to an excited state. Afterwards, it can relax to equilibrium excited state from which emission can occur instantaneously, within one hundred vibrations or even longer.

1.3.3.2 Excitation and Emission Band Shapes

The luminescent center ion is mostly a substitutional defect in the host lattice, and its vibrational modes differ markedly from those of the host. If both host lattice and the luminescent center were cooled to 0 K, then the electronic transition between a single Stark state of the ground state to a single Stark state of the excited state would be observed [18]. This would yield a single sharp energy line, which is called the “Zero Phonon (ZP)” mode. However, the energy states of both in the transition from the ground state and in the excited state are broadened by the presence of vibronic coupling. This is shown in the configurational – coordinate model by the variations in the $r_{\text{eff,rad.}}$ at each Stark state (see Figure 1.3). In other words, the vibronic coupling at temperatures
above the absolute zero will contribute to the formation of a broad band both for excitation and for emission. It is important to note that, unlike transition metal activator centers, the 4f emitting states of the rare-earth luminescent ions are shielded from the perturbation effects of the lattice by the outer valence \((5s^2, 5p^6)\) electron shells, and, thus, they emit sharper line spectra, in contrast to other activators which are coupled to the phonon modes of the host lattice [20].

As stated earlier, the absorption of energy will result in a density of states because of the random process of phonon perturbation of the excited state, both before it relaxes and afterwards. This random (Gaussian) formation of energy states contributes to a broad band in excitation, and to a broad band in emission [5,18]. As the temperature increases, phonon branching also increases, and the emission band will be even further broadened. In other words, as the temperature increases, the phonon spectrum becomes broadened, and this will lead to broadening of absorption and emission bands. The characteristic absorption and emission bands associated with phosphors are shown in Figure 1.4. The ZP line is the same as the characteristic electronic transitions of the luminescent centers which is shown in the configurational – coordinate diagram (Figure 1.3). Therefore, the Stokes shift occurs because of the change in \(r_{\text{eff.rad.}}\) radius with the contribution of vibronic coupling (phonon energy perturbations) which cause a broad band of emission and excitation.

In addition to the direct effect of the vibronic coupling, the presence of many activator sites in the host lattice, each of which, at any given moment, has a slightly different energy from its relaxed excited state, and this will also contribute
to the formation of a broad emission band [3]. Therefore, there is a Gaussian array of absorbers and emitters. The energy differences among the absorbers and the emitters originated from [3];

i) Vibronic coupling of the electronic excited state(s) of the luminescent center

ii) Phonon addition and subtraction in order to occupy the adjacent Stark states, especially in the excited state

iii) Characteristic relaxation processes.

The effect of the vibronic coupling of the excited states is more pronounced compared to that of the ground states of the luminescent center. As mentioned above, only certain types of activators can be used as an impurity in a crystalline host lattice to prepare a luminescent material. These involve cations (transition metal ions or rare-earth ions), which have a ground state and the vibronic coupling is minimized or zero because of the closed electron shells. In other words, the electrons spins and angular momentae are all coupled and this prevents the phonon perturbation.

In summary, the electronic transition in the luminescent center involves the ZP line, which is broadened above absolute zero temperature levels by quantized phonon interactions to form a band of permissible excitation and emission energies. As mentioned above, the electronic transitions of excitation and emission are dynamic processes and are perturbed by the vibronic coupling of the quantized phonon spectrum present in the host lattice. Therefore, the optical
properties of the host lattice are just as important as that of the luminescent ion center.

**Figure 1.4** Schematic representations of Excitation and Emission energy bands associated with phosphors.

### 1.3.3.3 The Influence of the Host Lattice

It is experimentally proven that a given activator doped into the different host lattices will give different absorption and emission characteristics because of the change in the crystallographic surroundings of the luminescent center [5,17]. It is critical to understand the effect of the host lattice on the luminescence. If we can understand how the luminescent properties of a luminescent center depend on
Covalency is one of the main factors responsible for the different spectral properties of a given luminescent ion in different host lattices [21,22]. By increasing the covalency, the interaction between electrons will be reduced. As a result, electronic transitions between energy levels will be determined by electron interaction shift to lower energy for increasing covalency. This is also known as the "nephelauxetic effect" [21]. Higher covalency means that the electronegativity difference between the constituting ions is lower, so that charge-transfer (CT) transitions between these ions become relatively lower energy [21].

Another factor responsible for the change of the luminescent properties of a given activator ion’s dependence on the host lattice is the “crystal field”. This is basically the electric field at the site of the activator ion due to the crystallographic surroundings [3]. The spectral position of certain optical transitions is determined by the strength of the crystal field. The crystal field is also responsible for the splitting of certain optical transitions such as the transition metal ions. In other words, different host lattices would provide different crystal fields and different splittings. In this way, the luminescent center can serve as a probe of the crystallographic surroundings, and the observed splittings provide information about the symmetry of the site [3].

It is important to note that for phosphors in powder form, the external and internal surface areas may be large, and the luminescent ions near the surface
experience a covalency (and hence a crystal field) that differs from the bulk. These luminescent ions may have their characteristic optical transitions at slightly different energies than those in the bulk. This will lead to “inhomogeneous broadening” in the spectra [3,5]. Additionally, point defects in the crystal structure can also contribute to this broadening. For example, in the bright-red colored phosphor Eu\(^{3+}\) doped Y\(_2\)O\(_3\), the host lattice yttria provides two different crystallographic sites with different symmetry for the luminescent ion, Eu\(^{3+}\). The Eu\(^{3+}\) ions populate both crystallographic sites with different spectral properties. On the other hand, glasses, as a host lattice, have a significant inhomogeneous broadening because of the absence of translational symmetry, and luminescent centers differ from site to site. Therefore, the spectral bands in glasses are generally broader than in crystalline solids with symmetrical structures.

1.3.3.4 The Energy Level Diagrams of Luminescent Ions

The main effect of the luminescent centers in crystals is to introduce new energy levels within the energy gap of the crystal, so that the transitions among these levels produce new optical bands that are not present in the perfect crystal or in the crystalline host lattice. Because of these characteristic absorption and emission bands, optical centers in crystals are relevant for a variety of applications such as phosphors for plasma displays, fluorescent lamps, cathode ray tubes, solid state lasers, etc. The majority of industrial and technological applications are based on the incorporation of impurity ions in crystalline host lattices. In principle, all of the elements of the periodic table can be used to
incorporate impurity ions in crystalline host lattices. However, in practice, only a limited number of elements have been used for optically-active centers in inorganic crystalline compounds. In other words, only certain elements can be incorporated in ionic form and give rise to energy levels (within the valence and conduction bands of the host lattice) separated by optical energies. Transition and rare-earth (lanthanides) elements are the most common active centers which have been doped into the crystalline host lattices as an impurity. The transition and lanthanide groups yield quite different characteristics due to their particular electronic configurations. Transition metal ions have optically-active unfilled outer 3d shells whereas rare-earth ions have unfilled optically-active 4f shells screened by outer filled shells. Both types of ions are paramagnetic because of their unfilled shells [5].

In addition to the intentional doping of impurity ions, optically-active centers can also be created by structural defects. These optically active centers are called "color centers" and they produce optical bands in the otherwise colorless perfect crystal. This phenomenon has been used to develop solid state lasers [18]. It is important to note that these optically-active centers can be formed unintentionally during crystal growth and unexpected optical bands may be observed.

In the following sub-section, the absorption characteristics of both rare-earth ions and transition metal ions in crystalline inorganic host lattices will be given in detail.

**Rare-Earth Ions:** The rare earth ions (lanthanides) have been commonly used as activator centers in phosphors, lasers, and amplifiers [18]. Lanthanide
ions are formed by ionization of a number of atoms located in periodic table after lanthanum: from Cerium with an atomic number of 58 to ytterbium with an atomic number of 70. Cerium has an outer electronic configuration of 5s² 5p⁶ 5d¹ 4f¹ 6s², and Ytterbium has an outer electronic configuration of 5s² 5p⁶ 4f¹⁴ 6s². Rare earth elements are usually used to dope the inorganic crystalline host lattices as divalent or trivalent cations. Rare earth ions with different valences show very different optical characteristics. In trivalent rare-earth ions 5d, 6s, and some 4f electrons are removed and, hence the transitions between electronic energy sub-levels of the 4fⁿ configuration gives rise to the characteristic absorption and emission bands. On the other hand, divalent rare-earth ions contain one more f electron such as the Eu²⁺ ion has the same electronic configuration as the Gd³⁺ ion, which is the next element in the periodic table, and they tend to show f → d optical transitions. These differences in inter-configurational transitions cause very different luminescent properties between divalent and trivalent ions.

**Trivalent Rare-Earth Ions:** Trivalent rare-earth ions are characterized by an incompletely filled 4f shell with an outer electronic configuration 5s² 5p⁶ 4fⁿ, where n varies from 1 for Ce³⁺ to 13 for Yb³⁺. These 4fⁿ electrons are the valence electrons which are responsible for the electronic transitions and the characteristic optical properties.

Table 1.2 shows the number of 4f electrons for each trivalent rare-earth ion of the lanthanide series. The 4f orbital lies inside the ion and the valence electrons are shielded from the surroundings by the 5s and 5p outer electrons of the 5s² and 5p⁶ less energetic configurations. Therefore, the valence electrons of trivalent
rare earth ions are weakly affected by ligand ions of the host lattice because of this shielding effect.

When the trivalent rare-earth ions are incorporated in crystals, their \( ^{2S+1}L_J \) states are slightly perturbed. The crystal field causes a slight shift in the energy of these states and leads to additional level splitting. However, the amount of this shift and the splitting energy are much smaller than the spin-orbit splitting. Therefore, the luminescent characteristics of the trivalent rare-earth ions are expected to be very similar to those for free ions. Furthermore, this suggests that the main optical features (including absorption, emission, and decay time) will be very similar from one crystalline host lattice to another. It is very common practice to

**Table 1.2** The number of 4f valence electrons (n) in trivalent rare-earth ions.

<table>
<thead>
<tr>
<th>Rare-earth Ion</th>
<th>4f valence electrons “n”</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce(^{3+})</td>
<td>1</td>
</tr>
<tr>
<td>Pr(^{3+})</td>
<td>2</td>
</tr>
<tr>
<td>Nd(^{3+})</td>
<td>3</td>
</tr>
<tr>
<td>Pm(^{3+})</td>
<td>4</td>
</tr>
<tr>
<td>Sm(^{3+})</td>
<td>5</td>
</tr>
<tr>
<td>Eu(^{3+})</td>
<td>6</td>
</tr>
<tr>
<td>Gd(^{3+})</td>
<td>7</td>
</tr>
<tr>
<td>Tb(^{3+})</td>
<td>8</td>
</tr>
<tr>
<td>Dy(^{3+})</td>
<td>9</td>
</tr>
<tr>
<td>Ho(^{3+})</td>
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</tr>
<tr>
<td>Er(^{3+})</td>
<td>11</td>
</tr>
<tr>
<td>Tm(^{3+})</td>
<td>12</td>
</tr>
<tr>
<td>Yb(^{3+})</td>
<td>13</td>
</tr>
</tbody>
</table>
interpret the absorption and emission spectra of trivalent rare-earth ions in different crystalline host lattices based on the systematic spectral measurements made in a particular host lattice, LaCl$_3$. These characteristic spectra of trivalent lanthanide ions were documented by Dieke and co-workers [23] with the well-known energy level diagram, which is called Dieke diagram, shown in Figure 1.5. The Dieke diagram shows the energy levels originating from the 4f$^n$ configuration as a function of “n” for the trivalent rare-earth ions in LaCl$_3$. The width of each state (shown as bars) indicates the magnitude of the crystal field splitting, whereas the center of gravity of each multiplet gives the approximate location of its corresponding free ion $^{2S+1}L_J$ energy level. The magnitude of the crystal field splitting in rare-earth ions is very small compared to that of the transition metal ions. It is expected that the energy splitting and center of gravity of the $^{2S+1}L_J$ energy levels for a rare-earth ion can change slightly when it is incorporated into other crystalline host lattices other than LaCl$_3$, but the general characteristics of its energy level diagram remain the same.

The absorption and emission spectra of trivalent rare-earth ions consist of sharp lines because the inter-configurational 4f$^n$ transitions have $\Delta r = 0$ (see Figure 1.3). Optical absorption transitions in trivalent rare-earth ions are strongly forbidden by the parity selection rule. Vibronic coupling has only a very weak influence on the rare-earth ions incorporated in a crystalline host lattice [3,18,23]. The Dieke diagram provides information regarding how to predict or make a proper assignment of the light emission spectra corresponding to trivalent rare-earth ions in crystalline inorganic host lattices. As can be seen in the Dieke
diagram (Figure 1.5), some energy states are marked with a semicircle below them, which correspond to light-emitting levels, i.e., energy levels from which a direct transition produces luminescence. On the other hand, energy levels with no semicircle below them do not lead to direct emission of light (at least, has not been observed). These energy levels can give rise to luminescence, but from lower energy states populated by non-radiative relaxations.

In general, the Dieke diagram can be used to roughly predict the average wavelength for each \( ^2S+1L_J \rightarrow ^2S'+1L'_{J'} \) transition of a given trivalent rare-earth ion in any given inorganic crystalline host lattice. As an example, Figure 1.6 shows the emission spectrum of the \( \text{Eu}^{3+} \) ion in the \( \text{LiNbO}_3 \). The luminescent trivalent europium ions have the characteristic red light emission with four groups of lines. These corresponding lines are the different transitions from the singly degenerate excited state \( ^5D_0 \) to the different sub-energy levels within four terminal states of \( ^7F_J \), from \( J = 1 \) to \( 4 \). The \( ^5D_0 \rightarrow ^7F_0 \) emission is forbidden at the electric dipole order and will not be observed. On the other hand, for example, \( ^5D_0 \rightarrow ^7F_2 \) emission transitions shows two peaks, because the terminal level \( ^7F_1 \) splits into two different sub-levels, which are the singly-degenerate and the doubly-degenerate levels. The remaining characteristic emission peaks related to the \( ^5D_0 \rightarrow ^7F_J \) transitions can be analyzed the same way by describing the splitting components of the other \( ^7F_J \) terminal energy levels.
Figure 1.5 Energy levels of the $4f^n$ configurations of the trivalent rare-earth ions in Lanthanum Chloride [23].
Figure 1.6 The characteristic emission spectrum of Eu$^{3+}$ ion in LiNbO$_3$. The part of the Dieke diagram, which corresponds to the emission spectra of Eu$^{3+}$ ion, is also included [5,24].

As stated above, the $f \rightarrow f$ transitions are parity-forbidden; however, most of these transitions become partially allowed at the electric dipole order as a result of mixing with other orbitals that have different parity due to the presence of non-inversion symmetry crystal field [17,18]. Therefore, it is possible to obtain a variety of trivalent rare-earth ion transitions with “forced electric dipole” transitions based on the crystallographic site symmetry, i.e., the crystallography of the host lattice.

**Divalent Rare Earth Ions and Charge-Transfer Transitions:**

Divalent rare-earth ions, like trivalent rare-earths, also have an outer electronic
configuration of $4f^n$, but the “n” includes one more electron than for the equivalent trivalent rare-earth. They have $4f^n \rightarrow 4f^{(n-1)}5d$ transitions, which are parity-allowed transitions, with intense and broad absorption and emission bands, i.e., $\Delta r \neq 0$ (see Figure 1.3). Similarly, the charge-transfer reactions, $4f^n \rightarrow 4f^{n+1}L-1$ (where L = Ligand), is also allowed with $\Delta r \neq 0$, and appear in the spectra as broad absorption. Charge transfer reactions are common among the rare-earth ions, which have a tendency to be reduced. On the other hand, $4f \rightarrow 5d$ transitions for the rare-earth ions like to be oxidized [17]. The tetravalent rare-earth ions such as Tb$^{4+}$, Ce$^{4+}$, Pr$^{4+}$ show strong charge-transfer absorption bands [25]. For instance, orange light emission from Y$_2$O$_3$:Tb$^{4+}$ phosphors occurs because of the charge-transfer absorption band in the visible spectrum. On the other hand, divalent rare-earth ions such as Eu$^{2+}$, Yb$^{2+}$, Sm$^{2+}$ show the characteristic electronic transition of $4f^n \rightarrow 4f^{(n-1)}5d$ with the emissions in the visible range for Sm$^{2+}$ and in the long wavelength ultraviolet range for Eu$^{2+}$ and Yb$^{2+}$.

The trivalent ions that have a tendency to become divalent, such as Eu$^{3+}$, Sm$^{3+}$, Yb$^{3+}$, exhibit charge-transfer absorption bands in the ultraviolet range. On the other hand, the trivalent ions that have a tendency to become tetravalent such as Tb$^{3+}$, Ce$^{3+}$, Pr$^{3+}$ show the $4f^n \rightarrow 4f^{(n-1)}5d$ absorption bands in the ultraviolet region [26].

**Transition Metal Ions:** Transition metal ions have been used as active dopants in commercial phosphors, scintillators, and in tunable solid state lasers. Transition metal ions cover the range of elements beyond the calcium atom with
electronic configuration of (Ar)4s², up to zinc with electronic configuration of (Ar)3d¹⁰4s². They tend to lose the outer 4s electrons, and alternatively lose or gain 3d electrons. Basically, they have an electronic configuration 1s²2s²2p⁶3s²3p⁶3dⁿ, where n (1 < n < 10) indicates the number of 3d electrons. These outer valence electrons are responsible for the characteristic optical transitions. Table 1.3 shows the most common transition metal ions used in inorganic luminescent materials with their corresponding 3dⁿ valence electrons.

<table>
<thead>
<tr>
<th>Transition metal ions</th>
<th>3dⁿ (valence electrons “n”)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti³⁺, V⁴⁺</td>
<td>1</td>
</tr>
<tr>
<td>V³⁺, Cr⁴⁺, Mn⁵⁺</td>
<td>2</td>
</tr>
<tr>
<td>V²⁺, Cr³⁺, Mn⁴⁺</td>
<td>3</td>
</tr>
<tr>
<td>Cr²⁺, Mn³⁺</td>
<td>4</td>
</tr>
<tr>
<td>Mn²⁺, Fe³⁺</td>
<td>5</td>
</tr>
<tr>
<td>Fe²⁺, Co³⁺</td>
<td>6</td>
</tr>
<tr>
<td>Fe⁺, Co²⁺, Ni³⁺</td>
<td>7</td>
</tr>
<tr>
<td>Co⁺, Ni²⁺</td>
<td>8</td>
</tr>
<tr>
<td>Ni⁺, Cu²⁺</td>
<td>9</td>
</tr>
</tbody>
</table>

Table 1.3 The transition metal ions commonly used in phosphors and their corresponding 3d valence electrons.

In transition metal ions, the 3d orbitals have relatively large radii and are not shielded by the outer shells; thereby, strong luminescent ion – lattice coupling occurs. Based on this coupling, the characteristic luminescence spectra of transition metal ions consist of both broad (Δr ≠ 0) and sharp (Δr ≈ 0) bands, in
contrast to the spectra of trivalent rare-earth ions, which only have sharp bands ($\Delta r \approx 0$) and broad charge transfer bands.

**3d\(^1\) Transition Metal Ions:** It was shown in the configurational – coordinate diagram (Figure 1.3) that the energy level of the free ion can be found at the utmost left-hand side, where $\Delta r \approx 0$. However, in a crystalline solid, many of these energy levels split into two or more levels for $\Delta r \neq 0$, and the ground state, which is the lowest energy level, coincides with the x-axis (r-effective radius). The levels for the free ion states of the transition metal ions are governed by the electron-electron interaction and so are marked as \(^{2S+1}L\), which is usually called L-S terms, where “S” is the total spin quantum number, and “L” is the total orbital angular momentum. Racah parameters (A, B, and C) show the energy separation between different \(^{2S+1}L\) states, and these parameters describe the strength of the electrostatic interactions between the electrons [27]. The values of L can be 0 for S, 1 for P, 2 for D, 3 for F, etc. The degeneracy of these levels is \(2L+1\) and it may be increased by the presence of the crystal field. On the other hand, the crystal field levels are labeled as \(^{2S+1}X\), where X can be A for no degeneracy, E for two-fold degeneracy, T for threefold degeneracy.

The energy levels for the transition metal ions with 3d\(^1\) outer electronic configuration, such as Ti\(^{3+}\) and V\(^{4+}\), as a function of the octahedral crystal field is given in Figure 1.7. The free transition metal ion has five-fold orbital degeneracy (\(^2D\)) which is split into two levels, \(^2E\) and \(^2T_2\), in an octahedral crystal field. The octahedral coordination is the most common crystal field for transition metal ions. The only feasible optical absorption transition for transition metal ions with 3d\(^1\)
electronic configuration in octahedral crystal symmetry is $^2T_2 \rightarrow ^2E$. The energy difference between the $^2E$ and $^2T_2$ is equal to the crystal field strength, $\Delta r$. The Stokes shift for the trivalent transition metal ions is around 20,000 cm$^{-1}$ and this energy difference between the emission and excitation band peaks corresponds to the emission in the visible region. It is important to note that this transition occurs between energy levels of the $d$ shell and is forbidden. Hence, the parity does not change. However, the parity relaxation rule is relaxed by coupling of the electronic transition with the vibrations (or distortions) of the suitable symmetry [28].

A typical example is Ti$^{3+}$ ion doped Al$_2$O$_3$ (sapphire) [29]. Both excitation and emission spectra correspond to transitions between $t_{2g}$ (ground) and $e_g$ (excited) energy levels, which arise from the splitting of the 3$d^1$ level caused by the octahedral crystal field. The characteristic absorption and emission bands are

![Energy levels](image)

**Figure 1.7** Energy levels of the transition metals with 3$d^1$ electronic configuration as a function of the octahedral crystal field. $^2D$ is the free ion level [18].
broad and a large Stokes shift is observed in accordance with a strong electron–lattice coupling [18,29]. Furthermore, transitions from the ground state (t_{2g}) to the excited state (e_g) are dipole allowed due to the crystal field around the Ti^{3+} luminescent ions in the sapphire host lattice. Therefore, the radiative lifetime is very short (3.9 µs), which is typical for an allowed electric dipole transitions. Ti–sapphire crystals have high luminescent efficiency, even at room temperature, and they have been used in the development of tunable solid state lasers in the red–near infrared spectral region [28].

3d^n Transition Metal Ions (n>1) and Sugano – Tanabe Diagrams:

As stated above, transition metal ions have an incompletely filled d shell, and the related energy levels originating from such a configuration can be calculated using the Sugano – Tanabe diagram considering the mutual interaction between the d electrons and the crystal field. These energy level calculations are represented in the so-called Sugano – Tanabe diagrams, which are used to interpret the characteristic absorption and emission spectra of transition metal ions in a variety of crystalline host lattices. Sugano – Tanabe diagrams generated for transition metal ions exhibit how the \(^{2S+1}L\) free ion levels split up as the ratio between the crystal field strength and the inter-electronic interaction increases. As an example, the Sugano – Tanabe diagram for a 3d^3 transition metal ion, such as Cr^{3+}, V^{2+}, Mn^{4+}, is shown in Figure 1.8. The x-axis, Dq/B, represents the inter-electronic interactions. The free ion energy levels of \(^4F\), \(^4P\), \(^2G\), and \(^2F\) are shown on the y-axis measured in E/B energy units. Furthermore, the split components of each free ion energy level in an increasing
Figure 1.8 The Sugano – Tanabe diagram of a rare-earth ion with 3d$^3$ electronic configuration. The inset shows the energy level diagrams for relatively strong crystal fields [30].

octahedral crystal field are also shown on the graph. As an example, it can be seen how the ground state $^4F$ splits into three separate energy levels, which are $^4A_{2g}$ ground level and two excited levels, $^4T_{2g}$ and $^4T_{1g}$, in an octahedral crystal field. The other excited free ion levels also split into different A, T, and E, energy
levels [30]. Additionally, the C/B ratio changes depending on the specific ion and slightly on the host matrix and varies from 4.19 for Ti$^{4+}$ to 4.88 for Ni$^{2+}$. Moreover, there are some levels $^2E_g^2T_1g$, and $^2T_2g$ (for Dq/B >1) with energies (almost zero slope) that are independent of the crystal field.

As a result, the spectral positions of the transitions between the $^4A_{2g}$ ground level and the $^2E_g$, $^2T_{1g}$, and $^2T_{2g}$ energy levels are also independent of the crystal field strength. In a broader sense, this means that the mentioned transition energies are practically constant with the configurational – coordinate (r$_{\text{eff.rad.}}$), and they give rise to narrow optical bands with $\Delta r \approx 0$, as they have nearly the same electron-lattice coupling behavior as the $^4A_{2g}$ ground level. In contrast, other energy levels, $^4T_{1g}$, $^4T_{2g}$, $^2A_{1g}$, and $^4A_{2g}$ (of $^4F$) have a large slope in the diagram, and, hence, the energy separation of these levels and the $^4A_{2g}$ (of $^4F$) ground level is strongly dependent on the crystal field strength [5,30]. It is important to mention that the main reason for the different slopes for the two states is the different participation of the $e_g$ and $t_{2g}$ orbitals in these two states. For example, the $^2E_g$ and $^4A_{2g}$ ground states derive from $t_{2g}^3$ orbitals, so they have similar phonon coupling, i.e., $S \approx 0$, and hence the $^2E_g$ ground state has almost zero slope in the Sugano – Tanabe diagram. On the other hand, the $^4T_{2g}$ state derives from $t_{2g}^2 e_g$ orbitals and so there is a strong difference in the photon coupling in respect to the $^4A_{2g}$ ground state.

As a result, the electronic transitions from the $^4A_{2g}$ (of $^4F$) to these large-slope energy levels are strongly dependent on the crystal field. In a broader sense, the mentioned transition energies are very sensitive to small displacements of the
local crystalline environment (crystallographic site) and, hence the transition energy strongly dependent on the configurational – coordinate and broad absorption and emission bands are associated with these transitions.

The inset in Figure 1.8 shows the splitting of the free ion energy levels for relatively strong crystal fields approximation. The electrostatic interactions among the 3d electrons are ignored because of the relatively larger crystal field. The orbitals are products of three single electron orbitals, and each single orbital is either a t_{2g} or an e_g orbital. As a result, the following four different combinations, which are t_{2g}, (t_{2g}^2 e^1_g), (t_{2g}^2, e^2_g), and e^3_g, are possible and t_{2g}^3 has the lowest energy.

The vertical line at the value of Dq/B = 2.2, at which the $^4T_{2g}$ and $^2E$ states are equal in energy, and this value of Dq/B is so-called the crossover value. Luminescent material systems of host lattice and luminescent center, with Dq/B value of less than the crossover value are known as low crystal field materials. The lowest energy level for these materials is $^4T_{2g}$ and they show a characteristic broad and intense emission band due to the spin allowed $^4T_{2g} \rightarrow ^4A_{2g}$ vibronic transition. On the other hand, other optically materials on the right hand side of the crossover line are called high crystal field materials and they show a narrow-line emission due to the spin-forbidden $^2E_g \rightarrow ^4A_{2g}$ transition, which is also known as R-line emission.

In summary, the Sugano – Tanabe diagram is a useful guide for crystal field engineering, luminescent material design with transition metal ions, and has been used to deduce the information about the nature of the optical bands of
transition metal ions. Mn$^{2+}$ ion doped phosphors of more than 500 inorganic host lattices with broad luminescence characteristics, covering a wavelength range from about 490 nm to 750 nm, has led to the development of phosphors for plasma display panels, cathode ray tubes, and fluorescent lamps. Additionally, Cr$^{4+}$ ion doped crystals are a very active research area because of the possibility of producing broadly-tunable solid state lasers in the infrared and can be operated at room temperature.

1.3.3.5 Photoluminescence Types in Phosphors

Photoluminescence in crystalline solids is classified according to the nature of the electronic transitions [17].

**A. Intrinsic Luminescence:**

There are three kinds of intrinsic luminescence; i) Band-to-band luminescence, ii) Cross-luminescence, and iii) Exciton luminescence.

i) **Band-to-Band Luminescence:** Band-to-band luminescence refers to the combination of an electron in the conduction band with a hole in the valence band of the host lattice. It is mainly observed in very pure crystals at relatively high temperatures [17]. Band-to-band luminescence has been observed in semiconductors like Si, Ge, and some of the IIIb – Vb compounds such as GaAs. At low temperatures, this type of luminescence is transformed into exciton luminescence, which will be detailed in the following sub-section. It is important to
mention that the light emission mechanism from very bright LEDs (Light Emitting Diodes) and semiconductor lasers is this band-to-band luminescence.

ii) Cross-Luminescence: Cross luminescence is produced by recombination of an electron in the valence band with a hole created in the outermost core band [31]. Cross luminescence can take place when the energy difference between the top of the valence band and that of the outermost core band is smaller than the bandgap energy. In other words, cross luminescence requires that $E_{c-v} < E_g$ [32]. On the other hand, when $E_{c-v} > E_g$, an Auger process takes place so that the hole at the outermost core band is filled nonradiatively with an electron in the valence band and another electron in the valence band is raised to the conduction band. This type of luminescence was first observed in BaF$_2$ under X-ray pulse excitation in 1982 [31]. In the case of BaF$_2$, $E_g = 10.5$ eV and $E_{c-v} = 7.8$ eV, and the peak of the luminescence spectrum is 5.6 eV. One important characteristic of cross luminescence is that the decay time is very fast, on the order of nanoseconds or less. In BaF$_2$, the decay time is 0.8 ns. It is their decay time characteristics that enable crystals showing efficient cross-luminescence to be used as scintillators.

iii) Exciton Luminescence: An exciton is a combination of an excited electron and a hole interacting with one another, i.e., is a composite particle. The exciton moves in a crystal conveying energy and
produces luminescence due to the recombination of the electron and the hole. There are two types of excitons: the Wannier-Mott exciton and the Frenkel exciton [17]. The Wannier-Mott exciton represents the exciton as composed of an electron in conduction band and a hole in the valence band, bound together by Coulombic forces. Therefore, the Wannier-Mott exciton model is analogous to a hydrogen atom. The Wannier-Mott exciton moves in a crystal but does not contribute to electric conduction, and it shows luminescence by the recombination of the electron and hole composing it. The expanse of the wavefunctions of the electron and hole in a Wannier-Mott exciton is much larger than the lattice constant. This model explains the properties of inorganic semiconductors such as IIIb – Vb and IIb – VIb compounds [5]. Another important feature of the Wannier-Mott exciton is that they are stable only at relatively low temperatures, where the binding energies of excitons are higher than the thermal energy, and hence the characteristic luminescence of this type of excition is observed only at such temperatures [18]. At higher temperatures, the excitons are no longer stable and result in band-to-band luminescence. The other type exciton model, the Frenkel exciton, is used in cases where the expanse of the electron and hole wavefunctions is smaller than the lattice constant. Typical examples are inorganic complex salts including transition metal ions such as vanadates (e.g., YVO₄), tungstates (e.g., CaWO₄), cyanoplatines {e.g., BaPt(CN)₄ · 4H₂O},
uranyl salts (e.g., Cs₂UO₂Cl₄), etc. In these luminescent materials, the excited state of an isolated molecule or a complex ion transfers from one molecule to another, or from complex ion to ion, usually due to the presence of dipole – dipole interactions. Therefore, it is accepted as the exciton state and the luminescence characteristics are very similar to those of isolated molecules or complex ions.

B. Extrinsic Luminescence:

Luminescence caused by intentionally-incorporated impurity ions, mostly metallic impurities, or defects, is classified as extrinsic luminescence. Most of the observed types of luminescence that have practical applications belong to this category. Intentionally-incorporated (or doped) impurities are called activators (or luminescent centers) and materials made luminescent in this way are called phosphors.

Ionic crystals and semiconductors which show extrinsic luminescence are classified into two main types; unlocalized and localized. In the unlocalized type, the electrons and holes of the host lattice, i.e., the free electrons in the conduction band and free holes in the valence band, participate in the luminescence process, while in the case of the localized type, the luminescence excitation and emission processes are confined in a localized luminescence center.
C. Localized Type Luminescence:

Rare-earth ions and transition metal ions have been used as impurity ions doped in inorganic crystalline solids and semiconductors to make active luminescence centers. There are two main types of localized luminescence centers based on the electric dipole transitions: Allowed transition type and forbidden transition type. The electric dipole (electronic) transitions between levels with the same parity because it is forbidden by the parity selection rule.

The selection rule for the electronic transition in luminescent atoms is for the $\Delta l = \pm 1$, where $l$ is the azimuthal quantum number. As it was stated earlier, when luminescence ions are incorporated in crystalline host lattices, the forbidden electric–dipole transition is changed by the perturbation of the crystal field, and this may lead to allowed transitions.

A catalog of allowed and forbidden transition types for the luminescent ions incorporated in host lattices which covers all the technically important phosphors is given below [17]:

i) **Allowed transitions**

1. $s \leftrightarrow p$ transition; an electron trapped at an anion vacancy, e.g., Ti$^0$
2. $s^2 \leftrightarrow sp$ transition; e.g., Ti$^+$, Pb$^{2+}$, Sn$^{2+}$, Bi$^{3+}$, Sb$^{3+}$
3. $f \leftrightarrow d$ transition; e.g., Ce$^{3+}$, Eu$^{2+}$.

ii) **Forbidden transitions**

1. $d \leftrightarrow d$ transition; Cr$^{3+}$, Cr$^{4+}$, Mn$^{2+}$, Mn$^{4+}$, Ti$^{3+}$, Fe$^{2+}$, Fe$^{3+}$
2. f $\leftrightarrow$ f transition; Eu$^{3+}$, Er$^{3+}$, Sm$^{3+}$, Nd$^{3+}$, and other rare-earth luminescent ions

One of the main differences between the allowed and forbidden transitions is the life time of the excited state. For allowed emission transitions in phosphors, the decay time is relatively short, 10 - 100 ns, whereas, for forbidden transitions, the decay time is relatively longer and can reach to a few milliseconds [18].

A schematic description of the energy levels of different localized centers located within the energy band of the host lattice is shown in Figure 1.9. It is important to mention that the relative locations of the energy levels of an activator center to the conduction and valence energy bands of the host lattice are usually determined by their depths from the vacuum level, and these relative energy positions are not well known and understood, even for luminescence centers.

When the ground and excited states of the luminescent center are located between the conduction and valence bands, as in the case of A, it is a so-called forbidden gap. On the other hand, the absorption and emission states of the luminescent centers are located deep below the valence band of the host lattice, as shown as case B in Figure 1.9. In the case of C and D transitions, localized centers were excited by the band-to-band transitions. Transitions marked as C show an initial hole capture by the luminescence center and then an electron is captured and this hole – electron combination leads to the characteristic luminescence. Similarly, in the case of D, first an electron and then a hole was
captured by the luminescence center. It is also possible that, the localized centers can be excited by excitons that move in the crystal.

![Diagram](image)

**Figure 1.9** Relative locations of the energy levels of localized center to the host lattice energy bands. A, B, C, D, and E show the possible luminescence transitions [17].

D. **Unlocalized Type Luminescence:**

Donor – acceptor transitions in semiconductors dominate the semiconductive properties and that kind of transition takes place because of the presence of impurities that are donors and acceptors, i.e., luminescence centers. The transition of a free carrier to a bound carrier, and the transition of a bound
electron to a donor to a bound hole at an acceptor are the two types of transitions which result in luminescence in doped semiconductors, for instance, IIIb – Vb and IIb – Vlb compounds [17,18].

In semiconductors, the luminescence, because of the donor – acceptor transitions, is accepted as an intermediate type between localized and unlocalized luminescence. The donor – acceptor luminescence follows one of the following two luminescent mechanisms: The first is where the direct excitation of an electron in a compensated acceptor to an ionized donor level. The second is where an electron is trapped at an ionized donor, and a hole at a compensated acceptor, and they recombine right after the band-to-band excitation. The characteristic emission (energy) of the donor – acceptor luminescence depends on the spatial distance between the donor and the acceptor in a stated pair system.

1.4 Efficiency of Phosphors

The configurational – coordinate diagrams are the most commonly used models for non-radiative relaxation. The possibility of non-radiative relaxation via the conduction band is described by the model of Struck and Fonger [33].

The quantum efficiency (QE) of a phosphor indicates the relative contribution of non-radiative decay processes, and is defined as [17],

\[ \text{QE} = \frac{\text{Number of photons emitted}}{\text{Number of photons absorbed}} \]
Similarly, energy efficiency ($\eta$) is defined as the ratio between the amount of energy emitted and the amount absorbed. It can never exceed 100% and could be used as an alternative to the quantum efficiency [17,18].

An efficient phosphor refers to a high quantum efficiency. For instance, the phosphors used in fluorescent lamps have quantum efficiency close to 100%.

The quantum efficiencies of some phosphors which have practical applications are tabulated in Table 1.4.

Table 1.4 Quantum efficiencies (QE) for some well-known phosphors with practical applications. Excitation wavelength = 254 nm, and Temperature = 300K [18].

<table>
<thead>
<tr>
<th>Luminescent Material</th>
<th>QE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn$_2$SiO$_4$:Mn$^{2+}$</td>
<td>70</td>
</tr>
<tr>
<td>Y$_2$O$_3$:Eu$^{3+}$</td>
<td>93</td>
</tr>
<tr>
<td>SrP$_2$O$_7$:Sn$^{2+}$</td>
<td>86</td>
</tr>
<tr>
<td>CaWO$_4$</td>
<td>75</td>
</tr>
<tr>
<td>MgWO$_4$</td>
<td>84</td>
</tr>
</tbody>
</table>

It is very challenging to measure the absolute QE values accurately. The number of photons being absorbed has to be determined from diffuse reflectance spectra of the sample in comparison to BaSO$_4$, or another totally reflecting material. This process is rather laborious and there are many pitfalls in the calibration procedures. As a result, absolute quantum efficiencies of the same luminescent material have been measured and reported with different QE values [34]. On the other hand, measurement of relative quantum efficiencies has been used as a
good representation of the characteristic quantum efficiency of the phosphor [17,18]. The light outputs of the phosphor with unknown QE, and of a reference material with a known QE are measured under the identical conditions. Also, the amount of light that is absorbed at the excitation wavelength is determined for the sample and the reference material by diffuse reflectance spectroscopy. This analysis is used to get the relevant QE values of the new luminescent materials.

Alternatively, if the characteristic non-radiative decay processes can be neglected at low temperature, and if the radiative decay time is not a function of temperature, then the measurement of the temperature dependence of the decay time and/or the light output of a luminescent material can be used to estimate the quantum efficiencies [17].

For the given assumptions above, the QE approaches unity at low temperatures. Increasing the temperature causes thermal quenching of luminescence, which results in a reduction in the light output. Additionally, the decay time decreases due to the increased non-radiative transition probability from the excited state to the ground state

\[
\frac{1}{\tau} = A_r + A_{nr}
\]

Where \( A_r \) is the radiative decay rate which is assumed to be independent of temperature, and \( A_{nr} \) is the non-radiative decay rate which is assumed to be zero at lowest temperature levels.
1.5  Colorimetry

Colorimetry is the science and measurement of colors and human vision [2]. It is a scientific approach used to quantify and describe the human color perception by using mathematical models. A quantified description of color matching is a necessity because color perception through human vision is a psychophysical phenomenon. The physcophysical colors can be treated and measured in terms of the chromatic response of the eye to pure colors at different wavelengths [2]. On the other hand, the perceived colors, which are the second type of color, cannot be measured quantitatively as they are subjectively perceived by the eye. Based on this fact, a standardized method, the CIE system of colorimetry, will be presented. This system consists of the Red, Green, Blue (RGB) and the XYZ colorimetric systems to quantify color.

1.5.1 Human Vision

Although our vision is sensitive to the colors formed during optical emission with wavelengths between 380 and 760 nm, (i.e., visible light), we still need to be able to measure small differences of color. Two fundamental functions of the human eyes are the detection of the color and perception of the brightness. Human eyes consist of the eyeball, the visual center of the brain, and the optical nerves connecting the two [2]. The sensitivity of the eye over this wavelength range is not constant. For equal energies (for example), a yellow-green light produces a much stronger response in the human eye compared to a red or blue light [3],
i.e., the yellow-green light will be perceived as brighter than the red or blue lights. This phenomenon is called the luminosity of eyes. The main optical parts of the human eye are shown in Figure 1.10.a and Figure 1.10.b.

The retina, which is the light sensitive part of the eye, clads the inside of the eyeball, as shown in Figure 1.10.a. The cell structure of the retina including the light-sensitive rod cells and cone cells and the nerves transmitting the information to the brain is shown in Figure 1.10.b. Rod cells are more abundant and are

![Figure 1.10 Schematic drawing of the horizontal cross-section of the human eye (a) and the schematic view of the retina including rod and cone light receptors [36].](image)

sensitive to the light over the entire visible spectrum. There are three types of cone cells, giving three sets of color preceptors. Each cone cell is sensitive in the red, green, or blue regions of the visible spectrum. The associated cone cells are, therefore, denoted as the Red, Green, and Blue cones as shown in Figure 1.10.b.
In human eyes, rods have a much higher sensitivity than the cones. Human vision during daylight conditions with a high ambient light levels, is mediated by the cones and this is so-called photopic vision. On the other hand, human vision, during night (low light conditions), is mediated by rods, and is called scotopic vision. In the scotopic vision regime, the sense of color is essentially lost, i.e., objects lose their colors and only appear as objects with different gray levels. Photopic vision peaks at 550 nm whereas scotopic vision peaks at 520 nm.

1.5.2 Basic Radiometric and Photometric units

Visible light, in a broader sense, is defined as the electromagnetic radiation which is detectable by the human eye [2]. Radiometry is the measurement of optical radiation, which is electromagnetic radiation covering the ultraviolet, the visible, and the infrared spectral regions at wavelengths between 10 nm to $10^6$ nm [2]. Radiometric units such as watts/m$^2$, and photons/sec-steradian have been used to characterize the physical properties such as the photon energy, number of photons, optical power (or radiant flux), etc., of electromagnetic radiation [2]. However, these radiometric units are not appropriate when it comes to light perception by human vision. For instance, the spectral range for infrared radiation is well beyond the visible range and it causes no luminous sensation in the human eye. On the other hand, photometric units are used to characterize the light and color sensation by the human eye. Photometry is the measurement
of the light at wavelength ranges from 360 to 830 nm. Photometry is very similar to the radiometry except that everything is weighted by the spectral response of the human eye. The only real difference between radiometry and photometry is that radiometry covers the entire optical radiation spectrum whereas photometry is restricted to the visible spectral range as defined by the response of the eye. Typical photometric units are candela, lumens, lux, etc.

The light intensity of an optical source, as perceived by the human eye, is quantified by the luminous intensity and is measured in candela (cd), which is a SI-unit. A candela, as a unit of luminous intensity, is defined as 1/60 of the luminous intensity per square centimeter of a black-body radiator operating at the temperature of freezing platinum (1772 °C) [3].

The unit candela evolved from an older unit, the candlepower. One candlepower is the light intensity emitted from a candle, and one standardized candle emits a luminous intensity of 1.0 cd. Therefore, the luminous intensity of a light source can be represented by a number of standardized candles with the same luminous intensity. Both candlepower and candle are non-SI units that are not commonly used [2,3].

As another photometric quantity, the luminous flux represents light power of a source as perceived by the human eye. The luminous flux unit is the lumen, and one lumen is defined as a monochromatic light source emitting an optical power of (1/683) Watt at a wavelength of 555 nm. The illuminance represents the luminous flux per unit area. It is measured in lux, i.e., lumen/m² [3]. Both lumen and lux are SI-units.
The conversion between photometric and radiometric units can be done by using the eye-sensitivity function, $V(\lambda)$. The eye has its peak sensitivity at a wavelength of 555 nm, which is in the green range of the visible spectrum, as shown in Figure 1.11. A polynomial approximation and the numerical values of $V(\lambda)$ has been tabulated after the 1978 CIE data [37].

![Eye sensitivity function, $V(\lambda)$ and luminous efficacy (lumens/watt) of optical power at visible spectral range with the characteristic colors. The eye sensitivity is the highest at 555 nm where it is marked on the graph [36].](image)

**Figure 1.11** Eye sensitivity function, $V(\lambda)$ and luminous efficacy (lumens/watt) of optical power at visible spectral range with the characteristic colors. The eye sensitivity is the highest at 555 nm where it is marked on the graph [36].

### 1.5.3 CIE Chromaticity Diagrams

As was mentioned in the sub-section above, light causes different levels of excitation of the Red, Green, and Blue cones in the human eye. This leads to the
slight changes in the sensation of color and brightness of a color between individuals. Therefore, in order to quantify the color, a standardized color measurement using color matching functions and the chromaticity diagram was established by The International Commission for Illumination (Comission Internatiionale de l'Eclairage, (CIE) in 1931 based on visual experiments. It is important to mention that there have been several different versions of color matching functions and chromaticity diagrams reported [37,38].

Even though limitations are well recognized, the CIE system of colorimetry remains the only internationally-agreed system for color measurement, and all the official color-related standards and specifications use the CIE color system.

The CIE 1931 XYZ color matching functions denoted as x(λ), y(λ), and z(λ) are shown in Figure 1.12. These three color matching functions correspond to the eye sensitivity curves of the Red, Green, and Blue cones, respectively.

The green color matching function was chosen in such a way that its value is equal to the eye sensitivity functions, i.e., \( y(\lambda) = V(\lambda) \).

The degree of stimulation of the Red, Green, and Blue cones with any light stimuli having any spectral power distribution can be written as:

\[
X = \int \Phi(\lambda) x(\lambda) \, d\lambda \\
Y = \int \Phi(\lambda) y(\lambda) \, d\lambda \\
Z = \int \Phi(\lambda) z(\lambda) \, d\lambda
\]

where these integrated values X, Y, and Z are the tristimulus values that indicate the relative stimulation of each of the three cones, and \( \Phi(\lambda) \) is the spectral
Figure 1.12 CIE 1931 XYZ color matching functions. The y color matching function is identical to the eye sensitivity function $V(\lambda)$ [2].

distribution of light stimulus and $k$ is a normalizing constant. It is important to note that color matching functions and eye sensitivity function are dimensionless.

By projecting the tristimulus values on to the unit plane, i.e., $X+Y+Z = 1$, color can be defined in a two dimensional plane. This plane is known as the chromaticity diagram. Therefore, to specify a color, the chromaticity coordinates $x$ and $y$ can be calculated from the tristimulus values according to the following equations;

\[
x = X / (X + Y + Z) \\
y = Y / (X + Y + Z)
\]
The diagram using the chromaticity coordinates \((x, y)\) is known as the CIE 1931 chromaticity diagram (see Figure 1.13) [2]. The value of a chromacity coordinate represents the stimulation of one particular cone normalized to the entire stimulation. Similarly, the value of the \(z\) chromaticity coordinate can be calculated by the following:

\[
z = 1 - x - y = \frac{Z}{X + Y + Z}
\]

As the \(z\) chromaticity value can be obtained from \(x\) and \(y\), it is redundant, and doesn't need to be used in the chromaticity diagram.

**Figure 1.13** CIE chromaticity diagram [40].
1.6 Technical Importance of Phosphors and their Practical Applications

The scientific research, synthesis, and development of novel phosphors started more than 100 years ago with the preparation of zinc sulfide type phosphors, which eventually saw use in television tubes [17]. From the late 19th century to 20th century, active and extensive research had been done on the development and description of the concept of host lattices doped with luminescence activators, and alkaline-earth chalcogenides. In addition to the transition metals, some rare-earth ions were also used as activators.

The research on phosphors and solid-state luminescence evolved remarkably after the Second World War [2,17]. Development of spectroscopic techniques and luminescence mechanistic models lead to a variety of technically important practical applications for phosphors such as light sources, display devices, detector systems and many others [2].

Development, synthesis and preparation of inorganic luminescent phosphors are based on materials processing with physical and inorganic chemistry principles. On the other hand, interpretation and explanation of luminescence mechanisms can be done by solid-state physics. Therefore, research and development of phosphor technology require an interdisciplinary approach with the above mentioned methods and techniques.
Phosphors can be classified based on their application: 1) Lighting, 2) Display panels, 3) X-Ray screens and Scintillators, and 4) other relatively simpler applications such as luminescent paint with after-glow phosphors.

### 1.6.1 Solid State Lighting

*Lamp Phosphors:* A low pressure luminescent (or fluorescent) lamp is filled with a noble gas at a pressure of 400 Pa, containing 0.8 Pa mercury. About 85% of the emitted radiation from the excited mercury atoms is at 254 nm, 12 % at 185 nm, and the remaining 3% is emitted in the longer UV and visible regions [17]. The lamp phosphor converts the 254 and 185 nm radiation into the visible light. Therefore, a lamp phosphor should be able to be excited at these two wavelengths strongly and convert the absorbed radiation efficiently (high quantum efficiency, typically >85%) [2,17]. Also, it must have structural and chemical stability under UV radiation, it should be inert to mercury, and plasma discharge. For example, sulfides cannot be used in lamps because they react with mercury. A fluorescent lamp typically has to emit white light, hence the sun, black body radiator, is imitated [2].

**Phosphors used for Lamps:** MgWO₄ + (Be,Zn)₂SiO₄:Mn²⁺ mixtures: the tungstate has a broad bluish-white centered at 480 nm, and the ortho-silicates have an emission band from 500 to 700 nm centered at 600 nm. The main drawback of this blend is that Mn²⁺ ions pickup mercury from the gas discharge and is liable to decompose under UV radiation. Also, Be is highly toxic. Hence, in 1948, this phosphor blend was replaced with calcium halophosphate phosphors.
Ca$_5$(PO$_4$)$_3$(Cl,F):(Sb$^{3+}$, Mn$^{2+}$): The Sb$^{3+}$ acts both as sensitizer and activator. It absorbs the UV radiation and emits a broad band peaked near 480 nm, and part of this radiation is transferred to the Mn$^{2+}$ ions which emit at 580 nm [2]. By changing the Sb$^{3+}$/Mn$^{2+}$ and Cl/F ratios, different hues of white color is produced. However, because of the deficiency of the red color, the light is of poor color rendering (Ra = 50 to 76). High Ra~90 was obtained in deluxe phosphors (Sr$_5$(PO$_4$)$_3$(Cl,P):(Sb$^{3+}$, Mn$^{2+}$) + Sr$_3$(PO$_4$)$_2$:Sn$^{2+}$ mixtures) [2]. However, these deluxe phosphors have lower luminous efficiencies than those of other halophosphates. The main drawback of the halophosphate phosphors is that it is impossible to obtain high brightness and high Ra simultaneously. The use of rare-earth activated phosphors in 1970s allowed to have both the high luminous efficiency with high Ra value.

Tricolor lamps (triphosphors): Combination of three phosphors which emit in narrow wavelength intervals centered at 450, 550, and 610 nm resulted in high efficacy (100 lm/W) and CRI (~85). Triphosphors may comprise a variety of matrices doped with rare-earth ions. Y$_2$O$_3$:Eu$^{3+}$ is widely used as red; BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$, Sr$_3$(PO$_4$)$_5$Cl:Eu$^{2+}$, Sr$_2$Al$_6$O$_{11}$:Eu$^{2+}$, Sr$_{5-x-y}$Ba$_x$Ca$_y$(PO$_4$)$_3$:Eu$^{2+}$ for blue; and LaPO$_4$:Ce$^{3+}$, Tb$^{3+}$, CeMgAl$_{11}$O$_{19}$:Tb$^{3+}$, and GdMgB$_5$O$_{10}$:Ce$^{3+}$, Tb$^{3+}$ for green color [2,17,39]. Triphosphors are much more expensive, but they surpass halophosphates in quantum efficiency, lifetime, and color rendering.

**Special Lamp Phosphors:** Although a CRI of 85 yields a normal appearance for most objects, some colors will look unnatural under illumination with a tricolor lamp. Hence in some applications such as museum illumination and flower
displays, a higher CRI is required. However, the efficacy drops to 65 lm/W. The increase in CRI is obtained by using a blue-emitting phosphor with an emission maximum at 490 nm and by using a band instead of a line phosphor for the red and green components. Sr$_4$Al$_4$O$_{25}$:Eu$^{2+}$ is used for blue; GdMgB$_5$O$_{10}$:Mn$^{2+}$, Ce$^{3+}$ broad band red emitting; Ca$_5$(PO$_4$)$_3$(F,Cl):Sb$^{3+}$, Mn$^{2+}$ broad band green emitting green color.

When applied to the human skin, for $\lambda<$300 nm, sunburn (erythema) and $\lambda>$300 nm direct pigmentation (skin darkening) occurs [17]. As sun-tanning lamps using SrAl$_{12}$O$_{19}$: Ce$^{3+}$, Mg$^{2+}$ will induce sunburn, SrB$_4$O$_7$ gives direct pigmentation, and BaSi$_2$O$_5$:Pb$^{2+}$ provides a long lasting tan. Also, GdBO$_3$: Pr$^{3+}$ or (La,Gd)B$_3$O$_6$:Bi$^{3+}$ have emission at 312 nm and can be used to control psoriasis (skin disease) without too much sunburn [2,17].

(Sr,Mg)$_3$(PO$_4$)$_2$:Sn$^{2+}$ and YVO$_4$:Eu$^{3+}$ have been used for high-pressure mercury vapor lamps with red emissions and high quantum efficiency up to 300 °C.

**Phosphor Conversion LEDs (pcLED):** Devising equipment device for creating sources of white light is the ultimate goal of solid-state lighting technology. The ultimate target of LED development is the replacement of conventional incandescent and fluorescent lamps. There are two current approaches to producing white LEDs. The first approach is to mix light of different colors emitted by different chips (two electroluminescent emitters), called a white multichip (MC) LED [2,39]. Another way is to down-convert the emission from a blue or UV LED to a longer wavelength light using phosphors.
Dichromatic pcLEDs are an easy and efficient way to produce white LEDs by using an AlInGaN chip that emits blue light and a phosphor that emits in the yellow region. A portion of the blue light is absorbed in the phosphor layer and down-converted to yellow light. The rest of the blue emission escapes to complete the white spectrum. The spectral properties of $Y_3Al_5O_{12} \cdot Ce^{3+}$ (YAG) almost ideally meet the requirements for a dichromatic white LED [2]. The peak of the excitation spectrum around 460 nm coincides well with the peak wavelength of the most efficient blue AlInGaN LED and the emission spectra of the phosphor fit the complementary component around 570 to 590 nm [41]. In addition, tailoring the emission spectra of the garnet phosphor yields a white light with various color temperatures. ($Y_{1-a}Gd_a$)$_3(Al_{1-b}Ga_b)_5O_{12} \cdot Ce^{3+}$ phosphor emission bands peaked at 570 and 580 nm when excited at 460 nm. Red shifting the phosphor emission by 10 nm yields a significant change in color temperature and in the blue-to-yellow intensity ratio, with less effect on efficacy and color rendering. The luminous efficacies of the spectra exceed 300 lm/W and the Ra ~ 80 [42].

Trichromatic pcLEDs offer improved efficiency and color rendering. An appropriate combination of two inorganic phosphors such as SrGa$_2$S$_4$:Eu$^{2+}$ for conversion of blue light to green emission (~535 nm) and SrS:Eu$^{2+}$ for the conversion to red emission (~615 nm) by using an AlInGaN blue chip (~450 nm) [43]. Compared to a dichromatic AlInGaN/YAG:Ce$^{3+}$ LED, the trichromatic pcLED yields higher luminous efficacy and Ra. Unlike blue chips, for UV LEDs (InGaN chips emitting 370-420 nm range), the visible part of the spectrum is completely
generated by phosphors. Phosphors excited by InGaN chips are BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ for blue, ZnS:Cu$^+$,Al$^{3+}$ for green, and Y$_2$O$_2$S:Eu$^{3+}$ for red color [44]. Other systems such as blue chip combined with Sr$_2$Si$_5$N$_8$(orange-red) + SrSi$_2$O$_2$N$_2$ (yellow-green) gave a high luminous efficiency (25 lm/W), excellent color rendering index Ra>90, and very good color quality [45]. Nearly all current research studies to find new phosphors for LEDs use Eu$^{2+}$ or Ce$^{3+}$ as activators. Although AlINGaN/YAG:Ce$^{3+}$ is presently the most efficient technique, the light color is not true white because of a lacking of the red component. Therefore, the interest in development of blue-excitable red emitting phosphors is currently very high. Silicate phosphors are the most attractive candidates for the white LED applications besides nitrides such as LiSrSiO$_4$:Eu$^{2+}$ (580 nm), Ca$_3$Si$_2$O$_7$:Eu$^{2+}$ (600 nm), Ba$_2$MgSi$_2$O$_7$:Eu$^{2+}$ (505 nm) [46], Ba$_9$Sc$_2$Si$_6$O$_{24}$:Eu$^{2+}$ (500-520 nm) [47], Ba$_2$Si$_5$O$_8$:Eu$^{2+}$ [48], CaAlSi$_3$:Eu$^{2+}$ [49], Ca$_2$ZnSi$_2$O$_7$:Eu$^{2+}$ (600 nm) [50], CaAl$_2$Si$_2$O$_6$:Eu$^{2+}$, Mn$^{2+}$, SrGa$_2$S$_4$:Eu$^{2+}$ (green), Ca$_{1-x}$Sr$_x$S:Eu$^{2+}$ (red) [51], Gd$_2$Mo$_3$O$_9$:Eu$^{3+}$ etc.

**Outlook:** After July 2006, RoHS (Restriction of Hazardous Substances Directive) restricted the use of Pb, Hg, Cd, and Cr$^{6+}$ in the manufacture of electrical and electronic equipment, and they cannot be introduced to the European market [52]. Although the Hg-discharge based fluorescent lamps are not restricted equipment at present, Hg-based lighting will be prohibited in the near future. Because the patent for the original invention of white LEDs with YAG garnet conversion has been very prolonged, other lighting companies have been aggressively trying to find and patent phosphors for pcLEDs. There are
many alternative phosphors and new ones have still been explored. A potential practical concern is that each LED has maximum of a few mg of phosphors for down-conversion of the emitted chip light, hence the required capacity for manufacturing is in the kg scale not in tones. However, such a little amount of usage gives it a chance of being expensive.

1.6.2 Displays

**Cathode Ray Tubes:** Cathode rays are a beam of fast electrons with high accelerating voltage such as >10kV for a TV picture tube. ZnS and its derivatives are the main host crystals yielding the highest radiant efficiency. ZnS:Ag\(^{+}\) has been used as blue phosphor and the Ag is the acceptor. ZnS:Cu, Cl (or Al) are used as green color. For red emitting phosphor initially (Zn,Cd)S:Ag and Zn\(_3\)(PO\(_4\))\(_2\):Mn\(^{2+}\) were used, however after considering that the red emission should have a narrow emission band at 610 nm, YVO\(_4\):Eu\(^{3+}\) were used and then Y\(_2\)O\(_2\)S:Eu\(^{3+}\) with increased brightness was used, and Y\(_2\)(WO\(_4\))\(_3\):Eu\(^{3+}\) was proposed because of its high lumen equivalent [2,17].

**Projection Television phosphors:** Y\(_2\)SiO\(_5\):Tb\(^{3+}\), Y\(_3\)Al\(_5\)O\(_{12}\):Tb\(^{3+}\), and Y\(_3\)(Al,Ga)\(_5\)O\(_{12}\):Tb\(^{3+}\) are used as green; Y\(_2\)O\(_3\):Eu\(^{3+}\) as red; (La,Y)OBr:Ce\(^{3+}\) and (La,Gd)OBr:Ce\(^{3+}\) are attractive but there are currently no ideal phosphors for blue color because of the difficulty in screen making.

**Display Panels:** Tricolor inorganic phosphors have been used in plasma display panels (PDP) to emit red, green and blue light. These phosphors have to absorb the vacuum ultraviolet (VUV) source radiation at 147 nm from a He/Xe
gas plasma to emit visible light. \((Y, Gd)BO_3: Eu^{3+}\) has been used as the red-emitting phosphor, \(Zn_2SiO_4: Mn\) (525 nm) and/or \(BaAl_{12}O_{19}: Mn\) (515 nm) as green, and \(BaMg_2Al_{16}O_{27}: Eu^{2+}\) (450 nm) is used as the blue phosphor [2,39].

**Outlook:** As far as red phosphor is concerned, \((Y, Gd)BO_3: Eu^{3+}\) gives emission at 593—much higher than that of the red one at about 610nm, resulting in a poor chromaticity, i.e., poor color purity [53]. In addition, there exists a poor blue emission from \(BaMg_2Al_{16}O_{27}: Eu^{2+}\) after a relatively short time of absorbing the VUV light, hence the brightness of the blue color fades faster than the red and green components. For these reasons, research on red and blue phosphors is still important and active. However, PDP technology has to surpass its biggest competitor, LCD, to have a reasonable market share. LCD and PDP are definitely replacing the CRT-based screens in the display market.

### 1.6.3 X-Ray Phosphors and Scintillators

X-Ray phosphors and scintillators are often used interchangeably. The name X-ray phosphors is used when the application requires a powder screen and the term scintillator is used when a single crystal is required. Briefly, X-ray phosphors absorb X-rays and convert into luminescence with UV or visible emission. Typical applications include X-ray imaging in medical diagnostics, where an integrating technique measures the light intensity under continuous excitation. Additional applications include the use of scintillators in electromagnetic calorimeters in order to count photons, electrons, etc.
CaWO$_4$ was first used in 1896 and served for 75 years in X-ray intensifying screens. Today, nearly all commercial digital X-ray imaging systems use the photostimulable BaFBr:Eu$^{2+}$ phosphor. Some other X-ray storage and intensifying screen phosphors are: BaFCl:Eu$^{2+}$, LaOBr:Tm$^{3+}$, Gd$_2$O$_2$:Tb$^{3+}$, GdTaO$_4$:Tb$^{3+}$, Gd$_2$SiO$_5$:Tb$^{3+}$, and Gd$_3$Ga$_5$O$_{12}$:Tb$^{3+}$, Ba$_5$SiO$_4$Br$_6$:Eu$^{2+}$, Ba$_5$GeO$_4$Br$_6$:Eu$^{2+}$, Ba$_3$(PO$_4$)$_2$:Eu$^{2+}$, Y$_2$SiO$_5$:Ce$^{3+}$ [2,17,36,39].

**Outlook:** The search for new X-Ray phosphors for X-ray intensifying screens presently appears to have reached its end. A number of satisfactory materials are available, but for specialized applications there may be some need for improvement. However, the physics of the X-ray storage mechanism is not well understood.
SECTION 2

Synthesis of Inorganic Luminescent Materials

2.1 Introduction

Most solid structural and functional ceramics we encounter in the real world are in the form of powders of small crystallites with varying dimensions. Crystallites and particles have their own unique shapes varying from spheres to needles with characteristic diameter or size. Their size can be tailored by the method used to prepare them.

As noted earlier, inorganic phosphors consist of a crystalline host lattice with small amounts of active luminescent centers, “activators”. In some cases, co-activators are necessary to dissolve the active luminescent centers into the host crystal lattice. Both activator and co-activator ions are incorporated into the crystalline host lattice by diffusion at elevated firing temperatures (calcination). In general, the calcination temperature for inorganic materials is a little below the melting temperature of the host material.

Commercially-available high-purity raw materials are available in various grades (reagent grade, luminescent grade), and are conveniently used to prepare most inorganic luminescent materials, excepting sulfide-based phosphors due to their sensitivity to impurities.
Inorganic luminescent materials have been prepared by two general methods: one is by the conventional solid state method and the other is by precipitation from aqueous (less often from non-aqueous) solutions. Sometimes, both methods are used to prepare efficient phosphors for specific applications. Although they have some similarities, the phenomena governing particle growth caused by the conventional solid state reactions is quite different from the growth process of particles in solutions [3]. The conventional solid state synthetic approach requires the solid metal oxide or carbonate precursors be brought into contact by grinding and mixing, followed by calcination of this mixture at high temperatures with intermediate grinding when necessary to facilitate the diffusion of atoms in the chemical reaction [2,3,17].

Most inorganic luminescent powders used in practical applications are commercialized in the form of powder. In other words, these light sensitive ceramic materials are in the form of discrete small particles of varying size, i.e., crystallites. The main difference between the single-crystal and polycrystalline (crystallite) states of matter is the size of the crystal itself. For the single-crystal, the crystal size is typically large (>10 cm) whereas in the poly-crystalline state, the size of crystals is small in scale (10 µm or less) [3].

Ceramic powders consist of particles, and each particle has its own characteristic diameter and size. The performance of inorganic luminescent materials depends on their physicochemical properties. The characteristic properties in turn depend on the atomic structure, homogeneity in composition, microstructure, defects, and interfaces which are controlled by thermodynamics and kinetics of synthesis.
from various raw materials [54,55]. The size of powder particles can be tailored by the method used to prepare them.

Both the conventional solid state and chemical synthesis and processing methods involve the formation of nuclei and the growth of the formed nuclei. Nucleation can be homogeneous or heterogeneous. In precipitation from aqueous solutions to form crystalline particles, nucleation occurs via a combination of both mechanisms [3].

A large variety of inorganic luminescent materials has been produced by the conventional solid state method under a wide range of conditions. However, the low temperature chemical synthesis and processing routes are of greater interest, as they offer better control of the microstructure, stoichiometry, and phase purity.

In this chapter, conventional solid state and chemical methods of synthesis will be discussed. Additionally, nucleation and growth mechanisms will also be explained as they relate to both solid state reactions and chemical synthesis routes for obtaining discrete crystalline particles. This chapter also deals with the standard equipment needed to characterize the synthesized phosphor powders and to measure their photoluminescence properties.
2.2 Types of reactions encountered in the synthesis of ceramic particles

In basic chemistry terms, the starting raw materials of a chemical reaction are called the *reactants*, and the material to which the reactants are chemically converted the *products*. The reactants can be in the form of solid, liquid, or gas phase, or any combination of phases. They may be used in the form of pure elements, or multi-component compounds [55]. A multi-element compound is called a *precursor* and the components of the final product are in an intimate mixture with atomic scale mixing. There are many types of chemical reactions have been employed for the synthesis of solid inorganic particles. Some of the most common reactions used for the synthesis of solid inorganic compounds are [56]:

i) *Decomposition reactions*

\[ A(s) \rightarrow B(s) + C(g) \]

for example, \( \text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g) \)

ii) *Combination reactions*

\[ A(s) + B(g) \rightarrow C(s) \]

for example, \( \text{YBa}_2\text{Cu}_3\text{O}_6(s) + \text{O}_2(g) \rightarrow \text{YBa}_2\text{Cu}_3\text{O}_7(s) \)

iii) *Metathetic reactions* (combining decomposition (i) and combination (ii) reactions)
A(s) + B(g) → C(s) + D(g)

For example, Pr$_6$O$_{11}$(s) + 2H$_2$(g) → 3Pr$_2$O$_3$(s) + 2H$_2$O(g)

iv) Addition reactions

A(s) + B(s) → C(s)

For example, ZnO(s) + Fe$_2$O$_3$(s) → ZnFe$_2$O$_4$(s)

A(s) + B(l) → C(s)

A(g) + B(g) → C(s)

For example, GaMe$_3$(g) + 4NH$_3$(g) → GaAs(s) + 3CH$_4$(g)

v) Exchange reactions

AX(s) + BY(s) → AY(s) + BX(s)

AX(s) + BY(g) → AY(s) + BX(g)

For example, ZnS(s) + CdO(s) → CdS(s) + ZnO(s)

Complex reactions involving more than one type of chemical reaction have been commonly employed in ceramic material synthesis. In the preparation of multi-oxide compounds, it is common to carry out calcination at elevated temperatures. This serves as thermal decomposition of a compound followed by oxidation in air or oxygen in a single step [57]; for example,

2Ba$_{0.5}$Mn$_{0.5}$CO$_3$(s) + 1/2O$_2$ → BaMnO$_3$(s) + 2CO$_2$(g)
Similarly, the reactants in the vapor phase can react with solid compounds to yield products in solid phase such as [57],

\[ \text{MgO(s) + Cr}_2\text{O}_3 + \text{O}_2(\text{g}) \rightarrow \text{MgCr}_2\text{O}_4(\text{s}) \]

In the synthesis of inorganic solid compounds, during the calcination step, specific reagents and reaction conditions can be used to carry out various processes such as oxidation, reduction, halogenation, etc. The reduction of oxides is commonly done by calcining in an atmosphere of flowing pure hydrogen, a hydrogen-nitrogen mixture, or alternatively, CO or CO-CO\(_2\) mixtures [3,55,57]. Additionally, vacuum annealing or decompositions at low pressures have also been used for the reduction of oxides by lowering the oxygen content of the calcination atmosphere. In addition to the reduction of oxides, concentrated or diluted hydrogen atmospheres have been used for halides and other compounds.

\[ \text{M}_2\text{O}_3(\text{s}) + \text{H}_2(\text{s}) \rightarrow 2\text{M}(\text{s}) + \text{H}_2\text{O}(\text{g}) \quad (\text{e.g., } \text{M = Fe}) \]

\[ \text{ABO}_3(\text{s}) + \text{H}_2(\text{g}) \rightarrow \text{ABO}_{2.5}(\text{s}) + \frac{1}{2}\text{H}_2\text{O}(\text{g}) \quad (\text{e.g., } \text{ABO}_3 = \text{LaCO}_3) \]

Similarly, elemental carbon and any suitable metal can be used for the reduction of oxides for example,

\[ 2\text{MCl}_3 + M \rightarrow 3\text{MCl}_2 \quad (\text{e.g., } M = \text{Nd, Fe, etc.}) \]
2.3 Solid State Reactions

2.3.1 Functional Ceramic Synthesis and Processing by Conventional Routes

The most common synthesis method of preparing functional ceramic materials is by the reaction of the raw materials in the solid state at elevated temperatures. The desired composition and conditions for the synthesis of a ceramic compound with the right stoichiometry can be determined by using the knowledge of the specific phase diagram [58-60]. Platinum, alumina, and silica are commonly used as containers for the synthesis of complex metal oxides, whereas graphite containers are more suitable for sulfides and other chalcogenides as well as pnictides [3,17,60]. Alternatively, sealed-evacuated capsules are used for the synthesis of ceramic materials if one of the constituents is volatile or sensitive to the ambient atmosphere. Most functional ceramic material preparation by the conventional routes require relatively high temperatures and resistance heating is the most common method to attain the elevated temperatures.

The conventional ceramic material preparation method suffers from several inherent disadvantages. The entire reaction to form the desired ceramic phase is in solid state form when no melt is formed during the firing stage. Reactions in the solid state start with a phase boundary reaction at the contact points between the components and continues by diffusion of constituents through the product phase to obtain the desired stoichiometry [3,61]. As the solid state reaction progresses, diffusion paths for the constituents become increasingly longer, and thus the reaction rate becomes slower. Furthermore, the product interface
between the reacting particles acts as a transport barrier for the development of the final product. Intermittent grinding via ball mills between heating cycles can be used to break up particles, creating new surfaces, speeding up the characteristic reactions and shortening the diffusion distances to form the targeted compounds with the right stoichiometry [3,55].

There is no simple known way to monitor the progress of the reaction between the reacting particles in the conventional solid state route. It is very common to use X-Ray diffraction measurement techniques to determine the proper synthesis conditions that lead to completion of the reaction by identifying the characteristic crystalline phases. This is done by trial and error. The solid state method usually results in mixtures of reactants and products because of the difficulty in controlling the progress of the characteristic reactions. It is very difficult (sometimes impossible) to separate the compound with the desired stoichiometry from other secondary phases. In some cases, it is difficult to obtain a compositionally homogeneous ceramic material, even when the reaction proceeds to completion.

Despite the fact that the conventional solid state method has the mentioned characteristic disadvantages, it is, nonetheless, widely used for the preparation of functional ceramic materials.
2.3.2 Modified Conventional Solid State Route

2.3.2.1 Overview and Historical Perspective

The mechanical milling and alloying of materials is of great interest in the mineral, ceramic processing, and powder metallurgy industries [62]. A powder mixture is placed in the ball mill and is subject to high energy collisions to produce finer scale powders from the coarser starting elemental powders. The most common types of materials used for grinding vessels include tool steel, hardened steel, stainless steel, and WC-Co [63]. Both flat-ended and round-ended mill containers have been used [64].

This mechanochemical synthesis technique involves repeated welding, fracturing, and re-welding of powder particles in a high-energy ball mill. Nanostructures, metastable crystalline, and quasi-crystalline phases, supersaturated solid solutions, and amorphous alloys are typical non-equilibrium products synthesized [63].

Although, historically, oxide dispersion strengthened (ODS) alloys have been the primary application of mechanical alloying, the mechanochemical technique has been extended to synthesize many thermodynamically non-equilibrium structures including nanocrystalline [65], amorphous [66], and quasi-crystalline materials [67,68].

In solid state method, a large number of lattice defects are produced by introducing the energy into the crystalline powder particles. This causes a reduction in the average crystallite size by a factor of $10^3 – 10^4$ because of the
creation and self-organization of small-angle and high-angle grain boundaries within the powder particles during the mechanochemical activation process [63]. Therefore, significant changes in the mechanical, chemical and thermodynamic properties of these mechanically treated particles have been observed. The properties of nanophase materials are often controlled by the grain size distribution and the cohesive energy of the grain and interphase boundaries.

Mechanical alloying was developed first by John Benjamin at the International Nickel Company in the late 60’s in order to synthesize complex Oxide Dispersion Strengthened (ODS) nickel-based superalloys (Ni-20%Cr alloy strengthened by approximately 1 vol%Al₂O₃) for gas turbine applications and other heat resistant alloys. The repeated cold welding and fracturing of the powder particles eventually lead to formation of oxide layers on the surface of the powder particles as well as layered structures [69]. At this stage, this mechanochemical activation process was referred to as “milling/mixing”. The term “mechanical alloying” was later introduced by E.C. MacQueen in the late 1960’s [70]. Mechanical alloying is done when the mixtures of powders of different metals or alloys/compounds are milled together and the chemical composition of the powder particles change due to the continuous welding, fracturing, and re-welding at the atomic scale. On the other hand, milling of uniform powders such as pure materials, intermetallics, pre-alloyed powders, etc., without any material transfer for homogenization is called as mechanical mixing [63]. In a broader sense, mechanical alloying of the powders results in compositional and microstructural changes, whereas
mechanical mixing produces smaller scale and structurally-changed single component powders.

In the early 1970's, high energy milling of powder particles combined with subsequent high temperature sintering was developed as an important industrial process to produce new alloys and phase mixtures. This powder metallurgical process allows the preparation of alloys and composites which cannot be produced via conventional casting methods.

In the 1980's, mechanical attrition and mechanical alloying received great attention as meta-stable solid state process resulting in materials with nanoscale structures.

2.3.2.2 Mechanochemical Activation Process and Mechanics

The initial raw materials used for milling usually have particle sizes in the range of 1 to 200 µm [71]. During mechanochemical activation, the raw powder particles in the grinding medium are continuously impacted by the balls and cold welding between particles and fracturing of the particles take place repeatedly as shown in Figure 2.1. Although the initial powder particle size is not very critical, it should be smaller than the milling ball size [72].

Both mechanical milling and mixing techniques have been widely used in the manufacture of structural and functional ceramic materials. Mechanical alloying processes can be described by four different stages: the initial, intermediate, final, and completion stage [69]. At the initial stage of milling, the powder
particles are readily flattened by the compressive forces because the material is relatively soft at this stage. The ductile particles can easily be deformed under compressive loading, and hence they are flattened into thin flakes. On the other hand, relatively hard particles tend to resist compressive forces. If the powder mixture contains both ductile and brittle particles, the brittle ones may remain less deformed and the ductile ones tend to bind the hard particles. Fracture is expected to be predominant in bcc and hcp metals as compared to cold welding in fcc metals. As a result of the difference in ductility of the raw particles, a wide distribution of particles size is observed at the initial stage of the mechanical alloying process.

At the intermediate stage, fracturing and cold welding are now significant and greater plastic deformation leads to the formation of layered structures. The
laminated structure is further refined as additional fracturing takes place. Diffusion in the solid state is responsible for the formation of non-equilibrium (meta-stable) phases. It has been proposed that the change in lamellae thickness is a function of the collision energy, mechanical properties of the mixed powder, and the mechanical milling duration.

Considerable grain refinement and particle size reduction are evident at the final stage of the mechanochemical activation process. The microstructure of the particles is more homogeneous and that homogeneity results from the established equilibrium between the continuous fracturing and cold welding. Fracture tends to break individual particles into smaller pieces and de-agglomerates the particles that have been cold welded. As a consequence, a particle may either become smaller in size through fracturing or may agglomerate by welding depending on the local dominant forces as alloying and mixing time progress. At the final stage, cold welding and fracturing will ultimately reach a steady-state equilibrium [69,73]. The average particle size and particle size distribution depend on the balance between cold welding and fracturing. Crystallite size may reach less than 10 nm depending on the properties of the materials being processed. Further deformation is almost impossible because it requires very high deformation stresses, best described by Hall-Petch relation

\[ \sigma = \sigma_0 + kd^{1/2}, \]

where \( \sigma \) is the stress, \( \sigma_0 \) and \( k \) are the constants, and \( d \) is the average grain size. Therefore, very high deformation stress has to be applied to get a very small crystallite [69].
In the completion stage of the mechanical alloying process, the powder particles possess an extremely deformed meta-stable microstructure. The characteristic lamellae structure may no longer be resolvable by electron microscope, and further mechanical alloying cannot improve the particle size distribution [69,73].

2.3.2.3 Mechanochemical Activation Process Variables

The Milling time is so chosen as to get a steady-state balance between fracturing and cold welding of the particles. The powder mixture should be milled for the required duration, otherwise, if milled for longer than required, it is possible that contamination will increase and some undesirable phases will form [74]. X-Ray diffraction techniques are used to check for the presence of the targeted compound depending on the milling time. It varies depending on the mill type, the ball-to-powder ratio, the intensity of the milling, and the temperature of the milling medium.

The Milling speed depends on the design of the mill. The temperature of the medium can reach very high values at high speeds. This increase in temperature may be advantageous if diffusion is required to promote homogenization or alloying. On the other hand, it may be a disadvantage because the increased temperature accelerates the phase transformation process and results in the decomposition of supersaturated solid solutions or other meta-stable phases formed during mechanical alloying [75]. Furthermore, during nano-crystalline structure formation, an increase in medium temperature leads to an increase in the average crystal size (via Ostwald ripening), and a reduction in the internal
strain at relatively higher milling intensities because of the dynamic recrystallization [76]. High milling medium temperatures can be overcome by following a sequence of milling and resting or cooling with a cooling system to keep the milling temperature at desirable levels.

The Grinding medium should have enough specific gravity to apply sufficient impact force on the powder in the charge. It is desirable to have the grinding vessel and grinding medium made of the same material to prevent cross-contamination. A larger size of the grinding medium (balls) will transfer more impact energy to the powder particles and the final constitution of the powder is dependent upon the medium size [71]. Alternatively, relatively higher collision energy can be obtained if the mixtures of balls with different sizes are used because of the increase in the random motion of the grinding medium [77].

The Degree of filling the grinding vessel influences the milling intensity. Ideally, there should be enough space for the balls and the powder particles to move freely and impact each other [71]. If the quantity of the balls and the powder is very small, then the milling intensity will be very low. On the other hand, in the case of overfilling, there won’t be enough space for the milling media to move freely. Typically, half of the vessel is left empty.

The Ball-to-Powder weight ratio directly influences the collision frequency during the milling. A higher the ball-to-powder weight ratio will cause higher collision frequency and thus this will lead to an increase in milling temperature and shorter milling time [71,75].
The Temperature rise induced in the powders by the kinetic energy of the milling media and the ambient temperature are important milling variables. Besides the external heating, an inner localized temperature rise also takes place because of the kinetic energy of the milling medium. During milling, at the time of rupture, for a very short time (ns) and within a very thin surface layer (~10nm) around $10^3\text{K}$ temperature rise takes place and this thermal shock causes localized melting or structural changes in the formed new surfaces [78]. The industrial equipment used for milling process is often equipped with a water cooling jacket surrounding the milling chambers. There are too many uncontrollable and unknown variables to state any definitive model for temperature rise in milling process, but it may be possible to draw some conclusions about the magnitude of the temperature rise depending on the microstructure of the synthesized powders [63,79].

Process Control Agents (PCA) can be added to powder mixture during milling to minimize the cold welded agglomeration of ductile particles by decreasing the surface tension of the powders. The energy ($E$) required to reduce the particle size can be written as [71];

$$E = \gamma \Delta S$$

where $\gamma$ is the specific surface energy and $\Delta S$ is the increase in surface area. Therefore, a reduction in surface energy results in finer powders or the use of shorter milling times.
2.3.3 Solid State Reaction Mechanisms

2.3.3.1 Overview

Solid state reaction mechanisms include phase changes, nucleation, nuclei formation rate, formation of phase boundaries, diffusion, and diffusion controlled solid state reactions [3,55,80]. Heterogeneous solid state reactions take place between two different phases, whereas homogeneous solid state reactions take place in a single phase.

If there is a heterogeneous reaction between two solid particles, it can only progress if the particles are in direct contact [80,81]. Although those that adjoin each other will undergo solid state reaction easily, those that are not in close proximity will not react because the cations and anions from one structure have to be transported or interchanged by certain mechanisms to another structure in order to form a new compound. Therefore, the overall mechanism of solid state reaction strongly depends on the degree of dispersion and intimate mixing of the reaction solids [81]. Incomplete mixing of different solids, i.e., lack of molecular level dispersion, is the main reason for the synthesis of undesirable secondary phases.

2.3.3.2 Phase Boundary Formation and Hopping Mechanisms

As stated above, the solid state reaction can proceed to form the desirable compounds if different phases to be reacted are mixed thoroughly. When two different powders are in contact during calcination, any solid state reaction which
may proceeds can only take place at the local contact layer of the powders [3,81]. If the dominant reaction is: $X + Y \rightarrow XY$, then the solid reaction product forms a phase boundary between the contact layers as shown in Figure 2.2. This two-dimensional phase boundary model exists in a typical solid state reaction between two different crystallites with discrete compositions. When $X$ reacts with $Y$, a phase boundary forms at each interface and this $XY$ phase grows outward in the direction of $X$ and $Y$. Once the phase boundary is formed, then the reaction species of $X$ and $Y$ have to diffuse through the $XY$ phase to access its opposite phase boundary in order to react [3,81]. Therefore, the overall solid state reaction is a function of the rate of the diffusion of the $X$ and $Y$ through the phase boundary $XY$. These two diffusion rates may or may not be the same. It is assumed that the $X$ and $Y$ do not react in the middle during passing the $X$ phase because $XY$ has a certain ordered structure and the diffusion by $X$ through $XY$ occurs until $X$ encounters $Y$ on the other side, and vice versa.

![Figure 2.2](image.png)

**Figure 2.2** Schematic representation of the formation of a phase boundary [3].
In reality, the boundaries of the XY phase move in a three-dimensional direction at the expense of both of the X and Y volumes. In other words, X atoms do not move through XY to the phase boundary of X and XY. Any given atom displaces one of the X atoms in XY and the displaced X atom subsequently causes another displacement by a “hopping” motion until the other edge of the phase boundary is encountered [3]. At the opposite phase boundary, the final displaced X atom reacts with Y atom to form XY. At the same time, displaced Y atoms diffuse to the left by the same “hopping” motion.

Typically, the diffusion rate of X atoms is different from that of Y atoms. It is also important to note that a change in the crystallographic structure happens while the XY arrangement grows. For example, the reaction between particles of BaO and SiO$_2$ involves diffusion of species and their reactivity [3].

$$\text{BaO} + \text{SiO}_2 = \text{BaSiO}_3$$

At room temperature, BaO has a cubic structure, whereas SiO$_2$ has a crystallographic structure consists of a three-dimensional network of SiO$_4$ tetrahedra bound at the apices through mutual oxygen atoms. The solid state reaction between BaO and SiO$_2$ is very slow, even at elevated temperatures, because it is diffusion limited and occurs at the interface of the two phases. The only possible reaction that occurs is the diffusion of Ba$^{2+}$ atoms within the three-dimensional silica network. It is important to note that diffusion takes place primarily in one direction because the three-dimensional network of tetrahedra are not free to move and the silica tetrahedral is being rearranged to form another thermodynamically feasible structure. Therefore, the nature and the
speed of the solid state reaction strongly depends on the crystallographic structure and composition of the reacting species [80,81]. Conversely, if BaCO$_3$ is used as a reactant, the solid state reaction proceeds very fast.

$$\text{BaCO}_3 + \text{SiO}_2 = \text{BaSiO}_3 + \text{CO}_2(g)$$

The first reaction during the heat treatment is the formation of very fine nanoparticles of BaO which can react very fast to form the barium silicate.

$$\text{BaCO}_3 = \text{BaO} + \text{CO}_2(g)$$

The rate of the solid state reaction is a function of the number of nuclei produced per unit volume [3,81]. A nucleus is a crystallographic point where atoms are reacted to form the crystallographic structure of the product. When BaO is used as reactant, the number of nuclei formed per unit volume and time is small and the formation of the structure is strictly dependent on the diffusion. On the other hand, in the case of BaCO$_3$, the release of CO$_2$ leaves an atomic scale BaO which reacts with SiO$_2$ immediately when it is formed and thus the number of nuclei formed per unit volume and time increases significantly. Therefore, one way to increase the solid state reaction rates is to use a decomposition reaction to supply the reacting species in a finer and more dispersed manner. Moreover, the reduced particle size and greater homogeneity accelerate the reaction kinetics resulting in lower calcination temperatures to obtain the single phase compound [81].
2.3.4 Solid State Nucleation Processes and Mechanisms

The rate of solid state reaction is described very similar to the chemical reaction rate and the volume is used as limiting factor.

The rate of homogeneous and heterogeneous nucleation can be written as [3];

\[
\text{r (Homogeneous)} = \frac{1}{V} \left( \frac{dn_i}{dt} \right)
\]

\[
\text{r (Heterogeneous)} = \frac{1}{V_f} \left( \frac{dV_f}{dt} \right)
\]

where \(n_i\) is the initial mols of reactants, \(V_i\) is volume at a given time \(t\), and \(V_f\) is the final product.

In order to define the number of nuclei formed per unit time, the following general equation gives the volume formed as a function of time [3];

\[
V(t) = \int \{ \theta \left( \int x dt \right)^2 \left( \frac{dN}{dt} \right)_{t=y} \} dy
\]

where \(N\) is the number of nuclei formed in \(t = y\), and \(\theta\) is a geometrical factor.

If we assume that the nucleus is in spherical form;

\[
V(t) = \int \{ \theta \left( 4\pi/3 \left( \int x dt \right)^3 \left( \frac{dN}{dt} \right)_{t=y} \} \} dy
\]

Transforming the volume based analysis of nucleus formation into the rate,

Rate of nucleation = Number of nuclei formed/unit time/unit volume

If the nucleation formation process is random, it is called **homogeneous nucleation**, whereas if it is associated with foreign or phase boundary walls it is called **heterogeneous nucleation** [81]. After the nucleation, only the successful growth can lead to the formation of the desirable phases. During the growth process, kinetic factors such as reaction rates, diffusion rates of reactants, accommodation, redistribution of matter, etc., compete with the thermodynamics of the system [80,81]. The reaction and transport rates are affected by the
concentration level of reactants, temperature, and mixing. The reaction rate and impurities influence the structure and crystallinity of the prepared particles [80-82]. The produced particle morphology is influenced by nucleation & growth rates, recrystallization and the ageing processes. The growth is interface controlled when the particles are very small, however, after reaching a critical size, it becomes diffusion-controlled [81,82].

2.3.4.1 Heterogeneous Nucleation

The heterogeneous nucleation process is more commonly observed in solid state reactions [3,81]. Nucleation occurs when a cluster (or embryo) of two, three or some other small number of particles grows to a size large enough to continue to grow rather than shrink. In other words, the embryo has to form first before it is transformed into the larger nucleus, which will be the basis for the growth of the particle. The nucleation rate is the net number of clusters per unit time which grow larger than the critical size [55,81]. A critical-sized nucleus is a cluster of a size such that its rate of growth is equal to its rate of decay. Therefore, clusters which fluctuate to a size larger than the critical size will possibly continue to grow to macroscopic size, while clusters smaller than the critical size most likely will shrink. The formed new phase usually has a different parameter and crystal structure so that the transformation leads to the dimensional changes. The changes in volume and shape cannot occur freely because of the rigidity of the surrounding matrix, and hence elastic strains are induced during the transformation [3,81]. The strain energy and surface energy created by the nuclei
of the new phase increase the free energy and tends to prevent the phase transition.

The formation of a cluster Y within the crystallite X is shown schematically in Figure 2.3.

![Figure 2.3 The formation of a cluster Y within the crystallite X [3].](image)

The free energy change during the transition from X to Y will be a function of both volume and surface area & shape. Therefore, in addition to the interfacial surface energy between X and Y, the internal energy of these two phases must be defined separately. The free energy change for a general case can be given by [3]:

$$
\Delta G = N \left( G_v + \sigma \right) \lambda + \beta N^{2/3} \gamma
$$

where N is the number of nuclei, $G_v$ is the difference of free energy of Y within X, $\sigma$ is the interfacial tension or surface energy, $\lambda$ is the nuclei volume, $\beta$ is the geometrical (shape) factor, and $\gamma$ is the interface exchange energy. In this free
change equation, the first part \((N (G_v + \sigma) \lambda)\) represents the volume factor, whereas the second part \((\beta N^{2/3} \gamma)\) represents the surface factor.

For a spherical nucleus,

\[
\Delta G = 4/3 \pi r^3 N (G_v + \sigma) + 4 \pi r^2 N^{2/3} \gamma
\]

In order to define the zero surface energy condition, we have to differentiate the free energy change by the cluster radius,

\[
d(\Delta G) / dr = 4 \pi N r^2 (G_v + \sigma) + 8 \pi N^{2/3} \gamma
\]

In order to represent the zero surface energy state, we have to set the \(d(\Delta G)/dr\) and \(\sigma\) equal to zero, and this gives (assume that \(N^{2/3} / N \equiv 1\));

\[
r_{cr} = -2 \gamma / \Delta G_v
\]

which is also known as the Gibbs-Thompson equation, to define the critical radius required for a cluster to form.

The internal energy \((W_{int})\) can be found the same way,

\[
W_{int} = 1/3 (4 \pi r_{cr} \gamma) = 16/3 (\pi \gamma^3 / \Delta G_v)
\]

From thermodynamics, we know that the change in the difference of free energy of \(Y\) within \(X\) can be written as,

\[
\Delta G_v = RT \ln P / P_{eqm} .1 / V_{cr}
\]

then

\[
\Delta G_v = H_v [ (T - T_{eqm}) / T_{eqm} ]
\]

where \(V_{cr}\) is the critical volume, eqm stands for the equilibrium state, and both \(G_v\) and \(H_v\) refer to the difference between the states of \(X\) and \(Y\).

Using the equations given above, the rate of nucleation \((n)\) can be written as,
\[ n = Z \exp \left( -\frac{E_o}{RT} \right) \exp \left( -\frac{W_{\text{int}}}{RT} \right) \]

where \( Z \) is the coefficient, \( E_o \) is the cluster motion energy.

If we know the number of original cluster nuclei present, then the rate of nucleation can be written as,

\[ n = \frac{dN}{dt} = k (N_o - N)^s \]

where “\( k \)” is the rate constant and “\( s \)” is the number of steps involved in the interface change of the structure.

Therefore, the number of nuclei at any given time can be given as;

\[ N = N_o \left[ 1 - \exp \left( -kt \right) \right] \]

or the nucleation rate is;

\[ n = k N_o \exp \left( -kt \right). \]

As stated earlier, the growth of nuclei strongly depends on the motion of the phase boundary. The interface structure between the cluster (\( Y \)) and the crystallite (\( X \)) can be distinguished in terms of how well the crystalline lattices match each other. In other words, what degree the cluster lattice matches that of the nucleus and the formed particle.

A coherent interface is formed when the two lattices are continuous across the interface [3,55]. This typically happens when the interfacial phase has the same atomic configuration in both phases. When the match at the interface is not perfect, coherency can be maintained by straining one or more lattices. For large misfits, the energy increase due to the strains leads to the formation of a semi-coherent interface in which the mismatch is periodically taken up by misfit dislocations. The interfacial energy for semi-coherent interfaces arises from the
change in composition across the interface as for fully coherent interfaces, plus the dislocation energy [55,83]. The energy of a semi-coherent interface increases with decreasing the dislocation spacing, i.e., increasing the dislocation population, until the dislocation strain fields overlap. As a result, the interface becomes incoherent. The incoherent interface is somewhat similar to the High Angle Grain Boundary and is relatively independent of the orientation [83].

In the case of coherence across the interface, it is the strain energy factor which controls the shape of the particle [3,83]. For instance, a spherical shaped particle is associated with maximum strain energy but the minimum surface energy. On the other hand, a platelike particle is associated with the least strain energy and the surface energy determines the crystallographic plane on which a plate shaped precipitate forms.

In summary, the interface structure has a large effect on both the interfacial energy and the thermodynamics of change from X to Y, and the rate of nuclei formed.

### 2.3.4.2 Homogeneous Nucleation

Homogeneous nucleation is associated with a random process within a single compound whereas the heterogeneous nucleation involves more than one phase or compounds as explained above. For example, in a decomposition reaction such as a carbonate decomposing to form an oxide $\text{ZnCO}_3 \rightarrow \text{ZnO}$, the nuclei formation and growth can be explained based on the homogeneous nucleation
process because only the heat is involved in the decomposition reaction, not another compound or external reactant.

As mentioned earlier, a change in phase during the nucleation will change the free energy ($\Delta G$). This will be related to the total volume ($V$) and the total surface area ($A$) [3];

$$\Delta G = V \Delta g + A \sigma$$

where $\Delta G$ is the free energy per unit volume, $\Delta g$ is the individual free energy of nuclei, and $\sigma$ is the surface energy of the individual nuclei.

For a spherical nuclei,

$$\Delta G = \frac{4}{3} \pi r^3 \Delta g + 4 \pi r^2 \sigma$$

The critical radius for nucleus ($r_{cr}^*$) formation can be found by $d(\Delta G) / dr = 0$, i.e., the total free energy, $\Delta G$, does not change with nuclei radius;

$$r_{cr}^* = - \frac{2 \sigma}{\Delta g}$$

Combining the equation gives the change in free energy ($\Delta G^*$) at the critical radius for nucleus formation;

$$\Delta G^* = 16 \pi \sigma^3 / 3 (\Delta g)^2$$

We can write the $\Delta g$ in terms of the temperature change and the heat of transformation of nuclei ($\Delta h$);

$$\Delta g = \Delta g \left[ (T - T_0) / T_0 \right] \text{ or } \Delta g = \Delta h \left( \Delta T / T_0 \right)$$

Then,

$$\Delta G^* = 16 \pi \sigma^3 T_0^2 / 3 (\Delta h)^2 \Delta T^2$$

Boltzmann distribution can be used to describe the number of nuclei.
In general, it is difficult to obtain homogeneous nucleation because it requires a positive energy and opposes the loss of energy associated with creating the volume of the particle.

### 2.4 Chemical Synthesis and Processing

The conventional solid-state synthesis method, as was mentioned above, includes bringing the solid reactants (or precursors) such as metal oxides or carbonates into close physical contact by grinding and mixing, and to subsequently fire this mechanically activated intimate mixture at elevated temperatures to form the products by providing the required diffusion of atoms and/or ions. Additionally, the mixing and grinding steps are usually repeated to obtain an intimate mixture of the raw materials at the nano-scale and also to provide newly formed surfaces for further reactions. Long diffusion distances for the reactant atoms is one of the main disadvantages of the conventional solid state methods.

In order to overcome the inherent disadvantages of the conventional solid state routes, various modifications have been reported. Best results were obtained when the diffusion path lengths were shortened. It has been reported that, in a polycrystalline mixture of reactants with the average particle size of 10 µm the diffusion distances would be roughly 10,000 unit-cells [81]. Therefore, very thorough mixing of the starting raw materials before calcination is extremely important for the successful preparation of highly efficient phosphors.
By using freeze-drying (cryochemical), and spray-drying, it became possible to reduce the particle size to a few tens of nanometers and thus provide a more intimate mixing and alloying of reactants. In freeze-drying, reactants in a solvent are frozen by immersing in a liquid nitrogen bath and the solvent is removed at low pressures. On the other hand, in spray drying, suitable raw materials are dissolved in a common solvent and then sprayed in the form of fine droplets into a hot chamber. The solvent evaporates immediately and leaves behind an intimate mixture of reactants [84]. A subsequent heat treatment at elevated temperatures is required in order to convert the precursors to the final oxide product. The main disadvantage of cryochemical synthesis is its rather long duration. The process takes from several hours to several days depending on the amount and type of product and the geometry of the freeze-drying machine [84].

In addition to the cryochemical synthesis, solvothermal processing and hydrothermal synthesis are also used in combination with mechano-chemical or microwave activation. Hydrothermal inorganic phosphor powders can be prepared by the dissolution-precipitation process, which is based on the dissolution of precursors and precipitation (nucleation & growth) of supersaturated cations under hydrothermal conditions [85]. Hydrothermal synthesis requires considerably higher temperature and long reaction times under strongly basic conditions because the dissolution-precipitation process is governed by the dissolution rate as well as the nucleation-growth rate. Furthermore, the alkaline cations such as K and Na are known to be difficult to remove and can influence the performance of the prepared powders, for instance
the electronic properties of the ceramics [85,86]. The main disadvantage of all these techniques is that they require specific processing equipment and costly maintenance of the process.

Diffusion of matter in the liquid or gas phase is typically many orders of magnitude larger than in the solid phase, and thus, compared to solid-state synthesis, the synthesis of nano-structured functional materials can be obtained at lower temperatures when the chemical routes are used [81]. Many functional ceramic materials can be prepared in aqueous or non-aqueous solutions.

The chemical synthesis parameters such as reactant and precursor temperatures, pH, reactant concentration, and time should be properly correlated with thermodynamic factors such as saturation, supersaturation, nucleation and growth rates, surface energy, and diffusion coefficients in order to prepare the same product by ensuring the reproducibility of characteristic reactions. Moreover, special procedures such as recrystallization, purification may be used to remove any entrapped impurities from the product and to prevent the post-synthesis contamination [87].

Many laboratory-scale reactions can be scaled up to economically-desirable large quantities of material, however the laboratory-scale reaction parameters may not be linearly related to that of the large-scale reaction. Additionally, in chemical synthesis of materials, reactants and precursors should be handled carefully by considering the potential by-products and post-reaction wastes, especially when complex, reactive and hazardous materials are involved.
Chemical synthesis and processing of nanostructured materials is very broad, spanning structural and functional ceramics including optical, electronic, magnetic, biological, catalytic, and biomedical materials. Advanced functional ceramics such as phosphors are usually manufactured by conventional processes, however there is increasing interest in alternative synthetic routes for several reasons. First, undesirable chemical impurities have a deleterious effect on the luminescence efficiency so that greater purity derived from novel synthesis methods can lead to improved luminescence properties. Secondly, conventional synthesis techniques are not versatile for producing a wide range of coatings to make reproducible component fabrication because of the non-uniform powder compositions, chemical inhomogeneity and voids in the microstructure [88]. Therefore, physical characteristics of phosphor powders should allow reliable fabrication. Finally, there is no definite reason why only powder feedstocks should be suitable for manufacturing of inorganic luminescent materials.

2.5 The Chemistry of Precursor Solutions

Chemical synthesis of inorganic luminescent materials is usually performed by using chemical reactants dissolved in a liquid medium. The chemical reactant which contains the cation “M” present in the final inorganic sol or gel is called the chemical precursor. All types of precursors can be used as long as they are miscible. The chemical transformation of precursors involves a competition at the
molecular level between the reaction for the formation of open structures and the one resulting to dense solid.

There are two main groups of miscible precursors can be used for the synthesis of inorganic materials: the metallic salts and the alkoxides [39,87]. In general, metallic salts are represented by the $M_aX_b$ where $M$ is the metal, $X$ a corresponding anionic group, $m$ and $n$ are stoichiometric coefficients, e.g., magnesium chloride, $\text{MgCl}_2$. On the other hand, the general formula for the alkoxides is $M(\text{OR})_n$ where $M$ is the metal cation and $n$ alcohol groups ROH, e.g., Magnesium ethoxide $\text{Mg(OC}_2\text{H}_5)_3$. The choice of the solvent medium would be dependent on the precursor type because of the differences in the solution chemistry between the metal salts and metal alkoxides. Ceramic materials synthesized by precipitation, sol-gel, modified sol-gel routes, etc., are mainly oxides and the water is the choice as a liquid medium in order to transform the precursor. Therefore, the electronic properties of the water will take an important role in the transformation process of the chemical precursors.

There are some precursors other than the metal salts and alkoxides such as organometallic compounds in which a metal $M$ is directly bonded to a carbon atom [87-89]. Unlike oxides, it is difficult to synthesize carbides, nitrides, or sulfides directly in a liquid medium by chemical reactions. Non-oxide ceramics are typically synthesized in multi stages: first step includes the thermal decomposition of metal salts and possibly grinding. In a second step, fine particles are dispersed in a liquid medium to obtain the gelation of colloidal
particles by controlling the agglomeration. The final step is the formation of an aerosol by nucleation and growth from a vapor phase [89].

As stated above, the choice of liquid medium for the synthesis of oxide luminescent materials is the water, and thus the electronic properties of water and its effects on the chemical reactions will be detailed in the next subsection.

\section*{2.5.1 Water as a Solvent}

A water molecule is formed when two atoms of hydrogen bond covalently with an atom of oxygen. The water molecule is V-shaped in the Lewis representation as shown Figure 2.4. The oxygen atom is surrounded by four electron pairs and there is one covalent bond with each of the two hydrogen atoms and two unshared electron pairs. Therefore, based on the Valence Shell Electron Pair Repulsion (VSEPR) model, the oxygen occupies the center position of a tetrahedron and the two hydrogen atoms occupy two of its corners. In the liquid state the angle $\theta$ (H-O-H) varies from 118° to 120°, and in the gaseous state it is 104.5°.

The asymmetrical molecular configuration provides the permanent polarization of the water molecule with a dipole moment (see Figure 2.4).

$$\mu = (\delta q) \times d$$

where $\mu$ is the dipole moment, $\delta q$ is the charge, and $d$ is the distance vector. The distance vector originates at the center of the negative charges
(-δq) and ends at the center of the positive charges (+δq). For a water molecule the magnitude of the dipole moment is \( \mu = 1.85 \text{D} = 6.17 \times 10^{-30} \text{C.m.} \) (1 D = 1 Debye = \(3.336 \times 10^{-30}\) C.m) [90].

The theoretical calculations of the molecular orbitals of water can be made by linear combination of the 2s and 2p atomic orbitals of the oxygen atom and the 1s orbital of the two hydrogen atoms. Therefore, the electrons of the water molecule are placed on the four molecular orbitals with the following wave functions and energies [83,91],

\[
\begin{align*}
\psi_W(2a_1) &= 0.85 \psi_O(2s) + 0.13\psi_O(2p_z) + 0.81(\psi_{HA}(1s) + \psi_{HB}(1s)) \quad E = -36 \text{ eV} \\
\psi_W(1b_2) &= 0.4 \psi_O(2p_y) + 0.78(\psi_{HA}(1s) - \psi_{HB}(1s)) \quad E = -19 \text{ eV} \\
\psi_W(3a_1) &= 0.46 \psi_O(2s) - 0.83\psi_O(2p_z) - 0.33(\psi_{HA}(1s) + \psi_{HB}(1s)) \quad E = -14 \text{ eV}
\end{align*}
\]

Figure 2.4 Lewis representation of a water molecule (V-shaped) with asymmetrical distribution of charge [83].
\[ \Psi_W(1b_1) = \Psi_O(2p_x) \ E = -12 \text{ eV} \]

where \( \Psi_W \) is the molecular orbitals of the water, \( \Psi_O \) is the atomic orbitals of the oxygen atom, and \( \Psi_{HA} \) and \( \Psi_{HB} \) are the atomic orbitals of the two hydrogen atoms A and B, respectively. The corresponding energy diagram is shown in Figure 2.5. The electron presence probability clouds of the molecular orbitals of water shows that the 3a1 molecular orbital of water is largely delocalized outside the water molecule. The Lewis base character of the water originates from this orbital of 3a1. Therefore, the water molecule is able to donate a pair of electrons to a ligand group and build a stable “s” bond with it. However, the 1b1 molecular orbital has non-binding character, and thus has a very weak \( \pi \) donor character.

Molecular orbital wave functions can be used to estimate the partial electrical charge \( \delta q \) carried by each atom. The electronic charge density is obtained by integrating on the whole volume because the wave functions \( \Psi_M \) for an AB molecule can be obtained by linear combination of \( \Psi_A \) and \( \Psi_B \) [91],

\[ \Psi_M = a \Psi_A + b \Psi_B \]

hence,

\[ \Psi_M^2 = a^2 \Psi_A^2 + b^2 \Psi_B^2 + 2ab \Psi_A \Psi_B \]
Figure 2.5 Schematic representation of energy diagram and possible shapes of the electron presence probability clouds for the molecular orbitals of water [91].

where the $a^2$ coefficient is the electron charge density contributed by the A atom, the $b^2$ coefficient is the electron charge density contributed by the B atom, and the overlap integral of $2ab\Psi_A\Psi_B$ is equally by the A and B
atoms. The partial charge \( \delta(A) \) carried by the A atom can be calculated from the difference between the total charge density of the A atom in the molecule AB and in the isolated state. For the water molecule, a negative partial charge for the oxygen atom \( \delta(O) = -0.4 \) and a positive partial charge of \( \delta(H) = 0.2 \) was found to be for hydrogen atom. Therefore, water molecules are polarized due to the charge differences and thus it is an excellent medium to dissolve the ionic solutes. This characteristic is expressed by the coulomb electrostatic force \( F \) between two electrical charges \( q \) and \( q' \),

\[
F = \frac{1}{4\pi \varepsilon_r \varepsilon_0} \frac{qq'}{r^2}
\]

Where \( \varepsilon_0 \) represents the dielectric permittivity of vacuum \( (8.8542 \times 10^{-12} \text{ F/m}) \) and \( \varepsilon_r \) is the relative dielectric constant of the medium which is dimensionless. Water has a relative dielectric constant of \( \varepsilon_r = 78.4 \) at room temperature and it largely attenuates the coulomb interaction between two electrical charges [83,91].

Hydrogen bond formation between oxygen and hydrogen atoms of different molecules takes place because of the polar structure of water molecules. In hydrogen bonds, a hydrogen atom fluctuates by tunnel effect between two minimum energy positions separated by a very small energy barrier on the order of 20 to 40 kJ/mol. As a consequence of these hydrogen bonds, based on the molecular dynamic calculations, only very few water molecules can be isolated in the pure liquid state [92]. Most water molecules are bound by up to four hydrogen
bonds to neighboring molecules and these random groups have an average lifetime of around $10^{-10}$ s [92].

Another characteristic property of the water is that it is protic solvent [93]. Water molecules can auto-dissociate according to the following reaction,

$$2\text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{OH}^-$$

with the corresponding equilibrium constant of $K = 10^{-14}$ at room temperature. Furthermore, the hydronim ion (H$_3$O$^+$) and hydroxyl (OH$^-$) ions can also associate themselves with other water molecules by hydrogen bonds, and these two ions actually exist in liquid phase water as [H$_9$O$_4$]$^+$ and [H$_7$O$_4$]$^-$. The [H$_7$O$_4$]$^-$ is the strongest possible base in aqueous solution. Therefore, oxygen ion (O$^{2-}$) practically does not exist in water, and it immediately undergoes an acid-base protonation reaction when a solid oxide is dissolved [93].

### 2.5.2 Non-Aqueous Solvents

The polar non-aqueous solvents, similar to water, have a molecular structure characterized by a permanent dipole moment $\mu$ and by a relative dielectric constant $\varepsilon_r$. Additionally, $\varepsilon_r$ depends on the polarizability ($\alpha$) of the molecule according to the following relation [94],

$$\mu^* = \alpha E$$

where $\mu^*$ is the induced dipole moment when the molecule is exposed to an electric field $E$. 
In general, a high relative dielectric constant ($\varepsilon_r > 40$) is attributed to the existence of a permanent dipole moment [94]. Molecules with relatively high dielectric constants have good ionizing properties and thus can dissolve other polar solute. On the other hand, if the solvent’s relative dielectric constant is less than 20, it has a weak ionizing property and can dissolve less polar solute [94]. Table 2.1 illustrates a list of commonly used non-aqueous solvents with their relative dielectric constant and dipole moment.

**Table 2.1**
List of frequently used non-aqueous solvents with their relative dielectric constant ($\varepsilon_r$) and dipole moment ($\mu$) [94].

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Type</th>
<th>$\varepsilon_r$</th>
<th>$\mu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone ($C_3H_6O$)</td>
<td>Aprotic</td>
<td>20.7</td>
<td>3.00</td>
</tr>
<tr>
<td>Acetic acid ($C_2H_4O_2$)</td>
<td>Protic</td>
<td>6.2</td>
<td>0.99-1.51</td>
</tr>
<tr>
<td>Ammonia (NH$_3$)</td>
<td>Protic</td>
<td>16.9</td>
<td>0.90</td>
</tr>
<tr>
<td>Benzene ($C_6H_6$)</td>
<td>Aprotic</td>
<td>2.3</td>
<td>0.00</td>
</tr>
<tr>
<td>Chloroform (CHCl$_3$)</td>
<td>Aprotic</td>
<td>4.8</td>
<td>1.11</td>
</tr>
<tr>
<td>Dimethylsulfoxide ((CH$_3$)$_2$SO)</td>
<td>Aprotic</td>
<td>45</td>
<td>3.90</td>
</tr>
<tr>
<td>Water (H$_2$O)</td>
<td>Protic</td>
<td>78.5</td>
<td>1.85</td>
</tr>
<tr>
<td>Methanol (CH$_3$OH)</td>
<td>Protic</td>
<td>32.6</td>
<td>1.70</td>
</tr>
<tr>
<td>Ethanol ($C_2H_5OH$)</td>
<td>Protic</td>
<td>24.3</td>
<td>1.71</td>
</tr>
<tr>
<td>Formamide (CH$_3$ON)</td>
<td>Protic</td>
<td>110</td>
<td>3.39</td>
</tr>
<tr>
<td>Dimethylformamide ($C_3H_7ON$)</td>
<td>Aprotic</td>
<td>36.7</td>
<td>3.86</td>
</tr>
<tr>
<td>Tetrahydrofuran ($C_4H_8O$)</td>
<td>Aprotic</td>
<td>7.3</td>
<td>1.63</td>
</tr>
<tr>
<td>Carbon tetrachloride ($CCl_4$)</td>
<td>Aprotic</td>
<td>2.2</td>
<td>0.00</td>
</tr>
<tr>
<td>Diethyl ether ($C_4H_10O$)</td>
<td>Aprotic</td>
<td>4.3</td>
<td>1.15</td>
</tr>
<tr>
<td>Pyridine ($C_5H_5N$)</td>
<td>Aprotic</td>
<td>14.2</td>
<td>2.19</td>
</tr>
</tbody>
</table>

Protic solvents can exchange a proton whereas aprotic solvents cannot exchange a proton. Alternatively, solvents can be classified as acidic when they are able to donate a proton (Bronsted) or when they are able to accept a pair of electrons (Lewis). On the other hand, a base is able to accept a proton
(Bronsted) and to donate a pair of electrons (Lewis). Amphoteric solvents behave both as a base and as an acid. Typical amphoteric solvents include mineral acids (HNO$_3$, H$_2$SO$_4$, H$_2$S, etc.), water, the first alcohols (CH$_3$OH, C$_2$H$_5$OH, etc.), ammonia and amines (RNH$_2$, RR’NH), amides (R-CO-NH$_2$, R-CO-NHR’), and carboxylic acids (R-COOH) [89,94].

Organic solvents have been commonly used for controlling the reaction of alkoxide precursors with water in order to tailor the structure of sol-gel products [87-89].

2.5.3 Metal Salts Solutions

In ceramic material synthesis, when metal salts are used they are usually dissolved in an aqueous medium. When the metal salt MX dissolves in water, it dissociates into ions which disperse in the medium and the negative charge of the anions ($X^{z-}$) balances the positive charge of the metal cation ($M^{z+}$). Anions are sometimes considered as impurities and they must be removed in order to synthesize oxide ceramics with high purity.

When the metal salt dissolves in water, the positive charge $z+$ of the cation attracts the partial negative charge of water molecules ($\delta$(O) < 0) [89]. As a result, the cation is entrapped by a number (N) of water molecules which constitute the first solvation shell as these water molecules are the first neighbors of the dissolved cation. This water molecule based solvation shell is tightly bonded to the metal cation $M^{z+}$ so that the chemical formula of the complex formed by the solvated ion is represented by $[M(H_2O)N]^{z+}$ [83,89]. The
value of $N$ often ranges from 4 to 8 depending on the cation type. It is important to note that water also solvates the proton and the most frequent value of $N$ for proton is 4, $[H_5O_4]^+$. Similarly, anions are also solvated by water molecules. In this case, hydrogen atoms of water molecules oriented toward the anion. In ceramic processing, the solvatation of anions is not as important as that of the cations because the solvatation of cations is responsible for the hydrolysis of precursors to form a complex chemical transformations leading to the formation of oxide products [84,89].

In addition to the first solvatation shell, there is also a second shell of water molecules in which the oxygen atoms are turned toward the hydrogen atoms of the first shell. However, this second shell is not taken into consideration in the chemical evolution of the precursor due to its less rigid character [89].

2.5.4 Hydrolysis

Deprotonation of one or more water molecules surrounding the dissolved metal $M$ in the first solvatation cell is called “Hydrolysis”. As a result, the aquo ligand molecule that is bonded to the metal is either transformed into an hydroxo ligand, $OH^-$, when only one proton leaves, or into an oxo ligand, $O^{2-}$, when two protons are removed from the first solvatation shell [95].
2.5.4.1 Formation of Hydroxo Ligands

When the solvated metal has an acidic nature, water acts as a Lewis base and leads to the formation of hydroxo ligands [96]. This can be represented as,

\[
[M(OH_{2})_n]^{2+} + H_{2}O \rightarrow [M(OH)(OH_{2})_{n-1}]^{(z-1)+} + H_{3}O^{+}
\]

Acid + Lewis base = Conjugated base + Conjugated acid

This hydrated complex can lose other protons, hence the following general reaction of k consecutive deprotonation reaction,

\[
[M(OH_{2})_n]^{2+} + k H_{2}O = [M(OH)_k(OH_{2})_{n-k}]^{(z-k)+} + k H_{3}O^{+}
\]

Here, \([M(OH_{2})_n]^{2+}\) is the most acidic form of the metal complex since all the ligands are water molecules. On the other hand, \([M(OH)_k(OH_{2})_{n-k}]^{(z-k)+}\) is the most basic form of M, which is also an "aquo-hydroxo" complex.

If the dissolved metal cation has an acidic oxide, the following deprotonation reaction shows the formation of hydroxo ligands by addition of a base to the solution, \([M(OH_{2})_n]^{z+} + OH^- = [M(OH)(OH_{2})_{n-1}]^{(z-1)+} + H_2O\)

The corresponding mechanism is then [97]:

\[
\text{Nucleophile} + M^{\delta+} + H_2O \rightarrow [M-OH]^\delta \rightarrow [M-OH]^\delta + H_2O
\]
A free hydroxyl nucleophilic ion attacks one of the hydrogen atom of one of the water molecule of the first solvataion shell of the metal M. The hydrogen carries a positive partial charge (δ(H) > 0), an electron charge takes place between the hydroxyl ion and the original solated metal complex. As a result, the partial charge of the water group consisted of the incoming hydroxyl ion and the attacked hydrogen atom increases until it becomes null, i.e., δ(H₂O) = 0 and leaves the metal complex as a water molecule. This type of deprotonation reaction can successively continue as long as δ(O)_{free \text{ water}} < δ(O)_{complex} < 0.

A hydroxo ligand can still be produced with an acid when a free H⁺ ion attacks the nucleophilic oxygen of an oxo ligand [98]. In the case of water,

\[
[M\text{O(OH}_{2})_{N-1}]^{(z-2)+} + H_2O = [M\text{(OH)(OH}_{2})_{N-1}]^{(z-1)+} + OH^-
\]

Similarly, in the case of an acid,

\[
[M\text{O(OH}_{2})_{N-1}]^{(z-2)+} + H_3O^+ = [M\text{(OH)(OH}_{2})_{N-1}]^{(z-1)+} + H_2O
\]

the reaction can be represented by the following mechanism,

This reaction continues as long as δ(O)_{free \text{ water}} > δ(O)_{complex} > 0 [98].
2.5.4.2 Formation of Oxo Ligands

As described previously, an oxo ligand will form by the deprotonation of an hydroxo ligand according to the acid-base reaction to bond O$^{2-}$ anion to a metal M within an aqueous complex [98],

$$[\text{M(OH)(OH}_2]_{N-1}]^{(z-1)+} + \text{H}_2\text{O} = [\text{MO(OH}_2]_{N-1}]^{(z-2)+} + \text{H}_3\text{O}^+$$

Acid + Lewis base = Conjugated base + Conjugated acid

The product {[[MO(OH)$_2]_{N-1}]^{(z-2)+}]} is called an “aquo-oxo” since it contains both water and oxo ligands. In addition to the aquo-oxo, “oxo-hydroxo” and “oxo-hydroxo-aquo” complexes with the chemical formula $[\text{MOx(OH)}_y(\text{OH}_2)]_{N-x-y}^{(z-y-2x)+}$ are also exist in aqueous medium such as $[\text{VO(OH)}_2(\text{OH}_2)_3]^+$ vanadium complex.

2.5.4.3 Application of the Partial Charge Model to the Hydrolysis of Cations

As stated previously, chemical precursors used to produce the ceramic materials undergo chemical reactions both with water and with the other species present in the solution. Partial Charge Model (PCM) is one of the most efficient models used to predict the reactions in the solution [99,100]. It considers the electrical interactions between the partial electric charges “$\delta$” carried by each atom or molecule. The chemical potential of the electrons in an atom "I" or a molecule "C" depends on the partial electric charges $\delta(i)$ or $\delta(C)$ carried by I and C, respectively. It is also reported that the electronegativity $\chi(i)$ of an atom or $\chi(C)$ of
a molecule is directly related to the chemical potential and thus the model can be expressed in terms of the particles’ electronegativities [101]. Therefore, according to the partial charge model, the electronegativity of any complex can be calculated from its formal charge and the Allred and Rochow electronegativity, which is based on the charge experienced by an electron on the surface of an atom, of each atom present in the complex. For example, the electronegativity of an aquo-hydroxo complex \( C = [\text{M(OH)}_h(\text{OH}_2)^{N-h}]^{(z-h)^+} \) and then the number \( h \) of hydroxo ligands present in the aquo-hydroxo complex formed by the metal \( M \) can be calculated by using the Point Charge Model [83,101].

\[
\chi(C) = (\chi_M^{0.5} + N\chi_O^{0.5} + (2N-h) (\chi_H^{0.5} + 1.36(z-h)/\chi_M^{0.5} + \chi_O^{0.5} + \chi_H^{0.5}))
\]

If \( \chi(C) = \chi(H_2O) \), then

\[
\chi(H^+) = \chi(H_2O) = 2.631 - 0.02 \text{ pH} = \chi(C)
\]

after adjusting the number of \( h \) hydroxo ligands can be found by using the following equation,

\[
h = (1/(1+0.014\text{pH})) [1.36z - N(0.236-0.038\text{pH}) -(2.621-0.02\text{pH}-\chi_M^{0})/\chi_M^{0.5}].
\]

For instance, for Si \( (z =4, N = 4) \), most acidic complex is \( \text{Si(OH)}_3(\text{OH})^2^+ \) which has an \( h \) value of 3, and the calculated \( h \) 3.8. The most basic complex for the same element is \( \text{SiO}_2(\text{OH})_2 \) with an \( h \) value of 6 and the calculated \( h \) value is 5.1. These examples show that PCM estimates the number of hydroxo ligands relatively accurate.

The PCM also gives a good estimate of the domains of formation of aquo \([\text{M(H}_2\text{O)}_N]^Z^+ \) and oxo \([\text{MO}_m]^{(2m-z)^-} \) ligands. Figure 2.6 shows the domains as a function both of the formal charge \( z \) of the cation \( M \) and of the pH of the solution.
Figure 2.6 shows two extreme types of cations; those with a low formal charge e.g., \( z = 1 \) will form very basic oxides and pure aquo cations such as \( \text{Li}^+ \) ion will form \([\text{Li(OH}_2\text{)}_4]^+\). Those with a higher formal charge, on the other hand, such as \( z = 6 \) will produce very acidic oxides and pure oxo anions. For example, S forms the acidic oxide \( \text{SO}_3 \) and the oxo anion \( \text{SO}_4^{2-} \).

According to the Partial Charge Model, the electrostatic character of the hydrolysis process reveals the correlation between the first deprotonation constant \( (K_{1p}) \) of a cation \( M \) with a formal charge of \( z \), and the interatomic distance \( d \) between the metal and the corresponding oxygen atoms, \( M - O \). This relationship can be shown as,

\[
\log K_{1p} = A + 11 \left( \frac{z}{d} \right)
\]

Where \( A \) is a constant and varies depending on the metal. Metals in group I and II have the most resistance to deprotonation and hydrolysis and thus the constant
A has a very low value; $A = -22$. On the other hand, the transition metals are slightly less resistant to hydrolysis and $A = -20$. Post-transition metals such as Bi$^{2+}$ can also go extensive hydrolysis and $A$ has a higher value. Figure 2.7 shows the relationship between the deprotonation constant and the ratio charge for cations.

![Figure 2.7 Relationship between the deprotonation constant ($K_{1p}$) and the ratio charge ($z/d$) to cation to oxygen distance (M-O) for cations [98].](image)

**2.6 Sol-Gel Route**

The sol-gel processing method has emerged to become an important means of preparing inorganic oxides in last two decades. It is classified as a wet chemical method with multi-step processes involving both chemical and physical processes such as hydrolysis, polymerization, drying, and densification [89]. The term sol-gel is given to the method because of the distinctive increase in viscosity, which occurs during the gel formation step.
A sol is a stable suspension of colloidal solid particles within a liquid medium [89,103]. The solid particles are denser than the surrounding liquid environment. For a sol to be stable, the solid particles in the precursor must be small enough to have dispersion forces greater than the associated gravitational forces. The term “colloidal” was originally used for referring to molecular particles that could not pass through a dialysis membrane [90]. However, this definition does not give an accurate size range for the macroscopic particles. It has been reported that the particles in a colloidal sol must have a size range between 2 nm and 200 nm and this corresponds to $10^3$ to $10^9$ atoms per macroscopic particle [90]. In nature, particles in this specified colloidal size range is divided into three categories. They can either consist of subdivided parts of bulk matter (e.g., nanoscale silica particles), of macromolecules with adequate size to be colloidal (e.g., proteins), or of small particles that can be considered both tiny parts of bulk matter and macromolecules (e.g., lacey). In the case of the first category, the subdivided parts of bulk matter can have two thermodynamic phases and the formed sol is considered as lyophobic or hydrophobic if water is used as the main solvent.

A gel is defined as a porous three-dimensionally inter-connected solid network that expands in a liquid medium [82,87,89]. It expands in a stable fashion and is only limited by the size of the container. If the solid network is made of colloidal sol particles the gel is called “colloidal”. On the other hand, if the solid network is made of sub-colloidal chemical units, then the gel is said to be “polymeric” [104]. Formed gel properties depend on the equilibrium of the coexistence between the
solid network and the liquid medium. The solvent is present between the mesh of solid network that forms the gel and it is in thermodynamic equilibrium with the solid network. If the liquid medium is mostly composed of water, then the corresponding formed gel is a hydrogel (or aquagel) [87-89]. A hydrogel is very soft and can be easily cut with a knife. On the other hand, if the liquid phase is mostly composed of an alcohol then the gel is called as “alcogel”. A brittle solid structure, called a xerogel (or areogel), will be obtained after removing most of the liquid from the gel [87-89].

In the sol-gel process, synthesis of inorganic oxides is typically achieved from inorganic or organometallic precursors, mostly metal alkoxides. The main advantages of the sol-gel techniques are better homogeneity compared with the traditional ceramic routes, high purity, lower processing temperatures, more uniform phase distribution in multicomponent ceramic systems, relatively better size and morphological control, the possibility of synthesizing new crystalline and amorphous materials, and relatively easier preparation of thin films and coatings [87-89,104].

Important steps in sol-gel synthesis [89]:

1. **Hydrolysis**: The process of hydrolysis starts with a mixture of a metal salts or alkoxide and water in a solvent (usually alcohol) at the ambient or a slightly elevated temperature. Acid or base catalysts are added to speed up the hydrolysis reaction.

2. **Polycondensation**: The polymerization step involves condensation of adjacent molecules wherein H₂O and ROH are eliminated and metal oxide
linkages are formed. Polymeric networks grow to colloidal dimensions in the liquid (sol) state. A sol, or a solution, can be transferred to a colloidal or polymeric gel by going through the gel-point [105]. The sol abruptly changes from a viscous liquid state to a solid phase, i.e., gel.

3. **Gelation**: During the gelation step, the polymeric network link up to form a three-dimensional network throughout the liquid. The gelled system becomes somewhat rigid, which is the characteristic of the gel. The solvent alcohol and water remain inside the pores of the gel. Ageing of the gel will lead to the aggregation of smaller polymeric units to the main network progressively.

4. **Drying**: Water and alcohol are removed at moderately low temperatures (< 250 °C) during the drying stage, leaving a hydroxylated metal oxide with residual organic content. Typically, the solvent is removed supercritically, if the objective is to prepare a high surface area of aerogel powder with low bulk density.

5. **Dehydration**: Organic residues and chemically bound water is driven off during the dehydration stage which is carried out between 400 °C and 850 °C. Dehydration step yields a glassy metal oxide with up to 20% - 30% microporosity.

6. **Densification**: Dense oxide products are obtained after the calcination of dehydrated precursors at and beyond 1000 °C.
2.6.1 Advantages of the Sol-Gel Synthesis Method

There are a number of reasons to apply sol-gel processing for the synthesis of advanced ceramic materials. In addition to the preparation of materials with oxide compositions, the sol-gel route allows the production of new hybrid organic-inorganic materials which do not exist naturally [89]. Temperature ranges required for the first steps are relatively low and thus the thermal degradation of both the material itself and any entrapped species is minimized. This minimizes the chemical interactions between the material and the container walls compared to the conventional high temperature synthesis methods.

High-purity products can be obtained by simply purifying the precursors either by distillation, crystallization, or electrolysis [87,89]. Since organometallic precursors with different metals are usually miscible, homogeneous controlled doping is very easy to obtain. Another advantage is the formation of a stable combination of the solid colloidal state with a liquid medium. This avoids any pollution by the eventual dispersion of dust. This explains why the biggest industrial application of sol-gel synthesis is for nuclear fuels [83].

The chemical conditions during the sol-gel synthesis are very mild. Hydrolysis and condensation can be catalyzed by acids and bases without any extreme pH conditions. The nucleation and growth of the primary colloidal particles can also be controlled in order to tailor the shape, size, and size distribution of the particles [87]. The structure of sol-gel ceramics may be as easily controlled as the size of the produced particles. Many new types of amorphous or semi-vitreous glasses such that were not feasible by the conventional quench
techniques can be synthesized by the sol-gel route. Using functionalized precursors, covalent attachment of organic and biological compounds to porous glass structures is also feasible. By controlling the ageing and drying conditions, further pore size and mechanical strength control may be achieved. Since liquid precursors are used, it is possible to cast ceramic materials in a range of complex shapes and to produce thin films or fibers without the need for melting. Sol-gel processing offers the most significant advantages for mixed oxide systems in which the chemical homogeneity of the various elements may be controlled at atomic scales. This condition can not be, however, obtained with conventional solid state methods when solid powders are mechanically mixed [106].

2.6.2 Limitations of the Sol-Gel Synthesis Method

Despite all these advantages, the sol-gel synthesis method has some inherent limitations. The precursors, especially metal alkoxides, are often expensive and sensitive to moisture [89,106]. Ageing and drying steps are very critical and time-consuming. The problems of dimensional change during densification, and of shrinkage and stress cracking on drying also require careful attention [89]. The sol-gel synthesis of ceramic materials can not presently compete for the mass production of some mass-manufactured materials such as window glass in which conventional methods are preferred because less expensive raw materials can be used. Nonetheless, sol-gel processing is one of the best routes for advanced technical ceramics.
2.7 Modified Sol-Gel Synthesis Routes

The processing steps in the sol-gel technique outlined above may not be strictly followed in practice to synthesize inorganic luminescent materials. For example, many multi-component phosphor powders can be prepared by a modified sol-gel route without preparing inherently unstable metal alkoxides.

Although it has been known that alkoxy-derived gel powders are very fine and reactive [107,108], in multicomponent systems such as cordierite ceramics, the difference in hydrolysis rates of each alkoxide causes inhomogeneity in the resultant oxides [109]. Yoldas [110] demonstrated that the degree of hydrolysis of alkoxides could be controlled by hydrolysis temperature, concentration of alkoxide, the type of catalyst, and the water amount. However, it is very difficult to determine the optimum conditions for hydrolysis. Another disadvantage is that the gel-derived compacts often show crystallization before the complete densification, which leads to large pores within the sintered body [89,108]. For example, in the case of SiO$_2$ - containing gels, it is very difficult to remove the remaining pores after the commencement of crystallization because densification by atomic diffusion is much slower than densification by viscous sintering, which is the dominant mechanism for densification before crystallization [89,111]. Hence, the kinetics of viscous sintering should be faster than those of crystallization in order to produce dense sintered bodies. It has been found that the modified sol-gel routes such as the Pechini process [112], PVA – metal ion complex [113] routes were found to be very effective in solving the densification
problems of the synthesized powders by producing stable and atomistically-homogeneous multi-oxide powders.

The modified sol-gel route process has been extensively studied for the synthesis of various advanced functional ceramic powders due to the merits of fine size, relatively-easier composition control, better homogeneity, and low processing temperatures in comparison to the conventional solid state reaction processes. For these reasons, modified sol-gel techniques were employed in the present work to prepare pure, and efficient phosphors with the desired stoichiometry.

2.7.1 The Pechini Process as a Solution – Polymerization Route

One of the most successful synthesis techniques for single-phase mixed-oxide powders is the so-called Pechini process [112]. In general, the Pechini process is considered a solution – polymerization method [114] and it relies on the ability of κ-pyroxycarboxylic acids such as citric and lactic acids to chelate metal ions in combination with polyhydroxyl alcohols such as ethylene glycol to form a resin through condensation reactions. [115,116]. The synthesis process employs the Pechini resin as the polymeric carrier of the per-ceramic powders. The resin consists of citric acid as the chelating agent and ethylene glycol to promote polymerization during the esterification process. The esterification reaction leads to the formation of polymerized resin that has the various cations distributed uniformly in stoichiometric proportions. The polymerized resin with the chelated cations is also called a “pre-ceramic powder”, which can be calcined at elevated
temperatures in order to produce the oxide powders. In the Pechini method, the cation sources are usually selected from the nitrate salts of the metals, dissolved, and mixed in stoichiometric proportions in the aqueous resin solutions. The molar ratio of citric acid to ethylene glycol that gives the best powder characteristics is 1:1 [117]. After mixing the stoichiometric amounts of all components, the pH of the solution must be maintained at an acidic level in order to prevent precipitation [118].

It has been proposed that the chelation of the dissolved metal cations by the carboxylic acid end of the citric acid (step I) [119] as shown in Figure 2.8.

Figure 2.8 Proposed chemical reactions for the solution – polymerization (Pechini) method [119].
The polyesterification reaction follows the chelation of metal cations after heating at relatively low temperatures (<300°C) (step II).

It is commonly accepted that the chelating action of the organics is responsible for the formation of a stable, atomistically-homogeneous, pre-ceramic, multi-cation, precursor. However, there are some studies related to the synthesis of different multi-oxide material systems using the Pechini method, which revealed that the resin can accommodate higher amounts of cations than it can chelate in the aqueous solutions [119].

### 2.7.2 The PVA-metal ion complex route

Although several chemical routes have been used successfully for the preparation of multi-oxide ceramic powders, the considerations of affordability and versatility of a preparation method still remain as major challenges. The use of polymers to prepare multi-oxide ceramics has gained great interest over the last decade. Resin intermediates based on a starch-type organic precursor were successfully used to replace the citric acid and ethylene glycol in the Pechini process for the synthesis of complex ceramic oxide powders [120]. Several ferrites and garnets prepared by this method with fine and pure structures [121-123]. In these synthesis methods, polyvinyl alcohol (PVA) was used to cover the metal cation within the solution so that precipitation from the synthesis solution was prevented [113,124]. The nitrate ions have the role of oxidizing agents for the decomposition of PVA [125]. Chandramouli et.al. [126] used a ratio of metal cation to vinyl alcohol monomer units of 1:2.5 and suggested that during the
decomposition of nitrate salt, the nitrogen dioxide combines with water to form nitric acid.

Polyvinyl alcohol (PVA) is produced and available in fully or partially hydrolyzed forms. Fully hydrolyzed PVA has a degree of hydrolysis of 98% or higher, whereas partially hydrolyzed PVA is less than 98%. The physicochemical properties of PVA depend on its degree of polymerization, degree of hydrolysis, and the distribution of the degree of hydrolysis [127]. The hydroxyl groups reduce the solubility of the PVA because of the strong hydrogen bonding between the intra-molecular and inter-molecular OH groups. The intra-molecular and inter-molecular bonding can be reduced if residual acetate groups are hydrophilic.

During pyrolysis, PVA decomposes as a result of dehydration and depolymerization reactions. Dehydration of the PVA molecule occurs at 245 °C and the reaction is represented as [127]:

\[
-\text{(CH} - \text{CH}_2\text{)}_n - \text{CH} - \text{CH}_2 \xrightarrow{} -\text{(CH} = \text{CH})_n - \text{CH} - \text{CH}_2 - + n \text{H}_2\text{O}
\]

\[
\text{OH} \quad \text{OH} \quad \text{OH}
\]

After the water releases at 245 °C, the polyenes are finally broken into carbons and hydrocarbons at 450 °C. When PVA is heated in air, ketone groups form as a result of the oxidation of the unsaturated polymeric residue. PVA can form complexes with metal cations because of the presence of hydroxyl functional groups [127a]. This provides a homogeneous distribution of cations within the precursor solution without any precipitation.
As mentioned above, to date it has been suggested that chelation, or the chemical fixation of the cation by the organic molecule, is the prerequisite for the formation of a stable – homogeneous multi-cation precursor. However, it has also been reported by several research groups that the precursors were able to carry a higher amount of cations than they could chelate during the synthesis of multi-oxide ceramic using Pechini precursors with very high metal ion:monomer ratios [113,119]. It has also been reported that a fine, pure multi-oxide powder synthesis is possible with only PVA solution where the chelation is not necessary for the formation of a stable precursor to form the desired ceramic phases [118,119,128]. A generic flowchart for the PVA – metal ion complex route is given in Figure 2.9.

Unlike the Pechini process, which involves chelation and polymerization, the PVA – metal ion complex route primarily involves steric entrapment of cations into the polymer network [113,118]. Its polymeric network structure ensures the homogeneous distribution of metal ions and inhibits their segregation or precipitation from the solution [129]. Water is able to diffuse through the polymer and stretch it, and the long chain polymer prevents contact between cations and limits their precipitation and agglomeration. The cationic entrapment mechanism is schematically illustrated in Figure 2.10.

The spatial distribution of cations depends on the relative amount of dissolved polymer and its molecular length. It has been suggested that the homogeneous steric entrapment between the hydroxyl groups of the polymer and cations is enhanced by the weak hydrogen bonding in an aqueous medium [121,130]. The
length and amount of PVA polymer chains affect homogeneity and distance between metal ions in the organic-inorganic precursor during the steric entrapment mechanism [121,130]. The PVA – metal ion complex process produces carbonaceous species that give heat through combustion, and thus a single-phase, pure, highly-reactive, and homogeneous powder at molecular level is obtained at relatively-low calcination temperatures [121,131]. Several different groups of functional and structural oxide ceramics such as calcium aluminate (CaAl$_2$O$_4$) [119], lanthanum and yttrium aluminates (La$_4$Al$_2$O$_9$, Y$_4$Al$_2$O$_9$) [132], calcium silicates (Ca$_2$SiO$_4$, Ca$_3$SiO$_5$) [130], cordierite (Mg$_2$Al$_4$Si$_5$O$_{18}$) [131], yttrium aluminum garnet (Y$_3$Al$_5$O$_{12}$) [118] etc., have been successfully produced by PVA – metal ion complex route.

Figure 2.9 Generic flowchart of the PVA – metal ion complex route.
$\text{Zn}_2\text{SiO}_4:\text{Mn}$ and $\text{Zn}_2\text{SiO}_4:\text{Mn,Mg}$ green-emitting phosphors were prepared by the PVA-Metal Ion Complex Route and Photoluminescence & materials characteristics were presented in Section 3.

![Figure 2.10](image)

**Figure 2.10** Schematic illustration of cationic entrapment with (a) non-optimal amount of polymer and (b) optimal amount of polymer [130].

### 2.7.2.1 Polymeric Stabilization

Polymeric stabilization is a generic term used to describe all aspects of the stabilization of metal ions and colloidal particles by organic polymer molecules. This principle has been used for more than 4500 years, since the Egyptians
applied it empirically in the production of ink [133]. The polymeric stabilization mechanism has been used for a variety of industrial products such as inks, paints, glues, food emulsions, pharmaceuticals, detergents, (etc.), and has very important role in many biological systems [133]. In the processing of ceramics, this stabilization technique has been commonly used for the production of stable suspensions of the ceramic powders during consolidation techniques such as slip casting and tape casting [81,84].

When polymeric macromolecules are adsorbed on colloidal particles, steric interactions will take place as a consequence of the interaction between the polymer macromolecules and the solvent. Therefore, a mathematical explanation of the steric entrapment energy can be given by using the theory for polymer solutions derived by Flory and Huggins [134,135].

### 2.7.2.2 Characteristics of Polymer solutions

In general, the solubility of a polymer in a given solvent depends on the temperature & pressure of the system and the molecular weight of the polymer. It will dissolve in a solvent if at constant temperature and pressure the total Gibbs free energy decreases, and thus the necessity for the polymer solubility is given as [136],

\[ \Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}} < 0. \]

For most polymers, the enthalpy change on mixing is positive, and hence the change in entropy should be sufficiently positive if mixing takes place.
There are two main phenomena which dictate the behavior of a polymer in a solvent. First, Brownian motion causes each polymer macromolecule to extend in the solvent. This extension is limited by the finite length of each polymer chain and its elasticity. Second, interactions such as the Van der Waals interaction takes place between the atoms in the polymer chain itself, and between the atoms in the chain and the atoms in the solvent [136]. All these interactions indicate the affinity of the polymer (as a solute) for the solvent.

According to the classical Flory-Huggins theory, the change in total Gibbs free energy of dilution of a polymer ($p$) in a solvent ($s$) is [134,135]

$$\Delta G_{\text{mix}} = k_b T \left[ n_s \ln(1-\Phi_p) + n_p \Phi_p + \chi_s n_s \Phi_p^2 \right],$$

where $n_p$ and $n_s$ are the number of polymer and solvent molecules, respectively, $\Phi_s = 1 - \Phi_p$ are their volume fraction and $\chi_s$ is a dimensionless number.

The molar chemical potential of the solvent can be calculated using

$$\mu_s - \mu_s^0 = R T \left[ \ln(1-\Phi_p) + \left(1-1/x\right) \Phi_p + \chi_s \Phi_p^2 \right],$$

where $x$ is the ratio of the polymer volume to the solvent molar volume ($=V_p/V_s$).

In the dimensionless coefficient “$\chi_s$”, a separate contribution of enthalpy “$H_s$” and a contribution of entropic nature $S_s$ were associated with the partial enthalpy and entropy of dilution [137],

$$\Delta H_s = R T H_s \Phi_p^2$$

$$\Delta S_s = R S_s \Phi_p$$

These relationships of the enthalpic and entropic nature contributions with the $\chi_s$ are

$$\chi_s - 1/2 = H_s - S_s = - S_s \left(1-\theta/T\right),$$
where $\theta$ is known as the *Flory Huggins’ theta temperature*, which is a characteristic of the solvent-polymer couple.

For a large value of $\chi_s$, the solvent will behave as a poor solvent for the polymer because of the large increase of the free energy of mixing ($\Delta G_{\text{mix}}$). On the other hand, a low value of $\chi_s$ can give a negative $\Delta G_{\text{mix}}$ and thus the solvent will dissolve the polymer. A critical value “$\chi_{sc}$” of the transition between the high and low $\chi_s$ values shows the stability of the polymer – solvent system. When $\chi_s > \chi_{sc}$, there will be a separation of solution into two phases. For endothermic solution ($\Delta H_s > 0$), $\chi_s$ decreases as the temperature increases, which results in better mixing.

As mentioned earlier, temperature is also an important parameter and when $T = \theta$, there is no net interaction between the polymer chains and the solvent. On the other hand, when $T > \theta$, a thorough mixture of the polymer in the solvent will occur. The polymer macromolecules have a tendency to extend in the solvent in order to have good contact between the polymer and the solvent, and thus it forms a stable solution. On the contrary, when $T < \theta$, the polymer chains contract and agglomerate within the solution in order to minimize the contact between the polymer and the solvent, and such a solvent acts as a poor solvent for the polymer.

In addition to dependence on the temperature, the volumetric proportion of the polymer will also affect the interaction between the polymer and the solvent. If the solute volume proportion ($\Phi_s$) is beyond the critical value of the solute volume proportion ($\Phi_{sc}$), phase separation will occur. The critical value of the solute
volume proportion \( (\Phi_{s2}) \) and \( \chi_{sc} \) can be calculated from the following equations [138]:

\[
\frac{d\mu_s}{d\Phi_p} = \frac{d^2\mu_s}{d\Phi_p^2} = 0,
\]

and thus \( \Phi_{s2} = \frac{1}{1+x^{1/2}} \), and \( \chi_{sc} = \frac{1}{2} + \frac{1}{x^{1/2}} + \frac{1}{2}x \).

These results indicate the presence of an upper critical temperature as illustrated in Figure 2.11.

\[\text{Figure 2.11} \text{ Liquid phase diagrams for polymer solutions indicating an upper critical solution temperature [138].}\]

Although it may be only a qualitative comparison between the observed phase diagrams and those calculated, it contributes to our understanding of the behaviors of polymers in solution.

Flory [138], alternatively, established the “State Equation Theory” which depends on a derivation of the thermodynamic equation of state of the solution from a general partition function. State equation theory requires seven independent parameters, determined experimentally. The advantage of the State Equation
Theory relies on the incorporation of the individual characteristics of the components present in the solution and the ability to explain the possible occurrence of a lower critical solution temperature qualitatively. However, similar to the Flory-Huggins theory, in the case of the State Equation Theory, the agreement between the experiments and the theory is only qualitative.

### 2.7.2.3 Steric Entrapment of Metal Ions

As indicated before, when polymeric macromolecules are adsorbed on the colloidal particles, steric interactions play a significant role as a consequence of the polymer-solvent interaction. It is well known that when the adsorbed polymer only anchors by one end to a particle, it will produce either a repulsion or an attraction between two particles depending on the temperature of the solution. When \( T > \theta \), where \( \theta \) is the Flory-Huggins theta temperature of the polymer-solvent couple, the polymer macromolecules have a tendency to extend in the solvent and this leads to a good contact between polymer and solvent. If these polymers have one end of their chains adsorbed on a colloidal particle, they will make a swollen polymer shell around the particle [136,137]. They stay in the swollen state due to the penetration of the osmotic diffusion flow of the solvent in between the polymer macromolecules. In this case, particles will remain dispersed in the solution because the polymer in both shells tends to avoid interpenetration to maximize the contact solvent-polymer when colloidal particles happen to collide. Hence, the polymer is responsible for an effective repulsion between the particles within the solution [136,137]. This phenomenon is of
potential use when trying to produce well-dispersed particles in a sol-gel reaction process.

On the other hand, when $T < \theta$, the polymer macromolecules will contract and agglomerate with each other in order to minimize polymer-solvent contacts. When two colloidal particles with adsorbed polymers happen to collide, particles will be agglomerated because the polymer in both shells remains in contact. Therefore, the polymer is responsible for the attraction between the colliding particles.

In summary, the adsorbed polymer shell will have a tendency to swell when the temperature of the polymer-colloid-solution system is heated to relatively higher temperatures i.e., $T > \theta$. As a result, particles will repel each other. On the other hand, when $T < \theta$, particles will attract each other because of the contraction of the polymer shell.

### 2.7.3 The Sucrose-metal ion complex route

Sucrose ($C_{12}H_{22}O_{11}$) is the most abundant pure organic molecule produced at the industrial scale (>1.25 Mt/yr) from renewable resources such as sugar cane and sugar beets [139]. It is a disaccharide constructed with a glucose moiety and a fructose one connected at their anomeric carbon atoms as shown in Figure 2.12. Derivatisation of sucrose by oxidation, esterification, halogenation, isomerization, and fermentation leads to many potential applications such as detergents, surfactants, sequestrants, and sweeteners [140].
Many research studies have been done with respect to the conformation of and hydrogen bonding in the sucrose molecule. Brown et al. [141a] has performed the single crystal X-Ray analysis to determine the conformation of the sucrose molecule. It has been reported that, in the crystal structure, the glucose part of the molecule is in the $^{4}C_1$ conformation and the fructose moiety exists in the $^{4}T_3$ twist conformation. The conformation of sucrose in solution and the question of whether solvation would disrupt hydrogen bonding characteristics of the molecule has been the subject of many discussions. There are two important hydrogen bonds between 6'-OH of fructose and the ring oxygen of glucose (1.89 Å), and from 1'-OH$_f$ to O-2$_g$ (1.85 Å) which are present in each sucrose molecule. Bock et al. [142], and McCain et al. [143], reported that the two above-mentioned hydrogen bonds are still intact in aqueous solutions, based on $^{13}$C NMR spin-lattice experiments together with hard-sphere exo-anomeric calculations. However, Raman spectroscopy analysis was in conflict with this result for dilute sucrose solutions [144]. The presence of an extra hydrogen bond between O-2$_g$
and OH-3' was demonstrated by isotope-shift measurements with SIMPLE \(^1\)H-NMR. This extra hydrogen bond is in competition with the one between O-2\(\text{g}\) and OH-1'\(\text{f}\). Additional NMR work and MM calculations on sucrose and 2-deoxy-sucrose showed evidence of a dynamic equilibrium between several conformations of sucrose in solution [145]. Tran et al. [146], however, identified three low-energy regions for sucrose identified by constrained conformational energy minimizations.

Sucrose is a typical non-reducing sugar and it hydrolyses to fructose and glucose in the presence of acids in experimental salt solutions [139]. This allows the reduction of the metal salts by glucose and fructose. The hydrolyzed sucrose products, glucose and fructose, are successfully utilized to reduce the metal salts into metal particles [147]. Glucose is a stronger reducing agent compared to fructose and it gives smaller particles initially, but these smaller particles do not generate the required repulsion in order to have the colloidal stability, and coalescence will be rapid [148]. Such particles cannot repel, and coalescence is irreversible according to the normal Derjaguin-Landau-Verwey-Overbeek (DLVO) system [149]. On the other hand, fructose is a relatively weaker reducing agent than the glucose and the initial particle diameter is larger. For the larger particles, however, the barrier to coalescence is large and the colloid particles will experience weak flocculation forces [148].

It is well-known that sucrose is readily soluble in water and, in the acidic conditions, -COOH and –OH functional groups will form, which hence can lead to stable binding with metal ions in homogeneous solution. Therefore, sucrose can
also act as an efficient metal ion stabilizer to produce fine ceramic particles. In recent years, several attempts have been made to prepare fine nanoceramic powders using sucrose as a chelating agent and fuel [150-152].

The generic flow chart for the preparation of nanoceramic powders by using the sucrose templated sol-gel route is shown in Figure 2.13.

**Figure 2.13** Flow chart for the preparation of ceramic nanopowders by the sucrose templated sol-gel route.

The hydrolysation of sucrose and the complexing processes can be represented by the following main reactions.

Firstly, disaccharide sucrose will hydrolyze into glucose and fructose with the catalysis of protons provided by the nitric acid according to the following reaction [153,154],

\[
C_{12}H_{22}O_{11} + H_2O + H^+ \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6
\]
The nitric acid also prevents the re-crystallization of sucrose in aqueous solution. The primary hydrolysis products, fructose and glucose, will be further oxidized by nitric acid according to,

\[
\begin{align*}
\text{CH}_2\text{OH-(CHOH)}_4\text{-CHO} + \text{HNO}_3 & \rightarrow \text{COOH-(CHOH)}_4\text{-COOH} \\
\text{CH}_2\text{OH-(CHOH)}_3\text{-CO-CHO} + [\text{O}] & \rightarrow \text{CH}_2\text{OH-COOH} + \text{CH}_2\text{OH-(CHOH)}_2\text{-COOH}
\end{align*}
\]

The product of the oxidation of glucose sugar is known as aldose which is a saccharic acid. On the other hand, fructose sugar (ketose) will be oxidized into two types of hydroxyl acids; glycolic acid and trihydroxy-butyric acid [154]. These oxidation products contain the functional groups of –COOH and –OH, which would complex the dissolved metal ions to prevent the precipitation. The saccharic acid with two –COOH groups will interact with the metal ions to form stable –COOM\(^{3+}\), while the hydroxyl acid can complex with metal ions through the carboxyl groups. The characteristic complexing equations are;

\[
\text{COOH-(CHOH)}_4\text{-COOH} \rightarrow \text{COOM}^{3+} -(\text{CHOH})_4\text{-COOM}^{3+}
\]

\[
\text{CH}_2\text{OH-(CHOH)}_n\text{-CHOOH} \rightarrow \text{CH}_2\text{OH-(CHOH)}_n\text{-COOM}^{3+} \quad n=0.2
\]

Additionally, the –OH groups can also chelate the metal ions within the solution. Hydroxyl groups, however, have rather weak chelating ability when compared with carboxyl groups. As a result, homogeneous aqueous solutions will form with metal ions well-complexed on the molecular-scale and no precipitation will form during the evaporation stage. The metal – ion complex will decompose during
heating of the precursor by releasing nitrous and carbonaceous gases and heat will be generated, which helps the formation of nano-scale particles. The Sucrose-Metal Ion complex route was used to synthesize blue-emitting novel phosphors, Ce$^{3+}$-doped SrZnO$_2$. Materials characterization and Photoluminescence results were reported in Section 4.

2.7.4 The PVA-Sucrose-metal ion complex route

An aqueous sucrose solution in the presence of nitric acid will be oxidized to saccaric acid, and it has been reported that the saccaric acid is an excellent chelating agent for metal ions [139-147]. PVA (10-20 mol%), in the presence of saccaric acid at medium temperatures (∼200 °C), undergoes a polyesterification (polycondensation) reaction [155]. A schematic representation of this reaction is shown in Figure 2.14. During heating at <250 °C, a polycondensation reaction occurs and most of the water molecules are removed, resulting in a highly-viscous polymeric resin. The utility of the polymeric approach comes from the chemical bonding of the cations in to the polymeric chains and ensures good molecular-level mixing of the cations throughout the polymeric network. Further heat-treatment of the polymeric resin at <250 °C causes charring. It is assumed that the metal ions are homogeneously distributed into the charred mass and oxidized at relatively low temperatures into the stoichiometric nano-crystalline ceramic materials.
The PVA-Sucrose-Metal Ion complex route was used to prepare the $M_3Al_2O_6$ (M = Ca, Sr, Ba) red-emitting phosphors and characterization results with optical properties were presented in Section 4.

![Chemical Structures](image)

**Figure 2.14** Aqueous chemistry of Sucrose-PVA-metal ion complex route [155].

### 2.7.5 The Adipic Acid-metal ion complex route

Adipic acid is an industrial chemical used for the manufacture of nylon-6,6, which is used in carpet fibers, tire reinforcements, upholstery, auto parts, and other products [155a]. More recently, adipic acid has also played an important role in the elimination of the use of chlorofluorocarbons during the manufacture of solid state electronics [156]. Mild solutions of adipic acid are used instead of conventional resin flux to remove metal oxides from circuit boards in preparation for soldering. The worldwide industrial use of adipic acid is around 2.2 million metric tons per year [157]. It is a large molecule with two carboxylic groups as shown in Figure 2.15.
The metal ion-adipic acid gel precursors can be obtained when the carboxylic groups in the adipic acid interacts with the dissolved metal ions so that they become very viscous gelled polymeric resins. Lee et al. [158] used adipic acid as a chelating agent and fuel in the synthesis of spinel LiMnO$_2$ cathode materials for lithium secondary batteries with high energy density. Thirunakaran et al. [159] synthesized novel cathode materials by using adipic acid as the chelating agent. However, to the best of our knowledge, no attempt to use the adipic acid as a templating agent to synthesize luminescent ceramic materials has been reported. The synthetic procedure of polycrystalline nano powders by adipic acid assisted sol-gel method is shown in Figure 2.16.

A stoichiometric amount of metal salts will be dissolved in DI water and mixed well with an aqueous solution of adipic acid. A slow evaporation at 80 °C to 90 °C for 8 to 12 hours will lead to the formation of a transparent sol. Further drying of the sol yields metal ions-adipic acid gel precursors.
Figure 2.16 Flow chart for the preparation of ceramic nanopowders by the adipic acid templated sol-gel route.

Adipic acid not only functions as a chelating agent but also provides the heat of combustion for the synthesis of metal oxides [158]. In addition to the pH, the relative concentration of adipic acid within the gel precursor affects the powder characteristics. It has been reported that the smaller the amount of adipic acid used in the preparation of gel precursors, the shorter the cation-to-cation distance, and hence the higher the probability of the crystallization and agglomeration between the cations [158-160]. This may lead to lower homogeneity in the gel precursors and less combustion heat will be generated from the adipic acid. Conversely, the homogeneity of the gel precursors will be better with large amounts of adipic acid, because more cross-linked gel precursors will hinder the cation mobility and a large amount of combustion heat will be generated from the adipic acid content. This will lead to the formation of
the metal oxide phase together with fine powders because of the void volumes formed by the evolution of CO and CO$_2$ gases during the thermal decomposition of adipic acid [158-161]. Furthermore, the increased amount of combustion heat increases the crystallinity of the synthesized metal oxides.

The adipic acid templated sol-gel route was used to synthesize the novel blue-emitting SrZnO$_2$:Pb phosphors. Photoluminescence and materials characterization results were reported in Section 4.

2.8 Characterization of Luminescent Powders

2.8.1 Physical Characteristics

The powder characteristics, as discussed earlier, have a significant influence on the luminescence properties. Synthesized luminescent powders are composed of discrete particles and each particle may be single crystal or contain grain boundaries. Particle distribution and the sizes of luminescent particles are very critical because many of their physical and some of the chemical properties are dependent upon particle size. The most important physical properties of a luminescent powder are its particle size distribution, particle morphology, and the state of agglomeration.

2.8.1.1 Dynamic Light Scattering

The scattering of light from a monochromatic source has been commonly used to determine the particle size and particle size distribution. Powder particle size
distributions were measured in this work by using Dynamic Light Scattering techniques. When a beam of light strikes an assembly of particles, some fraction of it is absorbed, some is scattered, and some is transmitted. The variation in the intensity of the forward-scattered light is used to find the particle size. Smaller particles scatter a small and definite amount of light through a fixed but larger angle. On the other hand, larger particles scatter a greater amount of light but through a smaller angle.

In general, light-scattering instruments for particle size analysis utilize measuring techniques that give the particle size based on the volume or projected area of the particle.

The particle sizes and size distributions were measured using a dynamic light scattering (DLS) on a Microtrac® Nanotrac NPA 250 instrument.

### 2.8.1.2 X-Ray Diffraction and Line Broadening

X-ray diffraction (XRD) is often an appropriate starting point for phase identification for inorganic luminescent materials. It reveals long-range structural order, but not oxidation states.

In X-ray diffraction, a collimated beam of X-rays, with wavelength $\lambda = 0.5 – 2 \text{ Å}$, is incident on a specimen and is diffracted by the crystalline phases present in the specimen according to Bragg’s law ($n \lambda = 2 d \sin \theta$, where $d$ is the spacing between atomic planes) [162]. Typically, the intensity (a.u.) of the diffracted X-rays is measured as a function of the diffraction angle ($2\theta$) and the specimen’s
orientation. This characteristic diffraction pattern is used to identify the sample’s crystalline phases (i.e., long-range structural order) and to measure its other structural properties such as the size and orientation of crystallites and strain [55,162]. X-ray diffraction techniques can also be used to determine the concentration profiles, film thicknesses, and atomic arrangements in amorphous materials and multilayers [80].

It is possible to determine the number and type of all major phases present. However, the structure of individual regions such as grains, inclusions, interfacial layers, etc. cannot be easily be identified by XRD techniques because of the lack of spatial resolution [55,80]. Detection of a second phase amounts is usually on the order of several percent for favorable conditions and much less for very complex mixtures with a very similar crystal structure and size, or those containing amorphous or micro-crystalline materials.

The X-ray scattering power of the lighter elements is very low and this limits the ability to accurately determine numbers or positions of such important atoms such as carbon, oxygen, and hydrogen in the crystalline lattice [80,162]. In addition, it provides little information about the nature of the bonding and site symmetry for amorphous or microcrystalline materials.

Although the penetration depth of X-rays is significantly greater than for optical wavelengths, measurements by X-ray diffraction are still largely restricted to the surface layer of the powders [162]. Penetration is typically a few µm but is material dependent. In order to detect interior phases, crushing, sectioning, etc. are required.
Compounds that are present in small localized quantities such as luminescence centers obtained by small impurities often cannot be detected by X-ray methods. Detection limits are material dependent, but it is typically ~3% in a two phase mixture, and it can be reduced to ~0.1% with synchrotron radiation [80]. Crystalline structures of produced powders in these studies were identified using X-ray diffraction (XRD).

**X-Ray diffraction line broadening** is often used to determine a powder's average crystallite size and is applicable when crystallite sizes are less than 1000 Å. The origins of the X-ray line broadening effect, like the other diffraction effects of crystals, can be explained by the reciprocal lattice [162]. In principle, the width of the diffraction peak is inversely proportional to the size of the crystal. As the size of the crystal increases, the width of the peak decreases and diffraction peaks becomes sharper. In addition to crystallite size, other factors such as lattice strain and the presence of crystal defects also can produce broadening of the X-ray peaks. However, the diffraction peak broadening due to size will be the dominant factor for crystallite sizes less than ~20 nm.

The crystallite size, D, is calculated by using the Scherrer equation [162],

$$D = \frac{(A \lambda)}{(\beta \cos \theta)},$$

where $A$ is a constant (~0.9), $\lambda$ is the characteristic wavelength of the X-rays, $\beta$ is the width of the diffraction peak at half-maximum , and $\theta$ is the Bragg angle of reflection.

The crystallization behavior and crystal structure of the synthesized phosphor powders were checked by using a room temperature X-Ray Diffractometer
(Philips PW 2273) with CuK\textsubscript{\alpha} radiation (\(\lambda = 1.5406 \, \text{Å}\)) at 40 kV and 30 mA between 2\(\theta\) values of 10° and 70° with a step size of 0.02°. The crystal size measurements were made by using the Williamson-Hall technique based on the broadening of the diffraction peaks with the built-in XRD software program (Jade 6.1).

2.8.1.3 Electron Microscopy

The most common tool for examining surface morphology of synthesized powders is scanning electron microscopy (SEM). In the SEM an accelerated electron beam is focused into a fine probe and subsequently raster scanned over a small rectangular area. Depending on the energy of the electron beam and the thickness of the sample, some fraction of the accelerated electrons will be scattered in the forward direction, another fraction will be absorbed, and the remaining fraction will be scattered in the backward direction [55,80]. As the beam interacts with the sample it forms various emissions such as secondary electrons, backscattered electrons, photons, internal currents, etc., all of which can be detected. These characteristic signals are highly localized to the area under the beam. In particular, the energetic incident electrons can knock electrons out of their orbits around an atom and if these electrons are located near the surface of the sample, within ~20 nm, they may have enough energy to escape from the sample and are called secondary electrons. These secondary electrons ejected from the sample surface are used to produce an image [55,80].
Submicron sized powders and their surface morphologies can be studied at a very large range of magnifications because of the very large depth of field. It is important to note that most inorganic phosphors will need to have a conducting overcoat deposited before SEM analysis to prevent surface charging problems during analysis.

Lateral resolution in the secondary electron mode is 1 – 50 nm [80]. The depth to which the incident electron penetrates into the sample varies from a few nm to a few µm depending upon the sample type, accelerating voltage, and the mode of analysis. For electron energies of 1 MeV, the penetration depth is around 1 µm. For electron energies in the range of 20-1000 eV, the penetration depth is ~ 1nm, and thus an incident electron beam with energy below 1 keV is used to probe surface layers with one to two monolayers thick [55,80].

The particle morphology of the synthesized phosphors was investigated by cold field emission scanning electron microscopy (FE-SEM, Hitachi S-400) after coating with Pt on carbon tape.

### 2.8.1.4 Infrared (IR) Spectroscopy

The vibrational motions of the chemically bound constituents of matter have frequencies in the infrared (IR) regime that are far away from the visual range. The infrared region of radiation lies between the visible and microwave regions of the electromagnetic spectrum. The fundamental vibrational region of typical
chemical bonds is located in the mid–infrared region with a range of 400-4000 cm\(^{-1}\) [163].

According to IR spectroscopy theory, the oscillations induced by certain vibrational modes provide a means for matter to couple with an impinging beam of infrared electromagnetic radiation and to exchange energy with it when the frequencies are in resonance. In other words, when a broad frequency range of IR energy is applied to a material, the energy at specific frequencies is absorbed by the sample. A molecule may absorb IR radiation of the appropriate frequency to excite it from one vibrational or rotational level to another [80,163].

Infrared absorption spectra are generally measured by Fourier Transform Infrared (FTIR) spectrometers. The absorption spectrum of the sample is produced in the form of a graph of energy absorbed versus frequency and such a spectrum is an exclusive characteristic of the particular molecules present and their molecular motions. Therefore, the spectrum can be accepted as a “fingerprint” of the chemical species and it has been used in qualitative analysis to identify the molecules present. In addition to the qualitative analysis, IR spectroscopy has also been used for quantitative analysis because the intensity of absorption is proportional to the amount of species present in the sample [163].

The IR spectroscopy technique is not applicable to ranges from undetectable to \(<10^{13}\) bond/cc and sub-monolayers sometimes [80].

The basic configuration of an FTIR spectrometer is schematically shown in Figure 2.17. The essential component of this spectrometer is a Michelson
interferometer that consists of a fixed mirror, a movable mirror, and a beamsplitter. When the IR beam from a source reaches the beamsplitter, it will be divided into two halves. Half of the beam is reflected in the beamsplitter to the fixed mirror, while the other half passes through the beamsplitter toward the moving mirror. These two beams are reflected in the fixed and moving mirrors, respectively, and come back to the beamsplitter, where they recombine into a new beam that passes through the sample and is finally focused on to the detector.

![Diagram of an FTIR spectrometer](image)

**Figure 2.17** A schematic diagram of an FTIR spectrometer [163].

Unless otherwise stated, Infrared spectra of the precursor and calcined samples at different temperatures were recorded in the range 400 to 4000 cm\(^{-1}\) by the KBr pellet method, using a Fourier transform infrared spectrometer (FTIR) (Perkin Elmer Spectrum 2000).
2.8.2 Luminescent Properties

2.8.2.1 The Measurement of Absorption Spectra: the Spectrophotometer

Characteristic absorption spectra of phosphors are usually recorded by using spectrophotometers. A schematic diagram of a single-beam spectrophotometer and the spectral shape of the light after passing through each element are shown in Figure 2.18. The single-beam spectrophotometer consists of a light source (a deuterium lamp for the UV spectral range and a tungsten lamp for the VIS and IR spectral ranges) that is focused on the entrance to a monochromator used to select a single wavelength and to scan over a desired wavelength range, a sample holder, followed by a light detector (photomultiplier for the UV-VIS range and a SPb cell for the IR range) to measure the intensity of each monochromatic beam after traversing the sample, and finally a computer to display and record the absorption spectrum.

Figure 2.18 A schematic diagram of a single-beam spectrophotometer and the spectral shape of the light after passing through each elements [5].
Optical spectrophotometers measure the optical density (OD), absorbance (A), or transmittivity (T) in different modes. The optical density (OD = \log (I_0/I)) can be transformed to other well-known optical magnitudes such as the transmittance (T = I/I_0) and the absorbance (A = 1 – I/I_0):

\[ T = 10^{-\text{OD}} \] and \[ A = 1 - 10^{-\text{OD}}. \]

The spectra obtained from a single-beam spectrophotometer are affected by spectral and temporal variations in the illumination intensity. The combined effects of the lamp spectrum and the monochromator response will cause the spectral variations, while the temporal variations take place due to the lamp stability. These effects can be reduced by using the double-beam spectrophotometers as shown in Figure 2.19.

**Figure 2.19** A schematic diagram of a double-beam spectrophotometer [5].

The illuminating beam is split into two beams of equal intensity which are directed toward a reference channel and sample channel. Two similar detectors D1 and D2 are used to detect the outgoing intensities corresponding to I_0 and I, respectively. The spectral and temporal intensity variations of the illuminating
beam affect the sample and reference beams similarly thereby these effects are minimized in the resulting absorption spectrum.

### 2.8.2.2 The Measurement of Photoluminescence: the Spectrofluorimeter

Excitation and emission spectra analysis, as mentioned earlier, provides information on the energy-level scheme of the synthesized phosphor. Photoluminescence spectra are often measured by using compact instruments called spectrofluorimeters. A schematic diagram showing the main elements for measuring the photoluminescence spectra is shown in Figure 2.20.

![Schematic diagram showing the main elements for measuring photoluminescence spectra](image)

**Figure 2.20** A schematic diagram for measuring photoluminescence spectra of phosphors. Lamp and the excitation monochromator combination can be replaced by using a laser to provide the excitation energy [5].

The sample is typically excited at a specific wavelength with a lamp, followed by an excitation monochromator or a laser beam. Then, the emitted light is collected by a focusing lens and analyzed by utilizing a second monochromator (emission
monochromator), which is followed by a suitable detector connected to a computer. Both emission spectra and excitation spectra can be registered on spectrofluorimeters. When the emission spectrum is registered, the emitted light intensity is measured at different wavelengths by scanning the emission monochromator at a fixed excitation wavelength. Similarly, when the excitation spectrum is registered, the emission monochromator is fixed at any emission wavelength while the excitation wavelength is scanned in a specific spectral range.

Excitation and emission characteristics of the phosphor powders were recorded at room temperature on a Hitachi F-4500 fluorescence spectrophotometer equipped with a 150W Xe-lamp as an excitation source at a scanning speed of 240nm/min and a sampling interval of 0.5 nm.

2.8.2.3 Time-Resolved Spectroscopy

For luminescent materials, the lifetime of an excited state gives very valuable information regarding the nature of the state and the environment of the luminescent ion in the crystalline host lattice. There are two types of lifetimes which are applicable to luminescent materials [17]: the first lifetime is the population lifetime, which is determined by the radiative and non-radiative transition rates to the ground state or other excited states. The second lifetime is the dephasing time, which is determined by the rate of dephasing interactions affecting the coherence of an excited state. Between these two lifetimes,
population lifetime has been used to describe the decay time behavior of phosphors.

Many different techniques have been developed to measure the lifetime of an excited state in phosphors over the years, some even capable of measuring at femto-seconds levels.

The lifetime of an excited state in phosphors represents the rate at which the population in the excited state changes depending on the time. It is commonly measured by applying a short, intense excitation pulse at the initial time \( t = 0 \), which creates a population \( N_e \) in the excited state, and then recording the temporal evolution of the emission intensity in time \([18]\). For a simple two level system, which consists of an excited and a ground state (see Figure 1.3), the change in the population of the excited state as a function of time can be written as \([18]\):

\[
\frac{dN_e}{dt} = -N_e P_{se}
\]

where \( N_e \) is the number of luminescent ions in the excited state after the pulse excitation at \( t = 0 \), and \( P_{se} \) is the probability of spontaneous emission from the excited state to the ground state.

Integration gives

\[
N_e(t) = N_e(0) \exp(P_{set}),
\]

which can also be written as

\[
N_e(t) = N_e(0) \exp(-1/\tau),
\]

where \( \tau = 1/P_{se} \) is the radiative decay time, which is the inverse of the spontaneous emission (or transition probability).
As the luminescence intensity is proportional to $N_e(t)$, it will decrease exponentially and can be written as

$$I(t) = I(0) \exp(-t/\tau).$$

The values of the radiative decay vary from "ns" to "s", depending on the characteristics of the transition involved. In the case of spin allowed transitions very short decay times are observed and the emission process is called *fluorescence* whereas spin-forbidden transitions cause relatively longer decay times and the emission process is called *phosphorescence*.

Decay curves of phosphors are not always in single exponential character. Energy transfer rates and the transfer mechanism can be obtained from the analysis of the nature of the decay curve. Di Bartolo et al., [35] reported how to analyze the decay curves to obtain information on energy transfer processes.

A continuous light source in combination with a mechanical shutter can be used to create a pulsed excitation for the measurement of long decay times, i.e., 1ms or longer [18]. On the other hand, for relatively faster decay time (\(\mu s\)) measurements, a continuous light in combination with a chopper wheel can be used. Pulse laser systems and flash-lamps are the most commonly used pulsed excitation sources [18].

Decay time measurements of the phosphors were made with the pulsed laser induced fluorescence and the combined data acquisition system is shown in Figure 2.2.1. The 4\(^{th}\) harmonic of a nanosecond pulsed Nd:YAG laser at 266 nm was directed at approximately 45\(^{\circ}\) angle from the normal to the powdered sample of phosphors with some absorption and the majority of the beam specularly
reflected. Fluorescence was measured 90° to the solid sample surface collected by a lens and directed into a SPEX 1680 equipped with 0.22 m double monochromator. The fluorescence transmitted through the monochromator was detected by a photomultiplier tube. The time-dependent fluorescence was recorded by a digital oscilloscope (LeCroy Wavesurfer 452).

Figure 2.21 Spectroscopic setup used for the measurements of fluorescence decays based on laser induced fluorescence. PMT: Photomultiplier tube.

2.8.2.4 Diffuse Reflectance Spectroscopy

Diffuse reflectance spectroscopy provides similar and complementary information to the absorption measurements. The reflectivity spectra $R(\nu)$ can identify the singularities caused by the absorption process when the absorption coefficients
are as high as $10^5 - 10^6$ cm$^{-1}$ [5]. The reflectivity, $R(\nu)$, and the absorption spectra, $\alpha(\nu)$ can interrelated by using the Kramers Kronig relations [164].

The reflectivity at each frequency is defined by

$$R = \frac{I_R}{I_0},$$

where $I_0$ is the beam of intensity incident on a solid sample and $I_R$ is the reflected intensity.

Reflectivity spectra can be recorded in two different modes; viz. direct reflectivity or diffuse reflectivity. Direct reflectivity measurements are made with polished samples at normal incidence, whereas diffuse reflectivity is typically used for unpolished or powdered samples. For direct reflectivity measurements, monochromatic light is passed through a semi-transparent lamina (beamsplitter) as shown in Figure 2.2.a. This beamsplitter deviates the light reflected in the sample toward the detector.

For diffuse reflectance studies, a sphere with a fully reflective inner surface (integrating sphere) is used (Figure 2.2.b). The integrating sphere has a pinhole through which the light enters and is transmitted toward the sample. The diffuse reflected light reaches the detector after experiencing multiple reflections in the inner surface of the sphere.

The diffuse reflectance spectra of the powdered phosphor samples were recorded on a Shimadzu UV-240 spectrophotometer.
Figure 2.22 A schematic diagram showing the experimental arrangement used to measure direct reflectivity spectra (a). A schematic diagram of an integrating sphere for measuring diffuse reflectivity spectra (b). [5].
SECTION 3

Synthesis of pure Zn$_2$SiO$_4$·Mn green phosphors by simple PVA-Metal ion complex route

(Comparative Study)

3.1. Introduction

Willemite (α-Zn$_2$SiO$_4$), with the penacite structure, occurs naturally and belongs to the group of ortho-silicates [165]. Zinc ortho-silicate (a.k.a., willemite) has a wide range of industrial applications such as phosphor host compounds [166,167], glazes, pigments [168], electrical insulators [169], and it is an important component in glass ceramics [170].

The manganese-doped zinc-orthosilicate, Zn$_{2-x}$Mn$_x$SiO$_4$, is an efficient green luminescent phosphor commercially used in cathode ray tubes (CRTs), fluorescent lamps, and plasma display panels (PDPs) because of its high saturated color, very bright luminescence, long life span, lack of moisture sensitivity, and chemical stability [166,167,171]. Manganese-doped zinc orthosilicate phosphors such as high luminance phosphor and antiflicker phosphor in low refresh-rate display applications when co-activated with arsenic (10-500 ppm) are commercially available under the name P1 and P39 respectively. [172]
Phosphors with good color purity, high quantum efficiency, and desirable decay times are required to produce high definition color flat panels and plasma display panels [166]. Many research efforts have been dedicated to the development of novel low-voltage cathodoluminescent (CL) luminescent materials with high efficiency and chemical stability under electron-beam exposure in high-vacuum systems for the next generation of enhanced field emission displays [173,174]. Non-sulfide based inorganic phosphors have been favored as the best suitable materials for this application because sulfide phosphors are unstable under electron beam bombardment in a high vacuum ($10^{-7}$ Torr), resulting in a chemical degradation of the phosphor layer and a large degradation on CL efficiency [175,176]. Zn$_2$SiO$_4$:Mn was found to be a promising alternative to the conventional thin film phosphors in electroluminescent devices [177], and appropriate for medical imaging detectors for low-voltage radiography and fluoroscopy [178,179].

The photoluminescence properties of phosphors mainly depend on the dopant level and the synthesis methods used. For enhancing the brightness and the resolution of the displays, it is critical to produce phosphors with high quantum efficiency, controlled morphology, and relatively small particle sizes. The conventional method to synthesize Zn$_2$SiO$_4$:Mn phosphor powders is the solid state reaction of component oxides or precursors, which requires high firing temperatures and a milling process as a post-treatment method. This mechano-chemical activation process generates largely-agglomerated and irregular particles with relatively weak luminescence properties [180]. For this reason,
the last two decades, much effort has been dedicated to synthesis of Zn$_2$SiO$_4$:Mn phosphor particles using newer processing methods with solutions and sols as starting materials such as sol-gel [181-183], concentration gradient uniform particle size (CGUPS) [184], hydrothermal [185], spray pyrolysis [167,186], fume pyrolysis [187], polymer pyrolysis [188], combustion synthesis [189] – each method producing the phosphor material with the desirable luminescence and satisfy all the requirements of homogeneity, relatively low processing temperatures, chemical purity of phases, and relatively-fine particle sizes with uniform size distributions. Although several chemical methods have been applied to the production of fine phosphor particles with good luminescence characteristics, challenges remain in reducing process complexity, controllability, and cost. Therefore, new synthetic routes are being explored to potentially overcome some of these difficulties in commercialization of green phosphor materials. During recent years, novel organic-inorganic polymerization synthesis routes have been applied to produce a variety of mixed oxide metals. For example, poly(vinyl alcohol) (PVA) $-[CH_2-CH(OH)]_n$ and poly(ethylene glycol) (PEG) $H[O-CH_2-CH_2]_n-OH$ have been reported for use in synthesis as an organic component, with water dissoluble metal cations added as the inorganic component [190-192]. Detailed information about the chemical and processing characteristics of the PVA-metal ion complex method can be found in Chapter 2. In this study, manganese doped willemite (Zn$_2$SiO$_4$:Mn) green phosphor particles were produced by a simple PVA-metal complex route. This material was selected based partially on the interest in new synthesis routes for this phosphor, and the
existence of numerous studies in this material produced using alternative approaches (and the attending characterization data). The photoluminescence properties, crystallinity, particle size and morphology were investigated, and the results are presented in the following subsections.

3.2. Experimental Procedure

As outlined in Section 2, the synthesis process used in this work involves the preparation of cationic precursors and mixing them with a viscous PVA–H₂O solution. This blend was then heated to evaporate the water, leaving behind an intermediate powder which was calcined at elevated temperatures to significantly improve purity, crystallinity, and create uniform doping in the resulting phosphor powders. All polymeric and cationic solutions were prepared fresh. The flowchart for the PVA-metal ion complex processing of the Zn₂₋ₓMnₓSiO₄ phosphors is given in Figure 3.1.

The PVA-metal complex precursor for Zn₂₋ₓMnₓSiO₄ was prepared using Zn(NO₃)₂·6H₂O (99%, Alfa Aesar), Mn(NO₃)₂·4.4H₂O (99.98%, Alfa Aesar), Ludox TMA colloidal silica solution (ChemPoint.com), and PVA (molecular weight of 145,000) with a degree of polymerization of 3300 (Sigma-Aldrich, Inc.). Co-doping with magnesium was done by dissolving the required amount of Mg(NO₃)₂·6H₂O (ACS Reageant Grade, Sigma-Aldrich) in water. According to the PVA product specifications, the nominal “100 mol% hydrolyzed PVA” actually contains up to 2 mol% of acetate groups, which replace the OH-cation bonds.
used in our process. Thus, in our calculations, we assumed an average 99 mol% degree of hydrolysis.

The process begins with a 5 wt% PVA–H₂O solution, prepared on a hot plate at ~85 °C (with mixing) until a clear viscous solution formed. Stoichiometric amounts of the cationic nitrates were dissolved in the minimal necessary amount of D.I. water by stirring in a separate container at room temperature and then were added to the heated PVA aqueous solution. Typically, 120 gram batches of the PVA-metal solutions were prepared for each set of conditions. The proportions of the PVA and cation sources in the precursor solution were adjusted to provide a targeted PVA monomer unit:metal ion mole ratio of 2:1 to provide sufficient hydroxyl (OH) groups for cation dispersion in the PVA. Ideally, this is done in a manner that avoids cation (metal) precipitation and agglomeration. Each monomer part of the long PVA polymeric chains has one hydroxyl group in the aqueous solution and the relative stoichiometric values of the cations in the solution were calculated based on the total number of hydroxyl functional groups, given the solution concentration, degree of hydrolysis, and degree of polymerization. The PVA–metal aqueous solution was then heated on a hot plate at a temperature of ~150 °C with continuous mixing. After evaporation (8 to 10 hours), a dark brown, soft, loosely–connected phosphor precursor powder typically remains. Each sample powder batch was then calcined at different temperatures for a fixed 2–hour period and then air cooled to obtain the final manganese–doped green phosphors.
The crystallization behavior and the crystallite size measurements of the phosphors were studied as a function of the calcination temperature using X-Ray diffraction (XRD) with CuKα radiation. All XRD data were collected at room
temperature, after the powder had been cooled. The particle sizes and size distributions were measured using a Microtrac® Nanotrac NPA 250 particle size analyzer. For the particle size measurements, powders were dispersed in a 20 wt% glycerin–D.I. water solution, via ultrasonication. Photoluminescence characteristics in the visible range were recorded on a Hitachi F-4500 fluorescence spectrometer with a 150W Xe lamp using a 254 nm (ultraviolet) excitation wavelength. Scanning electron microscopy (SEM) was conducted using a Hitachi S-4700 cold field emission SEM, with the powder samples coated with Pt. IR spectroscopy analysis was done using Thermo-Nicolet (Nexus 470) FTIR.

Using the above–described procedures, we prepared a set of powders at three different manganese doping concentrations (4, 8, and 12 mol%) and examined a range of calcination temperatures between 750 ºC and 1175 ºC to determine the influence these parameters had on the material properties.

3.3. Results and Discussion

3.3.1. XRD Analysis

The stable, crystalline α-Zn$_2$SiO$_4$ (willemite) structure is well characterized in the literature. The Zn$_2$SiO$_4$ crystal lattice has a phenacite structure with a rhombohedral space group and both Zn$^{2+}$ and Si$^{4+}$ ions coordinated tetrahedrally with four oxygen atoms [18,193]. It has two distinct zinc sites, both having four nearest-neighbor oxygen ions in a slightly distorted tetrahedral (Td) configuration.
Silicon atoms in $\alpha$-Zn$_2$SiO$_4$ also are tetrahedrally coordinated. The Si-O and Zn-O bond lengths are reported to be 1.62 Å and 1.96 Å [193]. Two inequivalent tetrahedral and one Si tetrahedron alternate in chains parallel to the c-axis in such a way that neighboring inequivalent zinc tetrahedra form pairs by sharing corners, with the pair axes lying approximately parallel or perpendicular to the crystal c-axis. Nearest neighbor cation interactions between ions on Zn sites therefore occur between the inequivalent Zn sites.

As the difference in ionic radii of Zn$^{2+}$ (0.74 Å) and Mn$^{2+}$ (0.80 Å) is relatively small, both Zn$^{2+}$ sites can be substituted by doped-in Mn$^{2+}$ ions [194,195]. The zinc atoms occupy two crystallographically-different sites. However, these two crystallographic environments differ only slightly [18]. Although the willemite structure contains conspicuous “empty” channels, it is not known whether interstitial manganese or any other impurity positions are also possible.

XRD patterns for the Mn-doped Zn$_2$SiO$_4$ phosphor powders prepared at various temperatures and for the commercial phosphor are shown in Figure 3.2. The as-synthesized powders showed unreacted ZnO peaks at around 2$\theta$ = 36° with an amorphous structure. The characteristic zinc orthosilicate crystal structure with similar crystallinity to that of the commercial powder started to form at ~850 °C at 2 hours. All particles had a white color, showing that manganese is in the right Mn$^{2+}$ state [171] post heat treating at (and above) 950 °C.

The peak positions of Figure 3.2 match well with those of the standard pattern (JCPDS 37-1485) for Zn$_2$SiO$_4$ in the phenacite structure. In order to investigate the crystallinity dependence on the calcination temperatures, the FWHM values
of the main peaks were measured. The FWHM values decreased from 0.30° to 0.24° as the temperature increased from 950 to 1175 ºC. Also, the peak intensities increased with increasing calcination temperatures leading to the conclusion that the crystallinity of phosphor particles was increased with calcination temperature. Individual crystallite sizes were found to shift from 25 nm

![X-Ray diffraction spectra for Mn-doped Zn$_{2-x}$Mn$_x$SiO$_4$ phosphors prepared at various temperatures and the commercial one. Conditions are as follows: a) As-synthesized, b) 750 ºC (2hrs) c) 850 ºC (2hrs), d) 950 ºC (2hrs), e) 1050 ºC (2hrs), f) 1150 ºC (2hrs), and g) Commercial P39 powder. (Note: * denotes ZnO peaks).](image-url)
to 38 nm as the temperature was increased from 850 to 1175 °C. At high temperatures above 1200 °C, zinc oxide will possibly evaporate and this will cause a decrease in crystallinity and low excitation and emission intensities [186]. Measured lattice parameters (a,c) and the calculated cell volume depending on the manganese concentration levels are reported in Table 3.1 and are in good agreement with those reported in literature [196].

Table 3.1
Composition and lattice parameters of Zn$_{2-x}$Mn$_x$SiO$_4$ (0<x<0.12) phosphors (R = Rhombohedral).

<table>
<thead>
<tr>
<th>Mn$^{2+}$ concentration (x)</th>
<th>Crystal Structure</th>
<th>Lattice Parameter</th>
<th>Cell Volume ($\text{Å}^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>R3H</td>
<td>a 13.947</td>
<td>c 9.314</td>
</tr>
<tr>
<td>0.04</td>
<td>R3H</td>
<td>13.949</td>
<td>9.312</td>
</tr>
<tr>
<td>0.08</td>
<td>R3H</td>
<td>13.944</td>
<td>9.312</td>
</tr>
<tr>
<td>0.12</td>
<td>R3H</td>
<td>13.946</td>
<td>9.315</td>
</tr>
</tbody>
</table>

3.3.2. SEM Analysis

Scanning electron microscope (SEM) images for the as-synthesized powders and the 4 mol% Mn doped samples prepared at 1150 °C for 2h are illustrated in Figure 3.3. The SEM morphology shows that the as-synthesized particles are highly agglomerated at the micron-scale.
Figure 3.3 SEM micrographs of 4 mol% Mn doped powder samples, a) As-synthesized b) calcined at 1150 °C for 2h in air.
On the other hand, the calcined sample shows that the individual green phosphor particles have a solid-filled (minimal pores) morphology without any porosity, and with bigger particle sizes, and smooth and rounded morphologies. Particles of 200 to 500 nm dimensions were observed to be either agglomerated to form larger phosphor particles in the order of 1 to 3 µm diameter range or separate particles without any agglomeration in the order of sub micron range. On calcination, the agglomeration size increases. It has been reported that the particles synthesized using other techniques such as solid state, co-precipitate, and hydrothermal treatment are irregular in shape and large [171,184,195]. The use of spherically-shaped particles and round-shaped grains will increase the screen brightness of the evolved light and higher packing densities than irregular shaped phosphor particles [17,18].

It is widely accepted that photoluminescent properties of phosphors depend on their shape, size, surface texture, and purity. These properties of the phosphors should be optimized to obtain the maximum quantum efficiency through energy absorption [166]. Highly crystalline phosphor particles without any porosity and with smooth, rounded surface texture gives very good luminescence properties as shown in Figure 3.3.

3.3.3. Particle Size & Distribution Analysis

A typical particle size distribution for phosphor particles calcined at 1150 °C is shown in Figure 3.4. Phosphor particles were dispersed in 20 wt% glycerin-water
solution by ultrasonication prior to particle size analysis. The average particle size is 1 µm, ranging from 200 nm to 3 µm for each manganese doping level.

![Particle size distribution graph](image)

**Figure 3.4** Particle size distribution of 4 mol% Mn doped Zn$_2$SiO$_4$:Mn phosphors calcined at 1150 °C for 2 h in air.

### 3.3.4. FTIR Analysis

IR spectra for the precursor powders (as-synthesized) and calcined Zn$_2$SiO$_4$:Mn phosphor samples (950 °C and 1160 °C for 2 hours) are shown in Figure 3.5. The IR band located at 3390 cm$^{-1}$ and bending mode at 1620 cm$^{-1}$ in the precursor material can be attributed to the presence of moisture in the precursor material (Figure 3.5.a). The intensity of these bands disappears with the increase in calcination temperatures. The absorption bands located at 1620 cm$^{-1}$ (strong), 1120 cm$^{-1}$ (strong), and at 827 cm$^{-1}$ in the precursor material can be assigned to the the various vibrational modes of the carboxylate (COO$^-$) ions [121]. The bands located at 1440 cm$^{-1}$ and 960 cm$^{-1}$ are due to the presence of nitrates in the precursor material [128]. IR spectra for the samples
Figure 3.5 FTIR spectra of the PVA-metal ion complex route derived manganese doped α-Zn$_2$SiO$_4$ powders (a) as-synthesized (precursor), (b) calcined at 950 °C for 2 hours, (c) and (d) calcined 1160 °C for 2 hours.
calcined at 950 °C and 1160 °C indicated that all characteristic carboxylate and nitrate absorbance peaks were diminished and the characteristic α-Zn₂SiO₄ absorption peaks starts to appear. It was observed that the main absorption peaks of the manganese doped Zn₂SiO₄ phosphor fall in the frequency region
500-1100 cm\(^{-1}\), which is in a good agreement with other reported data [196]. (see Figure 5.d). The IR bands and corresponding vibrational modes for Zn\(_2\)SiO\(_4\) are 870 cm\(^{-1}\) (\(\nu_1\) SiO\(_4\)); 896, 931, and 978 cm\(^{-1}\) (\(\nu_3\) SiO\(_4\)); 569 and 578 cm\(^{-1}\) (\(\nu_1\) ZnO\(_4\)); and 615 cm\(^{-1}\) (\(\nu_3\) ZnO\(_4\)), where \(\nu_1\) corresponds to totally symmetric stretching, \(\nu_3\) is asymmetric stretching [197,198]

3.3.5. Photoluminescence Analysis of Zn\(_2\)SiO\(_4\):Mn Phosphors

3.3.5.1. Electronic States of Mn\(^{2+}\)-doped Phosphors

Transition metal ions have an incompletely-filled d\(^n\) shell (0 < n < 10). The energy levels formed by such an electronic configuration can be calculated by Tanabe and Sugano considering the mutual interaction between the d electrons and the crystal field applied by the host lattice [199]. Figure 3.6 shows the energy levels of the d\(^5\) configuration as a function of the octahedral crystal field, which is known as Orgel’s diagram. For the 3d\(^5\) configuration, Orgel’s diagram applies for both octahedral and tetrahedral symmetry. The crystal field on the utmost left-hand side is equal to zero which gives the energy levels of the free ion. However, in a solid host lattice, many of these levels split into two or more levels because the crystal field is not zero. The ground state, which is the lowest energy level, coincides with the x-axis. For the free ion the levels are marked \(^{2S+1}L\), where S is the total spin quantum number, and L is the total orbital angular momentum. Values of L can be 0 (for S), 1 (for P), 2 (for D), 3 (for F), etc. The degeneracy of these energy levels is 2L+1. On the other hand, the crystal field levels are
marked $^{2S+1}X$, where X can be A (without degeneracy), E (two-fold degeneracy) and T (three-fold degeneracy). Certain symmetry properties are indicated by the subscripts.

The Mn$^{2+}$ ion with d$^5$ configuration is used in many luminescent materials and it has a characteristic emission with a broad band. However, the position of the spectrum depends on the host lattice. In a cubic crystalline field of low to moderate strength, the five d electrons of Mn$^{2+}$ ion are distributed in the t$_{2g}$ and e$_g$ orbitals, with three in the former and two in the latter. Thus the ground state configuration is $(t_{2g})^3 (e_g)^2$. This configuration gives rise to the electronic states, $^6A_{1g}$, $^4A_{1g}$, $^4E_g$, $^4T_{1g}$, $^4T_{2g}$, and to a number of doublet states of which $^6A_{1g}$ lies lowest according to Hund’s rule. The luminescence spectra of Mn$^{2+}$ ions have only spin-forbidden transitions because all the excited states of Mn$^{2+}$ ion with d$^5$ configuration are either quartets or doublets [196].

The spectra of Mn$^{2+}$ activated phosphors, as mentioned earlier, fall in two classes, those with green emission, and those with orange-to-red emission.

The observed position of the $^4A - ^4E$ level for the green emitters is found to be about 23,500 cm$^{-1}$, while for the orange-to-red emitters, the level is found at about 24,700 cm$^{-1}$ [196,199]. The decay time of the emission is relatively long,
Figure 3.6 Orgel’s diagram for Mn$^{2+}$ ion with $d_5$ configuration as a function of the octahedral symmetry [199]. The abscis is the ground state.

of the order of ms. From the Tanabe-Sugano diagram (Figure 3.6) it can be seen that the emission corresponds to the $^4T_1 \rightarrow {}^6A_1$ transition. The ground level is $^6A_1$ and all optical absorption transitions are parity and spin forbidden. Therefore, the characteristic broad emission band is due to different slopes of the energy levels, its relatively long decay time (ms range) is due to the spin selection rule, and different emission colors depend on the host lattice type due to the dependence on crystal field. In general, tetrahedrally-coordinated Mn$^{2+}$, which is a weak crystal field, gives a green emission, on the other hand, octahedrally coordinated Mn$^{2+}$, which is a stronger crystal field, gives an orange to red emission.
### 3.3.5.2. Photoluminescence Characteristics of Zn$_2$SiO$_4$·Mn

Emission spectra (under 254 nm excitation) for phosphor particles prepared at various calcination temperatures are shown in Figure 3.7. As the temperature increases, the emission peak intensity increases, with the highest intensities obtained from calcinations in the 1160-1175 °C range. The observed intensities were 120% that of the commercial particles. As the manganese content is increased from 4 mol% to 12 mol%, the maxima of the emission band shifts to higher wavelength from 523 nm to 526 nm with a bandwidth change of Δλ = 38 nm to Δλ = 39 nm at half maximum respectively. These characteristic wavelength values resulted from the presence of Mn$^{2+}$ cations, which acts as an activation center in willemite structure. The manganese-doped Zn$_2$SiO$_4$ phosphors had the characteristic green emission, which can be attributed to the relatively-weak crystal field on tetrahedrally coordinated luminescent centers (Mn$^{2+}$).

Small differences between the absorption and emission profiles of Mn$^{2+}$ ions occupying each of the two non-equivalent crystallographic sites have been reported [200]. The Mn$^{2+}$ ion has 3d$^5$ configuration with high spin and the emission band is assigned to transition from the lowest excited state $^4T_1$ to the ground state $^6A_1$ [200]. The mechanism for the green emission from the manganese doped willemite is explained by the excitation of the electron from the ground state of Mn$^{2+}$ ($^6A_1$) to the conduction band of the Zn$_2$SiO$_4$ by photons and can be shown as

$$\text{Mn}^{2+} + h\nu \rightarrow \text{Mn}^{3+} + e^-,$$
where $h\nu$ is the required energy for the excitation of Mn$^{2+}$ in the Zn$_2$SiO$_4$ system (Figure 3.8). The free electrons in the conduction band can relax to the $^4T_1$ excited state by non-radiative process, followed by a radiative transition to the $^6A_1$ ground state emitting a bright green light ($^4T_1 \rightarrow ^6A_1$) [196].

![Emission spectra](image)

**Figure 3.7** Emission spectra, (excited at 254 nm) of 4 mol% Mn doped Zn$_2$SiO$_4$:Mn phosphor particles calcined at different temperatures for 2 h in air, including a commercially-available sample with 8.1 mol% Mn doping.
Figure 3.8 Schematic representation of the characteristic energy level scheme for the green emission process in Zn$_{2-x}$Mn$_x$SiO$_4$ (0.01<x<0.12) phosphor samples upon excitation with 254 nm.

Because Zn$^{2+}$ has a d$^{10}$ configuration, it exhibits an intense and broad UV absorption in the short wavelength range and then an energy transfer to Mn$^{2+}$ takes place, resulting in the green emission from the Zn$_2$SiO$_4$:Mn phosphor [18,201]. It is not well understood how the UV absorption transition takes place, but it has been proposed that it includes a charge transfer transition from the 2p orbital of oxygen to an anti-bonding orbital, which is localized partly on the d$^{10}$ ion of Zn$^{2+}$ and partly on the 2p ion of oxygen. [18]. The emission spectra of
Zn$_2$SiO$_4$:Mn show a tailing in the long wavelength side of the emission because of some coordinate displacement of the potential energy curves, which is in agreement with other studies [202].

Figure 3.9 shows the excitation spectrum for 4 mol% Mn and 12 mol% Mn doped samples prepared at 1160 ºC for 2 h, and the commercial powder with 8.1 wt% Mn. The strong excitation peak at 254 nm could be attributed to a charge transfer transition from the divalent manganese ground state $^6A_1(S)$ of Mn$^{2+}$ ion to the conduction band (CB) of the host lattice.

![Excitation spectra of Zn$_2$SiO$_4$:Mn](image)

**Figure 3.9** Excitation spectra of 4 mol%, 8 mol%, and 12 mol% Mn doped samples prepared at 1160 ºC for 2 h, and commercial (8.1 wt% Mn) Zn$_2$SiO$_4$:Mn phosphor particles, all excited at 254 nm.
Figure 3.10 shows the observed relative peak emission intensities of 4 mol\%, 8 mol\%, and 12 mol\% Mn doped Zn$_2$SiO$_4$:Mn phosphor samples at various calcination temperatures ranging from 950 to 1175 °C. The peak emission intensity of 4 mol\% Mn doped phosphor prepared at 1175 °C is almost 17 times higher than that prepared at 950 °C. This correlates with the crystallite size differences, and the right divalency of manganese ions replaced Zn$^{2+}$ ions in

![Graph comparing peak emission intensity vs. temperature](image)

**Figure 3.10** Comparison of peak emission intensity of 4 mol\%, 8 mol\%, and 12 mol\% Mn doped Zn$_2$SiO$_4$:Mn phosphors as a function of the calcination temperatures. Excitation wavelength was 254 nm.

lattice structure. For both concentration levels, emission intensities were increased sharply when the calcination temperatures increased. Overall, phosphors with 8 mol\% Mn showed higher emission intensities than the one with
4 mol% and 12 mol% Mn because of the concentration quenching phenomenon [166,200].

3.3.5.3. Concentration Quenching of Luminescence

In principle, an increase in the concentration of activators in a given host lattice should be accompanied by an increase in the emitted light intensity due to the corresponding increase in the absorption efficiency. However, in reality, the emitted light intensity increases up to a certain critical luminescent center concentration. Beyond this concentration, the luminescence intensity will start to decrease and this phenomenon is known as concentration quenching of luminescence [5,18].

Figure 3.10 illustrates the concentration quenching effect for the main green emission (around 528 nm) of Mn$^{2+}$ ions in crystalline Zn$_2$SiO$_4$ host lattice. In this figure, the green emission intensity of Mn$^{2+}$ ions in Zn$_2$SiO$_4$ is shown as a function of the Mn$^{2+}$ content for a fixed excitation wavelength of 254 nm. Up to about 8% Mn$^{2+}$ concentration, the emitted light intensity grows monotonously with the Mn$^{2+}$ content. At higher manganese doping levels, the luminescence starts to decreases.

In general, the concentration quenching of luminescence can be explained by the very efficient energy transfer among the luminescent centers. The quenching takes place at a certain activator concentration level where there is a sufficient reduction in the average distance between these luminescent centers and thus the energy transfer between the luminescent centers will be favored [18].
Quenching traps (killers) and cross-relaxation are two different mechanisms of quenching of luminescence and are commonly encountered in inorganic luminescent materials [5,18]:

i. The absorbed energy can migrate a large amount of luminescent centers before being emitted because of the very efficient energy transfer. However, in even the purest polycrystalline materials, there are certain amounts of defects or impurities (trace ions) that can act as acceptors and the migrating excitation energy can finally be absorbed by them. These centers can relax to their ground state by multiphonon emission or by infrared emission. Therefore, they can cause the quenching of luminescence by acting as an energy sink within the absorbed energy transfer chain. These energy receiving centers within the host lattice are called quenching traps.

ii. The cross-relaxation mechanism becomes dominant when the absorbed excitation energy is lost from the emitting state without actual migration of the excitation energy through the luminescent centers. Inorganic luminescent materials have this type of relaxation mechanism by resonant energy transfer between two identical adjacent active centers, because of the particular energy-level structure of these centers. Figure 3.11 illustrates a simple energy-level scheme involving cross-relaxation processes between pairs of active centers. For isolated active centers, radiative emission (III → G) from the excited level III dominates. However, the presence of a close active
center can cause a resonant energy transfer and one of the centers, acting as donor, transfers part of its excitation energy \((E_{\text{III}} - E_{\text{II}})\) to the other center (acceptor). The resonant energy transfer becomes feasible because of the particular disposition of the energy levels, in which the energy for the transition \(\text{III} \rightarrow \text{II}\) is equal to that for the transition \(\text{G} \rightarrow \text{I}\). Therefore, as a result of the cross-relaxation, the donor center, located in state \(\text{III}\), will be in the excited state \(\text{II}\), while the nearby acceptor center will jump to the excited state \(\text{I}\). These states will give a non-radiative relaxation or photon emission with energies lower than \(E_{\text{III}} - E_{\text{G}}\) and thus the \(\text{III} \rightarrow \text{G}\) emission will be quenched.

![Diagram](image)

**Figure 3.11** Schematic representation of the cross-relaxation mechanism between pairs of active luminescent centers [5].
It is important to note that in addition to the possibility of energy transfer, a high concentration of luminescent centers within the host lattice can contribute to the formation of new kinds of centers such as clusters, formed by coagulation of individual centers. These new active centers can give different absorption and emission bands than that of the isolated centers. This also is another concentration mechanism for the luminescence of isolated luminescent centers. When the Mn$^{2+}$ dopant concentration increases, there will be a high rate of energy transfer between Mn$^{2+}$-Mn$^{2+}$ ions. This will take the excitation energy far from the crystallographic site where the absorption took place and the excitation is lost without any radiation because of this quenching site. Therefore, the luminescence efficiency in this case will be very low or zero [18,198]. At low concentrations of Mn$^{2+}$ ions (<8 mol%), the quenching effect is negligible because the average distance between Mn$^{2+}$ ions is relatively large and the energy migration is prevented.

3.3.5.4. Time Resolved Spectroscopy

Emission decay time studies at $I_0/e$ ($\tau_{I_0/e}$) of the initial emission revealed that the 4 mol% Mn doped phosphor has $\tau_{I_0/e} = 13.4$ ms and the 12 mol% Mn doped Zn$_2$SiO$_4$ sample has $\tau_{I_0/e} = 5.0$ ms. The 8 mol% Mn doped Zn$_2$SiO$_4$ phosphor has $\tau_{I_0/e} = 9.8$ ms. Figure 3.12 shows that the decay time decreases as the manganese concentration increases. The commercial product, with 8.1 wt% Mn doping, has an emission decay time of 7.1 ms. Both the decay time and the
luminance vary with manganese concentration in the same manner as reported earlier in literature [166]. Morell et. al. [171] reported that the decrease in decay time at higher Mn concentrations is closely related to the concentration quenching. It was also argued that two different types of color centers, with different decay times, exist in manganese-doped zinc orthosilicate phosphors [172].

![Decay curves of 4 mol%, 8 mol%, and 12 mol% Mn\(^{2+}\) and commercial Zn\(_2\)SiO\(_4\):Mn phosphor particles. Phosphors were prepared by calcining the precursors at 1150 °C for 2 hours.](image)

**Figure 3.12** Decay curves of 4 mol%, 8 mol%, and 12 mol% Mn\(^{2+}\) and commercial Zn\(_2\)SiO\(_4\):Mn phosphor particles. Phosphors were prepared by calcining the precursors at 1150 °C for 2 hours.

Ronda and Amrein [203] suggested that the exchange interaction between Mn\(^{2+}\) ions indeed results in allowable optical transitions in Mn\(^{2+}\) ion pairs, which then results in a shortening of the decay time at relatively high manganese concentrations. Therefore, the decay behavior is governed by the energy
migration between the Mn$^{2+}$ active centers. It is possible to obtain the critical
distance between the Mn$^{2+}$ ions from the concentration quenching data [204].
The critical distance ($R_c$) between the Mn$^{2+}$ ions can be calculated using

$$R_c = 2\left[ \frac{3V}{(2\pi x_c N)} \right]^{1/3},$$

where, $x_c$ is the critical concentration corresponding to the concentration of
maximum intensity (8 mol% Mn), $N$ is the number of Zn ions in the Zn$_2$SiO$_4$ host
lattice (Mn ions substitutionally replace the Zn sites) and $V$ is the volume of the
unit cell ($1569 \times 10^{-30}$ m$^3$ for Zn$_2$SiO$_4$). Using the above equation, the critical
distance between the Mn-Mn pairs is 34 Å.

The decrease in decay time at higher Mn concentrations doesn’t reflect a
concentration quenching at non-radiative centers in the crystals, but rather an
energy transfer to complex centers involving Mn$^{2+}$ ions with faster radiative rates
[205].

For Mn$^{2+}$ doped Zn$_2$SiO$_4$ phosphors, the maximum intensity (excitation efficiency
$B_o$), decay time ($\tau_{0/e}$), time integration (luminous efficiency, $S_N$), and total
luminance ($B_o \times S_N$) are presented in Table 3.2. As a result, 4 mol% and 8 mol%
Mn$^{2+}$ doped Zn$_2$SiO$_4$ phosphors prepared by the PVA-metal ion complex route
provide a good combination of favorable luminance and acceptable decay time,
particularly for plasma display applications. Several other research groups have
also suggested that a Mn concentration range of 5 mol% to 11 mol% could be
suitable for display panel applications [206,207].
Table 3.2
Maximum Intensity, Decay Time, Time Integration, Radiation Efficiency, and Luminance, together with the results of regression fitting for various Zn$_{2-x}$Mn$_x$SiO$_4$.

<table>
<thead>
<tr>
<th>Mn$^{2+}$ Content (x)</th>
<th>Maximum Intensity, $B_0$ (A.U.)</th>
<th>Decay Time, $\tau_{10/e}$ (ms)</th>
<th>Time Integration, $S_N$</th>
<th>Luminance $B_0 \times S_N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04</td>
<td>108.83</td>
<td>13.4</td>
<td>14.014</td>
<td>1525.14</td>
</tr>
<tr>
<td>0.08</td>
<td>115.26</td>
<td>9.8</td>
<td>10.349</td>
<td>1192.83</td>
</tr>
<tr>
<td>0.12</td>
<td>62.70</td>
<td>5.0</td>
<td>6.515</td>
<td>408.49</td>
</tr>
<tr>
<td>Commercial</td>
<td>90.07</td>
<td>7.1</td>
<td>7.189</td>
<td>647.51</td>
</tr>
</tbody>
</table>

3.3.5.5. Diffuse Reflectance Spectroscopy

The diffuse reflectance spectra of 4 mol% and 8 mol% Mn-doped Zn$_2$SiO$_4$ phosphors are shown in Figure 3.13. By extrapolating the sharp slope to the level of no absorption in the reflectance, it was found that the prepared Zn$_2$SiO$_4$ host lattice has two main absorption energies located at ~225 nm and ~254 nm. The characteristic absorption at around 225 nm corresponds to the band gap energy of the host lattice Zn$_2$SiO$_4$, which is found to be \((1240 \text{ nm.eV}) / (225 \text{ nm}) = 5.51 \text{ eV}\).

The band gap of the Zn$_2$SiO$_4$ host lattice was determined by Kroger [208] to be 5.6 eV from optical absorption. More-precise measurements with an increment of
Figure 3.13 Diffuse Reflectance Spectra of 4 mol% and 12 mol% Mn doped Zn$_2$SiO$_4$ phosphors prepared at 1100 °C for 2 hours. Recorded at room temperature.

1 nm revealed that the band gap energy of the Zn$_2$SiO$_4$ host lattice is 5.5 eV [209]. Similarly, the other characteristic UV absorption at around 254 nm is
attributed to the presence of active luminescent centers (manganese) within the crystalline host lattice. As a result, electrons located in the ground state of the manganese ions will jump to the Zn$_2$SiO$_4$ conduction band due to the absorption at 254 nm (see Figure 3.8).

3.4. Effect of co-doping on the Photoluminescence of Zn$_2$SiO$_4$:Mn Phosphors

Based on the study we performed to understand the luminescence characteristics and performance of the manganese-doped Zn$_2$SiO$_4$ host lattice, it was concluded that a moderate Mn concentration of around 4-8 mol% with desirable luminescence intensity levels and decay time could be suitable for Plasma Display Panels (PDP).

One potential way of enhancing the photoluminescence performance of inorganic phosphors is to co-dope the host lattice at the main activator ion site. For the Zn$_2$SiO$_4$:Mn phosphors, the co-doping species possibilities can be classified into two categories. First, Zn ions in the host lattice can be replaced by some of the transition metals and/or alkali earths. Second, the Si ion site in Zn$_2$SiO$_4$ can be replaced with other elements such as Ga, Ge, or Al, co-doping with Mn ions. These were found to have a favorable influence on the brightness and performance in other studies [180,210]. On the other hand, several transition metals and alkali earth metals have also been co-doped with Mn ions in order to improve the luminescence and for shortening the decay time of the Zn$_2$SiO$_4$:Mn
phosphors [197,206,211,212]. However, only a few elements have provided higher emission intensity and shorter decay time.

### 3.4.1. Co-doping with Mg ions

The present investigation of luminescent properties of Zn$_2$SiO$_4$:Mn phosphors in terms of Mn ion concentration revealed that the 8 mol% Mn-doped Zn$_2$SiO$_4$ phosphors exhibited the highest green emission, however the decay time decreases consistently when increasing the Mn ion concentration. Therefore, the co-doping experimentation was started with the 8 mol% Mn-doped Zn$_2$SiO$_4$ phosphors in order to further improve the photoluminescent characteristics. Figure 3.14 shows the emission spectra and decay curve of Mg co-doped (Zn$_{1.92-y}$SiO$_4$:0.08Mn, yMg) green phosphors with $y = 0.0$, 0.005, 0.01, 0.025. All phosphor powders were calcined at 1160 °C for 2 hours. Photoluminescence analysis revealed that the Mg co-doping resulted in approximately a 29% enhancement in characteristic green emission intensity; however, the emission peak height does not change depending over the range of Mg concentrations examined.
Figure 3.14 Emission spectra of 8 mol% Mn, 8 mol% Mn and 1 mol% Mg co-doped and commercial Zn$_2$SiO$_4$ green phosphors. Powders were prepared at 1160 °C for 2 hours.

Zn$_{1.92}$SiO$_4$:Mn$_{0.08}$ green phosphors co-doped with 0.5 mol%, 1 mol%, and 2.5 mol% Mg yielded the same amount of increase in brightness, in accord with previous observations [206]. It is important to note that 8 mol% Mn + Mg co-doped Zn$_2$SiO$_4$ phosphors produced 56% brighter emission compared with the commercial Zn$_2$SiO$_4$:Mn phosphors.

Although Mg co-doping caused a significant increase in characteristic green emission, time resolved spectroscopy analysis revealed that the decay time for 8 mol% Mn doped Zn$_2$SiO$_4$ slightly increased from $t_{10/e} = 9.8$ ms to $t_{10/e} = 10.2$ ms as shown in Figure 3.15.
Figure 3.15 Decay curves of Zn$_2$SiO$_4$:Mn,Mg phosphors with 8 mol% Mn phosphor co-doped with 1 mol% Mg, and commercial one.

When Mg ions were co-doped into the Zn$_2$SiO$_4$ host lattice with Mn ions, the formation of Mg$_2$SiO$_4$ (forsterite) and MgSiO$_3$ (enstatite) phases, which have a six-coordinated crystallographic sites for Mg ions and four-coordinated crystallographic sites for Si ions, is expected. However, X-ray diffraction measurement for the synthesized Mg co-doped Zn$_2$SiO$_4$:Mn phosphors, as shown in Figure 3.16, revealed that the only stable crystalline phase is Zn$_2$SiO$_4$, and diffraction results did not show any evidence for the existence of these solid solutions in the Mg co-doping range used. The possible minor phases Mg$_2$SiO$_4$ and MgSiO$_3$ in the synthesized phosphor are not detected because of their relatively smaller quantities. Note that Mn-doped MgSiO$_3$ phosphor is a
commercial light-red colored phosphor (P13), which has been used as a storage phosphor [17,18]. It has been reported that Mn-doped MgSiO$_3$ phosphors show a broad emission band centered around 660 nm and this characteristic red emission is attributed to the transition $^4T_1$ ($^4G$) $\rightarrow$ $^6A_1$ ($^6S$) of Mn$^{2+}$ [213]. On the other hand, the emission spectra of Mn$^{2+}$ doped Mg$_2$SiO$_4$ phosphors consist of two broad bands peaked at

$$647 \text{ and } 748 \text{ nm, which are attributed to the } ^4T_1(^4G) \rightarrow ^6A_1(^6S) \text{ transitions of Mn}^{2+}$$

ions occupying two non-equivalent Mg$^{2+}$ crystallographic sites: inversion

**Figure 3.16** X-ray powder diffraction patterns for Zn$_{1.92-x}$SiO$_4$:(0.08Mn, xMg), green phosphors calcined at 1160 °C for 2 hours. x = 0.005, 0.01, 0.025.
symmetric octahedron (M1) and mirror symmetric octahedron (M2) in Mg$_2$SiO$_4$ [214,215]. The crystal field strength of M2 sites is weaker because the average Mg-O bond length of M2 crystallographic sites is larger than that of M1. Based on this fact and the Tanabe-Sugano diagram, the emission bands peaked at 647 and 748 nm could be attributed to the characteristic luminescence of Mn$^{2+}$ ions occupying M2 and M1 crystallographic sites, respectively. Therefore, if there had been some crystalline and stable MgSiO$_3$ and/or Mg$_2$SiO$_4$ phase formation during the co-doping of Zn$_2$SiO$_4$·Mn with Mg$^{2+}$, it would be possible some of the Mn$^{2+}$ ions would occupy the Mg ions octahedral site, so that this would give the characteristic red colored emission. It would be expected that such a red emission would alter or reduce the characteristic green emission of the Mn$^{2+}$ doped Zn$_2$SiO$_4$ phosphor. However, the Mg$^{2+}$ co-doping resulted in a significant improvement in emission intensity, which corroborates that no MgSiO$_3$ and/or Mg$_2$SiO$_4$ peaks were observed in the X-Ray Diffraction spectra.

Sohn et.al., [206] attempted to explain the dominant mechanisms for the improvement in green emission intensity upon co-doping Mg$^{2+}$ into the Zn$_2$SiO$_4$·Mn phosphor based on the schematic energy band diagram as shown in Figure 3.17. It could be assumed that almost all Mn$^{2+}$ ions tend to occupy the tetrahedral Zn$^{2+}$ sites in the Zn$_2$SiO$_4$ host lattice and that Mg$^{2+}$ ions can also be considered as occupying the tetrahedral Zn$^{2+}$ sites in the Zn$_2$SiO$_4$ matrix. When Mg$^{2+}$ is co-doped into Zn$_2$SiO$_4$·Mn, the unoccupied energy levels (3s and 3p components) of Mg are located near the lowest unoccupied molecular orbitals (LUMO) of down-spin in Mn$^{2+}$ ions. The energy of Mn$^{2+}$ transition between spin-
up and spin-down is shortened from 2.6 to 2.5 eV when Mn$^{2+}$ and Mg$^{2+}$ ions are co-doped together.

Figure 3.17 Schematic energy band diagram for Mn and Mg co-doped Zn$_2$SiO$_4$ phosphors with their relative locations between the conduction and valence band of the crystalline host lattice [206].

The energy difference between spin-up and spin-down states of the 3s and 3p energy levels in the Mg$^{2+}$ ion was reported to be about 0.2 eV and the Mg$^{2+}$ ions' 3s and 3p electron of spin-up can jump down to the manganese level of spin-up state. This transition is spin allowed and, hence, it can facilitate the green emission and contribute to the characteristic green emission intensity. However, the probability of such a transition is very low because of the presence of two different charge transfer steps, Mn$^{2+}$ to Mg$^{2+}$ and vice versa, it is enough to enhance the green emission. Even such a slight assist of Mg$^{2+}$ co-doping would
be effective by considering the fact that the probability of manganese spin flip transition itself is also very low.
SECTION 4

Development of New Phosphors by Modified Sol-Gel Routes

4.1. Introduction

Inorganic luminescent materials have a wide range of applications from light emitting diodes to luminescence immunoassay. The development of new solid inorganic luminescent materials has provided improvements in lighting and display systems. In recent years, great efforts have been dedicated to invent new rare earth or transition metal ion doped material systems as luminescent materials with high absorption in the UV or near UV spectral region. In particular, cerium, europium, terbium, and lead ions are well-known dopants for many different inorganic host lattices and are of great scientific and technological interest. However, because of the refractory nature of the ceramic host lattices with rare-earth and transition metal oxides, conventional synthesis of inorganic luminescent materials requires longer preparation and higher calcination temperatures. Therefore, simple and economical processing of ceramic materials with modified sol-gel techniques can be used in the preparation of inorganic luminescent materials efficiently and these techniques contribute to the development of novel phosphors because of their versatility.

The technological importance of the sol-gel and modified sol-gel routes and their advantages over the conventional synthesis techniques were summarized in Chaper II. In this chapter, successful application of these modified sol-gel routes for the development of new phosphors will be presented. In addition to the
processing details and the characterization results for the produced phosphors, the luminescence properties and associated mechanisms will be explained in a detailed manner.

4.2. SrZnO₂ as a Host Lattice

The crystal structure of SrZnO₂ was reported to be in the orthorhombic system with the space group of Pnma [216]. In this orthorhombic crystalline system, the ZnO₄ tetrahedra share edges with each other and from waved layers on the ab plain as shown in Figure 4.1. On the other hand, the Sr atoms are located at the cavity between the ZnO₄ tetrahedra layers. Overall, there is one crystallographic site for the Sr atom, one for the Zn atom, and two for the O atoms.

Kubota et al., [217] reported a new luminescent material by co-doping the SrZnO₂ with Ba²⁺ and Mn²⁺ ions. Their emission spectra (Sr₁₋ₓBaₓ)Zn₀.₉₉Mn₀.₀₁O₂ studies revealed that it was a broad peak extending from 550 nm to 630 nm. The peak of emission shifted from 578 to a longer wavelength, 582 nm, however the emission intensity decreased with the Ba ion concentration. The excitation spectra of (Sr₁₋ₓBaₓ)Zn₀.₉₉Mn₀.₀₁O₂ were also very broad, from around 200 to 450 nm, and consisted of five or six peaks [217]. This broad emission was attributed to the d-d, ⁴T₁ (⁶S) – ⁶A₁ (⁴G) transitions of Mn²⁺ ions. ⁶A₁ represents the ground level and the ⁴T₁ is the lowest excitation level at which the energy deceased with the increase of the crystal field. Therefore, the energetic transitions were strongly influenced by the crystal field within the SrZnO₂ host lattice.
Figure 4.1 Crystalline structure of the SrZnO$_2$. The Sr atoms located between the ZnO$_4$ tetrahedra layers [216].

By using the same host lattice, a new luminescent material is obtained by doping with terbium [218]. The emission spectra of SrZnO$_2$:Tb$^{3+}$ exhibited the characteristic Tb$^{3+}$ ion energy transmissions, $^5D_{3,4} \rightarrow ^7F_j$ ($j=3-6$), and the maximum emission peak was located at 543 nm when the phosphor was excited at 262 nm. On the other hand, the excitation spectra consist of two strong absorption bands located at 250 nm and 262 nm when measured with the emission wavelength of 543 nm.

Activating this new host matrix, SrZnO$_2$, with different rare-earth and transition metal ions might provide new luminescent materials having potential applications in optical devices. In this chapter, Ce$^{3+}$, Pb$^{2+}$, and Tb$^{3+}$ doped SrZnO$_2$ phosphors prepared with novel modified sol-gel routes and their material and optical characteristics are reported.
4.3. Pb\textsuperscript{2+} doped SrZnO\textsubscript{2} Phosphors

4.3.1. Electronic States of Pb\textsuperscript{2+}-doped Phosphors

The luminescence of compounds containing metal ions with ns\textsuperscript{2} configuration can be used in X-ray imaging devices, low pressure lamps, and high energy physics [219]. Ti\textsuperscript{3+}, Pb\textsuperscript{2+}, Bi\textsuperscript{3+} (all with 6s\textsuperscript{2} configuration) and Sn\textsuperscript{2+}, Sb\textsuperscript{3+} (both with 5s\textsuperscript{2} configuration) are well known ns\textsuperscript{2} class luminescent ions used as impurities in inorganic host lattices.

The optical properties of Pb\textsuperscript{2+} have been progressively studied as an activator in the host matrix [220,221]. An energy level diagram for an impurity ion with the ns\textsuperscript{2} ground state configuration is shown in Figure 4.2. In principle, the luminescence properties of the Pb\textsuperscript{2+} ion with 6s\textsuperscript{2} configuration are described by the ground state \(^1S_0\) and two excited states of singlet \(^1P_1\) and triplet \(^3P_{0,1,2}\) [222,223]. For the free ion, the ground level is \(^1S_0\) originating from the s\textsuperscript{2} configuration, and the lowest excited energy levels are \(^3P_0\), \(^3P_1\), and \(^1P_1\) derived from the excited sp configuration. In principle, the absorption spectra of Pb\textsuperscript{2+} ions in solids consist of three bands labeled A, B, and C in order of increasing energy corresponding to electronic transitions \(^1S_0 \rightarrow ^3P_0\), \(^3P_1\), \(^3P_2\) and \(^1P_1\), respectively as shown in Figure 4.2. The C band is associated with the allowed transitions, whereas transitions corresponding to A and B bands are partly allowed by spin-orbit coupling and vibronic coupling, respectively [17,18]. The energy levels of A band lies in the UV range and it has been reported to be markedly sensitive to the surroundings.
The influence of host lattice on the optical properties of ns$^2$ ions is found to be significant but it is relatively less understood. Strong interactions of s$^2$ ions with the host lattice are expected because the transitions on s$^2$ ions involve the outer valence shells [219]. This is also supported by the s$^2$ ion effect which explains the off-centre positioning of the s$^2$ ion in the ground state due to the lone pair of electrons, i.e., pseudo Jahn-Teller effect [222]. As a result, the electrons will be positioned in an asymmetric orbital in a way that an overlap with the wavefunctions will be enhanced on one side of the s$^2$ ion.

![Energy Level Diagram](image)

**Figure 4.2** Schematic representation of the Energy level diagram for an impurity ion with the ns$^2$ ground-state configuration [223].

Studies on the luminescence of Pb$^{2+}$ ion in several host lattices have shown that the interaction of the impurity ion with the host lattice strongly influences the
value of the Stokes shift of the emission from the $^3P_0$ excited state of Pb$^{2+}$, but can also give rise to emission from a Pb$^{2+}$ related charge-transfer state [224,225]. It is important to note that the border between the $^3P_0$ excited state and the Pb$^{2+}$-related charge transfer is not very distinct because of the contribution of Pb$^{2+}$ ion and ligand wavefunctions to the charge-transfer states can change significantly depending on the host lattice type. As a result, the characteristic emission of ions with ns$^2$ configuration varies significantly depending on the host lattice, and hence Pb$^{2+}$ emission is very difficult to predict [226].

4.3.2. Synthesis of SrZnO$_2$:Pb phosphors by the Adipic Acid Templated Sol-Gel Route

The general characteristics and technological importance of adipic acid is given in Chapter II. As a major application, adipic acid, (HOOC(CH$_2$)$_4$COOH), has been used as the monomer for the production of polyamides (Nylon-6,6) by the polycondensation reaction with hexamethylene diamine [227]. It was also used as a chelating agent to synthesize cathode material for lithium secondary batteries [158,159]. The main advantage of this method is the capability of preparing complex mixed oxide solutions, obtaining molecular level homogeneity in solution, stoichiometric control at lower temperature calcinations with shorter time.
4.3.3 Experimental Procedure

$\text{Sr}_{1-x}\text{Pb}_x\text{ZnO}_2$ powders were prepared from the starting materials of $\text{Sr(NO}_3\text{)}_2$ (>99%, Alfa Aesar), $\text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}$ (99%, Alfa Aesar), $\text{Pb(NO}_3\text{)}_2$ (99.3%, J.T. Baker Chemical Co.) and adipic acid, (99%, Sigma Aldrich). The flowchart for the Adipic acid templated sol-gel processing of the $\text{Sr}_{1-x}\text{Pb}_x\text{ZnO}_2$ phosphors is given in Figure 4.3.

![Flowchart](chart.png)

**Figure 4.3** Flow chart for the synthesis of $\text{Sr}_{1-x}\text{Pb}_x\text{ZnO}_2$ blue-white phosphors prepared with the novel adipic-acid templated sol-gel route.
Aqueous solutions of all the starting materials were made by dissolving them in deionized water. In a typical batch, 10 ml of 2 M cation solution was added to 50 ml of 0.2 M adipic acid solution prepared at a mild temperature (~45 °C). The clear mixture was then heated to 80 °C on a hot plate with continuous stirring. After evaporation of all the water, a translucent sol was formed and was further heated in an oven at 120 °C for 2 h in air to get a white-colored, crispy, and loosely-connected powder that was subsequently fired at the desired temperatures for 2h in air. In the precursor solution, the molar ratio of the metal ions to adipic acid was set to different ratios in order to find the best cation to organic ratio for gel formation. The results are presented in Table 4.1. The molar ratio of 1:0.5 for Metal:Adipic Acid content was found to give stable, transparent gel formation. Other ratios yielded white-colored, non-transparent, hard precipitates.

**Table 4.1**
Stable Gel formation for different metal to adipic acid ratio.

<table>
<thead>
<tr>
<th>Metal:AA</th>
<th>Cation #</th>
<th>(COO-) #</th>
<th>Stable Gel Formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0.5</td>
<td>1</td>
<td>1</td>
<td>Yes</td>
</tr>
<tr>
<td>1:1</td>
<td>1</td>
<td>2</td>
<td>No</td>
</tr>
<tr>
<td>1:2.5</td>
<td>1</td>
<td>5</td>
<td>No</td>
</tr>
<tr>
<td>1:5.0</td>
<td>1</td>
<td>10</td>
<td>No</td>
</tr>
</tbody>
</table>

Based on this, all phosphor particles were synthesized using the 1:0.5 ratio for the Metal:Adipic Acid content. The molar doping concentrations of Pb²⁺ in the phosphor were 0.1%, 0.5%, 1.0%, 1.5%, 2.5%, and 5%, respectively.
The crystallization behavior and crystal structure of the phosphor powders were checked by using a room temperature X-Ray Diffractometer (Philips PW 2273) with CuKα radiation. Crystal size measurements were made using the built-in Jade program for this instrument. Excitation and emission characteristics of the phosphor powders were recorded at room temperature on a Hitachi F-4500 fluorescence spectrophotometer with a 150W Xe-lamp as an excitation source. Time-resolved spectroscopy was used to measure the decay time with the same equipment. Scanning electron microscopy (SEM) was performed using a Hitachi S-4700 cold field emission SEM and the powder samples were coated with Pt. The particle sizes and size distributions were measured using a dynamic light scattering (DLS) on a Microtrac® Nanotrac NPA 250 instrument. The diffuse reflectance spectra were recorded on a Shimadzu UV-240 spectrophotometer. IR spectroscopy analysis was done using Thermo-Nicolet (Nexus 470) FTIR.

4.3.4. Results and Discussions

4.3.4.1. XRD Analysis

The crystallinity of the SrZnO₂:Mn (x = 0.001, 0.005, 0.01, 0.015, 0.025, 0.05) powders fired between 800 and 1100 °C in ambient air for 2 h were characterized using XRD patterns and are shown in Figure 4.4. Samples prepared at 800 °C still have raw materials, however at 900 °C, the SrZnO₂ crystallographic structure was obtained with some weak lines corresponding to ZnO and SrCO₃ as secondary phases in trace amounts. These secondary phase
peaks disappeared and a single phase of SrZnO₂, corresponding to the standard JCPDS file # 41-0551, was obtained at and above 1000 °C. It suggests that the introduction of Pb²⁺ ions into the SrZnO₂ host lattices does not change the XRD pattern of the sample. Phosphors prepared at 1000 °C have an average crystallite size of 48 nm.

![X-ray diffraction patterns of Pb doped SrZnO₂ calcined at 800 °C (a), 900 °C (b), 1000 °C (c), and 1100 °C (d). SrZnO₂ phase start to form at 900 °C with ZnO and SrCO₃ phases and single phase orthorhombic structure of SrZnO₂ formed at 1000 °C.](image)

**Figure 4.4** X-ray diffraction patterns of Pb doped SrZnO₂ calcined at 800 °C (a), 900 °C (b), 1000 °C (c), and 1100 °C (d). SrZnO₂ phase start to form at 900 °C with ZnO and SrCO₃ phases and single phase orthorhombic structure of SrZnO₂ formed at 1000 °C.
The crystal structure of SrZnO$_2$ is orthorhombic and in the space group of Pnma (see subsection 4.2). It has a layered structure which consists of ZnO$_{4/2}$ tetrahedra linked through common vertexes (Zn-O-Zn), and Sr atoms are located between these waved vertex layers [228]. The ionic radii of Zn$^{2+}$, Sr$^{2+}$, and Pb$^{2+}$ are 74, 121, and 123 pm, respectively [229]. Therefore, when the SrZnO$_2$ host lattice is doped with Pb$^{2+}$ ions, they likely substitutionally replace strontium atoms from the host lattice.

**4.3.4.2. SEM Analysis**

A typical scanning electron micrograph of the Pb$^{2+}$-doped SrZnO$_2$ samples prepared at 1000 °C for 2 hours is shown in Figure 4.5. The calcined phosphor

![Figure 4.5](image)

**Figure 4.5** A typical SEM image of the Pb$^{2+}$-doped SrZnO$_2$ phosphors prepared by calcining the precursors at 1000 °C for 2 hours.
particles have an irregularly-rounded morphology and range in size from 50 to 250 nm. These submicron particles formed larger aggregates in micron and submicron sizes.

4.3.4.3. Particle Size & Distribution Analysis

Particle size and distribution analysis were made via dynamic light scattering, with results shown in Figure 4.6. The average particle size is 918 nm with a range of sizes extending from 400 nm to 4600 nm.

![Graph of particle size distribution](image)  
*Figure 4.6* Particle size distribution of Pb²⁺-doped phosphor powders prepared by calcining the precursors at 1000 °C for 2 hours. The average particle size is 918 nm.

4.3.4.4. FTIR Analysis

The infrared spectrum of the precursor of 1 mol% Pb doped SrZnO₂ prepared by Adipic acid templated sol-gel route and the same precursor calcined at 1100 °C for 2 hours are shown in Figure 4.7(a) and Figure 4.7(b), respectively.
Figure 4.7 Precursor of 1 mol% Pb$^{2+}$-doped SrZnO$_2$ phosphors prepared by the adipic acid-templated sol-gel route (a), and the same precursor fired at 1100 °C for 2 hours.
The IR spectrum of the precursor material with the broad band covering a range from 3500 to 2500 cm$^{-1}$ is due to the stretching vibrations of O-H bonds. On the other hand, the characteristic peaks that appear at 1700 cm$^{-1}$ and 1220 cm$^{-1}$ belong to C=O stretching of carboxylic group of adipic acid. The IR bands located at 2950 and 2880 are attributed to the symmetric stretching of (C-H) [230]. The bands located at 1450 and 948 cm$^{-1}$ are due to the presence of nitrates in the precursor material. The band located at 1400 cm$^{-1}$ of the symmetric stretching vibrations for carboxyl ions of the adipic acid complex. The wagging vibrations of adipic acid are observed at 1270 and 1340 cm$^{-1}$ [231]. The band located at 905 cm$^{-1}$ is attributed to CC stretching vibrations, while the bands located at 738 and 815 cm$^{-1}$ are due to the CH$_2$ rocking (rocking-twisting) due to the presence of adipic acid complex with metal ions [231]. The IR spectrum of the same precursor calcined at 1100 °C for 2 hours showed that the characteristic carboxylate and nitrate absorbance bands disappeared, and new bands located at 862 and 995 cm$^{-1}$ start to appear. These low-IR range bands indicate the formation of metal oxide compounds. The wide band located at 1460 cm$^{-1}$ can be associated with the presence of trace amounts of adipic acid.
4.3.4.5. Diffuse Reflectance Spectroscopy Study of Pb\(^{2+}\)-doped SrZnO\(_2\) Phosphors

The diffuse reflectance spectra of the undoped SrZnO\(_2\) samples are very similar to that of the dilute Sr\(_{1-x}\)ZnO\(_2\):Pb\(_x\) system with x = 10\(^{-2}\) and are shown in Figure 4.8. The characteristic bandgap energy of 3.4 eV (364 nm) was found for SrZnO\(_2\) by extrapolating the sharp slope to the level of no absorption in the reflectance spectra. The absorption wavelength at 283 nm was seen for doped and undoped samples, but the peak at 317 nm becomes detectable in reflectance spectra only when SrZnO\(_2\) is doped with Pb\(^{2+}\).

![Diffuse Reflectance Spectra](image)

**Figure 4.8** Diffuse Reflectance Spectra of SrZnO\(_2\):Pb for undoped, 1 mol% and 5 mol% Pb doped. Data recorded at room temperature.
4.3.4.6. Photoluminescence Characteristics of Pb$^{2+}$-doped SrZnO$_2$ Phosphors

Figure 4.9 shows the excitation and emission spectra for Sr$_{1-x}$Pb$_x$ZnO$_2$ ($x = 0.015$) phosphors fired between 800 and 1100 °C. Excitation spectra monitored at 455 nm and consist of two broad intense bands of 283 nm, 317 nm, and a weak shoulder at 275 nm.

![Photoluminescence spectra](image)

**Figure 4.9** Photoluminescence properties of 1.5 mol% Pb doped SrZnO$_2$ phosphors, depending on the calcination temperatures between 800 and 1100 °C, with excitation spectra monitored at 455 nm and the emission spectra excited at 283 nm. (a: 800°C, b: 900°C, c: 1000 °C, d: 1100°C)
When temperature increases, the relative intensity of the peak centered at 317 nm increases, although the band at 283 nm decreases and shifts towards higher wavelengths. When excited at 283 and 317 nm, a broad emission band was observed, extending from 374 to 615 nm with a maximum at about 451 nm. The emission spectrum of SrZnO$_2$:Pb$^{2+}$ changes depending on the excitation wavelength and the calcination temperature of the prepared phosphors (Figure 4.10). Under 283 nm excitation, phosphors prepared at 1000 °C show higher emission intensity than phosphors under 317 nm excitation as shown in Figure 4.10(a).

However, the relative intensity of the 451 nm emission peak ($\lambda_{ex} = 283$ nm) of phosphors prepared at 1100 °C is slightly lower than the intensity when the phosphor prepared under 317 nm excitation. These observations suggest that two different luminescent centers are possibly formed when Pb$^{2+}$ is doped into the host lattice. In SrZnO$_2$, all Sr atoms are crystallographically equivalent and only one site is available. Because of the large ionic radii difference between Pb$^{2+}$ and Zn$^{2+}$, only Sr atoms will be replaced substitutionally when doped with Pb$^{2+}$ ions. Therefore, the second active luminescent center of Pb$^{2+}$ ions can only be the interstitial positions in SrZnO$_2$ host lattice.

The excitation and emission spectra of SrZnO$_2$ activated with different Pb concentrations prepared at 1000 °C for 2 h are illustrated in Figure 4.11(a) and Figure 4.11(b), respectively. The undoped samples have no PL properties of emission. However, broad bands have been observed from the Pb$^{2+}$ doped samples with an emission peak at the fixed position centered at 451 nm.
Figure 4.10 The emission spectrum of $\text{Sr}_{0.99}\text{Pb}_{0.01}\text{ZnO}_2$ depending on the excitation wavelength and calcination temperatures. Calcined at 1000 °C (a) and 1100 °C (b).
The calculated full width at half maximum (FWHM) is about 95 nm for the brightest emission (1 mol% Pb). The two bands in the excitation spectrum coincide with the two absorption bands at 283 nm and 317 nm, respectively, in the diffuse reflectance spectrum of Sr$_{1-x}$Pb$_x$ZnO$_2$ phosphors. The Pb$^{2+}$-induced absorption band at 317 nm is not observed in the diffuse reflectance spectrum of the undoped SrZnO$_2$ host lattice (see Figure 4.8). This lowest energy absorption band is due to the $^1S_0 \rightarrow ^3P_1$ (A-band) transition on the Pb$^{2+}$ ion. The higher energy absorption may be assigned to the allowed $^1S_0 \rightarrow ^1P_1$ transition (C-band). This assignment would yield an energy difference between $^1P_1$ and $^3P_1$ states of about 4000 cm$^{-1}$. However, in crystalline solids, the energy separation between $^1P_1$ and $^3P_1$ states usually amounts to about 12,000 cm$^{-1}$ [232]. Although the absorption edges of the doped and undoped samples at around 283 nm cannot be clearly distinguished from the diffuse reflectance spectra in Figure 4.8, the excitation band shows that the host lattice has a weak absorption centered at 269 nm and has no luminescence when excited at 283 nm, as shown in Figure 4.11(b). Other research groups have also reported that SrZnO$_2$ has no characteristic excitation and emission bands [218]. From the weakness of the host lattice excitation band in the excitation spectrum, it can be assumed that an energy transfer from the host to the Pb$^{2+}$ impurity is not efficiently present. Moreover, there is no emission from the SrZnO$_2$ host lattice which overlaps with the absorption spectrum of the Pb$^{2+}$-doped samples, hence it is not expected that the Pb$^{2+}$ impurity would be excited by excitation of the host followed by an interband energy transfer from the SrZnO$_2$ host to Pb$^{2+}$ impurity [233]. The
Figure 4.11 Effect of Pb-dopant level from 0.1 to 5 mol% on photoluminescent properties of SrZnO$_2$. (a) Excitation and (b) Emission characteristics. Samples prepared by calcining at 1000 °C for 2 hours.
presence of Pb$^{2+}$ ions provides an efficient excitation centered at 283 nm, which is thus tentatively assigned to the absorption into the excitonic state. Increasing the calcination temperature from 1000 to 1100 °C for the same Pb$^{2+}$ concentration resulted in an increase in the population of A-band absorption at the expense of the excitonic states, as shown in Figure 4.10.

It has been reported that the absorption and emission spectra of Pb$^{2+}$ in many host lattices are in the near-UV spectral region due to the 6s$^2$-6s6p inter-configurational transition ($^3P_1 \rightarrow ^1S_0$) [234,235]. However, Sr$_{1-x}$Pb$_x$ZnO$_2$ phosphors showed a broad emission band covering the near-UV spectral region and the visible part of the spectrum, This can be explained by the large stokes shift of the emission around 13,000 cm$^{-1}$. Similar observations were reported for different luminescent materials with high Stokes shift emissions [236].

Despite extensive studies with different host lattices, the origin of the visible emission in s$^2$ ion-doped material systems remains unresolved and varies from host to host. There are three popular mechanisms proposed as impurity-trapped exciton type [237,238], D-level emission (ligand-to-metal charge transfer transitions or perturbed exciton emission) [223,239], and s$^2$-ion effect (pseudo Jahn-Teller effect) [239]. The host lattice with narrow band-gap allows Pb$^{2+}$ ions to ionize under UV excitation into their first excited states, located just below the conduction band of the host crystal [237]. In Sr$_{1-x}$Pb$_x$ZnO$_2$ phosphors, the visible emission band is associated with the ionization process described above, in which the active Pb$^{2+}$ center injects an electron into the host lattice conduction
band. Based on this, the blue-centered emission is an impurity-centered exciton state that is populated by an electron transfer from the $^1P_{0,1}$ excited state of the Pb$^{2+}$ ion to the SrZnO$_2$ conduction band. The emission due to the ionization mechanism is not only valid for the Pb$^{2+}$ ion, but has also been observed in luminescence of ions such as Yb$^{2+}$ [238], Eu$^{2+}$ [240], Cu$^+$ [241], and Bi$^{3+}$ [242]. The impurity-trapped exciton structure consists of the hole localized on the luminescent ion and the electron delocalized over the surrounding cations; for instance, a Yb$^{3+}$ core with the electron delocalized over the 12 nearest neighbors Sr$^{2+}$ ion forms the trapped exciton in SrF$_2$:Yb$^{2+}$ [238]. As previously described, the SrZnO$_2$ structure consists of a two-dimensional array of ZnO$_{4/2}$ tetrahedra which share corners with each other to form waved layers, and Sr atoms are located in the cavity between the layers. Therefore, the exciton structure in SrZnO$_2$:Pb$^{2+}$ can be considered to consist of the hole residing on the Pb$^{3+}$ ion and the electron over the ZnO$^{2-}$. It has been reported that the M(d$^{10}$)-O(II) complexes delocalize easily when their concentration is high [243]. It is also noteworthy that the Stokes shift of impurity-trapped excitonic state emission is reported to be much larger than that of the localized ($^3P_{0,1} \rightarrow ^1S_0$) transitions [237,242].

In addition to the impurity-trapped exciton, the visible emission can also be perceived as an emission arising from a charge-transfer transition between the activator Pb$^{2+}$ ($6s^2$) and the Zn$^{2+}$ ($3d^{10}$) ions of the host lattice. The occurrence of luminescence from complexes consisting of d$^{10}$ metal ions surrounded by oxygen ions in solids and molecules such as Zn$_4$O(Acetate)$_6$ [243] and Zn$_4$O(BO$_2$)$_6$ [244], in which the Zn$^{2+}$ ion is tetrahedrally coordinated, has been reported. The
relevant strongly Stokes-shifted broad emission was associated with a considerable amount of charge-transfer character, like the well-known luminescence of oxo-complexes of the d^0 metal ions such as vanadates and molybdates [243,245]. Since the D-level in the energy scheme of ns^2 ions is thought to be of a charge-transfer type, the visible emission in SrZnO_2:Pb^{2+} can be assigned to a D → ^1S_0 radiative transition.

It has been reported that the pseudo-Jahn-Teller effect (s^2 ion effect) also contributes to the formation of the large stokes shifts because the s^2 ion will possibly shift to a more centered position in excited state relative to the off-centre positioning in the ground state, which will cause a large stokes shift [239].

The relative intensities of the emission peaks change dramatically depending on the doping level of the Pb^{2+} ions (Figure 4.12). With increasing Pb^{2+} concentration, the emission intensity of the samples increases and reaches a maximum at 1 mol% Pb, and then decreases when the mole concentration of Pb^{2+} ion exceeds this.

The concentration dependence of the emission intensity can be explained by the well-known concentration quenching of the emission (see Chapter III). Concentration quenching in inorganic phosphors has been attributed to migration of excitation energy to the quenching centers (traps) or to cross relaxation mechanisms [246]. In Pb^{2+} doped SrZnO_2 phosphors, it can be attributed to the former one, when the distance between the excited luminescent center and a trap is close enough to transfer excitation energy readily to the trap, where the excitation energy is lost non-radiatively. The produced phosphors have low
concentrations of quenching centers, mainly originating from the defects produced during the synthesis and unwanted trace impurities contained in

![Graph](image)

**Figure 4.12** The relative intensity of emission at 455 nm as a function of Pb\(^{2+}\) concentration for SrZnO\(_2\):Pb\(^{2+}\) phosphors prepared at 1000 °C for 2 hours.

starting materials [247]. When the concentration of Pb\(^{2+}\) ions (activators) is less than 1 mol%, then these luminescent centers can be accepted as “isolated” and the excitation energy transfer to traps is too small to account for luminescence quenching. However, beyond 1 mol% Pb, the distance between activators will potentially be close enough to transfer the excitation energy from one center to another which causes non-radiative transitions extensively. Therefore, the luminescence intensities of samples decrease when the Pb\(^{2+}\) ion amount exceeds 1 mol% in SrZnO\(_2\) host lattice.

The color coordinates of the SrZnO\(_2\):Pb phosphors were found to be \(x = 0.2267\), and \(y = 0.2227\).
Mao et al. [248] reported that co-doping of Pb\(^{2+}\) and Cu\(^+\) in the host lattice of ZnS resulted in better luminescence and longer decay times in a way which Cu\(^+\) and the host matrix form the active luminescent center and Pb\(^{2+}\) forms a deep level as a sensitizer. When SrZnO\(_2\) host lattice was co-doped with Pb\(^{2+}\) and Cu\(^+\) at different concentrations resulted in no luminescence, however the synthesized powder was green color in body which might have a potential application as a pigment material.

**4.3.4.7. Time-Resolved Spectroscopy**

Phosphorescence lifetime studies with time-resolved spectroscopy revealed that the brightest luminescence with 1 mol% and 1.5 mol% Pb-doped SrZnO\(_2\) phosphors showed an exponential decay curve with a decay time of \((t_0/e)\) about 33 ms (Figure 4.13). This slow decay property is very abnormal compared with

![Graph](image_url)

**Figure 4.13** Decay curves for 1 mol% and 1.5 mol% Pb\(^{2+}\) doped SrZnO\(_2\) phosphors.
other Pb$^{2+}$ doped host lattices. A strong decrease in the luminescent decay time from ms to μs with increasing temperature is usual for A- and D-level emissions. At low temperatures, $^3P_0 \rightarrow ^1S_0$ emission has a ms range lifetime because of the forbidden transitions ($\Delta J = 0$) [18]. At higher temperatures, $^3P_1$ level is thermally populated, and due to mixing of $^1P_1$ and $^3P_1$ states, the spin selection rule is partially-lifted and the decay time of this allowed emission is shortened to μs. Although the exact nature of the D-level emission is still unknown, the same behavior has been attributed to the D-level emission of charge-transfer transitions [233]. For allowed charge-transfer transitions, ns level decay times are typically observed; however, a small wavefunction overlap and spin-forbidden character can increase the decay time to ms ranges at low temperatures for Pb$^{2+}$-doped phosphors similar to the charge-transfer transitions in $d^0$ complexes [233,239]. An impurity trapped exciton type emission from different host lattices has been reported to have a typical decay time in μs at high temperatures [237,241]. The long decay time of SrZnO$_2$:Pb can be associated with the release of holes from the trapping center, to restore the radiative decay of the luminescence centers. After excitation, the majority of the excited Pb$^{2+}$ ions immediately release photo energy by emitting and then returning to the ground state (in μs). However, a very small fraction may produce holes by taking an electron from the valence band and stay as Pb$^+$. These mobile holes can be trapped by any cationic defects, such as possible Sr$^{2+}$ vacancies formed in nanocrystals during the synthesis and fast cooling of the heat-treated samples in
air. A reverse combination process in which holes turn back to Pb\(^+\) to form Pb\(^{2+}\) accompanies the characteristic emission. The exponential character of the decay curve shows that there is no re-trapping after the recombination process. Such an interpretation runs parallel to the case of Bi\(^{3+}\)-doped Ca\(_{1-x}\)Sr\(_x\)S phosphors with a persistent phosphorescence and a direct cation vacancy formation was observed because of the valence difference between Ca\(^{2+}\) and Bi\(^{3+}\) [249].
4.4. Ce\textsuperscript{3+} doped SrZnO\textsubscript{2} Phosphors

4.4.1. Electronic States of Ce\textsuperscript{3+}-doped Phosphors

Cerium-doped inorganic host lattices are known as very efficient luminescent material systems, with quantum efficiencies close to one in some cases [250]. This high quantum efficiency can be explained in terms of the electronic structure of trivalent cerium ion. It has the simple (4f\textsuperscript{1}) ground state with one-electron case and the excited configuration is represented by 5d\textsuperscript{1}. The 4f\textsuperscript{1} ground state configuration can give two levels, \(^2\text{F}_{5/2}\) and \(^2\text{F}_{7/2}\), separated by \(-2,000\) cm\(^{-1}\) due to spin-orbit coupling [18]. On the other hand, the first excited 5d\textsuperscript{1} configuration is split by the crystal field in two to five components with a total amount of 15,000 cm\(^{-1}\) (Figure 4.14). The characteristics of emission from cerium ions depends on both the overall 4f-5d separation and the crystal field splitting of the excited d-levels [251,252]. The visible emission occurs from the lowest excited state energy level component (\(^2\text{E}_g\) for cubic, and \(E'_1\) for the non-cubic structures) of the 5d\textsuperscript{1} configuration to the spin-orbit split ground state. The transition from the energetically lowest 5d excited level to the 4f ground state is parity allowed and spin selection is not applicable, and hence the Ce\textsuperscript{3+} ion emission transition is fully allowed. Typically, the 4f\textsuperscript{1} ground state leads to a 20,000-40,000 cm\(^{-1}\) large gap between the spin-orbit split ground state and the lowest level of the 5d orbital. Therefore, the possibility of non-radiative multi-phonon relaxation processes is very unlikely and the characteristic luminescence is typically observed in the blue and UV spectral region with a very short decay time, on the order of \(10^{-8}\) s [18].
Figure 4.14 The simplified energy level diagram of the Ce$^{3+}$ ions showing the lowest energy ground state components and the first excited 5d states of Ce$^{3+}$ in cubic and non-cubic host lattices. $\Delta$: crystal field splitting.

It has been reported that the decay time is longer if the characteristic emission is at longer wavelengths, such as 20 ns for the 300 nm emission of CeF$_3$, on the other hand it is 70 ns for the 550 nm emission from Ce$^{3+}$ doped Y$_2$Al$_5$O$_{12}$ phosphors. The decay time ($\tau$) for a given transition on Ce$^{3+}$ ion in an host lattice is reported to be proportional to the square of the emission wavelength ($\lambda$) [18]

$$\tau \sim \lambda^{-2}.$$
Studies on many different host lattices revealed that the Stokes shift of the Ce$^{3+}$ emission is not very large and typically varies from a thousand to a few thousand wavenumbers. The spectral position of the cerium ion induced emission band are influenced by three factors; [18]

i. The Stokes shift.

ii. The nephelauxetic effect (covalency) which reduces the energy difference between the ground state (4f$^1$) and the excited state (5d$^1$) configurations.

iii. Crystal field splitting ($\Delta$) of the excited state of 5d$^1$ configuration is very critical. A low symmetry crystal field reduces the lowest crystal field component (E’$_1$) from which the ultraviolet or visible emission originates.

Although non-radiative transitions are not very likely, the emission from some Ce$^{3+}$ doped host lattices such as Y$_2$O$_3$, La$_2$O$_3$, and La$_2$O$_2$S [253] is completely quenched, however other rare earth ions like Eu$^{3+}$ provide efficient luminescence in these same host lattices [17,18]. The luminescence quenching phenomenon specific to cerium ions can be explained by the large Stokes shift, electron transfer, and photoionization [253]. It is a general assumption that the Stokes shift is too small for the cerium ion to cause a complete quenching of emission. Therefore, the electron transfer to neighboring ions or to the conduction band of the host lattice are the dominant mechanisms for the luminescence quenching of cerium ions. For instance, electron transfer to neighboring ions quenches the
emission in cerium doped vanadates [20]. Photoionization as a mechanism for the luminescence quenching and the correlation of the luminescence efficiency with the bandgap energy of the host material has been reported [252,253]. In relatively-small bandgap host materials, the lowest 5d excited energy level will be located very close or even inside the conduction band, hence leading to photoionization of the Ce$^{3+}$ ion when excited into the 5d level and to quenching of the characteristic emission as a non-radiative relaxation process. Yen et al., [254] concluded that the presence of an absorption band corresponding to the acceptor-like electron transfer in the oxidized samples provides information about the location of the cerium levels within the bandgap of the host material using the Born cycle. It states that the sum of the acceptor-like and donor-like (transfer of the cerium ground state electron (4f) into the host material conduction band) thresholds must equal the energy gap between the host valence and conduction band. Table 4.2 shows a selection of Ce$^{3+}$-doped host materials with the observed luminescence characteristics, viz. quenched or unquenched. The host absorption energy of the host materials listed in Table 4.1 corresponds to the onset of the host absorption and the actual band gap reduced by the binding energy of the exciton. Based on this table, the boundary between the luminescent and quenched Ce$^{3+}$-doped material systems lies between 5.58 eV and 6.19 eV of host absorption energies. It is important to note that close to the mentioned boundary, the luminescence efficiency does not change gradually, instead it drops from a certain value close to unity (unquenched) to zero (quenched).
Table 4.2
A selection of inorganic host lattices with the corresponding host absorption energies and the presence of the characteristic Ce$^{3+}$ emission [254 and references therein].

<table>
<thead>
<tr>
<th>Host Material</th>
<th>$E_{\text{host}}$ (eV)</th>
<th>Ce$^{3+}$ emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$_2$O$_3$S</td>
<td>4.46</td>
<td>No</td>
</tr>
<tr>
<td>La$_2$O$_3$</td>
<td>5.33</td>
<td>No</td>
</tr>
<tr>
<td>Lu$_2$O$_3$</td>
<td>5.58</td>
<td>No</td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td>5.58</td>
<td>No</td>
</tr>
<tr>
<td>Y$_2$(SiO$_4$)O</td>
<td>6.19</td>
<td>Yes</td>
</tr>
<tr>
<td>Y$_3$Al$<em>5$O$</em>{12}$</td>
<td>6.44</td>
<td>Yes</td>
</tr>
<tr>
<td>LaF$_3$</td>
<td>9.91</td>
<td>Yes</td>
</tr>
</tbody>
</table>

All in all, the luminescence of cerium ion doped systems should be considered based on the correlation between the host band gap energy and the influence of the host material on the separation and location of the cerium levels with respect to the host bands. Furthermore, the crossover from the luminescent to non-luminescent systems occurs in the host absorption energy range between 5.58 eV and 6.19 eV. Unfortunately, the luminescence efficiency at this crossover range changes abruptly from very high values close to unity to zero.

4.4.2. Synthesis of SrZnO$_2$:Ce phosphors by the Sucrose Templated Sol-Gel Route

For the preparation of Ce$^{3+}$-doped SrZnO$_2$ phosphors, a very convenient sucrose templated sol-gel route was used. Several advanced functional ceramic materials were successfully synthesized and characterized by using the sucrose as a chelating agent and template material, and the effect of the molar ratio of the sucrose to metal cation ratio on the produced nanopowders was studied extensively [255,256]. As an inexpensive agricultural product, sucrose provides a
very cation-complexing nature through hydrolysis in very acidic aqueous media and the subsequent formation of oxidation products with chelating –COOH and –OH groups. Although, the oxidation of sucrose in water was performed by decreasing the pH with HNO₃, Souza et al. [257] prepared nanoscale NiO and NiFe₂O₄ particles without using the nitric acid by only using the sucrose as the chelating agent.

Sucrose can also be used as both fuel and chelating agent in order to synthesize the oxide powders with combustion method. Xu et al., [258] used the sucrose combustion method to investigate the luminescent properties of Y₂O₃:Eu³⁺. Unlike other combustion synthesis fuels such as urea, citric acid, glycine, carbohydrazine etc., sucrose burns and propagates slowly, rather than a quick combustion with more gas liberation, regardless whether initiation of the combustion occurs with heating on a hot plate, microwave irradiation, or with direct flame via matchsticks [258,259].

4.4.3. Experimental Procedure

Phosphor powders were prepared from the starting materials of Sr(NO₃)₂ (>99%, Alfa Aesar), Zn(NO₃)₂·6H₂O (99%, Alfa Aesar), Ce(NO₃)₃·6H₂O (99.5%, Alfa Aesar), and sucrose (ACS Reagent, Sigma Aldrich). Aqueous solutions of all the starting materials were made by dissolving them in deionized water. Cerium-doped and undoped SrZnO₂ phosphor samples were prepared by using sucrose. In a typical batch, 5 ml of 4 M sucrose solution was mixed with 10 ml of 0.5 M metal cation solution and pH was set to 1 using concentrated nitric acid. This
solution was aged at 120 °C for 1 h and then heated at 200 °C with continuous mixing. After all water evaporates, the sample was heated in a furnace at 120 °C for 2 h. The flowchart for the sucrose-templated sol-gel processing of the SrZnO₂:Ce phosphors is given in Figure 4.15.

Unless otherwise stated, a black colored fluffy char and metal ion precursor was crushed and then heated on a hot plate at 400 °C to burn all the remaining sucrose and the black precursor became a gray-colored powder. This powder was finally calcined at higher temperatures to obtain pure phosphor particles. In order to ensure trivalent valency of the doped cerium ions, calcination was done at 1000 °C for 6h under a reducing atmosphere (90%N₂, 10% H₂) in a tube furnace.

The crystallization behavior and crystal structure of the phosphor powders were checked by using a room temperature X-Ray Diffractometer (Philips PW 2273) with CuKα radiation (λ = 1.5406 Å) at 40 kV and 30 mA between 2θ values of 10° and 70° with a step size of 0.02°. The crystal size measurements were made by using the Williamson-Hall technique based on the broadening of the diffraction peaks with the built-in XRD software program (Jade 6.1). The powder
morphology was investigated by cold field emission scanning electron microscopy (FE-SEM, Hitachi S-400) after coating with Pt on carbon tape. IR spectroscopy analysis was done using Thermo-Nicolet (Nexus 470) FTIR. Excitation and emission characteristics of the phosphor powders were recorded at room temperature on a Hitachi F-4500 fluorescence spectrophotometer equipped with a 150W Xe-lamp as an excitation source at a scanning speed of 240nm/min and a sampling interval of 0.5 nm. Decay time measurements of the phosphors were made with the pulsed laser induced fluorescence and the
combined data acquisition system as shown in Figure 2.21. The 4th harmonic of a nanosecond-pulsed Nd:YAG laser at 266 nm was directed at approximately 45° angle from the normal to the powdered sample of phosphors with some absorption and the majority of the beam speculally reflected. Fluorescence was measured 90° to the solid sample surface collected by a lens and directed into a SPEX 1680, equipped with 0.22 m double monochromator. The fluorescence transmitted through the monochromator was detected by a photomultiplier tube. The time-dependent fluorescence was recorded by a digital oscilloscope (LeCroy Wavesurfer 452).

Quantum efficiency (QE) values were calculated by comparing the luminescence intensity of the prepared samples with the luminescence intensity of the commercial green phosphor Zn$_2$SiO$_4$:Mn (2284C phosphor, Osram Sylvania Products, Inc.), which is reported to have a 70% QE at room temperature [18].

The particle sizes and size distributions were measured using dynamic light scattering (DLS) on a Microtrac® Nanotrac NPA 250 instrument. Infrared spectra of the polymerized black char (precursor), pretreated at 400 °C, and calcined at different temperatures were recorded in the range 400 to 4000 cm$^{-1}$ by the KBr pellet method, using a Fourier transform infrared spectrometer (FT-IR) (Perkin Elmer Spectrum 2000). The diffuse reflectance spectra of the powdered samples were recorded on a Shimadzu UV-240 spectrophotometer.
4.4.4. Results and Discussions

4.4.4.1. XRD Analysis

The x-ray powder diffraction patterns of Sr$_{1-x}$Ce$_x$ZnO$_2$ phosphors with x=0.0 to 0.06 are shown in Figure 4.16. As-synthesized samples without calcination are totally amorphous and shows that all cations were homogeneously mixed throughout the black char obtained during the synthesis. Undoped and 1 mol% Ce- doped samples have a pure SrZnO$_2$ phase after firing at 1000 °C for 2h in air, corresponding to the standard JCPDS file # 41-0551. Phosphors containing 3 mol% and higher cerium concentrations have a secondary phase of Sr$_2$CeO$_4$ (50-0115) present in addition to the SrZnO$_2$ phase. The crystallite size of undoped SrZnO$_2$ samples prepared at 1000 °C was found to be 64 nm.

As mentioned earlier, the crystal structure of SrZnO$_2$ is orthorhombic and in the space group of Pnma [216]. It has a layered structure which consists of ZnO$_{4/2}$ tetrahedra linked through common vertexes (Zn-O-Zn), and Sr atoms are located between these waved vertex layers [228]. Each strontium atom is surrounded by seven oxygen atoms and there is only one site for each Zn and Sr atoms but there are two sites are available for oxygen atoms [228]. The ionic radii of Zn$^{2+}$, Sr$^{2+}$, and Ce$^{3+}$ are 74, 121, and 107 pm, respectively [229]. Therefore, based on the ionic radii values, when SrZnO$_2$ host lattice is doped with Ce$^{3+}$ ions, they can substitutionally replace strontium atoms from the host lattice. However, an increase in concentration of cerium resulted in more Sr$_2$CeO$_4$ secondary phase
formation as can be seen in Figure 4.16. This suggests that cerium dopant ions preferentially take the 4+ valency to form the more stable $\text{Sr}_2\text{CeO}_4$ phase.

Figure 4.16 X-ray diffraction patterns of $\text{SrZnO}_2$:Ce depending on the concentration of Cerium ion, calcined at 1000 °C. a) As-synthesized (no calcination), b) 0 mol% Ce, c) 1 mol% Ce, d) 3 mol% Ce, e) 6 mol% Ce.
Figure 4.17 shows the effect of the pre-heat treatment at 400 °C for 20 min in air on the crystalline phase formation of 12 mol% Ce doped SrZnO₂ prepared at 1000 °C for 2h in air. The same muffle furnace was used to calcine the same

[Image of XRD patterns]

**Figure 4.17** XRD patterns for 12 mol% Ce doped SrZnO₂ heat treated at 1000 °C for 2h, a) no pretreatment at 400 °C, b) with pretreatment at 400 °C for 20 min. (●: SrZnO₂; ▼: Sr₂CeO₄; ◊: ZnO).

batch samples. It is very clear that pretreatment at 400 °C caused the formation of SrZnO₂ as a primary phase in addition to very small amounts of secondary ZnO and Sr₂CeO₄ phases. On the other hand, samples prepared without pretreatment resulted in formation of Sr₂CeO₄ as the major phase in addition to the secondary phase of SrZnO₂. This big difference in crystalline phase formation
for the same samples can be associated with the properties of the sucrose, which is used as a templating agent in the synthesis. This can be explained by the fact that samples prepared without pretreatment at 400 °C produced more COₓ and NOₓ gases during calcination and prevented sintering or agglomeration of the particles, yielding more open-structured calcined samples without minimal sintering effect. Therefore, more surface area of the precursor would be exposed to the free oxygen in ambient air, promoting oxidation of the cerium ions and formation of the Sr₂CeO₄ phase. On the other hand, for the same concentration of sucrose to metal ratio, preheating at 400 °C for 20 min resulted in small amounts of burning and combustion of sucrose with a large volume of gases (CO, CO₂, NOₓ) during the calcination stage.

4.4.4.2. SEM Analysis

Scanning electron microscopy (SEM) was used to observe the particle size and morphology of the Ce-doped SrZnO₂ powder. A typical scanning electron micrograph of the 12 mol% Ce³⁺-doped SrZnO₂ samples prepared at 1000 °C for 2h with pre-heat-treatment at 400 °C for 20 min and untreated ones are shown in Figure 4.18 (a) and (b), respectively. The calcined phosphor particles have an irregularly-rounded morphology and range in size from 100 to 300 nm. Since these submicron phosphor particles formed larger aggregates in micron and submicron sizes, dynamic light scattering measurements were made to observe the degree of agglomeration and particle size distribution of them.
**Figure 4.18** SEM micrograph of the 12 mol% Ce doped SrZnO$_2$ phosphors prepared at 1000 °C a) pre-heat-treated at 400 °C for 20 min and b) untreated. Samples calcined after pre-heat-treatment resulted in relatively larger sized aggregates forming nanoscale particles.
4.4.4.3. Particle Size & Distribution Analysis

The particle size distribution of 12 mol% Ce doped SrZnO$_2$ powders with a typical average particle size of 1.07 $\mu$m is shown in Figure 4.19. Also, these prepared phosphor particles in agglomerated form have a range of sizes extending from 200 nm to 2000 nm.

![Particle Size Distribution](image)

**Figure 4.19** Dynamic light scattering results for 12 mol% Ce-doped SrZnO$_2$ phosphor particles with an average particle size of 1.07 $\mu$m.

4.4.4.4. FTIR Analysis

In Figure 4.20 FT-IR spectra in the range 400-4000 cm$^{-1}$, recorded at different steps of the cerium-doped SrZnO$_2$ synthesis are shown. The IR spectrum of the sucrose-metal complex (black char) in Figure 4.20(a) shows a complex spectra with bands at 3410, 2920, 1766, 1710, 1623, 1384, and 824 cm$^{-1}$. The common
broad bands located between 2800 and 3600 cm\(^{-1}\) are attributed to the stretching vibrations of the hydrogen-bonded OH\(^-\) groups.

**Figure 4.20** FTIR spectra of as synthesized precursor, i.e., black char (a), pre-heat treated at 400 °C for 20 min (b) and calcined samples at 1000 °C for 2 hours in air.

A very small band of free carboxyl (COO\(^-\)) groups near 1766 cm\(^{-1}\) are also observed [260]. The band located at 1623 cm\(^{-1}\) is attributed to the asymmetric stretching of the complexed COO\(^-\) groups of sucrose ions complexed to the metal ions in polymeric intermediates. The band around 1400 cm\(^{-1}\) of the symmetric stretching vibrations for carboxyl ions of the sucrose complex is shielded by an intense band of nitrate ions centered at 1384 cm\(^{-1}\).
The bands close to 1384 and 824 cm⁻¹ are assigned to [NO₃]⁻ corresponding to N-O stretching and bending vibrations, respectively [261]. The presence of the characteristic band of NO₃⁻ group indicates that this species is enclosed in the sucrose-metal ion gel during the black char formation. On heating the black char at 400 °C, the organic matrix is decomposed and, as a result, the absorption at 3400 cm⁻¹ and between 1300 and 1800 cm⁻¹ drastically decreases in intensity. The vibration absorption bands of [CO₂] and [NO₃]⁻ in this material system are very weak and no N-O bending at 824 cm⁻¹ was found while are present the band characteristics of adsorbed water molecules with bands located at around 3400 and 1630 cm⁻¹. On the other hand, samples calcined at 1000 °C for 2h showed new bands located between 450 and 650 cm⁻¹ which indicates the formation of the metal oxide compounds, confirmed by XRD as SrZnO₂ phase.

4.4.4.5. Diffuse Reflectance Spectroscopy Analysis of SrZnO₂:Ce phosphors

The diffuse reflectance spectra of the undoped SrZnO₂ and the 1 and 12 mol% Ce-doped SrZnO₂ and Sr₂CeO₄ phosphors are shown in Figure 4.21. The characteristic bandgap energy of 3.4 eV was found for SrZnO₂ by extrapolating the sharp slope to the level of no absorption in the reflectance spectra. This result is consistent with the same host lattice prepared with the adipic acid templated sol-gel route (see subsection 4.3.4.5). It was also observed that the absorption edge shifted from 363 nm to 367 nm when doped with 12 mol% Ce.
Figure 4.21 Diffuse Reflectance Spectra of Sr\(_{1-x}\)Ce\(_x\)ZnO\(_2\) for x = 0.0, 1.0 and 12.0, and Sr\(_2\)CeO\(_4\).

The absorption edge for the Sr\(_2\)CeO\(_4\) samples prepared at 1100 °C for 4h was found to be around 290 nm (Figure 4.21). The position of the CT band of the rare earth ions can be theoretically calculated by the given formula which is proposed by Resfeld and Jorgensen [262] as

\[
E_{CT} \ (cm^{-1}) = [\chi_{opt}(X) - \chi_{opt}(M)] * 30,000 \ cm^{-1},
\]
where, the $\chi_{\text{opt}}(X)$ and the $\chi_{\text{opt}}(M)$ are the optical electronegativity of the anion and the central metal cation, respectively. Utilizing the reported values of $\chi(O^{2-}) = 3.2$ and the $\chi(Ce^{4+} = 2.1)$ [263]. The calculated position of the CT band of Ce$^{4+}$ - O$^{2-}$ is at about 33,000 cm$^{-1}$ ($\approx$303 nm), which is in good agreement with the experimental values obtained at the absorption edge of the Sr$_2$CeO$_4$ in the diffusion reflectance spectrum, and with the PL excitation spectrum (peak intensity is 294 nm) when monitored at 467 nm (see Figure 4.22).

4.4.4.6. Photoluminescence Characteristics of SrZnO$_2$:Ce phosphors

Characteristic excitation and emission spectra for 12 mol% Ce-doped SrZnO$_2$ phosphors with and without heat treatment at 400 °C for 20 min. before heat treating at 1000 °C for 2h in air are shown in Figure 4.22, Figure 4.23, and Figure 4.24, respectively. In order to facilitate the comparison between the absorption characteristics of the phosphors prepared with and without pretreatment at 400 °C, a decomposition of the recorded bands by using a Cauchy-Lorentz model is also presented. Pretreatment at 400 °C caused the absorption maxima from 294/339 to 292/343 nm, however the location of the emission bands for these samples remained the same. The PL intensity of the cerium doped SrZnO$_2$ system increased with an increase in the cerium dopant concentration because of the formation of more Sr$_2$CeO$_4$ phase formation as shown in XRD results in Figure 4.16. Single phase Sr$_2$CeO$_4$ phosphors prepared at 1100 °C for 4h via the
sucrose sol-gel method showed the same absorption and emission spectral band locations (see Figure 4.24). The cerium-doped SrZnO$_2$ samples prepared at 1000 °C for 6h under strong reducing atmosphere resulted in no luminescence. Therefore, the characteristic blue-centered broad emission resulted from the Ce-doped SrZnO$_2$ host lattice, and can be attributed to the formation of the stable Sr$_2$CeO$_4$ compound. As stated in the earlier subsection, there are three main non-radiative relaxation mechanisms, which were proposed for cerium-doped compounds [20]: photoionization, large stokes shift, and electron transfer. It has been accepted that the cerium ion has a relatively-small stokes shift and this wouldn't cause a complete non-radiative relaxation. In the literature, it has also been reported that the electron transfer from the excited 5d electron of the cerium ion to the neighboring ions quenches the luminescence such as in vanadates [253]. However, the photoionization mechanism correlates the band gap energy of the host lattice in a way that when the lowest 5d cerium ion level is resonant with the conduction band of the host lattice, no Ce$^{3+}$ luminescence is observed. Since the optical bandgap of the SrZnO$_2$ compound was found to be 3.4 eV from the
**Figure 4.22** Photoluminescence properties of 12 mol% Ce doped SrZnO$_2$ sample heat treated at 1000 °C for 2h in air, with (A) no pretreatment at 400 °C, i.e., the black char was directly fired at calcination temperature. Excitation spectra were monitored at 467 nm. Straight lines represent the experimental data, small dot lines show the decomposed bands drawn by using the Cauchy-Lorentz model, and solid filled circles state for entirely calculated curve by using the Cauchy-Lorentz model.
Figure 4.23 Photoluminescence properties of 12 mol% Ce doped SrZnO$_2$ sample heat treated at 1000 °C for 2h in air, (B) with pre-treatment at 400 °C for 20 min. Excitation spectra were monitored at 467 nm. Straight lines represent the experimental data, small dot lines show the decomposed bands drawn by using the Cauchy-Lorentz model, and solid filled circles state for entirely calculated curve by using the Cauchy-Lorentz model.
**Figure 4.24** Photoluminescence properties of 12 mol% Ce doped SrZnO$_2$ sample heat treated at 1000 °C for 2h in air. Excitation spectra were monitored at 467 nm. A) no pretreatment at 400 °C, i.e., the black char was directly fired at calcination temperature, B) with pretreatment at 400 °C for 20 min.

diffuse reflectance spectroscopy (see Figure 4.21), which is a relatively small bandgap, the lowest 5d electronic level of the cerium ion is possibly located very close or inside the conduction band of the host lattice. In such a case, the excited electron relaxes to the bottom of the conduction band, which is located below the lowest cerium 5d energy level. This electron at the bottom of the conduction band returns to the ground state of the cerium ion with a non-radiative relaxation. Therefore this scheme of electron transfer leads to photoionization of
the cerium ion in the SrZnO₂ host lattice and non-radiative relaxation phenomena is observed. Quenching of the luminescence of cerium ions has been observed in several host lattices such as Y₂O₃ [20], La₂O₃, La₂O₂S [253], etc., although these host lattices have very good luminescence properties when doped with other rare earth or transition metals. Samples prepared without pretreatment at 400 °C resulted in better absorption and emission characteristics because of the more efficient formation of the Sr₂CeO₄ phase and more surface of the compounds was exposed to the free air during gas release and calcinations at higher temperature. It was observed that calcinations of the black char without pretreatment resulted in a more open-structured morphology in final powder form. Serra et al. [264] reported that the presence of oxygen during the calcinations of the Sr₂CeO₄ samples increases both absorption bands and gives brighter emission without changing the emission band location. However, the luminescence mechanism of the Sr₂CeO₄ is the charge transfer transition in which an electron is excited from the oxygen ligand to the Ce⁴⁺ ion, not the oxygen vacancies. Therefore, the presence of oxygen increases the formation of the luminescent Sr₂CeO₄ phase on the surface of the prepared samples and resulted in better luminescent properties. Until now, the Sr₂CeO₄ lattice is the only reported host lattice in which charge transfer luminescence of Ce⁴⁺ has been observed at room temperature [265]. Many novel synthesis techniques have been employed to synthesize Sr₂CeO₄ phosphors and films due to its efficient luminescence under excitation with cathode-rays, X-rays, or UV light [265-270]. All these studies revealed that the
emission spectrum of the Sr$_2$CeO$_4$ phosphors is very broad. However, the excitation spectra are influenced by the synthesis technique of Sr$_2$CeO$_4$ phosphors. It is possible that the differences in the absorption characteristics can originate from the differences in phosphor particle size and the chemical surrounding of the host matrix.

The differences in the characteristic excitation spectra of the Sr$_2$CeO$_4$ phosphor have four different aspects. First is the number of peaks. Two [265] or three [267-270] excitation peaks were reported in the literature. Second is the position of the excitation peaks. Pieterson et al. [265] observed two absorption peaks located at 285 nm and 328 nm, whereas Liu et al. [271] reported two absorption peaks at about 290 nm and 340 nm. Third is the spike of the peaks [272]. Two separated broad spectrum, or a strong peak with a shoulder, or a strong peak with two shoulder peaks have been reported [264,265,269]. Fourth is the charge transfer mechanism. It has been reported that the presence of two absorption peaks in the excitation spectra can be attributed to the two different charge transfer transitions because of the two different Ce$^{4+}$ - O$^2-$ bond lengths available in Sr$_2$CeO$_4$ structure [273]. Park, et al. [267], however, reported three excitation peaks, among which, the two highest energy bands were attributed to the parity forbidden $t_{1g} \rightarrow f$ transition and the parity-forbidden $t_{1u} \rightarrow f$ transition, respectively. The lowest energy excitation band was not associated with any known transitions.

Phosphors prepared with the sucrose-templated sol-gel route showed two characteristic absorption peaks located at about 294 nm and 340 nm (see Figure
4.22 and Figure 4.23). This observation runs parallel with the earlier reports and these two absorption peaks originate from the two different Ce-O bond lengths within the Sr₂CeO₄ structure. The CIE color coordinates of the 12 mol% Ce doped SrZnO₂ phosphors were x = 0.2299 and y = 0.2568.

4.4.4.7. Time Resolved Spectroscopy

The luminescence decay times of Ce-doped SrZnO₂ phosphors were determined by fitting a constant term plus a sum of double exponentials to the time resolved decay curve data. For the Sr₂CeO₄ samples only a single exponential function was used (Figure 4.25). The emission intensity is described by the following equation as [274-275],

\[ I(t) = I_0 + \sum_{i=1}^{\infty} \left[ \frac{I_i}{\tau_i} \right] \cdot \exp \left[ \frac{-(t-t_0)}{\tau_i} \right], \]

where the fractions sum to unity,

\[ A_i = \sum_{i=1}^{\infty} \left[ \frac{I_i}{\tau_i} \right] = \sum_{i=0}^{\infty} I_i = 1, \]

and the average lifetime, \( \tau_{ave} \) is calculated by

\[ \tau_{ave} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}. \]
The average time constant of the PL decay for the 12 mol% Ce-doped SrZnO$_2$ is 44.7 µs and the relevant time constants obtained by curve fitting are $\tau_1 = 4.4$ µs, $\tau_2 = 47.4$ µs, and relative amplitudes are $A_1 = 42.1$, $A_2 = 57.9$. On the other hand, the Sr$_2$CeO$_4$ phosphors have a single decay time of 52.4 µs. This value is very close to the previous reports used wet chemical methods to prepare Sr$_2$CeO$_4$ phosphors [273,276]. As mentioned earlier, there are two crystallographically-different oxygen ions present in Sr$_2$CeO$_4$ with different absorption energies and it might be expected that there would be different CT emissions, resulting in biexponential decay kinetics. However, the decay studies show only one time constant and this can be explained by the fact that in the CT state the complex relaxes to the lowest energy excited state and only the emission from this lowest energy CT state is observed. It also has a faster radiative decay than the higher excited energy state [265].

In cerium-doped SrZnO$_2$ samples, the second time constant of (47.4 µs) with a relative amplitude of 57.9 can be attributed to the decay of luminescence of Sr$_2$CeO$_4$ phase, and the first very fast decay constant can be attributed to the non-radiative relaxation process of possible Ce$^{3+}$ ionization reaction. Calcinations at 1000 °C for 2h didn’t result in a single Sr$_2$CeO$_4$ phase. In other words, not all cerium ions transferred from 3+ valence to 4+, therefore, it is possible that some portion of Ce$^{3+}$ is left in the SrZnO$_2$ lattice, and contributed to the non-radiative relaxation process.

The long decay character of Sr$_2$CeO$_4$ (~50 µs) can be attributed to the spin-forbidden character of the Ce$^{4+}$ - O$^{2-}$ charge transfer [265].
Figure 4.25 Luminescence decay curves of a) 12 mol% Ce doped SrZnO₂ (1000 °C, 2h) monitoring at 467 nm, b) Sr₂CeO₄ (1100 °C, 4h) monitoring at 467 nm. Phosphors were excited at 266 nm by using the fourth harmonic of a nanopulsed Nd-YAG laser.
4.5. Tb\textsuperscript{3+} doped SrZnO\textsubscript{2} Phosphors

4.5.1. Electronic States of Tb\textsuperscript{3+}-doped Phosphors

The energy levels of trivalent rare-earth ions originating from the 4fn electronic configuration were given and mentioned in Chapter II. In reality, these given energy levels are split by the crystal field. However, this crystal field splitting for the rare-earth activators is very small due to the shielding by the 5s\textsuperscript{2} and 5p\textsuperscript{6} electrons. Moreover, the characteristic emission transitions yield sharp lines in the emission spectra.

In general, the emission of Tb\textsuperscript{3+} ions in host materials is attributed to the transitions $^5\text{D}_4 \rightarrow ^7\text{F}_j$ and the emission bands are usually located in green light wavelengths [17,18]. In many host lattices, a significant contribution to the emission is from the higher level emission $^5\text{D}_3 \rightarrow ^7\text{F}_j$ and this transition usually has a characteristic blue-centered emission. The crystal field significantly affects the $^7\text{F}_j$ in a way that many sublevels will be active and this gives the spectrum a very complicated appearance.

4.5.2. Synthesis of SrZnO\textsubscript{2}:Tb Green-Emitting phosphors by the Sucrose Templated Sol-Gel Route

Terbium-doped SrZnO\textsubscript{2} phosphors were prepared by the sucrose-templated sol-gel route, and the processing details are given in section 4.4.3.
Figure 4.26 shows the X-ray diffraction patterns for Tb$^{3+}$-doped SrZnO$_2$ phosphors prepared at different calcination temperatures from 800 to 1100 °C for 2 hours.

**Figure 4.26** XRD patterns of the Tb$^{3+}$-doped SrZnO$_2$ phosphors under different heat treatment. (▼: SrZnO$_2$; ●: SrCO$_3$; +: ZnO).

Single phase SrZnO$_2$:Tb phosphors were obtained at and beyond 900 °C without any shift of the diffraction peaks as the terbium impurity concentration increased because the amount of the Tb$^{3+}$ is beyond the detection limit of the XRD technique.
4.5.3. Photoluminescence Characteristics of SrZnO$_2$·Tb Phosphors

The characteristic excitation and emission characteristics of 0.25 mol% Tb$^{3+}$-doped SrZnO$_2$ phosphors prepared by sucrose templated sol-gel route are shown in Figure 4.27. The excitation spectrum measured at an emission wavelength of 543 nm consists of a broad absorption band peaked at 283 nm.

![Graph showing PL characteristics](image)

**Figure 4.27** PL characteristics of 0.25 mol% Tb$^{3+}$-doped SrZnO$_2$ phosphors prepared at 1100 °C for 2h in air. Excitation spectrum was recorded when monitoring at 543 nm and the excitation wavelength was 283 nm.

and ranges from 220 nm to 300 nm. This characteristic absorption band attributed to the parity allowed $4f^8 \rightarrow 4f^75d$ transitions. The characteristic
emission spectrum of Tb$^{3+}$-doped SrZnO$_2$ phosphor under 283 nm excitation is also shown in Figure 4.27. It shows the characteristic Tb$^{3+}$ emissions with the associated electronic transitions $^{5}D_4 \rightarrow ^7F_j$ ($j = 3\text{-}6$). The specific green emission band of terbium centers at 543 nm, and is due to the $^{5}D_4 \rightarrow ^7F_5$ electronic transition inside the Tb$^{3+}$ ion with 4f$^7$ configuration. In principle, when the terbium ion in phosphors is excited by ultraviolet excitation, the electrons located in the 4f$^8$ state would be excited to higher 4f$^7$5d$^1$ levels and subsequently feed to $^{5}D_3$ and/or $^{5}D_4$ excited states nonradiatively [17,18]. The energy gap between these excited levels and the multiplet ground state ($^7F_j$) is large enough to produce emissions in the visible spectral regime. The host lattice, SrZnO$_2$, did not produce any absorption or excitation under the same conditions, indicating that the characteristic green emission is only due to the electronic transitions within the Tb$^{3+}$ ions.

Yu et al. [277] reported the maximum characteristic green emission of Tb$^{3+}$-doped SrZnO$_2$ was at a dopant level of ~0.3 mol%, prepared with the conventional solid-state method. It was reported that the absorption band of the samples had two separate and sharp peaks, located at 250 and 262 nm [277]. It was commented that there are possibly two different luminescence centers, based on the differences in the ionic radii of cations and the emission spectra when excited at these two maxima of the absorption. The ionic radii of Zn$^{2+}$, Sr$^{2+}$, and Tb$^{3+}$ are 74, 112, and 92.3 pm, respectively [229]. It was speculated that Tb$^{3+}$ ions may occupy both Zn$^{2+}$ and Sr$^{2+}$ crystallographic sites within the SrZnO$_2$ host matrix because the ionic radii difference between the Tb$^{3+}$ and Sr$^{2+}$ is very
close to that of Tb$^{3+}$ and Zn$^{2+}$, and hence different luminescence centers can form. On the other hand, Tb$^{3+}$-doped SrZnO$_2$ phosphors prepared with the sucrose-templated sol-gel route showed only one absorption band with a single peak located at 283 nm.

The decay profile of the $^5$D$_4$ emission was non-exponential and was deconvoluted into two exponents (Figure 4.28). Tb$^{3+}$-doped SrZnO$_2$ samples showed very fast fluorescence with an average fluorescence decay time of 13.8 ns with the related time constants of $\tau_1 = 17.68$ ns, $\tau_2 = 9.79$ ns, and relative amplitudes are $A_1 = 36.5$, $A_2 = 63.5$. This suggests that two different luminescent centers form when the SrZnO$_2$ host material is doped with Tb$^{3+}$ ion because the decay kinetics show a biexponential character (see Figure 4.28).

The relative intensity of the 543 nm emission peak as a function of the Tb$^{3+}$ ion concentrations of SrZnO$_2$:Tb$^{3+}$ phosphor is shown in Figure 4.29. The green emission intensity increases up to 0.25 mol% Tb$^{3+}$ and then decreases this critical terbium concentration level is exceeded. Berdowski et al. [278] reported that the blue emission attributed to the transition from $^5$D$_3$ excited state to $^7$F$_j$ vanished when the Tb$^{3+}$ concentration for cross-relaxation to take place. The process of cross-relaxation is explained in terms of the occurrence of a number of transitions between the crystal-field components of the $^7$F$_6$ ground level of Tb$^{3+}$ and the $^7$F$_1$ and $^7$F$_0$ states which are quasi resonant with $^5$D$_3 \rightarrow ^5$D$_4$ transition [279]. The occurrence of cross-relaxation process in SrZnO$_2$:Tb$^{3+}$ phosphors can be explained by the resonance between the excited states and the ground states of Tb$^{3+}$-Tb$^{3+}$ pairs and can be represented by [80],
\[ \text{Tb}^{3+} (^5D_3) + \text{Tb}^{3+} (^7F_6) \rightarrow \text{Tb}^{3+} (^5D_4) + \text{Tb}^{3+} (^7F_0). \]

Figure 4.28 Luminescence decay curve of 0.25 mol\% \text{Tb}^{3+} doped \text{SrZnO}_2 (1100 °C, 2h) monitored at 543 nm. Phosphors were excited at 266 nm by using the fourth harmonic of a nanopulsed Nd-YAG laser.

As a result, the transitions from $^5D_3$ to $^7F_j$ are significantly quenched because of the cross-relaxation, and those green to red emissions peaked at 489 nm ($^5D_4 \rightarrow ^7F_6$), 543 nm ($^5D_4 \rightarrow ^7F_5$), 587 nm ($^5D_4 \rightarrow ^7F_4$), 621 nm ($^5D_4 \rightarrow ^7F_3$) are enhanced. Beyond the critical \text{Tb}^{3+} concentration of 0.25 mol\% within the \text{SrZnO}_2 host lattice, the emission intensity decreases and this can be explained by the concentration quenching mechanism. The details are given in Chapter III.
Figure 4.29 Effect of Tb\textsuperscript{3+}-dopant level from 0.1 to 2.5 mol% on relative peak intensity of 543 nm emission from SrZnO\textsubscript{2}:Tb phosphors.
4.6. Eu$^{3+}$ doped Ba$_2$YAlO$_5$ Phosphors

4.6.1. Electronic States of Eu$^{3+}$-doped Phosphors

The europium ion, with 4f$^6$ configuration, has found significant applications in lighting and display devices [281]. The characteristic Eu$^{3+}$-centered emission is in the red spectral regime and usually consists of sharp lines. These lines are associated with the transitions from the excited $^5D_0$ level of the Eu$^{3+}$ ion to the $^7F_J$ ($J = 0$-6) ground levels of the 4f$^6$ configuration. The splitting of the emission transitions leads to the crystal-field splitting of the $^7F_J$ ground states. On the other hand, the $^5D_0$ excited level will not be split by the crystal field because $J = 0$ [17,18]. In addition to the radiative relaxation from the $^5D_0$ excited level, it is also possible to have emission from higher $^5D$ excited levels such as $^5D_1$, $^5D_2$, and $^5D_3$.

In principle, if the crystallographic site of the rare-earth ion within the host matrix has inversion symmetry, the associated optical transitions between the 4f$^n$ ground state are strictly forbidden as electric-dipole transition. These transitions within the ground state take place as magnetic-dipole transitions and it follows the selection rule $\Delta J = 0, \pm 1$ or as vibronic electric-dipole transitions [18]. In contrast, if there is no inversion symmetry at the crystallographic site of the luminescent rare-earth ions, the electric dipole transitions will not be strictly forbidden and the transitions between the ground state will appear as weak lines in the emission spectra. In particular, transitions with $\Delta J = 0, \pm 2$ will appear
dominantly in the emission spectrum even for small deviations from the inversion symmetry.

4.6.2. Synthesis of Ba$_2$YAlO$_5$:Eu$^{3+}$ Red-Emitting Phosphors by the PVA-metal complex route

4.6.2.1. Experimental Procedure

The generic flowchart for the PVA-metal complex method was given in Chapter III. Ba$_2$(Y$_{1-x}$Eu$_x$)AlO$_5$ phosphors were prepared by the facile polymer-metal complex route. The raw materials were Ba(NO$_3$)$_2$ (99+%, ACS Reagent, Sigma-Aldrich), Y(NO$_3$)$_3$6H$_2$O (99.9%, Aldrich), Al(NO$_3$)$_3$9H$_2$O (99+% ACS Reagent, Alfa Aesar), Eu(NO$_3$)$_3$.5H$_2$O (99.9%, Aldrich), and PVA (MWt \(\sim\)145,000) with degree of polymerization of 3300 (Sigma-Aldrich). The stoichiometric amounts of all cationic salts were dissolved in the least amount of deionized water, and the aqueous 3 wt% PVA solution was prepared at \(\sim\)85 °C on a hot plate. The metal cation solution was added to the PVA solution and this PVA-metal aqueous solution was then heated to a temperature of \(\sim\)150 °C with continuous mixing. The molar ratio of the metal ions to hydroxyl group of PVA was set to 1:2. The mixed solution was clear and no precipitation was observed. After evaporation of all water, a dark brown, loosely-connected phosphor precursor powder was obtained. The precursor powder was calcined at temperatures of 800-1200 °C for 2 h in air and then cooled to room temperature in open air.
The purity and phases formed in the phosphor samples were investigated using a Phillips PW 1710 X-ray diffractometer (45 kV-30 mA) with CuKα radiation. All XRD data were collected at room temperature. The morphology of the particles was examined using a Hitachi S-4700 cold field emission scanning electron microscope (FE-SEM). The particle size distribution was analyzed using a Microtrac Nanotrac NPA 250 particle size analyzer and the powders were homogeneously dispersed in 40 wt% glycerin-deionized water solution. Diffuse reflection spectra were measured with a Shimadzu UV-240 spectrophotometer. Photoluminescence characteristics were recorded on a Hitachi F-4500 fluorescence spectrometer with a 150 W Xe lamp.

4.6.3. Results and Discussions

4.6.3.1. XRD Analysis

Kovba et al., [282] reported the crystal structure of Ba₂YAlO₅ as perovskite-like and monoclinic, with a = 7.231 Å, b = 7.430 Å, c = 6.022 Å, γ = 117.23˚ and Z = 2. It also has a pseudo-bcc subcell, as found for the perovskite structure ABX₃. The superstructure is ascribed to an ordered arrangement with the Y and Al ions on the B position, and with the oxygen ions and oxygen vacancies on the X position. In the perovskite structure, the A site is twelve-fold coordinated by oxygen ions. Since in Ba₂YAlO₅ one oxygen position out of six is vacant, the average coordination number of the barium ion site is assumed to be ten. For a
random distribution of the oxygen vacancies, this would result in a large number of different Ba-sites.

The crystallization of \( \text{Ba}_2(\text{Y}_{1-x}\text{Eu}_x)\text{AlO}_5 \) phosphors with \( x = 0.05 \) prepared at different temperatures and with \( x = 0.1 \) calcined at 1100 °C for 2 h in air were characterized by using the XRD patterns, which are shown in Figure 4.30. The monoclinic structure of \( \text{Ba}_2\text{YAlO}_5 \) is well-formed at temperatures ≥1100 °C and all

![X-ray diffraction patterns](image)

**Figure 4.30** X-ray diffraction patterns of 5 mol% Eu\(^{3+} \) doped \( \text{Ba}_2\text{YAlO}_5 \) phosphors prepared at 900 °C (a), 1000 °C (b), 1100 °C (c), 1200°C (d), and 10 mol% Eu doped samples calcined at 1100 °C (e) for 2 h in air. (* : unknown)

the peaks are due to the characteristic reflections of \( \text{Ba}_2\text{YAlO}_5 \) (JCPDS # 37-0292), except two relatively small peaks of an unknown secondary phase. Even
heat-treating at 1200 °C for 20h was not enough to produce a single phase of monoclinic Ba₂YAlO₅. Similar results were obtained and reported in literature [282,283]. Phosphor powders prepared at 900 and 1000 °C have secondary phases of BaCO₃ (45-1471). Elevated calcination temperature cause an increase of diffraction peak intensity and a decrease of the peak’s full-width at half-maximum (FWHM) value due to the enhanced crystallinity and the coarsening of grains. It is noteworthy that even 10 mol% Eu³⁺-doped phosphor powders calcined at 1100 °C show a single phase of Ba₂YAlO₅ with two weak peaks of unknown phase (Fig. 4.30(e)). This suggests that when Eu³⁺ ions are introduced into the host lattice, they can replace Y³⁺ ions effectively without changing the crystal structure and unit cell parameters significantly.

4.6.3.2. SEM Analysis

SEM studies revealed that individual phosphor particles of around 200 nm are irregularly rounded and formed larger-sized loose aggregates in micron and submicron sizes as shown in Figure 4.31.
Figure 4.31 A typical scanning electron micrograph for 10 mol% Eu-doped Ba$_2$YAlO$_5$ powder calcined at 1100 °C for 2h.

4.6.3.3. Particle Size & Distribution Analysis

The particle size and distribution analyses were made using photon correlation spectroscopy. Results for 10 mol% Eu$^{3+}$-doped Ba$_2$YAlO$_5$ samples are shown in Figure 4.32. The average particle size is 1.5 μ with a range extending from 200 nm to 2500 nm.
Figure 4.32 Particle size distribution of Ba$_2$Y$_{0.9}$Eu$_{0.1}$AlO$_5$ phosphor powders prepared at 1100 °C. The average particle size is around 1.5 µ.

4.6.3.4. Diffuse Reflectance Spectroscopy Study of Eu$^{3+}$-doped Ba$_2$YAlO$_5$ Phosphors

The diffuse reflectance spectra of the undoped Ba$_2$YAlO$_5$ sample is shown in Figure 4.33. By extrapolating the sharp slope to the level of no absorption in the reflectance, it was found that the Ba$_2$YAlO$_5$ host lattice has a very high characteristic bandgap energy of 6.0 eV. Furthermore, the reflectance spectra of Eu$^{3+}$-doped samples exhibited the characteristic absorption of Eu$^{3+}$ ions located at 395 nm ($^7F_0 \rightarrow ^5L_6$).
Figure 4.33 Diffuse Reflectance Spectra of Ba$_2$Y$_{1-x}$Eu$_x$AlO$_5$ for $x = 0$, 3, and 10, recorded at room temperature.

4.6.3.5. Photoluminescence Characteristics of Eu$^{3+}$-doped Ba$_2$YAlO$_5$ Phosphors

The PL spectra of 5 mol% Eu$^{3+}$-doped samples prepared under different heat-treated temperatures from 800 to 1200 °C for 2 h are shown in Figure 4.34. The sample calcined at 800 °C shows emission bands with the peaks corresponding to the $^5D_0 \rightarrow ^7F_{1,2}$ transitions of Eu$^{3+}$ ions appearing in a broad manner. When the calcination temperature increased to 900 and 1000 °C, characteristic emission
Figure 4.34 The PL spectra of Ba$_2$Y$_{0.95}$Eu$_{0.05}$AlO$_5$ phosphors prepared under different heat treatment for 2h in air. (a: 800 °C, b: 900 °C, c: 1000 °C, d: 1100 °C, e: 1200 °C). The excitation wavelength was 254 nm.

peaks started to form due to the formation of the crystalline Ba$_2$YAlO$_5$ host lattice. The samples heat-treated below 1100 °C exhibit a single emission peak centered at 611 nm and other peaks in a broad manner. However, samples prepared at 1100 °C and above showed maxima at 582, 595, and 610 nm plus a shoulder located at 616 nm. The relative intensity of emission peaks increase and becomes sharper with increasing calcination temperature. Further, increasing temperature causes to form other characteristic emissions of $^5D_1\rightarrow^7F_2$ and $^5D_0\rightarrow^7F_0$ transitions.
Figure 4.35 shows excitation spectra of Ba$_2$Y$_{1-x}$AlO$_5$:xEu$^{3+}$ ($0 \leq x \leq 0.15$) monitored at 610 nm in the UV region. The broad bands located between 210 and 300 nm, with the maximum at about 254 nm, are attributed to charge transfer bands (CTB) from 2p orbital of O$^{2-}$ to an empty 4f orbital of Eu$^{3+}$ ion, and the other lines associated with the characteristic 4f-4f transitions of the Eu$^{3+}$ ions.

![Excitation Spectra](image)

\[ \lambda_{em} = 610 \text{ nm} \]

**Figure 4.35** Emission spectra for the emission at 610 nm as a function of Eu$^{3+}$ content for Ba$_2$Y$_{1-x}$Eu$_x$AlO$_5$ phosphors prepared at 1100 °C for 2h.

Upon excitation with a wavelength of 254 nm UV light, the PL spectra showed the characteristic $^5D_0 \rightarrow ^7F_J$ ($J = 0, 1, 2, 3$) line emissions of the Eu$^{3+}$ ions with
strong emissions for $J = 1$ (582 and 595 nm) and $J = 2$ (610 nm) (Figure 4.36). The $^5D_0 \rightarrow ^7F_1$ transition is magnetic dipole (MD) allowed, and not restricted by any symmetry [284]. Its high intensity in Ba$_2$YAlO$_5$ is the consequence of the low

![Emission Spectra](image)

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**Figure 4.36** The PL emission spectra of the Ba$_2$(Y$_{1-x}$Eu$_x$)AlO$_5$ phosphors for $0 \leq x \leq 15$ excited at 265 nm. The inset shows the dependence of PL emission intensity on Eu$^{3+}$ doping concentration for the samples prepared at 1100 °C.

probability of the 4f-4f electric-dipole (ED) transitions. On the other hand, the $^5D_0 \rightarrow ^7F_2$ transition is ED forbidden, and is sensitive to the chemical bonds in the vicinity of the Eu$^{3+}$ ions. A short peak located at 578 and a shoulder at 575 nm are attributed to the $^5D_0 \rightarrow ^7F_0$ transition, which is both spin and electric dipole
forbidden, and it is sensitive to the different lattice field. Therefore, both $^5D_0$ and $^7F_0$ levels of Eu$^{3+}$ are non-degenerate and cannot be split by the crystal field. The observation of more than one $^5D_0 \rightarrow ^7F_0$ peak in the emission spectra suggests the presence of Eu$^{3+}$ in more than one different crystalline environments [285]. This observation proves that Eu$^{3+}$ ions have different crystallographic sites by replacing Y$^{3+}$ ions with different coordination numbers because of the presence of one oxygen vacancy out of six in the host lattice.

The dependence of the photoluminescence intensities on Eu$^{3+}$ content is given in the inset of Figure 4.36. The intensities at 582, 595 and 610 nm increase with Eu$^{3+}$ content until saturation occurs, then it decreases. The saturation point was found to be 10 mol% for Eu$^{3+}$ concentration.
4.7. Eu$^{3+}$ doped M$_3$Al$_2$O$_6$ (M = Ca, Sr, Ba) Phosphors

Alkaline earth aluminates doped with transition and rare-earth cations, such as SrAl$_2$O$_4$ doped with Eu$^{2+}$, Eu$^{2+}$ and Dy$^{3+}$ [286,287], have been extensively studied as efficient luminescent materials. Alkaline-earth aluminates with the general formula M$_3$Al$_2$O$_6$ (M = Ca, Sr, Ba) form a component of refractory materials such as portland and some specialty cements [288]. Among them, Sr$_3$Al$_2$O$_6$ activated with rare earth ions Eu$^{2+}$ [289] and Eu$^{3+}$ [290] were studied. It has been reported that Sr$_3$Al$_2$O$_6$ phase is converted to SrAl$_2$O$_4$ at 1250 °C [291]. It is required to investigate the low temperature synthesis without a secondary phase.

4.7.1. Synthesis of M$_3$Al$_2$O$_6$:Eu$^{3+}$ (M = Ca, Sr, Ba) Red-Emitting Phosphors by the Sucrose-PVA-Metal Complex Route

All phosphor samples were synthesized using the sucrose-PVA-metal ion complex technique. Based on a certain stoichiometric ratio, 1M aqueous cationic solution were prepared from Al(NO$_3$)$_3$·9H$_2$O (99.5%), Eu(NO$_3$)$_3$·6H$_2$O (99.9%), and M(NO$_3$)$_2$·XH$_2$O (>99.5%). M = Ca, Ba, Sr was added to 5 wt% aqueous PVA and aqueous solution of sucrose and this mixture was aged at 80 °C for 1h. A molar ratio of 4:1 sucrose to metal ions was used for the preparation. Further heating of this aged solution at 250 °C yielded a highly viscous liquid and complete evaporation of the solution occurred with the release of fumes of NO$_x$ gases. No visible precipitation or turbidity was observed during heating and viscous polymeric resin formation. Complete evaporation yields a black,
voluminous, fluffy precursor which was easily ground to fine powders. A generic flowchart for the Sucrose-PVA-metal complex route was given in Chapter III. The precursor powders were then calcined at temperatures of 800-1100 °C for 2 h in air and then cooled to room temperature in open air in order to obtain the desired nano-crystalline phosphor materials. All phosphor powders obtained were white color in body.

The phase identification was performed by x-ray powder diffractometer (Phillips PW 2273) using CuKα radiation (40 kV, 35 mA). The average crystallite size was calculated using the Williamson-Hall technique with the built-in software (JADE 6.1). The average particle size was measured using photon correlation spectroscopy on a Microtrac Nanotrac™ ULTRA instrument. The excitation and emission characteristics of the samples were recorded at room temperature using a Hitachi F-4500 fluorescence spectrophotometer equipped with a 150W Xe-lamp as an excitation source. IR spectroscopy analysis was done using Thermo-Nicolet (Nexus 470) FTIR.

4.7.2. Characterization of Eu³⁺-doped Ca₃Al₂O₆ Red Emitting Phosphors

4.7.2.1. XRD Analysis

X-ray powder diffraction patterns of Ca₃Al₂O₆ (C3A) phosphor samples calcined at different temperatures between 800 °C and 1200 °C for 2 h in air are shown in Figure 4.37. The as-synthesized phosphor precursors have an amorphous
structure, showing that all the cations were homogeneously distributed in the as-synthesized powders. When the precursor

![XRD patterns of the 4 mol% Eu³⁺-doped Ca₃Al₂O₆ samples calcined at different temperatures, a) As-synthesized, b) 800 °C, c) 900 °C, d) 1000 °C, e) 1100 °C, f) 1200 °C. (♀: CaO, ▼: Ca₃Al₂O₆).](image)

Figure 4.37 XRD patterns of the 4 mol% Eu³⁺-doped Ca₃Al₂O₆ samples calcined at different temperatures, a) As-synthesized, b) 800 °C, c) 900 °C, d) 1000 °C, e) 1100 °C, f) 1200 °C. (♀: CaO, ▼: Ca₃Al₂O₆).

was calcined at 800 °C, the characteristic peaks of C3A appeared with a secondary phase of CaO. However, at 1000 °C, a single phase of cubic C3A forms without any secondary phases and all peak positions agree well with the JCPDS #38-1429. Mondal and Jeffery [288] reported that pure C3A has a cubic unit cell with a very large lattice parameter (a = 15.263 Å) in the space group Pa3. In C3A, the Ca coordination is a distorted octahedral, but the AlO₄
tetrahedra are much less distorted rings of six $\text{AlO}_4$ tetrahedra ($\text{Al}_6\text{O}_{18}$), with eight to a unit cell, and with $\text{Ca}^{2+}$ ions holding the rings together. The crystallinity of samples increases with increasing calcination temperature, since the FWHM of diffraction peaks decreases. The average crystallite size for the phosphor samples calcined at 1100 °C for 2 hours was found to be 41 nm. Furthermore, no obvious shifting of the diffraction peaks was observed as $\text{Eu}^{3+}$ doping concentration increased, which means that when $\text{Eu}^{3+}$ were introduced into the lattice, the crystal structure and lattice parameters do not change largely.

4.7.2.2. SEM Analysis

Figure 4.38 shows a typical SEM micrograph of the $\text{Ca}_{2.96}\text{Eu}_{0.04}\text{Al}_2\text{O}_6$ phosphors prepared at 1100 °C. It reveals that the phosphor particles have

![SEM micrograph](image-url)

**Figure 4.38.** SEM micrograph of 4 mol% $\text{Eu}^{3+}$-doped $\text{Ca}_3\text{Al}_2\text{O}_6$ phosphor prepared at 1100 °C for 2 hours in air.
irregularly-rounded morphology and individual submicron size particles agglomerated.

4.7.2.3. Particle Size & Distribution

Photon correlation spectroscopy analysis revealed that the agglomeration of these phosphor grains formed powder particles with an average size of about 1.2 μm as shown in Figure 4.39. The phosphor particle size ranged from 600 nm to 2.5 μm.

![Particle size distribution](image)

**Figure 4.39** Particle size distribution of Eu³⁺-doped C3A phosphor powders prepared at 1100 °C for 2 hours. The average particle size is around 1.2 μm.

4.7.2.4. FTIR Analysis

Figure 4.40 illustrates the FTIR spectra of precursor and calcined C3A powders at 1100 °C for 2 hours. IR spectrum analysis was used to follow the dehydration
Figure 4.40 FTIR spectrum of C3A precursor and calcined precursor at 1100 °C for 2 hours in air.

reaction of the precursor and the formation of AlO₄ tetrahedra within the crystalline C3A phase. The common broad bands located between 2800 and
3600 cm\(^{-1}\) are attributed to the stretching vibrations of the hydrogen-bonded OH\(^-\) groups. The band located at 1450 cm\(^{-1}\) is attributed to the formation of calcium carbonates in the precursor powders. The absorption bands located in 1200-1400 cm\(^{-1}\) regions corresponding to C-H and C-O bands and also the peaks between 700 and 900 cm\(^{-1}\) region are attributed to the vibration of the AlO\(_4\) tetrahedron [292]. The decrease in intensities of mentioned bands and disappearance of them at 1100 °C, accompanied with strengthening of Al-O bands in the AlO\(_4\) groups that prove the formation of the calcium aluminate phase. The bands located near 840, 805, and 780 cm\(^{-1}\) are ascribed to AlO\(_4\) groups. However the bands around 720, 685, 640 and 570 cm\(^{-1}\) correspond to AlO\(_6\) groups [293].

4.7.2.5. Photoluminescence Characteristics of Eu\(^{3+}\)-doped C3A phosphors

The characteristic photoluminescence spectra of 4 mol% Eu\(^{3+}\)-doped C3A phosphor samples, prepared under different calcination temperatures from 800 to 1200 °C and excited at 265 nm, are shown in Figure 4.41. Samples prepared at 800 and 900 °C showed characteristic emission peaks in a broad manner and the emission maxima at 612 nm shifted to 614 nm and a peak starts to form at 619 nm when the calcinations temperature was increased to 1000 °C and beyond. The relative PL emission peak intensity increases with temperature, which suggests that the degree of crystallinity is in favor of the emission of Eu\(^{3+}\) ions.
Figure 4.41 The PL emission spectra of 4 mol% Eu$^{3+}$-doped Ca$_3$Al$_2$O$_6$ phosphor samples prepared under different calcination temperatures. Excitation wavelength was 265 nm. (a: 800 °C, b: 900 °C, c: 1000 °C, d: 1100 °C, e: 1200 °C).

The excitation spectra of Ca$_3$Al$_2$O$_6$ doped with different Eu$^{3+}$ concentrations monitored at 614 nm in UV region are illustrated in Figure 4.42. They consist of a broad intense band with a maximum at 265 nm and several characteristic line excitation peaks of Eu$^{3+}$. Broad bands between 210 and 330 nm are attributed to charge transfer bands (CTB) between Eu$^{3+}$ ions and the surrounding O$_2^-$ anions. The 395 nm photons were absorbed by the most intense 4f-4f transition peak ascribed to $^7F_0 \rightarrow ^5L_6$ transition [294,295]. The phosphors of Eu$^{3+}$-activated Ca$_3$Al$_2$O$_6$ exhibited bright red color luminescence under UV excitation.
Figure 4.42 The PL excitation spectra monitored at 614 nm as a function of Eu$^{3+}$ concentrations for Ca$_3$Al$_2$O$_6$:Eu$^{3+}$ phosphors prepared at 1100 °C for 2h.

Figure 4.43 shows the room temperature photoluminescence spectra in the range of 550-710 nm of the Ca$_3$Al$_2$O$_6$ phosphors doped with different Eu$^{3+}$ concentrations under 265 nm excitation. All samples were prepared at 1100 °C for 2h and air cooled. There are 6 obvious emission maxima which are the $^5D_1 \rightarrow ^7F_2$ (558 nm), $^5D_0 \rightarrow ^7F_0$ (579 nm), $^5D_0 \rightarrow ^7F_1$ (592 nm), $^5D_0 \rightarrow ^7F_2$ (614 and 619 nm), $^5D_0 \rightarrow ^7F_3$ (648 nm), and $^5D_0 \rightarrow ^7F_4$ (695 and 698 nm) transitions, which arise from the characteristic f-f transitions of Eu$^{3+}$ [295,296]. The highest emission peaks located at 610-630 nm range ($^5D_0 \rightarrow ^7F_2$) are a forced electric dipole transition and are induced by the non-inversion symmetry at the Eu$^{3+}$ ion.
site. However, the band centered at 592 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_1$) is a magnetic dipole transition which is allowed when the Eu$^{3+}$ ion is located at a site of inversion symmetry [297]. The asymmetry ratio of the 4 mol% Eu$^{3+}$-doped Ca$_3$Al$_2$O$_6$ was found to be 1.15, which indicates that the majority of Eu$^{3+}$ ions did not occupy the inversion symmetry center [298].

![Graph showing PL emission spectra](image)

**Figure 4.43** The PL emission spectra of the Ca$_3$Al$_2$O$_6$ phosphors doped with different Eu$^{3+}$ concentrations excited at 265 nm. The inset shows the dependence of PL emission intensity on Eu$^{3+}$ doping concentration for the samples prepared at 1100 °C.

In the Ca$_3$Al$_2$O$_6$ host lattice, Eu$^{3+}$ ions can only occupy Ca$^{2+}$ sites because the ionic radii of Eu$^{3+}$ (107 pm) and Ca$^{2+}$ (112 pm) for octahedral coordination are very close to each other. Furthermore, Eu$^{3+}$ ions are too large to occupy
tetrahedral locations of Al\(^{3+}\). There is no split on the \(^5D_0 \rightarrow ^7F_0\) transition (579 nm), which is both spin and electric dipole forbidden, and this suggests that Eu\(^{3+}\) ions occupy only one site [295].

The emission intensity of luminescent materials is always dependent on the doping concentration. The concentration quenching effect depending on the Eu\(^{3+}\) content for phosphor samples prepared at 1100 °C is given in the inset of Figure 4.43. At low doping concentration, the PL emission intensity increased with the Eu\(^{3+}\) doping until a saturated PL intensity was reached, and beyond this saturation point it decreased. The saturation point of Eu\(^{3+}\) content in Ca\(_3\)Al\(_2\)O\(_6\) was found to be 4 mol%.

Figure 4.44 shows the decay behavior of the 4 mol% Eu\(^{3+}\)-doped Ca\(_3\)Al\(_2\)O\(_6\) red-emitting phosphors. The time resolved \(^5D_0 \rightarrow ^7F_2\) transition (619 nm) presents a single exponential decay behavior, revealing the decay mechanism of the \(^5D_0 \rightarrow ^7F_2\) transition is a single decay component between Eu\(^{3+}\) ions. The decay curve can be represented by [5],

\[ I = I_0 \exp(-t/\tau) \]

Where \(I\) and \(I_0\) are the luminescence intensities at time \(t\) and 0 and \(\tau\) is the radiative decay time. The characteristic decay time (\(\tau\)) was found to be 1.22 ms.
Figure 4.44 The decay time curve of 4 mol% \( \text{Eu}^{3+} \)-doped C3A red-emitting phosphors.

4.7.2.6. Photoluminescence Characteristics of \( \text{Eu}^{3+} \)-Doped \( \text{M}_3\text{Al}_2\text{O}_6 \) (\( \text{M} = \text{Ca, Sr, Ba} \)) Phosphors

X-ray powder diffraction patterns of \( \text{Sr}_3\text{Al}_2\text{O}_6 \) (S3A) and \( \text{Ba}_3\text{Al}_2\text{O}_6 \) (B3A) phosphor samples calcined at different temperatures between 800 °C and 1100 °C for 2 h in air are shown in Figure 4.45 and Figure 4.46, respectively.

The crystal structure of \( \text{Sr}_3\text{Al}_2\text{O}_6 \), S3A, was reported to be cubic, Pa3, with \( a = 15.8556 \) Å [300]. The S3A structure is a puckered, six-membered \( \text{AlO}_4 \) tetrahedral ring, with an average bridging Al-O bond length of 1.768 Å.
Figure 4.45 X-Ray diffraction patterns of Eu$^{3+}$-doped Sr$_3$Al$_2$O$_6$ samples calcined at different temperatures ranging from 800 °C to 1100 °C.

When the precursor was calcined at 800 °C, the characteristic peaks of S3A appeared with a secondary phase of SrCO$_3$ (JCPDS # 99-0099). At 1000 °C, however, a single phase of cubic S3A forms without any secondary phase and all peak positions agree well with JCPDS #24-118 (see Figure 4.45).

The crystal structure of tribarium aluminate, B3A, was determined by Walz from single crystal data [301]. It is reported to be an orthorhombic cell in combination
Figure 4.46 X-Ray diffraction patterns of Eu$^{3+}$-doped Ba$_3$Al$_2$O$_6$ samples calcined at different temperatures ranging from 800 °C to 1100 °C. Samples prepared at 1100 °C show secondary phases as shown above.

with a cubic unit cell. The topological arrangement in the substructure of the barium atoms conforms to the cubic space group Pa3. Furthermore, the individual Al-O distances of the [AlO$_4$]$^-$ tetrahedra scatter between 1.61 Å and
1.95 Å. The principal building unit of B3A is highly puckered 12-membered rings of [AlO₄]⁻ tetrahedra, which are cross-linked via the barium cations [293]. The B3A precursor samples calcined even at 1200 °C for 2 hours did not yield a single phase B3A. The secondary phases were shown in Figure 4.46. Photon correlation spectroscopy analysis revealed that the particle size distribution of the agglomerated nanocrystalline phosphor particles prepared at 1100 °C (2h) have a range extending from 400 nm to 3 μm (Figure 4.47). The average particle size of phosphors was found to be 1.2 μm for C3A, and 1.5 μm for Ba₃Al₂O₆ and Sr₃Al₂O₆ powders.

![Particle size distribution analysis](image)

**Figure 4.47** Particle size distribution analysis of phosphors calcined at 1100 °C for 2 hours with photon correlation spectroscopy.

The photoluminescence characteristics of M₃Al₂O₆:Eu (M = Ca, Sr, Ba) phosphors were measured at a fixed 3 mol% Eu³⁺ concentration level. No excitation and emission bands were observed for the undoped host lattices. This
suggests that all photoluminescence characteristics are due to the active Eu$^{3+}$ ions in the three investigated host lattices. Figure 4.48 shows the room temperature photoluminenscence excitation (PLE) spectra of the phosphors synthesized at 1100 °C for 1h in air when monitored at $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (614 nm) emission band. The absorption spectrum of Ca$_3$Al$_2$O$_6$:Eu$^{3+}$ consists of two regions. First, a very intense and broad band extending from 210 to 330 nm is assigned to charge transfer bands (CTB) between the Eu$^{3+}$ ions and the surrounding O$^{2-}$ anions. Second, the narrow peaks located at wavelengths longer than 330 nm can be attributed to the characteristic f-f transitions of Eu$^{3+}$ (see subsection 4.6.2.5). The f-f transitions of Eu$^{3+}$ include sharp absorption lines $^7\text{F}_0 \rightarrow ^5\text{L}_6$ at 396 nm and $^7\text{F}_0 \rightarrow ^5\text{D}_2$ at 465 nm with intensities comparable to the broad CTB. The absorption spectra of Ba$_3$Al$_2$O$_6$:Eu$^{3+}$ and Sr$_2$Al$_2$O$_6$:Eu$^{3+}$ consist of a broad CTB band similar to Ca$_3$Al$_2$O$_6$:Eu$^{3+}$ without any visible f-f transitions. Unlike Ca$_3$Al$_2$O$_6$ and Sr$_2$Al$_2$O$_6$, Ba$_3$Al$_2$O$_6$ phosphors do not show a noticeable peak in the absorption spectra under the same measurement parameters. The maxima of the absorption bands (CTB) of Sr$_3$Al$_2$O$_6$, and Ca$_3$Al$_2$O$_6$:Eu$^{3+}$ are centered at 267 and 265 nm, respectively. This blue-shift of the center of absorption peaks occurs when the M$^{2+}$ cation is changed from Sr$^{2+}$ to Ca$^{2+}$, and can be explained by the covalency dependence of CTB between Eu$^{3+}$ and O$^{2-}$ ions in host lattice [302]. In the bond structure of M$^{2+}$ - O$^{2-}$ - Eu$^{3+}$ (M = Sr, Ca), the degree of covalency of the O$^{2-}$ - Eu$^{3+}$ bond is stronger in the Sr$_3$Al$_2$O$_6$ than the Ca$_3$Al$_2$O$_6$ host lattice due to the fact that Ca$^{2+}$ cation has the smaller radius and the largest electronegativity [229,303]. Therefore, the electronic transition
from the 2p orbital of O$^{2-}$ to the 4f orbital of Eu$^{3+}$ ion in the Sr$_3$Al$_2$O$_6$ host lattice could be easier than in the Ca$_3$Al$_2$O$_6$, and hence the CTB energy of Eu$^{3+}$ increases in the synthesized Ca$^{2+}$ aluminate phosphors.

![Light emission spectrum of the $\text{Ca}_3\text{Al}_2\text{O}_6$:Eu$^{3+}$ phosphor](image)

**Figure 4.48** Photoluminescence absorption spectra of the 3 mol% Eu$^{3+}$ doped M$_3$Al$_2$O$_6$ (M = Ba, Ca, Sr) phosphors prepared at 1100 °C for 2h in air when monitored at 614 nm.

The emission spectrum of Ca$_3$Al$_2$O$_6$:Eu$^{3+}$ excited by 254 nm is shown in Figure 4.49. It exhibits red luminescence with emission peaks located at 556, 579, 592, 614, and 650 nm attributed to the transitions from the $^5\text{D}_{0,1}$ excited level to the $^7\text{F}_J$ ($J = 0, 1, 2, 3$) ground states of Eu$^{3+}$ ions (see subsection 4.6.2.5). Sharp and
relatively narrow emission peaks are observed because of the shielding effect of 4f electrons by 5s and 5p electrons in the outer shells of the Eu\(^{3+}\) ion [304]. The dominant emission peaks located in the 610-630 nm range (\(^{5}D_{0} \rightarrow ^{7}F_{2}\)) result from a forced electric dipole transition and are induced by the non-inversion symmetry at the Eu\(^{3+}\) ion site. However, the band centered at 592 nm (\(^{5}D_{0} \rightarrow ^{7}F_{1}\)) is a magnetic dipole

![Emission spectra](image)

**Figure 4.49** Emission spectra of 3 mol% Eu\(^{3+}\) doped phosphors excited at 254 nm (a) Ba\(_{3}\)Al\(_{2}\)O\(_{6}\), (b) Sr\(_{3}\)Al\(_{2}\)O\(_{6}\), (d) Ca\(_{3}\)Al\(_{2}\)O\(_{6}\), excited at 396 nm (e) Ca\(_{3}\)Al\(_{2}\)O\(_{6}\), and excited at 465 nm (c) Ca\(_{3}\)Al\(_{2}\)O\(_{6}\). All phosphors were prepared at 1100 °C for 2h in air.
transition, which is allowed when the Eu$^{3+}$ ion is located at a site of inversion symmetry [299]. In contrast, the orange luminescence located at 592 nm in the other two phosphors (Sr$_3$Al$_2$O$_6$ and Ba$_3$Al$_2$O$_6$) is much stronger than their red luminescence located around 614 nm. Additionally, Ca$_3$Al$_2$O$_6$ phosphors exhibited the $^5\!D_0 \rightarrow ^7\!F_0$ band, located at 579 nm, which is both spin and electric dipole forbidden, however this band is not detectable from the emission of other two phosphors. That there is no split on the $^5\!D_0 \rightarrow ^7\!F_0$ transition (579 nm), suggests that Eu$^{3+}$ ions occupy only one site in Ca$_3$Al$_2$O$_6$ phosphors [299]. It is well-defined that the $^5\!D_0 \rightarrow ^7\!F_2$ transition is only allowed when the Eu$^{3+}$ ion is embedded at a site of non-inversion symmetry and the $^5\!D_0 \rightarrow ^7\!F_1$ transition occurs at a site of inversion symmetry [297]. The asymmetry ratio ($I_{\text{red}}/I_{\text{orange}}$) gives a measure of the degree of distortion from inversion symmetry of the local environment around the europium ions in the host lattice. The asymmetry ratio of the Ca$_3$Al$_2$O$_6$, Sr$_3$Al$_2$O$_6$, and Ba$_3$Al$_2$O$_6$ phosphors doped with 3 mol% Eu$^{3+}$ is calculated from the Figure 4.49 to be 1.33, 0.73, and 0.32, respectively. For the same concentration of Eu$^{3+}$ ion in the prepared phosphors, Ca$_3$Al$_2$O$_6$:Eu$^{3+}$ showed the brightest luminescence, as shown in Figure 4.49. The luminescence quenching for the same activator concentration can be explained by the population of crystal defects introduced into the host lattice because of the size-mismatch of the Eu$^{3+}$ ions in the alkaline earth cationic sites, and the formation of oxygen vacancies because of the higher valence value of europium ion. The ionic mismatch between Eu$^{3+}$ (107 pm) and Ca$^{2+}$ (112 pm) is less than that of between Eu$^{3+}$ and Sr$^{2+}$ (126 pm) or Ba$^{2+}$ (142 pm) for the octahedral coordination
[229]. Moreover, the larger ionic radii mismatch will lead to a larger lattice distortion, causing an increase in the defect population around the Eu$^{3+}$ luminescent centers, and this results in weaker luminescence [305]. Based on this fact, Eu$^{3+}$ doped Ca$_3$Al$_2$O$_6$ phosphors will have relatively fewer crystal defects, and the luminescence becomes more favorable compared to the Eu$^{3+}$ doped Ba$_3$Al$_2$O$_6$ and Sr$_3$Al$_2$O$_6$ phosphors.
SECTION 5

Conclusions

Inorganic luminescent materials (phosphors) used in practical applications are typically commercialized in powder form. Photoluminescent properties of phosphors depend on their physical properties such as shape, size, surface texture, purity and their chemical properties such as the characteristic atomic structure, homogeneity in composition, microstructure, presence of defects, etc. All these physicochemical properties of inorganic luminescent powders are controlled by thermodynamics and kinetics of synthesis from raw materials and should be optimized to obtain the maximum quantum efficiency.

A large variety of inorganic luminescent materials have been produced by the conventional solid-state method under a wide range of conditions; however, the low temperature chemical synthesis and processing routes are of great interest, as they offer better control of the microstructure, stoichiometry, and phase purity. This dissertation described the synthesis of five new and commercial phosphors by the Organic-Metal-Ion complex route. This technique is employed for the synthesis of multi-oxide functional ceramic powders because of its versatility and affordability, as compared to conventional solid-state techniques and other
common wet-chemistry-based methods. Polyvinyl alcohol, sucrose, adipic acid and/or their combinations were used as the organic component because of their availability, affordability, and high solubility in water. The solubility limit of metal nitrate salts in water is very high and they are accepted as a relatively-less expensive sources of cations.

The Organic-Metal-Ion complex route provided an easy and convenient way to produce the desired crystalline phases with the right stoichiometry in a relatively shorter processing time—typically less than 8 hours. Synthesized powders were nanocrystalline, and the particle sizes ranged from a few hundred nm to a few microns, averaging out to about one micron. Furthermore, synthesized phosphor particles had a solid-filled and rounded morphology. It is well-known that all these general particle characteristics provide better luminescence and contribute to a higher luminescence efficiency. Molecular-level mixing of cations without aggregation led to the formation of homogeneous metal oxide-dopant complex systems. Additionally, precursors required relatively-lower calcination temperatures, which also contributed to the production of fine particle sizes with relatively-uniform size distributions.

Mn$^{2+}$-doped Zn$_2$SiO$_4$ green-emitting phosphors, prepared by the PVA-Metal-Ion complex route, had a luminescence intensity more than 120% of that of the commercial powders. Furthermore, co-doping with magnesium resulted in an additional 29% enhancement in luminescence intensity without adversely
affecting the decay behavior. These bright-green-emitting zinc-orthosilicate phosphors have the desirable optical properties to be used for display panels and thin film electroluminescent devices.

Optical devices with enhanced designs can be obtained by the development of efficient phosphors. A new host lattice, SrZnO$_2$, was doped with Ce, Tb, and Pb$^{2+}$ ions. Cerium and lead-doped SrZnO$_2$ host lattices gave blue centered emission, while the terbium doped samples yielded the characteristic green emission. In particular, the luminescence properties of Tb$^{3+}$-doped SrZnO$_2$ samples are very efficient and may potentially be suitable to replace other current solid-state lighting phosphors. Photoluminescence and material characterization of these new phosphors proved that the desired crystalline phases with the right stoichiometry formed very efficiently. Optical properties and associated mechanisms were explained based on the photoluminescence and time resolved spectroscopy analysis.

A new red-emitting phosphors was obtained by doping the Ba$_2$YAlO$_5$ host lattice with europium ions. This phosphor can be excited at 254 nm and can be an alternative orange-red colored phosphor for lamp applications. In addition to the general material characterization, photoluminescence properties of this new phosphor were reported. Similarly, the Eu$^{3+}$-doped Ca$_3$Al$_2$O$_6$ host lattice gave the characteristic red-emission. Ca$_3$Al$_2$O$_6$:Eu phosphors had a strong absorption peak at 396 nm in addition to the broad charge-transfer ban centered at around
265 nm. Therefore, it is possible that this phosphor can be used in phosphor-converted red light emitting diodes due to the presence of strong absorption at 396 nm.

Adipic acid and sucrose are found to be very efficient chelating agents for the metal salt solutions and provide excellent synthesis routes for multi-oxide ceramic material production. Precursor solutions yielded stoichiometric pure compounds with the desirable particle morphology and size after calcining at relatively-low temperatures.

Much of the work appearing in this dissertation has been published in peer-reviewed forums [306,307]. Copies of these manuscripts are attached in Appendix.
Future Work

In this study, attempts were made to prepare phosphor powders by using chemical synthesis techniques. In addition to the room temperature optical properties, general material characterization of the synthesized phosphors was presented. $\text{Zn}_2\text{SiO}_4:\text{Mn},\text{Mg}$ phosphors prepared by the PVA-Metal-Ion complex route have excellent optical properties for display and electroluminescent applications. This requires further study. Co-doping with chromium may optimize decay time characteristics.

SrZnO$_2$:Tb green emitting phosphors can potentially replace conventional green phosphors from lamps and similarly, Ca$_3$Al$_2$O$_6$:Eu red-emitting phosphors may have applications in solid state lighting devices such as light emitting diodes. Therefore, absolute quantum efficiency, the effect of heat on the absorption, and emission characteristics can be studied as an extension of this work.
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APPENDIX
Synthesis of pure Zn$_2$SiO$_4$:Mn green phosphors by simple PVA–metal complex route

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Abstract Green light emitting Zn$_{2-x}$Mn$_x$SiO$_4$ (willemite) particles were synthesized by a simple and cost-effective poly(vinyl alcohol) (PVA)-complex route. Microstructural studies on the calcined products show that particles are pure, single phase, nano-crystalline, and agglomerated morphology. A pure-phase willemite structure was obtained with calcination between 850 and 1,175 °C for 2 h in air. Particle size analysis indicates that the average particle size is ~1 μm. The photoluminescence properties of these 4 and 12 mol% Mn-doped Zn$_2$SiO$_4$ powders were measured by fluorescence spectroscopy. Particles with 4 mol% Mn doping prepared at 1,150 °C, with an emission decay time, $t_{0/e}$, of 13.4 ms showed the highest relative peak emission intensities. The emission intensity at this doping level was measured to be ~110% of a representative commercial product's, doped with 11.2 mol% Mn, and exhibiting a decay time of 7.1 ms. The effect of calcination temperature on the photoluminescence and crystallinity properties of synthesized green powders was also investigated.

Introduction

The manganese-doped zinc orthosilicate Zn$_{2-x}$Mn$_x$SiO$_4$ is used as a green luminescent phosphor in cathode ray tubes, lamps, and plasma display panels because of its high saturated color, very strong luminescence, long life span, lack of moisture sensitivity, and chemical stability [1–3]. Zn$_2$SiO$_4$:Mn was also found to be a promising alternative to the conventional thin film phosphors in electroluminescent devices [4], and appropriate for medical imaging detectors for low-voltage radiography and fluoroscopy [5, 6].

The photoluminescence properties of phosphors mainly depend on the dopant choice and composition, the choice of host lattice, and the synthesis methods used. The conventional method to synthesize Zn$_2$SiO$_4$:Mn phosphor is the solid-state reaction which requires high firing temperatures and a milling process as a post-treatment method. This mechano-chemical activation process generates largely agglomerated and irregular particles with relatively weak luminescence properties [7]. For this reason, in the last two decades, much effort has been dedicated to synthesize Zn$_2$SiO$_4$:Mn phosphors with new methods such as sol–gel [8–10], concentration gradient uniform particle size [11], hydrothermal [12], spray pyrolysis [2, 13], fume pyrolysis [14], polymer pyrolysis [15], and combustion synthesis [16]—each method producing material with the desirable luminescence. Although several chemical methods have been applied to the production of fine phosphor particles with good luminescence, challenges remain in reducing process complexity, controllability, and cost. Therefore, new synthesis routes are being explored to potentially overcome some of these difficulties in commercialization. During recent years, novel organic–inorganic polymerization synthesis routes have been applied to produce a variety of mixed oxide metals. For example, poly(vinyl alcohol) (PVA) –[CH$_2$–CHOH]$_n$ and poly(ethylene glycol) (PEG) H[O–CH$_2$–CH$_2$]$_n$–OH have been...
reported for use in synthesis as an organic component, with water dissoluble metal cations added as the inorganic component [17–21].

In this study, manganese doped willemite, Zn$_2$SiO$_4$·Mn, green phosphor particles were produced by a simple PVA–metal complex route. The photoluminescence properties, crystallinity, particle size, and morphology were investigated, with the results reported here.

**Experimental procedure**

The synthesis process used in this work involves preparation of cationic precursors and mixing them with a viscous PVA–H$_2$O solution. This is then heated to evaporate the water, leaving behind an intermediate powder which is calcined at elevated temperature to significantly improve purity and crystallinity, and create uniform doping in the resulting phosphor powders. All polymeric and cationic solutions were prepared fresh. This process is described more fully below.

The PVA–metal complex precursor for Zn$_2$Mn$_x$SiO$_4$ was prepared using Zn(NO$_3$)$_2$·6H$_2$O (99%, Alfa Aesar), Mn(NO$_3$)$_2$·4.4H$_2$O (99.98%, Alfa Aesar), Ludox TMA colloidal silica solution (ChemPoint.com) with an average colloidal particle size of 5.78 nm, and PVA (molecular weight of 145,000) with degree of polymerization of 3300 (Sigma-Aldrich Inc.). According to the PVA’s product specifications, the nominal “100 mol% hydrolyzed PVA” actually contains up to 2 mol% of acetate groups, which replace the OH–cation bonds used in our process. Thus, in our calculations, we assumed an average 99 mol% degree of hydrolysis.

Synthesis begins with a 5 wt.% PVA–H$_2$O solution, prepared on a hot plate at ~85 °C (with mixing) until a clear viscous solution results. Stoichiometric amounts of the cationic nitrates were dissolved in the minimal necessary amount of D.I. water by stirring in a separate container at room temperature and then added to the heated PVA–H$_2$O aqueous solution. Typically, 120 g batches of the PVA–metal solution were prepared for each set of conditions. The proportions of the PVA and cation sources in the precursor solution were adjusted to provide a targeted PVA monomer unit:metal ion mole ratio of 2:1 to ensure sufficient hydroxyl (OH–) groups were available for cation dispersion in the PVA. Ideally, this helps avoid cation (metal) precipitation and agglomeration. Each monomer part of the long PVA polymeric chains has one hydroxyl group in the aqueous solution and the relative stoichiometric values of the cations in the solution were calculated based on the total number of hydroxyl functional groups, given the solution concentration, degree of hydrolysis, and degree of polymerization. The PVA–metal aqueous solution was then heated on a hot plate at a temperature of ~150 °C with continuous mixing. After evaporation (8–10 h), a dark brown, soft, loosely connected precursor powder typically remains. Each sample powder batch (typically 0.2 g after evaporation) was calcined in air at different temperatures up to 1,175 °C, for a fixed 2-h period and then air cooled to obtain the final manganese-doped green phosphors.

The crystallization behavior and the crystallite size measurements of the phosphors were studied via room temperature X-ray diffraction (XRD) as a function of the calcination temperature using a Philips P.W. 2273/20 diffractometer with Cu Kα radiation (45 kV, 30 mA). The particle sizes and size distributions were measured using a Microtrac® Nanotrac NPA 250 particle size analyzer. For the particle size measurements, powders were dispersed in 20 wt.% glycerin–D.I. water solution, via ultrasonication. Photoluminescence characteristics in the visible range were recorded on a Hitachi F-4500 fluorescence spectrophotometer with a 150 W Xe lamp, using a 254 nm (ultraviolet) excitation wavelength. Decay time measurements were performed via time-resolved spectroscopy with the same equipment. Scanning electron microscopy (SEM) was conducted using a Hitachi S-4700 cold field emission SEM, with the powder samples coated with Pt. Mn dopant levels in a commercial powder (evaluated to serve as a baseline comparison) were measured using a Perkin-Elmer 2380 Atomic Absorption Spectrophotometer.

Using the above-described procedures, we prepared a set of powders at two different manganese doping concentrations (4 and 12 mol%) and examined a range of calcination temperatures between 750 and 1,175 °C to determine the influence these parameters had on the material properties. Comparisons were made with a commercially available Zn$_2$SiO$_4$·Mn product provided by OSRAM SYLVANIA Products Inc.

**Results and discussion**

**XRD analysis**

XRD patterns for 4 mol% Mn doped Zn$_2$SiO$_4$ phosphors, measured from samples calcined at various temperatures (as well as the commercial phosphor) are shown in Fig. 1. The as-synthesized powders and those
calcined at 750 °C showed unreacted ZnO peaks near 2θ = 36° with an amorphous structure. Single phase zinc orthosilicate crystal structures with similar crystallinity (i.e., the willemite phase, exhibiting the phenacite structure) to that of the commercial powder, start to form at calcination temperatures of ~850 °C after 2 h. The Mn doping concentration in the commercial phosphor was measured to be 11.2 mol% using atomic absorption spectroscopy, which is close to the composition of a commercial product Zn₇₂SiO₄·Mn reported elsewhere [22] (~10 mol%). All powders had a white color, indicative that the manganese is in the desired Mn²⁺ state [3] after heat treating at (and above) 950 °C. Other reports [1], indicate that synthesis using solid-state and solution reaction methods yielded the same single-phase willemite at 1,400 °C (for 4 h) and 1,200 °C (for 4 h), respectively. The spray pyrolysis method [13], has been reported to give the same phase at 1,200 °C (for 5 h). Combustion synthesis [16] and the hydrothermal method [12], resulted in single-phase willemite without any high temperature heat treatment.

The peak positions in Fig. 1 match well with those of the standard pattern (JCPDS 37-1485) for Zn₇₂SiO₄ in the phenacite structure. In order to investigate the crystallinity dependence on the calcination temperatures, the FWHM values of the main peaks were measured and found to decrease from 0.30° to 0.24° as the temperature increased from 950 to 1,175 °C. Also, the peak intensities increased with increasing calcination temperatures leading to the conclusion that the crystallinity of phosphor particles was increased with calcination temperature. Individual crystallite sizes were estimated using Scherrer’s formula and were found to shift from ~25 to ~38 nm as the temperature was increased from 850 to 1,175 °C.

Photoluminescence spectra characterization

Emission spectra (under 254 nm excitation) for phosphor particles prepared at various calcination temperatures are shown in Fig. 2. As the temperature increases, the emission peak intensity increases, with the highest intensities obtained in the 1,160–1,175 °C range. These intensities were ~120% that of the commercial product’s particles. Phosphors (5 mol% Mn) prepared with spray pyrolysis [13] at 800 °C and post-treated at 1,100 °C reportedly had an intensity maximum of ~112% of the commercial product. As the manganese content is increased from 4 to 12 mol%, the maxima of the emission band was observed to shift slightly to a higher wavelength, from 523 to 526 nm, and with a bandwidth change of Δλ = 38 nm to 39 nm at half maximum, respectively. These characteristic wavelength values are attributed to the presence of Mn²⁺ cations in the willemite structure. Both Zn²⁺ and Si⁴⁺ ions coordinate tetrahedrally with four oxygen atoms in the Zn₇₂SiO₄ crystal lattice [23], and in this host lattice, Mn²⁺, with a weak crystal field, usually gives green emission. There are reportedly two different Zn sites with nearest oxygen ions in a slightly distorted tetrahedral configuration [24]. As the difference in ionic radii of Zn²⁺ (0.074 nm) and Mn²⁺ (0.080 nm) is very small, both Zn²⁺ sites can be replaced by Mn²⁺ ions [25]. The Mn²⁺ ion has 3d⁵ configuration with high spin and the emission band is assigned to transition from the lowest excited state ⁴T₁ to the ground state ⁶A₁ [23, 24].

![Fig. 1 X-ray diffraction spectra for 4 mol% Mn doped Zn₇₂·Mn₂SiO₄ prepared for 2 h at various temperatures and the commercial one. Conditions are as follows: (a) as–synthesized, (b) 750 °C, (c) 850 °C, (d) 950 °C, (e) 1,050 °C, (f) 1,150 °C, and (g) commercial powder. (ZnO). Note that at temperatures above ~850 °C, crystallinity is significantly improved, and the primary ZnO peak disappears, suggesting a predominantly single-phase willemite material.](image-url)
Zn\(^{2+}\) exhibits an intense and broad UV absorption in the short wavelength, an energy transfer to Mn\(^{2+}\) takes place, resulting in the green emission from the Zn\(_2\)SiO\(_4\):Mn phosphor [23, 26]. The UV absorption–transition process has been suggested [23] to include a charge transfer transition from the 2p orbital of oxygen to an anti-bonding orbital, which is localized partly on the d\(^{10}\) level of the Zn\(^{2+}\) ion and partly on the 2p level of the oxygen.

Figure 3 shows the excitation spectrum for 4 and 12 mol\% Mn doped samples calcined at 1,160 °C for 2 h, and the commercial powder with 11.2 mol\% Mn.

Figure 4 shows the observed relative peak emission intensities of 4 and 12 mol\% Mn doped Zn\(_2\)SiO\(_4\):Mn samples at various calcination temperatures ranging from 950 to 1,175 °C. For both measured concentration levels, the emission intensity was increased sharply when the calcination temperatures increased. The peak emission intensity of the 4 mol\% Mn doped phosphor prepared at 1,175 °C is almost 17 times higher than that of phosphors prepared at 950 °C. Overall, phosphors with 4 mol\% Mn showed higher emission intensities than those doped with 12 mol\% Mn. This behavior has been attributed to the concentration quenching phenomenon [24].

When the Mn\(^{2+}\) dopant concentration increased, there is expected to be energy transfer between Mn\(^{2+}\)–Mn\(^{2+}\) ions [24]. This can take excitation energy too far from the absorption location, potentially losing the excitation at a quenching site, without any photon radiation and lead to a decrease in luminescence efficiency [23, 24]. At low concentrations of Mn\(^{2+}\) ions, the concentration quenching effect is negligible because the average distance between Mn\(^{2+}\) ions is relatively large and the energy migration is prevented.

**SEM characterization**

Scanning electron microscope (SEM) images for the as-synthesized powders and the 4 mol\% Mn doped samples prepared at 1,150 °C for 2 h are illustrated in Fig. 5. Micrographs show that the as-synthesized particles are highly agglomerated at the micron-scale. Additionally, the calcined phosphor particles have an irregularly rounded morphology and solid-filled
structure without any porosity in the range of 200–500 nm. These sub-micron particles formed irregularly rounded aggregates in micron size.

Particle size measurements

A typical particle size distribution for phosphor particles calcined at 1,150 °C is shown in Fig. 6. Phosphor particles were dispersed in 20 wt.% glycerin–water solution by ultrasonication prior to particle size analysis. The average discrete particle size is ~1 μm, with a range of sizes extending from 200 nm to 4 μm for all measured manganese doping levels.

Decay time measurements

It is widely accepted that photoluminescent properties of phosphors can depend on their shape, size, and surface texture, as well as the composition. These properties of the phosphors should be optimized to obtain the maximum quantum efficiency through energy absorption [1]. The intensity decay of a photoluminescence process can be expressed in the functional form: $I_{\text{em}} = I_0 e^{-t/\tau}$, where the lifetime $\tau$ refers to the time required for the intensity to drop to $I_0/e$ [27].

Figure 7 shows the measured intensity decay plots, including the measured lifetimes to reach intensities of $I_0/e$ and $I_0/10$. Phosphors calcined at 1,150 °C and doped with 4 mol% Mn decayed to $I_0/e$ in 13.4 ms and $I_0/10$ in 31.2 ms. The 12 mol% Mn phosphor (also calcined at 1,150 °C) decayed to $I_0/e$ in 5.0 ms and $I_0/10$ in 11.2 ms.

Similarly, the decay times for the commercial product we evaluated were found to be 7.1 ms at $I_0/e$, and 13.5 ms at $I_0/10$, placing the commercial product’s decay times in between the 4 and 12 mol% samples produced in this effort.

Similar comparisons have been made in the literature, which report that the decay times measured at $I_0/10$, (i.e., $\tau_{10\%}$), typically fall in the range

![Fig. 6 Particle size distribution of 4 mol% Mn doped Zn$_2$SiO$_4$:Mn phosphors calcined at 1,150 °C for 2 h in air. The size distribution is fairly large (200 nm to 3 μm), with a mean diameter of ~1 μm](image)

![Fig. 7 Decay curves of Zn$_{2-x}$Mn$_x$SiO$_4$ phosphors with 4 and 12 mol% Mn doping levels, as well as a commercial product (11.2 mol% Mn) shown for comparison](image)
of 5–25 ms [1–3, 22] at the same Mn doping levels. The emission decay time behavior is reported to be dictated by the energy migration between proximate manganese ions [24]. Thus, the Mn doping level can be expected to influence the diffusion-controlled emission decay time. The decay times for the phosphors produced here extend from as short as 5 ms, to over 31 ms. This overlaps the range of values reported elsewhere in the literature, as well as the commercial product included in this study. Whereas it was found in this effort that the decay time can be varied over a range, a systematic study of this behavior was beyond the scope of this effort. The range of decay times achieved here suggest that phosphors with decay times of 5–10 ms and very bright emission intensities, can likely be achieved simply through doping concentration. In general, additional studies would be needed to determine whether other controllable parameters would impact the photoluminescence behavior of these phosphors. Examples of potential utility include the degree of PVA polymerization, the degree of hydrolysis of the PVA, cation source selection, the mole ratio of PVA monomer to metal cations, and the use of different polymerizing and combustion agents.

Conclusions

Green light emitting Zn$_2$SiO$_4$:Mn phosphor particles with rounded and filled morphologies without any porosity, and with good luminescence properties were produced using a simple PVA–metal complex route. This method requires a short thermal processing time of 2 h in air at a minimum temperature of 950 °C. This results in phosphors with the desired willemite phase, and with Mn-doping in the desired Mn$^{2+}$ state yielding green light emission under 254 nm UV excitation. In general, as the calcination temperature is increased (within the range investigated here), the calcined samples exhibit emission intensities that are 110–120% that of the tested commercially available product. The calcined samples exhibit irregularly rounded particles of 200–500 nm size, agglomerated into an overall average particle size of ~1 µm for samples prepared at both manganese doping levels, i.e., the agglomeration behavior was insensitive to doping composition in the range of composition evaluated here. Highly crystalline phosphor particles without any porosity and with smooth, rounded surface texture are demonstrated here to give good luminescence properties in comparison with available commercial products, complementing the simple and reliable synthesis process used in their creation.

The data presented here indicate that there may be some potential for the application of a relatively simple PVA–metal complex synthesis method to produce phosphor materials such as the green phosphor, Zn$_2$SiO$_4$:Mn. Further development of this synthesis method for application in different phosphor systems is presently under way.

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References

A new blue-emitting phosphor, SrZnO$_2$:Pb$^{2+}$, synthesized by the adipic acid templated sol–gel route

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Abstract

A new blue-emitting phosphor, Sr$_{1-x}$Pb$_x$ZnO$_2$, was prepared by a novel adipic acid templated sol–gel route. Photoluminescence and crystalline properties were investigated as functions of calcination temperatures and the Pb$^{2+}$ doping levels. It was found that under UV excitation with a wavelength of 283 or 317 nm, the phosphors gave emission from 374 to 615 nm with a peak centered at 451 nm. This broad-band was composed of UV and the visible range was attributed to an impurity-trapped exciton-type emission. The maximum emission intensity of the Sr$_{1-x}$Pb$_x$ZnO$_2$ phosphors occurred at a Pb concentration of $x = 0.01$. The decay time was observed to be ~33 ms for the compound doped with 1 mol% Pb prepared at 1000 °C. Diffuse reflectance spectra revealed the characteristic absorption peaks and the bandgap energy of SrZnO$_2$ was found to be 3.4 eV. SEM analysis indicated that phosphor particles have an irregularly rounded morphology and the average particle size was found to be approximately 1 μm.

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1. Introduction

The development of new solid inorganic luminescent materials has provided improvements in lighting and display systems. In recent years, great efforts have been dedicated to discover and develop new rare-earth or transition-metal ion-doped material systems as luminescent materials with high absorption in the UV spectral region. The optical properties of Pb$^{2+}$ have been progressively studied as an activator or in the host matrix [1,2]. The luminescence properties of the Pb$^{2+}$ ion with 6$s^2$ configuration are attributed to the ground state $^1S_0$ and two excited states of singlet $^1P_1$ and triplet $^3P_{0,1,2}$ [3]. The luminescence of compounds containing metal ions with $s^2$ configuration can be used in X-ray imaging devices, low pressure lamps, and high-energy physics [4].

Recently, a new UV-absorbing luminescent host lattice material, SrZnO$_2$, with yellow emission after co-doping with Ba$^{2+}$ and Mn$^{2+}$ was reported [5]. SrZnO$_2$ doped with Tb$^{3+}$ has been shown to exhibit green emission [6]. Activating this new host matrix with different ions might provide new luminescent materials having potential applications in optical devices. In working towards this end, we reported our preliminary observations of doping SrZnO$_2$ with Pb to produce blue emission [7].

Several low-temperature chemical routes have been used to prepare inorganic luminescent materials during the last decade using sol–gel [8,9], combustion [10], polymer–metal precursor [11,12], co-precipitation [13], and other related methods. Adipic acid (HOOC(CH$_2$)$_4$COOH) has been used as the monomer for the production of polyamides (Nylon-6,6) through polycondensation reaction with hexamethylene diamine [14]. It has also been used as a chelating agent to synthesize cathode materials for lithium secondary batteries [15,16]. The main advantage of this method is the capability of preparing complex mixed-oxide solutions, with molecular-level homogeneity in solution, and stoichiometric control at lower temperature calcinations with shorter time.
In this work, we report a new blue-emitting luminescent material, \( \text{SrZnO}_2: \text{Pb}^{2+} \), synthesized by the sol–gel method, templated by adipic acid as a chelating agent. This material’s photoluminescence excitation and emission characteristics are also presented.

2. Experimental

\( \text{Sr}_{1-x}\text{Pb}_x\text{ZnO}_2 \) powders were prepared from the starting materials of \( \text{Sr(NO}_3)_2 \) (>99%, Alfa Aesar), \( \text{Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O} \) (99%, Alfa Aesar), \( \text{Pb(NO}_3)_2 \) (99.3%, J.T. Baker Chemical Co.), and adipic acid (99%, Sigma Aldrich). Aqueous solutions of all the starting materials were made by dissolving them in deionized water. In a typical batch, 10 mL of 2 M cation solution was added to 50 mL of 0.2 M adipic acid solution prepared at a mild temperature (~45 °C). The clear mixture was heated to 80 °C on a hot plate with continuous stirring. After evaporation of all the water, a translucent sol was formed and it was further heated in an oven at 120 °C for 2 h in air to produce a white-colored, crispy, and loosely-connected powder that was subsequently fired at the desired calcination temperatures for 2 h in air. In the precursor solution, the molar ratio of the metal ions to adipic acid was 1:0.5. The molar doping concentrations of \( \text{Pb}^{2+} \) in the phosphor were 0.1%, 0.5%, 1.0%, 1.5%, 2.5%, and 5%, respectively.

The crystallization behavior and crystal structure of the phosphor powders were examined using a room temperature X-ray diffractometer (Philips PW 2273) with CuK\( \alpha \) radiation. Average crystallite size was calculated from the broadening of diffraction peaks based on the Williamson–Hall technique, using the built-in instrument software (JADE). Excitation and emission characteristics of the phosphor powders were recorded at room temperature on a Shimadzu UV-240 spectrophotometer.

3. Results and discussion

The crystallinity of the \( \text{SrZnO}_2:x\text{Pb} \) powders with \( x = 1.5 \text{ mol}\% \) Pb calcined between 800 and 1000 °C in ambient air for 2 h was characterized by XRD (Fig. 1). Samples prepared at 800 °C appear to still have precursor materials present; however, at 900 °C, \( \text{SrZnO}_2 \) crystallographic structure was obtained with only weak lines corresponding to ZnO and \( \text{SrCO}_3 \) as secondary phases in trace amounts. These secondary phase peaks disappeared and a single phase of \( \text{SrZnO}_2 \), corresponding to the standard JCPDS file # 41-0551, was obtained at 1000 °C.

This suggests that the introduction of \( \text{Pb}^{2+} \) ions into the \( \text{SrZnO}_2 \) host lattices does not change the lattice structure of the sample. Phosphors prepared at 1000 °C have crystallite sizes of 48 nm. Calcination at 1200 °C resulted in very hard green-colored agglomerates separate from a white-colored matrix. The crystal structure of \( \text{SrZnO}_2 \) is orthorhombic and is in the space group of Pnma [17]. It has a layered structure which consists of \( \text{ZnO}_4 \) tetrahedra, linked through common vertexes (Zn–O–Zn), with Sr atoms located between these waved vertex layers [18]. Each strontium atom is surrounded by seven oxygen atoms. There is only one site for each Zn and Sr atom, but there are two sites available for oxygen atoms [5,17]. The ionic radii of \( \text{Zn}^{2+} \), \( \text{Sr}^{2+} \), and \( \text{Pb}^{2+} \) are 74, 121, and 123 pm, respectively [19]. Therefore, when the \( \text{SrZnO}_2 \) host lattice is doped with \( \text{Pb}^{2+} \) ions, they substitutionally replace strontium atoms from the host lattice.

A typical scanning electron micrograph of the 1 mol% \( \text{Pb}^{2+} \)-doped \( \text{SrZnO}_2 \) samples prepared at 1000 °C for 2 h is shown in Fig. 2. The calcined phosphor particles have an irregularly rounded morphology, ranging in size from 50 to 250 nm.

These submicron particles form larger aggregates in micron and submicron sizes. Particle size and distribution analysis was done using DLS (Fig. 3). The average particle size is 918 nm, with a range of sizes extending from 400 to 4600 nm.

The diffuse reflectance spectra of the undoped \( \text{SrZnO}_2 \) samples are very similar to those of the dilute \( \text{Sr}_{1-x}\text{ZnO}_2: \text{Pb}_x \) system, with \( x = 10^{-2} \) (Fig. 4).

The characteristic bandgap energy of 3.4 eV was found for \( \text{SrZnO}_2 \) by extrapolating the sharp slope to the level of no absorption in the reflectance spectra. The absorption near 283 nm was seen for doped and undoped samples, but the peak at 317 nm is detectable in reflectance spectra only when \( \text{SrZnO}_2 \) is doped with \( \text{Pb}^{2+} \).

![Fig. 1. X-ray diffraction patterns of 1.5 mol% Pb-doped SrZnO2 calcined at 800 °C (a), 900 °C (b), and 1000 °C (c). The SrZnO2 phase starts to form at 900 °C with ZnO and SrCO3 phases and the single-phase orthorhombic structure of SrZnO2 is formed at 1000 °C.](https://example.com/fig1.png)
Fig. 5 shows the excitation and emission spectra for Sr$_{1-x}$Pb$_x$ZnO$_2$ ($x = 0.015$) phosphors, calcined between 800 and 1100 °C, with excitation spectra monitored at 455 nm and the emission spectra excited at 283 nm. (a) 800 °C, (b) 900 °C, (c) 1000 °C, (d) 1100 °C.

The emission spectrum of Sr$_2$ZnO$_4$:Pb$^{2+}$ changes depending on the excitation wavelength and the calcination temperature of the prepared phosphors (Fig. 6). Under 283 nm excitation, phosphors prepared at 1000 °C show higher emission intensity than phosphors under 317 nm excitation as shown in Fig. 6(a). However, the relative intensity of the 451 nm emission peak ($\lambda_{ex} = 283$ nm) of phosphors prepared at 1100 °C is slightly lower than the intensity when the phosphors were prepared under 317 nm excitation.

When temperature increases, the relative intensity of peak centered at 317 nm also increases, although the band at 283 nm decreases and shifts towards higher wavelengths. When excited at 283 and 317 nm, a broad emission band was observed, extending from 374 to 615 nm with a maximum at about 451 nm.

The excitation and emission spectra of Sr$_2$ZnO$_4$:Pb$^{2+}$ changes depending on the excitation wavelength and the calcination temperature of the prepared phosphors (Fig. 6). Under 283 nm excitation, phosphors prepared at 1000 °C show higher emission intensity than phosphors under 317 nm excitation as shown in Fig. 6(a). However, the relative intensity of the 451 nm emission peak ($\lambda_{ex} = 283$ nm) of phosphors prepared at 1100 °C is slightly lower than the intensity when the phosphors were prepared under 317 nm excitation.

The excitation and emission spectra of Sr$_2$ZnO$_4$ activated with different Pb concentrations prepared at 1000 °C for 2 h are illustrated in Fig. 7. The calculated full-width at half-maximum (FWHM) is about 95 nm for the brightest emission (1 mol% Pb). The two bands in the excitation spectrum coincide with the two absorption bands at 283 and 317 nm, respectively, in the diffuse reflectance spectrum of Sr$_{1-x}$Pb$_x$ZnO$_2$. The Pb$^{2+}$-induced absorption band at 317 nm is not observed in the diffuse reflectance spectrum of the undoped material. This lowest energy absorption band is due to the $^1S_0 \rightarrow ^3P_1$ (A-band) transition on the Pb$^{2+}$ ion. The higher energy absorption may be assigned to the allowed $^1S_0 \rightarrow ^3P_1$ transition. This
assignment would yield an energy difference between \(^{1}\text{P}\text{1}\) and \(^{3}\text{P}\text{1}\) states of about 4000 cm\(^{-1}\). However, in crystalline solids, the energy separation between \(^{1}\text{P}\text{1}\) and \(^{3}\text{P}\text{1}\) states usually amounts to about 12,000 cm\(^{-1}\) [20]. Although the absorption edges of the doped and undoped samples at around 283 nm cannot be clearly distinguished from the diffuse reflectance spectra in Fig. 4, the excitation band shows that the host lattice has a weak absorption centered at 269 nm and has no luminescence when excited at 283 nm, as shown in Fig. 7. Other research groups reported that SrZnO\(_2\) has no characteristic excitation and emission bands [6]. From the weakness of the host lattice excitation band in the excitation spectrum, it can be assumed that an energy transfer from the host to the Pb\(^{2+}\) impurity is not efficiently present. In addition, there is no emission from the SrZnO\(_2\) host lattice which overlaps with the absorption spectrum of the Pb\(^{2+}\)-doped samples, hence it is not expected that the Pb\(^{2+}\) impurity would be excited by excitation of the host followed by an interband energy transfer from the SrZnO\(_2\) host to the Pb\(^{2+}\) impurity [21]. The presence of Pb\(^{2+}\) ions provides an efficient excitation centered at 283 nm, which is thus tentatively assigned to the absorption into the excitonic state. Increasing the calcination temperature from 1000 to 1100 °C for the same Pb\(^{2+}\) concentration results in an increase in the population of A-band absorption at the expense of the excitonic state, as shown in Fig. 6.

Pb\(^{2+}\)-doped SrZnO\(_2\) phosphors showed a broad emission band covering the near-UV spectral region and the visible part of the spectrum, and this can be explained by the large Stokes shift of the emission at around 13,000 cm\(^{-1}\). Similar observations were reported for different luminescent materials with high Stokes shift emissions [22]. Despite extensive studies with different host lattices, the origin of the visible emission in s\(^2\) ion-doped systems remains unresolved and varies from host to host.

There are three popular mechanisms proposed as impurity-trapped exciton type [23,24], D-level transition (ligand to metal charge transfer transitions or perturbed exciton emission) [25,26], and \(s^2\)-ion effect (pseudo Jahn–Teller effect) [25]. The host lattice with narrow bandgap allows Pb\(^{2+}\) ions to ionize under UV excitation into their first excited states, located just below the conduction band of the host crystal [23]. In Sr\(_{1-x}\).Pb\(_x\).ZnO\(_2\), the visible emission band is associated with the ionization process described above, in which the active Pb\(^{2+}\) center injects an electron into the host lattice conduction band. Based on this, the blue-centered emission is an impurity-centered exciton state that is populated by an electron transfer from the \(^{3}\text{P}\text{0},1\) excited states of the Pb\(^{2+}\) ion to the SrZnO\(_2\) conduction band. The emission due to the ionization mechanism is not only valid for Pb\(^{2+}\) ion, but has also been observed in luminescence of ions such as Yb\(^{3+}\) [24], Eu\(^{3+}\) [27], Cu\(^{+}\) [28], and Bi\(^{3+}\) [29]. The impurity-trapped exciton structure consists of the hole localized on the luminescent ion and the electron delocalized over the surrounding cations; for instance, a Yb\(^{3+}\) core with the electron delocalized over the 12 nearest neighbors Sr\(^{2+}\) ion forms the trapped exciton in SrF\(_2\):Yb\(^{3+}\) [24]. As previously described, the SrZnO\(_2\) structure consists of a two-dimensional array of ZnO\(_{4,2}\) tetrahedra which share corners with each other to form waved layers, and Sr atoms are located in the cavity between the layers. Therefore, the exciton structure in SrZnO\(_2\):Pb\(^{2+}\) can be considered to consist of the hole residing on the Pb\(^{2+}\) ion and the electron over the ZnO\(_{2,2}\). It has been reported that the M(d\(^{10}\))–O(II) complexes delocalize easily when their concentration is high [30]. It is also noteworthy that the Stokes shift of impurity-trapped excitonic state emission is reported to be much larger than that of the localized \((^{3}\text{P}\text{0},1\rightarrow^{1}\text{S}\text{0})\) transitions [23,29].

In addition to the impurity-trapped exciton, the visible emission can also be perceived as an emission arising from a charge-transfer transition between the activator Pb\(^{2+}\) (6s\(^2\)) and the Zn\(^{2+}\) (3d\(^{10}\)) ions of the host lattice. The
occurrence of luminescence from complexes consisting of d^{10} metal ion surrounded by oxygen ions in solids and molecules such as Zn_{4}O(acetate)_{6} [30] and Zn_{4}O(BO_{2})_{6} [31], in which the Zn^{2+} ion is tetrahedrally coordinated, has been reported. The relevant strongly Stokes-shifted broad emission was associated with a considerable amount of charge-transfer character, like the well-known luminescence of oxo-complexes of the d^{0} metal ions such as vanadates and molybdates [30,32]. Since the D-level in the energy scheme of ns^{2} ions is thought to be of a charge-transfer type, the visible emission in SrZnO_{2}:Pb^{2+} can be assigned to D→1S_{0} radiative transition.

The relative intensities of the emission peaks change dramatically depending on the doping level of the Pb^{2+} ions (Fig. 7). With increasing Pb^{2+} concentration, the emission intensity of the samples increases and reaches a maximum at 1 mol% Pb. It decreases when the mole concentration of Pb^{2+} ion exceeds this concentration level. The concentration dependence of the emission intensity can be explained by the well-known concentration quenching of the emission. The concentration quenching in inorganic phosphors has been attributed to the migration of excitation energy to the quenching centers (traps) or to the cross-relaxation mechanisms [33]. In Pb^{2+}-doped SrZnO_{2} phosphors, it can be attributed to the former one, when the distance between the excited luminescent center and the trap is close enough to transfer excitation energy readily to the trap, where the excitation energy is lost non-radiatively. The produced phosphors have low concentrations of quenching centers, mainly originating from the defects produced during the synthesis and unwanted trace impurities contained in starting materials [34].

When the concentration of Pb^{2+} ions (activators) is less than 1 mol%, these luminescent centers can be considered as “isolated”, and the excitation energy transferred is too small for luminescence quenching. However, beyond 1 mol% Pb, the distance between activators will potentially be close enough to transfer the excitation energy from one center to another, which causes non-radiative transitions extensively. Therefore, the luminescence intensities of samples would decrease when the Pb^{2+} ion amount exceeds 1 mol% in the SrZnO_{2} host lattice [33,34].

Phosphorescence lifetime studies with time-resolved spectroscopy revealed that the brightest luminescent 1 mol% Pb-doped SrZnO_{2} showed an exponential decay curve with a decay time of (I_{0}/e) ~ 33 ms. This slow decay property is very abnormal compared with other Pb^{2+}-doped host lattices. A strong decrease in the luminescent decay time from ms to μs with increasing temperatures is usual for A- and D-level emissions. At low temperatures, 1P_{0}→1S_{0} emission has a ms range lifetime because of the forbidden transition (ΔJ = 0) [35]. At higher temperatures 3P_{1} level is thermally populated, and due to mixing of 1P_{1} and 3P_{1} states the spin selection rule is partially lifted and the decay time of this allowed emission is shortened to μs. Although the exact nature of the D-level emission is still unknown, the same behavior has been attributed to the D-level emission of charge-transfer transitions [21]. For allowed charge-transfer transitions, ns level decay times are typically observed; however, small wavefunction overlap and spin-forbidden character can increase the decay time to ms ranges at low temperatures for Pb^{2+}-doped samples similar to the charge-transfer transitions in d^{0} complexes [21,25]. Impurity trapped exciton-type emission from different host lattices has been reported to have a typical decay time in μs at high temperatures [23,28]. The long decay time of Sr_{0.99}Pb_{0.01}O_{2} can be associated with the release of holes from the trapping center, to restore the radiative decay of the luminescent centers. After excitation,
majority of the excited Pb\(^{2+}\) ions immediately release photo energy by emitting and then returning to the ground state (in \(\mu s\)). However, a very small fraction of them may produce holes by taking an electron from the valence band and stay as Pb\(^{2+}\). These mobile holes can be trapped by any cationic defects, such as possible Sr\(^{2+}\) vacancies formed in nanocrystals during the synthesis and fast cooling of the heat-treated samples in air. A reverse recombination process in which holes turn back to Pb\(^{2+}\) to form Pb\(^{2+}\) accompanies the characteristic emission. The exponential character of the decay curve shows that there is no re-trapping after the recombination process. Such an interpretation runs parallel to the case of Bi\(^{3+}\)-doped Ca\(_1_{-}\)Sr\(_3\)S phosphors with a persistent phosphorescence and a direct cation vacancy formation was observed because of the valence difference in Ca\(^{2+}\) and Bi\(^{3+}\) [36].

Mao et al. [37] reported that co-doping of Pb\(^{2+}\) and Cu\(^{2+}\) in the host lattice of ZnS resulted in better luminescence and longer decay times in a way in which Cu\(^{2+}\) and the host matrix form the active luminescent center, and Pb\(^{2+}\) forms a deep level as a sensitizer. When the SrZnO\(_2\) host lattice was co-doped with Pb\(^{2+}\) and Cu\(^{2+}\) at different concentrations, it resulted in no luminescence. However, the synthesized powder was green in color, and so might have a potential application as a pigment material.

4. Conclusions

Pb\(^{2+}\)-doped SrZnO\(_2\) phosphor particles were prepared by the sol–gel route, templated by adipic acid as a chelating agent. The produced phosphor particles were nanocrystalline and irregularly rounded, with an average particle size of \(\sim 1 \mu m\). Doping with the Pb\(^{2+}\) ion resulted in a new UV-excited luminescent material with a very broad emission band, centered in the blue region with a wavelength of 451 nm. The excitation studies revealed that there are two consistent absorption bands located at 283 and 317 nm, which were assigned to the Pb\(^{2+}\) ion trapped exciton and A-band (\(^{1}S_0 \rightarrow ^{3}P_1\)), respectively. The emission peak intensities change depending on the concentration of Pb\(^{2+}\) in the host lattice and reached a maximum at 1 mol\%; however, the maxima of emission bands were fixed at 451 nm. The calculated FWHM was about 95 nm for the brightest emission and the Stokes shift was found to be 13,000 \(cm^{-1}\). Emission with such a big Stokes shift was attributed to an impurity-trapped exciton-type emission. Phosphors with the highest emission (1 mol\% Pb) have a decay time of \(\sim 33 \mu s\) and show an exponential decay character. This phosphorescence character was attributed to the possible defect-involved mechanism.

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