University of Nevada, Reno

Pressure-Temperature Phase Diagram Of Tris (Hydroxymethyl)Aminomethane And Phase Diagram Determination Of Tris(Hydroxymethyl)Aminomethane – 2-Amino-2-Methyl-1, 3-Propanediol(AMPL) Binary System

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Abstract

A pressure-temperature phase diagram of the tris(hydroxymethyl)aminomethane (TRIS) and a temperature-composition equilibrium phase diagram of the tris(hydroxymethyl)aminomethane (TRIS) -- 2-Amino-2methyl-1,3-propanediol (AMPL) binary system are developed. The component organic crystalline materials undergo solid-solid phase transitions and their property make them suitable for storage of thermal energy. The low temperature crystal structure of pure TRIS is orthorhombic, and that of the pure AMPL is monoclinic.

In this study, Raman spectroscopy was performed at different temperatures and pressures to determine structural changes in the P-T diagram of TRIS. In situ high-pressure/high-temperature Raman spectroscopy experiments were carried out using resistively heated heated diamond anvil cells up to 160 °C and 7 GPa. High pressure experiments performed at room temperature showed transformation of the orthorhombic α-TRIS to β-TRIS phase at ~1.17 GPa. As the temperature is increased to ~130 °C at ambient pressure, both α and β phases transform to γ-TRIS. The experiments were also run at different temperatures and pressures, by which a typical pressure-temperature phase diagram of TRIS has been developed.

The binary phase diagram of TRIS-AMPL was constructed using the PANalytical X-ray diffractometer and differential scanning calorimetric data. It was found that below ~75 °C, there is virtually no solubility of AMPL in TRIS or vice versa. The AMPL rich α phase transforms to an AMPL rich γ phase at ~75 °C. Between ~75 °C and 105 °C a wide β+γ phase region is observed. The maximum solubility of TRIS in AMPL is at ~12%
TRIS at 73 °C and that of AMPL in TRIS is 40% AMPL at ~125 °C. The phase diagram exhibits two eutectoidal transformations at 73 °C (γ→α+β) and at 108 °C (γ¹→β+γ) respectively. The phase diagram also exhibits a peritectic transformation at 128 °C (L+γ¹→γ). A two phase region with γ + γ¹ plastic phases rich in TRIS and AMPL is also observed between 105 °C and 125 °C. Lattice parameters changes with increase in temperature have also been studied.
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Chapter 1

INTRODUCTION

1.1 Materials under Extreme Conditions

High pressure and temperature studies of complex hydrides are an important scientific research area. High Pressure - Temperature studies have been performed in almost every element in the periodic table [1]. However, many complex hydrides with potential applications remain to be investigated. This chapter contains a brief introduction of high pressure and temperature science, and its relation with hydrogen storage materials, which is focus of this thesis. An introductory example of high temperature and pressure research is cited by using geophysical research, which is closely related with the earth and its conditions near the center (approximately 3.6 million atmospheres and few thousand Kelvin) [2]. It is interesting to recreate that environment, to analyze the materials and its behavior under those extreme conditions, or adjust the parameters for the situations presented in other planets and astrophysical systems like stars. The principal idea is to approximate a model to generate knowledge and comprehend the state of the matter in those places. It is desirable to observe how arrangement of atoms can change under extreme pressures, having transitions between solid, liquid and gas. The scientific community is becoming increasingly interested in solid-solid phase transitions,
which have been reported many elements and compounds. There are excellent publications regarding high pressure effects; papers written by Hemley and Ashcroft [3], and the review by Block and Piermarini [4] are important. Raman spectroscopy, x-ray diffraction and infrared spectroscopy are generally used to characterize materials under extreme pressures; this will give us information on molecular structure behavior. Other methods examine properties at macroscopic level, like the equation of state (PVT relations). Both types of measurements are complementary, providing information of a system at molecular and macroscopic level, respectively. More recently, high pressure studies related to energy and hydrogen storage materials are becoming increasingly considerable because of their promise as potential application related to reduce carbon emissions.

1.2 Thermal Energy Storage Materials

The global energy demands are ever increasing, and as our traditional energy reserves are consumed, other sources of energy must be found. Of the energy consumed in last 50 years, 90% of this is nonrenewable. It is not surprising that serious interest in alternative energy sources has arisen in recent decades. Possible answers are solar, fusion, wind, nuclear, geothermal, tidal, and hydrogen energy production.

There are four principle types of energy: 1) Potential, 2) Kinetic, 3) Electrical, and 4) Mass or radiation. It is often necessary to transform one form of energy into a more usable form for man’s specific needs. In transforming energy from one form to another, there is sometimes a mechanism for storage which enables a reserve of energy to be
established for subsequent use and at a rate that is not dependent on the initial rate of transformation. Energy flow and demand are not always constant; therefore, energy storage becomes a necessity. The criteria for an effective energy storage media is that it must be easy to transport, easy to store, and convenient to use. The primary energy storage mediums are pumped hydroelectric, compressed air, chemical, kinetic, and thermal energy storage.

In general, there are two thermal energy storage mechanisms available for used as storage media. The first is sensible heat storage and is based on the heat capacity of the storage medium. The second mechanism is latent heat storage that is associated with the change of phase for a particular storage medium. For a substance to be an effective thermal storage material, some of the following properties must be inherent [5].

1) High specific heat.

2) High thermal conductivity.

3) High density.

4) Reversible heating and cooling.

5) Chemical and geothermal stability.

6) Noncombustible, noncorrosive, and nontoxic.

7) Low vapor pressure to reduce cost of containment and

8) Low cost.
There are several types of materials used for thermal energy storage, the traditional ones being concrete, brick, adobe, and water. Builders of passive solar dwellings have incorporated these materials into the walls, ceilings, and floors of homes for years. The heat that is stored is sensible heat, that is, as the solar radiation is absorbed in the storage medium, the temperature of the material changes and this heat can be sensed. Other types of materials available for thermal energy storage are classified as phase change materials (PCMs). These materials undergo physical and/or chemical changes during heat absorption and release cycles. When the materials are heated or cooled, at the phase transition temperature, the latent heat of transformation is either absorbed or released. PCMs store the latent heat of transformation in addition to the sensible heat thus making the overall storage capacity per unit mass far greater than those materials storing sensible heats only.

There are three classes of phase change materials, those which undergo reversible solid-liquid, solid-gas, and solid-solid phase transformations. The solid-liquid PCMs have been investigated extensively by many researchers in the past two or three decades. Examples of solid-liquid PCMs are paraffins, non paraffin organic, salt hydrates, and metals. The salt hydrates such as sodium sulfate decahydrate and calcium chloride hexahydrate [6,7] have large enthalpies of transformation near or below room temperature; sodium triacetate hydrate is an example of this. As the melt is cooled, the liquid doesn’t solidify at its thermodynamic melting point. The reason for the high degree of supercooling is either the rate of nucleation or rate of growth of these nuclei is very slow. In such supercooled melts, initiation of the solidification process can be carried out
by simply bending a metallic disc inserted into liquid. These materials, although are candidates for certain thermal energy storage applications, have their limitations. Foremost, there is the need for proper containment to prevent leakage of the liquid phases. The phase transition for salt hydrates is more complex, the melts are often incongruent, leaving a solid residue along with a dilute solution as end products of the melt [8]. Water retention from partially hydrated or less soluble salt crystals contributes little to the reversible storage [9]. Nucleating agents are added to prevent the formation of less soluble salts, but due to differences in densities, segregation of the nucleating agent can occur. Paraffin’s exhibit fewer problems than the salts but require nucleating agents to counter under cooling problems. Also, paraffin’s have to be adequately sealed to prevent vaporization when subjected to continuous thermal cycling.

The solid-gas phase change materials, specifically metal hydrides, have also been considered for thermal energy storage. The phase change is the absorption of hydrogen into the lattice of the metal alloy, during a reaction of the following form: metal + hydrogen $\rightarrow$ metal hydride generate heat during transformation [10]. Substituted LaNi$_5$ – xMx, where M = Sn, Gd, Al, or excess Ni, is a potential candidate for this type of storage medium. In a unique experimental lab configuration [7], hydrogen at pressures exceeding 150 psi is allowed to saturate the host alloy. Once the compound is depressurized the temperature of the metal can exceed 125 °C. Through a series of chambers and valves, a metal hydride heat pump can be used for “on demand” heat release. A typical enthalpy of hydrogen reaction with the alloy is -35 KJ/mol. For cold weather applications, a charged MHHP containing -220 grams of an alloy at 0 °C upon discharge will increase in
temperature to 35 °C. This thermal energy storage system is being considered for space exploration situations. The obvious disadvantage to this system is pressurized hydrogen and the possibility of leakage but the metal hydride heat pump is a promising new approach to specific thermal energy needs. Other metal hydrides systems are being suggested for heating and air conditioning applications in commercial buildings.

The third class of phase change materials is which undergo solid-solid phase transitions. In particular, certain class of organic molecular crystals called polyalcohols is currently being developed for thermal storage applications. These polyalcohols are currently being developed for thermal energy storage applications. These polyalcohols such as pentaerythritol, pentaglycerine, neopemtylglycol, and Tris exhibit crystalline transformations which reversibly absorb and emit large amounts of heat [11]. Thermal storage of latent heat occurs with the change in crystal structure at a fixed transition temperature (T\textsubscript{t}). The low temperature structure is a low symmetry type which transforms to a symmetric crystalline form but disordered when these crystals are heated above the transition point. The thermal energy storage capacities of the different systems are compared on a volumetric and gravimetric basis as shown in figures below. In Figure 1(a) energy densities per unit mass for PCMs are plotted against their respective transition temperature. The calculated volumetric energy densities for the same materials are plotted as a function of transition temperature are shown in Figure 1(b). Volumetric energy densities are of significant importance for designing compact thermal energy storage systems. When compared to polyalcohols, salt hydrates or other eutectic salts, the hydridies have the highest volumetric densities.
Figure 1. Comparison of energy densities per unit mass (top) and energy densities per unit volume (bottom) of solid-solid, solid-liquid and solid-gas systems [3].
The polyalcohols, amines, and other families of compounds have two crystallographic forms. The high temperature crystalline phase had been designated as “phase I” and the low temperature phase had been designated as “phase II”, by the previous pioneering investigators such as Timmermann [12], Nitta [13], and others. Chandra [14] et. Al modified these designations to take into account the presence of additional phases in the case of binary or ternary systems. He has designated the high temperature phase for pure as well as solid solutions as “γ or γ’ phase”, replacing phase I which had applied to pure alcohols only. This change in nomenclature is more important in the low temperature phases which are designated as “α or β phase” to cover the entire region in the multicomponent systems. We will use Chandra’s specifications for this work. The large enthalpies of crystalline transformation in these materials have stimulated many investigations. The early studies on thermal energy store were mainly concentrated on the structure and thermodynamic properties of pure polyalcohols. Murrill and Breed [15] were commissioned in 1969 to evaluate the feasibility of thermal applications of selected SSPCMs on passive temperature control of satellites. Again the studies were confined to pure compounds. With the potential for an excellent energy storage resource in mind, investigators were initiated for passive energy storage in solar buildings. Benson and Colleagues [10] conducted thermal analysis on different compounds for the projects that were funded by the DOE. From their initial testing, these scientists realized that in order for the polyalcohols to be effective thermal energy storage mediums the phase transition temperatures would have to be adjusted. They covered that my mixing PE-PG, PE-NPG, and PE-NPG to form solid solutions, the transition temperature could be changed. They realized this was the key to depressing the phase
transition point for a number of compounds that have higher temperatures of transition. Benson’s work also revealed the undercooling nature of most polyalcohols.

In understating a binary mixture, phase diagrams are constructed with temperature and composition being the state variables. The development of phase diagram for a binary mixture is very important for thermal energy storage research. It reveals the compositional dependence in binaries on the phase transition temperature and the stabilities of the high temperature phases. Knowledge gained from certain binary systems may be applied to other systems in developing new and more practical thermal energy storage materials.

Thermal energy storage materials are becoming increasingly important as a renewable energy resource. Several types of phase change material (PCM) have been evaluated for thermal energy storage applications [16-21]. The solid-liquid PCM including paraffin and salt hydrates [22-25] have been extensively studied and solid-gas PCM in the form of metal hydrides have also been investigated [26, 27]. The solid-solid PCM (SSPCM) are the most promising ones as they undergo changes in crystal structure (well below their melting points) releasing or absorbing a large amount of stored energy. Pure SSPCM have an additional advantage of maintaining almost constant temperature during heat absorption and release cycles. A special class of organic molecular crystals exhibits polymorphisms that are characterized by high enthalpies of solid-solid transitions and a low enthalpy of fusion. Such organic “plastic crystals” are potential thermal energy storage materials that undergo solid-solid phase transitions storing a significant amount of thermal energy and can be incorporated in practical applications such as dry-wall and
thrombi walls in passive solar buildings. Timmermann [28] identified this group of molecules as globular molecules. An important characteristic of these molecules is that they undergo phase transition from a layered or chained low temperature structure (for example: tetragonal, monoclinic, orthorhombic etc.) to a disordered but isotropic high temperature cubic phase (FCC or BCC). This high temperature phase is referred to as orientationally disordered crystal (ODIC) or plastic crystal phase. Alcohol derivates of neopentane are examples of these “plastic crystals”. These materials are proposed for use in passive solar buildings, and can potentially be incorporated in building materials. These materials are far superior as compared to conventional sensible heat storage materials. Ordinary concrete or brick, store sensible heat of \(~ 0.01\) cal/gm, as compared to \(~ 0.5\) cal/gm sensible heat for polyalcohols in additions to the solid-solid phase transformation energies in the range of 20-80 cal/gm, depending upon the number of \(\text{O-H-O}\) bonds. In additions these plastic crystals can store a large amount of energy \textit{reversibly}.

Alcohol and amine derivatives of neopentane \([\text{NP}: \text{C(CH}_3\text{)}_4]\) belong to a special group of compounds that undergo solid–solid phase transition from a layered or chained low temperature structure (tetragonal, monoclinic, etc.) to a high temperature orientationally disordered cubic structure (FCC or BCC). The polyalcohol series of these compounds include pentaerythritol \([\text{PE}: (\text{CH}_2\text{OH})_2\text{C(\text{CH}_2\text{OH})}_2]\), pentaglycerine \([\text{PG}: (\text{CH}_3\text{)C(\text{CH}_2\text{OH})}_3]\), neopentylglycol \([\text{NPG}: (\text{CH}_3\text{)_2C(\text{CH}_2\text{OH})}_2]\), and neopentylalcohol \([\text{NPA}: (\text{CH}_3\text{)_3C(\text{CH}_2\text{OH})}]\). Examples of amine derivatives include 2-amino-2-methyl-1,3-propanediol \([\text{AMPL}: (\text{NH}_2\text{)}\text{C(\text{CH}_3\text{)}(\text{CH}_2\text{OH})}_2]\), and tris(hydroxymethyl) aminomethane
TRIS: \((\text{NH}_2)\text{C(\text{CH}_2\text{OH})}_3\). The ability of these compounds to reversibly absorb or release a large amount of heat at the phase transition temperature during the solid–solid phase transition makes them attractive as solid state thermal energy storage materials. After the pioneering study of Murrill and Breed [29], numerous researchers have conducted thermodynamic and crystallographic studies on pure as well as binary mixtures to design new thermal energy storage materials (TES) for practical applications. Earlier studies were primarily considered with evaluating the crystallographic and thermodynamic parameters of pure polyalcohols and their derivates. Nitta and Watanable [30] established crystallographic parameters of PE many years ago. Chandra et al. have reported high temperature structural details of PE [31] NPG [32] using the high resolution Guinier diffraction system. Several crystallographic studies have also been reported [33]. For practical materials, solid-solid phase transition temperatures \((T_{SSTR})\) of pure materials may range from -31 °C (NPA) to 188 °C (PE). Solid solutions of these polyalcohols are made to vary the phase transition temperature to suit a particular application [34].

Thermal applications of polyalcohols were investigated first by Murril and Breed [35] in 1969 under a NASA contract, in order to evaluate the feasibility of using polyalcohols for passive temperature control of satellites. However, only pure compounds were examined for space applications. Because of the remarkable potential for storage of energy during solid-solid phase transformations in polyalcohols, investigations were initiated by the US Department of Energy on passive thermal energy storage in solar buildings, by Benson et.al [36]; this necessitated adjustment of the phase transition
temperature. Thermal analysis showed significant changes in the transition temperature when these compounds were mixed to form solid solutions.

In the past M Barrio et al. developed the binary phase diagram of these two crystals, tris (hydroxymethyl)aminomethane (TRIS) and 2-amino 1,3-propanediol (AMPL) by the means of thermal analysis and powder diffraction between room temperature and 450 K. The binary phase diagram is shown below in Figure 2. In this phase diagram we can observe that the plastic phase is completely miscible, i.e. molecular alloys can be formed at any mole fraction. It can be concluded that the AMPL cubic phase has the same space group as TRIS [42]. This is a very good binary phase diagram and guided us in the right path. But, the high temperature plastic phases of the two compounds are not differentiated. In our phase diagram we used the X-ray diffraction to differentiate the two plastic phases and could present a detailed phase diagram.

1.3 Structure of TRIS and AMPL

The understanding of the molecular arrangement in the lattice of polyalcohols is important because this reveals the orientation of the molecules and the possible interstitial sites for the insertion of dopants [9]. In addition, the nature of solid-solid phase transitions can be revealed by structural studies. Most polyalcohol crystals have a layered or chain structure but differ in the molecular arrangement of the crystal lattice.
1. 3.1 Crystal Structure in Tris(hydroxymethyl)aminomethane

The most comprehensive study performed on the crystal structure of TRIS was done by Rudman in 1978 [37]. Besides being a potential candidate for thermal energy storage, TRIS is a widely used buffering agent in pH range 7 to 9. Also, it has been proposed as a standard for solution calorimetry and is being studied in peptide and enzyme research. This crystallizes in the orthorhombic system, with $a=8.844$, $b=7.794$,
and \( c = 8.795 \) angstroms. The experimental and X-ray densities are 1.320 and 1.327 g/ml, respectively, corresponding to four molecules per unit cell. Rudman observed systematic absences in the structure which were consistent with space group \( \text{pn2}_1 \alpha \) (space group 33) and then confirmed later during refinement of the structure. The data was collected on an automatic single-crystal diffractometer and then analyzed using standard crystallographic programs.

TRIS (hydroxymethyl)-aminomethane has a layered structure in its low temperature \( \alpha \) phase. The \( \alpha \) phase can be described as being ordered, with strong hydrogen bonds within each layer and weak hydrogen bonds between the layers. The important features of this structure are shown in the Figure 3 below.

![Diagram](image)

**Figure 3.** (left). Diagram of a single molecule of the unit cell and showing the intermolecular hydrogen bonding within each layer of molecules. Atoms N, O(1), (O)2, and (O)3 are designated by N, 1, 2, and 3, respectively. The hydrogen bonded distances are given in angstroms, and the values of the intramolecular distances given in Table 1. (right). Determination of crystalline tris looking down the \( c \) axis of the unit cell. The layers are approximately perpendicular to the \( a \) axis. The hydrogen bonds within each layer are shown by the light lines between the molecules; hydrogen bonds between layers are not included [37].
Table 1. Bond Lengths and Angles. [John Hansen’s Thesis]

<table>
<thead>
<tr>
<th>BOND</th>
<th>LENGTH (Å)</th>
<th>BOND</th>
<th>LENGTH (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A Cc-N</td>
<td>1.472(2)</td>
<td>C1-H11</td>
<td>0.928(31)</td>
</tr>
<tr>
<td>B Cc-C(1)</td>
<td>1.522(2)</td>
<td>C1-H12</td>
<td>0.959(32)</td>
</tr>
<tr>
<td>C Cc-C(2)</td>
<td>1.531(2)</td>
<td>C2-H21</td>
<td>0.998(30)</td>
</tr>
<tr>
<td>D Cc-C(3)</td>
<td>1.522(2)</td>
<td>C2-H22</td>
<td>0.964(35)</td>
</tr>
<tr>
<td>Average C—C</td>
<td>1.525(2)</td>
<td>C3-H31</td>
<td>1.031(27)</td>
</tr>
<tr>
<td>E C(1)-O(1)</td>
<td>1.412(2)</td>
<td>C3-H3</td>
<td>0.966(30)</td>
</tr>
<tr>
<td>F C(2)-O(2)</td>
<td>1.426(3)</td>
<td>Average C-H</td>
<td>0.974</td>
</tr>
<tr>
<td>G C(3)-O(3)</td>
<td>1.431(2)</td>
<td>O1-HO1</td>
<td>0.739(49)</td>
</tr>
<tr>
<td>Average C-O</td>
<td>1.423(2)</td>
<td>O2-HO2</td>
<td>0.878(45)</td>
</tr>
<tr>
<td>N-HN1</td>
<td>0.835(30)</td>
<td>O3-HO</td>
<td>0.984(42)</td>
</tr>
<tr>
<td>N-HN2</td>
<td>0.822(36)</td>
<td>Average O-H</td>
<td>0.867</td>
</tr>
<tr>
<td>Average N-H</td>
<td>0.828</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>BOND</th>
<th>BOND ANGLE (deg)</th>
<th>BOND</th>
<th>BOND ANGLE (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-C-C</td>
<td>108.7(0.2)</td>
<td>H-C-H</td>
<td>110.0(2.4)</td>
</tr>
<tr>
<td>C-C-C</td>
<td>110.3(0.2)</td>
<td>H-C-O</td>
<td>109.8(1.8)</td>
</tr>
<tr>
<td>O-C-C</td>
<td>110.3(0.2)</td>
<td>H-C-C</td>
<td>108.5(1.8)</td>
</tr>
<tr>
<td>H-N-H</td>
<td>107.4(2.9)</td>
<td>H-O-C</td>
<td>106.0(2.5)</td>
</tr>
<tr>
<td>H-N-C</td>
<td>108.4(2.2)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
In viewing the above figure, all three hydroxyl hydrogen bonds atoms are strongly intermolecularly hydrogen bonded to O(3), O(2), and N atoms within each layer, whereas one of the amine hydrogen atoms is weakly hydrogen-bonded to an O(1) atom on a molecule in an adjacent layer. The role of O(1) as an acceptor of this weak hydrogen bond (from the amine hydrogen) is clearly evident from the highly anisotropic thermal ellipsoid of O(1) and consequently from the artificially short O(1)-H(1) bond length.

The TRIS low temperature phase transforms to an orientationally disordered crystal ~ 134 °C, in a manner similar to the related polyhydric alcohol pentaerythritol. The structure is believed to have centers located on the lattice points of face-centered cubic unit cells. At the time of this literature search, no information could be found on high temperature cubic phase of TRIS. Rudman maintains that detailed structural studies of similar molecules are often sufficient to allow one to relate the changes in positional parameters that accompany the phase transitions to the mechanisms of these phase transitions. He suggests that the orthorhombic TRIS unit cell is formed by a contraction of the high-temperature FCC unit cell. He contends that even though the unit cell and crystal structure of the ordered phases of these two compounds are different, the gross features of the molecular packing in these ordered phases are similar. Therefore, similar transition mechanisms should exist between the two materials.

1.3.2 Crystal Structure of 2-Amino-2-Methyl-1,3-Propanediol (AMPL)

AMPL has large entropy of solid-solid phase transition and very low entropy of fusion [38]. Rose and Van Camp [39] reported the powder data on AMPL and concluded the structure to be monoclinic with lattice parameters; a = 8.62 Å, b = 11.00 Å, c = 6.1(3)
Å, $\beta = 93.32(1)^{\circ}$, $V = 580.3(5) \, \text{Å}^3$ at $20 (\pm 1)^{\circ}$C, $D_x = 1.211 \, \text{g. cm}^{-3}$ for $z = 4$ from the JCPDS card. In 1991, Chandra, Ding, and Lynch [40] reported powder diffraction patterns of binary solid-solutions with other organic compounds such as neopentylglycol and AMPL [41] which are indexed based on the JCPDS card 12-1111. Chandra, Ding and Lynch [41] have shown that AMPL has a propensity to undercool with substitutional doping of this organic plastic crystal. More recently in 1994, Chandra and coworkers determined the structural details of AMPL, in which interactions of N—H—O or O—H—O bond distance, which were not known before. The AMPL molecule, $\text{C}_4\text{H}_{11}\text{NO}_2$, with thermal vibration ellipsoids of non-hydrogen atoms drawn to encompass 50% of their electron density and hydrogen represented by arbitrary small diameter spheres is shown in Figure 3. The bond lengths of non-hydrogen atoms are listed in Table 2.

<table>
<thead>
<tr>
<th>Type</th>
<th>Length (Å)</th>
<th>Type</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_1$—C$_1$</td>
<td>1.425(4)</td>
<td>O$_2$—C$_3$</td>
<td>1.410(4)</td>
</tr>
<tr>
<td>C$_1$—C$_2$</td>
<td>1.534(4)</td>
<td>C$_2$—N</td>
<td>1.477(4)</td>
</tr>
<tr>
<td>C$_2$—C$_3$</td>
<td>1.525(4)</td>
<td>N—H$_{1a}$</td>
<td>0.93(5)</td>
</tr>
<tr>
<td>C$_2$—C$_4$</td>
<td>1.529(5)</td>
<td>N—H$_{2a}$</td>
<td>0.89(5)</td>
</tr>
<tr>
<td>O$<em>1$—H$</em>{10}$</td>
<td>0.82(6)</td>
<td>O$<em>2$—H$</em>{2o}$</td>
<td>0.86(5)</td>
</tr>
</tbody>
</table>

The monoclinic structure of the $\alpha$ phase of AMPL has a tetrahedral molecular chain joined via O—H and N—H bonds. The molecules have intermolecular O—H—O bonds along the linear chains and the chains are interconnected by alternating O—H—O
and O—H—N bonds leaving unbounded periodic hydrogen atom sites in the structure. The molecular arrangement may be explained by showing the bonds between four molecules in Figure 4. Computer generated projections of the molecules in the a-b, b-c, and a-c planes in the space group P2₁/n are given in Figure 4 with the unit cell outlined. There are inversion centers at the midpoints of each unit cell edge, at the corners of the unit cell, and at ½, ½, and ½. Bonding between the four AMPL molecules in Figure 4 can be viewed as follows; the central AMPL molecule is bonded to the right hand molecule (b) with hydrogen bonds, namely O2-H2o….O1b AND O1b-H2o-O1 bonds. The other two molecules, a and c, to the left are bonded alternately by O1-H1o….H2na-O2 and N-H2n….O2c, respectively. The average nitrogen acceptor (N) contact distance with donor oxygen is 2.725 Å and the average hydrogen distance, shown by the double dashed line in Figure 2, is 1.89 Å. The O—H bonds, however, involve two types of interactions. The first is donor O-H2o and the acceptor O1 distance is 1.86 Å. The second donor O—H2n and the acceptor is O2 bond with a distance of 3.068 Å, and the hydrogen to acceptor O2 bond with a distance of 2.18 Å. Figure 5 shows the orientation of O—H and N—H bonded molecules in the unit cell of AMPL. Figures 6 and 7 show the orientation of alternating bimolecular chains in the Y-Z and X-y planes, respectively.

In Figure 6, the atom positions are projected on the a-c plane. The molecules are bonded along the length of the chain with O—H bonds and alternate chains are joined by O—H and N—H bonds. In 1991, Chandra, Ding, and Lynch [41] reported the γ phase structure BCC a = 6.7 Å above approximately 84 °C at which the hydrogen/nitrogen bond
configuration changes and an isotropic but orientationally disordered BCC γ-phase is obtained unlike most of the other plastic crystals which have FCC structure [41].

Figure 4. The molecule of AMPL [C$_4$H$_{11}$NO$_3$] with non-hydrogen atoms represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density; hydrogen atoms are represented by arbitrarily small spheres. [Renee Russell’s Thesis]

Figure 5. Intermolecular bonding scheme showing a central and three AMPL molecules with N—H and O—H bonds. [John Hansen’s Thesis]
Figure 6. Orientation of O—H and N—H bonded molecules in the unit cell of AMPL. [Hansen’s Thesis]

Figure 7. Atom positions in AMPL unit cells projected showing chains of molecules in the b-c plane. [Hansen’s Thesis]
Chandra, Ding, and Lynch [41] determined the lattice expansions in the $\alpha$ phase of pure AMPL by X-ray diffraction. They are anisotropic with the $b$-direction having the greatest expansion and the $c$-direction the least with $\alpha_a = 3.9 \times 10^{-5}$ °C$^{-1}$, $\beta_b = 3.9 \times 10^{-5}$ °C$^{-1}$, and $\alpha_c = 2.4 \times 10^{-5}$ °C$^{-1}$ in the temperature range of 22 to 70 °C. There is a sharp increase in approximately 10.75% when $\alpha$ transforms to $\gamma$ in AMPL. The lattice expansion coefficient in the high temperature BCC $\gamma$ phase $\alpha_a = 1.4 \times 10^{-4}$ °C$^{-1}$ in the temperature range of 88 to 95 °C.

1.4 Transformation Mechanisms

The mechanism of a solid-solid phase transition in organic polyalcohol crystals have been explained in terms of a rotational/vibrational disorder transformation. Nitta
[13, 14] was the first researcher to suggest that the hydrogen bonding in PE holds the nearly spherical molecules rigid in the low temperature phase. As the transition temperature approaches, some segments of these bonds break, permitting molecular vibration and rotation upon further heating. This hypothesis has been used to qualitatively explain the similar solid-solid phase transitions in closely related compounds such as NPG, PG, Tris, and others.

Most molecular crystals are known to transform from a low symmetry, layered structure to a highly symmetric face centered cubic structure as the temperature is increased. X-ray, Raman and NMR line broadening studies have determined that the molecules in the high temperature phase are known to be rationally and vibrationally disordered. The low temperature crystals have more rigidly held molecules because of the intermolecular hydrogen bonding between the adjacent OH groups on the nearest neighbor molecules.
Chapter 2

Experimental Techniques

2.1 Raman Spectrometry

2.1.1 Diamond Anvil Cells

The highest pressures achievable in a static laboratory environment are obtained using an instrument known as a diamond anvil cell (DAC). A general review of DACs and their applications can be found in Jayaraman [43]. More detailed descriptions of their design and use can be found in the two articles by Dunstan and Spain [44, 45] and the book by Eremets [46]. The idea behind a DAC is to take two diamonds and polish the tips to a flat (commonly called a culet) of small diameter (typically 100 m - 1 mm). See Figure 9. The diamonds are mounted so that the culets are in opposition. The material of interest is then compressed between the two diamond culets to create large pressures. A hard metallic gasket material is nearly always used in order to contain the sample in the lateral direction. A tiny hole of approximately half the culet diameter is drilled in the gasket in order to form a sample chamber. The sample of interest, a hydrostatic pressure medium, and a pressure calibrant such as a ruby chip are then placed in the sample chamber. The first DACs were developed in the 1950s [43]. Lawson and Tang were the first to use a diamond cell [47]. Weir et al. performed the first infrared absorption experiments with samples inside a DAC [48]. Jamieson et al. used a DAC to obtain high-
pressure x-ray diffraction patterns for bismuth [49]. These first DACs did not use gaskets. The introduction of the gasket was important because it allowed pressure gradients to be reduced by filling the sample chamber with a hydrostatic or quasi-hydrostatic medium [43].

Figure 9. (a) Schematic diagram of DAC operation. (b) Picture of four-post high pressure cell. The tapped holes on the optical table are one inch apart. [Erik Emmons Thesis]

Several different types of DACs are used depending on the type of experiment to be performed and the pressures and temperatures reached. DACs with culet diameters greater than about 0.5 mm are used for low pressure work up to about 50 GPa (500 kbar) [46]. DACs with smaller culets can achieve pressures above 100 GPa (1 Mbar). The ability to achieve pressures of several hundred GPa allows scientists to simulate the conditions near the center of the Earth. These ultra-high pressure DACs typically have bevelled anvils with a small central flat of diameter less than 300 μm [50]. The beveled anvils act to concentrate the force into a smaller region, increasing the pressure.
There are several different factors that must be carefully considered when a DAC is designed. The diamonds must be seated on a hard material such as tungsten carbide that is ground flat to avoid stress concentrations. The diamond culets must be positioned so that they are concentric to a high degree of accuracy and so that the two faces are parallel to within a few wavelengths of light across them [44, 45, and 46]. This alignment must also be maintained at high pressure. The alignment can be checked with a microscope capable of using both transmitted and reflected light. Viewing the diamond culets from the side and rotating the DAC allows the concentricity to be checked. The concentricity can also be checked by viewing the culets along the axis of the DAC and looking for a crescent shape indicating that the diamonds are not concentric. Set screws can then be adjusted to move the diamonds so that they are concentric. The corners of the culets should also be aligned. In addition to aligning the culets for concentricity, the parallelism of a DAC can also adjusted under a microscope. The culets are brought very close to each other so that they are touching or nearly touching. When viewed with transmitted light which passes through the sample and is collected with the microscope, interference fringes (“Newton’s rings”) will then be observed [45]. The diamonds can then be adjusted until the interference fringing is minimized. Typically, only 3-4 rings could be seen during this procedure indicating parallelism to a few microns.

There are two different types of cells which are generally used. The first type was a four-post high pressure cell. A picture of this type of cell is shown in Figure 9. This type of DAC adopts a piston-cylinder arrangement. The holes that the posts slide through are very accurately machined in order to maintain the alignment of the culets as they are
pushed closer together. Allen head cap screws are used to tighten the cell and increase the pressure. Two of the screws are right handed, while two are left handed, to avoid introducing torques while adjusting the pressure. The screws should be tightened evenly and in small increments of a few degrees at a time, so as not to force the diamond culets to be tilted relative to each other. Belleville spring loaded washers are place on the screws in order to allow a more controllable tightening of the screws. The second type is the Merrill-Bassett cell. These are somewhat similar to the four-post high pressure cells. They are triangular in shape, and use only three Allen screws, all right handed, for increasing the pressure. A micrometer can be used to measure the thickness of the cell on all three corners in order to maintain parallelism while increasing the pressure. Spring loaded washers are not used with these cells.

At UNR, the high pressure measurements were performed using a four-post diamond anvil cell (High-Pressure Diamond Optics, Tucson, AZ) designed for use up to moderate pressures of 400-500 kilobars. The diamonds were seated on hardened steel or tungsten carbide backings for support. The cells were designed to have wide cone-angle openings in order for large solid angles to be used for good optical collection. The diamond anvil cell had 0.6 mm culets and the sample chamber consisted of a hole of approximately 250 μm diameter drilled in an inconel gasket. The inconel gasket was pre-indent to approximately the maximum pressure desired during operation before being drilled. For Raman measurements low fluorescence type I diamonds were used.
2.1.2 Ruby Fluorescence Technique

Probably the most common technique for measuring pressure in a diamond anvil cell is the ruby fluorescence technique [51, 52]. Ruby is sapphire (Al2O3) that is doped with a small percentage (typically <1%) Cr3+ ions that substitute for the Al3+ ions. As described by crystal field theory, the Cr3+ ions are in a d3 configuration and experience a field of octahedral symmetry from the surrounding ions, which splits the d orbitals into t2g and eg orbitals [53]. The ground state is t32 4A2 [53]. In the ruby fluorescence technique, a visible laser line such as the 488 or 514.5 nm lines of an argon ion laser are used to excite the broad Y (t22 e 4T1) and U (t22 e 4T2) absorption bands of ruby, which are centered near 400 and 550 nm, respectively [53]. These excited states then quickly decay by non-radiative processes to the metastable t32 2E state. This 2E state is split into 2A and E states by trigonal distortion of the crystal lattice and spin-orbit effects [53]. These states decay relatively slowly to produce the R2 and R1 line emission, respectively. Rubies gain their distinctive red color due to fluorescence of the R1 and R2 lines at 694.2 and 692.8 nm, respectively [52].

The ruby fluorescence spectrum can be used to diagnose the presence of nonhydrostatic conditions within the DAC sample chamber. Changes in the splitting and widths as the pressure is increased are an indication of deviatoric stresses and pressure gradients, respectively [54]. These lines redshift with pressure, both at a nearly linear rate of 0.365 nm/GPa [43, 55] at low pressure. For the experiments described in this dissertation (p < 12 GPa), the above linear pressure calibration was used to obtain the pressure. Nonlinear calibrations are available, such as the formula by Mao et al. [56],

\[ p(\text{Mbar}) = 3.808\left\{1 + \left(\lambda / \lambda_0\right)^5 - 1\right\}, \]

however, these calibrations are negligibly different
from the linear calibration for $p < 12$ GPa. Therefore, the linear calibration was used for all of the data reported here. The ruby fluorescence measurements were performed with the same setup that was used to perform Raman spectroscopy measurements. A microscopic video image of the DAC chamber with ruby is shown below in Figure 10.

![Image of DAC sample chamber in (a) transmitted and (b) reflected light. The polymer film sample and ruby calibration chip are indicated in (b). [Emmons Thesis]](image)

2.1.3 Sample Preparation

Meticulous sample preparation is important in high pressure experiments in order to obtain convincing results. It is mandatory to clean all the devices like DAC, its
diamonds, gasket needles, tweezers, etc. before each experiment in order to reduce the impurities in the sample. The cleaning can be done with lint-free wipes, ethyl alcohol and cotton swabs. The gasket is positioned in the DAC and an indentation is made on the gasket by applying moderate pressure. The indented gasket is removed from the DAC and placed in the EDM machine for drilling a hole in center of its indentation. The holes drilled in this whole experiment are of 120 micron diameter. The gasket is cleaned thoroughly and placed in the DAC once the whole is drilled. The sample is now loaded with the help of a needle under a microscope for better vision until the hole is completely filled. The ruby particles can now be added by placing them on the other DAC culet. When the DAC is closed, the diamonds will compact the sample and the ruby will be present. Then, the high pressure experiments can be started.

2.1.4 Raman Microspectrometry

Raman spectroscopy is another type of vibrational spectroscopy. Some care should be taken in performing Raman spectroscopy of samples in a DAC. The sample should be large enough to obtain a spectrum with adequate statistical precision, but at the same time enough room should be allowed to add pressure medium and a ruby chip for pressure calibration and production of a hydrostatic or quasi-hydrostatic environment.

The main components of a Raman spectrometer are the laser, the focusing and collecting optics, a diffraction grating, and a detector. Due to the high sensitivity and relatively low cost of visible CCD cameras, diffraction gratings are typically used rather than Fourier transform interferometers. However, sometimes it is desirable to use a laser
with a low photon energy such as a Nd:YAG laser, with a wavelength of 1064 nm, because these photons tend to excite less undesirable background fluorescence in the sample. In this case, it is most efficient to use an FTIR system to detect the Raman scattered light. This fluorescence is a result of electronic excitation of the sample or impurities in it. The samples can then reradiate at longer wavelengths when they relax. For some polymer samples in particular, this can overwhelm the Raman signal.

Again, a microspectroscopy system was used with the DAC in order to study the small samples that needed to be examined. At OPML a Renishaw InVia Raman microscope system was used. A low power argon ion laser (Spectra Physics Models 262A or 263C) was used to generate light at 488 or 514.5 nm. The laser emitted a total output power typically of around 10-25 mW. The laser light was then filtered with two different filters, since it contained undesirable light of different frequencies from the excitation lamp in the laser. This light, although low in intensity, can be collected by the spectrometer and produce artifacts in the spectra. A laser line filter was used that nominally passes only a small range of wavelengths near 488 or 514.5 nm. This should produce a monochromatic beam. However, it was found that sometimes radiation near ~700 nm could pass through these filters, since they performed poorly at longer wavelengths. Thus, a second short pass filter was used that would block radiation with wavelengths longer than 600 nm. The laser beam is then expanded using a beam expander and directed to a special optic known as a notch filter. This notch filter is a holographic interference filter that reflects the laser light wavelength while transmitting all other wavelengths.
The light then is focused by a high magnification microobjective onto the sample. The purpose of expanding the laser beam is to fill the back aperture of this microobjective, which leads to less diffraction and a smaller focal spot size. With high magnification objectives, spot sizes on the order of ~1 μm can be obtained. A 20× objective with a numerical aperture of 0.40 was used to obtain spectra for samples inside the DAC. The numerical aperture is defined by the formula \( NA = \sin \theta \), where \( \theta \) is half the cone angle of the light focused or collected by the objective. With higher numerical apertures, a tighter focal spot size can be obtained, along with a larger collection solid angle for the Raman scattered light. In general, the collected light depends on the square of the numerical aperture. However, the 2 mm diamond window present in the DAC leads to spherical aberration which limits the optimal NA that should be used. Also, it was necessary to use an objective that was designed with an extra-long working distance so that it could focus on the sample though the 2 mm diamond windows. The sample is then moved around on the microscope stage until it is brought into the laser focus. The high level of spatial resolution is helpful, especially when using rubies for calibration purposes. The strong fluorescence from the ruby interferes with the much weaker Raman spectrum from the sample if both are excited simultaneously. To give an idea of the magnitude of the signal levels, a very high quality ruby spectrum can typically be obtained in 100 ms with 10 μW of laser power. By contrast, most of the Raman spectrum obtained in this report were acquired in 100-400 s with 5-10 mW of laser excitation.

The Raman scattered light is collected in the backscattering geometry, i.e., scattered light that is emitted back through the same objective is sent to the spectrometer. Since the Raman scattered light is of different wavelength than the laser light, it passes
through the notch filter. It is then focused by a lens onto the entrance slit of the spectrometer. Typically the slit width was set to 50 μm, which corresponded to a resolution of ~5 cm\(^{-1}\) full-width at half-maximum (FWHM). Another lens recollimated the light and then it was dispersed by a diffraction grating with 1800 grooves/mm. The light was then detected by a CCD camera that was thermoelectrically cooled to reduce dark count noise. The wavelengths were dispersed along one dimension of the camera. Therefore, the signal could be integrated along the other dimension in order to obtain a spectrum with a high signal-to-noise ratio. The Raman microscopy system and its associated camera are controlled with software from Renishaw. The spectral data are recorded on disk for later analysis. A diagram of the Raman microscopy system is shown in Figure 11.
Figure 11. Schematic diagram of Renishaw In-Via Raman microscopy system. [Emmons Thesis]
2.2 Differential Scanning Calorimeter

Differential Scanning Calorimeter is a thermal analysis technique that measures the temperatures and heat flows associated with transitions in materials as a function of time and temperature. Such measurements provide qualitative and quantitative information about physical and chemical changes that involve endothermic or exothermic processes or changes in heat capacity. Typical measurements include:

1) Glass transitions in amorphous/semi-crystalline materials.
2) Melting points; boiling points.
3) Crystallization time and temperature; percent crystallinity.
4) Heats of fusion and reaction.
5) Oxidative stability.
6) Purity.
7) Rate of cure; Degree of cure.
8) Reaction kinetics.
9) Specific heat and heat capacity.
10) Thermal Stability.

The main component of the DSC is the DSC standard cell. It consists of a constantan (thermoelectric) sensor assembly as a primary heat flow element. A silver heating block, covered with a pair of vented silver lids, encloses the sensor assembly. The sample, contained in a sample pan and an empty reference pan are placed on the sensor platforms. Heat is transferred from the furnace through the constantan sensor to both the
sample and reference. Differential heat flow to the sample and reference is monitored by CHROMEL-constantan area thermocouples, formed by welding CHROMEL discs to the underside of the constantan sensor platforms. The base of the sensor has a CHROMEL and constantan thermocouple welded to its surface between the two platforms. This Tzero thermocouple measures the temperature of the base of the sensor. Sample temperature is determined by computing the difference in temperature between the Tzero thermocouple and the sample thermocouple and adding that difference to the Tzero temperature. DSC experiments should always be conducted with a purge gas. In our experiments we use nitrogen as the purge gas.

The cooling system used in the DSC is the Refrigerated Cooling System (RCS), consists of a two-stage, cascade, vapor compression refrigeration system with an attached cooling head. The cooling head, which is made up of an internal heat exchanger, anti-condensate heaters, and various other components, fits over the DSC cell. The RCS can be used for experiments requiring cooling within an operating range of -90° C to 550° C. The maximum rate of cooling depends on the temperature range of the experiment. The typical DSC machine used at UNR is shown in the Figure 12 below.

2.2.1 Working Principle of DSC

In a “heat flux” DSC, the sample material, encapsulated in a pan, and an empty reference pan sit on a thermoelectric disk surrounded by a furnace. As the temperature of the furnace is changed (usually by heating at a linear rate), heat is transferred to the sample and reference through the thermoelectric disk. The differential heat flow to the
sample and reference is measured by area thermocouples using the thermal equivalent
Ohms’s Law.

\[ Q = \frac{\delta T}{R} \]

where:
\[ Q = \text{sample heat flow.} \]
\[ \delta T = \text{temperature difference between sample and reference.} \]
\[ R = \text{resistance of the thermoelectric disk.} \]

Figure 12. DSC Q100 (with DSC Refrigerated Cooling System) from TA Instruments

This sample relationship, however, does not take into account extraneous heat flow
within the sensor or between the sensor pan. The TA instruments Q series DSC’s are
specifically designed to account for those latter heat flows.

The cell sensor consists of a constantan body with separate raised platforms to hold
the sample and reference. The platforms are connected to the heating block (base) by
thin-walled tubes that create thermal resistances between the platforms and the base. Area
detectors (thermocouples) on the underside of each platform measure the temperature of
the sample and reference. A third thermocouple measures the temperature at the base. The equation below shows the thermal network model which represents this cell arrangement, and the resultant heat flow expression that describes this cell arrangement is \( t/dt \).

\[
q = -\frac{\Delta T}{R_r} + \Delta T_0 \left( \frac{R_r - R_s}{R_r R_s} \right) + \left( C_r - C_s \right) \frac{dT_s}{dt} - C_r \frac{d\Delta T}{dt}
\]

The first term in this expression is the equivalent single-term DSC heat flow expression. The second and the third terms account for differences between the sample and reference resistances and capacitances respectively. These terms have their largest impact during regions of the thermal curve where the heat capacity of the sample is the predominant contributor to heat flow. The fourth term accounts for the difference in heating rate between the sample and reference. This term has its largest impact during enthalpic events. This equation can be further modified to account for pan heat flow effects.

**2.3 X-ray Diffraction Studies**

X-ray diffraction of crystals has been used for years in the investigating of fine structure of matter. The powder method has proven to be outstanding in the determination of crystal structure and phase boundaries of great importance in the high temperature analyses. A typical X-ray diffractometer used at UNR is shown in Figure 13.

A diffractometer is an instrument for studying crystalline materials by measurement of the way in which they diffract X-rays of known wavelength. In the
diffractometer, the intensity of a diffracted beam is measured directly by an electronic counter. The counter converts incoming x-rays into surges or pulses of electric current in the circuit connected to the counter. This circuit counts the number of current pulses per unit of time, and this number is directly proportional to the intensity of the x-ray beam entering the counter. The counter, set near $2\theta = 0$, is driven at a constant angular velocity through increasing values of $2\theta$ until the whole range is scanned, thus recording the diffraction lines one after the other. The result is a chart which gives a record of counts/sec (proportional to diffracted intensity) versus diffraction angle $2\theta$, see Figure 14. These diffraction patterns, peaks on the chart in this case, are unique for each type of unit cell, be it cubic, orthorhombic, monoclinic, etc., because the diffraction directions are determined solely by the shape and size of the unit cell. From the data acquired from the x-ray diffractometer, Bragg’s law, $\lambda = 2dsin\theta$, can be used to equate the distance between adjacent planes d. Further indexing on a standard crystallographic program or in a search manual will help identify these planes and the cell dimensions.
Minerals and other crystalline compounds have been indexed and catalogued over the years. The results are files in the form of search manuals that allow the scientist a tool for the easy identification of an unknown sample. Thus, the diffraction pattern serves as a fingerprint, so too peak, of the compound. Room temperature diffraction data was obtained using a Norelco diffractometer coupled to a microwave II DEC computer. The d-spacing and lattice parameter calculations were made employing Siemens software.

![X-ray Diffraction pattern of pure TRIS. The most prominent peaks correspond to their reflecting Planes. [John Hansen’s Thesis]](image-url)
TRIS and AMPL have a distinct boiling points and melting points. The melting point of TRIS is approximately the boiling point of AMPL. Because of this reason, at higher compositions of TRIS and at higher temperatures, AMPL present in the binary sample started to evaporate before TRIS started to melt and hence the composition changed giving unexpected X-ray patterns and results. For these reasons the sample is now loaded inside a 1 mm inner diameter capillary and sealed with the glue rather than directly heating on a flat sample holder. The sample is heated externally by using a tubular heater using air as the heating medium. As the sample is loaded inside a sealed capillary, AMPL cannot escape on evaporating instead it get condenses back into the capillary by which the composition of the binary sample remains the same. The pictures of the experimental setup with the capillary and also with the flat sample holder are shown later in this report.

2.4 Sample Preparation for DSC and X-Ray Diffraction

TRIS (99.99+% ultra high purity) and AMPL (99% purity) were bought from Sigma-Aldrich and were used without any further purification. The samples TRIS and AMPL are mixed to form a binary compound mixture by using the following procedure.

1) Calculate the masses of each compound on a 20 gm basis with different mole% compositions of TRIS (10, 20, 30, 40, 50, 60, 70, 80, and 90%).

2) Weigh them out accurately using a micro balance and transfer each 20 gm mixture with different compositions and also the pure compounds into 11 different glass tubes and seal the tubes tight with rubber corks.
3) Gently heat each glass tube until the solid mixture in each glass tube transforms completely into the liquid.

4) Let cool the samples to room temperature.

5) Place all the 11 glass tubes in a freezer for the next 12 hours.

6) Take them out one at a time and place the glass tube in the glove box filled with argon gas.

7) Scrap the solid chunk and grind them using a mortar and a pestle to obtain the powder form and transform all the powder into an empty glass container and sealed tight.

8) Remove all the glass containers from the glove box and place them in a freezer for the next 24 hours.

9) Remove each of the powdered samples from the freezer and mechanically press it to form a pellet and place all the pellets in the freezer for the next 24 hours.

10) Grind the pellets to again obtain the powdered form and the samples are ready for the experiments.

    The reason for mechanically pressing the sample is, when we have eutectics or peritectics, at the boundary they should precipitate out the equilibrium phases but they do not because nucleation of phases does not occur easily. (Nucleation is best at low temperature, and growth at high temperature.) For this reason we have to make sure that all the phases that precipitate out, are the expected "equilibrium phases." This is done by lowering the temperature by placing the samples in the freezer, and to doubly make sure it precipitates when we supply the activation energy by pressing mechanically. Sometimes we may not need the pressing step, but from the earlier work we found that
the phases sometimes do not precipitate out at freezer temperature, so we press the powders to ensure we are dealing with equilibrium phases.

The prepared samples are now used for the Differential Scanning Calorimetry (DSC) Study. The samples are placed in the DSC to determine the solid-solid transition and melting temperatures of the mixture. The samples are heated from -50 °C to 200 °C with a heating rate of 2°C/min. A DSC Q100 (with DSC Refrigerated Cooling System) from TA Instruments is used at UNR.

The prepared samples are also used in the high temperature X-ray diffraction Study to determine structures of \( \alpha \)- and \( \gamma \)-phase of TRIS-AMPL binary mixture at 1 atm pressure. A PANalytical X’Pert PRO X-ray Diffraction System is used at UNR.
Chapter 3

High Pressure Studies and Pressure-Temperature Phase Diagram Determination of TRIS [(NH$_2$)C(CH$_2$OH)$_3$]

3.1 Molecular Vibrations

This section gives a basic description of molecular vibrations. Molecules and solids have different types of motion and each of these types can lead to different forms of excitation. Three of the main types are rotational, vibrational, and electronic. Rotations are characterized by motion where the nuclei maintain constant separations relative to each other. Vibrations, by contrast, involve the nuclei moving relative to each other. The electronic state of a molecule describes the distribution of the negative electronic charge throughout the molecule. These degrees of freedom can be considered independent in many circumstances.

The vibrational potential energy surface of a molecule is determined by calculating the electronic energy of the molecule for fixed nuclear coordinates. The nuclear coordinates are then varied to construct the potential energy surface. This procedure is based on the Born-Oppenheimer approximation. Since the electrons are so much less massive than the nuclei, they move very fast by comparison. Thus, when calculating the electronic eigenfunction, the nuclei can be considered to be stationary. Let
the potential energy surface be denoted as $E(R_a)$, where $R_a$ contains all the nuclear coordinates. A Schrödinger equation for the wavefunction of the nuclei, $\psi_n$, can then be obtained [57].

$$H_n\psi_n = [T_n + E(R_a)]\psi_n = E\psi_n$$

where $H_n$ is the Hamiltonian of the nuclei and $T_n$ is the term for the kinetic energy of the nuclei. This new equation can be solved to find the vibrational eigenfunctions and eigenvalues. The position $R_a = 0$ gives the equilibrium positions of the nuclei. This is a minimum in the potential energy. For a specific type of vibrational mode, $R_a$ is typically reduced to a single coordinate. In general, for small displacements the potential will appear quadratic around this equilibrium point. Thus, the problem can be reduced to that of a quantum mechanical simple harmonic oscillator, with an equation of the form [58].

$$-\frac{\hbar^2}{2m} \frac{d^2\psi_n}{dx^2} + \frac{1}{2}kx^2\psi_n(x) = E\psi_n(x).$$

Eq 3.2

Here $\hbar = h/2\pi$, where $h$ is Planck’s constant, and $m$ and $k$ are the effective mass and spring constant, respectively. The energies of a simple harmonic oscillator are quantized and take the values $E_n = \hbar\nu(n+1/2)$, where $\nu$ is the vibrational frequency and $n$ is a positive integral quantum number [58]. There are in general small deviations from this formula due to cubic and higher order terms in the potential energy function. These deviations are called anharmonicities.

For the simple harmonic oscillator, the normalized wavefunctions take the form
\[
\psi_n(x) = \frac{1}{\sqrt{2^n n!}} \left( \frac{m\omega}{\pi\hbar} \right)^{1/4} \exp \left( -\frac{m\omega}{2\hbar} x^2 \right) H_n \left( \sqrt{\frac{m\omega}{\hbar}} x \right),
\]

where \( \omega = k/m \) and \( H_n(x) \) is the Hermite polynomial of order \( n \) [58]. As will be seen later, the intensity of a transition in the infrared absorption (or emission) spectrum will depend on the square of a matrix element of the form

\[
\langle \psi_m | x | \psi_n \rangle = \int_{-\infty}^{\infty} \psi^*_m(x)x\psi_n(x)dx.
\]

\[
= \sqrt{\frac{\hbar}{2m\omega}} \left[ \sqrt{n+1} \delta_{m,n+1} + \sqrt{n} \delta_{m,n-1} \right],
\]

Where \( \psi_m(x) \) and \( \psi_n(x) \) are the final and initial state wavefunctions, respectively, and \( \delta_{i,j} \) is the Kronecker delta function [58]. The delta functions show that there is a selection rule where a photon can only be absorbed or emitted if \( n \) changes by \( \pm 1 \). This selection rule also holds for Raman scattering, since matrix elements of this form also occur in the formula for the Raman scattering intensity. This will be described more in the next section. If \( \Delta n > 1 \), the transition is known as an overtone. Although weak, these transitions can occur if the potential has anharmonic terms, i.e., if it has terms of order higher than two. Another type of transition is a combination mode. This is when two different modes of a vibration are simultaneously excited. These transitions also tend to be rather weak.

There are several different types of vibrational modes. These include stretching (v), scissoring (\( \delta \)), rocking (\( \rho \) or \( \gamma_r \)), twisting (t or \( \gamma_t \)), and wagging (w or \( \gamma_w \)). The stretching modes can be symmetric or asymmetric depending on whether or not the atoms
move in phase or 180° out of phase. A diagram of these different types of vibrational motions is shown in Figure 15 below. Group theory, which will be described later in this chapter, is very useful for categorizing these types of vibrational modes.

3.2 Interpretation of the Ambient Raman Spectra of the TRIS

A series of Raman spectroscopy experiments were conducted on TRIS in order to observe the phase transition changes occurring at different conditions of temperatures and pressures. Different categories of Raman experiments were performed. For reference, conditions to know the initial conditions of the molecular symmetry and the first the ambient spectra of TRIS will be described. The sample was analyzed at ambient orientation of the atoms which are later compared with the spectra obtained at different conditions to know the initial conditions of the molecular symmetry and the first the

![Diagram of different types of vibrational modes. The + and – symbols indicate motion perpendicular to the plane of the paper. [Emmons Thesis]](image)
pressures and temperatures. The Raman spectrum of TRIS under ambient conditions is shown in Figure 16, and also its important modes are indicated in the Figure 17. Since an isolated TRIS molecule lacks any symmetry, all the vibrational modes are active in Raman spectrum. A list of mode frequencies and description of the atomic involved is given in the Table 3. The mode assignments for the bands at frequencies lower than 300 cm\(^{-1}\) were taken from analogies with pentaerythritol [59, 60]. The mode assignments for bands at frequencies higher than 300 cm\(^{-1}\) were taken from Schroetter and Bougeard [61]. The normal coordinate analysis of Schroetter and Bougeard indicates that most of the vibrational modes cannot be described simply, but rather are mixture of different types of motions.

The vibrational mode frequencies and assignments of internal modes of TRIS at room temperature and pressure are listed in Table 1 below. In order to compare the vibrational modes of TRIS obtained in this project, Table 1 shows band assignment and mode assignments reported earlier [59, 60, 61]. The data acquired in the present study is in agreement with the study made earlier.

The bands at frequencies below 300 cm\(^{-1}\) were identified by analogy with pentaerythritol [59, 60]. For the peaks at frequencies greater than 300 cm\(^{-1}\), the assignments and potential energy distribution (%PED) are based on normal mode calculations of Schroetter and Bougeard [61]; these modes of frequencies are compared to those of Schroetter and Bougeard. An unlabelled mode indicates that it was not observable. The stretching modes are good indicators for analyzing the pressure and temperature effects on the sample. These phenomena will be described in more detail
later, where the OH, NH₂ and CH₂ peaks softens and shifts to lower frequencies as temperature or pressure is increased. The frequency shifts indicate that the temperature increase in the system at constant pressure is producing a phase transition in TRIS. Figure 18 represents the comparison of the Raman spectrums at two different temperatures.

![Raman spectrum comparison](image)

Figure 16. Ambient temperature and pressure Raman spectrum of a bulk sample of TRIS. The left hand side of the figure shows the low frequency deformation modes while the right hand side of the figure shows the CH, OH and NH stretching modes. [64]

An increase in noise of the signal is visible in Raman spectrum at high temperature, being a normal phenomenon. A shifting in the band corresponding to the
stretching mode is probably the most notorious difference observed between the Raman spectrums at two different temperatures in Figure 18. The disappearance of some of the bands is also important to considerate a new organization in the molecular structure of the sample due to a phase transition.

Figure 17. Raman spectra of TRIS under ambient conditions of temperature and pressure indicating the different important modes.
Table 3. List of vibrational mode frequencies and assignments of internal modes of TRIS. [64]

<table>
<thead>
<tr>
<th>Label</th>
<th>Current Frequencies (cm(^{-1}))</th>
<th>Schroetter Frequency (cm(^{-1}))</th>
<th>Assignment and % PED</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v_3)</td>
<td>221.8</td>
<td>-</td>
<td>CC twist (skeletal)</td>
</tr>
<tr>
<td>(v_4)</td>
<td>250.1</td>
<td>-</td>
<td>(\tau) (CCO)</td>
</tr>
<tr>
<td>(v_5)</td>
<td>275.4</td>
<td>-</td>
<td>(\tau) (CCO)</td>
</tr>
<tr>
<td>(v_6)</td>
<td>308.7</td>
<td>311 (IR)</td>
<td>(\delta)(CCC) 62%</td>
</tr>
<tr>
<td></td>
<td>329.1</td>
<td>330 (IR)</td>
<td>(\tau)(CN) 90%</td>
</tr>
<tr>
<td>(v_7)</td>
<td>341.0</td>
<td>342</td>
<td>(\tau)(CN) 90%</td>
</tr>
<tr>
<td>(v_{10})</td>
<td>419.7</td>
<td>420 (IR) 424</td>
<td>(\delta)(NCC)– 42% (\delta)(CCC)– 20%</td>
</tr>
<tr>
<td></td>
<td>431.8</td>
<td>420 (IR) 424</td>
<td>(\delta)(NCC)– 42% (\delta)(CCC)– 20%</td>
</tr>
<tr>
<td>(v_{11})</td>
<td>474.2</td>
<td>470 (IR) 476</td>
<td>(\delta) (NCC)-63%</td>
</tr>
<tr>
<td>(v_{12})</td>
<td>520.3</td>
<td>524 530 (IR)</td>
<td>(\delta)(NCC)-49% (\delta)(HCC)-21%</td>
</tr>
<tr>
<td>(v_{13})</td>
<td>620.0</td>
<td>633 (IR) 655 (IR) 715 (IR) 790 (IR)</td>
<td>(\delta)(CCC) (\tau)(CO) (\tau)(CO) (\delta)(HNC)-54%</td>
</tr>
<tr>
<td>(v_{14})</td>
<td>800.6</td>
<td>804</td>
<td>(\nu)(CC)</td>
</tr>
<tr>
<td>(v_{15})</td>
<td>878.5</td>
<td>875</td>
<td>(\delta)(HCC)-45% (\tau)(CO)-27%</td>
</tr>
<tr>
<td>(v_{16})</td>
<td>891.6</td>
<td>896</td>
<td>(\delta)(HCC)-41% (\delta)(HNC)-22%</td>
</tr>
<tr>
<td>(v_{17})</td>
<td>918.1</td>
<td>917</td>
<td>???</td>
</tr>
<tr>
<td></td>
<td>925 (IR)</td>
<td></td>
<td>(\delta)(HCC)-57% (\tau)(CO)-21%</td>
</tr>
<tr>
<td>(v_{19})</td>
<td>980.3</td>
<td>983 (IR)</td>
<td>(\delta)(HNC)-43% (\nu)(CC)-27%</td>
</tr>
<tr>
<td>(v_{20})</td>
<td>1018.2</td>
<td>1024</td>
<td>(\nu)(CO)-67%</td>
</tr>
<tr>
<td>(v_{21})</td>
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<td>(\nu)(CO)-60%</td>
</tr>
<tr>
<td>(v_{23})</td>
<td>1069.3</td>
<td>1071</td>
<td>(\nu)(CO)-60%</td>
</tr>
<tr>
<td>(v_{25})</td>
<td>1095.6</td>
<td>1098</td>
<td>???</td>
</tr>
<tr>
<td>(v_{26})</td>
<td>1158.1</td>
<td>1161</td>
<td>(\delta)(HNC)-34%</td>
</tr>
<tr>
<td>(v_{28})</td>
<td>1211.8</td>
<td>1215</td>
<td>(\delta)(OH)-42%</td>
</tr>
</tbody>
</table>
normal phenomenon. A shifting in the band corresponding to the stretching mode is probably the most notorious difference observed between the Raman spectrums at two
3.3 High Pressure Behavior of TRIS

The results reported in this section show the behavior of TRIS under conditions of high pressure at room temperature. It is crucial to characterize the structural changes of the samples under these parameters, in order to understand if the polyalcohols can have potential commercial applications as an energy storage material. Raman spectra was acquired and analyzed in order to understand the nature of the molecular structure changes in materials. First Raman experiments on TRIS were performed at ambient conditions and then at variable pressure and constant room temperature. Initially at ambient conditions TRIS remains in the $\alpha$ phase and has a monoclinic structure. At each pressure, spectrum was recorded and one such spectrum is shown in Figure 19 which had a phase transition. In the left hand side of the Figure 19 a prominent peak is present at
~275 cm\(^{-1}\), gradually reducing its intensity until its disappearance at ~6.3 GPa. It is also possible to recognize the same intensity reduction in the adjacent bands present at 340 cm\(^{-1}\) and 475 cm\(^{-1}\). A similar result is observed at ~1158 cm\(^{-1}\) with a dramatic reduction of the intensity which completely disappears at 6.3 GPa. The peak at ~1095 cm\(^{-1}\) looses completely its intensity at 2.2 GPa. Similarly in the right hand side of the Figure 19, the peaks at ~2848 cm\(^{-1}\) and ~2876 cm\(^{-1}\) converge to a single peak above 1.17 GPa. The same convergence of the peaks is seen at 2924 cm\(^{-1}\) and 2949 cm\(^{-1}\). All these effects mark the change from \(\alpha\) to \(\beta\) phases of TRIS. Above 1.17 GPa there are signals of phase transition zone, with new peaks at ~651 cm\(^{-1}\), 785 cm\(^{-1}\) and 1026 cm\(^{-1}\) surviving only the first one in the new phase. The stretching and broadening of the OH, CH and NH modes in the right hand side of the Figure 19 also represents a significant phase change in the sample. The structure of TRIS in the \(\beta\) phase is cubic, which is determined from analogies with pentaerythritol.

Figure 20 shows another experiment performed, where the temperature was initially set to 50 °C at ambient pressure, to be slightly below the pressure-induced orientational-disorder phase transition of TRIS reported in the previous figure. The phase transition of TRIS from \(\alpha\) to \(\beta\) phase can be clearly seen in the low and high frequency Raman spectra acquired in the experiment, specifically when the pressure lies between 0.34 GPa and 2.14 GPa. The virtual disappearance of the peaks at ~275 cm\(^{-1}\), ~340 cm\(^{-1}\), ~475 cm\(^{-1}\), ~1095 cm\(^{-1}\) and ~1156 cm\(^{-1}\) above 0.34 GPa, indicates a significant change in the material that may be associated with the phase transition from \(\alpha\) to \(\beta\)-TRIS. Additionally the formation of new band at ~651 cm\(^{-1}\) provides substantial evidence of the
phase transition in the material. There is a softening in the intensity of the strong peaks at ~892 cm\(^{-1}\), ~916 cm\(^{-1}\), ~1472 cm\(^{-1}\), ~3351 cm\(^{-1}\) and the shoulder present at ~1395 cm\(^{-1}\).

Figure 19. Pressure-dependent Raman spectra of TRIS. By increasing the pressure of the sample at constant room temperature, reorganization in the structure of the material from \(\alpha\) to \(\beta\) phase was observed above 1.17 GPa.

Figure 20. Pressure-dependent Raman spectra of TRIS at 50 °C. The orientational order/disorder transition can be observed above 0.34 GPa phase transition in the material. There is a softening in the intensity of the strong peaks at ~892 cm\(^{-1}\), ~916 cm\(^{-1}\), ~1472 cm\(^{-1}\), ~3351 cm\(^{-1}\) and the shoulder present at ~1395 cm\(^{-1}\).
This phenomenon can be compared with the peak and shoulders present in Figure 19 and its minimization when the phase transition from $\alpha$ to $\beta$ phase occurs. Because of the temperature conditions and the differences in between each experiment, the spectra exposed in Figure 20 are a bit different compared to the spectra in Figure 19.

Figure 21 shows additional spectra in the region of the CH, OH, and NH stretches, in order to illustrate the evolution of the phase transition. Spectra were measured after increasing and decreasing pressure steps, and demonstrate considerable hysteresis. Approximately 20-30 mins were allowed for the system to evolve after increasing the pressure before beginning a spectral scan. With increasing pressure, indications of the phase transition are shown in the spectra measured at a pressure of 1.88 GPa. For example, the two NH stretching modes begin to show shoulders, indicating a mixture of two phases. After waiting for a further 30 minutes at the same nearly constant pressure (the measured pressure increased slightly to 1.90 GPa), the shoulders become more prominent, indicating that a larger fraction of the sample had transformed. The OH-stretching modes also become more prominent relative to the NH-stretching modes. The temporal evolution of the spectra indicates that the transition is marked by relatively sluggish kinetics. Upon decreasing pressure, the $\alpha$-phase was not recovered until the pressure was near ambient, providing further evidence for an energy barrier to the transition. This hysteresis effect is indicative of a first-order phase transition.

In Figure 21, the spectra on the left side were taken during pressure increase, while those on the right were taken during the pressure decrease. Considerable hysteresis is evident, indicative of slow kinetics for the first order phase transition.
The pressure induced frequency shifts for many of the vibrational modes of TRIS were measured. The results are tabulated below in Table 2 for the deformation modes of both the low and high pressure phases of TRIS. Table 3 shows similar coefficients for the OH and NH stretching modes. For the high pressure phase, it was found that quadratic fits were necessary to adequately fit the data for the NH stretching modes. Here a

Figure 21. Pressure dependent Raman spectra of TRIS in the region of C—H stretching (~2800-3000 cm⁻¹), O—H stretching (~3000-3400 cm⁻¹), and N—H stretching (~3200-3400 cm⁻¹) vibrations. [64]
quadratic function of the form \( v(p) = v_0 + (dv/dp)_0 p + (d^2v/dp^2) p^2 \) was used to fit the data. The CH stretching modes were not analyzed as a function of pressure.

Linear fits were used based on data acquired during pressure increase. For the \( \beta \)-phase, the “ambient frequencies” indicate the intercept of the linear fit with the \( p=0 \) axis. In the first column, unlabelled frequencies indicate that a mode was observable in a bulk sample in the infrared or Raman spectra but not in the Raman spectrum of the low-pressure phase in the DAC. Several modes could be tracked only in the high pressure phase. In addition, one mode (\( v_{24} \)) could be tracked in the low pressure phase but not in the high-pressure phase.

The three OH stretching modes could only be traced in the high-pressure phase due to low intensities in the low-pressure phase. In the high-pressure phase, it was necessary to use quadratic functions to accurately model the frequency shifts of the NH stretching modes. Errors in the linear fits for the OH stretching modes are shown in parentheses, and are very large for the \( v_{OH1} \) and \( v_{OH3} \) modes, due to significant scatter in the data.

3.4 NH and OH Stretching Modes

Figure 22 shows the pressure-induced frequency shifts for the \( NH_2 \) stretching vibrations. In the low-pressure phase, a linear function was suitable to describe the
Table 4. Pressure-induced frequency shifts for the deformation modes of the α and β phases of TRIS. [64]

<table>
<thead>
<tr>
<th>Mode and ambient frequency (α-phase, cm(^{-1}))</th>
<th>Mode and ambient frequency (β-phase, cm(^{-1}))</th>
<th>(\text{d}v/\text{d}p) (α-phase) cm(^{-1})/GPa</th>
<th>(\text{d}v/\text{d}p) (β-phase) cm(^{-1})/GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>–</td>
<td>(v_1) (146.6)</td>
<td>–</td>
<td>6.5</td>
</tr>
<tr>
<td>–</td>
<td>(v_2) (195.6)</td>
<td>–</td>
<td>1.4</td>
</tr>
<tr>
<td>(v_3) (221.8)</td>
<td>(v_3) (213.0)</td>
<td>7.6</td>
<td>9.5</td>
</tr>
<tr>
<td>(v_4) (250.1)</td>
<td>(v_4) (248.6)</td>
<td>–</td>
<td>6.4</td>
</tr>
<tr>
<td>(v_5) (275.4)</td>
<td>(v_5) (279.1)</td>
<td>6.5</td>
<td>7.5</td>
</tr>
<tr>
<td>(v_6) (308.7)</td>
<td>(v_6) (299.6)</td>
<td>–</td>
<td>9.1</td>
</tr>
<tr>
<td>(v_7) (341.0)</td>
<td>(v_7) (339.7)</td>
<td>10.8</td>
<td>7.2</td>
</tr>
<tr>
<td>–</td>
<td>(v_8) (379.2)</td>
<td>–</td>
<td>3.5</td>
</tr>
<tr>
<td>–</td>
<td>(v_9) (380.3)</td>
<td>–</td>
<td>10.7</td>
</tr>
<tr>
<td>(v_{10}) (419.7)</td>
<td>(v_{10}) (430.4)</td>
<td>6.4</td>
<td>4.6</td>
</tr>
<tr>
<td>(v_{11}) (474.2)</td>
<td>(v_{11}) (471.1)</td>
<td>8.0</td>
<td>7.5</td>
</tr>
<tr>
<td>(v_{12}) (520.3)</td>
<td>(v_{12}) (537.6)</td>
<td>7.5</td>
<td>5.0</td>
</tr>
<tr>
<td>(v_{13}) (620.0)</td>
<td>(v_{13}) (635.1)</td>
<td>–</td>
<td>3.8</td>
</tr>
<tr>
<td>(v_{14}) (800.7)</td>
<td>(v_{14}) (779.4)</td>
<td>9.3</td>
<td>6.0</td>
</tr>
<tr>
<td>(v_{15}) (878.5)</td>
<td>(v_{15}) (878.7)</td>
<td>–</td>
<td>4.0</td>
</tr>
<tr>
<td>(v_{16}) (891.6)</td>
<td>(v_{16}) (889.6)</td>
<td>8.0</td>
<td>5.4</td>
</tr>
<tr>
<td>(v_{17}) (918.1)</td>
<td>(v_{17}) (903.5)</td>
<td>3.6</td>
<td>4.8</td>
</tr>
<tr>
<td>–</td>
<td>(v_{18}) (928.7)</td>
<td>–</td>
<td>8.5</td>
</tr>
<tr>
<td>(v_{19}) (980.3)</td>
<td>(v_{19}) (957.7)</td>
<td>–</td>
<td>5.7</td>
</tr>
<tr>
<td>(v_{20}) (1018.2)</td>
<td>(v_{20}) (1006.6)</td>
<td>5.1</td>
<td>5.6</td>
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<td>(v_{21}) (1040.4)</td>
<td>7.0</td>
<td>4.0</td>
</tr>
<tr>
<td>–</td>
<td>(v_{22}) (1039.0)</td>
<td>–</td>
<td>7.0</td>
</tr>
<tr>
<td>(v_{23}) (1069.3)</td>
<td>(v_{23}) (1076.6)</td>
<td>5.2</td>
<td>5.8</td>
</tr>
<tr>
<td>(v_{24}) (1096.2)</td>
<td>–</td>
<td>7.2</td>
<td>–</td>
</tr>
<tr>
<td>–</td>
<td>(v_{25}) (1137.3)</td>
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<td>4.9</td>
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<tr>
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<td>(v_{26}) (1158.6)</td>
<td>3.4</td>
<td>2.7</td>
</tr>
<tr>
<td>–</td>
<td>(v_{27}) (1173.5)</td>
<td>–</td>
<td>4.3</td>
</tr>
<tr>
<td>(v_{28}) (1211.8)</td>
<td>(v_{28}) (1205.8)</td>
<td>7.6</td>
<td>3.8</td>
</tr>
<tr>
<td>(v_{29}) (1227.6)</td>
<td>(v_{29}) (1233.6)</td>
<td>7.3</td>
<td>4.3</td>
</tr>
<tr>
<td>(v_{30}) (1255.7)</td>
<td>(v_{30}) (1251.4)</td>
<td>4.4</td>
<td>4.2</td>
</tr>
<tr>
<td>(v_{31}) (1396.0)</td>
<td>(v_{31}) (1396.0)</td>
<td>4.8</td>
<td>5.7</td>
</tr>
<tr>
<td>(v_{32}) (1450.9)</td>
<td>(v_{32}) (1443.3)</td>
<td>–</td>
<td>1.9</td>
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<tr>
<td>(v_{33}) (1461.5)</td>
<td>(v_{33}) (1454.9)</td>
<td>–</td>
<td>2.2</td>
</tr>
<tr>
<td>(v_{34}) (1471.6)</td>
<td>(v_{34}) (1465.7)</td>
<td>2.0</td>
<td>2.8</td>
</tr>
<tr>
<td>(v_{35}) (1584.6)</td>
<td>(v_{35}) (1601.4)</td>
<td>4.9</td>
<td>1.2</td>
</tr>
<tr>
<td>–</td>
<td>(v_{36}) (1617.1)</td>
<td>–</td>
<td>4.7</td>
</tr>
</tbody>
</table>
Table 5. Pressure-induced frequency shifts of the OH and NH stretching modes of the \(\alpha\) and \(\beta\) phases of TRIS. [64]

<table>
<thead>
<tr>
<th>Mode (frequency) ((\alpha)-phase, cm(^{-1}))</th>
<th>Mode (frequency) ((\beta)-phase, cm(^{-1}))</th>
<th>(\frac{dv}{dp}) ((\alpha)-phase) (cm(^{-1})/GPa)</th>
<th>(\frac{dv}{dp}) ((\beta)-phase) (cm(^{-1})/GPa)</th>
<th>(\frac{d^2v}{dp^2}) ((\beta)-phase) (cm(^{-1})/GPa(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-)</td>
<td>(v_{\text{OH}1}(3159.9))</td>
<td>-</td>
<td>0.61(0.57)</td>
<td>-</td>
</tr>
<tr>
<td>(-)</td>
<td>(v_{\text{OH}2}(3218.0))</td>
<td>-</td>
<td>2.44(0.28)</td>
<td>-</td>
</tr>
<tr>
<td>(-)</td>
<td>(v_{\text{OH}2}(3268.6))</td>
<td>-</td>
<td>-0.43(0.69)</td>
<td>-</td>
</tr>
<tr>
<td>(v_{\text{NH}1}(3291.0))</td>
<td>(v_{\text{NH}1}(3316.8))</td>
<td>-4.18</td>
<td>-5.88</td>
<td>0.393</td>
</tr>
<tr>
<td>(v_{\text{NH}2}(3351.2))</td>
<td>(v_{\text{NH}2}(3351.3))</td>
<td>-2.92</td>
<td>5.12</td>
<td>-0.422</td>
</tr>
</tbody>
</table>

behavior of these modes. In the high-pressure phase, however, it was necessary to use a quadratic function. Quadratic functions have been shown before to be necessary to model the pressure shift of the frequencies for some modes [62, 63]. In the low pressure phase, both modes decrease in frequency as the pressure is increased. This is an indication of the increased importance of intermolecular hydrogen bonding of the NH\(_2\) groups. Above the phase transition, the dependence of the mode frequencies on pressure is more complex, and indicates that the nature of the hydrogen bonds is changing. There is a clear discontinuity in the frequencies at the phase transition, indicating that it is of first order. In addition, for some of the spectra measured near the phase transition, the two phases could be observed to coexist, indicating slow kinetics.

The solid symbols were obtained upon pressure increase while the open symbols were obtained upon pressure decrease. Linear fits were performed for the low-pressure phase, while quadratic fits were performed for the high-pressure phase. These fits used only the data obtained upon pressure increase.

Although the OH stretching modes could not be easily tracked in the low-pressure phase due to their low intensities, three OH-stretching modes could be observed and
tracked in the high-pressure phase. These modes, which do not have clear counterparts in the low pressure phase, were interpreted as stretching modes of OH groups involved in hydrogen bonding due to their broad nature; plots of the Raman shifts as a function of pressure are shown noting that there is significant scatter in these data. The lowest and highest frequency modes of these three had very small pressure-induced frequency shifts. The mode with a frequency near 3220 cm\(^{-1}\) at 2 GPa had a more significant positive slope. In the Figure 23, the solid symbols indicate data acquired during pressure increase,

Figure 22. Raman shift as a function of pressure for the symmetric and asymmetric NH\(_2\) stretching modes of TRIS. [64]
while the open symbols indicate data acquired during pressure decrease. The OH stretching modes were difficult to track at low pressures due to their low intensities, but became more intense relative to the CH and NH stretching modes at high pressures.

These fits were performed with data obtained only during pressure increase.

3.5 Deformation Modes

Finally, shifts of the low-frequency deformation modes are shown below in Figure 24. Not all of the modes could be traced to the highest pressures due to low and...
decreasing intensities with increasing pressure. Discontinuities in the mode frequencies and $d\nu/dp$ values could be observed for nearly all of the modes at the phase transition, indicating that the transition is of first order. Mode frequencies and $d\nu/dp$ values either decrease or increase, depending on the particular mode. The behavior of selected vibrational modes as a function of pressure will now be described. Modes in the vicinity of the 1332 cm$^{-1}$ Raman-active first-order phonon mode of diamond could not be tracked due to the large amount of interference from the diamond feature.

There are several modes of TRIS that are difficult to observe in the Raman spectra of the low pressure phase of the sample in the DAC which become significantly more intense in the high pressure phase. The $\tau$(CCO) mode at 250.1 cm$^{-1}$ and the $\delta$(CCC) mode at 308.7 cm$^{-1}$ are examples of this phenomena. In the ambient pressure Raman spectrum, only an extremely weak mode is observable in the Raman spectrum near 620 cm$^{-1}$. In the high-pressure phase, however, a significantly more intense mode is observed near 640 cm$^{-1}$ at a pressure of 1.9 GPa. Note that these modes become easily observable in the ODIC $\gamma$-phase as well.

The $\delta$(HNX) mode at 1158.1 cm$^{-1}$ (34%PED according to the normal coordinate analysis of Schroetter and Bougeard) appears to split into a triplet of peaks as a result of the phase transition. It appears that the effect may be the result of increased correlation splitting at higher pressures. It is also possible that modes near these frequencies that are weak in Raman spectra become observable in the high pressure phase.
The three mixed δ(CH\textsubscript{2})/δ(HCO) scissoring modes in the range of 1450-1472 cm\textsuperscript{-1} show significant changes in relative intensities above the phase transition. Only the strongest of the three modes at 1472 cm\textsuperscript{-1} could be tracked in the low-pressure phase; the other two peaks were weak and unresolved in the DAC. In the high-pressure phase, however, all three modes could be partially resolved and the relative intensities became more comparable. As a result, it was possible to track the mode frequencies as a function of pressure.

The δ(NH\textsubscript{2}) scissoring mode at 1585 cm\textsuperscript{-1} shows interesting behavior as a result of the phase transition. It splits into a clearly observable doublet in the high-pressure phase, possibly as a result of increased correlation splitting. The pressure induced frequency shifts of these two modes are significantly different, with the higher frequency mode shifting at a much faster rate. In addition, the frequency versus pressure plots tends to flatten out above ~4 GPa. A similar change in slope was observed for the ν(NH\textsubscript{2}) stretching modes, which is likely the result of changing hydrogen bond interactions. Discontinuities and changes in slope can be observed in Figure 24 above the phase transition. In addition, new modes can be tracked in the high-pressure phase that was difficult or impossible to observe in the low-pressure phase. Some of the lower intensity modes in the high pressure phase could not be tracked to the highest pressures due to poor statistics. The black triangles indicate modes observed under ambient conditions in the bulk sample in the infrared or Raman spectra. Some of these modes could not be
Figure 24. Pressure-induced frequency shifts of the low-frequency deformation modes of TRIS. [64]
observed in the DAC due to the small sample size.

3.6 High Temperature Behavior of TRIS

In the previous sections we have discussed the behavior of TRIS under pressure and in this section we will discuss the effects and changes the TRIS undergoes under high temperatures. Raman spectroscopy, X-Ray diffraction and Differential Scanning Calorimetry (DSC) methods are used to study the after effects of TRIS under high temperatures. Starting with Raman spectroscopy the sample has been loaded in the diamond anvil cell at ambient conditions of pressure and temperature. First, a spectra was collected at ambient conditions and then the spectra was collected at different temperatures keep the pressure same. One such spectra is shown below in Figure 25 where the pressure has been kept at atmospheric pressure and the temperature was raised to 152 °C. The phase transition of TRIS from \( \alpha \) to \( \gamma \) phase can be clearly seen in the low and high frequency Raman spectra acquired in this experiment, specifically when the temperature lies between 131 °C and 135 °C. The gradual disappearance of the low frequency modes above 131 °C, indicates a significant change in the material that may be associated with the phase transition from \( \alpha \) to \( \gamma \)-TRIS. The prominent peaks seen at ~225 cm\(^{-1}\) went on reducing its intensity until it disappeared in the spectrum obtained at 131 °C. It is also possible to see the same intensity reduction in the adjacent bands present at 277 cm\(^{-1}\), 340 cm\(^{-1}\), and 475 cm\(^{-1}\). The shoulders possibly recognized at 1094 cm\(^{-1}\) and 1395 cm\(^{-1}\) softened progressively till they completely disappeared above 131 °C. The convergence of the peaks at ~1061 cm\(^{-1}\), 2880 cm\(^{-1}\), and 2944 cm\(^{-1}\) and the broadening of
the peaks at 3292 cm\(^{-1}\) and 3351 cm\(^{-1}\) observed in the spectrum at 131 °C symbolizes that there is a change in the structure of the material. Additionally the formation of a new band at 624 cm\(^{-1}\) provides substantial evidence of the phase transition in the material. Finally we can show that the TRIS has been completely transformed into \(\gamma\) phase and the structure of TRIS in this phase is observed as body centered cubic (BCC). The structure of TRIS in this new phase has been determined from X-Ray diffraction of TRIS at high temperatures which is shown later in this report.

Figure 25. Temperature dependent Raman spectra for TRIS. By increasing the temperature of sample at constant atmospheric pressure 152 °C, a phase transition from \(\alpha\) to \(\gamma\) can be observed between 131 – 135 °C.

As seen in the previous Figure 25 the temperature of the sample has been raised keeping the pressure constant at ambient pressure. Similarly the DAC has been loaded again with the TRIS sample to make a high temperature run. But, this time the pressure has been initially set to 2.12 GPa before raising the temperature. Now the sample’s temperature is slowly raised from room temperature to 125.3 °C and the spectrum is acquired at each
temperature point. Figure 26 below shows the spectra. The figure shows that all the spectra acquired matches with the \( \beta \) phase spectra as seen in Figures 19 and 20. So, as soon the pressure was initialized to 2.1 GPa at room temperature the sample has entered into \( \beta \) phase and remained in the same phase even after increasing the temperature to 125.3 \( ^\circ \)C. There will be a pressure drop as the temperature keeps on increasing and the equivalent pressure has been measured at each temperature as indicated in the right side of the figure. This becomes an important spectrum to distinguish the \( \alpha \) and \( \beta \) phases in the pressure-temperature phase diagram. The phase transition shown in the above Figure 26 was also been justified by Differential Scanning Caloriemetry (DSC). TRIS sample was loaded in the DSC and the data has been acquired by heating the sample at a heating rate of 2 \( ^\circ \)C/min in the temperature range of -50 \( ^\circ \)C to 200 \( ^\circ \)C to observe if any solid-solid phase transitions were occurring. The DSC run is
shown below in Figure 27. The figure shows two peaks in which the peak on the left hand side of the figure represents that at 131 °C TRIS underwent a solid-solid transition which resembles the transition temperature shown in Figure 25. The second peak indicates the transition into liquid phase which happened at ~169 °C. The temperature indicating the liquid phase transition can be used to indicate the liquid phase region in the pressure-temperature phase diagram as Raman spectra is not active in liquid phases. The DSC can also show the energy released during the transition process with respect to the weight of the sample.

The phase transitions shown in Figures 25 and 26 have also been proved by high temperature X-Ray diffraction, where the sample TRIS has been loaded in the X-ray diffractometer and has been sealed. Vacuum conditions have been created using the inert nitrogen gas to prevent the sample from the moisture present in air. Now the X-Ray diffraction pattern has been collected at different temperatures by slowly increasing the temperature from room temperature to 145°C. All the diffraction patterns have been collected and stacked in an order to observe if any phase transition took place. The patterns are shown in Figure 28 below. It was been observed that above 130 °C new peak emerged in the pattern at ~25.5° and the peak has a new orientation of (200). The peak prominently seen in the 25 °C pattern at ~17.5° with an orientation of (111) has been changed its orientation to (110) above 130°C. All these effects prove that there is a phase change happening after 130 °C and the TRIS has been transforming into \( \gamma \) phase which as a body centered cubic structure.
Figure 27. DSC result of pure TRIS. The peak on the left hand side shows the solid-solid phase transition and the transition temperature 131.99 °C has been indicated. The peak on the right hand side shows the liquid phase transition and the transition temperature

3.7 High Pressure/Temperature Behavior of TRIS

Till now we have concentrated either on temperature dependent Raman spectra of TRIS or on pressure dependent Raman spectra of TRIS. Let’s see what happens to the Raman spectra of TRIS when we deal with both pressure and temperature in a single run. Taking into consideration the case of increasing the pressure to 3.97 GPa from atmospheric pressure and then gradually increasing the temperature. The spectrum is shown below in Figure 29. At ambient conditions of pressure and temperature the spectra remains in the α phase but when the sample was been pressurized to 1.8 GPa TRIS had entered into β phase. Then the sample was further pressurized to 3.97 GPa which still showed β phase. Now at this pressure of 3.97 GPa the temperature was gradually raised
to 134.4 °C without changing the pressure. However, the pressure keeps on changing due to the temperature increase and the corrected pressures were measured at each point of temperature increase. The lack of strong lattice modes in the high temperature phase indicates that a pronounced disruption of crystallinity is likely. The sample was showing β phase throughout the temperature run. This can be proved with the analogy of Figures 19 and 20.

Figure 28. X-Ray diffraction patterns of TRIS showing the phase transition above 130 °C. The phase transition has been taking place from α to γ phase.
Figure 30 shows one such similar run as Figure 29. Initially the sample is loaded at 0.16 GPa and at ambient temperature. The spectra acquired shows that the TRIS was in $\alpha$ phase at these initial conditions. The same $\alpha$ phase was seen in the spectra even after pressurizing the sample to 0.35 GPa. Now after still pressurizing the sample to 1.97 GPa we observe a phase change and it is seen in Figure 30. The sample remains in the same $\beta$ phase even after increasing the pressure to 6.04 GPa. The broadening of the NH and CH modes and dramatic shifting of the NH, CH modes indicate that there is a significant change in the material that may be associated with the phase transition above 0.35 GPa. The sample now at 6.04 GPa was heated gradually to 152.2 °C. The respective pressures at different temperatures have been corrected and are also indicated in Figure 31.
sample still remains in the $\beta$ phase even after raising the temperature to 152.2 °C at a pressure of 6.04 GPa.

Figure 30. Pressure dependent Raman spectra of TRIS showing the phase transition from $\alpha$ to $\beta$ phase above 0.35 GPa.

Figure 31. This figure shows the continuation of Figure 15 (a). The sample after pressurizing till 6.04 GPa in Figure 15 (a) is then slowly heated 152.2 °C and the sample still remained in the $\beta$ phase.
3.8 TRIS P-T Phase Diagram

Based on the changes to the vibrational modes discussed previously, the $PT$ phase boundaries of TRIS can be established and the resulting phase diagram is plotted in Figure 32. A dramatic weakening of the CH and NH bonds, stretching of the OH modes are seen in Figure 19 above 1.17 GPa which marks the phase transition from $\alpha$ to $\beta$ phase. Similar phenomenon can be seen in Figure 20 where the high pressure Raman spectra was run at 50 °C. Pressure induced frequency shifts of the low frequency modes are shown in Figure 24 which implies that there is a phase transition happening at higher pressures. Temperature dependent Raman spectra shown in Figure 26 at a constant pressure of 2.1 GPa shows that all the spectrum stay in the $\beta$ phase. The softening of the high frequency NH, CH modes, appearance of new bands and disappearance of some peaks observed in Figure 25 above 131 °C when the sample is heated to 152 °C shows that there is a phase transition from $\alpha$ to $\gamma$ phase. The $\gamma$ was also determined by X-Ray diffraction and DSC shown in Figures 27 and 28 also justifies Figure 25. The broadening of the high frequency modes shown in Figure 29 at 22 °C and 1.8 GPa proves that TRIS has transformed into $\beta$ phase. Taking into all these effects and approximating the phase boundaries the TRIS $PT$ phase diagram has been established.
Figure 16. Experimental pressure-temperature phase diagram of TRIS. The diagram is based on the variable pressure/temperature measurement.
Chapter 4

Phase Diagram Determination of AMPL, (NH\textsubscript{2})(CH\textsubscript{3})C(CH\textsubscript{2}OH\textsubscript{2}) – TRIS, (NH\textsubscript{2})C(CH\textsubscript{2}OH)\textsubscript{3} Binary System

The phase transitions in tris(hydroxymethyl)aminomethane and 2-amino-2-methyl-1,3-propanediol (TRIS – AMPL) binary system and the equilibrium TRIS – AMPL phase diagram determined by X-ray diffraction and differential scanning Calorimetry (DSC) are reported in this report. The DSC and high temperature X-ray experiments were performed on the several sets of TRIS – AMPL solid solution samples to gain understanding of the phase transitions and structural changes of these solid solutions through the construction of the phase diagram. The X-ray diffraction results obtained at different temperatures show the phase stability regions in certain ranges and the DSC results indicate the actual transition temperatures. The phase boundaries were obtained from the DSC results.

4.1 Thermal Analysis

The various phase transitions involved in the TRIS-AMPL binary phase system were initially screened by obtaining DSC plots from several compositions. At this point, the details of the nature of the phase transitions were not apparent. This data established the
high temperature phase boundaries; particularly the melting temperatures for the binaries. These studies led to the determination of temperature ranges for conducting studies on the X-ray diffractometer. The DSC spectra were analyzed to obtain the phase transition temperatures and enthalpies for the composition range. The results are shown in Figure 33.

- 1st phase transition, AMPL $\alpha \rightarrow \gamma$
- 2nd Phase transition, TRIS $\beta \rightarrow \gamma^l$
- 3rd phase transition, some solid $\rightarrow$ liquid
- 4th phase transition, all solid $\rightarrow$ liquid

Figure 33. Temperature Vs composition diagram of TRIS-AMPL obtained using the DSC data
The DSC data for pure AMPL gave two endothermic peaks, one of the peaks at 77.8 °C was interpreted as a solid-state transition and the other at 108.28 °C was the melting transition. The DSC data for pure TRIS also showed two transitions, one solid-state transition at 132 °C, and a melting temperature of 169.54 °C.

4.2 AMPL – Rich Region: Pure 2-amino-2-methyl-1, 3-propanediol

X-ray diffraction patterns of dry AMPL were obtained in various temperatures in the range of 35 to 114 °C. The patterns taken at 35 °C, till 77 °C have shown the room temperature monoclinic phase which is also the α phase of AMPL. As the sample was heated the structure changed from monoclinic to body centered cubic (BCC) phase which is also the γ phase of AMPL. This is indicated by the disappearance of the Bragg peaks at 86 °C and the appearance of the γ Bragg peak of 110. The sample turns into liquid at 114 °C.: The patterns are shown in Figure 34 below.

\[ \alpha \rightarrow \gamma \rightarrow L \]

35-77 °C  86-96 °C  114 °C

The DSC scan of pure AMPL is show in Figure 35. The solid-solid phase transition according to the DSC is shown by an endotherm at 77.8 °C which can be considered as the α to γ phase transition. Phase transitions based on DSC data can be summarized as:

\[ \alpha \rightarrow \gamma \rightarrow L \]

35-77  77-108  > 108 °C
During the heating process the lattice parameters of the unit cell behave differently. The lattice parameters and volume of the unit cell with respect to the temperature are shown below in figure 36. The lattice parameters ‘a’ and ‘c’ decreases as the temperature increases which means the unit cell is contracting in the direction of ‘a’ and ‘c’. But the value of ‘b’ predominantly increases in the direction of ‘b’ which says that the unit cell is expanding in this direction. The sudden volume difference shown after 80 °C says that the unit cell had expanded by 6.87 % which proves that there is a phase change happening above that temperature. The pure AMPL sample is turning into high temperature γ phase which is body centered cubic in structure.
Figure 35. The DSC scan of pure AMPL taken at various temperatures and the phase transitions are shown

4.3 Dilute Solution of TRIS-AMPL (10% TRIS)

The X-ray diffraction patterns for the 10% TRIS are shown in Figure 37. The analysis of these data shows three solid-state phase transitions. The AMPL and TRIS peaks are seen between 35 and 67 °C which is α+β Phase region. At 74 °C the γ peak appears at ~ 18.5°. This peak overlaps with the α peak at same angle and so we see a big change in the intensity of the peak at 74 °C. We can clearly see that there is no β peak which should be at 22.25° angle. This phase is α+γ and it continues till 78 °C. At 80 °C the α peaks completely disappear and we see only γ peak and this γ phase continues till 105 °C. Above this temperature at 112 °C the intensity of the γ peak decreases a lot which
proves that the sample is starting to enter into liquid phase and this is L+γ phase. At 119
°C all the peaks disappear which proves that the sample completely turned into liquid.

Figure 36. Lattice parameters and volume changes in pure AMPL with respect to temperature

Phase transitions based on X-ray diffraction data can be indicated as:

\[ \begin{align*}
\alpha & \rightarrow \alpha + \gamma \\
35-67 \degree C & \quad 74-78 \degree C \\
\gamma & \rightarrow L + \gamma \\
80-105 \degree C & \quad 105-112 \degree C \\
L & \rightarrow L \\
>119 \degree C & 
\end{align*} \]
Figure 37. X-ray diffraction patterns of 10% TRIS

The DSC scan shown in Figure 38 shows two endotherms. From the trends established in Figure 33, the first transition is interpreted as $\beta \rightarrow \gamma$ and the second as $\gamma \rightarrow \text{liquid}$ transition. Phase transitions based on the DSC data can be summarized as:

$$
\beta \quad 35-71 \\
\gamma \quad 80-115 \\
L \quad > 115 \degree C
$$

The lattice parameters and volume of the unit cell with respect to the temperature are shown below in figure 39 in regard with AMPL. As the $\beta$ phase of TRIS is in very little amount in this sample, the lattice parameters of TRIS are not calculated.
The lattice parameters ‘a’ and ‘c’ of AMPL decreases as the temperature increases which means the unit cell is contracting in the direction of ‘a’ and ‘c’. But the value of ‘b’ predominantly increases in the direction of ‘b’ which says that the unit cell is expanding in this direction. The sudden volume difference shown after 70 °C says that the unit cell had expanded by 6.37 % which proves that there is a phase change happening above that temperature. The pure AMPL sample is turning into high temperature γ phase which is body centered cubic in structure.
4.4 Transition and Stability in 20% TRIS-80% AMPL

X-ray diffraction data for 20% TRIS-80% AMPL binary are presented in Figure 40. These data show that the both $\alpha$ and $\beta$ phase Bragg peak lines are present in the patterns obtained at 35 and 75°C. In the diffraction pattern taken at 77 ºC, the Bragg lines for the $\alpha$ phase are not observed, but the characteristic Bragg lines of the $\gamma$ phase appear at 18.25º. Thus, the $\alpha$---$\gamma$ transition can be established between 75 and 77 ºC. The $\beta$+$\gamma$ continues till 95 ºC. At 105 ºC the $\beta$ peaks also completely disappear only the $\gamma$ peaks can be seen at 18.5º and 26º. So, the $\beta$+$\gamma$---$\gamma$ phase transition occurs at 105 ºC. At 116 and
128 °C the intensity of the γ peaks decreases which proves that the sample contains liquid. So, γ→L+γ transition occurs at 116 °C and remains till 128 °C. At 133 °C there are no peaks observed which proves that the sample completely turned into liquid phase.

\[
\alpha \rightarrow \beta + \gamma \rightarrow \gamma \rightarrow L + \gamma \rightarrow \text{Liq.}
\]

\[
\begin{array}{c}
133 ^\circ C \\
128 ^\circ C \\
116 ^\circ C \\
105 ^\circ C \\
95 ^\circ C \\
77 ^\circ C \\
75 ^\circ C \\
35 ^\circ C \\
\end{array}
\]

\[
\begin{array}{c}
\text{Liq.} \\
L+\gamma \\
\gamma \\
L+\gamma \\
\gamma \\
\beta + \gamma \\
\beta + \gamma \\
\alpha + \beta \\
\alpha + \beta \\
\end{array}
\]

Figure 40. X-ray diffraction patterns for 20%TRIS-80%AMPL

The DSC scan of the 20%TRIS-80%AMPL sample is shown in the Figure 41. The solid-state phase transformation temperatures are in agreement with those obtained by the X-ray diffraction method. The first transition is interpreted as \(\alpha \rightarrow \gamma\) and the
second as γ→liquid transition. Phase transitions based on the DSC data can be summarized as:

\[
\begin{align*}
\alpha & \rightarrow \gamma & \rightarrow & L \\
35-74.85 & 74.85-115.62 & > & 115.62 \, ^{\circ}C
\end{align*}
\]

Figure 41. DSC plot of the 20%TRIS-80%AMPL binary.

As both α phase AMPL and β phase TRIS is shown in the X-ray pattern of the 20% TRIS sample, the lattice parameters and volume of the unit cell with respect to the temperature are shown below in Figure 42 and 43 in each case of AMPL and TRIS. The AMPL’s lattice parameters ‘a’, ‘b’ and ‘c’ increases as the temperature increases which means the unit cell is expanding in all the directions. The sudden volume difference shown after 70 °C says that the unit cell had expanded by 12.9 % which proves that there
is a phase change happening above that temperature. The $\alpha$ phase AMPL turns into $\gamma$ phase above 70 °C. The TRIS’s lattice parameters ‘b’ and ‘c’ increases as the temperature increases which means the unit cell is expanding in the direction of ‘b’ and ‘c’. But the value of ‘a’ predominantly decreases in the direction of ‘b’ which says that the unit cell is contracting in this direction. As the $\beta$ phase TRIS disappears after the phase transition, the volume of the unit cell after the transition is solely dependent on AMPL.

Figure 42. Lattice parameters and volume changes in AMPL with respect to temperature in 20%TRIS-80%AMPL.
4.5 Phase Transitions in 30% TRIS-70% AMPL

The X-ray diffraction data for the 30% TRIS composition shows Bragg lines of the α and β phase up to 75 °C. The Bragg reflections of the α phase and also some of the principal reflections of the β phase, such as 111 and 200 lines have been shown. At higher temperatures (77 to 105 °C) Bragg peaks for the α phase at ~12.8° disappear and γ phase peak at ~18.3° appear, where as the β phase peaks still appear. So, the α→γ phase transition occurred between 75 and 77 °C and continued till 105 °C. Above 105 °C the characteristic peaks of TRIS β phase also dissappear, but the AMPL rich γ
phase lines are observed. The diffraction patterns taken at 110 °C and 115 °C show only the AMPL rich γ phase lines. Now at 120 and 130 °C the intensity of the γ peaks decreases a lot compared to the previous γ phase which proves that the sample has also a partial liquid in it. So, the current phase is L+γ. In this composition range, TRIS rich γ phase does not dissolve in the AMPL rich γ phase at higher temperatures, but transforms directly to the AMPL rich γ phase. At 135 °C all the peaks disappear because the sample completely transformed into liquid.

\[
\begin{align*}
\alpha & \rightarrow \beta + \gamma \rightarrow \gamma \rightarrow L + \gamma \rightarrow \text{Liq.} \\
35-75^\circ C & \quad 77-105^\circ C \quad 110-115^\circ C \quad 120-130^\circ C \quad > 130^\circ C
\end{align*}
\]

Figure 44. X-ray diffraction pattern of 30%TRIS-70%AMPL binary
The thermal analysis of the 30\%TRIS-70\%AMPL binary systems is given in Figure 45. The three endotherms with ascending temperatures are interpreted as the \(\alpha\rightarrow\gamma\), \(\beta\rightarrow\gamma\) and \(\gamma\rightarrow\) liquid phase transitions. Complete melting of the 30\%TRIS occurs at 140 \(^\circ\)C. This is reasonable as one would expect the increase in melting point with increase of TRIS content in AMPL. Phase transitions are briefed as:

\[
\begin{align*}
\alpha & \rightarrow \gamma & 35-74.73 \quad 74.73-115.8 \quad > 115.8 \, ^\circ\text{C} \\
\beta & \rightarrow \gamma & 107.71 \, ^\circ\text{C} \\
\alpha + \beta & \rightarrow 35 - 74.73 ^\circ\text{C} \\
\beta + \gamma & \rightarrow 74.73 - 115.8 ^\circ\text{C}
\end{align*}
\]

As in the previous 20\% TRIS – 80\%AMPL case the lattice parameters and volume of the unit cell with respect to the temperature are shown below in Figure 46 and 47 in each case of AMPL and TRIS. The lattice parameters ‘a’ and ‘b’ increases as the temperature increases which means the unit cell is expanding in the direction of ‘a’ and ‘b’. But the value of ‘c’ predominantly decreases in the direction of ‘c’ which says that the unit cell is contracting in this direction. The sudden volume difference shown after 70 \(^\circ\)C says that the unit cell had expanded by 8.37 \% which proves that there is a solid-solid phase change happening above that temperature. The \(\alpha\) phase AMPL turns into \(\gamma\) phase above 70 \(^\circ\)C. The TRIS’s lattice parameters ‘a’ and ‘c’ decreases as the temperature increases which means the unit cell is contracting in the direction of ‘a’ and ‘c’. But the value of ‘b’ predominantly increases in the direction of ‘b’ which says that the unit cell is expanding in this direction. As the \(\beta\) phase TRIS disappears after the phase transition, the
volume of the 30%TRIS – 70%AMPL unit cell after the transition is solely dependent on AMPL.

![30TRIS-70AMPL](image)

Figure 45. DSC plot of the 30%TRIS - 70%AMPL binary

4.6 Phase Transitions and Stability in 40%TRIS Binary

In viewing the diffraction patterns of the 40%TRIS composition, the characteristic Bragg lines for the $\alpha$ phase of AMPL and $\beta$ phase of TRIS are prominent in the temperature range between 35 and 75 °C. In the next temperature scan at 77 °C, the Bragg peaks of $\alpha$ phase of AMPL are disappear and the $\gamma$ peaks try start to appear at $\sim$18.5° which is over lapped with the $\beta$ peak. One can conclude that the $\alpha\rightarrow\gamma$ transition occurred between 75 and 77 °C. The $\beta+\gamma$ phase continues till 105 °C. At 115 °C, the $\gamma^1$
peak starts to appear which has been overlapped with the $\gamma$ peak. This $\gamma+\gamma'$ phase continues till 125 °C. At 130 °C the $\gamma$ peak disappear and the intensity of the $\gamma'$ peak also decreases which shows that the material started to melt. The L+$\gamma'$ phase continues till 140 °C. The sample completely melts at 145 °C.

Figure 46. Lattice parameters and volume changes in AMPL with respect to temperature in 30%TRIS-70%AMPL
Figure 47. Lattice parameters and volume changes in TRIS with respect to temperature in 30%TRIS-70%AMPL.

Overall phase transitions can be summarized as follows:

\[ \alpha + \beta \rightarrow \beta + \gamma \rightarrow \gamma + \gamma' \rightarrow L + \gamma' \rightarrow \text{Liq}, \]

\[ 35 - 75 \degree C \quad 77 - 105 \degree C \quad 115 - 125 \degree C \quad 130 - 140 \degree C \quad > 145 \degree C \]

The DSC plot of the 40%TRIS sample is shown in Figure 49. The data is agreeable with that of the X-ray patterns. From inspection, the \( \alpha \rightarrow \gamma \) shift is at \( \sim 74.86 \degree C \). The \( \beta \rightarrow \gamma' \) shift is at 115.2 \( \degree C \). The solid to liquid transition is at 122.31 \( \degree C \).

\[ \alpha \rightarrow \gamma \rightarrow L \quad 35-74.86 \quad 74.86-122.31 \quad > 122.31 \degree C \]

\[ \beta \rightarrow \gamma' \quad 115.2 \degree C \]
Figure 48. X-ray diffraction patterns of 40% TRIS – 60% AMPL binary.

The lattice parameters and volume of the unit cell with respect to the temperature are shown below in Figure 50 in each case of AMPL and TRIS. The lattice parameters ‘b’ and ‘c’ decreases as the temperature increases which means the unit cell is contracting in the direction of ‘b’ and ‘c’. But the value of ‘a’ increases in the direction of ‘a’ which says that the unit cell is expanding in this direction. The sudden volume difference shown after 70 °C says that the unit cell had expanded by 5.82 % which proves that there is a solid-solid phase change happening above that temperature.
4.7 Phase Transitions in the 50% TRIS-50% AMPL Binary

The X-ray diffraction pattern for 50% TRIS is same as the previous sample. The pattern is shown below in Figure 51. The $\alpha$ phase of AMPL and the $\beta$ phase of TRIS are observed along the line till 75 $^\circ$C. In the next temperature scan at 77 $^\circ$C, the Bragg lines
of $\alpha$ phase of AMPL disappear and the high temperature Bragg peak of the $\gamma$ phase at $\sim 18.5^\circ$ can be seen which concludes that there is a phase transition of $\alpha \rightarrow \gamma$. This transition can be observed until 105 °C. At 115 °C, the $\gamma^1$ peak starts to appear which has been overlapped with the $\gamma$ peak. This $\gamma + \gamma^1$ phase continues till 125 °C. At 130 °C the $\gamma$ peak disappear and the intensity of the $\gamma^1$ peak also decreases which shows that the material started to melt. The $L + \gamma^1$ phase continues till 145 °C. The sample completely melts at 150 °C.

Figure 50 (a): Lattice parameters and volume changes in AMPL with respect to temperature in 40%TRIS-60%AMPL
The transitions can be summarized as follows:

\[
\begin{align*}
\alpha + \beta & \rightarrow \beta + \gamma & \rightarrow \gamma + \gamma^1 & \rightarrow L + \gamma^1 & \rightarrow \text{Liq.}
\end{align*}
\]

- \(35 - 75 \, ^\circ\text{C}\)
- \(77 - 105 \, ^\circ\text{C}\)
- \(115 - 125 \, ^\circ\text{C}\)
- \(130 - 145 \, ^\circ\text{C}\)
- \(150 \, ^\circ\text{C}\)

Figure 50(b). Lattice parameters and volume changes in TRIS with respect to temperature in 40%TRIS-60%AMPL.

Thermal analysis of 50% TRIS as shown in the Figure 52 below indicate the \(\alpha \rightarrow \gamma\) transition at 74.67 \(^\circ\text{C}\). The \(\beta \rightarrow \gamma^1\) phase transition 115.07 \(^\circ\text{C}\). The third endotherm peak at 158 \(^\circ\text{C}\) is very pronounced as the liquid transition and can be concluded as the transition \(\gamma \rightarrow L\).
Figure 51. X-ray diffraction patterns of 50%TRIS – 50%AMPL binary sample.

The transitions together can be finalized as:

\[ \alpha \rightarrow \gamma, \beta \rightarrow \gamma^1 \rightarrow L \]

74.67 °C, 115.08 °C, 158 °C

The lattice parameters and volume of the unit cell with respect to the temperature are shown below in Figure 53 and 54 in each case of AMPL and TRIS. The lattice parameters ‘a’ and ‘b’ decreases as the temperature increases which means the unit cell is contracting in the direction of ‘a’ and ‘b’. But the value of ‘c’ predominantly increases in the direction of ‘c’ which says that the unit cell is expanding in this direction. The sudden volume difference shown after 70 °C says that the unit cell had expanded by 7 % which proves that there is a solid-solid phase change happening above that temperature. The \( \alpha \) phase AMPL turns into \( \gamma \) phase above 70 °C. The TRIS’s lattice parameters ‘a’, ‘b’ and
‘c’ increases as the temperature increases which means the unit cell is expanding in all the three directions. As the β phase TRIS disappears after the phase transition, the volume of the 50%TRIS – 50%AMPL unit cell after the transition is solely dependent on AMPL.

Figure 52. DSC plot of the 50TRIS-50AMPL binary.
Figure 53. Lattice parameters and volume changes in AMPL with respect to temperature in 50%TRIS-50%AMPL.
4.8 Phase Transitions and Stabilities in 60% TRIS-40% AMPL Binary

The X-ray diffraction patterns for 60% is shown below in Figure 55. The α phase of AMPL and the β phase of TRIS are observed along the line till 67 °C. In the next temperature scan at 77 °C, the Bragg lines of α phase of AMPL disappear and the high temperature Bragg peak of the γ phase at ~18.5° can be seen which concludes that there is a phase transition of α—>γ. This transition can be observed until 105 °C. At 114 °C the high temperature γ¹ phase Bragg line at ~18.25° can seen which overlapped with the β
peak and the $\gamma$ peak disappeared. At 124 °C the $\beta$ phase disappears and only $\gamma^1$ phase remains constant. From 133 – 142 °C the sample remains in L+$\gamma^1$ phase and completely turns into liquid at 152 °C. The transitions can be summarized as:

\[
\begin{align*}
\alpha + \beta & \rightarrow \beta + \gamma \rightarrow \beta + \gamma^1 \rightarrow \gamma^1 \rightarrow \gamma^1 + L \rightarrow \text{Liq.} \\
35-67^\circ C & \quad 77-105^\circ C \quad 114^\circ C \quad 124^\circ C \quad 133-142^\circ C \quad >152^\circ C
\end{align*}
\]

Figure 55. X-ray diffraction pattern of 60%TRIS-40%AMPL.

The DSC plots for the 60% TRIS sample can be viewed in the Figure 56 below. From these thermal analyses; the $\alpha \rightarrow \gamma$ phase transition takes place at 75.26 °C respectively. The second endotherm has been defined as the $\beta \rightarrow \gamma^1$ at 128 °C. The third endotherm indicates the $\gamma \rightarrow L$ phase transition at 141.88 °C. The broadening of the third
endotherm indicates that the liquid phase begins to dominate the $\gamma^1$ phase and slowly turns completely into the liquid phase at 162 °C. The transitions are summarized below.

\[ \alpha \rightarrow \gamma, \beta \rightarrow \gamma^1 \rightarrow L \]

\[ 75.26^\circ C \quad 128^\circ C \quad 141.88^\circ C \]

Figure 56. DSC plot of the 60%TRIS-40%AMPL binary.

The lattice parameters and volume of the unit cell with respect to the temperature are shown below in Figure 57 and 58 in each case of AMPL and TRIS. The lattice parameters ‘b’ and ‘c’ increases as the temperature increases which means the unit cell is expanding in the direction of ‘b’ and ‘c’. But the value of ‘a’ decreases in the direction of ‘a’ which says that the unit cell is contracting in this direction. The sudden volume difference shown after 70 °C says that the unit cell had expanded by 6.53 % which proves that there is a solid-solid phase change happening above that temperature. The $\alpha$ phase
AMPL turns into γ phase above 70 °C. The TRIS’s lattice parameters ‘a’, ‘b’ and ‘c’

Figure 57. Lattice parameters and volume changes in AMPL with respect to temperature in 60% TRIS–40% AMPL.

increases as the temperature increases which means the unit cell is expanding in all the
tree directions. As the β phase TRIS disappears after the phase transition, the volume of
the 60%TRIS – 40%AMPL unit cell after the transition is solely dependent on AMPL.
4.9 Phase Transitions and Stability in 70%TRIS-30%AMPL Binary Sample

Scanning the X-ray patterns of 70% TRIS shown in Figure 59 below, one sees the same trends as the previous temperature scans. Observance of the $\alpha+\beta$ phase region with the characteristic Bragg lines of both TRIS and AMPL till 72 °C. At 77 °C, the 110 and 200 diffraction lines of the $\gamma$ phase appear, while the $\alpha$ diffraction lines are not visible. One can reason, the $\alpha\rightarrow\gamma$ transition takes place between 72 and 77 °C. From 77 °C to 105 °C, no changes in the diffraction patterns are noticed, therefore, the $\beta+\gamma$ phase region is stable to 105 °C. In the pattern at 114 °C, the Bragg diffraction line for the $\gamma$ phase disappear and the $\gamma^1$ peak start to appear. This can be observed by the shift in the $\gamma$ peak at 18.5° to 18.25° which is the $\gamma^1$ peak merged with the $\beta$ peak at 18.25°. The $\beta+\gamma^1$ phase continues till 122 °C. After this the $\beta$ peaks disappear and what remains is only the $\gamma^1$ peak till 142 °C. The liquid phase starts after this and continues till 151 °C along with the $\gamma^1$ peak. The sample completely turns into liquid at 161 °C with no peaks at all. The overall phase transitions can be briefed as follows:

$\alpha + \beta \rightarrow \beta + \gamma \rightarrow \beta + \gamma^1 \rightarrow \gamma^1 \rightarrow \gamma^1 + L \rightarrow \text{Liq.}$

35 – 72 °C  77 – 105 °C  114 – 122 °C  133 – 142 °C  151 °C  >161 °C

Thermal analysis of the 70%TRIS-30%AMPL DSC plot is shown below in the Figure 60. The three endotherms indicate three major transitions. The first endotherm starting at 76.56 °C shows the initial $\alpha\rightarrow\gamma$ phase transition. The second endotherm indicates actually two transitions. The broadening of the second endotherm can be
Figure 58. Lattice parameters and volume changes in TRIS with respect to temperature in 60%TRIS-40%AMPL.
Figure 59. X-ray Diffraction pattern of 70%TRIS-30%AMPL binary.

explained as the β phase of TRIS slowly starting to convert into its high temperature γ\textsuperscript{1} phase at ~108 °C. The complete transformation of the β phase happens at 127.76 °C. The third endotherm can be taken as the solid-liquid transition happening at 157.52 °C. The transformations can be combined as

\[
\begin{align*}
\alpha & \rightarrow \gamma \\
\beta & \rightarrow \gamma^1 \rightarrow L
\end{align*}
\]

\[
\begin{align*}
& 76.56 \\
& 127.76 & 157.52
\end{align*}
\]
Figure 60. DSC plot of the 70%TRIS-30%AMPL binary sample

The lattice parameters and volume of the unit cell with respect to the temperature are shown below in Figure 61 and 62 in each case of AMPL and TRIS. The lattice parameters ‘b’ and ‘c’ increases as the temperature increases which means the unit cell is expanding in the direction of ‘b’ and ‘c’. But the value of ‘a’ decreases in the direction of ‘a’ which says that the unit cell is contracting in this direction. The sudden volume difference shown after 70 °C says that the unit cell had expanded by 6.75 % which proves that there is a solid-solid phase change happening above that temperature. The α phase AMPL turns into γ phase above 70 °C. The TRIS’s lattice parameters ‘a’, ‘b’ and ‘c’ increases as the temperature increases which means the unit cell is expanding in all the three directions.
Figure 61. Lattice parameters and volume changes in AMPL with respect to temperature in 70%TRIS-30%AMPL.
4.10 Phase Transitions and Stabilities in 80%TRIS-20%AMPL

This binary sample acts same as the previous sample. The scan is shown below in Figure 63. The scans at 35 and 68 °C show the Bragg peaks of both α and β phases of AMPL and TRIS respectively. In the 77 °C scan of the sample, we can observe the disappearance of the α phase peaks of AMPL. But, the formation of the new peak which corresponds to the high temperature γ phase is seen. The β phase of TRIS remains the same. We can conclude that α→γ phase transition happened between 68 and 77 °C. At 114 °C the high temperature γ phase of AMPL disappears and the Bragg peak of the high
temperature $\gamma^1$ phase of TRIS is seen and also the $\beta$ phase is visible and this continues till 124 °C. This means that the $\beta$ phase of TRIS is slowly starting to convert into the $\gamma^1$ phase of TRIS which is cubic. At 133 °C the scan shows that the $\beta$ phase Bragg peaks completely disappear. So at this point the transformation is complete into $\gamma^1$ phase and this continues till 142 °C. The sample completely turns into liquid at 162 °C with no peaks seen in the pattern. The phase transitions can be summarized as:

$$\alpha + \beta \rightarrow \beta + \gamma \rightarrow \beta + \gamma^1 \rightarrow \gamma^1 \rightarrow \text{Liq.}$$

35 – 68 °C  77 – 105 °C  114 – 124 °C  133 – 142 °C  162 °C

![Figure 63. X-ray diffraction scan of the 80%TRIS-20%AMPL binary sample](image)

The DSC plot for the above binary sample is shown in Figure 64 below. The small peak at 73.96 °C represents the solid-solid phase transition from $\alpha\rightarrow\gamma$ phase. The
second peak at 127.23 °C shows the transition from $\beta \rightarrow \gamma^I$ phase. The third endotherm represents the $\gamma^I \rightarrow \text{liq}$ phase transition at 166.57 °C.

\[
\begin{array}{c}
\alpha \rightarrow \gamma \\
73.96 \degree C \\
\beta \rightarrow \gamma^I \rightarrow \text{L} \\
127.23 \degree C \quad 166.57 \degree C
\end{array}
\]

![DSC plot of the 80%TRIS-20%AMPL binary showing two solid-solid phase transitions and one solid-liquid transition](image)

Figure 64. DSC plot of the 80%TRIS-20%AMPL binary showing two solid-solid phase transitions and one solid-liquid transition.

The lattice parameters and volume of the unit cell with respect to the temperature are shown below in Figure 65 and 66 in each case of AMPL and TRIS. The lattice parameters ‘b’ and ‘c’ increases as the temperature increases which means the unit cell is expanding in the direction of ‘b’ and ‘c’. But the value of ‘a’ decreases in the direction of ‘a’ which says that the unit cell is contracting in this direction. The sudden volume difference shown after 60 °C says that the unit cell had expanded by 11.9 % which proves
that there is a solid-solid phase change happening above that temperature. The α phase AMPL turns into γ phase above 60 °C. The TRIS’s lattice parameters ‘a’, ‘b’ and ‘c’ increases as the temperature increases which means the unit cell is expanding in all the three directions according to TRIS.

Figure 65. Lattice parameters and volume changes in AMPL with respect to temperature in 80%TRIS-20%AMPL
Figure 66. Lattice parameters and volume changes in TRIS with respect to temperature in 80%TRIS-20%AMPL

4.11 Phase Transitions and Stabilities in 90%TRIS-10%AMPL

The following binary is rich in TRIS because it contains 90% of TRIS. So, may be because of this reason we see the Bragg lines of the β phase of TRIS all the way till 110 °C and the α phase of AMPL is not visible.
At 125 °C the $\gamma^1$ phase of TRIS starts to appear at $\sim18.25^\circ$ which merges with the $\beta$ peak at the same angle. This can be observed by the sudden increase in the intensity of the $\beta$ peak at $18.25^\circ$. We can conclude that the phase transition $\beta \rightarrow \gamma^1$ is happening between 110 and 125 °C. At 135 °C the Bragg peaks of $\beta$ phase completely disappear, but the Bragg peak of the $\gamma^1$ phase of TRIS is still observed. This $\gamma^1$ phase continues till 152 °C. At 162 °C the sample starts to melt because we see a sudden decrease in the intensity of the $\gamma^1$ peak. The sample completely melts at 167 °C. The diffraction pattern is shown below in Figure 67.
Thermal analysis of the above sample that there are two transitions happening, one is the solid-solid transition ($\beta \rightarrow \gamma^1$) at 128.39 °C and the other transition is the solid-liquid transition ($\gamma^1 \rightarrow L$) at 168.55 °C. The DSC plot is shown below in Figure 68.

![DSC plot of the 90%TRIS-10%AMPL binary sample](image)

Figure 68. DSC plot of the 90%TRIS-10%AMPL binary sample

The lattice parameters and the volume of the unit cell for the above binary sample are measured at each pattern with respect to only TRIS because the AMPL was not visible in any of the pattern. The comparison is shown in below in Figure 69. The TRIS’s lattice parameters ‘a’, ‘b’ and ‘c’ increases as the temperature increases which means the unit cell is expanding in all the three directions according to TRIS. The sudden increase
in the volume is seen after 120 °C which proves that there is a solid-solid phase transition taking place/ occurring instead of happening above 120 °C.

4.12 Phase Transitions in Pure TRIS

The phase transitions in Pure TRIS by X-ray diffraction are presented below in Figure 70. The TRIS shows the normal low temperature β phase till 124 °C. In the temperature scan at 133 °C all the Bragg peaks of the β phase of TRIS completely
disappear and the Bragg peaks of the high temperature $\gamma^1$ phase appear. This states that TRIS underwent a solid-solid phase transition between 124 and 133 °C. The transition can be concluded as $\beta \rightarrow \gamma^1$. This $\gamma^1$ phase continues till 165 °C and so this phase is stable from 133 to 165 °C. The sample turns into liquid phase at 172 °C showing no peaks in the pattern.

Figure 70. X-ray diffraction of the pure TRIS showing a solid-solid phase transition above 130 °C.

Thermal analysis of the pure TRIS sample using the DSC is plotted below in Figure 71. The first endotherm indicates that there is a solid-solid phase transition happening at 131.99°C. One can conclude that transition as $\beta \rightarrow \gamma^1$. The second endotherm shows a solid-liquid transition happening at 169.54 °C, which means above this temperature the sample turns into liquid phase.
4.13 Complete AMPL-TRIS Equilibrium Phase Diagram

After plotting all the X-ray diffraction data points from different compositions, the DSC plot was superimposed over it. The DSC data was plotted using the onset temperatures. We know that the dynamic structural changes are taking place in and around this transition zone and that the onset temperature may not be very accurate information to plot for a given binary (i.e., max peak). One can see the discrepancies in the X-ray and DSC data collection for the $\alpha \rightarrow \gamma$ and $\beta + \gamma \rightarrow \gamma' + \gamma$ phase transitions. Furthermore, thermal analysis failed to reveal the $\beta \rightarrow \gamma$ phase transitions due to low
transitional energies of mixing. With this in mind, we combined these information bases and came up with a phase diagram that was thermodynamically sound which is shown in Figure 72.

Figure 72. Proposed phase diagram of AMPL-TRIS binary system.
4.14 Discussion of Results for the AMPL-TRIS Binary

The important feature to note on this phase diagram is that there are five different phase transitions occurring in this binary. At temperatures below 75 °C, it can be seen that there is essentially no solubility of one phase in the other. Heating above this temperature, we notice the solubility of β and γ phases increase. At ~75 °C, the α→γ solid state phase transition takes place. On the AMPL rich side of the phase diagram, above 75 °C, we observe the β→γ and β→γ\textsuperscript{l} phase transitions occurring. The two phase α+γ region can also be seen on the AMPL rich side. It is a narrow band that borders the eutectoid temperature zone on one side and has α phase field and γ phase field as boundaries for its outer extremes. These two different structures represent the low and high temperature phases of AMPL. There is an invariant point at ~73 °C, 19% TRIS. This point establishes the eutectoidal temperature and the end composition of this phase boundary. At 108 °C and very near 63%TRIS, an eutectoid reaction is observed. The high temperature γ\textsuperscript{l} phase, upon cooling, transforms into two different solid phases, β+γ. Another point of interest is the γ+γ\textsuperscript{l} phase region located in the upper mid compositional range of the diagram. This situation is very unique in polyalcohols and indicates the composition in which thermal energy is stored. In solid-liquid phase region of the TRIS rich side of the diagram there is a peritectic reaction; the γ\textsuperscript{l}+L→γ phase transformation occurring at ~128 °C, 57%TRIS. Also on the TRIS rich side of the diagram, at concentrations greater than 65%TRIS, the γ→γ\textsuperscript{l} phase transition has been observed.
Due to the size and crystal structure of the two polyalcohols, unusual expansion and contraction of the lattices were observed when heating the compounds through the different phase regions. The TRIS, orthorhombic structure, expands through much of a temperature series, but contracts at phase transition temperature, when it transforms to the high temperature cubic phase.

The AMPL monoclinic structure also demonstrated irregularities in expansion and contraction when subjected to varying amounts of TRIS. Inspecting the X-ray diffraction patterns of the low to mid range compositions, the lattice of the AMPL crystal expanded over a few temperature scans but a contraction is observed in most of the patterns. The unit cell apparently must contract in size in order to fit into the orthorhombic or cubic phase of TRIS. The DSC plots revealed very little energy absorption at these phase transitions.

### 4.15 Structural Measurements on Pure TRIS

The first data ever collected on TRIS was taken to General Electric Corporation in Vellecoto, California, and a d-space file was obtained using a high tech film scanner. The d-spacings were obtained from the major planes and unit cell volumes and lattice constants were measured over a range of temperatures for the TRIS crystal. The temperature range scanned was from 25 to 160 °C. This data was then graphed on the Cricket program to evaluate volume and lattice expansion. It is apparent from this data a contraction in the TRIS orthorhombic crystal structure occurs at the transition temperature. In Figures 73 and 74, the percent expansion in the a, b, and c directions is
plotted versus temperature (°C). Looking at the α phase (orthorhombic structure), we find expansion in the a and b direction with continuous heating. But the c direction of the unit cell shows a slight contraction at 80 °C and never regains its former dimension (that at 40 °C), prior to the anticipated β→γ′ phase change. At 140 °C, the TRIS transforms from the orthorhombic structure to a face centered cubic phase. It is apparent that there is a contraction in the unit cell of this lower symmetry β phase at the transition temperature. After the phase transformation occurs, the FCC phase expands with increased heating as would be expected.

Figure 73. Lattice expansion and contraction in pure TRIS before phase transformation
Figure 74. Lattice expansion and contraction in pure TRIS after phase transformation.
Chapter 5

CONCLUSIONS

Raman spectroscopy was used to study tris(hydroxymethyl)aminomethane at high pressures inside a diamond anvil cell. A phase transition was observed at ~2 GPa. In addition to discontinuous changes in many of the mode frequencies and slopes of the frequency versus pressure curves above this phase transition, new modes were present that were difficult to observe or not present in the low temperature phase. This indicates a significant change in the crystal lattice structure and/or the molecular conformations in the material. The phase transition is marked by slow kinetics and significant hysteresis, indicative of a first-order process. The $P$-$T$ phase diagram has been developed for TRIS. Further work is underway to measure the Raman spectra of other polyalcohol and amine derivatives of neopentane are being examined to order see how pressure affects the properties of these “plastic” crystal materials with globular molecules.

A binary phase diagram for the AMPL-TRIS system is proposed. The phase diagram was determined using a high temperature X-ray diffractometer and a Differential Scanning Calorimeter. The data acquired from this from this work established the lattice parameters, d-spacings, and plane indices for the two compounds. This also confirmed that no high temperature phases were present in the powder samples. The majority of the diagram was constructed with the data obtained from X-ray diffractometer. The DSC
results gave valuable information concerning solidus/liquidus temperatures and thermodynamic properties of selected binaries.

A progression of DSC patterns of the AMPL-TRIS binary is shown in Figure 75. These transitions can be correlated with the phase diagram. Although the DSC results are did not reveal transitions with very low heat effects, such as β→γ and γ→γ\textsuperscript{l} phase transitions, it did reveal the continuous phase transition, β→γ\textsuperscript{l}, higher concentration TRIS binaries.

In viewing the proposed phase diagram in Figure 72, some important points are worth noting. It was found that below ~75 °C, there is virtually no solubility of AMPL in TRIS or vice versa. The AMPL rich α phase transforms to an AMPL rich γ phase at ~75 °C. Between ~75 °C and 108 °C a wide β+γ phase region is observed. The maximum solubility of TRIS in AMPL is 11% TRIS at 73 °C and that of AMPL in TRIS is 34% AMPL at ~125 °C. The phase diagram exhibits two eutectoidal transformations at 73 °C (γ→α+β) and at 108 °C (γ\textsuperscript{l}→β+γ) respectively. The phase diagram also exhibits a peritectic transformation at 128 °C (L+γ\textsuperscript{l}→γ). A two phase region with γ+γ\textsuperscript{l} plastic phases rich in TRIS and AMPL is also observed between 108 °C and 128 °C. Another point to notice is a narrow band of α+γ phases prevailing on the AMPL rich portion of the diagram. One doesn’t notice this on the TRIS rich side, a β+γ\textsuperscript{l} region.
Lattice expansion measurements were taken on X-ray diffraction patterns of pure TRIS. As expected, the lattice expanded in (a) and (b) direction with increasing temperature, but surprisingly showed a slight contraction in the c direction prior to the anticipated phase change. Figure 73 shows this expansion behavior of the α phase, and a sudden contraction in the lattice is seen at the phase transition temperature in Figure 74. Once the γ phase is formed, the expected increase in the lattice parameter is observed.
Both AMPL and TRIS show promise for thermal energy storage applications. The combination of the two, the AMPL-TRIS binary system, may not be of use for room temperature operations.

One might ask what kind of applications the polyalcohols might have. For sometime phase change materials such as salt hydrates and lithium hydride have been used in large scale industrial heat transfer operations. Experiments in thermal energy storage integrated into power plants have also been conducted. A few examples are:

1) Stationary bulk PCM medium surrounding the high packing density tubes (JPL).
2) Stationary encapsulated PCM (Gruman, Boeing, Comstock, Wescott, and Institute of Gas Technology).
3) Moving PCM (Marshall Space Flight Center) and
4) Direct contact PCM and transport fluid (Naval Research Lab).

The operating temperatures are very high for these arrangements and material problems such as corrosion and heat shock have been incurred.

Due to high transition temperature of certain polyalcohols, binary solid solutions must be found for room temperature applications. The possible uses include impregnating wallboard with a binary solid solution for solar heating of buildings. Hot water heater insulation jackets, hot food container insulation wrap, and thermos are a few of the household items that come to mind. In the auto industry, heating of cold engines prior to ignition is being developed. One can extend this though to possible use in diesel engines, where pre ignition heating of the spark plug and cylinder wall is necessary in colder
climates. With a creative imagination, several other concepts and possible uses of this promising field in thermal energy storage can be envisioned. Hopefully, this might simulate reader’s minds and a second generation technology breakthrough will occur in the near future.

The X-ray diffraction is done by a PANalatical X-ray Diffractometer in which we use a special TTK 450 low temperature chamber for heating the samples which is shown in Figure 76. The sample is placed on the flat sample holder as shown and the chamber is sealed. The chamber should be evacuated twice and finally filled with helium to avoid any moisture present in the air. Now at higher temperatures AMPL vaporizes out of the TRIS-AMPL binary mixture and deposits all over the chamber, because AMPL has got a lower boiling point compared to TRIS. As the AMPL vaporizes from the binary mixture, the composition of the sample changes which is unknown and so we get unexpected results.

Figure 76. Low Temperature TTK 450 chamber showing the flat sample holder.
In order to get rid of this vaporization problem we came up with a new experimental setup. In this experimental setup we use a quartz capillary of 1 mm inner diameter instead of the flat and open sample holder. The experimental setup is shown in the Figure 77. The capillary is filled with the binary sample, and then stuffed with the industrial glass wool on the wide end of the capillary. The capillary is now completely sealed at the open end of the capillary using glue. The capillary is now placed in the custom made capillary metal holder as shown in the figure. The capillary is heated using an external tubular heater which uses air as the heat medium. The air flows through the tubular heater with a certain flow rate by which the capillary gets heated. As the X-rays hit the quartz capillary we see a lot of background and also we see a wide range of shift in the X-ray patterns.

![Figure 77. Capillary experimental setup for X-ray diffraction.](image-url)
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REFERENCES


APPENDIX I  Shows Temperature Calibration of the X-ray sample.

Figure A-1. Show temperature calibration of the x-ray diffraction XRK 450 low temperature stage on the PANalytical X-ray diffraction apparatus. The temperature ($T_{\text{measured}}$) is the temperature that was recorded by the temperature controller thermocouple (TC) at the bottom of the water cooled system (isolated by stainless, just below the sample holder slot). A flexible (thin) K type thermocouple was fed through 1/16" stainless steel tube in the x-ray stage. The TC leads were epoxied to the SS tube on the outside of the chamber; there was approximately 12 cm of free TC wire available inside the sample chamber. The actual bead