Superstrengthening $\text{Bi}_2\text{Te}_3$ through Nanotwinning

Guodong Li,1,2 Umut Aydemir,2,3 Sergey I. Morozov,4 Max Wood,2 Qi An,5,* Pengcheng Zhai,1 Qingjie Zhang,1,4 William A. Goddard III,6 and G. Jeffrey Snyder2,3

1State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China
2Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208, USA
3Department of Chemistry, Koc University, Sariyer, Istanbul 34450, Turkey
4Department of Computer Simulation and Nanotechnology, South Ural State University, Chelyabinsk 454080, Russia
5Department of Chemical and Materials Engineering, University of Nevada, Reno, Reno, Nevada 89557, USA
6Materials and Process Simulation Center, California Institute of Technology, Pasadena, California 91125, USA

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Bismuth telluride ($\text{Bi}_2\text{Te}_3$) based thermoelectric (TE) materials have been commercialized successfully as solid-state power generators, but their low mechanical strength suggests that these materials may not be reliable for long-term use in TE devices. Here we use density functional theory to show that the ideal shear strength of $\text{Bi}_2\text{Te}_3$ can be significantly enhanced up to 215% by imposing nanoscale twins. We reveal that the origin of the low strength in single crystalline $\text{Bi}_2\text{Te}_3$ is the weak van der Waals interaction between the Te1 atoms of adjacent quint substructures. However, we demonstrate here a surprising result that forming twin boundaries between the Te1 atoms of adjacent quints greatly strengthens the interaction between them, leading to a tripling of the ideal shear strength in nanotwinned $\text{Bi}_2\text{Te}_3$ (0.6 GPa) compared to that in the single crystalline material (0.19 GPa). This grain boundary engineering strategy opens a new pathway for designing robust $\text{Bi}_2\text{Te}_3$ TE semiconductors for high-performance TE devices.

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The continued use of fossil fuels to satisfy escalating global energy requirements is causing severe unacceptable environmental impact. This has generated renewed interest in thermoelectric (TE) conversion technology to convert waste heat directly into electricity, which involves no CO2 emissions. This has generated renewed interest in thermoelectric (TE) conversion technology to convert waste heat directly into electricity, which involves no CO2 emissions. This has generated renewed interest in thermoelectric (TE) conversion technology to convert waste heat directly into electricity, which involves no CO2 emissions. This has generated renewed interest in thermoelectric (TE) conversion technology to convert waste heat directly into electricity, which involves no CO2 emissions. This has generated renewed interest in thermoelectric (TE) conversion technology to convert waste heat directly into electricity, which involves no CO2 emissions. 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resulting in a dramatically improved $zT$ of 1.86 at 320 K [25]. This GB strategy has been further applied in other TE semiconductors such as PbTe, Mg$_2$Si, and CoSb$_3$ for enhancing their $zT$ values [26–28]. In addition, nanotwinned bismuth telluride also can promote superior TE performance and robust mechanical properties [29], which further suggest that nanoscale twins may play an essential role in the mechanical properties of TE semiconductors.

Here we use the Perdew-Burke-Ernzerhof (PBE) density functional to examine the shear stress-strain relationship of single crystalline and nanotwinned bismuth telluride (Bi$_2$Te$_3$). We find that the weak van der Waals interactions between the Te1 atoms dominate the failure process of crystalline Bi$_2$Te$_3$, leading to a very low ideal shear strength of 0.19 GPa. However, we show that the presence of nanoscale twins leads to increased covalency in the Te1 bonds between adjacent quints at the twin boundary, which significantly improves the structural stiffness. This strengthening mechanism results in a dramatically improved ideal shear strength of 0.60 GPa for nanotwinned Bi$_2$Te$_3$, triple the value (0.19 GPa) for single crystalline Bi$_2$Te$_3$.

All density functional theory (DFT) simulations were performed using the periodic code Vienna *ab initio* Simulation Package (VASP) with plane wave basis sets [30–32], adopting the projector augmented wave (PAW) method and the PBE exchange-correlation functional applied to account for the core-valence interactions [33]. We show that an energy cutoff of 600 eV with a $(10\times10\times2)$ Monkhorst-Pack grid in the $k$ point reciprocal space sampling gives excellent convergence on energy and geometries. The convergence for the electronic self-consistent field and the force criterion were set to less than $1\times10^{-6}$ eV and $1\times10^{-2}$ eV/$\text{Å}$, respectively. Spin-orbit coupling (SOC) was included in the structural optimization of Bi$_2$Te$_3$.

To examine the failure mechanism, we applied pure shear deformation by imposing the shear strain on a particular shear direction while allowing full structural relaxation along the other five strain components. The residual stresses for relaxation along the other strain components are all set to less than 0.1 GPa [34].

Bi$_2$Te$_3$ crystallizes in a rhombohedral structure with the space group $R3m(D_3^h)$, which can be visualized as a hexagonal lattice cell made of Te1–Bi–Te2–Bi–Te1 five-layer (quint) substructures along the [001] axis as shown in Fig. 1(a) [35,36]. The shorter covalent Bi–Te1 (3.11 Å) and longer (weaker) covalent Bi–Te2 (3.30 Å) bonds stabilize the quint five-layer substructure, while the quints are coupled via van der Waals interaction between the Te1 atoms of adjacent quints ($d_{\text{Te1–Te1}} = 3.82$ Å). These weak van der Waals interactions control the ease of cleavage along the (001) axis [35,36]. PBE gives equilibrium lattice parameters of $a = 4.47$ and $c = 31.15$ Å. These values agree well with the previous results ($a = 4.45$, $c = 31.15$ Å) using the PBE functional [37], and are only 1.8% and 3.3% larger than the experimental values of $a = 4.39$ and $c = 30.50$ Å at 300 K, respectively [38].

Here, we used DFT to determine the atomic structures of three nanotwinned Bi$_2$Te$_3$, with TBs lying along (i) the {702} plane, see Fig. 1(b), leading to an interfacial energy of 325.6 ml/m$^2$. The TB along the {702} plane contains 60 × Bi and 90 × Te atoms. The measured angle on each side of the TBs is 37°, and the twinning size is 2.4 nm. Along the TB plane of {702}, two new covalent Te1–Te1 bonds (3.48 Å) are formed, further coupling adjacent Te1–Bi–Te2–Bi–Te1. (ii) The {701} plane, see Fig. S1 [39], leading to an interfacial energy of 385.7 ml/m$^2$. (iii) The {210} plane, see Fig. S2 [39], leading to an interfacial energy of 440.7 ml/m$^2$. These three nanotwinned Bi$_2$Te$_3$ have been experimentally observed recently [29,40].

To understand the intrinsic failure mechanism of Bi$_2$Te$_3$, we examine the deformation process of single crystalline Bi$_2$Te$_3$. We used DFT to determine the shear-stress-shear-strain relationships of single crystalline Bi$_2$Te$_3$ along various directions within the (001) cleavage plane, as shown in Fig. 2(a). Each slip system shows extremely low ideal shear strength of (i) 0.16 GPa for the (001)/⟨50⟩ slip system, (ii) 0.19 GPa for the (001)/⟨50 − 1⟩ slip system, and (iii) 0.22 GPa for the (001)/⟨210⟩ slip system. This agrees well with the experimental observation that Bi$_2$Te$_3$ easily cleaves along the (000) plane [35,36]. Beyond the maximum shear stress point, each slip system exhibits an obvious “yielding” stage, indicating a softening structural.
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FIG. 2. Deformation behavior of single crystalline Bi₂Te₃.

(a) The shear-stress-shear-strain relationships under shear deformation along various slip systems. (b) The bond stretching ratio (Te₁–Te₁, Bi–Te₁, Bi–Te₂) with increasing shear strain along the (001)/⟨50–1⟩ slip system. (c) The atomic structure at 0.071 shear strain corresponding to the maximum shear stress along the (001)/⟨50–1⟩ slip system. (d) The atomic structure at 0.221 shear strain corresponding to highly softening Te₁–Te₁ bond along the (001)/⟨50–1⟩ slip system. The red dashed lines and red ellipses displayed in Figs. 2(d) highlight the van der Waals Te₁–Te₁ bond softening.

stiffness. To determine bond-response processes, we extracted the atomic configurations at critical strains and bond length changes, as shown in Figs. 2(b)–2(d). The van der Waals Te₁–Te₁ interactions dominate the ideal shear strength and its deformation modes of crystalline Bi₂Te₃. Along the (001)/⟨50–1⟩ slip system, the weak van der Waals Te₁–Te₁ interatomic distance stretches rapidly, with a bond stretching ratio of 42.5% at 0.22 shear strain. The Bi–Te₁ and Bi–Te₂ bonds exhibit negligible stretching, suggesting that the Te₁–Bi–Te₂–Bi–Te₁ substructure remains intact during the shear process. The atomic structures show clearly that the Te₁–Te₁ bond resists external deformation while the Te₁–Bi–Te₂–Bi–Te₁ substructure holds together. These deformation modes for the (001)/⟨502⟩ and (001)/⟨210⟩ slip systems are similar as shown in Figs. S3 and S4 in the Supplemental Material [39].

We find that nanotwins in Bi₂Te₃ dramatically change the material’s strength and its deformation mechanisms. To illustrate these effects, we used DFT to probe the shear deformation of the nanotwinned Bi₂Te₃ along the TBs, as shown in Fig. 3. In the elastic stage with shear strain less than 4%, the slope of the stress-strain response for nano-twinned Bi₂Te₃ is 59% higher than that of single crystalline Bi₂Te₃, illustrating the strengthening effect of the nanotwins. Indeed, we find that nanotwinned Bi₂Te₃ displays an ideal shear stress of 0.60 GPa, which is more than 3 times higher than that of single crystalline Bi₂Te₃ (0.19 GPa). This suggests that nanotwins can superstrengthen Bi₂Te₃.

In addition, the sudden drop of shear stress in twinned Bi₂Te₃ [Fig. 3(a)] indicates the brittle failure, totally different from the plastic deformation in single crystalline Bi₂Te₃. These can be attributed to intriguing bond rearrangements near the TBs. The newly formed Te₁(1)–Te₁(2) and Te₁(2)–Te₁(3) bonds (3.48 Å), which are considered weak covalent bonds, strengthen the interactions between different substructures. When nanotwinned Bi₂Te₃ is sheared [Fig. 3(c)], the lower half part shears along the same shear direction as single crystalline Bi₂Te₃, leading to the stretching of the Te₁(2)–Te₁(3) and Te₁(6)–Te₁(7) bonds [Fig. 3(b)]. However, the upper half part shears along the opposite shear direction, leading to a compression of the Te₁(1)–Te₁(2) and Te₁(4)–Te₁(5) bonds [Fig. 3(b)]. The newly formed Te₁(2)–Te₁(3) bond has a much smaller stretching ratio than the van der Waals

FIG. 3. Deformation modes of nanotwinned Bi₂Te₃ with TBs along the {702} plane. (a) The shear-stress–shear-strain relationships of nanotwinned Bi₂Te₃ compared with single crystalline Bi₂Te₃. (b) The bond stretching ratio [Te₁(1)–Te₁(2), Te₁(2)–Te₁(3), Te₁(4)–Te₁(5), Te₁(6)–Te₁(7)] with the increasing shear strain. (c) The atomic structure at 0.123 shear strain corresponding to the maximum shear stress. (d) The atomic structure at 0.134 shear strain corresponding to the breakage of Te₁(2)–Te₁(3) bond. (e) The atomic structure at 0.145 shear strain corresponding to the structural failure. The gray dashed line in Fig. 3(b) represents the critical strain before failure. The red ellipses displayed in Figs. 3(e) highlight the breakage of Te₁(2)–Te₁(3) and Te₁(1)–Te₁(2) bonds. The black curve in Fig. 3(e) guides the collapsed TBs.
The Te(6)–Te(7) bond, indicating the Te(1)(2)–Te(1)(3) bond is much stronger than the Te(1)(6)–Te(1)(7) bond in resisting external deformation, resulting in the strengthening effect of nanotwins at the elastic stage as shown in Fig. 3(a). Moreover, the strong Te(1)(1)–Te(1)(2) and Te(1)(2)–Te(1)(3) bonds suppress the softening of the van der Waals Te(1)–Te(1) bonds near the TBs, giving rise to the super-strengthened nanotwin (0.60 GPa) compared to the single crystal (0.19 GPa). The shear strain (0.123) corresponding to the mechanical strength in nanotwinned Bi(2)Te(3) is much larger than that (0.071) in single crystalline Bi(2)Te(3). This strain-stiffening effect would lead to the potential better manufacturability of this nanotwin. This effect is similarly found in inorganic crystalline solids [41], where the enhanced material’s strength mainly arises from newly formed atomic bonds under large structural deformations. At 0.134 shear strain, the Te(1)(2)–Te(1)(3) bond stretching ratio sharply increases from 8% to 17%. This indicates a highly softening or nonbonding interaction [Fig. 3(d)], leading to a sudden drop of the shear stress [Fig. 3(a)]. As shear strain increases to 0.145, the Te(1)(1)–Te(1)(2) bond breaks, destabilizing the TBs and resulting in structural failure [Fig. 3(e)]. This clearly suggests that this robust nanotwin leads to less plasticity compared with single crystalline Bi(2)Te(3).

In the other two nanotwinned Bi(2)Te(3) structures (Figs. S5–S6 in the Supplemental Material) [39], the nanotwins have no obvious influence on the mechanical properties because the TBs do not change the interaction between the Te(1)–Bi–Te(2)–Bi–Te(1) substructures which are coupled through their van der Waals Te(1)–Te(1) interactions.

Here, we compared the ideal shear strength of Bi(2)Te(3) with various high-performance TE materials [34,42–45]. As shown in Fig. 4, Bi(2)Te(3) has the lowest ideal shear strength (0.19 GPa) among all these TE materials, which can be attributed to the layered structure with very weak van der Waals Te(1)–Te(1) interactions. The calculated stretching force constant (SFC) [46] of a Te(1)–Te(1) bond using the atat code [47] is only 0.25 eV/Å², which is much lower than those of the Bi–Te2 bond (0.62 eV/Å²) and Bi–Te1 bond (2.24 eV/Å²). This well explains that the Te(1)–Te(1) bond is highly stretched to resist the deformation while the Te(1)–Bi–Te2–Bi–Te1 five-layer substructure holds together (Fig. 2), which is similarly found in layered SnSe [42]. Thus, Bi(2)Te(3) and SnSe exhibit low ideal strengths of 0.19 and 0.59 GPa, respectively, because the van der Waals-like bonding interactions dominate the shear deformations. In La(2)Te(4), Mg(2)Sb(2), CaMg(2)Sb(2), and CaZn(2)Sb(2), the ionic bonds are responsible for the ideal strength and deformation modes [43,44], leading to a higher ideal strength compared with that in Bi(2)Te(3), as shown in Fig. 4. Moreover, due to the strong covalent Co–Sb 3D framework in CoSb(3) and even much stronger TiSn 3D framework in TiNiSn, CoSb(3) and TiNiSn show an extremely high ideal strength of 7.17 and 10.52 GPa, respectively [34,45].

The weak van der Waals interaction between Te(1)–Bi–Te2–Bi–Te1 substructures leads to a significantly low ideal strength in bulk Bi(2)Te(3). However, in nanotwinned Bi(2)Te(3), a newly formed covalent bond in the vicinity of TBs can remarkably enhance the coupling interaction between different substructures, which strongly improves the structural stiffness. This suppresses the structural softening and strengthens the material as embedded in Fig. 4. This structure-stiffening mechanism can well explain recent experimental results reporting that Bi(2)Te(3) with TBs shows an eightfold and a sixfold increase in the compressive and flexural strength, respectively, compared with those of single crystalline Bi(2)Te(3) [29].

The mechanical properties of real samples of Bi(2)Te(3) are closely related to defects such as GBs and vacancies that are ubiquitous in real materials. Studying GB effects requires cell sizes much larger than practical for DFT. Thus, future studies fitting the DFT results in this Letter to a reactive force field for molecular dynamics simulations will be useful for testing how such defects affect the strength.

Here we examined how nanotwins influence the mechanical properties of Bi(2)Te(3) TE material. Previous experimental studies showed that nanotwins could be used...
to tailor the electronic structure and to suppress the lattice thermal conductivity of Bi$_2$Te$_3$ [29,40]. This is worthy of future studies.

In summary, we applied DFT to determine the role of nanowires on mechanical properties of Bi$_2$Te$_3$ revealing that the newly generated Te1—Te1 covalent bonds in the vicinity of the twin boundary significantly improves the coupling interaction between Te1—Bi—Te2—Bi—Te1 five-layer substructures. Formation of nanowires remarkably enhances the structural stiffness while suppressing the structure softening, leading to a much higher ideal strength of 0.6 GPa in nanowinned Bi$_2$Te$_3$, compared to that of the single crystalline Bi$_2$Te$_3$ (0.19 GPa). Our work proposes a new TB engineering strategy to enhance the mechanical integrity of Bi$_2$Te$_3$, where the stronger structural stiffness can be achieved by a structural modification rather than a traditional elemental doping. This work opens a new pathway to rationally design robust high-performance TE materials, which can be also applied to other TE or non-TE materials.

Another exciting application of Bi$_2$Te$_3$ is as a topological insulator (TI) [49]. Goddard et al. have shown theoretically that Bi$_2$Te$_3$ is a TI, with spectacular states in the gap for Bi$_2$Te$_3$ [50]. It may be that the incorporation of the TBs could modulate the TI properties while strengthening the materials.

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*Corresponding author.
qia@unar.edu
†Corresponding author.
zhangqj@whut.edu.cn
‡Corresponding author.
jeff.snyder@northwestern.edu

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[39] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.119.085501 for a detailed description of the nanotwinned Bi$_2$Te$_3$ structure with the TB along the (001) and (210) plane, respectively; Bond-responding process of single crystalline Bi$_2$Te$_3$ along the (001)/(502) and (001)/(210) slip system, respectively; deformation modes of nanotwinned Bi$_2$Te$_3$ with TB along the (701) and (210) plane, respectively.

[46] The calculation of a stretching force constant is similar to frozen phonon calculations. The stretching force constant is calculated by fitting a spring model to the force matrix resulting from imposed atomic displacements. In each perturbed system, only a small atomic displacement (0.1 Å in our calculation) was imposed along each direction ($\pm x$, $\pm y$, or $\pm z$). The total energy is evaluated for each system with a displacement pattern, and the force constant matrix is obtained by the derivatives of the total energy with respect to the displacement.