The Mechanism of Deformation and Failure of In_4Se_3 Based Thermoelectric Materials

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Supporting Information

ABSTRACT: The layered In_4Se_3 based material is recognized as a state-of-the-art n-type thermoelectric material for the middle temperature range of 500 to 900 K. Despite excellent thermoelectric properties, its inferior mechanical properties restrict its commercial possibilities. In this work, we use quantum mechanics (density functional theory) to investigate the ideal strength and failure mechanisms of ideal and Se deficient In_4Se_3 under pure shear and biaxial shear loads. We found that the lowest ideal shear strength of ideal In_4Se_3 is 1.25 GPa along the (100)/<001> slip system. Slippage between the In/Se layer dominates its deformation and failure. With Se vacancies, the ideal strength of $\text{In}_4\text{Se}_{2.75}$ drops to 1.00 GPa, while the failure mechanism remains almost the same as that of ideal In_4Se_3 . Moreover, under biaxial shear loads (as in nanoindentation experiments), the ideal strength of In_4Se_3 increases to 1.50 GPa, with compression now accounting for the failure. Even so, In_4Se_3 shows poorer mechanical properties under biaxial shear loads. These insights into the deformation and failure mechanism of In_4Se_3 compounds should help suggest designing modifications to improve mechanical properties.

KEYWORDS: In_4Se_3 , DFT, ideal shear strength, mechanical properties, failure mechanism

1. INTRODUCTION

The diversification and efficient multilevel utilization of energy have become important to systematically solve the enormous energy and environmental problems facing humanity.¹ In particular, thermoelectric (TE) conversion technology provides a key technology to support many modern industries due to its advantages of flexibility, diversity, and reliability for providing green energy and environmentally friendly refrigeration technology.² The dimensionless thermoelectric figure of merit (ZT) provides an important criterion for judging the thermoelectric properties of TE materials. According to $ZT = \alpha^2 \sigma T / \kappa$, high-performance thermoelectric materials should have a high Seebeck coefficient α and a high electrical conductivity σ ($\alpha^2 \sigma$ is defined as “power factor”) but a low

thermal conductivity κ . These three important parameters determining the thermoelectric properties of materials are closely related, so that increasing or decreasing one of the parameters often leads to deleterious variation in other parameters.³ This is the root cause of the difficulty in continuously improving the thermoelectric performance ZT . Consequently, the research in thermoelectric materials has focused on improving ZT , leading to development of successful material design theory and multiscale structural regulation strategies for improved thermoelectric, such as band engineer-

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Table 1. Calculated Slip Systems and Detailed Information

slip systems	<i>a</i> , <i>b</i> , <i>c</i> directions	supercell	gamma <i>k</i> -point reciprocal space sampling
(100)/<001>	<001>, <0-10>, <100>	4×1×1 (112 atoms)	5×5×5
(100)/<010>	<010>, <001>, <100>	1×4×1 (112 atoms)	5×5×5
(010)/<001>	<001>, <100>, <010>	4×1×1 (112 atoms)	5×5×5
(110)/<100>	<100>, <00-1>, <110>	1×4×1 (112 atoms)	3×3×3
(-110)/<110>	<110>, <00-1>, <-110>	1×1×1 (56 atoms)	3×10×3

ing,^{4–6} alloy solid solution,^{7,8} phonon resonance scattering,^{9,10} and nanocomposites.^{11,12} Despite this continuous development of improved *ZT* values, widespread industrial application of thermoelectric materials has not been realized. A main reason is the poor mechanical properties of thermoelectric materials.¹³ This makes the mechanical behavior and failure mechanisms of materials under static and dynamic loads a key issue in the development and application of TE materials. Macroscopic properties are affected by various scales, and the characteristics of materials are derived from the atomic configuration and microstructure of the materials. Therefore, understanding the microscopic physical nature of material mechanical behavior and the factors controlling the mechanical properties of materials are essential for developing robust TE materials.

Layered In₄Se₃ is a promising state-of-the-art n-type thermoelectric materials in the middle temperature range.^{14,15} It has unique layer crystal structure that leads to strong electron–phonon coupling arising from charge density waves (CDW) and Peierls lattice distortion in the layer plane that break the lattice translational symmetry to enhance random disorder. This effectively increases the Seebeck coefficient while decreasing thermal conductivity.^{16,17} Indeed, Rhyee et al. reported that In₄Se_{3–x} (*x* = 0.65) crystal achieves a high *ZT* value of 1.48 in the *b*–*c* plane at 705 K.¹⁶ Unfortunately, the electrical conductivity of In₄Se_{3–x} crystals is much smaller than other classical TE materials. One approach to optimize electrical conductivity is to introduce Se vacancies to regulate the carrier concentration.^{18,19} Thus, doping with various element can also enhance the *ZT* value of In₄Se₃.^{20–22} For example, doping with Cl into In₄Se_{3–x} single crystal has been used to optimize carrier concentration to enhanced the figure of merit over a wide temperature range, reaching a quite high *ZT* of 1.53 at 698 K.²¹ In order to decrease costs, polycrystalline In₄Se₃ is attractive because of its isotropic nature and relatively low cost.^{23–26} The Pb/Sn multiple-dopant polycrystalline In₄Pb_{0.01}Sn_{0.03}Sn₃ showed a remarkable *ZT* value of 1.4, comparable to In₄Se₃ single crystal.²⁵ Wu et al. reported that Se deficiency combined with CuI nanodoped In₄Se₃ polycrystalline obtains a *ZT* value 80% higher than undoped.²⁶ Despite this series of research making improvement in *ZT*, the mechanical properties of In₄Se₃ so important for practical application have not yet been studied.

In this paper, we use density function theory (DFT) to examine the mechanical behavior of ideal and Se deficient In₄Se₃ under pure shear and bi-shear (shear and compression) loads. We find that the (100)/<001> slip system has the lowest ideal shear strength (1.25 GPa), which agrees well with experimental observations that layered In₄Se₃ cleaves along the (100) plane.²⁷ During shear deformation, we find that the weak In–Se van der Waals bond, connecting the In/Se layers, softens and creates slippage that leads finally to the structure failure. Although Se deficient In₄Se₃ exhibits improved TE properties, the Se vacancy lowers its mechanical properties. Thus, the ideal strength of In₄Se_{2.75} drops to 1.00 GPa with a

deformation and failure mechanism similar to In₄Se₃. Moreover, the In₄Se₃ failure process accelerates under bi-shear loads even though the ideal strength increases to 1.50 GPa. We find that compression accounts for a larger proportion of structural failure than shearing. This ideal strength of In₄Se₃ is better than other excellent layer TE materials, such as SnSe (0.59 GPa) and Bi₂Te₃ (0.19 GPa),^{28,29} but it is much lower than the other ionic and covalent TE materials, like Mg₃Sb₂ (1.95 GPa),³⁰ BiCuSeO (2.0 GPa),³¹ PbTe (3.46 GPa),³² CoSb₃ (7.17 GPa),³³ and TiNiSn (10.52 GPa).³⁴ Thus, for commercial applications of In₄Se₃, we still need to strengthen the mechanical properties.

2. METHODOLOGY

All relaxation and shear calculations were performed using density function theory with the generalized gradient approximation (GGA) to include electronic exchange–correlation with Perdew–Burke–Ernzerhof (PBE) functional. We used the projected augmented wave (PAW) method as implemented in the Vienna Ab initio Simulation Package (VASP).³⁵ The In₄Se₃ unit cell convergence test shows that the plane wave cutoff of 500 eV gives good convergence for the total energies. We set 1×10^{-6} eV energy difference and 1×10^{-2} eV/Å force as the convergence criteria for solving the electronic wave function and geometry optimization. In the *k*-point reciprocal space sampling, we adopted the gamma-centered Monkhorst–Pack scheme with a fine resolution of $2\pi \times 1/40 \text{ Å}^{-1}$ in all DFT calculations. The fully relaxed In₄Se₃ unit cell parameter is *a* = 15.586 Å, *b* = 12.548 Å, *c* = 4.185 Å, which is only 1.90%, 1.94%, and 2.42% larger than the experimental value of *a* = 15.296 Å, *b* = 12.308 Å, *c* = 4.086 Å at room temperature.³⁶

Consistent with dislocation theory, we assume that shear stress is the driving force of dislocation motion. Thus, we studied the response of In₄Se₃ under shear loads. For all DFT shearing calculations, we obtained relaxed crystal structure by altering the lattice parameter in a certain direction with a gradient of 1% and fixing it, then optimizing the remaining five lattice parameters with the positions of all atoms. The detailed description is provided in our previous work.^{33,37} We considered five slip systems for the shear calculations, and the detailed information on supercells with redefined lattices are listed in Table 1.

3. RESULTS AND DISCUSSION

3.1. Crystal Structure of In₄Se₃. Layered In₄Se₃ has an orthorhombic structure belonging to the *Pnmm* space group (No. 58).¹⁴ It contains four elementary units within the unit cell. For each elementary unit, there are seven independent coordinate atoms (four In atoms and three Se atoms) at the 4g Wyckoff sites as shown in Figure 1. The metallic quasi-one-dimensional (1D) In1–In3 (In/In) chains covalent bonded with Se atoms to create [(In₃)⁵⁺(Se₃)^{6–}][–] zigzag clusters (In/Se pentagon frameworks). The [(In₃)⁵⁺(Se₃)^{6–}][–] clusters

Figure 1. Crystal structure of In_4Se_3 . (Parallel view of the a - b plane. In atoms are rose red spheres; Se atoms are green spheres.)

extend along the b - c plane to form quasi-two-dimensional (2D) corrugated In/Se layers, while the In/Se layers are stacked along the a -axis direction through weak van der Waals interaction. Furthermore, the In4 atoms sit between the layers to strengthen the layer-layer interaction by weak ionic bond.

3.2. Elastic Properties of In_4Se_3 . The elastic constants provide important characterizations of mechanical properties, indicating the ability of a material to retain its inherent shape and size under external forces. We calculated the elastic constants (C_{11} , C_{12} , C_{13} , C_{22} , C_{23} , C_{33} , C_{44} , C_{55} , C_{66}) of both In_4Se_3 and $\text{In}_4\text{Se}_{2.75}$ since intrinsic Se deficiency exists in In_4Se_3 based materials. Using the Voigt-Reuss-Hill calculation method,^{38–40} we obtain the elasticity mechanical properties, such as bulk modulus B , shear modulus G , elastic modulus E , Poisson's ratio ν and toughness index B/G . The calculation results of $\text{In}_4\text{Se}_{2.75}$ in Table 2 are basically consistent with the experimental values, which validates the calculations. The small discrepancy between the calculated and experimental value for $\text{In}_4\text{Se}_{2.75}$ may be because the Se deficient ratio of In_4Se_3 cannot be determined exactly. Based on Frantsevich's criteria,⁴¹ when B/G is less than 2.67, the material always features brittle character. The B/G of In_4Se_3 is 1.61, suggesting it is a brittle material.

3.3. Deformation and Failure Mechanism. **3.3.1. Ideal Shear Strength of In_4Se_3 .** Although elastic modulus and related theories are widely used in qualitative analysis of the mechanical properties of materials, these parameters (elastic modulus, shear modulus, and Young's modulus) are obtained within the elastic limit of a small strain range. Thus, they cannot predict the mechanical properties of materials subjected to large strain accurately. Calculations of ideal strength and deformation mechanism provide the possibility to compute the

mechanical properties of materials under the large strain. The ideal strength of a material can be obtained by a stress-strain relationship. Hence, we calculated the shear-stress response against shear strains along various slip systems for In_4Se_3 crystal, as shown in Figure 2. The stresses are proportional

Figure 2. Calculated shear stress vs strain of In_4Se_3 for different shear directions. (100)/<001> has the lowest critical stress of 1.25 GPa and is the most ductile, returning to zero stress at 0.20 strain. (110)/<100> has the highest critical shear stress of 2.35 GPa.

to the strains in all simulated systems at the initial stage. Shear in the (100)/<001> and (-110)/<110> slip system leads to a short yielding stage. The (100)/<001> slip system is much weaker than the other four in resisting external deformation, and the ideal shear strength, which is defined as the first maximum stress point, is found to be 1.25 GPa. The (010)/<001>, (100)/<010>, and (110)/<100> slip systems show the similar resistance under the pure shear load. The (010)/<001> structure undergoes a structural rearrangement at the strain of 0.173, with shear stress releasing from 1.59 to 0.92 GPa. The (110)/<100> slip system has the largest ideal shear strength of 2.35 GPa. This is because the covalent In-Se bond is much stronger than the van der Waals-like In-Se bond. As a layered compound connected by van der Waals interactions, the ideal shear strength (1.25 GPa) of In_4Se_3 is much higher than the other high-performance layered TE materials such as SnSe (0.59 GPa) and Bi_2Te_3 (0.19 GPa),^{28,29} probably due to the stronger In-Se interaction compared with Sn-Se interaction in SnSe and Te-Te interaction in Bi_2Te_3 .

3.3.2. Deformation Mechanism of In_4Se_3 under Shear Loads. To understand the stress-strain curve analysis, we analyzed the deformation mechanism in terms of the internal chemical bonds and atomic configuration. To elucidate the failure mechanism of In_4Se_3 , the typical structural patterns of In_4Se_3 crystal along (100)/<001> slip system are shown in

Table 2. Calculated Independent Elastic Constants (C_{11} , C_{12} , C_{13} , C_{22} , C_{23} , C_{33} , C_{44} , C_{55} , C_{66}) and Other Related Elastic Properties: Bulk Modulus (B), Shear Modulus (G), Elastic Modulus (E), Poisson's Ratio (ν), Ductility Index (B/G) of In_4Se_3 Based Materials and Comparison with Previous Molecular Calculations and Experimental Values^a

methods	C_{11}	C_{12}	C_{13}	C_{22}	C_{23}	C_{33}	C_{44}	C_{55}	C_{66}	B	G	E	ν	B/G
PBE (In_4Se_3)	63.2	23.3	39.4	87.1	16.1	76.2	17.0	39.9	39.2	42.6	26.6	66.0	0.24	1.61
PBE ($\text{In}_4\text{Se}_{2.75}$)	57.6	22.8	34.8	79.5	14.4	65.1	13.9	34.4	27.5	38.5	21.9	55.3	0.26	1.75
expt ⁴²	38.2	10.8	30.4	66.5	22.4	64.3	16.6	26.6	19.0	-	-	-	-	-
MD ⁴²	39.9	9.0	35.9	66.9	15.8	49.6	18.0	38.1	11.6	-	-	-	-	-
MD	49.8	15.6	26.1	58.9	21.7	52.2	18.7	33.0	16.1	-	-	-	-	-
MD ¹⁹	36.4	13.7	22.4	68.9	24.9	62.0	20.5	32.5	22.7	-	-	-	-	-

^aThe unit of elastic constants and various moduli are GPa. MD indicates molecular dynamics simulation using a force field instead of quantum mechanics. PBE indicates QM (DFT).

Figure 3. Structural changes of In_4Se_3 crystal along the $(100)/\langle 001 \rangle$ slip system under pure shear loads: (a) the initial atomic configuration, (b) the atomic configuration corresponding to the maximum stresses (strain = 0.094), (c) atomic configuration at the point of slipping (strain 0.127), (d) the failed structure at 0.196 strain, (e) various bond lengths and bond angle as a function of shear strain. The front and back layers are distinguished by deep and light colors.

Figure 3a–d. In the ideal structure (Figure 3a), the atoms are evenly ordered, and the In/Se layers overlap with each other in the a – c plane of the In_4Se_3 crystal. As the strain increases to 0.094, which corresponds to the maximum shear stress (1.25 GPa), the structure deforms uniformly to resist the external forces (Figure 3b). As the strain increases continuously to 0.127, the interlayers distort and a slightly slippage occurs between the layers (Figure 3c). When the strain reaches 0.196, the stress is released completely, with the atoms slipping from one equilibrium position to another (Figure 3d). During the whole shearing process, the In/Se pentagon framework structure within the layers changes little while there is a significant slippage between the layers. This is because the van der Waals intralayer interaction is much weaker than the covalent interlayer interactions.

To further understand the deformation mechanism of the $(100)/\langle 001 \rangle$ slip system of In_4Se_3 , we extract the critical intralayer bond lengths (In2–In3, In2–Se2, In3–Se3, In5–Se3, In5–Se2), interlayer bond length (In4–Se1), and the bond angle (In1–In2–In6) against shear strain (Figure 3e).

Plotting the In1–In2–In6 angle against shear strain is to clearly explain how In/Se layers slip with each other. The bond lengths of the In2–In3 and In5–Se2 bonds change slightly during the shearing process. In addition, the In2–Se2 and In5–Se3 bond lengths remain nearly unchanged before the shear strain reaches 0.127. Then these bonds elongate with increasing strain, from 2.756 to 2.847 Å and 2.693 Å to 2.704 Å, a stretching ratio of 3.3% and 0.41%, respectively. The In3–Se3 bond first changes slightly from 2.853 to 2.863 Å, then diminishes to 2.771 Å with a variation of 3.2% after a significant structural change at the strain of 0.127. The bond changes show clearly that the In/Se pentagon framework structure retains its structural integrity within the whole shearing process because all the bonds hold together with slight changes. Nevertheless, the In4–Se1 weak ionic bond length stretched remarkably from 3.202 to 3.664 Å in response to resist the shear deformation, leading to the short “yielding” stage. These bond deformations lead to a decrease in the In1–In2–In6 bond angle. The In1–In2–In6 angle decreases slowly at the same rate without sharp changes. At the beginning, the

Figure 4. Structural changes of In_4Se_3 crystal along the $(010)/\langle 001 \rangle$ slip system under pure shear loads: (a) the initial atomic configuration, (b) the atomic configuration before stress relaxation, (c) the atomic configuration after structural rearrangement, (d) various bond lengths and bond angle as a function of shear strain.

Figure 5. Structural patterns of In_4Se_3 crystal along the $(110)/\langle 100 \rangle$ slip system: (a) the initial atomic configuration, (b) the atomic configuration before structural failure, (c) the failed structure, (d) various bond lengths as a function of the shear strain.

In1-In2 and In2-In6 bonds are perpendicular to each other. With the continuously increased shear strain, the In1-In2-In6 bond angle becomes 76.06° at which point the structure can no longer resist external loads. The stretched In4-Se1 bond and the bent In1-In2-In6 bond angle lead to the structural slippage, accounting for the failure of In_4Se_3 .

Figure 4a–c shows the structural variation of the In_4Se_3 crystal under shearing along the $(010)/\langle 001 \rangle$ slip system while Figure 4d shows the critical bond lengths and bond angles as a function of shear strain. The shear stress increases monotonically as the shear strain increases to 0.173, then it undergoes a sudden drop from 1.59 to 0.92 GPa, indicating a

significant structural rearrangement. Below the shear strain of 0.173, corresponding to the maximum shear strength, the structure is slightly distorted to resist the deformation. As the strain increases to 0.184, the structure distorts further with the In1-In2-In3 angle changing from 152.34° to 133.79° without breakage of In/In chains. The bond lengths of In/Se pentagon framework (In2-In3 , In3-Se2 , In5-Se2 , In5-Se1 , In2-Se1) and the weak ionic In4-Se1 interlayer bond remain almost unchanged except for a slight twist around the critical shear strain 0.173. This shows that the structure is twisted to accommodate the deformation (Figure 4c,d). The In/In chains change to a more zigzag shape with a bent In1-In2-In3 bond

Figure 6. Structural changes for $\text{In}_4\text{Se}_{2.75}$ crystal along the (100)/<001> slip system under pure shear loads: (a) the shear stress–shear strain relationships for $\text{In}_4\text{Se}_{2.75}$, $\text{In}_4\text{Se}_{2.375}$, and In_4Se_3 , (b) the atoms configuration corresponding to the maximum stress point, (c) the failed structure, (d) various bond lengths and bond angle as a function of shear strain. The front and back layers are distinguished by deep and light colors.

angle, which leads to the structural weakening effects and release of the shear stress. While the (−110)/<110> slip system also presents a sudden drop of stress, its failure differs from that of (010)/<001>. There is no apparent structural rearrangement and the softened In4–Se2 bond dominates the structure failure, as presented in Supporting Information Figure S1.

We analyze the atomic configurations, bond lengths, and bond angles to understand the failure mechanism of (110)/<100> slip system plotted in Figure 5, which corresponds to the largest shear strength among all slip systems. It is clear that the structure deforms uniformly to resist the external loads until the strain of 0.335 (Figure 5a,b). With further shear strain increase to 0.349, the In4–Se3 bond length sharply increases to disconnect the pentagon framework. The newly formed In4–Se1 bond and disconnected pentagon framework suggest the structure cannot remain its rigidity (Figure 5c). The typical length of In–Se bonds are relatively unchanged until the failure strain of 0.335. Upon further increase in the strain, the In3–Se3 and In3–Se4 bond lengths change from 2.826 to 3.257 and 2.786 Å to 3.039 Å (Figure 5d). This results in disconnecting the pentagon framework and failure of In_4Se_3 . Except for the difference in fracture strain, the (100)/<010> slip system leads to almost the same shear-stress–strain relationship as the (110)/<100> slip system. However, the tilted In5–Se3 bond and increased Se2–In5–Se3 bond angle dominant the failure which is different from the (110)/<100> slip system as shown in Supporting Information Figure S2.

3.3.3. The Role of a Se Vacancy in the Mechanical Behavior of In_4Se_3 . A Se vacancy can increase the carrier concentration to enhance the ZT value, but its role on mechanical behavior has not been explored. To study the effect

of Se deficiency on the mechanical properties of In_4Se_3 , we chose $\text{In}_4\text{Se}_{2.75}$ and $\text{In}_4\text{Se}_{2.375}$ crystals since the Se vacancy of these two models lead to excellent TE performance. The formation energy calculation indicates that the Se3 site is most likely vacant.²² This is expected from crystal structure where Se3 atoms make less contribution in retaining structure rigidity. Thus, we considered only the Se3 atom vacancy in the following calculations. We constructed $1 \times 4 \times 4$ supercells to randomly distribute the vacancies, as shown in Supporting Information Figure S3.

Figure 6 shows the shear stress–strain response of $\text{In}_4\text{Se}_{2.75}$ and $\text{In}_4\text{Se}_{2.375}$ crystals is along the least stress slip system of In_4Se_3 , (100)/<001>. The ideal strength of $\text{In}_4\text{Se}_{2.75}$ and $\text{In}_4\text{Se}_{2.375}$ decrease to 1.00 and 1.08 GPa, respectively, much lower than the 1.25 GPa of ideal In_4Se_3 . The slopes of the response curves decrease gradually with increasing Se deficiency, suggesting that the mechanical stability of In_4Se_3 decreases with increasing the ratio of Se deficiency. This trend agrees well with the elastic modulus calculations, listed in Table 1. Figure 6b,c display the structural changes of $\text{In}_4\text{Se}_{2.75}$ showing no significant differences between the ideal and deficient crystals regarding the failure mode. As the strain increases to the failure strain, they all deform uniformly to resist the external deformation. Then, a relative slippage arises between the In/Se layers. Compared with the intact structure, the $\text{In}_4\text{Se}_{2.75}$ crystal is highly distorted around the neighbors to In4 atoms due to the absence of Se3 atoms, leading to large vacancies in the lattice that increasing the mobility of In atoms (a similar phenomenon for $\text{In}_4\text{Se}_{2.375}$ is presented in Supporting Information Figure S4). In addition, Figure 6d illustrates the bond length changes to provide an understanding of the effect of Se deficiency on mechanical behavior.

Figure 7. Structural patterns of In_4Se_3 crystal along $(100)/\langle 001 \rangle$ slip system under bilateral shear to mimic nanoindentation experiments: (a) the shear-stress–shear-strain relationship for bilateral shear compared with that of pure shear, (b) the atoms configuration before shearing, (c) the atomic configuration at the shear strain of 0.062, (d) the atomic configuration corresponding to the maximum stress point, (e) the structure after failure, (f) various bond lengths and c lattice parameter as a function of the shear strain.

Obviously, the In2-In3 , In2-Se2 , In3-Se3 , In5-Se3 , In5-Se2 bonds remain nearly stable for the whole period, showing the pentagonal frameworks remain nearly unchanged. The In4-Se1 bonds stretch remarkably from 3.462 to 5.258 Å while the In1-In2-In6 bond angle bends to 77.02° from strain 0 to 0.102. That is, the softening of In4-Se1 bond and In1-In2-In6 angle lead to the slippage between In/Se layers, hence the failure of $\text{In}_4\text{Se}_{2.75}$.

3.3.4. Simulation of Nanoindentation in In_4Se_3 . Nanoindentation technology can measure various mechanical properties at the nanoscale to characterize the mechanical behavior of a material. We simulate the nanoindentation experiment by applying bi-shear loadings on the In_4Se_3 system. Figure 7 provides insight into the ideal strength and failure mechanism of In_4Se_3 under bi-shear condition. Under bi-shear loads, the In_4Se_3 crystal displays an increased maximum shear stress (1.50 GPa) but a sudden destruction process (Figure

7a). As the shear strain increases to 0.062, the distance between layer decreases leading to a significant compression as presented in Figure 7b,c. As the shear strain increases further to 0.094, the layers remain connected as a whole (Figure 7d). After that, the structure can no longer retain its symmetry and destructs suddenly (Figure 7e). Figure 7e shows more detail information on how the length of In1-Se1 reduces dramatically, confirming the layer distance decreases. Furthermore, the sudden decrease in the c lattice parameter illustrates that the compression plays a more important role in the structural failure than shearing. The failure mechanism of $\text{In}_4\text{Se}_{2.75}$ under bi-shear loads is different from that of the In_4Se_3 system. It is the breaking of In3-Se3 and In5-Se2 bonds which leads to the collapse of In/Se pentagon frameworks (Supporting Information Figure S5).

4. CONCLUSIONS

In this work, we used DFT to explore the ideal shear strength and failure mechanism of In_4Se_3 based TE materials under pure shear and bi-shear loads. The main conclusions are

- The (100)/<001> is the easiest slip system of In_4Se_3 under shear loads leading to an ideal shear strength of 1.25 GPa. Here the structural failure involves slippage of In/Se layers connected by weak van der Waals interaction.
- The (110)/<100> slip system has the largest strength of 2.35 GPa.
- The Se deficiency reduces the mechanical properties of In_4Se_3 . Compared with intact structure, the strength of the Se-deficient structure $\text{In}_4\text{Se}_{2.75}$ drops to 1.00 GPa while the weak In/Se layers interaction dominate the structural softening and failure.
- Under bi-shear loads, the In_4Se_3 crystal displays an increased maximum shear stress (1.50 GPa); however, the sudden destruction process indicates that compression accelerates structural failure. The sudden decrease of c lattice parameter illustrates that compression plays an even more significant role in the failure of structure than shearing.

The ideal strength of In_4Se_3 is much lower than the other ionic and covalent TE materials, like Mg_3Sb_2 (1.95 GPa),³⁰ BiCuSeO (2.0 GPa),³¹ PbTe (3.46 GPa),³² CoSb_3 (7.17 GPa),³³ and TiNiSn (10.52 GPa).³⁴ Thus, In_4Se_3 must be strengthened for commercial applications.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsaem.9b02103>.

Shear deformation mechanisms of In_4Se_3 along the (-110)/<110> and (100)/<010> slip system; crystal structure of $\text{In}_4\text{Se}_{2.75}$ and $\text{In}_4\text{Se}_{2.375}$; shear deformation mechanism of $\text{In}_4\text{Se}_{2.375}$ along the (100)/<010> slip system; biaxial shear deformation mechanism of $\text{In}_4\text{Se}_{2.75}$ along (100)/<010> slip system (PDF)

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Notes

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■ REFERENCES

- (1) He, J.; Tritt, T. M. Advances in thermoelectric materials research: looking back and moving forward. *Science* **2017**, *357*, eaak9997.
- (2) Gaultois, M. W.; Sparks, T. W.; Borg, C. K. H.; Seshadri, R.; Bonificio, W. D.; Clarke, D. R. Data-driven review of thermoelectric materials: performance and resource considerations. *Chem. Mater.* **2013**, *25*, 2911–2920.
- (3) Zhu, T.; Liu, Y.; Fu, C.; Heremans, P. J.; Snyder, J. G.; Zhao, X. Compromise and synergy in high-efficiency thermoelectric materials. *Adv. Mater.* **2017**, *29*, 1605884.
- (4) Pei, Y.; Wang, H.; Snyder, G. J. Band engineering of thermoelectric materials. *Adv. Mater.* **2012**, *24*, 6125–6135.
- (5) Tan, G.; Zhao, L.; Kanatzidis, M. G. Rationally designing high-performance bulk thermoelectric materials. *Chem. Rev.* **2016**, *116*, 12123–12149.
- (6) Pei, Y.; Shi, X.; Lalonde, A.; Wang, H.; Chen, L.; Snyder, G. J. Convergence of electronic bands for high performance bulk thermoelectrics. *Nature* **2011**, *473*, 66–69.
- (7) Meisner, G. P.; Morelli, D. T.; Hu, S.; Yang, J.; Uher, C. Structure and lattice thermal conductivity of fractionally filled skutterudites: solid solutions of fully filled and unfilled end members. *Phys. Rev. Lett.* **1998**, *80*, 3551–3554.
- (8) Wang, H.; Lalonde, A. D.; Pei, Y.; Snyder, G. J. The criteria for beneficial disorder in thermoelectric solid solutions. *Adv. Funct. Mater.* **2013**, *23*, 1586–1596.
- (9) Yang, J.; Zhang, W.; Bai, S.; Mei, Z.; Chen, L. Dual-frequency resonant phonon scattering in $\text{Ba}_x\text{R}_y\text{Co}_4\text{Sb}_{12}$ ($\text{R} = \text{La}, \text{Ce}, \text{and Sr}$). *Appl. Phys. Lett.* **2007**, *90*, 192111.
- (10) Shi, X.; Kong, H.; Li, C.; Uher, C.; Yang, J.; Salvador, J. R.; Wang, H.; Chen, L.; Zhang, W. Low thermal conductivity and high thermoelectric figure of merit in n-type $\text{Ba}_x\text{Yb}_y\text{Co}_4\text{Sb}_{12}$ double-filled skutterudites. *Appl. Phys. Lett.* **2008**, *92*, 182101.
- (11) Faleev, S. V.; Léonard, F. Theory of enhancement of thermoelectric properties of materials with nanoinclusions. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2008**, *77*, 214304.
- (12) Yamini, S. A.; Wang, H.; Ginting, D.; Mitchell, D. R. G.; Dou, S. X.; Snyder, G. J. Thermoelectric performance of n-type $(\text{PbTe})_{0.75}(\text{PbS})_{0.15}(\text{PbSe})_{0.1}$ Composites. *ACS Appl. Mater. Interfaces* **2014**, *6*, 11476–11483.
- (13) Twaha, S.; Zhu, J.; Yan, Y.; Li, B. (2016). A comprehensive review of thermoelectric technology: materials, applications, modeling and performance improvement. *Renewable Sustainable Energy Rev.* **2016**, *65*, 698–726.
- (14) Yin, X.; Liu, J.; Chen, L.; Wu, L. High thermoelectric performance of In_4Se_3 -based materials and the influencing factors. *Acc. Chem. Res.* **2018**, *51*, 240–247.
- (15) Rhyee, J. S.; Kim, J. H. Chemical potential tuning and enhancement of thermoelectric properties in indium selenides. *Materials* **2015**, *8*, 1283–1324.
- (16) Rhyee, J. S.; Lee, K. H.; Lee, S. M.; Cho, E.; Kim, S. I.; Lee, E.; Kwon, Y. S.; Shim, J. H.; Kotliar, G. Peierls distortion as a route to high thermoelectric performance in $\text{In}_4\text{Se}_{3-x}$ crystals. *Nature* **2009**, *459*, 965–968.
- (17) Rhyee, J. S.; Cho, E.; Lee, K. H.; Lee, S. M.; Kim, S. I.; Kim, H. S.; Kwon, Y. S.; Kim, S. J. Thermoelectric properties and anisotropic electronic band structure on the $\text{In}_4\text{Se}_{3-x}$ compounds. *Appl. Phys. Lett.* **2009**, *95*, 212106.
- (18) Zhu, G.; Lan, Y.; Wang, H.; Joshi, G.; Hao, Q.; Chen, G.; Ren, Z. Effect of selenium deficiency on the thermoelectric properties of n-type $\text{In}_4\text{Se}_{3-x}$ compounds. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2011**, *83*, 115201.

- (19) Ji, H. S.; Kim, H.; Lee, C.; Rhyee, J. S.; Kim, M. H.; Kaviani, M.; Shim, J. H. Vacancy-suppressed lattice conductivity of high-ZT $\text{In}_4\text{Se}_{3-x}$. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2013**, *87*, 793–799.
- (20) Ahn, K.; Cho, E.; Rhyee, J. S.; Kim, S. I.; Lee, S. M.; Lee, K. H. Effect of cationic substitution on the thermoelectric properties of $\text{In}_{4-x}\text{M}_x\text{Se}_{2.95}$ compounds ($\text{M} = \text{Na}, \text{Ca}, \text{Zn}, \text{Ga}, \text{Sn}, \text{Pb}; x = 0.1$). *Appl. Phys. Lett.* **2011**, *99*, 102110.
- (21) Rhyee, J. S.; Ahn, K.; Lee, K. H.; Ji, H. S.; Shim, J. H. Enhancement of the thermoelectric figure-of-merit in a wide temperature range in $\text{In}_4\text{Se}_{3-x}\text{Cl}_{0.03}$ bulk crystals. *Adv. Mater.* **2011**, *23*, 2191–2194.
- (22) Ahn, K.; Cho, E.; Rhyee, J. S.; Kim, S. I.; Hwang, S.; Kim, H. S.; Lee, S. M.; Lee, K. H. Improvement in the thermoelectric performance of the crystals of halogen-substituted $\text{In}_4\text{Se}_{3-x}\text{H}_{0.03}$ ($\text{H} = \text{F}, \text{Cl}, \text{Br}, \text{I}$): effect of halogen-substitution on the thermoelectric properties in $\text{In}_4\text{Se}_{3-x}$. *J. Mater. Chem.* **2012**, *22*, 5730.
- (23) Kim, J. H.; Kim, M. J.; Oh, S.; Rhyee, J. S. Thermoelectric properties of Se-deficient and Pb-/Sn-codoped $\text{In}_4\text{Pb}_{0.01}\text{Sn}_{0.03}\text{Se}_{3-x}$ polycrystalline compounds. *J. Alloys Compd.* **2014**, *615*, 933–936.
- (24) Zhan, H.; Peng, K.; Alsharafi, R.; Chen, Q.; Yao, W.; Lu, X.; Wang, G.; Sun, X.; Zhou, X. Thermoelectric properties of Ce/Pb Co-doped polycrystalline $\text{In}_{4-x}\text{Ce}_x\text{Pb}_{0.01}\text{Se}_3$ Compounds. *J. Electron. Mater.* **2017**, *46*, 3215–3220.
- (25) Lin, Z.; Chen, L.; Wang, L.; Zhao, J.; Wu, L. A promising mid-temperature thermoelectric material candidate: Pb/Sn-codoped $\text{In}_4\text{Pb}_x\text{Sn}_y\text{Se}_3$. *Adv. Mater.* **2013**, *25*, 4800–4806.
- (26) Chen, Y.; Lin, H.; Wu, L. High thermoelectric performance of polycrystalline $\text{In}_4\text{Se}_{3-6}(\text{Cu})_x$: synergistic effect of Se-deficiency and CuI-doping. *Inorg. Chem. Front.* **2016**, *3*, 1566–1571.
- (27) Losovyj, Y. B.; Klinke, M.; Cai, E.; Rodriguez, I.; Zhang, J.; Makinistian, L.; Petukhov, A. G.; Albanesi, E. A.; Galiy, P.; Fiyala, Y.; Liu, J.; Dowben, P. A. The electronic structure of surface chains in the layered semiconductor $\text{In}_4\text{Se}_3(100)$. *Appl. Phys. Lett.* **2008**, *92*, 122107.
- (28) Li, G.; Aydemir, U.; Wood, M.; Goddard, W. A.; Zhai, P.; Zhang, Q.; Snyder, G. J. Ideal strength and deformation mechanism in high-efficiency thermoelectric SnSe. *Chem. Mater.* **2017**, *29*, 2382–2389.
- (29) Li, G.; Aydemir, U.; Morozov, S. I.; Wood, M.; An, Q.; Zhai, P.; Zhang, Q.; Goddard, W. A.; Snyder, G. J. Superstrengthening Bi_2Te_3 through nanotwinning. *Phys. Rev. Lett.* **2017**, *119*, 085501.
- (30) Li, G.; Aydemir, U.; Wood, M.; An, Q.; Goddard, W. A.; Zhai, P.; Zhang, Q.; Snyder, G. J. Deformation mechanisms in high-efficiency thermoelectric layered Zintl compounds. *J. Mater. Chem. A* **2017**, *5*, 9050.
- (31) Li, G.; Hao, S.; Morozov, S. I.; Zhai, P.; Zhang, Q.; Goddard, W. A.; Snyder, G. J. Grain boundaries softening thermoelectric oxide BiCuSeO . *ACS Appl. Mater. Interfaces* **2018**, *10*, 6772–6777.
- (32) Li, G.; Aydemir, U.; Duan, B.; Agne, M.; Wang, H.; Wood, M.; Zhang, Q.; Zhai, P.; Goddard, W. A.; Snyder, G. J. Micro- and macro-mechanical properties of thermoelectric lead chalcogenides. *ACS Appl. Mater. Interfaces* **2017**, *9*, 40488–40496.
- (33) Li, G.; An, Q.; Li, W.; Goddard, W. A.; Zhai, P.; Zhang, Q.; Snyder, G. J. Brittle failure mechanism in thermoelectric skutterudite CoSb_3 . *Chem. Mater.* **2015**, *27*, 6329–6336.
- (34) Li, G.; An, Q.; Aydemir, U.; Goddard, W. A.; Wood, M.; Zhai, P.; Zhang, Q.; Snyder, G. J. Enhanced ideal strength in the thermoelectric Half-Heusler TiNiSn by sub-structure engineering. *J. Mater. Chem. A* **2016**, *4*, 14625.
- (35) Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **1996**, *6*, 15–50.
- (36) Schwarz, U.; Hillebrecht, H.; Deiseroth, H. J.; Walther, R. In_4Te_3 und In_4Se_3 : Neubestimmung der Kristallstrukturen, druckabhängiges Verhalten und eine Bemerkung zur Nichtexistenz von In_4S_3 . *Zeitschrift Für Kristallographie*. **1995**, *210*, 342–347.
- (37) Li, G.; Morozov, S. I.; Zhang, Q.; An, Q.; Zhai, P.; Snyder, G. J. Enhanced strength through nanotwinning in the thermoelectric semiconductor InSb . *Phys. Rev. Lett.* **2017**, *119*, 215503.
- (38) Chung, D. H. Elastic moduli of single crystal and polycrystalline MgO . *Philos. Mag.* **1963**, *8*, 833–841.
- (39) Wu, Z.; Zhao, E.; Xiang, H.; Hao, X.; Liu, X.; Meng, J. Crystal structures and elastic properties of superhard IrN_2 and IrN_3 from first principles. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2007**, *76*, 54115.
- (40) Pugh, S. F. Relationship between the Elastic Moduli and the Plastic Properties of Polycrystalline Pure Metals. *Philos. Mag.* **1954**, *45*, 823–843.
- (41) Vaitheeswaran, G.; Kanchana, V.; Kumar, R. S.; Cornelius, A. L.; Nicol, M. F.; Svane, A.; Delin, A.; Johansson, B. High-pressure structural, elastic, and electronic properties of the scintillator host material KMgF_3 . *Phys. Rev. B: Condens. Matter Mater. Phys.* **2007**, *76*, 14101–14107.
- (42) Bercha, D. M.; Rushchanskii, K. Z.; Sznajder, M. Phonon spectrum of the layered In_4Se_3 crystal. *Phys. Status Solidi B* **1999**, *212*, 247–261.