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Grain Boundaries Softening Thermoelectric Oxide BiCuSeO

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Abstract: Engineering grain boundaries (GBs) is effective in tuning the thermoelectric (TE) properties of TE materials, but the role of GB on mechanical properties, which is important for their commercial applications, remain unexplored. In this paper, we apply *ab-initio* method to examine the ideal shear strength and failure mechanism of GBs in TE oxide BiCuSeO. We find that the ideal shear strength of the GB is much lower than that of the ideal single crystal. The atomic rearrangements accommodating the lattice and neighbor structure mismatch between different grains leads to the much weaker GB stiffness compared with grains. Failure of the GBs arises from either the distortion of the Cu-Se layers or the relative slip between Bi-O and Cu-Se layers. This work is crucial to illustrate the deformation of GBs, laying the basis for the development and design of mechanically robust polycrystalline TE materials.

Keywords: Atomistic modeling; Micro-mechanics; Grain boundary softening; Thermoelectric oxide BiCuSeO

1. INTRODUCTION

Since the 21st century, various environmental issues, which are caused by the excessive consumption of fossil fuels, are restricting the global ecological development. To balance the environment and economic development, it is extremely urgent to explore the eco-friendly and sustainable clean energy technology. Thermoelectrics (TEs), a type of solid-state technology capable of converting thermal energy into electrical energy, has potential important applications in solving the global energy and environmental crisis.¹ TE power generators, which are silent, scalable, and reliable devices without any mechanical moving parts, have been successfully applied in the radioisotope space power systems for NASA's missions and are being considered as an automobile exhaust heat recovery device.² An excellent TE material should simultaneously possess high conversion efficiency (the figure of merit, zT) and robust mechanical properties. During the past two decades, various novel concepts and advanced synthesis techniques have made the rapid progress in developing high-performance TE materials with high zT values.³⁻⁸ However, under the working conditions of TE devices, the thermal expansion coefficient difference between TE materials and the joint metal would dramatically degrade the thermo-mechanical reliability performance, resulting in the fatigue crack and failure of TE materials.^{9,10} Therefore, robust mechanical properties such as the attainment of strength or toughness are significant application requirements for TE materials.

TE oxides have received wide attention because of their high chemical stability and environmental compatibility.¹¹⁻¹³ In 2010, layered oxide BiCuSeO was found to be a potential high-performance TE oxide.¹⁴ The intrinsically low thermal conductivity of BiCuSeO (<1 W/mK) indicates that improving the power factor is an effective approach to optimize its TE properties.¹⁴ Since then, various optimization strategies such as hole carrier concentration optimization, band structure modification, as well as enhancing the hole carrier mobility, have been extensively developed to successfully increase the zT value from 0.4 to ~ 1.4 ,¹⁵⁻¹⁸ indicating that oxide BiCuSeO have become a strong candidate for TE applications in the high temperature range. Meanwhile, it requires as well that BiCuSeO has excellent mechanical properties and maintains the expected thermo-mechanical reliability during severe working conditions. However, the mechanical properties of BiCuSeO are seldom studied.

Recently, engineering GBs was reported as a novel strategy to optimize the power factor and thermal conductivity of TE materials.¹⁹⁻²¹ In 2015, Kim *et al.* reported that the zT value of Bi_{0.5}Sb_{1.5}Te₃ alloys can be enhanced to 1.86 at room temperature by remarkably reducing the lattice thermal conductivity through an effective GB scattering mechanism.¹⁹ In 2017, Zhang *et al.* achieved a high-performance bulk Yb-filled CoSb₃ TE material with a zT value of 1.43 at ~ 900 K

through the addition of carbon nanotubes at GBs. This results in the TE power generation modules demonstrating a high conversion efficiency of 9.3%.²⁰ Whereas, Tang *et al.* found that the GB scattering, which dominates the scattering mechanism in polycrystalline SnSe, is the origin why polycrystalline SnSe samples exhibit much lower electrical transport properties compared with its single-crystalline samples.²¹ GBs play an essential role in TE performance, but their influences on mechanical properties are still unexplored so far.

To illustrate the role of GBs on mechanical properties of TE oxide BiCuSeO, we employed *ab-initio* calculations to investigate the GB structure, the stress response against shear-strain, and the failure mechanism. Firstly, we studied the interfacial formation energies of many possible GB configurations, and found that BiCuSeO(100)/BiCuSeO(110) with the GB coupled with Cu–Se or Bi–Se interaction, which we named CuSe_GB or BiSe_GB, is energetically favorable. The CuSe_GB and BiSe_GB are found to have the ideal shear strengths of 0.41 and 0.15 GPa, respectively, which are much lower than that (2.0 GPa) of the ideal single-crystalline BiCuSeO. Atomic rearrangements in the GB largely weaken the GB stiffness. Failure of the CuSe_GB arises from the distortion of the Cu–Se layer and the Cu-Se bond breakage, while failure of the BiSe_GB arises from the relative slip between Cu–Se and Bi–O layers.

2. METHODOLOGY

ab-initio density functional theory (DFT) calculations were implemented within the VASP code, utilizing the project augmented wave (PAW) framework and generalized gradient approximation (GGA) - Perdew-Burke-Ernzerhof (PBE) exchange-correlation potential.²²⁻²⁴ The $6s^2 6p^3$ electrons of Bi, $3d^{10} 4s^1$ electrons of Cu, $4s^2 4p^4$ electrons of Se, and $2s^2 2p^4$ electrons of O were chosen as the valence state configuration. An energy cut-off of 500 eV was applied for the convergence on force and total energy. For Brillouin-zone integrations, an $11 \times 11 \times 5$ Monkhorst-Pack *k*-point sampling was used for the geometry optimization of BiCuSeO unit cell, while a $3 \times 3 \times 2$ Monkhorst-Pack scheme sampling is used for the structural relaxation and deformation of GBs. The detailed simulation setups are consistent with our previous published work on other important TE materials.²⁵⁻²⁷

3. RESULTS AND DISCUSSION

3.1 Crystal structure of BiCuSeO

Oxide BiCuSeO is a layered compound crystallizing in a ZrCuSiAs structure type with space group $P4/nmm$ (129). The crystal structure, which contains 8 atoms (2×Bi, 2×Cu, 2×Se, and

2×O atoms) in the unit cell, consists of the Bi-O layer alternatively stacked with the isostructural Cu-Se layer along the [001] axis (*a-c* plane), as shown in Figure 1(a). The covalent Bi–O (2.34 Å) and Cu–Se (2.53 Å) bonds couple Bi-O and Cu-Se layers, respectively, while the weak van der Waals-like Bi–Se bond (3.27 Å) links Bi-O and the Cu-Se layers. Figure 1(b) displays the structure along the [001] axis (*a-b* plane) highlighting the slightly distorted Bi₄O tetrahedral with the Bi–O–Bi bond angle of 106.97°. Our *ab-initio* calculations give optimized lattice parameters of $a = 3.95$ Å, $c = 9.09$ Å, which are only 0.5% and 1.8% larger than the reported experimental lattice parameters of $a = 3.93$ Å, $c = 8.93$ Å.¹⁸

Figure 1. Crystal structure of oxide BiCuSeO. (a) Structure of BiCuSeO along the [010] axis highlighting the Cu-Se and Bi-O layers, (b) Structure of BiCuSeO along the [001] axis highlighting the slightly distorted Bi₄O tetrahedral with the Bi–O–Bi bond angle of 106.97°. The Bi, Cu, Se, and O are shown with purple, dark-blue, light-green, and red balls, respectively.

3.2 Favorable grain boundaries in BiCuSeO

Recent experiment clearly showed a typical GB between BiCuSeO(100) and BiCuSeO(110) grains.²⁸ Here, BiCuSeO(100) and BiCuSeO(110) represents the oriented unit cell with lattice direction (*a*, *b*, *c*) along ($\langle 010 \rangle$, $\langle 001 \rangle$, $\langle 100 \rangle$) and ($\langle 110 \rangle$, $\langle 1-10 \rangle$, $\langle 100 \rangle$), respectively. Specifically, the structure of BiCuSeO(100) consists of 8 atoms in the unit cell, with the cell parameter $a = b = 3.95$ Å, $c = 9.09$ Å. The structure of BiCuSeO(110) consists of 16 atoms in the unit cell, with the cell parameter $a = b = 5.59$ Å, $c = 9.09$ Å.

As guided by the experimental observations,²⁸ the BiCuSeO(100)/BiCuSeO(110) GB structure is considered in this study. Due to different cutting surface along the *a-b* plane, as shown in Figure 1(a), we consider three types of interfacial structures for the BiCuSeO(100)/BiCuSeO(110) GB, namely BiO_GB structure, CuSe_GB structure, and BiSe_GB

structure. The detailed explanation and illustration of these three GB structures are shown in Figures S1-S3 in the supporting information. The BiCuSeO(100)/BiCuSeO(110) GB structure, which contains 136 atoms, consists of a (3×3×1)-BiCuSeO(100) oriented cell ($a = b = 11.85 \text{ \AA}$, $c = 9.09 \text{ \AA}$) and a (2×2×1)- BiCuSeO(110) oriented cell ($a = b = 11.18 \text{ \AA}$, $c = 9.09 \text{ \AA}$). It is clear that there is a 5.65% lattice mismatch along the a and b directions between BiCuSeO(100) and the BiCuSeO(110) oriented cell based on the above supercell size. Here, we enlarge the BiCuSeO(110) cell and reduce the BiCuSeO(100) cell through moving the Bi and Se atoms in the boundaries to eliminate lattice mismatch. Periodic boundary conditions were applied in all structures, thus each structure contains two GBs. It is noted here that no available experimental observation shows how the BiCuSeO(100) and BiCuSeO(110) grains cohered together in the a - b plane. Consequently, for each GB structure, several possible coherent models are constructed and the one with the minimum GB formation energy is considered as the favorable structure. The details of how we cohere these two grains are illustrated in Figure S4 in the supporting information.

To evaluate the structural stability of GBs, we can calculate the GB formation energy E_f as,^{29,30}

$$E_f = \frac{E_{GB} - \sum_i E_{bulk}^i}{2S} \quad (1)$$

where E_{GB} and E_{bulk}^i are the total energies of the constructed GB systems and the corresponding bulk system i ($i = \text{BiCuSeO(100)}, \text{BiCuSeO(110)}$), and S is the lateral area.

We calculated formation energies for various possible BiCuSeO(100)/BiCuSeO(110) GB structures, as listed in Table 1. The lowest formation energy is 0.373 J/m^2 for the CuSe_GB (structure 4), indicating it is the most favorable GB structure. However, the BiSe_GB (structure 1) is also found to have a very low formation energy of 0.428 J/m^2 , suggesting that it is energetically favorable as well. In addition, the formation energies of the BiO_GB are much higher than those of the CuSe_GB and BiSe_GB, implying the BiO_GB configurations are rarely formed. On the basis of above interfacial formation energies, we consider the most favorable configurations, the structure 4 for the CuSe_GB and the structure 1 for the BiSe_GB as shown in Figure 2 to illustrate the role of GB on ideal strength, deformation and failure mechanism of TE oxide BiCuSeO.

Table 1. GB formation energy (E_f) computed for constructed BiCuSeO(100)/BiCuSeO(110) GB structures. The favorable GB models, which are shown in bold type, are displayed in Figure 2. The unit is J/m².

Configurations	Possible coherent structures and formation energies (E_f)											
	1	2	3	4	5	6	7	8	9	10	11	12
BiO_GB	0.788	0.798	0.743	0.796	0.779	0.746	0.783	0.775	0.779	0.779	0.776	0.776
CuSe_GB	0.400	0.378	0.382	0.373	0.384	0.385	0.384	0.399	0.385	0.384	0.399	0.384
BiSe_GB	0.428	0.441	0.429	0.429	0.439	0.437	0.452	0.441	0.447	0.445	0.437	0.439

Figure 2. The favorable GB model with the minimum GB formation energy among constructed BiCuSeO(100)/BiCuSeO(110) structures. The CuSe_GB structure is found to have the lowest formation energy of 0.373 J/m², which corresponds to the structure 4 in Table 1, as shown in (a) before relaxation and (b) after relaxation. The BiSe_GB structure is found to have a low formation energy of 0.428 J/m², which corresponds to the structure 1 in Table 1, as shown in (c) before relaxation and (d) after relaxation..

3.3 Ideal shear strength of the BiCuSeO(100)/BiCuSeO(110) grain boundary

To determine the ideal shear strength of the BiCuSeO(100)/BiCuSeO(110) GB, we calculated the shear stress response against shear strains for favorable GB structures, as shown in Figure 3(a). In addition, we also investigated the shear stress-strain relationships of bulk BiCuSeO along the (001)/<100> and (001)/<110> directions (Figure 3(b)) for a comparison. The ideal shear strength of the CuSe_GB structure is found to be 0.41 GPa at shear strain of 0.04, while the BiSe_GB structure has a much lower ultimate shear strength of 0.15 GPa at 0.092 shear strain. The CuSe_GB structure has a lower formation energy than the BiSe_GB structure, as listed in Table 1, which suggests that the CuSe_GB is much more stable than the BiSe_GB. This leads to a much stronger structural rigidity of the CuSe_GB, giving rise to a much higher elastic moduli and ideal shear strength of the CuSe_GB as observed in Figure 3(a). However, compared with the single crystalline BiCuSeO shown in Figure 3(b), we found that the ideal shear strength (0.41 GPa at 0.04 shear strain) of the CuSe_GB structure is extremely lower than that (2.0 GPa at 0.13 shear strain) of the single-crystalline system. Although the CuSe_GB structure has the lowest formation energy (Table 1), it is thermodynamically unstable compared with the flawless BiCuSeO. Due to the lattice mismatch and the neighbor structure difference leading to the atomic rearrangement in the vicinity of the GB, the CuSe_GB structure is much weaker in the resistance to the shear deformation compared with the flawless crystal. This gives rise to the GB softening, as shown in Figure 3.

Figure 3. Calculated shear-stress – shear-strain relations for (a) favorable BiCuSeO(100)/BiCuSeO(110) GBs and (b) related single-crystalline BiCuSeO.

3.4 Deformation mechanism of the BiCuSeO(100)/BiCuSeO(110) grain boundary

To further understand the GB softening effect, we examined the atomic patterns and the related bond angle changes to illustrate shear induced deformation mechanism of the BiCuSeO(100)/BiCuSeO(110) GB, as shown in Figures 4-5. Figure 4 shows the atomic configurations of the CuSe_GB structure at critical shear strains. As shown in Figure 4(a), due to the atomic rearrangement in the GBs, the neighbor structure of the Cu-Se layer is different from that in the flawless crystal (Figure 1(a)), while the Bi-O layer can maintain structural integrity. As the shear strain increases to 0.04, which corresponds to the maximum stress point, the Cu-Se layer is distorted against the external deformation, while the Bi-O layer holds together, as displayed in Figure 4(b). At the failure strain of 0.06, the Cu-Se layer is further distorted leading to the Cu-Se bond breakage (Figure 4(c)). This relaxes the shear stress and results in the GB collapse. Figure 4(d) plots the Cu-Se bond and the distortion angle (α) changes as a function of shear strains. The distortion angle uniformly increases from 166.5° to 182.1° before the structural failure, while the Cu-Se bond length slightly increases from 2.57 to 2.59 Å. At 0.06 failure strain, the angle α sharply increases to 195.2° , while the Cu-Se length rapidly increases to 3.55 Å. This highly distorted angle leads to the Cu-Se bond breakage, resulting in the remarkably decreased structural rigidity. This indicates that the CuSe_GB structure can't resist the shear loads, indicating the destruction of this GB.

Figure 4. The atomic configurations of the CuSe_GB structure during shear deformation: (a) Intact structure, (b) Atomic structure at 0.04 shear strain, which corresponds to the maximum stress point, (c) Atomic structure at 0.06 failure strain. (d) The typical Cu–Se bond length and the distortion angle (α) against shear strain. The red dashed line highlights the Cu–Se bond breakage.

Figure 5 displays the structural patterns of the BiSe_GB at critical shear strains to further examine the deformation mechanism of the BiCuSeO(100)/BiCuSeO(110) GB. In the intact structure shown in Figure 5(a), the distance along the c axis between Bi–O and Cu–Se layers is 2.57 Å, which is larger than those (1.45 and 1.39 Å) in the BiCuSeO(100) and BiCuSeO(110) oriented grains. This suggests that the Bi–Se interaction in the GB is much weaker compared with those in (100) and (110) oriented grains, which creates pathways to slip between Bi–O and Cu–Se layers when the shear strain increases to 0.091, as displayed in Figure 5(b). At 0.102 failure strain, the Bi–O and Cu–Se layers further slides with each other (Figure 5(c)), deconstructing the weak Bi–Se bonding in the GB. This relaxes the shear stress and gives rise to the GB failure. The

related bond angle (α) as a function of shear strain is plotted in Figure 5(d). The bond angle, α , linearly decreases from 90.4° to 85.2° as the shear strain increases to 0.601, representing the structure uniformly resists shear deformation. This corresponds to the stress climbing stage as plotted in Figure 3(a). When the shear strain further increases to 0.092, the angle α decreases with a larger decline ratio. This indicates the Bi–Se interaction in the GB starts to weaken, corresponding to the plastic stage displayed in Figure 3(a). At 0.102 failure strain, the angle suddenly drops from 78.4° to 69.4° . This releases the interaction between Bi–O and Cu–Se layers, relaxing the shear stress and resulting in the GB destruction.

Figure 5. The atomic configurations of the BiSe_GB structure during the shear process: (a) the intact structure. In the vicinity the GB, the distance along the c axis between Bi–O and Cu–Se layers is 2.57 Å,

which is larger than those (1.45 and 1.39 Å) in the BiCuSeO(100) and BiCuSeO(110) oriented grains. (b) Atomic structure at shear strain of 0.0091, which corresponds to the maximum shear point, (c) Atomic structure at 0.102 failure strain. (d) The bond angle (α) change during the shear process. The red lines show the GB slip between Cu–Se and Bi–O layers.

It would be better if we can measure the ultimate shear strength of GBs, and compare them with our calculated values. Experimentally, however, the mechanical properties heavily depend on the defects such as cracks, vacancies, and dislocations, which are ignored in our work. This gives rise to a much higher ideal strength of an ideal single crystalline compared with that of a real sample. For example, the ideal strength of BiCuSeO bulk is 2.0 GPa as shown in Figure 3(b). Exploring such defects necessitates a much bigger model size. Therefore, the combination of large-scale atomistic modeling and experimental measurements would be helpful for illustrating the role of these defects on ultimate shear strength and failure mechanism of BiCuSeO GBs. It is worthy of future studies. Moreover, engineering GBs is reported as a novel approach to lower the lattice thermal conductivity and improve the zT values of such important TE materials as Bi₂Te₃,¹⁹ CoSb₃,²⁰ and SnSe.²¹ Illustrating how GBs influence the thermal transport as well as the scattering mechanism of TE materials is also worthy of future studies.

4. CONCLUSIONS

We apply *ab-initio* calculations to examine the role of GBs on such mechanical properties as the ideal shear strength and failure mechanism of BiCuSeO.

- (i) Interfacial formation energy calculation predicts that BiCuSeO(100)/BiCuSeO(110) with the GB coupled with Cu–Se or Bi–Se interaction is energetically favorable, with the formation energy of 0.373 and 0.428 J/m², respectively.
- (ii) The atomic rearrangements accommodating the lattice and neighbor structure mismatch between different grains gives rise to a much weaker GB stiffness compared with grains. This leads to much lower ideal shear strengths (0.41 and 0.15 GPa) of the GBs compared with that (2.0 GPa) of the ideal single-crystalline system.
- (iii) Failure of the GBs arises from either the distortion of the Cu-Se layers or the relative slip between Bi-O and Cu-Se layers.

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Supporting Information. Explanation and illustration of three GB structures, and how to cohere BiCuSeO(100)/BiCuSeO(110) GBs in the *a-b* plane.

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A TOC Figure: