

Lattice Vibrational Hierarchy and Mean-Free-Path Filtering in $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ Superlattice Thermoelectrics

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Heteroanionic thermoelectric (TE) oxides have attracted considerable attention due to their unique phonon and carrier transports. The recent investigation of $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ has opened new prospects for the development of n -type TE oxides. Herein, we first investigate the mechanism of superlattice formation and the origin of narrow band gap in $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$. The physical picture of lattice vibration hierarchy in $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ is indexed to the lone pair rattler of Bi and liquidlike behavior of Cu since more diffusons are observed as temperature increases. Additionally, the modified band structure and crystal defects are responsible for the stable n -type transport in $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ compared to the well-known p -type BiCuSeO . Combining phonon transport and carrier mean-free-path filtering, theoretical results demonstrate that n -type case exhibits two optimized carrier concentration regions with peak ZT values approaching ~ 1.0 at 300 K and ~ 1.4 at 900 K, respectively, while p -type case shows a higher power factor of $\sim 90 \mu\text{W cm}^{-1} \text{K}^{-2}$, leading to high-ranged TE performance among 300–900 K. Our results demonstrate $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ is a promising TE oxide with potential applications in both refrigeration and power generation. Moreover, understanding and establishing a physical and chemical link between the superlattice structure and TE properties enables the future development of TE oxides.

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I. INTRODUCTION

Thermoelectric (TE) technology enables the direct conversion of heat energy into electrical energy, providing a promising avenue for clean energy generation. Advances in TE technology are typically driven by the development of

functional materials, whose performance is quantified by the dimensionless figure of merit ZT [1–3]:

$$ZT = \frac{S^2 \sigma T}{\kappa_e + \kappa_l}, \quad (1)$$

where S , σ , T , κ_e , and κ_l represent Seebeck coefficient, electrical conductivity, absolute temperature, and electronic and lattice thermal conductivity, respectively. The interplay of TE parameters requires a balance to decouple the conflict between electrical and thermal transport [4–9]. In recent years, many efforts have been directed toward optimizing various TE materials [10–14]. Particularly, several novel strategies were adopted, including lattice plainification [15–19], mutiband synglisis [20–23], and crystal structure modification [24–26]. However, oxide-based TE materials

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with high physicochemical stability especially at high temperatures, consisting of earth-abundant, nontoxic and nonvolatile elements, have received limited exploration to date due to their inferior TE performance [27]. Nevertheless, heteroanionic oxide-based materials with the ZrCuSiAs-type structure have shown promise due to their complex electronic band structure, anisotropic superlattice, and ultralow κ_1 , making them efficient candidates as midtemperature TE oxides [28–31].

A typical example is the BiCuSeO-based TE materials, which consists of alternating conductive $[\text{Cu}_2\text{Se}_2]^{2-}$ and insulating $[\text{Bi}_2\text{O}_2]^{2+}$ units [32,33]. Theoretically, crystal defect analysis indicates that BiCuSeO is a native *p*-type semiconductor, with Cu vacancies (V_{Cu}) preferentially forming and ensuring holes as the majority carriers [34]. Also, the unique superlattice structure induces quantum confinement of holes, leading to large Seebeck coefficients [35,36]. Meanwhile, the interlayer van der Waals interaction promotes strong phonon scattering, resulting in ultralow κ_1 [37]. Building on these advantages, extensive efforts in experiments, in recent years, have focused on improving the carrier transport of *p*-type BiCuSeO, as its wide band gap ($E_g \approx 31k_B T$) inherently limits electrical conductivity [30,38]. Extensive achievements have been made in *p*-type BiCuSeO TEs, with an impressive peak *ZT* of ~ 1.5 by Pb and Ca dual doping [39] and an exceptional average *ZT* of ~ 0.9 across a broad temperature range from 300 to 923 K in BiCuSeO-Pb-Cu samples prepared using a three-step texturation [40]. However, the development of *n*-type BiCuSeO and other analog TE oxides remains both a critical and challenging endeavor [41–43]. Previous studies have primarily concentrated on elucidating the obstacle to achieving stable *n*-type transport in BiCuSeO, yet a definitive solution remains elusive [34,43,44].

Until recently, a novel superlattice semiconductor of $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ has been successfully synthesized, exhibiting stable *n*-type transport properties by halogen doping at Se sites [45]. Recent advancements in the optimization of *n*-type $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ have involved strategies including modulation doping and inducing resonant levels [46,47]. These efforts have led to significant improvements in its transport performance, demonstrating that *n*-type $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ holds considerable promise for TE applications [48]. However, the upper limit of TE performance optimization remain unclear whether it is *n*- or *p*-type case. The query also arises as to why *n*-type behavior can be achieved in $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ but not BiCuSeO. In addition, the unit cell of $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ can be conceptualized as the wide-band-gap $\text{Bi}_2\text{O}_2\text{Se}$ intercalated into the BiCuSeO interlayer, while the underlying driving mechanism has not yet been fully elucidated. The $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ has been reported as a relatively narrow-band-gap ($E_g \approx 18k_B T$) semiconductor, which might be more conducive to TE applications in its polycrystal form since it is easier for doping design than a wide band gap [49]. Intriguingly, the

mechanism by which the combination of two wide-band-gap materials results in the emergence of this narrow band gap remains to be clarified.

Most recently, materials with ultralow κ_1 have been rethought from the computational materials science. Typically, research interests involve Si [50], AgCrSe_2 [51], and SrSnSe_2 [52], which exhibit significant high-order phonon scattering, as well as Ti_3VSe_4 [53], $\text{La}_2\text{Zr}_2\text{O}_7$ [54], and $\text{Na}_2\text{CaCdSb}_2$ [55], which demonstrate glasslike behavior at elevated temperatures. The former can be reasonably explained within the phonon Boltzmann transport equation (BTE) framework [56–58], while the latter remains an open question with various possible solutions [59–61]. Inspired by the idea of vibrational hierarchy, the dual-phonon theory and numerical methods have been widely developed, providing new possibility for effectively obtaining fundamental and physical insights based on the BTE framework [54,55]. However, to the best of our knowledge, there has been a lack of study that uses physical and chemical picture to reveal the hierarchical nature of lattice vibrations. Moreover, previous work on the limited thermal transport properties of $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ has predominantly relied on self-consistent effective medium theory [47]. Experimental observations suggested that its κ_1 exhibited glasslike behavior at high temperatures, which was attributed to the strong anharmonicity [46]. However, the underlying physical and chemical driving forces responsible for its ultralow κ_1 and weak temperature dependence still require further investigation.

To summarize, the TE transport properties of $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ with superlattice structure remain unknown so far, and a comprehensive understanding of the physical and chemical origin of its ultralow κ_1 has yet to be fully established. With this motivation, we have synthesized $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ polycrystal sample, and constructed its primitive cell based on scanning transmission electron microscope (STEM) characterizations. Combined with crystal bonding and electronic band structure analysis, we have revealed the formation mechanisms of the superlattice structure and relatively narrow band gap in $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$, which is closely related to the lattice contraction caused by the spontaneous insertion of $\text{Bi}_2\text{O}_2\text{Se}$ layer into the original BiCuSeO layered structure, along with the splitting of Cu_{3d} orbitals and the hybridization of Bi_{6p} and O_{2s} orbitals. Based on experimental results and dual-phonon theory, we have discovered a large number of diffusons in $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ based on the full BTE framework, which can be attributed to the lone pair rattler of Bi and liquidlike behavior of Cu atoms. In addition, the reduction of band gap and the introduction of more *n*-type defects lead to the stable *n*-type electrical transport in $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ compared to BiCuSeO. Therefore, by combining phonon transport and electronic mean free path (MFP), we have evaluated the TE transport properties of *n*-type and *p*-type $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$. Theoretically, it was

found that *n*-type case exhibits two optimized carrier concentration regions, while the *p*-type shows a higher power factor, which is closely related to its complex electronic band structure with four valence band maxima near the Fermi level. Our current results not only enrich the physical and chemical understanding of transport properties in superlattice structures, but also shed light on more new possibilities for the future development of TE oxides.

II. LATTICE AND ELECTRON STRUCTURES

The polycrystalline $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ samples were synthesized by process solid-state reaction followed by spark plasma sintering at 923 K. The experimental details can be found in Supplemental Material (SM) [62]. The powder x-ray diffraction patterns of $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ sample were in accordance with the simulated pattern (see Fig. S1 in SM [62]). In order to observe the $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ sample on a smaller length scale (100 nm), the atomic resolution annular-bright-field (ABF) and annular-dark-field (ADF) STEM were performed. Figure 1(a) presents an ABF STEM image of $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ sample with corresponding energy dispersive spectroscopy (EDS) mapping showing a uniform distribution of the elements, indicating there is no significant phase separation or compositional deviation during the synthesis process [Fig. 1(b)]. In order to more clearly distinguish the atomic occupancy, Fig. 1(c) presents

the enlarged high-resolution magnified ADF STEM image viewed along the [100] direction. It can be observed that the atoms arrangement exhibits a long-range ordered crystal structure. Subsequently, the ADF STEM image at higher magnification indicates this crystal structure is formed by the alternating stacking of $\text{Bi}_2\text{Cu}_2\text{Se}_2\text{O}_2$ and $\text{Bi}_2\text{O}_2\text{Se}$ layer in a 1:2 ratio along the *c* axis [Fig. 1(d)]. From the atomically resolved EDS mapping analysis, we have observed that all atoms occupy their assigned positions with no mixed occupancy, reflecting a clear atomic arrangement [Fig. 1(e)]. The overlaid EDS mapping also indicates an ordered distribution of elements, presenting a superlattice form [Fig. 1(f)].

Based on the electron microstructural analysis, we have constructed the unit cell of $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ superlattice. For the basic components, the BiCuSeO (space group no. 129, $P4/nmm$) exhibits lower symmetry than the $\text{Bi}_2\text{O}_2\text{Se}$ (space group no. 139, $I4/mmm$), despite both being the tetragonal system. Experimentally, the measured lattice parameters of $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ ($a/b = 3.901 \text{ \AA}$, $c = 21.066 \text{ \AA}$) along the in-plane direction lie between that of BiCuSeO ($a/b = 3.921 \text{ \AA}$, $c = 8.913 \text{ \AA}$) and $\text{Bi}_2\text{O}_2\text{Se}$ ($a/b = 3.891 \text{ \AA}$, $c = 12.213 \text{ \AA}$), while in the out-of-plane direction, it is slightly larger than the sum of the two (Table S1 in SM [62]). The lattice matching laid the foundation for the further formation of superlattices [63]. Theoretically,

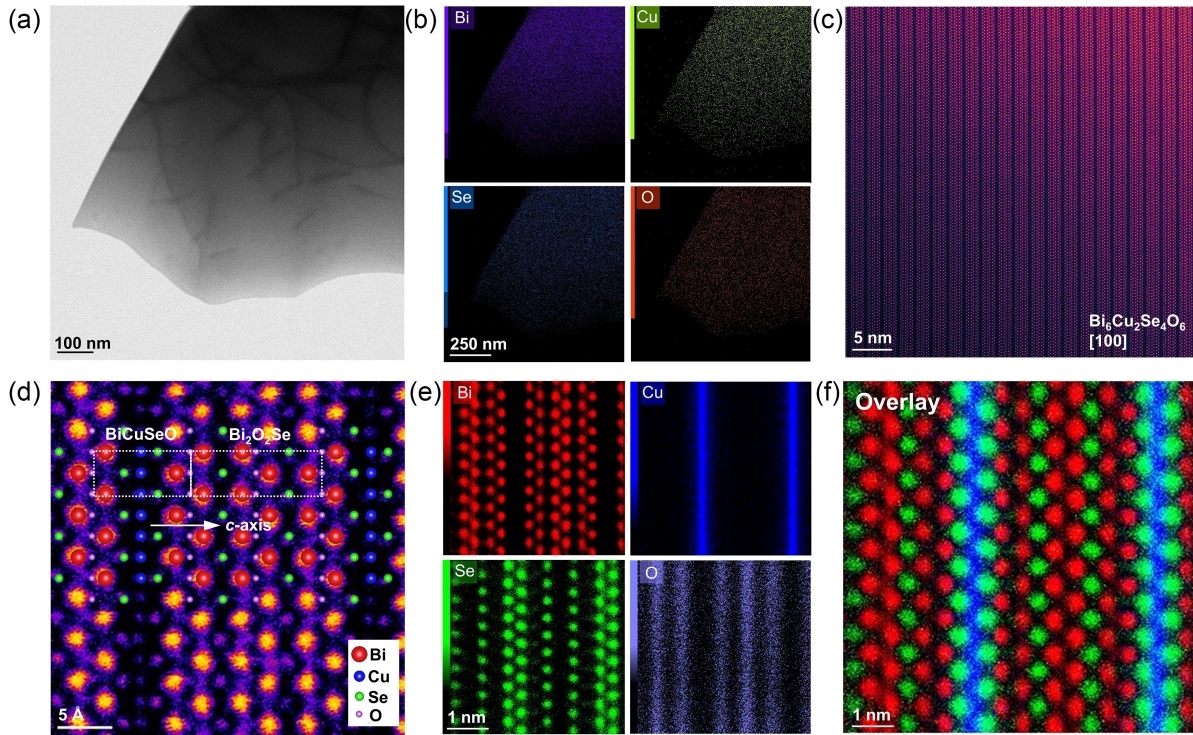


FIG. 1. Microstructure characterizations of $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ sample. (a) ADF STEM image of a large area and (b) its corresponding EDS mapping. (c) The enlarged ADF STEM image viewed along the [100] direction. (d) The high-magnification ADF STEM image and (e) its atomic-resolved EDS mapping, reflecting a clear atomic arrangement. (f) The overlay EDS mapping, indicating an ordered distribution of elements.

the calculated lattice parameters of $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ ($a/b = 3.884 \text{ \AA}$, $c = 21.049 \text{ \AA}$) based on PBEsol functional [64] were in agreement with the experimental results, which is consistent with a previous report [49]. Notably, because the $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ superlattice shares the same space group as BiCuSeO , we inferred that $\text{Bi}_2\text{O}_2\text{Se}$ can spontaneously and orderly intercalate into BiCuSeO interlayer by reducing its lattice symmetry. The cohesive energy of $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ was calculated (see SM for detail) and the negative value of -1.00 eV/atom has demonstrated its thermodynamic stability. Also, the *ab initio* molecular dynamics (AIMD) simulations of $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ supercell were performed at 300 and 900 K, respectively. We observed no significant bond breaking and structural phase transition (Fig. S2 in SM), indicating its dynamical stability across the entire temperature range.

Based on the reduced density gradient (RDG) as a function of $\text{sgn}(\lambda_2)\rho$, the noncovalent interaction analysis between atom pairs can be a powerful tool for investigating crystal structures with weak interactions [65]. Herein, the $\text{sgn}(\lambda_2)\rho$ represents the sign of the second eigenvalue for the electron density (ρ) Hessian matrix. The $\text{sgn}(\lambda_2)\rho$ is negative for attractive interaction and positive for repulsive interaction. Meanwhile, the spikes observed in the RDG, which approach zero at critical points within regions of low ρ , can be indicative of weak interactions, reflecting the

strength of the corresponding interaction. Figure 2(a) represents the schematic of interaction region indicator for the $\text{Bi}_2\text{O}_2\text{Se}$ and BiCuSeO layer. From the perspective of chemical bonding, the $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ superlattice was composed of $[\text{Se}]^{2-}$ unit originating from $\text{Bi}_2\text{O}_2\text{Se}$, $[\text{Cu}_2\text{Se}_2]^{2-}$ unit from BiCuSeO , and $[\text{Bi}_2\text{O}_2]^{2+}$ unit from both. We observed that the regions among different units appear green, indicating weak interactions.

In order to quantitatively describe the interaction between atomic pairs, Figs. 2(b) and 2(c) show the RDG as a function of $\text{sgn}(\lambda_2)\rho$ for $\text{Bi}_2\text{O}_2\text{Se}$ and BiCuSeO layer, respectively. The $\text{Bi}_1\text{-Se}_1$ and $\text{Bi}_4\text{-Se}_2$ interaction have exhibited a low RDG peak when the $\text{sgn}(\lambda_2)\rho$ approaches zero, which demonstrates that there is a weak van der Waals interaction among these units. Combined with topological properties of the bond critical points (BCPs), the quantitative chemical bonding in crystal can be analyzed in detail (Table S2 in SM [62]). According to the summarized topological descriptors [66], the properties of BCPs associated with polar bonding were characterized by a small density $\rho(r)$, positive $\nabla^2\rho(r)$, negative total energy density H , $V/G \geq 1.0$, and $G/\rho \leq 1.0$. For $[\text{Bi}_2\text{O}_2]^{2+}$ and $[\text{Cu}_2\text{Se}_2]^{2-}$ units, the Bi—O and Cu—Se bonding can be described as polar bonds. In contrast, the $\rho(r)$, H , and V/G of Cu—Se bonding is significantly lower than that of Bi—O, indicating weaker interaction. Moreover, we calculated

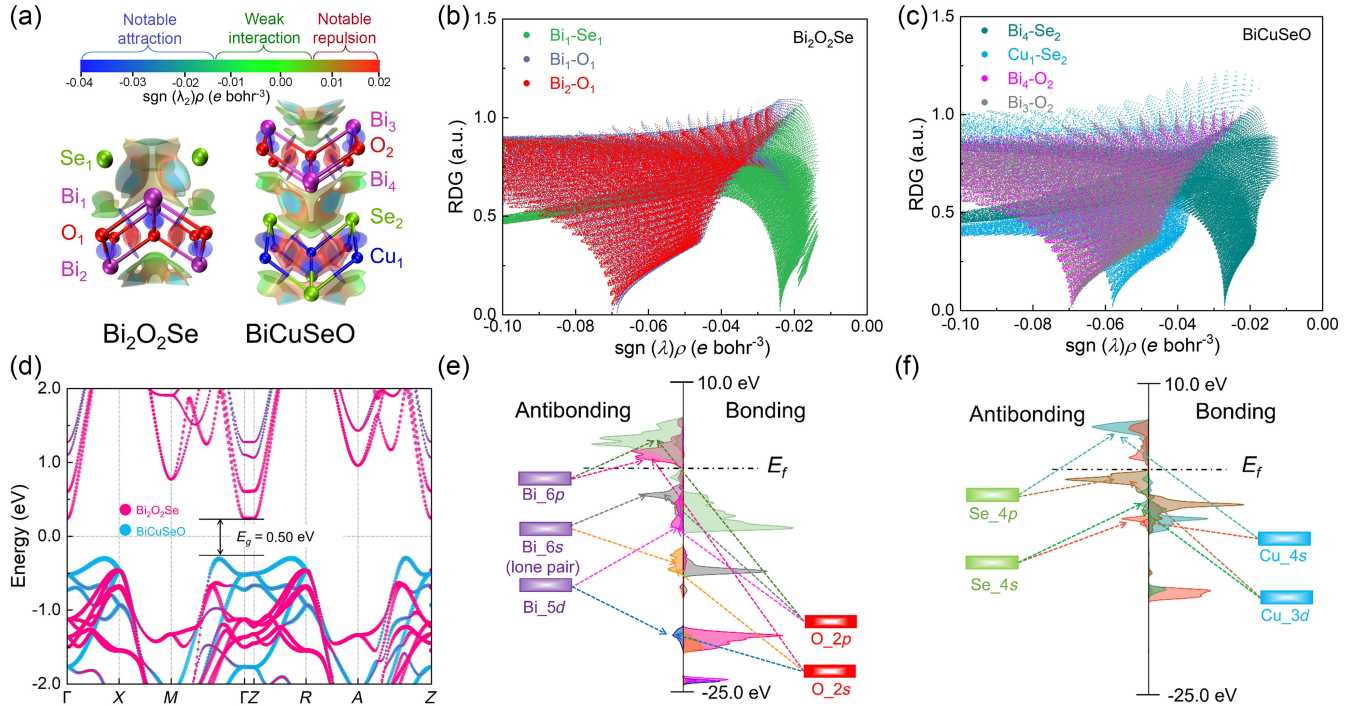


FIG. 2. Crystal bonding analysis and electronic band structure of $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$. (a) The schematic of interaction region indicator for $\text{Bi}_2\text{O}_2\text{Se}$ and BiCuSeO layer, which is colored on a blue-green-red (BGR) scale of $-0.04 < \text{sgn}(\lambda_2)\rho < 0.02 e \text{ bohr}^{-3}$. (b),(c) The reduced density gradient (RDG) as a function of $\text{sgn}(\lambda_2)\rho$ for $\text{Bi}_2\text{O}_2\text{Se}$ and BiCuSeO layers. (d) The projected electronic band structure for $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$. (e),(f) The crystal orbital Hamilton population (COHP) analysis for $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$.

that the $[\text{Cu}_2\text{Se}_2]^{2-}$ unit has the lowest degree of ionicity ($\sim 26.71\%$), reflecting Cu—Se with weaker polar covalent bond (Table S3 in SM).

To further explore the impact of crystal structure on the energy level distribution, we performed the electronic band structure calculation (see SM for details [62]). For $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$, the calculated band gap (~ 0.50 eV) was almost consistent with our experimental band gap (~ 0.48 eV), indicating an indirect narrow-band-gap semiconductor (Fig. S3 in SM). Also, experiments have confirmed that $\text{Bi}_2\text{O}_2\text{Se}$ (~ 1.81 eV) and BiCuSeO (~ 0.81 eV) are two wide-band-gap semiconductors, as in our previous work [49]. Intriguingly, the mechanism by which the interaction of $\text{Bi}_2\text{O}_2\text{Se}$ into BiCuSeO interlayer can induce the transition of the materials from wide band gap to narrow band gap deserves further exploration, facilitating polycrystalline TE applications. Figure 2(d) presents the projected electronic band structure of $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$. Obviously, the valence band maximum (VBM) mainly is primarily contributed by BiCuSeO layer, while the conduction band minimum (CBM) is mainly governed by $\text{Bi}_2\text{O}_2\text{Se}$ layer. Therefore, we calculated the electronic band structure of $\text{Bi}_2\text{O}_2\text{Se}$ and BiCuSeO (Fig. S4 in SM). The BiCuSeO has a higher VBM, whereas the $\text{Bi}_2\text{O}_2\text{Se}$ has shown a lower CBM. In contrast, the VBM of $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ is larger than that of BiCuSeO and $\text{Bi}_2\text{O}_2\text{Se}$, while its CBM lies between the two. We found the interaction of $\text{Bi}_2\text{O}_2\text{Se}$ into BiCuSeO interlayer can push VBM energy higher and lower CBM energy.

By crystal orbital analysis to understand the driving force, the crystal orbital Hamilton population (COHP) for $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ was presented in Figs. 2(e) and 2(f). Specifically, the VBM is predominantly derived from the hybridization of Cu_{3d} and Se_{4p} orbitals forming antibonding states, while CBM is primarily influenced by the hybridization of Bi_{6p} and O_{2s} orbitals forming antibonding states. In addition, an antibonding state, located 0.5 eV below the Fermi level, derives from the lone pair electrons $6s^2$ of Bi in $\text{Bi}_2\text{O}_2\text{Se}$ layer, driving the upward shift of all valence band extremes (VBs). According to the crystal field theory, the CuSe_4 tetrahedron becomes distorted due to a Jahn-Teller-like effect, breaking the degeneracy of electronic orbitals [67]. The bond length (d) and bond angle (α) of CuSe_4 tetrahedron in $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ [$d(\text{Cu—Se}) = 2.483$ Å, $\alpha = 102.92^\circ$] were slightly smaller than those in BiCuSeO [$d(\text{Cu—Se}) = 2.506$ Å, $\alpha = 102.95^\circ$], originating from the in-plane lattice contraction induced by the insertion of $\text{Bi}_2\text{O}_2\text{Se}$ (Fig. S5 in SM [62]). Also, compared with BiCuSeO , the $4d$ -orbital splitting of Cu is stronger in $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$, as indicated by the wide energy distribution for t_{2g} and e_g orbitals [Fig. S6(a) in SM]. Therefore, the $4d$ -orbital splitting of Cu is promoted. Electrons can fill the orbits with higher energy (t_{2g} orbitals), leading to an elevation of VBs. Similarly, lattice contraction can enhance the Bi—O bonding of BiO_4

square pyramids (Fig. S5 in SM), which in turn intensifies the hybridization between Bi_{6p} and O_{2s} orbitals, resulting in the reduction of CBM [Fig. S6(b) in SM].

Comprehensive crystal bonding analysis paves the way for understanding from structure to properties. We have known that $[\text{Cu}_2\text{Se}_2]^{2-}$ and $[\text{Bi}_2\text{O}_2]^{2+}$ units exhibit a weak van der Waals interlayer interaction, while $[\text{Se}]^{2-}$ exists in the interlayer in its ionic form and preferentially bonds $[\text{Bi}_2\text{O}_2]^{2+}$ unit with positive charge to form $\text{Bi}_2\text{O}_2\text{Se}$ layer (Table S2 in SM [62]). As a result, we confirmed the synergistic effect between these factors provides the driving force for the spontaneous incorporation of $\text{Bi}_2\text{O}_2\text{Se}$ layer into BiCuSeO interlayer. Compared with BiCuSeO , $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ have been observed in-plane lattice contraction, promoting the splitting of Cu_{4d} orbitals and enhancing the orbital hybridization between Bi_{6p} and O_{2p} , thereby making it narrow-band-gap semiconductor. In addition, $[\text{Cu}_2\text{Se}_2]^{2-}$ unit lays the foundation for the $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ as a potential TE oxide, as its bonding type and strength can govern the low thermal conductivity and carrier transport [37].

III. PHONON TRANSPORT AND LATTICE VIBRATIONAL DYNAMICS

Both the lone pair electrons from the $[\text{Bi}_2\text{O}_2]^{2+}$ unit and the polar covalent bonding in the $[\text{Cu}_2\text{Se}_2]^{2-}$ unit indicates that the phonon transport can be damped in $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$. This not only underlines potential as a candidate for TE oxides with ultralow κ_1 , but also motivates us to reveal phonon transport properties through physical and chemical picture. Figure 3(a) represents that the κ_1 of $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ as a function of temperature adopted by experimental and different theoretical scheme. For full BTE scheme, the phonon relaxation time (τ_{ph}) was evaluated by combining multiple scattering mechanisms (see SM for details [62]). A notable phenomenon is that the κ_1 calculation based on full BTE scheme does not provide a good description across the entire temperature range. The κ_1 calculation considering three-phonon (3ph) scattering is significantly overestimated (the maximum error of $\sim 51.8\%$), while the inclusion of both three- and four-phonon (3ph and 4ph) scattering leads to a severe underestimation in the high-temperature region (the maximum error of $\sim 60.2\%$).

To clarify this calculation error, we analyzed the norm of third- ($|\Phi^{3\text{rd}}|$) and fourth-order ($|\Phi^{4\text{th}}|$) interatomic force constants (IFCs), as they are fundamental and most significantly influenced by temperature and the chosen atomic cutoff radius [Fig. 3(b)]. We calculated that the $|\Phi^{3\text{rd}}|$ and $|\Phi^{4\text{th}}|$ converge when the maximum distance is set to >5.0 Å and >3.6 Å, respectively. Also, the phonon scattering rates ($\tau_{3\text{ph}}^{-1}$ and $\tau_{4\text{ph}}^{-1}$) and weighted phase space (WP3 and WP4) were evaluated in $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ (Figs. S7 and S8 in SM [62]). The results have shown that the triplets interaction ($\tau_{3\text{ph}}^{-1} \sim T\omega^2$, ω is phonon frequency) [50] is not sufficient to reflect the real scattering mechanism,

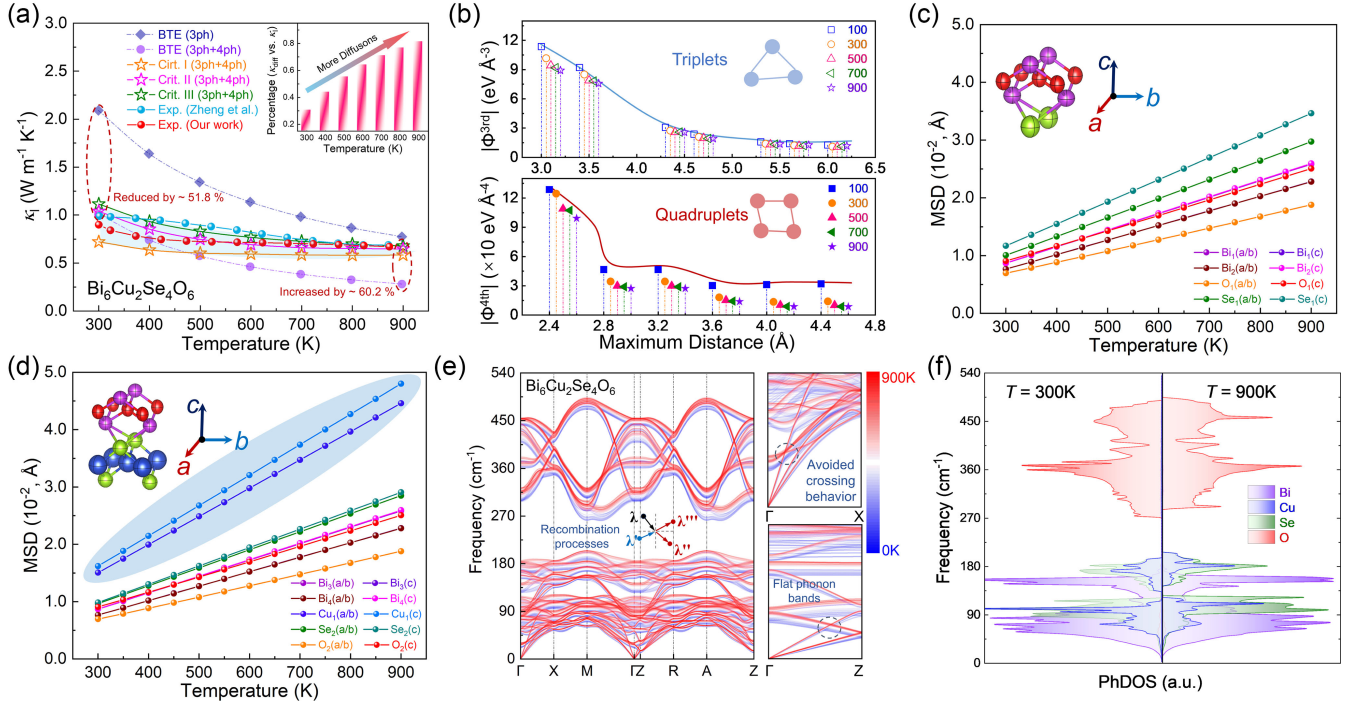


FIG. 3. Phonon and thermal transport properties. (a) The lattice thermal conductivity (κ_l) of $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ as a function of temperature. The inset presents the percentage of κ_{diff} (diffusons) versus κ_l as a function of temperature. (b) The norm of third ($|\Phi^{\text{3rd}}|$) and fourth order ($|\Phi^{\text{4th}}|$) of interatomic force constants (IFCs) of $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ as a function of maximum distance. (c), (d) The mean square displacement (MSD) of $\text{Bi}_2\text{O}_2\text{Se}$ layer and BiCuSeO layer as a function of temperature, respectively. The inset indicates atomic displacement ellipsoid at 900 K. (e) The temperature-dependence phonon spectrum of $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$, where blue to white to red represents from 0 to 900 K. (f) The projected phonon density of states (PDOS) of $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ at 300 and 900 K.

as evidenced by the $\text{WP4} > \text{WP3}$. In contrast, the quadruplets interaction ($\tau_{4\text{ph}}^{-1} \sim T^2 \omega^4$) [50] has shown strong temperature fluctuations at a low numerical level, which does not conform to the characteristics of heat carriers at high temperatures. As a result, the query raised was whether the full thermal vibration modes can still be viewed as phonons.

Inspired by dual-phonon transport theory in low κ_l materials, to address this query, we classified phonon vibrations mode by mode into diffusons and phonons and extended to the case of considering 3ph + 4ph scattering (see SM for details [62]), which is among the highest computationally feasible theoretical levels so far [54–56]. Derived from the Ioffe-Regel limit for phonons [53,54], a mode can be viewed as a diffuson if its phonon MFP is smaller than either wavelength (criterion I) or the minimum interatomic distance (criterion II), otherwise a phonon. Therefore, the phonon MFP as a function of frequency was evaluated using the criteria I and II (Fig. S9 in SM). We observed that under criterion I, the phonon number cannot be defined to reach a maximum at 900 K. In other words, a more stringent definition for diffuson description would be as criterion II. Meanwhile, this concept can also be applied to phonon (D_{phon}) and diffuson (D_{diff}) thermal diffusivity; that is, the diffusion coefficient of diffuson can be classified by $D_{\text{phon}} < D_{\text{diff}}$ based on random walk (RW) theory [68],

otherwise (criterion III). The experimentally measured κ_l aligns well with the criteria II and III. In summary, the criterion I, being less restrictive, was not fully applicable, as it does not accurately describe some phonons in $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ whose phase velocity exceeds the group velocity (Fig. S10 in SM) [69]. This situation is similar to the τ_{ph} criterion for acoustic phonons in the long-wavelength limit, as previously reported [53]. Therefore, although the κ_l calculation with 3ph + 4ph scattering can agree well with experimental measures near room temperature, we confirmed more diffusons as increasing temperature [inset of Fig. 3(a)], indicating the necessity of using RW theory to correct the calculation model [59].

To illustrate the driving forces behind these criteria, Figs. 3(c) and 3(d) show the atomic mean square displacement (MSD) as a function of temperature in $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ for $\text{Bi}_2\text{O}_2\text{Se}$ and BiCuSeO layers, respectively. For $\text{Bi}_2\text{O}_2\text{Se}$ layer, the Se atoms in $[\text{Se}]^{2-}$ unit show stronger vibrational modes, which is attributed to their weak interaction with the lone pair expression of Bi along the c axis. More notably, for BiCuSeO layer, the Cu atoms in $[\text{Cu}_2\text{Se}_2]^{2-}$ can vibrate more strongly with increasing temperature, as indicated by the steeper slope [blue region in Fig. 3(d)]. Meanwhile, we conducted the corresponding regular residuals analysis (RRA) to characterize atomic thermal vibrations and correlate them with different

scattering mechanisms (Fig. S11; see SM for detailed description [62]). For $\text{Bi}_2\text{O}_2\text{Se}$ layer, the RRA shape of Bi atoms along the c axis appears as a “ $\sim$ -like” pattern, and by the lone pair expression, it induces the case of Se atoms to form a “W-like” pattern. In BiCuSeO layer, the RRA shape of Cu atoms exhibited a W-like pattern, and through polar covalent bonding, it further drives the case of Se atoms to adopt a $\sim$ -like pattern. Combined with the above analysis, we inferred that the strongly vibrating Cu atoms are primarily responsible for 4ph scattering, while the Bi atoms through lone pair expression indirectly influenced the scattering mechanism by driving the vibrations of Se atoms. As a result, this also indicates that the sharp increase in the number of diffuson can be indexed to the chemical picture due to the large deviation of κ_1 (3ph + 4ph) calculation at high temperature. We concluded that the primary is the polar covalent bonding of Cu – Se followed by the lone pair expression of Bi.

Then, we performed temperature-dependent phonon dispersion calculations based on self-consistent phonon theory and renormalized IFCs (see SM for details [62]). Figures 3(e) and 3(f) represent the phonon spectrum and projected phonon density of states (PDOS) for $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ at different temperatures. Some intriguing physical pictures were captured. The first one was that the lone pair rattler of Bi atom leads to large phonon linewidth and avoided-crossing behavior in the low frequency range ($30\text{--}50\text{ cm}^{-1}$), which not only provide giant anharmonicity (lower τ_{ph}) but also reduce the phonon group velocity (Fig. S10 in SM). As the above MSD analysis, the lone pair expression as increasing temperature results in the weak bonding between $[\text{Bi}_2\text{O}_2]^{2+}$ and $[\text{Se}]^{2-}$ units, inducing significant displacement of Se atom. This shifts the vibrational frequency from Se atom upward further generating the avoided-crossing behavior in the phonon spectrum, which become more significant at high temperatures. The second one was that the flat phonon bands contributed by the Cu atom and Se atom can be observed near ~ 100 and $\sim 180\text{ cm}^{-1}$, which are expected to scatter phonons. Based on the previous COHP analysis, the antibonding states formed between Cu $3d$ and Se $4p$ below the Fermi level soften the phonon modes around those frequencies. The last one was that the larger optical phonon band gap can be observed in the high frequency region. Herein, the soften phonon mode is an important factor, while on the other hand, the mass differences between elements also play a role. Therefore, the existence of phonon band gap inhibits many 3ph scattering processes that have to simultaneously satisfy both energy and momentum conservation, resulting in $\text{WP}_4 > \text{WP}_3$ (Fig. S8 in SM). This also explains why the calculation considering 3ph + 4ph scattering near room temperature better matches experimental observations.

To better visualize the origin of vibrational hierarchy, Fig. 4(a) shows the phonon thermal diffusivity (D_{phon}) as a

function of frequency based on criterion III at 300 and 900 K. According to the RW theory, the frequency-dependent D_{phon} were divided into diffusons and phonons. Obviously, the phonons still dominate the low frequency region of $\omega < \sim 50\text{ cm}^{-1}$ as the increased temperature, while the vibration mode frequencies of some phonons at $\omega > \sim 50\text{ cm}^{-1}$ increase sharply and enter the region of diffusons. The MSD analysis has revealed that the atomic displacements of Cu and Se exhibit significant temperature dependence [Fig. 3(d)], and the PDOS analysis has further confirmed a notable upward shift in their vibrational frequencies [Fig. 3(f)]. Moreover, the AIMD simulation also has indicated that the Cu atom exhibits a relatively larger diffusion coefficient (Fig. S12 in SM [62]). Significantly, the atomic trajectory distribution of Cu exhibits a stronger disorder compared to other elements [Fig. 4(b)]. Combined with crystal bonding analysis, we attributed the vibrational hierarchy in the $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ to the polar covalent bonds of Cu – Se.

To further characterize the structural evolution, Fig. 4(c) presents the partial pair distribution functions (PDFs), $G(r)$, of $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ based on AIMD simulations at different temperatures. The first three stronger $G(r)$ peaks were found at Bi-O, Cu-Se, and Cu-Cu pairs, respectively, which are determined by the distance and interaction strength between their atomic pairs. Notably, the strongest $G(r)$ peak of Cu-Cu pairs survives significant broadening and shifts from ~ 2.7 to $\sim 2.5\text{ \AA}$, reflecting the strong electrostatic repulsion and a large-amplitude fluctuation of the short-range correlations. Meanwhile, the MSD analysis has shown that the vibration amplitude of Se atoms is second only to that of Cu atoms. However, the Se-Se pairs as a whole exhibited long-range order, which is significantly different from the Cu-Cu pairs. As a results, we believe that the Cu-Cu pairs exhibit disordered characteristics in long-range interactions, similar to amorphous liquids. In summary, the polar covalent bonds between Cu and Se can induce a liquidlike structural evolution of Cu atoms at high temperatures as the temperature increases, providing a clear physical and chemical insight into hierarchical vibrational mechanism.

IV. ELECTRICAL TRANSPORT MECHANISMS AND THERMOELECTRIC PERFORMANCE

The development of n -type BiCuSeO -based TE materials has long been a significant challenge, primarily due to its wide band gap and the strong p -type native dominated by Cu vacancies (V_{Cu}) [34,40,43]. In contrast, $\text{Bi}_2\text{O}_2\text{Se}$ semiconductor with wide band gap exhibits n -type behavior, attributed to the synergistic effects of Se vacancies (V_{Se}) and antisite defects (Bi_{Se}) [70]. Therefore, $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ can combine the characteristics of these two materials, offering a promising pathway for the development of n -type TE oxides, as demonstrated in

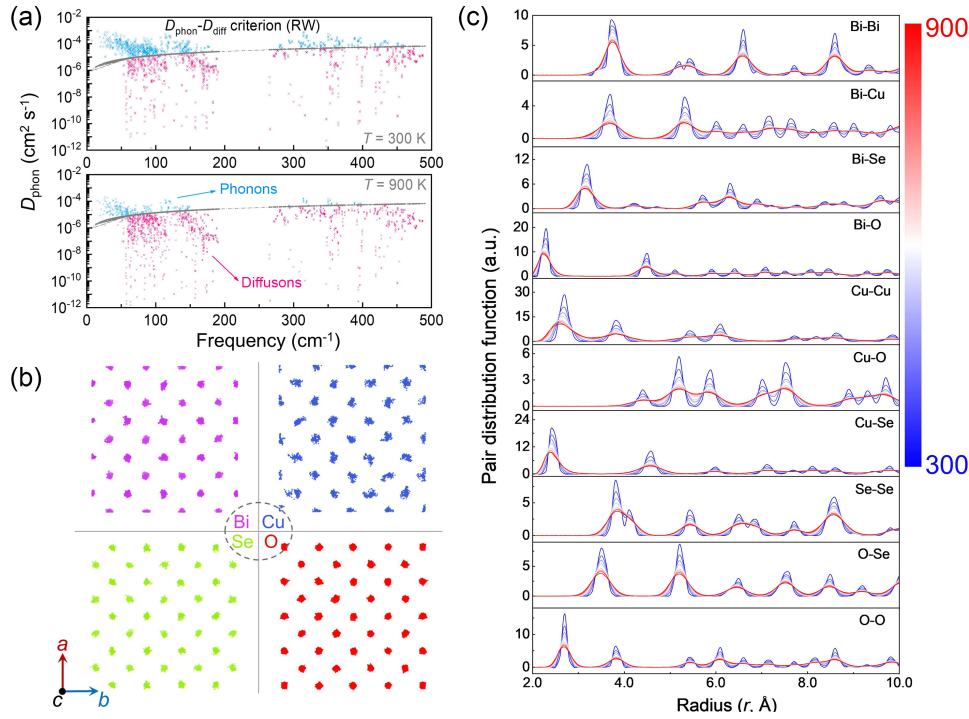


FIG. 4. Lattice vibrational and dynamics simulations. (a) The phonon thermal diffusivity (D_{phon}) of $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ as a function of temperature. The phonon modes of $D_{\text{phon}} > D_{\text{diff}}$ are assigned as phonon, otherwise diffuson, in which the D_{diff} is calculated based on the random walk (RW) theory. (b) The atomic thermal vibration trajectory diagram of $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ obtained from the AIMD simulations during the total time of 10 ps at 900 K. (c) The partial pair distribution functions (PDFs) of $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ at elevated temperatures.

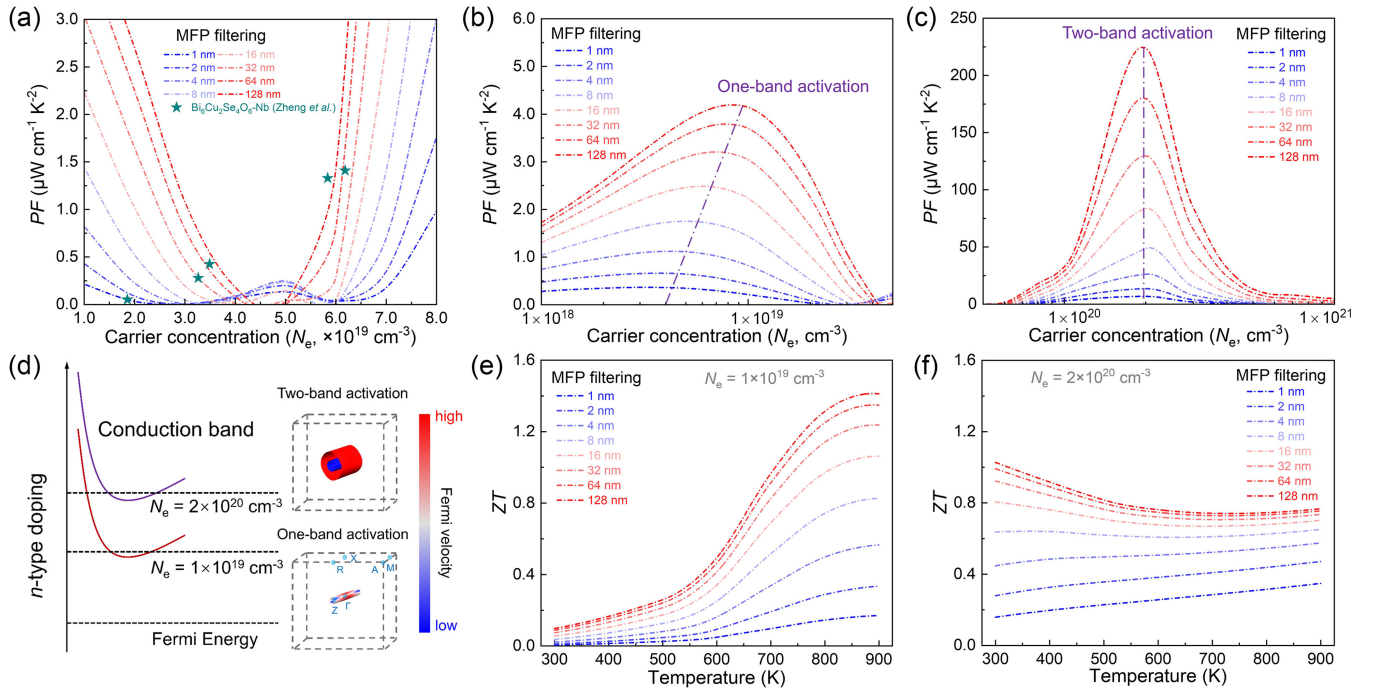


FIG. 5. Thermoelectric transport properties for n -type $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$. (a)–(c) The power factor (PF) as a function of carrier concentration at different carrier mean-free-path (MFP), including the experimental measurements [46]. (d) The schematic diagram of Fermi surface, including one-band activation and two-band activation situations. The color scale is the Fermi velocity, increasing from blue to red. (e), (f) The ZT as a function of temperature at different carrier MFP corresponding to electronic concentration $N_e = 1 \times 10^{19} \text{ cm}^{-3}$ and $N_e = 2 \times 10^{20} \text{ cm}^{-3}$, respectively.

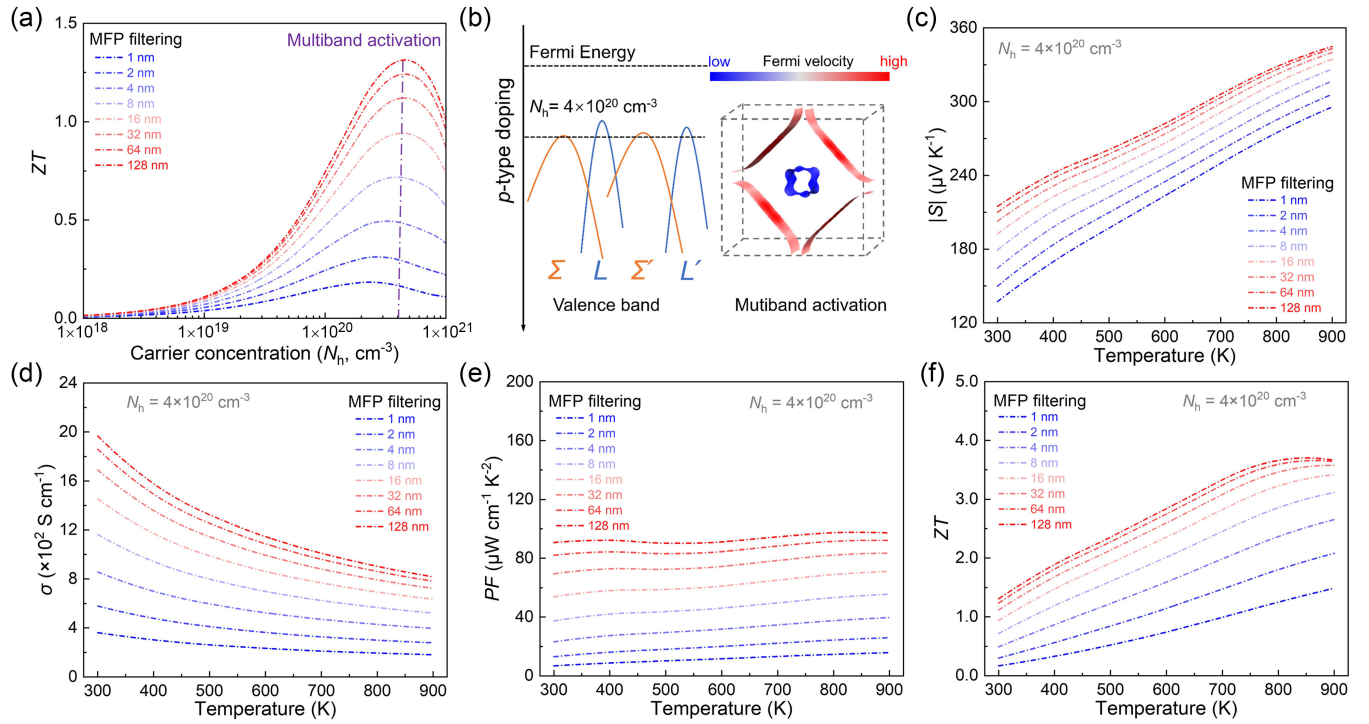


FIG. 6. Thermoelectric transport properties for p -type $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$. (a) The ZT as a function of carrier concentration at different carrier MFP. (b) The schematic diagram of Fermi surface at multiband activation situations. The color scale is the Fermi velocity, increasing from blue to red. (c)–(f) The Seebeck coefficient ($|S|$), electrical conductivity (σ), power factor (PF), and ZT as a function of temperature at different carrier MFP corresponding to hole concentration $N_h = 4 \times 10^{20} \text{ cm}^{-3}$.

our previous work [46–49]. Owing to the introduction of favoring n -type defects and the reduction in band gap, the intrinsic $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ exhibits a p - n transition behavior with increasing temperature [45,49]. Herein, we performed carrier transport calculations to evaluate the optimization potential of $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ under different electronic MFP for both n - and p -type cases, considering scattering mechanisms including elastic acoustic deformation potential scattering, ionized impurity scattering, carrier boundary scattering, and inelastic polar optical phonon scattering (Fig. S13 in SM [62]).

After calculating the Seebeck coefficient and electrical conductivity (Fig. S14 in SM [62]), we analyzed the power factor (PF) as a function of carrier concentration at room temperature, as shown in Figs. 5(a)–5(c), where the electronic MFP filtering was varied from 1 to 128 nm. Since the synthesis process and sample homogeneity affect grain size, the reported experimental PF values [46] were consistent with those calculated based on different electronic MFPs, demonstrating the robustness of the calculation results. An intriguing observation was that the calculated PF exhibits two peak values, indicating the presence of two carrier optimization regions in n -type $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$. In fact, this phenomenon was caused by the sequential activation of two conduction bands in the same momentum space [Fig. 5(d)], attributing to the overlapping fluctuations of Seebeck coefficients [Fig. S14(a) in SM].

In the case of one-band activation (low carrier concentration), the enhancement of electrical transport properties mainly originates from carrier mobility [4]. Consequently, the different carrier MFPs can significantly affect the carrier mobility (Fig. S15 in SM [62]), leading to a shift in the optimal PF . In contrast, the two-band activation occurs at higher carrier concentrations, where it already plays a dominant role in enhancing electrical transport properties. Thus, variations in electronic MFPs would affect only the peak value without causing a significant shift. Meanwhile, the Fermi surfaces corresponding to both activation scenarios are shown in Fig. 5(d). Combined with thermal transport properties, Figs. 5(e) and 5(f) present the ZT of n -type $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ as a function of temperature at electronic concentration of $\sim 1 \times 10^{19}$ and $\sim 2 \times 10^{20} \text{ cm}^{-3}$, respectively. The calculated results have indicated potential ZT optimization for different n -type $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ samples (variable carrier MFP), depending on crystallization and grain boundary size. For high-quality n -type samples, the electrical transport properties are primarily governed by the electronic band structure. Therefore, for TE cooling, the carrier concentration of n -type $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ should be increased to achieve two-band activation, enhancing the room-temperature ZT by up to ~ 1.0 . In addition, for TE power generation, the carrier concentration should be reduced to satisfying one-band activation, improving the high-temperature ZT by up to ~ 1.4 .

Many efforts on *p*-type TE oxides in recent years have been focused on BiCuSeO-based semiconductors [32,40]. However, the *p*-type Bi₆Cu₂Se₄O₆, exhibiting similar multivalence band characteristics, has not received sufficient attention. Therefore, it is necessary to theoretically evaluate their *p*-type TE performance before future experimental development. Figure 6(a) exhibits the room-temperature *ZT* of *p*-type Bi₆Cu₂Se₄O₆ as a function of carrier concentration. For high-quality *p*-type samples, the optimal *ZT* peak values were observed in the high carrier concentration region, unlike the *n*-type case. Based on the electronic band structure analysis, the VBMs of Bi₆Cu₂Se₄O₆ mainly are composed of two heavy (Σ and Σ') and two light (*L* and *L'*) bands, distributed across different momentum spaces. This characteristic has determined that optimal TE can be achieved by increasing the carrier concentration to activating more Fermi surfaces [Fig. 6(b)]. Therefore, for high-quality *p*-type samples, the optimal carrier concentration when *ZT* reaches its peak was approximate around $4 \times 10^{20} \text{ cm}^{-3}$.

Figures 6(c) and 6(d) present the Seebeck coefficients and electrical conductivity of Bi₆Cu₂Se₄O₆ as a function temperature with the carrier concentration of $4 \times 10^{20} \text{ cm}^{-3}$ under different MFPs. The Seebeck coefficient increases with rising temperature, while the electrical conductivity decreases as the temperature rises. Notably, the Seebeck coefficient and electrical conductivity achieve a trade-off with varying carrier concentration at the condition of multiband activation, leading to an optimized *PF* of $\sim 90 \mu\text{W cm}^{-1} \text{ K}^{-2}$ across the entire temperature range [Fig. 6(e)]. The calculated *PF* remains nearly constant with increasing temperature, aligning well with experimental observations of some TE materials with complex electronic band structure [11,22,71]. Combined with thermal transport properties, Fig. 6(f) presents the *ZT* of *p*-type Bi₆Cu₂Se₄O₆ as a function of temperature at a hole concentration of $4 \times 10^{20} \text{ cm}^{-3}$. We calculated that for high-quality *p*-type samples, the room-temperature performance of Bi₆Cu₂Se₄O₆ is expected to be *ZT* > 1.0, while this value might exceed 3.0 at elevated temperatures, highlighting its potential as a promising high-performance *p*-type TE oxides.

V. CONCLUSION

In conclusion, establishing the relationship between superlattice and TE properties provides valuable insights for improving TE performance. In this work, the Bi₆Cu₂Se₄O₆ polycrystal sample was synthesized, and the primitive cell of superlattice was constructed according to STEM characterizations. By crystal bonding and electronic band structure calculations, the formation of superlattice and the origin of narrow band gap were explored. Results demonstrated that Bi₂O₂Se can spontaneously enter BiCuSeO interlayer by reducing its lattice symmetry, inducing lattice contraction, which promoted the splitting

of Cu-3*d* orbitals and the orbital hybridization between Bi-6*p* and O-2*p*, causing a narrow band gap. Subsequently, combined with dual-phonon theory and experimental observations, more diffusons were found in high-temperature region. To illustrate the underlying mechanisms, we performed the MSD analysis, which exhibited significant vibrations occurring in Cu and Se atoms. Phonon spectrum further demonstrated that the lone pair rattler of Bi induced intense vibrations in adjacent Se atoms in [Se]²⁻ unit due to the avoided-crossing behavior. The COHP indicated that the antibonding states of Cu – Se in [Cu₂Se₂]²⁻ unit softened the phonon modes, reducing phonon group velocity and leading to WP₄ > WP₃. AIMD simulations and PDF together revealed that the polar covalent bond of Cu – Se drives a liquidlike structural evolution of Cu atoms at elevated temperatures, offering a clear physical and chemical understanding of the hierarchical vibrational mechanism. Eventually, by combining phonon transport and electronic MFP filtering, theoretical results demonstrated that the *n*-type case exhibited two optimized carrier concentration regions with peak *ZT* values approaching ~ 1.0 at 300 K and ~ 1.4 at 900 K, respectively, while *p*-type showed a higher *PF* of $\sim 90 \mu\text{W cm}^{-1} \text{ K}^{-2}$ owing to its complex electronic band structure, leading to high-ranged TE performance among 300–900 K. Our current results not only enrich the understanding of transport behavior in materials with superlattice structures, but also shed light on more possibilities for the future development of TE oxides.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

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