






**Optical phonon dominated heat transport: A first-principles thermal conductivity study of BaSnS<sub>2</sub>**Zhi Li <sup>1,2</sup>, Hongyao Xie <sup>2,\*</sup>, Shiqiang Hao <sup>3</sup>, Yi Xia,<sup>3</sup> Xianli Su <sup>1</sup>, Mercuri G. Kanatzidis,<sup>2,†</sup>  
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Acoustic phonons with long mean free paths have long been believed to control the lattice thermal conductivity  $\kappa_L$  in solids dominantly. In this study, however, we demonstrate an optical phonon dominated  $\kappa_L$  in BaSnS<sub>2</sub>. By solving the Peierls-Boltzmann transport equation, we predict a low diagonal lattice thermal conductivity  $\kappa_L(\text{D})$  of 0.34 W m<sup>-1</sup> K<sup>-1</sup> at 850 K, which is less than half the  $\kappa_L(\text{D})$  of SnS at the same temperature. Further calculations following the Allen-Feldman model suggest the additional off-diagonal lattice thermal conductivity  $\kappa_L(\text{OD})$  contributed by wavelike tunneling phonons. The  $\kappa_L(\text{OD})$  becomes pronounced at the high temperature (0.17 W m<sup>-1</sup> K<sup>-1</sup> at 850 K) and leads to a deviation of the temperature dependence of  $\kappa_L$  from  $T^{-1}$  to  $T^{-0.76}$ , suggesting the potential lattice anharmonicity in BaSnS<sub>2</sub>. Further analyses indicate BaSnS<sub>2</sub> has over 68% of  $\kappa_L$  contributed by optical phonons. We show this uncommon optical phonon dominated  $\kappa_L$  is due to the relatively high group velocities of optical phonons in BaSnS<sub>2</sub>. The phonon mode visualization suggests these relatively high-velocity optical phonons correspond to the antiphase vibrations in BaSnS<sub>2</sub> monolayers, which is originated from the unique permutation of SnS<sub>3</sub> tetrahedra. Finally, by investigating the mode-resolved group velocity, relaxation time, and Grüneisen parameter, we attribute the intrinsic low  $\kappa_L$  of BaSnS<sub>2</sub> to the soft lattice and the relatively high lattice anharmonicity induced by the Ba-S weak bonding and Sn(II) lone-pair electrons. Our study explicitly analyzes the microscopic mechanism of optical phonon dominated heat transport in BaSnS<sub>2</sub> and suggests it worthy of further experimental studies as an intrinsic low- $\kappa_L$  material.

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Materials with low lattice thermal conductivity  $\kappa_L$  have received much attention in many science and technology fields, including thermoelectricity [1,2], heat management [3,4], and thermal barrier coatings [5]. To search for these materials, we must first understand the underlying heat transport mechanism. In crystals, heat is transported, in part, by the propagation of vibration modes. The phonon gas model has been widely used to describe such particlelike heat-transport behaviors in the lattice. Depending on the vibration modes, phonons are classified as either acoustic or optical. Acoustic phonons represent the in-phase movements of all atoms in the lattice and generally have low frequencies as well as high group velocities and long mean free paths. Optical phonons at higher frequencies represent the out-of-phase movements of different atoms in the lattice and tend to possess low group velocities and short mean free paths. The lattice thermal conductivity in solids can be studied using kinetic theory [6], with  $\kappa_L = 1/3C_V\nu l$ , where  $C_V$  is the heat capacity,  $\nu$  is the phonon group velocity, and  $l$  is the phonon mean free

path. Because acoustic phonons usually have significantly higher  $\nu$  and longer  $l$  than optical phonons, they are typically considered the dominant contributors to the lattice thermal conductivity, and the role of optical phonons is far less studied in most materials. However, a recent study of SnS revealed that acoustic phonons are not the only source of  $\kappa_L$ , and more than 70% of the  $\kappa_L$  of SnS are actually contributed by its optical phonons [7]. Here,  $\kappa_L$  can be divided into the acoustic-phonon part  $\kappa_{La}$  and the optical-phonon part  $\kappa_{Lo}$ . In addition,  $\kappa_{Lo}$  has also been reported to account for over 20% of the  $\kappa_L$  in PbSe [8], PbTe [8], and CoSb<sub>3</sub> [9]. On the other hand, in some highly anharmonic crystals, heat is transported by the coupling of vibrational modes following the Allen-Feldman model [10]. This wavelike tunneling effect can be considered by calculating the off-diagonal elements of the heat-flux operators. A unified theory of both thermal transport mechanisms (i.e., particlelike propagation and wavelike tunneling) has been successfully applied in calculations of the  $\kappa_L$  in CsPbBr<sub>3</sub> [11] and Si [12].

Recently, we found a rarely reported SnS-based material, BaSnS<sub>2</sub> [13], possessing nearly the same Sn-S skeleton with SnS, but with the additional heavy element Ba. More importantly, we found the optical phonons are also predominant in the heat transport in BaSnS<sub>2</sub>, i.e., over 68% of  $\kappa_L$  contributed by its optical phonons, similar to that of 71% in SnS. Considering the similar Sn-S framework and the predominant optical phonon thermal conductivity in BaSnS<sub>2</sub> and SnS, it

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TABLE I. Lattice parameters of SnS and BaSnS<sub>2</sub> from this work and literature.

	SnS			BaSnS <sub>2</sub>		
	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)
PBEsol (this work)	11.09	3.99	4.23	6.06	12.11	6.23
PBE (this work)	11.43	4.02	4.45	6.19	12.54	6.35
LDA (this work)	10.97	3.95	4.19	6.00	11.91	6.16
PBE (Ref. [20])	11.42	4.02	4.46			
LDA (Ref. [21])	10.96	3.95	4.20			
Experiment (Ref. [22])	11.20	3.99	4.33			
Experiment (Ref. [23])	11.18	3.98	4.33			
Experiment (Ref. [13])				6.08	12.14	6.24

inspired our interest to study the correlation between the Sn-S framework and the optical phonon thermal conductivity in these materials.

In this work, we report the optical phonon dominated  $\kappa_L$  of BaSnS<sub>2</sub> and the underlying microscopic mechanism. The low diagonal lattice thermal conductivity  $\kappa_L(D)$  of BaSnS<sub>2</sub> was initially calculated using density-functional theory (DFT) combined with the Peierls-Boltzmann transport equation (PBTE) [14]. Further calculation based on the Allen and Feldman model indicates that the off-diagonal components in heat flux operators also have moderate contributions to  $\kappa_L$ , which we define as  $\kappa_L(OD)$ . The  $\kappa_L(OD)$  becomes pronounced at high temperatures and eventually leads to a deviation of the temperature dependence of  $\kappa_L$  from  $T^{-1}$  to  $T^{-0.76}$ , suggesting the potential lattice anharmonicity in BaSnS<sub>2</sub>. We then calculated the mode-specific  $\kappa_L$  contribution to identify the  $\kappa_L$ -dominant phonons. The result suggests that optical phonons with relatively high group velocities dominate the  $\kappa_L$ . By visualizing the corresponding vibration modes, we attribute these relatively high-velocity optical phonons to the antiphase vibrations in BaSnS<sub>2</sub> monolayers, which results from the unique permutation of SnS<sub>3</sub> tetrahedra. Finally, through investigating the mode-resolved group velocity, relaxation time, and Grüneisen parameter, we ascribe the intrinsic low  $\kappa_L$  in BaSnS<sub>2</sub> to the soft lattice and the relatively high lattice anharmonicity resulting from the Ba-S weak bonding and Sn(II) lone-pair electrons.

## II. CALCULATION METHODS

All the DFT calculations were performed using the Vienna *Ab initio* Simulation Package (VASP) [15] implemented with the projector augmented-wave method [16]. We used a high plane-wave cutoff energy of 500 eV, with Ba *5s5p6s* electrons, Sn *4d5s5p* electrons, and S *3s3p* electrons as valence electrons. The local density approximation (LDA) [17], Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) [18] and revised PBE-GGA for solids (PBEsol) [19] were all evaluated as the exchange-correlation functional. The comparison of the theoretical and experimental results [13,20–23] in Table I suggests that the LDA (or PBE) functional tends to underestimate (or overestimate) the lattice constants because of their well-known deficiency of overbinding (or underbinding) the chemical bonding. In

contrast, the revised PBEsol-GGA functional overcomes this problem and yields the closest lattice parameters to the experimental values. Therefore, we adopted the PBEsol-GGA functional to relax the crystal structure of SnS and BaSnS<sub>2</sub>, and then used it in the following self-consistent calculations. *k* grids of  $5 \times 13 \times 12$  and  $8 \times 4 \times 8$  were applied for SnS and BaSnS<sub>2</sub> structure relaxation, respectively. The convergence criterion energy of the self-consistent step was  $10^{-8}$  eV. The lattice parameters and atomic positions were fully relaxed until the Hellmann-Feynman forces between any two atoms were less than  $10^{-3}$  eV Å<sup>-1</sup>.

The lattice thermal conductivity  $\kappa_L$  can be obtained from Peierls-Boltzmann equation [24] as

$$\kappa_L = \frac{\hbar^2}{V_{\text{prim}} N k_B T^2} \sum_{\mathbf{q}n} n_{\mathbf{q}n} [n_{\mathbf{q}n} + 1] \omega_{\mathbf{q}n}^2 \mathbf{v}_{\mathbf{q}n} \otimes \mathbf{v}_{\mathbf{q}n} \tau_{\mathbf{q}n}, \quad (1)$$

where  $\hbar$ ,  $V_{\text{prim}}$ ,  $N$ ,  $k_B$ , and  $T$  are, respectively, the reduced Planck constant, volume of the primitive cell, the number of sampled  $q$  points, Boltzmann constant, and the absolute temperature.  $\mathbf{q}$  and  $n$  index the wave vector and phonon branch of the phonon mode.  $n$ ,  $\omega$ , and  $\mathbf{v}$ , are, respectively, the Bose-Einstein distribution function, frequency, and group velocity of the corresponding phonon mode. We used PHONOPY [25], a package implemented with the finite displacement method, to calculate the phonon dispersion and extract second-order interaction-force constants (2nd-order IFCs), which are used to construct the dynamical matrix and calculate the harmonic phonon properties we mentioned above. To calculate the relaxation time  $\tau$ , the anharmonic interaction must be considered. We employed the script `thirdorder.py` [14] to build the supercell configuration and extract third-order interaction force constants (3rd-order IFCs) to account for three-phonon scattering process. When generating the 2nd-order IFCs, we confirmed that a  $3 \times 3 \times 3$  supercell configuration for both SnS and BaSnS<sub>2</sub> was sufficient to cover all the long-range corrections. When generating the 3rd-order IFCs, a  $2 \times 4 \times 4$  supercell configuration and a  $2 \times 1 \times 2$  supercell configuration were built for SnS and BaSnS<sub>2</sub>, respectively. After the interaction-force convergence test, we used a strict force cut-off radius of 0.5 nm for both compounds. Interactions between atoms spaced further than this radius were neglected and were considered as not contributing to the  $\kappa_L$ . Finally, the  $\kappa_L$  from diagonal terms of the heat-flux operators was calculated by finding the full iterative solution to the PBTE using the SHENGBTE [14] package. The  $\kappa_L$  contribution from off-diagonal terms of the heat-flux operators was calculated following the unified theory proposed by Simoncelli *et al.* [11] based on the single-mode relaxation time approximation, which has been implemented and detailed in our earlier publications [26,27]

## III. RESULTS AND DISCUSSION

### A. Crystal structure

As portrayed in Fig. 1(a), BaSnS<sub>2</sub> crystallizes in a layered monoclinic structure (space group  $P2_1/c$ ,  $a = 6.08$  Å,  $b = 12.14$  Å,  $c = 6.24$  Å) and shares similar structural features with SnS (space group  $Pnma$ ,  $a = 11.18$  Å,  $b = 3.98$  Å,  $c = 4.33$  Å) shown in Fig. 1(b). The in-plane directions of BaSnS<sub>2</sub>

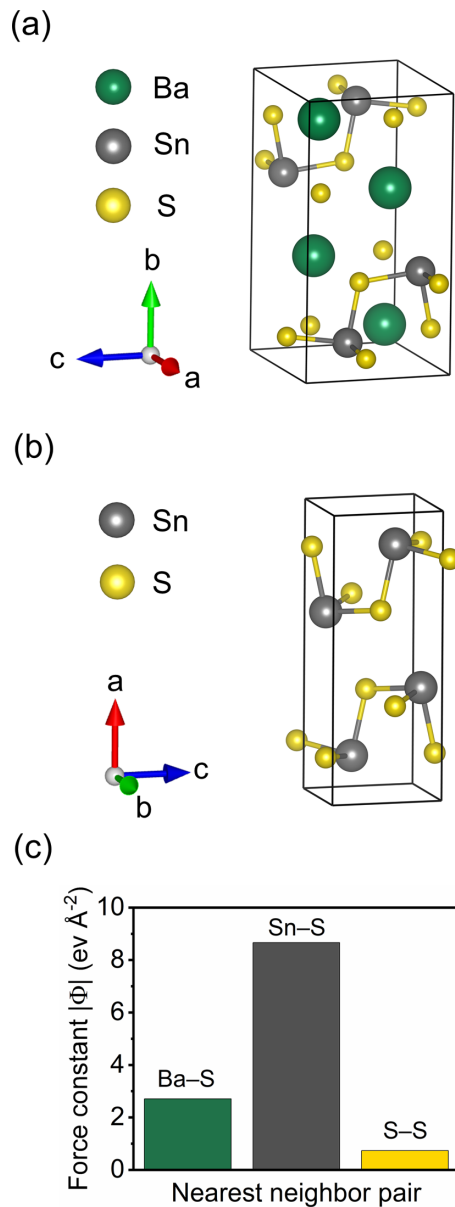


FIG. 1. Crystal structure of BaSnS<sub>2</sub>. (b) Crystal structure of SnS. (c) Second-order interatomic force constants of the nearest-neighbor pairs in BaSnS<sub>2</sub>. The 2nd-order IFC serves as an indicator for the bonding strength between the nearest-neighbor pairs. The higher 2nd-order IFC a nearest-neighbor pair has, the stronger bonding it presents.

can be viewed as accordionlike Sn-S chains with minor distortions expanding along the *c* axis. Ba<sup>2+</sup> ions fill the interval between neighboring Sn-S chains along the *a* axis. For the out-of-plane direction (the *c* axis), except for the weak bonding between Sn-S layers, there is also weak ionic bonding between Ba<sup>2+</sup> and S<sup>2-</sup> from different layers of BaSnS<sub>2</sub>. In SnS, the Sn(II) atom is in an asymmetric octahedral site. Instead of being in the octahedron center, it shifts closer to one of the triangular faces and coordinates with three S atoms via two short Sn-S bonds (2.57 Å) and one long Sn-S bond (2.60 Å), which permits the formation of a 5s<sup>2</sup> lone pair [28,29] that occupies one corner of the SnS<sub>3</sub> tetrahedron, as shown in Fig. S1(a) [30]. The neighboring corner-shared SnS<sub>3</sub> tetra-

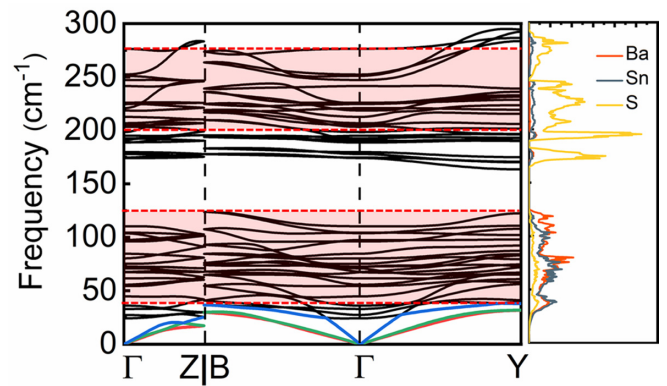


FIG. 2. Phonon dispersion and projected density of states of BaSnS<sub>2</sub>. Frequency ranges in red windows (45–125 and 200–275 cm<sup>-1</sup>) indicate optical phonons with group velocities close to or higher than acoustic phonons.

hedra tend to choose as distant as possible positions to accommodate their lone pairs because of the electrostatic repulsion, while the symmetry guarantees that every two neighboring SnS<sub>3</sub> tetrahedra can still coincide completely by rotating one of them towards the other. This unique zigzag accordionlike shape of Sn-S chains are inherited by BaSnS<sub>2</sub>, as illustrated in Fig. S1(b) [30], with minor distortions in bond lengths (three Sn-S bonds at the length of 2.538, 2.598, and 2.615 Å) and bond angles. The further distortions of SnS<sub>3</sub> tetrahedra in BaSnS<sub>2</sub> are due to the disturbance from weak bonding between Ba and S. In BaSnS<sub>2</sub>, Ba<sup>2+</sup> ions have distorted sixfold coordination with six S atoms from the neighboring Sn-S chains, with Ba-S bond lengths ranging from 3.12 to 3.19 Å. Such distorted structures in SnS and BaSnS<sub>2</sub> not only strengthen the lattice anharmonicity but also have a decisive influence on the prevalent vibration modes in the systems, which we will explain in detail in the vibration mode visualization section. In addition, we extracted the 2nd-order IFC of BaSnS<sub>2</sub> and used it as an indicator for the bonding strength between the nearest-neighbor pairs, as shown in Fig. 1(c). The higher 2nd-order IFC a nearest-neighbor pair has, the stronger bonding it presents. As the covalent bonding skeleton of the system, the Sn-S bonding is undoubtedly the strongest, with the 2nd-order IFC of 8.67 eV/Å<sup>2</sup>. The Ba-S bonding, in contrast, is significantly weaker, with the 2nd-order IFC of only 2.71 eV/Å<sup>2</sup>. The weak bonding between Ba<sup>2+</sup> ions and the Sn-S framework would significantly soften the lattice and slow down the phonon transport. The 2nd-order IFC of S-S interaction is 0.73 eV/Å<sup>2</sup>, indicating weak interlayer forces between Sn-S layers.

## B. Phonon dispersion

The phonon dispersion and projected density of states (DOS) for BaSnS<sub>2</sub> are presented in Fig. 2. In BaSnS<sub>2</sub>, most of the phonon bands are much flatter than those in SnS as shown in Fig. S2 [30]. As the group velocity of phonon modes is the derivative of the phonon frequency with respect to the wave vector, this result suggests that phonon modes in BaSnS<sub>2</sub> have overall low group velocity, which we attribute to the weak bonding induced by Ba<sup>2+</sup> ions. Meanwhile,

several optical phonon branches in the range of 45–125 and 200–275  $\text{cm}^{-1}$  (in red windows in Fig. 2) exhibit larger slopes than acoustic phonon branches, indicating relatively higher group velocities. This phenomenon is fairly uncommon as the group velocities of optical phonons in most materials tends to be much lower than acoustic phonons. These high-velocity optical phonons are related to anomalous high  $\kappa_{L0}$  in  $\text{BaSnS}_2$  according to our following analyses. On the other hand, all the optical phonon branches in Fig. 2 are spaced closely to each other. When their frequency differences are smaller than their linewidths, there is a high chance these phonon modes will couple with each other and contribute to a wavelike tunneling transport [11]. This feature suggests that extra  $\kappa_L$  might exist if we take into account these wavelike tunneling phonons when calculating the  $\kappa_L$  of  $\text{BaSnS}_2$ . From projected DOS, we can tell that acoustic phonons and low-frequency optical phonons are mainly contributed by  $\text{Ba}^{2+}$  ions and Sn atoms, while the high-frequency optical phonons are dominated by the vibrations of S atoms.

### C. Lattice thermal conductivity

Figure 3(a) displays the anisotropic  $\kappa_L(D)$  of  $\text{BaSnS}_2$  and SnS along the  $a$ -,  $b$ -, and  $c$ -axis calculated by solving the PBTE. The calculated room-temperature of SnS along the  $a$ -,  $b$ -, and  $c$ -axis are 1.0, 2.9, and 2.1  $\text{W m}^{-1} \text{K}^{-1}$ , which are close to the experimental results of He *et al.* [31].  $\text{BaSnS}_2$  exhibits a lower  $\kappa_L(D)$  than SnS in the corresponding directions. Especially along the  $b$  axis (the out-of-plane direction),  $\text{BaSnS}_2$  has a low  $\kappa_L(D)$  of merely 0.41  $\text{W m}^{-1} \text{K}^{-1}$  at 300 K and eventually 0.15  $\text{W m}^{-1} \text{K}^{-1}$  at 850 K. We also plotted the average  $\kappa_L(D)$  of  $\text{BaSnS}_2$  by calculating the arithmetic average of  $\kappa_L(D)$  along three axes, which goes from 0.94  $\text{W m}^{-1} \text{K}^{-1}$  at 300 K to 0.34  $\text{W m}^{-1} \text{K}^{-1}$  at 850 K. In contrast, SnS has the average  $\kappa_L(D)$  of 2.03  $\text{W m}^{-1} \text{K}^{-1}$  at 300 K and 0.73  $\text{W m}^{-1} \text{K}^{-1}$  at 850 K. This result implies that weak bonding and structural distortions induced by  $\text{Ba}^{2+}$  ions might suppress the heat transport in the Sn-S framework. Recent studies [11,12,27,32] have clarified the importance of off-diagonal components in heat-flux operators. Our phonon dispersion analysis also suggests the possible  $\kappa_L$  contributed by optical phonons with small frequency differences. Consequently, we calculated the off-diagonal lattice thermal conductivity  $\kappa_L(OD)$  separately to evaluate their contribution to the  $\kappa_L$ . Here, we define  $\kappa_L = \kappa_L(D) + \kappa_L(OD)$ . As shown in Fig. 3(b), the  $\kappa_L(OD)$  has a different anisotropy with  $\kappa_L(D)$ , i.e.,  $\kappa_L^{b \text{ axis}}(OD) > \kappa_L^{c \text{ axis}}(OD) > \kappa_L^{a \text{ axis}}(OD)$ . The  $\kappa_L^{b \text{ axis}}(OD)$  descends with the increasing temperature, while  $\kappa_L^{a \text{ axis}}(OD)$  and  $\kappa_L^{c \text{ axis}}(OD)$  ascend with the temperature. The total change of average  $\kappa_L(OD)$  with the temperature is less than 0.02  $\text{W m}^{-1} \text{K}^{-1}$ , suggesting a weak temperature dependence. The  $\kappa_L^{a \text{ axis}}(OD)$  and  $\kappa_L^{c \text{ axis}}(OD)$  at room temperature are negligible because they account for merely 10% of the  $\kappa_L$  along the corresponding direction. In comparison,  $\kappa_L^{b \text{ axis}}(OD)$  accounts for 35% of  $\kappa_L$  along the  $b$  axis. This is consistent with the phonon dispersion in Fig. 2, where the  $\Gamma$ -Z direction (corresponding to the  $b$  axis) presents flatter and denser optical phonon branches than the other two directions. With the temperature  $T$  increasing, the  $\kappa_L(D)$  decreases following a  $T^{-1}$  manner, which makes the weakly temperature-dependent

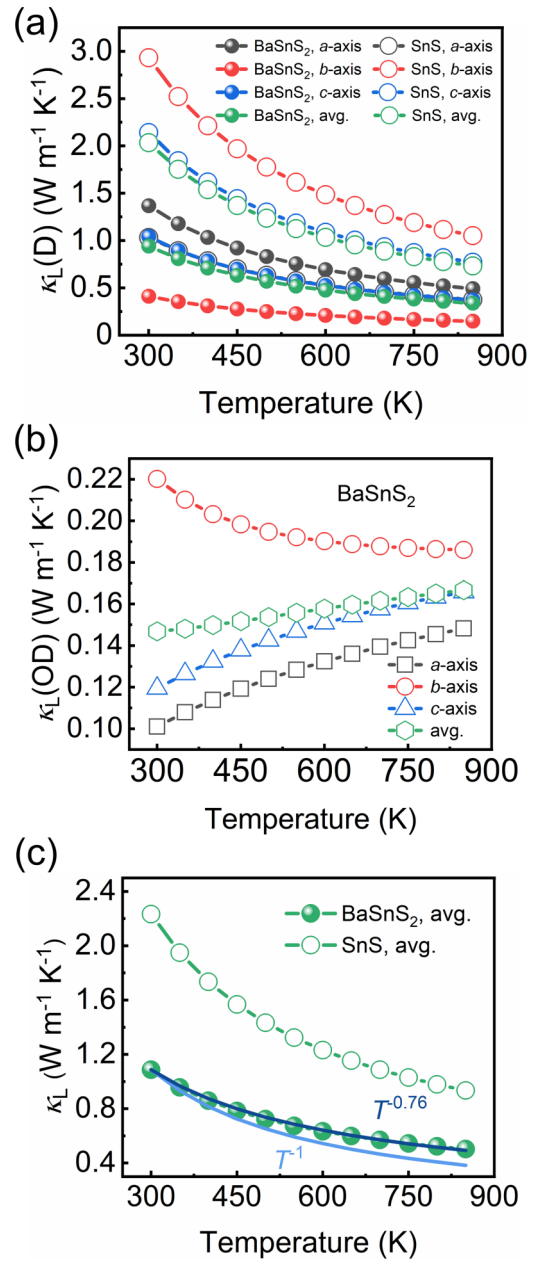


FIG. 3. Calculated diagonal lattice thermal conductivity  $\kappa_L(D)$  as a function of temperature in  $\text{BaSnS}_2$  and SnS. (b) Calculated off-diagonal lattice thermal conductivity  $\kappa_L(OD)$  as a function of temperature in  $\text{BaSnS}_2$ . (c) Calculated total lattice thermal conductivity  $\kappa_L = \kappa_L(D) + \kappa_L(OD)$  as a function of temperature in  $\text{BaSnS}_2$  and SnS. The solid lines without symbols are fitting lines indicating how  $\kappa_L$  decays with temperature  $T$ .

$\kappa_L(OD)$  gradually comparable to  $\kappa_L(D)$  at high temperatures. Eventually, the  $\kappa_L^{a \text{ axis}}(OD)$  and  $\kappa_L^{c \text{ axis}}(OD)$  reach 23 and 31% of the  $\kappa_L$  along the corresponding directions, and  $\kappa_L^{b \text{ axis}}(OD)$  even reaches 56% of the  $\kappa_L$  along the  $b$  axis. The gradually increasing average  $\kappa_L(OD)$  eases the decay of  $\kappa_L$  from  $T^{-1}$  to  $T^{-0.76}$ . Such deviation in the temperature dependence of  $\kappa_L$  is also found in some highly anharmonic systems such as  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  [27] and  $\text{TlInTe}_2$  [32], suggesting the potential lattice anharmonicity in  $\text{BaSnS}_2$ . Compared to SnS ( $\kappa_L(OD)$  plotted in Fig. S3 [30]),  $\text{BaSnS}_2$  has a higher proportion of

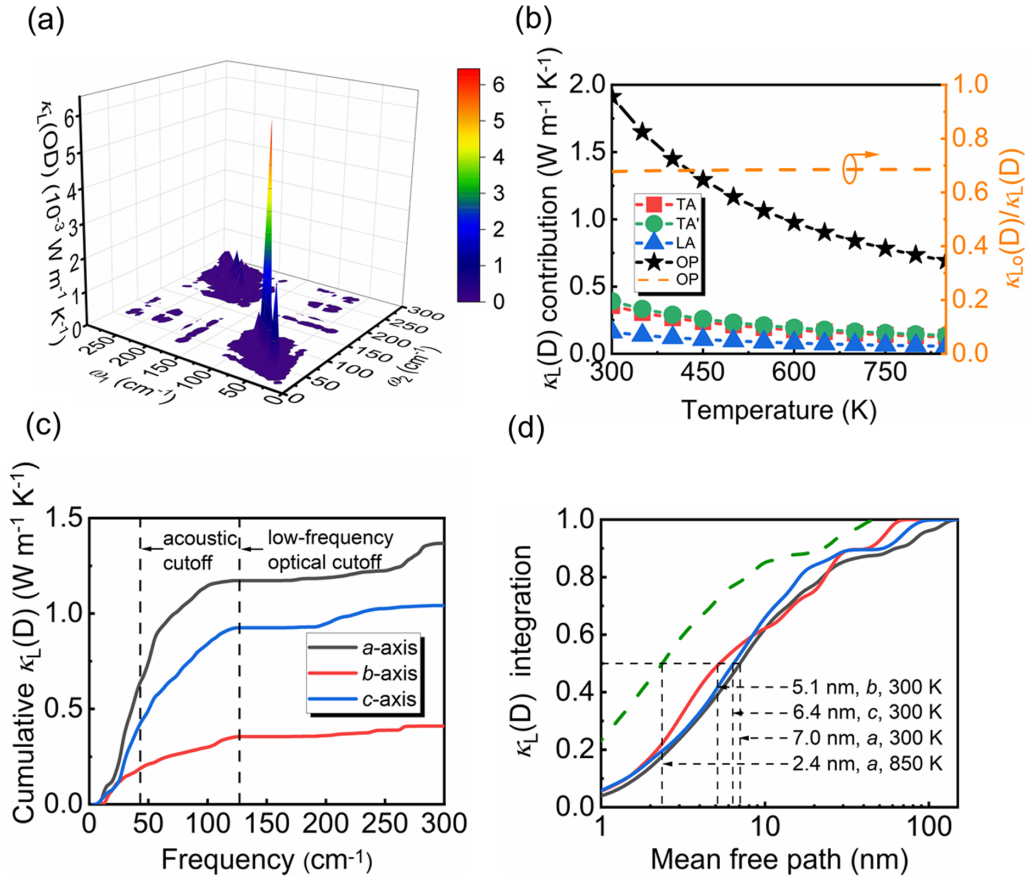


FIG. 4. Two-mode-dependent contributions to average  $\kappa_L(\text{OD})$  vs coupling phonon frequencies  $\omega_1$  and  $\omega_2$  at 300 K. (b) Temperature dependence of  $\kappa_L(\text{D})$  contribution from three acoustic phonon branches (TA, TA', and LA) and all the optical branches (OP) in BaSnS<sub>2</sub>. Note that  $\kappa_L(\text{D})$  here is the sum of diagonal lattice thermal conductivities along three axes. The right-hand axis indicates the ratio of optical phonon contributed lattice thermal conductivity  $\kappa_{L_o}(\text{D})$  to the  $\kappa_L(\text{D})$ . (c) Frequency dependence of cumulative  $\kappa_L(\text{D})$  at room temperature. (d) Mean free path dependence of  $\kappa_L(\text{D})$  integration at 300 and 850 K.

$\kappa_L$  contributed by off-diagonal components because of the stronger coupling between closely spaced phonon modes suggested by its denser phonon dispersion. Furthermore, the weak bonding between Ba and S results in a generally lower group velocity of both diagonal and off-diagonal operators, thus leading to the lower  $\kappa_L$  as plotted in Fig. 3(c).

In the phonon gas model, each phonon mode contributes to  $\kappa_L(\text{D})$  independently. In the Allen-Feldman model, however, as the wavelike tunneling effect is always concerning two coupling phonons, it is inappropriate to attribute the  $\kappa_L$  contribution from this effect to a single-phonon mode with a specific frequency and mean free path. Therefore, in the following  $\kappa_L$  contribution analyses, we discuss the  $\kappa_L$ -contribution from  $\kappa_L(\text{OD})$  and  $\kappa_L(\text{D})$  separately. In Fig. 4(a), we plot the two-mode dependent contributions to average  $\kappa_L(\text{OD})$  versus coupling phonon frequencies  $\omega_1$  and  $\omega_2$  at 300 K. This plot shows how much  $\kappa_L(\text{OD})$  is contributed by two coupling phonons with frequency  $\omega_1$  and  $\omega_2$ . The peaks mainly emerge around the diagonal ( $\omega_1 = \omega_2$ ) in the frequency ranges of 45–125 and 200–275  $\text{cm}^{-1}$ , indicating the  $\kappa_L(\text{OD})$  is mainly derived from the coupling of phonons with close frequencies. As we have observed in the phonon dispersion of BaSnS<sub>2</sub> that optical phonons in these frequency ranges tend to be more dispersive, the plot also suggests

that optical phonons with relatively high group velocities dominate the  $\kappa_L(\text{OD})$ . We further calculated the contributions to  $\kappa_L(\text{D})$  from three acoustic branches (the first transverse acoustic branch TA, the second transverse acoustic branch TA', and the longitudinal acoustic branch LA) and all the optical branches with respect to the temperature. As observed in Fig. 4(b), in BaSnS<sub>2</sub>, all the contributions to  $\kappa_L(\text{D})$  tend to decrease with increasing temperature because of the strengthening of Umklapp scattering, whereas  $\kappa_{L_o}(\text{D})/\kappa_L(\text{D})$  maintains approximately 68%, similar to that 71% in SnS (demonstrated in Fig. S4(a) [30]). Given that we already concluded  $\kappa_L(\text{OD})$  is mainly derived from the coupling of two optical phonons with similar frequencies, the results in Figs. 4(a) and 4(b) suggest the optical phonons have an even larger contribution to  $\kappa_L$  (over 68%) because they predominate in both  $\kappa_L(\text{OD})$  and  $\kappa_L(\text{D})$ . To further investigate which part of optical phonons has a major contribution to the  $\kappa_L(\text{D})$ , we calculated the frequency dependence of the cumulative  $\kappa_L(\text{D})$  at room temperature, as shown in Fig. 4(c). The cumulative  $\kappa_L(\text{D})$  increases with the increasing frequency, for  $\kappa_L(\text{D})$  contributions from phonons at different frequencies gradually add up. The cumulative  $\kappa_L(\text{D})$  along three directions increase significantly in the frequency range 0–45, 45–125, and 200–275  $\text{cm}^{-1}$ . The 0–45- $\text{cm}^{-1}$  frequency range is populated

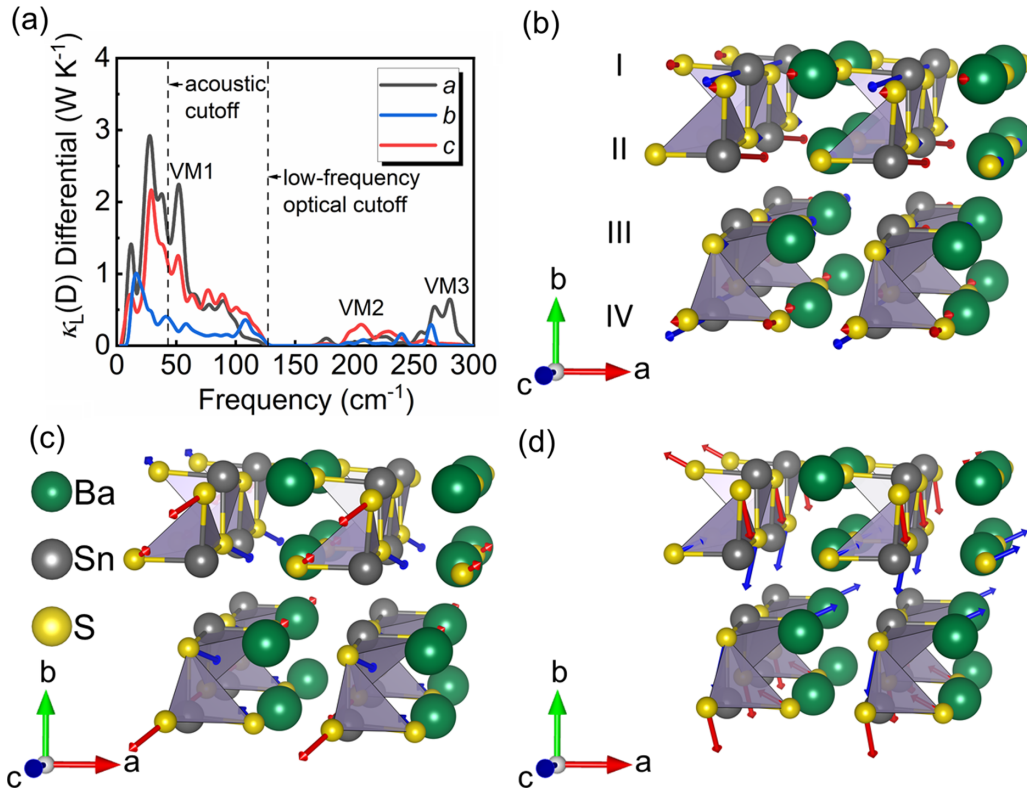


FIG. 5. (a)  $\kappa_L(D)$  differential with respect to phonon frequency in BaSnS<sub>2</sub>. The peaks of the most  $\kappa_L$ -contributive vibration modes are marked as VM1 at  $\sim 50$  cm<sup>-1</sup>, VM2 at  $\sim 200$  cm<sup>-1</sup>, and VM3 at  $\sim 275$  cm<sup>-1</sup>. (b), (c) Visualization of corresponding vibration modes. The  $2 \times 1 \times 2$  BaSnS<sub>2</sub> supercell is divided into IIV sublayers according to different orientations of SnS<sub>3</sub> tetrahedra between neighboring sublayers. Eigenvectors of vibrations are indicated by arrows. Arrows with different colors (blue and red) indicate pairs of antiphase vibrations in each BaSnS<sub>2</sub> monolayer. SnS<sub>3</sub> tetrahedra are colored in gray to better indicate their different orientations in each sublayer.

mainly by acoustic phonons, while the other two frequency ranges corresponding to the relatively high-group-velocity optical phonons. Now we find that optical phonons falling in these ranges lead to the high  $\kappa_{L0}(D)$  and  $\kappa_{L0}(OD)$  simultaneously, which deserves to be further analyzed. In addition, we also plotted the normalized  $\kappa_L(D)$  integration versus phonon mean free path at 300 K in Fig. 4(d). The results indicate that 50% of  $\kappa_L(D)$  of BaSnS<sub>2</sub> is contributed by phonons with mean free paths shorter than 7.0 nm. This value further decreases to 2.4 nm at 850 K. Similar results for SnS are exhibited in Fig. S4(c) [30]. Phonons with such small mean free paths can hardly be scattered by tens of nanometer scale impurity centers or grain boundaries introduced by nanostructuring. Therefore, this method is expected to have a limited effect on the  $\kappa_L$  of BaSnS<sub>2</sub> and SnS, while alloying might be effective to modify these short-mean free path optical phonons, as He *et al.* [33] has succeeded in suppressing the  $\kappa_L$  of SnS by alloying it with Se.

#### D. Visualization of high $\kappa_L$ -contribution optical phonon modes

To specifically locate the most  $\kappa_L$ -contributive optical phonon modes, we calculated the  $\kappa_L(D)$  differential with respect to the phonon frequency. Obviously, with 32% of the  $\kappa_L(D)$  in BaSnS<sub>2</sub> contributed by only three acoustic branches within a narrow frequency range (0–45 cm<sup>-1</sup>), the largest  $\kappa_L(D)$  differential should lie in the acoustic-phonon frequency range. However, because the total  $\kappa_L(D)$  contribution from

optical phonons is larger than that from acoustic phonons, we focus only on the optical-phonon frequency range. As shown in Fig. 5(a), some low-frequency (45–125 cm<sup>-1</sup>) optical phonons contribute significantly to the  $\kappa_L(D)$ . We can then visualize the vibration modes belonging to this range and select one of them with the highest peak at  $\sim 50$  cm<sup>-1</sup> (VM1) as a representative. In the same way, we choose VM2 and VM3 in the frequency range 200–275 cm<sup>-1</sup> to represent the vibration modes of high-frequency optical phonons. All the graphics of vibration mode visualization are made by VESTA 3 [34].

In Figs. 5(b)–5(d), we define the Ba-Sn-S layers stacking along the *b* axis as sublayers I–IV. The sublayers I and II, as well as sublayers III and IV, belong to the same BaSnS<sub>2</sub> monolayer. Atoms in each sublayer have identical vibration amplitude but opposite vibration directions, which we call the antiphase vibrations. For instance, in Fig. 5(b), all the atoms in sublayer I vibrate mainly towards the positive *c* axis, while in the neighboring sublayer II all the atoms vibrate mainly towards the negative *c* axis with the same amplitude. For the modes VM2 at  $\sim 200$  cm<sup>-1</sup> and VM3 at  $\sim 275$  cm<sup>-1</sup>, where S vibrations dominate, S atoms in the neighboring sublayers also have similar antiphase vibrations. As shown in Fig. 5(c), S atoms in sublayers I and IV vibrate mainly towards the positive *c* axis, whereas S atoms in sublayers II and III vibrate towards the negative *c* axis. In Fig. 5(d), S atoms present incomplete antiphase movements. They all have partial eigenvectors towards the negative *b* axis but combined with opposite partial eigenvectors along the *c* axis. It is worth noting that

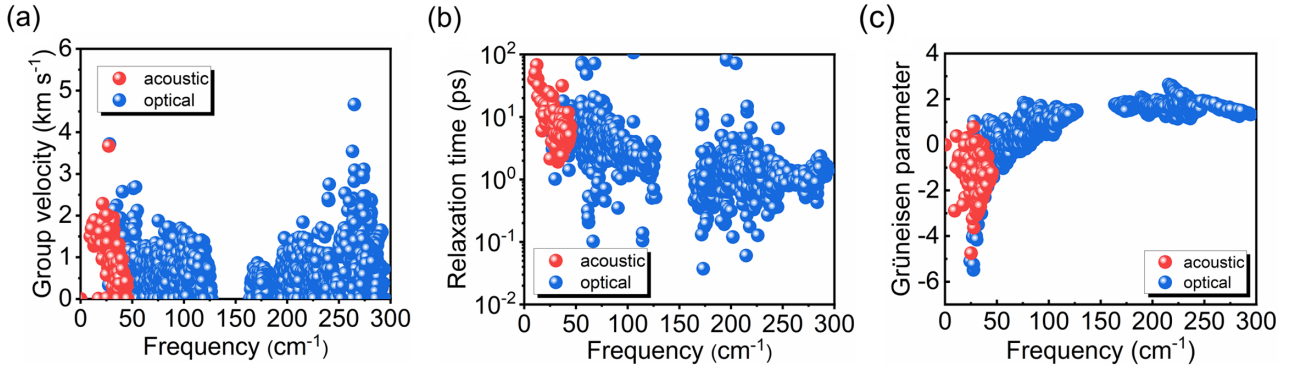


FIG. 6. Mode-resolved (a) group velocity (b) relaxation time, and (c) Grüneisen parameter vs phonon frequency in BaSnS<sub>2</sub> at room temperature.

owing to the influence of Ba<sup>2+</sup> ions, S atoms between Ba<sup>2+</sup> ions might have different vibrations with other S atoms that are exactly on the Sn-S chains, but they still present antiphase vibrations in each sublayer. The patterns of antiphase vibrations can be observed more intuitively in SnS, where there is only pristine Sn-S framework without the interference of Ba<sup>2+</sup> ions, as exhibited in Fig. S5 [30]. These antiphase vibrations are derived from the unique permutation of SnS<sub>3</sub> tetrahedra. As demonstrated in the crystal structure section, all the corner-shared neighboring SnS<sub>3</sub> tetrahedra have to accommodate the lone pairs at distant corners to diminish the electrostatic repulsion maximally. Consequently, the orientations of each neighboring SnS<sub>3</sub> tetrahedra are different from each other, but they can coincide with each other with certain rotating operations, as displayed in Figs. 5(b)–5(d). This unique symmetry combined with strong covalent Sn-S bonding inherited from SnS gives rise to highly synchronous antiphase movements in BaSnS<sub>2</sub>. We rarely see Sn and S in the same sublayer moving towards different directions even in other vibration modes that do not have as large  $\kappa_L$  contributions as VM1, VM2, and VM3. This special antiphase movement is similar to the famous pnictogen ring movement which is also corresponding to the heat-carrying optical phonon modes that account for 20% of the  $\kappa_L$  in skutterudite CoSb<sub>3</sub> [9,35,36]. The former is the synchronous movement of the entire Sn-S chain, and the latter is the synchronous movement of the local Sb<sub>4</sub> pnictogen ring. In Supplemental Material Sec. E [30], we demonstrate that three of the major heat-carrying optical modes in SnS also show these similar antiphase movements. All these high  $\kappa_L$ -contribution modes in BaSnS<sub>2</sub> and SnS fall into the previously mentioned frequency ranges that relatively high-velocity optical phonon belongs to. They are supposed to be the representatives of the prevailing vibration patterns in these high-velocity optical modes. In general, we visualized the vibration modes of optical phonons with the highest- $\kappa_L$  contributions in BaSnS<sub>2</sub>. They are highly synchronous antiphase movements in BaSnS<sub>2</sub> monolayer, which is attributed to the unique permutation of SnS<sub>3</sub> tetrahedra.

### E. Mode-dependent group velocity, relaxation time, and Grüneisen parameters

To further investigate the properties of heat-carrying phonons, we quantitatively characterized all the phonon modes in BaSnS<sub>2</sub> by giving the mode-resolved group velocity

$v$ , relaxation time  $\tau$ , and Grüneisen parameter  $\gamma$  from all the  $q$  points in the irreducible Brillouin zone at room temperature. We also calculated the same parameters of SnS as references in Fig. S6 [30]. As shown in Fig. 6(a), most of the phonon modes in BaSnS<sub>2</sub> present low group velocities less than 1 km s<sup>-1</sup>. The overall low group velocity in BaSnS<sub>2</sub> is consistent with the flat phonon bands observed in Fig. 2. Besides, the group velocities of optical phonons around 50 cm<sup>-1</sup> are very close to that of the acoustic phonons, and some optical phonons around 275 cm<sup>-1</sup> even possess higher group velocities than the acoustic ones, with a peak value of 4.7 km s<sup>-1</sup> at 270 cm<sup>-1</sup>. As we have mentioned above, these relatively high-velocity optical modes have high  $\kappa_L$ -contribution and correspond to those antiphase vibrations in BaSnS<sub>2</sub> monolayers. To give a more general description of the overall group velocity in BaSnS<sub>2</sub>, we defined the mode-average group velocity as

$$\bar{v} = \sqrt{\frac{\sum_{q_n} C_{Vq_n} v_{q_n}^2 \tau_{q_n} N_{q_n}}{\sum_{q_n} C_{Vq_n} \tau_{q_n} N_{q_n}}}, \quad (2)$$

where  $C_v$ ,  $v$ ,  $\tau$ , and  $N$  are, respectively, the mode heat capacity, group velocity scalar, relaxation time, and symmetry degeneracy of corresponding mode  $q_n$ . This parameter reflects the general level of all the phonon modes over the entire Brillouin zone. We calculated  $\bar{v}$  in BaSnS<sub>2</sub> to be 0.8 km s<sup>-1</sup>. Compared to  $\bar{v}$  of 1.1 km s<sup>-1</sup> in SnS, lower mode-average group velocity in BaSnS<sub>2</sub> confirms the lattice softening induced by Ba-S weak bonding.

Figure 6(b) shows the mode-resolved relaxation time (the reciprocal of phonon linewidths) with respect to the frequency. In BaSnS<sub>2</sub>, acoustic phonons have relaxation time ranging from 1 to 100 ps, while most optical phonons have short relaxation times less than 10 ps, which indicates optical phonons have larger phonon linewidths than acoustic ones. These highly broadening and closely spaced optical phonon modes couple with each other easily and contribute to a substantial wavelike tunneling heat transport, which explains the origin of  $\kappa_L$  (OD) in BaSnS<sub>2</sub>. The mode-average relaxation time reads

$$\bar{\tau} = \frac{\sum_{q_n} C_{Vq_n} v_{q_n}^2 \tau_{q_n}}{\sum_{q_n} C_{Vq_n} v_{q_n}^2}. \quad (3)$$

We obtained  $\bar{\tau}$  of 2.37 and 3.79 ps in BaSnS<sub>2</sub> and SnS, respectively. The likewise low  $\bar{\tau}$  in BaSnS<sub>2</sub> and SnS implies potential high lattice anharmonicity in both systems.

The lattice anharmonicity can be explicitly measured by mode Grüneisen parameters  $\gamma$  defined as  $\gamma_{qn} = -\partial \ln \omega_{qn} / \partial \ln V$  [37]. The  $\gamma$  quantifies the change of phonon frequencies  $\omega$  with respect to the change of unit-cell volume  $V$ . Positive or negative values of  $\gamma$  indicate the phonon frequency softening or hardening with the expansion of lattice. Larger absolute values of  $\gamma$  indicate the higher lattice anharmonicity in compounds. Solids with weak anharmonicity usually present  $\gamma$  lower than 1, while those with strong anharmonicity have  $\gamma$  close to or higher than 1 [38], such as InTe ( $\gamma \sim 1.00$ ) [39], PbTe ( $\gamma \sim 1.40$ ) [40], and BiCuSeO ( $\gamma \sim 1.50$ ) [41]. From Fig. S6(c) [30], we can tell that most heat-carrying phonons in SnS have  $\gamma$  larger than 1, especially those high-frequency optical phonons with  $\gamma$  ranging from 1 to 4. According to previous studies [28,42–44], the high lattice anharmonicity in SnS is originated from the lone-pair electrons of Sn(II). BaSnS<sub>2</sub> inherits this feature (we have elaborated in the crystal structure section) and presents even stronger lattice anharmonicity due to the extra disturbance that Ba<sup>2+</sup> ions bring to the Sn-S framework. As plotted in Fig. 6(c), phonon modes in the frequency range 0–125 cm<sup>-1</sup> present high Grüneisen parameters ranging from -6 to +2, suggesting high anharmonicity of certain acoustic phonon modes and low-frequency optical phonon modes in BaSnS<sub>2</sub>. The high-frequency optical phonon modes possess relatively lower Grüneisen parameters ranging from +1 to +2. We define the mode-average Grüneisen parameters as

$$\bar{\gamma} = \frac{\sum_{qn} |\gamma_{qn}| C_{Vqn}}{\sum_{qn} C_{Vqn}}. \quad (4)$$

The  $\bar{\gamma}$  of BaSnS<sub>2</sub> and SnS is 1.24 and 1.08, respectively, indicating overall higher lattice anharmonicity in BaSnS<sub>2</sub>. Our calculated Grüneisen parameters are derived from three-phonon interaction, as the strong lattice anharmonicity of SnS is reported more often at high temperatures [45–47]; we believe considering the phonon-frequency shifting induced by higher-order anharmonicity (such as quartic anharmonicity) at high temperature will offer a more comprehensive understanding of the lattice anharmonicity in both compounds. In Fig. S7 [30], the potential-energy surfaces (PES) were plotted and fitted with polynomials up to the second and fourth order, respectively, following the formalism proposed by Skelton *et al.* [48] The result shows PES of typical phonon modes in BaSnS<sub>2</sub> deviate more from the harmonic approximation than in SnS by considering up to quartic anharmonicity, implying potential higher lattice anharmonicity might be contributed from high-order anharmonic terms in BaSnS<sub>2</sub>. We realized that by performing phonon renormalization with cubic and quartic anharmonicity, a more explicit relation between the lattice anharmonicity and thermal conductivity could be unveiled. However, recent studies [49–51] have demonstrated the complex interplay between phonon renormalization, four-phonon scattering, and thermal expansion. In our previous study [26], the opposite influence that phonon renormalization and four-phonon scattering might have on the  $\kappa_L$  makes it nontrivial to clarify the relation between high-order

anharmonicity and  $\kappa_L$ . Given that BaSnS<sub>2</sub> has a large primitive cell (16 atoms), it requires tremendous resources and time to compute the four-phonon scattering rates and renormalize phonon frequencies with cubic and quartic anharmonicity. Therefore, it is practical to conclude with current results that BaSnS<sub>2</sub> has a stronger lattice anharmonicity than *Pnma* phase SnS whose low  $\kappa_L$  is previously attributed to the strong lattice anharmonicity [7,20].

In conclusion, the low group velocity, low relaxation time (large phonon linewidth), and high Grüneisen parameter indicate the soft and anharmonic lattice of BaSnS<sub>2</sub>, which slows down the entire phonon transport process and leads to an intrinsic low  $\kappa_L$ .

#### IV. CONCLUSION

Using the DFT methods combined with Peierls-Boltzmann transport theory, we first calculated the diagonal lattice thermal conductivity  $\kappa_L(D)$  derived from particlelike phonon transport in BaSnS<sub>2</sub>. The average  $\kappa_L(D)$  is less than half of that in SnS, with a low value of 0.34 W m<sup>-1</sup> K<sup>-1</sup> at 850 K. By taking into account the off-diagonal terms of general group velocity operators, we found additional off-diagonal lattice thermal conductivity  $\kappa_L(OD)$  contributed by wavelike tunneling phonon transport. With temperature increasing, the  $\kappa_L(OD)$  accounts for a higher proportion in  $\kappa_L$  and finally reaches 33% of the  $\kappa_L$  at 850 K. It leads to a milder decay of  $T$  dependence of  $\kappa_L$  from  $T^{-1}$  to  $T^{-0.76}$ , indicating the potential lattice anharmonicity in BaSnS<sub>2</sub>. Subsequent mode-specific  $\kappa_L$ -contribution investigations suggest that over 68% of  $\kappa_L$  in BaSnS<sub>2</sub> is contributed by optical phonons. This anomalous optical phonon dominated  $\kappa_L$  is ascribed to the relatively high group velocity of the heat-carrying optical phonons. These relatively high-velocity modes are then visualized as the antiphase vibrations in BaSnS<sub>2</sub> monolayers, resulting from the unique permutation of SnS<sub>3</sub> tetrahedra. Eventually, the low group velocity, low relaxation time, and high Grüneisen parameter are found in BaSnS<sub>2</sub>, suggesting the soft lattice and relatively high lattice anharmonicity induced by Ba<sup>2+</sup> ions and Sn(II) lone-pair electrons. All these factors suppress the phonon transport and contribute to the intrinsic low  $\kappa_L$ . BaSnS<sub>2</sub> is a special compound that nearly inherits the entire Sn-S conductive network from SnS while presenting much lower  $\kappa_L$ . Recent progress in experimental studies of SnS-based thermoelectrics implies that BaSnS<sub>2</sub> might also be a potential candidate for high-performance thermoelectric materials. Our study reveals the microscopic mechanism of heat transport in BaSnS<sub>2</sub> and suggests it worthy of further experimental studies as an intrinsic low- $\kappa_L$  material.

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