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Phys. Rev. B **94**, 115203 — Published 14 September 2016

DOI: [10.1103/PhysRevB.94.115203](https://doi.org/10.1103/PhysRevB.94.115203)

# Low phonon conductivity of layered BiCuOS, BiCuOSe, and BiCuOTe from first principles

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Combining the effect of layer mixing, mass mismatch, and intrinsic defects, we have investigated the origin of very low phonon conductivity  $k_p$  in thermoelectric (TE) BiCuOQ (Q: S, Se, Te) compounds. Based on the first-principles anharmonic, lattice dynamics calculations, we use the single-mode relaxation time approximation of the linearized phonon Boltzmann equation, which shows good agreement with experiments. Here, we found that the most important parameter for low  $k_p$  is the interlayer interaction between the BiO and CuQ layers. By analyzing the phonon linewidth distribution, which indicates the phonon scattering rate, we propose that the interlayer interactions play critical role on suppressing  $k_p$ , i.e., the hetero-layered crystal controls these interlayer interactions, achieving low  $k_p$  and optimal TE properties.

PACS number(s): 72.20.Pa, 66.70.Df, 31.15.A-, 63.22.Np

## I. INTRODUCTION

Lowering thermal conductivity is the most important issue in the thermoelectric (TE) material development. TE efficiency is quantified by the figure of merit  $ZT = S^2 \sigma_e T / k$ , where  $S$ ,  $\sigma_e$ ,  $T$ ,  $k$  are the Seebeck coefficient, electrical conductivity, absolute temperature, thermal conductivity. So, efficient TE materials essentially need the low  $k$  in addition to the optimization of the power factor (PF)  $S^2 \sigma_e$ . The total thermal conductivity  $k = k_e + k_p$  consists of both electronic and phonon contributions. For semiconductors (most of TE materials), the phonon contribution usually surpasses the electronic contribution, so lowering  $k_p$  becomes important. Indeed, there has been much research on achieving low  $k_p$ , such as the phonon glass-electron crystal [1], the construction of rattling ions in crystal [2-6], nanostructuring [7-10] and all-scale hierarchical architecting [11]. From the phonon perspective, the mass-mismatch of layers can lead to phonon scattering and low  $k_p$ . Indeed, the hetero-layered BiCuOQ compounds (Q: chalcogen elements S, Se, and Te) have been reported to be good candidates for high  $ZT$  with intrinsically low  $k_p$ .

The  $p$ -type BiCuOSe (BiCuSeO or BiOCuSe) is a recently reported high- $ZT$  thermoelectric (TE) material, i.e.,  $ZT = 1.4$  at 923 K [12]. The pristine compound exhibits intrinsically low  $k_p$  ( $< 1.0$  W/m-K), and its electrical conductivity is also small due to low hole mobility [13-16]. By doping with cations such as Ba<sup>2+</sup> into Bi<sup>3+</sup> site, however, the electrical conductivity as well as its PF have significantly increased. Further enhancement of the PF through doping with light atoms increases both the carrier concentration and the mobility. Although its PF is smaller than other high efficient TE materials, BiCuOSe can have high  $ZT$  values because of its very low  $k_p$ .

Figure 1(a) shows a typical BiCuOQ tetragonal crystal structure that is a ZrSiCuAs-type structure with the space group of  $P4/nmm$ . The unit cell consists of two different layers stacking along  $c$ -axis, which are the conducting  $[\text{Cu}_2\text{Q}_2]^{2-}$  and insulating  $[\text{Bi}_2\text{O}_2]^{2+}$  layers. It was reported that the mixing of two different layers allows the control of electronic band gap as well as the band structures around the band gap to induce the high PF [11]. The two different layers in this compound are intrinsically mixed with simple synthesizing technique, and various types of doping in each layer is available. For BiCuOSe,

the band gap is given by 0.8 eV with the valence band of  $[\text{Cu}_2\text{Se}_2]^{2-}$  character and the conduction band of  $[\text{Bi}_2\text{O}_2]^{2+}$  character as illustrated in Fig. 1 (b) [18, 19].

The TE properties  $S$  and  $\sigma_e$  of the BiCuOQ compounds have been predicted by the Boltzmann transport equation (BTE) combined with the first-principles band structure calculations. Using a simple rigid-band and the constant relaxation time approximation (RTA), the calculated PF showed good agreement with experimental results at same doping condition. Moreover, the electronic structure calculations also suggested the optimal charge carrier density doping maximizing the PF of BiCuOQ compounds [18] and verifying the origin of anomalous increases of hole carrier concentration of Pb doped BiCuOTe [20]. The  $k$ , however, cannot be described by the electronic structures only because the phonon contribution may dominate over the electronic contribution. So, accurate prediction of  $ZT$  in BiCuOQ compounds requires the prediction of  $k_p$ .

There are two common theoretical treatments of the phonon transport, namely, atomistic molecular dynamics (MD) technique and continuum transport theory. The MD simulations provides the insight into the lattice dynamics at the atomic level. With a given material structure and suitable interatomic potentials, the MD simulations have been used to match well the experimental lattice properties of simple two-atom TE materials. [21, 22] However, the semi-empirical interatomic potentials are generally obtained by fitting the experimental lattice properties. So the complex systems are very challenging to describe their atomic interactions with simple two-body and three-body interactions. To overcome this limitation, the *ab initio* MD simulations have been used for simple systems with advances in computing resources [23, 24]. The advantage is no need for fitting to existing experimental data, but it is computationally extensive. Another approach is the continuum transport theory (or kinetic theory), such as the phonon BTE, which is suitable for fast calculation of large systems. Recent development of the perturbation theory within density functional theory (DFT) allows for the third-order force constant matrices to be determined without resorting to the numerical differentiation. This facilitates the investigation of accurate phonon dispersion including anharmonicity [25]. Because the BTE only requires the phonon dispersion, the combination of the BTE and the first-principles phonon

calculations have enabled the accurate prediction of phonon transport properties [26].

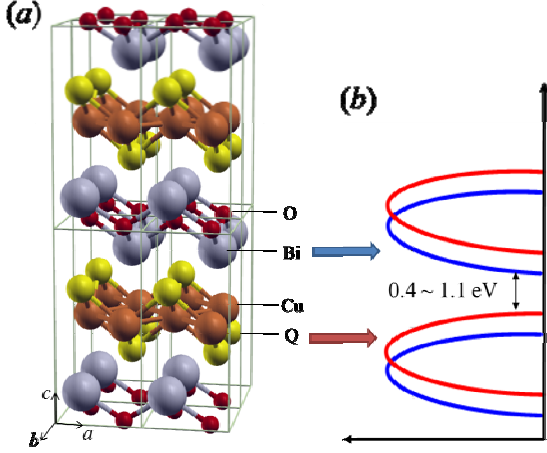


FIG. 1. (Color online) (a) Atomic structure of the ZrSiCuAs-type BiCuOQ compound. (b) Schematic diagram illustrating the electronic density of states (DOS) of BiCuOQ based on the concept of mixed-layer systems [17].

Recent investigations of  $k_p$  in BiCuOSe system have used the combined approach of the first-principles and the lattice dynamics calculations [19, 27]. Saha [19] has suggested the origin of low  $k_p$  by comparing the vibrational modes of BiCuOSe and LaCuOSe. The low  $k_p$  of BiCuOSe is ascribed to its heavy atomic mass of Bi and high anharmonicity indicated by Grüneisen parameter. Shao *et al.* [27] also have investigated  $k_p$  of BiCuOSe by solving the phonon BTE with anharmonic force constants and also emphasized the anharmonicity as an origin of the low  $k_p$ . They also pointed out the anisotropy and the importance of optical phonon in low  $k_p$  as a report. However, there have been few studies in the origin of high anharmonicity in this system as well as its control based on atomic doping or substitution. So, more systematic analysis in the anharmonic phonon calculation is needed to find key factor for low  $k_p$  in hetero-layered compounds.

Here, we investigate the  $k_p$  for the series of BiCuOQ compounds using a combined approach of the first-principles calculation and the phonon BTE under the RTA. For understanding the mechanism of low  $k_p$ , we also compare the phonon modal scattering rates of BiCuOQ compounds using many-body perturbation theory with the anharmonic force constants. Our results reproduce well the reported  $k_p$  and structural properties in experiments. Moreover, we show that the interlayer interaction has an important role to lower the  $k_p$ , based on the comparative analysis of the frequency-dependent scattering rate in three parent compounds BiCuOS, BiCuOSe, and BiCuOTe.

**Table I.** Calculated lattice parameters, Born effective charges  $z_{M,\alpha}$ , and dielectric constants  $\epsilon_{\infty,\alpha}$  of BiCuOQ. The lattice constants in parentheses are experimental results [16].

Compound	$a$ (Å)	$c$ (Å)	$z_{\text{Bi},\parallel}$	$z_{\text{Bi},\perp}$	$z_{\text{Cu},\parallel}$	$z_{\text{Cu},\perp}$	$z_{\text{O},\parallel}$	$z_{\text{O},\perp}$	$z_{\text{Q},\parallel}$	$z_{\text{Q},\perp}$	$\epsilon_{\infty,\parallel}$	$\epsilon_{\infty,\perp}$
BiCuOS (this work)	3.84 (3.86)	8.46 (8.56)	5.87	5.77	1.02	0.61	-3.71	-4.03	-3.10	-2.35	12.70	11.45
BiCuOSe (this work)	3.89 (3.93)	8.89 (8.93)	6.27	5.85	1.15	1.08	-4.09	-4.30	-3.13	-2.64	14.25	13.90
BiCuOTe (this work)	3.99 (4.04)	9.51 (9.52)	6.50	6.38	0.97	1.24	-4.44	-4.89	-2.59	-2.73	15.80	17.11
BiCuOSe (PBE, [27])	3.96	9.12	6.51	6.05	1.52	1.14	-4.31	-4.42	-3.73	-2.76	18.64	14.01
BiCuOSe (PBEsol, [19])	3.90	8.92	6.46	5.93	1.44	1.06	-4.28	-4.42	-3.67	-2.70	18.01	13.79

## II. METHODS

### A. *Ab initio* calculations

In the DFT calculations of BiCuOQ, we use the frozen-core projector augmented wave method [28, 29] encoded in the Vienna *ab initio* simulation package [30], and the generalized-gradient approximation of Perdew-Burke-Ernzerhof prescription for solid (PBEsol) [31] for the exchange-correlation functional with the plane-wave-cut-off energy of 500 eV. The Brillouin zones of the tetragonal unit cells were sampled by  $6 \times 6 \times 2$   $k$ -point meshes generated in accordance with the Monkhorst-Pack scheme [32]. The  $6s$ ,  $6d$ , and  $6p$  electrons of Bi atom, the  $3p$ ,  $4s$ , and  $4d$  electrons of Cu atom, the  $2s$  and  $2p$  electrons of O atom, and the  $ns$  and  $np$  electrons for Q atom ( $n = 3$  for S, 4 for Se, and 5 for Te) were treated as valence and the remaining electrons were kept frozen. To obtain atomic forces, the total energies were minimized until the energy convergences less than  $10^{-8}$  eV. The lattice parameters are then optimized under zero-pressure condition.

The second- and third-order force constants were obtained by the supercell approach [33, 34] with finite atomic displacement of 0.03 Å. In the finite-difference calculations, we use  $3 \times 3 \times 1$  supercells containing 72 atoms with 8 different atomic displacements for second-order and 1514 displacements for third-order force constants, while containing full nearest neighbors in  $3 \times 3 \times 1$  supercell. We have also verified the size effect on the phonon dispersion and  $k_p$  with  $3 \times 3 \times 2$  and  $4 \times 4 \times 1$  supercells by comparing with  $3 \times 3 \times 1$  results. The reciprocal cells of the supercells were sampled by  $2 \times 2 \times 2$   $k$ -point meshes using the Monkhorst-Pack scheme.

### B. Phonon conductivity and Modal scattering rate

To calculate the phonon conductivity, the BTE is used within the RTA, which is implemented in the PHONO3PY package [26]. The phonon conductivity tensor is [35]

$$\mathbf{K}_p = \sum_{\lambda} C_{\lambda} \bar{v}_{\lambda} \otimes \bar{v}_{\lambda} \tau_{\lambda}, \quad (1)$$

where  $C_{\lambda}$  is the modal-heat-capacity,  $\bar{v}_{\lambda}$  and  $\tau_{\lambda}$  are the group velocity and phonon relaxation time for phonon mode  $\lambda$ . Here the phonon modes including the wave vector  $\mathbf{q}$ , and the band indices  $j$  ( $\mathbf{q}, j$ ) and  $(-\mathbf{q}, j)$  have been abbreviated by  $\lambda$  and  $-\lambda$ , respectively.

The phonon relaxation time is calculated from the imaginary part of the self-energy considering up to three-phonon participating in scattering using many-body perturbation theory. It takes the form analogous to the Fermi golden rule [36],

$$\Gamma_{\lambda}(\omega) = \frac{18\pi}{\hbar^2} \sum_{\lambda', \lambda''} |\Phi_{-\lambda\lambda'\lambda''}|^2 \{ (f_{\lambda'} + f_{\lambda''} + 1) \delta(\omega - \omega_{\lambda'} - \omega_{\lambda''}) + (f_{\lambda'} - f_{\lambda''}) [\delta(\omega + \omega_{\lambda'} - \omega_{\lambda''}) - \delta(\omega - \omega_{\lambda'} + \omega_{\lambda''})] \}, \quad (2)$$

**Table II.** Calculated lattice properties of the BiCuO $Q$  compounds: elastic constants  $C_{ij}$ , bulk ( $B$ ), shear ( $G$ ), and Young ( $E$ ) moduli (in GPa), longitudinal and transversal sound speed ( $v_L, v_T$  in m/s), Debye temperature ( $T_D$  in K), and Debye frequency ( $\omega_D$  in THz). Available experimental results [39] of the BiCuOSe are also listed.

Compound	$c_{11}$	$c_{12}$	$c_{13}$	$c_{33}$	$c_{44}$	$c_{66}$	$B$	$G$	$E$	$v_L$	$v_T$	$T_D$	$\omega_D$
BiCuOS (this work)	173.8	80.1	73.5	116.2	51.0	41.0	99.6	46.2	120.1	4344	2326	310	6.5
BiCuOSe (this work)	158.1	71.2	66.6	102.8	46.8	36.2	89.6	42.1	109.3	4012	2157	280	5.8
BiCuOTe (this work)	143.9	57.2	58.3	98.8	37.8	22.5	80.3	34.7	91.1	3728	1953	244	5.1
BiCuOSe (exp. [39])									76.5	3290	1900	243	
BiCuOSe (PBE, [27])	137.3	57.7	53.5	94.5	23.8	38.9	76.2		79.6	3650	1814		

where  $f_\lambda$  is the phonon equilibrium occupancy and  $\Phi_{\lambda\lambda'\lambda''}$  is the strength of interaction among the three phonons  $\lambda, \lambda'$ , and  $\lambda''$  involved in the scattering which is explicitly given by Eq. (10) in Ref. [26].

The  $2\Gamma_\lambda(\omega_\lambda)$  is the phonon linewidth of the phonon mode  $\lambda$  whose inverse is phonon relaxation time [36],

$$\tau_\lambda = \frac{1}{2\Gamma_\lambda(\omega_\lambda)}. \quad (3)$$

Shao *et al.* [27] have already verified the RTA results negligibly underestimates  $k_p$  compared with the iterative solution. So, we focused on the results using the RTA.

### III. RESULTS AND DISCUSSION

#### A. Crystal structure and lattice properties

Table I shows the calculated equilibrium crystal-structure parameters of BiCuO $Q$  compounds. The PBEsol exchange potential based the DFT calculations gives smaller lattice constants compared to the experimental reports [16]. In general, the PBEsol underestimates the lattice parameter, while the PBE slightly overestimates it [27]. Our results for BiCuOSe are in good agreement with previous PBEsol results [19]. As the chalcogen atom changes from S to Te, the cross-plane  $c$ -axis is more elongated than in-plane  $a$  axis. The  $c/a$  ratio changes from 2.2 (BiCuOS) to 2.4 (BiCuOTe), which indicates the distance between BiO and Cu $Q$  layers are more sensitively changed than in-plane lattice with the change of atomic size of chalcogen atom. Table I also lists the Born effective charges and the dielectric constants of BiCuO $Q$ , which are related to the bond character and the optical phonon splitting in the dispersion relation. Our results indicate that the covalent character of the Bi-O bond is much greater than the Cu- $Q$  bond [19]. The trend with the change of chalcogen atom shows that the increase of the atomic number leads to increase in the covalent bond character of the Bi-O and Cu- $Q$  [37]. The increase in the dielectric constant also indicates low-frequency phonons in the dispersion and is consistent with the presence of heavy atoms in the BiCuOTe crystal.

Based on the optimized crystal structure, we have calculated the elastic properties of the BiCuO $Q$  compounds listed in Table II. We also estimate the bulk ( $B$ ) and shear ( $G$ ) moduli using the Hill average of the Voigt and Reuss bounds. The Young modulus ( $E$ ) is related to  $B$  and  $G$  [38] as

$$E = \frac{9BG}{3B+G}. \quad (4)$$

The longitudinal ( $v_L$ ) and transversal ( $v_T$ ) sound velocities of the tetragonal crystal are

$$\rho v_L^2 = B + \frac{4}{3}G, \quad \rho v_T^2 = G, \quad (5)$$

where  $\rho$  is the density. The Debye temperature ( $T_D$ ) and frequency ( $\omega_D$ ) are

$$\omega_D = v_A (6\pi^2 n)^{1/3}, \quad T_D = \frac{\hbar \omega_D}{k_B}, \quad (6)$$

where  $v_A$  is average sound velocity

$$\frac{3}{v_A^3} = \frac{1}{v_L^3} + \frac{2}{v_T^3}. \quad (7)$$

As the chalcogen atomic number increases, the overall stiffness decreases (soft bonding in the compounds). The underestimation of the lattice parameter gives large elastic properties compared with experimental reports [39] and those of Shao *et al.* [27], but comparable with those of Saha (93 GPa) [19].

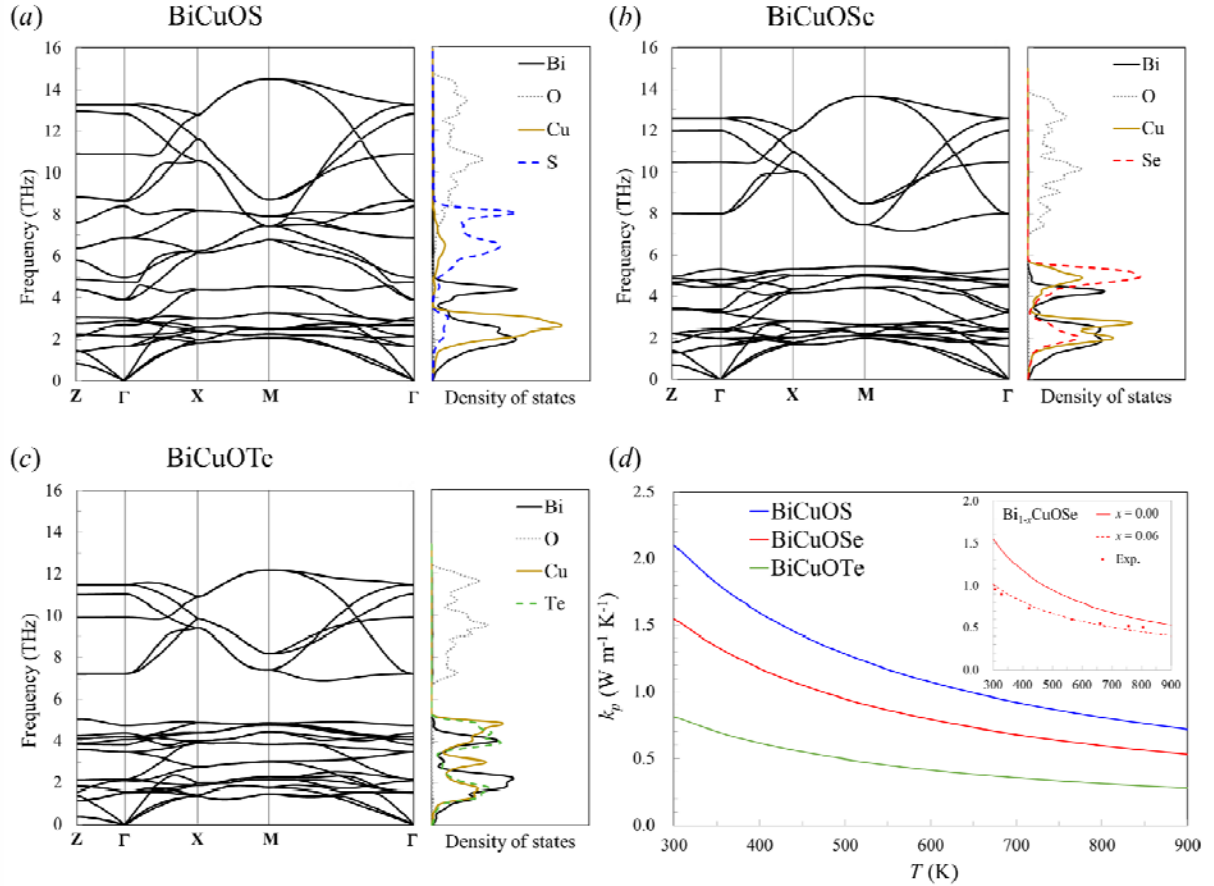
#### B. Phonon dispersion and conductivity

Figures 2(a)-(c) show the phonon dispersions and atomic-projected DOS for each BiCuO $Q$  compounds. Based on the lattice properties, the phonon frequencies become lower as the chalcogen atomic number increases, which are also well consistent with the elastic properties. The vibrations of the Bi and O atoms are completely decoupled and the acoustic vibration is mainly from the Bi vibration, for all three compounds. For the Cu- $Q$  layer, however, the strength of the coupling of the chalcogen vibration and the Cu vibration increases as the atomic mass increases. In the Cu-S layer, the S vibrational modes are spanning over 5-8 THz and are weakly coupled with the Cu vibrational modes below 3 THz. In the Cu-Se and Cu-Te layers, the chalcogen vibrational modes are red shifted to 2-5 THz and become coupled with the Cu vibrational modes. The overlap of the Cu and chalcogen phonon DOS shown in Fig. 2 indicates that the coupling between the Cu and  $Q$  modes becomes stronger as the atomic mass of  $Q$  increases. It also indicates that the covalent bonding of the Cu- $Q$  bonds becomes stronger as  $Q$  becomes heavier, which is well consistent with the results of the Born effective charge calculation mentioned above. The coupled phonon states of the Cu-Se and the Cu-Te layers show large overlap with the Bi state. Saha [19] discussed that the overlap between the Bi acoustic and the Cu optical (quasi-acoustic) vibrations can make for strong acoustic-optical phonon scattering. This is discussed in the next section with detailed analysis of our phonon-phonon interaction calculations.

The phonon BTE-based  $k_p$  results for the BiCuO $Q$  compounds show the expected temperature dependence, evident in Fig. 2(d). Our direction-averaged  $k_p = (k_{aa} + k_{bb} + k_{cc})/3$  for the BiCuOSe overestimates the available experimental results as illustrated in the inset of Fig. 2(d). To verify our predictions, we apply the point-defect phonon scattering model, due to deficiency of Bi atom in the crystal. In BiCuO $Q$ , it has been

known that the Bi atom can readily cause defects in the crystal, which in turn induces the phonon scattering. The detailed descriptions of the point-scattering model and its application are

available elsewhere [22, 40, 41]. Then the experimental results are consistent with the calculation of a Bi defect scattering for  $x = 0.06$  [Fig. 2(d) inset],



**FIG. 2.** (Color online) Phonon dispersions and atomic-projected phonon DOS of (a) BiCuOS, (b) BiCuOSe, and (c) BiCuOTe. (d) Variation of the calculated average phonon conductivity as a function of temperature for BiCuOS (blue), BiCuOSe (red), and BiCuOTe (green). Inset: Comparison between experimental (Reference [39], dots) and predicted average phonon conductivity for Bi<sub>1-x</sub>CuOSe (solid line for  $x = 0.00$ , dashed line for  $x = 0.06$ ).

dashed line] which is considered a reasonable Bi defect or doping level.

As the chalcogen atomic number increases, the  $k_p$  follows the expected trend in the elastic properties (Table II) and phonon dispersions [Figs. 2(a)-(c)], i.e., the  $k_p$  of the BiCuOQ is suppressed as the chalcogen atomic number increases. The extent of suppressions of  $k_p$ , however, is much larger than the expectation from the elastic properties, which are closely related with the phonon group velocities. The total mass of the BiCuOSe (734.98 amu) is 1.15 times heavier than that of the BiCuOS (641.19 amu) and BiCuOTe (832.26 amu) is 1.13 times heavier than BiCuOSe.

The square roots of mass differences are also well consistent with the inverse of the ratios of elastic properties and phonon dispersion among BiCuOQ compounds. However, the ratio of  $k_p$  between the BiCuOSe and the BiCuOS is 1.35 and even  $k_p$  of the BiCuOSe is 1.94 times larger than that of the BiCuOTe. This implies that a simple suppression of phonon frequencies due to mass difference is not the only factor on the  $k_p$  suppression.

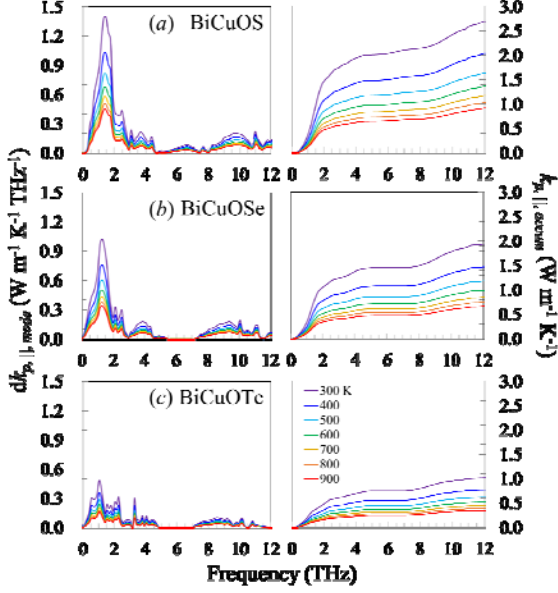
### C. Modal conductivity and phonon linewidth

To investigate the suppression of  $k_p$  in the BiCuOQ compounds further, the temperature dependent modal and

accumulated  $k_p$  of BiCuOQ compounds are shown in Figs. 3(a)-(c). To demonstrate more clearly the suppression of  $k_p$  for the BiCuOQ compounds, we focus on the in-plane  $k_p$ , which is the main contribution to the total  $k_p$ . The most dominant conductance comes from the acoustic phonon below 5 THz regime as indicated in phonon dispersion shown in Figs. 2(a)-(c). The remaining contribution to  $k_p$  is from the high frequency optical phonon above 7 THz regime. Similar to other semiconductors, the optical phonon shows small contribution to  $k_p$  and weak temperature dependence. The trend on chalcogen atom is much clear in Fig. 3. The modal  $k_p$  values of each compounds show similar sizes upto 0.5 THz, but they show clear difference above it. The modal  $k_p$  peak on acoustic phonon regime drops around 2 THz for the BiCuOS and BiCuOSe, but the size of peak around 1 THz is suppressed for the BiCuOSe. For the BiCuOTe, the peak drops rapidly at 1 THz and the overall peak size is much smaller than other compounds. Because the most important differences appear in the acoustic phonon regime, it is crucial to understand why the modal  $k_p$  is suppressed in heavy element compound. In addition to the change of group velocity, we expect that the phonon scattering should be considered as the origin of the rapid drop in the modal  $k_p$  in the acoustic phonon regime.

Since the phonon dispersions of these systems are similar and the suppression of dispersion is rather small as mentioned in previous section, the effect of phonon scattering is expected to

be critical in these systems. So, we begin by analyzing the suppression of the modal  $k_p$  in detail using the phonon linewidth  $2\Gamma$ , which is the inverse of relaxation time indicating the scattering strength of phonon, at 300 K. The low-frequency acoustic phonon regime below 5 THz is illustrated in Figs. 4(a)-(c). The larger linewidth indicates larger phonon scattering and shorter phonon relaxation time. The strong scattering occurs at the sudden drop in the modal  $k_p$  contribution.

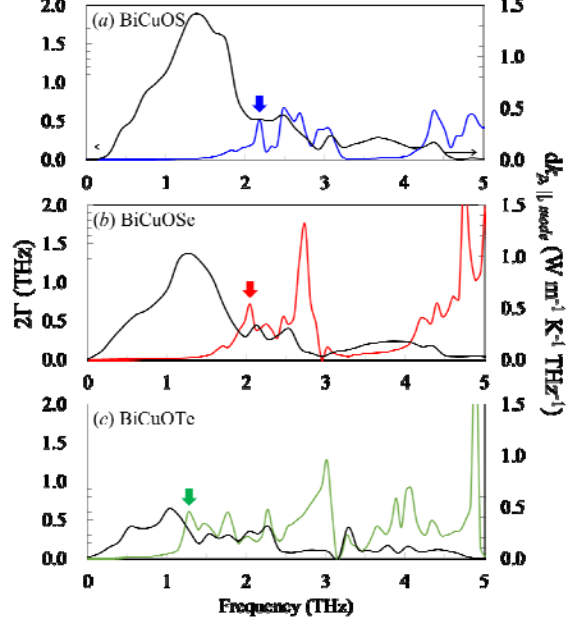


**FIG. 3.** (Color online) Frequency dependence of the in-plane modal phonon conductivity (left), and the accumulative phonon conductivity (right) of (a) BiCuOS, (b) BiCuOSe, and (c) BiCuOTe, which corresponds to the area under the modal phonon conductivity. The discrete temperatures are listed in (c).

Comparing BiCuOS and BiCuOSe, both shows modal  $k_p$  drop at 2 THz, but the BiCuOSe has a larger  $2\Gamma$  peak near 2 THz compared to the BiCuOS [Figs. 4(a)-(b)]. Strong suppression of the modal  $k_p$  in the BiCuOTe is clearly seen at 1.5 THz, which is also consistent with the  $2\Gamma$  peak at same frequency [Fig. 4(c)].

Note that the distribution of scattering rate ( $2\Gamma$ ) is related to the phonon DOS coupling as mentioned in the description of Fig. 2. Since the scattering is related to the phonon-phonon interaction strength, i.e., Eq. 2, the frequencies at peaks in the scattering rate distribution in Fig. 4 correspond to the peaks in the Cu vibrational mode overlapping with the acoustic Bi vibrational mode [DOS of Fig. 2] which makes the largest contribution to the  $k_p$ . As the chalcogen atomic number increases, the vibration of Cu atom shows strong coupling, which interrupts the Bi vibration and causes the acoustic-optical phonon scattering for these compounds. Comparing the BiCuOS with the BiCuOSe, the Cu vibration is weakly overlapping with the Bi vibration near 2 THz for the BiCuOS, showing rather small  $2\Gamma$ . In the BiCuOSe, however, the Cu vibration, which is coupled with the Se vibration, is strongly overlapped with the Bi vibration near the 2 and 5 THz, regimes, which are consistent with results presented in Fig. 4(b). Moreover, the heavier chalcogen lowers the peak frequency from 2.5 (BiCuOS) to 1.5 THz (BiCuOTe), as evident in the DOS of Fig. 2 and also indicated by the arrows in Fig. 4. Because the main contribution to  $k_p$  is around the 0–2 THz regime, which can be seen as a large area of modal  $k_p$  in Fig. 4, the first peak in  $2\Gamma$  is critical in the suppression of total  $k_p$ . Note that the Bi and Cu vibrations are contributions from different layers (Fig. 1), so the overlaid independent vibrational modes interrupt each other.

Our result indicates that the controlling the elements can control the phonon-phonon interaction and scattering of phonon by overlapping two independent vibrational states in the layered crystal system. Moreover, this result shows the different layer stacking along the  $c$ -direction can also affect the in-plane  $k_p$  suppression by the interruption of vibrational modes. So, we suggest that the intrinsically hetero-layered structure can be a potentially good TE candidate for its electrical properties as well as the phonon scattering. Further studies will verify this interlayer interaction concept by changing the elements in several layered structures both theoretically and experimentally.



**FIG. 4.** (Color online) Calculated modal phonon conductivity (black lines) and phonon linewidth ( $2\Gamma$ , colored lines) at 300 K, in the low-frequency regime, for (a) BiCuOS, (b) BiCuOSe, and (c) BiCuOTe. Colored arrows indicate the frequency of the first phonon linewidth peak, where the modal phonon conductivity is substantially suppressed.

#### IV. CONCLUSIONS

We have investigated the origin of very low phonon conductivity in the thermoelectric BiCuOS, BiCuOSe, and BiCuOTe compounds using the first-principles anharmonic, lattice dynamics calculations. The lattice properties and phonon conductivities are predicted considering natural Bi-defects in crystals, and our results show good agreement with the reported experiments. To investigate the origin of the low phonon conductivity, the phonon linewidth, which indicates the phonon scattering, has been analyzed for these three compounds with different interlayer interaction. We show that the large suppression of phonon conductivity originates from the interaction between vibration of two independent layers (BiO and CuQ), presented by both the modal phonon conductivity and the phonon lifetime. Strong overlap of the two vibrational frequencies causes strong scattering of the phonon modes, and the BiCuOTe compound offers the smallest phonon conductivity.

We conclude that the mixed-layer structures, including intrinsically hetero-layered crystals, are potentially favorable TE material candidates, allowing the engineering of both electronic band gap and phonon thermal conductivity controlled by the interlayer interactions.

#### ACKNOWLEDGMENTS

This research was supported by Global Frontier Program through the Global Frontier Hybrid Interface Materials (GFHIM) (2013M3A6B1078870) and Nano-Material Technology Development Program (2011-0030146) and Basic Science Research Program (2015R1D1A1A01059621) and grant funded by the Korea government (2015R1A2A1A15051540) through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning and by the National Institute of Supercomputing and Network/Korea Institute of Science and Technology Information with supercomputing resources including technical support (KSC-2015-C2-018). M.K. is thankful to the U.S. NSF program on Thermal Transport and Processes (Award No. CBET1332807).

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