Low thermal conductivity and high performance anisotropic thermoelectric properties of XSe (X = Cu, Ag, Au) monolayers†

Qing-Yu Xie, Jian-Jiang Ma, Qing-Yi Liu, Peng-Fei Liu, Pei Zhang, Kai-Wang Zhang and Bao-Tian Wang

Combining density functional theory (DFT) and semi-classic Boltzmann transport theory, we report the thermoelectric (TE) performance of a family of two-dimensional (2D) group IB-selenides XSe (X = Cu, Ag, Au). The results show that these monolayers exhibit small and anisotropic phonon velocities (0.98–3.84 km s⁻¹), large Grüneisen parameters (up to 100), and drastic phonon scattering between the optical and acoustic phonons. These intrinsic properties originate from strong phonon anharmonicity and suppress the heat transport capacity, resulting in low lattice thermal conductivities (12.54 and 1.22 W m⁻¹ K⁻¹) along the x- and y-directions for a CuSe monolayer. Among our studied monolayers, the 2D CuSe monolayer possesses the most remarkable TE performance with ultrahigh ZT (3.26) for n-type doping along the y-direction at 300 K. CuSe monolayer can achieve higher thermoelectric conversion efficiency at a lower synthetic preparation cost than the expensive AgSe and AuSe monolayers, and our work provides a theoretical basis for paving the way for further experimental studies.

1. Introduction

Thermoelectric (TE) materials can convert waste thermal energy into electrical energy directly and play an important role in the sustainable energy field.¹ The conversion efficiency of a TE system can be quantified by the TE figure of merit (ZT),²,³

\[ ZT = \frac{\sigma S^2}{k_L + k_e} T, \]

where \( \sigma \), \( S \), \( T \), \( k_L \), and \( k_e \) are the electrical conductivity, Seebeck coefficient, absolute temperature, lattice thermal conductivity, and electronic thermal conductivity, respectively. With years of development, several strategies have been developed to enhance the TE performance effectively: by improving the electrical transport properties by the band-structure engineering to obtain a high power factor (PF = \( \sigma S^2 \)) or suppressing the heat transport capacity through alloying and nanostructuring.⁵,⁶ Moreover, seeking materials with intrinsic low thermal conductivity can be another effective approach that avoids facing the rather rough barrier of optimizing phonon transport coefficients independently due to the intricate coupling among electrons, phonons, and magnons.⁷

According to Slack’s theory,⁸ to achieve low lattice thermal conductivity, materials with strong phonon anharmonicity (normally with large Grüneisen parameters), weak interatomic bonding, a complicated structure, and heavy elements are essential. For example, PbTe, a typical TE material with a low thermal conductivity of about 2 W m⁻¹ K⁻¹ at 300 K, exhibits strong anharmonic interaction between the transverse optical and longitudinal acoustic branches.⁹ α-MgAgSb has been demonstrated to have strong phonon anharmonicity combined with its static local structure distortion with an ultralow thermal conductivity of 0.54 W m⁻¹ K⁻¹ at 300 K.¹⁰ CsAg₅Te₃ also exhibits an ultralow lattice thermal conductivity of 0.18 W m⁻¹ K⁻¹ at room temperature due to the concerted rattling of a group of Ag ions promoting the Grüneisen parameters.¹¹ Unfortunately, the combination of heavy elements and complex structures tends to indicate higher synthetic preparation costs. Hence, low-cost materials with low lattice thermal conductivity are extremely attractive in the field of thermoelectricity.

β-Gold selenide, a relatively unexplored layered material, has been synthesized by colloidal synthesis, which is a mild method with inexpensive equipment, and scaling-up is easily achievable.¹²,¹³ It can be noted that its bulk phase compound was synthesized in 1968 and exhibits metallic properties.¹⁴
Owing to the strong interlayer quantum confinement effect, the $\beta$-AuSe monolayer has an indirect bandgap (1.82 eV); meanwhile, it exhibits a tunable bandgap and outstanding optical absorption coefficient offering perspectives for electric devices and photovoltaic solar cells. These extrinsic intrinsic properties suggest that it may be a good TE material. Sadly, there is a lack of studies on the phonon transport and TE properties of the system, motivating us to explore.

In our present work, we systematically study the TE properties of XSe ($X = \text{Cu, Ag, Au}$). We find that they have intrinsic low thermal conductivity and excellent electrical transport properties. For the CuSe monolayer, its thermal conductivities along the $x$- and $y$-directions are as low as 12.54 and 1.22 W m$^{-1}$ K$^{-1}$ at 300 K, respectively. The ratio $\kappa_x/\kappa_y$ of 10.27 for the CuSe monolayer is significantly higher than those of other conventional anisotropic 2D materials, like BP ($k_{\text{BP}}/k_{\text{arm}} = 1.4$)\cite{16} and SnSe ($k_{\text{SnSe}}/k_{\text{arm}} = 2.5$).\cite{17} Phonon velocity, Grüneisen parameters, and phonon relaxation time provide microscopic physical images to understand low and anisotropic thermal conductivity. The maximum value of $ZT$ for the CuSe monolayer can approach 1.61 along the $x$-direction and 3.26 along the $y$-direction for n-type doping at 300 K. Compared to the expensive AuSe and AgSe monolayers, the CuSe monolayer presents a tremendous economic advantage in terms of synthesis cost; meanwhile, its $ZT$ is nearly five times higher than that of the AuSe monolayer (0.63 for n-type doping), suggesting a great potential thermoelectric field.

2. Computational methods

In this work, first-principles calculations were performed using the Vienna $ab$ initio simulation package (VASP).\cite{18} To handle the exchange–correlation potential, the generalized gradient approximation (GGA)$^{19}$ was employed in the Perdew–Burke–Ernzerhof form.\cite{20} The cutoff energy of the plane was set as 500 eV on a $9 \times 6 \times 1$ Monkhorst-Pack $k$-point mesh. The geometric structure was fully optimized with a convergence threshold of $10^{-8}$ eV in energy and 0.01 eV Å$^{-1}$ for the force. To avoid the interaction between the adjacent images, a large vacuum layer of $20$ Å was set along the vacuum layer. To obtain an accurate band structure and electrical transport properties, all our present calculations about the electrical transport are based on the HSE06 method.

Based on the Boltzmann transport equation and rigid band approximation, the electronic transport properties were obtained from the BoltzTraP code.\cite{21} The energy-dependent relaxation time was calculated by deformation potential theory, which considers the main interaction between electrons and longitudinal-acoustic phonons in the low energy region based on the single parabolic band (SPB) model, ignoring the scattering of other phonons. To obtain sufficiently accurate transport properties, a dense $35 \times 25 \times 1$ $k$-mesh was employed for the Brillouin zone (BZ).

The harmonic second-order force interaction constants and the phonon dispersion curves were calculated using the Phonopy code\cite{22} via the finite-displacement method using a $5 \times 3 \times 1$ supercell on a $4 \times 2 \times 1$ $k$-mesh. The anharmonic third-order force constants (3rd IFCs) were calculated using the thirdorder.py code with the same supercell and method. Interactions including the sixth-nearest-neighbor were considered for 3rd IFCs. The lattice thermal conductivity and the phonon transport properties are obtained from the self-consistent iterative solution of the Boltzmann transport equation in the ShengBTE package.\cite{23} Here, a dense $45 \times 30 \times 1$ $k$-grid was employed in the calculation of lattice thermal conductivity which can reach good convergence criteria.

3. Results and discussion

3.1 Geometry and electronic band structure

The optimized crystal structure of the monolayer of XSe ($X = \text{Cu, Ag, Au}$) is shown in Fig. 1(a), the equilibrium lattice constants are $a = 3.54, 3.76, 3.73$ Å and $b = 5.53, 6.05, 6.35$ Å for CuSe, AgSe, and AuSe monolayers, respectively. The 2D XSe possesses a highly anisotropic structure (space group no. 10) belonging to monoclinic symmetry. The unit cell of this system consists of two non-equivalent metal atoms coordinated with two and four Se atoms (linear $X^I$ atom and square-planar $X^{IV}$ atom), and more details can be seen in Table 1. The electronic structure can reflect intrinsic characteristics of electrical transport, since the bandgap tends to be underestimated by using PBE functional, herein, the HSE06 method\cite{24} is employed, and the band structure of CuSe, AgSe, and AuSe monolayers are shown in Fig. 1(b)–(d). The results show that these monolayers are indirect bandgap semiconductors with the valence band maximum (VBM) located at the $Y$ points and the conduction band minimum (CBM) located along the $I$–$X$ direction. For

![Fig. 1](image-url)
Table 1  Calculated lattice constants (in Å), angle (in °), the distance \( h_{\text{Se-Se}} \) between the top Se atom and the bottom one, bandgap (in eV) based on the PBE and HSE06 methods

<table>
<thead>
<tr>
<th>Comp.</th>
<th>( a )</th>
<th>( B )</th>
<th>( \alpha )</th>
<th>( \beta )</th>
<th>( \gamma )</th>
<th>( h_{\text{Se-Se}} )</th>
<th>( \mu_{\text{B}} )</th>
<th>( \mu_{\text{S}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSe</td>
<td>3.54</td>
<td>5.53</td>
<td>90</td>
<td>90</td>
<td>95.45</td>
<td>2.58</td>
<td>0.57</td>
<td>1.12</td>
</tr>
<tr>
<td>AgSe</td>
<td>3.76</td>
<td>6.05</td>
<td>90</td>
<td>90</td>
<td>94.97</td>
<td>2.72</td>
<td>0.83</td>
<td>1.24</td>
</tr>
<tr>
<td>AuSe</td>
<td>3.73</td>
<td>6.35</td>
<td>90</td>
<td>90</td>
<td>98.08</td>
<td>2.55</td>
<td>1.21</td>
<td>1.81</td>
</tr>
</tbody>
</table>

The two-dimensional group IV-selenides, the valence band (VB) is mainly from Se-p orbitals while the conduction band (CB) is dominated by M-d orbitals near the Fermi level, in which group IV and Se atoms consist of the partial-ionic bond, polarized covalent bond, and lone-pair electrons (see Fig. S1, ESI†). In this case, the VB dominated by Se-p orbitals changes slightly while the shape of the CB is sharp, beneficial to high carrier mobility. These band intrinsic characteristics are in favor of good TE performance. More details will be discussed in the following.

3.2 Electrical transport properties

Deformation potential (DP) theory based on phonon-limited scattering has been widely used to calculate carrier mobility. 26 For 2D materials, the formula is written as 27,28

\[
\mu_{2D} = \frac{e h^2 C_{\text{2D}}}{8 \pi^2 k_B T nm^*(E_1)^2} \tag{2}
\]

\[
\tau_0 = \frac{\mu m}{e T} \tag{3}
\]

where \( C_{\text{2D}} \) is the 2D elastic modulus, \( m \) is the effective mass along the transport direction, \( m^* \) is the averaged effective mass \( (m^* = \sqrt{m_a m_b}) \), and \( E_1 \) represents the potential constant. All the calculation results are tabulated in Table 2. The search for two-dimensional materials with strong anisotropic carrier mobility has been a hot topic, especially for electrons along one direction, but holes along the other. Here, the carrier mobilities exhibit highly anisotropic behavior. The electron mobility along the x- and y-directions become increasingly larger from AuSe (5686.54, 346.8 cm² V⁻¹ s⁻¹) to CuSe (7594.62, 1413.78 cm² V⁻¹ s⁻¹) to AgSe (16604.68, 1706.81 cm² V⁻¹ s⁻¹) and their ratio \( \mu_a/\mu_b \) gradually increases from CuSe (5.37) to AgSe (9.73) and then AuSe (16.40). Interestingly, the hole mobility along the y-direction is remarkably higher than that along the x-direction, and the ratio \( \mu_b/\mu_a \) gradually increases from the CuSe (10.48) to AgSe (20.28) and then AuSe (39.18); more details can be seen in Table 2. That is, electrons and holes have a preferred transport direction due to the existence of mutually perpendicular ion channels for the system. 14 XSe monolayers have higher carrier mobility than most commonly studied semiconductors, such as MoS₂ (60–200 cm² V⁻¹ s⁻¹), 29 indicating an excellent prospect in electronic devices and highly efficiently polarization-sensitive devices.

In addition, determining the electronic relaxation time \( \tau \) is quite difficult because it varies with the carrier concentration, temperature, and scattering mechanism. In our work, we calculate the energy-dependent relaxation time \( \tau = \tau_0 e^r \) where \( r \) depends on the scattering mechanism, is set as -1/2 which considers the predominant scattering to stem from the coupling between electrons and longitudinal-acoustic phonons in the low energy region based on the single parabolic band (SPB) model. 28 Generally, the scattering model can well describe most materials, such as nonpolar crystals, 26 anisotropic 2D SiS, 30 and anisotropic 2D tellurene. 31 According to Fig. 2, the relaxation time decreases with increasing carrier (holes or electrons) concentration, which is reasonable due to the carrier aggregation giving rise to more frequent collisions between electrons and phonons.

Based on rigid band approximation, 32 it is assumed that as the carrier doping concentration increases, the band structure does not change, involving only a shift in the Fermi energy level. Electrical transport coefficients, Seebeck coefficient \( S \), electrical conductivity \( \sigma \) as the numerator of equ (1), directly reflect the TE power, and these coefficients can be obtained from the BoltzTraP code. 21 These coefficients are given by

\[
S = \frac{e k_B}{\sigma} \int \frac{\mathcal{E}(\varepsilon)}{\varepsilon} \left( -\frac{\partial f_0}{\partial \varepsilon} - \frac{\varepsilon - \mu}{k_B T} \right) d\varepsilon \tag{4}
\]

\[
\sigma = e^2 T \int \mathcal{E}(\varepsilon) \left( -\frac{\partial f_0}{\partial \varepsilon} - \frac{\varepsilon - \mu}{k_B T} \right) d\varepsilon \tag{5}
\]

where \( e, f_0, \varepsilon, \mu, \) and \( k_B \) are the electron charge, Fermi–Dirac distribution function, energy eigenvalue, chemical potential, and Boltzmann constant, respectively. The transport distribution function \( \mathcal{E} \) can be defined as

\[
\mathcal{E} = \sum_k U_k \nu_k \tau_k \tag{6}
\]

Table 2  Calculated carrier effective mass \( m_a/m_b \) (in \( m_0 \)), elastic modulus \( C_a/C_b \) (in J m⁻²), deformation potential \( E_a/E_b \) (in eV), carrier mobility for electrons and holes (in cm² V⁻¹ s⁻¹), and scattering time \( \tau_a/\tau_b \) (in ps) at 300 K

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Type</th>
<th>( m_a )</th>
<th>( m_b )</th>
<th>( E_a )</th>
<th>( E_b )</th>
<th>( C_a )</th>
<th>( C_b )</th>
<th>( \mu_a )</th>
<th>( \mu_b )</th>
<th>( \tau_a )</th>
<th>( \tau_b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSe</td>
<td>e</td>
<td>0.14</td>
<td>3.38</td>
<td>1.05</td>
<td>0.14</td>
<td>37.00</td>
<td>3.00</td>
<td>7594.62</td>
<td>1413.78</td>
<td>0.60</td>
<td>2.72</td>
</tr>
<tr>
<td></td>
<td>h</td>
<td>-1.36</td>
<td>-0.53</td>
<td>5.43</td>
<td>0.75</td>
<td>37.00</td>
<td>3.00</td>
<td>22.91</td>
<td>43.39</td>
<td>880.09</td>
<td>0.03</td>
</tr>
<tr>
<td>AgSe</td>
<td>e</td>
<td>0.15</td>
<td>2.56</td>
<td>0.55</td>
<td>0.19</td>
<td>22.30</td>
<td>4.60</td>
<td>16604.68</td>
<td>1706.81</td>
<td>1.44</td>
<td>2.48</td>
</tr>
<tr>
<td></td>
<td>h</td>
<td>-1.39</td>
<td>-0.36</td>
<td>3.34</td>
<td>0.66</td>
<td>33.50</td>
<td>8.00</td>
<td>346.81</td>
<td>346.81</td>
<td>0.48</td>
<td>0.44</td>
</tr>
<tr>
<td>AuSe</td>
<td>e</td>
<td>0.15</td>
<td>2.23</td>
<td>-1.21</td>
<td>-0.62</td>
<td>33.50</td>
<td>8.00</td>
<td>346.81</td>
<td>346.81</td>
<td>0.48</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>h</td>
<td>-1.13</td>
<td>-0.23</td>
<td>4.46</td>
<td>-0.43</td>
<td>33.50</td>
<td>8.00</td>
<td>346.81</td>
<td>346.81</td>
<td>0.48</td>
<td>0.44</td>
</tr>
</tbody>
</table>
where $v_k$ and $\tau_k$ are the group velocity and scattering time of the wavevector $k$. Combining with the energy-dependent relaxation time $\tau(E)$, all transport coefficients for p- or n-type doping for XSe monolayer at 300 K are shown in Fig. 3(a)–(f). For doping systems, the Seebeck coefficient is written as the following by the Mott relation $^{33}$

$$S = \frac{\pi k_B^2 T}{3e} \left( \frac{1}{n} \frac{dn(e)}{de} + \frac{1}{\mu} \frac{d\mu}{de} \right)_{\nu=\mu} \tag{7}$$

The bipolar effect should be considered in the case of a small bandgap and high temperature. However, in our work, the calculated bandgap values of these monolayers all belong to a middle or wide value (1.12–1.8 eV), and the electrical transport properties were calculated at 300 K; thus, in our view, the bipolar thermal conductivity can be ignored. As shown in Fig. 3(a) and (d), for both n-type and p-type doping, the absolute value of the Seebeck coefficient decreases linearly with the logarithm of the carrier concentration and it exhibits ultrahigh value of the Seebeck coefficient decreases linearly with the logarithm of the carrier concentration. On the one hand, it originated from the competitive relationship between electronic conductivity with Seebeck coefficient, and on the other hand, since the electrons obey the Fermi–Dirac distribution, as the concentration of carriers increases, the Fermi level moves toward the deeper level, resulting in an enhanced electrical conductivity. For n-type doping, $\sigma$ along the $x$-direction is almost one magnitude higher along the $y$-direction, whereas, the trend is exactly opposite for p-type doping, in good agreement with the previous analysis of carrier mobility. The electric thermal conductivity $\kappa_e$ expressed by the Wiedemann–Franz law $^{34}$

$$k_e = L\sigma T \tag{8}$$

where $L$ is the Lorentz number, is affected by temperature and carrier concentration, and it changes depending on the materials. The classic value $L = \frac{\pi^2 k_B^2}{3e^2}$ is employed which can accommodate most TE materials. Because of the linearity of $\kappa_e$ and $\sigma$, the trends of the two curves are similar. It is worth noting that when the doping concentration is high enough, the electronic thermal conductivity is not negligible, and it can reach and even exceed the phonon thermal conductivity.

### 3.2 Phonon spectrum and phonon thermal conductivity

The phonon dispersion curves and partial phonon density of states (PhDOS) for CuSe, AgSe, and AuSe monolayers are shown in Fig. 4. The phonon branches can be sorted by the continuity of their eigenvectors. $^{35,36}$

$$\sum c_{k,\alpha}^* e_{k+\Delta k,\beta} = |\delta_{\alpha,\beta} - o(\Delta)| \tag{9}$$

where $c_{k,\alpha}$ is the displacement of atom $j$ in the eigenvector of the vibrational mode and $\Delta$ is a small wave vector. The dynamic stability of these monolayers can be confirmed by the phonon spectrum with no imaginary frequency. To test the thermal stability of these monolayers, we run the ab initio dynamics (AIMD) simulations at 900 K (see Fig. S1, ESI†). Results show that these monolayers can be maintained for up to 10 ps at 900 K, suggesting that they are stable at high temperature. Since acoustic branches play a dominant role in the thermal transport process in narrow bandgap semiconductors, we highlight them and the lowest frequency optical branch with different colors while the other optical branches are black. As shown in Fig. 4, the highest vibrational frequency exhibits a decreasing trend following the order of CuSe (9.5 THz) > AgSe (7.2 THz) > AuSe (6.9 THz). The transverse acoustic (TA) and the out-of-plane (ZA) modes are coupled with the longitudinal...
acoustic (LA) mode of these monolayers, leading to the enhancement of phonon scattering.\(^\text{37}\) In addition, these monolayers exhibit a very low optical mode of CuSe (2.10 THz), AgSe (1.57 THz), AuSe (1.64 THz) approaching the long-wave limit, coupling with the transverse acoustic (TA), resulting in strong acoustic–optical coupling and providing a larger three phonon scattering phase space. This behavior is similar to other materials, such as PbSe (2 W m\(^{-1}\) K\(^{-1}\)),\(^\text{9}\) indicating severe optical mode softening for these monolayers, as we analysed.

Phonons are the main carrier for heat transport in semiconductors or insulators. Based on phonon Boltzmann transport equation (BTE), it can be given by the following formula:\(^\text{18}\)

\[
\kappa_L = \frac{1}{V} \sum q \frac{C_{iq} v_{iq}^2 \tau_{iq}}{\nu_{iq}}
\]

where \(C_{iq}\), \(v_{iq}\), and \(\tau_{iq}\) are the mode-specific heat capacity, phonon velocity, and phonon relaxation time for the \(i\)th phonon branch, respectively. As shown in Fig. 1(a), the lengths between the topmost Se and the bottom Se (\(h_{\text{se-se}}\)) of XSe are varying from 2.55 to 2.72 Å, and the van der Waals radii of Se are approximately 2.18 Å;\(^\text{39}\) hence, the effective thickness of monolayer XSe \(h_{\text{eff}} = 2.18 \times 2 + h_{\text{se-se}}\) is employed to compute the lattice thermal conductivity. Fig. 5 shows the dependence of thermal conductivity for these monolayers on the temperature along the \(x\)- and \(y\)-directions. \(\kappa_L\) decreases with increasing temperature with the enhancement of phonon anharmonicity. Unlike some superionic conductors such as 3D \(\beta\)-Cu2Se,\(^\text{40}\) Ag2Te,\(^\text{41}\) the cations can randomly move rather than their equilibrium positions, especially at high temperatures, leading to the lattice thermal conductivity show weak or even no distinct dependence on \(T\) at high temperatures experimentally. Meanwhile, it exhibits very low and highly anisotropic lattice thermal conductivity, the calculated \(\kappa_L\) along the \(x\)- and \(y\)-directions increasing from CuSe (12.54, 1.22 W m\(^{-1}\) K\(^{-1}\)) to AgSe (19.65, 3.38 W m\(^{-1}\) K\(^{-1}\)) and then AuSe (47.80, 15.69 W m\(^{-1}\) K\(^{-1}\)), and the ratio of \(\kappa_x/\kappa_y\) with the following order: CuSe (10.27) > AgSe (5.81) > AuSe (3.04). For the CuSe monolayer, the lattice thermal conductivity along the \(y\)-direction can compared to that of traditional TE materials, such as SnSe (0.62 W m\(^{-1}\) K\(^{-1}\)),\(^\text{42}\) PbTe (1.7–2.2 W mL\(^{-1}\))\(^\text{43,44}\) at 300 K.

3.3 Phonon transport properties

To further explore these monolayers low lattice thermal conductivity and the anisotropic behavior, phonon group velocity \(v_{iq}\), Grüneisen parameters \(\gamma_{iq}\), and phonon relaxation lifetimes \(\tau_{iq}\) are calculated. From eqn (10), \(\kappa_L\) and phonon group velocities are positively correlated. Here we calculated group velocities by the slope of the phonon dispersion curve for these monolayers, which expresses by \(v_{iq} = \partial \omega_{iq}/\partial q_i\). As shown in Fig. 6(a)–(c), we highlight three acoustic phonon group velocities for LA, TA, and ZA branches with different colors. Due to the flat phonon dispersion curve, the phonon group velocities for these monolayers are small, no more than 3.98 km s\(^{-1}\). As the frequencies increase, TA enters the higher energy optical area, the scatterings between acoustic and optical branches are enhanced significantly; thus, the velocities of TA phonons are suppressed naturally, which validates the previous analysis for the phonon spectra. Meanwhile, it is seen that the slopes of three acoustic branches along \(\Gamma-Y\) are far smaller than that along \(\Gamma-X\) from the phonon dispersion curves in Fig. 4(a)–(c). Furthermore, the insets in Fig. 6(a)–(c) show that the phonon group velocities along the \(x\)-direction (blue points) are much larger than those along the \(y\)-direction (red points), especially for the CuSe monolayer, giving rise to the anisotropic lattice thermal conductivity behavior of \(\kappa_L\) for these monolayers.

In general, low \(\kappa_L\) ideally needs weak harmonic and strong anharmonicity.\(^\text{45,46}\) The Grüneisen parameter \(\gamma_{iq}\) is a crucial dimensionless physical quantity to quantize the intensity of the phonon anharmonic effect.\(^\text{47}\) It can be obtained from the relation between phonon frequency and volume change as follows:

\[
\gamma_{iq} = -\frac{V}{\omega_{iq}(q)} \frac{\partial \omega_{iq}(q)}{\partial V}
\]

\(\gamma_{iq}\) as a function of frequency can be seen in Fig. 7(a)–(c). According our calculation, it exhibits a very large absolute value, especially near the long-wave limit (up to 100) for the CuSe monolayer, indicating that these monolayers’ phonon anharmonicities are strong. Additionally, its negative value implies these monolayers may be materials with negative thermal expansion, which is a favorable property for reducing the effect of high temperatures on the TE properties of materials by reducing the thermal stress, like graphene,\(^\text{48}\) and 2D \(\beta\)-tellurium.\(^\text{49}\)

![Fig. 5](image-url) Calculated lattice thermal conductivity \(\kappa_L\) along the \(x\)- and \(y\)-directions for CuSe, AgSe, and AuSe as a function of the temperature.

![Fig. 6](image-url) (a–c) Calculated phonon group velocity \(v_{iq}\) as a function of frequency with \(v_{iq}\) (blue point) and \(v_{iq}\) (red point) inset, for CuSe, AgSe, and AuSe monolayer. The red, blue, green, and orange dots represent for ZA, TA, LA, and optical branches, respectively.
Phonon relaxation times provide a deeper microscopic mechanism to understand the behavior of low thermal conductivity. According to eqn (10), the smaller the value of phonon relaxation time, the lower the thermal conductivity. Phonon relaxation times $t_{iq}$ with respect to frequency for these monolayers are shown in Fig. 8(a)–(c). It is seen that most of the phonon relaxation time becomes smaller and smaller from AuSe to AgSe and then the CuSe monolayer, deriving from the more frequent collisions between phonons, leading to a gradual decreasing behavior of the thermal conductivity for these monolayers.

The size effect of materials can regulate thermal conductivity to become a non-negligible factor for designing TE devices.\textsuperscript{50,51} Furthermore, we calculate the fitting normalized cumulative $k_L$ as a function of the phonon mean free path (MFP) at 300 K for these monolayers, which can be expressed as

$$k_L(l) = \frac{k_{L_{\text{max}}}}{1 + \frac{l_0}{l}}$$

where $k_{L_{\text{max}}}$ and $l_0$ are the ultimate thermal conductivity and the evaluated characteristic phonon MFP is shown in Fig. 9. The calculated thermal conductivity significantly decreases when the size of materials is shorter than that of phonon MFP due to the frequent phonon-surface scattering and increasing with the phonon MFPs until reaching the thermodynamic limit. The phonon MFP value corresponding to 50% $k_L$ for XSe monolayers can be seen in Fig. 9. In general, the value of nanostructures is no more than 100 nm, indicating that $k_L$ is not sensitive to the size effect. Compared with TaAs (110 nm),\textsuperscript{52} the value for CuSe, and AgSe monolayers along the $x$- and $y$-directions are only (47, 13 nm) and (92, 48 nm), which means that their size dependence on $k_L$ is not sensitive.

**3.4 Thermoelectric figure of merit**

Combining lattice thermal conductivity, electronic transport coefficients, the figure of merit ($ZT$) of these monolayers can be determined. Owing to the direction-dependent transport behavior of electrons and phonons, $ZT$ for these monolayers are highly anisotropic as well. As shown in Fig. 10. For p-type doping, the CuSe monolayer possesses more excellent thermoelectric performance ($ZT = 0.33, 0.63$) than AgSe ($ZT = 0.14, 0.61$) and AuSe ($ZT = 0.05, 0.57$) monolayers both along the $x$- and $y$-directions. For n-type doping, the maximum $ZT$ of the CuSe monolayer can reach 3.26 along the $y$-direction for carrier concentrations of about $1.77 \times 10^{13}$ cm$^{-2}$. Compared with the 3D Ag$_2$Se,\textsuperscript{53} the power factor of CuSe is nearly six times that of Ag$_2$Se, although the thermal conductivity ($k_e + k_p$) of 2.606 W m$^{-1}$ K$^{-1}$ is twice that of Ag$_2$Se. Thus, the $ZT$ value of CuSe is much larger than that (1.12) of Ag$_2$Se. Such a surprising high $ZT$ is comparable to the high-performance thermoelectric materials reported to date, such as PtTe$_2$ (2.60 at 600 K),\textsuperscript{54} CaP$_3$ (3.23 at 500 K),\textsuperscript{55} SnP$_3$ (3.7 at 300 K).\textsuperscript{56} The CuSe monolayer has a higher conversion efficiency, and is economically cheaper, environment friendly, and non-toxic compared conventional TE materials, such as Mg$_2$Sb$_3$,\textsuperscript{57} Bi$_2$Te$_3$,\textsuperscript{58,59} indicating that it is a promising TE material.

**4. Conclusions**

In summary, we study the TE performance of 2D group IB-selenides XSe ($X = \text{Cu, Ag, Au}$) by using first-principle
calculations and the Boltzmann transport equation. The results show that XSe monolayers have excellent electric transport performance (ultrahigh Seebeck coefficient and high carrier mobility); meanwhile, they exhibit a low and highly anisotropic lattice thermal conductivity. In particular, for the CuSe monolayer, the calculated $k_x$ values along the $x$- and $y$-directions are as low as 12.54 and 1.22 W m$^{-1}$ K$^{-1}$ at 300 K with a $k_x/k_y$ ratio of 10.27, which can be attributed to its large phonon anharmonic effect and anisotropic phonon velocities. As a result, the CuSe monolayer exhibits the best TE performance and the maximum $ZT$ value of 3.26 can be achieved along the $y$-direction for n-type doping at 300 K. The CuSe monolayer has a tremendous economic advantage in the synthesis process compared to expensive gold and silver elements, indicating a promising prospect for application in thermoelectric devices.

Conflicts of interest

There are no conflicts to declare.

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