Thermoelectric Performance of Two-Dimensional AlX (X = S, Se, Te): A First-Principles-Based Transport Study

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ABSTRACT: By using the first-principles calculations in combination with the Boltzmann transport theory, we systematically study the thermoelectric properties of AlX (X = S, Se, Te) monolayers as indirect gap semiconductors. The unique electronic density of states, which consists of a rather sharp peak at the valence band maxima and an almost constant band at the conduction band minima, makes AlX (X = S, Se, Te) monolayers excellent thermoelectric materials. The optimized power factors at room temperature are 22.59, 62.59, and 6.79 mW m\(^{-1}\) K\(^{-2}\) under reasonable electronic concentration for AlS, AlSe, and AlTe monolayers, respectively. The figure of merit (zT) increases with temperature and the optimized zT values of 0.52, 0.59, and 0.26 at room temperature are achieved under moderate electronic concentration for AlS, AlSe, and AlTe monolayers, respectively, indicating that two-dimensional layered AlX (X = S, Se, Te) semiconductors, especially AlSe, can be potential candidate matrices for high-performance thermoelectric nanocomposites.

INTRODUCTION

With the global energy crisis and environmental impact of fossil fuels, a compelling need exists for thermoelectric (TE) materials which can directly convert waste heat into electric power. Generally, the thermally driven electrical performance of TE materials is gauged by the dimensionless power factor PF = S\(^2\)\(\sigma\)\(fi\), in which \(S\) and \(\sigma\) are, respectively, Seebeck coefficient and electrical conductivity. The conversion efficiency of TE materials is governed by the dimensionless figure of merit \(zT = S^2\sigma T/\kappa\), where \(T\) is the absolute temperature, \(\kappa\) the sum of electronic (\(\kappa_e\)) and lattice (\(\kappa_l\)) thermal conductivity. A high-performance TE material not only requires a high power factor but also has to possess a low thermal conductivity. Unfortunately, it is complex to efficiently achieve waste heat recovery for the interdependency of transport parameters (\(S, \sigma, \kappa_e, \kappa_l\)). \(S\) and \(\sigma\) usually interweave and behave in an opposite trend.1 The improvement of TE devices thus strongly depends on the optimization of electronic and thermal transport properties. A strategy for achieving high TE performance is to identify materials with intrinsically high TE performance, which can be applied as potential matrices for high-performance TE nanocomposites. Since the arrival of graphene,7 the large number of the two-dimensional (2D) layered materials, such as black phosphorus (BP),5,6 transition metal dichalcogenides (TMDSs),3–8 and group III metal chalcogenides (GIIAMCs),9–13 have been synthesized and characterized. Unlike graphene, these 2D layered materials are semiconductors and can potentially play key roles in the fabrication of next-generation nano-electronic devices. In particular, these 2D semiconductors could alleviate the coupling between \(S\) and \(\sigma\) because of the quantum confinement effects, consequently enhancing TE performance.14–16

Indeed, TMDSs such as MoS\(_2\), MoSe\(_2\), WS\(_2\), and WSe\(_2\) exhibit thickness-dependent TE properties15 because of the thickness-dependent electronic band structure20,22 and maximum power factor of about 340 and 150 mW m\(^{-1}\) K\(^{-2}\) for n-type monolayer MoSe\(_2\), and p-type MoS\(_2\) monolayers,22 respectively, which are much higher than those of 20 and 30 mW m\(^{-1}\) K\(^{-2}\) for n-type bulk MoSe\(_2\) and p-type bulk MoS\(_2\), respectively. Experimentally, the Seebeck coefficient up to 30 mV K\(^{-1}\) for single-layer MoSe\(_2\) at room temperature is observed,23 which is significantly larger than the one observed in bulk MoS\(_2\) (~7 mV K\(^{-1}\)), and moreover can be tuned between 0.4 and 100 mV K\(^{-1}\) by an external electric field using a field effect transistor.25 As for BP, theoretical calculations in different approaches indicate that the BP monolayer shows a strong spatial anisotropy in electrical and thermal conductivities, which makes \(zT\) in the armchair direction larger than that in the zigzag direction.26,27 and using the electric-double-layer transistor configuration experimentally, the Seebeck coefficient of ion-gated BP reached 510 μV K\(^{-1}\) at 210 K in the hole-depleted state,28 which is much higher than the reported 335 μV K\(^{-1}\) of single crystal BP at 300 K.29

Among promising TE 2D layered semiconductors, monolayer layered GIIAMCs such as InSe, GaS, GaSe, or GaTe have entered the spotlight. These monolayer layered semiconductors have unique electronic structures, having a flat band at the valence band maxima (VBM) and a parabolic band at the conduction band minima (CBM), thus resulting in a rather sharp peak at VBM and an almost constant band at CBM in the density of states (DOS).30,31 Experimentally, the monolayer or few layers of InSe,11,32,33 GaS,12,34,35 GaSe,13,36–39 and GaTe10 have been synthesized, and much effort has been dedicated to reveal the electronic and optical properties and potential applications in many fields.9 It was recently reported that the carrier mobility in few-layer InSe was...
more than $10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature,\textsuperscript{40} which is much larger than $321 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ of n-type InSe polycrystalline samples with the PF of about $250 \mu \text{W m}^{-1} \text{ K}^{-1}$ and $zT$ of 0.42 at 700 K.\textsuperscript{41} The thickness-dependent TE properties of GaS, GaSe, InS, InSe monolayers have been theoretically investigated based on a constant relaxation time,\textsuperscript{42} and by more precise relaxation time calculation, the InSe monolayer has both a large $S$ and a large $\tau$, giving the maximum PF of 49 ($43$) mW m$^{-1}$ K$^{-2}$ for the p-type (n-type) InSe monolayer at room temperature in the armchair direction.\textsuperscript{43} Otherwise, it was theoretically reported that monolayer InSe exhibited unusual phonon behavior and ultralow thermal conductivities.\textsuperscript{44} The TE performance of two-dimensional layered semiconductor InSe was further effectively enhanced by reducing film thickness and modulating electron density.\textsuperscript{45} The study on the temperature-dependent TE properties of GaS, GaSe, and GaTe monolayers by the Boltzmann transport theory based on constant relaxation time showed the high $zT$ of GaS, GaSe, and GaTe monolayers at low temperature.\textsuperscript{46} Thus, it seems that monolayer II-VI monolayers such as InSe, GaS, GaSe, or GaTe are promising matrices for high-efficient TE nanocomposites.

Recently, other group III–VI monolayers such as AIX ($X = S$, Se, Te) have been proposed to have similar band structures with InSe, GaSe, GaSe, or GaTe monolayers and high mechanical stability.\textsuperscript{47} We thus expect that AIX ($X = S$, Se, Te) monolayers could be suitable candidates for applications in electronic and TE devices. However, relevant works about $\kappa$ and TE properties of AIX ($X = S$, Se, Te) are lacking till date. In this work, we present a detailed study on TE properties of 2D layered semiconducting AIX ($X = S$, Se, Te) by using first-principles in combination with the Boltzmann transport theory, which enables systematic analysis and comparison on TE performance for possible III–VI 2D semiconducting configurations.

## RESULTS AND DISCUSSION

### Crystal and Electronic Structures.

The structure of AIX ($X = S$, Se, Te) monolayers is modeled based on the geometry of InSe, GaSe, and GaS monolayers, which have already been synthesized experimentally,\textsuperscript{2,37,40} for they all belong to group III binary monolayers. All the AIX ($X = S$, Se, Te) compounds crystallize in a honeycomb structure belonging to space group $D_{3h}$. Figure 1 presents the top view and side view of the monolayer AIX unit cell which consists of four atoms (two Al and two $X$ atoms). In a monolayer AIX, there exist four

(a) Top view

(b) Side view

Figure 1. Ball-and-stick model of the AIX ($X = S$, Se, Te) monolayers from the top view (a) and side view (b).

In this work, we present a detailed study on TE properties of GaS, GaSe, and GaTe monolayers by the Boltzmann transport theory based on constant relaxation time showed the high $zT$ of GaS, GaSe, and GaTe monolayers at low temperature.\textsuperscript{46} Thus, it seems that monolayer II-VI monolayers such as InSe, GaS, GaSe, or GaTe are promising matrices for high-efficient TE nanocomposites.

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### Table 1. Optimized Lattice Constant ($a$), Bond Length ($d_{Al-X}$, $d_{X-X}$, $d_{Al-Al}$), Bond Angle ($\theta$), and Band Gap ($E_{g}$) of AIX ($X = S$, Se, Te) Monolayers

| AIX     | $a$ (Å) | $d_{Al-X}$ (Å) | $d_{X-X}$ (Å) | $d_{Al-Al}$ (Å) | $\theta$ (deg) | $E_{g}$ (eV) |
|---------|---------|----------------|---------------|----------------|----------------|-------------|
| AlS     | 3.46 (3.57) | 2.59 (2.57) | 4.82 (4.73) | 2.29 (2.32) | 98.22 | 2.05 (2.10) |
| AlSe    | 3.70 (3.78) | 2.57 (2.57) | 4.95 (4.90) | 2.45 (2.47) | 98.31 | 2.01 (1.99) |
| AlTe    | 4.10 (4.11) | 2.55 (2.58) | 5.11 (5.14) | 2.69 (2.70) | 99.30 | 1.86 (1.84) |

*The values in brackets are theoretical results in ref 47.
The obtained values of \(m^*\) for the two carriers in AlX (X = S, Se, Te) monolayers are collected in Table 2. Expectedly, the effective mass of electrons is smaller than that of holes in all the three monolayers, which is mainly attributed to a steeper CBM (for electrons) compared with a VBM (for holes). Table 2 also summarizes the calculated deformation potential (DP) constant \((E_1)\), obtained carrier mobility \((\mu)\), and relaxation time \((\tau)\) at room temperature. It is obvious to find that the carrier mobility of electrons is larger than that of holes resulting from the unusual DOS feature seen in Figure 2. The temperature dependence of the relaxation time \((\tau)\) is presented in Figure 3.

**TE Properties.** The carrier concentration \((n)\) dependence of transport coefficients including the Seebeck coefficient \((S)\), electrical conductivity \((\sigma)\), power factor \((PF = S^2\sigma)\), and electronic thermal conductivity \((\kappa_e)\) at 300, 500, and 700 K for AlX (X = S, Se, Te) monolayers are presented in Figure 4 (for n-type systems) and Figure 5 (for p-type systems). As can be seen from Figures 4 and 5a–c, the absolute Seebeck coefficients decrease for n-type and p-type AlS, AlSe, and AlTe monolayers with increasing carrier concentration, but they show an increasing trend when increasing the temperature at constant carrier concentrations, reflecting that \(S\) is inversely
for n-type and p-type AlS, AlSe, and AlTe monolayers is conductivity for a high power factor (PF). The calculated PF is inversely proportional to the value of obtaining a high Seebeck coefficient, but electrical conductivity and thermal conductivity but also simultaneously needs a balance between the Seebeck coefficient and electrical conductivity, while for the p-type systems, they are 652.39 (at 300 K), 680.89 (at 500 K), and 700.56 \( \mu V \) K\(^{-1}\) (at 700 K) at the carrier concentration of 10\(^{11}\) cm\(^{-2}\) for p-type AlSe. Otherwise, the absolute S of n-type AlTe monolayer is 350.18, 402.69, and 445.74 \( \mu V \) K\(^{-1}\) (at 700 K) for n-type AlSe, which are also smaller than 641.74 (at 300 K), 680.89 (at 500 K), and 700.56 \( \mu V \) K\(^{-1}\) (at 700 K) for p-type AlSe. Otherwise, the absolute S of n-type AlTe monolayer is 350.18, 402.69, and 445.74 \( \mu V \) K\(^{-1}\) at the temperature of 300, 500, 700 K, which are about twice of those for the n-type ones at the same condition. Also, the absolute S are 489.73 (at 300 K), 554.62 (at 500 K), and 578.94 \( \mu V \) K\(^{-1}\) (at 700 K) for n-type AlSe, which are also smaller than 641.74 (at 300 K), 680.89 (at 500 K), and 700.56 \( \mu V \) K\(^{-1}\) (at 700 K) for p-type AlSe. Otherwise, the absolute S of n-type AlTe monolayer is 350.18, 402.69, and 445.74 \( \mu V \) K\(^{-1}\) at the temperature of 300, 500, 700 K, which are about twice of those for the n-type ones at the same condition. Also, the absolute S are 489.73 (at 300 K), 554.62 (at 500 K), and 578.94 \( \mu V \) K\(^{-1}\) (at 700 K) for n-type AlSe, which are also smaller than 641.74 (at 300 K), 680.89 (at 500 K), and 700.56 \( \mu V \) K\(^{-1}\) (at 700 K) for p-type AlSe. Otherwise, the absolute S of n-type AlTe monolayer is 350.18, 402.69, and 445.74 \( \mu V \) K\(^{-1}\) at the temperature of 300, 500, 700 K, which are larger than 316.47, 292.24, and 321.46 \( \mu V \) K\(^{-1}\) for the p-type AlTe monolayer at the same carrier concentration and temperature. The consequent electrical conductivity (\( \sigma \)) is shown in Figure 4d–f (for n-type systems) and Figure 5d–f (for p-type systems). Contrary to the Seebeck coefficient, the electrical conductivity increases with \( n \) in the whole concentration range. The behavior of \( \sigma \) with respect to temperature, however, is completely inverse. All the three n-type systems hold bigger \( \sigma \) than p-type systems at the same carrier concentration, originating from the larger carrier mobility of electrons because of \( \sigma = ne\mu \). An ideal TE material not only requires to minimize the thermal conductivity but also simultaneously needs a maximized power factor (PF). However, transport coefficients are usually coupled with each other. As can be seen from above discussion, the presence of large effective mass is required for obtaining a high Seebeck coefficient, but electrical conductivity is inversely proportional to the value of \( \mu \). One should make a balance between the Seebeck coefficient and electrical conductivity for a high power factor (PF). The calculated PF for n-type and p-type AlS, AlSe, and AlTe monolayers is presented in Figures 4 and 5g–i. The curves first increase with carrier concentration to a maximum and then go down with further increasing in \( n \). For the n-type AlS monolayer, the power factor can be optimized to be as high as 22.59 (300 K), 22.45 (500 K), and 23.39 mW m\(^{-1}\) K\(^{-2}\) (700 K), which are all larger than that for the p-type system. This indicates the superior TE behavior of the n-type system with respect to the p-type system. The largest power factor (62.59 mW m\(^{-1}\) K\(^{-2}\)) among the three systems is obtained in the n-type AlSe monolayer at the carrier concentration of 5.5 \( \times \) 10\(^{12}\) cm\(^{-2}\) at \( T = 300 \) K because of the largest electrical conductivity. As discussed above, the largest electrical conductivity is mainly attributed to the highest carrier mobility of electrons in the AlSe monolayer (in Table 2).

We then turn to explore the phonon transport properties of AlX (X = S, Se, Te) monolayers, as the thermal transport in semiconductors is mainly contributed by the phonon. Figure 6a–c shows the dispersion of phonon modes of AlX (X = S, Se, Te) monolayers, no imaginary frequencies in all phonon branches confirm the dynamical stability of the AlX (X = S, Se, Te) monolayers, which are consistent with the previous theoretical work.\(^{37}\) The calculated phonon dispersions for the three systems are all composed of three acoustic modes and nine optical ones. The three acoustic modes contains two linear modes [longitudinal acoustic (LA) and transverse acoustic (TA)] for in-plane vibrations and a flexural one (ZA) for out-of-plane vibrations. The dispersion of all the three acoustic modes is quite stronger away from the zone center, thus giving higher velocity modes than typical optical phonons and possesses most of the heat. Besides, it is found that the acoustic modes are more dispersive from AlS to AlSe to AlTe monolayers, leading to a higher group velocity and thus an enhanced lattice thermal conductivity.\(^{39–51}\) The group velocity of ZA, TA, and LA phonons near the \( \Gamma \) point for the AlX (X = S, Se, Te) monolayers is calculated and listed in Table 3. For comparison, the corresponding results of MoS\(_2\), GaSe, and InSe monolayers are also presented.\(^{49,52}\) As a fact, the ZA branch plays a crucial role in \( \kappa \) of 2D materials.\(^{53,54}\)
MoS_2 monolayer. However, the calculated κ_l of the MoS_2 monolayer is much larger than that of AlX (X = S, Se, Te) monolayers, and thus suggesting lower Debye temperature in the AlX (X = S, Se, Te) monolayer. In Slack’s model,^56 κ_l has cubic dependence on Debye temperature, and accordingly, a higher Debye temperature corresponds a higher κ_l. A comparison of κ_l for three selenide-based monolayers, AlSe, GaSe, and InSe, is illuminating. The atomic mass of Al (27) is smaller than that of Ga (70) and In (115), and thus, one might expect a higher κ_l for the AlSe monolayer. Nevertheless, the calculated κ_l of the AlSe monolayer is the smallest among the three monolayers. To explain the unusually low κ_l of the AlSe monolayer, we consider the mechanical properties of the three selenide-based monolayers. Young’s modulus (E) of AlSe, GaSe, and InSe monolayers are, respectively, 26.71, 28.62, and 27.96 GPa. Poisson’s ratio (σ) of AlSe, GaSe, and InSe monolayers is listed as 0.24, 0.24, and 0.29.^57 The AlSe monolayer has very small E and σ, indicating lower vibrational strength. From the phonon dispersion of the AlSe, GaSe, and InSe monolayers shown in other literature,^47 the ZA modes are more and more flat from AlSe to GaSe to InSe monolayers. Therefore, we conclude that the AlSe monolayer has the smallest Debye temperature among the three selenide-based monolayers as discussed above. Therefore, a small Debye temperature together with low Poisson’s ratio always means a weak interatomic bonding, which will decrease the κ_l of the AlSe monolayer. As a result, the AlSe monolayer has a relative κ_l compared to GaSe and InSe monolayers. The calculated lattice thermal conductivity (κ_l) of the AlX (X = S, Se, Te) monolayers as a function of temperature in the range from 300 to 700 K is shown in Figure 6d–f. One can clearly see that the lattice thermal conductivity of all the three AlX, AlSe, and AlTe monolayers decreases as the temperature increases. The values of κ_l for AlS, AlSe, and AlTe monolayers are respectively 3.00, 4.21, and 4.45 W m⁻¹ K⁻¹ at room temperature. When taking the thickness into consideration, the thermal sheet conductances of two-dimensional AlS, AlSe, and AlTe are, respectively, 2.39, 3.61, and 3.86 nW K⁻¹ cm⁻² (300 K), which are comparable to those of high ZT bulk materials such as PbTe^48 but much smaller than those of Mo- and W-based dichalcogenides^59–63 and GIIAMCs such as InSe^60 at the same temperature. The low thermal conductivity of AlS, AlSe, and AlTe monolayers suggests that these three monolayers could have favorable TE performance.

Based on the obtained TE transport parameters (S, σ, and κ) of AlX (X = S, Se, Te) monolayers, the TE performance can be evaluated. Figure 7 plots the zT values as a function of carrier concentration and temperature for n-type and p-type monolayers. For p-type AlS, the optimal value of zT at room temperature is 0.33 at the carrier concentration of 1.9 × 10¹³ cm⁻². At a high temperature of 700 K, a maximal zT of 0.62 appears at the carrier concentration of 2.4 × 10¹³ cm⁻². The largest zT can be further improved to 0.52 (at T = 300 K and n = 1.5 × 10¹¹ cm⁻²) and 0.67 (at T = 700 K and n = 1.1 × 10¹¹ cm⁻²) for n-type AlS. As such, the n-type AlS monolayer exhibits a more favorable TE performance rather than the n-type system. Similar to the AlS case, the n-type AlSe monolayer has the largest zT of 0.59, 0.69, and 0.74 at the temperature of 300, 500, and 700 K because of the extremely large power factor. Notably, even at a lower temperature of 300 K, zT can also compete with that at higher temperatures. Thus, the n-type AlSe monolayer can exhibit promising TE performance even at relatively low temperatures. Similar to AlS and AlSe monolayers, n-type AlTe can be used as a promising TE material. The optimal zT at 300 and 700 K for the n-type AlTe monolayer are, respectively, 0.26 and 0.73 at the carrier concentration of 5.4 × 10¹¹ and 2.7 × 10¹¹ cm⁻². Including the results of AlS, it can be concluded that the n-type AlSe monolayer exhibits the largest TE figure of merit among the studied AlX (X = S, Se, Te) monolayers because of its intrinsic band structure. Although the DP theory has been widely used to calculate the relaxation time for two-dimensional systems, it still may be unstable for the DP model which fully ignores electron–optical–phonon interaction, polar scattering, and other scattering mechanisms. In order to make a comparison to the previous work easier, the zT values of AlX (X = S, Se, Te) monolayers at 300 K with a relaxation time range centered around the calculated ones from the DP model are plotted in Figure 8. The solid black lines stand for the zT values from the DP model and the open symbols stand for our obtained values of zT for both n- and p-type AlX (X = S, Se, Te) monolayers.

### Table 3. Calculated Group Velocities (v_g) (km/s) of ZA, TA, and LA Phonons Near the Γ Point for the AlX (X = S, Se, Te) Monolayers with MoS_2, GaSe, and InSe Monolayers for Comparison

| Monolayer | ZA   | TA   | LA   |
|-----------|------|------|------|
| AlS       | 1.726| 1.745| 2.967|
| AlSe      | 2.092| 2.518| 4.525|
| AlTe      | 3.036| 3.811| 4.882|
| GaSe      | 2.487| 4.162| 4.67  |
| InSe      | 1.853| 3.272| 4.67  |
| MoS_2     | 1.400| 3.96 | 6.47  |

### Figure 7. Figure of merit (zT) as a function of carrier concentration for n-type and p-type AlS (a–b), AlSe (c–d), and AlTe (e–f) monolayers at 300, 500, and 700 K.
Monkhorst–Pack uniform k-point sampling \(^7\) is selected as \(24 \times 24 \times 1\) in the whole Brillouin zone. The energy and force convergence criteria are, respectively, taken to be \(10^{-6}\) eV and \(0.01\) eV/Å. By conducting the energy minimization calculations on the basis of the conjugate gradient method, we determine the optimized configuration of the systems. A vacuum slab of 20 Å is enough to eliminate the interactions between the adjacent AlX (X = S, Se, Te) monolayers.

Based on the calculated accurate electronic structures and carrier relaxation time, the electronic transport properties are then calculated from the semiclassical Boltzmann theory.\(^7\) The obtained DFT results are used as an input of BoltzTraP to estimate TE performance of AlX (X = S, Se, Te) monolayers. In this approach, the temperature \((T)\) and chemical potential \((\mu)\) dependence of the Seebeck coefficient \((S_{\alpha\beta})\), electrical conductivity \((\sigma_{\alpha\beta})\), and electronic thermal conductivity \((\kappa_{\alpha\beta}^e)\) are expressed as\(^7\),\(^3\),\(^4\)

\[
S_{\alpha\beta}(T, \mu) = \frac{1}{eT\Omega_{\alpha\beta}(T, \mu)} \int \sigma_{\alpha\beta}(\epsilon) (\epsilon - \mu) \left[ \frac{\partial f_\mu(T, \epsilon)}{\partial \epsilon} \right] d\epsilon
\]

\[
\sigma_{\alpha\beta}(T, \mu) = \frac{1}{\Omega} \int \sigma_{\alpha\beta}(\epsilon) \left[ \frac{\partial f_\mu(T, \epsilon)}{\partial \epsilon} \right] d\epsilon
\]

\[
\kappa_{\alpha\beta}^e(T, \mu) = \frac{1}{e^2T} \int \sigma_{\alpha\beta}(\epsilon) (\epsilon - \mu)^2 \left[ \frac{\partial f_\mu(T, \epsilon)}{\partial \epsilon} \right] d\epsilon
\]

in which subscripts \(\alpha\) and \(\beta\) represent the two axis directions in the momentum space (or according to real space). Here, \(\Omega\) is the volume of the unit cell and \(f_\mu\) stands for the Fermi–Dirac distribution function. The \(\sigma_{\alpha\beta}(\epsilon)\) as a function of \(\epsilon\) is in the form of

\[
\sigma_{\alpha\beta}(\epsilon) = \frac{e^2}{N} \sum_{i,k} \tau_{\alpha\beta}(i,k) v_\alpha(i,k) v_\beta(i,k) \delta(\epsilon - \epsilon_{i,k})
\]

In this formula, \(i\) and \(k\) donate the band index and wave vector, respectively. Parameters \(N, \epsilon\), and \(\tau\) express the number of k-points samples, electron charge, and carrier relaxation time, respectively. The carrier group velocity \(v_\alpha(v_\beta)\) along the \(\alpha(\beta)\) direction can be calculated from

\[
v_\alpha(i,k) = \frac{1}{\hbar} \frac{\partial \epsilon(i,k)}{\partial k_\alpha}
\]

The electrical conductivity \((\sigma)\) and electronic thermal conductivity \((\kappa_e)\) are proportional to the relaxation time \((\tau)\). Therefore, the accurate treatment of \(\tau\) is of great importance. Many earlier theoretical calculations on TE properties were performed based on a constant relaxation time \(^2\),\(^3\),\(^6\) and the value is generally overestimated.\(^2\),\(^3\),\(^7\) In this study, the relaxation time is evaluated by adopting the DP theory,\(^7\) which is widely used to calculate the relaxation time for two-dimensional systems.\(^2\),\(^6\),\(^7\)–\(^8\) Accordingly, the relaxation time is calculated by

\[
\tau = \frac{\mu m^*}{e}
\]

in which the effective mass \((m^*)\) is obtained from the accurate band structure. For a 2D crystal, the carrier mobility \((\mu)\) can be expressed as

\[
\mu = \frac{\hbar}{k_B T} m^* \mu
\]

In the formula, the two-dimensional elastic modulus \((C_{2D})\) is calculated from

\[
C_{2D} = \frac{1}{S_0} \frac{\partial^2 E}{\partial (\Delta l/l_0)^2}
\]

where \(l_0\) is the optimized lattice parameter of the unit cell, \(\Delta l = l - l_0\) is the lattice variation when the compressed and expanded systems are compared with the optimized system, and \(E\) is the corresponding energy of the compressed and expanded systems. \(m_4\) is the average density-of-states effective mass dominated by \(m_4 = \sqrt{m_1^* m_2^*}.\) \(E_1\) is the DP constant defined as

\[
E_1 = \frac{\partial E_{edge}}{\partial (\Delta l/l_0)}
\]

The anisotropic in-plane lattice thermal conductivity under the relaxation time approximation can be calculated as the sum of the contributions of all phonon model \(\lambda\) with different wave vectors and branch indexes

\[
\kappa_{\alpha\beta} = \frac{1}{V} \sum_{\lambda} C_\lambda v_{\alpha,i} v_{\beta,j} \mathcal{S}_\lambda
\]

where \(V\) is the crystal volume, \(C_\lambda\) is the specific heat per mode, \(v_{\alpha,i}\) and \(\mathcal{S}_\lambda\) are the velocity components along the \(\alpha\) direction and the relaxation time of the phonon mode \(\lambda\). The lattice thermal conductivity \((\kappa_l)\) can be obtained by solving the phonon Boltzmann transformation related to the harmonic and anharmonic interatomic force constants (IFCs) as performed by the ShengBTE code.\(^8\)–\(^10\) The inputs for the ShengBTE are the second- and third-order IFCs. For this, a \(4 \times 4 \times 4\) supercell with \(5 \times 5 \times 1\) k-point sampling is used to calculate the second-order IFCs and phonon frequencies by the Phonopy package.\(^8\) The third-order IFCs are obtained by using the thirdorder.py module using a \(4 \times 4 \times 4\) supercell and \(\Gamma\)-point only calculations. Note that we use eq 4 to calculate the electronic thermal conductivity \((\kappa^e)\) because the Wiedemann–Franz law is only suitable for the system where the scattering of electrons in the material is dominated by...
elastic collision. Here, the effective van der Waals thickness of AlX (X = S, Se, Te) monolayers is 7.97, 8.57, and 8.68 Å, which is defined as the summation of the buckling distance and two van der Waals radii of the outermost surface atoms of structures.

**CONCLUSIONS**

To summarize, we have presented the electronic, phonon, and TE properties of AlX (X = S, Se, Te) monolayers by the density functional theory in combination with the Boltzmann transport theory. All the AlX (X = S, Se, Te) monolayers are indirect band gap semiconductors with unique electronic structures, having a flat band at VBM and a parabolic band at CBM, and consequently, a rather sharp peak at VBM and an anticrossing at CBM in DOS. No imaginary frequencies in all phonon branches verify the dynamical stability of the AlX (X = S, Se, Te) monolayers. A detailed study of TE properties as a function of carrier concentration and temperature is carried out. The largest power factors are around 22.59, 62.59, and 6.79 mW m⁻¹ K⁻² at room temperature and 23.40, 54.36, 10.42 mW m⁻¹ K⁻² at 700 K under reasonable electronic concentration for AlS, AlSe, and AlTe monolayers, respectively. The figure of merit (zT) increases with temperature, and the optimized zT values reach 0.52, 0.59, and 0.26 at room temperature and 0.67, 0.74, and 0.73 at 700 K under reasonable electronic concentration for AlS, AlSe, and AlTe monolayers, respectively, thus suggesting that the n-type AlX (X = S, Se, Te) monolayers, especially the AlSe monolayer can be used as potential candidate matrices for high-performance TE nanocomposites.

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**Notes**

The authors declare no competing financial interest.

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