Low thermal conductivities and excellent thermoelectric performances of the pyrite-type IIB-VIA₂ dichalcogenides: ZnS₂, CdS₂ and CdSe₂

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ABSTRACT

By solving the phonon and electron Boltzmann transport equations, we calculate the thermoelectric properties of three pyrite-type IIB-VIA₂ dichalcogenides (ZnS₂, CdS₂ and CdSe₂). The results show that they both have low lattice thermal conductivities and promising electrical transport properties. Comparing their detailed phonon properties with that of FeS₂, we find that their low lattice thermal conductivities come from their soft phonon modes and strong anharmonicity resulted by their weak bonds between the metal atoms with the nonmetal atoms. Analysis of their electronic band structures indicates that their promising electrical transport properties are contributed by the non-spherical isoenergy Fermi surface in the valence bands and the large energy valley degeneracies and light carrier effective masses in the conduction bands. Additionally, due to their calculated carrier relaxation times of p-type carriers are larger than that of n-type carriers, their thermopower factors of p-type doping are higher than that of n-type doping. As a result, their figure of merit, ZT values, can reach 1.45, 1.37 and 2.29 for p-type doping, and 1.01, 0.57 and 1.16 for n-type doping, respectively. This means that three IIB-VIA₂ dichalcogenides (ZnS₂, CdS₂ and CdSe₂) exhibit both excellent thermoelectric properties for p-type and n-type doping, and their thermoelectric properties of p-type doping are better than n-type doping.
INTRODUCTION

The thermoelectric conversion efficiency of a thermoelectric (TE) device depends on the dimensionless thermoelectric figure of merit, $ZT = S^2 \sigma T / \kappa$, where $T$ is the absolute temperature, $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity and $\kappa$ is the thermal conductivity including charge carrier ($\kappa_c$) and lattice ($\kappa_l$) contributions. The promising TE materials need have high thermopower factor ($PF = S^2 \sigma$) and low thermal conductivity. According to the Boltzmann transport theory\[1\], for most semiconductors, the thermopower factor is determined by the electrical transport properties ($S$ and $\sigma$), while the thermal conductivity is mainly contributed by phonon scattering properties ($\kappa_l$). However, due to the state-of-the-art TE materials still have relatively low $ZT$ values or contain toxic and expensive chemical elements, the commercial applications of TE devices are limited. Currently, there are two major strategies to increase the $ZT$ values of TE materials. One is to optimize the thermoelectric performance of the existing TE materials, such as, using band structure engineering to improve the $PF$\[2-5\] and increasing phonon scattering to decrease $\kappa_l$\[5-7\]. The other strategy is to seek new promising TE materials.\[8-10\]

Recently, the pyrite-type FeX$_2$ ($X$=S, Se and Te) have shown promising electrical thermoelectric performance in the first principle studies\[11-13\], and the experimental synthesized pyrite-type PtSb$_2$\[14\] and MnTe$_2$\[15\] exhibited excellent thermoelectric performance. Additionally, through our previous High-throughput computations\[9\] and theoretically research\[16\], we have predicted that ZnSe$_2$ have excellent thermoelectric performance due to not only the promising electrical transport properties but also the low lattice thermal conductivity. Such studies have motivated us to explore thermoelectric performances of other pyrite-type IIB-VIA$_2$ dichalcogenides, such as, ZnS$_2$, CdS$_2$ and CdSe$_2$.

The crystal structure of the pyrite-type MX$_2$ [M=transition metal (Zn and Cd), X=S and Se] is a cubic structure (space group Pa$_3$, depicted in Fig. 1) with Wyckoff position 4a(0,0,0) for M and 8c($u,u,u$) for X, where $u$ is the pyrite parameter, which can uniquely determine the atomic positions. In the structure, each M atom has six X atom and each X atom has three M atom and one X atom as the nearest neighbors. In 1968, some pyrite-type dichalcogenides (including ZnS$_2$, ZnSe$_2$, CdS$_2$ and CdSe$_2$) have been successfully synthesized at high pressures (6.5-8.9 GPa)\[17\]. Therefore, it is both theoretically and practically interesting to dig into the thermoelectric performances of ZnS$_2$, CdS$_2$ and CdSe$_2$. 
In this work, through calculating the detailed phonon vibrational properties, we solve the phonon Boltzmann transport equation, and evaluate the lattice thermal conductivity of ZnS$_2$, CdS$_2$ and CdSe$_2$. We find that they have both low lattice thermal conductivity. To analyze the source of the low lattice thermal conductivity, we compare their detailed phonon properties with FeS$_2$. After analyzing, we find that 1. The four pyrite-type dichalcogenides (ZnS$_2$, CdS$_2$, CdSe$_2$ and FeS$_2$) both have the nonmetallic dimers and the electrons are localized around the dimers. 2. However, in three pyrite-type IIB-VIA$_2$ dichalcogenides (ZnS$_2$, CdS$_2$ and CdSe$_2$), the nonmetallic dimers are very strong, and the bonds between the metal atoms with the nonmetal atoms are very weak. 3. The weak bonds can result in the soft phonon modes and strong anharmonicity, which lead to the low lattice thermal conductivity in three pyrite-type IIB-VIA$_2$ dichalcogenides. Additionally, we also calculate their electrical transport properties in the framework of electron Boltzmann transport theory. We find that they both have promising electrical transport properties for p-type and n-type doping, which caused by their complex non-spherical isoenergy Fermi surface in valence bands and the large energy valley degeneracies in conduction bands. Their low lattice thermal conductivity and promising electrical transport properties contribute to their excellent thermoelectric performances.
PHONON TRANSPORT PROPERTIES

A. Computational methodologies

Based on the phonon Boltzmann transport equation (BTE), the components of the thermal conductivity tensor along Cartesian axes $\alpha$ and $\beta$ ($\kappa_{\alpha\beta}$) can be calculated by summing the contributions of all phonon modes denoted by the wave vector ($q$) and the dispersion branch ($s$) as

$$\kappa_{\alpha\beta} = \sum_{qs} C_{qs} v_{qs}^\alpha v_{qs}^\beta \tau_{qs}$$

(1)

where $C$ is the volumetric heat capacity, $v$ is the phonon group velocity, and $\tau$ is the phonon relaxation time. In this work, to solve the phonon BTE, the first-principle phonon properties are calculated by utilizing the density-functional theory (DFT) performed in the Vienna Ab initio Simulation Package (VASP) [18] with the projector augmented-wave (PAW) method [19]. The electronic exchange and correlation energy are accounted by the generalized gradient approximation of Perdew, Burke, and Ernzerhof (GGA-PBE). [20] The energy cutoff for the plane-wave expansion is 420 eV. The geometry structures with a $7 \times 7 \times 7$ Monkhorst-Pack k-point mesh [21] are first relaxed until the total energies are less than $10^{-5}$ eV and the force components of each atom are below 0.01 eV/Å. And the more accurate crystal structures with a $8 \times 8 \times 8$ k-point mesh are obtained until the total energies are less than $10^{-8}$ eV and the force components of each atom are below $10^{-4}$ eV/Å. The $2 \times 2 \times 2$ supercells are used for the second- and third-order interatomic force constants (IFCs) calculations using the finite displacement method, as implemented in the PHONOPY software package [22] and the thirdorder.py code [23], which involves the displacements of one and two atoms, respectively. Based on the calculation of Born effective charges and the consideration of interatomic interactions up to the 5th coordination shell, a $7 \times 7 \times 7$ $\Gamma$-centered grids are used to solve the phonon BTE. The lattice thermal conductivities at different temperatures are calculated using the almaBTE code [24].

B. Phonon dispersions and densities of states

For these three pyrite-type IIB-VIA$_2$ dichalcogenides: ZnS$_2$, CdS$_2$ and CdSe$_2$, the calculated pyrite parameters ($u$) are 0.400, 0.406 and 0.397, which equal to the previous research results [25], and the calculated lattice constants ($a$) are 5.9965, 6.3990 and 6.7403 Å (at 0 GPa), which are in good agreement with the experimental measurement (5.9542, 6.3032 and 6.615 Å) [17]. To research their structural stabilities at zero pressure, we calculate their phonon dispersions along different high symmetry lines (refer to the Brillouin zone in Fig. 1b) and their partial phonon densities of states (PDOS), as shown in Fig. 2. In Fig. 2a, three acoustic
phonon modes [two transverse (TA, TA’) and one longitudinal (LA)] are highlighted. From Fig. 2, we can find that all phonon frequencies of these three compounds are real, which indicates that ZnS$_2$, CdS$_2$ and CdSe$_2$ are both mechanically stable at zero pressure. This suggests that even these compounds are synthesized at high pressure, they could be metastable at zero pressure. It is reasonable to theoretically research their physical thermoelectric behavior at 0 GPa.

Figure 2. Calculated phonon dispersions [The red, green and blue lines highlight two transverse (TA, TA’) and one longitudinal (LA) acoustic phonon modes, respectively. The black lines represent optical (O) phonon modes] (a), partial phonon densities of states (PDOS) (b), projected 2D electron localization function (ELF)
Comparing the shapes and the values of the phonon dispersions of three pyrite-type IIB-VIA$_2$ dichalcogenides (MX$_2$: ZnS$_2$, CdS$_2$ and CdSe$_2$) (Fig. 2a), we find that they have similar acoustic phonon dispersion curves along different high symmetry lines and the frequencies satisfied: $\omega$(ZnS$_2$) > $\omega$(CdS$_2$) > $\omega$(CdSe$_2$), such as, their maximum acoustic phonon frequencies are 74, 54 and 42 cm$^{-1}$, respectively, which can result in their corresponding sound velocities satisfied: $v$(ZnS$_2$) > $v$(CdS$_2$) > $v$(CdSe$_2$). Through analyzing their phonon dispersions and PDOS (Fig. 2b), we can find that their phonon modes both can obviously divide into two parts (there are big bandgaps in optical phonon modes), the high frequencies only contributed by the vibrations of X atom and the low frequencies contributed by the vibrations of M and X atoms together, which are very similar with the phonon properties of ZnSe$_2$. [16] Through calculating their electron localization function (ELF) [41] (Fig. 2c), we find that they both have a strong nonmetallic (X-X) covalent dimer. This indicates that similar with ZnSe$_2$, their high frequencies are contributed by the stretches of the nonmetal (X) atom along the X-X dimer. Additionally, for the part of low frequencies in PDOS (Fig. 2b), they both can be further separated into two regions, with the comparatively low frequencies mainly contributed by M atoms, and the comparatively high frequencies mainly contributed by X atoms. To study the reason for the lower frequencies of M atoms, we calculate the atomic displacement parameters (ADPs) of different atoms along different directions, as shown in Fig. 2d. The large ADPs means the large-amplitude atomic vibrations at different temperatures. From Fig. 2d, we can find that M atoms have larger ADPs than X atoms. This means that the metal (M) atoms are loosely bound in these three compounds, which can result in the phonon frequencies of the metal (M) atoms are lower than X atoms (Fig. 2b). Furthermore, we find that the phonon frequencies ($\omega$) and sound velocities ($v$) of these three compound have an opposite tendency with their ADPs, and they satisfied: $\omega$(ZnS$_2$) > $\omega$(CdS$_2$) > $\omega$(CdSe$_2$), $v$(ZnS$_2$) > $v$(CdS$_2$) > $v$(CdSe$_2$), and ADPs(ZnS$_2$) < ADPs(CdS$_2$) < ADPs(CdSe$_2$). This means that the larger ADPs can lead to softer phonons. Additionally, due to the relationship between sound velocities and atom mass ($m$) satisfied $v \sim \sqrt{k/m}$ [26], another mainly reason for the higher phonon frequencies and larger sound velocities of ZnS$_2$ maybe is the smaller atomic mass of Zn than Cd and S than Se.
C. Lattice thermal conductivities

Fig. 3a-c show the BTE calculated lattice thermal conductivities ($\kappa_\ell$) of ZnS$_2$, CdS$_2$ and CdSe$_2$ at different temperatures. The calculated $\kappa_\ell$ at 300 K is 1.55, 1.47 and 0.75 W/(m·K) for ZnS$_2$, CdS$_2$ and CdSe$_2$, respectively, which are lower than that of PbTe [2.4 W/(m·K)] [27]. This means these pyrite-type IIB-VIA$_2$ dichalcogenides both have low thermal conductivity, and they both have the potential to be good thermoelectric materials. To verify whether all pyrite-type dichalcogenides have low thermal conductivity, we calculate $\kappa_\ell$ of FeS$_2$ (the common pyrite-type dichalcogenides) at different temperatures using the same method, the results are shown in Fig. 3d. The calculated $\kappa_\ell$ of FeS$_2$ is 0.382, which can in good agreement with the experiment value 0.385 [28]. The calculated $\kappa_\ell$ of FeS$_2$ at 300 K is 65.8 W/(m·K), which is reasonable compared with previous experiment result [47.8 ± 2.4 W/(m·K)]. [29] This means that not all pyrite-type dichalcogenides have low thermal conductivity.

![Figure 3. Calculated lattice thermal conductivity ($\kappa_\ell$) at different temperatures of ZnS$_2$, CdS$_2$, CdSe$_2$ and FeS$_2$ (from a to d), respectively.](image)

D. Source of low lattice thermal conductivities

To research the source of low $\kappa_\ell$ of these pyrite-type IIB-VIA$_2$ dichalcogenides, we compare the phonon properties between FeS$_2$ with the three IIB-VIA$_2$ dichalcogenides (ZnS$_2$, CdS$_2$ and CdSe$_2$). The calculated phonon dispersions and partial phonon densities of states (PDOS) of FeS$_2$ are shown in Fig. 4a and 4b, respectively. Through comparing the calculated phonon dispersions and PDOS of FeS$_2$ (Fig. 4a and 4b) with these three IIB-VIA$_2$ dichalcogenides (Fig. 2a and 2b), we can find that 1. The maximum phonon frequency in the three pyrite-type sulfides (ZnS$_2$, CdS$_2$ and FeS$_2$) is both about 500 cm$^{-1}$, while the maximum phonon frequency in pyrite-type selenides (CdSe$_2$ and ZnSe$_2$ [16]) is both about 250 cm$^{-1}$. This means that the maximum phonon frequency in the pyrite-type dichalcogenides is mainly decided by their nonmetal (X) atom. 2. Unlike the separated optical phonon dispersions in IIB-VIA$_2$ dichalcogenides, there is no bandgap in optical phonon modes in FeS$_2$. This results in the maximum acoustic phonon frequency in FeS$_2$ is very high. 3. Additionally, the high-frequency
phonons in FeS$_2$ are contributed not only by nonmetal (S) atoms, but also by metal (Fe) atoms (Fig. 4c).

To explain the reason, we calculate the ELF and ADPs of FeS$_2$, as shown in Fig. 4c and 4d, respectively. From Fig. 4c, we can find that similar to the pyrite-type IIB-VIA$_2$ dichalcogenides, FeS$_2$ also has a nonmetal (S-S) dimer. By comparing their bond length of the nonmetal dimer, we find that the binding of the dimer in FeS$_2$ is weaker than these IIB-VIA$_2$ dichalcogenides, due to the bond length of S-S in FeS$_2$ (2.182 Å) is longer than IIB-VIA$_2$ dichalcogenides (2.079 and 2.086 Å in ZnS$_2$ and CdS$_2$, respectively). Additionally, from Fig. 4d, we find that the ADPs of Fe and S atoms in FeS$_2$ are both very small compared with those of M and X atoms in MX$_2$ (IIB-VIA$_2$ dichalcogenides) (Fig. 2c). This means that Fe and S atoms in FeS$_2$ cannot move easily, which indicates that FeS$_2$ doesn’t have soft phonon modes and the Fe-S and S-S bonds are both strong. The strong bonds can result in the high phonon frequency and the large sound velocity in FeS$_2$, which is consistent with the very high maximum acoustic phonon frequency of FeS$_2$ (243 cm$^{-1}$) in Fig. 4b. Therefore, comparing with FeS$_2$, the soft phonon modes (low phonon frequency and small sound velocity) in three IIB-VIA$_2$ dichalcogenides is one of the important reasons for their low conductivity.

Figure 4. Calculated phonon dispersions (a), partial phonon densities of states (PDOS) (b), projected 2D electron localization function (ELF) in (001) plane (c) and atomic displacement parameters (ADPs) (d) of FeS$_2$. 
Through calculating the contribution of different phonons to $\kappa_i$ in these four pyrite-type dichalcogenides (ZnS$_2$, CdS$_2$, CdSe$_2$ and FeS$_2$) (Fig. 5a), we find that their $\kappa_i$ are mainly contribute by the low-frequency phonons, and the contributions of their acoustic phonons to $\kappa_i$ are 59%, 59%, 55% and 69%, respectively. Except the phonon frequency and sound velocity, many previous studies have shown that the anharmonicity (the Grüneisen parameter $\gamma$, $\gamma = -\frac{V}{\omega} \frac{\partial \omega}{\partial \nu}$) is another main parameter to predict $\kappa_i$, and a large $\gamma$ can result in a low $\kappa_i$. [30,31] This means that the values of $\gamma$ in acoustic phonons have important effect in $\kappa_i$. To further understand the low $\kappa_i$ in IIB-VIA$_2$ dichalcogenides, we compare the calculated $\gamma$ at different phonon modes in these four dichalcogenides, as shown in Fig. 5b. From Fig. 5b, we can obtain the maximum Grüneisen parameter ($\gamma_m$) in acoustic phonons are 4.60, 3.18, 2.72 and 1.78 for ZnS$_2$, CdS$_2$, CdSe$_2$ and FeS$_2$, respectively, the calculated $\gamma_m$ satisfied: $\gamma_m$(ZnS$_2$) > $\gamma_m$(CdS$_2$) > $\gamma_m$(CdSe$_2$). This means that three IIB-VIA$_2$ dichalcogenides have stronger anharmonicities (larger $\gamma$) than FeS$_2$, which is another important reason for their low conductivity.

**E. Source of strong anharmonicities**

Comparing the values of $\gamma$ in different phonon modes (Fig. 5b), we can find that the calculated $\gamma$ of two transverse acoustic phonon modes (TA and TA’) in GM line are obviously different (the calculated $\gamma$ of TA mode are higher than that of TA’ mode) in three IIB-VIA$_2$ dichalcogenides, but they are very similar in FeS$_2$. And the calculated $\gamma_m$ in three IIB-VIA$_2$ dichalcogenides are both TA mode located in GM line, but not in FeS$_2$. These indicate that the anharmonicities of pyrite-type dichalcogenides are mainly decided by their TA mode in GM line. Through analyzing the phonon dispersions in these four pyrite-type dichalcogenides (Fig. 2a and 4b), we find that TA and TA’ mode are highly degenerate at different high symmetry lines except GM line. Through comparing the phonon vibrational properties of two transverse acoustic modes in GM line (GM line is shown in Fig. 1b), we find that all atoms in TA mode vibrate primarily in ab-plane but all atoms in TA’ mode vibrate primarily along c-axis (Fig. 1a). Due to the different bonding situations in ab-plane and c-axis in different pyrite-type dichalcogenides, the phonon frequencies of TA and TA’ modes in GM line are not degenerate. And because of the different kinds of atoms in these four pyrite-type dichalcogenides, their phonon frequency differences between the TA and TA’ modes in GM line are obviously different, such as, for ZnS$_2$, the phonon frequencies of TA mode are lower than those of TA’ mode; but for FeS$_2$, the phonon frequencies of TA mode are higher than those of TA’ mode.
As a result, the calculated average phonon frequency differences between the TA and TA’ mode ($\Delta \omega_{TA} = \bar{\omega}_{TA} - \bar{\omega}_{TA'}$) in GM line are -0.134, 0.028, 0.055 and 0.716 cm$^{-1}$ for ZnS$_2$, CdS$_2$, CdSe$_2$ and FeS$_2$, respectively. Comparing the values of $\Delta \omega_{TA}$ and $\gamma_m$ in these four dichalcogenides, we can find that $\gamma_m$ is decreased with the increase of $\Delta \omega_{TA}$. Therefore, we can infer that the large $\gamma$ and strong anharmonicities of three IIB-VIA$_2$ dichalcogenides may come from their the small $\Delta \omega_{TA}$.

Figure 5. The contributions of different phonons to the lattice thermal conductivity (the vertical and horizontal dot lines represent the maximum acoustic phonon frequencies and corresponding lattice thermal conductivities) (a) and the calculated anharmonicity parameters $\gamma$ at different phonon modes (the color denotes the values of $\gamma$) (b) for ZnS$_2$, CdS$_2$, CdSe$_2$ and FeS$_2$ (from left to right), respectively.

From analyzed above, we can know that three IIB-VIA$_2$ dichalcogenides (ZnS$_2$, CdS$_2$ and CdSe$_2$) both have soft phonon modes and strong anharmonicities, which contribute to their low lattice thermal conductivity. And due to their sound velocities satisfied: $\nu($ZnS$_2$) > $\nu($CdS$_2$) > $\nu($CdSe$_2$) but their anharmonicities satisfied: $\gamma_m($ZnS$_2$) > $\gamma_m($CdS$_2$) > $\gamma_m($CdSe$_2$), according the relationships between $\kappa_l$ and $\nu$ and $\gamma$ ($\kappa_l \propto \frac{\nu^3}{\gamma^2}$), [40] the calculated $\kappa_l$ satisfied: $\kappa_l($ZnS$_2$)~$\kappa_l($CdS$_2$) > $\kappa_l($CdSe$_2$).

ELECTRONIC TRANSPORT PROPERTIES

A. Computational methodologies

The electrical transport properties (σ/τ, S and κe) as functions of temperature (T) and chemical potential (μ) are calculated using the BoltzTraP2 code, [32] which is based on the solution of the electron Boltzmann transport equation under constant relaxation time approximation (CRTA), as

\[
\frac{\sigma_{\alpha\beta}}{\tau} = e^2 \frac{1}{\tau} \int - \frac{\partial f_0}{\partial E} g(E) \nu_\alpha(E) \nu_\beta(E) dE
\]

(2)

\[
S_{\alpha\beta} = -\frac{1}{eT} \int \frac{\partial f_0}{\partial E} g(E) \nu_\alpha(E) \nu_\beta(E) (E-\mu) dE
\]

(3)

\[
\kappa_{e\alpha\beta} = -\frac{1}{T} \left\{ \int - \frac{\partial f_0}{\partial E} g(E) \nu_\alpha(E) \nu_\beta(E) (E-\mu)^2 dE - \frac{\left[ \int - \frac{\partial f_0}{\partial E} g(E) \nu_\alpha(E) \nu_\beta(E) (E-\mu) dE \right]^2}{\int - \frac{\partial f_0}{\partial E} g(E) \nu_\alpha(E) \nu_\beta(E) dE} \right\}
\]

(4)

where α and β (α, β = x, y, z) are the tensor indices, τ is the carrier relaxation time, \( f_0 \) is the Fermi–Dirac distribution function, \( g(E) \) is the density of states, and \( \nu(E) \) is the carrier group velocity.

In a semiconductor, the acoustic phonon scattering is the dominant carrier scattering mechanism.[33] In this work, the carrier relaxation times (τ) are calculated using the single parabolic band (SPB) model through considering the acoustic phonon scattering mechanisms, as [33]

\[
\tau = \frac{2\pi \hbar^4 \rho \nu_l^2}{3E_d^2(m^* k_B T)^3 F_1^1(\eta)}
\]

\[
F_x(\eta) = \int_0^\infty \frac{E x}{1+\exp (E-\eta)} dE, \quad \eta = \frac{\mu}{k_B T}
\]

(5)

where \( \hbar \) is the reduced Planck constant, \( k_B \) is the Boltzmann constant, \( \rho \) is the mass density, \( \nu_l \) is the longitudinal acoustic phonon sound velocity, \( \eta \) is the reduced chemical potential, \( m^*_d \) is the density of states (DOS) effective mass, \( E_d \) is the deformation potential. Through first-principle calculation, \( \nu_l \) can be calculated from the phonon properties as \( \nu_l = \frac{\partial \omega}{\partial k} \), \( m^*_d \) at different carrier concentrations can be obtained by solving the electron Boltzmann transport equation as \( m^*_d = \frac{\hbar^2}{2k_B T} \left[ \frac{2 \pi^2 n}{F_{1/2}(\eta)} \right]^2 \) [34], and \( E_d \) can be evaluated through calculating the energy change of the band extrema with the volume dilation as \( E_d = \Delta E / (V/V_0) \) (\( V_0 \) is the equilibrium lattice volume). For these three IIB-VIA2 dichalcogenides, the calculated \( \nu_l \) and \( E_d \) are listed.
in Table 1, the calculated $m^*_d$ at different carrier concentrations and temperatures are shown in Fig. 6.

Table 1. Calculated longitudinal acoustic phonon velocity ($\nu_L$) and deformation potential ($E_d$) of ZnS$_2$, CdS$_2$ and CdSe$_2$, respectively.

|       | $\nu_L$ (m/s) | $E_d$ (eV) |
|-------|---------------|------------|
|       | $E_d$ (eV)    | p-type     | n-type     |
| ZnS$_2$ | 5300         | -11.2      | -11.9      |
| CdS$_2$ | 4297         | -9.9       | -11.8      |
| CdSe$_2$ | 3441         | -9.0       | -10        |

Figure 6. Calculated DOS effective mass ($m^*_d$) of ZnS$_2$, CdS$_2$ and CdSe$_2$ (from left to right) with respect to the carrier concentration for p-type and n-type at 300, 600 and 900 K, respectively.

**B. Electronic band structures**

Fig. 7 shows the PBE calculated electronic band structures of ZnS$_2$, CdS$_2$ and CdSe$_2$ from left to right, respectively. From Fig. 7, we can find that the band structure shapes of these three compounds are very similar. And their band gaps are 1.406, 1.146 and 0.588 eV, respectively. Their valence band maximums (VBM) are both located at $\Gamma$ point with two-fold band degeneracy (as shown in Fig. 7 as B1, B2). Comparing the band structure shapes of B1 and B2, we can find that they have very different shapes along $\Gamma$–X direction. These different band structure shapes will provide different carrier effective masses, such as, the calculated carrier effective masses ($m^*_{\alpha\beta} = \hbar^2 [\frac{\partial^2 E}{\partial k_\alpha \partial k_\beta}]^{-1}$) along $\Gamma$-X direction are 7.38$m_0$, 4.51$m_0$ and 5.47$m_0$ for B1, and 0.24$m_0$, 0.27$m_0$ and 0.22$m_0$ for B2 for ZnS$_2$, CdS$_2$ and CdSe$_2$, respectively (Table 2, $m_0$ is the electron rest mass), which means that these dichalcogenides have both light and heavy p-type carriers. For the conduction bands, their conduction band minimums (CBM) are both located within the R-$\Gamma$ line (the P point in Fig. 7), which has a big symmetry degeneracy.
And through comparing the calculated $m_{\alpha\beta}^*$ of CBM along different directions (Table 2), we find that all $m_{\alpha\beta}^*$ of CBM are both smaller than $m_0$, which means that these dichalcogenides have light n-type carriers.

Table 2. The carrier effective mass ($m_{\alpha\beta}^*$) of different energy valleys along different directions ($\vec{D}$) for ZnS$_2$, CdS$_2$ and CdSe$_2$, respectively.

| $\vec{D}$ | $m_{\alpha\beta}^*$ ($m_0$) |
|-----------|-----------------------------|
|           | VBM | CBM | VBM | CBM | VBM | CBM |
| $\vec{G}\vec{X}$ | 7.38 | 0.24 | 4.51 | 0.27 | 5.47 | 0.22 |
| $\vec{G}\vec{M}$ | 0.86 | 0.31 | 0.91 | 0.36 | 0.79 | 0.29 |
| $\vec{G}\vec{R}$ | 0.46 | 0.46 | 0.51 | 0.51 | 0.43 | 0.43 |
| $\vec{P}_x$ | 0.50 | 0.53 | 0.41 |
| $\vec{P}_{xy}$ | 0.51 | 0.54 | 0.43 |
| $\vec{P}_{\vec{R}}$ | 0.51 | 0.55 | 0.45 |

C. Electrical transport properties

Due to the PBE is well-known for underestimating the band gaps of semiconductors and insulators, we further calculate the band gaps of these three dichalcogenides using the Heyd–Scuseria–Ernzerhof (HSE06) [35,36] method. The HSE06 calculated band gaps are 2.526, 2.177 and 1.472 eV, respectively, which are in good agreement with the band gaps calculated from previous GW study. [37] Therefore, to improve the accuracy of the study, we calculate
the electrical transport properties by manually changing the band gaps to HSE06 calculated values, while keeping PBE calculated band structure shapes. Fig. 8 shows the calculated electrical transport properties [the carrier relaxation times $\tau$ (a), electrical conductivities $\sigma$ (b), Seebeck coefficients $S$ (c) and thermopower factors $PF = S^2\sigma$ (d)] at different carrier concentrations for p-type and n-type doping at 300, 600 and 900 K, respectively.

From Fig. 8a, for these three IIB-VIA$_2$ dichalcogenides, we can find that their calculated $\tau$ at 300 K are both in the range of $10^{-15}$ to $10^{-14}$ s, which indicates that our calculations are reasonable. [38] Due to the enhancement of the carrier scattering at high carrier concentration and high temperature, their calculated $\tau$ both show very similar reduction trend with the increase of carrier concentration and temperature. According to the Eq. 5, we can know that due to their calculated absolute values of $E_d$ (Table 1) and $m_d^*$ (Fig. 6) of p-type carriers are both smaller than n-type carriers, their calculated $\tau$ of p-type carriers is larger than n-type carriers at same carrier concentration and temperature (Fig. 8a).

From Fig. 8b, we can find that their calculated $\sigma$ are both increased with the increase of carrier concentration ($n$), which is caused by the relationship between $\sigma$ and $n$, as[38]

$$\sigma = ne\mu = \frac{ne^2}{m_c^*} \tau$$

where $m_c^*$, $m_c^*$ = $\left[\frac{1}{3} \sum_{\alpha\beta} \frac{1}{m_{\alpha\beta}}\right]^{-1}$, is the conductivity effective mass. As above analyzed about the electronic band structures of these three IIB-VIA$_2$ dichalcogenides, we can know that they both have light and heavy p-type carriers, and light n-type carriers. From Eq. 6, their light p-type and n-type carriers can contribute to their good $\sigma$ for p-type and n-type doping, respectively. Considering the influence of carrier relaxation time, due to their calculated $\tau$ of p-type carriers are larger than n-type carriers (Fig. 8a), their calculated $\sigma$ of p-type carriers are larger than n-type carriers (Fig. 8b).
Figure 8. Calculated carrier relaxation times $\tau$ (a), electrical conductivities $\sigma$ (b), Seebeck coefficients $S$ (c), and thermopower factors $PF = S^2\sigma$ (d) of ZnS$_2$, CdS$_2$ and CdSe$_2$ (from left to right) with respect to the carrier concentration for p-type and n-type at 300, 600 and 900 K, respectively.

From Fig. 8c, we can find that their calculated $S$ are both decreased with the increase of the carrier concentration and increased with the increase of temperature. At 300 K and $10^{19}$ cm$^{-3}$, the calculated absolute values of $S$ ($|S|$) are 359, 353 and 342 $\mu$V/K for p-type carriers and 390, 405 and 377 $\mu$V/K for n-type carriers for ZnS$_2$, CdS$_2$ and CdSe$_2$, respectively, which are larger than that of the well-studied PbTe ($\sim$100 $\mu$V/K for n-type doping) [39]. This means that these three IIB-VIA$_2$ dichalcogenides both have large $S$ and can provide high thermoelectric voltages. According to the Mott formula for the heavily doped semiconductors, the $S$ can be simply evaluated by [38]
From Eq. 7, we can know that $S$ is mainly controlled by the value of $m^*_d$. The relationship between $m^*_p$ and $m^*_d$ is $m^*_d = N_V K^* m^*_p$, where $N_V$ is the energy valley degeneracy and $K^*$ is the anisotropy parameter of a non-spherical isoenergy Fermi surface.[34] In these three IIB-VIA$_2$ dichalcogenides, due to the valence band B1 at VBM have very flat shape along $\Gamma$-X direction but very steep shapes along $\Gamma$–M and $\Gamma$-R directions (Fig. 7), the isoenergy Fermi surface of B1 will be very complex, and these three IIB-VIA$_2$ dichalcogenides will both have large $K^*$ for p-type doping. Besides, due to the symmetry degeneracy of P point at CBM (Fig. 7) is 8, these three IIB-VIA$_2$ dichalcogenides have a large $N_V$ for n-type doping. The large $K^*$ and $N_V$ can contribute to large $m^*_d$, and results in their large $S$.

Combining their good $\sigma$ and large $S$, their calculated $PF$ are first increased and then decreased with the increase of carrier concentration (Fig. 8d), and the maximum of $PF$ ($PF_{max}$) can reach 1.77, 1.55 and 1.86 mW/(mK$^2$) for p-type doping, and 1.48, 0.75 and 0.97 mW/(mK$^2$) for n-type doping for ZnS$_2$, CdS$_2$ and CdSe$_2$, respectively. For these three compounds, due to the larger $\sigma$ of p-type carriers, the calculated $PF_{max}$ of p-type carriers are larger than n-type carriers.

**FIGURE OF MERIT**

Combining the calculated thermal conductivity ($\kappa_\parallel$ and $\kappa_\perp$) and electrical properties ($PF$), the figure of merit $ZT$ values of these three IIB-VIA$_2$ dichalcogenides (ZnS$_2$, CdS$_2$ and CdSe$_2$) are evaluated at different carrier concentrations at 300, 600 and 900 K, respectively, as shown in Fig. 9. From Fig. 9, we can know that they both have high $ZT$ values, and their corresponding maximum $ZT$ values at 900 K are 1.45, 1.37 and 2.29 at $1.34\times10^{20}$, $1.43\times10^{20}$ and $8.23\times10^{19}$ cm$^{-3}$ for p-type doping, and 1.01, 0.57 and 1.16 at $2.89\times10^{20}$, $3.55\times10^{20}$ and $1.91\times10^{20}$ cm$^{-3}$ for n-type doping, respectively. For these three IIB-VIA$_2$ dichalcogenides, due to their p-type carriers have higher $PF$, they have higher $ZT$ values for p-type doping than n-type. Regardless, their maximum $ZT$ values for n-type doping are still higher than 0.5. This indicates that these three IIB-VIA$_2$ dichalcogenides are promising thermoelectric materials for both p-type and n-type doping, and they are worth for the future experimental investigations.
CONCLUSION

In this work, through solving the phonon and electron Boltzmann transport equations, we have systematically studied the thermal and electrical transport properties of three IIB-VIA$_2$ dichalcogenides (ZnS$_2$, CdS$_2$ and CdSe$_2$). The calculation of thermal transport properties shows that three IIB-VIA$_2$ dichalcogenides have very low lattice thermal conductivities compared with FeS$_2$. The detailed calculations of phonon properties and atomic displacement parameters explain that three IIB-VIA$_2$ dichalcogenides have soft phonon modes that are not possessed by FeS$_2$. The calculation and analyze of the Grüneisen parameters indicate that three IIB-VIA$_2$ dichalcogenides have stronger anharmonicities than FeS$_2$, and the anharmonicities of pyrite-type compounds are decided by the phonon frequency difference between their two transverse acoustic phonon modes. The soft phonon modes and strong anharmonicities result in low lattice thermal conductivities of three IIB-VIA$_2$ dichalcogenides. The calculation of electrical transport properties shows that three IIB-VIA$_2$ dichalcogenides have similar electronic band structures, and due to their VBM are contributed by different valence bands, they both have light and heavy p-type carriers, and due to their CBM are located in a high symmetric line, they both have light n-type carriers with high degeneracy. The heavy carriers and high degeneracy contribute to their high Seebeck coefficient for p-type and n-type doping, respectively. The light carriers contribute to their good electrical conductivity. Their high Seebeck coefficients and good electrical conductivities can guarantee their promising electrical transport properties. Besides, due to the calculated carrier relaxation times of p-type carriers are larger than n-type carriers, their electrical transport properties for p-type doping are better than n-type doping. Combining their low thermal conductivities and promising electrical transport properties, their maximum ZT values can reach 1.45, 1.37 and 2.29 for p-type doping, and 1.01, 0.57 and 1.16 cm$^3$K$^{-1}$ for n-type doping, respectively. Our work shows that three IIB-VIA$_2$ dichalcogenides (ZnS$_2$, CdS$_2$ and CdSe$_2$) exhibit excellent thermoelectric properties for both p-type and n-type
doping. Combining previous research about ZnSe$_2$, we can refer that all IIB-VIA$_2$ dichalcogenides have promising thermoelectric properties, and their thermoelectric properties maybe can be regulated by pressures. What’s more, we further infer that co-melting, doping or defect method can be used to adjust their thermoelectric properties future.

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