Quaternary compounds $\text{Ag}_2\text{XYSe}_4$ ($\text{X} = \text{Ba, Sr}; \text{Y} = \text{Sn, Ge}$) as novel potential thermoelectric materials

A J Hong$^{1,3}$, C L Yuan$^{1,3}$ and J-M Liu$^2$

1. Introduction

During the last few decades, with the increasing problems of energy exhaustion and environment pollution, thermoelectric (TE) materials have already aroused people’s widespread concern [1, 2], due to their special properties of directly converting heat to electricity and vice versa. One can use a dimensionless figure of merit, namely $ZT = S^2\sigma T / \kappa$, to assess the TE materials’ conversion efficiency from heat to electricity [3, 4]. Herein, $S$ and $\sigma$ represent the Seebeck coefficient and electrical conductivity, $T$ and $\kappa$ are the temperature (in unit of Kelvin) and total thermal conductivity composed of electronic $\kappa_e$ and lattice $\kappa_L$ contributions. Thus, a good TE material requires high $S$ and $\sigma$ and low $\kappa$. However, this is hard to achieve due to the complex interdependences between $S$, $\sigma$ and $\kappa$ [5]. Recently, it was reported that achieving large band degeneracy [6] or localized resonant states [7] via energy band engineering do improve the TE transport properties in few existing TE materials [8]. Nevertheless, this strategy has great blindness because one is difficult to decide which dopant can induce beneficial change to electronic structure. Another common strategy is to reduce lattice thermal conductivity by low-dimension [9] or solid solution strategies [10, 11] that usually require very rigorous preparation conditions. Thus, seeking new TE materials with medium TE performance and then improving $ZT$ value by tuning the carrier density remains a simple and feasible method [12, 13].

How to screen good TE materials through electronic structures has always been of concern to researchers. For example, Liu et al [14] propose the generalized material parameter $B^* \propto U^*E_g/\kappa_L$ as a screening criterion where the weighted mobility $U^*$, the total thermal conductivity $\kappa_L$, and the band gap $E_g$.

Good TE material should have $B^*$ as high as possible. Thus, theoretically, wide bandgap materials should possess better TE
performance than narrow bandgap materials. Unfortunately, the carrier density of wide bandgap materials is regulated nearly impossible to the optimal density. Due to adjustability in carrier density, materials with bandgap of less than 1.0 eV usually are as candidates for TE application. For example, star TE materials Bi2Te3, SnSe, PbS, PbSe, PbTe, CoSb3, NbFeSb, Mg2Si, Mg2Ge and Mg2Sn have band gaps of ~0.15 eV [20], ~0.86 eV [5], ~0.4 eV [21], ~0.29 eV [21], ~0.32 eV [21], ~0.77 eV [24], ~0.74 eV [25] and ~0.35 eV [26], respectively.

Recently, quaternary compounds Cu2ZnSn(S/Se)4 (CZTSSe) are considered as a promising photovoltaic absorber material due to high efficiency of about 12.6% [15]. It was reported that the band gaps of pure Cu2ZnSnSe4 (CZTSe) and Cu2ZnSnS4 (CZTS) were about 1.0 [16–18] and 1.5 eV [19, 20] close to ideal values of 1.3–1.4 eV for solar cell materials. By judging from band gaps, instead of CZTS, compound CZTSe seems to be a promising TE material due to smaller band gap suitable for carrier density regulation. Indeed, previous works have indicated that the ZT of In-doped CZTSe reached up to 0.95 at 850 K [22] and that of modified CZTS was only 0.36 at 700 K [22]. Therefore, we tried to replace Cu, Zn and Sn atoms of compound Cu2ZnSnSe4 with Ag, Ba/Sr and Sn/Ge atoms, constructing four new compounds Ag2XYSe4 (X = Ba, Sr; Y = Sn, Ge). The structures of Ag2BaGeSe4 and Ag2BaSnSe4 have been experimentally verified to be space group I222 (No. 23) [23] and the other two were theoretically predicted to be space group I222 [24], also. Obviously, Ag2XYSe4 structures possess lower symmetry than kesterite and stannite Cu2ZnSnSe4 belonging to space groups I4 (No. 82) and I42m (No. 121) [25], respectively. Low symmetry can favor the strengthening anharmonic vibration of phonon, and thus the low symmetry materials such as SnSe, ZnSb and MgAgSb usually possess low lattice thermal conductivity [26]. Furthermore, it is expected Ag2XYSe4 have high electrical conductivity due to containing two Ag atoms in each primitive cell.

To the best of our knowledge, there have been few theoretical reports on the TE properties of Ag2XYSe4 (X = Ba, Sr; Y = Sn, Ge). Hence, in this work, we used density functional theory (DFT) with semi-classical Boltzmann equation to explore the TE property of p- and n-type Ag2XYSe4 (X = Ba, Sr; Y = Sn, Ge). It was showed that band gaps of Ag2BaGeSe4, Ag2BaSnSe4, Ag2SrGeSe4 and Ag2SrSnSe4 are 0.909 eV, 0.832 eV, 0.708 eV and 0.729 eV, respectively. In addition, their lattice thermal conductivities are 2.2 W m⁻¹ K⁻¹, 1.95 W m⁻¹ K⁻¹, 2.26 W m⁻¹ K⁻¹ and 2.00 W m⁻¹ K⁻¹ at 300 K that are obviously lower than 3.2 W m⁻¹ K⁻¹ of Cu2ZnSnSe4 [21]. Lattice thermal conductivity at high temperature for each compound is below 1.0 W m⁻¹ K⁻¹. It is predicted that the n-type Ag2SrGeSe4, having ZT maximum of 1.22 (at 900 K), is the most excellent in the compounds Ag2XYSe4 (X = Ba, Sr; Y = Sn, Ge), and its p-type counterpart has a ZT maximum of 1.13. The ZT maximums of both p-type Ag2BaSnSe4 and Ag2SrSnSe4 are above unity. This paper reveals Ag2XYSe4 are a new family of promising candidates for TE materials and may pave a way for seeking TE materials with high the ZT values.

We organize the rest of this paper as follows: the detailed computational method and some important parameters for first-principles calculations are presented in section 2. The electronic structures, mechanical, thermal and TE properties are described and discussed in section 3. Finally, findings and conclusions are summarized in section 4.

2. Theoretical calculation details

Firstly, structure optimization was performed using the generalized gradient approximation of Perdew, Burke, and Ernzerhof (GGA-PBE) [27] as the electronic exchange-correlation functional in VASP code. The plane-wave energy cutoff and Monkhorst–Pack k-point mesh were set to 500 eV and 10 × 10 × 10, and the total-energy and force convergences were 10⁻⁶ eV and 10⁻³ eV Å⁻¹.

Secondly, we used the full potential method with GGA-PBE modified Becke and Johnson potential scheme (mBJ) [28] to perform atomic coordinate optimization and then calculate electronic structures for all the compounds in Wien2k code [29]. In the whole calculation procedure, the total-energy and charge convergences were taken as 0.0001 eV and 0.0001 e. 3000 k-points in the whole first Brillouin zone were sampled for calculations of such as band structure and density of states. Taking a very dense mesh of 20000 k-points, the electrical transport parameters such as the Seebeck coefficient, electrical conductivity and electronic thermal conductivity, were calculated using the semi-classical Boltzmann theory. In this theoretical framework, the electronic transport parameters can be described as follows [30]:

\[
\sigma_{\alpha\beta}(T,E_F) = \frac{1}{\Omega} \int \sigma_{\alpha\beta}(\varepsilon) \left[ -\frac{\partial f}{\partial \varepsilon} \right] d\varepsilon, \quad (1)
\]

\[
S_{\alpha\beta}(T,E_F) = (\sigma^{-1})_{\alpha\beta} \eta_{\alpha\beta}, \quad (2)
\]

\[
\kappa_{\alpha\beta}(T,E_F) = \kappa_0^{\alpha\beta} - T \eta_{\alpha\beta} (\sigma^{-1})_{\alpha\beta} \eta_{\alpha\beta}, \quad (3)
\]

where \( T, E_F, \Omega, \) \( f \) and \( \varepsilon \) are the absolute temperature, Fermi energy, unit cell volume, Fermi–Dirac distribution function and energy for electronic state. As noted, \( \kappa_{\alpha\beta} \) is the electronic thermal conductivity without the external electric field. The energy projected conductivity tensors, \( \sigma_{\alpha\beta} \), can be expressed as the following form:

\[
\sigma_{\alpha\beta}(\varepsilon) = \frac{\hat{e}^2 e^\tau}{N} \sum_{ik} \nu_{\alpha} \nu_{\beta} \delta(\varepsilon - \varepsilon_{ik}) \frac{d\varepsilon}{d\varepsilon}. \quad (4)
\]

Herein, \( \varepsilon \) is the charge of an electron, \( \tau \) is the carrier relaxation time, \( N \) is the total number of sampled k-points, \( \varepsilon_{ik} \) is the energy for the kth point at the ith band. The other physical parameters are given as follows:

\[
\eta_{\alpha\beta}(T,E_F) = \frac{1}{e^2 T \Omega} \int \sigma_{\alpha\beta}(\varepsilon) (\varepsilon - E_F) \left[ -\frac{\partial f}{\partial \varepsilon} \right] d\varepsilon, \quad (5)
\]

\[
\kappa_0^{\alpha\beta}(T,E_F) = \frac{1}{e^2 T \Omega} \int \sigma_{\alpha\beta}(\varepsilon) (\varepsilon - E_F)^2 \left[ -\frac{\partial f}{\partial \varepsilon} \right] d\varepsilon. \quad (6)
\]
Subsequently, we used Slack’s equation (see equation (7)) to calculate the lattice thermal conductivity for all systems [31].

\[ \kappa_L = A \frac{\Theta_D^3 V_{per} \bar{m}}{\gamma_a^{2/3} n_{tot}^2 T} \]  

(7)

Herein, A is a collection of physical constants with the value of about \(3.04 \times 10^{-6}\), \(\Theta_D\) is the Debye temperature, \(V_{per}\) is the volume per atom, \(\bar{m}\) is the average atom mass in the whole unit cell, \(n_{tot}\) is the total number of all atoms in the primitive cell. \(\gamma_a\) is the Grüneisen parameter for only acoustic phonons. Previous works [32–34] show lattice thermal conductivity attained by Slack’s equation is in good agreement with experimental data. For the purpose of comparison, we also used compressive sensing lattice dynamics (CSLD) method [35] combined with Boltzmann transport equation (BTE) [36] to compute the lattice thermal conductivity. In addition, we used the Phonopy code [37] to calculate the phonon spectrum.

3. Results and discussion

3.1. Crystal structures and electronic structures

Crystal structures of compounds \(\text{Ag}_2\text{XYSe}_4\) have been verified experimentally or theoretically to belong to group I222 (No. 23). There are 16 and 8 atoms in the conventional and primitive cells, respectively (see figure 1). The lattice constants of conventional cells in this work and other literatures are summarized in table 1. It is seen that our results for Sr compounds are in good agreement with the other theoretical data. However, for Ba compounds, there is a little difference compared to the experimental data. Experimental and theoretical lattice constants are determined at room and zero temperatures respectively, thus the difference is perfectly acceptable. The cell volume of \(\text{Ag}_2\text{SrGeSe}_4\) is smaller than that of \(\text{Ag}_2\text{SrSnSe}_4\) due to the difference in the atomic radii of Ge and Sn, which is the same as Ba compounds. Similarly, due to the Ba radius being smaller than the Sr radius, the cell...
volumes of $\text{Ag}_2\text{BaGeSe}_4$ and $\text{Ag}_2\text{BaSnSe}_4$ are smaller than those of $\text{Ag}_2\text{SrGeSe}_4$ and $\text{Ag}_2\text{SrSnSe}_4$, respectively.

Calculated band structures and corresponding density of states (DOS) of the four compounds are showed in figure 2. Sn compounds have indirect band gaps of 0.765 eV ($\text{Ag}_2\text{BaSnSe}_4$) and 0.694 eV ($\text{Ag}_2\text{SrSnSe}_4$), of which valence band maximum (VBM) and conduction band minimum (CBM) are at the $Z$ and $\Gamma$ points, respectively. However, the Ge compounds have direct band gaps of 0.870 eV ($\text{Ag}_2\text{BaGeSe}_4$) and 0.667 eV ($\text{Ag}_2\text{SrGeSe}_4$), with both CBM and VBM appearing at $Z$.
It is worth mentioning the difference between indirect and direct band gaps for each compound is very small. We have also noticed that other work [24] points Ag$_2$BaGeSe$_4$ and Ag$_2$SrGeSe$_4$ possess indirect band gaps. Perhaps, the full potential method with mBJ scheme was adopted in this work, which is different from the pseudopotential method, leading to this difference. The PBE, mBJ and HSE06-hybrid (from [24]) band gaps for the four compounds are also listed in table 1. The mBJ band gaps, close to the HSE06-hybrid band gaps, are obviously larger than the PBE band gaps. The normal PBE method usually underestimates the band gap, but the mBJ method, comparable with GW, usually gets band gap in good agreement with the experimental data.

The DOS diagrams show Se–Ag hybridization is the major ingredient of valence band (VB) in all the compounds, which implies Se–Ag covalent bonds are in the four compounds. The conduction band (CB) displays significant density of Se and Ge/Sn atoms. The Ba/Sr atoms have negligible contributions to both VB and CB in each compound. It is implied that doping vacancy or heterogeneous atom at the site of Ba/Sr atoms can result in little effect on electronic transport properties. The valence bandwidth (VBW) is ~2 eV greater than the conduction bandwidth (CBW) of less than 1 eV in each compound. This possibly implies that n-type carrier has larger effective mass than p-type carrier does.

Calculated effective mass along the $a$, $b$ and $c$ axes as a function of energy is plotted in figure 3. It is expected that the electron effective mass is larger than the hole effective mass along the $a$ and $b$ axes in each compound, although it is in the opposite case along the $c$ axis. In addition, the hole effective mass decrease with the increasing energy, which is the opposite of the electron effective mass. For each compound, the hole effective mass along the $c$ axis is larger than along the $a$ and $b$ axes in each compound, and the electron effective mass along the $b$ axis is larger than along the other axes. For instance, the effective mass for p-type Ag$_2$SrSnSe$_4$ along the $c$ axis can reach up to 1.33 $m_e$, and the effective mass for n-type Ag$_2$BaSnSe$_4$ is as large as 9.82 $m_e$ (not shown in figure 3) at ~0.01 Ry above the CBM.

### 3.2. Structure stabilities

In order to verify structural stability, phonon spectrum with corresponding phonon DOS for the four compounds was calculated and plotted in figure 4. There are eight atoms in one primitive cell and one atom can yield three phonon branches.
Thus, there are twenty four phonon branches composed of sixteen longitudinal branches and eight transverse branches, including one longitudinal acoustic (LA), two transverse acoustic (TA) modes.

Phonon DOS in the range of low frequency mainly comes from the contribution of Ag atom. The phonon thermal transport property is primarily decided by phonon modes of low frequency. This implies Ag atom play important role and then Sn atom has negligible effect in lattice thermal transport. As is known, for a system with dynamical stability, the frequency of each phonon mode should be not imaginary. Our result shows no obvious imaginary frequencies in the full Brillouin zone, thus ensuring structure stability.

Elastic constants were obtained by second-order-derivative of polynomial fit of energy as a function of strain at zero strain, which called energy approach. For the orthorhombic Ag$_2$XYSe$_4$, there are nine independent elastic constants ($c_{11}$, $c_{22}$, $c_{33}$, $c_{44}$, $c_{55}$, $c_{66}$, $c_{12}$, $c_{13}$ and $c_{23}$). The elastic constants $c_{11}$, $c_{22}$ and $c_{33}$ are indicative of the stiffness against principal strains that are along the a, b and c axes, respectively. The other elastic constants represent resistance against shear deformations, which are obviously smaller than the $c_{ii}$ ($i = 1, 2, 3$). Table 2 shows the $c_{11}$, $c_{22}$ and $c_{33}$ follow the order of $c_{11} > c_{22} > c_{33}$. Interestingly, the lattice constants follow the opposite order of $a < b < c$. The elastic constants can be used to assess structural mechanical stability. The criteria of mechanical stability for orthogonal crystals are expressed by [39]

\[ c_{11} > 0, c_{22} > 0, c_{33} > 0, c_{44} > 0, c_{55} > 0, c_{66} > 0, \]  
\[ c_{11} + c_{22} + c_{33} + 2c_{12} + 2c_{13} + 2c_{23} > 0, \]  
\[ c_{11} + c_{22} - 2c_{12} > 0, \]  

Figure 4. The phonon spectrums along high symmetry points for Ag$_2$XYSe$_4$ (X = Ba, Sr; Y = Sn, Ge) and phonon DOS.
It is clear that the four compounds are of mechanical stability. Some mechanical and thermal parameters can be calculated by the elastic constants [40]. For examples, using the Voigt–Reuss–Hill approximations bulk and shear moduli $B$ and $G$ can be calculated (summarized in Table 2). $B$ for each compound is larger than $G$. The $G/B$ ratio is indicative of the brittleness of materials. High $G/B$ ratio is indicative of the thermal resistivity (reciprocal thermal conductivity) origins from anharmonic vibrations of phonon and especially acoustic phonon. It is noted that recent experiential work shows the average Grüneisen parameter of Ag$_2$BaSnSe$_4$ is very small value of 0.65 [42] that is less than the acoustic Grüneisen parameter ~1.8 in this work. This implies that anharmonic vibrations of optical phonon are very weak.

3.3. TE properties

3.3.1. Carrier relaxation time. It is well known that the precise calculation for the carrier relaxation time is difficult to be implemented due to complex carrier-scattering mechanism. In this work, we calculated the relaxation time based on considering the carrier-phonon scattering using the Fermi-golden rule and the deformation potential (DP) theory. According to the Fermi-golden rule, the scattering rate $P_k$ at the electronic state $k$ can be described by

$$P_{kk'} = \sum_{k'} |M(k, k')|^2 \delta \left( \varepsilon(k) - \varepsilon(k') + \Delta E \right),$$

(18)

where the matrix element $M(k, k')$ represents the scattering from $k$ state to $k'$ state, which is known as the transition matrix element, $\Delta E$ is the phonon energy. In this work, we taken the phonon energy as $3k_BT$. Based on solid state physics theory, the reciprocal of the carrier relaxation time can expressed as:

$$\frac{1}{\tau(k)} = \sum_{k'} P_{kk'} (1 - \cos \theta) = \frac{2\pi}{h} \sum_{k'} |M(k, k')|^2 \delta \left( \varepsilon(k) - \varepsilon(k') + \Delta E \right) (1 - \cos \theta).$$

(19)

Herein, the angle $\theta$ is between the $k$ state to the $k'$ state. In the scattering process, the carrier absorbs or emits a phonon. Thus, by the DP theory, the effective transition matrix element around the valence band maximum (VBM) or conduction band maximum (CBM) can be given by [43].

| $\text{Ag}_2\text{BaGeSe}_4$ | $\text{Ag}_2\text{BaSnSe}_4$ | $\text{Ag}_2\text{SrGeSe}_4$ | $\text{Ag}_2\text{SrSnSe}_4$ |
|---|---|---|---|
| $c_{11}$ | 90.1953 | 90.8454 | 98.4429 | 99.8721 |
| $c_{22}$ | 56.0873 | 64.6186 | 66.9605 | 63.6739 |
| $c_{33}$ | 52.2170 | 52.8386 | 62.3014 | 65.6002 |
| $c_{44}$ | 24.5931 | 22.7369 | 24.7166 | 23.2939 |
| $c_{55}$ | 26.0964 | 21.4068 | 25.2265 | 23.4543 |
| $c_{66}$ | 33.7824 | 31.6366 | 29.2304 | 30.8721 |
| $c_{12}$ | 48.8688 | 53.5752 | 54.4242 | 56.4909 |
| $c_{13}$ | 33.0205 | 29.9881 | 35.1455 | 32.7599 |
| $c_{23}$ | 9.3571 | 30.3142 | 29.9960 | 30.7913 |
| $B$ | 44.207 | 45.954 | 49.460 | 48.150 |
| $G$ | 20.685 | 19.939 | 21.969 | 20.606 |
| $v_\gamma$ | 1944.30 | 1900.12 | 2016.75 | 1943.25 |
| $v_\nu$ | 3622.08 | 3624.24 | 3818.37 | 3722.74 |
| $\gamma_\alpha$ | 1.75 | 1.83 | 1.81 | 1.85 |
| $\Theta$ | 212.535 | 204.537 | 224.897 | 212.985 |
Figure 5. The relaxation time of p- and n-type carrier as a function of temperature for Ag$_2$XYSe$_4$ (X = Ba, Sr; Y = Sn, Ge).

Figure 6. Calculated Seebeck coefficient with respect to temperature $T$ and carrier density $n$ for p- and n-type Ag$_2$XYSe$_4$ (X = Ba, Sr; Y = Sn, Ge).
\[ |M|^2 = \frac{k_B T E_\beta^2}{\Omega c_\beta}, \]  
\[ \frac{1}{\tau(k)} = \frac{2\pi}{\hbar} \sum_{k'} |M(k, k')|^2 \delta [\varepsilon(k) - \varepsilon(k') \pm \Delta E]. \]  

Figure 7. Calculated electrical conductivity with respect to temperature \( T \) and carrier density \( n \) for p- and n-type \( \text{Ag}_2\text{XYSe}_4 \) (\( X = \text{Ba, Sr}; Y = \text{Sn, Ge} \)).

It is worth mentioning that the anisotropy is not completely ignored in the DP theory, and it arises from the anisotropic deformation potential constants and anisotropic elastic constants, which has small difference in the different directions. The carrier relaxation time was showed in figure 5. It is found that the \( \tau \) for each compound reduces with increasing \( T \) and is of the order of magnitude of \( 10^{-14} \)–\( 10^{-15} \). The \( \tau \) for p-type \( \text{Ag}_2\text{BaSnSe}_4 \) and \( \text{Ag}_2\text{SrSnSe}_4 \) is obviously higher than their n-type. However, for \( \text{Ag}_2\text{BaGeSe}_4 \) and \( \text{Ag}_2\text{SrGeSe}_4 \), p- and n-type carriers have close values of relaxation time. It is worth mentioning that the scatters from kinds of defects were not considered. Thus, the actual value should be lower that the calculated.

3.3.2. Electronic transport properties. According to Boltzman theory, Seebeck coefficient \( S \), electrical conductivity \( \sigma \) and electronic thermal conductivity \( \kappa_e \) are all related to temperature and chemical potential. The chemical potential corresponds to carrier density. Thus, calculated \( S \) with respect to...
temperature $T$ and carrier density $n$ for p- and n-type $\text{Ag}_2\text{XYSe}_4$ ($X = \text{Ba, Sr}; Y = \text{Sn, Ge}$) were calculated and then plotted in figure 6. The largest $|\sigma|$ of n-type system is higher than that of the p-type system. For example, the largest $|\sigma|$ of n- and p-type $\text{Ag}_2\text{BaSnSe}_4$ are 775 and 668 $\mu$eV respectively. The largest $|\sigma|$ for each n-type systems is above 700 $\mu$eV. $|\sigma|$ follows the following rules: 1. The $|\sigma|$ reduces with increasing carrier density at low temperatures, and reduces and then rises at high temperature. 2. The $|\sigma|$ rises and then reduces with increasing temperature at low carrier density. The $|\sigma|$ rises with increasing temperature at high carrier density.

Figure 7 shows that the electric conductivity is more sensitive to carrier density than to temperature. In the case of p-type $\text{Ag}_2\text{BaSnSe}_4$, $\sigma$ at 300 K changes from 4.12 S cm$^{-1}$ to $2.71 \times 10^5$ S cm$^{-1}$ with the carrier density increasing from $10^{17}$ to $10^{21}$ cm$^{-3}$. $\sigma$ at 300 K reduces to 1.46 S cm$^{-1}$ at 620 K and then rises to 7.33 S cm$^{-1}$ at 900 K. Figure 8 shows that electronic thermal conductivity at low carrier densities < $10^{19}$ cm$^{-3}$ has negligible contribution to the total thermal conductivity. At 300 K, $\kappa_e$ of p-type $\text{Ag}_2\text{BaGeSe}_4$ is 0.004 W m$^{-1}$ K$^{-1}$ at $10^{17}$ cm$^{-3}$, which can reach up to 0.37 W m$^{-1}$ K$^{-1}$ at $10^{19}$ cm$^{-3}$. $\kappa_e$ is not sensitive to the change of temperature like $\sigma$. At $10^{19}$ cm$^{-3}$, when temperature increases 300 K to 900 K, $\kappa_e$ reduces to 0.06 W m$^{-1}$ K$^{-1}$.

3.3.3. Phonon transport properties. Figure 9 shows the calculated specific heat at constant volume $C_v$ of the four compounds and experimental specific heat at constant press $C_p$ of $\text{Ag}_2\text{BaSnSe}_4$. Below 550 K, $C_v$ and $C_p$ of $\text{Ag}_2\text{BaSnSe}_4$ agree with each other. Above 550 K, $C_p$ is higher than $C_v$. The
difference between $C_v$ and $C_p$ above 550 K origins from the thermal expansion coefficient and isothermal compressibility, which is reasonable and acceptable. $\Theta$ was also obtained by fitting the calculated specific heat $C_v$ according to the following equation:

$$C_v = 9Nk_B \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} \, dx. \tag{22}$$

Herein, $N$ represents the total number of atoms in the primitive cell. In figure 9(b), $\Theta$ at 300 follows the order of $\text{Ag}_2\text{SrGeSe}_4$ (255.0K) > $\text{Ag}_2\text{BaGeSe}_4$ (249.9) > $\text{Ag}_2\text{BaSnSe}_4$ (228.3) > $\text{Ag}_2\text{SrSnSe}_4$ (228.0), which indicates the values are slightly higher than these by equation (15). Experimental $\Theta$ of $\text{Ag}_2\text{BaSnSe}_4$ is about 160K [42] that is obviously lower than the calculated value of 244.9K. We consider the different fitting equations lead to the difference of Debye temperatures between in this work and [42].

We used Slack’s equation and BTE to calculate the lattice thermal conductivity of $\text{Ag}_2\text{XYSe}_4$, respectively. Lattice thermal conductivities calculated by two equations both reduce with rising temperatures (see figures 10(a) and (b)). $\kappa_L$ obtained by Slack’s equation is higher than that by BTE. $\kappa_L$ of $\text{Ag}_2\text{BaSnSe}_4$ by BTE is closer to the experimental data (see figure 10(c)) from [42] but that by Slack’s equation seems more reasonable. The calculated $\kappa_L$ is without the effects of grain boundary, vacancy and doping, and only is average of anisotropic property, which should be higher than experimental data of materials containing all kinds of defects. Thus, we used $\kappa_L$ by Slack’s equation to calculated ZT.

3.3.4. Figure of merit. ZT with respect to $T$ and $n$ in a sufficiently broad region ($n$, $T$) were plotted in figure 11, where the red, green and blue areas denote the high, moderate, and low ZT. N-type $\text{Ag}_2\text{SrGeSe}_4$ and $\text{Ag}_2\text{SrSnSe}_4$ possess relatively low ZT maximums 0.72 and 0.92, although they have larger red closed region than the other systems have the red open region. ZT maximums for p- and n-type $\text{Ag}_2\text{SrGeSe}_4$ reach up to 1.22 and 1.13, respectively. However, these for n-type $\text{Ag}_2\text{SrGeSe}_4$ are below unit (0.91 and 0.97). ZT maximums for P-type $\text{Ag}_2\text{BaSnSe}_4$ and $\text{Ag}_2\text{SrSnSe}_4$ are 1.20 and 1.12, respectively. For all the p-type systems and n-type $\text{Ag}_2\text{BaGeSe}_4$ and $\text{Ag}_2\text{SrGeSe}_4$, ZT maximums appear at 900 K and in the range of $10^{19}$–$10^{20}$ cm$^{-3}$. However, these for n-type $\text{Ag}_2\text{BaSnSe}_4$ and $\text{Ag}_2\text{SrSnSe}_4$ appear in the range of $10^{20}$–$10^{21}$ cm$^{-3}$ and respectively at 670K and 810K.
In order to study TE properties in detail, we extract ZT as a function of carrier density \( n \) at 300 K, 600 K and 900 K from figure 11 and show them in figure 12. For all the systems, ZT rises to the peak value and then reduces with increasing carrier density. At most carrier densities, ZT rises with increasing temperature. In the range of \( 10^{18} \)–\( 10^{19} \) cm\(^{-3} \), ZT is sensitive to both carrier density and temperature. At high temperature, ZT is more sensitive to carrier density. In the case of p-type Ag\(_2\)BaSnSe\(_4\), the ZT at 900 K changes from 0.06 to 1.20 with the carrier density increasing from \( 10^{17} \) cm\(^{-3} \) to \( 3.3 \times 10^{19} \) cm\(^{-3} \).

In this work, we defined the optimal carrier density \( n_{\text{opt}} \) and the optimal temperature \( T_{\text{opt}} \) at which the system has the ZT maximum. The \( n_{\text{opt}} \) and \( T_{\text{opt}} \) of the four compounds with p- and n-type carrier were summarized in table 3. The \( n_{\text{opt}} \) for most systems are \( \sim10^{19} \) cm\(^{-3} \), but \( n_{\text{opt}} \) for n-type Ag\(_2\)BaSnSe\(_4\) and Ag\(_2\)SrSnSe\(_4\) reach up to \( 2.5 \times 10^{20} \) cm\(^{-3} \) and \( 2.7 \times 10^{20} \) cm\(^{-3} \), respectively. The optimal carrier density is very useful for promoting ZT by experimental doping. Theoretically, one can easily calculate the optimal carrier density, but the optimal carrier density and the optimal temperature are difficult to achieve experimentally. For example, when temperature rises to 900 K, material may undergo phase transition or melt. These are the issues to be considered and solved in the experiment, but we still consider Ag\(_2\)XYSe\(_4\) (\( X = \) Ba, Sr; \( Y = \) Sn, Ge) as a class of potential TE materials.

**Figure 11.** Calculated ZT with respect to temperature \( T \) and carrier density \( n \) for p- and n-type Ag\(_2\)XYSe\(_4\) (\( X = \) Ba, Sr; \( Y = \) Sn, Ge).
4. Conclusions

In summary, we use the first-principles method to systematically explore electronic structures, mechanical and thermal and TE properties of p- and n-type Ag$_2$XYSe$_4$ (X = Ba, Sr; Y = Sn, Ge). The results show that low crystal symmetry and suitable band gap mainly contribute to weak thermal transport and medium electrical transport performances. The largest ZT in the p-type Ag$_2$XYSe$_4$ comes from Ag$_2$BaSnSe$_4$ compound reaching up to 1.20 at 900 K, and the largest ZT in the n-type is 1.22 of Ag$_2$SrGeSe$_4$ at 900 K. Although the values for ZT is not very excellent, we believe the ZT for those compounds can be prompted by such as doping, low-dimensional strategy.

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ORCID iDs

A J Hong  https://orcid.org/0000-0002-5328-8760
C L Yuan  https://orcid.org/0000-0002-8088-0313

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