# High Performance of N-type thermoelectric Material AgInSe2 Originated from Strong Acoustic Phonon Scattering

<table>
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<th>Journal:</th>
<th>Materials Lab</th>
</tr>
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<tbody>
<tr>
<td>Manuscript ID</td>
<td>MATLAB-2023-0024.R1</td>
</tr>
<tr>
<td>Manuscript Type:</td>
<td>Original Article</td>
</tr>
<tr>
<td>Date Submitted by the Author:</td>
<td>17-Jun-2023</td>
</tr>
</tbody>
</table>
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| Keywords: | Thermoelectricity, Four-phonon interaction, Average figure of merit, Low thermal conductivity |
| Speciality: | Thermoelectrics |
High Performance of n-type thermoelectric Material AgInSe$_2$ Originated from Strong Acoustic Phonon Scattering

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Abstract

The chalcopyrite system, which consists of ABC$_2$ (where A can be Cu or Ag, B can be Ga or In, and C can be Se or Te), has potential uses in thermoelectric applications. However, the lack of high-performance n-type chalcopyrite thermoelectric has hindered their practical application. This study presents a new method for inhibiting cation vacancy in AgInSe$_2$, achieved through the addition of excessive amounts of Ag and Br doping, which further increases electronic concentration. The resulting n-type material, Ag$_{1.03}$InSe$_{1.99}$Br$_{0.01}$, exhibited superior thermoelectric performance at high temperatures, with a $ZT$ of 1.2 at 900 K and an average $ZT$ of 0.75 within a temperature range of 600-900 K. The remarkable thermal performance of this material is mainly due to its extremely low lattice thermal conductivity, which is attributed to the quartic anharmonicity and nondispersive phonon dispersion relation. These findings provide new insights into developing high-performance n-type chalcopyrite thermoelectric for practical use in energy conversion technologies.

Keywords: Thermoelectricity; Four-phonon interaction; Average figure of merit; Low thermal conductivity
1. Introduction

Thermoelectric technology, which involves the conversion of heat into electrical power and vice versa, has gained significant attention as a potential solution to global energy issues. Thermoelectric devices, including refrigeration and power generation devices, have several attractive features, such as being noiseless, low-maintenance, emission-free, and reliable. The efficiency of thermoelectric devices is proportional to the figure of merit \( ZT = S^2\sigma T/\kappa \), where the \( S \), \( \sigma \), \( \kappa \) are the Seebeck coefficient, electrical conductivity, and thermal conductivity, respectively.\(^1\) The total thermal conductivity \( \kappa \) can be described by the formula: \( \kappa = \kappa_e + \kappa_{lat} \), where the \( \kappa_e \) and \( \kappa_{lat} \) is electronic thermal conductivity and lattice thermal conductivity, respectively. Additionally, the \( \sigma \) and \( \kappa_e \) obey the Wiedemann-Franz law, indicating a coupling relationship between electrical and thermal parameters\(^2\).

To explore the decoupling of electronic and thermal transport in thermoelectrics, a number of strategies have been proposed to improve thermoelectric performance. These include defects manipulation, energy band convergence, strong spin-orbit coupling, strain, heterojunctions, nanostructures, and entropy engineering \(^3\). Among these methods, reducing lattice thermal conductivity is the most effective. For instance, low lattice thermal conductivity in room temperature (RT) thermoelectric Bi\(_2\)Te\(_3\) can be achieved through the use of dense dislocation arrays \(^4\). Ultralow lattice thermal conductivity of medium-temperature thermoelectric chalcogenides can be induced by high entropy, and the lattice thermal conductivity of high-temperature thermoelectric SiGe alloys can be substantially reduced by employing nanostructures \(^5\). Recently, a group of chalcopyrite ABC\(_2\) compounds (where A = Cu, Ag; B = Ga, In; and C = Se, Te) have drawn the attention of thermoelectric scientists due to their low lattice thermal conductivity. Examples of these compounds include CuInSe\(_2\) (3.9 W/m K at RT) \(^6\), CuGaTe\(_2\) (6.1 W/m K at RT) \(^7\), CuInTe\(_2\) (5.8 W/m K at RT) \(^8\), AgInSe\(_2\) (1.0 W/m K
at RT) \cite{9}, AgGaTe\textsubscript{2} (1.1 W/m K at RT) \cite{10}, and AgInTe\textsubscript{2} (1.4 W/m K at RT) \cite{8}. Among the chalcopyrite compounds, Ag-based chalcopyrites exhibit lower lattice thermal conductivity, and AgInSe\textsubscript{2} has a much lower lattice thermal conductivity than other chalcopyrite compounds due to the weak chemical bonds in Ag-based chalcopyrites, which results in a lower sound velocity and enhanced Umklapp process \cite{8,10}.

The attainment of desirable thermoelectric properties heavily relies on maintaining a low lattice thermal conductivity. The AgInSe\textsubscript{2} chalcopyrite has emerged as a prominent research material for its low lattice thermal conductivity \cite{9,11,12}. Three-phonon (3ph) scattering, including the normal-mode process and Umklapp process, is generally considered to play a dominant role in thermal transport \cite{13}, however, the theory only includes 3ph scattering usually overestimate the lattice thermal conductivity of many traditional thermoelectric materials (including AgInSe\textsubscript{2}) \cite{14-17}. Despite the number of ongoing research, the fundamental explanation behind the low thermal conductivity is yet to be fully understood. Our previous research has shown that AgCrSe\textsubscript{2}, another Ag-based material characterized by low lattice thermal conductivity with weakly Ag-bonded rattling constituents, exhibits strong four-phonon (4ph) scattering \cite{12}. It inspires us to consider whether AgInSe\textsubscript{2}, a material with similar composition and low thermal conductivity, may also exhibit strong 4ph scattering. In this study, our anharmonic lattice dynamics calculations and analysis of AgInSe\textsubscript{2} reveal that the strong localized phonon coupling is indeed due to 4ph interactions of low-frequency phonons in thermal transport. Including 4ph interaction, the lattice thermal conductivity of AgInSe\textsubscript{2} has been successfully predicted. We have found the impact of low-frequency optical phonons on thermal transport and resolve the issue of serious overestimation caused by 3ph interaction on lattice thermal conductivity in this work (which even led to the theoretical prediction value being more than twice the experimental value) \cite{18-21}.

2. Materials and methods
2.1. Synthesis:

The AgInSe$_2$ samples were synthesized by mixing elements (High-purity Ag (99.999%), In (99.999%), Se (99.999%), and Br (99.999 %)) in stoichiometric proportions and reacting in a molten state, then spark plasma sintering into bulk. The total mass of each sample was about 8 g. The specific process is as follows: The mixtures of elements were sealed in evacuated silica tubes and heated to 1323 K at 100 K/h, kept at this temperature for 12 h, and quenched in cold water to room temperature; The samples were then annealed at 673 K under vacuum for 12 h before cooling to room temperature. The annealed ingots were crushed, and ground into a fine powder, followed by spark plasma sintering at 773–823 K under a pressure of 50 MPa for 5 min to obtain densified samples.

2.2. Measurement Details

**X-ray Diffraction:** The obtained samples were analyzed by powder X-ray diffraction on a Rigaku smart lab system at 45 kV and 200 mA with Cu K$_\alpha$ radiation (LK$_\alpha$1 = 1.540593 Å, LK$_\alpha$2 = 1.544414 Å) at a scan rate of 2° min$^{-1}$ and a step size of 0.020°.

**Electron Microscopy:** STEM experiments were conducted on a Thermofischer Themis G2 60-300 electron microscope under 300 kV. The convergence angle is 30 and the collection angle is 60-200 mrad, respectively. EDS mapping was conducted using a Super-X EDX detector.

**Electronic Transport Measurements:** For all samples (~2 × 2 × 8 mm$^3$), the electrical resistivity and Seebeck coefficient were simultaneously measured using a ZEM-3 system (Ulvac-Riko, Japan) under a helium atmosphere from 300 to 900 K.

**Thermal Transport Measurements:** The thermal conductivity was calculated with the relationship $\kappa=\rho\lambda C_p$. The density $\rho$ was determined using the dimensions and mass of the samples, respectively. The specific heat capacities and the diffusivities $\lambda$ were measured using pellets cut and polished into square shapes of ~6×6×1.0 mm$^3$ and with
the laser flash diffusivity method by LFA-457 (Netzsch, Germany), using the Pyroceram 9606 as a calibration standard.

**Hall Measurements:**

The carrier concentration values were measured by the Van der Pauw method with an HMS-5500 Hall measurement system under a static magnetic field of 0.56 T.

### 2.3. Computational Details

In this study, electrical properties were calculated based on the crystal cell (16 atoms: 4 Ag, 4 In, and 8 Se/Br) within a $7 \times 7 \times 3$ mesh. The Perdew-Burke-Ernzerhof (PBE) with the generalized gradient approximation (GGA)\(^{[22]}\) was used for exchange and correlation energy in structural optimization and band structure computations. In the Vienna Ab-initio Simulation Package (VASP)\(^{[23–26]}\), the hybrid functional HSE06\(^{[27,28]}\) is further utilized to estimate the energy band. The cutoff energy for the wave function is 400 eV. To simplify the calculation, the phonon transport is calculated based on the original cell (8 atoms: 2 Ag, 2 In, and 4 Se). The anharmonic lattice dynamics of AgInSe\(_2\) were calculated using temperature-dependent effective potential (TDEP)\(^{[29,30]}\). An energy cut-off of 400 eV was used throughout Ab initio molecular dynamics simulation. During molecular dynamics simulation, lattice parameters of a $2 \times 2 \times 4$ supercell with 128 atoms were relaxed until the external pressure is smaller than 0.05 GPa. Then the results from molecular dynamics simulation were used to determine 2nd, 3rd, and 4th order force-constants (IFCs) by TDEP. The cut-offs for the 2nd, 3rd, and 4th order IFCs are 8.0 Å, 7.0 Å, and 4.5 Å, respectively.

Lattice thermal conductivity for 3ph scattering $\tau_{3ph}^{-1}$ was obtained by the Peierls-Boltzmann transport equation for phonons on a $26 \times 26 \times 26$ mesh, as implemented in the software TDEP\(^{[31]}\). Since the full solution of the 4ph transport equation needs expensive calculations, the 4ph scattering process is accounted for in a non-self-consistent way. The 4ph scattering $\tau_{4ph}^{-1}$ rate was added to the total scattering rate $\tau^{-1}$ as:

$$
\tau^{-1} = \tau_{3ph}^{-1} + \tau_{4ph}^{-1}.
$$  \hspace{1cm} (1)

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This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record.
The calculation of 4ph was carried out by interpolation method on an initial 6 × 6 × 6 mesh.

3. Results and discussion

AgInSe$_2$ is a semiconductor with a tetragonal structure and a wide bandgap of approximately 1.2 eV, which makes it suitable for various applications such as thermoelectricity, photovoltaic generation, and optical engineering $^{[32,33]}$. The crystal structure of AgInSe$_2$ is diamond-like, with each Se atom bonded to two other elements Ag and In. The space group of AgInSe$_2$ is $I4d$ as shown in Figure 1a. The difference in bond lengths between Ag-Se and In-Se provides a basis for the diversity of electron and phonon transport properties $^{[8]}$. The carrier concentration of undoped AgInSe$_2$ at room temperature is relatively low, ~$1.3 \times 10^{13}$ cm$^{-3}$, resulting in low electrical conductivity of $10^{-3}$ S/cm $^{[34]}$. Due to the wide bandgap of AgInSe$_2$, free carriers are difficult to be excited in electronic transport. Furthermore, most chalcopyrites are naturally p-type due to cation vacancy, making it difficult to achieve high thermoelectric performance and n-type thermoelectric applications $^{[9]}$. One approach to improve the conductivity of AgInSe$_2$ is through Ag doping $^{[34]}$. As Figure S1 shows, compared with the experiment data of AgInSe$_2$ without excess Ag, the electrical conductivity of Ag$_{1.03}$InSe$_2$ is much higher, and the total thermal conductivity is lower. The resulting larger $ZT$ values in a temperature range of 300-900 K mean that our strategy of 3% Ag over-doping, is effective. To improve the conductivity of AgInSe$_2$, 3% Ag over-doping is applied to each sample. This approach provides more electronic concentration than undoped AgInSe$_2$. The extranuclear 5s electrons in Ag provide extra electronic carriers for the whole system, resulting in a carrier concentration of $9.0 \times 10^{15}$ cm$^{-3}$ at room temperature for Ag$_{1.03}$InSe$_2$. This concentration is about three orders of magnitude higher than that of undoped AgInSe$_2$, which means that over-doping Ag is a very effective approach to improve the carrier concentration. In several n-type thermoelectric materials, the addition of Br dopants has been found to enhance the electronic concentration in chalcogenide compounds like SnS $^{[35]}$, SnSe $^{[36]}$, SnSe$_2$ $^{[37]}$, SnTe $^{[38]}$, and PbTe $^{[39]}$. 

https://mc03.manuscriptcentral.com/matlab
PbTe [38], and AgBiSe$_2$ [39]. Thus, we introduced Br doping into Ag$_{1.03}$InSe$_2$ and synthesized a series of samples with varying Br content (x= 0, 0.01, and 0.02) by mixing the elements in stoichiometric proportions and then reacting them in the molten state. The resulting mixtures were consolidated into bulk using spark plasma sintering. The powder X-ray diffraction (XRD) patterns of the synthesized samples were recorded at room temperature and are presented in Figure 1b. According to the PDF card (#No. 35-1099) of AgInSe$_2$, the secondary phase Ag is found in our sample. Scanning transmission electron microscopy high-angle annular dark field (STEM HAADF) images are shown in Figure 1c, the STEM images reveal the presence of secondary phase precipitates homogeneously distributed throughout the matrix, with a size ranging from 500 nm to 2 μm. Energy-dispersive X-ray (EDX) spectroscopy analysis confirms that these precipitates consist mainly of Ag, with minor amounts of In and Se, thus verifying that the synthesized samples meet our desired specifications.
Figure 1. (a) Crystal structure of AgInSe$_2$. (b) XRD patterns of Ag$_{1.03}$InSe$_{2-x}$Br$_x$ ($x=0$, 0.01, and 0.02). Low magnification STEM HAADF image (c), magnified STEM HAADF image (d), and EDX (e-g) of Ag$_{1.03}$InSe$_2$.

Our study also investigates the effect of Br doping on AgInSe$_2$ using ab initio calculations. The electronic band structures of AgInSe$_2$ and Br-doped AgInSe$_{1.75}$Br$_{0.25}$ are displayed in Figures 2a and 2b, respectively. Both have a direct bandgap at the $\Gamma$ high symmetry point, with the valence band maximum (VBM) and conduction band minimum (CBM) determined through calculation. The bandgap of AgInSe$_2$ is approximately 0.77 eV, which is lower than the experimental value due to ab initio calculations' tendency to underestimate the bandgap. While our model's precision may not be sufficient to determine the actual solid solubility of Br, our qualitative analysis shows that Br doping introduces the change of Fermi energy and enhances electronic concentration. We calculated the effective mass of holes and electrons by fitting a parabola to the CBM and VBM, respectively. The projected energy band diagram of CBM (Figure 2c) indicates an isotropic electronic effective mass of 0.16 $m_e$ in both a and c directions, where $m_e$ denotes electronic mass. The CBM in AgInSe$_2$ has only one valley, and the conduction band energy valley is isotropic, enabling the single parabolic band model to explain electronic transport properties$^{[40]}$. The effective mass of the hole, as shown in Figure 2d, is slightly anisotropic. The values of $m_x^*$ and $m_z^*$ are 0.79 and 0.62 $m_e$, respectively, which are relatively larger than those of the electron. Using the electronic effective mass for n-type AgInSe$_2$ at 300 K is $1.2 \times 10^{18}$ cm$^{-3}$ (details are provided in the Supplementary Information).
Figure 2. Band structures of AgInSe$_2$ (a) and AgInSe$_{1.75}$Br$_{0.25}$ (b), and Fermi energy $E_F$ is set to be zero. Projection of band dispersion of the conduction (c) and valence (d) band energies for AgInSe$_2$ in the first Brillouin zone.

Figure 3 displays the electronic transport properties of Ag$_{1.03}$InSe$_{1.99-x}$Br$_x$ ($x = 0$, 0.01, and 0.02). The comparison of other sample results, Ag$_{1.03}$InSe$_{1.99-x}$Br$_x$ ($x = 0.005$, 0.015), and the thermal and electrical transport properties of AgInSe$_2$ without excess Ag are shown in Figure S1. Ag$_{1.03}$InSe$_{1.99}$Br$_{0.01}$ and Ag$_{1.03}$InSe$_{1.98}$Br$_{0.02}$ exhibit higher room temperature (RT) electrical conductivity, with values of 3.9 and 4.3 S/cm, respectively, compared to Ag$_{1.03}$InSe$_2$ (~1.6 × 10$^{-3}$ S/cm). This increase in conductivity is due to the increase in electronic concentration and mobility. The electronic concentration of Ag$_{1.03}$InSe$_{2-x}$Br$_x$ ($x = 0.01$ and 0.02) at RT is 1.4 × 10$^{17}$ and 4.3 × 10$^{17}$ cm$^{-3}$, respectively. The relationship curves for the Seebeck coefficient and carrier concentration are shown in Figure 3c, and the fitted electronic effective mass and relaxation time values are presented in Table 1. Comparing Ag$_{1.03}$InSe$_{1.99}$Br$_{0.01}$ and Ag$_{1.03}$InSe$_{1.98}$Br$_{0.02}$, the relaxation time remains virtually unchanged with increasing Br doping concentration, implying that the decrease in mobility is mainly caused by the
increase in effective mass. The Seebeck coefficient values for Ag$_{1.03}$InSe$_{2-x}$Br$_x$ ($x=0.01$ and 0.02) at RT are $3.0 \times 10^2$ and $3.6 \times 10^2$ μV/K, respectively. The absolute value of the Seebeck coefficient $|S|$ for Ag$_{1.03}$InSe$_2$ decreases with an increase in Br content (Figure 3c). Additionally, $|S|$ for Ag$_{1.03}$InSe$_2$ sharply decreases in the temperature range of 300–400 K, which is a typical characteristic of two-band model dominant intrinsic semiconductors with a dramatic shift in Fermi energy, in general.[41] However, our DFT calculated band structure has shown that there is only one valley on CBM, which means the shift of Fermi energy has little contribution to electrical transport properties. Here, excess Br introduces many defects, which may enhance the energy-filtering effect. The electrons with lower energy are scattered by the defect barrier, only the electrons with high energy will cross the barrier, resulting in an increasing absolute value of the Seebeck coefficient. Compared to the results of the 1 % Br-doping sample, the electronic effective mass is enhanced due to the strong energy-filtering effect after 2 % doping, simultaneously. In addition, the $PF$ of Br-doped Ag$_{1.03}$InSe$_2$ is significantly enhanced with a maximum value of 53.7 μW/cm K$^2$ at 900 K for Ag$_{1.03}$InSe$_{1.99}$Br$_{0.01}$. The measured data indicate that Br doping can increase electronic concentration and conductivity, which is consistent with our ab initio calculation results.
Figure 3. Electrical conductivity $\sigma$ (a), Seebeck coefficient $S$ (b), $PF$ (d) of all samples from 300 to 900 K. (c) Electronic concentration $n$ dependent Seebeck coefficient $S$ for all samples at RT. The solid lines are calculated according to the single parabolic band model. The green and yellow regions represent the range of intrinsic semiconductors and degenerate semiconductors, respectively.

Table 1. Electrical conductivity $\sigma$, carrier concentration $n$, mobility $\mu$, electronic effective mass $m^*$ obtained by single parabolic band model, electronic relaxation time $\tau$ of all samples at RT.

<table>
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<th>Samples</th>
<th>$\sigma$ ($\text{S cm}^{-1}$)</th>
<th>$n$ ($\text{cm}^{-3}$)</th>
<th>$M$ ($\text{cm}^2 \text{V}^{-1}\text{s}^{-1}$)</th>
<th>$m^*$ ($m_e$)</th>
<th>$\tau$ (fs)</th>
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<tr>
<td>$\text{Ag}_{1.03}\text{InSe}_2$</td>
<td>$1.6 \times 10^{-3}$</td>
<td>$9.0 \times 10^{15}$</td>
<td>1.1</td>
<td>0.8</td>
<td>$5.1 \times 10^{-1}$</td>
</tr>
<tr>
<td>$\text{Ag}<em>{1.03}\text{InSe}</em>{1.99}\text{Br}_{0.01}$</td>
<td>3.9</td>
<td>$1.4 \times 10^{17}$</td>
<td>$1.9 \times 10^2$</td>
<td>0.08</td>
<td>8.6</td>
</tr>
<tr>
<td>$\text{Ag}<em>{1.03}\text{InSe}</em>{1.98}\text{Br}_{0.02}$</td>
<td>4.3</td>
<td>$4.3 \times 10^{17}$</td>
<td>$5.7 \times 10^1$</td>
<td>0.27</td>
<td>8.8</td>
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Figure S1 displays the temperature-dependent total thermal conductivity $\kappa$ of all samples. The total thermal conductivity comprises mainly two components, electronic
and lattice thermal conductivity. The electronic thermal conductivity $\kappa_e$ is determined by the Wiedemann-Franz relationship, $\kappa_e = LT\sigma$, where $L$ denotes the Lorenz number. The lattice thermal conductivity (Figure 4a) obtained for all samples exhibits similar RT values of approximately 0.85 W/m K, which suggests that Br doping has a weak effect on thermal transport. Compared to other conventional thermoelectric materials, such as Bi$_2$Te$_3$ (0.7 W/m K), PbTe (0.8 W/m K), and SnSe (1.3 W/m K), AgInSe$_2$ demonstrates relatively low lattice thermal conductivity.

To further investigate the origin of the low lattice thermal conductivity of AgInSe$_2$, the phonon dispersion at 300 K was calculated, as illustrated in Figure 4b. Low-frequency optical phonons were observed around 4 meV, which partially overlap with the acoustic phonons. Many avoided-crossing points were identified between the low-frequency optical phonons and acoustic phonons along the path from the zone center $\Gamma$ point to the boundary of the Brillouin zone, leading to a strong coupling effect between phonons. Furthermore, the acoustic branch and low-frequency optical branch display many flat dispersions, providing significant 4ph scattering phase space. The localized low-frequency acoustic phonon also implies low group velocities. These nondispersive low-frequency phonon dispersions are highly significant and suggest that strong phonon coupling excites not only 3ph but also 4ph interaction in thermal transport. Figure S2 vividly demonstrates the 3ph and 4ph scattering processes. In 3ph scattering processes, two phonons ($k_1$ and $k_2$) combine to create a new phonon ($k_3$). According to the law of energy conservation ($\hbar\omega_{k_1} + \hbar\omega_{k_2} = \hbar\omega_{k_3}$, where $\hbar$ is reduced Planck constant and $\omega$ is phonon frequency), the newly generated phonon energy must be higher than $\hbar\omega_{k_1}$ or $\hbar\omega_{k_2}$. This results in limited 3ph scattering when there is no higher energy phonon branch (dashed in Figure S2). However, in the 4ph scattering recombination processes, two phonons ($k_1$ and $k_2$) combine into two new phonons ($k_3$ and $k_4$), are permitted. If two phonon branches are parallel, both the laws of energy conservation ($\hbar\omega_{k_1} + \hbar\omega_{k_2} = \hbar\omega_{k_3} + \hbar\omega_{k_4}$) and momentum conservation ($k_1 + k_2 = k_3 + k_4 + G$ where $G$ is
a reciprocal lattice vector) are met. As a result, the cumulative 4ph scattering phase space is enormous, and 4ph must be considered in phonon transport. The projected phonon DOS (Figure 4c) shows that low-frequency phonons with an energy of ~4 meV mainly come from Ag, which can be the reason for the strong phonon-phonon coupling.[12].

To further confirm the significant role of 4ph in phonon transport in AgInSe$_2$, we directly performed lattice dynamics calculations for anharmonic phonons, as detailed in the Supplementary Information. Figure 4d shows the lineshape peaks $\omega_0$ of the transverse acoustic (TA) and longitudinal acoustic (LA) phonon spectrum functions at the P point, which are 3.2 meV and 4.1 meV, respectively. The imaginary part of phonon self-energy functions $\Gamma_\omega$ is closely related to the phonon scattering rate $\tau^{-1}$, where $\tau^{-1} = 2\Gamma_\omega(\omega_0)$. [12] At the characteristic frequency of the TA phonon (3.2 meV), the imaginary part of the 4ph is comparable to that of the 3ph. Additionally, at the characteristic frequency of the LA phonon (4.1 meV), the 4ph imaginary part is only slightly smaller than the 3ph imaginary part. This behavior is common for both TA and LA modes, as seen in Figure S3 where the intensity of 4ph phonon scattering is not lower than that of 3ph scattering at the Z point. Thus, 4ph interactions should not be ignored. The lattice thermal conductivity of 3ph interaction was calculated to be 2.1 W/m K in $a$ direction and 2.3 W/m K in $c$ direction, while the lattice thermal conductivity of 3ph and 4ph interactions was found to be 0.8 W/m K in $a$ direction and 0.9 W/m K in $c$ direction, respectively. The theoretical lattice thermal conductivity, taking into account the 4ph interaction, is in perfect agreement with the experimental value (Figure S4) [9,42,43]. Therefore, the underlying cause of the intrinsic low thermal conductivity in AgInSe$_2$ can be attributed to the four-phonon interaction. Figure 4e shows the temperature-dependent $ZT$ of various AgInSe$_2$ samples, including AgInSe$_2$, Ag$_{1.01}$InSe$_2$, Ag$_{1.03}$InSe$_2$, Ag$_{0.9}$Cd$_{0.1}$InSe$_2$, and Ag$_{1.03}$InSe$_{1.99}$Br$_{0.01}$. The addition of 1% Br doping significantly enhances the electronic transport performance without
substantially increasing the lattice thermal conductivity. Compared to undoped AgInSe₂, the ZT value of Ag₁.₀₃InSe₁.₉₉Br₀.₀₁ increases from 0.₇ to 1.₂ at 900 K, achieving an average ZT of 0.₇₅ over the temperature range of 6₀₀ to 9₀₀ K, which is comparable to many reported p-type chalcopyrite compounds.

Figure 4. (a) Lattice thermal conductivity $\kappa_{\text{lat}}$ of all samples from 3₀₀ to 9₀₀ K. Calculated phonon dispersion (b), phonon DOS (c) of AgInSe₂. (d) 4 curves that increase as phonon frequency rises represent the imaginary part $\Gamma_{\omega}$ of the 3ph and 4ph self-energy functions at P point, and the purple and orange peak lines represent the
lineshape of TA and LA at P point, respectively. (e) ZT and (f) average ZT (from 600 to 900 K) of all samples and other reported AgInSe$_2$ materials$^{[34, 44]}$.

4. Conclusions

In summary, we have successfully prepared Br-doped n-type AgInSe$_2$ with outstanding thermoelectric performance. Preparation of the n-type chalcopyrite materials has been a notable challenge primarily due to inherent cation vacancies. However, through the suppression of Ag vacancies using excessive Ag and the optimization of electronic transport via Br doping, n-type AgInSe$_2$ has been successfully achieved. This offers a viable method to hinder persistent cation vacancies in intrinsic p-type semiconductors while obtaining n-type semiconductors. It brings forth new insights into the design of thermoelectric devices aiming to acquire n-type counterparts for intrinsic p-type thermoelectric materials. In terms of thermal transport, ultralow lattice thermal conductivity is a crucial factor for ensuring excellent thermoelectric properties. The flat low-frequency phonon dispersion and avoided crossovers between acoustic phonons and low-frequency optical phonons in AgInSe$_2$ are the characteristics of strong phonon coupling. In general, 3ph scattering is dominant in most of the materials, whereas the high-order phonon scattering phase space is significantly enhanced in strong phonon coupling materials, which results in ultralow lattice thermal conductivity. This provides a new perspective for the high-throughput screening of potential high-performance thermoelectric materials with ultralow lattice thermal conductivity.

5. Acknowledgments
This work was supported by the National Natural Science Foundation of China (Grant No. 11934007, 11874194, and 12174176), the Science and Technology Innovation Committee Foundation of Shenzhen (Grant No. JCYJ20200109141205978, JCYJ20190809145205497), and the Outstanding Talents Training Fund in Shenzhen (2021108).

6. Author contributions

S. H. and J. Q. H. designed this work. Y. W. and L. X. performed the calculations. B. H. J. synthesized the samples and carried out the transport property measurements. B. H. J., Y. Y. and P. J. L carried out the experimental study and performed the TEM observations. S. H., Y. W., and J. Q. H. wrote and all authors edited this manuscript. The authors declare no conflict of interest.

7. References


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Supplementary Information

High Performance of n-type Thermoelectric Material AgInSe$_2$
Originated from Strong Acoustic Phonon Scattering

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**Single Parabolic Band Model:**

In the single parabolic band model\(^1\), the electron obeys the Fermi Dirac distribution. The carrier concentration is

\[
n = \frac{N_v (2m^* \hbar^2)}{2\pi^2} \int_0^\infty \frac{E^2}{e^{(E - E_{FtoC})/k_BT} + 1} dE,
\]

where \(N_v\) is band degeneracy, \(m^*\) is effective mass, \(E\) is band energy, \(E_{FtoC}\) is the difference between Fermi energy and CBM (Figure S6), \(\hbar\) is reduced Planck constant, \(k_B\) is Boltzmann constant, and \(T\) is temperature.

For the sake of simplicity, define the Fermi integrals as

\[
F_s(E^*_s) = \int_0^\infty \frac{E^*_s}{e^{E^*_s - E_{FtoC}} + 1} dE^*_s,
\]

where \(E^*_s = E/k_BT\) and \(E^*_s = E_{FtoC}/k_BT\). Carrier concentration \(n\), electrical conductivity \(\sigma\), Seebeck coefficient \(S\), Lorentz constant \(L_0\), \(ZT\), and simplified judgment criteria of thermoelectric performance \(\beta\) can be expressed as function of Fermi integrals:

\[
n = \frac{N_v (2m^* k_B T)}{2\pi^2} \frac{2}{\hbar^2} F_{1/2},
\]

\[
\sigma = \frac{N_v e^2 \tau}{3\pi^2 m^*} \left( \frac{2m^* k_B T}{\hbar^2} \right)^{3/2} \left( r + \frac{3}{2} \right) F_{r + 1/2} = \sigma_0.
\]

\[
|S| = \left( \frac{k_B T}{e} \right) \left[ \left( \frac{r + 3}{2} \right) F_{r + 3/2} - E_{FtoC} \right],
\]

\[
L_0 = \left( \frac{k_B T}{e} \right)^2 \left[ \left( \frac{r + 3}{2} \right) F_{r + 5/2} - \left( \frac{r + 3}{2} \right) F_{r + 3/2} - \right] F_{r + 1/2},
\]

\[
ZT = \frac{1}{2} + \left( \frac{r + 7}{2} \right) F_{r + 5/2} - \frac{\left( \frac{r + 3}{2} \right)^2 F_{r + 3/2}}{\left( \frac{r + 3}{2} \right) F_{r + 1/2}},
\]

\[
\beta = \frac{N_v (2m^* k_B T)^3}{3\pi^2 (\hbar^2)^3} \frac{1}{k_i}.
\]
where τ is relaxation time, and r is scattering parameter: r = −1/2 for acoustic phonon scattering, r = 1/2 for polar optical phonon scattering, and r = 3/2 for ionized impurity scattering. For AgInSe₂, acoustic phonon scattering plays a primary role in electron transport. The relationship between ZT and β is shown in Figure S7, thus the optimized carrier concentration at ZTmax is higher than the carrier concentration threshold of degenerate semiconductor. The carrier concentration threshold of degenerate semiconductor is when \( E_{F \text{toC}} = 0 \) and \( F_{1/2} = 0.68 \), and corresponding carrier concentration is

\[
n = \frac{0.68 N_v (2m^* k_B T)^{3/2}}{2\pi^2}.
\]

(S9)

The effective mass can be obtained from the band structure calculation, and here \( N_v = 1 \) and \( m^* = 0.16 m_e \). The threshold of degenerate semiconductors for n-type AgInSe₂ is \( 1.2 \times 10^{18} \text{ cm}^{-3} \) at 300 K

**Phonon Calculations:**

The phonon dynamics are calculated by phonon spectral function \( S_{k,s}^{(i)}(\omega) \)[3–5]:

\[
S_{k,s}^{(i)}(\omega) = \frac{2\omega_{k,s}^{(i)} \Gamma_{k,s}^{(i)}(\omega)}{[\omega^2 - \omega_{k,s}^{(i)} - 2\omega_{k,s} \Delta_{k,s}(\omega)]^2 + 4\omega_{k,s}^2 \Gamma_{k,s}^{(i)}(\omega)^2},
\]

(S10)

where \( \omega_{k,s}^{(i)} \) is the eigenfrequency of the phonon mode \( (\vec{k},s) \), \( \Delta_{k,s}(\omega) \) and \( \Gamma_{k,s}(\omega) \) are the real and imaginary part of phonon self-energy \( \Sigma_{k,s}(\omega) \), respectively. For simplicity, we approximate \( \Sigma_{k,s}(\omega) \) by its low order perturbations:

\[
\Sigma_{k,s}(\omega) \approx \Sigma_{k,s}^{(1)}(\omega) + \Sigma_{k,s}^{(2)}(\omega) = \left[ \Delta_{k,s}^{(1)}(\omega) + i\Gamma_{k,s}^{(1)}(\omega) \right] + \left[ \Delta_{k,s}^{(2)}(\omega) + i\Gamma_{k,s}^{(2)}(\omega) \right].
\]

(S11)

The first bracket is the first- and second-order perturbations as calculated from the loop and bubble diagrams. The imaginary part \( \Gamma_{k,s}^{(1)}(\omega) \) is essentially determined by 3ph and isotopic scattering. The second bracket is associated with 4ph interactions.[6,7] The phonon self-energy up to second-order quartic anharmonic perturbations can be written as:

\[
\Delta_{k,s}^{(2)}(\omega) = \frac{24}{\hbar} \sum_{k_1,s_1} V_4 \left( \vec{k},s; -\vec{k},s; \vec{k}_1,s_1; -\vec{k}_1,s_1 \right) \left( n_1 + \frac{1}{2} \right) - \frac{18}{\hbar^2} \sum_{k_1,s_1} \sum_{k_2,s_2} \left| V_3 \left( \vec{k},s; \vec{k}_1,s_1; \vec{k}_2,s_2 \right) \right|^2 \times \mathcal{P}
\]

S-3
\[
\left(\frac{n_1 + n_2 + 1}{\omega + \omega_1 + \omega_2} - \frac{n_1 + n_2 + 1}{\omega - \omega_1 - \omega_2} + \frac{n_1 - n_2}{\omega - \omega_1 + \omega_2} - \frac{n_1 - n_2}{\omega + \omega_1 - \omega_2}\right), \quad (S12)
\]

\[
\sum_{k_1,s_1} \sum_{k_2,s_2} |V_3(k_1s_1,k_1s_1;k_2s_2,k_2s_2)|^2 \times \left\{(n_1 + n_2 + 1)[\delta(\omega - \omega_1 - \omega_2) - \delta(\omega + \omega_1 + \omega_2)] + (n_1 - n_2)[\delta(\omega - \omega_1 - \omega_2) - \delta(\omega + \omega_1 + \omega_2)] \right\} + \Gamma_{iso}(\omega), \quad (S13)
\]

\[
\Delta_{k,2}^{(2)}(\omega) = \frac{-96}{\hbar^2}
\]

\[
\sum_{k_1,s_1} \sum_{k_2,s_2} \sum_{k_3,s_3} |V_4(k_1s_1,k_1s_1,k_2s_2,k_2s_2,k_3s_3,k_3s_3)|^2 \times \mathcal{P} \left\{(n_1 + 1)(n_2 + 1)(n_3 + 1) - n_1 n_2 n_3 \right\} \times \left(\frac{1}{\omega + \omega_1 + \omega_2} - \frac{1}{\omega - \omega_1 - \omega_2}\right) (n_3 + 1), \quad (S14)
\]

\[
\Gamma_{k,2}^{(2)}(\omega) = \frac{96\pi}{\hbar^2}
\]

\[
\omega_i = \omega_{k_1s_1}, \quad (S16)
\]

\[
n_i \equiv n_{k_1s_1}^2 = \frac{1}{e^{\frac{\hbar \omega_i}{k_B T}} - 1}, \quad (S17)
\]

where $V_3$ and $V_4$ are the anharmonic coefficients of cubic and quartic anharmonic force constants $\Phi_3$ and $\Phi_4$, respectively. $\delta$ and $\mathcal{P}$ denote Dirac $\delta$-function and the principal value.

**Figure S1.** Temperature dependence electrical and thermal transport performance of...
all samples. It is compared with the thermal and electrical transport properties of AgInSe₂ with previous work\cite{2}.

Figure S2. Schematic diagram showing the restricted 3ph scattering process and 4ph resonance process in strong phonon coupling dispersions.

Figure S3. 4 curves that increase as phonon frequency rises represent the imaginary
part $\Gamma_{\omega}$ of the 3ph and 4ph self-energy functions at Z point, and the purple and orange peak lines represent the lineshape of TA and LA at Z point, respectively.

Figure S4 The blue area represents the lattice thermal conductivity calculated from the 3ph interaction, and the red area represents the lattice thermal conductivity considering both 3ph and 4ph interaction. The experimental values are shown by data points.$^{[2, 8, 9]}$

References

Supplementary Information

High Performance of n-type Thermoelectric Material AgInSe₂ Originated from Strong Acoustic Phonon Scattering

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Single Parabolic Band Model:

In the single parabolic band model\(^\text{[1]}\), the electron obeys the Fermi Dirac distribution. The carrier concentration is

\[
n = \frac{N_v}{2\pi^2} \left( \frac{2m^*k_B T}{h^2} \right)^{3/2} \int_0^\infty \frac{E_{Ftoc}^{3/2}}{e^{(E-E_{Ftoc})/k_B T}+1} dE, \tag{S1}
\]

where \(N_v\) is band degeneracy, \(m^*\) is effective mass, \(E\) is band energy, \(E_{Ftoc}\) is the difference between Fermi energy and CBM (Figure S6), \(h\) is reduced Planck constant, \(k_B\) is Boltzmann constant, and \(T\) is temperature.

For the sake of simplicity, define the Fermi integrals as

\[
F_s(E_{Ftoc}) = \int_0^\infty \frac{E_{Ftoc}^{3/2}}{e^{(E-E_{Ftoc})/k_B T}+1} dE, \tag{S2}
\]

where \(E^* = E/k_B T\) and \(E_{Ftoc}^* = E_{Ftoc}/k_B T\). Carrier concentration \(n\), electrical conductivity \(\sigma\), Seebeck coefficient \(S\), Lorentz constant \(L_o\), \(Z\), and simplified judgment criteria of thermoelectric performance \(\beta\) can be expressed as function of Fermi integrals:

\[
n = \frac{N_v}{2\pi^2} \left( \frac{2m^*k_B T}{h^2} \right)^{3/2} \tilde{F}_{1/2}, \tag{S3}
\]

\[
\sigma = \frac{N_v e^2 \tau}{3\pi^2 m^*} \left( \frac{2m^*k_B T}{h^2} \right)^{3/2} \left( \frac{r+3}{2} \right) F_{r+1/2} = \sigma_0, \tag{S4}
\]

\[
|S| = \left( \frac{k_B}{e} \right) \left[ \frac{(r+5)^2 F_{r+3/2}}{(r+2)^2 F_{r+1/2}} - E_{Ftoc} \right], \tag{S5}
\]

\[
L_o = \left( \frac{k_B}{e} \right)^2 \left[ \frac{(r+5)^2 F_{r+3/2}}{(r+2)^2 F_{r+1/2}} \right] \left( \frac{r+3}{2} \right) F_{r+1/2} = \tilde{F}_{1/2}, \tag{S6}
\]

\[
ZT = \left[ \frac{1}{\tilde{F}_{1/2}} + \frac{1}{\tilde{F}_{3/2}} - \frac{1}{\tilde{F}_{1/2}} \right] F_{r+1/2} \left( \frac{r+3}{2} \right) F_{r+3/2} \left( \frac{r+2}{2} \right) F_{r+1/2}, \tag{S7}
\]

\[
\beta = \frac{N_v}{3\pi^2} \left( \frac{2m^*k_B T}{h^2} \right)^{3/2} \left( \frac{3}{32} \right) k_B T \frac{m^*}{\tilde{k}_l}. \tag{S8}
\]

where \(\tau\) is relaxation time, and \(r\) is scattering parameter: \(r = -1/2\) for acoustic phonon scattering, \(r = 1/2\) for polar optical phonon scattering, and \(r = 3/2\) for ionized impurity scattering. For AgInSe\(_2\), acoustic phonon scattering plays a primary role in electron transport.\(^\text{[2]}\). The relationship between \(ZT\) and \(\beta\) is shown in Figure S7, thus the optimized carrier concentration at \(ZT_{max}\) is higher than the carrier concentration threshold of degenerate semiconductor. The carrier concentration threshold of
degenerate semiconductor is when $E_{F_{loc}} = 0$ and $F_{1/2} = 0.68$, and corresponding carrier concentration is

$$n = \frac{0.68N_v}{2\pi^2} \left( \frac{2m^*k_BT}{h^2} \right)^\frac{3}{2},$$ (S9)

The effective mass can be obtained from the band structure calculation, and here $N_v = 1$ and $m^* = 0.16 m_e$. The threshold of degenerate semiconductors for n-type AgInSe$_2$ is $1.2 \times 10^{18}$ cm$^{-3}$ at 300 K.

**Phonon Calculations:**

The phonon dynamics are calculated by phonon spectral function $S_{\vec{k}S}(\omega)$[3–5]:

$$S_{\vec{k}S}(\omega) = \frac{2\omega_{\vec{k}S}r_{\vec{k}S}(\omega)}{(\omega^2-\omega^2_{\vec{k}S}-2\omega_{\vec{k}S}\Delta_{\vec{k}S}(\omega))^2+4\omega^2_{\vec{k}S}r^2_{\vec{k}S}(\omega)},$$ (S10)

where $\omega_{\vec{k}S}$ is the eigenfrequency of the phonon mode $(\vec{k}, S)$, $\Delta_{\vec{k}S}(\omega)$ and $r_{\vec{k}S}(\omega)$ are the real and imaginary part of phonon self-energy $\Sigma_{\vec{k}S}(\omega)$, respectively. For simplicity, we approximate $\Sigma_{\vec{k}S}(\omega)$ by its low order perturbations:

$$\Sigma_{\vec{k}S}(\omega) \approx \Sigma^{(1)}_{\vec{k}S}(\omega) + \Sigma^{(2)}_{\vec{k}S}(\omega) = \left[ \Delta^{(1)}_{\vec{k}S}(\omega) + i\Gamma^{(1)}_{\vec{k}S}(\omega) \right] + \left[ \Delta^{(2)}_{\vec{k}S}(\omega) + i\Gamma^{(2)}_{\vec{k}S}(\omega) \right].$$ (S11)

The first bracket is the first- and second-order perturbations as calculated from the loop and bubble diagrams. The imaginary part $\Gamma^{(1)}_{\vec{k}S}(\omega)$ is essentially determined by 3ph and isotopic scattering. The second bracket is associated with 4ph interactions.[6,7] The phonon self-energy up to second-order quartic anharmonic perturbations can be written as:

$$\Delta^{(1)}_{\vec{k}S}(\omega) = \frac{24}{h^2} \sum_{\vec{k},s_1} V_4(\vec{k}, s; -\vec{k}, s; \vec{k}_1, s_1; -\vec{k}_1, s_1)(n_1 + \frac{1}{2}) - \frac{18}{h^2} \sum_{\vec{k},s_1} \sum_{\vec{k}_2,s_2} V_3(\vec{k}, s; \vec{k}_1, s_1; \vec{k}_2, s_2)^2 \times \mathcal{P} \left( \frac{n_1 + n_2 + 1}{\omega + \omega_1 + \omega_2} - \frac{n_1 + n_2 + 1}{\omega - \omega_1 - \omega_2} + \frac{n_1 - n_2}{\omega - \omega_1 + \omega_2} - \frac{n_1 - n_2}{\omega + \omega_1 - \omega_2} \right),$$ (S12)

$$\Gamma^{(1)}_{\vec{k}S}(\omega) = \frac{18\pi}{h^2} \sum_{\vec{k},s_1} \sum_{\vec{k}_2,s_2} |V_3(\vec{k}, s; \vec{k}_1, s_1; \vec{k}_2, s_2)|^2 \times \left( (n_1 + n_2 + 1)[\delta(\omega - \omega_1 - \omega_2) - \delta(\omega + \omega_1 + \omega_2)] + (n_1 - n_2)[\delta(\omega + \omega_1 - \omega_2) - \delta(\omega - \omega_1 + \omega_2)] + \Gamma_{iso}(\omega) \right),$$ (S13)
\[ \Delta_{k,s}^{(2)}(\omega) = \frac{-96}{h^2} \sum_{k_1,s_1} \sum_{k_2,s_2} \sum_{k_3,s_3} |V_4(\vec{k}, s; \vec{k}_1, s_1; \vec{k}_2, s_2; \vec{k}_3, s_3)|^2 \times \mathcal{P} \left\{ [(n_1 + 1)(n_2 + 1)(n_3 + 1) - n_1 n_2 n_3] \times \left( \frac{1}{\omega + \omega_1 + \omega_2 + \omega_3} - \frac{1}{\omega - \omega_1 - \omega_2 - \omega_3} \right) + 3[n_1(n_2 + 1)(n_3 + 1) - (n_1 + 1)n_2 n_3] \times \left( \frac{1}{\omega + \omega_1 + \omega_2 + \omega_3} - \frac{1}{\omega - \omega_1 - \omega_2 - \omega_3} \right) - \frac{576}{h^2} \sum_{k_1,s_1} \sum_{k_2,s_2} \sum_{k_3,s_3} |V_4(\vec{k}, s; -\vec{k}, s; -\vec{k}_1, s_1; \vec{k}_1, s_2) V_4(\vec{k}, s; \vec{k}_1, s_1; -\vec{k}_2, s_2; \vec{k}_3, s_3; -\vec{k}_3, s_3)| \times \mathcal{P} \left( \frac{n_1 + n_2 + 1}{\omega_1 + \omega_2} - \frac{n_1 - n_2}{\omega_1 - \omega_2} \right) (n_3 + \frac{1}{2}) \right\} \right\} (S14) \]

\[ \Gamma_{k,s}^{(2)}(\omega) = \frac{96\pi}{h^2} \sum_{k_1,s_1} \sum_{k_2,s_2} \sum_{k_3,s_3} |V_4(\vec{k}, s; \vec{k}_1, s_1; \vec{k}_2, s_2; \vec{k}_3, s_3)|^2 \times [(n_1 + 1)(n_2 + 1)(n_3 + 1) - n_1 n_2 n_3] \delta(\omega + \omega_1 + \omega_2 + \omega_3) + 3[n_1(n_2 + 1)(n_3 + 1) - (n_1 + 1)n_2 n_3] \delta(\omega + \omega_1 + \omega_2 + \omega_3) - \delta(\omega - \omega_1 + \omega_2 + \omega_3)] (S15) \]

\[ \omega_i = \omega_{k_i,s_i} \]

\[ n_i \equiv n_{k_i,s_i} = \frac{1}{e^{\hbar \omega_i/kT} - 1} \] (S17)

where \( V_3 \) and \( V_4 \) are the anharmonic coefficients of cubic and quartic anharmonic force constants \( \Phi_3 \) and \( \Phi_4 \), respectively. \( \delta \) and \( \mathcal{P} \) denote Dirac \( \delta \)-function and the principal value.

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References

Figure 1

622x584mm (130 x 130 DPI)
Figure 2

247x179mm (300 x 300 DPI)
Figure 3

235x185mm (300 x 300 DPI)
Figure 4

175x190mm (150 x 150 DPI)