Research Article

Crystalline Structure-Dependent Mechanical and Thermoelectric Performance in Ag$_2$Se$_{1-x}$S$_x$ System

Jiasheng Liang$^{1,2}$, Pengfei Qiu$^1$, Yuan Zhu$^3$, Hui Huang$^{1,2}$, Zhiqiang Gao$^{1,2,4}$, Zhen Zhang$^3$, Xun Shi$^{1,4}$, and Lidong Chen$^{1,2}$

$^1$State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China
$^2$Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China
$^3$Division of Solid-State Electronics, Department of Electrical Engineering, Uppsala University, Uppsala, Sweden
$^4$School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China

Correspondence should be addressed to Pengfei Qiu; qiupf@mail.sic.ac.cn and Xun Shi; xshi@mail.sic.ac.cn

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Self-powered wearable electronics require thermoelectric materials simultaneously with a high dimensionless figure of merit ($zT$) and good flexibility to convert the heat discharged by the human body into electricity. Ag$_2$(S,Se)-based semiconducting materials can well satisfy these requirements, and thus, they are attracting great attention in thermoelectric society recently. Ag$_2$(S,Se) crystallizes in an orthorhombic structure or monoclinic structure, depending on the detailed S/Se atomic ratio, but the relationship between its crystalline structure and mechanical/thermoelectric performance is still unclear to date. In this study, a series of Ag$_2$Se$_{1-x}$S$_x$ ($x = 0, 0.1, 0.2, 0.3, 0.4$, and $0.45$) samples were prepared and their mechanical and thermoelectric performance dependence on the crystalline structure was systematically investigated. $x = 0.3$ in the Ag$_2$Se$_{1-x}$S$_x$ system was found to be the transition boundary between orthorhombic and monoclinic structures. Mechanical property measurement shows that the orthorhombic Ag$_2$Se$_{1-x}$S$_x$ samples are brittle while the monoclinic Ag$_2$Se$_{1-x}$S$_x$ samples are ductile and flexible. In addition, the orthorhombic Ag$_2$Se$_{1-x}$S$_x$ samples show better electrical transport performance and higher $zT$ than the monoclinic samples under a comparable carrier concentration, most likely due to their weaker electron-phonon interactions. This study sheds light on the further development of flexible inorganic TE materials.

1. Introduction

Recently, thermoelectric (TE) technology shows a great potential to be used as a sustainable power source in wearable electronics [1–3]. Via harvesting the heat discharged by the human body and converting it into electricity, the wearable electronics using TE technology can be self-powered without using any external batteries. The energy conversion efficiency of a TE material is determined by the dimensionless figure of merit, $zT = \alpha^2 T/\kappa$, where $\alpha$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $\kappa$ is the thermal conductivity, and $T$ is the absolute temperature. The TE material used in wearable electronics should possess high $zT$ to maximize the energy conversion efficiency and good flexibility to match the curved surface of skin and endure repeated bending during service [4–6]. To date, Bi$_2$Te$_3$-based alloys are still the best room-temperature TE materials, but their application in wearable electronics is limited due to their inherent brittleness [7–14]. In contrast, the organic TE polymers show good flexibility, but their $zT$s are low [15–20]. Recently, we reported a class of Ag,S-based flexible inorganic TE materials with excellent intrinsic flexibility and high $zT$s [21]. Monoclinic Ag$_2$S shows surprisingly high ductility at room temperature due to its wrinkled layer structure (space group $P2_1/n$, with the sketch map shown in Figure 1(a), and weak Ag-S chemical bonds [22, 23]. However, its relatively wide band gap (around 1 eV) yields low $\sigma$ only in the order of $10^3$ S m$^{-1}$. As a result, $zT$ of the stoichiometric Ag$_2$S around room temperature is very poor. Alloying Se or/and Te in Ag$_2$S can significantly improve $\sigma$ and enhance $zT$ to 0.26 for Ag$_2$S$_{0.5}$Se$_{0.5}$ and 0.44 for Ag$_2$S$_{0.5}$Se$_{0.45}$Te$_{0.05}$ at 300 K.
Particularly, previous study showed that the good ductility can be well maintained when the Se alloying content in Ag$_2$S reaches 50% or the Te alloying content reaches 20%, enabling these materials very suitable to be used in flexible wearable electronics. The above results arouse great interest on the Ag$_2$S-based materials in TE society [21, 23–25].

Being different with ductile Ag$_2$S, Ag$_2$Se is a brittle material. It adopts an orthorhombic structure (space group $P_{2_1}2_12_1$) with the sketch map shown in Figure 1(b). The band gap of orthorhombic Ag$_2$Se is around 0.2 eV, about one-fifth of that of monoclinic Ag$_2$S. Orthorhombic Ag$_2$Se has very high carrier mobility ($\sim$10$^3$ cm$^2$ V$^{-1}$ s$^{-1}$), excellent $\sigma$ ($\sim$10$^5$ S m$^{-1}$), and extremely low lattice thermal conductivity ($\sim$0.3–0.5 W m$^{-1}$ K$^{-1}$), resulting in high $zT$ about 0.4–1.0 at 300 K [26–32]. Despite the different crystalline structures of Ag$_2$S and Ag$_2$Se, Bindi and Pingitore [33] reported that Ag$_2$S and Ag$_2$Se can form a continuous solid solution. The room-temperature crystalline structure of Ag$_2$S$_{1-x}$Se$_x$ solid

![Figure 1: Crystalline structures for (a) monoclinic Ag$_2$S and (b) orthorhombic Ag$_2$Se. (c) Room-temperature X-ray diffraction patterns for Ag$_2$Se$_{1-x}$S$_x$ ($x = 0, 0.1, 0.2, 0.3, 0.4$, and $0.45$) samples. The right panel shows the magnification around 2$\theta = 30$–35°. (d) Backscatter electron (AsB) image and elemental energy dispersive spectroscopy (EDS) mappings of Ag$_2$Se$_{0.7}$S$_{0.3}$](image)
solution is the same with the monoclinic Ag$_2$S when $x \leq 0.6$, but the same with the orthorhombic Ag$_2$Se when $x \geq 0.7$. Considering that the carrier concentration of Ag$_2$Se is about several orders of magnitude higher than that of Ag$_2$S [22], Ag$_2$Se$_{1-x}$Se$_x$ solid solution might process continuous adjustable carrier concentrations and TE properties. The mechanical properties and TE performance of Ag$_2$Se$_{1-x}$Se$_x$ (0.5 $\leq x \leq 1$) have been already reported previously [33], but those of Ag$_2$Se$_{1-x}$S$_x$ (0 $\leq x \leq 0.5$) have not been investigated yet. Particularly, the relationship between crystalline structure and mechanical/TE performance for Ag$_2$Se$_{1-x}$S$_x$ solid solution is still unclear so far.

In this study, a series of polycrystalline Ag$_2$Se$_{1-x}$S$_x$ ($x = 0, 0.1, 0.2, 0.3, 0.4$, and 0.45) samples were prepared. Their crystalline structures, mechanical properties, and TE properties were systematically investigated. $x = 0.3$ in the Ag$_2$Se$_{1-x}$S$_x$ system was identified to be the transition boundary of the orthorhombic structure and monoclinic structure. Orthorhombic Ag$_2$Se$_{1-x}$S$_x$ ($x = 0, 0.1, \text{and} 0.2$) samples are brittle, while monoclinic Ag$_2$Se$_{1-x}$S$_x$ ($x = 0.4$ and 0.45) are ductile and flexible. Due to the stronger electron-phonon interaction, monoclinic Ag$_2$Se$_{0.6}$S$_{0.4}$ has lower PF and $zT$ than orthorhombic Ag$_2$Se$_{1-x}$S$_x$ ($x = 0, 0.1, \text{and} 0.2$). However, the superior TE performance and thermal stability to the organic TE materials and the intrinsically good flexibility still promise a great potential for monoclinic Ag$_2$Se$_{1-x}$S$_x$ to be used in wearable electronics.

2. Results and Discussion

Figure 1(c) shows the X-ray diffraction patterns for the prepared Ag$_2$Se$_{1-x}$S$_x$ ($x = 0, 0.1, 0.2, 0.3, 0.4$, and 0.45) obtained at room temperature. When the S content $x < 0.3$, the diffraction peaks are well indexed to the orthorhombic structure of Ag$_2$Se with the space group of P2$_1/2_1/2_1$. This indicates that Ag$_2$Se$_{0.9}$S$_{0.1}$ and Ag$_2$Se$_{0.8}$S$_{0.2}$ still adopt the same crystalline structure with Ag$_2$Se at room temperature. When $x = 0.4$ and 0.45, the diffraction peaks agree well with the monoclinic structure of Ag$_2$S phase with the space group of P2$_1/n$. Likewise, the Ag$_2$Se$_{1-x}$S$_x$ ($x \geq 0.5$) samples also crystalize in the same monoclinic structure of Ag$_2$S [21]. Elemental energy dispersive spectroscopy (EDS) mappings confirm that all elements are homogeneously distributed in Ag$_2$Se$_{0.9}$S$_{0.1}$, Ag$_2$Se$_{0.8}$S$_{0.2}$, Ag$_2$Se$_{0.6}$S$_{0.4}$, and Ag$_2$Se$_{0.5}$S$_{0.5}$. No obvious secondary phase is observed. Thus, these samples are phase pure. Likewise, scanning electron microscopy (SEM) performed on the cross-section of Ag$_2$Se$_{0.6}$S$_{0.4}$ indicates that it has an obvious layered structure (cf. Fig. S1).

One special composition in the Ag$_2$Se$_{1-x}$S$_x$ system is Ag$_2$Se$_{0.6}$S$_{0.4}$. As shown in Figure 1(c), its X-ray diffraction pattern looks like that of monoclinic Ag$_2$Se$_{0.6}$S$_{0.4}$. However, besides those belonging to the monoclinic structure, some extra diffraction peaks with weak intensities are also observed, such as at 2$\theta$ = 31’ and (112) at 2$\theta$ = 34’ (right panel in Figure 1(c)). These are indexed to the orthorhombic structure. Thus, Ag$_2$Se$_{0.6}$S$_{0.4}$ is believed to be a mixture rather than a pure phase, in which the main phase crystallizes in the monoclinic structure while the secondary phase crystallizes in the orthorhombic structure. This result is different from that proposed by Bindi and Pingitore [33] that Ag$_2$Se$_{0.6}$S$_{0.4}$ crystallizes in the same orthorhombic structure with Ag$_2$Se. Figure 1(d) shows the EDS mappings performed on Ag$_2$Se$_{0.8}$S$_{0.2}$. Surprisingly, all elements are still homogeneously distributed. Thus, it is concluded that the two different phases in Ag$_2$Se$_{0.8}$S$_{0.2}$ have very similar chemical compositions but different crystalline structures. A similar polymorphic feature has been also observed in the C$_2$H$_8$S$_4$ system [34]. Combining the above result, it can be concluded that the transition boundary between the monoclinic and orthorhombic structures in Ag$_2$Se$_{1-x}$S$_x$ solid solution should be around $x = 0.3$.

Ag$_2$Se$_{1-x}$S$_x$ ($x = 0, 0.1, 0.2, 0.3, 0.4$, and 0.45) samples possess structure-dependent mechanical properties. The three-point bending test and Vickers hardness test were performed on Ag$_2$Se$_{1-x}$S$_x$. The material with larger bending deformation or small Vickers hardness is usually a benefit for the application in flexible electronics [2, 3, 6]. Figure 2(a) shows that orthorhombic Ag$_2$Se can only endure a very small bending strain before cracking. The maximum bending deformation is about 0.56%. Likewise, orthorhombic Ag$_2$Se$_{0.8}$S$_{0.2}$ also possesses a maximum bending deformation around 1.5%. The case is different for monoclinic Ag$_2$Se$_{0.6}$S$_{0.4}$, which exhibits a bending deformation above 10% without cracking. Previously, large bending deformation was also observed for monoclinic Ag$_2$Se$_{1-x}$S$_x$ ($x = 0.5, 0.7, 0.9, \text{and} 1$) in the bending test. It should be noted that such deformation is plastic, which is different from the elastic deformation of brittle materials with low dimension. Likewise, Vickers hardness for orthorhombic Ag$_2$Se is 43.7 Hv at room temperature. It is monotonously increased to 51.5 Hv and 62.7 Hv for the orthorhombic Ag$_2$Se$_{0.6}$S$_{0.4}$ and Ag$_2$Se$_{0.8}$S$_{0.2}$, respectively. However, monoclinic Ag$_2$Se$_{0.6}$S$_{0.4}$ has low Vickers hardness of only 33.8 Hv, about half of that for orthorhombic Ag$_2$Se$_{0.8}$S$_{0.2}$. As shown in Figure 2(c), Ag$_2$Se$_{0.6}$S$_{0.4}$ can be directly cut into thin strips with thickness about 0.1 mm like metal. Furthermore, these metal-like strips can be twisted into various shapes without cracking, confirming that Ag$_2$Se$_{0.6}$S$_{0.4}$ has good ductility and flexibility.

The above test results prove that the monoclinic structure has significantly better ductility and flexibility in the Ag$_2$Se$_{1-x}$S$_x$ system. The high cleavage energy and low slipping energy, related to the unique wrinkled layer structure, are the fundamental reason for the good ductility observed in monoclinic Ag$_2$Se$_{1-x}$S$_x$. Previous investigation found that the S atoms in monoclinic Ag$_2$S always bonded to part of the surrounding Ag atoms during slipping [22, 35], which is benefit for preventing the material’s cleavage under mechanical stress. Likewise, it enables the bonding energy between Ag and S atoms to change fluently, yielding a low energy barrier for slipping. However, in the orthorhombic structure, such unique wrinkled layer structure does not exist; thus, the orthorhombic Ag$_2$Se$_{1-x}$S$_x$ samples are brittle. Here, it should be noted that although the main phase in Ag$_2$Se$_{0.7}$S$_{0.3}$ crystallizes in the monoclinic structure, Ag$_2$Se$_{0.7}$S$_{0.3}$ still has low maximum bending deformation around 0.88%. The reason should be attributed to the presence of brittle orthorhombic grains.
among the ductile monoclinic grains. The second phase strengthening effect caused by these brittle orthorhombic grains will impede the movement of atoms, dislocations, or interfaces under mechanical stress like that in the pure orthorhombic phase, yielding poor ductility for Ag$_2$Se$_{0.3}$.

Figure 3 shows the measured $\sigma$ and $\alpha$ for Ag$_2$Se$_{1-x}$S$_x$ ($x = 0, 0.1, 0.2, 0.3, 0.4,$ and $0.45$). All samples possess negative $\alpha$, indicating that they are $n$-type semiconductors with electrons dominating the electrical transports. This scenario is the same with those Ag$_2$Se$_{0.55}$S$_{0.45}$ samples. Obvious $\sigma$ and $\alpha$ discontinuous jumps are observed between 360 K and 420 K, which are attributed to the orthorhombic-cubic or monoclinic-cubic phase transition. For example, Ag$_2$Se experiences orthorhombic-cubic phase transition around 410 K. At 300 K, $\sigma$ for Ag$_2$Se is about $1.4 \times 10^5$ S·m$^{-1}$. It increases with increasing temperature, reaching around $3.1 \times 10^5$ S·m$^{-1}$ at 403 K, and then decreases to $1.9 \times 10^5$ S·m$^{-1}$ after the phase transition. The $\sigma$ value for Ag$_2$Se$_{0.55}$S$_{0.45}$ at 300 K is only $3.6 \times 10^4$ S·m$^{-1}$, almost one-fourth of the pristine Ag$_2$Se. Likewise, the $\alpha$ values vary from -146 $\mu$V·K$^{-1}$ to -105 $\mu$V·K$^{-1}$ at 300 K and from -45 $\mu$V·K$^{-1}$ to -109 $\mu$V·K$^{-1}$ at 420 K, without obvious chemical composition dependence. Furthermore, Fig. S2 shows that the prepared samples have good reproducibility. When the chemical composition and fabrication process are fixed, different batches of samples have comparable $\sigma$ and $\alpha$ data.

With the purpose to understand the electrical transport properties of Ag$_2$Se$_{1-x}$S$_x$, Hall measurements were performed. The Hall carrier concentration ($n_H$) and mobility ($\mu_H$) at 300 K are listed in Table SI. All Ag$_2$Se$_{1-x}$S$_x$ samples possess $n_H$ in the order of $10^{16}$ cm$^{-3}$. However, being similar with the above measured $\sigma$ and $\alpha$, the $n_H$ values do not have monotonous variation with the sulfur content. The different contents of intrinsic defects inside the lattice, such as Ag interstitials, are expected to be the reason for this scenario. Likewise, the $\mu_H$ values for the Ag$_2$Se$_{1-x}$S$_x$ samples are in the range of 309 cm$^2$·V$^{-1}$·s$^{-1}$ to 1337 cm$^2$·V$^{-1}$·s$^{-1}$. These $\mu_H$ values are quite high as compared with other state-of-the-art TE materials, such as 190 cm$^2$·V$^{-1}$·s$^{-1}$ for $n$-type Bi$_2$Te$_3$ [36] and 48 cm$^2$·V$^{-1}$·s$^{-1}$ for $n$-type filled skutterudites [37]. A single parabolic model (SPB) is used to further understand the electrical transports of Ag$_2$Se$_{1-x}$S$_x$. According to the SPB model, the Seebeck coefficient, carrier concentration, and carrier mobility can be correlated as follows [38–40]:

$$\alpha = \frac{K_B}{e} \left[ \frac{2 + \lambda}{1 + \lambda} F_{\Lambda \Sigma}(\eta) - \eta \right], \quad (1)$$

$$n_H = 4\pi \left( \frac{2m^*k_B T}{\hbar^2} \right)^{3/2} F_{1/2}(\eta) \frac{1}{\tau_H}, \quad (2)$$

$$\mu_H = \frac{3\sqrt{\pi} (1/2) + 2\lambda}{4} \frac{1}{1 + \lambda} \frac{1}{F(2 + \lambda)} F_{2\lambda-1/2} \mu_{ph}, \quad (3)$$

$$\mu_{ph} = \frac{(8\pi)^{1/2} e \hbar^2 \rho v_T^2}{3(k_B T)^{3/2} (m^*)^{5/2} \zeta^2}, \quad (4)$$

Figure 2: (a) Strain-stress curves for the three-point bending test of Ag$_2$Se$_{1-x}$S$_x$ ($x = 0, 0.1, 0.3,$ and $0.4$) samples at 300 K. The tests were performed by using a dynamic mechanical analyzer (DMA). The insets show the optical images of Ag$_2$Se$_{0.6}$S$_{0.4}$ sample before and after the bending test. The data for Ag$_2$S are included for comparison [22]. (b) Vickers hardness of Ag$_2$Se$_{1-x}$S$_x$ under the load of 0.3 kgf. The insets are micrographs of indentation. Vickers hardness of Ag$_2$S reported in Ref. 22 is included for comparison. (c) Ag$_2$Se$_{0.6}$S$_{0.4}$ strips twisted into various shapes. The thickness of Ag$_2$Se$_{0.6}$S$_{0.4}$ strips is 0.1 mm.
Figure 3: Temperature dependences of (a) electrical conductivity $\sigma$ and (b) Seebeck coefficient $\alpha$ for $\text{Ag}_2\text{Se}_{1-x}\text{S}_x$ ($x = 0, 0.1, 0.2, 0.3, 0.4,$ and 0.45). (c) Temperature dependence of power factor (PF) for $\text{Ag}_2\text{Se}_{1-x}\text{S}_x$ ($x = 0, 0.1, 0.2, 0.3, 0.4,$ and 0.45). (d) Seebeck coefficient $\alpha$, (e) Hall carrier mobility $\mu_H$, and (f) PF as a function of carrier concentration $n_H$ for $\text{Ag}_2\text{Se}_{1-x}\text{S}_x$ at 300 K. The dashed lines represent the theoretical curves based on the single parabolic band (SPB) model with a dominated scattering mechanism by acoustic phonons. The data for $\text{Ag}_2\text{Se}$ and $\text{Ag}_2\text{Se}_{0.5}\text{S}_{0.5}$ reported before are added for comparison [21, 26–29].
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Ag$_2$Se$_0.7$S$_0.3$ are not included because its polymorphic feature is nondegenerate limit, and $\Xi$ is the deformation potential. $F_m(\eta)$ is the Fermi integrals, and it is given by equation

$$F_m(\eta) = \int_0^\infty x^m dx/(1 + e^{-x})$$

where $x$ represents the reduced carrier energy and $\eta = E_f/k_B T$ is the reduced Fermi energy.

Figure 3(d) presents that the $\alpha$ and $n_{th}$ data for the present Ag$_2$Se$_{1-x}$S$_x$ ($x = 0, 0.1, 0.2, 0.3, 0.4,$ and 0.45) samples roughly fall around the calculated theoretical Pasarenko curve with $m^* = 0.25 m_e$ ($m_e$ is the mass of free electron) and $\lambda = 0$ (acoustic phonon scattering). For comparison, the previously reported data for Ag$_2$Se and Ag$_2$Se$_0.5$S$_0.5$ are also summarized in Figure 3(d). These data also fall around the theoretical curve. This scenario suggests that all these samples might possess a similar band structure near the Fermi level, despite the fact that some of them crystallize in the monoclinic structure while others in the orthorhombic structure. This is possible because the conduction band minimums of Ag$_2$S and Ag$_2$Se are at the same gamma point and both of them are mainly dominated by Ag-Ss electrons [21, 41]. Alloying S at the Se sites would mainly alter the valence band maximum instead of the conduction band minimum, yielding the similar $m^*$ mentioned above. In addition, the small $m^*$, about 0.25$m_e$ for these Ag$_2$(S,Se) samples, are responsible for their higher $\mu_{th}$ than those for n-type Bi$_2$Te$_3$ [36] and filled skutterudites [37] mentioned above.

Figure 3(e) plots the $\mu_{th}$ and $n_{th}$ relationship at 300 K for Ag$_2$Se$_{1-x}$S$_x$ ($x = 0, 0.1, 0.2, 0.4, 0.45,$ and 0.5). The data for Ag$_2$Se$_{0.5}$S$_{0.5}$ are not included because its polymorphic feature might introduce extra boundary scattering to electrons and interrupt the understanding on the carrier mobility. As shown in Figure 3(e), under the similar $n_{th}$, the Ag$_2$Se$_{1-x}$S$_x$ ($x = 0, 0.1,$ and 0.2) and the orthorhombic structure have higher $\mu_{th}$ than the Ag$_2$Se$_{1-x}$S$_x$ ($x = 0.4, 0.45,$ and 0.5) samples with a monoclinic structure. By fitting the experimental data of the $\mu_{th}$ and $n_{th}$ relationship using Equations (1)–(5), deformation potential values of 11 eV and 19 eV can be extracted for the orthorhombic Ag$_2$Se$_{1-x}$S$_x$ ($x = 0, 0.1,$ and 0.2) and the monoclinic Ag$_2$Se$_{1-x}$S$_x$ ($0.4, 0.45,$ and 0.5), respectively. The thermal vibrations of the crystal lattice can influence the energy-band structure and perturb the carrier transports. The intensity of such interaction between electrons and phonons can be reflected by the magnitude of $\Xi$ [42]. The lower $\Xi$ value for the orthorhombic Ag$_2$Se$_{1-x}$S$_x$ suggests that the electron-phonon interaction wherein is weaker than that in the monoclinic Ag$_2$Se$_{1-x}$S$_x$. This is responsible for the higher $\mu_{th}$ observed for the orthorhombic Ag$_2$Se$_{1-x}$S$_x$.

The power factors (PF) for Ag$_2$Se$_{1-x}$S$_x$ ($x = 0, 0.1, 0.2, 0.3, 0.4,$ and 0.45) samples calculated from the formula $\text{PF} = a^2 \cdot \sigma$ are shown in Figure 3(c). At 300 K, the PF value for Ag$_2$Se reaches 22.5 $\mu$W·cm$^{-1}$·K$^{-2}$. It gradually decreases with increasing the S-alloying content. At 300 K, the PF for Ag$_2$Se$_{0.55}$S$_{0.45}$ is just 5.2$\mu$W·cm$^{-1}$·K$^{-2}$, about one-fourth of that for Ag$_2$Se. The greatly reduced $\sigma$ is responsible for the lowered PF. The PF value for Ag$_2$Se$_{0.5}$S$_{0.5}$ is comparable with that for Ag$_2$Se$_{0.5}$S$_{0.5}$ reported before [21, 24], about 4.8 $\mu$W·cm$^{-1}$·K$^{-2}$ at 300 K. Based on the SPB model, the theoretical PF vs. $n_{th}$ curves at 300 K can be obtained for the orthorhombic and monoclinic Ag$_2$Se$_{1-x}$S$_x$ samples, respectively. As shown in Figure 3(f), the experimental PF and $n_{th}$ data basically fall around these lines. Under the comparable $n_{th}$, the PF for the orthorhombic Ag$_2$Se$_{1-x}$S$_x$ samples are much higher than those of the monoclinic Ag$_2$Se$_{1-x}$S$_x$ samples. The reason is that the orthorhombic samples have weaker electron-phonon interaction than the monoclinic samples, which yields lower $\Xi$ value for higher $\mu_{th}$ and PF. In addition, based on the SPB model, the optimal carrier concentration ($n_{opt,PF}$) corresponding to the peak PF is around 3.4 $\times$ 10$^{18}$ cm$^{-3}$ for both orthorhombic and monoclinic Ag$_2$Se$_{1-x}$S$_x$. $\mu_{th}$ for the present orthorhombic Ag$_2$Se$_{1-x}$S$_x$ ($x = 0, 0.1,$ and 0.2) and monoclinic Ag$_2$Se$_{1-x}$S$_x$ ($x = 0.4$) samples are already close to this $n_{opt,PF}$ value.

Figure 4(a) shows $\kappa$ as a function of temperature for Ag$_2$Se$_{1-x}$S$_x$ ($x = 0, 0.1, 0.2, 0.3, 0.4,$ and 0.45). The discontinuous jumps on the $\kappa$ curves are attributed to the orthorhombic-cubic or monoclinic-cubic phase transitions. $\kappa$ ranges from 0.7 W·m$^{-1}$·K$^{-1}$ to 1.4 W·m$^{-1}$·K$^{-1}$ for all samples. Ag$_2$Se$_{0.6}$S$_{0.4}$ exhibits the lowest $\kappa$ among all samples. $\kappa$ for Ag$_2$Se$_{0.6}$S$_{0.4}$ at 300 K is around 0.7 W·m$^{-1}$·K$^{-1}$. This value is about 36% decrement as compared with that for Ag$_2$Se$_{0.8}$S$_{0.2}$. Generally, $\kappa$ is composed of two parts: the electron part $\kappa_e$ and the lattice part $\kappa_L$. $\kappa_e$ can be calculated according to the Wiedemann-Franz law [43]. Figure 4(b) shows the calculated $\kappa_e/\kappa$ for Ag$_2$Se$_{1-x}$S$_x$ ($x = 0, 0.1, 0.2, 0.3, 0.4,$ and 0.45). It can be seen that the $\kappa_e/\kappa$ values are in the range of 48% to 80%, indicating that the carriers’ contribution is very important in the thermal transports. By subtracting $\kappa_e$ from $\kappa$, $\kappa_L$ can be obtained. The results at 300 K are listed in Table SI. They range from 0.20 W·m$^{-1}$·K$^{-1}$ to 0.48 W·m$^{-1}$·K$^{-1}$, which are very low values as compared with those for the state-of-the-art TE materials [44–49]. The proximity to the cubic superionic phase is responsible for the low $\kappa_L$ values observed in these orthorhombic and monoclinic phases [23].

Based on the measured $\alpha$, $\sigma$, and $\kappa$, $zT$ can be calculated according to $zT = \alpha^2 \sigma T / \kappa T$ for orthorhombic Ag$_2$Se is around 0.6 in the whole measured temperature range, which is comparable with those reported before [28–30]. Orthorhombic Ag$_2$Se$_{0.6}$S$_{0.4}$ and Ag$_2$Se$_{0.5}$S$_{0.5}$ possess comparable $zTs$ with Ag$_2$Se. However, $zTs$ for monoclinic Ag$_2$Se$_{0.6}$S$_{0.4}$ and Ag$_2$Se$_{0.5}$S$_{0.5}$ are much lower than those for orthorhombic Ag$_2$Se. At 300 K, $zT$ is just 0.26 for Ag$_2$Se$_{0.6}$S$_{0.4}$ and 0.23 for Ag$_2$Se$_{0.5}$S$_{0.5}$.

As shown in Figure 4(d), the theoretical $zT$ vs. $n_{th}$ curves for orthorhombic and monoclinic Ag$_2$Se$_{1-x}$S$_x$ samples at 300 K are given by assuming that all samples possess the same $\kappa_L = 0.4$ W·m$^{-1}$·K$^{-1}$. The experimental $zT$ and $n_{th}$ data basically fall around these lines. Under the comparable $n_{th}$, $zT$ for the orthorhombic Ag$_2$Se$_{1-x}$S$_x$ samples is much higher than that of the monoclinic Ag$_2$Se$_{1-x}$S$_x$ samples because their
weaker electron-phonon interaction yields lower $\Xi$ value and larger $\mu_H$ for higher PF. The optimal carrier concentration ($n_{\text{opt}}$) corresponding to the peak $\zeta T$ is around $1-2 \times 10^{18}$ cm$^{-3}$ for orthorhombic $\text{Ag}_2\text{Se}_{1-x}\text{S}_x$, while $2-3 \times 10^{18}$ cm$^{-3}$ for monoclinic $\text{Ag}_2\text{Se}_{1-x}\text{S}_x$, $n_{\text{H}}$ for the present orthorhombic $\text{Ag}_2\text{Se}_{1-x}\text{S}_x$ ($x = 0, 0.1, 0.2$, and $0.4$) and monoclinic $\text{Ag}_2\text{Se}_{1-x}\text{S}_x$ ($x = 0.4, 0.45$, and $0.5$) samples are still higher than these $n_{\text{opt}}$ values. Thus, if their carrier concentration can be further reduced, higher $\zeta T$ can be expected.

Although the TE performances for ductile monoclinic $\text{Ag}_2\text{Se}_{1-x}\text{S}_x$ are lower than those for brittle orthorhombic $\text{Ag}_2\text{Se}_{1-x}\text{S}_x$, their performances are still much higher than those for the organic TE materials reported before. This can be clearly reflected by the scenario shown in Figure 5. The PF values for most of the $n$-type TE organic TE materials are lower than $1 \mu\text{W} \cdot \text{cm}^{-1} \cdot \text{K}^{-2}$ at $300$ K. Even for the best $n$-type TE organic TE materials reported so far, poly(Ni-ett) [19], its PF, $3.6 \mu\text{W} \cdot \text{cm}^{-1} \cdot \text{K}^{-2}$ at $300$ K, is still lower than the present monoclinic $\text{Ag}_2\text{Se}_{1-x}\text{S}_x$. The superior PF values achieved in the monoclinic $\text{Ag}_2\text{Se}_{1-x}\text{S}_x$ samples would promise high power output when they are fabricated into TE devices. In addition, most $n$-type organic TE materials are unstable in the air because their electron affinity is too low to stabilize the $n$-type dopants [2, 50]. In contrast, the present ductile monoclinic $\text{Ag}_2\text{Se}_{1-x}\text{S}_x$ samples are inert to oxygen or water; thus, they can realize good service stability in real application. Combining the intrinsically good flexibility and ductility, these monoclinic $\text{Ag}_2\text{Se}_{1-x}\text{S}_x$ samples show great potential to be used in wearable electronics.

Figure 4: (a) Temperature dependence of thermal conductivity for $\text{Ag}_2\text{Se}_{1-x}\text{S}_x$ ($x = 0, 0.1, 0.2, 0.3, 0.4$, and $0.45$). (b) The ratio of electronic thermal conductivity to thermal conductivity ($\kappa_e/\kappa$) at $300$ K for $\text{Ag}_2\text{Se}_{1-x}\text{S}_x$. (c) Temperature dependence of TE figure of merit $\zeta T$ for $\text{Ag}_2\text{Se}_{1-x}\text{S}_x$ ($x = 0, 0.1, 0.2, 0.3, 0.4$, and $0.45$). (d) $\zeta T$ as a function of carrier concentration $n_H$ for $\text{Ag}_2\text{Se}_{1-x}\text{S}_x$ at $300$ K. The dashed lines represent the theoretical curves based on the single parabolic band (SPB) model. The data for $\text{Ag}_2\text{Se}_{0.5}\text{S}_{0.5}$ reported before are added for comparison.
3. Conclusion

In summary, this study systematically studied the crystalline structure, mechanical properties, and TE properties of Ag$_2$Se$_1$S$_x$ ($x = 0, 0.1, 0.2, 0.3, 0.4, \text{and} 0.45$). Ag$_2$Se$_1$S$_x$ samples crystallize in the orthorhombic structure when $x \leq 0.2$, while in the monoclinic structure when $x \geq 0.4$. Only the monoclinic Ag$_2$Se$_1$S$_x$ samples possess good ductility and flexibility. Under comparable carrier concentration range, the orthorhombic Ag$_2$Se$_1$S$_x$ samples have higher carrier mobility, larger power factor, and better $zT$ than the monoclinic samples because they have weaker electron-phonon interaction. This leads to lower $zT$ values of monoclinic Ag$_2$Se$_1$S$_x$ ($x = 0.4 \text{ and } 0.45$) samples than those of the orthorhombic Ag$_2$Se$_1$S$_x$ ($x = 0.1 \text{ and } 0.2$) samples. However, the higher PF and better thermal stability promise a great potential for monoclinic Ag$_2$Se$_1$S$_x$ to be used in wearable electronics.

Conflicts of Interest

The authors declare no competing financial interests.

Authors’ Contributions

P.Q., X.S., and L.C. conceived the idea. J.L. conducted the synthesis, TE transport property measurement, and bending test. Z.G. and H.H. conducted the Hall measurement and Vickers hardness measurements. J.L., P.Q., Y.Z. and Z.Z. contributed to data analysis, model interpretation, and paper drafting. J.L., P.Q., and X.S. completed the writing of the manuscript. All authors discussed the results and gave comments regarding the manuscript.

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Supplementary Materials

Materials and methods. Fig. S1: cross-section image of Ag$_2$Se$_{0.6}$S$_{0.4}$ bulk sample. Fig. S2: electrical properties for three batches of Ag$_2$Se$_{0.8}$S$_{0.2}$ and Ag$_2$Se$_{0.6}$S$_{0.4}$. Table S1: room-temperature thermoelectric properties of Ag$_2$Se$_{1-x}$S$_x$ samples. (Supplementary Materials)

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