Research Article

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

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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, $zT = \alpha^2\sigma T/\kappa$, 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 $zTs$ are low [15–20]. Recently, we reported a class of Ag$_x$S-based flexible inorganic TE materials with excellent intrinsic flexibility and high $zTs$ [21]. Monocrystalline Ag$_x$S shows surprisingly high ductility at room temperature due to its wrinkled layer structure (space group $P_{2_1}/n$, 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$_x$S around room temperature is very poor. Alloying Se or/and Te in Ag$_x$S can significantly improve $\sigma$ and enhance $zT$ to 0.26 for Ag$_{0.95}$Se$_{0.05}$ and 0.44 for Ag$_{2.5}$Se$_{0.5}$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 (~$10^3$ cm$^2$ V$^{-1}$ s$^{-1}$), excellent $\sigma$ (~$10^5$ S m$^{-1}$), and extremely low lattice thermal conductivity (~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$_{0.3}$. 

\[\text{Ag}\] 
\[\text{S}\] 
\[\text{Se}\] 

Red: Orthorhombic 
Blue: Monoclinic
solution is the same with the monoclinic Ag₂S when \( x \leq 0.6 \), but the same with the orthorhombic Ag₂Se when \( x \geq 0.7 \). Considering that the carrier concentration of Ag₂Se is about several orders of magnitude higher than that of Ag₂S [22], Ag₂Se₁₋ₓSₓ solid solution might process continuous adjustable carrier concentrations and TE properties. The mechanical properties and TE performance of Ag₂Se₁₋ₓSₓ (0.5 \( \leq x \leq 1 \)) have been already reported previously [33], but those of Ag₂Se₁₋ₓSₓ (0 ≤ \( x \leq 0.5 \)) have not been investigated yet. Particularly, the relationship between crystalline structure and mechanical/TE performance for Ag₂Se₁₋ₓSₓ solid solution is still unclear so far.

In this study, a series of polycrystalline Ag₂Se₁₋ₓSₓ (\( x = 0, 0.1, 0.2, 0.3, 0.4, \) and 0.45) samples were prepared. Their crystalline structures, mechanical properties, and TE properties were systematically investigated. \( x = 0.3 \) in the Ag₂Se₁₋ₓSₓ system was identified to be the transition boundary of the orthorhombic structure and monoclinic structure. Orthorhombic Ag₂Se₁₋ₓSₓ (\( x = 0, 0.1, \) and 0.2) samples are brittle, while monoclinic Ag₂Se₁₋ₓSₓ (\( x = 0.4 \) and 0.45) are ductile and flexible. Due to the stronger electron-phonon interaction, monoclinic Ag₂Se₀.₆S₀.₄ has lower PF and \( \eta \) than orthorhombic Ag₂Se₁₋ₓSₓ (\( x = 0, 0.1, \) 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 Ag₂Se₁₋ₓSₓ to be used in wearable electronics.

### 2. Results and Discussion

Figure 1(c) shows the X-ray diffraction patterns for the prepared Ag₂Se₁₋ₓSₓ (\( x = 0, 0.1, 0.2, 0.3, 0.4, \) 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 Ag₂Se with the space group of \( P₂₁ 2₁ 2₁ \). This indicates that Ag₂SeₙSₙ₋₁ and Ag₂SeₙSₙ₋₂ still adopt the same crystalline structure with Ag₂Se at room temperature. When \( x = 0.4 \) and 0.45, the diffraction peaks agree well with the monoclinic structure of Ag₂S phase with the space group of \( P₂₁ / n \). Likewise, the Ag₂Se₁₋ₓSₓ (\( x \geq 0.5 \)) samples also crystallize in the same monoclinic structure of Ag₂S [21]. Elemental energy dispersive spectroscopy (EDS) mappings confirm that all elements are homogeneously distributed in Ag₂Se₀.₉S₀.₁, Ag₂Se₀.₇S₀.₃, Ag₂Se₀.₅S₀.₅, and Ag₂Se₀.₃S₀.₇. No obvious secondary phase is observed. Thus, these samples are phase pure. Likewise, scanning electron microscopy (SEM) performed on the cross-section of Ag₂Se₀.₆S₀.₄ indicates that it has an obvious layered structure (cf. Fig. S1).

One special composition in the Ag₂Se₁₋ₓSₓ system is Ag₂Se₀.₇S₀.₃. As shown in Figure 1(c), its X-ray diffraction pattern looks like that of monoclinic Ag₂Se₀.₆S₀.₄. However, besides those belonging to the monoclinic structure, some extra diffraction peaks with weak intensities are also observed, such as (102) at 2θ = 31° and (112) at 2θ = 34° (right panel in Figure 1(c)). These are indexed to the orthorhombic structure. Thus, Ag₂Se₁₋ₓSₓ₃ 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 Ag₂Se₀.₇S₀.₃ crystallizes in the same orthorhombic structure with Ag₂Se. Figure 1(d) shows the EDS mappings performed on Ag₂Se₀.₇S₀.₃. Surprisingly, all elements are still homogeneously distributed. Thus, it is concluded that the two different phases in Ag₂Se₀.₇S₀.₃ have very similar chemical compositions but different crystalline structures. A similar polymorphic feature has been also observed in the CₓSe₁₋ₓSₓ system [34]. Combining the above result, it can be concluded that the transition boundary between the monoclinic and orthorhombic structures in Ag₂Se₁₋ₓSₓ solid solution should be around \( x = 0.3 \).

Ag₂Se₁₋ₓSₓ (\( x = 0, 0.1, 0.2, 0.3, 0.4, \) and 0.45) samples possess structure-dependent mechanical properties. The three-point bending test and Vickers hardness test were performed on Ag₂Se₁₋ₓSₓ. 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 Ag₂Se can only endure a very small bending strain before cracking. The maximum bending deformation is about 0.56%. Likewise, orthorhombic Ag₂Se₀.₃S₀.₇ also possesses a maximum bending deformation around 1.5%. The case is different for monoclinic Ag₂Se₀.₆S₀.₄, which exhibits a bending deformation above 10% without cracking. Previously, large bending deformation was also observed for monoclinic Ag₂Se₁₋ₓSₓ (\( x = 0.5, 0.7, 0.9, \) 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 Ag₂Se is 43.7 Hv at room temperature. It is monotonously increased to 51.5 Hv and 62.7 Hv for the orthorhombic Ag₂Se₀.₈S₀.₂ and Ag₂Se₀.₇S₀.₃, respectively. However, monoclinic Ag₂Se₀.₅S₀.₄ has low Vickers hardness of only 33.8 Hv, about half of that for orthorhombic Ag₂Se₀.₇S₀.₃. As shown in Figure 2(c), Ag₂Se₀.₅S₀.₄ can be directly cut into thin strips with thickness about 0.1 nm like metal. Furthermore, these metal-like strips can be twisted into various shapes without cracking, confirming that Ag₂Se₀.₅S₀.₄ has good ductility and flexibility.

The above test results prove that the monoclinic structure has significantly better ductility and flexibility in the Ag₂Se₁₋ₓSₓ 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 Ag₂Se₁₋ₓSₓ. Previous investigation found that the S atoms in monoclinic Ag₂S 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 fluidly, yielding a low energy barrier for slipping. However, in the orthorhombic structure, such unique wrinkled layer structure does not exist; thus, the orthorhombic Ag₂Se₁₋ₓSₓ samples are brittle. Here, it should be noted that although the main phase in Ag₂Se₀.₇S₀.₃ crystallizes in the monoclinic structure, Ag₂Se₀.₇S₀.₃ 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$_{0.7}$S$_{0.3}$.

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$_{1-x}$S$_x$ ($x \geq 0.5$) 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 $1.4 \times 10^3$ 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$_{0.5}$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 S1. All Ag$_2$Se$_{1-x}$S$_x$ samples possess $n_H$ in the order of $10^{18}$ 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]:

\[
\alpha = \frac{k_B}{e} \left[ \frac{(2 + \lambda) F_{1+1(\eta)} - \eta}{(1 + \lambda) F_{1(\eta)}} \right],
\]

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

\[
\mu_H = \frac{3\sqrt{\pi} (1/2) + 2\lambda}{4} \frac{1}{1 + \lambda} F_{1/(2+\lambda)} F_{1/2} \mu_{ph},
\]

\[
\mu_{ph} = \frac{(8\pi)^{1/2} e \hbar \rho v_F^2}{3(k_B T)^{3/2} (m^*)^{1/2}}.
\]
Figure 3: Temperature dependences of (a) electrical conductivity $\sigma$ and (b) Seebeck coefficient $\alpha$ for Ag$_2$Se$_{1-x}$S$_x$ ($x = 0, 0.1, 0.2, 0.3, 0.4,$ and $0.45)$. (c) Temperature dependence of power factor (PF) for Ag$_2$Se$_{1-x}$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 Ag$_2$Se$_{1-x}$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 Ag$_2$Se and Ag$_2$Se$_{0.5}$S$_{0.5}$ reported before are added for comparison [21, 26–29].
where $k_B$ is the Boltzmann constant, $\lambda$ is the scattering factor, $\epsilon$ is the electron charge, $m^*$ is the density-of-state effective mass, $r_{\parallel}$ is the Hall factor, $\rho$ is the sample density, $v_1$ is the velocity of longitudinal sound waves, $\mu_{\text{ph}}$ is the drift mobility for acoustic phonon scattering in the nondegenerate limit, and $\Xi$ is the deformation potential.

$F_m(\eta) = \int_0^\infty \frac{dx}{x} \frac{\eta^2}{(1 + e^{x-\eta})}$, where $x$ represents the reduced carrier energy and $\eta = E_c/k_B T$ is the reduced Fermi energy.

Figure 3(d) presents the $\alpha$ and $n_{\parallel}$ data for the present Ag$_2$Se$_{1-x}$S$_x$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.45$) samples roughly fall around the calculated theoretical Pisarenko curve with $m^* = 0.25m_e$ ($m_e$ 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 crystalize 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-$5s$ electrons [21, 41]. Alloying S at the Se sites would mainly alter the valence band maximum, 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 $\mu_{\parallel}$ than those for $n$-type Bi$_2$Te$_3$ [36] and filled skutterudites [37] mentioned above.

Figure 3(e) plots the $\mu_{\parallel}$ and $n_{\parallel}$ relationship at 300 K for Ag$_2$Se$_{1-x}$S$_x$ ($x = 0, 0.1, 0.2, 0.4, 0.45, 0.5$). 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 $n_{\parallel}$, the Ag$_2$Se$_{1-x}$S$_x$ ($x = 0, 0.1, 0.2$) samples with an orthorhombic structure have higher $\mu_{\parallel}$ than the Ag$_2$Se$_{1-x}$S$_x$ ($x = 0.4, 0.45$) samples with a monoclinic structure. By fitting the experimental data of the $\mu_{\parallel}$ and $n_{\parallel}$ 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$_x$ ($x = 0, 0.1, 0.2$) and the monoclinic Ag$_2$Se$_{1-x}$S$_x$ ($0.4, 0.45, 0.5$), 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 $\mu_{\parallel}$ observed for the orthorhombic Ag$_2$Se$_{1-x}$S$_x$.

The power factors (PF) for Ag$_2$Se$_{1-x}$S$_x$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.45$) samples calculated from the formula $PF = \alpha^2 / \cdot \sigma$ 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$_{0.25}$S$_{0.75}$ 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$_{0.4}$S$_{0.6}$ 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. $n_{\parallel}$ 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 $n_{\parallel}$ data basically fall around these lines. Under the comparable $n_{\parallel}$, 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 $\mu_{\parallel}$ and PF. In addition, based on the SPB model, the optimal carrier concentration ($n_{\text{opt,PF}}$) corresponding to the peak PF is around $3.4 \times 10^{28}$ cm$^{-3}$ for both orthorhombic and monoclinic Ag$_2$Se$_{1-x}$S$_x$. $n_{\text{opt,PF}}$ 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 $n_{\text{opt,PF}}$ value.

Figure 4(a) shows $\kappa$ as a function of temperature for Ag$_2$Se$_{1-x}$S$_x$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.45$). 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$_{0.4}$S$_{0.6}$ exhibits the lowest $\kappa$ among all samples. $\kappa$ for Ag$_2$Se$_{0.4}$S$_{0.6}$ at 300 K is around 0.7 W·m$^{-1}$K$^{-1}$. This value is about 36% decremented 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$_x$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.45$). 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 transport. 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 $zT = \alpha^2 \sigma T / \kappa$. 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$_{0.8}$S$_{0.2}$ and Ag$_2$Se$_{0.5}$S$_{0.5}$ possess comparable $zT$ with Ag$_2$Se. However, $zT$s for monoclinic Ag$_2$Se$_{0.4}$S$_{0.6}$ and Ag$_2$Se$_{0.8}$S$_{0.2}$ are much lower than those for orthorhombic Ag$_2$Se. At 300 K, $zT$ is just 0.26 for Ag$_2$Se$_{0.8}$S$_{0.2}$ and 0.23 for Ag$_2$Se$_{0.5}$S$_{0.5}$. 

As shown in Figure 4(d), the theoretical $zT$ vs. $n_{\parallel}$ 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 $k_i = 0.4$ W·m$^{-1}$K$^{-1}$. The experimental $zT$ and $n_{\parallel}$ data basically fall around these lines. Under the comparable $n_{\parallel}$, $zT$ 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 (\( n_{opt_{zT}} \)) corresponding to the peak \( zT \) is around \( 1-2 \times 10^{18} \) \( \text{cm}^{-3} \) for orthorhombic Ag\(_2\)Se\(_{1-x}\)S\(_x\), while \( 2-3 \times 10^{18} \) \( \text{cm}^{-3} \) for monoclinic Ag\(_2\)Se\(_{1-x}\)S\(_x\), \( n_{H} \) for the present orthorhombic Ag\(_2\)Se\(_{1-x}\)S\(_x\) (\( x = 0, 0.1, 0.2 \)) and monoclinic Ag\(_2\)Se\(_{1-x}\)S\(_x\) (\( x = 0.4, 0.45, \) and 0.5) samples are still higher than these \( n_{opt_{zT}} \) values. Thus, if their carrier concentration can be further reduced, higher \( zT \) can be expected.

Although the TE performances for ductile monoclinic Ag\(_2\)Se\(_{1-x}\)S\(_x\) are lower than those for brittle orthorhombic Ag\(_2\)Se\(_{1-x}\)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 Ag\(_2\)Se\(_{1-x}\)S\(_x\). The superior PF values achieved in the monoclinic Ag\(_2\)Se\(_{1-x}\)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 Ag\(_2\)Se\(_{1-x}\)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 Ag\(_2\)Se\(_{1-x}\)S\(_x\) samples show great potential to be used in wearable electronics.
3. Conclusion

In summary, this study systematically studied the crystalline structure, mechanical properties, and TE properties of Ag$_2$Se$_{1-x}$S$_x$ (x = 0, 0.1, 0.2, 0.3, 0.4, and 0.45). Ag$_2$Se$_{1-x}$S$_x$ samples crystallize in the orthorhombic structure when x ≤ 0.2, while in the monoclinic structure when x ≥ 0.4. Only the monoclinic Ag$_2$Se$_{1-x}$S$_x$ samples possess good ductility and flexibility. Under comparable carrier concentration range, the orthorhombic Ag$_2$Se$_{1-x}$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$_{1-x}$S$_x$ (x = 0.4 and 0.45) samples than those of the orthorhombic Ag$_2$Se$_{1-x}$S$_x$ (x = 0.1 and 0.2) samples. However, the higher PF and better thermal stability promise a great potential for monoclinic Ag$_2$Se$_{1-x}$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$_{0.95}S_{0.05}$ 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)

References

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