Achieving metal-like malleability and ductility in Ag$_2$Te$_{1-x}$S$_x$ inorganic thermoelectric semiconductors with high mobility

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GRAPHICAL ABSTRACT

PUBLIC SUMMARY
- Phase structure plays a crucial role in determining the mechanical properties of inorganic semiconductors Ag$_2$Te$_{1-x}$S$_x$
- Metal-like malleability and ductility with a record-high tensile elongation of 107.3% are achieved in Ag$_2$Te$_{1-x}$S$_x$
- The plastic Ag$_2$Te$_{1-x}$S$_x$ with decent thermoelectric performance could exhibit promising applications in the field of flexible/wearable electronics
Inorganic semiconductor Ag$_2$Te$_{1-x}$S$_x$ has been recently found to exhibit unexpected plastic deformation with compressive strain up to 30%. However, the origin of the abnormal plasticity and how to simultaneously achieve superb ductility and high mobility are still elusive. Here, we demonstrate that crystalline/amorphous Ag$_2$Te$_{1-x}$S$_x$ ($x$ = 0.3, 0.4, and 0.5) composites can exhibit excellent compressive strain up to 70% if the monoclinic Ag$_2$Te phase, which commonly exists in the matrix, is eliminated. Significantly, an ultra-high tensile elongation reaching 107.3% was found in Ag$_2$Te$_{0.7}$S$_{0.3}$, which is the highest one yet reported in the system and even surpasses those achieved in some metals and high-entropy alloys. Moreover, high mobility of above 1000 cm$^2$/V·s at room temperature and good thermoelectric performance are simultaneously maintained. A modified Ashby plot with ductility factor versus carrier mobility is thereby proposed to highlight the potential of solid materials for applications in flexible/wearable electronics.

INTRODUCTION

Over the last decade, the Internet of Things (IoT) and wearable electronics have experienced rapid growth owing to the demand for an intelligent society. Semiconductors with good thermoelectric (TE) properties have been found to be promising for powering IoT nodes and wearable electronics, such as wearable medical monitoring sensors and handheld devices. TE semiconductor devices, which have the advantages of being small in size, noise free, pollution free, and reliable long term, can realize the direct conversion of heat energy to electricity based on the Seebeck effect if a temperature difference exists. In human society, temperature difference exists everywhere, for instance, between the inside and outside of buildings or heat pipes or between the human body and the ambient environment, providing heat sources for powering IoT nodes and wearable electronics by TE devices. The TE performance can be evaluated by the materials’ dimensionless figure of merit $zT = S^2T/k\rho$, where $S$, $\sigma$, $T$, and $k$ are the Seebeck coefficient, electrical conductivity, absolute temperature, and total thermal conductivity, respectively. TE materials are usually brittle and are typically designed to be a cubic structure with two flat surfaces attaching to the heat source and sink for applications. However, in practical scenarios, the temperature difference can also exist in objects with curved surfaces, such as heat pipes and human body skin. These drive the ever-increasing demand for high-performance TE semiconductors with both superior deformability and high carrier mobility, facilitating mechanical processability and high carrier transport.

Conventional good TE materials are usually found in inorganic semiconductors, which are inherently brittle, limiting their applications for heat sources with curved surfaces. Organic conducting polymers have been used for fabricating flexible TE devices due to their mechanical flexibility and low thermal conductivity. Nevertheless, the power factor (PF), $PF = S^2\sigma$, of organic materials is usually too low, only about 10$^{-6}$–10$^{-4}$ W m$^{-1}$ K$^{-2}$, and the carrier mobilities are between $~1$ and 10 cm$^2$/V·s$^{-1}$, leading to poor TE performance. By combining the flexibility of organic materials and the good TE performance of inorganic materials, hybrid flexible TE generators have been fabricated by depositing the thin film of inorganic semiconductors, such as Bi$_2$Te$_3$ and Ag$_2$Se, atop flexible organic substrates, which could exhibit better TE performance than pure organic conducting polymers. However, the organic substrates induce additional thermal resistance and lower the actual temperature difference across TE materials, which is adverse to the power output of hybrid flexible TE devices.

Recently, an inorganic semiconductor, a-Ag$_2$S, was found to exhibit an unexpectedly good malleability with a compressive strain above 50% at room temperature, which was thought to be owing to the continuous formation of Ag–S bonds during the slippage process. The intrinsically ductile Ag$_2$S makes it a good candidate for application in full-inorganic flexible TE devices from the view of machinability and ductility. However, the $zT$ value of pristine Ag$_2$S is less than 0.02 at 300 K. A delicate balance between the high TE performance and good ductility of Ag$_2$S-based materials was achieved in the alloying system, e.g., Ag$_2$S$_{0.5}$Se$_{0.5}$ and Ag$_2$S$_{0.7}$Te$_{0.3}$, and the $zT$ at 300 K was improved to 0.26 and 0.3, respectively, without impairing the plasticity. The introduction of Se and/or Te into Ag$_2$S not only optimizes the carrier concentration but also decreases the phase transition temperature from monoclinic phase to cubic superionic conductor phase with highly disordered Ag$^+$ distribution. Ag$_2$S$_{0.7}$Te$_{0.3}$ with a body-centered cubic structure shows both the lower Young’s modulus and nano hardness compared with monoclinic a-Ag$_2$S. Density functional theory calculations indicate that the lower generalized stacking fault energy and the larger cleavage energy in cubic Ag$_2$S$_{0.7}$Te$_{0.3}$ are responsible for its good ductility. These results suggest the cubic superionic conductor phase is the origin of good ductility in the Si-rich Ag$_2$Te$_{1-x}$S$_x$ $(x \geq 0.7)$.

Unexpectedly, in the Te-rich Ag$_2$Te$_{1-x}$S$_x$ materials $(x = 0.3$ and 0.4), the amorphization was observed by He et al. Nevertheless, the studied amorphous Ag$_2$Te$_{0.7}$S$_{0.3}$ sample can still exhibit large plastic deformability with a maximum compressive strain up to 25% and tensile strain to 12.5%. The formation and extending of shear bands, which are the primary process accounting for the ductility of bulk metallic glasses, were thought to be responsible for the exceptional plastic deformability. Distinct from the ductile Ag$_2$Te$_{1-x}$S$_x$ materials, the studied Ag$_2$Te$_{0.3}$S$_{0.7}$ sample, which also exhibits amorphization, was brittle in the compressive test. More recently, Ag$_2$Te$_{0.5}$S$_{0.5}$, which was thought to exhibit an amorphous/crystalline composite structure, was reported to display larger plastic deformation with a compressive strain of 30%. These results suggest that Ag$_2$Te$_{1-x}$S$_x$ compounds are promising candidates for power generation applications in scenarios with curved surfaces. However, the relationship between plastic deformability and the phase structure, particularly the amorphization, in Ag$_2$Te$_{1-x}$S$_x$ remains elusive. The revelation of this relationship is crucial for promoting both the understanding of the deformation mechanism and the practical applications of ductile inorganic semiconductors.

In this study, the amorphous Ag$_2$Te$_{1-x}$S$_x$ $(x = 0.3, 0.4,$ and 0.5) samples were fabricated by directly quenching the molten ingots into cold water and subjecting them to different heat treatment processes to systematically investigate the correlation between phase structure and plastic deformability. Compared with the quenched ingots, the annealed Ag$_2$Te$_{1-x}$S$_x$ specimens with cubic-crystalline/amorphous structure exhibit the coexistence of metal-like malleability, superb ductility, high carrier mobility ($\sim 1000$ cm$^2$/V·s$^{-1}$) at 300 K), and decent TE performance. All the annealed Ag$_2$Te$_{1-x}$S$_x$ specimens exhibit large compressive strain up to 70% without fractures. Meanwhile, the maximum ductility was found in the Ag$_2$Te$_{0.5}$S$_{0.5}$ sample with a maximum elongation of 107.3% under a relatively low ultimate stress of 46.7 MPa, the highest one yet found in the Ag$_2$Te$_{1-x}$S$_x$ system. These results pave the way for applying ductile and high-mobility Ag$_2$Te$_{1-x}$S$_x$ TE semiconductors in the field of flexible and wearable electronics.

RESULTS AND DISCUSSION

Coexistence of superb ductility and carrier mobility

Both higher carrier mobility and mechanical ductility are prerequisites for the implementation of flexible/wearable devices. For TE devices, high carrier mobility can guarantee low power consumption. For flexible electronics, higher carrier mobility can enable a faster switching speed and higher operating frequencies of transistors. Meanwhile, ductility is required to optimize the mechanical behavior and facilitate the manufacture of the devices. Aimed at simultaneously evaluating these two parameters, a modified Ashby plot at ambient temperature is presented in Figure 1A. We define a ductility factor $d = \sigma/A$, to quantitatively
reflect the material’s ability to be stretched, where \( \varepsilon \) is the total elongation at break (%), and \( \sigma_f \) is the ultimate tensile strength (MPa). Specifically, a large ductility factor \( d \) suggests that the materials can exhibit a large elongation at low tensile strength.

As shown in Figure 1A, organic semiconductors such as polydimethylsiloxane- \( 0.25 \) and poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate- \( 0.25 \)) have been widely used in fabricating flexible devices, \( 3 \) showing the highest ductility factor for the large elongation value at extremely low stress. However, the low carrier mobility of organic semiconductors limits their application to low-frequency flexible electronics. \( 53,54 \) The emergence of two-dimensional (2D) nanomaterials, which are demonstrated to exhibit high device mobility (about \( 10^{5} \) cm\(^2\)/Vs for graphene), promotes the flexible technology transformation from electronics for sensors and display to integrated flexible nanoelectronics. \( 55,56 \) The low ductility factor for 2D nanomaterials, as shown in Figure 1A, is mainly due to their high modulus (for instance, 1000 GPa Young’s modulus for graphene). \( 57 \) Nevertheless, large-scale, reproducible synthesis of 2D nanomaterials has been difficult to achieve so far. \( 38 \) The values of the ductility factor for \( Ag_{2}Te_{1-x}S_x \) specimens in this work are between organic semiconductors and 2D nanomaterials, sufficient to meet the required mechanical properties for flexible electronics. Besides, the carrier mobility of \( Ag_{2}Te_{0.67}S_{0.33} \) and \( Ag_{2}Te_{0.6}S_{0.4} \) around \( 1000 \) cm\(^2\)/Vs is comparable to traditional silicon material (1400 cm\(^2\)/Vs for electrons) and superior to organic semiconductors and ductile binary \( Ag_xS_y \) alloys that show significant advantages for applications in the fields of flexible electronics.

Figures 1B and 1C show the mechanical properties of the previously reported plastic inorganic semiconductors, metals, metallic alloys, steels, and high-entropy alloys. The metal-like malleability of cubic-crystalline/amorphous structure \( Ag_{2}Te_{1-x}S_x \) is displayed in Figure 1B. The compressive strain reaches 70%, which is larger than that of plastic inorganic semiconductors \( 14,21,23 \) and comparable to typical metals. \( 41,42 \) Furthermore, the ductility for our crystalline/amorphous \( Ag_{2}Te_{1-x}S_x \) is much higher than that of the previously reported monolithic \( Ag_xS_y \) amorphous \( Ag_{2}Te_{0.67}S_{0.33} \), and van der Waals layered InSe, of which the elongation ranges are 4.2\%, \( 14,21,23,59,60 \) and 12.5\% \( 35 \) respectively. Additionally, the tensile strain above 50% is also comparable to that for coarse-grained metals. \( 43,44 \) High-entropy alloys display significantly improved mechanical properties compared with conventional engineering alloys, which overcome the strength–ductility trade-off and show not only high strength but also high tensile plasticity. \( 56,57,58,59 \) As displayed in Figure 1C, the studied \( Ag_{2}Te_{0.67}S_{0.33} \) and \( Ag_{2}Te_{0.6}S_{0.4} \) samples show superior ductility to the state-of-the-art high-entropy alloys and exhibit a high uniform tensile elongation of about 100%. By further considering the relatively small tensile stress applied, the studied \( Ag_{2}Te_{0.67}S_{0.33} \) and \( Ag_{2}Te_{0.6}S_{0.4} \) samples exhibit excellent machinability for potential wearable/ flexible applications on curved surfaces.

The detrimental role of monolitic \( Ag_{2}Te \) to plasticity

In the first set of our experiments, \( Ag_{2}Te_{1-x}S_x \) \((x = 0.05)\) ingots were synthesized by using a water-quench method to facilitate the formation of more amorphous phases. When \( x \leq 0.2 \), the \( Ag_{2}Te_{1-x}S_x \) samples crystallize in a monoclinic \( \alpha-Ag_{2}Te \) structure and exhibit brittle fracture in the compressive tests (Figure S1). The compressive and tensile properties of the quenched ingots \((x \geq 0.3)\) are displayed in Figures 2 and S2. Unexpectedly, only the \( Ag_{2}Te_{0.3}S_{0.7} \) sample is plastic, exhibiting a significant strain hardening process and around 27% compressive strain. Conversely, the compressive stress–strain curve of the \( Ag_{2}Te_{0.3}S_{0.7} \) sample displays linear elastic deformation behavior at the beginning of their stress–strain curves, and the sample breaks at the maximum compressive strain of 4% without yielding (Figure 2A). This suggests a typical compressive failure of brittle materials, which is much different from the previous reports \( 21,23,59 \) in which the compressive strain for \( Ag_{2}Te_{0.3}S_{0.7} \) and \( Ag_{2}Te_{0.6}S_{0.4} \) samples could reach 20%. These differences make us aware that the various phase structures, relating to the different preparation methods, might have significant impacts on the plastic deformability of \( Ag_{2}Te_{1-x}S_x \) materials and even result in a brittle–to-plastic transition. However, the factors that cause a considerable difference in the plastic deformability of \( Ag_{2}Te_{1-x}S_x \) samples with the same nominal composition were previously not studied.

In the second set of our experiments, the quenched ingots were subjected to an annealing process at 723 K for 7 days. The X-ray diffraction (XRD) patterns of bulk \( Ag_{2}Te_{1-x}S_x \) \((x = 0.3, 0.4, 0.5)\) obtained by quenching and annealing are displayed in Figures 2C and S2A. Firstly, it should be noted that the XRD patterns of samples with \( x = 0.3 \) and \( x = 0.4 \) in Figure 2C are different from those of \( Ag_{2}Te_{0.3}S_{0.7} \) and \( Ag_{2}Te_{0.6}S_{0.4} \) reported previously \( 21 \) which contain no sharp diffraction peak in the 2\( \theta \) range of 30° to 50° and exhibit an amorphous phase-dominated structure. A small diffraction peak at 2\( \theta \) = 12.5° is detected for all quenched samples, corresponding to the diffraction peaks of the monoclinic \( Ag_{2}Te \) (space group \( P2_1/c \)). Furthermore, the whole differential scanning calorimetry (DSC) curves for the quenched and annealed \( Ag_{2}Te_{1-x}S_x \) specimens during the heating and cooling process are displayed in Figure S3. The second heating cycle for quenched \( Ag_{2}Te_{0.3}S_{0.7} \) and the first heating cycle for annealed \( Ag_{2}Te_{0.3}S_{0.7} \) are displayed in Figures 2D and S2B for comparison. As can be seen, the DSC curves for quenched \( Ag_{2}Te_{0.3}S_{0.7} \) indicate the phase transition of \( Ag_{2}Te \) at 423 K from the monoclinic phase to the face-centered cubic phase, \( 3 \) confirming the existence of monoclinic \( Ag_{2}Te \) in the quenched samples. However, the electron probe microanalysis (EPMA) imaging and energy dispersive
spectroscopy (EDS) mapping for the quenched Ag₂Te₀.6S₀.4 sample (Figure S4) do not indicate the existence of monoclinic Ag₂Te phases, probably owing to their crystallization in the nanoscale.

After annealing at 723 K for 7 days, the diffraction peak of Ag₂Te at 2θ = 12.5° disappears in all annealed samples (Figures 2C and S2A). Meanwhile, no endo-

thermic peak is observed in the DSC measurement for the annealed samples, further verifying the elimination of the Ag₂Te phase during the annealing process. In addition, a slight dip, which is only observed in the first heating cycle of the thermal scan for all quenched and annealed Ag₂Te₀.₆S₀.₄ samples as displayed in Figure S3, might be due to the crystallization of the amorphous phase.

The sharp XRD peaks in the 2θ range of 20° to 55° are similar to those observed in cubic Ag₂S₀.₇Te₀.₃. Thus, the body-centered cubic structure, similar to the middle-temperature phase of Ag₂S with freely migrating Ag⁺, was adopted for the structure analysis. That is, Te and S atoms fully occupy the (0, 0, 0) site in which the atomic occupancy of S is 0.3, 0.4, and 0.5 for the x = 0.3, x = 0.4, and x = 0.5 samples, respectively, while Ag atoms are partially distributed over (0.25, 0, 0.5) and (0.25, 0, 0.5) sites. The simulated XRD peaks by VESTA software are partly consistent with experimental data, and the lattice parameters of Ag₂Te₀.₃, Ag₂Te₀.₄, and Ag₂Te₀.₅ are 5.224, 5.020, and 5.013 Å, respectively.

Moreover, the submicroscale vein-like dimple patterns with different depths are observed in the fracture surface of the brittle quenched x = 0.4 sample and the ductile annealed x = 0.4 sample (Figures 3A and 3B), showing a typical fracture morphology of BMGs, which indicates plastic flow on the microscale.

Accordingly, we think that the main phase of the studied quenched and annealed Ag₂Te₀.₆S₀.₄ samples is a crystalline/amorphous composite and that the annealed ones exhibit the elimination of monoclinic Ag₂Te. Additionally, Figures 3C–3F show that the EDS mappings performed on the polished surface of annealed Ag₂Te₀.₆S₀.₄, indicating all elements, Ag, Te, and S, are distributed homogeneously.

As shown in Figure 2A, all annealed Ag₂Te₀.₆S₀.₄ (x = 0.3 and 0.4) specimens show mechanical characteristics of typical ductile materials in the compressive test. The large-strain deformation under compressive loading reflects the excellent plastic deformability of Ag₂Te₀.₆S₀.₄ materials. To comprehensively evaluate the mechanical properties of plastic materials, here tensile tests were also performed to determine the ductility. Tensile stress–strain curves of the quenched and annealed Ag₂Te₀.₆S₀.₄ are shown in Figures 2B and S2D, where the tensile plasticity (ductility) has been enhanced in annealed specimens compared with quenched Ag₂Te₀.₆S₀.₄. The all annealed specimens exhibit large tensile strain above 50% with significant work hardening, and serrations are found in stress–strain curves for the annealed Ag₂Te₀.₆S₀.₄ and Ag₂Te₀.₅S₀.₅, resulting in larger tensile strain. Significantly, the annealed Ag₂Te₀.₅S₀.₅ exhibits an extremely good ductility with total elongation of 107.3% under a relatively low ultimate stress of 46.7 MPa (Figure 2B), and the inset presents dog-bone-shaped tensile samples before and after the tensile test, indicating large tensile deformation in the deformation region. The tensile strain can reach 75.1% for annealed Ag₂Te₀.₅S₀.₅ in Figure 2B and decreases to ~51.8% for annealed Ag₂Te₀.₅S₀.₅ in Figure S2D.

To examine the reproducibility of the plastic deformability in the Ag₂Te₀.₆S₀.₄ system, three cuboids and two dog-bone-shaped specimens were cut from various regions of the ingot for both quenched and annealed samples, and the stress–strain curves for compressive and tensile tests are shown in Figure S5. For quenched Ag₂Te₀.₃S₀.₇, the compressive strain range varies from 28.1% to 70%. Both brittle fracture and plastic deformation are observed in Ag₂Te₀.₅S₀.₅ samples, while all the quenched Ag₂Te₀.₃S₀.₇ cuboids exhibit brittle fracture. The inhomogeneity and uncontrollability of plastic deformability can be ascribed to the inhomogeneous distribution of the monoclinic Ag₂Te phase in quenched Ag₂Te₀.₆S₀.₄ samples. In contrast, when the quenched Ag₂Te₀.₆S₀.₄ is subjected to an annealing process at 723 K to eliminate the Ag₂Te phase as discussed above, an enhanced plastic deformation behavior is observed in annealed
Figure 4. Enhancement of the plastic deformability in AgTe0.6S0.4 (A and B) Compressive stress-strain curves (A) and room temperature bulk XRD patterns (B) for AgTe0.6S0.4 obtained by different heat treatments. The inset in (A) shows quenched and annealed cuboids before and after the compressive test. (C) Powder XRD patterns of the quenched AgTe0.6S0.4 at different temperatures.

Figure 5. Electrical transport properties of AgTe1-xSx 

Ag2Te1-xSx specimens, and, more importantly, the reproducibility of ductility for different pressure is pretty good. Distinctly, all annealed Ag2Te1-xSx specimens show mechanical characteristics of typical ductile materials in both the compressive and tensile tests. A large tensile strain above 50% is observed in all annealed Ag2Te1-xSx (x = 0.3, 0.4, and 0.5) specimens, which is larger than that in the previous reports (a tensile strain of around 12.5% in Ag2Te0.6S0.4), suggesting the importance of the elimination of monoclinic Ag2Te to obtain superb ductility.

As discussed above, the plastic deformability of Ag2Te1-xSx materials is significantly affected by the heat treatment process. To further explore the effect of the heat treatment on the mechanical properties, Ag2Te0.6S0.4 samples were melted at 1273 K and then followed by different heat treatments to obtain the final ingots: water quenching, furnace cooling, and annealing (annealing at 723 K within 7 days). Figure 4A displays the compressive property for Ag2Te0.6S0.4 ingots with different heat treatments. The quenched and furnace-cooled Ag2Te0.6S0.4 samples, of which the XRD patterns in Figure 4B suggest the existence of the monoclinic Ag2Te phase, exhibit relatively weak deformability with a compressive strain smaller than 10% (Figure 4A). In contrast, the compressive strain–stress curves for annealed Ag2Te0.6S0.4 indicate a superior plastic deformation with a compressive strain up to 70%. The quenched and annealed specimens before and after compressive loading are shown in the inset of Figure 4A, and the quenched cuboid broke directly at the maximum load while the annealed cuboid can be eventually pressed into a plate without fracture. Moreover, the variable temperature XRD measurement for the quenched Ag2Te0.6S0.4 is shown in Figure 4C. Three XRD reflections, appearing around 2θ of 40°–45°, can be indexed to the monoclinic Ag2Te phase in a temperature range from 323 to 673 K. Above 723 K, the monoclinic structure disappears while the cubic structure appears. This is also the reason why the annealed temperature of the quenched sample was determined to be 723 K to eliminate the monoclinic Ag2Te phase. To conclude, the existence of the monoclinic Ag2Te phase is responsible for the weak deformability in Ag2Te1-xSx materials, and the heat treatment of annealing at 723 K is crucial to achieving good plastic deformability, which promotes the phase transformation into the cubic phase and eliminates the brittle Ag2Te phase simultaneously. Consequently, excellent plastic deformability can be achieved in Ag2Te1-xSx samples with the coexistence of cubic-crystalline and amorphous phases.

TE properties

The Hall carrier mobility \(\mu_h\) of quenched and annealed Ag2Te1-xSx (x = 0.3 and 0.4) is shown in Figure 5A. The \(\mu_{\text{fi}}\) for annealed Ag2Te0.7S0.3 and Ag2Te0.5S0.5 reaches above 1000 cm² V⁻1 s⁻¹ at ambient temperature, which is about 40% higher than the quenched samples as well as the previously reported ones.21 The Seebeck coefficient \(S\) and the electrical conductivity \(\sigma\) for quenched and annealed Ag2Te1-xSx (x = 0.3, 0.4, and 0.5) under a temperature range of 300 to 575 K are shown in Figures 5B, 5C, and 5D. All specimens display a typical conducting behavior of a degenerate semiconductor without the occurrence of intrinsic excitation. The \(\sigma\) follows a \(T^{1.7} \sim T^{-1}\) dependency, implying that the acoustic phonon scattering dominates the charge transport. Notably, good electrical performance can be maintained in annealed specimens for Ag2Te1-xSx materials, the density of states effective mass \(m*\) at 300 K, estimated by the theoretical Pisarenko curves presented in Figure S6C, gradually increases with the increasing S content, from \(m* = 0.12 m_0\) (where \(m_0\) is the free electron mass) for Ag2Te0.7S0.3 to \(m* = 0.20 m_0\) for Ag2Te0.3S0.7, implying that alloying S at Te sites might alert the shape of the conduction band minimum and yield to a larger \(m*\). This could explain why the annealed Ag2Te0.7S0.3 sample has a relatively low carrier mobility \(\mu_{\text{fi}}\) of 580 cm² V⁻1 s⁻¹ compared with other ductile annealed specimens. Based on the SPB model, the calculated PF as a function of carrier concentration \(n_p\) is presented in Figure S6D, indicating that the electrical performance of Ag2Te1-xSx can be further enhanced by decreasing \(n_p\).

Figures 5E and 5F show the temperature dependence of the total thermal conductivity \(k\) for all the Ag2Te1-xSx (x = 0.3, 0.4, and 0.5) samples. The \(k\) values are in the range of 0.4 to 0.8 W m⁻¹ K⁻¹ and are independent of the temperature, which shows a typical thermal transport property of superionic conductors and amorphous solids as previously reported.48–70 The elimination of the Ag2Te phase in annealed specimens does not significantly affect the \(\kappa\) compared with the quenched one. The lattice thermal conductivity \(\kappa_\ell\) can be calculated by \(k = \kappa_\ell + \kappa_p\) in which the electronic thermal conductivity \(\kappa_p\) is evaluated via the Wiedemann–Franz law \(\kappa_p = L T\), where the Lorenz number \(L\) can be estimated according to the measured Seebeck coefficient using the SPB model. But it turns out that the values of \(\kappa_p\) for most of the quenched and annealed Ag2Te1-xSx samples are even negative near room temperature. This was also reported in other
typical superionic conductors, such as Cu2Te-based71 and Ag2Te-based72 materials. The unphysical determination of $\kappa_2$ can be ascribed to the overestimation of $\kappa_2$ using the Wiedemann–Franz law in the superionic conductor phase since the mobile cations may also contribute to the electrical conductivity. The accurate determination of $\kappa_2$ in Ag2Te1-$x$Sx materials with migrating Ag+ needs further investigation in future studies.

The dimensionless figure of merit $zT$ of all quenched and annealed Ag2Te1-$x$Sx ($x = 0.3, 0.4, and 0.5$) is presented in Figures 5F and S6F. Finally, the annealed Ag2Te0.6S0.4 exhibits the highest $zT$ in the range of 300 to 573 K, and a $zT$ of about 0.3 at 300 K and a maximum $zT$ of $\approx 0.8$ at 573 K were obtained. It is worth noting that the temperature-dependent $zT$ does not differ significantly for the quenched and annealed Ag2Te1-$x$Sx samples. This value is comparable to other ductile TE materials at room temperature, in which $zT$ values of 0.26 for Ag2S0.5Se0.517, 0.20 for Ag2Te0.7Se0.321, and 0.30 for Ag2Se0.7Te0.3 were achieved.18 At 573 K, this value is also comparable with that of the brittle n-type commercial Bi2Te2.7Se0.3 TE materials,73 suggesting the potential of Ag2Te1-$x$Sx for TE applications. In addition, the room temperature electrical properties of the annealed Ag2Te0.6S0.4 sample remain unchanged (Figure S7), while the $\kappa_2$ increases after the compressive deformation. This anomalous trend suggests that the plastic deformation mechanism of Ag2Te1-$x$Sx materials is independent of the movement of dislocations, as reported in plastic Ag2S–Ag2S.74

Conclusions

We have systematically investigated the processing–microstructure–property relationship of Ag2Te1-$x$Sx plastic inorganic semiconductors. It was found that the precipitation of the monoclinic Ag2Te phase is the major cause of the brittleness in the Ag2Te1-$x$Sx materials. Through long-term annealing at an appropriate temperature to eliminate the monoclinic Ag2Te phase, a large compressive strain of 70% and an excellent tensile elongation of 107.3% at room temperature are achieved in the cubic-crystalline/amorphous Ag2Te1-$x$Sx composites. Meanwhile, a high carrier mobility of 1000 cm$^2$V$^{-1}$s$^{-1}$ is also achieved at room temperature for the annealed Ag2Te1-$x$Sx ($x = 0.3$ and $0.4$) samples, which is 40% higher than that of the quenched ones. Moreover, the TE performance of Ag2Te1-$x$Sx is not impaired by the elimination of the monoclinic Ag2Te phase. Consequently, a room temperature $zT$ of 0.3 and a maximum $zT$ of 0.8 at 573 K are achieved in annealed Ag2Te0.6S0.4. This study demonstrates that high-mobility Ag2Te1-$x$Sx TE semiconductors with cubic-crystalline/amorphous structures can exhibit superb plasticity and thus have great potential in the field of flexible/wearable electronics.

MATERIAL AND METHODS

See the supplemental information for details.

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Figure 5. Temperature dependences of thermoelectric properties for Ag2Te1-xSx ($x = 0.3$ and $0.4$) (A) Room temperature carrier mobility $\mu_r$ for quenched and annealed Ag2Te1-xSx specimens, and the reference data are presented for comparison. (B–F) Temperature dependence of (B) Seebeck coefficient $S$, (C) electrical conductivity $\sigma$, (D) power factor, (E) total thermal conductivity $\kappa$, and (F) $zT$ values for quenched and annealed Ag2Te1-xSx ($x = 0.3$ and $0.4$) specimens.
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