A low-cost and eco-friendly Br-doped Cu$_7$Sn$_3$S$_{10}$ thermoelectric compound with zT around unity

Tingting Deng, Pengfei Qiu, Tong Xing, Zhengyang Zhou, Tian-Ran Wei, Dudi Ren, Jie Xiao, Xun Shi and Lidong Chen

Cu–Sn–S ternary compounds have attracted great attention in the thermoelectric community because they are composed of low-cost, earth-abundant, and non-toxic elements. Among them, Cu$_7$Sn$_3$S$_{10}$ shows promising thermoelectric performance in the middle temperature range. In this work, through doping Br in Cu$_7$Sn$_3$S$_{10}$, a peak dimensionless figure of merit (zT) around unity at 750 K has been achieved. Chemical composition analysis indicates that Br has a higher solubility in Cu$_7$Sn$_3$S$_{10}$ than Cl. On one hand, the Br dopant introduces additional electrons and tunes the initial high-carrier concentration to the optimal range. On the other hand, the Br dopant creates strong strain field fluctuation to significantly suppress the lattice thermal conductivity to as low as 0.4 W m$^{-1}$ K$^{-1}$ at 750 K. Its synthetic effects advance the realization of high zT around unity in Br-doped Cu$_7$Sn$_3$S$_{10}$.

1. Introduction

The rapid development of industry has aggravated the global environmental pollution and energy crisis. Since thermoelectric (TE) technology can convert low grade heat into useful electricity and improve the energy utilization efficiency, it is gaining increasing attention in both academic and industrial communities. TE conversion efficiency is mainly dependent on the TE material’s dimensionless figure of merit, defined as $zT = S^2\sigma T/k$, where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $T$ is the absolute temperature, and $k$ is the thermal conductivity. A high $zT$ needs a large $S$, a high $\sigma$, and a low $k$. Among the numerous TE materials reported so far, Cu–Sn–S ternary TE compounds attract great attention because all their component elements are low-cost, earth-abundant, and non-toxic. One typical p-type Cu–Sn–S TE compound is Cu$_7$Sn$_3$S$_{10}$, which adopts a monoclinic structure at room temperature. Stoichiometric Cu$_7$Sn$_3$S$_{10}$ has a low $zT$ due to the intrinsically low carrier concentration, about 1.4 $\times$ 10$^{17}$ cm$^{-3}$ at 300 K. Via doping external elements (e.g., Zn, Co, Mn, or Ni) or introducing non-stoichiometry to the optimal range. On the other hand, the Br dopant creates strong strain field fluctuation to significantly suppress the lattice thermal conductivity to as low as 0.4 W m$^{-1}$ K$^{-1}$ at 750 K. Its synthetic effects advance the realization of high zT around unity in Br-doped Cu$_7$Sn$_3$S$_{10}$.
work, we synthesize a series of Cu$_5$Sn$_3$S$_{10-x}$Br$_x$ ($x = 0, 0.05, 0.1, 0.3, 0.5, 0.7, 1.0, 1.5, and 2.0$) samples. It is found that the nominal solubility of Br in Cu$_5$Sn$_3$S$_{10}$ is above 1.5. Due to the higher solubility of Br, the carrier concentration is successfully tuned to the optimal range, leading to a peak $zT$ around unity for Cu$_5$Sn$_3$S$_9$Br at 750 K. This $zT$ value is not only a record-high value in Cu–Sn–S ternary TE compounds, but also superior to that of most TE sulfides reported so far (Fig. 1).

2. Experimental section

2.1 Synthesis

Cu$_5$Sn$_3$S$_{10-x}$Br$_x$ ($x = 0, 0.05, 0.1, 0.3, 0.5, 0.7, 1.0, 1.5, and 2.0$) samples were synthesized by the melting-annealing method. High-purity raw materials of Cu (shots, 99.999%, Alfa Aesar), Sn (shots, 99.999%, Alfa Aesar), S (pieces, 99.999%, Alfa Aesar), and CuBr (powder, 99.999%, Alfa Aesar) were weighed based on the chemical ratio as designed, and sealed in quartz tubes under vacuum in a glove box. The quartz tubes were heated to 723 K in 4.5 hours and held at this temperature for 2 hours. Then, they were further heated to 1273 K in 5.5 hours and kept at this temperature for 12 hours. After that, the temperature was decreased to 1073 K in 4 hours and this temperature was maintained for 2 days. Finally, the tubes were slowly cooled to room temperature in 16 hours. The ingots were ground in an agate mortar into fine powders and pelleted into disks. The disks were sealed into quartz tubes and annealed at 693 K for 3 days. Finally, the products were ground into powders again and sintered at 873 K under a uniaxial pressure of 65 MPa for 3–5 minutes by Spark Plasma Sintering (Sumitomo, SPS-2040). The sintering was conducted in an argon atmosphere with a low pressure of about 0.07 MPa.

2.2 Characterization

The crystal structure was determined by X-ray diffraction with Cu K$_\alpha$ sources (XRD, D/max-2550 V, Rigaku, Japan) and transmission electron microscopy (TEM, JEM-1400, Japan) with selected area electron diffraction (SAED). The structure refinement was carried out by the Rietveld refinement method employing the WinCSD program package. The chemical components were characterized by scanning electron microscopy (SEM, ZEISS supra 55, Germany) with energy dispersive X-ray spectroscopy (EDS, Oxford, UK). The electrical conductivity ($\sigma$) and Seebeck coefficient ($S$) were measured from 300 K to 750 K by using a ZEM-3 (Ulvac-Riko Japan). The thermal conductivity ($\kappa$) was calculated with the formula $\kappa = \rho C_p T$, where $\rho$ is the density measured based on Archimedes principle, $C_p$ is the heat capacity estimated via the Dulong–Petit law, and $\lambda$ is thermal diffusivity measured by using the Laser flash method (LFA457, Netzsch, Germany). The Hall carrier concentration ($p_H$) was calculated using $p_H = 1/R_H e$, where $R_H$ is Hall coefficient measured with a Physical Property Measurement System (PPMS, Quantum Design, USA). The Hall carrier mobility was obtained from the relation $\mu_H = R_H q/\sigma$.

3. Results and discussion

3.1 Phase and crystal structure

Fig. 2a shows the powder X-ray diffraction patterns for Cu$_5$Sn$_3$S$_{10-x}$Br$_x$ ($x = 0, 0.05, 0.1, 0.3, 0.5, 0.7, 1.0, 1.5, and 2.0$) samples. It should be noted that here $x$ is the nominal Br-doping content. The actual Br-doping content in the lattice (Table S1†) is less than the nominal one due to the loss of Br during the fabrication process. The pattern of the pristine Cu$_5$Sn$_3$S$_{10}$ matches well with the tetragonal structure (I42m, Fig. 2b). Upon doping a tiny amount of Br at S-sites ($x = 0.05$), the characteristic peaks of the tetragonal structure, such as those at $2\theta = 18.3^\circ$ and $2\theta = 29.7^\circ$, are significantly weakened (Fig. S1†). When the Br-doping content reaches $x = 0.1$, the characteristic peaks of the tetragonal structure completely disappear. A similar phenomenon has been also observed in Cl-doped Cu$_5$Sn$_3$S$_{10}$. With further increasing the Br-doping content from $x = 0.1$ to $x = 1.5$, the patterns look quite similar, except that the diffraction peaks gradually shift to low angles. This is reasonable considering the larger atomic radius of Br (1.15 Å) than S (1.00 Å). Impurity phase Cu$_5$S$_{10}$Sn$_4$ emerges when the doping content is $x = 2.0$. This can be more clearly observed in Fig. S2† and the BSE image (Fig. S3†) for Cu$_5$Sn$_3$S$_9$Br$_{2.5}$. Thus, the nominal solubility of Br in Cu$_5$Sn$_3$S$_{10}$ should be above 1.5. This value is much higher than the nominal solubility of Cl ($x < 0.9$). The closer electronegativity between Br and S than that between Cl and S might be responsible for the higher solubility of Br. EDS characterization confirms that there are no visible secondary phases at the micron scale in Cu$_5$Sn$_3$S$_{8.5}$Br$_{1.5}$. All elements exhibit a uniform distribution (Fig. S4†).

The disappearance of characteristic peaks belonging to the tetragonal structure indicates that Br-doping changes the crystal structure and improves the structure symmetry. To figure out the crystal structure of Br-doped Cu$_5$Sn$_3$S$_{10}$ Rietveld refinement was performed on the powder XRD pattern of Cu$_5$Sn$_3$S$_{8.5}$Br. As shown in Fig. 2c, it is found that the cubic structure (F43m) shown in Fig. 2b can help well interpret the measured XRD pattern. Cu and Sn atoms display completely disordered occupations at 4a sites, while S and Br atoms are located at 4c sites. The detailed crystallographic information for Cu$_5$Sn$_3$S$_9$Br obtained from the Rietveld refinement is shown in Tables S2–S4†. Cu$_5$Sn$_3$S$_{10}$ has a complex crystal structure within the
tetragonal unit cell, in which the locations of Sn and Cu partial disorder in the basic structural pattern of the sphalerite type (Fig. 2b). Substituting S with Br can introduce more disordered atomic distributions throughout the crystal lattice to increase configuration entropy, which should be responsible for the increased symmetry from the tetragonal structure to cubic structure. A similar composition-dependent symmetry change has also been found elsewhere.\textsuperscript{28,29}

In order to further confirm the cubic structure of Br-doped samples, high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) were performed on Cu\textsubscript{7}Sn\textsubscript{3}S\textsubscript{9}Br. As shown in Fig. 3a, three different areas were selected in a piece of a single crystal sample prepared by ion beam thinning. In each SAED pattern, the diffraction spots are clean and clear without any splitting, confirming the good crystallinity of the sample. The three SAED patterns well match the [1\overline{1}2] zone (Fig. 3b), [0\overline{1}1] zone (Fig. 3c), and [001] zone (Fig. 3d) with the cubic structure (F\overline{4}3m), respectively. These are consistent with the above X-ray refinement results. In Fig. 3d, the distance of the crystal plane (200) is 2.713 Å, being close to the value of 2.717 Å obtained by the X-ray refinement. In addition, as shown in Fig. 3e and f, obvious stacking faults, superlattices, and twin crystals are found in Cu\textsubscript{7}Sn\textsubscript{3}S\textsubscript{9}Br.

3.2 Electrical transport properties

Because Br has one more outermost electron than S, doping Br in Cu\textsubscript{7}Sn\textsubscript{3}S\textsubscript{10} would strongly influence the electrical properties. Fig. 4 shows the temperature dependences of electrical

![Fig. 2](image_url)  
(a) Powder X-ray diffraction (PXRD) patterns of Cu\textsubscript{7}Sn\textsubscript{3}S\textsubscript{10−x}Br\textsubscript{x} (x = 0, 0.05, 0.1, 0.3, 0.5, 0.7, 1.0, 1.5, and 2.0) samples. The inset picture is a close-up view for the 2θ ranging from 27.5° to 29.5°. (b) Crystal structures of tetragonal Cu\textsubscript{7}Sn\textsubscript{3}S\textsubscript{10} and cubic Cu\textsubscript{7}Sn\textsubscript{3}S\textsubscript{9}Br. (c) Total powder X-ray diffraction refinement profile for Cu\textsubscript{7}Sn\textsubscript{3}S\textsubscript{9}Br. The red circles represent the measured point intensities. The black lines represent the intensities calculated from the cubic structure. The blue rough lines show the difference between experimental and calculated intensities. The green vertical bars indicate Bragg positions.

![Fig. 3](image_url)  
(a) Low magnification TEM image for the Cu\textsubscript{7}Sn\textsubscript{3}S\textsubscript{9}Br sample prepared by ion beam thinning. (b–d) Selected area electron diffraction (SAED) patterns performed on the areas in (a). (e and f) The high-resolution TEM (HRTEM) images with stacking faults (white lines), superlattices (yellow lines), and twin crystals (blue lines).
conductivity ($\sigma$) and Seebeck coefficient ($S$) for the Cu$_7$Sn$_3$-S$_{10-x}$Br$_x$ samples. Here the data of Cu$_7$Sn$_3$S$_8$Br$_2$ are not included due to the existence of secondary phases. All samples demonstrate positive and metallic conducting behavior. With increasing the Br-doping content, the $\sigma$ decreases continually in the entire measured temperature range. At 750 K, the $\sigma$ for Cu$_7$Sn$_3$S$_{8.5}$Br$_{1.5}$ is $1.1 \times 10^4$ S m$^{-1}$, about one order of magnitude lower as compared with that for the pristine Cu$_7$Sn$_3$S$_{10}$. Likewise, Br doping significantly enhances the $S$. The $S$ for Cu$_7$Sn$_3$S$_{8.5}$Br$_{1.5}$ is around 240 mV K$^{-1}$ at 750 K, about 140% enhancement as compared with that for the pristine Cu$_7$Sn$_3$S$_{10}$. Moreover, Fig. S5† shows that the measured $S$ and $\sigma$ are reproducible when the test temperatures are not higher than 750 K, indicating that Br-doped samples are very stable.

Fig. 4c shows the plot of the $S$ and $\sigma$ of Cu$_7$Sn$_3$S$_{10-x}$Br$_x$ at 750 K as a function of the Br-doping content. For comparison, the data for Cu$_7$Sn$_3$S$_{10-x}$Cl$_x$ are also included. Clearly, due to the higher solubility of Br in Cu$_7$Sn$_3$S$_{10}$, doping Br can achieve higher $S$ and lower $\sigma$ than cannot be achieved by doping Cl. However, the $S$ enhancement is not enough to compensate the $\sigma$ reduction, thus the PF ($=S^2\sigma$) decreased continually with increasing Br-doping content. As shown in Fig. 4d, the PF for Cu$_7$Sn$_3$S$_{8.5}$Br$_{1.5}$ is 6.0 $\mu$W cm$^{-1}$ K$^{-2}$ at 750 K, only about one half of the value for the pristine Cu$_7$Sn$_3$S$_{10}$.

Hall carrier concentration ($p_H$) and Hall carrier mobility ($\mu_H$) were measured to further understand the electrical transport properties of Cu$_7$Sn$_3$S$_{10-x}$Br$_x$. As shown in Fig. 5a, upon introducing Br into Cu$_7$Sn$_3$S$_{10}$, the $p_H$ at 300 K is decreased from $2.6 \times 10^{21}$ cm$^{-3}$ to $0.9 \times 10^{21}$ cm$^{-3}$. Such $p_H$ reduction is partially responsible for the decreased $\sigma$ and enhanced $S$ shown in Fig. 4. Likewise, $\mu_H$ roughly declines with increasing the Br doping content. At 300 K, the $\mu_H$ for $x = 1.5$ is 1.7 cm$^2$ V$^{-1}$ s$^{-1}$, which is about one fifth that for the pristine Cu$_7$Sn$_3$S$_{10}$.

Fig. 5b shows the plot of the Pisarenko relationship for Cu$_7$Sn$_3$S$_{10-x}$Br$_x$. The data for Cu$_7$Sn$_3$S$_{10-x}$Cl$_x$ are also included. The $S$ decreases with increasing the $p_H$ at both 300 K and 750 K. Based on the single parabolic band model (SPB), the transport parameters can be written as:  

$$S = \frac{k_B}{e} \left( \frac{2F_1}{F_0} - \frac{\eta}{e} \right)$$  

(1)

$$n_H = \frac{8\pi(2m^*k_BT)^{3/2}}{3h^3} \frac{2F_0^2}{F_{z,1/2}}$$  

(2)

$$\mu_H = \frac{F_{z,1/2}}{2F_0}$$  

(3)

$$PF = S^2n_H\mu_He$$  

(4)
\[ zT = \frac{S^2 n_H \mu_H e^2 T}{k_B + \epsilon} \]  

(5)

where \( \eta \) is the reduced Fermi level, \( F(\eta) \) is the Fermi integral expressed by \( F(\eta) = \int_0^\infty \frac{x^2 dx}{1 + \exp(x - \eta)} \), \( m_d^* \) is the density-of-states (DOS) effective mass, \( k_B \) is the Boltzmann constant, \( e \) is the elementary charge, \( h \) is the Planck constant, and \( \mu_0 \) is the mobility parameter. Assuming that carriers are dominantly scattered by both acoustic phonons and alloy scattering, \( \mu_0 \) is given by

\[
\frac{1}{\mu_0} = \frac{1}{\mu_{ac,0}} + \frac{1}{\mu_{al,0}}
\]  

(6)

\[
\mu_{ac,0} = \frac{\pi e h^4 d n^2}{\sqrt{2} \Xi^2 (m_b^*)^{5/2} (k_B T)^{3/2}}
\]  

(7)

\[
\mu_{al,0} = \frac{8 e h^4 N_0}{3 \sqrt{2} \pi x (1 - x) (k_B T)^{1/2} (m_b^*)^{5/2} U^2}
\]  

(8)

where \( \mu_{ac,0} \) and \( \mu_{al,0} \) are the mobility parameters for acoustic phonon scattering and alloy scattering, respectively. Based on eqn (1) and (2), the calculated Pisarenko lines are plotted. As shown in Fig. 5b, the experimental \( S \) data of \( Cu_7Sn_3S_{10-x}Br_x \) and \( Cu_7Sn_3S_{10-x}Cl_x \) at 300 K are roughly located between the Pisarenko lines with \( m_d^* = 4.0 m_e \) and \( m_d^* = 5.0 m_e \) (\( m_e \) is the free electron mass). Assuming that the carrier concentrations are the same from room temperature to high temperature, the experimental \( S \) data of \( Cu_7Sn_3S_{10-x}Br_x \) and \( Cu_7Sn_3S_{10-x}Cl_x \) at 750 K are roughly located between the Pisarenko lines with \( m_d^* = 5.0 m_e \) and \( m_d^* = 6.0 m_e \). In addition, it can be seen that the \( m_d^* \) increases with increasing the Br or Cl doping content (Table S5†). This indicates that Br/Cl-doping might not only shift the Fermi level upward to the valence band maximum, but also modify the initial band structure of \( Cu_7Sn_3S_{10} \).

Since the scattering factor for both acoustic phonon scattering and alloy scattering is 0, the theoretical \( \mu_H \) vs. \( p_H \) relation can be given by considering that only acoustic phonon scattering dominates the carrier transport (named the first case) or both acoustic phonon scattering and alloy scattering dominate the carrier transport (named the second case). As shown in Fig. 5c, the dashed lines represent the theoretical \( \mu_H \) vs. \( n_H \) relation in the first case, while the violet solid lines represent that in the second case. Clearly, the first case cannot describe the experimental \( \mu_H \) vs. \( p_H \) relation, which shows a non-monotonic variation. This indicates that alloy scattering must
be considered for the present Br-doped samples, especially when the Br-doping content is higher than $x = 0.5$. The presence of additional alloy scattering is consistent with the scenario shown in Fig. S6$^{†}$ that the measured $\mu_H$ obviously deviates from the $T^{-1.5}$ dependence around 300 K, which is a typical character for acoustic phonon scattering. The additional alloy scattering is also responsible for the decreased $\mu_H$ with increasing Br-doping content in Fig. 5a.

According to eqn (1)–(4), the theoretical power factor (PF) vs. carrier concentration curves at 300 K and 750 K are calculated and plotted in Fig. 5d. The experimental data roughly fall in the area with assigned $m^*_d$ and $m_0$ values at each temperature. At 300 K, the predicted maximal PFs occur around the carrier concentration of $2.3 \times 10^{20} \text{cm}^{-3}$. At 750 K, the optimal carrier concentration corresponding to the maximal PF shifts to around $1.7 \times 10^{21} \text{cm}^{-3}$. Moreover, the lower $\mu_0$ results in the lower PF. Herein, the experimental $p_H$ value ($1.0 \times 10^{21} \text{cm}^{-3}$ at 300 K) of Cu$_7$Sn$_3$S$_9$Br is already close to the predicted optimal carrier concentration at 750 K. However, the low $\mu_0$ limits it to realize higher PF.

3.3 Thermal transport properties

Beyond the electrical transport properties, doping Br in Cu$_7$Sn$_3$S$_{10−x}$Br$_x$ also strongly influences the thermal transport properties. The thermal conductivity ($\kappa$) of all Cu$_7$Sn$_3$S$_{10−x}$Br$_x$ samples is shown in Fig. 6. The $\kappa$ gradually decreases with increasing the Br doping content (Fig. 6a). At 300 K, the $\kappa$ for Cu$_7$Sn$_3$S$_8$Br$_{1.5}$ is about 0.9 W m$^{-1}$ K$^{-1}$, just about one fifth that of the pristine Cu$_7$Sn$_3$S$_{10}$. It should be noted that doping Br in Cu$_7$Sn$_3$S$_{10}$ can yield lower $\kappa$ than doping Cl. For example, at 300 K, the lowest $\kappa$ achieved in the Cu$_7$Sn$_3$S$_{10−x}$Cl$_x$ system is 1.5 W m$^{-1}$ K$^{-1}$, about twice that in the Cu$_7$Sn$_3$S$_{10−x}$Br$_x$ system. This is related to the higher solubility of Br in Cu$_7$Sn$_3$S$_{10}$ than that of Cl. Doping Br reduces the $\kappa$ based on two aspects: carrier thermal conductivity ($\kappa_c$) and lattice thermal conductivity ($\kappa_L$). $\kappa_c$ and $\kappa_L$ can be calculated from the formulas $\kappa_c = L \frac{T}{\pi^2} T$ and $\kappa_L = \frac{k}{\pi^2} \frac{T}{\pi^2}$, respectively. $L$ is the Lorenz number, which is calculated from

$$L = \left( \frac{k_B}{e} \right)^2 \left\{ \frac{3F_2(\eta)}{F_0(\eta)} - \frac{2F_1(\eta)}{F_0(\eta)} \right\}$$

(9)

In Fig. S7$^{†}$ and 6b, both $\kappa_c$ and $\kappa_L$ decrease with the increase of the Br-doping content throughout the whole temperature range. The reduction of $\kappa_c$ is caused by the decreased electrical conductivity (Fig. 4a). When the Br-doping content is 1.0, the $\kappa_c/\kappa$ ratio is about 0.25 at 300 K, only 40% of that for the pristine Cu$_7$Sn$_3$S$_{10}$. Likewise, the $\kappa_L$ for the pristine Cu$_7$Sn$_3$S$_{10}$ is 1.6 W m$^{-1}$ K$^{-1}$.
m\(^{-1}\) K\(^{-1}\) at 300 K. This value is much lower than that of many other diamond-like compounds reported before, such as CuFeS\(_2\) and CuInTe\(_2\)\(^{18}\). This is attributed to the presence of intrinsic Cu/ Sn disorder at 2b and 4d sites in Cu\(_7\)Sn\(_3\)S\(_{10}\). Interestingly, the \(\kappa_l\) is increased to 2.0 W m\(^{-1}\) K\(^{-1}\) for Cu\(_7\)Sn\(_3\)S\(_9\)Br\(_0.1\) at 300 K. Such an increase should be related to the transition from the low-symmetry tetragonal structure to the high-symmetry cubic structure as mentioned above. In the tetragonal structure, the localized short-range non-cubic lattice distortions will introduce extra strain field fluctuation to interrupt the phonon transport. However, when the tetragonal structure converts into a cubic structure, such kinds of lattice distortions disappears, which is responsible for the higher \(\kappa_l\) observed in Cu\(_7\)Sn\(_3\)S\(_9\)Br\(_0.1\). With increasing the Br-doping content from 0.1 to 1.5, the \(\kappa_l\) gradually decreases in the entire measured temperature range. At 300 K, the \(\kappa_l\) for Cu\(_7\)Sn\(_3\)S\(_{0.9}\)Br\(_{0.1}\) is just 0.7 W m\(^{-1}\) K\(^{-1}\), about 50% reduction as compared with that of Cu\(_7\)Sn\(_3\)S\(_{10}\).

In order to understand the reason for the lowered \(\kappa_l\), the sound velocity of Cu\(_7\)Sn\(_3\)S\(_{10}\)–Br\(_x\) samples was measured. The results are plotted in Fig. 6d.\(^{11}\) It can be seen that the transverse sound velocity \(v_T\), longitudinal sound velocity \(v_L\), and average sound velocity \(v\) gradually decrease with increasing Br-doping content, indicating that Br-doping might soften the phonons and modify the phonon dispersions. However, the maximum decrement of \(v\) is just 6.6\%, which cannot account for the drastic \(\kappa_l\) reduction. Thus, the additional point defect scattering introduced by Br-doping should still be the dominant reason for the \(\kappa_l\) reduction.

The Callaway model is used to analyze the influence of additional point defect scattering on \(\kappa_l\) reduction in Cu\(_7\)Sn\(_3\)–S\(_{10}\)–Br\(_x\).\(^{31–33}\) With the purpose of ruling out the influence of structure transition, we just discuss the Br-doped samples with the cubic structure. Cubic Cu\(_7\)Sn\(_3\)S\(_{0.9}\)Br\(_{0.1}\) is treated as a pure compound and its lattice thermal conductivity is named \(\kappa_L\). The chemical formulas of other cubic Cu\(_7\)Sn\(_3\)S\(_{10}\)–Br\(_x\) are rewritten as Cu\(_7\)Sn\(_3\)Br\(_{0.1}\)S\(_{0.9}\)–Br\(_{y}\), where \(y (=x–0.1)\) is the normalized Br-doping content. Then, the relation between \(\kappa_L\) and \(\kappa_l\) of Cu\(_7\)Sn\(_3\)Br\(_{0.1}\)S\(_{0.9}\)–Br\(_{y}\) can be expressed as

\[
\frac{\kappa_L}{\kappa_l} = \frac{\tan^{-1} \frac{u}{u'}}{u'} \tag{10}
\]

\[
u'^{2} = \frac{\pi \Theta_B \Omega}{2 \hbar^2} \left(\frac{\Delta M}{\langle M \rangle}\right)^2 \tag{11}
\]

where \(u\) is the disorder scaling parameter, \(\Theta_B\) is the Debye temperature, \(\Omega\) is the average atomic volume, \(\hbar\) is the reduced Planck constant, and \(\Gamma\) is the scattering parameter. \(\Gamma = \Gamma_{\text{Mass}} + \Gamma_{\text{Strain}}\), where \(\Gamma_{\text{Mass}}\) and \(\Gamma_{\text{Strain}}\) are scattering parameters related to mass fluctuation and strain field fluctuation, respectively. They can be expressed as:

\[
\Gamma = \frac{1}{2} \left(\frac{M}{\langle M \rangle}\right)^2 z(1-z) \left[\left(\frac{\Delta M}{\langle M \rangle}\right)^2 + \varepsilon \left(\frac{\Delta r}{r}\right)^2\right] \tag{12}
\]

where \(z\) is the fractional occupation of Br atoms on S sites. \(\Delta M\) and \(\Delta r\) are the differences in mass and radius between the doped and the host atoms, respectively. \(M\) and \(r\) are the average atomic mass and radius, respectively. \(\langle M \rangle\) is the average atomic mass of the compound. \(\varepsilon\) is the strain field-related adjustable parameter, which can be obtained by fitting the experimental data. The detailed numbers for the parameters used in the Callaway model are listed in Table S6.\(^{†}\)

Fig. 6e shows the scattering parameters \(\Gamma_{\text{Mass}}\) and \(\Gamma_{\text{Strain}}\) as a function of the Br doping content. \(\Gamma_{\text{Strain}}\) is quite larger than \(\Gamma_{\text{Mass}}\) implying that the strain field fluctuation dominates the \(\kappa_l\) reduction in Cu\(_7\)Sn\(_3\)S\(_{10}\)–Br\(_x\). In Fig. 6d, the dashed lines represent the predicted \(\kappa_l\) at different temperatures. The parameters used to predict the \(\kappa_l\) are shown in Table S6.\(^{†}\) The experimental data are in good agreement with theoretical curves, proving that the mass and strain field fluctuations introduced by the Br dopant are responsible for the reduced \(\kappa_l\) in Cu\(_7\)Sn\(_3\)S\(_{10}\)–Br\(_x\) with cubic structures.

### 3.4 TE figure of merit \(zT\)

The TE figure of merit \(zT\) for Cu\(_7\)Sn\(_3\)S\(_{10}\)–Br\(_x\) samples is calculated based on the measured \(\kappa, \sigma,\) and \(S\) as shown in Fig. 7a. The \(zT\) is significantly increased upon doping Br in the entire measured temperature range. When the Br-doping content is \(x\)
= 1.0, a peak $zT$ around unity is achieved at 750 K, which is twice that of the pristine Cu$_7$Sn$_3$S$_{10}$. Actually, this value is a record-high value in Cu–Sn–S ternary systems. It is also superior to that of most TE sulfo-

fides reported so far. Based on the SPB model, we also calculate the theoretical $zT$ curves for Cu$_7$Sn$_3$S$_{10}$–Br$_x$. The parameters used in the calculation are listed in Table S7.† As shown in Fig. 7b, when $m_0^* = 5.0 m_e$, $\mu_0 = 3.3$ cm$^2$ V$^{-1}$ s$^{-1}$, and $\kappa_L = 0.6$ W m$^{-1}$ K$^{-1}$, the predicted optimal carrier concentration corresponding to the maximal $zT$ is around 4.5 × $10^{20}$ cm$^{-3}$ at 750 K. If the $m_0^*$ is larger, achieving the maximal $zT$ at 750 K requires higher carrier concentration. For example, when $m_0^* = 6.0 m_e$, $\mu_0 = 1.7$ cm$^2$ V$^{-1}$ s$^{-1}$, and $\kappa_L = 0.4$ W m$^{-1}$ K$^{-1}$, the predicted optimal carrier concentration corresponding to the maximal $zT$ is around 6.8 × $10^{20}$ cm$^{-3}$. All the experimental data of Cu$_{5.5}$Sn$_{6}$S$_{10}$–Br$_x$ and Cu$_7$Sn$_3$S$_{10}$–Cl$_x$ systems show a very nice agreement with the calculated curves. Because the $p_0$ obtained in Cu$_7$Sn$_3$S$_{10}$–Br$_x$ is already comparable with the optimal carrier concentration when $m_0^* = 6.0 m_e$, the experimental $zT$ at 750 K is close to the predicted maximal $zT$.

4. Conclusions

In this work, a series of high-purity Cu$_7$Sn$_3$S$_{10}$–Br$_x$ samples have been prepared. Their crystal structures, and electrical and thermal transport properties have been systematically investigated. The results show that Br has a high nominal solution limit with $x > 1.5$ in Cu$_7$Sn$_3$S$_{10}$. Through doping Br at S sites, the carrier concentration is successfully tuned to the optimal range for good electrical transport properties. Likewise, doping Br introduces additional mass and strain field fluctuations to significantly decrease the lattice thermal conductivity. Lastly, a maximum $zT$ around unity is obtained for Cu$_7$Sn$_3$S$_{10}$Br at 750 K, which is among the highest values reported for TE sulfides.

Conflicts of interest

There are no conflicts to declare.

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