Improvement in the thermoelectric performance of highly reproducible n-type (Bi,Sb)$_2$Se$_3$ alloys by Cl-doping†

Nadra Nasir,a Kyu Hyoung Lee,b Sang-il Kim,c Hyun-Sik Kim,d Jae-Hong Lim,e Liangwei Fu,f* and Sung Wng Kim f*af

(Bi,Sb)$_2$Se$_3$ alloys are promising alternatives to commercial n-type Bi$_2$(Te,Se)$_3$ ingots for low-mid temperature thermoelectric power generation due to their high thermoelectric conversion efficiency at elevated temperatures. Herein, we report the enhanced high-temperature thermoelectric performance of the polycrystalline Cl-doped Bi$_{2.8}$Sb$_{0.2}$Se$_3$ (x = 0.8, 1.0) bulks and their sustainable thermal stability. Significant role of Cl substitution, characterized to enhance the power factor and reduce the thermal conductivity synergistically, is clearly elucidated. Cl-doping at Se-site of both Bi$_{1.2}$Sb$_{0.8}$Se$_3$ and BiSbSe$_3$ results in a high power factor by carrier generation and Hall mobility improvement while maintaining converged electronic band valleys. Furthermore, point defect phonon scattering originated from mass fluctuations formed at Cl-substituted Se-sites reduces the lattice thermal conductivity. Most importantly, spark plasma sintered Cl-doped Bi$_{2.8}$Sb$_{0.2}$Se$_3$ bulks are thermally stable up to 700 K, and show a reproducible maximum thermoelectric figure of merit, $zT$, of 0.68 at 700 K.

1. Introduction

Bi$_2$Te$_3$-based alloys are the only commercialized thermoelectric materials for solid-state cooling and low-mid temperature (473–873 K) power generation, and their ingot-type materials are widely used due to a high thermoelectric figure of merit ($zT = S^2\sigma T/k_{\text{tot}}$, where $S$, $\sigma$, $k_{\text{tot}}$, and $T$ are the Seebeck coefficient, electrical conductivity, total thermal conductivity, and the absolute temperature, respectively) of about 1.0 near room-temperature. However, ingots of Bi$_2$Te$_3$-based alloys have a poor mechanical reliability (fracture strength of ~10 MPa) because of 00l-oriented structure weakly bonded by van der Waals forces, which limits their wider applications such as in automobile thermoelectric generator (ATEG). To address this, polycrystalline bulk form materials have been intensively studied, and an improved mechanical strength (~80 MPa) with a higher $zT$ ~1.1 at 300 K has been obtained in micro-grained p-type Bi$_2$Sb$_2$Te$_3$ prepared by ball milling (BM) and spark plasma sintering (SPS). Its n-type counterpart with a comparable mechanical strength and $zT$ is required to construct thermoelectric module with improved mechanical reliability as well as high performance, however, no marked improvement in $zT$ from n-type micro-grained materials was achieved in BMed and SPSed Bi$_{2.8}$Te$_{0.2}$Se$_3$ (~0.63 at 300 K). Furthermore, a severe reproducibility problem was also found in this polycrystalline sample owing to the uncontrollable defect structures such as vacancies (Te- or Se-site) and antisite defects. Polycrystalline bulk of n-type Bi$_2$Te$_{2.7}$Se$_{0.3}$ with high $zT$ (~0.98 at 300 K) and improved reproducibility has been demonstrated by combining a cold deformation and a hot extrusion benefitting from precise control of point defects, however, a simpler and yet easily scalable approach is always sought after. Bi$_2$Se$_3$ is a narrow-bandgap layered semiconductor (space group $\overline{R}3m$-$D_{6h}$) with tetradymite structure and it has singly degenerate conduction band. The conduction band minimum (CBM) is observed at the center of the Brillouin zone (Γ-point) and the second conduction band is located 150–250 meV (Z-point) above the CBM, thus the $zT$ of pristine Bi$_2$Se$_3$ is very low (~0.1 at 300 K) mainly due to low $S$ (~40 $\mu$V K$^{-1}$ at 300 K). High $\kappa_{\text{tot}}$ ~2.4 W m$^{-1}$ K$^{-1}$ at 300 K is another reason for the low $zT$ of Bi$_2$Se$_3$. Very recently, Te-free (Bi,Sb)$_2$Se$_3$-based alloys have been received attention as promising alternatives to Bi$_2$(Te,Se)$_3$-based alloys especially for low-mid temperature power...
2. Results and discussion

In the present study, we selected two different matrixes; (1) BiSbSe₃ with an orthorhombic phase and (2) Bi₁.₂Sb₀.₈Se₃ with orthorhombic and rhombohedral phases. Fig. 1a shows the XRD patterns for BiSbSe₃-yCl₂ samples. All the peaks can be indexed as a pure orthorhombic structure of Sb₂Se₃ without any secondary phases, suggesting the Cl substitution at Se-site. Structure factors including lattice parameters of BiSbSe₃-based compounds with orthorhombic phase (Fig. S1†) and those of Bi₁.₂Sb₀.₈Se₃-based compounds with mixed (orthorhombic and rhombohedral) phases (Fig. S3†) were extracted by the Rietveld refinement (GSAS II suite) after refinements with different structural models at the condition of convergence with the best pattern match. The slight decrease in lattice parameters (a and c) of BiSbSe₃ after the Cl doping is another evidence for Cl substitution due to the smaller ionic radius of Cl⁻ (167 pm) when compared to that of Se²⁻ (184 pm) (Fig. S1†). On the other hand, as reported in the previous report,⁴⁴ both orthorhombic and rhombohedral phases are clearly detected in Bi₁.₂Sb₀.₈Se₃-yCl₂ samples as shown in Fig. 1b. Peaks for the rhombohedral structure of BiSbSe₃ were observed at 2θ ~18.58° and ~29.35°. The strongest intensity of (402) indicates the preferred crystal orientation generated during the SPS process. Oriented grain structure is also found in TEM images for the fractured surface of SPSed Bi₁.₂Sb₀.₈Se₃-yCl₂, (Fig. 1c and S2†). The mole fraction of rhombohedral phase estimated by Rietveld refinement is about 0.74, and this value does not show significant change with Cl doping contents (see the Table S1†). And slight decrease in cell volume by Cl-doping is observed in orthorhombic phase (Fig. S3†). Cl-related impurity phase

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(Bi$_3$Se$_4$Cl) was observed in Bi$_{1.2}$Sb$_{0.8}$Se$_{2.76}$Cl$_{0.24}$, suggesting that the solubility limit of Cl for Se-site is about 8 at% in Bi$_{1.2}$Sb$_{0.8}$Se$_3$ (Fig. S41).

The temperature dependences of $\sigma$ for both BiSbSe$_{3-y}$Cl$_y$ ($y = 0.12, 0.18, 0.24$) and Bi$_{1.2}$Sb$_{0.8}$Se$_{3-y}$Cl$_y$ ($y = 0.12, 0.18, 0.24$) samples are plotted in Fig. 2a. All thermoelectric transport properties ($\sigma$, $S$, and $k$) are measured perpendicular to SPS pressing direction since the electrical transport is dominant along the in-plane direction. The $\sigma$ values of BiSbSe$_3$ and Bi$_{1.2}$Sb$_{0.8}$Se$_3$ are effectively increased by Cl-doping. Interestingly, the $\sigma$ values of Cl-doped Bi$_{1.2}$Sb$_{0.8}$Se$_3$ are higher than those of Cl-doped BiSbSe$_3$ in the whole measured temperature range. The $\sigma$ values of the BiSbSe$_{2.76}$Cl$_{0.24}$ are 132 S cm$^{-1}$ and 61.2 S cm$^{-1}$ at 300 K and 700 K, respectively, while those of Bi$_{1.2}$Sb$_{0.8}$Se$_{2.76}$Cl$_{0.24}$ are 397 S cm$^{-1}$ and 159 S cm$^{-1}$ at 300 K and 700 K, respectively. To clarify this, we estimated the $n_e$ and $\mu_H$ of both Cl-doped BiSbSe$_3$ and Bi$_{1.2}$Sb$_{0.8}$Se$_3$ at 300 K (Fig. 2b). The improvement in $\sigma$ by Cl-doping is resulted from the increase of $\mu_H$ as well as $n_e$ both in BiSbSe$_3$ and Bi$_{1.2}$Sb$_{0.8}$Se$_3$. It is noted that $\mu_H$ values of Cl-doped Bi$_{1.2}$Sb$_{0.8}$Se$_3$ are much higher than those of Cl-doped BiSbSe$_3$. The $\mu_H$ values of BiSbSe$_{3-y}$Cl$_y$ ($y = 0.12, 0.18, 0.24$) at 300 K is ranged from 8.44 to 9.01 cm$^2$ V$^{-1}$ s$^{-1}$, whereas that of Bi$_{1.2}$Sb$_{0.8}$Se$_{2.88}$Cl$_{0.12}$ is $\sim$50.4 cm$^2$ V$^{-1}$ s$^{-1}$. Moreover, the $\mu_H$ value of highly Cl-doped BiSbSe$_{2.76}$Cl$_{0.24}$ is retained in value about 27.3 cm$^2$ V$^{-1}$ s$^{-1}$ despite of the high $n_e \sim 9.0 \times 10^{19}$ cm$^{-3}$. This high $\mu_H$ has been also reported in I-doped Bi$_{1.2}$Sb$_{0.8}$Se$_{3}$.

Unexpected difference between electronic transport properties of Cl-doped Bi$_{1.2}$Sb$_{0.8}$Se$_3$ and those of I-doped Bi$_{1.2}$Sb$_{0.8}$Se$_3$ is observed in S. Fig. 3a depicts the temperature dependences of $S$ for both BiSbSe$_{3-y}$Cl$_y$ ($y = 0.12, 0.18, 0.24$) and Bi$_{1.2}$Sb$_{0.8}$Se$_{3-y}$Cl$_y$ ($y = 0.12, 0.18, 0.24$) samples. The $S$ values of all samples are negative in the whole measured temperature range, indicating n-type semiconductors. The large |$S$| values of Cl-doped BiSbSe$_3$ samples due to the convergence of conduction band by phase transition are well demonstrated both in I-doped and Br-doped BiSbSe$_3$.\textsuperscript{5,9} To investigate the change in band structure by Cl-doping especially in Bi$_{1.2}$Sb$_{0.8}$Se$_3$, we calculate the $m_d^*$ by using measured $S$ and $n_e$ at 300 K based on the following eqn (1):\textsuperscript{3}

$$S = \frac{8\pi^2 k_B^2 T \left( \frac{\pi}{3m^*_{e}} \right)^{2/3}}{3e^2 h^2} m_d^*,$$  \hspace{1cm} (1)

where $k_B$, $e$, and $h$ are the Boltzmann constant, elementary charge, and Planck constant, respectively. The $m_d^*$ values are listed in Table 1 together with those for I-doped BiSbSe$_3$ and Bi$_{1.2}$Sb$_{0.8}$Se$_3$ samples, which are estimated from eqn (1) by using previously reported data.\textsuperscript{5} Large $m_d^*$ values of 1.55$m_0$ and 1.67$m_0$ are obtained both in BiSbSe$_{2.82}$Cl$_{0.18}$ and BiSbSe$_{2.91}$I$_{0.09}$, respectively, with pure orthorhombic phase benefiting from converged electronic band valleys. However, the $m_d^*$ values of Cl-doped Bi$_{1.2}$Sb$_{0.8}$Se$_3$ and those of I-doped Bi$_{1.2}$Sb$_{0.8}$Se$_3$ are smaller than those of Cl- and I-doped BiSbSe$_3$ mainly due to the large mole fraction of rhombohedral phase (Table S1) with singly-degenerate conduction band. It is noted that $m_d^*$ value of Bi$_{1.2}$Sb$_{0.8}$Se$_{2.76}$Cl$_{0.24}$ reaches value about 0.90$m_0$, which results
in a large $S$ even in Bi$_{1.2}$Sb$_{0.8}$Se$_3$ systems. Fig. 3c shows the Pisarenko plots ($n_c - |S|$) for both BiSb$_{2.88}$Cl$_{0.12}$ ($y = 0.12$, 0.18, 0.24) and Bi$_{1.2}$Sb$_{0.8}$Se$_{2.76}$Cl$_{0.24}$ ($z = 0.12$, 0.18, 0.24) samples at 300 K. Those for I-doped BiSbSe$_3$, I-doped Bi$_{1.2}$Sb$_{0.8}$Se$_3$, and Br-doped Bi$_{1.2}$Sb$_{0.8}$Se$_3$ and Cl- and I-doped Bi$_{1.2}$Sb$_{0.8}$Se$_3$ at 300 K.

As clearly shown in Fig. 3c, similar value of $S$ is obtained in Bi$_{1.2}$Sb$_{0.8}$Se$_{2.76}$Cl$_{0.24}$ despite of the large increase in $n_c$ when compared to that of I-doped Bi$_{1.2}$Sb$_{0.8}$Se$_3$ samples. Resultantly, a maximum power factor values of $\sim 3.19 \mu$W cm$^{-1}$ K$^{-2}$ and $\sim 5.61 \mu$W cm$^{-1}$ K$^{-2}$ at 300 K and 700 K, respectively, are obtained in Bi$_{1.2}$Sb$_{0.8}$Se$_{2.76}$Cl$_{0.24}$ (Fig. 3b), which ensures the enhanced $zT$ especially at higher temperatures. This beneficial characteristic feature for the realization of highly-efficient low-mid temperature thermoelectric power generation system is only found in Cl-doped Bi$_{1.2}$Sb$_{0.8}$Se$_3$ among other (Bi,Sb)$_2$Se$_3$-based alloys.

Table 1  The density-of-states effective mass ($m^*_d$) values of Cl-doped BiSbSe$_3$ and Bi$_{1.2}$Sb$_{0.8}$Se$_3$. Those of I-doped BiSbSe$_3$ and Bi$_{1.2}$Sb$_{0.8}$Se$_3$, which are estimated from the reported data ref. 5, are also shown for comparison.

| Compositions (nominal) | $m^*_d (m_0)$ | Compositions (nominal) | $m^*_d (m_0)$ |
|------------------------|--------------|------------------------|--------------|
| BiSbSe$_{2.88}$Cl$_{0.12}$ | 1.17          | BiSbSe$_{2.82}$I$_{0.03}$ | 1.50          |
| BiSbSe$_{2.82}$I$_{0.18}$ | 1.55          | BiSbSe$_{2.82}$I$_{0.06}$ | 1.63          |
| BiSbSe$_{2.76}$I$_{0.24}$ | 1.38          | BiSbSe$_{2.82}$I$_{0.09}$ | 1.67          |
| Bi$_{1.2}$Sb$_{0.8}$Se$_{2.88}$Cl$_{0.12}$ | 0.54          | Bi$_{1.2}$Sb$_{0.8}$Se$_{2.94}$I$_{0.03}$ | 0.33         |
| Bi$_{1.2}$Sb$_{0.8}$Se$_{2.82}$Cl$_{0.18}$ | 0.66          | Bi$_{1.2}$Sb$_{0.8}$Se$_{2.94}$I$_{0.06}$ | 0.65         |
| Bi$_{1.2}$Sb$_{0.8}$Se$_{2.76}$Cl$_{0.24}$ | 0.90          | Bi$_{1.2}$Sb$_{0.8}$Se$_{2.94}$I$_{0.09}$ | 0.43         |

Fig. 4a shows the temperature dependence of $k_{\text{tot}}$ for BiSbSe$_{3-y}$Cl$_y$ ($y = 0.12$, 0.18, 0.24) and Bi$_{1.2}$Sb$_{0.8}$Se$_{3-z}$Cl$_z$ ($z = 0.12$, 0.18, 0.24) samples. The $k_{\text{tot}}$ values of Cl-doped Bi$_{1.2}$Sb$_{0.8}$Se$_3$ are higher than those of Cl-doped BiSbSe$_3$. The room temperature $k_{\text{tot}}$ values of both Cl-doped BiSbSe$_3$ and Bi$_{1.2}$Sb$_{0.8}$Se$_3$ are $\sim 0.58$–$0.62$ W m$^{-1}$ K$^{-1}$ and $\sim 0.72$–$0.83$ W m$^{-1}$ K$^{-1}$, respectively. This is considered to be related to the increased electronic contribution ($k_{\text{ele}}$) originated from the higher $s$ of Cl-doped Bi$_{1.2}$Sb$_{0.8}$Se$_3$. On the other hand, as shown in Fig. 4a, the $k_{\text{tot}}$ of all the samples gradually decrease with temperature, suggesting the small contribution of bipolar thermal conduction ($k_{\text{bp}}$). We estimated the $k_{\text{lat}}$ and $k_{\text{ele}}$ by using the relationship of $k_{\text{tot}} = k_{\text{ele}} + k_{\text{lat}}$. Details for the calculation are described in Section 6 of ESI.†
by Cl-doping is relatively small compared to that of Cl-doped Bi$_{1.2}$Sb$_{0.8}$Se$_3$ due to cumulative phonon scattering by soft bonding and point defect. Thus the significantly reduced $\kappa_{\text{lat}}$ (~0.56 W m$^{-1}$ K$^{-1}$ at 300 K and ~0.39 W m$^{-1}$ K$^{-1}$ at 700 K) is obtained in Bi$_{1.2}$Sb$_{0.8}$Se$_{2.76}$Cl$_{0.24}$ mainly due to the intensified mass-defect phonon scattering. The slightly higher $\kappa_{\text{lat}}$ of Bi$_{1.2}$Sb$_{0.8}$Se$_{2.82}$Cl$_{0.18}$ than that of Bi$_{1.2}$Sb$_{0.8}$Se$_{2.88}$Cl$_{0.12}$ is considered to be related with the difference in preferred orientation (Fig. 1b).

Fig. 5a and b show the temperature dependent $\zeta T$ of BiSbSe$_3$$_y$Cl$_y$ ($y = 0.12, 0.18, 0.24$) and that of Bi$_{1.2}$Sb$_{0.8}$Se$_{2.76}$Cl$_{0.24}$ ($z = 0.12, 0.18, 0.24$), respectively. The Cl-doping effectively enhances the $\zeta T$ both in BiSbSe$_3$ and Bi$_{1.2}$Sb$_{0.8}$Se$_3$ due to improvement of electronic and thermal transport properties. High $\zeta T$ of Cl-doped BiSbSe$_3$ with pure orthorhombic phase is mainly due to the enlarged $m^*_d$ benefitting from the increased valley degeneracy and flattened band, which results in a larger $S$. Reduced $\kappa_{\text{lat}}$ by the bond softening in orthorhombic phase is another origin for high $\zeta T$ of Cl-doped BiSbSe$_3$. On the other hand, higher $\zeta T$ found in Cl-doped Bi$_{1.2}$Sb$_{0.8}$Se$_3$, despite of high rhombohedral phase fraction (~0.74) is attributed to the simultaneous improvement of electronic (enlarged $m^*_d$ and improved $\mu_H$) and thermal (reduced $\kappa_{\text{lat}}$) transport properties by Cl-doping. The highly-reproducible maximum $\zeta T$ reaches in value about 0.68 ± 0.04 at 700 K for three different Bi$_{1.2}$Sb$_{0.8}$Se$_{2.76}$Cl$_{0.24}$ samples. Moreover, high $\sigma$ values of 397 S cm$^{-1}$ at 300 K and 159 S cm$^{-1}$ at 700 K make this material a promising candidate for practical applications.

We verify the thermal stability of Bi$_{1.2}$Sb$_{0.8}$Se$_{2.76}$Cl$_{0.24}$ via the cyclic measurement of $\zeta T$ within temperature range from 300 K to 700 K (Fig. 6a) and remeasurement of power factor after annealing at 800 K for 10 h (Fig. 6b). Fig. 6a and b indicate that the Cl-doped Bi$_{1.2}$Sb$_{0.8}$Se$_3$ alloys are chemically stable up to 700 K.

4. Conclusions

In summary, temperature dependent thermoelectric transport properties of Te-free Cl-doped BiSbSe$_3$ and Bi$_{1.2}$Sb$_{0.8}$Se$_3$ are systematically investigated. Improved Seebeck coefficient and electrical conductivity are simultaneously obtained due to the enlarged density-of-states effective mass by high content Cl-doping (~8 at%), while maintaining intrinsic high mobility of Bi$_{1.2}$Sb$_{0.8}$Se$_3$-based alloys. This provides the optimized power factor of ~5.61 $\mu$W cm$^{-1}$ K$^{-2}$ at 700 K. Additionally, despite of the weaker phonon scattering owing to decreased bond softening effect in Bi$_{1.2}$Sb$_{0.8}$Se$_3$ compared to that in BiSbSe$_3$, lattice thermal conductivity is effectively reduced in value about 0.39 W m$^{-1}$ K$^{-1}$ at 700 K by 8 at% Cl-doping from the intensified mass-defect phonon scattering. This synergetic effect contributes to a high electrical conductivity of ~159 S cm$^{-1}$ and the high $\zeta T$ ~0.68 at 700 K.

Conflicts of interest

There are no conflicts to declare.

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