

N-Type Layered Oxyselenide Thermoelectric Materials

Subjects: Others

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$\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ is a new type of layered oxyselenide thermoelectric material. The crystal structure of $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ can be regarded as a 1:2 ratio of BiCuSeO and $\text{Bi}_2\text{O}_2\text{Se}$ heaping along the c -axis by turns, so there are insulative layers Bi_2O_2 and conductive layers Cu_2Se_2 and Se_2 in the structure. The $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ system not only maintains the low thermal conductivity of BiCuSeO but also can utilize the intrinsic electron carrier concentration of $\text{Bi}_2\text{O}_2\text{Se}$, considered to be a promising n -type oxyselenide thermoelectric material.

Keywords: thermoelectric ; n -type oxyselenide ; BiCuSeO ; $\text{Bi}_2\text{O}_2\text{Se}$; $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$

1. Introduction

Thermoelectric (TE) materials can achieve the direct transition between heat and electricity without producing other pollutants, providing an effective solution to the energy crisis and environmental problems [1][2]. The dimensionless figure of merit ZT defines the efficiency of a thermoelectric device, which derives from three related physical quantities: electrical conductivity (σ), Seebeck coefficient (S) and thermal conductivity (κ), $ZT = (\sigma S^2 T / \kappa)$, with absolute temperature T . However, the tightly-coupled relationship among these parameters makes it difficult to improve the overall ZT [2][3][4][5][6].

Intrinsic p -type semiconductor BiCuSeO possesses a layered ZrCuSiAs structure with space group $P4/nmm$ [2][7]. The special layered crystal structure of BiCuSeO is constituted by insulative $[\text{Bi}_2\text{O}_2]$ layers and conductive $[\text{Cu}_2\text{Se}_2]$ layers heaping along the c -axis by turns [8][9]. Due to the weak Van der Waals interaction between layers [10][11][12][13], the large displacement of the Cu atom [14][15] and the heavy Bi atom [3][16][17], BiCuSeO has intrinsically low thermal conductivity [18], which is an inherent advantage as a thermoelectric material. However, most of the reported BiCuSeO are p -type semiconductor materials at present, and researches on n -type BiCuSeO are relatively few and unsuccessful. The main problems are that no effective electronic dopant was found, and BiCuSeO -based materials with stable n -type transport properties have not been obtained yet.

Different from BiCuSeO , the intrinsic $\text{Bi}_2\text{O}_2\text{Se}$ exhibits n -type transport properties due to a large number of Se vacancies in the crystal structure [19][20]. However, the crystal structure of $\text{Bi}_2\text{O}_2\text{Se}$ is very similar to BiCuSeO in which insulative $[\text{Bi}_2\text{O}_2]$ layers and conductive $[\text{Se}_2]$ layers stack along the c -axis alternatively [21][22][23]. Similarly, $\text{Bi}_2\text{O}_2\text{Se}$ also has intrinsically low thermal conductivity due to the weak interlayer interaction [21][24][25][26], but its intrinsic carrier concentration ($\sim 1.5 \times 10^{15} \text{ cm}^{-3}$) is too low, resulting in poor electrical transport performance [27][28]. Therefore, current research is mainly focused on increasing the carrier concentration, thus improving the electrical transport performance of $\text{Bi}_2\text{O}_2\text{Se}$.

Recently, several studies on n -type layered oxyselenide thermoelectric materials were reported, which motivates us to systematically summarize the recent progress of these researches. The outline of this review is shown in **Figure 1**. First, several attempts to realize n -type BiCuSeO are summarized. Then, some typical approaches to optimize the thermoelectric performance of $\text{Bi}_2\text{O}_2\text{Se}$ are presented. Next, a new type layered oxyselenide $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ is introduced, and n -type transport properties can be obtained through halogen doping and optimized by introducing transition metal elements. At last, some prospective and outlooks were provided for future research in the end.

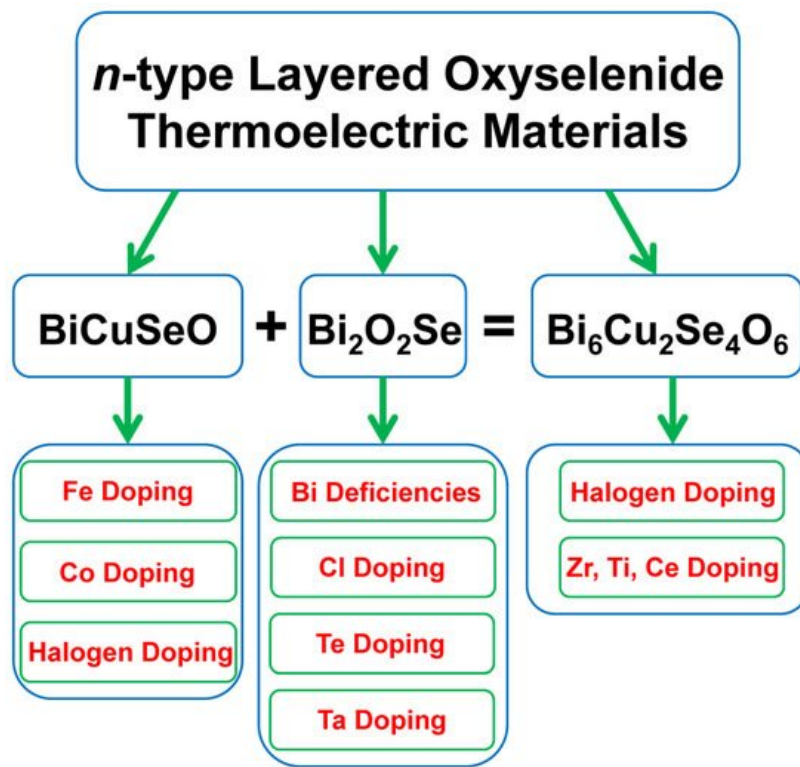


Figure 1. The outline of this review.

2. Various Attempts to Realize *n*-Type BiCuSeO

The peak Seebeck coefficient and corresponding temperature increase with the increase in Fe content, indicating the increase of band gap in those samples. Clearly, *n*-type transport properties can be found in the $x = 0.03$ sample at a low-temperature range, indicating that appropriate Fe content can achieve *n*-type BiCuSeO in a circumscribed temperature range.

Figure 2 a shows the temperature-dependent Seebeck coefficient (S) for Co-doped samples. For $x = 0.05$ and 0.10 samples, the S is positive within the entire temperature boundaries, indicating the dominant carrier is *p*-type. However, when the doping content of Co reaches 15%, the S begins to appear negative, indicating that the system exhibits *n*-type electrical transport properties. The negative S values of $x = 0.20$ sample within the entire temperature region indicate stable *n*-type electrical transport properties in the BiCuSeO system below room temperature.

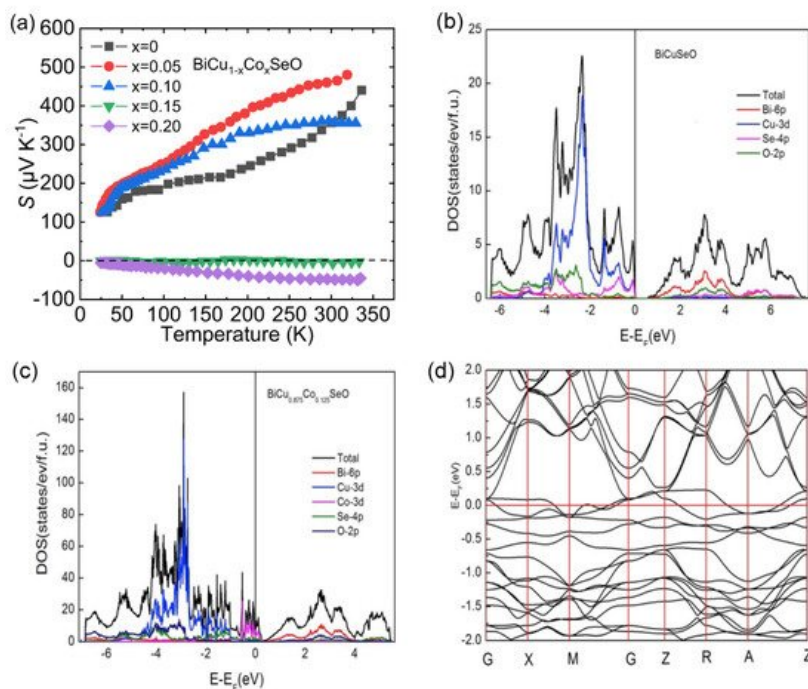


Figure 2. (a) The temperature-dependent Seebeck coefficient of BiCu_{1-x}Co_xSeO ($x = 0.05$ – 0.20). Data were adopted from Reference [29]. Copyright 2019, Elsevier Masson SAS. Calculated density of states (DOS) of (b) BiCuSeO and (c)

$\text{BiCu}_{0.875}\text{Co}_{0.125}\text{SeO}$, and (d) electronic band structure of $\text{BiCu}_{0.875}\text{Co}_{0.125}\text{SeO}$. (b–d) Reproduced with permission from Reference [29]. Copyright 2019, Elsevier Masson SAS.

Zhang et al. designed a series of continuous experimental steps to obtain n -type BiCuSeO [30]. Firstly, considering that the existence of Bi/Cu vacancies is the main reason for the p -type behavior of pristine BiCuSeO [31][32], extra Bi/Cu was introduced into the matrix to fill the vacancies which may produce holes. Finally, the optimal concentrations of extra Bi and Cu are determined as $x = 0.04$ and 0.05 , respectively. To increase electron carrier concentration, halogen elements (Br, I) were selected as donor dopants at Se sites and introduced into the Bi 1.04 Cu 1.05 SeO matrix. The S as a function of temperature for I/Br doped Bi 1.04 Cu 1.05 SeO samples is presented in **Figure 3** a,b. The introduction of Br/I can successfully transform Bi 1.04 Cu 1.05 SeO from p -type to n -type within a certain temperature range, and the negative S for I-doped Bi 1.04 Cu 1.05 SeO traverses a narrower temperature range than Br-doped one. In the high-temperature range, p -type behavior appears again, indicating that vacancies reproduced as the temperature rises, which may be relevant to the instability of Cu–Br and Cu–I bonds [33][34].

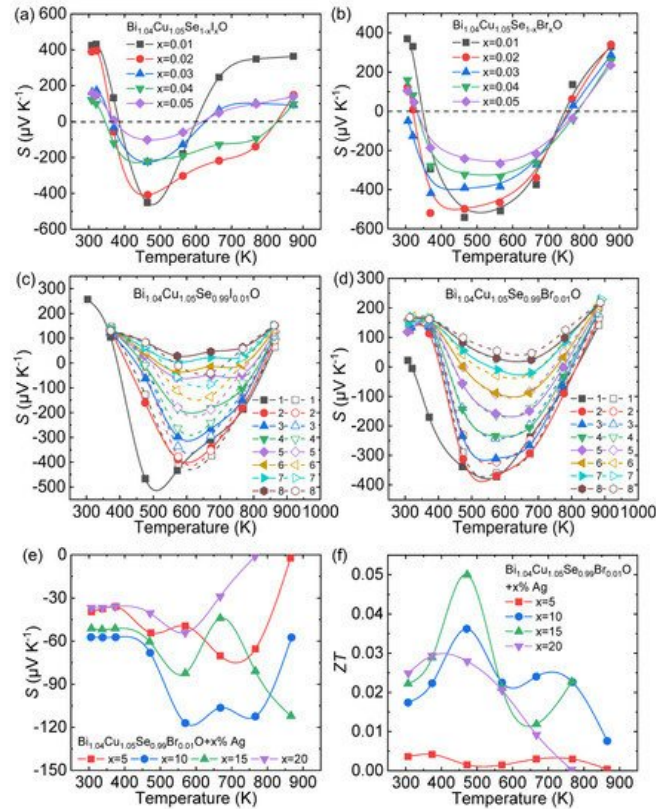


Figure 3. The temperature dependence of Seebeck coefficient for (a) $\text{Bi}_{1.04}\text{Cu}_{1.05}\text{Se}_{1+x}\text{I}_x\text{O}$ ($x = 0.01–0.05$) and (b) $\text{Bi}_{1.04}\text{Cu}_{1.05}\text{Se}_{1+x}\text{Br}_x\text{O}$ ($x = 0.01–0.05$). The temperature-dependent Seebeck coefficients obtained through heating-cooling cycle measurements: 8 cycles for (c) $\text{Bi}_{1.04}\text{Cu}_{1.05}\text{Se}_{0.99}\text{I}_{0.01}\text{O}$ and (d) $\text{Bi}_{1.04}\text{Cu}_{1.05}\text{Se}_{0.99}\text{Br}_{0.01}\text{O}$, respectively. The solid symbols and lines express the heating process, while the dashed symbols and lines express cooling process. The temperature dependence of (e) Seebeck coefficients and (f) ZT value of $\text{Bi}_{1.04}\text{Cu}_{1.05}\text{Se}_{1+x}\text{Br}_x\text{O} + x\% \text{Ag}$ ($x = 5–20$). Data shown in (a,b,e,f) were adopted from Reference [30]. Copyright 2017, Elsevier Inc. Data shown in (c–d) were adopted from Reference [35]. Copyright 2019, Elsevier Ltd and Techna Group S.r.l.

In order to further explore the p - n - p -type behavior in the obtained system, a heating–cooling measurement was carried out for halogen doped BiCuSeO samples [35], as shown in **Figure 3** c,d. As can be seen, Bi 1.04 Cu 1.05 Se 0.99 X 0.01 O ($X = \text{Br, I}$) changes completely from n -type to p -type transport behavior after eight heating–cooling cycle measurements. The above results indicate that halogens are effective dopants to obtain n -type BiCuSeO but exhibit poor stability. To improve the stability of n -type transport, metallic particles were introduced into the halogen-doped Bi 1.04 Cu 1.05 SeO. The temperature dependence of S for Bi 1.04 Cu 1.05 Se 0.99 Br 0.01 O + $x\% \text{Ag}$ samples is negative within the entire temperature range, and the maximum $|S|$ is $\sim 125 \mu\text{V/K}$ (**Figure 3** e). The maximum $ZT \sim 0.05$ can be reached at 475 K in Bi 1.04 Cu 1.05 Se 0.99 Br 0.01 O + 15% Ag (**Figure 3** f).

3. Various Attempts to Enhance Thermoelectric Properties of $\text{Bi}_2\text{O}_2\text{Se}$

At room temperature, the σ hikes from $\sim 0.019 \text{ S cm}^{-1}$ for $\text{Bi}_2\text{O}_2\text{Se}$ to $\sim 101.6 \text{ S cm}^{-1}$ for $\text{Bi}_2\text{O}_2\text{Se}_{0.985}\text{Cl}_{0.015}$, and then declines obviously as the Cl content increases (**Figure 4** a). One Cl - doped into the Se 2- sites can provide an extra electron, and the measured carrier concentration increased from $1.5 \times 10^{15} \text{ cm}^{-3}$ to $1.38 \times 10^{20} \text{ cm}^{-3}$ ($x =$

0.015). However, when the Cl content exceeds the solubility limit, the formation of the low-conductivity second phase $\text{Bi}_{12}\text{O}_{15}\text{Cl}_6$ [36] will reduce the effective doping amount of Cl, thereby deteriorating the σ . The small polaron hopping conduction theory was chosen to study the impact of Cl dopant on the σ . This theory could be expressed as the following Formula (5) [37]: $(5) \sigma = n e \mu = (C T) \exp(-E_a / k_B T)$ where n , e , μ , C , k_B , E_a and T express the carrier concentration, carrier charge, carrier mobility, the pre-exponential terms, Boltzmann constant, activation energy and the absolute temperature, respectively. **Figure 4 b** shows the linear relationship between $\ln(\sigma T)$ and $1000/T$, and the E_a can be obtained by calculating the slope of the straight line. As shown in the inset of **Figure 4 b**, the E_a of Cl-doped samples is obviously lower than $\text{Bi}_2\text{O}_2\text{Se}$, indicating that the introduction of Cl is conducive to carrier excitation. In summary, the high σ achieved in Cl-doped $\text{Bi}_2\text{O}_2\text{Se}$ is estimated to be the result of higher n coupled with lower E_a .

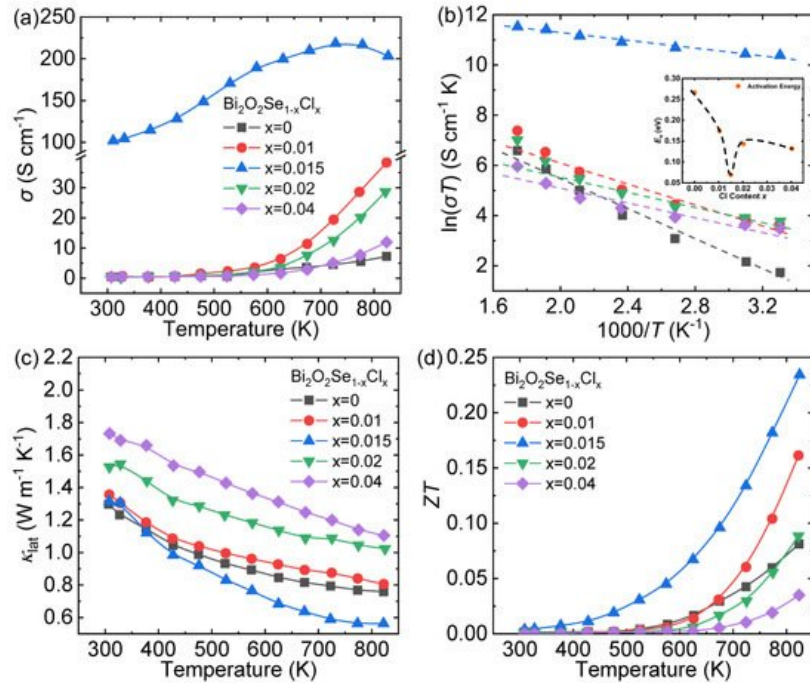


Figure 4. Thermoelectric transport properties of $\text{Bi}_2\text{O}_2\text{Se}_{1-x}\text{Cl}_x$ ($x = 0-0.04$): (a) electrical conductivity, (b) the fitting plots of the small polaron model and the activation energy (E_a) shown in the inset, (c) lattice thermal conductivity and (d) ZT . Data shown in (a–d) were adopted from Reference [28]. Copyright 2017, The American Ceramic Society.

Lattice thermal conductivity (κ_{lat}) of $\text{Bi}_2\text{O}_2\text{Se}_{0.985}\text{Cl}_{0.015}$ declines evidently after 423 K, reaching the lowest value $\sim 0.56 \text{ W m}^{-1} \text{K}^{-1}$ at 823 K (**Figure 4 c**). This effective decrease in κ_{lat} is derived from point defect scattering introduced by Cl substitution coupled with the enhanced grain boundaries scattering. However, for the $\text{Bi}_2\text{O}_2\text{Se}_{0.98}\text{Cl}_{0.02}$ and $\text{Bi}_2\text{O}_2\text{Se}_{0.96}\text{Cl}_{0.04}$ sample, the considerable augment in κ_{lat} is the result of the secondary phase $\text{Bi}_{12}\text{O}_{15}\text{Cl}_6$.

Benefitting from both the enhancement of the σ and the depression of the κ_{tot} , the peak ZT value ~ 0.23 at 823 K is achieved in $\text{Bi}_2\text{O}_2\text{Se}_{0.985}\text{Cl}_{0.015}$ (**Figure 4 d**), which demonstrates that Cl is an effective dopant to optimize the thermoelectric performance of $\text{Bi}_2\text{O}_2\text{Se}$.

The carrier engineering and hierarchical microstructure by Ta doping remarkably enhance the ZT values in $\text{Bi}_{1.90}\text{Ta}_{0.10}\text{O}_2\text{Se}$, reaching ~ 0.30 at 773 K, which is an increase of $\sim 350\%$ compared to pristine $\text{Bi}_2\text{O}_2\text{Se}$ (**Figure 5 f**).

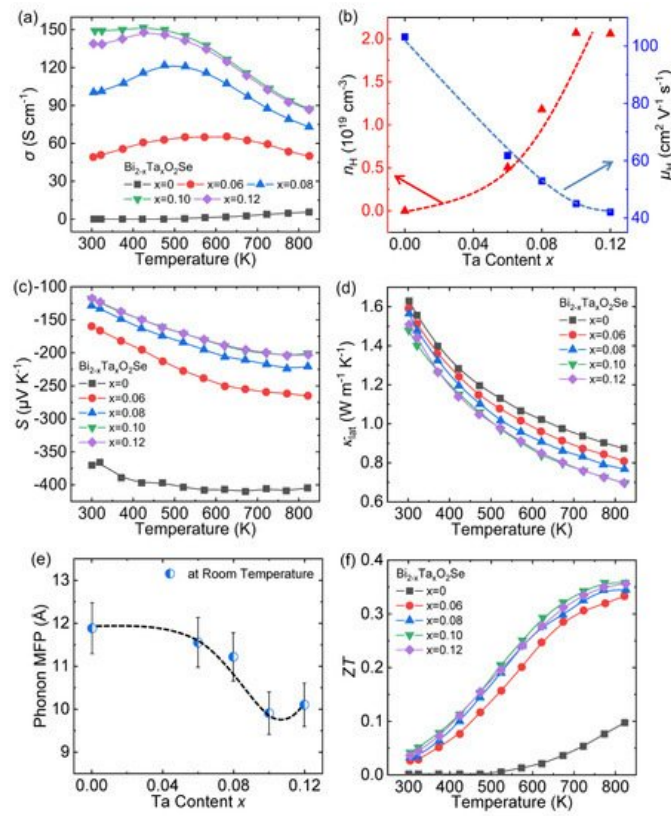


Figure 5. Thermoelectric transport properties of $\text{Bi}_{2-x}\text{Ta}_x\text{O}_2\text{Se}$ ($x = 0\text{--}0.12$): (a) electrical conductivity, (b) the carrier concentration and mobility at room temperature, (c) Seebeck coefficient, (d) lattice thermal conductivity, (e) phonon mean free path (MPF, l_{ph}) at room temperature, and (f) ZT. Data shown in (a–f) were adopted from Reference [38]. Copyright 2019, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

4. Attempts to Realize a New Kind of n-Type OxyseLENide: $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$

Because of the strong phonon scattering caused by layered structure [10], the lone pair electrons of Bi^{3+} [39][40], and the local vibration of Cu^{+} [14], BiCuSeO exhibits inherent low thermal conductivity. Another well-known thermoelectric oxyseLENide, $\text{Bi}_2\text{O}_2\text{Se}$ reveals stable n-type transport properties due to Se vacancies [19][20]. To fully utilize the features of BiCuSeO and $\text{Bi}_2\text{O}_2\text{Se}$, a new type layered oxyseLENide $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ was synthesized through solid state reaction (SSR) with the 1:2 ratio of BiCuSeO and $\text{Bi}_2\text{O}_2\text{Se}$ (Figure 6 a) [41][42][43], and stable n-type conductive transports were observed in this system through halogen element doping [42].

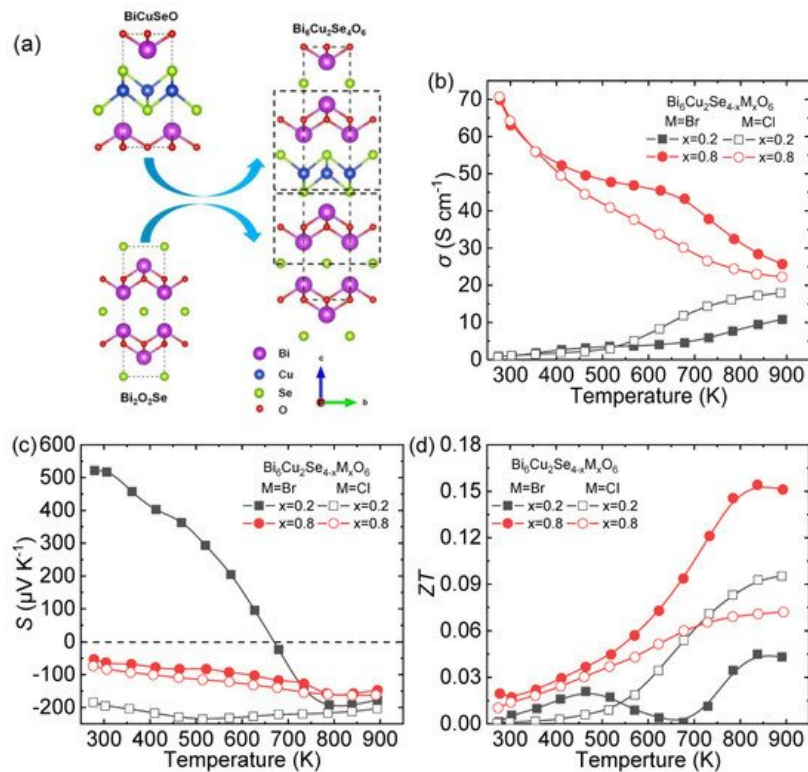


Figure 6. (a) The crystal structure of $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$. The temperature dependence of thermoelectric transport properties for $\text{Bi}_6\text{Cu}_2\text{Se}_{4-x}\text{M}_x\text{O}_6$ ($\text{M} = \text{Cl}/\text{Br}$, $x = 0.2/0.8$): (b) electrical conductivity, (c) Seebeck coefficient, (d) ZT . Data shown in (b–d) were adopted from Reference [42]. Copyright 2019, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

The σ of Cl-doped $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ is higher than Br-doped one at high temperature for the doping content $x = 0.2$. When the doping content x is increased to 0.8, the σ was significantly improved to $\sim 70 \text{ S cm}^{-1}$, and the Br-doped sample was better σ than the Cl-doped one at high temperature (Figure 6 b). The $\text{Bi}_6\text{Cu}_2\text{Se}_{3.8}\text{Br}_{0.2}\text{O}_6$ exhibits p-type semiconductor characteristics below 673 K and transfer to n-type with the temperature increasing; while $\text{Bi}_6\text{Cu}_2\text{Se}_{3.8}\text{Cl}_{0.2}\text{O}_6$ has a negative S value within the entire temperature boundaries indicating that a small amount of Cl doping ($x = 0.2$) can achieve stable n-type semiconductor behavior (Figure 6 c). When the doping content raises up to 0.8, the S of Cl/Br-doped samples has little difference, varying from ~ -60 to $-160 \mu\text{V K}^{-1}$. The maximum ZT value ~ 0.15 at 823 K is achieved in $\text{Bi}_6\text{Cu}_2\text{Se}_{3.2}\text{Br}_{0.8}\text{O}_6$ (Figure 6 d).

Zheng et al. chose $\text{Bi}_6\text{Cu}_2\text{Se}_{3.6}\text{Cl}_{0.4}\text{O}_6$ as the matrix and doped transition metal elements (Zr, Ti and Ce) at Bi sites to enhance its thermoelectric performance [43]. The introduction of transition metal elements can effectively increase the carrier concentration (n_H) and maintain the carrier mobility (μ_H ; Figure 7 a), thereby optimizing the electric conductivity (σ) of the matrix. The S of all doped samples remains negative throughout the entire temperature range, indicating the stable n-type semiconductor properties (Figure 7 b). Thanks to the optimized σ and maintained S , the power factor (PF) is effectively enhanced (Figure 7 c). Finally, due to the enhanced electrical transport properties and reduced thermal conductivity [43], the peak ZT value reached ~ 0.16 at 873 K in $\text{Bi}_{5.9}\text{Zr}_{0.1}\text{Cu}_2\text{Se}_{3.6}\text{Cl}_{0.4}\text{O}_6$ (Figure 7 d), which is 60% higher than that in $\text{Bi}_6\text{Cu}_2\text{Se}_{3.6}\text{Cl}_{0.4}\text{O}_6$ (~ 0.10 at 873 K).

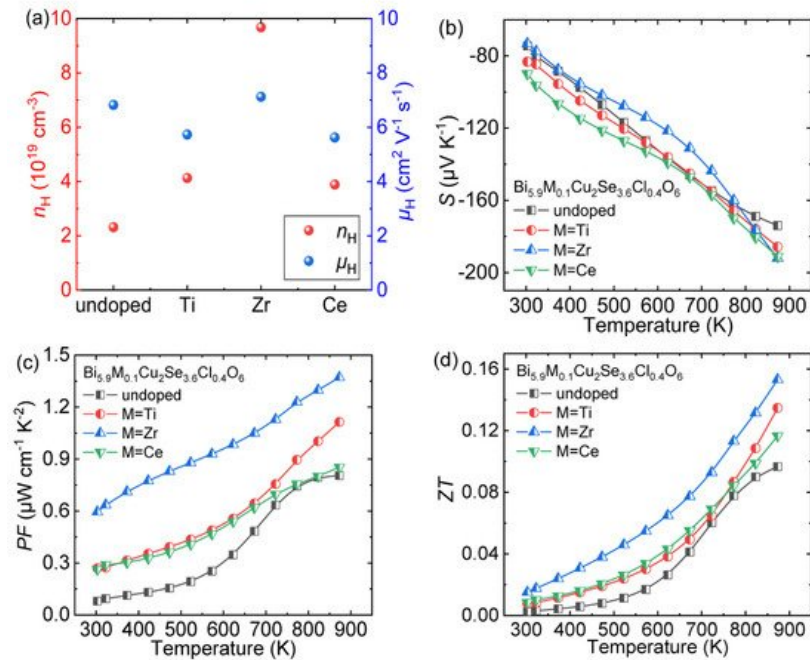


Figure 7. Thermoelectric transport properties of $\text{Bi}_6\text{Cu}_2\text{Se}_{3.6}\text{Cl}_{0.4}\text{O}_6$ and $\text{Bi}_{5.9}\text{M}_{0.1}\text{Cu}_2\text{Se}_{3.6}\text{Cl}_{0.4}\text{O}_6$ ($\text{M} = \text{Ti}, \text{Zr}, \text{Ce}$): (a) carrier concentration (n_H) and mobility (μ_H) at room temperature, (b) Seebeck coefficient, (c) power factor and (d) ZT . Data shown in (b–d) were adopted from Reference [43]. Copyright 2021, Acta Materialia Inc.

As a new type of layered oxyseLENIDE thermoelectric material, $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ maintains the advantages of BiCuSeO and $\text{Bi}_2\text{O}_2\text{Se}$, such as lower-cost and nontoxic elements, better thermal and chemical stability. Moreover, $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ can exhibit stable n-type semiconductor behavior by simple halogen doping and has intrinsic low thermal conductivity due to complex crystal structure. Thereby, $\text{Bi}_6\text{Cu}_2\text{Se}_4\text{O}_6$ is a new kind of n-type layered oxyseLENIDE thermoelectric material with broad development prospects.

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