Synergistic effects of Bi Deficiencies and Fe-doping on the thermoelectric properties and hardness of BiCuSeO ceramics

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Bi$_{1-x}$CuSeO + $x$ Fe ($x =$ 0, 0.01, 0.02, 0.04, 0.06, 0.08, 0.1, and 0.12) ceramics have been prepared by mechanical alloying and resistance pressing sintering process, and the synergistic effects of Bi Deficiencies and magnetic Fe doping on the thermoelectric properties and hardness of BiCuSeO ceramics have been investigated in detail. The results indicate that the band gap of the doped sample has narrowed down, which could be confirmed by the infrared absorption spectra. This leads to the dramatical increase of carrier concentration. The corresponding electrical conductivity increases significantly. The Seebeck coefficient decreases, but maintains high values in the high temperature zone. The maximum power factor of 0.38 mWm$^{-1}$K$^{-2}$ and ZT of 0.76 were obtained for the Bi$_{0.92}$CuSeO + 8% Fe sample at 873 K, which was ~1.4 and ~1.3 times as that of the pristine BiCuSeO. The hardness of pristine BiCuSeO is up to 200.0 HV, and increases greatly with the increase of $x$ for solid solution strengthening.

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1. Introduction

In recent years, more and more scientists have paid attention to thermoelectric materials because of their mutual conversion between thermal energy and electric energy. So far, materials with excellent thermoelectric properties at low temperature range, middle temperature range and high temperature range are basically alloy-based thermoelectric materials, such as tellurides,3–4 heuslers,5,6) and silicides,7) etc. However, the thermal/chemical stability of alloy-based thermoelectric materials are very poor, which would aggravate the service life of thermoelectric devices. Therefore, it is necessary to find thermoelectric materials with both good thermoelectric properties and excellent thermal/chemical stability in order to promote the large-scale applications of thermoelectric generation devices.

Compared with alloy-based thermoelectric materials, oxide thermoelectric materials exhibit well thermal/chemical stability, environmental friendliness and low cost of raw materials.8) However, because of the ionic nature, most oxide thermoelectric materials exhibit low electrical conductivity, high thermal conductivity and low ZT value.5) In recent years, because of the special natural superlattice structure and low Young’s modulus (~76.5 GPa), the layered oxysulfurides BiCuSeO exhibits extremely low thermal conductivity and very high Seebeck coefficient, which has attracted the attention of scholars.9,10) However, its intrinsic carrier concentration (~1.0 × 10$^{18}$ cm$^{-3}$) and carrier mobility (~20 cm$^2$ V$^{-1}$s$^{-1}$) are not desirable, which lead to relatively low electrical conductivity and ZT value.11,12)

Since 2010, various methods have been used to enhance the thermoelectric properties of BiCuSeO by monovalent ions (e.g., K$^+$,13) Na$^+$,14,15) and Ag$^{+}$16) doping at the Bi site, or at the Cu site (e.g., Ag$^{+}$17), divalent ions (e.g., Mg$^{2+}$,18) Ca$^{2+}$,19) Sr$^{2+}$,20) Ba$^{2+}$21) (Pb$^{2+}$,22) Cd$^{2+}$,23) Zn$^{2+}$,24),) trivalent ions (e.g., Sh$^{3+}$,25) La$^{3+}$,26),) tetravalent ions (Sn$^{4+}$,8) doping at the Bi site, dual doping with Ca$^{2+}$/Pb$^{2+}$ or Ba$^{2+}$/Pb$^{2+}$ at the Bi site,10,27) or with Ba at the Bi site and Co/Ni at the Cu site,9,28) Cu/Bi-deficiencies,29,30 preferred orientation,31) 3D Modulation Doping32) and compositing33,34) etc. However, there are few reports focused on the effects of dual-doping at both Cu and Bi sites. In this report, the magnetic transitional element, Fe, is used to optimize the thermoelectric properties of BiCuSeO combined with Bi-deficiencies for that Bi-
deficiencies are able to increase the hole concentration and magnetic Fe is able to give rise to extra spin entropy, contributing to a rise of Seebeck coefficient. Besides, the hardness of BiCuSeO has also been studied, and the influence of doping on hardness has also been investigated.

2. Experimental procedures

Weigh commercial Bi₂O₃ (99.99%), Bi (99.99%), Cu (99.99%), Se (99.99%), Fe (99.99%) according to the ratio of stoichiometry of Bi₁₋ₓCuSeO + x Fe (x = 0, 0.01, 0.02, 0.04, 0.06, 0.08, 0.1, 0.12) (called as BCSO below). The stoichiometric mixture of powders were ground by mechanical alloying (MA) in argon atmosphere for 5 h with rotating speed = 400 rpm, ball to powder weight ratio = 20:1, followed by MA with analytical reagent (AR) ethanol absolute (99.7%) for 1 h, and then sintered by resistance pressing sintering (RPS) under the axial compressive pressure of 50 MPa under argon atmosphere at 873 K for 10 min, resulting in a disk-shaped sample of Φ20 × 13 mm. Highly dense disk-shaped samples can have ≥97% of the theoretical density. The phase purity and crystal structure were examined by X-ray diffraction with an X’Pert Pro diffractometer using CuKa radiation (k = 1.5418 Å). The microstructure of the samples was observed by field emission scanning electron microscopy (FESEM) (FEI, Nova 400 Nano SEM) and the chemical compositions were analyzed by energy-dispersive X-ray spectroscopy (EDS). The sintered bulks were cut into bar-shaped specimens of 3 mm × 5 mm × 15 mm along the radial direction to test the electrical transport properties. The electrical resistivity (ρ) and Seebeck coefficient (S) were measured by commercial equipment (ZEM-2, Ulvac-Riko, Japan). The bulk samples were cut into small wafer with an approximate dimension of φ12.7 mm × 2 mm for measuring the thermal transport properties. The thermal diffusivity (D) and specific heat (Cₚ) were measured by a Laser Flash apparatus (LFA457, Netzsch). The volume density (d) was measured by the Archimedes method. The thermal conductivity (κ) was calculated from the relationship κ = DCₚd. The carrier concentration and mobility at room temperature were measured by the van der Pauw method using the Hall-effect measurement system (HMS-5500, Ekkops).

3. Results and discussion

Figure 1(a) shows the X-ray diffraction patterns of the BCSO bulks. All the Bragg diffraction peaks coincide with the standard cards (PDF#45-0296) of BiCuSeO, with no miscellaneous phase was not detected. Through the Rietveld refinement of the X-ray diffraction data, the variation of lattice constants as a function of Bi deficiencies/Fe doping content were obtained as shown in Fig. 1(b). With the increase of doping amount from 0 to 0.12, the lattice constant a and c decreases monotonously. It is plausible for that the radius of Fe³⁺ ions (0.055 nm)/Fe²⁺ ions (0.061 nm) are smaller than that of Cu¹⁺ ions (0.077 nm) and the distortion of the BiCuSeO matrix caused by Bi deficiencies. For that the radius of Bi³⁺ ions (0.103 nm) is far larger than that of Fe²⁺ ions (0.055 nm)/Fe³⁺ ions (0.061 nm) and Cu¹⁺ ions (0.077 nm), Fe³⁺ ions/Fe²⁺ ions are not supposed to substitute at Bi site, but in Cu site. For the excess Cu or Fe, some may enter into the Cu vacancies because there are a large number of Cu vacancies in BiCuSeO; the other part may form inclusions, only because the amount is too small, X-ray diffraction (XRD) has not been detected.

Figure 2 shows the FESEM micrographs of the fractured morphologies of BCSO (x = 0, 0.06, and 0.12) bulks. The grains are tightly arranged and few pores between grains are found, indicating that the density of the RPSed samples is very high (the relative densities are above 97%). As shown in Figs. 2(c) and 2(d), the grains of the samples is plate-like, 1–3 μm in length. Meanwhile, there are some nanosized grains with size about 100–300 nm. The EDS results indicate that the nano spots here are still Bi₁₋ₓFeₓCuSeO, but Fe-rich as shown in Figs. 2(e) and 2(f). During the RPS process, the effective discharge between particles can induce local high temperature and make the surface partial melting and peeling off, resulting in the formation of the nanoparticles. The reason for Fe-rich may contribute to the overrange of solubility limit of Fe ions into BCSO when x = 0.12.

![Fig. 1. XRD patterns (a) and lattice parameters (b) of BCSO bulks.](image-url)
Figure 3(a) shows the temperature dependence of the electrical conductivity ($\sigma$) for BCSO samples. The $\sigma$ of all the samples increases with the increase of temperature in the whole temperature zone, indicating a semiconducting behavior. In addition, the $\sigma$ ($\sigma = n\mu e$, $e$ is carrier charge, $n$ carrier concentration and $\mu$ mobility\cite{1}) of all the
doped samples is higher than that of the pristine sample in the whole temperature range, which is attributed to the increase of carrier concentration as shown in Table 1. Specifically, the doping amount increased from 0 to 0.10, and the corresponding \( n \) increased from \( 1.21 \times 10^{19} \) to \( 4.80 \times 10^{19} \text{cm}^{-3} \). When the doping amount increased to 0.12, the carrier concentration did not increase further. It indicates that the doping content is overranging the solid solubility limit and the excess of Fe cannot enter the lattice. As a consequence, it is difficult to further promote the carrier concentration.

Table 1. The carrier concentration \((n)\), mobility \((\mu)\) and \(n^+\) for the BCSO series at room temperature

| Sample | \( S \) (\( \mu \text{V K}^{-1} \)) | \( n \) \( (10^{19} \text{cm}^{-3}) \) | \( \mu \) \( (\text{cm}^2 \text{V}^{-1} \text{s}^{-1}) \) | \( m^+ / m_0 \) |
|--------|----------------------------|----------------------------|-----------------|-----------------|
| \( x = 0 \) | 380 | 1.21 | 3.09 | 0.986 |
| \( x = 0.01 \) | 277 | 1.91 | 2.54 | 0.975 |
| \( x = 0.02 \) | 235 | 2.40 | 2.35 | 0.963 |
| \( x = 0.04 \) | 210 | 2.82 | 2.12 | 0.958 |
| \( x = 0.06 \) | 180 | 3.45 | 2.03 | 0.939 |
| \( x = 0.08 \) | 152 | 4.29 | 1.87 | 0.917 |
| \( x = 0.10 \) | 140 | 4.80 | 1.69 | 0.910 |
| \( x = 0.12 \) | 151 | 4.15 | 1.91 | 0.907 |

Fig. 3. The temperature dependence of (a) Electrical conductivity, (b) Seebeck coefficient, (c) Power factor, (d) Thermal conductivity, (e) Lattice thermal conductivity and (f) ZT values of BCSO.
In order to find out the relationship between the band gap and \( x \), the transmittance (\( T \)) of infrared spectroscopy was obtained by Fourier transform infrared spectrometer. The band gap can be calculated from the following formula:  \[ (a\nu)^2 = C(\nu - E_g) \] 
where \( a \) is absorption coefficient, \( h \) is the Plank constant, \( \nu \) is the photon frequency, \( C \) is a constant and \( E_g \) is the band gap. The band gap can be traced by extrapolating the linear region near the onset in a plot of \( (a\nu)^2 \) versus \( \nu \). According to the Beer–Lambert Law:  \[ A = \log(1/T) = abc \]
where \( T \) is the transmittance, \( b \) is the thickness of sample, \( c \) is the concentration and the value of \( b \) and \( c \) are fixed, which means that \( a \) is proportional to \( A \). As \( A \) can be calculated by \( T \); the band gap can be traced by extrapolating the linear region near the onset in a plot of \( (a\nu)^2 \) versus \( \nu \) as shown in Fig. 4. It can be seen that the band gap is narrowing down with the increase of \( x \).

In a word, the increase of the electrical conductivity as \( x \) increasing from 0 to 0.10 is supposed to be ascribed to the narrowed band gap, and the corresponding increased carrier concentration. The highest conductivity of \( \sim 46 \text{ S cm}^{-1} \) has been obtained for the Bi\(_{0.90}\)Fe\(_{0.10}\)CuSeO bulks at 823 K, which is higher than that of Sb doping (\( \sim 43 \text{ S cm}^{-1} \) at 873 K),\(^{22}\) Mg doping (\( \sim 38 \text{ S cm}^{-1} \) at 923 K),\(^{17}\) NaF doping (\( \sim 36 \text{ S cm}^{-1} \) at 923 K),\(^{37}\) and Ag doping (\( \sim 27 \text{ S cm}^{-1} \) at 873 K);\(^{16}\) and less than that of La doping (\( \sim 60 \text{ S cm}^{-1} \) at 923 K),\(^{25}\) Zn doping (\( \sim 54 \text{ S cm}^{-1} \) at 823 K)\(^{23}\) and Ba doping (\( \sim 200 \text{ S cm}^{-1} \) at 923 K)\(^{20}\) as shown in Table 2.

The Seebeck coefficient of BCSO samples are shown in Fig. 3(b). The Seebeck coefficients of all the samples are positive in the whole temperature range, indicating a p-type electrical transport behavior. It can be found that the pristine BiCuSeO presents very large Seebeck coefficient from \( \sim 380 \mu \text{V K}^{-1} \) at room temperature to \( \sim 330 \mu \text{V K}^{-1} \) at 873 K due to its natural superlattice structure and the corresponding carrier confinement effect.\(^{12}\) Upon doping, the Seebeck coefficient shows a decreasing trend. As is known, the Seebeck coefficient can be given roughly by the Pisarenko relation:  \[ S = \frac{8\pi^2k_B^2T}{3eh^2}m^*(\frac{\pi}{3n})^2/3 \] (1)
where \( S \) is Seebeck coefficient, \( k_B \) is Boltzman constant, \( T \) is the absolute temperature, \( e \) is carrier charge, \( h \) is Plank constant, \( m^* \) is the effective mass at Fermi level, and \( n \) is the carrier concentration. That is to say, the Seebeck coefficient is determined by two competitive factors, the effective mass \( m^* \) and the carrier concentration \( n \). The effective masses \( m^* \) were estimated using Pisarenko relation as shown in Table 1. It is clear that the increasing \( n \) and the decreasing \( m^* \) resulted in the decrease of the Seebeck coefficient with the increase of \( x \) from 0 to 0.10. When \( x \) increases further from 0.10 to 0.12, the Seebeck coefficient increases slightly due to the decreased carrier concentration.

It is worth noting that when the doping content is low, the Seebeck coefficient changes slightly with the increase of testing temperature, and maintaining high values in the whole temperature range. However, the Seebeck coefficients of the heavily doped samples increase greatly with increasing testing temperature due to the enhanced alloy scattering effect in higher temperature range. Similar phenomenon has also been found in the Ag doped,\(^{16}\) Ba doped\(^{20}\) and Sb doped\(^{24}\) BiCuSeO.

As shown in Fig. 3(c), the power factor (\( PF \)) of all samples increases with increasing testing temperature. In the high temperature zone, the \( PF \) increases significantly with increasing \( x \) from 0 to 0.08 and the highest power factor of 0.38 mWm\(^{-1}\)K\(^{-1}\) is obtained at 873 K for the BCSO with \( x = 0.08 \), which is 41% higher than the pristine BiCuSeO sample. Compared with the other element doping results, it is also quite considerable, \( \sim 5\% \) higher than Sb doping (\( \sim 0.36 \)),\(^{24}\) \( \sim 18\% \) higher than Mg doping (\( \sim 0.32 \)),\(^{17}\) \( \sim 22\% \) higher than Ag doping (\( \sim 0.31 \)),\(^{16}\) and \( \sim 58\% \) higher than NaF doping (\( \sim 0.24 \)).\(^{33}\) It is 87% lower than Ba doping (\( \sim 0.6 \))\(^{20}\) as shown in Table 2.

Table 2. The comparison of thermoelectric properties to BCSO ceramics with other dopants

| Doping element | \( \sigma_{\text{MAX}} \) (S cm\(^{-1}\)) | \( PF_{\text{MAX}} \) (m Wm\(^{-1}\)K\(^{-1}\)) | \( ZT_{\text{MAX}} \) |
|----------------|----------------------------|----------------|------------------|
| Fe             | 46                         | 0.38           | 0.76             |
| Sb             | 43                         | 0.36           | 0.73             |
| Mg             | 38                         | 0.32           | 0.67             |
| NaF            | 36                         | 0.21           | 0.42             |
| Ag             | 27                         | 0.31           | 0.68             |
| La             | 60                         | 0.42           | 0.74             |
| Zn             | 54                         | 0.37           | 0.65             |
| Ba             | 200                        | 0.60           | 1.10             |

Fig. 4. The optical band gaps of BCSO (\( x = 0 \) 0.02, 0.06, 0.10).
In addition, the $\kappa$ of all BCSO samples decrease with increasing testing temperature. As $x$ increased from 0 to 0.10, the $\kappa$ shows a slightly increasing trend. On one hand, due to the large difference of atomic mass between Fe (56) and Cu (64), Fe is “lighter” than Cu, which could induce the increase of the lattice thermal conductivity ($\kappa_{\text{lat}}$) with increasing $x$ as shown in Fig. 3(e). The smaller the molar mass of constituent elements, the greater the amplitude of lattice vibration, and the higher of the lattice thermal conductivity. On the other hand, the increase of $\sigma$ would also result in the increase of the carrier thermal conductivity ($\kappa_{\text{ele}} = L\sigma T$, $L$ is the Lorenz number). So, the total thermal conductivity increases with the increase of $x$ due to the increased $\kappa_{\text{lat}}$ and $\kappa_{\text{ele}}$. While $x$ increased from 0.10 to 0.12, the thermal conductivity shows a slightly decreasing trend, which might be attributed to the exceeding for the solid solubility limit of Fe in BiCuSeO and the formation of second phase.

By using the electrical and thermal transport properties, the figure of merit ZT is calculated as shown in Fig. 3(f). The largest ZT = 0.76 has been achieved at 873 K for BCSO with $x = 0.08$, which is 31% higher than that of the pristine BiCuSeO sample. For comparison, the present ZT value is $\approx 81\%$ higher than NaF doping ($\approx 0.42$), $\approx 13\%$ higher than Mg doping ($\approx 0.67$), $\approx 12\%$ higher than Ag doping ($\approx 0.68$), $\approx 7\%$ higher than Te doping ($\approx 0.71$), $\approx 4\%$ higher than Sb doping ($\approx 0.73$), and comparable to Sr doping ($\approx 0.76$), La doping ($\approx 0.74$), and 44% lower than Ba doping ($\approx 1.1$) as shown in Table 2.

The good mechanical properties of TE materials can provide sufficient ability to bear cutting load and improve the reliability for applications in thermoelectric generators. So far, no investigation on the mechanical properties of BiCuSeO oxyselenides has ever been reported. In the following parts, the HVs of these eight samples were measured, and the results are illustrated in Fig. 5. The HVs of all BiCuSeO oxyselenides are more than 200.0 HV. Besides, the hardness of the BiCuSeO bulks is sensitive to Fe-doping content and increases significantly with the increase of Fe-doping content, which might be caused by the solution strengthening in the doped sample. The highest hardness of BCSO samples reached 400.9 HV for $x = 0.08$, nearly twice as that of the pristine one.

## 4. Conclusions

The BCSO oxycalogenides were synthesized by MA followed by RPS process. And the effect of Fe doping and Bi deficiencies on the thermoelectric properties of p-type BiCuSeO ceramics. The results indicated that the band gap narrowed, which resulted in the dramatically increase of carrier concentration and electrical conductivity while still keeping a relatively high Seebeck coefficient and low thermal conductivity. As a result, the maximum power factor of 0.38 mWm$^{-1}$K$^{-2}$ and ZT value of 0.76 were obtained for the Bi$_{0.92}$Cu$_{0.08}$SeO + 8% Fe bulk at 873 K, which was 41 and 31% higher than that of the pristine BiCuSeO ceramic. These results indicate that the Bi deficiencies and Fe doping is an effective approach for improving the thermoelectric performance of p-type BiCuSeO.

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