Effect of synthesis processes on the thermoelectric properties of BiCuSeO oxyselenides

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ABSTRACT

The BiCuSeO based ceramics have been prepared by mechanical alloying (MA) and resistance pressing sintering (RPS) process. The effects of the parameters of annealing, ball milling and sintering on the microstructure, thermoelectric properties, and mechanical properties are investigated systematically. The results indicate that the samples prepared by MA exhibit higher carrier concentration due to higher Cu vacancies concentration, smaller grain size resulting in stronger phonon scattering, and correspondingly higher thermoelectric properties than those prepared by annealing. By prolonging milling time and increasing ball milling strength, it can further refine grains, increase the carrier concentration, enhance phonon scattering and further improve thermoelectric properties. Coupled with Ca/Pb doping, the electrical conductivity at room temperature increased to 445 S cm⁻¹. The total thermal conductivity is below 0.90 W m⁻¹ K⁻¹ in the whole measured temperature range, which is attributable to the increased defects and gain boundaries. The maximum power factor of 0.75 mW m⁻¹ K⁻¹ and ZT value of 1.15 were obtained for the Bi₀.8₄Ca₀.0₈Pb₀.0₈CuSeO with BM time (t) = 16 h at 873 K.

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1. Introduction

Thermoelectric materials, which are capable of converting waste heat into electrical power, are currently receiving significant scientific attention. However, the widespread use of thermoelectric technology is constrained by the relatively low conversion efficiency of present available thermoelectric materials. Thermoelectric oxides are vigorous candidates in terms of large-scale structural optimization [4]. Up to now, the highest ZT value of substituted BiCuSeO can be as high as 1.5, which is superior to all the other thermoelectric oxides [4]. However, the thermoelectric properties of pristine BiCuSeO are not desirable due to the intrinsic low carrier concentration (~1.0×10¹⁸ cm⁻³) and carrier mobility (~20 cm² V⁻¹ s⁻¹) [5]. In the past few years, tremendous efforts have been made to modify the electrical/thermal transport properties by monovalent elements (K [6], Na [7] and Ag [8]), divalent elements (Mg [9], Ca [10], Sr [11], Ba [12], Pb [13], Cd [14] and Zn [15]), trivalent elements (Sb [16] and La [17]) and tetravalent element (Sn [18]) doping at Bi site, monovalent element (Ag [19]) doping at Cu site, monovalent element (Ag [10]) doping at Cu site, dual doping with Ca and Pb at Bi site [4], dual doping with Pb at Bi site and Te at Se site [20], Cu-deficient [21] and texturation [22], 3D Modulation Doping [23] and composite structure [24]. Up to now, the highest ZT value of 1.5 was obtained for the Ca/Pb-dual-doped BiCuSeO oxyselenides coupled with all-scale structural optimization [4].

Persistent efforts have been devoted to improve ZT values through boosting power factor while most of them neglecting lowering thermal conductivity. In particular, nanostructuring has

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been proven to be an effective approach to reduce the thermal conductivity by embedding nanoscale precipitates in the matrix [25]. Beside, it is well known that the preparation process has a great influence on the properties of materials, especially for the thermoelectric materials which are extremely sensitive to the composition and structure. However, few studies have paid attention to the preparation process (ball milling [26,27], ultra-fast self-propagating high-temperature synthesis [28,29], and flux synthesis [30]) of BiCuSeO. And no reports have ever studied the mechanical properties of BiCuSeO before. However, mechanical properties have a decisive influence on the machinability during the use of thermoelectric materials. Herein, we synthesize BiCuSeO by ball milling and annealing, respectively, followed by sintering, and report the effect of the parameters of annealing, ball milling and sintering on the thermoelectric and mechanical properties of BiCuSeO ceramics.

2. Experimental sections

2.1. The synthesis of powder

A series of samples with the chemical composition of BiCuSeO (called as BCSO below) and Bi$_{1-2x}$Ca$_x$Pb$_x$CuSeO ($x = 0, 0.01, 0.02, 0.04, 0.06, 0.08$) (called as BCPCSO below) were prepared from commercial powders (Bi$_2$O$_3$ (99.99%), Bi (99.999%), Cu (99.999%), Se (99.99%), CaO (99.99%), Pb (99.99%)). We synthesize the powder by ball milling and annealing, respectively.

1) The stoichiometric mixture of powders were ground: high-energy ball milling was performed at 300 or 400 rpm in argon atmosphere for 2 h/4 h/6 h/8 h/12 h and 4 h/8 h/12 h/16 h/20 h, respectively, followed by MA with analytical reagent (AR) ethanol absolute (≥99.7%) for 1 h.

2) The stoichiometric mixture of powders were placed in a quartz glass tube, vacuum sealed, then annealed at 300 or 800 °C for 3 h/8 h in a muffle furnace. Take out the powder, and grind with agate mortar.

2.2. The sintering for bulk

Then, the powder with high phase purity were sintered by resistance pressing sintering (RPS) at 823/873/923 K for 10 min under the axial compressive pressure of 40/50/60 MPa under argon atmosphere to form disk-shaped sample of Φ20 × 13 mm.

2.3. Characterization

The phase identification were characterized by X-ray diffraction
with an X’Per Pro diffractometer using Cu Kα radiation (\(\lambda = 1.5418 \, \text{Å}\)). The microstructures were studied by field emission scanning electron microscopy (FESEM) (FEI, Nova 400 Nano SEM) and the elemental compositions were determined using energy-dispersive X-ray spectroscopy (EDS). The sintered bulks were cut into bar-shaped specimens of 3 mm \times 3 mm \times 15 mm along the radical direction to test the electrical transport properties. The electrical resistivity (\(\rho\)) 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 \(\phi 12.7 \, \text{mm} \times 2 \, \text{mm}\) for measuring the thermal transport properties. The thermal diffusivity (\(D\)) and specific heat (\(C_p\)) were measured by a Laser Flash apparatus (LFA457, Netzsch). The volume density (\(d\)) was measured by the Archimedes method. The thermal conductivity (\(\kappa\)) was calculated from the relationship \(\kappa = D C_p d\). Both of the electrical transport properties and the thermal diffusivities were measured along the direction perpendicular to the RPS press direction. The carrier concentration and mobility at room temperature were measured by the van der Pauw method using the Hall-effect measurement system (HMS-5500, Ekopia). For the measurement of the band gap between the valence band and conduction band, the infrared spectroscopy was obtained by Fourier transform infrared/Raman spectrometer (VERTEX 70, Bruker, Germany). All the specimens were polished with two parallel planes and the plane close to the central part was utilized for Vickers hardness (HV) measurement, which were conducted on HV-10008 with a load of 25 g and a loading time of 15 s. Every sample was tested with 5 data points, and the average HV was used for characterizing mechanical properties.

Table 1
The relative density (\(r\)), carrier concentration (\(n\)), mobility (\(\mu\)) and \(m^*\) for the BCSO samples at room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(r) (%)</th>
<th>(S) ((\mu\text{VK}^{-1}))</th>
<th>(n) (10^{19}\text{cm}^{-3})</th>
<th>(\mu) (cm$^2$V$^{-1}$s$^{-1}$)</th>
<th>(m^*/m_o)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800 °C, (400)</td>
<td>97.6</td>
<td>400</td>
<td>0.84</td>
<td>13.96</td>
<td>0.81</td>
</tr>
<tr>
<td>800 °C, (t=8)</td>
<td>98.4</td>
<td>371</td>
<td>1.5</td>
<td>8.85</td>
<td>0.97</td>
</tr>
<tr>
<td>800 °C, (t=12)</td>
<td>97.9</td>
<td>355</td>
<td>1.9</td>
<td>7.73</td>
<td>1.24</td>
</tr>
<tr>
<td>800 °C, (t=16)</td>
<td>97.6</td>
<td>334</td>
<td>2.1</td>
<td>5.15</td>
<td>1.36</td>
</tr>
</tbody>
</table>

Fig. 2. SEM of the fractured surfaces for BCSO bulks ((a) stands for 800 °C annealing; (b)–(d) stand for ball milling time \(t=8\) h, 12 h, 16 h, respectively).

Fig. 3. The average grain size and proportion of grain (<500 nm) counted by Nano Measurer from SEM of the fractured surfaces for BCSO samples (samples 0 stands for 800 °C annealing; 1–3 stand for ball milling time \(t=8\) h, 12 h, 16 h, respectively).
3. Results and discussion

X-ray diffraction patterns at room-temperature for all the BCSO samples are shown in Fig. 1. It can be seen from Fig. 1(a) that the formation of BiCuSeO phase happened at 350 °C annealing, but the generation efficiency is very low. After 8 h, there are still a large number of strong impurity peaks as shown in Fig. 1(b), indicating that the kinetic condition of the reaction is too poor. When the annealing temperature is up to 800 °C, the generation efficiency of BiCuSeO is greatly improved. After 3 h, the intensity of the impurity peak is very weak. It’s contributed to the improvement of the kinetic conditions with increased temperature based on the}

![Fig. 4. 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.](image)
unreacted core kinetics model [31]. After 8 h, there is no detectable
impurity peak. In the process of ball milling, as shown in Fig. 1(c) and (d), the reaction efficiency of BiCuSeO is lower than that of the
annealing method. When the ball milling speed is 300 rpm, there is
no apparent heterozygosity after 12 h. When the milling speed
increased to 400 rpm, the reaction efficiency of BiCuSeO is
increased, no apparent heterozygosity after 8 h. This is contributing
to the increased milling intensity with faster ball milling speed for
more accelerated cold welding, welding process [32]. Moreover,
with the further prolongation of t, the XRD peaks become wider,
indicating that the grains get smaller, and a small amount of het-
teroraphse (CuSe) is found.

The relative density of the samples sintering at 823 K, 873 K, and
923 K is 96%, 98.2%, 93%, respectively. The sample sintering at 823 K
has micro cracks and is easily broken in cutting. During cracking,
bridges formed by matrix grains remain intact behind the crack tip.
Such bridges are formed by crack bridging of microcrack [33].
When the sintering temperature is too low, the bonding between
grains is not intact enough. The bridge is weakened greatly,
resulting in easy cracking. Melting out was found on the mold when
grains is not intact enough. The bridge is weakened greatly,
Such bridges are formed by crack bridging of microcrack [33].
When the sintering temperature is too low, the bonding between
grains is not intact enough. The bridge is weakened greatly,
resulting in easy cracking. Melting out was found on the mold when
when the sintering temperature is too high, the mechanical property of the sample is very poor, and it can be
pinched by hand. When the sintering pressure is 60 MPa, the
sample is cracked when removed from the mold. When the pres-
sure is low, bridges of microcrack are not easily formed, the
subcritical crack growth (SCG) or creep damage accumulation are
not being effectively curbed [34]. When the pressure is too high, the
SCG or creep damage accumulation increases instead. As a result,
the most appropriate sintering pressure is 50 MPa.

Considering the high production efficiency of 800 °C annealing
and ball milling with 400 rpm, the corresponding powder is sin-
tered (the sintering temperature is 873 K and the sintering pressure
is 50 MPa) into bulk. Fig. 2 shows the SEM images of the fractured
surfaces of BCSO bulks. The samples consist of lath-like micro-
grains which is stacked densely and there are few pores after the
process of densification by RPS. The relative densities of all the
samples are above 97% obtained by the Archimedes principle as shown in Table 1. The grain size of the annealed sample is obviously
larger than that of the BM sample. The average grain size and proportion of grain (<500 nm) counted by Nano Measurer from
SEM of the fractured surfaces for BCSO bulks are shown in Fig. 3.
The average grain size of the annealed sample is 1481 nm, much
larger than 952 nm for the BM sample with t = 8 h. With the pro-
longation of ball milling time, the average size of grain significantly
decreases, from 952 nm for t = 8 h to 598 nm for t = 12 h, and
further down to 400 nm for the 16 h. And the proportion of fine
grains (<500 nm) increases markedly, from 24% for t = 8 h to 44%
for t = 12 h, and further up to 62% for the 16 h. The grain size tends
to decrease monotonically with milling time towards a steady-state
grain size before the saturation in stored enthalpy, which is in line
with the previous literature on the ball mill [35].

Fig. 4 (a) shows the temperature dependence of the electrical
conductivity (σ) for BCSO samples. No obvious bipolar conduction
is observed for all the BCSO samples. And the σ increases with
increasing testing temperature, typical of a semiconducting behavior. The σ of the sample prepared by annealing is much lower
than that of ball milling in the whole temperature range, which is
contributing to the larger grain size (as shown in Figs. 2 and 3), and
the corresponding lower concentration of Cu vacancies. The σ is
known to depend on the carrier concentration and mobility as
shown in the relationship σ = nμe (e is carrier charge, n carrier
concentration and μ mobility) [4]. The Hall carrier concentration (n)
and mobility (μ) of BCSO bulks at room temperature are shown in
Table 1. The n of the sample prepared by annealing is far lower than
that of the BM sample. With the prolongation of t, the σ shows an
upward trend and increases with increasing testing temperature.
Specifically, the room temperature σ significantly increases from
–11 Scm−1 for t = 8 h to –16 Scm−1 for t = 12 h, and further up to
–20 Scm−1 for t = 16 h. This is attributed to the increase of n as
shown in Table 1. With the prolongation of t, and the severe plastic
deposition during ball-milling process could promote the formation
of Cu vacancies, which act as electron acceptor for BiCuSeO,
and correspondingly the increase of n [36]. The hole mobility
decreases with the prolongation of t, from 8.85 cm−2V−1s−1 for t = 8 h
to 5.15 cm−2V−1s−1 for t = 16 h. Generally, the inverse of the effective
hole mobility of the whole material can be expressed by Ref. [37]:
\[ S = \frac{8\pi^2 k_B^2 T}{3e \hbar^2} m^* (\frac{n}{3n})^{2/3} \]  

where \( S \) is Seebeck coefficient, \( k_B \) is Boltzmann constant, \( T \) is the absolute temperature, \( e \) is carrier charge, \( \hbar \) 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 inversely proportional to the carrier concentration. As mentioned above, the carrier concentration increased significantly as the prolongation of \( t \), which has touched off the decrease of the Seebeck coefficient.

The power factor (PF) of BCSO samples are shown in Fig. 4(c). As can be seen, the PF of the annealed BCSO increases as the temperature rises, and the maximum value is 0.26 mW m\(^{-1}\) K\(^{-2}\). The PF...

Fig. 6. Temperature dependence of (a) Electrical conductivity, (b) Seebeck coefficient, (c) Power factor (d) Thermal conductivity, (e) Lattice thermal conductivity and (f) ZT values of BCPCS.
of the ball milled samples are higher than the annealed sample over the entire temperature range, which is aroused by the significantly increased electrical conductivity. The highest power factor of 0.31 mWm\(^{-1}\)K\(^{-2}\) is obtained at 873 K for the BCSCO with \(t = 16\) h.

Fig. 4 (d) shows the total thermal conductivity (\(\kappa_t\)) as a function of testing temperature for the BCSCO bulks. The \(\kappa_t\) of all the samples decreases with increasing testing temperature over the entire temperature range, which is aroused by the enhancing phonon scattering. The \(\kappa_t\) of the annealed BCSCO decreases from 0.92 Wm\(^{-1}\)K\(^{-1}\) at 300 K to 0.61 Wm\(^{-1}\)K\(^{-1}\) at 873 K. The intrinsically low thermal conductivity is related to the weak chemical bonds, phonon confinement due to the layered structure, and the presence of heavy element. The \(\kappa_t\) of all the ball milled samples is lower than the annealed one for finer grains and stronger interface scattering. With the prolongation of \(t\), the \(\kappa_t\) shows an downward trend, mainly attributed to the decrease of lattice thermal conductivity (\(\kappa_l\)) as shown in Fig. 4 (e). The calculated \(\kappa_l\) follows the relationship as \(\kappa_l = T^{-1}\), which suggests that the phonon-phonon Umklapp scattering is predominant in phonon transport. In general, \(\kappa_l\) can be qualitatively expressed as:

\[
\kappa_l = \frac{1}{3} C v P = \frac{1}{3} C v^2 \tau (P = \nu \tau) \tag{3}
\]

or

\[
\kappa_l = \frac{1}{3} \int C(\omega) \nu^2(\omega) \tau(\omega) d\omega \tag{4}
\]

where \(C, v, P\) and \(\tau\) are specific heat, speed of sound, phonon mean free path, and phonon relaxation time, respectively. As \(t\) is prolonged, the grain size becomes smaller as shown in Figs. 2 and 3, the phonon scattering increases, the average free path of the phonon and the phonon relaxation time decreases, leading to the decrease of the \(\kappa_l\).

The dimensionless thermoelectric figure of merits (\(ZT\)) all the BCSCO bulks are plotted in Fig. 4 (f). It can be seen that the \(ZT\) value of the annealed BCSCO is notably low, whose peak is at 873 K with \(ZT\) of 0.43. The \(ZT\) values of all the ball milled samples are much higher than that of the annealed one, and dramatically rise up with \(t\), ranging from 0.51, 0.55 to 0.62 of peak value at 873 K with \(t = 8\) h, 12h, 16h, respectively.

Besides the thermoelectric properties, mechanically robust is also very important for applications in TEGs. Up to now, few studies \cite{39} have been reported to investigate the mechanical properties of BiCuSeO oxyselenides. In this work, the HV of the BCSCO samples were measured as shown in Fig. 5. It can be seen that the HV of the annealed BCSCO is \(-171\) HV. In addition, the hardness of the ball milled bulks is larger than the annealed one and show an increasing trend with the increase of \(t\), which might be caused by the fine-grained strengthening \cite{40}. Besides, as we can see from Fig. 2, as \(t\) is prolonged, the grain size becomes smaller, the size of the porosity is smaller, the number of porosity decreases, which indicates that the microstructure is more compact. This may also be one of the reasons for the higher hardness. The highest hardness of 270 HV is obtained for the ball milled sample with \(t = 16\) h.

In fact, a series of BCPCSCO samples were also obtained via the best optimal synthetic parameters (BM: 400 rpm, 16 h; RPS: 873 K, 50 MPa). Fig. 6 shows the temperature dependence of the thermoelectric properties for BCPCSCO samples. It can be seen that the thermoelectric properties have been greatly improved with the increase of the amount of Ca/Pb doping. Ca\(^{2+}\)/Pb\(^{2+}\) doping at Bi\(^{3+}\) site introduces holes, and correspondingly increase \(n\) and \(\sigma\). The \(S\) decreased to a certain extent upon Ca/Pb doping, which is attributed to the increase \(n\) according to (5). The \(\kappa\) increases obviously mainly driven by the increase of the electrical thermal conductivity. Finally, the maximum power factor reached 0.75 mWm\(^{-1}\)K\(^{-2}\) and the highest \(ZT\) value reached 1.15.

4. Conclusions

In this work, we have proposed an effective and feasible method to improve the thermoelectric/mechanical performance of BiCuSeO based thermoelectric materials through preparation process optimization and Ca/Pb co-doping. A series of p-type polycrystalline BiCuSeO samples with different preparation process parameters and different contents of Ca/Pb (\(x = 0, 0.01, 0.02, 0.04, 0.06, 0.08\)) were prepared by a combined method of MA and RPS. The results show that the sample prepared by MA has higher carrier concentration due to higher Cu vacancies concentration, smaller grain size resulting in stronger scattering for phonons, and thus higher thermoelectric properties than those prepared by annealing. By prolonging milling time and increasing ball milling strength, it can further refine grains, increase carrier concentration, enhance phonon scattering and further improve thermoelectric properties. The optimum process parameters are as follows: 400 rpm for ball milling speed, 16 h for ball milling time, 873 K for sintering temperature, 50 MPa for sintering pressure. The corresponding maximum power factor reached 0.31 mWm\(^{-1}\)K\(^{-2}\) and the highest \(ZT\) value reached 0.62 for the pristine BiCuSeO. Through Ca/Pb doping, the maximum power factor increased to 0.75 mWm\(^{-1}\)K\(^{-2}\) and the highest \(ZT\) value increased to 1.15. This significant improvement in thermoelectric properties coupled with good mechanically robust underlines that fine-grained polycrystalline BiCuSeO obtained by MA is very promising for thermoelectric applications.

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References


