Fabrication of thermoelectric CuAlO\textsubscript{2} and performance enhancement by high density

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**ABSTRACT**

CuAlO\textsubscript{2} compacts were prepared by SPS at 1273 K for 10 min. The crystal phases of resultant compacts were strongly dependent on the designed composition of starting powders: \( x \) CuO + (1–\( x \)) Cu\textsubscript{2}O + (1–2\( x \)) Al\textsubscript{2}O\textsubscript{3}. Single delafossite phase CuAlO\textsubscript{2} compacts with different density were obtained when \( x = 0.15, 0.20, 0.40 \) and 0.60, and the correspondent SPS pressure were 40 MPa, 20 MPa, 10 MPa and 5 MPa respectively. The relative density of the compacts increased with SPS pressure increasing and led to a maximum about 97.7%. Electrical conductivity, power factor and thermoelectric figure of merit of the compacts were all enhanced by increasing density, reaching 300 Sm\textsuperscript{-1}, 1000 Sm\textsuperscript{-1} and 5 \times 10\textsuperscript{-3} Wm\textsuperscript{-1} K\textsuperscript{-1}\textsuperscript{-1} respectively at 873 K. The features of electrical resistivity and thermal conductivity of the compacts were predicted by GEM equation. The evaluated results agreed well with the experimental results.

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**1. Introduction**

Thermoelectric materials play an important role in thermoelectric generator which directly covert the heat from various power source (solar, geothermal, and exhaust from automobiles or other industrial processes) into electricity, the most convenient energy form in life [1]. CuAlO\textsubscript{2}, a kind of p-type semiconductive materials, belonging to the delafossite group of ternary oxides, is viewed as a promising high temperature thermoelectric material for the temperature dependence thermoelectric properties along \( ab \)-plane of single crystal CuAlO\textsubscript{2} for Seebeck coefficient, electrical conductivity, power factor reaching 325 \( \mu \)V/K, 1000 Sm\textsuperscript{-1}, and \( 1 \times 10^{-4} \) Wm\textsuperscript{-1} K\textsuperscript{-1}\textsuperscript{-1} at 1200 K, respectively [2,3]. However, compared to single crystal, polycrystal CuAlO\textsubscript{2} has relative poor performance in thermoelectric properties. In general, the microstructure of the polycrystal, i.e., density, grain size, defects, grain boundary, grain orientation and doping greatly affect material thermoelectric properties [4–7].

In our previous work [8], by doping oxygen, the reaction behavior during the formation of CuAlO\textsubscript{2} from CuO and Al\textsubscript{2}O\textsubscript{3} powders was studied, and the results showed about 2.5% excess oxygen doping by annealing leading to a maximum for power factor as high as \( 2 \times 10^{-3} \) Wm\textsuperscript{-1} K\textsuperscript{-1}\textsuperscript{-1} at 850 K. In present work, we aim to improve the CuAlO\textsubscript{2} thermoelectric performance by tailoring the microstructure through increasing samples density using SPS technology. The mechanism of the formation of single phase CuAlO\textsubscript{2} from starting materials is discussed. The density dependence of thermoelectric properties of CuAlO\textsubscript{2} compacts is mainly focused on.

**2. Experiments and methods**

2.1. Mixture powders

The CuAlO\textsubscript{2} compacts were prepared by SPS using the commercial CuO (purity: 90.0%, average diameter: 3 \( \mu \)m), Cu\textsubscript{2}O (purity: 99.0%, average diameter: 1 \( \mu \)m) and Al\textsubscript{2}O\textsubscript{3} (purity: 99.98%, average diameter: 3 \( \mu \)m) powders as starting materials. The designed compositions of mixed powders were: \( x \) CuO + (1–\( x \)) Cu\textsubscript{2}O + (1–2\( x \)) Al\textsubscript{2}O\textsubscript{3}, where \( x = 0, 0.15, 0.20, 0.40, 0.60, 0.80 \) and 1. They were mixed using acetone as wetting media in an agate mortar for an hour at 100 rpm by a magnetic stirrer firstly, then the powders were...
drying for an hour at 373 K and mixed again without wetting media for 3 h at 300 rpm.

2.2. Fabrication of CuAlO₂ compacts

The obtained mixture powders were sintered by using SPS (SPS-1030, Sumitomo coal mining Co., Japan) technology. Specifically, about 15 g powders were filled into a graphite and placed in the SPS chamber. They were heated from room temperature to 973 K at 100 K/min, 973 K—1173 K at 50 K/min, 1173 K—1273 K at 25 K/min, and holding for 10 min at the final temperature with a certain SPS pressure. The obtained compacts were processed mechanically into rectangular blocks 40 mm × 5 mm × 2 mm in dimensions for the measurement of Seebeck coefficient (S) and electrical conductivity (ρ) and 10 mm × 1 mm × 1 mm for the measurement of thermal conductivity (κ).

2.3. Characterization and measurement of thermoelectric properties

The samples density was measured through Archimedes principle. For phase characterization, the X-ray diffraction (XRD) patterns were obtained using an automated diffraction meter (JDX-3530, JEOL, Japan) with CuKα₁ radiation. A scanning electron microscope (JSM-5300, JEOL, Japan) was used to investigate the microstructure of the sintered compacts. The thermoelectric properties, ρ and S, were simultaneously measured along the pressed plane of the compacts by the four-probe direct current method in air atmosphere using a computer controlled equipment. The thermal conductivity (κ) was determined from the specific heat capacity and the thermal diffusivity measured by laser flash technique (XFA500, Linseis Gmbh, Germany) from 273 K to 873 K.

3. Results and discussion

3.1. CuAlO₂ compacts

Fig. 1 shows the XRD patterns of resultant compacts prepared by SPS with the pressure of 40 MPa. These patterns show the single phase CuAlO₂ compacts can’t be obtained only using CuO as the sole Cu source. As seen from Fig. 1, on one hand, when x = 0.20, 0.40, 0.60, 0.80 and 1, the phases of CuAlO₂, CuAl₂O₄ and CuO exhibit, moreover, with an increase of x, the typical diffraction peaks of CuAl₂O₄ and CuO are more obvious; On the other hand, when x = 0 and 0.10, except for the major phase of CuAlO₂, the minor phases of Cu₂O and Al₂O₃ appear. This phenomenon is attributed to the formation of CuAlO₂ sensitive to O₂ pressure. Fig. 2 [9] shows the temperature vs O₂ pressure phase diagram for the Cu-Al-O system at 1 atm of total pressure. It is clear that at 1273 K, just the holding temperature for annealing of mixing powders, the phase of CuAlO₂ is stable over the O₂ pressure range from about 10⁻⁷ Pa—10 Pa. If O₂ pressure is higher than 10 Pa, the CuAlO₂ gradually decomposes into CuAl₂O₄ and Cu₂O, or CuAl₂O₄ and CuO. To the contrary, if O₂ pressure is less than 10⁻⁷ Pa, the CuAlO₂ decomposes into Cu and Al₂O₃. Therefore, using CuO and Al₂O₃ as the starting materials, in sintering process by SPS, the O₂ coming from reaction (1) can’t discharge from the interior of the compacts instantly,

\[
\text{CuO} + \text{Al}_2\text{O}_3 \rightarrow \text{CuAlO}_2 + \frac{1}{2} \text{O}_2
\]  

(1)

leading to high O₂ pressure, consequently, the phases of Cu₂O and CuAl₂O₄ present according to reaction (2). Hence, to reduce O₂ pressure, a certain amount of Cu₂O is added into starting materials, which exhausts a portion of O₂ through reaction (3). Of course, there is a maximum for the addition

\[
2\text{CuAlO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{CuAl}_2\text{O}_4 + \text{CuO}
\]  

(2)

Fig. 2. Temperature vs. \(\log p_{O_2}\) phase diagram for the Cu–Al–O system at 1 atm of total pressure.

Fig. 1. The XRD patterns of resultant compacts prepared from designed composition of starting mixtures: \(x\) CuO + \((1-x)\) Cu₂O + \((1-x) / 2\) Al₂O₃ by SPS with the pressure of 40 MPa.
of Cu$_2$O, otherwise, the O$_2$ pressure is so low as to the Al$_2$O$_3$ presents. Further, from Fig. 1, through the optimization of designed composition, the single phase CuAlO$_2$ compacts are fabricated by SPS with the pressure of 40 MPa when $x = 0.15$. It's noted that for obtaining single phase CuAlO$_2$ compacts, $x$, the designed composition of starting powders, is dependent on SPS pressure for the external pressure great affecting O$_2$ pressure. In sintering process of the mixture powders CuO, Cu$_2$O and Al$_2$O$_3$ with a fixed composition by SPS, the O$_2$ generated can't discharge immediately, the larger of the SPS pressure, the much difficult of the discharge of O$_2$, and the higher of the O$_2$ pressure. To keep O$_2$ pressure within a proper range in which the phase of CuAlO$_2$ can't decompose, when the SPS pressure increases, the proportion of Cu$_2$O in starting mixtures should increase. Therefore, $x$ or $x;1−x$ (mole ratio of CuO and Cu$_2$O) decreases with SPS pressure increasing. In our experiments, when $x = 0.60, 0.40, 0.20$ and 0.15, and the correspondent SPS pressure is 5 MPa, 10 MPa, 20 MPa and 40 MPa respectively, the single phase CuAlO$_2$ compacts with different density are successfully fabricated. Table 1 shows the relationship of SPS pressure and the relative density of compacts. In our imagination, the relative density increases with SPS pressure increasing, reaching as high as 97.7%, which is far higher than that of the samples prepared in air.

Fig. 3 shows the SEM images of the cross-sections of CuAlO$_2$ compacts polished using diamond abrasive paper, therein, (a) the CuAlO$_2$ by normal sintering in air, and (b, c) the CuAlO$_2$ by SPS with the pressure of 5 MPa and 40 MPa respectively. As seen in Fig. 3(a), the average grain size is less than 5 µm, but the micro morphology of the samples shows great inhomogeneity. In most region, the pores locate at the grain boundaries so as to the grains combine loosely by each other, even the small amount of grains disperse alone somewhere, which are all attributed to the low density and high porosity of the samples. As shown in Table 1, the relative density of EF-pre samples is as low as 44.3%. Fig. 3(b) and (c) show the micro morphology of the samples by SPS are more homogeneous, although the very few unreacted Cu$_2$O particles (white points) present in Fig. 3(b) and the composition inhomogeneity (dark region) is observed in Fig. 3(c). What's important is that with an increase of SPS pressure, the grains combine closely together, especially, the samples of SPS-40 are almost free of pores for the relative density of that is about 97.7%. As we know, the high density is responsible for a significant increase in the electrical conductivity and also the thermal conductivity, hence affecting the thermoelectric properties.

### 3.2. Thermoelectric properties

The temperature dependence of electrical resistivity ($\rho$) of CuAlO$_2$ compacts is shown in Fig. 4. The $\rho$(T) curves of all samples shows a decrease of the resistivity when the temperature increases,

\[
\text{Cu}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{CuO} \quad (3)
\]
indicating the semiconducting behavior. Meanwhile, compared to the $\rho$ of EF-pre samples, the $\rho$ of compacts by SPS shows an obvious decline. What is more, the $\rho$ decreases monotonically with SPS pressure increasing, in other words, with the density increasing, leading to a minimum for SPS-40 samples about 3.25 $\mu$mm (307 Sm/C0 1) at 925 K about 90% lower than that for EF-pre samples, but about doubled higher than that for CuAlO2 single crystal [2]. It’s no doubt that the increase of the fraction of conducting phase CuAlO2 responsible for the decline of the $\rho$ in dense samples. The increase of the concentration of hole and valance of copper under high O2 pressure (SPS pressure) may also make $\rho$ decline based on the following reaction (4) [5], but that needs to be proved by near future research.

$$O_2(g) = 2O_6^x + V_{Cu} + V_{Al}^{3+} + 4h$$

(4)

Fig. 5 shows the temperature dependence of Seebeck coefficient (S) of CuAlO2 compacts. The sign of Seebeck coefficient is positive for the whole measured temperature range, indicating hole conduction. The values of Seebeck coefficient for all samples decrease up to 673 K firstly, then increase till to the highest measured temperature 925 K. This behavior can be explained simply by formula [11]: $S = \gamma - \ln n_e$, where $\gamma$ is the scattering factor and $n_e$ is the carrier concentration. It’s no doubt that the intrinsic carrier concentration for un-doping CuAlO2 increases with the temperature increasing, however the $\gamma$ which is related to the interaction between the carrier and phonon, crystal defects i.e., grain boundary, impurity, pores, varies non-monotonicity with the temperature increasing. Also seen from Fig. 5, the values of Seebeck coefficient for all samples are over than 400 $\mu$V/K, and the density has few effects on it at high temperature so as to that for all samples fall a narrow range around 475 $\mu$V/K at 925 K.

The power factor ($P$) of CuAlO2 is calculated by $P = S^2/\rho$. Fig. 6 shows the temperature dependence of $P$ for the samples. It is seen that the $P$ of all samples increase with an increase in temperature. Although the $S$ almost has no change with the density increasing, the dense samples still show higher power factor than that for loose ones over the whole temperature range from 373 K to 925 K due to the significant reduction in $\rho$. Moreover, $P$ shows an increase for the compacts by SPS with the SPS pressure increasing, leading to $6 \times 10^{-5}$ Wm$^{-1}$K$^{-1}$ 1 at 925 K about half of that of single crystal [2].

The temperature dependence of thermal conductivity ($k$) of CuAlO2 compacts from 273 K to 873 K is shown in Fig. 7, the dense samples show higher $k$, and the $k$ changes obviously over the measured temperature range which means the intrinsic $k$ of CuAlO2 is strongly dependent on the temperature. However, to the samples with high porosity, the $k$ almost keeps constant with the temperature increasing, due to the $k$ of the air non-sensitive to the temperature.

The dimensionless thermoelectric figure of merit ($ZT$) of CuAlO2 compacts is calculated by $ZT = S^2/\rho k$, and it is shown in Fig. 8. As can be seen, the $ZT$ are enhanced from 2.6 $\times 10^{-3}$ K$^{-1}$ to 5 $\times 10^{-3}$ K$^{-1}$ at 873 K by increasing the sample density from 2.27 g/cm$^3$ of EF-pre samples to 5.0 g/cm$^3$ of SPS-40 samples because of the dense sample with higher power factor.

3.3. Discussion by GEM

From measurement of the density and characterization of the morphology by SEM for the compacts, it’s clear that the compacts are composed of air pores randomly embedded in a conducting CuAlO2 phase, so they can be called porous CuAlO2 to a certain extent. It is well know that the electrical resistivity and thermal conductivity of porous materials are a function of conducting phase volume fraction. In the next paragraph, the features of electrical
respectively as follows:

\[
\phi_1 \left\{ \left( \rho_e^{-1} \right)^{1/t} - \left( \rho_c^{-1} \right)^{1/t} \right\} + \left( \rho_e^{-1} \right)^{1/t} + \left( \phi_c \right)^{1/t} \left( \rho_c^{-1} \right)^{1/t} = 0
\]

\[
\phi_1 \left( k_e^{-1/t} - k_c^{-1/t} \right) + \left( \phi_c \right)^{1/t} \left( k_c^{-1/t} - k_e^{-1/t} \right) = 0
\]

where \( \phi_1 \) is volume fraction of the conducting phase, \( \rho_1 \) and \( \rho_2 \) are the electrical resistivities of the conducting phase and the air respectively; Similarly, \( k_1 \) and \( k_2 \) are the thermal conductivities of the conducting phase and the air; \( \phi_c \) is the critical concentration of percolation to a certain composites system and the exponent \( t \) is assumed to be universal, depending on the dimensionality of researched system.

Table 2 summarizes the essential parameters to evaluate the thermoelectric properties of the compacts at 873 K. It’s noted that the CuAlO₂ compacts with relative density of 100% is difficult to obtain, herein, the value of \( \rho \) and \( \kappa \) of CuAlO₂ comes from that of SPS-40. To the air, assuming the \( \rho \) is \( 1 \times 10^9 \) \( \Omega \) mm, and the \( \kappa \) of it is abstracted from the literature [13].

Fig. 9 shows the volume fraction dependence of electrical resistivity and thermal conductivity of sintered CuAlO₂ compacts by experiment and GEM (at 873 K).

4. Conclusions

CuAlO₂ compacts are prepared by SPS. The crystal phases of resultant compacts are strongly depended on the designed composition of starting powders: \( x \) CuO + \((1-x)\) Cu₂O + \((1-x/2)\) Al₂O₃. Single phase CuAlO₂ compacts are obtained when \( x = 0.15\),
0.20, 0.40, and 0.60, and the correspondent SPS pressure is 40 MPa, 20 MPa, 10 MPa and 5 MPa respectively. With the SPS pressure increasing, the largest relative density of the compacts is as high as 97.7%. The density has few effects on $S$, but $1/p$, $P$ and $ZT$ are all enhanced by increasing density, reaching 300 Sm$^{-1}$, $6 \times 10^{-5}$ Wm$^{-1}$K$^{-1}$ and $5 \times 10^{-3}$ K$^{-1}$ respectively at 873 K. The features of electrical resistivity and thermal conductivity of the compacts are predicted by GEM equation and the evaluated results agree well to the experimental results.

References