Preparation and thermoelectric properties of CuAlO₂ compacts by tape casting followed by SPS

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A B S T R A C T

We applied a novel method of tape casting followed by spark plasma sintering (SPS) to prepare CuAlO₂ compacts. During the tape casting process, plate-like Al₂O₃ particles distributed along the flow direction of slurry under the action of the shear-thinning effect. It greatly elevated the orientation degree of the CuAlO₂ compacts formed during the following SPS. Meanwhile, the relative density of these compacts was also considerably increased due to the reduction in porosity. The green compacts and as-sintered compacts were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). The thermoelectric properties including electrical resistivity, Seebeck coefficient, thermal conductivity, power factor, and the dimensionless figure of merit were measured. The results show that sample CuO-45-TC exhibited the highest thermoelectric performance with a ZT value of 0.042 at 973 K. The value should be the highest performance reported in the literature as far as we know. The remarkable increase in orientation degree and relative density should be responsible for the improvement in the thermoelectric performance of CuAlO₂.

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1. Introduction

CuAlO₂ compound classified into the delafossite group of ternary oxides with the chemical formula A²⁺B³⁺O₂ has attracted increasing interest in the field of low-cost thermoelectric materials and devices [1–3]. For delafossite crystals, charge carriers can easily move two-dimensionally along the O–Cu–O dumbbell layer than across the Al–O insulating layer. Hence, a thermal gradient along O–Cu–O place could restrain the carriers and phonons along the plane, and therefore a high ZT value can be expected depending on the Hicks model [4]. It is well known that excellent thermoelectric performance is expected if a large dimensionless figure of merit (ZT) was achieved [5].

\[ ZT = S^2σT/k \]  

(1)

Where S, σ, T, and k represent the Seebeck coefficient, electrical conductivity, temperature, and thermal conductivity, respectively. Therefore, to enhance thermoelectric performance, the Seebeck coefficient and electrical conductivity have to be increased, and meanwhile, thermal conductivity has to be decreased. However, CuAlO₂, as a kind of p-type semiconductor, always shows several orders of magnitude smaller electrical conductivity than those of n-type semiconductors, leading to low thermoelectric performance [5,6]. Despite its many merits including non-toxicity, ease of synthesis, chemical stability at elevated temperature, low cost of its raw materials [7–9], CuAlO₂ has to acquire superior electrical conductivity and maintain low thermal conductivity before its practical thermoelectric application.

In our reported studies, we prepared CuAlO₂ bulks by spark plasma sintering (SPS) from the mixture green compacts of CuO, Cu₂O, and Al₂O₃ powder [10]. The power factor of the CuAlO₂ compacts reached 6 × 10⁻⁵ Wm⁻¹K⁻² at 925 K. After that, we
prepared high-orientated CuAlO₂ compacts with high density by multi-press forming followed by SPS [3]. The thermoelectric performance also ran up to the same level. Last year, we made full use of the synergetic effect of high density, orientation control, and element doping to improve the thermoelectric performance of CuAlO₂ compacts [11]. Its power factor and ZT value were elevated to $1.54 \times 10^{-4} \text{Wm}^{-1} \text{K}^{-2}$ and 0.015 at 973 K. The performance value was greater compared with those of CuAlO₂ in documents. Meanwhile, an increase in orientation degree also improved the SPS. A higher density could lead to greater carrier mobility.

In the present work, we prepared CuAlO₂ bulks with high density and high orientation degree using tape casting followed by SPS. A higher density could lead to greater carrier mobility. Meanwhile, an increase in orientation degree also improved the effective two-dimensional confinement of charge carriers and phonons along a certain crystallographic plane under an anisotropic environment. At last, the thermoelectric performance was significantly enhanced compared to that of the CuAlO₂ compacts prepared by multi-press forming followed by SPS.

2. Experimental

2.1. Preparation of CuAlO₂ compacts

Plate-like Al₂O₃ powder (average diameter: 10 µm, thickness: 0.8 µm, purity: 98.8%) [VFA10030, Kinsei Matec Co., Ltd., Japan], CuO powder (average diameter: 3 µm, purity: 99.9%) and Cu₂O powder (average diameter: 3 µm, purity: 99.0%) were mixed together. To obtain the individual CuAlO₂ crystal phase, the mole ratio of Cu: Al was set at 1:1 and meanwhile the mole ratio of CuO to Cu₂O was adjusted as $x$ (100-$x$) (0 ≤ $x$ ≤ 100). Total weight of 30.0 g mixed powders and 50 mL acetone was poured into a vessel made of Al₂O₃ with a volume of 250 mL. Subsequently, mechanical mixing was done by a planetary ball mill at a revolution speed of 100 rpm keeping for 60 min (Pulverisette 6, Fritsch, Germany). Afterward, to execute the tape casting process well, 1.0 g PVB or 1.5 g KC-7000 (Kyoeisha Co., Ltd., Japan) as a binder and 0.15 g stearic acid as a dispersant were added in the mixed powders and then mechanically mixed by the above same planetary ball mill at 200 rpm for 180 min. After that, we prepared the slurry for tape casting as following. 0.4 g dibutyl phthalate, 15 mL ethanol, and above mixed powders were poured into the same vessel as above. Mechanical mixing was carried out again at 200 rpm for 30 min and the slurry for tape casting was acquired. Subsequently, the tape casting process was executed with the schematic diagram displayed in Fig. 1. We used a film applicator to form a green compact on oil-resistant paper with a gap varying from 100 to 200 µm between the oil-resistant paper and the curing edge of the applicator.

After the fabrication of the green compacts, the compacts were filled into a graphite mold of 40 mm in diameter, which was then sintered at 1273 K using spark plasma sintering (SPS) (SPS–1030, Sumitomo, Japan). The heating rate, the pressure, and the holding time are given in Table 1. Samples of $40 \times 5 \times 2 \text{mm}^3$ were prepared from the sintered compacts and used for thermoelectric performance measurement.

2.2. Characterization and evaluation

Phase types of the as-sintered samples were characterized by X-ray diffraction (JDX-3530, JEOL, Japan). Depending on Lotgering’s method, the orientation degree was calculated with the Lotgering factor (F), which was obtained from the XRD patterns. The detailed calculation can be found in our published work [3]. The surface morphology of the as-sintered samples was observed by scanning electron microscopy (JSM-6510, JEOL, Japan). The as-sintered samples with a dimension of $40 \times 5 \times 2 \text{mm}^2$ were used to measure their Seebeck coefficient $S$ and electrical conductivity $\rho$ using a four-probe direct current method within the temperature range of 373–973 K. The thermal conductivity was estimated depending on the formula $\kappa = \frac{\rho S}{\kappa_{\text{ph}}}$ where $\kappa$, $\rho$, and $S$ correspond to thermal diffusivity, density, and specific heat capacity, respectively. The thermal diffusivity and heat capacity was measured by the laser flash method (LFA 427 Microflash, Netzsch, Germany) [12]. The density of the as-prepared samples was evaluated using the Archimedean method.

3. Results and discussion

Fig. 2 shows the XRD patterns of the as-sintered samples with different preparation conditions listed in Table 2. From the XRD patterns, diffraction peaks at 15.75°, 31.75°, 36.80°, 37.90°, 42.37°, 48.41°, 57.27°, 65.38°, 66.20°, 66.90°, and 74.40° were detected. These diffraction peaks are indexed to correspond to the (003), (006), (011), (012), (104), (009), (018), (110), (0012), and (1010) orientations of the delafossite structure of 3R–CuAlO₂, which belongs to the R-3m space group (JCPDS PDF#35–1401) [a = 2.8567 Å and c = 16.943 Å] [11,13]. From the relative diffraction intensity of diffraction peaks, we can determine the 3R–CuAlO₂ is dominant. Meanwhile, trace 2H–CuAlO₂ phase coexisted in the present CuAlO₂ particles according to JCPDS PDF#75–1792 (a = 2.8809 Å and c = 11.4023 Å) [14–16]. In sample No. 1 and 3, a certain number of CuAl₂O₄ and CuO were also discovered according to JCPDS PDF#33–0448 and JCPDS PDF#48–1548, respectively. The appearance of CuAl₂O₄ and CuO is believed to be the decomposition result of the CuAlO₂ at or higher than 800 °C in the air as follows: $2\text{CuAlO}_2 \rightarrow \text{CuAl}_2\text{O}_4 + \text{CuO}$ (1) [17]. On the other hand, the absence of CuAl₂O₄ and CuO in sample No. 2 just confirms this statement since the preparation temperature of sample No. 2 was 100 °C lower than that of sample No. 1 and No. 3.

We calculated the orientation degree of these as-sintered samples according to the method in our published work [3]. The values are 0.49, 0.28, and 0.77 from sample No. 1 to 3, respectively. Therefore, to obtain the sample with a higher purity of CuAlO₂ and a higher orientation degree, we chose the preparation condition of sample No. 3 as the standard preparation condition, which made the degreasing process involved in the SPS process simultaneously. In present work, the following as-sintered samples were fabricated using the standard preparation process although the ratio of CuO to Cu₂O could be changed.

Fig. 3 represents the XRD patterns of the as-sintered samples with different ratios of CuO to Cu₂O ranging from 40:60 to 100:0. It
can be found that intense diffraction peaks of $3R\text{–CuAlO}_2$ appeared in all the samples. It indicates that the $3R\text{–CuAlO}_2$ phase was dominant in these as-sintered samples. In sample CuO-100-TC (TC means tape casting), obvious diffraction peaks of CuO and CuAl$_2$O$_4$ were detected. According to the reference [18], when the temperature rises to 700 °C, the following reaction occurs.

$$\text{CuO} + \text{Al}_2\text{O}_3 \rightarrow \text{CuAl}_2\text{O}_4$$  \hspace{2cm} (2)

When it further rises to higher than 950 °C, another reaction happens as follows.

$$2\text{CuO} + 2\text{CuAl}_2\text{O}_4 \rightarrow 4\text{CuAlO}_2 + \text{O}_2 \uparrow$$  \hspace{2cm} (3)

We can exclude that CuAl$_2$O$_4$ was derived from the decomposition of CuAlO$_2$ at high temperature because other samples prepared at the same temperature did not contain CuO and CuAl$_2$O$_4$. Therefore, we conclude that added CuO was excess for the reaction to form CuAlO$_2$ from Al$_2$O$_3$, CuO, and Cu$_2$O.

On the other hand, in Sample CuO-40-TC, diffraction peaks of CuO were observed, which suggests that Cu$_2$O was too much for the reaction to prepare CuAlO$_2$. Therefore, to obtain the CuAlO$_2$ sample with high purity, we need to determine a reasonable ratio of CuO to Cu$_2$O. From this point of view, the ratio of CuO to Cu$_2$O should be 45:55 and 50:50.

**Table 1**

<table>
<thead>
<tr>
<th>Temperature range (K)</th>
<th>Heating rate (K/min)</th>
<th>Pressure (MPa)</th>
<th>Holding time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298–973</td>
<td>100</td>
<td>10</td>
<td>–</td>
</tr>
<tr>
<td>973</td>
<td>–</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>973–1173</td>
<td>50</td>
<td>40</td>
<td>–</td>
</tr>
<tr>
<td>1173–1273</td>
<td>25</td>
<td>40</td>
<td>–</td>
</tr>
<tr>
<td>1273</td>
<td>–</td>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>1273–298</td>
<td>furnace cooling</td>
<td>0</td>
<td>–</td>
</tr>
</tbody>
</table>

**Fig. 2.** XRD patterns of the as-sintered samples.

Table 2 shows the density, relative density, and orientation degree of the as-sintered samples. With the ratio change of CuO to Cu$_2$O, the relative density of the as-sintered samples also varied from 97.8% to 98.7%. The orientation degree reached 0.60 to 0.77. Compared with the sample prepared by multi-press SPS (CuO-5-pre) [3], the relative density and orientation degree of the as-sintered samples prepared by tape casting followed by SPS increased to varying degrees. Therefore, we believe that tape casting followed by SPS is an effective way to improve the relative density and orientation degree of thermoelectric compacts. Furthermore, considering the purity of CuAlO$_2$ in the as-sintered samples, as well as the relative density and the orientation degree, we guess that sample CuO-50-TC should have a higher thermoelectric performance. The issue will be discussed in detail later.

**Fig. 4.** compares the reaction resultants of the as-sintered samples CuO-50-TC with different sintering pressure and gap value of tape casting. Sample CuO-50-TC and TC-10MPa were fabricated with an SPS pressure of 40 and 10 MPa, respectively. The XRD patterns of both the samples are almost the same, which means that the change in SPS pressure has little effect on the reaction process and resultant. Meanwhile, with the gap decreased from 200 μm (CuO-50-TC) to 100 μm (TC-100 μm), residual CuO and by-product of CuAl$_2$O$_4$ were detected. It may be related to the small gap that made the additives’ separation in green compacts easier. Therefore, to obtain higher purity CuAlO$_2$ compacts, the gap value of 200 μm is better than 100 μm when the reactant composition, sintering temperature and sintering pressure are the same.

**Table 2**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Binder</th>
<th>Dibutyl phthalate</th>
<th>Stearic acid</th>
<th>Degreasing and pressure</th>
<th>SPS sintering</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PVB, 1.0 g</td>
<td>0.4 g</td>
<td>0.15 g</td>
<td>–</td>
<td>5 → 40 MPa</td>
</tr>
<tr>
<td></td>
<td>1273 K/10min</td>
<td></td>
<td></td>
<td>1273 K</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>KC-7000, 1.5 g</td>
<td>0.4 g</td>
<td>0.15 g</td>
<td>1373 K/0.5 h</td>
<td>40 MPa</td>
</tr>
<tr>
<td></td>
<td>390 MPa/10min</td>
<td></td>
<td></td>
<td>1173 K/10min</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>KC-7000, 1.5 g</td>
<td>0.4 g</td>
<td>0.15 g</td>
<td>–</td>
<td>10 → 40 MPa</td>
</tr>
<tr>
<td></td>
<td>1273 K/10min</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 5a** shows the SEM images of the used plate-like Al$_2$O$_3$ powder particles. The average size of the particles in the plane is nine ~ ten μm and their thickness is about 800 nm. After tape casting, a layered structure formed with the plate-like Al$_2$O$_3$ particles distributed along the flow direction of the slurry (Fig. 5b). Furthermore, no obvious hollow structure is observed. From the surface morphology of the green compact of CuO-50-TC (Fig. 5c), no
distinct aggregation of the plate-like Al₂O₃ particles, CuO particles, and Cu₂O particles is discovered. The uniform distribution of the reactant particles can ensure a complete chemical reaction in the following SPS. After SPS, we have not seen the boundaries of the reactant particles, because these boundaries have become highly blurred. What’s more, the boundaries connected, which indicates that these powder particles have undergone the chemical reaction as follows [11]. From the XRD patterns (Fig. 3), we conclude that the main product during SPS is 3R–CuAlO₂ and therefore 3R–CuAlO₂ is dominant in Sample CuO-50-TC. Combined with the XRD patterns, we confirm that the main phase is 3R–CuAlO₂ in Fig. 5d.

4CuO + 4Cu₂O + 6Al₂O₃ → 12 CuAlO₂ + O₂ (4)

Fig. 6 shows the thermoelectric performance of the as-sintered samples. From Fig. 6a, we noted that the electrical resistivity of all the samples declined with the increase in measure temperature, which is similar to a semiconductor material. In all the samples, CuO-50-TC showed the smallest electrical resistivity. We see from Fig. 6b that the Seebeck coefficients of all the as-sintered samples are positive, which suggests that the charge carriers are holes rather than electrons. In other words, all the as-sintered samples are typical p-type semiconductors. The Seebeck coefficient of Sample CuO-100-TC decreased as the operating temperature increased over the range of 373–973 K. Normally, the Seebeck coefficient is inversely proportional to the carrier concentration and electrical conductivity according to the following equation [1,19].

\[
S = \frac{8\pi k_b^2}{3e^2} n^* \left( \frac{\pi}{3n} \right)^{\frac{1}{2}} T \sqrt{T} \tag{5}
\]

where \(n\) is the carrier concentration and \(m^*\) is the effective mass of the carrier, \(k_b\) and \(T\) are the Boltzmann constant and the measurement temperature, respectively. Generally, \(n\) increases with the measurement temperature for semiconductor materials. At high temperatures, the decrease of \(S\) for Sample CuO-100-TC suggest that \(n\) might play a dominant role [16]. A similar trend was observed by other researchers [1]. On the other hand, the Seebeck coefficients of the other sample reduced and then increased over the same temperature range. The change in trend may be directly related to the change in phase composition in the as-sintered samples. Specifically, in these as-sintered samples, the influence importance of temperature and carrier concentration on the Seebeck coefficient has changed because of the absence of the CuAl₂O₄ phase. From Fig. 6c, we observed that the power factor of all the samples also increased as measure temperature was increased. Sample CuO-100-TC and CuO-45-TC possessed the lowest and highest power factor values, respectively. When the temperature was elevated to 973 K, the power factor of sample CuO-45-TC reached 1.19 × 10⁻⁴ W m⁻¹ K⁻². In our published work [3], the power factor of multi-press formed CuAlO₂ followed by SPS was as high as 5.95 × 10⁻⁵ W m⁻¹ K⁻² at 928 K. The power factor of sample CuO-45-TC is twice that of the multi-press formed CuAlO₂ followed by SPS.

We also examined the effect of the SPS pressure and the gap between the oil-resistant paper and the curing edge of the applicator on the thermoelectric properties of the as-sintered samples with the results shown in Fig. 7. When SPS pressure was decreased from 40 to 10 MPa, the electrical resistivity was also decreased when temperature varied from 373 to 773 K. Within the same

![Fig. 3. XRD patterns of the as-sintered samples with different ratio of CuO to Cu₂O.](image)

![Fig. 4. XRD patterns of the as-sintered samples with different sintering pressure and gap value of tape casting.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density (g/cm³)</th>
<th>Relative density (%)</th>
<th>(F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO-5-pre [3]</td>
<td>4.99</td>
<td>97.5</td>
<td>0.57</td>
</tr>
<tr>
<td>CuO-100-TC</td>
<td>5.02</td>
<td>98.2</td>
<td>0.77</td>
</tr>
<tr>
<td>CuO-70-TC</td>
<td>5.01</td>
<td>97.8</td>
<td>0.60</td>
</tr>
<tr>
<td>CuO-50-TC</td>
<td>5.06</td>
<td>98.7</td>
<td>0.66</td>
</tr>
<tr>
<td>CuO-45-TC</td>
<td>5.01</td>
<td>97.8</td>
<td>0.67</td>
</tr>
<tr>
<td>CuAlO₂</td>
<td>5.12</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

Table 3
Density, relative density, and orientation degree of the as-sintered samples.
Fig. 5. SEM images of (a) the used plate-like Al₂O₃ powder, (b) and (c) cross section and surface morphology of the green compact of CuO-50-TC, respectively, (d) surface morphology of the as-sintered sample CuO-50-TC.

Fig. 6. Thermoelectric performance of the as-sintered samples: (a) electrical resistivity, (b) Seebeck coefficient and (c) power factor.
temperature range, the Seebeck coefficient of the as-sintered samples at 10 MPa was greater than that of the sample prepared at 40 MPa. As a result, the power factor the sample prepared at 10 MPa was also greater than that of the sample at 40 MPa during 373–673 K. When it was increased to 773 K, the power factor of the latter became larger than that of the former. On the other hand, the gap change affected the thermoelectric properties of the as-sintered samples. When the gap was decreased from 200 to 100 μm, the electrical resistivity was increased while the Seebeck coefficient was decreased. Therefore, the power factor was reduced.

Fig. 8 compared the thermoelectric properties of CuAlO₂ samples prepared by different methods. From Fig. 8a, the thermal conductivity of Sample SPS-40 prepared by multi-press forming followed by SPS decreased from 28 to 11 W·m⁻¹·K⁻¹ when measurement temperature was increased from 303 to 873 K [3]. Yanagiya and his coworkers [20] prepared CuAlO₂ compacts using SPS followed by annealing. The thermal conductivity decreased from 12 to 8 W·m⁻¹·K⁻¹ when the temperature was increased from 623 to 1023 K. Sakulkalavek and his team [8] prepared CuAlO₂ compacts using cold pressing followed by sintering. The thermal conductivity decreased from 10 to 4 W·m⁻¹·K⁻¹ when it was elevated from 298 to 573 K. In present work, we controlled the thermal conductivity of Sample CuO-45-TC between 8.7 and 2.5 W·m⁻¹·K⁻¹ when it was elevated from 374 to 975 K. The successful control of thermal

![Fig. 7. Thermoelectric performance of the as-sintered samples with different preparation parameters: (a) electrical resistivity. (b) Seebeck coefficient and (c) power factor.](image)

![Fig. 8. Comparison of thermoelectric properties of CuAlO₂ samples prepared by different methods: (a) thermal conductivity and (b) dimensionless figure of merit, ZT.](image)
conductivity can provide a lot of room for improvement of thermoelectric properties.

Fig. 8b shows the dimensionless figure of merit, $ZT$ of CuAlO$_2$ compacts prepared by different methods. In the present work, we greatly elevated the $ZT$ value of the as-sintered sample (CuO-50-TC) to 0.042 when measure temperature was increased to 973 K. Ruttanpun prepared CuAlO$_2$ compacts using cold pressing followed by sintering [21]. The maximum $ZT$ value of the CuAlO$_2$ bulk sample was 0.017 at 960 K. Yanagiya [20] prepared CuAlO$_2$ doped with Zn and Ag using SPS followed by annealing and the $ZT$ value reached 0.016 at 1060 K. Pantian [8] prepared (CuAlO$_2$)$_{1-x}$(Ag$_2$O)$_x$ specimens by sintering with a $ZT$ value of 0.0044 at 573 K. Through the addition of Fe and graphene, the $ZT$ value of CuAlO$_2$ prepared by sintering was as high as 0.0114 at 573 K [6]. Zhu and his coworkers also used sintering to prepare CuAlO$_2$, which had a maximum $ZT$ value of 9.82 x 10$^{-3}$ at 773 K [22]. Therefore, as far as I know, a $ZT$ value of 0.042 should be the highest performance among CuAlO$_2$ thermoelectric materials in published work.

CuAlO$_2$ belongs to the delafossite group of ternary oxide thermoelectrics with the chemical formula A$^+$ B$^{3+}$ O$_2$ [3]. In its crystal structure shown in Fig. 9a, alternate layers of two-dimensional close-packed copper cations with linear O–Cu$^+$–O bonds and slightly distorted edge-shared Al$^{3+}$O$_6$ octahedra [23]. Each Cu$^+$ cation is bonded to two O$^{2-}$ anions producing dumbbell-shape [O–Cu–O] structure along the c axis. Marquardt [24] has proved that the Cu layers can serve as the conduction path for charge carriers. The electrical conductivity of the CuAlO$_2$ single crystal along the c axis and the a-b plane is 600 and 1000 S m$^{-1}$, respectively. In other words, the charge carriers are easier to move two-dimensionally along the a-b plane than to move across the c axis [4]. Therefore, CuAlO$_2$ shows a strong dependence of thermoelectric performance on its orientation.

Shear-thinning is a phenomenon that occurs in polymer liquids and emulsions, and when the liquid is subjected to shear stress, the apparent viscosity decreases [25]. The anisotropic particles in the solvent are oriented along with the orientation of the molecular chains. In this work, the viscosity of the slurry can be lowered by the orientation degree of plate-like Al$_2$O$_3$ particles along with the flow direction of the slurry as shown in the schematic diagram in Fig. 9b. Therefore, the orientation degree of the as-sintered CuAlO$_2$ compacts was greatly increased to more than 0.60. During the SPS process, the chemical reaction among CuO, Cu$_2$O, and Al$_2$O$_3$ happened and laminar CuAlO$_2$ was formed. The interlayer surface of CuAlO$_2$ is just the a-b plane. Therefore, a higher orientation degree means that the a-b plane of the formed CuAlO$_2$ has a smaller angle with the direction of the temperature gradient. Based on the above discussion, we believe that the increase in orientation degree is the main reason for the improvement of the thermoelectric performance of CuAlO$_2$ compacts. Orientation control is believed to be an effective method for improving the thermoelectric performance of metal oxides. The method has been applied to improve the thermoelectric performance of metal oxides [26~29].

Another important reason for improving thermoelectric performance should be ascribed to the increased density. Compared with the as-sintered CuAlO$_2$ compacts prepared by multi-press forming followed by SPS, the as-sintered CuAlO$_2$ bulk prepared by tape casting followed by SPS possessed higher density and relative density (Table 3). The increase in relative density can increase the thermal conductivity since it can decrease the scattering of phonons. On the other hand, the relative density increase also improves electrical conductivity hence improving thermoelectric performance [10,11].

4. Conclusions

We developed a novel method of tape casting followed by SPS to prepare thermoelectric CuAlO$_2$ compacts. The orientation degree of the as-sintered CuAlO$_2$ compacts was greatly increased due to the distribution of plate-like Al$_2$O$_3$ particles along the direction of the slurry flow under the action of the shear-thinning effect during tape casting. The influence of some important processing parameters including the ratio of CuO to Cu$_2$O, additives, sintering pressure, and applicator gap on the thermoelectric properties of the as-sintered CuAlO$_2$ compacts was investigated. The optimized processing parameters were determined. The results showed that sample CuO-45-TC possessed the most excellent thermoelectric performance among all the as-sintered samples with a $ZT$ value of 0.042 at 973 K. The value should be the highest thermoelectric performance of CuAlO$_2$ compact as far as we know. The improvement in thermoelectric performance should be attributed to the increase in orientation degree and relative density.

![Fig. 9. (a) Schematic CuAlO$_2$ crystal structure [4] and (b) schematic diagram of anisotropy of the as-sintered CuAlO$_2$ samples.](image-url)
Compliance with ethical standards

No author has financial or other contractual agreement that might cause conflict of interest.

CRediT authorship contribution statement

Liang Hao: Writing - review & editing. Yan Zhang: Writing - review & editing. Ryota Kubomura: Writing - review & editing. Shingo Ozeki: Writing - review & editing. Shiqi Liu: Data curation, Writing - review & editing. Hiroyluki Yoshida: Data curation, Writing - review & editing. Yingrong Jin: Formal analysis, Writing - review & editing. Yun Lu: Conceptualization, Writing - original draft, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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