



Power factor improvement of delafossite CuAlO_2 by liquid-phase sintering with Ag_2O addition



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ARTICLE INFO

Keywords:

CuAlO_2

Ag_2O addition

Liquid-phase sintering

Power factor

ABSTRACT

Thermoelectric delafossite $(\text{CuAlO}_2)_{1-x}(\text{Ag}_2\text{O})_x$ with $0 < x < 0.06$ is prepared at three different sintering temperatures, 1323 K, 1373 K, and 1473 K. The samples are obtained from a mixture of CuO , Al_2O_3 , and additive Ag_2O powders. The mixture is ground and then pressed with uniaxial pressure into pellets. Differential scanning calorimetry and X-ray diffraction spectroscopy show that the sintering temperature to synthesize delafossite CuAlO_2 with Ag_2O addition is below 1473 K. X-ray diffraction patterns show the major phase of delafossite 3R- CuAlO_2 along with a trace amount of 2H- CuAlO_2 . A small amount of the Ag phase is present in the samples depending on the amount of Ag_2O addition and sintering temperature. Energy dispersive spectroscopy and backscattered electron image analyses show that the Ag phase is segregated around the grain boundary. Liquid-phase sintering is used to explain the growth mechanism. The CuAlO_2 samples with Ag_2O addition obviously exhibit enhanced bulk density, grain size, and electrical conductivity. The highest power factor (PF), obtained by CuAlO_2 with 2 at% of Ag_2O sintered at 1373 K, is $8.23 \times 10^{-5} \text{ W}/(\text{m K}^2)$ at 873 K. Hence, our findings show an improvement for delafossite CuAlO_2 by Ag_2O addition.

1. Introduction

Thermoelectricity is the phenomenon that describes the conversion of thermal energy into electricity or vice-versa. The thermoelectric performance of materials depends on both a temperature gradient across the material (ΔT) and a figure of merit (Z). The product of Z and absolute temperature (T) is a dimensionless parameter defined by $ZT = \frac{S^2\sigma}{k}T$, where S is the Seebeck coefficient, σ is the electrical conductivity, and k is the thermal conductivity. Additionally, Z is the power factor and $PF = S^2\sigma$ divided by k . The PF is one of the parameters that is commonly used to evaluate the performance of thermoelectric materials. Chalcogenides, such as Bi_2Te_3 and Sb_2Te_3 , are well-known materials for room-temperature thermoelectric applications [1]. The chalcogenides show a poor chemical and physical stability under high temperatures, and relatively high toxicity, which make them incompatible for use in major energy conversion technologies, such as combustion engines, concentrated solar radiation sources, or furnaces. However, thermoelectric oxide materials are very low cost compared with the chalcogenides because tellurium (Te) is an extremely rare element in the earth.

Oxide materials, such as NaCo_2O_4 , $\text{Ca}_3\text{Co}_4\text{O}_9$, ZnO , and SrTiO_3 , have been introduced to be candidate thermoelectric materials because of their high performance, high chemical and thermal stability at high

temperatures in air, and their simple and low-cost manufacturing process [3–9]. Recently, delafossite CuAlO_2 has attracted the attention of researchers. Delafossite CuAlO_2 can be formed with two different structures, which are the 3R structure (space group $R\bar{3}m$; no.166) and 2H structure (space group $P6_3/mmc$; no.194) [10] as shown in Fig. 1. The lattice constants a and c are approximately 2.8813 and 17.1006 Å for 3R- CuAlO_2 , and 2.8809 and 11.4023 Å for 2H- CuAlO_2 [11]. The thermoelectric properties of CuAlO_2 were first studied in 2001 [11]. The solid-state reaction and sintering process from 1323 to 1623 K in air ambient were conventional processes to synthesize the delafossite CuAlO_2 structure with low cost [13–18]. In another process, Tawat et al. synthesized the single phase of CuAlO_2 by using microwave radiation followed by the spark plasma sintering (SPS) process. The thermoelectric properties were measured and calculated from room temperature to 1073 K. The highest PF and ZT were $3.5 \times 10^{-5} \text{ W}/\text{m K}^2$ and 9×10^{-3} at 1073 K, respectively [19]. Two approaches for improving the thermoelectric properties have been suggested. An approach to increase the thermoelectric properties was the substitution of several elements, such as Ca [14,15], Fe [16,17], and Ni [18], to the Al sites. The findings from these studies indicated that substitution of 10% of the Al with Fe and sintering CuAlO_2 at 1473 K for 20 h yielded a compound with the highest power factor of $1.1 \times 10^{-4} \text{ W}/\text{m K}^2$ at 1140 K [16]. In addition, SPS at 1273 K for 10 min was used to

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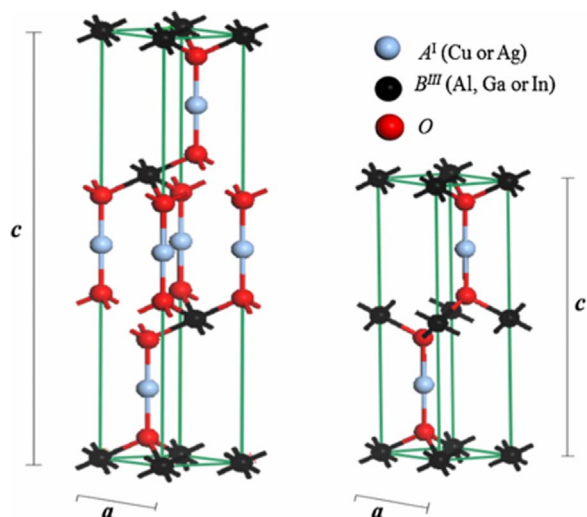


Fig. 1. Crystal structure of delafossite compounds for the (a) 3R polytype and (b) 2H polytype [2].

enhance the density of the CuAlO_2 compound. Using the SPS process, the relative density of the compound was as high as 97.7%. The highest PF and ZT were $6 \times 10^{-5} \text{ W/m K}^2$ and 5×10^{-3} , respectively, at 873 K [20]. Another approach, involving the effect of element substitution for the Cu sites in CuAlO_2 , has been studied. Yanagiya et al. studied the effect of Ag, Ni, and Zn substitution for Cu sites by SPS at 1123 K for 20 min and isothermal annealing at 1373 K for 24 h. The results indicated that Ag addition would enhance the microstructure (grain size) of the CuAlO_2 compound [21], while the thermoelectric properties of delafossite CuAlO_2 are decreased. However, the effect of the Ag sites on the delafossite structure is still unclear. In addition, it has been reported that the addition of Ag to some ceramics, such as $\text{Ca}_3\text{Co}_4\text{O}_9$ [22,23], can successfully enhance the power factor. Therefore, our objective is to verify the effect of Ag addition on the crystal structure, grain size, density, and thermoelectric properties of delafossite CuAlO_2 prepared by the sintering process.

2. Materials and methods

Delafossite $(\text{CuAlO}_2)_{1-x}(\text{Ag}_2\text{O})_x$ with $0 < x < 0.06$ were prepared from mixtures of CuO (Sigma-Aldrich, 99.99%), Al_2O_3 (Sigma-Aldrich, $\geq 98\%$), and Ag_2O (Sigma-Aldrich, 99.99%) powders. The mixtures were ground for 6 h using an alumina mortar. Differential scanning calorimetry (DSC; Mettler Toledo Model TGA/DSC) was carried out to obtain preliminary information of the phase transformations in Ag_2O and the mixture of CuO, Al_2O_3 , and Ag_2O powders. DSC was analyzed in air with the temperature increasing at a rate of 5 K/min. From the DSC results, as shown in Fig. 2(b), three sintering temperatures of 1323 K, 1373 K, and 1473 K, corresponding with before-phase transition, at-phase transition, and after-phase transition, respectively, were used for the synthesized delafossite CuAlO_2 . The as-ground samples with and without Ag_2O were pressed into a rectangular bar and sintered in air at design temperatures for 12 h and then rapidly cooled at room temperature. After that, the sintered samples were ground, pressed, and sintered again for two times to obtained homogeneous samples and reduce the sintering time. In this work, the calcination stage of the solid-state reaction was bypassed. The crystal structure and surface morphology/phase segregation of the as-sintered samples were analyzed by X-ray diffraction (XRD; Bruker D8 Advance) and scanning electron microscopy (SEM; EVO-MA10), respectively. Energy dispersive X-ray spectroscopy (X-max 20; Oxford Instruments) was then used to analyze the chemical composition of different phases in the samples. The Seebeck coefficient and electrical conductivity were measured at temperatures ranging from 300 to 873 K using the DC

four-terminal method (ZEM-3;Ulvac, Inc.). Finally, the Archimedes method (ASTMC373-88) was used to measure the density of the as-sintered samples.

3. Analysis and discussion

Fig. 2 shows the DSC results for Ag_2O and the mixture of CuO, Al_2O_3 and additive Ag_2O powders. Two exothermic peaks were observed at the temperature ranges of 623–663 K and 1220–1230 K for the Ag_2O powder, as shown in Fig. 2(a). The first exothermic peak (623–663 K) is the reaction of $2\text{Ag}_2\text{O} \rightarrow 4\text{Ag} + \text{O}_2$ [24]. The second exothermic peak (1220–1230 K) corresponds to the melting point of Ag [25]. For the mixture of CuO, Al_2O_3 , and Ag_2O powders, two exothermic peaks and one endothermic peak are observed, as shown in Fig. 2(b). The small broad peak is the melting point of Ag, as shown in the inset of Fig. 2(b). A sharp exothermic peak in the temperature range of 1300–1350 K corresponds to the delafossite formation reaction [4,13,14]. It is very interesting to observe a broadening endothermic peak in the temperature range of 1470–1500 K. We cannot identify this reaction from previous work. We were able to identify the reaction of the endothermic peak by using XRD results of the sample sintered at 1473 K. To investigate the effect of Ag_2O addition on the sintering temperature of delafossite CuAlO_2 , the mixture of CuO, Al_2O_3 , and Ag_2O powders were sintered in air at 1323 K, 1373 K, and 1473 K.

Figs. 3 and 4 show the XRD patterns of the as-sintered samples with 0–6 at% of Ag_2O at two different sintering temperatures (1323 and 1373 K). XRD patterns of as-sintered samples were compared with the JCPDS database of 3R- CuAlO_2 (No.35-1401), 2H- CuAlO_2 (No.75-1792), CuO (No.05-0661), Ag (No.03-0931), and Al_2O_3 (No.83-2080). Ag_2O was decomposed into Ag metal and oxygen in the temperature range of 1220–1230 K, so the sintering process produced Ag metal particles that were then mixed with CuO and Al_2O_3 powder. Four different compounds were found on the as-sintered samples, that is, 3R- CuAlO_2 (space group $R\bar{3}m$; no. 166), 2H- CuAlO_2 (space group $P6_3/mmc$; no. 194), Ag, and CuO. The spectrum of as-sintered samples without Ag_2O matched well with the database of 3R- CuAlO_2 . The XRD patterns of the samples sintered at 1323 K are more dominant phase of 2H- CuAlO_2 than that of the samples sintered at 1373 K, when we consider the intensity of 2H- CuAlO_2 peaks in Fig. 3 and 4. The calculated lattice parameters, obtained by using the Rietveld method, were close to those obtained in previous work [13,14,26]. The as-sintered samples were the single phase of CuAlO_2 . A small amount of CuO crystalline phase on the samples with and without Ag_2O addition was observed. The CuO content on the as-sintered samples depended on the sintering temperature and Ag_2O addition. The CuO content increased with an increase of the sintering temperature and the Ag_2O addition. This result was consistent with that reported by Park et al. [13,16] and Lu et al. [27]. The decomposition reaction of delafossite CuAlO_2 during annealing at high temperature in air was investigated. It has been reported that CuAlO_2 decomposes into CuAl_2O_4 and CuO above 1073 K [27]. However, CuAl_2O_4 was not detected in this work. This might arise from a smaller CuAl_2O_4 phase quantity than the detectable limit of the XRD machine. However, an increasing amount of 2H- CuAlO_2 from Ag_2O has not previously been discussed. 2H- CuAlO_2 crystal phases were found on as-sintered samples with the Ag_2O addition. A small amount of 2H- CuAlO_2 peaks ($2\theta \approx 37.15^\circ$, 39.73° , 54.99°) presented in samples with the Ag_2O addition. Liu et al. used density functional theory to calculate the enthalpy variation owing to the tensile stress that could enhance a phase transformation from the 3R phase to the 2H phase. The stress of 3R-to-2H phase transformation was approximately -26.0 GPa [12]. However, we found another approach to achieve the 3R-to-2H phase transformation, by the Ag_2O addition, where the 2H- CuAlO_2 content depends on the sintering temperature.

From previous work, CuAlO_2 with and without Fe and Ca dopants have been effectively sintered at 1473 K [13]. The XRD patterns of the

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