



Temperature dependent thermoelectric properties of cuprous delafossite oxides

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ABSTRACT

The use of nanostructured delafossite oxides in thermoelectric (TE) applications has attracted a great interest due to their high performance and long-term stability at elevated temperatures. Cuprous delafossites, CuMO_2 ($M = \text{Al, Cr, Fe, Ga, Mn}$), compared to conventional TE materials, such as Bi_2Te_3 , PbTe and SiGe , are non-toxic and more earth abundant. In particular, CuAlO_2 compound shows a great potential for high performance thermoelectric materials.

In this work, a systematic study of temperature dependent TE properties of cuprous delafossite materials, CuAlO_2 , is reported. The optimization of the TE properties has been realized by controlling nanostructure size around 80 nm CuAlO_2 powder was prepared using a solid-state synthesis method at ~ 1373 K in nitrogen/air atmosphere. The nanostructure size was controlled by a high energy ball milling process. Reducing the particle size of nanostructured bulk materials decouples interdependent electron and phonon transport and results in a lattice thermal conductivity decrease without deteriorating electrical conductivity. The high effective mass plays a dominant role in the high Seebeck coefficient and low electrical conductivity. The power factor reached $\sim 0.78 \times 10^{-5} \text{ W/mK}^2$ at 780 K. Temperature dependent TE properties, including Seebeck coefficient, electrical conductivity, and thermal conductivity are analyzed. The processing-structure-property correlation of these materials are discussed.

1. Introduction

There is an increasing need to supply clean and renewable energy to fulfill the world's high energy demand. Harvesting waste heat for electricity is one approach to improve sustainability. Thermoelectric materials have the ability to directly convert thermal energy into electricity via Seebeck effect [1–3]. Thermoelectric generators are silent, reliable solid-state devices with no moving parts, making them attractive for other applications, such as power generation in remote environments (e.g. space) or autonomous sensors [4,5]. However, there are still challenges using TE technology for applications. One of biggest challenges is optimized TE properties of existing TE materials since three parameters (S , σ , κ_T) are affected by each other [6]. The quality of materials for TE applications is described by a dimensionless parameter

zT [7,8], which is defined as the following:

$$zT = \frac{S^2\sigma}{k_T} T \quad (1)$$

where S is the Seebeck coefficient, σ is the electrical conductivity, k is the thermal conductivity. In physics, κ_T is the sum of the electronic contribution (κ_e , due to carrier transport) and lattice contribution (κ_l , due to phonon transport). The term $S^2\sigma$ is called the power factor (PF). A high PF indicates that a TE power generator can achieve a high power output. In our previous theoretical work, one effective way to improve the TE properties is by using small-nanostructure-size (SNS) limit to reach a high zT [9]. Also, cuprous delafossite oxides are promising candidates for thermoelectric materials due to their electronic properties can be tuned from insulator behavior to metallic behavior by

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manipulating their crystal structures, chemical compositions and doping concentrations [10,11].

In 1997, Kawazoe et al. reported the p-type conductivity of transparent thin film CuAlO_2 as 1 S/cm at room temperature [12]. Also, the previous study shows CuAlO_2 has a relatively large electronic bandgap (~ 3.4 eV) and flat band structure [13]. Moreover, Hao et al. has conducted a computational-driven TE materials search and identified CuAlO_2 is a promising p-type candidate [9]. CuAlO_2 has a layered, delafossite structure that can be considered a natural superlattice, which is more stable and easy for synthesis [14]. Superlattice structures show a lot of promise for TE materials [15–17]. Other layered oxide materials used for TE, such as NaCo_2O_4 [18], and SrTiO_3 [19] have demonstrated relatively large zTs. However, temperature dependent thermoelectric transport properties of CuAlO_2 have not been fully exploited in existing literature.

To fill this knowledge gap, we have conducted a systematic study of thermoelectric properties of CuAlO_2 with the function of temperatures from 300 K to 780 K. Solid-state synthesis of CuAlO_2 created a material with a nanostructured grain size, which affects electrical and thermal conductivity. Cold-pressed pellets kept powder maintained the grain size during the annealing process. Annealing temperature and time were optimized for microstructure, which will significantly affect thermoelectric properties [20]. The effects of different annealing times for CuAlO_2 , on resulting microstructure, and related thermoelectric properties of CuAlO_2 were studied.

1.1. Experimental design

High purity CuO and Al_2O_3 were stoichiometrically mixed with alcohol, and ball milled for 6 h using 3 mm yttria stabilized zirconia grinding media at a 40:1 ratio. The resulting powder was dried in oven at 363 K, then pressed into pellets with 13 mm diameter and 1.5 mm thick at 394 K under 8 Tons for 30 min. The pressed pellets were annealed at 1373 K for 5 h, 8 h and 12 h, respectively, in a combination of nitrogen and ambient environments. All samples were furnace cooled.

The crystal structure, and purity of the samples were analyzed via powder X-ray diffraction (XRD) using a Panalytical Empyrean Powder X-ray Diffractometer at 40 kV, 40 mA with Bragg-Brentano mode with $\text{Cu K}\alpha$ radiation. The diffraction patterns were collected from 10–80° for five times. The average crystalline size of the powders was calculated according to Scherrer's equation. A high-resolution transmission electron microscope (FEI Tecnai F20ST) was used to investigate crystal structure of annealed powders. Seebeck coefficient was determined through a home-built measurement system that applies a temperature gradient through the sample and measures the resulting voltage output as described elsewhere [6,21]. The Seebeck coefficient was calculated from the slope of temperature vs voltage. Electrical conductivity was directly measured by four-probe hall measurement system (Ecopia AHT55T5). The thermal conductivity was determined using transient time-dominant method from the thermal diffusivity and specific heat measured by laser flash method (LFA 467, NETZSCH, Germany). All the thermoelectric properties were measured from 300 K to 780 K in a nitrogen environment.

2. Results and discussion

Fig. 1 shows the results of powder x-ray diffraction patterns for CuAlO_2 powder with varying annealing times at 1373 K. It can be seen that higher purity of CuAlO_2 powder were obtained annealing at 1373 K for 12 h, due to the complete reaction between CuO and Al_2O_3 . The main reactions for the formation of CuAlO_2 are: $\text{CuO} + \text{Al}_2\text{O}_3 \rightarrow \text{CuAl}_2\text{O}_4$ and $\text{CuAl}_2\text{O}_4 + \text{CuO} \rightarrow 2\text{CuAlO}_2 + 1/2\text{O}_2$. There will be a formation of CuAl_2O_4 at annealing temperature between 1173 K and 1273 K. The following reactions will result in impurities of CuAlO_2 : $\text{CuAlO}_2 + \text{O}_2 \rightarrow 1/2\text{CuAl}_2\text{O}_4 + 1/2\text{CuO}$ and $\text{CuAl}_2\text{O}_4 \rightarrow \text{CuAlO}_2 + 1/2\text{Al}_2\text{O}_3 + 1/4\text{O}_2$ as shown in XRD pattern with

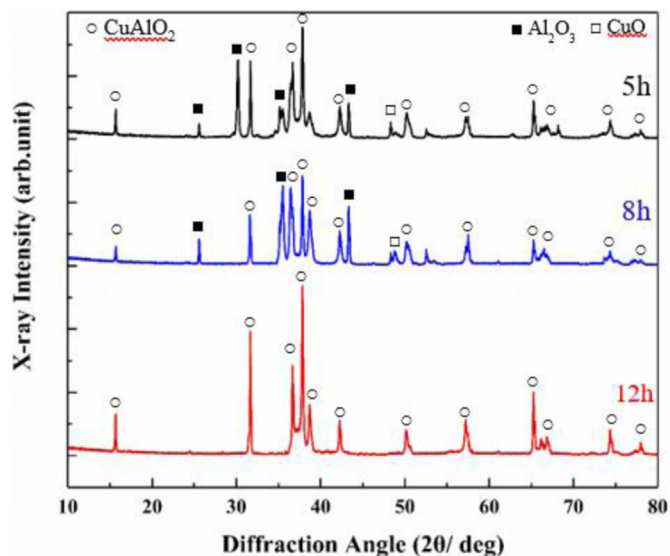


Fig. 1. The XRD patterns of CuAlO_2 powder with different annealing time at 1373 K.

CuO and Al_2O_3 peaks. The crystalline structure of the annealed CuAlO_2 bodies is rhombohedral, $R\bar{3}m$, $a = 2.8567$ Å and $c = 16.943$ Å (JCPDS Card File: 00-035-1401).

Further investigation on microstructure of annealed CuAlO_2 powder is done by using high resolution transmission electron microscope (HRTEM). Clear lattice fringes of CuAlO_2 is observed as shown in Fig. 2 (a), which indicates high quality of crystal structure. Furthermore, using Fast Fourier Transform (FFT) image obtained by Digital Micrograph software the d-spacing of the lattice orientation was calculated. The d-spacing of the lattice fringes (Fig. 2b) was found to be 2.47 Å, which corresponded to the reported d-value (2.4474 Å) of (10 $\bar{1}$ 1) plane of r- CuAlO_2 (JCPDS Card File: 00-035-1401). The FFT image as shown in Fig. 2c indicates the rhombohedral structure. The HRTEM results are confirmed with an XRD pattern of crystalline structure of r- CuAlO_2 .

Thermoelectric properties strongly depend on the microstructure of the materials. Fig. 3 shows the temperature dependent Seebeck coefficient of CuAlO_2 powder annealing at 1373 K for 12 h. The Seebeck coefficient shows a positive sign over the measured temperature range indicating p-type conductor behavior, which is due to the behavior of hole majority carriers. The Seebeck coefficient increases with the increase of temperature and the highest Seebeck coefficient reaches 665 $\mu\text{V}/\text{K}$ at 780 K. No bipolar effect was observed due to the large band gap of CuAlO_2 (~ 3.4 eV) [13]. Lu et al. reported the Seebeck coefficient value as 460 $\mu\text{V}/\text{K}$ at 780 K for CuAlO_2 pellets prepared by SPS method [22], which is lower due to the crystal defects i.e., impurity. Also, the grain size will grow during SPS pressing, which leads to more complicated electron scattering mechanisms. This will affect electrical properties of materials. However, the overall values of Seebeck coefficient for CuAlO_2 samples are relatively high. Seebeck coefficient is an intrinsic material property, which measures the thermoelectric voltage induced in response to a temperature difference across the material. High effective mass of the charge carriers will lead to high Seebeck coefficient. The high hole effective mass will increase the density of states at an energy E in the valence band as shown below:

$$g_v(E) = \frac{m_p^* \sqrt{2m_p^*(E_v - E)}}{\pi^2 \hbar^3}, \quad E \leq E_v \quad (2)$$

For semiconductors, the relationship among Seebeck coefficient, effective mass and carrier concentration can be expressed below:

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{2/3} \quad (3)$$

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