Dependence of mechanical and electrical properties on crystal orientation of CuCr$_{0.95}$Mg$_{0.05}$O$_2$ ceramics

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Abstract. Mg-doped CuCrO$_2$ material has emerged as a p-type semiconductor, especially in the field of thermoelectric materials because of its lowest resistivity in delafossite material family. In this work, CuCr$_{0.95}$Mg$_{0.05}$O$_2$ bulk materials were prepared in a series of sintering temperatures including 1000, 1200, and 1400°C using solid-state reaction method. From XRD results, all samples exhibit the significant existence of delafossite phase CuCrO$_2$, and a small portion belongs to the spinel phase MgCr$_2$O$_4$. An interesting finding in this study is that the Vickers hardness is mainly governed by the crystallite size of (110) plane. Besides, the change in the crystallite size of (110) plane also indirectly affects the carrier concentration of the compounds with increasing sintering temperature. The highest power factor (PF) was reached for the sample prepared at the sintering temperature 1400°C with the value of 193 $\mu$W/mK$^2$ along with the Seebeck coefficient value of 600 μV/K measured at 400°C.

1. Introduction

Cuprous delafossite materials which has a general formular Cu$^I$B$^{III}$O$_2$ (where, B is a trivalent cation (Cr, Fe, Ga, In, or Al)) have emerged as a good p-type oxide semiconductor [1–3]. In this structure, Cu atoms align with two oxygen atoms to form a O-Cu-O dumbbell structure paralleled c-axis, while B atoms form a BO$_6$ coplanar octahedral block. Besides, delafossite materials behave as a quasi-two-dimensional structure, in which the triangular Cu layer alternately stacks with the BO$_6$ octahedral layer along c axis of crystal cell [4], and therefore it can be considered as a natural superlattice. In the
family of cuprous delafossite materials, CuCrO$_2$ seems to be a superior compound in terms of natural p-type conductivity by doping magnesium [5]. Therefore, this materials have several potential applications, such as thermoelectric or optoelectronic devices [6].

There are many publications in which most of the authors just try to improve the electrical properties of CuCrO$_2$ compound by doping group two elements like Mg or Zn with an appropriate concentration [5,7,8]. For example, M. Ahmadi et al. [5] prepared (Mg, N)-doped CuCrO$_2$ thin films by a sputtering method and with an appropriate Mg concentration of 2.5 at.% the film reaches the highest electrical conductivity in the family of delafossite materials, which makes this compound become a potential candidate for optoelectronic applications. For thermoelectric applications, most authors have to deal with a big issue that doping Mg for improving the electrical conductivity of CuCrO$_2$ compound gives rise to a significant decrease of Seebeck coefficient [9–12]. Although there are many efforts for improving the electrical conductivity and Seebeck coefficient of CuCrO$_2$ compound, there are few reports on the mechanical properties and their relationship with electrical properties, while mechanical property is one of important properties of thermoelectric materials. J. Monteiro et al. [13] is one of rare authors who has a detailed report about the mechanical property of CuCrO$_2$ compound. In their publication, they found that the hardness of an $ab$-plane is significantly smaller than that of an $a(b)c$-plane and there is not any connection with those mechanical properties with electrical properties. In another publication, M. A. Madre et al. [14] prepared a series of CuCrO$_2$ sample doped divalent elements (Mg, Ca, Sr, and Ba) by conventional solid-state reaction method and they conclude that the higher hardness sample is, the worse electrical property is. However, it is hard to evaluate the correlation between mechanical properties and electrical properties of samples with different doping element because each element contributes to mechanical and electrical properties in a different way.

Therefore, in this study, we focus on investigating the correlation between structural, mechanical, and electrical properties of CuCrO$_2$ compounds with only 5% Mg doping concentration and at different sintering temperatures.

2. Experimental details

2.1 Synthesis

The CuCr$_{0.95}$Mg$_{0.05}$O$_2$ bulk samples were prepared by a conventional solid-state reaction method at different sintering temperatures (1000 – 1400°C). The raw materials were used to synthesis these compounds including Cu$_2$O, Cr$_2$O$_3$, and MgO (minimum 99% purity for all) with an appropriate quantity to preserve the stoichiometry. All raw materials were mixed along with distilled water with the ratio of 1 : 1 and then grinded that mixture in a planetary ball mill for 5 hours. After that, the wet mixture was dried in an oven at a drying temperature of 100°C for 24 hours to evaporate the water. The dried mixture was then grinded by hand on an agate mortar and pressed into a pellet with the dimensions of 30×30×8 mm$^3$. The green compacts were then sintered in the high-temperature furnace at a series of the temperature of 1000 – 1400°C.

2.2 Characterization

The powder X-ray diffraction (XRD) measurements (Bruker D8 Advanced) in 2θ scan = 30 – 75° (step = 0.02°) was used to detect the crystal structure of the compounds. Fourier Transform Infrared (FTIR) system (Bruker's VERTEX 70v spectrometer), a supporting tool for XRD result in this work, was employed to detect the featured vibration modes of atoms in solid materials. A Vickers indentation system (Vickers Hardness tester, Nova series system) was used to determine the hardness of the bulk samples. The Hall measurements (Ecopia HMS-3000) carried out at room temperature were used to measure the hole concentration and mobility of those bulk samples. The Seebeck coefficient and electrical conductivity of 1400°C sample were measured in the temperature range of 50 – 500°C using the LSR-3 system (Linseis GmbH, Germany).
3. Results and Discussions

Figure 1. XRD patterns of CuCr$_{0.95}$Mg$_{0.05}$O$_2$ compounds prepared at various sintering temperature. The insets in the red dot circles are the magnification of a narrow 2θ = 34.5 – 37.5°. XRD results of 1400 °C sample published in Ref. [15].

Figure 1 shows the variation of XRD patterns of CuCr$_{0.95}$Mg$_{0.05}$O$_2$ compounds as increasing sintering temperature. There is not much change in the XRD curves or the intensity of each peak with the increase of sintering temperature and all samples show the completely predominant existence of
CuCrO$_2$ phase based on powder diffraction file (PDF) # 74-0983. Noticeably, 1000°C sintering sample has a very weak signal of MgCr$_2$O$_4$ phase (PDF #77-0007) in comparison with higher sintering temperature samples as seen in the insets in each XRD pattern. Mg dopant concentration in delafossite CuCrO$_2$ materials has a very low solubility (solubility means that Mg could substitute for Cr and do not form new secondary phase). There are lots of literatures which investigates the influence of Mg dopant concentration on structural properties of CuCrO$_2$ material and depending on the synthesis conditions the solubility limit of Mg in CuCrO$_2$ compound is various around 0.5 – 5.0 % [12,16]. From XRD results, it can be clearly observed that the increase of sintering temperature gives rise to the growth of MgCr$_2$O$_4$ phase.

**Figure 2.** FTIR spectra of of CuCr$_{0.95}$Mg$_{0.05}$O$_2$ compounds at different sintering temperature. FTIR results of 1400 °C sample published in Ref. [15].

Figure 2 shows the change of FTIR spectra of CuCr$_{0.95}$Mg$_{0.05}$O$_2$ compounds with the variation of sintering temperature. All samples exhibit two big absorption peaks belonged to Cu–O and Cr(Mg)–O vibrations in delafossite material located at around 534–543 cm$^{-1}$ (vibrating along the c-axis) and 718–732 cm$^{-1}$, respectively [15,17,18]. A small absorption peaks located at 420 cm$^{-1}$ for all sample is assigned for the vibration of Mg–O in the spinel phase [15] which is also detected by XRD results. The appearance of spinel phase also exhibits via an absorption peak located around 674–703 cm$^{-1}$ and 463–477 cm$^{-1}$ which relates to the vibration of Cr–O in the octahedrons of the spinel phase [15]. Besides, 1400°C sintering sample appears a small absorption peak located at 590 cm$^{-1}$ which is assigned for the vibration of O-Cu-O in delafossite materials. The red shift of all FTIR absorption peaks may relate to lattice crystal distortion caused by point defects appeared in the compounds at high sintering temperature.
Figure 3. (a, b) $a$ and $c$ lattice parameters and (c, d) the crystallite size of (110) and (006) planes of CuCrO$_2$ delafossite material.

To get more details of effects of sintering temperature on structural properties, $a$ and $c$ lattice parameters belonged to delafossite materials derived from (110) and (006) planes, respectively, are calculated in Figure 3 (a, b) and exhibit a decrease trend with the increase of sintering temperature. As in our previous study [15], the decrease of $a$ and $c$ lattice parameters derives from the appearance of defects inside bulk sample, such as: Cr vacancies ($V_{\text{Cr}}$), Cu vacancies ($V_{\text{Cu}}$),… which also contributes to the increase of hole concentration of CuCrO$_2$ material. Based on those explanations, the decrease of lattice parameters is also contributed from above mentioned point defects which implies that the increase of sintering temperature causes the formation of point defects in the compounds. The crystallite size of (110) and (006) plane shows an increase trend with sintering temperature which is appropriate for sample prepared ceramic method because of mixing raw particles which in turn increases the grain size.
Interestingly, from Figure 4, there is a tight correlation between hardness and the crystallite size of (110) plane with the increase of sintering temperature. From this correlation, it can be considered that the hardness of CuCrO$_2$ materials is mainly governed by the crystallite size of (110) plane. J. Monteiro et al. [13] investigated the mechanical properties of CuCrO$_2$ single crystal and they found out that the hardness of this material is anisotropic in which the hardness of $a(b)c$-plane is harder than that of $ab$-plane. However, in the best of our knowledge, there is not any publications which reported on the hardness of CuCrO$_2$ polycrystal material oxide in terms of its relationship with crystal orientation.

Figure 4. The correlation between hardness and crystallite size of (110) plane of CuCr$_{0.95}$Mg$_{0.05}$O$_2$ compounds with sintering temperature. Hardness results of 1400°C sample published in Ref. [15].

Figure 5 shows hole carrier concentration, hole mobility, and conductivity of CuCr$_{0.95}$Mg$_{0.05}$O$_2$ samples sintered at different sintering temperature. The carrier concentration in Figure 5 (a) has an increase trend with the sintering temperature, in which in the low sintering temperature range (1000 –
1200°C) the hole concentration has a small increase, and dramatically increases at high sintering temperature range (1200 – 1400°C). There are some factors which contributes to the increase of hole concentration, including the substitution of Mg for Cr, $V_{Cu}$, $V_{Cr}$, or interstitial oxygen [19,20]. In Figure 5 (b) the hole mobility has a significant decrease at high sintering temperature, which may be contributed by the increase of ionized scattering center like $Mg_{Cr}', V_{Cu}'$ or $V_{Cr}'''$ (Kröger-Vink notation) [21], which is known as a generating p-type defects in delafossite materials, which explains the significant increase of hole concentration at high sintering temperature. Besides, the increase of crystallite size as seen in Figure 3 confirms the independence of hole mobility with grain boundary. The electrical conductivity of CuCr$_{0.95}$Mg$_{0.05}$O$_2$ compounds was derived from the relation of $p$ and $\mu$ based on equation $\sigma = p.\mu.e$ (1) and was plotted in Figure 5 (c).

![Figure 6](image_url)

**Figure 6.** The correlation between carrier concentration and crystallite size of (110) plane of CuCr$_{0.95}$Mg$_{0.05}$O$_2$ compounds with sintering temperature.

Figure 6 shows the curves hole concentration and crystallite size of (110) plane with the variation of sintering temperature. Interestingly, there is a similarity between two curves which implies that there may be correlation between $p$ and $D_{(110)}$ plane. In case of p-type delafossite materials, the main transporting mechanism is “hopping mechanism” between Cu atoms on $ab$ plane [20,22–24] which means that the grain boundary scattering could be ignored. Therefore, in this case, the increase of crystallite size $D_{(110)}$ with the sintering temperature may contribute a certain indirect effect related to the enhancement of carrier concentration. This means that the growth of crystallite size may also generate more defects simultaneously which contributes hole concentration to improve electrical conductivity as mentioned above.
Figure 7. (a) Seebeck coefficient, (b) electrical conductivity, and (c) power factor of CuCr$_{0.95}$Mg$_{0.05}$O$_2$ compounds prepared at 1400°C as a function of measuring temperature. This thermoelectric results were published in ref. [15].

To evaluate the ability of CuCr$_{0.95}$Mg$_{0.05}$O$_2$ compound applied for thermoelectric applications, the sample prepared at 1400°C has the highest electrical conductivity determined via Hall measurement as seen in Figure 5 is used to measure the Seebeck coefficient and electrical conductivity depending on temperature as seen in Figure 7. The Seebeck coefficient as seen in Figure 7 (a) shows positive sign which indicates p-type characteristics and has high value in comparison with other published reports with the similar compound [14,25]. In Figure 7 (b), the electrical conductivity shows an increase trend with the elevation of measuring temperature which indicates the semiconducting behavior of this compound and reaches the highest value of ~ 7 S/cm at 500°C. As a result of the simultaneously high Seebeck coefficient and electrical conductivity at measuring temperature range of 400 – 500°C, the power factor has the highest value of ~ 193 µW/mK$^2$ as seen in Figure 7 (c).

4. Conclusions

In summary, we have investigated the effect of sintering temperature on structural, mechanical, and electrical properties of CuCr$_{0.95}$Mg$_{0.05}$O$_2$ compounds. This study brings out the fact that the crystal structure, mechanical, and electrical properties has a significant correlation, which means that the change in the crystal structure consequently gives rise to the variation in mechanical and electrical properties. We find out that the Vickers hardness is mainly governed by the crystallite size of (110) plane. In addition, the change in the crystallite size of (110) plane also indirectly effects on the carrier concentration of the compounds with the increase of sintering temperature. The high Seebeck coefficient and electrical conductivity results of 1400°C sintering sample show the ability of this compound on thermoelectric applications.

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