

Synthesis and Characterization of Delafossite CuLaO_2 for Thermoelectric Application

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Abstract

The preparation of single-phase CuLaO_2 with delafossite-type structure by means of the solid-state reaction method was investigated using X-ray diffraction. The results showed that notwithstanding the fact that there was a trace of metallic copper, nearly single-phase CuLaO_2 was obtained by using $\text{La}(\text{OH})_3$ as a lanthanum source and by firing the mixed powder with nonstoichiometric composition ratio of $\text{La}(\text{OH})_3:\text{Cu}_2\text{O} = 1:1.425$ in a vacuum at 1273 K for 10 h. The measurement of electrical conductivity and Seebeck coefficient showed that CuLaO_2 thus obtained was a p-type semiconductor and had a Seebeck coefficient of approximately 70 $\mu\text{V}/\text{K}$.

Keywords : CuLaO_2 , delafossite, single-phase, reduction of pressure, $\text{La}(\text{OH})_3$, nonstoichiometry, thermoelectric properties

1. Introduction

Delafossite-type ternary oxides such as CuAlO_2 , CuInO_2 have received much attention as a material for thermoelectric application [1,2] and transparent semiconductor[3,4]. CuLaO_2 covered in this study is one of delafossites and hence is expected to have interesting properties. In order to clarify the properties, high-quality single-phase CuLaO_2 are needed,. However, there have only been a few reports on the synthesis of CuLaO_2 . One of the problems is that the reproducible preparation of single-phase CuLaO_2 is difficult. Haas et al. reported that CuLaO_2 is unstable and can not be prepared under normal temperature and pressure [5]. Cava et al. also reported that the synthesis of single-phase CuLaO_2 is considerably difficult and single-phase is synthesized only through complicated and troublesome route [6].

The purpose of this study is to find a method for reproducibly preparing single-phase CuLaO_2 through a simple route. This paper reports the effect of an atmosphere pressure during synthesizing, a starting lanthanum source and its composition ratio, and sintering temperature and the time on the preparation of CuLaO_2 .

2. Experimental and Results

CuLaO_2 was synthesized by firing the mixed powder of Cu_2O (Kokusaan Chem.Co., Japan) and La_2O_3 (99.9%, Soekawa Phys.Chem.Co., Japan) or $\text{La}(\text{OH})_3$ (99.9%, High Purity Chem.Co., Japan) with a desired composition ratio at 973-1273 K. La_2O_3 was prebaked at 1273 K for 10 h in air. Before firing, the powders were ground mechanically for 1 h in air and pressed into pellets of 1mm thick and 25 mm diameter at 500 kg/cm^2 . The pellets were placed on an

aluminum plate in the remaining powder in an aluminum crucible. The sintering was mainly carried out in a vacuum of about 10^{-2} Torr, for comparison and under an argon flow. We tried to prepare CuLaO_2 in a vacuum in order to eliminate the effect of O_2 thoroughly. The XRD result is shown in Fig.1. Here, we used $\text{La}(\text{OH})_3$ as a lanthanum source, and did not use La_2O_3 . Fig. 2 shows XRD patterns for samples prepared by firing the stoichiometrically mixed powder using (a) La_2O_3 and (b) $\text{La}(\text{OH})_3$ as a lanthanum source at 973 K for 10 h in a vacuum. When La_2O_3 was used as a lanthanum source, only unreacted La_2O_3 (unmarked peaks) and Cu_2O were detected. On the other hand, when $\text{La}(\text{OH})_3$ was used, the reaction occurs and CuLaO_2 is already formed even at 973 K. This suggests that H_2O produced by a decomposition of $\text{La}(\text{OH})_3$ accelerates the reaction between La_2O_3 and Cu_2O . Fig. 1 shows the XRD pattern for the sample prepared by firing the stoichiometrically mixed powder using $\text{La}(\text{OH})_3$ as a lanthanum source at 1273 K for 10 h in a vacuum. As can be seen in the figure, there were still traces of La_2O_3 and metallic copper remaining in the sample. In this method,

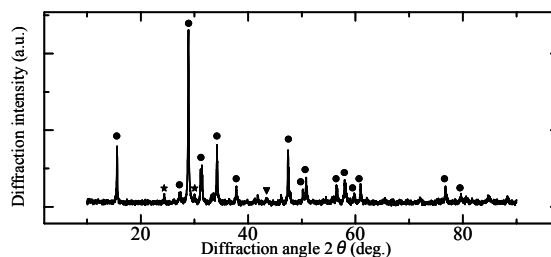


Fig. 1. XRD pattern for sample prepared by firing the stoichiometrically mixed powder using $\text{La}(\text{OH})_3$ as a lanthanum source at 1273 K for 10 h in a vacuum. (●: CuLaO_2 ★: La_2O_3 ▼: Cu)

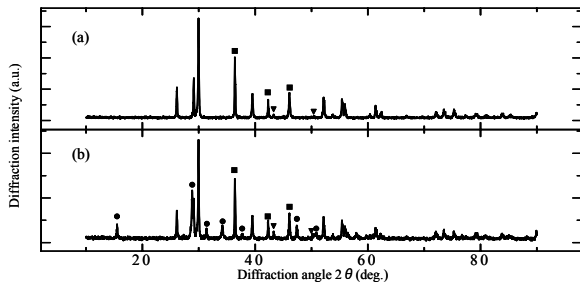


Fig. 2. XRD patterns for samples prepared by firing the stoichiometrically mixed powder using (a) La_2O_3 and (b) $\text{La}(\text{OH})_3$ as a lanthanum source at 973 K for 10 h in a vacuum. (●: CuLaO_2 ■: Cu_2O ▼: Cu)

some troublesome routes such as mechanically grinding under N_2 , use of zirconium setter and synthesis under N_2 flow for preventing trace amounts of O_2 from getting to the sample [9] were excluded in the preparation of CuLaO_2 . The result indicates that the method using $\text{La}(\text{OH})_3$ as a lanthanum source and keeping in a vacuum during firing process gave better results for the synthesis of CuLaO_2 than that by Cava et al.. In other words, this preparation route is simpler than that by Cava et al.. As can be seen in Fig.1, even in the method above-mentioned traces of La_2O_3 and metallic copper were still detected. Fig.3 shows the XRD pattern for sample prepared by firing the mixed powder with a composition ratio of $\text{La}(\text{OH})_3:\text{Cu}_2\text{O}=1:1.425$ at 1273 K for 10 h in a vacuum. The comparison of Fig.1 and Fig.3 shows that the trace of La_2O_3 disappears and a nearly single phase is prepared using Cu_2O -excess composition ratio of $\text{La}(\text{OH})_3:\text{Cu}_2\text{O}=1:1.425$. Here, a trace of metallic copper is still detected. Therefore, in order to eliminate a trace of metallic copper, the effect of firing temperature and firing time were also examined. At temperatures below 1223 K, the metallic copper trace did not disappear and besides La_2O_3 and Cu_2O were detected. The firing time was 10 h. At firing times below 7 h, it did not disappear and in addition Cu_2O was detected. The temperature dependence of the electrical conductivity for CuLaO_2 including a trace of metallic copper is shown in Fig.4 (a). The value at room temperature is approximately 0.032 S/cm. The electrical conductivity increases with increasing temperature, and typical of semiconducting behavior. The drop in the

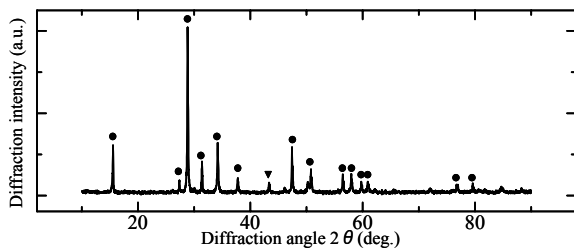


Fig. 3. XRD pattern for sample prepared by firing the mixed powder with a composition ratio of $\text{La}(\text{OH})_3:\text{Cu}_2\text{O}=1:1.425$ at 1273 K for 10 h in a vacuum. (●: CuLaO_2 ▼: Cu)

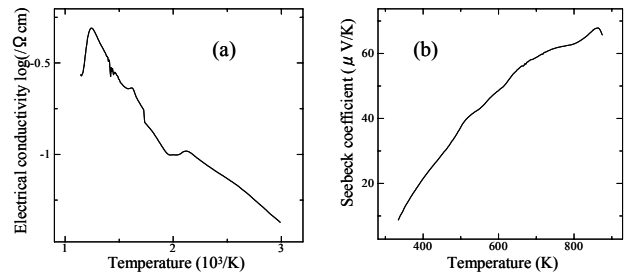


Fig. 4. Temperature dependence of (a) electrical conductivity and (b) Seebeck coefficient for the same sample as Fig.3

electrical conductivity at temperature around 500 K is probably due to a decrease in carrier mobility as temperature increases. Furthermore, the drastic decrease at above 850 K is probably due to the composition of CuLaO_2 . The temperature dependence of the Seebeck coefficient for the same sample as Fig.4(a) is shown in Fig.4(b). The Seebeck coefficient has a positive sign at all measurement temperature, indicating that CuLaO_2 is a p-type semiconductor. The Seebeck coefficient of CuLaO_2 increases with temperature and reaches a maximum of approximately 70 $\mu\text{V}/\text{K}$ at 850 K.

3. Summary

We investigated the preparation condition for obtaining the high-quality single-phase delafossite-type CuLaO_2 in a simple route. The results showed nearly single-phase CuLaO_2 , although a trace amount of metallic copper was included, was obtained by using $\text{La}(\text{OH})_3$ as a lanthanum source and firing the mixed powder with nonstoichiometric composition ratio of $\text{La}(\text{OH})_3:\text{Cu}_2\text{O}=1:1.425$ in a vacuum at 1273 K for 10 h. Electrical conductivity and Seebeck coefficient of CuLaO_2 thus obtained were measured.

4. References

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