A novel synthesis method of delafossite-type CuYO₂ using a layered yttrium hydroxide as an yttrium source

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A facile synthesis method of delafossite-type CuYO₂ using a layered yttrium hydroxide (LYH) was developed. LYH microplates and Cu₂O nanoparticles were both prepared from aqueous solutions and used as raw materials for the solid-state reaction to form CuYO₂. It was found that CuYO₂ could be obtained by heating LYH–Cu₂O mixed powder at 900°C for 4 h under a N₂ atmosphere. Although the product contained a slight amount of Y₂O₃, the heating time used in the proposed method was much shorter than that required for the conventional synthesis method via the Cu₂Y₂O₅ precursor phase. Analysis of the X-ray diffraction pattern showed that the CuYO₂ powder synthesized using LYH contained the 3R-type polymorph as the major content, whereas a larger content of the 2H-type polymorph was included in the powder synthesized by the conventional method. Based on these results, a topotactic reaction maintaining the layered structure of LYH was proposed as the formation mechanism for CuYO₂ in LYH–Cu₂O mixed powder.

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A. Introduction

Delafossite-type ternary oxides with the general formula ABO₂ have been widely studied for various applications, such as transparent conductors,¹ photocatalysts,² and multiferroics.³ The delafossite structure consists of two alternating layers: a layer of A cations in a triangular pattern, and a layer of edge-sharing BO₆ octahedra, which are stacked along the c-axis and bonded together by a dumbbell-shaped O-A-O liner bonding. The A site can be occupied only by monovalent noble metal cations (Pd⁺, Pt⁺, Cu⁺, and Ag⁺), whereas the B site can be composed of a wide variety of trivalent cations, including p-block metal cations (Ga³⁺, In³⁺, and Al³⁺), transition metal cations (Fe³⁺, Co³⁺, Y³⁺, etc.), and rare earth metal cations (La³⁺, Nd³⁺, Eu³⁺, etc.).³ Depending on the orientation of each layer in the stacking, two different delafossite structures can be formed, as illustrated in Fig. 1.⁵ Stacking the pairs of the A and BO₆ layers so as to rotate the BO₆ layers 180° relative to each other forms the hexagonal 2H type with the space group P₆₃/mmc [Fig. 1(a)]. When the pairs of the A and BO₆ layers are stacked without rotation but with an in-plane shift in a three-layer sequence, on the other hand, the rhombohedral 3R type with the space group R₃m is formed [Fig. 1(b)].

Some Cu-based delafossite-type compounds, such as CuAlO₂, CuCrO₂ and CuFeO₂, have also been regarded as promising p-type semiconducting oxides for use in thermoelectric energy conversion.⁵⁻⁷ Among these, Singh has pointed out based on first-principles band calculations that the heavily hole-doped delafossite-type CuYO₂ has the potential to show high thermopower \( \alpha S \) (where \( \sigma \) is electrical conductivity and \( S \) is the Seebeck coefficient).⁶ It is known that the thermal conductivity (κ) of the Cu-based delafossite-type compounds can be largely reduced by B-site substitution,⁸ moreover, which is beneficial for enhancement of the thermoelectric energy conversion efficiency. Thus, CuYO₂ is regarded as a promising ther-
moelectric material with potential for showing a high thermoelectric figure of merit $Z = \alpha S^2/\kappa$.

Cu-based delafossite-type compounds are generally synthesized via a conventional solid-state reaction in air or N₂ atmosphere using oxide raw materials. When it comes to CuYO₂, however, the solid-state reaction between Y₂O₃ and Cu₂O is too slow, and single-phase CuYO₂ can thus not be obtained by this usual solid-state reaction. Other synthesis methods, such as the hydrothermal route, are also unavailable for synthesis of CuYO₂. For this reason, a two-step synthesis method via a Cu₂Y₂O₅ precursor phase has been used to obtain CuYO₂. In this method, the Cu₂Y₂O₅ precursor phase containing the divalent copper ion Cu²⁺ is synthesized first via a conventional solid-state reaction and then reduced into CuYO₂ by heat treatment in a N₂ atmosphere. Although this method is effective for obtaining CuYO₂ powder without other impurity phases, it requires extended heat treatment lasting a total of from 10 h to several days. The product of the Cu₂O-ethanol suspension, followed by additional ball-milling for 1 h. The resulting Cu₂O-LYH mixed powder was dried and uniaxially pressed into pellets with a thickness of about 1 mm and a diameter of 11 mm. The pellets were embedded in sacrificial CuYO₂ powder, which was prepared by the conventional route described below, and heated in a tube furnace under a N₂ flow of 200 mL/min. The heating rate was fixed at 25 °C/min, and the heating temperature and time were varied from 1 to 4 h and from 700 to 900°C, respectively.

For purposes of comparison, CuYO₂ was also synthesized by the conventional method via the Cu₂Y₂O₅ precursor phase. Stoichiometric amounts of copper (II) oxide (Cu₂O, ≥ 99.9%, Wako) and yttrium oxide (Y₂O₃, ≥ 99.9%, Nippon Yttrium) were ball-milled in ethanol. The mixture was dried and fired at 1000°C for 5 h in air to form Cu₂Y₂O₅. The Cu₂Y₂O₅ powder was subsequently reduced in a tube furnace at 900°C for 5 h under a N₂ flow of 200 mL/min.

2.3 Characterizations

Phase determination of the samples was performed by the X-ray diffraction (XRD) technique using an X-ray diffractometer (D8 ADVANCE, Bruker AXS) equipped with a Cu Kα radiation source. The XRD profiles of the CuYO₂ powder were analyzed by the RIETAN-SEP Rietveld refinement program to determine the proportions of 2H and 3R types in the powder. The particle morphology of the LYH powder was observed by field-emission scanning electron microscopy (FE-SEM; type S-4700, Hitachi). The thermal behavior of the LYH powder in the N₂ atmosphere was examined by thermogravimetry–differential thermal analysis (TG–DTA; DTG-60, Shimadzu) at a heating rate of 5 °C/min up to 800°C.

3. Results and discussion

The XRD pattern of the LYH powder prepared by the homogeneous precipitation method is shown in Fig. 2. The observed diffraction peaks are well consistent with the previously reported XRD pattern of Y₂(OH)₅NO₃·nH₂O, which is a member of the LYH family containing NO₃⁻ as an interlayer anion, and which can be indexed to

2.2 Synthesis of CuYO₂

To prepare a mixed powder of LYH and Cu₂O, the synthesized Cu₂O was first ball-milled in ethanol for 5 h. Stoichiometric amounts of LYH and Cu₂O, the synthesized Cu₂O was then added to the Cu₂O-ethanol suspension, followed by additional ball-milling for 1 h. The resulting Cu₂O-LYH mixed powder was dried and uniaxially pressed into pellets with a thickness of about 1 mm and a diameter of 11 mm. The pellets were embedded in sacrificial CuYO₂ powder, which was prepared by the conventional route described below, and heated in a tube furnace under a N₂ flow of 200 mL/min. The heating rate was fixed at 25 °C/min, and the heating temperature and time were varied from 1 to 4 h and from 700 to 900°C, respectively.

2.2 Synthesis of CuYO₂

To facilitate direct formation of CuYO₂ in a solid-state reaction, we focused on the present study on a layered yttrium hydroxide (LYH) as the yttrium source. A powder of LYH with a plate-like particle morphology was synthesized from an aqueous solution. It was found that a CuYO₂ powder with only a slight amount of Y₂O₃ could be obtained in one step by heating a mixed powder of LYH and Cu₂O at 900°C under a N₂ atmosphere. The mechanism of this reaction using LYH was discussed based on the similarities in the layered structures of LYH and CuYO₂.

2. Experimental procedures

2.1 Preparation of LYH and Cu₂O

A powder of LYH for use in the synthesis of CuYO₂ was prepared by the homogeneous precipitation method. 2.298 g (6 mmol) of yttrium nitrate n-hydrate [Y(NO₃)₃·nH₂O, ≥ 99.9%, Wako] was dissolved in 60 mL of deionized water. 3.364 g (24 mmol) of hexamethylenetetramine (C₆H₁₂N₂, ≥ 99.0%, Wako) was then added to the solution as an alkaline source. After stirring for 60 min at room temperature, the solution was kept at 90°C for 3 h. The resulting white precipitate was filtered, washed with deionized water and dried at 60°C overnight to obtain a powder of LYH.

A fine powder of copper (I) oxide (Cu₂O) for use in the synthesis of CuYO₂ was also prepared by the following solution process. 9.989 g (40 mmol) of copper (II) sulfate pentahydrate (CuSO₄·5H₂O, ≥ 99.5%, Wako) was dissolved in 50 mL of deionized water. Separately, 3.944 g (20 mmol) of sodium L-ascorbate (NaC₆H₇O₆·3H₂O, ≥ 98.0%, Wako) and 7.353 g (25 mmol) of trisodium citrate dihydrate (Na₃C₆H₅O₇·2H₂O, ≥ 99.0%, Wako) were dissolved in 100 mL of deionized water. These solutions were mixed together, and a 1.0 M aqueous solution of sodium hydroxide (NaOH, ≥ 95%, Taisei Kagaku) was then added under stirring at a dropping rate of approximately 5 ml/min to adjust the pH value to 9.0. A light-brown precipitate was formed during the addition of the NaOH solution. The precipitate was centrifuged, washed twice with deionized water, and dried at 60°C overnight. This process yielded a fine Cu₂O powder with a particle size of under 50 nm.

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its orthorhombic unit cell with the $P2_12_12_1$ space group. Although there are some other LYH compositions with different interlayer anion species,\textsuperscript{18)} we will denote the prepared $\text{Y}_2(\text{OH})_5\text{NO}_3\cdot n\text{H}_2\text{O}$ by LYH for simplicity hereafter. Note that the unindexed small peaks in Fig. 2 are not attributed to secondary phases, but are caused by the overlapping of many diffraction peaks of LYH. The crystal structure of LYH is constructed by alternate packing of positively charged $[\text{Y}_2(\text{OH})_5\cdot n\text{H}_2\text{O}]^+$ unit layers and the intercalated $\text{NO}_3^-$ anions in the interlayer spaces along the $c$-axis with additional water molecules, as illustrated in the inset in Fig. 2. The FE-SEM image of the prepared LYH powder (Fig. 3) shows that many $\mu$m-sized hexagonal plates are assembled to form a secondary particle with a flower-like morphology. The main face of the hexagonal plate is composed of the (001) plane of LYH.\textsuperscript{18)}

**Figure 2** shows the TG–DTA curves of the LYH powder measured in a $\text{N}_2$ atmosphere. Three main distinct weight losses with strong endothermic peaks are observed at 84, 286, and 509°C. According to the literature, these weight losses can be attributed to the following pyrolysis reactions.\textsuperscript{18)} The first weight loss is due to the removal of bound water:

$$\text{Y}_2(\text{OH})_5\text{NO}_3 \cdot n\text{H}_2\text{O} \rightarrow \text{Y}_2(\text{OH})_5\text{NO}_3 + n\text{H}_2\text{O} \uparrow \quad (1)$$

From the observed weight loss in the range from room temperature to 160°C, the $n$ value for LYH prepared in this study is calculated to be 1.56. The second weight loss at around 300°C is caused by partial dehydration from the hydroxide layers:

$$\text{Y}_2(\text{OH})_5\text{NO}_3 \rightarrow \text{Y}_2\text{O}_2(\text{OH})\text{NO}_3 + 2\text{H}_2\text{O} \uparrow \quad (2)$$

The final decomposition into $\text{Y}_2\text{O}_3$ then occurs at around 500°C, as follows:

$$\text{Y}_2\text{O}_2(\text{OH})\text{NO}_3 \rightarrow \text{Y}_2\text{O}_3 + 0.5\text{H}_2\text{O} \uparrow + \text{NO}_2 \uparrow + 0.25\text{O}_2 \uparrow \quad (3)$$

The observed weight loss values corresponding to the second and third reactions are 11.9 and 15.4%, which are comparable to the theoretical values (10.2 and 17.8%, respectively). The total weight loss including a slight additional loss at above 600°C is 37.1%. It should be noted that the $\text{Y}_2(\text{OH})_5\text{NO}_3$ and $\text{Y}_2\text{O}_2(\text{OH})\text{NO}_3$ formed by the decomposition of LYH also have layered structures similar to that of LYH, whereas $\text{Y}_2\text{O}_3$ is not a layered compound. Stoichiometric amounts of LYH and $\text{Cu}_2\text{O}$ were weighed out based on the weight loss data for LYH shown above, mixed together, and heated in a $\text{N}_2$ atmosphere. **Figure 5(a)** compares the XRD patterns of the products heated at 700, 800, or 900°C for 1 h. It is obvious that the products prepared at 700 and 800°C are composed mainly of $\text{Cu}_2\text{Y}_2\text{O}_5$ containing $\text{Cu}^{2+}$, indicating that the oxidation of $\text{Cu}^{+}$ ion occurs during heating at these temperatures. As for the sample heated at 900°C, on the other hand, strong sharp peaks attributed to $\text{CuYO}_2$ are observed. The XRD profile of this sample, however, also shows small peaks due to the impurity phases of $\text{Y}_2\text{O}_3$ and $\text{Cu}_2\text{Y}_2\text{O}_5$. As the heating time is prolonged to 2 and 4 h, the relative intensity of these impurity peaks become smaller, as show in
Fig. 5(b). As a result, a CuYO₂ powder containing only a small amount of Y₂O₃ was obtained by heat treatment at 900°C for 4 h. It should be emphasized that no CuYO₂ phase can be obtained by direct solid-state synthesis using Y₂O₃ as the yttrium source. It is also worth noting that the heating time of 4 h employed in this study is much shorter than the total heating time required for the conventional two-step process via the intermediate Cu₂Y₂O₅ phase.

To discuss the mechanism underlying the formation of CuYO₂ from LYH–Cu₂O mixed powder, the XRD patterns of CuYO₂ powders prepared by the conventional method via Cu₂Y₂O₅ or from LYH–Cu₂O mixed powder were analyzed by the Rietveld method. In the analysis, we used a two-phase mixture model of 2H-type and 3R-type CuYO₂ to refine the proportions of these phases. Figure 6(a) shows the results of Rietveld refinement for the powder prepared by the conventional method. Although most peaks from the 2H and 3R types overlap each other, some distinct characteristic peaks (at 2θ = 33° for the 2H type and 2θ = 36° for the 3R type, marked by arrows) can be observed, indicating that the powder is a mixture of these types. The diffraction profile of this powder is well fitted by the two-phase mixture model, and the relative proportions of the 2H and 3R types are determined to be 66 and 34%, respectively.

Compared to the powder prepared by the conventional method, the CuYO₂ powder prepared from the LYH–Cu₂O mixture shows weaker diffraction peaks attributed to the 2H type and stronger diffraction peaks attributed to the 3R type, as shown in Fig. 6(b). This indicates that the relative proportion of the 3R type is increased in this sample. Actually, the Rietveld refinement results show that the
ratio of the 3R type in this powder is 67\%, which is much larger than that in the powder prepared by the conventional method.

Based on the Rietveld refinement discussed above, it has been found that Cu$_2$YO$_2$ powder synthesized using LYH contains the 3R type as the major portion. This result suggests that the formation pathway to Cu$_2$YO$_2$ in the LYH–Cu$_2$O mixed powder is different from that via Cu$_2$Y$_2$O$_5$. As shown in Fig. 2, the coordination environment of yttrium ions in the [Y$_2$(OH)$_5$$\cdot$H$_2$O]$^+$ hydroxide layers of LYH is not simple and is different from that in the layers of YO$_6$ octahedra in Cu$_2$YO$_2$. Nevertheless, the hydroxide layers have no in-plane rotation relative to one another, as can be seen in Fig. 2, which is a characteristic they share with the YO$_6$ layers in 3R-type Cu$_2$YO$_2$. Thus, the higher proportion of the 3R type in the Cu$_2$YO$_2$ powder derived from the LYH–Cu$_2$O mixed powder can be attributed to the influence of the layered structure of LYH. We consider that the formation of Cu$_2$YO$_2$ from the LYH–Cu$_2$O mixed powder occurs through a topotactic reaction maintaining the layered structure of LYH. As observed by TG–DTA, the layered structure of LYH was maintained until the final decomposition into Y$_2$O$_3$ at around 500°C. In the coexistence of Cu$_2$O, Cu$^+$ ions can be intercalated between the layers of the dehydrated LYH, leading to direct formation of Cu$_2$YO$_2$. This reaction should preferentially provide 3R-type Cu$_2$YO$_2$ due to the similarity of its stacking pattern to that of LYH. Similar topotactic solid-state reactions from a layered hydroxide into a complex oxide with a similar layered structure have been reported for some systems. Itahara et al. reported, for example, that textured ceramics of Ca$_3$Co$_4$O$_9$ with layers of edge-sharing Co$_6$ octahedra can be fabricated by a topotactic reaction conducted using layered $\beta$-Co(OH)$_2$ as a raw material.$^{19}$

Because the intercalation of Cu$^+$ ions and the final decomposition of LYH into Y$_2$O$_3$ are competitive during heating, the heating rate has a great influence on the product. We found that the high heating rate of 25 °C/min employed in this study was important to prevent the formation of Y$_2$O$_3$ during heating: a product mainly composed of Y$_2$O$_3$ and Cu$_2$O was obtained when the heating rate was much lower (for example, 3 °C/min). The holding temperature is also important. As shown in Fig. 5(a), Cu$_2$Y$_2$O$_5$ is formed when the holding temperature is 700 or 800°C. This is because the Cu$^+$ ion in Cu$_2$YO$_2$ formed by the topotactic reaction or in unreacted Cu$_2$O was oxidized into Cu$^{2+}$ during heating, although the heat treatment was performed under a N$_2$ environment. It is known that commercially available pure N$_2$ often contains a small amount of O$_2$ impurities (on the order of 10$^{-4}$–10$^{-5}$ atm).$^{20}$ The thermal decomposition of LYH also generates a small amount of O$_2$ as shown by Eq. (3). Because the equilibrium oxygen partial pressure of the Cu$_2$O–CuO system below 800°C is lower than 10$^{-3}$ atm,$^{21}$ Cu$^+$ is oxidized by the O$_2$ impurities, leading to the formation of Cu$_2$Y$_2$O$_5$. For these reasons, a sufficiently high heating rate and holding temperature are necessary for achieving a high yield of Cu$_2$YO$_2$ from the LYH–Cu$_2$O mixture.

In this study, the Cu$_2$YO$_2$ powder prepared using LYH also contained a non-negligible amount of the 2H-type polymorph. This may be due to the large size of the LYH plates, which is a drawback for the progress of the topotactic conversion into Cu$_2$YO$_2$. During the topotactic conversion through the intercalation of Cu$^+$, a part of the LYH plate simultaneously crystallizes into Y$_2$O$_3$. The remaining Cu$_2$O is oxidized by O$_2$ generated by the pyrolysis of LYH and then reacted with Y$_2$O$_3$ to form Cu$_2$Y$_2$O$_5$ during heating. The resulting Cu$_2$Y$_2$O$_5$ phase is then reduced again to form mainly 2H-type Cu$_2$YO$_2$ during holding at 900°C. We believe that selective synthesis of the single-phase 3R-type Cu$_2$YO$_2$ can be achieved with careful control of both the morphology of LYH and the heating conditions. These efforts are now under way.

4. Conclusions

In this study, we have demonstrated that a powder of Cu$_2$YO$_2$ can be directly synthesized by heating LYH–Cu$_2$O mixed powder at 900°C for 4 h. Rietveld refinement of the XRD profile showed that the sample prepared from LYH–Cu$_2$O mixed powder contained the 3R phase as the major content, whereas the sample prepared by the conventional route via Cu$_2$Y$_2$O$_5$ contains a larger content of the 2H type. Based on our structural analysis, a topotactic reaction maintaining the layered structure of LYH was proposed as the main formation route for Cu$_2$YO$_2$ in the LYH–Cu$_2$O mixed powder, which enabled faster formation of Cu$_2$YO$_2$ compared to the conventional solid-state reaction using Y$_2$O$_3$ as the yttrium source. The results presented here indicate that hydroxides with a layered crystal structure are effective raw materials for facile synthesis of delafossite-type ternary oxides.

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