Preparation of Heteronuclear $La_2Cu(C_4O_4)_4(H_2O)_{16}\cdot 2H_2O$ Complex and its Thermal Decomposition into Single Phase La_2CuO_4

Youichi Shimamoto, Hiromichi Aono,* Nobuyuki Kondo,† Masato Kurihara,†† Masatomi Sakamoto,†† and Yoshihiko Sadaoka*
Department of Materials Science and Engineering, Faculty of Engineering, Ehime University, Matsuyama 790-8577
†*Graduate Program of Human Sensing and Functional Sensor Engineering, Graduate School of Science and Engineering, Yamagata University, Yamagata 990-8560*
††*Department of Material and Biological Chemistry, Faculty of Science, Yamagata University, Yamagata 990-8560*

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A heteronuclear complex, $La_2Cu(C_4O_4)_4(H_2O)_{16}\cdot 2H_2O$, was synthesized and its thermal decomposition products were studied. Results of chemical analysis and TGA agreed with theoretical values for $La_2Cu(C_4O_4)_4(H_2O)_{16}\cdot 2H_2O$ complex. The La_2CuO_4 single phase having ca. 100 nm in crystal size was obtained by the thermal decomposition at 700 °C for 1 h.

Polymetallic oxides containing lanthanoid (Ln) and a transition metal (M), such as $LnMO_3$ and Ln_2MO_4, have been investigated for their useful functional properties and for many applications.

We have reported that homogeneous heterometallic oxides with relatively high specific surface areas were formed by the thermal decomposition of heteronuclear Ln:M = 1:1 complexes, such as $Ln[M(CN)_6]\cdot nH_2O$ and $LnM(dhbaen)(NO_3)\cdot nH_2O$ (dhbaen is *N*,*N*′-bis(3-hydroxysalicylidene)ethylenediamine).[1–5] In the case of the LaCu complex, we have synthesized $CuLa(dhbaen)(NO_3)\cdot nH_2O$ complex and it was decomposed to La_2CuO_4 and CuO.[3] The single-phase Ln_2MO_x (Ln:M = 2:1) have not been synthesized by the thermal decomposition of the heteronuclear complexes at all. To obtain the Ln_2MO_4 single phase, the complexes containing the Ln:M = 2:1 ratio are needed for the thermal decomposition method. However, the Ln_2M complexes have been rarely reported up to now. Bouayad et al. synthesized $La_2Cu(C_4O_4)_4(H_2O)_{16}\cdot 2H_2O$ complex and described its crystal structure.[6] Although we tried to prepare the La_2Cu complex according to the reported method,[6] we could not obtain the single-phase La_2Cu complex for the precursor of La_2CuO_4. In this paper, we investigated the synthesis method of $La_2Cu(C_4O_4)_4(H_2O)_{16}\cdot 2H_2O$ complex and its thermal decomposition products.

Aqueous solutions (total 200 mL) of $LaCl_3\cdot 7H_2O$ (6 mmol, 100 mL) and $CuCl_2\cdot 2H_2O$ (4 mmol 100 mL) were mixed together with continuous stirring, and then an ammonia solution was added to control the pH of the solution. This pH control was not described in Ref. 6. An aqueous solution (2 mmol, 300 mL) of squaric acid ($C_4H_2O_4$:3,4-dihydroxy-3-cyclobutene-1,2-dione) was added to this solution with continuous stirring. The resulting precipitate was collected by suction filtration, washed with water, ethanol and diethyl ether, before drying in ambient air at room temperature.

C, H, and N elemental analyses were carried out at the Instrumental Analysis Center of Chemistry, Faculty of Science, Tohoku University, Japan. The contents of La and Cu were determined by chelatometric titration method. The thermal decomposition behavior of the heteronuclear complex was examined by simultaneous thermogravimetric and differential thermal analyses (TG/DTA, Seiko Instrument TG/DTA 32), performed at a heating rate of 5 °C/min in flowing *syn*-air. The heat-treated samples were prepared by holding the complex at various temperatures in ambient air for 1 h. X-ray diffraction (XRD, Cu Kα radiation, Rint 2000, Rigaku, sweep rate 2°/min. 40 kV, 20 mA) analysis was used to study the phases present in the decomposition products. The surface microstructure was observed using a surface electron microscope (SEM, Model JSM-5310), JEOL.

Initially, we tried to prepare $La_2Cu(C_4O_4)_4(H_2O)_{16}\cdot 2H_2O$ complex according to the preparation method of Bouayad et al.[6] However, the obtained powder was a mixture of white and yellow crystals. The results of the elemental analysis for the collected white crystals were La: 32.3 wt %, Cu: 0%, C: 17.0%, and H: 3.1%, which suggested the formation of a La complex, $La_2(C_4O_4)_3(H_2O)_n$, $n = 13$. In this case, the pH value was around 2.2 for the mixed chloride solution in the preparation process. The pure yellow powder was obtained when the pH value was controlled at 3.0–9.0 by the addition of ammonia. The excessive addition of ammonia allowed the formation of copper hydroxide. For this yellow powder, the results of the elemental analyses for La, 24.5% (24.9%); Cu, 5.6% (5.7%); C, 17.2 % (17.3 %); and H, 3.2% (3.3%) were in good agreement with the estimated theoretical values in brackets for $La_2Cu(C_4O_4)_4(H_2O)_{16}\cdot 2H_2O$ complex. In pH = 3.0–9.0 range, the single-phase La_2Cu complex was obtained even if the La:Cu ratio of the starting chlorides was changed to another ratio such as 1:1 and 3:1.

Figure 1 shows the TG curve for the La_2Cu complex. The result of measurement showed that dehydration started below 50 °C and a gentle slope was observed around 200 °C. The weight percentage at 200 °C was ca. 72 wt % which agreed with the theoretical value of 70.9 %, due to the loss of 18 molecules of crystallization water. The TG curve showed an abrupt weight loss at 300–500 °C followed by a slower loss that ended at about 650 °C, which can be attributed to the decomposition of the ligand. The weight percentage of 36.8 wt % measured in the last plateau range was in good agreement with the theoretical value of 36.4 wt %, calculated by assuming the formation of La_2CuO_4 from the complex. From these results, the complex was also confirmed to be $La_2Cu(C_4O_4)_4(H_2O)_{16}\cdot 2H_2O$.

Figure 2 shows the XRD powder diffraction patterns for the products of the decomposition of the La_2Cu complex at various temperatures. The main peaks in the XRD patterns was assignable to La_2CO_5 and CuO with a broad "halo" for the sample decomposed at 500 °C. For the heated sample at 600 °C, the in-

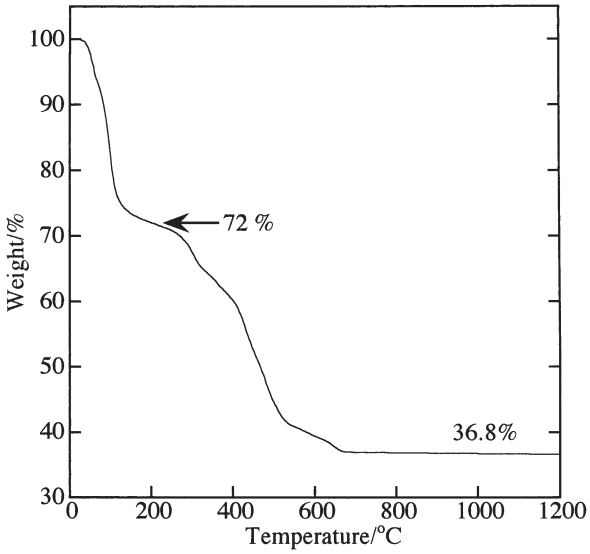

Figure 1. TGA result of $La_2Cu(C_4O_4)_4(H_2O)_{16}\cdot 2H_2O$.

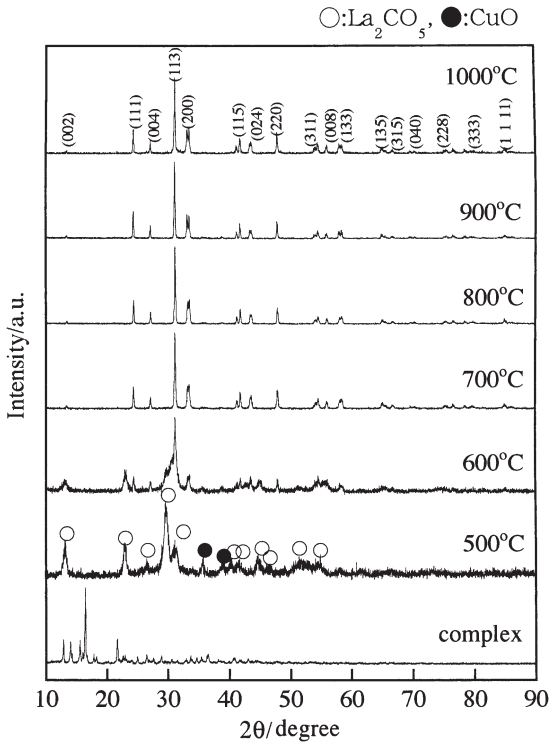

Figure 2. XRD results of La_2Cu complex decomposed at various temperature for 1 h.

tensity of the La_2CuO_4 peaks was higher than those of La_2CO_5 and CuO. The broad "halo" disappeared and only the La_2CuO_4 peaks were observed for the sample obtained at 700 °C. It was confirmed that the full-width-at-half-maximum (FWHM) of all the La_2CuO_4 peaks decreased with an increase in the decomposition temperature because of crystal growth. The XRD peaks for La_2CuO_4 were indexed with an orthorhombic phase. The lattice constants were $a = 5.362$ nm, $b = 5.406$ nm, and $c = 13.155$ nm for the sample sintered at 800 °C.

It is one of paramount importance to characterize the microstructure of the obtained powders, given that it is well known

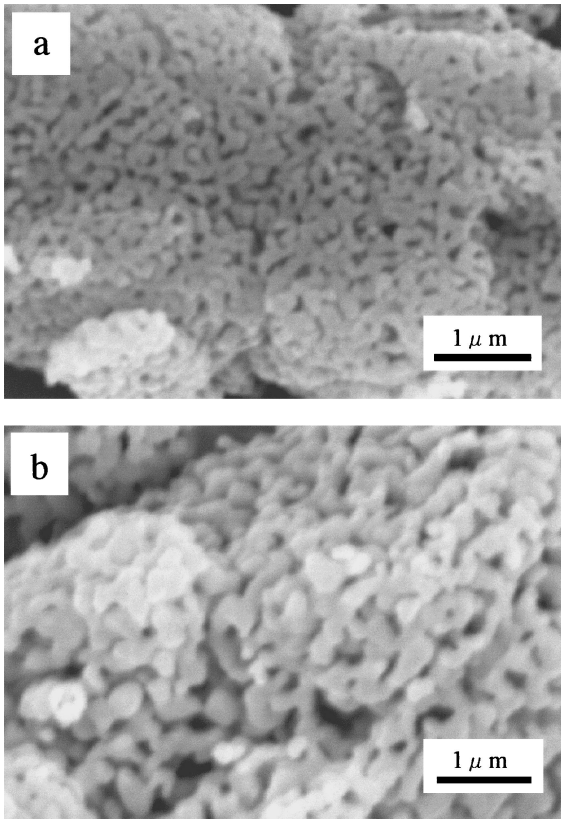

Figure 3. SEM photos for the La_2Cu complex decomposed at (a) 700 °C and (b) 800 °C.

that many oxide properties such as the catalytic activity and the gas sensing characteristics are strongly influenced by particle size. Figure 3 shows SEM photographs for La_2CuO_4 obtained by thermal decompostition of complex at 700 and 800 °C for 1 h. The uniform particles were obtained by the thermal decomposition. The average particle size was estimated to be about 100 and 200 nm for the samples decomposed at 700 °C (Figure 3a), and 800 °C (Figure 3b), respectively.

In conclusion, a heteronuclear complex, $La_2Cu(C_4O_4)_4(H_2O)_{16}\cdot 2H_2O$, was synthesized and its thermal decomposition products were analyzed. The La_2CuO_4 single phase having a crystal size of 100 nm was obtained by heating at 700 °C. Further work will be performed for the preparation of another combination of Ln_2M complexes, their decomposition products, and their applications.

References

1 Y. Sadaoka, K. Watanabe, Y. Sakai, and M. Sakamoto, *J. Alloys Compd.*, **224**, 194 (1995).
2 Y. Sadaoka, E. Traversa, and M. Sakamoto, *J. Mater. Chem.*, **6**, 1355 (1996).
3 M. Sakamoto, T. Igoshi, M. Sato, S. Matsushima, M. Miwa, H. Aono, and Y. Sadaoka, *J. Alloys Compd.*, **260**, 59 (1997).
4 H. Aono, M. Tsuzaki, A. Kawaura, M. Sakamoto, E. Traversa, and Y. Sadaoka, *J. Am. Ceram. Soc.*, **84**, 969 (2001).
5 H. Aono, M. Sakamoto, and Y. Sadaoka, *J. Ceram. Soc. Jpn.*, **109**, 419 (2001).
6 A. Bouayad, C. Brouca-Cabarrecq, and J.-C. Trombe, *Inorg. Chim. Acta*, **195**, 193 (1992).

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