Thermally Decomposed Products of Heteronuclear Complexes,
CuRE(dhbaen) (NO$_3$)$_m$(dmso)$_n$(H$_2$O)$_p$ (RE = Sm, Eu, Gd, Tb, Dy, Y, Ho, Er, Tm, Tb, and Lu)

Hiromichi AONO, Masatomi SAKAMOTO* and Yoshihiko SADAOKA

Department of Materials Science and Engineering, Faculty of Engineering, Ehime University, 3, Bunkyo-cho, Matsuyama-shi 790-8577
*Department of Material and Biological Chemistry, Faculty of Science, Yamagata University, 1-4-12, Koshirakawa-cho, Yamagata-shi 990-8560

The thermally decomposed products of the CuRE(dhbaen) (NO$_3$)$_m$(dmso)$_n$(H$_2$O)$_p$ complex were investigated by differential thermal analysis (TGA), X-ray diffraction patterns (XRD), energy dispersive X-ray analysis (EDX), and X-ray photoelectron spectroscopy (XPS). A mixed phase of RE$_2$O$_2$SO$_4$ and CuO was formed at a low temperature. The particle size of CuO in the mixed phase was estimated to be 30-90 nm by XRD. When the ionic radius of RE$^{3+}$ ion is small, the RE$_2$O$_2$SO$_4$ phase decomposed and formed a heterometallic 

1. Introduction
Heterometallic oxides such as perovskite-type materials and copper rare earth oxides have been investigated for determining their functional electrical properties and applications in fuel cells, catalysts, materials for gas sensors, and high $T_c$ superconductors. Heterometallic oxide powders having a controlled stoichiometry and microstructure are required for these applications.

In our previous studies, RE-T-O$_2$ heterometallic oxides containing rare earth (RE=Ln and Y) and transition (T) metals (RE : T = 1:1) were prepared by the thermal decomposition of heteronuclear complexes such as RE(T(CN)$_6$)$_2$. The crystal structure of the decomposed products is strongly influenced by the ionic size of the RE$^{3+}$ ions. For the thermal decomposition of heteronuclear complexes such as RE(T(CN)$_6$)$_2$, the RE$_2$O$_2$SO$_4$ phase decomposed and formed a heterometallic RE$_2$Cu$_2$O$_5$ at 850-1100°C. It appears that one dmso directly interacted with the RE ion (RE-O=S(-CH$_3$)$_2$) for the complex and the RE-O=S bond remained as RE$_2$O$_2$SO$_4$ after the decomposition. CuO in the mixed phase did not interact with SO$_4$ which was confirmed by XPS.

2. Experimental
2.1 Preparation of heteronuclear complexes
The mononuclear copper (II) complex has been synthesized by the reaction of copper (II) acetate monohydrate with $N,N'$-bis(3-hydroxysalicylidene)-ethylenediamine (H$_2$dhaen) in methanol. The following procedure was employed to synthesize the heteronuclear Cu-RE complex. A methanolic solution (10 cm$^3$) of lithium hydroxide monohydrate (4 mmol) was added to a suspension of the mononuclear copper (II) complex (4 mmol) in methanol (80 cm$^3$) which yielded a transparent solution. RE(III) nitrate hydrate (4 mmol) in methanol (5-10 cm$^3$) was then added. After warming the mixture with stirring for 2 h, the precipitated CuRE(dhbaen)(NO$_3$)(H$_2$O)$_p$ crystals were collected by suction filtration, washed with methanol and diethyl ether and then dried under reduced pressure. After drying under reduced pressure, this complex was dissolved in 20-70 ml dimethylsulfoxide (dmso) and the insoluble impurities were then filtered. Large quantities of diethyl ether (3-6 times greater than the solution) were slowly added to the solution and the precipitated CuRE(dhbaen)(NO$_3$)(dmso)$_m$(H$_2$O)$_p$ crystals were collected by suction filtration, washed with methanol and diethyl ether. The synthetic procedure is similar to a method in the literature. Elemental analyses of C, H, N, and S in the complex were carried out at the Instrumental Analysis Center of Chemistry, Faculty of Science, Tohoku University, Japan. The elemental analyses of RE and Cu were performed using an X-ray fluorescence (XRF) analyzer along with a Seiko Instrument analyzer (SEA2010).

2.2 Measurements
The thermal decomposition behavior was examined by TGA analysis using a Seiko Instrument analyzer (TG/DTA32) and performed at a heating rate of 5°C/min in syn-
Thermally Decomposed Products of Heteronuclear Complexes, CuRE(dhbaen)(NO$_3$)$_m$(dmso)$_n$(H$_2$O)$_n$

(RE = Sm, Eu, Gd, Tb, Dy, Y, Ho, Er, Tm, Tb, and Lu)

thesis-air. The heat-treated samples were prepared by holding at various temperatures in ambient air for 1 h after raising the temperature at the rate of 5°C/min. In order to characterize the decomposition products, the X-ray diffraction patterns (Cu Kα) were recorded (Rint 2000, Rigaku, sweep rates of 1 and 2°/min. 40 kV, 20 mA). The surface structures were characterized by energy dispersive X-ray analysis (EDX) (Link ISIS300, Oxford Instruments) and X-ray photoelectron spectroscopy (XPS) using a Perkin-Elmer XPS1600E (Mg Kα). All binding energies for XPS were obtained by referring to the C1s photoemission line spectrum at 284.5 eV. For the surface analysis, the pressed powders at a pressure of 1 × 10$^8$ Pa were heated once at 800°C in air to remove most of the contaminants. The powders were cooled in air and transferred to a high-vacuum chamber (<3 × 10$^{-7}$ Pa). To compare the XPS results for the sulfates, samples of anhydrous Eu$_2$(SO$_4$)$_3$ and CuSO$_4$ were obtained by heating Eu$_2$(SO$_4$)$_3$·10H$_2$O at 500°C and drying CuSO$_4$ at 160°C for 1 h, respectively. Eu$_2$O$_2$(SO$_4$) was also obtained by heating Eu$_2$(SO$_4$)$_3$·10H$_2$O at 1000°C for 1 h.

3. Results and discussion

3.1 Analyses of CuRE(dhbaen)(NO$_3$)$_m$(H$_2$O)$_n$ complexes

The existence of dmso in the CuRE(dhbaen)(NO$_3$)$_m$(dmso)$_n$(H$_2$O)$_n$ complex was confirmed by the chemical analysis. The m and n values were in the ranges of 2–4 and 1–4, respectively. These values did not depend on the element number or ionic radius of RE$^{3+}$. The RE/Cu elemental ratio determined from XRF was 1.00 ± 0.10 for each examined complex. From the results of these elemental analyses, it was confirmed that the Cu:RE = 1:1 complexes containing dmso, i.e., the CuRE(dhbaen)(NO$_3$)$_m$(dmso)$_n$(H$_2$O)$_n$ complexes, were obtained by the treatment with dmso.

3.2 Decomposed products

In the case of the CuRE(dhbaen)(NO$_3$)$_m$(H$_2$O)$_n$ complexes untreated with dmso, the thermal decomposition products were clearly controlled by the ionic radius of the RE$^{3+}$ ions. The XRD results for the decomposed samples at 900°C are shown in Fig. 1. The orthorhombic RE$_2$Cu$_2$O$_5$ single phase was obtained for RE = Tb, Dy, Y, Ho, Er, Tm, Tb, and Lu (JCPDS files; 330511 and 330458). In this phase, the RE$^{3+}$ ion has a sixfold coordination number (C.N. = 6). The observed peak positions were regularly shifted to a higher value in 2θ with decreasing ionic size of RE$^{3+}$. For RE = Gd, most of the peaks could be assigned to the tetragonal Gd$_2$CuO$_4$ (JCPDS file; 240422) (C.N. = 8) and some peaks due to CuO were detected. The formation of RE$_2$Cu$_2$O$_5$ could not be confirmed for the decomposed complex when the ionic radius for the RE$^{3+}$ ion was greater than Gd$^{3+}$. The signals due to CuO were also detected even for the complexes decomposed at 1000°C for RE = La, Eu, and Gd. In the case of RE = La, the orthorhombic La$_6$Cu$_2$O$_4$ phase (JCPDS files; 300487 and 380709) having C.N. = 9 was obtained. The obtained mixed rare earth oxides were categorized into two groups; the composite phase of RE$_2$Cu$_2$O$_5$–CuO for RE = La, Eu, and Gd, and the single RE$_2$Cu$_2$O$_5$ phase with RE = Tb, Dy, Y, Ho, Er, Tm, Tb, and Lu. The crystal structure of the mixed oxides was controlled by the coordination number of the RE$^{3+}$ ion due to the RE$^{3+}$/O$^{2-}$ ratio. A more detailed discussion has been reported in a previous paper.15)

Figure 2 shows the TGA results observed in synthesis-air (5°C/min) for the CuEr(dhbaen)(NO$_3$)$_m$(dmso)$_n$(H$_2$O)$_n$ complex (the m and n values were estimated by chemical analysis) which was obtained by the treatment of the CuEr(dhbaen)(NO$_3$)(H$_2$O)$_n$ complex with dmso. The dehydration started at room temperature and a plateau was observed in the temperature range of 60–150°C. This weight loss was caused by that of crystallized water molecules. Weight loss due to the exothermal decomposition of the ligand (confirmed by DTA/DSC) occurred by further heating at 200–280°C. Further heating induced a further gradual decrease in weight. The 36.6% weight at around 800°C was very close to 37.3% which was estimated as the Er$_2$O$_2$SO$_4$ formation. A small weight loss was observed at about 900°C. The final weight (33.0%) agreed with the calculated value (32.5%) for Er$_2$Cu$_2$O$_5$. In the case of other RE samples having a small ionic radius, the temperature for the small weight loss decreased with a decrease in the ionic radius of the RE$^{3+}$ ion.
Figure 3 shows the XRD results for the decomposed CuEr(dhbaen)(NO$_3$)$_m$(H$_2$O)$_n$ complex. The XRD pattern of the complex decomposed at 1000°C and higher temperatures was consistent with that of the CuEr(dhbaen)(NO$_3$)(H$_2$O)$_n$ complex decomposed at 900°C, i.e., the Er$_2$Cu$_2$O$_5$ single phase as shown in Fig. 1. For the complex decomposed at 900°C and lower temperatures, the XRD patterns are completely different from that of Er$_2$Cu$_2$O$_5$. When the complex decomposed at 1000°C or higher temperatures, the signals assigned to CuO disappeared and the Er$_2$Cu$_2$O$_5$ phase was obtained. The temperature of the XRD pattern change between 900°C and 1000°C agreed with that around 940°C for the weight loss of the TG result in Fig. 2, corresponding to the decomposition of Er-oxysulfate. The products decomposed and reacted with CuO at this temperature forming Er$_2$Cu$_2$O$_5$. The main product formed in the range of 400–900°C may be Er$_2$O$_4$SO$_4$ and the crystal size increased with the decomposition temperature. The crystal size growth was also confirmed by SEM and TEM observations. The average sizes of the CuO crystallites evaluated from the broad XRD line using Scherrer’s equation for the signals at 35.50 (hkl: -111, 002) and 38.80 degrees (hkl: 111, 200) in 2θ are shown in Fig. 3. For the decomposed Er-Cu-complex, the average sizes of the CuO crystallities increased with the decomposition temperature, i.e., 30 nm for 600°C, 67 nm for 700°C, 75 nm for 800°C, and 84 nm for 900°C. For the other products, broad XRD peaks were also observed for the complex decomposed at a low temperature. We tried to clarify the distribution of CuO especially on the surface, and its particle size by SEM–Auger for the CuSm(dhbaen)(NO$_3$)$_m$(H$_2$O)$_n$ sample decomposed at 800°C. However, no useful results could be detected by the charge up phenomena since the products are insulators. The surface structure was also examined by SEM–EDX. The observed particle size is lower than 100 nm. The examined surface is shown in Fig. 4. The spots of bright (A) and dark (B) positions were analyzed to compare the distributions of two phases. The atomic ratios of O : S : Cu : Sm at the spot areas indicated by A and B were 67.6 : 5.8 : 11.7 : 14.9 and 70.4 : 3.7 : 13.1 : 12.8, respectively. Based on the wide-range analysis, the atomic ratios became 69.0 : 5.4 : 13.1 : 12.5. The atomic ratios were similar (not departed) for all the spots based on the measurements. In the measurement for A and B spots, the detected area and depth are 0.5 (μm)$^2$ and 0.6 μm, respectively. It is concluded that the particle size of CuO is on the order of several tens of nm and a bigger particle composed of CuO was not formed, especially on the surfaces.

Figure 5 shows the XRD results of the dmso-treated complex decomposed at 900°C. The existence of CuO was confirmed for all the examined products. Furthermore, it was confirmed that the lattice parameters (tenorite: monoclinic, $a=0.4684$ nm, $b=0.3420$ nm, $c=0.5129$ nm) of the CuO are...
Thermally Decomposed Products of Heteronuclear Complexes, CuRE(dhbaen)(NO3)(dmso)m(H2O)n
(RE=Sm, Eu, Gd, Tb, Dy, Y, Ho, Er, Tm, Tb, and Lu)

hardly influenced by the ionic radius of the RE3+ ions. Except for the signals assigned to CuO, the detectable peak positions are regularly shifted to higher degree side with the decrease in ionic size of RE3+. This is expected for the formations of rare earth oxysulfides RE2O2SO4 and/or sulfates RE2(SO4)3. It is known that rare earth oxysulfates are formed by oxysulfide oxidation of the RE3+. The oxysulfates were also observed during the thermal decomposition of the rare earth sulfates.25 In general, the temperatures at which the decomposition of the anhydrous rare-earth sulfates to the rare-earth oxysulfates becomes noticeable lie in the range from 855 to 946°C.26 The crystal parameters of lanthanum oxysulfate have been examined by Fahey.27 He prepared the lanthanum oxysulfate from hydrated lanthanum sulfate by heating in the air at 1000°C for 6 h. The refined parameters for La2O2SO4 are as follows: Space group: I222, No. 23, Z = 2, cell dimensions a = 0.4286 nm, b = 0.4194 nm, and c = 1.372 nm. Some crystal parameters of the rare earth oxysulfates have been reported, but regularity in the RE species could not be interpreted. Recently, the crystal parameters for the lanthanum oxysulfate were reported by Zhukov and his coworkers; Space group: C2/c, No. 15, Z = 4, cell dimensions a = 1.4342 nm, b = 0.4283 nm, c = 0.8385 nm, α = 90.0°, β = 107.0°, and γ = 90.0°.28 The observed peaks, except for the peaks due to CuO, can be assigned to rare earth oxysulfate and the estimated crystal parameters as space group I222 are shown in Fig. 6 along with some results that (dref, berf, and cref) appeared in the JCPSD card and ICSD collection. The estimated parameters for the examined samples from the complexes suggest good regularity with the correlation between a parameters and the ionic radii of RE3+.

Figure 7 shows the XRD results of the complexes decomposed at 1100°C. The thermal stability of the rare earth oxysulfate is influenced by the ionic radii of RE3+. For RE = Sm, Eu, Gd, and Tb, the product decomposing at 1100°C was a mixture of RE2O2SO4 and CuO. For the samples having a small RE3+ ionic radius, a single-structure-type RE2Cu2O5 was obtained for RE = Y, Ho, Er, Tm, Tb and Lu. In the case of the Dy system, a mixture of Dy2O2SO4, Dy2Cu2O5 and CuO was formed because of the boundary between the two groups. From the XRD and TGA results, it appears that the thermal stability in air for the rare earth sulfates decreases along with the decrease in the ionic radii of RE3+.

3.3 Surface analysis by XPS

We examined the composite of the RE2Cu2SO4 phase with CuO for the samples sintered at low temperatures by XRD analysis. To confirm the interaction between the sulfate and metal ions (RE and Cu) on the surface, the XPS measurements were conducted for the decomposed samples (within 3 or 4 layers from the top surface; depth detectable by XPS).

Figure 8 shows the XPS results of Cu2p for the decomposed samples at 900°C of (a) CuEu(dhbaen)(NO3)(H2O)n and (b) CuEu(dhbaen)(NO3)(dmso)m(H2O)n. The Cu2p peak for CuSO4 is also shown in the figure. It is confirmed by XRD, as shown in Fig. 1, that the decomposed product of the CuEu(dhbaen)(NO3)(H2O)n complex was a composite with Eu2CuO4 and CuO. For this composite of oxides, Cu2p3/2 and Cu2p1/2 bands were observed at 932.9 and 952.7 eV (binding energy (BE) difference was 19.8 eV) and additionally, the shake-up peaks due to the paramagnetic property of Cu2+ of CuO were observed with peak positions at around 942 and 962 eV. In the case of CuEu(dhbaen)(NO3)(dmso)m(H2O)n, Eu2O2SO4 and CuO were confirmed by XRD (Fig. 5) as the decomposed products at 900°C. The XPS peaks of the Cu2p3/2 and Cu2p1/2 were observed at around 932.9 and 952.8 eV (BE difference was 19.9 eV) with the shake-up peaks of CuO. On the other hand, it is confirmed that the BE of Cu2p3/2 for CuSO4 was 935.4 eV.27 If a higher BE is observed for the products from the complex treated with dmso, the existence of an electronic interaction between Cu and S (charge transfer from Cu to S via oxygen) is suggested for these samples. It is confirmed that the interaction between Cu and sulfate did not occur for the samples from the dmso-treated complexes. Figure 9 shows the XPS results of Eu4d for the decomposed products at 900°C. The peak positions of 136.1 eV for the product from the dmso-containing complex is similar to the
135.9 eV band for Eu$_2$O$_2$SO$_4$. The O1s spectrum for the products from the complexes is shown in Fig. 10. The O1s peaks for the composite with CuO and Eu$_2$CuO$_4$ observed at 528.6 and 531.3 eV are assignable to the lattice oxygen and adsorbed oxygen, respectively.\(^{17,27}\) For the Eu$_2$O$_2$SO$_4$-CuO composite, the O1s peaks are observed at 528.9 and 531.8 eV. This peak position of high BE agreed with those for Eu$_2$O$_2$SO$_4$ and Eu$_2$(SO$_4$)$_3$. The higher BE value (531.6-531.8 eV) is due to the O1s signal of the SO$_4$ group. In the case of the S2p signal, the BE causing the sulfide and sulfate should be observed at around 162 and 169 eV, respectively. For the products from the complex containing dmso, the signals of S2p causing sulfates were detected at 168.9 eV (S2p$_{3/2}$) and at 170.1 eV S2p$_{1/2}$) as shown in Fig. 11. Additionally, a broad signal with a peak position at
165.9 eV was detected for the decomposed product from the dmso-treated EuCu-complex and Eu₂O₂SO₄, while for Eu₂(SO₄)₂, only the signals of S2p₁/₂ and S2p₃/₂ were observed at 168.9 and 169.9 eV, respectively. At this stage, although the signal at around 166 eV for the decomposed EuCu-complex could not be identified, this is due to the existence of Eu₂O₂SO₄. It was reported that one dmso in the heteronuclear YCu-complex treated with dmso interacted with the RE ion (RE-O=S(CH₃)₂).20 From the XRD results, it could not be formed by the thermal decomposition of the RE₂CuO₄ and CuO were obtained for the small E³⁺ ions (Tb, Dy, Y, Ho, Er, Tm, Yb, and Lu) and large ions (La, Nd, Sm, Eu and Gd), respectively. For the complex treated with dmso, the thermally decomposed products consisted of a mixture of RE₂O₂SO₄ and CuO. For the complex treated with dmso, the RE₂Cu₂O₅ single phase and the composite treated with dmso, the thermally decomposed products contained one dmso which interacted with the RE ion. RE–O=S bonding remained which resulted in the formation of RE₂O₂SO₄ at a low temperature. The XPS results showed that the sulfate and sulfide did not interact with the CuO particles.

Acknowledgment The present work was supported by a Grant-in-Aid (Nos. 10045045 and 10650811) from the Ministry of Education, Science and Culture.

References

26) ICSD Collection Code 66823.