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

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多核錯体 $\text{CuRE}(\text{dhbaen})(\text{NO}_3)_m(\text{dmsO})_n(\text{H}_2\text{O})_n$, ($\text{RE} = \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Y}, \text{Ho}, \text{Er}, \text{Tm}, \text{Tb}, \text{Lu}$) の熱分解生成物

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The thermally decomposed products of the $\text{CuRE}(\text{dhbaen})(\text{NO}_3)_m(\text{dmsO})_n(\text{H}_2\text{O})_n$ 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 $\text{RE}_2\text{O}_2\text{SO}_4$ 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 $\text{RE}_2\text{O}_2\text{SO}_4$ phase decomposed and formed a heterometallic $\text{RE}_2\text{Cu}_2\text{O}_5$ at 850–1100°C. It appears that one dmsO directly interacted with the RE ion ($\text{RE}-\text{O}=\text{S}(-\text{CH}_3)_2$) for the complex and the $\text{RE}-\text{O}=\text{S}$ bond remained as $\text{RE}_2\text{O}_2\text{SO}_4$ after the decomposition. CuO in the mixed phase did not interact with $-\text{SO}_4$ which was confirmed by XPS.

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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,¹⁾ catalysts,²⁾ materials for gas sensors,^{3)–7)} and high T_c superconductors.⁸⁾ Heterometallic oxide powders having a controlled stoichiometry and microstructure are required for these applications.

In our previous studies, $\text{RE}-\text{T}-\text{O}_x$ heterometallic oxides containing rare earth ($\text{RE} = \text{Ln}$ and Y) and transition (T) metals ($\text{RE}:\text{T}=1:1$) were prepared by the thermal decomposition of heteronuclear complexes such as $\text{RE}[\text{T}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ and $\text{RE}-\text{T}(\text{dhbaen})(\text{NO}_3)_m(\text{H}_2\text{O})_n$, where dhbaen is the N,N' -bis(3-hydroxysalicylidene)-ethylenediamine.^{9)–19)} The heterometallic oxides obtained by this method have a very fine particle size with a homogeneous elemental distribution on the particle surface.¹⁷⁾ The crystal structure of the decomposed products is strongly influenced by the ionic size of the RE^{3+} ions. For the thermal decomposition of the $\text{RE}-\text{Cu}(\text{dhbaen})(\text{NO}_3)_m(\text{H}_2\text{O})_n$ complexes, the homogeneous $\text{RE}_2\text{Cu}_2\text{O}_5$ and the composite with RE_2CuO_4 and CuO were obtained for the small RE^{3+} ions (Tb, Dy, Y, Ho, Er, Tm, Yb, and Lu) and large ions (La, Nd, Sm, Eu and Gd), respectively.¹⁵⁾ Casellato et al. reported that the heteronuclear $\text{Y}-\text{Cu}$ complex treated with dimethylsulfoxide (dmsO) was prepared and its crystal structure was determined as a tetranuclear complex $[\text{CuY}(\text{dhbaen})(\text{NO}_3)(\text{dmsO})]_2(\text{dmsO})_2(\text{H}_2\text{O})_n$.²⁰⁾ However, the thermal decomposition process for dmsO containing the $\text{RE}-\text{T}$ complexes has not been investigated until now.

In this study, we synthesized new heteronuclear complexes, $\text{CuRE}(\text{dhbaen})(\text{NO}_3)_m(\text{dmsO})_n(\text{H}_2\text{O})_n$, ($\text{RE} = \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Y}, \text{Ho}, \text{Er}, \text{Tm}, \text{Tb}, \text{and Lu}$) and investigated their thermal decomposition processes.

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_4dhbaen) in methanol.^{20),21)} The following procedure was employed to synthesize the heteronuclear $\text{Cu}-\text{RE}$ complex. A methanolic solution (10 cm^3) of lithium hydroxide monohydrate (8 mmol) was added to a suspension of the mononuclear copper (II) complex (4 mmol) in methanol (80 cm^3) which yielded a transparent solution. $\text{RE}(\text{III})$ nitrate hydrate (4 mmol) in methanol (5–10 cm^3) was then added. After warming the mixture with stirring for 2 h, the precipitated $\text{CuRE}(\text{dhbaen})(\text{NO}_3)_m(\text{H}_2\text{O})_n$ 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 into the solution and the precipitated $\text{CuRE}(\text{dhbaen})(\text{NO}_3)_m(\text{dmsO})_n(\text{H}_2\text{O})_n$ crystals were filtered, and washed with methanol and diethyl ether. The synthetic procedure is similar to a method in the literature.²⁰⁾ 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-

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 $5^\circ\text{C}/\text{min}$. In order to characterize the decomposition products, the X-ray diffraction patterns ($\text{Cu K}\alpha$) were recorded (Rint 2000, Rigaku, sweep rates of 1 and $2^\circ/\text{min}$, 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 ($\text{Mg K}\alpha$). All binding energies for XPS were obtained by referring to the C1s photoemission line spectrum at 284.5 eV .²² For the surface analysis, the pressed powders at a pressure of $1 \times 10^8\text{ Pa}$ 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 ($<3 \times 10^{-7}\text{ Pa}$). To compare the XPS results for the sulfates, samples of anhydrous $\text{Eu}_2(\text{SO}_4)_3$ and CuSO_4 were obtained by heating $\text{Eu}_2(\text{SO}_4)_3 \cdot 10\text{H}_2\text{O}$ at 500°C and drying CuSO_4 at 160°C for 1 h, respectively. $\text{Eu}_2\text{O}_2(\text{SO}_4)$ was also obtained by heating $\text{Eu}_2(\text{SO}_4)_3 \cdot 10\text{H}_2\text{O}$ at 1000°C for 1 h.

3. Results and discussion

3.1 Analyses of $\text{CuRE}(\text{dhbaen})(\text{NO}_3)_m(\text{dmsO})_n(\text{H}_2\text{O})_n$ complexes

The existence of dmsO in the $\text{CuRE}(\text{dhbaen})(\text{NO}_3)_m(\text{dmsO})_n(\text{H}_2\text{O})_n$ 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 $\text{Cu}:\text{RE}=1:1$ complexes containing dmsO, i.e., the $\text{CuRE}(\text{dhbaen})(\text{NO}_3)_m(\text{dmsO})_n(\text{H}_2\text{O})_n$ complexes, were obtained by the treatment with dmsO.

3.2 Decomposed products

In the case of the $\text{CuRE}(\text{dhbaen})(\text{NO}_3)_m(\text{H}_2\text{O})_n$ 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 $\text{RE}_2\text{Cu}_2\text{O}_5$ 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_2CuO_4 (JCPDS file; 240422) ($C.N.=8$) and some peaks due to CuO were detected. The formation of $\text{RE}_2\text{Cu}_2\text{O}_5$ 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_2CuO_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 $\text{RE}_2\text{CuO}_4\text{--CuO}$ for RE = La, Eu, and Gd, and the single $\text{RE}_2\text{Cu}_2\text{O}_5$ 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 $\text{RE}^{3+}/\text{O}^{2-}$ ratio. A more detailed discussion has been reported in a previous paper.¹⁵

Figure 2 shows the TGA results observed in synthesis-air ($5^\circ\text{C}/\text{min}$) for the $\text{CuEr}(\text{dhbaen})(\text{NO}_3)_m(\text{dmsO})_3(\text{H}_2\text{O})_3$ complex (the m and n values were estimated by chemical analysis) which was obtained by the treatment of the $\text{CuEr}(\text{dhbaen})(\text{NO}_3)_m(\text{H}_2\text{O})_n$ complex with dmsO. The dehydra-

Fig. 1. XRD results of $\text{CuRE}(\text{dhbaen})(\text{NO}_3)_m(\text{H}_2\text{O})_n$ complexes decomposed at 900°C . The RE species are shown in the figure.

Fig. 2. TGA results of the $\text{CuEr}(\text{dhbaen})(\text{NO}_3)_m(\text{dmsO})_3(\text{H}_2\text{O})_3$ complexes.

tion started at room temperature and a plateau was observed in the temperature range of $60\text{--}150^\circ\text{C}$. 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 $200\text{--}280^\circ\text{C}$. 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 $\text{Er}_2\text{O}_2\text{SO}_4$ formation. A small weight loss was observed at about 900°C . The final weight (33.0%) agreed with the calculated value (32.5%) for $\text{Er}_2\text{Cu}_2\text{O}_5$. 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 $\text{CuEr}(\text{dhbaen})(\text{NO}_3)_m(\text{dmsO})_m(\text{H}_2\text{O})_n$ complex. The XRD pattern of the complex decomposed at 1000°C and higher temperatures was consistent with that of the $\text{CuEr}(\text{dhbaen})(\text{NO}_3)_m(\text{H}_2\text{O})_n$ complex decomposed at 900°C, i.e., the $\text{Er}_2\text{Cu}_2\text{O}_5$ 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 $\text{Er}_2\text{Cu}_2\text{O}_5$. When the complex decomposed at 1000°C or higher temperatures, the signals assigned to CuO disappeared and the $\text{Er}_2\text{Cu}_2\text{O}_5$ 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 $\text{Er}_2\text{Cu}_2\text{O}_5$. The main product formed in the range of 400–900°C may be $\text{Er}_2\text{O}_2\text{SO}_4$ 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 crystallites 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 $\text{CuSm}(\text{dhbaen})(\text{NO}_3)_m(\text{dmsO})_m(\text{H}_2\text{O})_n$ 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 $0.5(\mu\text{m})^2$ and $0.6\mu\text{m}$, 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, $a = 0.4684\text{ nm}$, $b = 0.3420\text{ nm}$, $c = 0.5129\text{ nm}$) of the CuO are

Fig. 4. SEM–EDX results for the $\text{CuSm}(\text{dhbaen})(\text{NO}_3)_m(\text{dmsO})_m(\text{H}_2\text{O})_n$ complex decomposed at 800°C.

Fig. 3. XRD results for decomposed $\text{CuEr}(\text{dhbaen})(\text{NO}_3)_m(\text{dmsO})_m(\text{H}_2\text{O})_n$ complex. The decomposition temperatures in °C are shown in the figure.

Fig. 5. XRD results of $\text{CuRE}(\text{dhbaen})(\text{NO}_3)_m(\text{dmsO})_m(\text{H}_2\text{O})_n$ complex decomposed at 900°C. The RE species are shown in the figure.

hardly influenced by the ionic radius of the RE^{3+} 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 RE^{3+} . This is expected for the formations of rare earth oxysulfates $\text{RE}_2\text{O}_2\text{SO}_4$ and/or sulfates $\text{RE}_2(\text{SO}_4)_3$. It is known that rare earth oxysulfates are formed by oxysulfide oxidation of the RE^{3+} . The oxysulfates were also observed during the thermal decomposition of the rare earth sulfates.²³⁾ 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.²⁴⁾ The crystal parameters of lanthanum oxysulfate have been examined by Fahey.²⁵⁾ He prepared the lanthanum oxysulfate from hydrated lanthanum sulfate by heating in the air at 1000°C for 6 h. The refined parameters for $\text{La}_2\text{O}_2\text{SO}_4$ are as follows; Space group: I_{222} , No. 23, 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, $\alpha = 90.0^\circ$, $\beta = 107.0^\circ$, and $\gamma = 90.0^\circ$.²⁶⁾ 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 I_{222} are shown in Fig. 6 along with some results that (a_{ref} , b_{ref} , and c_{ref}) appeared in the JCPDS 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 RE^{3+} .

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 RE^{3+} . For RE = Sm, Eu, Gd, and Tb, the product decomposing at 1100°C was a mixture of $\text{RE}_2\text{O}_2\text{SO}_4$ and CuO. For the samples having a small RE^{3+} ionic radius, a single-structure-type $\text{RE}_2\text{Cu}_2\text{O}_5$ was obtained for RE = Y, Ho, Er, Tm, Tb and Lu. In the case of the Dy system, a mixture of $\text{Dy}_2\text{O}_2\text{SO}_4$, $\text{Dy}_2\text{Cu}_2\text{O}_5$ 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 RE^{3+} .

3.3 Surface analysis by XPS

We examined the composite of the $\text{RE}_2\text{Cu}_2\text{SO}_4$ 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) $\text{CuEu}(\text{dhbaen})(\text{NO}_3)(\text{H}_2\text{O})_n$ and (b) $\text{CuEu}(\text{dhbaen})(\text{NO}_3)(\text{dmsO})_m(\text{H}_2\text{O})_n$. The Cu2p peak for CuSO_4 is also shown in the figure. It is confirmed by XRD, as shown in Fig. 1, that the decomposed product of the $\text{CuEu}(\text{dhbaen})(\text{NO}_3) \cdot n\text{H}_2\text{O}$ complex was a composite with Eu_2CuO_4 and CuO. For this composite of oxides, Cu2p_{3/2} and Cu2p_{1/2} 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 Cu^{2+} of CuO were observed with peak positions at around 942 and 962 eV. In the case of $\text{CuEu}(\text{dhbaen})(\text{NO}_3)(\text{dmsO})_m(\text{H}_2\text{O})_n$, $\text{Eu}_2\text{O}_2\text{SO}_4$ and CuO were confirmed by XRD (Fig. 5) as the decomposed products at 900°C. The XPS peaks of the Cu2p_{3/2} and Cu2p_{1/2} were observed at around 932.9 and 952.8 eV (BE difference was

Fig. 6. Relationship between the ionic radius of RE^{3+} and the lattice parameters for the $\text{RE}_2\text{O}_2\text{SO}_4$ phase obtained by the thermal decomposition $\text{CuRE}(\text{dhbaen})(\text{NO}_3)(\text{dmsO})_m(\text{H}_2\text{O})_n$ at 900°C.

Fig. 7. XRD results for $\text{CuRE}(\text{dhbaen})(\text{NO}_3)(\text{dmsO})_m(\text{H}_2\text{O})_n$ complex decomposed at 1100°C. The RE species are shown in the figure.

19.9 eV) with the shake-up peaks of CuO. On the other hand, it is confirmed that the BE of Cu2p_{3/2} for CuSO_4 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 peaks for $\text{Eu}_2\text{O}_2\text{SO}_4$ and $\text{Eu}_2(\text{SO}_4)_3$ are also shown in the figure. The BE of Eu4d was 134.9 and 136.1 eV for the decomposed products of the $\text{CuEu}(\text{dhbaen})(\text{NO}_3)(\text{H}_2\text{O})_n$ complex and $\text{CuEu}(\text{dhbaen})(\text{NO}_3)(\text{dmsO})_m(\text{H}_2\text{O})_n$, respectively. The peak position of 136.1 eV for the product from the dmsO-containing complex is similar to the

Fig. 8. XPS results of Cu_{2p} for (a) the decomposed CuRE (dhbaen)(NO₃)(H₂O)_n (at 900°C) and (b) CuEu(dhbaen)(NO₃)(dmsom)(H₂O)_n complexes decomposed at 900°C together with that for CuSO₄.

Fig. 10. XPS results of O_{1s} for (a) the decomposed CuRE (dhbaen)(NO₃)(H₂O)_n (at 900°C) and (b) CuEu(dhbaen)(NO₃)(dmsom)(H₂O)_n complexes decomposed at 900°C together with those for Eu₂O₂SO₄ and Eu₂(SO₄)₃.

Fig. 9. XPS results of Eu_{4d} for (a) the decomposed CuRE (dhbaen)(NO₃)(H₂O)_n (at 900°C) and (b) CuEu(dhbaen)(NO₃)(dmsom)(H₂O)_n complexes decomposed at 900°C together with those for Eu₂O₂SO₄ and Eu₂(SO₄)₃.

Fig. 11. XPS results of S_{2p} for (b) CuEu(dhbaen)(NO₃)(dmsom)(H₂O)_n complex decomposed at 900°C together with those for Eu₂O₂SO₄ and Eu₂(SO₄)₃.

135.9 eV band for Eu₂O₂SO₄. The O_{1s} spectrum for the products from the complexes is shown in Fig. 10. The O_{1s} peaks for the composite with CuO and Eu₂CuO₄ observed at 528.6 and 531.3 eV are assignable to the lattice oxygen and adsorbed oxygen, respectively.^{17),27)} For the Eu₂O₂SO₄-CuO composite, the O_{1s} peaks are observed at 528.9 and 531.8 eV. This peak position of high BE agreed with those

for Eu₂O₂SO₄ and Eu₂(SO₄)₃. The higher BE value (531.6–531.8 eV) is due to the O_{1s} signal of the SO₄ group. In the case of the S_{2p} 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 dmsom, the signals of S_{2p} causing sulfates were detected at 168.9 eV (S_{2p}_{3/2}) and at 170.1 eV S_{2p}_{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 $\text{Eu}_2\text{O}_2\text{SO}_4$, while for $\text{Eu}_2(\text{SO}_4)_3$, only the signals of $\text{S}2\text{p}_{3/2}$ and $\text{S}2\text{p}_{1/2}$ were observed at 168.8 eV 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 $\text{Eu}_2\text{O}_2\text{SO}_4$. It was reported that one dmsO in the heteronuclear YCu -complex treated with dmsO interacted with the RE ion ($\text{RE}-\text{O}=\text{S}(\text{CH}_3)_2$).²⁰⁾ From the XRD results, it appears that one dmsO which interacted with the RE ion directly decomposed and remained as the $\text{RE}-\text{SO}_4$ bond, resulting in $\text{RE}_2\text{O}_2\text{SO}_4$ at a low temperature. The XPS results showed that the sulfate and sulfide did not interact with the CuO particles.

4. Conclusion

The thermal decomposition products from the heteronuclear $\text{RE}-\text{Cu}$ complexes were examined by TGA, XRD, SEM-EDX and XPS. The thermally decomposed products of the complexes were strongly influenced by the pretreatment with and without dmsO. For the complex untreated with dmsO, the $\text{RE}_2\text{Cu}_2\text{O}_5$ single phase and the composite with RE_2CuO_4 and CuO were obtained for the small RE^{3+} 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 $\text{RE}_2\text{O}_2\text{SO}_4$ and CuO . For the complex treated with dmsO, one dmsO directly interacted with the RE ion ($\text{RE}-\text{O}=\text{S}(\text{CH}_3)_2$) and did not interact with the Cu ion. $\text{RE}-\text{O}=\text{S}$ bonding remained which resulted in the formation of rare earth oxysulfates during the oxidative decomposition. The particle size of CuO was estimated to be on the order of several tens of nm. It appears that the composite with the homogeneously dispersed finer CuO particles is a preferable functional material for removing hydrogen sulfide under ambient conditions, since CuO is a reactive oxide with organic compounds containing sulfur and hydrogen sulfide.²⁷⁾ While the composite with RE_2CuO_4 and CuO could not be formed by the thermal decomposition of the corresponding complex for $\text{RE}=\text{Tb}-\text{Lu}$ and Y, the existence of CuO was confirmed for the decomposed products of the complexes treated with dmsO. We propose a new route to prepare CuO dispersed composite materials from the heteronuclear complex.

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