

ing down with ice bath, and quenched with 8 N HCl (8 ml) solution. After removal of solvents, the residue was washed with ethyl ether, providing light-yellow solid, acetic acid of 2a-c containing NaCl. (Z)-2-(2-Aminothiazolo[3,2-b][1,2,4]-triazol-5-yl)-2-(methoxyimino)acetic acid: 2.58 g, 97% (exclude NaCl), mp. 180°C (dec.); <sup>1</sup>H NMR (60 MHz, DMSO-d<sub>6</sub>) δ 4.01 (s, 3, OCH<sub>3</sub>), 6.29 (bs, 2), 7.56 (s, 1). To phosphorus pentachloride (660 mg, 3.2 mmol) in dried CH<sub>2</sub>Cl<sub>2</sub> (10 ml) at -20°C was added crude acetic acid of 2a-c (2.0 mmol). The mixture was stirred at -20°C for 2 h. 7-ACA (522 mg, 1.92 mmol) in dried CH<sub>2</sub>Cl<sub>2</sub> (5 ml) and bis(trimethylsilyl)acetamide (BSA, 1.8 ml, 7.28 mmol) was added dropwise, and the mixture was stirred at -20°C for 50 min and at 0°C for 2 h. The mixture was poured into cold water. Solid was removed by filtration and the resulting liquid was extracted with EtOAc. Drying (Na<sub>2</sub>SO<sub>4</sub>) and evaporation of organic layer afforded a yellow solid 1a-c. 1a: 284 mg, 29%, mp. 149-151°C; <sup>1</sup>H NMR (60 MHz, DMSO-d<sub>6</sub>) δ 2.15 (s, 3, CH<sub>3</sub>), 3.43-3.62 (m, 2, CH<sub>2</sub>), 4.15 (s, 3, OCH<sub>3</sub>), 4.78-5.25 (m, 4, NHCHCH + CH<sub>2</sub>), 5.83 (dd, 2, J = 8.2, 4.8 Hz, CH<sub>2</sub>), 7.15 (s, 2, NH<sub>2</sub>), 8.74 (s, 1, CH), 9.28 (d, 1, J = 8.0 Hz, NH). 1b: 35%, mp. 158-161°C; <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>) δ 2.07 (s, 3, CH<sub>3</sub>), 3.41 (d, 1, J = 18.2 Hz, CH<sub>2</sub>), 3.62 (d, 1, J = 18.2 Hz, CH<sub>2</sub>), 4.14 (s, 3, OCH<sub>3</sub>), 4.84 (d, 1, J = 13.2 Hz, CH<sub>2</sub>), 5.09 (d, 1, J = 13.2 Hz, CH<sub>2</sub>), 5.13 (d, 1, J = 4.8 Hz, CH), 5.85 (dd, 1, J = 8.0, 4.8 Hz, CH<sub>2</sub>), 7.57 (s, 1, CH), 8.21 (s, 1, CH), 9.82 (d, 1, J = 8.0 Hz, NH). 1c: 12%; <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>) 2.10 (s, 3, CH<sub>3</sub>), 2.53 (s, 3, CH<sub>3</sub>), 3.44 (d, 1, J = 18.5 Hz, CH<sub>2</sub>), 3.65 (d, 1, J = 18.5 Hz, CH<sub>2</sub>), 4.09 (s, 3, OCH<sub>3</sub>), 4.96 (d, 1, J = 13.4 Hz, CH<sub>2</sub>), 5.12 (d, 1, J = 4.8 Hz, CH), 5.20 (d, 1, J = 13.4 Hz, CH<sub>2</sub>), 5.95 (dd, 1, J = 9.0, 4.8 Hz, CH<sub>2</sub>), 7.35 (s,

1, CH), 7.78 (d, 1, J = 9.0 Hz, NH).

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## Formation Process of a Red Phosphor, Y<sub>2</sub>O<sub>2</sub>S:Eu<sup>3+</sup>

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Yttrium oxysulfide incorporated with europium has been prepared by direct heating the mixture of Y<sub>2</sub>O<sub>3</sub>, Eu<sub>2</sub>O<sub>3</sub>, NaOH (or Na<sub>2</sub>CO<sub>3</sub>), and S. The reaction of the mixture at low temperatures and treatment at higher temperatures are studied. The formation of Y<sub>2</sub>O<sub>2</sub>S is completed at lower temperature (ca. 500°C) and incorporation of Eu<sup>3+</sup> into Y<sub>2</sub>O<sub>2</sub>S lattice proceeds at higher temperature (above 1000°C) along with crystal growth. Small amount of the unknown phase considered to be Y<sub>2</sub>O<sub>2</sub>S<sub>2</sub> is formed along with Y<sub>2</sub>O<sub>2</sub>S in the temperature range from 400°C to 460°C.

### Introduction

Yttrium oxysulfide incorporated with europium, Y<sub>2</sub>O<sub>2</sub>S:Eu<sup>3+</sup>, is widely used as a red phosphor for color monitors because of its bright luminescence and high energy efficiency.<sup>1-6</sup> It is usually prepared from yttrium oxide coprecipitated with europium oxide.<sup>7</sup> In the present work the reaction of the mixture of Y<sub>2</sub>O<sub>3</sub> (neat or 3~4 at % Eu<sub>2</sub>O<sub>3</sub> added),

Na<sub>2</sub>CO<sub>3</sub> (or NaOH), and S has been studied in a wide range of temperatures in order to understand the formation and particle growing processes of the host material, Y<sub>2</sub>O<sub>2</sub>S, and incorporation process of Eu<sup>3+</sup> into it.

### Experimental

Europium-incorporated yttrium oxysulfide phosphors,

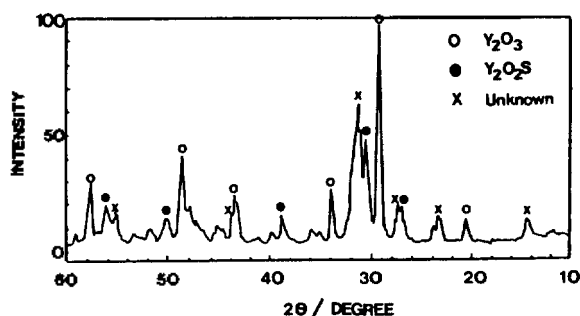


Figure 1. XRD pattern of the reaction product from the mixture.  $Y_2O_3:Na_2CO_3:S = 1:3:17.6$  at  $400^\circ C$  for 1.5 hours.

$Y_2O_2S:Eu^{3+}$ , were prepared directly by heating the mixtures of  $Y_2O_3$  (99.99%, Aldrich),  $Eu_2O_3$  (99.99%, Aldrich),  $Na_2CO_3$  (or NaOH, E. P. Kanto Chemical Co.), and sulfur (E. P. Kanto Chemical Co.) of certain mole ratios at desired temperatures. A flux of  $Na_2S_x$  ( $x = 1-5$ , melting temperature ranges from  $200^\circ C$  to  $950^\circ C$  depending on  $x$ )<sup>8</sup> is produced from the reaction mixture at around  $270-350^\circ C$ .<sup>9</sup> The yield of  $Y_2O_2S$  was monitored with an X-ray powder diffractometer (XRD, Rigaku, D/MAX-3A, Cu  $K\alpha$ ). The XRD peak intensities of  $Y_2O_2S$  and  $Y_2O_3$  were measured to estimate the fraction of  $Y_2O_2S$  in the product. The particle shapes and sizes of the product were observed with a scanning electron microscope (SEM, Akashi, ISI-SX-30E). Excitation and emission spectra were obtained by the fluorescence spectrometer composed of a Xe arc lamp (120W), monochromators (Oriel, 1200 lines/mm), a PM tube (Hamamatsu R928, type S20), and a microcomputer. Monochromator grating was driven by a stepper motor (16 steps per nm). The spectra were corrected for the system responses.

## Results and Discussion

**Formation of Oxysulfides.** Formation process of  $Y_2O_2S$  from  $Y_2O_3$  using  $Na_2S_x$  flux was investigated by XRD and SEM techniques. The main peaks of  $Y_2O_3$  and  $Y_2O_2S$  in the XRD pattern are at  $2\theta = 29.3^\circ$  and  $30.6^\circ$ , respectively. XRD patterns of the reaction products prepared by heating the mixture of  $Y_2O_3:Na_2CO_3:S = 1:3:17.6$  in the temperature range from  $350^\circ C$  to  $500^\circ C$  for 1.5 hours were taken. There are only peaks of  $Y_2O_3$  and no peaks of  $Y_2O_2S$  in the spectra of the product reacted at  $375^\circ C$ . This means that  $Y_2O_2S$  has not been produced yet. Intensities of the peaks corresponding to  $Y_2O_3$  increase as the reaction temperature increases above  $375^\circ C$ . XRD spectra of the reaction products obtained above ca.  $500^\circ C$  show only peaks of  $Y_2O_2S$  and no peaks of  $Y_2O_3$ , which implies that the formation of  $Y_2O_2S$  from  $Y_2O_3$  using  $Na_2S_x$  flux is completed below  $500^\circ C$ . XRD spectra of the product obtained between  $400^\circ C$  and  $460^\circ C$  show unidentified peaks ( $d = 3.80, 3.26, 2.86, 2.84$  Å) in addition to those of  $Y_2O_2S$  and  $Y_2O_3$  (Figure 1). The color of the unknown phase is mustard-yellow. The peak intensities of  $Y_2O_3$  ( $2\theta = 29.3^\circ$ ),  $Y_2O_2S$  ( $2\theta = 30.3^\circ$ ), and unknown phase ( $2\theta = 31.3^\circ$ ) are plotted against reaction temperature (Figure 2). As the reaction temperature increases, the peak intensities of  $Y_2O_3$  decrease and those of  $Y_2O_2S$  increase. The intensities of the unidentified peaks increase at first and then decrease. Only peaks of  $Y_2O_2S$  are detected above  $460^\circ C$ .

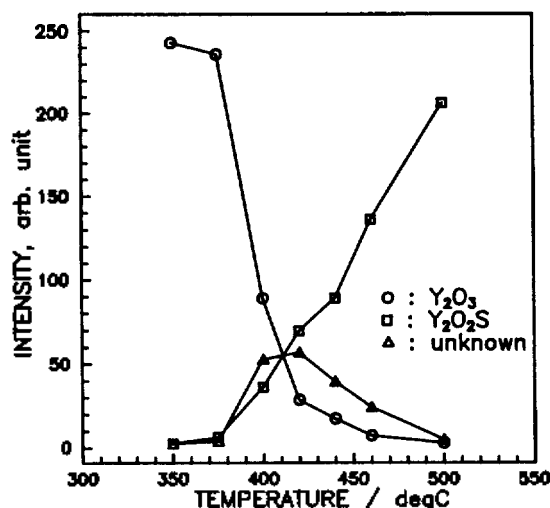


Figure 2. XRD peak intensities of  $Y_2O_3$  ( $2\theta = 29.3^\circ$ ),  $Y_2O_2S$  ( $2\theta = 30.3^\circ$ ), and unknown phase ( $2\theta = 31.3^\circ$ ) vs. reaction temperature.

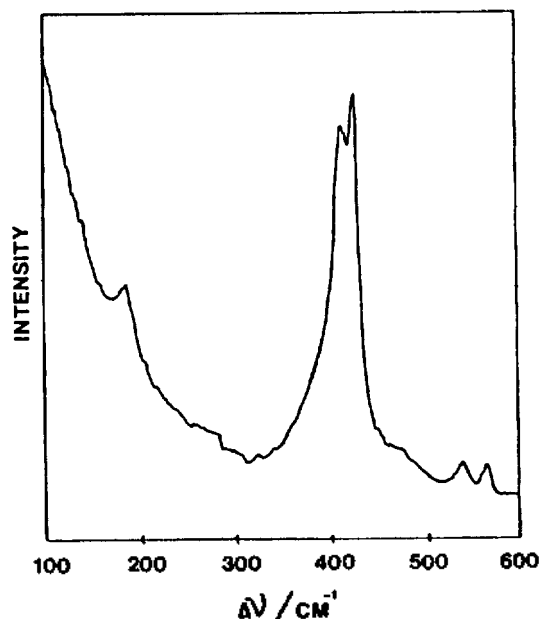
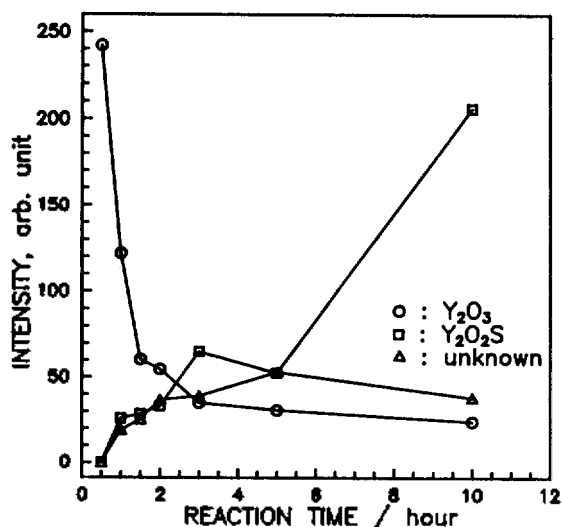


Figure 3. Raman spectrum of  $Y_2O_2S_2$ .

Since separation of the unknown phase was unsuccessful, an attempt was made to identify it in the product obtained at  $400^\circ C$  by various methods. Elemental analysis gave the weight percentages of Y, O, S, C, and Na to be 68.73, 18.0, 12.5, 0.94, and 0.31, respectively. Sodium and carbon can be regarded as minor contaminants from the flux. From this it is concluded that the unknown phase is composed of Y, O, and S. When the reaction product is dissolved in dilute HCl solution,  $H_2S$  is generated and the solution becomes slightly turbid. When the solution is extracted with carbon disulfide,  $CS_2$  layer becomes yellow which indicates the presence of free sulfur. This implies the presence of the  $S_2^{2-}$  in the product. The reaction product gives a doublet at 414 and 427  $cm^{-1}$  in Raman spectrum (Figure 3), which is similar to the S-S vibrational mode of  $LaS_2$ <sup>10</sup>. From these analyses the unknown phase in the reaction product is considered to be  $Y_2O_2S_2$ .



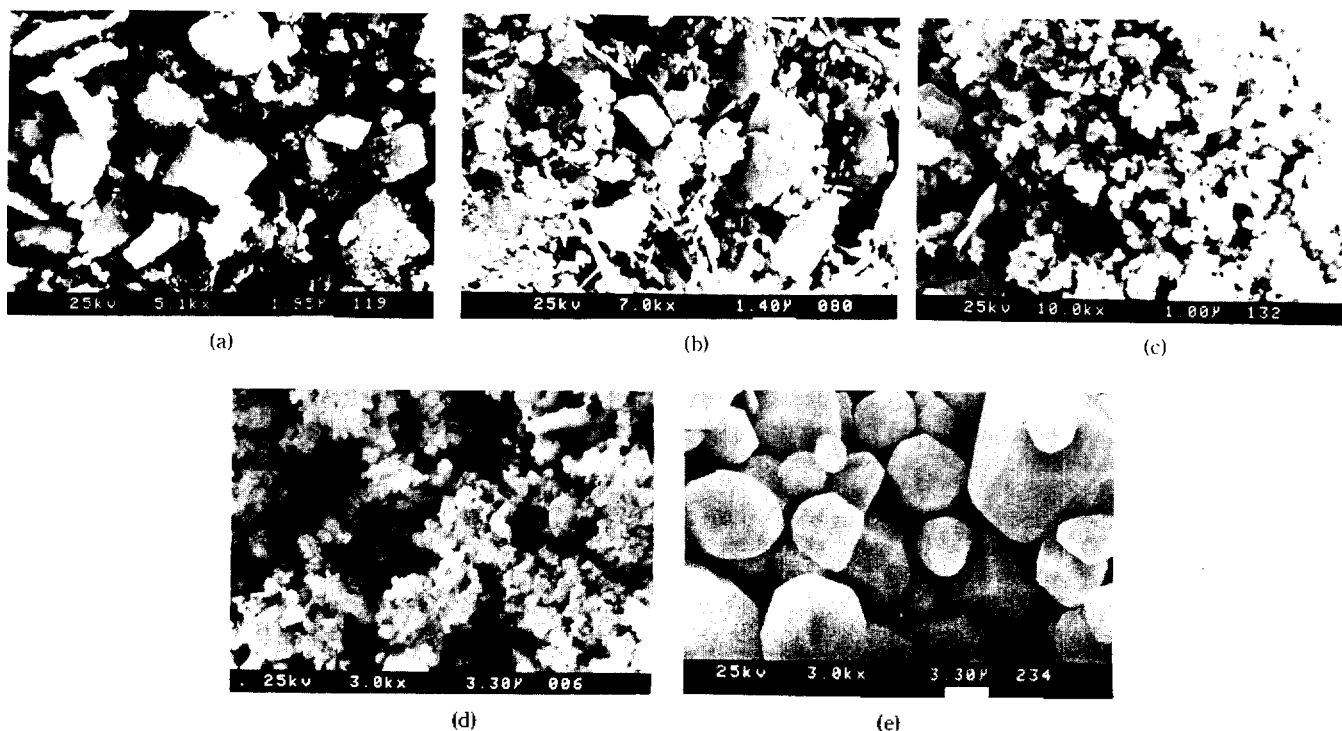
**Figure 4.** XRD peak intensities of  $Y_2O_3$ ,  $Y_2O_2S$ , and  $Y_2O_2S_2$  vs. reaction time.

Also the nature of the unknown phase was studied by fluorescence measurements using europium as a probe. Fluorescence intensity of the reaction product obtained by heating at 400°C the mixture of  $Y_2O_3$ : $Eu_2O_3$ : $Na_2CO_3$ :S at the ratio of 1:0.04:3:17.6 is weak. The fluorescence spectrum shows not only peaks of  $Eu^{3+}$  in  $Y_2O_2S$  and in  $Y_2O_3$  but also a weak broad band at 650 nm which could not be accounted for.

In order to clarify whether  $Y_2O_2S_2$  is formed concurrently with  $Y_2O_2S$  from  $Y_2O_3$ , or by further reaction of  $Y_2O_2S$  with excess (or unreacted yet) sulfur, XRD patterns and Raman spectra have been examined for the following reaction products. Instead of  $Y_2O_3$ , yttrium oxysulfide was reacted with

sulfur in the flux at 400°C for 1.5 hours with two different compositions of the reaction mixture,  $Y_2O_2S$ : $Na_2CO_3$ :S = 1:3:17.6 and 1:3:52.8, respectively. Neither products shows yellow tint, unknown peaks in XRD pattern, nor Raman peaks, which is indicative of the absence of  $Y_2O_2S_2$ . Consequently,  $Y_2O_2S_2$  is not produced from the reaction of  $Y_2O_2S$  and S. To examine if  $Y_2O_2S_2$  is decomposed to  $Y_2O_2S$  even at low temperatures, reaction time was varied in series at 400°C for the fixed ratio of  $Y_2O_3$ : $Na_2CO_3$ :S = 1:3:17.6. Peak intensities of XRD for  $Y_2O_3$ ,  $Y_2O_2S$ , and  $Y_2O_2S_2$  in the reaction product were plotted against the reaction time (Figure 4). As the reaction time is prolonged, the amount of  $Y_2O_2S$  increases, that of  $Y_2O_2S_2$  increases at first then decreases, and that of unreacted  $Y_2O_3$  is reduced. These result in the following conclusions: Both  $Y_2O_2S$  and  $Y_2O_2S_2$  are formed at the reaction temperature between 400°C and 460°C. The dioxidisulfide decomposes to  $Y_2O_2S$  above 500°C, and partially decomposes to  $Y_2O_3$  even at 400°C with prolonged reaction time. Only  $Y_2O_2S$  is obtained above 500°C. Dioxidisulfide,  $Y_2O_2S_2$ , is not formed from  $Y_2O_2S$  even at 400°C.

Particle size and shapes were observed with a scanning electron microscope in order to study the formation and particle growing processes of  $Y_2O_2S$ . Scanning electron micrographs of the products at various reaction temperatures are shown in Figure 5. The particle sizes of the  $Y_2O_2S$  (Figure 5c) produced at low temperatures are much smaller than those of the reactant  $Y_2O_3$  (Figure 5a). The needle-shaped particles in the product between 400°C and 460°C (Figure 5b) are considered to be  $Y_2O_2S_2$ . Smaller particle sizes of  $Y_2O_2S$  obtained at intermediate temperatures can be explained as follows: The reaction of  $Y_2O_3$  with S starts at the surface of  $Y_2O_3$ . Once  $Y_2O_2S$  is formed at the surface of  $Y_2O_3$ , it could be cracked due to the difference in densities and formed  $Y_2O_2S$  are peeled off. Therefore, sulfur is considered to



**Figure 5.** Scanning electron micrographs of the reaction products at various temperatures: (a) 350°C, (b) 400°C, (c) 500°C, (d) 1000°C, (e) 1200°C.

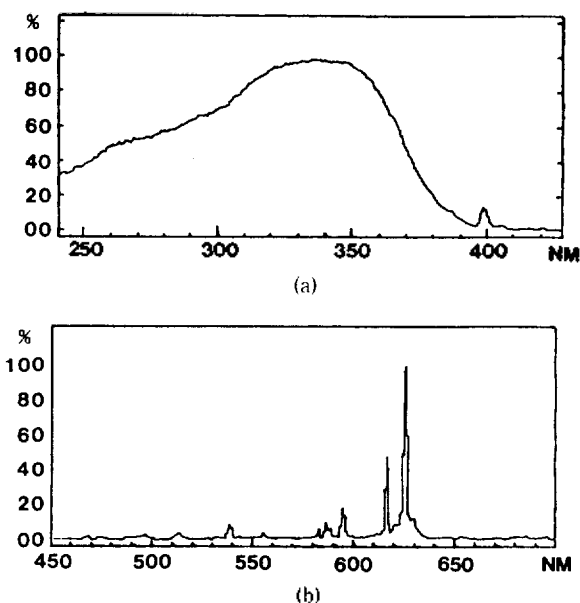


Figure 6. (a) Excitation and (b) fluorescence spectra of  $Eu^{3+}$  in  $Y_2O_2S$ .

react always with new  $Y_2O_3$  surfaces, and in this process diffusion of S into  $Y_2O_3$  particle is unnecessary. Particle growing of  $Y_2O_2S$  is observed above  $1000^\circ C$  (Figure 5d). At high temperatures above  $1000^\circ C$ , small particles may dissolve and recrystallize on the larger ones, leading to growth of particles. The sizes of  $Y_2O_2S$  particles heated at  $1200^\circ C$  are larger and their surfaces become smoother (Figure 5e).

**Incorporation of  $Eu^{3+}$  into  $Y_2O_2S$  and its Fluorescence Intensity.** Excitation and fluorescence spectra of  $Eu^{3+}$  in  $Y_2O_2S$  are shown in Figure 6. When  $Y_2O_2S$  particles are small, i.e., when the reaction temperature is low (below  $1000^\circ C$ ), the fluorescence intensity is very weak. This could be explained by incomplete incorporation. Fluorescence intensity is high when the sample is prepared above  $1000^\circ C$ , where the particles are larger (Figure 7a). Europium can be incorporated into  $Y_2O_2S$  not only by diffusion from the  $Y_2O_2S$  surface but also by recrystallization from the melt on  $Y_2O_2S$  crystals. In order to study the effects of each process, the fluorescence intensities of  $Y_2O_2S:Eu^{3+}$  (3%) prepared by two different routes were examined. Firstly, fluorescence intensities of  $Eu^{3+}$  of the reaction products by heating the mixtures of  $Y_2O_3$  (containing 3%  $Eu_2O_3$ ):NaOH:S = 1:7.9:19.7 at temperatures from  $500^\circ C$  to  $1200^\circ C$  for 0.5 to 2 hours were measured (Figure 7a). In this case,  $Eu^{3+}$  is incorporated into  $Y_2O_2S$  structure both by diffusion and by recrystallization from the melt. Secondly,  $Eu^{3+}$  is incorporated into larger grains of  $Y_2O_2S$  by heating the mixtures of  $Y_2O_2S:Eu_2O_3:NaOH:S = 1:0.03:7.9:19.7$  at temperatures from  $500^\circ C$  to  $1200^\circ C$  for 0.5 to 2 hours. The larger grains of  $Y_2O_2S$  were prepared by heating mixture of  $Y_2O_3:NaOH:S = 1:7.9:19.7$  at  $1200^\circ C$  for 2 hours. Fluorescence intensity of  $Eu^{3+}$  of each product is shown in Figure 7b. In this case incorporation of  $Eu^{3+}$  into  $Y_2O_2S$  occurs only by diffusion from the  $Y_2O_2S$  surface unless the solubility of  $Y_2O_2S$  in the flux is appreciable, since larger grains of  $Y_2O_2S$  are used.

Both  $Y_2O_2S:Eu^{3+}$  prepared at  $1200^\circ C$  for 2 hours from  $Y_2O_3$  and from  $Y_2O_2S$  were etched in 1M HCl solution to dif-

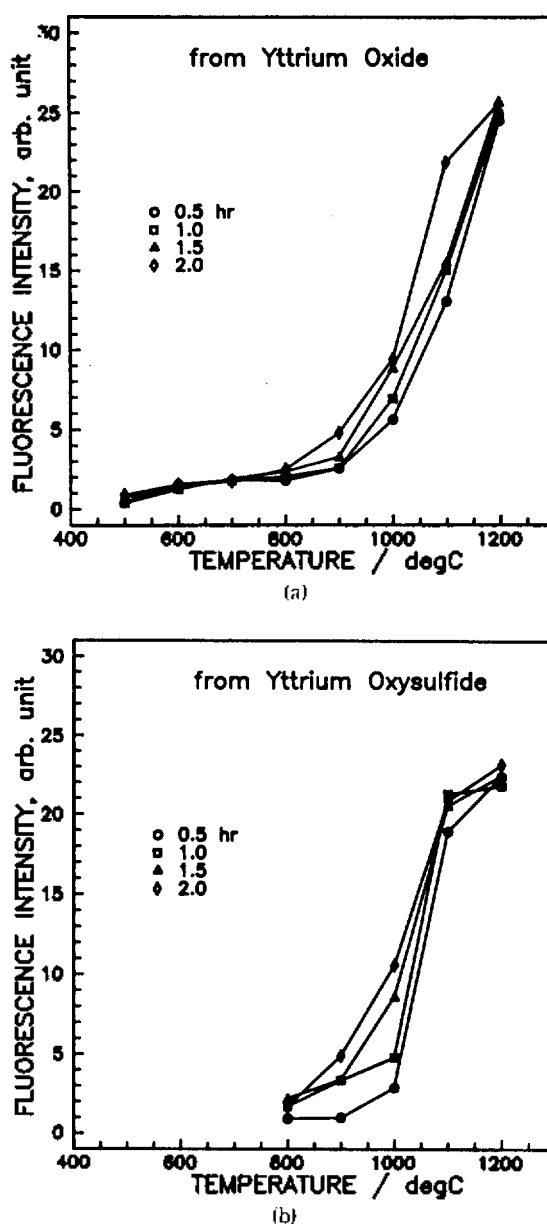
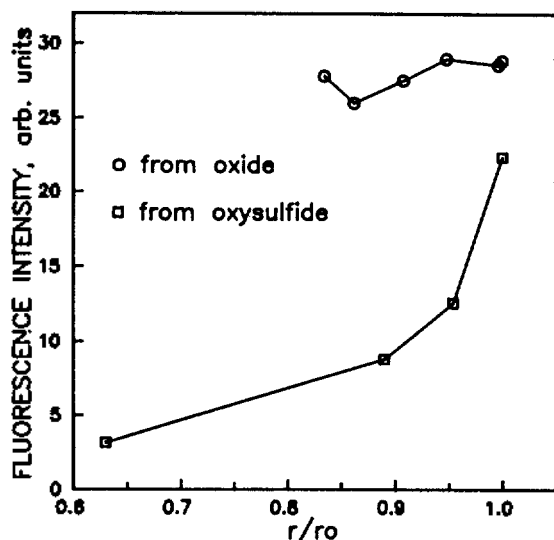


Figure 7. Fluorescence intensities of  $Eu^{3+}$  in  $Y_2O_2S$  prepared at different temperatures for 0.5-2 hours (a) from  $Y_2O_3$  and (b) from  $Y_2O_2S$  as starting materials.

ferent degrees by controlling the etching time and fluorescence intensities were measured. The fluorescence intensities are plotted against the particle radius ( $r$ ) derived from the weight ( $w$ ) by the equation,  $r = (3w/4\pi d)^{1/3}$ , where  $d$  is density, assuming spherical uniform particles (Figure 8). Fluorescence intensities for  $Y_2O_2S:Eu^{3+}$  (3%) prepared from the grown  $Y_2O_2S$  decrease exponentially as the surface of particles are etched away. This means the  $Eu^{3+}$  concentration decreases inside the particle exponentially and confirms that  $Eu^{3+}$  is incorporated by diffusion. Fluorescence intensities are the same inside the particle for  $Y_2O_2S:Eu^{3+}$  (3%) produced from  $Y_2O_3$ , which means that  $Eu^{3+}$  are incorporated homogeneously inside the particles, where the incorporation of  $Eu^{3+}$  into  $Y_2O_2S$  proceeds via recrystallization from the melt rather than by diffusion.



**Figure 8.** Fluorescence intensities of  $\text{Eu}^{3+}$  in  $\text{Y}_2\text{O}_2\text{S}$  prepared from  $\text{Y}_2\text{O}_3$ (○) and from  $\text{Y}_2\text{O}_2\text{S}$ (□) vs. degree of etching. The  $r_0$  and  $r$  represent radii of phosphor particles before and after etching, respectively.

Fluorescence intensities of  $\text{Eu}^{3+}$  in  $\text{Y}_2\text{O}_2\text{S}$  heated at temperatures below  $1000^\circ\text{C}$  by either method are too low to be used as a red phosphor (Figure 7). For  $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$  (3%) prepared from  $\text{Y}_2\text{O}_3$  as a starting material, the fluorescence intensities increase as the reaction temperature varies from  $1000^\circ\text{C}$  to  $1200^\circ\text{C}$ . On the other hand, for  $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$  (3%) prepared from the grown  $\text{Y}_2\text{O}_2\text{S}$  as a starting material the fluorescence intensities are about the same for the products reacted at  $1100^\circ\text{C}$  and at  $1200^\circ\text{C}$ . Also, we found that fluorescence intensity of  $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$  (3%) prepared from  $\text{Y}_2\text{O}_3$  is stronger than that from  $\text{Y}_2\text{O}_2\text{S}$  grown at  $1200^\circ\text{C}$ .

### Conclusion

Formation of  $\text{Y}_2\text{O}_2\text{S}$  is completed at lower temperature (*ca.*

$500^\circ\text{C}$ ) and incorporation of  $\text{Eu}^{3+}$  into  $\text{Y}_2\text{O}_2\text{S}$  proceeds at higher temperature (above  $1000^\circ\text{C}$ ). The second phase, presumably dioxysulfide,  $\text{Y}_2\text{O}_2\text{S}_2$ , is formed along with  $\text{Y}_2\text{O}_2\text{S}$  between  $400^\circ\text{C}$  and  $460^\circ\text{C}$ . Dioxysulfide decomposes slowly to  $\text{Y}_2\text{O}_2\text{S}$  even at  $400^\circ\text{C}$ . Only  $\text{Y}_2\text{O}_2\text{S}$  is obtained above  $500^\circ\text{C}$ . Particles of  $\text{Y}_2\text{O}_2\text{S}$  produced below  $1000^\circ\text{C}$  are much smaller than those of the starting  $\text{Y}_2\text{O}_3$ . This suggests that  $\text{Y}_2\text{O}_2\text{S}$  formed at the surface of  $\text{Y}_2\text{O}_3$  by the reaction with  $\text{Na}_2\text{S}_2$  flux are peeled off due to the difference in densities. Consequently, fresh  $\text{Y}_2\text{O}_3$  surfaces are exposed to sulfur and the formation rate is high. Particles of  $\text{Y}_2\text{O}_2\text{S}$  grow above  $1000^\circ\text{C}$ , and are larger with smoother surfaces at  $1200^\circ\text{C}$ . Europium is incorporated homogeneously through recrystallization from the melt at  $1200^\circ\text{C}$  rather than diffusion.

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