

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.); ¹H NMR (60 MHz, DMSO-*d*₆) δ 4.01 (s, 3, OCH₃), 6.29 (bs, 2), 7.56 (s, 1). To phosphorus pentachloride (660 mg, 3.2 mmol) in dried CH₂Cl₂ (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 CH₂Cl₂ (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 (Na₂SO₄) and evaporation of organic layer afforded a yellow solid **1a-c**. **1a**: 284 mg, 29%, mp. 149–151 °C; ¹H NMR (60 MHz, DMSO-*d*₆) δ 2.15 (s, 3, CH₃), 3.43–3.62 (m, 2, CH₂), 4.15 (s, 3, OCH₃), 4.78–5.25 (m, 4, NHCHCH + CH₂), 5.83 (dd, 2, J = 8.2, 4.8 Hz, CH₂), 7.15 (s, 2, NH₂), 8.74 (s, 1, CH), 9.28 (d, 1, J = 8.0 Hz, NH). **1b**: 35%, mp. 158–161 °C; ¹H NMR (200 MHz, DMSO-*d*₆) δ 2.07 (s, 3, CH₃), 3.41 (d, 1, J = 18.2 Hz, CH₂), 3.62 (d, 1, J = 18.2 Hz, CH₂), 4.14 (s, 3, OCH₃), 4.84 (d, 1, J = 13.2 Hz, CH₂), 5.09 (d, 1, J = 13.2 Hz, CH₂), 5.13 (d, 1, J = 4.8 Hz, CH), 5.85 (dd, 1, J = 8.0, 4.8 Hz, CH₂), 7.57 (s, 1, CH), 8.21 (s, 1, CH), 9.82 (d, 1, J = 8.0 Hz, NH). **1c**: 12%; ¹H NMR (200 MHz, DMSO-*d*₆) δ 2.10 (s, 3, CH₃), 2.53 (s, 3, CH₃), 3.44 (d, 1, J = 18.5 Hz, CH₂), 3.65 (d, 1, J = 18.5 Hz, CH₂), 4.09 (s, 3, OCH₃), 4.96 (d, 1, J = 13.4 Hz, CH₂), 5.12 (d, 1, J = 4.8 Hz, CH), 5.20 (d, 1, J = 13.4 Hz, CH₂), 5.95 (dd, 1, J = 9.0, 4.8 Hz, CH₂), 7.35 (s,

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

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Formation Process of a Red Phosphor, Y₂O₂S:Eu³⁺

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Yttrium oxysulfide incorporated with europium has been prepared by direct heating the mixture of Y₂O₃, Eu₂O₃, NaOH (or Na₂CO₃), and S. The reaction of the mixture at low temperatures and treatment at higher temperatures are studied. The formation of Y₂O₂S is completed at lower temperature (ca. 500 °C) and incorporation of Eu³⁺ into Y₂O₂S lattice proceeds at higher temperature (above 1000 °C) along with crystal growth. Small amount of the unknown phase considered to be Y₂O₂S₂ is formed along with Y₂O₂S in the temperature range from 400 °C to 460 °C.

Introduction

Yttrium oxysulfide incorporated with europium, Y₂O₂S:Eu³⁺, is widely used as a red phosphor for color monitors because of its bright luminescence and high energy efficiency.¹⁻⁶ It is usually prepared from yttrium oxide coprecipitated with europium oxide.⁷ In the present work the reaction of the mixture of Y₂O₃ (neat or 3~4 at % Eu₂O₃ added),

Na₂CO₃ (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, Y₂O₂S, and incorporation process of Eu³⁺ into it.

Experimental

Europium-incorporated yttrium oxysulfide phosphors,

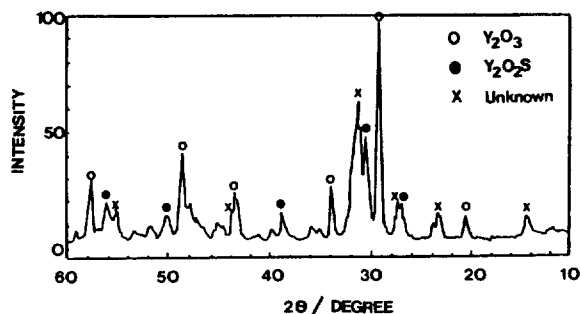


Figure 1. XRD pattern of the reaction product from the mixture, $Y_2O_3:Na_2CO_3:S = 1:3:17.6$ at $400^\circ C$ for 1.5 hours.

$Y_2O_2S:Eu^{3+}$, 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)⁸ is produced from the reaction mixture at around $270-350^\circ C$.⁹ The yield of Y_2O_2S was monitored with an X-ray powder diffractometer (XRD, Rigaku, D/MAX-3A, Cu K_α). 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° , 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 $\approx 500^\circ C$ 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_3S ($2\theta = 30.3^\circ$), 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 $460^\circ C$.

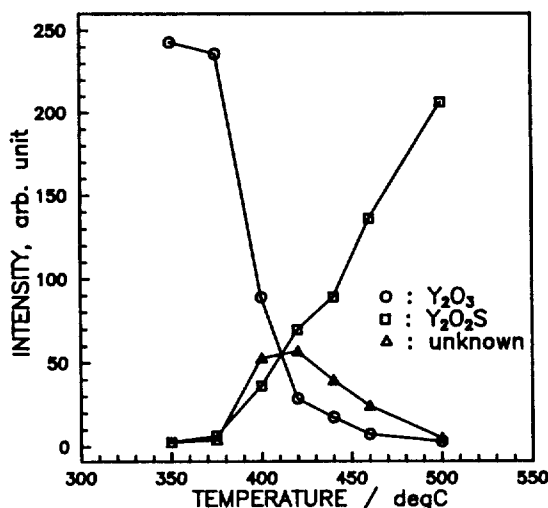


Figure 2. XRD peak intensities of Y_2O_3 ($2\theta = 29.3^\circ$), Y_2O_2S ($2\theta = 30.3^\circ$), and unknown phase ($2\theta = 31.3^\circ$) vs. reaction temperature.

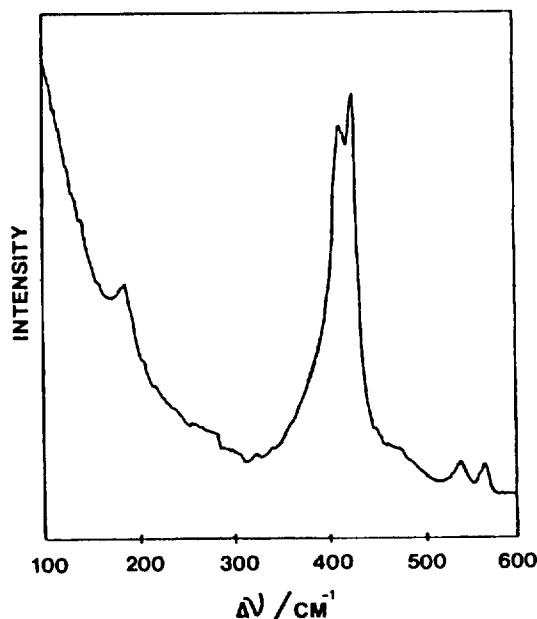


Figure 3. Raman spectrum of $Y_2O_2S_2$.

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 ¹⁰. From these analyses the unknown phase in the reaction product is considered to be $Y_2O_2S_2$.

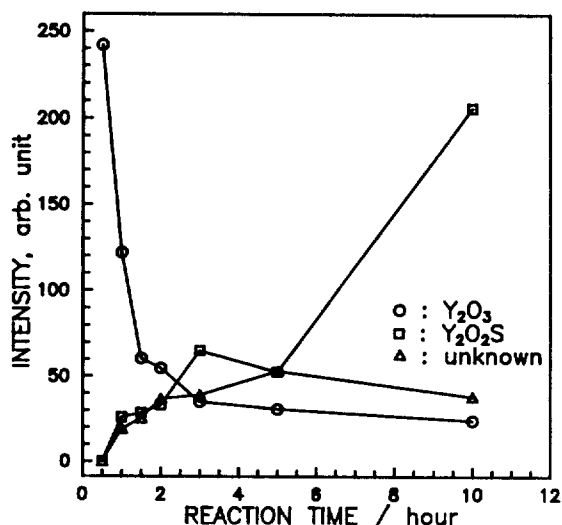


Figure 4. XRD peak intensities of Y_2O_3 , Y_2O_2S , and $Y_2O_2S_2$ vs. reaction time.

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 dioxydisulfide decomposes to Y_2O_2S above 500 °C, and partially decomposes to Y_2O_2S even at 400 °C with prolonged reaction time. Only Y_2O_2S is obtained above 500 °C. Dioxydisulfide, $Y_2O_2S_2$, 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 , it could be cracked due to the difference in densities and formed Y_2O_2S are peeled off. Therefore, sulfur is considered to

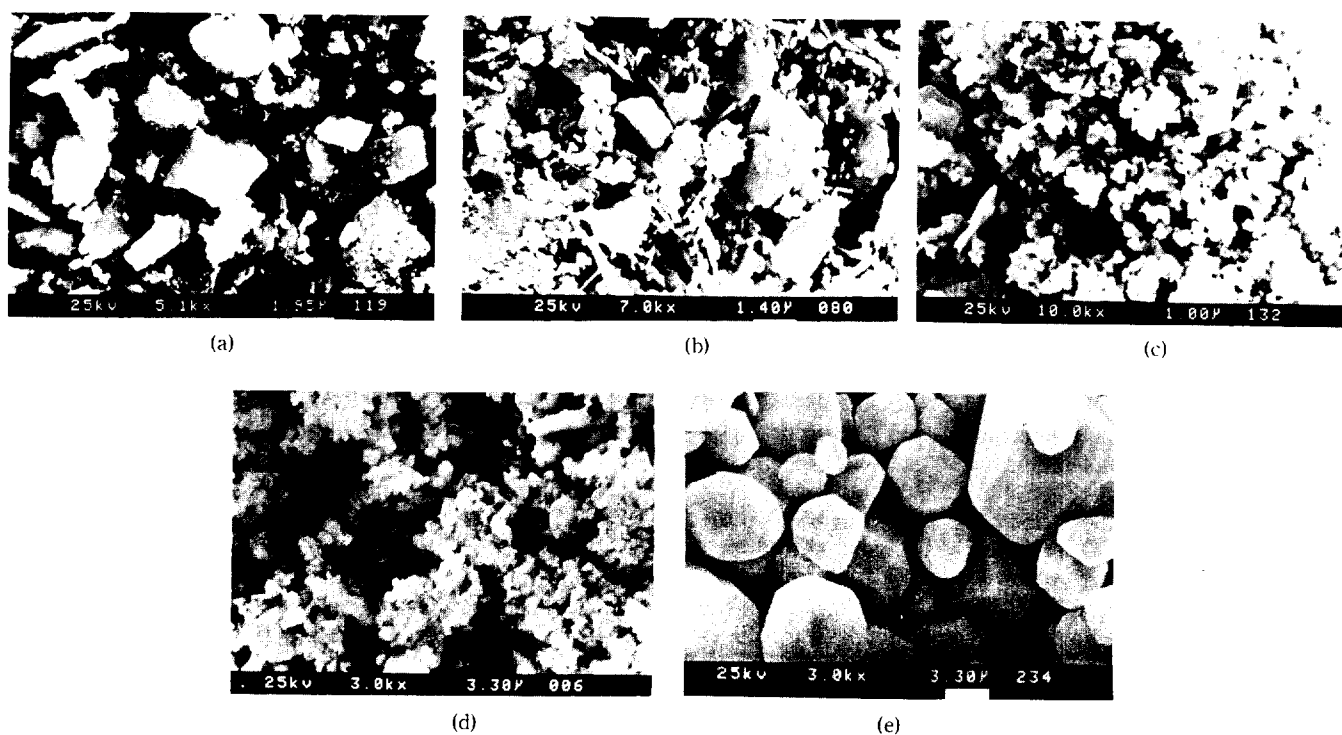


Figure 5. Scanning electron micrographs of the reaction products at various temperatures: (a) 350 °C, (b) 400 °C, (c) 500 °C, (d) 1000 °C, (e) 1200 °C.

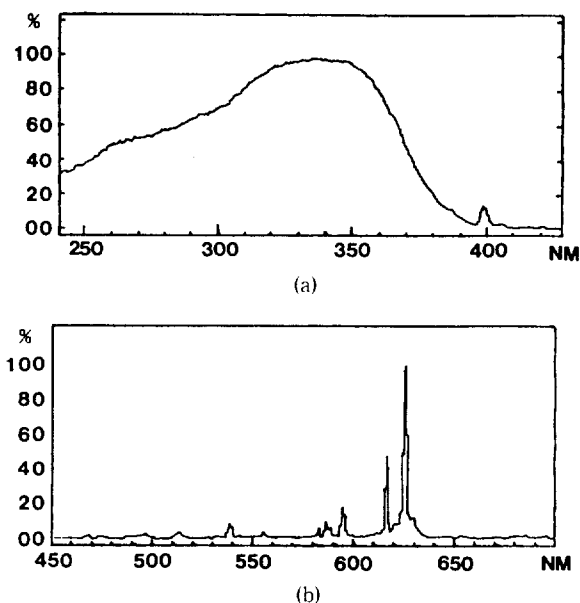


Figure 6. (a) Excitation and (b) fluorescence spectra of Eu^{3+} in Y_2O_2S .

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-

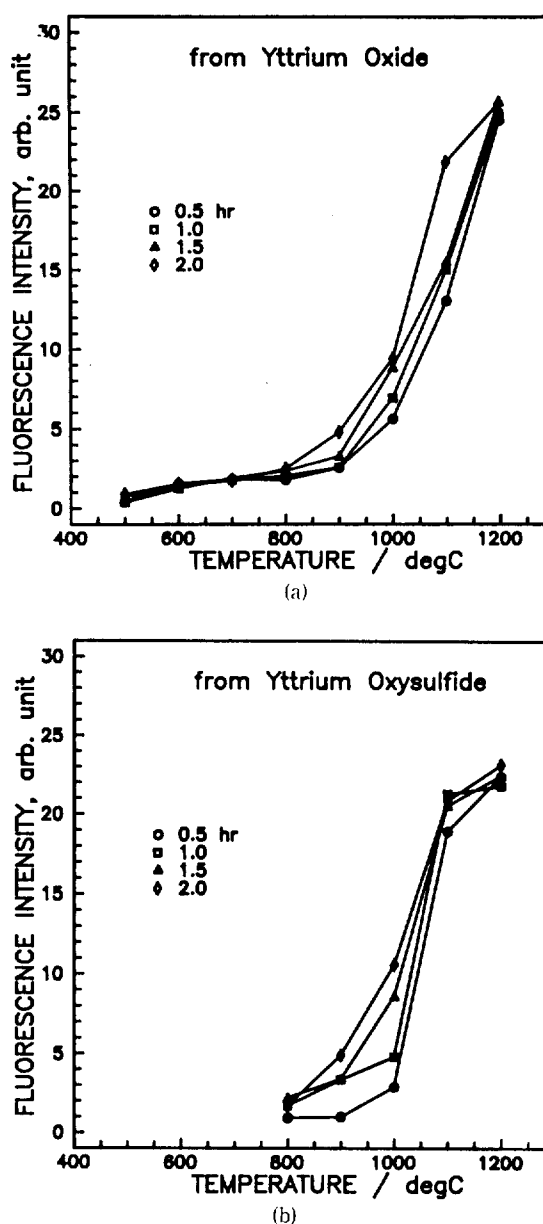


Figure 7. Fluorescence intensities of Eu^{3+} in Y_2O_2S prepared at different temperatures for 0.5–2 hours (a) from Y_2O_3 and (b) from Y_2O_2S as starting materials.

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.

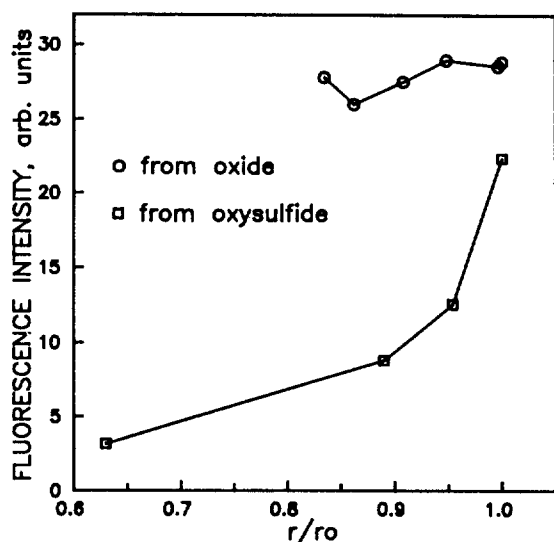


Figure 8. Fluorescence intensities of Eu^{3+} in $\text{Y}_2\text{O}_2\text{S}$ prepared from Y_2O_3 (○) and from $\text{Y}_2\text{O}_2\text{S}$ (□) vs. degree of etching. The r_0 and r represent radii of phosphor particles before and after etching, respectively.

Fluorescence intensities of Eu^{3+} in $\text{Y}_2\text{O}_2\text{S}$ heated at temperatures below 1000°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 Y_2O_3 as a starting material, the fluorescence intensities increase as the reaction temperature varies from 1000°C to 1200°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°C and at 1200°C . Also, we found that fluorescence intensity of $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ (3%) prepared from Y_2O_3 is stronger than that from $\text{Y}_2\text{O}_2\text{S}$ grown at 1200°C .

Conclusion

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

500°C) and incorporation of Eu^{3+} into $\text{Y}_2\text{O}_2\text{S}$ proceeds at higher temperature (above 1000°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°C and 460°C . Dioxysulfide decomposes slowly to $\text{Y}_2\text{O}_2\text{S}$ even at 400°C . Only $\text{Y}_2\text{O}_2\text{S}$ is obtained above 500°C . Particles of $\text{Y}_2\text{O}_2\text{S}$ produced below 1000°C are much smaller than those of the starting Y_2O_3 . This suggests that $\text{Y}_2\text{O}_2\text{S}$ formed at the surface of Y_2O_3 by the reaction with Na_2S_x flux are peeled off due to the difference in densities. Consequently, fresh Y_2O_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°C , and are larger with smoother surfaces at 1200°C . Europium is incorporated homogeneously through recrystallization from the melt at 1200°C rather than diffusion.

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