

was placed in front of the flask. A total of 10 g (0.10 mol) of *N*-nitrosomethylurea¹⁸ was added to the flask in 0.5 g portions at such a rate that the reaction temperature did not exceed 5 °C. The mixture was stirred for an additional 20 min and the bright yellow organic layer was quickly decanted into a glass tube (3×25 cm) cooled in a dry ice/acetone bath. Vapors of diazomethane were swept by nitrogen gas (5 mL/min) from the decalin solution into a 10 cm branched glass vessel containing a stirring bar and 2 g (20 mmol) of vinyltrimethylsilane.¹⁹ A spiral condenser, cooled to 0 °C, and a cold finger, kept at -78 °C were attached to the branched glass vessel. After 6h, introduction of the gaseous diazomethane was nearly complete as indicated by diminution of the bright yellow color.

Preparative GC on an OV-17 (20% on Chromosorb W 80/100, 1/4 in×2 ft; detector temp., 110 °C; injector temp., 105 °C; oven temp., 65 °C; flow rate, 65 mL/min) appeared one major peak. A total of 1.4 g (57% yield based on the amount of vinyltrimethylsilane) was isolated. UV (cyclohexane): λ_{max} 320 nm (ϵ 536); ¹H NMR (neat): δ 0.34 (s, 9H, Si(CH₃)₃), 1.11 (m, 2H), 3.88 (br m, 3H); ¹³C NMR (neat) δ : -0.37 (q), 82.91 (d), 18.51 (t), 74.91 (t); MS *m/z* 142 (M⁺, 41), 127 (91), 100 (19), 73 (100), 59 (95), 43 (52).

1-Trimethylsilyl-2-pyrazoline (2). Purification of **1** by a preparative GC on a 22 ft OV-17 (20% an Chromosorb W) column at 80 °C led to complete isomerization to **2**. UV (cyclohexane): λ_{max} 250 nm (ϵ 9836); ¹H NMR (neat): δ -0.24 (s, 9H, Si(CH₃)₃), 2.91 (app t, 2H, CH₂N), 2.18 (m, 2H, CH₂CC), 6.03 (t, 1H, *J*=10.1 Hz HC=N); ¹³C NMR (neat) δ : -1.95 (q), 44.35 (t), 33.28 (t), 137.67 (d); MS *m/z* same as **1**.

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Luminescence Characteristics of Y₂O₂S:Eu³⁺, Tb³⁺ Phosphor

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An inorganic phosphor basically consists of a host lattice in which activator ions are incorporated. These ions usually determine the energy levels responsible for the luminescence process.¹ When lanthanide(III) ions are incorporated into the insulating ionic host as an activator, characteristic 4f-4f transition sharp line spectra are resulted. Because of the shielding nature by the outer filled orbitals, perturbation by surrounding neighbors is negligible and the spectral characteristics are nearly independent of the host lattice.

The red emitter Eu³⁺ activated yttrium oxysulfide, Y₂O₂S:Eu³⁺, has been widely used in cathode ray tubes (CRT) for color TVs and color monitors because of its high efficiency and brightness.²⁻⁷ The characteristics and the efficiency of Y₂O₂S:Eu³⁺ luminescence have been extensively studied since it has been introduced by Royce.^{2,3} The Y₂O₂S:Eu³⁺ surpasses the (Zn, Cd)S:Ag (red 670 nm) in cathodoluminescence (CL) efficiency by 30% and the YVO₄:Eu³⁺ in brightness by 40%. The energy level diagram for Eu³⁺ in Y₂O₂S is shown in Figure 1(a). Stimulation by photons (absorption λ_{max} =365 nm; photoluminescence; PL) or high energy elect-

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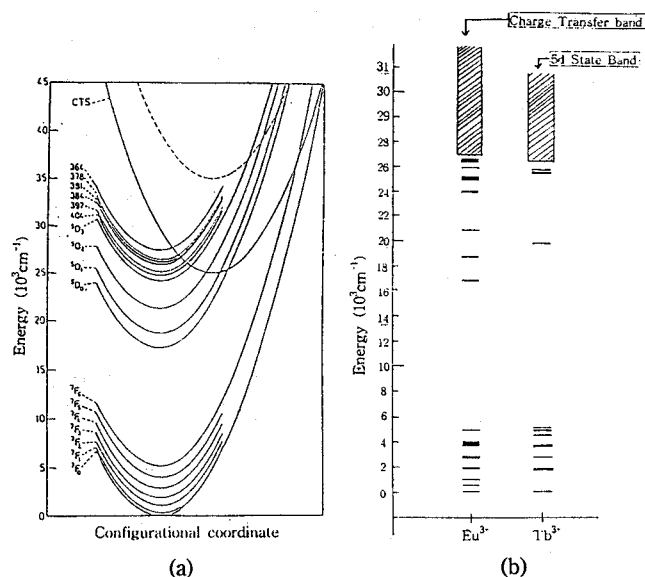


Figure 1. (a) Configuration coordinate model for the $4f^7$ and CTS of Eu^{3+} in $\text{Y}_2\text{O}_2\text{S}$, (b) Energy level diagrams of Eu^{3+} and Tb^{3+} .

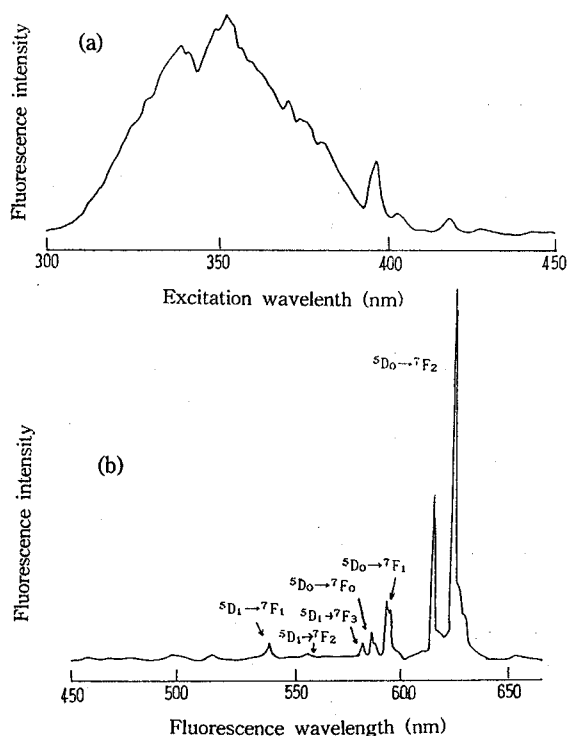


Figure 2. (a) Excitation and (b) Fluorescence spectra of $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$.

ron beam (CL) excites the Eu^{3+} ion to the charge transfer state (CTS) from the ground state. The excitation transition results in the charge transfer from p orbitals of oxygen and sulfur ligands to the f orbitals of the metal ion, Eu^{3+} , which has substituted the Y^{3+} sites. The increased electron density in the vicinity of the Eu^{3+} ion induces the dipole. This excited state would then relax, through nonradiative decay, to the emitting levels ^5D followed by radiative transition to the

^7F levels. Of these radiative transition peaks, $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ are most prominent. Figure 2 displays the luminescence and the excitation spectra of $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$. The intense peak at 627 nm corresponds to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu^{3+} ion.

Incorporation of other lanthanide ions as sensitizers to the $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ phosphor has been attempted to increase the luminescence efficiency.⁸⁻¹⁰ The Tb^{3+} is known as a good sensitizer for enhancing the red luminescence of $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$. The Tb^{3+} ion is incorporated into $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ in order to investigate the effect of sensitizer Tb^{3+} to the red luminescence and its radiative mechanism. The energy level diagram of Tb^{3+} ion is depicted in Figure 1(b) along with that of Eu^{3+} . It is desirable to have a radiative transition from the lowest level of ^5D levels, $^5\text{D}_0$, to improve the color purity of red phosphor. The transitions from the $^5\text{D}_1$ and the $^5\text{D}_2$ levels to the ^7F levels result green and blue emission, respectively. Tb^{3+} may facilitate the nonradiative transition from the $^5\text{D}_1$ and $^5\text{D}_2$ levels to the $^5\text{D}_0$ level of Eu^{3+} by efficient energy transfer between Eu^{3+} and Tb^{3+} . As shown in Figure 1(b), the $^5\text{D}_4$ level of Tb^{3+} is lying between the $^5\text{D}_1$ and $^5\text{D}_2$ levels of Eu^{3+} and this could facilitate the nonradiative transition to the $^5\text{D}_1$ level. Nonradiative relaxation rate increases as the energy gap between the two levels decreases. If the energy transfer between Tb^{3+} and Eu^{3+} is efficient, we might expect an improvement of color purity and brightness of $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$, Tb^{3+} phosphor without having emission from Tb^{3+} . With this scheme, $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$, Tb^{3+} phosphor was prepared by coprecipitation of Y_2O_3 , Eu_2O_3 , and Tb_4O_7 , followed by reaction with Na_2S_x flux. The spectroscopic characteristics, focused on its energy transfer and luminescence mechanism in photoluminescence and cathodoluminescence are reported.

Experimental

Two sets of fluorometer, as described earlier, were used in spectroscopic study to compare and evaluate the quantitative photoluminescence (PL) intensity.^{11,12} For the cathodoluminescence measurement, phosphor powder was deposited on the indium tin oxide (ITO) glass (10 mm diameter) by a conventional sedimentation method in a potassium silicate solution. Samples were excited by the 20 kV accelerated electron beam with 55 μA beam current. The crystalline phase of the phosphor was characterized by X-ray diffraction (XRD) measurement.

$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, Tb^{3+} phosphor was prepared by coprecipitation method since this method has some advantages in convenient stoichiometric control of trace elements and in homogeneous incorporation of activator Eu^{3+} and sensitizer Tb^{3+} ions in atomic scale into host lattice. Appropriate amounts of Y_2O_3 (99.99%, Aldrich), Eu_2O_3 (99.99%, Aldrich), and Tb_4O_7 (99.99%, Aldrich) were dissolved in 6 N HNO_3 solution. Excess of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution was added slowly with gentle stirring while heated to 50-60 $^\circ\text{C}$. The coprecipitated oxalates were fired at 800 $^\circ\text{C}$ for 2 hours to produce homogeneously incorporated metal oxides. This was confirmed by XRD measurement. $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$, Tb^{3+} was prepared from thus formed mixed oxide homogeneous in atomic scale using Na_2S_x flux, by the method previously established.¹¹ Though there are Tb^{3+} and Tb^{4+} ions in Tb_4O_7 with 1:1 ratio, only Tb^{3+} ion

is found in solution.¹³ With this method, 0.0, 1×10^{-3} , 2×10^{-3} , 2×10^{-2} , 0.2, and 1.3 mole% of total terbium ion was incorporated along with 4.0% of Eu^{3+} ion in $\text{Y}_2\text{O}_2\text{S}$ host lattice. Since we utilize the coprecipitation method from solution, this phenomenon might be an important variable for determining the luminescence characteristics of the phosphor. Phosphors of $\text{Y}_2\text{O}_2\text{S}:\text{Tb}^{3+}$ (4.0%) and $\text{Y}_2\text{O}_2\text{S}:\text{Tb}^{3+}$ (8.0%), without Eu^{3+} activator, were also prepared to investigate the luminescence characteristics of Tb^{3+} and its effect as a sensitizer on the Eu^{3+} activator in $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}, \text{Tb}^{3+}$.

Results and Discussion

The photoluminescence intensity was monitored by varying the Eu^{3+} concentration in $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ phosphor from 1.0% to 10% (Figure 3). The photoluminescence intensity increased monotonically as the Eu^{3+} concentration increased up to 5-6 mole% and decreased its intensity at higher Eu^{3+} concentration because of the concentration quenching effect. If $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ phosphor is excited to the charge transfer state by UV light, electron density is shifted toward Eu^{3+} and a dipole between metal and ligand is induced. As Eu^{3+} concentration is increased, energy transfer among Eu^{3+} ions through the dipole interactions becomes important. This phenomenon would facilitate the nonradiative decay and thus quench the luminescence intensity.

In order to study the effect of sensitizer Tb^{3+} on the Eu^{3+} luminescence in $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}, \text{Tb}^{3+}$ phosphor, the activator Eu^{3+} concentration was fixed at 4.0%, slightly lower than the concentration of maximum luminescence intensity (5-6%), and the sensitizer Tb^{3+} concentration was varied in the range of 0.0 to 1.3%. The peak positions and their relative intensities in PL and CL spectra of $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}, \text{Tb}^{3+}$ are very similar to those of $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ phosphor. No new peak attributable to the Tb^{3+} was observed. The luminescence and excitation spectra of $\text{Y}_2\text{O}_2\text{S}:\text{Tb}^{3+}$ were also measured as references (Figure 4). Although the luminescence and excitation features are independent of the presence of Tb^{3+} ion, the luminescence intensity is strongly influenced by Tb^{3+} ion concentration in $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}, \text{Tb}^{3+}$. Figure 5 shows the

PL and CL intensities as a function of Tb^{3+} concentration. CL intensities are measured at the luminescence peak at 627 nm which is corresponding to the ${}^5\text{D}_0\text{-}{}^7\text{F}_2$ transition. PL intensities are measured by exciting to the CTS of Eu^{3+} at 365 nm and monitoring the most intense luminescence peak at 627 nm. As was expected from the previous reports,⁸⁻¹⁰ CL intensities are increased when the trace amount of terbium ion is incorporated. Incorporation of Tb^{3+} up to 0.02% into $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ (4.0%) enhances the CL intensity up to 75%, though the peak positions and relative intensities are identical. In contrary to the CL, the PL intensity decreased significantly by the incorporation of terbium ion. It is noteworthy that the intensity of charge transfer band was decreased more significantly than those of f-f transition peaks

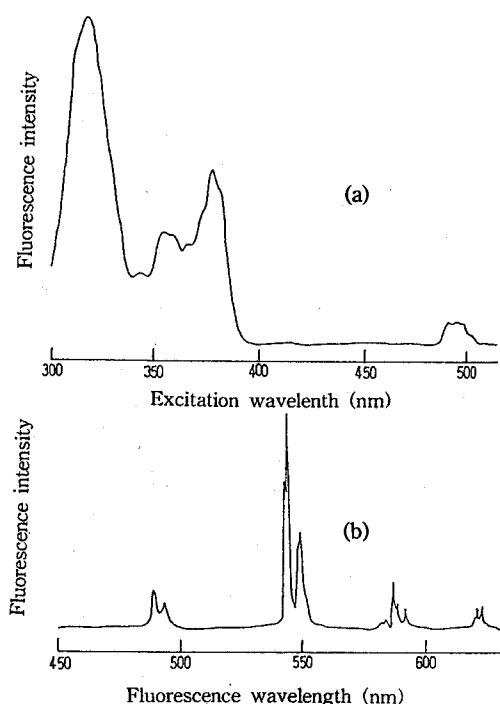


Figure 4. (a) Excitation and (b) Fluorescence spectra of $\text{Y}_2\text{O}_2\text{S}:\text{Tb}^{3+}$

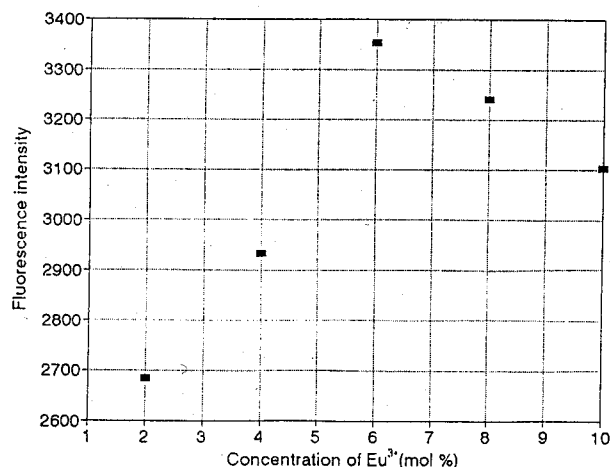


Figure 3. Plot of PL intensities (exciting at $\lambda_{\text{exc}}=365$ nm (CTS) and monitoring at $\lambda_{\text{flu}}=627$ nm (${}^5\text{D}_0\text{-}{}^7\text{F}_2$)) versus Eu^{3+} concentrations in $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$.

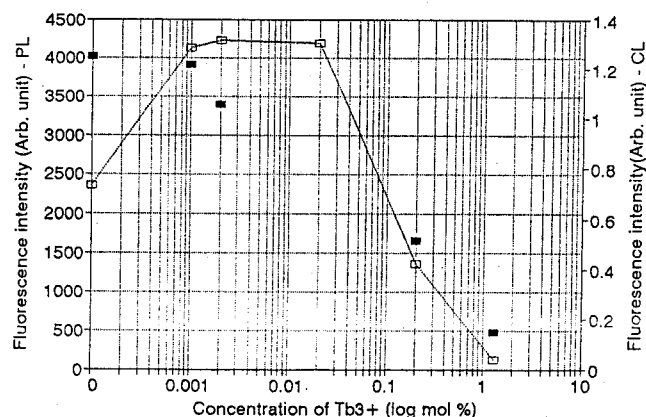


Figure 5. Plot of PL (\blacksquare) and CL (\square) intensities of Eu^{3+} (measuring at $\lambda_{\text{exc}}=365$ nm (CTS) and $\lambda_{\text{flu}}=627$ nm (${}^5\text{D}_0\text{-}{}^7\text{F}_2$)) versus Tb^{3+} concentrations in $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ (4%), Tb^{3+} .

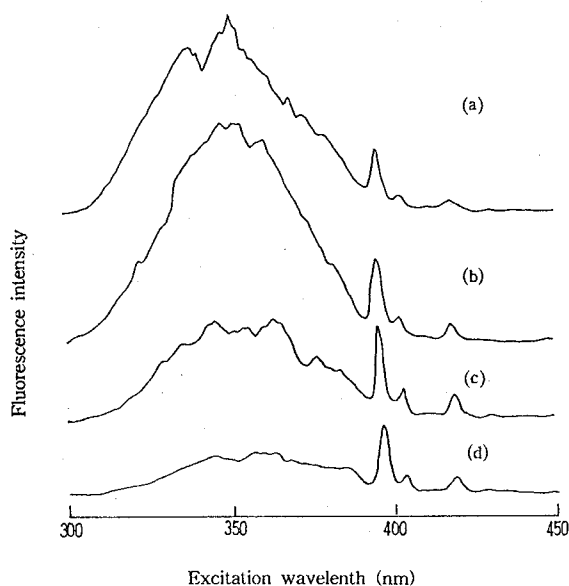


Figure 6. Excitation spectra (monitoring at $\lambda_{em} = 627$ nm (${}^6D_0 \rightarrow {}^7F_2$)) of (a) $Y_2O_2S:Eu^{3+}$ (4%), (b) $Y_2O_2S:Eu^{3+}$ (4%), Tb^{3+} (0.002%), (c) $Y_2O_2S:Eu^{3+}$ (4%), Tb^{3+} (0.2%), (d) $Y_2O_2S:Eu^{3+}$ (4%), Tb^{3+} (1.4%).

in excitation spectra (Figure 6). The electron density is shifted toward Eu^{3+} from O and S ligands in the charge transfer state. In $Y_2O_2S:Eu^{3+}, Tb^{3+}$ phosphor, some of Eu^{3+} in CTS could be dissociated to Eu^{2+} and a hole and the hole be trapped by Tb^{3+} ion. Nonradiative recombination of Eu^{2+} and the hole could quench the luminescence. On the other hand, for cathodoluminescence the phosphor is excited by high energy electron beam (20 KeV) and instantaneously the secondary electrons are ejected.¹⁴ Because of the momentarily high concentrations of electron on (or in) the phosphor, the dissociative holes could not be thought to be formed in the CTS. Hence, the nonradiative quenching of the luminescence by recombination could not be observed in cathodoluminescence. In addition, the energy transfer between Tb^{3+} and Eu^{3+} may enhance the luminescence efficiency of the $Y_2O_2S:Eu^{3+}, Tb^{3+}$ phosphor. Further work on this phosphor will be conducted in near future.

In conclusion, luminescence characteristics and red emission efficiency of $Y_2O_2S:Eu^{3+}$ as a result of incorporation of sensitizer Tb^{3+} have been studied. Coprecipitated metal oxalates were utilized as a reaction base to incorporate the

Tb^{3+} ion homogeneously into the red phosphor, $Y_2O_2S:Eu^{3+}$. The incorporation of Tb^{3+} into $Y_2O_2S:Eu^{3+}$ did not change the feature of the luminescence spectrum. The CL intensity of $Y_2O_2S:Eu^{3+}$ (4.0%), Tb^{3+} increased up to 75% in the Tb^{3+} concentration of $1 \times 10^{-3}\%$ and $2 \times 10^{-2}\%$ range. In contrary to the CL intensity change, the PL intensity decreased significantly as the Tb^{3+} concentration increased. In the excitation spectrum of $Y_2O_2S:Eu^{3+}, Tb^{3+}$, the intensity of charge transfer band is decreased more significantly than those of f-f transition peaks as the Tb^{3+} concentration increased. It is speculated that the Eu^{3+} in the charge transfer state is dissociated to the Eu^{2+} and a hole in the presence of Tb^{3+} . This hole could be trapped by Tb^{3+} ion and recombine non-radiatively with Eu^{2+} , which results in quenching the luminescence.

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