特別寄稿

Cathodoluminescence Color of Y_2O_2S: Eu Phosphors

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The brigtness and color coordinates of the cathodoluminescence of Y_2O_2S: Eu phosphors, including Fe_2O_3 pigmentation, have been studied. A concentration dependence curve of the $^5D_0$ Eu^{3+} cathodoluminescence of Y_2O_2S: Eu, which gives a red luminescence color, smoothly fits on the curve of $C^{0.22}(1-C)^{12}$. The brightness of practical Y_2O_2S: Eu phosphor is closely correlated with the color coordinates of cathodoluminescence. Color coordinates and brightness as a function of Eu concentrations are determined with good reproducibility (± 0.005 of x-values).

1. Introduction

Yttrium oxysulfide activated with europium (Y_2O_2S: Eu) is an important red primary of color cathode ray picture tubes[1] used in color TV sets and graphic work stations for computers, because it has high brightness in red, and because nearly 100% phosphor powder is screened on face plates by rejuvenation (reclaim) of scraped Y_2O_2S: Eu phosphor powder. Y_2O_2S: Eu phosphor is a very expensive phosphor powder, even though 100% of powder is used. The high cost of the red phosphor powder is due to the use of rare earths, especially europium. Many attempts to find a replacement phosphor have failed; therefore, reducing the Eu concentration in Y_2O_2S: Eu phosphors has become an important subject.

A discussion on cathodoluminescence (CL) of Y_2O_2S: Eu phosphors always encounters vagueness of Eu^{3+} CL as a function of Eu concentrations. For instance, they are color coordinates of CL and brightness. We have extensively studied the CL of Y_2O_2S: Eu phoshor powder as a function of Eu concentrations to clarify the vagueness of the CL properties. The results obtained are listed below.

2. Spectrum of Eu^{3+} Luminescence

The CL of Y_2O_2S: Eu phosphor occurs by recombination of electrons and holes at Eu^{3+} ions which occupy Y^{3+} lattice sites in an Y_2O_2S crystal.[2] **Figure 1** show the recorded (i.e., not corrected) luminescence and excitation spectra of Y_2O_2S: Eu. Activator concentrations are 1×10^{-3} mole fraction. The shadowed area indicates the wavelengths for the excitation spectrum. The numerals on the lines and bands indicate peak wavelengths in nm units (omitted in the figure).

The Eu^{3+} luminescence lines, which are attributable to the electron transitions from excited states of $^5D_0$ and $^5D_1$ to ground states of ^7F_J Eu^{3+}, are distributed in the wavelengths of the entire visible spectrum. The relative intensities of the Eu^{3+} luminescence lines in the spectrum markedly change with Eu concentrations.

3. Concentration Dependence Curves

Figure 2 shows the concentration dependence (CD) curves of Eu^{3+} CL, corresponding to the transitions of $^5D_0\rightarrow{}^7F_2$, $^5D_1\rightarrow{}^7F_1$ and $^5D_2\rightarrow{}^7F_3$, in the concentrations from 10^{-6} to 10^{-1} mole fractions. Below the 3×10^{-4} mole fraction, each curve has a straight line with the same slope of 0.66 on log-log bases, giving rise to the luminescence color of orangish white. Above the 3×10^{-4} mole fraction, each curve has a different behavior caused by different concentration quenching mechanisms.[3] The change in the luminescence intensitities with Eu^{3+} concentrations can be classified according to the emitting states, $^5D_0$, $^5D_1$, and $^5D_2$.

The concentration quenching interaction of the $^5D_1$ and $^5D_2$ states is due to electrostatic multipolar interactions; dipole-quadrupole interaction can be assigned for $^5D_2$ luminescence, and dipole-

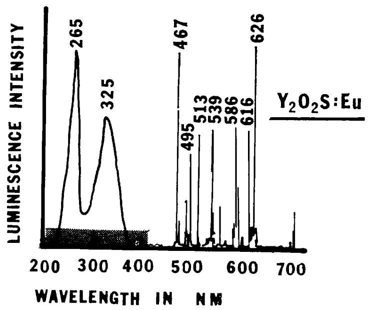

Fig. 1 Luminescence and excitation spectra of Y_2O_2S: Eu. Shadowed wavelengths are for the excitation spectrum.

dipole interaction is responsible for $^5D_1$ luminescence.[3] The self-concentration quenching mechanism for the $^5D_0$ luminescence is magnetic dipole-dipole interaction (magnetic coupling) which occurs between Eu^{3+} ions occupied at the nearest cation lattice sites.[4] Among them, electrostatic dipole-quadrupole interaction occurs at the lowest Eu concentration, and then the electrostatic dipole-dipole interaction occurs at slightly higher Eu concentrations. Magnetic dipole interaction only occurs at high Eu concentrations. Thus the self-concentration quenchings of the ^5D_j emitting states of Eu^{3+} occur in the order of $^5D_2$ (the lines fall in the violet to green spectral region); $^5D_1$ (blue to orange spectral region); and finally $^5D_0$ (orange to near infrared region). Hence the color of CL of Y_2O_2S : Eu phosphor alters from orangish white to red with Eu concentrations above the 3×10^{-4} mole fraction. The $^5D_0$ luminescence is practically used as a major component of red primary in screens of color cathode ray picture tubes.

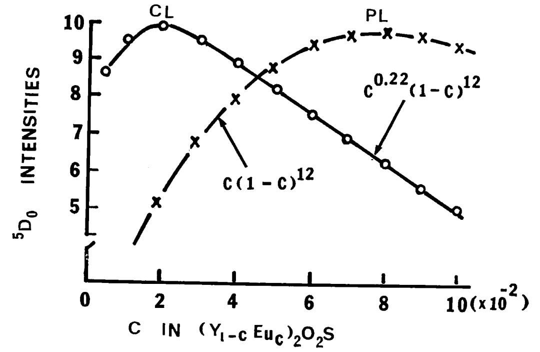

Fig. 3 Concentration dependence curves of the $^5D_0$ Eu^{3+} luminescence of Y_2O_2S: Eu phosphors under excitation of a cathode ray (CL) and 467 nm light (PL) in Eu concentrations between 0.01 to 0.1 mole fraction.

Figure 3 shows the normalized CD curves of the $^5D_0$ Eu^{3+} CL and photoluminescence (PL) of Y_2O_2S : Eu in the practical Eu concentrations, i.e., 0.01 to 0.1 mole fraction. The curve of PL is obtained under irradiation of the 467 nm blue light that is weakly and directly absorbed by Eu^{3+} in Y_2O_2S : Eu.[3] The curve of CL is obtained under irradiation of a steady electron beam of 15 kV, 1 $\mu A/cm^2$. The data of PL (x) fit smoothly on the theoretical curve of the relative number of Eu^{3+} that luminesces in Y_2O_2S : Eu and which is expressed by[4]

$$C(1-C)^{12}, \qquad (1)$$

where C is Eu concentration in mole fraction in a finite volume of the particles, and exponential

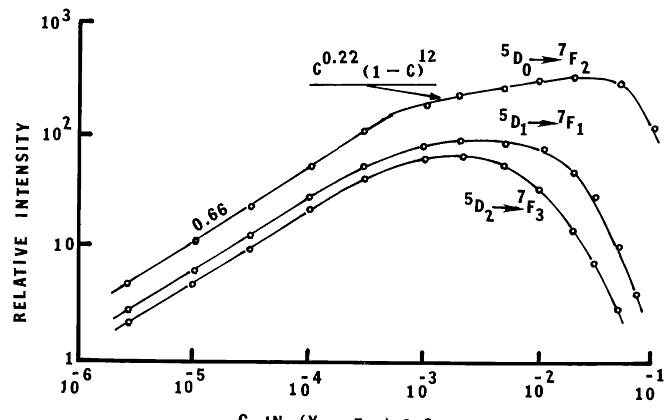

Fig. 2 Concentration dependence curves of $^5D_0$, $^5D_1$, and $^5D_2$ Eu^{3+} cathodoluminescence of Y_2O_2S : Eu for Eu concentrations between 10^{-6} to 10^{-1} mole fractions.

12 is the weighted number of the nearest cation sites in the Y_2O_2S crystal. $(1-C)^{12}$ is a fraction that indicates that excited Eu^{3+} ions are emissive. The optimal activator concentration is given by a differential of Eq. (1) to be zero: i.e., $C_{opt}=0.08$ mole fraction.

In contrast with PL, the curve of CL (o) completely deviated from the curve of Eq. (1), indicating that the CL intensities are not in accordance with the number of luminescent Eu^{3+} in the particles. It is found that CL data smoothly fit onto a curve which is calculated from the equation

$$C^{0.22}(1-C)^{12}, \qquad (2)$$

where exponential 0.22 is an empirically determined value for Y_2O_2S : Eu phosphor. $C^{0.22}$ indicates that the number of excited Eu^{3+} ions under an electron beam changed with $C^{0.22}$ instead of C. The value of 0.22 is one third of the slope (0.66) of the CD curve below the 3×10^{-4} mole fraction as shown in Fig. 2.

Equation (2) is applicable to the $^5D_0$ Eu^{3+} luminescence intensities in the Eu concentrations above 1×10^{-3} mole. The optimum intensity of the $^5D_0$ Eu^{3+} CL is given by the difftrential of Eq. (2) to be zero. This gives $C=0.019$, corresponding to Eu=2.9 wt%. It can practically be said that the optimal concentration of the $^5D_0$ Eu^{3+} CL is around 3.0 wt%. Above 3.0 wt%, the intensities of all Eu^{+3} CL lines in the spectrum, consequently the brightness, decrease monotonically with an increase in Eu concentration.

It should be noted that we obtained a high reproducibility (±3% error) for the curves in Fig. 3. If the Y_2O_2S : Eu phosphor powder is prepared by an improper process, the CD curve of the $^5D_0$ Eu^{3+} CL always shifts to high Eu concentrations from the CL curve calculated by Eq. (2). Hence the CL curve calculated from Eq. (2) provides a new tool for examining the preparation process of Y_2O_2S : Eu phosphor.

In practice, the Eu concentrations are commonly expressed by wt% instead of by mole fraction. We therefore use wt% in the following discussion. **Figure 4** shows the relative brightness of CL of Y_2O_2S : Eu phosphor powder in the Eu^{3+} concentrations between 2 to 10 wt%, which are of practical interest. The CL brightness of Y_2O_2S : Eu phosphor powder indeed monotonically decreases as Eu concentrations are increased. The shadowed area is the contribution of the $^5D_1$ luminescence to the brightness (giving blue to orange). Thus

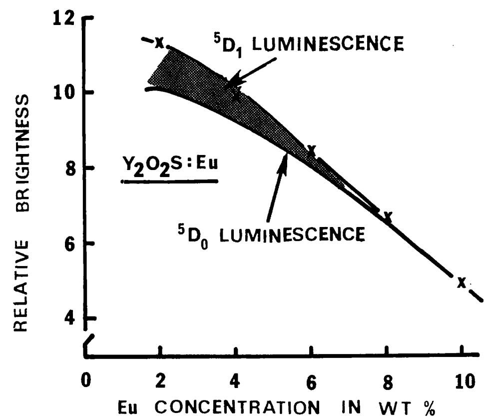

Fig. 4 Relative brightness of cathodoluminescence of Y_2O_2S : Eu phosphor as a function of Eu concentrations. Phosphors are excited by a steady electron beam of 15 kV, 1 $\mu A/cm^2$.

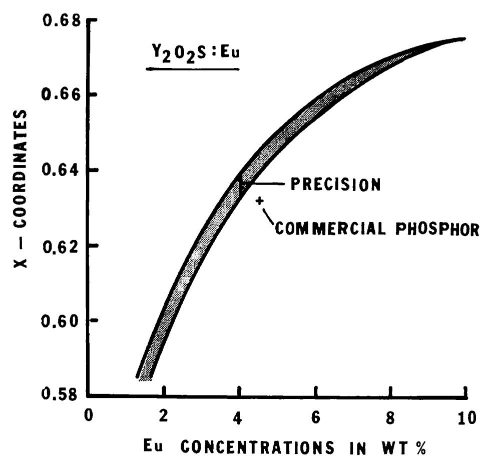

Fig. 5 x-values of color coordinates of cathodoluminescence of Y_2O_2S : Eu phosphors as a function of Eu concentrations between 1 to 10 wt%. Phosphors are excited by an electron beam of 15 kV, 1 $\mu A/cm^2$.

the brightness of Y_2O_2S : Eu phosphor in the practical Eu concentrations is strongly correlated with the luminescence color in Eu concentrations lower than 8 wt%.

4. Luminescence Color

The CL color is expressed by x-y color coordinates. In the practical Eu concentrations, the values of color coordinates are $x+y\simeq1.0$, so that we can use the x-value, instead of both x and y values, to discuss the color coordinates. **Figure 5** shows x-values obtained with CL of Y_2O_2S : Eu phosphor powder. The x-values were obtained from the measurements by using the color meter "Spectra." To ensure the reproducibility (precision) of the measurements and the sample preparations, three different instruments with the samples prepared on different days were examined. The data are scattered in the shadowed area, indicating a variation range of 0.005 of the x-values at the given Eu concentration. If Eu ions are unhomogenously distributed in individual Y_2O_2S : Eu phosphor particles, a deviation to the right side occurs. The deviation occurs in the production process, mainly in the handling of raw Eu_2O_3 powder.

In Eu concentrations in Fig. 5, the intensities of the $^5D_1$ Eu^{3+} luminescence lines are incompletely quenched and contribute to determination of the luminescence color. The contribution of the $^5D_1$ Eu^{3+} luminescence lines is large for low Eu concentrations. Above 10 wt%, the intensities of the $^5D_1$ Eu^{3+} luminescence lines are of a negligibly small value and no longer contribute to the determination of the Eu^{3+} luminescence color. The luminescence color of Y_2O_2S : Eu becomes $x=0.675$.

5. Brightness vs Color Coordinates

Figure 6 shows the relationship between color coordinates (x-values) and brightness. Color coordinates of the screens of color TV picture tubes were initially determined by NTSC to be $x=0.67$ and $y=0.33$. The present color coordinates of many color picture tubes are, however, $x=0.637$ and $y=0.345$. The brightness of Y_2O_2S : Eu red phosphor is significantly increased with a color shift to the yellow side, even though intrinsic CL efficiency remains at a constant. Brightness increases 95% with a decrease in x-values from NTSC's value (e. g., 0.637 from 0.67). An improvement of intrinsic CL efficiency, even at 3 %, is a very hard task. Shifting color not only increases the brightness, but it also significantly reduces the Eu concentration. The Eu concentration in Y_2O_2S: Eu to give the color $x=0.637$ is reduced to around 4.2 wt% from 8.5 wt% for NTSC color, saving 4.3 wt% Eu.

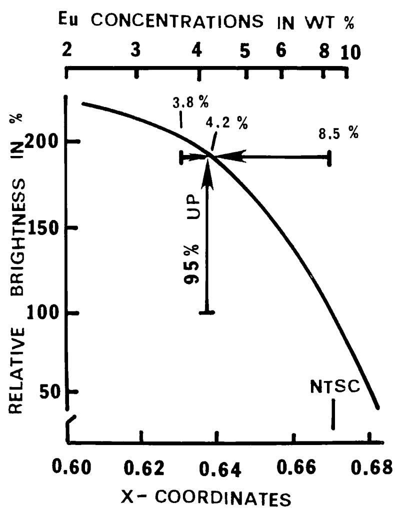

Fig. 6 Relationship between relative brightness and x-values of color coordinates of Y_2O_2S : Eu phosphors which are excited by a steady electron beam of 15 kV, 1 $\mu A/cm^2$.

Further decreases in Eu concentrations beyond 4 wt% cause a large color shift to the yellow side, resulting in poor color fidelity for color TV screens and only a small improvement in the brightness. The luminescence color of $x=0.637$ may be the limit of color shift of CL of Y_2O_2S : Eu phosphor as a red primary of color picture tubes. To give the luminescence color at $x=0.637$, some amount of the $^5D_1$ Eu^{3+} luminescence is absolutely necessary in the luminescence spectrum.

The luminescence efficiency and color of Y_2O_2S : Eu are not affected by the shape of particles (e. g., round, plate, and column) or by particle sizes greater than 2 μm as observed by microscope. This is because Eu^{3+} luminescence is determined by the conditions of the short-range environment surrounding Eu^{3+} ions in the particles, rather than by long-range perfection.

6. Pigmentation

To maintain the same luminescence color at $x=0.637$, a further reduction of Eu concentration is expected with the application of pigment. By partial absorption of the $^5D_1$ Eu^{3+} luminescence with Fe_2O_3 pigment,[5)] the Eu concentration in Y_2O_2S : Eu phosphor is indeed reduced to the level of around 3.8 wt% from 4.2 wt%, saving 0.4 wt% Eu.

An ideal pigment material absorbs the $^5D_1$ Eu^{3+} luminescence (green-orange) while being transparent to the $^5D_0$ Eu^{3+} luminescence (orange red) in the phosphor screen. Organic pigment cannot be applied to picture tubes since the heat generated during the production process of the CRT causes the material to decompose. Only inorganic compounds can be considered as pigment for phosphor screens. In earlier times, Cd(S, Se) pigment was applied to red phosphor powder. More recently, Fe_2O_3 powder (i. e., pigment of red paint) has been

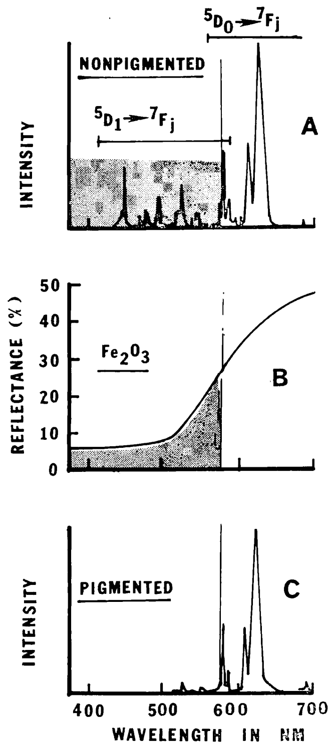

Fig. 7 Cathodoluminescence spectrum of unpigmented Y_2O_2S:Eu (A); reflectance spectrum of Fe_2O_3 pigment (B); and cathodoluminescence spectrum of pigmented Y_2O_2S: Eu phosphor (C).

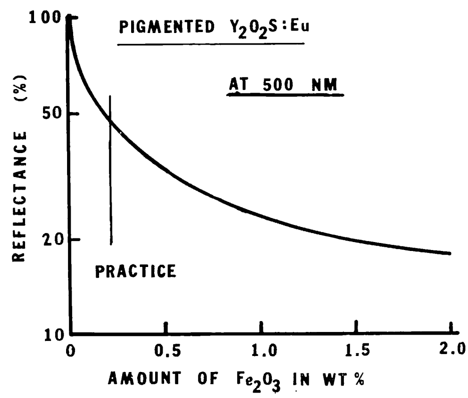

Fig. 8 Reflectance at 500 nm of Y_2O_2S: Eu phosphors pigmented with various amounts of Fe_2O_3.

substituted for Cd (S, Se).

Figure 7 (A) shows a CL spectrum of Y_2O_2S: Eu (0.005 mol). Figure 7 (B) shows a reflectance spectrum of Fe_2O_3 pigment powder. The shadowed wavelengths in Fig. 7 (B) indicate the subject of absorption by Fe_2O_3. Figure 7 (C) shows a CL spectrum of practical Y_2O_2S: Eu pigmented with Fe_2O_3 (0.2 wt% of phosphor powder). It can be seen that the luminescence intensities of the lines in the wavelengths shorter than 580 nm are effectively absorbed.

The magnitude of absorption of green-yellow lights in the CL spectrum of the Y_2O_2S: Eu phosphor screen is a function of the amount of Fe_2O_3 powder attached to the surfaces of phosphor particles. **Figure 8** shows a curve of the diffused reflectance of the pigmented Y_2O_2S: Eu phosphor screen at 500 nm plotted against the amount of Fe_2O_3 pigment. The reflectance (1-absorption) of phosphor powder pigmented with Fe_2O_3 is not a simple function of the amount of Fe_2O_3. The curve follows neither exponential nor bimolecular rules. First, at 0.2 wt%, the reflectance sharply decreases with Fe_2O_3 pigment (50% decrease), and then becomes dull. For instance, the reflectance decreases only 10% (totally 60% down) with the addition of another 0.2 wt% Fe_2O_3 (totally 0.4 wt%). Therefore, it can be said that 0.2 wt% Fe_2O_3 may be the appropriate amount of pigmentation of Y_2O_2S: Eu phosphor. With the pigmentation of 0.2 wt% Fe_2O_3 to Y_2O_2S: Eu, the Eu concentration giving the luminescence color of $x=0.637$ of the final product is substantially reduced to the level of 3.8 wt% from 4.2 wt%. A further reduction of Eu concentrations is expected with Fe_2O_3 of more than 0.2 wt%, but the brightness decreases when more Fe_2O_3 pigment is added.

Although Y_2O_2S: Eu phosphor powder is pigmented with the amount of exactly 0.2 wt% Fe_2O_3, the reflectance at 500 nm changes slightly (within 10%) with the (a) particle size of Fe_2O_3: (b) shape of phosphor particles; (c) surface conditions of phosphor particles; and (d) adhesion process of the pigment (e.g., aggregation of pigment) on the surfaces of phosphor particles. This is because the absorption of light in phosphor powder largely depends on optical scattering in the phosphor screen where the magnitude is determined by the conditions described above. To obtain good reproducibility, these conditions should be controlled.

7. Concluding Remarks

The brightness and color coordinates of cathodoluminescence of Y_2O_2S:Eu phosphors, including Fe_2O_3 pigmentation, have been studied as a function of Eu concentrations. The brightness of the practical phosphors strongly correlates with the luminescence color. An improvement of 3 % cathodoluminescence efficiency is very difficult, but a large improvement (about 95% increase) in the brightness is easily produced by the shift of the luminescence color to yellow. The color shift of cathodoluminescence may be optimized with the color coordinates of $x=0.637$ and $y=0.345$. The amount of the $^5D_1$ Eu^{3+} luminescence in the spectrum at a given Eu concentration is effectively and substantially controlled by application of Fe_2O_3 pigment to Y_2O_2S: Eu phosphor powder.

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