Low-Voltage Cathodoluminescence Properties of the Y_2O_2S:Eu Red Light Emitting Phosphor Screen in Field-Emission Environments

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Y_2O_2S:Eu phosphors doped with different concentrations of Eu were fabricated by a high-temperature flux fusion method. For applications in field emission displays, phosphor powders were electrophoretically deposited on an indium-tin oxide coated glass substrate to form a phosphor screen. Cathodoluminescence properties of phosphor screens were examined at a low excitation voltage of 5 kV in a high-vacuum chamber (5×10^{-8} Torr), and characteristics of Y_2O_2S:Eu phosphors, including brightness and wavelength data, are presented and discussed. The red emission brightness for the Y_2O_2S:Eu phosphor screens can be significantly improved by adjustment of the Eu additions, which decrease the x coordinate slightly, while having no significant influence on the color performance. Considering the effects of Eu concentrations on red light emission spectra and brightness for Y_2O_2S:Eu phosphor screens, it is found that brightness for Y_2O_2S:Eu phosphor screens could be obtained up to 120 cd/m^2 with chromaticity of $x = 0.63$ and $y = 0.36$, and the Eu dopant concentration is suggested to be in the range 6-7.5 wt %.
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Due to its outstanding features such as wide viewing angle, energy efficiency, large temperature range of operation, and compact size, the field emission display (FED) is believed to have a high potential for flat panel display applications.[1-3] The materials and technology utilized in FEDs are close to those of cathode ray tubes (CRTs). The basic structure of FEDs is to put fluorescent phosphors and microtip field emitters on two separate plates. Emitting electrons are attracted from the microtips through a high electric field on the backplate. Visible light is generated from a phosphor screen on the other end by using high-voltage accelerated electronic impact.

Yttrium oxysulfide doped with europium (Y_2O_2S:Eu) has sharper emission lines, leading to better colorimetric definition and higher cathodoluminescence (CL) efficiency than the other red phosphors.[4,5] Therefore, Y_2O_2S:Eu is a basic phosphor material that could be used in anode screens for FED devices. It is known that the shape and size of phosphor particles are critical in the fabrication of high-quality screens. Reducing the particle size gives a higher resolution.[6-9] Optimizing the particle size distribution will lead to a higher packing density for phosphor layers, and thus higher resolution can be achieved. Spherical particles also give a high packing density and a small light-scattering coefficient.[10,11] Moreover, the final quality of the information display in a view of phosphors can be determined by the brightness of phosphor screens. Consequently, not only the intrinsic properties of phosphor powders but also the optical characteristics of the phosphor screens should be taken into account to obtain a good anode plate for FED applications. In our previous study,[12] the uniform particle size distribution and sphere-like Y_2O_2S:Eu phosphor powders were successfully fabricated by the high-temperature flux fusion method. Those results indicated that the as-fabricated Y_2O_2S:Eu phosphors are suitable for application of the screening process in FED devices. Moreover, to estimate the validity of as-fabricated Y_2O_2S:Eu phosphor powders for FED applications, samples of Y_2O_2S:Eu red powders were prepared by a high-temperature flux fusion method and electrophoretically deposited on an indium-tin oxide (ITO) coated glass substrate to form a phosphor screen. A series of CL measurements were examined under excitation voltage of 5 kV in a high-vacuum chamber ($\sim 5 \times 10^{-8}$ Torr). In this study, the spectral and optical properties of Y_2O_2S:Eu phosphor screens were evaluated. Furthermore, the effects of Eu additive contents on the emission color shifting and brightness for Y_2O_2S:Eu red phosphor screens were investigated to optimize the performance of red phosphor screens for FED applications.

Experimental

Y_2O_2S:Eu powders were prepared by the sulfide-fusion method. Appropriate amounts of Y_2O_3 and Eu_2O_3 were mixed with the flux, containing S, Na_2CO_3, K_2CO_3, Li_2CO_3, and Li_3PO_4, and then fired at high temperature in the range 1000-1200°C to undergo a solid-melt reaction. The atmosphere in the heating tube was controlled to be oxygen-free during firing. After the firing process, powders were washed with water to remove the residual flux and flux by-products and then etched with 5% HNO_3 solution for a clean, smooth particle surface. The detailed process to fabricate the Y_2O_2S:Eu phosphor powders was reported elsewhere.[12,13] The concentrations of Eu in Y_2O_2S of as-derived powders were evaluated by inductively coupled plasma (ICP, GVM-1000P, Shimadzu, Japan). In order to determine the optimum Eu additive content in Y_2O_2S:Eu compositions to optimize the performance of phosphor screens for FED applications, the concentrations of Eu in Y_2O_2S phosphors were controlled in the range 4-9 wt %. The mean particle size of the as-fabricated phosphor powders used in the screen process was measured as 3 μm.

The phase and crystal structure of the synthesized phosphors were analyzed with a X-ray diffractometer (D/MAX-B, Rigaku, Japan) with a wavelength of Cu Kα ($\lambda = 1.5406$ Å). The scanning rate was 2θ/min.

To derive a phosphor screen, Y_2O_2S:Eu phosphor powders were coated onto the ITO glass substrate by an electrophoretic deposition method. Electrophoretic deposition is a materials processing technique in which particles suspended in liquid are deposited onto a substrate under the influence of an applied electric field.[14,15] Phosphor powders were first suspended in isopropyl alcohol (IPA) which contained dissolved magnesium nitride. ITO glass anode and copper plate cathodes were assembled at 10 mm distance apart in the cell. The voltage of the electrode connecting with the dc power supply was 150 kV.

In the CL measurement system, the electron-beam was generated and accelerated by an electron gun, and focused on the phosphor screens with a certain spot size. Y_2O_2S:Eu phosphor screens were operated in the chamber at a pressure under 5×10^{-8} Torr and excited by an electron-beam with controlled accelerating voltage (5 kV) and emission current (0.5 μA/cm^2). The CL emitting light passed through a lens to focus on an optical fiber and the emission
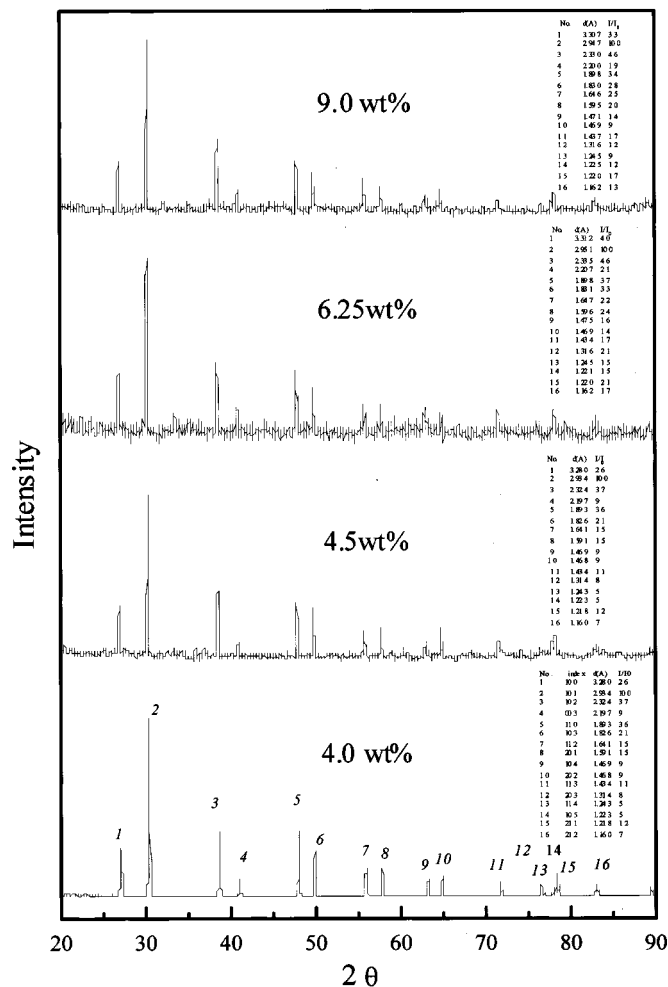
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Figure 1. The XRD patterns of Y$_2$O$_2$S:Eu phosphors with different concentrations of Eu.

Figure 2. The relationship of lattice parameters with respect to Eu concentrations in Y$_2$O$_2$S:Eu phosphors.

spectrum was recorded by Fourier transfer analysis (Nicolet MX-1, Acton Research Corp.), with the detecting range 360-830 nm. The measurement temperature was kept at room temperature. Moreover, the CIE (Commission International de l'Eclairage) color coordinates and brightness of emitting light for Y$_2$O$_2$S:Eu phosphor screens were determined with a Chroma Meter (Minolta CS-100, Japan). Five measurements were carried out and luminance data were averaged.

Results and Discussion

It is noted that Y$_2$O$_2$S is hexagonal crystal structure and the lattice parameter is defined as $a = 0.37$ and $c = 0.65$ nm. In this study, the Eu activator was doped into yttrium oxysulfide. Figure 1 is the X-ray diffraction (XRD) patterns of phosphors with different Eu addition in starting materials derived under the same fabrication process. All the XRD lines observed in Y$_2$O$_2$S:Eu phosphor with different Eu concentration matched the lines given in JCPDS data files. According to XRD patterns the as-fabricated phosphors were well crystallized. It seems that the addition of dopant activator as Eu would not affect the growth and phase transformation of Y$_2$O$_2$S phase, which is the host phosphor.

Moreover, from the plane space d_{hkl} data of the peaks in Fig. 1 and the overall plane index, the lattice parameters of unit cell for Y$_2$O$_2$S:Eu crystalline can be obtained by calculation as follows. The host phase of Y$_2$O$_2$S:Eu is a hexagonal unit cell characterized by
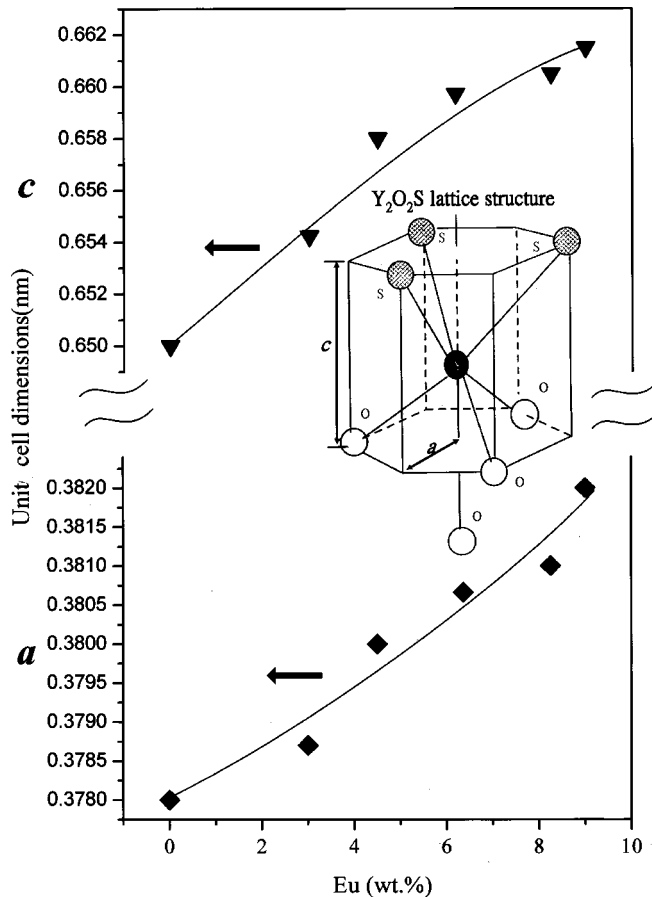
two variable parameters, a and c. The plane-spacing equation for a hexagonal system is

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2} \qquad [1]$$

The lines in Fig. 1 are designated as line 1 to line 16, in which the four highest intensity lines are designated to be 2, 3, 5, and 6. One can obtain the unit cell parameters a and c for each sample doped different concentration of Eu$_2$O$_3$, as shown in Fig. 2. It appears that unit cell parameters for Y$_2$O$_2$S hexagonal crystalline are slightly enlarged with the increasing amounts of Eu$_2$O$_3$ addition in Y$_2$O$_2$S:Eu phosphor. Considering the crystalline structure of Y$_2$O$_2$S, it contains a group of three oxygen ions and a group of three sulfurs. Yttrium is in the central site on the C_3 axis and the other single oxygen is on the other side of the C_3 axis, being slightly apart from the base plane. Thus, Y-S and Y-O bond length are approximately 0.29 and 0.223 nm. From crystallographic study,[16] it is found that the additional Eu ions are expected to occupy the yttrium ion sites. Because the radius of Eu ion (0.113 nm) is slightly larger than that of yttrium ion (0.106 nm), the lattice parameters would be somewhat enlarged when the Eu ions occupy the site of yttrium ions. Thus, the more Eu dopant into the Y$_2$O$_2$S:Eu phosphor, the larger the unit cell parameters.

The basic CL properties of a Y$_2$O$_2$S:Eu phosphor screen were analyzed in a high vacuum chamber (5×10^{-8} Torr) with an electron gun to obtain the information. The CL spectra in the wavelength range between 500 and 630 nm for phosphor screens with different Eu activator concentrations are given in Fig. 3. Obviously, the emission spectra of Eu^{3+} activated Y$_2$O$_2$S:Eu phosphor screens shows
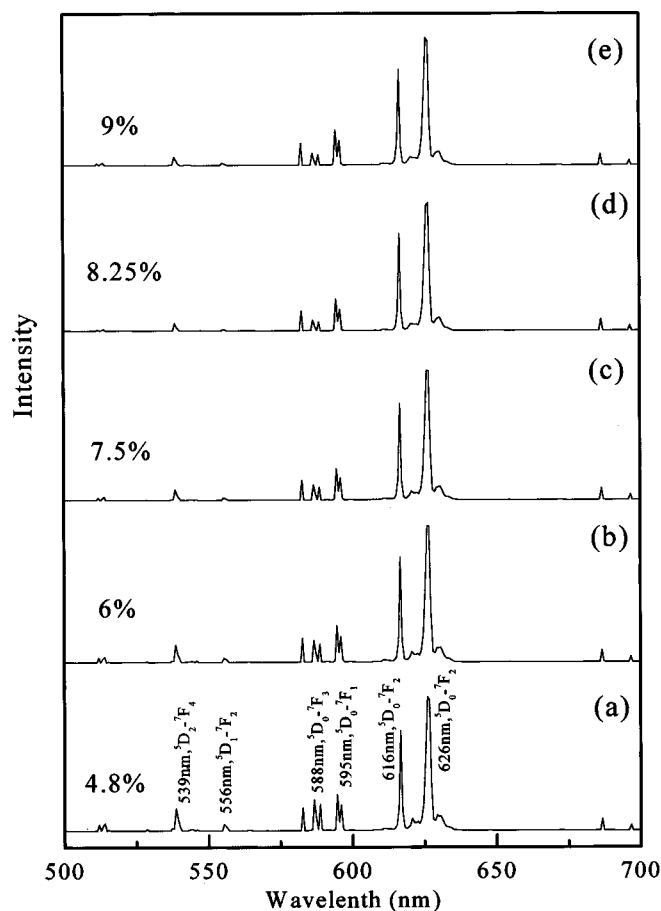
Figure 3. CL spectra of Y_2O_2S:Eu phosphors with various Eu activator concentrations: (a) 4.8, (b) 6, (c) 7.5, (d) 8.25, and (e) 9%.

Figure 4. Intensity ratio of $^5D_0 \rightarrow {}^7F_2$ (626 nm) to $^5D_1 \rightarrow {}^7F_4$ (556 nm) line as a function of Eu concentration.

three different regions peaking at 539, 556, and 626, indicating excited states $^5D_2$ (bluish-green light emitting), $^5D_1$ (greenish-orange light emitting), and $^5D_0$ (red light emitting), respectively. All the emission lines for Y_2O_2S:Eu phosphors are very well addressed in literature.[17,18] Typically, the red color emitting of Y_2O_2S:Eu is due to the transition from $^5D_0 \rightarrow {}^7F_j$ of Eu^{3+}, in which the wavelength of 626 nm shows the strongest intensity. On the other hand, the short wavelength lines (*i.e.*, $^5D_0 \rightarrow {}^7F_2$ and $^5D_1 \rightarrow {}^7F_4$ transition) were disadvantages in view of the location of the CIE color coordinates for red color phosphor application. Figure 4 shows the intensity ratio of the $^5D_0 \rightarrow {}^7F_2$ (626 nm) line to $^5D_1 \rightarrow {}^7F_2$ (556 nm) line. Figure 5 indicates the intensity ratio of the $^5D_0 \rightarrow {}^7F_2$ (626 nm) line to $^5D_2 \rightarrow {}^7F_4$ (539 nm) line with 5 kV accelerating voltage and 0.5 $\mu A/cm^2$ emission current applied. Results indicate that the intensity of the short wavelengths such as 539 nm ($^5D_2 \rightarrow {}^7F_4$) and 556 nm ($^5D_1 \rightarrow {}^7F_2$) are relatively degraded with the Eu concentrations. Accordingly, as the Eu dopant concentration is raised, the relative intensity for 626-556 or 539 nm is also increased. This indicates that the luminescence light emitted from Y_2O_2S:Eu phosphors containing enriched Eu tends to become red. With the increase of Eu concentration, the emission in the short-wavelength region (blue and green region) disappears completely. Moreover, the color shifting of the emission light could be identified more definitely with the aid of CIE color coordinates. Figure 6 shows a curve representing both the *x* and *y* value of CIE coordinates vs. the Eu dopant concentrations in Y_2O_2S:Eu phosphor. By addition of various concentrations of Eu activators in the Y_2O_2S:Eu red phosphor, the *x* values in CIE coordinates show a linear dependence with respect to the Eu concentration. Generally speaking, for *x* > 0.625, the color
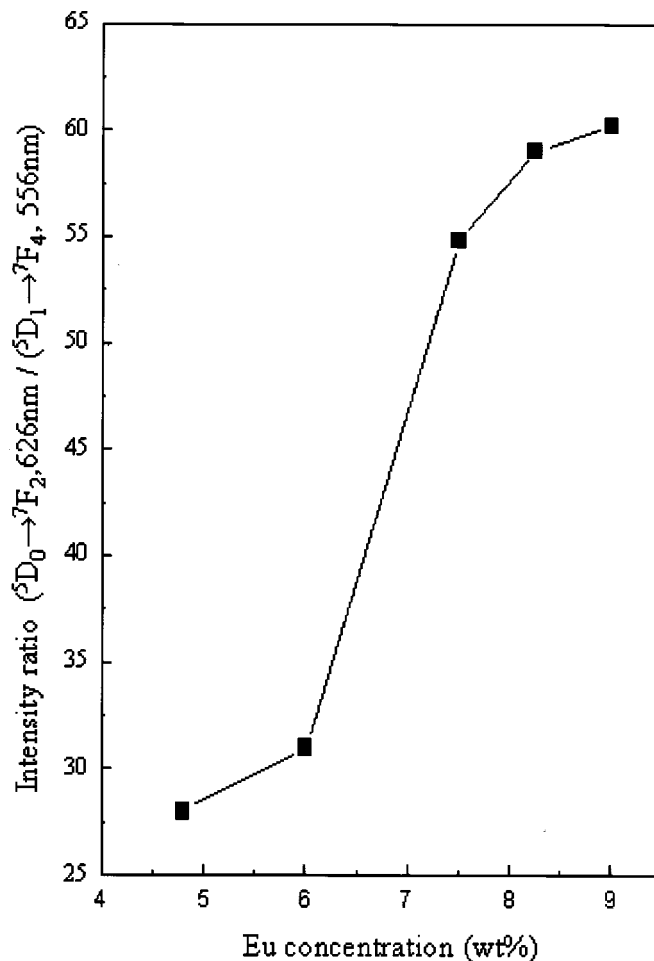
is red in viewing, while for *x* < 0.625, it is reddish orange. The color of emitting light shifts from reddish orange to red with the increase of Eu activator concentration, as presented in Fig. 6. This is another evidence that the relative intensity of the main transition from $^5D_0$ to $^7F_2$ provides the red-emitting light. Besides, the intensity of other spectra peaks becomes smaller as the Eu dopant concentration increases. This results in the red color for high Eu concentration phosphor.

Not only emission color but also brightness is one of the important CL properties for phosphor screens. Brightness also depends on the activator concentration. Figure 7 shows the dependence of CL brightness of Y_2O_2S:Eu phosphor screens on the Eu dopant concentrations. It is apparent that the relative brightness degrades substantially with increasing Eu dopant concentrations. The Y_2O_2S:Eu phosphors containing 7.5 wt % Eu exhibit more than twice the brightness (90 cd/m²) of those with 9 wt % (35 cd/m²). Similarly, Y_2O_2S:Eu phosphors with 6 wt % Eu activator show nearly four times brightness (120 cd/m²) than those with 9 wt % Eu activator. According to the spectra analysis, the brightness of Y_2O_2S:Eu phosphor is mainly contributed by the intensity of wavelength at 626 nm, corresponding to the electron transition from the state $^5D_0$ to $^7F_2$. Figure 8 illustrates the relationship between the intensity of the 626 nm ($^5D_0 \rightarrow {}^7F_2$) line in the CL spectra diagram and the Eu dopant concentration of Y_2O_2S:Eu red phosphor. The relative intensity of wavelength of 626 nm also depends on the Eu concentration in Y_2O_2S:Eu phosphor. By combining the color coordinates shift with Eu addition and brightness dependence on Eu concentration, a rela-
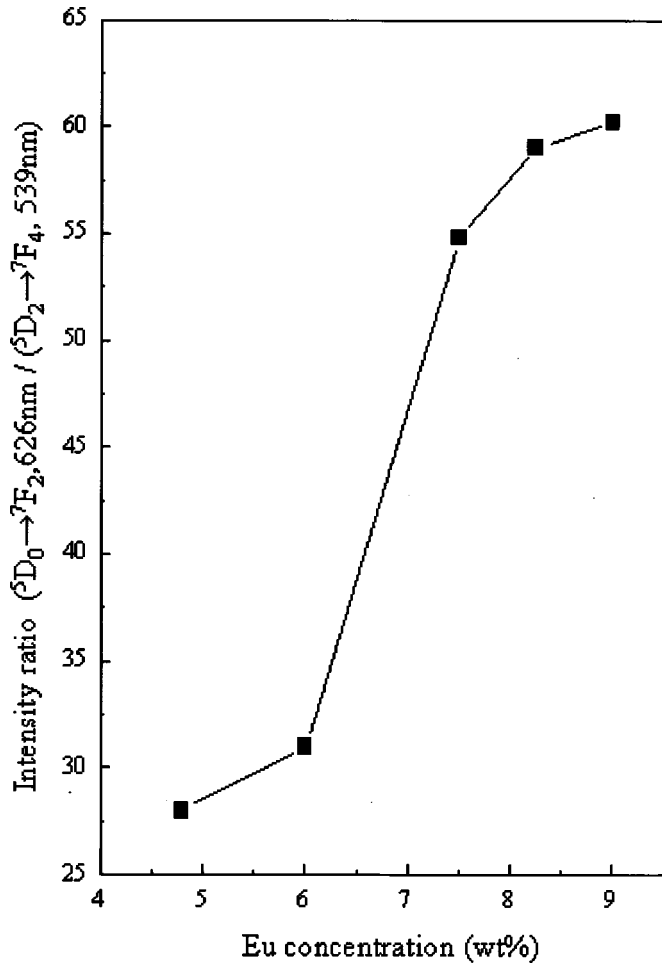
Figure 5. Intensity ratio of $^5D_0 \rightarrow {}^7F_2$ (626 nm) to $^5D_2 \rightarrow {}^7F_4$ (539 nm) as a function of Eu concentration.
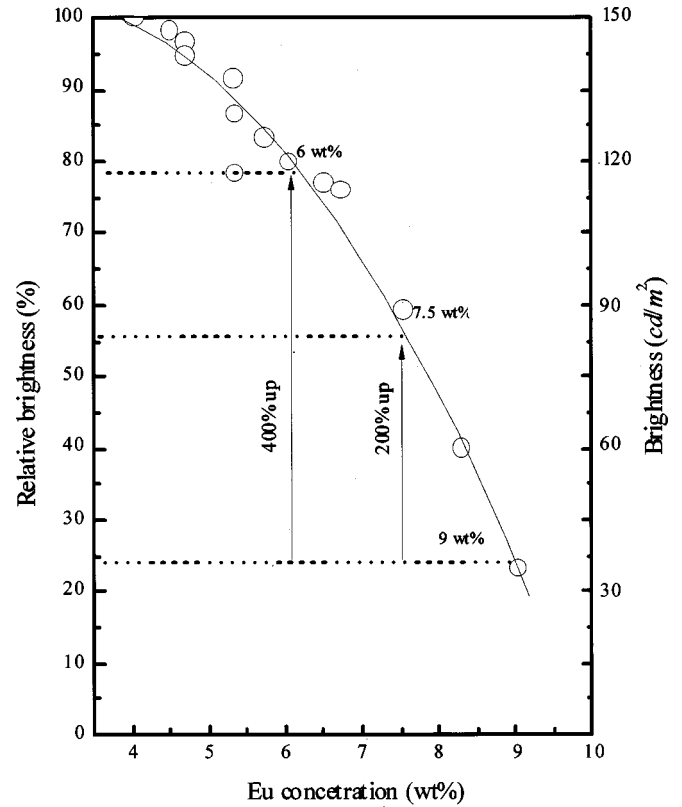

Figure 7. The relative brightness as a function of Eu concentration in the Y_2O_2S:Eu phosphor.
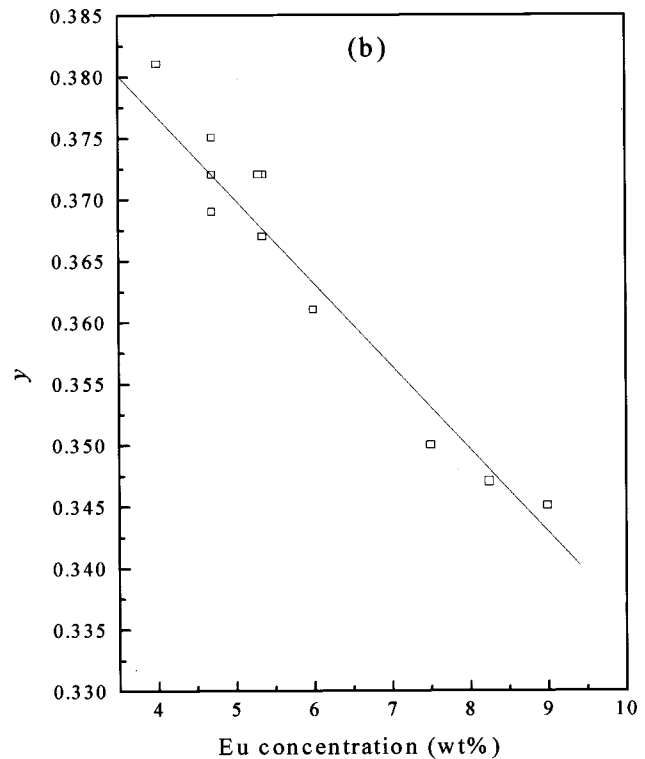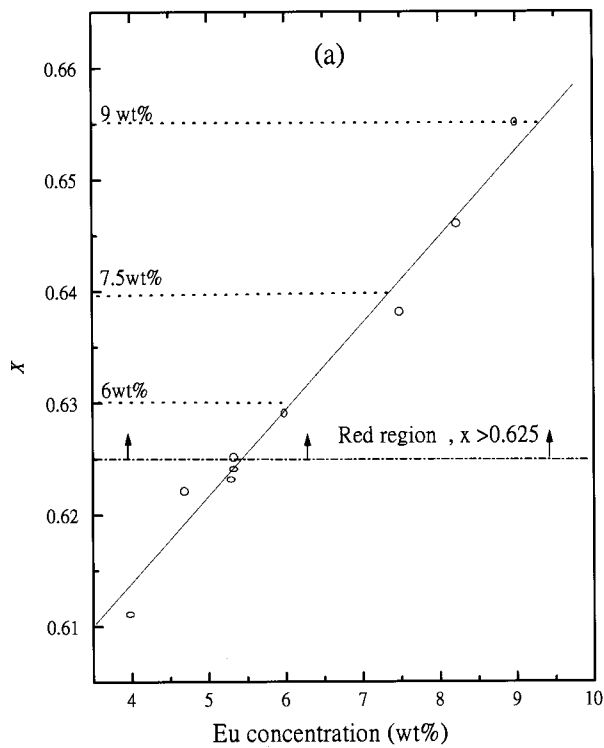

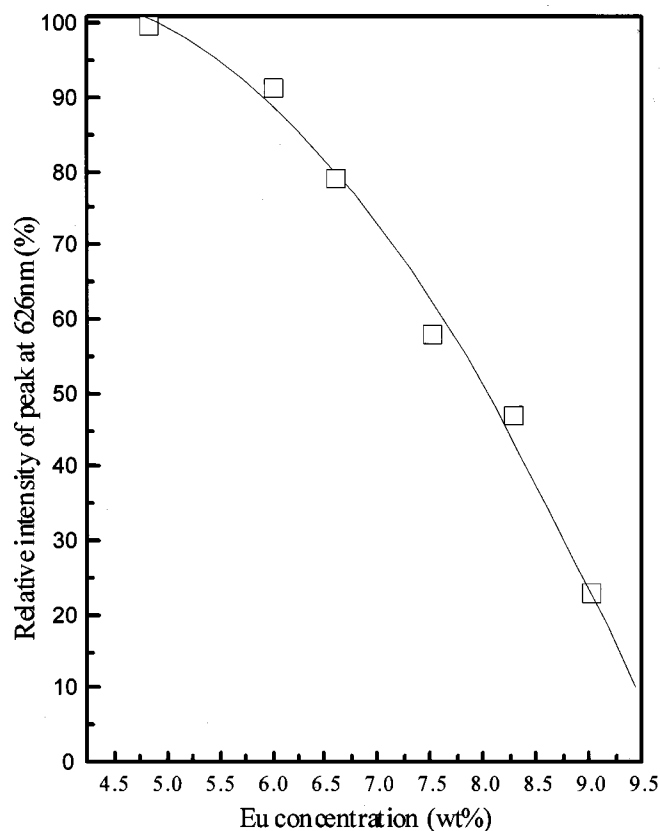**Figure 6.** (a) x and (b) y coordinate of Y_2O_2S:Eu as a function of Eu concentration.

Figure 8. Relative intensity of 626 nm line in CL spectra as a function of Eu concentration.

Figure 9. The relationship between the relative brightness and *x* coordinates of CIE for the Y_2O_2S:Eu phosphor.

tionship curve between brightness and color coordinates is attained in Fig. 9. It shows a similar tendency as those in Fig. 7 and 8, in which brightness degrades as the, *x* value increases (increasing Eu concentration). The CL emitting light of a larger *x* coordinate shows the lower brightness.

It can be noted that the greater tendency for the emission light to turn red, the lower the relative brightness that is observed, *i.e.*, the brightness of 0.63 in CIE coordinate is 270% up from that of *x* = 0.65 in CIE coordinates, and the brightness of *x* = 0.64 in CIE coordinate is 200% up from that of *x* = 0.65 CIE coordinate. For application of Y_2O_2S:Eu red phosphor in FEDs, the availability of color shift is, in fact, an advantage. According to the current measurement, the emission brightness for the Y_2O_2S:Eu phosphor screen can be significantly enhanced by reducing the addition concentration of Eu activator, which decreases the *x* coordinate slightly and would not affect the color shift. In fact, the color shift from *x* = 0.655 to *x* = 0.63 is not easily resolved by the naked eye. Therefore, to achieve sufficient brightness ($\sim$120 cd/m^2) in Y_2O_2S:Eu phosphor screens, Eu dopant concentration is suggested to be in the range 6-7.5 wt %.

Conclusions

Through CL measurement in a high-vacuum chamber with a acceleration voltages of 5 kV, the feasibility of Y_2O_2S:Eu phosphors for FED applications was presented. The brightness of red light emission for Y_2O_2S:Eu phosphor screens was significantly improved by reducing the doping concentrations of Eu activator in Y_2O_2S:Eu phosphor. The performance of phosphor screens was optimized based on the brightness and the CIE color coordinate of the emitting light. With the red light emitting in CIE color coordinates (*x* = 0.63 and *y* = 0.36), the brightness of the phosphor screen for
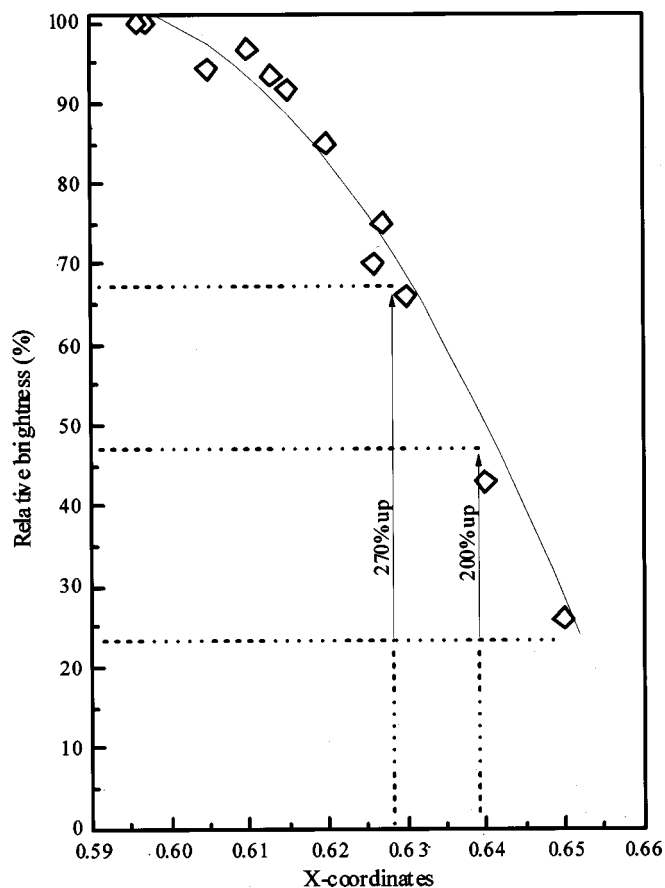
Y_2O_2S:Eu doped with 6 wt % Eu activator exhibited four times higher than those doped with 9 wt % Eu activator. The CL brightness of the electrophoretically deposited Y_2O_2S:Eu phosphor screens at low voltage in a high vacuum of 5×10^{-8} was up to 120 cd/m^2.

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