Moderate Voltage Cathodoluminescence of Y_2O_2S:Eu, $SrGa_2S_4$:Eu, and ZnS:Ag,Al for CNT-FEDs

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Received July 26, 2006

Key Words : Y_2O_2S:Eu, $SrGa_2S_4$:Eu, ZnS:Ag,Al, Cathodoluminescence, CNT-FED

Field emission displays (FEDs) are promising technologies for the realization of thin flat panel displays characterized by high contrast, wide viewing angle, and low power consumption. The materials and technology utilized in FEDs resemble those of cathode-ray tubes (CRTs). The basic structure of a FED is two separate plates, one with phosphors and the other with field emitters. Electrons emitted from the emitter tips are attracted through an electric field to the back plate. Many researchers have studied the cathodoluminescence (CL) properties of phosphors for use in low voltage (< 2 kV) Spindt-type FEDs.[1-5] Carbon nanotubes (CNTs) have been considered prime candidates for use as the field emitters for FEDs due to their high aspect ratios, sharp tips, high chemical stabilities, and high mechanical strengths.[6-8] Moderate voltages (3-8 kV) are required for operating the CNT-FEDs in order to obtain adequate brightness.

At present, however, there is limited information on the CL properties of sulfide phosphors at moderate voltages. In the present study, Y_2O_2S:Eu, $SrGa_2S_4$:Eu, and ZnS:Ag,Al, which are red-, green-, and blue-emitting phosphors respectively, were synthesized by solid-state reaction. The CL properties of the three sulfide phosphors were investigated at applied voltages of 3-8 kV to determine whether they are suitable for use in CNT-FEDs.

Experimental Section

Y_2O_3 (99.99%, Rhodia), Eu_2O_3 (99.99%, Aldrich), SrS (99.9%, Strem), Ga_2S_3 (99.99%, High Purity), S (99.998%, Aldrich), $(CH_3)_4NCl$ (98%, Aldrich), $Eu(NO_3)_3 \cdot 6H_2O$ (99.99%, Aldrich), $(CH_3)_2NCS_2Na \cdot 2H_2O$ (98%, TCI), Li_2CO_3 (Aldrich), Na_2CO_3 (Aldrich), and K_2HPO_4 (Aldrich), ZnS (99.9%, Sakau), $AgNO_3$ (Samchun), AlF_3 (Junsei), NH_4Cl (Aldrich) were used as received. The red emitting Y_2O_2S:Eu phosphor with activator concentration of 6.0% was prepared via solid-state reactions. Briefly, a mixture of $Y_2O_3/Eu_2O_3/S/Na_2CO_3/K_2HPO_4$ with a weight ratio of 1.76:0.18:0.8:1.2:0.27 was fired at 1250 °C for 4 h. Green emitting $SrGa_2S_4$:Eu phosphor with an europium activator concentration of 4.0% was synthesized by firing a mixture of SrS, Ga_2S_3, S, Li_2CO_3, and the europium complex $\{[(CH_3)_4N]Eu[(CH_3)_2NCS_2]_4\}$ with a weight ratio of 4.53:9.29:15.2:1.11:0.15 at 850 °C for 1.5 h. The europium complex, $\{[(CH_3)_4N]Eu[(CH_3)_2NCS_2]_4\}$, was obtained by precipitation of mixed solutions of $(CH_3)_4NCl$, $Eu(NO_3)_3 \cdot 6H_2O$, and $(CH_3)_2NCS_2Na \cdot 2H_2O$. Blue emitting ZnS:Ag,Al phosphor, in which the Ag activator and Al coactivator concentration was fixed at 0.046%, was prepared by firing a $ZnS/AgNO_3/AlF_3/NH_4Cl$ mixture of weight ratio 98.0:0.078:0.039:1.0 at 980 °C for 3 h under 5% H_2 in N_2 gas flow. All phosphors were washed with water to remove the flux residue, then filtered and dried under vacuum at room temperature.

The structures of the three sulfide phosphors were analyzed with powder X-ray diffraction (XRD, Phillips PW 1710) using Cu K_α radiation. The morphologies of the phosphors were characterized with scanning electron microscopy (SEM, Phillips XL30 ESEM-FEG). CL measurements were carried out in a high-vacuum (5×10^{-7} torr) chamber for various excitation energies. Patch-type samples were prepared on metal holders. The phosphor patches were placed in a demountable CRT and excited with electron beams with various DC excitation energies.

Results and Discussion

Figure 1 shows the XRD patterns and Miller indices of Y_2O_2S:Eu, $SrGa_2S_4$:Eu, and ZnS:Ag,Al. The XRD pattern of

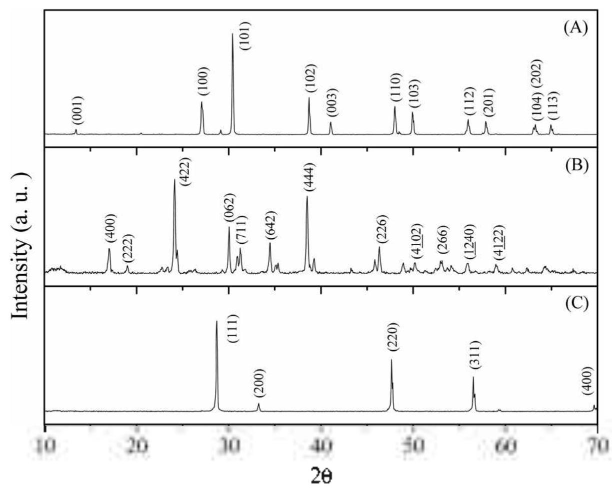

Figure 1. X-ray diffraction patterns and Miller indices of (A) Y_2O_2S:Eu, (B) $SrGa_2S_4$:Eu, and (C) ZnS:Ag,Al.

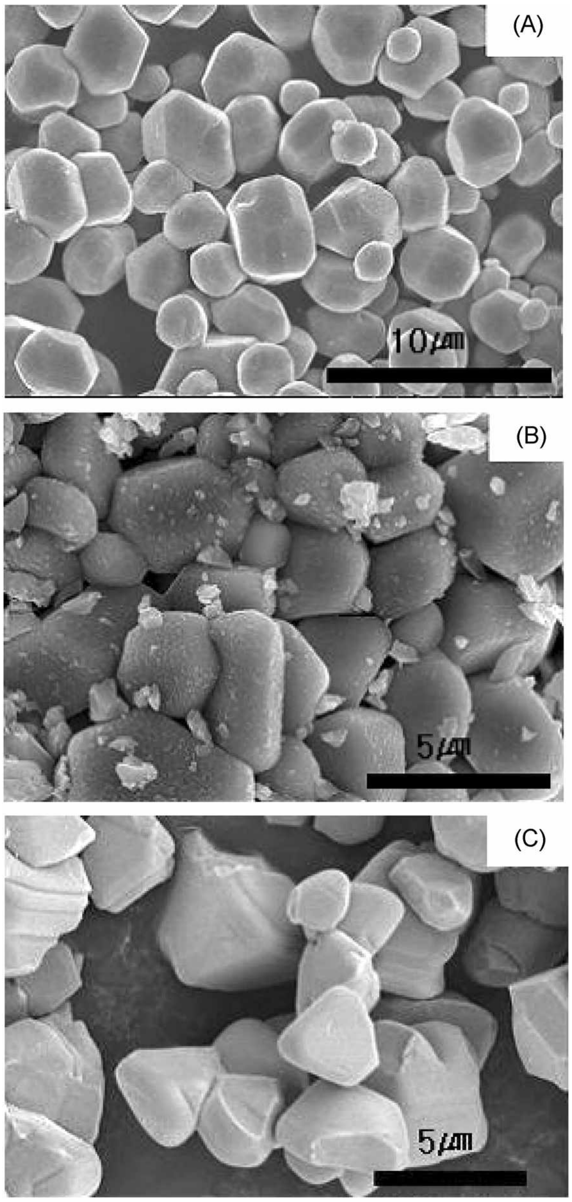

Figure 2. SEM images of (A) Y_2O_2S:Eu, (B) $SrGa_2S_4$:Eu, and (C) ZnS:Ag,Al.

Y_2O_2S:Eu matches that of hexagonal Y_2O_2S (JCPDS 24-1424) with a unit cell characterized by a = 3.81 Å and c = 6.59 Å.[9] The XRD pattern of $SrGa_2S_4$:Eu is identical to that of orthorhombic $SrGa_2S_4$ (JCPDS 25-0895), which has a unit cell characterized by a = 20.84 Å, b = 20.50 Å, and c = 12.20 Å.[10] The XRD pattern of ZnS:Ag,Al coincides with that of cubic ZnS (JCPDS 05-0566) with a = 5.41 Å.[11] In the Y_2O_2S:Eu phosphor, the Eu^{3+} ions occupy Y^{3+} sites. In the $SrGa_2S_4$:Eu phosphor, the Sr^{2+} ions are substituted by Eu^{2+} ions. In the ZnS:Ag,Al phosphor, the Ag activator and Al coactivator are introduced with nearly equal concentrations at the Zn^{2+} sites in the ZnS lattice. Since Ag is monovalent and Al is trivalent, charge compensation is realized in the ZnS lattice. Figure 2 shows SEM images of the Y_2O_2S:Eu, $SrGa_2S_4$:Eu, and ZnS:Ag,Al phosphors. The particles of Y_2O_2S:Eu, $SrGa_2S_4$:Eu, and ZnS:Ag,Al had average sizes of

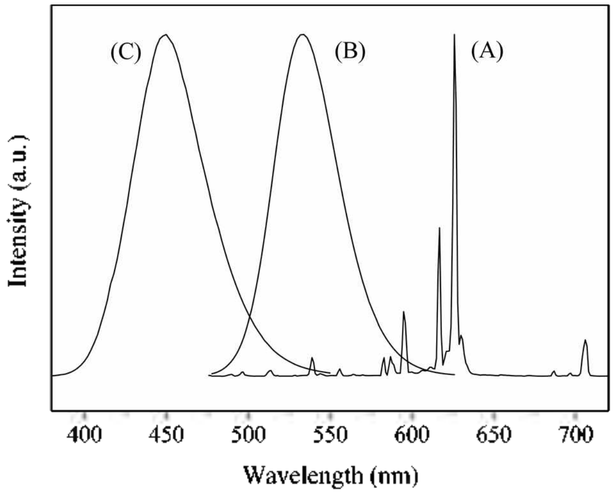

Figure 3. Normalized cathodoluminescence spectra of (A) Y_2O_2S:Eu, (B) $SrGa_2S_4$:Eu, and (C) ZnS:Ag,Al.

4 μm, 3 μm, and 3 μm, respectively.

Figure 3 shows the normalized CL spectra of the Y_2O_2S:Eu, $SrGa_2S_4$:Eu, and ZnS:Ag,Al phosphors. For the Y_2O_2S:Eu phosphor, main emission peaks are observed at 626 and 617 nm, which are assigned to the Eu^{3+} transition $^5D_0 \rightarrow {}^2F_2$.[12] $SrGa_2S_4$:Eu exhibits an emission band at 535 nm, which is due to the $4f^65d^1$ (a_1) $\rightarrow 4f^7$ transition of the Eu^{2+} ion.[13,14] ZnS:Ag,Al has an emission band at 450 nm, which is caused by a donor-acceptor pair type transition from the Ag^+ donor level to the Al^{3+} acceptor level.[15] These findings therefore show that Y_2O_2S:Eu, $SrGa_2S_4$:Eu, and ZnS:Ag,Al phosphors can be used as red-, green-, and blue-emitting CL phosphors, respectively.

The CL brightness characteristics of the Y_2O_2S:Eu, $SrGa_2S_4$:Eu, and ZnS:Ag,Al phosphors under applied voltages of 3 to 8 kV are shown in Figure 4. For all phosphors, the CL brightness is roughly proportional to the applied voltage. At an applied voltage of 7 kV and a current density of 3 μA/cm^2, the CL brightnesses of the Y_2O_2S:Eu, $SrGa_2S_4$:Eu, and ZnS:Ag,Al phosphors are 764, 1431, and

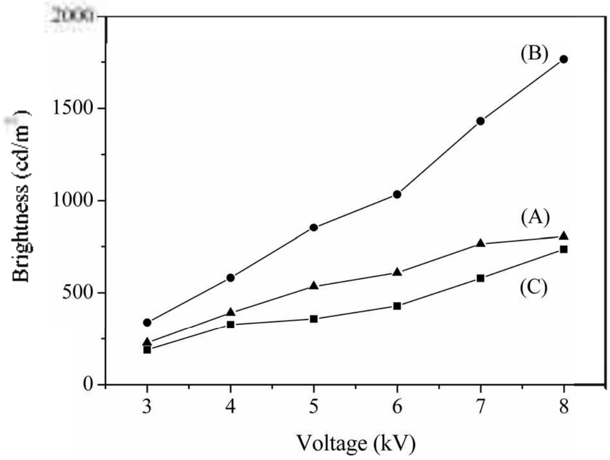

Figure 4. Cathodoluminescence brightness as a function of applied voltage for (A) Y_2O_2S:Eu, (B) $SrGa_2S_4$:Eu, and (C) ZnS:Ag,Al.

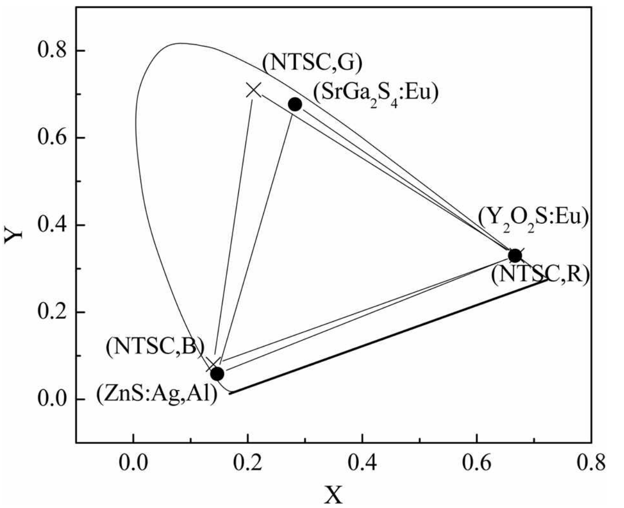

Figure 5. The CIE diagram and chromaticity coordinates of Y_2O_2S:Eu, $SrGa_2S_4$:Eu, and ZnS:Ag,Al, as well as NTSC red, NTSC green, and NTSC blue.

579 cd/m^2, respectively. Previously it has been proposed that the red, green, and blue luminescences should be 460, 1100, and 270 cd/m^2 in order to achieve the level of white required for a typical display, 200 cd/m^2.[16] Therefore, the CL brightnesses of the Y_2O_2S:Eu, $SrGa_2S_4$:Eu, and ZnS:Ag,Al phosphors exceed the levels required for CNT-FED applications.

Figure 5 shows the Commission International de l'Eclairage (CIE) diagram and chromaticity coordinates of the Y_2O_2S:Eu, $SrGa_2S_4$:Eu, and ZnS:Ag,Al phosphors, as well as the red, green, and blue of the NTSC (National Television Standard Committee).[17] The chromaticity coordinates of Y_2O_2S:Eu and ZnS:Ag,Al, (0.67, 0.33) and (0.15, 0.06), almost coincide with the NTSC red and blue coordinates, (0.67, 0.33) and (0.14, 0.08), respectively, indicating that Y_2O_2S:Eu and ZnS:Ag,Al have excellent color purities. However, the chromaticity coordinates of $SrGa_2S_4$:Eu, (0.28, 0.68), are not close to those of NTSC green, (0.21, 0.71). The area of the region inside the triangle drawn by connecting the NTSC red, green, and blue coordinates is used as the reference value for the color purity of a display panel. The area of the triangle drawn by connecting the positions of the Y_2O_2S:Eu, $SrGa_2S_4$:Eu, and ZnS:Ag,Al phosphors is 90.8% of that of the NTSC triangle. Given that a typical display panel is required to have a color purity of at least 70% of that of the NTSC triangle, the color purity of a CNT-FED based on Y_2O_2S:Eu, $SrGa_2S_4$:Eu, and ZnS:Ag,Al phosphors would be much better than that typically required for display panels.

In conclusion, the moderate voltage CL properties of three sulfide phosphors have been investigated to determine their suitability for use in CNT-FEDs. Y_2O_2S:Eu, $SrGa_2S_4$:Eu, and ZnS:Ag,Al were chosen as red-, green-, and blue-emitting CL phosphors, respectively. The CL brightnesses of the Y_2O_2S:Eu, $SrGa_2S_4$:Eu, and ZnS:Ag,Al phosphors at a voltage of 7 kV and a current density of 3 μA/cm^2 were 764, 1431, and 579 cd/m^2, respectively, which are sufficient to generate the level of white required by a typical display. In addition, the chromaticity coordinates of Y_2O_2S:Eu, $SrGa_2S_4$:Eu, and ZnS:Ag,Al were such that these phosphors would give excellent color purity in display applications. The present results therefore indicate that Y_2O_2S:Eu, $SrGa_2S_4$:Eu, and ZnS:Ag,Al are excellent red-, green-, and blue-emitting phosphors for CNT-FED applications, respectively.

Acknowledgments. This work was supported by the Ministry of Commerce, Industry and Energy of Korea through a Components and Materials Technology Development project (No. 0401-DD2-0162). This work was also supported by a grant number 2005-02522 (M10503000255-05M0300-25510) from the Nano R&D Program of the Ministry of Science and Technology. Professor Huh also thanks to Brain Korea 21 project.

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