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Research Article

Rare Earth Doped Alkali Earth Sulfide Phosphors for White-Light LEDs

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CaS:Eu and SrS:Eu phosphors were synthesized by solid-state reaction. The effects of doping concentrations on luminescent properties of phosphors are investigated. The samples are excited using electroluminescent blue light emitting diode (460 nm) to examine them as potential coating phosphors for white-light LEDs. The excitation and emission spectra of these phosphors are broadband which can be viewed as the typical emission of Eu^{2+} ascribed to the 4f–5d transitions. Because of their broadband absorption in the region 400–630 nm, these phosphors meet the application requirements for blue LED chips. A white-light LED was fabricated through the integration of a 460 nm chip. The results indicate that these phosphors can be considered as candidates for the application in blue LED chip-based white-light LEDs.

1. Introduction

There has been much interest in light emitting diodes (LEDs) with emission wavelengths in the ultraviolet-to-infrared range. Major developments in wide bandgap III–V nitride compound semiconductors have led to the commercial production of high-efficiency LEDs [1–4]. Traditional colored LEDs have proven effective in signal applications, as indicator lights, and in automotive lightning. The development of white LEDs as a cost-competitive, energy-efficient alternative to conventional electrical lightning is very important for expanding LED applications toward general white lightning [5–7]. Phosphors activated with rare earth metal have been widely investigated in the past few decades on account of their technological importance [8]. In particular, phosphors for LED applications have received significant attention in recent years with the rapid development of white LEDs, which have such merits as high efficiency, long lifetime, and low power consumption [9]. Alkali earth sulfide phosphors, such CaS:Eu^{2+} (red) and SrS:Eu^{2+} (orange) are also good candidates for LED applications because all of them have strong absorption in the blue region that is suitable to blue LED pumping. Sulfide phosphors have been ignored for a long time because they are not chemically stable. However, sulfide phosphors fit well for LED applications with adhesive seal and blue excitation.

In the present study, we therefore investigated the optical properties of Eu^{2+} doped alkali earth sulfides, with particular focus on the photoluminescence (PL) characteristics of these phosphors and the color variations of phosphor-converted colored LEDs pumped by blue LEDs.

2. Experimental

SrS:Eu and CaS:Eu powdered samples have been prepared using a solid-state reaction method. Raw materials of assay 99.9% $SrCO_3$ and $CaCO_3$ are mixed with sulfur in a 3 : 2 wt. ratio. Dopant compound Eu_2O_3 was added with a specified doping concentration for each sample. Ammonium fluoride NH_4F was used as flux. The samples are weighed, mixed, and then ground into fine powder using agate mortar and pestle about an hour and then heated to 950°C and kept for 2 h in reducing environment. Body colors are orange and red for SrS:Eu^{2+} and CaS:Eu^{2+}, respectively. Emission and excitation

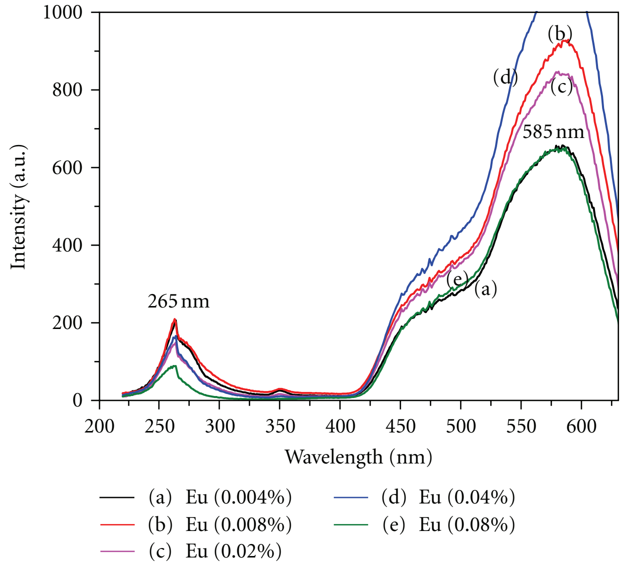

FIGURE 1: Excitation spectrum of CaS:Eu^{2+} at different wt%, monitored under 650 nm wavelength. Edited by Foxit Reader Copyright© by Foxit Corporation, 2005–2009 For Evaluation Only.

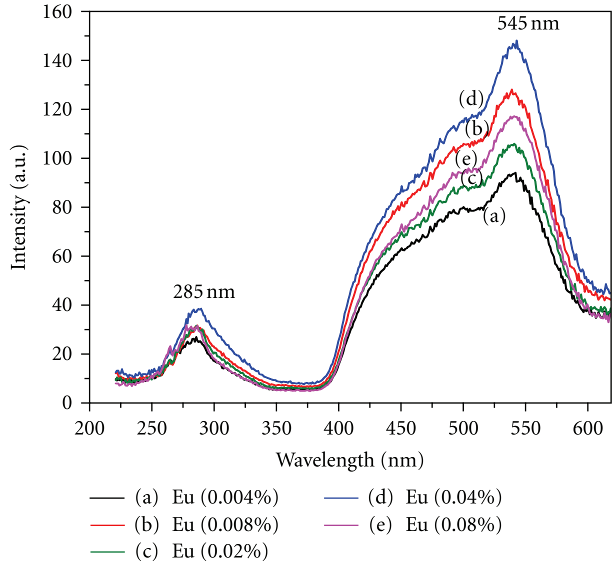

FIGURE 3: Excitation spectrum of SrS:Eu^{2+} at different wt%, monitored under 650 nm wavelength. Edited by Foxit Reader Copyright© by Foxit Corporation, 2005–2009 For Evaluation Only.

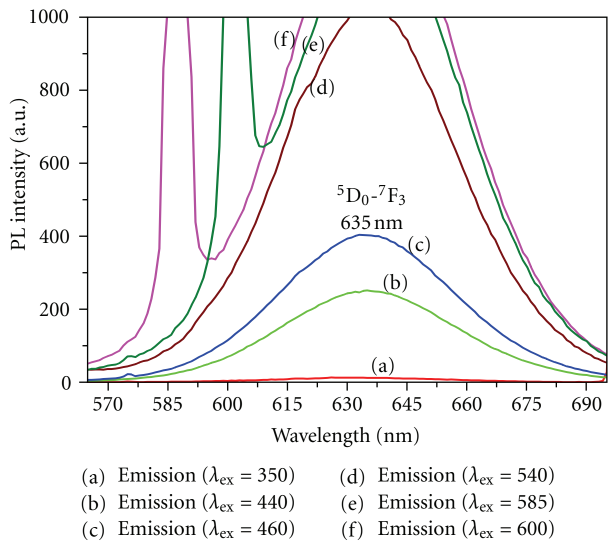

FIGURE 2: Emission of CaS:Eu^{2+} (0.04 wt%) under different excitation wavelengths. Edited by Foxit Reader Copyright© by Foxit Corporation, 2005–2009 For Evaluation Only.

spectra of the samples are measured with a Shimadzu RF 5301 PC spectrofluorophotometer. Blue LED with a 460 nm emission is also used as an excitation source. LEDs are coated by the prepared phosphors.

3. Results and Discussion

3.1. Red and Orange Emissions of CaS:Eu^{2+} and SrS:Eu^{2+}. CaS:Eu^{2+} is a very efficient phosphor with a red emission that can be excited with visible light. Its emission is a single broad-band range from 550 nm to 700 nm peaked at 635 nm resulting from the $4f_65d_1$ to $4f_7$ transition. Figure 1 shows the excitation spectrum of CaS:Eu at different wt%, which is monitored under 650 nm wavelength. The broad excitation bands of the 635 nm emission are found at 265 nm and 585 nm, which can be attributed to the e_g and t_{2g} field splitting 5d bands of Eu^{2+},respectively. Figure 2 shows the emission of CaS:Eu^{2+} (0.04 wt%) studied under different excitation wavelengths 350, 440, 460, 540, 585, and 600 nm. The 635 nm emission is very high under 585 nm excitation. The emission intensity is high for Eu (0.04 wt%), concentration quenching is observed. There is no charge transfer transition observed from Eu^{2+} ground state to the host conduction band, implying that the Eu^{2+} ground state is close to the host valence band [10], or the lowest 5d band overlaps with the host conduction band [11]. Bandgap of SrS is 4.32 eV that is smaller compared to CaS (4.434 eV). Lattice constant of SrS is 6.019 Å that is bigger than that of CaS (5.697 Å). The ligand field splitting of 5d level of Eu^{2+} results in red shifts for both emission and excitation peaks from CaS host to SrS host. A single broad-band emission of Eu^{2+} in SrS is blue shifted to 600 nm as shown in Figure 4. The broad-band excitation peaks of 5d field splitting components e_g and t_{2g} are found, respectively, to have a red shift to 285 nm and a blue shift to a region from 390 nm to 585 nm as shown in Figure 3. This indicates a weaker field splitting of the Eu^{2+} 5d state due to a weaker ligand field generated by a larger lattice. SrS and CaS have similar lattice symmetry, making them easier to have a solid solution in order to adjust the positions of absorption and emission and to obtain better color rendering for white LED applications [12].

3.2. Orange and Red Emissions Excited by LEDs. CaS:Eu^{2+} and SrS:Eu^{2+} with absorption peaks at 440 nm and 460 nm,

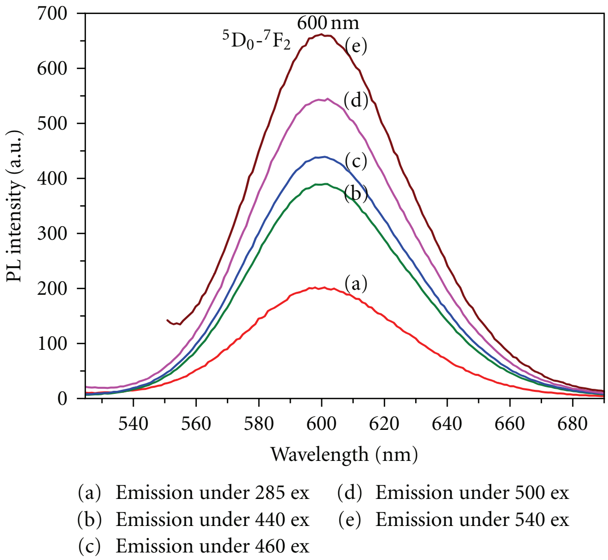

Figure 4: Emission of $SrS:Eu^{2+}$ (0.04 wt%) under different excitation wavelengths.

respectively, are of interest for blue LED applications. Upon excitation at 460 nm from the blue LED, these alkali earth sulfide phosphors emit strong orange and red light. Each of singly doped phosphors is individually blended into transparent adhesives and coated onto the blue LEDs. The resulting luminous efficiency of W-LED was found as high as 30 and 23.6 lm/W under 20 mA driving current. The CIE coordinates of W-LED are $x = 0.3395$, $y = 0.3434$ and $x = 0.3356$, $y = 0.2832$ with Ra values are 84.3 and 85.8, respectively.

4. Conclusion

The excitation and emission spectra of these phosphors show that all are broadband, which can be viewed as the typical emission of Eu^{2+} ascribed to the 4f–5d transitions. Because of their broadband absorption in the region 400–630 nm, these phosphors meet the application requirements for blue LED chips. The critical quenching concentration of Eu^{2+} in both phosphors is observed. Moreover, a white light LED was fabricated through the integration of a 460 nm chip. The results indicate that CaS:Eu phosphor can be considered as the most promising candidate for the application in blue LED chip-based white-light LEDs.

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