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Alkali earth sulfide phosphors doped with Eu^{2+} and Ce^{3+} for LEDs

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Abstract

$CaS:Eu^{2+}$, $SrS:Eu^{2+}$, $CaS:Ce^{3+}$, $SrS:Ce^{3+}$, $CaS:Eu^{2+}$, Ce^{3+} and $SrS:Eu^{2+}$, Ce^{3+} phosphor samples have been prepared using a solid state chemical reaction method. Emission and excitation spectra of the samples are investigated. $SrS:Ce^{3+}$, $CaS:Ce^{3+}$, $SrS:Eu^{2+}$ and $CaS:Eu^{2+}$ emit greenish blue (482 nm), green (515 nm), orange (606 nm), and red (648 nm) light, respectively. For the co-doped samples, $SrS:Eu^{2+}$, Ce^{3+} and $CaS:Eu^{2+}$, Ce^{3+}, energy transfer from Ce^{3+} to Eu^{2+} is observed. Ce^{3+} emission has been totally quenched because of the energy transfer. Eu^{2+} emissions are estimated to be enhanced by 28% and 18% in SrS and CaS hosts, respectively, at the present doping concentration. The samples are also excited by blue light emitting diodes (450 nm) to exam them as potential coating phosphors for the diodes.

Keywords: Phosphor; Energy transfer; Luminescence, LED

1. Introduction

Light emitting diode (LED) is one of the most efficient solid state lighting sources. For lighting applications, white light LEDs are very comparable to sunlight spectrum. Currently, white light LEDs can be achieved by combining blue, green, and red LEDs, or by coating the three color phosphors to a UV LED or green and red phosphors to a blue LED [1–3]. The coating methods are commonly used because of the lower cost. Coating on blue LEDs is more popular because of the higher energy conversion efficiency. Therefore, green and red phosphors with strong blue absorption are needed.

For both white light UV LEDs and white light blue LEDs, the efficiency of the devices is largely dependent on the efficiency of the phosphors. Color rendering of the phosphors is also critical to obtain a spectrum close to sunlight. Highly efficient green/red emitting phosphors are important components for white light LEDs [4].

Most of the LED phosphors are from the traditional lamp phosphors with absorption at the LED emissions. For example, a blue LED emitting at 460 nm in combination with Ce^{3+} doped yttrium aluminum garnet ($YAG:Ce^{3+}$), a yellow emitting phosphor, is one of the best white light LED systems [5,6]. Alkali earth sulfide phosphors, such $CaS:Eu^{2+}$ (red), $CaS:Ce^{3+}$ (green), $SrS:Ce^{3+}$ (blue) 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. When sulfides exposed to moisture they decomposed to carbonates or sulfates that eliminate the original luminescence [7]. Sulfide phosphors may also degrade under high energy UV or electron beam strike [8]. However, sulfide phosphors fit well for LED applications with adhesive seal and blue excitation .

In this work Ce^{3+} and Eu^{2+} singly doped and co-doped alkali earth sulfides are studied. Strong blue absorptions of

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SrS:Ce^{3+}, CaS:Ce^{3+}, SrS:Eu^{2+} and CaS:Eu^{2+} are found in these phosphors, making them good candidates for LED applications. In the co-doped samples, Ce^{3+} is used to improve the Eu^{2+} emissions in SrS and CaS through energy transfer from Ce^{3+} to Eu^{2+}. Enhanced luminescence of Eu^{2+} in CaS and SrS is obtained. These alkali earth sulfide phosphors are coated on 450 nm blue LEDs and yielded similar emissions to that obtained from the photoluminescence study using a xenon lamp.

2. Experimental

CaS:Eu^{2+}, SrS:Eu^{2+}, CaS:Ce^{3+}, SrS:Ce^{3+}, CaS:Eu^{2+}, Ce^{3+}, and SrS:Eu^{2+}, Ce^{3+} powdered samples have been prepared using a solid state reaction method. Raw materials of $Sr(NO_3)_2$ and $CaCO_3$ are mixed with excess sulfur in a 1:4 mole ratio. Dopant compounds, $Ce(NO_3)_3$ and $Eu(NO_3)_3$, are added with a specified doping concentration for each sample: 0.5 mole% of Eu^{2+} and 1 mole% of Ce^{3+} in SrS and 0.02 mole% Eu^{2+} and 0.1 mole% of Ce^{3+} in CaS. Na_2CO_3 was used as flux. Na_2CO_3 is used as a flux. All samples are heated to 1100 °C and kept for 1 h in reducing environment. Body colors are white for CaS:Ce^{3+} and SrS:Ce^{3+} and are orange and red for SrS:Eu^{2+} and CaS:Eu^{2+}, respectively.

Emission and excitation spectra of the samples are measured with a SPEX FluoroMax II spectrometer. The spectra in the singly doped Eu^{2+} and co-doped Eu^{2+}, Ce^{3+} samples have been normalized to the emission spectra from singly doped Eu^{2+} sample in each host. All the samples are much larger than the excitation light spot. The excitation intensity and all the slits are fixed for all the measurements. The normalization can be realized by setting the samples at the same configuration and fine tuning the position to maximize the Eu^{2+} emissions in each case. Blue LEDs with a 450 nm emission are also used as an excitation source. LEDs are coated by the phosphors/adhesives layer by layer until the blue LED emission is blocked. Emission spectra of the phosphors under LED excitation are measured using a Linespec M125 monochromator equipped with a UV enhanced CCD. Efficiency of energy conversion from electrical energy to optical energy for each phosphor is also studied.

3. Results and discussion

3.1. Green and blue emissions of CaS:$Ce^{3+}$and SrS:Ce^{3+}

Emission and excitation spectra of CaS:Ce^{3+} are shown in Fig. 1a. The broad band emissions peaked at 515 nm and 570 nm are due to the transitions from 5d state of Ce^{3+} to the two 4f states, $^2F_{7/2}$ and $^2F_{5/2}$, respectively. Three broad excitation bands are found at 280 nm, 365 nm and 450 nm. The excitation bands at 280 nm and 450 nm can be assigned to the e_g and t_{2g} 5d bands of Ce^{3+}. The 365 nm band is due to a charge transfer transition of Ce^{3+} from 4f to conduction band [9].

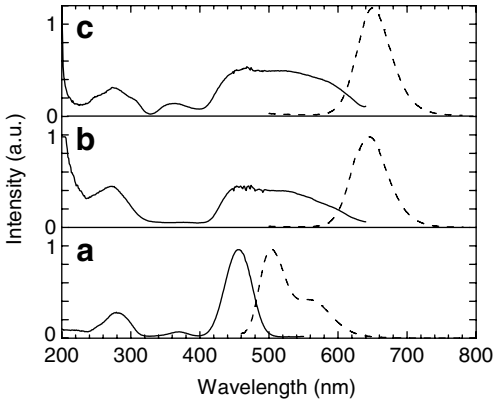

Fig. 1. Emission (dashed lines) and excitation (solid lines) spectra in CaS host ($\lambda_{ex} = 365$ nm). (a) CaS:Ce^{3+}; (b) CaS:Eu^{2+}; (c) CaS:Eu^{2+}, Ce^{3+}. All spectra in part (b) and (c) are normalized to CaS:Eu^{2+} emission. Peak emissions of Ce^{3+} (a) or Eu^{2+} (b) and (c) are monitored for excitation spectra.

SrS has a similar structure to CaS where Ce^{3+} sits in a six fold Ca^{2+} site surrounded by S^{2-} ions to make an O_h symmetry [10]. Band gap 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). For a different lattice constant, the ligand field splitting of Ce^{3+} 5d state in SrS is different from that in CaS. This will result in a peak shift in the emission and excitation bands of Ce^{3+}.

A broad band emission of SrS:Ce^{3+} is peaked at 482 nm with a shoulder at 535 nm as shown in Fig. 2a. These two emission peaks can be attributed to the transitions from Ce^{3+} 5d state to the two 4f states, $^2F_{5/2}$ and $^2F_{7/2}$, respectively. The excitation spectrum of Ce^{3+} emission at 482 nm is also shown in Fig. 2a. Three broad excitation bands are found respectively at 277 nm, 374 nm and 433 nm. Similarly to CaS, 277 nm and 433 nm absorption peaks can be assigned to the e_g and t_{2g} 5d bands but they have a few nm blue shifts due to the different ligand field influence [11,12]. The absorption peak at 374 nm, however, has a red shift comparing to Ce^{3+} in CaS, which is related

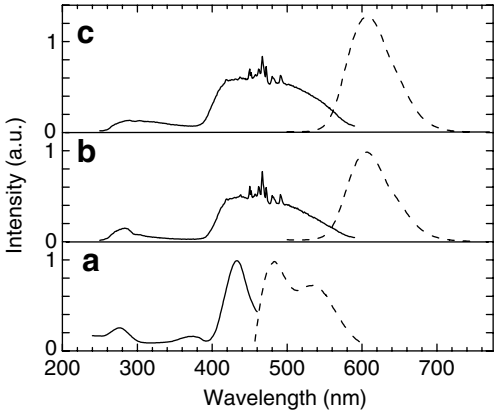

Fig. 2. Emission (dashed lines) and excitation (solid lines) spectra in SrS host ($\lambda_{ex} = 365$ nm). (a) SrS:Ce^{3+}; (b) SrS:Eu^{2+}; (c) SrS:Eu^{2+}, Ce^{3+}. All spectra in part (b) and (c) are normalized to SrS:Eu^{2+} emission. Peak emissions of Ce^{3+} (a) or Eu^{2+} (b) and (c) are monitored for excitation spectra.

to a charge transfer transition from Ce^{3+} 4f ground state to the SrS conduction band. The red shift can be caused by a narrower band gap or position difference of 4f ground state relative to the host band gap [10,13].

3.2. 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 peaked at 648 nm resulting from the $4f^6 5d^1$ to $4f^7$ transition. The broad excitation bands of the 648 nm emission are found at 275 nm and 500 nm, as shown in Fig. 1b, which can be attributed to the e_g and t_{2g} field splitting 5d bands of Eu^{2+}, respectively. Different from Ce^{3+}, 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 [14], or the lowest 5d band overlaps with the host conduction band [15,16].

Similar to Ce^{3+}, the ligand field splitting of 5d level of Eu^{2+} also 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 606 nm as shown in Fig. 2b. The broad band excitation peaks of 5d field splitting components e_g and t_{2g} are found, respectively, to have a red shift to 283 nm and a blue shift to a region from 390 nm to 590 nm. 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 [17,18].

3.3. Enhanced red and orange emissions of CaS:Eu^{2+}, Ce^{3+} and SrS:Eu^{2+}, Ce^{3+}

There is no Ce^{3+} emission observed in the co-doped CaS:Eu^{2+}, Ce^{3+} system when Ce^{3+} absorption is excited at $\lambda_{em} = 365$ nm. Instead, Eu^{2+} emission is observed at 650 nm as depicted in Fig. 1c for the same excitation, indicating an energy transfer process occurs from Ce^{3+} to Eu^{2+}. In addition, the 500 nm excitation band increases much higher over the excitation peak at 275 nm comparing the situation in Fig. 1c that is due to the Ce^{3+} t_{2g} band contribution. The 275 nm excitation peak of Eu^{2+} is also broadened and shifted to 280 nm (Ce^{3+} excitation peak). All these evidences show strong Ce^{3+} contributions to Eu^{2+} emission through energy transfer.

The overlap of Ce^{3+} emission and Eu^{2+} absorption for CaS:0.02% Eu^{2+}, 0.1% Ce^{3+} is presented in Fig. 3a, which is perfect for energy transfer. For a dipole–dipole interaction, the energy transfer rate between Ce^{3+} and Eu^{2+} in this concentration is $1.7 \times 10^8\ s^{-1}$ [19], which is one orders of magnitude higher than the decay rate of Ce^{3+}, $2.7 \times 10^7\ s^{-1}$ [20], therefore, Ce^{3+} emission has been quenched by Ce^{3+}–Eu^{2+} energy transfer [21–23].

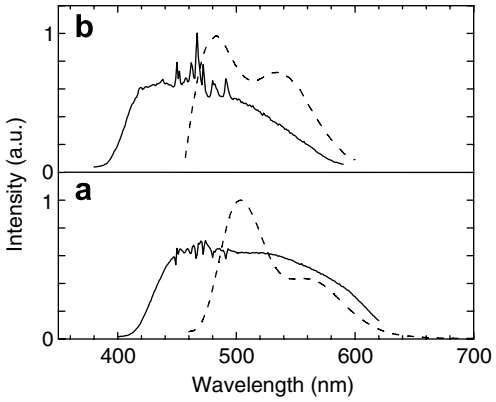

Fig. 3. Spectral overlap between Ce^{3+} emission (dashed lines) and Eu^{2+} excitation (solid lines) in (a) CaS and (b) SrS.

Emissions in Fig. 1b and c are normalized to the emission of singly doped CaS:Eu^{2+}. An 18% increase of Eu^{2+} emission is estimated based on the spectra due to the Ce^{3+} sensitization. This emission enhancement could be greater if the doped concentrations of Ce^{3+} and Eu^{2+} in the host are optimized.

Emission and excitation spectra of SrS:Eu^{2+}, Ce^{3+} are presented in Fig. 2c. The emission peak is found at 607 nm and the excitation bands for this emission observed at 290 nm and ~460 nm. The excitation profile is modified from singly doped SrS:Eu^{2+} system. Contribution from Ce^{3+} contents is found clearly by observing the shift of excitation edge from 390 nm to 380 nm due to the absorption of Ce^{3+} at 374 nm. Excitation shift and broadening at 290 nm is also due to the 374 nm as well as 277 nm absorptions. The evidences indicate that energy transfer from Ce^{3+} to Eu^{2+} also takes place in SrS:Eu^{2+}, Ce^{3+} [24]. The spectral overlap of SrS:Ce^{3+} emission and SrS:Eu^{2+} absorption is shown in Fig. 3b. Similarly, Ce^{3+} emission has not been observed in SrS:Eu^{2+}, Ce^{3+} sample upon Ce^{3+} excitation. The emission intensities in Fig. 2b and c have been normalized to the Eu^{2+} emission in singly doped SrS sample, suggesting a 28% increase of Eu^{2+} emission due to the energy transfer from Ce^{3+}.

3.4. Blue, green, orange and red emissions excited by LEDs

CaS:Ce^{3+}, SrS:Ce^{3+}, CaS:Eu^{2+}, and SrS:Eu^{2+} with absorption peaks at 450 nm, 433 nm, 450 nm, and 420 nm, respectively, are of interests for blue LED applications [25,26]. Upon excitation at 450 nm from the blue LED, these alkali earth sulfide phosphors emit strong blue, green, orange, and red light.

Each of six singly doped and co-doped phosphors is individually blended into transparent adhesives and coated onto the blue LEDs. The *V–I* curves and electrical to optical power conversion curves of the blue LEDs are shown in Fig. 4a and b, respectively. The turn-on voltage or power of the LED is 2.34 V or 3.1 mW. The specific operating voltage or power is at 3.2 V or 50 mW. The light output

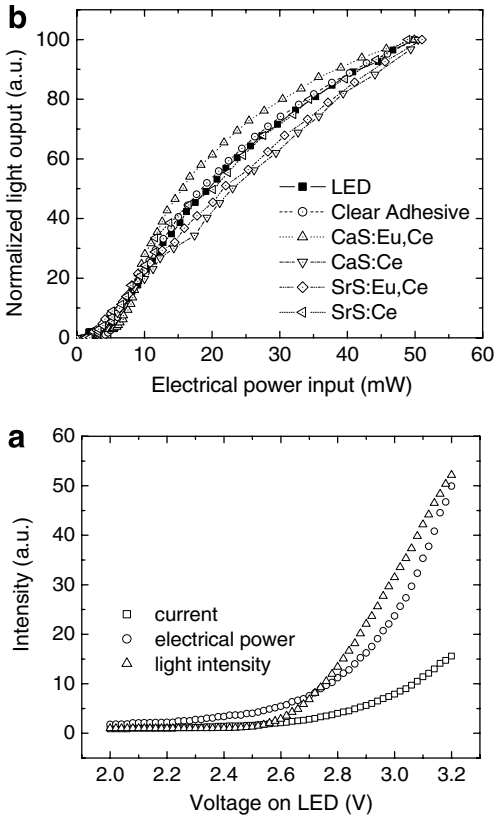

Fig. 4. (a) Current (□), electrical power input (○), and optical power output (Δ) of a blue LED as a function of the operating voltage; (b) Conversion of electrical power input to LED and phosphor optical power output (■: LED, ○: clear adhesive, Δ: CaS:Eu^{2+}, Ce^{3+}, ∇: CaS:Ce^{3+}, ◇: SrS:Eu^{2+}, Ce^{3+}, and ◁: SrS:Ce^{3+}).

intensity is not linearly dependent on the electrical power but shows a tendency of saturation as electrical power increases.

The emission spectra of the alkali earth phosphors excited with the LEDs are given in Fig. 5. The emission spectra are similar to corresponding photoluminescence emissions discussed earlier. Slight blue shifts of blue and green emissions are observed due to the leak of LED emissions. All the phosphor emissions in Fig. 5 have been normalized to the LED excitation profile to show the intensity differences, and the contributions of the residual LED emission have been corrected during the normalization. The co-doped samples show stronger emissions than the singly doped samples. The Ce^{3+} sensitization obviously improves the performance of red and orange phosphors under LED excitation. The differences among the conversion curves for different emissions, as shown in Fig. 4b, can be partially attributed to the thermal shift of the LED emissions as electric input power increases. Influence of the clear adhesives on light output is small, meaning that the transmittance of adhesives remains unchanged over the visible region.

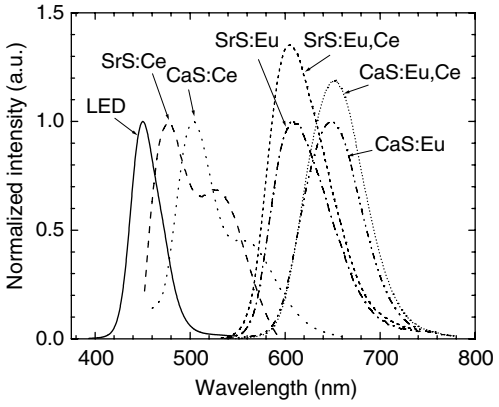

Fig. 5. Emission spectra of the alkali earth sulfide phosphors excited by 450 nm blue LEDs. Emissions from Eu^{2+}, Ce^{3+} co-doped samples are normalized to Eu^{2+} singly doped emissions in CaS and SrS, respectively. LED emission is also shown there as a reference.

For LED lighting applications, light extraction from LED is one of the major issues. A better light extraction will yield a higher efficiency. Alkali earth sulfide hosts have a high refractive index of 2.1 that is much closer to the refractive index of LED windows (~2.4) than that of commonly used YAG phosphors (~1.83). The smaller difference in refractive indices will increase the escape cone and obtain a better light extraction.

In addition, SrS and CaS have similar structures and similar refractive indices. Thus, when these two materials are mixed (not as a solid solution) for better color rendering, the well matched refractive indices at the boundaries between the grains will greatly reduce the internal light scattering.

4. Conclusion

CaS:Eu^{2+}, SrS:Eu^{2+}, CaS:Ce^{3+}, SrS:Ce^{3+}, CaS:Eu^{2+}, Ce^{3+} and SrS:Eu^{2+}, Ce^{3+} phosphors have been prepared and studied. Strong blue absorption is observed in these phosphors. Blue (482 nm), green (515 nm), orange (606 nm) and red (648 nm) emissions are obtained in SrS:Ce^{3+}, CaS:Ce^{3+}, SrS:Eu^{2+} and CaS:Eu^{2+}, respectively, being good candidates for blue LED applications. Codoping Ce^{3+} in SrS:Eu^{2+} and CaS:Eu^{2+} yielded 28% and 18% emission enhancements, respectively, due to the efficient energy transfer from Ce^{3+} to Eu^{2+}. Emission spectra of the phosphors excited by blue LEDs are also studied. *V–I* curves and energy efficiencies are measured.

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