

Spectral dependency of Eu^{2+} -activated silicate phosphors on the composition for LED application

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Abstract—An $\text{Sr}_2\text{SiO}_4\text{-Ba}_2\text{SiO}_4$ material system doped by Eu^{2+} was studied for light emitting diodes (LEDs) application. The main concern was the precise control of excitation and emission spectra for maximum light yield and color coordinate, which was carried out by changing the composition of the alkaline earth ions in host lattice. The Sr_2SiO_4 : $\text{Eu-Ba}_2\text{SiO}_4$: Eu system was found to be excellent for white LED applications with excitation in the 380-465 nm region. Especially, the yellow light intensity from $(\text{Sr,Ba})\text{SiO}_4$: Eu phosphors was comparable to $\text{YAG} : \text{Ce}$ phosphors in case of blue LED excitation.

Key words: White LED, Phosphor, Silicate, Spectrum

INTRODUCTION

Recently, intensive attention has been given to the development of white light emitting diodes (LEDs), because of their high efficiency as well as longevity. Phosphor-converted white LEDs have long been in the commercial markets. A structure widely reported is the use of blue-emitting LED covered by a yellow emitting phosphor such as $\text{Y}_3\text{Al}_5\text{O}_{12} : \text{Ce}$ (YAG:Ce), encapsulated in an epoxy resin [Narendran et al., 2004]. They are used for the backlight of a color cellular phone and the illumination lamp in an automobile. To date, many kinds of phosphors have been selected and even many new materials have been reported for the LED application [Starick et al., 2003; Proceedings of Phosphor Global Summit, 2004]. For the device application, it is very important to obtain the proper white CIE (International Commission on Illumination) point for realizing full color images as well as high efficiency. The white color coordinate is very sensitive to the emission spectrum of the phosphors in case of the phosphor-converted LED. Also, to obtain the maximum quantum yield, the excitation spectrum of the phosphor needs to be overlapped by the emission spectrum from LED as much as possible. The emission spectrum of the LED, which is available and high efficiency, shows peaks near 405 nm or 460 nm. Therefore, much effort has gone into development of phosphors with the proper emission (550-700 nm) and excitation (380-470 nm) wavelengths.

As of now, most phosphor-converted LEDs have used $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) doped by Ce^{3+} , which is excited by blue light (~460 nm) and emits orange light (~560 nm). Besides Ce^{3+} ions, the ions of Eu^{2+} , Tb^{3+} , and Mn^{2+} are known to have luminescent transitions suitable for LED applications, but proper selection of the host lattice remains a great challenge to phosphor engineers. The main factors responsible for different spectral properties of given activator ions in different host lattices are known to be covalency and crystal field around activator ions.

Blasse et al. reported on the fluorescence of Eu^{2+} -activated sili-

cates [Blasse et al., 1968]. The main factors controlling the excitation and emission wavelengths of a given activator ion were the host lattice and the alkaline-earth ion. Poort et al. [1996] examined the luminescence of Eu^{2+} in silicate host lattices with alkaline earth ions and reported that the spectrum peaks could be controlled by the preferential orientation of a d orbital in the chain direction. Recently, we reported that a very efficient blue-emitting silicate phosphor could be excited near 400 nm [Hong et al., 2003].

In this work, we focused on the variation of crystal fields by changing the ratio of the Ba/Sr in the $\text{Sr}_2\text{SiO}_4\text{-Ba}_2\text{SiO}_4$ material system. The proper control of PLE (Photoluminescence Emission) and PL (Photoluminescence) was the major concern of this work in that the orange light would be maximized near 465-nm excitation.

EXPERIMENTAL

The starting materials for the phosphor were high purity BaCO_3 , SrCO_3 , SiO_2 , and Eu_2O_3 , all 99.99% pure. Stoichiometric amounts of the starting materials were mixed thoroughly, and NH_4Cl (99.99%) was added as a flux. The mole fraction of the NH_4Cl flux was taken as an independent variable to maximize the light output. The weighed materials were ball-milled for longer than 48 hours in isopropyl alcohol. After evaporating the alcohol in air, the samples were preheated in a muffle furnace at 600 °C for 4 hrs. Then, they were heat-treated in the reducing atmosphere ($\text{N}_2+2\% \text{H}_2$) at a temperature between 1,200 and 1,400 °C for several hours. The final reaction time and temperature were optimized for maximum PL intensity. After washing with DI (Distillation) water to remove the flux, the samples were sintered again for 3 hr at 1,300 °C in $\text{N}_2+2\% \text{H}_2$ to improve crystallinity.

The phosphor powders were characterized by scanning electron microscopy (SEM-Philips Model 515). The crystal structure was identified by X-ray diffractometry (XRD-Scintag, Model SDS 2000) using $\text{Cu K}\alpha$ ($\lambda=1.540562$). The excitation spectra were measured by photoluminescence on an optical bench using scanned monochromatized excitation from a xenon lamp (ORC Model LH1751300), while the emission spectra were measured at a particular excitation

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wavelength with a second monochromator and photomultiplier detector.

RESULTS AND DISCUSSION

This work was undertaken in an attempt to study the spectral variation in excitation as well as in emission spectra for LED applications. The emission and absorption spectra of the Eu^{2+} are broad due to the transitions between the $4f^7$ ground state and the crystal field components of the $4f^65d$ excited state configuration. The emission varies from ultraviolet to red, depending on the covalency, the size of the cation, and the strength of the crystal field in host lattices. Here, we partially replaced strontium ions with the Ba ions in a strontium ortho-silicate system doped by Eu^{2+} activators to investigate

the spectral variation. Since the ionic radius of Eu^{2+} (0.117 nm) is similar to that of Sr^{2+} (0.113 nm), Sr salts are believed to be suitable host lattices for Eu^{2+} activation. Also, we assumed that Eu^{2+} ions occupy Sr-site in host lattices. Typical X-ray diffraction patterns of $\text{Sr}_x\text{Ba}_{2-x}\text{SiO}_4:\text{Eu}$ phosphors in this work are shown in Fig. 1. As all preparations are known to have a single-phase material [Barry, 1968], crystal planes were grown a little bit differently, depending on the Ba contents. Also, the emission and excitation spectra for $\text{Sr}_x\text{Ba}_{2-x}\text{SiO}_4:\text{Eu}$ are depicted in Fig. 2. The photoluminescence intensity of $\text{Sr}_x\text{Ba}_{2-x}\text{SiO}_4:\text{Eu}$ was very sensitive to the preparation conditions, such as ball milling, temperature of heat-treatment and reaction time. The results shown in Fig. 2 were from powders preheated at 600°C as described above, at heat treated at $1,300^\circ\text{C}$ for 4 hours.

SEM images of the typical morphology of the $\text{YAG}:\text{Ce}$ and for $\text{Sr}_x\text{Ba}_{2-x}\text{SiO}_4:\text{Eu}$ samples are shown in Fig. 3. As seen in SEM image, we observed that the solid and well-rounded phosphor powders with a large size or grains were synthesized. The body color of powders was dependent on the contents of Ba ions in our experimental regime. It ranged from green to yellow in our material system. However, small nano-sized particulates could be observed on the surface of the $\text{Sr}_x\text{Ba}_{2-x}\text{SiO}_4:\text{Eu}$ phosphors. Washing with warm water was not enough to completely remove these particulates from the surface. They might be segregated metal ions that we have not been able to identify so far. Obviously, they have an

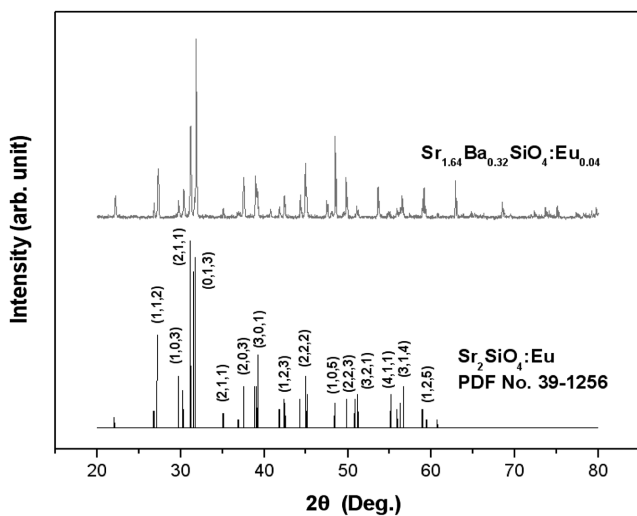


Fig. 1. Typical X-ray diffraction pattern of $\text{Sr}_x\text{Ba}_{2-x}\text{SiO}_4:\text{Eu}$ phosphors.

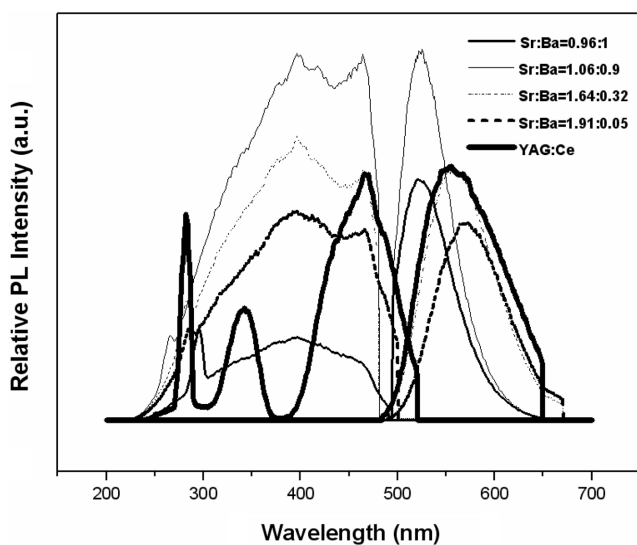
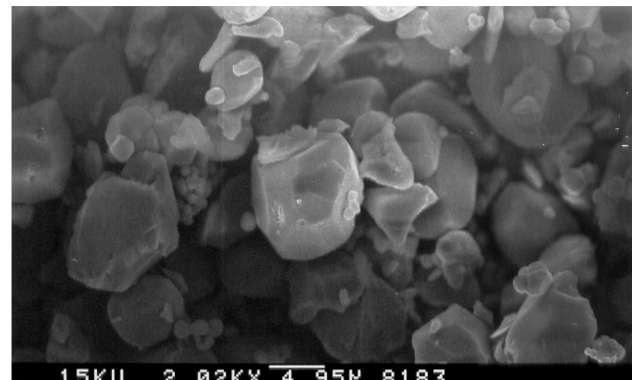
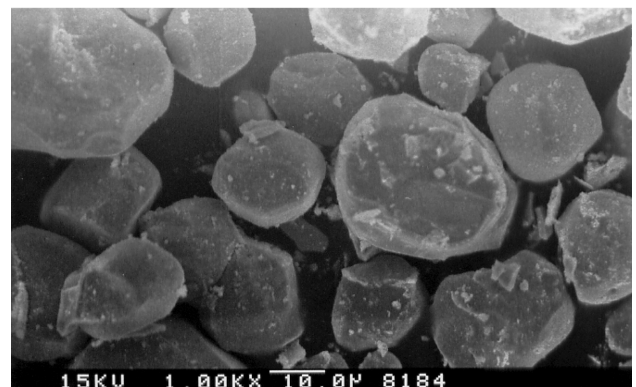


Fig. 2. The excitation and emission spectra from $\text{Sr}_{2-x}\text{Ba}_x\text{SiO}_4:\text{Eu}$ phosphors. The emission spectra were obtained with 465 nm excitation, while the excitation spectra were measured at peak emission wavelength of each phosphor material.



(a) $\text{YAG}:\text{Ce}$



(b) $\text{Sr}_{1.64}\text{Ba}_{0.32}\text{SiO}_4:\text{Eu}_{0.04}$

Fig. 3. SEM images of the $\text{Sr}_{1.64}\text{Ba}_{0.32}\text{SiO}_4:\text{Eu}$ and commercial $\text{YAG}:\text{Ce}$ phosphor particles.

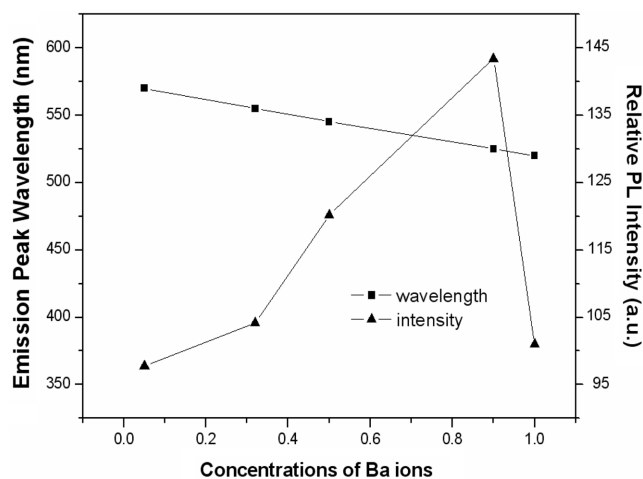


Fig. 4. The relationship between the composition of Ba ions in $\text{Sr}_{2-x}\text{Ba}_x\text{SiO}_4:\text{Eu}$ phosphors and peak emission. Also, relative luminous intensity was inserted. The emission spectra were obtained at 465 nm excitation.

effect on the luminous intensity. For instance, such a sample shows a peak at near 290 nm in excitation, which is generally ascribed to Eu^{3+} ions. This peak did not disappear even after successive heat-treatments under reducing atmosphere and deteriorated the luminous efficiency in our case. Usually, this was determined on the initial stage of processing such as ball milling and first heat treatment.

In all cases, we could observe a continuous shift in emission wavelength. A continuous shift from 570 nm to 525 nm in emission wavelength (excited with $\lambda=465$ nm) was observed with increasing Ba concentration, as shown in Fig. 4. As the concentration of Ba increases, the relative PL intensity of the emission peaks increases. The excitation spectra (determined at the peak emission wavelength) for $\text{Sr}_x\text{Ba}_{2-x}\text{SiO}_4:\text{Eu}$ phosphors where $1.06 \leq x \leq 1.64$ are ranged from ~340 nm to ~470 nm, as shown in Fig. 2, are similar to the spectra from commercially produced $\text{YAG}:\text{Ce}$ powder phosphor. Note that the excitation peak at 465 nm is good for efficient generation of white light with a blue LED. Compared to $\text{YAG}:\text{Ce}$, the $\text{Sr}_x\text{Ba}_{2-x}\text{SiO}_4:\text{Eu}$ phosphors exhibit a much broader excitation structure between 380 nm and 470 nm, which is important for efficient LED excitation. In contrast, more efficient emission spectra are observed to blue-shift with increasing Ba concentration relative to the $\text{YAG}:\text{Ce}$ emis-

sion, which is undesirable for proper color balance in a white LED.

CONCLUSION

An $\text{Sr}_2\text{SiO}_4\text{-Ba}_2\text{SiO}_4$ material system doped by Eu^{2+} was synthesized for LED applications and found to show broad excitation peaks from ~340 to 470 nm, which is excellent for photo-pumping with a blue or near UV LED. The emission spectra were also broad and controllable by changing the composition of Ba ions. In particular, the emission wavelength varied from 570 nm for $\text{Sr}_{1.64}\text{Ba}_{0.32}\text{SiO}_4:\text{Eu}_{0.04}$ to 525 nm for $\text{Sr}_{1.06}\text{Ba}_{0.94}\text{SiO}_4:\text{Eu}_{0.04}$, and the photo luminescence intensity increased as the emission wavelength decreased, i.e., as the Ba concentration increased. For white light emitting phosphor-LED devices, the PL emissions intensity of $(\text{Sr,Ba})_2\text{SiO}_4:\text{Eu}$ was comparable to $\text{YAG}:\text{Ce}^{3+}$ phosphors, with a much broader tunability in the pumping wavelength from the LED.

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