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# Luminescent properties of $\text{Eu}^{3+}$ and $\text{Sm}^{3+}$ activated $\text{M}_2\text{SiO}_4$ (M=Ba, Sr and Ca) red-emitting phosphors for WLEDs

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## ABSTRACT

$\text{Eu}^{3+}$  and  $\text{Sm}^{3+}$  activated  $\text{M}_2\text{SiO}_4$  (M=Ba, Sr and Ca) red-emitting phosphors were synthesized by a solid state reaction. The results of XRD and SEM measurements show that the samples are single phase and have irregular shape. The excitation and emission spectra indicate that these phosphors were effectively excited by ultraviolet (395 nm) and blue (466 nm) light and exhibited red performance. The charge compensator  $\text{R}^+$  ( $\text{R}^+=\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$ ) injecting into the host efficiently enhanced the luminescence intensity of the  $\text{M}_2\text{SiO}_4:\text{Eu}^{3+}$  and  $\text{M}_2\text{SiO}_4:\text{Sm}^{3+}$  phosphors. The emission intensity of  $\text{M}_2\text{SiO}_4:\text{Eu}^{3+}$  and  $\text{M}_2\text{SiO}_4:\text{Sm}^{3+}$  doping  $\text{Li}^+$  were higher than that of  $\text{Na}^+$  or  $\text{K}^+$ .

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## 1. Introduction

In recent years, white light-emitting diodes (WLEDs) have attracted considerable attention owing to their advantages of long life span, low energy consumption, and reliability, and their potential applications in indicators, backlights, automobile headlights and general illuminations [1,2]. Compared with traditional lighting engineering (incandescent, fluorescent lamps), WLEDs are considered as a novel generation of light source [3,4]. The first commercial WLED solid-state lighting was obtained by combining blue-emitting LED and yellow phosphor  $\text{YAG}:\text{Ce}^{3+}$  in 1997 [5]. However, this type of white light has a rather low color render index because the output light is deficient in the red region of the sunlight spectrum (above 600 nm) [6]. WLEDs can also be made by combination of a near-UV LED and red, green and blue color phosphors [7]. The WLEDs fabricated with UV chip has the following advantages: white color generated by phosphors, i.e. high tolerance to UV chip's color variation, and excellent color rendering index [8].

It is well known that a suitable UV-LED phosphor should have a stable host, exhibit strong absorption around 400 nm and show strong emission under 400 nm excitation. The current red phosphors for WLEDs based on UV GaN-LEDs are (Ca, Sr)S:  $\text{Eu}^{2+}$  [9] and  $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$  [10]. However, the red phosphor  $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$  shows lower efficiency and chemical stability than green ( $\text{ZnS}:\text{Cu}^+$ ,  $\text{Al}^{3+}$ )

phosphor and blue phosphor ( $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ ) under the excitation of near-UV light. Therefore, great efforts have been made to explore good phosphors for application in WLEDs. Haque et al. [11] synthesized a series of red phosphors  $\text{NaMY}(\text{MoO}_4)_3:\text{Eu}^{3+}$  (M=Sr and Ca) and measured their photoluminescent properties for white light-emitting diodes. Cao et al. [12] investigated the luminescent properties of  $\text{Ca}_x\text{Sr}_{1-x}(\text{MoO}_4)_y(\text{WO}_4)_{1-y}:\text{Eu}^{3+}$  red-emitting phosphors for WLEDs.

Recently, rare earth doped alkaline earth silicate has been extensively studied because of its long-wavelength excitation properties, excellent chemical stabilities, facile synthesis and cheap raw material ( $\text{SiO}_2$ ) [13]. Blasse had reported the luminescence properties of alkaline earth silicates activated by  $\text{Eu}^{2+}$  [14]. Alkaline earth silicates doped with  $\text{Eu}^{2+}$ , such as  $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$  [15],  $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$  [16] and  $\text{BaMgSiO}_4:\text{Ce}^{3+}, \text{Eu}^{2+}$  [17], have been systematically studied. However, photoluminescence properties of  $\text{M}_2\text{SiO}_4:\text{RE}$  (RE= $\text{Eu}^{3+}$  and  $\text{Sm}^{3+}$ ) excited by near-UV radiation have not yet been investigated.

In this work,  $\text{M}_2\text{SiO}_4:\text{RE}$  (RE= $\text{Eu}^{3+}$  and  $\text{Sm}^{3+}$ ) phosphors were prepared using the conventional solid-state reaction method and their luminescent properties were investigated. These phosphors were excited by UVLED chips, and emit red light.

## 2. Experiment

The phosphor  $\text{M}_2\text{SiO}_4:\text{RE}$  (RE= $\text{Eu}^{3+}$  and  $\text{Sm}^{3+}$ ) was synthesized through the solid-state reaction method. The starting materials were  $\text{BaCO}_3$  (A.R.),  $\text{CaCO}_3$  (A.R.),  $\text{SrCO}_3$  (A.R.),  $\text{SiO}_2$

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(G.R.),  $\text{Eu}_2\text{O}_3$  (99.99%) and  $\text{Sm}_2\text{O}_3$  (99.99%). Appropriate amounts of  $\text{Li}_2\text{CO}_3$  (A.R.),  $\text{Na}_2\text{CO}_3$  (A.R.),  $\text{K}_2\text{CO}_3$  (A.R.) were added as the charge compensator for  $\text{Eu}^{3+}$  and  $\text{Sm}^{3+}$  doped samples. The raw materials with stoichiometric amounts were mixed thoroughly in anagate mortar by grinding and subsequently sintering at 1573 K with a constant heating rate of 600 °C/h in air atmosphere.  $\text{M}_2\text{SiO}_4$ :  $\text{Eu}^{3+}$  and  $\text{M}_2\text{SiO}_4$ :  $\text{Sm}^{3+}$  phosphors were obtained.

The resulting powder samples were characterized by a DMAX-RB X-ray diffraction with  $\text{Cu K}\alpha$  radiation of wavelength 1.5406 Å at 40 kV and 150 mA. The morphology and size of the calcined particles were observed by field emission scanning electron microscopy (FESEM, JSM-6700F). The emission and excitation spectra were recorded using a fluorescent spectrofluorometer equipped with a 450 W Xenon lamp as an excitation source. All the photoluminescence properties of the phosphors were measured at room temperature.

### 3. Results and discussion

#### 3.1. Phase characterization and SEM

To determine the phase purity of the samples, XRD measurements for all synthesized products were conducted. Fig. 1 shows the XRD patterns of  $\text{M}_2\text{SiO}_4$ : 0.04RE (RE= $\text{Eu}^{3+}$  and  $\text{Sm}^{3+}$ , M=Ba, Sr and Ca). The XRD patterns of  $\text{Ba}_2\text{SiO}_4$ : 0.04RE (RE= $\text{Eu}^{3+}$  and  $\text{Sm}^{3+}$ ),  $\text{Sr}_2\text{SiO}_4$ : 0.04RE (RE= $\text{Eu}^{3+}$  and  $\text{Sm}^{3+}$ ) and  $\text{Ca}_2\text{SiO}_4$ : 0.04RE (RE= $\text{Eu}^{3+}$  and  $\text{Sm}^{3+}$ ) samples were consistent with JCPDS standard card (nos. 26-1403, 39-1256 and 49-1673). No impure phases were observed, indicating that the doping  $\text{Eu}^{3+}$  and  $\text{Sm}^{3+}$  ions did not influence the crystal structures of

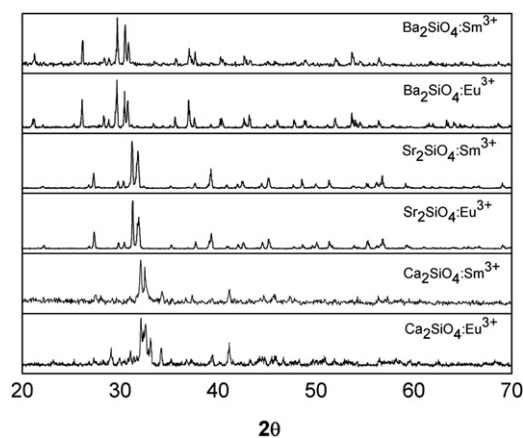


Fig. 1. XRD patterns of  $\text{Eu}^{3+}$  and  $\text{Sm}^{3+}$  doped  $\text{M}_2\text{SiO}_4$  (M=Ba, Sr, Ca) phosphors.

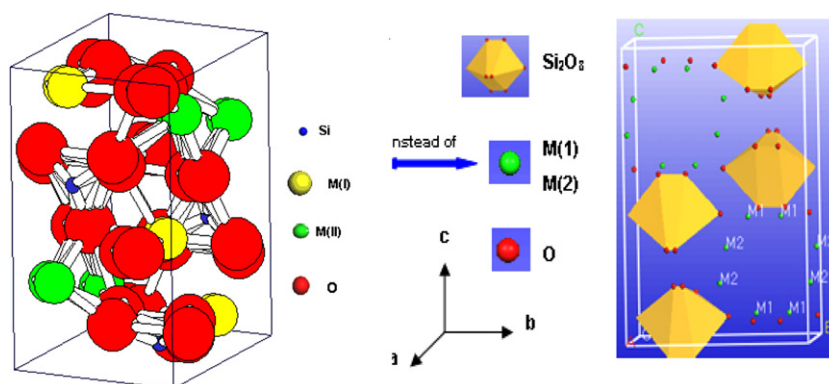


Fig. 2. Crystal structure of  $\text{M}_2\text{SiO}_4$ .

phosphors. The samples of  $\text{M}_2\text{SiO}_4$  (M=Ba, Sr and Ca) were of isostructure, as shown in Fig. 2, in which  $\text{M}_2\text{SiO}_4$  has two different cation sites in the lattice: M(I) and M(II) sites [18,19]. The site M(I) is coordinated by ten  $\text{O}^{2-}$  ions and forms a chain along  $c$ -axis with one side of  $\text{Si}^{4+}$  ion and the other side of M(I). The other site M(II) is surrounded by nine oxygen, which linked to form chains along the  $b$ -axis. The asymmetry of M(II) site is stronger than that of M(I) in  $\text{M}_2\text{SiO}_4$ . Therefore,  $\text{Eu}^{3+}$  and  $\text{Sm}^{3+}$  doped in  $\text{M}_2\text{SiO}_4$  probably occupied two different sites of M (I) and M (II) and led to the red emission of different color purity. Fig. 3(a)–(c) shows the SEM images of  $\text{Ca}_2\text{SiO}_4$ :  $\text{Eu}^{3+}$ ,  $\text{Sr}_2\text{SiO}_4$ :  $\text{Eu}^{3+}$  and  $\text{Ba}_2\text{SiO}_4$ :  $\text{Eu}^{3+}$  phosphors, respectively. The  $\text{Ca}_2\text{SiO}_4$ : 0.04 $\text{Eu}^{3+}$ ,  $\text{Sr}_2\text{SiO}_4$ : 0.04 $\text{Eu}^{3+}$  and  $\text{Ba}_2\text{SiO}_4$ : 0.04 $\text{Eu}^{3+}$  phosphors exhibited irregular morphology with no uniform shape and size and no obvious agglomeration.

#### 3.2. The luminescence properties of $\text{M}_2\text{SiO}_4$ : $\text{Eu}^{3+}$

The excitation spectra of  $\text{M}_2\text{SiO}_4$ : 0.04 $\text{Eu}^{3+}$  phosphors monitored at 613 nm emission are given in Fig. 4(a). The broad band from 250 to 320 nm is attributable to the charge transfer (CT) transition. The sharp lines included 363 nm ( ${}^7\text{F}_0$ – ${}^5\text{D}_4$ ), 385 nm ( ${}^7\text{F}_0$ – ${}^5\text{L}_7$ ), 395 nm ( ${}^7\text{F}_0$ – ${}^5\text{L}_6$ ), 466 nm ( ${}^7\text{F}_0$ – ${}^5\text{D}_2$ ) in the range of 350–500 nm were due to configurational 4f–4f transitions of  $\text{Eu}^{3+}$  in the host. The  ${}^7\text{F}_0$  to  ${}^5\text{L}_6$  at 395 nm and  ${}^7\text{F}_0$  to  ${}^5\text{D}_2$  transitions at 466 nm were the two strongest absorptions. The intensities of mentioned f–f transitions are higher than that of broad band. From Fig. 4(a) it can be seen that the shapes of excitation spectra were similar for the phosphors of  $\text{M}_2\text{SiO}_4$ : 0.04 $\text{Eu}^{3+}$  (M=Ba, Sr and Ca). However, the intensities of the peaks in the excitation spectra increased in the order of Sr, Ca and Ba.

Fig. 4(b) shows the emission spectra of  $\text{M}_2\text{SiO}_4$ : 0.04 $\text{Eu}^{3+}$  phosphors. Under the 395 nm excitation, the emission spectrum of our obtained samples were composed of a series of sharp emission lines, corresponding to transitions from the excited states  ${}^5\text{D}_0$  to the ground state  ${}^7\text{F}_j$ :  ${}^5\text{D}_0$ → ${}^7\text{F}_1$  (591 nm),  ${}^5\text{D}_0$ → ${}^7\text{F}_2$  (613 nm),  ${}^5\text{D}_0$ → ${}^7\text{F}_3$  (654 nm) and  ${}^5\text{D}_0$ → ${}^7\text{F}_4$  (703 nm). In the case of  $\text{Ba}_2\text{SiO}_4$ :  $\text{Eu}^{3+}$ , the red emission of  ${}^5\text{D}_0$ → ${}^7\text{F}_2$  was the strongest, which suggests that the  $\text{Eu}^{3+}$  mainly occupied at Ba(II) (asymmetric) cation. As is well known, if  $\text{Eu}^{3+}$  occupies an inversion symmetry site in the crystal lattice, the magnetic-dipole transitions  ${}^5\text{D}_0$ → ${}^7\text{F}_1$  of  $\text{Eu}^{3+}$  dominate. If there is no inversion symmetry at the site of  $\text{Eu}^{3+}$ , the main emission is the electric-dipole transition  ${}^5\text{D}_0$ → ${}^7\text{F}_2$  [20]. In the case of  $\text{Ca}_2\text{SiO}_4$ : 0.04 $\text{Eu}^{3+}$  and  $\text{Sr}_2\text{SiO}_4$ : 0.04 $\text{Eu}^{3+}$ , the orange-red emission of the transition  ${}^5\text{D}_0$  to  ${}^7\text{F}_1$  was as strong as the red emission of the transition  ${}^5\text{D}_0$  to  ${}^7\text{F}_2$ , revealing the equal probability that  $\text{Eu}^{3+}$  occupied at M(I) (symmetric) and M(II) (asymmetric) sites for the  $\text{Ca}_2\text{SiO}_4$  and

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