

# Preparation mechanism and luminescence of Sr<sub>2</sub>SiO<sub>4</sub>:Eu phosphor from (Sr,Eu)CO<sub>3</sub>@SiO<sub>2</sub> core-shell precursor

Yunsheng Hu<sup>1</sup>, Weidong Zhuang<sup>1\*</sup>, Jianhua Hao<sup>2\*</sup>, Xiaowei Huang<sup>1</sup>, Huaqiang He<sup>1</sup>

<sup>1</sup>National Engineering Research Center for Rare Earth Materials, General Research Institute for Nonferrous Metals, and Griem Advanced Materials Co., Ltd., Beijing, China

<sup>2</sup>Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong, China

Email: \*[vdzhuang@126.com](mailto:vdzhuang@126.com); \*[apjhao@polyu.edu.hk](mailto:apjhao@polyu.edu.hk)

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## ABSTRACT

Sr<sub>2</sub>SiO<sub>4</sub>:Eu phosphor for white light emitting diodes (LEDs) was synthesized by employing an as-prepared (Sr,Eu)CO<sub>3</sub>@SiO<sub>2</sub> core-shell precursor as starting materials, and the effect of the core-shell precursor was also discussed on the crystal structure, particle morphology and luminescent properties of the resultant phosphor. The results showed that the hybrid β- and α'-Sr<sub>2</sub>SiO<sub>4</sub>:Eu phosphor with fine particle size and narrow distribution could be obtained at a lower firing temperature than that in conventional solid-state reaction method, and its formation mechanism was deduced to be (Sr,Eu)CO<sub>3</sub> diffusion controlled reaction process. Responded to its hybrid crystal structure, this phosphor exhibited the combined luminescence of β- and α'-Sr<sub>2</sub>SiO<sub>4</sub>:Eu.

**Keywords:** Phosphor; Precursor; Core-Shell Structure; Preparation Mechanism; Luminescence

## 1. INTRODUCTION

Since Eu<sup>2+</sup>-activated alkaline earth orthosilicate phosphor was firstly reported on its fluorescence by Barry in 1968 [1], Me<sub>2</sub>SiO<sub>4</sub>:Eu (Me = Ca, Sr, Ba) had attracted little attention until the advent of white light emitting diodes (LEDs). Due to its high light conversion efficiency for near ultraviolet (NUV) and blue light, Me<sub>2</sub>SiO<sub>4</sub>:Eu has been an excellent commercial phosphor for white LEDs. Compared with the most popular (Y,Gd)<sub>3</sub>(Al,Ga)<sub>5</sub>O<sub>12</sub>:Ce (YAG:Ce) phosphor for white LEDs, Me<sub>2</sub>SiO<sub>4</sub>:Eu is not only suitable for blue LED but also for NUV LED; moreover, Me<sub>2</sub>SiO<sub>4</sub>:Eu can produce more colorful emission to satisfy the demands of the white LEDs with lower color temperature and higher color rendering index [2-6].

Currently, the commercial Me<sub>2</sub>SiO<sub>4</sub>:Eu phosphor is produced by high temperature solid-state reaction method [5-10]. Such a method can achieve high light con-

version efficiency of phosphor; however, it usually requires high firing temperature and introduction of flux to promote crystallization, which results in big particle size (>10 μm), broad particle distribution and irregular morphology, even flux contamination for phosphor. Taking the application properties into account, the phosphors for LEDs should have suitable particle size (<10 μm) and narrow distribution besides high brightness and desirable color coordinates. So some efforts have made to improve the particle properties of Me<sub>2</sub>SiO<sub>4</sub>:Eu phosphor by soft-chemistry methods [11-14]. For instance, Chang and co-authors synthesized nanometer Sr<sub>2</sub>SiO<sub>4</sub> by employing SrCO<sub>3</sub>@SiO<sub>2</sub> core-shell precursor as the starting materials; however, the luminescent center Eu was not considered and doped into the Sr<sub>2</sub>SiO<sub>4</sub> host in their work [14]. In the previous work, we also developed a homogenous (Sr,Eu)CO<sub>3</sub>@SiO<sub>2</sub> core-shell precursor, in which (Sr,Eu)CO<sub>3</sub> represents the homogenous mixture of Sr<sup>2+</sup> and Eu<sup>3+</sup> carbonates [15]. In this study, we employed this as-prepared core-shell precursor as starting materials to synthesize Sr<sub>2</sub>SiO<sub>4</sub>:Eu phosphor, and investigated its effect on the crystal structure, morphology and luminescent properties of the phosphor. Based on these results, the formation mechanism and the luminescence of Sr<sub>2</sub>SiO<sub>4</sub>:Eu was also discussed.

## 2. EXPERIMENTAL

The as-prepared (Sr,Eu)CO<sub>3</sub>@SiO<sub>2</sub> core-shell precursor in our previous work [15] was directly employed as the starting materials to synthesize Sr<sub>2</sub>SiO<sub>4</sub>:Eu phosphor in the present work, wherein the molar ratio of Sr, Eu and Si was 1.9:0.1:1. To be specific, the core-shell precursor was put into an alumina crucible and directly fired in a horizontal tube furnace at 1000°C for 2 h under reducing atmosphere (95% N<sub>2</sub> + 5% H<sub>2</sub>). And then the obtained phosphor powder was cooled to room temperature in the furnace for characterization.

FTIR measurements were performed on a Nicolet Magna-IR 760 Fourier transform infrared spectrometer

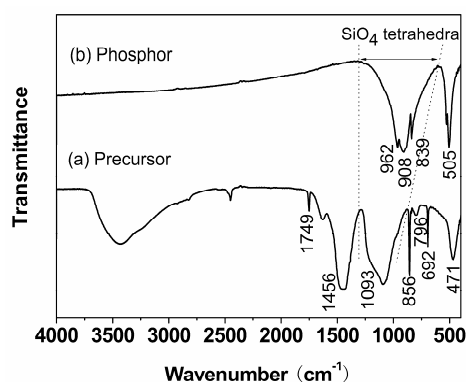
\*Corresponding authors.

using the standard KBr pellets technique, in the frequency interval 4000 - 400  $\text{cm}^{-1}$ . X-ray diffraction (XRD) identification was determined by Burker D8 Advance X-ray powder diffractometer running Cu  $K\alpha$  radiation at 40 kV and 40 mA, and the XRD patterns were collected in the range of  $15^\circ \leq 2\theta \leq 65^\circ$ . The microstructure and morphology were detected by a JEOL JSM-6335F field emission scanning electronic microscope. The emission and excitation spectra of the phosphor were acquired by using Edinburgh FLS920P fluorescence spectrometer equipped with a 450W xenon lamp as an excitation source. All the measures were carried out at room temperature.

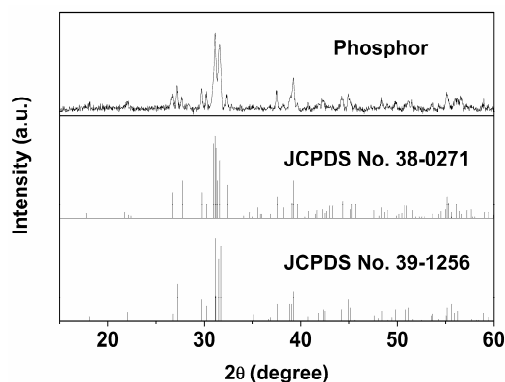
### 3. RESULTS AND DISCUSSION

**Figure 1** shows the FTIR spectrum of the obtained phosphor sample (curve b). For comparison, the FTIR spectrum of  $(\text{Sr},\text{Eu})\text{CO}_3@\text{SiO}_2$  precursor is also presented as curve (a). Obviously, the FTIR spectrum of the precursor mainly exhibits the characteristic vibrations of  $\text{SiO}_2$  (1093, 796 and 471  $\text{cm}^{-1}$ ),  $\text{CO}_3^{2-}$  group (692, 856, 1456 and 1749  $\text{cm}^{-1}$ ), CTAB (1630 and 2823  $\text{cm}^{-1}$ ) and  $\text{H}_2\text{O}$  (3435  $\text{cm}^{-1}$ ). After the precursor was fired into phosphor, the obtained sample shows different FTIR spectrum. As displayed in curve (b), the characteristic vibrations of  $\text{CO}_3^{2-}$  group, CTAB and  $\text{H}_2\text{O}$  disappear, and the characteristic vibration bands of  $\text{SiO}_2$  are replaced by multiple bands at 1000 - 800  $\text{cm}^{-1}$  and 600 - 500  $\text{cm}^{-1}$ , which could be attributed to the stretching and bending vibrations of Si-O bonds in  $\text{SiO}_4$  tetrahedra, respectively [16]. It means that the vibration bands of the phosphor sample are shifted to lower frequency compared with that of pure  $\text{SiO}_2$ . As O/Si ratio increases from 2 ( $\text{SiO}_2$ ) to 4 (orthosilicate), the Si-O bond length increases from 0.161 nm to 0.163 nm due to the presence of modifier oxides in the silica network, and the polymerization degree of  $\text{SiO}_4$  tetrahedral gets lower, which generally corresponds to a lower vibration frequency in FTIR spectrum [17,18]. Meanwhile, it is noticed that the stretching vibrations of the phosphor sample cover a broader range (1300 - 600  $\text{cm}^{-1}$ , the region between both dot lines in curve (b)) than that of pure  $\text{SiO}_2$  (1300 - 880  $\text{cm}^{-1}$ , the region between both dot lines in curve (a)) and split into three groups: 962, 908, and 839  $\text{cm}^{-1}$ , which is probably arisen by the different NBO/Si ratio (NBO/Si: non-bridging oxygen per silicon) in  $\text{SiO}_4$  tetrahedra [19].

To further investigate and clearly identify the phase structure, **Figure 2** depicts the XRD pattern of the phosphor sample obtained by directly firing  $(\text{Sr},\text{Eu})\text{CO}_3@\text{SiO}_2$  precursor at 1000°C for 2 h. This pattern agrees well with the standard diffraction data of  $\alpha'$ - $\text{Sr}_2\text{SiO}_4$  (JCPDS No. 39-1256) and  $\beta$ - $\text{Sr}_2\text{SiO}_4$  (JCPDS No. 38-0271), so it can be deduced that this phosphor sample is a mixture of



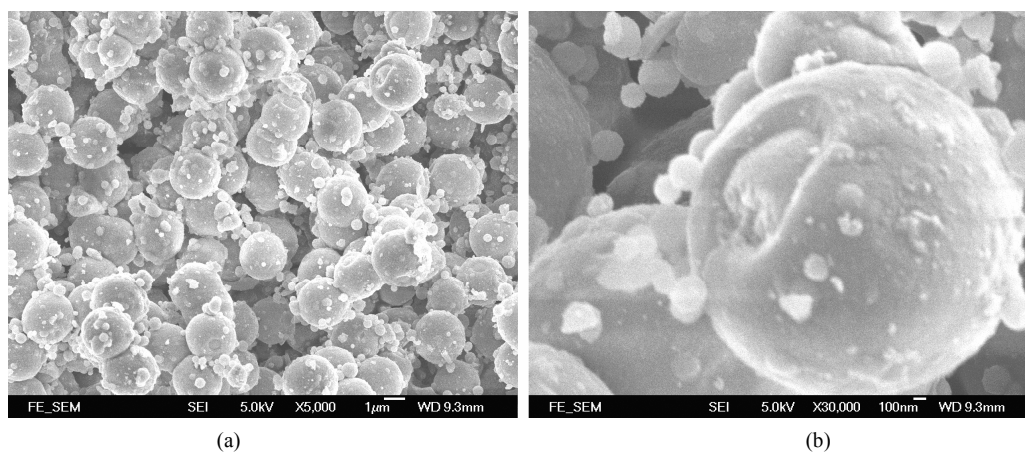
**Figure 1.** FTIR spectra of  $(\text{Sr},\text{Eu})\text{CO}_3@\text{SiO}_2$  precursor (a) and the obtained  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  phosphor sample (b).



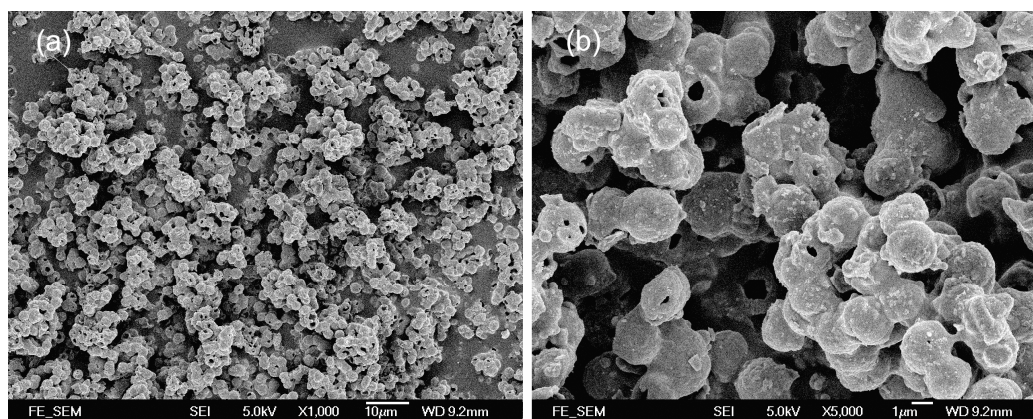
**Figure 2.** XRD pattern of  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  phosphor sample prepared by directly firing  $(\text{Sr},\text{Eu})\text{CO}_3@\text{SiO}_2$  precursor at 1000°C for 2 h.

orthorhombic  $\alpha'$ - $\text{Sr}_2\text{SiO}_4:\text{Eu}$  and monoclinic  $\beta$ - $\text{Sr}_2\text{SiO}_4:\text{Eu}$ . The  $\alpha'$  and  $\beta$  forms are the two modifications of  $\text{Sr}_2\text{SiO}_4$ , and the phase transition between low temperature  $\beta$  phase and high temperature  $\alpha'$  phase occurs at about 358 K [20,21], whereas  $\alpha'$  phase can also be stabilized at room temperature by substituting more Eu ( $\geq 0.1$ ) or small amounts of  $\text{Ba}^{2+}$  for  $\text{Sr}^{2+}$  [22,23]. In this work, the concentration of Eu activator is 0.1, so  $\alpha'$ - $\text{Sr}_2\text{SiO}_4:\text{Eu}$  is stably crystallized as well as  $\beta$ - $\text{Sr}_2\text{SiO}_4:\text{Eu}$  as expected. Approximately estimated from the intensity of the diffraction peaks,  $\alpha'$ - $\text{Sr}_2\text{SiO}_4:\text{Eu}$  has much more content percentage than  $\beta$ - $\text{Sr}_2\text{SiO}_4:\text{Eu}$  in this mixture. It is noted that not only is the present synthesized temperature (1000°C, no flux) lower than that in the conventional flux-assisted solid-state reaction method (usually 1300°C), but also the contamination of flux can be avoided due to the absence of flux.

To investigate the effect of core-shell precursor on the morphology of the resultant  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  phosphor, **Figure 3** and **Figure 4** demonstrate the SEM images of the precursor and phosphor sample, respectively. In this precursor (**Figure 3**), most of  $\text{SiO}_2$  are induced to coat on



**Figure 3.** SEM images of  $(\text{Sr,Eu})\text{CO}_3@\text{SiO}_2$  core-shell precursor observed at different magnifications: (a)  $\times 5000$ ; (b)  $\times 30,000$ .



**Figure 4.** SEM images of  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  phosphor sample observed at different magnifications: (a)  $\times 1000$ ; (b)  $\times 5000$ .

the surface of  $(\text{Sr,Eu})\text{CO}_3$  core to form  $(\text{Sr,Eu})\text{CO}_3@\text{SiO}_2$  core-shell structure with  $\text{SiO}_2$  shell layer about 100 ~ 200 nm thickness; however, a few nucleate directly into  $\text{SiO}_2$  nano-particles (100 ~ 200 nm) and locate onto the surface of core-shell structure. The formation mechanism and the composition of this precursor have been disclosed in our previous work [15]. It can be noted that this precursor has imperfect core-shell structure, and there appears an apparent gap without coated by  $\text{SiO}_2$  on every core-shell particle. However, the existence of the gap accesses us to clearly understand the reaction mechanism between core and shell by morphology observation and comparison.

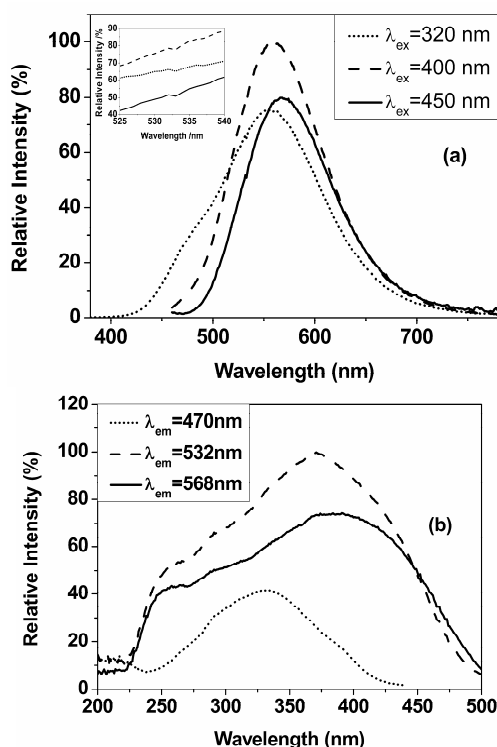
After the precursor was fired at  $1000^\circ\text{C}$  for 2 h, the obtained  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  phosphor sample seems to inherit the external contour of the precursor. Overall, the particles of the phosphor still appear uniform and near-spherical morphology, as shown in **Figure 4(a)**, and the particle size is about 2  $\mu\text{m}$ , slightly less than that of the precursor, which results from the condensation reaction between  $(\text{Sr,Eu})\text{CO}_3$  core and amorphous  $\text{SiO}_2$  shell at

the high temperature. Observed from the enlargement figure (**Figure 4(b)**), the condensation reaction also leads to slight aggregation and adhesion among particles, but the profile of the single particle can be clearly recognized, which indicates that every  $(\text{Sr,Eu})\text{CO}_3@\text{SiO}_2$  particle in the core-shell precursor would act as a separate reaction unit, and it is of the suitable stoichiometrical ratio to situ produce an isolated  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  micrometer particle. More noticeably, all the particles of the  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  phosphor exhibit hollow morphology with an opening, and the wall thickness is slightly thicker than that of  $\text{SiO}_2$  shell layer of the precursor. Combined with the results of XRD analysis, it seems that the shell of the precursor has transformed into thicker  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  layer, while the core has disappeared past the chemical reaction at the high temperature. That is to say, the fact that the phosphor particles still maintain near single and hollow spherical shape suggests that  $(\text{Sr,Eu})\text{CO}_3$  would diffuse into  $\text{SiO}_2$  shell and react into hollow  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  phosphor until the exhaust of  $(\text{Sr,Eu})\text{CO}_3$  core. It can be deduced intuitively that this reaction mechanism can be regarded as  $(\text{Sr,Eu})\text{CO}_3$

diffusion controlled process, which is consistent with the theoretical inference in Lu and Wu' work [24].

The luminescent properties of  $\alpha'$ - $\text{Sr}_2\text{SiO}_4\text{:Eu}$  or  $\beta$ - $\text{Sr}_2\text{SiO}_4\text{:Eu}$  have been researched widely [25-28]; however, the hybrid luminescence of the co-existent phase of  $\alpha'$ - and  $\beta$ - $\text{Sr}_2\text{SiO}_4\text{:Eu}$  has seldom been separately distinguished. In order to systematically understand the dependence of luminescent properties on the crystal structure of  $\text{Sr}_2\text{SiO}_4\text{:Eu}$  phosphor, we further investigated and analyzed the photoluminescence of this hybrid phosphor sample.

**Figures 5(a)** and **(b)** show the emission and excitation spectra of the phosphor sample, respectively. As illustrated in **Figure 5(a)**, the peak of the dominant emission band moves from 555 to 568 nm with the increase of the excitation wavelength from 320 to 450 nm. Whichever the excitation wavelength is, a turn at 532 nm is observed in the emission spectra as clearly shown in the inset of **Figure 5(a)**, which implies that the peak at 532 should be classified as a different emission band from the dominant one in the emission spectra. Both emission bands are the response to the co-existence of  $\alpha'$ - $\text{Sr}_2\text{SiO}_4\text{:Eu}$  and  $\beta$ - $\text{Sr}_2\text{SiO}_4\text{:Eu}$ . The orientations of  $\beta$  and  $\alpha'$  lattices are related by a simple rotation of x axis, and  $\beta$ - $\text{Sr}_2\text{SiO}_4\text{:Eu}$  with stronger Si-O bond valence produces stronger crystal field and then yields shorter wavelength emission compared with  $\alpha'$ - $\text{Sr}_2\text{SiO}_4\text{:Eu}$ , so it can be deduced that the emission band centered at 532 nm originates from  $\beta$ - $\text{Sr}_2\text{SiO}_4\text{:Eu}$ , and its emission peak position is independent on the excitation wavelength; while the dominant emission band at longer wavelength should be ascribed to  $\alpha'$ - $\text{Sr}_2\text{SiO}_4\text{:Eu}$ , and this emission can occur blue- or red-shift with the change of the excitation wavelength. It can be noted that  $\alpha'$ - $\text{Sr}_2\text{SiO}_4\text{:Eu}$  shows stronger emission intensity than  $\beta$ - $\text{Sr}_2\text{SiO}_4\text{:Eu}$  in our sample, which is contrary to the results confirmed by many work [10,22,26]. The reason is that  $\alpha'$ - $\text{Sr}_2\text{SiO}_4\text{:Eu}$  has much more mass percentage than  $\beta$ - $\text{Sr}_2\text{SiO}_4\text{:Eu}$  in this phosphor sample. Both of the emission band are produced by the 5d-4f transition of the activator  $\text{Eu}^{2+}$  occupied the ten oxygen coordinated  $\text{Sr}^{2+}$ (I). As well known, there is another  $\text{Sr}^{2+}$  site,  $\text{Sr}^{2+}$ (II), surrounded by nine oxygen in  $\beta$ - and  $\alpha'$ - $\text{Sr}_2\text{SiO}_4\text{:Eu}$ . When  $\text{Eu}^{2+}$  replaces  $\text{Sr}^{2+}$ (II), a shorter blue light emission band will be produced with peak at about 470 nm. As shown in **Figure 5(a)**, the 470 nm blue emission is obviously resolved as gibbous shoulder when the excitation wavelength is as short as 320 nm, while it disappears when the excitation wavelength is set at 400 or 450 nm. On the other hand, the phosphor sample has the strongest emission peak intensity when excited by 400 nm (NUV, near ultraviolet), and the intensity still maintains about 80% under 450nm blue light excitation. That is to say, the  $\text{Sr}_2\text{SiO}_4\text{:Eu}$  phosphor can applied to combine with NUV-LED or blue



**Figure 5.** Emission (a) and excitation (b) spectra of the obtained  $\text{Sr}_2\text{SiO}_4\text{:Eu}$  phosphor sample.

LED.

The applicability of this  $\text{Sr}_2\text{SiO}_4\text{:Eu}$  phosphor for white LED can also be certificated by the excitation spectrum. Three excitation spectra were illustrated in **Figure 5(b)**, with monitoring emission wavelength at 568, 532 and 470 nm, respectively. Obviously, there is a very broad excitation band in 300 - 500 nm spectral regions when monitoring wavelength at 532 and 568 nm, which assures that this phosphor has high efficient light conversion for NUV and blue light. As for 470 nm blue emission, it has much lower efficiency, and its suitable excitation region is narrower (250 - 400 nm). That is the reason that 470 nm emission is nearly unresolved when this phosphor is excited by long-wavelength light.

#### 4. CONCLUSIONS

The hybrid  $\alpha'$ - and  $\beta$ - $\text{Sr}_2\text{SiO}_4\text{:Eu}$  phosphor was successfully developed by firing  $(\text{Sr,Eu})\text{CO}_3\text{@SiO}_2$  core-shell precursor directly at 1000°C, and it appeared uniformly hollow near-spherical morphology with particle size about 2  $\mu\text{m}$ . The morphology was resulted from the core-shell structure of the precursor and the reaction mechanism between  $(\text{Sr,Eu})\text{CO}_3$  core and  $\text{SiO}_2$  shell. The mechanism was acquired visually to be  $(\text{Sr,Eu})\text{CO}_3$  diffusion controlled reaction process. Responded to its hybrid crystal structure, the phosphor exhibited the combined luminescence of  $\alpha'$ - and  $\beta$ - $\text{Sr}_2\text{SiO}_4\text{:Eu}$ .  $\alpha'$ - $\text{Sr}_2\text{SiO}_4\text{:Eu}$

has the longer emission wavelength, and its emission peak can blue- or red-shift with the change of the excitation wavelength; while the 532 nm emission of  $\beta$ - $\text{Sr}_2\text{SiO}_4:\text{Eu}$  is independent on the excitation wavelength. Compared with the conventional high temperature solid-state reaction method, this method requires lower firing temperature and no flux contamination, and produces finer particles with narrow size distribution. More importantly, the reaction mechanism will provide some ideas to improve the particle performance of silicate phosphors, for instance, the spherical and solid  $\text{Sr}_2\text{SiO}_4:\text{Eu}$  phosphor could be obtained by employing a spherical  $\text{SiO}_2@(\text{Sr},\text{Eu})\text{CO}_3$  core-shell precursor as starting materials.

## 5. ACKNOWLEDGEMENTS

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