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Photoluminescent and thermal properties of $(Sr_{0.995-x-y-z}Ca_xBa_yMg_z)_2SiO_4$:0.01$Eu^{2+}$ phosphors for warm white light-emitting diodes

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ABSTRACT

A series of phosphors $(Sr_{0.995-x-y-z}Ca_xBa_yMg_z)_2SiO_4$:0.01$Eu^{2+}$ ($0 \le x \le 0.45$, $0 \le y \le 0.015$, $0 \le z \le 0.35$) were synthesized by solid state reaction. Their phase compositions and photoluminescent properties were investigated in detail. The X-ray diffraction analysis indicates the impurity phase of $SrSiO_3$ is formed only when $z \ge 0.25$. A photoluminescence investigation shows, with x increasing the emission spectra of the phosphors ($0 \le x \le 0.45$, $0 \le y \le 0.015$, $z = 0$) obviously red-shift, the corresponding color tones shift from yellow to orange–yellow and their CCTs reduce from 2875 to 2237 K. All the results are beneficial for the phosphors to combining blue light-emitting diode chips to generate warm white light. Besides, the thermal stability of the phosphor ($x = 0.36$, $y = z = 0$) is enhanced by doping Ba^{2+}, due to the greater activation energy for the compounds containing barium.

1. Introduction

Recently, the phosphor-converted light-emitting diodes (LEDs) have been used as backlight, flashlight, automobile headlamp, and etc., which would be regarded as the next-generation lighting sources. They have a tendency to replace the conventional incandescent and fluorescent lamps because of their high energy efficiency, durability, reliability, and capability to be used in products with various sizes and eco-friendly spectral component [1–3]. Currently, a yellow-emitting $Y_3Al_5O_{12}$:Ce (YAG:Ce) phosphor has been used most widely on blue LED chips to generate white light. Nevertheless, the color-rendering index of such a white-light LED is poor [4,5]; thus, a warm-white illumination could not be achieved by this approach owing to lack of red component. In reality, since YAG phosphors are very tightly patented, it is impossible to use YAG:Ce without paying patent royalties. In addition to that, another concern is that there are few phosphor materials suitable for blue-LED chips at present. Thus, improvement of commercial phosphors appears to be greatly important [6–8]. As we known, there is increasing evidences that Eu^{2+} replacing a smaller equivalent cation may result in a bigger crystal field splitting of the d-manifold and a red-shift of the emission spectrum; and vice versa [7]. And Ba^{2+} substituting for a smaller equivalent cation may give rise to an enhancement of the thermal stability (TS) due to the bigger activation energy for the compounds containing barium [9,10]. In view of this, researchers have attempted a lot to improve the properties of commercial phosphors, including the positions of absorption and emission bands and the thermal stability through modifying host components [7,11,12].

Sr_2SiO_4:Eu^{2+} phosphor has been concerned as a yellow element for white LEDs because of its superior performances [13–17], such as chemical stability and thermal stability. It has been known, the orthosilicate Sr_2SiO_4, which crystallizes in the tetragonal space group *Pmnb*, contains two Sr^{2+} sites in the host lattice, one site I is 10-coordinated and the other site II is 9-coordinated by oxygen atoms [18]. Sr_2SiO_4:Eu^{2+} had been developed as yellow phosphors by Blasse et al. [19], and subsequently has been applied in white LEDs by Park et al. [14], their research results indicated that Sr_2SiO_4:Eu^{2+} possesses excellent absorption properties in the range of 300–450 nm and shows asymmetric broad emission spectra upon near ultraviolet excitation, whose emission spectra can be decomposed into two parts, i.e., the short-wavelength emission originating from EuII and the long-wavelength emission originating from EuI [20,21]. Moreover, it was reported that Sr_2SiO_4:Eu^{2+} exhibits a stronger yellow emission than that of YAG:Ce [22].

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Kim et al. reported the shift of the emission spectra of M_2SiO_4:Eu^{2+} (M&9552;Ba, Sr, Ca) phosphors under 375 nm excitation [23], and found that doping Ba^{2+} into Sr_2SiO_4:Eu^{2+} brings about a blue-shift of the emission spectrum and an enhancement of the thermal stability (TS) under 400 nm excitation [10]. Baginskiy et al. [9] investigated the temperature dependent emission of $(Sr_{2-x}Ba_x)SiO_4$:Eu^{2+} phosphors under 460 nm excitation. However, the photoluminescent and thermal properties of the phosphors $(Sr_{0.995-x-y-z}Ca_xBa_yMg_z)_2SiO_4$:$0.01Eu^{2+}$ (SCBM:$0.01Eu^{2+}$, $0 \le x \le 0.45$, $0 \le y \le 0.015$, $0 \le z \le 0.35$) under 450 nm excitation have not been researched yet. In this work, in order to improve the properties of the yellow Sr_2SiO_4:Eu^{2+} phosphor to realize a red-shift of the emission spectrum (by doping Ca^{2+} or Mg^{2+} ions) and enhance the TS of the phosphor (by doping Ba^{2+}), we synthesized a series of phosphors SCBM:$0.01Eu^{2+}$ ($0 \le x \le 0.45$, $0 \le y \le 0.015$, $0 \le z \le 0.35$) by solid state reaction and carefully investigated their photoluminescent and thermal properties.

2. Experimental

2.1. Synthesis

The orthosilicate compounds, SCBM:$0.01Eu^{2+}$ ($0 \le x \le 0.45$, $0 \le y \le 0.015$, $0 \le z \le 0.35$), were synthesized by solid state reaction. Stoichiometric amounts of $SrCO_3$ (Xiamen Tongshida Co., Ltd., 99%), $CaCO_3$ (Tianjin Guangfu Co., Ltd., 99%), $BaCO_3$ (Shanghai Silian Chemical Co., Ltd., 99%), $Mg(NO_3)_2{\cdot}6H_2O$ (Shanghai Shanpu Chemical Co., Ltd., AR), SiO_2 (Tianjin Meiyu Chemical Co., Ltd., 98%), and Eu_2O_3 (Beijing Non-ferrous Metal Research Institute, 99.99%) were ground in an agate mortar for 30 min to mix them homogeneously. Then the mixtures were placed in alumina crucibles and sintered at 1350 °C for 4 h in reducing atmosphere (N_2:H_2 = 95:5) in the tube furnace. After sintering the resulting products were ground again, yielding fluffy crystalline powder. All the samples were doped with 1 mol% of Eu^{2+}.

2.2. Characterization

The phase purity was determined by using a Rigaku D/max-2400 powder X-ray diffractometer with Cu Kα radiation (λ = 1.54178 Å) operating at 40 kV and 20 mA. The 2θ ranges of all the data sets are from 10° to 75° with the step size of 0.02°. The photoluminescence excitation (PLE) and emission (PL) spectra were recorded on an FLS-920T fluorescence spectrophotometer equipped with a 450 W Xe light source. To study the thermal quenching from 20 to 220 °C, the same spectrophotometer was equipped with a home-made heating cell. All the measurements were performed at room temperature.

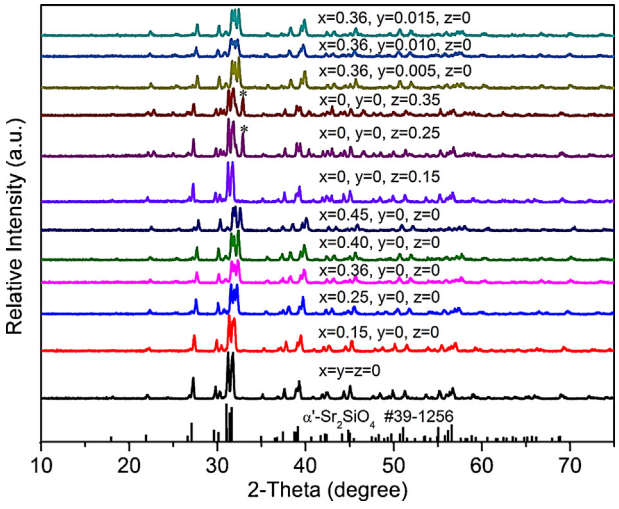

Fig. 1. XRD patterns of SCBM:$0.01Eu^{2+}$ ($0 \le x \le 0.45$, $0 \le y \le 0.015$, $0 \le z \le 0.35$).

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the XRD patterns of SCBM:$0.01Eu^{2+}$ ($0 \le x \le 0.45$, $0 \le y \le 0.015$, $0 \le z \le 0.35$). All the diffraction peaks of the phosphors doped with Ca^{2+} and Ba^{2+} ($0 \le x \le 0.45$, $0 \le y \le 0.015$, $z = 0$) are indexed to the phases of α′-Sr_2SiO_4 (JCPDS No. 39-1256), indicating that doping Ca^{2+} and Ba^{2+} into Sr_2SiO_4:$0.01Eu^{2+}$ does not cause significant change. But for the phosphors doped with Mg^{2+} ($x = y = 0$, $0 \le z \le 0.35$), when the doping content is above $z = 0.25$ the impurity phase of $SrSiO_3$ is obviously generated (see asterisk in Fig. 1), this may be because Mg^{2+} ion (0.06 nm) is much smaller than Sr^{2+} (0.11 nm). Besides, the diffraction peaks of the phosphors doped with Ca^{2+} ($0 \le x \le 0.45$, $0 \le y \le 0.015$, $z = 0$) shift towards high angles, due to the substitution of the smaller Ca^{2+} ions (0.09 nm) for larger Sr^{2+} ions (0.11 nm) in the host lattice.

3.2. Photoluminescent properties

The PLE and PL spectra of the series phosphors are shown in Fig. 2. In which, Fig. 2a illustrates the PLE and PL spectra of SCBM:$0.01Eu^{2+}$ ($x = y = z = 0$), its peak values of PLE spectra monitored at 490 and 550 nm are 338 and 367 nm, respectively, and its PLE intensity monitored at 490 nm is higher than that monitored at 550 nm, exhibiting clear selective excitation characteristic. This is consistent with the situation of its PL spectra. It is observed that, upon both 338 and 370 nm excitations, its PL spectra contain two bands: one's peak is 498 nm and the other's is 563 nm, which coincides with the research conclusion that Eu^{2+} may occupy two Sr^{2+} sites in Sr_2SiO_4 lattice. Upon 338 nm excitation, the short-wavelength emission band (emission peak (EP) at 498 nm) becomes dominant. And upon 370 nm excitation, the peak intensity of the long-wavelength emission (EP at 563 nm) is slightly higher than that of the short-wavelength emission, the PL spectrum presents a broad and nearly flat band in the range of 450–670 nm. Besides, under 450 nm excitation the long-wavelength emission becomes predominant and virtually hides the

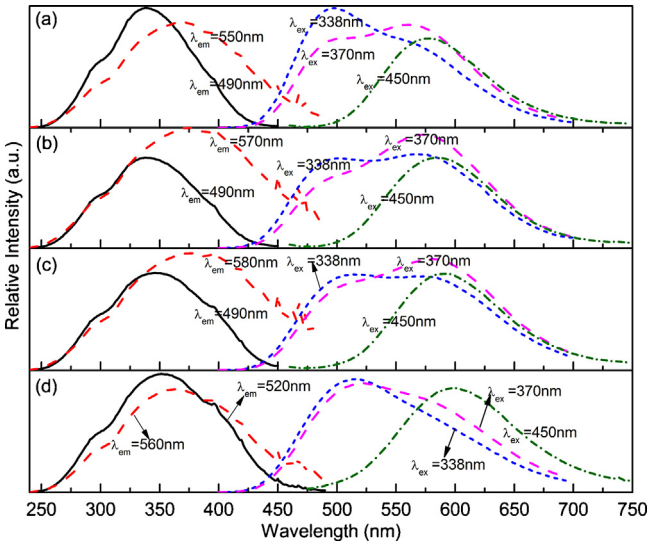

Fig. 2. PLE and PL spectra of SCBM:$0.01Eu^{2+}$ (a) $x = y = z = 0$; (b) $x = z = 0$, $y = 0.15$; (c) $x = 0.25$, $y = z = 0$; (d) $x = 0.36$, $y = 0.01$, $z = 0$.