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Properties of $Sr_{2.13}Ba_{0.8}SiO_5$:$0.07Eu^{2+}$ phosphor synthesized by microwave assisted with SiC method

Zhenxing Du, Quansheng Liu*, Yulong Chen, Hongbin Wang

School of Materials Science and Engineering, Changchun University of Science and Technology, Changchun, Jilin, 130012, China

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ABSTRACT

Nano-sized $Sr_{2.13}Ba_{0.8}SiO_5$:$0.07Eu^{2+}$ yellow phosphor was synthesized by microwave assisted with SiC method (MASM). The phase, morphology, luminescence properties and formation mechanism of nanoparticles were studied. Results indicate that the phosphor is a tetragonal system with space group *P*4/*ncc* (130). The SEM shows a smooth surface and regular morphology with homogeneous size distributed from 80 to 100 nm. The formation of nano-sized particles ascribed to the interaction of microwave and reactive material, and that is the high speed vibration of product particles induced by microwave interaction inhibits the growth of the crystal grain size. The excitation spectrum is a broad band spectrum from 250 to 550 nm, which attributed to $4f$–$5d$ transition of Eu^{2+} ions. The emission spectrum excited at 460 nm is a broad band peaking at 577 nm attributed to the transition of $4f^65d \rightarrow 4f^7(^8S_{7/2})$ of Eu^{2+} ions. The color temperature and color coordinate of white LED prepared with the phosphor are 2658 K and (x = 0.3976, y = 0.2955) respectively.

1. Introduction

White light-emitting diodes (W-LEDs), the fourth-generation of solid-state lighting, have been paid significantly attention to due to their potential application in many fields [1–5]. Phosphor conversion type W-LED combined with the blue LEDs and yellow phosphors has induced enormously interest for many years. Recently, in particular, warm W-LEDs achieved by the blue light LEDs combined with Sr_3SiO_5:Eu^{2+} yellow phosphors were extensively investigated. Since then, Sr_3SiO_5:Eu^{2+} yellow phosphor became a hotpot. Sr_3SiO_5:Eu^{2+} phosphor displayed some fascinating properties, such as long emitting wavelength, broad spectral range, superior stability, low-cost, and so on. The Eu^{2+} ion-activator concentration, fluxing agents and alkaline-earth metal replacing etc. had been systematically studied [6,7]. It is found that the emission band could be controlled by adding Ba^{2+} ions to replace the Sr^{2+} ions in the host [8]. When a little Ba^{2+} ion was doped into Sr_3SiO_5:Eu^{2+} phosphor, the emission peak would shift to red [9–11]. Therefore, we selected $Sr_{2.13}Ba_{0.8}SiO_5$:$0.07Eu^{2+}$ as a research object. The traditional synthetic method of the phosphor was high temperature solid phase method, which not only waste power but also generate large particle-size in synthetic phosphor [12,13]. At the process of using, the phosphor must be ground, which would cause luminescent intensity obvious decrease. How to get tiny size phosphor, simultaneously keep high luminescent intensity, also became difficult to handle. Given this, we provided a microwave assisted with SiC method to synthesize nano-sized $Sr_{2.13}Ba_{0.8}SiO_5$:$0.07Eu^{2+}$ phosphor. Through systematic exploratory research, the nano-sized $Sr_{2.13}Ba_{0.8}SiO_5$:$0.07Eu^{2+}$ phosphors were obtained by MASM. The formation mechanism of nanoparticles and luminescent properties were studied.

2. Experimental

The typical synthetic procedure was shown as follow. The appropriate stoichiometric mixture of $SrCO_3$(A. R.), $BaCO_3$(A. R.), SiO_2(A. R.) and Eu_2O_3(99.99%) were weighted according to the chemical formula and milled homogeneously. All materials were utilized directly without a further treatment. Then the powder was calcined in silicon-molybdenum furnace and microwave furnace respectively at 1400 °C for 2 h in corundum crucible with the atmosphere of N_2/H_2(N_2: 90%, H_2: 10%). SiCs, acting as microwave absorbent, absorb microwave in the whole process. Last but not least, the as-obtained phosphor was cooled to room temperature naturally.

The crystal structure and phase composition of samples were

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* Corresponding author.
E-mail address: liuqs@cust.edu.cn (Q. Liu).

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characterized by a Japanese Rigaku Ultima IV powder X-ray diffraction (CuKα 40 kV, 20 mA, λ = 1.5406 Å). The emission and excitation spectra were measured by a RF-5301PC spectrophotometer equipped with a 150 W Xe lamp, which was manufactured by the Japanese Shimadzu Corporation. The SEM image was measured by a Japanese JSM-6701F field emission scanning electron microscope. All tests were carried out at room temperature.

3. Results and discussions

3.1. Structure of the phosphors

Fig. 1 shows the XRD patterns of $Sr_{2.93}SiO_5:0.07Eu^{2+}$ phosphors, Fig. 1(a) is the sample synthesized by MASM, Fig. 1(b) is the sample synthesized by a traditional high temperature solid-state method and Fig. 1(c) and (d) are the standard PDF data of Sr_2SiO_4 and Sr_3SiO_5 respectively. According to compare with standard PDF cards (No. 39-1256 and No.26-0984), the two samples are the tetragonal crystal structure of Sr_3SiO_5. However, the sample prepared by conventional high temperature solid-state method appears to some impurity diffraction peaks at around 27°, 31° and 39° of Sr_2SiO_4 phase, which indicates that a small amount of Sr_2SiO_4 phase exist. Some research results reveal that it is too difficult to obtain pure Sr_3SiO_5 and to wipe out Si_2SiO_4 phase by traditional high temperature solid-state method [11,12,14]. Nevertheless, by using the MASM, the pure Sr_3SiO_5 phase can obtain, which is ascribed to the rapid, homogeneous heating process of microwave and accurate temperature control.

In order to determine the influence on crystal structure of Ba^{2+} ion-doping, $Sr_{2.93}SiO_5:0.07Eu^{2+}$ phosphor was studied. The XRD patterns of $Sr_{2.93}SiO_5:0.07Eu^{2+}$(a) and $Sr_{2.13}Ba_{0.8}SiO_5:0.07Eu^{2+}$ (b) phosphors are shown in Fig. 2. The diffraction patterns are almost pure Sr_3SiO_5 phase, which are well matched the index of JCPDF card No.26-0984. Except the diffraction of Sr_3SiO_5 phase, there is not found any other impurity phase, which again indicates $Sr_{2.13}Ba_{0.8}SiO_5:0.07Eu^{2+}$ phosphor is obtained by MASM and the doped Eu^{2+} ions does not change the crystal structure. When doping of Ba^{2+} ions, the diffraction peaks shift to small angle, which indicates the lattice increases. Because the radius of Ba^{2+} ion is bigger than that of Sr^{2+} ion, so when Ba^{2+} ion replaces Sr^{2+} ion, the unit cell is enlarged.

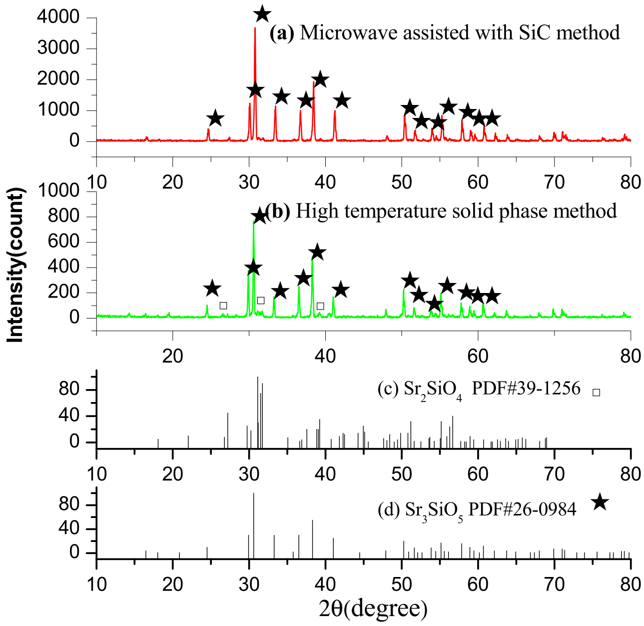

Fig. 1. XRD patterns of $Si_{2.93}SiO_5:0.07Eu^{2+}$ ((a) MASM (b) high temperature solid-state method (c)and (d) standard PDF cards).

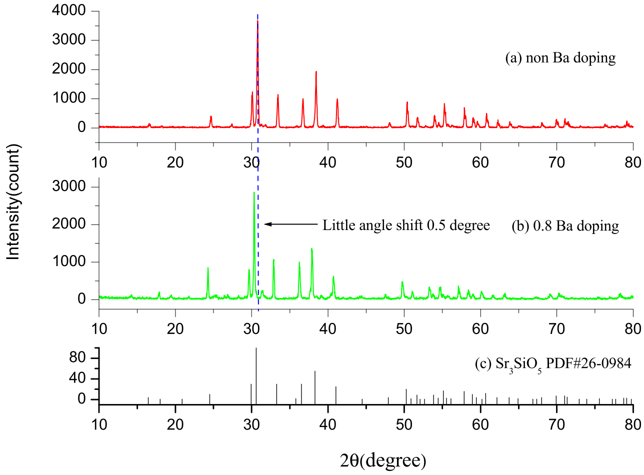

Fig. 2. XRD patterns of $Sr_{2.93}SiO_5:0.07Eu^{2+}$(a) and $Sr_{2.13}Ba_{0.8}SiO_5:0.07Eu^{2+}$ (b) phosphors.

Fig. 3 depicts the crystal structure of Sr_3SiO_5 and the crystal structure of $Sr_{2.13}Ba_{0.8}SiO_5:0.07Eu^{2+}$. The crystal structure of Sr_3SiO_5 is shown in Fig. 3(a). The Sr_3SiO_5 is a tetragonal crystal structure with a space group of *P4/ncc*. Each Sr^{2+} ion coordinates with six oxygen atoms and forms [SrO6] distorted octahedron and has two types of lattice positions [15]. Fig. 3(b) shows that the positions of Sr^{2+} ions are occupied by Eu^{2+} and Ba^{2+} ions in the $Sr_{2.13}Ba_{0.8}SiO_5:0.07Eu^{2+}$ structure. When Sr^{2+} ion-sites are substituted by Eu^{2+} and Ba^{2+} ions, the tetragonal phase is well maintained. However, since the radii of Eu^{2+} and Ba^{2+} ions are longer than that of Sr^{2+} ions, the octahedron is further more enlarged and distorted, which is consistent with ahead XRD results. Last, the grown lattice leads to the distance increase of central cations and surrounding anions, which will decrease the attraction of anions to the central Eu^{2+} ions.

3.2. Luminescent properties of phosphors

Fig. 4 shows the excitation (a) and emission (b) spectra of the $Sr_{2.93}SiO_5:0.07Eu^{2+}$ and $Sr_{2.13}Ba_{0.8}SiO_5:0.07Eu^{2+}$ phosphors. It is found that the excitation spectrum is a broad band spectrum ranging from 250 to 550 nm. There are two peaks at 276 and 373 nm and one excitation shoulder at 467 nm, indicating that these phosphors could be excited by UV or blue light chip. The

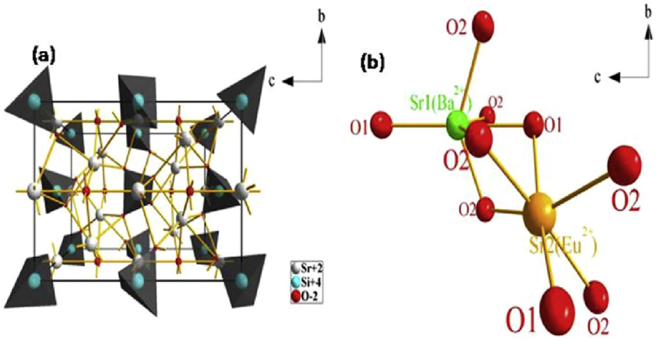

Fig. 3. Crystal structure models of $Sr_{2.13}Ba_{0.8}SiO_5:0.07Eu^{2+}$ phosphor (a) lattice (b) coordination of anions and cations.