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Synthesis and luminescent properties of a novel red-emitting phosphor: Eu^{3+}-activated Ba_2ScO_3F

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ABSTRACT

A novel red-emitting $Ba_2ScO_3F:Eu^{3+}$ phosphor was prepared by high-temperature solid-state reaction method. The structure and luminescence properties of the obtained phosphors were investigated. The crystallographic occupancy of Eu^{3+} in Ba_2ScO_3F was studied and verified to be the site of Sc^{3+} ions. Photoluminescence of the optimized $Ba_2Sc_{0.94}O_3F:0.06Eu^{3+}$ phosphor showed that the phosphor can be efficiently excited by ultraviolet (395 nm) and blue (464 nm) light, and exhibits an intense red emission at 612 nm (due to $^5D_0 \rightarrow {}^7F_2$ electric dipole transition of Eu^{3+} ions). The dependence of the luminescence intensity on temperatures was measured, and showed a satisfactory thermal quenching effect. These results suggest that the phosphor could be a potential for applications in w-LEDs.

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1. Introduction

White light-emitting diodes (w-LEDs) have demonstrated such outstanding advantages as long lifetime, high energy efficiency, and environmental friendliness while comparing with incandescent and fluorescent lamps for solid-state lighting [1,2]. Commercial w-LEDs generally employ blue LED chips combining with yellow-emitting phosphors [3], which have a color deficiency in the red region, and result in low color rendering index (CRI) [4] and high correlated color temperature (CCT). In order to solve this problem, red-emitting phosphors are added to fulfill the spectrum deficiency in red region. Meanwhile, near-ultraviolet (n-UV) LED chips combining with red-, green-, and blue-emitting phosphors are also used to obtain high color rendering index w-LEDs [5]. Therefore, red-emitting phosphors play an important role in producing high quality white light. However, the current red-emitting phosphors, no matter Eu^{3+} or Eu^{2+} ions activated phosphors, confront many problems like poor chemical stability for sulfide-based red-emitting phosphors [6], rigorous synthesis conditions and high prices for nitride-based red-emitting phosphors [7]. Consequently, it is essential to develop a high efficiency, excellent chemical stability and inexpensive red-emitting phosphors.

Recently, oxyfluoride materials, such as Sr_3AlO_4F [8], $Ca_2Al_3O_6F$ [9], $Ca_4Si_2O_7F_2$ [10,11], Sr_2LiSiO_4F [12] etc, have attracted more and more attentions as phosphor hosts due to their good stability, simple synthesis conditions and excellent luminescence properties. Moreover, Eu^{3+} doped phosphors can emit pure red light due to the sharp emission lines, and display a sufficient absorption at UV or blue band for LED chips [13]. Hence, Eu^{3+} activated red-emitting oxyfluoride phosphors is a favorable choice. In this letter, a Eu^{3+}-activated oxyfluoride Ba_2ScO_3F phosphor was synthesized, the crystallographic site and luminescence properties of Eu^{3+} ions in this phosphor were investigated in detail.

2. Experimental

Eu^{3+}-activated Ba_2ScO_3F phosphors were prepared by high-temperature solid-state reaction method. The starting materials, $BaCO_3$ (99.95%), Sc_2O_3 (99.99%), BaF_2 (99.99%), and Eu_2O_3 (99.99%) were weighed out according to the stoichiometric ratio. The mixed powder was grounded evenly in an agate mortar, and then homogeneous mixtures were put in an alumina crucible and continually fired at 1300 °C for 4 h in air. The crystal structure of the phosphor was characterized by an X-ray diffraction (XRD) analysis using an X-ray diffractometer with Co-*Ka* radiation (λ=0.178892 nm). The photoluminescence spectra and thermal quenching were measured by a spectrofluorometer, which are composed of a Xe high-pressure arc lamp, a photomultiplier tube and a heating apparatus.

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3. Results and discussion

Phase and structure: The crystal structure of Ba_2ScO_3F, first reported by Richard L. et al. [14], has a tetragonal space group *I4/mmm* (PDF card no. 89-0397) with cell parameters of $a=b=4.1480(2)$ Å, $c=13.5441(8)$ Å, $\alpha=\beta=\gamma=90^\circ$, $Z=2$. The XRD patterns of the synthetic products with assumed compositions Ba_2ScO_3F and $Ba_2Eu_{0.06}Sc_{0.94}O_3F$ (showed in Fig. 1a) matched well with JCPDS standard card, except for the intensities of the diffraction peaks for the preferred orientation in Miller (00L) planes, no peaks of impure phases were observed in the experimental range, which indicated the well formed single phase of these two samples. While a small amount of Sc_2O_3 was detected from the phase analysis of X-ray diffraction for the synthetic products with assumed composition $Ba_{1.94}Eu_{0.06}ScO_3F$ (showed in Fig. 1a). Therefore, it could be preliminarily inferred that the Sc^{3+} ions are partial substitution by Eu^{3+} ions. In addition, the XRD patterns of the samples $Ba_{1.94}Eu_{0.06}ScO_3F$ and $Ba_2Eu_{0.06}Sc_{0.94}O_3F$ showed that all the diffraction peaks shift to lower angles compared with Ba_2ScO_3F (showed in Fig. 1b), which demonstrated the lattice expansion while doping Eu^{3+} ions. In the structure of Ba_2ScO_3F (showed in Fig. 2), Ba^{2+} ions are coordinated by nine atoms with ionic radii approximately 1.47 Å [15] ($>r(Eu^{3+})=1.12$ Å [15] CN=9), while Sc^{3+} ions are coordinated by four oxygen and two disordered apical anion (O/F), forming distorted octahedrons [3,17] with ionic radii approximately 0.745 Å [15] ($<r(Eu^{3+})=0.947$ Å [15], CN=6). Obviously, the expansion of the lattices is most probably due to the partial substitution of Sc^{3+} ions by Eu^{3+} ions. The reason for Eu^{3+} ions occupying the sites of Sc^{3+} ions should be attributed to the ionic radii of Eu^{3+} ions matching Sc^{3+} ions better than Ba^{2+} ions.

Photoluminescence properties: As we know, practical phosphors for LEDs usually suggest two exciting approaches of LED chips (UV-LED chip with the wavelength of 380–420 nm and blue-LED chip, 450–480 nm) [2]. The excitation spectrum (showed in Fig. 3) of $Ba_2Sc_{0.94}O_3F$:$0.06Eu^{3+}$ in UV and blue range (monitored at 612 nm) contains several f–f transition lines of Eu^{3+} attributed to the transitions from $^7F_0$ ground state to the different excited states, with peaks at 320 nm, 362 nm, 379 nm, 387 nm, 395 nm, 409/414 nm and 464 nm, corresponding to the transitions from the $^7F_0$ ground state to the $^5H_4$, $^5D_4$,$^5G_2$, $^5G_3$, $^5L_6$, $^5D_3$ and $^5D_2$ states of Eu^{3+} [16], respectively. Among them, two strong excitation peaks exist, located at 395 nm and 464 nm, indicating the potential applications for UV- and blue-LEDs.

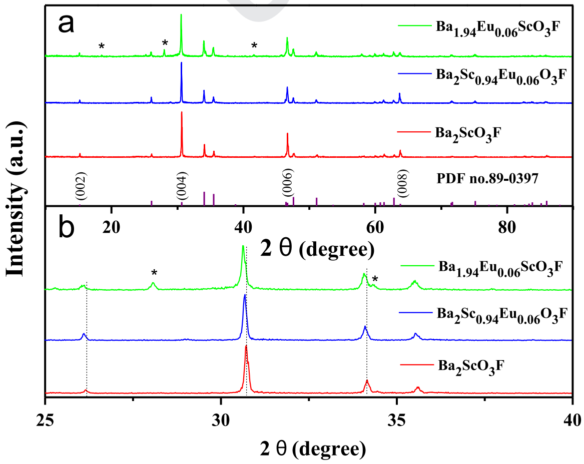

Fig. 1. The XRD patterns of the synthetic products with assumed composition $Ba_{1.94}Eu_{0.06}ScO_3F$ (green line), $Ba_2Eu_{0.06}Sc_{0.94}O_3F$ (blue line) and Ba_2ScO_3F (red line), (The asterisk marks the impurity phase, which is Sc_2O_3), 2θ ranges from (a) 10°–90°, (b) 25°–40°. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

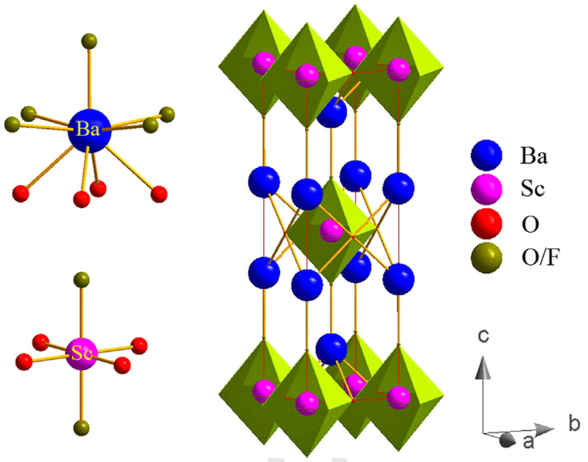

Fig. 2. The crystal structure model of Ba_2ScO_3F and coordination environment of Ba^{2+} and Sc^{3+}.

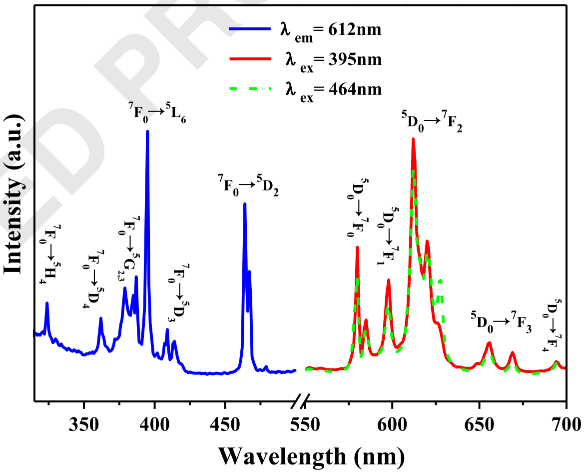

Fig. 3. Excitation and emission spectra of the $Ba_2Sc_{0.94}O_3F$:$0.06Eu^{3+}$ phosphor. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The emission spectra of $Ba_2Sc_{0.94}O_3F$:$0.06Eu^{3+}$ under 395 nm and 464 nm excitation are showed in Fig. 3. The positions of emission peaks almost have no changes, while the emission intensity at 612 nm excited by 395 nm is remarkably stronger than that of 464 nm. The emission peaks at 580 nm, 585/598 nm, 612/620/628 nm, 656/669 nm, 695 nm are ascribed to transitions of $^5D_0 \rightarrow {}^7F_J$ ($J=0$–4) [16], respectively. It is known that the magnetic dipole $^5D_0 \rightarrow {}^7F_1$ transition is insensitive to the local environment surrounding Eu^{3+} ions, while the electric dipole $^5D_0 \rightarrow {}^7F_2$ transition is sensitive to the local coordination environment [13]. In this phosphor, the Eu^{3+} ions exhibited the largest emission intensity at 612 nm ($^5D_0 \rightarrow {}^7F_2$), because the Eu^{3+} ions occupied the sites of Sc^{3+} ions, which are distorted for the disordered apical anion (O/F) [3,17].

The dependence of emission intensities of $Ba_2Sc_{1-x}O_3F$:xEu^{3+} phosphors on Eu^{3+} concentrations are shown in Fig. 4a. The emission intensities excited by 395 nm increase with Eu^{3+} content increasing until a maximum intensity is reached when $x=0.06$, and then decrease due to concentration quenching. The concentration quenching occurs because the nonradiative energy transfers among Eu^{3+} ion within a certain distance. The critical distance R_c can be calculated by the following formula $R_c=2[3V/(4\pi x_c N)]^{1/3}$, where V is the volume of the crystallographic unit cell, x_c is the

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