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Hydrothermal synthesis and luminescence properties of Eu^{2+}-doped $BaSiF_6$ microrods

Ruinian Hua *, Xin Zhao, Wei Zhang, Liyan Na, Jun Zhao

College of Life Science, Dalian Nationalities University, Dalian, Liaoning 116600, PR China

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ABSTRACT

Eu^{2+}-doped $BaSiF_6$ microrods with average diameter of 200 nm, and length of 1–4 μm were synthesized via a facile hydrothermal method. The crystal structure and morphology of final products were characterized by X-ray powder diffraction (XRD) and transmission electron microscope (TEM). Upon the excitation of 257 nm UV light, the as-prepared samples exhibit strong and sharp line emission, which originates from the transitions within the $4f^7$ electron configuration of Eu^{2+} ions. The optimal doping concentration of Eu^{2+} ions in $BaSiF_6$ matrix was confirmed to be about 15 mol%.

1. Introduction

Inorganic materials with special morphologies have been attracting more and more attention owing to their potential in fundamental studies and technological applications [1–3]. By far, plenty of efforts have been devoted to the fabrication of various kinds of inorganic materials with different morphologies and sizes [4–7]. Among these compounds, fluorides have attracted great interest for their low phonon energy and optical transparency over a wide wavelength range [8–10]. Therefore, as the matrix materials, fluorides doped with rare earth ions have excellent optical characteristics, such as high luminescent efficiency, long excited state lifetime, etc. [11]. Furthermore, fluorides possess good thermal and environmental stability. Recently, output of laser has been achieved in several fluorides systems [12,13]. Therefore, fluorides doped with rare earth ions have potential applications in high-definition display, solid state laser, infrared detection, biological analysis, medical diagnosis and so on.

The fluorescence of divalent europium has been investigated in many compounds, such as aluminates, silicates, phosphates, sulfides, nitride-silicates, fluorides, etc. [14]. Among these Eu^{2+}-activated phosphors, two types of emissions, including the band emission normally associated with Eu^{2+} 5d to 4f transition, and line emission from transitions within the $4f^7$ configuration have been found [15,16]. The band or line emission depends on crystal field, nephelauxetic effect, coordination number and temperature [17]. Although 4f→4f transition is parity forbidden, under certain conditions, sharp line emission due to the $4f^7(^6P_{7/2}) \rightarrow 4f^7(^8S_{7/2})$ also can be observed [18].

Because of the weak crystal field environment, $BaSiF_6$ is considered as a good host for the spectral research of Eu^{2+} ions. Blasse [17] has proposed the rule of f–f transition of Eu^{2+} and further predicted that a composition like $BaSiF_6$:Eu^{2+} should be a good sharp line emitter. However, there is no report on the 4f→4f transition of Eu^{2+} in $BaSiF_6$ phosphor synthesized by a hydrothermal method by far. Herein, the Eu^{2+}-doped $BaSiF_6$ phosphors were prepared by a simple hydrothermal method. The final products were characterized with X-ray diffraction (XRD), transmission electron microscopy (TEM), and photoluminescence (PL) spectroscopy. Strong sharp line emission from the 4f→4f transition of Eu^{2+} in $BaSiF_6$ is observed, indicating that the as-prepared products could be used for sensing and solid-state lasers.

2. Experimental

2.1. Hydrothermal synthesis

The stoichiometric amounts of $Ba(OH)_2 \cdot 8H_2O$ (1.8 mmol), $EuCl_2$ (0.2 mmol), H_2SiO_3 (4 mmol), NH_4HF_2(4 mmol) were dissolved in 30 mL of distilled water, and the pH value of solution was adjusted to 3–4 with HF under magnetic stirring at room temperature. After substantially stirring, the as-obtained solution was transferred into a 50 mL stainless Teflon lined autoclave and heated at 180 °C for 72 h. The resulting suspension was allowed to cool to room temperature naturally. After 12 h of aging, the final

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* Corresponding author.
E-mail address: rnhua@dlnu.edu.cn (R. Hua).

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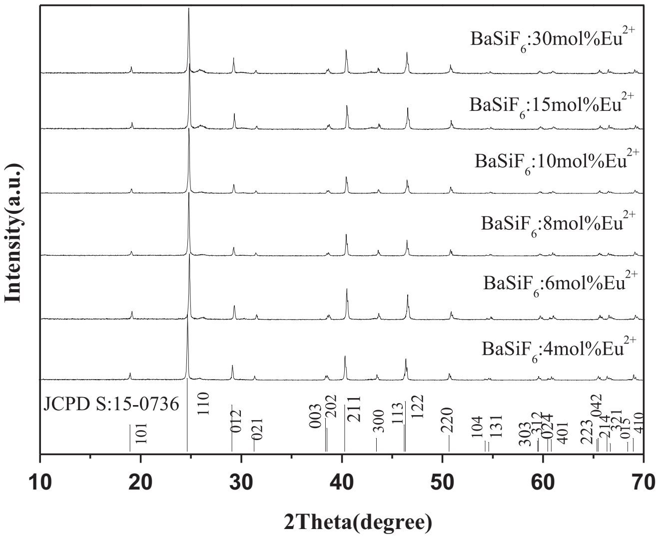

Fig. 1. XRD patterns of the $BaSiF_6$ microrods doped with various Eu^{2+} concentrations.

products were collected and washed several times with distilled water. Finally, the $BaSiF_6$:10 mol%Eu^{2+} phosphor was obtained after the sample was centrifuged and dried at 80 °C. The same process was employed to prepare $BaSiF_6$:x mol% Eu^{2+} ($x=4$, 6, 8, 15, 30) phosphors as well.

2.2. Characterization

The structures and morphologies of all the as-prepared products were characterized by an X-ray powder diffraction (XRD-6000, Shimadzu, Japan) with Cu $K_{\alpha 1}$ radiation ($\lambda=0.15406$ nm) and a transmission electron microscopy (JEM-2100F, JEOL, Japan) with an acceleration voltage of 200 kV, respectively. The excitation & emission spectra and fluorescent decays were recorded with a Hitachi F-4600 spectrophotometer equipped with a 150 W xenon lamp as excitation source. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Crystal structure

The typical XRD patterns of Eu^{2+}-doped $BaSiF_6$ phosphors are shown in Fig. 1. It can be seen that all the diffraction peak from the as-prepared Eu^{2+}-doped $BaSiF_6$ phosphors with different Eu^{2+} concentrations are well consistent with that of the pure rhombohedral phase of $BaSiF_6$ with space group *R-3m(166)*, which was reported in JCPDS card with No. 15-0736. No extra diffraction peaks corresponding to any impurities are observed even in the sample with highest concentration of 30 mol%Eu^{2+}. This fact indicates that the rhombohedral phase of $BaSiF_6$ microrods can be formed directly via a facile hydrothermal process, and the crystal structure of the products is influenced slightly by the introduction of Eu^{2+} ions. Herein, Eu^{2+} ions should substitute the sites of Ba^{2+} ions in $BaSiF_6$ host lattice because of the similar ionic radius. In addition, we can also see that the XRD peaks of the as-prepared samples are intense and sharp, suggesting that the products are crystallized well. This is in the favor of high efficient luminescence of rare earth ions as well.

3.2. Morphology and size

The TEM images of the $BaSiF_6$ microrods doped with 10 and 15 mol% Eu^{2+} are shown in Fig. 2. It can be found that the $BaSiF_6$:Eu^{2+} phosphors have regular morphology and the products exhibit rod-like shape. The resultant microrods have uniform diameter of around 200 nm and length ranging from 1 to 4 μm. When Eu^{2+} ions concentration exceeds over 15 mol%, as shown in Fig. 2b, it can be found that the surface of the microrods becomes rough, and there are some small particles on the surface of the microrods. This suggests that some surface defects are formed in this case [19].

3.3. Photoluminescent properties

The room temperature excitation and emission spectra of $BaSiF_6$:Eu^{2+} microrods are shown in Fig. 3. The excitation spectrum shows that $BaSiF_6$:Eu^{2+} has a broad excitation bands ranging from 220 to 320 nm, centered at 257 nm. Under an excitation of 257 nm, the emission spectra consist of four peaks from 348 to 374 nm (Fig. 3b). Two peaks located at 353 nm and 359 nm can be ascribed to the $4f^7(^6P_{5/2})\rightarrow 4f^7(^8S_{7/2})$ and $4f^7(^6P_{7/2})\rightarrow 4f^7(^8S_{7/2})$ parity forbidden transitions of Eu^{2+} ion, respectively. Because the influences of the crystal field and nephelauxetic effect in $BaSiF_6$ are weak, the lowest component of the 5d configuration of Eu^{2+} lies in such a position that the energy is higher than the excited 4f state. Under an excitation of 257 nm, the divalent europium ions are excited from the ground state ($^8S_{7/2}$) to $4f^65d^1$ configuration first. Then, the electrons will relax to the excited 4f configuration ($^6P_{7/2}$, $^6P_{5/2}$) nonradiatively. Thereafter, the excited 4f configuration electrons return to ground state, generating the $4f^7(^6P_{5/2})\rightarrow 4f^7(^8S_{7/2})$ and $4f^7(^6P_{7/2})\rightarrow 4f^7(^8S_{7/2})$ transition [20]. In the present

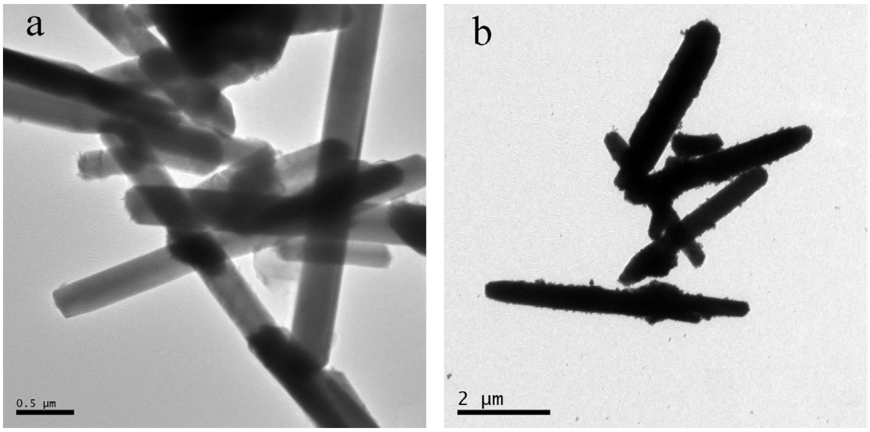

Fig. 2. TEM images of (a) $BaSiF_6$:10 mol%Eu^{2+} and (b) $BaSiF_6$:15 mol%Eu^{2+}.