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Short communication

A new green luminescent material $Ba_3Bi(PO_4)_3$:Tb^{3+}

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Abstract

A novel green phosphor Tb^{3+} doped $Ba_3Bi(PO_4)_3$ was synthesized by the conventional solid-state reaction at 1250 °C in air. The phosphor shows prominent luminescence in green due to the $^5D_4$–$^7F_5$ transition of Tb^{3+}. Structural characterization of the luminescent material was carried out with X-ray powder diffraction (XRD) analysis. The XRD measurements indicated that there were no crystalline phases other than $Ba_3Bi(PO_4)_3$. Luminescence properties were analyzed by measuring the excitation and photoluminescence spectra. Photoluminescence measurements indicated that the phosphor exhibited bright green emission at about 545 nm under UV excitation. The measured chromaticity for the phosphors $Ba_3Bi(PO_4)_3$:Tb^{3+} under UV excitation is (0.2699, 0.4831).

Keywords: A. solid-state reaction; C. Optical properties; Luminescence; Phosphors

1. Introduction

In recent years, new lighting and display technologies such as LEDs (light-emitting diodes), Hg-free lamps, PDPs (plasma display panels), and FEDs (field emission displays) have been proposed or developed in industry, which results in great interest in searching novel suitable phosphors for these new applications [1]. Tb^{3+}-doped materials have been widely used as green emitting phosphors due to their intense $^5D_4$–$^7F_5$ emission in the green spectral region. Previous studies have shown that Tb^{3+}-doped phosphates, aluminates or borates exhibit relatively strong absorption in the near-UV region and intense green emission with good color purity [2].

As a member of metal phosphate, $Ba_3Bi(PO_4)_3$ is an important optical material which has attracted particular interest due to its superior luminescent and structural properties. In 1970, Blasse firstly reported the new compounds with eulytine structure of $Ba_3Bi(PO_4)_3$ and its luminescence [3]. Thereafter, El Hassan Arbib et al. studied the structure of $Ba_3Bi(PO_4)_3$ in detail [4]. Moreover, some novel optical properties of this classic phosphor can be obtained by doping with rare-earth ions [5,6]. Previous study indicated that the $Ba_3Bi(PO_4)_3$ compound is a promising host materials for rare earth ions doped phosphor. However, to the best of our knowledge, there have been no researches on the luminescent properties of Tb^{3+} ions in $Ba_3Bi(PO_4)_3$ compound.

The aim of this work is to report our results on the synthesis, Photoluminescence (PL) and color chromaticity of the new green $Ba_3Bi(PO_4)_3$:Tb^{3+} phosphors and their corresponding spectroscopic properties under UV excitation. The results indicate that the phosphors can be efficiently activated by UV light.

2. Experimental

Powder samples $Ba_3Bi_{1-x}(PO_4)_3$:xTb^{3+} with different doping concentrations were prepared by solid-state reaction. The starting materials included $BaCO_3$ (A.R.), Bi_2O_3 (A.R.), $NH_4H_2PO_4$ (A.R.), and Tb_4O_7 (99.99%). Stoichiometric amounts of the starting reagents were thoroughly mixed and ground together by an agate mortar. An excess (2%) of $NH_4H_2PO_4$ was used to compensate for the

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evaporation of $NH_4H_2PO_4$ at high temperature in solid-state reactions. In order to obtain the target compound with pure phase, two firing steps were necessary. The mixture was firstly heated at 500 °C for 5 h in a covered alumina crucible, then reground thoroughly after cooled down to the room temperature. The second firing was conducted at 1250 °C for 3 h. Finally, the samples are ground into powder for characterizations.

The powder sample was characterized by X-ray diffraction (XRD) in a Bruker AXS D8 advanced automatic diffractometer (Bruker Co., German) with Ni-filtered Cu K_α radiation ($\lambda = 1.54178$ Å). A scan rate of 0.02°/s was applied to record the patterns in the 2θ range 10–90°. PL excitation and emissions spectra were collected in a fluorescence spectrophotometer (Hitachi F-4600). The chromaticity data were taken by using the PMS-80 UV–VIS-NEAR IR spectra analysis system. All the measurements were conducted at room temperature.

3. Results and discussion

The $Ba_3Bi(PO_4)_3$ compound has the structural type of eulytine, and Bi^{3+} ion occupies a distorted octahedron of oxygen ions due to three short and three long Bi–O distances [4]. $Ba_3Bi(PO_4)_3$ has an cubic crystal structure with a space group of I-43d (No. 220) and lattice parameters values $a=b=c=10.517$ Å, $Z=4$ and $V=1163.26$ Å^3. When Tb^{3+} ions doped in $Ba_3Bi(PO_4)_3$ compound, We assume that Bi^{3+} ions are replaced by Tb^{3+} ions because they have the same valence and ionic radii [7,8]. Fig. 1 represents the XRD patterns of $Ba_3Bi_{0.9}(PO_4)_3$:$0.10Tb^{3+}$ and JCPDS data (No. 33-0137). The comparison of measured powder XRD patterns of $Ba_3Bi_{0.9}(PO_4)_3$:$0.10Tb^{3+}$ with that of JCPDS data (No. 33-0137) indicates that the as-synthesized products are well crystallized with the $Ba_3Bi(PO_4)_3$ structure and no (detectable) additional phases (such as Tb_4O_7, $TbPO_4$) or other crystalline impurity phase present. The concentration of Tb^{3+} is only 10 atom percent in the as-synthesized $Ba_3Bi(PO_4)_3$ materials and the substitution of Bi^{3+} by the Tb^{3+} ion is expected to be random in the framework. Therefore, no obvious differences in the XRD peaks positions are noted between the as-synthesized material and the JCPDS data (No. 33-0137). These results indicated that Tb^{3+} ions were undoubtedly doped into and entered the $Ba_3Bi(PO_4)_3$ crystal lattice.

Fig. 2 displays the excitation spectra of $Ba_3Bi_{0.9}(PO_4)_3$:$0.10Tb^{3+}$ phosphors monitoring wavelength $\lambda_{em}=549$, 488 and 436 nm. When the x value changed from 0.005 to 0.10, the excitation spectra were similar except the intensity of excitation peaks (not shown). When monitoring at 549 nm which corresponds to $^5D_4 \rightarrow {}^7F_5$ emission of Tb^{3+} ions, the spectra were made up of a series of bands. The peaks located at 316, 340, 350, 356, 368, and 375 nm belong to the intrinsic f–f transitions of Tb^{3+} from the ground state $^7F_6$ to the excited state $^5D_0$, $^5L_7$, $^5L_9$, $^5L_{10}$, $^5G_5$, and $^5G_6$, respectively [9]. Of these excitation bands, the intensities of the 375 nm excitation peak are much stronger than the others, indicating near-UV LEDs are efficient pumping sources in obtaining Tb^{3+} emissions.

Fig. 3 shows (a) the emission spectra of typical $Ba_3Bi_{0.9}(PO_4)_3$:$0.10Tb^{3+}$ phosphors excited by 375 nm UV light and (b) the change of emission intensity of $Ba_3Bi_{1-x}(PO_4)_3$:xTb^{3+} as a function of Tb^{3+} concentration ($x=0.005$, 0.01, 0.03, 0.05, 0.08, 0.10). It can be seen from the emission spectra of $Ba_3Bi_{0.9}(PO_4)_3$:$0.10Tb^{3+}$ that one peak at 414 nm ($^5D_3 \rightarrow {}^7F_5$), one peak at 436 nm ($^5D_3 \rightarrow {}^7F_4$), two peaks at 488 and 496 nm ($^5D_4 \rightarrow {}^7F_6$),

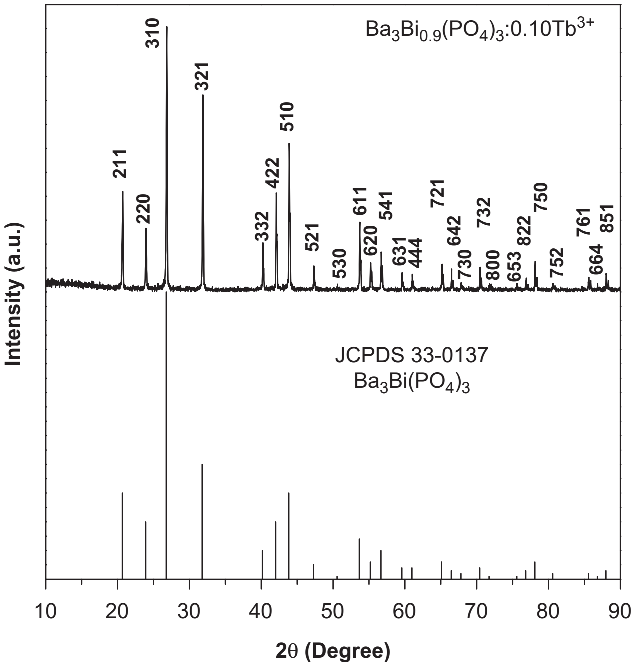

Fig. 1. The XRD patterns of typical sample $Ba_3Bi_{0.9}(PO_4)_3$:$0.10Tb^{3+}$ and the standard data JCPDS card No. 33-0137 of $Ba_3Bi(PO_4)_3$.

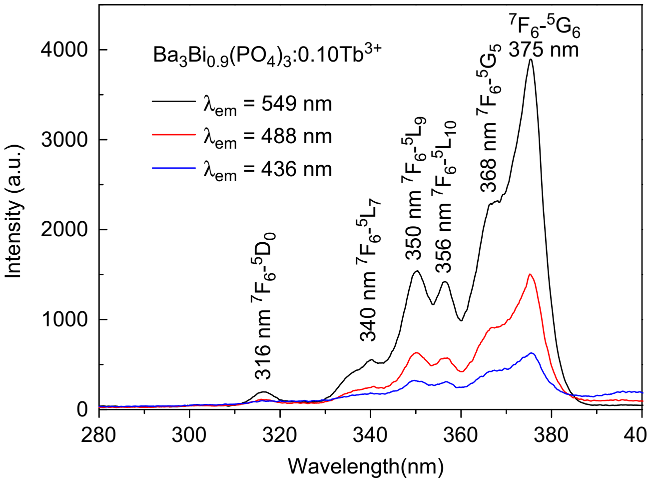

Fig. 2. The excitation spectra of the typical samples $Ba_3Bi_{0.9}(PO_4)_3$:$0.10Tb^{3+}$ (monitoring wavelength $\lambda_{em}=549$, 488 and 436 nm).

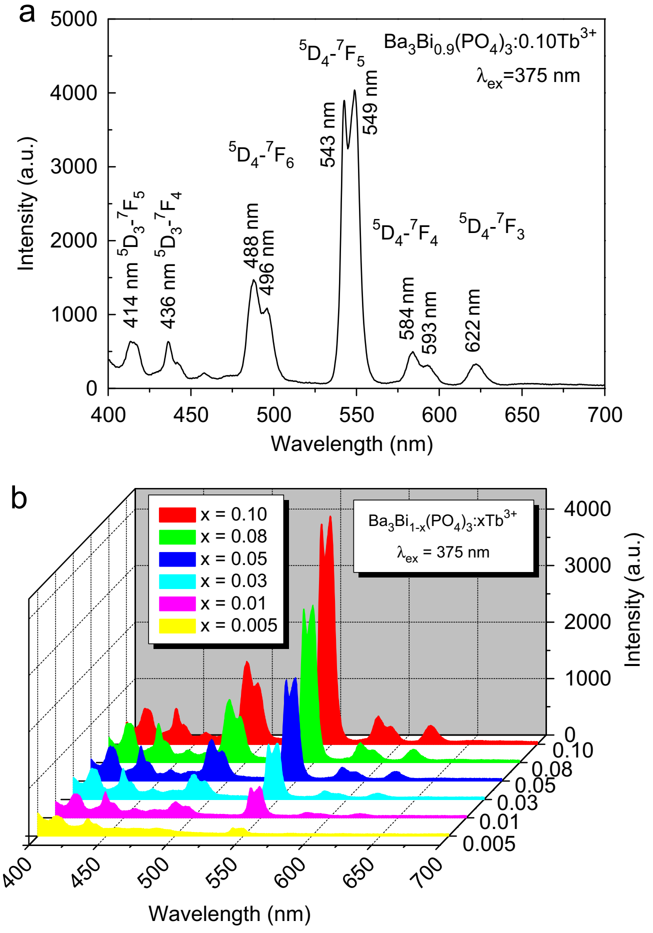

Fig. 3. (a) Emission spectra of typical phosphors $Ba_3Bi_{0.9}(PO_4)_3$: 0.10Tb^{3+} under 375 nm excitation (b) The emission intensity of Ba_3Bi_{1-x} $(PO_4)_3$:$x$$Tb^{3+}$ as a function of Tb^{3+} concentration. (λ_{ex}=375 nm).

two peaks at 543 and 549 nm ($^5D_4 \rightarrow {}^7F_5$), two peaks at 584 and 593 nm ($^5D_4 \rightarrow {}^7F_4$), and one peak at 622 nm ($^5D_4 \rightarrow {}^7F_3$) were observed [10,11]. The green emission transition $^5D_4 \rightarrow {}^7F_5$ is dominant among the others. Of two peaks due to $^5D_4 \rightarrow {}^7F_5$ transition, the intensity of the peak at 549 nm is stronger than that of the peak at 543 nm. Examining the emission spectral profiles from Fig. 3(b), it can be seen that the increase in dopant concentration is having absolutely no effect on the positions of the emission transitions except their change in the emission intensities. It is well known that cross relaxation phenomenon occurs with sufficient high dopant concentration. With the dopant concentration used in this paper, cross relaxation is not observed here. It also can be seen from Fig. 3(b) that the concentration quenching is not occurred in this case ($0.005 \leq x \leq 0.10$). This absence of cross relaxation and concentration quenching is under further investigation. The results demonstrate that this novel phosphor $Ba_3Bi_{0.9}$ $(PO_4)_3$:0.10Tb^{3+} can be well excited by UV 375 nm.

Color coordinates are one of the important factors for evaluating phosphors' performance. It is a well known fact that the color coordinates are the same if the spectra profiles are identical. In such case, the color coordinates for the sample doped with 10 mol% Tb^{3+} were calculated using the intensity-calibrated emission spectra data and the chromatic standard issued by the Commission Internationale de I'Eclairage in 1931 (CIE 1931). The CIE chromaticity coordinate for the prepared samples $Ba_3Bi_{0.9}(PO_4)_3$: 0.10Tb^{3+} are shown in Fig. 4 with the cross symbol (λ_{ex}=375 nm). It can be seen that the color coordinates of $Ba_3Bi_{0.9}(PO_4)_3$:0.10Tb^{3+} for full emissions are x=0.2699, y=0.4831, indicating $Ba_3Bi(PO_4)_3$: Tb^{3+} samples have good color coordinate as a green phosphor for white LEDs. In order to further improve the CIE colorcoordinates and achieve good quality white light emission, other rare earth dopants, emitting blue and red may need to be introduced into this phosphor system.

4. Conclusions

The novel green phosphate phosphor $Ba_3Bi(PO_4)_3$:Tb^{3+} is reported in this paper. The crystal structure of the phosphor was characterized by XRD. The PL properties of $Ba_3Bi(PO_4)_3$:xTb^{3+} were investigated. The $Ba_3Bi(PO_4)_3$: Tb^{3+} phosphor shows intense green emission under the UV excitation of 375 nm. The chromatic properties of the typical sample $Ba_3Bi_{0.9}(PO_4)_3$:0.10Tb^{3+} phosphor have been found to have chromaticity coordinates of x=0.2699 and y=0.4831 under the excitation wavelength λ_{ex}=375 nm. Consequently, the $Ba_3Bi(PO_4)_3$:Tb^{3+} phosphor is a promising candidate as a new green-emitting material for LEDs and fluorescent lamps.

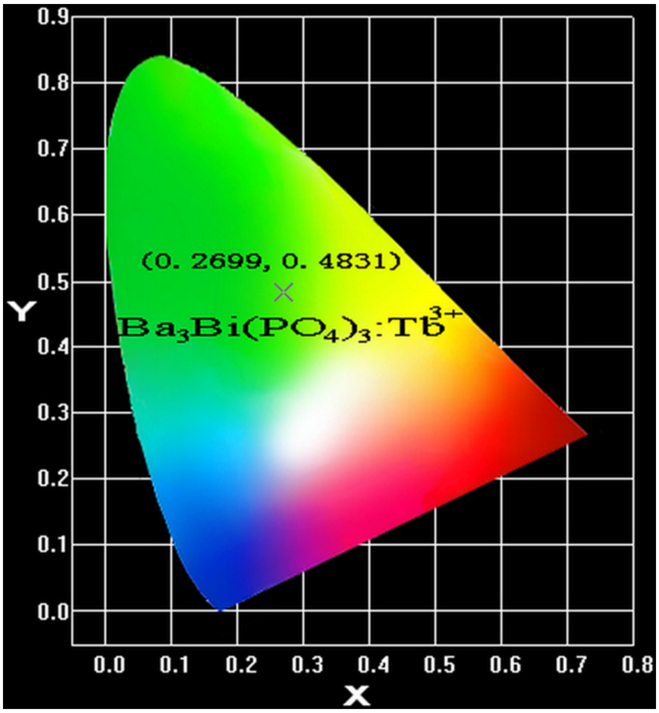

Fig. 4. The CIE chromaticity coordinate for the prepared typical samples $Ba_3Bi_{0.9}(PO_4)_3$:0.10Tb^{3+} under the excitation wavelength of 375 nm.

Acknowledgments

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