



Broadband orange emission from Bi activated calcium fluorophosphate



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ABSTRACT

Bi doped $\text{Ca}_5(\text{PO}_4)_3\text{F}$ phosphors were synthesized by the solid state reaction in air, and characterized by XRD and photoluminescence spectra. Including typical violet luminescence from Bi^{3+} , broadband orange emission peaked at about 521 nm can be observed under UV light excitation. Emission data with the size available lattice sites suggest that there are two types of Bi, Bi^{3+} and Bi^{2+} , in $\text{Ca}_5(\text{PO}_4)_3\text{F}$ lattice, and each locates on one of the two available Ca^{2+} sites. Bi^{2+} occupying $\text{Ca}^{2+}(1)$ sites is considered to be reduced from Bi^{3+} to Bi^{2+} and presents efficient orange emission.

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1. Introduction

Bismuth ion is an increasing important luminescence active center used in displaying and lighting fields, and since 2001, the reports of Bi doped glasses with ultra-broad near infrared (NIR) emission have dramatically improved the development of Bi active luminescent materials owing to their promising applications in broadband optical amplification and tunable lasers [1–4]. Besides the applications in NIR optical sources [5–9], bismuth also exhibits a broad variety of optoelectronic properties and potential applications, due to the large number of possible valence states, strong interaction with the surrounding lattice and, in some cases, clusters formation, as dopant in inorganic matrices [8–18].

It is noteworthy that, like rare earth ions with $5d-4f$ transition, e.g. Eu^{2+} and Ce^{3+} , the properties of Bi ion in solid-state compounds that splitting of $6p$ -excitation level depends strongly on the strength of crystal field, provides greatly multifold emission bands. However, comparing with wide researches and applications of Bi^{3+} doped crystals [17,18], mostly giving ultraviolet (UV) and blue emissions, research on Bi^{2+} doped materials, having been considered as an promising orange or red emitting phosphor excited by

UV or blue light emitting diodes (LEDs) [9,10], is still rare because of the relatively high oxidation tendency for low valence Bi in most host materials. And up to known, only a handful of matrix materials are reported, such as alkali metal borates [10,11], sulfates [12] and porous silica glass [13].

Calcium fluorophosphate, belongs to the large family of the apatite structure compounds, are well known for their applications as phosphor, laser and biocompatible materials, and the optical properties of these types of compounds have been the subject of numerous investigations [19,20]. For example, alkaline earth chlorophosphates activated by Eu^{2+} [20] are efficient phosphor materials, which are extensively used as the blue component in high efficiency trichromatic fluorescent lamps. However, to the best of our knowledge, the luminescent properties of Bi doped calcium fluorophosphates have not received attention up to now. In the present work, we reported the luminescence properties of Bi doped $\text{Ca}_5(\text{PO}_4)_3\text{F}$ synthesized by solid state reaction method in air. Under the excitation of UV light, typical violet emission from Bi^{3+} and broadband orange emission maybe due to Bi^{2+} were observed. The possible reason for the formation of Bi^{2+} emitting center was discussed according to the structure of $\text{Ca}_5(\text{PO}_4)_3\text{F}$ crystal.

2. Experimental details

The bismuth doped $\text{Ca}_5(\text{PO}_4)_3\text{F}$ samples were synthesized via solid state reaction method in air atmosphere. For that, analytical grade reagents CaCO_3 (99.99%), $(\text{NH}_4)_2\text{HPO}_4$ (99%), NH_4F (99%) and

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Bi_2O_3 (99.99%) were used as raw materials. Individual batches of 5×10^{-3} mol were weighed according to stoichiometric compositions of $\text{Ca}_{5-x}(\text{PO}_4)_3\text{F} : x\text{Bi}$ ($x = 0.5\%$, 1% , 1.5% , 2% and 4%) and mixed thoroughly. NH_4F was added in excess of 10 mol.% in order to compensate for volatilization losses. The raw materials were mixed homogeneously in an agate mortar and ethanol was used as a mixing agent. The grinded powder mixtures were then transferred into crucibles for a two-step heating. First, the mixed raw materials were preheated at 400°C for 4 h and ground together for a second time. Subsequently, all products were sintered at elevated temperature about 1100°C for 2 h again in the air condition. Then, the resulting samples were obtained.

Crystal structures of the obtained samples were analyzed by X-ray powder diffraction (XRD) with a Rigaku D/max 2200 Diffractometer with $\text{Cu K}\alpha$ ($\lambda = 1.542 \text{ \AA}$) radiation at 36 kV and 30 mA. The emission and excitation spectra were obtained with a HITACHI F-7000 fluorescence spectrophotometer, using a static Xe lamp (150 W). All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Identification of crystalline phase of $\text{Ca}_5(\text{PO}_4)_3\text{F} : \text{Bi}$

The XRD patterns of Bi doped $\text{Ca}_5(\text{PO}_4)_3\text{F}$ sample is given in Fig. 1. The diffraction peaks of the sample can be indexed as a pure phase, which coincide well with the reference data of $\text{Ca}_5(\text{PO}_4)_3\text{F}$ (PDF Cards No. 15-0876). It indicates that the doped Bi ions have not caused any significant change in the host structure and clearly confirms that the obtained sample has a hexagonal crystal structure with a space group of $P6_3/m$.

The crystallography of $\text{Ca}_5(\text{PO}_4)_3\text{F}$ is well documented in the previous work [21]. In $\text{Ca}_5(\text{PO}_4)_3\text{F}$ lattice, the position of F^- ion is responsible for the difference in the symmetry, there are two asymmetrical cationic (Ca^{2+}) sites possible in this system with the first site $\text{Ca}^{2+}(1)$ at the center of a slightly distorted tricapped trigonal prism constituted by six oxygen atoms of the PO_4 network corresponding to C_3 point group symmetry. The second type of site $\text{Ca}^{2+}(2)$ is coordinated with six oxygen atoms plus two F^- ion, with the local symmetry around the $\text{Ca}^{2+}(2)$ site described by C_s point group. These two cationic sites and crystal structure can be pictorially represented as shown in Fig. 2.

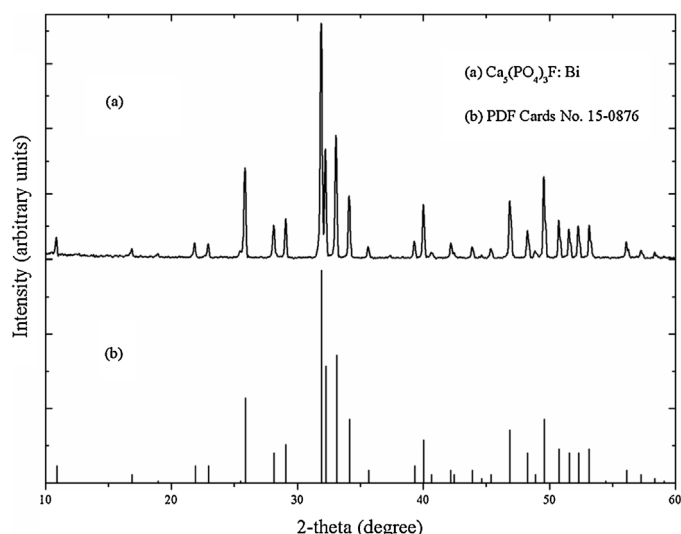


Fig. 1. XRD patterns of the sample for $\text{Ca}_{4.98}(\text{PO}_4)_3\text{F} : 2\% \text{Bi}$.

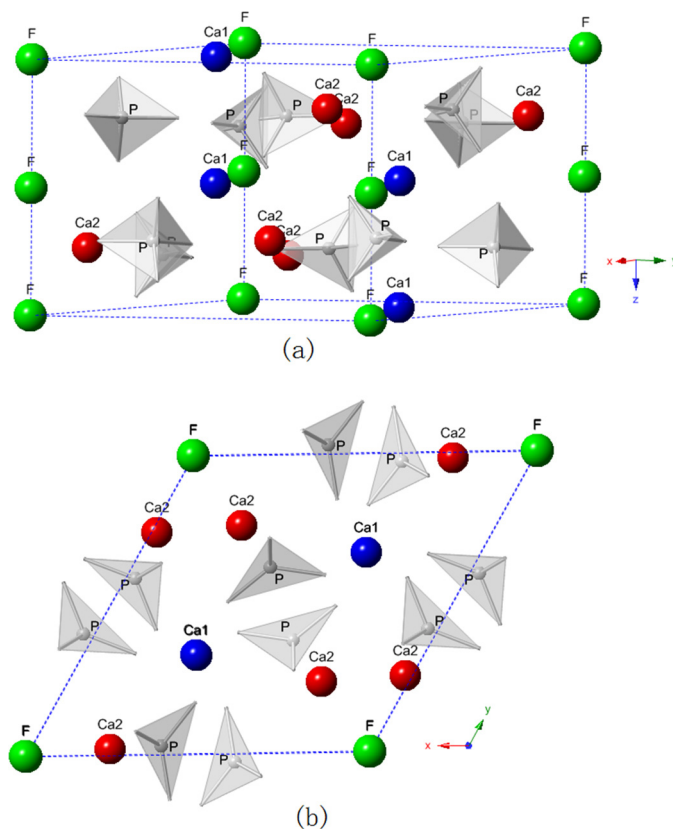


Fig. 2. Crystal structure of $\text{Ca}_5(\text{PO}_4)_3\text{F}$ (a) and two types of cationic sites (b), $\text{Ca}^{2+}(1)$ and $\text{Ca}^{2+}(2)$, available in $\text{Ca}_5(\text{PO}_4)_3\text{F}$ lattice.

3.2. The luminescence of $\text{Ca}_5(\text{PO}_4)_3\text{F} : \text{Bi}$ synthesized in air

Fig. 3 shows the excitation and emission spectra of $\text{Ca}_{4.98}(\text{PO}_4)_3\text{F} : 2\% \text{Bi}$ prepared in air. It exhibits that there are two excitation bands in the excitation spectra monitored at 397 nm, one dominating at 354 nm and another weak shoulder centering at 284 nm, which can be attributed to the fact that Bi^{3+} will replace Ca^{2+} on two different cation sites in $\text{Ca}_5(\text{PO}_4)_3\text{F}$ lattice. The emission centered at 397 nm can be ascribed to Bi-related

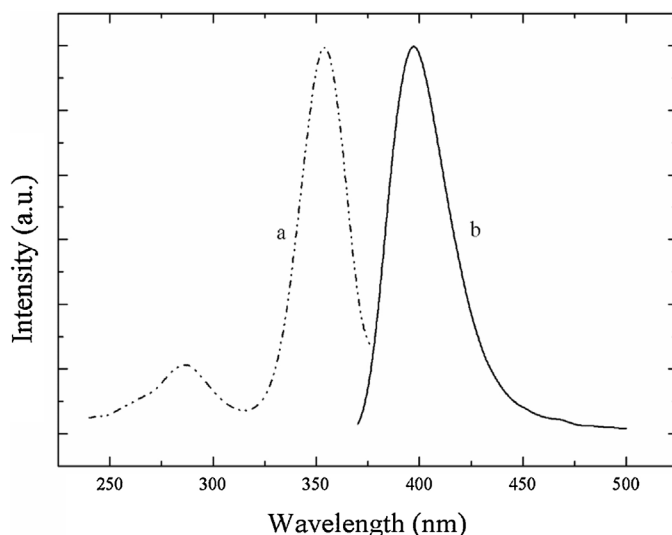


Fig. 3. Excitation (a) and emission (b) spectra of $\text{Ca}_5(\text{PO}_4)_3\text{F} : \text{Bi}^{3+}$ phosphor synthesized in air atmosphere.

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