

Luminescent performance of rare earths doped $\text{CaBi}_2\text{Ta}_2\text{O}_9$ phosphor

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Abstract: A series of red-emitting phosphors of $\text{CaBi}_2\text{Ta}_2\text{O}_9:\text{Pr}^{3+}$ and $\text{CaBi}_2\text{Ta}_2\text{O}_9:\text{Eu}^{3+}$ were synthesized by the solid-state reaction method. The crystal structure and photoluminescence properties were investigated by X-ray diffraction (XRD) and photoluminescence spectra. The emission spectra showed that the red emission peaks were located at 622 nm for Pr^{3+} and 615 nm for Eu^{3+} , respectively. The optimal doping concentrations for $\text{Ca}_{1-x}\text{Bi}_2\text{Ta}_2\text{O}_9:x\text{Pr}^{3+}$ and $\text{Ca}_{1-y}\text{Bi}_2\text{Ta}_2\text{O}_9:y\text{Eu}^{3+}$ were $x=0.02$ and $y=0.15$, respectively. The effect of fluxes (H_3BO_3 , NH_4F , CaCl_2 and CaF_2) and charge compensations (Li_2CO_3 , Na_2CO_3 and K_2CO_3) on luminescent properties were investigated in detail. It was found that the relative emission intensity of $\text{Ca}_{0.98}\text{Bi}_2\text{Ta}_2\text{O}_9:0.02\text{Pr}^{3+}$ with 10 mol.% H_3BO_3 flux was about 2.9 times higher than that of the sample without flux. The relative emission intensity of $\text{Ca}_{0.7}\text{Bi}_2\text{Ta}_2\text{O}_9:0.15\text{Eu}^{3+}$, 0.15K^+ was about the 2.1 times higher than that of $\text{Ca}_{0.85}\text{Bi}_2\text{Ta}_2\text{O}_9:0.15\text{Eu}^{3+}$.

Keywords: photoluminescence; rare earths; flux; charge compensation

Recently, rare earth ions doped bismuth layered-structure ferroelectrics (BLSFs) has become a novel luminescent material with an excellent luminescence performance. The BLSFs compounds can be written in the form of the formula $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$, where $\text{A}=\text{K}^+$, Na^+ , Ca^{2+} , Sr^{2+} , Pb^{2+} , Ba^{2+} , Bi^{3+} , La^{3+} , etc., $\text{B}=\text{Ti}^{4+}$, Ta^{5+} , Nb^{5+} , etc. and m is the number of perovskite layers ($m=1-5$)^[1-3]. $\text{ABi}_2\text{Ta}_2\text{O}_9$ ($\text{A}=\text{Ca}$, Ba , Sr) is a member of the BLSFs compounds and has a potential application in high-density nonvolatile ferroelectric random access memories (FeRAMs) owing to its high Curie temperature, low leakage current, fast switching speed and high fatigue resistance^[4-7]. The structure of $\text{CaBi}_2\text{Ta}_2\text{O}_9$ (CBTO) can be described as a stacking of Bi_2O_2 and the double perovskite layers^[8].

Rare earth elements are often used in luminescence materials due to their special electronic structure. It is found that the rare earth ions doped BLSFs materials show novel photoluminescence properties while possessing the ferroelectric performance^[9-12]. The coexistence of ferroelectrics and luminescence performance will make it possible to use BLSFs as a potential advanced material in the design of next generation novel multifunctional optoelectronic devices. To the best of our knowledge, there have been few reports about the photoluminescence of rare earth doped CBTO. It is necessary to better understand the photoluminescence of Pr^{3+} or Eu^{3+} doped CBTO.

In the process of synthesizing luminescence materials, the fluxes are often added to raw materials to reduce the sintering temperature and improve the photoluminescence performance^[13]. It is known that when a metal cation is substituted by an ion with different valence in host matrix, charge compensator such as Li^+ , Na^+ or K^+ is employed to keep the charge balance. For $\text{Ca}_{1-y}\text{Bi}_2\text{Ta}_2\text{O}_9:y\text{Eu}^{3+}$ system, the charge compensation mechanisms are: (a) two Ca^{2+} ions are replaced by one Eu^{3+} and one monovalent alkali cation, $2\text{Ca}^{2+}\rightarrow\text{Eu}^{3+}+\text{M}^+$, where M^+ is an alkaline cation like Li^+ , Na^+ or K^+ ; (b) the charge compensation is provided by a calcium vacancy, $3\text{Ca}^{2+}\rightarrow 2\text{Eu}^{3+}+\text{V}_{\text{Ca}}$ ^[14].

In this paper, the $\text{Ca}_{0.98}\text{Pr}_{0.02}\text{Bi}_2\text{Ta}_2\text{O}_9$ (CBTO:0.02 Pr^{3+}) powders with H_3BO_3 , NH_4F , CaCl_2 or CaF_2 fluxes were synthesized through a solid-state reaction method, and the effect of fluxes on crystal structure, luminescent properties of CBTO:0.02 Pr^{3+} was investigated. Meantime, the influence of charge compensators (Li^+ , Na^+ , K^+) on the luminescent properties of Eu^{3+} doped CBTO was also investigated.

1 Experimental

A series of $\text{Pr}^{3+}/\text{Eu}^{3+}$ doped CBTO phosphors were synthesized using solid-state reaction method. The starting raw materials were CaCO_3 (99.99%), Bi_2O_3 (99.999%), Ta_2O_5 (99.99%), Pr_6O_{11} (99.9%) and Eu_2O_3

(99.9%). Stoichiometric raw materials were mixed by an agate mortar thoroughly and sintered at 1200 °C for 4 h in air. In some cases, appropriate amount of H_3BO_3 (A.R.), NH_4F (A.R.), CaCl_2 (A.R.) or CaF_2 (A.R.) was added as the flux and certain amount of Li_2CO_3 (99.99%), Na_2CO_3 (A.R.) or K_2CO_3 (A.R.) was added as the charge compensator. The sintered mixtures were ground again for measurement.

The crystal structure of sintered samples was identified by an X-ray diffractometer (XRD) with Cu $\text{K}\alpha$ radiation (model D/Max-RA, Rigaku). The measurements of photoluminescence (PL) were performed by a fluorescence spectrophotometer (Horiba FluoroMax-4) equipped with a 150W-xenon lamp. The excitation and emission slits were set at 1.0 nm. All the measurements were carried out at room temperature.

2 Results and discussion

2.1 XRD analysis

The XRD patterns of CBTO:0.02Pr^{3+} with 5 mol.% fluxes (H_3BO_3 , NH_4F , CaCl_2 and CaF_2) are shown in Fig. 1, which matches well with the standard JCPDS-Card (No. 72-2365). It is worth mentioning that the three diffraction peaks of the sample with H_3BO_3 flux at about 33.68°, 47.86° and 48.66° are much weaker than the others in the XRD patterns. This preferred orientation growth is attributed to the different nucleation mechanism. The decomposition of H_3BO_3 happens under 445 °C, and the produced liquid of B_2O_3 could provide a convenience to the contact reaction between the raw materials. This may be helpful to the growth of crystal and it will reduce the crystal defect.

2.2 Luminescent properties of CBTO:Pr^{3+}

Fig. 2 shows the excitation and emission spectra of CBTO:0.02Pr^{3+} . The excitation spectrum (Fig. 2(1)) is monitored at 622 nm, and its three charge transfer bands are attributed to the f-f transitions of Pr^{3+} : $^3\text{H}_4 \rightarrow ^3\text{P}_2$ transition at 449 nm, $^3\text{H}_4 \rightarrow ^3\text{P}_1$ transition at 472 nm and $^3\text{H}_4 \rightarrow ^3\text{P}_0$ transition at 491 nm^[12]. The emission spectrum

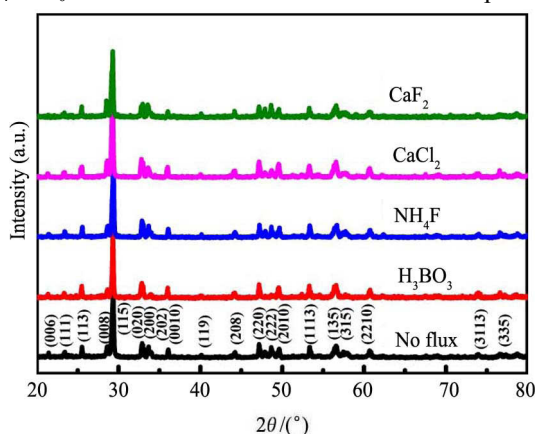


Fig. 1 XRD patterns of CBTO:0.02Pr^{3+} with different fluxes

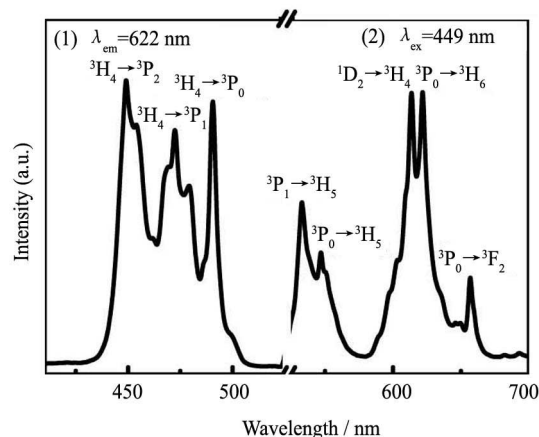


Fig. 2 Excitation and emission spectra of CBTO:0.02Pr^{3+}

(Fig. 2(2)) excited at 449 nm shows the red part emission peaks at 614 nm ($^1\text{D}_2 \rightarrow ^3\text{H}_4$), 622 nm ($^3\text{P}_0 \rightarrow ^3\text{H}_6$) and 657 nm ($^3\text{P}_0 \rightarrow ^3\text{F}_2$), respectively. The green part peaks at 533 nm ($^3\text{P}_1 \rightarrow ^3\text{H}_5$) and 547 nm ($^3\text{P}_0 \rightarrow ^3\text{H}_5$)^[12,15]. With the strong absorption band ranging from 430–500 nm, it could be used in white LEDs as a potential eco-friendly red phosphor excited by all commercial blue LED chips (420–470 nm).

The emission spectra of $\text{Ca}_{1-x}\text{Bi}_2\text{Ta}_2\text{O}_9:x\text{Pr}^{3+}$ ($x=0.0025, 0.005, 0.01, 0.02, 0.03$ and 0.04) are shown in Fig. 3. With the increase in Pr^{3+} concentration, the emission intensity enhances firstly, and then gets to a maximum at $x=0.02$. Then with the continuous increase of Pr^{3+} concentration, the emission intensity starts to decrease. This may be attributed to the concentration-quenching effect. This consequence is corresponding with the report in Ref. [12]. The main quenching process of Pr^{3+} is the cross-relaxation between $^3\text{P}_0 \rightarrow ^1\text{D}_2$ and $^3\text{H}_4 \rightarrow ^3\text{H}_6$, $^1\text{D}_2 \rightarrow ^1\text{G}_4$ and $^3\text{H}_4 \rightarrow ^3\text{F}_4$.

Fig. 4 shows the emission spectra of CBTO:0.02Pr^{3+} with different fluxes. The emission peak position has no difference with that of CBTO:0.02Pr^{3+} without flux. The samples with fluxes exhibit an enhancement of emission intensity. The emission intensity of CBTO:0.02Pr^{3+} with 5 mol.% H_3BO_3 , NH_4F , CaCl_2 or CaF_2 is about 1.63, 1.43,

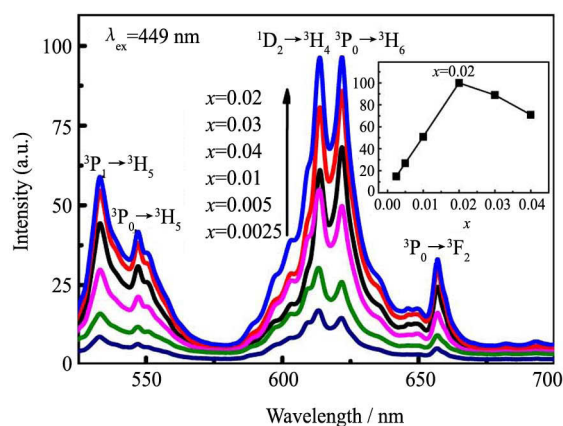


Fig. 3 Emission spectra of $\text{Ca}_{1-x}\text{Bi}_2\text{Ta}_2\text{O}_9:x\text{Pr}^{3+}$ ($x=0.0025, 0.005, 0.01, 0.02, 0.03$ and 0.04) (inset: relative emission intensity of $\text{Ca}_{1-x}\text{Bi}_2\text{Ta}_2\text{O}_9:x\text{Pr}^{3+}$ at 622 nm)

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