



Photoluminescence properties and effects of dopant concentration in $\text{Bi}_2\text{ZnB}_2\text{O}_7:\text{Tb}^{3+}$ phosphor



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ABSTRACT

A novel green phosphor, Tb^{3+} doped $\text{Bi}_2\text{ZnB}_2\text{O}_7$ was synthesized by conventional solid state reaction method. The phase of synthesized materials was determined using the XRD, DTA/TG and FTIR. The photoluminescence characteristics were investigated using spectrofluorometer at room temperature. $\text{Bi}_2\text{ZnB}_2\text{O}_7:\text{Tb}^{3+}$ phosphors excited by 270 nm and 485 nm wavelengths. The emission spectra were composed of three bands, in which the dominated emission of green luminescence $\text{Bi}_2\text{ZnB}_2\text{O}_7:\text{Tb}^{3+}$ attributed to the transition $^5\text{D}_4 \rightarrow ^7\text{F}_5$ is centered at 546 nm. The dependence of the emission intensity on the Tb^{3+} concentration for the $\text{Bi}_{2-x}\text{Tb}_x\text{ZnB}_2\text{O}_7$ ($0.01 \leq x \leq 0.15$) was studied and observed that the optimum concentration of Tb^{3+} in phosphor was 13 mol% for the highest emission intensity at 546 nm.

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1. Introduction

In recent years, the phosphor has attracted increasing attention because of its applications to solid-state lighting, display devices, detector systems and luminous paint with long persistent phosphorescence. A phosphor is generally composed of a transparent microcrystalline host and a luminescence activator formed by impurity metallic atoms intentionally incorporated. In the case of metallic impurities, a large number of rare-earth ions have been used as the luminescence activators of phosphors, especially trivalent rare-earth ions that generally exhibit stable emission due to the f–f electron transition [1]. Trivalent Tb ions have been expected as one of the promising species that provide optical devices in blue and green color regions and many investigations have been conducted in various compounds [2–6].

Borates have been receiving more and more attention due to their interesting physical properties and applications, such as non-linear optical (NLO), luminescent, magnetic, Li-ion battery, high laser damage tolerance, and high optical quality. A variety of BO atomic groups are considered to be a dominant for the physical properties, in particular the optical properties, of borates. Among the researches on these properties in borates, the discovery and synthesis of optical materials are the most intensively made [7–12].

In this paper, $\text{Bi}_2\text{ZnB}_2\text{O}_7:\text{Tb}^{3+}$ phosphors were prepared by conventional solid state reaction method. The phase of synthesized materials was determined using the XRD, DTA/TG and FTIR. After synthesis and characterization of the phosphors, the photoluminescence properties of the synthesized phosphors were studied using a spectrofluorometer at room temperature. Also, the dependence of the emission intensity on the Tb^{3+} concentration for the $\text{Bi}_{2-x}\text{Tb}_x\text{ZnB}_2\text{O}_7$ ($0.01 \leq x \leq 0.15$) was studied in detail.

2. Experimental

A series of Tb^{3+} doped $\text{Bi}_2\text{ZnB}_2\text{O}_7$ phosphors were obtained by solid state reaction in air. The reactants including Bi_2O_3 (99.00%), H_3BO_3 (99.80%), ZnO (99.99%) and $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99%) were weighted in the appropriate stoichiometric ratio. The chemical equation can be expressed as follows:



The chemicals weighted ground well in agate mortar at room temperature and later it was collected into an alumina crucible for its appropriate heating. The powder mixtures are firstly calcined at 450 °C during 4 h. After grinding and homogenization of pre-annealed mixtures were heat treated at 600 °C for 40 h.

A DTA/TG combined system (PERKIN ELMER Diamond, USA) was used to determine the reaction conditions in the temperature range of 50–1000 °C under an inert N_2 atmosphere with the heating rate of 10 °C/min.

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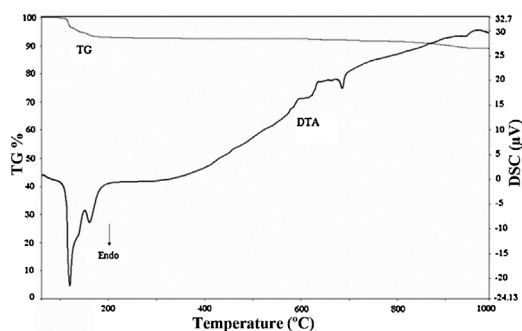


Fig. 1. TG/DTA plot of the stoichiometric mixture of Bi_2O_3 , H_3BO_3 and ZnO powders heated at the rate of $10^\circ\text{C}/\text{min}$.

Structural characterization was analyzed by X-ray diffraction (XRD; Bruker AXS D8) spectra with a $\text{CuK}\alpha$ line of 1.5406 \AA .

The Fourier transform infrared spectrum between 500 and 1500 cm^{-1} were measured at room temperature with a Perkin Elmer Spectrum 400 FTIR spectrometer.

All the luminescence characteristics of these phosphors were investigated at room temperature with a Scinco FluoroMate FS-2 spectrofluorometer equipped with a 150 W Xe-arc lamp.

3. Results and discussion

3.1. Thermogravimetry (DTA/TG) analysis

Typical DTA and TG plot for the stoichiometric powder mixture of Bi_2O_3 , H_3BO_3 and ZnO heated at $10^\circ\text{C}/\text{min}$ is shown in Fig. 1. The thermograms showed an endothermic peak corresponding to melting of H_3BO_3 at 129°C . Subsequently, another small endothermic peak appeared at 165°C , which indicated the dissociation of H_3BO_3 to B_2O_3 and H_2O . This was confirmed from the DTA of boric acid and the thermodynamic data. The weight of the sample decreased drastically just after the dissociation of boric acid. The thermograms revealed a small endothermic peak at 692°C due to the melting of $\text{Bi}_2\text{ZnB}_2\text{O}_7$. This means that the decomposition is almost complete and the crystallization of the $\text{Bi}_2\text{ZnB}_2\text{O}_7$ occurs at 600°C .

3.2. X-ray powder diffraction analysis

The XRD patterns of phosphors are presented in Fig. 2, which is in agreement with the XRD data of $\text{Bi}_2\text{ZnB}_2\text{O}_7$ in Ref. [13]. All phosphors crystallizes in the orthorhombic system having a space group $\text{Pba}2$ and with the lattice parameters of $a = 10.823$, $b = 11.016$, $c = 4.8844\text{ \AA}$ and $Z = 4$. $\text{Bi}_2\text{ZnB}_2\text{O}_7$, $\text{Bi}_2\text{ZnB}_2\text{O}_7:3\%\text{Tb}^{3+}$, $\text{Bi}_2\text{ZnB}_2\text{O}_7:7\%\text{Tb}^{3+}$, $\text{Bi}_2\text{ZnB}_2\text{O}_7:11\%\text{Tb}^{3+}$ and $\text{Bi}_2\text{ZnB}_2\text{O}_7:13\%\text{Tb}^{3+}$ were prepared in the same condition and second phase as well

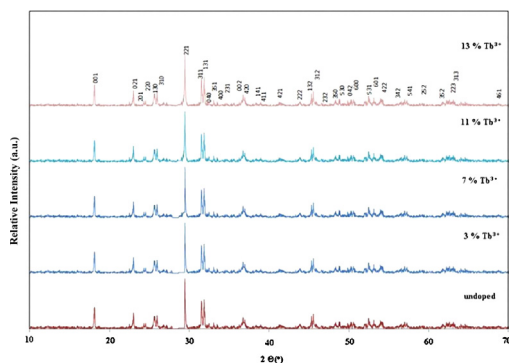


Fig. 2. XRD pattern obtained for $\text{Bi}_2\text{ZnB}_2\text{O}_7$ prepared by a solid state synthesis.

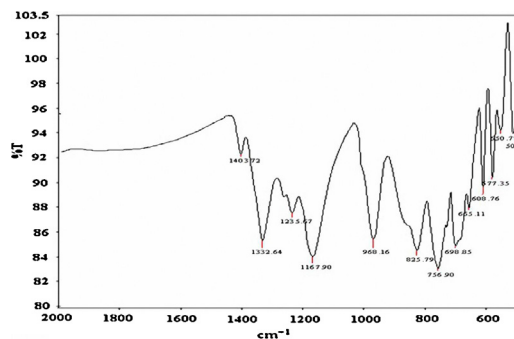


Fig. 3. Infrared spectrum of $\text{Bi}_2\text{ZnB}_2\text{O}_7$ at room temperature.

as obvious shifting of the diffraction peaks were not observed as Tb^{3+} doping concentration increasing, which means that when Tb^{3+} were introduced into the lattice, the crystal structure does not change largely. According to the ionic radius, the Tb^{3+} ions ($\text{Tb}^{3+} = 92\text{ pm}$) are expected to occupy the Bi^{3+} ion ($\text{Bi}^{3+} = 103\text{ pm}$) sites in the $\text{Bi}_2\text{ZnB}_2\text{O}_7$ host lattice, and no Tb^{3+} ions are expected to occupy the Zn^{2+} ($\text{Zn}^{2+} = 74\text{ pm}$) or B^{3+} ($\text{B}^{3+} = 23\text{ pm}$) sites.

3.3. Infrared spectrum analysis

The FTIR spectrum of the product is shown in Fig. 3. For an isolated, triangular BO_3 group, the vibrations are in the region $\nu_3 = 1100\text{--}1400\text{ cm}^{-1}$ (asymmetric stretch of B-O), $\nu_1 = 900\text{--}1000\text{ cm}^{-1}$ (symmetric stretch of B-O), $\nu_2 = 700\text{--}900\text{ cm}^{-1}$ (out-of-plane bend), and ν_4 : $450\text{--}650\text{ cm}^{-1}$ (in-plane bend) [14,15]. The absorption band at 500 cm^{-1} is the stretching mode of ZnO [16]. It is clearly shown that the crystal system of $\text{Bi}_2\text{ZnB}_2\text{O}_7$ ($\text{Bi}_2\text{ZnB}_2\text{O}_7$) has mainly had basic structural units of BO_3^{3-} .

3.4. Photoluminescence properties

The excitation spectra of undoped- $\text{Bi}_2\text{ZnB}_2\text{O}_7$ and $\text{Bi}_2\text{ZnB}_2\text{O}_7:13\%\text{Tb}^{3+}$ phosphor, which were obtained by monitoring the green emission at 546 nm , are shown in Fig. 4. The excitation spectrum show a broad band centered at about 270 nm , which is attributed to the $4f^8 \rightarrow 4f^7 5d^1$ ($f \rightarrow d$) transition of Tb^{3+} . In the longer wavelength region ($300\text{--}400\text{ nm}$), few weak excitation bands are observed and are attributed to the $f\text{--}f$ transitions of Tb^{3+} . The band at 485 nm (${}^7F_6 \rightarrow {}^5D_4$) has the maximum intensity among all the excitation bands [17].

The emission spectra of $\text{Bi}_2\text{ZnB}_2\text{O}_7:\text{Tb}^{3+}$ excited by 270 nm and 485 nm at room temperature and electronic transitions is similar to the emissions. Fig. 5 shows emission spectra (within the range of $500\text{--}700\text{ nm}$) of $13\text{ mol}\%\text{Tb}^{3+}:\text{Bi}_2\text{ZnB}_2\text{O}_7$ phosphor. The phosphors show emission bands ranging from 500 to 650 nm , originating from one excited states of Tb^{3+} transitions from the

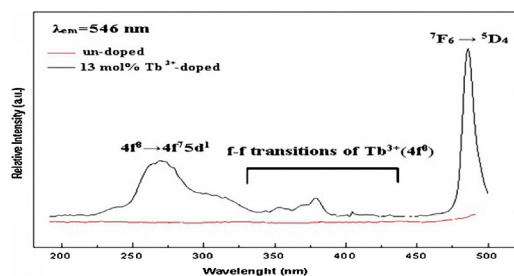


Fig. 4. Excitation spectra of undoped- $\text{Bi}_2\text{ZnB}_2\text{O}_7$ and $13\text{ mol}\%\text{Tb}^{3+}:\text{Bi}_2\text{ZnB}_2\text{O}_7$ phosphor.

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