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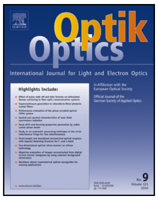

Green emitting Tb doped $LiBaB_9O_{15}$ phosphors

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ABSTRACT

A successful preparation of a Tb^{3+}-doped $LiBaB_9O_{15}$ phosphors was achieved through the use of a solution-combustion method. The preparation of the powders of the Tb^{3+}-doped $LiBaB_9O_{15}$ phosphor was confirmed by X-ray diffraction (XRD) results; furthermore, the size and morphology of these powders were further examined using a scanning electron microscope (SEM). A study of the luminescent proprieties under a UV excitation showed a dominant and strong green luminescent peak at 542 nm that is due to the d–f transition. When monitored at 542 nm, the excitation spectrum exhibited a broad band centered at 230 nm and several weak peaks in the wavelength range of 300–400 nm that are attributed to the f-d transitions and the intra-4f-4f transitions of the Tb^{3+} ions, respectively. The addition of the Tb^{3+} concentration greatly improved the photoluminescent properties of the present phosphors, and the Commission International de I'Eclairage (CIE) chromaticity coordinates are located in the green region. The present study suggests that the potential applications of the Tb^{3+}-doped $LiBaB_9O_{15}$ phosphors might be in the lighting and display fields.

1. Introduction

Phosphors, which are rare-earth-activated luminescent materials, have been used in significant developments in the revolutionizing of the solid-state-lighting industry. Phosphors are usually made from a suitable host material with the added activator rare-earth, and they have attracted great attention because of their excellent luminescent properties, whereby they are applicable for lasers, lighting, displays, scintillators, light-emitting diodes (LEDs), X-ray-imaging detectors, electroluminescent devices, and solar concentrators [1–4]. In general, phosphors including oxides, silicates, aluminates, aluminoborates, nitrides, and borates play significant roles as the host materials for the possible applications regarding ultraviolet (UV) devices. Among these, the borates represent an effective host-structure candidate for luminescent ions because of the large bandgap, an easy synthesis, a stability, and a low cost [5–9].

As the large bandgap of borates makes them suitable as the host lattices of luminescent ions, Tb^{3+}-doped borate phosphors have been widely studied over the last several years [10–13]. Currently, it is important to develop near-UV (NUV)-visible phosphors for light-emitting diode (LED) applications [14]. Recently, Shyichuk et al. reported that the excitation spectra

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Table 1
Sample Compositions, Sample Codes, and Starting Materials.

Sample Composition	Sample Code	Starting Materials				
$LiBaB_9O_{15}$:$Tb_{0.005}$	LB1	Li = 0.1856 g	Ba = 0.7037 g	B.A = 1.5 g	U = 0.5 g	Tb = 0.0058 g
$LiBaB_9O_{15}$:$Tb_{0.01}$	LB2	Li = 0.1856 g	Ba = 0.7037 g	B.A = 1.5 g	U = 0.5 g	Tb = 0.0087 g
$LiBaB_9O_{15}$:$Tb_{0.02}$	LB3	Li = 0.1856 g	Ba = 0.7037 g	B.A = 1.5 g	U = 0.5 g	Tb = 0.0146 g
$LiBaB_9O_{15}$:$Tb_{0.03}$	LB4	Li = 0.1856 g	Ba = 0.7037 g	B.A = 1.5 g	U = 0.5 g	Tb = 0.0292 g
$LiBaB_9O_{15}$:$Tb_{0.04}$	LB5	Li = 0.1856 g	Ba = 0.7037 g	B.A = 1.5 g	U = 0.5 g	Tb = 0.0380 g
$LiBaB_9O_{15}$:$Tb_{0.05}$	LB6	Li = 0.1856 g	Ba = 0.7037 g	B.A = 1.5 g	U = 0.5 g	Tb = 0.0497 g
$LiBaB_9O_{15}$:$Tb_{0.06}$	LB7	Li = 0.1856 g	Ba = 0.7037 g	B.A = 1.5 g	U = 0.5 g	Tb = 0.0625 g

Abbreviations: Li = $LiNO_3$, Ba = $Ba(NO_3)_2$, B.A. = Boric acid, U = Urea, Tb = $Tb(NO_3)_3 \cdot 5H_2O$.

of Tb^{3+}-doped $Sr_3RE_2(BO_3)_4$ borates contain intense bands in the range of 230–390 nm; as a result, the luminophores can be potentially used with different excitation sources such as vapor discharges or LEDs [15]. Typically, borate phosphors are mercury (Hg)/vapor/UV-oriented and are characterized by charge-transfer bands in the excitation spectra from 200 to 250 nm [16–18]. Here, Tb^{3+}-doped $LiBaB_9O_{15}$ borate phosphors with a wide excitation range of 230–390 nm are presented.

To the best of the authors' knowledge, a dearth exists regarding the reports on Tb^{3+}-doped $LiBaB_9O_{15}$ phosphors. Accordingly, a need for the knowledge about the results of Tb doping has motivated the present work, while the true potentialities of these materials in terms of these applications remain unexplored. The present study comprises a report on the structural, surface-morphology, and luminescent properties of Tb^{3+}-doped $LiBaB_9O_{15}$ phosphors that were synthesized using a solution-combustion method.

2. Material preparation and analysis

A series of Tb-doped $LiBaB_9O_{15}$ powders were synthesized using a solution-combustion method at a relatively low temperature. The details of the sample compositions, sample code and the starting materials are given in Table 1. As per the typical synthesis of lithium nitrate ($LiNO_3$) and barium nitrate ($Ba[NO_3]_2$), boric acid (H_3BO_3) was used as the oxidizer and urea ($[NH_2]_2CO$) was used as the fuel; moreover, terbium(III) nitrate pentahydrate ($Tb[NO_3]_3 \cdot 5H_2O$) was used as the activator. The starting materials were taken according to the stoichiometric ratio; then, they were dissolved in the minimum quantity of double-distilled water in a 100-ml china dish and kept in an oven at 80 °C for 20 min to obtain a homogeneous solution. The china dish was subsequently introduced into a muffle furnace that had been preheated to 500 ± 10 °C. Initially, the solution reached its boiling point and underwent dehydration followed by a decomposition, resulting in the escape of large amounts of gases such as the oxides of nitrogen and carbon. This was followed by spontaneous ignitions, and the solution underwent a smoldering combustion with an enormous swelling. The subsequent crushing of the foamy powder produced a white-color powder. The obtained white product was annealed for 2 h at 800 °C in the muffle furnace, and the resultant sample was used for a further characterization.

The powdered X-ray diffraction (XRD) patterns of the samples were recorded using the Miniflex II diffractometer (Rigaku, Japan) that was operated in the Bragg–Brentano focusing geometry at 40 kV and 30 mA, while Cu-Kα radiation ($\lambda = 1.5406$ Å) was used as the X-ray source. The XRD patterns were taken with a scan rate of 5°/min in the range of 10–80°. The morphology was investigated using the S-3400 scanning electron microscope (SEM) device (Hitachi, Japan). The photoluminescent emission and excitation spectra of the samples were recorded using the RF-5301PC spectrofluorophotometer (Shimadzu, Japan) equipped with a xenon lamp.

3. Results and discussion

3.1. Crystal-structure and crystallite-size analyses

Fig. 1 shows the XRD patterns of the $LiBaB_9O_{15}$:Tb (LB1–LB7) phosphors. The crystallization of the $LiBaB_9O_{15}$ compounds occurred in the noncentrosymmetric space group *R*3*c* [19]. The barium ions occupied the center of an almost-regular icosahedron (12-vertex polyhedron), while the lithium ions are simultaneously surrounded by three oxygen atoms that are nearly on the same plane; the consequent formation of a triangular environment facilitated the discovery of unusual environments [19]. All of the diffraction peaks are indexed to the hexagonal $LiBaB_9O_{15}$ structure [8]. Compared with the standard diffraction data (JCPDS No. 47-0341), the results indicate the absence of a significant difference between the LB1 and LB7 samples. The uniform diffraction patterns mean that the $LiBaB_9O_{15}$-phase formation was not influenced by a slight Tb^{3+} amount. An extra peak that is marked by the symbol ♦ was observed with the increasing of the Tb^{3+}-ion concentration. The average crystallite size was calculated using the Scherrer equation, as follows:

$$d = 0.9\lambda/\beta cos\theta \tag{1}$$

where λ is the radiation wavelength ($\lambda = 1.5406$ Å), θ is the diffraction-peak angle, and β is the full width at half maximum (FWHM) of the diffraction peak (in radians). The calculated crystallite sizes of the $LiBaB_9O_{15}$:Tb phosphors are in the range of 28–41 nm, indicating a nanocrystalline nature, and are given in Table 2.