

# Photoluminescence and electron-beam excitation induced cathodoluminescence properties of novel green-emitting $\text{Ba}_4\text{La}_6\text{O}(\text{SiO}_4)_6:\text{Tb}^{3+}$ phosphors

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## ABSTRACT

$\text{Tb}^{3+}$  ions activated  $\text{Ba}_4\text{La}_6\text{O}(\text{SiO}_4)_6$  (BLSO: $\text{Tb}^{3+}$ ) phosphors were synthesized by a citrate sol-gel method. The X-ray diffraction pattern confirmed their oxyapatite structure. The field-emission scanning electron microscope image established that the BLSO: $\text{Tb}^{3+}$  phosphor particles were closely-packed and acquired irregular shapes. The photoluminescence (PL) excitation spectra of BLSO: $\text{Tb}^{3+}$  phosphors showed intense f-d transitions along with low intense peaks corresponding to the f-f transitions of  $\text{Tb}^{3+}$  ions in the lower energy region. The PL emission spectra displayed the characteristic emission bands of  $\text{Tb}^{3+}$  ions, and the optimized concentrations were found to be at 1 and 6 mol% for blue and green emission peaks, respectively. The cathodoluminescence (CL) spectra exhibited a similar behavior that was observed in the PL spectra except the intensity variations in the blue and green regions. The CL spectra of the BLSO:6 mol%  $\text{Tb}^{3+}$  phosphor unveiled accelerating voltage induced luminescent properties.

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## 1. Introduction

Recently, the research has been focused on the multifunctional sources for lighting (incandescent light bulbs, compact fluorescent lamps, and phosphors and non-phosphors based semiconductor light-emitting diodes (LEDs)) and display (cathode ray tubes, field-emission displays (FEDs), and plasma display panels) applications [1–5]. Among the lighting sources, increasing attention has been paid towards the development of phosphor converted LEDs (pc-LEDs) because these devices provide an energy efficient and reliable source for indoor and outdoor lighting along with LEDs based display devices [1]. It is fortunate that the ultraviolet (UV) LED sources with different emission wavelengths in the UV-A (315–400 nm), UV-B (280–315 nm) and UV-C (100–280 nm) regions of the electromagnetic spectrum have been developed in recent years [6–11]. These UV sources are useful to provide tri-band (blue, green and red) based pc-white LEDs (pc-WLEDs), and the tri-band emissions not only cover the entire visible region but also provide high color-rendering index (CRI) and color purity [6]. In the case of the tri-band WLEDs, it is well known that the oxides based inorganic phosphors would be one of the best candidates in terms of both chemical stability and luminescence efficiency [12].

Nowadays, the oxide phosphors have been also used to fabricate efficient FED systems [3]. Therefore, the availability of phosphors operating under UV excitation as well as low voltage electron-beam excitation with better performance is of prime importance for such LEDs and FEDs. In previous work, we have developed and reported efficient red phosphors for promising multifunctional applications [13]. Now, our efforts have been focused on the development of green phosphors for LED and FED applications.

In this paper, we report on the  $\text{Tb}^{3+}$  ions doped  $\text{Ba}_4\text{La}_6\text{O}(\text{SiO}_4)_6$  phosphors (referred to it as BLSO: $\text{Tb}^{3+}$ ) by a sol-gel process for the first time. This phosphor exhibited efficient photoluminescence (PL) properties of the  $\text{Tb}^{3+}$  ions under the excitation of UV wavelength region. The cathodoluminescence (CL) properties were explained under electron-beam excitations and exhibited the accelerating voltage induced emission properties. The obtained results suggested that the BLSO: $\text{Tb}^{3+}$  phosphors are a promising novel green-emitting material for multifunctional applications.

## 2. Experimental

$\text{Ba}_4\text{La}_{6(1-x)}\text{O}(\text{SiO}_4)_6:6x\text{Tb}^{3+}$  phosphors were synthesized by a citrate sol-gel process by taking the appropriate amounts of barium nitrate [ $\text{Ba}(\text{NO}_3)_2$  ( $\geq 99\%$ )], lanthanum nitrate hexahydrate [ $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (99.99%)], terbium nitrate pentahydrate [ $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (99.9%)], tetraethyl orthosilicate (TEOS) [ $\text{Si}(\text{OC}_2\text{H}_5)_4$

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(98%), and citric acid [ $\text{HOC}(\text{COOH})(\text{CH}_2\text{COOH})_2$  ( $\geq 99.5\%$ )]. Initially, the solution was prepared by dissolving 4 mM of barium nitrate, 6(1-x) mM of lanthanum nitrate, and 6x mM of terbium nitrate in 200 ml of de-ionized (DI) water and 32 mM citric acid was added to the solution (metal ions and citric acid ratio of 1:2). The silicate source was prepared by dissolving the appropriate amount of TEOS in 20 ml of 2-PrOH. The two solutions were stirred individually using a magnetic stirrer until the homogeneous solutions were formed. Finally, the two solutions were mixed and the magnetic stirring was continued until the homogeneous solution formed. The mixed solution was heated on a hot plate and the solution temperature was maintained at 80 °C. The beaker was wrapped with a polythene cap for 1 h to get a homogeneous heating throughout the solution and then the cap was removed. The solution was evaporated gradually until the yellowish wet gel was formed. The obtained sol-gel was then dried in an oven at 120 °C for 24 h. The obtained xerogel was decomposed on further heating at 500 °C for 4 h, thus producing black-colored flakes with highly fine particles. The resulting powders were further annealed at 1400 °C for 12 h.

The X-ray diffraction (XRD) patterns of BLSO:6Tb<sup>3+</sup> phosphors were recorded on a Mac Science (M18XHF-SRA) X-ray powder diffractometer with  $\text{CuK}\alpha = 1.5406 \text{ \AA}$ . The morphological features were observed by field-emission scanning electron microscope (FE-SEM: CARL ZEISS, SUPRA) image. The room-temperature PL spectra were measured by using a Scinco Fluoromate FS-2. The CL properties were measured by a Gatan (UK) MonoCL3 system attached with the SEM (Hitachi S-4300 SE).

### 3. Results and discussion

Fig. 1 shows the XRD pattern of the BLSO:6Tb<sup>3+</sup> phosphor after annealed at 1400 °C in reduced atmosphere. The XRD pattern was in good agreement with the standard JCPDS No. 27-0037 for oxyapatite hexagonal structure and space group  $\text{P6}_3/\text{m}$  (176). The crystallite size has been estimated by the well-known Scherrer equation [14],  $D_{\text{hkl}} = k\lambda/\beta \cos \theta$ , where  $D$  is the average grain size,  $k$  (0.9) is a shape factor,  $\lambda$  is X-ray wavelength (1.5406 Å),  $\beta$  is the full width at half maximum (FWHM) and  $\theta$  is the diffraction angle of an observed peak, respectively. The strongest diffraction peaks

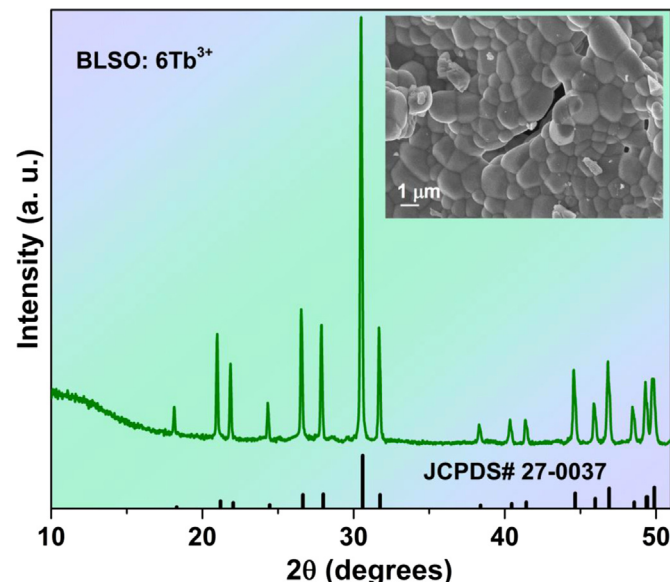


Fig. 1. XRD pattern of the BLSO:6Tb<sup>3+</sup> phosphor. Inset shows the SEM image of the corresponding sample.

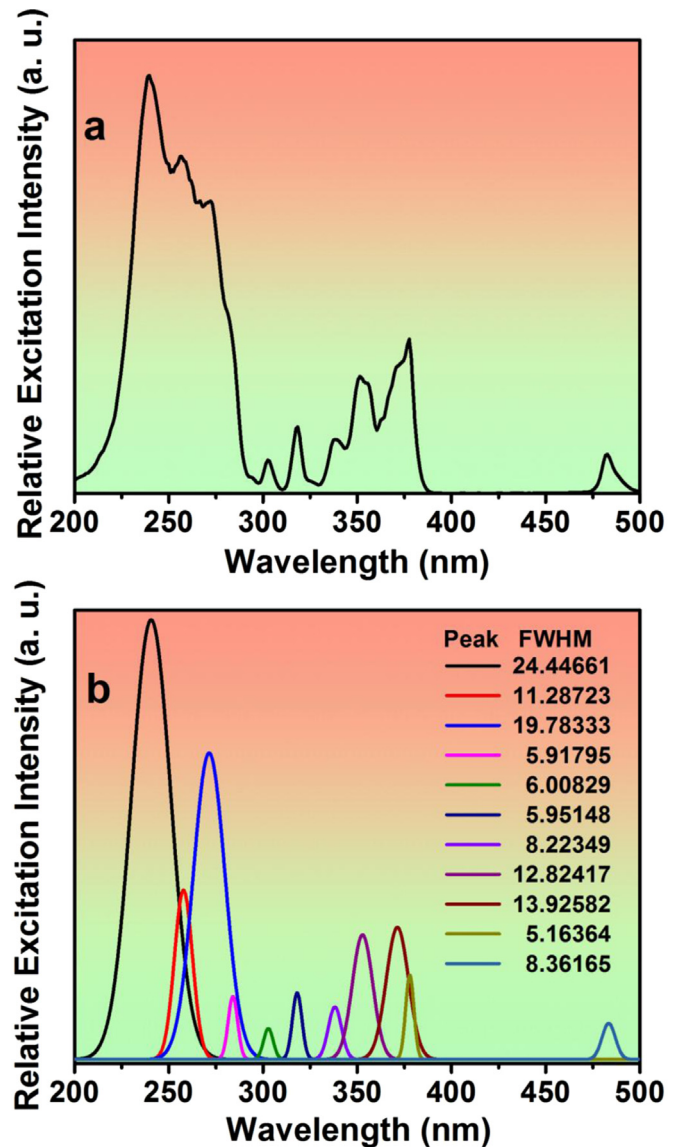


Fig. 2. (a) PLE spectrum and (b) Gaussian fitting curves of the BLSO:6Tb<sup>3+</sup> phosphor.

were used to calculate the crystallite size of CGZO: Tb<sup>3+</sup> nanophosphors, which yields an average value of 98.8 nm. The calculated lattice constants are  $a = 9.7732 \text{ \AA}$ ,  $c = 7.3015 \text{ \AA}$ , and  $v = 603.97 \text{ \AA}^3$ . The inset of Fig. 1 shows the SEM image of the BLSO:6Tb<sup>3+</sup> phosphor with irregular morphology and closely-packed particles.

Fig. 2a shows the PL excitation (PLE) spectrum of the BLSO:6Tb<sup>3+</sup> phosphor by monitoring the emission wavelength of 543 nm. The PLE spectrum consists of a broad excitation band between 200 and 300 nm and narrow bands due to 4f intra-configurational transitions. It is clearly observed that the broad band is due to the inter-configurational f-d transitions of Tb<sup>3+</sup> ions. The f-d transition appeared between 210 and 300 nm with a band maximum at 240 nm [15]. However, the f-d transitions are composed of low spin (LS) and high spin (HS)  $4f^8 \rightarrow 4f^7 5d^1$  transitions [15,16]. For more clarity, the PLE spectrum was deconvoluted by Gaussian fitting and exhibited eleven excitation peaks in the total spectrum (Fig. 2b). The bands centered at 241, 258 and 271 nm are related to the spin allowed (LS) and spin forbidden (HS) transitions, respectively. The position of these f-d transitions depends upon the nature of the host lattice [15,16]. The other group of

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