

Luminescence, Optical and Surface Studies of Green Emitting $\text{KCaBO}_3:\text{Tb}^{3+}$ Nanophosphors

A.K. Bedyal¹, Vinay Kumar^{1,2*}, O.M. Ntwacaborwa² and H.C. Swart²

¹School of Physics, Shri Mata Vaishno Devi University, Katra-182320 (J&K) India

²Department of Physics, University of the Free State, P.O. Box 339, Bloemfontein, ZA9300, South Africa

Abstract— Intense green emitting Tb^{3+} (0.5 – 4 mol %) doped KCaBO_3 nanocrystalline phosphors were synthesized by combustion method at 550 °C, followed by post annealing at 800 °C for 2 hours. X-ray diffraction (XRD), diffuse reflectance (DR) spectroscopy and photoluminescence (PL) spectroscopy were utilized to investigate the structural, optical and PL properties of the phosphors. XRD results revealed that the phosphors have monoclinic crystal structures with space group $P2_1/c$. The average crystallite sizes of the phosphors calculated using the XRD data were found to be in the range of 27–42 nm. Under UV excitation, the phosphors showed several emission bands centered at 487 nm, 544 nm, 586 nm and 622 nm which corresponded to $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$ and $^5D_4 \rightarrow ^7F_3$ characteristic transition of the Tb^{3+} ion, and the green emission band ($^5D_4 \rightarrow ^7F_5$) located at 544 nm was dominant. In order to determine the optimum PL emission intensity, the concentration of Tb^{3+} was varied. A maximum intensity was obtained from the phosphor with 3.0 mol% of Tb^{3+} . The calculated CIE coordinates were ($x = 0.30$, $y = 0.59$), which corresponded to the green shade of the gamut, was in good agreement with the CIE coordinates of the well known green phosphors. In addition, the chemical compositions and electronic states of the powders were analyzed with X-ray photoelectron spectroscopy.

Keywords— phosphors; photoluminescence; XPS; LED,

PACS Code— 33.50.Dq; 78.55.Qr; 79.60.-I; 85.60.Jb

1. INTRODUCTION

Currently, research in the field of phosphors for white light-emitting diodes (WLED) to produce white light is considering the attention of the researchers. Research in this field started in 1991 when there was a first improvement in solid state lightning (SSL) given by Nakamura [1] by his discovery of blue light-emitting diode (LED). Later, in 1996, the first white LED was fabricated which used yellow phosphor usually made of cerium- doped yttrium aluminum garnet (YAG:Ce) combined with blue GaN LED [2]. But this particular method of producing white light has certain demerits such as halo effect, low color rendering index due to two colors mixing. Therefore a new approach has been given to overcome the above limitations, which utilizes the combination of blue, green and red phosphor with UV LED and has excellent color rendering index and high color tolerance [3]. Hence, presently the studies on phosphors for second approach are fascinating much more consideration compared with the first one.

The orthoborates of the type MNBO_3 (M = alkali, N = alkaline) have admirable properties such as low thermal conductivity, high melting point, ability to accommodate defects, high thermal expansion coefficient and high

stability [4]. Recently, advances in these orthoborates doped with rare earth (RE) /transition metal ion demonstrated their significance in solid state lightening, Dosimetry, Nonlinear optics etc. [5–7]. In particular, KCaBO_3 has not been studied much. Das *et al.* for the first time reported the upconversion of Er^{3+} – Yb^{3+} co-doped KCaBO_3 phosphor under near-infrared excitation also the tunable visible upconversion emission had been achieved by introducing Ho^{3+} ions [8, 9]. Das *et al.*, [10] also reported the controllable white light emission from Dy^{3+} – Eu^{3+} co-doped KCaBO_3 phosphor for the potential optoelectronic applications such as white light-emitting phosphor for blue LEDs chips. However, to our best knowledge, there are no reports in the literature on luminescence of Tb^{3+} doped KCaBO_3 nanophosphors.

In this paper, we have synthesized the Tb^{3+} doped KCaBO_3 nanocrystalline phosphor by combustion method to explore its potential application in wLEDs. Luminescence, optical and surface studies properties of the $\text{KCaBO}_3:\text{Tb}^{3+}$ have been discussed.

2. EXPERIMENTAL DETAILS

Tb^{3+} doped KCaBO_3 phosphors were synthesized by combustion method using urea as a fuel. The concentration of the activator (Tb^{3+}) varied from 0.5 to 3.5 mol%. The potassium nitrate [KNO_3], calcium nitrate tetrahydrate [$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$], terbium oxide [Tb_2O_3]

* Corresponding author: vinaykdhiman@yahoo.com, vinaykumar@smvdu.ac.in

(99.99%) and boric acid [H_3BO_3] were used as precursors. In a typical preparation, all the reactants were taken according to the balanced reaction (Eq. 1) and dissolved, stoichiometrically, in a few drops of distilled water with vigorous stirring until a thick paste was formed. The thick paste was transferred into the crucible and was kept in a preheated muffle furnace at 550°C . Initially (1)

The crystalline phase of the synthesized samples was identified by X-ray powder diffractometer (XRD) (Bruker Advance D8 X-ray diffractometer), operating at 40 kV and 40 mA using $\text{Cu K}\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$). The photoluminescence (PL) measurements of the phosphors were done on a Cary-Eclipse Spectrofluorometer equipped with a 150 W xenon discharge lamp as an excitation source. For optical properties, the diffuse reflectance spectra of the powder samples were recorded using a UV-VIS -2600 double beam spectrophotometer; attached with an ISR (Integrating Sphere Assembly). To study the surface and the chemical states of the nanophosphors, the x-ray photoelectron spectroscopy (XPS) was performed on a PHI 5000 versa probe spectrometer using monochromatic $\text{Al K}\alpha$ radiation. The details for measuring the high resolution spectra were described in a previous report [11].

3. RESULTS AND DISCUSSIONS

3.1 XRD Studies

Fig. 1 shows the XRD pattern of the $\text{KCaBO}_3:\text{Tb}^{3+}$ (3 mol %) nanophosphor. The XRD pattern is consistent with the reported pattern [8,9] for KCaBO_3 and depicts that the pattern belongs to the pure monoclinic phase with space group $\text{C2}_1/\text{c}$. Also, it has been observed that the addition of small amounts of Tb^{3+} (activator), did not alter the crystal structure of the host lattice, which suggested that the activator ion is fully incorporated in the host lattice. The average crystalline size of the nanophosphors was calculated from the full width half maxima of the diffraction peaks by using Scherrer's equation [12] and is approximated to be $27 \times 42 \text{ nm}$.

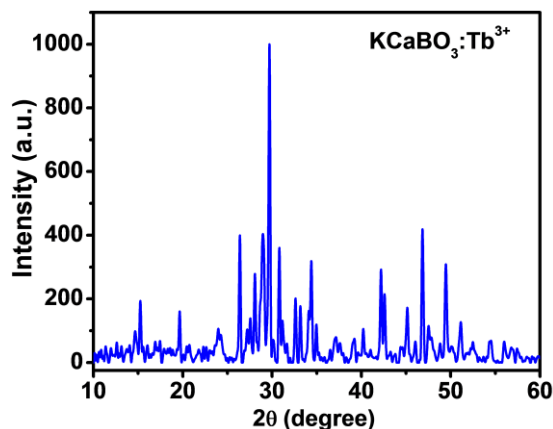


Fig. 1: XRD pattern of the $\text{KCaBO}_3:\text{Tb}^{3+}$ nanophosphors.

3.2 Photoluminescence Studies

Fig. 2 shows the excitation(a) and the emission spectra (b) of Tb^{3+} doped KCaBO_3 (3 mol%) nanophosphor. The excitation spectrum of the nanophosphor was recorded by keeping the emission wavelength at 544 nm. The spectrum shows an intense broad band at 222 nm corresponding to $^4\text{F}_8 \rightarrow ^4\text{F}_7^5\text{D}_1$ with some less intense peaks from 280–385 nm, due to characteristic 4f-4f transitions of the Tb^{3+} ion. The emission spectrum of the nanophosphor monitored at 378 nm excitation, consists of several emission peaks in the region of 475–635 nm with prominent emission at 544 nm occurred due to the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition of the Tb^{3+} ion, while the other emission peaks at 487 nm, 586 nm and 622 nm corresponds to the $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_5$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$ and $^5\text{D}_4 \rightarrow ^7\text{F}_3$ characteristic transition of the Tb^{3+} ion[13].

Fig. 4 presents the plot of Tb^{3+} ion concentration as a function of maximum intensity. It shows that the intensity was enhanced with increasing concentration of the activator ion and reached a maximum at $x=3 \text{ mol\%}$ where after it starts decreasing due to the well-known concentration quenching phenomenon [14]. The concentration quenching occurred due to the energy transfer between the activator (Tb^{3+}) ions.

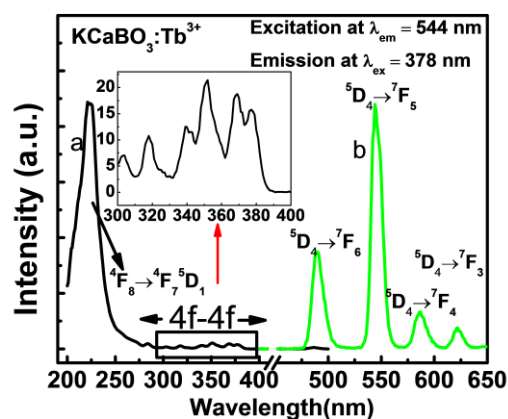


Fig. 2: The excitation and the emission spectrum of the $\text{KCaBO}_3:\text{Tb}^{3+}$ (3 mol%) nanophosphors.

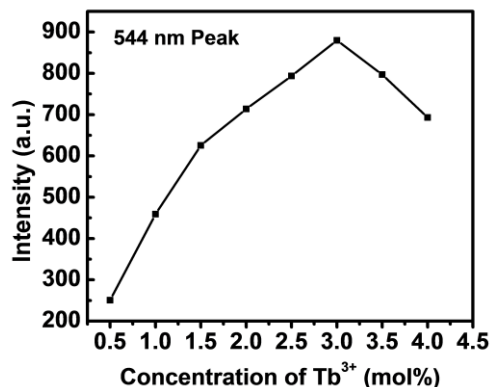


Fig. 3: Variation in PL intensity of the 544 nm PL emission peak as a function of Tb^{3+} concentration

3.3 UV-VIS Studies

The diffuse reflectance (DR) spectrum of the $\text{KCaBO}_3:\text{Tb}^{3+}$ (3 mol %) nanophosphor measured from 190–1400 nm is presented in Fig. 4. The spectrum consists of some less intense absorption peaks in the range of 300 nm \square 400 nm corresponds to the characteristic $4f \rightarrow 4f$ transitions of the Tb^{3+} ion. Along with a sharp absorption edge approximately equal to 222 nm corresponding to the band gap of the nanophosphor, which can also serve as the absorption wavelength of this particular nanophosphor.

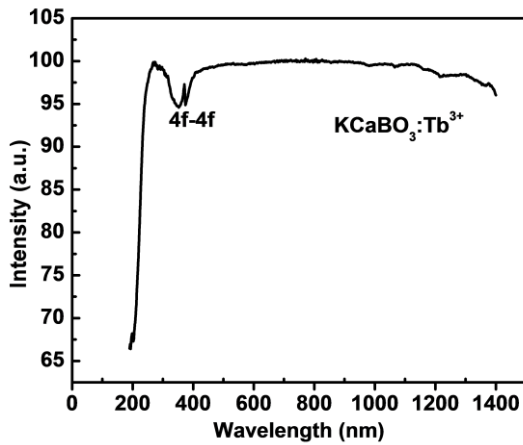


Fig. 4: Diffuse reflectance spectra of $\text{KCaBO}_3:\text{Tb}^{3+}$ (3 mol%) nanophosphor.

3.3.1 Band Gap Determination

From the DR spectrum, the band gap of the $\text{KCaBO}_3:\text{Tb}^{3+}$ (3 mol %) nanophosphor was determined by using the Kubelka–Munk [15] theory. The absorption spectrum (Fig. 5) of the phosphor was transformed from the DR spectra by using the Kubelka–Munk function, given as:

$$F(R) = \frac{(1-R)^2}{2R} = \frac{K}{S} \quad (2)$$

where, R = the diffuse reflectance of the sample, K = absorption coefficient and S = scattering coefficient.

The direct band gap (E_g) and linear absorption coefficient (α) are related by the well-known Tauc relation:

$$\alpha h\nu = C(h\nu - E_g)^{1/2} \quad (3)$$

where $h\nu$ = energy of light and C = constant. The above Tauc relation is modified by using equation (2) and is given by

$$[F(R)h\nu]^2 = C(h\nu - E_g) \quad (4)$$

Fig. 5 presents the plot of $[F(R)h\nu]^2$ as a function of photon energy ($h\nu$), constructed by using Eq (4). The value of the band gap (E_g) was determined by extrapolating the linear fitted region. The point on the energy axis, at which the extrapolating line meets with the $h\nu = 0$, corresponds to the direct band gap of the phosphor. In the present case the band gap of the $\text{KCaBO}_3:\text{Tb}^{3+}$ nanophosphor was approximated to be 5.66 eV.

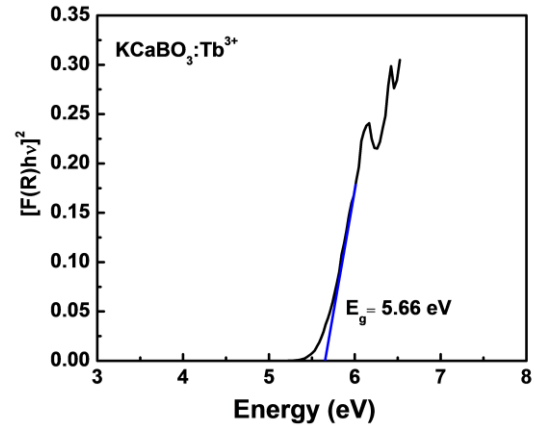


Fig. 5: Energy Band gap in the $\text{KCaBO}_3:\text{Tb}^{3+}$ nanophosphors

3.4 CIE Parameters

To evaluate the performance of the phosphor, the Commission Internationale de l'Eclairage (CIE) parameters were calculated.

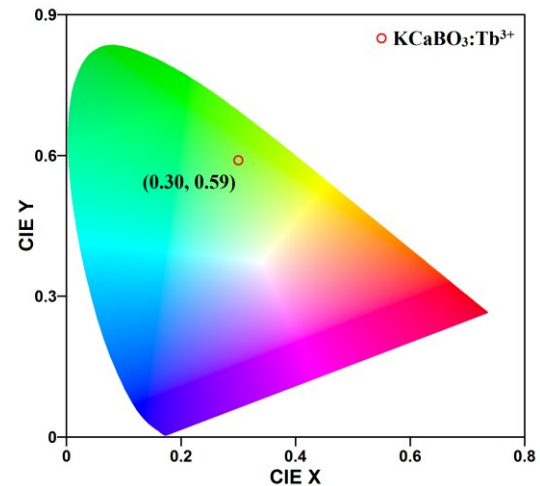


Fig. 6: The color gamut of the $\text{KCaBO}_3:\text{Tb}^{3+}$ nanophosphor.

The CIE chromaticity coordinates for $\text{KCaBO}_3:\text{Tb}^{3+}$ (3 mol%) nanophosphors under excitation wavelength of 378 nm is shown in Fig. 6. From the CIE diagram it can be found that the calculated CIE coordinates were

($x = 0.30$, $y = 0.59$), which corresponded to the green shade of the gamut and close to the CIE coordinates of the well known green phosphors $\text{ZnS:Au0.05, Cu0.01}$ (0.267, 0.582) [16].

3.5 XPS Study

XPS is a characterization technique extensively used to investigate the chemical constitution and chemical bonding state of elements in the materials. The technique is based on collecting the electrons that are ejected from atoms of the sample being examined when irradiated by X-rays. The technique is highly surface sensitive and non destructive. It provides compositional analysis of approximately the top 5 nm of material below the studied samples surface.

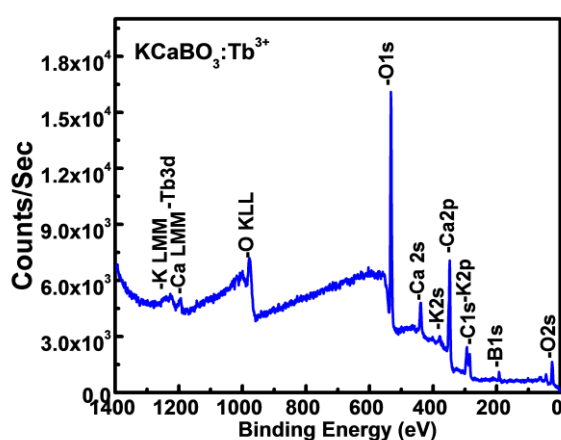


Fig. 7: The XPS survey scan spectrum of the $\text{KCaBO}_3:\text{Tb}^{3+}$ nanophosphor.

In order to examine the composition and to determine the chemical states of the K, Ca, B and O in the prepared nano-phosphors, XPS analyses were carried out and the energy scale was calibrated with the C1s peak of the carbon contamination at 284.60 eV as this peak comes from hydrocarbon contamination and its binding energy accepted as remaining constant, irrespective of the chemical state. Fig. 7 presents the survey scan spectrum of the $\text{KCaBO}_3:\text{Tb}^{3+}$ nanophosphors, which clearly confirms the presence of all the elements of the synthesized material from their corresponding binding energy.

4. CONCLUSIONS

In the present work, $\text{KCaBO}_3:\text{Tb}^{3+}$ nanophosphor was successfully synthesized by combustion method using urea as fuel. The excitation spectrum reveals that the phosphor could easily be excited by near UV-chips, to emit light corresponded to the green shade of the gamut CIE coordinates ($x = 0.30$, $y = 0.59$). The band gap and average crystalline size of the material are approximated to be 5.66 eV and 27–42 nm, respectively. In addition the XPS study confirms the presence of all the elements of $\text{KCaBO}_3:\text{Tb}^{3+}$ on the surface of the material.

ACKNOWLEDGEMENT

AKB is highly thankful to Inter University Accelerator Centre, New Delhi for financial support in the form of fellowship under UFR project code—MS/30505.

REFERENCES

- [1] S. Nakamura, Jpn. J. Appl. Phys. 30 (1991) L1705.
- [2] Y. Narukawa, Opt. Photonics News 15 (2004) 24.
- [3] Y. H. Won, H. S. Jang, W. B. Im, D. Y. Jeon, Appl. Phys. Lett. 89 (2006) 231909.
- [4] V. Kumar, et al., J. Alloys. Compd. 554 (2013) 214.
- [5] P. Li, et al., Mater. Res. Bull. 44 (2009) 2068.
- [6] Z. Wang, et al., J. Rare Earths, 28 (2010) 30.
- [7] L. Wu, et al., Inorg. Chem. 44 (2005) 6409.
- [8] S. Das, A. A. Reddy, G. V. Prakash, Chemical Physics Letters, 504 (2011) 206.
- [9] S. Das, et al, Materials Letters, 120 (2014) 232.
- [10] S. Das, et al., J Mater. Sci., 46 (2011) 7770.
- [11] A. K. Bedyal, et al., J. Mater. Sci. 48 (2013) 3327.
- [12] B. D. Cullity, Element of X-ray Diffraction, second ed. Addison-Wesley (New York) 1956.
- [13] P. A. Nagpure, S. K. Omanwar J. Rare Earths 30 (2012) 856.
- [14] G. Blasse, B. C. Grabmaier, Luminescent Materials, Springer (Verlag) 1994.
- [15] A. E. Morales, E. S. Mora, U. Pal., Rev. Mex. Fis. S. 53 (2007) 18.
- [16] W.M. Yen, S. Shionoya, H. Yamamoto, Phosphor Handbook, CRC Press, New York, 2006.