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# Synthesis and Thermoluminescence Studies of Gamma Ray Induced Ca<sub>3</sub>B<sub>2</sub>O<sub>6</sub>:Bi<sup>3+</sup> Nanophosphor

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Abstract— This paper reports on the synthesis and thermoluminescence (TL) properties of  $Bi^{3+}$  doped  $Ca_3B_2O_6$ nanophosphor. The phosphor  $Ca_3B_2O_6:Bi^{3+}$  was synthesized by combustion method at 600, using urea as fuel. The crystal structure of the phosphor was confirmed by the X-ray diffraction method after annealing the phosphor at 900, which belongs to the rhombohedral phase with space group R-3C. For the TL study, the phosphors were exposed with gamma rays in the dose ranges from 10 Gy to 5000 Gy. The TL glow curve of the phosphors consists of two glow peaks centered at 357 K and 584 K. The TL dose response curve shows sub-linear response for the studied dose. In addition, the effect of heating rate on the TL properties of  $Ca_3B_2O_6: Bi^{3+}$  phosphor was analyzed. Also, the kinetic parameters such as activation energy (E), frequency factor (s) and order of kinetics (b') as a function of heating rate after the deconvolution of the TL glow curve were also determined by using Chen's peak shape method. TLAnal computer program was used to deconvolution the TL glow curve.

Keywords—X- ray diffraction; Thermoluminescence; Combustion synthesis

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# 1. INTRODUCTION

The properties of any TL materials generally depend on the kinetic parameters of its glow curve peak. These parameters give important information about the mechanism responsible for the TL emission in the material. The energy released from the TL material on heating is plotted as a function of temperature form a glow curve. The shape, position and intensities of the glow curve peaks are related to the properties of the trapping states responsible for TL. The most important parameters to be determined is the activation energy (E) which is the thermal energy needed to empty the trap, frequency factor (s) and order of kinetics (b) [1]. From last few years, borate materials have attracted much attention of various researchers due to their potential applications as phosphor materials in thermoluminescence (TL) dosimeters [2-4], the detection of dose of various energetic radiations [5], X-ray medical imaging system [6]. Among these borates, Ca<sub>3</sub>B<sub>2</sub>O<sub>6</sub>:Bi<sup>3+</sup> phosphor is one of the most interesting type of host material because of their large band-gap, low cost, excellent physical and chemical stability. The crystal structure of Ca<sub>3</sub>B<sub>2</sub>O<sub>6</sub> was reported to crystallize in the rhombohedral phase with a space group of  $R-3_C$  and the lattice parameters are a = 8.6377Å, b = 8.6377Å and c = 11.849 Å by *Vegas et.* al.[7]. The luminescence properties of rare earth doped  $Ca_3B_2O_6$ 

phosphor have been reported by many researchers [8-10] for their application potentials in wLEDs. *Sun et. al.* [11] in 2011 has reported the thermoluminescence properties of  $Ca_3B_2O_6$ : Dy phosphor co-doped with  $Na^+$  ion synthesized by high temperature solid-state method.

To the best of our knowledge, no work has been reported on the thermoluminescence and TL parameters of  $Bi^{3+}$ doped Ca<sub>3</sub>B<sub>2</sub>O<sub>6</sub> phosphor. In this work, we have discussed the synthesis, structural, and thermoluminescence properties of Ca<sub>3</sub>B<sub>2</sub>O<sub>6</sub>:  $Bi^{3+}$  phosphor synthesized by combustion method. In addition, the effect of dose response and different heating rates on the TL glow curve has been discussed. The trapping parameters such as activation energy (E), frequency factor (s) have been determined by using the glow shape method [12] after the deconvolution of glow curve at different heating rates by using the TLAnal computer program [13].

# 2. EXPERIMENT

# 2.1 Synthesis of Ca<sub>3</sub>B<sub>2</sub>O<sub>6</sub>: Bi<sup>3+</sup> Nanophosphor

 $Ca_3B_2O_6$ : Bi<sup>3+</sup> phosphors were synthesized by using the combustion method. Calcium nitrate [Ca (NO<sub>3</sub>)<sub>2</sub>.

# 4H<sub>2</sub>O], Boric acid [H<sub>3</sub>BO<sub>3</sub>], Urea [CH<sub>4</sub>N<sub>2</sub>O] and

Bismuth oxide  $[Bi_2O_3]$  of Merck made with analytical reagent (AR) grade was used as starting materials. The chemical reaction used to synthesize the nanophosphor is given below:-

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 $3(1-x)Ca(NO_3)2H_2O + 2H_3BO_3 + CH_4N_2O +$  $1.5xBi_2O_3 \rightarrow Ca_{3(1-x)}Bi_3xB_2O_6 + 25H_2O + CO_2 + 8N_2$ 

#### The stoichiometric composition of the metal nitrate (oxidizer) and urea (fuel) was calculated taking O/F = 1, in order to have the maximum release of energy for complete combustion. The calculated amounts of reactants and urea were dissolved with few drops of distilled water and thoroughly were mixed together in an agate mortar pastel up to 40 minutes, until a mixture turns into a viscous liquid. The liquid was transferred to a beaker and then introduced into a preheated muffle furnace at 600°C to produce the corresponding phosphors by undergoing a flaming combustion. After that white foamy product was cooled to room temperature and grounded to obtained fine powder. The fine powder was then annealed at 900°C for three hours to get complete crystallinity.

The crystal structure of the prepared nanophosphor was examined by using Bruker D8-advance X-ray diffractometer with  $\theta$  in the range of  $20^{\circ} \le \theta \le 66^{\circ}$  with scanning step size of  $0.001^{\circ}$  operating at 40kV and 40mA and using CuK<sub>a</sub> radiation ( $\lambda$ =1. 54056 Å). The lattice parameters of the phosphor were calculated by using the UnitCellWin program [21]. The prepared phosphors were exposed to different doses of  $\gamma$  - rays at room temperature in the range of (10Gy – 5000Gy) by using a gamma chamber containing a <sup>60</sup>Co source. The TL glow curves of the exposed phosphors were recorded on the HARSHAW QS 3500 TLD reader, using a linear heating rate of 5K/s by taking 5 mg of the sample each time.

#### 3. RESULTS AND DISCUSSION

#### 3.1 Structural Analysis

The XRD pattern of  $Ca_3B_2O_6$ :  $Bi^{3+}$  nanophosphor was shown in Fig. 1. It can be seen from the Fig.1 that all the diffraction peaks matched well with the standard JCPDS data 022-0142, corresponds to that of rhombohedral phase of  $Ca_3B_2O_6$  with space group R-3C and its lattice parameters calculated to be a = b = 8.642 Å, c = 11.866 Å and V= 767.66 Å<sup>3</sup> by using Unitcellwin software [14]. The addition of a small amount of impurity atoms Bi<sup>3+</sup> did not affect the crystal structure of the host matrix, suggesting that the Bi<sup>3+</sup> ion (radius = 1.17 Å) successfully replaced the Ca<sup>2+</sup> ion (radius = Ca<sup>2+</sup> 1.12 Å) due to the approximately close ionic radius. The average crystallite size of the nanoparticles was estimated from the line broadening of the XRD peaks by the well known Debye -Scherrer's formula [15].

$$d = \frac{0.89\lambda}{\beta Cos\theta_B} \tag{1}$$

Where d is the average crystallite size of the particles,  $\lambda$  is the wavelength of  $CuK_{\lambda}$  (1.5406 Å) radiation,  $\beta$  (in radian) is full width at half maxima (FWHM) and  $\theta_B$  is the Bragg's angle. The average crystallite sizes were found to be in the range of 33–35 nm.



Fig. 1: XRD pattern of Ca<sub>3</sub>B<sub>2</sub>O<sub>6</sub>:Bi<sup>3+</sup> nanophosphor.

#### **3.2** Thermoluminescence

Fig.2 shows the (TL) glow curves of Ca<sub>3</sub>B<sub>2</sub>O<sub>6</sub>: Bi<sup>3+</sup> nanophosphor recorded at a heating rate of 5 K/s, exposed by gamma rays in the dose range of (10-5000) Gy. The TL glow curve shows two prominent peaks centered at 357 K and 584 K. The glow curve at lower doses (10-1000) Gy shows different shape as compared to higher doses. Moreover, The TL intensity increases with an increase in gamma dose range (10-5000) Gy as shown in Fig. 2. This increase in the TL intensity is due to the reason that with an increase in gamma dose, more and more trapping centers responsible for glow peak get filled. On heating the sample, the release of charge carriers from the trapping centers take place and the successive recombination of the charge carriers with their counterparts at recombination centers increases the TL intensity [16].



Fig. 2: TL glow curve of Ca<sub>3</sub>B<sub>2</sub>O<sub>6</sub>: Bi<sup>3+</sup> phosphor irradi- ated to gamma rays at different doses

#### 3.3 Linear Dose Response

For a good TL material it is important to know whether it exhibit linear, sublinear or supralinear behavior between TL intensity and absorbed doses. TL dose response behavior can be explained by using an equation of the form,  $TL = x(Dose)^y$ . Taking logarithms both sides of this equation,  $[\log (TL) = \log (x) + y \log (Dose)]$  can be obtained. The slope (y = linearity factor) will be found with a linear fit of log (TL) versus log (Dose). The dose response is linear for y = 1, sub linear for y < 1 and supralinear for y > 1 [17]. Fig. 3 shows the dose response curve of  $Ca_3B_2O_6:Bi^{3+}$  phosphor as log (TL) intensity Vs log (Dose) exposed by gamma rays in the range of (10  $\Box$ 5000) Gy in which peak heights were used for measuring the TL intensities. Fig.3 shows a linear response up to 2000Gy which corresponds to 3.307 from the graph. The values of y = 0.845, is less than 1 which means that the dose response shows sub linear behavior.

# 3.4 Effect of Heating Rates on the TL Response of Ca<sub>3</sub>B<sub>2</sub>O<sub>6</sub>: Bi<sup>3+</sup>Nanophosphor

The effect of different heating rates on TL response of 5000Gy gamma exposed Ca<sub>3</sub>B<sub>2</sub>O<sub>6</sub>:Bi<sup>3+</sup> nanophosphor has been investigated. Fig. 4 shows the TL glow curve of  $Ca_3B_2O_6$ : Bi<sup>3+</sup> phosphor at different heating rate, i.e. 3K/s, 5K/s and 10k/s. It has been observed that with increase in heating from 3K/s - 10K/s TL intensity increases and then decreases. When the heating rate increase from 3K/s to 5K/s the TL intensity and the total area of the glow peak increases, also the peak temperature shift toward higher temperature side. With further increase in heating rate from 5K/s to10K/s a drastic change in the peak behavior was observed, i.e. the TL intensity and total area of glow peak decreases with a peak temperature shift toward the higher temperature. The increase and decrease in TL intensity may be due to the reason that at lower heating rates the charge carries responsible for the thermoluminescence have enough time to get trapped at the recombination Centre and are not involved in producing luminescence. When the heating rate increase, the phenomenon of thermal quenching of TL intensity



Fig. 3: Linear dose response of Ca<sub>3</sub>B<sub>2</sub>O<sub>6</sub>:Bi<sup>3+</sup> nanophosphor irradiated to gamma rays at different doses.



Fig. 4: Effect of heating rates on the TL response of Ca<sub>3</sub>B<sub>2</sub>O<sub>6</sub>: Bi<sup>3+</sup> nanophosphor

arises due to which the TL intensity decreases. The similar behavior with different heating rates was available in many reports by [18, 16].

#### 3.5 Kinetic Parameters

The knowledge about the kinetic parameters such as activation energy (E), order of kinetics (b) and frequency factor (s), of TL glow curves of any thermoluminescent material has now become an important area of research and plays an important role in the understanding of the basic TL mechanism. Fig.5 shows the deconvoluted peak by using the TLAnal program at heating rate of 5K/s exposed by 5000Gy. This peak is deconvoluted by using five traps of different order. The peak shape method, also known as Chen's (1969) method [19] were used to determine these kinetic parameters at different heating rate. This method is mainly depends on the peak temperatures  $T_m$ ,  $T_1$  and  $T_2$ , Where  $T_m$  is the peak temperature at maximum TL intensity,  $T_1$  and  $T_2$  are the temperatures on either side of them corresponding to half peak intensity and the total half intensity width  $\omega = T_2 - T_1$ , the high temperature half width  $\delta = T_2 - T_m$  and the low temperature half width  $\tau = T_m - T_1$  parameters.

Order of kinetics (b') can be calculated from the symmetric factor  $(\mu_g)$  of the glow curve. Symmetry factor  $(\mu_g)$  of the glow peak is calculated from the known peak shape parameters given by equation (2):

$$\mu_g = \frac{T_2 - T_m}{T_2 - T_1} \tag{2}$$

Theoretically, the values of symmetry factor  $(\mu_g)$  for first and second order kinetics are close to 0.42 and 0.52, respectively. The activation energy  $(E_{\alpha})$  or trap depth which is the thermal energy required to liberate the trapped electron and holes can be determined by the Chen's [19] equation valid for any kinetics given by:-

Table 1: Kinetic parameters of Ca<sub>3</sub>B<sub>2</sub>O<sub>6</sub>: Bi<sup>3+</sup> phosphor calculated by Chen's formula

Heating Rate	Peak	$T_m(K)$	Order of kinetics	Activation	Frequency
(K/s)			$(\mu_g)$	Energy $E_{avg}(eV)$	factor $s(s^{-1})$
3	1	362.11	0.43(1)	1.09	5.91×10 <sup>14</sup>
	2	382.14	0.52(2)	1.34	$1.73 \times 10^{17}$
	3	525.21	0.50(2)	1.41	6.42×10 <sup>12</sup>
	4	573.12	0.51(2)	2.19	$4.82 \times 10^{18}$
	5	599.12	0.58(2)	2.35	6.15×10 <sup>18</sup>
5	1	366.14	0.42(1)	0.84	3.48×10 <sup>14</sup>
	2	442.35	0.51(2)	1.07	3.22×10 <sup>13</sup>
	3	517.00	0.52(2)	1.43	3.00×10 <sup>17</sup>
	4	567.16	0.54(2)	2.03	$1.78 \times 10^{14}$
	5	597.72	0.60(2)	2.06	1.30×10 <sup>9</sup>
10	1	368.14	0.41(1)	1.03	1.19×10 <sup>14</sup>
	2	384.15	0.53(2)	1.14	$1.01 \times 10^{15}$
	3	536.15	0.51(2)	1.50	8.26×10 <sup>13</sup>
	4	594.17	0.52(2)	1.52	3.97×10 <sup>12</sup>
	5	640.21	0.61(2)	1.54	5.17×10 <sup>11</sup>

$$E_{\alpha} = C_{\alpha} \left( \frac{kT_m^2}{\alpha} \right) - \dot{b_{\alpha}} (2kT_m)$$
(3)

Where

$$\begin{split} &\alpha = \tau, \, \delta, \, \omega; \, \tau = T_m - T_{1;} \, \delta = T_2 - T_1; \, \omega = T_2 - T_1; \, \text{and} \\ &C_\tau = 1.51 + 3.0 \, (\mu_g - 0.42); \, b'_\tau = 1.58 + 4.2 \, (\mu_g - 0.42) \\ &C_\delta = 0.976 + 7.3 \, (\mu_g - 0.42); \, b'_\delta = 0 \\ &C_\omega = 2.52 + 10.2 \, (\mu_g - 0.42); \, b'_\omega = 1. \end{split}$$

The frequency factor was calculated from equation given below:-

$$\frac{\beta E}{kT_m^2} = s \exp\left\{\frac{-E}{kT_m}\right\} \left[1 + (b'-1)\Delta m\right]$$
(4)

Where  $\beta$  is the linear heating rate, and k is Boltzmann constant (8.6 ×10<sup>-5</sup> eV K<sup>-1</sup>).

The calculated trapping parameters for  $Ca_3B_2O_6$ :  $Bi^{3+}$  nanophosphor at different heating by using Chen's method has been given in table 1. The activation energy (E) and frequency factor are calculated by using eqn. (3) and eqn.(4) at different heating rates from 3K/s to 10K/s. For calculations first and second order kinetic equation have been used with  $\mu_g = 0.42$  for the first order and 0.52 for second orders respectively. The activation energies are calculated by taking the average ( $E_{avg}$ ) of  $E_{\delta}$ ,  $E_{\tau}$  and  $E_{\omega}$  and increasing with increase in peak temperature, which is also in agreement.



Fig. 5: Deconvolution of the TL glow curve of  $Ca_3B_2O_6$ : Bi<sup>3+</sup> nanophosphor  $\beta = 5K/s$ 

# 4. CONCLUSION

We have successfully synthesized  $Ca_3B_2O_6$ :  $Bi^{3+}$ nanophosphors with combustion method at a reaction temperature of 600 °c. The TL studies of  $Ca_3B_2O_6$ :  $Bi^{3+}$ phosphor exposed by gamma rays shows that the TL glow curve consists of two peaks centered at 357K and 584K. It is observed that the TL intensity of the glow curves increase with increase in gamma doses. The TL dose response curve shows sub-linear behavior for the studied doses in the range of (10–5000) Gy. Kinetic analysis of the TL glow curve has been carried out by using the TLAnal software of deconvolution by adding five peaks of first and second order traps in different heating rates (3–10) K/s glow curves. The activation energy obtained for  $Ca_3B_2O_6$ :  $Bi^{3+}$  nanophosphor at different heating rates increases with increase in peak temperature. Moreover, with the different heating rates the effect on shape, position and a shift in peak temperature towards the higher side in glow curves have been observed.

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