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# Thermally stimulated luminescence studies of $BaB_4O_7$ compound

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In this paper thermally stimulated luminescence (TSL) studies of $BaB_4O_7$ compound are reported for the first time. The polycrystalline sample of $BaB_4O_7$ was prepared by a melting method and the formation of the $BaB_4O_7$ compound was confirmed by an X-ray diffraction study. The compound has orthorhombic structure at room temperature. The TSL glow curves of $BaB_4O_7$ compound when heated at a constant heating rate of 4°C/s exhibit two thermoluminescence (TL) glow peaks at 110 and 150°C followed by a shoulder around 210°C. The trapping parameters associated with the prominent glow peak of $BaB_4O_7$ are reported using isothermal luminescence decay method (ILDM). As a check the trap parameters are also calculated by glow curve shape (Chen's) method after isolating the prominent glow peak by thermal cleaning technique. Our results show a very good agreement between the trapping parameters calculated by the two methods. 

## 1. Introduction

Thermally stimulated luminescence studies of borate compounds were started in 1974 by the work of Kazanskaya [1]. Since then, detailed TL studies on various alkali and alkaline earth tetraborates were reported. These compounds find several interesting applications e.g., lithium and magnesium borates are phosphors used in thermoluminescence dosimetry [2, 3], barium borate is used as a non-linear optical material for laser harmonic generation [4]. Many researchers [5, 6] carried out the TSL studies of lithium and magnesium borate compounds. However, so far no work has been reported on the thermally stimulated luminescence studies of barium borate compound. Keeping this in view, an attempt was made to study the TSL of $BaB_4O_7$ compound. The results of trapping parameters such as order of kinetics ($b$), activation energy ($E$) and frequency factor ($s$) for the prominent glow peak (peaking at 150°C) of RT, X-irradiated barium borate are reported.

## 2. Experimental

The polycrystalline sample of $BaB_4O_7$ was prepared by a melting method [7]. The preparation of barium borate sample was made by mixing barium carbonate (99%, Loba Chemie, Bombay) and boric acid (99.5%, S.d. fine-chem Ltd., Boisar) in stoichiometric ratio and the mixture was melted at 900°C in a platinum crucible for 4.5 h and then cooled at a rate of about 60 K/min. The crystalline material was ground and sieved to a grain size of 200 $\mu$m.

The characterization of $BaB_4O_7$ was carried out by an X-ray diffraction study. X-ray diffractogram of the compound was taken at room temperature in a wide range of Bragg angle $2\theta(10^\circ \leq 2\theta \leq 80^\circ)$ using a X-ray diffractometer type PW 1710, Holland with Cu target and at a scanning rate of 3°/min.

The samples was heated to 400°C for 10 min and then quenched to room temperature before X-irradiating them. The powder sample was irradiated by X-rays obtained from Cu target of Machlett tube operated at 20 kV and 15 mA. The TSL studies were made by using Personal Computer Based Thermoluminescence Analyzer System (type 1007) supplied by Nucleonix Systems Private Limited, Hyderabad, India. The glow curves were recorded by heating the samples at a uniform rate of 4°C/s with the help of a temperature controller (type 575) made by Nucleonix Systems Private Limited, Hyderabad, India and the luminescence emission was detected by a photo-multiplier tube (type 9924 B) imported from U.K. The photo-current from PM tube was amplified by a DC amplifier (type 552) made by Nucleonix Systems Private Limited, Hyderabad, India which was interfaced to a personal computer. The TSL out put was finally recorded by a printer connected to the personal computer.

## 3. Results

### 3.1. Structural study

In order to ascertain the structure of prepared $BaB_4O_7$ compound, X-ray diffraction pattern of powder sample

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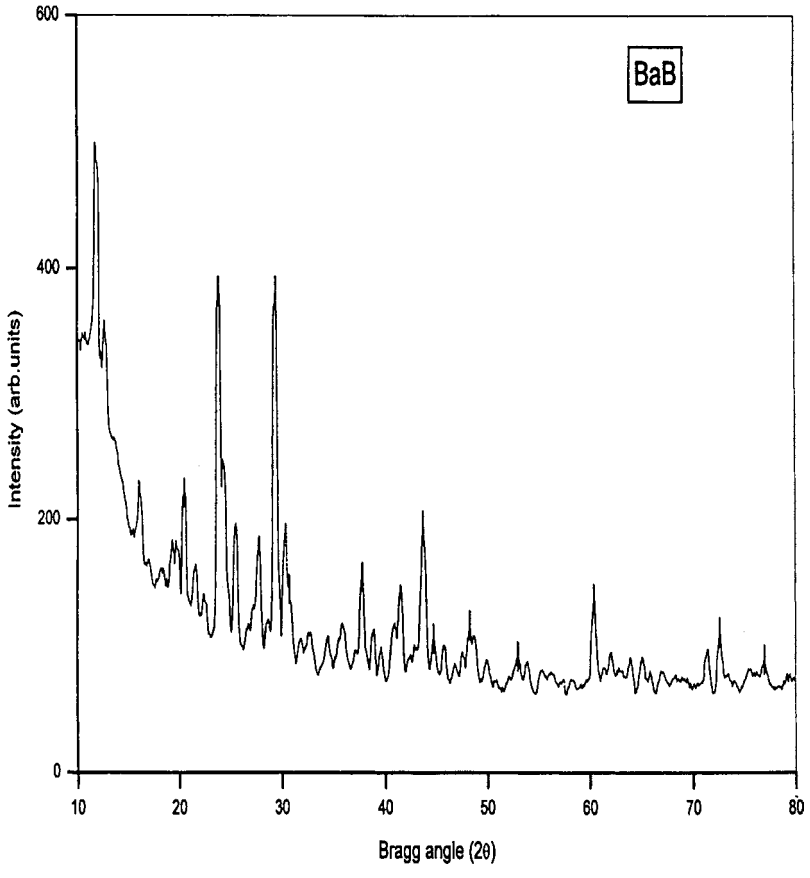


*Figure 1* XRD pattern of $BaB_4O_7$ sample at room temperature.

$BaB_4O_7$ was recorded (Fig. 1). The sharp and single diffraction peaks of the XRD pattern suggested the formation of new compound. From the $2\theta$ values of the diffraction lines, interplanar spacing ($d$) of the peaks was calculated. The diffraction lines were indexed using a computer program package 'Powdmult' [8]. Out of those a suitable orthorhombic unit cell was selected for which $\sum \Delta d (= d_{obs} - d_{cal})$ was found to be minimum. The lattice parameters of the unit cell were refined using least-squares method and were found to be: $a = 5.8496\,\text{Å}, b = 9.9283\,\text{Å}, c = 9.5291\,\text{Å}$. A good agreement between the observed and calculated $d$-values (Table I) suggests the suitability of the crystal structure and unit cell parameters. It is worth mentioning that the ($hkl$) values of most prominet diffraction peaks are (120), (301), (161), (201) and (104).

TABLE I Comparison of observed and calculated $d$-values (Å) of some reflections of a $BaB_4O_7$ sample at room temperature

| $h$ | $k$ | $l$ | $d_{obs}$ | $d_{cal}$ | $I/Io^*100$ |
|---|---|---|---|---|---|
| 1 | 2 | 0 | 3.7856 | 3.7849 | 100 |
| 2 | 0 | 1 | 2.7968 | 2.7961 | 46 |
| 1 | 0 | 4 | 2.2064 | 2.2063 | 44 |
| 2 | 1 | 3 | 2.1034 | 2.1028 | 32 |
| 3 | 0 | 1 | 1.9103 | 1.9103 | 76 |
| 2 | 3 | 3 | 1.8039 | 1.8039 | 36 |
| 0 | 3 | 5 | 1.6529 | 1.6515 | 36 |
| 1 | 6 | 1 | 1.5704 | 1.5705 | 76 |
| 1 | 1 | 6 | 1.5162 | 1.5148 | 29 |
| 0 | 3 | 7 | 1.2578 | 1.2590 | 31 |
| 5 | 0 | 1 | 1.1611 | 1.1612 | 29 |
| 3 | 0 | 7 | 1.1158 | 1.1162 | 39 |
| 4 | 3 | 5 | 1.0950 | 1.0949 | 21 |
| 2 | 9 | 0 | 1.0325 | 1.0322 | 23 |
| 5 | 6 | 4 | 0.8866 | 0.8866 | 27 |
| 4 | 8 | 6 | 0.8129 | 0.8129 | 19 |
| 1 | 11 | 5 | 0.8079 | 0.8079 | 22 |
| 4 | 2 | 10 | 0.7883 | 0.7882 | 18 |

## 3.2. TSL study

Under this study, TSL glow curves of $BaB_4O_7$ sample are recorded for the different times of X-irradiation. The TSL glow curve of $BaB_4O_7$ powder sample was recorded after X-irradiating at room temperature for 1, 2, 3, 4 and 5 min (Fig. 2). The room temperature X-irradiated $BaB_4O_7$ sample when heated at a constant heating rate of 4°C/s exhibit two glow peaks at 110 and 150°C followed by a shoulder around 210°C. The intensity of 150°C glow peak is the strongest. The appearance of different glow peaks indicates that different species of traps are being activated within the particular temperature range, each with its own value of activation energy ($E$) and frequency factor. Moreover the intensities of the glow peaks are found to increase with the increase of X-ray dose.

## 3.3. Trap parameters

Trap parameters such as order of kinetics ($b$), activation energy ($E$) and frequency factor ($s$) are calculated for the 150°C glow peak of $BaB_4O_7$ phosphor using the isothermal luminescence decay method (ILDM).

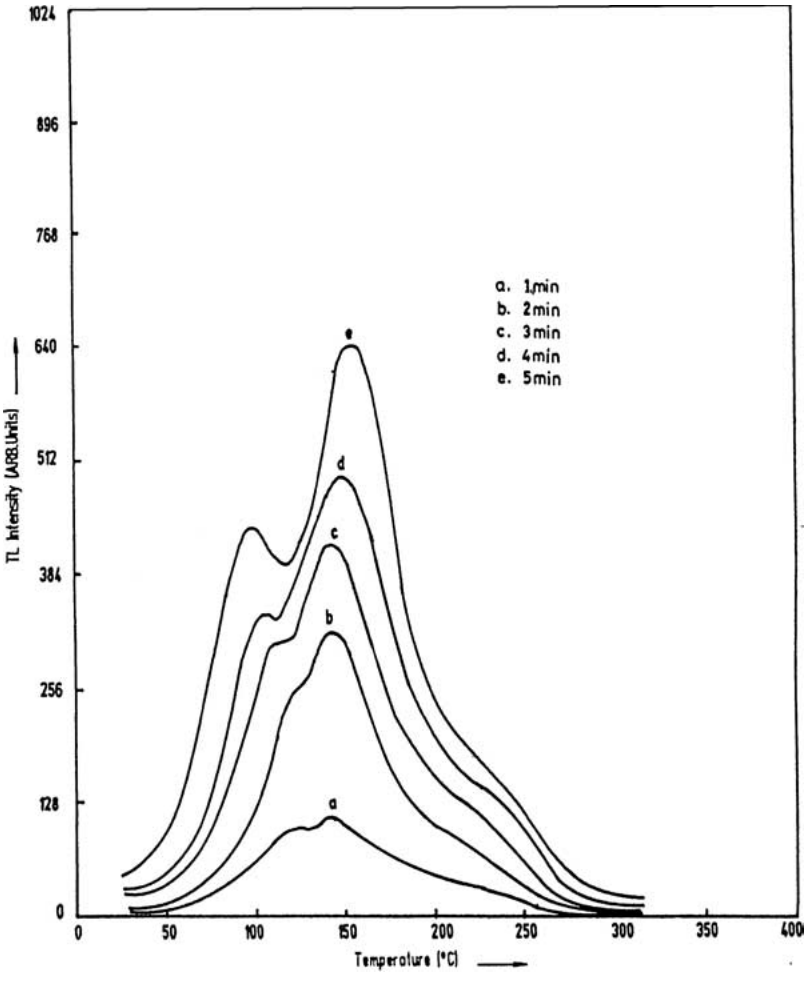


*Figure 2* TSL glow curves of $BaB_4O_7$ sample for different times of X-irradiation.

Amongst the various methods for finding the trapping parameters associated with the TSL glow curves, the isothermal luminescence decay method is the effective, reliable and versatile technique for the evaluation of trapping parameters because there are no prerequisite conditions in this method and can be applied not only for TSL processes involving first and second order kinetics but also for general order kinetics. The theory and experimental details of the method is described elsewhere [9]. As a check the trap parameters are also calculated by glow curve shape (Chen's) method.

### 3.3.1. Isothermal luminescence decay method

The isothermal luminescence decay method is based on recording the decay of luminescence intensity with respect to time at a constant temperature. In this method three temperatures are to be chosen on the rising side of the glow peak whose trapping parameters are to be determined. After irradiating the sample by X-rays or $\gamma$-rays of suitable doses, it is to be heated to one of the chosen temperatures and the decay of luminescence intensity is to be recorded at a constant temperature. This procedure is repeated for other two temperatures. Then experimental data is tested for finding the order of kinetics.

*First order kinetics:*

The TL intensity equation for the first order kinetics is:

$$I = -\left(\frac{\mathrm{d}n}{\mathrm{d}t}\right) = ns \exp\left(-\frac{E}{kT}\right)$$

The solution of intensity equation for the isothermal case:

$$I(t) = n_{\mathrm{o}} s \exp\left(-\frac{E}{kT}\right) \exp\left[-st \exp\left(-\frac{E}{kT}\right)\right]$$

or,

$$\mathrm{Ln}[I(t)] = -\left[s \exp\left(-\frac{E}{kT}\right)\right] t + \left[\mathrm{Ln}\,(n_{\mathrm{o}} s) - \frac{E}{kT}\right] \tag{1}$$

So for the first order case, plot of Ln $[I(t)]$ vs. time should yield a straight line.

*General order kinetics:*

The TL intensity equation for the general order kinetics is:

$$I = -\left(\frac{\mathrm{d}n}{\mathrm{d}t}\right) = s' n^{\mathrm{b}} \exp\left(-\frac{E}{kT}\right)$$

where $s' = \frac{s}{n_o^{b-1}}$ is the pre-exponential factor and $n_o$ is initial concentration of the trapped electrons.

The solution of intensity equation for the isothermal case:

$$\left(\frac{I_o}{I}\right)^{\frac{b-1}{b}} - 1 = s \exp\left[-\frac{E}{kT}\right](b-1)t \qquad (2)$$

so for the general order case, plot of $(I_o/I)^{(b-1)/b} - 1$ vs. time should yield a straight line where $b$ is the order of kinetics ($1 < b \leq 2$), $I_o$ is the intensity at $t = 0$ and $I$ is the intensity at any instant $t$. The experimental data is tested by choosing different test values of $b$, among which the value of $b$ that gives the best fit as straight line gives the order of kinetics ($b$).

The slope of this straight-line Equation 2 is:

$$m = (b-1)s \exp\left(-\frac{E}{kT}\right) \qquad (3)$$

The determination of slope ($m$) of straight line plots of $(I_o/I)^{(b-1)/b} - 1$ vs. time at different temperatures will give the value of frequency factor according to the relation:

$$s = \frac{(m_2)^{\frac{T_2}{T_2-T_1}}}{(b-1)(m_1)^{\frac{T_1}{T_2-T_1}}} \qquad (4)$$

where $m_1$ and $m_2$ are the slopes corresponding to the temperatures $T_1$ and $T_2$ respectively. From Equation 3.

$$\mathrm{Ln}[m(T)] = -\frac{E}{kT} + \mathrm{Ln}[s(b-1)] \qquad (5)$$

Now to find the thermal activation energy ($E$) a graph $\mathrm{Ln}[m(T)]$ vs. $1/T$ was plotted, which was a straight line (Equation 5). The slope $m' = -E/k$ of this straight line graph will give the value of thermal activation energy ($E$).

In order to calculate the trapping parameters corresponding to 150°C glow peak, three temperatures namely 140, 145 and 150°C were chosen and decay of luminescence intensity with time at these temperatures were recorded by X-irradiating the sample for 5 min. The plots of Ln $I$ vs. time were drawn at these temperatures which do not fit into the straight line nature which establish that the glow peak at 150°C does not obey first order kinetics. This indicates that TSL mechanism at this temperature is not associated with first order kinetics. Then plots of $(I_o/I)^{(b-1)/b} - 1$ vs. time were drawn for different values of $b(1 < b \leq 2)$ . The best straight line fitting was obtained for $b = 1.5$ as shown in Fig. 3. This established that 150°C glow peak is associated with general order kinetics ($b = 1.5$). To find the thermal activation energy ($E$), the slopes ($m$) of these straight lines for the temperatures 140, 145 and 150°C were noted and were plotted as Ln ($m$) vs. $1/T$ as shown in Fig. 4 which was a straight line as expected. The activation energy ($E$) was calculated from the slope ($m' = -E/k$) of this straight line and was found to be $0.75 \pm 0.02$ eV. The value of frequency factor ($s$) was found from the slopes of the

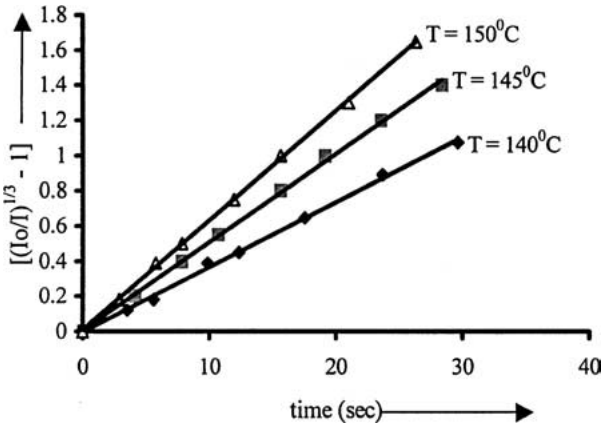


*Figure 3* Isothermal luminescence decay curves of $BaB_4O_7$ sample for 150°C glow peak.

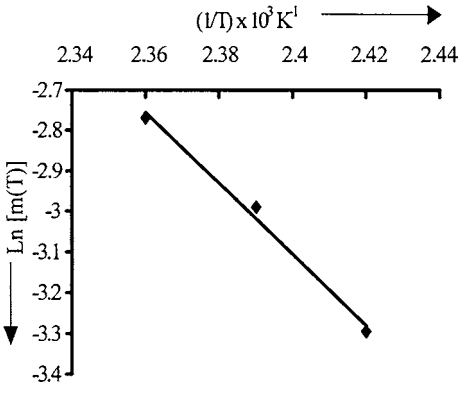


*Figure 4* Plot of Ln [m(T)] vs. 1/T for 150°C glow peak of $BaB_4O_7$ sample.

straight lines of $[(I_o/I)^{1/3} - 1]$ vs. time plots at 140 and 150°C by using the Equation 4 and was found to be $(2.57 \pm 1.00)10^8$ s$^{-1}$.

### 3.3.2. Glow curve shape method

The glow curve shape method proposed by Chen was used to verify the above calculated trapping parameters. The TSL glow curve of $BaB_4O_7$ powder sample, X-irradiated at room temperature for 5 min is shown in the Fig. 5a. In order to calculate the trapping parameters associated with the 150°C glow peak, by glow curve shape method the peak on the low temperature side and the shoulder on the high temperature side with respect to the prominent peak are first to be removed by thermal cleaning technique. For doing this, the sample was X-irradiated and heated upto 180°C and then rapidly cooled to room temperature. Now the TSL glow curve was recorded which exhibited one isolated peak at 210°C. This glow curve was normalized to the required height as shown in the Fig. 5b. Now again the sample was X-irradiated and heated upto 140°C and then rapidly cooled to room temperature. Now the TSL glow curve was recorded which exhibited one peak at 150°C along with one shoulder around 210°C. This glow curve was normalized to the required height as shown in the Fig. 5c. The isolated peak was obtained by substracting the normalized glow curve (Fig. 5b) from the glow curve (Fig. 5c) as shown in Fig. 5d.

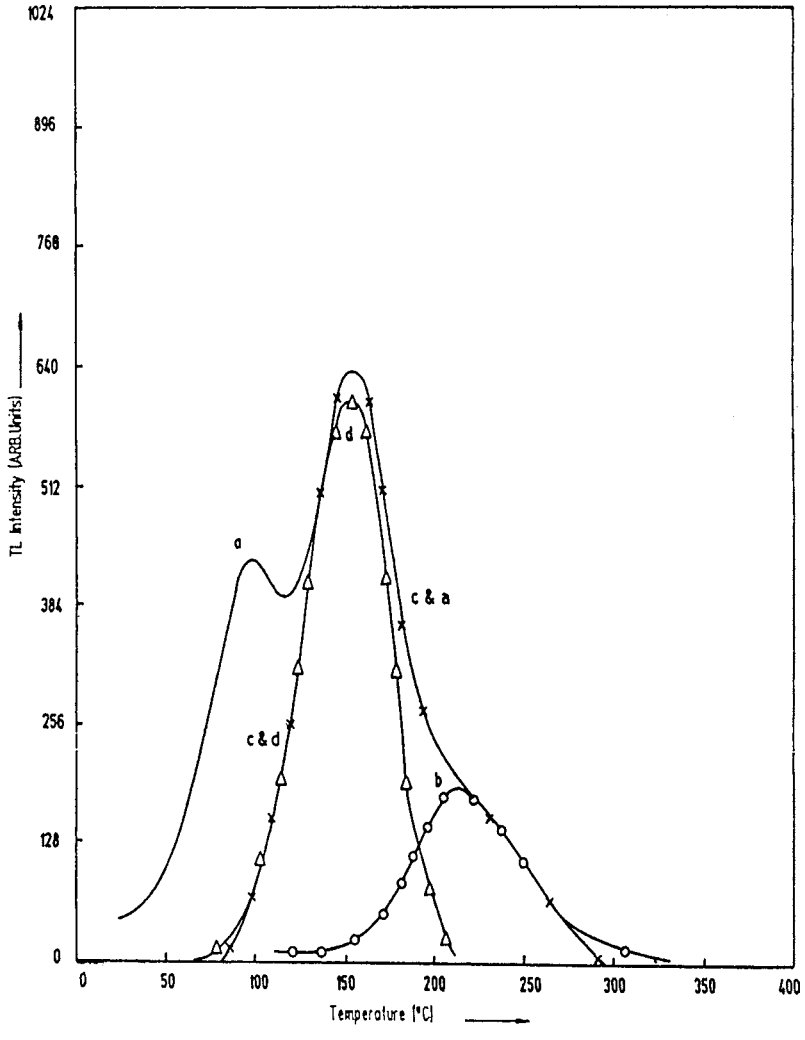


*Figure 5* Isolation of 150°C glow peak of $BaB_4O_7$ sample: (a) TSL glow curve of $BaB_4O_7$ sample for 5 min. X-irradiation (−), (b) Normalized TSL glow curve obtained after heating the $BaB_4O_7$ sample up to 180°C (○), (c) Normalized TSL glow curve obtained after heating the $BaB_4O_7$ sample up to 140°C (×) and (d) Isolated peak obtained after subtracting curve (b) from curve (c) (△).

To determine the trapping parameters associated with the prominent peak (peaking at 150°C) the following shape parameters were determined: the total half intensity with ($\omega = T_2 - T_1$), the high temperature half width ($\delta = T_2 - T_m$), the low temperature half width ($\tau = T_m - T_1$), where $T_m$ is the peak temperature and $T_1$ and $T_2$ are the temperatures on either side of $T_m$ corresponding to half peak intensity.

*Order of kinetics:*

Order of kinetics ($b$) was determined by calculating the symmetry factor ($\mu_g$) of the glow peak from the known values of shape parameters:

$$\mu_g = \delta/\omega = (T_2 - T_m)/(T_2 - T_1) \tag{6}$$

The shape factor ($\mu_g$) for the 150°C glow peak of $BaB_4O_7$ was found to be 0.48 which shows that this peak obeys general order kinetics with $b = 1.5$.

*Activation energy:*

Activation energy ($E$) was calculated by using the Chen's equations [10, 11] which gives the trap depth in terms of $\tau$, $\delta$, $\omega$. A general formula for $E$ was given by:

$$E = c_\gamma(kT_m{}^2/\gamma) - b_\gamma(2kT_m) \tag{7}$$

where $\gamma$ is $\tau$, $\delta$ or $\omega$. The constants $c_\gamma$ and $b_\gamma$ for these equations corresponding to $\tau$, $\delta$ and $\omega$ for general order kinetics are give in Table II.

The activation energy for the 150°C glow peak of $BaB_4O_7$ when calculated by Equations 7 using low temp. half width, high temp. half width and full width of the peak at its half height were found to be $0.74 \pm 0.01$ eV, $0.78 \pm 0.01$ eV and $0.76 \pm 0.01$ eV giving the mean value of activation energy $0.76 \pm 0.01$ eV.

*Frequency factor:*

Once order of kinetics and activation energy were determined, the frequency factor ($s$) was calculated by the equation given by Chen and Winer [12]:

$$qE/kT_m^2 = s[1 + (b-1)2kT_m/E]\exp(-E/kT_m) \tag{8}$$

where $q$ is the heating rate.

TABLE II Values of constants used in Chen's equations for general order kinetics

| $C_\tau$ | $b_\tau$ | $C_\delta$ | $b_\delta$ | $C_\omega$ | $b_\omega$ |
|---|---|---|---|---|---|
| $1.51 + 3(\mu_g - 0.42)$ | $1.58 + 4.2(\mu_g - 0.42)$ | $0.976 + 7.3(\mu_g - 0.42)$ | 0 | $2.52 + 10.2(\mu_g - 0.42)$ | 1.0 |

The frequency factor for the 150°C glow peak of $BaB_4O_7$ when calculated by using Equation 8 was found to be $(1.35 \pm 0.38) \times 10^8\ s^{-1}$.

The values of trapping parameters of the 150°C glow of $BaB_4O_7$ phosphor calculated by isothermal decay method are $b = 1.5$, $E = 0.75 \pm 0.02$ eV and $s = (2.57 \pm 1.00)10^8\ s^{-1}$ whereas the values obtained by Chen's method are $b = 1.5$, $E = 0.76 \pm 0.01$ eV and $s = (1.35 \pm 0.38)10^8\ s^{-1}$. The results shows a very good agreement between the trapping parameters calculated by the two methods and indicates the reliability of two methods and accuracy of the measurement of parameters.

As an extra check of the results, the value of activation energy ($E$) was also obtained by initial rise method. For this, the initial rise portion of the TSL glow curve was considered and a graph was plotted between Ln $I$ and $1/T$, which was a straight line. The value of activation energy was calculated from the slope of this straight-line plot and was found to be $E = 0.62 \pm 0.02$ eV. This method gives only an approximate value of activation energy ($E$) because the numbers of data points in the initial rise range are limited.

## 4. Conclusions

(i) The compound $BaB_4O_7$ has orthorhombic structure at room temperature.

(ii) The TSL glow curve of $BaB_4O_7$ compound when heated at a constant rate of 4°C/s exhibits two glow peaks at 110 and 150°C along with a shoulder around 210°C.

(iii) The prominent glow peak (peaking at 150°C) of $BaB_4O_7$ phosphor is due to the general order kinetics ($b = 1.5$) with an activation energy $E = 0.75 \pm 0.02$ eV and frequency factor $(s) = (2.57 \pm 1.00)10^8\ s^{-1}$.

(iv) The results show that the isothermal luminescence decay method is not only applicable to first and second order kinetics but also to general order kinetics.

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