Thermoluminescence of Li$_2$B$_4$O$_7$:Cu and La

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Computerized Glow Curve Deconvolution (CGCD) in the framework of kinetic formalism and Various Heating Rate (VHR) methods are subjected to the glow curves of Li$_2$B$_4$O$_7$:Cu,La phosphor. It was observed that the trapping parameters obtained by the two methods are similar which is well-supported by statistical analysis. The curves show three peaks with the distribution of trap depth in the range 0.79-1.42 eV.

Keywords: Thermoluminescence, Activation energy, Glow peak, Frequency factor

1 Introduction

Lithium tetraborate (Li$_2$B$_4$O$_7$) is a suitable material for thermoluminescence (TL) dosimetry because of its effective atomic number ($Z_{eff}$) 7.3 is very close to that of human tissue ($Z_{eff} = 7.4$). Lithium tetraborate based TL dosimeters have attracted much attention in radiation dosimetry$^1$ and have been used in research and applications for several decades$^2$. The first TL material based lithium tetraborate which was introduced in radiation dosimetry was Li$_2$B$_4$O$_7$:Mn phosphor$^5$, but it gives low TL sensitivity, caused partly by the emission in the 600 nm region of the spectra, which is far from the ideal wavelength region for most commercial photomultipliers (~ 400 nm). Different methods of preparation of these TL materials have subsequently been developed, but different activators give rather different TL characteristics i.e., glow curves, TL sensitivity, linearity etc.$^6$-$^8$. More recently, sintered Li$_2$B$_4$O$_7$ co-doped with several dopants have been introduced in order to produce TLD materials with better dosimetric characteristics$^9$. In this paper, TL characteristic of lithium tetraborate doped with Cu and La in powder form was presented. The key trapping parameters namely activation energy ($E$) and frequency factor ($s$) relevant to dosimetry in terms of mean life of trap electrons have been retrieved using Computerized Glow Curve Deconvolution (CGCD) and Various Heating Rates (VHR) methods.

CGCD is the curve fitting of TL curves consists of one or more TL peaks. This technique is widely used in various area of TL studies and is well documented$^9$-$^{10}$. The technique is based on Chen’s general order kinetic formalism and has been performed within the framework of kinetic formalism$^{11}$-$^{12}$. VHR method is simple but accountable based on repeated measurement of certain glow curve keeping all the parameters constant as suggested by many researchers$^{13}$-$^{14}$ as early as 1954. Using the maximum condition of the first order kinetic equation$^{15}$, Hoogenstraaten$^{16}$ suggested the calculation of the trapping parameters ‘$E$’ and ‘$s$’ using several linear heating rates. Many researchers have also studied its applicability in other kinetic orders to a very good approximation$^{17}$-$^{18}$. Munish et al.$^{19}$ have also investigated theoretically as well as experimentally the effect of heating rate on the TL glow curves.

2 Materials and Methods

Li$_2$B$_4$O$_7$:Cu,La phosphors were prepared by sintering method$^{20}$ with the addition of CuCl$_2$.2H$_2$O with 0.20 wt% and LaN$_2$O$_3$.6H$_2$O with 0.04%. The mixtures were mixed with acetone then homogenized by stirring for 30 min using a magnetic stirrer with hot plate. Afterwards acetone was allowed to evaporate at ambient temperature in the hot plate. Drying was completed in a laboratory oven at 100°C for 15 h. The dry powder was kept in a quartz crucible and sintered at 800°C for 3 h and rapidly cool down to room temperature in air. The material was then grounded to fine powder and annealed at 525°C for 30 min.
The powder samples were irradiated with γ-ray from $^{60}$Co source at Radiotherapy Department, IMS, Imphal (Manipur) to a dose of 5Gy and recorded the TL glow curves using the commercial PC based TL Reader, Model 1009I (Nucleonix Systems Pvt. Ltd, Hyderabad, India) at Luminescence Dosimetry Laboratory, Thoubal College, Thoubal, (Manipur). The different heating rates used in the present analysis were 0.5, 1.0, 2.0 and 5.0° Cs\(^{-1}\). 20 mg of the sample was used for each TL readout. A second readout was performed to record the background radiation which includes the back body radiation. The data presented are all with the background subtraction.

2.1 Methods of Analysis

2.1.1 Computerized Glow Curve Deconvolution (CGCD)

The model used here for analyzing these TL glow curves assumes a set of discrete electron traps and a set of hole traps (recombination center). All the glow curves of different heating rates are subjected to CGCD in the kinetic formalism. Computing and fitting of the glow peaks following the general order kinetic formalism including the famous first order and second order equation were done from the CGCD program given in the classical text of Chen and Kirsh, the modification incorporated here is the selection of the peak temperature within ± 2°C. The fitting quantity in the program is judged from the minimum value of the root mean square deviations.

In the CGCD program, the general order kinetics for the TL intensity $I(T)$ depending on the absolute temperature $T$ as developed by Chen is given as:

$$I(T) = \frac{dn}{dt} = s' n' \exp(-E/kT)$$

where $s' = s'n'^{b-1}$ is the frequency factor, $n'$ the initial concentration of trapped electrons, $b$ the kinetic order, $E$ the activation energy and $k$ is the Boltzmann’s constant.

For a linear heating profile:

$$T = T_0 + \beta t$$

where $T_0$ is the initial temperature, $T$ the temperature at time $t$ and $\beta$ the linear heating rate.

From Eqs (1) and (2), we get Randall and Wilkins equation ($b = 1$):

$$I(T) = n_s \exp(-E/kT) \times \left[ 1 + \frac{s(b-1)}{\beta} \exp\left(-\frac{E}{kT}\right) \right]^{-\frac{b}{b-1}}$$

with successive integration by parts over a limited number of terms, Chen and Winer approximated the integral as:

$$\int \exp(-E/kT)dT' = \frac{kT^2}{E} \exp\left(-\frac{E}{kT}\right) \left( 1 - 2 \frac{E}{kT} \right)$$

Then, the TL intensity may be written on the general form as:

$$I(T) = I_m b^{-\beta} \exp(E/kT) \left( \frac{T - T_m}{T_m} \right) \left( b - 1 \right) \left( 1 - 2 \frac{E}{kT} \right) \times \frac{T^2}{T_m^2} \exp\left( \frac{E}{kT} \right) \left( \frac{T - T_m}{T_m} \right) + \left[ 1 + \frac{2kT_m(b - 1)}{E} \right]^{-\frac{b}{b-1}}$$

where, $I_m$ and $T_m$ are the maximum intensity and peak temperature, respectively.

And one may deduce the frequency factor $s$ also as:

$$s = \left( \frac{\beta E}{kT_m^2} \right) \left( \frac{1}{1 + \frac{(b - 1)kT_m}{E}} \right) \exp\left( \frac{E}{kT_m} \right)$$

Though Chen’s general order kinetic formalism does permit order of kinetic ‘b’ beyond two (i.e. $b > 2$), but conventional analysis reported in the literature shows $1 \leq b \leq 2$.

The goodness of fit of the measured TL glow curve was again tested using $\chi^2$-test of normality which measure goodness of fit in term of normality of error distribution. As a cross check, Figure of Merit (FOM) was also calculated.

Another important point that has been taken into consideration to avoid errors in the kinetic parameters determination by CGCD is the effective heating rate ($\beta_{eff}$) between the heating element and the thermoluminescent sample during the TL readout in the reader (using contact heating). A simple method of heating correction was used to avoid this problem and determine the exact effective heating rate of the TL sample by using the equation:
\[ \beta_g = \frac{(T_g - T_o - \Delta T)}{(T_g - T_o)} \beta = \frac{(T_m - T_o)}{(T_g - T_o)} \beta \] 

where \( \Delta T = T_g - T_m \), \( T_g \) is the observed peak temperature (K) and \( T_m \) is the real peak temperature (i.e., with thermal lag correction), \( T_o \) is room temperature (25°C).

### 2.2 Various Heating Rate (VHR)

From the maximum condition of the first-order kinetics Eq. (3), that can be written as:

\[ \frac{\beta E}{k T_m^2} = s \exp \left( -\frac{E}{kT_m} \right) \]  

or

\[ \ln \left( \frac{\beta}{T_m^2} \right) = \ln (sk/E) - \frac{E}{kT_m} \]  

The plot of \( \ln \left( \frac{T_m^2}{\beta} \right) \) versus \( \frac{1}{T_m} \) using several linear heating rates in the Eq. (10), which yields a straight line with slope ‘\( E/k \)’, from which \( E \) can be calculated\(^{16} \). The value of ‘\( s \)’ is calculated by extrapolation of the straight line to \( 1/T_m = 0 \). This method is independent of the order of kinetics and applicable for any heating rate\(^{31} \). Similar in the case of CGCD, another very important point that has been taken into account for the evaluation of the trapping parameters by VHR method is the temperature lag between the heating element and the phosphor during the TL readout in reader using contact heating. The thermal lag between the heating element and the phosphor during the TL readout in the reader is calculated by the method developed by Kitis and Tuyn\(^{30} \).

### 3 Results and Discussion

TL glow curves of the \( \text{Li}_2\text{B}_4\text{O}_7\cdot\text{Cu,La} \) phosphor with various heating rates namely 0.5, 1.0, 2.0 and 5.0° Cs\(^{-1} \) are shown in Fig. 1. In all the cases, the glow peak with heating rates \( \beta_j \) and \( \beta_i \), respectively and \( c \) is a constant which is usually evaluated by using two very low heating rates preferably below 1°Cs\(^{-1} \) in which the temperature lag can be considered to be negligible\(^{32} \). In this work, the heating rates 0.5° Cs\(^{-1} \) and 1.0°Cs\(^{-1} \) were used to determine the constant ‘\( c \)’.  

![Fig. 1 — Glow curves of Li\(_2\)B\(_4\)O\(_7\)·Cu,La phosphor with different heating rates (0.5, 1.0, 2.0 and 5° Cs\(^{-1} \))](image)

<table>
<thead>
<tr>
<th>Peak</th>
<th>( T_m ) (°C)</th>
<th>( E ) (eV)</th>
<th>( s ) (s(^{-1} ))</th>
<th>( b )</th>
<th>FOM (%)</th>
<th>( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Heating rate = 0.5° Cs(^{-1} )</td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>I</td>
<td>117.67 ± 2.91</td>
<td>0.79 ± 0.02</td>
<td>(4.75 ±3.17)\times10^8</td>
<td>1.47 ± 0.16</td>
<td>1.63</td>
<td></td>
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<tr>
<td>II</td>
<td>183.20 ± 3.25</td>
<td>0.91 ± 0.00</td>
<td>(2.67±0.50)\times10^8</td>
<td>1.40 ± 0.15</td>
<td>0.99 (d.f =3)</td>
<td></td>
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<tr>
<td>III</td>
<td>288.51 ± 0.20</td>
<td>1.30 ± 0.14</td>
<td>(2.19±1.28)\times10^9</td>
<td>1.43 ± 0.11</td>
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<tr>
<td></td>
<td>Heating rate = 1.0° Cs(^{-1} )</td>
<td></td>
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<tr>
<td>I</td>
<td>125.79 ± 1.45</td>
<td>0.79 ± 0.00</td>
<td>(4.03±1.49)\times10^8</td>
<td>1.39 ± 0.06</td>
<td>3.37</td>
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<td>II</td>
<td>190.70 ± 1.32</td>
<td>0.91 ± 0.02</td>
<td>(5.39±0.54)\times10^8</td>
<td>1.47 ± 0.05</td>
<td>0.83 (d.f =4)</td>
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<td>III</td>
<td>293.60 ± 1.40</td>
<td>1.30 ± 0.01</td>
<td>(1.65±0.21)\times10^10</td>
<td>1.65 ± 0.07</td>
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<tr>
<td></td>
<td>Heating rate = 2.0° Cs(^{-1} )</td>
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<tr>
<td>I</td>
<td>137.63 ± 3.13</td>
<td>0.79 ± 0.00</td>
<td>(5.23±1.02)\times10^8</td>
<td>1.55 ± 0.12</td>
<td>1.51</td>
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<tr>
<td>II</td>
<td>203.12 ± 3.70</td>
<td>0.90 ± 0.00</td>
<td>(3.26±0.48)\times10^9</td>
<td>1.56 ± 0.20</td>
<td>0.85 (d.f = 5)</td>
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<td>III</td>
<td>306.39 ± 0.86</td>
<td>1.21 ± 0.01</td>
<td>(2.83±0.94)\times10^9</td>
<td>1.29 ± 0.05</td>
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<tr>
<td></td>
<td>Heating rate = 5.0° Cs(^{-1} )</td>
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<tr>
<td>I</td>
<td>150.34 ± 3.05</td>
<td>0.79 ± 0.01</td>
<td>(6.01±0.51)\times10^8</td>
<td>2.00 ± 0.01</td>
<td>3.17</td>
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<tr>
<td>II</td>
<td>216.97 ± 3.85</td>
<td>0.89 ± 0.01</td>
<td>(2.94±0.67)\times10^10</td>
<td>1.54 ± 0.05</td>
<td>0.67 (d.f = 4)</td>
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<tr>
<td>III</td>
<td>316.22 ± 1.15</td>
<td>1.40 ± 0.02</td>
<td>(2.16±0.85)\times10^11</td>
<td>1.33 ± 0.07</td>
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Fig. 2 — (a) CGCD of Li₂B₄O₇:Cu,La phosphor, heating rate = 0.5°C s⁻¹
- ooooooooo Experimental curve
- Numerically generated curve
- Sum of the numerically generated best curves
(b) Second derivative plot of the experimental glow curve

Fig. 3 — (a) CGCD of Li₂B₄O₇:Cu,La phosphor, heating rate = 2.0°C s⁻¹
- ooooooooo Experimental curve
- Numerically generated curve
- Sum of the numerically generated best curves
(b) Second derivative plot of the experimental glow curve

Fig. 4 — Plot of ln(T²/β) versus (1/Tₘ) after thermal lag correction of all thermoluminescence glow peaks. Inset: values of E and s
I, II, III corresponds to the 1st, 2nd and 3rd Peak

same pattern of glow curves is observed with a systematic shifting of peak positions from lower to higher temperature region as the heating rates are increased. All the curves show three prominent peaks. These glow curves are subjected to CGCD within the framework of kinetic formalism after thermal correction. These glow curves may be deconvoluted to three constituent peaks. The location of the glow peak temperatures are determined by the minima of the second derivative plot of the curves. The trapping parameters of the analysis are presented in Table 1 and some of the typical fittings along with the 2nd derivative plots of the curves are shown in Figs 2 and 3. The outcome of the analysis shows that the key trapping parameters namely E, s and b are in the physically realistic range and also the fittings are subjected to statistical analysis and found FOM less than 1% and χ²-test passed at 5% level of probability.

The trapping parameters also calculated by using VHR method of Hoogenstraaten which are shown in Fig. 4 for the three constituents peaks. The results of the outcomes compare with the mean values of the
trapping parameters obtained by CGCD, are presented in Table 2. The values of the trapping parameters obtained from CGCD and VHR have similar values indicating the reliability of our result.

4 Conclusions
Glow curves of Li$_2$B$_4$O$_7$:Cu, La follow non-first order kinetics. Trapping parameters obtained by the analysis of the glow curves using two methods namely CGCD and VHR are found to be in agreement with each other with the distribution of trap depths in the range 0.79-1.42 eV and frequency factor $10^8$ to $10^{11}$ s$^{-1}$.

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