Analysis of the thermoluminescent of borate glass by computerized glow curve deconvolution in kinetic formalism

S. Nabadwip Singh
Department of Physics, Oriental College (Autonomous)
Takyel, Imphal-795001, Manipur (India)
E-mail: singhnabadwip@gmail.com

Abstract: Borate based phosphor is a suitable material for thermoluminescence dosimetry. Glow curves of β-irradiated pure borate glass has been analyzed by restoring to Computerized Glow Curve Deconvolution (CGCD) technique and evaluate the trapping parameters namely activation energy (E), frequency factor (s) and order of kinetics (b). It is observed that there are stable peaks in the range 110° to 150°C even to various extent of thermal cleaned ones also. The activation energies of the phosphor are in the range 0.898 to 1.325 eV and frequency factors are in the order of $10^{11}$ to $10^{13}$ s$^{-1}$.

1. Introduction

The phenomenon of thermoluminescence (TL) is the emission of light during the heating of preirradiated material due to the released of initially trapped electrons from the defect centers or trap centers in the material [1]. Among the several methods that have been developed for analyzing TL glow curves, Computerized Glow Curve Deconvolution (CGCD) becomes one of the important methods for decoding trapping parameters in the kinetic formalism [2-3]. The CGCD technique based on Chen’s General Order Kinetic formalism becomes the most rigorous method for TL glow curves fitting consisting of one or more TL peaks. This method is well documented and widely used in the analysis of various area of thermoluminescence [4-7]. Not only this method provides the mathematical description of the TL phenomenon, but it can describe the experimental glow curves with reasonable degree of confidence and retrieves the key trapping parameters namely the activation energy (E), the frequency factor (s) and order of kinetics (b) of the glow curve. The fitting of the glow curve by this technique has been generalised to fit the entire glow curve and the location of glow peak temperature was guided by the minima of the second order derivative plot of the glow curve [8]

Even the traps are not discrete in the cases of non-crystalline materials, rather they follow some form of distribution. However, the distributed traps become nearly discrete allowing the use of the technique under thermal cleaning (Tc) more than the peak temperature [9]. On the similar grounds Singh et. al., [10] evaluate the trapping parameters from a variety of glow curves of post irradiated thermally cleaned Cu-doped borate glass (a typical non-crystalline material) and shows that the distribution of traps in borate glass is exponential. With this background in mind CGCD in kinetic formalism was applied to TL glow curves pure borate glass measured after the irradiation of β-ray to evaluate the key trapping parameters E, s and b. The goodness of fit was tested using standard statistical tests i.e., Chi – square ($\chi^2$) test of normality [11-12] which measures the goodness of fit in terms of normalcy of error distribution. Figure of Merit (FOM) [13] also evaluated for cross check of the goodness of fit.

Borate based phosphor as having their effective atomic number is much closed to effective atomic number of human tissue ($Z_{eff} = 7.42$), become a suitable material in the field of radiation dosimetry and
due to this property attract the attention of many researchers to the study of borate-based TL phosphor. Because of peculiarities of their structure these phosphors have been the subjected to numerous infrared studies [14-15]. This phosphor is also relatively stable compound and can easily doped with the TL sensitive elements like copper or manganese ions [6].

2. Experiment

The chemical composition of borax is NaB$_4$O$_7$.10H$_2$O, which on heating released water molecules present in it and borate glass of composition of 69.2 wt% B$_2$O$_3$ and 30.8 wt% Na$_2$O was obtained. The phosphor used in this analysis is in the form of circular pellets of diameter ~ 4 mm and thickness ~ 1mm. These phosphors were first heated to a temperature ~ 500°C in order to erase any pre dose radiation absorbed by the material. Then the glow curves of the phosphor after the irradiation of β-ray to different doses 10, 20, 40, 60, 80 and 100Gy were measured with a uniform heating rate of 5°C/s using a commercial Risø TL/OSL (Model TL/OSL –DA-15) reader [16] in the flowing Nitrogen atmosphere at Luminescence Dating Laboratory, Manipur University. This TL/OSL reader has inbuilt Sr-90 source facility and the strength of the source at the time of irradiation of the phosphor is 0.83Gy/s. The use of optical filter Schott UG-11 in conjunction with Schott BG-39 filtered out the unwanted radiation and allowed the transmission in the wavelength 300 ~ 400 nm range to the EMI 9635 photomultiplier tube in the operating voltage of 950 volts of the reader.

Measurements were also taken at two low heating rates viz. 0.5 and 1°C/s for the calculation of the effective heating rate. The glow curves of phosphor irradiation at 100 Gy were also recorded at the heating rate 2°C/s after various extents of thermal cleaning at 80, 100, 110, 120, 130 and 140°C. To remove the back ground radiation including the black body radiation, a second read out of each glow curve was also measured. All the presented data in this work were subtracted their background radiation.

3. Results and Discussion

Thermoluminescence glow curves of pure borate glass measured after the irradiation of β-ray at various doses at a constant heating rate of 5°C/s are presented in Figure 1. The glow curves are appeared to be a single broad peak is at around 110°C with a systematic increase of peak temperature from 108° to 116° with the increase of dose of radiation.

Figure 1. Glow curves of pure borate glass with different doses of β-radiation with constant heating rate (5°C/s) (Curves a, b, c, d, e and f corresponds to the curves of 100, 80, 60, 40, 20, 10 Gy irradiation)

Figure 2. Dose Response curve of pure borate glass
The dose response curve (DRC) of the material shows a linear behaviour at lower doses but has tendency of saturation at higher doses which is presented in Figure 2. The peak parameters of the glow curves are presented in Table 1.

Table 1. Peak parameter of the glow curves of pure borate glass with different doses of β-irradiation.

| Dose of irradiation (Gy) | \(T_m\) (°C) | \(\omega = (T_2 - T_1)\) (°C) | \(\mu_g = \delta / \omega\) | \(I_m\) | Area (25-400°C) |
|-------------------------|-------------|-----------------|------------------|------|----------------|
| 10                      | 111         | 60              | 0.567            | 5605 | 381729         |
| 20                      | 112         | 58              | 0.569            | 10609| 731261         |
| 40                      | 113         | 58              | 0.586            | 19096| 1316420        |
| 60                      | 114         | 60              | 0.583            | 26471| 1866540        |
| 80                      | 115         | 60              | 0.600            | 34908| 2568690        |
| 100                     | 117         | 62              | 0.581            | 43635| 3210880        |

The shape factor \(\mu_g\) is given by

\[
\mu_g = \frac{T_2 - T_m}{T_2 - T_1}
\]

where \(T_m\) is the peak temperature and \(T_1\) and \(T_2\) are the temperatures at half of maximum intensity on the rising and falling sides of the peak. The values of shape factor are in the range 0.58 – 0.60, indicating that the peaks follow second order kinetics [17].

The phosphor irradiated at 100 Gy was subjected to various extent of thermal cleaning and measured their corresponding glow curves at a constant heating rate 2°C/s which are presented in Figure 3. Even thermal cleaning up to 140°C cannot erase all the peaks between 110° to 150°C. It means that there are stable dosimetric peaks in this region. A plot of \(T_m \sim T_{stop}\) produces a linear straight line (inset Figure 3) with a slope of 0.77, which shows that the glow peaks are closely overlapped or follow a quasi-continuous distribution [18].

Figure 3. TL curves of β-irradiated (100Gy) pure borate glass without Tc and with Tc at different temperature. (Heating rate = 2°C/s).

Inset show \(T_{stop} \sim T_m\) plot.
After the correction of heating rate following the work of Kitis and his Co-workers [19], the glow curves measured at different doses of irradiation of β-ray were subjected to CGCD in the kinetic formalism assuming the peaks are single peak. The outcomes of the deconvolution are presented in Table 2 and Figure 4 (a) and 4 (b) shows some of the fitted curves.

Table 2. Outcome of the CGCD of the pure borate glass (assuming the peaks are single peak).

| Dose (Gy) | $T_m$ (°C) | E (eV) | b | $s$ (s$^{-1}$) | FOM (%) | $\chi^2$-calculated value (d. f.) |
|-----------|------------|--------|---|--------------|---------|-----------------------------------|
| 10        | 110.80     | 0.88   | 2.09 | $2.22 \times 10^{11}$ | 1.97    | 8.00* (2)                         |
| 20        | 112.12     | 0.91   | 2.72 | $0.45 \times 10^{11}$ | 2.40    | 10.27 (2)                         |
| 40        | 114.21     | 0.85   | 2.55 | $0.75 \times 10^{10}$ | 1.65    | 8.51 (3)                          |
| 60        | 114.81     | 0.90   | 3.01 | $0.19 \times 10^{11}$ | 2.36    | 9.88 (2)                          |
| 80        | 116.03     | 0.87   | 2.75 | $0.97 \times 10^{10}$ | 1.98    | 9.65 (1)                          |
| 100       | 118.01     | 0.91   | 3.21 | $1.57 \times 10^{11}$ | 2.04    | 22.81 (3)                         |

* pass at 1% level of probability.

The outcome of the deconvolution shows that even the fittings seem acceptable from the point of FOM values and at least two from $\chi^2$ values (10Gy) but the value of order of kinetics >2 which has no physical significance [6]. The outcome of the deconvolution shows that the glow curves of borate glass seem to be a single peak, but they consist of multiple peaks [4].
The glow curves irradiated at different doses are again subjected to CGCD in kinetic formalism assuming that the curves are multi-peak system. The outcome of the deconvolution shows that all the glow curves are the combination of four constituent peaks and some of the fittings are presented in Figure 5(a) and 5(b). In the deconvolution, the glow peak temperatures were located by the minima of second order derivative plot of the glow curves [8].

![Figure 5. Fitted curves β-radiated pure borate glass by CGCD method in the kinetic formalism (a) 100 Gy β-radiated curve (b) 20 Gy β-radiated curve. ooooo is the experimental curve, ——— is the numerically generated total best fit curve.](image)

The trapping parameters (mean values) obtained during the deconvolution of the curves with different doses of irradiation are presented in Table 3. The outcome of the analysis shows that the key trapping parameters namely activation energy (E), frequency factor (s) and order of kinetic (b) are in the physically realistic range.

| Glow Peak | $T_m$ (°C) ± s.d | E (eV) ± s.d | s(s$^{-1}$) ± s.d | b ± s.d |
|-----------|-----------------|-------------|-----------------|--------|
| I         | 107.5 ± 1.9     | 0.898 ± 0.015 | (1.80 ± 0.92)$\times10^{11}$ | 1.678 ± 0.057 |
| II        | 136.8 ± 2.5     | 1.075 ± 0.029 | (6.42 ± 0.69)$\times10^{12}$ | 1.650 ± 0.238 |
| III       | 169.5 ± 4.1     | 1.248 ± 0.021 | (5.91 ± 1.30)$\times10^{13}$ | 1.538 ± 0.0131 |
| IV        | 208.8 ± 2.8     | 1.325 ± 0.017 | (2.82 ± 0.83)$\times10^{13}$ | 1.998 ± 0.005 |

The fitting also subjected to statistical analysis to test the goodness of fit and found $\chi^2$-test passed at 5% level of probability for all the curves and the value of FOM less than 1.3%. From the deconvolution of the glow curves of borate glass by CGCD in kinetic formalism and thermally cleaned glow curves it infers that with or without thermal cleaning there is stable peaks in the range 110° to 150°C.
4. Conclusion

The intense peak temperature of TL glow curves of borate glass is around 110°C, when the glow curves were analyzed by CGCD in kinetic formalism found that they have four constitutes peaks. There are stable peaks in the range 110° to 150°C with trapping levels distributed in the range 0.896 to 1.325 eV with realistic values of frequency factor in the range $10^{11} \leq s \leq 10^{13}$ s$^{-1}$.

Acknowledgement

The author is thankful to Prof. R.K. Gartia, Department of Physics, Manipur University, Imphal for suggesting this work and for allowing to take all the measurements in his Luminescence Dating Laboratory.

References

[1] Chen R and Kirsh Y 1981 *Analysis of Thermally Stimulated Processes* (Pergamon Press, London, U.K.)
[2] Randall J T and Wilkins M H F 1945b *Proc. Roy. Soc. London*. A184 p366
[3] Garlick G F J and Gibson A F 1948 *Proc. Phys. Soc. 60* p 574
[4] Horowitx Y S and Yossian D 1995 *Radiat. Prot. Dosim. 60(1)* p 3
[5] Gartia R K and Singh S D 1993 *Physica Status Solidi (a)* 135 (2) p 83
[6] McKeever S W S, Moscovitch M and Townsend P D 1995 *Thermoluminescence Dosimetry: Properties and Uses* (Ashford, England; Nucl. Tech. Publ)
[7] Sharma B A, Singh A N, Singh, S N and Singh O B 2009 *Radiation Measurement*. 44 p32
[8] Singh B Th 2001 *Indian J. of Phys*. A75(3) p 229
[9] Gartia R K and Singh S N 2000 *Int. Symposium of Luminescence & its Application* (eds) T.R. Joshi et al (Baroda, India), Vol TL-3 p15.
[10] Singh S N, Sharma B A, Gartia R K and Singh A N 2004 *Indian J. Pure & Appl. Phys. 42* p 886
[11] Spigel M R 1980 *Schaum’s Outline of Theory and Problem of Probability and Statistics SI (Metric)* (Mc Graw Hills Inc. Singapore) pp. 347.
[12] Sharma B A, Singh T B and Gartia R K 2004 *Indian J Pure & Appl. Phys. 43* p 492
[13] Misra S K and Eddy N W 1979 *Nucl. Instrum Meth*. 166 p 537
[14] Wang J and Angell C A 1976 Glass *structure by spectroscopy* (New York: Dekker) Ch 7
[15] Kitis G and Tuyn J W N 1998 *J. Phys. Chem. Glasses*. 30 p 19
[16] Bøtter-Jensen L 1997 *Radiat. Meas. 27* p 749
[17] Halperin A and Briner A A 1960 *Phys. Rev. 117* p 408
[18] Mckeever S W S 1980 *Phy. Stat. Sol (a). 62* p 331
[19] Kitis G and Tuyn J W N 1998 *J. Phys. D: Appl. Phys. 31* p 2065