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Energy storage behaviour of some binary alkali borate glasses by thermoluminescence studies

RITA NASIPURI, H. D. BANERJEE, A. PAUL
Materials Science Centre, Indian Institute of Technology, Kharagpur 721302, India

Thermoluminescence behaviour of a series of binary alkali borate glasses has been investigated to study their energy storage mechanism. Sodium borate glasses of varying composition have been prepared and their glow curves recorded after exposing them to X-rays (Cu$K\alpha$ radiation, 30 kV, 10 mA) of different dosages at room temperature. The effect of the nature and concentration of alkali oxide and the dose of irradiation on the nature of thermoluminescent glow curves were also studied. Borate glasses containing different concentrations of Na_2O exhibit significantly different glow curves. These glow curves have been analysed and the nature of traps responsible for TL emission are tentatively identified. The broad and complex nature of the glow pattern is attributed to distribution of trap depths in these materials. The viability of borate glasses in the construction of TL dosimeters are discussed.

1. Introduction

High energy radiations are known to interact with oxide glasses causing electronic and/or ionic displacements [1–6]. These induced imperfections in glass are commonly known as 'colour centres'. An electron excited by high-energy radiation may either:

(a) recombine with its original centre giving fluorescence emission, (however, in most of the cases non-radiative modes of recombination are also possible); or

(b) it can fall into a trap existing within the glass structure; it will escape from the trap when sufficient energy to overcome the activation barrier is available, and then recombine with an empty centre giving phosphorescence emission. The thermal activation energy required to liberate a trapped electron is called 'trap depth'.

During the last few years much work has been reported on electroluminescent phosphors, LED materials and other semiconducting/luminescent materials for opto-electronic displays. It is known that radiation-induced traps (both electron and hole type) play a very important role in controlling various physical properties of these materials [7]. The present report, which forms a part of the programme for the development of luminescent glassy materials, deals with the energy-storage properties of some binary alkali borate glasses studied using X-rays as the source of excitation with a view to assessing their viability in the construction of thermoluminescent dosimeters. The information regarding trap depths and trap sites, which will emerge from these studies, will also help in the better understanding of the structure of these glasses. In the present investigation, the effects of the nature and concentration of alkali oxide and the dose of irradiation on the nature of thermoluminescence glow curves were studied.

2. Experimental details

Binary alkali borate glasses (compositions given in Table I) were prepared with AnalaR grade chemicals. Calculated amounts of orthoboric acid (H_3BO_3) and the corresponding carbonate were accurately weighed and thoroughly mixed in a platinum crucible. The mixture was then melted in an electric furnace at 1000° C for about 1 h. The melt was cast into a rectangular brass mould and

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TABLE I Composition of glasses

Glass no.	Target composition (from batch) (mol%)		Actual composition (from analysis) (mol%)	
	Na_2O	B_2O_3	Na_2O	B_2O_3
1	–	100.00	–	100.00
2	10.00	90.00	10.14	89.86
3	16.00	84.00	15.99	84.01
4	20.00	80.00	20.56	79.44
5	25.00	75.00	25.50	74.50
6	33.33	66.67	33.10	66.90
7	20.00 (K_2O)	80.00	18.75 (K_2O)	81.25
8	20.00 (Li_2O)	80.00	19.46 (Li_2O)	80.54

annealed at appropriate temperatures to remove strain. These glasses were cut into pieces (5 mm × 5 mm × 2 mm) and polished for thermoluminescence measurement. Precautionary measures were taken to avoid contamination during melting and polishing of the samples. Alkali oxide and boric oxide contents of all the glasses were chemically estimated with conventional acid base titrations.

Suitably shaped samples were exposed to X-rays (Cu*Kα* radiation, 30 kV, 10 mA) at room temperature for different lengths of time. The distance between the target of the X-ray tube and the sample was kept constant (1.0 cm) during every exposure. After irradiation, the sample was rigidly fixed to a sample holder inside a vacuum chamber (10^{-3} Torr) and the light emitted by the material under a constant rate of heating ($28 \pm 1°\,C\,min^{-1}$) was recorded using a RCA 1P28 photomultiplier tube as the detecting device in conjunction with an ECIL EA812 electrometer amplifier and two millivolt recorders. A block diagram of the experimental apparatus is given in Fig. 1.

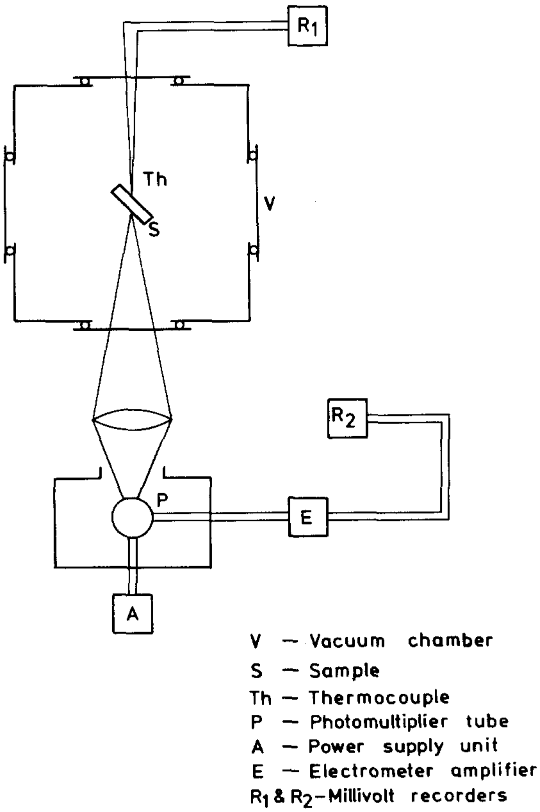

Figure 1 Schematic diagram of the experimental apparatus for studying the thermoluminescence of glass.

The thermoluminescent emission from the samples could be recorded only after 10 min X-ray irradiation, as this length of time has generally elapsed in transferring the samples from the irradiation spot and evacuating the vacuum chamber. The temperature of the sample during heating is measured using a copper–constantan thermocouple. To check the reproducibility of the results, several samples of the glass specimens were studied; even after repeated cycles of irradiation and heating they showed identical emission patterns. The thermoluminescence could be measured with good precision by operating the amplifier in its sensitive range (10^{-9} A).

3. Results and discussion

The thermoluminescence measurement with a constant rate of heating gives information regarding nature of defect centres and relative depths of trap formed by irradiation. Thermoluminescence results from the recombination of thermally released electrons with the holes. The glow curves give information about the thermal stability of traps. The trap depth, E (in electron volts), can be calculated using the Urbach relation [8]:

$$E = T/500$$

where T is the absolute temperature at which the thermoluminescence emission is maximum.

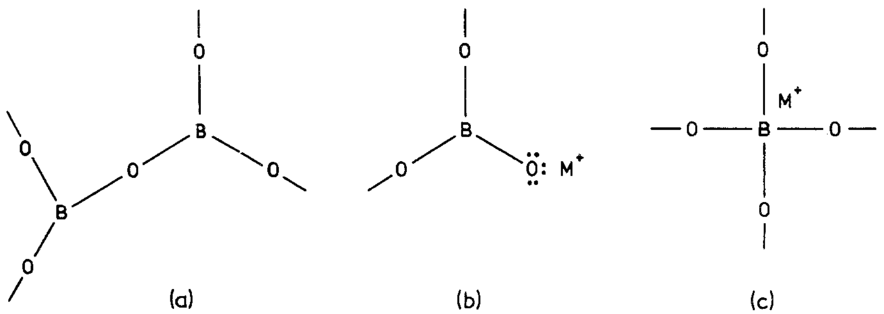

Figure 2 Three types of major structural groupings in alkali borate glasses: (a) each boron atom triangularly co-ordinated with three bridging oxygen atoms; (b) a boron atom triangularly co-ordinated with a mixture of bridging and non-bridging oxygen atoms; (c) a boron atom tetrahedrally co-ordinated with four bridging oxygen atoms.

It is generally accepted from X-ray [9–17], infra-red [18–21], and NMR [22–25] studies that in alkali borate glasses the mean co-ordination number of boron increases from 3 to 4 with the increase of alkali oxide concentration up to a limit of about 33 mol% alkali oxide, and then decreases again with further addition of alkali oxide. In alkali borate glasses, the presence of three types of major structural groupings have been suggested [15]:

(1) each boron atom being triangularly co-ordinated with three bridging oxygen atoms (Fig. 2a);

(2) a boron atom triangularly co-ordinated with a mixture of bridging and non-bridging oxygen atoms (Fig. 2b), and

(3) a boron atom tetrahedrally co-ordinated with four bridging oxygen atoms (Fig. 2c).

The amount of each type of structural unit in a particular glass depends on the concentration and nature of the alkali ion in it. Upon irradiation, defect centres are formed into these structural units. Beekenkamp [26] studied the optical absorption and ESR spectra of radiation-induced defect centres in different alkali borate glasses. He also tried to establish the structure of defect centres derived from these building units and consistent with optical and ESR data.

3.1. Effect of time of irradiation on the thermoluminescence glow curve

Two glasses of molar compositions: $Na_2O \cdot 9B_2O_3$ and $Na_2O \cdot 2B_2O_3$ were irradiated with X-rays (Cu*Kα*) for varying lengths of time (5 to 60 min) at room temperature. The TL glow curves of these samples are shown in Figs. 3 and 4. The time of irradiation (dose) significantly alters the thermoluminescence spectrum in both the glasses. Two broad asymmetric TL bands were obtained; in the case of $Na_2O \cdot 2B_2O_3$ glass the high temperature band is considerably overlapped by another suspected band/bands at higher temperatures. Since the high temperature band of $Na_2O \cdot 9B_2O_3$ glass occurs around 280° C (compared to 310° C in the case of $Na_2O \cdot 2B_2O_3$ glass) the overlap of the unidentified high-temperature emission on band-II (high-temperature TL band) is not significant. Both the TL bands in all the glasses are highly asymmetric indicating the presence of a number of component bands hidden under these envelopes. In this complicated situation, identification of true peak temperature and its shift, if any, with the dose of irradiation cannot be satis-

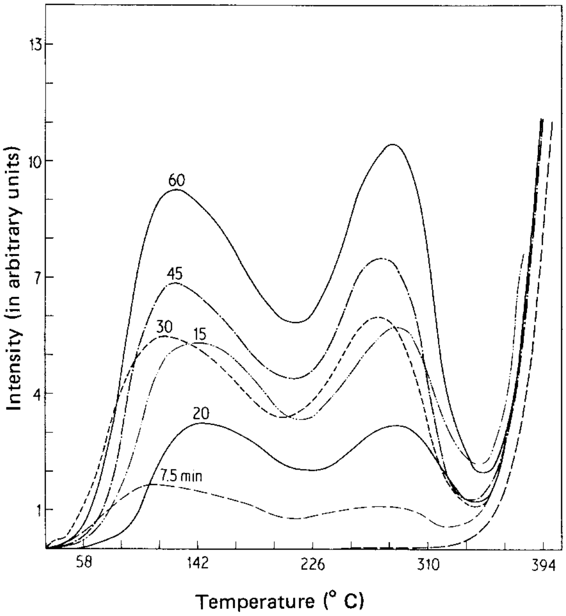

Figure 3 Thermoluminescence glow curves of sodium borate glass ($Na_2O \cdot 9B_2O_3$) after different times of irradiation as indicated in the figure.

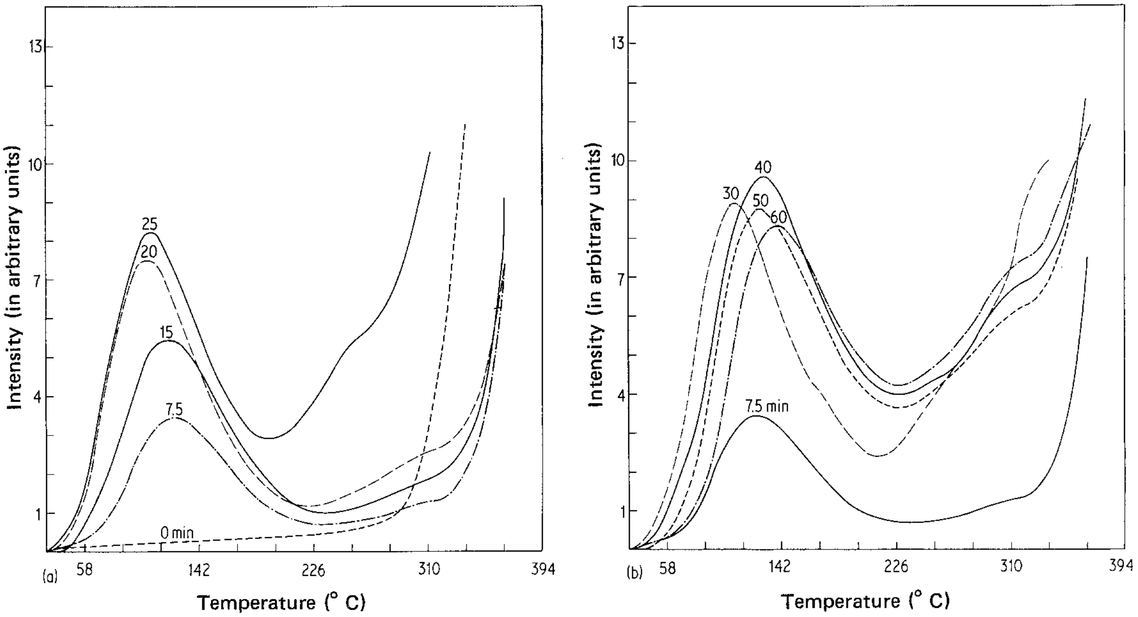

Figure 4 Thermoluminescence glow curves of sodium borate glass ($Na_2O \cdot 2B_2O_3$) after different times of irradiation as indicated in the figure.

factorily made. However, looking at the spectra it can be qualitatively deduced that under the envelope of band I at least two bands exist and the relative intensity of both these component bands change with the dose of irradiation. That is why when the dose of irradiation was gradually increased the apparent band maximum shifted to slightly higher temperatures. In the case of $Na_2O \cdot 9B_2O_3$ glass the high-temperature band (where it is reasonably pure) does not show any significant change in peak temperature or half-width of the band as the dose of irradiation increases. For quantitative analysis of the problem (number of TL bands and their intensities with different doses of irradiation) a computer technique for curve analysis is under development.

3.2. Effect of concentration of the alkali oxide on thermoluminescence glow curves

The TL spectra of a series of sodium borate glasses having different concentrations of soda are shown in Fig. 5. All these glasses were irradiated for a constant time of 25 min with Cu*Kα* X-rays. Unlike the reported optical and ESR spectra of radiation-induced colour centres [7], the TL spectra change very significantly with increasing alkali oxide concentration in these glasses. In the case of pure boric oxide glass two TL bands of nearly equal intensity are obtained having glow maxima around 74 and 150° C. As the soda content increases the intensity of both these bands increases. However, the increase of the low-temperature band supersedes that of the band around 150° C. As soda is added to boric oxide glass a number of extra TL bands also appear around 250 and 300° C. The intensity of all these extra bands also increases with increasing soda content of the glass, although

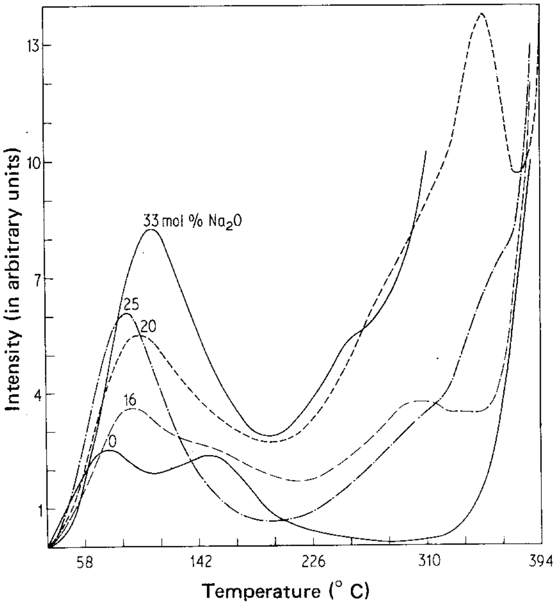

Figure 5 Thermoluminescence glow curves of a series of sodium borate glasses having different concentrations of soda.

the intensity of individual bands under the envelope does not seem to increase at equal rate. Thus the shape and apparent band maxima change in an unsystematic way with increasing soda content of the glass. For satisfactory correlation, as discussed previously, a complete band analysis is yet to be made.

3.3. Effect of the nature of the alkali ion on thermoluminescence glow curves

Fig. 6 shows the TL spectra of a lithium borate, a sodium borate and a potassium borate glass all containing 20 mol % alkali oxide and irradiated for a constant time of 25 min. The TL spectra change dramatically with the nature of alkali ion in these glasses. The apparent TL glow maximum of band I (low-temperature band) shifts to lower temperature with increasing size of the alkali ion. This shift of band maximum may be due to a difference in trap depth caused by the alkali ions in these glasses or may be due to formation of different kinds of defect centres giving TL bands hidden under the same envelope, the relative concentration of which changes with the nature of alkali ion. There appears to be a good correlation between the peak temperature of band I and the ionic potential of the alkali ions. However, before a satisfactory band resolution technique is developed and the relative intensity and temperature of occurrence of the component bands are established, this type of correlation is not expected to produce any meaningful conclusion. The position of the high-temperature band (band II) does not appear to have any straightforward relation with the size of the alkali ion.

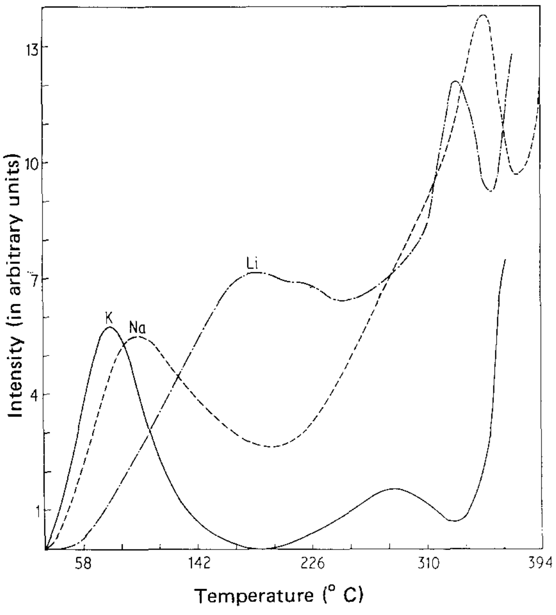

Figure 6 The glow curves of a lithium borate, a sodium borate and a potassium borate glass, all containing ~ 20 mol% alkali oxide and irradiated for a constant time of 25 min by X-rays (Cu$K\alpha$, 30 kV, 10 mA) at room temperature.

4. Conclusions

A material exhibiting a reproducible single glow peak at a reasonably high temperature is ideal for TL dosimetry work. The thermoluminescence given by glasses of the present investigation is reproducible; isolated single glow peaks are obtained in the case of low-alkali borate glasses. However, the TL output is much weaker compared to commercial phosphors.

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