TL Properties of X-ray Irradiated Li$_2$O-MO-B$_2$O$_3$ (MO=ZnO, CaO, CdO) Glasses Doped with Europium Ions

J. Anjaiah$^{1,2}$

$^1$Department of Physics, The University of Dodoma, Tanzania, East Africa
$^2$Department of Physics, Geethanjali College of Engineering & Technology, Keesara, RR Dist. TS, 501301, India

Abstract: Thermoluminescence (TL) characteristics of X-ray irradiated pure and doped with Eu$^{3+}$ ions Li$_2$O-MO-B$_2$O$_3$ (MO=ZnO, CaO, CdO) glasses have been studied in the temperature range 303-573K; all the pure glasses have exhibited single TL peak at 382K, 424K and 466 K respectively. When these glasses are doped with Eu$^{3+}$ ions no additional peaks are observed but the glow peak temperature of the existing glow peak shifted gradually towards higher temperatures with gain in intensity of TL light output. The area under the glow curve is found to be maximum for Eu$^{3+}$ doped glasses mixed with cadmium oxide as modifier. The trap depth parameters associated with the observed TL peaks have been evaluated using Chen’s formulae. The possible use of these glasses in radiation dosimetry has been described. The result clearly showed that europium doped cadmium borate glass has a potential to be considered as the thermoluminescence dosimeter.

Keywords: Infrared spectra, Thermoluminescence, Borate glasses, Europium

1. Introduction

Thermoluminescence is the phenomenon of emission of light from a solid which has been previously exposed to ionizing radiation under conditions of increasing temperature. Oxylithiumborate glasses are considered as good materials for dosimetry applications since they are relatively moisture resistant when compared with the pure borate glasses. The understanding of the glass structure by detailed studies on radiation induced defect centres has been an interesting subject of investigation in recent years. Recently some recommendable work has done on thermoluminescence mechanisms in borate based glasses. The influence of induced structural changes on thermoluminescence characteristics of $\gamma$-ray irradiated PbO-Al$_2$O$_3$-SiO$_2$: a Dy$^{3+}$ glass is reported by Sundara Rao et al. [1]. Thermoluminescence study of MnO doped borophosphate glass samples for radiation dosimetry is reported by Swamy et al. [2] and Rojas et al. reported the structural, thermal and optical properties of CaBO and CaLiBO glasses doped with Eu$^{3+}$ [3]. Thermoluminescence properties of CaO-B$_2$O$_3$ glass system doped with GeO$_2$ reported by Tengku Kamarul Bahri et al. [4]. Haydar Aboud et al. reported the thermoluminescence properties of the Cu-doped lithium potassium borate glass [5].

It is well known that boric acid (B$_2$O$_3$) is one of the good glass formers and can form glass alone with good transparency, high chemical durability, thermal stability and good rare-earth ion solubility [6]. The glass containing Li$_2$O as network modifier was seen as bubble free, highly stable and moisture resistant, suitable for a systematic analysis [7]. Among the three modifier oxides chosen to mix in the present glass system, viz., CaO, ZnO and CdO; ZnO is expected to shorten the time taken for solidification of glasses during the quenching process and glasses containing ZnO have high chemical stability and less thermal expansion. Their wide band gap, large exciton binding energy and intrinsic emitting property make them as promising candidate for the development of optoelectronic devices, solar energy concentrators, ultraviolet emitting lasers and gas sensors [8]. Both ZnO and CdO are thermally stable and appreciably covalent in character [9].

Lithium tetraborate glass system is a known and important starting material in the development of applications of radiation dosimetry for a long period, since its effective atomic number $Z_{\text{eff}} \approx 7.25$ has the property of being nearly tissue equivalent that makes it as a very promising material in the field of personal and clinical dosimetry and for other applications like X-ray phosphors, scintillators and thermoluminescent detectors [2,10-13]. However, pure borate glasses have certain disadvantages to use in radiation dosimetry since they are highly hygroscopic and exhibit weak glow peak at relatively low temperatures.

Schulman et al. [14] were the first to be acknowledged for starting the TL studies on lithium borate compounds and since then various details on TL studies of alkali and alkaline earth tetra borates continued up to present times especially on magnesium and lithium borate compounds. Several attempts were also made to enhance thermoluminescence sensitivity of these glass materials by adding different transition and rare earth or lanthanide metal ions to these glass samples [15-20].

The study on the influence of europium ions on thermoluminescence light output of these glasses is also carried out with a view to examine the suitability of these glasses in the radiation dosimetry.
2. Experimental Methods

Undoped and following europium ion doped glasses in mole% are prepared by using standard melting and quenching techniques and used for the present study [21-23].

\[
\begin{align*}
\text{ZnB} & : 30 \text{Li}_2\text{O}-10 \text{ZnO}-60 \text{B}_2\text{O}_3, \\
\text{ZnBEu} & : 30 \text{Li}_2\text{O}-10 \text{ZnO}-59 \text{B}_2\text{O}_3:1\text{Eu}_2\text{O}_3, \\
\text{CaB} & : 30 \text{Li}_2\text{O}-10 \text{CaO}-60 \text{B}_2\text{O}_3, \\
\text{CaBEu} & : 30 \text{Li}_2\text{O}-10 \text{CaO}-59 \text{B}_2\text{O}_3:1\text{Eu}_2\text{O}_3, \\
\text{CdB} & : 30 \text{Li}_2\text{O}-10 \text{CdO}-60 \text{B}_2\text{O}_3, \text{and} \\
\text{CdBEu} & : 30 \text{Li}_2\text{O}-10 \text{CdO}-69 \text{B}_2\text{O}_3:1\text{Eu}_2\text{O}_3.
\end{align*}
\]

Appropriate amounts of raw materials ZnO, CaCO\(_3\), CdO, H\(_3\)BO\(_3\), Li\(_2\)CO\(_3\) and Eu\(_2\)O\(_3\) were thoroughly mixed and grounded in an agate mortar and melted in a platinum crucible. The chemicals used in the work were of high purity (99.9%). These compositions were heated in a PID temperature controlled furnace at 450°C for 2 hour for the decarbonization from CaCO\(_3\) and Li\(_2\)CO\(_3\) and then the temperature maintained within the range 1000-1050°C and kept the melt at this temperature for an hour till a bubble free liquid was formed. The crucibles were shaken frequently for the homogeneous mixing of all the constituents. At still higher temperatures an amorphous glass was formed. The glasses were subsequently annealed at glass transition temperature in another furnace to remove mechanical stress and were polished.

The density ‘ρ’ of these glasses was determined by the standard principle of Archimedes’ using xylene (99.99% purity) as the buoyant liquid. The glass transition temperatures \(T_g\) and crystallization temperature \(T_m\) of these glasses were determined (to an accuracy of ± 1°C) by differential scanning calorimetry (DSC) traces, recorded using universal V23C TA differential scanning calorimeter with a programmed heating rate of 1°C per minute in the temperature range 30-750°C.

Infrared transmission [IR] spectra for these glasses were recorded using a Perkin Elmer Spectrometer in the wavenumber range 400-4000 cm\(^{-1}\) by KBr pellet method. For recording thermoluminescence emission, the glasses were irradiated with X-rays for one hour at room temperature with Norelco X-ray Unit operated at 35 kV, 10 mA; TL output of these glasses was recorded on a computerized Nucleonix-TL set up with a heating rate of 1°C/s.

3. Results and Discussion

3.1. Physical properties and characterization

From the measured values of density and the average molecular weight \(\bar{M}\), various other physical parameters such as europium ion concentration \(N_i\), mean europium ion separation distance and field strength are calculated and presented in the Table 1.

Our visual examination, absence of peaks in X-ray diffraction spectra, existence of glass transition temperature \(T_g\) and crystallization temperature \(T_m\) in differential thermal analysis curves, indicate that the glasses prepared were of amorphous in nature.

![Figure 1: DSC patterns of pure and Eu\(^{3+}\) doped Li\(_2\)O-MO-B\(_2\)O\(_3\) glasses. Insets a) the variation of Hruby's parameter and b) the variation of \((T_c-T_g)\) for different modifier oxides.](image-url)

Table 1: Various physical properties of Li\(_2\)O-MO-B\(_2\)O\(_3\): Eu\(_2\)O\(_3\) glasses

<table>
<thead>
<tr>
<th>Property/ Glass</th>
<th>ZnB</th>
<th>ZnBEu</th>
<th>CaB</th>
<th>CaBEu</th>
<th>CdB</th>
<th>CdBEu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refractive index, (n_d)</td>
<td>1.517</td>
<td>1.521</td>
<td>1.519</td>
<td>1.522</td>
<td>1.523</td>
<td>1.524</td>
</tr>
<tr>
<td>Density, (\rho) (g/cm(^3))</td>
<td>2.181</td>
<td>2.839</td>
<td>2.845</td>
<td>2.972</td>
<td>2.799</td>
<td>3.118</td>
</tr>
<tr>
<td>Average molecular weight, (\bar{M})</td>
<td>46.001</td>
<td>44.833</td>
<td>46.017</td>
<td>44.832</td>
<td>46.028</td>
<td>44.841</td>
</tr>
<tr>
<td>Europium ion concentration, (N_i) (10(^2)/cm(^3))</td>
<td>--</td>
<td>3.81</td>
<td>--</td>
<td>3.99</td>
<td>--</td>
<td>4.19</td>
</tr>
<tr>
<td>Inter-ionic distance of europium ions, (R_i) (Å)</td>
<td>2.97</td>
<td>--</td>
<td>2.93</td>
<td>--</td>
<td>2.88</td>
<td></td>
</tr>
</tbody>
</table>
For the Eu$^{3+}$ ions doped glasses mixed with different modifier oxides, the glass transition temperature $T_g$ is in between 535°C and 550°C. For all glasses with the introduction of europium ions the values of $T_g$ and $T_c-T_g$ is found to decrease gradually.

### 3.2. Infrared Spectroscopy

Figure 2 represents IR spectra of the pure as well Eu$^{3+}$ ions doped Li$_2$O-MO-B$_2$O$_3$ glasses. The infrared transmission spectra of pure and europium ion doped Li$_2$O-MO-B$_2$O$_3$ glasses exhibit three groups of bands: (i) in the region 1300-1380 cm$^{-1}$, (ii) in the region 930-1040 cm$^{-1}$ and (iii) a band at about 710 cm$^{-1}$.

It is well known that the effect of introduction of alkali oxides into B$_2$O$_3$ glass is the conversion of sp$^2$ planar BO$_3$ units into more stable sp$^3$ tetrahedral BO$_4$ units and may also create non-bridging oxygens. Each BO$_4$ unit is linked to two such other units and one oxygen from each unit with a europium ion and the structure leads to the formation of long tetrahedron chains. The presence of such BO$_4$ units in the present glasses is evident from the IR spectral studies. The second group of bands is attributed to such BO$_4$ units whereas the first group of bands is identified as due to the stretching relaxation of the B-O bond of the trigonal BO$_3$ units and the band at 710 cm$^{-1}$ is due to the bending vibrations of B-O-B linkages in the borate network [26-29]. A weak band observed around 456 cm$^{-1}$ is an indicative of the presence of ZnO$_4$ units in the ZnB series glass network [30,31].

The intensity of the second group of bands (band due to the trigonal BO$_4$ units) is found to increase at the expense of first group of bands (bands due to tetrahedral BO$_3$ units) with the introduction of Eu$^{3+}$ ions with the shifting of meta-centres of first and second group of bands, respectively towards slightly lower and higher wave number for all the glasses. No significant change in position and intensity of the other bands are observed in the spectra of the glass by introducing the europium ions. The summary of the data on the positions of various bands in the IR spectra of pure and Li$_2$O-MO-B$_2$O$_3$:Eu$_2$O$_3$ glasses are presented in Table 3.

### 3.3. Thermoluminescence

Thermoluminescence glow curves of all the glasses doped with europium ions have shown in Fig 3. Pure Li$_2$O-MO-B$_2$O$_3$ (M=ZnO, CaO and CdO) glasses exhibit a glow peak at

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**Table 2: Data on differential scanning calorimetric studies of Li$_2$O-MO-B$_2$O$_3$: Eu$_2$O$_3$ glasses.**

<table>
<thead>
<tr>
<th>Glass</th>
<th>$T_g$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$T_c/T_m$</th>
<th>$(T_c-T_g)$</th>
<th>$(T_c-T_g)/T_m$</th>
<th>$K_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnB</td>
<td>553.0</td>
<td>636</td>
<td>0.805</td>
<td>83.0</td>
<td>0.121</td>
<td>1.637</td>
</tr>
<tr>
<td>ZnBEu</td>
<td>550.0</td>
<td>632</td>
<td>0.804</td>
<td>82.0</td>
<td>0.120</td>
<td>1.577</td>
</tr>
<tr>
<td>CaB</td>
<td>544.7</td>
<td>625</td>
<td>0.800</td>
<td>80.3</td>
<td>0.118</td>
<td>1.434</td>
</tr>
<tr>
<td>CaBEu</td>
<td>543.2</td>
<td>622</td>
<td>0.799</td>
<td>78.8</td>
<td>0.116</td>
<td>1.359</td>
</tr>
<tr>
<td>CdB</td>
<td>537.0</td>
<td>613.8</td>
<td>0.792</td>
<td>76.8</td>
<td>0.113</td>
<td>1.196</td>
</tr>
<tr>
<td>CdBEu</td>
<td>535.0</td>
<td>611</td>
<td>0.790</td>
<td>76.0</td>
<td>0.112</td>
<td>1.152</td>
</tr>
</tbody>
</table>

**Table 3: Peak positions (cm$^{-1}$) of IR spectra of Eu$^{3+}$ doped Li$_2$O-MO-B$_2$O$_3$ glasses.**

<table>
<thead>
<tr>
<th>Glass</th>
<th>Band due to B-O bond stretching in BO$_3$ units</th>
<th>Band due to B-O bond stretching in BO$_4$ units</th>
<th>Band due to B-O-B linkage in borate network</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnB</td>
<td>1378</td>
<td>939</td>
<td>710</td>
</tr>
<tr>
<td>ZnBEu</td>
<td>1337</td>
<td>984</td>
<td>710</td>
</tr>
<tr>
<td>CaB</td>
<td>1352</td>
<td>979</td>
<td>710</td>
</tr>
<tr>
<td>CaBEu</td>
<td>1319</td>
<td>1013</td>
<td>710</td>
</tr>
<tr>
<td>CdB</td>
<td>1336</td>
<td>992</td>
<td>710</td>
</tr>
<tr>
<td>CdBEu</td>
<td>1304</td>
<td>1036</td>
<td>710</td>
</tr>
</tbody>
</table>

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**Figure 2: Infrared spectra of pure (dotted line) and Eu$^{3+}$ doped (solid line) Li$_2$O-MO-B$_2$O$_3$ glasses.**
Table 4: Data on various trap depth parameters of Li₂O-MO-B₂O₃: Eu₂O₃ glasses

<table>
<thead>
<tr>
<th>Glass</th>
<th>TM (K)</th>
<th>τ (K)</th>
<th>δ(K)</th>
<th>µg</th>
<th>Et(eV)</th>
<th>Ed(eV)</th>
<th>TL light output (rel. units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnB</td>
<td>382</td>
<td>30</td>
<td>28</td>
<td>0.483</td>
<td>0.526</td>
<td>0.432</td>
<td>502</td>
</tr>
<tr>
<td>ZnBEu</td>
<td>404</td>
<td>27</td>
<td>22</td>
<td>0.449</td>
<td>0.673</td>
<td>0.615</td>
<td>740</td>
</tr>
<tr>
<td>CaB</td>
<td>445</td>
<td>51</td>
<td>30</td>
<td>0.370</td>
<td>0.382</td>
<td>0.548</td>
<td>770</td>
</tr>
<tr>
<td>CaBEu</td>
<td>438</td>
<td>74</td>
<td>43</td>
<td>0.368</td>
<td>0.217</td>
<td>0.370</td>
<td>1149</td>
</tr>
<tr>
<td>CdB</td>
<td>466</td>
<td>76</td>
<td>44</td>
<td>0.367</td>
<td>0.244</td>
<td>0.409</td>
<td>1142</td>
</tr>
<tr>
<td>CdBEu</td>
<td>486</td>
<td>68</td>
<td>37</td>
<td>0.352</td>
<td>0.318</td>
<td>0.530</td>
<td>1355</td>
</tr>
</tbody>
</table>

382K in ZnB glass, 424K in CaB glass and 466 K in CdB glass. When these glasses are doped with Eu³⁺ ions no additional peaks are observed but the glow peak temperature Tm of the existing glow peak shifted gradually towards higher temperatures with a gain in the intensity of TL light output. The glow peaks of europium doped ZnBEu, CaBEu and CdBEu glasses shifted to 399K, 438K and 475K respectively.

The relative TL light outputs (area under the glow curve) of pure and Eu³⁺ ion doped Li₂O-MO-B₂O₃ glasses have shown in the inset of Fig. 3. Pure glasses have the TL light output intensity area under the glow curve is 502, 770 and 1142. The area under the glow curve is also found to be maximum for CdBEu doped glass comparing to all other glass systems. The trap depth parameters for these glow peaks are computed using Chen’s formulae.

The trap depth parameters for these glow peaks are computed using Chen’s formulae [32]:

\[ E_\tau = 1.52 \left( \frac{k_B T_M}{\tau} \right)^{-1.58} (2k_B T_M) \]

\[ E_\delta = 0.976 \left( \frac{k_B T_M^2}{\delta} \right) \]

for the first order kinetics.

In the above equation \( k_B \) is Boltzmann constant, \( \tau = T_M - T_i \), \( \delta = T_2 - T_M \), \( \mu_g = \delta T_2 / (T_2 - T_1) \), where \( T_M \) is the glow peak temperature and \( T_1 \) (rising end) and \( T_2 \) (falling end) are the temperature at the half widths of the glow peaks. The summary of the data on thermoluminescence peaks with corresponding trap depth parameters of the present glasses is furnished in Table 4. The trap depth parameters of pure glasses are found to be ≈0.422 eV and observed to increase by doping with Eu₂O₃. Such value of trap depth indicates that the lifetime (τ) of electron in these traps is of the order of several months [2, 33].

Prior to TL measurements, the optical absorption spectra of all the glasses before and after X-ray irradiation are recorded. After the X-ray irradiation no additional absorption bands are observed other than those obtained in non-irradiated glasses; however the relative intensities of these bands are slightly affected [34].

Figure 3: Thermoluminescence emission of pure (dotted line) and Eu³⁺ ions doped (solid line) Li₂O-MO- B₂O₃ glasses. Inset figure represents the relative TL light output of pure and Eu³⁺ ions doped glasses.
The action of X-ray irradiation on glasses is to produce secondary electrons from the sites where they are in a stable state and have an excess energy. Such electrons may traverse in the glass network depending upon their energy and the composition of the glass and are finally be trapped, thus forming colour centres (or alternatively they may form excitons with energy states in the forbidden gap). The trapping sites may be the europium ions which constitute the glass structure, ions of admixtures to the main composition and the structural defects due to impurities in the glass. Thus this process leads to the formation of 1) boron electron centres, 2) non-bridging oxygen hole centres and 3) boron oxygen hole centres [35-37].

Thermoluminescence is a consequence of radiative recombination between the electrons (released by heating from electron centre) and an anti-bonding molecular orbital of the nearest of the oxygen hole centres. The observed TL peaks in the present glasses can be attributed due to such radiation.

The Li+ ions have closed structure, do not have energy levels within 10 eV of the ground state and hence these ions do not participate directly in luminescence but may act as activator ions [38]. Let us assume that the Eu3+ ions are uniformly distributed throughout the sample. In the absence of Eu3+ ion in the network, each electron released by heating from electron centre would be caught by an anti-bonding molecular orbital of the nearest of the oxygen hole centre. The process is followed by a radiative recombination. The observed TL peak in the present glasses is attributed to such radiation. If Eu3+ ion is present in the glass network, we have observed such a radiative recombination to enhance with respect to that of corresponding pure glass indicating that the europium ions are acting as TL activators in all the glasses. The comparison of TL emission of Eu3+ doped glasses shows a low percentage of enhancements of TL light output for ZnB doped glasses and a low percentage of enhancements of TL light output for CdBEu glasses.

Finally our studies on properties of Li2O-MO-B2O3 glasses doped europium ions indicate that i) Differential scanning calorimetric studies indicate high glass forming ability is for ZnBEu glass. ii) The IR spectral studies indicate relatively less disorder in ZnBEu glass network. iii) The analysis of the TL data suggests that the CdBEu glass can be used more effectively in radiation dosimetry since they exhibit high TL light output in high temperature region.

### Table 4: Data on various trap depth parameters of Li2O-MO-B2O3: Eu3+O3 glasses

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<thead>
<tr>
<th>Glass</th>
<th>Tm(K)</th>
<th>τ (K)</th>
<th>δ(K)</th>
<th>μg</th>
<th>E(g) (eV)</th>
<th>E(h) (eV)</th>
<th>TL light output (rel. units)</th>
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### References


Author Profile

Dr. J. Anjaiah is received M. Sc. (Physics) degree with distinction in 1998 and awarded Ph. D. in 2005 from Osmania University, India. He is a Professor in Geethanjali College of Engineering & Technology, Keesara, TS, India. His areas of specialization are Glass Science and Solid State Spectroscopy. He has 7 International publications (Peer Reviewed). Now he is working as lecturer, at Department of Physics, The University of Dodoma, Tanzania, East Africa.