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TL Properties of X-ray Irradiated Li_2O-MO-B_2O_3 (MO=ZnO, CaO, CdO) Glasses Doped with Europium Ions

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Abstract: ***Thermoluminescence (TL) characteristics of X-ray irradiated pure and doped with Eu^{3+} ions Li_2O-MO-B_2O_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 γ-ray irradiated PbO-Al_2O_3-SiO_2: a Dy3+ 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_2O_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_2O_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_2O 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 $Z_{eff} \approx 7.25$ 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.

Table 1: Various physical properties of Li_2O-MO-B_2O_3: Eu_2O_3 glasses

Property/ Glass	ZnB	ZnBEu	CaB	CaBEu	CdB	CdBEu
Refractive index, n_d	1.517	1.521	1.519	1.522	1.523	1.524
Density, ρ (g/cm^3)	2.181	2.839	2.415	2.972	2.799	3.118
Average molecular weight, $\overline{M}$	46.001	44.833	46.017	44.832	46.028	44.841
Europium ion concentration, N_i (10^{22}/cm^3)	--	3.81	--	3.99	--	4.19
Inter-ionic distance of europium ions, R_i (Å)	--	2.97	--	2.93	--	2.88

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].

ZnB : 30 Li_2O-10 ZnO-60 B_2O_3,
ZnBEu : 30 Li_2O-10 ZnO-59 B_2O_3:1Eu_2O_3,
CaB : 30 Li_2O-10 CaO-60 B_2O_3,
CaBEu : 30 Li_2O-10 CaO-59 B_2O_3:1Eu_2O_3,
CdB : 30 Li_2O-10 CdO-60 B_2O_3, and
CdBEu : 30 Li_2O-10 CdO-59 B_2O_3:1Eu_2O_3.

Appropriate amounts of raw materials ZnO, $CaCO_3$, CdO, H_3BO_3, Li_2CO_3 and Eu_2O_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 decorbonization from $CaCO_3$ and Li_2CO_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. The resultant melt was poured on a rectangular brass mould held at room temperature. The samples 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% pure) as the buoyant liquid. The glass transition temperatures T_g and crystallization temperature T_c 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 15°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 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 $\overline{M}$, 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_c in differential thermal analysis curves, indicate that the glasses prepared were of amorphous in nature.

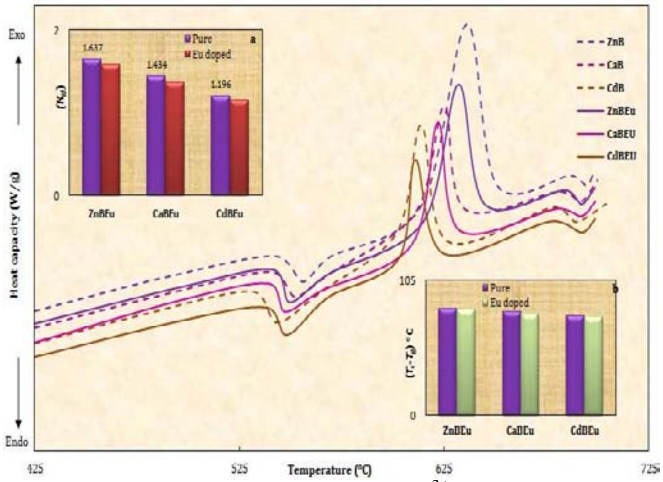

Figure 1: DSC patterns of pure and Eu^{3+} doped Li_2O-MO-B_2O_3 glasses. Insets a) the variation of Hruby's parameter and b) the variation of (T_c-T_g) for different modifier oxides

Fig.1 represents the thermograms of pure and Li_2O-MO-B_2O_3:Eu_2O_3 glasses; the pure glasses exhibit an endothermic effect due to the glass transition temperature T_g. Presence of single transition temperature T_g at 553°C in ZnB glass, 544.7°C in CaB glass and 537°C in CdB glass indicates homogeneity of the glasses. At still higher temperatures an exothermic peak T_c due to the crystal growth followed by an endothermic effect due to the re-melting of the glass symbolized by T_m are observed. The glass forming ability (Hruby's) parameter K_{gl} = (T_c-T_g)/(T_m-T_c) is calculated, which gives the information about the stability of the glass against devitrification [24,25] are evaluated and presented in Table 2. The highest values of these parameters are obtained for ZnO-modifier glass (ZnBEu) indicating it's relatively high glass forming ability among the three glasses. Insets of Fig.1 represent; (a) the variation of Hruby's parameter and (b) the variation of (T_c-T_g) for Eu^{3+} ions doped glasses mixed with different modifier oxides.

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_2O-MO-B_2O_3 glasses. The infrared transmission

Table 2: Data on differential scanning calorimetric studies of Li_2O-MO-B_2O_3: Eu_2O_3 glasses.

Glass	T_g (°C)	T_c (°C)	T_m (°C)	T_g/T_m	(T_c-T_g) (°C)	(T_c-T_g)/T_m	K_{gl}
ZnB	553.0	636	686.7	0.805	83.0	0.121	1.637
ZnBEu	550.0	632	684	0.804	82.0	0.120	1.577
CaB	544.7	625	681	0.800	80.3	0.118	1.434
CaBEu	543.2	622	680	0.799	78.8	0.116	1.359
CdB	537.0	613.8	678	0.792	76.8	0.113	1.196
CdBEu	535.0	611	677	0.790	76.0	0.112	1.152

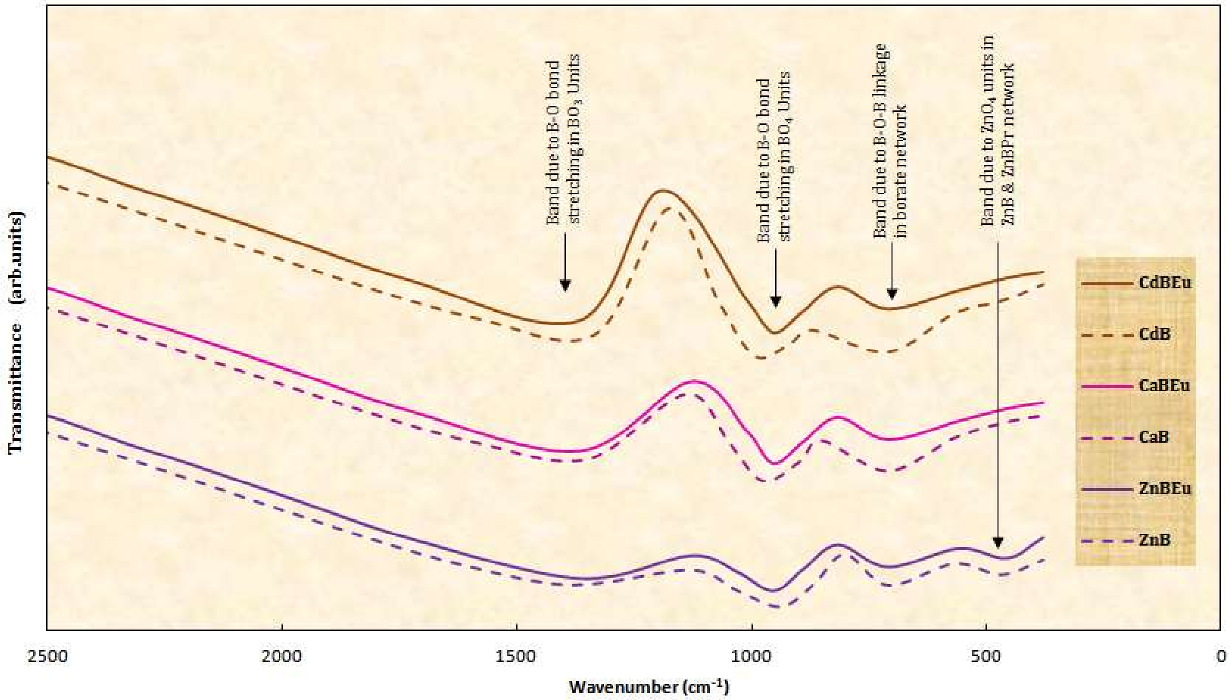

Figure 2: Infrared spectra of pure (dotted line) and Eu^{3+} doped (solid line) Li_2O-MO-B_2O_3 glasses.

spectra of pure and europium ion doped Li_2O-MO-B_2O_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_2O_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 where as 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_2O-MO-B_2O_3:Eu_2O_3 glasses are presented in Table 3.

Table 3: Peak positions (cm^{-1}) of IR spectra of Eu^{3+} doped Li_2O-MO-B_2O_3 glasses

Glass	Band due to B-O bond stretching in BO_3 units	Band due to B-O bond stretching in BO_4 units	Band due to B-O-B linkage in borate network
ZnB	1378	939	710
ZnBEu	1337	984	710
CaB	1352	979	710
CaBEu	1319	1013	710
CdB	1336	992	710
CdBEu	1304	1036	710

3.3. Thermoluminescence

Thermoluminescence glow curves of all the glasses doped with europium ions have shown in Fig 3. Pure Li_2O-MO-B_2O_3 (M=ZnO, CaO and CdO) glasses exhibit a glow peak at

Table 4: Data on various trap depth parameters of Li_2O-MO-B_2O_3: Eu_2O_3 glasses

Glass	T_M (K)	τ (K)	δ(K)	μ_g	E_τ (eV)	E_δ (eV)	TL light output (rel. units)
ZnB	382	30	28	0.483	0.526	0.432	502
ZnBEu	404	27	22	0.449	0.673	0.615	740
CaB	445	51	30	0.370	0.382	0.548	770
CaBEu	438	74	43	0.368	0.217	0.370	1149
CdB	466	76	44	0.367	0.244	0.409	1142
CdBEu	486	68	37	0.352	0.318	0.530	1355

382K in ZnB glass, 424K in CaB glass and 466 K in CdB glass. When these glasses are doped with Eu^{3+} ions no additional peaks are observed but the glow peak temperature T_m 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 Eu^{3+} ion doped Li_2O-MO-B_2O_3 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 activation energies for these glow peaks are computed using Chen's formulae [32]:
$E_\tau = 1.52\ (k_B T_M^2/\tau) - 1.58\ (2k_B T_M)$,
$E_\delta = 0.976\ (k_B T_M^2/\delta)$, for the first order kinetics.

In the above equation k_B is Boltzmann constant, $\tau = T_M - T_1$, $\delta = T_2 - T_M$, $\mu_g = \delta/(T_2 - T_1)$, 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 Eu_2O_3. 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].

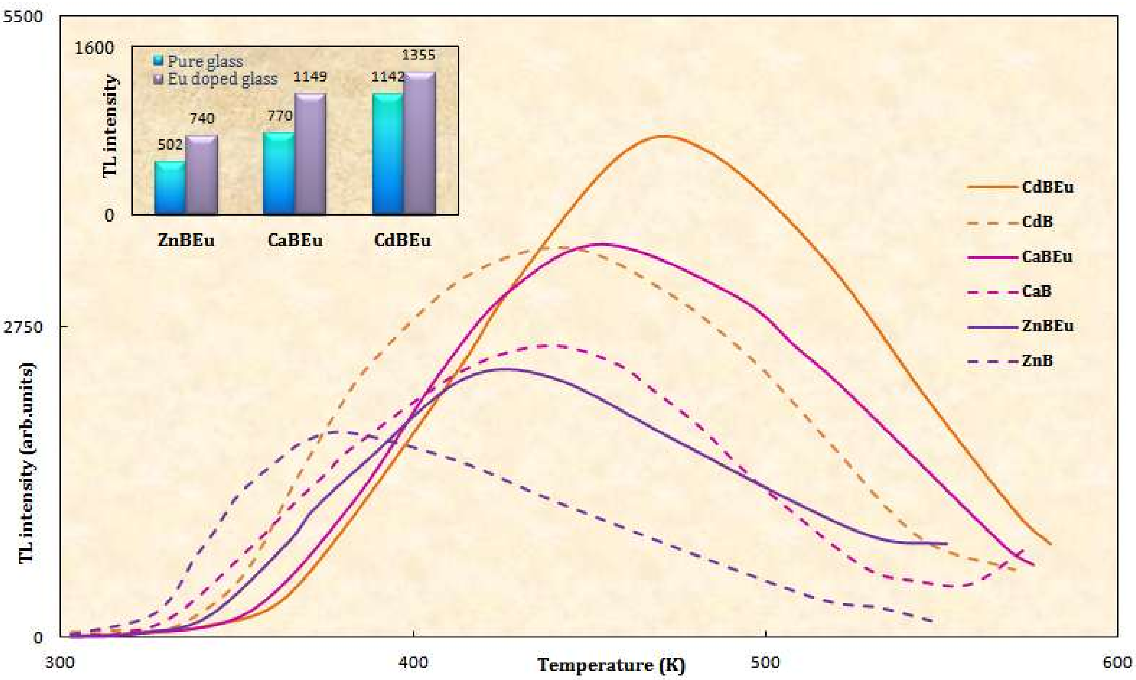

Figure 3: Thermoluminescence emission of pure (dotted line) and Eu^{3+} ions doped (solid line) Li_2O-MO- B_2O_3 glasses. Inset figure represents the relative TL light output of pure and Eu^{3+} ions doped glasses

Table 4: Data on various trap depth parameters of Li_2O-MO-B_2O_3: Eu_2O_3 glasses

Glass	T_M (K)	τ (K)	δ(K)	μ_g	E_τ (eV)	E_δ (eV)	TL light output (rel. units)
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CdB	466	76	44	0.367	0.244	0.409	1142
CdBEu	486	68	37	0.352	0.318	0.530	1355

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 color 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 Eu^{3+} ions are uniformly distributed throughout the sample. In the absence of Eu^{3+} 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 Eu^{3+} 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 Eu^{3+} doped glasses shows a low percentage of enhancements of TL light output for ZnBEu glasses.

The larger the number of Eu^{3+} ions in the glass network, the higher is the TL light output. Relatively larger concentration Eu^{3+} ions in CdBEu glasses cause relatively higher light output as observed (Inset of Fig. 3). Thus the analysis of the TL data of Li_2O-MO-B_2O_3:Eu_2O_3 glasses suggests that the CdBEu glass to be a better candidate for TL emission among the three Eu^{3+} doped glasses.

4. Conclusions

Finally our studies on properties of Li_2O-MO-B_2O_3 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.

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