Materials Science-Poland, 33(1), 2015, pp. 144-151
http://www.materialsscience.pwr.wroc.pl/
DOI: 10.1515/msp-2015-0028

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Infrared luminescence and thermoluminescence of lithium borate glasses doped with Sm^{3+} ions

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Thermoluminescence (TL) characteristics of X-ray irradiated pure and doped with Sm^{3+} ions Li_2O–MO–B_2O_3 (where MO=ZnO, CaO, CdO) glasses have been studied in the temperature range of 303 to 573 K. All the pure glasses exhibited single TL peaks at 382 K, 424 K and 466 K. When these glasses were doped with Sm^{3+} ions no additional peaks have been 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 was found to be maximum for Sm^{3+} doped glasses mixed with cadmium oxide as a 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 results clearly showed that samarium doped cadmium borate glass has a potential to be considered as a thermoluminescence dosimeter.

Keywords: *infrared spectra; thermoluminescence; borate glasses; samarium ions*

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 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. Li et al. reported the effects of calcium oxide addition on the structure and thermal properties of iron phosphate glasses [1]. Thermoluminescence study of MnO doped borophosphate glass samples for radiation dosimetry was reported by Swamy et al. [2] and the thermoluminescence properties of CaO–B_2O_3 glass system doped with GeO_2 was reported by Tengku Kamarul Bahri et al. [3]. Influence of induced structural changes on thermoluminescence characteristics of γ-ray irradiated PbO–Al_2O_3–SiO_2: Dy^{3+} glasses was reported by Rao et al. [4]. 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 with good transparency, high chemical durability, thermal stability and good rare-earth ions solubility [6]. The glass containing Li_2O as the network modifier is 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

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expected to shorten the time taken for solidification of glasses during the quenching process, and glasses containing ZnO have high chemical stability and lower thermal expansion. Their wide band gap, large exciton binding energy and intrinsic emitting properties make them promising candidates 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 material in the development of the applications for long-term radiation dosimetry, since its effective atomic number $Z_{eff} \approx 7.25$ is nearly tissue equivalent, which makes it a very promising material in the field of personal and clinical dosimetry and for other applications, such as 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 who had started 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 the 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 samarium ions on the thermoluminescence light output of these glasses has been also carried out with a view to examine the suitability of these glasses in the radiation dosimetry.

2. Experimental

Undoped and samarium ion doped glasses with the compositions presented below, were prepared using standard melting and quenching techniques and used for the present study [21–23]:

ZnB: 30 Li_2O-10 ZnO-60 B_2O_3,
ZnBSm: 30 Li_2O-10 ZnO-59 B_2O_3:1Sm_2O_3,
CaB: 30 Li_2O-10 CaO-60 B_2O_3,
CaBSm: 30 Li_2O-10 CaO-59 B_2O_3:1Sm_2O_3,
CdB: 30 Li_2O-10 CdO-60 B_2O_3, and
CdBSm: 30 Li_2O-10 CdO-59 B_2O_3:1Sm_2O_3.

Appropriate amounts of raw materials ZnO, $CaCO_3$, CdO, H_3BO_3, Li_2CO_3 and Sm_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 decarbonization of $CaCO_3$ and Li_2CO_3 and then, the temperature was maintained within the range of 1000 to 1050 °C and the melt was kept 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 into 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 then 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 temperature T_g and crystallization temperature T_c of these glasses were determined (within an accuracy of ±1 °C) using differential scanning calorimetry (DSC) traces, recorded using a universal V23C TA differential scanning calorimeter with a programmed heating rate of 15 °C per minute in the temperature range of 30 to 750 °C.

Infrared transmission [IR] spectra of these glasses were recorded using a Perkin Elmer spectrometer in the wavenumber range of 400 to 4000 cm^{-1} by KBr pellet method. For recording the thermoluminescence emission, the glasses were irradiated with X-rays for one hour with Norelco X-ray unit operated at 35 kV, 10 mA. The thermoluminescence output of these glasses was recorded on a computerized Nucleonix-TL setup 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 M, various other physical parameters, such as samarium ion concentration N_i, mean samarium ion separation distance and field strength were calculated and presented in 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 prepared glasses are amorphous in nature.

Fig. 1 shows the thermograms of pure and Li_2O–MO–B_2O_3:Sm_2O_3 glasses; the pure glasses exhibit an endothermic effect due to the glass transition temperature T_g. The 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 these glasses. At 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, is observed.

The glass forming ability (Hruby's) parameters $K_{gl} = (T_c - T_g)/(T_m - T_c)$, which give the information about the stability of glass against devitrification [24, 25], have been evaluated and presented in Table 2. The highest values of these parameters have been obtained for ZnO-modified glass (ZnBSm) indicating its relatively high glass-forming ability among the three glasses. Insets in Fig. 1 represent: (a) the variation of Hruby's parameter and (b) the variation of $(T_c - T_g)$ for Sm^{3+} ion doped glasses mixed with different modifier oxides.

For the Sm^{3+} ion doped glasses mixed with different modifier oxides, the glass transition temperature T_g is 549.8 °C for ZnBSm glass, 541.0 °C for CaBSm glass and 533.3 °C for CdBSm glass. For all the glasses the values of T_g and $T_c - T_g$ have been found to decrease gradually with the introduction of samarium ions.

3.2. Infrared spectroscopy

Fig. 2 shows IR spectra of pure and Sm^{3+} ion doped Li_2O–MO–B_2O_3 glasses. The infrared transmission spectra of pure and samarium ion doped Li_2O–MO–B_2O_3 glasses exhibit three groups of bands: (i) in the region 1310 to 1380 cm^{-1}, (ii) in the region 930 to 1030 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 results in 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 other units, and one oxygen from each unit is connected with a samarium ion, which finally leads to the formation of long tetrahedron chains. The presence of such BO_4 units in the investigated glasses is evident from the IR spectral studies. The second group of bands is attributed to such BO_4 units, where the first group of bands is due to the stretching relaxation of the B–O bond of 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} indicates the presence of ZnO_4 units in the ZnB series glass network [30, 31].

The intensity of the second group of bands (the bands due to the trigonal BO_4 units) is found to increase at the expense of the first group of bands (bands due to tetrahedral BO_3 units) with the introduction of Sm^{3+} ions causing the shifting of meta-centres of the first and the second group of bands, respectively, towards slightly lower and higher wave numbers for all the glasses. No significant changes in position and intensity of the other bands are observed in the spectra of the glass as a result of introducing the samarium ions. The summary of the data about the positions of various bands in the IR spectra of pure and Li_2O–MO–B_2O_3:Sm_2O_3 glasses is presented in Table 3.

3.3. Thermoluminescence

Thermoluminescence glow curves of all the glasses doped with samarium ions are shown in Fig. 3. Pure Li_2O–MO–B_2O_3 (M=ZnO, CaO and

Table 1. Physical properties of Li_2O–MO–B_2O_3:Sm_2O_3 glasses.

Property/ Glass	ZnB	ZnBSm	CaB	CaBSm	CdB	CdBSm
Refractive index, n_d	1.517	1.523	1.519	1.525	1.523	1.529
Density, ρ (g/cm^3)	2.181	2.916	2.415	3.023	2.799	3.221
Average molecular weight, $\overline{M}$	46.001	44.831	46.017	44.827	46.028	44.839
Sm^{3+} ion concentration, N_i (10^{22}/cm^3)	–	3.92	–	4.06	–	4.33
Inter-ionic distance of Sm^{3+} ions, R_i (Å)	–	2.94	–	2.91	–	2.85

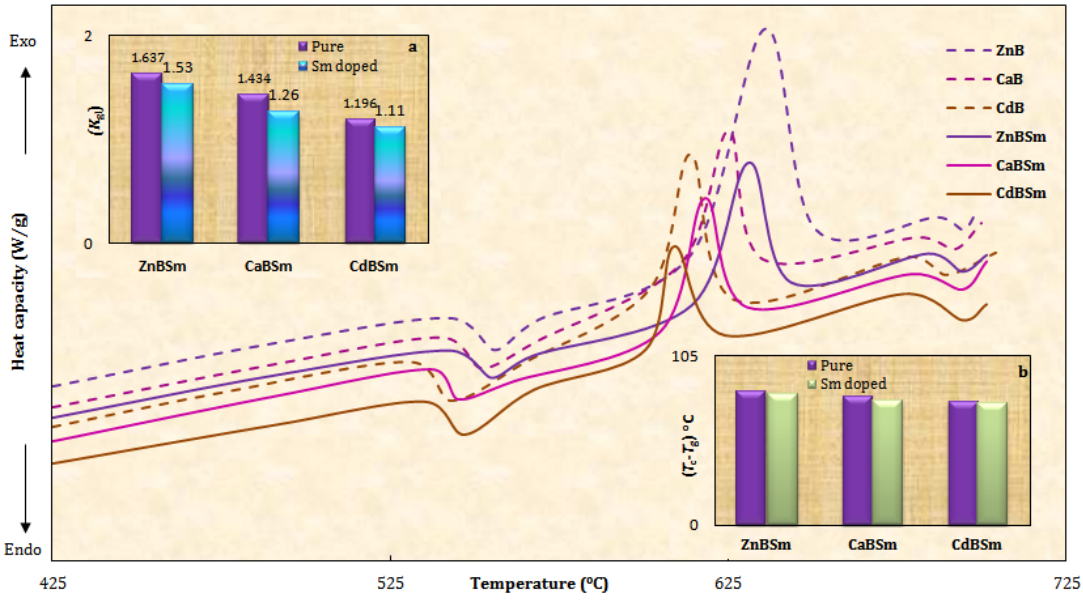

Fig. 1. DSC patterns of pure and Sm^{3+} doped Li_2O–MO–B_2O_3 glasses. Insets (a) the variation of Hruby's parameter and (b) the variation of ($T_c - T_g$) for different modifier oxides.

CdO) glasses exhibit a glow peak at 382 K in ZnB glass, 424 K in CaB glass and 466 K in CdB glass. When these glasses are doped with Sm^{3+} ions no additional peaks are observed but the glow peak temperature T_m of the existing glow peaks shifts gradually towards higher temperatures with a gain in the intensity of TL light output. The glow peaks of samarium ion doped ZnBSm, CaBSm and CdBSm glasses are shifted to 399 K, 442 K and 482 K, respectively.

The TL light outputs (area under the glow curve) of pure and Sm^{3+} ion doped Li_2O–MO–B_2O_3 glasses are shown in the inset of Fig. 3. Pure glasses have the TL light output intensity area under the glow curve of 502, 770 and 1142. For the Sm^{3+} ions doped glasses mixed with different modifier oxides the glow peaks of samarium ion doped ZnBSm, CaBSm and CdBSm glasses are 654, 1055 and 1286, respectively. The area under the glow curve is also found to be maximum for CdBSm doped glass comparing to all other glass systems.

The trap depth parameters and activation energies for these glow peaks have been computed using Chen's formulas [32]:

$$E_\tau = 1.52(k_B T_M^2/\tau) - 1.58(2k_B T_M) \quad (1)$$

$$E_\delta = 0.976(k_B T_M^2/\delta) \quad (2)$$

for the first order kinetics.

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

Table 2. Data from differential scanning calorimetric studies of Li_2O–MO–B_2O_3: Sm_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
ZnBSm	549.8	631	684.0	0.804	81.2	0.119	1.532
CaB	544.7	625	681	0.800	80.3	0.118	1.434
CaBSm	541.0	618	679	0.797	77.0	0.113	1.262
CdB	537.0	613.8	678	0.792	76.8	0.113	1.196
CdBSm	533.3	609.0	677	0.788	75.7	0.112	1.113

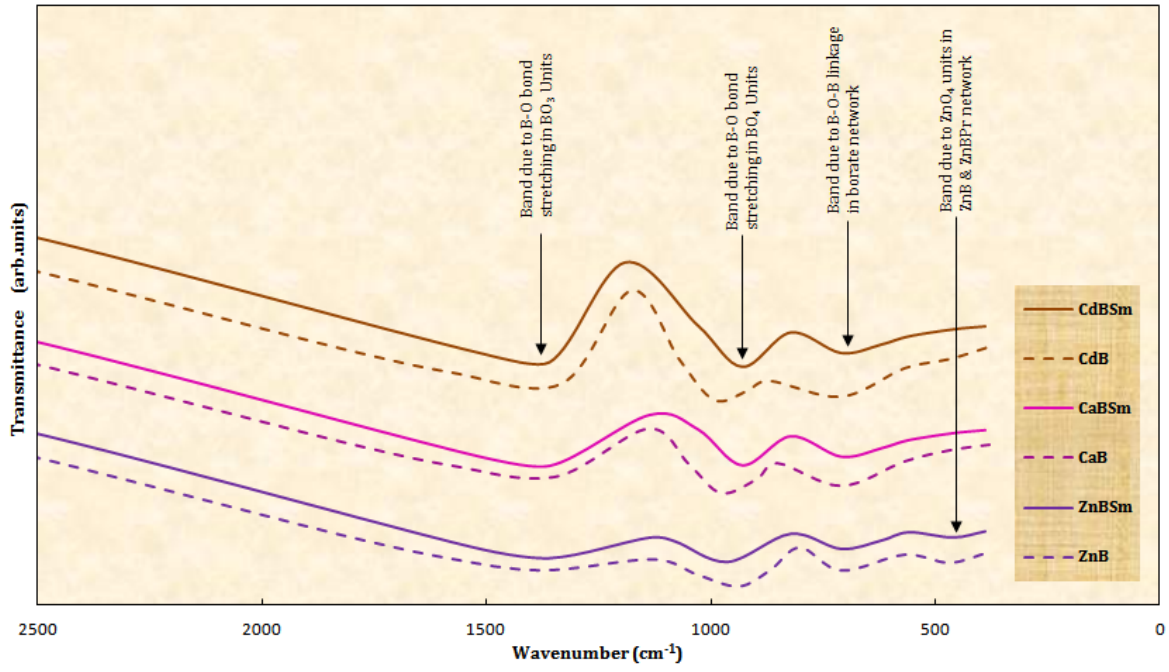

Fig. 2. Infrared spectra of pure (dotted line) and Sm^{3+} doped (solid line) Li_2O–MO–B_2O_3 glasses.

Table 3. Peak positions (cm^{-1}) of IR spectra of Sm^{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
ZnBSm	1353	975	710
CaB	1352	979	710
CaBSm	1327	1002	710
CdB	1336	992	710
CdBSm	1316	1027	710

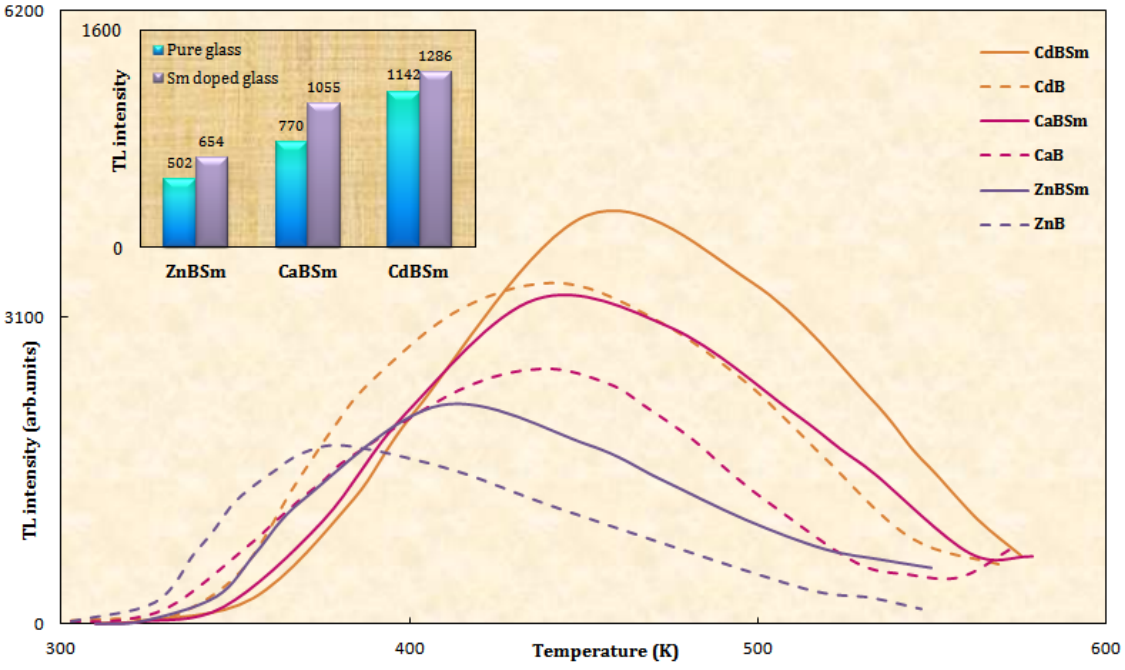

Fig. 3. Thermoluminescence emission of pure (dotted line) and Sm^{3+} ion doped (solid line) Li_2O–MO–B_2O_3 glasses. Inset figure represents the relative TL light output of pure and Sm^{3+} ion doped glasses.

where T_M is the glow peak temperature and T_1 (rising end) and T_2 (falling end) are the temperatures at the half widths of the glow peaks. The summary of the data on thermoluminescence peaks with corresponding trap depth parameters of the studied glasses is furnished in Table 4. The trap depth parameters of pure glasses are found to be ~0.422 eV and tend to increase with Sm_2O_3 doping. 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 were recorded. After the X-ray irradiation, no additional absorption bands other than those obtained in the non-irradiated glasses were observed, however, the relative intensities of these bands were slightly affected [34].

X-ray irradiation of glass produces secondary electrons from the sites, where they are in a stable state and have an excess energy. Such electrons may traverse the glass network depending upon their energy and the composition of the glass and are finally trapped, thus, forming color centres (or alternatively, they may form excitons with energy states in the forbidden gap). The trapping sites may be the samarium 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 centres) and an antibonding molecular orbital of the nearest of the oxygen hole centres. The observed TL peaks in the studied glasses can be attributed to such radiation.

The Li^+ ions have closed structure, do not have energy levels within 10 eV of the ground state, hence, these ions do not participate directly in luminescence but may act as activator ions [38]. Let us assume that the Sm^{3+} ions are uniformly distributed throughout the sample. In the absence of Sm^{3+} ions in the network, each electron released by heating from such electron centre would be caught by an anti-bonding molecular

Table 4. Trap depth parameters of Li_2O–MO–B_2O_3:Sm_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
ZnBSm	399	28	24	0.462	0.627	0.550	654
CaB	424	53	35	0.398	0.324	0.426	770
CaBSm	442	52	31	0.373	0.367	0.523	1055
CdB	466	76	44	0.367	0.244	0.409	1142
CdBSm	482	72	38	0.345	0.287	0.507	1286

orbital of the nearest of the oxygen hole centres. The process is followed by a radiative recombination. The observed TL peak in the studied glasses is attributed to such radiation. If Sm^{3+} ion is present in the glass network, we can observe that such radiative recombination is enhanced with respect to that of corresponding pure glass, indicating that the samarium ions act as TL activators in all the glasses. A comparison of TL emission of Sm^{3+} doped glasses shows only a low percentage of enhancement of TL light output for ZnBSm glasses.

The larger the number of Sm^{3+} ions in the glass network, the higher is the TL light output. Relatively larger concentration of Sm^{3+} ions in CdBSm glasses causes relatively higher light output as can be observed in the inset of Fig. 3. The vibrational transitions are less intense for optical absorption process of glasses containing Sm^{3+} ions, which may be more favourable for the formation of high concentration of color centers at deeper depths in these glasses; the maximum TL output at higher temperatures obtained for the Sm^{3+} ion doped glasses can be attributed to these reasons [39]. Thus, the analysis of the TL data of Li_2O–MO–B_2O_3:Sm_2O_3 glasses suggests that the CdBSm glass is the best candidate for thermoluminescence emission among the three Sm^{3+} doped glasses.

4. Conclusions

In conclusion, our studies on the properties of Li_2O–MO–B_2O_3 glasses doped with samarium ions indicate that (i) ZnBSm belongs to the glasses with high glass forming ability, confirmed by differential scanning calorimetric studies; (ii) the IR spectral studies indicate relatively less disorder in ZnBSm glass network; (iii) the analysis of the TL data suggests that the CdBSm glasses can be used more effectively in radiation dosimetry since they exhibit high TL light output in high temperature region.

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Received 2014-07-28
Accepted 2014-12-10