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Spectroscopic properties and luminescence behaviour of europium doped lithium borate glasses

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ABSTRACT

Li_2O–MO–B_2O_3 (MO=ZnO, CaO and CdO) glasses doped with europium are prepared by using the melt quenching technique to study their absorption and luminescence properties to understand their lasing potentialities. The XRD pattern of the glasses confirmed the amorphous nature and the IR spectra reveal the presence of BO_3 and BO_4 units in the glass network. Judd–Ofelt intensity parameters Ω_λ (λ=2, 4, 6) are evaluated from the intensities of various absorption bands of optical absorption spectra. The J–O parameters have been used to calculate transition probabilities (A), lifetime (τ_R), branching ratios (β_R) and stimulated emission cross-section (σ_P) for the $^5D_0 \rightarrow {}^7F_J$ (J=1–4) transitions of the Eu^{3+} ions. The decay from the $^5D_0$ level of Eu^{3+} ions in these glasses has been measured and analysed. Branching ratios and stimulated emission cross-sections measured for all these glasses show that the $^5D_0 \rightarrow {}^7F_1$ transition under investigation has the potential for laser applications. The high stimulated emission cross-section and branching ratios from the present glasses suggests their potential for infra red lasers. The study of the thermoluminescence is also carried out and the data suggests that the CdBEu glass is suitable for thermoluminescence emission output among the three Eu^{3+} doped glasses.

1. Introduction

Optical properties of rare-earth [RE] doped glasses are extensively studied for their potential applications in the fields of lasers, fluorescent display devices, optical detectors, waveguides and fibre amplifiers [1–4]. There has been a considerable attention in the study on optical, structural and dielectric behaviour of borate based glasses [5–8].

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 [9]. 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 candidates for the development of optoelectronic devices, solar energy concentrators, ultraviolet emitting lasers and gas sensors [10]. Both ZnO and CdO are thermally stable and appreciably covalent in character [11]. Addition of alkaline-earth oxide CaO into these glass matrices is expected to increase the resistance of the glasses to the moisture [12]. The glass containing Li_2O as network modifier was seen as bubble free, highly stable and moisture resistant, suitable for a systematic optical analysis [13].

In the present work, the trivalent europium ion Eu^{3+} ($4f^6$) has been chosen as a dopant due to its well characterised visible spectrum with pure luminescence transitions. Also the lower energy level structure of the Eu^{3+} ion is relatively effortless compared to other RE ions. Normally, the trivalent europium ion, Eu^{3+} emits narrow band, almost monochromatic with longer lifetime and it can used as a red emitting material for field emission technologies and LEDs. The excitation and emission transitions are due to the transitions among the 4f electronic states in the trivalent RE ions, which are highly sensitive to the symmetry, structure of the local environment and phonon energy of the host matrix [14,15].

Recently, Eu^{3+} ion doped sodium–lead borophosphate glasses for red light emission were reported by Nallamala Kiran [16]. Spectroscopic investigation and optical characterisation of Eu^{3+} ions in K–Nb–Si glasses were reported by Mohan et al. [17]. Concentration dependent luminescence studies on Eu^{3+} doped telluro fluoroborate glasses were reported by Vijayakumar et al. [18]. Nico et al. [19] reported the Eu^{3+} luminescence in aluminophosphate glasses. Rojas et al. [20] reported the structural, thermal and optical properties of CaBO and CaLiBO glasses doped with Eu^{3+}.

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Due to the technological importance of europium ion and the advantages of above research, the Eu_2O_3 doped $Li_2O–MO–B_2O_3$ (MO=ZnO, CaO and CdO) glasses have been prepared and investigated. The present study (i) determines the J–O intensity parameters for trivalent europium ions and the radiative properties for significant levels, (ii) compares the experimental and predicted radiative properties for $^5D_0$ level, (iii) studies the luminescence efficiencies with the aid of IR spectra data, (iv) studies the thermoluminescence properties to examine the possible use of these glasses in radiation dosimetry applications.

2. Experimental

Undoped and following Eu^{3+} ion doped glasses are prepared by using standard melting and quenching techniques and used for the present study [21–23].

ZnBEu: $30Li_2O–10ZnO–59B_2O_3$:$1Eu_2O_3$,
CaBEu: $30Li_2O–10CaO–59B_2O_3$:$1Eu_2O_3$ and
CdBEu: $30Li_2O–10CdO–59B_2O_3$:Eu_2O_3.

Appropriate amounts of raw materials ZnO, $CaCO_3$, CdO, H_3BO_3, Li_2CO_3 and Eu_2O_3 (all in mol%) 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 h 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. Optically transparent and bubble free glasses were selected for optical studies.

The glass transition temperatures T_g and crystallisation 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.

The optical absorption spectra of the glasses were recorded at room temperature in the wavelength range 350–650 nm using Shimadzu-3100 UV–VIS–NIR Spectrophotometer. By using xenon arc lamp, the intense line $\lambda_{exc} = 393.8$ nm was identified and the same was used to record the photo-luminescence spectrum of all the glasses. The photo-luminescence spectra of the glasses were recorded on Hitachi-F 3010 Fluorescence Spectrophotometer in the wavelength range 460–750 nm up to a resolution of 0.1 nm.

Infrared transmission 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; thermoluminescence output of these glasses was recorded on a computerised Nucleonix-TL set up with a heating rate of 1 °C/s.

3. Results and discussion

3.1. Characterisation

The existence of glass transition temperature T_g and crystallisation temperature T_c in differential scanning calorimetry study curves and absence of peaks in X-ray diffraction pattern indicate that the glasses prepared were of high quality glasses.

Fig. 1 shows the differential scanning calorimetry traces of three glasses. All the glasses exhibit an endothermic change between 535 °C and 550 °C, which is attributed to the glass transition temperature T_g. At still higher temperature, T_c an exothermic peak due to the crystal growth followed by another endothermic effect at temperature T_m due to the re-melting of the glass are also observed. The appearance of single peak due to the glass transition temperature in DSC pattern of all the glasses indicates the high homogeneity

Table 1
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)	$(T_c-T_g)/T_m$	K_{gl}
ZnBEu	550.0	632	684	0.804	82.0	0.120	1.577
CaBEu	543.2	622	680	0.799	78.8	0.116	1.359
CdBEu	535.0	611	677	0.790	76.0	0.112	1.152

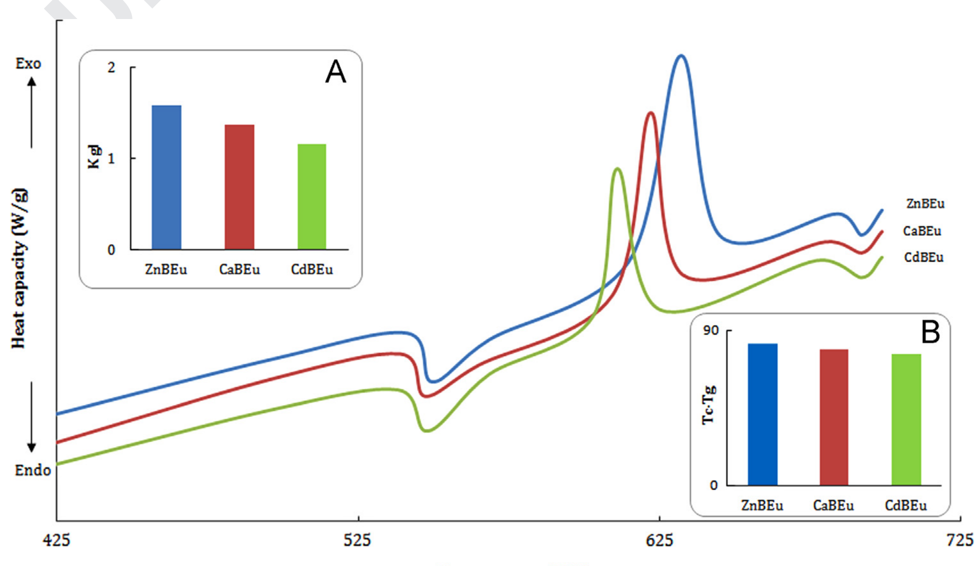

Fig.1. DSC patterns of Eu^{3+} doped $Li_2O–MO–B_2O_3$ glasses.