Journal of Non-Crystalline Solids 475 (2017) 184–189

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Synthesis and characterization of Dy^{3+} doped lithium borate glass for thermoluminescence dosimetry

Bhaskar Sanyal[a,*], M. Goswami[b], S. Shobha[b], V. Prakasan[a], S.P. Chawla[a], M. Krishnan[b], Sunil K. Ghosh[a]

[a] Food Technology Division, Bhabha Atomic Research Centre, Mumbai 400 085, India
[b] Glass & Advanced Materials Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

ARTICLE INFO

Keywords:
Thermoluminescence
Radiation dosimetry
Lithium borate glass
Dy^{3+} doping

ABSTRACT

Lithium borate glass systems were synthesized to study their feasibility for measuring high radiation doses using thermoluminescence (TL) technique. Lithium borate glass with a composition (mol%) of $30Li_2O–70B_2O_3$ was prepared by conventional melt quenched technique. To see the effect of Dy^{3+} on thermoluminescence, photoluminescence and thermal properties of the glass, 0.5 wt% of Dy_2O_3 was added prior to the glass making. One more glass with exact lithium tetraboarte ($Li_2B_4O_7$) composition doped with 0.5 wt% Dy_2O_3 was also prepared. Thermo-physical properties like density, and glass transition did not show significant changes with addition of Dy_2O_3. However, optical properties like band gap, UV visible absorption and photoluminescence showed substantial changes. The optical band gap decrease from 3.05 to 2.78 eV with addition of Dy_2O_3. Photoluminescence (PL) analysis showed a broad emission at around 475 nm in all the glasses and very sharp intense emission at 570 nm for Dy_2O_3 doped glasses. After gamma irradiation in the dose range of 0.5–5 kGy the samples exhibited TL peak at around 136 and 152 °C for Dy_2O_3 doped lithium borate and tetraborate samples, respectively. A linear dose response in TL intensity was also observed which was useful for quantitative estimation of absorbed dose.

1. Introduction

Rare-earth doped luminescent materials play a significant role as radiation detectors in many fields of basic and applied research. They are used for monitoring of ionizing radiation in nuclear power plants, radiotherapy, personnel exposure and environmental release. The rare-earth impurities incorporated into the host may cause the changes in its TL features as well as the dosage properties [1]. Most of TL based dosimetry systems having polycrystals as host matrices showed saturation in dose response in higher dose range thus employed for low dose measurements in the field of radiation protection dosimetry [2]. However, TL technique could be an interesting area of research to measure higher doses incurred during various radiation processing applications, such as food irradiation, radiotherapy and medical product sterilization. Development of amorphous systems is therefore of paramount importance for this specific application. New amorphous materials are now being developed with more sensitivity and linearity of TL output over a broad range of radiation doses [3,4]. Rare-earth doped borate glasses could be interesting systems having properties useful for various dosimetric applications. However, studies on rare-earth doped borate glasses are very few [5]. Furthermore, borate glasses have an effective atomic number close to that of the human tissue (Z_{eff} = 7.42) [6,7]. This is an important parameter because the dosimeter used to measure radiation dose in biological materials preferably should have similar atomic properties with biological tissue.

Many researchers investigated the TL properties of lithium tetraborate (LTB) doped materials with different activators such as: Mn, Cu, Ag, and Mg [8–10]. Kelemen et al. [11] reported the radioluminescence (RL) and TL data for Mn doped glassy samples of LTB, characterized by a very broad peak at about 150 °C. In case of rare-earth doped samples, TL sensitivity is dependent on the trivalent dopant, which may form complex defects in borates by creating hole or electron trap centres depending on the boron–oxygen arrangement in the glass structure [8]. Amongst the different rare earths, the Dy^{3+} ion is recognized as an active luminescence centre. It is identified as an f-localized trap-creating ion and found to increase the afterglow for a protracted time [14]. Moreover, the structure of borate glasses is very interesting due to the widely known “boron anomaly phenomenon” which is the coordination changes of the network forming cations in the glass structure that influence behavior in several physical properties [12,13].

Although LTB has been a well-studied material in terms of thermoluminescence, no report investigating the relationship between TL

* Corresponding author.
E-mail addresses: sanyal@barc.gov.in, bhasbarc@gmail.com (B. Sanyal).

http://dx.doi.org/10.1016/j.jnoncrysol.2017.09.016
Received 30 May 2017; Received in revised form 21 August 2017; Accepted 5 September 2017
Available online 12 September 2017

response and rare earth dopant (Dy_2O_3) has been encountered, especially for the measurement of higher doses applicable for radiation processing. The objective of the present work is to evaluate the thermal, structural and optical properties of the undoped lithium borate and Dy^{3+} doped lithium borate glasses by means of thermoluminescence (TL), X-ray diffraction (XRD), differential scanning calorimetry (DSC), Raman spectroscopy, ultraviolet–visible optical absorption (UV–vis), and fluorescence spectroscopy. The principal aim of these studies was to assess the feasibility of this material as a potential thermoluminescence based dosimeter for the measurements of high radiation dose.

2. Experimental

2.1. Synthesis of glass system

Lithium borate glasses with compositions in mol% $30Li_2O$ - $70B_2O_3$ (LB-00) was prepared by conventional melt quenched technique. In order to study the effect of rare earth dysprosium (Dy^{+3}) on TL, 0.5 wt % of Dy_2O_3 was added to the glass sample. The doped glass system was therefore $30Li_2O$ - $70B_2O_3$:Dy_2O_3 (LB-01). Another glass based on lithium tetraborate composition ($Li_2B_4O_7$:$Li_2O{\cdot}2B_2O_3$) doped with 0.5 wt % of Dy^{3+} (LBD-01) was also prepared. Stoichiometric amount of Li_2O and B_2O_3 in the form of Li_2CO_3 and H_3BO_3 as initial constituents were taken for glass preparation. Each batch of weight approximately 50 g was prepared by thorough mixing and grinding of initial constituents. The charge was calcined at 800 °C after holding at 110 °C for 2–4 h for complete removal of moistures and complete decomposition of boric acid to their respective oxide forms. The temperature was slowly raised from 110 °C to 800 °C with controlled heating and kept constant for a period of 20–25 h. The calcined charge was weighed to ensure complete decomposition of the initial constituents. The calcined charge was further grounded and mixed properly followed by melting in a covered alumina crucible inside a raising and lowering furnace. Melting was carried out at around 1000 °C and held for 1–2 h for complete homogenization of the glass. A part of the melt was poured in a graphite mould of 10 mm diameter × 40 mm length and remaining part of the material was poured on a metal plate. The density of the glass was around 2.27 g/cm^3, so the volume of the glass was around 22 cm^3. Afterwards all the poured glasses were transferred into an annealing furnace operating at 450 °C for removal of thermal stress. The melting and annealing furnaces were operated within a accuracy of ± 1 °C. The glass was then cooled down slowly to room temperature. The obtained glass was transparent and bubble free. The glass was cut into pieces for different experiments. Hereafter the glass samples are referred by their generic names of LB-00 for $30Li_2O$:$70B_2O_3$, LB-01 for $30Li_2O$:$70B_2O_3$:Dy_2O_3, and LBD-01 for $Li_2B_4O_7$:Dy_2O_3.

2.2. Irradiation

Lithium borate glass samples of generic names LB-00, LB-01, and LBD-01 were powdered for irradiation and distributed in eight parts. One part was kept as control (nonirradiated). Remaining seven parts were exposed to gamma radiation from a Cobalt 60 source at 0.25, 0.5, 0.75, 1, 2, 3, and 5 kGy doses using a gamma chamber GC 5000 (BRIT, Mumbai, dose rate 38 Gy/min) at BARC, Mumbai, India. The calibration and absorbed dose rate of the irradiator were carried out using Fricke reference standard dosimeters [15]. The powder samples were kept at the body centre of the irradiation volume of the gamma chamber where the dose rate was determined as mentioned above. In order to further confirm the actual absorbed dose in glass samples, a set of alanine dosimeters was used and absorbed dose was evaluated using an EPR spectrometer [16]. A variation in absorbed dose with respect to the desired dose was observed within ± 2.5%.

2.3. Characterization

The density of these samples was measured by Archimedes principle using water/xylene as solvent. The accuracy of the measurement was up to ± 0.02 g/cm^3. Following analyses were then carried out on these samples.

2.3.1. Phase identification by X-ray diffractometer

Powdered glass samples were characterized for phase formation using X-ray diffractometer. For X-ray analysis Cu K_α of 1.5408 Å radiation source with Ni filter was used. Measurements were carried out in 2θ range of 10–70°.

2.3.2. Thermoluminescence measurements

The thermoluminescence (TL) of the samples were measured by increasing the temperature from ambient to 300 °C with a heating rate of 5 °C/s using a TL reader (Intech Dosimeters Pvt. Ltd., New Delhi, India).

2.3.3. Thermal and optical analysis

For TG/DTA experiment on these samples, approximately 40 mg of powdered sample was placed in a Pt-10%Rh crucible and heated in the temperature range of 30–900 °C with a heating rate of 10 °C/min under Argon atmosphere. Glass transition and crystallization temperatures were determined from the measurements. Tangents were plotted to find out the glass transition temperature and peak and onset of the crystallization temperatures. Accuracy of the measurement was within ± 2 °C. The thermo-mechanical analyzer (TMA) was used for measuring thermal expansion coefficient and dilatometric softening temperature of these glasses. The measurements were carried out in the temperature range of 30–600 °C in Argon atmosphere using silica as the probe material with a heating rate of 10 °C/min. Samples with 10 mm diameter and thickness of 2–3 mm were used for these experiments. The average thermal expansion in the temperature range of 30–300 °C was calculated from the TMA plot. The reported CTE values were within the accuracy of ± 0.02 and T_g was measured by plotting tangents and values were within the accuracy limit of ± 2 °C.

Optical measurements such as absorbance/transmission characteristics were carried out in the spectral range of 200–2700 nm with spectral band width 4 nm using UV–vis–NIR spectrophotometer (Model JASCO). Optical band gap (E_{opt}) was calculated from absorbance data. The photoluminescence characteristics of these samples were determined using PL fluorimeter (Model FL 980). The measurements were carried out using Xenon flash lamp as an excitation source and emission was recorded in vis-NIR region.

3. Results

The density values of these glass samples were found around 2.27 g/cm^3. No significant change of density value was observed with Dy_2O_3 incorporation in this glass. The thermo-physical parameters of these glasses are shown in Table 1.

3.1. Phase analysis and thermal properties

Fig. 1 shows the merged XRD patterns of different lithium borate glasses. Two broad low intense peaks in the range of 20–25° and 40–45° were observed. No significant changes have been observed in the patterns of these glasses in presence of Dy_2O_3. The glasses are found to be transparent and free from any phase separation or inhomogeneity.

Fig. 2a shows merged DTA plots for three different lithium borate glass samples. A broad endothermic shift around 450–500 °C was observed. The plot shows a sharp and intense exothermic peak at around 591 °C for Dy^{+3} doped lithium borate glass. In case of base glass (LB-00) two exothermic peaks were observed, one at around 575 °C and other one at 634 °C, with relatively less intensity compared to first