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Structural, optical and thermoluminescence study of Dy^{3+} ion doped sodium strontium borate glass

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ABSTRACT

In the present work physical, optical and thermoluminescence studies of Dy^{3+} ion doped sodium strontium borate glasses have been reported. XRD study confirms the amorphous nature of glass and the increasing concentration of Dy_2O_3 results in broadening and shifting of the XRD peak. FTIR shows no change in structure with the inclusion of Dy_2O_3 but the optical band gap is sensitive to dopant concentration. Glow curve possess single prominent peak in the temperature range 390–393 K and the glass sample with 0.4 mol% Dy_2O_3 concentration has the most appropriate TL response. The Glow curve width also changes with the dopant concentration. The calculation of kinetic parameters shows that all the glass samples exhibit second order kinetics.

1. Introduction

The study of different properties of borate glasses is of great interest and has been done by different researchers on account of their easy preparation, suitable strength, excellent transparency, isotropic nature and low cost. The study generally includes the effect of modifiers and dopants on the structural, optical, thermal & magnetic properties of the glasses through the techniques namely Fourier transform infrared spectroscopy (FTIR), UltraVoilet-visible spectroscopy (UV–Vis), Differential thermal analysis (DTA), Nuclear magnetic resonance spectroscopy (NMR) to name a few [1]. Borate is one of the best and extensively used glass former because of the properties like low melting point, good host for alkali, alkaline and rare-earth (RE) metals [2–5]. But the hygroscopic nature of the borate glasses has unfavorable effect on their performance, since they absorb moisture and becomes unstable. However their properties can be modulated with the addition of modifiers like alkali and alkaline earth metals [6].

Nowadays many researchers are working in the area of radiation dosimetry because dosimeters are useful tool in medicine, radiotherapy treatment, industry and environmental monitoring [7]. For a material to be accepted as dosimeter it must have human tissue equivalency, which means that the interaction of photon with the dosimeter material is same as that with the human soft tissue [8]. Dosimeters made from borate glasses serve this purpose very well as their effective atomic number is close to human soft tissue (Z_{eff} ~ 7.42) [6,9–13]. Continuous efforts are being directed towards the improvement of the sensitivity of dosimeters. Recently in addition to alkali and alkaline, RE ions attracted the researchers' attention as literature suggest they can create electron trapping levels in the intra band gap of the host material. Among the rare-earth ions Dy^{3+} ion is identified as active luminescence centre [14,15]. Due to radiation exposure Dy^{3+} ions goes to excited state and there is direct transfer of electrons from these states to trap centers which contributes to thermoluminescence (TL) emission [14, 16–18]. In view of this an attempt has been made to study the effect of rare-earth ion doping on the physical, structural, optical and TL properties of prepared sodium-strontium-borate (NaSrB) glasses.

2. Experimental

2.1. Sample preparations

The conventional melt quenching technique was used to prepare a series of NaSrB glasses of composition (70-x) B_2O_3-20 Na_2O-10 SrO: x Dy_2O_3 (where $x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$). The detailed composition and notation of the glass samples is given in Table 1. For each of the glass sample experimental thermal conditions (melting temperature, annealing temperature and annealing time) were kept similar. High purity oxides of H_3BO_3, Na_2CO_3, $SrCO_3$ and Dy_2O_3 were used in sample preparation. The oxides were weighed on an electronic balance with an accuracy of 1 mg and were grinded in an agate mortar to obtained uniform mixture. The mixture was then melted in silica crucible in the

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Table 1
Details of the chemical compositions of Dy_2O_3 doped sodium strontium borate glass samples.

	Chemical compositions (in mol%)			
Sample notation	B_2O_3	Na_2O	SrO	Dy_2O_3
NaSrB0.0	70.0	20.0	10.0	–
NaSrB0.2	69.8	20.0	10.0	0.2
NaSrB0.4	69.6	20.0	10.0	0.4
NaSrB0.6	69.4	20.0	10.0	0.6
NaSrB0.8	69.2	20.0	10.0	0.8
NaSrB1.0	69.0	20.0	10.0	1.0

range of temperature 900–1000 °C in an electric furnace at Department of Physics, Punjabi University, Patiala and stirred frequently to obtained homogeneous molten glass. The molten glass was then poured in a preheated graphite mould and immediately annealed at temperature of 400 °C for 2 h to remove the thermal stress. Finally, the sample was left in the furnace and allowed to cool with an average cooling rate of 5 °C/min. The glass sample was crushed to obtained fine powder which was then used for XRD, FTIR, UV–Vis and TL Glow curve measurements.

2.2. Characterization

2.2.1. Density and molar volume

Archimedes principle was employed to measure the density of glass sample at room temperature. High purity Benzene was used as buoyant liquid to avoid any type of hygroscopic effect and all the measurements were performed three times to minimize the error. The density was calculated as follows:

$$\rho = \frac{x}{x-y} \times 0.8765 \ \text{g cm}^{-3} \tag{1}$$

where $x$the density of glass in air is, y is the density of glass in benzene and 0.8765 g cm^{-3} is the density of benzene at room temperature.

The molar volume of the glass was computed using the following equation.

$$V_m = \frac{M}{\rho} \ \text{cm}^3 \ \text{mole}^{-1} \tag{2}$$

where V_m is the molar volume, M is the molar weight and ρ is the density of the sample.

To see the effect of dopant concentration on glass matrix, average boron-boron separation was calculated using Eq. (3) [19]

$$\langle d_{B-B} \rangle = \left[\frac{V_m^b}{N_A}\right]^{\frac{1}{3}} \tag{3}$$

where V_m^b is volume of boron atoms per mole and calculated as:

$$V_m^b = \frac{V_m}{2(1-X_B)} \tag{4}$$

where X_B is the mole fraction.

2.2.2. Ion concentration

The Dy^{3+} ion concentration in the interior of the prepared samples was calculated by using following formula given by Eq. (5),

$$N = \frac{\text{Mol percent of dopant} \times \text{Density of glass} \times \text{Avogadro No.}}{\text{Average molecular weight of glass}} \ \text{ions cm}^{-3} \tag{5}$$

Using ion concentration we can also calculate three other important parameters as follows,

Polaron radius

$$r_p(\text{A}) = \frac{1}{2}\left(\frac{\pi}{6N}\right)^{\frac{1}{3}} \tag{6}$$

Inter-nuclear distance

$$r_i(\text{A}) = \left(\frac{1}{N}\right)^{\frac{1}{3}} \tag{7}$$

Field strength

$$F = \frac{Z}{(r_p)^2} \tag{8}$$

2.2.3. X-ray diffraction

Rigaku miniflex 600 pro-powder X-ray diffractometer was used to determine the amorphous phase of the prepared samples. The diffractometer uses CuK_α radiations of wavelength 1.54 Å and operating at 40 kV, 15 mA in the range of 2θ from 10° to 90° with step width of 0.02° and scan speed of 4°/min at room temperature. The prepared glass samples were crushed to fine powder and the X-ray diffraction pattern was obtained for the same.

2.2.4. Infrared spectroscopy (FT-IR)

The infrared spectrum was taken to study the structure of the prepared glass samples. The FT-IR spectroscopy tells us about the molecular vibrations and rotations corresponding to a covalent bond [20]. For this the glass was grinded with potassium bromide (KBr) so that fine mixture was obtained and that mixture was pressed in a hydraulic press with a pressure of 100 kg cm^{-2}. Then thin transparent pellets of approximate thickness 1 mm were obtained and these pallets were used for data analysis. The spectrum was taken in the range of 450 cm^{-1} to 4000 cm^{-1}.

2.2.5. UV–vis spectroscopy

The reflectance spectrum of the glass in the range 200–800 nm was taken at room temperature to calculate the optical band gap using Hitachi U-3900H UV–vis double beam spectrometer in diffuse reflectance mode. The value of E_g was found out using Kubelka-Munk method [21], which used the following equation

$$\text{F}(R) = \frac{(1-R)^2}{2R} \tag{9}$$

where R is the reflectance and F(R) is analogous to Extinction coefficient (α). For more details refer to [22,23] of paper [21].

By plotting $(\text{F(R)h}\nu)^n$ versus hv and extrapolating the slope to $(\text{F(R)h}\nu)^{1/2} = 0$ the band gap was calculated. Where $n = 1/2$ is for indirect allowed transition and $n = 2$ is for direct allowed transition.

2.2.6. Thermoluminescence spectra

The thermoluminesence spectra was measured using Intech TLD reader, model (I-1501 DC). The samples were exposed to 15 Gy dose with Gamma chamber GC-1200 having a Co-60 source available at Inter University Accelerator Centre (IUAC), New Delhi, India. The glow curves were recorded from room temperature to 400 °C at heating rate 5 °C/s.

2.2.7. Kinetic parameters (peak shape method)

The variation in the glow curve peak, shape and intensities of TL spectra is due to the trapping levels [22]. Kinetic parameter gives us valuable information about the TL phenomenon occurring in the materials. The different importanat kinetic parameters are activation energy (E) or trap depth, frequency factor (s) and order of kinetics (b). Chen's