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Structural, thermal, optical and dielectric studies of Dy^{3+}: B_2O_3-ZnO-PbO-Na_2O-CaO glasses for white LEDs application

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Dy^{3+}-doped borate glasses with nominal composition (60-x) B_2O_3-10 ZnO-10 PbO-10 Na_2O-10 CaO-(x) Dy_2O_3 (x = 0, 0.1, 0.2, 0.5, 0.75, 1.0, 1.5 and 2.0 mol%) were prepared by the melt quenching technique. The XRD and SEM confirm the amorphous nature of the glasses and through EDAX, all the related elements were found in the synthesized glasses. The vibrations of metal cations such as Pb^{2+} and Zn^{2+}, B—O—B bond bending vibrations from pentaborate groups, bending vibrations of BO_3 triangles, and stretching vibrations of tetrahedral BO_4^- units etc. are identified from the respective FTIR and Raman spectra including the non-hygroscopic nature of the synthesized glasses. The TGA and DSC measurements were performed to study thermal properties, where $\Delta T > 100$ °C ($\Delta T = T_x - T_g$) for all the glasses. Among all the Dy^{3+}-doped glasses, the 0.75 mol% Dy^{3+}-doped glass shows the highest PL intensity with four emissions, where the two transitions corresponding to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (blue) and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (yellow) are observed more intense than the others. The CIE chromaticity (x,y) coordinates for BZPNCDy 0.1 mol% glass are (0.398, 0.430), close to the white light region in the CIE 1931 chromaticity diagram. The dielectric properties of the 0.75 mol% Dy^{3+}-doped glass such as dielectric constant, dielectric loss and AC conductivity were studied in the various frequencies and temperature.

1. Introduction

Much consideration is given lately by numerous researchers towards examining the optical properties of rear-earth (RE)-doped crystalline and additionally amorphous materials because of their use in optoelectronics, lasers, light emitting diodes, optical fiber amplifiers, and sensors so forth [1–4]. The amorphous/glassy materials have been widely employed as the host matrix for RE ions doping as they exhibit huge advantages over crystalline materials like wide transparency, excellent recycling capability, flexibility of choosing various glass compositions, less fabrication time, ability to accept large number of RE ions and the possibility of constructing larger laser gain media with good optical quality in different shapes (rod, disc) etc. [4–7]. Further, RE-doped glasses are the favorable materials for the mentioned applications because they hold advantages like fluorescence over UV–Vis-IR spectral regions, longer lifetimes and higher quantum efficiency [4]. Basically, optical properties and quantum efficiency are an important parameters to consider for a compatible host for RE ions doping because of their valuable contribution to the improvement of optoelectronic devices [8,9]. Borate (B_2O_3) glasses among different hosts are observed to be promising candidates for RE-doping because of their properties like low melting point, thermal stability, and formation of various structural units. However, higher phonon energy (~1300–1500 cm^{-1}) demerits that lead to restrict their use in several applications because of the non-radiative transitions [4,6]. With an inclusion of appropriate network modifier oxide Na_2O and heavy metal PbO oxide, phonon energy of the borate glass can be reduced for the higher quantum efficiency [6,10]. The addition of ZnO into the borate network gives an advantage as non-hygroscopic nature, and non-toxicity, which in turn increases the possibility for optoelectronic applications [4,11]. As well, it is known that ZnO can enter the glass network structure as a modifier

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or network former depending on the ZnO molar concentration. It is established that at low concentration of ZnO as a network modifier, it breaks B-O-B bonds and leads to the formation of non-bridging oxygens (NBOs) together with the defects known as dangling bonds [6,12]. Calcium borate glasses are very attractive to evaluate the effects of the chemical environment on the optical properties of RE ions by contributing to low melting temperature, high thermal stability and non-hygroscopicity [13]. White light emitting diodes (W-LEDs) play a crucial role in solid state lighting technology because of their significant properties like low electrical power consumption, longer lifetime, high efficiency, environmental friendliness, and high brightness etc., over the conventional light sources [14]. Among the several RE ions, Dy^{3+}-doped glasses are found to be the suitable candidates for white light applications because they exhibit two intense emissions in the blue and yellow regions due to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions, respectively. The suitable cooperation of these yellow and blue emission bands creates white light and can be adjusted by changing the synthetic composition, pumping wavelengths and Dy^{3+} content [15,16]. Hence, special attention has been paid to Dy^{3+}-doped glass systems towards the fabrication of light emitting sources. The present work reports the effect of Dy^{3+} content on the thermal, structural, spectroscopic and dielectric properties of Dy^{3+}-doped borate glasses for white light emission applications.

2. Experimental

2.1. Glass synthesis

By using the conventional melt quenching technique borate glasses doped with various Dy_2O_3 concentrations were prepared along with the host glass. High purity chemicals from Sigma-Aldrich were used for the current work: B_2O_3 (99.98%), ZnO (99%), PbO (99.5), Na_2CO_3 (99.5%), CaO (99.9%) and Dy_2O_3 (99.9%). The synthesized eight glasses for this work are presented in Table 1 and labeled as “BZPNC”, “BZPNCDy0.1”, “BZPNCDy0.2”, “BZPNCDy0.5”, “BZPNCDy0.75”, “BZPNCDy1.0”, “BZPNCDy1.5” and “BZPNCDy2.0”, respectively. Each 20 g batches were weighed separately and then each one powder is placed into a high purity alumina crucible and then heated inside an electric furnace to melt at 950 °C for 60 min. The homogeneous melt was poured onto the stainless-steel plate and quickly covered by another steel plate. Optically transparent and bubble free disk glasses were obtained with 3–4 cm diameter and ~0.3 cm thickness. All the glasses were annealed for 5 h at 300 °C and cooled down naturally to ambient temperature in air. Annealing was used for removal of internal stress of the glasses during the process of melt quenching.

2.2. Characterization

The X-ray diffraction (XRD) profile of the BZPNC glass was obtained by using Ital Structure APD 2000 diffractometer with CuKα (λ = 1.542 Å) radiation at 40-kV applied voltage and anode current 20 mA. Here, 2°/min. was the scanning rate, and the scan range was between 10° and 80°. The surface morphology was monitored using FE-SEM equipment FEI-NOVA NanoSEM 230 with an acceleration voltage 5 kV, equipped with an EDX detector from EDAX-Ametek that allowed semi-quantitative analysis of elements. The Fourier transform infrared (FTIR) spectra of all the glass powders were measured over the 280-4000 cm^{-1} range by a Perkin Elmer Spectrum 100 FTIR spectrometer with a resolution of ~4 cm^{-1}. The Raman spectra of the synthesized glasses were acquired with a WITec alpha 300R Confocal Raman system equipped with a Nd: YAG laser (532 nm) as the excitation source. The incident power of 10 mW was commonly utilized. The Raman spectrum was recorded in the range of 0–3800 cm^{-1} for the Raman shift, with a 5s an integration time. Thermogravimetric (TGA) and differential scanning calorimetry (DSC) measurements were performed with a Mettler Toledo TGA/DSC 1 HT Integrated Thermal Gravimetric Analyzer using high purity nitrogen for carrying the gas and a flow rate of 50 mL/min. Powders of 15–20 mg glass were used in an Al_2O_3 crucible for the measurement. 10 K/min. is the heating rate applied for the glass sample up to 1000 °C from ambient temperature, utilizing Al_2O_3 as a reference sample. The test was run 3 times for the same sample to determine errors in analysis. The optical absorption spectrum for the 0.75 mol% Dy^{3+}-doped glass was investigated at room temperature in the 200–2500 nm spectral range by a dual-beam spectrophotometer (Hitachi U-4100 UV–Vis–NIR), and the resolution is 2 nm. For the Dy^{3+} doped glasses, the room temperature photoluminescence excitation (PLE) and photoluminescence (PL) spectra in the wavelength range 200–700 nm with spectral resolution of 1.0 nm were measured using Hitachi F-7000 fluorescence spectrophotometer equipped with a 150 W Xenon lamp as the excitation source. Dielectric properties of the 0.75 mol % Dy^{3+}-doped glass was determined using a high-resolution dielectric analyzer (Novocontrol) connected to a BDS 1200 sample holder over a frequency range of 5–100 MHz with an applied potential of 1 V and temperature range of 323–473 K. The temperature sensor used was a PT100 platinum sensor and temperature was controlled to a limit of ±0.1 K from the set-point by a Novotherm controller unit. All measurements control and evaluations were carried out by the WinDETA software.

Table 1
The nominal composition of the synthesized glasses (mol%).

Glass code	B_2O_3	ZnO	PbO	Na_2O	CaO	Dy_2O_3
BZPNC	60	10	10	10	10	–
BZPNCDy0.1	59.9	10	10	10	10	0.1
BZPNCDy0.2	59.8	10	10	10	10	0.2
BZPNCDy0.5	59.5	10	10	10	10	0.5
BZPNCDy0.75	59.25	10	10	10	10	0.75
BZPNCDy1.0	59	10	10	10	10	1.0
BZPNCDy1.5	58.5	10	10	10	10	1.5
BZPNCDy2.0	58	10	10	10	10	2.0

3. Results and discussion

3.1. Structural properties

As an example, Fig. 1(a) shows the X-ray diffraction (XRD) pattern of the BZPNC glass in the range of $10° \le \theta \le 80°$, where remaining all other glasses also show similar XRD profiles and not presented here. The XRD pattern exhibits broad diffuse and scattering in low angles without any sharp crystalline diffraction peaks, which confirms the amorphous glass sample nature [17,18]. The Scanning electron microscopy (SEM) image of the BZPNC glass was examined and presented in Fig. 1(b). This SEM image shows uniformity in glass phase of prepared glass. The results presented in Fig. 1(a) and (b) are characteristically confirm the amorphous nature of the synthesized glass. Similar SEM images were obtained for all Dy^{3+}-doped glasses also. Using energy dispersive X-ray analysis (EDAX), we detected all of the chemical elements (O, B, Zn, Pb, Na, Ca, and Dy) that dispersed in the studied glass network. As an example, the EDAX spectrum measured for the BZPNC glass is shown in Fig. 1(c) and it clarifies all main components of the glass. In addition to these host glass elements, Dy element is also identified in all the Dy^{3+}-doped glasses (not shown here).

In Fig. 2 is shown the FTIR spectrum of the BZPNC glass. For the Dy^{3+}-doped glasses also, similar IR profiles were obtained except