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Effect of Nd_2O_3 addition on structure and characterization of lead bismuth borate glass ☆

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ABSTRACT

The effect of different contents of Nd_2O_3 on the thermal transition temperature, density and structure of 25 Bi_2O_3 – 25 PbO – 50 B_2O_3 has been investigated using X-ray diffraction (XRD), differential thermal analysis (DTA), infrared spectrophotometer (FTIR) and optical absorption. The amorphous phase has been identified based on X-ray diffraction analysis. The neodymium oxide plays the role as a glass-modifier and influences on $BO_3 \leftrightarrow BO_4$ conversion. The observed increase in T_g with Nd_2O_3 reflects an increase in bond strength. The decrease of the density and the increase of the molar volume with the addition of Nd_2O_3 contents attributed to an increase in the number of Non-bridging oxygen (NBOS). The optical absorption results are indicating the higher covalency of the Nd–O bond for glass containing 2 mol% of Nd_2O_3. In addition, a lowest covalency is observed in glass with 1 mol% Nd_2O_3. In addition, it is considered necessary in the construction of compact and efficient laser source.

Introduction

The development in information technology depends on the materials that are effective for information transmission, power transmission and nonlinear applications.

Glasses based on heavy metals such as Bismuth and Lead has high refractive index, due to their higher hyperactive polarizable nature. Since these glasses exhibit nonlinear phenomenon, they are valuable in optical fibers and in optical switches [1–3].

Borate glass has many properties such as, high transparency, low melting temperature, high thermal stability, different coordination numbers, and good solubility of rare earth ions, although it is very suitable for optical material. The addition of heavy metal oxide to borate glasses decreases the phonon energy. Thus, leads to an increase in its quantum efficiency of luminescence from the exited state of rare earth ions. Further, the addition of rare earth oxide to alkali borate glasses is interesting for studying effects of its ions on the glass forming network [4–6].

Mohan [7] investigated the physical and spectroscopic properties for sodium lead borate glasses doped with varying amounts of Nd^{3+}. Density measurement indicates that the density decreases with the increase in concentration of Nd^{3+} ions up to 1.75 mol%. The decrease in density could be due to the formation of non-bridging oxygen (NBO's) atoms. From the spectroscopic measurements obtained the indirect and direct mobility gap have a maximum for 2 mol% and a minimum for 1 mol% of Nd_2O_3. The direct mobility gap shows the same behavior of density, and the indirect mobility gap does not follow a uniform variation.

Borate glasses have two groups of different coordination; first one is trigonal BO_3 coordination and the second is the tetrahedral BO_4 coordination. These two fundamental coordinations can be combined to form different groups like boroxol rings, orthoborate, pentaborate, tetraborate, metaborate and diborate groups, etc. The BO_4 units give rise to tetrahedral network features in the glass structure [8], where BO_4 units are always negatively charged ($[BO_{4/2}]^-$), whereas BO_3 units may be present as ($\equiv [BO_{3/2}]^0$), charged units $[BO_{2/2}O]^-(\equiv B_2)$, $[BO_{1/2}O_2]^{2-}(\equiv B_1)$ or even $[BO_3]^{3-}(\equiv B_0)$ [9].The fraction of these BO_4 and structural units depends on the nature and concentration of the added modifiers [10–15].

Thermal and optical properties of glasses $Bi_2O_3{\cdot}B_2O_3$ system were studied. The optical transparent glasses $Bi_2O_3{\cdot}B_2O_3$ containing rare earth ions or nano-regions of ferroelectric crystals are of more interest, because such materials have potential for laser host, tunable waveguide and tunable fiber grating [16–19]. Heavy metal oxide glasses (Bi_2O_3 and PbO) have many applications in the field of glass ceramics, layers for optical and electronic devices, thermal and mechanical sensors, reflecting windows, etc. [20].

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Neodymium oxide is used to dope glass, including sunglasses, make solid-state lasers, and to color glasses and enamels. Also, used in ceramic capacitors, color TV tubes, high temperature glazes, coloring glass, carbon-arc-light electrodes, and vacuum deposition.

In the present work, the effect of Nd_2O_3 on the structure, glass forming ability and density of glass samples were studied using different techniques such as XRD, DTA, IR and optical absorption measurements.

Experimental

Reagent grades $H_3\ BO_3$, Bi_2O_3, PbO and $Nd_2\ O_3$ were used as starting materials for preparing glasses having the composition 25 Bi_2O_3 – 25 PbO – 50 B_2O_3 – x Nd_2O_3 mol%, ($0 \leqslant x \leqslant 2$) where x varies from 0 to 2 in steps of 0.5. Initially the samples were maintained at about 550 °C for 2 h for de-carbonization of carbonate. Then the temperature was raised up to 800 °C and maintained for two hours. Subsequently, the temperature was further increased up to 1000 °C and maintained for one and half an hour depending upon the composition. Then the molten liquid was poured between two stainless steel mold plates kept at room temperature for the formation of glassy composition of required shape.

The glassy nature of the samples were confirmed by XRD studied using Philips Analytical X-ray diffraction system, type PW3710 based with Cu tube anode of wave length $K_{\alpha 1}$ = 1.54060 Å and $K_{\alpha 2}$ = 1.54439 Å. The generator tension was 40 kV and the generator current was 30 mA. The start angle (2θ) was 10° and the end angle was 70°, the step size (2θ) was 0.02 and the time per step was 1.0 s.

In the present work, analysis by infrared spectrometer was carried out using FTIR 6300; Tosco, Japan absorption spectra in the region 400–4000 cm^{-1} were recorded for all the samples using KBr pellets technique.

The glassy nature of the prepared glasses was confirmed by the differential thermal analysis (DTA) in the temperature range from 30 to 1200 °C with the heating rate of 30 °C/min (in N_2 gas atmosphere) of using Al_2O_3 powder as a reference material (Shimadzu DTA-50 analyzer). The density of the glass samples was measured using the Archimedes principle. The measurements were done using a digital balance and toluene as inert immersion liquid. The density was obtained from the relation

$$d(g/cm^3) = [a/(a - b)] \times (\text{density of the toluene})$$

where 'a' is the weight of the glass sample in the air, 'b' is the weight of the glass sample when immersed in toluene and the density of the toluene is 0.86 (g/cm^3).

Results and discussion

XRD analysis

The glass samples of neodymium doped lead bismuth borate were identified by XRD, the investigated glass samples as shown in Fig. 1.

The X-ray diffraction pattern shows no sharp peaks indicating the absence of crystalline nature, and observed broad humps in the glass samples, characteristic of the amorphous phase at diffraction angles (2θ) to be fully amorphous indicating that these glass samples are composed of glassy phase .

FTIR spectral analysis

Infrared spectroscopy studies were used to get essential information about the arrangement of the structural units of the glass samples. It is assumed that vibrations of characteristic groups of atoms in the glass network are independent of vibration of the other neighboring groups in the glass [21].

The fundamental absorption bands of borate glasses are clear at three principal bands the first band, which occurs between 800 and 1200 cm^{-1}, is due to the B–O bond stretching of tetrahedral BO4 units. The second band that occurs between 1200 and 1600 cm^{-1} is due to stretching vibration of B–O of trigonal BO_3 units [22,23]. The third band is observed around 700 cm^{-1} is due to

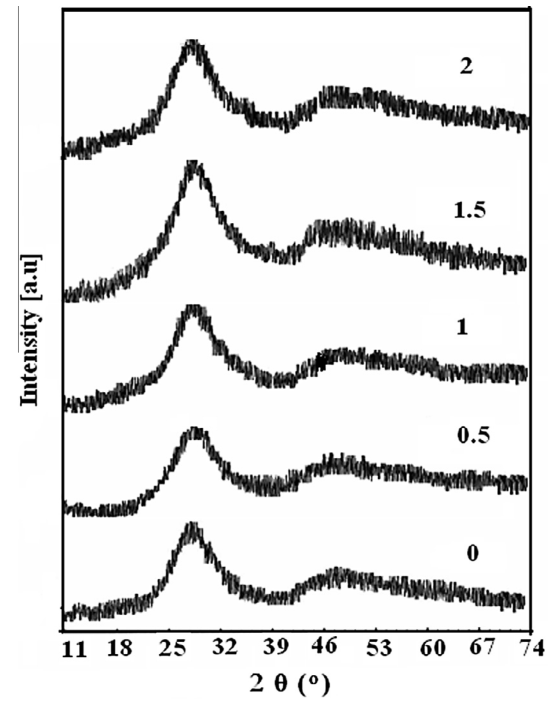

Fig. 1. The X-ray diffraction pattern of neodymium doped lead bismuth borate glasses.

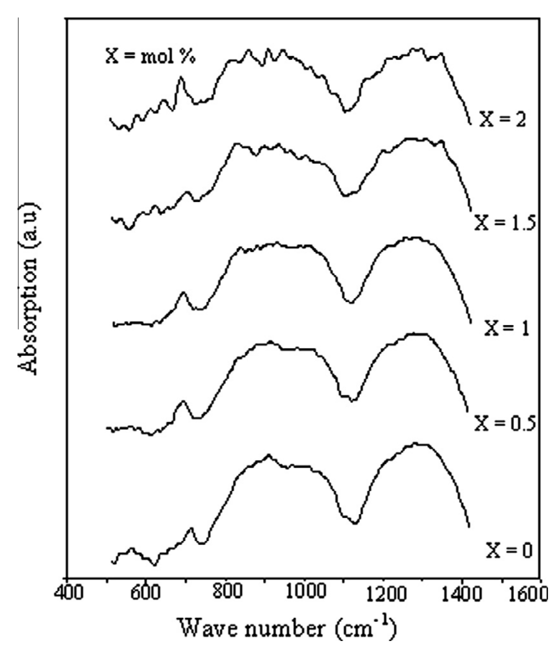

Fig. 2. Infrared spectra of [50 B_2O_3 – 25 PbO – 25 Bi_2O_3 – x Nd_2O_3] mol% glasses, with x = 0, 0.5, 1.0, 1.5 and 2.0.