Physical, optical and structural characterizations of Dy\(^{3+}\)-doped lead borate glasses

Neetu Chopra\(^{1,3}\), Sandeep Kaur\(^{1,2}\), O P Pandey\(^{2}\), Gopi Sharma\(^{1}\) and Surbhi Sharma\(^{3}\)

\(^{1}\)Department of Physics, Kanya Maha Vidyalaya, Jalandhar, Punjab-144004, India
\(^{2}\)School of Physics and Materials Science, Thapar Institute of Engineering and Technology, Patiala, Punjab -147004, India
\(^{3}\)neetuverma75@yahoo.co.in

Abstract. In the current studies optical, physical and structural properties of rare-earth doped borate glasses have been reported. Bulk samples were prepared by using melt quenching technique with nominal composition 70B\(_2\)O\(_3\)-(17-x)ZnO-10PbF\(_2\)-3Na\(_2\)O-xDyF\(_3\) and 60B\(_2\)O\(_3\)-(27-x)ZnO-10PbF\(_2\)-3Na\(_2\)O-xDyF\(_3\), where (x=0,1). XRD analysis was used to confirm the amorphous nature of prepared samples. Optical and structural properties of as prepared samples were studied using UV-Visible and FTIR absorption spectra. The undoped and doped glasses exhibit characteristic absorption bands due to the presence of rare earth ion. A decrease in the band gap has been observed with the addition of rare earth ion. Variations in density have been observed with the addition of rare earth ion.

Keywords: Rare Earth elements, XRD, UV-Visible Spectroscopy, FTIR absorption spectra.

1. Introduction

Glasses doped with rare earth (RE) ions owing to their optical transitions within 4f-level structure and excellent photoluminescence properties furnishes them great attention in optical and photonic technology as well as have emerged as the important candidate for various applications such as optical amplifiers, infrared lasers, hole-devices, white light emitting diodes, light-converting diodes [1-5]. In particular, Dy\(^{3+}\) has excellent mid-infrared emission which makes it fit for Q-switch devices and solid state lasers [6]. Two intense bands in the blue (470-500nm) and yellow(560-600 nm) wavelength region gives Dy\(^{3+}\) doped glasses good opportunity to produce white light by adjusting its Y/B intensity ratio [7-9]. Dy\(^{3+}\) activated glasses are considered to have potential application in designing optical devices viz. optical waveguides, lasers, LED’s etc. [10]. Dy\(^{3+}\) ions creates electron trapping levels in the host band gap which makes them desirable candidates for fibre optics amplifiers [11-12]. Ox fluoride glasses owing to the low-phonon character, enhances the radiative transitions and hence increases the quantum efficiency [13].

Among all the glass formers, borates glasses (B\(_2\)O\(_3\)) shows remarkable properties viz. high thermal stability, lower degree of expansion in volume due to change in temperature, high transparency, low melting point and good rare-earth ion solubility owing to its network [14]. Borate glasses constitute three dimensional random network of either BO\(_3\) triangles with non-bridging oxygen or BO\(_4\) tetrahedrons with all bridging oxygen. Addition of modifiers in borates leads to the formation of combinations of these units to form stable diborates, triborates, tetraborates and pentaborates [15]. In addition to its low glass transition temperature Borate glasses also acts as an excellent host for transition metals as well as for rare earth metals. In the current study, we have chosen ZnO, PbO and...
Na$_2$O as network modifiers to mix in the present glass sample. Among these modifiers, ZnO is expected to increase the chemical stability and reduce the time taken for solidification of glasses [16]. ZnO doped alkali borate glasses are non-toxic and non-hygrosopic in nature and its wide band gap, large exciton binding energy make them a suitable candidate for opto-electronic devices, UV emitting laser, solar converter etc. [17-18]. Addition of Pb in borate glasses reduces its phonon energy ($\sim$ 1400 cm$^{-1}$) and also helps in lowering of melting temperature for glass stability [19]. Metal oxide modifier (Na$_2$O) can also decrease the viscosity and hence due to forming new non-bridging oxygens in the glass system. The present study reports the structural, optical and physical properties of the Dy$^{3+}$-doped lead borate glasses modified with zinc and sodium via density, XRD, UV-Vis and FTIR spectroscopy.

2. Sample preparation and Experimental
The two series of Dy$^{3+}$-doped lead borate samples modified with zinc and sodium with the composition (in mol %) 70B$_2$O$_3$-(17-x) ZnO-10PbF$_2$-3Na$_2$O-xDyF$_3$ and 60B$_2$O$_3$-(27-x) ZnO-10PbF$_2$-3Na$_2$O-xDyF$_3$ where (x=0,1) were prepared by using melt quench technique. All the samples were prepared using chemicals of approximately 99.99% of purity. Nominal compositions of the prepared samples are presented in table 1. The amount of oxides and fluorides were weighed by using digital electronic balance and were mixed in a pestle mortar for half an hour. The alumina crucible containing the batch was placed in an electric furnace at 950°C for half an hour. Substances were stirred in the furnace to have bubble free sample. The melt was annealed in an annealing furnace kept at 350°C for two hours in a preheated brass mould to remove residual stresses present in the glass sample. Then the furnace was switched off and glass was allowed to cool inside until it reached room temperature.

The amorphous nature of the melt quenched glasses was verified by using Xpert Pro MPD, Cu K$\alpha$ =1.5405 Å in the range of 10° $\leq$ 2$\theta$ $\leq$ 80° while the optical properties were studied by UV-Vis Spectroscopy using Shimadzu UV-2600 spectrophotometer with air as reference. Structural properties were studied with the help of IRAffinity-1(Shimadzu Co. Japan) instrument equipped with DRS-8000A between ranges of 300-1500 cm$^{-1}$ using KBr pellet technique. To study the physical properties like density standard Archimedes Principle with ethanol as immersion liquid was employed on Shimadzu specific gravity measurement kit. Weight measurements were carried out using a Shimadzu (AUX220 series) analytical balance with accuracy up to 0.001gcm$^{-3}$. All the measurements were taken at room temperature.

| Sample Code | B$_2$O$_3$ (mol%) | ZnO (mol%) | PbF$_2$ (mol%) | Na$_2$O (mol%) | DyF$_3$ (mol%) |
|-------------|-------------------|------------|----------------|----------------|----------------|
| B70Dy0      | 70                | 17         | 10             | 3              | -              |
| B70Dy1      | 70                | 16         | 10             | 3              | 1              |
| B60Dy0      | 60                | 27         | 10             | 3              | -              |
| B60Dy1      | 60                | 26         | 10             | 3              | 1              |

3. Results and Discussion

3.1 X-Ray Diffraction (XRD):
In order to confirm the amorphous nature of the as prepared glasses, the X-ray Diffraction (XRD) has been performed. Fig.1 shows the XRD pattern of the doped and undoped samples. The XRD results exhibited a broad diffuse scattering at lower angle which is due to short range order in glass samples.
3.2 UV-Vis Spectroscopy: Optical band gap and Urbach Energy

Fig. 2 shows UV-visible absorption spectra of present glasses recorded in the wavelength range between 200 to 900 nm. The absorption spectra of the Dy$^{3+}$-doped samples reveal electronic transitions at 325 nm, 350 nm, 364 nm, 388 nm, 427 nm, 453 nm, 474 nm, 753 nm and 801 nm corresponding to transitions arise from ground state of Dy$^{3+}$ ($^6$H$_{15/2}$) to excited states $^6$P$_{7/2}$, $^6$P$_{3/2}$, $^4$P$_{3/2}$, $^4$I$_{15/2}$, $^4$F$_{9/2}$, $^6$F$_{3/2}$ and $^6$F$_{5/2}$ respectively [20, 21]. A blue shift is observed in absorption edge of B70Dy1 with respect to its corresponding host glass (i.e. B70Dy0). This shifting can be due to Dy$^{3+}$ ions, as these ions may be responsible for the delocalization of localized states of energy levels. The study of optical band gap is an important factor for describing the electronic nature of the glasses. A model, proposed by Mott and Davis [22] is used...
in the calculations. According to this model, the absorption coefficient varies with the angular frequency in the following formula:

\[ (h\nu) \alpha = A (h\nu - E_0)^n \]  

(1)

where A is a constant, \( E_0 \) is the optical band gap energy in eV, A is a constant, n is an index which can be assumed to have values of 1/2, 2 etc., depending on the nature of the electronic transition which is responsible for absorption.

A decrease in the values of both direct and indirect band gap was found with the addition of rare earth in the prepared glass system as indicated in table 2. It can be attributed to the structural changes induced in the system due to increase of the Non-Bridging Oxygens (NBO’s). As with the addition of DyF3, more of the BO4 units were converted to BO3+1 and hence increased the concentration of NBO’s. The NBO’s being easily polarizable leads to decrease in the band gap [23]. In order to study the disorderness in the as prepared glasses, Urbach energy is calculated by plotting a natural logarithm of absorption coefficient \( \alpha(h\nu) \) as a function of \( h\nu \) and then calculating inverse of its slope using the formula.

\[ \alpha(h\nu) = \beta \exp \left( \frac{h\nu}{\Delta E} \right) \]  

(2)

where \( \beta \) is constant, \( \nu \) is the photon energy and \( \Delta E \) is the Urbach energy which is the width of tail of localized sates in forbidden gap. It was observed that Urbach energy values increased with doping of dysprosium. This further indicated that with the addition of Dy3+ more NBO’s were formed in the system which increased the disorderedness in the prepared glasses.

| Sample Code | Band Edge (nm) | Direct Band Gap (eV) | Indirect Band Gap (eV) | Urbach Energy (eV) | Density (g/cm\(^3\)) |
|-------------|----------------|---------------------|------------------------|-------------------|----------------------|
| B70Dy0      | 300            | 3.67                | 3.73                   | 0.810             | 2.96                 |
| B70Dy1      | 285            | 3.58                | 3.69                   | 0.856             | 3.11                 |
| B60Dy0      | 286            | 3.69                | 3.56                   | 0.751             | 2.94                 |
| B60Dy1      | 289            | 3.61                | 3.51                   | 0.789             | 3.16                 |

3.3 Fourier transform infrared spectra (FTIR)

![Infrared spectra of the prepared samples](image-url)

*Figure 3.* Infrared spectra of the prepared samples
To analyze the local structure and prominent structural units of as prepared glasses with the change in the concentration of rare earth, FTIR analysis was done. FTIR analysis is generally inferred by the bending and stretching vibrations of the different structural units which the network is made of. The infrared absorption spectrum for the prepared series was recorded at room temperature in the wave number range 400 to 1600 cm⁻¹. With the addition of Dy³⁺ ions, several number of peaks in the FTIR spectrum can be evinced which specifies local structure of as prepared samples. Bands present in the spectrum correspond to the vibrations of various structural units present in the glass system. It can be observed from Fig. 3 three broad bands in range 600-800 cm⁻¹, 800-1100 cm⁻¹ and 1100-1600 cm⁻¹ were observed. Assignments of as observed bands with respect to their position are presented in table 3. Some of the variations in the IR spectra are observed with the addition of Dy³⁺ ions in the intensities due to formation of NBOs. This result is in accordance with the UV-Vis absorbance data.

Table 3. Assignment of bands observed

| S. No. | Band position (cm⁻¹) | Band assignment |
|--------|---------------------|-----------------|
| 1.     | 600-800             | B-O-B bending of diborate linkages [24-26] |
| 2.     | 800-1175            | B–O stretching vibration of [BO₄] units in di-, tri-, tetra- and pentaborate groups [25,27] |
| 3.     | 1175-1300           | B-O stretching vibrations in [BO₃] units from boroxol rings [26] |
| 4.     | 1300-1400           | Stretching vibrations of the B-O of trigonal [BO₃]³⁻ units in metaborate, pyroborates and orthoborates [26] |
| 5.     | 1350                | Anti- symmetric stretching vibrations with three NBOs of B-O-B groups [25,26] |

3.4 Physical Properties: Density

Density is an important physical property to study the compactness and structure of the prepared samples. The value of density has been derived from Archimedes principle using following formula.

\[ \rho = \frac{w_a}{w_a - w_l} \rho_l \]  

where \( \rho \) is density to be calculated, \( w_a \) is weight of sample in air and \( w_l \) is weight of sample in immersing liquid and \( \rho_l \) is density of liquid [28,29]. The temperature was 11ºC and density of ethanol at 11ºC = 0.7969 g/cm³. It has been observed from Table 2 that density of prepared samples increases with the addition of dysprosium. As it is a well-known fact that density is mass per unit volume. Addition of DyF₃ leads to increase in molecular mass of the system but Dy³⁺ ions occupy interstitial sites which leads to no variation in the volume and hence density increases.

4. Conclusion

We have prepared glass samples 70B₂O₃-(17-x) ZnO -10PbF₂-3Na₂O-xDyF₃ and 60B₂O₃-(27-x) ZnO-10PbF₂-3Na₂O-xDyF₃ where (x= 0, 1) using melt quenching technique. The amorphous nature of prepared system was confirmed through XRD studies. The effect of DyF₃ on borate glasses have been explained with the aid of UV- Vis and infrared spectroscopy. A decrease in the band gap value was observed with dysprosium introduction. Decrease in the band gap value is as a result of increase in the non-bridging oxygens. An Urbach energy results show the increase in the disorderedness owing to doping. Absorption spectra and band gap values reveals that the present system is sensitive to Dy³⁺ ions. The FTIR spectra confirms the result of the absorption spectra that doping of Dy³⁺ increases the NBO’s in the present system. Spectra as obtained using UV-Vis and FTIR spectroscopy suggest that glasses under study can be used in UV sensing devices and for lasing materials.
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