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SYNTHESIS AND STRUCTURAL STUDY ON BORATE & RARE EARTH DOPED GLASSES

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Abstract: This paper describes the synthesis and structural studies of the borate & rare earth doped borate glass system, $Na_2O–ZnO–ZnF_2–B_2O_3$ prepared by melt quenching method. Sodium borate containing ZnF_2 glasses have been synthesized by melt quenching technique over a wide composition range. The analyses of DSC and XRD did not show the crystallinity of the glass sample. ^{11}B MAS–NMR shows the presence of sharp peak around –14 ppm. From the IR studies, the broadening of the peak around 1200–1400 and 800–1100 cm–1 shows the presence of mixed linkages like B–O–B, B–O–Zn in the network. The rare earth substitution in to the host glass system does not change the glass transition temperature.

Keywords: Glasses, Melt quenching, XRD , Rare earths & Density.

INTRODUCTION:

B_2O_3 is one of the most common glass formers and is present in almost all commercially important glasses and it is often used as a dielectric material. Borate glasses can be formed over a wide range of modifier concentration at relatively lower melting temperatures (Pye et al 1978). In borate glasses, B_2O_3 is a basic glass former because of its higher bond strength, lower cation size and smaller heat of fusion. Therefore, the structural investigations of boron in these glasses are one of the most attractive points of borate glass formation and related doped systems. In the borate glasses, B^{3+} ions are triangularly co-ordinated by oxygen atoms and triangle units are corner bonded in a random configuration. The ^{11}B MAS NMR investigation (Greenblatt and Bray 1967; Kim and Bray 1974;) and the IR (Krogh-Moe 1965; Kamitsos et al 1987b) studies were important in identifying several borate groups consisting of boron–oxygen triangles and tetrahedra which form the glass network at various modification levels. The optical properties of rare earth ions and transition metal ions are decided by the structure of the host glass in which they are doped. These ions have absorption and fluorescence bands mainly in the visible and near IR regions and they are narrow for rare earth ions compared to those of transition metal ions. The absorption and fluorescence bands in rare earth ions are due to the electronic transitions which occur within the *4f* shell, which is well shielded by the outer *5s* and *5p* shells. On the other hand, in transition metal ions, the electronic transitions occur in the *3d* shell which is the outermost shell. The strong/sharp line absorption and fluorescence from rare earth doped glasses allow them to be used extensively as active media in optically pumped laser devices.

EXPERIMENTAL

Glasses having general formula 20Na2O-60B2O3-(20-x)ZnO-xZnF2 (BNZF) and $60B_2O_3$-$20TeO_2$-(20-x)ZnO-xZnF_2-0.2Eu^{3+} (x = 0, 5, 10, 15, 20) (x=0, 5,10,15,20) were prepared by mixing together the appropriate weights of analar grade chemicals Na2Co3, ZnO, ZnF2, H3BO3. The amorphous nature of the Eu-BTZF glasses was confirmed using X-ray diffraction (Philips PW1050/37) technique. Broad humps have been observed, a characteristic feature of amorphous materials. The glassy nature has also been ascertained and the glass transition temperatures (T_g) were determined using differential thermal analysis (Mettle Toledo-DTA 850) in the temperature range 50-400 ^{0}C. 11B MAS–NMR was recorded with a MSL-300 solid state high resolution spectrometer operating at 96·28 MHz. The chemical shift Raman spectra was recorded using 'SPEX 1403, 0.85 double spectrometer' with 90^0 scattering geometry. values were recorded with respect to resonance signal of BF3Et2O. The IR spectroscopic measurements were carried out in the range 400–1600 cm–1 using 'Perkin Elmer spectrum 1' in KBr media. All NMR/IR spectra were recorded at room temperature. All the glasses exhibited characteristic glass transition temperature and varied systematically as a function of alkali/divalent oxide concentration. The density of the glass samples were measured by Archimedes principle using benzene as an immersion liquid (density, ρ = 0·879 g/cc).

RESULTS AND DISCUSSIONS

The figure 1 shows the DTA graph of these glasses and figure 2 shows the variation of T_g with ZnF_2 mol%. The The DTA curves show endothermic changes, for all compositions, which are attributed to the glass transition temperature T_g. The progressive insertion of fluorine with a gradual introduction of (ZnO+ZnF_2) in Eu-BTZF glass system, in higher proportion, affects the glass transition temperature following the continuous tendency of increase.

The density of the glass samples were measured by Archimedes principle using benzene as an immersion liquid. Molar Volume was calculated from the molecular weight and density values. The density of Eu-BTZF glasses varies between 2.77 to 6.48 gm/cc. It is low for ZnF_2 free (Eu-0) glasses. The dependence of density and molar volume on composition is in agreement with the weight and size of the constituent oxides.

11B MAS–NMR spectra of BNZF glass series shows the presence of a sharp resonance peak at around –14 ppm (with respect to resonance signal of BF3 Et2O), which arises from boron atom in four coordination [BO4/2]–. There is a split peak at the base of all the [BO4/2]– signals which arises from boron atoms in [BO3/2]0 coordination (Silver and Bray 958:Bray 1985: Zhong and Bray 1989: Prabhakar et al 1992; Muthupari and Rao 1994). We have also examined variation of the fraction, N4 [N4 = B4/B3 + B4] of boron atoms in [BO4] units by finding area under the [BO4/2]– and [BO3/2]0 peaks. From figure 3, it is observed that the peak shifts towards longer wavelengths with increase in ZnF_2 i. e. for x = 0, 5, 20 mol% of ZnF_2. This indicates that the degree of covalency of Re-O band increases with ZnF_2 content. This is due to the tightening of the structure with the formation of BO_4 units and ZnO_4 units which results in increased interaction between the rare earth ions and charged NBO oxygens. Henrie and Choppin [28] have reported that in halide complexes, the degree of covalency of Nd-O increases in order Cl < Br < I as indicated by the shift of the peak wavelength by the transition of Nd^{3+} to longer wavelengths. The same behaviour is also seen in T_g behavior of the present glass system . But for x =10, 15 mol% of ZnF_2, the positions of the peak wavelengths of the bands of these glasses are

F→D transitions. And these are not allowed by either electric or magnetic dipole mechanisms as selection rules forbid certain of the transitions for which very weak absorption bands are observed.

CONCLUSIONS:

A synthesized glass confirms the glassy nature by XRD & Tg analysis. ^{11}B MAS–NMR, IR and DSC studies on Na2O–ZnO– ZnF2–B2O3 glass system have been carried out to ascertain the role of Zn2+ ion in these glasses. Analysis of 11B MAS–NMR indicates the dual role of Zn2+ as former and modifier. IR spectra indicate the presence of mixed linkages like B–O–B and B–O–Zn. The glass structure has been confirmed by XRD and DSC measurements

FIGURES:

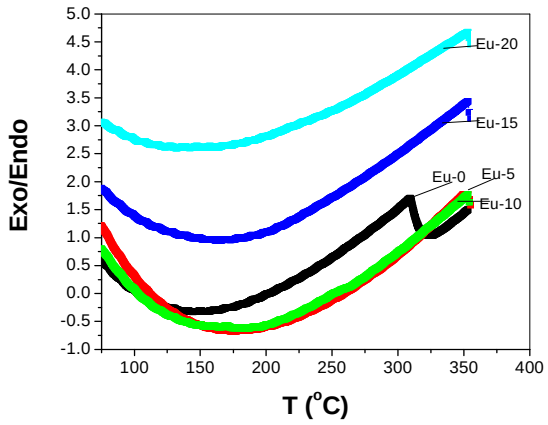

Figure 1 DTA Graph of Eu-BTZF glasses

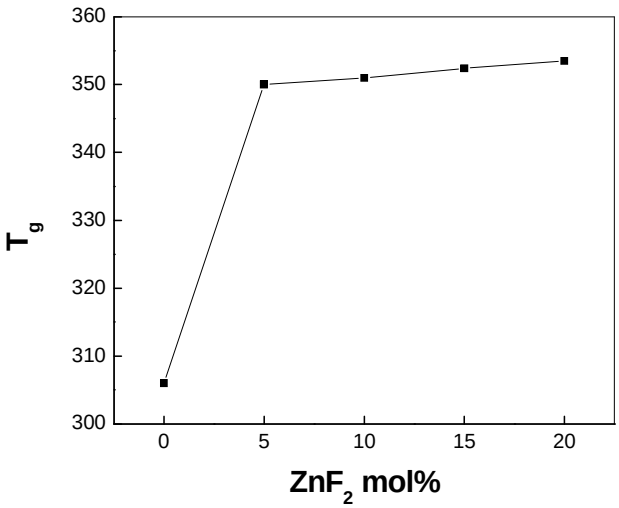

Figure 2 Variation of T_g with ZnF_2 mol% of Eu-BTZF glasses

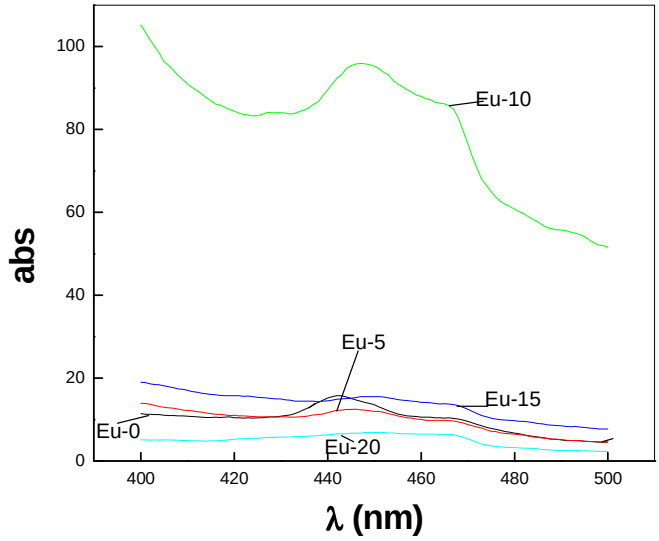

Figure 3. Fluorescence spectra of Eu-BTZF glasses.

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