# Synthesis and structural studies of $Na_2O$–$ZnO$–$ZnF_2$–$B_2O_3$ oxyfluoride glasses

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**Abstract.** This paper describes the synthesis and spectroscopic studies of the glass system, $20Na_2O$–$(20–x)$ $ZnO$–$xZnF_2$–$60B_2O_3$ ($x$ = 0, 5, 10, 15, 20), prepared by melt quenching method. 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.

**Keywords.** Borate glasses; oxyfluoride glasses; glass structure; MAS–NMR; IR.

## 1. Introduction

Oxyfluoride glasses are promising host glasses for optical applications because of their excellent optical properties, high refractive index, low dispersion and good transparency in the UV and IR regions. These glasses also possess good chemical and thermal stability as well (Sidebottom *et al* 1997). Oxyfluoride glasses can be formed in various glass matrices such as $SiO_2$, $TeO_2$, $P_2O_5$, $B_2O_3$ etc. Among all these, oxyfluoride glasses formed with $B_2O_3$ shows interesting behaviour because of the unique structure of $B_2O_3$.

$B_2O_3$ 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; Prabhakar *et al* 1990) and the IR (Krogh-Moe 1965; Kamitsos *et al* 1987b; Kamitsos and Chryssikos 1991) studies were important in identifying several borate groups consisting of boron–oxygen triangles and tetrahedra which form the glass network at various modification levels. It is known that in alkali modified borate glasses, up to 33·3 mol% of $Na_2O$, there is continuous formation of $BO_3 \rightarrow BO_4$ units and further increase in the alkali leads to reconversion of $BO_4 \rightarrow BO_3$ with non-bridging oxygen. PbO and ZnO can enter the glass network as a network former and also as a network modifier (Veeranna Gowda and Anavekar 2004). Due to this the structure of glass is expected to be different from that of alkali borate glasses (Kim and Bray 1974; Munia *et al* 1999). In the present study, we report the synthesis and structural studies of $Na_2O$–$ZnO$–$ZnF_2$–$B_2O_3$ oxyfluoride glasses and study the role of intersubstitution of ZnO by $ZnF_2$.

## 2. Experimental

### 2.1 *Materials and methods*

A series of five glasses were synthesized having the general formula, $20Na_2O$–$(20–x)$ $ZnO$–$xZnF_2$–$60B_2O_3$ ($x$ = 0, 5, 10, 15, 20), BNZF. Glasses were prepared by mixing together the appropriate weights of analar grade chemicals, $Na_2CO_3$, ZnO, $ZnF_2$ and $H_3BO_3$. The mixture was taken in a porcelain crucible and melted in an electric furnace at 1200°C to get a homogeneous melt. Different pieces of glasses with dimension $1 \times 1 \times 1$ cm were obtained by quenching the melt between two copper blocks.

The amorphous nature of glasses was confirmed using X-ray diffractometer (Philips, PW1050/37) by employing $CuK_\alpha$ radiation. The X-ray diffractogram did not show any sharp peaks, a characteristic of amorphous nature. The samples were crushed to powder and ^{11}B MAS–NMR was recorded with a MSL-300 solid state high resolution spectrometer operating at 96·28 MHz. The chemical shift

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values were recorded with respect to resonance signal of $BF_3Et_2O$. 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 variation of $T_g$ was determined using differential scanning calorimeter (Modulated DSC 2820) with small pieces of the samples in the temperature range 95–550°C. The density of the glass samples were measured by Archimedes principle using benzene as an immersion liquid (density, $\rho = 0.879$ g/cc).

## 3. Results and discussion

### 3.1 *Density*

Figure 1 shows the variation of density as a function of $ZnF_2$ concentration. As one can see from the figure the intersubstitution of ZnO by $ZnF_2$ leads to an increase in the density (from 2 g/cc to 3·4 g/cc) when 20ZnO is replaced by $20ZnF_2$. However, in the intermediate composition one can see that density fluctuates between 2·46 and 4·25 g/cc. This behaviour could probably be due to structural origin resulting from intersubstitution of ZnO by $ZnF_2$ and it is described again in the later sections.
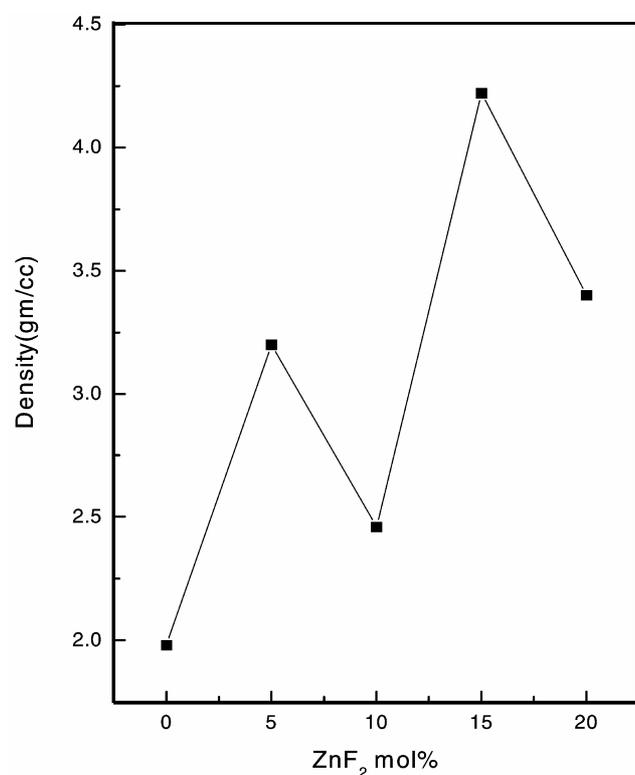
### 3.2 *Differential scanning calorimetry*

Figure 2 shows the variation of glass transition temperature, $T_g$, with $ZnF_2$ mol%. In general, $T_g$ is found to decrease with $ZnF_2$ concentration. A decrease in $T_g$ is a manifestation of the degradation of the glass network. This is because of the bigger size of $ZnF_2$ than ZnO that leads to open structure resulting in a decrease of $T_g$.

### 3.3 $^{11}B$ *MAS–NMR*

$^{11}$B MAS–NMR spectra of BNZF glass series are shown in figure 3. The spectra reveals the presence of a sharp resonance peak at around −14 ppm (with respect to resonance signal of $BF_3$ $Et_2O$), which arises from boron atom in four coordination $[BO_{4/2}]^-$. There is a split peak at the base of all the $[BO_{4/2}]^-$ signals which arises from boron atoms in $[BO_{3/2}]^0$ coordination (Silver and Bray 1958: Bray 1985: Zhong and Bray 1989: Prabhakar *et al* 1992; Muthupari and Rao 1994). We have also examined variation of the fraction, $N_4$ [$N_4 = B_4/B_3 + B_4$] of boron atoms in $[BO_4]$ units by finding area under the $[BO_{4/2}]^-$ and $[BO_{3/2}]^0$ peaks (Muniya *et al* 1999).

Figure 4 shows the variation of $N_4$ as a function of $ZnF_2$ concentration. As can be seen from the figure, the $N_4$ values do not vary systematically with intersubstitution of ZnO by $ZnF_2$. However, the values of $N_4$ are well below the diborate composition ($N_4 \approx 0.5$). Further, the



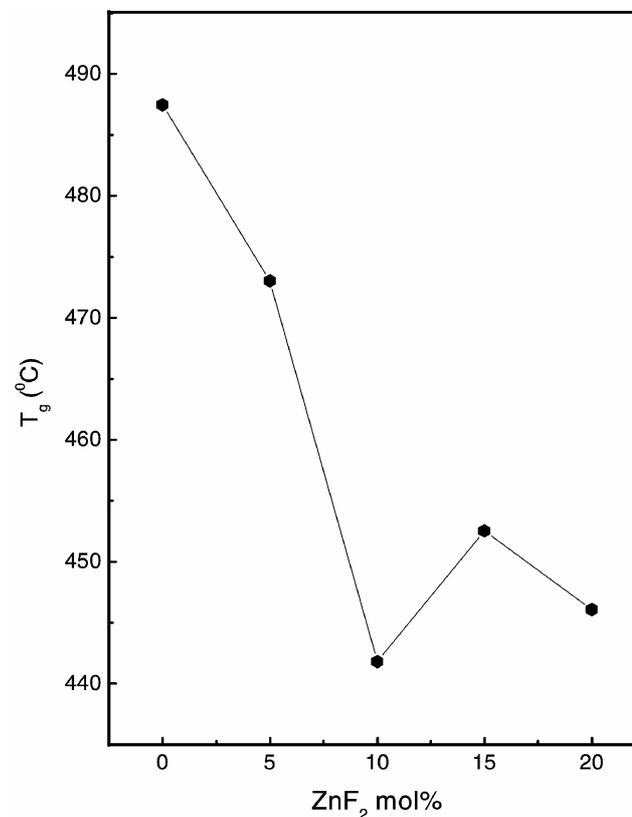**Figure 1.** Variation of density with $ZnF_2$ mol%.



**Figure 2.** Variation of $T_g$ with $ZnF_2$ mol%.

$N_4$ values of $ZnF_2$ free glasses are higher than those glasses containing $ZnF_2$. This is likely due to the dual role of $Zn^{2+}$ as former and modifier. The dual role of $Zn^{2+}$ is also reflected in the density variation as a function of $ZnF_2$ concentration.

### 3.4 *IR*

Infrared spectra of the BNZF glass series are shown in figure 5. IR spectra consists of three strong absorption regions. The vibrations in the region between 1200 and 1400 cm$^{-1}$ arises from borate units in which the boron atom is connected to three oxygens, $[BO_{3/2}]^0$ and the broadening in this region is due to the mixed linkages present. The response in the region between 800 and 1100 cm$^{-1}$ is due to boron atom in tetrahedral oxygen co-ordination $[BO_{4/2}]^-$ units. The B–O–B bending vibrations manifest in the lower frequency region between 600 and 800 cm$^{-1}$ (Krogh-Moe 1965; Selvaraj and Rao 1984; Kamitsos *et al* 1987a). The relative intensities of the peak also undergo significant changes as $ZnF_2$ concentration increases. The broadening of the peaks in the region
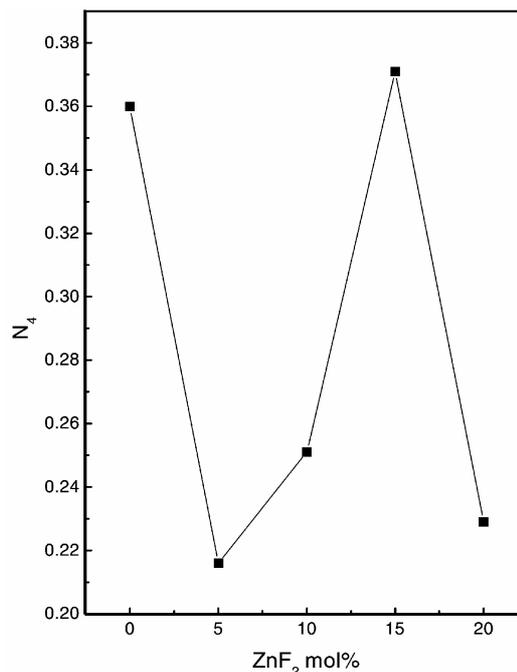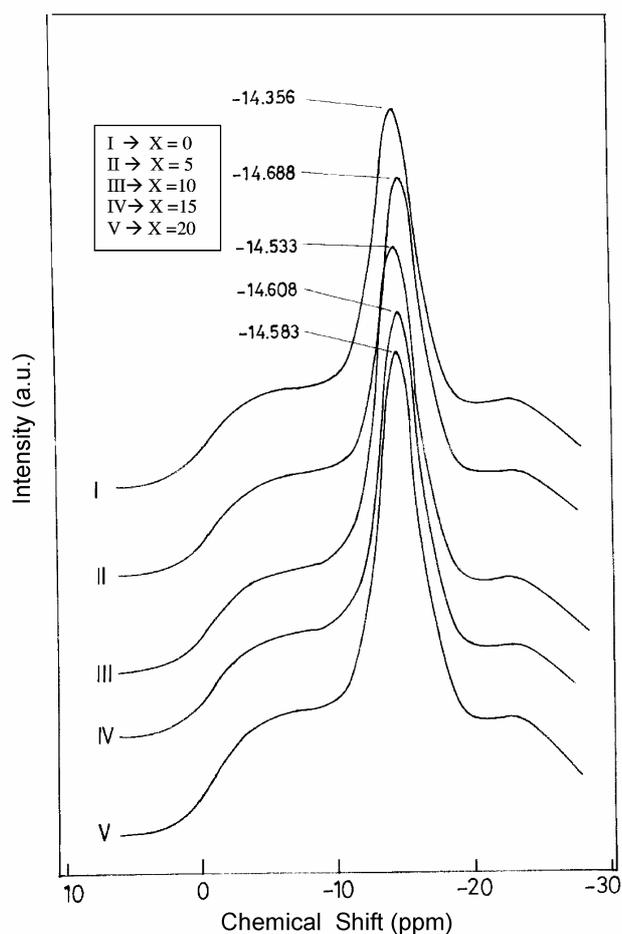


**Figure 4.** Variation of $N_4$ with $ZnF_2$ mol%.
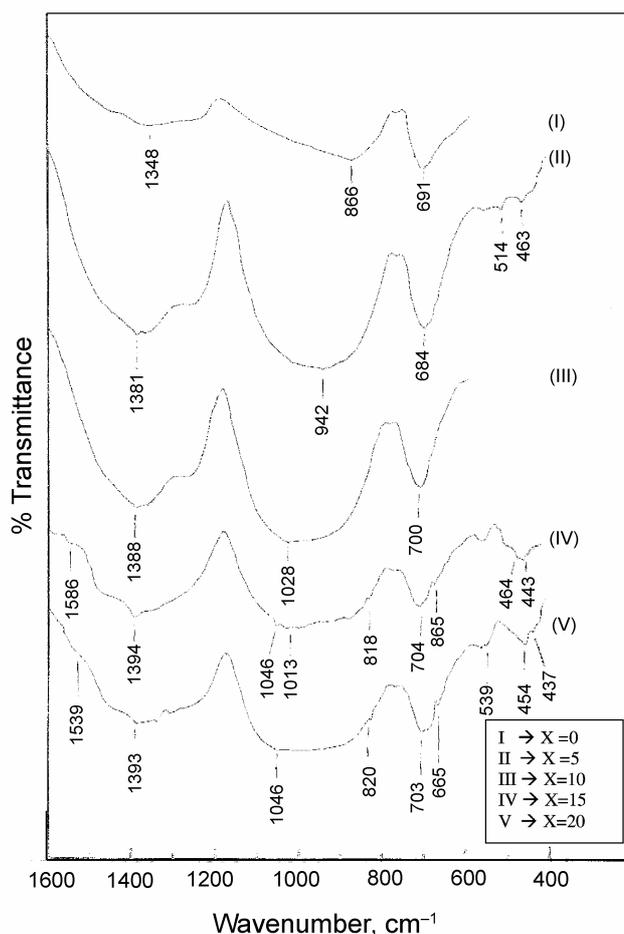


**Figure 3.** $^{11}$B MAS NMR spectra of BNZF glass system.



**Figure 5.** IR spectra of BNZF glass system.

1200–1400 cm$^{-1}$ and 800–1100 cm$^{-1}$ strongly indicates the presence of mixed bonding such as B–O–B and B–O–Zn. This observation is consistent with the variation of $N_4$ values.

## 4. Conclusions

$^{11}$B MAS–NMR, IR and DSC studies on $Na_2O$–$ZnO$–$ZnF_2$–$B_2O_3$ glass system have been carried out to ascertain the role of $Zn^{2+}$ ion in these glasses. Analysis of $^{11}$B MAS–NMR indicates the dual role of $Zn^{2+}$ 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.

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