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# Elastic properties of $Na_2O$–ZnO–$ZnF_2$–$B_2O_3$ oxyfluoride glasses

**SHANTALA D PATIL, V M JALI* and R V ANAVEKAR†**

Department of Physics, Gulbarga University, Gulbarga 585 106, India

†Department of Physics, Bangalore University, Bangalore 560 056, India

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**Abstract. Elastic properties of $Na_2O$–ZnO–$ZnF_2$–$B_2O_3$ oxyfluoride glasses with different $ZnF_2$ concentrations have been investigated using ultrasonic velocity measurements at room temperature, at a frequency of 10 MHz. Glasses prepared by melt quenching method were suitably polished for the ultrasonic velocity measurements using pulse-echo superposition method. Various elastic moduli have been calculated and their compositional dependence has been examined. The compositional dependence of elastic moduli with the concentration of $ZnF_2$ shows decrease in the moduli initially, with further increase in $ZnF_2$ the moduli sharply increases and then again tend to decrease when $ZnF_2$ concentration is 20 mol%. The values of Poisson's ratio lie in the range of 0·24–0·30, which is typical to covalent bonded network. The variation of $\theta_D$ with $ZnF_2$ indicates complex behaviour of the glass network. The results have been analysed in view of the modified borate glass network. Addition of $ZnF_2$ into the pure glass seems to influence the borate network by replacement of B–O–B linkages with B–O–Zn.**

**Keywords. Borate glasses; oxyfluoride glasses; elastic properties; dual role of $Zn^{2+}$.**

## 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). Recent interest extends to fast ion conductors, lasers and non-linear optical materials. The search for transparent glasses over a wide spectral range resulted in the recent developments in fluoride glasses. $B_2O_3$ is one of the most common glass formers and is present in almost all commercially important glasses. It is often used as a dielectric material and borate glasses possess scientific interest because of the occurrence of boron anomaly (Pye *et al* 1978). $B_2O_3$ is a basic glass former because of its higher bond strength, lower cation size and smaller heat of fusion. Synthesis and study of lanthanum borate, aluminum borate whiskers and borate glasses, in particular, have become subjects of great interest due to their structural peculiarities (Kamitsos and Karakassides 1989). The structure of borate glasses mainly consists of $[BO_{3/2}]^0$, $[BO_{4/2}]^-$ groups which get further modified into $[BO_{2/2}O]$, $[BO_{1/2}O]$ (Ardeleana and Toderasa 2006). The concentrations and modifications mainly depend on the amount of modifier oxide present in the glass system. It is a well known fact that addition of alkali oxide and alkaline earth oxide breaks the B–O–B bonds leading to compactness in the structure. As a consequence of structural changes, the properties of borate glasses vary in a non-linear way.

Elastic properties of borate glasses through ultrasound velocity measurements is one of the important techniques to elucidate the structure of glasses, since their properties have direct bearing on the bonding and interatomic forces. Sound velocity measurement at ultrasonic frequencies is used to determine the mechanical properties of glasses which can be directly related to the interatomic potential in the system. Several such elastic property-structure studies have been reported for oxide glasses (Kodama 1991a, b; Kodama *et al* 1995). Therefore, the structural investigation on boron in these glasses is one of the most attractive points of borate glass formation and related doped systems. The measurement of ultrasonic parameters such as velocity and attenuation as a function of composition, temperature and frequency is of great interest in glasses. These ultrasonic parameters besides density and molar volume are sensitive and informative about the changes occurring in the structure of glass network (Yasser Saddeek 2004). The properties of glasses are closely related to inter-atomic forces and potential in the lattice structure. Therefore, any change in the lattice due to modifier doping can be directly noted. These aspects need a basic understanding of the relationship between the structure of the glass and its macroscopic behaviour for the design of materials suitable for specific

*Author for correspondence (vmjali@rediffmail.com)

applications. Alkali borate glasses have been extensively studied over the years to elucidate the nature and relative concentration of various borate units constituting the glass network. The ability of boron to exist in three and four oxygen coordinated environments and the high strength of covalent B–O bonds enable borates to form stable glasses. In $Na_2O$–$B_2O_3$ glass system (Krause and Kurkjian 1978), the elastic properties have been discussed in terms of boron coordination. The elastic properties of various borate glasses have also been reported (Yawale *et al* 1992; Pakade *et al* 1995). The structure of borate glasses is completely different from other glasses such as phosphate and silicate glasses. It has been shown that $Zn^{2+}$ ions in $Na_2O$–ZnO–$B_2O_3$ glass system prefer to be in the network forming positions (Veeranna Gowda and Anavekar 2004). They have pointed out that the oxyfluoride glasses are potential candidates because of their unique optical properties. In this communication, we report the effects of the addition of $ZnF_2$ in the $Na_2O$–ZnO–$B_2O_3$ glasses.

## 2. Experimental

### 2.1 *Sample preparation*

Glasses having general formula, $20Na_2O$–$(20–x)$ZnO–$xZnF_2$–$60B_2O_3$ [BNZF] ($x = 0$, 5, 10, 15, 20), were prepared (Shantala *et al* 2008) by mixing together the appropriate weights of analar grade chemicals $Na_2CO_3$, ZnO, $ZnF_2$ and $H_3BO_3$. The mixtures were taken in a porcelain crucible and melted in an electric furnace at about 1200°C to get a homogeneous melt. Glasses were obtained by quenching the melt between two copper blocks. For ultrasonic measurements, a special sample mould was used (10 × 10 mm). The cylindrical shaped samples were obtained for ultrasonic measurements by quenching the melt in a brass mould which was pre-heated (at about 200°C) to avoid breaking of the samples due to thermal strains. All the samples were annealed below their glass transition temperature. A high degree of parallelism and flatness of the surfaces of the sample are essential to obtain good echo pattern during the measurement of the ultrasonic delay times. Utmost care was taken to achieve the flatness on the glass surfaces.

The amorphous nature of the glasses was confirmed by X-ray diffraction using X-ray diffractometer (Philips, PW1050/37) by employing $CuK_\alpha$ radiations. The X-ray diffractogram did not show any sharp peaks, a characteristic of amorphous nature. The density of the glass samples was measured by Archimedes principle using benzene as an immersion liquid (density, $\rho = 0{\cdot}879$ g/cc). Molar volume ($M_V$) was calculated from the molecular weight ($M$) and density ($\rho$) using the relation, $M_V = M/\rho$.

### 2.2 *Elastic measurements*

The various elastic properties of the glasses were calculated using the following relations (Mcskimin 1965)

Longitudinal modulus, $L = \rho V_l^2$,

Shear modulus, $G = \rho V_t^2$,

Bulk modulus, $K = L - \frac{4}{3}G$,

Young's modulus, $E = (1 + \sigma)2G$,

Poisson's ratio, $\sigma = (L - 2G)/2(L - G)$,

and

Debye temperature, $\theta_D = \frac{h}{k}\left[\frac{3\rho q N_A}{4\pi M}\right]^{1/3} V_m$,

where $L$, $G$, $K$ and $E$ are longitudinal, shear, bulk and Young's modulus, respectively. $\rho$, $\sigma$, $\theta_D$, $V_l$ and $V_t$ are the density, Poisson's ratio, Debye temperature, longitudinal and shear sound velocities, respectively. The mean sound velocity, $V_m$, is defined by the relation

$$\frac{3}{V_m^3} = \frac{1}{V_l^3} + \frac{2}{V_t^3}.$$

For elastic measurements, samples were polished using a lapping tool method and uniform parallel surface of the samples were achieved. Ultrasonic velocity measurements were carried out at room temperature, at a frequency of 10 MHz using $x$-cut and $y$-cut quartz transducers. A pulse superposition technique was employed using ultrasonic interferometer (System Dimensions, Bangalore). Salol (phenyl salicilate) was used as a bonding material between the glass sample and the transducers. Using Mcskimin $\Delta t$ criteria, the round trip delay time, $\tau$, has been calculated (Mcskimin 1961; Mcskimin and Andreatch 1962). By measuring the thickness of the sample ($d$), longitudinal ($V_l$) and transverse ($V_t$) wave velocities were calculated using the relation, $V = 2d/\tau$.

## 3. Results and discussion

The values of density, molar volume, sound velocities, elastic moduli, Poisson's ratio and Debye temperature and the glass transition temperature for BNZF glasses are given in table 1. Density is one of the effective tools to explore the degree of structural compactness as can be seen from figure 1. Modification of the geometrical configurations of the glass network leads to changes in the coordination and variation of the interstitial holes. This behaviour could be probably due to structural origin resulting from intersubstitution of ZnO by $ZnF_2$ which is attributed to the rearrangement of the structure with addition of $ZnF_2$ in $Na_2O$–$B_2O_3$–ZnO glass network. This is

**Table 1.** The code, density, molar volume, transition temperature, velocity, dimensionality, elastic moduli, Debye temperature and $N_4$ values for BNZF glasses.

| The code | Density (g/cc) | Mol. vol. (cc) | $V_l$ (m/s) | $V_t$ (m/s) | $V_m$ (m/s) | $T_g$ (°C) | $K$ (GPa) | $E$ (GPa) | $L$ (GPa) | $G$ (GPa) | $\sigma$ | $D$ | $\theta_D$ (K) | $N_4$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BNZF0 | 1·98 | 35·58 | 4787 | 2800 | 3107 | 487 | 24·79 | 38·44 | 45·40 | 15·50 | 0·24 | 2·50 | 375 | 0·36 |
| BNZF5 | 3·20 | 22·36 | 4085 | 2103 | 2351 | 473 | 34·64 | 37·22 | 53·40 | 14·10 | 0·32 | 1·60 | 325 | 0·22 |
| BNZF10 | 2·46 | 29·53 | 2567 | 1283 | 1442 | 441 | 10·81 | 10·77 | 16·20 | 4·05 | 0·33 | 1·49 | 318 | 0·25 |
| BNZF15 | 4·22 | 17·47 | 5540 | 2773 | 3107 | 452 | 86·34 | 86·32 | 129·50 | 32·45 | 0·33 | 1·50 | 483 | 0·37 |
| BNZF20 | 3·40 | 22·01 | 2680 | 1421 | 1587 | 446 | 15·27 | 17·84 | 24·40 | 6·86 | 0·30 | 1·79 | 323 | 0·23 |

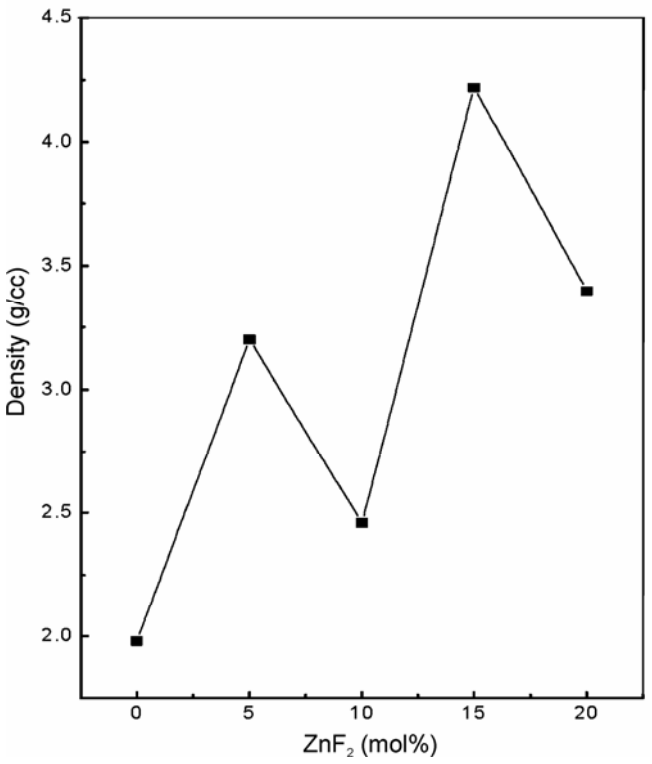


**Figure 1.** Variation of density with $ZnF_2$ mol%.

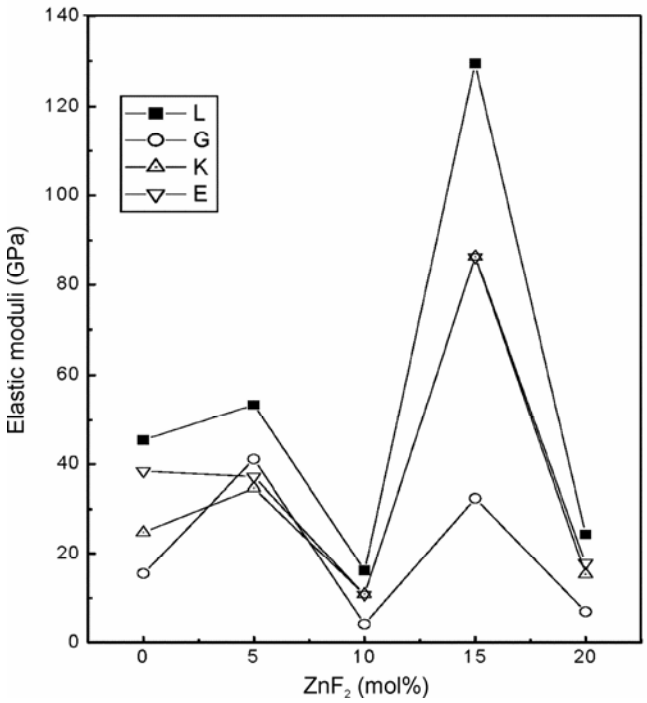


**Figure 2.** Variation of elastic moduli with $ZnF_2$ mol%.

also reflected in the variation of molar volume with $ZnF_2$ concentration.

The compositional dependence of the various elastic moduli as a function of $ZnF_2$ concentrations is shown in figure 2. Initially, with increase in $ZnF_2$ (5 mol%) the moduli increase and tend to decrease with further increase in $ZnF_2$ (up to 10 mol%). It then increases almost by a factor of 3 (pronounced in case of L) and at 20 mol% of $ZnF_2$, the moduli again decrease. The trends in the variation of moduli with $ZnF_2$ clearly suggest that the addition of $ZnF_2$ in base glass $Na_2O$–ZnO–$B_2O_3$ leads to significant structural rearrangements in the network. It is well known that pure $B_2O_3$ glass structure is two-dimensional comprising of boroxyl rings and boron in three coordinated ($BO_{3/2}$). With the addition of modifiers such as $Na_2O$ (up to 33·3 mol%) the structure becomes three-dimensional due to conversion of boron to form four coordinated ($BO_{4/2}$). The scheme of modification is represented by the following equation

$$2BO_{3/2} + O^{2-} \rightarrow 2[BO_{4/2}]^{-}.$$

With further addition of the modifier, the coordination of boron changes from ($BO_{4/2}$) to three coordinated boron $(BO_{2/2}\,O)^{-}$, this is referred to as reconversion.

In the present glass system, the modifier composition ($Na_2O$ + ZnO + $ZnF_2$) is 40 mol% i.e. quite above 33·3 mol%. In this composition, both four and three co-ordinated boron with non-bridging oxygen (NBO) are present. The presence of NBO would weaken the structure and the moduli would decrease. However, as seen from figure 2, the moduli tend to decrease and increase in the intermediate concentration of $ZnF_2$, clearly suggesting the dual role of $Zn^{2+}$ in this glass system. It is possible that due to addition of $Zn^{2+}$ into the glass network,

$Zn^{2+}$ acts as a network former and modifier by transfer of bridging and non-bridging oxygens. A similar observation has been made in $BiO_2$–$TeO_2$–PbO glass system.

The compositional dependence of Poisson's ratio and Debye temperature as a function of $ZnF_2$ concentration are shown respectively, in figures 3 and 4. The values of Poisson's ratio lie in the range of 0·24 to 0·30. These values are typical of a covalently bonded network. The initial increase in the Poisson's ratio is likely to be due to weakening of the structure due to the presence of non-bridging oxygens. It increased in the reconversion region from 0·24 to 0·32 after doping 5 mol% of $ZnF_2$ to ZnO and is not much affected by the crossover from reconversion to conversion region. As can be seen from figure 4, $\theta_D$ decreases with increase of $ZnF_2$ (up to 10 mol%) and there is a sharp increase in $\theta_D$ followed by a decrease at 20 mol% of $ZnF_2$. The initial decrease in $\theta_D$ is associated with the weak network and further increase is indicative

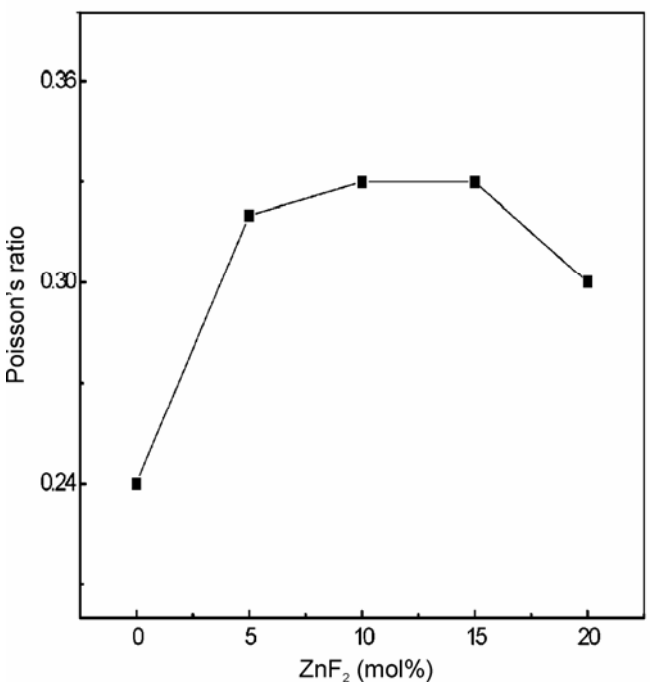


**Figure 3.** Variation of Poisson's ratio with $ZnF_2$ mol%.

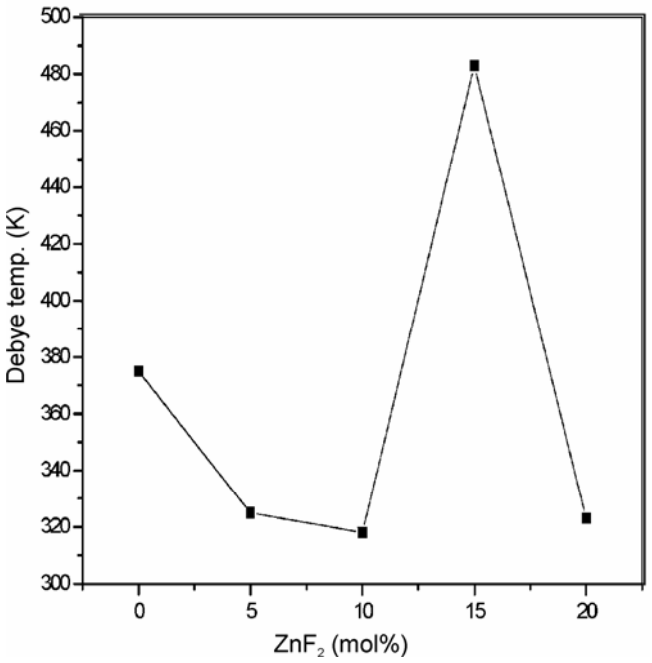


**Figure 4.** Variation of Debye temperature with $ZnF_2$ mol%.

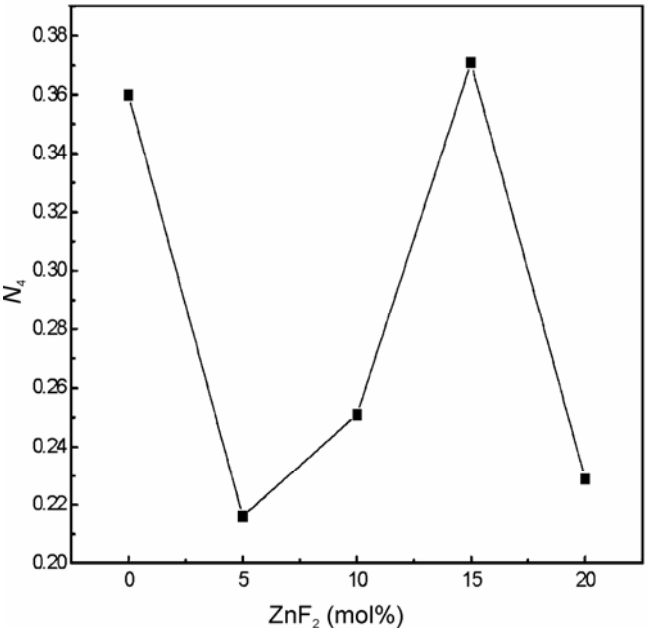


**Figure 5.** Variation of $N_4$ with $ZnF_2$ mol%.

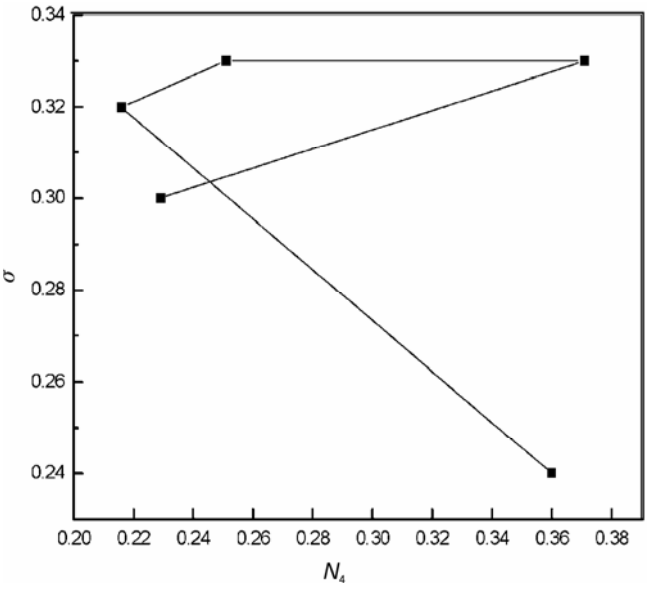


**Figure 6.** Variation of Poisson's ratio with $N_4$.

of the compactness in the structure. This behaviour is likely to be due to dual role of $Zn^{2+}$ and presence of non-bridging oxygens. As can be seen from figure 5, $N_4$ values lie in the range of 0·20–0·36 which are well below the diborate composition, $N_4 = 0{\cdot}5$. These values of $N_4$ suggest the possible dual role of $Zn^{2+}$. The dimensionality factor is evaluated using $D = 2(B_3) + 3(B_4) + (B_2)$ which also varies in a similar way as $\theta_D$. Variation of Poisson's ratio as a function of $N_4$ is shown in figure 6. The increase of Poisson's ratio in the reconversion region is associated with a corresponding decrease in $N_4$ value. In the conversion region, Poisson's ratio is insensitive with the variation of $ZnF_2$ and $N_4$. We have also carried out $^{11}B$ MAS-NMR studies (Shantala *et al* 2008) on this glass system and calculated the $N_4$ values.

The present study attempts to correlate the changes in elastic moduli to the anticipated structural changes in the borate network. This is supported by the observed changes in molar volume and elastic moduli. Such type of non-linear changes in sound velocities is associated with the role of $Zn^{2+}$ in the network forming position.

## 4. Conclusions

Elastic properties of $Na_2O$–ZnO–$ZnF_2$–$B_2O_3$ oxyfluoride glasses have been investigated to ascertain the role of $Zn^{2+}$ ions in these glasses. The changes in elastic moduli are correlated to the anticipated structural changes in the borate network. The values of Poisson's ratio lie in the range of 0·24–0·30, which is typical to covalent bonded network. The variation of $\theta_D$ with $ZnF_2$ indicates complex behaviour of the glass network. This type of non-linear changes in sound velocities, elastic moduli are associated with the role of $Zn^{2+}$ in the network forming position. The results have been analysed in view of the modified borate glass network. The present glass system to begin with itself is in reconversion region. Therefore, a decrease in sound velocity is expected. Addition of $ZnF_2$ into the pure glass seems to influence the borate network by replacement of B–O–B linkages with B–O–Zn.

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