Elastic properties and spectroscopic studies of Na_2O–ZnO–B_2O_3 glass system

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Abstract. Elastic properties, ^{11}B MAS–NMR and IR spectroscopic studies have been employed to study the structure of Na_2O–ZnO–B_2O_3 glasses. Sound velocities and elastic moduli such as longitudinal, Young's, bulk and shear modulus have been measured at a frequency of 10 MHz as a function of ZnO concentration. Both sound velocities and elastic moduli increase with increasing ZnO concentration. Poisson's ratio and Debye temperature were also found to increase with ZnO concentration. ^{11}B MAS–NMR and IR spectra show characteristic features of borate network and compositional dependence trends as a function of Na_2O/ZnO concentration. The results are discussed in view of borate network and dual structural role of Zn^{2+} ion into the network. The results indicate that the Zn^{2+} ions are likely to occupy network forming positions in this glass system.

Keywords. Borate glasses; elastic properties; MAS–NMR; IR; network former.

1. Introduction

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 co-ordinated environments and the high strengths of covalent B–O bonds enables borates to form stable glasses. The ^{11}B NMR investigation (Greenblatt and Bray 1967; Kim and Bray 1974; Prabakar *et al* 1990) and the IR work (Krogh-Moe 1965; Kamitsos *et al* 1987a,b; Kamitsos and Chryssikos 1991) were important in identifying several borate groups consisting of boron–oxygen triangles and tetrahedra which forms the glass network at various modification levels. Alkali borate glasses containing divalent oxide such as PbO, MgO and ZnO show an interesting behaviour. Structural and NMR studies on Li_2O–PbO–B_2O_3 and Na_2O–MgO–B_2O_3 glasses show that the divalent ions, Pb^{2+} and Mg^{2+}, are in network forming and network modifying positions (Kim and Bray 1974; Munia *et al* 1999a). The pressure dependence studies of Na^+ ion conductivity on Na_2O–ZnO–B_2O_3 glasses has also indicated that the Zn^{2+} ions prefer network forming positions (Anavekar *et al* 1989). The dual role of divalent ions is not only seen in borate glasses but also in silicate and phosphomolybdate glasses and these aspects have been thoroughly investigated by using various techniques (Damodaran *et al* 1988).

Among the various experimental methods available for studying structure–property relations, elastic properties of solid materials are of considerable significance. Because their measurement yields information concerning the forces that are operative between the atoms or ions comprising solid. This is fundamentally important in interpreting and understanding the nature of bonding in the solid state. Therefore, the choice of the most appropriate material for particular application requires a knowledge of its mechanical properties. Hence, elastic properties are suitable for describing the glass structure as a function of composition (Schreiber *et al* 1973). There have been studies reported (Kodama 1991; Kodama *et al* 1993, 1995) on several binary alkali borate glasses which show that there is a correlation between elastic properties and borate glass structure. 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 (Singh *et al* 1990; Yawale *et al* 1992; Pakade *et al* 1995). In this communication, we examine the role of Zn^{2+} ion in Na_2O–B_2O_3 glass system using elastic properties and ^{11}B MAS–NMR and IR spectroscopy.

2. Experimental

Three series of glasses were synthesized having general formulae:

(1) $x$$Na_2O$–$y$ZnO–$(100 - x - y)$$B_2O_3$ constant B/Na series (CBNa),

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(2) xNa$_2$O–10ZnO–(90 – x)B$_2$O$_3$ constant Zn series (CZn) (x = 5, 10, 15, 20, 25 and 30 mol%) and
(3) 10Na$_2$O–xZnO–(90 – x)B$_2$O$_3$ constant Na series (CNa) (x = 5, 10, 15, 20, 25 and 30 mol%).

Glasses were prepared by mixing together the appropriate weights of analar grade chemicals, Na$_2$CO$_3$, ZnO and H$_3$BO$_3$. The mixtures were then 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 fabricated (10 × 10 mm). The cylindrical shaped samples were obtained for ultrasonic measurements by quenching the melt in a brass mould which was preheated (about 200°C) to avoid breaking of the samples due to thermal strains. All the samples were annealed below their glass transition temperature. The glasses were checked by X-ray diffraction for their amorphous nature using X-ray diffractometer (model Rigaku DMAX-1C) by employing Cr-Ka 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 spectra were recorded with a Bruker MSL-300 solid state high resolution spectrometer operating at 96·28 MHz. The chemical shift values were recorded with respect to the resonance signal of BF$_3$ Et$_2$O. The infrared spectroscopic measurements have been carried out in the range 400–1600 cm^{-1} using Nicolet 740 FTIR spectrometer. All NMR/IR spectra were recorded at room temperature.

The density of glass samples were measured by Archimedes principle using toluene as immersion liquid (density = 0·86 g/cm^3). Molar volume was calculated from the molecular weight (M) and density (r) using the relation, $M_v = M/r$.

2.1 *Elastic measurements*

For elastic measurements, samples were polished using a lapping tool and uniform parallel surfaces of the samples were achieved. Ultrasonic velocity measurements were carried out 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 samples and transducers. Using Mcskimin's Δt criteria the round trip delay time 't' have 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, $V = 2d/t$.

The various elastic properties of the glasses were calculated using the following relations.

Longitudinal modulus, $L = rV_l^2$,   (1)

Shear modulus, $G = rV_t^2$,   (2)

Bulk modulus, $K = L - (4/3)G$,   (3)

Young's modulus, $E = (1 + s)2G$,   (4)

Poisson's ratio, $s = (L - 2G)/2(L - G)$ and   (5)

Debye temperature, $q_D = (h/k)[(3rqN_A)/(4pM)]^{1/3}V_m$,   (6)

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

$$3/V_m^2 = 1/V_l^3 + 1/V_t^3.$$ (7)

3. Results and discussion

3.1 *Density and molar volume*

The variation of density and molar volume of CBNa glass series is shown in figure 1. It can be seen from figure 1 that the density increases monotonically while the molar volume decreases with the increase of ZnO concentration. The variation of density with ZnO concentration can be explained by considering the structural changes occurring in the coordination of boron glass network. The structure of crystalline as well as amorphous B$_2$O$_3$ is made up of planar [BO$_{3/2}$]^0 triangles (Bray and O'Keefe 1963; Bray
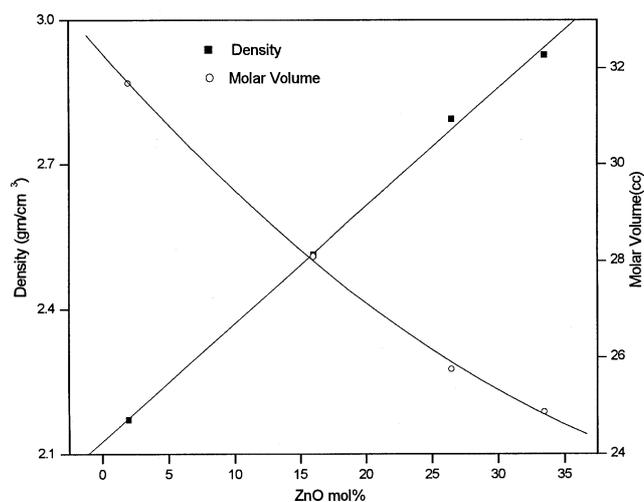

Figure 1. Variation of density and molar volume vs ZnO mol% for xNa$_2$O–yZnO–(100 – x)B$_2$O$_3$ glass system.

1996). In amorphous B$_2$O$_3$, most of these triangles are arranged into boroxyl rings in which three oxygens are part of the ring and three oxygens are outside the ring. These rings are randomly interconnected through loose $[BO_{3/2}]^0$ units. Due to the addition of modifying alkali oxide such as Li$_2$O, Na$_2$O, the three coordinated triangle boron $[BO_{3/2}]^0$ units are converted to four coordinated boron tetrahedra $[BO_{4/2}]^-$ and thus the network dimensionality and connectivity increases (Warren 1941; Abe 1952). This would lead to efficient packing and compactness in the structure. This is also reflected in the variation of molar volume vs ZnO concentration.

3.2 *Elastic properties*

3.2a *Sound velocities:* The elastic moduli are proportional to the square of velocity and a plot of sound velocities vs composition is indicative of relative structure. The compositional dependence of longitudinal (V_l) and transverse (V_t) sound velocities are shown in figure 2. Figure 3a shows the variation of elastic moduli as a function of ZnO concentration. As can be seen from figures 2 and 3a, both V_l, V_t and elastic moduli increase with the increase of ZnO concentration over the entire composition studied.

This variation of ultrasonic wave velocities and elastic moduli can be explained on the basis of the structural consideration of borate network. As pointed out in the earlier section, the vitreous B$_2$O$_3$ consists of planar $[BO_{3/2}]^0$ triangles (Bray and O'Keefe 1963; Bray 1996). The addition of alkali oxide to B$_2$O$_3$ network creates $[BO_{4/2}]^-$ units. This leads to increase in the network dimensionality and connectivity. Hence, both velocities and elastic moduli increase with the increase of ZnO concentration. It may also be noted from figure 3a that the rate
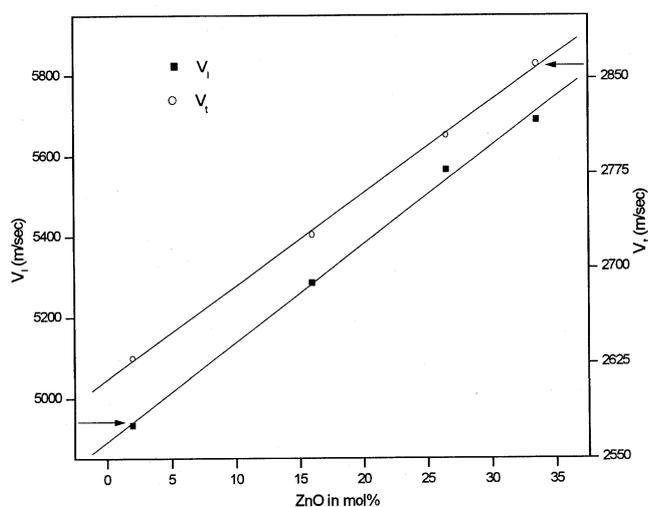
of change of elastic moduli is more pronounced in *L* and least in case of *G*. This indicates resistance to deformation and it is most probably due to presence of large number of covalent bonds (Rao *et al* 1984; Wang *et al* 1991; Munia *et al* 1999a).

It is a well known fact that in borate glasses, addition of alkali oxide to B$_2$O$_3$ network creates $[BO_{4/2}]^-$ units up to 33·3 mol% of modifying oxide, further addition of modifying oxide leads to reconversion of $[BO_{4/2}]^-$ to $[BO_{3/2}]^-$ units (Bray 1996) and this leads to loose structure because of the presence of non bridging oxygens (NBOs). In the present glass system if ZnO were to be incorporated into the network as a glass modifier, one would have expected decrease in both velocities and elastic moduli when the effective concentration of modifier oxide (Na$_2$O + ZnO) were to exceed 33·3 mol% (Krause and Kurkjian 1978). Therefore, above 33·3 mol% of modifier concentration the network consists of only $[BO_{4/2}]^-$ tetrahedra along with $[BO_{3/2}]^0$ triangles. This strongly suggests that the excess of oxygens supplied by the modifier has been utilized by Zn^{2+} and it is likely to be incorporated into the network as a glass former.

3.2b *Poisson's ratio:* The compositional dependence of Poisson's ratio and Debye temperature as a function of ZnO concentration is shown in figure 3b. Poisson's ratio is the ratio of transverse and linear strains for a linear stress. Poisson's ratio has also been discussed in terms of the dimensionality of glass network and it is observed that the Poisson's ratio for a three dimensional network is less than that of a two dimensional structure, which in turn is less than that of a one dimensional structure. This has been attributed to the fact that the concentration of bonds resisting a transverse deformation decreases in that order (Damodaran and Rao 1989a).

As it can be seen from figure 3b, the Poisson's ratio is found to increase even when the effective concentration of modifier is > 33·3 mol%. This again suggests that there are no $[BO_{3/2}]^-$ groups formation with NBOs. Further, the values of Poisson's ratio are that of covalently bonded structure. The gradual increase of Debye temperature also suggests increase in the compactness in the structure leading to increase in mean sound velocity (Damodaran *et al* 1989b).

The above observation based on the elastic properties indicates that the Zn^{2+} ion prefers network forming position and the observation seems to be consistent with the spectroscopic studies which are discussed below.

3.3 ^{11}*B MAS–NMR studies*

^{11}B MAS–NMR spectra of CZn and CNa glass series are shown in figures 4a and b, respectively. The spectra reveals the presence of a sharp resonance peak at around –2 ppm (with respect to resonance signal of BF$_3$ Et$_2$O)


Figure 2. Variation of sound velocities vs ZnO mol% in xNa$_2$O–yZnO–(100 – x)B$_2$O$_3$ glass system.
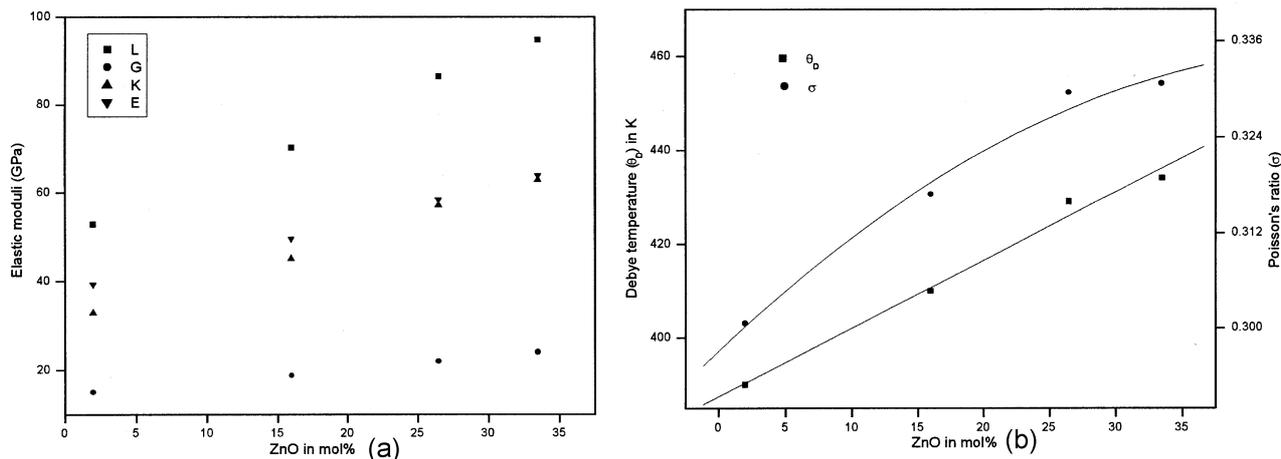
Figure 3. **(a)** Variation of elastic moduli vs ZnO mol% in xNa$_2$O–yZnO–$(100 - x)$B$_2$O$_3$ glass system and **(b)** variation of Poisson's ratio and Debye temperature ZnO mol% in xNa$_2$O–yZnO–$(100 - x)$B$_2$O$_3$ glass system.
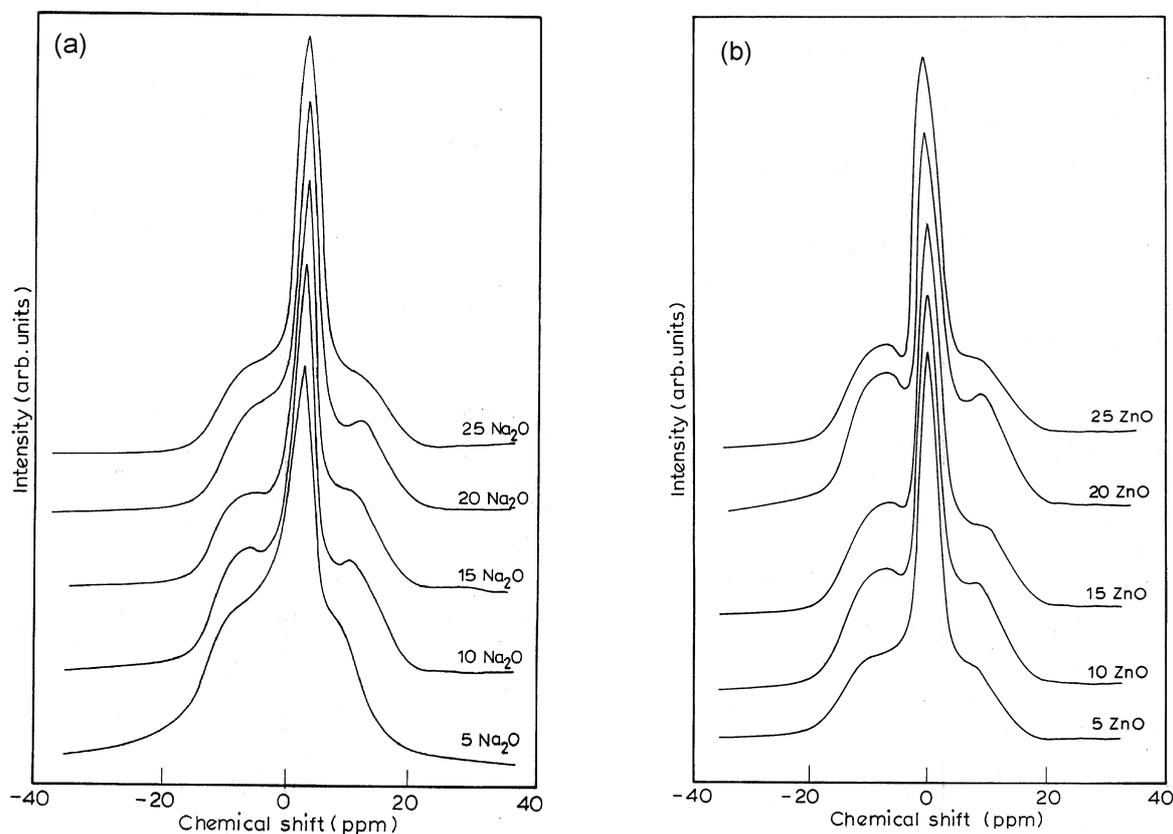
Figure 4. ^{11}B MAS NMR spectra of **(a)** xNa$_2$O–10ZnO–$(90 - x)$B$_2$O$_3$ glass system and **(b)** 10Na$_2$O–xZnO–$(90 - x)$ B$_2$O$_3$ glass system.

which arises from boron atom in four-coordination [BO$_{4/2}$]$^-$ (Silver and Bray 1958; Bray 1985; Zhong and Bray 1989; Prabakar *et al* 1992; Muthupari and Rao 1994). 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; Prabakar *et al* 1992; Muthupari and Rao 1994). In CZn glass series the intensities of BO$_4$ peak are found to increase with increase of Na$_2$O concentration at the expense of BO$_3$ peak. Whereas in CNa glass series the peak intensities are almost constant. We have also examined variation of the fraction, N_4 [$N_4 = B_4/(B_3 + B_4)$] of
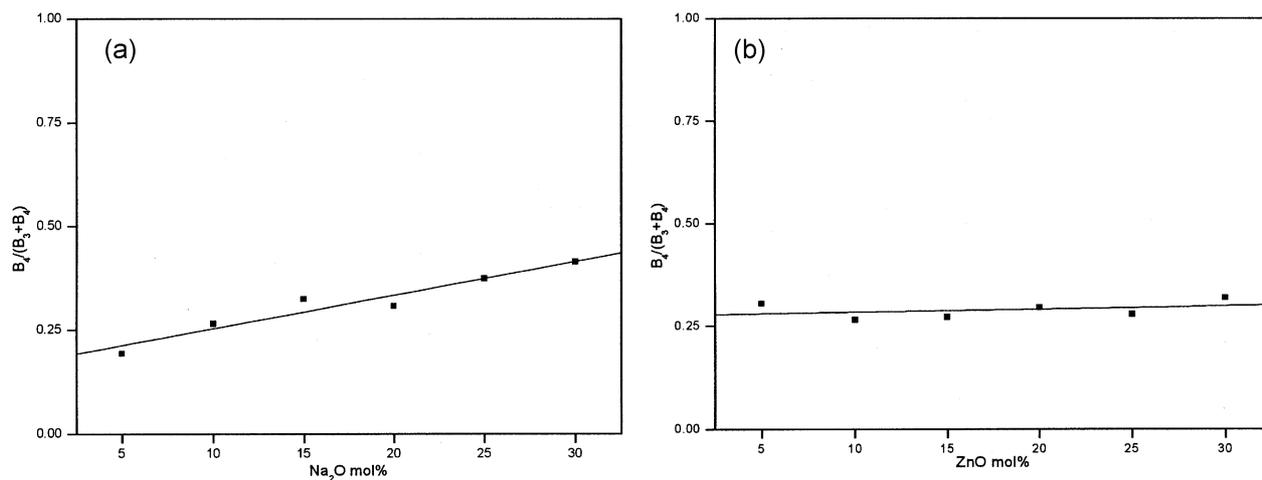
Figure 5. **(a)** Variation of N_4 vs Na$_2$O mol% in xNa$_2$O–10ZnO–$(90 - x)$B$_2$O$_3$ glass system and **(b)** variation of N_4 vs ZnO mol% in 10Na$_2$O–xZnO–$(90 - x)$B$_2$O$_3$ glass system.
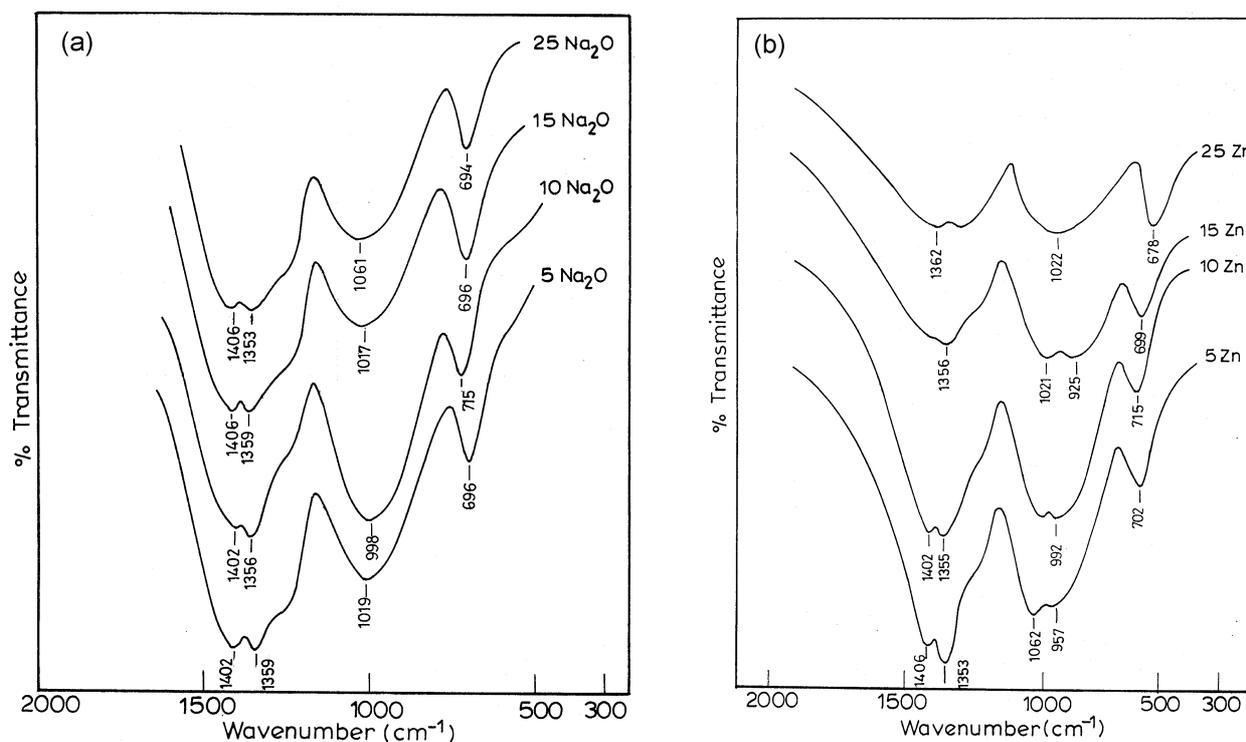
Figure 6. Infrared spectra of **(a)** xNa$_2$O–10ZnO–$(90 - x)$B$_2$O$_3$ glass system and **(b)** 10Na$_2$O–xZnO–$(90 - x)$B$_2$O$_3$ glass system.

boron atoms in [BO$_4$] units by finding the area under the [BO$_{4/2}$]$^-$ and [BO$_{3/2}$]^0 peaks (Munia *et al* 1999b).

Figures 5a and b show the variation of N_4 as a function of Na$_2$O and ZnO composition. As can be seen in figure 5a that in CZn glass series the values of N_4 continuously increase with increase of Na$_2$O concentration and tend to reach the typical diborate composition value of $N_4 = 0.5$. This clearly suggests that the added oxygen supplied by

Na$_2$O has been utilized for the formation of [BO$_{3/2}$]^0 and [BO$_{4/2}$]$^-$ groups. In CNa glass series the variation of N_4 values shows a interesting feature. As seen in figure 5b the values of N_4 remain constant over the entire composition studied and the N_4 values are well below the diborate composition. This behaviour can be explained by considering the reconversion of [BO$_{4/2}$]$^-$ to [BO$_{3/2}$]$^-$ and the structural role of Zn^{2+} ions.

As pointed out in the earlier section, beyond the modifier concentration of 33·3 mol% the four coordinated boron atoms $[BO_{4/2}]^-$ are reconverted into $[BO_{3/2}]^-$ and one would expect decreasing trend in N_4. However, in the present glass system as seen from figures 5a and b, such a trend has not been observed in both CZn and CNa glass series. This ascertains the fact that the excess of oxygens beyond 33·3 mol% of effective modifier concentration has not been utilized by B_2O_3 in the glass matrix. Therefore, it is possible that some of Zn^{2+} ions are present in the form of $[ZnO_4]$ tetrahedrons which can be represented by following scheme of reaction

$$2ZnO \Rightarrow [ZnO_{4/2}]^{2-} + Zn^{2+}.$$

Similar structural changes are known to occur in Na_2O–MgO–B_2O_3 (Kim and Bray 1974) and Li_2O–PbO–B_2O_3 glasses (Munia *et al* 1999a), where the Mg/Pb ion is present in tetrahedral network positions.

3.4 *Infrared absorption*

Infrared spectra of representative compositions of CZn and CNa glass series are shown in figures 6a and b, respectively. IR spectra found to consist of three absorption regions. The region between 1200 and 1400 cm^{-1} arises from borate units in which the boron atom is connected to three oxygens $[BO_{3/2}]^0$. The region between 900 and 1100 cm^{-1} is due to boron atom in tetrahedra oxygen coordination $[BO_{4/2}]^-$ units (Krogh-Moe 1965; Selvaraj and Rao 1984; Kamitsos *et al* 1987a). 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 these peaks also undergo significant changes as ZnO/ Na_2O concentration increases.

In CZn series the intensities of the peak at 1000 cm^{-1} corresponding to $[BO_{4/2}]^-$ units increases with increase of Na_2O concentration indicating an increase in production of $[BO_{4/2}]^-$ units. In case of CNa glasses the structural features of IR spectra are almost identical to that of CZn series. However, as can be seen in figure 6b, there is a split band feature seen in the peak at 1400 cm^{-1} and 1065 cm^{-1}, which could be probably due to linkages like B–O–Zn in the network, suggesting the entry of Zn^{2+} ions into the network.

4. Conclusions

Elastic properties, ^{11}B MAS–NMR and IR studies on Na_2O–ZnO–B_2O_3 glass system have been investigated to ascertain the role of Zn^{2+} ion in these glasses. The sound velocities, V_l and V_t, elastic properties, Poisson's ratio and Debye temperature show increasing trend even when the effective modifier concentration is $> 33·3$ mol%. The

increase in Poisson's ratio suggests formation of a weaker B–O–Zn linkages in place of strong B–O–B linkages. Analysis of ^{11}B MAS–NMR and IR spectra indicates that Zn^{2+} ions are incorporated into the network as a former presumably in the form of ZnO_4 tetrahedra.

Acknowledgements

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