Microwave synthesized zinc-boro-vanadate glasses: Structural elucidation by employing ultrasonic and MAS NMR studies

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Abstract

Correlation between mechanical properties and MAS NMR spectroscopic revelations have been carried out on the glass system, $xZnO - 50\ B_2O_3 - (50 - x)\ V_2O_5$ where $15 \leq x \leq 40$ is prepared by a novel microwave heating method. Elastic moduli were computed from ultrasound velocities measured by a pulse echo superposition method. Both ultrasound velocities and elastic properties increase monotonically as a function of ZnO content. The variations observed in the mechanical properties were explained in view of modifications occur in the network structure consisting of borovanadate units. The bulk and shear moduli increase due to the presence of four coordinated borons along with diborovanadate units, which increases the dimensionality and connectivity of the glass network. Surprisingly, the process of the reconversion of four coordinated borons into three coordinated borons beyond 33.3mol% of modifier concentration is not initiated in these glasses, which is essentially due to the formation of $[B_2V_2O_9]^{2-}$ units similar to the $[B_4O_7]^{2-}$ units. This is well supported by the monotonic increase in N_4 - values even above the 33.3 mol% of modifier content. Materials with enhanced elastic properties find application in cathode materials. Copyright © 2017 VBRI Press.

Keywords: ^{11}B MAS-NMR, borovanadate groups, ultrasound velocity, vickers hardness, elastic moduli.

Introduction

The microwave synthesis of solid materials is a new technology, which offers several advantages such as the method is energy saving and environment friendly. The products obtained by this method exhibit enhanced properties [**1**]. Some new applications of microwave heating in the synthesis of materials have been reported recently [**2-6**]. There are reports on the microwave processing of materials where the enhancement of properties like density, strength, fracture toughness, electrical permittivity, thermal conductivity and reduction in grain growth have also been observed [**7-9**].

Glasses doped with transition metal ions (TMI) such as FeO_3, V_2O_5, MoO_3, WO_3 etc. exhibit semiconducting properties and find potential technological applications in solid state batteries [**10-12**]. In particular, glasses with a high dielectric constant are used as capacitors [**13**]. The characterizations of TMI containing glasses using non-destructive ultrasound method to study their structure by using mechanical properties yield good results. The coordination and connectivities of the B_2O_3 and V_2O_5 species in borovanadate glasses can vary in complexity as

a consequence of network modifications [**7-9**]. Also, the structure of these glasses consists of $[BO_{3/2}]^0$ and $[VOO_{3/2}]^0$ units which are inter-connected connected. There is a topological similarity with pure B_2O_3 glass, because it is equivalent to a random substitution of B by V=O in the B_2O_3 glass structure. The addition of modifier oxides gives rise to similar structural modifications in B_2O_3 and borovanadate glasses leading to the formation of various borovanadate units similar to diborate units [**3**]. The ^{11}B MASNMR spectra of borovanadate glasses provided quantitative information regarding the trigonally (B_3) and tetrahedrally (B_4) coordinated borons exist in these glasses [**13-14**].

Elastic properties of glasses formed by covalent networks are affected sensitively by modification. It is particularly true in the case where the network connectivities are affected drastically. Elastic properties can also be very informative since they are related to the cohesive energies and vibrational properties. Hence, study of elastic moduli and their variation as a function of modifier content can be very useful in providing supportive evidences about network structure of glasses. Elastic properties of several oxide glasses studied using

ultrasonic methods have been reported in literature [**1, 6, 15**]. In the present work elastic properties and structural aspects of borovanadate glasses have been examined with a view to understand structural features such as $N_4 \left(= \frac{B_4}{B_3 + B_4} \right)$ values and formation of structural units which results from network modification.

Experimental

Glasses having the general formula x ZnO – 50 B_2O_3 – (50 - x) V_2O_5, where x = 15, 20, 25, 30, 35 and 40 mol% and designated ZBV1, ZBV2, ZBV3, ZBV4 and ZBV5, respectively, were synthesized using analar grade zinc monoxide (Sd fine chemicals), boric acid (Sd fine chemicals) and vanadium pentoxide (Merck) as chemical ingredients.

Synthesis

Required quantities of the chemicals were ground and mixed using agate mortar and 30 gram batches of the ground mixture were taken in a silica crucible and kept inside a microwave Kitchen oven operating at 2.5 GHz (power level = 850 Watts). When the oven was switched on, the decomposition of water vapor take place in 2-3 minutes. Homogeneous melt free from air bubbles was obtained in less than 10 minutes which is highly rapid compared to melt quenching method. In a solidstate microwave synthesis of oxides, at least one of the reactants should be microwave active material. The melt was stirred to ensure homogeneity and quenched in a cylindrically designed brass moulds. The glass samples were annealed for 3 hours at 150^0C in a muffle furnace to make the glasses strain free.

Characterizations

The glassy nature of the investigated specimens was confirmed by an X-ray powder diffractometer. Density of the glass samples free from air bubbles were carried out using Archimedes principle using alcohol of known density as the immersion liquid. The DSC thermograms of all the investigated glasses were obtained using Perkin-Elmer-DSC-2, differential scanning calorimeter. Care has

been taken to minimize thermal drifts during the experiment by pre-warming the pans to the temperature range required for the measurement. Microhardness of the investigated glasses was measured using TTS Unlimited Inc (Model: HWMMT Japan with a Vickers indenter). The ultrasound velocity measurements were carried out at frequency 12MHz using quartz transducers (X-Cut and Y-Cut) at room [**6-15**] temperature.

Results and discussion

Sample code, composition, density and molar volume of zinc-boro-vanadate glasses along with glass transition temperature, ultrasonic velocities and elastic properties are listed in **Table.1**. The uncertainties in these quantities are also shown in **Table.1**. The investigated glasses show a monotonic increase in density with ZnO content and the values of density lie in the range of 3.88 to 4.26 g/cm^3. The molar volume of these glasses decreases marginally by 3.3%, when ZnO content increases from 15 to 40 mol%. These variations are attributed to the structural changes brought about by the addition of ZnO. Borate and vanadate structural units are the basic units which form the network structure of glass. Borate can exist in both triangular and tetrahedral coordinations while vanadium units retain their tetragonality [**16-18**]. Along with B_3, B_4 and V_3 species, diborovanadate units similar to diborate units exist in these glasses due to the network modification. One can expect that the monotonic increase in density with ZnO mol% is due to the fact that the triangular borate units are converted into tetrahedral borate units and diborovanadate units of type-I and type-II. As a result of this, the network dimensionality and connectivity increases [**19-20**]. Consequently, the packing of the glass network becomes efficient, which is reflected in elastic properties.

Glass transition temperature increases with ZnO mol% linearly, when ZnO varied from 15 to 40 mol%. The linear variation confirms the continuous conversion of $[BO_{3/2}]^0$ to $[BO_{4/2}]^-$ along with $[B_2V_2O_7]^{2-}$ (type I & II). As the modifier oxide, ZnO increases, the weaker V-O bonds of energy 637 kJmol^{-1} are replaced by stronger B-O bonds of energy 809 kJmol^{-1} [**21**]. As reported in alkali borate glasses, glass transition temperature should show

Table 1. Composition, density (ρ), molar volume (M_v), glass transition temperature (T_g) and elastic moduli of Zinc – boro –vanadate glasses.

Property (with appropriate error)	Codes					
	ZBV1	ZBV2	ZBV3	ZBV4	ZBV5	ZBV6
Density ρ (±0.005 gm/cm^3)	3.88	3.95	4.02	4.10	4.17	4.26
Molar Volume M_V (±0.03cm^3)	34.51	34.33	34.16	33.89	33.74	33.39
Glass transition temperature T_g (±1K)	601	603	609	613	617	621
Vicker's hardness (GPa)	3.93	4.01	4.09	4.17	4.26	4.35
Longitudinal velocity V_l (±10 m/s)	4138	4468	4813	5156	5516	5888
Transverse velocity V_s (±10 m/s)	2486	2693	2922	3137	3392	3647
Mean sound velocity V_m (±10 m/s)	2750	2978	3229	3465	3743	4021
Longitudinal modulus L (±0.88 GPa)	66.44	78.85	93.12	108.99	126.88	147.69
Shear modulus G (±0.44 GPa)	23.98	28.65	34.32	40.35	47.98	56.67
Young's modulus E (±0.61 GPa)	56.1	66.86	79.71	93.55	110.38	129.64
Bulk modulus K (±0.54 GPa)	34.46	40.66	47.36	55.2	62.91	72.14
N_4 - Values	0.24	0.30	0.39	0.42	0.49	0.53

an opposite trend, when the modifier content exceeds 33.3 mol% [**22**]. Because the reconversion of B_4 into B_3 species is expected to be initiated above 33.3 mol%. In the present glass system V_2O_5 content facilitate the formation of four connected borons in diborovanadate groups. Thus, the glass transition temperature monotonically increases for the entire range of composition. Vickers microhardness of the investigated glass lie between 3.93 GPa and 4.35 GPa. The variation of H_v with ZnO content is presented in **Fig. 1** as inset. Further, the variation seen in **Fig. 1** (inset) may be related to the network connectivities and bond energies [**23**]. In ZnO – B_2O_3 – V_2O_5 glass system the basic covalent linkages which determine the cohesive energies of the network are B-O, V-O and V-O-B. As mentioned above, the weak V-O linkage is replaced by a strong B-O linkage when ZnO concentration increases from 15-40 mol%.
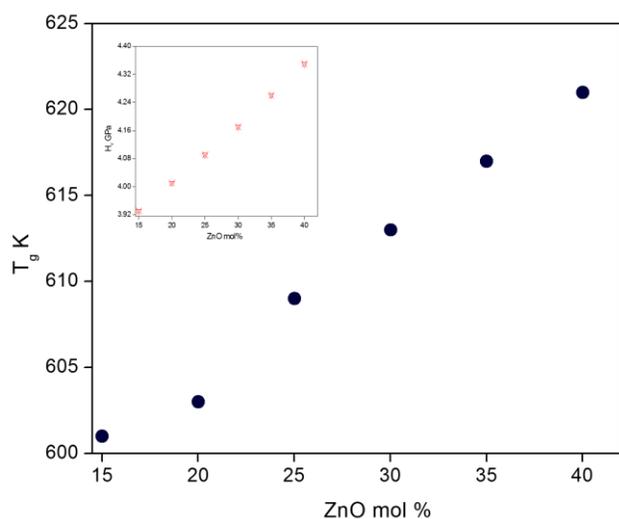
Fig. 1. Variation of T_g with ZnO mol%. Inset: Variation of Vickers hardness with ZnO mol%.

The ultrasonic velocities (viz longitudinal and transverse) and elastic properties are listed in **Table 1**. It is evident form **Table 1** that the longitudinal and transverse sound velocities (V_l and V_t), elastic moduli gradually increase with ZnO content. The observed variation in V_l, V_t, L, G, E and K can be substantiated using structural considerations of the borate and vanadate interlinked network. As pointed out above B_2O_3 is a strong glass former while V_2O_5 is a conditional glass former. When V_2O_5 is added to $B_2 O_3$, it readily forms glass and the glass forming region is enhanced. Addition of a divalent modifier oxide ZnO to boro-vanadate glass, the boro-vanadate network undergoes a modification. Vitreous boro-vanadate glass basically consists of triangular $[BO_{3/2}]^0$, tetrahedral $[BO_{4/2}]^-$ and tetragonal $[VOO_{3/2}]^0$ units. The modifier role of ZnO can be explained as;

$$ZnO \rightarrow Zn^{2+} + O^{2-}$$

One unit of B_2O_3 consists of two units of $[BO_{3/2}]^0$. Similarly one unit of V_2O_5 consists of two units of

$[VOO_{3/2}]^0$, These, $[BO_{3/2}]^0$ and $[VOO_{3/2}]^0$ units can be interlinked in the network with the formation of B-O-B, V-O-V and V-O-B connectivities depending upon the stoichiometry of the glass composition. The triagonal boron with three connectivities and vanadium is three connected but four coordinated are given below:

$[BO_{3/2}]^0$ $[VOO_{3/2}]^0$

● Boron ,   ● Vanadium ,   ● Oxygen
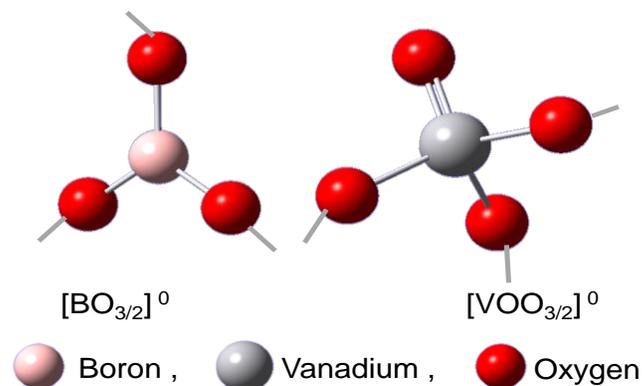
The main connectivities between B, O and V are broken when ZnO is added to B_2O_3 – V_2O_5 glass. This network modification can be explained by considering Sanderson's principle of electronegativity [**24**]. Since $[BO_{3/2}]^0$ and $[VOO_{3/2}]^0$ groups have the same electronegativity [χ=2.79], the oxide ion reacts with an equal probability and the oxide ion, O^{2-} is equally shared by basic borate and vanadate groups in structure. The network modification takes place in the following order:

$$2[B_2O_3] + 2[V_2O_5] + O^{2-} \rightarrow [B_2V_2O_9]^{2-} \text{ (Type I)} + [B_2V_2O_9]^{2-} \text{ (Type II)} \qquad \text{(i)}$$
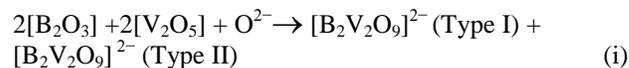
where, $[B_2V_2O_9]^{2-}$ is a diborovanadate group which similar to that of diborate. The diborovanadate groups of type 1 and 2 are shown below:

$[B_2V_2O_9]^{2-}$ (I) $[B_2V_2O_9]^{2-}$ (II)

● Boron ,   ● Vanadium ,   ● Oxygen

$$0.5[B_2V_2O_9]^{2-} \text{ (Type-II)} + ZnO \rightarrow [BO_{2/2}O]^- + [VOO_{1/2}O_2]^{2-} + Zn^{2+} \qquad \text{(ii)}$$

where, $[BO_{2/2}O]^- \equiv B_2 \equiv B_3$ and $[VOO_{1/2}O_2]^{2-} \equiv V_1$

$$0.5[B_2V_2O_9]^{2-} \text{ (Type-I)} + ZnO \rightarrow [VOO_{2/2}O]^- + [BO_{1/2}O_2]^- + Zn^{2+} \qquad \text{(iii)}$$
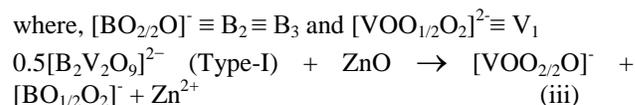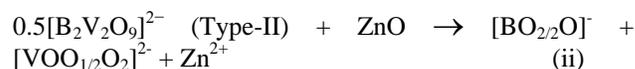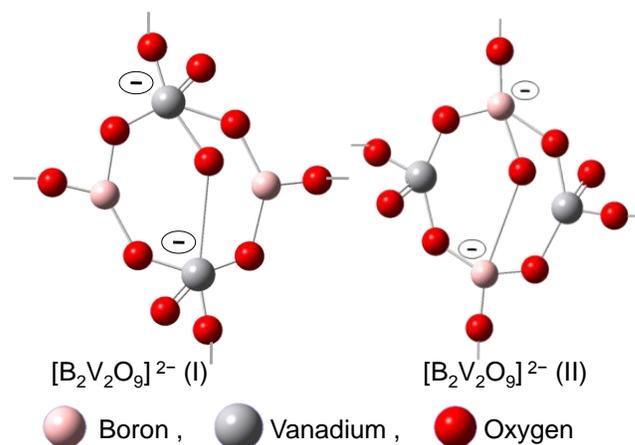
Since the modifier concentration is limited to 40 mol%, the network modification is limited only to the second stage of modification (*i.e.;* $[B_2V_2O_9]^{2-}$ (Type-II)). The network modification reveals that, the ZnO in the investigated glasses plays a modifier role, which results in the formation of diborovanadate groups and borons in their four coordination. The formations of these groups are in accordance with the variations found in sound velocities and elastic moduli (see **Fig. 2**). Modified network has more number of B-O bonds per mole compared to unmodified boro-vanadate glass.
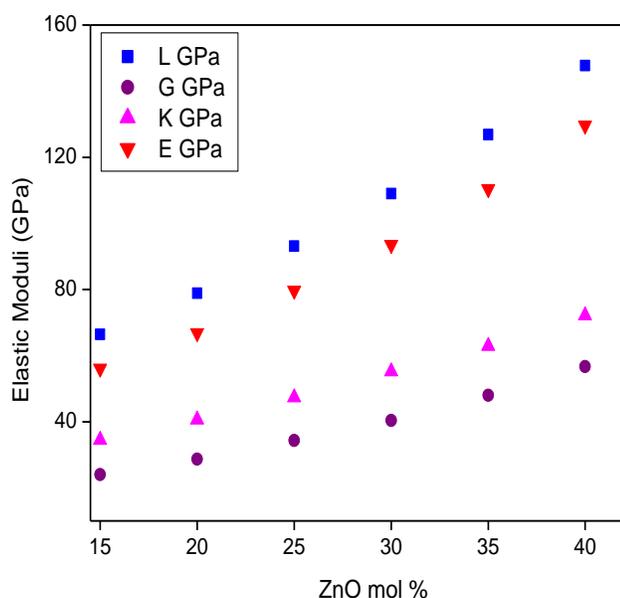
Fig. 2. Variation of elastic moduli with ZnO mol%.

The formation of network motifs explained above is further examined using ^{11}B high resolution MASNMR spectroscopic studies. **Fig. 3** show representative ^{11}B MASNMR spectra. The spectrum clearly shows that the resonance is centered at 19 ppm with respect to a resonance signal of trimethyl boron, the peak arises due to the resonance of B_4 species. As can be seen from **Fig. 3**, B_3 units are quadrupolar split with two typical asymmetric peaks while tetrahedrally coordinated B_4 units, exhibit a single peak. The spectra are deconvoluted to sort-out the area under B_3 and B_4 peaks. The N_4-values have been calculated using the relation $N_4 \left(= \frac{B_4}{B_3 + B_4} \right)$ [25-26]. The values are listed in Table.1. It is evident form **Table 1** that the N_4-vlues increases with ZnO content monotonically but there is no inflexion, which is expected when the reconversion of 4-coordinated borons into 3-coordinated borons [27]. ^{11}B MASNMR study reveals a continuous conversion of B_3 to B_4 units even beyond 33.3 mol% of modifier oxide. Further, the weakening of the borate network with the addition of another glass former such as vanadium pentoxide does not affect the structural sustainability of the ratio B_4/B_3. This is because B_3 and B_4 units are always formed in pairs during the formation of diborovanadate units.

Conclusion

The elastic moduli, Vickers microhardness glass transition temperature, density and molar volume studies on $ZnO - B_2O_3 - V_2O_5$ glasses have been carried out.
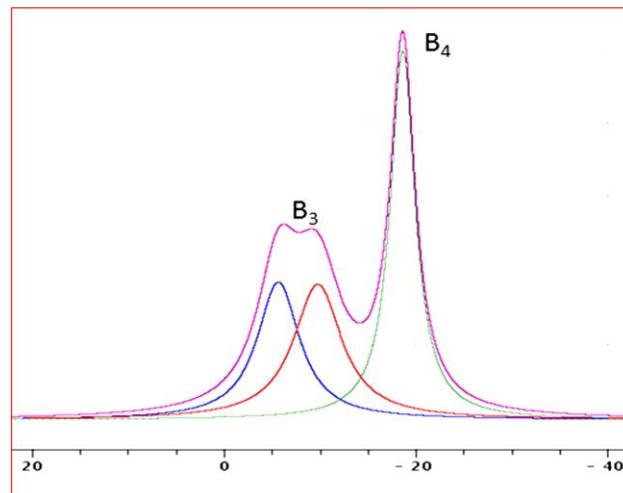
Fig. 3. ^{11}B MAS NMR spectra of ZBV1 glass.

The mechanical, physical and thermal properties were discussed and correlated to the structure of the glass formers. The structure was well explained on the basis of the structural motifs formed due to the network modification. Modifying role of ZnO is obeyed by the Sanderson's electronegativity principle and the main feature of the investigated glass is that the conversion of triangular borons into 4-coordinated borons was seen even beyond 33.3 mol% of ZnO. The boron coordinations are well supported by the ^{11}B MASNMR studies. Further, the continuous increase in N_4-values with ZnO mol% is consistent with variations seen in elastic moduli, microhardness and glass transition temperature.

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