Study on ultrasound velocities and elastic properties of sodium diboro-vanadate glasses

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Abstract: Glasses with general formula $xNa_2O-15V_2O_5-(85-x)B_2O_3$ where $x$ is varied from 5 to 50 mol% in steps of 5 mol%, are fabricated using melt quenching technique. Ultrasound velocities, elastic moduli and Poisson’s ratio exhibit composition dependent trends. Both ultrasound velocities and elastic moduli increases with the addition of Na$_2$O mol% whereas Poisson’s ratio decreases. The introduction of V$_2$O$_5$ results in the formation of diboro-vanadate units similar to that of a diborate. Formation of these diboro-vanadate units leads to a monotonic increase in both sound velocities and elastic moduli.

Keywords: Ultrasound velocities, elastic moduli, semiconducting, Poisson’s ratio.

1. Introduction

Among oxide glasses, borate glass continue to attract scientific investigations because of their superior physical, optical and mechanical properties and find applications in the fiber optic communication systems, nonlinear optical devices and lasers [1-3]. In addition these glasses possess wide range of applications which include glasses for lightening, laboratory, cookware, medical, LCD screens and optical glasses [4, 5]. Glasses containing large quantity of transition metal oxide are known to exhibit electronic conductivity. The study of semiconducting glasses containing transition metal oxide (TMO) is very important because of their applications in memory switching devices and electrochemical batteries [6-8]. Many glasses containing V$_2$O$_5$ exhibit semiconducting properties which arises due to the conduction mechanism taking place through hopping of electrons between different oxidation states V$^{5+}$ and V$^{4+}$ of vanadium [9].

Elastic properties of glasses are very important because they provide deep insight to understand the structure of glasses as well as provide important information about interatomic forces, nature of bonding and vibrational frequencies. Glasses exhibit perfect elasticity and it
has been reported by Makishima and Mackenzie [10] that the bulk modulus of glasses are strongly dependent on packing density and bond dissociation energies. Yamane and Sakaino [11] estimated the Young’s modulus as a function of melting temperature of constituent oxides which depends on the strength of cohesive forces in the network. The variation in the network connectivity as a result of modification in the structure can be observed in elastic properties. The variation of elastic properties of glasses as function of composition can provide important information about the role of network formers and modifiers [12-21]. The measurement of elastic moduli and Poisson’s ratio in vanadium containing glasses [12-16], borate [17-20] and phosphate [21] as a function of composition were studied. The elastic properties of alkali borate [22], alkali molybdo-phosphate and alkali phosphate glasses [23] were reported to reflect in ultrasound velocities. Special feature of the present work is to introduce V$_2$O$_5$ content into sodium-borate glasses and to study the role of V$_2$O$_5$ and Na$_2$O on the structure of borate glass as a function of elastic properties by performing ultrasound measurements.

2. Experimental
Glasses with general formula xNa$_2$O-15V$_2$O$_5$-(85-x)B$_2$O$_3$ are fabricated using melt quenching technique, where x is varied from 5 to 50 mol% in steps of 5 mol%. Analar grade sodium carbonate, vanadium pentoxide and boric acid (Sd fine chemicals) were used. The chemicals were taken in exact proportions ground together to uniform mixture and melted inside a muffle furnace maintained at a temperature around 1200\degree C. The hot melt is quenched to obtain cylindrical glass pieces. The obtained glass pieces are annealed for 2 hours at 200\degree C in a muffle furnace to remove thermal strains. The faces of the cylindrical glasses are polished using silicon carbide to obtain flat and smooth surface. Ultrasound velocity measurements were performed at room temperature of 298 K and at frequency 12 MHz using quartz transducers (X-Cut and Y-Cut). Glasses are bonded to transducers using phenyl salicylate.

3. Results and discussion
3.1 Ultrasound velocities
Ultrasound velocities, longitudinal and transverse (V$_l$ and V$_t$) of sodium-vanado-borate glasses show composition dependence. Figure 1 gives the variation of V$_l$ and V$_t$ with Na$_2$O mol%. A monotonic increase in ultrasound velocities unlike a similar variations seen lithium borate lasses. Binary alkali-borate glasses were investigated by Kodama [24]. Kodama [24] report reveals a non-linear variation in sound velocities as a function of alkali concentration. Surprisingly the present investigation reveals that the sound velocities increase monotonically as a function of modifier oxide concentration (Na$_2$O) for the full range of composition. This can be attributed to structural changes occur due to the addition of alkali oxide. Details are given in the latter sections.

The modulus of elasticity and Poisson’s ratio have been calculated using the density and sound velocities. The values are shown in the Table 1.
Table 1: Composition, ultrasound velocities ($V_l$ and $V_t$), Longitudinal modulus $L$, Shear modulus $G$, Young’s modulus $E$, Bulk modulus $K$ and Poisson’s ratio $\sigma$ of sodium diboro-vanadate glasses.

| Composition (in mol%) | Sound velocities (m/s) | Elastic moduli (GPa) | $\sigma$ |
|-----------------------|------------------------|----------------------|---------|
| $Na_2O$ | $B_2O_3$ | $V_2O_5$ | $V_l(\pm10)$ | $V_t(\pm10)$ | $L(\pm0.88)$ | $G(\pm0.44)$ | $E(\pm0.61)$ | $K(\pm0.54)$ |
| 5 | 80 | 15 | 4033 | 2295 | 36.18 | 11.71 | 29.53 | 20.56 | 0.261 |
| 10 | 75 | 15 | 4252 | 2428 | 40.91 | 13.34 | 33.57 | 23.12 | 0.258 |
| 15 | 70 | 15 | 4455 | 2560 | 45.52 | 15.01 | 37.64 | 25.50 | 0.254 |
| 20 | 65 | 15 | 4655 | 2713 | 50.22 | 17.04 | 42.37 | 27.50 | 0.243 |
| 25 | 60 | 15 | 4855 | 2898 | 54.93 | 19.57 | 47.88 | 28.84 | 0.223 |
| 30 | 55 | 15 | 5017 | 3001 | 59.19 | 21.17 | 51.73 | 30.96 | 0.222 |
| 35 | 50 | 15 | 5220 | 3132 | 64.14 | 23.09 | 56.28 | 33.38 | 0.219 |
| 40 | 45 | 15 | 5335 | 3207 | 67.03 | 24.22 | 60.96 | 34.93 | 0.217 |
| 45 | 40 | 15 | 5417 | 3280 | 71.89 | 27.57 | 64.58 | 36.47 | 0.189 |
| 50 | 35 | 15 | 5570 | 3399 | 75.48 | 29.09 | 68.98 | 39.37 | 0.186 |

Fig.1 Variation of ultrasound velocities $V_l$ and $V_t$ as a function $Na_2O$ mol%.

3.2 Elastic moduli
The longitudinal modulus ($L$) varies from 36.18 to 75.48 GPa, shear modulus ($G$) varies from 11.71 to 29.09 GPa, Young’s modulus ($E$) varies from 29.53 to 68.98 GPa and bulk modulus ($K$) varies from 20.56 to 39.37 GPa when the alkali oxide concentration is varied from 5 to 50 mol%. Figure 2 represents the variation of moduli of elasticity with $Na_2O$ mol%. All the moduli show the same trend except the change of slope. The observed variations are different from literature reports. The literature reports reveal the non-linear variations in elastic moduli. The observed trends of elastic moduli can be better explained using structural analogy. The structure of boron trioxide consists of triangular boron and tetrahedral boron units. These units are interconnected to planar ring structures, chains and tightly bound diborates. Addition of sodium oxide results in the modifications of the basic structure of $B_2O_3$ which leads to conversion of $B_3 \equiv [BO_3]_2^-$ units into $B_4 \equiv [BO_4]_2^-$ up to the modifier to $B_2O_3$ ratio reaches 1:2, further increase in the modifier oxide concentration results in the reconversion of $B_4$ into $B_3$. If this is expected to happen one can observe only non-linear variation. In the present work $V_2O_5$ is introduced into $Na_2O-B_2O_3$ glass system. Basic structure of $B_2O_3-V_2O_5$ consists
of $[\text{BO}_3/2]^0$ and $[\text{VOO}_3/2]^0$ units connected internally. Further, the glass network contain B-O-B, V-O-V and B-O-V linkages. The modification of boro-vanadate network is given below.

$$\text{Na}_2\text{O} \rightarrow 2\text{Na}^+ + \text{O}^2-$$

The liberated oxide ion $(\text{O}^2-)$ reach the basic structural group which has higher electronegativity and can participate in modification. Since both $[\text{BO}_3/2]$ and $[\text{VOO}_3/2]$ has the same electronegativity $(\chi = 2.79)$, the oxide has an equal a priori probability to modify and lead to the formation of boro-vanadate groups.

$$[\text{BO}_3/2]^0 + \frac{1}{2}\text{O}^2- \rightarrow [\text{BO}_4/2]^2-$$
$$[\text{VOO}_3/2]^0 + + \frac{1}{2}\text{O}^2- \rightarrow [\text{VOO}_2/2\text{O}]^-$$
$$[\text{BO}_4/2]^2- + \frac{1}{2}\text{O}^2- \rightarrow [\text{BO}_2/2\text{O}]^2-$$
$$[\text{VOO}_2/2\text{O}]^- + + \frac{1}{2}\text{O}^2- \rightarrow [\text{VOO}_1/2\text{O}_2]^2-$$

$2[\text{B}_2\text{O}_3] + 2[\text{V}_2\text{O}_5] + 2\text{O}^2- \rightarrow [\text{B}_2\text{V}_2\text{O}_5]^2-$(Type I) $+ [\text{B}_2\text{V}_2\text{O}_5]^2-$(Type II)

The diboro-vanadate groups of type (I) and type (II) are always formed in pairs. Further the formation of these groups are in proportion to the composition of the component oxides in the formula unit. Even though the concentration of modifier oxide (Na$_2$O) increased from 5 to 50 mol%, the reconversion of tetrahedral boron into triagonal boron units is not initiated but these two units continue to form in pairs. Therefore, in the investigated glasses B-O-B, V-O-V and B-O-V connectivities are possible. Instead of routine modification in alkali-borate glasses, the presence of V$_2$O$_5$ leads to the formation of diboro-vanadate units. Such structures in the glass network increases the strength, rigidity and dimensionality of the network. As a result of this the ultrasound velocities and elastic moduli tend to increase.

![Graph](image.png)

**Fig.2:** Variation of elastic moduli L, G, E and K as a function of Na$_2$O mol%.

Poisson’s ratio is an important parameter which provide good details about the cross link density of the glass network. It is known that a high cross link density network has a Poisson’s ratio in the range of 0.1 to 0.2, while a low cross-link density has a Poisson’s ratio
between 0.3 and 0.5 [25]. In the present study, sodium diboro-vanadate glasses possess Poisson’s ratio from 0.261 to 0.186 indicating that the glasses exhibit intermediate cross link density. The variation of Poisson’s ratio with Na₂O mol% is shown in Fig.3. It can be observed from the Table.1, that the Poisson’s ratio decreases with addition of Na₂O mol%, indicating increase in cross link density as a result of network dimensionality.

![Fig.3 Variation of Poisson’s ratio, σ as a function Na₂O mol%.

4. Conclusions
Glasses with general formula xNa₂O-15V₂O₅-(85-x)B₂O₃ are fabricated using melt quenching technique. Ultrasound velocities, elastic moduli and Poisson’s ratio exhibit composition dependent trends. Both ultrasound velocities and elastic moduli increases with the concentration of Na₂O whereas Poisson’s ratio decreases. The introduction of V₂O₅ results in the formation of diboro-vanadate units similar to that of a diborate. Formation such units leads to a monotonic increase in both sound velocities and elastic moduli. Another special feature of the investigated glass system is that it exhibited good homogeneous glass formation over a wide range of composition.

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