Comparative Study for Structure of Alkali Borate Glasses with and without Aluminum Oxide – Density Measurements

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ABSTRACT

This paper reports on density measurements of alkali aluminoborate glass system ($xR_2O - yAl_2O_3 - (1 - x - y)B_2O_3$, R = Li, Na where x = 20 or 30 mol% and y = 10 or 15 mol%), correlated with the glass structure. The samples have been prepared by using the melt-quenching technique. The density has been obtained by Archimedes principle using benzene as buoyant. The effect of nature of alkali and its composition with and without alumina is well studied. It is found that number of trigonal and tetrahedral boron units are related to the type of alkali oxide as well as the total concentration of alkali oxide in alkali borate glasses. The addition of aluminum oxide at the cost of borate induces the changes in the structure of glass network which further depends upon aluminum oxide and alkali oxide content.

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1. INTRODUCTION

Density of a glass is a strong function of its composition. Density is a tool in revealing the degree of change in structure with composition of glasses as the change in geometrical configuration, coordination number, cross-link density and dimensions of interstitial space of glass. Thus, measurement of density of metal oxide glasses is carried out which makes use of structural ideas of Krogh-Moe [1], Shibata et al. [2], Feil and Feller [3] and Karki et al. [4]. The atomic arrangements in metal oxide glass system had been defined in terms of fraction of trigonal borons with three bridging oxygens (f_1), four coordinated borons (f_2), two bridging oxygens with one non-bridging oxygen (f_3), and one bridging oxygen with two non-bridging oxygens (f_4). Density and molar volume of borate glasses with different modifiers have been well studied by Stehle et al. [5], George et al. [6], Stenz et al. [7] and Singh et al. [8]. The nature of various structural units present in glasses can be determined from density comparisons. Density data were used to calculate the volumes of structural units present in various types of glass. Doweidar et al. [9–14] have shown that volume of structural units remain constant for alkali silicate, alkaline earth silicate glasses as well as for alkali alumino silicate glasses. While in alkali borate glasses, volume of BO_3 and BO_4 units changes with the glass composition, as the behavior of alkali in borate glasses is not same as that in silicates. In this paper, our aim is to study the changes in the structure of borate glasses in presence of alkali with and without alumina. The present work is

an attempt to correlate the density of alkali alumino borate glasses with composition of alkali and nature of alkali with and without alumina. The role of aluminum in structure of borate glasses is studied with respect to formation of tetrahedral or trigonal units which further depend upon the amount of alumina. The variation in density is attributed to different sizes of metal ion present.

2. EXPERIMENTAL TECHNIQUE

The samples $(xR_2O−yAl_2O_3−(1–x−y)B_2O_3$, R = Li, Na where x = 20 or 30 mol% and y = 10 or 15 mol%) have been prepared by using the melt-quenching technique. Chemical composition for all the glasses is shown in Table I. All chemicals used were of analytical reagent grade. Purity level of all the starting materials Li_2O (Fluka Chemical Company), Na_2O (Fluka Chemical company), K_2O (Fluka Chemical company), B_2O_3(Aldrich Chemical Company), Al_2O_3 (Fluka Chemical Company) was 99.99%. Various starting materials were calculated as follows:

$$\frac{W_1}{W_2} = \frac{xM_1}{(1-x)M_2}$$

where W_1 and W_2 are the weights to be taken and M_1 and M_2 are molecular weights of oxides respectively. The amounts of oxides were weighed by using digital electronic balance. The chemicals were then mixed in a pestle mortar for half an hour. The silica crucible containing the batch was placed in an electric furnace capable of reaching 1400 °C.

The melting points of all the glass samples were in the range of 800 − 950 °C.

Appropriate amounts of oxides were weighed by using an electronic balance having an accuracy of 0.001 g. The chemicals were then mixed in a pestle mortar for half an hour. A silica crucible containing the batch was then placed in an electric furnace capable of reaching a temperature of 1600 °C and it was heated at a temperature of 900 °C for one hour under normal atmospheric conditions. The melt was then poured into copper mould for quenching. The glass samples were then annealed in a separate annealing furnace for 12 hours. The samples were grounded with the help of an electric machine using different grades of SiC abrasives and aluminum oxide with machine oil by setting the sample in a specially designed holder to maintain the two faces parallel. The polishing was done with cerium oxide to obtain flatness.

The density was obtained by Archimedes principle using benzene as buoyant. The density was determined employing the following relation:

$$\rho = \frac{W_a}{W_a - W_b} \times \rho_b$$

Where W_a is the weight in air, W_b the weight in buoyant and ρ_b the density of buoyant. All the weight measurements have been made using a digital balance (M/s. Sartorius, Model: BP221S, USA). The accuracy in the measurement of weight is ± 0.1 mg. The

experiment was repeated five times to get an accurate value in density. The overall accuracy in the density measurement is ± 0.5 kg m^{-3} and hence, the percentage error in the measurement of density is $\pm 0.05\%$.

In order to confirm the amorphous nature of glass samples, X-ray diffraction (XRD) study has been made on each glass sample using Rigaku Mini-flex table-top spectrometer with Cu-Kα line of wavelength $\lambda = 1.5418$ A° at the

scanning rate of $2°$ /min and 2θ was varied from $10°$ to $80°$.

3. RESULTS

3.1. XRD Results

Figure 1 shows the X-ray diffraction patterns for lithium borate series with and without alumina (LB2, LAB2, LB3, LAB3) and Figure 2 shows the X-ray diffraction patterns for sodium borate series with and without alumina (NB2, NAB2, NB3, NAB3).
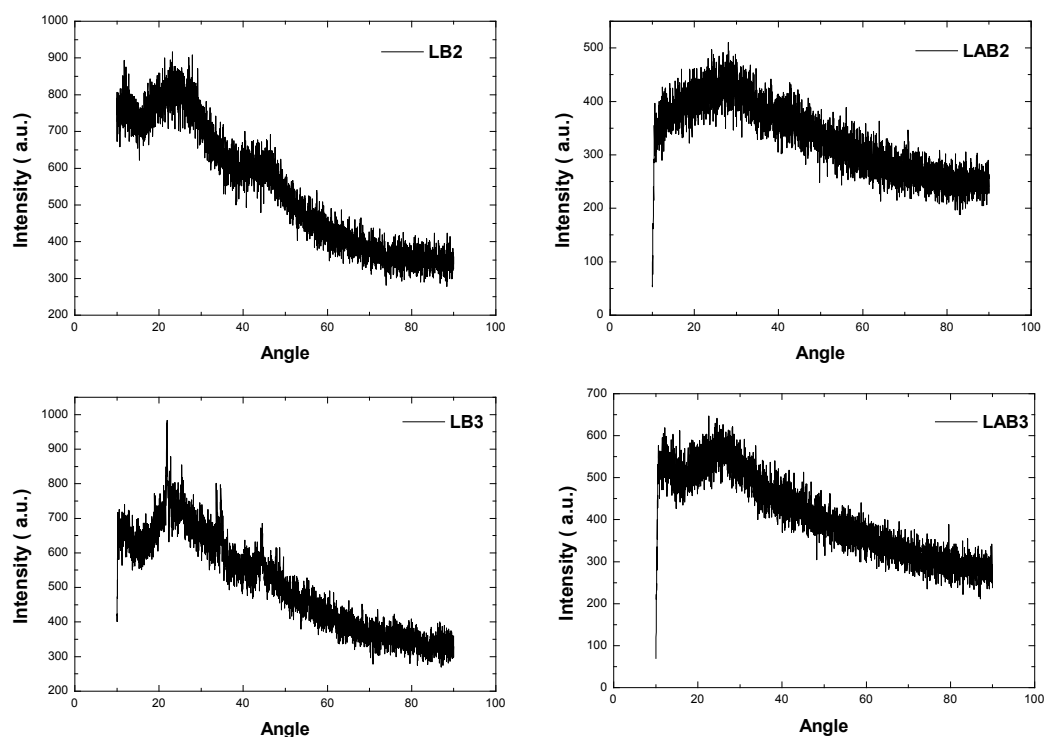
Fig. 1: *XRD Spectra of Lithium Borate Glasses without Alumina (LB2, LB3) and with Alumina (LAB2, LAB3).*
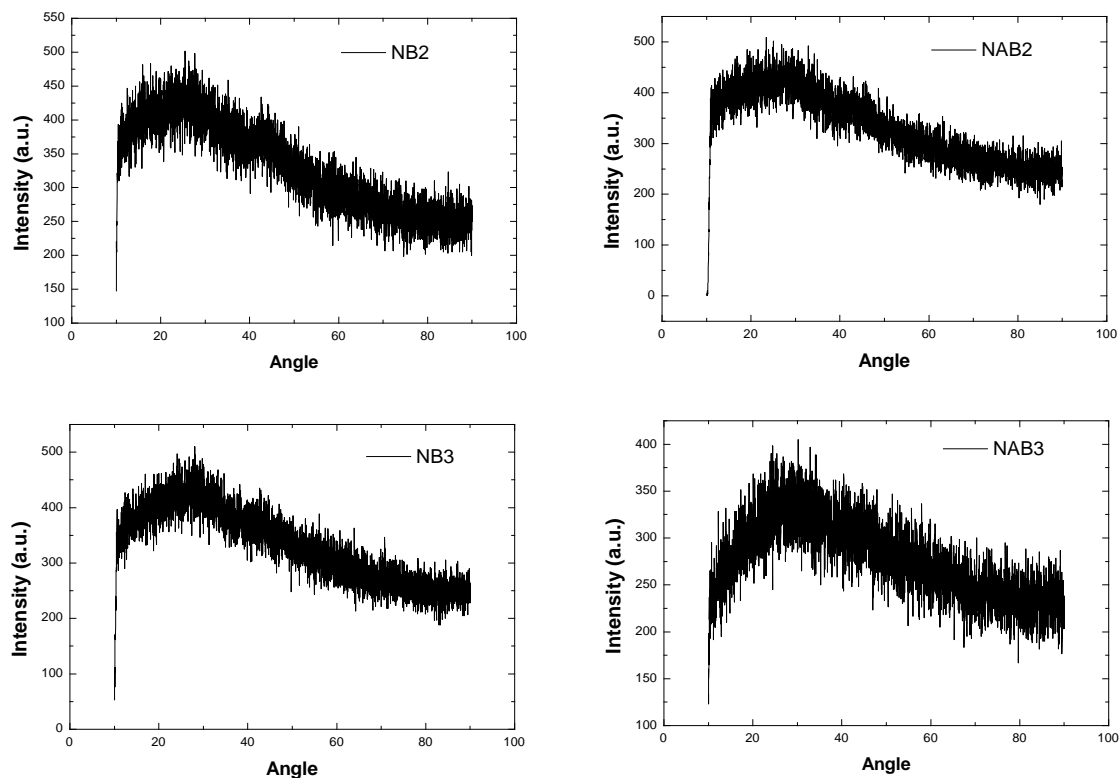
Fig. 2: XRD Spectra of Sodium Borate Glasses without Alumina (NB2, NB3) and with Alumina (NAB2, NAB3).

Table I: Sample Code and Chemical Composition of Prepared Glasses.

S.No.	Sample Code	Composition in mol%			
		Li_2O	Na_2O	B_2O_3	Al_2O_3
1.	LB2	0.20	-	0.80	-
2.	LAB2	0.20	-	0.70	0.10
3.	LB3	0.30	-	0.70	-
4.	LAB3	0.30	-	0.55	0.15
5.	NB2	-	0.20	0.80	-
6.	NAB2	-	0.20	0.70	0.10
7.	NB3	-	0.30	0.70	-
8.	NAB3	-	0.30	0.55	0.15

Table II: *Density, Molar Volume of Prepared Glasses.*

S.No.	Sample Name	Density gm/cm^3	R (molar ratio of alkali to boron)	Molar Volume cm^3
1.	LB2	2.033	0.25	30.33
2.	LAB2	2.184	0.285	29.70
3.	LB3	2.431	0.428	23.73
4.	LAB3	2.256	0.545	27.71
5.	NB2	2.141	0.25	31.80
6.	NAB2	2.179	0.285	32.73
7.	NB3	2.327	0.428	28.93
8.	NAB3	2.23	0.545	32.35

3.2 . Density

Table II shows the density and molar volume measurements of our glass samples along with their R values (ratio of alkali oxide content to that of boron oxide). It is found that density of borate glass increases by addition of 20 mol% alkali oxide (Li_2O or Na_2O). As the content of alkali oxide increases to 30 mol% (LB3, NB3), density follows the same trend, i.e., it increases. From Table II, it is observed that addition of 10 mol% aluminum oxide at the cost of boron oxide in glass system having 20 mol% of alkali oxide (LAB2, NAB2), there is rise in the density in comparison to the glass system without aluminum oxide having same molar percentage of alkali oxide (LB2, NB2). It is also found that role of aluminum oxide in alkali borate glasses depends on the alkali composition. Density of glasses (LAB3 and NAB3) containing 15 mol% of alumina at the cost of boron oxide for glass system with 30 mol% of alkali oxide, decreases as

compared to LB3 and NB3 respectively. Figure 4 shows the variation in density of the studied glasses as a function of R and it is clear from the graph that density increases with increase in R and it is maximum for the value of R = 0.425 and after it, increase in R causes decrease in the density. Figure 4 shows the variation in the molar volume of glasses as a function of R and it is found that as value of R increases up to 0.425, the molar volume decreases and has minimum value at R = 0.425 and for R > 0.425, molar volume increases.

4. DISCUSSION

4.1. XRD

Absence of sharp peaks and presence of broad humps confirms amorphous nature of glasses. In glasses the probability of finding atoms is neither regularly spaced nor uniform as in

crystals. Because of variations in the interatomic distances, the peaks get broader.

4.2. Effect of Composition of Alkali on Density

Density is a powerful tool capable of exploring changes in the structure of glasses. The change in coordination number and structural softening or compactness on the addition of modifier in glasses affect density. The density of B_2O_3 glass former is 1.812–1.84 g/cm^3 [15] and in vitreous form of boric oxide, boron exists in triangular coordination. Boron can have coordination of three/ four [16–19], the addition of each alkali ion to boron oxide causes one boron to change from B_3 state to B_4 state. In borate glasses, the trend in density is controlled by the fraction of four coordinated borons [20]. In the present study, for glasses LB2 and NB2 (Table II), it is observed that with addition of 20 mol% of alkali in borate glasses, density increases with the variation of 2.0–2.25 g/cm^3. Thus density of borate glasses increases by adding 20% of modifier as alkali. This increase in density in comparison to vitreous boric oxide is due to conversion of triangular borate groups into tetrahedral borate. With the addition of alkali in boric oxide, non-bridging oxygen atoms are not formed. The excess oxygen enters the network by covalently bonded to two boron atoms [21–24]. This results in boron atoms bonded to four bridging oxygen atoms and these boron atoms are tetrahedral borons. The tetrahedral borons are more stable as compared to non-bridging oxygen atoms. The tetrahedral BO_4 groups are

strongly bonded than the triangular BO_3 groups. This change increases the connectivity and thus molar volume decreases. Hence, a compact structure leads to increase in density. For LB3 and NB3 glasses (Table II), the alkali content changes from 20 mol% to 30 mol%, and increase in density is observed. Thus as the content of alkali increases from 20 mol% to 30 mol% in borate glasses, density also increases. The addition of network modifying components increases the density, since the network modifying ions attempt to occupy the interstices within the network. The separation between BO_4 tetrahedra and a neighboring BO_3 should be less than the separation between two adjacent BO_3 triangles. Thus conversion from B_3 to B_4 leads to network contraction [25, 26]. For binary glass composition xR_2O $(100−x)$ B_2O_3, the fraction of four coordinated boron units (N_4) and the fraction of three coordinated boron units (N_3) for $x < 33.3$ mol% can be calculated by the relation $N_4 = x/1 − x$ and $N_3 = 1 − N_4$, from which we can find the connectivity number of the system for desired composition [14, 15]. For 20 mol% of alkali addition (LB2 and NB2), $N_4 = 0.25$, $N_3 = 0.75$ and connectivity number=4x0.25+3x0.75=3.25 while for 30 mol% of alkali addition (LB3 and NB3) $N_4 = 0.43$, $N_3 = 0.57$ and connectivity number = 4x0.43 + 3x0.57=3.43. The increase in connectivity number with increase in alkali shows the increase in connectivity of the network that causes the compact structure and thus density of system increases that is in agreement with our present studied system. Density depends on molar ratio of alkali to

boron (R). Density increases as R increases and becomes maximum for R = 0.5 and it decreases for R > 0.5 [15]. Figures 3 and 4 for lithium and sodium borate glasses respectively show the variation of density as a function of R and show that density increases as value of R increases. Density follows the same trend up to R = 0.5 and density decreases for R = 0.545
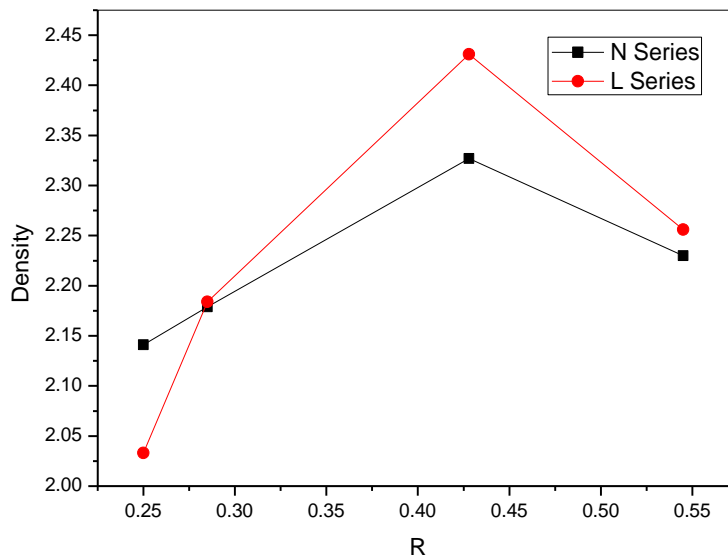

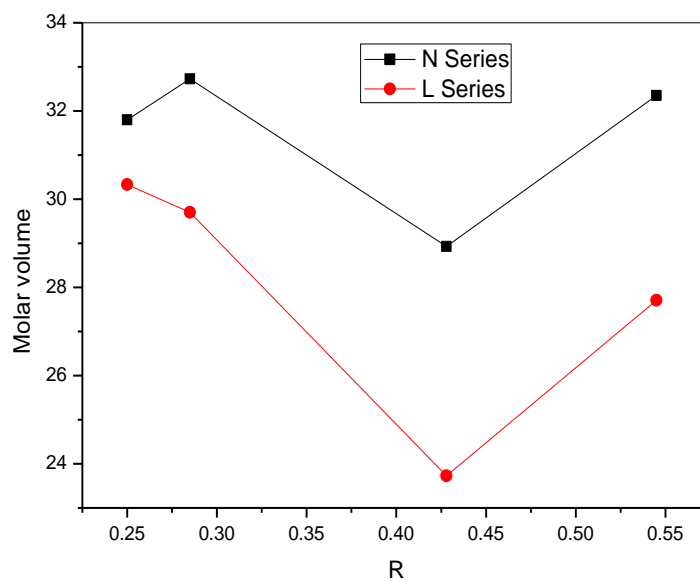*Fig. 3: Variation of Density as a Function of R (Molar Ratio of Alkali Oxide to Boron Oxide).*

Fig. 4: Variation of Molar Volume of Glasses with R (Molar Ratio of Alkali Oxide to Boron Oxide).

4.3. Dependence of Cation Nature on Density

Table II lists the values of densities for LB2 and NB2 as 2.033 and 2.141 respectively. It is justified as volume of tetrahedrally coordinated boron unit increases with the alkali ion size [15], by which the structure gets compact as more interstice space gets occupied. Thus, with 20 mol% potassium addition, density is more than that with sodium addition, which is more than that with lithium substitution. By adding 30 mol% of alkali (Table I), density increases as compared to 20 mol% of alkali. A similar trend (as in 20 mol%) is observed for 30 mol% for the nature of alkali, i.e., density of NB3 > LB3. Higher value of density for sodium borate glasses is attributed to increase in the volume of tetrahedrally coordinated boron unit that increases with the increase in alkali ion size. The increase in density by changing the content of alkali from 20 mol% to 30 mol%, is more pronounced with lithium addition as compared to sodium. This may be due to small ionic radii of lithium which can occupy the interstice spaces within the network of boron atoms [27]. Due to filling of empty spaces within the network, the structure becomes dense and thus the density of glass increases.

4.4. Role of Aluminum on Density in Alkali Borate Glasses

The addition of aluminum at the cost of borate in alkali borate glasses causes variation in density due to structural changes in the network. In the present study, 10 mol% of alumina is added to alkali borate glasses (LAB2 and NAB2) at the cost of borate, keeping alkali content same that is 20 mol% as in (LB2 and NB2). It is found that density increases in alumina containing alkali borate glasses in comparison to alumina free glasses (Table II) while density decreases for addition of 15 mol% of alumina (LAB3 and NAB3) in alkali borate glasses with 30 mol% of alkali (LB3 and NB3). Without adding aluminum, addition of only alkali, in borate glasses, there is change of trigonal borate units to tetrahedral boron units. But if aluminum is added to alkali borate, aluminum oxygen tetrahedral would form in preference to boron oxygen tetrahedra. Boron can remain in threefold coordination when alumina is added to glass, but aluminum ions must be fourfold coordinated [28]. As the atomic weight and size of aluminum is more than that of boron so volume of aluminum tetrahedral is more than that of boron. Thus, the density of aluminum containing alkali borate glasses is more than that of alumina-free alkali borate glasses for 20 mol% of alkali. But there is decrease in density for addition of alumina in 30 mol% of alkali borate glasses for LAB3 and NAB3. The presence of 15 mol% of Al_2O_3 causes lower density due to decrease in coordination shift of BO_3 to BO_4. The effect of Al_2O_3 in the glass causes an increase in BO_3 units where it consumes some oxygen atoms in R_2O (where R = Li, Na) which are required to convert BO_3 to BO_4. This leads to increase in molar volume, i.e., decrease in density.

Density also depends on the molar ratio of alkali to boron R. Density increases as R increases and becomes maximum for R = 0.5 and it decreases for R > 0.5 [15]. In our system, containing 15 mol% of alumina, R = 0.545, so density decreases for this glass composition in comparison to alumina-free composition of 30 mol% of alkali. This is in agreement with the results of addition of alumina in alkali borate glasses [28]. In such a glass composition, molar ratio of alkali to boron R is greater than 0.5, so density decreases, as density depends on the value of R (molar ratio of alkali to boron). Density increases as R increases and becomes maximum for R = 0.5 and it decreases for R > 0.5.

5. CONCLUSIONS

Density of borate glasses increases with addition of alkali oxide. As the composition of alkali increases from 20 mol% to 30 mol%, density increases due to increase of BO_4 units and this increase is more pronounced for lithium addition. Density of glasses having 20 mol% of alkali with 10 mol% of alumina is more than that without alumina due to formation of tetrahedral aluminum units but for glasses having 30 mol% of alkali, role of 15 mol% alumina is contrary to the previous case, i.e., density decreases with alumina addition due to formation of NBO.

ACKNOWLEDGEMENT

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