FACTA UNIVERSITATIS
Series: **Physics, Chemistry and Technology** Vol. 9, N° 1, 2011, pp. 29 - 36
DOI: 10.2298/FUPCT1101029C

DENSITY AND MOLAR VOLUME STUDIES OF PHOSPHATE GLASSES †

UDC 666.11.016.25 : 546.185 + 544.038.1

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Abstract. *The density and molar volume of some phosphate glasses ($xNa_2O\cdot(100\text{-}x)P_2O_5$, x = 30, 35, 40, 45, 50); $xB_2O_3\cdot(1\text{-}x)NaPO_3$, x = 5, 10, 15, 20, 25; $xNa_2O\cdot(30\text{-}x)\,K_2O\cdot10Al_2O_3\cdot25B_2O_3\cdot35P_2O_5$, x= 5, 10, 15, 20, 25) glasses were determined, in order to study their structure. The density of the glasses increased while their molar volume values decreases with the increase of sodium oxide content in phosphate glasses. The results obtained could be correlated to several factors such as the polarization, the field strengths and the ionic radii of the different incorporated cations.*

Key words: *density, molar volume, glass composition, mixed alkali effect, mixed glass former effect*

1. INTRODUCTION

Density of solids is mostly the simplest physical property that can be measured. However, it would be a highly informative property if the structure of material could be well defined. Density can be used for finding out the structure of different types of glasses. Some workers considered that density of the glass is additive and can thus be calculated on the basis of the glass composition [1-4]. Several formulas have been derived to correlate the glass density to the glass composition [5-9]. Jen and Kalinowski [10] suggested a model for describing the bridging to non-bridging oxygen ratio as a function of the glass composition and the calculated values of glass density based on this model, were excel-

Received March 9th, 2011; revised June 23th, 2011; accepted September 1st, 2011.
† Acknowledgement: One of the authors, U.B. Chanshetti, expresses his thanks to UGC for providing the financial assistance in the form of minor research project.
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lent agreement with the experimental values. The glass structure can be explained in terms of molar volume rather than density, as the former deals the spatial distribution of the ions forming that structure. The change in the molar volume with the molar composition of an oxide indicates the preceding structural changes through a formation or modification process in the glass network [11].

2. EXPERIMENTAL

2.1. Glass preparation

The phosphate glasses of following compositions: i) $xNa_2O{\cdot}(100\text{-}x)P_2O_5$ (x= 30, 35, 40, 45, 50), ii) $xB_2O_3{\cdot}(1\text{-}x)NaPO_3$ (x= 5, 10, 15, 20, 25) and iii) $xNa_2O{\cdot}(30\text{-}x)K_2O{\cdot}10Al_2O_3{\cdot}25B_2O_3{\cdot}35P_2O_5$ (x= 5, 10, 15, 20, 25) were prepared by conventional melt-quench technique. As a starting material, $NaNO_3$, K_2CO_3, H_3BO_3, $NH_4H_2PO_4$ and $AlCl_3$ of AR (Analytical Reagent) grade, purchased from S.D. Fine-chem Ltd, were used. These chemicals were thoroughly mixed and ground for 30-40 min in a mortar pastel and then the charge (25g) was melted in alumina crucible using muffle furnace for 4-5 hrs at temperature ranging from 800-1100 $^{\circ}$C depending on composition. When the melt was thoroughly homogenized and attained desirable viscosity it was poured either onto metal plate or into graphite moulds. The prepared glass was the annealed at appropriate temperatures (between 300 and 400 $^{\circ}$C) for 2 hrs and stored in desiccator prior to evaluation.

2.2. Density measurements

Density was measured for all glass samples at room temperature using xylene as the immersion liquid. Density is generally measured by the fluid displacement method depending on Archimedes principle. According the Archimedes principle, the buoyancy equals the weight of the displaced fluid. Archimedes Principle using xylene as the buoyant medium evaluated the density of the glass samples. The density was obtained by employing the relation:

$$\rho = W_a \, \rho_b / (W_a - W_b) \tag{1}$$

Where w_a is the weight of glass sample in air, w_b is the weight of glass sample in buoyant liquid, $(w_a\text{-}w_b)$ is the buoyancy, ρ_b is density of buoyant. All the measurements were made using a digital balance (contech). In case when sample reacts with water, a suitable inert liquids such as xylene, toluene etc. can be selected as the immersion medium.

2.3. Molar volume calculations

The molecular weight of the glass was also calculated as described below and using these molecular weights and density, the molar volume of the glass samples can be calculated from following expression:

$$V_m = M/\rho \tag{2}$$

Here, V_m is molar volume, ρ is the density of the sample and M is the molecular weight of the sample. In the present immersion fluid and the reported density values are the average of at least three independently measured values.

2.3. Molecular weight calculation

An example batch calculation may be demonstrated here for $xNa_2O{\cdot}(1\text{-}x)P_2O_5$ (x = 35, 40, 45, 50, 55, 60) glass system (Steps 1 and 2, see belpw). The results obtained in the case where x = 35 are sumerized in the Table 1:

Table 1. Parameters calculated for $35Na_2O{\cdot}65P_2O_5$ glass system

Glass system **$35Na_2O{\cdot}65P_2O_5$**	**Na_2O**	**P_2O_5**
Mole %	35	65
Mole Wt.	62	141,9
Wt/mole	21,70	92,26

Step 1 – Calculation of wt/mole

As molar weight of Na_2O is 62, if 100% Na_2O contains 62 mg of Na_2O (correspoonds to 10^{-3} mol), then 35% of Na_2O contains following mass (mg) of Na_2O:

100% Na_2O ≡ 62 mg of Na_2O
35% Na_2O ≡ X mg of Na_2O
X ≡ 62x35/100
X ≡ 21.7 mg of Na_2O

Similarly, if 100% of P_2O_5 (molar weight 141,9) contains 141.94 mg (correspoonds to same amount of substance, i.e. 10^{-3} mol) of P_2O_5, then 65% of P_2O_5 contains following mass (mg) of P_2O_5:

100% of P_2O_5 ≡ 141.94 mg of P_2O_5
65% of P_2O_5 ≡ Y mg of P_2O_5
Y ≡ 141.94x65/100
Y ≡ 92.26 mg of P_2O_5

Step 2 – Calculation of molecular weight of sample (M)

Molecular weight of respective glass sample is nothing but the summation of wt/mole of its constituent oxides, i.e. molecular weight of $35Na_2O{\cdot}65P_2O_5$

M ≡ wt/mole of Na_2O + wt/mole of P_2O_5
≡ X + Y
≡ 21.7 + 92.26

Hence, molecular weight of $35Na_2O{\cdot}65P_2O_5$ glass sample ≡ 113.96.

3. RESULTS AND DISCUSSION

The calculated values of density (ρ) and molar volume (V_m) for all the sodium phosphate, sodium borophosphate and mixed alkali borophosphate investigated glass samples have been displayed in Table 2-4. Variation of density (ρ) and molar volume (V_m) with Na_2O mole% for all glass samples is shown in Figure 1-3.

Table 2. Chemical composition (mol %), density values and molar volume of sodium phosphate glasses $xNa_2O{\cdot}(100\text{-}x)P_2O_5$

Sr. No.	Glass composition		Molar Mass (M)	Density (ρ)	Molar Volume (V_m)
	Na_2O	P_2O_5			
1	35	65	113.96	2.11	54.00
2	40	60	109.96	2.51	43.80
3	45	55	105.96	2.55	41.55
4	50	50	101.96	2.63	38.76
5	55	45	97.97	2.72	36.02
6	60	40	93.97	2.85	32.97

Table 3. Chemical composition (mol%), density values and molar volume of sodium borophosphate glasses $xB_2O_3{\cdot}(1\text{-}x)NaPO_3$

Sr. No.	Glass composition			Molar Mass (M)	Density (ρ)	Molar Volume (V_m)
	Na_2O	B_2O_3	P_2O_5			
1	47.5	5	47.5	100.35	2.425	41.38
2	45	10	45	98.74	2.326	42.45
3	42.5	15	42.5	97.12	2.209	43.96
4	40	20	40	95.52	2.127	44.90
5	37.5	25	37.5	93.90	2.053	45.73
6	35	30	35	92.28	2.03	45.45

Table 4. Chemical composition (mol%), density values and molar volume of mixed alkali borophosphate glasses $xNa_2O\text{-}(30\text{-}x)K_2O\text{-}10Al_2O_3\text{-}25B_2O_3\text{-}35P_2O_5$

Sr. No.	Glass composition		Molar Mass (M)	Density (ρ)	Molar Volume (Vm)
	Na_2O	K_2O			
1	05	25	103.95	2.21	47.036
2	10	20	102.33	2.32	44.107
3	15	15	100.72	2.34	43.042
4	20	10	99.11	2.44	40.62
5	25	05	97.50	2.48	39.314

The following could be concludes from the obtained results:

1. The value of density increased from 2.11 to 2.85 g/cm^3; while the values of the molar volume decreased from 54 to 32.97 cm^3 with the gradual increase of the Na_2O content in the sodium phosphate glasses. The variation of density and molar volume with mol% of sodium oxide for $xNa_2O{\cdot}(100\text{-}x)P_2O_5$ glass system is shown in Figure 1.
2. The value of density increased from 2.03 to 2.425 g/cm^3; while the values of the molar volume decreased from 45.45 to 41.38 cm^3 with the gradual increase of the Na_2O content in the sodium borophosphate glasses. The variation of density and molar volume with mol% of Na_2O for $xB_2O_3{\cdot}(1\text{-}x)NaPO_3$ glass system is shown in Figure 2.
2. The value of density increased from 2.21 to 2.48 g/cm$^{3;}$ while the values of the molar volume decreased from 47.03 to 39.31 cm^3 with the gradual increase of the Na_2O content in the mixed alkali borophosphate glasses. The variation of density

and molar volume with mol % of Na_2O for $xNa_2O \cdot (30\text{-}x)K_2O \cdot 10Al_2O_3 \cdot 25B_2O_3 \cdot 35P_2O_5$ glass system is shown in Figure 3.

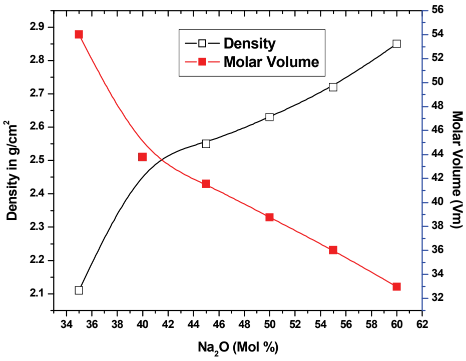

Fig. 1. Variation of density and molar volume of sodium phosphate glasses with the Na_2O content

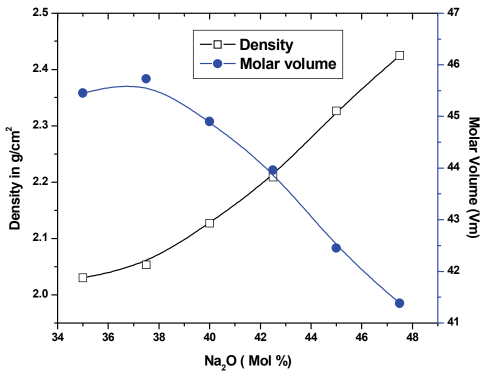

Fig. 2. Variation of density and molar volume of sodium borophosphate glasses with the Na_2O content

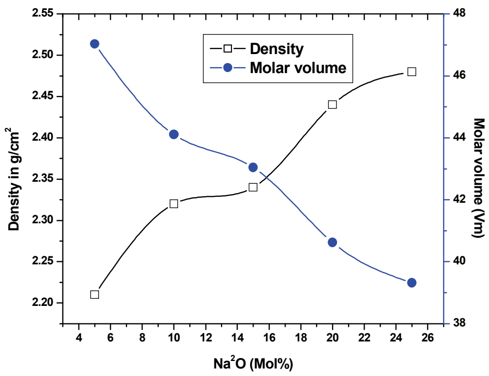

Fig. 3. Variation of density and molar volume of mixed alkali borophosphate glasses with the Na_2O content

Win Kelman and Scott [1] have proved that the additive calculation of glass density is possible by multiplication of a suitable factor of various oxide percentage in the glass. Hence, the glass is a mixture of the constituent oxides. The density is in close connection with the volume and is expressed in 10^{-24} cm^3. For simple oxide glasses, the value of the volume is always higher than that for the crystalline modifications of the corresponding oxides [12].

The density of the glass is the volume of the constituent ions and it depends on nature, the number of ions and the way by which ions can enter the glass structure [13]. The experimental results obtained can be discussed as follows.

3.1. Alkali phosphate glasses

In the alkali phosphate glasses, the introduction of sodium oxide acts as modifier oxide. The added alkali oxide causes the formation of non-bridging oxygen ions (NBOs) in the phosphate matrix. This type of ions represents broken bonds in the network. The sodium ions are linked to the surrounding oxygens by bonds which are much more ionic and also much weaker than the P-O bond. Thus, the structure of sodium phosphate glass is weaker than the other phosphate glasses. As the soda content is increased, non-bridging oxygens are formed until eventually the material consist of isolated PO_4 tetrahedra linked together by ionic Na-O bonds. Accordingly, the increase of the soda content in the glasses studied is responsible for increasing the number of the non-bridging oxygens and this may cause a decrease in the volume of the network structure and this may be the reason for the increase in the value of density, i.e. decrease in the value of molar volume with the increase of the soda content in the sodium phosphate glasses studied.

3.2. Alkali borophosphate glasses

In the sodium borophosphate glasses introduction of B_2O_3 acts as glass former along with P_2O_5. This type of glass is called as 'mixed glass former glasses' (MGFGs) [14] Fig 2 shows the composition dependence of the density and calculated molar volumes for the series of $xB_2O_3 – (1-x)NaPO_3$ glasses studied in this work. While the density values decreases from 2.425 to 2.03g/cm^3 and volume increases from 41.38 to 45.45 cm^3 with increasing B_2O_3 content at the expense of Na_2O and P_2O_5 which shows the mixed glass former effect (MGFE). Since the density can often be dominated by short range atomic packing of constituent atoms (ions) in the glass, the lack of a strong MGFE in the molar volume may indicate that the short range order, the first co-ordination sphere around each atom (ion) in the glass, is not strongly affected by mixing the glass formers. Since both end members are oxide materials, it could be expected (to the first approximation) that mixing of these two glass formers (B_2O_3 and P_2O_5) would not cause changes in the first coordination sphere around each glass forming cation, B and P. However, MGFE might cause changes in the second coordination sphere [14]. As can be seen from Fig 2, there is a linear change in both ρ and V_m when increasing the content of one of the modifier oxides, at the expense of the other. This behavior suggests a systematic difference in mentioned properties when substituting one molecule of a modifier oxide with a molecule of the other oxide. The trends observed in Fig 2 are consistent with the results of other studies [15, 16].

3.3. Mixed alkali borophosphate glasses

Figure 3 shows the composition dependence of the density and calculated molar volumes for the series of $xNa_2O\cdot(30\text{-}x)K_2O\cdot10Al_2O_3\cdot25B_2O_3\cdot35P_2O_5$ glasses studied in this work. The density values increases in the range 2.21 to 2.48 g/cm^3 and molar volume decreases from 47.03 to 39.31 cm^3 with increasing alkali ratio. As the replacement of potassium by sodium reduces molar volume causing shrinkage of the glass network which results the increase in density [17]. The increase in density observed is attributed to increase in the rigidity of glass. A sodium ion with higher field strength attracts the oxygen ions more than potassium, leading to a decrease in the size of the interstices. The effect of mixed alkali on density and molar volume is of small magnitude. The variations in density and molar volume with increase in concentration of Na_2O by replacing K_2O in MA glasses indicate that the glass network become continuously close packed. This is in agreement with the previous results [18-20].

4. CONCLUSION

The density of the glasses increased while their molar volume values decreases with the increase of sodium oxide content in phosphate glasses. All the above conclusions are in complete agreement with the experimental results obtained.

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ODREĐIVANJE GUSTINE I MOLARNE ZAPREMINE FOSFATNIH STAKALA

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U cilju proučavanja strukture pojedinih tipova fosfatnih stakala ($xNa_2O\cdot(100\text{-}x)P_2O_5$, x= 30, 35, 40, 45, 50); $xB_2O_3\cdot(1\text{-}x)NaPO_3$, x= 5, 10, 15, 20, 25; $xNa_2O\cdot(30\text{-}x)K_2O\cdot10Al_2O_3\cdot25B_2O_3\cdot35P_2O_5$, x= 5, 10, 15, 20, 25), određivane su njihova gustina i molarna zapremina. Sa povećanjem sadržaja natrijum-oksida, povećavala se i gustina fosfatnih stakala, dok se odgovarajuća molarna zapremina smanjivala. Dobijeni rezultati se mogu dovesti u vezu sa nekoliko faktora kakvi su polarizacija, jačina polja i josnki radijusi različitih inkorporiranih katjona.

Ključne reči: gustina, molarna zapremina, sastav stakla, efekat mešanjat katjona, efekat mešanja graditelja stakla