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Study of Physical Properties of Sodiumborophosphate Glasses

KEYWORDS: Average molecular weight, Density, Molar volume, Oxygen packing density, Ionic Concentration, Inter ionic distance, Polaron radius

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ABSTRACT *Glass samples of the Sodium borophosphate 42.5Na2O• (57.5-x) B2O3-xP2O5, x=0-57.5 in the step of 5.75, were prepared by conventional melt-quench technique. In order to study structure, The physical parameters like, Average molecular weight , Density , Molar volume , Oxygen packing density, Ionic Concentration , Inter ionic distance ,and Polaron radius were determined. Average molecular weight, Molar volume, Inter ionic distance, and Polaron radius are increasing; where as Oxygen packing density, and Ionic Concentration decreases with increasing the mol% of P2O5. The density of the glasses increased while their molar volume values decreases. Molar volume increases linearly as mol % of P2O5 increases. Oxygen packing density is exactly apposite to that of molar volume. Ionic concentration decreases, where as inter ionic distance and polaron radius increases with increases the mol % of P2O5, respectively. Inter-ionic separation & polaron radius, Molar refractivity & Molar polarizability are also increases parallel with increase in mol% of P2O5. Inter-ionic distance, Polaron radius and molar refraction, molar polarizability varies linearly.*

1. INTRODUCTION

Oxide glasses are classically described as a network composed by building entities such as SiO_2, B_2O_3, P_2O_5, TeO_2 and modifiers such as alkaline oxides: Li_2O, Na_2O, K_2O, Ag_2O or alkaline earth oxides: CaO, MgO, SrO [1]. In such glasses, the oxygen from the metal oxide becomes part of the covalent glass network, creating new structural units. The cations of the modifier oxide are generally present in the neighborhood of the non-bridging oxygen (NBO) in the glass structure. The extent of the network modification obviously depends on the concentration of the modifier oxide present in the glass. A glass network affects various physical properties such as density, molar volume, glass transition temperature, polarization, etc.

The mixed glass former (MGF) effect (MGFE) is defined as a nonlinear and non-additive change in the ionic conductivity with changing glass former composition at constant modifier composition. Sodium borophosphate glasses are characterized by an interesting structure on account of the presence of two glass-forming components.

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.

The density of the glass is additive and can thus be calculated on the basis of the glass composition [...]. Several formulas have been derived to correlate the glass density to the glass composition [...]. 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 [...].

The density, molar volume and packing fraction [...] could be directly related to the short range structure of alkali oxide modified borate glasses. The densities prove changes in both short range order and co-ordination as the modification, while the molar volume is sensible in terms of size and packing. The packing of the borate based glasses with ions having volume smaller than the oxygen is considered to be covalent, controlled by oxygen covalent network, and heavily dependent on the glass former.

Physical properties such as refractive index, dielectric constants are well known parameters. At an interface of two media with different refractive indices, the loss that occurs because, a fraction of the incident wave is reflected back toward the light source. At normal incidence, the fraction of reflection is expressed by the relation $R = (n_1 - n_2)^2/(n_1 + n_2)^2$ where R is the refraction loss [1]. For an air-glass interface $n_2 = 1$

The molar refractivity [...], is a constitutive-additive property which represents the real volume of the molecules. That is calculated by the Lorenz-Lorentz formula. Electric polarizability [17-23], is the relative tendency of a charge distribution, like the electron cloud of an atom or molecule, to be distorted from its normal shape by an external electric field; similarly ionic concentration [17,22,23], inter ionic distance[17,22] When an electron in the conduction band of a crystalline insulator or semiconductor polarizes or otherwise deforms the lattice in its vicinity. The polaron comprises the electron plus its surrounding lattice deformation. (Polarons can also be formed from holes in the valence band.) If the deformation extends over many lattice sites, the polaron is "large," and the lattice can be treated as a continuum. Charge carriers inducing strongly localized lattice distortions form "small" polarons [22]. These are the recent study in case of glasses. In this work, these parameters have studied to explain structural features.

2. EXPERIMENTAL TECHNIQUES

2.1. PREPARATION OF GLASSES

The Sodium-borophosphate glass samples having the general chemical formula $42.5Na_2O{\cdot}(57.5\text{-}x)B_2O_3\text{-}xP_2O_5$, (x=0-57.5 in the step of 5.75) were prepared by conventional melt-quench technique from high-purity reagent grade Na_2CO_3,H_3BO_3 and $(NH_4)_2HPO_4$ The raw materials were mixed up in the desired proportions and thoroughly ground in an agate mortar. The mixtures were fired in air in a porcelain crucible in the following manner:

(a) reaching 500°C and keeping steady at this temperature for 30 min to allow the evaporation of water from the powders to be as complete as possible; (b) reaching 800°C and keeping steady at this temperature for 30 min to allow all the gases

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removal (CO_2, NH_3,); (c) reaching 1100°C depending on composition, 4-5 hrs and keeping steady at this temperature for 30 min to allow a complete homogenization of the melt and attained desirable viscosity it was poured onto metal plate. The prepared samples was then annealed at 300-400 °C temperature for 2 hrs and then kept in vacuum desiccators to avoid possible moisture absorption before testing.

The prepared glass samples are polished and the surfaces are made perfectly plane and smoothened by 120 No. emery paper. Thickness of the samples has been measured using digital vernier calipers with an accuracy of 0.0001mm.

The composition of glass samples along with there conductivity, activation energy, and glass transition temperature is listed in Table 2.1.

2.2. DENSITY MEASUREMENTS

Density of all samples was measured at room temperature using xylene as 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:

$$\rho = \frac{W_a \rho_b}{(W_a - W_b)}$$

Where W_a is the weight of glass sample in air, W_b is the weight of glass sample in buoyant liquid, (W_a - W_b) is the buoyancy, ρ_b is density of buoyant. All the measurements were made using a digital balance.

Table 2.1: Composition of glass samples with there nomenclature, conductivity, activation energy, and glass transition temperature.

Sample No.	Name of samples	Composition in mol %			σ (SCm^{-1})	T_g °C	E_a (eV)
		Li_2O	B_2O_3	P_2O_5			
1	NBP 1	42.5	57.5	0	4.265 * 10^{-4}	436	0.65
2	NBP 2	42.5	51.75	5.75	1.202 * 10^{-4}	452.3	0.75
3	NBP 3	42.5	46	11.5	1.288 * 10^{-4}	473.7	0.72
4	NBP 4	42.5	40.25	17.25	2.951 * 10^{-4}	433.2	0.6
5	NBP 5	42.5	34.5	23	3.090 * 10^{-4}	408.0	0.59
6	NBP 6	42.5	28.75	28.75	1.949 * 10^{-4}	405.7	0.68
7	NBP 7	42.5	23	34.5	2.630 * 10^{-4}	400.8	0.66
8	NBP 8	42.5	17.25	40.25	1.288 * 10^{-4}	384.3	0.60
9	NBP 9	42.5	11.5	46	5.754 * 10^{-5}	301	0.80
10	NBP 10	42.5	5.75	51.75	1.819 * 10^{-5}	365.4	0.77
11	NBP 11	42.5	0	57.5	3.715 * 10^{-5}	371	0.78

2.3. MOLAR WEIGHT CALCULATIONS

Step I – Calculation of wt/mole

Weight/mole = molar weight of the constituents * mole% / 100

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

The molecular weight of the sample (M) is nothing but the summations of Wt/mole of its constituents.

Step III – Calculation of Molar volume (V_m)

Using molecular weight and density calculated as from above, the molar volume of the glass samples can be calculated from following expression:

$$V_m = \frac{M}{\rho}$$

Here, V_m is molar volume, ρ is the density of the sample and M is the molecular weight of the sample.

2.4. OXYGEN PACKING DENSITY (O)

The oxygen packing density of the glass samples were calculated using the following relation []

$$O = n\left(\frac{\rho}{M}\right)$$

where ρ, the density of desired glass samples, M, molecular weight of the sample and n, the number of oxygen atoms in the composition.

2.5 THE IONIC CONCENTRATIONS (N)

The ionic concentrations of the glass samples are determined using the following relation,

$$N = \left(\frac{6.023x10^{23}\ \text{mol}^{-1} * mol\%ofcation * valencyofcation}{V_m}\right)$$

2.6 INTER-IONIC DISTANCE (R)

Inter ionic distance (R) of the glass samples is given as,

$$R = \left(\frac{1}{N}\right)^{\frac{1}{3}}$$

Where N = ionic concentrations.

3. RESULT AND DISCUSSION

Average molecular weight, Density, Molar volume, Oxygen packing density Ionic concentrations, Inter-ionic distance and Polaron radius Parameters values of Sodium-borophosphate glasses are listed in Table 3.1.

Table 3.1 Average molecular weight, Density, Molar volume, Oxygen packing density Ionic concentrations , Inter-ionic distance and Polaron radius for $Na_2O{\cdot}B_2O_3$-P_2O_5 glass system.

Name of samples	Average molecular weight M (gm/mol)	Density ρ (gm/cm^3)	Molar volume V_m (cm^3/mol)	Oxygen packing density O (10^{-6} m^3/mol)	Ionic Concentration N (10^{21} / cm^3)	Inter ionic distance r_i (A°)	Polaron radius r_p (A°)
NBP.1	66.372	2.28	29.111	73.855	8.793	1.043	0.195
NBP.2	70.531	2.28	30.934	73.218	8.274	1.065	0.199
NBP.3	74.689	2.22	33.644	70.740	7.608	1.095	0.204
NBP.4	78.848	2.275	34.658	71.987	7.385	1.106	0.206
NBP.5	83.007	2.32	35.778	72.947	7.154	1.118	0.209
NBP.6	87.165	2.38	36.624	74.404	6.989	1.126	0.210
NBP.7	91.324	2.3	39.706	71.525	6.446	1.157	0.216
NBP.8	95.483	2.28	41.878	70.561	6.112	1.178	0.220
NBP.9	99.641	2.2	45.291	67.782	5.651	1.209	0.226
NBP.10	103.801	2.215	46.862	67.964	5.462	1.223	0.228
NBP.11	107.959	2.22	48.630	67.859	5.263	1.238	0.231

From Table 3.1 (Figures 3.1, and 3.2) increasing the mol% of P_2O_5 at the cost of B_2O_3 by keeping modifier Na_2O con-

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stant, the molar volume, inter ionic distance, polaron radius increasing; while oxygen packing density, ionic concentration decreases, which suggests the increased free space within the glass structure, [ ], it means that the glass structure becomes loosely packed[]. The polaron comprises the electron plus its surrounding lattice deformation. (Polarons can also be formed from holes in the valence band.) Due to the increasing values of polaron radius the deformation extends over many lattice sites, and the lattice can be treated as a continuum.

Transformation of BO_3 triangle units to BO_4 tetrahedral units can be expected to increase the network linkage of the glass which is reflected in the monotonically increasing density. []

Figure3.1. Variation of Ionic concentration and Inter ionic distance with respective to mol% of P_2O_5.

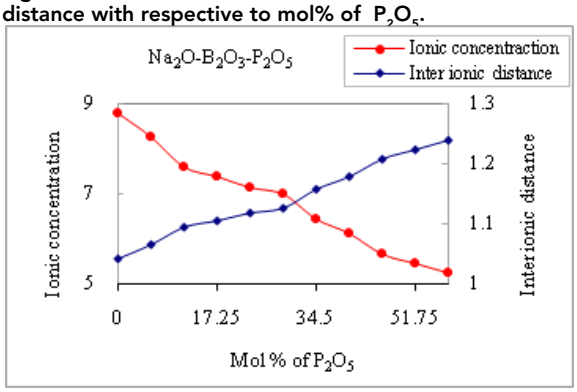


Figure3.2. Variation of Ionic concentration, Molar volume with respective to mol% of P_2O_5

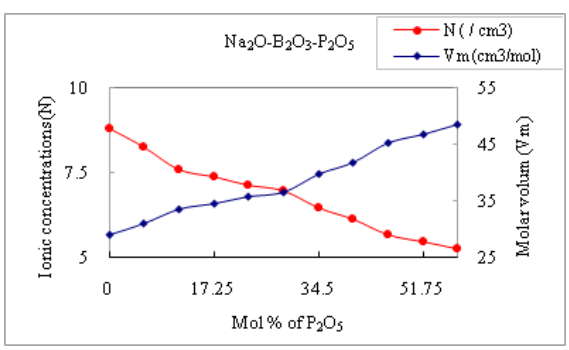
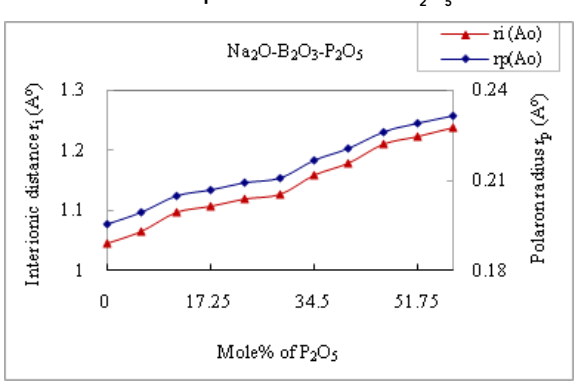


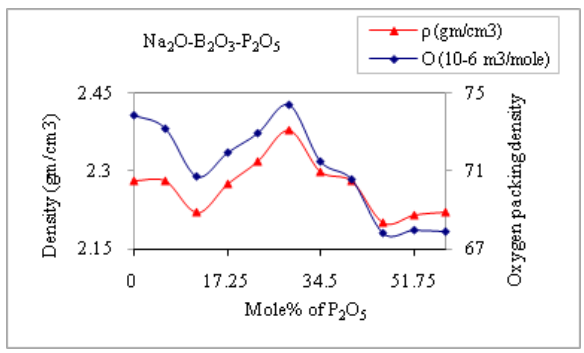
Figure3.3. Comparison of inter ionic separation and polaron radius with respective to mol% of P_2O_5



Comparison of inter-ionic separation and polaron radius is increases parallel with increase in mol% of P_2O_5, which is due to the constant value of modifier (Figure 3.3).

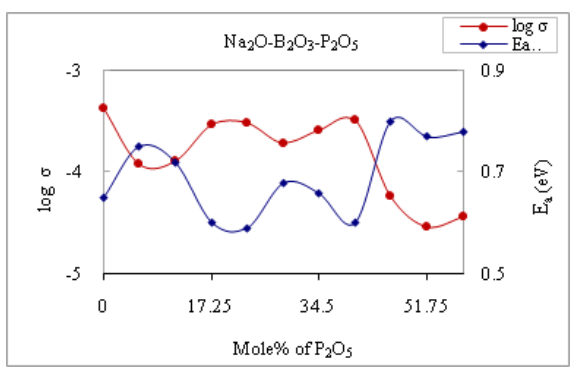
Inter-ionic distance and Polaron radius varies linearly with slope 0.187 intercept is 0.185 and R^2 is 1; similarly molar refraction and molar polarizability is also varies linearly having slop 0.396 intercept 8 and R^2 is 1

Figure3.4. Comparison of density and oxygen packing density with respective to mole% of P_2O_5



Oxygen packing density is a measure of tightening of packing of oxide network. Increase in oxygen packing density indicates that the glasses are tightly packed where as, decreasing is due to the glass structure becomes loosely packed (Figure 3.4).

Figure3.5. Comparison of log σ and E_a (eV) with respective to mol% of P_2O_5



The comparison of log σ and E_a (eV) with respective to mole% of P_2O_5 (Figure 3.5). Conductivity increases on addition of P_2O_5 up to 23 mol%, latter on it decreases due to decrease of mol % of B_2O_3.

CONCLUSION

Increasing the mol% of P_2O_5 with respective to the B_2O_3 by keeping modifier Na_2O constant, the molar volume, inter ionic distance, polaron radius increasing, suggests the increased free space within the glass structure, it means that the glass structure becomes loosely packed. Oxygen packing density, ionic concentration decreases, because the polaron comprises the electron plus its surrounding lattice deformation. Hence, the deformation extends over many lattice sites and the lattice can be treated as a continuum. Transformation of BO_3 triangle units to BO_4 tetrahedral units can be expected to increase the network linkage of the glass which is reflected in the monotonically increasing density.

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