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Influence of alkali and post transition metal oxide on physical and optical properties of lithium based phosphate glasses

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Abstract: Sodium aluminophosphate glasses containing lithium ions of composition X Li_2CO_3 - (30-X) Na_2 CO_3- 60 NH_6PO_4 -10Al_2O_3 (where $20 \leq x \geq 5$) have been prepared by melt quenching technique. The XRD spectra reveal the presence of no sharp peak confirms that the prepared glass samples were of an amorphous nature. The physical and optical properties of the glasses were investigated with the support of density and molar volume. The density of the glass matrix increases with lithium content and its molar volume shows non-linear variation. The metallic and non-metallic nature of the glass was predicted through the calculation of its physical properties. The optical properties of the prepared glass show mole fraction dependent and are mainly dependent on the basicity and polarizability of the Al_2O_3 content. The metallization criterion of the glass matrix clearly indicates the size of the conduction and valance band. Optical band gap values were found to decrease from 3.276 to 2.634 eV with aluminium content. The refractive index values were found to increase with lithium content in the glass samples. Inter-nuclear distance, field strength, oxygen packing density, polaron radius, transmission coefficient, reflection loss, dielectric constant and molar refraction were determined to study the physical properties of the glass matrix.

Keywords: borate, metallization criterion, XRD, optical band gap.

1. INTRODUCTION

The presence of alkali oxides such as lithium, potassium, or sodium oxides as glass modifier in the host phosphate glass improves the physical properties, glass forming capability, and their moisture resistance [1,2]. Besides, alkali fluorides like NaF, LiF, etc. tend to remove the hydroxyl (–OH) groups from phosphate glasses and form a three dimensional network. Also, it improves the fluorescence but decreases the phonon energy by suppressing the non-radiative losses [3]. Hence, alkali fluorophosphates glass have various applications in solar energy converters, radiation dosimetry, phosphorus, and have good mechanical strength than pure phosphate glasses[4].

High lithium ionic conducting solids are potential electrolyte materials for high energy density batteries and other electrochemical devices [5]. Phosphate glasses have good properties such as high ultraviolet (UV) transmission, high refractive index, low melting temperature, high electrical conductivity, and low glass transition temperature, which make them suitable in technological applications such as optical fibers for communication, luminescent solar energy concentrators, host glasses for solid state lasers, immobilization of nuclear wastes, glass-to-metal sealing and solid state batteries [6–8] but some of the properties like low chemical durability, poor thermal stability against crystallization, volatile and hygroscopic nature of phosphate glasses limit their extensive practical applications. These properties can be enhanced by introducing different metal oxides into the glass matrix [9,10]

Aluminium is one of the frequently used oxides which will play an intermediate role between glass modifier and glass former in the glass matrix due to three different coordination numbers [11]. The formation of P–O–Al chains, the $Al(OP)_4$ behave as the glass former, while excess Al^{3+} ions lead to $Al(OP)_6$ and behaves as the glass modifier.
In the present work we concentrated on behaviour of alkali oxide in aluminophosphate glasses, in which we could see the decrease in density and non-linear variation in molar volume using these values we were in a position to see the variation of physical and optical properties of investigated glass matrix. Also we calculate the refractive index of the glass to check whether it is suitable for optical fiber in communication purpose.

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2. EXPERIMENTAL

Pure Aldrich chemicals of lithium carbonate(Li_2CO_3), sodium carbonate(Na_2CO_3), ammonium dihydrogen phosphate(NH_6PO_4) and aluminium oxide(Al_2O_3) have used to prepare different glasses of composition X Li_2CO_3 - (30-X) Na_2CO_3- 60 NH_6PO_4 -10Al_2O_3 in mole fraction. Table 1 shows the chemical composition in mole fraction of the prepared glass. The value x varies from 0 to 25 in steps of 5 mole fraction to make desired glass to study its physical properties. To make the glass, mixture of raw materials of each batch about 14g taken in crucible. These batches taken in porcelain crucible were kept in electrical furnace to melt at 950^0 C for 2 hours. The molten liquid was shacked in between for every 20 min to obtain homogeneity in liquid. After the melting process, the liquid was quenched between pre heated copper blocks. The obtained glasses were kept for 1h in furnace at 300^0 C for annealing to remove the strain formed during the quenching process.

3. RESULTS AND DISCUSSION

3.1 Density and molar volume measurement

The density of the samples was measured using Archimedes method at room temperature with the help of acetone liquid. Glass samples were weighed in air (W_{air}) and in acetone ($W_{acetone}$) (density of acetone ρ = 0.791g/cc). The density was calculated by the formula

$$\rho = \frac{W_{air}}{W_{air} - W_{acetone}} \text{ X } 0.791 \text{ g/cc}$$

The molar volume (Vm) of the glass sample was calculated by the expression Vm=M/ ρ where M is the molecular weight of the samples. Each glass sample was measured three times for its consistence to avoid uncertainty of the measurement. Table1 represents the values of density and molar volume.

Molar volume and density of the glass samples could be an important physical parameter to study the structural compactness of the glass matrix. Molar volume and density of the samples found to be non-linear and decreases respectively. Non-linear molar volume is due to conversion of bridging and non-bridging oxygen atoms during the modification of the structure in the glass network. Figure.1 shows the variation of density and molar volume with the lithium content. Oxygen packing density (OPD) indicate the rigidity of the glass matrix can be calculated by the relation $OPD = \frac{n}{V_m} X\ 1000$ where n is the number of oxygen atoms of the glass composition. Table 2 shows the marginal change in OPD values implies the rigidity in the glass matrix.[12]

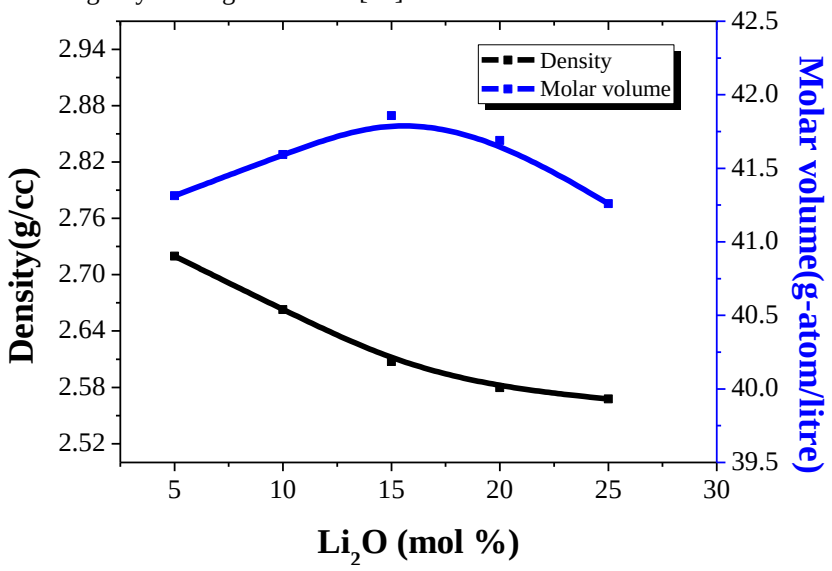

Figure 1. Variation of density and molar volume

3.2 Refractive index and molar refraction relationship

To understand the reaction of the electrons to an electromagnetic field, the Lorentz-Lorentz equation was used for the glass materials [13]. The Lorentz-Lorentz equation is correlated to molar volume (Vm), refractive index (n) and molar refraction(Rm).

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$$R_m = \left[\frac{n^2-1}{n^2+2}\right] V_m$$

The linear density of the glass matrix is strongly depending on molar volume or refractive index of the glass. Duffy [14] projected a link between the optical band gap and molar refraction as

$$R_m = V_m\left[1-\sqrt{\frac{E_g}{20}}\right]$$

Similarly, the optical dielectric constant ε_{opt} of the glass can be found using the relation $\varepsilon_{opt} = n^2$ [15].The values obtained for linear refractive index, molar refraction and optical dielectric constant are listed in Table 2. In order to estimate the metallization criterion M for the investigated glasses, the value of R_m/V_m is very important to know the nature of materials as metallic (>1) and insulator (<1) behaviour[16,17]. The metallization criterion can be calculated using $M = 1 - R_m/V_m$ and the obtained values are tabulated in Table 2. It observed that M values are found to decrease with increase in Li_2O content, depicts that the glass matrix incline towards the metallic behaviour. The metallization criterion based on band gap energy and refractive index using the Lorentz-Lorentz equation can be calculated from the expression

$$M = \left[1-\left(\frac{n^2-1}{n^2+2}\right)\right] = \left(\frac{E_g}{20}\right)^{\frac{1}{2}}$$

Metal state of the glass matrix occurred when above equation and energy gap equals to zero. Based on comparison of both quantities incline to zero, Duffy proposed that there is a relationship between molar refraction and energy gap of the glass oxide[18]. Dimitrov and Sakka calculated the metallization criterion for oxide glasses and observed that oxides with high refractive index and low energy gap holds low metallization criterion compared with low refractive index and high energy gap [19]. The values of metallization criterion are listed in. It is observed that the metallization criterion of the glasses on the basis of refractive index is in the range 0.425-0.376. Metallization criterion based on band gap energy is in the range 0.432-0.382. (shown in figure 2.)

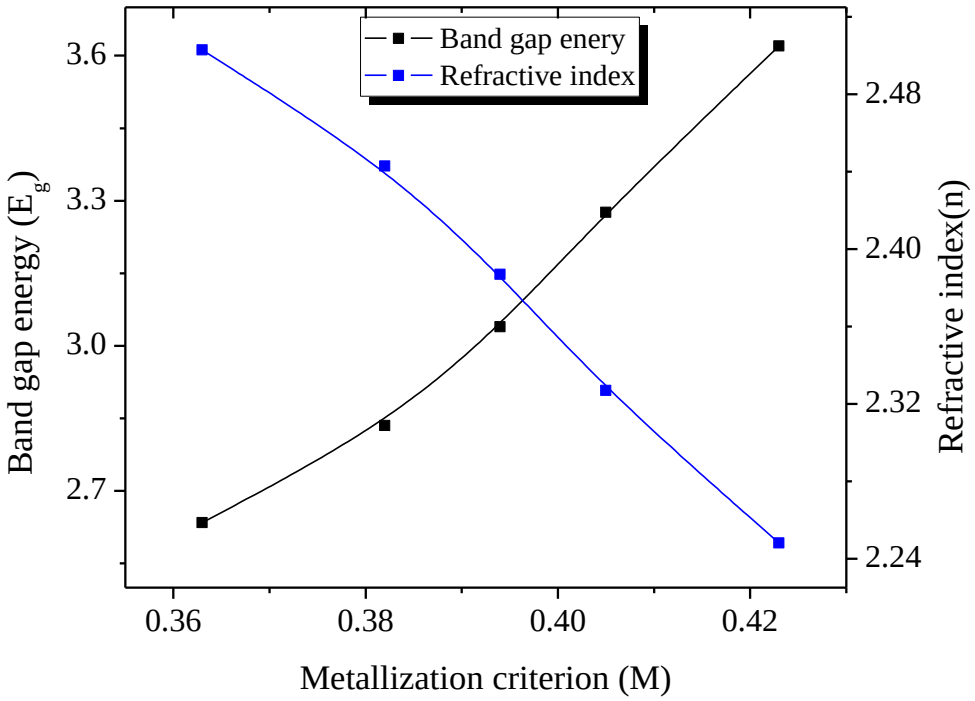

Figure 2. Variation of band gap energy and refractive index with metallization criterion.

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Table 1. Code, composition, density, molar volume, oxygen packing density and band gap energy.

Code	Composition in mol %				ρ	V_m	OPD	Band gap energy
	Li_2O	Na_2CO_3	P_2O_5	Al_2O_3	(g/cm^3)	(cm^3/mol)	(g-atom/litre)	(eV)
LNPA 1	5	25	60	10	2.719	41.312	58.094	3.620
LNPA 2	10	20	60	10	2.663	41.593	57.702	3.276
LNPA 3	15	15	60	10	2.608	41.858	57.337	3.039
LNPA 4	20	10	60	10	2.579	41.688	57.570	2.835
LNPA 5	25	5	60	10	2.568	41.258	58.169	2.634

3.3 Optical basicity and electronic polarizability

The electronic polarizability of ions can be understood when an electromagnetic filed is applied to the glass matrix, the cloud deformation occurred.[17,20] Polarizability of oxide glass is linked to macro and micro physical and chemical properties of the materials like dielectric properties, electro optical effects, chemical stability and ferroelectricity. The electronic polarizability of the glass matrix can be calculated using xApOq-yBrOs-zC$_t$Ou-wDL$_i$d from the refractive index values.

$$\alpha_{O^{2-}Li^{+}}(n) = \left[\left(\frac{V_m}{2.52}\right)\left(\frac{n^2-1}{n^2+2}\right) - \sum \alpha_i\right](N_{O^{2-}Li^{+}})^{-1}$$

where $\sum \alpha_i$ is the cation polarizability and $(N_{O^{2-}Li^{+}})$ is the number of oxide and lithium ions in the chemical formula xq+ys+zu+wd, the data of Li, Na, P and Al ions are collected from Dimitrov and Komatsu articles[17] and the obtained values are listed in Table 2. On the other hand, optical basicity ∧[19] is the means to measure the acid-base properties of glasses, alloys etc. transmitting the electron density to nearest cations by oxygen or lithium ions depends on polarization effect. The optical basicity ∧ of the glass matrix is calculated by the Duffy formula [21] based on the electronic polarizability and their values are presented in Table 2

$$\wedge = 1.67\left(1 - \frac{1}{\alpha_{O^{2-}Li^{+}}}\right)$$

The optical basicity values are found to increase with increase of lithium content which depicts the increasing of thermodynamic stability of the glass matrix due to increasing charges on aluminium and lithium[20,22]

3.4 Ion concentration (N), polaran radius (r_p), inter nuclear distance (r_i) and field strength (F)

Lithium ion concentration (N), polaran radius (r_p), inter nuclear distance (r_i) and field strength (F) can be calculated using the relations. [23]

$$N = \frac{(\text{Avogadro's number})\,(\text{sample density})}{(\text{sample average molecular weight})}\ (\%\ \text{of Lithium})$$

$$\text{Polaron radius,}\quad r_p = \left(\frac{1}{2}\right)\left(\frac{\pi}{6N}\right)^{1/3}$$

$$\text{Inter nuclear distance, } r_i = \left(\frac{1}{N}\right)^{1/3}$$

$$\text{Field strength, } F = \left(\frac{z}{r_p^2}\right)$$

Where N: Lithium ion concentration. Z: atomic mass of lithium. The calculated values for lithium ion concentration, polaran radius, inter nuclear distance and field strength are tabulated in **Table 2.** As observed from the **table 2,** the concentration of lithium ions increases in the sample with the percentage of lithium ions. Because of ratifying the compactness of the system with the addition of lithium ions. Furthermore, a decrease in inter nuclear distance and polaron radius with lithium ion concentration. This result leads to the Li-O bond strength increases which enable the strong field near the lithium ion. Field strength gives information about the arrangement of ions in the sample, the obtained values show the rigidity of the sample increases with lithium content. The variation of polaron radius and field strength with

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lithium concentration is shown in figure.3. From the figure, we observed that field strength increases while polaron radius decreases. In general field strength and polaron radius shows the opposite behaviour and which is observed in our study.

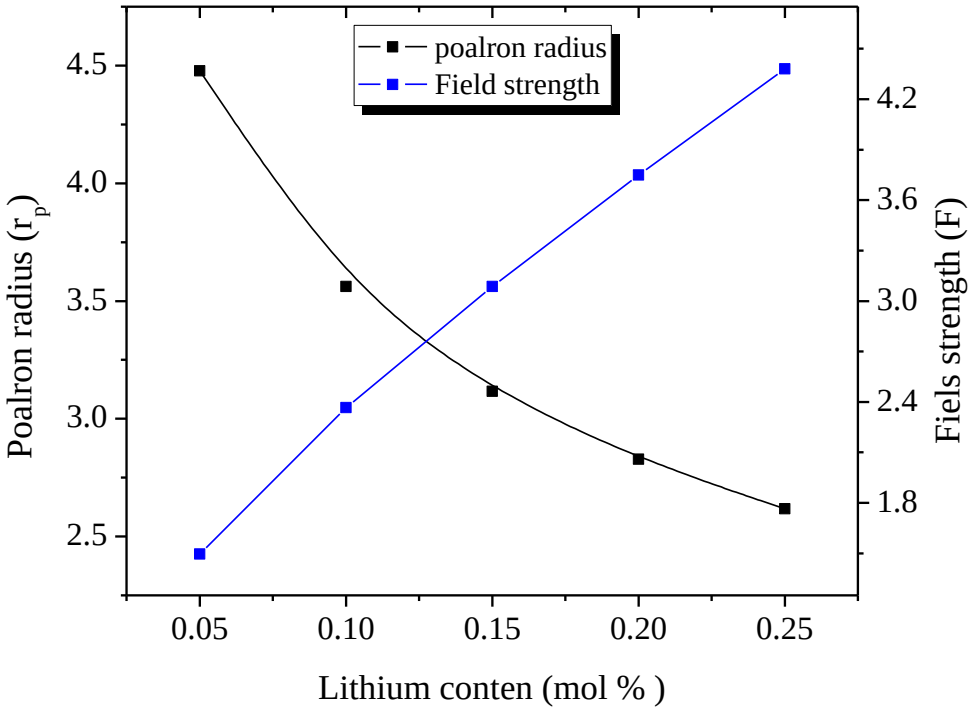

Figure 3. Variation of polaron radius and field strength with lithium content

Table 2. The physical and optical properties of LNPA glasses.

	Codes of the glass sample				
	LNPA1	LNPA2	LNPA3	LNPA4	LNPA5
Li^{2+} ion concentration ($x10^{20}$ ion/cm^3)	7.289	14.481	21.584	28.895	36.495
Polaron radius (r_p)($x10^{-8}$cm)	4.477	3.561	3.117	2.828	2.617
Inter nuclear distance (r_i) ($x10^{-8}$cm)	11.111	8.839	7.738	7.021	6.495
Field Strength (F)($x10^{15}$ cm^{-2})	1.496	2.365	3.086	3.748	4.380
Refractive Index (n)	2.247	2.326	2.386	2.443	2.503
Reflection loss (R)	0.147	0.159	0.167	0.175	0.184
Dielectric constant (ε)	5.052	5.413	5.696	5.968	6.266
Optical dielectric constant(dpt/dp)	4.052	4.412	4.696	4.968	5.266
Molar Refraction (R_M) (cm^{-3})	23.736	24.759	25.541	25.992	26.285
Electronic polarizability(α_e)(A^0)^3	9.413	9.819	10.129	10.308	10.424
Glass oxide polarizability(α_m^{2-})(A^0)^3	3.401	3.644	3.847	3.996	4.119
Optical basicity (Λ)	0.6468	0.7152	0.7657	0.7995	0.8254
Metallization criterion (M)	0.425	0.405	0.389	0.376	0.363

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CONCLUSION

Lithium sodium aluminophosphate glasses have been investigated by UV-Visible, XRD, density and molar volume. Electronic polarizability, metallization criterion and optical basicity of lithium based aluminophosphate were analysed and studied on the basis of refractive index and band gap energy. The electronic polarizability shows a tendency of increase with increasing refractive index and decreasing band gap energy. The increase of oxide ion polarizability results in increasing non-bridging oxygen atoms in the glass matrix (NBO). The optical basicity value infer the glass matrix is more basic and depicts the linear increase with increasing oxide ion polarizability. As a result of which oxide ion has ability to donate electrons to neighbouring cations. The decreasing value metallization criterion with the lithium content shows that the glass is metalizing. The refractive index value for prepared glass is suitable for using as optical fiber.

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