ROLE OF MnO_2 ON OPTICAL, PHYSICAL AND THERMAL PROPERTIES IN SODIUM ZINC PHOSPHATE GLASSES

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ABSTRACT: *Different concentration of sodium-zinc-phosphate glasses containing manganese ions were prepared by melt quenching method. The samples were analysed to study its structural, optical and thermal properties. Densities of the samples were increased where as their molar volume decreases. In addition, the field strength, manganese ion concentration, refractive index, dielectric constant, reflection loss, optical dielectric constant and electronic polarizability values were found to increase where as the corresponding inter nuclear distance, transmission coefficient and metallization criterion were decreased. The glass transition temperature was found to increase with MnO_2 content.*

1.Introduction

Phosphate glasses mixed with transition metal ions have much attracted towards optical, electrical and magnetic properties[1–6]. Paramagnetic probes comprising manganese ions used for exploring structure and properties of glasses[7–9]. In the field of low temperature sealing, phosphate glasses are much used because of their low melting and glass transition temperature. The sealing application is restricted due to the poor solubility of phosphate glass. However, solubility can be increased by adding metal oxides such as MnO_2,ZnO etc. these glasses treated to be a good for radiation shielding[10]. Sodium phosphate glasses containing transition metals plays a vital role in field of photonic applications[11,12]. The addition of ZnO in oxide glasses makes structural changes in the glass matrix due to its dual nature as former and modifier. ZnO in the glass matrix behaves as ZnO_4 and octahedrally coordinated when it behaves as former and modifier respectively[13].

In the present study MnO_2 was selected to vary its concentration in sodium zinc phosphate glass to see its variation of metallization criterion and glass transition temperature. Optical band gap energy was calculated using UV-visible analysis. Density and molar volume were calculated to study some of the properties like refractive index, polaron radius, field strength, molar refraction, inter nuclear distance, oxygen packing density,electronic polarizability, reflection loss, dielectric constant, optical dielectric constant and Mn^{2+} ion concentration.

2.Experimental

The glass matrix of 25 Na_2O-(75-x)(0.6P_2O_5-0.4 ZnO)-x MnO_2 ($0.5 \leq x \leq 20$ mol%) have been prepared using high purity chemicals Na_2O, P_2O_5, ZnO and MnO_2 in suitable proportion. Mixture of these chemicals were melted at 1000^oC. The homogenous molten liquid was quenched by pre heated copper blocks. These prepared glasses of thickness around 1mm were kept for sintering for about 3 hours to remove thermal strain produced at the time of quenching. Samples were analysed by x-ray diffraction for its amorphous confirmation. Density of all glasses was measured by Archimedes principle using acetone as immersion liquid. Oxygen packing density, molar volume and other Physical parameters were calculated for all glasses investigated. The reflectance, absorbance and transmittance were measured in the wavelength range of 200-2000nm using UV-visible spectrometer at room temperature.The spectral range of 200-2000 cm^{-1} was used to study FTIR absorption spectra using a JASCO FTIR 6200 spectrometer in which KBr pellet technique was used for IR absorption measurement.

3. Result and discussion

3.1 Density and molar volume

Density measurement for the glasses gives an information about structural changes in glass matrix. Density of glass depends on coordination number, geometrical configuration, structural compactness and cross link density[14]. Molar volume can be calculated using density and molar mass.A graph of density and molar volume variation with manganese content is shown in **Fig.1a**and the values of density and molar volume are reported in Table1. The increase of density and the corresponding decrease in molar volume with the addition of manganese makes the network rigid[15]. Oxygen packing density(OPD) is the measure of tightness of oxide network in the glasses. Increase in OPD value indicates rigidness of the glass network.

3.2 Glass transition temperature (Tg)

The glass material does not have distinct property as that of crystal for its complete structural information. The thermal differential scanning calorimeter characterisation provides complete structural information[16]. The glass transition temperature(Tg) values are found to be gradual increase with manganese concentration and is shown in **Fig. 1b**. This impedes the openness of the glass network and thereby improvesthe chemical durability of the glass.

Table 1: Code, chemical compositions, density, molar volume, OPD, and glass transition temperature.

Code	Composition (mol%)				Density (gcm^{-3})	Molar volume(cm^3)	OPD (g- atom/litre)	T_g (^oC)
	Na_2O	P_2O_5	ZnO	MnO_2				
Mn0.5	25	44.7	29.8	0.5	2.974	34.847	59.259	288
Mn1	25	44.4	29.6	1	2.982	34.704	59.935	291
Mn5	25	42	28	5	3.033	33.709	65.264	317
Mn10	25	39	26	10	3.16	31.862	73.755	338
Mn20	25	33	22	20	3.821	25.549	103.72	364

3.3 Physical Properties

For the investigated glasses, physical properties like Polaron radius (r_p), Field strength (F), Inter nuclear distance (r_i)and OPD have been calculated using the standard equations[17] and the values are listed in Table 2.

3.3.1 Polaron radius

Polaron radius is calculated using the relation

$$r_p = \frac{1}{2}\left(\frac{\pi}{6N}\right)^{\frac{1}{3}} \quad (1)$$

Where N is Avogadro number

Quasi particle polaron obtained from conduction electron in alkali oxides by its own induced polarization. The study of Polaron describes polaron interaction among electron and optical phonons[18,19].Polaron is said to be small polaron if the polaron radius is of the order of lattice constant and is said to be large polaron if its radius is larger than lattice constant. Polaron radiusvalues found to be lessor than inter nuclear distance and the values are found to decrease with increase in manganese content in the glass network.

3.3.2 Inter nuclear distance

Inter nuclear distance is estimated using Eq.2 and the values are found to decrease with manganese concentration which results in compactness of the glass.

$$r_i = \left(\frac{1}{N}\right)^{\frac{1}{3}} \quad (2)$$

Where N is ion concentration in the glass sample.

Table 2. Physical and optical parameters of the sodium zinc phosphate glasses.

Parameters	**Code**				
	Mn0.5	**Mn1**	**Mn5**	**Mn10**	**Mn20**
Polaron radius (r_p) (A^0)	11.15	11.13	11.03	10.82	10.06
Mn2+ concentration (x 10^{20} ions/cm^3)	0.864	1.735	8.933	18.9	47.15
Inter nuclear distance (r_i) (A^0)	27.6	27.56	27.3	26.8	24.91

Field strength (F) (x 10^{15} cm^{-2})	2.012	2.018	2.056	2.135	2.472
Refractive index (n)	2.291	2.34	2.383	2.424	2.56
Reflection loss(R_L)	0.153	0.161	0.167	0.173	0.192
Transmission coefficient(T)	0.733	0.722	0.713	0.705	0.677
Dielectric constant (ε)	5.246	5.475	5.679	5.875	6.554
Optical dielectric constant ($P_{dt/dp}$)	4.246	4.475	4.679	4.875	5.554
Molar refraction (R_M) (cm^3)	20.42	20.77	20.54	19.72	16.58
Electronic polarizability $(A^0)^3$	8.09	8.209	8.129	19.31	22.01
Metallization criterion(M)	0.414	0.401	0.391	0.381	0.351

3.3.3 Field strength

Field strength is the ability to attract electrons, the value of field strength for Zn^{2+} will be greater than Na^{2+} and therefore shielding of phosphorous atom is more for zinc phosphate glass[20]. The values for the investigated glass are calculated using Eq. 3

$$F = \frac{Z}{r_p{}^2} \qquad (3)$$

Where Z and R be the cationic charge and radius respectively.

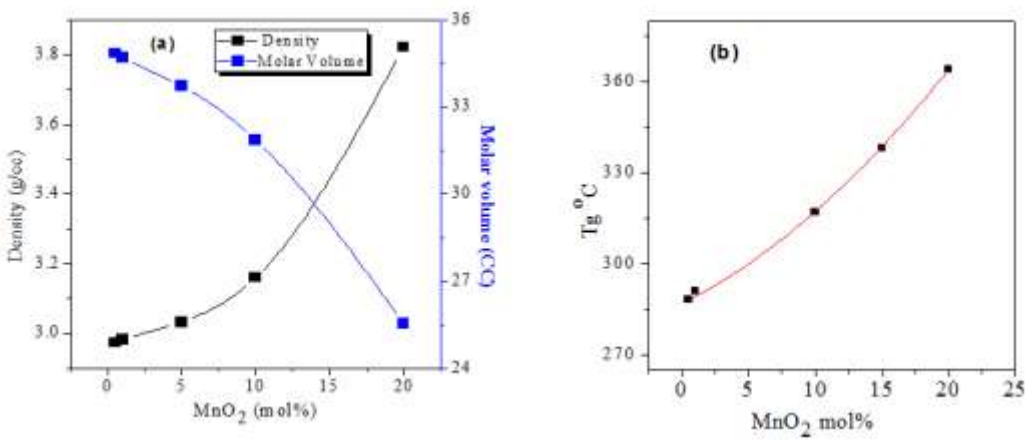

Figure1:(a) Variation of density and molar volume and (b) variation of glass transition temperature.

3.3.4 Oxygen packing density

Oxygen packing density is calculated using Eq. 4 [21] and the values are listed in Table 1.

$$OPD = X\left(\frac{\rho}{m_w}\right) \qquad (4)$$

Where ρ is density, X is number of oxygen atom and m_w is molar weight of the glass sample respectively.Decrease in molar volume due to the increase of higher field intensity causes increase in OPD which gives rise to rigidness in the glass matrix.

3.4 Optical Properties

Optical properties like, refractive index(n), molar refraction (Rm), electronic polarizability $\alpha_e(A^o)^3$, reflection loss(R_L), transmission coefficient(T), metallization criterion(M), dielectric constant(ε), optical dielectric constant ($P_{dt/dp}$), Mn^{2+} ion concentration (N) (10^{23} ion/cm^3) have been calculated using the standard equations[22] and the corresponding values are given in Table 2.

3.4.1Refractive index

Refractive index can be calculated by the value of E_{opt} using the relation given by Dimitrov and Sakka[23].

The calculated values of the refractive index listed in the Table 2 and it is noticed that the refractive index slightly increase with increasing MnO_2 content. The estimated values of the refractive index also correlated with the values calculated from Moss and Kumar-Singh relations[24,25]. The refractive index, n is one of the basic tool to describe the optical properties of the materials which are associated to local field of the material and electronic polarizability of ions[26].

3.4.2 Molar refraction and electronic polarizability

Molar refraction (R_m) for the glass sample can be calculated using relation[27]and is given by

$$R_m = \left(\frac{n^2-1}{n^2+2}\right)V_m \quad (5)$$

Where n is refractive index and V_m is molar volume of the glass

The values of molar refraction and electronic polarizability shows opposite behaviour and are presented in Table 2. The structure of the glass can be explained based on the molar refraction which is directly proportional to the electronic polarizability in accordance with Clausins-Mossotti relation[28].

$$\alpha_e = \left(\frac{3}{4\pi N}\right)R_m \quad (6)$$

Where N is polarizable ion assumed to be equal to Avogadro number (N_A)

Electronic polarizability of an ion depends on the properties of the material such as optical nonlinearity along with optical basicity, refraction and conductivity which is also show significant interest to study the polarization state of ions in crystalline and amorphous materials[29].

3.4.3 Reflection loss and transmission coefficient

Reflection loss for the investigated sample can be calculated using Fresnel's equation[18].

$$R_L = \left[\frac{n-1}{n+1}\right]^2 \quad (7)$$

Where n is the refractive index

The transmission coefficient(T) can be calculated by the relation

$$T = \frac{2n}{n^2+1} \quad (8)$$

The values of reflection loss and transmission coefficient are given in Table 2 and are found to be partial inverse proportionality with each other.

3.4.4 Dielectric constant and optical dielectric constant

The dielectric constant of the glass directly depends on its band gap energy and it is calculated using the equation[30].

$$\varepsilon = n^2 \quad (9)$$

Optical dielectric constant can be calculated by using dielectric constant[31].

$$P_{\frac{dt}{dp}} = \varepsilon_{opt} = \varepsilon - 1 \quad (10)$$

Dielectric constant and optical dielectric constant values areshown in Table 2and are found to increase with MnO_2 content.

3.4.5 Mn^{2+} ion concentration and metallization criterion

Ion concentration can be calculated using the equation[32]

$$N = \frac{\rho\, X\, N_A}{M_w} \quad (11)$$

Where ρ is density and X is molar fraction of Mn^{2+} ion

The metallization criterion can be calculated using the relation[33,34],

$$M = 1 - \frac{R_m}{V_m} \quad (12)$$

Metallic and non-metallic nature of the glass material can be verified by looking at the values of metallization criterion which can also examine the insulating behaviour of the glass samples. In accordance with Herzfeld theory value of $R_m / V_m \geq 1$ the material is said to be a metallic nature and is said to be non-metallic if $R_m / V_m \leq 1$[35]. The metallization criterion values for the glass investigated are lies in the range 0.414-0.351 and are listed in Table 2. Thisclearly suggest that glass samples have non-metallic in nature. The decreasing value of metallization criterion indicates narrow band gap energy due to the increasing width of valence band and conduction band.

3.4.6 Band gap energy

The optical band gap energy for the investigated sample is calculated using Mott and Davis theory[36]. Electronic band structure and optical transitions were studied by considering absorption effect which intern gives rise to explain the optical band gap energy[37]. The energy related to the fundamental

absorption edge will be the optical band gap energy. In accordance with Tauc's theory, following information have been pointed out based on absorption coefficient with photon energy like, Tauc region related to the higher energy linked with the inter band transitions and continuous absorption because of exciton-photon coupling. The glass material shows direct and indirect allowed transitions. The absorption coefficient $\alpha(\vartheta)$ with the photon energy $h\vartheta$ can be written as $\alpha h\vartheta = B\left(h\vartheta - E_{opt}\right)^n$ where B is the band tailing parameter, E_{opt} is the optical band gap energy and n is index parameter which can take the values as n=2 for indirect allowed transitions and n=1/2 for direct allowed transitions. **Fig. 2** shows the plot of direct allowed transitions for the zinc phosphate glass with manganese dopant. Band gap energy values were obtained by extrapolating the linear region of the curves to the zero absorption at $(\alpha h\vartheta)^{1/2} = 0$ and $(\alpha h\vartheta)^2 = 0$ for indirect and direct allowed transitions respectively. The values of the band gap energy are given in Table 3.

Table 3: Direct and indirect band gap energy for MnO_2 glasses.

Code	Band gap energy (eV)	
	Direct	Indirect
Mn0.5	5.578	3.428
Mn1	4.259	3.221
Mn5	3.464	3.052
Mn10	3.254	2.902
Mn20	2.542	2.460

3.5 FTIR study

FT-IR spectra of manganese doped glass network are as shown in **Fig3**, in which most of IR bands are broad and asymmetric. The absorption band at 574 cm^{-1} may be due to the O–P–O bonds[38]. The manganese content up to 10 mol% shows a maximum phosphorous bridging with oxygen atoms. The significant change in the amount of these bridges may reveal the modification in the glass structure because of depolymerisation of the phosphate network with increasing manganese concentration. The bands between 720cm^{-1} to 760 cm^{-1} are attributed to P-O-P symmetric stretching vibrations[39],whereas bands from 900 cm^{-1} to 940 cm^{-1} are assigned to P-O-P asymmetric stretching vibrations[40]. Up to 10 mol% of MnO_2 in the glass matrix the relative band area increases and then decreases beyond this region due to the formation of Mn-O-P bonds. This bridging would enhance the cross link density of the glass matrix besides chemical durability of the glasses. The bands 1030 cm^{-1}, 1090 cm^{-1} and 1170 cm^{-1} are due to symmetric stretch of the$(PO_3)^{2-}$ terminal group, low frequency component of asymmetric stretch of the $(PO_3)^{2-}$ terminal group and the high frequency component of the asymmetric stretch of the $(PO_3)^{2-}$ terminal grouprespectively[41]. The assigned band values of the investigated glasses are given in Table 4.

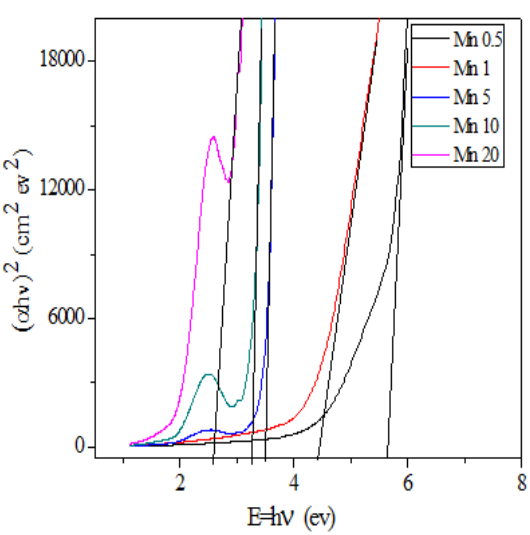

Figure 2: Tauc's plot for Mn glasses

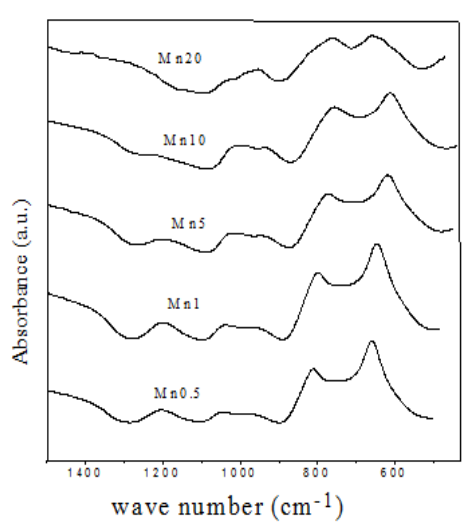

Figure 3: FT-IR spectra for Mn glasses

Table 4: IR band assignment for manganese doped sodium zinc phosphate glasses

Band frequency (cm^{-1})	Band assignment
574	Bridging O-P-O bond
720-760	P-O-P symmetric stretching vibrations
900-940	P-O-P asymmetric stretching vibrations
1030	Symmetric stretching $(PO_3)^{2-}$ group
1090	Low frequency asymmetric stretch of $(PO_3)^{2-}$ group
1170	High frequency asymmetric stretch of $(PO_3)^{2-}$ group
1200	Asymmetric stretch of the $(PO_2)^-$ group

Conclusion

Manganese containing sodium zinc phosphate glasses have been prepared using melt quenching technique. Optical, physical and thermal properties were studied by analysing density, molar volume, UV-visible and FT-IR spectroscopy. Various parameters have been calculating for the investigated samples to study the nature of the glass network. Addition of manganese ions increasesthe polarizability implies decrease in the polaron radius of the glass samples. Transmission coefficient of the manganese glass decreases leading to increased field strength of manganese ions, which results in restriction of phosphate chain structure for its stable glass structure. The metallization criterion data reveals that the prepared glass samples are found to be non-metallic in nature.

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