Lead Oxide Influence on Chemical Durability of Sodium Lead Metaphosphate Glasses

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ABSTRACT

Sodium lead metaphosphate glasses belonging to the *(50-x)Na₂O–xPbO–50P₂O₅ (x = 0, 10, 30, 50)* metaphosphate glasses series have been prepared by conventional melt-quenching method. The glass samples were characterized using X-ray diffraction (XRD), molar volume, glass transition temperature and chemical durability techniques in distilled water at 25°C. The X-ray diffraction pattern confirms the amorphous nature of the glass samples. The dissolution behavior of the samples depends on glass composition and its structure. The lowest release rate is observed for the *lead-metaphosphate matrix (x =50)* in demineralized water. The dissolution rate is found to be higher in the first day, and decreases up to five days. However, the pH of leaching solution increases continuously during the first three days and slows down progressively for last time.

Introduction

Among various conventional oxide glasses, phosphate glasses are known to have comparatively low softening point, low melting sealing glasses, optical glasses for precision molding, and active fiber devices [1–7], optoelectronics and nuclear waste storage [8,9]. However, these glasses were of poor chemical durability that limits their usefulness [10-18]. It is well known that the water durability of phosphate glasses is improved by introduction of one or more of divalent metal oxides (M_eO) (M_e = Cu, Zn, Cd, Pb) [19-24], or trivalent metal oxides ($M_{e2}O_3$) (M_e = Al, Bi, Fe) [25-27] to P_2O_5 network, which results in the formation of M_e-O-P bonds leading to increase the degree of condensation of the phosphate network.

The adding of alkali oxides (A_2O) or alkaline earth oxides (MO) to P_2O_5 glasses results in conversion of the three-dimensional network to linear metaphosphate chains when the molar ratio of alkali or alkaline earth oxide to P_2O_5 [R=A_2O/P_2O_5 =MO/P_2O_5] increases from 0 to1. The A_2O and MO act only as the network modifiers. Among various modifier oxides that play the role of glass modifiers in P_2O_5 glass network, the lead-oxide (PbO) is considered as unique since PbO is known to play a dual structural role as well as a network modifier and a network former. Recently, extensive studies have been made on PbO-P_2O_5 glasses using Raman, FTIR, NMR, X-ray diffraction techniques [23-24, 28–35]; these studies revealed that lead oxide takes the role of both glass former and glass modifier. As a glass former, PbO enters the network with PbO_4 structural units by sharing the corners of phosphate network which in turn form P-O-Pb linkages. When PbO acts as a network modifier, Pb becomes of octahedral coordination like any other conventional alkali oxide modifier.

In the present work, we report the results study of density, molar volume, glass transition temperature, chemical durability in *(50–x)Na₂O–xPbO–50P₂O₅ (x = 0, 10, 30, 50) metaphosphate glasses*, where Na₂O has the role of a network modifier; this is developed in order to determine the role of PbO in improving the water dissolution of *Na₂O–PbO–P₂O₅ phosphate glass system*.

Experimental

Commercial chemical reagents of sodium carbonate Na_2CO_3, lead oxide PbO and diammonium hydrogen phosphate $(NH_4)_2HPO_4$ were used as starting material. The batch compositions are listed in Table 1. The samples were prepared by using 10g of ingredients mixture in an alumina crucible. The crucible was initially heated in a furnace at 200°C for an hour and then at 300°C for another hour to minimize evaporation of P_2O_5 during heating at elevated temperatures. The temperature was then progressively increased to 1000 °C and held constant at this value for 15 min to homogenize the melt before quenching. The molten glasses were then quenched to room temperature under atmospheric air in order to produce vitreous samples.

The X-ray diffractograms of the powdered samples were recorded at room temperature using a Siemens D5000 diffractometer with Cu_K radiation (λ = 1,5418 Å) in the 2θ ranges of 10°–60° at a scanning rate of 2° per minute. The XRD analysis was used to confirm the amorphous nature of the glasses.

The Density measurements were carried out at room temperature, using Archimedes method with diethyl orthophthalate as an immersion fluid. The relative error in the measurements was about ±0.03 gcm⁻³. The molar volume(V_m) was calculated from the density($ρ$) determined

Table 1: Composition, density ρ, molar volume V_m, crystalline molar volume V_c, glass transition temperature T_g and dissolution rates DR in 5 days of $(50\text{-}x)Na_2O\text{–}xPbO\text{–}50P_2O_5$ metaphosphate glasses

Sample	Composition (mol%)			ρ (g/cm³)	V_m (cm³/mol)	V_c (cm³/mol)	ΔV[a]	T_g (°C)	DR (g/cm²×min)
	Na_2O	PbO	P_2O_5						
1	50	0	50	2.52	40.16	43.4	3.24	282	5×10^{-4} [b]
2	40	10	50	2.91	39.62	43.02	3.40	303	$10^{-5,8}$
3	20	30	50	3.80	38.93	42.26	3.33	320	$4,74 \times 10^{-7}$
4	0	50	50	4.69	38.75	41.5	2.75	361	10^{-7}

(a) $\Delta V = V_c\text{-}V_m$, (b) Dissolution rates DR was given in 20 hours of *$50Na_2O\text{–}50P_2O_5$ phosphate glass*

experimentally according to the relation: $V_m = M/\rho$, where M is the molar weight of the glass.

The Differential scanning calorimetry of powder samples was made at a heating rate of 10 K.min^{-1} using the DSC-SETRAM type apparatus 121 to determine the glass transition temperature (T_g); the estimated error is ±5 °C.

The chemical durability of the bulk glasses was evaluated from the weight loss of samples immersed in deionized water for 5 days. The samples were polished to 600 grit finishes with SiC paper, cleaned with acetone and suspended in glass flasks containing 100 ml of deionized water at 25 °C ±3°C. The weight loss of the samples was measured at regular time intervals. The samples were measured before and after different immersion times, by using an analytic balance of sensitivity 0.1mg. The dissolution rate (DR) was calculated by the formulae: $DR = \Delta w/(S \times t)$, where Δw is the weight loss (g), S is the sample area (cm²) before the dissolution test and t is the dissolution time (min).

Results and Discussion

The obtained results concerning nominal compositions, density, molar volume and glass transition temperature for all studied samples are listed in Table 1.

X-ray diffraction

As shown in Fig. 1, the X-ray diffraction patterns of typical glass sample, with nominal composition of *$20Na_2O\text{-}30PbO\text{-}50P_2O_5$* confirms their amorphous nature, since there is no sharp peak observed in the diffraction pattern.

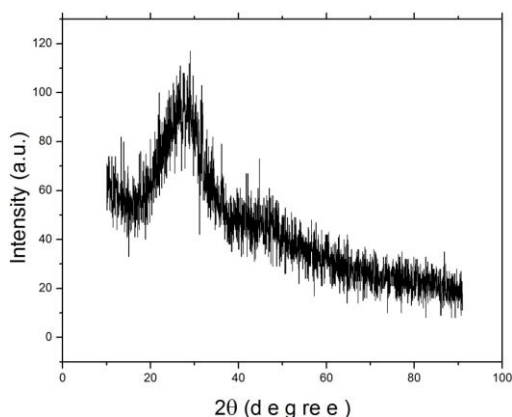**Figure 1:** X-ray diffraction patterns for typical sample $20Na_2O$– $30PbO$–$50P_2O_5$

Density and molar volume

The measured density of the glass samples is shown in Table 1. The experimental molar volume (V_m) of the glasses has been estimated from the molecular weight (M) and density (ρ). The corresponding molar volume for ideal close packing is also calculated, simply by summing up the

molar volumes of the crystalline Na_2O (27.3cm³.mol^{-1}), PbO (23.5 cm³.mol^{-1}) and P_2O_5 (59.5 cm³.mol^{-1}) in the molar ratio ($V_c = \Sigma V_i$, where i represents the ith component of the glass). Both values are listed in Table 1 for comparison. The glass molar volumes are smaller than the crystalline molar volumes in all the compositions indicating more compact structures in the glasses than in hypothetical mixed crystalline phase of the same compositions. The significant difference between the experimental molar volume and the molar volume for ideal close packing shows that Pb^{2+} ions reticule the phosphate network of the glass, and this contract the arrangement of oxygen ions.

DSC study

The glass transition temperatures for all the studied glasses are listed in Table 1. T_g increases from 282°C (for $50Na_2O\text{-}50P_2O_5$) to 361°C (for $50PbO\text{-}50P_2O_5$) [36]. The increase in glass transition temperature reflects an increase of the cross-link strength of the glass network as Pb^{2+} ions are introduced. This result can be explained by the charge densities (z/a^2) being larger in the order Pb^{2+} ($z/a^2 = 31nm^{-2}$)>Na^+ ($z/a^2 = 18$ nm^{-2}). Similar behavior was observed for other phosphate glasses containing Ca^{2+} ions [37].

Chemical durability
Weight loss

Under the operating conditions described above, it can be observed, after about twenty hours, that the glass of sodium metaphosphate $50Na_2O\text{-}50P_2O_5$ dissociates completely in the demineralized water.

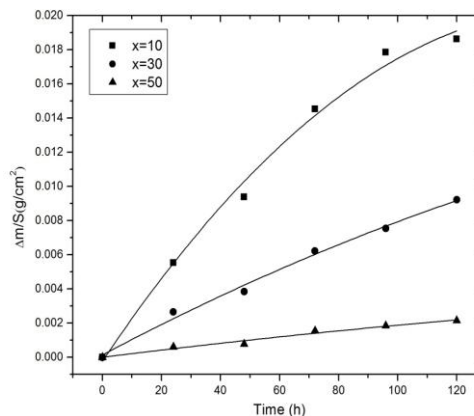**Figure 2:** Loss in weight of $(50\text{-}x)Na_2O\text{-}xPbO\text{-}50P_2O_5$ glasses attacked by water at 25 °C for different periods of time

The Fig. 2 represents the evolution of the weight losses per unit area ($\Delta m/S$) as a function of time for a few glasses of *$(50\text{–}x)Na_2O\text{–}xPbO\text{–}50P_2O_5$ (x=10, 30 and 50) metaphosphate glasses*. The substitution of Na_2O by PbO leads progressively to a considerable reduction of the chemical attack in the medium concerned.

The Figure 3 shows the effect of PbO concentration in the glass on the dissolution rates at different times of *(50–x)Na₂O–xPbO–50P₂O₅ (x=10, 30 and 50) metaphosphate glasses* immersed in distilled water at 25°C. The dissolution rate DR is higher (5×10^{-4}g.cm^{-2}.min^{-1}) for free lead glass (50Na₂O-50P₂O₅) than those observed for all other glasses (completely dissociates after about 20 hours). In 5 days, the dissolution rate DR decreases from $10^{-5,8}$ g.cm^{-2}.min^{-1} for *40Na₂O-10PbO-50P₂O₅ glass* to 10^{-7}g.cm^{-2}.min^{-1} for the glass containing 50 mol% PbO. This result indicates that the substitution sodium oxide with lead oxide in metaphosphate glasses will improve their chemical durability.
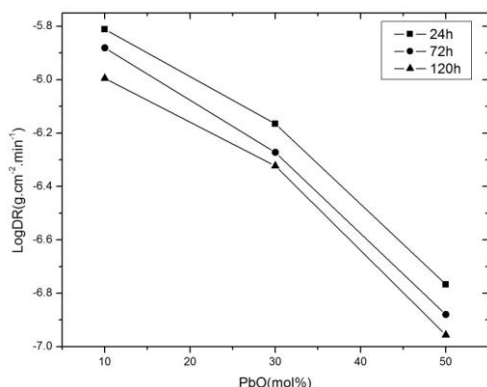

Figure 3: Composition dependence of dissolution rates (DR) for *(50-x)Na₂O-xPbO-50P₂O₅ glasses* after immersion in distilled water at 25 °C from 1 to 5 days

Variation of the pH:

The pH of each solution was measured at regular time intervals. The figure 4 shows the evolution of the pH as a function of the time of immersion. It is noticed that the pH of the solution increases continuously during a times being less than 72 hours, and beyond this value it slows down progressively, irrespective of the composition of the glass; this increase is more pronounced for rich glasses Na₂O or poor in PbO. A similar behavior was observed by Hamilton and al. [38] in the study of the silicate glass of the Na₂O-Al₂O₃-SiO₂ system.
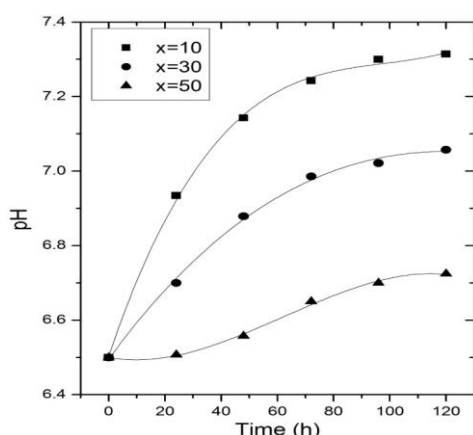
Figure 4: The pH values of the solution in which (50-x)Na₂O-xPbO-50P₂O₅ metaphosphate glasses were immersed at 25°C for different periods of time

The dissolution rates of sodium lead metaphosphate glasses of composition *(50-x)Na₂O-xPbO-50P₂O₅(x = 0, 10, 30 and 50)* studied in deionized water at 25 °C, is higher when the sample is rich in Na₂O, so the substitution of

sodium oxide by lead oxide greatly reduces the dissolution rate of glasses.

The increase in the pH of the leaching solutions is related to the inter-diffusion of the hydronium (H$^+$) ions of the solution and the sodium (Na$^+$) ions of the glass. Thus, the dissolution of sodium lead metaphosphate glasses can be directly related to the concentration of non-bridging oxygen (NBOs) in these glasses. Indeed, when a water molecule diffuses towards the vitreous network, it becomes immobile in the neighborhoods of non-bridging oxygen (NBOs). The formation of the groups (PO$^-$H$^+$) is made simultaneously with the diffusion of the Na$^+$ ion with its hydroxyl (OH$^-$) co-ion at the glass/solution interface. This process can be schematized as follows:
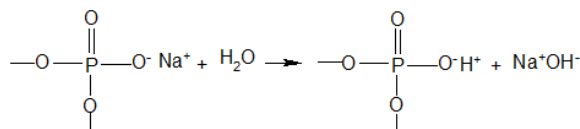

After 72 hours, the pH becomes almost constant, this can be explained by the depletion of the bridging oxygen (BOs) and consequently the glass becomes saturated with H$^+$ ions of the solution. Thus, it can be concluded that dissolution rates are limited by the diffusion of water molecules in the glass.

The Substitution of sodium oxide Na₂O with lead oxide PbO leads to the formation of P-O-Pb bonds by replacing the P-O$^-$ ... Na$^+$ bonds. This reduces the non-bridging oxygen (NBOs) and consequently there is an improvement in the chemical durability of the glass in an aqueous medium. Indeed, the structure of all the phosphate glasses consists of a network of PO₄ tetrahedral units with three bridging (P–O–P) and one terminal double bonded non-bridging (P = O) oxygen atoms. When sodium oxide (Na₂O) is added into the PO₄ network of phosphate glass, it results in conversion of three-dimensional network into linear phosphate chains with the cleavage of P–O–P linkages and creation of non-bridging oxygen (NBOs) atoms. For each introduced molecule Na₂O in the network of P₂O₅, one process occurs as it is represented in the following figure:

Network of P₂O₅   Creation of NBOs
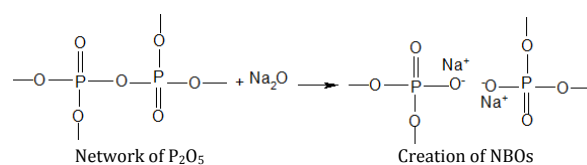
The substitution of sodium oxide with lead oxide (PbO$_{2/2}$) (since PbO itself can almost generate [PbO$_{2/2}$] unit in the network), in sodium metaphosphate glasses, leads to the formation of tetrahedral structural [PbO₄]$^{2-}$ units which share summits with ortho-phosphate PO₄ groups and the neutrality is ensured by converting the units [POO$_{3/2}$] to [PO$_{4/2}$]$^+$ [24, 30]. The process of reticulation of lead oxide PbO in the vitreous network can be schematized by the following model.
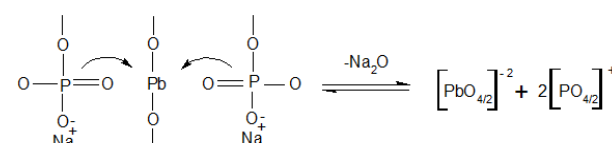
A similar behavior was observed in lead phosphate glasses [39-40] reveal that the formation of P—O—Pb bonds

linkage reticule the lead-phosphate network glasses offer these glasses a high chemical durability, reduce the dissolution rate and melting temperature.

Conclusions

Density, molar volume, thermal and chemical durability studies of *(50-x)Na₂O-xPbO-50P₂O₅ (0≤x≤50)* metaphosphate glasses system have been investigated. The amorphous nature of the synthesized material was confirmed by X-ray diffraction. The change of density and molar volume with PbO content reveals that the increase in density is related to the replacement of sodium with lead, while the decrease in the molar volume can be attributed to the smaller molar volume of PbO than that of Na₂O. The substitution of sodium oxide with lead oxide in *(50-x)Na₂O-xPbO-50P₂O₅* metaphosphate glasses reticules the network glasses by the formation of PbO₄ polyhedra and results in a large increase in T_g and in an improvement distilled water durability for these glasses.

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