

Study of the mechanical and chemical properties of potassium manganese phosphate glasses

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Abstract. Homogeneous phosphate glasses having the general formula $20K_2O-xMnO-(80-x)P_2O_5$ were synthesized using a melt-quenching method. The amorphous nature of the samples was asserted by X-ray diffraction. The glasses are studied in order to evaluate the influence of MnO addition on the chemical and mechanical properties, such as, dissolution rate, average compressive strength (R_c), Young's modulus (E) and limit strain (ϵ_{lim}). Some studies show that the addition of MnO significantly reduces the degradation rate (D_R) of soluble phosphate glasses and enhanced chemical stability of both alkali-resistance and acid-resistance. MnO interfere with the chemical structure of the glass, and consequently improve their mechanical properties. Indeed, the mechanical measurements showed that the glass structure was modified by the addition of MnO oxide, becoming more rigid, and as a result, increasing the compressive strength (R_c), Young's modulus (E). These new materials could be an important opportunity for applications in the fields of building, construction, civil engineering, etc...

Keywords: Phosphate glasses, mechanical properties, chemical durability, compressive strength, elastic modulus, strain limit.

1 Introduction

Nowadays, the study of the phosphate glasses represents a special part in the large field of material science because of their applications in the different domains [1-2]. The scientific and technological applications of glasses have encouraged researchers to custom-build the novel glasses for the industry. Glasses are receiving considerable attention due to their unique physical properties like hardness, good strength, transparency, excellent corrosion resistance and high chemical stability [3-5]. These properties of glasses to a large extent are controlled by the composition, structure and nature of the bonds of the glasses formed. Phosphate based glasses have

several advantages such as bioactivity; they are degradable and non-toxic and have been used as soluble inhibitors and conversion coating materials [6-8]. However, those glasses present poor mechanical and chemical durability properties when compared to silica based glasses. One approach to increasing these properties is to add various oxides to phosphate glasses, such as PbO, MgO, and TiO₂, and MnO, etc. These oxides lead to the formation of Pb-O-P, Mg-O-P, Ti-O-P and Mn-O-P bonds which replace the easily hydrolysable P-P-P bonds and improve dramatically the chemical durability of the modified phosphate glasses [9-13]. Similarly, the properties of these glasses in terms of mechanical, structural, and electrical properties can be also improved by adding some oxides cited

above. The presence of P–O–Mn bands in higher concentration makes the glass more hydration resistant. The addition of metal oxides to the glass leads to a depolymerisation of the network, with the breaking of P–O–P linkages and the creation of non-bridging. Mechanical strength is a crucial factor for structural application of a material. Although all the characters of applied force, temperature, shape, and surface defects significantly influence the strength of a glass product, the mechanical properties of a glass are basically determined by its elastic module values (e.g., bulk, shear, and Young’s modulus). To the best of our knowledge, there is no work related to the effect of metallic oxides addition on the mechanical and chemical and properties of a K-containing phosphate glass. The aim of this work was to investigate the effect of MnO addition on the dissolution rates and mechanical properties of potassium phosphates glasses, such as degradation rate (D_R), compressive strength (R_c), Young’s modulus (E), and limit strain (ϵ_{lim}).

2 Materials and methods

The glass samples were prepared from reagent grades of K_2CO_3 , $MnCO_3$ and $NH_4H_2PO_4$, mixed according to the molar composition. Were prepared by mixing proportionally weighed raw materials and melted at $1100^\circ C$ for 1h. Details of the procedure adopted in the preparation of these glasses have been described in our earlier work [13].

X-ray diffraction patterns were recorded at room temperature with a Simens D5000 diffractometer using CuK radiation.

For the chemical durability analysis, samples they were then immersed into a beaker filled with 50 mL of different medium at $25^\circ C$ for 6, 12 and 24 hours. The dissolution rate (DR) was determined from the weight loss during the aqueous treatment at $25^\circ C$. The dissolution rate (DR) was calculated as:

$$DR = \frac{\Delta w}{S \cdot t}$$

Where Δw is the weight loss (g), S is the sample area (cm^2) before the dissolution test and t is the dissolution time (min).

Compression testing of four glasses (V1), (V2), (V3) and (V4) are also performed on cylindrical specimens of dimensions $h = 5mm$ and diameter = 8mm. These specimens are made by a static compaction with an effort of 5MPa associated

with the different dosages of manganese oxide 15, 20, 25 and 30 mol % (Figure 1).

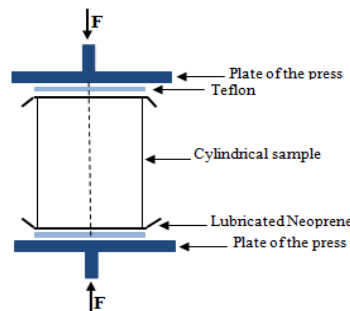


Fig.1. Experimental material of compression test

Glass shows an almost perfect brittle-elastic behavior at temperatures lower than the transformation point. The strain is proportional to the stress according to Hooke’s law. If the ends of a rod are exposed to a stress σ , its relative elongation is given by:

$$\sigma = E \cdot \epsilon$$

Where:

σ : is stress [MPa]

E: modulus of elasticity [MPa]

ϵ : strain

3 Glass-forming region

The glass forming region is shown in triaxial K_2O , MnO , P_2O_5 diagram by area enclosed by the solid line in fig.2.

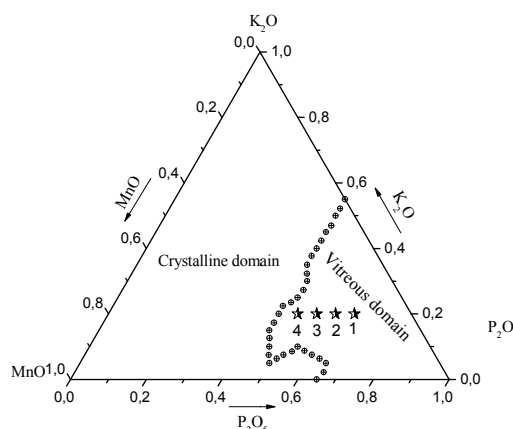


Fig.2. The glass-forming region in the system K_2O - MnO - P_2O_5 at $1100^\circ C$ [12] (see Table 1 for the correspondence between the batch numbers and chemical composition)

Table 1. Composition (mol %), density ρ ($\text{g}\cdot\text{cm}^{-3}$) of the studied specimens.

Glass no.	K ₂ O	MnO	P ₂ O ₅	ρ
V1	20	15	65	2.64
V2	20	20	60	2.72
V3	20	25	55	2.81
V4	20	30	50	2.89

3 results and discussion

3.1 X-ray diffraction

As shown in Fig. 3, the X-ray diffraction patterns for all the studied compositions, confirms their amorphous nature, since there is no sharp peak observed in the diffraction pattern.

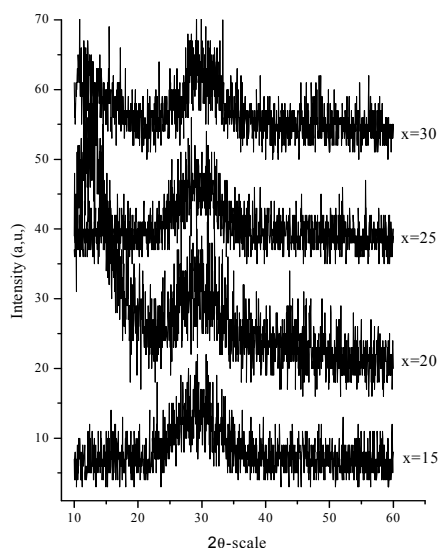


Fig.3. X-ray powder diffraction patterns of the K₂O-MnO-P₂O₅ system.

3.2 Chemical durability

The dissolution rates D_R of the potassium manganese phosphate glasses, measured from their weight loss in distilled water at 25 °C, are given in Table 2 and fig.3.

All the leaching experiments were carried out at pH = 4, 6 and 11. The leaching experiments at ambient temperature were carried out on all glasses from V1 to V4 at all leaching times of 6 h, 12 h and 24 hours, with leaching solutions of HCl (pH = 4), distilled water (pH = 6), and NH₃ (pH = 11).

Table 2 summarizes the values of the dissolution rates DR changes for all of these leaching

experiments. In a general manner, all the glasses studied exhibit similar behavior as a function of the pH and whatever the time of alteration. The dissolution rates DR of the leachate decreases in an initially neutral and basic medium whereas it increases in an initially acidic medium.

3.2.1 Variation of the dissolution rates (DR)

Fig. 4 shows the effect of MnO concentration on the dissolution rate at different times of 20K₂O-xMnO-(80-x)P₂O₅ (x=15, 20, 25 and 30) glasses immersed in distilled water at 25°C. The dissolution **Table 2.** Dissolution rate DR ($\text{g}\cdot\text{cm}^{-3}\cdot\text{min}^{-1}$) of 20K₂O-xMnO-(80-x)P₂O₅ glasses in three different middle (pH= 4,6 and 11) at 25°C for 24 hours.

Initial pH	Composition (x)	DR values after an immersion time of 6, 12 and 24 hours		
		6	12	24
4	15	$3,89\cdot 10^{-6}$	$4,26\cdot 10^{-6}$	$3,31\cdot 10^{-6}$
	20	$6,91\cdot 10^{-6}$	$6,45\cdot 10^{-6}$	$5,49\cdot 10^{-6}$
	25	$7,76\cdot 10^{-6}$	$7,24\cdot 10^{-6}$	$6,30\cdot 10^{-6}$
	30	$8,51\cdot 10^{-6}$	$7,26\cdot 10^{-6}$	$6,60\cdot 10^{-6}$
6	15	$1,69\cdot 10^{-5}$	$1,28\cdot 10^{-5}$	$1,23\cdot 10^{-5}$
	20	$1,54\cdot 10^{-5}$	$1,20\cdot 10^{-5}$	$9,54\cdot 10^{-6}$
	25	$8,91\cdot 10^{-6}$	$7,24\cdot 10^{-6}$	$6,30\cdot 10^{-6}$
	30	$4,17\cdot 10^{-6}$	$3,39\cdot 10^{-6}$	$2,29\cdot 10^{-6}$
11	15	$7,08\cdot 10^{-6}$	$6,92\cdot 10^{-6}$	$6,76\cdot 10^{-6}$
	20	$5,50\cdot 10^{-6}$	$5,24\cdot 10^{-6}$	$4,78\cdot 10^{-6}$
	25	$4,78\cdot 10^{-6}$	$3,98\cdot 10^{-6}$	$3,80\cdot 10^{-6}$
	30	$4,46\cdot 10^{-6}$	$3,31\cdot 10^{-6}$	$2,75\cdot 10^{-6}$

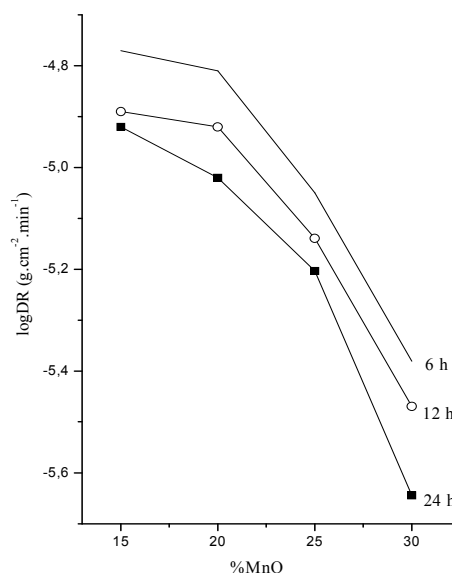


Fig.4. Composition dependence of dissolution rates (DR) for 20K₂O-xMnO-(80-x)P₂O₅ glasses after immersion in distilled water at 25 °C for 6 h, 12 h and 24 hours.

rate decreases slightly between 15 and 20 mol% MnO. For MnO additions >20 mol%, the dissolution rate decreases rapidly as MnO concentration increases.

The increasing addition of MnO gives a decrease in solubility. Therefore, in our case we assumed that the higher dissolution rate for less than 20% MnO corresponds to the release of metaphosphate chains into the solution. As it was discussed in our previous works [12,13] from IR and Raman spectra, the addition of less than 20 mol% MnO shows that MnO has a smaller effect on the glass structure with infinite long chains of PO₄ tetrahedra. When increasing MnO concentration, the metaphosphate chains are broken into smaller groups of short chain phosphates such as P₄O₁₃⁶⁻, P₃O₁₀⁵⁻ and P₂O₇⁴⁻, which are linked to manganese through P–O–Mn bonds. The formation of P–O–Mn bonds increases the cross-link between the phosphate chains and leads to enhanced chemical durability, in accordance with the increase of T_g [12-13]. These variations can be explained by the effect of the cation substitution on the reticulation of the glasses. The MnO addition causes a shrinking of the phosphate network and creates a more entangled and reticulated metaphosphate chains [14]. In addition, the P-O-K bonds are more sensitive to the hydration process compared to P-O-Mn bonds. These combined effects make the high MnO glasses composition more resistant toward water attack and delay its diffusion into the glasses [15].

3.2.1 Variation of the pH

The table 3 summarizes the pH vales as a function of the time of immersion in three different middles.

Table 3. Composition dependence of pH of 20K₂O-x MnO-(80-x)P₂O₅ glasses in three different middle (pH= 4,6 and 11) at 25°C for 24 hours.

Initial pH	Composition (x mol %)	pH values after an immersion time of 6, 12 and 24 hours		
		6	12	24
4	15	6.99	7.13	7.17
	20	7.18	7.22	7.32
	25	7.82	7.93	7.98
	30	8.28	8.42	8.78
6	15	8.40	8.75	9.22
	20	8.11	8.53	8.70
	25	7.81	8.02	8.26
	30	7.78	7.96	8.07
11	15	10.55	10.37	10.17
	20	10.58	10.45	10.26
	25	10.61	10.48	10.32
	30	10.79	10.6	10.44

The figure 5 shows the evolution of the pH as a function of the MnO content. It is noticed that the pH of the solution decreases continuously during a times being less than 12 hours, and beyond this value it slows down progressively.

This figure shows that from an initial value of 6 for distilled water, increases continuously with the immersion time to reach a maximum value of 9.22. A similar behavior was observed for the medium of pH = 4.

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 potassium (K⁺) ions of the glass. Thus, the dissolution of potassium manganese 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 (P-O-H⁺) is made simultaneously with the diffusion of the K⁺ ion with its hydroxyl (OH⁻) co-ion at the glass/solution interface [16].

This process can be schematized as follows:

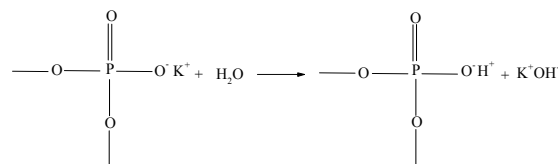


Table 4. Experimental results means the mechanical characteristics of the studied glasses

	E(MPa)	Rc(MPa)	ε _{lim} (%)
V1	417	31.73	28.17
V2	2193	37.45	19.64
V3	2474	42.64	17.73
V4	2759	54.91	15.34

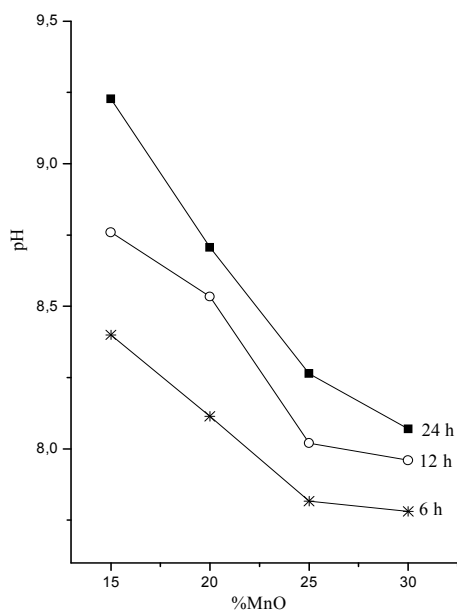


Fig.5. Composition dependence of pH for $20K_2O-xMnO-(80-x)P_2O_5$ glasses after immersion in distilled water at $25^\circ C$ for 6 h, 12 h and 24 hours.

The basification of the pH = 4 and pH = 6 solutions can be attributed to the alkali extraction by ion exchange mechanisms between the protons of the solution and the network modifying elements, this exchange process is responsible for the increase of pH due to the increase of residual OH^- ions in the solution.

For solutions initially basic pH = 11, the evolution of pH over time is less meaningful than for solutions of pH = 4 and 6 for all glasses. Indeed, we notice a drop in pH. It evolves with time and reaches its minimum value at 24 hours certainly due to a consumption OH^- ion.

3.4 Mechanical properties

3.4.1 Effect of the chemical constituents of the glass on the mechanical behavior of the vitreous material

The experimental results of the average compressive strength (R_c), the Young modulus (E) and the limit strain (ϵ_{lim}) of four glasses, associated with different dosages of manganese oxide, are summarized in Table 4.

Table 4. Experimental results means the mechanical characteristics of the studied glasses

Figs.6 and 7 give the evolution of the compressive strength, the Young's modulus and the limit strain of four glasses (V1), (V2), (V3) and (V4).

As can be seen from Fig. 6, the Young's modulus values increase with MnO content. The influence of the manganese oxide content on the strength characteristics of glasses is illustrated by the data presented in Table 4 and Fig. 6. The glasses contains over 20 mol% manganese oxide, and present a greater rigidity than the glass (V1).The rigidity is generally dependent upon the bond strength and cross-link density. The increase in elastic modulus with an increase in MnO content is attributed to increasing in the cross-link density and rigidity of glass. In addition, MnO enters into the glass network in a position which create a cross-linking between Mn^{2+} ions and the phosphate tetrahedral (Mn-O-P instead of P-O-P). Thus, the enhancement of the structure with addition of MnO beyond 30 mol% results in the increase in modulus, as noticed in Figs. 6-7, and Table 4. That MnO has the ability to enter into the vitreous arrangements.

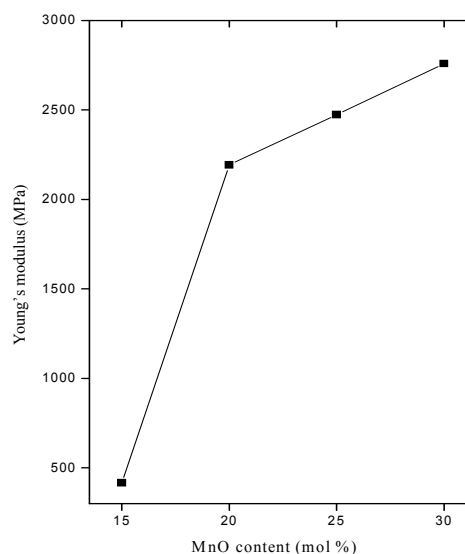


Fig. 6. Variation of Elastic modulus versus MnO content mol%.

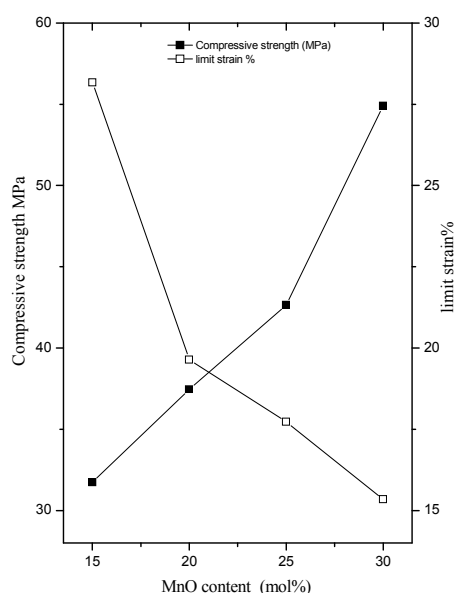


Fig.7. Variation of compressive strength and limit strain versus MnO content in mol%.

and thus, creates a stronger Mn–O–P linkage and increases the O/P ratios in the network are causes depolymerisation in the phosphate network. In consequently, the glass network becomes compact and thereby increases elastic modulus as observed in Figs. 6 and 7. This result is in agreement with our recently studies [12,13]. The addition of manganese oxide to the glass increases the density of glasses which ranged from 2.64 g/cm³ for (V1) to 2.89 g/cm³ for (V4) (Table 1). The glass transition temperature also increased with the addition of MnO to the 20K₂O-xMnO-(80-x)P₂O₅ glasses. Results presented in Tables 1 and 4, and Figures 6 and 7 show that the density and the compressive strength increase with increasing MnO in the glass, stiffens the material and reduces its ability to deform as showed in figure 7.

. This is due to the presence of MnO oxide which provides more density and more strength than K₂O. This indicates that replacement of K⁺ ion by Mn²⁺ ion increase the density as well as compressive strength of the of glass.

The potassium manganese phosphate network becomes stronger with increasing MnO content. The improved durability with increased MnO content is attributed to the easy hydrated P-O-P bonds being replaced by more chemically resistant Mn-O-P bonds. The elastic modulus of the glass

samples shows an improvement in their mechanical properties with the increase in the MnO content.

This increase in strength is believed to be due to the replacement of monovalent potassium ions by divalent manganese ions which increases the cross-link density in the glass structure and makes the glass stronger. The combination of high strength and good chemical durability of the manganese phosphate glasses, along with the fact that they can be prepared at relatively low temperatures, are valuable advantages for potential technological applications. The observed decrease in limit strain can be attributed to the resulted increase in rigidity and the glass network connectivity. Similar results were found by Hsu et al. [17] and by Hand and Tadjiev [18] when studying, respectively Nb–Sr-phosphate glasses and Mg-silicate glasses.

Conclusions

In this work, we presented the preliminary results obtained for 20K₂O-xMnO-(80-x)P₂O₅ (15≤x≤30) glasses investigated by XRD and chemical durability. It was confirmed that the prepared glasses are amorphous. The improved chemical durability with increasing manganese content is attributed to the easily hydrated P-O-P bond being replaced by more chemically resistant Mn-O-P bond. The mechanical properties of potassium manganese phosphate have been investigated. On increasing the amount of MnO in the glass samples, density, Young's moduli and compressive strength were found to increase accordingly. The results revealed that chemical durability is in good agreement with the mechanical properties. Glasses containing more than 20 mol% of MnO had excellent chemical resistance, good mechanical strength and rigidity.

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