



## Role of manganese in $20\text{K}_2\text{O}-x\text{MnO}-(80-x)\text{P}_2\text{O}_5$ phosphate glasses and model of structural units

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### Abstract

Glasses with composition  $20\text{K}_2\text{O}-x\text{MnO}-(80-x)\text{P}_2\text{O}_5$  with  $0 \leq x \leq 30$  mol% were prepared by conventional melt quenching technique at  $1100^\circ\text{C}$  mixtures of  $\text{K}_2\text{CO}_3$ ,  $\text{MnCO}_3$  and  $\text{NH}_4\text{H}_2\text{PO}_4$ . Their density, molar volume, glass transition temperature and infrared spectroscopy have been investigated. Differential Scanning Calorimetry (DSC) measurements give the variation of glass transition temperature ( $T_g$ ) from  $225^\circ\text{C}$  for  $x=0$  to  $440^\circ\text{C}$  for  $x=30$  mol %. The density ( $\rho$ ) measurements increase from 2.28 to  $2.89 \text{ g}\cdot\text{cm}^{-3}$ . The evolution of infrared spectra with the composition is studied and the oxide forming character is discussed. When manganese oxide is added to potassium phosphate glass, phosphate chains are depolymerized by the incorporation of distorted (4) units through P-O-Mn bonds. It is assumed to be presented as  $[\text{MnO}_4]^{2-}$  structural units a corner sharing geometry and the electrical neutrality in the system is achieved by the conversion of  $[\text{POO}_{3/2}]$  into  $[\text{PO}_{4/2}]^+$  units.

**Keywords:** Phosphate glasses, Glass transition temperature, DSC, IR spectroscopy, X-Ray Fluorescence

### 1. Introduction

Phosphate glasses are technologically important materials, because of their relatively large thermal expansion coefficients, low optical dispersions and low glass transition temperatures ( $T_g$ ) [1-3]. They have found important applications in glass-to-metal seals, laser hosts and biocompatible materials. Glasses containing transition metals like  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$  possess better semiconducting properties and hence they are used for several applications such as memory switching, electrical threshold [4-6]. Among all transition metal ions, manganese (Mn) is particularly interesting because it exists in multivalent states with different coordination in glass matrices [7-9].

In the last years, various searchers have been interested in manganese polyphosphate glasses [10-15]. The structural and physical properties of these glasses have been studied by means of DTA, EPR, magnetic susceptibility and FT-IR measurements. A strong dependence of structural and physical properties with concentration of manganese ions has been noticed.

However, phosphate glasses typically have a relatively poor chemical durability, which often limits their applications. One approach to increasing the chemical durability is to add various oxides to phosphate glasses, such as  $\text{SnO}$ ,  $\text{PbO}$ ,  $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{MnO}$ , etc. These oxides lead to the formation of Sn-O-P, Pb-O-P, Zn-O-P, Al-O-P, Fe-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 [3, 15, 16-22]. Similarly, the properties of these glasses in terms of physical, structural, and electrical properties can be also improved by adding some oxides cited above.

In the present work physical properties such as density ( $\rho$ ), the molar volume ( $V_m$ ) and the glass-transition temperature ( $T_g$ ), are put together with the results of the infrared spectra (IR) study of  $20\text{K}_2\text{O}-x\text{MnO}-$

(80-x)P<sub>2</sub>O<sub>5</sub> phosphate glasses with 0 ≤ x ≤ 30 mol%, where the phosphorus oxide is replaced by manganese oxide by maintaining the amount of K<sub>2</sub>O constant. A correlation between thermal and structural properties of the studied glasses has been established in order to determine the structural role of MnO in these glasses.

## 2. Materials and methods

Glasses were prepared using analytical-grade K<sub>2</sub>CO<sub>3</sub>, MnCO<sub>3</sub> and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>. Batches of 4 or 6 g were weighed to prepare glass compositions of 20K<sub>2</sub>O-xMnO-(80-x)P<sub>2</sub>O<sub>5</sub> with 0 ≤ x ≤ 30 mol%. The batches were introduced in an alumina crucible and melted at 1100°C during 30 min. Details of the procedure adopted upon the preparation of glasses have been described in our previous paper [23]. Figure 1 and Table 1 give the chemical compositions of the studied samples.

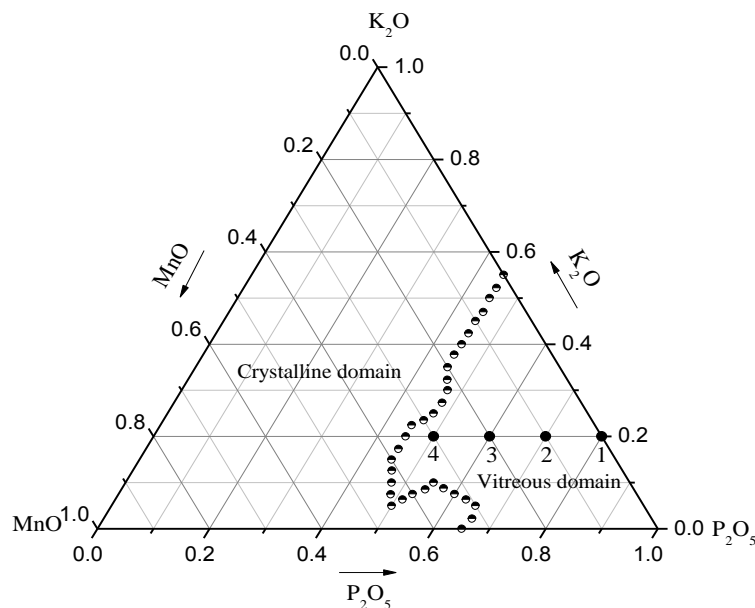
X-ray diffractograms of the powdered samples were recorded at room temperature using a Siemens D5000 diffractometer with CuK radiation (λ = 1,5418 Å) in the 2θ ranges of 10°-60° at a scanning rate of 2° per minute. The XRD analysis was used to confirm the amorphous nature of the glasses.

Density was measured at room temperature by Archimedes principle using diethyl phthalate as an immersion fluid. The relative error of measurements was about ± (0.03g.cm<sup>-3</sup>).

The glass transition temperatures were measured on 20-30 mg of samples using the DSC- SETRAM type apparatus 121 with a heating rate of 10 °C/min under argon atmosphere whose accuracy is ± 5°C.

FTIR-ATR characterization of the samples was performed using a Jasco FT/IR 4600 spectrometer equipped with a Jasco ATR PRO ONE module. The samples were scanned in transmission mode 4 cm<sup>-1</sup> resolution at the range 4000-400 cm<sup>-1</sup>.

The elemental composition of materials was analyzed using X-Ray fluorescence spectroscopy (XRF, Panalytical Epsilon 5). Each sample (~4g) was mixed with 4g of boric acid, followed by grinding the mixture in order to homogenize the whole. The nominal and analyzed glass compositions are reported in Table 1.



**Figure 1:** The glass-forming region in the system K<sub>2</sub>O-MnO-P<sub>2</sub>O<sub>5</sub> at 1100 °C [23].

**Table 1:** Analyzed (A) and nominal (N) composition (mol %), density ρ (g.cm<sup>-3</sup>), molar volume V<sub>m</sub> (cm<sup>3</sup>.mol<sup>-1</sup>) and glass transition temperature T<sub>g</sub> (°C) of the studied specimens.

Glass no.	K <sub>2</sub> O N/A	MnO N/A	P <sub>2</sub> O <sub>5</sub> N/A	ρ	V <sub>m</sub>	T <sub>g</sub>
1	20/17	0/0	80/83	2.28	52.48	255
2	20/19	10/10	70/71	2.67	48.27	342
3	20/18	20/19	60/63	2.72	43.94	388
4	20/18	30/28	50/54	2.89	41.32	440

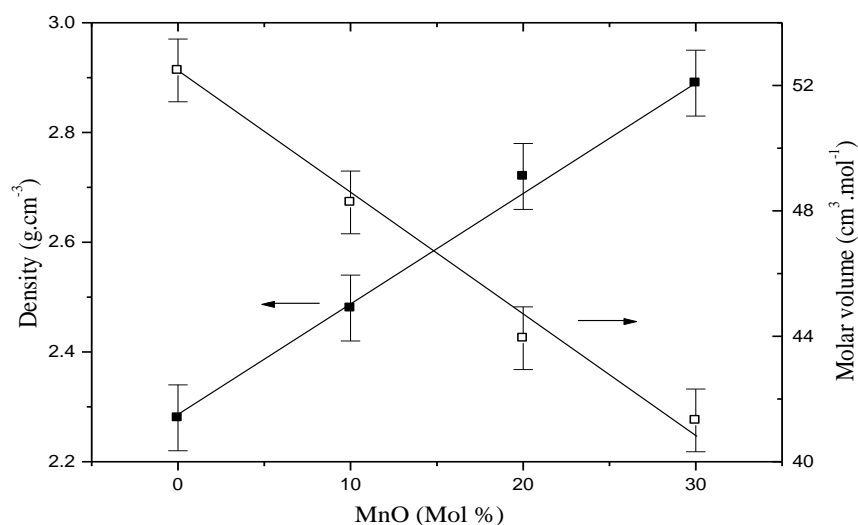
### 3. Results and discussion

X-ray diffraction patterns of all potassium phosphate glasses with different concentrations of manganese exhibit a broader continuum and no sharp peak was detected, which confirm the amorphous nature of all the synthesized glassy samples.

#### 3.1. Density and molar volume

Density is one of the effective tools to explore the degree of structural compactness. The density and molar volume of the glass network depend upon many factors such as structure, coordination number, cross-link density, and dimensionality of interstitial spaces [24].

The molar volume of glass was calculated from the density data:  $V_m = M/\rho$ . Where  $V_m$  is the molar volume as calculated from the determined density  $\rho$ , and  $M$  is the molecular weight of the glass. The variation in the density and molar volume of  $20K_2O-xMnO-(80-x)P_2O_5$  glasses with composition are listed in Table 1 and graphically presented in Figure 2. From Table 1 and Figure 2, it is indicated that the density gradually increases with increasing concentration of MnO while corresponding molar volume decreases. The density of these glasses should decrease due to replacement of high molecular weight  $P_2O_5$  by low molecular weight MnO. But it is found that the density of these glasses increases with addition of MnO and correspondingly molar volume decreases, indicating that the manganese polyhedral form some new interconnections with the structural network and thus stabilize the glass structure. This behavior can be explained by the formation of P—O—Mn bonds linkage which reticulate the phosphate network and lead to the close structure of the glasses. Similar result has also been observed in  $(50-x/2)Na_2O-xMnO-(50-x/2)P_2O_5$  ( $0 \leq x \leq 33$  mol%) [15] and in  $K_2O-MnO-P_2O_5$  ( $0 \leq x \leq 40$  mol%) [23] phosphate glasses.



**Figure 2:** The variation density and molar volume of glasses with manganese concentrations

#### 3.2. DSC study

In Figure 3, a typical DSC curve of chosen glass composition of  $20K_2O-10MnO-70P_2O_5$  is reported. Similar curves have been recorded for all other samples given in Table 1. From the DSC data, we can obtain the glass transition temperature ( $T_g$ ) for each composition (Table 1).

The variation of glass transition temperature  $T_g$  with composition is shown in Figure 4.  $T_g$  values increase with MnO content. A systematic rise of  $185^\circ C$  in  $T_g$  is recorded between extreme compositions. The large increase of  $T_g$  shows that the structure is strongly modified. This is due to increasing of the network cross-link strength when  $Mn^{2+}$  ions are introduced in the structure [15, 25].

The variation of glass transition temperature is strictly related to the nature of bonding in the vitreous network.  $20Na_2O-80P_2O_5$  glasses are predominately ionic and become covalent with the addition of MnO, leading to the formation of P-O-Mn linkage. This result can be explained by the electrical field strength which is larger for  $Mn^{2+}$  than for  $K^+$ . A similar behavior was observed for other phosphate glasses containing  $Mn^{2+}$ ,  $Cd^{2+}$  and  $Pb^{2+}$  [9, 25-26].

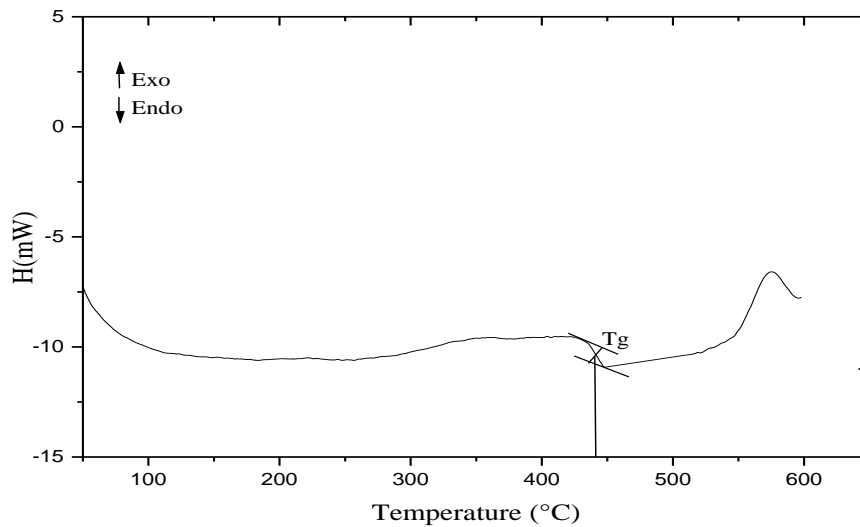


Figure 3: DSC curve of glass with composition of 20K<sub>2</sub>O-30MnO-50P<sub>2</sub>O<sub>5</sub>

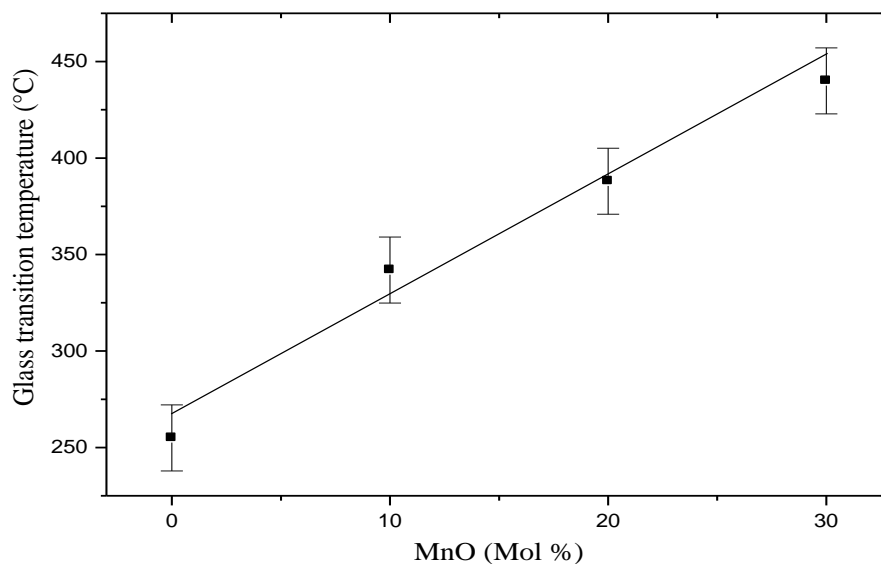
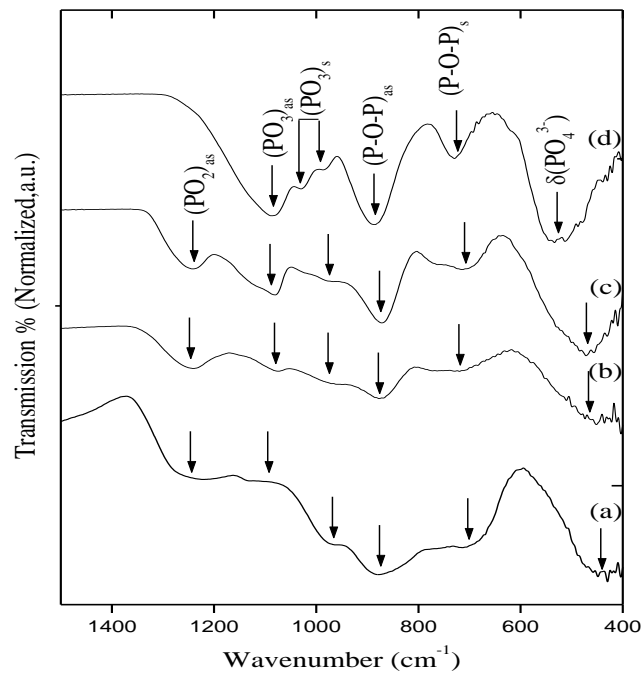


Figure 4: Composition dependence of glass transition temperature for 20K<sub>2</sub>O-*x*MnO-(80-*x*)P<sub>2</sub>O<sub>5</sub> glasses (0 ≤ *x* ≤ 30 mol %)

### 3.3. FT-IR spectroscopy

FTIR spectra of 20K<sub>2</sub>O-*x*MnO-(80-*x*)P<sub>2</sub>O<sub>5</sub> glasses with various contents of manganese oxide ranging from 0 to 30 mol%, in the frequency range between 400 and 1400 cm<sup>-1</sup> are shown in Figure 5. The IR bands assignment is given in Table 2.

For the glass sample without MnO (*x* = 0 mol%), six absorption bands at 1245, 1098, 970, 880, 705 and 440 cm<sup>-1</sup> can be clearly seen. Based on previous infrared studies on phosphate glasses, the band at 1245 cm<sup>-1</sup> has been attributed to the asymmetric stretching vibration band of the non bridging oxygen atoms (NBO) bonded to phosphorus atoms PO<sub>2</sub> (Q<sup>2</sup> structural units) [27]. The absorptions bands around 1098 and 970 cm<sup>-1</sup> are assigned to asymmetric and symmetric stretching of PO<sub>3</sub> groups characteristic of Q<sup>1</sup> structural units (chain-end groups) respectively [28-29]. The band at 880 cm<sup>-1</sup> is assigned to asymmetric stretching of P-O-P bridges [30], while the band at 705 cm<sup>-1</sup> is due to symmetric stretching of O-P-O bridges [31]. The band around 440 cm<sup>-1</sup> is due to bending vibrations of P-O<sup>-</sup> bonds δ PO<sub>4</sub><sup>3-</sup> [29, 32].



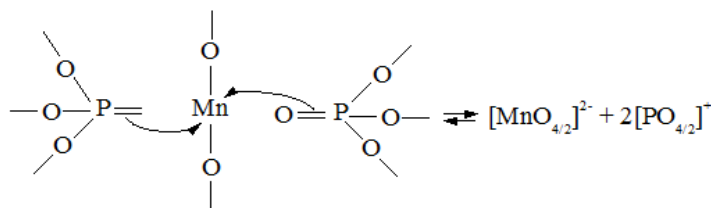
**Figure 5:** Infrared spectra of the  $20\text{K}_2\text{O}-x\text{MnO}-(80-x)\text{P}_2\text{O}_5$  glasses: (a) 0 mol%, (b) 10 mol%, (c) 20 mol% and (d) 30 mol %

**Table 2:** Infrared band assignments ( $\text{cm}^{-1}$ ) of  $20\text{K}_2\text{O}-x\text{MnO}-(80-x)\text{P}_2\text{O}_5$  ( $0 \leq x \leq 30$  mol%)

Glass no	$\nu_{\text{as}}(\text{PO}_2)$	$\nu_{\text{as}}(\text{PO}_3)$	$\nu_{\text{s}}(\text{PO}_3)$	$\nu_{\text{as}}(\text{POP})$	$\nu_{\text{s}}(\text{POP})$	$\delta(\text{PO}_4^{3-})$
1	1245	1098	970	880	705	440
2	1245	1080	975	876	705	445
3	1245	1080	980	870	705	470
4	-	1085	1025-980	885	727	525

With increasing MnO content, FTIR spectra remain the same except the band around  $1245 \text{ cm}^{-1}$  which disappears at  $x = 30$  mol%. Moreover, the asymmetric band of P-O-P stretching mode shifts towards higher wavenumber values, which is characteristic of the transition from longer chains to pyrophosphate groups  $(\text{P}_2\text{O}_7)^{4-}$  [15, 27, 33]. This change indicates that the P-O-P linkages in phosphate chains are disrupted by the addition of MnO oxide.

When MnO is added to phosphate glasses, it can be incorporated into the network which is referred as the network former. We assume that in this case, manganese is present in the network as corner-sharing  $[\text{MnO}_4]^{2-}$  tetrahedral units. The formula  $[\text{MnO}_4]^{2-}$  suggests that additional oxygen atoms are required to complete the coordination of manganese (since MnO itself can almost generate  $[\text{MnO}_{2/2}]$  in the network), this can be achieved through the host network [34]. The incorporation process of MnO in the network can be represented schematically as show bellow.



## Conclusion

Ternary potassium manganese phosphate glasses with composition  $(\text{K}_2\text{O})_{20}(\text{MnO})_x(\text{P}_2\text{O}_5)_{80-x}$  with  $0 \leq x \leq 30$  mol% were prepared and the amorphous nature of the synthesized material was confirmed by X-ray diffraction. Based on the physical property results, it has been shown that the density increases and the molar volume

increases when MnO content was added to the phosphate glasses. The increase in density was also affected by the change in crosslink density and the coordination number of  $Mn^{2+}$  ions. The addition of MnO and a decrease of the  $P_2O_5$  concentration in the glass network cause an increase in density values. These results agree with a closer structure and act in a manner that MnO enters the glassy matrix as a network former character. The decrease in the molar volume might be attributed to the formation of P—O—Mn bonds linkage which reticulate the phosphate network and leads to the closed structure of glasses. FTIR spectra fact evidence the presence of short polyphosphate groups as  $(P_2O_7)^{4-}$ . When manganese oxide acts as network former, it is assumed to be presented as  $[MnO_{4/2}]^{2-}$  structural units in a corner sharing geometry and the electrical neutrality in the system is achieved by the conversion of  $[POO_{3/2}]$  into  $[PO_{4/2}]^+$  units.

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