Elaboration, Thermal and Structural Approach of Manganese Phosphate Glasses Inside the System of K$_2$O-MnO$_2$-P$_2$O$_5$

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Elaboration, Thermal and Structural Approach of Manganese Phosphate Glasses Inside the System of K₂O-MnO₂-P₂O₅

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Abstract. Glasses of the composition (50-x/2) K₂O-xMnO₂-(50-x/2) P₂O₅ with (0≤x≤30%mol), have been prepared by standard melt quenching procedures. The amorphous state of the glasses is evidenced using the X-Ray diffraction. Their physical properties were characterized by thermal analysis and density measurements. The density and the glass transition temperature increase with increasing MnO₂ content. To study the structural role of MnO₂ oxide in studied glasses, the FTIR and Raman spectroscopies have been employed. It was highlighted that the presence of MnO₂ allows the depolymerisation of the phosphate chains and formation of covalent bonds P-O-Mn, which replace P-O-P and P=O linkages.

Keywords: Manganese glasses, Glass transition temperature, density, Infrared spectroscopy, Raman spectroscopy.

1. Introduction

This article will introduce manganese phosphates glasses as consider among the glasses containing transitions metal ions (TMI), which have drawn much attention, because of their electric, optical and magnetic properties. These properties come from the presence of TMI in different multivalent states [1]. The most interesting glass structure modifier is manganese; it was used in metallurgy, as a component and alloy addition increasing their hardness and resistance to abrasion [2]. It was reported in the literature, that the manganese ions exist in different valence states with different coordination in glasses matrices [3, 4]. The content of manganese in different coordination in different valence state is related to the quantitative properties of modifiers and glasses formers, size of the ions in the glass, and the mobility of the modifier cation…[4]. Due to their interesting properties and their coordination, the glasses containing manganese have been subject of several publications [5, 1, 6].

In the present work, the structure of glasses with the general composition of (50-x/2) K₂O-xMnO₂-(50-x/2)P₂O₅ (0 ≤ x ≤ 30 % mol) is investigated using FTIR and Raman spectroscopies to elucidate the
structural change as a function of composition. Other physical properties such as density, molar volume and glass transition temperature were also studied with the composition.

2. Experimental procedure

The phosphate glasses of composition \((50-x/2)K_2O-xMnO_2-(50-x/2)P_2O_5\); \(x=0,10,20\) and \(30\)% mol of \(\text{MnO}_2\), were prepared by melt-quench process. The \(\text{NH}_4\text{H}_2\text{PO}_4\), \(\text{K}_2\text{CO}_3\), and \(\text{MnO}_2\) are used as raw materials. Each composition was carefully weighted and then mixed in a porcelain crucible placed in the electrical furnace. The mixture was initially heated at 300°C for 12 hours in order to remove \(\text{NH}_3\) and \(\text{H}_2\text{O}\). Then, the temperature increases at 600°C in order to remove \(\text{CO}_2\) gas in \(\text{K}_2\text{CO}_3\). The batch was finally quenched to room temperature under air in order to produce vitreous structure. The obtained glasses were homogeneous and colored. The solids were kept in desiccator to prevent possible moisture.

3. Results and discussions

3.1. Glassy formation and XRD analysis

Fig.1 displays the ternary diagram which report the all formulations investigated in this work. The X-ray diffractograms of the \((50-x/2)K_2O-xMnO_2-(50-x/2)P_2O_5\) glasses are shown in Fig.2. No peak of crystallization was observed, which indicates the amorphous state of all the elaborated materials.

![Figure 1](image_url)  
**Figure 1.** Location of studied glasses in the system \((50-x/2)K_2O-xMnO_2-(50-x/2)P_2O_5\) in the ternary diagram.
Figure 2. X-ray patterns of the studied glasses

3.2. Density and molar volume

The density values for different bulk of samples are represented in Fig.3. For the studied glasses, \((50-x/2)K_2O-(50-x/2)P_2O_5-xMnO_2\), we observe that the density values increase from 2.35 for \(x=0\) to 2.76 for \(x=30\) %mol in MnO₂ content. This can be proved by the formation of P-O-Mn covalent bonds linkage which reticule the phosphate network. However, the molar volume decreases from 50.24 for \(x=0\) to 39.39 \(\text{cm}^3/\text{mol}\) for \(x=30\) %mol in MnO₂ content. This variation can be due to the decrease of the interstitial space between the polyhedra. Therefore, the planned structure is closed. One can suppose that the substitution of KPO₃ by MnO₂ induces the conversion of some bridging oxygen (BO) to non-bridging oxygen (NBO). Similar variation of the density and molar volume have also been observed in systems contain manganese oxide, in \(20K_2O-xMnO-(80-x)P_2O_5\) [7], in\((50-x)K_2O-xMnO-50P_2O_5\) [6], and \((50-x/2)Na_2O-xMnO-(50-x/2)P_2O_5\) [1].

Figure 3. Variation of the density and molar volume of glass with manganese concentration
3.3. DSC study

The DSC curves of the studied glasses are shown in Fig.4. The evolution of glass transition temperature $T_g$ as a function of MnO$_2$ amount is represented in Fig.5. An increase in $T_g$ from 214°C for $x=0$ to 372°C for $x=30$ %mol MnO$_2$ was seen in prepared glasses. The increase of $T_g$ indicates an increase of the network crosslink strength of the structure as Mn$^{2+}$ ions are introduced to the glassy matrix. It is worth to mention, that the nature of bonding is responsible for this variation in $T_g$. For instance, the K$_2$O rich glasses are predominantly ionic and become covalent with the addition of MnO$_2$ in KPO$_3$ matrix, leading to the formation of P-O-Mn covalent bonds. This result is explained by the electrical field strength which is larger for Mn$^{2+}$ than that of K$^+$. The same change of $T_g$ with manganese content was also observed in the system 20K$_2$O-$x$MnO-$x$P$_2$O$_5$[6] and the (50-$x$)K$_2$O-$x$MnO-50P$_2$O$_5$ system [7].

![Figure 4. Differential scanning calorimetry (DSC) curves for glass samples](image)

![Figure 5. Composition dependence of glass transition temperature for the studied glasses.](image)

3.4. FTIR and RAMAN spectroscopy

FTIR and Raman spectra of (50-$x$/2)K$_2$O-$x$MnO$_2$-(50-$x$/2)P$_2$O$_5$ glasses with various concentration of manganese oxide are presented in Fig.6 and Fig.7 respectively. The assignment of different bands is realized based to the comparison of our result with the literature data [1,8].

FTIR spectra (Fig.6), reveal the disappearance of the $\nu_{as}(P=O)/\nu_{as}(PO_2)$ band at 1274 cm$^{-1}$ as the concentration of MnO$_2$ increases. This statement was be explained by the conversion of some P=O bonds into P-O-Mn bonds. A shoulder at about 1031 cm$^{-1}$ is an indicator of the presence of some pyrophosphates unities. These structural groups are also evidenced from Raman analysis. From the Raman spectra (Fig.7), we notice the appearance of a new band at 1020 cm$^{-1}$ attributed to pyrophosphate groups ($Q^1$). Therefore, we can state that the MnO$_2$ causes a depolymerisation of the glassy matrix; its presence induces the conversion of some metaphosphate structural units ($Q^2$) to pyrophosphate ones ($Q^1$).
The introduction of MnO$_2$ causes progressive spectral changes. In particular, the stretching mode band of P-O-P shifted to higher frequencies from 689 cm$^{-1}$ in KPO$_3$ to 710 cm$^{-1}$ for 35K$_2$O-30MnO$_2$-35P$_2$O$_5$ glass. This result can be interpreted in term of the increase of the covalent character of P-O-P bonds as Mn$^{2+}$ ions replace the K$^+$ ions. Since the potassium belongs to column one of the periodic table, it has a strong ionic character compared to Mn.
4. Conclusion

In this work, we have investigated phosphate glasses belonging to the ternary K$_2$O-MnO$_2$-P$_2$O$_5$ system. The amorphous state of the samples was confirmed by X-Ray diffraction. From the physical properties results, it has been shown that the density and $T_g$ increase, which indicate that MnO$_2$ reticule the phosphate network by the formation of P-O-Mn bonds. Infrared and Raman spectroscopies allowed us to follow the evolution of glass structure as the introduction of MnO$_2$ content. One can notice the modification of the vitreous network when MnO$_2$ oxide is introduced suggesting the shortening of the infinite metaphosphate chains.

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