

Preparation and characterization of phosphate glass system $A_2MnMP_2O_{10}$ (A = Li, Na, K) and (M = W, Mo)

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Abstract. New materials based glassy phosphates and transition elements $A_2MnMP_2O_{10}$ (A = Li, Na, K) and (M = Mo, W) were prepared by direct fusion of the mixture of the reactants followed by quenching in the air. Analysis by X-ray diffraction showed that the obtained materials are amorphous. Differential scanning calorimetry DSC was used to determine the glass transition (T_g) and crystallization (T_c) temperatures. The thermal stability of tungsten glasses is higher than that of molybdenum ones. Tungsten plays, certainly, a role of cross-linking polyphosphate groups by creating more covalent new bonds P-O-W and W-O-W. Moreover, it has been shown that lithium glasses are more stable than sodium and potassium, probably due to the potassium hygroscopy. Raman analysis confirms that the studied glasses have similar structures and the predominant structural units are PO_4 , P_2O_7 and MO_6 polyhedra (M = W, Mo, Mn).

INTRODUCTION

The phosphate glasses compared to borate and silicate ones have very interesting physical properties. The low melting temperature of phosphate and their ability to vitrify make easy their development. They are characterized by low glass transition temperatures and high thermal expansion coefficients. These characteristics, allow them to be used for original applications: sealing glasses [1], oxidation resistant coatings, their interesting optical properties permit them to be operate as template for laser [2], waste containment matrixes. However, the use of these materials is limited by their low chemical durability. To overcome this drawback, the corrosion resistance of phosphate glasses has been improved by the introduction of cations that enhance the glassy network against the hydrolysis (P-O-M more covalent). Include Al^{3+} , Fe^{3+} , Pb^{2+} [3,4] or anions such as N^{3-} that increase the linking entities phosphate [5]. Thus some phosphate-based glasses have comparable or higher durability to silicate glasses and are used as containment of waste [6]. In order to obtain new performance phosphate glassy materials, we have prepared and characterized the glasses system $A_2MnMP_2O_{10}$ with (A = Li, Na, K) and (M = W, Mo).

1. PREPARATION OF GLASSES

The preparation of $A_2MnMP_2O_{10}$ glass with (A = Li, Na, K) and (M = W, Mo) is formed by direct heating, in air, the mixture of ANO_3 , $MnCO_3$, MO_3 (M = W, Mo) and $(NH_4)_2HPO_4$. Reagents, taken in stoichiometric proportion, are finely ground to obtain a homogeneous mixture. The reaction takes place in a platinum crucible. A first heat treatment is performed at 200° C to decompose the ammonium dihydrogen phosphate $(NH_4)_2HPO_4$ and a second at 400° C to decompose the manganese carbonate $MnCO_3$. The temperature is then gradually raised to

600° C to decompose completely nitrates of alkali metals ANO_3 .

The fusion is reached by heating the mixture at 900° C for 20 to 30 minutes. The resulting liquid is then quenched on a nacelle preheated to 200° C to avoid thermal shock. The obtained glasses are brown.

These materials were characterized by: X-ray diffraction, density measurement, differential scanning calorimetry DSC and Raman vibrational spectroscopy.

2. RESULTS

2.1. XRD, density measurement, DSC

The diffractograms X of prepared materials are typical of non crystallized compounds (no diffraction lines); therefore they confirm they are amorphous.

Measurements of density and molar volume of $A_2MnWP_2O_{10}$ and $A_2MnMoP_2O_{10}$ (A = Na, K, Li) glasses show that for all the glasses (tungsten and molybdenum) the density increases gradually as the molecular weight of alkali metal increases.

The glass transition T_g and crystallization T_c temperature are determined from the DSC thermograms (Figure 1). We note the evolution of T_g and T_c as a function of alkali ions, glasses tungsten and molybdenum ones. We found that the glass transition temperature T_g increases from lithium to potassium.

2.2. Study by Raman Spectroscopy

Raman spectra are reported in figures (2 and 3). The analysis of these spectra shows that their appearance is identical and indicates that their structures are almost similar. The most intense Raman band observed at 920 cm^{-1} , decreases in intensity and width in the order $Li > Na > K$.

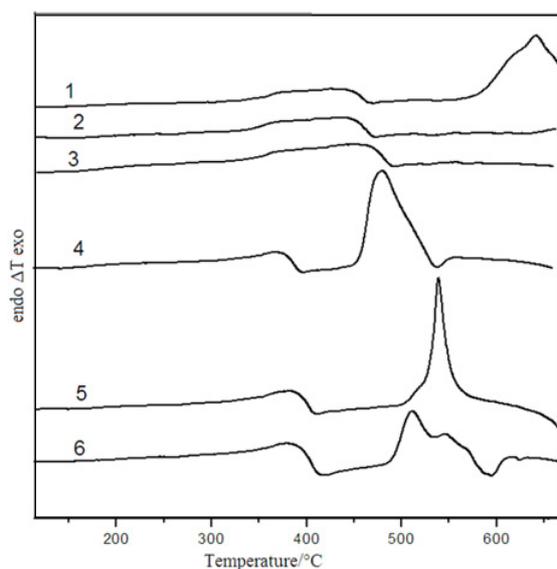


Figure 1. DSC curves of glasses $\text{Li}_2\text{MnWP}_2\text{O}_{10}$ (1), $\text{Na}_2\text{MnWP}_2\text{O}_{10}$ (2), $\text{K}_2\text{MnWP}_2\text{O}_{10}$ (3), $\text{Li}_2\text{MnMoP}_2\text{O}_{10}$ (4), $\text{Na}_2\text{MnMoP}_2\text{O}_{10}$ (5) and $\text{K}_2\text{MnMoP}_2\text{O}_{10}$ (6).

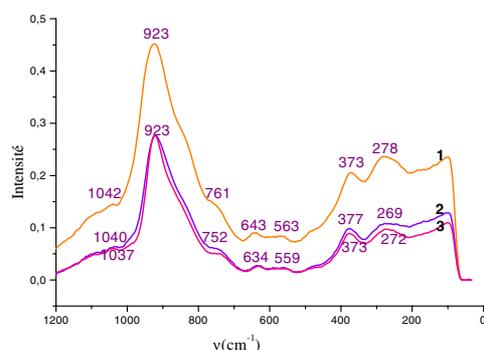


Figure 2. Raman spectra of the glasses $\text{Li}_2\text{MnWP}_2\text{O}_{10}$ (1), $\text{Na}_2\text{MnWP}_2\text{O}_{10}$ (2) and $\text{K}_2\text{MnWP}_2\text{O}_{10}$ (3).

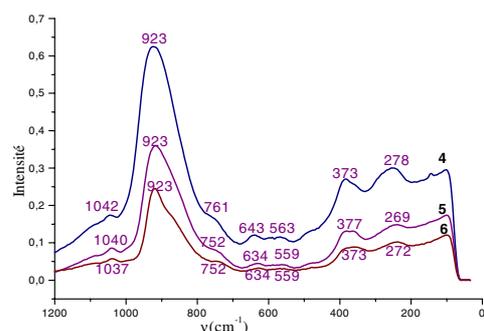


Figure 3. Raman spectra of the glasses $\text{Li}_2\text{MnMoP}_2\text{O}_{10}$ (4), $\text{Na}_2\text{MnMoP}_2\text{O}_{10}$ (5) and $\text{K}_2\text{MnMoP}_2\text{O}_{10}$ (6).

3. DISCUSSION

3.1. Density, thermal stability

In the case of glasses with tungsten and molybdenum, the density increases gradually as the molecular weight of the alkali metal increases. It is known that changes in the molar volume (V_m) depend on the molecular weight of alkali metal ions introduced into the glass. This reflects

the impact of the latter within the glass network. If the molar volume remains constant, we can conclude that the cation introduced is placed in the cavities of the network. A decrease in the molar volume shows that the introduced cation strengthens the network: it decreases the chaining of oxygen ions. An increase in molar volume is indicative of a network expansion [8]. We can thus explain the decrease of the molar volume by network cross-linking [9].

The analysis of the DSC curves (Fig. 1) of two sets of glasses (Tungsten (W), molybdenum (Mo)) allowed us to identify several types of thermal stability. The first one on tungsten glasses which have higher T_g than molybdenum ones, the second type relates to molybdenum glasses which have a difference ($T_c - T_g$) relatively low (94 to 144°C) compared to tungsten glasses, the third observation corresponds to the absence of exothermic crystallization peaks for both $\text{Na}_2\text{MnWP}_2\text{O}_{10}$ and $\text{K}_2\text{MnWP}_2\text{O}_{10}$ glasses.

Therefore their thermal stability could not be evaluated numerically, but it is probably very high. In addition, the difference ($T_c - T_g$) (>170°C): Case of (lithium - tungsten) glass is higher than that on the molybdenum glass, confirming the high thermal stability of these glasses. The fourth type relates to $\text{K}_2\text{MnMoP}_2\text{O}_{10}$ glass having two exothermic peaks (510 and 545°C) rather broad. They, probably, can be attributed to two crystalline phases.

The behavior of studied glasses is close to that of $\text{A}_2\text{MgWP}_2\text{O}_{10}$ ($A = \text{K}, \text{Cs}, \text{Rb}$) [10]. The stability of the glasses devote them a great importance for future applications. For example, it is known that a temperature difference ΔT less than 100°C is suitable in industrial processes.

3.2. Raman

In last few years [11], numerous studies on the structure of the glasses were conducted. Nevertheless, the study of the structure of glasses is not easy to implement because they are characterized by a substantial disorder and a lack of large-scale three-dimensional periodicity. Vibrational spectroscopy (Raman and infrared) was the most suitable techniques for study of the glassy materials.

Previous studies [12] have reported that the addition of various oxides to P_2O_5 leads the depolymerization of the network and the formation of different structures. It is also known that the structure of the glass depends on the O/P (oxygen/phosphorus) ratio and on the properties of the introduced oxides. The studied glasses contain MO_3 ($M = \text{W}, \text{Mo}$), MnO and oxides of alkali A_2O ($A = \text{Li}, \text{Na}, \text{K}$). Oxides of alkali ions are considered as network modifiers. However, oxides and MO_3 do not readily form the glass network. The O/P ratio for $\text{A}_2\text{O} - \text{MnO} - \text{P}_2\text{O}_5$ composition is 3.5 and corresponds to a pyrophosphate structure. The addition of MO_3 increases the O/P ratio in $\text{A}_2\text{MnMP}_2\text{O}_{10}$ glasses to 5. The real O/P is probably close to 3.5 than 5 because the $\text{W}(\text{Mo})\text{O}_3$ oxides does not act as modifiers. The structure of the glass may be composed mainly of the pyrophosphate Q_1 and orthophosphate Q_0 groups (Q_n : n is the number of bridging oxygen atoms by PO_4 tetrahedron). A great similarity was found between the Raman spectra of $\text{A}_2\text{MnMP}_2\text{O}_{10}$ glasses studied in this work and those of $[\text{Rb}_2\text{MgWO}_2(\text{PO}_4)_2]$ crystalline

phases (13) which consist of PO_4 groups, octahedra WO_6 and MgO_6 . That suggests that the $\text{A}_2\text{MnMP}_2\text{O}_{10}$ glassy network contains also the same structural units. However, the presence of Raman bands near 750 cm^{-1} not observed in the crystal structure of $\text{Rb}_2\text{MgWO}_2(\text{PO}_4)_2$ and which can be assigned to symmetric stretching modes of P_2O_7 groups indicates that the $\text{A}_2\text{MnMP}_2\text{O}_{10}$ glass structure is formed of a large amount of pyrophosphate. We note that the Raman bands near 920 cm^{-1} decrease in intensity and width in the order $\text{Li} > \text{Na} > \text{K}$, they can be assigned to symmetric vibrations of MO_6 octahedra ($\text{M} = \text{Mn}, \text{W}, \text{Mo}$). A Raman band very similar and with the same intensity was observed for the $[(80-0.8x)\text{NaPO}_3-(20-0.2x)\text{BaF}_2-x\text{WO}_3]$ glasses [13]. The high intensity of this band, probably, indicates that the MO_6 octahedra are more distorted. The Raman band 1040 cm^{-1} can be attributed to symmetric and asymmetric stretching of PO_3 terminal group [15]. The Raman band near 750 cm^{-1} can be attributed to symmetric vibration modes of pyrophosphates POP units (Q_1). Early studies on phosphates showed a band near 640 cm^{-1} which is characteristic of deformation vibrations of metaphosphate groups (P_3O_9)³⁻. The band observed at 550 cm^{-1} can be assigned to deformation vibrations of pyrophosphates and orthophosphates groups. Raman bands observed between 270 and 370 cm^{-1} can be assigned to deformation vibrations of MO_6 octahedra resulting from short (M-O) and long (O-M-O) links.

4. CONCLUSION

The X-ray diffraction analysis showed that the synthesized materials are amorphous. The differential scanning calorimetry (DSC) confirmed that the thermal stability of tungsten glasses is higher than that of molybdenum ones. Tungsten plays, probably, a role of cross-linking polyphosphate groups by creating P-O-W and W-O-W bonds more covalent, which justified their thermal stability. The analysis by Raman of $\text{A}_2\text{MnMoP}_2\text{O}_{10}$ ($\text{A} = \text{Li}, \text{Na}, \text{K}$) and ($\text{M} = \text{W}, \text{Mo}$) glass compositions showed that their structure is mainly formed by pyrophosphates groups and P-O-T, T-O-T ($\text{T} = \text{Mn}, \text{W}, \text{Mo}$) chains similar to those existing in other phosphate glassy materials.

The studied materials contain some small amounts of metaphosphate and orthophosphate units.

This work has enabled us to provide structural information on the new phosphate-based vitreous transition elements. However, several work remains to be done to explain some structural phenomena, in particular the structural study of annealed glasses obtained and the magnetic properties of materials containing manganese (Mn^{2+}).

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