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The structural changes induced by the addition of MoO_3 and Fe_2O_3 in lead-phosphate glasses

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The relationship between the composition and structure of $x(MoO_3 \cdot Fe_2O_3)(1-x)[2P_2O_5 \cdot PbO]$ with $0 \le x \le 50$ mol% glass system has been investigated by FT-IR and Raman spectroscopy. With the increasing of modifier oxide content, the shapes of the IR and Raman bands change due to the replacement of the P-O-P bonds for the most moisture resistant Fe-O-P bonds and also, due to the appearance of the Mo-O-Mo asymmetric stretching vibrations in $[MoO_4]$ tetrahedron. The very strong depolymerization which appears in these glasses is observed by decreasing in intensity of the specific bands of phosphate network and by increasing of the characteristic bands of the very short chain phosphate units Q^0 and Q^1.

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1. Introduction

The practical applications of phosphate glasses are limited by their poor chemical durability. The physical and chemical properties of phosphate glasses can be optimized by controlling the melting conditions and chemical composition [1]. The chemical durability of lead-phosphate glasses increases dramatically with the addition of Fe_2O_3, this fact is attributed to the replacement of P-O-P bond by more moisture resistant P-O-Fe bonds [2]. This durability is consistent with the shortening of the phosphate chain length, which leads to a strengthening of the glass network, through the formation of Fe-O-P bonds [3, 4].

The molybdenum cations could act both as a network former as well as network modifier depending upon its concentration. Due to the presence of two glass formers in molybdenum phosphate glasses, Mo-O^- and P=O bonds are transformed into Mo-O-Mo and Mo-O-P bridging bonds when the Mo/P ratio increases [5].

In order to obtain further information of the role of iron and molybdenum ions in phosphate glasses a new glass system $x(MoO_3 \cdot Fe_2O_3)(1-x)[2P_2O_5 \cdot PbO]$ with $0 \le x \le 50$ mol% was prepared and investigated by FT-IR and Raman spectroscopy.

2. Experimental

The starting materials used in the present investigation were $(NH_4)_2HPO_4$, PbO, MoO_3 and Fe_2O_3 of reagent grade purity. The samples were prepared by weighing suitable proportions of the components, powder mixing and mixture melting in sintered corundum crucibles at 1250^0 C for 5 min. The mixtures were put into the furnace directly at this temperature. The obtained glass-samples were quenched by pouring the molten glass on a steel plate.

The FT-IR absorption spectra of the glasses in the 400-1500 cm^{-1} spectral range were obtained with an Equinox 55 Bruker spectrometer. The IR absorption measurements were done using the KBr pellet technique. In order to obtain good quality spectra, the samples were crushed in an agate mortar to obtain particles of micrometer size. This procedure was applied every time to fragments of bulk glass to avoid structural modifications due to ambient moisture.

The FT-Raman spectra were recorded with a Bruker FRA 106/S Raman accessory attached to the Bruker Equinox 55 FT-IR spectrometer equipped with an InGaAs detector working at room temperature. The FT-Raman spectra were recorded in backscattering geometry with a resolution of 4 cm^{-1}.

3. Results and discussion

The FT-IR spectra of $x(MoO_3 \cdot Fe_2O_3)(1-x)[2P_2O_5 \cdot PbO]$ with $0 \le x \le 50$ mol% show the characteristic bands of $2P_2O_5 \cdot PbO$ matrix and also the bands of iron oxide and molybdenum oxide respectively (Fig. 1).

For x=0 mol% the band around 500 cm^{-1} is described like fundamental frequency of Q^0 species or like the harmonics of bending frequency of P-O bond [6]. In the Q^n terminology, n represents the number of bridging oxygens (BO) per PO_4 tetrahedron. The peak around 700 cm^{-1} is due to the bending vibration of PO_4 units [7]. The strong band around 900-950 cm^{-1} is due to the asymmetric stretching vibration of P-O-P bond, while the band at 1043 cm^{-1} is attributed to the asymmetric stretching vibrations of the ending-groups $(PO_3)^{2-}$ in Q^1 [8]. Another weak shoulder at 1103 cm^{-1} is attributed to the stretching of P-$O^{(-)}$ ionic groups [9] and the band at 1260 cm^{-1} is due to the asymmetric stretching vibrations of Q^2 units [10, 11]. Taking in consideration the IR results [12] reported for some phosphate glasses we can attribute the peaks at about 1400 cm^{-1} to the P=O stretching vibrations, too.

With the increasing of modifier oxide content the spectra shape is changing (Fig. 1). The band around 500 cm^{-1} becomes narrower and shifts to higher wavenumber.

This shift is due to the overlapping of phosphate bands with the specific bands of Fe-O [7]

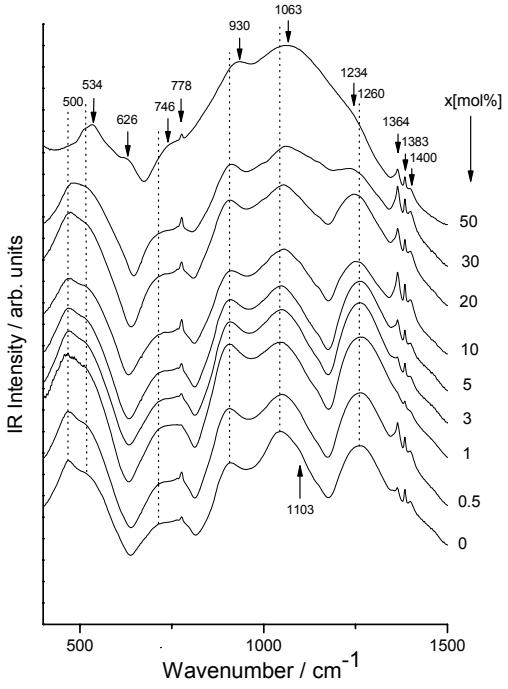

Fig. 1. FT-IR spectra of $x(MoO_3 \cdot Fe_2O_3)(1-x)[2P_2O_5 \cdot PbO]$ with 0≤x≤50 mol%.

vibration and the Mo-O-Mo bending vibration also [13]. The asymmetric stretching band from 900 cm^{-1} shifts to higher frequencies as the amount of the modifier oxides increases. The larger wavenumber of the P-O-P band is a result of the smaller P-O-P bond angle, which results from shorter phosphate chain length or smaller metal cation size [14, 15]. In the structural study of iron phosphate glasses, it was found that the band near 1047 cm^{-1} shifted to higher frequency together with an increase in its intensity with increasing the Fe_2O_3 content, and suggests that the Fe-O-P bonds would replace the P-O-P bonds in the glass structure [3]. The 1260 cm^{-1} band decreases in intensity with the addition of modifier oxide, this result indicated a smaller number of Q^2 groups, therefore shorter chains lengths. The weak shoulder from 626 cm^{-1} which appears for concentrations more then 50 mol% of modifier oxides can be attributed to the asymmetric stretching vibrations of Mo-O-Mo [16-18], this fact suggests the presence of the $[MoO_4]$ tetrahedral species in these glasses [19].

From these results we can observe that with the increasing of the modifier oxides content, the Q^2 groups characteristics for the long phosphate chains start to decrease, this fact indicates a very strong depolymerization which appears in these glasses. For higher modifier oxides content the band from 626 cm^{-1}, characteristic for Mo-O-Mo asymmetric stretching vibrations in $[MoO_4]$ tetrahedral is observed. This fact indicates that the Mo atoms prefer to bridge with oxygen do not participate in phosphate structural groups and thus MoO_3 confirms its network former role.

The Raman spectra of $x(MoO_3 \cdot Fe_2O_3)(1-x)[2P_2O_5 \cdot PbO]$ glass system with 0≤x≤30 mol% is show in Fig. 2. For x=0mol% the Raman spectrum shows the characteristic bands of $2P_2O_5 \cdot PbO$ matrix. The presence in this spectrum of two bands at 300 cm^{-1} and 380 cm^{-1} may be attributed to the presence of PbO in these glasses [20]. The 684 cm-1 band is attributed to the P-O-P symmetric stretching vibrations of the Q^2 tetrahedrons [14, 21-22], while the weak shoulder from 1080 cm^{-1} is due to symmetric stretching vibration (PO_3) in Q^1 groups [23]. The bands from 1149 cm^{-1} and 1243 cm^{-1} have been attributed to symmetric and asymmetric stretching motions of the two non-bridging oxygen (NBO) atoms bonded to phosphorous atoms (PO_2) in the Q^2 phosphate tetrahedron [20, 24].

With the increases of modifier oxides content, the band from 684 cm^{-1} shifts to higher wavenumber and also decreases gradually in intensity. For higher concentration of modifier oxides (x= 30 mol%) this band almost disappears. This fact could be explain trough the gradual depolymerization of the long phosphate chain with the increase of the modifier oxides content.

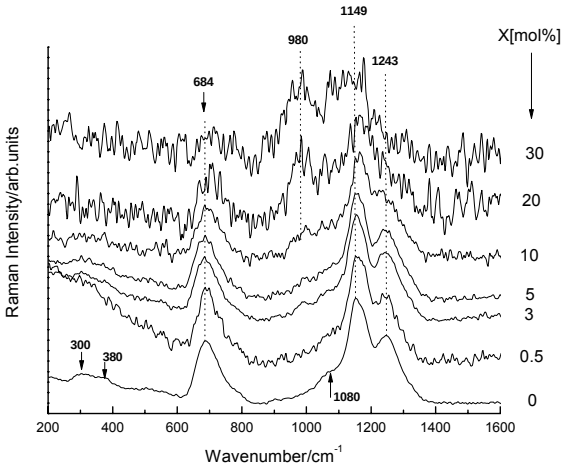

Fig. 2. Raman spectra of $x(MoO_3 \cdot Fe_2O_3)(1-x)[2P_2O_5 \cdot PbO]$ with 0≤x≤50 mol%.

The same tendency was observed for the bands from 1149 and 1234 cm^{-1} which decrease in intensity with the addition of modifier oxides content. On the other hand, for concentrations more then 10 mol % of modifier oxides a new characteristic band at about 980 cm^{-1} due to the symmetric stretching vibrations in Q^0 groups appears. The weak shoulders from 1080 cm^{-1}, attributed to the symmetric stretching (PO_3) in Q^1 groups increases also in intensity with the network modifiers content.

From these results we can say that with the addition of network modifiers in phosphate matrix, a very strong depolymerization appears. The bands characteristic to phosphate glasses decrease strongly in intensity, except the specific bands of very short chain phosphate units Q^1 and Q^0.

4. Conclusion

The FT-IR and Raman spectra of this glass system indicate that with increase of modifier oxides content a very strong depolymerization appears in these glasses. The characteristic bands of phosphate glasses strongly decrease in intensity except the specific bands of the very short chain phosphate units Q^1 and Q^0.

With the addition of the two modifier oxides, the band from 1047 cm^{-1} shifted to higher frequency together with an increase in its intensity due to the replacement of P-O-P bonds by more moisture resistant Fe-O-P bonds.

For higher modifier oxides content the band from 626 cm^{-1}, characteristic for Mo-O-Mo asymmetric stretching vibrations in [MoO_4] tetrahedron is observed. This fact indicates that the Mo atoms prefer to bridge with oxygen, do not participate in phosphate structural groups and thus MoO_3 confirms its network former role.

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