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Structural investigation of calcium-soda-phosphate glasses with small content of silver oxide

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Calcium-soda-phosphate glasses of (100-x)[$50P_2O_5 \cdot 30CaO \cdot 20Na_2O$)$\cdot$x$Ag_2O$ system, with x ≤ 0.25 mol % were prepared by classical melting and casting method. The samples were investigated using X-ray diffraction (XDR), Raman, infrared (IR) and ^{31}P magic angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopies. The X-ray powder diffraction patterns consist in a broad line, typical of vitreous systems. The Raman and IR spectra show significant distorsion of the phosphate groups with silver doping level. Both Raman, IR and ^{31}P MAS-NMR results reveal the presence of Q^1 and Q^2 species.

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1. Introduction

The calcium-soda-phosphate materials have potential application as biomaterials, because their chemical composition is close to that of natural bone mineral phase. The pure phosphate glasses do not have enough chemical stability for application. The addition of silver oxide to calcium-soda-phosphate matrix is aimed at minimizing the risk of microbial contamination through the potential antimicrobial activity of the leaching Ag^+ ions [1,2]. Vitreous P_2O_5 has a three-dimensional network build up with PO_4 tetrahedra connected by three of their four corners. The fourth one is occupied by terminal double-bonded oxygens. Introducing the glass network modifiers, results in breaking P-O-P bonds, and non bridging oxygens (NBO) are formed. Depending on the number of the bridging oxygen the phosphate tetrahedra can be described as Q^n, where n represents the number of the bridging oxygens and can have a value of 0, 1, 2, 3 [3]. A framework built up with Q^3 denotes a fully polymerized structure, while Q^2 unit gives only a two dimensional structure based on chains or rings. Q^1 and Q^0 units are characteristic for ortophosphate structures.

The aim of this study is to characterize the structure of the glasses and to determine the change that occurs with increasing Ag_2O content.

2. Experimental

Glass samples of (100-x)[$50P_2O_5 \cdot 30CaO \cdot 20Na_2O$)$\cdot$x$Ag_2O$ compositions with x≤0.25 mol % were prepared using as starting materials: $NH_4H_2PO_4$, $CaCO_3$, $Na_2CO_3 \cdot 10H_2O$ and Ag_2O reagents of purity grade. The mixtures were melted in air, in sintered corundum crucibles in an electric furnace Carbolite RF 1600 at 1200 °C for 15 minutes. The melts were quickly undercooled at room temperature by pouring and pressing between two stainless steel plates.

The samples were characterized by X-ray diffraction (XRD), Raman, Fourier transform infra-red (FTIR) and high resolution magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopies using Bruker equipments. All measurements were carried out at room temperature. XRD data for glass samples were collected with a D8 Advance diffractometer. The Raman spectra were performed on a Dilor Labram system equipped with a 0.90 × 100 microscope objective, a 1800 lines/mm grating and an external laser with an emission wavelength of 514 nm. In the recording of the micro-Raman spectra a power of 100 mW on the sample has been employed. The spectral resolution in this case was 2 cm^{-1}. The IR spectra were recorded with a Bruker Equinox 55 spectrometer, the spectral resolution in this case was 2 cm^{-1}. The ^{31}P spectra were measured using the Bruker AVANCE 400 spectrometer, a frequency of 12 kHz. As reference for the chemical shift was used H_3PO_4.

3. Results and discussion

The X ray diffraction (XRD) patterns of investigated samples consist of a broad line typical of vitreous systems (Fig. 1). The patterns do not evidence any narrow line of crystalline phases.

The Raman and IR spectra are displayed in Fig. 2 and Fig. 3. For all samples the profiles of spectra consist of large bands typical for disordered systems, in accordance with the X-ray patterns.

The addition of silver oxide to the calcium-soda-phosphate matrix determines structural changes evidenced both in the Raman and IR spectra. In the Raman spectra, especially, for x = 0.25 mol % Ag_2O it can be observed the increase in intensity of the bands situated at 340, 750 and 1160 cm^{-1}. The first and the second band are attributed to the O-P-O bending and P-O-P stretching vibrations in PO_4 tetrahedra, respectively [4-8]. It was shown that the increase in asymmetry of the band around 692 cm^{-1}, which is assigned to the P-O-P stretching vibrations of the long-chain species, is caused by the increase of the number of very short phosphate units [9]. Other signals appears around 1025, 1160 and 1250 cm^{-1}. The bands recorded at 1160 cm^{-1} and 1250 cm^{-1} were attributed to asymmetric stretching vibrations of $(PO_2)^-$ (Q^2) species [4].

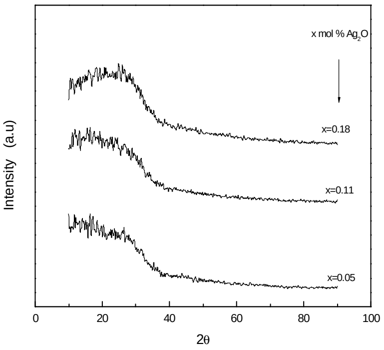

Fig. 1. XDR patterns (100-x)[50P_2O_5·30CaO·20Na_2O]·xAg_2O samples.

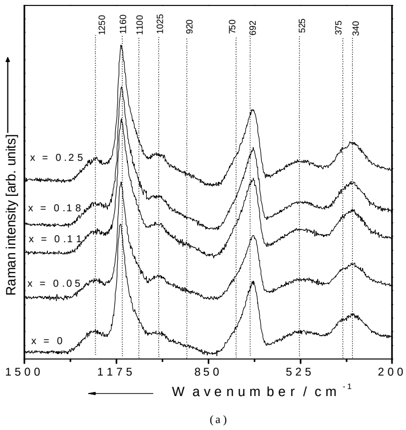

Fig. 2. Raman spectra of (100-x)[50P_2O_5·30CaO·20Na_2O]·xAg_2O glasses.

The FTIR spectra of the investigated samples (Fig. 3) show the presence of large bands typical for systems with short range order. Similar features a those observed in the Raman spectra were shown. The band at 487 cm^{-1} is attributed to deformation modes of different fragments of structure units. Lower frequency shoulders appear at 544 cm^{-1} and 619 cm^{-1}. These features can by associated with deformation modes of PO_2 fragment, their increase in intensity with increasing Ag_2O content showing significant distortion of the phosphate groups. The main band located around 1122 cm^{-1} is due to the asymmetric stretching vibrations of $(PO_3)^{2-}$ (Q^1 species) [4,10]. The addition of silver oxide to the matrix determines the increase in intensity of the band recorded at 1122 cm^{-1}. It can be also seen the progressive increase in intensity of the band situated at 1255 cm^{-1} due to $(PO_2)^-$ (Q^2 species) asymmetric stretching vibrations. These changes in the IR spectra show the distorsion of the phosphate units. With the increase of the silver doping level one remarks an increase of the non bridging oxygens (NBO) number as a result of the depolymerization process of the phosphate glass network.

MAS-NMR spectroscopy has proved to be a powerful tool to resolve the different Q^n units according to the ^{31}P chemical shift, which is sensitive to the phosphorus local environmets. Fig. 4 presents the evolution of the ^{31}P 1-D MAS NMR spectra (12 kHz) of the glasses samples without Ag_2O and with the highest content of Ag_2O introduced in the [50P_2O_5·30CaO·20Na_2O]·matrix. The spectrum of matrix (x = 0) shows two isotopic resonances at about –35.3 ppm and –11 ppm attributed to Q^2 and Q^1 species, respectively.

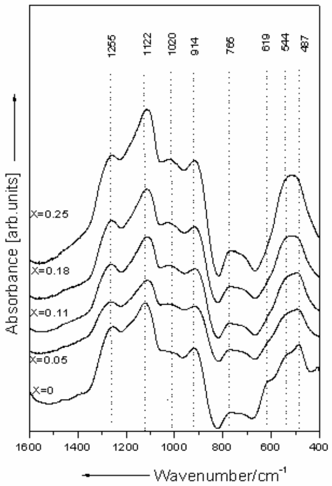

Fig. 3. IR spectra of (100-x)[50P_2O_5·30CaO·20Na_2O]·xAg_2O glasses.

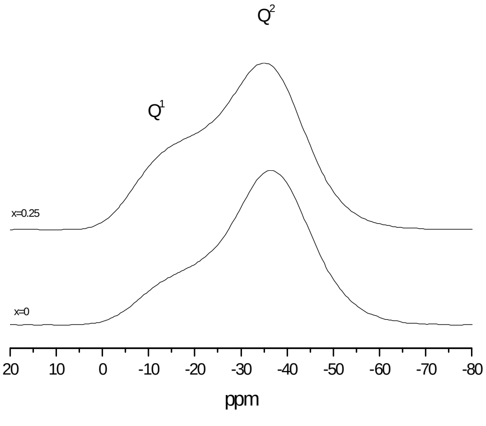

Fig. 4. ^{31}P MAS NMR spectra of the (100-x)[50P_2O_5·30CaO·20Na_2O)·xAg_2O glasses.

The addition of silver oxide to matrix determines the increase in intensity of the ^{31}P resonance attributed to Q^1 species because structural changes in the phosphorus coordination appears. The NMR results confirm the structural changes evidenced in the Raman and FTIR spectra.

It is remarkable that in our previous study [11] on the same Na-Ca-phosphate glasses, but doped by Fe_2O_3, we observed a partial replacement of P-O-P bonds with P-O-Fe and, consequently, a depolymerization of the glass network.

4. Conclusions

The structure of $(100-x)[50P_2O_5 \cdot 30CaO \cdot 20Na_2O) \cdot xAg_2O$, $x \leq 0.25$ mol % glasses is modified by doping with Ag_2O. The glass network structure of the investigated sample is mainly formed by anionic Q^2 $(PO_2)^-$ and Q^1 $(PO_3)^{2-}$ species. The vibrational spectral features indicate a depolymerisation procces of the phosphate network with silver content by increase of NBO number. This result is also confirmed by the MAS NMR data.

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