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Spectroscopic studies of some silver calcium phosphate glasses

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Phosphate based glasses doped with small quantities of silver oxide have been prepared and studied by means of two spectroscopic methods: FT-IR absorption and Raman scattering. Both techniques provide information regarding the local structure and the molecular dynamics analyzing the transition between the vibrational and vibration-rotational levels. Analysis of the FT-IR and Raman spectra of the investigated glasses reveals a network structure arising mainly from the phosphate structural units: Q^3 ($[P(OP)_3OP^-)_1]$), Q^2($[P(OP)_2OP^-)_2]$), Q^1 ($[P(OP)OP^-)_3]$ and Q^0 tetrahedra linked through P-O-P bonds. The occurrence of the de depolimerization process in these phosphate glasses with the addition of silver oxide was followed.

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1. Introduction

Phosphate-based glasses are technologically important materials due to their high thermal expansion coefficient, lower transition temperature and high electric conductivity rather than silicate and borate based glasses [1]. Giving these properties, phosphate-based glasses have potential for application in optical data transmission, solids states batteries, and laser technologies [2].

The interest for phosphate-based glasses increased nowadays because they have great prospective for use as biomaterials. It is well known that among the phosphate-based glasses, those containing calcium, magnesium, sodium and potassium has received a great deal of attention because of their chemical composition close to that of natural bone [4]. The addition in very small quantities of boron into the calcium-phosphate glasses is motivated by the fact that boron is thought to be a factor in helping keeping calcium, magnesium and phosphorus in our body and bones, protecting against osteoporosis.

However, the newest applications for biomaterials requires glasses with higher solubility including glasses that slowly release active ingredients used to cure trace element deficiencies in animals, suture thread and bone fracture fixation [5]. Still, the prevention of infections post-implantation remains a central need. Silver, due to his well-known antibacterial and antimicrobial [6] effect might be the answer to this problem. The development of new materials, silver-calcium-phosphate based glasses having low bacterial adhesion and biocompatibility represents one of the possible solutions to prevent post-implantation infections.

Experimental and theoretical investigations of phosphate glasses have been undertaken by numerous investigators [1-3]. As a conclusion of theirs results the network of the vitreous P_2O_5 is formed from PO_4 tetrahedra which are connected through P-O-P linkages forming a polymeric structure. The addition of a modifier oxide (alkaline or alkali-earth) changes the characteristics of the network from the three-dimensional random network to one of linear phosphate chains. In terms of Q^n (where n represents the number of bridging oxygen atoms per PO_4 tetrahedron) terminology proposed by Lippma et al. [7] the phosphate structural groups pass from Q^3 to Q^2 to Q^1 to Q^0. As the concentration of the modifier oxide increases the infinitely long phosphate chains are shortened causing a break in the network coherency.

The aim of the present study was to obtain information concerning the influence of the Ag_2O addition on the short-range order of the network structure through spectroscopic methods FT-IR absorption and Raman scattering.

2. Experimental procedure

The prepared glass compositions were $xAg_2O\cdot(1-x)[2P_2O_5\cdot CaO\cdot 0.05B_2O_3]$ with $0 \le x \le 0.01$. The batch of the mixture of the reagent grade $(NH_4)_2HPO_4$, H_3BO_3, $CaCO_3$, $AgNO_3$ was melted in air, in sintered corundum crucibles, in an electric furnace at 1200 ˚C for 1 hour. The melts were quickly cooled at room temperature by pouring them onto stainless steel plates.

The FT-IR absorption spectra were recorded with a 6100 Jasco spectrometer, at room temperature, in the 350-4000 cm^{-1} range using the KBr pellet technique. The Raman spectra were obtained with a micro-Raman setup (HR LabRam inverse, Jobin-Yvon-Horiba). As excitation wavelengths was used the 532 nm line of a frequency-doubled Nd:YAG laser (Coherent Compass) with a laser power of 10 mW incident on the sample. The Raman signal wad collected with a charge-coupled-device camera operating at 220 K.

3. Results and discussion

The experimental FT-IR spectra of the glass system are shown in Fig. 1. It has been reported that in the infrared spectra of calcium-phosphate glasses are present four fundamental vibration peaks for the phosphate structure [8]:

1. the 470-800 cm^{-1} spectral range reveals the harmonics of symmetric bending and asymmetric stretching modes;
2. in the 530-780 cm^{-1} spectral range are present the symmetric stretching vibrations;
3. in the 780-940 cm^{-1} are present the symmetric bending modes;
4. in the 1230-1390 cm^{-1} it can be observed the asymmetric stretching modes.

Generally, the phosphate glasses exhibits well absorption bands characteristic to the molecular groups as follows: P=O, $P\text{-}O^-$, PO^{3-}_4, P-O-P and P-O [9, 10]. Any shift from the characteristic frequency of each group depends on the type of the network modifier.

In our system the infrared spectrum of the glass matrix reveals three well defined absorption bands attributed to the fundamental O=P-O bending vibrations (~500 cm^{-1}), symmetric stretching vibrations of P-O-P ring (~760 cm^{-1}) and to the P=O symmetric stretching mode associated with Q^3 tetrahedra (~1297 cm^{-1}); two week peaks around 1400 cm^{-1} assigned to the $P\text{-}O^-$ correlated to the self network vibration and ~1447 cm^{-1} attributed to the P-O-H stretching vibrations.

Regarding the 800-1200 cm^{-1} spectral region a computer program (PeakFit v4.12) has been use to deconvolute this domain (for example see Fig. 2) using the same number of peaks at approximately the same frequencies.

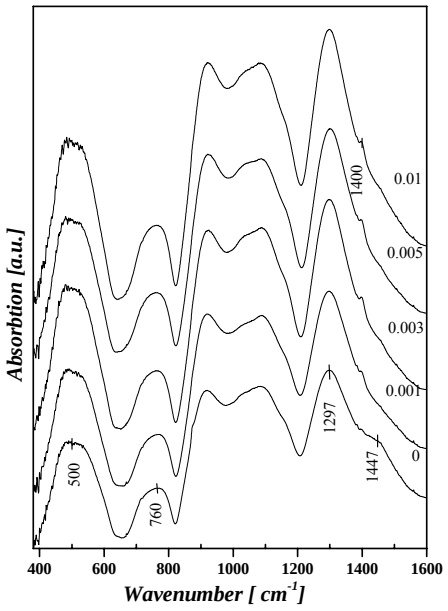

Fig. 1. FT-IR spectra of $xAg_2O\cdot(1\text{-}x)[2P_2O_5\cdot CaO\cdot 0.05B_2O_3]$ glasses.

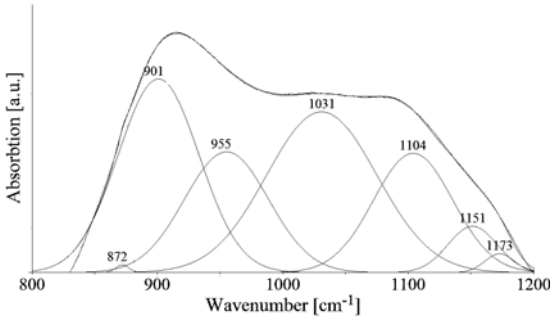

Fig. 2. Deconvoluted infrared bands of $0.001Ag_2O\cdot 0.009[2P_2O_5\cdot CaO\cdot 0.05B_2O_3]$ glass between 800-1200 cm^{-1} spectral range.

Under the absorption envelop between 800-1200 $cm^{-1}$are present several bands revealing the presence of the υ_{as}(P-O-P) mode (~872 cm^{-1}), asymmetric stretching vibrations of P-O-P bonds linked with linear metaphosphate chains (~901 cm^{-1}), asymmetric stretching vibrations of P-O-P bonds linked with large metaphosphate rings (~955 cm^{-1}), PO^{3-}_4 ionic groups (~1031 cm^{-1}), υ_{as} PO^{2-}_3 vibrations (~1151 cm^{-1}) and the $\upsilon_s(PO_2)^-$ mode in metaphosphate groups (~1173 cm^{-1}). The band from ~1104 cm^{-1} can be associated with an overlap of several modes namely: stretching of the PO_3 terminal and PO_2 middle groups.

No supplementary absorption bands were detected with the addition of silver oxide. Slight modifications resulting from increasing the Ag_2O content in the system can be related to the fact that increasing the silver oxide some of the ring structures open and form smaller structures such as short chains and terminal structures revealed by the decrease in intensity of the band form ~901 cm^{-1} and the increase in intensity of the band from ~1104 cm^{-1} respectively.

Raman measurements made on calcium-phosphate glasses reveals three type of vibrations present in the phosphate structural units: the presence of the υ_s(P-O-P) in the 630-850 cm^{-1} spectral range, υ_{as} and $\upsilon_s(PO_2)$ in the 950-1400 cm^{-1} domain [11].

For the glass matrix the main Raman bands are assigned to the P-O-P symmetric stretching vibrations from the quasi-infinite metaphosphate chains (~693 cm^{-1}), "strained" $(PO_2)_s$ (~1178 cm^{-1}) and P=O vibrations (~1282 cm^{-1}), along with υ_{as}(P-O-P) mode (~787 cm^{-1}), P-O symmetric stretching vibrations of triply degenerate T_2 mode of PO_4 (~949 cm^{-1}), $\upsilon_s(PO_3)$ stretching mode (~1081 cm^{-1}), and network bending (~350 $cm^{-1}$and ~560 cm^{-1}). Basely the matrix contains bands coming from ultraphosphate, metaphosphate, pyrophosphate and orthophosphate units. No supplementary bands were detected with the addition of silver oxide.

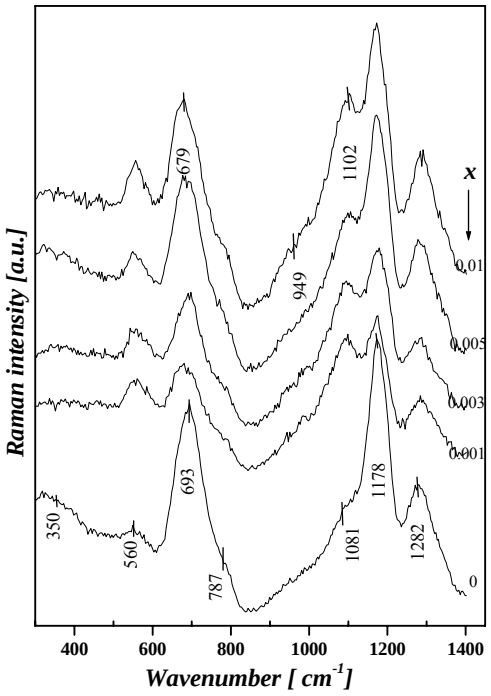

Fig. 3. Raman spectra of $xAg_2O·(1-x)[2P_2O_5·CaO·0.05B_2O_3]$ glasses.

In case of the glass matrix doped with 0.001 Ag_2O there is an increase in intensity of the bands from ~560 cm^{-1} and ~1081 cm^{-1} on the expense of the band from ~693 cm^{-1} and ~1178 cm^{-1}. On the other hand, the band centered at 693 cm^{-1} is shifted to 679 cm^{-1}; this shift might be explained by the increase of P-BO (bridging oxygen) length or due to a change in the in-chain P-O-P bond angles as an effect of the modifiers on the network structure. Moreover the band from the ~1081 cm^{-1} is shifted to higher frequency namely ~1102 cm^{-1}, due to the changes from the average bond characteristics. For the rest of the compositional domain the addition of silver oxide determine an increase in the intensity of the Raman bands denoting for this compositional range some stability in the local order of the network.

4. Conclusions

Glasses from $xAg_2O·(1-x)[2P_2O_5·CaO·0.05B_2O_3]$ with $0 \leq x \leq 0.01$ were prepared on relatively small composition domain in order to preserve the vitreous character of the samples. FT-IR absorption and Raman measurements revealed a network structure based on ultra-, meta-, pyro- and orthophosphate units. Following the quantitatively the structural changes as a function of the glass composition it was found a slight depolimerization of the glass network with the increase of Ag_2O content.

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