

# Structural investigation of calcium – phosphate glasses with silver oxide

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$x\text{Ag}_2\text{O}\cdot(100-x)[\text{P}_2\text{O}_5\cdot\text{CaO}]$  glass system with  $0 \leq x \leq 5$  mol% was prepared and investigated in order to evidence the structural changes induced by the silver ions in controlled addition. The samples local structure were investigated using X-ray diffractions, IR and Raman spectroscopy. The X-ray diffraction patterns consist in a broad line, typical for a vitreous system. The phosphate structural units of the network former revealed from FT-IR and Raman spectra are ultra-, meta-, pyro- and ortho- phosphate units. Both FT-IR and Raman spectra do not evidence directly the presence of silver structural units in the studied glasses. A continuously depolymerization process of these calcium phosphate glasses structure was evidenced by the Raman spectroscopy.

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## 1. Introduction

The interest for the investigation of phosphate glasses was stimulated by the many applications of these materials in the different fields of technique. The phosphate glasses have potential application as biomaterials because their chemical composition is close to natural bone mineral phase. Phosphate glasses containing  $\text{Ag}^+$ ,  $\text{Cu}^+$  or  $\text{Zn}^+$  are studied for their potential applications as antimicrobial materials. Such materials could be used in the cosmetic industry or for implants; it's known that certain metal ions penetrate in bacteria and inactivate their enzymes or some metal ions can generate hydrogen peroxide and in final bacteria is kill [1].

The main unit of the phosphate network is  $\text{PO}_4$  tetrahedra which connected through P-O-P linkages forming a polymeric structure. They are bonded between them through maximum three bonds, the fourth being inactive from the chemical point of view. Depending on the number of the bridging oxygen the phosphate tetrahedra can be describe as  $\text{Q}^i$ , where  $i$  represents the number of the bridging oxygen and can have a value of 0, 1, 2 and 3 [2]. Introducing the glass network modifiers, results in breaking P-O-P bonds and non bridging oxygens are formed. As the concentration of modifier oxide increases the infinitely long phosphate chains are shortened causing a break in network coherency and forming non bridging oxygens [2].

The aim of this study is to characterize the local structure of the  $\text{P}_2\text{O}_5\cdot\text{CaO}$  based glasses when the controlled amount of  $\text{Ag}_2\text{O}$  is introduced in this composition.

## 2. Experimental

Glass samples of  $x\text{Ag}_2\text{O}\cdot(100-x)[\text{P}_2\text{O}_5\cdot\text{CaO}]$  compositions with  $0 \leq x \leq 5$  mol % have been prepared

from corresponding quantities of  $\text{AgNO}_3$ ,  $(\text{NH}_4)_2\text{H}_2\text{PO}_4$  and  $\text{CaCO}_3$  of reagents grade purity. The mixture were melted in sintered corundum crucibles at  $1200^\circ\text{C}$  for an hour. The melts are quickly under cooled at room temperature by pouring and pressing between stainless steel plates. The pure calcium phosphate glasses were transparent. When we doped with silver oxide, samples with  $x > 1\%$  were yellow.

The structure of samples was analyzed by means of X-ray diffraction using a Bruker D8 Advanced X-ray diffractometer with a graphite monochromator for  $\text{CuK}\alpha$  radiation with  $\lambda = 1.54 \text{ \AA}$ . The pattern obtained did not reveals any crystalline phase in all samples.

The FT - IR spectra have been recorded using a FT - IR 615 Fourier Transform-Infrared Spectrometer using the KBr pelt technique with a spectral range from 4000 to  $300 \text{ cm}^{-1}$ .

The Raman spectra were performed by HR LabRaman Horiba Jobin Yvon equipped with a 10X microscope objective. For all measurements it was used an external laser with a wavelength of emission 532 nm and a power of 5 mW incidents on the samples has been employed. The Raman spectra were obtained from different points on the surface of the same fragments of bulk glass to avoid structure modifications caused by the ambient moisture.

All measurements were performed at room temperature.

## 3. Results and discussion

The assignment of vibrational modes had been done by using the literature data related to various crystalline and glass phosphate structure [7,8]. The infrared spectra recorders on investigated samples are present in Fig. 1.

IR spectra of  $\text{P}_2\text{O}_5\cdot\text{CaO}$  glass matrix reveals in the first part of spectral range two large bands:  $\sim 500 \text{ cm}^{-1}$

assigned to the fundamental O=P-O bending vibrations and  $\sim 752\text{ cm}^{-1}$  corresponding to symmetric stretching vibrations of P-O-P [3,4]. In the 800-1300  $\text{cm}^{-1}$  spectral region we found vibrations of P-O-P bonds linked with linear metaphosphate chain ( $\sim 914\text{ cm}^{-1}$ ) and asymmetric stretch of P=O ( $\sim 1280\text{ cm}^{-1}$ ) [3,5]. The band from  $\sim 1112\text{ cm}^{-1}$  can be associated with symmetric stretching ( $\text{PO}_2$ ) and asymmetric stretching of  $(\text{PO}_3)^{2-}$  terminal groups [4,6].

For all glasses with  $x \leq 1\text{ mol\%}$  appears a weak band at  $1400\text{ cm}^{-1}$  attributed to the P-O- correlated to the self network vibrations [3].

IR spectra of glasses showed a very weak band at  $\sim 1620\text{ cm}^{-1}$  which may be attributed to the bending vibrations of free  $\text{H}_2\text{O}$  molecules [7]. The presence of water molecules in our glasses was probably because the mixtures had absorbed some water during the investigate process.

In addition of  $\text{Ag}_2\text{O}$  a weakening of P=O might be expected with this bond being ruptured by network forming cations. If instead the cation entered the network interstitially as an ion, the network is gradually broken down and new spectral bands may appear corresponding to the vibrational character of free charged structural units.

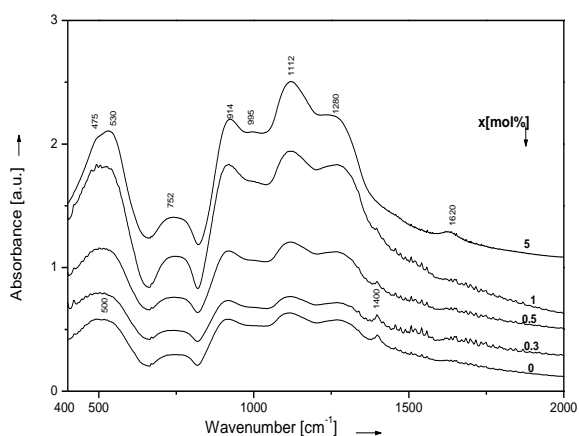


Fig. 1. IR spectra of  $x\text{Ag}_2\text{O} \cdot (100-x)[\text{P}_2\text{O}_5 \cdot \text{CaO}]$ .

The increasing of  $\text{Ag}_2\text{O}$  content has a result the appearance of two new band at:  $\sim 470\text{ cm}^{-1}$  – attributed to the  $\delta(\text{PO}_2)$  modes of  $(\text{PO}_2)$  chain groups and  $\sim 995\text{ cm}^{-1}$  for symmetric stretching of P-O bonds in the  $(\text{PO}_3)^{2-}$  end groups [1].

The partial break down of the covalent vitreous network at high  $\text{Ag}_2\text{O}$  content is show by the band at  $\sim 1112\text{ cm}^{-1}$ , assigned to stretching vibrations of P-O groups, the intensity of this band reaches a fairly strong maximum at 5 mol% [4,6].

It's clearly observed (for 5 mol %) that the intensity of P=O absorption band starts to decrease, we attributed this to the increasing replacement of P=O bonds by P-O-Ag bridging units.

Fig. 2 shows the Raman spectra of all investigated glasses. Raman spectra of  $\text{P}_2\text{O}_5 \cdot \text{CaO}$  glass matrix reveals six well definite bands at:  $\sim 340\text{ cm}^{-1}$ ,  $\sim 540\text{ cm}^{-1}$ ,  $\sim 700\text{ cm}^{-1}$ ,  $\sim 1162\text{ cm}^{-1}$ , and  $\sim 1240\text{ cm}^{-1}$ . There we can see

two strong bands at  $\sim 700\text{ cm}^{-1}$  attributed to the symmetric stretching vibrations of P-O-P bonds and  $\sim 1162\text{ cm}^{-1}$  assigned to the asymmetric stretching vibrations of the  $(\text{PO}_2)^-$  groups [9,10]. Bues and Gehrke [12] attributed in glass the well defined band observed at  $\sim 340\text{ cm}^{-1}$  to the  $\text{PO}_2$  and chain O-P-O bending vibrations [7,12]. Other bands (two shoulders) appear around  $1032\text{ cm}^{-1}$  typical of  $\text{P}_2\text{O}_7$  group with  $\gamma_s(\text{PO}_3)$  [13,14,10] and  $\sim 1240\text{ cm}^{-1}$  due to the vibrations of P=O bonds [10,15].

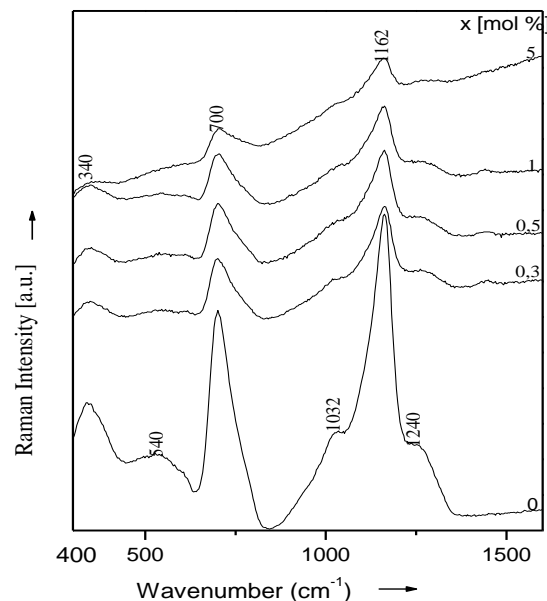


Fig. 2. Raman spectra  $x\text{Ag}_2\text{O} \cdot (100-x)[\text{P}_2\text{O}_5 \cdot \text{CaO}]$ .

The large band  $450\text{-}630\text{ cm}^{-1}$  (centered app.  $540\text{ cm}^{-1}$ ) belongs to P-O-P chains complex vibrations [8,16]. This band is well observed only for  $\text{P}_2\text{O}_5 \cdot \text{CaO}$  glass matrix. Their intensity decrease up to disappearance (when silver oxide is added to the matrix up to 1 mol%) because of breaking of P-O-P bonds and forming of new P-O- and P-O-Ag bonds.

The decrease in intensity of all bands with the increase of silver oxide to the glass network matrix concludes the depolymerization process of phosphate glasses structure.

#### 4. Conclusions

Homogeneous glasses of  $x\text{Ag}_2\text{O} \cdot (100-x)[\text{P}_2\text{O}_5 \cdot \text{CaO}]$  system were obtained for  $0 \leq x \leq 5\text{ mol\%}$ . FT-IR and Raman spectroscopies have been used in order to analyze the local structure and to identify the contributions of each component on the glass network structure.

From FT-IR it can be observed that the network structure of the studied glasses consist of randomly connected  $\text{PO}_4$ ,  $(\text{PO}_3)^{2-}$  and  $(\text{PO}_2)^-$  structural units.

Raman spectra confirm the structure proposed by FT-IR measurements and reveal supplementary the presence of  $\text{P}_2\text{O}_7$  groups. No new absorption bands in Raman

spectra were detected with the addition of silver oxide to glass matrix.

Both FT-IR and Raman spectra do not evidence directly the presence of silver structural units in the studied glasses.

The investigation of FT-IR and Raman spectra of this glass matrix show that the increasing of silver oxide content leads to the appearance of gradually depolymerization process of the calcium phosphate network.

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