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Structural characterization of phosphate glasses doped with silver

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ABSTRACT

The present paper reports the influence of silver oxide addition on the local structure of $2P_2O_5 \cdot CaO \cdot 0.05ZnO$ glass matrix. The glass samples were investigated through several methods: X-ray powder diffraction (XRD), scanning electron microscopy (SEM), infrared absorption (FT-IR) and Raman scattering. The X-ray diffraction patterns confirm the vitreous character of these samples over the explored compositional range and the SEM pictures confirm this information. The phosphate structural units of the network former are assessed from FT-IR and Raman spectra as ultra-, meta-, pyro- and orthophosphate units. A slight structural depolymerization process of these phosphate-based glasses was evidenced for higher silver oxide content. *In vitro* behavior of the bulk glass sample with the highest silver oxide content was tested by immersion in simulated body fluid (SBF). X-ray diffraction and SEM measurements made on the SBF treated sample revealed growth of a crystalline phase on the surface sample.

1. Introduction

In addition to their applicability in optical data transmission, solid state batteries, and laser technologies, and owing to their high thermal expansion coefficient, low transition temperature and high electric conductivity [1–6], phosphate-based glasses are nowadays also studied because of their great potential for use as biomaterials [7–9].

Simple phosphate glasses do not have high chemical stability when compared with multicomponent phosphate-based glasses. Among the phosphate-based glasses, those containing calcium, magnesium, sodium and potassium have received a great deal of attention because of their chemical composition is close to that of natural bone [7].

However, the newest applications for biomaterials also requires glasses with higher solubility, e.g. glasses that slowly release active ingredients used to cure trace element deficiencies in animals, suture thread and bone fracture fixation [10–12]. Moreover, the prevention of post-implantation infections remains a central need. Silver, due to his well-known antibacterial and antimicrobial [13] activity, might be an answer to this problem. On the other hand, zinc is also needed for the health and maintenance of the bones. The development of new materials, like silver–calcium–zinc–phosphate based glasses, having low bacterial adhesion and biocompatibility, represents one of the possible solutions to prevent post-implantation infections.

Numerous investigators [1–6] have undertaken experimental and theoretical research on phosphate glasses. It was established that 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 (usually alkali 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 terminology (where n represents the number of bridging oxygen atoms per PO_4 tetrahedron) [4], the phosphate structural groups pass from ultraphosphate Q^3 ($[P(OP)_3(OP^-)_1]$) to metaphosphate Q^2($[P(OP)_2(OP^-)_2]$) to pyrophosphate Q^1 ($[P(OP)(OP^-)_3]$) to orthophosphate 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 prepare zinc calcium phosphate glasses containing silver oxide and to investigate their structure through various methods (X-ray diffraction, scanning electron microscopy, FT-IR absorption and Raman scattering). The sample with the highest concentration of silver oxide was investigated both before and after immersion in simulate body fluid (SBF) in order to see if there is any structural change denoting bioactive properties.

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Table 1
Ion concentration (mM) in SBF and in human blood plasma.

Ion	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	HCO_3^-	HPO_4^{2-}	SO_4^{2-}
SBF	142.0	5.0	1.5	2.5	147.8	4.2	1.0	0.5
Human plasma	142.0	5.0	1.5	2.5	103.0	27.0	1.0	0.5

2. Experimental procedure

The following glass compositions $Ag_2O \cdot (100 - x)[2P_2O_5 \cdot CaO \cdot 0.05ZnO]$ with $0 \leqslant x \leqslant 1$ mol% were prepared by the conventional melt quenching technique. The starting materials used were of analytical grade, i.e. $(NH_4)_2HPO_4$, ZnO, $CaCO_3$, $AgNO_3$. The appropriate amounts of chemicals were manually mixed in an agate pellet. The mixtures corresponding to the desired compositions were melted in air, in sintered corundum crucibles, in an electric furnace at 1200 °C for 1 h. The melts were quickly cooled at room temperature by pouring and stamp them between two copper plates to avoid any undesired crystallization process.

The structure of the samples was investigated by X-ray diffraction measurements using a standard Bruker X D8 Advance diffractometer with a monochromator of graphite for CuK_α (λ = 1.54 Å). The diffractograms were performed in a 2θ degree range 10°–90° with a speed of 2.4°/min. A scanning electron microscope type Jeol JSM 5510 LV of high resolution 3.5 nm with 100 kV acceleration voltage and 300 000× magnification order was also use to investigate the surface morphology. To perform the SEM measurements the samples were glued on an aluminum sample holder with conductive carbon cement. For FT-IR measurements the glasses were powdered and mixed with KBr in order to obtain thin pellets with a thickness at about 3 mm. The spectra were recorded at room temperature in the 350–4000 cm^{-1} range with a 6100 Jasco spectrometer with a maximum resolution of 0.5 cm^{-1} and S/N (signal/noise) ratio: 42 000:1. The Raman spectra were obtained with a micro-Raman setup (HR LabRam inverse, Jobin-Yvon-Horiba). As excitation wavelength 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 was collected with a charge-coupled-device camera operating at 220 K.

In vitro bioactivity of the glasses, reflected in their capability for self-assembly of hydroxyapatite layer onto their surface [9], was investigated by immersion in SBF solution at 37 °C. The SBF solution was prepared using the Kokubo recipe [14], which is the closest to the human plasma, as shown in Table 1, [15] buffered at pH 7.38 by tris-hydroxymethyl-amminomethane (Tris, 50 mM) and hydrochloric acid.

Due to the small quantities of silver oxide introduced in the glass matrix the sample $Ag_2O \cdot 99[2P_2O_5 \cdot CaO \cdot 0.05ZnO]$, having the highest concentration of silver oxide (keeping the vitreous character) was choused to be soaked into the SBF and sealed in a sterilized glass container. Afterward the container was stored in a thermostat at 37 °C. After 3 h, the sample was removed from the solution washed with distilled water and dried in air. The surface changes were then, investigated through X-ray diffraction and SEM measurements.

3. Results and discussion

The absence of Bragg peaks in the X-ray diffraction patterns (Fig. 1) confirmed the vitreous character of the obtained glasses which were colorless and transparent through the choused compositional domain. If we increase the content of the silver oxide content, over those particular compositions $Ag_2O \cdot (100 - x)[2P_2O_5 \cdot CaO \cdot 0.05ZnO]$ with *x = 0,* 0.1, 0.3, 0.5 and 1 mol% the obtained samples revealed inhomogeneous areas.

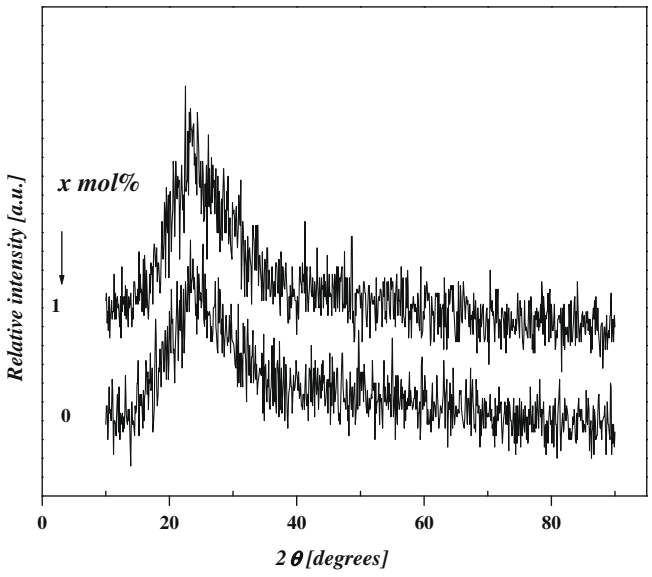

Fig. 1. X-ray diffraction patterns of glasses with $x = 0$ and $x = 1$ mol%.

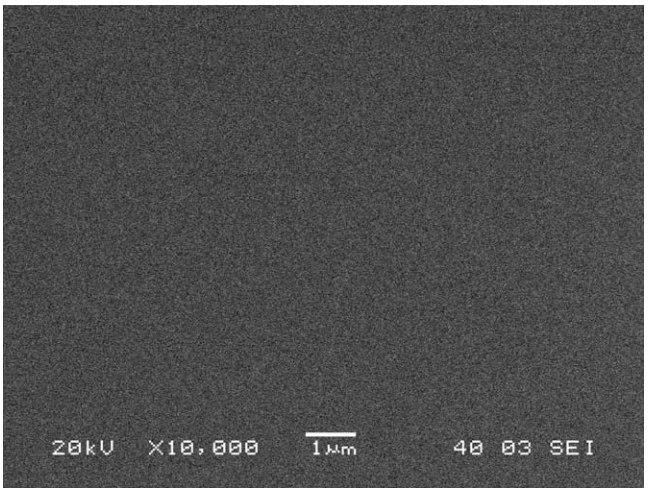

Fig. 2. SEM picture of the glass with $x = 1$ mol%.

The SEM picture of the sample with $x = 1$ mol% Ag_2O content revealed only homogenous areas characteristic of a glassy network (Fig. 2) and this result is in agreement with the information provided by the X-ray diffraction patterns.

The experimental FT-IR spectra of the $xAg_2O \cdot (100 - x)[2P_2O_5 \cdot CaO \cdot 0.05ZnO]$ glasses are shown in Fig. 3.

The spectra consist of relatively broad absorption bands. The width may reflect the structural rearrangements of different phosphate structural group. These groups may be interconnecting in several ways increasing the number of allowed vibrational modes.

The IR absorption spectrum of the matrix reveals in the 400–800 cm^{-1} spectral range bands assigned to the bending vibrations of O–P–O bonds, δ (PO_2) modes of $(PO_2)^-$ chain groups (~470 cm^{-1}), fundamental O=P–O bending vibrations (~530 cm^{-1}) and symmetric stretching vibration of P–O–P ring (~760 cm^{-1}) [4].

Regarding the 800–1200 cm^{-1} spectral region a computer program (PeakFit v4.12) was used to deconvolute this domain using the same number of peaks at approximately the same wavenumber (for example, see Fig. 4). Normalization procedure was applied before deconvolution analysis. Under this absorption envelop are present bands revealing the existence of: asymmetric stretching