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Dedicated to Academician Professor Dr. Emil Burzo on His 80th Anniversary

STRUCTURAL PARTICULARITIES OF THE SILVER AND COPPER DOPED SiO_2–CaO–P_2O_5 BASED BIOACTIVE GLASSES

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ABSTRACT. Silver and copper oxidesdoped SiO_2–CaO–P_2O_5 based bioactive glasses were obtained and structurally investigated taking into consideration their possible use as biomaterials for bone regeneration. The samples synthesized by the sol-gel method have shown the existence of a preponderantly amorphous structure, as indicated by the X-ray diffraction (XRD) data. The samples were further heat treated at 600 °C and investigated by means of XRD, Fourier Transform Infrared Spectroscopy (FT-IR) and UV-vis spectroscopy. The XRD data revealed features that can be associated with theexistence of apatite like crystallization centers. UV-vis absorption spectra indicate the presence of a small amount of metallic silver in the glass matrix, while the FT-IR spectra of silver and copper doped SiO_2–CaO–P_2O_5 samples shown common characteristics to the bioactive glasses.

Keywords: *bioactive glasses, FT-IR, silver, copper*

INTRODUCTION

The development of bioactive glasses is one of the most important subjects in the field of hard tissue implants. Almost 40 years after being discovered by Prof. Hench, bioactive glasses still attract the attention of many researchers all over the world [1, 2].

Sol-gel represents one of the main process alongside the melt-quenching method [3]. It has been claimed that one of the essential advantages of this process relates to its resource to produce new glasses from structures which would normally crystallize if processed by quenching a melt [4, 5].

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Sol-gel glasses based on SiO_2–CaO–P_2O_5 are recognized as bioactive in a very different chemical proportion [6]. Some authors have originally reported about sensitive compositions of the glass to reach and maintain bioactivity. They did the investigation through in vitro studies [6, 7]. A benefit of sol-gel synthesized glasses is that they can be formed with different metallic nanoparticles to create a particular composition [8].

It is well known that silver exhibitsantibacterial properties [8, 9] and copper is recognized to have, besides antibacterial properties, very significantly angiogenetic properties [8]. In a previous study, we demonstrated that the glasses with a minimum of 0.2 mol% Ag_2O displayeda good antibacterial effect against L. monocytoges ATCC 19115, but once the Ag_n clustersoccurred this effect was diminished [10].

The release of copper *in vivo* has been figured to minimise the risk of ischemia in skin flaps. It was discovered that copper-composition scaffolds not only provided guided vascularization, but also improves wound healing [11]. Wu et al. [12] has reported that a Cu-containing bioactive porous scaffold was successfully prepared by incorporating Cu^{2+} into glass. In the same study it has been demonstrated that it is possible to develop multifunctional scaffolds by combining enhanced angiogenesis potential, osteostimulation, and antibacterial properties for the treatment of large bone defects.

The main purpose of this study is to obtain and structurally characterize glasses, whose bioactive and biocompatible properties can be further evaluated, the most efficient materials could be eventually used in tissue engineering applications. In order to get more insight concerning the structural characteristics of the samples obtained in the present study, X-ray diffraction analysis (XRD), and FT-IR spectroscopy measurements were performed. To assess the silver/copper incorporation into the samples network, UV-Vis absorption spectroscopic measurements were also involved.

EXPERIMENTAL

Formation of Glass

The glass compositions belonging to the $60SiO_2\cdot(32\text{-}x)CaO\cdot8P_2O_5\cdot xCuO$ and $60SiO_2\cdot(32\text{-}y)CaO\cdot8P_2O_5\cdot yAg_2O$ (x, y=0, 0.5 and 2.5 mol%) system were prepared by sol-gel method. The used precursors were tetraethyl orthosilicate (TEOS), triethyl phosphate (TEP), calcium nitrate tetrahydrate ($Ca(NO_3)\cdot4H_2O$), silver nitrate ($AgNO_3$) and $Cu(NO_3)\cdot3H_2O$ hydrolyzed in the presence of nitric acid. The (HNO_3+H_2O)/(TEOS+TEP) molar ratio was constant and equal to 8. Reactants were added consecutively after 1-h intervals, with continuous stirring. The solution (*sol*) was poured into closed containers that were kept at 37°C temperature until gelation (*gel*) was reached (1-2 days depending on the sol composition). The resultant gel was by atmospheric dried in an oven 110^0C for 24 h. Nitrate elimination and material stabilization was carried out at 600^0C/3h. This temperature was determined by differential thermal analysis of the dried gels.

Methods

The XRD analysis was carried out on a Shimadzu XRD- 6000 diffractometer using CuKα radiation (λ=1.54), with Ni-filter. The diffractograms were recorded in 2θ range from10° to 80° with a speed of 2°/min.

The FT-IR absorption spectra were recorded with a JASCO 4100 (Jasco, Tokyo, Japan) spectrometer, at room temperature, in the 400–4000 cm^{-1} spectral range with a spectral resolution of 4 cm^{-1} and by using the well-known KBr pellet technique.

UV–Vis Spectroscopy absorption measurements were performed with an Analytic Jena Specord 250 plus UV-Vis spectrometer. The spectral resolution was of 2 nm.

RESULTS AND DISCUSSION

Structural characterization

The XRD patterns of the as-prepared powders is presented in Fig. 1 and revealed broad characteristics recorded around 2Θ~22° that denoted the preponderantly amorphous character of the samples. The irregular shape of the XRD signals obtained from the thermally treated samples can be owed to the presence of the second signal centered at 2θ~32° that shows the possible existence of a few crystallization centers associated with the formation of tricalcium phosphate phase, identified as $Ca_3(PO_4)_2$ H_2O (Fig. 2)[13].

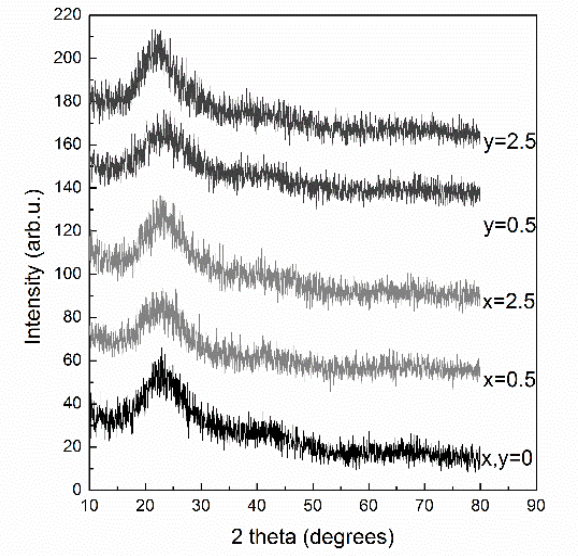

Fig. 1. XRD patterns of the as-prepared samples belonging to the $60SiO_2·(32\text{-}x)CaO·8P_2O_5·xCuO$ and $60SiO_2·(32\text{-}y)CaO·8P_2O_5·yAg_2O$systems, with x and y values as indicated.

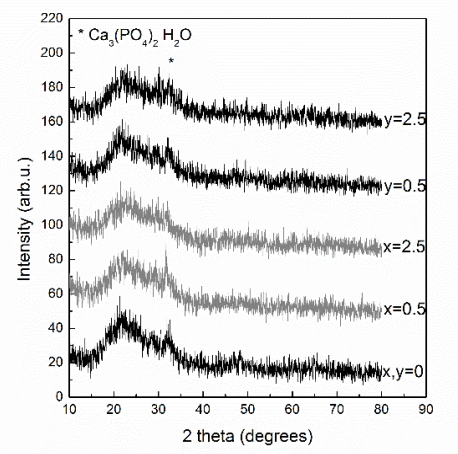

Fig. 2. XRD patterns of the thermally treated samples belonging to the $60SiO_2 \cdot (32\text{-}x)CaO \cdot 8P_2O_5 \cdot xCuO$ and $60SiO_2 \cdot (32\text{-}y)CaO \cdot 8P_2O_5 \cdot yAg_2O$ systems, with x and y values as indicated.

The FT-IR spectra of the heat treated samples exhibit absorption bands characteristic for bioactive glass (Fig. 3).Thereby, one can see features that can be assigned to the Si-O-Si stretching (1040 and 860 cm^{-1}) and Si-O-Si bending vibrations (510 cm^{-1}). The presence of water is indicated by the wide absorption signal at around 1640 cm^{-1}. The band at 1440 cm^{-1} is associated with the existence of the carbonate group and the 560 and 580 cm^{-1} signals show the presence of the phosphate groups [13]. By inspecting the recorded FTIR spectra no significant changes can be noticed, this result indicated that no important structural changes occurred in the glass structure with the addition of silver or copper, as expected for their low content.

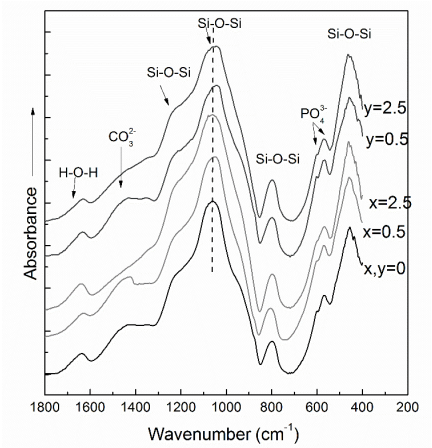

Fig. 3. FT-IR spectra of the thermally treated samples belonging to the $60SiO_2 \cdot (32\text{-}x)CaO \cdot 8P_2O_5 \cdot xCuO$ and $60SiO_2 \cdot (32\text{-}y)CaO \cdot 8P_2O_5 \cdot yAg_2O$systems, with x and y values as indicated.

In order to get more details about the structure of the investigated bioactive glasses, UV-vis absorption measurements were performed. UV-vis spectrum of the sample with 2.5 mol% CuO (Fig. 4a) shows a band centered at 800 nm characteristic to d-d transitions of Cu^{2+} in octahedral coordination [14]. According to the literature, the samples containing silver could give rise to plasmon resonance bands in the 400-500 nm spectral region of the UV-vis spectra as a consequence of Ag nanoparticles presence [10]. Thus, by analyzing the Figure 4b one can observe the appearance of an absorption signal with a maximum of around 420 nm for the samples with silver, this signal being associated with the existence of very small, spherical silver particles, formed inside the glass matrix [10]. For the glass sample with 2.5 mol% Ag_2O content, a less intense signal appears between 300 and 330 nm due to electronic transitions in Ag metallic species [15].

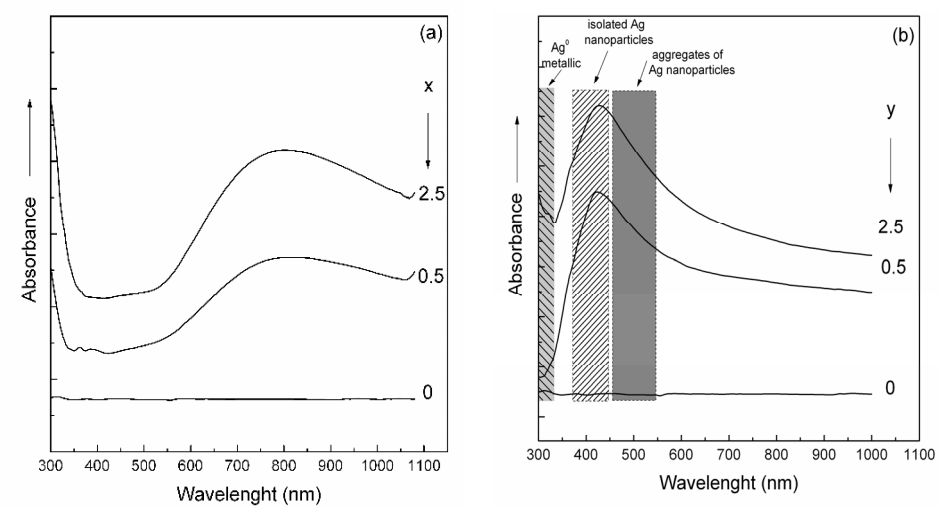

Fig. 4. UV-vis spectra of the (a) $60SiO_2 \cdot (32\text{-}x)CaO \cdot 8P_2O_5 \cdot xCuO$ (b) $60SiO_2 \cdot (32\text{-}y)CaO \cdot 8P_2O_5 \cdot yAg_2O$ samples with x and y values as indicated

CONCLUSIONS

In this study several compositions of silver and copper oxides containing bioactive SiO_2–CaO–P_2O_5 based glasses were synthesized. The structural particularities determined after the silver or copper addition to the bioactive glass network was investigated by three different techniques. The XRD pattern of the as prepared samples revealed the amorphous structure of the glass. Thermally treatment applied to the both set of samples revealed the occurrence of a second broad maximum centered at $2\theta \sim 32°$ that show the possible existence of a few crystallization centers associated with the formation of tricalcium phosphate phase. UV-vis absorption spectra indicate the presence of a small amount of metallic silver into the glass matrix, as indicated

by the absorption signal recorded around 420 nm. For 2.5% Cu containing sample, the UV-vis spectra emphasize a band centered at 800 nm characteristic of d-d transitions of Cu^{2+} in octahedral coordination.The FT-IR spectra of the obtained sol-gel glass samples exhibit absorption bands characteristic for bioactive glass, no influence of the silver and copper addition have been noticed.

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