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SYNTHESIS AND CHARACTERIZATION OF STRONTIUM CONTAINING PHOSPHOSILICATE BIOGLASSES

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ABSTRACT. The structural properties of strontium containing silicophosphate glasses synthesized by sol-gel process were studied and compared with those of the strontium-free material. The samples were characterized by differential thermal analysis (DTA), X-ray diffraction (XRD), Fourier transform infrared spectroscopy, and BET surface area analysis. Based on the DTA results, the 100 ºC dried gels were subjected to heat treatments at 300 ºC and 650 °C. X-ray diffractograms show a predominant amorphous character for all samples, even after the thermal treatments. The FT-IR analysis indicates weak changes in the local structure of Sr-free samples induced by progressive addition of SrO addition, as well as by increasing treatment temperature. The BET data reveal that the glasses are mesoporous.

Keywords: *silicophosphate bioglasses; sol-gel; strontium; mesoporosity.*

INTRODUCTION

Bioceramics and bioglasses are extensively used in the treatment of bone defects and osteoporotic problems [1]. An important requirement for bioglasses to be used as bone implant is to have osteoinductive properties. If a bone is damaged, the osteoclasts remove the damaged fragments and the osteoblasts reconstruct the bone. However, the natural reconstruction is slow and usually bone ceramics and glasses are used in order to assist bone reparation. The properties of bioglasses for stimulation and acceleration of new bone formation can be improved by incorporating bone stimulating ions into their chemical composition [2]. Besides zinc and magnesium, strontium is another element that has a positive effect on osteoblastic cell proliferation, differentiation and bone mineralization [3-5].

It is demonstrated that strontium reduces bone resorption and stimulates the bone formation. In vitro and in vivo studies have indicated `that strontium increases bone formation and reduces osteoporosis, leading to a gain in bone mass and improved bone mechanical properties in animals and humans [6–7].

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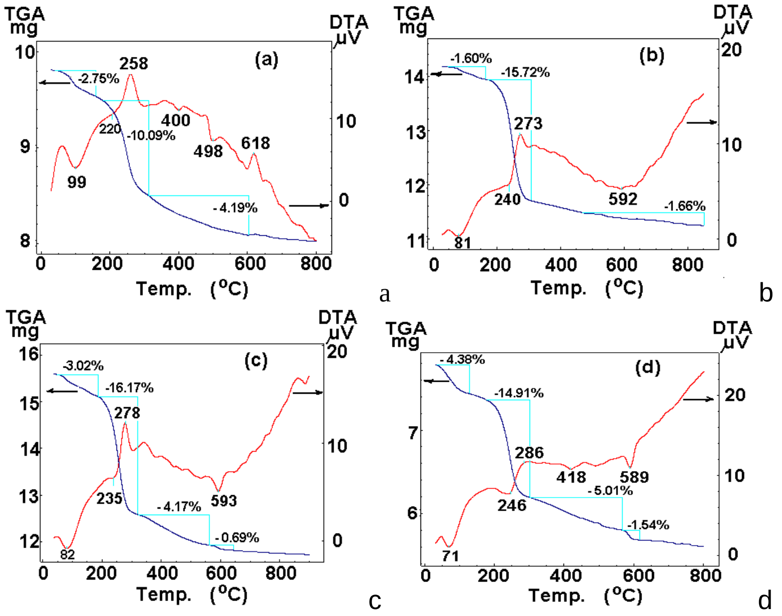
The aim of the present study was to produce sol-gel derived silicophophate glasses with different SrO contents and to compare their physico-chemical properties to those of strontium-free glass using proper analytical techniques.

RESULTS AND DISCUSSION

Samples of (95-x)$SiO_2 \cdot xSrO \cdot 5P_2O_5$ glass system, $0 \le x \le 10$ mol%, with four different SrO/SiO_2 molar ratios (Table 1) treated at 100, 300 and 650 ^oC were investigated.

Table 1. Compositions and codes of samples**.**

Sample code	SiO_2 (mol %)	SrO (mol %)	P_2O_5(mol %)
M	95	-	5
S1Sr	92	3	5
S2Sr	88	7	5
S3Sr	85	10	5



a b c d

Figure 1. DTA and TGA runs of sol-gel derived samples: (a) M; (b) S1Sr; (c) S2Sr; (d) S3Sr.

The TGA curves for all the samples present several regions of weight loss (Figure 1). The first weight loss that occurs around 90 ^oC coincides with an endothermic peak in DTA signal and it can be associated with the removal of free water molecules. A second weight loss with two corresponding peaks in the DTA curve can be observed until 300 °C. This loss can be associated with the elimination of water caged in the pores and the decomposition of residual ammonium nitrate. Further weight losses are observed until 650°C and correspond to the elimination of hydroxyl groups. Based on this result, a thermal treatment at 650 °C was also considered.

The XRD patterns of the 100°C dried samples (Figure 2) indicate a prevalent amorphous state in all samples. It can be observed that with the increase of the strontium amount, besides the large diffraction peak that dominates the XRD patterns, there are peaks indicating the presence of minor crystalline phases, that could be assigned to some strontium nitrate crystals (JCPDS 25-0746) from the precursor used as SrO source, or formed during the samples synthesis. After thermal treatment at 300 °C the peaks corresponding to strontium nitrate crystals are still present. The XRD patterns of 650 °C heat treated samples indicate an amorphous phase for all the samples, excepting S3Sr which evidences the tendency to develop a nanocrystalline phase.

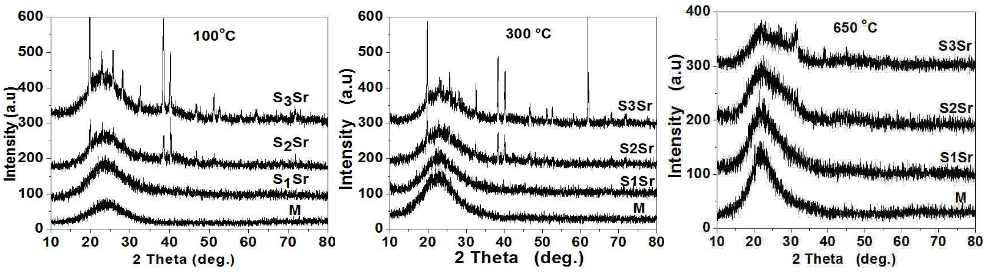


Figure 2. XRD patterns after treatments at different temperatures.

The FT-IR spectra (Figure 3) consist of broad absorption bands recorded in the spectral range 3750-2600 cm^{-1} which are assigned to vibrations of Si-OH bonds, molecular water and organic residues [8-12]. The peak at 3540 cm^{-1} is associated to silanol groups linked to molecular water through hydrogen bonds. The large absorption band at 3400 cm^{-1} is assigned to molecular water. The bands at 3300-2600 cm^{-1} correspond to the symmetric and asymmetric fundamental stretching vibration of CH_2 and CH_3 groups belonging to residues from the TEOS precursor used in the sol-gel process. After thermal treatment the broad band from 3750-2600 cm^{-1} decreased in intensity by eliminating of water and hydroxyl groups. The peak at 1620 cm^{-1} also corresponds to vibration of molecular water. The absorption band recorded around 1360 cm^{-1} is assigned to symmetric stretching vibration modes of C-H bonds, but also to the stretching vibration of NO_3^- ions [13]. A decrease in the intensity of this band is observed with increase of SrO content and after thermal treatments too. The bands at 1265-830 cm^{-1} are due to the Si-O-Si and P-O stretching mode [14, 15]. A decrease in intensity is noticed with increasing of SrO content on the account of SiO_2 content. By addition of SrO, a shift of the absorption band assigned to Si–O–Si vibrations to lower wavenumbers was also observed, that suggests the shortening of Si–O–Si bonds in the vicinity of large Sr cations [16]. This peak may also indicate the presence of Si–O–Sr bond in silicate compounds [17]. The bands at 780 and 445 cm^{-1} are assigned to Si-O-Si bonds [18], and that at 610 cm^{-1} to Si-Si stretching vibrations [19].

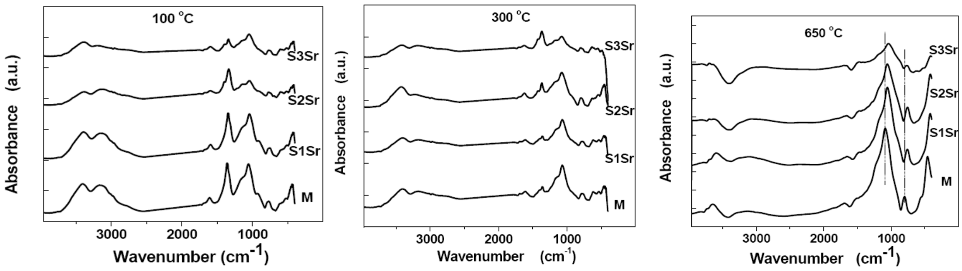


Figure 3. FT-IR spectra of the samples treated at different temperatures.

Figure 4 illustrates the mesopores distribution as a function of the amount of strontium. The strontium containing samples versus the strontium-free sample exhibit a more uniform and narrow size distribution of the mesopores with a pore diameter between 2 and 7 nm.

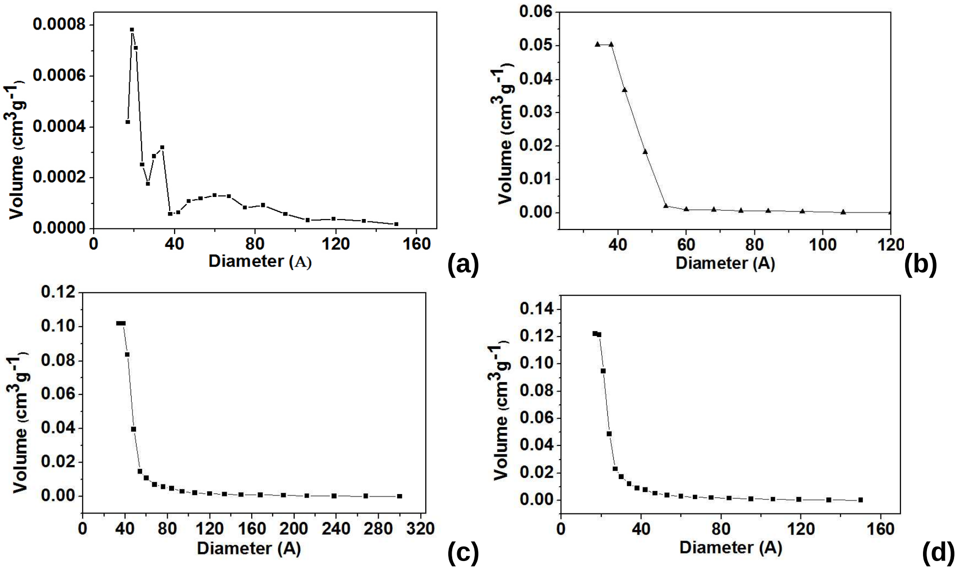


Figure 4. Textural pore size distribution of the prepared sample, obtained from BJH analysis of nitrogen desorption branch: (a) M, (b) S1Sr, (c) S2Sr and (d) S3Sr.

On the other hand, it was observed that the specific surface area of the investigated samples (Table 2) pronouncedly increases as only 3 mol % SrO is added into the phosphosilicate glass matrix, but with further increase of strontium concentration the specific surface area slightly diminishes.

Table 2. Specific surface area of the samples

Sample	M	S1Sr	S2Sr	S3Sr
Specific surface area (m^2/g)	27	191	187	172

In the calcosilicate sol-gel derived bioactive glasses no significant effect of strontium addition on specific surface area is observed [20], while in phosphosilicate glasses strontium induces pronounced textural changes.

CONCLUSIONS

Both sol-gel derived glasses based on SiO_2-P_2O_5-SrO system and strontium-free phophosilicate glass matrix have a prevalent amorphous character and remain amorphous after thermal treatments up to 650 ^oC. The FT-IR analysis shows weak changes in the local structure of strontium-free samples induced by SrO addition, as well as in function of SrO content. The BET data indicate that the glasses are mesoporous. The specific surface area pronouncedly increases from 27 m^2/g, for the phophosilicate glass matrix, to 191 m^2/g, by addition of only 3 mol % SrO, but it slightly decreases for higher SrO contents. The samples can be considered for further investigation with respect to their bioactivity required for biomaterials used as scaffolds in bone tissue regeneration.

EXPERIMENTAL SECTION

The $(95-x)SiO_2 \cdot xSrO \cdot 5P_2O_5$ glass samples, $0 \leq x \leq 10$ mol%, were prepared following the sol-gel route. The indicated compositions (Table 1) are related to the amounts of the SiO_2, SrO and P_2O_5 precursors used in the synthesis of these samples. The precursors were TEOS ($Si(OC_2H_5)_4$), strontium nitrate ($Sr(NO_3)_2$) and dibasic ammonium phosphate ($(NH_4)_2HPO_4$). Nitric acid (HNO_3) was used as catalyst in TEOS solution. The precursors were separately stirred with distillated water, for 30 min. Then both strontium and phosphorous containing solutions were added to TEOS solution under continuous stirring. The obtained solution was left overnight for gelation at room temperature. After 7 days of aging at room temperature, the samples were heat treated for 24 h at 100º C.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on a Shimadzu type derivatograph DTG-60H, with a heating rate of 5ºC/min using alumina open crucibles, in order to investigate the thermal behavior of the dried samples, and to assess the heat treatment temperatures.

The structure of the samples was characterized by X-ray diffraction (XRD) analysis using X-ray Shimadzu XRD-6000 diffractometer with Ni-filter, and CuKα radiation (λ = 1.5418Ǻ). The operation voltage and current were 40 kV and 30 mA, respectively. The measurements were performed at a scan speed of 2^o/min in 2θ scan range from 10^o to 80^o.

After 100 ºC drying, the samples were ground in an agate ball mixer mill Retsch MM300, and then they were thermally treated at 300 ºC and 650ºC.

FT-IR spectra were recorded in the range of 4000-400 cm-1 in transmission mode on a FT/IR-6200 Spectrometer by Jasco using the KBr pellet technique. Samples were prepared by mixing 1 mg of powder with 250 mg of KBr and pressing into pellets.

The specific surface area, pore volume, and pore radius of the samples were obtained from N_2-adsorption measurements, using a Sorptomatic 1990 apparatus. The BET method was used for calculation of surface area, and the BJH method was used for determination of porosity parameters.

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