



# Novel selenium containing boro-phosphate glasses: Preparation and structural study



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## ARTICLE INFO

### Article history:

Received 18 June 2013

Received in revised form 27 January 2014

Accepted 17 February 2014

Available online 22 February 2014

### Keywords:

Boro-phosphate glass network

Selenium oxide

Glass microstructure

Depolymerization

## ABSTRACT

We synthesized a new boro-phosphate glass system with different %mol SeO<sub>2</sub> content by conventional melt quenching technique. All samples were obtained in a glassy state with the vitreous structure confirmed by X-ray diffraction analysis. Scanning electron microscopy (SEM) revealed some non-homogeneous domains on the glasses surface, and their tendency to link each other once the selenium oxide content increases. Energy-dispersive X-ray analysis (EDAX) indicated similar elemental composition in different regions of each sample. X-ray photoelectron spectroscopy (XPS) was used to determine the nature of chemical bonding and the elemental composition at the sample surfaces, and Fourier transform infrared (FT-IR) spectroscopy was used to determine the structural groups in the obtained glass structure. Based on FT-IR results, the glass structure at short range order consists mainly of small phosphate units such as pyrophosphate (i.e. P<sub>2</sub>O<sub>7</sub><sup>2-</sup> dimers or terminating groups at the end of phosphate chains) and some metaphosphate (i.e. PO<sub>3</sub><sup>-</sup> middle groups in the phosphate chains) units. The boron atoms are mainly placed in three-coordinated sites in BØ<sub>3</sub> or BØ<sub>2</sub>O<sup>-</sup> units. A small contribution of BØ<sub>4</sub><sup>-</sup> units was also detected from the FT-IR spectra of glasses. For SeO<sub>2</sub> content higher than 5 mol%, the modifier role of selenium ions is strongly reflected on the local structure dominated in this case by pyrophosphate units.

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## 1. Introduction

The category of materials called glass network formers comprises a large diversity of substances that are able to form glasses by themselves. In the light of structural and kinetic theories, the properties needed by a substance to be able to vitrify itself were observed for the most common oxides used as glass network formers like SiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub> and P<sub>2</sub>O<sub>5</sub> [1]. From these materials in the last decades, phosphate glasses and glass ceramics containing calcium ions have attracted much attention in the field of materials with major application in the bone tissue engineering. These biomaterials were in the beginning selected for structural restoration based on their biomechanical properties [2]. Presently, scaffolds are engineered to be bioactive or bioresorbable to enhance tissue growth because of their chemical similarity to the inorganic phase of human bone [3]. However, one of the major demands in bone tissue engineering remains the fabrication of scaffolds exhibiting mechanical, structural, surface-chemical, topographical and biological properties suitable to regenerate substantial (critical size) cortical bone and able of functioning under relevant loads. These scaffolds are frequently porous and/or made of biodegradable materials that envelope different growth factors, drugs or genes [4]. It is known that phosphate glasses are water soluble, and the degradation rate can be adjusted by altering their composition

[5]. Boron is an element that can be considered as a potential stimulating agent for bone tissue engineering. Besides, its degradation rate can be adjusted by adjusting boron content in the glass composition. It was shown that boron affects the RNA synthesis in fibroblast cell [6]. *In vivo* studies on rabbits have indicated that dietary boron can stimulate bone formation [7]. Generally, borate glasses present low chemical durability, some of them being able to convert faster and more completely to hydroxyapatite (HA) when immersed in an aqueous phosphate solution, such as simulated body fluids [3,8,9].

Moreover, bioactive glasses and glass-ceramics find a variety of biological applications such as in cell separation, drug delivery and magnetic intracellular hyperthermia treatment of cancer [10]. Presently, the bioactive glasses are rather limited to simple form in clinically applications because of their strong tendency to crystallize during heat treatments usually required for manufacturing special products or shape. It was shown that besides decelerating the HCA development, it also inhibits protein adsorption, contributing to a decrease in bone bonding [10]. Thus, small changes in the oxide composition of a glass can have large effects on the glass structure. Consequently, a comprehensive understanding of glass behaviour with small changes in the oxide composition of the glass is a necessity for a successful product with potential biomedical application. By introducing it into the scaffold materials of therapeutic ions (Zn, Sr, Cu, Co, Mg, and Se), the subsequent release of these ions after exposure to a physiological environment is believed to favourably affect the human cell response and to enhance the bioactivity of the scaffolds related to both osteogenesis and angiogenesis [11].

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In this context, we propose to study the influence of  $\text{SeO}_2$  addition to  $\text{P}_2\text{O}_5\text{-CaO-B}_2\text{O}_3$  vitreous system. Selenium is an essential component of a key antioxidant enzyme (glutathione peroxidase) necessary for the normal growth and development of human body and is playing an important role in both the detoxification of heavy metals and the production of antibodies by the immune system [12,13]. Selenium acts as a cofactor with the enzyme glutathione peroxidase that prevents the cell degeneration of tissues due to its antioxidant role [14]. The basic function of this enzyme is to maintain low levels of hydrogen peroxide in the cells, reducing the negative effect of free radicals. In addition, *in vitro* tests have evidenced the antimicrobial character of selenium containing materials through its positive role in formation of superoxide radicals [12,15]. Though selenium is an essential mineral trace of the human body, its influence on the structural properties and biological performance in phosphate glasses was poorly analyzed [11,12,16].

The present study aims to establish the right synthesis conditions (melting temperature, melting time, the selenium oxide concentration range for vitreous composition) for samples that belong to the  $x\text{SeO}_2 \cdot (100 - x)[48\text{P}_2\text{O}_5 \cdot 50\text{CaO} \cdot 2\text{B}_2\text{O}_3]$  system to analyze their local structure, the surface composition and the morphology with a special emphasize on the influence of selenium ion in the glasses structure and composition.

## 2. Materials and methods

### 2.1. Glass synthesis

$48\text{P}_2\text{O}_5 \cdot 50\text{CaO} \cdot 2\text{B}_2\text{O}_3$  glass samples with different %mol  $\text{SeO}_2$  content were prepared by conventional melt quenching technique. Appropriate quantities of reagent grade  $\text{NH}_3 \cdot \text{H}_2\text{PO}_4$ ,  $\text{CaCO}_3$ ,  $\text{H}_3\text{BO}_3$  and  $\text{SeO}_2$  were mixed in an agate mortar. The  $x\text{SeO}_2 \cdot (100 - x)[48\text{P}_2\text{O}_5 \cdot 50\text{CaO} \cdot 2\text{B}_2\text{O}_3]$  batches ( $x = 0, 0.1, 0.5, 1, 5, 10$  and  $20$  mol%  $\text{SeO}_2$ ) were melted in air, in sintered corundum crucibles, in an electric furnace at  $1100^\circ\text{C}$  for 45 min. The melts were quickly cooled at room temperature by pouring and stamped between two copper plates, initially cooled with liquid nitrogen. Glass frit was ground to powder in a Retsch Planetary ball mills, type PM 100, for 45 min and revolution speed of 450 rpm in order to reach a final fineness lower than  $30\ \mu\text{m}$ .

### 2.2. Methods of glass characterization

The sample structure was investigated by X-ray diffraction using a standard Bruker X D8 Advance diffractometer with a monochromator of graphite for  $\text{CuK}\alpha$  ( $\lambda = 1.54\ \text{\AA}$ ). The diffractograms were recorded in  $2\theta$  range from  $10^\circ$  to  $90^\circ$  with a speed of  $2.4^\circ/\text{min}$ .

The sample morphology was explored by SEM using an FEI Quanta 3D FEG dual beam in high vacuum work mode using Everhart Thornley Detector and accelerating voltage of 30 kV. Quantitative elemental analyses were provided by energy-dispersive X-ray (EDX) equipment combined with SEM.

X-ray photoelectron spectroscopy (XPS) analysis was performed using a SPECS system, with appropriate computer-controlled data collection. The base pressure in the analysis chamber spectrometer was less than  $5 \times 10^{-9}$  mbar. XPS spectra were obtained using a monochromated  $\text{Al K}\alpha$  radiation, operated at 280 W. All of the spectra presented in this paper have been corrected for the charging effect. Surveys were measured in steps of 1 eV and high-resolution spectra with 0.05 eV steps. Analysis of the data was carried out with Casa XPS software [17]. For the survey spectra, 10 scans were performed for each sample, while for the high-resolution spectra, 20 scans were recorded for each element. The anode of the monochromated X-ray source in our experiments was used in the non-focusing mode, which allows the X-ray source to operate at maximum power. In this operation mode, the X-ray spot size on the anode is  $3.5 \times 4\ \text{mm}^2$ , which corresponds to  $3.5 \times 1\ \text{mm}^2$  on the sample, larger than the analyzed powder particles size.

For Fourier transform infrared (FT-IR) measurements, identical amounts of glasses were powdered and mixed with KBr in order to obtain thin pellets containing approximately 1.03-wt% glass powders. The pellet thickness was about 3 mm. The spectra were recorded at room temperature in the  $350\text{-}4000\text{-cm}^{-1}$  range, with a 6100 Jasco spectrometer with a maximum resolution of  $0.5\ \text{cm}^{-1}$  and signal-to-noise ratio 42,000:1.

## 3. Results and discussion

All samples were obtained in a glassy state with the vitreous structure confirmed by X-ray diffraction patterns (Fig. 1). The simultaneous presence of both network formers  $\text{P}_2\text{O}_5$  and  $\text{B}_2\text{O}_3$  in the glasses composition gives rise to two large bands observed in the XRD pattern: a dominant one centred at  $2\theta = 25^\circ$  followed by a second one at  $2\theta = 45^\circ$ . This is a commune observed feature in glasses containing two network former cations.

After milling the samples, the particle dimensions of the powdered samples are bigger for the samples with  $x > 5$  mol%. Fig. 2a shows the SEM micrographs recorded from the powdered samples at high magnification. The elemental composition of different regions of the samples was determined using the EDX analysis (Fig. 2b). For different domains of the same sample, minor differences in the composition appeared, even if morphologically they look rather different.

X-ray photoelectron spectra survey scans (Fig. 3) were recorded first to determine the chemical species developed on the  $\text{P}_2\text{O}_5\text{-CaO-B}_2\text{O}_3\text{-SeO}_2$  sample surface. The survey spectra are quantified in terms of peak intensities and peak positions. All XPS and Auger peaks from the constituent elements of the obtained glasses were clearly identified and marked on the spectra (see Fig. 3). The binding energy of  $\text{C1s}$  photoelectron peak has been used as an energy reference for the spectra. The comparison of the obtained XPS intensities of the investigated samples was done with Casa XPS software via the so-called percentage atomic concentrations, based on the ratio of the intensity to the total intensity of electrons in the measurement. The results obtained are listed in the Table 1. At the sample surface, the Se content as estimated by XPS is not higher than 1 at%. Earlier reported work [18] on selenium doped hydroxyapatite coatings for biomedical applications revealed that 0.6 at% in the coating is efficient for clinical application, a value that is close to that obtained in this case at the analyzed sample surface.

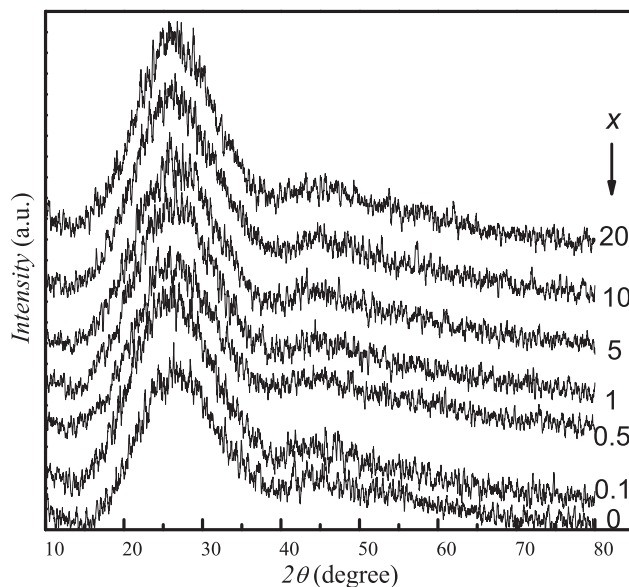


Fig. 1. X-ray diffraction patterns of the  $x\text{SeO}_2 \cdot (100 - x)[48\text{P}_2\text{O}_5 \cdot 50\text{CaO} \cdot 2\text{B}_2\text{O}_3]$  glass system.

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