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Preparation, structure and bioactivity of $xAu_2O_3\cdot(100-x)[P_2O_5\cdot CaO]$ glass system

Adriana N. Regos *, I. Ardelean

Faculty of Physics, Babes-Bolyai University, Cluj Napoca 400084, Romania

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ABSTRACT

Gold doped calcium phosphate glasses were prepared by the melting method. The structure of Au_2O_3–P_2O_5–CaO glasses is investigated using X-ray diffraction, infrared absorption and Raman scattering. The depth characterization of their structures is essential for the understanding of the properties of biocompatible materials. Thermal analysis DTA and TGA were also made to study behavior under different temperature regions and to see chemical changes versus time and temperature of these glasses. Bioactivity of the glasses was investigated in vitro by examining apatite formation on the surface of glasses treated in acellular simulated body fluid (SBF) with ion concentrations nearly equal to those in human blood plasma. Formation of bioactive apatite layer on the samples treated in SBF for 28 days at 37 °C was confirmed by X-ray diffraction (XRD) and scanning electron microscope (SEM). The effect of SBF soaking induces structural changes on the surface, reflected by the appearance of nano-crystalline particles agglomerated into micro-aggregates.

1. Introduction

Phosphate glasses have a large interest for many technological applications due to the high refraction index, thermal expansion coefficient, low melting temperature and viscosity, and their transmission in UV. Also phosphate glasses have the ability to immobilize the radioactive waste in their matrix, and are use as raw material for optical instruments, fiber glass, implant, etc. [1–5].

During the last 20 years, bioactive materials have been applied to repair bone defects. In this way, the applications of these materials have avoided problems arising from shear–stress failure in orthopedic implants. Unfortunately, the synthetic materials develop up to date cannot replace all the function of a lost tissue or adapt to the aging changes of the body [6,7].

The first bioactive glass, 45S5 bioglass was reported by Hench [8]. It is one of the most studied and well characterized bioglass materials. Particularly, the main unit of the phosphate network is PO_4 tetrahedra which connected through P–O–P linkages forming a polymeric structure. They are bonded between them through maximum three bonds, the forth being inactive from the chemical point of view. Depending on the number of the bridging oxygen the phosphate tetrahedra can be describe as Q^i groups, where i represents the number of the bridging oxygen and can have a value of 0, 1, 2 and 3 [1–7]. Introducing the glass network modifiers in phosphate glass results in breaking P–O–P bonds and non-bridging oxygen are formed. When the concentration of modifier oxide increases the infinitely long phosphate chains are shortened causing a break in network coherency and forming non-bridging oxygen.

Calcium phosphate (CP) materials have been extensively used for bone replacement augmentation due to their similarity to the mineral component of bone [9–14]. In addition to being non-toxic, they are biocompatible, not recognized as foreign in the body, and most importantly, exhibit bioactive behavior, being integrated into the tissue by the same process active in remodeling healthy bone.

The analysis of trace heavy elements in animal bone by spectra chemical analysis has been studied although currently (multiple procedures with major use made of neutron activation analysis, X-ray fluorescence, emission spectroscopy, and spark-source mass spectrometry). This studies show that bone is a non-stoichiometric calcium phosphate arranged in a hexagonal apatite lattice. Bone mineral closely resembles synthetic hydroxyapatite $[Ca_{10}(PO_4)_6(OH)_2]$. Bone contains type I collagen, which is arranged in robust fibrils [14–18].

In modern times, injectable gold has been proven to help to reduce the pain and swelling of rheumatoid arthritis and tuberculosis. Gold alloys are used in restorative dentistry, especially in tooth restorations, such as crowns and permanent bridges. Colloidal gold is used in research applications in medicine, biology and materials science. The technique of immunogold labeling exploits the ability of the gold particles to absorb protein molecules onto their surfaces. Colloidal gold particles coated with specific antibodies can be used as probes for the presence and position of antigens on the surfaces of cells. Colloidal gold is also the form of gold used as gold paint on ceramics prior to firing [19–22,25].

The purpose of this investigation is in the first part to prepare gold doped calcium phosphate and to study the influence of

* Corresponding author. Tel.: +40 0264 405300; fax: +40 0264 591906.
E-mail addresses: dadrianad@yahoo.com (A.N. Regos), ioan.ardelean@phys.ubbcluj.ro (I. Ardelean).

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Au_2O_3 of the structure P_2O_5–CaO glass matrix, and in the second part is to exanimate in vitro bioactive behaviors of some samples of Au_2O_3–P_2O_5–CaO in acellular medium. Differential thermal analysis (DTA) and thermo gravimetric analysis (TGA) were also used to study the thermal properties of these glasses and the influence of Au_2O_3 to the thermal properties of glass matrix. Measurements regarding structure of glass samples were made through different analytical characterization techniques, including Fourier transform infrared (FT-IR) and Raman spectroscopy (sensitive methods for detecting local changes in the network symmetry). Complementary techniques were also used, namely X-ray diffraction and high resolution transmission electron microscopy with electron diffraction to characterize the surface of samples.

2. Experimental

2.1. Glass preparation

Glasses were prepared in five different compositions ($0 \leqslant x \leqslant 3$ mol%) by taking the starting materials as reagent grade ammonium dihydrogen phosphate $(NH_4)_2HPO_4$, calcium carbonate $CaCO_3$ and gold chloride $AuCl_3$ in the required stoichiometric ratio in wt.%. The chemicals are ground into fine powders using an agate mortar so as to get homogeneity of the mixture. The mixtures melted in sintered corundum crucibles, introduced in an electric furnace directly at 1250 °C, and kept at the same temperature for 50 min. When time expired, they are quickly cooled at room temperature by pouring onto stainless plates. This results in the formation of the respective calcium phosphate glasses $xAu_2O_3{\cdot}(100-x)[P_2O_5{\cdot}CaO]$ system with $0 \leqslant x \leqslant 3$ mol%. The prepared glass samples were used for further studies without any treatments.

2.2. X-ray diffraction measurements

The structure of samples was analyzed by means of X-ray diffraction using a Bruker D8 Advanced X-ray diffractometer with a graphite monochromatic for Cu Kα radiation with $\lambda = 1.54$ Å.

2.3. Structure analysis using infrared spectroscopy and Raman scattering

The FT-IR spectra have been recorded using a FT-IR 615 Fourier Transform-Infrared Spectrometer with a spectral range from 400 to 1700 cm^{-1} at room temperature. To obtain IR absorption spectra of a glass samples, KBr pelt technique is employed. The glass samples were ground in a clean mortar to a fine powder and weighed quantity (~0.004 g) of the powder was intimately mixed with desiccated highly purified (~99.99%) KBr powder (~0.2 g). The mixture was then pressed with a pressure of 7 ton per square inch to yield a transparent pellet of approximate thickness 0.1 mm suitable for mounting in spectrophotometer.

The Raman spectra were performed by HR Lab Raman Horiba Jobin Yvon equipped with a 10× microscope objective. For all measurements it was used an external laser with an wavelength of emission 532 nm and a power of 5 mW incidents on the samples has been employed. The Raman spectra were obtaining from points on the surface of sample.

2.4. Thermal analysis

The differential thermal analysis (DTA) and thermogravimetry (DTA–TGA) were carried out on Stanton Redcroft STA780 apparatus with a heating rate of 10 °C/s in argon flow using Al_2O_3 as a reference material.

Table 1
Ion concentrations of the SBF and human blood [26,38].

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
Blood plasma	142.0	5.0	1.5	2.5	103.0	27.0	1.0	0.5

2.5. Surface analysis of glass samples and pH values of SBF solution

In vitro assay of bioactivity were performed by soaking the material in simulated body fluid (SBF), an acellular aqueous solution, with inorganic ions composition almost equal to human plasma (Table 1). The SBF solution was prepared by dissolving reagent grade chemicals of NaCl, $NaHCO_3$, KCl, $K_2HPO_4{\cdot}3H_2O$, $MgCl_2{\cdot}6H_2$ and $CaCl_2$ in ion distilled water, as described by Kobuko et al. [26]. The concentration of Cl^- and HCO_3^- were selected to provide stability and reproducibility of apatite formation on the prepared glass samples (Table 1). The glass samples were immersed in SBF solution for 28 days at 37 °C. After this period the samples were gently rinsed with water, dried and analyzed by scanning electron microscopy with a JSM5510LV Joel microscope. The thickness of the layers that grew as a consequence of the bioactive process was measured on SEM images with 500× and 1300× microscope objective.

Variation of pH values in SBF solution was measured every day for 28 days using a pH meter (model-720A Thermo Orion) for all glass samples under identical conditions. The electrode was calibrated using the standard pH value of 4.00, 7.00 and 10.0 before taking the pH measurements.

All measurements were performed at room temperature.

3. Results and discussion

3.1. FT-IR spectroscopy

The infrared absorption spectroscopy is one of the most important techniques used in the investigation of matter. The IR radiation is absorbed by molecules and converted in molecular vibration energy. When the radiant energy coincides with specific molecular vibrations, the absorption appears. The appearances in the IR spectrum of absorption intensity maxima corresponds necessarily to the presence of certain functional groups in the molecule and the wavenumbers at which the radiation is absorbed by the molecule can be directly correlated with the links of the given compound.

The infrared absorption spectra obtained for the $xAu_2O_3{\cdot}(100-x)[P_2O_5{\cdot}CaO]$ glasses with $0 \leqslant x \leqslant 3$ mol% are present in Fig. 1. The spectra reflect the minor structural rearrangements of different phosphate structural groups. These groups may connect in several ways increasing the number of allowed vibration modes.

IR analysis spectra reveal that the low frequency envelope around 500 cm^{-1} consists of two component bands at ~490 and ~536 cm^{-1}. The band about 490 cm^{-1} is assigned to the bending vibrations of P–O–P units, $\delta(PO_2)$ modes of $(PO_2^-)n$ chain groups, and the band at ~536 cm^{-1} is described as a fundamental frequency of (PO_4^{3-}) or as harmonics of P═O bending vibration. The large band centered at ~753 cm^{-1} is attributed to a P–O–P stretching vibrations from Q^2 units [3,4,27].

The absorption band at ~920 cm^{-1} is attributed to asymmetric stretching vibration of P–O–P groups linked with linear metaphosphate chain.

It has been suggested that the band at the highest wave number ~1279 cm^{-1} is caused by the P═O double stretching bond from Q^2 species. The band at ~1120 cm^{-1} is due to PO_3^{2-} asymmetric and symmetric vibrations (Q^1) [3–5]. This band increases in its intensity