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Thermal investigations of Ti and Ag-doped bioactive glasses

E. Wers, H. Oudadesse*, B. Lefeuvre, B. Bureau, O. Merdrignac-Conanec

University of Rennes 1, SCR, UMR CNRS 6226, 263 av. du Général Leclerc, 35042 Rennes, France

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ABSTRACT

The purpose of this paper is to explore the effect of titanium and silver on the characteristic temperatures of 46S6 glass and the excess entropy. The results show that the adding of these metals in the chemical composition does not affect the amorphous character of glasses. The introduction of these elements greatly reduces the melting temperatures of glasses and involves similar variations on the crystallization and glass transition temperatures. These elements also increase the thermal stability of glasses. The excess entropy calculations show a decrease when the content of Ti or Ag increases. Contrary to crystals, synthesized glasses have entropy different to zero at $T = 0$ K.

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1. Introduction

Bone grafts (heterografts, xenografts) are capable of transmitting viruses and/or infections. The synthetic biomaterials are an excellent alternative to replace grafts because they are available in unlimited quantities, they can be adapted to the needs of patients and their chemical composition can be controlled [1,2]. The efficiency of the bioactive glasses is well proven [1–3] and they are the subject of numerous studies and many developments all over the world in order to improve their properties for biomedical use.

Hench has discovered the first bioactive glass: 45S5 or Bioglass® in the quaternary SiO_2, Na_2O, CaO and P_2O_5 system [1–3]. Their bioactive character results of their ability to form a hydroxyapatite layer $Ca_{10}(PO_4)_6(OH)_2$ on their surface when they are immersed in a simulated body fluid (SBF) [4–6]. The hydroxyapatite is the major inorganic compound of the human bone. It induces a bone bonding improving the bone growth.

However, complications such as bacterial infections may occur during implantation of a biomaterial. The particularity of this investigation is based on the introduction of Ag and Ti in the pure bioactive glass 46S6. Each of these chemical elements presents interesting biological properties that may expand the field of use of bioactive glasses.

Titanium is present in several inert biomaterials such as hip prosthesis made of titanium alloy, screws and plates to repair bone damages. It does not induce inflammatory response because it is a good biocompatible material [7]. It is also used in the materials for aerospace because it has high mechanical properties. It allows reinforcing biomaterials [7].

The antibacterial properties of the silver ion Ag^+ have been used for many years in the medicine [8]. A lot of studies on 12 species of bacteria including *Escherichia coli* [9,10] confirmed its biological properties. The introduction of silver into implants is promising method in reducing the infection rate, while exhibiting low toxicity toward cells and tissues [11,12]. Moreover, its use in the surgical tools (pins, scalpel) decreases bacterial colonization and infections [13]. The incorporating of silver ions into the glass matrix allowed the controlled delivery of this anti-bacterial agent at the site of the bone defect [14]. News studies about bioactive glasses doped with silver showed that these glasses have a bacteriostatic potential and induce bacteria reactions [8–15].

Glasses are composed of network forming, modifying and intermediate oxides. They present an amorphous character reflecting a structural disorder. Metal elements introduced in the glass matrix may involve specific changes on thermal behavior. In a previous work, the introduction of zinc has showed a decrease of the fusion temperature and the excess entropy of the pure glass 46S6 [16]. In the glassy matrix, if there are no enough alkaline ions, the intermediate element will be a network modifier by creating two oxygen bridges. Conversely, if there are enough alkaline ions, the intermediate element will be a network former [16,17].

Studies have showed the impact of silver and titanium on the thermal properties.

Numerous researches about borophosphate glasses have showed the effect of the addition of TiO_2 on their thermal characteristics. The results showed a non-linear increase of glass

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* Corresponding author. Tel.: +33 223236659.
E-mail address: hassane.oudadesse@univ-rennes1.fr (H. Oudadesse).

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transition temperature [18]. In glasses in the ternary system Na_2O–TiO_2–P_2O_5, the addition of TiO_2 (from 0 to 5 mol% TiO_2) resulted in a non linear increase of glass transition temperature and dilatation softening temperature. The increase of TiO_2 content involves the increase of the contribution of the surface crystallization mechanism. With the increase of TiO_2 content, the temperature of maximum nucleation rate is also gradually shifted from a value close to the glass transition temperature toward the crystallization temperature. The chemical durability of the glasses without titanium oxide is very poor, but with the replacement of Na_2O or P_2O_5 by TiO_2, it increases sharply [19]. It has been proved shown that TiO_2 changes from a glass network former to a glass network modifier with increasing TiO_2 content in this system [20]. TiO_2 is also an effective nucleating agent for promoting the crystallization of apatite and wollastonite.

In chalcogenide glasses, the introduction of a content of silver causes several changes in the thermal behavior. Indeed, the thermal stability and the glass-forming ability increase with the Ag content. Results show that $Se_{80.5}Bi_{1.5}Te_{16}Ag_2$ composition is thermally more stable and has a little tendency to crystallize in comparison to other compositions without silver. The increase in thermal stability with increasing Ag concentration is attributed to an increase in the cohesive energy [21]. Moreover, the introduction of silver in polyurethane composites improves and increases both the thermal conductivity and the stability in comparison with a reference polyurethane sample without silver [22]. In Ag–As–Se chalcogenide glasses, the enthalpy of primary crystallization decreases with increasing Ag content, accompanied by an increase of the activation energy of primary crystallization and the thermal stability of the supercooled liquid, which suggests a change of the crystallization mechanism [23]. Moreover, the glass transition temperature is independent of the Ag content [23]. For other materials, for example syndiotactic polystyrene, the adding of silver enhances the thermal stability, probably due to the higher thermal conductivity that silver exhibits [24].

This work comes after the thermal study of bioactive glasses doped with zinc [16]. The aim of this study is to investigate the impact of titanium and silver ions on the characteristic temperatures and the excess entropy of bioactive glasses. The excess entropy was calculated according to the changes of thermal characteristics [16]. This entropy represents the difference between the melting entropy of crystal and the entropy of glass [16]. Unlike crystals which have a zero entropy, synthesized glasses have entropy different to zero at $T = 0$ K and versus T_f [25].

2. Materials and methods

2.1. Elaboration of bioactive glasses

The pure bioactive glass 46S6 (46 wt% SiO_2, 24 wt% CaO, 24 wt% Na_2O and 6 wt% P_2O_5) was studied doped by introduction of different concentrations of silver and titanium: 46S6-*x*Ag and 46S6-*x*Ti (where $x = 0$, 0.1, 1, 5 and 10 in wt%).

For the preparation of bioactive glasses, sodium metasilicate (Na_2SiO_3), silicon oxide (SiO_2), calcium metasilicate ($CaSiO_3$), sodium metaphosphate ($Na_3P_3O_9$), silver oxide (Ag_2O) and titanium oxide (TiO_2) were weighed and mixed in a polyethylene bottle, for 2 h using a planetary mixer. Ag_2O and TiO_2 were introduced at the expense of Na_2O and CaO.

The premixed mixtures were melted in platinum crucibles that were placed in an electric furnace. The first rise of temperature rate was 10 °C/min and it was hold at 900 °C for 1 h to achieve the decarbonation of all products. The second rise of temperature rate was 20 °C/min and it was hold to 1350 °C for 3 h. The samples were casted in preheated brass molds, in order to form cylinders of 13 mm in diameter, and annealed at 565 °C for 4 h near the glass transition temperature of each glass [16].

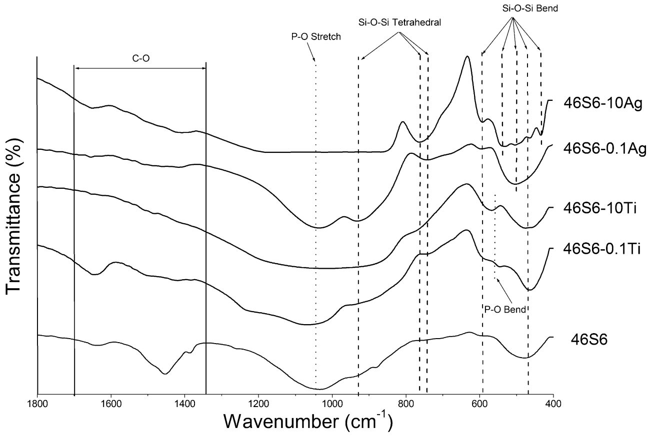

Fig. 1. FTIR spectra of pure and doped glasses.

2.2. Differential thermal analysis

Differential Thermal Analysis (DTA) was used to measure the thermal characteristics of different bioactive glasses. The DTA principle is based on the detection of exothermic or endothermic phenomenon. The glass transition temperature T_g, the crystallization temperature T_c and the fusion temperature T_f have been recorded using a Setaram Labsys 1600TG-DTA/DSC thermal analyzer under N_2 gas atmosphere. The onset temperature of crystallization $T_{onset}c$ represented the beginning of the crystallization have been recorded. All characteristics temperatures were obtained thanks to SETSOFT software which uses the tangent method. Bioactive glasses were studied under heating rate of 5 °C/min raised from room temperature to 1400 °C. 40 mg of the glass powder was heated in platinum crucible and another empty platinum crucible for use as control. The thermal stability (*TS*) of bioactive glasses has been expressed by the difference between T_g and $T_{onset}c$ introduced by Dietzel [26]: $TS = T_{onset}c - T_g$

3. Results and discussion

3.1. Characterizations of Ag-doped glasses and Ti-doped glasses

In the order to see the impact of a high amount of Ti or Ag on the structure of the glass network, measures by X-ray diffraction were undertaken. The diffractograms of bioactive glasses were obtained between 5 and 80 ($2\theta°$) using a Bruker D8 advance diffractometer with Cu K_α radiation. A halo of diffraction, characteristic of an amorphous system, was visible between 24 and 40 ($2\theta°$) for pure and doped glasses. Thereby, a content of 10 wt% of Ti or Ag introduced in the glass matrix does not affect the amorphous character of these glasses.

To analyze the eventual new chemical bonds formed by introduction of metal elements, analyses by infrared spectroscopy were performed by using Fourier Transformer InfraRed (FTIR) spectrometer Bruker Equinox 55 between 4000 and 400 cm^{-1} with a resolution of 2 cm^{-1}. The infrared spectra of bioactive glasses are presented in Fig. 1.

For all glasses, bands characteristic of bend vibrations of Si—O—Si bonds are visible at 479 cm^{-1}. Between 1350 and 1700 cm^{-1}, vibrations of C—O bonds are due to the carbon dioxide present during the analysis. A band characteristic at 592 cm^{-1} reveals bend vibrations of Si—O—Si bonds for all glasses except to that of 46S6-10Ag which is more pronounced. For 46S6-0.1Ti and 46S6-0.1Ag, a band

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