



# A novel tantalum-containing bioglass. Part I. Structure and solubility



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## ARTICLE INFO

### Article history:

Received 17 June 2016

Received in revised form 2 October 2016

Accepted 17 November 2016

Available online 18 November 2016

### Keywords:

Bioactive glass

Solubility

Glass characterization

Silicate glasses

Tantalum

## ABSTRACT

Bioglasses are employed for surgical augmentation in a range of hard tissue applications. Tantalum is a bioactive and biocompatible transition metal that has been used as an orthopedic medical device. It has a range of biological and physical properties that make its incorporation into ionic form into bioactive glass systems promising for various clinical applications. The work herein reports the characterization and properties of novel tantalum-containing glasses. A series of glasses based on the system  $48\text{SiO}_2-(36-X)\text{ZnO}-6\text{CaO}-8\text{SrO}-2\text{P}_2\text{O}_5-X\text{Ta}_2\text{O}_5$  with X varying from 0 mol% (TA0) to 0.5 mol% (TA2) were synthesized. The addition of small amounts of  $\text{Ta}_2\text{O}_5$  did not cause crystallization of the glasses but increasing  $\text{Ta}_2\text{O}_5$  content at the expense of ZnO was found to result in an increased number of bridging oxygens (BOs). This, along with the data recorded by differential thermal analysis (DTA) and magic angle spinning-nuclear magnetic resonance (MAS-NMR), confirms that Ta acts as a glass former in this series. Solubility experiments showed that minor changes in the glass structure caused by Ta incorporation (0.5 mol%) exhibited greater cumulative % weight loss, pH values and cumulative  $\text{Zn}^{2+}$  and  $\text{Sr}^{2+}$  ion concentration over a period of 30 days of maturation, when compared to  $\text{Ta}_2\text{O}_5$ -free glasses. The results presented in this article confirm that replacing ZnO with  $\text{Ta}_2\text{O}_5$  in silicate glasses results in the formation of stronger bonds within the glass network without any adverse effects on the solubility of the glasses prepared from them.

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## 1. Introduction

Bioactive glasses are candidate materials for a wide variety of biomedical applications as they can bond to bone and be formulated to release bioactive ions into the local environment, resulting in antimicrobial activity and enhanced cell response [1,2].

Silicate-glasses are inorganic amorphous solids composed of  $\text{SiO}_4^{4-}$  tetrahedral units. In other words, silicon is coordinated to 4 oxygen atoms and each oxygen atom is coordinated to 2 silicon units so that the structure is a three-dimensional (3-D) network of corner connected  $[\text{SiO}_{4/2}]$  tetrahedra [3]. These  $\text{SiO}_4^{4-}$  tetrahedral units form the backbone of the glass structure while modifying cations charge balance the silicate chains. The ionicity of the Si—O bond, resulting from the difference in the electronegativity of Si and O, allows for the formation of Si—O—Si bonds [4], forming the backbone of various bioglass systems. Si can also bond to other atoms depending on the glass composition [5,6]. Indeed, bond formation corresponds to a state of electronegativity equalization stated by Sanderson [7]. When a bond is formed between two atoms, X and Z, with different electro-negativities, there is an electron

flow from the less to the more electronegative atom. Further, it is accepted that silica glasses undergo modification in response to the addition of other cations/atoms [8]. As an example, the alkali ions locate themselves in the structure near the non-bridging oxygen (NBO) when added to silica glasses resulting in the formation of meta, pyro and ortho-silicates.  $[\text{SiO}_{4/2}]^0$ ,  $[\text{SiO}_{3/2}\text{O}]^-$ ,  $[\text{SiO}_{2/2}\text{O}_2]^{2-}$ ,  $[\text{SiO}_{1/2}\text{O}_3]^{3-}$  and  $[\text{SiO}_4]^{4-}$ , which are present in silicate glasses, are designated as  $Q^4$ ,  $Q^3$ ,  $Q^2$ ,  $Q^1$  and  $Q^0$  respectively, where the superscripts indicate the number of bridging oxygens (BOs) centered on the given Si atom through which it is connected to other Si atoms in the glass structure [9].

The solubility of a bioglass network is related to alkali ion content [9]; the addition of glass former cations will result in a systematic decrease in the solubility of these systems. Readers are referred to the work of Hoppe et al. [1] for detailed information on the degradation kinetics of these biomaterials and the specific effect of the released ionic dissolution products, for example  $\text{Sr}^{2+}$  and  $\text{Zn}^{2+}$  ions, impart on biological performance.

Transition metals can play a dual role in oxide glasses [10]. In some concentrations the transition metal may enter the network structure while in other concentration amounts, they may allow the oxygen ions of their former cation to break the oxygen bridges in the system, therefore acting as a glass modifier. Tantalum (Ta) is a transition metal that has been used as a bone implant [11–13] due to its physical and biological properties. The Ta ion is reported to be bioactive and

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biocompatible due to the formation of a stable tantalum pentoxide ( $\text{Ta}_2\text{O}_5$ ) component on its surface [14,15]. Studies [11,16] have shown that Ta surfaces exhibit lower contact angles and higher surface energies than titanium (Ti) or hydroxyapatite (HA) surfaces offering a favorable biological environment for adhesion, growth and differentiation of human cells. Despite some processing challenges [13,17], the inclusion of Ta and other transition metals into ionomer glasses can improve their thermal and chemical stability [6,18–20].

In a previous article [6], the authors synthesized and characterized a wholly new silicate-glass series in which ZnO was substituted with up to 8 mol%  $\text{Ta}_2\text{O}_5$ . In that work, Alhalawani and Towler showed that Ta incorporation into silicate-based glasses was possible by the melt-quenching process. They also confirmed that Ta behaved as a glass former whereas Zn acted as a glass intermediate, depending on its content, in that particular glass system. These novel glasses were designed specifically to formulate a series of glass polyalkenoate cements (GPCs) for use in sternal fixation. Initial, unpublished data has confirmed that high Ta-containing glasses have rheology (setting and working times) that are deemed unsuitable for sternal applications. The work herein expands the understanding of this particular bioglass system where a new series of the previously formulated glass [6] was synthesized containing lower  $\text{Ta}_2\text{O}_5$  contents (0.0 to 0.5 mol%). The manuscript also aims to characterize the structure and solubility of the glass system under study.

## 2. Experimental methods

### 2.1. Glass synthesis

Three glasses were proposed for this study (Table 1), a  $\text{Ta}_2\text{O}_5$ -free  $\text{SiO}_2$ -ZnO-CaO-SrO- $\text{P}_2\text{O}_5$  glass (TA0) and two  $\text{Ta}_2\text{O}_5$ -containing glasses (TA1 and TA2). Appropriate amounts of analytical grade silica, zinc oxide, calcium carbonate, strontium carbonate, ammonium dihydrogen phosphate and tantalum oxide (Fisher Scientific, Ottawa, ON, Canada; Sigma-Aldrich, Oakville, ON, Canada) were weighed out and hand-mixed using a spatula. Platinum (Pt.) crucibles and a Lindberg/Blue M model furnace (Lindberg/Blue M, Asheville, NC USA) with a UP550 controller were used for melting the sieved powders (1650 °C, 1.5 h). The melts were shock quenched in water to obtain frit which was then dried in an oven (100 °C, 1 h), ground using a ball mill (400 rounds per minute, 15 min), and sieved once more through a 45  $\mu\text{m}$  mesh. TA0, TA1 and TA2 were then annealed at 670 °C, 666 °C and 677 °C, respectively for 12 h to relieve internal stresses within the glass network. The furnace (Lindberg/Blue M, Asheville, NC, USA) was programmed to reach to the annealing temperature in 3 h and to cool down to the room temperature ( $25 \pm 2$  °C) in 3 h. The glass powders of the selected compositions were then sieved through a 45  $\mu\text{m}$  mesh and utilised for subsequent characterization.

### 2.2. Glass structural and thermal characterization

#### 2.2.1. X-ray diffraction (XRD)

A Bruker D2 Phaser desktop X-ray diffractometer (Bruker AXS Inc., WI, USA) was used to obtain X-ray diffraction patterns from the glasses

at room temperature ( $23 \pm 1$  °C). Glass powder samples were packed into stainless steel sample holders. With the X-ray generator set at 30 kV and 30 mA, a copper anode was used to produce a divergent beam with an average  $K\alpha$  wavelength of 1.541874 Å. The range of  $10$ – $80^\circ 2\theta$  with a step size of  $0.02^\circ 2\theta$  and a count time of 10 s per step were used for the measurements. X'Pert Highscore™ data analysis software version 1.0 d (PANalytical, Almelo, The Netherlands) was employed to find peak parameters.

#### 2.2.2. Particle size analysis (PSA)

The particle size distribution (PSD) of each glass series was recorded using a Multisizer 4 Particle size analyzer (Beckman Coulter, Fullerton, CA, USA). The glass powder samples ( $n = 5$ ) were evaluated in the range of 2 to 60  $\mu\text{m}$  with a run length of 60 s. A background analysis was performed and subtracted for accurate results. The fluid used in this case was a sodium chloride (NaCl) electrolyte solution at a temperature range of  $10$ – $37$  °C. The relevant volume statistics were calculated on each glass composition. The average diameters ( $n = 5$ ) at the 10%, 50%, and 90% of the cumulative volume distribution ( $d_{10}$ ,  $d_{50}$  and  $d_{90}$ , respectively) were recorded.

#### 2.2.3. Scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS)

Sample imaging was carried out with an FEI Co. Quanta 200F Environmental Scanning Electron Microscope equipped with an EDAX Genesis Energy-Dispersive Spectrometer (Oxford Instruments X-max, Netherlands). Secondary electron (SE) and backscattered electron (BSE) images were taken on glass particles and polished disc surfaces. All EDS spectra were collected at 20 kV using a beam current of 26 nA. Quantitative EDS spectra was subsequently converted into relative concentration data ( $n = 3$ ).

#### 2.2.4. Differential thermal analysis (DTA)

A combined differential thermal analyzer–thermal gravimetric analyzer (DTA-TG; SDT 2960 Simultaneous DSC-TGA, TA Instruments, DW, USA) was used to study the thermal properties of the glasses. A heating rate of 20 °C/min was employed using an air atmosphere with alumina in a matched platinum crucible as a reference and then cooled to room temperature at the same rate. Sample measurements were carried out every 6 s between 30 °C and 1200 °C. Data analysis was performed using NETZSCH Proteus software, V. 6 (Netzsch-Gerätebau GmbH, Selb, Germany).

#### 2.2.5. X-ray photoelectron spectroscopy (XPS)

The powders' chemical compositions as well as local chemical environment were analyzed using PHI Quantera Scanning X-ray photoelectron Microprobe (XPS). The XPS data sets were collected with Al  $K\alpha$  X-rays (monochromatic, beam size = 100  $\mu\text{m}$ ) at an output power of 26.2 watts, with a photon energy of 1486.6 eV and a step size of  $\sim 0.025$  eV. Survey scans ( $\sim 0.5$  eV step size) were performed with a pass energy of 140 eV to gain qualitative information such as peak identification and peak position. Peaks identified in all survey scans were used to adjust high resolution scan binding energy range, pass energy (26 eV) and beam dwelling time ( $\sim 100$  ms). The beam sweeps for each high resolution scan was adjusted to yield a signal-to-noise ratio of  $> 100:1$ . The analyzed area was 1–2 mm in diameter.

#### 2.2.6. Magic angle spinning-nuclear magnetic resonance (MAS-NMR)

$^{29}\text{Si}$  MAS-NMR spectra were recorded at 7.05 T (Tesla) on a Varian Unity Inova 300 FT-NMR spectrometer (Palo Alto, CA, USA), equipped with a cross polarization-magic angle spinning (CP-MAS) probe. The glass samples were placed in a zirconia sample tube with a diameter of 7 mm. The sample spinning speed at the magic angle to the external magnetic field was 5 kHz.  $^{29}\text{Si}$  MAS NMR spectra were taken at 59.59 MHz with 7.0- $\mu\text{s}$  pulse length (pulse angle,  $p/2$ ), 100-s recycle delays, where the signals from 2126, 1837 and 1880 pulses were

**Table 1**  
Composition of the glass series.

	$\text{SiO}_2$	ZnO	CaO	SrO	$\text{P}_2\text{O}_5$	$\text{Ta}_2\text{O}_5$
mol%						
TA0	48.0	36.0	6.0	8.0	2.0	0.0
TA1	48.0	35.8	6.0	8.0	2.0	0.2
TA2	48.0	35.5	6.0	8.0	2.0	0.5
wt%						
TA0	35.8	36.4	7.5	14.7	5.7	0.0
TA1	35.5	35.8	7.4	14.5	5.7	1.1
TA2	35.0	35.1	7.3	14.3	5.6	2.7

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