Journal of Non-Crystalline Solids 432 (2016) 300–306

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/ locate/ jnoncrysol

Effect of zinc substitution for calcium on the crystallisation of calcium fluoro-alumino-silicate glasses

Siqi Zhang, Artemis Stamboulis *

Biomaterials Group, School of Metallurgy and Materials, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

ARTICLE INFO

Article history:
Received 27 January 2015
Received in revised form 3 September 2015
Accepted 11 October 2015
Available online 23 October 2015

Keywords:
Fluoro-alumino-silicate glass;
Crystal phases;
Gahnite

ABSTRACT

A series of 25, 60, 75 and 100 mol% zinc substituted for calcium ionomer glasses of the composition $4.5SiO_2$–$3Al_2O_3$–$1.5P_2O_5$–3CaO–$2CaF_2$ were produced following a well-established melt quench route. Similar glass compositions have been widely used in dentistry as the glass component in glass ionomer cements. The glasses crystallise to an apatite and mullite phase after appropriate heat treatments and are interesting materials for bone repair. Zinc is a bactericidal agent and has shown ability to stimulate osteogenesis. The new zinc containing glass compositions were characterised by Helium Pycnometer, DSC, TGA, SEM and EDX. The density of the zinc substituted glasses and glass–ceramics increased with increasing the zinc content as expected. The glass transition temperature decreased with zinc substitution, whereas the crystallisation temperature increased with zinc substitution. Zinc substituted glasses lead to the formation of gahnite in expense of mullite. Fluorapatite formation was not favoured in high zinc content glass ceramics, whereas loss of fluorine in the form of SiF_4 was suggested. SEM and EDX analysis showed significant changes in the morphology of glass ceramics with zinc substitution. The formation of gahnite during glass crystallisation may open new application avenues for these materials in the field of semiconducting materials.

1. Introduction

Calcium fluoro-alumino-silicate glasses are commonly used for the formation of polyalkenoate cements and have a range of applications especially in dentistry. Previous studies have shown that such glasses can crystallise to form fluorapatite [1–4]. Apatite and fluorapatite glass–ceramics have attracted a lot of interest due to apatite being an important mineral phase of tooth and bone. Recently, a strontium containing glass ceramic ($4.5SiO_2$–$3Al_2O_3$–$1.5P_2O_5$–3SrO–$2SrF_2$) exhibiting a strontium fluorapatite phase was reported to be non-biodegradable and osteoconductive similar and comparable to a bioactive HA–bioglass composite that was used as control [5]. The above study established the osteointegration of the strontium containing glass ceramic during short term implantation in a rabbit model [6]. Although, a number of cation substitutions for calcium studies in the above glass composition have been reported and the cation size effect on the structure of the glass and glass ceramics has been investigated [5], the effect of Zn addition on the apatite-forming ability of this glass has not been reported.

Two zinc glass compositions have attracted research attention in the literature; CaO–ZnO–SiO_2 and Al_2O_3–ZnO–SiO_2 [7–9]. In the CaO–ZnO–SiO_2 ternary system, zinc oxide acts as both a network modifier and an intermediate oxide like alumina as reported by R. Hill et al. [7]. In addition, the release of zinc enhances bone formation and mineralization by directly activating the aminoacyl-tRNA synthetase in osteoblastic cells as well as stimulating cellular protein synthesis [8]. Moreover, zinc is important for the function of the immune system and has been recognized as an antibacterial agent [9,10]. Due to the abovementioned advantages, zinc silicate glasses may have a great potential as cement formers and as glass ceramics in hard tissue replacement. However, reports suggest that the zinc glass based cements have inferior mechanical properties compared to the corresponding aluminosilicate glass based cements for use in clinical dentistry [11–13]. Recently, zinc was incorporated into a Ca–Si system, forming a material referred as hardystonite ($Ca_2ZnSi_2O_7$), which possesses improved mechanical properties with increased bending strength and fracture toughness as compared to hydroxyapatite (HAP) [14]. Furthermore, reports on zinc oxide addition in bioactive glasses and phosphor-silicate glasses have shown that zinc addition results in a decrease in the solubility of glasses as well as cytotoxic effects at levels of zinc ion release of higher than 2 ppm [15,16]. Due to the properties of glass and glass–ceramics being determined critically by their composition (network modifiers and their atomic environment), the crystallisation process and the microstructure, both the design and characterisation of these glasses play a very important role in the development of new medical glasses.

In the present study, addition of zinc oxide to the following ionomer glass composition $4.5SiO_2$–$3Al_2O_3$–$1.5P_2O_5$–(3-x)CaO–(2-y)CaF_2–xZnO–$yZnF_2$ is expected to have an effect on the structure of the glass as well as the formed glass–ceramics. It is also expected that the produced glass ceramics might have stimulatory effects on bone formation. More

* Corresponding author.
E-mail address: a.stamboulis@bham.ac.uk (A. Stamboulis).

http://dx.doi.org/10.1016/j.jnoncrysol.2015.10.025
0022-3093/

importantly, if Zn would act as an intermediate oxide, this will allow the design of new aluminium free glass compositions for bioceramic applications as well as dental and bone cements.

The purpose of the present work was to study the influence of zinc substitution on the crystallisation and specifically the apatite forming ability of fluorine containing calcium-alumino-silicate glasses. All the substituted glasses are based on the composition of $4.5SiO_2$–$3Al_2O_3$–$1.5P_2O_5$–3CaO–$2CaF_2$, which can crystallise to fluorapatite (FAP) and mullite on appropriate heat treatments. The samples were all characterised by DSC, TGA, XRD, SEM and EDX in order to observe the effect of zinc substitution on the crystallisation of glasses.

2. Materials and methods

2.1. Materials preparation

The molar composition of the fluorine containing alumino-silicate glasses is shown in Table 1. The glass components silicate dioxide (SiO_2), aluminium oxide (Al_2O_3), phosphorus pentoxide (P_2O_5), calcium fluoride (CaF_2), zinc oxide (ZnO), zinc fluoride (ZnF_2) and calcium carbonate ($CaCO_3$), supplied by Sigma Aldrich, were weighed out to give approximately 100 g of glass for each composition.

The oxide powders were well mixed in a plastic container and transferred to a platinum rhodium (Pt, 5% Rh) crucible. The crucible was then placed in an electric furnace (EHF 17/3, Lenton, UK) for a period of 1.5 h at a temperature of 1450 °C. The glass melt was then quenched into deionized water to prevent phase separation and crystallisation. The frit glasses were milled followed by sieving. Fine (<45 μm) and coarse glass particles (45 μm–100 μm) were obtained for further analysis. X-ray diffraction showed that all glasses were amorphous with the exceptions of 75%Zn, that was possible to quench but was partly crystallised and 100%Zn that was crystallised in the crucible and was not possible to quench. It is worth mentioning, that the 75%Zn glass was still transparent. As this glass was partly crystallised it could not be directly compared to the rest of the amorphous glasses but it was included to the results as an example of the effect of high zinc substitution.

2.2. Characterisation of glasses and glass ceramics

Differential scanning calorimetry was used in order to examine the thermal transitions of the glass compositions in the temperature range from 300 to 1300 °C. The instrument used was a NETZSCH 404C DSC with pairs of matched platinum-rhodium crucibles. All the measurements were performed using 20 mg of glass samples in dry argon at a heating rate of 10 °C/min. For the TGA measurements, the instrument used was a NETZSCH Thermal Analysis STA 449C with pairs of matched platinum-rhodium crucibles. All the measurements were performed with 20 mg of glass samples in dry argon at a heating rate of 10 °C/min.

The density of glasses and glass ceramics was measured by a helium pycnometer (AccuPyc II 1340 Series). The standard deviation of all measurements was less than 0.0009 g/cm^3. The samples had a particle size of <45 μm and the mass of the samples was approximately 1 g. In order to calculate the density of glasses and glass ceramics, the average of ten consecutive measurements was taken.

Table 1
Molar composition of Zn substituted alumino-silicate glasses.

Glass code	SiO_2	Al_2O_3	P_2O_5	CaO	CaF_2	ZnO	ZnF_2
0%Zn	4.5	3	1.5	3	2	0	0
25%Zn	4.5	3	1.5	1.75	2	1.25	0
60%Zn	4.5	3	1.5	0	2	3	0
75%Zn	4.5	3	1.5	0	1.25	3	0.75
100%Zn	4.5	3	1.5	0	0	3	2

The oxygen density (OD) was calculated by using the following equation:

$$OD = D \times \frac{\text{no. of moles of oxygens in the glass}}{\text{molecular weight of glass}} \quad (1)$$

where D is the density of the glass measured by helium pycnometer.

X-ray powder diffraction was used in order to identify the crystal phases present and study the effect of cation substitution on the crystallisation of glasses. All glass samples were heat treated in a furnace at 1100 °C for 1 h. X-ray diffraction was then performed on the heat treated samples using a continuous scan between $2\theta = 10°$ and 60°, with a step size of $2\theta = 0.0200°$. A Philips analytical X-Pert XRD was used with Cu KA at 40 kV and 40 mA.

An XL 30 SEM&EDX FEG electron microscope was used in order to investigate the morphology of the glass ceramics operated at 20 kV. Prior to characterisation all glass ceramics were etched with HF (10%). All the glass ceramic samples were coated with carbon using an SB250 coating machine. The standard deviation for EDX results was less than 0.15 wt.%.

3. Results

3.1. Density study of Zn substituted glasses and glass ceramics

The measured density and oxygen density for zinc containing alumino-silicate glasses are shown in Figs. 1 and 2. It is indicated, that the density increased proportionally with zinc substitution with the lowest density for 0%Zn and the highest density for 60%Zn. In the case of 75%Zn, the density measured 3.03 g/cm^3 but cannot be compared directly to the rest of the glasses as this one was partly crystallised. Similarly, the oxygen density increased with increasing zinc substitution as shown in Fig. 2.

In the case of glass ceramics, the density was increased with zinc substitution from 2.88 g/cm^3 for 0%Zn to 3.17 g/cm^3 for 75%Zn (Fig. 3). It is clear, that there is a linear relationship between the density and the zinc molar content.

3.2. DSC and TGA thermal analysis

Tables 2 and 3 present the glass transition, the crystallisation and the crystal dissolution temperatures of both fine (<45 μm) and coarse glass powders (>45 and <100 μm). From Table 2, it is clear that the glass transition temperature of all fine glass powders decreased with zinc substitution. The first crystallisation temperature increased with substitution with the exception of the 75%Zn substitution, where a small decrease was observed compared to the 60%Zn substitution. As mentioned

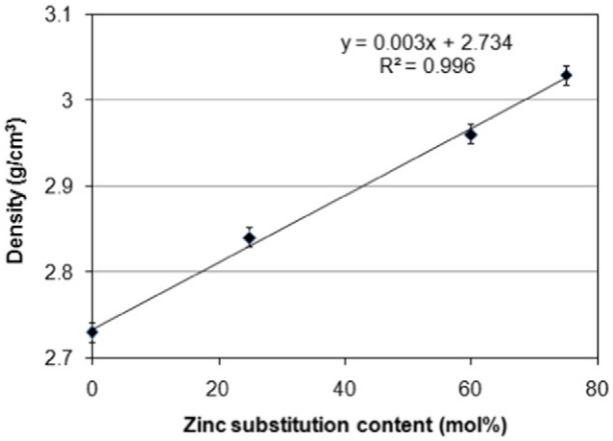

Fig. 1. Density of zinc containing glasses.