Journal of Non-Crystalline Solids 376 (2013) 221–228

Contents lists available at SciVerse ScienceDirect

Journal of Non-Crystalline Solids

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

Structural and surface studies on calcium phospho-silicate glass-ceramics containing zinc and iron oxide

K. Sharma [a,*], S. Bhattacharya [b], K.G. Bhushan [b], M.N. Deo [c], G.P. Kothiyal [a,1]

[a] Glass and Advanced Materials Division, Bhabha Atomic Research Centre, Mumbai 400 085, India
[b] Technical Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India
[c] High Pressure & Synchrotron Radiation Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

ARTICLE INFO

Article history:
Received 15 November 2012
Received in revised form 16 April 2013
Available online 2 July 2013

Keywords:
Glass-ceramic;
XPS;
XRD;
BSA

ABSTRACT

Effects of ZnO addition on structural and microstructural properties of glass/glass-ceramic with nominal composition $25SiO_2$–$50CaO$–$15P_2O_5$–$(10 - x)\,Fe_2O_3 - x\,ZnO$ (where $x = 0$–5 mol%) have been studied. Glasses were prepared by melt-quench technique and converted into glass-ceramics by controlled heat treatment. The glass-ceramics samples were immersed in bovine serum albumin (BSA) and their surfaces were investigated using Fourier transform infrared spectroscopy (FTIR) and time of flight-secondary ion mass spectrometry (TOF-SIMS). Microstructure of glass-ceramic exhibited a granular microstructure. Calcium phosphate, calcium silicate ($Ca_3Si_2O_7$), hematite and magnetite phases were observed. Surface morphology of glass-ceramics after immersion in BSA showed the formation of Si – OH functional groups. Absorption of BSA took place by interacting with the silanol groups present at the surface. The fraction of non-bridging oxygen decreased with the increase in the amount of ZnO, which led to a decrease in the surface dissolution; thereby decreasing the adhesion of BSA.

1. Introduction

A large number of glass/glass-ceramics possessing a variety of functional attributes have been developed. Bioactive glass and glass-ceramics have been used clinically in dental, craniomaxillofacial and spinal applications [1–3]. The development of ferrimagnetic crystallites in bioactive glasses induces the magnetic properties in the materials, which arise from the conversion of iron oxide into magnetite, maghemite and hematite [4]. Some of the bioactive glass compositions have also been studied as possible vehicles for the delivery of ions like Ag and zinc [5–7].

A bioactive glass/glass-ceramic forms a biologically active hydroxyapatite layer on the surface, which permits bonding with bone and soft tissue [8]. The rate of reaction between bioactive glass/glass-ceramics and body fluid depends on the structural and microstructural features of glass/glass-ceramics, which in turn depends on the composition. Thus, optimum response of glass/glass-ceramics can be obtained by varying the composition of alkaline earths like CaO, MgO and ZnO in a glass matrix. Oliveira et al. [9] reported that the glasses with improved surface activity are obtained when calcium oxide is replaced by magnesium oxide. Ebisawa et al. [10] reported an improvement in the response of ferromagnetic glasses with the addition of small amount of P_2O_5.

Zinc is known to have stimulatory effects on bone formation [11]. It is an essential mineral required to synthesis about 300 enzymes in human body. These enzymes control the vital functions such as cell reproduction, immunity, protein synthesis, wound repair, vision, free radical protection and immunity inside the body. Balamurugan et al. [12] studied the apatite-forming ability of SiO_2–CaO–P_2O_5–ZnO system in vitro and in vivo and reported that the incorporation of Zn into a bioglass does not diminish the apatite-forming ability of the material. Zinc is also known to prolong chemical durability of glass, by retarding its dissolution and reaction in aqueous solutions, and thus improving the mechanical properties of the implant [13]. The addition of zinc to iron containing glass may lead to the formation of zinc ferrites, which enhance the magnetic properties, thus, a number of glass systems containing iron and zinc have also been studied and developed [14,15]. Sing et al. [16] observed an increase in the apatite-forming ability of ZnO containing glass-ceramic samples with the evolution of Zinc ferrites in the glass-ceramics.

El-Ghannam et al. reported that the superior bioactive effect of glass/glass-ceramics as compared to hydroxyapatite was due to its ability to induce the adhesion of biopolymer (fibronectin) on its surface [17]. The material composition and surface mineralization are not the only reasons for successful osteointegration, but the selective adsorption of proteins at the interface is also important for bone bonding behavior of the materials [18].

We had observed an improvement in the magnetic and surface response of iron and ZnO containing glass-ceramics when tested in SBF [14,19]. The work reported here is an extension of previous work. As

* Corresponding author. Tel.: +91 22 25595660; fax: +91 22 25505296.
E-mail address: ksharma_iit@yahoo.co.in (K. Sharma).
[1] Superannuated.

0022-3093/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jnoncrysol.2013.04.021

mentioned above the adsorption of proteins at the surface plays an important role in determining the ultimate response of materials in physiological environment, thus it will be interesting to study these glass/glass-ceramics in bio-polymers. Since the absorption of protein on bio-glass/glass-ceramics is influenced by the surface properties of the materials, the objective is to analyze the response of materials in bovine serum albumin. Serum albumin has been chosen to investigate the protein adhesion since it is the most abundant protein found in human blood. Therefore, in the present work, we report the effect of ZnO addition on the surface properties of $25SiO_2$–$50CaO$–$15P_2O_5$–$(10 - x)\,Fe_2O_3 - x\,ZnO$ (where $x = 0$–5 mol%) glass-ceramics. Structural and microstructural measurements were studied using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The surface morphology of glass-ceramics was studied as a function of immersion time in bovine serum albumin (BSA).

2. Materials and methods

2.1. Preparation of glass/glass-ceramics

Base glasses with nominal compositions $25SiO_2$–$50CaO$–$15P_2O_5$–$(10 - x)\,Fe_2O_3 - x\,ZnO$ (where $x = 0$–5 mol%) were prepared by melt quench technique. About 100 g batches were prepared by mixing reagent grades SiO_2, $CaCO_3$, $NH_4H_2PO_4$, ZnO and Fe_2O_3. The charge was calcined at a maximum of 900 °C for 12 h, holding at intermediate temperature for 6–8 h, decided by the decomposition temperatures of various precursors. To ensure complete decomposition of carbonates into oxides, the batch was weighed before and after calcinations of the precursors. The calcined charge was melted under air ambient at 1500 °C in a Pt–Rh crucible. The base glass was powdered in a ball mill and pelletized. These were converted into glass-ceramics (hereafter called MGC) through controlled heat treatment. Glass-ceramics MGC0, MGC2 and MGC5 with ZnO concentrations 0, 2 and 5 mol% respectively, were heat treated at 1000 °C for 6 h.

Table 1
Ratio of non-bridging and bridging structure units for different glass samples obtained from XPS data (Fig. 1b).

Sample	Ratio of non-bridging to bridging oxygen groups
MG0	0.30 ± 0.04
MG2	0.193 ± 0.02
MG5	0.057 ± 0.05

2.2. DTA analyses

DTA measurements on glass powders were performed on a Setaram Labsys (TG/DTA) apparatus, which was calibrated using the melting points of high purity indium and zinc. The non-isothermal experiments were performed by heating approximately 40 mg powder of the samples in Al_2O_3 crucibles under protective ambient, using empty Al_2O_3 crucible as a reference. A heating rate of 10° K/min was employed in the range of 25–1000 °C.

2.3. Structural study

2.3.1. XPS

For XPS measurements, glass samples were mounted on a specimen holder using silver paste. The conducting path was provided from bottom to the top surface of the sample by silver paste, to avoid the surface charging effect. The sample chamber was then evacuated to a vacuum better than 1×10^{-9} Torr. The sample was excited by Mg-K_α radiations

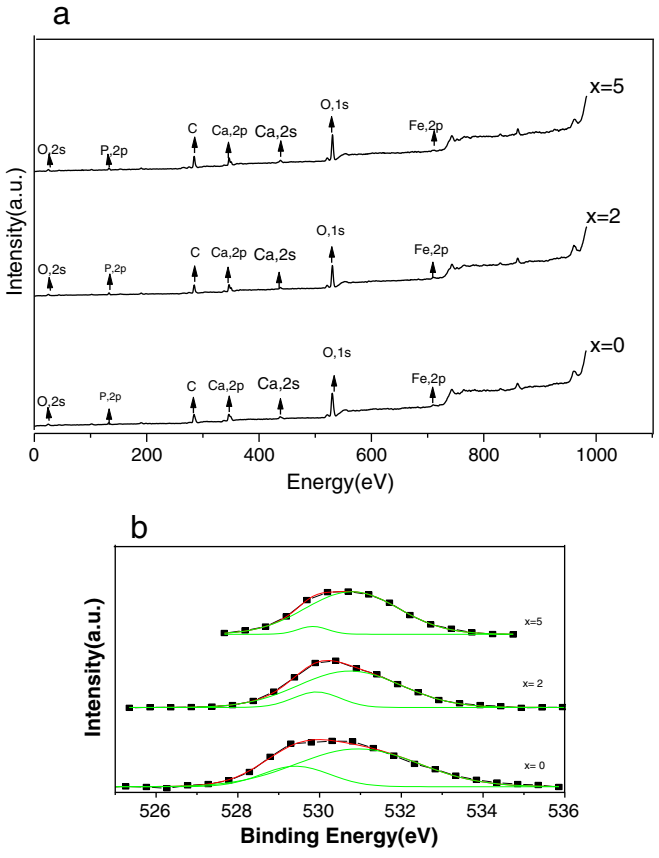

Fig. 1. (a) XPS of glass samples having different ZnO (x (mol)%) contents, and (b) oxygen spectra of glass samples with peak fitting.

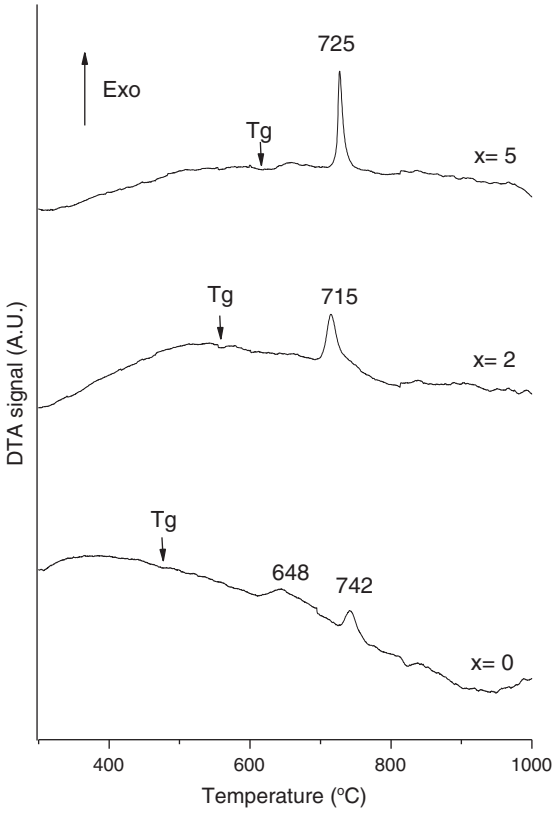

Fig. 2. DTA of glass samples having different ZnO (x (mol)%) contents.