

Fabrication of Bioactive Glass Powder Based on $\text{SiO}_2\text{-CaO-Na}_2\text{O-P}_2\text{O}_5$ System at Lower Melting Temperature

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ABSTRACT. In the present work, melt-derived method was deployed to fabricate new composition of bioactive glass (BG) from $\text{SiO}_2\text{-CaO-Na}_2\text{O-P}_2\text{O}_5$ system at lower melting temperature. Amorphous glass nature is discovered through X-ray diffraction (XRD) for all glass composition. Formation of silica network is established with the formation of functional groups Si-O-Si (bend), Si-O-Si (tetrahedral) and Si-O-Si (stretch) within all glass. The bioactivity of all BG composition is evaluated by incubation in Tris buffer solution for 7 days. Several crystalline peaks appeared in XRD after 7 days of incubation with characteristic of carbonate group (C-O) and P-O bands detected in FTIR on hydroxyl carbonate apatite (HCA) formation. Hence, the objective to develop new composition of BG fabricated at lower temperature was achieved with preservation of BG bioactivity.

Keywords: Melt-derived, Water quench, Bioactive glass powder, Bioactivity;

Received: 15.10.2017, *Revised:* 15.12.2017, *Accepted:* 30.02.2018, and *Online:* 20.03.2018;

DOI: 10.30967/ijcrset.1.S1.2018.112-117

Selection and/or Peer-review under responsibility of Advanced Materials Characterization Techniques (AMCT 2017), Malaysia.

1. INTRODUCTION

Bioactive glass (BG) is a well-known bioactive material that has the ability to develop hydroxyl carbonate apatite (HCA) layer on the surface which is essential for bond formation with tissue upon implantation in the body [1]. The classic bioactive glass was developed based on silicate network along with other oxides such as calcium oxide (CaO), sodium oxide (Na_2O) and phosphorus pentoxide (P_2O_5). The most widely researched bioactive glass is 45S5 composition and composed of 45 SiO_2 -24.5 Na_2O -24.5 CaO -6 P_2O_5 in weight percentages (wt.%), also known as Bioglass®. It was reported that 45S5 was successfully used as bone filler in clinical treatment of periodontal diseases and in middle ear surgery [1,2]. The use of BG in such clinical treatment applications is due to the osteoproduction characteristics shown by BG. The prime character is obtained due to the rapid release reaction on BG surface which facilitate in releasing critical concentration of soluble silicon, calcium, sodium and phosphorus ions that induce the attachment, proliferation and differentiation of osteoblast (bone-forming cell) [3].

The capability of implant material to evoke hydroxyapatite (HA) like layer on the surface upon immersion in simulated body fluids *in vitro* is often used as denotation of its bioactivity [4]. The rate of bioactivity of BG is dependent on the rate of ion release from the glass through its aqueous interface [5]. The bioactivity can be tailored and improved by several factors such as modification on the glass composition, pH of surrounding

environment, particle size and surface characteristic of BG [2,5]. Features such as low silica (SiO_2), high sodium and calcium oxides (Na_2O and CaO) content along with high ratio of calcium to phosphorus content [4,6,7] should be the factors in modification of glass composition. The concentration of phosphorus oxides (P_2O_5) in BG composition is also vital in stimulating optimum bioactivity of BG. It is reported that increase in P_2O_5 concentration resulted in faster apatite formation due to enhancement in glass reactivity [8]. A wide range of glass composition has been proposed to improve the biological, mechanical and processing of BG. However, the golden composition of 45S5 is still being used commercially and as subject of researches until today [7]. In addition, most of literature reported on higher melting temperature along with longer soaking time deployed during BG powder fabrication through melt-derived route [9-11].

Hence, the aim of the present work is to develop new composition of BG powder based on SiO_2 - CaO - Na_2O - P_2O_5 glass network system that can be melted at lower melting temperature and to characterize the BG properties fabricated at different composition and melting temperature. The bioactivity of the BG is evaluated by immersion in Tris-buffer solution.

2. MATERIALS AND METHODS

2.1 Sample preparation. BG powder was produced using high purity and reagent grade silicon dioxide (SiO_2), sodium carbonate (Na_2CO_3), calcium carbonate (CaCO_3) and phosphorus pentoxide (P_2O_5). Briefly, two batches of BG composition were fabricated through melt-derived route. Table 1 presents the detailed on studied glass composition in mole percentages (mol.%). Bioglass (45S5[®]) composition was used as a control. The weight of each oxide powder was measured prior mixing using analytical balance. The correct amount of each oxide was mixed inside a polyethylene bottle for 24 hours on a horizontal roller at 125 rpm for homogeneity. The powder mixtures were then melted in a platinum crucible at 1400°C for 1 hour with rate of 10°C per min inside an electrical furnace. The molten glass was quenched immediately into distilled water to obtain glass frit and dried overnight at 110°C inside an oven. Glass powder was obtained through dry milling using planetary mill, milled at 400 rpm for 1 hour. The glass powder was then sieved to obtain particle size less than 38 μm for material characterization. Similar methods were applied to melt glass with melting temperature defined based on previous work [12].

Table 1 Different glass composition in mole percentages (mol.%) and network connectivity (N_c)

Glass	SiO_2	CaCO_3	Na_2CO_3	P_2O_5	N_c	T_m
45S5	46.13	26.91	24.35	2.60	2.12	1377
50S8P	51.89	24.47	20.12	3.51	2.69	1348

2.2 In vitro testing

The glass powder was immersed in Tris-buffer solution, pH 8 inside an incubator shaker with temperature set to 37°C at 100 rpm for 7 days. After immersion, the glass powder was filtered using filter paper and dried inside an oven for 1 hour at 70°C.

2.3 Sample characterization

The properties of glass powder were studied before and after immersion in Tris-buffer solution.

2.4 X-ray diffraction (XRD)

The phase composition of each glass composition was verified using X-ray diffraction (XRD) (Bruker D8 Advance) with copper anode (Cu K α , $\lambda = 1.5406 \text{ \AA}$) where the patterns were recorded in a 2θ range from 10° to 70° .

2.5 Fourier transform infrared spectroscopy (FTIR)

The surface structural analysis of glass powders was identified using FTIR. The sample was analyzed with transmission technique using KBr pellets as a reference. The glass powder and KBr was mixed with ratio of 9 to 1 and pressed into pellet with diameter less than 5mm using handpressed machine. FTIR spectra for each glass composition were recorded between wavenumber 2000 and 400 cm^{-1} .

3. RESULTS AND DISCUSSION

3.1 Characterization on BG powder before immersion in Tris-buffer solution

X-ray diffraction Analysis. Amorphous structure is observed for all glass composition with broad peaks between 30° - 35° after glass melting without appearance of sharp Bragg peaks as shown in Fig. 1. This result indicated that the process step in forming glass via melt-derived is consistent although it was melted at different melting temperatures. The amorphous structure is obtained as glass melt is rapidly quenched in water in order to prevent phase separation [13].

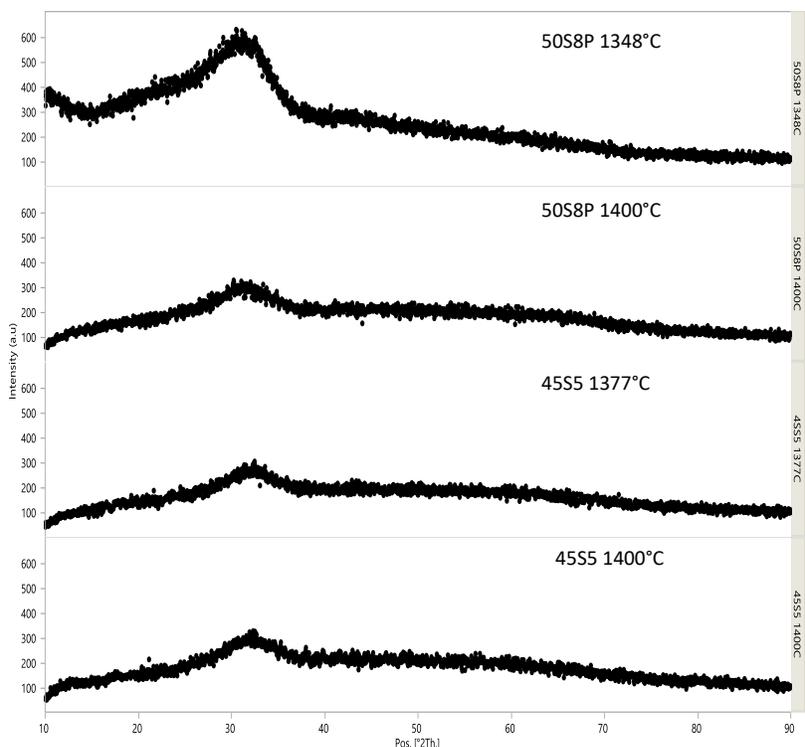


Fig. 1 X-ray diffraction of glass powder prior immersion in Tris-buffer solution

3.2 Fourier transform infrared spectroscopy (FTIR). Characteristic of silica network is observed for all glass composition with peaks observed at 508 cm^{-1} indicated the Si-O-Si bending mode, 751 - 768 cm^{-1} assigned to Si-O-Si symmetric stretching mode of bridging oxygen atoms between tetrahedron, 902 - 1082 cm^{-1} corresponding to asymmetric stretching mode of Si-O-Si bonding, shown in Fig. 2 [14-16]. Existence of

residual carbonate group is observed at band located at 1459 cm^{-1} while presence of water adsorption at glass surface is notified at 1654 cm^{-1} [16].

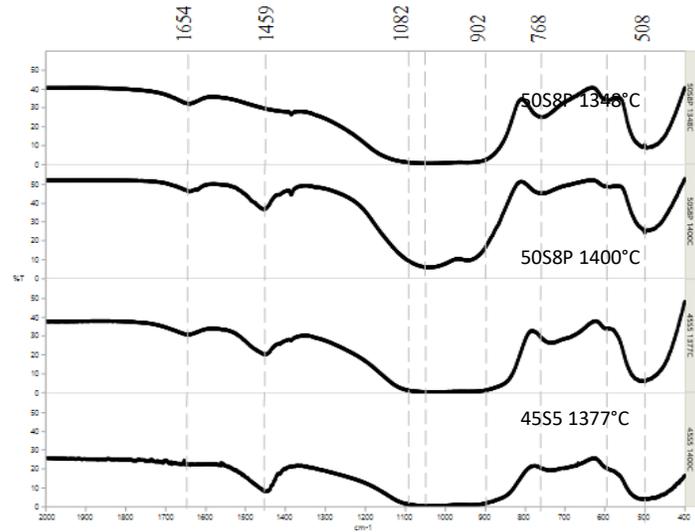


Fig.2 FTIR spectra of glass powder prior immersion in Tris-buffer solution
45S5 1400°C

3.3 Characterization on BG powder after immersion in Tris-buffer solution

X-ray diffraction (XRD). Structural changes observed for all glass composition after 7 days immersion in Tris-buffer solution is shown in Fig. 3. However, lower intensity of crystalline peaks is observed for BG melted at lower melting temperature. The crystalline peak emerged at 26° observed for all glass composition is equivalent to the plane (002) in HA [16, 17]. This indicates process of ion leaching of glass occurred which initiates the formation of silica rich layer and calcium phosphate ($\text{CaO-P}_2\text{O}_5$) leading to the growth of apatite layer on glass surface [1].

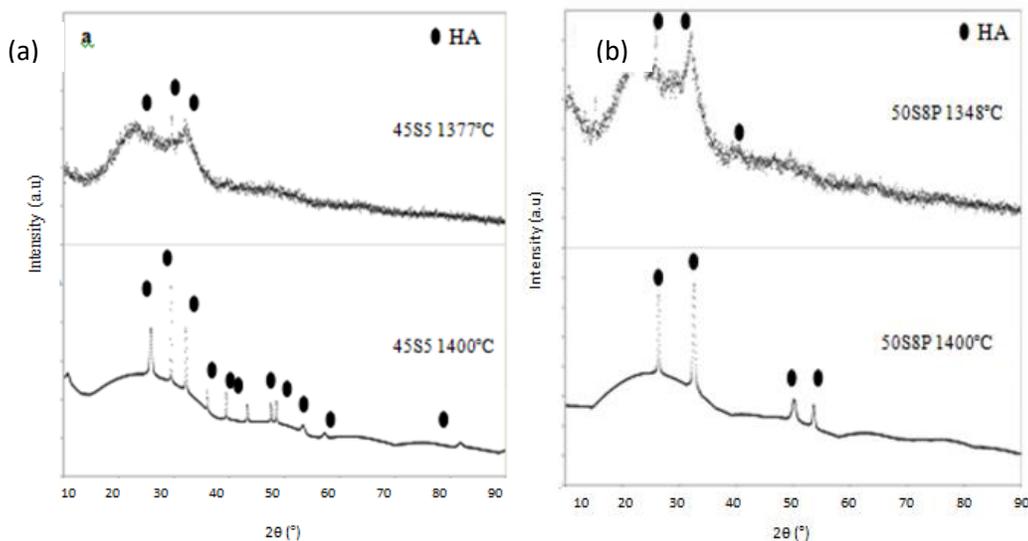


Fig.3 XRD pattern for 45S5 (a) and 50S8P (b) after immersion in Tris-buffer solution for 7 days

3.4 Fourier transform infrared spectroscopy (FTIR). Formation of apatite is observed for all BG powder after 7 days immersion in Tris-buffer solution, shown in Fig. 4. Bands appeared at 803 cm^{-1} and 997 cm^{-1} indicating the formation of Si-O symmetric and O-Si-O asymmetric stretching vibration which highlights formation of Si-OH group due to ion exchange from solution after glass leaching leading to the growth of silica-gel layer on the glass surface [16, 18]. The present of split dual band at range of 550 to 600 cm^{-1} show characteristic of P-O (crystalline) in HA [16, 19]. Decomposition of original peak at 1459 cm^{-1} into split dual band at range of 1400 to 1500 cm^{-1} signify the characteristic of carbonate group (C-O) along with weak characterization of C-O at 875 cm^{-1} . This finding suggests the growth of HA in the form of hydroxyl carbonate apatite (HCA).

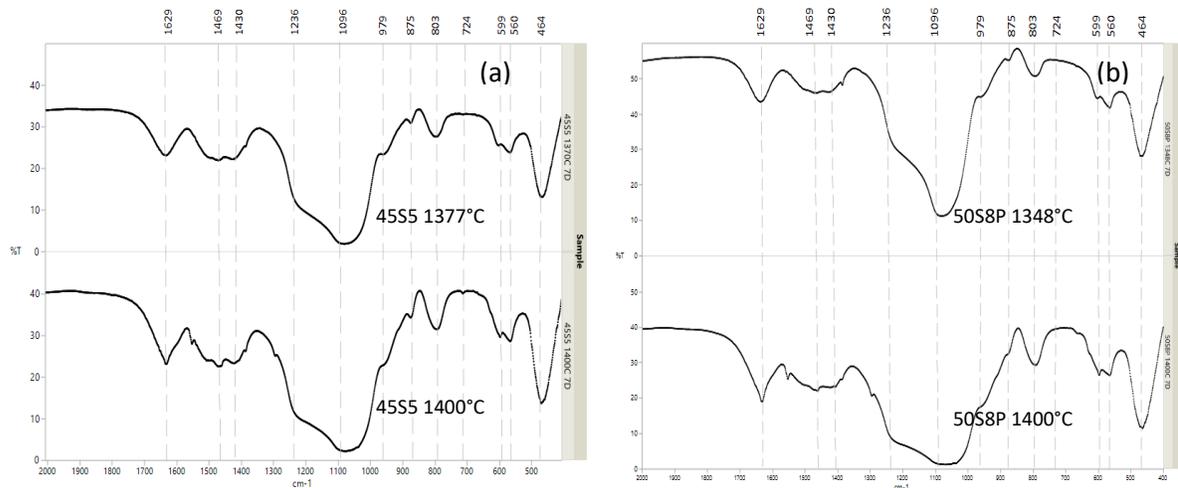


Fig. 4 FTIR spectra for 45S5 (a) and 50S8P (b) after immersion in Tris-buffer solution for 7 days

4. SUMMARY

Melt-derived BG was successfully fabricated at lower melting temperature with formation of HCA observed on all BG samples after 7 days of immersion in Tris-buffer solution.

ACKNOWLEDGEMENT

The authors acknowledged the Research University Grant, Universiti Sains Malaysia (1001/CIPPT/814258) for financial assistance.

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