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In-vitro bioactivity of zirconia doped borosilicate glasses

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In-Vitro Bioactivity of Zirconia Doped Borosilicate Glasses

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Abstract. Glass composition $31B_2O_3$-$20SiO_2$-$24.5Na_2O$-(24.5-x) CaO-xZrO_2 x=1,2,3,4,5 were prepared by melt-quenching Technique. The formation of hydroxyapatite layer on the surface of glasses after immersion in simulated body fluid (SBF) was explored through XRD, Fourier transform infrared (FTIR) and Scanning electron microscopy (SEM-EDX) analyses. In this report, we observed that hydroxyapatite formation for 5days of immersion time. Also observed that with increasing the immersion time up to 15days, higher amount of hydroxyapatite layer formation on the surface of glasses. The varying composition of zirconia in glass samples influences shown by XRD, FTIR studies. The present results indicate that, in-vitro bioactivity of glasses decreased with increasing zirconia incorporation.

Keywords: melt-quenching Technique, Hydroxyapatite, Simulated body fluid, Bioactivity**.**

PACS: 81, 87

INTRODUCTION

Bioactive glasses and glass ceramics are playing key role in medical applications due to their unique property as a bone bonding material for the past few decades. They form a fast direct bond with bone. However, formation of a bond with the apatite layer depends upon initial glass composition, its volume and processing conditions [1]. Hench reported for the first time the formation of an apatite layer on bioactive glasses in Na_2O–CaO–SiO_2–P_2O_5 system, through in vitro as well as in vivo studies [1]. Till now 45S5 glass is the highly bioactive glass, but it is having low mechanical strength [2]. Hench reported that, to get bioactivity, phosphate ions play important role in the glass composition. But Kokubo [3] and Oktsuki et al. [4] demonstrated that phosphate free calcium silicate glass also formed the apatite layer when the glass was exposed to a simulated body fluid. To improve mechanical strength as well as bioactivity we are adding ZrO_2 because of its higher yield strength and fracture toughness [5, 6].

The objective of the present work is to synthesize and characterize $31B_2O_3$-$20SiO_2$-$24.5Na_2O$-(24.5-x) CaO-xZrO_2 x=1,2,3,4,5 bioactive glasses and study the effect of ZrO_2 on bioactivity, structural properties of these glasses.

EXPERIMENTAL PROCEDURE

The glasses were prepared from chemically pure grade materials. Materials Commercial grade reagents of B_2O_3, SiO_2, Na_2O, CaO, ZrO_2 having 99.9% purity level were used as starting materials. Appropriate amounts of oxides were weighed by using an electronic balance having an accuracy of 0.001 g. The reagents were then thoroughly mixed and ground in an agate mortar. The weighed batches were melted in Platinum crucibles at 1200^{o}C for 3h. The melts were rotated at intervals of 30 min apart to ensure homogeneity of the melts. The homogenized melts were cast into Preheated Brass molds of the required dimensions. The prepared samples were characterized with an X-ray Diffractometer (Model: SHIMADZU XRD-7000) using CuKα as a radiation source at a scanning angle ranging between 10^o and 60^o. The structure and formation of the apatite layer on the surface of glasses after immersion in SBF solution were studied in all specimens using FTIR transmittance spectroscopy (model S 100; PerkinElmer). The surface morphologies of the glasses were examined using SEM-EDX (model 5WEGA 3 LMU; TESCAN).

RESULTS AND DISCUSSION

Figure 1, shows the XRD analysis of all glass samples before and after in-vitro studies. Figure 1(a) shows the XRD analysis of prepared glasses shows no diffraction peaks. The observed results confirm the amorphous character of glasses. Figure 1(b), shows the crystalline phases on the glass surfaces after 5days of immersion in simulated body fluid. The observed peaks at 26^o, 31.74^o and 45.34^o related to (002), (211) and (203) planes respectively which confirms the formation of apatite layer on the glass surfaces [7]. From the XRD analysis on examining all the samples, hydroxyapatite formation is observed. But formation is decreased with increasing zirconia content. We can also observe that more number of hydroxyapatite phases in GZ1 and GZ2 compared to the other glass samples. It is clear that

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in samples GZ1, GZ2 we can observe better layer formation compare to the all other glass samples.

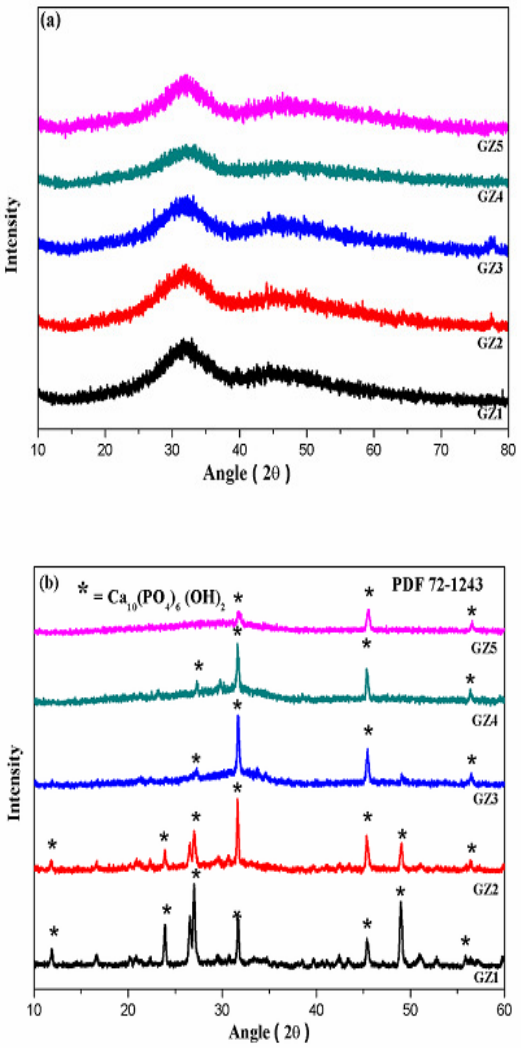

FIGURE 1. XRD analysis of Glasses before (a) and after (b) in-vitro studies

Figure 2 shows FTIR spectra of all glass samples before and after in-vitro studies. Figure 2(a) shows, In all glass samples wavenumber 474-494 cm^{-1} corresponds to rocking vibrations of Si-O-Si bridges and modifier cations (Na^{+}, $Ca^{+)}$ [8]. Characteristic wave number 520-530,720-730 related to Zr–O stretching and Zr–O_2–Zr asymmetric modes [9]. 720-730 cm^{-1}, 930-1197 cm^{-1} related to B-O-B linkages, stretching vibration of BO_4 units in various structural groups respectively. The peaks at 1200-1500 cm^{-1} B–O stretching vibrations of trigonal BO_3 units only [8],with increasing zirconia content we can observe the shoulder peaks in all glass samples before in vitro studies. The FTIR spectra [Figure 2(b)] of all glasses after 5 days of immersion in SBF, the obtained peak values positioned at 460, 561, 609, 875, 967, 1024, 1111, 1425, 1513, 1639 cm^{-1}.The band at 460 cm^{-1} corresponds both Si-O-Si rocking vibrations[10] and B-O-B bond bending vibrations[11]. The appearance of double peak at 561, 609 cm^{-1} is due to P-O bending vibrations in PO_4 tetrahedra and characteristic band of HA phase [12, 13].

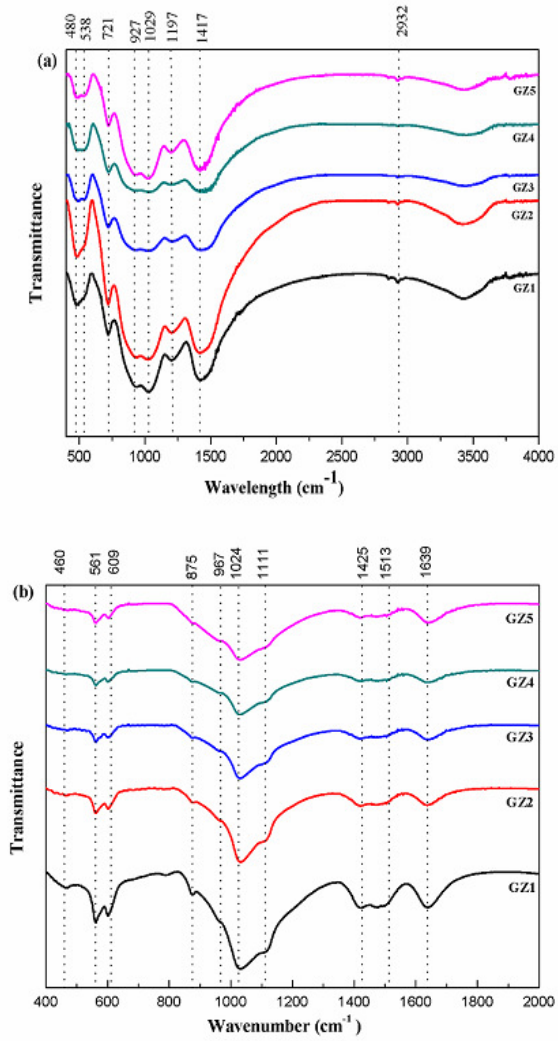

FIGURE 2. FTIR spectra of glasses before (a) and after (b) in-vitro studies

The small shoulder around 875cm^{-1}, is related to the stretching vibration of SiO_4^{4-} units (Q^0) and to A-type carbonate-substituted hydroxyapatite (CHA) phase [14,15]. The band at 1024cm^{-1} indicates the formation of apatite layer [16]. In GZ1 we can observe increased double peak intensity compared to all remaining glasses. From this FTIR data we can say that GZ1 sample is more bioactive than other glass samples.

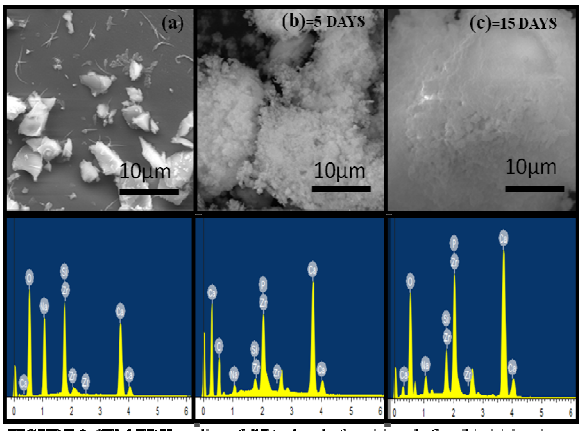

FIGURE 3. SEM-EDX studies of GZ1 glass before (a) and after (b), (c) in-vitro studies

Figure 3, shows the SEM micrograph of the GZ1 glass before and after in-vitro studies. Which shows the formation of precipitate on the surface of the glass. SEM figures show that the formed HAp was in the form of agglomerated globular crystals similar to the one reported for the HAp crystals formed on the silica gel [17]. The SEM image 3(b) shows that, the rich precipitate is observed for 5 days of immersion time. On increasing immersion time from 5days to 15 days (image 3c), higher amount of hydroxyapatite layer formation, which is also confirmed by EDX. XRD and Fourier transform infrared (FTIR) studies confirmed that the above precipitate is Hydroxyapatite.

CONCLUSION

In summary, we have successfully synthesized zirconia doped borosilicate glasses by melt-quenching method. The XRD studies confirmed the formation of Hydroxyapatite on all the glass samples by observing the maxima at 31.74^{o}. The FTIR studies confirmed with double shoulder peaks positioned at 561, 609 cm^{-1} and the band at 1024 cm^{-1} with high intensity confirms the formation of hydroxyapatite layer. Among the all glasses GZ1 showed good bioactivity. Then, it may be used as bioactive material.

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