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Influence of strontium on structure, bioactivity and corrosion behaviour of B_2O_3–SiO_2–Na_2O–CaO glasses-investigation by spectroscopic methods

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ABSTRACT

Strontium mixed borate based bioactive glasses of the composition (55–x)B_2O_3–5SiO_2–20CaO–20Na_2O: xSrO (with x = 2,4,6,8 and 10 mol%) were synthesized using conventional melt quenching technique. Structural variations in the glasses due to addition of SrO were assessed from FTIR and optical absorption spectroscopy methods. Degradation and bioactivity studies of the glasses were performed by immersing the glasses in simulated body fluid (SBF). Degradation studies of these glasses measured as function of immersion time were analyzed in terms of structural modifications taken place due to strontium mixing. The formation of hydroxy apatite (HA) layer on the surface of glasses, treated in SBF solution was examined by XRD, FTIR, optical absorption and scanning electron microscopy studies. The observed bone like apatite formation on glass surface demonstrated the potentiality of the chosen glass for integration with bone. Quantitative analysis of results of the studies on the bioactive behavior of the titled glass indicated that the mixing of SrO to the optimum levels improved its bioactivity.

1. Introduction

Bioactive glasses (BGs) are mainly being used in bone filling, implant coating and in bone tissue engineering applications [1–4]. These glasses react with the body fluids to form hydroxyapatite (HA) layer which is responsible for an intimate bond with bone [5]. This layer is predicted to play a crucial role for attachment of proteins such as fibronectin (a high molecular weight glycoprotein) and vitronectin (which is also glycoprotein present in the platelets) with osteoblasts (the bone cells responsible for forming new bone) and proliferate and thereby pave the way to grow a strong bone [6]. Most of the bioactive studies are confined to 45S5 [7] glass composition. Though, these glasses exhibit excellent bioactivity, the conversion process of these glasses in to HA is very slow. Moreover, borate-based BGs exhibit interesting properties related to osteogenesis and angiogenesis and are predicted to be viable alternative for poly methyl methacrylate (PMMA) in the treatment of deep bone diseases [8]. Besides this, boron plays a vital role in bone formation and depends on its concentration in glass composition. The highest concentrations of boron are found in bone, nails and hair in the human body [9,10]. By adding some modifier oxides like SrO to B_2O_3 containing bioactive glasses the release of toxic BO_3^{3-} ions could be controlled [11]. It was also shown that boron affects the RNA synthesis in fibroblast cells [12] and hence such glasses are of special interest. However, the localized high concentration of boron due to its rapid degradation may result in cytotoxicity which is of high concern.

Further, bioactive glasses incorporated with strontium have gained considerable attention recently. Strontium (Sr) ions normally stimulate osteoblastic bone formation and facilitate for anabolic and anti-catabolic effects in bioactive glasses. These ions were also reported to play a important role in inhibiting osteoclastic bone resorption both *in vitro* and *in vivo* [13–15]. It was also observed that the chemical similarities between Ca and Sr, enabled strontium to accumulate in bone by exchanging with Ca in the crystalline hydroxy apatite [16]. It has also been predicted that Sr acts as a promising agent in treating osteoporosis [17]. Yet, Sr is known to be an essential element for metabolic processes associated with the formation and calcification of bone tissue [18,19]. Recently, O'Donnell et al. [20,21] have investigated the influence of strontium and importance of glass chemistry, structure while designing bioactive glasses for bone regeneration. Their studies have indicated that immersion of the Sr-glasses in SBF lead to the formation of biomimetic apatite and cell proliferation assays and the all the

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compositions of the glass supported normal cell attachment and proliferation.

There are number of other studies devoted to investigate the influence of SrO on bioactivity of glasses carried out by immersing SrO mixed glasses in simulated body fluid (SBF). These studies also indicated the formation of biomimetic apatite and cell proliferation assays and also demonstrated that all such glasses supported normal cell attachment and proliferation [22–26]. Overall review of some of the available studies on SrO mixed bioactive glasses indicated that these glasses are highly potential for bone regeneration.

Motivated by these positive aspects on addition of Sr to the original bioglass and also with the anticipation that SrO controls the release of toxic boron (to avoid the problem of cytotoxicity) from the original glass, in the present investigations, we have designed a new multi component glass system *viz.,* $B_2O_3-SiO_2-Na_2O-CaO$: SrO and investigated the role of Sr on structure, biological response and corrosion behavior using spectroscopic techniques viz., optical absorption and IR spectra.

2. Materials and methods

The details of the chemical composition selected for the studied BGs are presented in Table 1. Specific techniques employed for preparation of the glass samples, SBF and for measuring density, weight loss and particulars of the apparatus used for recording XRD, FTIR and optical absorption spectra were reported elsewhere [11]. Scanning electron microscope (Tescan, Model VEGA3 LMU) is used to obtain surface image of glass samples to explore its surface morphology which is helpful to ascertain the deposition of crystalline hydroxy apatite layer on glass samples.

For *in vitro* studies the specimens were immersed in SBF solution [27–29] (maintained 36.5 °C) for a period of 30 days. Formation of white thin layer is observed on the surface of the samples after the immersion. The surface morphology of the post immersed samples is evaluated by XRD, MIR, SEM and optical absorption measurements.

3. Results

Using the values of density *d*, average molecular weight of the glasses, several physical parameters of the titled glasses are computed using standard formulae [30,31] and furnished in Table 2.

In the studied samples, we have fixed the concentrations of SiO_2, Na_2O and CaO while content of SrO is increased from 0 to 10 mol% at the expense of B_2O_3. A slight increase in the density of the glasses is observed with the increase of SrO content. Interestingly, we have observed a considerable decrement of densities of the glasses after the SBF treatment with respect to those of corresponding pre-immersed samples.

Fig. 1 shows the optical absorption spectra of $B_2O_3-SiO_2-Na_2O-CaO$:SrO glasses recorded at ambient temperature in the wavelength region 300–800 nm. Absorption edge for SrO free glass is observed at 319 nm. Gradual addition of SrO up to 10 mol %, the edge exhibited spectrally red shift (Table 3). Optical band gap (E_o) of the samples were evaluated from Tauc plots (Fig. 2) and presented in Table 3. The value of E_o exhibited decreasing trend with the increase of SrO content.

Table 1
Details of the chemical composition of the glasses in mol%.

Sample label	B_2O_3	SiO_2	Na_2O	CaO	SrO
Sr_0	55	5	20	20	0
Sr_2	53	5	20	20	2
Sr_4	51	5	20	20	4
Sr_6	49	5	20	20	6
Sr_8	47	5	20	20	8
Sr_{10}	45	5	20	20	10

Fig. 3 shows the IR spectra recorded in mid infrared region of all the pre-immersed samples. Spectra exhibited standard vibrational bands due to BO_3, BO_4, B-*O*-B linkages and due to Si–O–Si asymmetric vibrations at 1525 cm^{-1}, 1078 cm^{-1}, 700 cm^{-1} and 1022 cm^{-1} respectively [32–35]. Due to addition of SrO, no new bands are developed in the IR spectra (Table 4). However, with the gradual increase of SrO content from 2 to 10 mol% intensity of the bands due to BO_3 and Si–O–Si asymmetric vibrations is observed to increase, while that of band due to BO_4 structural units is observed to decrease.

Fig. 4(a) shows the variation of weight loss % *vs* dissolution time of studied glasses during the degradation in SBF solution. Variation indicated the maximal loss for the glass Sr_{10} at any interval of time. The graph indicates a gradual increase of degradability of the sample with the increase of SrO content from 2 to 10 mol%. Change in the pH of the residual SBF solution measured at regular intervals of immersion time is shown in Fig. 4(b). The trend observed for pH variation is found to be similar to that of degradation study.

Fig. 5(a) shows the X-ray diffractogram of Sr-free sample recorded after immersion in SBF solution. The diffractogram exhibited well-defined sharp diffraction peaks at 2θ = 38.43°, 41.57°, 44.67°, 48.8°, 65.03°, 72.57° and 78.13° assigned to (2 2 0), (1 3 1), (4 0 0), (2 3 0), (5 1 1), (2 0 5) and (2 5 2) reflections of hydroxy apatite, respectively (JCPDS card No. 72–1243). The diffraction peaks clearly indicate formation of crystalline HA layer on the surface of the sample.

To have some knowledge over the dependence of magnitude of HA formation on SrO content, we have compared XRD patterns (recorded after 30 days of immersion in SBF) of SrO mixed samples (with the lowest and the highest contents *viz.*, 2.0 and 10.0 mol%) in Fig. 5(b). Diffractogram of Sr_2 sample exhibited three sharp diffraction peaks at 2θ = 21.68° 32.96° and 44. 99° due to the reflections from (2 0 0), (3 0 0) and (2 0 3) planes of crystalline HA layer. On other hand, the diffractogram of post-immersed Sr_{10} glass exhibited two broad peaks at 2θ = 28.88° and 44.01° due to the reflections from (2 1 0) and (4 0 0) planes of HA layer (JCPDS Card no. 72–1243). In the diffraction pattern of post-immersed Sr_{10} specimen, the reflections from the crystalline apatite are observed to be comparatively broader, probably due to overlapping of diffraction peaks of different planes. This observation indicates the degree of crystallinity of the apatite layer increases with the increase in the concentration of strontium ions. In other words, it suggests, the crystallization of the apatite layer formed on the glass surface after soaking in physiological fluid depends on the amount of the strontium content introduced in the glass matrix. In some reports, it was stated that, the broadening mighty be an indication of poor crystallization of form HA layer or the size of HA crystallites is on a nanometre scale [36]. In fact, according to the studies of Le-Geros et al. [37] to obtain XRD maxima of an apatite phase, HA should contain crystals more than 20 unit cells and studies by Vallet-Regi et al. [38] have indicated that the minimum crystals also crystal size should be ~140 Å.

Fig. 6(a)–(b) represent SEM pictures (recorded with the magnification 500x) of two of the SBF treated glass samples *viz.*, Sr_0 and Sr_{10}, respectively. The pictures clearly indicated the deposition of some small crystalline grains (predicted as apatite crystals) on the specimens.

Band gap measurements before and after immersion give us some understanding over the apatite formation on the surface as it involves different reactions like glass dissolution, precipitation etc. [5]. These reactions cause some surface structural changes which in turn result in changes in the optical transmission and the optical band gap E_o of the glass sample. Comparison of the values of E_o of the samples before and after immersion in SBF exhibited significant difference (Fig. 7). In fact, E_o is found to decrease due to immersion in SBF.

Fig. 8(a) shows the MIR spectra of HA layer formed on the glass surface after immersing in SBF solution for 30 days. The spectra of post-soaked samples exhibited significant differences when compared with those of corresponding pre-immersed samples (Fig. 3). For better