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Influence of barium substitution on bioactivity, thermal and physico-mechanical properties of bioactive glass

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ABSTRACT

Barium with low concentration in the glasses acts as a muscle stimulant and is found in human teeth. We have made a primary study by substituting barium in the bioactive glass. The chemical composition containing (46.1 − X) SiO_2–24.3 Na_2O–26.9 CaO–2.6 P_2O_5, where X = 0, 0.4, 0.8, 1.2 and 1.6 mol% of BaO was chosen and melted in an electric furnace at 1400 ± 5 °C. The glasses were characterized to determine their use in biomedical applications. The nucleation and crystallization regimes were determined by DTA and the controlled crystallization was carried out by suitable heat treatment. The crystalline phase formed was identified by using XRD technique. Bioactivity of these glasses was assessed by immersion in simulated body fluid (SBF) for various time periods. The formation of hydroxy carbonate apatite (HCA) layer was identified by FTIR spectrometry, scanning electron microscope (SEM) and XRD which showed the presence of HCA as the main phase in all tested bioactive glass samples. Flexural strength and densities of bioactive glasses have been measured and found to increase with increasing the barium content. The human blood compatibility of the samples was evaluated and found to be pertinent.

1. Introduction

Bioactive glasses degrade in physiological solutions, forming a hydroxyl-carbonate apatite (HCA) layer on surface of the bioactive glass, which are an intimate bond between the glass and living bone [1,2]. Bioactive glasses can be produced by the traditional melting method which is regarded as simple and suitable for mass production [3]. The bioactive glass systems containing SiO_2–Na_2O–CaO–P_2O_5 have shown higher bioactivity in comparison to hydroxy apatite [4–6]. The bioactive glasses were able to bind to bone and to promote bone formation, which are also of interest for use as bone grafts and implant coatings [7–9]. The 45S5 bioactive glass is a very successful biomaterial for clinical applications and many researchers have studied with an incorporation of some ions such as Li, Zn, Ti, K, Zr, Mg, Fe, and Sr in the base bioactive glass because of their unique effect on osteoblastic cell proliferation of different ions in the base bioactive glasses [10–13]. It was reported that in 45S5 bioactive glass, SrO can easily be substituted for calcium oxide due to their similar ionic charge and radius [14,15]. Donnell and Hill [16] discussed the difference in atomic weight of Sr = 87.62 and Ca = 40, while Sr^{2+} containing bioactive glasses were shown to combine with bone regenerative properties of bioactive glasses [16]. The ^{89}Sr 1488 keV beta radiation has been used for the treatment of pain in the bone due to metastases from prostatic cancer [17].

It is well known that the general formula for apatite is $[M_{10}(XO_4)_6Y_2]$, where M represents a bivalent cation, X represents a trivalent anion and Y represents a monovalent anion [18]. The divalent cations (Mg^{2+}), (Sr^{2+}) and (Ba^{2+}) with a similar charge of (Ca^{2+}) calcium can readily be substituted in the lattice of hydroxyapatite. Barium is one of the alkaline earth metals like calcium. It has been reported that low doses of barium in glasses act as a muscle stimulant [19]. Austin et al. [20] confirmed that the barium distributions in the teeth of human children and found early life dietary transitions in primates. Kaur et al. [21] studied the bioactivity in the system of barium–zinc-borosilicate glass containing 30 mol% of barium in their compositions. Leenakul et al. [22] substituted BaO–Fe_2O_3 in 45S5 bioactive glass and showed the improvement in bioactivity. Though, the barium is radioactive but the lower concentration in the amorphous state is worth to investigate its role which is due to be studied. There is a continuous demand for bone implant formulations such as bioactive glasses which have better osteoblastic properties. One of the approaches to improve bone stimulating properties of these biomaterials is incorporation of bone stimulator ions into their chemical compositions. Moreover, there are limited studies on barium containing bioactive glass for bone substitutes. This makes Ba^{2+} substitution in bioactive glass an interesting group of materials to study and hence we carried out the preliminary screening tests as a biomaterial.

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2. Materials and methods

2.1. Preparation of bioactive glasses

The chemicals were used in this experiment are analytical reagent grade (all from Loba Chemie, Mumbai, India) such as quartz, sodium carbonate, calcium carbonate, barium carbonate and ammonium dihydrogen orthophosphate as a source of SiO_2, Na_2O, CaO, BaO and P_2O_5, respectively with a purity of 98–99.9%. All were introduced in the form of their respective anhydrous state. The weighed batches were mixed thoroughly for 30 min and melted in pure alumina crucibles to get the desired bioactive glasses as given above in Table 1. The melting was carried out in an electric furnace at 1400 ± 5 °C for 2 h in air as furnace atmosphere and homogenized melts were poured on preheated aluminum sheet. The prepared bioactive glass samples were directly transferred to a regulated muffle furnace at 500 °C for annealing. Further, the glass samples were cooled gradually under a controlled rate of 10 °C per minute to room temperature after annealing for 1 h at 500 °C. In order to explore the possibility for contamination of aluminum in the glass samples melted in 99.9% pure alumina crucibles at 1400 °C for 2 h, the XRF (Thermo Scientific, USA) and the chemical analysis of the samples were done for aluminum content. The chemical analysis of the glass samples for determination of aluminum by $Al(OH)_3$ precipitation method did not show any presence of Al^{3+} ion in the glass [23]. Further, the XRF analysis also did not show any appreciable contamination of aluminum in the glass melts prepared at above temperature in a small duration of 2 h. Since the glass samples have been melted in alumina crucibles as such the problem of contamination of silicon in the melts does not arise. Hence the results obtained for the present investigation on SiO_2–CaO–Na_2O–P_2O_5–BaO bioactive glasses have not been affected by contamination of aluminum and silicon from the crucibles.

2.2. Preparation of SBF

To carry out in vitro studies, we prepared simulated body fluid according to Kokubo [24] that has inorganic ion concentrations similar to those of human body fluid in order to reproduce formation of apatite on bioactive materials in vitro. The SBF solution was prepared at 37 °C by dissolving reagent grade NaCl, KCl, $NaHCO_3$, $MgCl_2 \cdot 6H_2O$, $CaCl_2$ and KH_2PO_4 into double distilled water and it was buffered at pH = 7.4 with TRIS (trishydroxy methyl aminomethane) and 1 N HCl.

2.3. Characterization of samples

2.3.1. Thermal behavior

In order to identify the thermal behavior of the barium substituted bioactive glasses, the differential thermal analysis (SETARAM Instrumentation, France) was carried out on powdered samples in air up to 1000 °C using powdered alumina as a reference material with the heating rate of 10 °C min^{-1}. The glass nucleation and crystallization temperatures were obtained from the DTA results which were used for proper heat treatment for converting glass to their corresponding glass–ceramic.

Table 1
Chemical composition of the bioactive glasses (mol%).

Constituents	Ba-0	Ba-1	Ba-2	Ba-3	Ba-4
SiO_2	46.1	45.4	44.6	43.9	43.1
Na_2O	24.3	24.5	24.6	24.8	25.0
CaO	26.9	27.1	27.3	27.4	27.6
P_2O_5	2.6	2.6	2.6	2.7	2.7
BaO	0.0	0.4	0.8	1.2	1.6

2.3.2. Heat-treatment system

Sometimes the bioactive glasses are used as coating materials on metal implants and composites therefore they are subjected to heat-treatment. Hence it is better to know their crystalline phases present. The prepared bioactive glass samples were heat-treated in two-step system, firstly nucleation temperature for the formation of nuclei sites and after holding for the specific time, it was then further heated to reach the second selected crystal growth temperature after holding for the specific time. The samples were left to cool inside the muffle furnace to room temperature at a cooling rate of 10 °C per min.

2.3.3. Powder X-ray diffraction analysis

In order to identity the crystalline phase present in the bioactive glasses, glass-ceramics and SBF treated glass samples were ground to 75 μm and the fine powders were subjected to X-ray diffraction analysis (XRD) using RIGAKU-Miniflex II diffractometer adopted Cu-Kα radiation (λ = 1.5405 Å) with a tube voltage of 40 kV and current of 35 mA in a 2θ range between 20° and 80°.

During measurement the step size and speed were set to 0.02° and 1° per min, respectively and were followed in the present investigation. The JCPDS-International Centre for diffraction Data Cards were used as a reference.

2.3.4. Structural analysis of bioactive glasses

The functional groups of bioactive glasses were investigated at room temperature in the frequency range of 4000–400 cm^{-1} using a Fourier transform infrared (FTIR) spectrometer (VARIAN scimitar 1000, USA). The fine bioactive glass powdered samples were mixed with spectroscopic grade KBr in the ratio of 1 part of sample with 99 parts of KBr. The mixtures were subjected to an evocable die at load of 10 MPa to produce clear homogeneous discs. The discs were immediately put in the instrument for FTIR spectral transmission measurements and the spectra of samples were recorded.

2.3.5. In vitro bioactivity study of bioactive glass

The bioactivity of the prepared bioactive glass samples were examined through in vitro test. The test was performed by immersing 1 g of each samples in 10 mL of SBF solution contained in a small polyurethane container and incubated at 37 °C in a static condition for time periods of 1, 3, 7, 14 and 30 days. After soaking, the samples were filtered, rinsed with double distilled water and dried in an electric air oven at 100 °C for 1 h. The formation of hydroxy carbonate apatite layer (HCA) on the surface of the bioactive glass samples were determined using FTIR, XRD and SEM techniques.

2.3.6. pH behavior

The stages of formation of hydroxyl carbonate apatite layer on the surface of the samples were checked by pH behavior of the SBF solution containing bioactive glasses. Each 1 g of powdered bioactive glass samples was soaked in 10 mL of SBF solution at 37 °C for 7 days and the pH of the leached solution was measured continuously using Universal Biomicroprocessor pH meter at room temperature. The pH values were recorded timely after definite intervals of time. The instrument was calibrated each time with standard buffer solutions of pH 4.0 and 7.0.

2.3.7. Surface morphology of bioactive glass sample by SEM

The surface morphology of samples was analyzed before and after SBF treatment using a scanning electron microscope (SEM) (Inspect S50, FEI). The bioactive glass samples were cut into required dimensions and immersed into SBF for 14 days at 37 °C. Further, the samples were removed, washed with double distilled water and dried at 100 °C for 1 h and they were coated with gold by sputter coating instrument before their examination with SEM.