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Structural investigations on P_2O_5-CaO-Na_2O-K_2O: SrO bioactive glass ceramics

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ABSTRACT

In the present work, glasses of a particular composition (60-x) P_2O_5-20CaO-17Na_2O-3K_2O: xSrO ($0.5 \le x \le 1.5$) mol% were synthesized using conventional melt quenching technique. Further, samples were characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Differential Thermal Analyses (DTA) techniques and Fourier Transform Infrared (FT-IR) spectra. In vitro bioactivity was evaluated by soaking glass ceramic powders in SBF solution for 7 and 15 days. XRD patterns of glass ceramics have clearly confirmed the formation of various crystalline phases $K_2Sr(PO_3)_4$, α-$Ca_2P_2O_7$, $Ca_2Sr(PO_4)_2$, $Ca_5(PO_4)_3(OH)$ and $Ca_3(PO_4)_2$. Random spreading of uneven sized micro crystals with distinct boundaries in the glass matrix have been observed from SEM pictures. DTA scans revealed an increase in the content of SrO with heating rate causes the glass transition (T_g) and crystallization temperatures (T_c) towards lower side, that confirms the decrease in rigidity of glass network. FT-IR spectra showed that there is an increase in the degree of structural disorder and the formation of a crystalline hydroxyapatite layer with soaking time. From the analyses of all the above results, it can be concluded that the sample doped with 1.5 mol% of strontium is found to exhibit high bioactivity.

1. Introduction

Bioactive glasses and glass ceramics are being used as potential candidates for bone tissue engineering applications [1–3]. Nowadays, special attention has been paid towards the development of phosphate based bioactive glasses and glass ceramics due to their high dissolution rate in physiological fluids and due course, it has been replaced by natural tissue, which enables these materials suitable for prominent applications in the field of medicine [4–8]. Apart from high dissolution, biomaterials also have other advantages viz., availability, reproducibility, reliability and biocompatibility. When bioactive materials are kept in contact with human plasma, they develop a reactive hydroxyapatite layer at the glass surface which forms a chemical bond between the implant and the host tissue [9]. The nature of hydroxyapatite layer is chemically and structurally very similar to the mineral component of natural bone that improves a firm bond with the surrounding bone tissue. The high chemical surface reactivity of bioactive materials makes them to produce precipitation of bone-like apatite from the body fluids after ions leaching. Subsequently, the precipitated calcium phosphate layer develops a strong muscular chemical bonding with tissues [10–12].

Calcium phosphate based glasses and glass ceramics have been of interest for medical uses due to their unique properties. In particular, a bioactive calcium phosphate based-implant after integration with bone forms a biologically active hydroxyapatite layer at the bone/implant interface which favors bonding with bone and soft tissues. Owing to the advantages of phosphate based bioactive glasses over silicate and considering its high dissolution rate, significant attempts have been made in improving the biological properties of bioactive glasses to a greater extent by doping them with certain metallic ions [13–16].

The addition of cations or network modifiers viz., Ca, Na, K to a glass network former will be leading to the formation of non-bridging oxygens (NBO's) along with network disorder that triggering high reactivity of glasses in aqueous situations. High reactivity between glasses and physiological fluids plays an important role in forming hydroxyapatite layer. This high reactivity has become a significant benefit in bone repair and bone augmentation applications.

Among various transition metal ions, strontium ion is widely

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investigated in various bioactive glasses due to the fact that they stimulate prompt bone growth [16–20]. Strontium ions are known to up regulate osteoblasts and down regulate osteoclasts to prevent bone resorption. Strontium is a naturally occurring trace element in the human body. Once it enters the bloodstream, it is distributed throughout the body and it behaves very much like calcium. In the human body, about 99% of the strontium is concentrated in the bones only. It is found that the compound of strontium known as strontium ranelate, can increase bone formation and prevent bone loss during osteoporosis treatment [16,17]. It has similar chemical and physical properties as calcium and magnesium. In particular, the structural modifications found in the phosphate glass network after the substitution of strontium are almost similar to calcium. It is also important to note that the resulting structural modifications alter the surface chemical reactivity based on network disorder.

Many interesting studies being available on bioactive glasses and glass ceramics with better bioactivity after addition of strontium content [4,18–20]. Dziadek et al have reported high bio-activity in calcium rich glass ceramics with the addition of SrO content. Even though, it is still felt that there is a lot of scope to investigate the influence of the addition of strontium ions on structural changes and bioactivity of calcium phosphate bioglasses, an attempt has been made with a goal of finding a glass ceramic that exhibit high bioactivity of prepared samples. Thus, the present work mainly focuses on synthesizing bioactive glasses of a composition (60-x) P_2O_5-20CaO-17Na_2O-3K_2O: xSrO ($0.5 \le x \le 1.5$ mol%), exploring the changes in bioactivity and the structural modifications to the content of strontium oxide along with soaking periods.

2. Experimental Methods

For the present study, a glass composition (60-x) P_2O_5-20 CaO-17 Na_2O-3 K_2O: x SrO ($0.5 \le x \le 1.5$ mol%) is chosen. The details of the composition and corresponding nomenclature are as follows:

SR_5: 59.5 P_2O_5-20 CaO-17 Na_2O- 3 K_2O: 0.5 SrO
SR_{10}: 59.0 P_2O_5-20 CaO-17 Na_2O- 3 K_2O: 1.0 SrO
SR_{15}: 58.5 P_2O_5-20 CaO-17 Na_2O- 3 K_2O: 1.5 SrO

Phosphorous pentaoxide (P_2O_5) was added in the form of ammonium dihydrogen orthophosphate ($NH_4H_2PO_4$) whereas sodium, potassium, calcium and strontium were introduced in the form of their respective anhydrous carbonates. All the raw materials of chemicals were of analytical grade and were used without further purification. The reagents were thoroughly mixed in an agate mortar and melted in a platinum crucible in the temperature range of 1200 °C to 1300 °C in a PID temperature controlled furnace for about one and half hour. The resultant melts were rotated several times 30 min apart to achieve homogeneity and then bubble free melts were cast into preheated brass molds of the required dimensions. The prepared glasses were directly transferred to a regulated muffle furnace maintained at 350 °C for annealing. After 2 h, furnace was left cool to room temperature at a rate of 30 °C h^{-1}. Further, prepared glasses were heat treated in a furnace at 670 °C for 18 h to convert them into glass-ceramics. The automatic controlling furnace was used to keep the temperature at the desired level with the heating rate 10 °C. After the heat treatment in the furnace, at above specified temperature, the samples were chilled in air to room temperature. Then, they were ground and optical polished to the dimensions of 1.2 cm×1.2 cm×0.2 cm. The amorphous/crystalline nature and phase compositions of strontium-doped bioactive glass powders were examined with an X-ray diffractometer (XRD, Rigaku D/Max ULTIMA III) operating at 50 kV and 30 mA with a CuKα radiation source. Scanning electron microscopy studies were also carried out on these bioactive glasses to observe the crystallinity using ZEISS Scanning Electron Microscope. Differential thermal analysis traces were carried out by Netzsch Simultaneous DSC/TG Thermal Analyzer STA409C with 32-bit controller to determine the glass transition temperature and temperatures of crystallization. The density of the bulk samples was determined to an accuracy of (±0.0001) by the standard principle of Archimedes' using *o*-xylene (99.99% pure) as the buoyant liquid. In-vitro studies of bioactive glasses were carried out by soaking them in simulated body fluid (SBF at 37 °C) for different intervals of time 7 and 15 days. The ratio of the sample weight to the SBF volume was 10 mg mL^{-1}. The SBF solution was prepared according to Kokubo [21]. After soaking of desired time, samples were taken out from SBF, washed with deionized water and finally dried at room temperature to make them ready for SEM analysis. Infrared absorption spectra were recorded on a JASCO-FT/IR–5300 spectrophotometer, up to a resolution of 0.1 cm^{-1}, in the spectral range 400–4000 cm^{-1} using potassium bromide pellets (300 mg), containing pulverized sample (1.5 mg). These pellets were pressed in a vacuum die at ~680 MPa.

3. Results and discussion

Physical parameters such as strontium ion concentration N_i, mean strontium ion separation r_i, and polaron radius r_p have been evaluated (Table 1). A slight decrease in density and increase in average molecular weight with the rise in the content of SrO has been observed. The decrease in density of SrO doped bioactive glasses might be due to extended structure of the loose phosphate glass network as a result of addition of SrO. The slightly larger molecular weight and atomic radius of strontium than calcium could also be another reason for density variations [22]. There may be some other factors viz., change in the coordination of the phosphate ions, the degrees of structural compactness, the modification of the geometrical configuration of the phosphate glassy network and the fluctuations in the dimensions of the interstitial holes caused by dopant ions that influence the density of the glasses [10]. Interionic distance (r_i) and polaron radius (r_p) were evaluated using the formulae [33], the decreasing trend of interionic distance and polaron radius with SrO content is another indication of loosely packed glass network, which is a result of the more structural degree of disorder.

3.1. X-Ray Diffraction (XRD)

The XRD patterns of all pre-heated glasses before soaking in SBF have exhibited wide ranging halo that confirms non-crystalline nature of all the glasses (Fig. 1.) The samples were heat treated at 670 °C which was identified from DTA. The observed broad halo may be an indication of initializing development of different crystalline phases among all glasses [23]. This wide halo found to be very slightly increased with the content of SrO. Initially, an attempt of immersing glasses in SBF for 12 h has been carried out. Then a broad halo still observed in the XRD patterns for all the glasses after soaking in SBF for 12 h supports amorphous nature (not shown in Fig). XRD patterns for post heat treated glass samples were presented in Fig. 2. These patterns clearly evidenced the presence of different crystalline phases. The observed results have clearly confirmed the formation of various crystalline phases $K_2Sr(PO_3)_4$, α-$Ca_2P_2O_7$, $Ca_2Sr(PO_4)_2$, $Ca_5(PO_4)_3(OH)$ and $Ca_3(PO_4)_2$ that are found to be present in all post heat treated samples and JCPDS card numbers

Table 1
Physical parameters of P_2O_5-CaO-Na_2O-K_2O: SrO glass ceramics.

Sample	Avg. Mol. Wt. (g/mol)	Density (g/cm^3)	Conc. of 'Sr' ions N_i (10^{21}/cm^3)	Interionic distance of 'Sr' ions r_i (A°)	Polaron radius r_p (A°)
SR_5	172.8	2.654	4.62	6.00	2.41
SR_{10}	173.2	2.604	9.05	4.79	1.93
SR_{15}	174.1	2.596	13.47	4.20	1.69