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Effect of MgO on bioactivity, hardness, structural and optical properties of SiO_2–K_2O–CaO–MgO glasses

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Abstract

Glass composition $55SiO_2$–$10K_2O$–$(35-x)$CaO–xMgO is synthesized by a melt quench technique. The as quenched and simulated body fluid (SBF) soaked glasses are investigated for their bioactive, optical and structural properties. These properties are discussed in the light of the role of MgO. The hardness increases with content of MgO instead of CaO. No remarkable change in the XRD pattern has been observed in unsoaked and soaked glasses in SBF for 28 days. The pH values initially increases rapidly and later stage of soaking it changes slowly. The soaked glasses exhibit some new FTIR bands as compared to virgin glasses. The optical band gap of the soaked samples is higher and Urbach energy lower with respect to pristine glass powder. The ion released into the SBF solution and consequent pH rise are maximum for glass sample containing minimum amount of Mg. The higher MgO containing glasses show low dissolution rate of Mg^{2+}, K^+ and Ca^{2+} cations. Among all the glasses G2 show highest bioactivity.

Keywords: Biomedical; Urbach energy; In-vitro; Bioactivity

1. Introduction

The field of biomaterials has been revolutionized by the bio ceramics due to their some advantages over tradition materials such as metals, alloys and composites as implant materials. Undoubtedly, metals, alloys and composites offer good mechanical properties as well as good tissue interaction [1]. However, in some cases, the composites release toxic elements into the human body. On the other hand, metals and alloys are prone to corrosion inside the body fluid [1,2]. So, bioceramics like Al_2O_3, ZrO_2, hydroxyapatite, bone cement, tricalcium phosphate and bioactive glasses are extensively used to repair damaged hard tissues [3,4]. In these materials bioactive glasses have received special attention after the invention of first bioglass by Hench and coworkers [5] due to their better bone bonding ability in vivo. Owing to good bioactive, osteoconductive, osteostimulative and tailorable degradation properties, use of glasses for various biomedical applications like bone graft, filler, dental, implant coating and craniomaxilofacial application have been investigated extensively [6,7].

Bioactivity simply means bone bonding capacity of the materials which are characterized by formation of interfacial layer of apatite or carbonate layer when dipped in stimulated body fluid (SBF) solution. The SBF solution mimics human blood plasma in terms of pH and ionic concentration as proposed by Kokubo. Thus, SBF test is a preliminary test done in-vitro to asses bioactivity of a potential biomedical materials. The sequential steps for formation of interfacial layer were explained by Hench et al. [5]. Conclusively, cation exchange with hydronium ions leads to pH rise initially followed by formation of silica rich layer on the surface of the materials. In later stage of apatite formation, the incorporation of calcium, phosphorous and other ions to form calcium rich layer which may further crystallize to form hydroxy carbonated apatite (HCA) layer. The process is dynamic in nature and kinetics of layer formation continuously changes during soaking in SBF solution. The same is also influenced by

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Table 1
Glass sample labels and their compositions in mol%.

Label	Amount (mol%)			
	SiO_2	K_2O	CaO	MgO
G2	55	10	30	5
G4	55	10	20	15
G6	55	10	10	25
G8	55	10	0	35

physio-chemical parameters viz.-a-viz. hydrophobity, weight loss, pH change, particle size and chemical compositions. Concerning the role of Si–O (NBO) in determination of bioactivity via dissolution of silica through formation of silanol group at the surface, it is very important to monitor the change in NBO concentration with soaking in SBF.

Bioactivity of the glass has also been depended on its initial composition [8,9]. Many bioactive silicate and borate glass compositions containing variable types of modifiers have been developed [10–14]. In present work, we have synthesized glass composition inspired from the 45S5 Bioglass®. K_2O has been used in place of Na_2O. It is expected to reduce tendency of the glass to crystallize [15]. It is well reported in the literature that crystallized glass inhibits the bioactivity of the glass [16,6]. It would be very interesting to study the effect of replacement of CaO by MgO on bioactivity especially in the presence of K_2O since K_2O is chemically similar to Na_2O. Mg is key element of the bone and it stimulates the osteoblast proliferation [17]. Many authors have reported the positive influence of MgO on bioactivity [18–20]. However, some of the researchers have reported either negative or no effect of MgO on bioactivity [21,22]. The contradictory behavior of magnesium on bioactivity originates due to dual role of MgO in silicon network. Based on Pauling scale of electronegativity, MgO behaves like intermediate oxide. Some of the MgO may enter in the form of $[MgO_4]^{2-}$ tetrahedron in the glass as network former [23]. The motivation of the present work is to investigate the effect of CaO replacement by MgO on bioactivity since the ionic radii of Mg^{2+} (0.72 Å) is close to ionic radii of Ca^{2+} (0.99 Å) ions. It is expected that the replacement of CaO by MgO might retard the formation of HCA layer. However, on the other hand, it can increase the mechanical properties of the glass. The as prepared and soaked glasses were investigated using X-ray diffraction, mass plasma atomic emission spectroscopy (MP-AES), pH variations, UV–visible spectrophotometer, Fourier transform infrared spectroscopy (FTIR), micro-hardness tester, Scanning electron microscopy (SEM) and Energy dispersive spectroscopy (EDS).

2. Materials and methods

2.1. Preparation of samples

Composition of $55SiO_2$–$10K_2O$–$(35-x)$CaO–xMgO; $x=5$, 15, 25, 35 was prepared using the melt quench technique. SiO_2, CaO, MgO, and K_2CO_3 (Loba Chemie, Purity ≥ 99.0%) were mixed using an agate mortar pestle in acetone for 1 h (h). The CaO was directly stored in wet media (acetone) due to its hygroscopic nature. The K_2CO_3 was taken in appropriate amount using a gravimetric factor of 1.47. The ground mixture was melted at 1550 °C in a recrystallized alumina crucible using a programmable electric furnace at a heating rate ~5 °C min^{-1}. The furnace was held at different intermediate temperatures i.e. 400, 800 and 1200 for 15 min each, to enhance the fusibility of the oxides with each other. At 1550 °C, the melt was held for 2 h to obtain homogenization. After that, the melt was quenched on a thick copper plate using another copper plate. The composition with their label is given in Table 1.

2.2. Micro-hardness test

Micro-indentations were performed on the polished surfaces of the unsoaked glass specimens using a diamond Vickers indenter on a micro-hardness testing machine (Mitutoyo MVK-HO, Japan). The rectangular glass slice was cut using a diamond cutter (Buehler, IsoMet Low speed saw). The glass slice was mounted in thermoset polymer (acrylic) for proper handling of the samples during hardness test. The mounted slice of glass was thoroughly polished using emery paper grit no. 600, 1000 and 1200. The diagonal of the pyramidal shape indentations made for loads of 100 g (g) were taken at three different points on the polished glass slice. The micro-hardness in HV unit was calculated using the following equation:

$$H = 1.854P/d^2 \quad (1)$$

where P is the applied load and d is the average length of the diagonal of pyramidal indentation.

2.3. In-vitro tests

In-vitro bioactivity and degradation study were carried out in SBF solution. It contains an ionic concentration of Ca^{2+} (2.5), Na^+ (142), K^+ (5.0), Mg^{2+} (1.5), Cl^- (147.8), HCO_3^{2-} (4.2), SO_4^{2-} (0.5) mmol/dm^3 [24]. The as prepared glasses were crushed in powder. The powder of 1 g amount was immersed in 50 ml SBF solution into polyethylene bottles and was kept at 37 °C in an incubator [25]. The initial pH of the SBF was kept at 7.4, which lies in the range of normal pH of human blood plasma [26]. The pH of the SBF was measured every day after soaking powder sample of glasses. To observe the formation of any crystalline phase particular apatite or carbonate group on the surface of the soaked glass, XRD patterns were obtained after 28 days of soaking in SBF solution. A PANalytical X'Pert PRO X-ray diffractrometer with Cu Kα radiations ($\lambda=1.54$ Å) was used to take the XRD patterns of the samples after soaking. The step size was equal to 0.017° and scan rate was ~3° min^{-1} during the XRD measurements. For comparison, the XRD pattern of virgin samples was also taken.

The quantitative information about the ions leached into the SBF solution from the glass surfaces was obtained by MP-AES using an Agilent 4100 MP-AES system. Samples were prepared 1 normal in nitric acid (HNO_3). MP-AES measurements were repeated three times to check the reproducibility of the results. The FTIR spectra of the powdered samples, after 28 days of soaking, were taken to check the presence of