Influence of MgO on Sol-Gel Derived SiO$_2$-CaO-Na$_2$O-P$_2$O$_5$ Bioglass System

S.A.S. Salim$^1$, H. Mohamad$^1$, S.N.F.M. Noor$^2$

$^1$School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, Nibong Tebal, Penang, Malaysia
$^2$Craniofacial and Biomaterials Sciences Cluster, Universiti Sains Malaysia, Advanced Medical and Dental Institute, Penang, Malaysia.

Email: hasmaliza@usm.my

Abstract. Sol-gel derived SiO$_2$-CaO-Na$_2$O-P$_2$O$_5$ (45S5) bioactive glass (BG) is well known for its enhanced bioactivity properties towards bone regeneration. The synthesis of 45S5 and the addition of MgO (1, 2, 3 and 5 mole percentages) in the 45S5 system was prepared using sol-gel method. The prepared bioactive glass powder was immersed in simulated body fluid (SBF) at room temperature for 7 days. The effect of MgO on the BG structure and bioactivity were characterized through X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). The results showed that increasing MgO concentration within the 45S5 influenced the glass structural phases formation. In addition, FTIR proved the presence of Si-O bending and Si-O stretching as the main transmission bonds. The addition of MgO affected the apatite layer formation on the glass surface following SBF bioactivity test.

1. Introduction

Bioactive glass (BG) 45S5 was first invented by Professor Larry Hench in 1969 composed of 45% SiO$_2$, 24.5% CaO, 24.5% Na$_2$O, 6% P$_2$O$_5$ which are able to bond to bone via the formation of apatite layer [1]. Bioglass® 45S5 possessed unique properties such as biocompatibility, outstanding bioactive behaviour and regenerative characteristics which greatly facilitate the application in bone regeneration. The interest of 45S5 is geared towards their bioactivity with the surrounding tissues. Bioactivity reflects the material property and it depends on the environment and the solution used for in vitro test. The common methods to produce bioactive glass materials are melt-quenching and sol-gel techniques. BG fabricated via sol-gel derived have many advantages compared to melt quench including lower fabrication temperature, better controlled homogeneity, larger surface area which increases dissolution rate and hence its bioactivity [2].

The bone-bonding ability of BG occurs through the formation of a biological apatite layer at the glass surface. This layer is observed after immersion in simulated body fluid (SBF), and during in vivo experiments. Apatite layer promotes the adhesion of tissues and permits an intimate bone-bonding with the implants. Upon BG contact with SBF, a silica hydrogel layer formation is generated on the
BG surface. The formation of this silica rich layer is related to the dissolution of the glass surface. This layer allows the subsequent crystallization of the apatite-like phase at the glass interface. However, the dissolution kinetics of glass in the biological environment, and consequently the bioactivity of the upper thin layer depend on many variables such as chemical composition, glass structure and interaction with surrounding medium [3]. Bioactivity of glass provides the information regarding the growth of apatite layer, whereas structural and dissolution rate properties appraise the strength of BG. To improve the bioactivity of glass system, a few types of alkaline earth element can be added into the BG composition. Magnesium addition into BG by substituting with calcium may provide excellent bioactivity over time. Hence, magnesium may influence hard tissue mineralization by binding strongly to phosphate through the formation of hydroxyapatite [5], however, contribution of magnesium to the BG properties can act as network modifier and network former [6].

The purpose of this work is to provide information on physical and chemical behavior of sol-gel pure and doped BG 45S5 with MgO (1, 2, 3 and 5 mol.%) and subsequently evaluate their chemical reactivity and bioactivity. Magnesium contribution to the properties of the apatite-like phase requires a broad investigation of doped Mg-based bioactive glass.

2. Experimental study

The 45S5 BG composition consisted of 46.13% SiO2, 26.91% CaO, 24.35% Na2O and 2.60% P2O5 (in mole percentages, mol.%) and addition of MgO (1, 2, 3 and 5 mol.%) in the BG 45S5 system was prepared using sol-gel technique. Initially, tetraethylorthosilicate (TEOS) was added into a mixture of nitric acid and deionized water, followed by stirring for 60 minutes to allow TEOS hydrolysis. Then, triethylphosphate (TEP) was added into the solution, followed by the addition of calcium nitrate and sodium nitrate at 45 minutes interval. Then, Mg(NO3)2·6H2O at different compositions (1, 2, 3 and 5 mol.%) was added into the glass mixture using the similar procedure at 45 minutes interval. The obtained solution was stirred overnight to allow completion of hydrolysis. The solution was left for 2 days at 70°C to allow gelation to occur. Gel obtained was then dry for 2 days at 120°C to ensure complete liquid vaporization within the gel. The dried gel was sintered at 700°C for 1 hour with 10°C per minute heating rate. The as-synthesized BG powder was grinded by using agate mortar to avoid agglomeration and stored inside a container in a desiccator prior to test. The BG powder was subjected to FTIR, XRD and SEM analyses. For in vitro SBF testing, the SBF solution were prepared by dissolving of NaCl, NaHCO3, KCl, K2HPO4·3H2O, MgCl2·6H2O, HCl, CaCl2 and Na2SO4 following Kokubo’s method [7]. In each experiment, the BG samples were removed from SBF after 7 days. Then, the samples were filtered and dried at 70°C and characterized using XRD, FTIR and SEM.

3. Results and discussion

3.1 Fourier transform infrared spectroscopy (FTIR)

Figure 1 shows the BG 45S5 and BG doped MgO (1, 2, 3 and 5 mol.%) infrared spectra in the mid-range of wavelength from 400 cm\(^{-1}\) to 2200 cm\(^{-1}\) before and after soaking in SBF for 7 days. The transmission spectra of all samples show numerous peaks related to crystalline and amorphous structures. All bioactive glass powders before soaking in SBF solution exhibit vibrational bands around 440 cm\(^{-1}\) due to Si-O-Si bending. Whereas for BG 45S5, the main transmission bonds which represent amorphous phase are Si-O-Si bending and Si-O-Si stretching. Characteristic band of sol-gel BG as wide absorption bands occur at 810 cm\(^{-1}\), 850 cm\(^{-1}\), 930 cm\(^{-1}\) and a peak at 460 cm\(^{-1}\) refers to Si-O-Si bending bond. Besides, there are two small peaks at 580 cm\(^{-1}\) and 625 cm\(^{-1}\) reflecting a crystalline sodium calcium silicate (Na\(_2\)Ca\(_2\)Si\(_3\)O\(_8\)). There were also three peaks occurring at 980 cm\(^{-1}\), 1040 cm\(^{-1}\) and 1106 cm\(^{-1}\) that reflects the Si-O-Si stretching (asymmetric) bands.
Figure 1. FTIR spectra of BG 45S5 and BG doped MgO (1, 2, 3 and 5 mol.%) before and after soaking in SBF for 7 days.
The FTIR spectra of BG 45S5 after soaking in SBF solution for 7 days reveal Si-O-Si tetrahedral (700-800 cm\(^{-1}\)) which indicates the formation of the silica-rich layer and presence of P-O bending peak at 500 cm\(^{-1}\) indicating the formation of an amorphous calcium phosphate surface layer.

For BG doped MgO (1, 2, and 3 mol.% after soaking in SBF solution for 7 days immersion, a band located at 510 cm\(^{-1}\) are observable and corresponded with crystalline calcium phosphate. However, this band is not clearly observed in BG doped MgO at 5 mol.% MgO at 7 days. The precipitation of pure hydroxyapatite in SBF is likely less to occur since the surrounding solution is saturated with respect to carbonated apatite where the orthophosphates are substituted with carbonates in the crystal lattice as reported in previous research [8]. Therefore, the phases formed at the surface of the bioactive glass samples were further confirmed by X-ray diffraction.

### 3.2 X-ray diffraction (XRD)

![Figure 2](image-url)

**Figure 2.** XRD pattern of BG 45S5 and BG doped MgO (1, 2, 3 and 5 mol.%) before and after soaking in SBF for 7 days. (+ hydroxy-apatite)

The XRD pattern of the bioactive glass before and after soaking in SBF for 7 days are shown that the pattern are amorphous state indicated the glassy structure. The BG 45S5 apatite phase is detected at 25.7 and 31.9 diffraction peaks following SBF immersion for 7 days. For BG doped MgO (1, 2, and 3 mol.%), the intensity of apatite increases with the increasing addition of MgO since the 1 mol MgO replaces 1 mol CaO, hence, Mg is substituted for Ca in biological apatite. However, the intensity of
apatite at 5 mol.% MgO substitution showed less crystalline apatite formation. The retardation of the apatite formation could be attributed by the basis of apatite layer formation mechanism proposed by Hench and co-workers where the initial stage for hydroxyapatite formation on bioactive glass surface was delayed due to the rapid ion exchange between Ca\(^{2+}\) and Mg\(^{2+}\) as shown by the existence of Si-O-Ca-O-Si and Si-O-Mg-O-Si, non-bridging oxygen bond, H\(^+\) or H\(_3\)O\(^+\) ions in SBF solution. Hence, this indicates that the rapid ion exchange corresponds to higher bioactivity of the BG. Consequently, the higher Mg-O bond energy compared to Ca-O resulting in glass containing more MgO content tend to be less reactive in solution and the rate of ions exchange might be slower. Thus, this would result in lower apatite formation on the surface of BG doped with higher MgO content [9].

### 3.3 Scanning Electron Microscopic (SEM)

Figure 3 shows the SEM analysis for BG 45S5 and BG doped MgO (1, 2, and 3 mol.%) before and after soaking in SBF for 7 days. Based on the figure, before soaking in SBF solution, all BG showed fine particles with a few agglomerations probably due to high water absorption ability of the BG.

![Figure 3](image)

**Figure 3.** SEM microstructure and EDX for 45S5 and (1,2,3 and 5) mole % MgO before soaking in SBF after soaking in SBF for 7 days.
After soaking in SBF for 7 days, BG doped MgO showed that the tiny spherical crystalite indicating the homogeneous crystallization behaviours. Such similar behaviour can also be detected on BG particles with MgO addition (1 to 3 mol.%). However, for BG doped with 5 mol.% MgO, the dendritic crystal instead of homogenous spherical crystalite were observed. With even more MgO addition, surface was partially covered with less amount of HA. The growth of HA for BG 45S5 can be explain by ionic dissolution of Ca²⁺ and Na⁺, while for BG doped MgO, it is explained by ionic dissolution of Ca²⁺, Mg²⁺ and Na⁺. It is notable that Mg²⁺ has larger ionic field strength (4.73 Å) than Ca²⁺ (2.04 Å), indicating that the glass modifying role of Ca is larger than Mg. Therefore, the glass network become tighter when MgO was incorporated into the BG structure [10].

4. Conclusion

45S5 bioactive glass and the addition of MgO (1, 2, 3 and 5 mol.%) in the 45S5 system was synthesized using sol-gel route. The FTIR proved that the main transmission bond was crystalline structure (Si-O-Si bending and Si-O-Si stretching). Whereas the phase found in all glass was calcium phosphate. For SBF in vitro study, all glasses exhibited apatite layer growth at their surface after immersion in SBF at 7 days. The incorporation of MgO especially with higher content (5 mol.%) tend to slow down the formation rate of apatite layer formation on glass surface. The influence of MgO on glass properties are explained in terms of internal structure. The obtain result proved that the 45S5 bioglass with addition of MgO in BG showed potential for application in wide range of hard and soft tissue regeneration.

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