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# Preparation of nano bioactive glass and investigation of its properties in different volume of solution

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**ABSTRACT:** Nano Bioactive glass material of the type CaO–$P_2O_5$–$SiO_2$ was obtained by the sol-gel processing method at considerably lower temperatures than required for conventional melting methods. As a new modification, volume of solution was changed in order to investigate its effects on the properties of bioglass samples. The obtained material was characterized by X-ray powder diffraction (XRD), surface electron microscopy (SEM) and Transmission electron microscopy (TEM) to evaluate the properties of the sol-gel derived bioactive powders. More homogeneous nano bioactive glass with almost 20 nm particles was obtained by higher volume of solution.

**Keywords:** *Bioactive; Nano bioglass; Sol gel processing; Volume of solution*

## INTRODUCTION

Glasses and glass-ceramic materials based on the $SiO_2$-CaO-$P_2O_5$ system constitute an important group of materials that have found wide application in medicine as bone implants (Balamurugan, *et al.*, 2007, Oki, *et al.*, 2004). The prerequisite for glasses and glass-ceramics to bond to living bone is the formation of a layer of biologically active hydroxylcarbonate apatite (HCA) on the surface of these biomaterials when they are exposed to physiological fluids (Yan, *et al.*, 2006). Hench has described a sequence of five reactions that result in the formation of a hydroxy-carbonate (HCA) apatite layer on the surface of these bioactive glasses. These reactions are summarized on Table 1. The first reactions are the ion exchange between the alkali in the glass and water. This is followed by a breakdown of the silica network, forming silanol bonds that repolymerize to form a hydrated, high surface-area, silica rich layer. This silica rich surface attracts organic molecules (proteins, mucopolysaccharides, and collagen) and facilitates the formation of the HCA layer on the glass (Zhong and Greenspan, 2000, Hench and LaTorre, 1993, Saravanapavan, *et al.*, 2003). The rate of apatite layer formation, a measure of bioactivity, depends on morphological parameters such as surface area, pore size, and glass chemical composition (Greenspan, *et al.*, 1994, Li, *et al.*, 1992). The basic components of bioactive glasses are oxides of calcium, phosphorus,

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(*) Corresponding Author - e-mail: nimanabian@mazust.ac.ir and silicon in proportions that provide the material with surface activity (Stoor, *et al.*, 1998). The silica and phosphate compositions of this glass are within the range that allows dissolution and calcium phosphate formation at the surface, while maintaining an appropriate rate of degradability (Schepers and Ducheyne, 1997, Marcolongo, *et al.*, 1998).

Bioactive glasses can be formed either from the traditional melt-quenching or by the modern sol-gel method. Sol-gel processing, an alternative to traditional melt processing of glasses, involves the synthesis of a solution (sol), typically composed of metal organic and metal salt precursors followed by the formation of a gel by chemical reaction or aggregation, and lastly thermal treatment for drying, organic removal, and sometimes crystallization (Olding, *et al.*, 2001). This technology is a low temperature preparation method, and the glasses prepared by sol–gel method have porous structure with high specific surface area (Sepulveda, *et al.*, 2001). An increase of the specific surface area and pore volume of sol–gel BG may greatly accelerate the deposition of hydroxyapatite and therefore enhance the bonding of materials to osseous tissue (Vallet-Regi and Ramila, 2000, Pereira, 1995, Li, *et al.*, 1991). It has also been proved that an increase in the growth rate of apatite-like layer as well as the wider bioactivity were observed depending on the compositional range used for the preparation of bioglass by sol-gel method (Vallet-Regi, *et al.*, 2003, Vallet-Regi and Ramila, 2001). The objective of the present study is to synthesize $SiO_2$-CaO- $P_2O_5$ bioactive glass system by different volumes of solution through sol-gel method to investigate its effect on bioactive glass particle size, size distribution, morphology and homogeneity.

## EXPERIMENTAL

### *Reagents and standard solutions*

The composition studied was bioactive glass 58S (58 % $SiO_2$-33 % CaO-9 % $P_2O_5$, based on mol %). The sol-gel precursors used in this study were Tetraethyl orthosilicate (TEOS), Triethyl phosphate (TEP), calcium nitrate tetrahydrate ($Ca(NO_3)_2{\bullet}4H_2O$), distilled water , 1 M ammonia, 2 M nitric acid (Merck, Germany). No additional purification was done on materials.

### *Nano bioactive glass preparation*

The initial procedure involved mixing TEOS, distilled water, $HNO_3$ in order. Ethanol as an alcoholic media was added to solution and allowed to react for 30 min for the acid hydrolysis of TEOS to proceed almost to completion. The following reagents were added in sequence allowing 20 min for each reagent to react completely: TEP, calcium nitrate tetrahydrate, ammonia solution. After the final addition, mixing was continued until the gel was formed. Four volumes of solution including 0.5, 1, 1.5 and 2 times of the base volume was employed for synthesizing nano bioactive glass to study its effect on size and morphology of nanopowders (named as BG-0.5Base, BG-Base, BG-1.5Base and BG-2Base). The gel was kept in the oven and heated at 70°C for one day to remove the residual

Table 1. Reaction stages of bioactive glass

| | |
|---|---|
| Stage (1) | Rapid exchange of cations such as $Na^+$ or $Ca^{2+}$ with H+ or $H_3O^+$ from solution:<br>$Si—O—Na^+ + H^+ + OH^- \longrightarrow Si—OH + Na^+(solution) + OH^-$ |
| Stage (2) | Loss of soluble silica in the form of $si(OH)_4$ to the solution resulting from breakage of Si—O—Si bonds and formation of Si—OH (silanols) at the glass solution interface.<br>$2\ (Si—O—Si) + H_2O = Si—OH + OH — Si$ |
| Stage (3) | Condensation and repolymerization of a SiO2-rich layer on the surface depleted in alkali and alkaline earth cations:<br>$Si—OH + OH — Si = —Si—O—Si— + H_2O$ |
| Stage (4) | Migration of $Ca^{2+}$ and $PO_4^{3-}$ group to the surface forming CaO— $PO_4^{3-}$ clusters on the top of the $SiO_2$-rich layer, followed by growth of the amorphous CaP |
| Stage (5) | Crystallization of the amorphous CaP by incorporation of $OH^-$ , $CO_3^{2-}$ anions from solution to form a hydroxyl-carbonate apatite layer. |

water and ethanol. During about 3 hours the temperature was raised to 600°C slowly and then was calcined for 2 additional hours at 600°C to stabilize the glass and eliminate residual nitrate.

### *Characterization*

The crystal structure and the phase present in resulting powders were analyzed with X-ray diffraction (XRD). This instrument (Philips PW 3710) works with voltage and current settings of 30 kV and 35 mA, respectively and uses Cu–Kα radiation (1.540510 Å). For qualitative analysis, XRD diagrams were recorded in the interval $20° \leq 2\theta \leq 50°$ at scan speed of 2°/min. The mean crystallite sizes "D" were determined according to the Scherrer equation ($D = 0.9\lambda/\beta \cos\theta$, where $\lambda$ is the X-ray wavelength (1.5405 Å), $\beta$ is the full width at half maximum of the diffraction line, and $\theta$ is the diffraction angle). Scanning electron microscopy (SEM XL30) was used to characterize the morphology and grain size of nano bioactive glass powders. The samples were coated with gold before the examination.

## RESULTS AND DISCUSSION

The XRD result of calcified sample BG-Base can be seen in Fig 1. As you can see in this figure, the pattern confirms the formation of the bioactive glass nano powder with approximately amorphous structure. It can be detected that β-TCP and wollastonite (pseudowollastonite, JCPDS No. 19-0248) are the main phases in the bioglass samples. The calculation of the crystallite size from specimens is shown in Table 2. It can be seen that with higher volume of solution, crystallite size markedly has been decreased.

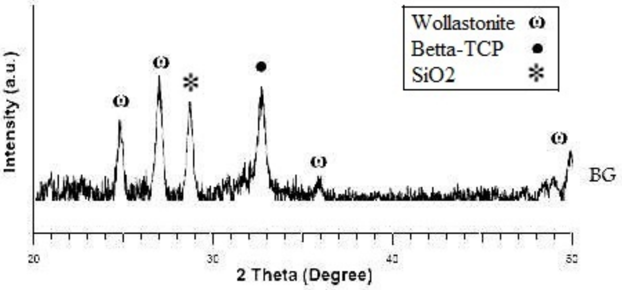

Fig. 1. XRD pattern of sample BG-Base

SEM images of produced bioactive glass powders that could be used for study of the size, morphology and homogeneity of samples (BG-Base and BG-2Base) are shown in Figs. 2A & 2B. Comparing these SEM Figures, it is clearly seen that bioactive glass prepared by higher volume of solution has smaller size, more homogeneous and more spherical particles. The size of the bioactive glass particles could be controlled in the range of 50 nm by controlling the volume of solution. It was indicated from TEM photograph of nano-bioactive glass–ceramic in Fig. 2 that most particle sizes were from 20 to 40 nm, and a few of particles presented less than 10 nm, while some small particles were conglomerated even though their size were also less than 60 nm. So, nano-bioactive glass–ceramic could be successfully prepared through this method.

Table 2. The crystallite size due to volume of solution

| Volume of Solution | Crystallite Size (nm) |
|---|---|
| 0.5 Base | 81 |
| Base | 72 |
| 1.5 Base | 59 |
| 2 Base | 49 |

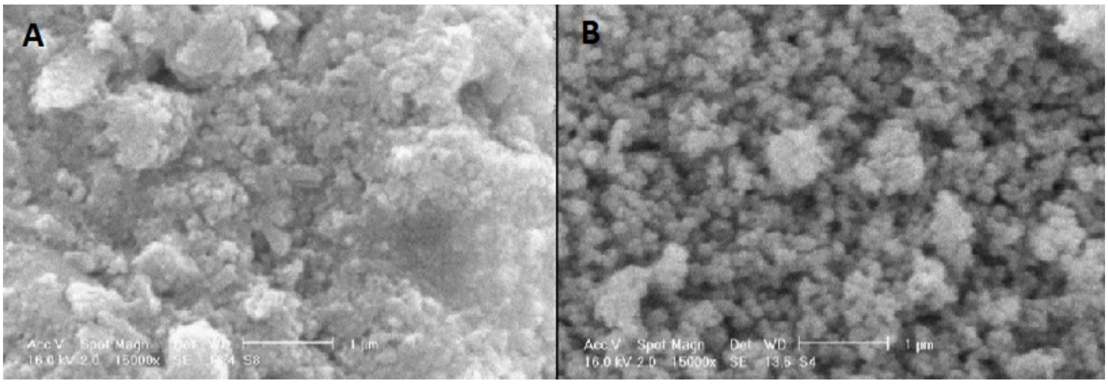

Fig. 2. SEM picture of two samples: A) sample BG-Base B) sample BG-2Base

## CONCLUSIONS

In conclusion, this study showed that the sol–gel low temperature process could be useful for producing nano bioactive glass-ceramic. The size and homogeneity of the particles are dependent on the rate of stirring. It can be concluded that when the rate of stirring increases, the size of particles decrease.

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