

## Effect of SrO Doping on Structural and Morphological Properties of Sol-Gel Derived Bioglass

Thet Thet Swe<sup>1,2</sup>, Hasmaliza Mohamad<sup>1</sup> and Khairul Anuar Shariff<sup>1</sup>

<sup>1</sup>School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

<sup>2</sup>Department of Physics, University of Yangon, 11041 Kamayut, Yangon, Myanmar

---

### Abstract

Bioglass (BG) has a broad variety of bone tissue applications because of its distinctive ability to bond with bone. This study concerns sol-gel derived strontium doped bioglass (BG) composition:  $50.77\text{SiO}_2-24.12\text{Na}_2\text{O}-(23.39-x)\text{CaO}-x\text{SrO}-1.72\text{P}_2\text{O}_5$  with different mol% of strontium ( $x=0, 3, 5$  and  $8$ ) i.e. Sr(0), Sr(3), Sr(5) and Sr(8) respectively. The structure and morphology of prepared samples were evaluated by X-ray powder diffraction (XRD) and Scanning electron microscope (SEM). In XRD, the amorphous peak is slightly shifted to smaller diffraction angle after SrO was doped into glass matrix. Moreover, the surface morphology of prepared Sr-BG exhibited an obvious sensitively changed grain boundary with the addition of Sr to BG.

**Keyword:** Bioglass, Glass-ceramics, Quaternary, Sol-gel Method, Strontium

---

### Article Info

Received 23<sup>rd</sup> October 2019

Accepted 23<sup>rd</sup> December 2019

Published 1<sup>st</sup> April 2020

\*Corresponding author: Hasmaliza Mohamad; email: hasmaliza@usm.my

Copyright Malaysian Journal of Microscopy (2020). All rights reserved.

ISSN: 1823-7010, eISSN: 2600-7444

## Introduction

Bioglass (BGs) are synthetic biomaterials which is particularly interest in orthopedic as bone substitute due to the formation of bone-like phase on their surface after implanted into bone defects [1]. In 1969, Professor Hench prepared the very first bioglass named as 45S5 (Bioglass®) which has been synthesized by melt-quenching method and this method needs very high temperature ( $>1300^{\circ}\text{C}$ ) to melt all precursors homogeneously and suddenly quenched to get amorphous glass [2]. Generally, there are two different methods to fabricate the bioglass: (1) melt-quenching method and (2) sol-gel method. However, sol-gel method is increasingly applied because of higher purity and lower processing temperatures than melting method. Lower processing temperature makes it energy-efficient and environmentally friendly to use this proposed method. In addition, the rate of bioactivity (apatite formation) of sol-gel derived bioglass is increased due to its high surface area although similar composition fabricated by melting method [3].

After the invention of first bioglass, many researchers have studied and synthesized different compositions of bioglass by varying the oxide compositions and they are being used in biomedical applications [4,5]. Since the biocompatibility of bioglass, they have been used in soft and hard tissue treatment of biomaterial, such as bone regeneration, dental treatment, wound healing and maxillofacial therapy [6]. Since last decade, the addition of different ions have been proposed to the different compositions of bioglass; such as silver (Ag)[7,8], magnesium (Mg)[8-10], aluminum (Al) [11], zinc (Zn) [12], strontium (Sr)[13,14], copper (Cu) [15] and potassium (K) [16].

Among the aforementioned therapeutic ions, Sr also has a beneficial effect on the patient who suffer osteoporosis disease because it can enhance the bone formation, increase bone density and bone mass since the chemical analogy to Ca [17]. Fredholm et.al claimed that complete SrO replacement for CaO enables enhanced apatite development [18]. Contrary to this study Goel et.al stated that the apatite formation was significantly reduced when SrO 10 mol% was substituted in CaO [19]. Fujikura et.al studied that complete replacement and influence of  $\text{Sr}^{2+}$  substitution on the crystallization of melt-derived 45S5 bioglass [20] and claimed that more than 50 mol% substitution of Sr influences the silicate network of bioglass. According to our previous study, the sol-gel derived new quaternary S50P4 BG was successfully synthesized [21]. Hence, in order to understand the effect of Sr substitution in bioglass matrix with narrow down the concentration of dopants, the aim of this study is to dope partially Sr into our previous bioglass composition. The phase and structure of prepared glass and their surface morphology were studied by X-ray powder diffraction (XRD) and Scanning Electron Microscope (SEM) respectively.

## Materials and Methods

### *Synthesis of Bioglass*

The Sr-doped  $50.77\text{SiO}_2-24.12\text{Na}_2\text{O}-(23.39-x)\text{CaO}-x\text{SrO}-1.72\text{P}_2\text{O}_5$  ( $x=0, 3, 5$  and  $8$  mol%) bioglass was synthesized by sol-gel method as our previous report [21,22] and the oxide compositions and their respective codes are presented in Table 1. The starting materials: triethyl phosphate (TEP) (Merck, 99%), tetraethyl orthosilicate (TEOS) (Aldrich, 99%), strontium nitrate (Aldrich, 99%), calcium nitrate tetrahydrate (Merck, 99%) and sodium nitrate (Merck, 99.5%), were used as precursors for  $\text{P}_2\text{O}_5$ ,  $\text{SiO}_2$ , SrO, CaO and  $\text{Na}_2\text{O}$  respectively.

**Table 1: Oxide compositions (mol %) of the prepared bioglass in this study**

<i>Glass Code</i>	<i>SiO<sub>2</sub></i>	<i>P<sub>2</sub>O<sub>5</sub></i>	<i>Na<sub>2</sub>O</i>	<i>CaO</i>	<i>SrO</i>
Sr (0)	50.77	1.72	24.12	23.39	0
Sr (3)	50.77	1.72	24.12	20.39	3
Sr (5)	50.77	1.72	24.12	18.39	5
Sr (8)	50.77	1.72	24.12	15.39	8

The synthesis of Sr doped BG were synthesized by sol-gel method at room temperature. Firstly, TEOS (37.06 mL) and 1 M of HNO<sub>3</sub> solution were mixed under stirring condition for 1 h and then TEP (1.90 mL), sodium nitrate (13.42 g), calcium nitrate (18.09 g) and strontium nitrate (for Sr doped BG) were added into the mixture solution one after another for 45 mins interval with constant stirring. For the completion of hydrolysis process, the final mixture solution was continuously stirred for 1 h after the final raw material was added. The final solution was sealed and kept for 5 days to obtain gel and then the resulting gels were transferred into Petri dishes and dried at 100°C for 2 days in a hot air oven. The dried gel were ground into fine powder which was pressed using a hydraulic press (Specac Atlas®, USA) at 60 MPa using a 10 mm diameter pressing mould. Subsequently, these pellets were calcined at 700°C for 5 hours to stabilize and remove residual nitrate of starting materials.

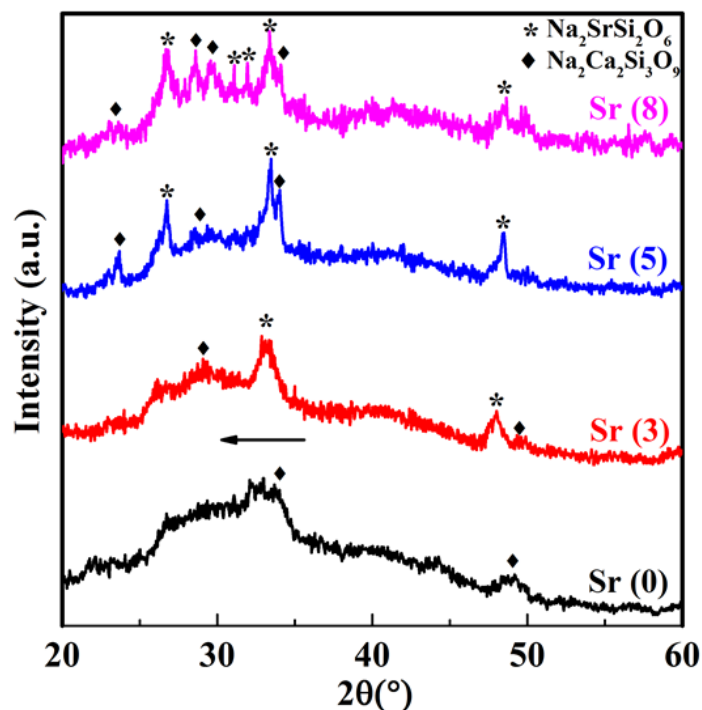
### **Characterization**

Phase and structure of synthesized glass powder were analyzed by X-ray diffraction (XRD, Bruker DX 8) operating with CuK $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) in the range of  $2\theta$  (20-60°). The percentage of crystallinity was calculated from XRD pattern by dividing the total area of crystalline peaks by the total area under the diffraction curve. The surface morphology of the glass pellets was characterized by Hitachi S-3400N Scanning Electron Microscope (SEM). The surface of the samples were coated with gold because of poor electrical conductivity of bioactive samples. The apparent porosity (AP) of calcined bioglass pellets were calculated in accordance with ASTM C 830-00 based on Archimedes' principle [23].

### **Results and Discussions**

The XRD patterns displayed in Figure 1 showed that BG Sr(0) presented broad amorphous phase between 26° and 35° ( $2\theta$ ) but low intense of combeite (Na<sub>2</sub>Ca<sub>2</sub>Si<sub>3</sub>O<sub>9</sub>, ICDD 002-1445) peaks were also observed. This partial crystallization has been observed in other quaternary glasses after calcination (700°C) process and these results were consistent with other studies of Na containing sol-gel derived bioglass [24,25]. There were several crystalline sodium calcium silicate phases observed within the amorphous structure of the bioactive glass. Among them, Clupper and Hench found that combeite is the most interesting one as it is known to influence the bioactivity [26]. However, the XRD patterns of Sr(3), Sr(5) and Sr(8) are similar with Sr(0) but the obtained patterns were shifted to smaller diffraction angle with

increasing strontium content due to the radius of doping ion ( $\text{Sr}^{2+}$ ) is larger than the host ion ( $\text{Ca}^{2+}$ ) [27] as shown in Figure 1. Moreover, there were some new peaks after incorporation of Sr to BG and these could be related to the presence of Sr compound like  $\text{Na}_2\text{SrSi}_2\text{O}_6$  (ICDD 007-9839). It was noticed that the crystallinity was linearly increased with doping amount by comparing with Sr(0), as presented in Table 2.



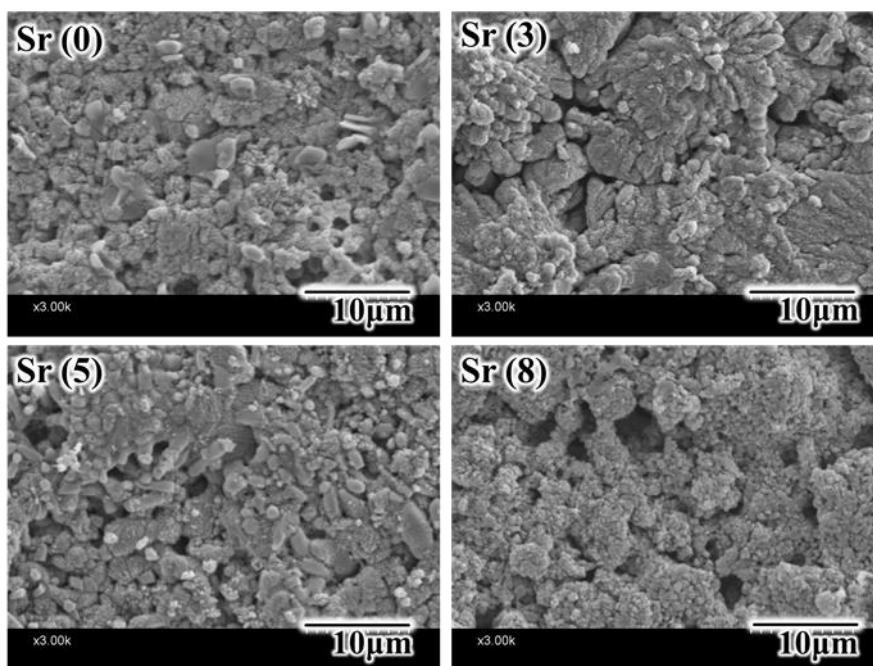
**Figure 1: XRD patterns of synthesized undoped and Sr doped BG**

**Table 2: Crystallinity percentage of prepared undoped and Sr-doped BG**

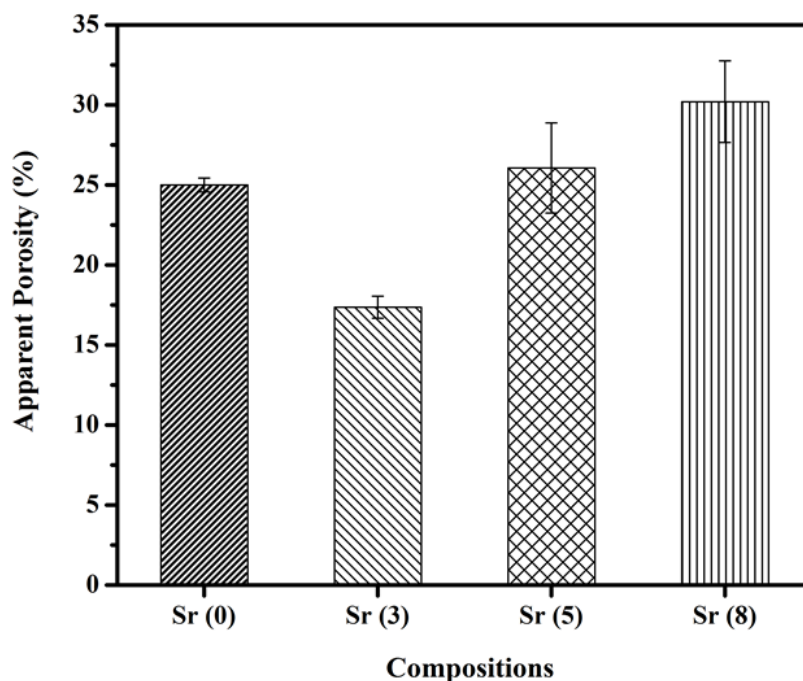
<i>Glass Code</i>	<i>Crystallinity (%)</i>
Sr (0)	35.83
Sr (3)	44.42
Sr (5)	45.61
Sr (8)	51.83

The SEM images of Sr doped BG calcined at 700°C for 5 hours were presented in Figure 2. According to SEM images, all compositions possess porous microstructure. However, the microstructures of prepared pellets were sensitive with increasing of Sr doping amounts. Although the size of the granules were irregular to be defined by a particular morphological shape, they exhibited an increase in the size for Sr (3), due to difference of ionic radii between  $\text{Sr}^{2+}$  and  $\text{Ca}^{2+}$ . Meanwhile, the apparent porosity was also decreased from 25% to 17.36%. However, on further addition of Sr dopant, the size of granules only witnessed a decrease for

Sr (5) and Sr (8). This evident decrease with increasing Sr content could be attributed to the effect of solubility limits of the low melting point of  $\text{Sr}(\text{NO}_3)_2$  dopant in BG matrix and results in aggregation at the grain boundaries [28]. Furthermore, the porosity was increased by further increase in Sr content to 8%. Thus, this observation inferred that Sr addition above a particular threshold i.e. Sr (3) retarded the grain growth in BG system. The results for porosity measurement supported these microstructure SEM images and presented in Figure 3.



**Figure 2: SEM images of synthesized undoped and Sr doped BG**



**Figure 3: Apparent porosity of undoped and Sr doped BG**

## Conclusions

Pure and Sr doped quaternary bioactive glass were synthesized by sol-gel method. According to XRD results, it can be concluded that Sr is successfully doped to BG structure as the amorphous peak was shifted to lower angles. Moreover, it was interesting to note that more crystalline sharp peaks formed in higher Sr dopants and along with increasing the crystallinity. Besides, the microstructure changes significantly with the addition of SrO above a particular threshold i.e. 3 mol% retarded the grain growth and reduction in porosity.

## Acknowledgments

Authors are grateful to AUN/SEED-Net grant (6050368) and Research Universiti grant (8014045) for financial support of this study.

## Author Contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

## Disclosure of Conflict of Interest

The authors report no conflicts of interest in this work.

## Compliance with Ethical Standards

The work is compliant with ethical standards.

## References

- [1] Profeta, A. C., and Huppa, C. (2016) Bioactive-glass in Oral and Maxillofacial Surgery Craniomaxillofac Trauma Reconstr 9 (1) 1
- [2] Hench, L. L. (2006) The story of Bioglass (R). J. Mater. Sci-Mater. M. 17 (11) 967
- [3] Li, R., Clark, A., Hench, L. (1991) An investigation of bioactive glass powders by sol-gel processing J. Appl. Biomater 2(4) 231
- [4] Bairo, F., Novajra, G., Miguez-Pacheco, V., Boccaccini, A. R., Vitale-Brovarone, C. (2016) Bioactive glasses: special applications outside the skeletal system. J. Non. Cryst. Solids 432 15
- [5] Jones, J. R. (2015) Reprint of: Review of bioactive glass: From Hench to hybrids. Acta biomater. 23 S53
- [6] Ojha, N. (2016) Borosilicate glass with enhanced hot forming properties and conversion to hydroxyapatite (M. Sci. Thesis, Tampere University of Technology, Finland) pp. 10-40
- [7] El-Kady, A. M., Ali, A. F., Rizk, R. A., Ahmed, M. M. (2012) Synthesis, characterization and microbiological response of silver doped bioactive glass nanoparticles. Ceram Int 38 (1) 177
- [8] Kaur, K., Singh, K., Anand, V., Bhatia, G., Singh, S., Kaur, H., Arora, D. S. (2016) Magnesium and silver doped CaO–Na<sub>2</sub>O–SiO<sub>2</sub>–P<sub>2</sub>O<sub>5</sub> bioceramic nanoparticles as implant materials. Ceram Int 42 (11) 12651
- [9] Sharifi Sedeh, E., Mirdamadi, S., Sharifianjazi, F., Tahriri, M. (2015) Synthesis and evaluation of mechanical and biological properties of scaffold prepared from Ti and Mg with different volume percent Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry 45 (7) 1087

- [10] Ma, J., Chen, C., Wang, D., Hu, J. (2011) Synthesis, characterization and in vitro bioactivity of magnesium-doped sol-gel glass and glass-ceramics *Ceram Int* 37 (5) 1637
- [11] El-Kheshen, A., Khaliafa, F., Saad, E., Elwan, R. (2008) Effect of Al<sub>2</sub>O<sub>3</sub> addition on bioactivity, thermal and mechanical properties of some bioactive glasses *Ceram Int* 34 (7) 1667
- [12] Goh, Y.-F., Alshemary, A. Z., Akram, M., Kadir, M. R. A., Hussain, R. (2013) In vitro study of nano-sized zinc doped bioactive glass *Mater. Chem. Phys* 137 (3) 1031
- [13] Solgi, S., Khakbiz, M., Shahrezaee, M., Zamanian, A., Tahriri, M., Keshtkari, S., Raz, M., Khoshroo, K., Moghadas, S., Rajabnejad, A. (2017) Synthesis, characterization and in vitro biological evaluation of sol-gel derived sr-containing nano bioactive glass *Silicon-Neth* 9 (4) 535
- [14] Dziadek, M., Zagrajczuk, B., Menaszek, E., Wegrzynowicz, A., Pawlik, J., Cholewa-Kowalska, K. (2016) Gel-derived SiO<sub>2</sub>-CaO-P<sub>2</sub>O<sub>5</sub> bioactive glasses and glass-ceramics modified by SrO addition *Ceram Int* 42 (5) 5842
- [15] Kaur, K., Singh, K., Anand, V., Kaur, H., Arora, D. S., (2015) In-vitro study of copper doped SiO<sub>2</sub>-CaO-P<sub>2</sub>O<sub>5</sub> system for bioactivity and antimicrobial properties. *AIP Conference Proceedings*, Place, vol. 1675, p 020020
- [16] Salman, S., Salama, S., Abo-Mosallam, H. (2012) The role of strontium and potassium on crystallization and bioactivity of Na<sub>2</sub>O-CaO-P<sub>2</sub>O<sub>5</sub>-SiO<sub>2</sub> glasses *Ceram Int* 38 (1) 55
- [17] Boivin, G., Deloffre, P., Perrat, B., Panczer, G., Boudeulle, M., Mauras, Y., Allain, P., Tsouderos, Y., Meunier, P. J. (1996) Strontium distribution and interactions with bone mineral in monkey iliac bone after strontium salt (S 12911) administration *J. Bone Miner. Res.* 11 (9) 1302
- [18] Fredholm, Y. C., Karpukhina, N., Brauer, D. S., Jones, J. R., Law, R. V., Hill, R. G. (2011) Influence of strontium for calcium substitution in bioactive glasses on degradation, ion release and apatite formation *J. R. Soc. Interface* 9 (70) 880-889
- [19] El-Fiqi, A., Kim, J.-H., Kim, H.-W. (2015) Osteoinductive fibrous scaffolds of biopolymer/mesoporous bioactive glass nanocarriers with excellent bioactivity and long-term delivery of osteogenic drug *ACS Appl. Mater. Interfaces.* 7 (2) 1140-1152
- [20] Fujikura, K., Karpukhina, N., Kasuga, T., Brauer, D., Hill, R., Law, R. (2012) Influence of strontium substitution on structure and crystallisation of Bioglass® 45S5 *J. Mater. Chem* 22 (15) 7395-7402
- [21] Swe, T. T., Mohamad, H., Shariff, K. A., Noor, A. F. M., Ishikawa, K., Thant, A. A., (2018) Synthesis and Characterization of Bioactive Quaternary Silicate Gel-glasses. In *RCM-AMC 2018*, IOP Publishing, Penang, Malaysia, vol. 1082, p 012070
- [22] Swe, T. T., Mohamad, H., Shariff, K. A., Thant, A. A., (2019) Fabrication of sol-gel derived new quaternary silicate Bioglass S55P4. In *ICXRI 2018*, AIP Conference Proceedings, Kelantan, Malaysia, vol. 2068, p 020070
- [23] ASTM C830-00, Standard Test Methods for Apparent Porosity, Liquid Absorption, Apparent Specific Gravity, and Bulk Density of Refractory Shapes by Vacuum Pressure, *ASTM Int.* West Conshohocken, PA,. (2016)
- [24] Chen, Q.-Z., Li, Y., Jin, L.-Y., Quinn, J. M., Komesaroff, P. A. (2010) A new sol-gel process for producing Na<sub>2</sub>O-containing bioactive glass ceramics *Acta Biomater* 6 (10) 4143
- [25] Bejarano, J., Caviedes, P., Palza, H. (2015) Sol-gel synthesis and in vitro bioactivity of copper and zinc-doped silicate bioactive glasses and glass-ceramics *J. Biomed mater* 10 (2) 025001
- [26] Clupper, D., and Hench, L. (2003) Crystallization kinetics of tape cast bioactive glass 45S5 *J. Non-Cryst. Solids* 318 (1-2) 43-48
- [27] Massera, J., and Hupa, L. (2014) Influence of SrO substitution for CaO on the properties of bioactive glass S53P4 *J. Mater. Sci.: Mater. Med* 25 (3) 657-668
- [28] Chen, G., Chen, J., Fu, C., Peng, X., Cai, W., Deng, X. (2014) Effect of strontium doping on the microstructures and dielectric properties of lanthanum titanate ceramics *T Can Soc Mech Eng* 73 (4) 307