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Sol-Gel Method for Bioactive Glass Synthesis

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***Abstract*—Bioactive glasses are a group of ceramic materials that may stimulate bone regeneration. These materials are shown to be biocompatible and bioactive, making them widely studied to be used as implants within the human body to repair and replace defective bones. This article provides readers with information about the synthesis of bioactive glasses by sol-gel method, which has been growing rapidly in recent years. We revolved the bioactive glasses synthesized by the conventional sol-gel, and also the modified sol-gel processes.**

Keywords—bioactive glass, bioactivity, in vitro, hydroxyapatite, sol-gel method, characterization

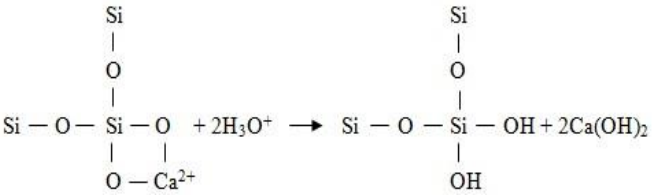
I. INTRODUCTION

The first bioactive glass was developed by Prof. L.L. Hench in 1969, it represents a group of reactive materials capable of binding to mineralized bone tissue within the physiological medium [1]. The bioactive glass of L.L. Hench has the composition of $45SiO_2$ - $24.5CaO$ - $24.5Na_2O$ - $6P_2O_5$ (wt.%) (noted as 45S5) with the commercial name of Novamin or Bioglass®. Through testing, L.L. Hench has discovered a very important property of this glass material that's bioactivity. it's the ability to create a replacement layer of hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (noted as HA) on the glass's surface when the material is implanted at the defective bone sites within the human body. The mineral hydroxyapatite (HA) layer is analogous to the inorganic component of human bone, so it's the bridge connecting the artificial graft manufactured from glass material and natural bone, through which the defective bones are repaired, and filled [2-3].

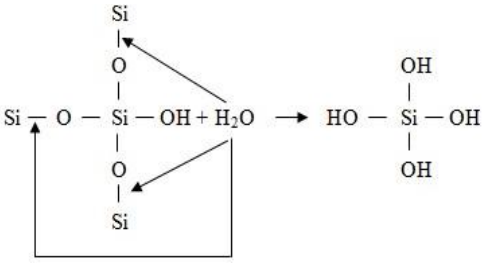
The ''in vitro'' experiment is taken into account to be a quick and effective method to check the bioactivity of synthetic glass systems. This is the method developed by T. Kokubo & H. Takadama, and widely applied until now [4]. Samples of bioactive glass were immersed within the Simulated Body Fluid (SBF) solution that's a synthetic solution with inorganic ionic components like the blood of the human body. After different time periods, a layer of hydroxyapatite (HA) minerals will form on the glass's surface if it's bioactive.

The scientists have explained the mechanism of bioactivity of bioactive glass materials in the SBF medium. This mechanism is accepted to this day, and is summarized in the following stages [4-7]:

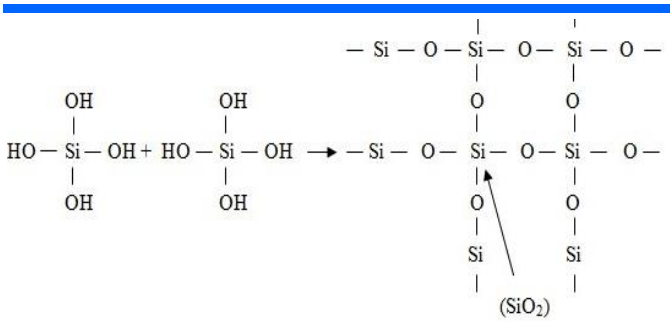
Stage 1: Quick exchange of Na^+ or Ca^{2+} cations with H^+ in the medium, creating silanol bonding groups (Si-OH) on the glass surface.



Stage 2: Release of $Si(OH)_4$ silicic acids into the environment by the fracture of Si - O - Si bonds.



Stage 3: Polymerization of saturated $Si(OH)_4$ silicic acids to form a SiO_2 silica gel layer on the surface of the glass.



Stage 4: Movement of Ca^{2+} and PO_4^{3-} ions in the network of glass structure as well as their movement from the physiological environment to the surface of SiO_2 gel layer to create a layer rich in Ca and P.

Stage 5: Combination of Ca^{2+}, PO_4^{3-}, OH^- ions to form Hydroxyapatite (HA) mineral layer similar to inorganic composition of bone. Thanks to this mineral layer, defective bones are repaired and filled.

After the invention of L.L. Hench, many bioactive glass systems with different components are studied, synthesized and applied. There are two main methods for the synthesis of bioactive glasses. The first method is melting the precursors at a high temperature. The second method is related to synthesizing the glass systems in solution, called the sol-gel (sol-gel) method. The melting method can quickly synthesize glass systems with a large number of products, but there are also disadvantages such as requiring a high temperature synthesis (above 1300 °C). At high temperature, the P_2O_5 component is easily volatile, leading to deviation in composition. Moreover, the resulting glass systems generally have a dense structure and low value of specific surface area [7-8]. The sol-gel method overcomes the disadvantages of the melting method such as synthesis of materials at lower temperatures, resulting glass systems having porous structures and larger specific surface areas. On the other hand, the sol-gel method is favorable for combining bioactive glasses with active organic molecules to form inorganic/organic functional composite systems with more superior properties [9].

This paper presents the essential information, focused on the sol-gel method for synthesizing bioactive glasses, and the characterization of synthetic materials.

II. PRINCIPLE OF THE SOL-GEL METHOD

The sol-gel method undergoes two main stages: hydrolysis of precursors to sol and converting sol particles into gel. After that, the gel is dried, and processed at a temperature of about 700 °C to obtain the glass systems [7-10]. The sol-forming and gelling processes are described and briefly illustrated according to the following reactions:

Reaction 1: $Si(OC_2H_5)_4 + 4H_2O \rightarrow Si(OH)_4 + 4C_2H_5OH$, creating sol particles $Si(OH)_4$, catalyst medium H^+);

Reaction 2: $nSi(OH)_4 \rightarrow x(SiO_2).\ y(OH) + zH_2O$, forming gel $x(SiO_2)y(OH)$ after several days.

The gel system is inorganic polymer with an orderly bonding arrangement - Si - O - Si - O - Si -. When synthesizing bioactive glass material systems, cations such as Ca^{2+} or Na^+ from salts or oxides are introduced to disrupt the bonding order, creating the amorphous structural lattice of synthetic glasses. An orderly bond breaking process usually occurs when treating a dry gel system at high temperatures. The breakdown of links - Si - O - Si - O - Si - O - is depicted in Fig. 1 below:

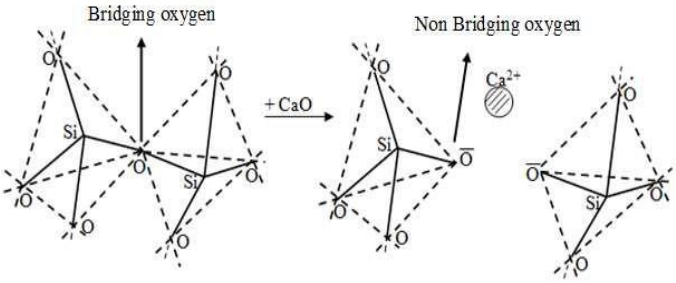


Fig. 1. Breaking process of bonding order, creating an amorphous structure of glass

III. BIOACTIVE GLASSES SYNTHESIZED BY SOL-GEL METHOD

Based on the sol-gel method, some typical biomedical glass material systems have been studied, and synthesized. J. Ma et al have synthesized the 58S bioactive glass system with the composition of $58SiO_2$ - $38CaO$ - $4P_2O_5$ (wt.%) from the precursors TEOS - $Si(OCH_2CH_3)_4$; TEP - $(CH_3CH_2O)_3P$; $Ca(NO_3)_2.4H_2O$ in solution with the 2N HNO_3 acid catalyst. The dried gel samples are heated at temperatures 700 °C, 900 °C, 1000 °C and 1200 °C. The analyses of thermal effect showed that the crystallization occurred with the formation of pseudowollastonite $Ca_3Si_3O_9$ and $CaSiO_3$ wollastonite phases at the heating temperature above 900 ^oC. In addition, with the increase in heating temperature, the pseudowollastonite phase composition decreased while the wollastonite phase content increased. The ‘‘in vitro’’ test was done in the simulated body fluid

(SBF) solution. The bioactivity of the 58S glass system was confirmed through the formation of bone mineral layer hydroxyapatite (HA). Moreover, the crystallization of the crystal phase at high temperatures during gel treatment does not inhibit the bioactivity of the synthetic glass material [10].

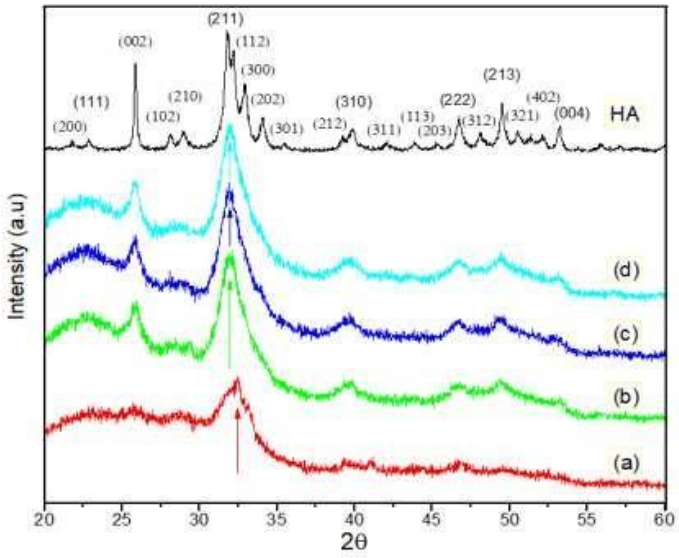


Fig. 2. XRD diagrams of the bioactive glass 58S before (a) and after soaking in the SBF for b) 2, c) 5 and d) 10 days [11]

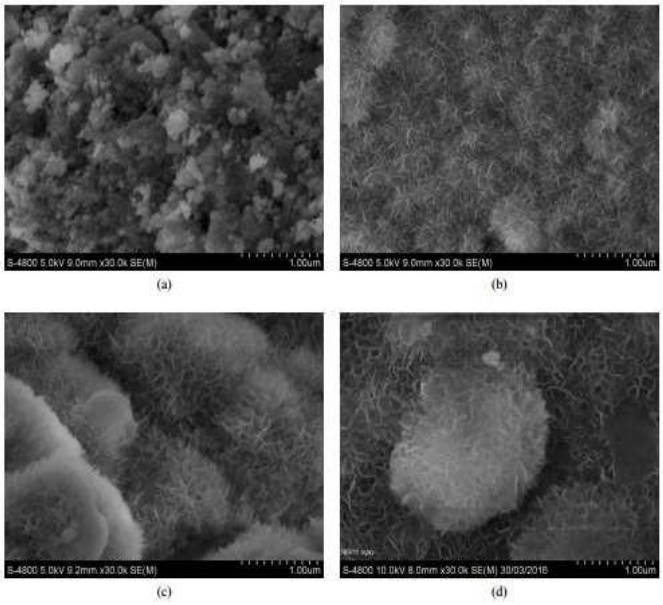


Fig. 3. SEM observations of bioactive glass 58S before (a) and after soaking in SBF solution: b) 2, c) 5 and d) 10 days [11]

X. V. Bui and T. H. Dang synthesized and evaluated the 58S bioactive glass system by using an improved sol-gel method [11]. In this study, the authors added NH_3 agent to sol solution to stimulate gel formation, thereby reducing gelation time to only 1 to 2 hours compared to 5 days in conventional sol-gel method. The XRD analyses showed that the 58S glass system synthesized by the new sol-gel method gives an amorphous structure in accordance with the nature of the glass material. ‘‘In vitro’’ experiment `` in SBF solution confirmed the high bioactivity of synthetic glass through the formation of the apatite mineral layer on the surface of the glass’s sample after 2 days of testing (Fig. 2-3).

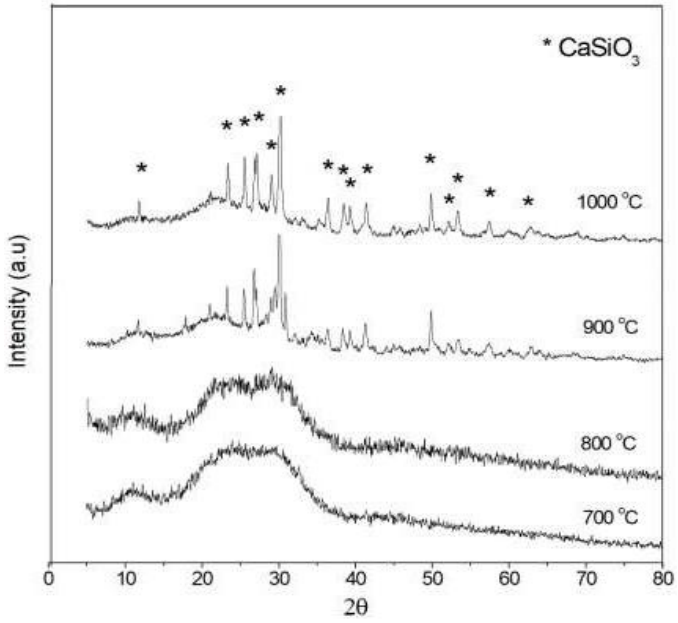


Fig. 4. XRD patterns of synthetic glass $70SiO_2$-30CaO at 700, 800, 900 and 1000 ◦C [13]

Different glass systems of $70SiO_2$ - 30CaO (mol.%) and $55SiO_2$ - 41CaO - $4P_2O_5$ (mol.%) were synthesized and studied by J. Roman et al [12]. The dried gels are converted to ceramics with a temperature range from 700 to 1400 ^oC. The ‘‘in vitro’’ experiment was done in the simulated body fluids (SBF). The analytical results showed that all glasses obtained in the form of amorphous materials or glass-ceramics, and they are bioactive. In addition, the bioactivity is affected by the composition of the initial glass and heat treatment conditions in the synthesis of material systems.

Bioactive glass $70SiO_2$-30CaO (mol.%) has been successfully synthesized with the modified sol-gel process in hot water without using acid catalyst [13]. The thermal analysis showed that the bioactive glass with the amorphous state can be synthesized by sintering the dried gel sample at 700 ^oC for 3 hours. Furthermore, the synthetic bioactive glass exhibited interesting biological activity and good biological compatibility after in

vitro experiments in the simulated body fluid (SBF) and in the cellular culture environment (Fig. 4-5).

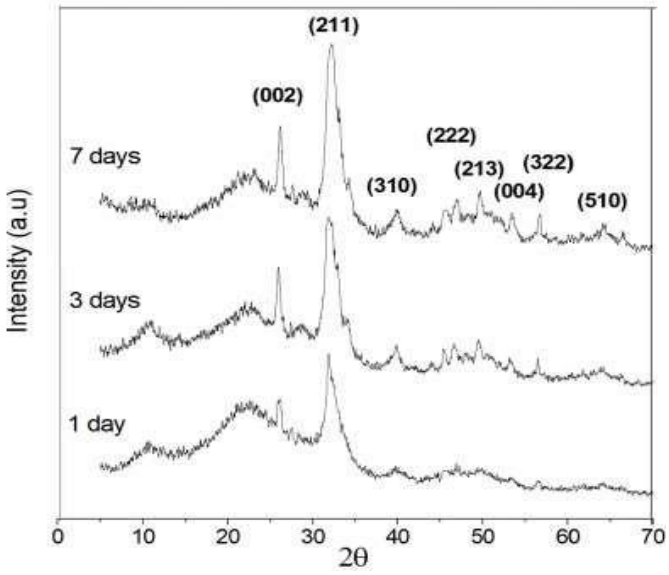


Fig. 5. XRD diagrams of glass $70SiO_2$-30CaO in SBF for 1, 3 and 7 days [13]

The ternary glass system SiO_2-CaO-P_2O_5 with different CaO/P_2O_5 ratios was studied by S. M. Ahmadi et al [14]. The ‘‘in vitro’’ experiment highlighted that the glass’s sample with the ratio of CaO/P_2O_5 = 9.5 show the highest bioactivity. In addition, the cellular biocompatibility test confirmed the biocompatibility of this synthetic material system.

The development of bioactive glasses has a history of 50 years. In this period, scientists have found out extensive explorations on the special properties of bioactive glasses. However, bioactive glasses have not yet reached their application potentials while research activity is growing. This is both a challenge and a prospect for the development of bioactive glasses in the future.

IV. CONCLUSIONS

This presentation essentially focuses on the sol-gel method for synthesis of bioactive glasses which are the biomaterials used for defective bone replacement. The basic processing of sol-gel method is described succinctly. To illustrate this approach, the typical bioactive glasses were selected, and presented to provide readers with main information on the synthetic strategy, special feature, and principal results.

REFERENCES

[1] L. L. Hench, ‘‘Bioceramics: From Concept to Clinic,’’ *Journal of the American Ceramic Society*, Vol. 74, No. 7, pp. 1487-1510, 1991.

[2] L. L. Hench, R. J. Splinter and T. K. Jr. Greenlee, “Bonding Mechanisms at the Interface of Ceramic Prosthetic Materials,” *Journal of Biomedical Materials Research,* Vol. 5, No. 6, pp. 117141, 1971.

[3] I. Elgayar, A. E. Aliev, A. R. Boccaccini and R. G. Hill, ‘‘Structural analysis of bioactive glasses,’’ Journal of Non-Crystallization Solid, Vol.361, No. 2, 173-183, 2005.

[4] T. Kokubo and H. Takadama, ‘‘How useful is SBF in predicting in vivo bone bioactivity,’’ *Biomaterials*, Vol. 27, No. 15, pp. 2907-2915, 2006.

[5] S. Sepulveda, J. R. Jones, L. L. Hench. (2001). Characterizationof melt-derived 45S5 and solgel-derived 58S bioactiveglasses. *Journal Biomedical Material Research, 58(*6), 734–740.

[6] O. Peitl, E. D. Zanotto, F. C. Serbena, and L. L. Hench. (2012). Compositional and microstructural design of highly bioactive P_2O_5–Na_2O–CaO–SiO_2 glass-ceramics. *Acta Biomaterialia, 8*(1), 321-332.

[7] G. J. Owens, R. K. Singh, F. Foroutan, M. Alqaysi, C. M. Han, C. Mahapatra, H. W. Kim, and J. C. Knowles. (2016). Sol–gel based materials for biomedical applications. *Progress in Materials Science*, *77*, 1-79.

[8] O. Peitl, E. D. Zanotto, F. C. Serbena, and L. L. Hench. (2012). Compositional and microstructural design of highly bioactive P_2O_5–Na_2O–CaO–SiO_2 glass-ceramics. *Acta Biomaterialia*, *8*(1**),** 321-332.

[9] J. R. Jones. (2013). Review of bioactive glass: From Hench to hybrids, Acta Biomaterialia, 9, 4457-4486.

[10] J. Ma, C. Z. Chen, D. G. Wang, X. G. Meng, J. Z. Shi. (2010). Influence of the sintering temperature on the structural feature and bioactivity of sol-gel derived SiO_2-CaO-P_2O_5 bioglass, *Ceramics International*, *36*(6), 1911-1916.

[11] X. V. Bùi, T. H. Dang. (2019). Bioactive glass 58S prepared using an innovation sol-gel process. *Processing and Application of Ceramics*, *13*(1), 98-103.

[12] J. Roman, S. Padilla and M. Vallet-Regi. (2003). Sol-Gel Glasses as Precursors of Bioactive Glass Ceramics. *Chemistry Materials, 15*(3), 798-806.

[13] T. H. Dang et al. (2020). Characterization of Bioactive Glass Synthesized by Sol-Gel Process in Hot Water. *Crystals* 10 (529) 1-10.

[14] S. M. Ahmadi, A. Behnamghader, A. Asfnejaad. (2017). Sol-gel synthesis, characterization and in vitro evaluation of SiO_2-CaO-P_2O_5 bioactive glass nanoparticles with various CaO/P_2O_5 ratios. *Digest Journal of Nanomaterials and Biostructures, 12*(3), 847-860.