

# Research Article

# Investigation of Bioactive Glass-Ceramic 60SiO<sub>2</sub>-30CaO-10P<sub>2</sub>O<sub>5</sub> Prepared by Hydrothermal Method

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Received 24 August 2019; Accepted 11 October 2019; Published 3 November 2019

Guest Editor: Lavinia C. Ardelean

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Bioactive glass-ceramics (BGCs) with the composition of  $60SiO_2$ -30CaO- $10P_2O_5$  (wt. %) have been synthesized by the hydrothermal method. The BGC samples were prepared at two reaction temperatures of 150 and 220°C, named BGC-150 and BGC-220. The XRD and FTIR analyses highlighted that the degree of crystallinity of BGCs increased linearly with hydrothermal reaction temperature. FE-SEM and TEM results indicated that the surface of BGC samples is covered by the nanosized particles which grow into larger sizes as a function of reaction temperature. The bioactivity of BGCs was investigated by the immersion of powder samples in the SBF solution. The results confirmed the dissolution and the interaction of BGC samples in the SBF solution which led to the formation of a new apatite phase on their surface.

#### 1. Introduction

Bioactive glasses (bioglasses) have been discovered in 1969 by Hench [1]. These materials possess a special property, called "bioactivity", which is the ability to form an interfacial bond to the bone through the quick formation of hydroxyapatite (HA) layer on the surface of bioglasses when they are implanted in the human body or in the simulated body fluid (SBF). The composition of HA is similar to that of the natural bone, and it is able to make a strong linkage between the artificial implant and natural bone [1, 2]. Due to their bioactivity, bioactive glasses are an important component of injectable materials for replacing and repairing bone defects in orthopedic surgery or in dental filling [3, 4].

Although bioglasses have been widely used, there still remain some disadvantages such as low fracture strength and brittleness [5, 6]. One of the efficient methods to enhance the mechanical properties of bioglasses is to convert them into glass-ceramics by partial crystallization, forming a new kind of biomaterial named as bioactive glass-ceramics (BGCs) [6]. Bioactive glass-ceramics (BGCs) include both the amorphous phase of glass and the crystalline phase of ceramics. These materials not only have the bioactivity similar to bioglasses but also have improved mechanical properties. Due to the interesting properties, bioactive glassceramics are more suitable for biomedical applications than conventional bioglasses.

Among various techniques, melting and sol-gel are the two main methods for the preparation of BGCs. For the melting method, bioactive glass-ceramics are synthesized by melting precursors at high temperatures, according to a special heat treatment process in which the glass sample has to go through the annealing stage for partial crystallization. This technique is fast and suitable for the massive production but retains some obstacles such as energy consumption or evaporation of  $P_2O_5$  at high temperatures [7].

For the sol-gel method, the synthesis process undergoes through several steps consisting of hydrolysis of precursors to form the sol state, conversion of a sol into a gel, gel drying, and finally, heating treatment of dried gel at temperatures in the range of 600–800°C [8]. Even though the sol-gel method is quite complex, it has some benefits such as the use of lower temperatures than the melting method and producing nano-BGCs with high porosity and specific surface area that enhances the bioactivity of biomaterials [9].

Recently, bioactive glass-ceramics have been prepared by the hydrothermal method, in which the BGC samples were synthesized at relatively low temperatures and the compression of samples under hydrothermal conditions stimulated the gelation process. According to the literature, a few of BGCs were prepared and evaluated such as ternary system  $58SiO_2$ -33CaO- $9P_2O_5$  (wt. %) and quaternary systems  $40SiO_2$ .27CaO- $27Na_2O$ - $6P_2O_5$  (mol. %) and  $60SiO_2$ .30-CaO- $6Na_2O$ - $4P_2O_5$  (mol. %) [10, 11].

In this study, the BGCs with a composition of  $60SiO_2.30CaO-10P_2O_5$  (wt. %) were selected to synthesize by the hydrothermal method. The chemical composition of synthetic materials is very close to a ternary conventional system ( $58SiO_2.33CaO-9P_2O_5$ ) as reported in previous research studies [10, 11]. The samples of BGCs were synthesized and evaluated at two hydrothermal reaction temperatures of 150 and 220°C. The effect of temperature on phase crystallization, surface morphology, and the bioactivity of BGCs was investigated.

# 2. Materials and Methods

2.1. Hydrothermal Preparation of Bioactive Glass-Ceramics (BGCs). A bioactive glass-ceramic with a composition of  $60 SiO_{2\mathchar`-} 30 CaO\mathchar`-10 P_2 O_5$  (wt. %) was prepared by the hydrothermal method. The principal precursors for the preparation including tetraethyl orthosilicate (TEOS, Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>, 99.999% in purity), triethyl phosphate (TEP, OP(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>, 99.8% in purity), and calcium nitrate tetrahydrate (Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, 99% in purity) were purchased from Sigma-Aldrich (Singapore). First, 4.17 g of TEOS and 0.51 g of TEP were added in 15 mL of distilled water. The pH of the mixture was adjusted to a value of 2 by adding a 1M HNO<sub>3</sub> solution. After stirring for 30 minutes at room temperature, 2.53 g of calcium nitrate tetrahydrate was added and the reaction mixture was continuously stirred at the same time as the previous step. Then, the resulting sol was transferred into a Teflon-lined stainless steel autoclave, which was then heated in an oven at 150 and 220°C for 24 hours. From here, the samples were named as BGC-150 and BGC-220, respectively. In this study, the hydrothermal temperature of 220°C was chosen according to the previous research [10], while the other one of 150°C was selected for the purpose of comparison. After the hydrothermal process, the samples were cooled to room temperature and then dried at 100°C for 24 hours. The powder samples of BGC-150 and BGC-220 were served for physic-chemical characterizations. The process of BGC synthesis is briefly presented in Scheme 1.

2.2. In Vitro Experiment. The in vitro experiment was effectuated to evaluate the bioactivity of BGCs by soaking the powder samples in the simulated body fluid (SBF) solution



SCHEME 1: Schematic of the hydrothermal process for synthesis of bioactive glass ceramics.

following the ratio of 1/2 (mg/mL). The SBF solution has a similar ionic composition as human blood plasma. It was prepared according to Kokubo's method [12]. The samples of BGC-150 and BGC-220 were soaked in the SBF solution for 20 days. In this time, the mixture was stirred using a magnetic mixer with a speed of 50 rpm at a temperature of 37°C. At the end of the soaking time, the samples were removed from the solution, gently rinsed with distilled water, and dried at 50°C for 1 day.

2.3. Physic-Chemical Characterizations. The structural phase of BGC materials was identified by X-ray diffraction (XRD) on a Bruker D8 Advance diffractometer. Powder samples were homogeneously mixed with cyclohexane, dropped on the surfaces of plastic tablets, and then dried to remove the solvent. The XRD data were acquired with a scanning speed of 1°/min. Fourier-transformed infrared spectroscopy (FTIR) was employed to determine the functional groups of BGC materials. Powder samples were ground and then mixed thoroughly with KBr with a ratio of 1/100. The FTIR spectra were recorded on Bruker Equinox 55 with the wave number in the range from 400 to 4000 cm<sup>-1</sup>, at a resolution of 2 cm<sup>-1</sup>. The structural morphologies of BGC samples were observed by using field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). The degradation of the BGC samples in the SBF solution was investigated through Ca, Si, and P

concentrations by using inductively coupled plasma-optical emission spectroscopy (ICP-OES).

#### 3. Results and Discussions

3.1. Phase Characterization of Bioactive Glass-Ceramics. Figure 1 presents the XRD diagrams of the bioactive glassceramic 60SiO<sub>2-</sub>30CaO-10P<sub>2</sub>O<sub>5</sub> at reaction temperatures of 150 and 220°C. While broad peaks at 22° (2 $\theta$ ) are depicted to the amorphous phase, well-defined peaks are assigned to crystalline phases of hydroxyapatite (JCPDS 90432). Based on the literature [13], the appearance of the crystalline phase can be explained by the following hypotheses. The thermal energy of hydrothermal processing is the cause of the diffusion of silicate ions (SIO<sub>4</sub><sup>4-</sup>) and phosphate ions (PO<sub>4</sub><sup>3-</sup>) in the structural network of bioceramics. Consequently, more free phosphate groups combine with calcium ions  $(Ca^{2+})$  to form the apatite phase. For BGC-150, three crystalline peaks with low intensity were defined at 31.9, 32.4, and  $33.1^{\circ}$  (2 $\theta$ ). When increasing the temperature up to 220°C, these three peaks became sharper and clearer; additionally, other new peaks appeared at 26, 29.2, 34.2, 40.2, 47, 48.3, 49.7, 50.8, 51.7, and 52.5° ( $2\theta$ ). The XRD results indicated that the BGC-150 exhibited a lower degree of crystallinity in comparison to the BGC-220, and the crystallization was enhanced as increasing the temperature. This result probably due to the higher thermal energy at 220°C compared to that of 150°C facilitates the diffusion of silicate and phosphate ions in the structural network of bioceramics. The observation in this analysis is slightly different from the previous study [10]. In this work, the BGC with the composition of 58SiO<sub>2-</sub>33CaO-9P2O5 (wt. %) was prepared by using the hydrothermal method at the reaction temperature of 220°C, which expressed the amorphous and two crystalline phases of HA and quartz.

Figure 2 shows the FTIR spectra of the BGC-150 and BGC-220. For the BGC-150 sample, a majority of characteristic bands of the silica network were determined according to the previous investigations [10, 14, 15]. The band at 470 cm<sup>-1</sup> is attributed to the Si-O-Si bending vibration, while two bands at 811 and 1101 cm<sup>-1</sup> correspond to Si-O-Si symmetric stretching and Si-O-Si asymmetric stretching, respectively. A weak band at 972 cm<sup>-1</sup> is characterized for the stretching modes of Si-OH, confirming the appearance of nonbridging oxygen in the ceramic matrix. The band with slight intensity at 570 cm<sup>-1</sup> is related to the bending vibration of P-O liaisons in  $PO_4^{3-}$  groups. The band at 1374 cm<sup>-1</sup> mentions the presence of nitrate ions as a result of using HNO<sub>3</sub> as a catalyst in the synthesis process. In comparison, for the BGC-220 sample, all bands were characterized by the silica network but they were moved to the right side. The band at 972 cm<sup>-1</sup> for nonbridging oxygen was decreased in intensity. The band at 570 cm<sup>-1</sup> was split in two well-defined bands of 560 and 605 cm<sup>-1</sup> which correspond to the bending vibration of the P-O bond in the crystalline phase of hydroxyapatite material. The aforementioned phenomena confirmed the temperature-dependent structure effect of reaction temperature on the structural formation of ceramic material; the crystallinity of



FIGURE 1: XRD diagrams of BGC-150 and BGC-220 samples.



FIGURE 2: FTIR spectra of BGC-150 and BGC-220 samples.

the crystalline phase was enhanced with increasing hydrothermal temperature. The obtained results are consistent with the XRD analyses.

3.2. Structural Morphology of Bioactive Glass-Ceramics. The FE-SEM images of BGCs prepared by the hydrothermal method at 150 and 220°C for 24 hours are presented in Figure 3. The micrographs of the two BGC samples were measured at different magnifications of 20.000 and 100.000 times. The results highlighted that the surfaces of both BGC-150 and BGC-220 samples were covered by the particles at nanosize as observed in both images at the lower and higher magnifications. These observed nanoparticles can be assigned to apatite crystals that are formed and covered on the surface of BGC granules in the hydrothermal reactions. As the hydrothermal reaction temperature increased from 150 to 220°C, the particles were grown to larger sizes but still



FIGURE 3: FE-SEM micrographs of BGC-150 and BGC-220 samples at different magnifications.

in the nanoscale. The growth of particles could consist of the partial crystallization of the crystal phase when the reaction temperature increased as observed in the previous section.

Figure 4 shows the TEM images of BGC-150 and BGC-220 samples. The sizes of spherical particles of both samples are in the nanoscale, in the range of 15–25 nm and 20–40 nm for the BGC-150 sample and BGC-220, respectively. These results are consistent with the observation by FE-SEM images. The results also confirmed the effect of reaction temperature on the particle size of the apatite phase in the synthetic samples.

3.3. Bioactivity of Bioactive Glass-Ceramics. Figures 5 and 6 show the XRD diagrams of BGC-150 and BGC-220 samples after 20 days of immersion in the SBF solution. The XRD pattern of pure hydroxyapatite (HA) was presented as a reference to identify the formation of HA phase on the surface of BGCs after *in vitro* experiment. It is clearly shown that the amorphous phase of BGC-150 and BGC-220 totally disappeared after the immersion of BGC samples in the SBF solution. This confirmed the dissolution of BGC samples in the SBF solution. After *in vitro* experiment, the XRD diagrams of BGC samples characterized by the crystalline materials in which the sharp peaks corresponded to HA

phase were detected at 31.8° and 45.5° ( $2\theta$ ) (JCPDS 90432). It could be noticed that the peak at 31.8° was grown from the initial peak of the BGC samples, while the peak at 45.5° is a new appearance. In addition, the peaks characterized by the CaSiO<sub>3</sub> phase with low intensity were also determined in the XRD diagrams of BGCs after immersion in the SBF solution [15, 16]. Therefore, the bioactivity of BGC-150 and BGC-220 samples was confirmed by the development of a new apatite phase on the surface of BGC samples after the *in vitro* experiment.

Figure 7 showed the SEM images of BGC-150 and BGC-220 samples after 20 days of immersion in the SBF solution. The observation indicated that the new apatite crystals were totally covered on the surface of both samples. Clearly, the larger size of apatite crystals was observed in BGC-220 compared to BGC-150 sample, reflecting the effect of the initial structure of BGCs on the bioactivity of synthetic biomaterials. Due to the larger particle size covering on the surface, the surface of BGC-220 is more porous than that of BGC-150, results in better reactivity between the sample and the SBF solution and efficient formation of apatite crystals. As seen in the FE-SEM images in Figure 3, the surface of sample BGC-220 was covered with the larger-sized particles and created more porosity than the one of sample BGC-150. The porous surface could make the reaction between the



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FIGURE 4: TEM images of BGC-150 and BGC-220 samples.



FIGURE 5: XRD pattern of BGC-150 after 20 days of immersion in SBF solution.

sample and the SBF solution faster, producing more new apatite crystals, and they grow faster on the porous structural surface of the sample.

3.4. Degradation of Bioactive Glass-Ceramics in the SBF Solution. The pH and Si, Ca, and P concentrations are related to the dissolution of BGC samples and then the mineralization of new apatite crystals on the surface of biomaterials [3, 14]. The pH was measured by using a pH



FIGURE 6: XRD pattern of BGC-220 after 20 days of immersion in SBF solution.

meter, while the concentrations of Si, Ca, and P in the SBF solution were identified by the ICP-OES (Figure 8). For both samples BGC-150 and BGC-220, the pH values recorded a sharp increase during the first 7 days and then a slight increase until 20 days of immersion. The Si concentrations in the SBF solution increased with a high rate after the first 7 days for both BGC samples. After that, the Si concentrations were almost constant. The release of Si ions is related to the dissolution of the BGC networks in the SBF solution. Compared to the BGC-150 sample, the Si concentration in the SBF solution for the BGC-220 sample is lower. This can



FIGURE 7: SEM micrographs of BGC-150 and BGC-220 at different magnifications after 20 days of immersion.





FIGURE 8: Evaluations of pH and Ca, Si, and P concentrations in the SBF solution after 0, 7, 14, and 20 days.

be explained by the initial surface of the BGC-220 sample which contained more apatite crystals. These apatite crystals were covered on the surface of the sample and could prevent the release of Si from the structural network versus the SBF solution. The behaviors of Ca and P concentrations for both BGC samples were quite similar, beginning with a significant decrease in the first 7 days and following by a saturate step in the days after. The consumptions of these ions are consistent with the formation of a new apatite layer on the surface of BGC samples after soaking times. The consumed rate of Ca and P for the sample BGC-220 is higher than that of the sample BGC-150. This could be attributed to the faster formation of a new apatite layer on the surface of the sample BGC-220 compared to that of the sample BGC-150.

# 4. Conclusion

Ternary bioactive glass-ceramics (BGCs) with a composition of 60SiO<sub>2-</sub>30 CaO-10P<sub>2</sub>O<sub>5</sub> (wt. %) have been prepared by the hydrothermal method. Two hydrothermal reaction temperatures were selected at 150 and 220°C for the synthesis of BGC-150 and BGC-220 samples. The obtained results showed that the crystallinity and the particle nanosize of BGCs increased when increasing the reaction temperature from 150 to 220°C. In vitro experiment was effectuated by the immersion of BGC powders in the SBF solution. The bioactivity of BGCs was confirmed by the dissolution and the formation of the apatite phase on their surface after in vitro experiments. The hydrothermal technique has been proved to be effective and simple to synthesize BGC samples at low temperature in comparison with melting and conventional sol-gel methods. The crystallinity and particle size could be well controlled by the hydrothermal reaction temperature.

# **Data Availability**

The data used to support the findings of this study are included in the article.

# **Conflicts of Interest**

The authors declare that they have no conflicts of interest.

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