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Fabrication and characterization of ferrimagnetic bioactive glass-ceramic containing $BaFe_{12}O_{19}$

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Abstract

Bioactivity of ferrimagnetic glass-ceramics is useful as thermo seeds for hyperthermia treatment of cancer. Ferrimagnetic glass-ceramics were prepared from the $BaFe_{12}O_{19}$(BF)–SiO_2–CaO–Na_2O–P_2O_5 system using the incorporation method. The mixture was then further sintered at 800 °C to form the glass-ceramic samples. The structure and microstructure of the samples were characterized by X-ray diffraction, energy dispersive X-ray analysis (EDXA) and scanning electron microscopy. Magnetic hysteresis loops of the glass-ceramic samples were obtained with maximum field of 10 kOe, in order to evaluate the potential of these samples for hyperthermia treatment of cancer. *In vitro* bioactivity was investigated in simulated body fluid (SBF) for 14 days. The results showed that $Na_2Ca_2Si_3O_9$ and $BaFe_{12}O_{19}$ were the main phases in the glass-ceramic samples. Apatite was formed on the surface layers of the glass-ceramics, confirming their biocompatibility. It was found that the bioactivity increased with an increase in BF contents.

Keywords: A. Sintering; Glass–ceramic; Ferrimagnetic

1. Introduction

Since the discovery of Bioglass® by Hench in 1970s [1], a variety of bioactive glasses and glass ceramics have been developed for clinical applications due to their good bioactivity [2,3]. Recently, development of bioglass-ceramics with good bioactivity containing magnetic properties has received much attention as a thermo-seed in hyperthermia treatment of cancer, especially deep seated bone tumors [2]. When granular seeds of glass-ceramics are implanted around tumors and then subjected to alternating magnetic fields, heat is generated from magnetic loss, killing the tumors. Generally, such tumors are effectively heated and destroyed at temperatures around 42–45 °C, without the damage of normal tissue. Ferrimagnetic glass-ceramics are potential candidates for magnetic induction hyperthermia [3,4]

Since bioactive ferrimagnetic glass-ceramics possess both bioactivity and magnetic properties having good prospect in hyperthermia, various kinds of such materials have been widely investigated. Abdel-Hameed [5] prepared glass-ceramics containing magnetite phase in a matrix of SiO_2–CaO–P_2O_5–Na_2O based glass which showed ferrimagnetism and good bioactivity after soaking in SBF for 1 week. Another interesting work[6] revealed that the dopant of Mg ferrite to wallastonite-fluorapatite bioglass-ceramics led to the development of magnetic properties but decreased the bioactivity of the materials. However, the Ba ferrite phase, which also has good magnetic properties, has been scarcely used for this type of application. As known, Fe can react with P and Si easily at high temperature to form non-magnetic phase [6]. In order to solve this problem, the present work, therefore attempted to synthesize SiO_2–CaO–Na_2O–P_2O_5 bioactive glass-ceramics containing the Ba ferrite (BF) phase using the incorporation method. In this method, BF crystals were

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firstly produced using the solid-state reaction technique and then added to the glass precursors as a glass batch, which was then further mixed and sintered to form the glass-ceramic. The influence of BF addition on the structural and magnetic properties of the prepared glass-ceramic was studied and the bioactive properties of these materials were analyzed.

2. Experimental procedures

Firstly, barium ferrite ($BaFe_{12}O_{19}$) powder was produced by solid-state reaction technique using Fe_2O_3 and $BaCO_3$ as starting materials with ratio of 6:1. The mixture was ball-milled and calcined at 1100 °C for 3 h.

Secondly, 45S5 bioglass was produced by melting appropriate combinations of SiO_2 45 wt%, Na_2O 24.5 wt%, CaO 24.5 wt% and P_2O_5 6 wt% in an alumina crucible. The mixture was melted at 1300 °C for 2 h and quenched in water. The glass was crushed and ground into powder which was then mixed with the calcined barium ferrite $BaFe_{12}O_{19}$ at 5, 10, 20, and 40 wt.%.The samples were labelled as 5BF, 10BF, 20BF, and 40BF, correspondingly. The green bodies were sintered at 800 °C for 2 h.

The glass transition temperature (T_g) and crystallization temperature (T_c) were estimated using a differential thermal analysis (DTA: 1600 DTA, Du Pont Instrument) and the phase identification of the samples was carried out with an X-ray diffractometer (XRD: Siemen D-500). Then, a scanning electron microscope (SEM: JSM-6335F) was used to observe the microstructures of the prepared glass-ceramics. The magnetic properties were measured using a vibrating sample magnetometer (VSM: LakeShore 7404) at room temperature. *In vitro* test was carried out by soaking in SBF [7]. The SBF was buffered at pH 7.4 and maintained at 37 °C for 14 days. After that, the glass-ceramic samples were analysed for the apatite formation by using a scanning electron microscope based energy dispersive X-ray spectrometer (EDS).

3. Results and discussion

The DTA traces of the investigated glass samples are presented in Fig. 1. It is shown that both T_g and T_c increase when the level of BF increases from 5 to 40 wt %. The increasing trends of T_g and T_c with BF content are attributed to the higher density of BF (4.32 g/cm^3) compared to normal 45S5 glass (2.7 g/cm^3). Generally, the change in T_g with composition reflects a structural evolution in the glass network, and linear trend observed in this work (the inset in Fig. 1) confirms that there is no change in the glass networks of the 45S5 samples with the addition of BF compounds. The sample with 5 wt% BF however exhibits two T_c values at 594 °C and 664 °C, while the higher BF content samples show only one T_c. This may be due to the occurrence of phase separation in the 5 wt% BF glass.

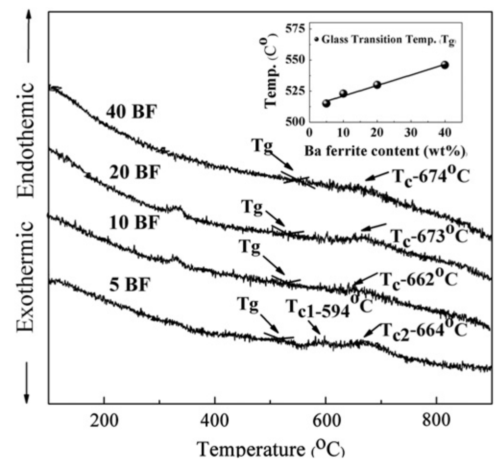

Fig. 1. DTA traces.

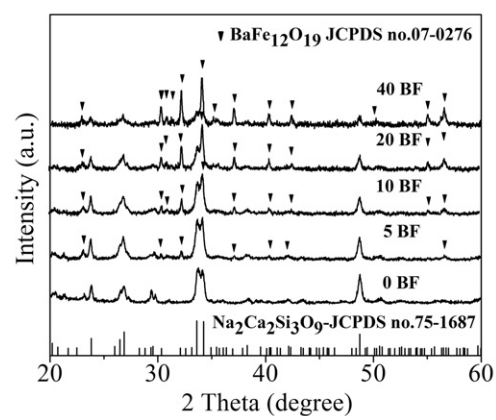

Fig. 2. XRD patterns of the glass ceramic samples sintered at 800 °C.

The X-ray diffraction patterns of the samples sintered at 800 °C are shown in Fig. 2. Two major phases, sodium calcium silicate ($Na_2Ca_2Si_3O_9$) and barium iron oxide ($BaFe_{12}O_{19}$), were identified in all of the sintered samples containing BF. Sodium calcium silicate is nontoxic and its presence indicates the biocompatible nature of the glass-ceramics [8]. By increasing the BF content, the intensity of $BaFe_{12}O_{19}$ increases whereas the intensity of $Na_2Ca_2Si_3O_9$ decreases.

Magnetic hysteresis loops of glass-ceramic samples are shown in Fig. 3. All of the bioglass–ceramic samples display similar magnetic behaviours [5,6]. The results are summarized in Fig. 4. The remanence (M_r) and maximum magnetization increase with an increase in BF contents. It is well known that the saturation magnetization (M_s) depends on the concentration of magnetic phase. With increasing BF contents, the magnetic response of the samples increases. The 40BF sample has the highest magnetic phase with the highest value of saturation magnetization as shown in the inset of Fig. 3. On the other hand, the coercivity changed from 4.4 kOe in 5BF to 2.9 kOe in 40BF. It can be noted that the coercivity of the samples decreases with a rise in BF levels present in the samples as indicated in the inset of Fig. 3 showing the plot of coercivity versus $1/d$.

This result is consistent with the finding that crystallite size depends on the coercivity [7]. In consideration of the multi-domain structure, coercivity decreases with increasing crystallite size because the domain walls can rotate easily along the magnetic field [9]. In contrast, for the pseudo-single domain structure, the coercivity increases with increasing crystallite size [9]. From the result, it may be assumed that the $BaFe_{12}O_{19}$ crystals growing in the glass matrices have a multi-domain structure because the coercivity values decrease with an increase in crystallite size.

The magnetic loss of the materials can be calculated and presented in Fig. 4. It is clearly shown that, for an applied field of ± 10 kOe, the area of the hysteresis loop increased with increasing content of barium ferrite from 5 wt% to 40 wt%. The maximum area was obtained from the 40BF glass ceramic sample exhibiting the highest magnetic content and the highest magnetization.

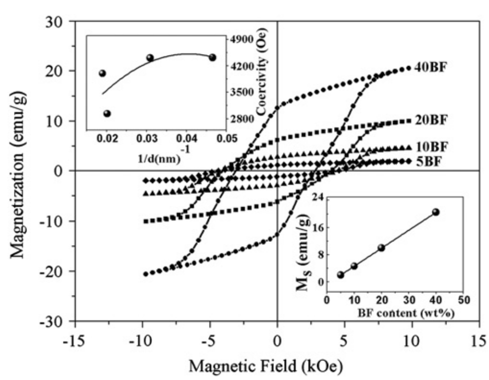

Fig. 3. Hysteresis loops of different glass-ceramic samples containing different BF concentrations.

Fig. 5 shows the SEM micrographs of all samples sintered at 800 °C before incubating in SBF. The micrographs reveal the small granular crystals distributed on the glass ceramic fracture surface. EDS analysis indicated that these granular crystals (bright areas) contained high concentration of Fe, O, and Ba. It may be assumed that these crystals are $BaFe_{12}O_{19}$ phase. The dark areas illustrate glass matrix after sintering at 800 °C (Si, O, Na and Ca). Moreover, the uniform distribution of $BaFe_{12}O_{19}$ crystals increased with increasing BF content while their grain size decreased.

Fig. 6 shows the SEM photographs of all sintered samples after soaking in SBF for 14 days. New layers covering the surface of all samples after incubating in SBF are revealed. EDS analyses showed that the layers contained P and Ca, indicating the formation of apatite layers, confirming that all samples are bioactive. The surface of 5BF sample was plentifully covered by apatite layers with numerous spherical particles. In higher BF samples (10BF and 20BF), the particle sizes of the apatite phase were slightly increased. In addition, EDS analysis confirmed the increase in Ca and P concentrations with simultaneous decrease in Si, Fe, and Ba ions. Especially, the samples having higher BF content exhibited better apatite cell growth. The sharp increase in P concentration is due to the migration of Ca^{2+} and PO_4^{3-} from the solution to the surface whereas the decrease in Si from the surface to the solution resulted in the formation of Si–OH [8]. This is consistent with pH value of SBF solution as shown in Fig. 7. The pH of the initial SBF solution increased due to the ionic exchange between the species H^+ of SBF solution with Ca^+ and Na^+ from sample, and the continuous formation of Si–OH layers. However, in the 40BF sample the spherical particle did not continue to fill the surface layer, with some localized coagulation of the particle (Fig. 6(d)).

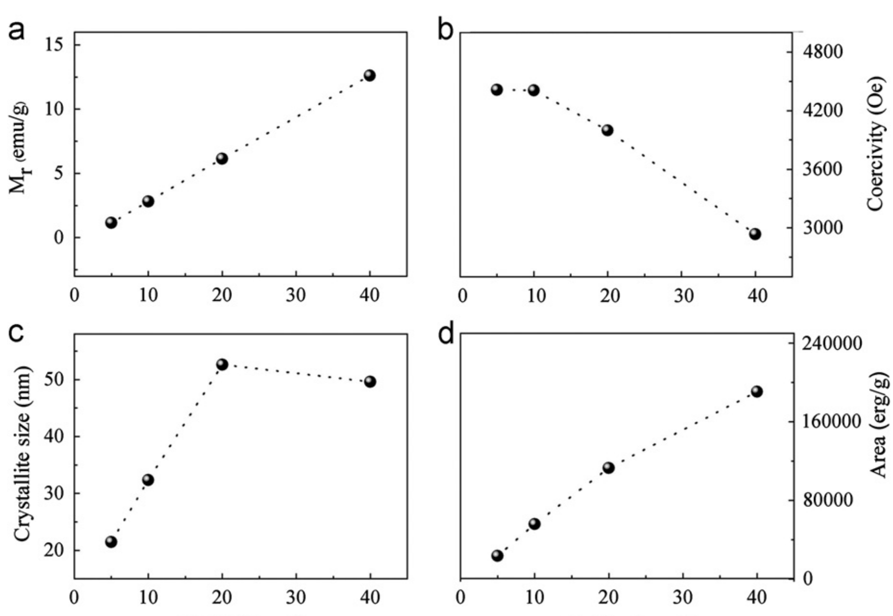

Fig. 4. Magnetic properties evaluated from hysteresis loops.

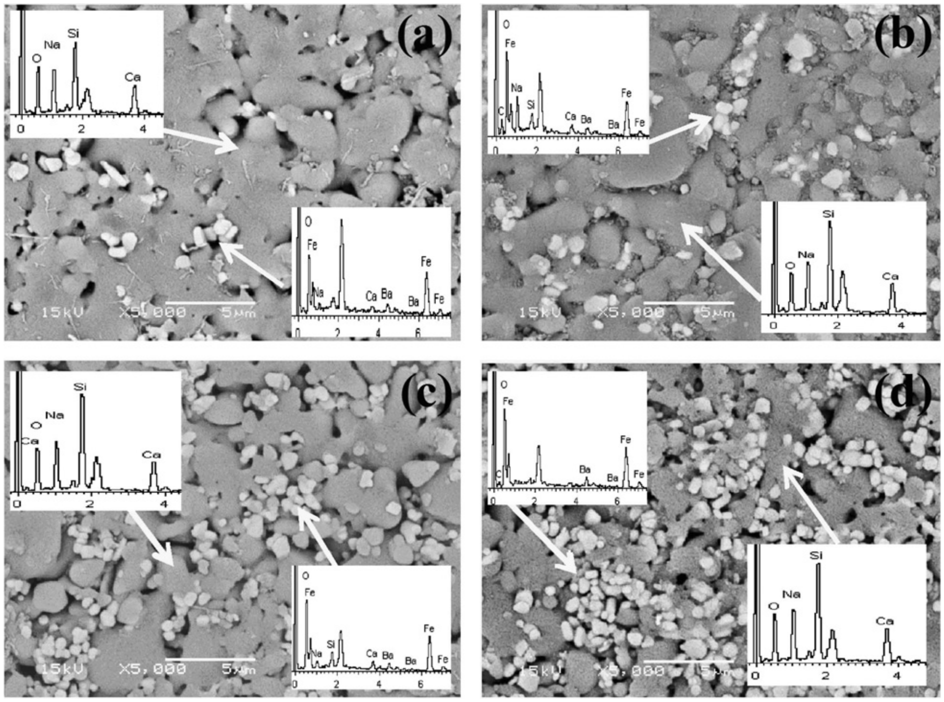

Fig. 5. SEM micrographs and EDS analyses of glass-ceramics: (a) 5BF, (b) 10BF, (c) 20BF and (d) 40BF.

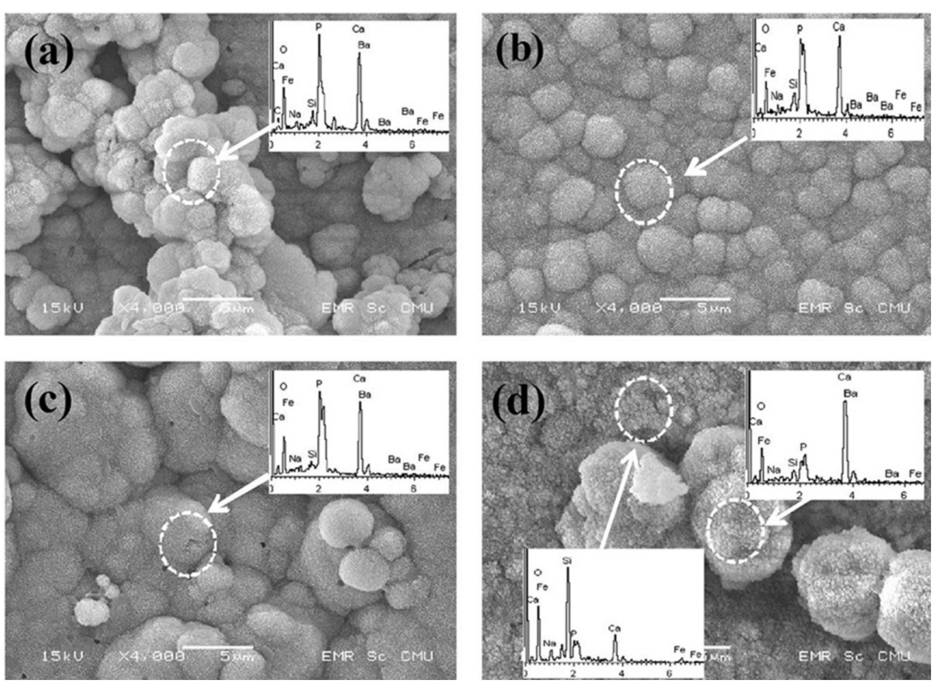

Fig. 6. SEM micrographs and EDS analyses of glass-ceramic samples: (a) 5BF, (b) 10BF, (c) 20BF and (d) 40BF after 14 days in SBF.

EDS analysis showed lower Ca and P than that of the lower BF samples whereas Si ions were higher. These changes in ion concentrations may be associated with the crystallization in glass matrices.

For the XRD results of the sintered samples (Fig. 2), the higher BF content samples, in particular the 20BF sample, had lower crystallinity ($Na_2Ca_2Si_3O_9$) those that of the lower BF samples. This can be clearly observed by the decrease in intensity of the corresponding XRD peaks of $Na_2Ca_2Si_3O_9$ phase with increasing BF content. This higher glassy amorphous phase also has a positive effect on the bioactivity behavior of the samples because the appearanceof a crystal phase has an effect on hindering ion exchange and delaying the formation of the apatite layer resulting in

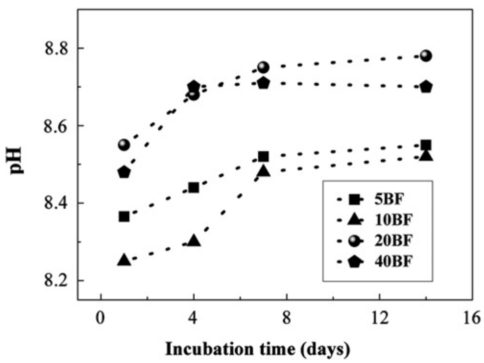

Fig. 7. The pH of the SBF media with incubation time.

reduction of the apatite formation. This is consistent with the work done by Sinsh and Shrinivasan. [7] reporting that the apatite formation increased when the iron oxide contents increased because SiO_2 with Fe_2O_3 did not disturb the formation of Ca and P on the material surface. It is confirmed that the addition of the magnetite phase does not inhibit bioactivity. However, for the 40BF, sample apatite cell growth decreased dramatically. This might be because the amount of $Na_2Ca_2Si_3O_9$ phase which has predominant effect on bioactivity behavior is less in this sample, resulting in the inhibition of apatite cell growth.

4. Conclusion

New ferrimagnetic glass-ceramics from the $BaFe_{12}O_{19}$ (BF)–45S5 system were successfully prepared using the two-step mixed oxide method. Two major phases, sodium calcium silicate and barium iron oxide, were obtained and developed in all sintered samples. The saturation magnetization and hysteresis area increase when BF content increases. The BF crystallite has a multi-domain structure. All of the glass ceramics possess good bioactivity *in vitro* with the formation of a bone-like apatite phase. Hence, the addition of BF into bioglass 45S5 can improve both the magnetic properties and bioactivity of the glass materials.

Acknowledgments

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