EFFECTS OF BZT ADDITION ON PHYSICAL AND ELECTRICAL PROPERTIES OF CALCIUM PHOSPHATE BIOGLASS

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Abstract

The effects of $BaZr_{0.1}Ti_{0.9}O_3$ (BZT) addition on dielectric and piezoelectric properties of calcium phosphate glass (CPG) were investigated. The $BaZr_{0.1}Ti_{0.9}O_3$-40CaO-45P_2O_5-15Na_2O glass was prepared by the conventional melt quenching technique. This study has been carried out in the formula of (1-x) CPG-xBZT where x = 0.00-0.40. Then powder was compacted and sintered at various temperatures. The structural properties were characterized by X-ray diffraction (XRD). From the XRD result, BZT (JCDPS file no. 031-0019), β-$Ca_2P_2O_7$ (JCDPS file no. 03-0604), and $NaPO_3$ (JCDPS file no. 011-0650) were found to precipitate in all glass ceramics. The amount of the BZT phase was found to increase with an increasing BZT content. It was found that the dielectric, piezoelectric, and also the microhardness properties of the glass ceramics could be enhanced by the addition of BZT. The glass ceramics had good bioactivity except for the glass ceramic sample with x = 0.2, which showed no evidence of apatite growth in simulated body fluid for 7 days. Piezoelectric bioglass may be of particular interest in the development of biomaterials for repairing bone defects by regeneration of bone and support of cellular growth.

Keywords: Dielectric, piezoelectric, BZT, calcium phosphate glass, bioglass

Introduction

Developments of biomaterials such as bioactive glass, glass-ceramics, and calcium phosphate for use in dental and orthopedic applications have been extensively carried out (Hench and Ethridge, 1982; Kokubu *et al*., 1982; Nakamura *et al*., 1985; Legeros, 1988; Hench and Wilson, 1993; Xin *et al*., 2005;). Phosphate based glass is of particular interest as it has a low glass transition temperature (T_g), low melting temperature, and a high thermal expansion coefficient. Moreover, it is biodegradable and biocompatible with some human connective tissue cells (Tiwari *et al*., 2007; Marikani *et al*., 2008).

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The calcium phosphate glasses (CPGs) from the ternary P_2O_5-CaO-Na_2O system are considered as a one of the best approaches to obtain materials suitable for bone replacement and regeneration (Zhang and Santos, 2000). The CPGs have a potential for uses in bone substitution application and reconstruction of bone because of their similar chemical composition to the inorganic phase of natural bone (Dias *et al*., 2005; Thonglem *et al*., 2010; Ahmed *et al*., 2011). They also have non-toxicity, bioresorbability, and good biocompatibility, and are able to dissolve in physiological fluids when they are replaced by regenerated tissue (Thonglem *et al*., 2010).

Unfortunately, in various situations, bone substitution by biomaterials has not been completely successful as there is a problem in reconstructive surgery, mainly due to the bad quality of the bone growth around the implants. To solve this problem, a new biomaterial with an optimal osteogenesis function was introduced. (Miara *et al*., 2005). The scope of biomaterials for repairing bone defects has been extended by the addition of lead-free piezoelectric ceramics, such as alkaline niobate and barium titanate-based dielectric compositions, because of their stable piezoelectricity and biocompatibility (Pisitpipathsin *et al*., 2012).

Limited research has attempted to combine the bioactive properties of hydroxyapatite (HA) with a piezoelectric and high permittivity ferroelectric material, such as $BaTiO_3$. Feng *et al*. (1997) prepared HA–$BaTiO_3$ composites, which promoted osteogenesis in the jawbones of dogs. No reaction phases between the 2 phases were observed from X-ray diffraction analysis and the composites exhibited a d_{33} piezoelectric charge coefficient of 6 pC/N. There was, however, no indication of the precise composition of the composites. Almeida *et al*. (2004) presented optical and electrical properties of screen-printed HA–$BaTiO_3$ thick films along with a detailed XRD study but the piezoelectric properties were not reported.

Recently, lead-free ceramics have been intensively studied in large numbers because of their potential as environmentally friendly materials (Maiti *et al*., 2011). Barium zirconium titanate ($Ba(Zr_xTi_{1-x})O_3$, BZT) has attracted great attention for its potential application due to its high dielectric constants and piezoelectric properties (Cai *et al*., 2009; Ricinschi *et al*., 2010). Li *et al*. (2010) reported that the Ba $(Zr_xTi_{1-x})O_3$ at x = 0.10 possessed a Curie temperature at 56°C and $d_{33} \sim 158^{o}$C/N. It is, therefore, interesting to further investigate the effects of piezoelectric materials on the properties of bioactive materials, especially based on the assumption that these composites may be able to stimulate the growth and differentiation of bone tissue when subjected to electromechanical loading.

The aim of this study is to fabricate the (1-x)CPG-xBZT glass-ceramic (x = 0-0.4) in order to study phase formation and the relationship between the electrical properties and bioactivity of CPG-xBZT glass-ceramics. The optimum condition for obtaining the new biomaterials was also reported.

Materials and Method

Material Preparation

The calcium phosphate glass (CPG) containing 45, 40, and 15 mol% of P_2O_5, CaO, Na_2O was prepared by the conventional melt quenching method, using $(NH_4)_2HPO_4$, $CaCO_3$, and Na_2CO_3 as starting materials. The starting materials were weighed following the desired glass composition and melted in an electrical furnace at 1000°C for 1 h using alumina crucibles. The melt was poured onto a stainless-steel plate and quickly pressed by another stainless steel plate for quenching in air. After that the CPG was ground and sieved. Subsequently, the barium zirconium titanate ($Ba(Zr_{0.1}Ti_{0.9})O_3$, BZT) powder was added to the prepared CPG powder. The CPG-BZT ((1-x)CPG-xBZT where x = 0.0, 0.1, 0.2, 0.3 and 0.4) ceramic composites were prepared

by the conventional sintering method. It can be noted that the unit of x is in mole and, therefore, the molecular weight (MW) of CPG glass powder was estimated as 95.6028 g/mol which was further used for batch calculations. The mix powder was milled for 24 h in ethanol media, dried, and pressed into disk-shaped pellets, which were sintered at temperatures ranging from 500°C to 650°C for 2 h in an electric furnace.

Materials Characterizations

The microstructures of all samples were investigated by scanning electron microscopy (SEM). The glass-ceramic samples were sputtered with gold in sputter equipment and then the microstructure of the surface of the samples was observed by SEM operated at the acceleration voltage of 25 kV.

To determine the phase purity and lattice parameters of the calcined powders and ceramics samples, X-ray diffraction technique was performed in the 2θ scan range of 20°-60°. The source of the X-ray is Cu-K_α radiation with a wavelength of 1.54 Å, using a tube voltage and current of 40 kV and 20 mA, respectively. Room temperature XRD data were collected with a step size of 0.02-0.05° per second as a scanning rate. The X-ray diffraction patterns were determined and analyzed by an X'pert High Score Plus program.

The densities of the ceramics were obtained using the Archimedes method which is described in the following Equation (1):

$$\rho_{bulk} = \frac{w_d}{w_{sat} - w_{sus}} \times \rho_w \quad (1)$$

From Equation 1, w_d is dry weight; w_{sus} is sample weight in water; and w_{sat} is the weight of the sample after being taken out of the water. ρ_w is the density of the water which is temperature dependent, as described in following Equation (2):

$$\rho_w = 1.0017\text{-}0.0002315T \quad (2)$$

where T is the temperature of water in degrees Celsius.

Before the measurement, the samples were boiled in distilled water for 5 h and then soaked for an additional 24 h to allow water to replace air in the pores of the samples.

For electrical measurement, the samples were polished and made conductive with a sputtered coating of gold using a sputtering machine. The room temperature dielectric constant (ε_r) of all glass ceramics was measured using an LCZ meter (Model 4276A, Hewlett Packard) at 100 Hz to 2 MHz. The dielectric constant was calculated from the capacitance by the following Equation (3) (Cai *et al*., 2009):

$$\varepsilon = \frac{cd}{\varepsilon_0 A} \quad (3)$$

where C is the capacitance (farads), ε_0 is the free space dielectric constant value (8.854×10^{-12} Fm^{-1}), A is the capacitor area (m^2), and d is the thickness (m) of the samples.

The piezoelectric charge constant (d_{ij}) is defined as the electric polarization generated in a material per unit of the mechanical stress applied to it. Alternatively, it is the mechanical strain experienced by the material per unit of the electric field applied to it. The first subscript refers to the direction of polarization generated in the material (at $E = 0$) or to the applied field strength; the second refers, respectively, to the direction of the applied stress or to the direction of the induced strain.

d_{33} is the induced polarization per unit of the applied stress in direction 3 or the induced strain per unit of the electric field in direction 3.

In this work, the piezoelectric properties properties were measured at room temperature by using a piezoelectric-d_{33}-meter (S5865 d_{33} METER).

Results and Discussion

Figure 1 shows the differential scanning calorimeter (DSC) trace of the CPG quenched

glass. The glass transition temperature (T_g) of this glass was found around 427°C. The exothermic peak at 575°C indicated crystallization occurring in the glass at elevated temperatures. We use the DSC result as a suggestion for an appropriate range of sintering temperatures to further produce glass ceramics which were between 550-650°C.

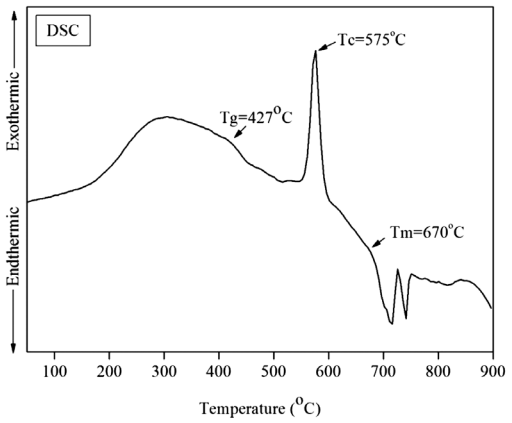

Figure 1. DSC trace of CPG glass where T_g = glass transition temperature, T_c = crystallization temperature, and T_m = melting temperature

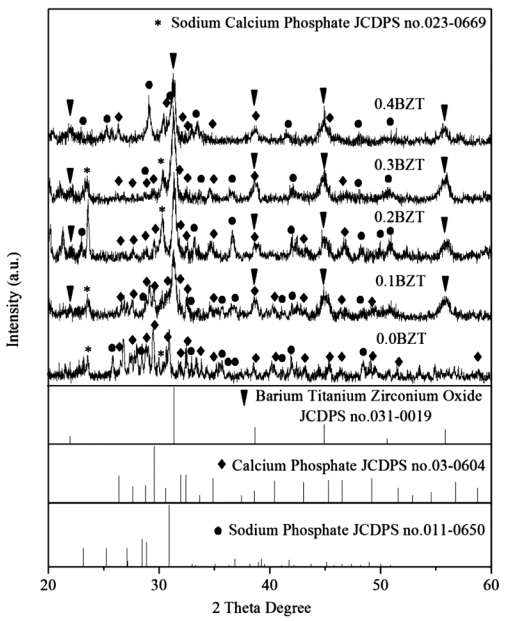

Figure 2. X-ray diffraction patterns of CPG-BZT glass ceramics at various BZT compositions

The XRD spectra of CPG-BZT glass ceramics at various compositions are presented in Figure 2. All XRD signatures obtained for glass ceramics were in good agreement with the stoichiometry of the barium zirconium titanate phase (JCDPS file no. 031-0019), calcium phosphate phase of β-$Ca_2P_2O_7$ (JCDPS file no. 03-0604), and sodium phosphate of $NaPO_3$ (JCDPS file no. 011-0650). As expected, the amount of BZT phase was found to increase with an increasing BZT content.

The experimental density and microhardness data are given in Table 1 for different compositions of CPG- BZT glass ceramics and corresponding graphs were plotted as shown in Figure 3, where the similar trends of both density and microhardness as a function of BZT content are clearly seen. The density of the CPG- BZT glass ceramics varied between 1.90 g/cm^3 and 3.36 g/cm^3, while their microhardness presented between 0.55 GPa and 2.52 GPa. The maximum density could be observed at the x=0.4 BZT sample which also possessed the highest microhardness value.

The electrical properties of CPG-BZT glass ceramics are shown in Figure 4. The highest dielectric constant was obtained for the CPG-BZT glass ceramics at 0.4 BZT

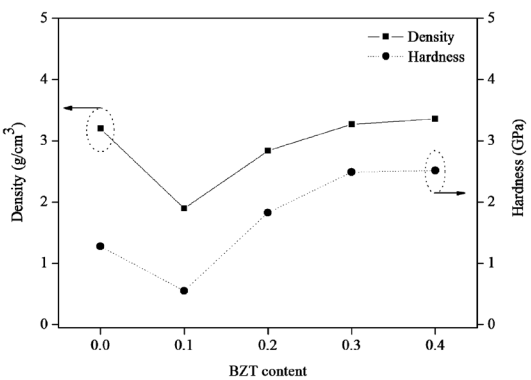

Figure 3. Density and hardness of CPG-BZT glass ceramics at various BZT contents

as a result of the highest density of this sample. The frequency depends on the relative permittivity (ε_r) indicating that all CPG-BZT glass ceramic samples gave a degree of dielectric dispersion at a low frequency (f<10 kHz). The permittivity magnitude and degree of dispersion increased with an increasing BZT content. The dispersion in the CPG-BZT glass ceramics, probably, is attributed to the dipole moment of ions in CPG-BZT glass ceramics. The trend of piezoelectric coefficient (d_{33}) is shown in the inset of Figure 4. It was seen that the d_{33} value increased with an increasing BZT content, which may be attributed to the presence of the BZT ferroelectric phase. In their previous work, Feng *et al*. (1997) prepared HA–$BaTiO_3$ composites and found that their composites with d_{33} with 6 pC/N could promote osteogenesis in the jawbones of dogs. In our study, the CPG-BZT glass ceramic with x = 0.4 possessed the d_{33} of 7 pC/N which was a good sign for the possibility to use this composite for generating osteogenesis in *vitro*.

The scanning electron micrographs of the surface of CPG-BZT glass-ceramics before and after immersion in the stimulated body fluid (SBF) for 7 days are illustrated in Figure 5. It was observed that apatite-like layers were found on most of the glass ceramic surfaces except for the glass ceramic samples with x = 0.2. From the XRD results, it was interesting that only the glass ceramic

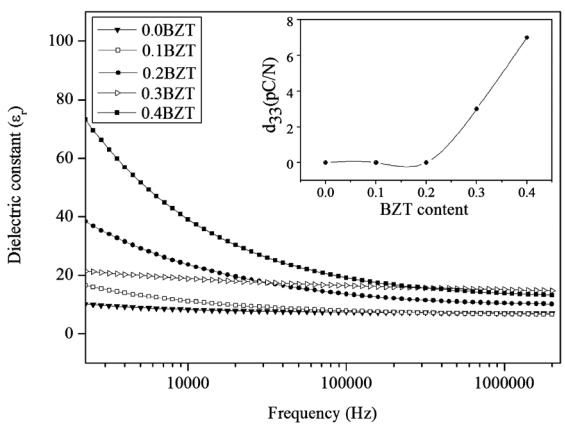

Figure 4. Frequency dependence of dielectric constant of CPG-BZT glass ceramics at various BZT contents

Table 1. The hardness, density and piezoelectric constant (d_{33}) of CPG-BZT glass ceramics

Condition	Hardness (GPa)	Density (g/cm^3)	Piezoelectric constant (d_{33})
0.0	1.28	3.20	0
0.1	0.55	1.90	0
0.2	1.83	2.84	0
0.3	2.49	3.27	3
0.4	2.52	3.36	7

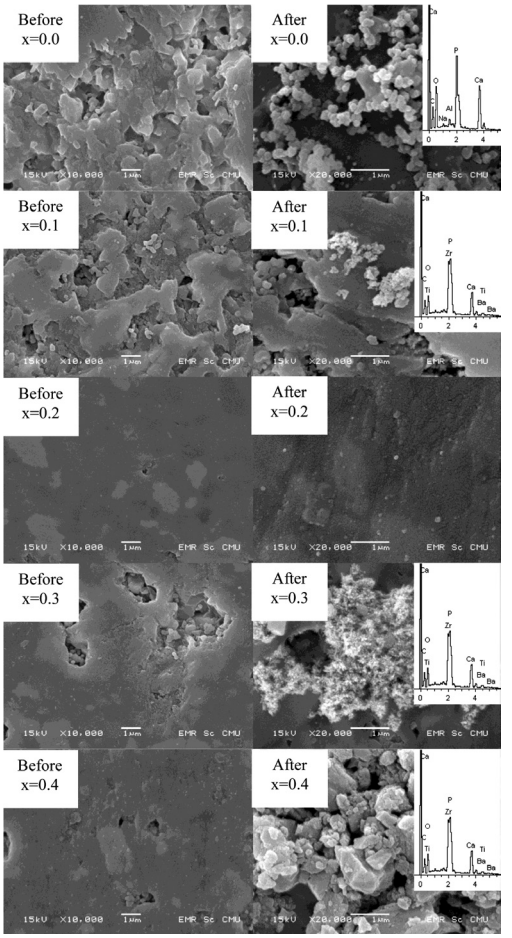

Figure 5. SEM micrographs of CPG-BZT glass ceramics before and after immersion in SBF for 7 days

samples with x = 0.2 and 0.3 (BZT) containing sodium calcium phosphate, and especially the corresponding peaks were maximum for the x = 0.2 sample. This phase may, in turn, inhibit or retard the growth of apatite-like phase in SBF. However, further study should be carried out in order to verify this assumption.

Conclusions

Bioactive ferroelectric (1-x)CPG-xBZT glass ceramics for orthopedic applications have been produced by adding BZT in CPG bioglass, where x were ranged from 0 to 0.4 mole. It was found that the addition of BZT improved the dielectric property of materials which may be attributed to the presence of the ferroelectric BZT phase. Moreover, the hardness of CPG bioglass was improved with the addition of the BZT content. The bioactivity of the CPG-BZT glass ceramics was evident by the formation of bone-like apatite layers on the surface of the x = 0.3-0.4 samples after soaking in SBF for 7 days. The optimized composition for the CPG-BZT system was found to be x = 0.4, the maximum value of density of 3.36 g/cm^3, and hardness of 2.52 GPa with suitable bioactivity.

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References

Ahmed, A.A., Ali, A.A., Mahmoud, A.R., and El-Fiqi, A.M. (2011). Study on the preparation and properties of silver-doped phosphate antibacterial glasses (Part I), Solid State Sci., p. 13.

Almeida, A.F.L., Fechine, P.B.A., Sasaki, J.M., Ayala, A.P., Góes, Pontes, J.C.D., Margulis, L.W., and Sombra, A.S.B. (2004). Optical and electrical properties of barium titanate-hydroxyapatite composite screen-printed thick films. Solid State Sci.., 6:267–278.

Cai, W., Fu, C., Gao, J., Chen, X., and Zhang, Q. (2009). Microstructure and dielectric properties of barium zirconate titanate ceramics by two methods. Integr. Ferroelectr., 113: 83–94.

Dias, A.G., Skakle, J.M.S., Gibson, I.R., Lopes, M.A., and Santos, J.D. (2005). In situ thermal and structural characterization of bioactive calcium phosphate glass ceramics containing TiO_2 and MgO oxides: High temperature–XRD studies. J. Non-Cryst. Solids, 351:810–817.

Feng, J.Q., Yuan, H.P., and Zhang, X.D. (1997) Promotion of osteogenesis by a piezoelectric biologicalceramic. Biomaterials, 18(23):1531-1534.

Hench, L.L. and Ethridge, E.C. (1982). Biomaterials: An Interfacial Approach. Vol. 4. Academic Press, NY.

Hench, L.L. and Wilson, J. (1993). An Introduction to Bioceramics: Advanced Series in Ceramics. Vol. 1. World Scientific, Singapore, 303p.

Kokubo, T., Nagashima, Y., and Tashiro, M. (1982). Preparation of apatite-containing glass ceramics by sintering and crystallization of glass powder. Japanese Ceramic Society, 90(3):151.

Legeros, L.Z. (1988). Calcium phosphate materials in restorative dentistry: a review. Advances in Dental Research, 2:164-183.

Li, W., Xu, Z., Chu, R., Fu, P., and Zang, G. (2010) Dielectric and piezoelectric properties of $Ba(Zr_xTi_{1-x})O_3$ lead-free ceramics. Braz. J. Phys., 40(3):353-356.

Maiti, T., Guo, R., and Bhalla, A.S. (2011). Evaluation of experimental resume of $BaZr_xTi_{1-x}O_3$ with perspective to ferroelectric relaxor family: An overview. Ferroelectrics, 425:4–26.

Marikani, A., Maheswaran, A., Premanathan, M., and Amalraj, L. (2008). Synthesis and characterization of calcium phosphate based bioactive quaternary P_2O_5–CaO–Na_2O–K_2O glasses. J. Non-Cryst. Solids, 354:3929–3934.

Miara, B., Rohan, E., Zidic, M., and Labat, B. (2005). Piezomaterials for bone regeneration design-homogenization approach. J. Mech. Phys. Solids, 53:2529–2556.

Nakamura, T., Yamamuro, T., Higashi, S., Kokubo, T., and Ito, S. (1985). A new glass-ceramic for bone replacement: evaluation of its bonding to bone tissue. J. Biomed. Mater. Res., 19: 685-698.

Pisitpipathsin, N., Kantha, P., Leenakul, W., Sriprapa, P., Pengpat, K., Eitssayeam, S., and Rujijanagul, G. (2012). Effect of $BaZr_{0.05}Ti_{0.95}O_3$ addition on microstructure and piezoelectric properties of Hydroxyapatite bone. Adv. Mat. Res., 56:166-169.

Ricinschi, D., Ciomaga, C.E., Mitoseriu, L., Buscaglia, V., and Okuyama, M. (2010). Ferroelectric–relaxor crossover characteristics in Ba $(Zr_xTi_{1-x})O_3$ ceramics investigated by AFM-piezoresponse study. J. Eur. Ceram. Soc., 30:237–241.

Thonglem, S., Pengpat, K., Rujijanagul, G., Eitssayeam, S., Punyanitya, S., and Tunkasiri, T. (2010). Effects of CaO on properties of P_2O_5-CaO-Na_2O glasses and glass ceramics. Journal of Metals, Materials and Minerals, 20(3):173-177.

Tiwari, B., Dixit, A., and Kothiyal, G.P. (2007). Preparation and characterization of phosphate glasses containing titanium. BARC Newsletter.

Xin, R., Leng, Y., Chen, J., and Zhang, Q. (2005). A comparative study of calcium phosphate formation on bioceramics in vitro and in vivo. Biomaterials, 26:6477–6486.

Zhang,Y. and Santos, J.D. (2000). Crystallization and microstructure analysis of calcium phosphate-based glass ceramics for biomedical applications. J. Non-Cryst. Solids, 272:14-21.