

CHARACTERIZATION OF PIEZOCERAMIC-HYDROXYAPATITE COMPOSITES FOR BONE TISSUE ENGINEERING

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Abstract

Hydroxyapatite (HA) has been widely used as bone repairing material, as its chemical composition resembles human bone composition. However, different clinical reports reveal that pure HA has a low bone induction while having low mechanical properties; in addition, it is understood by scientist that piezoelectric properties can be observed in human bone tissue. Therefore, this study anticipates that use of the piezoelectric effect in lead-free piezoceramics would be feasible for bone repair applications. The crystal structure, microstructure, and electrical properties of barium titanate (BT), barium calcium zirconate titanate (BCZT), 90BT-10HA composites and 90BCZT-10HA composites were therefore investigated. X-ray diffraction (XRD) patterns revealed that apure perovskite phase was observed in pure BT and BCZT ceramics, while HA decomposition was found in 90BT-10HA and 90BCZT-10HA ceramics. Furthermore, addition of HA into BT and BCZT ceramics caused a decrease in average grain size and dielectric permittivity as well as polarization. In summary, results showed that 90BT-10HA ceramics is a promising candidate for use in bone implants and for bone repair applications, since it exhibited good dielectric permittivity and polarization.

Keywords: Lead-free piezoceramics, electrical properties, biomaterials, bone-repair applications

Introduction

Hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] (HA) is a bioceramic that has been widely used as a synthetic bone that substitutes in orthopedic applications due to its excellent bioactivity. Equally important, HA composition is similar to the natural bone (Suchanek and Yoshimura, 1998; Nakamura *et al.*, 2007). However, some limitations of HA, such as low bone induction may be observed in medical applications (Zhou and Lee, 2011).

Basically, human bones can produce biological electricity under the application of mechanical stress, which is called the piezoelectric effect (Fukada and Yasuda, 1957). Recently, there has been a growing interest in producing piezoceramic composites between HA and lead-free piezoelectric materials for bone implants materials (Prakasam *et al.*, 2017; Sikder *et al.*, 2019). In addition, some in-vivo studies suggested that the enhancement

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of nerve repair, bone regeneration, cell proliferation and cell adhesion between bone tissue and the implant material made of piezoceramics could be observed (Rajabi *et al.*, 2015; Jacob *et al.*, 2018).

Alternatively, Barium Titanate or BaTiO₃ (BT) is an interesting lead-free piezoelectric candidate for using in bone-repair applications due to its excellent bioactivity, biocompatibility, high dielectricity and mechanical properties as reported by Park and Jacob (Park *et al.*, 1977; Jacob *et al.*, 2018). Moreover, Gittings observed that the addition of BT, at least 80% volume into HA, was required to improve the piezoelectric properties (Gittings *et al.*, 2007); whereas, Baxter and Tang found that the composite between BT and HA in the ratio of 90:10 weight percent was shown not to be cytotoxic while exhibiting the best biocompatibility and bone-inducing activities with human cells (Baxter *et al.*, 2009; Tang *et al.*, 2017).

Recently, the excellent piezoelectric coefficient (d_{33}) at a low Curie temperature (T_c) was observed in (Ba_{0.85}Ca_{0.15})(Zr_{0.1}Ti_{0.9})O₃ (BCZT) lead-free piezoceramic (Cheng *et al.*, 2005; Li *et al.*, 2010; Wang *et al.*, 2011; Wu *et al.*, 2012). Therefore, the BCZT piezoceramic is also an interesting material for use in bone implants. Hence, this work aims to investigate the microstructure, crystal structure, and electrical properties of BT and BT-HA composite in comparison to the BCZT and BCZT-HA composite at the ratio between BT or BCZT: HA of 90wt%: 10wt%, since Tang reported that the 90wt% BaTiO₃: 10wt% HA ceramic showed the best biocompatibility and bioactivity at this composition.

Materials and Methods

HA or Ca₁₀(PO₄)₆(OH)₂ in this work was prepared via aqueous precipitation method using Ca(OH)₂, H₃PO₄ and NH₃ solutions as precursors, while BaTiO₃ and (Ba_{0.85}Ca_{0.15})(Ti_{0.9}Zr_{0.1})O₃, or BT and BCZT respectively, were prepared via solid-state reaction. The starting materials for preparing BT and BCZT, which were barium carbonate (BaCO₃, 99.0%), calcium carbonate (CaCO₃, 99.0%), titanium dioxide (TiO₂, 99.0%), and zirconium dioxide (ZrO₂, 99.0%), were weighed and milled for 24 h in ethanol using zirconia balls as the grinding media and then dried for 24 h prior to calcination at 1,250°C for 3 h in high-purity alumina crucible at a heating and cooling rate of 5°C/min. In order to prepare the BT-HA and BCZT-HA powders, the powder mixture ratio was 90wt% BT or BCZT powder to 10wt% HA powder (90BT-10HA and 90BCZT-10HA) which were milled for 24 h in ethanol followed by drying at 90°C for 24 h.

Afterwards, the BT, BCZT, 90BT-10HA and 90BCZT-10HA powders were weighed at 0.3 g prior to mixing with 1 drop of PVA binder solution and then subsequently pressed at 94 MPa for 30 sec into a pellet with diameter of 13 mm and thickness of ~1 mm. Once that process was completed, all green samples were heated at 500°C for 1 h in order to eliminate the PVA binder prior to further heating, using the sintering process, to 1,350°C for 3 h at a heating and cooling rate of 5°C/min.

The density of BT, BCZT, 90BT-10HA, and 90BCZT-10HA were measured applying Archimedes' principle. The theoretical density of 90BT-10HA and 90BCZT-10HA composite was calculated by using Equation (1)

$$\frac{1}{\rho_t} = \frac{1-x}{\rho_1} + \frac{x}{\rho_2} \quad (1)$$

where ρ_t is the theoretical density of composite, ρ_1 and ρ_2 are the theoretical density of BT or BCZT and HA, respectively, and x is volume fraction of a HA.

The surface microstructure of all sintered samples was observed by using the Scanning Electron Microscopy instrument analyzer (Benchtop SEM, Model JEOL JCM6000, JAPAN), while the crystal structure was investigated by examined using an X-Ray Diffractometer (XRD, Bruker AXS Model D8 Advance, Germany). To obtain electrical measurements, the parallel surfaces of the ceramic pellets were ground using P800-grade SiC paper before coating the pellets with an air-dried silver paint (SPI-5001) used as electrode. The dielectric permittivity and loss tangent were measured using a LCR Meter (Alilent, E4980A) with frequency at 100Hz to 1,000kHz at room temperature. In addition, a Radiant Technology ferroelectric tester was employed to measure the ferroelectric hysteresis loop (P-E loop) under the application of electric field from 0.012 kV/cm to 20 kV/cm.

Results and Discussion

The XRD patterns of BT, BCZT, 90BT-10HA, and 90BCZT-10HA ceramics sintered at 1,350°C for 3 h are presented in Figure 1. It was found that the perovskite structure (JCPDS 03-0725) was observed in all compositions. Regarding BT and 90BT-10HA ceramics, the splitting of (002) and (200) peaks at 2 θ around 44°-46° was identified clearly, which indicated that the tetragonal phase was found in these compositions. However, the lattice parameters of 90BT-10HA was slightly lower than the pure BT,

as shown in Table 1. This may be attributed to the occurrence of Ca^{2+} (ionic radius $\sim 1.34 \text{ \AA}$) from HA phase substitution into the Ba^{2+} site (ionic radius $\sim 1.64 \text{ \AA}$) of BT main phase (Chen *et al.*, 2015). As a result, a decrease amount of lattice parameters was observed in 90BT-10HA ceramic. Moreover, the ratio of BT to HA was 90:10 wt%, the tetragonality (c/a), was also reduced from 1.0099 to 1.0090 $\text{\AA}$ which suggested that the degree of distortion was lower as well. Correspondingly, Keswani found that the addition of Ca^{2+} into BT ceramic, sintered occurred at $1,400^\circ\text{C}$, which led to the decrease of crystallographic parameters a from 3.9917 to 3.9814 $\text{\AA}$, c from 4.0307 to 4.0175 $\text{\AA}$, and c/a from 1.0098 to 1.0091 $\text{\AA}$ (Keswani *et al.*, 2018).

In contrast, the XRD pattern of BCZT ceramic showed the broad peak at 2θ around $44^\circ\text{--}46^\circ$. According to the BCZT phase diagram, this composition occurs near to the convergence region; the coexistence of tetragonal-orthorhombic-

rhombohedral phases may be observed at room temperature (Bai *et al.*, 2015; Yang *et al.*, 2016). For XRD pattern of 90BT-10HA and 90BCZT-10HA ceramics, the diffraction peaks of HA were in agreement with JCPDS 09-0432. Moreover, the decomposition of HA into α -tricalcium phosphate ($\alpha\text{-Ca}_3(\text{PO}_4)_2$, JCPDS 09-0348) and β -tricalcium phosphate ($\beta\text{-Ca}_3(\text{PO}_4)_2$, JCPDS 03-0713) was observed, as obviously shown in Figure 1. This can be explained by the fact that the loss of OH^- in HA lead to the presence of β -tricalcium phosphate upon further heating to above $1,200^\circ\text{C}$, at which point the β -tricalcium phosphate was decomposed into α -tricalcium phosphate with CaO (Gittings *et al.*, 2009). This reaction shown in Equation (2) is in consistent with (Dosen and Giese, 2011; Prakasam *et al.*, 2017; Senra *et al.*, 2020). However, Ou mentioned that the amount of CaO was too small and could not be detected by XRD which corresponded to this work (Ou *et al.*, 2013).

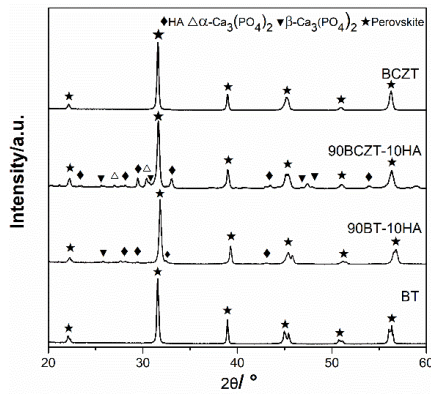
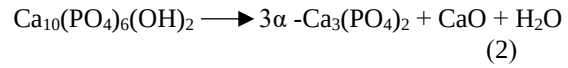


Figure 1. XRD patterns of BT, BCZT, 90BT-10HA, and 90BCZT-10HA ceramics

Table.1. Summary of the crystallographic parameters of the tetragonal phase for pure BT and 90BT-10HA ceramics sintered at $1,350^\circ\text{C}$ for 3h

composition	a ($\text{\AA}$)	c ($\text{\AA}$)	c/a
BT	3.9888	4.0284	1.0099
90BT-10HA	3.9601	3.9957	1.0090

Figure 2 illustrates the surface microstructures of BT, BCZT, 90BT-10HA, and 90BCZT-10HA ceramics observed by SEM, while Table 2 presents the summary of their densities, grain size, and

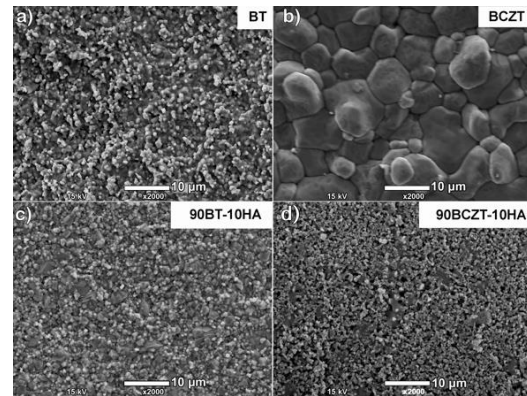


Figure.2. SEM micrographs (x2000) of a) BT b) BCZT c) 90BT-10HA and d) 90BCZT-10HA ceramics sintered at 1350°C for 3h

Table 2. Summary of measured density, theoretical density, relative density, average grain size, dielectric permittivity, and loss tangents for BT, BCZT, 90BT-10HA, and 90BCZT-10HA ceramics sintered at $1,350^\circ\text{C}$ for 3h

Composition	Measured density ($\text{g}\cdot\text{cm}^{-3}$)	Theoretical density ($\text{g}\cdot\text{cm}^{-3}$)	Relative density (%)	Grain size (μm)	$f = 1\text{kHz}$	
					ϵ_r	$\tan\delta$
BT	5.54 ± 0.28	6.020	92.06 ± 4.7	0.92 ± 0.18	2,901.08	0.11366
BCZT	4.50 ± 0.53	5.620	80.05 ± 9.39	6.44 ± 1.14	2,421.06	0.061432
90BT/10HA	4.31 ± 0.21	5.519	78.05 ± 3.89	0.91 ± 0.05	605.54	0.03964
90BCZT/10HA	4.16 ± 0.19	5.21	79.91 ± 3.71	0.74 ± 0.06	210.23	0.107517

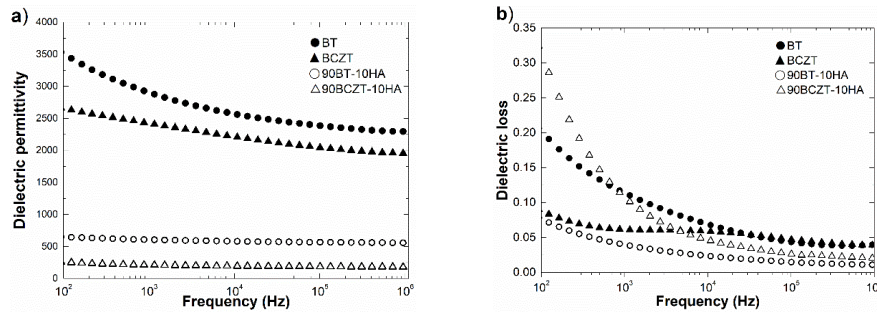


Figure 3. a) Dielectric permittivity, b) Dielectric loss tangent at 100Hz-1000kHz for pure BT, pure BCZT, 90BT-10HA, and 90BCZT-10HA ceramics

room-temperature dielectric properties measured at frequency of 1 kHz. The average grain size of pure BT ($\sim 0.92 \mu\text{m}$) was significantly smaller than pure BCZT ceramics ($\sim 6.44 \mu\text{m}$). This observation was common for BCZT ceramic prepared by solid-state reaction (Wang *et al.*, 2011). However, when adding HA into BT and BCZT for 10wt%, the average grain size of 90BCZT-10HA ceramic dropped dramatically to less than $1 \mu\text{m}$, whereas 90BT-10HA ceramic found a slight drop of grain size. This is attributed to the addition of HA which commonly observed small grain size (Tavangar *et al.*, 2020). Furthermore, the relative density also decreased from 92.06% (for BT) to 78.05% (for 90BT-10HA) and 80.05% (for BCZT) to 79.91% (for 90BCZT-10HA), as presented in Table 2. However, measured density of 90BT-10HA and 90BCZT-10HA ceramics was significantly lower than its theoretical density, calculated from Equation (1). This can be explained by the fact that the decomposition of HA (theoretical density = 3.14 g/cm^3) into α -tricalcium phosphate (theoretical density = 2.86 g/cm^3) and β -tricalcium phosphate (theoretical density = 3.07 g/cm^3) was observed in 90BT-10HA and 90BCZT-10HA ceramics, leading to the occurrence of a huge difference between measured and theoretical densities of 90BT-10HA and 90BCZT-10HA ceramic observed in this work (Ahmad *et al.*, 2012).

In addition, it was found, by adding HA into BT or BCZT a uniform pore distribution was observed, as seen in Figure 2(c) and 2(d). As a result, the densities of 90BT-10HA and 90BCZT-10HA ceramics were lower than pure BT and BCZT ceramics. However, the increase of pore distribution by adding HA into BT and BCZT can enhance the interconnection between the osteogenic cells and the open pores when used in bone-tissue engineering, as reported by Bose *et al.* (Bose *et al.*, 2012).

To evaluate the electrical properties, the room-temperature dielectric and ferroelectric properties of BT, BCZT, 90BT-10HA, and 90BCZT-10HA

ceramics were measured in this work. Figure 3 shows the dielectric permittivity (ϵ_r) and a loss tangent ($\tan\delta$) as a function of frequency in a range of 100Hz to 1,000kHz at room temperature. The dielectric properties can be related to the microstructures, crystalline phases distributions, and the densification degree (Wang *et al.*, 2011; Vouilloz *et al.*, 2017; Tavangar *et al.*, 2020). This work observed that the addition of HA into BT or BCZT ceramics caused a significant drop in ϵ_r , as seen in Figure 3(a). At 1 kHz, the addition of 10wt% HA into BT caused a decrease of ϵ_r from 2,901.08 (pure BT) to 605.54 (90BT-10HA), whereas adding HA into BCZT caused the drop of ϵ_r from 2,421.06 (pure BCZT) to 210.23 (90BCZT-10HA). Moreover, it was found that pure BT and BCZT ceramics showed a stronger frequency dependence than 90BT-10HA and 90BCZT-10HA ceramics, which are shown in Figure 3(b). This suggested that the relaxor behavior was observed in BT and BCZT ceramics (Parjansri *et al.*, 2015). According to Table 2, it was found that pure BT ceramic showed the highest $\tan\delta$ at 1 kHz.

Interm of ferroelectric properties, the polarization-electric field (P-E) hysteresis loops measured at room temperature for BT, BCZT, 90BT-10HA, and 90BCZT-10HA are shown in Figure 4. Basically, the area of the P-E hysteresis loop is proportional to the loss tangent, whereas the slope proportional to the capacitance of ceramics (Stewart *et al.*, 1999). Figure 4(a) shows that a rounded with large area of hysteresis loop was observed in pure the BT ceramics, indicating the characteristic of lossy capacitor response. This outcome correspond to the result shown in Table 2 that shows the highest $\tan\delta$ was observed in the pure BT ceramic. In contrast, the slim P-E hysteresis loop with saturation polarization (P_{sat}) of $11.881 \mu\text{C/cm}^2$, remnant polarization (P_r) of $3.283 \mu\text{C/cm}^2$, and coercive field (E_c) of 2.332 kV/cm were found in the BCZT ceramic, as shown in Figure 4(a). The occurrence of lossy P-E loop found

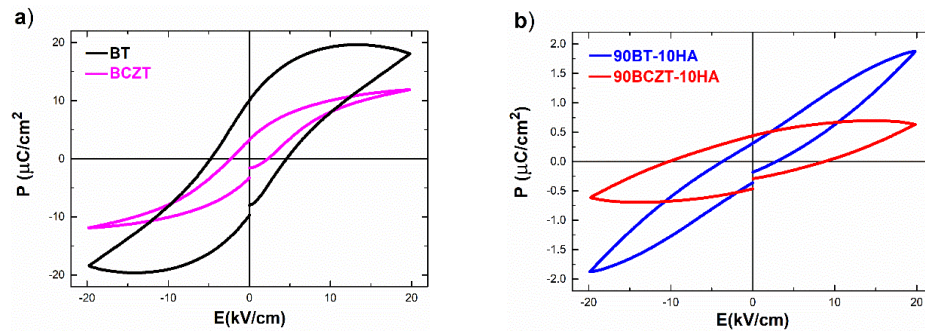


Figure 4. P-E hysteresis loops for: a) BT and BCZT, b) 90BT-10HA and 90BCZT-10HA ceramics measured at room temperature with the applied field of 20kV/cm

Table 3. The saturation polarization (P_{sat}), remnant polarization (P_r), and coercive field (E_c) of BT, BCZT, 90BT-10HA, and 90BCZT-10HA ceramics

Composition	P_s ($\mu\text{C}/\text{cm}^2$)	P_r ($\mu\text{C}/\text{cm}^2$)	E_c (kV/cm)
BT	19.631	9.667	4.720
BCZT	11.881	3.283	2.332
90BT/10HA	1.878	0.312	2.840
90BCZT/10HA	0.697	0.464	8.661

in pure BT ceramic may be attributed to its density that may not be dense enough, since a higher sintering temperature (at 1,475°C) was required for sintering BT as reported (Bai *et al.*, 2015). However, a sudden drop of polarization was observed when adding 10wt% of HA into BT and BCZT, as seen in Figure 4(b). The P_{sat} of 1.878 $\mu\text{C}/\text{cm}^2$ and P_r of 0.697 $\mu\text{C}/\text{cm}^2$ were observed in the 90BT-10HA ceramic; whereas, the 90BCZT-10HA ceramic showed that there were different values between the P_{sat} of 0.312 $\mu\text{C}/\text{cm}^2$ and P_r of 0.464 $\mu\text{C}/\text{cm}^2$. This corresponds to the Phromyoo's report that the P_{sat} was 1.75 $\mu\text{C}/\text{cm}^2$ while the P_r was 1.5 $\mu\text{C}/\text{cm}^2$ in the composite of BZT and HA, 80%vol and 20%vol, respectively (Phromyoo *et al.*, 2018). The summaries of P_{sat} , P_r , and E_c for BT, BCZT, 90BT-10HA, and 90BCZT-10HA ceramics are presented in Table 3.

Conclusions

In summary, the crystal structure, microstructure and electrical properties of BT, BCZT, 90BT-10HA and 90BCZT-10HA ceramics sintered at 1,350°C for 3 h were investigated in this work. The XRD result showed that the perovskite phase was found in BT and BCZT, while the decomposition of HA occurred in both 90BT-10HA and 90BCZT-10HA ceramics. Regarding the microstructure, the addition of HA into the BT and BCZT ceramics

caused a decrease of the average grain size. Furthermore, the addition of HA into BT and BCZT led to a significant drop of the dielectric permittivity as well as the polarization. For biomedical applications, the electrical properties of bone implant materials could be improved by using the composites of piezoelectric materials and HA. As a result, the 90BT-10HA composite can be considered as a promising candidate for bone-repair applications.

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