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The Electrical Properties of BCZT Lead-Free Ceramics Induced by $BaZrO_3$ Seeds

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Abstract. $Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$ (BCZT) ceramics were produced by using the seed-induced method. The nano-particle BZ ($BaZrO_3$) seeds were mixed with $BaCO_3$, $CaCO_3$, ZrO_2 and TiO_2 powder for preparing by the mixed oxide method. The XRD results indicated that all powder and sintered ceramic samples showed a pure perovskite phase with coexistence between rhombohedral and tetragonal phase. As the BZ seed content increased, the density of ceramics tended to decrease from 5.61 g/cm^3 to 5.37 g/cm^3. The average grain size of the ceramics was in the range of 12.15 - 13.50 μm. The dielectric loss (tanδ) was less than 0.03 for all samples at room temperature (at 1 kHz). Other electrical properties, including dielectric constant (ε_r), remnant polarization (P_r), and piezoelectric charge coefficient (d_{33}) values decreased with increasing BZ seed doping with relates to the decreasing grain size and density of BCZT ceramics. However, the values of coercive field (E_c) decreased and piezoelectric voltage coefficient (g_{33}) increased with BZ seed doping.

Introduction

Nowadays, lead-free ceramics have received considerable attention because of their good electrical properties and are widely employed for piezoelectric device applications [1-2]. Recently, many researchers have studied and reported modified $BaTiO_3$ (BT)-based ceramics. $Ba_{(1-x)}Ca_xZr_{(x)}Ti_{(1-x)}O_3$ can be obtained by modification of BT ceramic with the addition of cacium (Ca) into the Ba site (A-site) and zirconium (Zr) into Ti site (B-site) [3]. These ceramics have received wide interest because of their high piezoelectric, and dielectric properties. A high d_{33} value of ~600 pC/N was obtained for BCZT ceramic with the composition of $Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$, obtained using high calcinations temperatures and dwelling times for forming pure perovskite phase [4]. In recent years, the procedures which can reduce calcination temperature such as using template grain growth (TGG) or seed-induced method and also doping with various elements have been studied [5-7]. Normally, the template or seed materials were prepared by sol-gel [6] and molten-salt method [7] because these methods can produce nano-particle size powder. The seed-induced method to form a pure perovskite phase at low temperature has been studied by Li et al [6]. Template grain growth to produce good electrical properties of BCZT ceramic has been reported by Ye et al [7]. Ye and co-workers found that BT template added samples show excellent piezoelectric coefficients and have Curie temperatures higher than non-template samples. From the above reports, it can be concluded that the seed-induced method and template grain growth can reduce calcination temperatures and enhance the electrical properties of piezoelectric ceramics. However, using $BaZrO_3$ seed has not been reported. Thus, in the present work, we studied the preparation and electrical properties of $Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$ ceramic by using $BaZrO_3$ (BZ) as seed in different concentrations.

Experimental Procedure

$Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$ (BCZT) ceramics were prepared by using the seed-induced method. The seeds were prepared via the molten salt method using $BaCO_3$ and ZrO_2 oxides as starting materials. The starting materials were mixed by ball milled for 24 h and mixed with KCl - NaCl salt (1:1) for 30 min and then heated at 1100 °C for 2 h. After that, they were washed with hot deionized water several times until no trace of anion was found, and then dried in an oven at 120°C. The BZ seed powder was then mixed with $BaCO_3$ (99%, Sigma Aldrich), $CaCO_3$ (98.5 - 100.5%, Sigma Aldrich), and ZrO_2 (99%, Sigma Aldrich), TiO_2 (99 - 105.5%, Sigma Aldrich) powder. The BZ seed content was varied from 0.0 to 7.5 mol% (0.0, 2.5, 5.0 and 7.5 mol%). The mixed powder was ball milled for 24 h in ethanol with zirconia grinding media and then dried. All ceramic powders were calcined at 1250 °C for 2 h. Then, the calcined powder was pressed into a disk shape of thickness and diameter about 2.0 mm and 10 mm, respectively and afterwards they were sintered at 1450 °C for 4 h.

The microstructure and phase structure of BCZT : BZ seed ceramics were observed by using scanning electron microscope (SEM) and an X-ray diffractrometor (XRD). For electrical properties, ceramic samples were polished and coated with silver plate to make the electrodes. The dielectric constant and dielectric loss of ceramics were measured as a function of frequency and temperatures by an E4980A, precision LCR meter. The electrode coated samples were poled in a silicone oil bath by applying a DC field of 3kV/mm for 30 min at room temperature. After 24 h, the piezoelectric charge coefficient (d_{33}) was measured by using a S5865 d_{33} meter (KCF Technologies). The coated samples had an applied electric field of 1-2 kV/mm for measuring ferroelectric properties using a Sawyer Tower circuit (Radiant Technologies, Inc.). The ac conductivity and the piezoelectric voltage coefficient (g_{33}) were calculated and plotted as a function of the mol% BZ seed.

Results and discussions

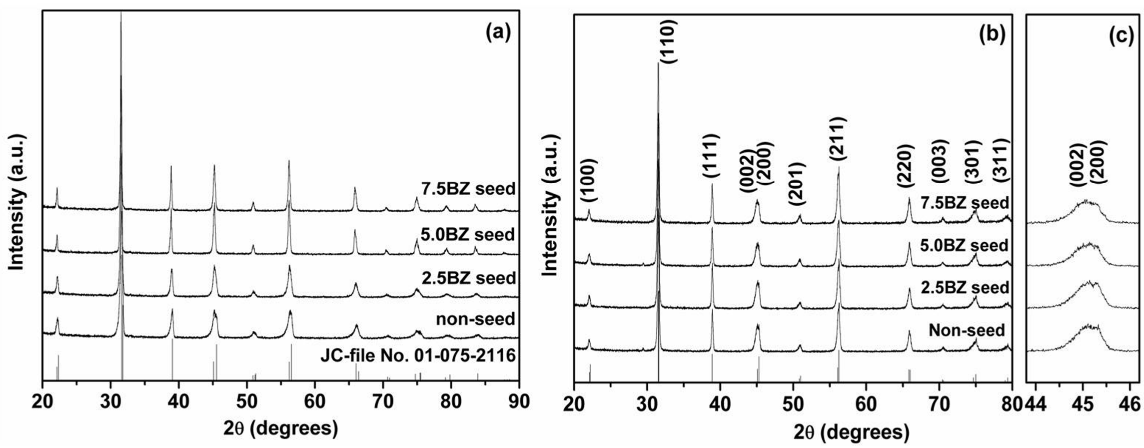

Fig. 1 XRD patterns of BCZT: (a) BZ seed powder, (b) ceramics and (c) 2θ in the range of 44°-46°

Fig.1 illustrates the XRD spectra patterns of powder and ceramic samples. It was found that all powder samples showed pure perovskite phase corresponding to JCPDS No. 01-075-2116 which is the $BaTiO_3$ phase structure. A pure phase for BZ seed added samples confirmed that the small BZ seed particle can completely dissolve in BCZT solution [8]. The XRD spectra patterns of sintered ceramic samples are displayed in Fig.1 (b). The results showed that the ceramics possess pure perovskite phase for all samples. From an expanded range of 44 - 46° it was seen that all samples exhibited coexistence between rhombohedral and tetragonal phase which was observed by the peaks of (002)/(200) reflection [4].

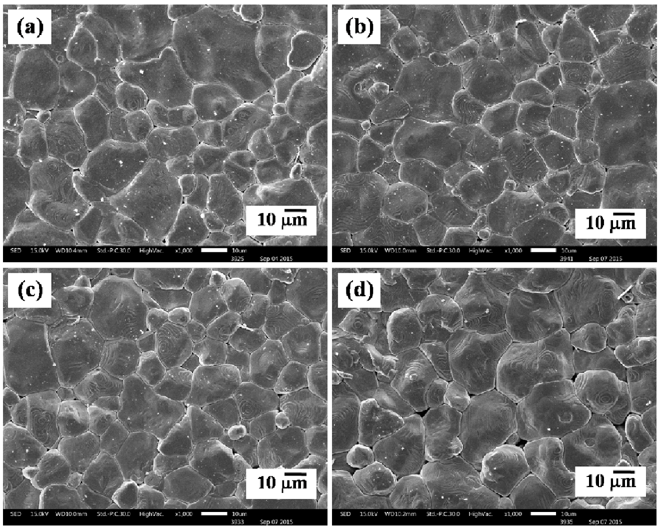

Fig. 2 SEM micrographs of the surface of BCZT: x mol% BZ seed ceramics; (a) Non-seed, (b) x=2.5, (c) x=5.0 and (d) x=7.5

Fig. 2 shows SEM micrographs of the sintered surface of non-BZ seed and seed-added ceramic samples. It was observed that the grain morphology of non-seed, 2.5 mol% and 5.0 mol% BZ seed added samples had no significant change and found that BZ seed of 2.5 and 5.0 mol% showed uniform and homogeneous grains. Increasing the BZ seed content to 7.5 mol% resulted in the appearance of pores. The result might be the grain boundary starts to melt which results from the excess BZ seed particle content. The density and average grain size of all ceramic samples are listed in Table 1. The density of ceramics slightly decreased with increasing BZ seed addition. The density of ceramics were in the range of 5.40 – 5.60 g/cm^3. Decreasing density of BZ seed doped ceramics might be a result of the improper BZ seed content which was not enough to enhance the densification in BCZT ceramics especially for sample of 7.5 mol%. Grain size values of ceramics was measured by the line intercepts method from SEM micrographs in Fig. 2. It was found that the average grain size of ceramics decreased from 13.5 to 12 μm with BZ seed doping from 0.0 mol% to 5.0 mol%. The decreasing grain size may result from the excess BZ seed content accumulating near the grain boundary area leading to interrupted grain growth during the sintering process for BCZT ceramic [9].

Table 1, Density, grain size and electrical properties of the BCZT ceramic systems

Samples (x mol% BZ)	Density (g/cm^3)	Grain size (μm)	ε_r (T_r)	tanδ (T_r)	d_{33} (pC/N)	g_{33} (10^{-3} Vm/N)
0.0	5.61	13.50	3797	0.0163	564	16.77
2.5	5.50	13.19	3598	0.0163	553	17.36
5.0	5.47	12.15	3285	0.0159	498	17.12
7.5	5.37	13.23	2811	0.0278	324	13.02

The dielectric constant (ε_r) and dielectric loss (tanδ) of ceramic samples measured at room temperature and 1 kHz are also listed in Table 1. It was found that the BZ seed had an effect on the dielectric properties of BCZT ceramic. The ε_r value tended to decrease with increasing BZ seed content which related to the decreasing density. The ε_r values were in the range of 2811-3797. For the tan δ observed at a frequency of 1 kHz, the 7.5 mol% BZ seed had a higher value than the other samples while non-seed and BZ seed added (2.5 mol% and 5.0 mol%) samples showed tanδ less than 0.02.

Fig. 3 presents ac conductivity of non-seed and BZ seed added ceramics measured as a function of frequency at room temperature. The ac conductivity (σ_{ac}) can be defined as the following equation (1) [10];

$$\sigma_{ac} = \omega\varepsilon_o\varepsilon_r \tan\delta \qquad (1)$$

where ω is angular frequency (ω=2πf), f is frequency, ε_o and ε_r are the permittivity of vacuum and dielectric constant, respectively and tanδ is the dielectric loss. The σ_{ac} value showed clear frequency dependence and tended to increase with increasing BZ seed content as observed at frequencies lower than 10 kHz. Over the frequency range of 10 kHz to 1MHz, the σ_{ac} value tended to decrease with BZ seed content.

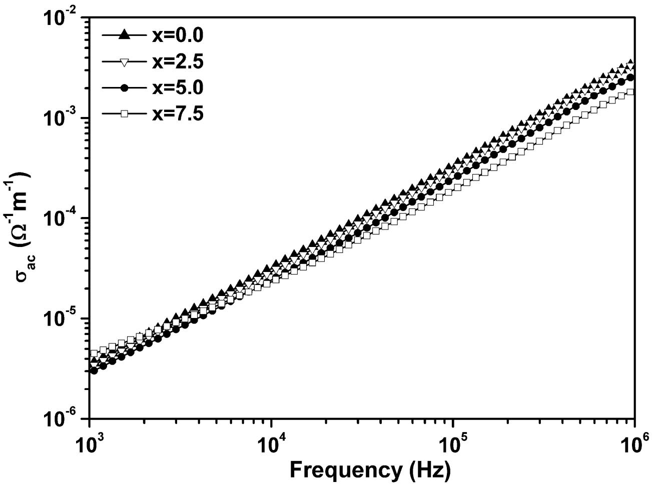

Fig. 3 The ac conductivity as a function of frequency for BCZT: BZ seed measured at room temperature

The high σ_{ac} value of high BZ seed content at low frequency may be caused by defects or impurities or the unbalance of valence in the BCZT structure [11]. Note that the decreasing σ_{ac} value corresponds to increasing resistance. From the results it should be noted that the BZ seed increases the resistance of BCZT ceramics.

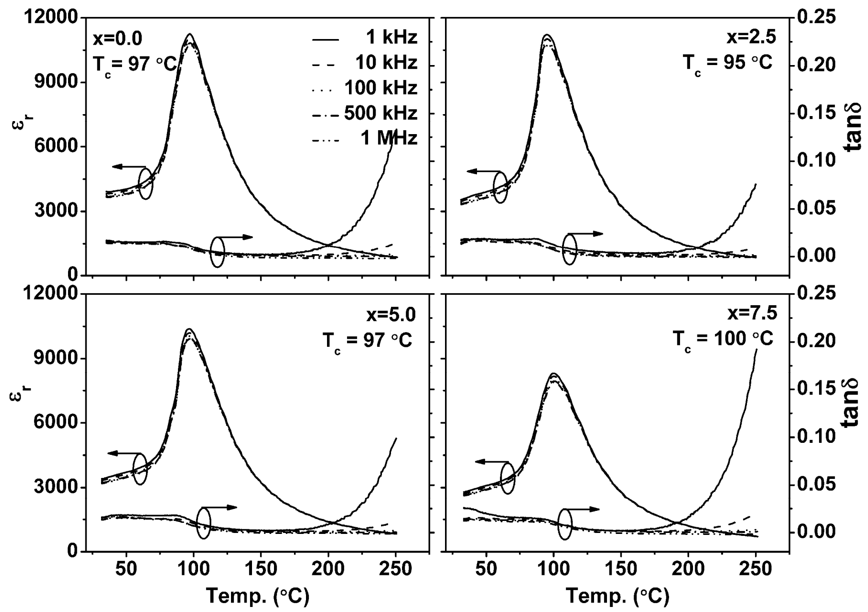

Fig. 4 The temperature dependent of dielectric constant (ε_r) and dielectric loss (tanδ) of BCZT: BZ seed ceramics

The relationship between dielectric properties and temperatures from 30 °C to 250 °C is shown in Fig 4. It can be seen that all the ceramics have a normal peak of dielectric constant and also no significant change with frequency. The maximum dielectric constant (ε_r) at Curie temperature tended to decrease slightly with increasing BZ seed content ranging from 11253 - 8296 (measured at 1 kHz). Dielectric loss (tanδ) showed similar behavior to the dielectric constant behavior having no significant change with the increasing frequency and BZ seed content. The tan δ values of all samples measured at the temperature range of 30 °C to 200 °C were lower than 0.02. Results concluded that the BZ seed doping had little effect on the dielectric loss of BCZT ceramics. In addition, it were observed that the Curie temperatures (T_c) of the ceramics showed little change with BZ seed content which were in the range from 95 to 100 °C. The highest T_c was obtained for the sample with 7.5 mol% BZ seed.

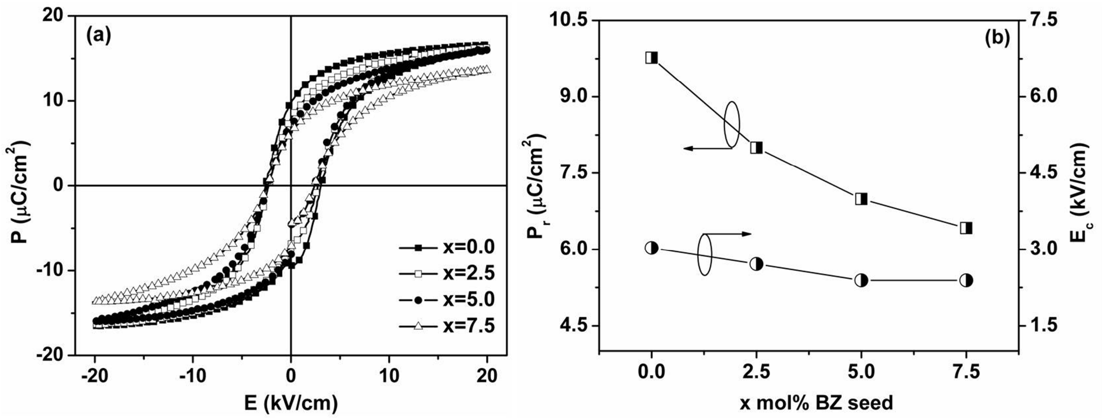

Fig. 5 Ferroelectric properties; (a) P-E ferroelectric loop, (b) remnant polarization (P_r) and coercive field (E_c) for BCZT:BZ seed ceramics.

Fig. 5 shows the ferroelectric properties at room temperature; the P-E ferroelectric loop (Fig.5 (a)) and the parameters of ferroelectric properties (Fig. 5(b). It was found that all ceramic samples exhibited a slim ferroelectric behavior. Plots of the ferroelectric parameters such as remnant polarization (P_r) and coercive field (E_c) as a function of BZ seed content are shown in Fig. 5(b). From the results, it was observed that seed content significantly effected the P_r values. The P_r value decreased with increasing BZ seed content as shown in Fig. 5(b). Decreasing P_r value with higher BZ seed doping could be associated with the decreasing density and grain size values. Also, this result might be due to inhibited domain walls reorientation and polarization switching during the applied electric field cycle [12-13]. The E_c values of ceramic samples show little change and tended to decrease with increasing BZ seed content. The E_c values were in the range of 2.39-3.03 kV/cm with lowest E_c value found for the samples of 5.0 and 7.5 mol% BZ seed.

Piezoelectric charge (d_{33}) and voltage (g_{33}) coefficients as a function of x mol% BZ seed are listed in Table 1. It can be seen that d_{33} value decreased slightly from 564 to 324 pC/N with increasing BZ seed from x=0.0 to x=7.5 mol%. According to the theory of ferroelectricity, as reported by Haun et al. [14], the d_{33} value depends on the P_r value. From the d_{33} result, it can be noted that the decreasing d_{33} for BZ seed added samples may result from the P_r values decrease because the polarization switching decreased during the electric field that was applied in poling process [13, 15-16]. The value of g_{33} slightly increase from 16.77×10^{-3} to 17.36×10^{-3} Vm/N for x=0.0 to x=2.5 mol% BZ samples and then decreased with increasing BZ seed content.

Conclusions

Effect of $BaZrO_3$ (BZ) seed on the density, dielectric, ferroelectric and piezoelectric properties of BCZT ceramics was investigated. Results found that BZ seeds lead to changes of all properties of BCZT ceramics. The XRD patterns showed perovskite structure without impurity phase for all ceramic samples. Density and average grain size of ceramics were in the range of 5.37-5.61 g/cm^3 and 12.15-13.50 μm, respectively. The values of ε_r, d_{33} and P_r decreased with increasing BZ seed content. Curie temperature (T_c) of the ceramic increased from 97 to 100 °C for the samples of non-seed to 7.5 mol% BZ seed. Dielectric loss (tanδ) was lower than 0.03 for all samples. The g_{33}, and E_c of BCZT ceramic were improved with BZ seed addition.

Acknowledgments

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