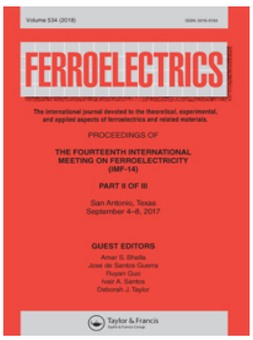

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Effects of MnO_2 doping on the electrical properties of BCZT ceramics prepared by seed-induced method

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ABSTRACT

The effects of MnO_2 doping on the electrical properties of $Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$ (BCZT) ceramics prepared by adding 1.0 mol% BCZT seed were studied Results were found that the ceramics showed pure perovskite phase phase for all samples. Density and grain size values were in the range of 5.45–5.57 g/cm^3 and 6.79–9.85 μm, respectively. The highest values of ε_r and P_r measured at room temperatures were 3900 and 8.22 μC/cm^2, respectively which were obtained for the sample of 1.0 mol% MnO_2. Tan δ of all ceramic samples was lower than 0.02. In addition, d_{33} and g_{33} values were changed with MnO_2 content.

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Electrical properties; perovskite; lead-free ceramics

1. Introduction

Barium titanate ($BaTiO_3$; BT) is a lead-free ceramic which has been widely studied because the phase transition temperature of BT ceramic can be modified by A-site or B-site substitutions such as the addition of calcium (Ca) into the barium (Ba) site (A-site) or zirconium (Zr) into the titanium (Ti) site (B-site) [1]. BCZT ceramic is one of the lead free piezoelectric ceramics which has been widely reported because it has good electrical properties such as high piezoelectric coefficient (d_{33}∼600 pC/N) and high planar electromechanical coefficient (k_p∼0.50) at the composition of $Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$ [2]. However, it uses high calcination and sintering temperatures (∼1350°C and 1500°C, respectively), and a very long dwelling time to form the pure perovskite phase [2–4]. Consequently, many researchers have focused on the study of different methodologies to reduce the calcination and sintering temperatures and also to improve the electrical properties of BCZT ceramics. Many researchers have focused on the study of the doping effects of various metal ions to reduce the temperatures and also to improve the electrical properties of BCZT ceramics [5–7]. A methodology of the synthesis of piezoelectric ceramics to improve the electrical properties by modifying the textured structure of the ceramics has been are applied by using nanometric perovskite ceramics as a template such as the seed-induced method and the template grain growth method [8–10]. The report have been studied by Ye et al. [11] found that $BaTiO_3$ (BT) template particles which were prepared by the molten salt method had a good effect on

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the electrical properties of $Ba_{0.85}Ca_{0.15}Zr_{0.10}Ti_{0.90}O_3$ ceramic. Their ceramics used a low calcination temperature of 1100°C and the textured BCZT ceramics (BT templates added) showed piezoelectric coefficient (d_{33} =470 pC/N), electromechanical coefficient (k_p =40%) and Curie temperature (T_C) higher than the sample without using BT templates. Zhao and coworkers [12] have reported that in the $Ba_{0.85}Ca_{0.15}Zr_{0.10}Ti_{0.90}O_3$ ceramic prepared by the template grain growth (TGG) using BT as the template, the condition of 10 wt% BT template (sinter at 1400°C for 5 h) gave the highest d_{33} ~455 pC/N and a high ε_r ~3500. Previously, we studied the fabrication of $Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$ (BCZT) ceramics by the seed-induced method varying the seed content (0.0–4.0 mol%) and found that pure perovskite phase was formed at a low calcination temperature. Some electrical properties, especially the d_{33} property of BCZT were enhanced with BCZT seed adding. However, the dielectric constant measured at room temperature of the seed added samples was lower than for the non-seeded ceramics. As in previous reports, the doping of various metal oxides to improve the dielectric properties of piezoelectric ceramics and also other electrical properties will be investigated. The metal oxide proposed is MnO_2. MnO_2 is an interesting additive because the multi-valence of Mn ion allows it to act as donor and acceptor dopant [13]. Reports of MnO_2 doped lead-free ceramic found that MnO_2 can improve the densification of ceramics, dielectric constant and reduce the dielectric loss [8, 14]. Jiang et al. [15] studied the effects of MnO_2 on microstructure, ferroelectric, and piezoelectric properties of $Ba_{0.85}Ca_{0.15}Ti_{0.90}Zr_{0.10}O_3$ lead-free ceramics and found that the ceramic with Mn (x) = 0.25 had the maximum piezoelectric properties $d_{33} = 306$ pC/N and $k_p = 42.2\%$, respectively. Moreover the ferroelectric and piezoelectric properties decreased when higher MnO_2 doping. Di Loreto and co-works [16] have investigated the MnO_2-doped lead free $0.5[Ba(Zr_{0.2}Ti_{0.8})O_3]$-$0.5[(Ba_{0.7}Ca_{0.3})TiO_3]$ ceramics, result showed that a small amount of MnO_2 ($x < 0.5$ mol.%) doping improve the dielectric and ferroelectric properties of the BCZT ceramics. However, MnO_2 doped BCZT ceramic using the seed-induced method has not been reported. In this work we studied the effect of MnO_2 doping on the electrical properties of BCZT ceramics prepared by adding 1.0 mol% of BCZT seed.

2. Experimental

Lead-free ceramic ($Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$) components with 1.0 mol% BCZT seed was mixed with x mol% MnO_2 ($x = 0.00$, 0.5, 1.0, 1.5 and 2.0) and prepared by the mixed oxide method. The BCZT seed was synthesized by the molten-salt method and heated at 1000°C for 2 h. After that, 1.0 mol% of BCZT seed powder was mixed in with the BCZT ceramic system and then doped with MnO_2. The mixed powder was ball-milled for 24 h, then calcined at 1200°C for 2 h and the calcined powder pressed into a disk-shaped pellet of diameter 10 mm under 1.0 ton (25 kg/cm^2) and sintered at 1450°C for 4 h. The phase formation and microstructure of the ceramic systems were analyzed by X-ray Diffraction (XRD) and scanning electron microscope (SEM). For case of electrical properties, the ceramics were polished and coated with silver paste on the faces as electrodes. The dielectric constant and dielectric loss were measured as a function of temperatures and Mn contents. For piezoelectric coefficient d_{33} properties, the electrode

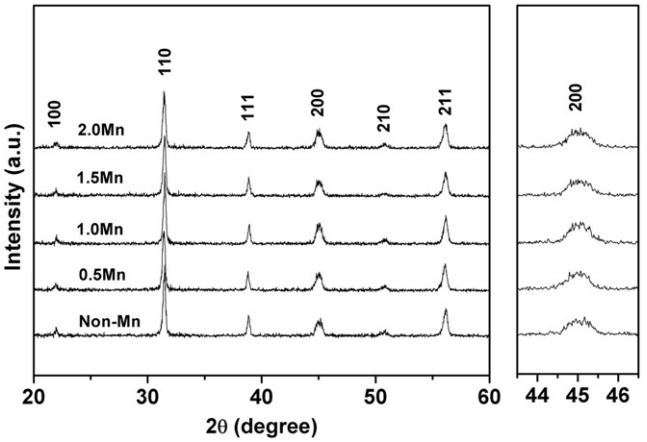

Figure 1. XRD pattern of BCZT: Mn ceramics prepare by mixed oxide method.

samples were poled at room temperature in a silicone oil bath with an electric field of 3 kV/mm for 30 min. After 24 h, the piezoelectric coefficient was measured by using a d_{33} meter. In addition, ferroelectric properties as a function of Mn content were measured at room temperature using a Sawyer Tower circuit.

3. Results and discussion

The XRD patterns of un-doped and Mn doped ceramics are shown in Figure 1. It was found that all ceramic samples showed pure perovskite phase with XRD peaks corresponding to the perovskite peak of (100), (110), (111), (200), (210) and (211) directions. The pure perovskite phase of both un-doped and Mn dope BCZT ceramics suggested that the Mn ion dissolved into the solid solution of BCZT ceramic. Figure 2 displays the density and average grain size values of the ceramic systems. It can be seen that the density values decreased from 5.57 to 5.48 g/cm^3 for un-doped to 0.5 mol% Mn doped, then increased for 1.0 mol% Mn doped. The reduced density value might be due to pores in the ceramic structure, which were observed in SEM micrographs as shown in Figure 3. The highest density value of 5.57 g/cm^3 was obtained for the samples of un-doped and 1.0 mol% Mn. The average grain size decreased from 9.85 to 6.79 μm with increasing Mn content. The small grain size of higher Mn doped samples may be due to excess Mn particles accumulating near the grain boundaries, leading to grain growth being interrupted [17, 18]. The dielectric constant (ε_r) and dielectric loss (tanδ) at 38°C and the phase transition temperature (Curie temperature; T_C) are displayed in Figure 4. The dielectric constant (ε_r) was in the range of 3300–3900 and 9950–11300 for temperatures of 38°C and T_C, respectively. The highest dielectric constant at 38°C was found for the 1.0 mol% Mn sample. This result may be because to the sample of 1.0 mol% Mn had the highest density. Results suggested that the lower Mn content, the Mn ion may enter in the A-site and created a donor effect [14, 15]. Dielectric loss (tanδ) tended to increases with increasing Mn content at room temperature. At the Curie temperature, it was found that tanδ had no significant change with increasing of the Mn content from 0.0 to 1.5 mol%. Note that the tanδ value at 1 kHz was less than 0.016 for samples of

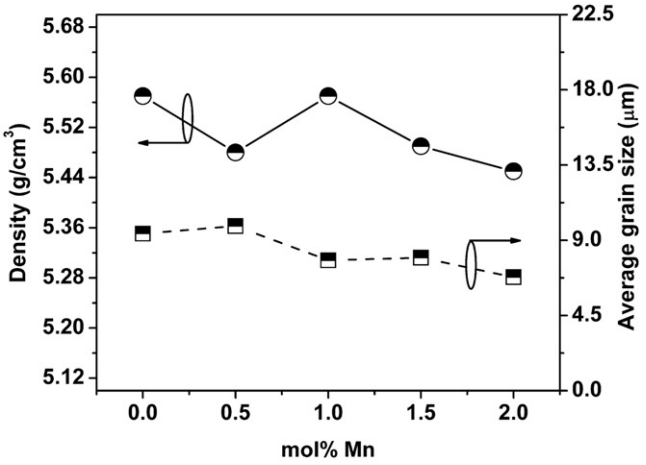

Figure 2. Density and average grain size values for un-doped and Mn doped ceramics.

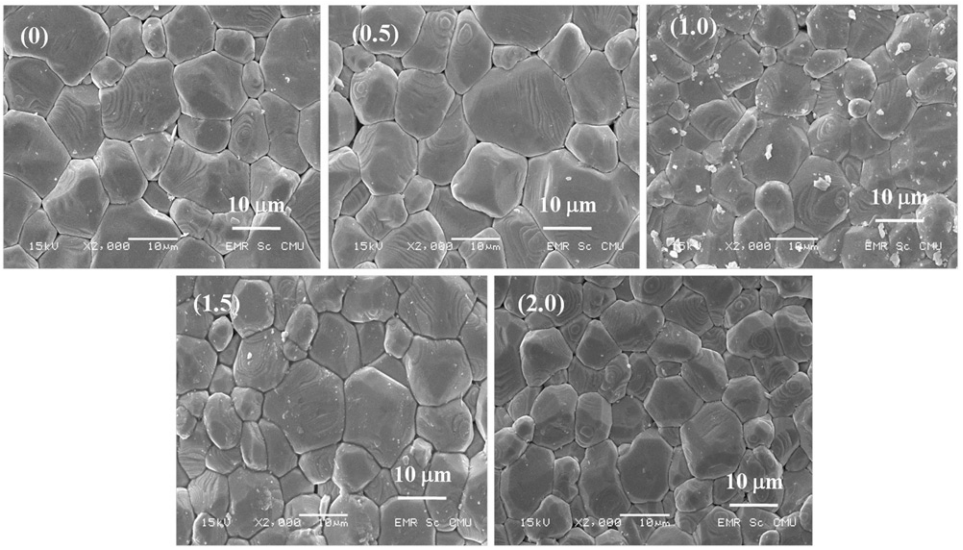

Figure 3. Microstructure of un-doped and Mn doped BCZT ceramics.

un-doped and 1.0–1.5 mol% Mn doped. Figure 5 plots the dielectric constant and dielectric loss as a function of frequency and temperature. From the figure, it can be seen that the dielectric constant at the phase transition temperature (Tc) position had a sharp peak for all samples. However, the T_C changed slightly with increasing Mn content. The dielectric loss of the un-doped sample and 0.5 mol% Mn doped samples were clearly dispersed with frequency around the T_C position. Figure 6 shows the P-E hysteresis loops and ferroelectric parameters of BCZT: Mn ceramics. It was found that the un-doped and Mn doped showed normal ferroelectric behavior and had a slim P-E loop. It was found that the P-E hysteresis loop because the wide loop with increasing Mn content and was clearly observed for the sample of 2.0 mol% Mn. This result might be caused by the higher dielectric loss value (seen in Figure 6(a)). The ferroelectric

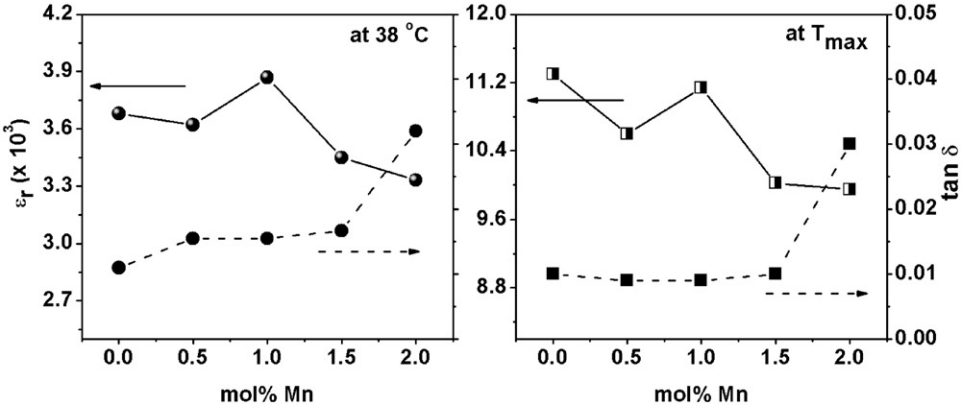

Figure 4. Dielectric properties as a function of mol% Mn at temperature of 38 °C and phase transition temperature (measured at 1 kHz).

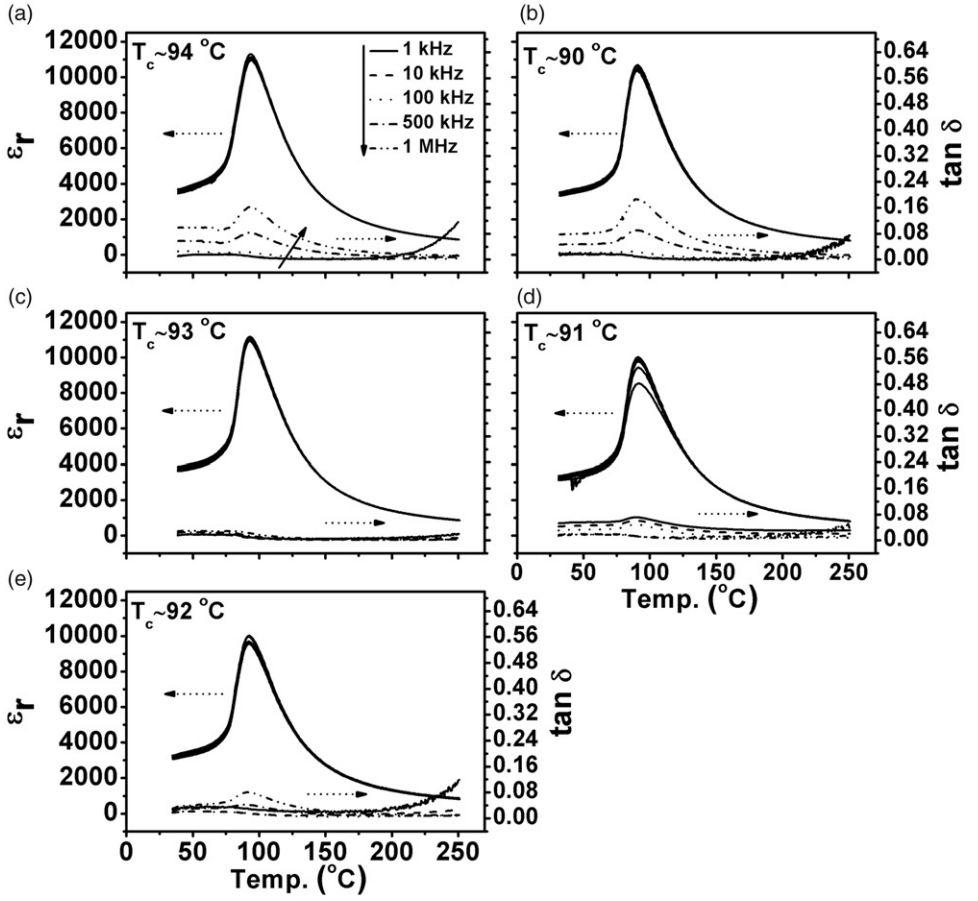

Figure 5. Dielectric constant (ε_r) and dielectric loss (tanδ) as a function of frequency and temperature for ceramic samples: (a) un-doped, (b) 0.5Mn, (c) 1.0 Mn, (d) 1.5Mn and (e) 2.0Mn.

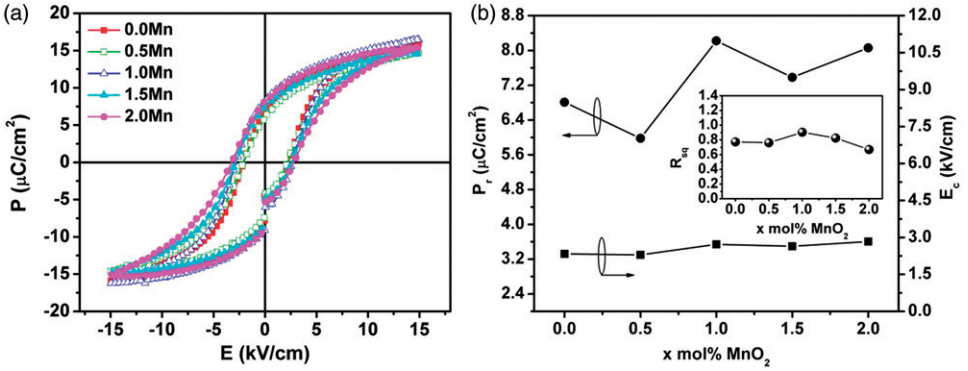

Figure 6. (a) Polarization vs electric field hysteresis loops, (b) remnant polarization (P_r), coercive field (E_c) and R_{sq} for ceramic samples.

parameters including remnant polarization (P_r), coercive field (E_c) and squareness of the hysteresis loop (R_{sq}) are shown in Figure 6(b). Results found that the value both P_r and E_c tended to increase with increasing Mn content with in the range of 6.81–8.06 $\mu C/cm^2$ and 2.33–2.83 kV/cm, respectively. It this can be noted that the Mn doping improved the P_r of BCZT ceramics. Increasing P_r value may be due to a more uniform domain structure in ceramics [19]. Increasing of E_c value might be from the decreasing in grain size because small grain ceramics indicating higher E_c valued for non-lead ceramics is well-known [20]. From R_{sq} (inserts in Figure 6(b)) can be determined the quantification of changes in the hysteresis loop, Haertling and Zimme [21] derived a relationship through the Eq. (1):

$$R_{sq} = \frac{P_r}{P_s} + \frac{P_{1.1E_c}}{P_r} \tag{1}$$

where R_{sq} is the squareness of the hysteresis loop, P_s is the saturate polarization, P_r is the remanent polarization, and $P_{1.1Ec}$ is the polarization at an electric field equal to 1.1 times of the coercive field. It was found that the R_{sq} changed with Mn content, so Mn changed the hysteresis loops of BCZT ceramics. The piezoelectric coefficient (d_{33}), piezoelectric voltage coefficient (g_{33}), planar electromechanical coupling factor (k_p) and mechanical factor (Q_m) for ceramic samples are listed in Table 1. The d_{33} values of the ceramic decreased with increasing Mn content. Decreasing d_{33} may be an effect of oxygen vacancies which may be due to the domain wall pinning mechanical and induced internal field in grain [14, 22]. Also, it might be the result of decreasing grain size and increasing E_c value. These will lead to more difficulty of domain movement and the switching of polarization during the poling process [15, 23]. The k_p value decreased from 49% to 25% with increasing Mn content. The decrease in k_p values may be due to the higher amount of Mn content which created more oxygen vacancies and affected the domain wall mechanically.

The g_{33} factor can be calculated through an equation following [24]. It was found that the g_{33} value showed a similar behavior to d_{33} and k_p values with a range of 15.62×10^{-3}–9.44×10^{-3} Vm/N for the sample of un-doped to 0.5–2.0 mol% Mn doped BCZT ceramics. The Q_m value was calculated using an equation following the IEEE standards [25]. The Q_m value can be defined in terms of the mechanical loss

Table 1. Piezoelectric coefficient (d_{33} and g_{33}) and electromechanical factor (k_p and Q_m) of BCZT: Mn ceramics.

Samples	d_{33} (pC/N)	g_{33} ($\times 10^{-3}$ Vm/N)	k_p	Q_m
0.0Mn	509	15.62	49	39
0.5Mn	487	15.18	34	50
1.0Mn	450	13.14	39	53
1.5Mn	386	12.64	30	93
2.0Mn	278	9.44	25	78

which is proportion at to Q_m^{-1} [26]. When increasing the Mn content from un-doped to 2.0 mol% Mn, the Q_m value increased from 39 to 78. The increasing Q_m values resulted from the decreasing of mechanical loss. These results can suggest that the Mn doping enhanced the mechanical loss of the BCZT ceramics.

4. Conclusion

The effect of MnO_2 doping on the electrical properties of BCZT ceramic with 1.0 mol% BCZT seed was successfully investigated. The ceramics showed pure perovskite phase in all samples. The dielectric properties were enhanced with MnO_2 doping. The highest ε_r ~3900 was found for 1.0 mol% Mn. Tanδ at the Curie temperature was 0.009 for 0.5 and 1.0 mol% Mn. The P_r value increased with increasing Mn content and d_{33} and g_{33} values were clearly changed with Mn doping.

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