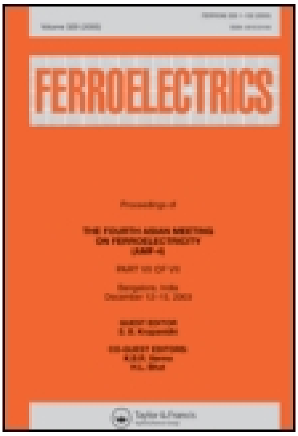

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The effects of Zn^{2+} and Nb^{5+} co-doping (x mol%ZN) on the electrical properties of lead-free $Ba_{0.90}Ca_{0.10}Zr_{0.10}Ti_{0.90}O_3$-Seed ceramic systems, where x = 0.0–1.0 mol% have been studied. The ceramics were prepared using the solid state reaction technique. The phase of the samples showed pure perovskite structure. The density values of the ceramics were in the range of 4.86–5.78 g/cm^3. The maximum dielectric constant was 40893 for 0.8 mol% ZN. The highest values of $P_r \sim 5.85$ μC/cm^2, $d_{33} \sim 381$ pC/N and $k_p \sim 38\%$ were obtained for the sample of 0.4 mol% ZN.

Keywords Lead free ceramics; phase formation; piezoelectric properties; perovskite structure

1. Introduction

In recent years, lead-free materials have received considerable attention because of their good piezoelectric properties and high curie temperatures and they have great potential for use in piezoelectric devices [1–3]. Work on lead free materials has been focused on modified $BaTiO_3$-base ceramics because of the phase transition temperature of BT which can be modified by A-site or B-site substitutions such as by the addition of calcium (Ca) into the barium (Ba) site or zirconium (Zr) into the titanium (Ti) site [4]. Lead free $(Ba_{1-x}Ca_x)(Zr_yTi_{1-y})O_3$ (BCZT) ceramic is one of the modified barium titanates which attracts considerable attention because of its high piezoelectric properties, good dielectric properties and large tunability [5–6]. From previous reports, these properties are found for $Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}$ and it can be easily sintered because no volatile composition exists for this system [5–6]. However, these ceramics require very high calcining and sintering temperatures of about 1300–1350 °C and 1500–1540 °C, respectively for forming pure perovskite phase. Recently, the doping of various elements in BCZT ceramics (such as CeO or ZnO) has been widely reported due to their denser microstructure with lower calcining and sintering temperatures which results in improved electrical properties [7–8]. In addition, the Nb_2O_5 doping was reported to help promote domain wall motion, enhancing

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the densification and resistivity of piezoelectric ceramics [9–10]. However, BCZT doped with ZnO and Nb_2O_5 co-doping has not been reported. In the present work, we studied the effect of $Zn^{2+}$and Nb^{5+} co-doping on the properties of $Ba_{0.9}Ca_{0.1}Zr_{0.1}Ti_{0.9}$ ceramic systems by seed-induced method. Using seed compound to induce formation of the perovskite phase at low temperature because the energetic barrier of phase formation was decreased [11].

2. Experimental

$Ba_{0.9}Ca_{0.1}Zr_{0.1}Ti_{0.9}O_3$ (BCZT)-Seed ceramics doped with x mol% of Zn^{2+} and Nb^{5+} were prepared by the solid state reaction technique. BCZT seed was synthesized from $Ba_{0.9}Ca_{0.1}Zr_{0.1}Ti_{0.9}O_3$ powder by the molten-salt route. Reagent grade metal oxide powders were ball-mill for 24 h in ethanol with zirconia grinding media. The powders were then mixed with KCl-NaCl salt (1:1) and calcined at 1000°C for 2 h.

The powders were then washed with hot deionized water and dried in an oven at 120°C. Then, 5 mol% of the BCZT seed powders were mixed with BCZT and x mol% of Zn-Nb (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0). The slurry was dried and calcined in crucibles at 1200°C for 2 h. The dried powders were then mixed with organic binder (3 wt% PVA) and pressed into cylindrical pellets 10 mm in diameter and 1 mm in thickness using a force of 1 ton. The pellets were sintered at 1400°C for 2 h (after the PVA binder was burned out at 500°C for 1 h). Phase formation and microstructure of the samples was studied via X-ray diffraction (XRD) and scanning electron microscopy (SEM). For electrical properties characterization, the sintered ceramics were ground to obtain parallel faces and the faces were then coated with silver as electrodes. The dielectric constants and dielectric loss of the sintered ceramics were measured as a function of frequency and temperature with an automated dielectric measurement system. The ferroelectric properties were measured using a Sawyer Tower circuit. The electrode specimens were poled in a silicone oil bath at 28°C by applying a DC field of 3 kV/mm for 30 min. Then, the poled samples were characterized for piezoelectric properties using a KCF S5865 d_{33} meter. The electromechanical coupling coefficient k_p of poled samples was investigated by a resonance and anti-resonance method with using an impedance analyzer.

3. Results and Discussions

The XRD patterns of the ceramic samples as a function of x mol% Zn-Nb for BCZT-seed ceramics are illustrated in Fig. 1(a). The samples exhibited pure perovskite phase for all conditions. All samples exhibited coexistence between the orthorhombic phase and tetragonal phase. The existence of tetragonal phase in ceramics is confirmed by the splitting of the (002)/(200) peaks at 2θ of 44–46° [5, 12–13]. Fig. 1(b) shows grain size and density values of the samples. It was observed that as the ZN content increased from 0.0–0.4 mol% the grain size increased. As the ZN content increased from 0.6 to 1.0 mol% it was found that the grain size decreased. The sample of 0.4 mol% ZN showed the largest grain size of 13.5 μm. (Grain size was measured by the line intercept method from SEM micrographs). The increasing grain size was found to have an effect on the density of ceramics. However, for these conditions there is very little change in density value.

Figure 2 indicates the dielectric constant (a) and dielectric loss values (b) as a function of frequency at room temperature. The graph is expanded for the frequency range of 1–100 kHz (as shown in Fig. 2(a1) and (b1)). The results show that the dielectric constant (ε_r) and dielectric loss (tan δ) values of samples at 0.0–0.6 mol% ZN change with frequency

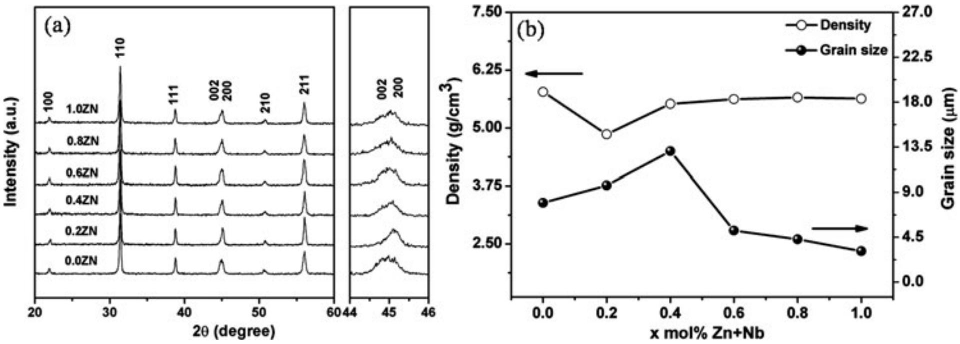

Figure 1. (a) XRD diffraction patterns and (b) density and grain size values of the sintered BCZT-seed-mol% ZN ceramic samples.

and significantly change with ZN content of 0.8–1.0 mol%. The ε_r of ceramic were in the range of 1500–45000 (measured at 1 kHz) with the highest value found for 0.8 mol% ZN content. The high dielectric constant can be due to the densification and mechanisms of domain wall mobility when Zn-Nb dope the ceramics [14]. Dielectric loss for ceramics showed significant change with frequency because the concentration of charge carriers was not constant [15].

Moreover, the tan δ values in the frequency range of 1–100 kHz were less than 0.04 for the samples of 0.0–0.6 mol%ZN.

The relationship between dielectric properties and temperature is displayed in Fig. 3. From the figure, the ceramics exhibit two phase transitions corresponding to the orthorhombic-tetragonal ($T_{O\text{-}T}$) at ~50 °C and tetragonal-cubic (T_c) phase transitions were observed for the samples with mol% ZN = 0.0–0.4 [12]. With increased ZN content

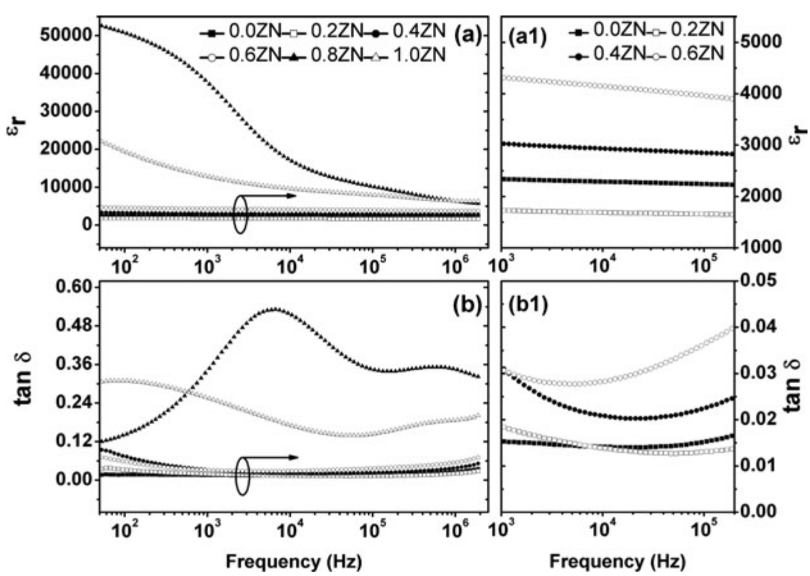

Figure 2. Dielectric constant (a) and dielectric loss (b) as a function of frequency at room temperature.

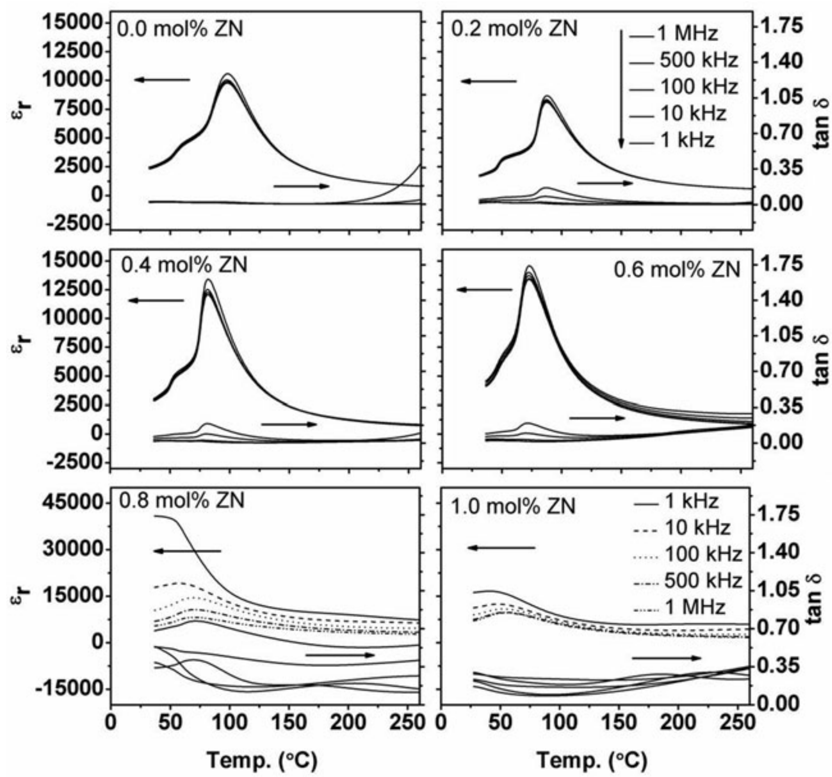

Figure 3. Dielectric constant (ε_r) and dielectric loss (tan δ) as a function of temperature and frequency for BCZT-seed-x mol% ZN ceramic samples.

(ZN = 0.8–1.0 mol%) the transition of orthorhombic to tetragonal phase at room temperature was not observed. The tetragonal-cubic (T_c) phase transitions temperature was reduced from 100°C to 40°C with increased ZN content. These results suggest that the Curie temperature decreased because the substitutions of Zn^{2+} and Nb^{5+} ions lead to deformation of the ABO_3 lattice [5]. Thus, the increasing ZN content had an effect on the phase formation from tetragonal to cubic phase at lower temperatures [7]. Also, the dielectric peak at T_c becomes broader with temperature for samples of 0.8–1.0 mol% ZN which may be the diffuseness of the phase transition in BCZT ceramics [16]. In addition, the maximum dielectric constant (dielectric constant at T_c) tended to increase with increase of ZN content from 0.0–0.8 mol% ZN and then decrease at 1.0 mol% ZN. The highest dielectric constant of 40893 was found for the 0.8 mol% ZN sample. The dielectric loss shows similar behavior as the dielectric constant behavior. Hence ZN co-doping improved the dielectric properties of BCZT ceramics.

The samples of 0.0–0.6 mol% ZN content were selected for investigation of the ferroelectric and piezoelectric properties because these samples exhibited low dielectric loss at 1 kHz (lower than 0.03). The hysteresis loops (P-E loop) of the samples for 0.0–0.6 mol% ZN are shown in Fig. 4(a). It can be seen that all samples indicated ferroelectric behavior with a slim loop. The remanent polarization (P_r) of the ceramics tended to increase with increasing ZN content (as shown in Fig. 4(b)). Maximum $P_r \sim 5.85\ \mu C/cm^2$ was obtained for sample with 0.4 mol% ZN and the coercive field (E_c) value decreased with increasing

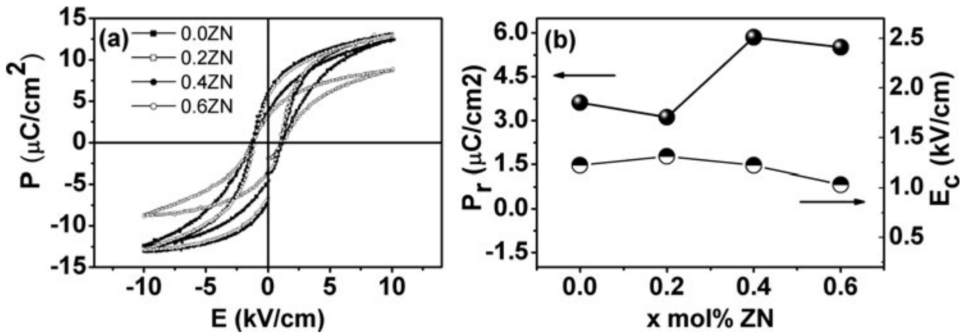

Figure 4. (a) Polarization vs electric field hysteresis loops and (b) P_r and E_c values for BCZT-seed-mol% ZN ceramic samples.

ZN content. The decrease of E_c for ceramics may be because the Nb^{5+} doped BCZT can promote domain wall motion in ceramics [10]. The 0.4 mol% ZN sample showed highest P_r which suggests that this sample should have better piezoelectric properties [17]. Fig. 5 illustrates the piezoelectric coefficient d_{33}, voltage piezoelectric coefficient g_{33} and planar mode electromechanical coupling coefficient k_p of ceramics as a function of mol% ZN. The coefficient g_{33} was calculated by the equation [18]. It can be observed that ZN co-doping has a large effect on the d_{33}, k_p and g_{33} values.

The value of d_{33} and k_p tended to increase with increased ZN content for 0.0–0.4 mol% and then decrease for sample of 0.6 mol% ZN (maximum values of d_{33} and k_p were 381 pC/N and 38%, respectively). The value of g_{33} increases from 10×10^{-3} Vm/N for 0.0 mol% ZN to 23×10^{-3} Vm/N for 0.2 mol% ZN and then gradually decreased with increasing ZN content. The highest values of d_{33} and k_p for BCZT ceramics may be attributed to the coexistence of orthorhombic phase and tetragonal phase near room temperature [5, 19]. The large P_r and low E_c values for sample of 0.4 mol% ZN may result in enhanced piezoelectric properties because these values indicate improvement of the poling process [20]. Moreover, it was found that the piezoelectric properties were associated with grain size of BCZT ceramics. The decreased d_{33} and k_p values of 0.6 mol% ZN may be due to the decreased domain size (grain size decreases) which constrain the movement of the domain walls in polarization process [21].

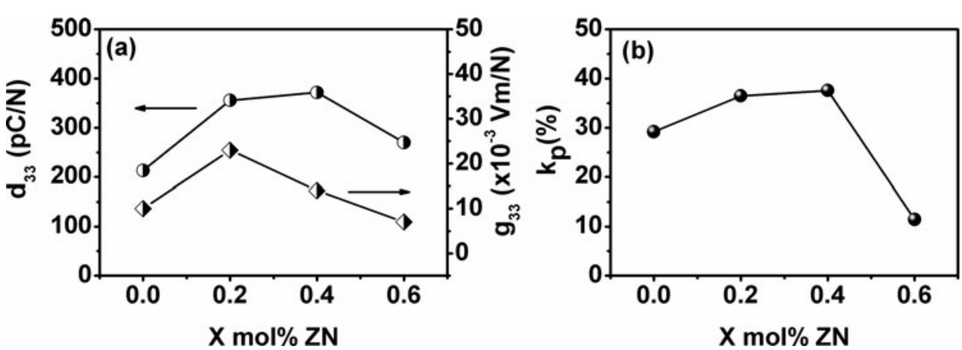

Figure 5. (a) Piezoelectric coefficient (d_{33}), piezoelectric voltage coefficient (g_{33}) and (b) electromechanical coupling coefficient (k_p) for BCZT-seed-mol% ZN ceramics.

4. Conclusion

The effect of Zn-Nb co-doping on the electrical properties of BCZT ceramics produced by seed-induce method were investigated. It was found that the seed induce method reduced the calcination temperature to a lower temperature (by ~100–150°C). All ceramics indicated existence of orthorhombic phase and tetragonal phase. The ZN co-doping demonstrated enhancement of the dielectric constant ($\varepsilon_{max} \sim 40893$). The highest values of $P_r \sim 5.85\ \mu C/cm^2$, $d_{33} \sim 381$ pC/N and $k_p \sim 38\%$ were obtained for the sample of 0.4 mol% ZN.

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