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Influence of Ca substitution on microstructure and electrical properties of Ba(Zr,Ti)O_3 ceramics

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Abstract

In the present work, lead-free $(Ba_{1-x}Ca_x)(Zr_{0.04}Ti_{0.96})O_3$ ($x=0.00$–0.09) ceramics were fabricated via a solid-state reaction method. The microstructure and electrical properties of the ceramics were investigated. The microstructure of the BCZT ceramics showed a core shell structure at compositions of $x=0.03$ and 0.06. The substitution of small amount of Ba^{2+} by Ca^{2+} resulted in an improvement of the piezoelectric, dielectric and ferroelectric properties of the ceramics. The orthorhombic–tetragonal phase transition was found in the composition of $x \leq 0.03$. Piezoelectric coefficient of $d_{33} \sim 392$ pC/N and lowest $E_c \sim 3.3$ kV/cm with highest $P_r \sim 14.1$ μC/cm^2 were obtained for the composition of $x=0.03$ while its Curie temperature (T_C) was as high as 125 °C. However, the ferroelectric to paraelectric transition temperature had slightly shifted towards room temperature with increasing Ca^{2+} concentration.

Keywords: C. Dielectric properties; C. Diffusion; C. Piezoelectric properties

1. Introduction

For a half century, Pb-based piezoelectric ceramics, such as lead zirconium titanate [$PbTiO_3$–$PbZrO_3$ (PZT)], have dominated the field of piezoelectric ceramics worldwide. However, the volatilization of PbO during processing and the waste products containing Pb cause a series of environmental problems. For this reason, numerous researchers have been developing a number of lead-free piezoelectric ceramics to substitute the Pb-based ceramics.

Ferroelectric, dielectric and piezoelectric properties of barium zirconium titanate, $BaZr_xTi_{1-x}O_3$ (BZT), a classical perovskite-type compound, has been extensively studied fundamentally and as a material for applications in electronic devices.

Recently, many researchers have reported that the substitution of Ca^{2+} to replace Ba^{2+} in $Ba_{1-x}Ca_xTiO_3$ solid solutions can cause a slight change in T_C, but has strongly lowered the orthorhombic to tetragonal T_{O-T} transition temperature, which is of great value in improving the temperature stability of piezoelectric materials for many practical applications [1,2]. Liu et al. [3] reported that a high piezoelectric coefficient (d_{33} about 300–600 pC/N) was achieved in Ca doped BZT ceramics. Unfortunately, their optimal composition with high d_{33} values exhibited a low T_C (93 K), which limited their use in real applications.

In order to obtain excellent piezoelectric properties and a high T_C, we redesigned the $(Ba_{1-x}Ca_x)$ $(Zr_{0.04}Ti_{0.96})O_3$ (BCZT) system. The effect of Ca doping on the structure, microstructure, dielectric, piezoelectric and ferroelectric properties of the BCZT lead-free ceramics were systematically studied.

2. Experimental procedure

The $(Ba_{1-x}Ca_x)(Zr_{0.04}Ti_{0.96})O_3$ (BCZT) ceramics for $x=0.00$, 0.03, 0.06 and 0.09 were prepared via a solid state reaction method. High purity (> 99.0%) powders of $BaCO_3$, $CaCO_3$, ZrO_2 and TiO_2 were mixed, dried and calcined at 1200 °C for 4 h. After that, the calcined powders were pressed into pellets of 10 mm diameter and the pellets were sintered between 1300 and 1450 °C for 4 h. The phase identification and density of the BCZT ceramic samples were investigated using X-ray diffraction (XRD)

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and Archimedes' method. Scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) were used to observe the surface microstructures and quantitative element analysis of selected sintered ceramics with maximum density. The linear intercept method was used to estimate the grain size of ceramics. The dielectric constant (ε_r) and dielectric loss (tan δ) of the samples were measured at 1 kHz for various temperatures from room temperature to 250 °C using a LCZ meter. Polarization and strain were measured as a function of electric field by using a Sawyer–Tower circuit. The ceramic samples were polled in a silicone oil bath at 40 °C at 3 kV/cm for 20 min and the piezoelectric properties were measured at room temperature by using a piezoelectric-d_{33}-meter.

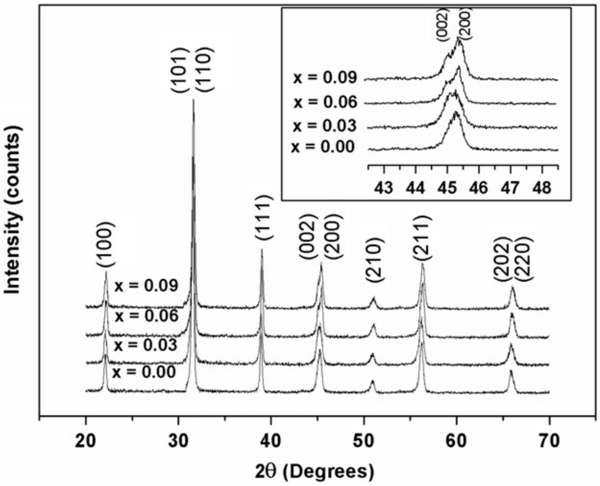

Fig. 1. XRD patterns at 2θ ranging from 20°–70° and inset: a reduced range for 43°–48° of BCZT ceramics.

3. Results and discussion

The XRD patterns for 2θ ranging from 20°–70° and smaller range of 43°–48° for the BCZT ceramics with different compositions are shown in Fig. 1. All of the ceramics show patterns suggesting that Ca and Zr diffuse into the $BaTiO_3$ lattices during sintering to form a solid solution of highly pure perovskite structure. At room temperature, the BCZT ceramic for $x=0.00$ possessed orthorhombic structure seen as a single peak of the (200) between 2θ of 43–48°. It is also noticed that ceramics with $x=0.03$ possess a mixture of orthorhombic and tetragonal structure. When Ca was added ≥ 0.06, BCZT ceramics showed a tetragonal structure, with splitting of (002)/(200) peaks between 2θ of 43°–48°.

The SEM micrographs of the BCZT ceramics are shown in Fig. 2. As can be seen here, samples with a high density and low porosity are obtained from solid state reaction method. However, it was found that the core-shell could be observed at compositions of $x=0.03$ and 0.06. Also, the addition of Ca inhibited grain growth as shown in Fig. 2b and c for the SEM and EDS of the BCZT ceramics with $x=0.03$ and 0.06. The Zr-rich phase with a trace of Ca noticeably occurred at the grain boundary as confirmed by EDS, which led this phase to form the core-shell structure. However, the XRD could not detect the phase of these core shells which may be due to the very small amount of this phase in the ceramic samples.

Fig. 3 shows the temperature dependence of the dielectric constant and dielectric loss for the BCZT ceramics at 1 kHz. The BCZT ceramics for $0.00 \leq x \leq 0.03$ display two obvious polymorphic phase transitions corresponding to the orthorhombic to tetragonal ($T_{O\text{–}T}$) and tetragonal to

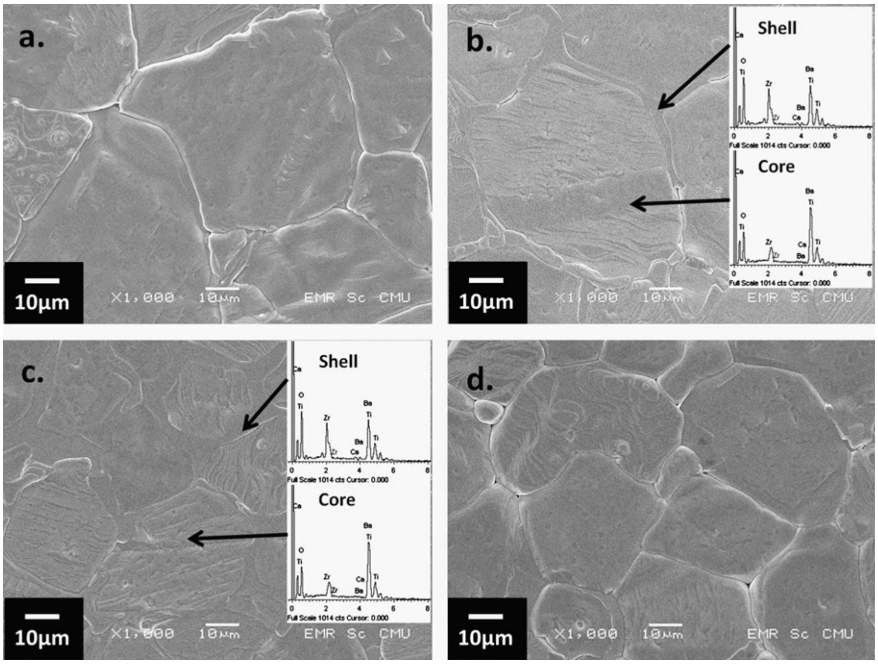

Fig. 2. The SEM and EDS of the BCZT ceramics: (a) $x=0.0$, (b) $x=0.03$, (c) $x=0.06$, and (d) $x=0.09$.

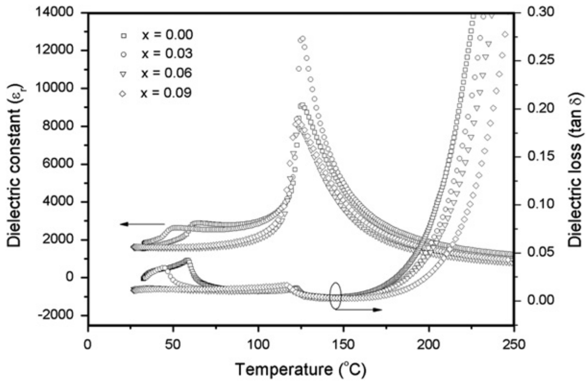

Fig. 3. Temperature dependence of dielectric constants (ε_r) and dielectric loss (tan δ) of BCZT ceramics at 1 kHz.

Table 1
Physical and electrical properties of BCZT ceramics.

X (mol)	0.00	0.03	0.06	0.09
Density	5.93	5.98	5.81	5.73
Porosity	1.51	0.27	0.60	1.18
ε_{max}	9122.0	12716.1	7882.7	8239.6
T_m (°C)	126.0	125.4	123.9	123.0
T_{O-T}	62.3	49.0	–	–
P_r (μC/cm^2)	13.2	14.1	12.3	11.5
P_{max} (μC/cm^2)	22.0	22.0	21.5	21.2
E_c (kV/cm)	5.2	3.3	6.9	7.3
d_{33}	262	392	158	232
Grain size (μm)	38.9	36.1	23.8	24.1

cubic phase (T_m or T_C). The T_{O-T} transition peaks shifted towards lower temperatures with the Ca addition. Moreover, it can be clearly seen that the ε_r maximum ($\varepsilon_{r,max}$) increased with the addition of Ca at $x=0.03$ ($\varepsilon_{r,max}\sim 12716$) which is ~40% higher than that of the undoped sample. However, a slight decrease of T_m of $x=0.03$ was detected at 125 °C. The considerable increase in ε_r values for $x=0.03$ may be due to the coexistence of orthorhombic and tetragonal phases near room temperature and their core shell structure. Furthermore, the density and microstructure may play a role in controlling the ε_r of these ceramics. The average density and grain size values of the BCZT ceramics are shown in Table 1. It can also be noticed that the ε_r of the $x=0.06$ sample is lower than that of the $x=0.03$ sample, which may be attributed to the reduction of its grain diameter as it is well known that ferroelectric materials like the BT ceramics have a grain size dependence on the ferroelectricity [4,5]. The decrease in ε_r with decreasing grain diameter was also observed in Reference [6].

The core shell structure in the $x=0.06$ sample seems to have insignificant effect on the improvement of ε_r which is in contrast to that of the $x=0.03$ sample. The core-shell ceramics were generally considered to be especially difficult to possess high ε_r in fine grain ceramics such as the $x=0.06$ sample [7]. Moreover, the grain growth was inhibited during sintering as in the core-shell ceramics. The inhibition of grain growth results in large stresses in the grains and thus the $\varepsilon_{r,max}$ at the Curie temperature is reduced by surface stress of the grains [8].

Dielectric diffusivity can be clearly found in most Ca content BCZT ceramics. The diffuseness of the phase transition can be determined from the modified Curie–Weiss law, using the following expression [9]:

$$\frac{1}{\varepsilon_r}=\frac{1}{\varepsilon_{max}}+\frac{(T-T_m)^{\gamma}}{2\varepsilon_{max}\delta^2} \tag{1}$$

where ε_{max} is the maximum dielectric constant, T_m is the phase transition temperature and ε_r is the dielectric constant of the sample. For BCZT compositions, the diffusivity and diffuseness parameters can be assessed from the slope and intercept of the dielectric data displayed in Fig. 4, which should be linear. The values of γ and δ are both material constants depending on the composition and structure of the materials. The value of γ is the degree of dielectric relaxation, which normally ranges from 1 for a normal ferroelectric to 2 for an ideal relaxor ferroelectric, while the parameter δ is used to measure the degree of diffuseness of the phase transition. The value of γ of the prepared BCZT ceramics was found to vary between 1.28 and 1.52, which confirms the occurrence of the diffuse phase transition. It was also found that the value of δ increased with increasing Ca content ($x\geq 0.06$), confirming that the addition of Ca promoted the diffuse phase transition of the BCZT ceramics.

Fig. 5 shows the plots of the *P–E* loops at room temperature for the four tested compositions of BCZT ceramics. These results display the most prominent features, which is slightly changed with increasing Ca content. The values of coercive field E_c and the remnant polarization P_r of BCZT ceramics are shown in Table 1. The value E_c reduced with the addition Ca at $x=0.03$; however, it then increased with increasing Ca content for $x\geq 0.06$. The value of P_r of BCZT ceramics was maximum at $x=0.03$ and then decreased with increasing Ca content for $x\geq 0.06$.

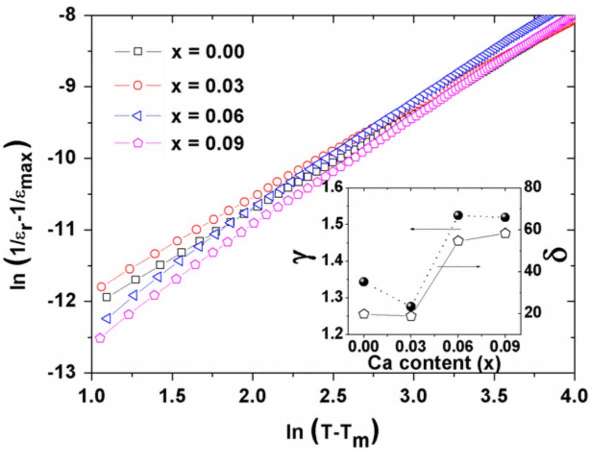

Fig. 4. Variation of $\ln(1/\varepsilon_r-1/\varepsilon_{max})$ vs $\ln(T-T_m)$ of samples at 1 kHz as function of Ca content.

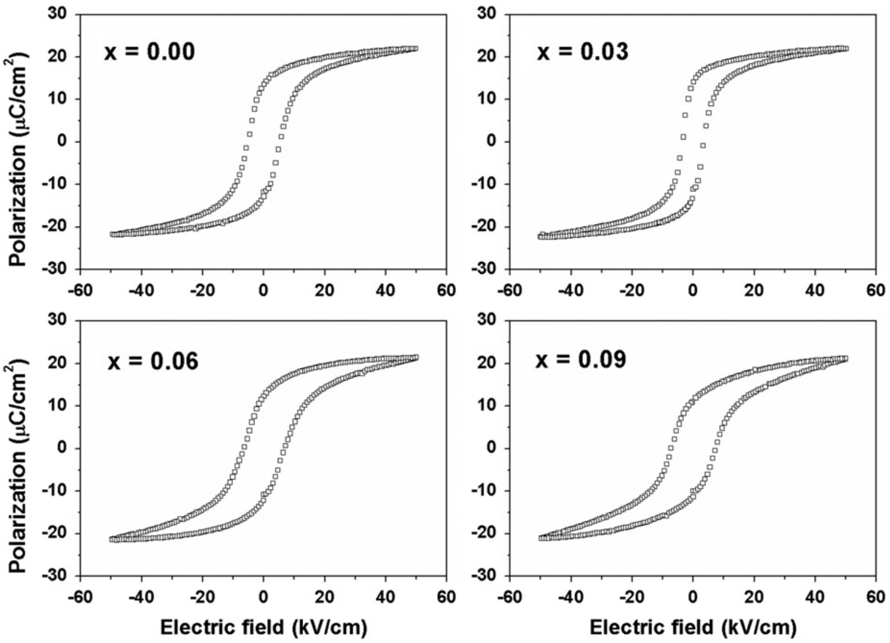

Fig. 5. *P–E* loops for BCZT ceramics at room temperature at frequency 1 kHz.

The unipolar electric field-induced strain curves of the BCZT ceramics with various *x* contents at room temperature are shown in Fig. 6. The normalized strain ($d^*_{33} = S_{max}/E_{max}$) of the BCZT ceramics for all studied compositions is summarized in the inset of Fig. 6 and was calculated from the maximum strain (S_{max}) to the maximum electric field (E_{max}) [10]. The values of d^*_{33} for the compositions $x=0.00$, 0.03, 0.06 and 0.09 are 332, 416, 383 and 513 pm/V, respectively. These values indicate that Ca doping has improved the normalized strain of the ceramics.

d_{33} of the undoped sample is 262 pC/N. With increasing Ca content ($x=0.03$), d_{33} of these ceramics reached the maximum average value of 392 pC/N. The maximum value of d_{33} of the BCZT ceramic at $x=0.03$ could be attributed to the high P_r of 14.1 μC/cm^2 and relative low E_c of 3.3 kV/cm, which indicate an improvement in the poling process. Furthermore, the improved piezoelectric properties are considered to be reasonably consistent with the occurrence of both tetragonal and orthorhombic phase near room temperature. The composition of the induced orthorhombic–tetragonal phase transition results in instability in the polarization state, therefore the polarization direction can be easily rotated by external stress or electric field, thus resulting in a high piezoelectricity [11].

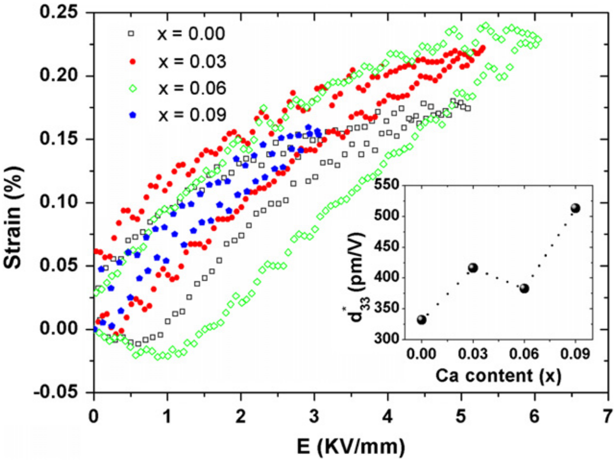

Fig. 6. Unipolar *S–E* loops and normalized strain (d^*_{33}) of the BCZT ceramics.

4. Conclusions

Ceramics with compositions of $(Ba_{1-x}Ca_x)(Zr_{0.04}Ti_{0.96})O_3$ ceramics were prepared using solid state reaction technique. The coexistence of orthorhombic and tetragonal phases at room temperature of the composition $x=0.03$ leads to the most extreme increase in the dielectric and piezoelectric properties of $\varepsilon_{max}=12716$ and $d_{33}=392$ pC/N. The core shell structure found in the compositions of $x=0.03$ and 0.06 had accounted for the reduction of dielectric and piezoelectric properties of the BCZT ceramics. However, further development of this system may be a future candidate for lead free piezoelectric materials.

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