

Effect of grain size on the electrical properties of (Ba,Ca)(Zr,Ti)O₃ relaxor ferroelectric ceramics

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(Ba_{0.90}Ca_{0.10})(Zr_{0.25}Ti_{0.75})O₃ (BCZT) relaxor ferroelectric ceramics with grain sizes of 0.85, 2.5, 15, and 30 μm were prepared from powders synthesized using a sol-gel process. The effects of grain size and dc field on the dielectric properties and tunabilities of BCZT ceramics were investigated. As the grain size decreased, the maximum dielectric constant decreased and the transition temperature increased. The BCZT ceramics with various grain sizes showed a typical relaxor ferroelectric behavior. The dielectric relaxation rate follows the Vogel–Fulcher relation. The dielectric constant is greatly suppressed and the low loss is obtained under a dc electric field. At room temperature (300 K) and 20 kV/cm, the tunabilities and figures of merit are 42% and 62, 51% and 98, 56% and 193, and 51% and 182, respectively, for the BCZT ceramics with grain sizes of 0.85, 2.5, 15, and 30 μm. © 2005 American Institute of Physics. [DOI: 10.1063/1.1849817]

I. INTRODUCTION

Barium strontium titanate (Ba_{1-x}Sr_x)TiO₃ (BST) is the most common ferroelectric oxide in the perovskite ABO₃ structure. Insulating BST is widely used as dielectrics in capacitors because of its high dielectric constant. The high dielectric constant value makes BST one of the promising candidates for dynamic random access memory (DRAM) applications. In order to increase the tunability of the dielectric constant under a biasing field and to reduce the dielectric loss tangent at low frequencies, MgO, Al₂O₃, and ZrO₂ are added.^{1,2} Recently, Ba(Zr_yTi_{1-y})O₃ (BZT) has been chosen as an alternative to BST in the fabrication of ceramic capacitors because Zr⁴⁺ is chemically more stable than Ti⁴⁺.³⁻⁹ The solid solution of barium titanate (BaTiO₃) and barium zirconate (BaZrO₃), Ba(Zr_yTi_{1-y})O₃ (BZT), shows a lot of analogies to BST solid solution.² The nature of the ferroelectric phase transition at the Curie temperature (T_C) of BZT bulk ceramics is known to change strongly with the Zr content. At higher Zr contents ($y > 0.08$), BZT bulk ceramics show a broad dielectric constant-temperature ($\epsilon \sim T$) curve near T_C , which is caused by inhomogeneous distribution of Zr ions in Ti sites and mechanical stress in the grain. This can be considered as a result of pinch off of the three phase transitions of pure BaTiO₃ at high Zr concentration ($y \geq 0.15$).⁴ As the Zr content increases, the phase-transition temperatures approach each other, until, at a Zr content of $y \sim 0.20$, only one phase transition exists.¹ Below this temperature, the rhombohedral phase is stable; above this temperature, the cubic phase is stable.⁶ The related system of (Ba_{1-x}Ca_x)(Zr_yTi_{1-y})O₃ (BCZT) ceramics is reported to ex-

hibit a broad dielectric constant-temperature curve near T_C with values as high as $\epsilon \sim 18\,000$.¹⁰ While it is known that the dielectric constant of BCZT ceramics is high,¹⁰ we reported the field dependence of dielectric constant of BCZT ceramics.¹¹ Not much work has been performed on the dielectric properties and tunabilities of BCZT ceramics. The fabrication of BCZT thin films by metal-organic decomposition¹² and radio frequency magnetron sputtering,¹³ and their dielectric properties and tunability have been reported recently. There are a few papers reporting on the diffuse phase-transition characteristics and effects of grain size and dc electric field on the dielectric properties of (Ba,Ca) × (Zr_yTi_{1-y})O₃ ceramics.

In this work, (Ba_{1-x}Ca_x)(Zr_yTi_{1-y})O₃ ($x=0.10$, $y=0.25$) ceramics have been prepared by a sol-gel method. The diffuse phase transitions and the effects of grain size and dc electric field on the dielectric properties and tunabilities of the BCZT ceramics are reported.

II. EXPERIMENT

(Ba_{0.90}Ca_{0.10})(Zr_{0.25}Ti_{0.75})O₃ (abbreviated as BCZT) powders and ceramics were prepared by a sol-gel process.^{11,14} Weighted amounts of the appropriate proportions of high-purity barium acetate, calcium acetate, zirconium-*n*-propoxide, and titanium *n*-butoxide were used as precursors. Acetic acid and 2-methoxyethanol were selected as solvents. Barium acetate, calcium acetate, zirconium-*n*-propoxide, and titanium *n*-butoxide were dissolved in acetic acid and 2-methoxyethanol, respectively. By controlling the hydrolysis condition of the complex solution, a BCZT gel was formed. The dry gel was calcined at 1100 °C for 2 h in atmosphere and after grinding, BCZT powders were obtained. The annealed powders were dried

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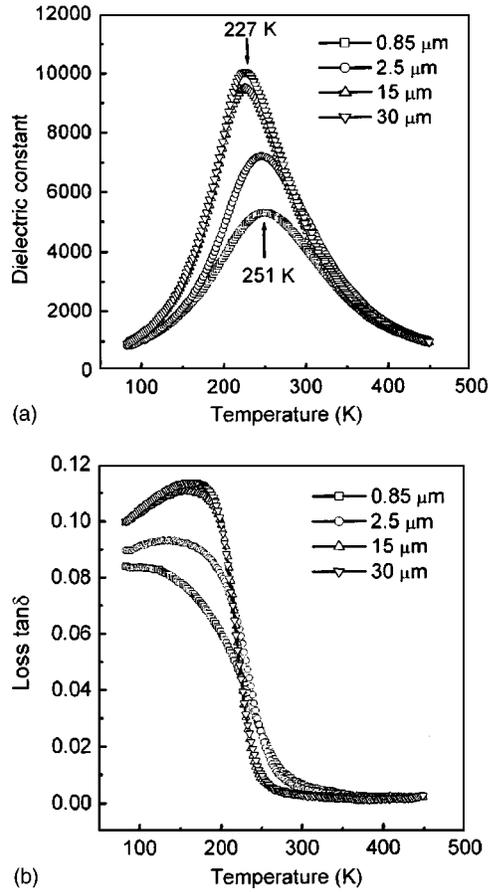


FIG. 1. Temperature dependence of the dielectric constant (ϵ) and loss $\tan \delta$ for the BCZT ceramics with various grain sizes at 10 kHz.

and pressed into disks. The pellets were sintered at 1250–1400 °C for 5 h and cooled in a furnace. Various grain sizes of BCZT ceramics were obtained. Silver paste was coated to form electrodes on both sides of the sintered ceramic specimens for dielectric measurements.

The grain size was determined by averaging over the total number of grains in a scanning electron microscopy (SEM) (Leica Stereoscan 440) micrograph. The capacitance and loss $\tan \delta$ of the samples were measured using a HP4194A LCR meter from 0.1 to 1000 kHz. The capacitance and loss $\tan \delta$ were also measured under various dc biases using a blocking circuit, a multifrequency LCR meter (Model SR720 of Stanford Research System), and a dc power source of 1000 V (Keithley 6517A).

III. RESULTS AND DISCUSSION

A. Dielectric behavior

The temperature (T) dependence of dielectric constant and loss ($\tan \delta$) of BCZT samples with grain sizes of 0.85, 2.5, 15, and 30 μm at 10 kHz is shown in Figs. 1(a) and 1(b). For coarse-grained ($>15 \mu\text{m}$) sample, the permittivity maximum temperature (T_m) is found at ~ 227 K, the dielectric constant (ϵ_m) is $\sim 10\,025$. For medium- (2.5 μm) and fine-grained (0.85 μm) samples, more diffuse peaks occurred at 245 and 251 K, respectively. The shifts of T_m are up to 18 K for samples with various grain sizes. ϵ_m decreases

TABLE I. Sintering temperature of BCZT ceramics and their dielectric properties at 10 kHz.

Sintering temperature (°C)	Grain size (μm)	ϵ_m	T_m (K)	ΔT_{res}^a (K)
1250	0.85	5280	251	12
1300	2.5	7190	245	14
1350	15	9486	226	14
1400	30	10 025	227	15

$$^a \Delta T_{\text{res}} = T_{m(100 \text{ kHz})} - T_{m(100 \text{ Hz})}.$$

from 10 025 to 5280 with a decrease in grain size from 30 to 0.85 μm . The dielectric constant maximum ϵ_m and maximum temperature T_m at 10 kHz, for all the samples, are shown in Table I.

The temperature dependence of dielectric constant and loss $\tan \delta$ of BCZT ceramics with various grain-size samples at four different frequencies is shown in Figs. 2(a)–2(d). These curves demonstrate a typical relaxor behavior around 240 K with a magnitude of the dielectric constant decreasing with increasing frequency and the maximum shifted to higher temperatures. For coarse-grained sample [see Fig. 2(d)], the frequency dispersion of ϵ_m corresponds to a relatively high value of loss $\tan \delta$ for the relaxor phase ($T = 198 \text{ K} < T_m$). On the contrary, ϵ_m does not vary with frequency and the loss $\tan \delta$ is very low above $T = 300 \text{ K} > T_m$. Other samples with smaller grain sizes display similar permittivity-temperature curves compared to the coarse-grained sample. The effect of grain size on the dielectric properties is that ϵ_m increases and T_m decreases with increasing grain size. In order to quantify the frequency dispersion of T_m , a parameter ΔT_{res} defined as $\Delta T_{\text{res}} = T_m(100 \text{ kHz}) - T_m(100 \text{ Hz})$ was used. ΔT_{res} for various grain-size samples are also shown in Table I. It is seen that ΔT_{res} increases slightly with increasing grain size, indicating an increase in the frequency dispersion of T_m .

B. Diffuse phase transition in BCZT ceramics

It is known that the dielectric permittivity of a normal ferroelectric above the Curie temperature follows the Curie-Weiss law described by

$$1/\epsilon = (T - T_0)/C \quad (T > T_C), \quad (1)$$

where T_0 is the Curie-Weiss temperature and C is the Curie-Weiss constant. T_0 of 383 K and C of 1.56×10^5 K have been obtained for a pure BaTiO₃ crystal.¹⁵ For the BCZT ceramics with various grain sizes, the dielectric constant (ϵ) was fitted to the Curie-Weiss law. The parameters are shown in Table II. For coarse-grained sample, $T_0 = 309$ K and $C = 1.35 \times 10^5$ K were obtained. Figure 3 shows the plots of temperature versus inverse dielectric constant at 10 kHz fitted to the Curie-Weiss law (solid line in Fig. 3) for the four samples. A deviation from the Curie-Weiss law starting at T_{CW} can be seen and T_{CW} is different from different samples.

The parameter ΔT_m which is often used to show the degree of the deviation from the Curie-Weiss law is defined as

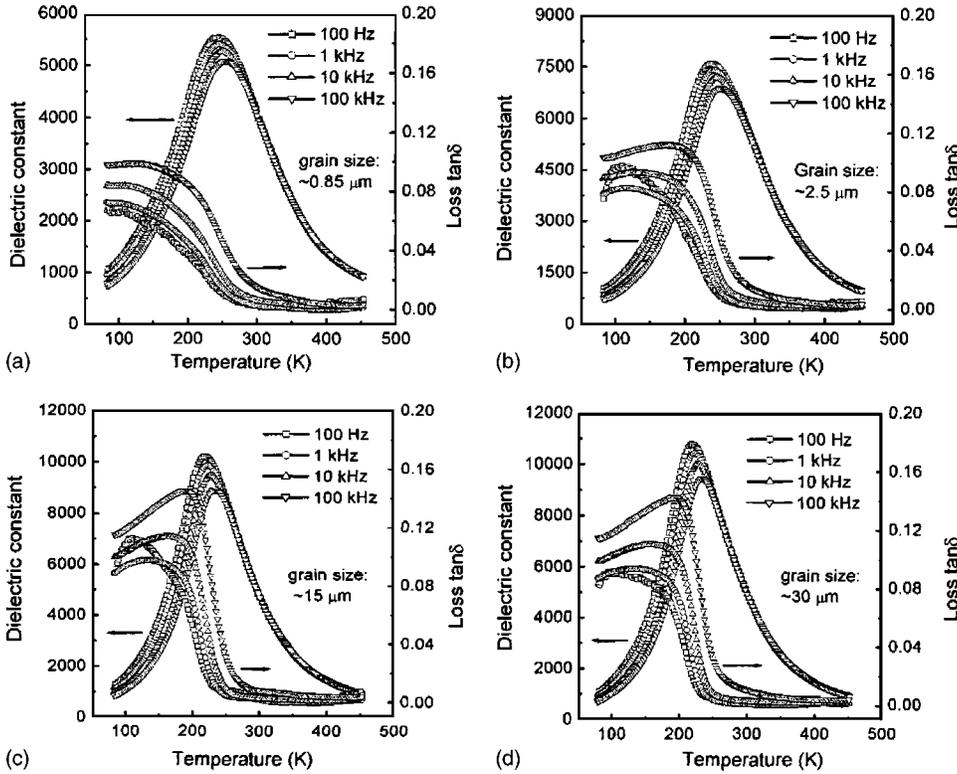


FIG. 2. Temperature dependence of the dielectric constant (ϵ) and loss $\tan \delta$ for the BCZT ceramics at 0.1, 1, 10, and 100 kHz for the four samples with different grain sizes: (a) 0.85, (b) 2.5, (c) 15, and (d) 30 μm .

$$\Delta T_m = T_{CW} - T_m, \quad (2)$$

where T_{CW} denotes the temperature from which the permittivity starts to deviate from the Curie–Weiss law and T_m represents the temperature of dielectric constant maximum. For 30-, 15-, 2.5-, and 0.85- μm -grained samples, $\Delta T_m = 151$, 146, 130, and 122 K, respectively. It can be seen from Table II that the ΔT_m decreases with decreasing grain size.

A modified empirical expression was proposed by Uchino and Nomura¹⁶ to describe the diffuseness of the ferroelectric phase transition as

$$1/\epsilon - 1/\epsilon_m = (T - T_m)^\gamma / C_1, \quad 1 \leq \gamma \leq 2, \quad (3)$$

where γ and C_1 are assumed to be constant. The parameter γ gives information on the character of the phase transition: for $\gamma=1$, a normal Curie–Weiss law is obtained and $\gamma=2$ describes a complete diffuse phase transition.^{16,17}

The plots of $\ln(1/\epsilon - 1/\epsilon_m)$ as a function of $\ln(T - T_m)$ for the four samples are shown in Fig. 4. A linear relationship is observed for the four samples. By fitting Eq. (3) to the data, the critical exponent γ determining the degree of diffuse transitions is obtained from the slope of the fitting

curves. At 10 kHz, it is found that $\gamma=1.88$, 1.94, 2.07, and 2.01 for BCZT ceramics with grain sizes of 30, 15, 2.5, and 0.85 μm , respectively. In the coarse-grained sample, the fitted value of γ decreases from 1.92 to 1.81 when the frequency increases from 100 Hz to 100 kHz, clearly implying that BCZT ceramics with different grain sizes exhibit different features of diffuse phase transition.

C. Vogel–Fulcher relationship

As observed, the BCZT ceramics with different grain sizes present the main characteristic of relaxor ferroelectrics, namely, strong frequency (ν) dependence of T_m and different maximum temperatures for dielectric constant. The plot of $\ln(\nu)$ vs T_m is shown in Fig. 5 for the BCZT ceramics with various grain sizes. An obvious nonlinear behavior, indicating that the data cannot be fitted with the Debye equation, is observed. In order to analyze the main relaxation features of the fine-grained ceramics, the experimental curve (Fig. 5) was fitted using the Vogel–Fulcher^{18,19} relationship

TABLE II. The maximum dielectric constant (ϵ_m), the Curie–Weiss temperature (T_0), the Curie–Weiss constant (C), and the temperature above which the dielectric constant follows the Curie–Weiss law (T_{CW}), $T_{CW} - T_m$, and the critical parameter γ for BCZT ceramics with various grain sizes at 10 kHz.

Grain size (μm)	ϵ_m	T_0 (K)	C ($\times 10^5$ K)	T_{CW} (K)	$T_{CW} - T_m$ (K)	γ
0.85	5288	300	1.40	372	122	2.01
2.5	7206	314	1.35	376	130	2.07
15	9690	309	1.37	373	146	1.94
30	10 024	309	1.35	378	151	1.88

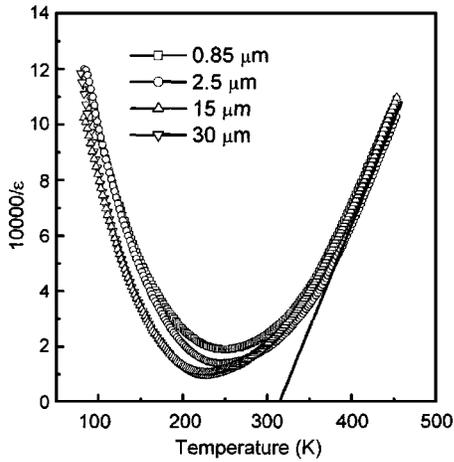


FIG. 3. The inverse dielectric constant ($1/\epsilon$) as a function of temperature at 10 kHz for different grain sizes. (Symbols: experimental data, solid line: fits the Curie-Weiss law).

$$\nu = \nu_0 \exp[E_a/k_B(T - T_{VF})], \quad (4)$$

where ν_0 is the attempt frequency, E_a is the measure of the average activation energy, k_B is the Boltzmann's constant, and T_{VF} is the static freezing temperature. The fitted curve is shown in Fig. 5 (solid line). For fine-grained sample, the fitting parameters are $E_a=0.0495$ eV, $T_{VF}=219$ K, and $\nu_0=1.59 \times 10^{12}$ Hz. The T_{VF} values are 219, 207, 189, and 187 K for BCZT ceramics with grain sizes of 0.85, 2.5, 15, and 30 μm , respectively, as shown in Table III. In addition, a parameter ΔT_1 , defined as $\Delta T_1 = T_m(100 \text{ kHz}) - T_{VF}$, is also listed in Table III, to compare the relative freezing temperatures of the various grain-size samples. For the grain size of BCZT ceramics $>2.5 \mu\text{m}$, the freezing temperatures and ΔT_1 do not vary with grain size.

As can be seen by comparison with the values in Tables I-III, degree of diffuseness γ and T_m of the phase transition decreased with increasing grain sizes while ϵ_m , ΔT_{res} , $T_{CW} - T_m$, and ΔT_1 increase with increasing grain size.

The relaxor behavior can be induced by many reasons, such as microscopic composition fluctuation, the merging of

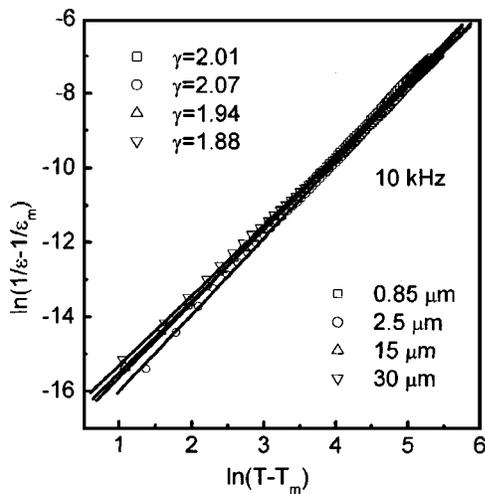


FIG. 4. $\ln(1/\epsilon - 1/\epsilon_m)$ as a function of $\ln(T - T_m)$ for different grain sizes. [Symbols: experimental data, solid line: fits to Eq. (3)].

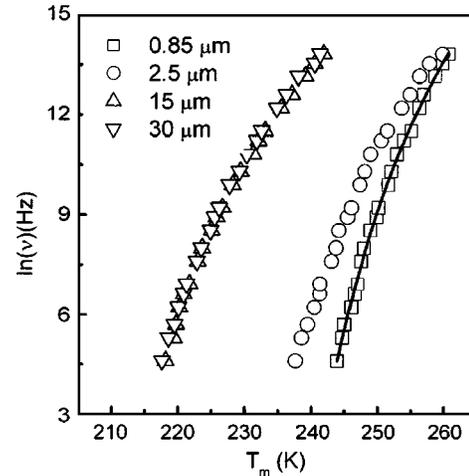


FIG. 5. T_m vs $\ln(\nu)$ curve and Vogel-Fulcher fits for different grain sizes. [Symbols: experimental data, solid line: fits to Eq. (4)].

micropolar regions into macropolar regions, or a coupling of order parameter and local disorder mode through the local strain.^{17,20,21} Vugmeister and Glinichuk reported that the randomly distributed electrical field/or strain field in a mixed oxide system was the main reason leading to the relaxor behavior.²² In the solid solution of $(\text{Ba}_{1-x}\text{Ca}_x)\text{Zr}_y\text{Ti}_{1-y}\text{O}_3$, Ba and Ca ions occupy the A sites of the ABO_3 perovskite structure with the ionic radius of Ca^{2+} (0.99 Å) being smaller than that of Ba^{2+} (1.35 Å). Zr and Ti ions occupy the B sites with the ionic radius of Zr^{4+} (0.98 Å) being larger than that of Ti^{4+} (0.72 Å); therefore, at higher Zr contents ($y > 0.08$), $(\text{Ba}_{1-x}\text{Ca}_x)\text{Zr}_y\text{Ti}_{1-y}\text{O}_3$ bulk ceramics show a broad dielectric constant-temperature ($\epsilon \sim T$) curve near T_C , which is caused by inhomogeneous distribution of Ca ions in Ba, Zr ions in Ti sites, and mechanical stress in the grain. Stress was introduced into the lattice during cooling after sintering, which is due to the cubic to rhombohedral phase transition below the Curie temperature.¹ Internal stress occurs to a lesser extent in ceramics with larger grains because of the lower concentration of grain boundaries. On the other hand, it is known that BaZrO_3 , CaTiO_3 , and CaZrO_3 show nonferroelectric (cubic paraelectric phase) behavior at room temperature because, Ca locates at the central equilibrium position of the BaTiO_3 lattice and Zr locates at the central equilibrium position of the BaZrO_3 lattice. In this case, the macrodomains in BaTiO_3 should be divided into microdomains with increasing Ca and Zr-ion doping, which may also result in the appearance of the relaxor behavior.

TABLE III. The Vogel-Fulcher temperature (T_{VF}), attempt frequency (ν), activation energy (E_a), and $\Delta T_1 = T_m(100 \text{ kHz}) - T_{VF}$ for BCZT ceramics with various grain sizes.

Grain size (μm)	T_{VF} (K)	E_a (eV)	ν ($\times 10^{10}$ Hz)	ΔT_1 (K)
0.85	219	0.0495	159	36
2.5	207	0.0708	271	44
15	189	0.0498	5.54	44
30	187	0.0590	22	46

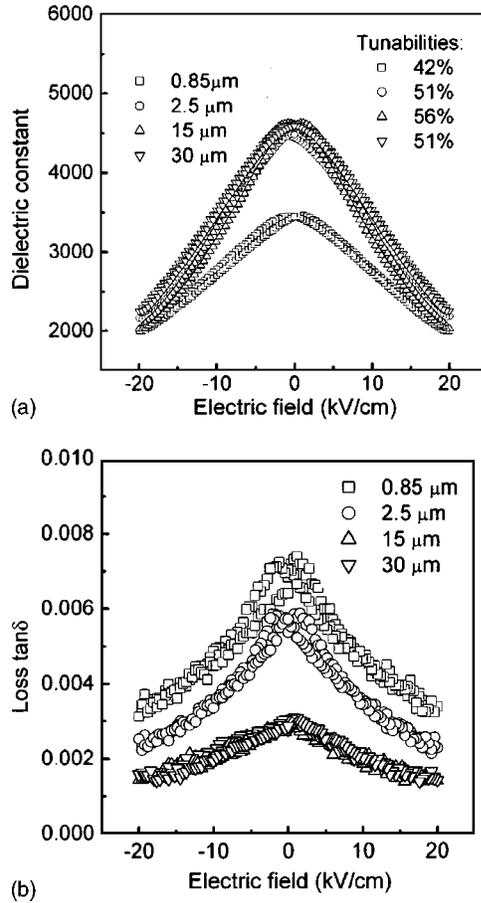


FIG. 6. (a) Dielectric constant and (b) loss $\tan \delta$ as a function of dc electric field at room temperature and 10 kHz for different grain sizes.

D. Electric-field dependence of dielectric constant of BCZT ceramics

The dc field dependence of the dielectric constant (ϵ) and loss $\tan \delta$ for the four samples at room temperature (300 K) is shown in Fig. 6. The dielectric constant is greatly suppressed and low loss is obtained under a dc electric field. As a hysteresis in ϵ with the variation of the dc electric field is observed; it implies that the influence of the existence of the micropolar regions above T_m cannot be neglected because of its relaxor ferroelectric characteristic.^{4,15} For the fine-grained sample, the dielectric constant and loss decrease from 3443 and 0.0068 to 1992 and 0.0034 when the dc electric field increases from 0 to 20 kV/cm. For coarse-grained samples, the dielectric constant and loss decrease from 4610 and 0.0028 to 2256 and 0.0014 when the dc electric field increases from 0 to 20 kV/cm.

The tunability (k) was calculated by using the expression

$$k = [\epsilon(0) - \epsilon(E)]/\epsilon(0), \quad (5)$$

where $\epsilon(0)$ and $\epsilon(E)$ represent the dielectric constant without and at a certain field E , respectively.

It can be seen that k exhibits the highest value of $\sim 56\%$ for the 15- μm -grained sample at 300 K and 20 kV/cm. And $k=42\%$, 51%, and 51%, respectively, for 0.85-, 2.5-, and 30- μm -grained samples. BCZT with larger grain size has higher dielectric constant and tunability and has lower loss. In addition, the high dielectric constant ϵ value permits room

TABLE IV. The tunabilities and figure of merits (FOM) for BCZT ceramics with various grain sizes at room temperature, 10 kHz and 20 kV/cm.

Grain size (μm)	Tunability (%)	Loss	FOM
0.85	42	0.0068	62
2.5	51	0.0052	98
15	56	0.0029	193
30	51	0.0028	182

for further decreasing the loss $\tan \delta$. It is expected that the properties, in particular, the dielectric loss can be further improved by adding additives, such as MgO and Al_2O_3 . It is anticipated that by varying Zr/Ti ratio of the solid solution, the dielectric constant can be tailored to suitable values for tunable capacitor applications.

The figure of merit (FOM) is calculated based on the expression below,²³

$$\text{FOM} = k/\tan \delta, \quad (6)$$

where k is expressed in Eq. (5). At room temperature, the tunabilities and figures of merit of BCZT ceramics with various grain sizes are listed in Table IV. It can be seen that, at 20 kV/cm and 10 kHz, the figures of merit are 62, 98, 193, and 182, respectively, for the BCZT ceramics with 0.85, 2.5, 15, and 30 μm .

IV. CONCLUSIONS

$(\text{Ba}_{0.90}\text{Ca}_{0.10})(\text{Zr}_{0.25}\text{Ti}_{0.75})\text{O}_3$ (BCZT) ceramics with grain sizes of 0.85, 2, 15, and 30 μm were prepared from powders synthesized by a sol-gel process. As the grain size decreased, the maximum dielectric constant decreased and the transition temperature increased, respectively. The BCZT ceramics with various grain sizes showed a relaxor ferroelectric behavior which follows the Vogel-Fulcher relation. The dielectric constant is greatly suppressed and low loss is obtained under a dc electric field. At room temperature (300 K) and 20 kV/cm, the tunabilities and figures of merit of BCZT ceramics with 0.85, 2.5, 15, and 30 μm , are 42% and 62, 51% and 98, 56% and 193, and 51% and 182, respectively. These ceramics are promising materials for tunable capacitor applications.

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