Research Article

Effect of grain size on dielectric and ferroelectric properties of nanostructured $Ba_{0.8}Sr_{0.2}TiO_3$ ceramics

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Abstract: Barium strontium titanate ($Ba_{0.8}Sr_{0.2}TiO_3$, BST) nanocrystalline ceramics have been synthesized by high energy ball milling. As the sintering temperature increases from 1200 ℃ to 1350 ℃, the average grain size of BST ceramics increases from 86 nm to 123 nm. The X-ray diffraction (XRD) studies show that these ceramics are tetragonal. The phase and grain size of the sintered pellets have been estimated from the XRD patterns, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images. The effect of grain size on dielectric and ferroelectric properties is studied. The dielectric and piezoelectric parameters are greatly improved at room temperature with increase in grain size. The Curie transition temperature is found to shift slightly towards higher temperatures as the grain increases from 86 nm to 123 nm. The coercive field decreases and the remnant polarization and spontaneous polarization increase as the grain size of BST nano ceramics increases. These ceramics are promising materials for tunable capacitor device applications.

Keywords: nanocrystalline ceramics; lead free ceramics; crystallization; electron microscopy; dielectric properties; hysteresis

1 Introduction

Piezoelectric and ferroelectric ceramic materials are mature and ubiquitous materials for advanced technology. These ceramic materials are active elements in a range of piezoelectric devices and perform functions such as sensing and actuation. Ferroelectric materials are characterized by a switchable macroscopic polarization, which have drawn extensive attention due to their applications in nonvolatile memories, micro-electromechanical systems, nonlinear optics and sensors. However, at nano-scale, the ferroelectric structure will exhibit quite different properties from the bulk materials. For example, the ferroelectric properties, including the Curie temperature, mean polarization, area of hysteresis loop, coercive electric field, piezoelectric strain and remnant polarization, will become size dependent.

Barium strontium titanate (($Ba_{1-x}Sr_x$)TiO_3, BST) is

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the most common ferroelectric oxide in the perovskite ABO_3 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 high speed random access memories (FRAMs), dynamic random access memories (DRAMs), multilayer ceramic capacitors, piezoelectric transducers and wireless communication devices, and pyroelectric elements have also increased in recent years. The tendency of the electronic industry towards miniaturization and the need to achieve higher performances in smaller structures lead to high interest in understanding the changes of properties while passing from bulk to the nanosized systems, and determining the ultimate structure (particle or grain size (GS) whilst still preserving ferroelectric properties) as well [1,2].

It is well known that ferroelectric materials, such as $BaTiO_3$ and $PbTiO_3$, show "size effect". The size effect means that the properties of ferroelectrics are dependent on the size of materials and show different behavior from a single crystal [3]. However, there are many causes for size effect in ferroelectrics and it is often difficult to separate true size effect from other factors that change with the size of the system. For instance, the results have been reported in the literature about the size effect in ferroelectric particles associated with the variety of synthesis routes and processing techniques adopted [4–8].

In the present study, the dependence of the dielectric properties on the average grain size down to tens of nanometers range in dense BST ceramics has been investigated. In particular, we explored the possibility of achieving a system, which is expected to realize temperature dependent transformation from one phase to another phase and elevate Curie transition temperature T_C. For that purpose, the nanostructure powders prepared from a blend of elemental oxides by high energy ball milling were compacted by means of conventional sintering technique. The grain size of these nano ferroelectric materials has been modified by varying the sintering temperature from 1200 ℃ to 1350 ℃. The microstructure results obtained by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were correlated with measurements of relative permittivity, ferroelectric loop and piezoelectric coefficient d_{33} calculations. The phase analysis and dielectric property measurements in these specimens with different grain size revealed several novel features

of these materials.

Recently, a mechanical alloying technique (i.e., high energy ball milling) has successfully been used to synthesize the nanocrystalline ferroelectric materials [9,10]. Indeed, mechanical alloying is found superior to the high temperature solid state reaction method/wet chemical process because it lowers the calcination and sintering temperature due to the nanocrystalline nature of the resultant powders. The properties of nanocrystalline materials are found superior to those of conventional polycrystalline coarse-grained materials.

2　Experimental conditions

2. 1　Sample preparation

The nano ceramic $Ba_{0.8}Sr_{0.2}TiO_3$ samples were prepared through high energy ball milling, i.e., mechanical alloying. Stoichiometric amounts of $BaCO_3$, $SrCO_3$ and TiO_2 were weighed with "Sr" content. The milling was carried out in a Fritsch Pulverisette P5 planetary ball mill at room temperature for different milling time 0, 5 h, 10 h, 15 h and 20 h, in tungsten carbide (WC) milling media at a speed of 300 rpm and a ball-to-powder weight ratio of 10:1. The milling was suspended for 30 min after every half an hour of milling to cool down the system. The powders thus obtained were compacted at 100 MPa to form the pellets with size 10 mm in diameter and 2 mm in thickness by using microprocessor controlled uniaxial compaction unit. The pellets were sintered at different sintering temperatures (1200–1350 ℃) for 2 h in air. The densities were determined by Archimedes method, and this densification process then enabled better electric characterization of the ceramics. The measured density of the sintered BST pellets was found to be within 95%–99% of their theoretical value.

2. 2　Microstructural investigations

For XRD measurements, the sample surfaces were ground and polished to remove the sintering layer. The phase identification was performed with an X-ray diffractometer (Philips, PW-1710 XRD) with Cu Kα radiation, $\lambda = 0.15418$ nm. Typical 2θ angular scans ranging from 20° to 80° in a 0.02° step were used in these experiments. The lattice parameters were also calculated. The average crystalline size was calculated from X-ray peak broadening using the Scherer formula after eliminating the instrumental broadening [11] and

strain contribution which was confirmed by TEM and SEM. Microstructure characterization measurements were performed on polished and chemically etched samples by means of SEM. For etching, a solution of 5 mL HCl and 95 mL distilled water, containing a few drops of HF acid, was used. 10 s exposure gave clear images of the grains. TEM was used to characterize the present sample products by using a Philips CM 20 microscope.

2. 3   Electrical measurements

The flat polished surfaces of the sintered pellets were electroded with high-purity silver paste and then dried at 150 ℃ before making electrical measurements. The capacitance measurements were made on polled pellets by using a HIOKI-3535-50 LCR Hi-Tester under an electric field (with the maximum magnitude 1 V) in the temperature range of 25–150 ℃ at different frequencies varying from 100 kHz to 100 MHz at a heating rate of 5 ℃/min. The dielectric constant can be calculated by the equation $\varepsilon_r = Cd/(\varepsilon_0 A)$, where C is the

capacitance (F); ε_0 is the free space dielectric constant value (8.854×10^{-12} F/m); A is the capacitor area (m^2); and d is the thickness (m) of the ferroelectric material.

Electroded pellets were poled in silicon oil at 150 ℃ by applying a DC field of 10 kV/cm for 2 h. This gave balanced poling processes to enable observations of any changes in piezoelectric properties independent of poling levels. The piezoelectric coefficient (d_{33}) was measured using a Piezo d_{33} meter. Ferroelectric hysteresis measurements were done at room temperature by using an automatic PE loop tracer based on Radiant Technologies ferroelectric test system with virtual ground mode at 1 kHz.

3   Results and discussion

3. 1   Phase, structural and crystallite size analysis

XRD analysis was used to determine lattice parameters and degree of tetragonality of each ceramic specimen. Figure 1(a) compares the XRD patterns of starting
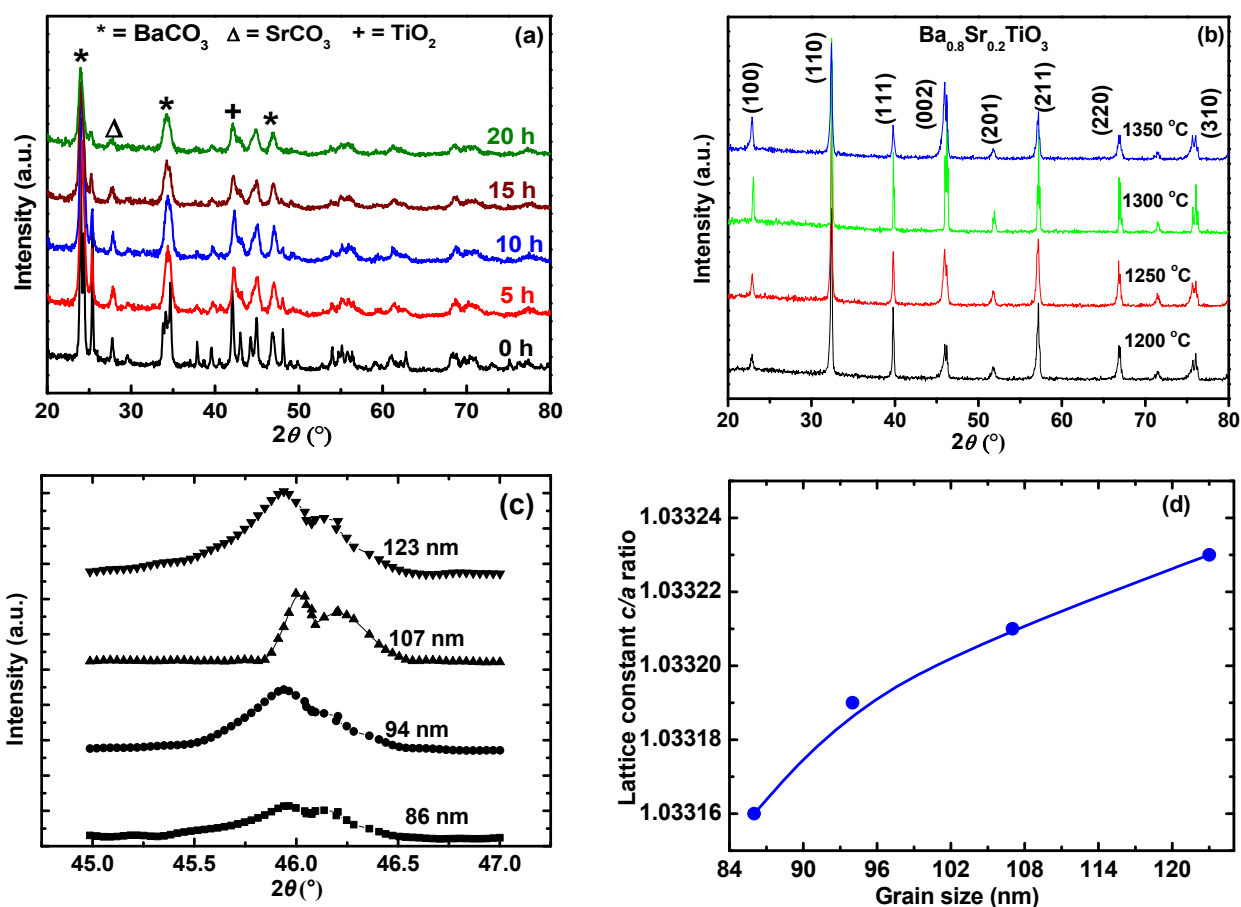

Fig. 1   (a) XRD patterns of mechanically activated BST ceramics at different ball milling time; (b) XRD of BST composition at different temperatures; (c) XRD profile around 45° to 47°; (d) lattice constants of the samples dependent on the mean grain size.

powder mixtures of BST subjected to different durations of milling. After 20 h of milling, alloying starts and some of the XRD peaks of the starting oxides have vanished. The peaks become increasingly broader with milling time and a number of new broadened peaks appear. The new peak patterns have tetragonal structure suggesting the formation of a new phase during mechanical alloying of mixtures of oxides. However, to form single phase tetragonal BST, it requires sintering. Figure 1(b) compares the XRD patterns of mechanically alloyed BST pellets sintered at different temperatures (1200–1350 ℃). The indexing of XRD peaks and the determination of lattice parameters of BST were carried out using a software package POWD. All these peak patterns depict the formation of a single phase with a tetragonal perovskite structure. The results also clearly show that there are no diffraction peaks from impurity phases after sintering. As the sintering temperature is increased, the peaks are sharpened suggesting the increase in the crystallite size. The grain growth of BST nano ceramics as a function of sintering temperature is shown in Table 1. As the sintering temperature increases from 1200 ℃ to 1350 ℃, the crystallite size also increases from ~80 nm to ~120 nm. In order to realize the sub-micron microstructure in the sintered ceramics, it is essential to have the nanocrystalline powders as starting milled powders. Figure 1(c) shows the XRD patterns of the (002) peak as a function of grain size. The diffraction peaks are obtained in the range of $2\theta = 45°–47°$ determined by analyzing the individual peak using Lorentzian curve fit function. As expected from the shape of the XRD spectra, the fit procedure yields a significant increase of the tetragonal phase content with increase in grain size. As the temperature decreases, the grain size is too small for domain twinning to occur; resulting high internal stress is expected to reduce the tetragonal distortion. From the XRD patterns, the lattice distortion is calculated as a function of grain size shown in Fig. 1(d). As the grain size increases, the c/a ratio also increases. These results are in agreement with the previous observations of PMN-PT relaxor ferroelectric ceramics and the grain and particle size effects on microwave properties of $BaTiO_3$ ceramics [4,12].

Average grain sizes of the $Ba_{0.8}Sr_{0.2}TiO_3$ ferroelectric ceramics are estimated using SEM and high resolution TEM. Figure 2(i) shows the typical

Table 1 Lattice parameters of BST nanocrystalline ferroelectric ceramics

Composition	Preparation method	Parameter	Sintering temperature			
			1200 ℃	1250 ℃	1300 ℃	1350 ℃
$Ba_{0.8}Sr_{0.2}TiO_3$	Ball milled for 20 h	a (Å)	3.9982	3.9981	3.9982	3.9982
		c (Å)	4.1308	4.1307	4.1310	4.1311
		c/a	1.03316	1.03319	1.03321	1.03323
		Crystallite size from XRD (nm)	86	94	107	123

SEM micrographs of nanocrystalline BST ferroelectric ceramics sintered at different temperatures. The ceramics are very dense, smooth and crack free. The average grain sizes of the present ceramics are estimated in the range of 150 nm to 300 nm after sintering, suggesting that the nanocrystalline nature is retained even after sintering at high temperature. Figure 2(ii) shows the typical TEM micrograph of the $Ba_{0.8}Sr_{0.2}TiO_3$ ferroelectric ceramics; it reveals that, the grain sizes in the range of 20–50 nm are much smaller than those reported elsewhere [3,4,12]. Such fine-grained microstructure is produced for the first time in BST ceramics and the size of these particles is comparable to crystallite sizes calculated by the XRD peak broadening. The results of the SEM and TEM analyses reveal fine morphology of the nanocrystalline BST ferroelectric ceramics.

The relative density and grain size of the nanocrystalline BST ferroelectric ceramics densified at different temperatures in the range of 1200–1350 ℃ are shown in Fig. 3. The values are determined on polished cross sections by image analysis and are averaged over all chemical compositions and plotted in dependence of the sintering temperature. As expected, the density of sintered samples increases with increasing sintering temperature (Fig. 3(a) and Table 2). The values range from about 95% theoretical density for lower sintering temperature to about 99% theoretical density after sintering at 1350 ℃. Figure 3(b) displays that, the grain size increases from 86 nm to 123 nm as the sintering temperature increases from

Table 2 Variations in grain size, density, dielectric constant at T_R and T_C and piezoelectric coefficient d_{33} with different sintering temperatures

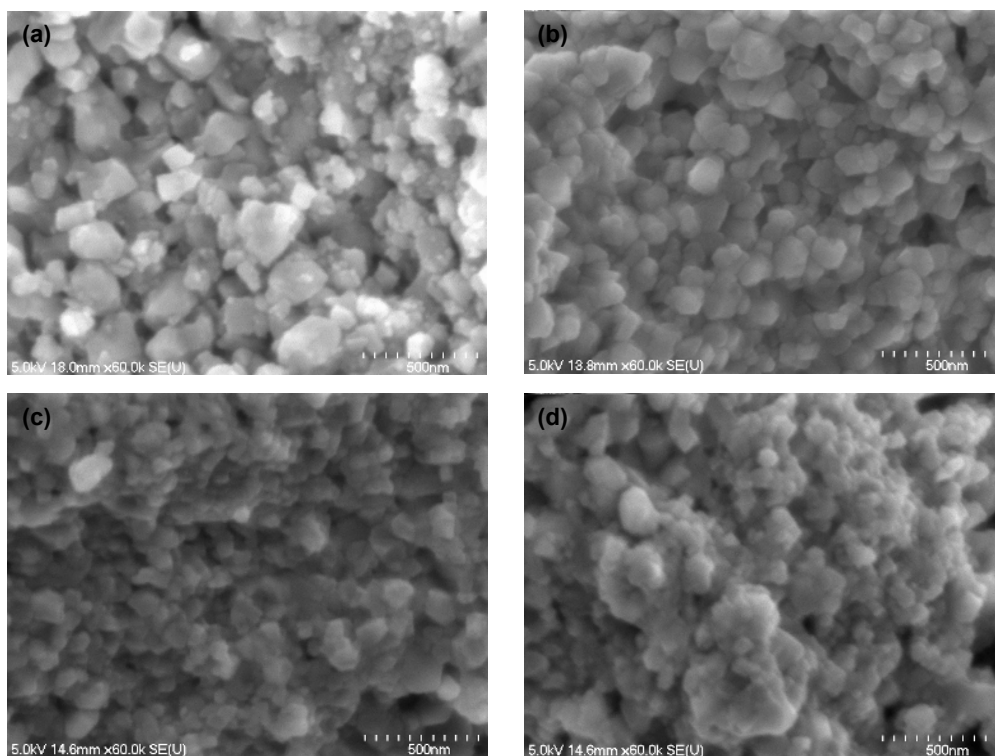| Sintering temperature (℃)	Grain size (nm)	Relative density (%)	ε' at T_R	ε' at T_C	d_{33} (pC/N)
1200	86	95	731	1520	160
1250	94	97	1028	2071	182
1300	107	98	1123	2504	198
1350	123	99	1530	3062	212

Fig. 2(i) SEM of BST ceramics ball milled for 20 h and sintered at (a) 1200 ℃, (b) 1250 ℃, (c) 1300 ℃ and (d) 1350 ℃ for 2 h.
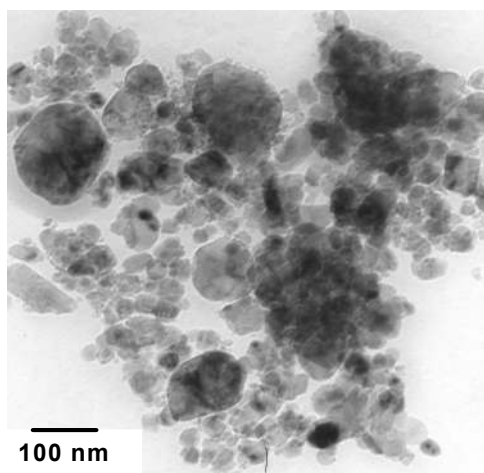

Fig. 2(ii) TEM of BST ceramics ball milled for 20 h and sintered at 1350 ℃ for 2 h.

1200 ℃ to 1350 ℃. The reduced grain sizes of the specimens in the present work can be related to the fine morphology of the starting powders and a good grain connection (Fig. 2(i)) for each constituent phase in the ceramic specimens.

3. 2 Dielectric constant

The grain size dependence of dielectric constant of nanocrystalline BST compositions at 100 kHz is shown
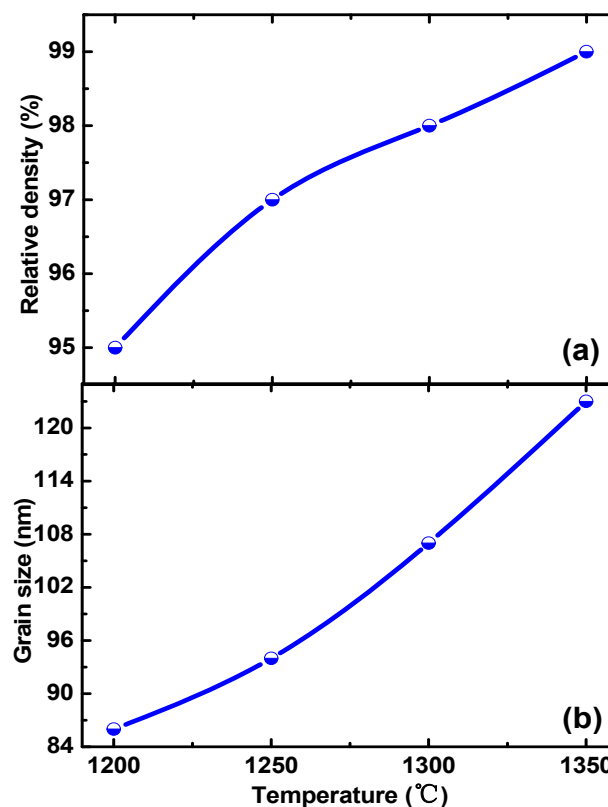

Fig. 3 (a) Relative density and (b) grain size as a function of sintering temperature.

in Fig. 4(a) as a function of temperature. The dielectric constant increases with increasing temperature for all the grain sizes. As expected, it reaches a maximum value at transition temperature (T_C) and then decreases, with further increase in temperature. Dielectric constant is observed to increase from 731 to 1530 as the sintering temperature increases; this is due to the increase in the density of the samples. Chen *et al.* [3] and Xu *et al.* [13] also observed similar variation in dielectric constant in these compositions prepared by thin films and ceramics, respectively. The dielectric anomaly is clearly observable for all the samples, indicating a ferroelectric behavior. The hopping of charge carriers is thermally activated with temperature rise; hence, the dielectric polarization increase causes an increase in ε_r. The dielectric constants at T_R and T_C are also shown in Fig. 4(b). From Fig. 4(b), it is described that the dielectric constants at T_R and T_C increase with the grain size increasing. It is found that at T_C the dielectric constant increases as 1520, 2071, 2504 and 3062 with grain size of 86 nm, 94 nm, 107 nm and 123 nm, respectively (Table 2). The dielectric constant of the nanocrystalline samples is remarkably less sensitive to temperature in contrast to the coarse ceramics. As is well known, the dielectric anomaly can be ascribed to a ferroelectric phase (tetragonal)–paraelectric phase (cubic) transition at T_C and it is also noticed that the Curie transition temperature shifts from 70 ℃ to 80 ℃ as the grain size increases.

There are two possibilities to gain the high dielectric properties of BST nano ceramics. The first possibility is the crystal structure of the phase. The smaller *c/a* means the smaller tetragonality, which also means that the crystal structure is closer to the cubic structure. This leads to an easier transformation from tetragonal to cubic phase, which explains why the dielectric constant at room temperature decreases with decreasing *c/a*. The second possibility is the grain size which also has a significant effect on the dielectric properties. The dielectric properties of BST ceramics are affected by both crystalline structure of phase and microstructure. Grain size also has significant effect on the dielectric constant. A ferroelectric single crystal often has multiple ferroelectric domains separated by interfaces called domain walls, which are transition between different dipole alignment. The dielectric constant is dependent on the population of domains and mobility of the domain walls [14]. It is also believed that when the grain size is uniform, the
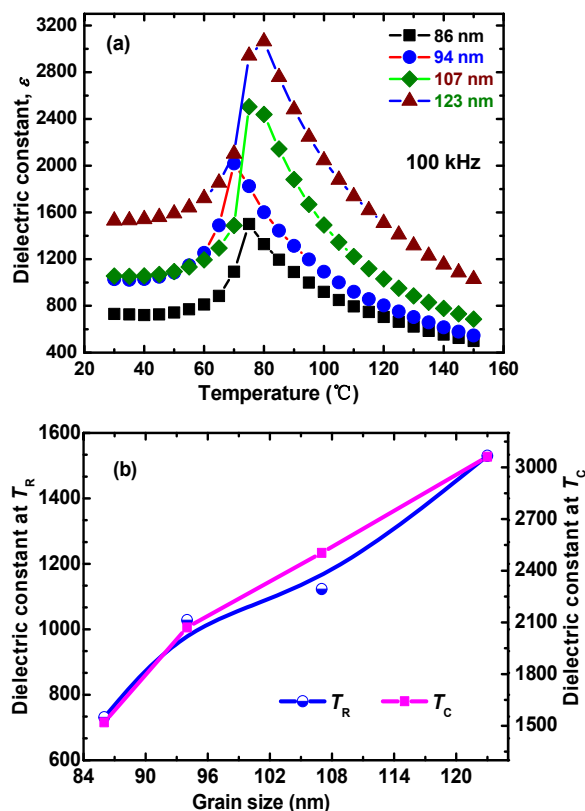

Fig. 4　(a) Temperature dependence of the dielectric constant at 100 kHz with different grain sizes; (b) grain size dependence of the dielectric constant at T_R and T_C.

domain wall movement is relatively easy and regular, and dielectric constant increases. Internal stress arises in the material at Curie transition temperature due to the mechanical deformation of the unit cells that comes from the phase transformation. It is understandable that this internal stress is affected by the grain size and uniformity. Uniform grain size generates less internal stress, resulting in easier domain wall motion.

3. 3 Piezoelectric coefficient

The nanocrystalline BST ferroelectric ceramics were poled in silicon oil at 150 ℃ by applying a DC field of 10 kV/cm for 2 h. This gives balanced poling processes to enable observations of any changes in the piezoelectric independent of poling levels. In general, the piezoelectric properties at room temperature decrease consistently with grain size reduction [15–17]. The grain size dependence of piezoelectric coefficient (d_{33}) is shown in Fig. 5. It can be noticed that the piezoelectric constant of our experiment can be decreased from 212 pC/N for 123 nm to 160 pC/N for 86 nm (Table 2). Generally the piezoelectric constant is
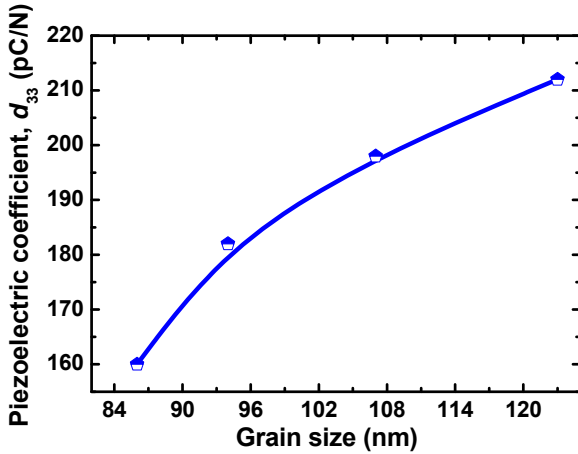
Fig. 5 Grain size dependence of the piezoelectric constant d_{33} of BST ceramics.

determined by crystal structure, relative density as well as grain size. Since there is no apparent difference in crystal structure and relative density, the grain size should be a main factor such that the piezoelectric constant increases apparently with increasing grain size. However, a study by Shao *et al.* [18] indicated that for the conventional sintered $BaTiO_3$ ceramics with larger grain size, the piezoelectric constant decreases from 419 pC/N to 185 pC/N when the average grain size increases from 7 μm to 19 μm. Hence, there could be a critical grain size with which the piezoelectric constant of BST has a maximum value.

3.4 *P–E* hysteresis loop behavior

Figure 6(a) shows the polarization versus electric field (*P–E*) hysteresis loops of the nanocrystalline BST ferroelectric ceramics with different grain sizes at room temperature. It is found that the hysteresis loops change significantly with grain size. The grain size dependence of the remanent polarization (P_r) and the coercive electric field (E_c) of BST nano ceramics are shown in Fig. 6(b). It is found that the coercive electric field (E_c) decreases as grain size increases. For the small grain (86 nm) $E_c = 3.2$ kV/cm, and for the largest grain (123 nm) $E_c = 2.04$ kV/cm. Energy barrier for switching ferroelectric domain must be broken through and energy barrier decreases as grain size increases. So reversal polarization process of a ferroelectric domain is much easier inside a large grain than in a small grain [19]. Moreover, it is also found that the remanent polarization (P_r) increases with the increase of grain size of BST ceramics (Table 3). Effect of grain
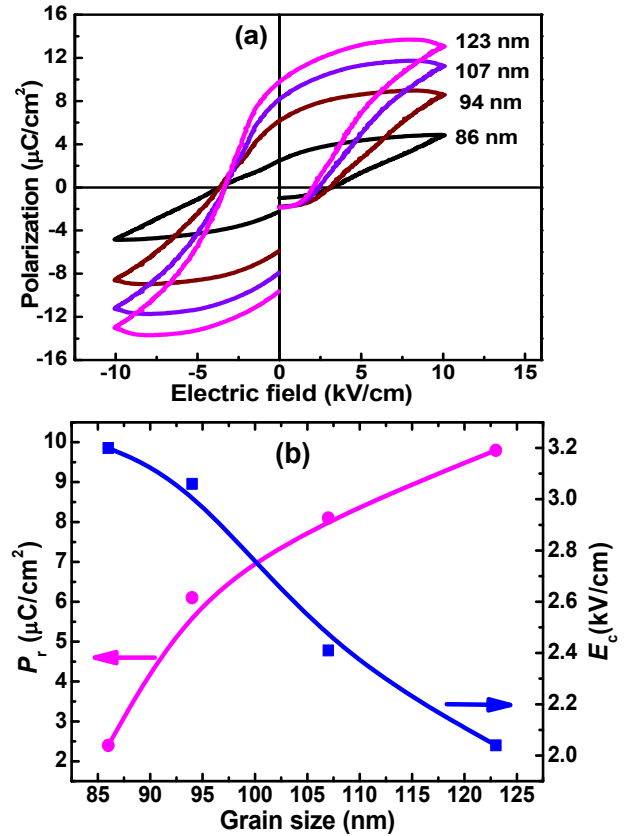

Fig. 6 (a) Ferroelectric hysteresis loops at room temperature and 1 kHz with different grain sizes; (b) grain size dependence of the remanent polarization (P_r) and the coercive field (E_c) of BST ceramics.

Table 3 Values of E_c, P_{max} and P_r obtained from the hysteresis loops of BST ceramics with different grain sizes

Grain size (nm)	E_c (kV/cm)	P_r (μC/cm^2)	P_{max} (μC/cm^2)
86	3.20	2.4	4.82
94	3.06	6.1	8.56
107	2.41	8.1	11.24
123	2.04	9.8	13.06

boundary on polarization includes two facets. On one hand, grain boundary is a low-permittivity region. That means the grain boundary has poor ferroelectricity. Therefore, polarization of grain boundary may be little, and even none. On the other hand, space charges in grain boundary exclude polarization charge on grain surface, and depletion layer on grain surface can be formed. That results in polarization discontinuity on grain surface to form depolarization field, and polarization decreases. The number of grain boundary increases as grain size decreases. Consequently, the remanent polarization increases as the grain size increases.

4   Conclusions

In this study, nanocrystalline barium strontium titanate ferroelectric ceramics have been synthesized from the fine constituent powders by high energy ball milling at sintering temperatures of 1200–1350 ℃. From the results of XRD, it is evident that BST is of perovskite crystal structure. As the sintering temperature increased, the average grain size of BST ceramics increased from 86 nm to 123 nm. As the grain size increased, the dielectric constant both at room temperature and the Curie transition temperature increased. It can be noticed that the piezoelectric constant of our experiment can be increased with grain size. It is found that the ferroelectric hysteresis loops change significantly with grain size, and the coercive electric field (E_c) decreases as grain size increases. For the small grain (86 nm) $E_c = 3.2$ kV/cm, and for the largest grain (123 nm) $E_c = 2.04$ kV/cm. In addition, it is also found that the remnant polarization (P_r) increases with the increase of grain size of BST ceramics. So, BST systems are very attractive as an alternative promising lead free material for piezoelectric and tunable capacitor device applications.

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