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Phase structure and nano-domain in high performance of $BaTiO_3$ piezoelectric ceramics

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Abstract

$BaTiO_3$ ceramics were prepared by conventional sintering technique with a special emphasis on the effects of sintering temperature (1100–1230 °C) on the crystalline structure and piezoelectric properties. XRD patterns indicated that the crystallographic structure changed from tetragonal phase to orthorhombic one with raising sintering temperature from 1160 °C to 1180 °C. Domains were shaped in a stripe and a herringbone in orthorhombic samples for $BaTiO_3$ ceramics. The domain width and domain density increased with raising sintering temperature. The $BaTiO_3$ ceramic sintered at 1190 °C showed the excellent electrical properties, $d_{33} = 355$ pC/N, $k_p = 40\%$, $P_r = 10.2$ μC/cm^2, respectively, which are originated to the contributions of both the crystallographic structure transition and nano-domain.

Keywords: A. Sintering; B. Grain size; C. Piezoelectric properties; D. $BaTiO_3$ and titanates; Domain sizes

1. Introduction

Lead zirconate titanate (PZT) based piezoelectric ceramics have long played a leading role in piezoelectric ceramics area because of their excellent piezoelectric properties and good temperature stability. However, the content of PbO in PZT is over 60%, which has made a great threat for human health and environment. Many efforts have been made on lead-free piezoelectric ceramics with excellent properties in order to replace the PZT. Barium titanate ($BaTiO_3$), the first material practically used to fabricate piezoelectric ceramics, was widely used before the discovery of PZT.[1–3] Recent researches on the fabrication of high-performance $BaTiO_3$ lead-free piezoelectric ceramics have attracted much attention again. For example, high piezoelectric constant d_{33} values of 350, 416, 460 and 788 pC/N were separately reported for $BaTiO_3$ ceramics prepared by microwave sintering, spark plasma sintering, two-step sintering and templated grain growth using hydrothermally synthesized fine $BaTiO_3$ powders.[4–7] In addition, Shao et al.[8] reported a high d_{33} value of 419 pC/N for $BaTiO_3$ ceramics obtained through conventional solid-state reaction route starting from ordinary $BaCO_3$ and TiO_2 powders.

Although $BaTiO_3$ is one of the promising lead-free piezoelectric materials, the origin of high piezoelectric properties for $BaTiO_3$ ceramics is still controversy so far. The piezoelectric properties are considered to be closely related to both grain and domain sizes.[4,6,9–12] Takahashi et al.[4] reported the piezoelectric constant $d_{33} = 350$ pC/N of the sample fabricated by microwave sintering, in which the grain size was 2.1 μm and domain width was less than 50 nm. Tomoaki[6] acquired excellent piezoelectric properties of $d_{33} = 460$ pC/N by two-step sintering, whose grain size was 1.6 μm. It is commonly considered that much smaller grain size and domain size should be required to obtain much higher piezoelectric properties.[9–12]

The theoretical investigation indicated that the domain width was proportional to (grain size)$^{1/2}$ in unpoled $BaTiO_3$ ceramics.[10] On the other hand, Shao et al.[8] reported that domain length, which reflects the areas of domain walls in the three-dimensional, rather than domain width, significantly influences the piezoelectric properties in normally sintered $BaTiO_3$ ceramics. The larger the grain size, the longer the domain length. They revealed that the piezoelectric constant d_{33} values decreased from 419 pC/N to 185 pC/N when its average grain size increased from 7 to 19 μm, while its average domain width remained

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approximately constant at around 480 nm. High piezoelectric properties were acquired by microwave sintering, spark plasma sintering and two-step sintering, which were also attributed to the small grain size. Shen and Li[5] reported the high piezoelectric properties (416 pC/N) owing to nano-domain structure in large grains (>10 μm) for the sample prepared by spark plasma sintering. It is known that crystallographic structure affects greatly piezoelectric properties for (Na,K)NbO_3-based ceramics. Little attention was paid to the influence of crystallographic structure on piezoelectric properties of $BaTiO_3$ ceramic besides the grain size and domain size so far. The issue is whether high piezoelectric properties and nano-domain can be obtained or not in large grains (>50 μm). Does the crystallographic structure influence the piezoelectric properties of $BaTiO_3$ ceramics? In the present study, the dependence of piezoelectric properties on crystallographic structure, grain size and ferroelectric domain structure was investigated. It was found that the $BaTiO_3$ with large grain also exhibited excellent piezoelectric properties, which may be due to the crystallographic structure transition and small domain existed in large grains (>50 μm).

2. Experimental procedure

Hydrothermally synthesized $BaTiO_3$ powders shown in Fig. 1 were used as raw material. The powders were first pressed into disks of 10 mm in diameter at 80 MPa using PVA as a binder, followed by normal sintering at 1100–1230 °C for 2 h. Silver electrodes were fired on the top and bottom surfaces of the sintered samples and fired at 600 °C for 30 min. Poling was performed under an electric field of 3 kV/mm in silicone oil bath for 30 min.

Density of the sintered samples was determined by the Archimedes method. The crystal structure of poled samples was determined using XRD with Cu Kα radiation ($\lambda = 1.5416$ Å) filtered through a Ni foil (Rigaku, RAD-B System, Tokyo, Japan). The microstructure of $BaTiO_3$ powders was observed by field emission scanning electron microscopy (FESEM, SUPRA^{TM} 55, Germany). After chemical etching the samples surface in $HCl:HF:H_2O = 1:1:20$ solution for 40 s, the microstructure of the poled samples was observed by scanning electron microscope (SEM, ZEISS-EVO18, Germany) or optical microscopy (BX60, Olympus, Japan). The domain of poled ceramic samples was observed by transmission electron microscopy (TEM, JEM-2010, Japan). The grain size was determined by the linear intercept method, which was statistically averaged by the careful examination of each grain size. The domain width and length were also determined by linear intercept method, and the domain density was determined by calculating the average number of domain in a certain length. The piezoelectric constant d_{33} was measured using a quasi-static piezoelectric coefficient testing meter (ZJ-3A, Institute of Acoustics, Chinese Academy of Sciences, Beijing, China). The temperature dependence of the dielectric properties was examined using a programmable furnace with an *LCR* analyzer (TH2828S, Tonghui Electronics, Shenzhen, China) at 1 kHz between 7 and 200 °C. The electromechanical coupling coefficient was determined by resonance–antiresonance method using an Agilent 4294A precision impedance analyzer (Hewlett-Packard, Palo Alto, CA). Ferroelectric hysteresis loops were measured using a ferroelectric tester (RT6000HVA, Radiant Technologies Inc., Albuquerque, NM).

3. Results and discussion

3.1. Phase structure and microstructure

Fig. 2 shows the XRD patterns of poled $BaTiO_3$ ceramics sintered at 1100–1230 °C. All the samples exhibit a pure perovskite structure without any trace of impurity phase. The diffraction peaks cited from the tetragonal $BaTiO_3$ (PDF#05-0626) and the orthorhombic one (PDF#81-2200) are indicated by vertical lines for comparison, whose ratios of two diffraction peaks around 45° are obviously different as shown in the enlarged XRD patterns of angles ranged from 44° to 46° in Fig. 1(b). The former ratio of (2 0 0) to (0 0 2) is greater than 1, while the later ratio of (2 0 0) to (0 2 2) is less than 1. All the diffraction peaks correspond well to those of the PDF#05-0626 for the samples sintered at 1100–1160 °C and of the PDF#81-2200 for the counterparts sintered at 1180–1230 °C, respectively. The result suggests that the crystallographic structure changes from tetragonal symmetry to orthorhombic one with raising sintering temperature from 1160 °C to 1180 °C. Although a discontinuous change appears between 1160 °C and 1180 °C, the diffraction peaks shift to a lower angle with raising temperature in the range of 1180–1230 °C. The decreased diffraction 2θ peak corresponds to the enlargement of the lattices. There may be some oxygen vacancies in lattice due to inadequate oxygen supply in the environment with raising sintering temperature, leading

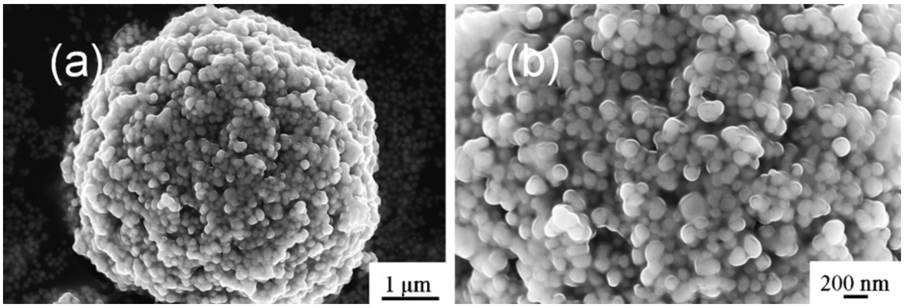

Fig. 1. FESEM images of commercial $BaTiO_3$ powders under different magnifications.

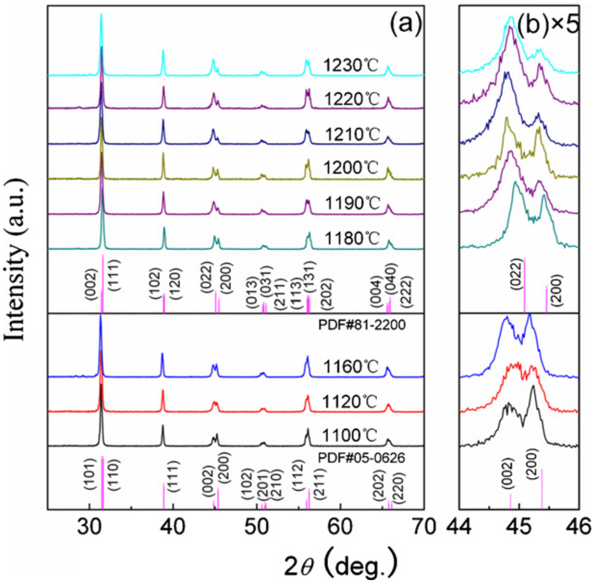

Fig. 2. XRD patterns of the poled $BaTiO_3$ ceramics sintered at 1100–1230 °C.

to the substitution of Ti^{3+} (0.72 Å) for Ti^{4+} (0.68 Å), which results in the enlargement of lattice.[13–15] Maiwa[11] reported the crystallographic structure transition with increasing sintering from 1100 °C to 1300 °C for conventionally sintered $BaTiO_3$ ceramics. The sample sintered at 1100 °C showed a mixing of cubic/orthorhombic phases with a broad diffraction peak splitting into (0 2 2) and (2 0 0). But a tetragonal character was observed in the XRD pattern for the ceramics sintered at 1200 °C and 1300 °C in which the intensity ratio of (0 0 2) and (2 0 0) was about 1:2. However, little attention had been paid to the influence of crystallographic structure to piezoelectric properties. Shao[8] reported the same orthorhombic phase for $BaTiO_3$ ceramics sintered at 1210 °C, 1250 °C and 1300 °C, which showed excellent piezoelectric properties ($d_{33} = 419$ pC/N) for the sample sintered normally at 1210 °C. Shen and Li[5] obtained a $d_{33} = 193$ pC/N for the sample sintered normally at 1210 °C which had a tetragonal symmetry. The results suggest that the crystallographic structure of $BaTiO_3$ may have a great influence on the piezoelectric properties which is similar to the (Na,K)NbO_3-based ceramics.[16,17]

Fig. 3 shows the lattice parameters of the $BaTiO_3$ ceramics as a function of sintering temperature. The sample sintered at 1100 °C shows a single perovskite structure with a tetragonal symmetry, whose lattice parameters are $a = b = 4.0078$ Å and $c = 4.0454$ Å. Lattice parameter a drops to about 3.992 Å as the temperature was raised to 1180 °C, while b and c suddenly increase to 5.7289 Å and 5.6729 Å. The change on the lattice parameters is consistent with the shift of diffraction peaks (Fig. 2). It suggests that the transition between tetragonal phase and orthorhombic one occurred in the $BaTiO_3$ samples sintered at 1160–1180 °C. This behavior is quite similar to the temperature sensitivity of the phase in the (Na,K)NbO_3-based ceramics,[16,17] although no much attention was paid to the phase transition for the $BaTiO_3$ system.

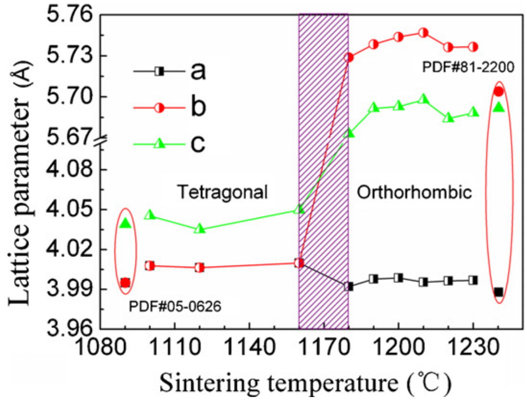

Fig. 3. Lattice parameters of the poled $BaTiO_3$ ceramics sintered at 1100–1230 °C.

Fig. 4 gives the SEM and OM images of the poled $BaTiO_3$ ceramics sintered at 1100–1230 °C. The $BaTiO_3$ ceramic sintered at 1100 °C shows a loose and porous structure with an average grain size of about 0.8 μm. The grain grows rapidly to 50 μm as raising sintering temperature to 1180 °C. Further raising the temperature to 1220 °C and 1230 °C, the grain size gradually increases to 60 μm, which is similar to the grain size (>50 μm) in the sample which were sintered normally at 1210 °C by Shen and Li.[5]

Fig. 5 shows OM images of the domain pattern for the poled $BaTiO_3$ ceramics sintered at 1180–1230 °C. Stripe and/or herringbone domain patterns are clearly observed in the larger grain under high magnification for all the samples except for the porous samples sintered at 1100 °C and 1160 °C. The herringbone domains result from the combination of two alternating pairs of 90° domains.[8] There are several stripe domains orderly arrayed in a grain, in which each stripe domain composes of many paralleled domain bunches and the domain bunch is made up of single domain. The length of a single domain is actually the width of stripe domain. The detailed domain structure is shown schematically in Fig. 6 . Such stripe and herringbone domains were reported usually to be a typical feature of domain configuration for $BaTiO_3$ ceramics with tetragonal symmetry,[18–21] which are observed presently in the orthorhombic phase. The stripes correspond to the 90° domain patterns. The 90° domains are small in length comparable to their corresponding grain size. The domain length is about 8 μm in length with a uniform distribution in each grain for the samples sintered at 1180–1210 °C. However, for the samples sintered at 1220 °C and 1230 °C, the domain lengths show a great difference in a grain, about 6.5–9 μm and 7–13 μm, respectively. The long thin stripes are orderly arrayed in a grain. The stripes almost array in parallel and keep a certain distance from each other for the samples sintered at 1180–1210 °C. The distances between two strips are gradually reduced with raising sintering temperature. On the other hand, when the samples were sintered at 1220 °C and 1230 °C, the stripes array more tightly and several herringbone patterns can be observed individually in a grain. The smaller the domain length means the smaller the areas of domain walls. The domain walls with small areas rotate easily and respond more actively to the external electrical signal, which is considered to be the most likely reason that contributes to the excellent piezoelectric properties.[8] Both of the samples sintered at 1220 and

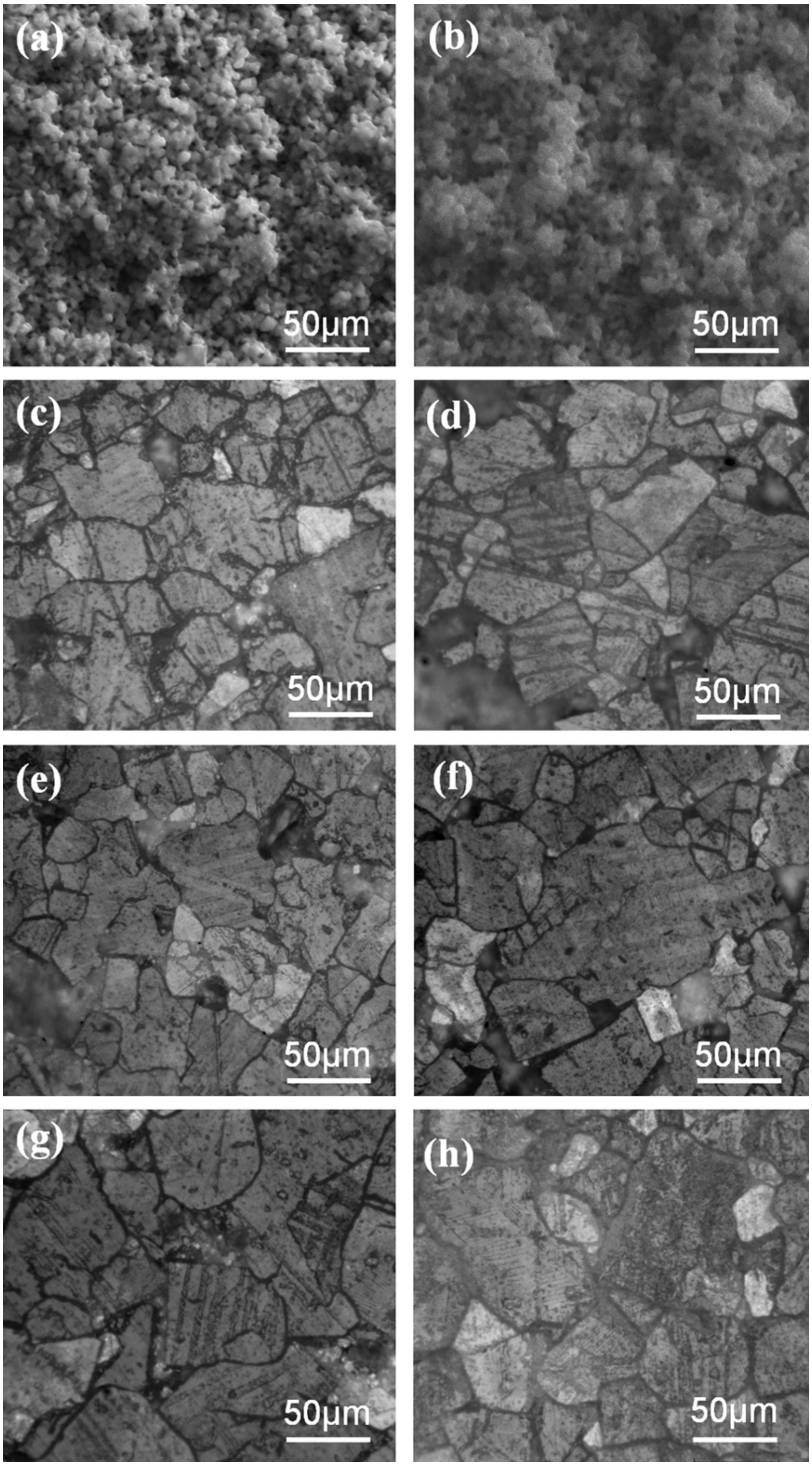

Fig. 4. SEM (a and b) and OM (c–h) images of the poled $BaTiO_3$ ceramics sintered at 1100 °C (a), 1160 °C (b), 1180 °C (c), 1190 °C (d), 1200 °C (e), 1210 °C (f), 1220 °C (g) and 1230 °C (h).

1230 °C have more domain stripes and longer domains compare to other samples sintered at lower temperatures. There may be not enough space for the domain walls to rotate sufficiently in an individual grain with the tightly arrayed longer stripes, which induces the piezoelectric properties to decrease for the samples sintered at 1220 °C and 1230 °C.

The HRTEM images of a typical of nano-domain for the poled samples sintered at 1190 °C and 1220 °C are shown in Fig. 7. Stripe domains are also clearly observed. The single domain width is about 10 nm for the sample sintered at 1190 °C and about 20 nm for the counterpart sintered at 1220 °C, respectively, which are much smaller comparable to their corresponding

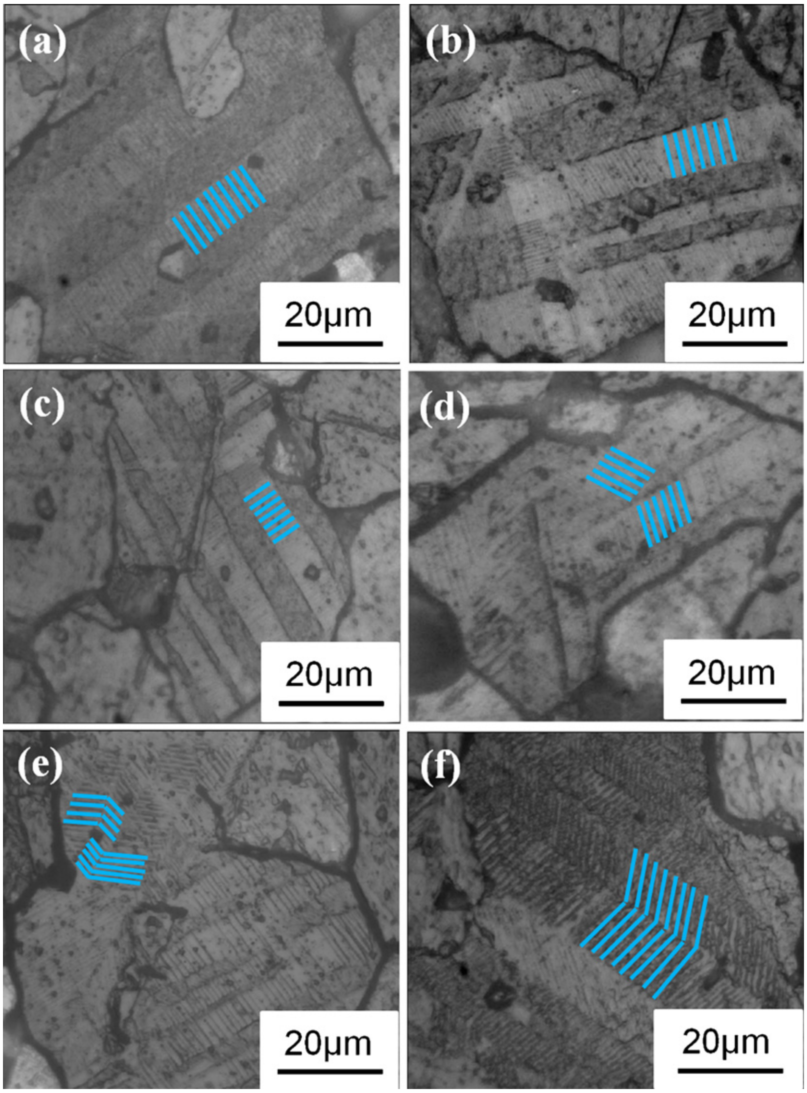

Fig. 5. OM images of the domain pattern for the poled $BaTiO_3$ ceramics sintered at 1180 °C (a), 1190 °C (b), 1200 °C (c), 1210 °C (d), 1220 °C (e) and 1230 °C (f).

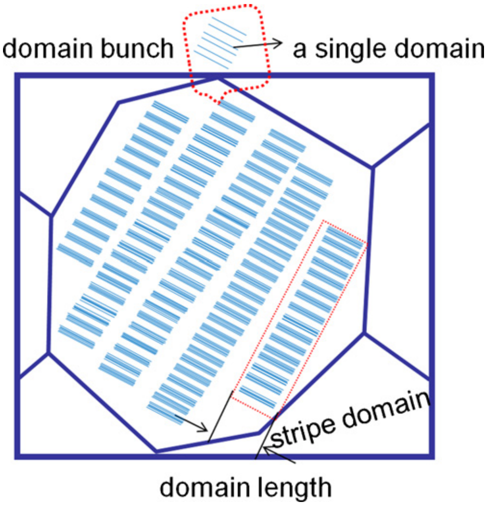

Fig. 6. Schematic image of domain for the $BaTiO_3$ ceramics.

grain size. The single domains have the similar width and uniformly distribute in each domain bunch for the samples sintered at 1190 °C and 1220 °C. It is clearly that the domain density increases and the distances between single domains reduce in one domain bunch with raising sintering temperature. Therefore, the sample sintered at 1220 °C has more domain walls in a certain area than that sintered at 1190 °C, which result in a decrease of the piezoelectric properties. According to the previous reports,[5,9–11] the high piezoelectric properties should be attributed to this kind of nano-domain structure. Takahashi et al.[4] suggested that nano-domain structure was contributed to the enhanced piezoelectric properties in $BaTiO_3$ ceramics prepared by microwave sintering. The domain width was less than 50 nm for the sample with grain size of 2.1 μm. Shen and Li[5] also observed the nano-domain of about 20 nm in width for the sample prepared by spark plasma sintering, whose grain size was larger than 10 μm. It is generally accepted that the smaller grain size is required to reduce the domain size.[9–11] However, the nano-domain structure not only can be obtained in the case of small grain size,[4] but also can be acquired in large grain size

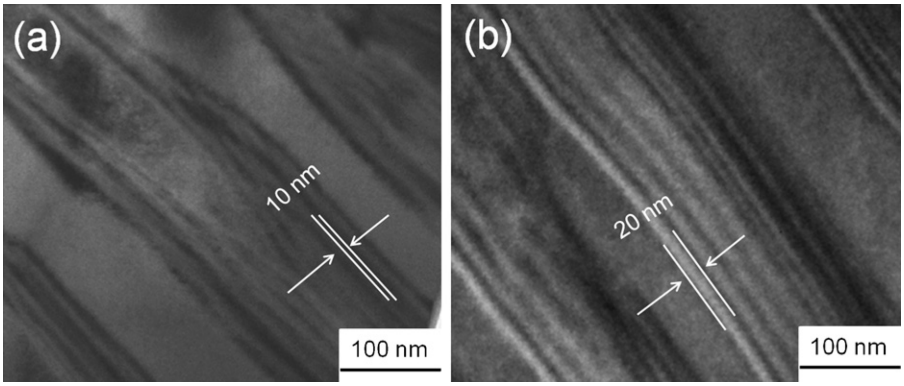

Fig. 7. TEM images for the poled $BaTiO_3$ ceramics sintered at 1190 °C and 1220 °C.

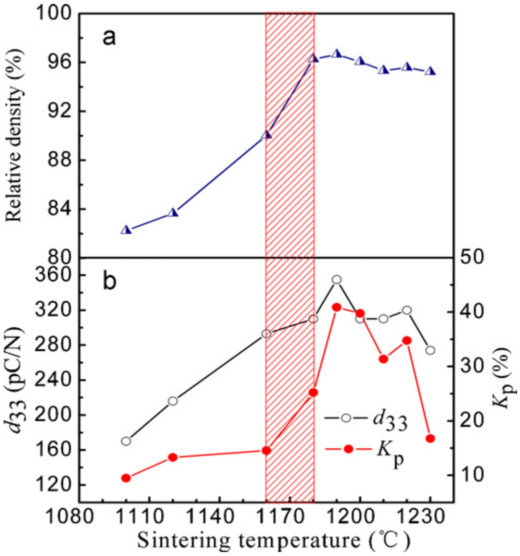

Fig. 8. Relative density, piezoelectric constant d_{33} and electromechanical coefficient k_p of the $BaTiO_3$ ceramics as functions of the sintering temperature.

(>50 µm) for $BaTiO_3$ ceramics prepared by the conventional solid sintering process using nano-powders. A small domain width may be another reason to induce high piezoelectric properties for $BaTiO_3$ with large grains. Hydrothermally synthesized $BaTiO_3$ powders in which many micro-scale spherical particles are composed of nano particles were used in the study as shown in Fig. 1. The powders with nano-micro composite structure may be contributed to the large grains with small domains.

3.2. Dielectric and piezoelectric properties

Fig. 8 delineates the variation of relative density, piezoelectric constant d_{33} and electromechanical coefficient k_p with sintering temperature. The relative density increases from 79.7% to a maximum value of 98.7% with raising sintering from 1100 °C to 1190 °C and then reduces to a constant value of about 95.0% as further raising temperature. Both d_{33} and k_p show a similar varying trend to the relative density with raising sintering temperature. When the sintering temperature was lower than 1190 °C, the d_{33} and k_p rapidly increase with increasing temperature, which indicates that the relative density is an important factor to influence the d_{33} and k_p. The higher relative density value, the larger d_{33} and k_p values.[22] The optimized values are $d_{33} = 355$ pC/N and $k_p = 40\%$ in the sample sintered at 1190 °C. It is notable that when the sintering temperature rises from 1190 °C to 1230 °C, the d_{33} and k_p decrease rapidly while the relative density still stays above 95.0%. Shao et al.[8] reported a high d_{33} value (419 pC/N) and suggested that the d_{33} value is not only determined by relative density but also by grain size. But the grain size is about 50 µm and the relative density also changes a little between 98.7 and 95.9% for the present samples sintered at 1180–1210 °C. There must be other factors to influence the d_{33} and k_p if the samples both have a close relative density and a close grain size. Besides the high relative density and moderate grain size, the sample sintered at 1190 °C is closer to the phase transition between tetragonal symmetry and orthorhombic one (Figs. 2 and 3), which provides a favorable condition for easier motion of domain and thus gives rise to high piezoelectric properties. This may be the main reason for the excellent piezoelectric properties of the sample sintered at 1190 °C. Moreover, this sample has a small domain width about 10 nm (Fig. 7(a)) and its domain width increases to 20 nm (Fig. 7(b)) with rising sintering temperature to 1220 °C. It was reported that the small domain width contributes to the enhanced piezoelectric properties.[5,9] Further raising the temperature to 1220 °C and 1230 °C, the grain size gradually increases to 60 µm. The samples have more domain stripes and longer domains, which induces the decrease of piezoelectric properties. Otherwise, more oxygen vacancies were created with increasing sintering temperature, which pin the movement of the ferroelectric domain walls and result in both decrease of the d_{33} and k_p.

Fig. 9 shows the temperature dependence (7–200 °C) of dielectric constant ε_r for the $BaTiO_3$ ceramics measured at 1 kHz. The T_C of the $BaTiO_3$ samples sintered at 1120, 1160, 1190 and 1230 °C is 115, 120, 120, and 125 °C, respectively. The sample sintered at 1190 °C shows the highest dielectric constant at the T_C. It is well known that the cavities can dissipate the energy and deteriorate the dielectric properties. The improved densification results in the reduction of cavities, thereby the dielectric constant would be increased.[23] The inner figure in Fig. 9 shows the temperature dependence of dielectric constant at 7–15 °C. It should be noted that a dielectric constant

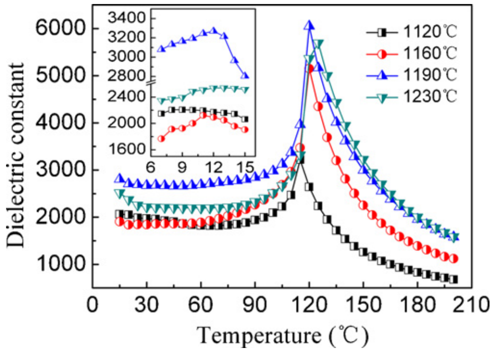

Fig. 9. Temperature dependence of the dielectric constant at 1 kHz for the $BaTiO_3$ ceramics sintered at 1100–1230 °C.

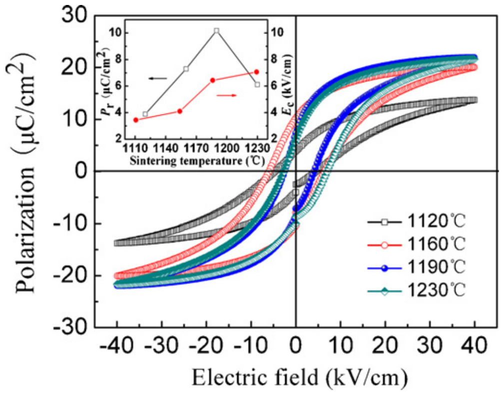

Fig. 10. Ferroelectric hysteresis loops of the $BaTiO_3$ ceramics sintered at 1100–1230 °C.

peak exists in the range of 7–15 °C, which corresponds to the orthorhombic–tetragonal ($T_{O\text{–}T}$) phase transition. The $T_{O\text{–}T}$ is 8, 11, 12, and 13 °C for samples sintered at 1120, 1160, 1190 and 1230 °C, respectively, which shows a slightly increased trend of $T_{O\text{–}T}$ with raising sintering temperature. The sample sintered at 1190 °C is close to the transition between tetragonal phase and orthorhombic one at the room temperature as shown in Fig. 2, resulting in the excellent piezoelectric properties.

Fig. 10 shows the ferroelectric hysteresis loops of the ceramics sintered at different temperatures. All samples possess a typical ferroelectric polarization hysteresis loop. The inset in Fig. 10 illustrates the variation of the remanent polarization P_r and coercive field E_C for the $BaTiO_3$ sintered at different temperatures. The P_r first increases and then decreases, while the E_C increases with raising temperature. The sample sintered at 1190 °C shows the maximum P_r value of 10.2 μC/cm^2, with a corresponding E_C value of 6.4 kV/cm, which indicates that this ceramic is easier to pole and has higher piezoelectric properties. However, oxygen vacancies were easier created at high sintering temperature, which strengthen the pinning effect to the ferroelectric domain under an electric field, thereby inducing a continuous increase of the E_C and a decline of the P_r.[24]

4. Conclusions

Both tetragonal and orthorhombic structures were formed in the $BaTiO_3$ samples sintered normally at 1100–1160 °C and at 1180–1230 °C, respectively. The samples sintered at 1180–1230 °C showed the grain size of 50–60 μm, which were insensitive to the sintering temperature. Stripes or/and herringbones of domain configuration were observed in the samples sintered at 1180–1230 °C and the distances between two strips were gradually reduced with raising temperature. The single domain width and the domain density increased with raising temperature. The $BaTiO_3$ ceramic sintered at 1190 °C showed the highest electrical properties, $d_{33} = 355$ pC/N, $k_p = 40\%$, $P_r = 10.2$ μC/cm^2, respectively. The crystallographic structure transition and nano-domain are most likely the origin of the high d_{33} of the $BaTiO_3$ ceramics.

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