

# Ferroelectricity of 30 nm BaTiO<sub>3</sub> ceramics prepared by high pressure sintering

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**Abstract** BaTiO<sub>3</sub> ceramics with a grain size of 30 nm were prepared at 6 GPa, 1,273 K using a three-step high pressure sintering method. The sintered bulk is uniform and the relative density is above 96% of the theoretical value. Similar to normal BaTiO<sub>3</sub>, successive phase transitions were observed in 30 nm BaTiO<sub>3</sub> ceramics by X-ray diffraction method with the change of temperature. After annealing in O<sub>2</sub>, a broadened ferroelectric transition was obtained at 398 K and the relative dielectric constant is 1,700 at 10 kHz.

**Keywords** BaTiO<sub>3</sub> nanocrystalline ceramics · High pressure sintering · Ferroelectricity

## 1 Introduction

Barium titanate (BaTiO<sub>3</sub>) with a perovskite structure has been widely used as ferroelectric material for multilayer ceramics capacitors, embedded capacitance in printed circuit boards, thermal imaging, and actuators, owing to its high dielectric constant and low losses [1, 2]. It is well known that bulk BaTiO<sub>3</sub> undergoes successive phase transitions from cubic to tetragonal (C–T), tetragonal to orthorhombic (T–O), and orthorhombic to rhombohedral (O–R) with temperature decreasing. The phase transition

occurs near 403 K ( $T_C$ ), 298 K ( $T_{T-O}$ ) and 183 K ( $T_{O-R}$ ), respectively [3]. Effects of various factors on ferroelectric properties of BaTiO<sub>3</sub> crystal have been studied both theoretically [4] and experimentally [5–11]. It is generally observed that the grain size has a significant effect on the dielectric properties of BaTiO<sub>3</sub>. The room temperature permittivity has a pronounced maximum for a grain size of about 1 μm [5] and further reducing grain size leads to a decrease of permittivity. Consequently the study of size-dependent properties of nano grain is important both to find the possible limit of ferroelectricity and to elucidate the microstructural characteristics of the ferroelectrics components. Experimentally, it is difficult to obtain nanocrystalline ceramics using conventional sintering methods due to agglomeration and exaggerated grain growth. Zhao et al. [12] reported dielectric data for dense BaTiO<sub>3</sub> ceramics with grain sizes from 50 to 1,200 nm fabricated by spark plasma sintering. They found that with decreasing grain size from 1,200 to 50 nm, the Curie temperature shifted to lower values, and the permittivity decreased. Recently, Deng et al obtained dense BaTiO<sub>3</sub> ceramics with grain sizes less than 20 nm [13] and investigated its successive phase transition.

High pressure sintering can significantly increase the densification driving force and dramatically reduce growth rate as a result of the decrease of diffusivity [14, 15]. Thus, high pressure sintering is a very effective method to obtain dense nanocrystalline ceramics.

In this paper, we report that dense BaTiO<sub>3</sub> ceramics with a homogeneous grain size of 30 nm can be easily prepared from the 10 nm BaTiO<sub>3</sub> raw powder by using a specified high pressure sintering route, i.e. the three-step high pressure sintering method. Using the X-ray diffraction method under various temperatures, the dependence of phase transitions on temperatures of BaTiO<sub>3</sub> ceramics with

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a grain size of 30 nm was investigated. The dielectric properties were measured.

## 2 Experimental procedure

Ten nanometer raw BaTiO<sub>3</sub> powder was synthesized by sol-gel processing [16]. In order to eliminate nano grain agglomeration, which happens generally in nano materials, a three-step method involving high pressure was adopted to synthesize the dense uniform nanocrystalline BaTiO<sub>3</sub> ceramics. High pressure experiments were carried out using a cubic anvil type high pressure apparatus. The pyrophyllite was used as the pressure-transmitting medium. The procedure of the three-step high pressure sintering method was following the route. The first step was to press the raw powder into a pellet uniaxially at 8 MPa at room temperature. No binders were added. In the second step, the pellet was pressed under higher pressure, such as 3 GPa, and then it was unloaded and ground into powder in a mortar without any additives. The grinding time was 15 min. The processed powder was repressed using the same method as the first step. This step was repeated several times. The second step is crucial to crack the agglomerations and avoid exaggerated grain growing in the following high pressure sintering. The third step was to process the pellet by high pressure sintering. The pellet with the dimension of 6 mm in diameter and 2 mm in thickness was wrapped by Ag foil to prevent from contaminating. The pellet was inserted into a BN spacer tube that was in turn put into a graphite heater. The sample was first pressurized up to 6 GPa and then heated at 1,273 K in air. The sintering time was 5 min. After temperature quenching, the sample was recovered by slow releasing pressure.

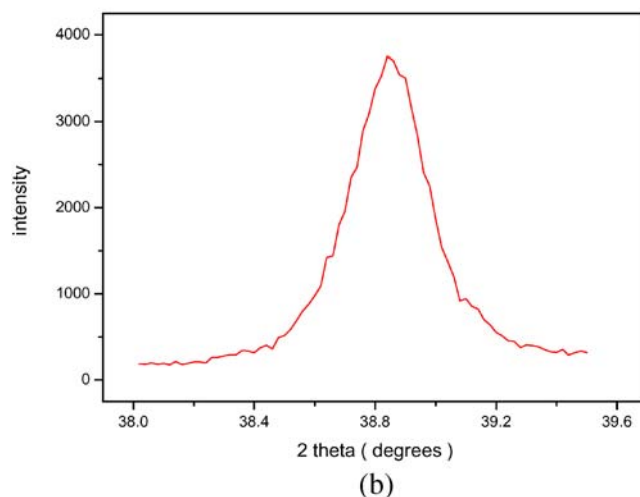
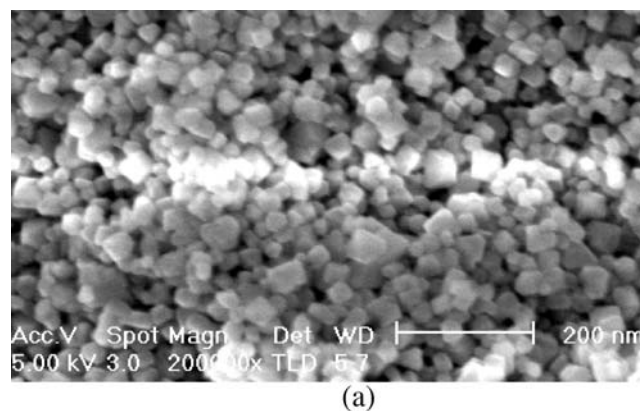
The ceramics samples were characterized with different techniques. The microstructure was observed by scanning electron microscopy (SEM, XL30-FEG) on fracture surfaces. Using CuK $\alpha$  radiation with a step size of 0.02° and a time step of 5 s, the crystallite size of BaTiO<sub>3</sub> sintered bulk could be calculated by the Scherrer equation from the broadened X-ray diffraction (111) peak at room temperature. Phase composition and crystal structure were characterized by X-ray diffraction (Rigaku D/max-2500). The dielectric properties were measured using HP4194A LF impedance analyzer in the vicinity of the Curie temperature at 10 kHz, 100 kHz and 1 Vrms.

## 3 Results and discussion

The microstructure of sintered bulk is shown in Fig. 1(a). The sintered bulk exhibits homogeneous grain size distribution,

and the mean grain size is 30 nm. From the X-ray diffraction pattern in Fig. 1(b) at room temperature, the grain size is calculated to be 28 nm from the (111) peak according to the Scherrer equation. By means of Archimedes' method, the relative density of the BaTiO<sub>3</sub> ceramics is measured to be 96–98% of the theoretical value (6.02 g/cm<sup>3</sup>).

The crystal structure of 30 nm BaTiO<sub>3</sub> ceramics is investigated by X-ray diffraction at variable temperatures. Figure 2(a) shows X-ray diffraction patterns of 30 nm BaTiO<sub>3</sub> ceramics at temperatures ranging from 84 to 443 K. The peaks indexing are simply based on the cubic structure of the single crystal. Owing to the presence of high levels of chemisorbed gases, the 10 nm raw powder can absorb some impurities such as CO<sub>2</sub>, so that there are some carbonate impure phases denoted by the asterisks in X-ray diffraction patterns. The diffraction peaks cannot be separated accurately since the peaks remarkably broaden and incline to overlap when particle size is reduced to the nanoscale [17]. So we only trace the shift trend of some X-ray diffraction peaks, for example (200) peak. Figure 2(b)



**Fig. 1** (a) SEM image of BaTiO<sub>3</sub> ceramics sintered by the three-step high pressure method. (b) (111) XRD peak pattern of BaTiO<sub>3</sub> nanocrystalline ceramics at room temperature

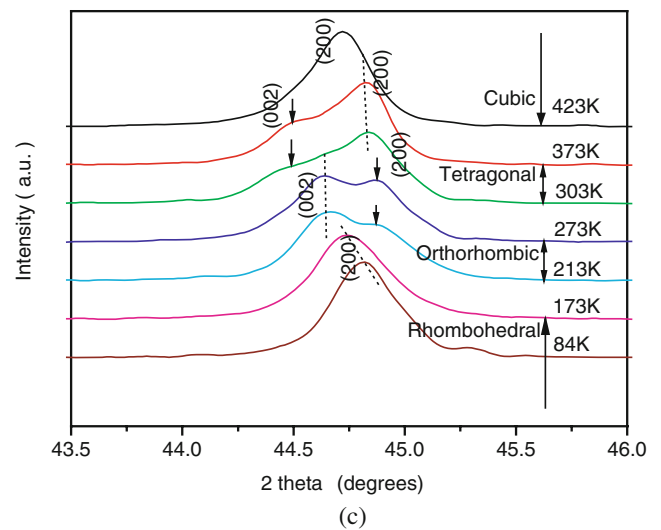
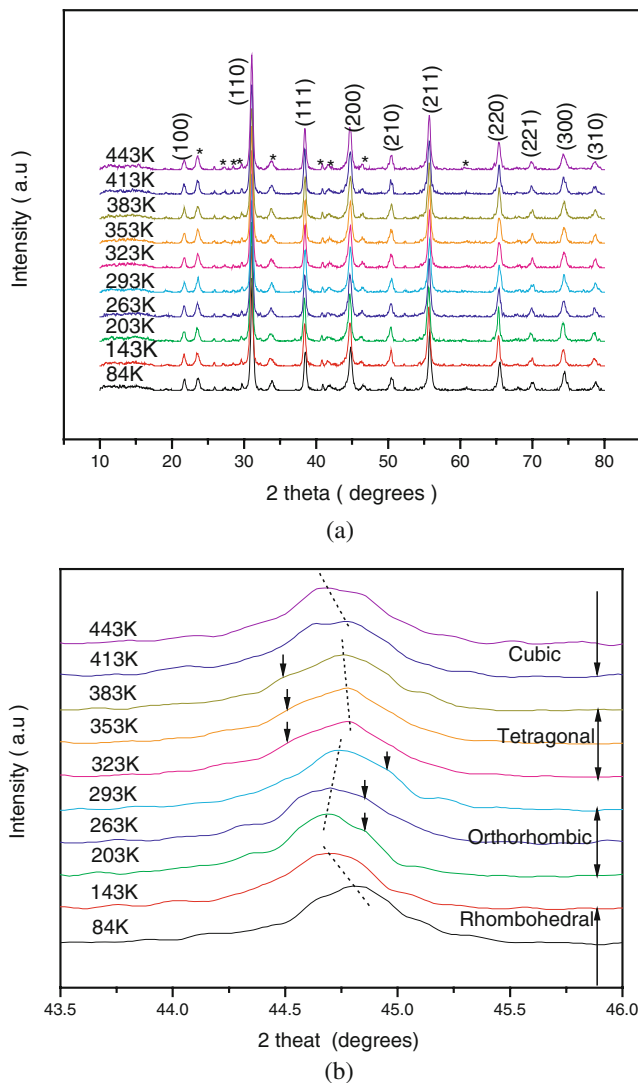


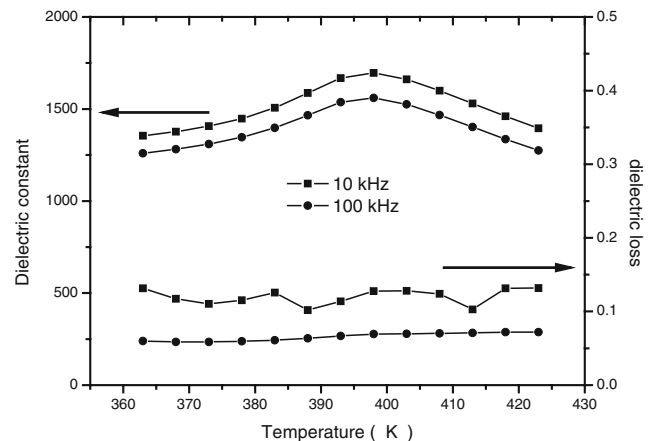
Fig. 2 (continued)

The diffraction peaks of 30 nm BaTiO<sub>3</sub> ceramics at various temperatures cannot clearly show the characteristics for every phase owing to the peaks broadening in Fig. 2(b). Compared with the 600 nm ceramics, it is inferred that successive phase transitions occur in 30 nm BaTiO<sub>3</sub> ceramics. The phase transitions may be assigned to from cubic to tetragonal, then to orthorhombic, and to rhombohedral phase in turn with decreasing temperature.

In order to eliminate the oxygen vacancies and stresses in 30 nm BaTiO<sub>3</sub> ceramics, the sample was annealed in O<sub>2</sub> at 873 K for 8 h. Figure 3 shows the dielectric constant and the dielectric loss in the vicinity of the Curie temperature (*T<sub>c</sub>*) of 30 nm BaTiO<sub>3</sub> ceramics at 10 and 100 kHz. It is found that there is a broadened dielectric peak at 398 K. The relative dielectric constant is 1,700, which is far less than 6,000 for normal bulk, and the dielectric loss is less than 0.15 at 10 kHz. The broadened dielectric peak may attribute to the size-induced diffuse phase transition [18, 19].

**Fig. 2** (a) XRD patterns of 30 nm BaTiO<sub>3</sub> ceramics in various temperature. The asterisks denote peaks to BaCO<sub>3</sub>. (b) Enlarged (200) X-ray diffraction peaks of 30 nm BaTiO<sub>3</sub> ceramics at various temperatures between 2θ=43.5 and 46.0°. (c) Enlarged X-ray diffraction peaks of 600 nm BaTiO<sub>3</sub> ceramics between 2θ=43.5 and 46.0° at various temperatures. The change trends of the peaks are characterized by the dotted lines (the stronger peaks) and the arrows (the weaker peaks)

represents enlarged X-ray diffraction peaks between 2θ=43.5 and 46.0° with increasing temperature. In order to explicitly explain the phase transitions for the 30 nm BaTiO<sub>3</sub> ceramics, we also studied the 600 nm BaTiO<sub>3</sub> ceramics sintered by the same method. Figure 2(c) represents the enlarged X-ray diffraction patterns of 600 nm BaTiO<sub>3</sub> ceramics between 2θ=43.5 and 46.0° with increasing temperature, and the change trends of peaks at various temperatures are outlined by the dotted lines and the arrows. The four typical diffraction patterns obviously exhibit the characteristic of cubic, tetragonal, orthorhombic, and rhombohedral phases, indicating that the successive phase transitions happened with changing temperature.



**Fig. 3** The temperature dependence of the dielectric constant and the dielectric loss of 30 nm BaTiO<sub>3</sub> ceramics at 10 and 100 kHz

When the grain size is below 500 nm, due to the reduced average tetragonal  $c/a$  ( $a$  and  $c$  are the unit cell parameters), the dielectric constant of  $\text{BaTiO}_3$  ceramics decreased dramatically [5, 20]. Moreover the fraction of grain boundary volume increases with decreasing grain size in nanocrystalline ceramics. Thus the dielectric constant is strongly depressed in 30 nm  $\text{BaTiO}_3$  ceramics.

#### 4 Conclusions

Dense  $\text{BaTiO}_3$  ceramics with a grain size of 30 nm were fabricated by using three-step high pressure sintering. We investigated the X-ray diffraction of 30 nm  $\text{BaTiO}_3$  ceramics with the change of temperature. The results indicated that successive phase transitions occurred in 30 nm  $\text{BaTiO}_3$  ceramics with increasing temperature and the ferroelectricity still retained in 30 nm  $\text{BaTiO}_3$  ceramics.

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