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Ferroelectric behaviour of 30 nm $BaTiO_3$ ceramics prepared by high pressure assisted sintering*

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Dense nanocrystalline $BaTiO_3$ ceramics with a homogeneous grain size of 30 nm was obtained by pressure assisted sintering. The ferroelectric behaviour of the ceramics was characterized by the dielectric peak at around 120 °C, the *P*-*E* hysteresis loop and some ferroelectric domains. These experimental results indicate that the critical grain size for the disappearance of ferroelectricity in nanocrystalline $BaTiO_3$ ceramics fabricated by pressure assisted sintering is below 30 nm. The ferroelectric property decreasing with decreasing grain size can be explained by the lowered tetragonality and the 'dilution' effect of grain boundaries.

Keywords: $BaTiO_3$, pressure assisted sintering, nanocrystalline ceramics, ferroelectric behaviour
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1. Introduction

The development of microelectronics and communications requires the miniaturization and integration of ferroelectric components. Consequently the study of size effect in the nanometric range is one of the most attractive subject in the industrial as well as scientific research. Among the most popular ferroelectrics, barium titanate ($BaTiO_3$) is a well-known material with high room temperature permittivity and is extensively used in the electronics industry, especially as material of multilayer ceramic capacitors (MLCC).[1] However, its ferroelectricity decreases with decreasing particle or grain size, and disappears below a certain critical size. The critical size was investigated theoretically, and was predicted to be about 44 nm for $BaTiO_3$ particles.[2−4] Experimentally, for $BaTiO_3$ nanoparticles, owing to the different powder preparation methods, the critical size has been reported to be from 10 to 100 nm.[5] For $BaTiO_3$ thin film, the ferroelectric response was absent when the grain size was 25 nm.[6] For $BaTiO_3$ ceramics prepared by spark plasma sintering, the critical size was reported to be below 20 nm.[7] Because fabricating dense nanocrystalline ceramics must be adopted the special sintering method,[5,7,8] few data on structural, dielectric, ferroelectric behaviours of dense $BaTiO_3$ ceramics with grain size below 100 nm are available.

High pressure significantly promotes densification. Further, during the high pressure assisted sintering, the nucleation rate is increased due to the reduced energy barrier height for nucleation, and the reduced growth rate due to the decrease of diffusivity. Thus high pressure enables the specimen to be fabricated under relatively lower temperature, which results in shorter production period for producing dense nanocrystalline ceramics.[9,10]

In this paper, a novel sintering method, i.e. the three-step pressure assisted sintering, was adopted to prepare the dense nanocrystalline $BaTiO_3$ ceramics. Its ferroelectric behaviours were investigated by observing the dielectric peak, the *P*-*E* hysteresis loop and some ferroelectric domains.

2. Experiment

The raw $BaTiO_3$ powder with a grain size of 10 nm was synthesized by chemical processing,[11] and it was pressed into a pellet under a uniaxial pressure of 7 MPa. No binders were added. The pellet

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was pressed again at ambient temperature under a higher pressure, such as 3 GPa, and then unloaded and ground into powder. The processed powder was repressed into a pellet. In order to sinter the sample under high pressure, the pellet was wrapped by Ag foil to prevent from contamination and then inserted into a BN spacer tube that was in turn put into a graphite heater. The high pressure experiment was performed using a cubic anvil type apparatus. The pyrophyllite was used as the pressure-transmitting medium. The pellet was first pressurized up to 6 GPa and then heated at 1000 °C for 5 min in air. After temperature quenching, the sample was obtained by slow releasing of pressure. To eliminate oxygen vacancies and stress, the as-sintered sample was annealed in O_2 at 600 °C for 8 h.

The ceramics sample was characterized with different techniques. The microstructure was observed by scanning electron microscope (SEM, XL30-FEG). The grain size was determined by x-ray diffraction (XRD, Rigaku D/max-2500 diffractometer). Dielectric measurement was made on a HP 4192A impedance analyser, *P-E* measurement was performed on a TF2000 axiACCT Analyser FE and scanning nonlinear dielectric microscopy (SNDM) was carried out using scanning force microscope (SPM, SEIKO SPI3800N/SPA400).

3. Results and discussion

Figure 1 shows the microstructure of the sintered sample. From the SEM image, the sample was seen to have a homogeneous grain size distribution and the grain size is estimated to be about 30 nm by the line intercept method. The average grain size is calculated to be 28 nm from the full width at half maximum (FWHM) of the broadening of (111) peak using Scherrer formula, which is consistent with the SEM result. The relative density of the sample, determined by the Archimedes' method, is above 96% of the theoretical density.

Figure 2 shows the dielectric constant and the dielectric loss in the vicinity of the Curie temperature (T_C) of the 30 nm $BaTiO_3$ ceramics at 1 kHz. It is found that there is a broadened dielectric peak at 120 °C, indicating the occurrence of ferroelectric-to-paraelectric phase transition. The relative dielectric constant ε_r is 1920, which is far less than the maximum of $BaTiO_3$ ceramics,[12] and the dielectric loss is less than 0.15. The broadening of dielectric peak is in agreement with the general behaviour that the decrease of grain size leads to the broadening and flattening of the permittivity anomaly located at the ferroelectric-to-paraelectric transition temperature (T_C). Thus the sharp dielectric peak at T_C typical of coarse ceramics is replaced by a broadened one. The broadened dielectric peak is characteristic of the size-induced diffuse phase transition.[13,14]

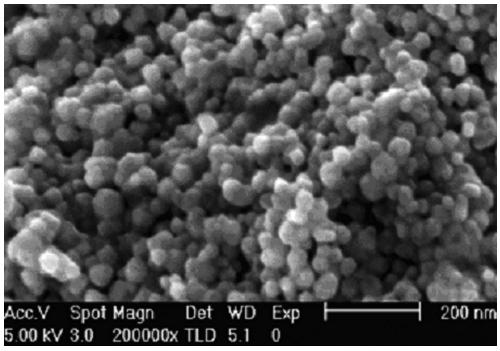


Fig.1. SEM image of 30 nm $BaTiO_3$ ceramics sintered by the high pressure assisted method.

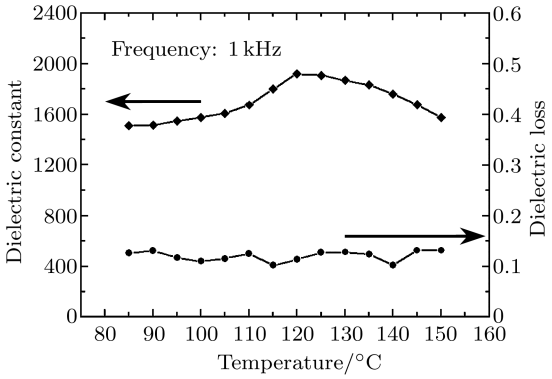


Fig.2. Temperature dependence of dielectric constant and dielectric loss of 30 nm $BaTiO_3$ ceramics at 1 kHz.

In order to further investigate the ferroelectric characteristic, the polarization vs. applied electric field measurement was performed. Figure 3 is a typical polarization hysteresis loop obtained in 30 nm $BaTiO_3$ ceramics at room temperature, which indicates that the ferroelectric behaviour is still retained. At the same time, we also observe that its polarization value is remarkably lower than those reported for $BaTiO_3$ single crystal.

Recently, the scanning nonlinear dielectric microscopy (SNDM) was proposed and developed,[15–17] and its resolution has been improved down to one nanometre.[18] Therefore, it is suited for investigating the nanoscale ferroelectric domains of ferroelectric

materials.[19,20] Figure 4 shows the SNDM image of 30 nm $BaTiO_3$ ceramics. From the image, it is clearly seen that some regions are brighter than the others, indicating the existence of ferroelectric domains. The present experimental evidence of the ferroelectric domains occurring at local regions reveals that ferroelectricity still remains in 30 nm $BaTiO_3$ ceramics.

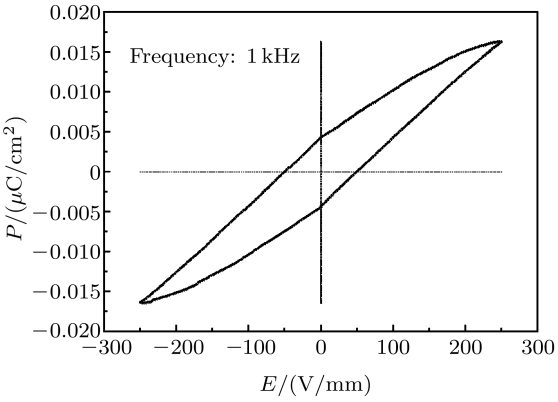


Fig.3. Polarization vs. applied electric field hysteresis loop of 30 nm $BaTiO_3$ ceramics at room temperature at 1 kHz.

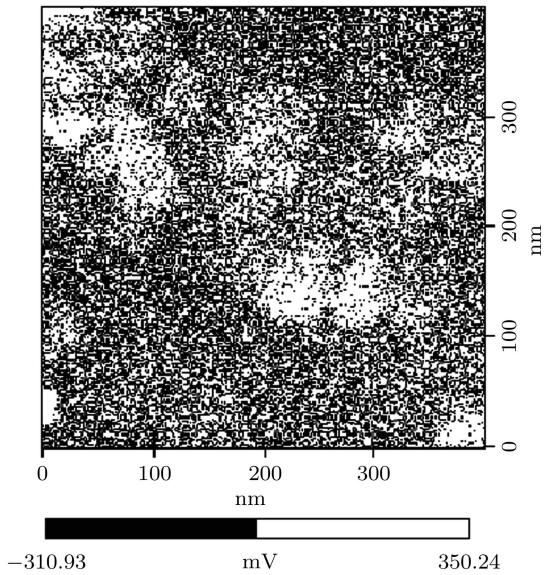


Fig.4. SNDM images of domain pattern in 30 nm $BaTiO_3$ ceramics.

It has been found that tetragonal distortion, heat of transition, Curie temperature, and relative dielectric constant are progressively reduced with grain size decreasing from 1200 to 50 nm.[5] In 30 nm $BaTiO_3$ ceramics, the tetragonal distortion of the lattice, defined as c/a (c and a are the tetragonal lattice parameters), was evaluated by the Rietveld refinement method to be 1.0058. The low tetragonal distortion leads to a reduced spontaneous polarization and the lowering of the dielectric constant. Besides, the lowered dielectric constant has been explained by a brick-wall model of the ceramics corresponding to a diphasic system consisting of ferroelectric grain cores of size-dependent permittivity separated by a continuous network of nonferroelectric grain boundaries with lower permittivity.[5,21,22] The values of permittivity and thickness of the grain boundaries were estimated theoretically to be $\varepsilon_d = 100$ and $d = 0.7$ nm, respectively, which was in reasonable agreement with the experimental data.[22] Experimentally, their thickness was observed to be 0.8 nm.[23] Moreover, the fraction of grain boundary volume increases with decreasing grain size. The total dielectric constant of a grain is made of the intrinsic dielectric constant that results from ferroelectric core and the extrinsic effect of the grain boundary layers. Therefore, the 'dilution' effect of the grain boundary layers results in the decrease of permittivity with decreasing grain size.

4. Conclusion

High pressure significantly promotes densification and dramatically suppresses the grain growth. Thus dense $BaTiO_3$ ceramics with a homogeneous grain size of 30 nm can be fabricated by pressure assisted sintering. The ferroelectric behaviour was characterized by the dielectric peak at around 120 °C, the P-E hysteresis loop, and the existence of some ferroelectric domains. The experimental results indicate that the critical grain size of disappearance of ferroelectricity in nanocrystalline $BaTiO_3$ ceramics fabricated by pressure assisted sintering is below 30 nm.

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