Dielectric Properties of Fine-Grained BaTiO$_3$ Ceramics under High Pressure *

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We investigate the temperature dependence of the dielectric constant of BaTiO$_3$ ceramic with coarse to nano-grain size under different hydrostatic high pressures up to 5000 bar in the range between room temperature and 200°C. The ferroelectric-to-paraelectric phase transition temperatures T_c are determined from the peak of dielectric constant versus temperature. The values of average grain-size are estimated from the SEM images. It is found that the magnitude of dT_c/dp varies considerably from sample to sample depending on grain size. The Curie point T_c of the sample with small grain size decreases more sharply than that of samples with larger one.

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Since miniaturization of ferroelectric components is the present endeavour in the microelectronic industry, the study of the grain size (GS) effect is an important topic in science and technology.[1] It is well known that BaTiO$_3$ (BT) undergoes successive phase transitions from cubic to tetragonal (C-T), tetragonal to orthorhombic (T-O), and orthorhombic to rhombohedral (O-R) with temperature decreasing.[2] Compared with coarse-grained BaTiO$_3$ ceramics, fine-grained ceramics have diffusive and lower dielectric constants due to the size effects and complicated grain boundary conditions.[3] To better understand the different dielectric properties in nano-BaTiO$_3$ ceramic, external electrical fields,[4] atomic substitution,[5,6] chemical ordering,[7] and pressure[8−10] can be used as effective tools to probe the property evolution. Although there has been great research effort focused on coarse BaTiO$_3$ ceramics under high pressure, the properties of nano-BaTiO$_3$ ceramics under high pressure are less studied due to the difficulty in preparing the fully dense nano-ceramics. Based on the two-stage/three-stage[11] and spark plasma sintering (SPS) methods,[12,13] almost fully dense nano-BaTiO$_3$ ceramics are obtained. It is crucial, at least essential to study the properties of nano-BaTiO$_3$ ceramics under high pressure, to elucidate the thermodynamic behaviour, which is closely related to the ferroelectricity. On the one hand, it is a pathway to distinguish what is the intrinsic difference between coarse-grained ceramic and nano-ceramic. On the other hand, combined with other methods, more information, such as microstructure, stress in the grain and at the grain boundary,

the grain size effect on the long-range coulomb interaction and short-range interaction, can be comprehended more deeply through investigating pressure behaviour.

There are some experimental studies on the properties of single crystals and coarse grain-sized BaTiO$_3$ ceramics under the high pressure.[14−16] The transition temperatures T_{C-T} decreases linearly with increasing pressure up to 3 GPa with the initial slope $dT_c/dp = −55$ K/GPa. Above 4 GPa it decreases rather steeply, but each phase exists stably even in the vicinity of $T = 0$ K. The value of the respective critical pressure at $T_c = 0$ K, is 6.5 GPa.[14] For higher pressure, when pressure reaches a critical value, it enhances the ferroelectricity.[15] With increasing pressure, the intensity of ε near T_c increases for BaTiO$_3$ single crystals, and decreases for BaTiO$_3$ ceramics.[16] At present, there are no reports on investigation of dielectric properties of nanometre sized BaTiO$_3$ ceramics under high pressure. Our experiments aim at perceiving the influence of microstructure on nano-ceramic characteristics. In this Letter, we study the temperature-dependent dielectric properties of nano-BaTiO$_3$ ceramic under different hydrostatic pressures. In order to investigate the ferroelectricity (FE), the ferroelectric hysteresis loops are measured.

A 40-nm sample was synthesized by high-pressure solid-state reaction. Other samples are synthesized with the SPS method.[13] The grain size of the nanocrystalline ceramics was estimated from the SEM images of fracture surfaces (Fig. 1). The average grain sizes in Figs. 1(a) and 1(b) are 70 nm and 100 nm, re-

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spectively. For ferroelectric, ferromagnetic and ferroe-lastic materials, the critical size is always performed in many phenomena related to the so-called superpara-ferroic behaviour.[17−19] However, as mentioned by Buscaglia *et al.*,[1] the 40-nm BaTiO$_3$ system can still preserve its ferroelectricity at room temperature.[20]
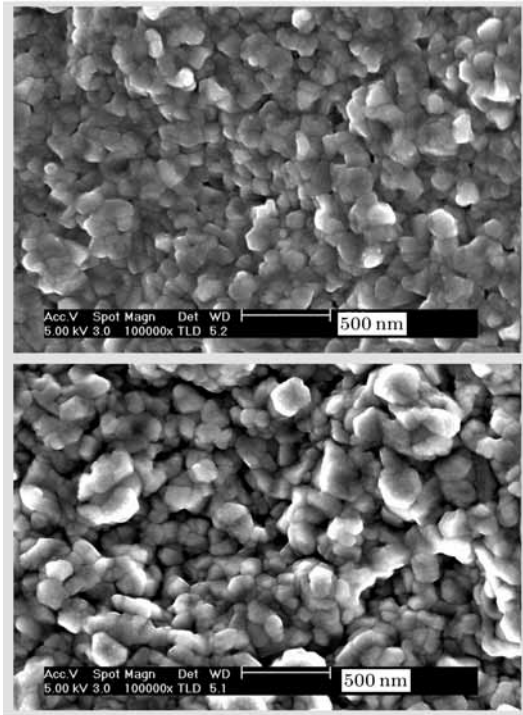

Fig. 1. SEM image of fracture surface for sintered ceramic with average grain size of 70 nm (a) and 100 nm (b).

Figure 2 exhibits the dielectric temperature curves of BaTiO$_3$ with the different grain sizes at 10 kHz over the temperature range of 20–200° C. Figure 2(a) shows the dielectric temperature curve under 1 bar at 10 kHz. Figures 2(b) and 2(c) present the dielectric tempera-ture curves under pressures 2000 bar and 5000 bar at 10 kHz, respectively. As mentioned above, the dielec-tric constant of nano-BaTiO$_3$ ceramic is lower than those of BaTiO$_3$ crystals and coarse-grained BaTiO$_3$ ceramics, and a diffusive phase transition with a broad maximum is found.[21,22] This behaviour has been ex-plained in terms of structural changes, the twinning mechanism in polycrystalline BaTiO$_3$ ceramics and in-ternal stresses induced by the reduction of the grain size.[1] As shown in Fig. 2, the dielectric constant at T_c decreases and T_c shifts to lower temperature with decreasing grain size. Wang *et al.*[13] have attributed these phenomena to the decreasing tetragonal content and internal stress remained in the pellets with re-duced grain size. Pressure can suppress the dielec-tric properties and shift T_c of BaTiO$_3$ to the lower temperature,[14] as shown in Fig. 3.

The reduction of the dielectric constant under high pressure is strongly related to the change of the in-

frared contribution of the total polarization under high pressure. The pressure dependence of ε in the cubic phase obeys a similar relationship as the Curie–Weiss law,[16]

$$\varepsilon = C^*/(p - p_0), \qquad (1)$$

where C^* and p_0 are constants at a given temper-ature. The decrease of T_c with increasing pressure is expected from a consideration of the strains in-troduced into the lattice at the onset temperature of the spontaneous polarization. Since pressure favours the smaller volume and higher symmetric phase (at least for BaTiO$_3$), with the increasing pressure, a sta-bilization of cubic phase or a decrease of T_c as well as a
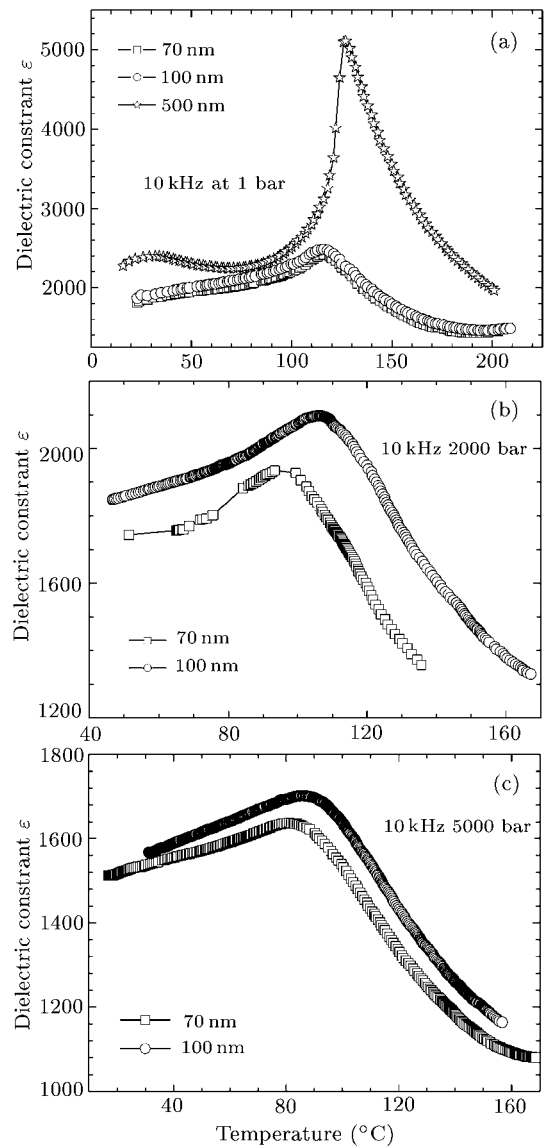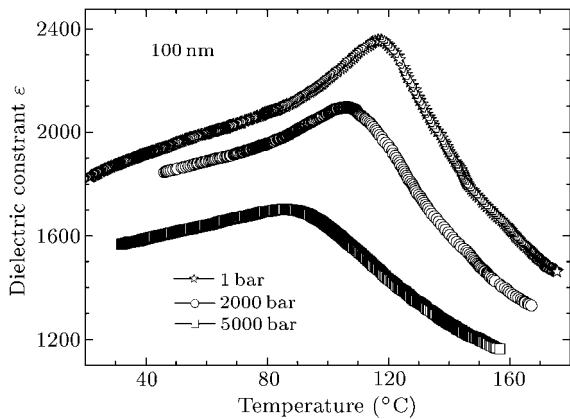

Fig. 2. The relative dielectric constant as a function of temperature at fixed-frequency (10 kHz) for BaTiO$_3$ with different grain sizes: (a) at 1 bar, (b) at 2000 bar and (c) at 5000 bar.

Fig. 3. The relative dielectric constant as a function of temperature at fixed-frequency (10 kHz) for $BaTiO_3$ with grain size 100 nm under different pressures.

considerably larger shift of T_c for higher tetragonality is observed.[16] The tetragonal-to-cubic transition in $BaTiO_3$ is a first-order phase transformation, thus obeys the Clausius–Clapeyron equation

$$dT_c/dp = T_c \Delta V/Q, \qquad (2)$$

where p is the pressure, ΔV and Q are the transition volume and latent heat, respectively. As is seen from Table 1, the magnitude of dT_c/dp varies considerably from sample to sample due to their different grain sizes. The slightly higher value of T_c for the 40-nm sample is expected for its high pressure preparation processing compared to the SPS method. The Curie point of the sample with small grain size drops more sharply than that of the samples with larger ones. It seems that the sample with small grain sizes is more sensitive to and easily affected by the pressure.

Table 1. Curie points T_c and its pressure derivatives for the $BaTiO_3$ samples investigated.

Grain size	T_c (°C) (1 bar)	T_c (°C) (2000 bar)	T_c (°C) (5000 bar)	dT_c/dp (°C/kbar)
40 nm	120.84	98.54	82.34	7.7
70 nm	114.93	94.43	81.03	6.78
100 nm	116.11	106.61	93.81	4.66

Although this variation is unrealized based on the current experiments, certain possible causes can be listed below for referring. The nano-$BaTiO_3$ ceramics are composed of a mixture of tetragonal and orthorhombic crystallites.[13] The orthorhombic structure is a low temperature form of $BaTiO_3$ crystals and coarse-grain ceramics, thus it is metastable at room temperature. The metastable phase is more sensitive to external perturbations. When applying pressure, orthorhombic structure can easily change into the stable cubic structure. It is supposed that the smaller grain will gain higher fraction of orthorhombic crystallites,[13] so a larger shift of T_c is expected.

In conclusion, the Curie point of $BaTiO_3$ decreases with increasing hydrostatic pressure, but at a rate which varies from -4.66 to -7.7 °C/kbar for samples with different grain sizes. This change is attributed to the novel evolution of crystallines at nano scales. Further experiments under higher pressure are necessary to enrich the understanding of nano-level ferroelectric ceramic, which will be helpful to comprehend more deeply the nano-characteristics of $BaTiO_3$ ceramics.

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