

## Phase transition and dielectric properties of nanograin BaTiO<sub>3</sub> ceramic under high pressure

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(Received 31 March 2008; accepted 19 May 2008; published online 17 June 2008)

Temperature dependence of the dielectric constant of nanograin BaTiO<sub>3</sub> ceramic has been investigated under hydrostatic pressure  $\sigma$  up to 5 GPa. We found that the paraelectric-ferroelectric phase transition temperature  $T_C$  decreases with  $\sigma$  at a rate of  $dT_C/d\sigma = -40.0(\pm 1.1)$  K/GPa for coarse-grain ceramic and  $-34.3(\pm 1.4)$  K/GPa for ceramic with 60 nm grains. The variation of intergranular stresses with reducing grain size is considered as the main factor causing the decrease of  $T_C$  and the change of  $dT_C/d\sigma$ . © 2008 American Institute of Physics. [DOI: 10.1063/1.2944253]

As a classic ferroelectric material, BaTiO<sub>3</sub> (BTO) has been studied for more than half a century and has found many applications, especially for making multilayer ceramic capacitors that made the miniaturization of electronic devices possible.<sup>1</sup> As the layer thickness of multilayer structures becomes thinner and thinner, the grain size required for the BTO ceramic is down to the order of submicrons, or even nanometers. A strong size effect begins to appear at such small scale that affects the physical properties of the material and the performance of devices. In recent years, size effect has become one of the most important topics in physics and materials science communities.

The influence of grain size on the dielectric properties of barium titanate ceramics has been studied since 1966.<sup>2-6</sup> It was found that the permittivity of BTO ceramic changes nonlinearly with the reduction of grain size. At room temperature, the dielectric constant increases with the reduction of the grain size until a maximum value is reached, and then it begins to decrease on further decreasing the grain size.<sup>7,8</sup> At the same time, the number of 90° ferroelectric domains, which are formed to relieve the transformation strain in the tetragonal phase of BTO, begins to reduce as the grain size of BTO ceramic reaches the nanometer scale.<sup>8</sup> Eventually, each nanograin becomes a single domain crystal. Consequently, the internal stresses produced during sintering process and by the paraelectric to ferroelectric phase transition will not be fully released due to the lack of 90° ferroelectric domains in nanograin BTO ceramic. Such internal stresses will change the cubic to tetragonal phase transition temperature  $T_C$  (~130 °C in coarse-grain BTO ceramic when grain size > 1 μm).

It is known that higher hydrostatic pressure suppresses spontaneous polarization in the tetragonal phase of BTO and may even induce transition to the cubic phase in favor of smaller volume in the cubic phase. Therefore, increasing compressive pressure will result in a shift of  $T_C$  to lower temperature and may also significantly suppress the peak dielectric constant. For the nanosize grain ceramics, the internal stresses are mainly compressive and isotropic, like an applied hydrostatic pressure, so that  $T_C$  will be lowered. In

this work, we apply hydrostatic pressure to study the change of  $T_C$  with pressure and use the result to explain the size effect occurred in nanograin BTO ceramic.

From experience, the internal stresses caused by the reduction of 90° ferroelectric domains in nanosized BTO ceramics are sensitive to the applied hydrostatic pressure. However, up to date, there are no documented studies on the progressive decrease of  $T_C$  in nano-BTO ceramic under high pressure. Samara,<sup>9</sup> Merz,<sup>10</sup> and others<sup>11-13</sup> have reported the change of the paraelectric-ferroelectric phase transition temperature for coarse-grain BTO in the 1950s and 1960s. They reported that the Curie point of BTO decreased linearly with pressure at a rate in the range from -35 to -76 K/GPa. Recently, several authors also reported studies on the ferroelectric phase transition of perovskite like materials under high pressure.<sup>14,15</sup> Demartin and Damjanovic<sup>16</sup> have reported the direct piezoelectric effect in fine and coarse-grain barium titanate ceramics under external alternating and static pressure. They mentioned that internal stress model is required to explain the ac and dc pressure dependences of the piezoelectric coefficient in barium titanate ceramic.

In our work here, ultrafine pure BTO powders were obtained by a modified oxalate precipitation method as described in Ref. 17. All ceramic samples were prepared by a two-stage<sup>18</sup> solid-state reaction method under high pressure. The pellets with a diameter of 5 mm were pressed uniaxially under 4 MPa pressure, followed by an initial calcination at 600 °C for 12 h in ambient pressure; then, the sintered samples were heated up to 1000 °C for a few seconds (to increase density) under 5 GPa pressure using a cubic anvil type apparatus, followed by second heat treatments at 1000, 900, and 830, respectively, for 30 min at the same pressure to prepare 5000, 100, and 60 nm grain size BTO ceramic samples. In order to keep the stoichiometric ratio of all BTO samples, the initial starting powders were the same ultrafine nano-BTO powders, and all pellets were encapsulated in Au foil to prevent contamination and maintain the Ba/Ti ratio. Samples obtained from high pressure sintering were then annealed at 600 °C for 48 h in oxygen atmosphere to reduce oxygen vacancies and release stresses generated by the pressure gradient during pressure sintering. Therefore, influences from other sources, such as chemical impurities, lattice defects, and Ba/Ti/O ratio change, which could also affect the

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Curie temperature, were kept to the minimum.

The temperature dependence of the dielectric constant of BTO ceramic was measured at 100 kHz using an electrical impedance analyzer (HP 4192A) under a hydrostatic pressure from ambient up to 5 GPa. The temperature and dielectric constant values were recorded by a personal computer in an automated measurement setup.

The electrodes on the samples were prepared by applying a thin coating of Ag paint on the two parallel planes of each sample. During the experiment, the sample was placed at the center of a pyrophyllite cube ( $25 \times 25 \times 25 \text{ mm}^3$  in size) surrounded by a pressure transmitting medium (boron nitride). A Cu wire of 0.1 mm in diameter encapsulated by a Teflon tube was used to make a flexible contact with the sample at the diagonal corners of the pyrophyllite cube and the external leads were screened by a metal net. The sample was placed in a graphite tube with two metal pellets attached to the top and bottom anvils serving as heat transmitters and contacts for the electric circuit. Temperature was monitored by a NiCr–NiSi thermocouple mounted very close to the sample. The pyrophyllite cube was placed in the center cavity of the cubic anvil apparatus, which could generate pressure up to 5 GPa. The grain size of the samples was determined by the mean intercept length measured by scanning electron microscope.

Figure 1 shows the dielectric constant of BTO ceramic as a function of temperature measured at 100 kHz under different hydrostatic pressures. It was found that the peak value of the dielectric constant is strongly suppressed by decreasing grain size, which may be explained by the “dead layer” model for the grain boundaries that have very low dielectric constant.<sup>19</sup>

The maximum of the dielectric constant at ambient pressure is located at 128, 120, and 111 °C for the 5000, 100, and 60 nm grain size BTO ceramic samples, respectively. Although the dielectric peak becomes more diffused for the nanograin BTO ceramic, a dielectric anomaly indicating the paraelectric-ferroelectric phase transition is clearly visible for all samples, as shown in Fig. 1. The transition temperature  $T_C$  is determined by two different methods: (i) The Curie temperature is estimated by using the maximum value of the dielectric constant after subtracting the background using a fitted line; (ii) using the interception of the two tangents on both sides of the peak, which differ less than 5 K compared to the first method. We used the  $T_C$  value from the first method and considered the uncertainties in the measurements of pressure ( $\pm 0.05 \text{ GPa}$ ) and temperature ( $\pm 0.5 \text{ K}$ ) and the distinction between the first and second methods to estimate the error, as shown in Fig. 2. Figure 2 shows the dependence of the transition temperatures  $T_C$  on pressure and grain size. The diffuse transition peak in nanograin BTO ceramic is attributed to both the grain size distribution and the presence of inhomogeneous internal stresses.<sup>20,21</sup>

Since the internal stresses in the ceramic are compressive type because of the volume increase at the cubic to tetragonal phase transition, the cubic structure is more favored for smaller grain size.<sup>22</sup> Therefore, the behavior of nanograin BTO ceramic is very much like a system under a hydrostatic pressure. Internal compressive stresses will shift  $T_C$  to lower temperature. Based on the  $T_C$  difference between different grain size samples, the internal compressive stresses are estimated at the level of kilobars. To reduce the Curie temperature comparable to the effects caused by an external

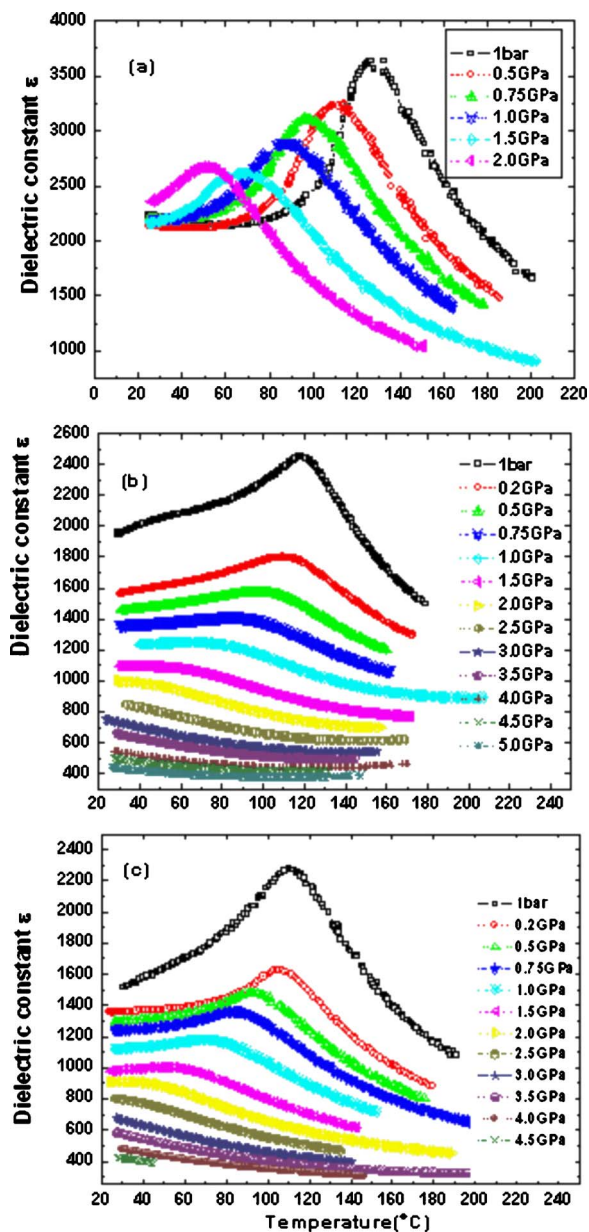


FIG. 1. (Color online) Dielectric constant vs temperature under different pressures at 100 kHz for BTO with different grain sizes: (a) 5000 nm, (b) 100 nm, and (c) 60 nm.

hydrostatic pressure, the levels of internal pressures in 5000, 100, and 60 nm ceramic should be 0, 0.3, and 0.5 GPa, respectively. Following the expression in terms of surface tension in Ref. 23:  $\sigma = 2\gamma/R$ ,  $\gamma$  is estimated to be 15 N/m, which can produce 6 MPa, 0.3 GPa, and 0.5 GPa internal stresses for 5000, 100, and 60 nm ceramics, respectively.

Considering that a positive volume strain is produced at the cubic paraelectric to tetragonal ferroelectric phase transition, reducing tetragonality  $c/a$  and decreasing  $T_C$  with compressive stress are expected.<sup>10</sup> In the pressure range from 0 to 2 GPa,  $T_C$  decreases linearly with pressure.<sup>14</sup> The rate of change are  $dT_C/d\sigma = -40.0 (\pm 1.1) \text{ K/GPa}$ ,  $-37.1 (\pm 1.3) \text{ K/GPa}$ , and  $-34.3 (\pm 1.4) \text{ K/GPa}$ , respectively, for 5000, 100, and 60 nm grain size BTO ceramic samples, as shown in Fig. 2. This reduction of  $T_C$  is consistent with the increase of bulk moduli on decreasing grain size in nanograin BTO ceramic.<sup>24</sup>

Figure 3 gives the pressure dependence of the dielectric constant at 30 °C measured at 100 kHz. The change of the

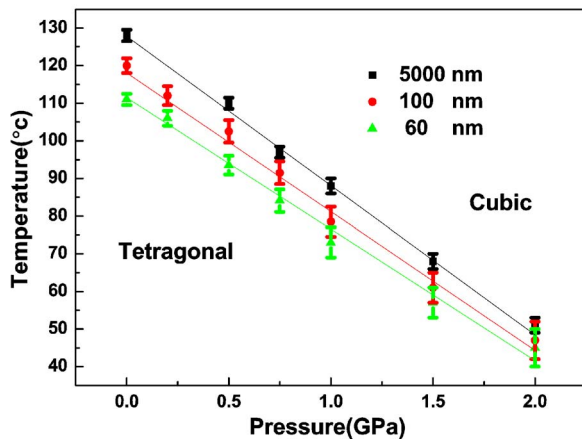


FIG. 2. (Color online) Dependence of the transition temperatures  $T_C$  on pressure and grain size. The solid lines are fitting results and the symbol points are experimental data. The error bar was determined according to the uncertainties in the measurements of pressure ( $\pm 0.05$  GPa) and temperature ( $\pm 0.5$  K) and the distinction between the first and second methods.

dielectric constant with pressure is a result of the competition between the dielectric constant increase caused by the downward  $T_C$  shift and the permittivity suppression caused by external pressure. In coarse-grain BTO ceramic, the permittivity increase due to  $T_C$  shift caused by pressure is bigger than the permittivity suppression; hence, the total dielectric constant increases, which can be seen from the results of our coarse-grain BTO and from the results of Ref. 9, as shown in Fig. 3. On the contrary, for the two nanograin BTO ceramic samples, the dielectric peak becomes more diffuse under high pressure. The pressure suppression of the dielectric constant is bigger than the dielectric constant increase due to the pressure induced  $T_C$  shift; therefore, the total effective dielectric constant at 30 °C decreases with applied pressure. In addition, the coexistence of tetragonal and orthorhombic phases in nanograin BTO ceramic may also contribute to the diffused dielectric peak.<sup>25</sup>

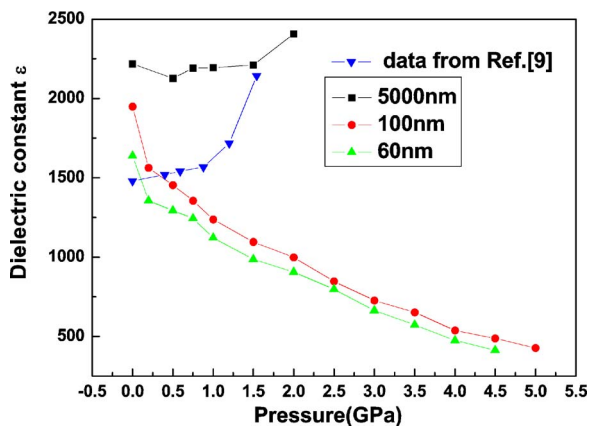


FIG. 3. (Color online) Dependence of the dielectric constant on pressure at 100 kHz at 30 °C. The experimental data from Ref. 9 are also listed for comparison.

In summary, we have systematically measured the dielectric property change of different grain size BTO ceramic under a hydrostatic high pressure up to 5 GPa. Our results showed that the paraelectric-ferroelectric phase transition temperature  $T_C$  becomes lower with reducing grain size. Another interesting finding is the opposite trend of the pressure dependence of the dielectric constant in nanograin and coarse-grain BTO ceramic.

In the pressure range of 0–2 GPa,  $T_C$  decreases linearly with pressure. The experimentally measured rates of change for 5000, 100, and 60 nm BTO ceramics are  $dT_C/d\sigma = -40.0 (\pm 1.1)$  K/GPa,  $-37.1 (\pm 1.3)$  K/GPa, and  $-34.3 (\pm 1.4)$  K/GPa, respectively. The variation of  $dT_C/d\sigma$  in different grain size ceramic is mainly caused by the modification of the internal stresses by the external high pressure. It was found that the amplitude of the changing rate  $|dT_C/d\sigma|$  becomes smaller as the grain size gets smaller.

This research was supported by NSF and MOST of China through research projects (2002CB61330; 2005CB724402; 2007CB925003) and by the NIH under Grant No. P41-EB2182.

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