# Ceramic Processing Research

## Effect of internal stress on the dielectric properties of barium titanate ceramics

#### Byeong Woo Lee\* and Keun Ho Auh<sup>a</sup>

Department of Materials Engineering, Korea Maritime University, Pusan 606-791, Korea <sup>a</sup>Ceramic Processing Research Center (CPRC), Hanyang University, Seoul 133-791, Korea

Grain size effects on the dielectric properties of BaTiO<sub>3</sub> ceramics were characterized in the light of an effect of internal stress. Fine grained BaTiO<sub>3</sub> with an average grain size of 1  $\mu$ m exhibited higher dielectric constant, lower ferroelectric transition temperature ( $T_c$ ), and lower transition energy in comparison with those of coarser grained material. For the fine grained BaTiO<sub>3</sub>, the dielectric constant decreased with increasing one-dimensional compressive pressure, whereas, for the coarse grained material, the value increased before decreasing with the pressure. The one-dimensional pressure caused an increment of  $T_c$  in both the fine and coarse grained BaTiO<sub>3</sub>. The pressure affected more significantly the coarse grained material. The relationship between these results and internal stress, and the effect of external pressure imposed on the internally stressed lattice, is discussed.

Key words: BaTiO<sub>3</sub>, internal stress, grain size effects, dielectric properties, ferroelectric

## Introduction

A great deal of work has been performed to establish the relationship between the grain size and the dielectric properties of BaTiO<sub>3</sub> [1-8]. A dense fine grained (1 μm) BaTiO<sub>3</sub> showed a high dielectric constant reaching to 6000, while a coarser grained ceramic exhibited values of 1500 to 2000 at room temperature [1, 2]. The value obtained in fine grained material was much greater than the average value calculated on singlecrystal BaTiO<sub>3</sub>, where as the value was 4000 along the nonpolar a-axis and 400 along the polar c-axis [9]. Buessem et al. [2-4] suggested that fine grained BaTiO<sub>3</sub> had no or very few ferroelectric 90° domains, and thus such a high dielectric constant resulted from the internal stress, whereas the stress was easily dissipated by the formation of 90° domains in coarse grained BaTiO<sub>3</sub>. As an alternative approach, Arlt *et al.* [5], by contrast, showed numbers of 90° domains in fine grained ( $\approx 1 \mu m$ ) BaTiO<sub>3</sub> and explained the high dielectric constant as a 90° domain wall contribution.

The influence of grain size on the ferroelectric phase transition temperature  $(T_c)$  is still obscure. Some authors expected that  $T_c$  increased with decreasing grain size [6, 7]. They have suggested that a stable space charge layer formed inside every domain, which results in increased ferroelectric phase stability. The space charge layer is especially important in fine grained ferroelectric materials, where  $T_c$  may increase with decreasing

grain size, due to the increased influences of the surface area of the space charge layer with decreasing grain (domain) size. Some authors [1, 8], however, have shown that  $T_c$  decreases with decreasing grain size.

In order to interpret the conflicting theories of the basic dielectric properties in polycrystalline  $BaTiO_3$ , a systematic series of experiments on the grain size dependence of the dielectric constant and ferroelectric-paraelectric phase transition, and an interpretation of the internal stress need to be carried out.

The aim of this study is to establish the  $T_c$  and abnormally high dielectric constant in fine grained BaTiO<sub>3</sub>. One-dimensional pressure was applied to the BaTiO<sub>3</sub> with grain sizes of 1 to 40 µm and the effect of the onedimensional pressure on domain switching and dielectric properties was investigated. The dielectric properties were analyzed in the light of internal stress.

## **Experimental Procedure**

The BaTiO<sub>3</sub> powders used in this study were synthesized by a co-precipitation process. A stoichiometric mixture of Ba(NO<sub>3</sub>)<sub>2</sub>, TiCl<sub>4</sub>, and H<sub>2</sub>O<sub>2</sub> aqueous solution was added to a NH<sub>4</sub>OH solution. Single-phase BaTiO<sub>3</sub> powders with sub-micrometer size were obtained by heating the filtered and washed precipitates at 300°C. The disk-shaped bodies were made by ordinary pressing, and then cold isostatic pressed (CIP) under 103 MPa prior to firing at 1150-1400°C for 1-5 h in air. The sintered ceramic pieces were thin and disk shaped measuring 1.2 mm thick and 10-12 mm in diameter; electrodes formed by silver paste were applied to both faces to measure the electrical properties. The dielectric constant was determined by inductance, capacitance,

<sup>\*</sup>Corresponding author:

Tel:+82-51-410-4356 Fax:+82-51-404-3986

E-mail: bwlee@kmaritime.ac.kr

and resistance (LCR) meter at 1 kHz during heating and cooling the specimens in a silicone oil bath. The rates of heating and cooling were 1°C/minute and the rates were reduced to 0.2°C/minute near the transition temperature. To determine the grain size, chemical etching was conducted on the polished specimens using a dilute solution of HCl and HF. The transition temperature was also determined by differential thermal analysis (DTA), with a heating rate of 5°C/minute. To measure the tetragonality (c/a), X-ray diffraction measurements using Cu  $K_{\alpha}$  were carried out on sintered specimens. The dielectric properties of fine and coarse grained BaTiO<sub>3</sub> during heating under one-dimensional pressure were measured using a temperature-controlled pressure vessel as shown in Fig. 1. The uni-axial compression was applied normal to the electrode and the dielectric constant under the pressure was measured within 10 s after each pressure was applied.

#### **Results and Discussion**

The sintered bodies showed average grain sizes of 1



Fig. 1. Diagram of the temperature-controlled pressure vessel.



Fig. 2. Variation in dielectric constant  $(e_r)$  and apparent density as a function of grain size.

to 40 µm. Figure 2 shows the dielectric constant and the apparent density of sintered BaTiO<sub>3</sub> as a function of grain size. The dielectric constant of BaTiO<sub>3</sub> with an average grain size of 1 µm is around 5000 and the value decreases with increase in grain size. The apparent densities are above 92%. The variation of dielectric constants of coarse grained (30 µm) and fine grained (1 μm) BaTiO<sub>3</sub> as a function of (silicone oil) temperature is shown in Fig. 3. The dielectric constant peak of fine grained BaTiO<sub>3</sub> is broadened at the transition temperature  $(T_c)$  at which the tetragonal (ferroelectric) phase is transformed to cubic (paraelectric). The  $T_c$  of fine grained BaTiO<sub>3</sub> is about 2°C lower than that of the coarse one. The phase transformation is known to be a first-order transition and thus the transition is accompanied by a latent heat during nucleation and growth [10]. This could result in a  $T_c$  difference ( $dT_c = T_{c, \text{heating}}$  $-T_{c, \text{ cooling}}$ ) during heating and cooling. However, no appreciable difference in  $dT_c$  is detected for both fine and coarse grained BaTiO<sub>3</sub>. DTA analysis (Fig. 4) shows that the fine grained BaTiO<sub>3</sub> has a 2°C lower transition temperature and 5% lower transition energy than the coarse grained one. These results imply that the fine grained BaTiO<sub>3</sub> ceramic could be subject to an internal stress, which alleviated the energy barrier of the transition. For the series of specimens with different average grain sizes, the tetragonality was determined by X-ray diffraction; the value of the tetragonality is 1.01 for samples with an average grain size larger than 25 µm and down to 1.009-1.0095 for 0.8-2.5 µm specimens. The slightly lower tetragonality of the fine grained BaTiO<sub>3</sub> could also be one of the evidences of the internal stress. The transition temperature of single and poly-crystal BaTiO<sub>3</sub> can be decreased with hydro-static (isostatic) compression [11]. This result has been interpreted as a stabilization of the cubic phase, with decreased volume accomplished by lower tetragonality under hydrostatic pressure. Taking into consideration these facts, the



**Fig. 3.** Variation in the dielectric constant on temperature for specimens of fine  $(1 \ \mu m)$  and coarse  $(30 \ \mu m)$  grained BaTiO<sub>3</sub>.



**Fig. 4.** DTA curves and measured transition energy for (a) fine  $(1 \ \mu m)$  and (b) coarse  $(30 \ \mu m)$  grained BaTiO<sub>3</sub>.

lower tetragonality, transition tempe-rature, and transition energy of the fine grained  $BaTiO_3$  could have originated from the internal stress existing in the form of isostatic compression.

A different result, as described, has been reported by other authors [6]. A space-charge layer formed inside each BaTiO<sub>3</sub> domain, particularly in fine grained material with a small domain size, could play an important role in determining  $T_c$ . The ferroelectric polarization was locked in by the space-charge layer in the fine grained material, and the ferroelectric phase would be stable far beyond the usual Curie temperature,  $T_c$ . The space charge field in a porous fine grained ceramic is known to be larger than that in a dense fine grained ceramic because the field in the dense fine grained ceramic was removed more easily by the charge of the surrounding grains. If the  $T_c$  of BaTiO<sub>3</sub> increased with decreasing grain size because of the locked-in ferroelectric polarization, the transition of cubic to tetragonal during cooling, should occur at the same temperature in both fine and coarse grained BaTiO<sub>3</sub>, since there is no ferroelectric polarization in the cubic phase. In addition, the  $dT_c$  of the fine grained ceramic should be much larger than the  $dT_c$  of the coarse grained material. However, the experimental results show that the  $dT_c$  is almost the same in both the fine and coarse grained BaTiO<sub>3</sub>, and the fine grained material always exhibits a lower  $T_c$  during heating and cooling. Since the porosity of the fine grain BaTiO<sub>3</sub> (1 µm-92% apparent density) was higher than that of the coarse grained (30 µm-98% apparent density) one, the space-charge field should be higher in the porous fine grained material than that in



**Fig. 5.** Variation of the dielectric constant with one-dimensional pressure for specimens of different grain sizes.

the dense coarse grained BaTiO<sub>3</sub>. However, this does not accord well with our observations either. There is no or very little influence of the space charge field on  $T_c$  in BaTiO<sub>3</sub> in range of 1-40 µm grain size.

Figure 5 shows variations of the dielectric constant as a function of the compressive pressure for the specimens with different grain sizes. For the specimen with a fine grain size (1  $\mu$ m), the dielectric constant shows a continuous decrease until it levels off at a pressure above 70 MPa. Whereas, for the specimens with a coarse grain size, the dielectric constant increases with the pressure up to higher pressures before decreasing continuously. The peak pressure, at which the maximum value of the dielectric constant occurs, increases with an increase in grain size. These results in coarse grained specimens can be explained as follows. The shorter aaxes (higher dielectric constant) were preferentially aligned by 90° domain switching along the normal to the electrode with increasing pressure, leading to an increase in the average dielectric constant. The peak pressure increases with grain size because the larger grains contain more domains, which are loosely constrained, and easily switchable by mechanical stress. Therefore, when the alignment (90° domain switching) leveled off, further compression was imposed mainly on immobile a-axes, which led to a decrease in the dielectric constant. Figure 6 shows a schematic explanation of the induced 90° domain switching by the mechanical stress and the pressure imposing on the immobile a-axes. For the fine grained material, the continuous decrease of the dielectric constant is also explained in the same way, i.e., the compression on immobile a-axes resulting from domain pinning at grain boundaries, because the domain length in the fine grained material was comparable with the grain size



Fig. 6. Schematic diagram of domain switching in coarse grained material by a one-dimensional pressing and the pressure imposed on immobile a-axis.

[5].

According to the internal stress model [2-4], the internal compressive stress along the c-axis and equal tensile stress along the two a-axes could be the origin of the high dielectric constant in the fine grained (  $\approx 1$  $\mu$ m) BaTiO<sub>3</sub>. It is assumed that the major contribution to the dielectric constant of fine or coarse grained BaTiO<sub>3</sub> originates from the tensile stress along the aaxes, because the dielectric constant along the a-axes is almost 10 times higher than that along the c-axis, and tetragonal materials have two a-axes. Therefore, the dielectric constant decreasing with pressure in the fine grained BaTiO<sub>3</sub> and decreasing over the peak pressure in the coarse grained material can be explained by the internal stress model, i.e., a compressive stress on immobile a-axes, which are under tensile stress, resulted in a reduction in the dielectric constant.

Above  $T_c$ , the internal stress system would be changed. The dielectric constant measured at above  $T_c$  (150°C) as a function of the external compressive pressure is shown in Fig. 7. Regardless of the grain size, there is only a decrease in the dielectric constant with the pressure. The result is also interpreted as the effect of the compressive stress on immobile a-axes, because there is no switchable domain in the cubic (paraelectric) phase and all three axes are the same a-axes.

Figure 8 shows the variations of  $T_c$  as a function of the compressive pressure for fine (1 µm) and coarse (30 µm) grained BaTiO<sub>3</sub>. The  $T_c$  increases with increasing pressure. For the fine grained material, however, the increase of the  $T_c$  is smaller than that of coarse grained one at the same pressure. This result indicates that the one-dimensional compression acts as a tension, which results in a tetragonality increase, i.e., stabilization of the tetragonal phase and increase in  $T_c$ . For the fine grained BaTiO<sub>3</sub>, the one-dimensional pressure, which resulted in tetragonality increasing, was partially com-



**Fig. 7.** Variation of the dielectric constant measured above  $T_c$  (150°C) with one-dimensional pressure for specimens of fine (1  $\mu$ m) and coarse (30  $\mu$ m) grained BaTiO<sub>3</sub>.



Fig. 8. Variation of the transition temperature with one-dimensional pressure for specimens of fine  $(1 \ \mu m)$  and coarse  $(30 \ \mu m)$  grained BaTiO<sub>3</sub>.

which caused a tetra- gonality decrease, and thus the transition temperature increase was smaller than that of the coarse grained  $BaTiO_3$ .

We agree with Buessem *et al.*'s internal stress system as mentioned [2], but disagree with their single-domain model of internally stressed grains resulting form the absence of 90° domains since the fine grained ( $\approx 1 \ \mu m$ ) BaTiO<sub>3</sub> also has numbers of 90° domains [5]. The origin of the internal stress is unclear. It seems to be related to the surface energy of the fine grains or to the stress field formed in the fine lamellar domain structures. On the basis of the above discussions, it is believed that the low  $T_c$  and high dielectric constant of the fine grained BaTiO<sub>3</sub> arises from the internal stress.

#### Conclusions

It has been shown that the fine grained ( $\approx 1 \,\mu$ m) BaTiO<sub>3</sub> had an internal stress resulting in isostatic compression. The internal stress in the fine grained BaTiO<sub>3</sub> contributed to the stabilization of the cubic phase. The reduced tetragonality, ferroelectric transition temperature, and transition energy in the fine grained BaTiO<sub>3</sub> were also attributed to the internal stress. The dielectric constant decreasing with one-dimensional pressure in the fine grained BaTiO<sub>3</sub> and the decreasing over the peak pressure in the coarser grained materials were interpreted to be due to a pressure imposed on the immobile *a*-axes. The one-dimensional compression stabilized tetragonal phase and resulted in a  $T_c$  increase for both the fine and coarse grained BaTiO<sub>3</sub>. For the fine grained material, however, the  $T_c$  increase with pressure was smaller due to the compensation of external pressure by the internal stress.

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