Ferroelectric-to-Paraelectric Phase Transition in Barium Titanate Ceramics Investigated by Pyrocharge Measurements

VASILE TURA, LILIANA MITOSERIU, CONSTANTIN PAPUSOI, TOSHIO OSAKA[1]
& MASANORI OKUYAMA[2]

Department of Electricity and Magnetism, Faculty of Physics, Al. I. Cuza University, Bd. Copou 11, Iasi, 6600, Romania
[1]*Department of Applied Physics, Faculty of Science, Science University of Tokyo, Kagurazaka 1-3, Shinjuku-ku, Tokyo 162, Japan*
[2]*Department of Electrical Engineering, Faculty of Engineering Science, Osaka University, 1-3 Machikaneyama-cho, Toyonaka, Osaka 560, Japan*

Abstract. Temperature dependencies of the pyrocharge were recorded in view of investigating the ferroelectric-to-paraelectric phase transition in barium titanate ceramics with average grain sizes between $0.5\,\mu m$ and $20\,\mu m$. The transition temperature decreased with decreasing the grain size. The relatively small shift of the Curie temperature detected in these pyrocharge experiments suggests that internal stresses are the main cause of the observed grain size effects.

1. Introduction

Barium titanate is a well known ferroelectric material, extensively investigated in the last 50 years because of its various applications to electronic devices. In single crystal form, barium titanate has four structural phases: rhombohedral, orthorhombic, tetragonal and cubic with phase transitions occurring at transition temperatures of $-90°C$, $5°C$ and $130°C$ [1,2], respectively. These four structural phases of crystalline barium titanate are also present in the ceramic form. The physical properties of ceramics are different from those of single crystals and strongly dependent on parameters like: grain size, density, impurities and defects due to various preparation conditions. The modifications in phase transformation behavior and other physical properties of ceramics with different average grain sizes are usually called ''grain size effects''. Since Kniepkamp and Heywang [3] discovered that the ferroelectric properties of barium titanate are nearly nonexistent if the size of crystals is less than $1\,\mu m$, grain size effects became a very interesting subject. The interest increased more after Jonker and Noorlander [4] prepared a fine

grained barium titanate ceramic with $\approx 1\,\mu m$ average grain size and recorded the temperature dependence of its dielectric permittivity $\varepsilon_r(T)$, between $0°C$ and $170°C$. They noticed an important increase of the relative dielectric permittivity at room temperature of $\varepsilon_r \approx 4000$, and a decrease of the ε_r maximum value at the ferroelectric-to-paraelectric transition point. Because the main application of barium titanate was as a dielectric material of high permittivity, the increase of the dielectric constant with decreasing grain size of the ceramic turned into a size effect of great importance. An extensive study of this feature started and many reports relative to grain size effects on the ferroelectric properties of barium titanate ceramics were published.

Kinoshita and Yamaji [5] gave a detailed $\varepsilon_r(T)$ diagram in the temperature range from $-140°C$ to $230°C$ with respect to mean grain sizes between $1.1\,\mu m$ and $53\,\mu m$. They reported a decrease of the Curie temperature and an increase of the other two transition temperatures as the grain size decreases. Kanata et al. [6] studied barium titanate ceramics with grain sizes in the range $(0.1, 110)\,\mu m$ and observed through the $\varepsilon_r(T)$ dependencies that the

orthorhombic-to-tetragonal phase transition is more influenced by the grain size than the tetragonal-to-cubic one.

Uchino et al. [7] investigated by X-ray methods the particle size effect on crystal structure and Curie temperature of barium titanate powders and ceramics. They found that for ceramics with particle sizes smaller than $0.2\,\mu$m, no Curie temperature exists above room temperature. However, using dielectric constant measurements Wada et al. [8] observed a Curie temperature of about 90°C for a ceramic with 58 nm particle size. Frey and Payne [9] published differential scanning calorimetry data showing for a 35 nm grain size sample a tetragonal-to-cubic transition temperature $T_c \approx 110$°C, that suggests a grain size dependence of the Curie point in barium titanate ceramics even slower than Wada et al. [8] observed. Lobo et al. [10] studied the ferroelectric-to-paraelectric phase transition and its diffuse character in fine grained barium titanate ceramics and found a maximum of $\varepsilon_r(T)$ at 108°C for a sample with $0.2\,\mu$m grain size.

It can be seen that all the above mentioned authors reported a decrease of the Curie temperature with decreasing grain size of barium titanate ceramics. In the present work we verified if a similar tendency of the grain size dependence of ferroelectric-to-paraelectric transition temperature can be observed by another investigation technique, i.e. by recording the temperature dependence of the pyrocharge.

2. Experiment

2.1. Ceramic Samples

The experiments in this work were performed on barium titanate ceramic samples with four average grain sizes: $0.5\,\mu$m, $2.5\,\mu$m, 10 μm and 20 μm denoted in the following by A, B, C and D, respectively. Details concerning ceramics preparation and their characteristics have been given in a previous work [11]. The samples were obtained from a hydrothermally grown barium titanate fine powder of 50 nm grain size, pressed into disks and subjected to different sintering conditions shown in Table 1. The sintered ceramics were disks of 8 mm diameter and 0.35 mm thickness. Silver paste electrodes were applied directly to the natural surfaces of the sintered ceramics, to obtain ferroelectric capacitors. We did

Table 1. Characteristics of barium titanate ceramics obtained from hydrothermally grown powders subjected to different sintering conditions

Sample	Sintering conditions	Average grain size (μm)	Density (g/cm^3)	Log(R) (R in Ω)
A	1200°C, 2 h	0.5	5.7	12.8
B	1250°C, 2 h	2.5	5.8	12.8
C	1300°C, 2 h	10	5.9	11.6
D	1300°C, 20 h	20	5.8	11.5

not perform any polishing in order to avoid surface domain reorientation and stresses induced by plastic deformation [12]. The natural status of stresses in these ceramics was not altered.

2.2. Experimental Set-up

A block diagram of the pyrocharge measurement system is shown in Fig. 1, where the symbols denote: C_f—ferroelectric ceramic capacitor; C_0—reference capacitor; Th—thermocouple; ZCU—zero Celsius reference unit; VRE—vibrating reed electrometer; H—heater; PPS—programmable power supply. The ferroelectric capacitor C_f is the barium titanate ceramic sample under investigation. A stainless steel cylinder acts as a thermally stable sample chamber filled with dry air at atmospheric pressure. The sample chamber was in thermal contact with a heater connected to a home-made programmable power
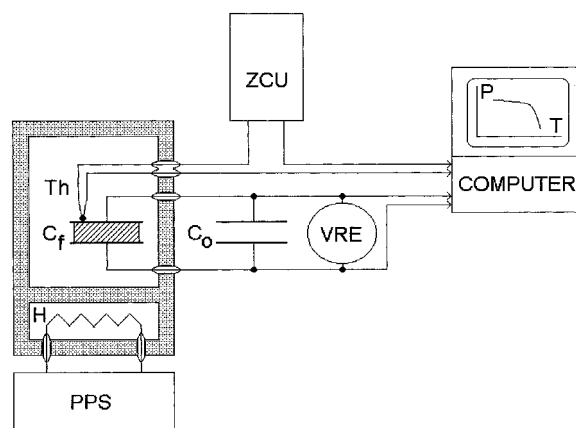

Fig. 1. Block diagram of the pyrocharge measurement system: C_f—ferroelectric ceramic capacitor; C_0—reference capacitor; Th—thermocouple; ZCU—zero Celsius reference unit; VRE—vibrating reed electrometer; H—heater; PPS—programmable power supply.

supply that ensured a heating/cooling rate of 5°C/h. A chromel-constantan thermocouple and a zero Celsius reference unit (Komatsu Electronics Inc. Model ZC-114) were used to measure the sample temperature during the heating/cooling process. The electric charges released from C_f during heating were collected on a reference capacitor $C_0 = 0.614 \mu F (C_0 \gg C_f)$ with practically no losses. The voltages at the thermocouple ends and on C_0 were measured with a HP 3478A Multimeter and with a vibrating reed electrometer (Takeda Riken TR B401), respectively. Both these voltages were periodically read and stored by a computer and used to draw the temperature dependence of the pyrocharge.

3. Results and Discussion

After a preliminary study we selected a poling method consisting of heating the ceramic sample up to the specific Curie temperature, applying an electric field of 30 kV/cm at constant temperature for one hour, and cooling under field down to room temperature with a cooling rate of 5°C/h. When room temperature was reached, the electric field was removed and the plates of the ferroelectric capacitor were connected. The short-circuit connection was maintained until no current between plates was detected. After a short-circuit duration of 24 h, all the poled ceramic samples reached an equilibrium state.

Temperature dependencies of the remanent polarization derived from the pyrocharge measurements are reproduced in Fig. 2. The detail given in Fig. 3 shows that the ferroelectric-to-paraelectric transition temperature increases with increasing the grain size. The variation is rapid in the range of small sizes and tend to saturate for large grain sizes. The values of the remanent polarization at room temperature for each ceramic sample are given in Fig. 4, where we can see that the maximum value of P_r is that of the ceramic B (2.5 μm average grain size). We must accentuate that the results depicted in Fig. 4 do not represent the saturation polarization dependence on the grain size. Finding an exact value of the saturation polarization from pyrocharge measurements is possible only for single-domain single-crystal samples, with the ferroelectric axis oriented perpendicular to the plates of the ferroelectric capacitor. In a real ceramic sample there are grains with various sizes and axis orientation. Therefore, the physical properties of a ceramic are
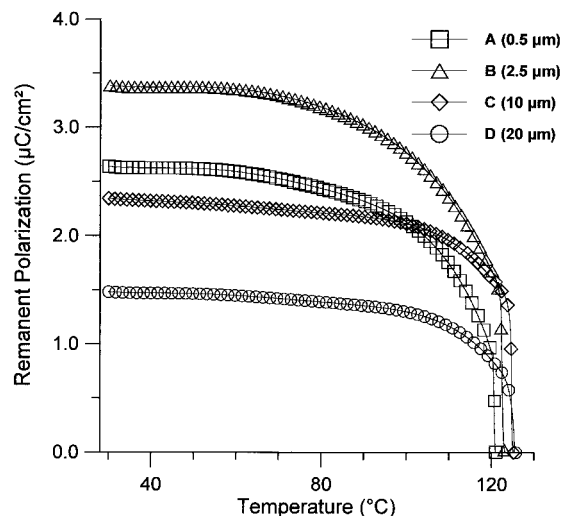

Fig. 2. Temperature dependencies of the remanent polarization for barium titanate ceramics with different average grain sizes: A—0.5 μm; B—2.5 μm; C—10 μm and D—20 μm.

described by parameters like particle size and particle axis orientation. Moreover, in the case of barium titanate ceramics, for a given grain size there are one or more possible ferroelectric domain configurations and for each configuration there is a specific set of possible values of the total polarization [13]. To derive P_s from the experimental values of P_r one should know the exact form of the above mentioned
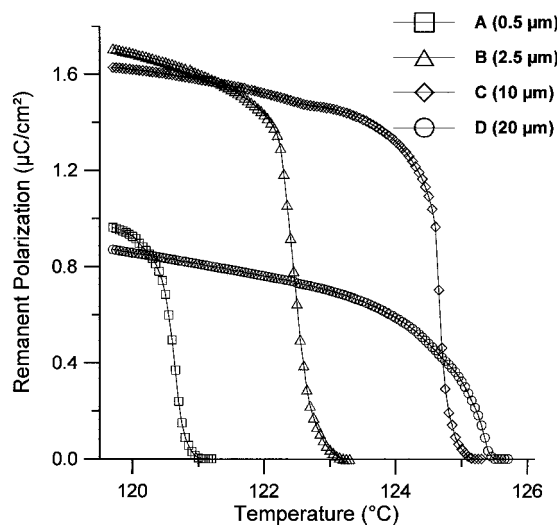

Fig. 3. Temperature dependencies of the remanent polarization in the proximity of ferroelectric-to-paraelectric phase transition. Detailed representation of the dependencies shown in Fig. 2.
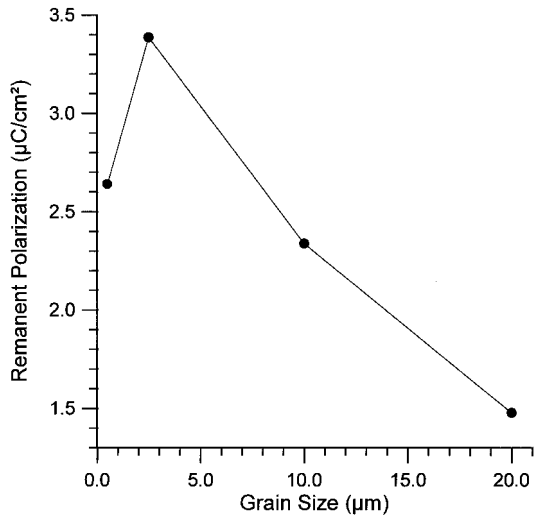
Fig. 4. Grain size dependence of the remanent polarization of barium titanate ceramics at room temperature.

distribution functions, for each ceramic sample. It is clear now that the results given in Fig. 4 cannot be related in a simple way to the real P_s values of the investigated ceramics.

Figure 5 shows the $P(E)$ hysteresis loops of the ceramic samples investigated in this study, recorded in a Sawyer-Tower circuit supplied with triangular electric field of 0.1 Hz frequency. The $P(E)$ loops show that the saturation polarization P_s and the remanent polarization P_r increase with increasing the
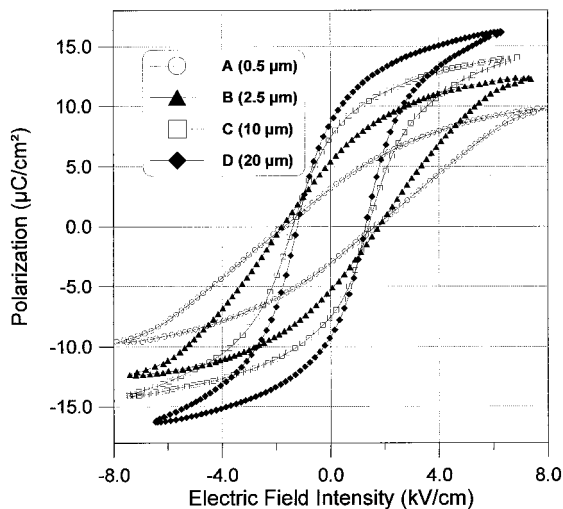
grain size. However, the ceramic B (2.5 μm) has the maximal coercive field (1.85 kV/cm) in the sample group, which is an unusual behavior. Recently, we described in a paper concerning the grain size influence on the ferroelectric-to-paraelectric phase transition in barium titanate ceramics similar to those studied here, another peculiar phase-transition behavior of the ceramic B observed by ac calorimetry [11]. The temperature dependencies of the heat capacity of each ceramic sample are illustrated in Fig. 6. We can see that the heat capacity of the ceramic B has the largest thermal hysteresis and the smallest jumps at the transition points.

The experimental results presented in this work, show that both the pyrocharge and the calorimetric measurements revealed a decrease of the ferroelectric-to-paraelectric transition temperature as the average grain size of the barium titanate ceramics decreased. Figure 7 displays the transition temperatures observed by heat capacity measurements together with the results of the present pyrocharge study. We can see that there is no significant difference between the two dependencies.

In order to explain the grain size dependence of the transition temperature of barium titanate powders or ceramics, most of the scientists considered two main possible causes: the depolarization field [14] and the internal stresses [13]. We consider that the two different type of investigations performed, i.e.
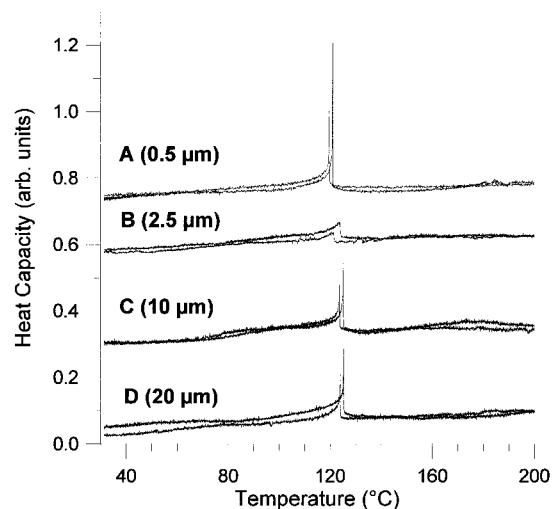

Fig. 5. Grain size influence on the $P(E)$ hysteresis loops of barium titanate ceramics with different average grain sizes: A—0.5 μm; B—2.5 μm; C—10 μm and D—20 μm.

Fig. 6. Temperature dependencies of the heat capacity, in case of barium titanate ceramics with different average grain sizes: A—0.5 μm; B—2.5 μm; C—10 μm and D—20 μm.
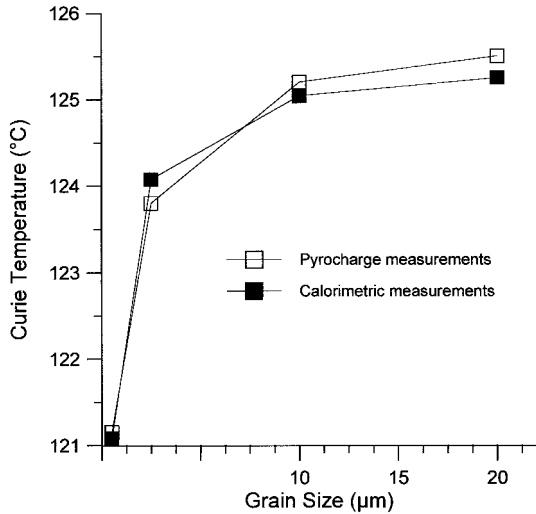
Fig. 7. Grain size dependencies of the ferroelectric-to-paraelectric transition temperature of barium titanate ceramics observed by pyrocharge and calorimetric measurements.

pyrocharge and calorimetric, allow us to decide which one of the two above mentioned causes has the main influence on the ferroelectric-to-paraelectric phase transition behavior of barium titanate ceramics. Each one of the two investigation methods has its own specific advantages. For instance, during the calorimetric experiments, the ceramics were never subjected to electric fields, preserving in this way the natural ferroelectric domain configuration formed in ceramics after sintering. Of course, the polishing performed for thinning the samples as requested by the ac calorimetric method, probably induced a surface domain reorientation [12] but there is no reason to expect changes of bulk domain structures. Thus, all the possible causes leading to grain size effects were able to influence the phase transition observed by heat capacity measurements. Besides, during the calorimetric measurements, the barium titanate ceramic samples could not exchange electrical charges with an external circuit, allowing a maximum influence of the depolarization field on the phase transition process.

A completely different situation exists in case of pyrocharge measurements. During the poling process, the ceramic is subjected to an intense electric field and a large amount of electric charges are coming inside the sample from the external circuit. Some of these charges screen the polarization and some are trapped by crystal defects. When the poling field is removed

and the plates of the ferroelectric capacitor are connected, the ferroelectric ceramic evolves towards a stable state. Until the equilibrium state is reached a current between plates can be detected. Part of this current is due to charges released by a slow domain rearrangement and another part is due to charges released from crystal defects. The contribution of these charges to the total depolarization current can be assessed by looking at Fig. 8, where the short-circuit time influence is analyzed in case of sample D (20 μm average grain size). After 24 h short-circuiting time at room temperature, the apparent remanent polarization is much lower because the ceramic reached an equilibrium state where no charges are released by domain wall movements or from crystal defects. However, there is no reason to consider that even after a 24 h short-circuit at room temperature all the charges trapped on defects were released. It is more reasonable to consider that the crystal defects have a distribution of their barrier energies and the releasing of charges will continue all the time during the heating. These charges inevitably affect the observed value of remanent polarization and make more difficult the evaluation of the saturation polarization. But, the presence of the charges released from defects ensures that during the phase transition the depolarization field is considerably reduced by screening.
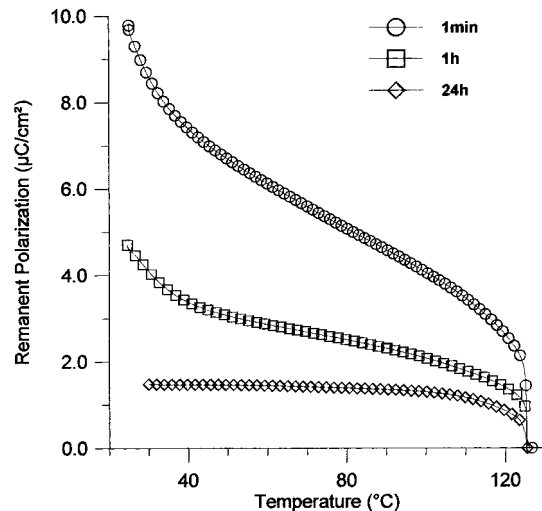

Fig. 8. Short-circuit time influence on the temperature dependence of remanent polarization, for a barium titanate ceramic sample with 20 μm average grain size (sample D).

While in case of the calorimetric measurements we cannot be sure about the importance of the depolarization field action at the particle level, in the case of poling and thermally stimulated depolarization, a seriously diminished action of this field is certain. If the depolarization field would have an important influence on the phase transition behavior of barium titanate ceramics, a notable difference between the transition temperatures observed by pyrocharge measurements and those obtained by calorimetric measurements should be detected. But, as Fig. 7 shows, there is no significant difference between the two dependencies. Since the observed grain size dependence of the transition temperature is much slower than that computed within the depolarization field model [14], and because no major differences were noticed between the results of pyrocharge and calorimetric measurements, we concluded that the internal stresses have the main influence on the ferroelectric-to-paraelectric behavior of barium titanate ceramics.

Now, some comments on the differences between the remanent polarizations observed on hysteresis loops and those derived from pyrocharge measurements are needed. We can see in Fig. 5 that the remanent polarization on the $P(E)$ loops are in the range $(3, 10)$ $\mu C/cm^2$, in very good agreement with the values previously reported by Arlt [15]. The remanent polarization observed in our pyrocharge study are in the range $(1.4, 3.4)$ $\mu C/cm^2$, much lower than those seen on the $P(E)$ hysteresis loops. This is a normal result, if we are taking into account that the two kinds of data correspond to two different processes: a dynamic process under strong electric field (hysteresis) and a long time relaxation under zero electric field (short-circuit after poling). If the short-circuit interval in the poling procedure is very short, Fig. 8 shows that the apparent remanent polarization at room temperature is practically equal to that seen on the hysteresis loop. But, only a slight heating up to 40°C is enough to produce an important decrease of this value. It is clear now that the high values of the remanent polarization observed on the hysteresis loops are due to the polar defects and their important contribution to the time dependent polarization of the ceramic.

In the end of this discussion, another aspect of the phase transition behavior exhibited by the barium titanate ceramic samples investigated in our study need to be discussed more. Looking at the results of our calorimetric, pyrocharge and $P(E)$ hysteresis investigations, we notice that the B-type ceramic always had a singular behavior: the largest value of the thermal hysteresis of heat capacity, the maximum value of the remanent polarization after poling and the maximum value of the coercive field. In our calorimetry study [11] we explained the peculiar ferroelectric-to-paraelectric phase transition behavior taking into account that inside the ceramic B, about 26% of the grains have sizes in the range $(0.5, 2.5)$ μm, as revealed by AFM images of the natural ceramic surfaces. In this interval of sizes, many of the physical properties of barium titanate ceramics have a rapid grain size dependence with a singular point at 1.1 μm [15,16]. Even the average grain size of the particle assembly is 2.5 μm, the presence of this important percent of grains with sizes close to 1.1 μm, determines significant effects on the physical properties of the B ceramic sample. We consider that the maximum value of the remanent polarization after poling is also due to the presence of this important number of particles with sizes close to the critical one of 1.1 μm, that turn the B-type ceramic into a ferroelectric system with a relatively high mechanical and electrical inhomogeneity, where the rearrangement of ferroelectric domains and the redistribution of internal stresses is more difficult than in a homogeneous one.

4.   Conclusions

In the present work we investigated by pyrocharge measurements the grain size dependence of the ferroelectric-to-paraelectric transition temperature of barium titanate ceramics sintered from hydrothermally grown powders. The observed transition temperature increased from 121°C to 126°C with increasing grain size from 0.5 to 20 μm. The increase was faster in the range of small grain sizes, with a tendency to saturate for large grain sizes.

The largest remanent polarization at room temperature was observed in case of a ceramic with 2.5 μm average grain size. This maximum value of the remanent polarization is probably caused by the relatively high mechanical and electrical inhomogeneity of this special ceramic sample which have 26% of its grains with sizes in the vicinity of the critical value of 1.1 μm where many of the physical

properties of barium titanate ceramics have a rapid variation.

A large amount of charges released from defects was observed during the short-circuit interval after poling and during the heating. The presence of these charges ensured a considerably diminished influence of the depolarization field on the phase transition behavior. Considering this diminution, a difference between grain size dependencies of the ferroelectric-to-paraelectric phase transition observed by ac calorimetric measurements and by pyrocharge measurements was expected. Because the two observed dependencies were almost identical, it was concluded that the internal stresses have the main influence on the ferroelectric-to-paraelectric phase transition behavior of barium titanate ceramics.

References

1. H.E. Kay and P. Vousden, *Philos. Mag.*, **40**, 1019 (1949).
2. C.J. Johnson, *Appl. Phys. Lett.*, **7**, 221 (1965).
3. H. Kniepkamp and W. Heywang, *Z. Angew. Phys.*, **6**, 385 (1954).
4. G.H. Jonker and W. Noorlander, in *Science of Ceramics*, edited by G.H. Stewart (Academic Press, London and New York, 1962) p. 255.
5. K. Kinoshita and A. Yamaji, *J. Appl. Phys.*, **47**, 371 (1976).
6. T. Kanata, T. Yoshikawa, and K. Kubota, *Solid State Commun.*, **62**, 765 (1987).
7. K. Uchino, E. Sadanaga, and T. Hirose, *J. Am. Ceram. Soc.*, **72**, 1555 (1989).
8. S. Wada, T. Suzuki, and T. Noma, *J. Mater. Res.*, **10**, 306 (1995).
9. M.H. Frey and D.A. Payne, *Phys. Rev.*, **B 54**, 3158 (1996).
10. R.P.S.M. Lobo, N.D.S. Mohallem, and R.L. Moreira, *J. Am. Ceram. Soc.*, **78**, 1343 (1995).
11. V. Tura, L. Mitoseriu, C. Papusoi, T. Osaka, and M. Okuyama, accepted for publication in *Jpn. J. Appl. Phys.*
12. B.W. Lee and K.H. Auh, *J. Mater. Res.*, **10**, 1418 (1995).
13. G. Arlt, *J. Mater. Sci.*, **25**, 2655 (1990).
14. W.Y. Shih, W.H. Shih, and I.A. Aksay, *Phys. Rev.*, **B 50**, 15575 (1994).
15. G. Arlt, *Ferroelectrics*, **104**, 217 (1990).
16. G. Arlt, D. Hennings, and G. de With, *J. Appl. Phys.*, **58**, 1619 (1985).