

Particle-size-induced diffuse phase transition in the fine-particle barium titanate porcelains

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1997 J. Phys.: Condens. Matter 9 9445

(<http://iopscience.iop.org/0953-8984/9/43/027>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.209

The article was downloaded on 14/05/2010 at 10:54

Please note that [terms and conditions apply](#).

Particle-size-induced diffuse phase transition in the fine-particle barium titanate porcelains

Yung Park[†], Won-Jae Lee and Ho-Gi Kim

Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Kusong-dong, Yusong-gu, Taejon 305-701, Korea

Received 18 December 1996, in final form 4 June 1997

Abstract. The effect of particle size on the ferroelectric transition in fine-particle BaTiO₃ porcelain produced by the inorganic sol–gel method was investigated. The phase transition was measured by dielectric properties, variable temperature x-ray diffraction, and differential scanning calorimetry (DSC). The tetragonal distortion of the unit cell decreases with size and vanishes at 0.037 μm . The T_c decreases gradually but the transition becomes diffuse with a decrease in the size of 0.081 to 0.040 μm , below which there is no peak in the dielectric constant or DSC curve, though ferroelectric distortion (c/a) persists down to 0.037 μm .

1. Introduction

In a number of studies on phase transitions in complex perovskite-type ferroelectrics, broadened maxima and/or minima are observed in physical properties in the vicinity of the apparent Curie temperature [1]. Yet it is not clear what kind of phase transition indeed occurs at these broadened maxima and/or minima because different transition temperatures are displayed by different physical parameters. Also, it is not clear what physical process is responsible for such gradual and diffuse phase transitions in certain systems.

In a number of perovskite ABO₃-type ferroelectrics, especially in compounds with a multiple-ion occupation of A and/or B sites in the crystal lattice, deviations from the Curie–Weiss behaviour have been reported. The notable characteristic of deviations is the fact that the transition temperature is not sharply defined and physical properties change rather gradually over a temperature range. This type of phase transition is named a diffuse phase transition, and DPT characteristics have been summarized by previous researchers [2–6] as the following: (i) broadened maxima in the dielectric constant curves, (ii) different transition temperatures displayed by different physical parameters, (iii) frequency dependent character of the dielectric properties in the transition region accompanied by the shift in the apparent transition temperature, (iv) gradual decrease of spontaneous or remanent polarization beyond the apparent transition, and (v) deviation from the Curie–Weiss behaviour in the vicinity of the apparent transition temperature. So far the existence of such characteristics of the DPT have only been qualitatively established. The experimental relative dielectric constant data

[†] Corresponding author. E-mail address: yp204@cam.ac.uk

of most polar dielectrics can be successfully fitted by a semi-empirical equation of the form [7]

$$1/\varepsilon = 1/\varepsilon_{max} + 1/A(T - T_a)^\gamma \quad (1)$$

where ε_{max} is the maximum dielectric constant value at the apparent transition temperature T_a , A is a constant, and γ is an exponent varying between 1 and 2. Exponent γ is 1 when the transition is Curie–Weiss type, while it is considered to be 2 when the transition is a complete DPT.

Equation (1) may be more conveniently rewritten in a new form

$$(\varepsilon_{max} - \varepsilon)/\varepsilon = (T_a/\sigma)^\gamma (T/T_a - 1)^\gamma \quad (2)$$

where σ may be defined as a constant showing the degree of thermal diffuseness or a Curie–Weiss constant at $\gamma = 1$. Both γ and σ can together indicate the degree of deviation from the ideal Curie–Weiss law. Exponent γ can be determined from the slope of the log–log plot of equation (2), while σ can be determined from the y-axis intercept of the same plot.

Kanata *et al* [8] have shown that in fine particles of BaTiO₃ with grain size less than 20 μm , the T_c decreases with decreasing particle size. They attributed this shift to superparaelectricity and pointed out the importance of the internal stresses that develop spontaneously in small grains. Uchino *et al* [9] made a detailed study of the variation of the tetragonal distortion (c/a) with particle size in BaTiO₃ and, having identified the T_c as that temperature at which c/a becomes 1, estimated the critical size for the existence of ferroelectricity to be 0.12 μm .

Arlt *et al* [10] showed that 25 °C high dielectric constant and broadened maxima for small-grain-size BaTiO₃ ceramic were related to the internal stress by means of measuring the elastic modulus and average width of a 90° domain. Moreover, internal stress made the dielectric curve broad for Zr-doped BaTiO₃ [11] and for Ce-doped BaTiO₃ [12]. For sintered ceramics of BaTiO₃ with high density, it was also found that with a decrease in grain size in the 1 to 5 μm range, (1) there is a decrease in the peak dielectric constant ε_{max} , (2) the peak in the dielectric constant curve becomes broader and (3) the ferroelectric transition temperature (T_c) goes up [13–15].

Park [16] made a Raman study of BaTiO₃ particles with different average particle size as a function of temperature. The ferroelectric T_c was indirectly measured as the temperature at which the frequency ω_s of the soft E (1TO) mode vanishes. Furthermore it was found not only that T_c decreases with decrease in particle size, but also that the ω_s at room temperature shifts towards lower frequencies with decreasing particle size, which implies that decrease in particle size lowers T_c . For fine particles of PbTiO₃, similar phenomena for the ω_s were reported by Burns and Scott [17, 18] and Zhong *et al* [19].

Depolarization fields result from an uncompensated spontaneous polarization for a ferroelectric material [20]. When a ferroelectric material spontaneously polarizes, the free surface accumulates compensating charge from the environment. After doing so, the full spontaneous polarization can be realized. If for some reason a spontaneous polarization cannot be compensated by charge, the consequence of the necessary boundary condition of zero polarization at the free surface would be an internal electric field oriented opposite to the polarization itself. Thus, the gradient in the polarization from the bulk to the surface would become a source for a depolarization field. In the absence of compensating charge, the depolarization field can become sufficiently strong. In the present study, the depolarization field might play a substantial role in size-related phenomena for BaTiO₃. In order to minimize the depolarization field effect, the sintered porcelains were coated with Mn(NO₃)₂·4H₂O solution.

We prepared commercial fine particles of BaTiO₃, and particle size was measured by x-ray diffraction (Hall–Williamson method) and compared with the light intensity fluctuation particle size and transmission electron microscope (TEM) observations. The object of this study was to examine the effect of the BaTiO₃ particle size on the diffuse phase transition. In order to obtain a complete understanding, the phase transition in the fine-particle BaTiO₃ porcelains was studied by dielectric dispersion against temperature, measurement of the temperature dependence of tetragonal distortion (c/a), DSC, γ and σ (diffuseness coefficient).

2. Experimental details

The commercial high-purity (99.99%) BaTiO₃ powders A to J used in the present study were Rhone Poulenc's electric grade BaTiO₃ manufactured by the inorganic sol–gel process. The Ba/Ti atomic ratio was determined by means of x-ray fluorescence (XFA) to be Ba/Ti = 1:1.008 ± 0.001.

The particle size of starting BaTiO₃ (d_{light}) and standard deviation (σ_{light}) were measured by a light intensity fluctuation type particle size analyser (Malvern's Autosizer 2C). The crystallite size (d_{XRD}) was also estimated using x-ray diffraction (Hall-Williamson method), which separates size influence and residual strains from line broadening [21, 22]. The particle size (d_{TEM}) and standard deviation (σ_{TEM}) were also measured from micrographs obtained from a transmission electron microscope (Hitachi H9000NA analytical TEM, Japan).

The starting BaTiO₃ powders were pressed into a disc shape of 10 mm diameter and 0.5 mm thickness and sintered at 700–1000 °C for 1–20 min. The relative density of sintered specimens ranges from 50% to 70%, and, henceforth, the sintered specimens were regarded as porcelain. The BaTiO₃ powders C and I were cold isostatically pressed at 2 GPa and thereafter hot pressed for 10 min in air at 1100 °C at uniaxial pressures of about 0.2 GPa. The highly dense ceramics (0.3% porosity) were then cut and electroded for dielectric measurements. The porcelains were maintained in Mn(NO₃)₂·4H₂O solution for 10 days and Auger conformed Mn²⁺ and NO₃²⁻ layers on the surface of the porcelain. It is believed that Mn²⁺ and NO₃²⁻ might supply the compensating charge. The average grain size (d_{porce}) and standard deviation (σ_{porce}) were calculated from the grain boundary intercept distance of the fractured surface of the porcelain, using a scanning electron microscope (SEM) (model JXA-840, JEOL, Tokyo, Japan). Disc surfaces were cleaned and electroded with silver paste. The dielectric constant and dielectric loss were measured at 1 kHz, 100 kHz and 1 MHz using a Hewlett Packard 4294A impedance gain phase analyser. The heating rate was maintained at 3 °C h⁻¹. At least three discs were scanned for each sample corresponding to a particle size. The ferroelectric T_c was identified as the temperature corresponding to the maximum value of dielectric constant curves.

The temperature dependence on tetragonal distortion c/a ratio was determined from x-ray diffraction in the –250 to 130 °C range using a Rigaku x-ray diffractometer coupled with high-temperature attachment and an He closed cycle refrigerator. The tetragonal lattice constants a and c were calculated from the (200) and (002) reflection, respectively. Diffraction angles were corrected by a standard silicon target. More than five diffractions from 20° to 100° (Cu K α , 2 θ) were collected to calculate the lattice constants by using commercial least-squares determination. Diffraction patterns were recorded after stabilizing at each temperature for at least 15 min. The T_c was identified as the temperature at which c/a becomes 1. The T_c was also determined from differential scanning calorimetry performed in

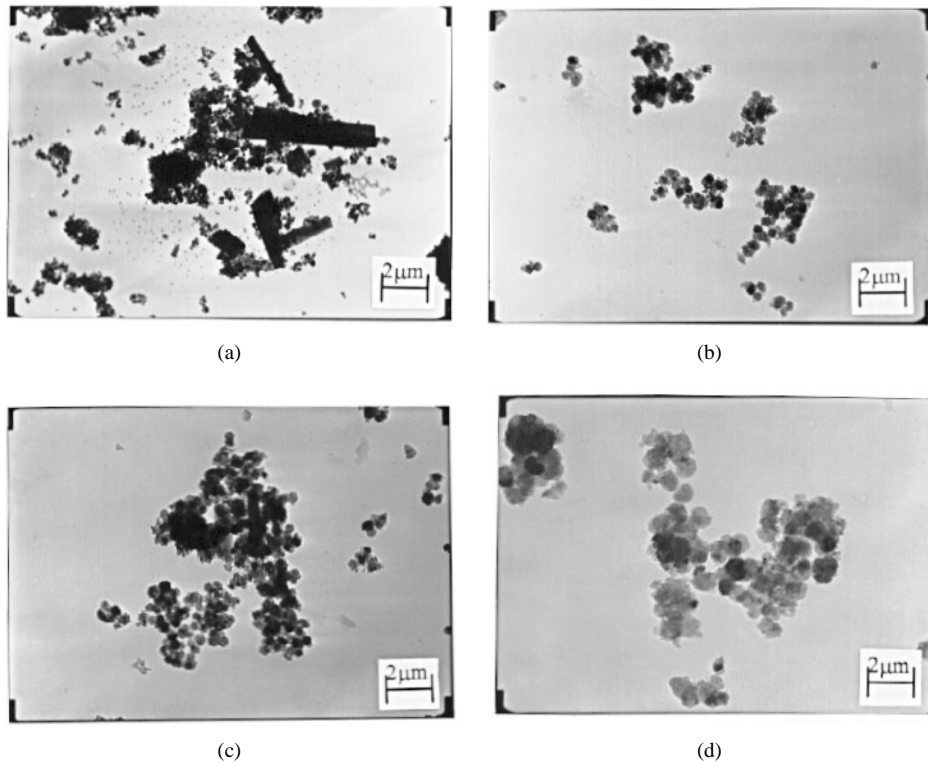


Figure 1. TEM images of the starting BaTiO₃ powders with different particle sizes: (a) A, (b) B, (c) G and (d) J.

the range of $-130\text{ }^{\circ}\text{C}$ to $+150\text{ }^{\circ}\text{C}$ using a Stanton DSC thermal analyser. The measurements were made in the temperature increasing mode with a scan rate of $5\text{ }^{\circ}\text{C h}^{-1}$.

3. Results

3.1. X-ray and thermal analysis

TEM images for the BaTiO₃ powders with different average sizes are shown in figure 1. The BaTiO₃ particles prepared by the inorganic sol-gel method are shown to have a narrow size distribution. As can be seen in table 1, the particle size (d_{light}) determined from light intensity measurements compares very well with the average particle size (d_{TEM}) seen in the TEM pictures. However, d_{XRD} is consistently smaller than d_{light} , which is only to be expected since each particle could consist of several coherently diffracting domains. It is clear from table 1 that the larger the particle, the greater is the number of domains it contains. Since ferroelectric phenomena in perovskite systems are associated with lattice vibrational mechanisms, henceforth, (unless otherwise specified), all references to particle size indicate d_{XRD} . Figures 2(a)–(d) show SEM images of specimens A, B, G and J which reveal the porous porcelains, while figures 2(e) and (f) exhibit SEM images of hot-pressed ceramics C and I. d_{porce} is nearly proportional to the starting particle size of d_{TEM} and d_{light} . Therefore, we can ignore the complicated stress effect induced by c -axis expansion and a -axis contraction in the ferroelectric transition of fine-grained BaTiO₃ ceramics.

Table 1. Variation of the ferroelectric transition temperature (T_c) and diffuseness coefficient (γ, σ) with different particle size and grain size in BaTiO₃.

Sample No	d_{XRD}^a (μm)	d_{light}^b (μm)	σ_{light}^c (μm)	d_{TEM}^d (μm)	σ_{TEM}^e (μm)	d_{porce}^f (μm)	σ_{porce}^g (μm)	$d_{ceramic}^h$ (μm)	T_c (dielectric) (°C)	T_c (DSC) (°C)	γ (diffuseness)	σ (diffuseness)
A	0.033	0.05	0.032	0.042	0.35	0.061	0.40		no peak	no peak		
B	0.037	0.10	0.040	0.095	0.035	0.104	0.050		no peak	no peak		
C	0.040	0.12	0.060	0.134	0.068	0.132	0.080	0.135	70	62	1.74	230
D	0.047	0.14	0.035	0.145	0.060	0.152	0.093		82	75	1.71	194
E	0.053	0.16	0.097	0.167	0.105	0.174	0.123		95	90	1.61	190
F	0.060	0.18	0.103	0.187	0.122	0.193	0.135		114	108	1.45	170
G	0.064	0.20	0.100	0.22	0.110	0.23	0.130		123	120	1.39	138
H	0.073	0.25	0.113	0.245	0.124	0.265	0.140		124.5	122	1.312	115
I	0.081	0.30	0.145	0.29	0.135	0.34	0.159	0.36	127	125	1.17	77
J	0.140	1.13	0.35	1.10	0.55	1.27	0.65		130	130	1.00	50

^a XRD particle size.

^b Light intensity particle size.

^c Standard deviation of d_{light} .

^d Particle size observed from TEM figure.

^e Standard deviation of d_{TEM} .

^f Grain size of porcelain observed from SEM figure.

^g Standard deviation of d_{porce} .

^h Grain size of hot-pressed ceramics observed from SEM figure.

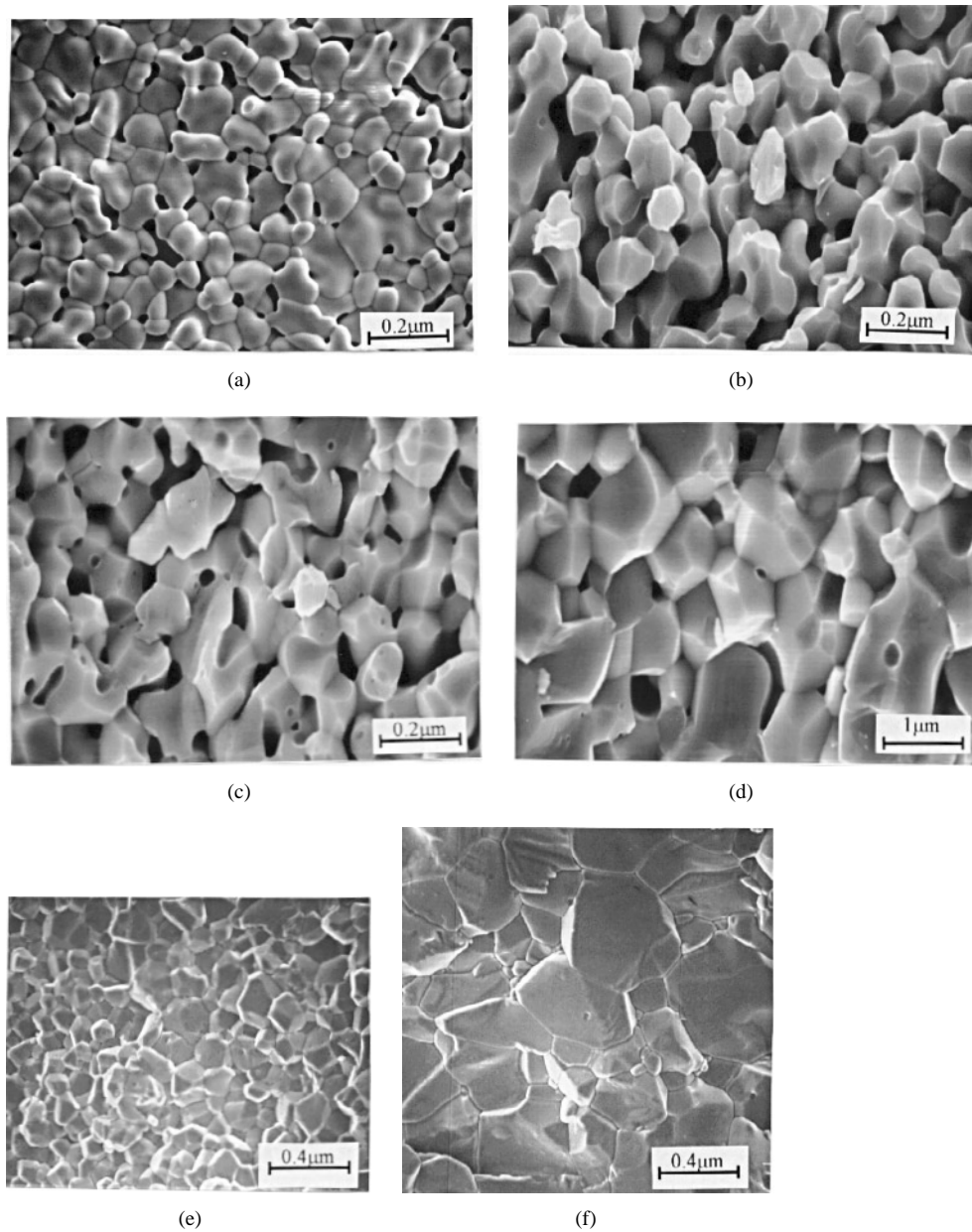


Figure 2. SEM images of the fractured surfaces of (a) A porcelain, (b) B porcelain, (c) G porcelain, (d) J porcelain, (e) C ceramic and (f) I ceramic.

Figure 3 shows the variation of the lattice constants a and c with particle size at room temperature. The unit cell does not change its dimensions down to $0.081 \mu\text{m}$, below which c decreases and a increases with decreasing size. The resulting reduction in the tetragonal distortion c/a becomes rapid when the particle size goes below about $0.073 \mu\text{m}$. This suggests that there is a decrease in the spontaneous polarization (P_s) in fine-particle BaTiO_3 porcelain, since the tetragonal distortion (c/a ratio) in the ferroelectric phase scales with the spontaneous polarization.

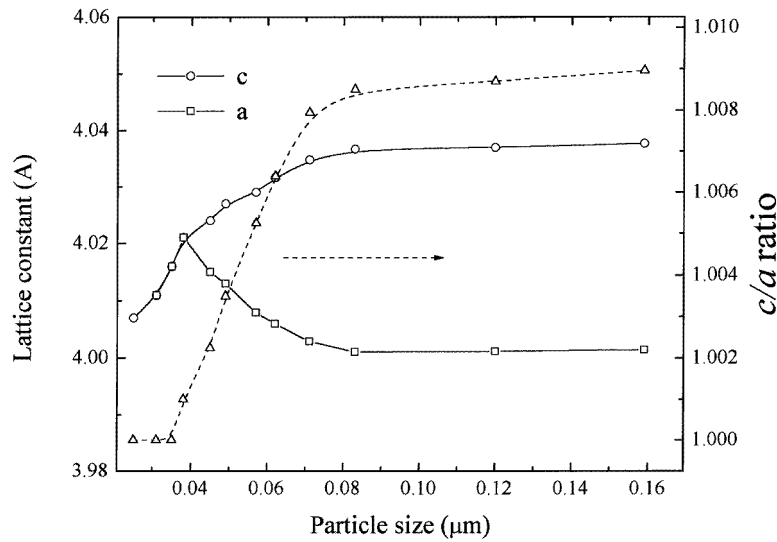


Figure 3. Particle size dependence of the lattice constants (*a* and *c*) and the tetragonal distortion *c/a* in BaTiO₃ porcelain at room temperature.

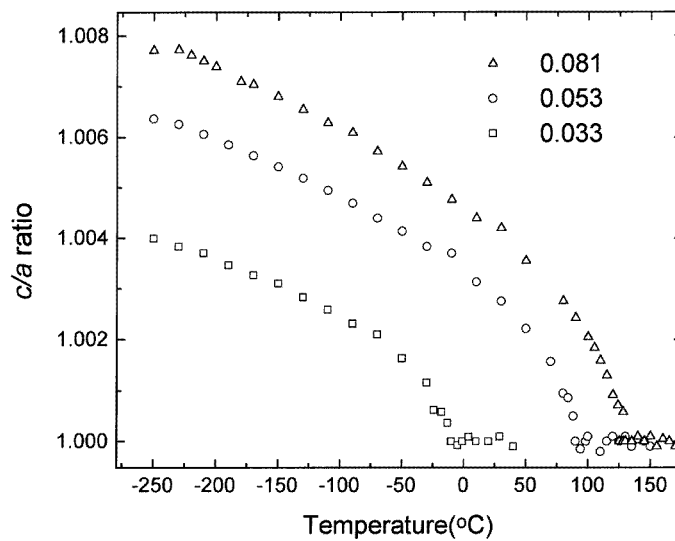


Figure 4. Temperature dependence of the tetragonal distortion (*c/a*) for BaTiO₃ porcelains with different particle sizes.

Figure 4 shows that the particle-size-induced reduction in the value of *c/a* persists even at low temperature. The XRD pattern at temperatures 150 °C to −250 °C tells us about the particle size dependence of the structural *T_c*. We define this as the temperature at which the (100)–(001) and the (200)–(002) line splittings disappear, i.e. the ferroelectric distortion, *c/a* becomes 1, as can be seen in figure 4.

Figure 5 shows the specific heat capacity (*C_p*) as a function of temperature for BaTiO₃ porcelains of different particle sizes. The thermal *T_c* was identified with the temperature

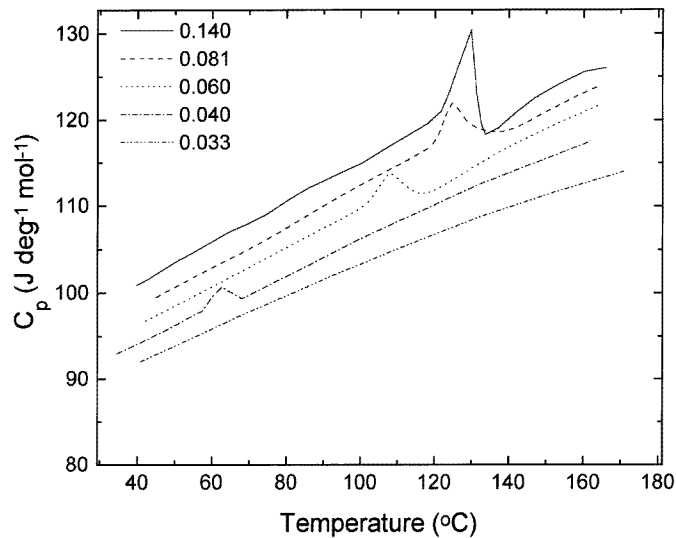


Figure 5. Specific heat capacity of BaTiO₃ porcelains with different particle sizes (as a function of temperature).

of the peak in the specific heat capacity curve associated with the disappearance of the ferroelectric order. The T_c was again found to decrease with a decrease in particle size (table 1) and there was also a progressive increase in peak width. For samples with particle size $\leq 0.035 \mu\text{m}$, no transition peaks were observed in the specific heat capacity curves.

3.2. Dielectric temperature characteristics

The temperature dependence of the dielectric constant and dielectric loss was measured in the vicinity of the Curie temperature at four different grain sizes. Figure 6 shows the grain size dependence of the hot-pressed ceramics. This is in accordance with the predictions of the internal stress model proposed by Buessem *et al* [23, 24]. When a fine-grained ceramic is cooled through T_c , each grain is subjected to a complex system of internal stresses which depend on the orientation of all the surrounding grains. The structural transition accompanying the ferroelectric transition cannot develop fully due to such intergranular contacts, so that unrelieved strains remain within the grains. According to Buessem *et al* [23, 24], the stress system would tend to suppress the spontaneous deformation and force the grain back towards the cubic state. Moreover the stress system would consist of a combination of uniform mechanical compression along the c -axis and tensions along both the a -axes. Such a stress system would lead to a decrease in the T_c .

On the other hand, figure 6 shows that with a decrease in grain size of porcelain, T_c decreases, ϵ_{max} decreases and the peaks become increasingly broader. For samples with a particle size of $0.037 \mu\text{m}$ and below, no peaks were observed in the dielectric constant curves. The nature of the dielectric and the thermal transitions reveal qualitatively similar changes with a reduction in the particle size.

Figure 7 illustrates that for a sample with the particle size of $0.081 \mu\text{m}$, a decrease in frequency leads to an increase in the ϵ_{max} , but the ferroelectric T_c remains constant at 127°C . Also the peak in the dielectric loss curves occurs at 120°C . On the other hand, the T_c for the particle size $0.040 \mu\text{m}$ moves up with an increase in frequency from 70°C at

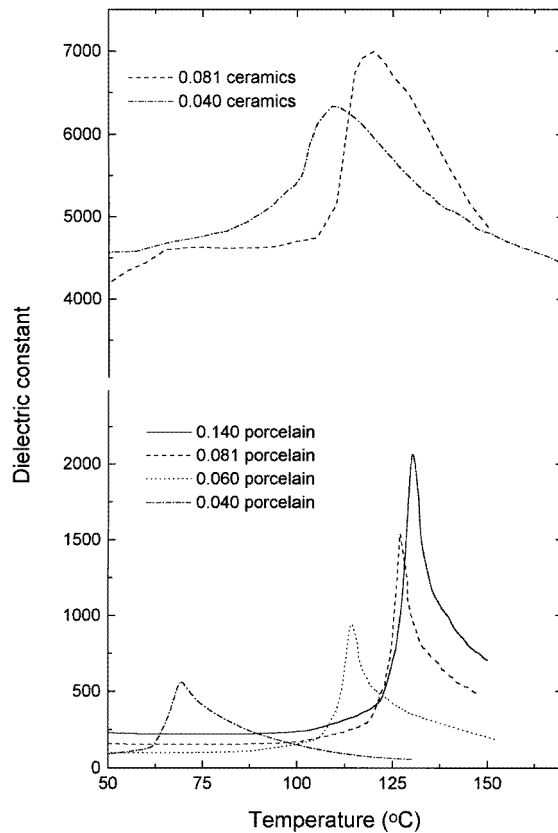


Figure 6. Temperature dependence of the dielectric constant for BaTiO₃ porcelains and hot-pressed BaTiO₃ ceramics with different particle sizes all measured at 1 kHz.

1 kHz to 78 °C at 1 MHz, as can be seen in figure 8. A similar behaviour was also observed in other samples with small particle size. It is noted that the temperature difference between the dielectric loss maxima and dielectric constant maxima is larger in fine particles. These properties are typical of materials with a diffuse phase transition.

4. Discussion

The particle size reduction progressively increases the symmetry of the crystal structure, which was reflected by a monotonic decrease in the tetragonal distortion (c/a ratio) from 1.0085 at the particle size of 0.081 μm to 1.00 at the particle size of 0.037 μm.

Dielectric and thermal T_c measurements appear to indicate that the ferroelectric transition is suppressed in nanocrystalline BaTiO₃ when d_{XRD} is reduced below 0.035 μm. This is in apparent contradiction with the structural measurements since the ferroelectric distortion corresponding to 0.033 μm does not actually vanish even in the finest particles studied. Therefore, we suggest that the nonappearance of a peak in the dielectric and thermal response need not be construed as indicative of an absence of ferroelectric ordering.

The broadening of dielectric constant and DSC peaks in fine-particle porcelain is typical of materials which exhibit the diffuse phase transition. Our study of BaTiO₃ fine-

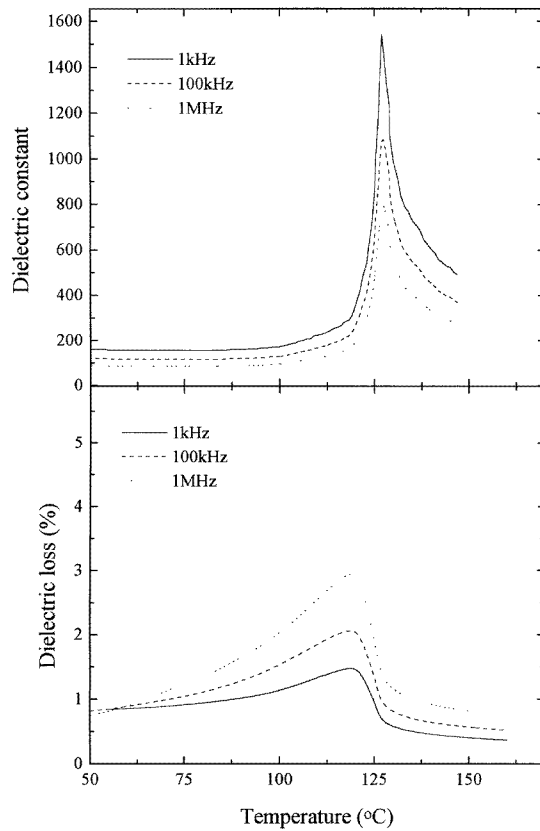


Figure 7. Temperature dependence of dielectric constant and dielectric loss in BaTiO₃ porcelain with 0.081 μm particle size for three different frequencies (1 kHz, 100 kHz, 1 MHz).

particle porcelain suggests that with a decrease in particle size, (1) the dielectric constant peaks become broader, (2) the difference between peaks of dielectric constant maxima and dielectric loss maximum becomes larger, (3) there is an increasing deviation from the Curie–Weiss law in the vicinity of T_c , (4) both dielectric constant curve and dielectric loss curve are frequency dependent, (5) the decrease in c/a , which is assumed to scale with spontaneous polarization, becomes more gradual, (6) T_c values obtained from different measurements do not coincide, as shown in table 1, and (7) with a decrease in frequency, T_c decreases and ε_{max} increases.

A quantitative analysis of the diffuseness of the ferroelectric phase transition in fine-particle BaTiO₃ porcelain can be made by fitting the dielectric constant curve for $t > T_{max}$ with the equations (1) and (2). For a system exhibiting intermediate degrees of diffuseness, γ has the value of 1 to 2. We determine the value of γ from the slope of a straight line fitted to the logarithmic plots of the reciprocal dielectric constant ($1/\varepsilon - 1/\varepsilon_{max}$) measured at 1 MHz as a function of $(T - T_a)$. Table 1 shows that with a decrease in particle size, the ferroelectric transition becomes increasingly diffuse. The BaTiO₃ porcelain with particle size 0.140 μm (1.13 μm) shows γ and σ values of 1.0 and 50, while γ and σ are 1.74 and 230 for the sample with particle size 0.040 μm , below which the transition peak is totally smeared.

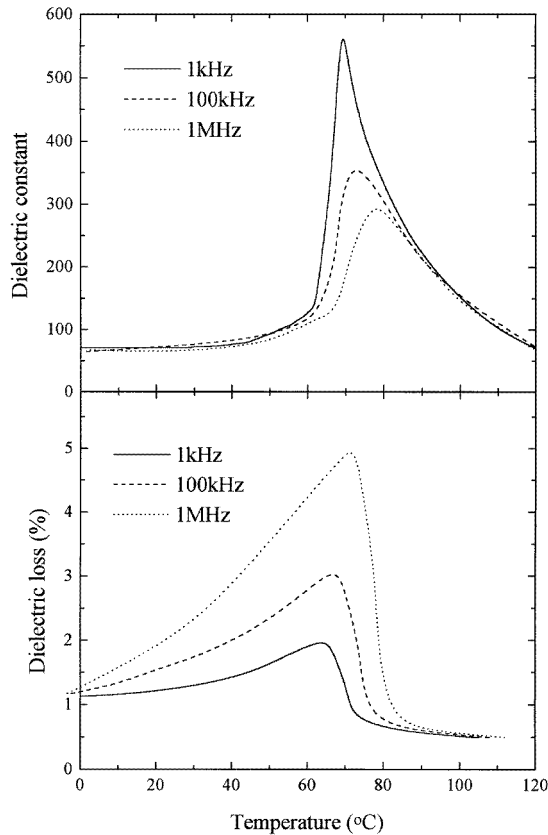


Figure 8. Temperature dependence of dielectric constant and dielectric loss in BaTiO₃ porcelain with 0.040 μm particle size for three different frequencies (1 kHz, 100 kHz, 1 MHz).

The DPT is explained in terms of polarization fluctuation. Fritzberg's polarization (structural) fluctuation theory [1, 25] of DPT has been based on the assumption that there are spatial variations in polarization because of the small thermodynamic free energy difference caused by the thermal fluctuations between the ferroelectric and paraelectric phases around the transition. Local polarization fluctuations must be present throughout the crystal; i.e. it would consist of microregions of paraelectric and ferroelectric phase and transition temperature varies from one microregion to another. There could be also an intermixture of ferroelectric and paraelectric regions if only one of the constituent phases is ordered at the temperature of interest. The scale of heterogeneity is believed to be 100 to 200 \AA , which suggests a physical similarity between a solid solution and a fine-particle porcelain.

A fine-particle ferroelectric with an average size of 100–200 \AA would consist of a collection of crystallites with varying sizes, whose T_c depends on the different c/a ratio associated with different sized particles. Since the variation of T_c with particle size is clearer in finer particles, a more diffused phase transition is observed. A T_c distribution model had also been argued to explain the dielectric behaviour of certain sintered ceramics, where a complicated stress distribution occurs due to the high compaction. In comparatively loosely aggregated fine-particle porcelain, the observed T_c appears to depend directly on the

particle size. Subsequently, for fine-particle porcelain, increase in diffuseness (γ , σ) relates to particle size.

5. Conclusions

The study of the ferroelectric phase transition in a fine-particle BaTiO₃ porcelain suggests that with a decrease in average particle size, (i) below a size of 0.081 μm , the tetragonal distortion (c/a ratio) decreases monotonically. The decrease in c/a ratio is accompanied by a decrease in the T_c by about 57 °C corresponding to a change in d_{XRD} from 0.081 μm to 0.040 μm , (ii) a decrease in the particle size makes the ferroelectric transition increasingly diffuse. The diffuseness coefficient (γ) increases from 1.00 for 0.140 μm particles to 1.74 for 0.040 μm . Accordingly, the dielectric and thermal transitions at T_c become progressively broader and shallower before they disappear altogether at 0.037 μm , (iii) BaTiO₃ fine particles with $d_{XRD} < 0.037 \mu\text{m}$ do not exhibit any peak corresponding to the ferroelectric transition in DSC and dielectric dispersion. It is believed that these particles are ferroelectrically ordered since the tetragonal distortion is still comparatively high in particles of this size and (iv) the tetragonal distortion approaches unity when d_{XRD} is 0.037 μm . This should be considered as the critical size at which a ferroelectric–paraelectric transition takes place at room temperature in BaTiO₃.

References

- [1] Fritzberg V Ya 1968 *Sov. Phys.–Solid State* **10** 304
- [2] Stenger C G F and Burggraaf A G 1980 *J. Phys. Chem. Solids* **41** 25
- [3] Smolenskii G 1970 *J. Phys. Soc. Japan Suppl.* **28** 26
- [4] Uchino K and Nomura S 1982 *Ferroelectr. Lett.* **44** 55
- [5] Cross L E 1987 *Ferroelectrics* **76** 241
- [6] Tiwari V S and Pandey D 1994 *J. Am. Ceram. Soc.* **77** 1819
- [7] Clarke R and Burfoot J C 1974 *Ferroelectrics* **6** 505
- [8] Kanata T, Yoshikawa T and Kubota K 1987 *Solid State Commun.* **62** 765
- [9] Uchino K, Sadanaga E and Hirose T 1989 *J. Am. Ceram. Soc.* **72** 1555
- [10] Arlt G, Hennings D and With de G 1985 *J. Appl. Phys.* **58** 1619
- [11] Armstrong T R and Buchanan R C 1990 *J. Am. Ceram. Soc.* **73** 1268
- [12] Park Y, Kim Y and Kim H G 1996 *J. Phys. D: Appl. Phys.* **29** 2483
- [13] Okazaki K and Nagata K 1973 *J. Am. Ceram. Soc.* **56** 82
- [14] Martirena H T and Burfoot J C 1974 **7** 3182
- [15] Srinivasan M R, Multani M S, Ayyub P and Vijayaraghavan R 1983 *Ferroelectrics* **51** 137
- [16] Park Y unpublished work
- [17] Burns G and Scott B A 1970 *Phys. Rev. Lett.* **25** 167
- [18] Burns G and Scott B A 1973 *Phys. Rev. B* **7** 3088
- [19] Zhong W L, Jiang B, Zhang P L, Ma J M, Cheng H M, Yang Z H and Li L X 1993 *J. Phys.: Condens. Matter* **5** 2619
- [20] Lines M E and Glass A M 1977 *Principles and Application of Ferroelectrics and Related Materials* (Oxford: Clarendon)
- [21] Hall W H and Williamson G K 1951 *Proc. Phys. Soc. B* **64** 937
- [22] Williamson G K and Smallman R E 1955 *Proc. Phys. Soc. B* **68** 577
- [23] Buessem W R, Cross L E and Goswami A K 1966 *J. Am. Ceram. Soc.* **49** 33
- [24] Buessem W R, Cross L E and Goswami A K 1966 *J. Am. Ceram. Soc.* **49** 36
- [25] Fritzberg V Ya 1977 *Bull. Acad. Sci. Latvian USSR* **2** 355