

Grain-size effects on the ferroelectric behavior of dense nanocrystalline BaTiO₃ ceramics

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(Received 28 April 2004; published 30 July 2004)

A progressive reduction of tetragonal distortion, heat of transition, Curie temperature, and relative dielectric constant has been observed on dense BaTiO₃ ceramics with grain size decreasing from 1200 to 50 nm. The correlations between grain size, extent of tetragonal distortion, and ferroelectric properties strongly support the existence of an intrinsic size effect. From the experimental trends the critical size for disappearance of ferroelectricity has been evaluated to be 10–30 nm. The strong depression of the relative permittivity observed for the nanocrystalline ceramics can be ascribed to the combination of the intrinsic size effect and of the size-dependent “dilution” effect of a grain boundary “dead” layer.

DOI: 10.1103/PhysRevB.70.024107

PACS number(s): 77.84.–s, 64.70.–p, 81.07.–b

I. INTRODUCTION

Ferroelectric ceramics with perovskite structure, like barium titanate (BaTiO₃) and lead zirconate titanate [Pb(Zr,Ti)O₃], are extensively used in the electronic industry for the fabrication of multilayer ceramic capacitors, piezoelectric transducers, pyroelectric elements, and ferroelectric memories. The continuous advance in microelectronics and communications is leading to the miniaturization and integration of ferroelectric components. However, the reduction of the physical sizes of ferroelectrics seems to have a significant effect on polarization and this could represent a limitation for the miniaturization process. Beside the technological implications, the existence of a critical size for ferroelectricity is of great fundamental interest.

Above the Curie temperature ($T_C \approx 130^\circ\text{C}$), the structure of barium titanate is cubic and paraelectric. Below the Curie point, the structure is slightly distorted and three ferroelectric polymorphs with nonzero dipole moment exist depending on temperature. The tetragonal modification is stable between $\approx 10^\circ\text{C}$ and 130°C . Below 10°C the structure becomes orthorhombic and a further transition to rhombohedral structure occurs at $\approx -80^\circ\text{C}$. The size dependence of polarization, Curie temperature (T_C) and tetragonal distortion ($c/a-1$, where c and a are the unit cell edges) of the ferroelectric phase has been calculated by means of theoretical models based on the Landau-Ginsburg-Devonshire (LGD) theory in the case of isolated particles.¹ The instability of the ferroelectric phase (suppression of polarization) in isolated particles is mainly the consequence of the surface effect in a confined system. According to this approach, a transition from the ferroelectric phase to a cubic paraelectric phase at room temperature for a critical particle size from a few nanometers to a few tens of nanometers is predicted.¹ Recent local piezoresponse force microscopy measurements have indicated a critical size of the same order of magnitude (4–20 nm) for isolated PbTiO₃ nanograins.² Critical sizes in the range 10–100 nm were reported in previous studies on BaTiO₃ and

PbTiO₃.^{3,4} In ferroelectric thin films and ultrafine particles, mainly inhibition and occasionally enhancing of polarization was reported.³ Both types of behavior have been explained in the frame of modified LGD theory.¹

However, there are many causes for size effects in ferroelectrics and is often difficult to separate true size effects from other factors that change with the size of the system. For instance, the extreme spreading of the results reported in literature about the size effect in ferroelectric particles is associated with the variety of synthesis routes and processing techniques adopted.³ The stability of the ferroelectric phase can be determined by additional factors like defect chemistry, incorporation of foreign atoms and bulk hydroxyl groups, aggregation level of the particles, porosity level, residual stresses, etc.^{3–5} Generally, in ferroelectrics the boundary conditions can have a strong influence on the stability of the polar phase and on the nature of the size effect.^{6,7} Because of the large electrostrictive coupling between spontaneous lattice strain and polarization, the elastic boundary conditions must be considered. Compressive or tensile stresses are expected to change the transition temperature of a ferroelectric material. For instance, it is well known that the application of a hydrostatic pressure shifts the Curie temperature of BaTiO₃ of $\approx -5.8 \times 10^{-3} \text{ }^\circ\text{C}/\text{atm}$.⁶ In contrast, the application of a bidimensional pressure to a single crystal of BaTiO₃ rises the transition temperature, since the spontaneous strain of the lattice is increased and the crystal is prevented to become cubic. These trends can be correctly reproduced within the LGD theory.⁶ It should be noted that the mechanical boundary conditions of isolated particles, particles embedded in a nonferroelectric matrix, grains in a ceramic, and thin films are quite different. This explains why the behavior of powders, composite materials, ceramics, and films is generally distinct.^{3–8} In the same way, the size effect in films rigidly clamped to a substrate may deviate from that of the same film when removed from its support. This because growth stresses, as well as lattice and thermal expansion mismatch between film and substrate impose appreciable in-plane stress on the film. An additional consideration concerns

the electric boundary conditions in ferroelectric materials. The spontaneous polarization creates depolarization fields that require compensation charges near or at the surfaces/interfaces. Consequently, the properties of the system are expected to strongly depend on the electric boundary conditions limiting the ferroelectric phase. Two types of interfaces can be considered in ferroelectric materials like polycrystalline ceramics or films: ceramic/electrode interfaces and grain boundaries. The first ones are highly important in the case of ferroelectric thin (≤ 1000 nm) films, because the distribution of screening charges in the electrodes, very near to the interface with the dielectric, leads to thickness-dependent electrical properties.^{7,9} However, in the case of bulk ceramics, with thickness of the order of 10^6 nm or more, the influence of the depolarization field related to the screening charges in the electrodes is negligible and the main depolarizing effect is coming from charges located at the grain boundaries. The depolarization field is normally reduced by domain patterns formation, but this process is not energetically favorable in fine grained ceramics (the grains of BaTiO_3 are essentially single domain when their size is reduced below 500–300 nm)^{10,11} and compensation only via surface charges and/or polarization gradients is thus possible. Another important effect which has to be considered is related to the dipole-dipole interaction which is quite different depending on the location of dipoles (grain core or grain boundary). As the physical size of the confined system is reduced (i.e., decreasing the grain size), the fraction of dipoles located at interfaces increases substantially and changes on the dipolar interaction in nanosized system may be expected.

The dielectric properties of bulk ferroelectric materials result from the combination of the intrinsic response of the system (i.e., the appropriate directional average of the response expected from a single domain crystal with well-defined boundary conditions) and extrinsic effects, like those associated with domain structure, grain boundaries, and defects. Both contributions are, in general, influenced by the grain size (GS). Nevertheless, ceramic seems a more convenient system to study size effects in comparison to thin films and powders for the reasons discussed before and for the average isotropic characteristics. The size dependence of the relative permittivity (ϵ) in dense BaTiO_3 ceramics has been well characterized for materials with $\text{GS} > \approx 0.5 \mu\text{m}$.^{3,7,10–12} The room-temperature permittivity has a pronounced maximum for a GS of $\approx 1 \mu\text{m}$ which was considered to be caused by the increase of the domain walls mobility at this particular grain size.¹⁰ Further reduction of GS leads to a decrease of permittivity. For really nanocrystalline ceramics there are scanty data available. This is mainly related to the difficulty to obtain fully dense materials with $\text{GS} < 0.5 \mu\text{m}$. In a recent study, Frey *et al.*¹¹ reported the dielectric data of dense BT ceramics with GS from 70 to 1700 nm fabricated by pseudoisostatic hotpressing in a multianvil press at a pressure of 8 GPa. The progressive suppression of the relative dielectric constant for GS below ≈ 500 nm was explained by a brick-wall model of the ceramic corresponding to a diphasic system consisting of ferroelectric grain cores of size-independent permittivity separated by a lower- ϵ grain-boundary region. In other words, the size effect in dense BaTiO_3 nanoceramics would be only apparent, coming from

a “dilution” effect due to a large number of nonferroelectric grain boundaries. However, the authors give no details on the crystal structure as well as on the tetragonal/cubic transition of their samples, i.e., on the possible existence of intrinsic size effects in addition to the apparent size effect induced by grain boundaries.

In this paper, the results of a systematic investigation of the size effect on tetragonal distortion, phase transitions, and dielectric properties of dense BT ceramics with GS of 50–1200 nm are reported and discussed. The main objective is to show the existence of an intrinsic size effect on the ferroelectric behavior of bulk nanocrystalline BaTiO_3 ceramics. Particular attention was devoted to the preparation of dense samples, because structure and dielectric properties of nanocrystalline BaTiO_3 can be significantly affected by porosity. First, grains partially surrounded by pores have increased possibility to accommodate the strain resulting from the paraelectric to ferroelectric transition. Second, gas/solid interfaces have a different energy in comparison to solid/solid interfaces (grain boundaries). Finally, since a porosity level $> 5\%$ generally leads to a strong depression of the apparent dielectric constant, a high density guarantees a meaningful comparison between different samples.

II. EXPERIMENT

Dense nanocrystalline BaTiO_3 ceramic samples (diameter: 1.2 cm; thickness: 0.1–0.2 cm) with GS in the range 50–300 nm were produced by spark plasma sintering (SPS). The ability of SPS in producing fully dense materials with fine and sometimes unique microstructure at relatively low temperatures in a time of a few minutes has been demonstrated for a wide variety of ceramics and ceramic composites.¹³ Very fine, undoped BaTiO_3 powders for the SPS process were obtained by a chemical aqueous method described elsewhere.¹⁴ The powders had a specific surface area of $\approx 30 \text{ m}^2/\text{g}$ and a particle size of 30–40 nm. The main impurity (as determined by inductively coupled plasma spectroscopy) contained in the powders was Na (≈ 400 ppm), while Sr was < 50 ppm. The Ba/Ti atomic ratio was controlled within 1 ± 0.01 for all the powders. The BaTiO_3 powder was loaded directly into a cylindrical graphite pressure die. The samples were heated up ($200^\circ\text{C}/\text{min}$) in a SPS equipment (Dr. Sinter 2050, Sumitomo Coal Mining Co., Tokyo, Japan) by allowing a pulsed direct current to pass through the pressure die, while an uniaxial pressure of 100 MPa was applied. Sintering was carried out in a vacuum. No sintering aids were added. The holding time at the sintering temperature ($800\text{--}1000^\circ\text{C}$) was 2–5 min. The samples were cooled at a rate of $400^\circ\text{C}/\text{min}$ with no pressure. The sintered ceramics were finally polished and then annealed in air for 1–10 h at a temperature of 700 or 800°C , depending on GS. This treatment should guarantee the relief of residual stresses and the elimination of excess oxygen vacancies possibly produced during SPS. Samples S50 and S100 were translucent.

The ceramic samples were characterized with different techniques. Microstructure was observed by scanning electron microscopy (SEM) and atomic force microscopy (AFM)

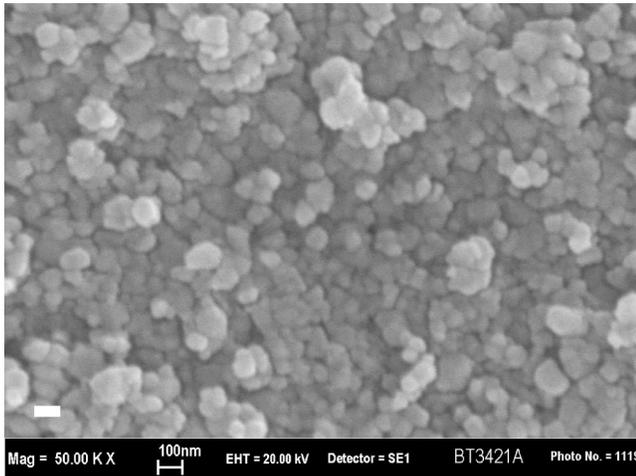


FIG. 1. Microstructure (SEM, after polishing and chemical etching) of a ceramic with average grain size of ≈ 50 nm. Bar: 100 nm.

on fracture surfaces as well as on polished surfaces after chemical etching. Phase composition, crystallite size, and crystal structure were investigated by x-ray diffraction (XRD) using the $\text{Co } K_\alpha$ radiation. Differential scanning calorimetry (DSC) measurements were performed in the range -20 – 180°C at a heating/cooling rate of $10^\circ\text{C}/\text{min}$. The heat of transition was obtained from the area of the DSC peaks. Permittivity measurements were carried out in the frequency range 10^2 – 10^6 Hz using an impedance analyzer (Solartron SI1260). Pd-Ag electrodes were applied on the upper and lower surfaces of the sintered disk after polishing obtaining a parallel-plate capacitor configuration. The measurements were performed in air in the range 40 – 180°C (heating/cooling rate of $0.5^\circ\text{C}/\text{min}$) with an applied voltage of 1 V.

III. RESULTS

The mean GS (mean intercept length measured by SEM) of the samples obtained by SPS was 282 (S300), 94 (S100), and 51 nm (S50). The microstructure of sample S50 is shown in Fig 1. The ceramic exhibits a grain size distribution: grains from ≈ 20 to ≈ 100 nm can be observed. The grain size distribution measured from the AFM topography is in reasonable agreement with the SEM results. A multidomain structure could be observed only on few larger grains (≈ 500 nm) of sample S300 after proper chemical etching of the polished surface, meaning that the grains in the nanocrystalline ceramics essentially consist of single domains. Imaging by piezoresponse force microscopy revealed no multidomain structures on sample S50.¹⁵ These results are in agreement with previous observations of the disappearance of multiple domain grains for a grain size of 300 – 500 nm.^{10,11} Coarser ceramics (S500, GS of 530 nm, and S1200, GS of 1200 nm) were obtained by conventional sintering in air of powders produced with the same method as those used for SPS. The relative density was $\geq 97\%$ (reference density: 6.02 g cm^{-3}) for all samples with the exception of S500(94%).

Secondary phases, if any, are below the XRD detection limit (≈ 1 wt. %). The crystallite size determined from the

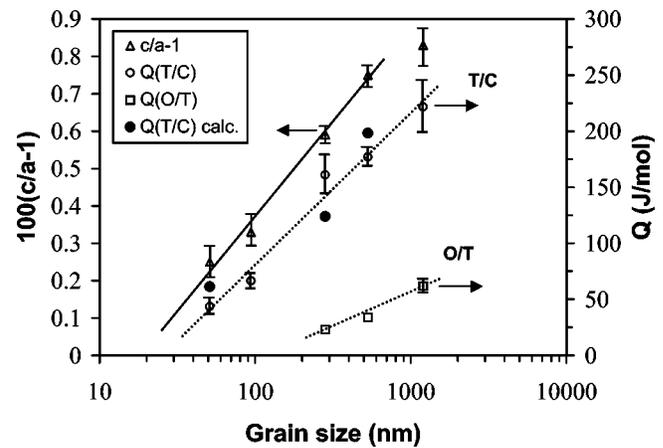


FIG. 2. Room temperature tetragonal deformation (Δ), heat of transition of the tetragonal to cubic (\circ) and of the orthorhombic to tetragonal (\square) transformations of BaTiO_3 as a function of grain size. The full circles (\bullet) represent the heat of transition calculated from Eq. (4).

broadening of the (111) and (222) peaks was 96 nm for sample S100 and 54 nm for sample S50, in good agreement with SEM results. Measurements of the crystallite size before and after postannealing of ceramics did not show any significant change, meaning that there was not appreciable grain growth during heat-treatment. The splitting of the XRD peaks characteristic of coarse-grained BaTiO_3 and related to the tetragonal deformation of the structure is less and less pronounced as the grain size decreases, i.e., the lattice becomes progressively less tetragonal. Splitting is no longer observed in S50 and S100 ceramics. However, the existence of a distorted lattice at room temperature is revealed by the pronounced broadening of most of the diffraction peaks in comparison to the hhh reflections, which are not subjected to splitting during the cubic to tetragonal transition. With increasing temperature this broadening effect gradually reduces and, above T_C , it disappears indicating a fully cubic structure. The cubic cell edge of S50 at 200°C was 4.013 \AA , in agreement with literature values reported for single crystals.⁶ The stability of the tetragonal modification of BaTiO_3 around room temperature in S50 and S100 was confirmed by a detailed study of the infrared and Raman activity in the range -190 – 300°C ,¹⁶ which also proved the existence of the orthorhombic and rhomboedral phases at lower temperature. Tetragonal lattice parameters were obtained by Rietveld refinement of the full XRD pattern, including all reflections from (100) to (400). The tetragonal distortion ($c/a-1$) decreases from 0.83% to 0.26% as the GS decreases from 1200 to 50 nm (Fig. 2). The value measured for the 50 nm sample is about $\frac{1}{4}$ of the reference value (1%) reported for single crystals and ceramics with $\text{GS} > 10 \mu\text{m}$.^{6,10} The lowering of c/a is the result of the decrease of c and the increase of a , likewise the behavior observed for isolated particles.³⁻⁵ Thus, the decrease of grain size produces an effect qualitatively similar to an increase of temperature,⁶ in the sense that both reduce the spontaneous strain and the stability of the ferroelectric phase.

The heat of transition (Q) corresponding to the tetragonal to cubic (T/C) and to the orthorhombic to tetragonal (O/T)

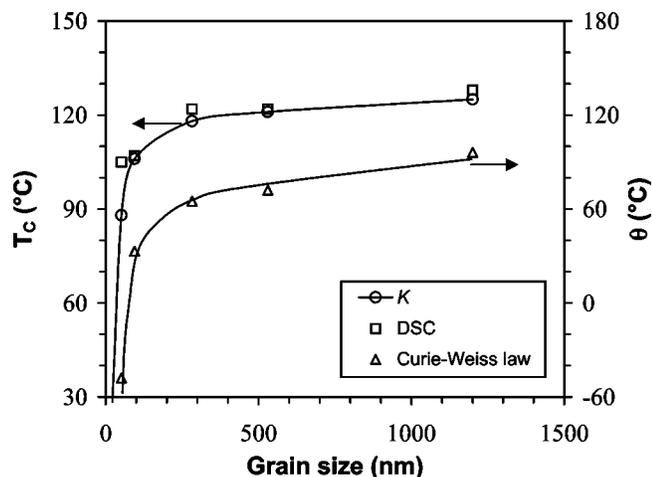


FIG. 3. Critical temperatures of BaTiO₃ ceramics as a function of grain size. Curie temperature (T_C) from: (○) dielectric measurements, (□) DSC measurements, (△) Curie-Weiss temperature (θ). The solid curves are a guide for the eyes.

transformations was measured. The results are shown in Fig. 2. Likewise the c/a ratio, the GS has a remarkable effect on Q . For the T/C transformation, Q of the samples with a GS of 50 nm (44 J/mol) is only 20% of the value measured for the 1200 nm ceramic, 220 J mol⁻¹. The value reported for single crystals is 210±20 J mol⁻¹.⁶ The temperature corresponding to the maximum of the DSC peak is gradually shifted to lower temperatures with decreasing grain size, from 127°C for the 1200 nm sample to 105°C for the 50 nm samples (Fig. 3). The latent heat of the O/T transition could be measured only for ceramics with GS ≥ 300 nm. The maximum of the differential thermal analysis peak lies at 14–18°C. For the finer ceramics, the thermal effect, if any, is below the instrumental detection limit (≈5–10 J mol⁻¹).

The relative dielectric constant and the dielectric losses ($\tan \delta$) of the nanocrystalline ceramics are reported in Fig. 4. The behavior of a coarser ceramic is shown for comparison.

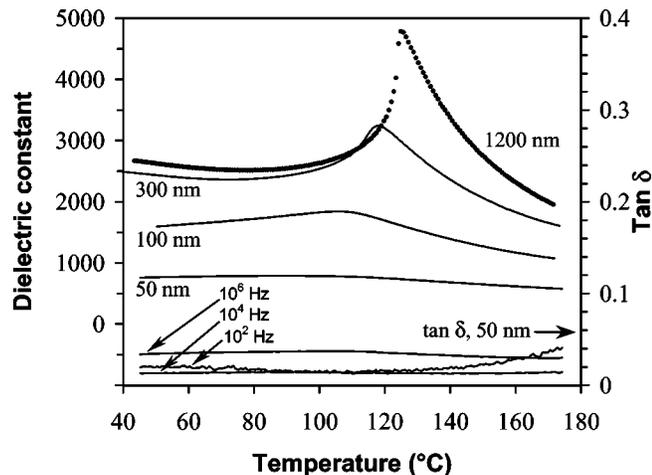


FIG. 4. Relative dielectric constant (ϵ) at 10⁴ Hz and loss tangent ($\tan \delta$) of BaTiO₃ ceramics as a function of temperature. $\tan \delta$ is reported for the 50 nm sample at three frequency values: 10², 10⁴, and 10⁶ Hz.

A dielectric anomaly is clearly observable for all samples, indicating a ferroelectric behavior. ϵ is strongly depressed for fine grained samples; at 70°C and 10⁴ Hz, ϵ is 2520 for S1200, 2200 for S300, 1680 for S100, and 780 for S50. These values are lower than those reported by Frey *et al.*¹¹ but comparable with the trend found by Arlt *et al.*¹⁰ The dielectric constant of nanocrystalline samples is remarkably less sensitive to temperature in contrast to coarse ceramics. The maximum variation for S50 in the range 40–170°C is <30% of the room temperature value, because the permittivity peak is remarkably broadened and rounded in comparison to coarse ceramics. The dielectric losses of the fine grained ceramics (50–300 nm) are rather small, <5% in the whole frequency range and comprised between 1% and 2% in the range 3 × 10³–3 × 10⁵ Hz. These figures give an indication of the dielectric quality of the samples. It is worth noting that the strong increase (about one order of magnitude) of $\tan \delta$ and the deviation from the Curie-Weiss behavior noticed at frequencies below 1 kHz in the as sintered samples were completely removed by the postannealing treatment. The losses of the S50 sample, selected as representative, are reported in Fig. 4. Despite the significant broadening of the permittivity peak, the position of ϵ maximum can still be considered as an indication of the ferroelectric/paraelectric transition temperature, T_C . The Curie temperature is progressively lowered with decreasing grain size, from 125(1200 nm) to 88°C(50 nm), as shown in Fig. 3 (10⁴ Hz). For a given grain size, T_C is almost unaffected by frequency, being the variations within 1–2°C.

In the paraelectric region, ϵ of all fine grained ceramics closely follows the Curie-Weiss law, $\epsilon = C/(T - \theta)$, for $T > 125^\circ\text{C}$, as proved by a series of parallel lines obtained if $1/\epsilon$ is plotted against temperature. The Curie-Weiss temperature (θ) gradually decreases with decreasing grain size: from 96°C(1200 nm) to -48°C(50 nm), as shown in Fig. 3 (10⁴ Hz). The Curie constant (C) is nearly the same, (1.5–1.6) × 10⁵ K, for all samples with GS ≥ 100 nm. For the 50 nm sample, C is lower: 1.3 × 10⁵ K. θ and C are practically independent of frequency in the range 3 × 10³ to 10⁶ Hz. At lower frequencies a moderate increase of C (up to 1.7 × 10⁵) and a decrease of θ (down to -76°C for S50) is observed.

IV. DISCUSSION

As the surface to volume ratio of the individual grains in a ceramic increases with decreasing grain size, the observed variations of tetragonal strain, heat of transition, and Curie temperature can be ascribed to an intrinsic size effect. However, the internal stresses originated in the ceramic when cooled through the Curie point might also play an effect. The transition from the cubic to the tetragonal structure of barium titanate is accompanied by a spontaneous strain and a small volume increase. In a perfect, single domain crystal, if the surfaces are not constrained, the full strain can be developed without stress generation. If the surfaces of the crystal are constrained, like a grain in a dense ceramic, the change of dimensions and the internal stresses can be minimized by twinning (formation of 90° domain patterns). However, in

fine grained (<500 nm) BaTiO₃, 90° twins are absent and the grains essentially consist of single domains. Consequently, the resulting stresses cannot be longer relieved by the twinning process. The stress distribution in an individual grain will in general be very complex, depending on the orientation of the neighboring grains. In average, however, it is expected that the stresses are of compressive type because of the volume increase, thus tending to suppress the spontaneous deformation and forcing the grains back toward the cubic state. This effect can be assimilated to the application of an hydrostatic pressure, as considered by Mitoseriu *et al.*¹⁷ The magnitude of the internal stresses can be roughly evaluated using the elastic properties of BaTiO₃¹⁸ and assuming a volume change at T_C of 0.062 Å³.⁶ The result is a stress of the order of 0.06 GPa. Malinowski *et al.*¹⁹ have measured the lattice parameter of BaTiO₃ as a function of hydrostatic pressure at room temperature. They found a cubic lattice for pressures higher than 2.1 GPa, in agreement with the dielectric measurements of Samara.²⁰

According to their results, for an applied pressure of 0.1 GPa, the decrease of the tetragonal strain is only ≈5% of the spontaneous strain at ambient pressure. This is a small variation in comparison to the reduction of tetragonality observed for the present nanocrystalline ceramics.

Although the earlier considerations are rather approximate, they reasonably indicate a minor role of the residual stresses resulting from the tetragonal deformation on the behavior of the fine grained ceramics. Thus, the existence of an intrinsic size effect in nanocrystalline barium titanate ceramics is strongly supported. Extrapolation of the experimental trends (Fig. 2) suggests a critical size in the range 10–30 nm for disappearance of ferroelectricity in dense BaTiO₃ ceramics, in agreement with theoretical studies.¹ Using some results of the LGD thermodynamic theory of ferroelectrics it is possible to show, at least qualitatively, how the variation of tetragonality induced by the intrinsic grain size effect can influence the ferroelectric properties in this system. The Gibbs free energy G of the ferroelectric phase is usually written as a power series of the polarization P as^{6,21}

$$G = G_0 + \frac{1}{2}\beta(T - \theta)P^2 + \frac{1}{4}\gamma P^4 + \frac{1}{6}\delta P^6, \quad (1)$$

where β , γ , and δ are phenomenological coefficients and θ is the Curie-Weiss temperature. The parameter β is directly related to $1/C$. On the basis of the present results, β is virtually independent of GS (at least for GS > 50 nm). Because of the electrostrictive coupling between lattice strain and polarization in BaTiO₃, the deformation of the lattice along the a and c tetragonal directions is proportional to the square of the spontaneous polarization, P_s .^{6,21} Therefore, the tetragonal distortion η can be written, with good approximation (error <0.3%), as

$$\eta = \frac{c}{a} - 1 = kP_s^2, \quad (2)$$

where k is the difference $Q_{11} - Q_{12}$ of the electrostrictive coefficients. Irrespective of the cause (variation of temperature, external stress, grain size, etc.), a change in lattice deformation determines a variation of polarization. As a result, the

decrease of P_s with decreasing grain size observed by Frey *et al.*¹¹ and by others²² can be ascribed to the reduction of tetragonality. The heat of transition at T_C is related to P_s by the relationship⁶

$$\frac{Q}{T_C} = \frac{1}{2}\beta P_s^2 + \frac{1}{4}AP_s^4, \quad (3)$$

where A is the derivative ($\partial\gamma/\partial T$). Insertion of Eq. (2) in Eq. (3) gives

$$\frac{Q}{T_C} = \frac{\beta}{2k}\eta + \frac{A}{4k^2}\eta^2. \quad (4)$$

The lattice deformation of BaTiO₃ is temperature dependent.⁶ Therefore, the tetragonality of samples S500, S300, and S50 was measured also 10°C below T_C . The resulting values were introduced in Eq. (4) and the heat of transition calculated using $\beta = 7.5 \times 10^5$ J mC⁻² K⁻¹ and literature values²³ for k (0.16 m⁴/C²) and A (1.5×10^7 J m⁵C⁻⁴ K⁻¹). The results are shown in Fig. 2 as full circles. The agreement with experimental values is reasonable and supports the idea of a direct influence of GS on the ferro/para transition. A size dependence of A can not be excluded; nevertheless the contribution of the second term on the right hand side of Eq. (4) is relatively small (10–25%). The combination of a well know result of the LGD theory^{6,21} and Eq. (2) leads, near T_C , to

$$P_s^2 = -B \frac{\gamma}{\delta} = \frac{\eta}{k}, \quad (5)$$

where B is a numeric constant of the order of unit. It results that the ratio γ/δ is affected by GS and, near T_C , it displays the same GS dependence as η . Equations (4) and (5), have a very general meaning because they show the interplay among tetragonal strain, ferroelectric to paraelectric transition, and spontaneous polarization. A change of grain size, likewise a change of temperature or an external stress, produces a variation of the tetragonal strain and a modification of the spontaneous polarization and, consequently, affects the phase transition and the related ferroelectric properties.

The effect of GS on T_C and on the dielectric constant is not easy to be correlated to the tetragonality change. In contrast to Frey *et al.*,¹¹ an evident lowering of T_C with decreasing GS has been observed in the present samples, even from the calorimetric measurements. The study of the Raman activity¹⁶ also supports the shift of the Curie point at lower temperatures (95°C for S50) and shows, in addition, that all the phase transitions becomes more diffuse with decreasing grain size. The shifting of the phase transition temperature as well as the broadening, lowering, and rounding of the permittivity anomaly described for the present nanocrystalline ceramics are characteristic features expected for intrinsic size effects.²⁴ A decrease of T_C is reported by most papers,^{3,4,8} including also some recent studies carried out on fine grained dense ceramics obtained from high-purity commercial hydrothermal powders.²² A decrease of T_C with particle size is predicted also by modified forms of the LGD theory where surface and gradient effects are included.¹ From the LGD approach it turns out that the dielectric constant (c direction)

of the ferroelectric phase near T_C is directly related^{6,21} to the ratio γ^2/δ . Therefore, an intrinsic effect of GS on the dielectric properties of BaTiO₃ ceramics is qualitatively expected from Eq. (5). A more quantitative interpretation of the size dependence of dielectric properties in the ferroelectric regime is not an easy task as it would require an expression for the effective permittivity of the ceramics. Such an expression should account for the temperature and size dependence of the coefficients γ and δ and for the anisotropy of permittivity in BaTiO₃ ($\epsilon_{11}=\epsilon_{22}\neq\epsilon_{33}$). However, the evaluation of γ and δ separately cannot be carried out from the present data and requires direct measurement of other properties, like spontaneous polarization. The grain size distribution of the ceramics can contribute to the rounding and broadening of the permittivity anomaly because, according to our results, grains with different size have different Curie temperatures. Consequently, the observed permittivity will correspond to the superposition of all the contributions and to the directional average of the dielectric response. Furthermore, the presence of a continuous low-permittivity nonferroelectric grain boundary layer (“dead” layer) can contribute to the depression of permittivity with decreasing grain size, as suggested in Ref. 11. According to the series dielectric mixing rule, even a dead layer of ≈ 1 nm can significantly reduce the apparent permittivity when its relative dielectric constant is much smaller than that of the ferroelectric phase and GS is $< 200\text{--}300$ nm.¹¹

Although the calculation of the effective permittivity of a ferroelectric nanocrystalline ceramic is beyond the scope of this paper, some insight into existence of an apparent size effect related to the grain boundaries can be gained from the observed strong decrease of θ with decreasing GS (see Fig. 3). Indeed, even if a shift of θ with decreasing GS is imposed by the condition $T_C > \theta$ (the T/C transition of BaTiO₃ is a first order transition), a drop of θ of $\approx 150^\circ\text{C}$ is hardly justified by the intrinsic size effect alone. Recently, an expression of the effective permittivity as a function of grain size for a polycrystalline material composed of ferroelectric grains separated by a continuous low-permittivity layer has been obtained in the paraelectric regime by Emelianov *et al.*²⁵ The solution is based on the effective medium approximation and results in the renormalization of the Curie-Weiss law. The apparent Curie constant C^* and the apparent Curie-Weiss temperature θ^* of the ceramic can be calculated as a function of the grain size g and of the thickness d of the grain boundary layer as

$$C^* = C \frac{[g^3 + 2(g - 2d)^3]}{[2g^3 + (g - 2d)^3]}, \quad (6)$$

$$\theta^* = \theta - \frac{C}{\epsilon_d} \frac{[g^3 - (g - 2d)^3]}{[2g^3 + (g - 2d)^3]}, \quad (7)$$

where C and θ are the Curie constant and the Curie-Weiss temperature of the ferroelectric region, respectively, and ϵ_d is the relative dielectric constant of the grain boundary layer. It is worth noting that C^* is independent of ϵ_d . The experimental trends can be reasonably reproduced by setting $\theta = 110^\circ\text{C}$, $C = 1.53 \times 10^5$ K, $\epsilon_d = 70\text{--}120$, and $d = 2\text{--}3$ nm. An

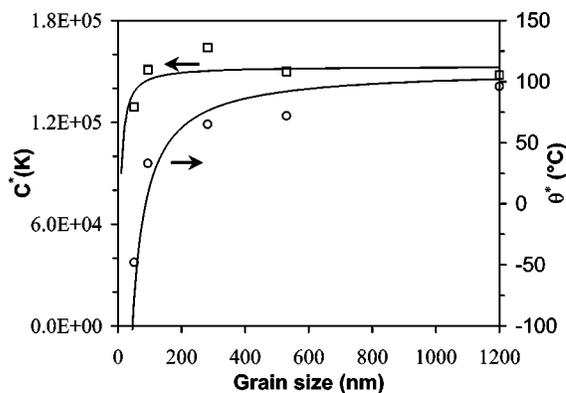


FIG. 5. Apparent Curie constant (C^*) and apparent Curie-Weiss temperature (θ^*) of BaTiO₃ ceramics as a function of grain size. (□) Curie constant. (○) Curie-Weiss temperature. Solid lines: computed from Eqs. (6) and (7) using the model of Emelianov *et al.* (in Ref. 25). The involved parameters were taken to be $\theta = 110^\circ\text{C}$, $C = 1.53 \times 10^5$ K, $\epsilon_d = 80$, and $d = 2.5$ nm.

example is shown in Fig. 5. Although the model does not exactly reproduce all the observed features, it strongly supports an extrinsic effect of the grain boundaries on the dielectric properties. A good fit of the data reported by Frey *et al.*¹¹ can be obtained by taking $\epsilon_d = 100$, and $d = 0.7\text{--}0.8$ nm. Therefore, the low permittivity grain boundary layer in the present samples is at least three times thicker than in the ceramics investigated in Ref. 11. The volume fraction of the grain boundary layer in the 50 nm ceramic corresponds to 20%–30% of the whole sample volume. Such a large volume cannot be accounted for by the presence of a secondary phase located at grain boundaries, because this is incompatible with the level of impurities and the maximum deviation from stoichiometry (± 1 mol%) of the present samples. Rather, it should be admitted the existence of a paraelectric or quasiparaelectric shell on the surface of the BaTiO₃ grains near the grain boundary. This interpretation is reasonable and coherent with the grain size independent thickness of the dead layer assumed in Eqs. (6) and (7). However, the different value of d found for the samples of Frey *et al.*¹¹ indicates a possible stabilizing/destabilizing effect of the grain boundary layer related to segregation of specific impurities or defects. The existence of a layer with reduced polarization at the surface of ferroelectric particles is predicted by theoretical model as a result of the depolarization field.¹ It should be also noted that, for the finest ceramics, the grains with a size below the critical value corresponding to suppression of ferroelectricity can contribute to the dead layer.

Recently, measurements of the local switching properties of dense BaTiO₃ nanocrystalline ceramics were performed by means of piezoresponse force microscopy.¹⁵ The application of electric fields induced stable domain structures and typical piezoelectric hysteresis loops were recorded. Changes in the polarization state far away from the probed area and related to transgranular dipole interaction, as reported for coarser ceramics,²⁶ were observed in many experiments. This is an indirect evidence that the presence of a grain boundary dead layer does not hamper the long-range interaction of

domains separated by grain boundaries. As a result, the boundary conditions of the grains in a nanocrystalline ceramic are significantly different from those experienced by isolated crystallites embedded in a low-permittivity matrix, like the situation encountered in BaTiO₃ glass ceramics.⁸ The nature and the properties of the interfaces in ceramics are sometimes very different than expected. For example, in the case of ceramics of the incipient ferroelectric SrTiO₃, there are convincing evidences of the existence of frozen dipole moments at the grain boundaries which induce a polar phase in the grain bulk at low temperature.²⁷ High-resolution transmission electron microscopy studies have shown that there are two kinds of interfaces in SrTiO₃ with different properties.²⁸ “Special” grain boundaries have a well defined structure, contain oxygen vacancies and show a substantial lattice relaxation near the interface. On the contrary, “random” grain boundaries reveal the existence of an amorphous or disordered film with a thickness of the order of 1 nm. With respect to the earlier considerations, the interpretation of grain boundaries and interfaces simply as dead layers is, maybe, too restrictive and probably needs to be reconsidered.

V. CONCLUSIONS

The results of a systematic investigation on crystal structure, phase transitions, and permittivity of dense BaTiO₃ ceramics with grain size in the range 50–1200 nm give evidence of the existence of size effects. With decreasing grain size, the crystal structure at room temperature becomes pro-

gressively less tetragonal and the heat of the tetragonal (ferroelectric) to cubic (paraelectric) transition is gradually reduced. The Curie temperature, either obtained from permittivity measurements or from calorimetric measurements, is shifted to lower values. The effect of grain size on the ferroelectric properties can be qualitatively described on the basis of the corresponding variation of the tetragonal strain in the framework of the Landau-Ginsburg-Devonshire theory. A change of grain size, likewise a change of temperature or an external stress, produces a variation of the tetragonal strain and a modification of the spontaneous polarization and, consequently, affects the phase transitions and the ferroelectric properties. The critical grain size corresponding to suppression of ferroelectricity is estimated to be 10–30 nm. In addition to the intrinsic size effect, some properties of nanocrystalline ferroelectrics can be also affected by the extrinsic effect of grain boundaries. In particular, the permittivity of BaTiO₃ ceramics with grain size below 500 nm seems quite sensitive to the presence of a low permittivity, nonferroelectric grain boundary layer. The strong decrease of the Curie-Weiss temperature with decreasing grain size supports the presence of such a dead layer. As a result, the effective permittivity will be determined by the combination of the intrinsic size effect and of the “dilution” effect due to the nonferroelectric grain boundaries. As a general conclusion, the measurement of the dielectric properties alone can not provide a conclusive evidence about the origin of the size effects in ceramics.

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