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Dielectric properties of fine-grained barium titanate ceramics

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Dielectric properties, lattice- and microstructure of ceramic $BaTiO_3$ showing grain sizes of 0.3–100 μm were studied. At grain sizes $< 10\,\mu$m the width of ferroelectric 90° domains decreases proportionally to the square root of the grain diameter. The decreasing width of the domains can be theoretically explained by the equilibrium of elastic field energy and domain wall energy. The smaller the grains, the more the dielectric and the elastic constants are determined by the contribution of 90° domain walls. The permittivity below the Curie point shows a pronounced maximum $\epsilon_r \approx 5000$ at grain sizes 0.8–1 μm. At grain sizes $< 0.7\,\mu$m the permittivity strongly decreases and the lattice gradually changes from tetragonal to pseudocubic.

I. INTRODUCTION

Since the discovery of the high permittivity ϵ_r of ferroelectric barium titanate in 1943 ceramic materials based on this compound are utilized in the manufacture of ceramic capacitors.

The permittivity of ceramic $BaTiO_3$ strongly depends on the grain size a. Coarse-grained ceramics of pure $BaTiO_3$ ($a = 20$–$50\,\mu$m) show $\epsilon_r \approx 1500$–2000 at room temperature. Many years ago, several investigators[1–3] observed higher values $\epsilon_r \approx 3500$–4000 in dense, fine-grained $BaTiO_3$ ceramics with $a \approx 1\,\mu$m. In hot-pressed $BaTiO_3$ with $a \approx 1\,\mu$m, Brandmayr *et al.*[4] found an ϵ_r value of ≈ 6000 at room temperature. At even smaller grain sizes, however, the same authors observed a strong decrease of ϵ_r. It was concluded that the room-temperature permittivity of $BaTiO_3$ obviously has a maximum at a grain size of about 1 μm.

The permittivity of $BaTiO_3$ single crystals is strongly anisotropic with $\epsilon_c = 400$ along the tetragonal c axis and $\epsilon_a = \epsilon_b = 4000$ perpendicular to the c axis[5] at room temperature. For ceramic $BaTiO_3$ an average of $\epsilon_r \approx 950$–1200 was calculated.[6–9]

Up to now several authors ascribed the higher values of $\epsilon_r \approx 1500$–2000 observed in ceramic $BaTiO_3$ to the effect of internal stress in the grains.[2,10–12] These authors suggest that the width of ferroelectric 90° domains remains constant at about 1 μm. Thus no ferroelectric domains can exist in fine-grained $BaTiO_3$ with $a \leqslant 1\,\mu$m. In that case the tetragonal distortion of the perovskite unit cell below the Curie point then can no longer be compensated by formation of 90° domains and strong internal stress should appear in the microstructure of such fine-grained $BaTiO_3$. Using the Devonshire theory, Buessem *et al.*[10,11] and recently Bell *et al.*[12] showed that internal stress (uniaxial as well as biaxial) should give rise to an increase of ϵ_r in fine-grained $BaTiO_3$ ceramics. In their models these authors presumed the existence of single-domain grains, i.e., the absence of 90° domain walls in $BaTiO_3$ ceramics with $a \leqslant 1\,\mu$m. A decreased frequency of 90° twinning was observed by Yamaji *et al.*[13,14] in fine-grained Dy-doped (0.4–1.2 at. %) $BaTiO_3$. These authors studied replicas of etched surfaces in TEM. At the average grain size of 1.25 μm only 10% of the grains showed 90° twins.

Martirena and Burfoot[15] tried to explain the high permittivity of fine-grained $BaTiO_3$ by means of a distribution model of the dielectric Curie peak using Gauss distributions of the ferroelectric Curie point T_c. The $\epsilon_r(T)$ curves calculated by these authors, however, do not agree with the experimental curves. Furthermore, the high values of $\epsilon_r \approx 5000$ at temperatures between 25 and 100 °C cannot be explained using such models.

The authors[10–12,15] suggest in their models that the width of 90° domains in $BaTiO_3$ not become smaller than 1 μm. Thus the existence of ferroelectric 90° twins and their contribution to the permittivity of fine-grained $BaTiO_3$ was not considered in the models of these authors.

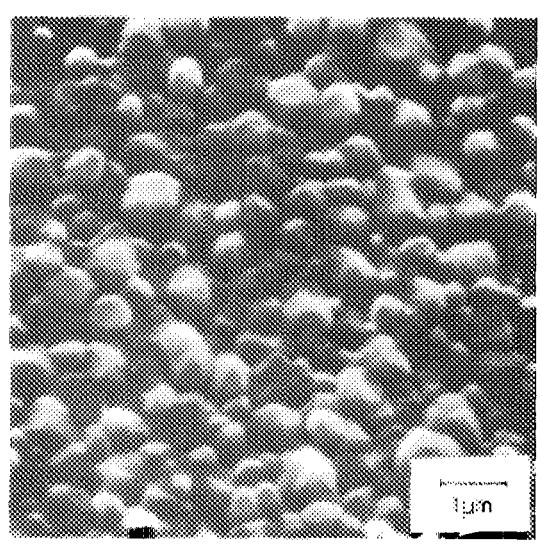

FIG. 1. Thermal etching of fine-grained $BaTiO_3$, 1 h in air at 1100 °C; $BaTiO_3$ hot pressed at 1130 °C.

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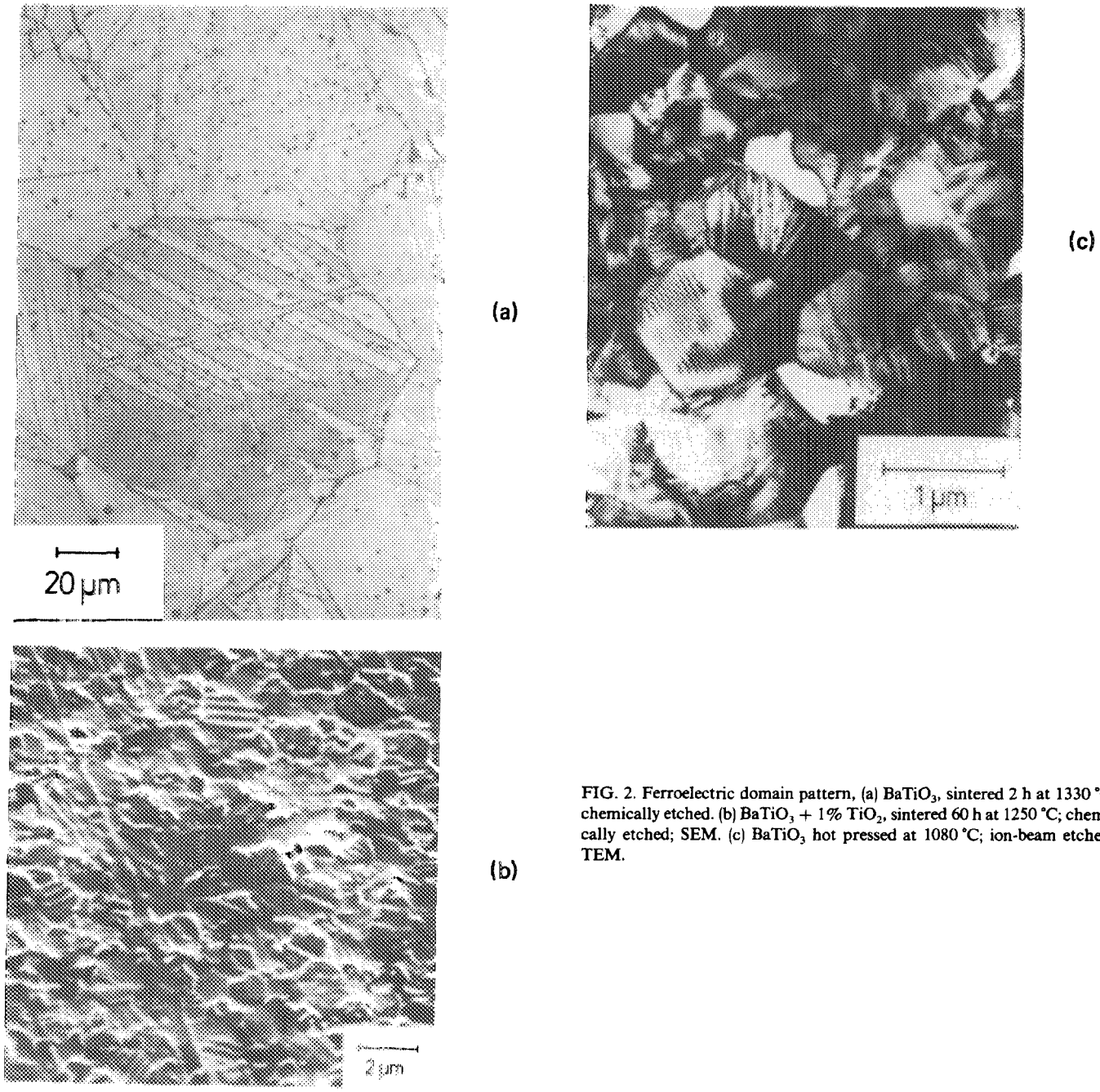

FIG. 2. Ferroelectric domain pattern, (a) $BaTiO_3$, sintered 2 h at 1330 °C; chemically etched. (b) $BaTiO_3$ + 1% TiO_2, sintered 60 h at 1250 °C; chemically etched; SEM. (c) $BaTiO_3$ hot pressed at 1080 °C; ion-beam etched; TEM.

This paper presents a systematic experimental and theoretical study of the sizes of 90° domains as a function of the average grain diameter of ceramic $BaTiO_3$. The measured dielectric properties are discussed alternatively in the light of a new model on the contribution of 90° domain walls to the permittivity of fine-grained $BaTiO_3$ ceramics.

II. EXPERIMENTS

A. Preparation and sintering of the $BaTiO_3$ samples

The $BaTiO_3$ used for preparing very dense ceramics in the grain size range 0.7–1.2 μm was a highly pure material (HPB-Lot 579, TAM Corporation, Niagara Falls). The impurity level of this material (SiO_2, Al_2O_3, Fe_2O_3, Cl, Na_2O) was determined in total to be less than 250 wt. ppm. The Ba/Ti atomic ratio was determined by means of x-ray fluorescence (XFA) to be Ba/Ti = 1:1.006 $\pm$ 0.0015. For preparing dense ceramics of 0.3–0.5 μm grain size, barium-titanyl-oxalate was prepared and calcined at 1000 °C to $BaTiO_3$. The main impurity of this powder was 0.05 wt. % Al_2O_3 wear of the alumina milling balls. The atomic ratio of this powder was Ba/Ti = 1:1.004 $\pm$ 0.0015.

The $BaTiO_3$ powders were cold isostatically pressed without binder at 2 GPa and thereafter hot pressed during 15–60 min in air at 1080–1120 °C at uniaxial pressures of about 0.1 GPa. The highly dense ceramics (0.1% porosity) were then cut and lapped to discs of 5 mm diameter and 0.2–0.5 mm thickness. For electrical measurements thin CrNi/Au electrodes were evaporated.

Coarse-grained ceramics of 10–50 μm average grain size were produced by conventional sintering of $BaTiO_3$ (HBP) in air at temperatures > 1330 °C. $BaTiO_3$ ceramics showing grain sizes in the range 1–7 μm could only be prepared from

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mixed oxide prepared powders with an atomic ratio of Ti/Ba≈0.998. These materials were brought to high densities by means of hot isostatic pressing (HIP) in nitrogen after sintering.

Using various annealing procedures at temperatures between 1150 and 1450 °C in air the average grain sizes of the $BaTiO_3$ ceramics prepared covered the range 0.3–100 μm.

B. Determination of the average grain size

The average grain size was determined on thermally etched ceramics using the line intercept method. For thermal etching we annealed the hot-pressed samples at 1100 °C and the normally sintered samples at 1200 °C over 1 h in air. Figure 1 shows the scanning electron microscope (SEM) photograph of a thermally etched, fine-grained $BaTiO_3$ ceramic.

C. Determination of the domain width

The domain width, i.e., the average distance between single 90° domain walls, could easily be determined in coarse-grained materials using the light microscope after chemical etching [Fig. 2(a)]. In fine-grained materials showing grain sizes of about 1 μm the domains are only visible in the SEM after chemical etching [Fig. 2(b)]. Ferroelectric domains in ceramics of even smaller grain size were studied in the transmission electron microscope (TEM) [Fig. 2(c)]. For the TEM investigation the samples were thinned to about 0.05 μm using ion-beam etching.

Since the 90° domain walls cut the surface of the samples under various angles $\neq 90°$, the widths of the domains determined show a strong scatter. The true width of the domains is therefore always smaller or at most equal to the experimentally determined widths. Furthermore, in the thin TEM foils the grains are not fully clamped, which may also influence to some extent the measured domain widths.

D. Dielectric measurements, x-ray investigations

The dielectric properties of the ceramics were determined in an automatic capacitance bridge at 1 kHz and 4 V/mm during cooling the samples from 200 to − 100 °C with 3 °C/min.

The lattice structure of the samples was studied in a hot-stage x-ray diffractometer using the (400)/(004) and (222) reflections. Crystallographic surface textures were largely avoided by carefully polishing the samples using Syton.

E. Elastic measurements

The Young's modulus of the $BaTiO_3$ ceramics was determined from the sound velocity on planparallel tiles using a pulse-echo delay line transducer at 15 MHz.

III. RESULTS

A. Dielectric temperature curves

The dielectric temperature curves (Fig. 3) show clearly the grain size dependence of the permittivity, as described by the authors.[1–4] The highest values of $\epsilon_r(T)$ at $T < T_C$ are in

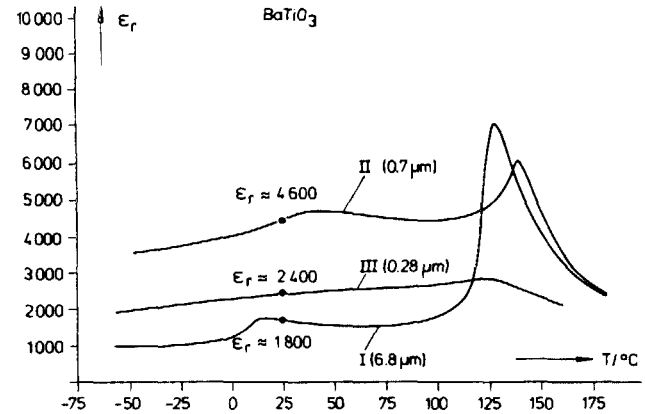

FIG. 3. Dielectric constant vs temperature of $BaTiO_3$ showing various grain sizes.

fact observed at grain sizes of 0.7–1 μm. At even smaller grain sizes the dielectric maximum at the Curie point T_C broadens and the $\epsilon_r(T)$ values decrease. This observed decrease of $\epsilon_r(T)$ is contradictory to the statements of Martirena and Burfoot[15] who predict a strong increase of $\epsilon_r(T)$ when the dielectric peak is smeared out. In contrast to the results observed on pure $BaTiO_3$ by Kinoshita and Yamaji[16] we never found similar high and sharp Curie peaks in hot-pressed samples of pure fine-grained $BaTiO_3$. Unfortunately, these authors give in Ref. 16 very few preparational details. The permittivity values measured at 25 °C and 70 °C (Fig. 4) show a maximum at grain sizes $d = 0.7$–$1\,\mu$m. Above 10–20 μm the permittivity obviously remains at a constant value of $\epsilon_r \approx 1700$. The observed scatter is probably caused by preparation parameters.

B. The width of 90° domains as a function of the mean grain diameter

The evaluation of the width of the 90° domains reveals a clear dependence on the grain size. From Fig. 5 can be seen that the width becomes much smaller than the 1 μm stated before by several authors[2,10–12] We observe in fine-grained

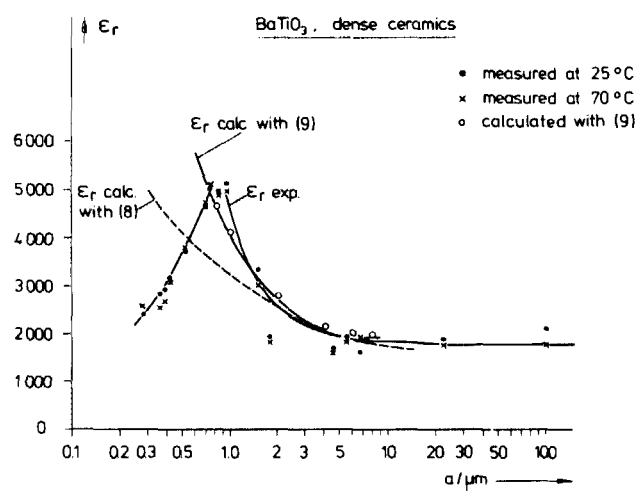

FIG. 4. Dielectric constants of $BaTiO_3$, measured at 25 and 70 °C, plotted vs the average grain diameter.

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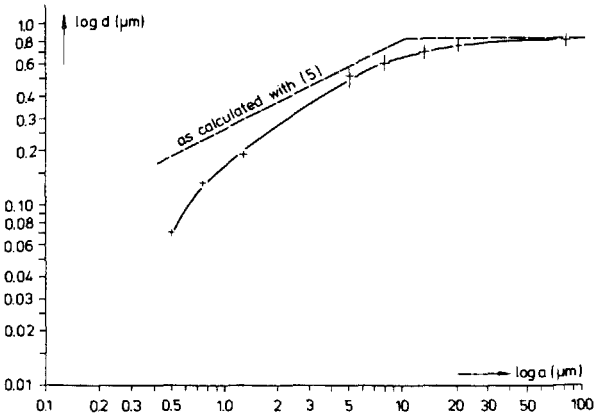

FIG. 5. Average width of 90° domains of $BaTiO_3$ in dependence on the average grain diameter, as observed in various domain patterns; double logarithmic plot.

$BaTiO_3$ ceramics with $a \approx 0.5\ \mu m$ a domain width of $d \approx 0.1\ \mu m$. The results of the present work are contradictory to those of Yamaji *et al.*[13,14] and of the authors.[2,10–12] A possible explanation for the lower frequency of 90° twins in the materials of Yamaji *et al.* is the content of 0.6 at. %Dy. Dy is considered a typical donor dope which is compensated in oxidizing atmosphere (sintering in O_2) by metal vacancies. It is well known that metal vacancies have a strong influence on the mobility and stability of ferroelectric domains in $BaTiO_3$.[17] Thus the $BaTiO_3$ in this work and the Dy-doped $BaTiO_3$ of Yamaji *et al.* are not quite comparable. The much higher frequency of 90° twins observed in our SEM micrographs [Fig. 2(b)] of $BaTiO_3$ with $\approx 1\ \mu m$ average grain size is a clear experimental fact. The $BaTiO_3$ of Fig. 2(b) was sintered at 1260 °C (with 1% TiO_2 as a grain growth inhibitor) and surface etched. Chemical etching of 90° twins in fine-grained ceramics generally provides problems. The usual agency (1–2% solution of HF + NHO_3 or HCl) etches the grain boundaries much more intensively than the domains. Thus the small grains ($\approx 1\ \mu m$) are often completely eliminated from the surface before the 90° twins begin to etch. In the thin TEM foils, on the other hand, we cannot principally exclude any artifacts caused by ion-beam etching which give rise to enhanced frequency of 90° twins.

Extrapolating in a semilogarithmic plot d vs $\log a$ to smaller grain sizes we can expect the 90° walls to vanish at grain diameters $a < 0.4\ \mu m$. At grain sizes $a \approx 10\ \mu m$, the width is $d \approx 0.7$–$0.8\ \mu m$. The domain width remains essentially constant at grain sizes larger than $10\ \mu m$. At $a > 10\ \mu m$, Arlt and Sako[19] observed in $BaTiO_3$ the appearance of a novel type of ferroelectric domain walls being a combination of 90° and 180° walls. Thus the simple correlation of domain width and grain size seems to end at grain sizes of about 10 μm.

In the range $1 < a < 10\ \mu m$ the decrease of the domain width can be roughly expressed by the correlation: $d \sim \sqrt{a}$, as shown in Sec. IV. According to the decreasing width, the area of the 90° domain walls per volume strongly increases in fine-grained $BaTiO_3$. The observed strong increase of ϵ_r in fine-grained $BaTiO_3$ can be therefore interpreted in terms of the increasing contribution of domain walls to the permittivity.

Arlt and Peusens[7] obtained in coarse-grained $BaTiO_3$ $\epsilon_r \approx 1700$ of which the volume contribution is $\epsilon_{r,vol} \approx 1000$ and the domain wall contribution is $\epsilon_{r,dom} \approx 700$. The permittivity of $BaTiO_3$ ceramics can be regarded as the sum of a volume contribution which is based on the single-crystal dielectric constants and of the contribution of the ferroelectric domain walls moving in the electric field.

$$\epsilon_r(T) = \epsilon_{r,vol}(T) + \epsilon_{r,dom}(T).$$

If ferroelectric domains are no longer present above the Curie point the dielectric behavior of coarse- and fine-grained $BaTiO_3$ becomes more or less equivalent. At rather small grain sizes, $a \lesssim 0.5\ \mu m$, however, the dielectric Curie maximum is smeared out more and more. At grain sizes below 0.7 μm an increasing number of grains no longer shows the 90° twins in TEM. One possible explanation is the presence of internal stress in the material[20] which shifts the Curie point[21,22] and gives rise to phase changes. In accordance to the Devonshire calculations of Bell *et al.*[12] we observe in hot-pressed $BaTiO_3$ of 0.7 μm average grain size an increased transition temperature orthorhombic/tetragonal (Fig. 3).

C. The lattice structure at grain sizes below 0.7 μm

The surprising decrease of ϵ_r observed at grain sizes below 0.7 μm obviously correlates to structural changes of the $BaTiO_3$. At grain sizes $a > 1.5\ \mu m$ we observe a constant ratio of the lattice parameters $(c/a - 1) = 1.02\%$ (Fig. 6). At $a < 1\ \mu m$ the tetragonal distortion of the $BaTiO_3$ unit cell decreases at room temperature to $(c/a - 1) < 1\%$. Moreover, a change from the tetragonal to a pseudocubic structure gradually takes place (Fig. 7). We thus have at room temperature the coexistence of different ferroelectric phases, just as recently observed in the mixed crystal series $BaTiO_3$-$BaZrO_3$.[22] At $a = 0.84\ \mu m$ a third pseudocubic reflection appears, [cf. Fig. 7(b)] lying between the tetragonal (400)/(004) reflections [cf. Fig. 7(a)]. This "pseudocubic" reflection can be most probably ascribed to the orthorhombic phase, normally existing at temperatures below 10 °C. Also the dielectric temperature curves (Fig. 3) show that in fine-grained hot-pressed materials the transition temperature of the or-

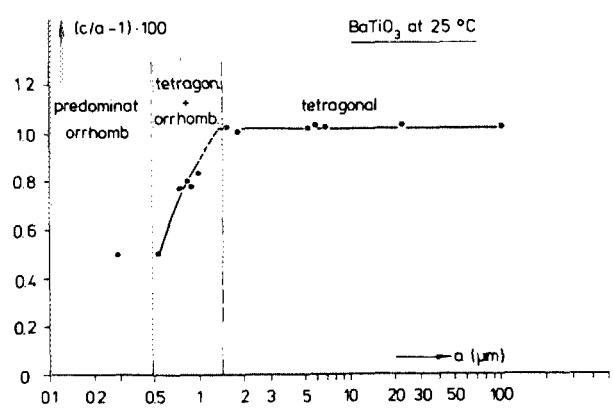

FIG. 6. Ratio of the lattice constants $(c/a - 1)\%$ of tetragonal $BaTiO_3$ ceramics in dependence on the average grain diameter.

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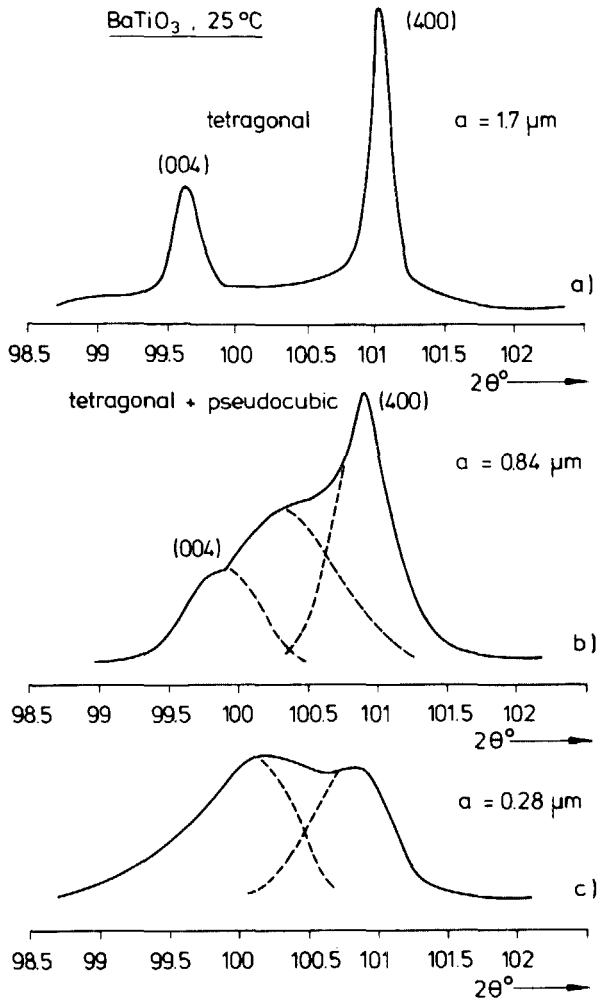

FIG. 7. Deformation of the tetragonal (400)/(004) x-ray diffraction peaks (Cu-$K\alpha$rad.) of $BaTiO_3$ at various grain sizes (α_2 suppressed).

thorhombic to the tetragonal phase is shifted to about 25 °C. The sole existence of the orthorhombic phase showing the triple reflection (400), (040), (004) (which should be equal in intensity) can be excluded with regard to the measured intensity ratios. At $a = 0.28\,\mu$m [cf. Fig. 7(c)] only two reflections are observed which cannot be ascribed to any of the known ferroelectric phases of $BaTiO_3$.

The ferroelectric domain structure of such fine-grained $BaTiO_3$ can be throughout different from that of normal tetragonal $BaTiO_3$. Using electron microdiffraction we found in small particles of $BaTiO_3$ ferroelectric domains of the rhombohedral phase showing 71° walls instead of the "normal" 90° walls.[23] From this we may conclude that the dielectric properties of fine-grained $BaTiO_3$ are unlike the "normal" tetragonal $BaTiO_3$.

D. Elastic properties

Just as in the case of the dielectric properties also the elastic properties are assumed to depend on the number of ferroelectric domains per volume. Since the velocity of sound is strongly influenced by the porosity of the material only highly dense hot-pressed ceramics could be used. We thus measured the sound velocity on each six hot-pressed samples of the average grain size $a \approx 0.3\,\mu$m and $a \approx 0.7\,\mu$m from which the Young's modulus was determined.

$a \approx 0.3\ \mu$m:

$v = 5.566 \pm 0.033$ km/s,

$E = 186$ GPa;

$a \approx 0.7\ \mu$m:

$v = 5.293 \pm 0.021$ km/s,

$E = 168$ GPa.

The measured velocity of sound and Young's modulus of the material with $a \approx 0.7\,\mu$m which has the maximum number of domains per volume are distinctly lower than in the material with $a \approx 0.3\,\mu$m. Unfortunately the normally sintered ceramics show a too high (0.5–2%) porosity for evaluating domain size effects on Young's modulus. Thus the results obtained with the two dense materials still have a somewhat tentative character.

IV. THEORETICAL TREATMENT

The observation of decreasing domain width with decreasing grain size can be explained on a theoretical basis. It is well known that the equilibrium size of domains whether magnetic or ferroelectric is determined by a balance of energies. The smaller the domains, the higher the domain wall energy per volume w_w. On the other hand, the larger the domains, the larger the electric and stress fields resulting in electrical and mechanical field energy densities, w_e and w_m, respectively. The equilibrium size of the domain is determined by the minimum in the sum of the energies

$$w_w + w_e + w_m = \text{minimum}. \tag{1}$$

A. Domain wall energy w_w

The calculations of the wall energy of 90° domains in $BaTiO_3$ has been carried out by several authors.[24–26] An often used value is that of Zhirnov[24]:

$$\sigma = 3 \times 10^{-3}\ \text{J/m}^2$$

In a cubic grain of size a (Fig. 8) the total wall energy per volume will be

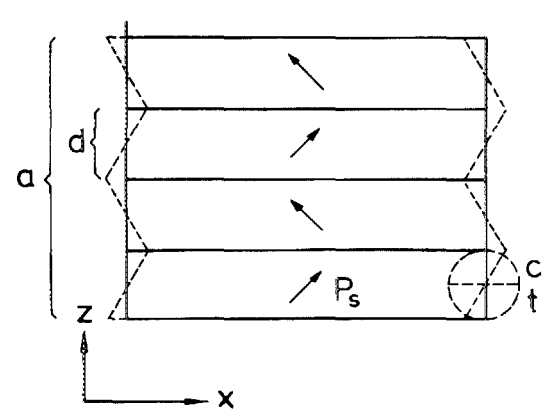

FIG. 8. A cubic grain split into in 90° domains, embedded in an isotropic dielectric medium. The distortion if the grains were free and not clamped is shown by dotted lines. The circle indicates the region of elastic energy in the upper half with compressional c and in the lower half with tensile stress t.

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$$w_w = \frac{(n-1)a^2\sigma}{a^3} \approx \sigma/d, \tag{2}$$

if n is the number of walls in the grain and d is the domain width.

The electric and elastic field energies will be discussed for a grain which is for simplicity cubic and which is embedded in hypothetic $BaTiO_3$ being dielectrically and elastically isotropic, as represented in Fig. 8. The grain is clamped by its surrounding.

B. Electric field energy w_e

This energy which is depolarization energy has been analyzed by several authors as reviewed by Lines and Glass.[28]

The electric field emerging from the polarization charges at the grain boundary is of the order $P_s/\epsilon \approx 10^8$ V/cm. It might be lowered by dielectric displacement in the grain and in the surrounding near the boundary. However, even a field of 10^6 V/cm will cause charge separation in defects or even in atoms on lattice sites producing free charges which will be transported to screen off the polarization charges. Accumulation of free charge carriers at the grain boundaries thus will reduce the depolarization energy to negligible values.

C. Mechanical field energy w_m

This energy is due to the tetragonal distortion in the ferroelectric state. The dotted lines in Fig. 8 show, greatly exaggerated, what kind of surface ripple would exist if the grains were not clamped. In order to get a smooth boundary, compressional stress will exist in the regions c and tensile stress in the regions t. An estimate of this kind of elastic energy is accomplished in Ref. 18. It results in

$$w_m = \frac{a\,d^2\,c_{11}\,S_s^2\,2}{64\,\pi\,4} \tag{3}$$

as the elastic energy of one domain of width d and length a (in y direction). Here c_{11} and S_s are the average longitudinal elastic constant resp. the spontaneous deformation $c/a - 1$. Compared with Eq. (3) in Ref. 18 a factor $\frac{1}{4}$ is applied because the geometrical mismatch is constrained by the grain, not by the embedding matrix. The other factor 2 accounts for the fact that the same distortional energy appears at the right and the left boundaries of the grain. The cubic grain in total thus will have an elastic energy density

$$w_m = \frac{d\,c_{11}\,s_s^2}{128\,\pi\,a}. \tag{4}$$

Whereas w_m increases linearly with the domain width d, the wall energy density w_w according to Eq. (2) decreases with $1/d$.

Using the minimum energy condition (1) and $w_e \ll w_m$ one calculates the equilibrium domain width

$$d = \sqrt{\frac{128\,\pi\,\sigma\,a}{C_{11}\,S_s^2}}, \tag{5}$$

which is proportional to $\sqrt{a}$.

For the grain size of $a = 10\,\mu$m the width of the domain is calculated from Eq. (5) to be

$$d \approx 0.8 \quad \mu\text{m}. \tag{6}$$

Here $c_{11} = 1.7\times10^{11}$ N/m^2 and $S_s = 10^{-2}$ and $\sigma = 3\times10^{-3}$ J/m^2 are used as was done in Ref. 18. Considering that Eq. (3) is a rough estimate only, there is a quite good agreement of d with the observed value (cf. Fig. 7) without any matching of constants.

For $a > 10\,\mu$m, the domain width remains constant. The origin is a new kind of domain wall which acts as artificial grain boundary. These mixed walls have a distance of about $10\,\mu$m and limit thus the length of the 90° domains. In addition to the calculated elastic energy density, Eq. (4), there is some tensile stress in the whole grain along the y direction (Fig. 8). By the spontaneous deformation the grain in this direction gives rise to tensile stress if the embedding matrix is isotropic. This extensional stress may shift the orthorhombic/tetragonal phase transition to higher temperatures as observed by Kinoshita and Yamaji.[16] Additionally this approaching of the transition temperature to room temperature may increase the dielectric constant of the bulk. Analogous to the statements of Buessem *et al.*[11] who predicted a decrease of ϵ_r if compressional stress is applied perpendicular to the c axis of the grains, we can expect the increase of ϵ_r if tensile stress is applied.

V. DIELECTRIC CONSTANT

Mobile 90° domain walls give contributions to the real and imaginary parts of the permittivity, of the elastic compliance, and of the piezoelectric constant as shown by several authors.[24–26] The mobility of the wall is assumed to be independent of the grain size.

The contribution of the 90° domain walls to the real part of the dielectric constant is proportional to the total area A of 90° walls per volume as mentioned in Sec. III B.

$$\epsilon_r = \epsilon_{r,\text{vol}} + (k\,A_{\text{tot}}), \tag{7}$$

$$\epsilon_r = 1000 + 2200/\sqrt{a/\mu\text{m}}, \tag{8}$$

$$\epsilon_r = 1000 + 500/d \tag{9}$$

(with d determined experimentally).

According to Ref. 18, $\epsilon_{r,\text{vol}} \approx 1000$ and $(k\,A_{\text{tot}}) \approx 700$ at $a \approx 10\,\mu$m. With decreasing grain size, $a < 10\,\mu$m, the total 90° domain area will increase $A \sim 1/d \sim \sqrt{1/a}$. The domain wall contribution to ϵ_r therefore will increase to $\epsilon_{r,\text{dom}} = 2200/\sqrt{a/\mu\text{m}}$. A similar relation was found for PLZT ceramics by Okazaki *et al.*[32] ϵ_r as derived on this line is shown by the dashed curve in Fig. 6.

If instead of the calculated values of the domain width d according to Eq. (5) the measured values d as shown in Fig. 5 are introduced in Eq. (9), then the curve with open dots (Fig. 4) for ϵ_r results (matched at $a = 10\,\mu$m). It is evident that the domain contribution to the permittivity explains the steep increase of the permittivity at small grain sizes. The differences in the calculated curve for d according to Eq. (5) possibly arises by the gradual change from the tetragonal to the pseudocubic structure and by the coexistence of both phases below $a = 1\,\mu$m. The strong decrease of ϵ_r for grain sizes smaller than $0.7\,\mu$m cannot be explained on the basis of this model. It appears obvious, however, that (i) the spontaneous

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polarization and deformation, (ii) the wall energy and mobility, (iii) the domain configuration, and (iv) the contribution of the volume and the domains to ϵ_r undergo variations when the c/a ratio is no longer constant.

VI. CONCLUSIONS

The observation of domains, the measurement of the dielectric constant and Young's modulus, and a theoretical analysis confirm that the equilibrium domain width is dependent on the grain size. The equilibrium domain width decreases for grain sizes $a < 10\,\mu$m and is effectively constant at $a > 10\,\mu$m. The high dielectric constant of fine-grained $BaTiO_3$ can be explained by domain size effects. At grain sizes smaller than $a = 1\,\mu$m, however, the ferroelectric structure changes. This may cause the observed decrease in the dielectric constant.

The observed increase of the transition temperature orthorhombic/tetragonal can be explained with respect to the earlier theories[10–12] by the existence of tensile stress in the grains of the hot-pressed materials. Therefore the importance of internal stress should not be neglected in these materials. Accordingly, it is not the intention of this paper to set aside the earlier theories suggesting a stress-induced increase of the dielectric constant in fine-grained $BaTiO_3$. The increase of the permittivity is possibly caused by a summation of domain size and stress effects. Further theoretical and experimental work should aim at the assessment of these two effects.

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