Size effect in Mn²⁺-doped BaTiO₃ nanopowders observed by electron paramagnetic resonance

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Barium titanate (BaTiO₃) ultrafine powders have been prepared from a monomeric metallo-organic precursor through combined solid-state polymerization and pyrolysis. This particular preparation route enables an adjustment of the mean particle size in a wide range from a few nanometers up to micrometer size by choosing an appropriate reaction temperature and tempering atmosphere. Doping by paramagnetic probe ions such as Mn^{2+} is readily done by adding the corresponding metal acetates. The ultrafine doped BaTiO₃ powder samples with an average grain size varying from 15 nm to 155 nm were studied by x-ray diffraction (XRD) and electron paramagnetic resonance (EPR) techniques, taking EPR spectra in the X (9.5 GHz), Q (34.2 GHz), and W (94.1 GHz) frequency bands. The determined quantities such as grain size, unit cell deformation c/a-1, the axial fine structure parameter D, the distribution width ΔD of the latter, and the EPR intensity ratio of cubic and tetragonal $Mn_{T_i}^{2+}$ sites are used to develop a more comprehensive insight into small particles. Sufficiently large crystallites consist of a regular ferroelectric core with a tetragonality gradient towards the outer surface range, surrounded by a peripheral particle layer with strongly distorted translational symmetry. In particles smaller than about 40 nm the regular core no longer exists at room temperature. EPR spectroscopy along with second-harmonic generation and Raman measurements at room temperature reveals the occurrence of a locally acentric structure in very small particles whereas XRD measurements can only indicate an averaged cubic structure. In agreement with findings in the literature, the presented results give evidence of a regular grain core undergoing a size-driven transition into the paraelectric phase, and they lay stress on a heavily distorted surface layer which does not participate in this transition. The size-driven transition is considerably smeared out by the grain-size distribution. Thus, application of Landau theory to a particular BaTiO₃ particle brings out a critical size of about 50 nm at room temperature whereas in the size-distributed nanopowder a considerably lower mean size (~ 25 nm) represents the effective threshold for the size-driven transition into the paraelectric phase.

I. INTRODUCTION

Since the 1950s, continuous studies of size effects on ferroelectric properties of barium titanate (BaTiO₃) have experienced great impetus (Ref. 1 and references cited therein). Curie temperature, electrical polarization, coercive field, switching time, etc., potentially depend on particle size or, more generally, correlation length.² Thus, the purity of the sample material attains great importance in investigations of size effects. The availability of high-quality ferroelectric fine powders is a prerequisite for preparing optimized technologically promising ferroelectric polymer-ceramic composite films offering both high dielectric permittivity and low losses.³ Recent thermal wave measurements on such ferroelectric polymeric composite films^{4,5} brought out a rather complex electrical poling and switching behavior which turned out to critically depend on the mean size of the ceramic powder component. Thus, investigating size effects on ferroelectric properties on an extended methodical scale is, in addition to basic interest, also of significant practical importance.

So far, a temperature shift of the tetragonal-to-cubic phase transition has been considered by theory,^{6,7} as a particular size effect due to the depolarization effect and the inhomogeneous distribution of polarization within the small par-

ticles. The critical size at which polarization disappears is still under controversial discussion. A study of the crystal structure dependence on the size of BaTiO₃ particles revealed a critical size magnitude of approximately 120 nm at room temperature.⁸ Moreover, knowledge about the real lattice structure of nanocrystalline BaTiO₃ particles is still insufficient. Thus, in x-ray diffraction (XRD) investigations of BaTiO₃ nanopowders at room temperature, Takeuchi et al.⁹ were faced with the coexistence of tetragonal and cubic phases. The latter was supposed to occur in a surface layer of the BaTiO₃ grains, thus gaining prevalence with decreasing particle size. On the other hand, in accordance with Niepce's model,¹⁰ one expects a gradual change in tetragonality in the surface region, and the deformation (c/a-1) of the unit cell should continuously decrease from a definite bulk value to zero at the very surface, thus precluding an assignment of definite lattice parameters to BaTiO₃ nanocrystallites. The XRD technique is based on coherent scattering at extended crystallographic planes and is therefore insensitive to subtle structural short-range changes in BaTiO₃ nanocrystallites. However, magnetic resonance methods, among them electron paramagnetic resonance (EPR), can sensitively probe small changes in the local symmetry at the particular crystal sites.

The Mn^{2+} ion (with free-ionic ground state ${}^{6}S_{5/2}$) forms a

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very suitable probe for studying size effects in nanocrystalline BaTiO₃ powders by means of EPR spectroscopy: In the $BaTiO_3$ host lattice it substitutes for the Ti^{4+} ion within an octahedron formed by six O^{2-} ions. Owing to the orbital singlet state, the spin-lattice relaxation time is long enough to probe the local symmetry over a wide temperature range. Moreover, the fine structure (FS) interaction is determined by a second-order ligand field term produced by the nearestneighboring O^{2-} ions. This makes this particular paramagnetic ion so sensitive to the symmetry changes which occur at the Ti⁴⁺ site at all the structural transmutations (rhombohedral, orthorhombic, tetragonal, cubic; as for the respective bulk measurements see Refs. 11-17). On the other hand, due to the orientational disorder of the paramagnetic ions in the BaTiO₃ powder samples, the hyperfine structure (HFS) interaction (I = 5/2 for ⁵⁵Mn) imparts a considerable complexity to the Mn²⁺ EPR spectra. However, by investing sufficient effort towards analyzing the Mn^{2+} HFS spectra, these complex spectral features can even be a rich source of additional structural information. Particular clarity and unambiguousness of the discussion is attained by combining EPR measurements in the various (X, Q, and W) microwave frequency bands and by employing a sophisticated spectra simulation program.

The present investigations are based on an advanced sample preparation route allowing reproducible adjustment of the mean particle size and doping by paramagnetic probe ions. Combining EPR as a local probe technique with common XRD measurements proves particularly efficient in elucidating structure and size effects in the ferroelectric nanopowder samples. This endeavor is supported by numerical model calculations using Landau's phase transition theory.

II. PREPARATION AND CHARACTERIZATION

Different ways of preparing nanocrystalline BaTiO₃ particles are known, such as hydrothermal,¹⁸ sol-gel,¹⁹ microemulsion,²⁰ and gas-condensation processes²¹ as well as by metallo-organic precursor pyrolysis (MOPP),²² hydrolytic decomposition,²³ and chemical precipitation from solutions.^{24,25} Notwithstanding the high level of success attained in the various preparation routes, a serious disadvantage still remains: Either a particular route furnishes particles in the 10 nm size range, but only poor possibilities for straightforward size adjustment, or, alternatively, the preparation method yields submicron powders with adjustable mean grain size, but does not reach the size range (below 100 nm) which is of particular interest in a study of size effects on ferroelectricity. Besides a more efficient size adjustment in the wide range from 10 nm up to about 1.5 μ m, the route developed by us aims at homogeneous doping by paramagnetic ions with concentrations ranging from typically 0.005 mol % BaTiO₃ for EPR measurements up to some mol % for materials with positive temperature coefficient of resistance (PTCR).²⁶

Our preparation route of $BaTiO_3$ nanopowders may be briefly described by four reactions: In a first step, barium titanium methacrylate is obtained as a monomeric metalloorganic precursor from metallic barium, titanium (IV) isopropylate, and methacrylic acid in boiling methanol. Then, the solid-phase polymerization and the concomitant pyrolysis proceed simultaneously at temperatures above 200 °C. Nucleation and growth of BaTiO₃ particles start at about 600 °C, where the temperature and reaction atmosphere determine the resulting particle size (e.g., 2 days 600 °C/N₂ yield 10 nm particles, whereas 2 days 1350 °C/O₂ lead to 1.5 μ m mean particle size). The ability to adjust the particle size by just choosing an appropriate reaction temperature and to introduce paramagnetic dopants form the salient advantageous features of our preparation route. The dopant was introduced in the first stage of the preparation route by adding the corresponding acetates [e.g., Mn(ac)₂ for doping with manganese ions]. Tempering was done under inert conditions (N_2 atmosphere). Since doping by manganese ions can affect the grain size of BaTiO₃ samples to a significant extent,^{26,27} the size dependence on the reaction temperature was carefully remeasured by means of XRD.

The product (yield 97%) was verified with the aid of elemental analysis and numerous spectroscopic means: nuclear magnetic resonance (137 Ba NMR), EPR (Gd³⁺, Mn²⁺, Cr³⁺), and Fourier transform (FT) Raman as well as by recording the x-ray absorption near edge structure (XANES) at the Ti *K* edge. For further details of preparation and characterization the interested reader is referred to Ref. 1.

III. FERROELECTRICITY IN SMALL PARTICLES

It appears quite obvious that the particle size influences the dielectric properties of fine-grained ferroelectric powders, ceramics, and ferroelectric thin films at least in the limiting case when the grain size or film thickness falls below the correlation length of the cooperative ferroelectric long-range interactions. But even if the size considerably exceeds the correlation length, one has to reckon with polarization inhomogeneities within a surface layer of the thickness of some correlation lengths which may remarkably affect the overall ferroelectric behavior. In order to comprise the sizedependent phenomena, the Landau-Devonshire theory has meanwhile been successfully extended,^{6,28–30} and the considerations in this section follow the main ideas developed in this context.

A. Landau theory

In calculating the spontaneous polarization within a small isolated spherical grain one cannot consider only the free energy density as in an extended solid but, instead, one has to comprehensively minimize its total free energy

$$F = \int_{V} dV \left[\frac{1}{2} A'_{0}(T - T_{0}) P^{2} + \frac{1}{4} B'^{4} P^{4} + \frac{1}{6} C'^{6} P^{6} + \frac{1}{2} D' (\nabla P)^{2} \right] + \frac{D'}{2\delta} \int_{S} dS P^{2}.$$
 (1)

Here, *P* is the polarization, *T* the absolute temperature, T_0 the Curie-Weiss temperature, and, A'_0 , B', C', D', and δ are material parameters (primed symbols have been chosen here in order to avoid a nomenclature conflict with the parameters of the spin Hamiltonian at a later stage). The first three terms in the volume integral are the conventional ones of the homogeneous bulk solid whereas the gradient term

[the fourth one in Eq. (1)] takes into account the distortion energy from the polarization inhomogeneity. Finally, the "surface" term [the last one in Eq. (1)] is physically and mathematically closely related to the gradient term because it comprises the surface field contribution in the formation of the polarization gradient. Formally, the close interrelation of both terms is reflected by the use of the same prefactor D'where the so-called extrapolation length δ measures the strength of the surface effect. From the mathematical point of view, minimization of the free energy forms an Euler-Lagrange problem with natural boundary conditions. Using the variational principle, the Euler-Lagrange equation

$$D'\nabla^2 P = A'P + B'P^3 + C'P^5$$
(2)

is obtained with the boundary condition for the normal derivation of the polarization at the grain surface:

$$dP/dn = -P/\delta.$$
 (3)

The extrapolation length δ depends on the intersite dipole interaction as well as the coordination number of a dipole within the surface layer. For a spherical particle it is size dependent and given by

$$1/\delta = 5/d + 1/\delta_{\infty}(1 - a_0/d), \tag{4}$$

where d, δ_{∞} , and a_0 are the particle diameter, the extrapolation length for an infinitely large grain, and the unit cell length of the bulk material, respectively. The assumption of a unidirectional polarization of a purely radial-dependent amount introduces considerable simplification into the solution of this particular Euler-Lagrange problem. However, it brings forth additional errors in the model from the physical point of view. As P is assumed to be only radial dependent, P^2 becomes constant at the whole surface of a spheric grain which is in contradiction to the real physical situation. This leads to an overestimation of the surface term in Eq. (1) and, therewith, the polarization gradient at the grain border. But this overestimation plays now a crucial role in the numerical calculations as it is balanced out due to parameter adaption of the relevant physical values, such as, e.g., the critical size, to the experimental observations. As expected, the numerical calculations disclose a size-driven ferroelectric-toparaelectric phase transition and, equivalent to it, a reduction in the Curie temperature when going to a smaller particle size.

B. Numerical calculations

As mentioned above, the magnitude of polarization P(r)in Eqs. (1)–(3) is assumed to depend only on the radial position *r* and, hence, polar coordinates may be used. But even in this simplified case, the differential equation (3) can only be solved numerically. For this purpose a standard solution method was employed.³¹ The adopted model parameters are the corresponding bulk values taken from standard sources,³² i.e., $A'_0 = 6.66 \times 10^5$ J m C⁻² K⁻¹, B' = -3.56 $\times 10^9$ J m⁻⁵ C⁻⁴, $C' = 2.7 \times 10^{11}$ J m⁹ C⁻⁶, and T_0 = 391 K, whereas $\delta = 5/d$, and $D' = 0.025 \times 10^{-7}$ J m⁵ C⁻² have been chosen so as to attain best fits to the experimental data. Figure 1 shows polarization profiles within the grains for grain diameters up to 200 nm. The calculated size depen-



FIG. 1. Calculated radial dependences of polarization at room temperature for spherical particles with diameters up to 200 nm. Every separate curve is the polarization profile of a grain of definite size. It starts at the grain center at zero-grain-size scale and ends at the grain border where the grain radius is identical to the value on the grain size scale for the curve end.

dence of the polarization at the grain center and the grain border as well as the average polarization shown in Fig. 2 discloses the occurrence of significant size effects at geometrical sizes below 100 nm. Finally, a pronounced temperature reduction of the ferroelectric-to-paraelectric phase transition is observed at particle sizes below 100 nm (cf. Fig. 3). Note that these temperature-size characteristics also enable one to deduce the critical size below which the ferroelectric state is no longer stable in this small particle at a given temperature.

IV. EXPERIMENTAL RESULTS

A. XRD measurements

XRD investigations were performed at room temperature with a powder diffractometer (Philips X Pert) in Bragg-Brentano configuration, using Cu $K\alpha$ radiation. Figure 4 shows the x-ray diffraction patterns of two samples which were prepared at reaction temperatures of 700 °C and 1300 °C, respectively. In the sample prepared at the higher temperature, the tetragonal splitting of the Bragg reflections



FIG. 2. Dependence of the polarization on grain size at room temperature: (a) polarization at the grain center (dashed line), (b) average polarization $\langle P \rangle$ of the grain (dark line), (c) polarization at the grain border (dotted line), and (d) polarization difference between grain center and border (dash-dotted line) The polarization *P* is related to that for infinite grain size P_0 .



FIG. 3. Ferroelectric-to-paraelectric phase transition temperature T_C in dependence on particle diameter *d*.

became well visible although the tetragonal distortion of the BaTiO₃ unit cell was quite small (c/a = 1.0095). The peaks of the other samples were broadened so that the tetragonal splitting could no longer be observed (Fig. 5).

The line profile analysis according to Warren³³ takes into account the angular dependence of the broadening effects, thus enabling a separate determination of mean crystallite size and lattice strain. For this purpose, the (111) and (222) [the (222) reflex is off scale in Fig. 4] Bragg reflections were used which are not split by the tetragonal distortion. Deconvolution of the measured diffraction pattern with the (111) and (320) reflections of the LaB₆ reference sample allows for an elimination of instrumental effects. The dependence of the mean particle size of manganese-doped powders on the reaction temperature proves particularly critical in an upper temperature region (Fig. 6). In addition, with growing reaction temperature, the proportion of surface regions to volume becomes smaller and, as expected, a decreasing lattice strain is found.



FIG. 4. X-ray diffraction patterns of $BaTiO_3$ powder samples prepared at 700 °C and 1300 °C.



FIG. 5. Expanded view of (002) and (200) Bragg reflections of BaTiO₃ powder samples prepared at various reaction temperatures.

The determination of the tetragonal lattice parameters a and c in dependence on the particles size was based on the (002) and (200) Bragg reflections. For the 1300 °C sample these reflections reveal a pronounced $K\alpha_1/K\alpha_2$ splitting, thus furnishing evidence of largely homogenous crystallites and small lattice strain. With decreasing reaction temperature (and, hence, particle size) the two-component feature of the $K\alpha$ x-ray line is increasingly smeared out (Fig. 5), and a Voigt profile fit was applied to determine the Bragg angles of the two line components. Then, these peak positions were corrected with respect to the (220) reflection of the internal standard (Si), and the lattice parameters a and c were determined. In rather good agreement with the data by Frey and Payne^{34,35} the results in Fig. 7 indicate a decreasing tetragonal distortion when going to a lower reaction temperature and, correspondingly, smaller particle size. For the largest particles the obtained lattice parameters largely agree with corresponding literature data.^{10,34} The smallest particles



FIG. 6. Mean crystallite size of $BaTiO_3$ powders in dependence on reaction temperature determined from the (111) and (222) XRD peak profiles.



FIG. 7. Lattice parameters a and c of BaTiO₃ determined at room temperature in dependence on reaction temperature and, hence, crystallite size.

(<20 nm in Fig. 7) explicitly reveal a pseudocubic structure. The residuals of the Rietveld refinements of the XRD features of the larger particles could also be substantially reduced by taking into account a pseudocubic peak. The relative pseudocubic proportion decreases with growing particle size, e.g., amounting to about 25% and about 10% for particle sizes of 25 nm and 155 nm, respectively.

B. Mn²⁺ EPR powder spectra and local symmetry

1. Spin Hamiltonian and spectra simulation

In principle, a discussion of the Mn²⁺ EPR spectra and their line shapes of nanocrystalline BaTiO₃ powder samples should be based on the most general form of the spin Hamiltonian including the fourth-order FS terms.³⁶ However, the available spin-Hamiltonian parameters of the Mn²⁺ ions incorporated in barium titanate single crystals and ceramic samples¹² as well as the results of our W-band measurements justify considerable simplifications: Thus, neither line broadening effects nor additional splittings were observed in the W-band EPR spectra. Hence, the anisotropy of the g and the HFS tensors yields much smaller angular-dependent EPR resonance shifts than the peak-to-peak widths ΔB_{pp} (0.25) mT) of the W-band lines. Consequently, the Zeeman and HFS interactions may be represented by the g and A constants, respectively. Moreover, in the Mn²⁺ EPR powder spectra no indication was found of the fourth-order FS terms and, hence, they were omitted. However, in the calculation of the resonance fields and intensities of the forbidden HFS transitions, the nuclear Zeeman and quadrupole terms were taken into consideration:

$$\hat{H} = g\beta\vec{B}\cdot\hat{\vec{S}} + D\left[\hat{S}_{z}^{2} - \frac{1}{3}S(S+1)\right] + A\cdot\hat{\vec{S}}\cdot\hat{\vec{I}} - g_{n}\beta_{N}\vec{B}\hat{\vec{I}} + Q\left[\hat{I}_{z}^{2} - \frac{1}{3}I(I+1)\right],$$
(5)

with S and I being 5/2 each.

The axial FS term $D[\hat{S}_z^2 - \frac{1}{3}S(S+1)]$ contains the major part of structural information, where the ligand field parameter *D* is temperature dependent and drops to zero at the tetragonal-to-cubic phase transition and vanishes in the cubic phase. The conditions $|D|, |A| \leq g \beta B$ proved valid in all the microwave frequency bands, and third-order perturbation theory may be applied in calculating the resonance magnetic fields $B_{RES}(M_S, M_I, i)$ for allowed $(\Delta M_I = 0, i = 0)$ and forbidden $(\Delta M_I = \pm 1, i = \pm 1)$ transitions. In the Mn²⁺ EPR spectra of the nanopowder samples only the central FS transition $M_S = -1/2 \Leftrightarrow M_S = 1/2$ could be detected. Therefore, the corresponding formula by Kliava³⁷ supplies a comprehensive description:

$$B_{RES}\left(\frac{1}{2}, M_I, i\right) = B_0(M_I, i) + \frac{2D^2}{B_0} (8\sin^2\Theta - 9\sin^4\Theta) - (2M_I + i) \left[\frac{D^2A}{B_0^2} (72\sin^2\Theta - 73\sin^4\Theta) + \frac{2DA^2}{B_0^2} (3\cos^2\Theta - 1)\right] - iQ(3\cos^2\Theta - 1)(2M_I + i), \quad (6)$$

with

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$$B_{0}(M_{I},i) = B_{c} - (2M_{I}+i)\frac{A}{2} + [(2M_{I}+i)^{2} + (17-i)^{2} - 324]\frac{A^{2}}{8B_{c}} + i\frac{g_{N}B_{c}}{g}, \quad B_{c} = \frac{h\nu}{g\beta}.$$
 (7)

 M_S and M_I are the electronic and nuclear quantum numbers; Θ is the angle between the static magnetic field *B* and the symmetry axis of the local crystal field which in the present case is identical with the crystallographic *c* axis. Note that in Eq. (6) a linear *D* expression only occurs in the third-order term which is of minor importance here. Furthermore, the cubic FS parameter *a* was found to be quite small [*a* <2 mT (Refs. 12 and 13)] and therefore omitted.

In order to deduce the spin-Hamiltonian parameters from the EPR powder spectra, it appeared inevitable to employ a simulation program (written in FORTRAN 77). It is based on two assumptions: First, equal probabilities are assigned to all orientations of the paramagnetic centers in the macroscopic powder sample, and the EPR powder pattern can be obtained by averaging the angular-dependent single-crystal spectra:

$$I(B)\alpha \sum_{i} \sum_{M_{I}=-5/2}^{5/2} \int_{0}^{\pi/2} \int W(\Theta, M_{I}, i) \\ \times \left| \frac{dB_{RES}\left(\frac{1}{2}, M_{I}, i\right)}{d(h\nu)} \right| F\left(\frac{B_{RES}\left(\frac{1}{2}, M_{I}, i\right) - B}{\Delta B_{pp}} \right) \sin \Theta d\Theta.$$
(8)

In Eq. (8), $W(\Theta, M_I, i)$ denotes the transition probability and $F((B_{RES}-B)/\Delta B_{pp})$ is the line shape function which was assumed to be Gaussian. The effective field conception by

Bir³⁸ provides a more adequate description of the transition probability $W(\Theta, M_I, i)$ than furnished by common perturbation theory because Bir's method takes into account the difference between the quantization axes of the nuclear spin in different electronic M_S states. Second, we presuppose that the BaTiO₃ nanocrystallites reveal an inhomogeneous structure which translates into statistical parameter distributions with mean values g_0 , A_0 , and D and widths Δg , ΔA , and ΔD . Including the linewidth ΔB_{pp} , seven parameters are to be determined from the experimental spectra. In particular, only a statistical distribution of the FS parameter D yielded a comprehensive description of all the EPR measurements in the various frequency bands (X, Q, W). Assuming a Gaussian distribution P(D), the EPR spectrum I(B) of Mn^{2+} ions in nanocrystalline BaTiO₃ is obtained as

$$I(B) \propto \sum_{i} \sum_{M_{I}=-5/2}^{5/2} \int_{-\infty}^{+\infty} dD \int_{0}^{\pi/2} P(D) \times W(\Theta, M_{I}, i) F\left(\frac{B_{RES}\left(\frac{1}{2}, M_{I}, i\right) - B}{\Delta B_{pp}}\right) \sin \Theta d\Theta.$$
(9)

Particularly, owing to the weak angular dependence of the central FS transition, the term $dB_{RES}/d(h\nu)$ in Eq. (8) can be treated as a constant in Eq. (9).

2. Centered model and fine structure parameter

The superposition model³⁹ enables the determination of the spin-Hamiltonian parameters for a known structure of a defect in a solid-state material or, vice versa, the deduction of the local environment of a paramagnetic center from the EPR data. The main assumption of the model is that the spin-Hamiltonian parameters are sums of individual contributions from each nearest neighbor of the paramagnetic ion. In this approximation the axial FS parameter may be determined from the lattice parameters *a* and *c* (centered model):^{12,13}

$$D_{\rm cm} = 2\overline{b}_2 \left(\frac{c}{2}\right) \left[1 - \left(\frac{c}{a}\right)^{t_2}\right],\tag{10}$$

with the intrinsic parameter \overline{b}_2 depending on the lattice parameter c and the exponent $t_2=7$. For the system BaTiO₃:Mn²⁺ the functional dependence of \overline{b}_2 is

$$\bar{b}_2\left(\frac{c}{2}\right) = \bar{b}_2(0.2101[\text{nm}]) \left[\frac{0.2101[\text{nm}]}{c/2[\text{nm}]}\right]^{t_2}, \qquad (11)$$

with $\bar{b}_2(0.2101 \text{ nm}) = -148.5 \text{ mT}$. Using the sizedependent lattice parameters deduced from the XRD measurements, the axial FS parameter can be evaluated and compared with the corresponding EPR results.

Because of $(c/a-1) \ll 1$, an expansion of Eq. (10) leads to a direct relation between the fine structure parameter *D* and the ferroelectric order parameter *P* of the tetragonal phase:



FIG. 8. Mn^{2+} EPR spectra measured with Q band of (a) microcrystalline and (b) nanocrystalline BaTiO₃ samples.

$$D \propto P^2 \propto \left(\frac{c}{a} - 1\right). \tag{12}$$

This relation meets the constraints of symmetry according to which for paramagnetic center at a centrosymmetric site, the fine structure parameter is to be comprised of terms with even powers of P only.

3. Mn²⁺ spectra taken at room temperature

EPR measurements were carried out in the X band (9.5 GHz) with a Bruker ESP 380 spectrometer, in the Q band (34.2 GHz) with a Bruker EMX device, and in the W band (94.1 GHz) with a Bruker ELEXSYS E 600 spectrometer with 100 kHz field modulation. The magnetic fields were determined by means of a proton magnetic-resonance probe (X and Q band). For g-factor determination the standard sample DPPH (g=2.0036) was used. The temperature dependences of the EPR spectra were taken using a Varian E 112 spectrometer with variable temperature accessory E257, attaining a stability better than 0.5 K in the temperature range from 60 °C to 160 °C.

At first, in order to investigate the influence of the mean particle size on the EPR spectra we measured Mn^{2+} -doped BaTiO₃ micropowders, prepared as a reference sample by the application of the common solid-state reaction. The pertinent powder pattern of the central FS transition in Fig. 8(a) is a superposition of tetragonal and cubic spectra, with the lines of the latter being marked by asterisks. Obviously, the six intense line groups observed both for micropowders and nanopowders arise from the ⁵⁵Mn HFS interaction. Each group shows absorptionlike features and derivative shapes in the first derivative powder spectra where the following condition is satified:³⁷

$$\frac{dB_{RES}\left(\frac{1}{2}, M_I, i, \Theta\right)}{d\Theta} = 0.$$
(13)

In our case of a spin Hamiltonian of axial symmetry with isotropic *g* and *A* terms, an absorptionlike feature is expected for $\Theta = 0^{\circ}$ whereas derivative shapes are to be attributed to



FIG. 9. Central Mn²⁺ FS lines $(M_S = 1/2 \Leftrightarrow M_S = -1/2, M_I = -3/2, -5/2)$ taken at room temperature in the *Q* band for powder samples of various mean sizes.

 Θ angles of 41.8° and 90°, respectively. The distance between the outer peaks ($\Theta = 90^{\circ}$, 41.9°) is determined by the second-order term D^2/B_0 and, due to the third-order terms in Eq. (6), is additionally superposed by a weak dependence on the quantum number M_I [cf. Eq. (6)].

From the simulation of this axial EPR spectrum the crystal field parameter D is estimated, yielding a value of about 24.5 mT for the micropowder sample at room temperature. Both this value and the temperature dependence of the FS parameter are in agreement with the respective data of ceramic samples.¹⁴ However, the magnitudes of the absorptionlike features for $\Theta = 0^{\circ}$ cannot be fully explained on the basis of this axial spin Hamiltonian. For the axial case, the simulation vields more intense derivative lines ($\Theta = 90^{\circ}$ and 41.8°) than the absorptionlike feature between them (see also Ref. 40). Therefore, an additional Mn²⁺ EPR spectrum of cubic symmetry must be taken into consideration. Having in mind that the cubic FS parameter a of Mn^{2+} ions in BaTiO₃ is smaller than 2 mT,^{12,13} the pertinent spectrum consists of only six narrow HFS lines. The g factors and HFS constants of Mn²⁺ ions on tetragonal and cubic lattice sites are equal and, hence, the lines of the cubic spectrum overlap with those of the tetragonal central ones ($\Theta = 0^{\circ}$).

When going from micropowder to nanopowder samples (Fig. 8), the resolution of Mn^{2+} EPR spectra becomes quite poor. The spectra taken in the various frequency bands (for the *Q*- and *W*-band spectra see Figs. 9 and 10) reveal a size effect on the line shapes: At first, for the 155-nm-sized sample, the outer derivative features are broadened and an asymmetric line occurs between them. In the EPR spectra of powders with a small grain size (<100 nm) these two outer peaks are no longer observed and the central FS transition consists of six allowed and ten forbidden HFS lines with asymmetric shapes. Their linewidths depend on the microwave frequency and are smallest at *W* band. A comparison of the *X*-, *Q*-, and *W*-band spectra shows that any anisotropy of the *g* and HFS tensors as well as their distributions Δg and ΔA may even be neglected in the *W*-band spectra. Conse-



FIG. 10. The same as in Fig. 9 for the W band.

quently, the line shapes can provide information on the FS parameter D and its distribution ΔD .

Simulations of the Q- and W-band spectra readily reproduce all the spectral details of both the allowed and forbidden transitions (Figs. 11 and 12), thus furnishing confidence in the spin-Hamiltonian parameters employed. The best-fit values of the g factor (2.002±0.001), the HFS constant $A(8.64\pm0.02 \text{ mT})$, and the quadrupole coupling constant $Q(0.2\pm0.05 \text{ mT})$ do not vary with particle size and are typical of Mn²⁺ ions incorporated into BaTiO₃ single crystals.^{11–13} The amounts of the mean FS parameters D and the widths ΔD of the distribution in Table I reveal a pro-



FIG. 11. Experimental and simulated *Q*-band spectra for the 155 nm sample.



FIG. 12. Experimental and simulated W-band Mn²⁺ EPR spectra of the 25 nm sample (central FS lines $M_S = 1/2 \Leftrightarrow M_S = -1/2$, $M_I = -3/2, -5/2$ only).

nounced grain-size dependence, with the |D| value of the finest powder sample being only one-third of the singlecrystal value. It is worth mentioning that optimal simulation of the spectra of powder samples with intermediate grain size (e.g., 155 nm) is attained by superposing two axial spectra. One of the two FS parameters still is quite close to that of single crystals^{11–13} and microceramics.¹⁴ The other FS parameter set (|D| = 13.5 mT, $\Delta D = 8.0 \text{ mT}$) opens a series in which the amount of the mean FS parameter decreases and the distribution width ΔD grows with decreasing particle size. The tremendous increase in the widths of the FS parameter distribution indicates a growing breaking of translational symmetry in an outer particle region. Moreover, a cubic spectral proportion (D=0) is worth mentioning which substantially reduced the fit residuals in all cases. For greater grain sizes (with $|D| > \Delta D/2$) a cubic spectral component has to be explicitly taken into account whereas for the finer nanopowder samples the broad FS parameter distribution $(|D| < \Delta D/2)$ inherently contained the adequate cubic proportion.

For comparison, Table I also contains the corresponding FS parameters D_{cm} which were deduced from the XRD results (cf. Fig. 8) with the aid of the centered model. Notwithstanding a qualitative agreement, the size dependence of |D|

TABLE I. Size dependence of the FS parameter D and its distribution witdth ΔD (as determined by EPR spectra fitting) and the corresponding values $D_{\rm cm}$ which were obtained from XRD data with the aid of the centered model.

Size (nm)	D (mT)	ΔD (mT)	<i>D</i> _{cm.} (mT)
2000	24.0	< 1.0	32.2, 21.5, ^a 33.3 ^b
155	24.0, 15.5	4.0, 8.0	28.1
75	13.5	8.0	22.9
25	10.0	30.0	3.0
15	8.0	45.0	0.0

^aMeasured single crystal data.

^bCalculated from Refs. 12 and 13.



FIG. 13. Mn^{2+} *X*-band spectra of a microcrystalline sample recorded in the ferroelectric tetragonal (a) and in the paraelectric cubic (b) phases, with the latter being taken at reduced gain (by a factor of 50). The EPR lines at 335.2 mT and 340.2 mT on the top spectrum are to be attributed to Fe³⁺ and Cr³⁺ impurities, respectively.

reveals the occurrence of local acentric crystal symmetry with growing particle size, well before the detection of any tetragonal structure by XRD measurements.

4. Mn^{2+} spectra taken at the Curie temperature T_C

At the ferroelectric-to-paraelectric phase transition (T_C) ≈ 120 °C) of bulk BaTiO₃, the symmetry of the unit cell increases from tetragonal to cubic, clearly affecting the Mn²⁺ micropowder spectra: In the paraelectric cubic phase the axial FS parameter D vanishes, yielding an intense cubic six-line HFS spectrum (upper part of Fig. 13). Thus, the disappearance of the cubic spectrum must not be traced back to an oxidation stage alteration as has been assumed in the literature.^{16,17} However, in the ferroelectric tetragonal phase, remnants of this cubic spectrum survive and compete in intensity with the tetragonal Mn²⁺ spectrum. The temperaturedependent intensities of the cubic Mn²⁺ spectra in Fig. 14 reflect a pronounced size dependence: The samples with greater particle sizes (e.g., 155 nm) undergo a relatively sharp phase transition reminiscent of the crystalline bulk system. In addition, the intensity of the cubic Mn^{2+} spectrum reveals a thermal hysteresis (Fig. 15) similar to that measured for the lattice parameters in bulk systems by crystallographic means.⁴¹ At smaller particle sizes (below 155 nm in Fig. 14) such a pronounced tetragonal-to-cubic phase transition behavior is no longer observed in the range around the Curie temperature T_C . In addition, the thermal hysteresis is also no longer detectable.

V. DISCUSSION

At first, we compare the XRD and EPR data from our room temperature measurements with the model calculations outlined in Sec. III. The centered model [Eq. (12)] allows

1.0

D, (c/a - 1), P² (normalized)

0.5





(da

D, this work

1), this work

FIG. 14. Temperature dependence of the relative intensity of the cubic Mn^{2+} spectrum in BaTiO₃ powder samples of different mean particle sizes.

correlation of the amount of the axial fine structure parameter D with the tetragonality parameter c/a - 1. The normalization in Fig. 16 was based on the results obtained for samples with a mean particle size of $2 \mu m (|D|)$ = 24 mT, c/a - 1 = 0.01077), with the latter values falling quite close to the corresponding bulk values. Note that particularly at small mean particle sizes (<50 nm), the XRD data reveal a suppression of the tetragonal phase which is remarkably more pronounced than that delivered by EPR. In discussing the apparent discrepancy we again refer to the different local resolution of both methods [for comparison, see the discussion in the literature³⁴ of XRD data versus second-harmonic generation (SHG) and Raman measurements]. For comparison, some literature data have been included in Fig. 16. At first glance, our experimental data agree well with pertinent literature data.^{8,34,35} In a consideration of



FIG. 15. Temperature hysteresis of the relative EPR intensity of the cubic Mn^{2+} spectrum for the 155 nm powder sample.

FIG. 16. Correlation between measuring data D and c/a-1 with calculated mean square of polarization P where $\langle P^2 \rangle_r$ is the radial average of P^2 and $\langle P^2 \rangle_{r,d}$ additionally accounts for a particle size distribution (cf. text).

the remaining discrepancies one has to take into account the particle-size distribution. The best theoretical verification of our measuring data could be achieved on the assumption of a relatively broad particle size distribution (Gaussian with a width of 80% of the mean grain size-cf. Fig. 16). The lines drawn in Fig. 16 correspond to theoretical calculations according to Sec. III. The solid bold line is the numerical solution of Eqs. (2) and (3) using the parameters given in Sec. IIIB. The dashed line, however, additionally takes into account the grain-size distribution by averaging over a Gaussian distribution P(d). The inevitable assumption of a pronounced grain-size distribution in the simulation of experimental data throws some new light on the presumed coexistence of tetragonal and cubic phases within a particular BaTiO₃ particle deduced primarily from the XRD results.⁹ In reality, the apparent coexistence of tetragonal and cubic phases stems from the superposition of particle sizes, which allows for ferroelectricity in the sufficiently large grains and the size-driven transition into the paraelectric cubic state in the smaller ones.

Furthermore, the amounts of the EPR fine structure parameter D reveal a relatively good correlation with the corresponding values $D_{\rm cm}$ (cf. Table I) inferred from the XRD data with the aid of the centered model.^{12,13} The rather good agreement between the results obtained for the microcrystalline powder samples and the literature data for single crystals^{12,13} furnishes additional confidence in the size dependences of the amounts of the axial FS parameter D and their distribution widths ΔD . The distribution of the tetragonal FS parameters D requires a separate discussion. Obviously, only particles with sizes close to the critical value make considerable contributions to the D-parameter distribution. Note that for small particles the distribution width ΔD becomes remarkably larger than the average |D|. As the powder line position depends only on D^2 [see Eq. (6)] this situation means a strongly asymmetric distribution of D^2 ranging from approximately zero with the highest probability up to $(|D| + \Delta D)^2$. The resulting fine structure values |D|



FIG. 17. Simulation of the dependence of the cubic Mn^{2+} spectrum intensity on temperature and mean particle size (again assuming a broad particle size distribution—cf. text).

 $+\Delta D$ clearly exceed the pertinent bulk value, thus providing clear evidence of subregions with strong distortions going beyond the ferroelectric tetragonal unit cell deformation of the bulk. Consequently, the ΔD values measured for the 25 nm and 15 nm grains indicate strong local distortions which have nothing to do with the limited tetragonal distortions occurring in the ferroelectric phase but are caused by distortions.

Of particular interest is of course the extent to which our simulation can reproduce the measured intensity decrease of the cubic Mn^{2+} spectrum (cf. Fig. 14) when going either to a lower temperature or a smaller mean particle size in the vicinity of the apparent Curie temperature T_C^a . In particular, the same broad particle-size distribution has to be assumed (with the width again being 80% of the mean size; as for the results; see Fig. 17). A detailed inspection of the temperature-dependent intensity of the cubic Mn²⁺ EPR spectrum (Fig. 14) reveals, for the finest nanopowders, the most intense cubic remnants below T_C^a and, vice versa, the weakest intensities above T_C^a . Starting from the assumed geometrical size distribution, the effect of a distorted outer layer was accounted for by estimating the cubic volume fractions $p_{cub}(T,d^0)$ of the sufficiently small particles using the numerically ascertained size dependence of the ferroelectric transition temperature (cf. Fig. 3):

$$p_{cub}(T,d^0) \propto \int_0^{x_{crit}(T)} \exp\left[-\left(\frac{x-d^0}{\sqrt{2}\sigma}\right)^2\right] (x-d_r)^3 dx.$$
(14)

In Eq. (14), d^0 is the mean particle size in the nanopowder, d_r the thickness of the distorted surface layer, and $x_{crit}(T)$ the inverse function of the size-driven phase transition temperature. Conformity with the experimental results, especially for the decreasing EPR intensity with lower particle size, has been achieved on the presupposition that the manganese ions in this particular surface layer make no contribution to the cubic spectrum because of the heavy distortions

of translational symmetry going far beyond the ones expected in the tetragonality gradient layer of the generalized Landau theory. The thickness of this distorted layer has been estimated at about 15 nm for all nanopowders under investigation. Because of the dominant role of the grain-size distribution in the discussion of the spectroscopic data of nanopowder samples, the greatest progress in future work will have to be achieved with regard to size homogeneity, either in a direct way by further optimizing the preparation route or, alternatively, by size fractionation with the aid of gel permeation chromatography.

Our picture of a small particle as an aggregate of inner regular core and heavily distorted outer layer mediated by a tetragonality gradient (cf. the so-called tetragonal anisotropy defect¹⁰) is largely consistent with the one presented by An-liker *et al.*⁴² who devised from their x-ray scattering and surface-sensitive electron scattering experiments a quite similar two-component model. The detailed structure and nature of the nonferroelectric outer layer is unknown.

Finally one should mention the consistency of the present EPR data with preceding studies¹ of these particular topics, carried out with the aid of vibrational (FT-Raman) and nuclear magnetic resonance (137 BaNMR) spectroscopy. In the Raman investigations, it was particularly the tetragonal spectral feature at 309 cm⁻¹, and in NMR a line broadening due to axial nuclear quadrupole coupling, which corroborated the present idea of small BaTiO₃ particles according to which they are formed by an inner regular tetragonal core, a strongly distorted surface layer, and a mediating tetragonal gradient layer between them.

VI. CONCLUSIONS

We have used XRD measurement and EPR spectroscopy in combination with numerical calculations based on Landau theory to study the size effects of ferroelectric BaTiO₃ nanoparticles. Owing to the highly local character of its information, EPR spectroscopy in conjunction with SHG and Raman measurements, reveals the existence of a locally acentric surface layer at room temperature with about 15 nm thickness surrounding the crystalline bulk. Sufficiently large particles consist of a regular ferroelectric core with a tetragonality gradient towards the heavily distorted (15-nm-thick) outer layer. With decreasing particle size this surface layer increasingly determines the properties of the grains. The tetragonal distortion measured by XRD and EPR can be systematized by Landau theory only on the presupposition of a pronounced grain-size distribution. In future work, the most progress can be attained by improving the size homogeneity of the nanopowder samples.

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