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BRIEF REPORTS

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Surface relaxation in ferroelectric perovskites

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Lattice relaxation on the surface of PbTiO_3 and BaTiO_3 is investigated under the assumption that the spurious lattice expansion in perovskite nanocrystals is caused by the surface relaxation. By comparing the observed peak position and full width at half maximum with those of the calculated x-ray diffraction patterns from a cubic lattice containing surface relaxation, the maximum relaxation on the surface of PbTiO_3 is found to be 0.035 nm, and 0.015 nm for BaTiO_3 . The relaxation is decreased to $1/e$ at 1.5 layers in PbTiO_3 and 8 layers in BaTiO_3 . These values are consistent with the extrapolation lengths predicted by a modified Landau theory explaining the size effect on the phase transition temperature. [S0163-1829(99)11341-9]

Finite-size effects in ferroelectric nanoparticles have attracted renewed interest, giving information on the smallest size limit to make a computer simulation of the phase transition in electric dipole systems or on the upper limit of the density of nonvolatile ferroelectric memories in practical applications.

Känzig and co-workers studied the size effect in ferroelectric fine particles of potassium dihydrogen phosphate and barium titanate (BaTiO_3) in the 1950s.¹⁻³ They predicted the existence of a critical size below which no spontaneous polarization could occur. Considering the depolarization field effect in the film, Batra *et al.* proposed a model and predicted that T_c decreased as the film thickness decreased.⁴ By Raman scattering, Ishikawa *et al.* found a steep drop of T_c with decreasing the size of lead titanate (PbTiO_3) fine particles and pointed out that the ferroelectric state was unstable in PbTiO_3 particles less than 11 nm in diameter.⁵ The critical size for BaTiO_3 has been investigated by many research groups and the reported values range from 15 to 100 nm, generally larger than that for PbTiO_3 .⁶

Phenomenological models to describe the size effects in ferroelectric thin films based on Landau theory have been developed by adding the surface contribution to the usual expansion of the free energy F in terms of the electric polarization P for a first-order displacive ferroelectrics. The following is the simplest form of such an expression:

$$F = \int \left[\frac{1}{2} A (T - T_{c\infty}) P^2 + \frac{1}{4} B P^4 + \frac{1}{6} C P^6 + \frac{1}{2} D (\nabla P)^2 \right] dv + \int \frac{1}{2} D \delta^{-1} P^2 dS, \quad (1)$$

where $T_{c\infty}$ is T_c of the bulk crystal.⁷ The designations A , B , C , and D are parameters which should be determined by experiments. The last term describes the surface effects and δ is the extrapolation length by which one takes the surface effect into account phenomenologically. The magnitude of the polarization must satisfy the Euler-Lagrange equation and the following boundary condition to minimize the free energy:

$$\left. \frac{\partial P}{\partial x} \right|_{\text{surface}} = - \frac{P_{\text{surf}}}{\delta}, \quad (2)$$

where P_{surf} is the polarization on the surface. Extending the phenomenological model to a spherical case, Zhong *et al.* explained the observed shift of T_c in PbTiO_3 and BaTiO_3 fine particles.⁸ They obtained

$$\begin{aligned} \delta &= 3 \text{ nm for } \text{PbTiO}_3, \\ \delta &= 43 \text{ nm for } \text{BaTiO}_3, \end{aligned} \quad (3)$$

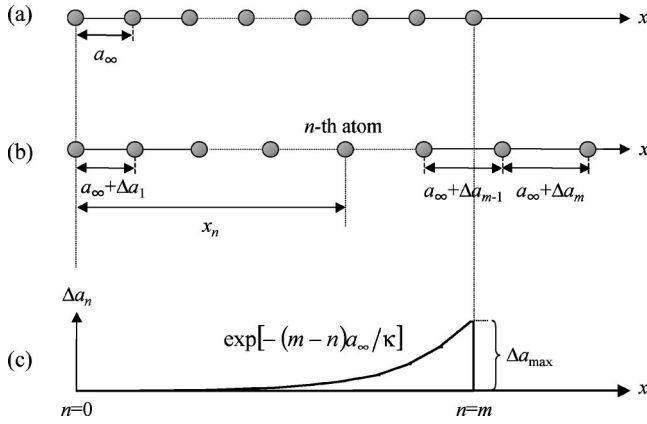


FIG. 1. Schematic illustration of the lattice relaxation in the positive half of a linear chain: (a) without relaxation and (b) with relaxation. The relaxation is assumed to be maximum at the surface and changes exponentially with distance from the surface. (c) The change of the relaxation is shown vertically for visual convenience.

by the best fit of their theoretical calculations to the experimental results. The phenomenological theory concludes that the shift of T_c towards a low temperature by decreasing size is accompanied by a reduction of the polarization in the surface region. What causes the spatial distribution in the polarization? It could be, for example, the surface relaxation of the crystal lattice and/or the change in the local electric field at the surface. We believe the surface relaxation is one of the most important factors. It is, however, very difficult to observe the relaxation extending to several layers below the surface with low-energy electron diffraction (LEED), for example, due to the multiscattering effect of electrons.

In this paper, we propose a very simple method to estimate the surface relaxation by using ultrafine particles as a sample. The lattice parameters of PbTiO_3 or BaTiO_3 fine particles measured by x-ray diffraction (XRD) are known to increase with the decrease of the particle size.^{9,10} We regard this expansion as caused by the lattice relaxation on the surface. The spurious expansion of the lattice thus occurs due to the increase of the contribution of the relaxed surfaces in small particles. Since the size of the fine particles is usually determined by Scherrer's equation in which one assumes the crystal to be homogeneous, the relation cannot be used to estimate the size of the particle containing relaxation. Therefore, we made rigorous calculations of XRD patterns from the lattice with various magnitudes of surface relaxation and compared them with experiments to determine the real magnitude of the surface relaxation and its distribution below the surface. It is not necessary to use any expensive apparatus but a flask, some chemicals, a conventional x-ray diffractometer, and a personal computer.

An XRD pattern from a particle was obtained from the calculation by taking a cube composed of equivalent N^3 atoms. The scattered radiation was summed over all the atoms in the cube associated with the lattice relaxation on the surface. We first consider a linear chain of $N=2m+1$ atoms separated by a_∞ , the lattice constant along the a axis in the bulk, as shown in Fig. 1(a). Our assumption is that the relaxation occurs along the a axis, taking the maximum value ($=\Delta a_{\max}$) on the surface, and decreases exponentially with distance from the surface as shown in Figs. 1(b) and 1(c). Let us

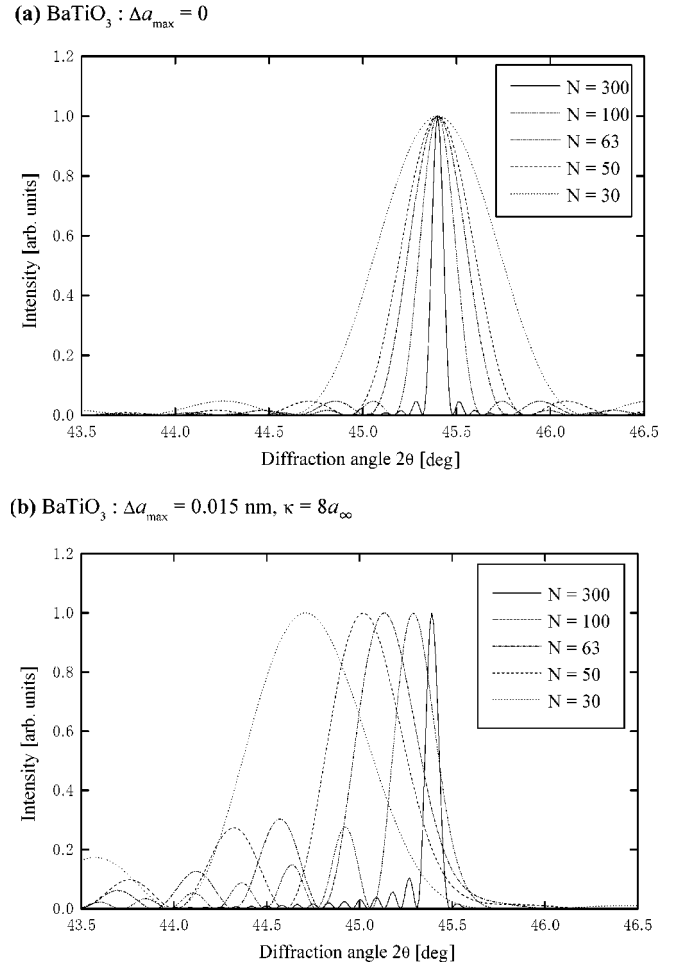


FIG. 2. Some examples of the calculated patterns for BaTiO_3 in case of (a) $\Delta a_{\max}=0$ and (b) $\Delta a_{\max}=0.015$ nm and $\kappa=8a_\infty$, for various N .

take the origin $n=0$ to be the center of the chain. Then the $\pm m$ th atoms are at both ends. We assume that the relaxation of n th atom from the center is expressed as

$$\Delta a_n = \Delta a_{\max} \exp[-(m-n)a_\infty/\kappa] \quad (0 < n \leq m), \quad (4)$$

where κ , named the ‘‘relaxation length’’ here, is a parameter which is a measure of the decay of relaxation from the surface. This situation is shown in Fig. 1(c) where the relaxation is drawn vertically for convenience. The position of the n th atom x_n is expressed as

$$\begin{aligned} x_n &= \sum_{j=1}^n (a_\infty + \Delta a_j) \\ &= na_\infty + \Delta a_{\max} \exp[-(m-1)a_\infty/\kappa] \\ &\quad \times \frac{1 - \exp(na_\infty/\kappa)}{1 - \exp(a_\infty/\kappa)} \quad (0 < n \leq m). \end{aligned} \quad (5)$$

Next, we consider a cube, three-dimensional lattice with relaxation. For example, the x-ray intensity scattered from the (200) plane is expressed as

$$I = \frac{f_c}{|\mathbf{R}|^2} \left| \sum_{n=-m}^m \exp \frac{2\pi i}{\lambda} (2x_n \sin\theta) \right|^2. \quad (6)$$

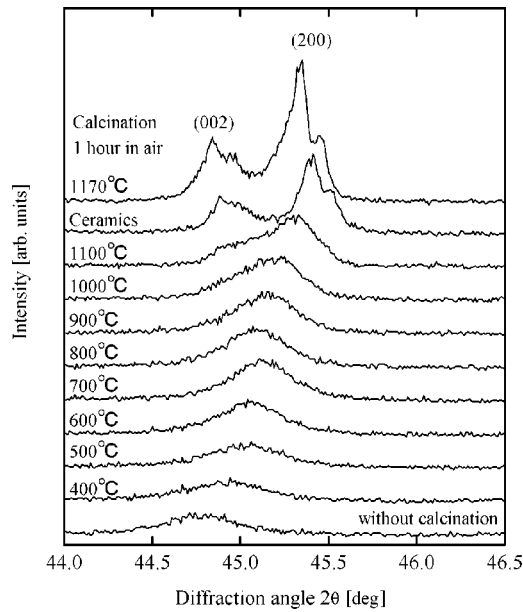


FIG. 3. XRD patterns from BaTiO₃ fine particles for various calcination durations.

Intensities were numerically calculated for various values of Δa_{\max} , κ , and N , using this expression. The dependence of the peak position $2\theta_{\text{calc}}$ and the full width at half maximum (FWHM) β_{calc} on N were derived for different values of Δa_{\max} and κ . Figure 2 shows an example of the calculated patterns for BaTiO₃ in the cases of (a) $\Delta a_{\max}=0$ and (b) $\Delta a_{\max}=0.015$ nm, and $\kappa=8a_{\infty}$, for various N . Then, the calculated values of $2\theta_{\text{calc}}$ and β_{calc} were compared with those obtained experimentally for samples with different size to determine Δa_{\max} and κ .

In our experiments, fine particles of PbTiO₃ and BaTiO₃ were obtained by hydrolyzing each mixture of the constituent alkoxides. Precipitates of PbTiO₃ were calcined in the air at 450 °C for various durations to control the average particle size. BaTiO₃ powders were calcined at temperatures from 400 to 1100 °C for 1 h. The ratio of the standard deviation of the particle size distribution to the average diameter was

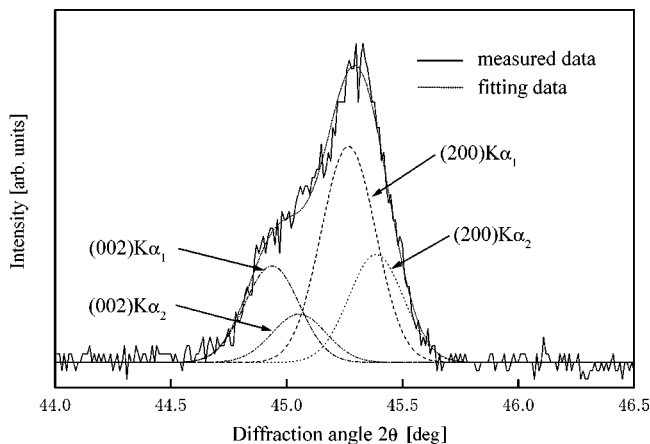
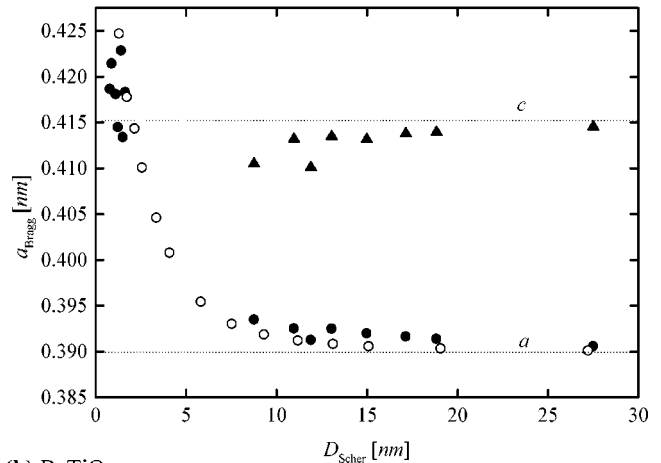


FIG. 4. Illustration of peak separation procedure. An observed peak was separated into four peaks. Each peak shape was assumed to be Gaussian. We also assumed that the intensity ratio of $K\alpha_1$ to $K\alpha_2$ of Cu was 2:1.

(a) PbTiO₃



(b) BaTiO₃

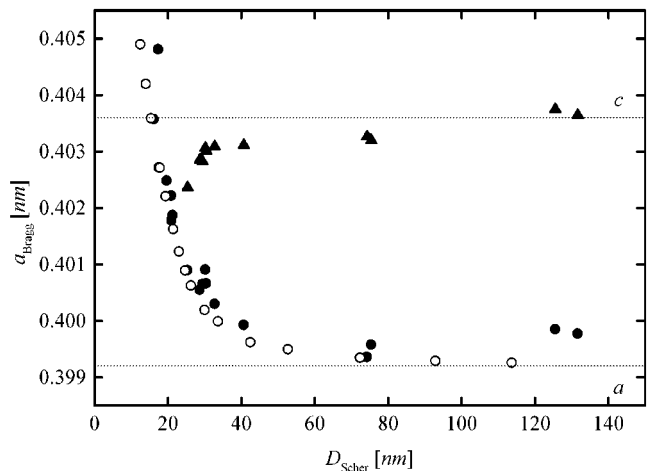


FIG. 5. Effective lattice parameter a_{Bragg} of (a) PbTiO₃, and (b) BaTiO₃ nanoparticles as a function of the effective diameter $D_{\text{Scher}} \equiv K\lambda/(\beta \cos \theta)$ along the a axis (solid circle) and c axis (solid triangle). Open circles were obtained by the calculation (see text). Dotted lines denote the bulk lattice constants.

from 0.1 to 0.2. Details were described in our previous paper.¹¹ Figure 3 shows the XRD patterns from BaTiO₃ fine particles for various calcination durations. Similar patterns were obtained for PbTiO₃ which were reported elsewhere.¹⁰ Figure 4 is an example of the peak separation. In this case, the observed peak should be separated into four peaks, which are composed of (002) and (200) diffraction peaks, each containing a contribution from $K\alpha_1$ and $K\alpha_2$ components of Cu target. We assumed that the shape of each peak was Gaussian type and the intensity ratio of $K\alpha_1$ to $K\alpha_2$ was 2:1. The FWHM and the peak position of each pattern were determined after the peak separation procedures. We obtained a set of the peak position and FWHM for the sample with different particle sizes.

Figures 5(a) and 5(b) show the change in the “effective lattice parameter” a_{Bragg} along the c axis (solid triangle) and a axis (solid circle) as a function of the “effective diameter” D_{Scher} obtained from samples with various particle sizes, where the former was determined by the Bragg condition, the latter by Scherrer’s equation $D_{\text{Scher}} = K\lambda/(\beta \cos \theta)$. The quantity λ is the wavelength of the x ray, 2θ the peak posi-

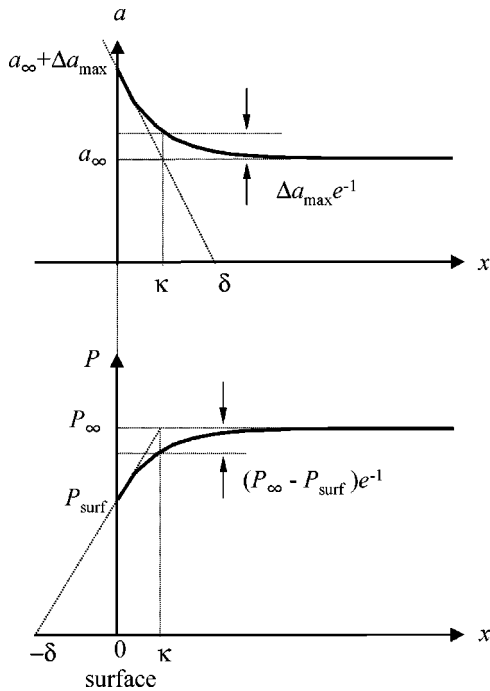


FIG. 6. Schematic illustration of the extrapolation length δ and the relaxation length κ derived by assuming both the derivatives of a and P on the surface to be equal.

tion of the XRD pattern, β the FWHM, and K the Scherrer constant ($= 0.9$). The reason for using the term “effective” is that both the Bragg condition and Scherrer’s equation assume a perfect crystal lattice and are not suitable for the crystal with relaxation. They only give the approximate lattice parameters and the diameters for particles with lattice relaxation.

We have determined the maximum relaxation Δa_{\max} and relaxation length κ by curve fitting with experimental data. The calculated results are shown by open circles in Fig. 5. The values giving the best fit are $\Delta a_{\max} = 0.035$ nm, $\kappa = 1.5a_{\infty}$ ($a_{\infty} = 0.390$ nm) for PbTiO_3 and $\Delta a_{\max} = 0.015$ nm, $\kappa = 8a_{\infty}$ ($a_{\infty} = 0.399$ nm) for BaTiO_3 .

The magnitude of the relaxation in PbTiO_3 is 9% of the bulk lattice constant and 3.8% in BaTiO_3 . The relaxation decreases to $1/e$ at 1.5 layer in PbTiO_3 and at the eighth layer in BaTiO_3 .

Jian *et al.* investigated the surface structures of BaTiO_3 particles by high-resolution transmission electron microscopy (HRTEM).¹² They reported that there might be a sur-

face relaxation of 10% outward in the (100) plane. They mentioned, however, that possible errors due to fringe shifts exist. Dorfman *et al.* investigated the surface relaxation of cubic BaTiO_3 by using the shell model and found that the Ba ion in the top layer of (001) moved inside of the crystal by 3.7% and the oxygen ion moved outside by 1%.¹³ Landree *et al.* studied the surface relaxation in MgO (100) surfaces by grazing incidence x-ray diffraction and found that the surface relaxed inward by 0.56% of the lattice constant.¹⁴ At present, there are not any definite results on the surface relaxation.

Next, we compare our results with the extrapolation lengths reported by Zhong *et al.* [see Eq. (3)]. The extrapolation length is defined by Eq. (2) which implies that the tangent line to P on the surface intersects with the x coordinate at $-\delta$. On the other hand, the relaxation length κ is defined as the distance from the surface to the point where the deviation of the lattice parameter from the bulk value decreases to $1/e$ from the maximum on the surface as shown in the lower part of Fig. 6. We are not able to calculate the change in the polarization from Δa_{\max} and κ because knowledge of the positions and effective charges of each ion is necessary to calculate the polarization. However, it is natural to assume that the deviation of the polarization from the bulk value P_{∞} changes with distance from the surface exponentially and that the absolute values of two derivatives of a and P on the surface are equal. Then, we can estimate the extrapolation lengths from the relaxation lengths as follows:

$$\delta = 7 \text{ nm for PbTiO}_3,$$

$$\delta = 88 \text{ nm for BaTiO}_3.$$

These values are in good agreement with the extrapolation lengths given in Eq. (3).

We regard that the difference in the relaxation between PbTiO_3 and BaTiO_3 originates from the difference in the depth of the potentials of the Ti ion.¹⁵ The difference should be related to cooperative phenomena in the dipole system. We believe that the technique developed in this study is useful to study the relaxation which expands over several layers below the surface and the results obtained in this work throw light on a microscopic understanding of the size effects in ferroelectrics, although some simplified assumptions are used.

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