

Size effect on the ferroelectric phase transition in PbTiO_3 ultrafine particles

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We report a size effect on the ferroelectric phase transition in PbTiO_3 ultrafine particles. The samples were synthesized by an alkoxide method. The size was determined by x-ray analysis with the aid of Scherrer's equation. When the particle size is less than 50 nm, the transition temperature T_c , determined by Raman scattering, decreases from its bulk value (500 °C) as the size decreases. The temperature T_c is described by an empirical expression, $T_c = 500 - 588.5/(D - 12.6)$ (°C), where D is the average particle size (nm).

I. INTRODUCTION

Size effects on the ferroelectric phase transition have been investigated theoretically¹⁻⁵ and experimentally^{6,7} for a long time since Känzig *et al.* studied dielectric properties of ferroelectric fine particles.^{8,9} It is quite natural that small ferroelectric particles or thin films show different dielectric properties from those of bulk crystals because the long-range Coulomb force plays an important role in them.

Känzig and co-workers extensively studied the dielectric properties of potassium dihydrogen phosphate (KDP)⁸ and BaTiO_3 (Ref. 9) fine particles by x-ray and electron diffraction. According to them, KDP fine particles embedded in an insulating medium show no ferroelectric phase transition if the size is less than 150 nm, while the transition temperature T_c of BaTiO_3 increases as the particle size decreases. They attributed the change of the ferroelectric properties in fine particles to the presence of domain walls or surface layers.

Batra *et al.* have shown the phase transition in ferroelectric thin films is strongly affected by depolarization fields.¹ Their phenomenological discussion on the ferroelectrics shows that the Curie temperature shifts towards lower temperature as the thickness of the film becomes small.

These studies have clarified many problems concerned with the size effects on the ferroelectric phase transition. But microscopic knowledge about this problem, such as the soft-mode behavior, has not yet been obtained. The main aim of this paper is to give experimental information about the problem.

II. EXPERIMENTS

In recent years, a new method called the alkoxide method has been developed to synthesize ultrafine particles of ionic crystals including metal oxides as small as several tens of nanometers.¹⁰ This enables us to obtain small particles with fewer mechanical distortions and to study the size effect on the phase-transition properties in ferroelectrics.

The sample was synthesized by hydrolyzing a stoichiometric mixture of a solution of titanium tetraisopropoxide in isopropyl alcohol and that of lead isopropox-

ide in isopropyl alcohol, both with concentration of 10 wt.%. By sintering the precipitate at a temperature higher than 600 °C in the air, we have obtained crystalline PbTiO_3 fine particles. The particle size increases with the rise of sintering temperature.

The average size was determined from the full width at half maximum (FWHM) of the x-ray diffraction peak using Scherrer's equation¹¹

$$D = K\lambda / (B \cos\theta) , \quad (1)$$

where D is the particle diameter, λ the x-ray wavelength, B the FWHM of a diffraction peak, (101) in our case, θ the diffraction angle, and K is the Scherrer's constant of the order of unity for usual crystals.¹¹ The value of the FWHM includes errors originated from noises and the apparatus conditions such as the slit width of the x-ray diffractometer. Since samples including lead generally give weak x-ray signals, we adopted smoothing procedure to eliminate the noises. In general, it is difficult to calculate deconvolutions when observed signals have noises of high level. We therefore estimated the particle size by assuming a Gaussian-type distribution for the diffraction line. The observed spectra were separated into two peaks originated from $K\alpha_1$ and $K\alpha_2$ lines of Cu target, by a curve-fitting procedure. The FWHM of the peak obtained was compared with that calculated from a diffraction pattern of large particles, 1 μm in size, using the Scherrer's equation. We can regard the system transfer function as a δ function when the sample size is sufficiently large. The calculated size of our specimens ranges from 22 to 52 nm.

Figure 1 shows an electron micrograph of the sample of size 22 nm determined by the x-ray diffraction. The stripe pattern in the enlarged picture must be Moiré fringes formed by the crystal lattice since the distance of the adjacent lines estimated from the picture is around 1.5 nm, 4 times larger than the lattice constant of PbTiO_3 . The particle size estimated from the picture is about 60 nm and is different from the value calculated by the x-ray analysis. Twin structure, often found in some microcrystals, might be present in this material and cause the disagreement in sizes. The line broadening of x-ray patterns is mainly due to small particles while the electron microscopic observation tends to overlook the smaller particles. This might cause the disagreement. Generally, overestimation of

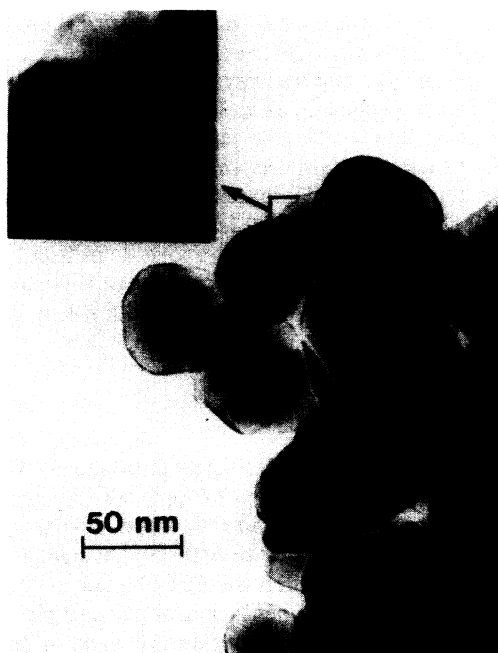


FIG. 1. Electron micrograph of PbTiO_3 fine particles used in the experiments. At the corner of the picture, an enlarged picture of Moiré fringes is shown.

more than 30% is possible when the distribution of the sample size has a Gaussian type.¹²

We studied the soft-mode behavior of PbTiO_3 fine particles in the tetragonal ferroelectric phase by Raman scattering measurements with a backscattering arrangement. An Ar laser at 514.5 nm was used as an exciting light source. The output of the laser was carefully chosen to eliminate the local heating of the sample due to the laser irradiation since the temperature rise turned out to be more significant in smaller particles. The dependence of the soft Raman line on the laser power suggests the temperature rise of order 1°C for the laser power of 5 mW. The temperature of the sample was controlled within $\pm 1^\circ\text{C}$.

III. RESULTS

Raman spectrum of PbTiO_3 of $1\ \mu\text{m}$ has almost the same profile and the same temperature dependence as that of a bulk crystal.^{13,14} Figure 2 shows a Raman spectrum of PbTiO_3 fine particles having average size of 28 nm. We can observe a soft mode, designated as $E(1\text{TO})$ by Burns,¹³ shifting towards a low-frequency region with decreasing temperature. All Raman lines become inactive in the paraelectric region where the crystal has cubic symmetry. Even very small particles such as 22 nm show a well-defined soft-mode line at lower temperature. Soft-mode peaks can be clearly separated by subtracting the Rayleigh component from the observed spectrum when the shape of the Rayleigh scattering is assumed as a Lorentzian line profile. The line shapes, however, become

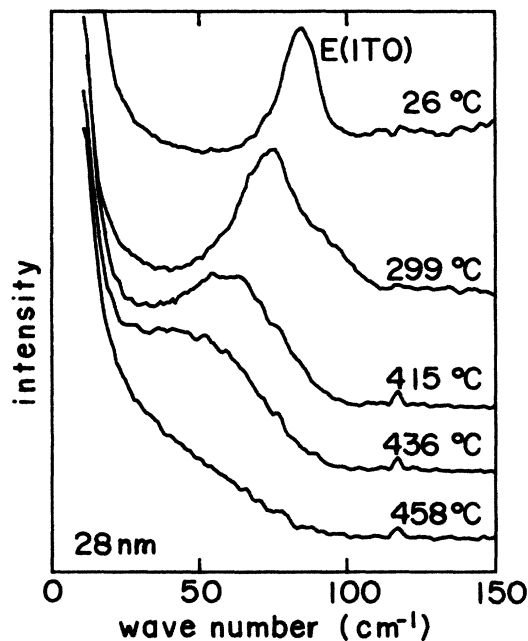


FIG. 2. Raman spectrum of PbTiO_3 fine particles at various temperatures (particle size 28 nm).

broad as the temperature approaches T_c . The soft-mode frequencies and the damping factors were determined by assuming a damped oscillator model following Burns *et al.*¹⁴ The frequencies of soft $E(1\text{TO})$ mode are plotted in Fig. 3 as a function of temperature for various particle sizes. The Raman shift of the soft $E(1\text{TO})$ mode in the samples larger than 52 nm coincides with that in the bulk crystal obtained by Burns *et al.* within experimental er-

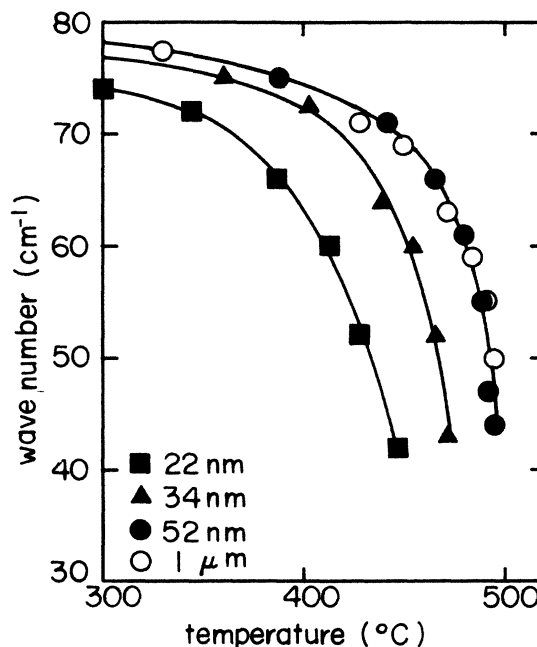


FIG. 3. Temperature dependence of the soft $E(1\text{TO})$ mode frequency in PbTiO_3 fine particles of different size.

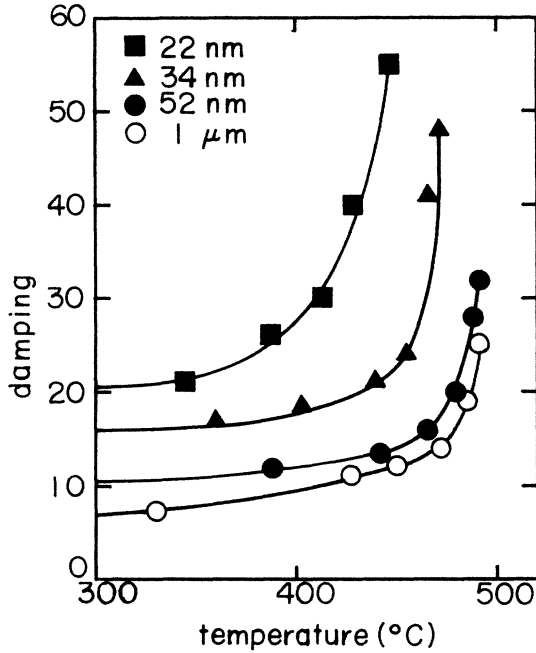


FIG. 4. The damping factors of PbTiO_3 fine particles of different size.

rors. The lattice vibration of smaller particles is softer than that of larger ones because the soft-mode frequency at an arbitrary temperature decreases as the size decreases. Other modes, $E(2\text{TO})$ and $A(1\text{TO})$, show similar size dependence at $E(1\text{TO})$ while the "silent mode" observed at 290 cm^{-1} does not depend on the size. The change in the damping factor of the soft $E(1\text{TO})$ mode is shown in Fig. 4. The damping factor increases near T_c . Smaller particles have larger damping factors.

IV. DISCUSSION

According to Känzig *et al.*, the transition temperature of BaTiO_3 fine particles increases as their size decreases. They attributed the increase to the presence of a surface layer having a higher transition temperature. But our results obtained by Raman scattering show well-defined soft-mode lines which can be assigned to the bulk phonon lines and should not originate from the surface layer. Therefore, the decrease of T_c observed in our experiments may be due to a different mechanism.

Batra *et al.* have pointed out that the ferroelectric phase in ferroelectric films, for example, 10^{-5} cm thick, becomes unstable by the presence of strong depolarization fields if the surface charges due to the polarization are not fully compensated and that below "transition length," the polarizations are not stable. According to them, the transition temperature $T_c(D)$ in thin films with thickness D varies as $\Delta T_c(D) \equiv T_c(\infty) - T_c(D) \propto 1/D$ when the depolarization field is compensated.

There seems to be no general theory at the present stage to describe the size effects in three-dimensional ferroelectric fine particles. We therefore assume the similar depen-

dence to the two-dimensional thin film case, where ΔT_c is in inverse proportion to the sample size. Figure 5 shows the change of T_c , the temperature at which the soft $E(1\text{TO})$ line disappears, as a function of particle size. The transition temperature of particles larger than about 50 nm is almost the same as that of bulk crystals. The transition temperature decreases as the particle size decreases below 50 nm. The difference $\Delta T_c(D) \equiv T_c(\infty) - T_c(D)$, similar to the above definition but the parameter D is the average particle size in this case, can be expressed by the following equation with fitting parameters C and D_{crit} ,

$$\Delta T_c(D) = C/(D - D_{\text{crit}}) . \quad (2)$$

The solid line in Fig. 5 is the value obtained by Eq. (2) with $C = 588.5^\circ\text{C nm}$, $D_{\text{crit}} = 12.6\text{ nm}$. We assume here T_c of PbTiO_3 bulk crystal is 500°C , since reported values of T_c scatter in the range 490 to 510°C .¹⁵ We regard D_{crit} as a critical size below which the ferroelectricity becomes unstable. The charge compensation in our sample should be insufficient because the samples are kept in the air. According to Batra *et al.*, the ferroelectric phase is known to be unstable if the compensation is insufficient. For the explanation of the size effect, we are expecting a new model applicable to ferroelectrics in three dimensions.

A different viewpoint may be possible for small particles in which the interaction length is comparable to the sample size. All the ferroelectric soft modes are of TO type because the depolarization field associated with LO phonons suppresses the local field. But in particles smaller

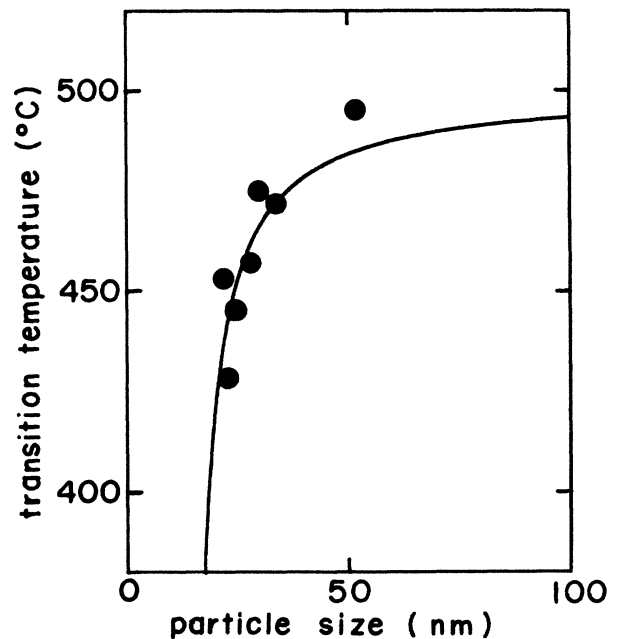


FIG. 5. The transition temperature, at which the Raman line disappears, vs the particle size; observed values are denoted by full circles, the solid curve is obtained by an empirical expression $T_c = 500 - 588.5/(D - 12.6)$ ($^\circ\text{C}$), where D is the particle diameter in nm.

than the Coulomb interaction length, the depolarization field should work also in TO phonon mode. This obscures the increase of the local field due to the Lorentz field. Lorentz correction term should have less contribution in smaller particles because the dipole summation runs over a limited volume. These might cause the disappearance of the ferroelectric phase transition.

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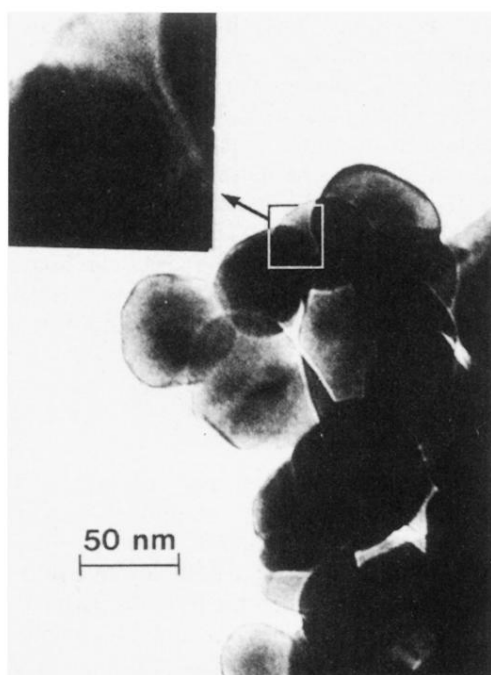


FIG. 1. Electron micrograph of PbTiO₃ fine particles used in the experiments. At the corner of the picture, an enlarged picture of Moiré fringes is shown.