Phase transition in PbTiO$_3$ ultrafine particles of different sizes

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Abstract. The size effect on the ferroelectric phase transition in PbTiO₃ ultra-fine particles is reported. Samples with particle sizes from 20 to 200 nm were prepared by a sol–gel process followed by calcining at different temperatures. The particle size was determined by x-ray diffraction from the integrated width of diffractions. The soft-mode frequency at room temperature was measured by Raman scattering. It decreases with decreasing particle size. The ferroelectric phase transition was traced by specific-heat measurement. The transition temperature decreases and the transition becomes diffused as the particle size decreases. The size dependence of T_C can be described by $T_C(D) = 766 - 256/(D - 8.8)$ (K), where 766 K is the T_C for bulk PbTiO₃ and D (nm) is the particle size. This equation gives a critical size of 9.1 nm below which ferroelectricity disappears.

1. Introduction

The dependence of ferroelectric behaviour on the particle or grain size has been investigated for a long time ever since the 1950s [1–13]. However, many of the earlier experiments were performed on sintered ceramics, mechanically ground powder or particles embedded in some other matrix. They were complicated by additional effects due to grain boundaries or internal stress, and usually the grains or particles were not sufficiently small. In order to study the finite-size effect straightforwardly, isolated, ultrafine and homogeneous particles are required. They have been available only in recent years owing to advanced ultrafine powder synthesis techniques. Using these particles, Ishikawa *et al* [9] investigated the size effect on the ferroelectric phase transition in PbTiO₃, and Uchino *et al* [10] studied it in BaTiO₃. For particle samples, measurement of the electrical properties is difficult; hence Raman scattering [9] and x-ray diffraction [10] were employed. In the present work, we use specific-heat measurement to trace the phase transition in PbTiO₃ ultrafine particles derived from the sol–gel process. In addition, Raman scattering was also used to study the size dependence of the soft-mode frequency at room temperature.

2. Experimental details

The ultra-fine PbTiO₃ particles were derived from the sol–gel process. Lead acetate was dissolved in 2-ethoxyethanol at about 80 °C. To eliminate the water associated with lead

acetate, the solution was heated to 120 °C, and then stoichiometric titanate *n*-butoxide was added to the solution. To make the synthesis reaction complete, the solution was heated to 130 °C and then cooled to room temperature. To prepare the powders, water droplets were added to the solution while stirring. With increasing turbidity, the precipitate was washed with water and acetone three times, filtered and then dried at 80 °C for 24 h. The dried powder was calcined at temperatures between 550 and 700 °C for 1 h. Particles of average size 20–200 nm in a pure perovskite structure were thus obtained for different calcining temperatures.

The average size was determined from the integrated width of diffraction peak using Scherrer's equation [14, 15]

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

where D is the size, λ is the wavelength, θ is the diffraction angle, B is the integrated width of a diffraction (100 and 200 in our case) and K is a constant which is near unity for the usual crystals. The integrated width depends on three factors: the apparatus parameters, the $K\alpha_2$ line of the target (Cu, in our case) and the particle size. By comparison with the diffraction of a standard material (Si, in our case), the width due to the apparatus can be eliminated. By use of the modified Ranchinger method, the width due to the $K\alpha_2$ line can be eliminated. Therefore, the true integrated width induced by the particle size can be obtained and the size can be calculated using Scherrer's equation.

The particle size was also observed by TEM. Sizes given by the two methods are in fairly good agreement with each other. As an example, figure 1 shows the transmission electron micrograph of the sample with particle size 30 nm determined by the x-ray diffraction. The magnification was 10^5. From the micrograph, the size is about 35 nm.

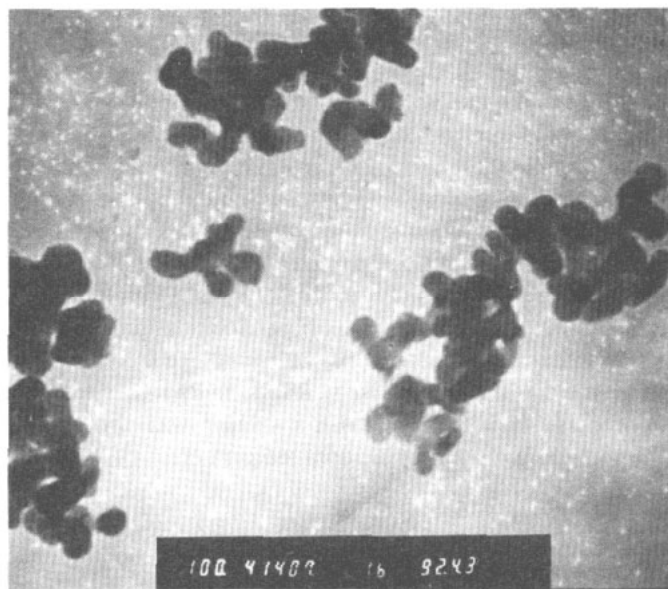**Figure 1.** Electron micrograph of the $PbTiO_3$ ultrafine particles. (Magnification, $10^5 \times$).

Table 1. Size dependence of the soft-mode frequency and the tetragonality c/a.

Average size (nm)	Raman shift (cm^{-1})	c/a
200	85	1.065
115	85	1.064
70	82	1.064
50	81	1.064
30	78	1.062
22	71	1.059
Bulk	89 [16]	1.0652 [20]

The tetragonality c/a was measured by x-ray diffraction at room temperature. It increases with increasing particle size as is shown in table 1.

The soft-mode behaviour was studied by Raman scattering. It was carried out on a Spex 1403 double-grating spectrometer. The light source was an argon ion laser with 5145 Å radiation and a laser output 30 mW. The scattered radiation was measured at an angle of 90° to the incident radiation using a photomultiplier coupled to photon-counting electronics. The spectral width of the slits was about 2 cm^{-1}.

A differential scanning calorimetry (DSC) study was performed in the temperature range from room temperature to 550 °C using a Perkin–Elmer DSC-2 thermal analyser. The sample was encapsulated. The average mass was about 2 mg. Sapphire was used as the standard reference for the specific-heat determination. The linear heating rate was 20 K min^{-1}.

3. Results and discussion

Figure 2 shows the Raman spectra of some PbTiO₃ ultrafine particles of different sizes. The spectra were taken at a resolution of 0.3 cm^{-1}. A soft mode, designated by Burns and Scott [16] as E(1TO) was observed. It was located by subtracting the Rayleigh line component from the observed spectrum assuming that the Rayleigh line is a Lorentzian profile. The assumption was checked experimentally. The soft mode shifts toward a low-frequency region with decreasing size. The lowering of the soft-mode frequency implies a lowering of the phase transition temperature with decreasing particle size. The size dependence of the soft-mode frequency is listed in table 1.

Figure 3 shows the curves of specific heat versus temperature for different-sized PbTiO₃ ultrafine particles. They were obtained in the process of heating. For each particle size, at least three samples were measured. The reproducibility was fairly good. The scatter of the measured peak position temperature increases with decreasing size, but in any case the scatter was less than 6 K. It is seen that the specific-heat peak moves toward lower temperatures as the particle size decreases. The transition temperature was identified with the position of the specific-heat peak. The specific heat is due to the energy associated with the construction (or destruction) of the spontaneous polarization and is an indication of the ferroelectric phase transition. It therefore provides an alternative way of obtaining the ferroelectric phase transition temperature. The lowering of the phase transition temperature with decreasing size is plotted in figure 4.

The same measurement was also carried out during cooling. The peak position temperatures obtained were 5–10 K lower than those obtained during heating. Thermal hysteresis is expected because this transition is first order.
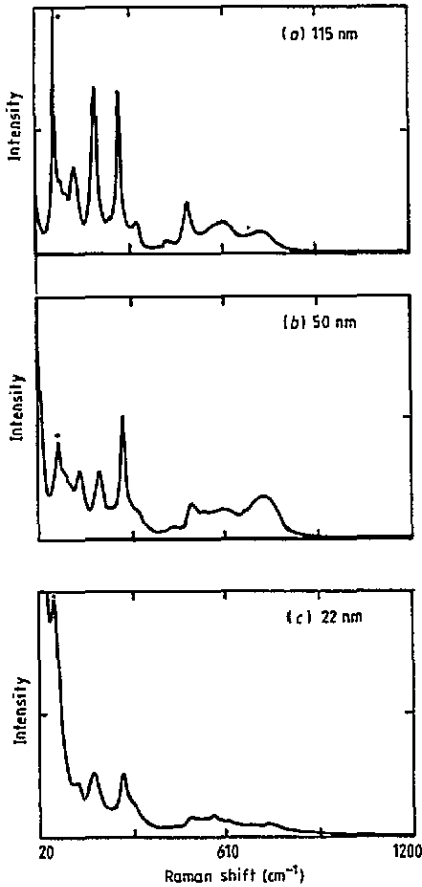
Figure 2. Raman spectra of the PbTiO₃ ultrafine particles. The full circle denotes the soft mode.
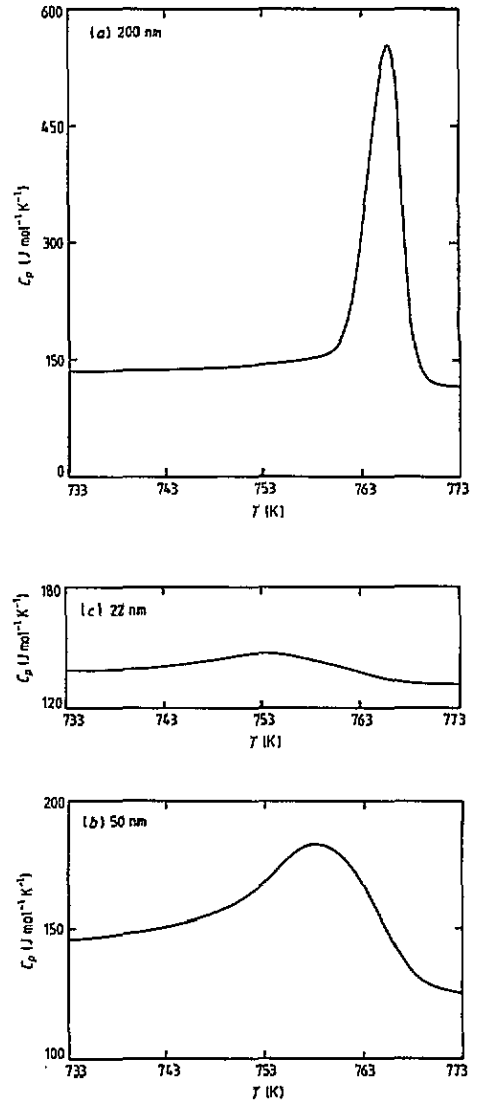
Figure 3. Temperature dependence of the specific heat.

Another feature in figure 3 is that the specific-heat peak is lowered and broadened as the particle size decreases. Integrating the area under the specific-heat peak, one can obtain the heat ΔQ of phase transition and the change ΔS in entropy at the transition given by $\Delta S = \Delta Q / T_C$. The resulting ΔQ versus particle size is shown in figure 5. ΔQ decreases with decreasing particle size, indicating a decrease in the spontaneous polarization. It is therefore expected that, below some critical size, spontaneous polarization will disappear even at low temperatures.

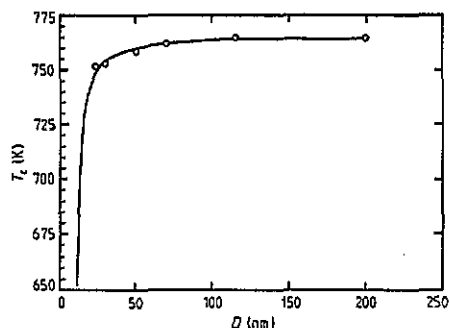The full curve in figure 4 is obtained from the following equation [9]

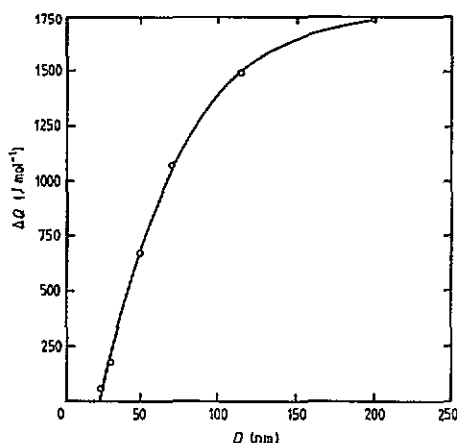**Figure 4.** Size dependence of the phase transition temperature.

Figure 5. Size dependence of the heat of transition.

$$T_C(D) = T_C(\infty) - C/(D - 8.8) \text{ (K)}$$

with $C = 256$ K nm. In this equation, $T_C(\infty)$ is the Curie temperature of the bulk PbTiO₃ which is taken to be 766 K. If we define a critical size D_{crit} as the size at which $T_C = 0$ K, then, from the equation, $D_{crit} = 9.1$ nm.

The above equation was first proposed in [9] but the critical size used in it was 13.8 nm. Apart from other factors, the critical size is very sensitive to $T_C(\infty)$. The $T_C(\infty)$ that we used was 493 °C [17] and that in [9] was 500 °C.

Although there is not yet a quantitative theory describing the size effect in ultrafine ferroelectric particles, qualitative understanding could be obtained from the soft-mode picture. Ferroelectricity is intrinsically a long-range cooperative phenomenon. The 'freezing out' of the soft mode depends on the balance of the short-range force and the long-range Coulomb force [18]. The latter depends on the field E_s due to the dipole summation and the depolarization field E_d. E_s can be expressed in the simplest case as the Lorentz field: $E_s = (4\pi/3)P$, where P is the polarization. E_d is shape dependent and can be written $E_d = -\gamma P$, where γ is a constant. For the TO mode in an infinite crystal, $E_d = 0$ and E_s is strong enough to balance out the short-range force. However, in particles of very small size, E_s is weakened because the dipole summation runs over limited numbers, and $E_d \neq 0$ since the surface can no longer be neglected. When the size reaches the critical value, the long-range force cannot balance out the short-range force even at low temperatures; thus ferroelectricity cannot appear.

The correlation length to sustain ferroelectricity was estimated to be several to tens of nanometres [19]. The critical size obtained in this work is in this region.

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