### **Iowa State University**

From the SelectedWorks of Alexander H. King

March, 2005

## Size-driven domain reorientation in hydrothermally derived lead titanate nanoparticles

Zhiyuan Ye, *Purdue University* Elliot B. Slamovich, *Purdue University* Alexander H. King, *Purdue University* 



Available at: https://works.bepress.com/alex\_king/30/

# Size-driven domain reorientation in hydrothermally derived lead titanate nanoparticles

Zhiyuan Ye, Elliott B. Slamovich,<sup>a)</sup> and Alexander H. King School of Materials Engineering, Purdue University, West Lafayette, Indiana 47907-2044

(Received 11 October 2004; accepted 22 December 2004)

High-resolution transmission electron microscopy studies of hydrothermally derived platelike lead titanate nanoparticles reveal that below a critical size of approximately 70 nm, the single ferroelectric domain polarization axis reorients from perpendicular to parallel to the plate. We suggest that during particle growth, ions in the hydrothermal processing medium compensate for the ferroelectric depolarization energy. When the processing medium is removed by washing and drying, single domain nanoparticles minimize their depolarization energy by *c*-axis flipping.

The effects of particle size on ferroelectricity in perovskites have been known since the 1950s.<sup>1,2</sup> Due to the application of ferroelectric perovskites in nonvolatile memory,<sup>3,4</sup> the size effects in ferroelectric materials have been extensively studied experimentally<sup>5–12</sup> and theoretically.<sup>13–19</sup> Research has focused on size effects on the Curie temperature, spontaneous polarization, dielectric response, and phase stability. As the grain size decreases, the Curie temperature and the spontaneous polarization typically decrease.<sup>5,7,8,10,17</sup>

In recent years, new synthesis technologies have made it possible to study size effects in isolated nanocrystalline particles. For example, as the particle size in ZrO<sub>2</sub> decreases to the nanometer range, the high-temperature tetragonal phase becomes stable at room temperature.<sup>20</sup> Similar phenomena have been reported for ferroelectric perovskites. Bulk BaTiO<sub>3</sub> has a Curie temperature of about 130 °C. However, the paraelectric phase is stable at room temperature for particles less than a critical size ranging from 30 to 115 nm, depending on the study.<sup>7,9,11</sup> The critical size of PbTiO<sub>3</sub> ranges from 7 to 13.8 nm in experimental studies<sup>5,8,10,21</sup> and 4.2 nm according to a theoretical model.<sup>17</sup> In nonferroelectric systems, sizedriven phase transitions may be attributed to the large surface energy contribution to the total free energy. Determining the origin of phase stabilization in ferroelectric materials is complicated by spontaneous polarization, the presence of ferroelectric domains, and piezoelectricity. The mechanisms proposed for the size effects in ferroelectric materials, summarized by Frey and Payne,<sup>11</sup> fall into four categories: depolarization effects, correlation

length of ferroelectric interaction, influence of point defects, and elastic constraints. Also, the surface layers of ferroelectric particles may behave differently from the ferroelectric core.<sup>17</sup> Recent work suggests that depolarization effects may dominate phase stabilization,<sup>22–25</sup> as indicated by the observation that individual nanoscale BaTiO<sub>3</sub> particles were observed in the cubic paraelectric phase, while clusters of the same particles were tetragonal and ferroelectric.<sup>23</sup> Also, coating the same nanoparticles with Cu stabilized the tetragonal phase.<sup>24</sup> Both clustering and coating with a conductive material compensate for the depolarization energy and stabilize the bulk phase.

The majority of research on size effects in ultrafine ferroelectric perovskites has been conducted using nanoparticles prepared by processes requiring a hightemperature calcination step to form crystalline particles.<sup>6,8,10–12</sup> These-high temperature processes have at least four effects. First, the particles will go through the Curie temperature, which might introduce some undesirable residual strain due to the phase transition. Second, the high temperature will also increase the electrical conductivity of the particles and reduce the depolarization effect by compensating the polarization charges through carrier conduction. Third, the particles will typically have a spherical or spherelike polyhedral morphology, eliminating any effects of anisotropy on the depolarization geometry factor. Fourth, particularly for PbTiO<sub>3</sub>, the high-temperature process tends to introduce lead deficiency in the particles, thus altering their properties.

In the present work,  $PbTiO_3$  nanoparticles were synthesized by a hydrothermal process through which high crystallinity and high phase purity can be achieved at temperatures much lower than the Curie temperature of 493 °C. The hydrothermally derived particles used in this

<sup>&</sup>lt;sup>a)</sup>Address all correspondence to this author.

e-mail: elliotts@ecn.purdue.edu

DOI: 10.1557/JMR.2005.0097

study are typically faceted, enabling study of depolarization geometry effects that appear in the form of a novel phase transformation.

Nanocrystalline TiO<sub>2</sub> (P25, Degussa, Dublin, OH) was mixed with lead acetate trihydrate  $[Pb(CH_3COO)_2 \cdot 3H_2O]$ , Aldrich, 99+% purity] at a 1:1 molar ratio, then suspended in 1.0 M aqueous potassium hydroxide (KOH, Mallinkcrodt, 88%, Phillipsburg, NJ) in a Teflon lined autoclave (Model No. 4748, Parr Instrument Co., Moline, IL). The autoclave was then sealed and placed into a preheated force-air oven at 200 °C for reaction under autogenous conditions for 6 h. The suspension was vacuum-filtered and washed repeatedly with CO2-free de-ionized water. The collected powders were dried overnight at 90 °C. The phases of the collected powders were identified by x-ray diffraction (XRD; Siemens D500 diffractometer, New York, NY) using Cu  $K_{\alpha}$  radiation. To characterize the morphology of the nanoparticles, 2-3 mg dried powder samples were dispersed ultrasonically in methanol for 5 min and then collected on carbon films supported on 200 mesh copper grids for investigation by transmission electron microscopy (TEM; JEOL 2000/FX/EX, Peabody, MA).

X-ray diffraction (XRD) showed that after hydrothermal processing, the powder consisted of PbTiO<sub>3</sub> and unreacted anatase or rutile TiO<sub>2</sub>. TiO<sub>2</sub> and PbTiO<sub>3</sub> were easily distinguished by TEM because the TiO<sub>2</sub> particles were spherical and had a diameter of approximately 25 nm, while the PbTiO<sub>3</sub> particles were typically faceted rectangular plates with sizes ranging from 20 to 200 nm. Size is defined as the average of the sides of the rectangle. Estimates of the aspect ratio of the PbTiO<sub>3</sub> particles, made by tilting, ranged from 3:3:1 to 5:5:1, and selected-area electron diffraction (SAED) indicated that the particles typically had {100} facets. Considering the isotropic growth environment and the tetragonal symmetry of the PbTiO<sub>3</sub> lattice, it is reasonable to conclude that the caxis is perpendicular to the plate while the a axis lies within the plate. If we assume that the particle shape represents a local energy minimum during growth, the surface energy ratio of  $\gamma_{(100)}$ : $\gamma_{(010)}$ : $\gamma_{(001)}$  ranges from 3:3:1 to 5:5:1.

For particles greater than 70 nm in size, SAED showed that the *c* axis was perpendicular to the plate, in agreement with the symmetry argument presented above [Fig. 1(a)]. However, for particles smaller than 70 nm, high-resolution transmission electron microscopy (HRTEM) showed that the *c* axis often lay in the plane of the plate [Fig. 1(b)]. HRTEM was used to measure the axial ratio of the two perpendicular interatomic spacings for approximately 50 PbTiO<sub>3</sub> nanoparticles ranging from 20 nm to 200 nm in size. The axial ratio of each HRTEM lattice was obtained by computing a Fourier transform of the lattice image, then measuring the distance between the relevant intensity maxima (Fig. 1, insets). The results are summarized as a plot of particle size versus axial ratio



FIG. 1. HRTEM images of  $PbTiO_3$ : (a) particle with the *c* axis perpendicular to the plate and (b) particle with the *c* axis parallel to the plate.

(Fig. 2). While the particles with axial ratio close to 1.0 had sizes widely spread over the range of 20 to 200 nm, the particles with axial ratio close to 1.07 (i.e., the c/a ratio of bulk PbTiO<sub>3</sub>) displayed a much narrower size distribution, with no particles exceeding 70 nm. The observation indicates that there exists a critical size, between 50 and 70 nm, above which the c axis of the



FIG. 2. Particle size versus axial ratio. The majority of particles with size less than 50 nm have an axial ratio close to 1.07. The majority of particles with size greater than 50 nm have their *c* axis perpendicular to the plate.

particles lies within the plane of the plate. The ferroelectric phase is stable below the critical size but adopts a morphology in which the crystal symmetry and the particle symmetry are different.

The observed morphologies could result from thermodynamic (equilibrium) effects or from kinetic processes that occur at higher rates than the relaxation processes that would return the system to equilibrium. A kinetic process resulting in the growth of rectangular-shaped plates with the *c* axis in the plane of the plate implies that the growth rate in the  $\langle 100 \rangle$  and  $\langle 010 \rangle$  are different by a factor of 3–5 times. This is unlikely considering that the hydrothermal growth medium is isotropic, and the  $\langle 010 \rangle$ and  $\langle 100 \rangle$  directions for PbTiO<sub>3</sub> are identical both physically and chemically. Also, particles above the critical size were never observed with the *c* axis lying within the plate. Large and small particles with in-plane *c* axes should have the same probability of formation if the selection mechanism is related to the mode of growth.

Since the processing temperature of 200 °C is below the PbTiO<sub>3</sub> Curie temperature of 493 °C, the PbTiO<sub>3</sub> particles grow in the ferroelectric phase. Normally, the domain size in ferroelectrics is determined by the minimization of depolarization energy (favoring the formation of many small domains) and domain wall energy (favoring the formation of a single domain). In a conductive environment, or for a conductive ferroelectric crystal, the depolarization energy can be fully compensated by free charge flow.<sup>26</sup> Consequently, the ferroelectric interaction will dominate over the depolarization energy favoring a single domain structure. The 1.0 M KOH solution in which the PbTiO<sub>3</sub> nanoparticles grow is rich in ions that may compensate the depolarization energy, thereby resulting in single-domain nanoparticles. Under hydrothermal processing conditions the polarization direction, or c axis, will be perpendicular to the plate during particle growth regardless of size (see illustrations in Fig. 2). When the particles are washed with de-ionized

water and dried, the compensating ions are desorbed from the nanoparticle surface, allowing the buildup of depolarization energy. In larger particles, alternating multiple domain structures can form to minimize the total free energy, and the c axis will still be perpendicular to the plate. However, in smaller particles only a single domain can exist. The BaTiO<sub>3</sub> particles were found to be monodomain for particle sizes smaller than 100-400 nm.<sup>6,9</sup> The corresponding size for sol-gel processed PbTiO<sub>3</sub> is 20 nm.<sup>12</sup> For the anisometric PbTiO<sub>3</sub> particles in our study, the depolarization energy will dominate the ferroelectric interaction and may destabilize the ferroelectric phase if the c axis is perpendicular to the plane of the plate. However, because of the greater separation of the positive and negative charged particle surfaces, and their smaller area, the polarization energy with the c axis parallel to the plate is much lower than the polarization energy with the c axis perpendicular to the plate. Therefore, the total free energy can be minimized by flipping the domain axis into the plane of the plate and maintaining the ferroelectric phase. Our observations suggest that particles smaller than ~70 nm undergo a flipping of the c axis from lying perpendicular to the plate to lying parallel within the plate.

The platelike morphology of the particles indicates that the (100) and the (001) surface energies are very different. Therefore, changes in surface energy must be overcome for domain flipping to occur. Assuming that the (100) and the (001) have a surface energy of 1 and  $0.25 \text{ J/m}^2$ , respectively, for particles of size  $40 \times 40 \times 10$  nm, the total surface energy will be  $2.4 \times 10^{-15}$  J when the *c* axis is perpendicular to the plate surface. After the *c* axis flips, the surface energy will be  $4.2 \times 10^{-15}$  J. Therefore, the surface energy change will be on the order of  $2.0 \times 10^{-15}$  J.

Using the parallel plate capacitor approximation, the energy associated with the ferroelectric surface charge can be expressed as

$$E = \frac{1}{2} \frac{Q^2}{C} = \frac{1}{2} \frac{(P/\epsilon_0)^2 \times A^2}{A/(\epsilon_r \epsilon_0 d)} = \frac{1}{2} \frac{\epsilon_r}{\epsilon_0} P^2 V$$

where Q is the charge, P is the polarization, A is the plate area, V is the volume,  $\epsilon_r$  is the relative dielectric constant, and  $\epsilon_0$  is the permittivity of a vacuum. However, when the polarization direction lies within the plate, edge effects cannot be excluded and the approximation is no longer valid. For a single ferroelectric domain, the depolarization energy is<sup>26</sup>

$$E = \frac{1}{2} \int \frac{\epsilon_{\rm r,c}}{\epsilon_0} L^2 P^2 \mathrm{d}V$$

where L is a geometry factor ranging from 0 for a long rod to 1 for a thin disk. The depolarization energy formulation includes the edge effects in the geometry factor L. Generally, the polarization P is not the spontaneous

polarization  $P_{\rm s}$  due to the existence of the depolarization field. For a thin slab with a linear dielectric response,  $P = P_{\rm s}/\epsilon_{\rm r}$ . However, since the response of ferroelectric  $PbTiO_3$  is nonlinear, the determination of P requires a self-consistent calculation because the depolarization field E, and the polarization P are mutually dependent. Also, the dielectric constant  $\epsilon_r$  is known to be sizedependent, and drops quickly when the particle size is less than about 40 nm. The reported  $\epsilon_r$  ranged from 40 to 120 for nanocrystalline PbTiO<sub>3</sub> specimens.<sup>10,27</sup> If r is considered to be anisotropic, with  $\epsilon_{r,a}$  an order of magnitude larger than  $\epsilon_{r,c}^{6,26}$  the reported value of  $\epsilon_r$  corresponded to a bulk polycrystalline specimen, which can significantly overestimate  $\epsilon_{r,c}$ . Assuming  $\epsilon_{r,c} = 40$  and  $P_{\rm s} > 50 \ \mu\text{C/cm}^2$ , <sup>26</sup> P is approximately 1.5  $\mu\text{C/cm}^2$ . To simplify the calculation, L is approximated using an ellipsoid with the same aspect ratio. According to Osborn,<sup>28</sup> for an aspect ratio of 1:4,  $L \sim 0.7$ , while for 4:1,  $L \sim 0.15$ . Thus the energy difference due to the geometry factor will be  $L^2$  or 0.40. For a 40 × 40 × 10 nm particle, the polarization energy change is  $-4.0 \times 10^{-15}$  J, which is about 2 times higher than the surface energy change. The depolarization energy may be significantly underestimated due to simplifying assumptions. There are several theoretical calculations of polarization in nano-ferroelectric particles based on the Landau-Ginsburg-Devonshire approach showing that the polarization will be 1/2 to 1/5 of the  $P_{s}$ .<sup>17</sup> If this is taken into account, the polarization energy can be 2 orders of magnitude higher. Domain flipping is therefore energetically favorable.

The critical size for domain flipping is about 70 nm. Considering that the particles have an aspect ratio of 3:3:1 to 5:5:1, the particles of critical size will have a thickness of 14-24 nm. This number agrees well with literature reporting a 7–13.8 nm critical size for a sizedriven ferroelectric-paraelectric phase transition in spherical PbTiO<sub>3</sub> nanoparticles.<sup>5,8,10,21</sup> The geometry factor for a sphere is 0.333, which is between the two geometry factors of the platelike particle (0.7 and 0.15 in the above calculation, respectively). Thus, the critical size in the thickness direction for a platelike shape will be larger than that of a spherical shape, and the critical size parallel to the plate will be much smaller. Therefore, the ferroelectric phase will be stable in the direction parallel to the plate even when it is not stable in the perpendicular direction.

Our TEM observations show that hydrothermally derived  $PbTiO_3$  nanoparticles have a rectangular platelike morphology. The HRTEM studies indicate that there is a new type of size effect for such ferroelectric particles. Below a critical size of about 70 nm, the single ferroelectric domains of the particles will flip into the plane of the plate. We attribute this to the strong depolarization effect.

#### ACKNOWLEDGMENTS

We are grateful to Applied Materials, Inc., Santa Clara, CA, for providing a graduate fellowship to Z. Ye, and to the Purdue Electron Microscopy Consortium for laboratory facilities. We thank Professor Keith Bowman for enlightening discussions.

### REFERENCES

- M. Anliker, H.R. Brugger, and W. Känzig: The behavior of colloidal ferroelectrics III, barium titanate. *Helv. Phys. Acta.* 27, 99 (1954).
- 2. W. Känzig: Space charge layer near the surface of a ferroelectric. *Phys. Rev.* **98**, 549 (1955).
- J.F. Scott and C.A. Paz De Aranjo: Ferroelectric memories. *Science* 246, 1400 (1989).
- J.F. Scott: Ferroelectric Memories (Springer-Verlag, Berlin, Germany, 2000).
- K. Ishikawa, K. Yoshikawa, and N. Okada: Size effect on the ferroelectric phase transition in PbTiO<sub>3</sub> ultrafine particles. *Phys. Rev.* B37, 5852 (1988).
- A.S. Shaikh, R.W. Vest, and G.M. Vest: Dielectric-properties of ultrafine grained BaTiO<sub>3</sub>. *IEEE Trans. Ultrason. Ferroelectr. Freq. Control.* 36, 407 (1989).
- K. Uchino, E. Sadanaga, and T. Hirose: Dependence of the crystal-structure on particle-size in barium-titanate. *J. Am. Ceram. Soc.* 72, 1555 (1989).
- W.L. Zhong, B. Jiang, P.L. Zhang, J.M. Ma, H.M. Cheng, Z.H. Yang, and L.X. Li: Phase-transition in PbTiO<sub>3</sub> ultrafine particles of different sizes. *J. Phys. Condens. Matter* 5, 2619 (1993).
- H.I. Hsiang and F.S. Yen: Effect of crystallite size on the ferroelectric domain growth of ultrafine BaTiO<sub>3</sub> powders. *J. Am. Ceram. Soc.* 79, 1053 (1996).
- S. Chattopadhyay, P. Ayyub, V.R. Palkar, and M. Multani: Sizeinduced diffuse phase-transition in nanocrystalline ferroelectric PbTiO<sub>3</sub>. *Phys. Rev.* B52, 13177 (1995).
- M.H. Frey and D.A. Payne: Grain-size effect on structure and phase transformations for barium titanate. *Phys. Rev.* B54, 3158 (1996).
- B. Jiang, J.L. Peng, L.A. Bursill, and W.L. Zhong: Size effects on ferroelectricity of ultrafine particles of PbTiO<sub>3</sub>. *J. Appl. Phys.* 87, 3462 (2000).
- D.L. Mills: Surface effects in magnetic crystals near the ordering temperature. *Phys. Rev.* B3, 3887 (1971).
- I.P. Batra, P. Würfel, and B.D. Silverman: New type of first-order phase transition in ferroelectric thin films. *Phys. Rev. Lett.* **30**, 384 (1973).
- R. Krestschmer and K. Binder: Surface effects on phase transitions in ferroelectrics and dipolar magnets. *Phys. Rev.* B20, 1065 (1979).
- D.R. Tilley and B. Zeks: Landau theory of phase-transitions in thick-films. Solid State Commun. 49, 823 (1984).
- W.L. Zhong, Y.G. Wang, P.L. Zhang, and B.D. Qu: Phenomenological study of the size effect on phase-transitions in ferroelectric particles. *Phys. Rev.* B50, 698 (1994).
- W.L. Zhong, B.D. Qu, P.L. Zhang, and Y.G. Wang: Thickness dependence of the dielectric susceptibility of ferroelectric thin films. *Phys. Rev.* B50, 12375 (1994).
- 19. H.T. Huang, C.Q. Sun, T.S. Zhang, and P. Hing: Grain-size effect on ferroelectric  $PbZr_xTi_{1-x}O_3$  solid solutions induced by surface bond contraction. *Phys. Rev. B.* **6318**, 184112 (2001).
- 20. T. Chraska, A.H. King, and C.C. Berndt: On the size-dependent

phase transformation in nanoparticulate zirconia. *Mater Sci.* Eng. A **286**, 169 (2000).

- A. Roelofs, I. Schneller, K. Szot, and R. Waser: Piezoresponse force microscopy of lead-titanate nanograins possibly reaching the limit of ferroelectricity. *Appl. Phys. Lett.* 81, 5231 (2002).
- W.Y. Shih, W.H. Shih, and I.A. Aksay: Size dependence of the ferroelectric transition of small BaTiO<sub>3</sub> particles—Effect of depolarization. *Phys. Rev.* B50, 15575 (1994).
- 23. X.P. Li and W.H. Shih: Size effects in barium titanate particles and clusters. J. Am. Ceram. Soc. 80, 2844 (1997).
- 24. X.H. Liu, W.Y. Shih, and W.H. Shih: Effects of copper coating on

the crystalline structure of fine barium titanate particles. J. Am. Ceram. Soc. 80, 2781 (1997).

- 25. J. Junquera and P. Ghosez: Critical thickness for ferroelectricity in perovskite ultrathin films. *Nature* **422**, 506 (2003).
- M.E. Lines and A.M. Glass: Principles and Applications of Ferroelectrics and Related Materials (Oxford University Press, Oxford, U.K., 1977).
- B.D. Qu, B. Jiang, Y.G. Wang, P. Zhang, and W.L. Zhong: Size and temperature-dependence of dielectric-constant of ultrafine Pb-TiO<sub>3</sub> particles. *Chin. Phys. Lett.* **11**, 514 (1994).
- 28. J.A. Osborn: Demagnetizing factors of the general ellipsoid. *Phys. Rev.* 67, 351 (1945).