Surface bond contraction and its effect on the nanometric sized lead zirconate titanate

LETTER TO THE EDITOR

Surface bond contraction and its effect on the nanometric sized lead zirconate titanate

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Abstract.   The grain size effect of lead zirconate titanate $PbZr_{1-x}Ti_xO_3$ (PZT, $x \geqslant 0.6$) caused by surface bond contraction has been investigated by using the Landau–Ginsburg–Devonshire (LGD) phenomenological theory. It has been shown that, due to the surface bond contraction, both the Curie temperature and the spontaneous polarization of tetragonal PZT decrease with decreasing grain size. These effects become more significant when the grain size is in the nanometre range. A dielectric anomaly appears with decreasing grain size, which corresponds to a size dependent phase transformation. The ferroelectric critical size below which a loss of ferroelectricity will happen is estimated from the results obtained.

It has long been recognized since the early part of this century that the ionic radius of an atom contracts with the reduction of the atomic coordination number. Goldschmidt has pointed out that the ionic radius contracts by 4%, 6% and 12%, when the coordination number reduces from 12 to 8, 6 and 4, respectively [1]. The ionic radius contraction has also been noticed by Pauling [2]. For instance, the ionic radius contracts from 0.128 to 0.117 nm when its coordination number changes from 12 to 1. Obviously, the coordination number reduction takes place at the surface. Recently, the effect of surface bond contraction has been intensively studied. It is realized that the surface bond contraction plays an important role in the oxygen chemisorption [3, 4], the band-gap enlargement [5, 6] of nanoclusters and the photoluminescence of nanometric SiO_2 [7]. The surface bond contraction is expected to affect the material properties when the materials go to nanometre size range, i.e. when the surface–volume ratio becomes very large.

The lead zirconate titanate (PZT) solid-solution system has many applications, such as in smart structures [8] and memory devices [9]. As the device elements become smaller and smaller, the grain size effect should be taken into consideration in order to optimize their properties. The grain size dependence of the dielectric permittivity in barium titanate ceramics [10, 11] and thin films [12] has been known for many years. The Curie temperature, polarization, coercive field, switching speed etc all depend on the film thickness and grain size [9]. Several models, including the presence of internal stresses in fine-grained ceramics, which are due to the absence of 90° domain walls [10], the domain-wall contribution to the dielectric response in fine-grained ceramics [11] and shifts of the phase transition temperatures with grain size [12] have been proposed by different authors. However, due to the complexity of the phenomenon, the origins of the grain size effect in fine-grained ferroelectric ceramics are still not well understood. In this letter, we try to study the grain size effect from a different starting point, i.e., the effect of surface bond contraction is studied and some interesting results are obtained.
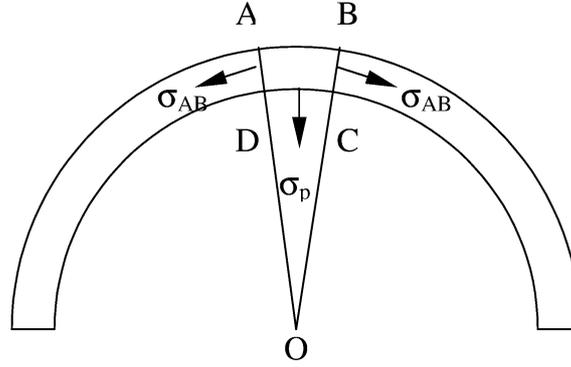
Figure 1. Schematic drawing of part of the outer layer of a spherical grain. O is the centre position.

For a curved surface the surface bond contraction will produce a strain along the surface. This effect can be clearly seen in the following discussion. Figure 1 shows part of the outer layer of a spherical grain with a centre at O. For simplicity, we only consider the bond contraction on this outer layer since the coordination number reduction happens only in the first few layers at the surface and below. The inner part of the grain has no bond contraction. Due to the surface bond contraction, the radius of the grain will shrink by a small amount,

$$\delta R = n\delta a \tag{1}$$

where R is the radius of the grain, a is the lattice parameter and n is the number of unit cell layers which perform surface bond contraction.

Consider a very small part ABCD in the outer layer; the contraction of the radius R will induce a contraction along arc AB. Thus a strain is produced in the outer layer of the grain. The corresponding stress along arc AB is

$$\sigma_{AB} = \frac{\delta R}{R}E = \frac{n\delta a}{Na}E \tag{2}$$

where N is the total number of unit cell layers along the radius direction OA and E is the Young's modulus of the material. This surface stress in the tangential direction will cause a compressive stress on the inner part of the grain,

$$\sigma_p = -\frac{n^2\delta a}{N^2a}E. \tag{3}$$

The negative sign is used for compressive stress. As shown above, a hydrostatic pressure is induced on the inner part of the grain due to the surface bond contraction.

According to the LGD theory, the elastic Gibbs free energy function for a tetragonal PZT under a hydrostatic pressure σ_p can be expressed as a Taylor series in powers of polarization and stress [13–22],

$$\begin{aligned}
\Delta G = {} & \alpha_1(P_1^2 + P_2^2 + P_3^2) + \alpha_{11}(P_1^4 + P_2^4 + P_3^4) + \alpha_{12}(P_1^2 P_2^2 + P_2^2 P_3^2 + P_3^2 P_1^2) \\
& + \alpha_{111}(P_1^6 + P_2^6 + P_3^6) + \alpha_{112}[P_1^4(P_2^2 + P_3^2) + P_2^4(P_3^2 + P_1^2) + P_3^4(P_1^2 + P_2^2)] \\
& + \alpha_{123}P_1^2 P_2^2 P_3^2 - \tfrac{3}{2}(s_{11}^P + 2s_{12}^P)\sigma_p^2 - (Q_{11} + 2Q_{12})(P_1^2 + P_2^2 + P_3^2)\sigma_p
\end{aligned} \tag{4}$$

where P_i $(i = 1, 2, 3)$ are the magnitude of the polarization vector along the direction i; α_1, α_{ij} $(i, j = 1, 2)$ and α_{ijk} $(i, j, k = 1, 2, 3)$ are the dielectric stiffness and higher-order dielectric stiffness coefficients at a constant stress; s_{ij}^P $(i, j = 1, 2)$ are the elastic compliance

Table 1. Values of the coefficients of the Gibbs free energy at 25 °C for $PbZr_{1-x}Ti_xO_3$.

	$x = 0.6$	$x = 0.7$	$x = 0.8$	$x = 0.9$	$x = 1.0$
$T_{C\infty}$ (°C)	418.4	440.2	459.1	477.1	492.1
C (10^5 °C)	2.664	1.881	1.642	1.547	1.500
α_1 (10^7 m F^{-1})	−8.340	−12.47	−14.84	−16.17	−17.08
α_{11} (10^7 m^5 C^{-2} F^{-1})	3.614	0.6458	−3.050	−5.845	−7.253
α_{111} (10^8 m^9 C^{-4} F^{-1})	1.859	2.348	2.457	2.518	2.606
Q_{11} (10^{-2} m^4 C^{-2})	8.116	7.887	8.142	8.504	8.900
Q_{12} (10^{-2} m^4 C^{-2})	−2.950	−2.480	−2.446	−2.507	−2.600
Q_h (10^{-2} m^4 C^{-2})	2.216	2.927	3.250	3.490	3.700

at constant polarization; Q_{ij} ($i, j = 1, 2$) are the electrostrictive constants. The dielectric stiffness constant α_1 is assumed to be a linear function of temperature near the Curie point,

$$\alpha_1 = \frac{T - T_0}{2C\varepsilon_0} \tag{5}$$

where T is the temperature, T_0 is the Curie point, C is the Curie constant and ε_0 is the vacuum dielectric permittivity. All the other coefficients in equation (4) are assumed to be temperature independent [15–22]. Their optimized values [17] are listed in table 1.

It should be noted that when applying the LGD theory to a finite-size and inhomogeneous ferroelectrics, the total free energy instead of the energy density function is usually used [23, 24],

$$F = \int [g + D(\nabla P)^2] \, dv + \int D\lambda^{-1} P^2 \, dS \tag{6}$$

where the energy density g has the same form as equation (4), λ is the extrapolation length describing the difference between the surface and bulk and D is connected with the correlation length. However, even for a very simple case, the spontaneous polarization and Curie temperature cannot be derived analytically from the above integration. In order to avoid the tedious numerical calculation and to find out the 'pure' effect of the surface bond contraction, we assume that the surface and bulk have the same ferroelectric properties and the averaged value of polarization is used. The free energy density function of equation (4) will then be used instead of the total free energy. As will be seen later, the effect of surface bond contraction actually has similar effects on the ferroelectric properties as the term of polarization gradient in equation (6) does. A numerical calculation which includes both the effects of bond contraction and polarization gradient will be given in a future paper.

For the paraelectric cubic phase P_C, $P_1^2 = P_2^2 = P_3^2 = 0$, we have

$$\Delta G = -\tfrac{3}{2}(s_{11}^P + 2s_{12}^P)\sigma_p^2 \tag{7}$$

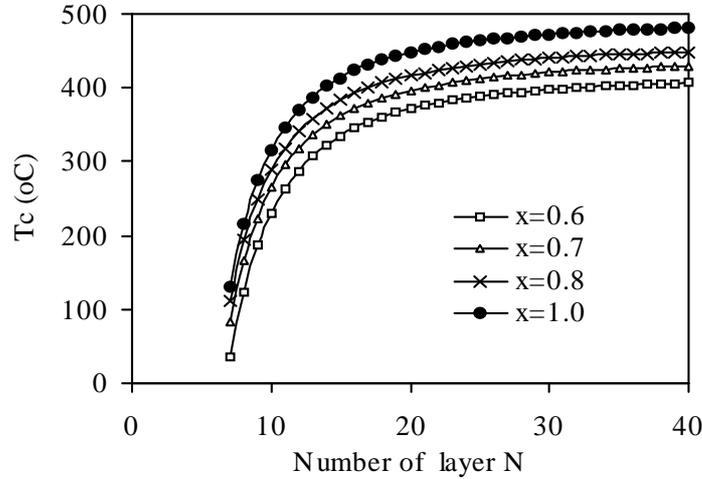$$\frac{1}{\varepsilon} = 2\varepsilon_0(\alpha_1 - Q_h\sigma_p) \tag{8}$$

where $Q_h = Q_{11} + 2Q_{12}$ and ε is the dielectric constant.

For the ferroelectric tetragonal phase F_T, $P_1^2 = P_2^2 = 0$, $P_3^2 \neq 0$, we have

$$\Delta G = -\tfrac{3}{2}(s_{11}^P + 2s_{12}^P)\sigma_p^2 + (\alpha_1 - Q_h\sigma_p)P_3^2 + \alpha_{11}P_3^4 + \alpha_{111}P_3^6 \tag{9}$$

$$P_3^2 = \frac{-\alpha_{11} + [\alpha_{11}^2 - 3\alpha_{111}(\alpha_1 - Q_h\sigma_p)]^{1/2}}{3\alpha_{111}} \tag{10}$$

$$\frac{1}{\varepsilon} = 2\varepsilon_0(\alpha_1 + 6\alpha_{11}P_3^2 + 15\alpha_{111}P_3^4 - Q_h\sigma_p). \tag{11}$$

Figure 2. Curie temperature T_C of PZT ($x = 0.6$, 0.7, 0.8 and 1.0) versus number of unit cell layers.

The Curie temperature can be obtained by equalizing the free energy of the ferroelectric and paraelectric phases,

$$T_C = T_{C\infty} + 2C\varepsilon_0 Q_h \sigma_p = T_{C\infty} - \frac{2n^2\delta a}{N^2 a} C\varepsilon_0 Q_h E \tag{12}$$

where $T_{C\infty}$ is the Curie temperature of bulk materials as given in table 1.

Figure 2 shows the Curie temperature T_C decreases with decreasing number of unit cell layers, i.e., the grain size. It is assumed that the surface bond contracts by an average of 10% within the top three layers. The Young's modulus is chosen to be 200 GPa. This value is reasonable for tetragonal PZT as compared with the bulk modulus of 209 GPa for PbTiO$_3$ obtained by first-principles calculation [25]. It can be seen that the Curie temperature drops slowly with N for $N > 15$. For $N < 15$, the Curie temperature drops dramatically. The equivalent grain size for $N = 15$ is about 12 nm since the lattice parameter is about 0.4 nm as determined by Glazer *et al* [26]. A similar result for PbTiO$_3$ is confirmed in experiment [27]. It should be pointed out that below a certain grain size (critical size) the Curie temperature reaches 0 K which implies a lost of ferroelectricity. This critical size obtained by our model is about 4 nm ($N = 5$). This value is comparable with the theoretical value of 4.2 nm obtained by Zhong *et al* [23]. They have used the total free energy of equation (6) to study the size effect in PbTiO$_3$. However, this critical size is smaller than those obtained by various experiments, such as, 12.6 nm by Raman scattering [28], 8.8 nm by specific heat measurement [29], 7 nm by x-ray diffraction [27]. This could be due to the oversimplification of our model but a more sensitive measurement is needed to verify different models since the existing results are too scattered.

By using equation (10) the room temperature spontaneous polarization can be calculated. Figure 3 shows that the spontaneous polarization decreases with decreasing grain size. Again it decreases slowly with N for $N > 15$. When $N < 15$, it drops very fast. The same trend for PbTiO$_3$ is experimentally verified by Chattopadhyay *et al* [27] as they found that the lattice parameter c decreases and a increases when the grain size decreases below 100 nm. The resulting reduction in the tetragonal distortion (c/a) implies a decrease in spontaneous polarization. At room temperature the spontaneous polarization becomes zero for grain size below 5.6 nm ($N = 7$). As the temperature increases, this size will also increase.
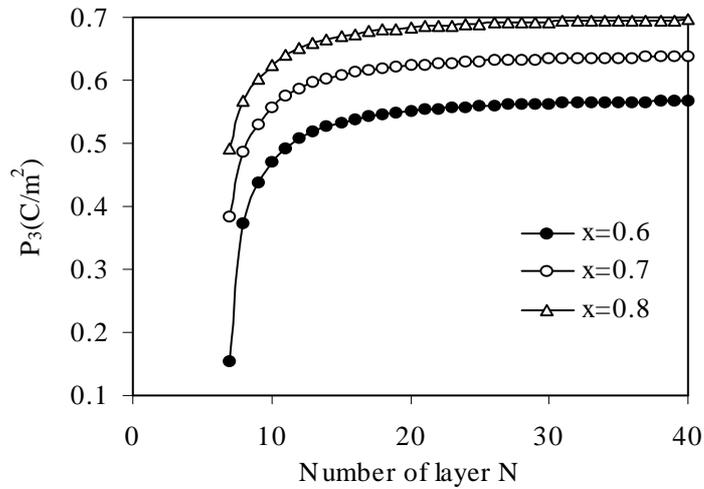
Figure 3. Room temperature spontaneous polarization of PZT ($x = 0.6$, 0.7 and 0.8) against number of unit cell layers.
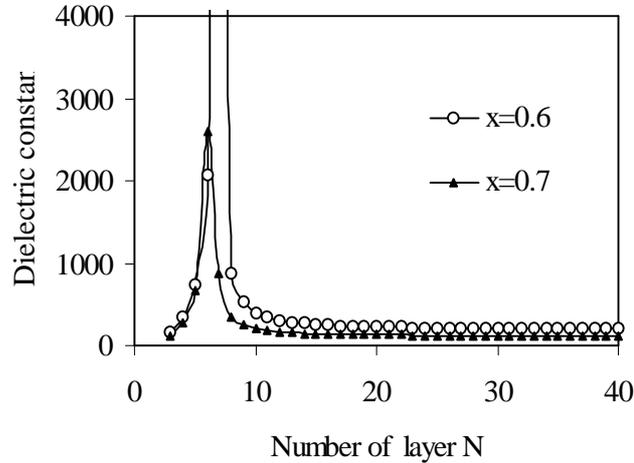
Figure 4. Room temperature dielectric constant of PZT ($x = 0.6$ and 0.7) against number of unit cell layers.

The room temperature dielectric constant is shown in figure 4. A dielectric anomaly can be clearly seen which indicates a phase transformation from a ferroelectric phase to a paraelectric one. The size at which this phase transition takes place is about 5.6 nm ($N = 7$). It is the same size at which the spontaneous polarization becomes zero. Our result has a similar feature as that obtained by using the total free energy (equation (6)) method [24]. However, this result differs from the experiment work of Chattopadhyay *et al* [27]. They found the dielectric constant decreases with decreasing size in a size range of 26–100 nm. The reason is that our calculation has not taken the domain wall contribution into account so that the calculated relative permittivity is lower than the experimental value. Actually the domain wall contribution has an opposite effect as compared with the surface bond contraction induced effect. When the grain size decreases to a value comparable to the width of domain

walls, pinning points would develop inside the grains and the domain wall motion would be inhibited [27]. The reduced wall mobility will cause a decrease in the relative permittivity. The measured value is a competition between the increase of relative permittivity by the surface bond contraction effect and its decrease by the domain wall pinning effect.

From the above results it can be concluded that the surface bond contraction induces a compressive stress on the inner part of a grain and this effect should be taken into account for ferroelectric materials in the nanometre size range. The induced stress causes decreases of Curie temperature and spontaneous polarization with decreasing grain size. A size driven dielectric anomaly can be seen due to the surface bond contraction. The theoretical results correspond well with the experiment ones. However, experimental information on the value of surface bond contraction of ferroelectric materials is still needed for a more precise description of the surface bond contraction induced effect. As can be seen from equations (10) and (12), the spontaneous polarization decreases with increasing surface bond contraction ratio $\delta a/a$, and the Curie temperature decreases linearly with increasing bond contraction ratio $\delta a/a$.

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