
Volume 62, No. 16, 15 June 2008
ISSN 0167-577X
ELSEVIER
materials letters
An interdisciplinary journal affiliated with the
Materials Research Society-Japan devoted to the rapid publication of short
communications on the science, applications and processing of materials
Editors: J. Hojo, G.L. Messing, L.S. Shvindlerman, A.F.W. Willoughby, H.Q. Ye
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ScienceDirect
Materials Letters 62 (2008) 2438 – 2440
materials letters
www.elsevier.com/locate/matlet

Size-dependent piezoelectric coefficient d_{33} of $PbTiO_3$ nanoparticles

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Received 12 July 2007; accepted 11 December 2007
Available online 3 January 2008

Abstract

Size-dependent piezoelectric coefficient $d_{33}(D)$ (D shows particle diameter) for small ferroelectrics is modeled in this paper. It is found that taking account of size effect is essential in understanding piezoelectric characteristics of nanoferroelectrics. The model prediction is in good agreement with the experimental results for $PbTiO_3$ nanoparticles, where $d_{33}(D)$ increases correspondingly as D decreases. In addition, the size effect of the dielectric susceptibility coefficient $\eta_{33}(D)$ is also predicted since $\eta_{33}(D) \propto d_{33}(D)$ is considered. Our model estimations for $\eta_{33}(D)$ function are consistent with other theoretical evidences.

Keywords: Ferroelectrics $PbTiO_3$; Piezoelectric materials; Size-dependent

1. Introduction

The continuous advance in microelectronics and communications is leading to the miniaturization and integration of ferroelectric components. On the other hand, higher strain piezoelectric materials also have drawn much attention for the fabrication of microelectrictromechanical systems, such as microactuators, pressure transducers, and high-frequency ultrasound transducers [1–3]. As a candidate, $PbTiO_3$ nanoparticles are extensively used in the piezoelectric transducer [1-3], and can well satisfy the technological requirements mentioned above since the piezoelectric coefficient of $PbTiO_3$ is observed to increase with size dropping [2]. It is known that, nanoparticles with higher surface-to-volume ratio, have substantial difference of physical, chemical and mechanical properties from their counterparts in bulk materials. Therefore, piezoelectric property is also a function of D (D denotes particle diameter) and it plays an important role in determining the application of nanoferroelectrics.

$PbTiO_3$ with perovskite structure, is cubic and paraelectric above the Curie temperature, while tetragonal structure is stable below the Curie temperature. Since the polarization direction of the tetragonal $PbTiO_3$ with nonzero dipole moment ($P_1 = P_2 = 0$, $P_3 = P_s \neq 0$, where the subscripts denote polarization axis directions and P_s is spontaneous polarization) is the desired one in devices for technological applications, and expected to be stable and the largest [4–6], the investigation on the piezoelectric coefficient (d_{33}) in this direction becomes valuable and possible. To clarify the size effect on ferroelectric properties such as phase transition, many efforts have been made [5,7–10]. They show that Curie temperature shifts towards lower temperature with the decrease of D, and the corresponding spontaneous polarization P_s also decreases. Furthermore, Akdogan et al. [2] have found that electrostrictive coefficients of $PbTiO_3$ particles exhibit an order of magnitude increase when the size decreases to nanoscale, which leads to an increase of the intrinsic piezoelectric coefficient d_{33}. They attributed this abnormal behavior into the inherent cooperative nature of ferroelectricity arising from long-range dipolar coupling. However, quantitative explanation for d_{33} variation with size is rarely reported. In this work, the model for $d_{33}(D)$ function of $PbTiO_3$ particles is established.

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doi:10.1016/j.matlet.2007.12.015

The model predictions are used to compare with the evidences obtained from experiments.

2. Model

According to the Landau–Ginsburg–Devonshire (LGD) theory for tetragonal $PbTiO_3$ ferroelectrics, piezoelectric coefficient d_{33} is expressed as [11],

$$d_{33} = 2\varepsilon_0\eta_{33}Q_{11}P_s \quad (1)$$

where ε_0 is permittivity of free space, Q_{11} shows electrostrictive coefficient, and η_{33} denote relative dielectric susceptibility coefficient and can be written [11],

$$\eta_{33} = \left[\left(2\alpha_1 + 12\alpha_{11}P_s^2 + 30\alpha_{111}P_s^4\right)\varepsilon_0\right]^{-1} \quad (2)$$

where α_1, α_{11}, and α_{111} are the dielectric stiffness and higher-order stiffness coefficients which can be obtained from the available thermodynamic amounts.

To determine d_{33} values, the parameters concerned in Eq. (1) should be known. As shown in Refs. [12,13], there is a second-order relationship between P_s and Q_{11} via $x_3=Q_{11}P_s^2$ with x_3 being elastic strains. Since both x_3 and P_s are fundamentally related to atomic shifts (Δz) with respect to the equilibrium positions in the cubic lattice, P_s (or x_3) ~ Δz is assumed [12,14]. As a result, Q_{11} ~ Δz^{-1} can be expected according to the above relationship. Taking the multiply of $Q_{11}P_s$ in Eq. (1) as an ensemble for simplicity, $Q_{11}P_s$ as a constant is considered. Therefore, in terms of Eq. (1), there exists an approximate relationship $d_{33} \propto \eta_{33}$ where ε_0 is assumed to be size-independent.

On the other hand, it is necessary to allow for the size effect of the parameters α_1, α_{11}, α_{111} and P_s appearing in Eq. (2). In light of Curie–Wess law, α_1 is read,

$$\alpha_1 = (T-\theta)/(2\varepsilon_0 C) \quad (3)$$

where T is absolute temperature, C is Curie constant and θ Curie–Weiss temperature. Since the tetragonal-cubic transition is first order in light of the thermodynamic considerations, the difference value of $(T_C-\theta)$ being a constant is taken [13], where T_C is the Curie temperature. Therefore, by introducing size-dependent $T_C(D)$ and $\theta(D)$ functions, there will be: $T_C(D)-\theta(D) \approx T_C(\infty)-\theta(\infty)$ with ∞ denoting the bulk value. $T_C(D)$ has been proposed as [7],

$$\frac{T_C(D)}{T_C(\infty)} = \exp\left(-\frac{2S_0}{3R}\frac{1}{D/D_0-1}\right) \quad (4)$$

where S_0 is the transition entropy from ferroelectric tetragonal phase to paraelectric cubic one, and R the ideal gas constant. D_0 is defined as a critical particle size where the ferroelectric phase cannot exist or the Curie transition is absent. Combining Eq. (4) and the available expression for $\theta(D)$ function, $\alpha_1(D)$ is obtained,

$$\alpha_1(D) = [T + T_C(\infty) - \theta(\infty) - T_C(D)]/(2\varepsilon_0 C) \quad (5)$$

Although the study on size effects of α_{11} and α_{111} parameters are few, their temperature dependences have been investigated [11], showing that the temperature contribution to both α_{11} and α_{111} is small enough to be neglected. Moreover, as particle size decreases, the corresponding Curie temperature or melting temperature will decreases correspondingly. As a result, size decreasing can be regarded as working temperature enhancing to some extent. Based on the discussion above, α_{11} and α_{111} are supposed to be size-independent in this paper.

Table 1
The thermodynamic data of $PbTiO_3$

Parameters	Quantity
$T_C(\infty)$ (K)	765.4 [11]
$\theta(\infty)$ (K)	752 [11]
$T_C-\theta$ (K)	13.4 [11]
$\alpha_1(\infty)$ (10^6 m F^{-1}) at T_C	5.045 [11]
α_{11} (10^7 m^5 C^{-2} F)	−7.252 [11]
α_{111} (10^8 m^9 C^{-4} F)	2.606 [11]
$P_s(\infty)$ (C m^{-2}) at 298 K	0.75 [11]
$d_{33}(\infty)$ (PC N^{-1}) at 298 K	79.1 [11]
η_{33} (∞) at 298 K	66.6 [11]
S_0 (J mol^{-1} K^{-1})	2.3 [17]
D_0 (nm)	13.8 [9]
$\varepsilon_0 C$ (10^{-6} K m^{-1} F)	1.3 [a]

[a] $\varepsilon_0 C$ is determined by the Curie–Wess law in terms of Eq. (3) where T is taken as Curie transition temperature T_C and the value of α_1 is the value at T_C.

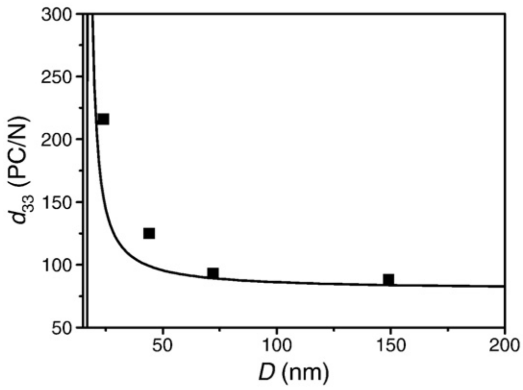

Fig. 1. A comparison for $d_{33}(D)$ function of $PbTiO_3$ particles between model prediction in terms of Eq. (7) (solid line) and the experimental results (■) [2] at 298 K.

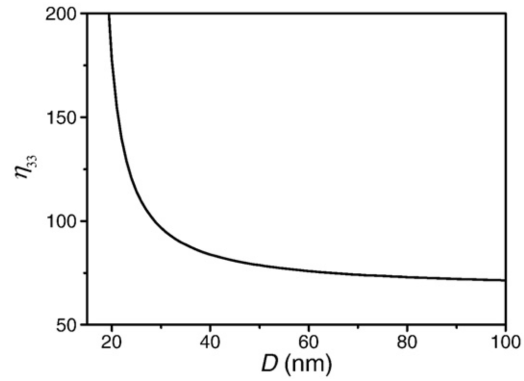

Fig. 2. Model prediction of $\eta_{33}(D)$ for $PbTiO_3$ particles.

In addition, the contribution of surface layer to P_s becomes significant because the dipoles located at surfaces differ from that inside the materials and thus results in the alteration of P_s [15]. Size-dependent spontaneous polarization $P_s(D)$ has been extended [10],

$$\frac{P_s(D)}{P_s(\infty)} = \exp\left(-\frac{S_0}{3R}\frac{1}{D/D_0-1}\right) \tag{6}$$

where the related parameters are same with that in Eq. (4). Based on the consideration above, an analytical expression for size-dependent intrinsic piezoelectric coefficient $d_{33}(D)$ and the corresponding $\eta_{33}(D)$ function can be determined,

$$\frac{d_{33}(D)}{d_{33}(\infty)} = \frac{\eta_{33}(D)}{\eta_{33}(\infty)} = \frac{2\alpha_1(\infty)+12\alpha_{11}P_s^2(\infty)+30\alpha_{111}P_s^4(\infty)}{2\alpha_1(D)+12\alpha_{11}P_s^2(D)+30\alpha_{111}P_s^4(D)} \tag{7}$$

where $\alpha_1(D)$ and $P_s(D)$ are determined by Eqs. (5) and (6) respectively.

3. Results and discussion

Fig. 1 presents a comparison between the model prediction of piezoelectric coefficient $d_{33}(D)$ at 298K in terms of Eq. (7) and the experimental results for $PbTiO_3$ particles, where the related parameters are listed in Table 1. The both are consistent each other. As shown in Fig. 1, $d_{33}(D)$ increases with D decreasing, especially when $D<100$ nm, and $d_{33}(D)\rightarrow d(\infty)$ as $D\rightarrow\infty$. $\eta_{33}(D)$ function is also shown in Fig. 2. Due to a lack of necessary experimental data obtained, a comparison between model prediction and experimental results fails. However, the trend of η_{33} with size is consistent with that of other theoretical estimations [2,16].

According to Eq. (7), $d_{33}(D)$ and $\eta_{33}(D)$ functions are related not only with size, but also with temperature. For bulk $PbTiO_3$, Haun et al. [11] demonstrated that $d_{33}(\infty)$ and $\eta_{33}(\infty)$ increase with T rising due to the enhanced α_1, which indirectly implies that $d_{33}(D)$ and $\eta_{33}(D)$ increase as D decreases, when the concerned T is fixed. By observing Eq. (7), the parameters related to determine $d_{33}(D)$ are determined by thermodynamic quantities of a material, which are available from experiments. Thus, our model seems to be applicable for other ferroelectrics particle, such as $BaTiO_3$, if the relative parameters are known. Moreover, the success of Eq. (7) implies that the assumptions used in this paper are reasonable.

4. Conclusion

In summary, size effect on the piezoelectric coefficient $d_{33}(D)$ and dielectric susceptibility coefficient $\eta_{33}(D)$ for $PbTiO_3$ particles is investigated, and can be determined as long as the relative thermodynamic parameters are clear. As the particle size decreases, $d_{33}(D)$ and $\eta_{33}(D)$ increase correspondingly. The obtained results are in agreement with the theoretical and experimental observations.

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