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Applied Study on Piezoelectric Properties of Ferroelectric Nanomaterials

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This paper presents the theoretical model d_{33}(D) for the size dependence of the piezoelectric coefficient of the ferroelectric lead titanate $PbTiO_3$ nano particles, where D is the diameter of nano particles. Through the model, it is found that the key to obtaining the piezoelectric coefficient of nano-ferroelectric material is to introduce its size effect. The research shows that d_{33}(D) increases with the decrease of size D, and that the prediction results of the theoretical model are consistent with the experimental results of the piezoelectric coefficient of ferroelectric nanomaterials. In addition, based on the assumption that the dielectric susceptibility coefficient η_{33}(D) is directly proportional to d_{33}(D), this paper also successfully predicts the size effect of the dielectric susceptibility coefficient, and the η_{33}(D) function predicted by the proposed model is consistent with those by other theoretical models.

1. Introduction

With the continuous development of microelectronics and communications, ferroelectric devices also need to be miniaturized and integrated. In this process, high-strain piezoelectric materials are starting to receive the attention in micro-electromechanical systems, such as microprocessors, pressure sensors and high-frequency ultrasonic transducers (Kim et al., 2006; Akdogan et al., 2000). Among them, ferroelectric nanomaterials are an excellent piezoelectric material, which is widely used in piezoelectric transducers (Kim et al., 2006; Akdogan et al., 2000) and can well meet the above-mentioned miniaturization requirement. This is because the piezoelectric coefficient of ferroelectric nanomaterials increases with the size decreasing. As is known to all, nano particles have a high surface-to-volume ratio, which makes the physical, chemical and mechanical properties of nano materials essentially different from bulk materials. Therefore, the size change directly affects the piezoelectric performance of the piezoelectric material, and the piezoelectric coefficient exhibits a strong size dependence and plays an important role in nano ferroelectric applications.

$PbTiO_3$ is of a perovskite structure. It is cubic structure above the Curie temperature and stable tetragonal structure below it. Since the polarization direction of the tetragonal lead titanate is a non-zero dipole moment, that is, $P_1=P_2=0$ and $P_3= P_s\neq0$, where the subscripts indicate the directions of the polaxis and P_s means spontaneous polarization, which is maximized in the polarization direction. Therefore, this polarization direction is most commonly used in applications (Rarnesh et al., 2002; Fong et al., 2004; Zembilgotov et al., 2002). Researchers have done a great deal of work on the size dependence of various performances of ferroelectric(Fong et al., 2004; Jiang et al., 2004; Fu et al., 2003; Ishikawa et al., 2003; Lang et al., 2007). For example, it was found that, as the size decreases, the Curie temperature decreases and the spontaneous polarization also decreases. Akdogan et al (2000) also found that when the $PbTiO_3$ particle size is reduced to nano size, the electrostrictive coefficient tends to increase, even by an order of magnitude, resulting in an increase in its piezoelectric coefficient d_{33}. However, few research studied the change of d_{33} with size. Therefore, with $PbTiO_3$ nano particles as the object, this paper studies in detail the intrinsic relation between

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the piezoelectric coefficient d_{33} and the nano particle size D, and establishes the mathematical size-dependent model d_{33}(D) for $PbTiO_3$ particles. Finally, the theoretical prediction results of the model are compared with the experimental results to verify the effectiveness of the model.

2. Model

According to the Landau–Ginsburg–Devonshire (LGD) theory for tetragonal lead titanate ferroelectric, the piezoelectric coefficient d_{33} can be expressed by the following equation (1): \

$$d_{33} = 2\varepsilon_0 \eta_{33} Q_{11} P_s \tag{1}$$

where, ε_0 is the spatial dielectric constant, Q_{11} is the electrical modulus, and η_{33} is the relative dielectric susceptibility coefficient, which may be expressed by the following equation (2):

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

where, α_1, α_{11} and α_{111} are the dielectric stiffness and high-order stiffness coefficients, respectively, and their values can be obtained from the thermodynamic parameters. In this paper, they are directly given.

From equation (1), it can be seen that if we want to determine d_{33}, we need to know all the parameter values in equation (1). The followings are the steps to obtain these parameters. First of all, in this paper, we adopt the reported second-order approximation relation between P_s and Q_{11} (Newnham et al., 1997; Akdogan et al., 2005): $x_3=Q_{11}P_s^2$, where x_3 is the elastic deformation. Since both x_3 and P_s are closely related to the displacement (Δz) of the atoms from the equilibrium position, there is a relationship between P_s (or x_3) and Δz (Newnham et al., 1997; Sundar et al., 1992). However, $Q_{11}\sim\Delta z^{-1}$ also holds approximately. Then we take the product of $Q_{11}P_s$ in equation (1) as one constant, regardless of size. Then according to equation (1), we obtain an approximate relation: $d_{33}\propto\eta_{33}$. Here ε_0 is assumed to be a size independent parameter.

The parameters α_1, α_{11}, α_{111} and P_s in equation (2) are size dependent. According to the Curie-Weiss Law, α_1 is expressed by equation (3):

$$\alpha_1 = (T-\theta)/(2\varepsilon_0 C) \tag{3}$$

where, T is the absolute temperature; C is the Curie constant; and θ is the Curie-Weiss temperature. Since from the thermodynamics point of view, the transition from tetragonal crystal to cubic crystal is a first-order phase change process, ($T_C-\theta$) can be seen as a constant (Akdogan et al., 2005), where T_C is the Curie temperature. Therefore, by introducing the size-dependent T_C(D) and θ(D) functions, we obtain the relationship $T_C(D)-\theta(D)\approx T_C(\infty)-\theta(\infty)$, where ∞ represents the corresponding bulk material, and $T_C(\infty)$ and θ(∞) are the corresponding block values. Then the function T_C(D) can be expressed as follows - (4):

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

S_0 is the transformational entropy from ferroelectric tetragonal body to the para-electric cubic; R is the ideal gas constant; and D_0 is the critical size, at which, the ferroelectric phase or Curie transition does not exist. By combining equation (4) and the existing θ(D) function, we haveα1(D) (5):

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

Although few studies have investigated the size effects of the α_{11} and α_{111} parameters, the studies on their temperature dependence show that temperature has very small or even negligible impact on α_{11} and α_{111}. In addition, as the particle size decreases, the corresponding Curie temperature or melting temperature decreases accordingly. Therefore, the reduction in size can be considered as an increase in temperature. Based on the above discussion, we consider in this paper that α_{11} and α_{111} are independent of size change.

In addition, the presence of the surface layer has particularly significant impact on P_s becomes particularly significant, mainly because the dipoles on the surface are different from those inside the material. When the size of the material gradually decreases, the surface effect becomes more obvious, fundamentally changing the value of spontaneous polarization P_s (Wang et al., 1996). Here we adopt the size-dependent model for spontaneous polarization P_s (D) proposed by Lang and Jiang (2007) from Jilin University, as shown in equation (6):

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

The relevant parameters in equation (6) are the same as in equation (4). Based on the above parameter derivation and assumptions, the size-dependent piezoelectric coefficient $d_{33}(D)$ and corresponding $\eta_{33}(D)$ functions can be expressed by the following equation (7):

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

where, $\alpha_1(D)$ and Ps(D) can be obtained using equations (5) and (6), respectively.

3. Results and Discussion

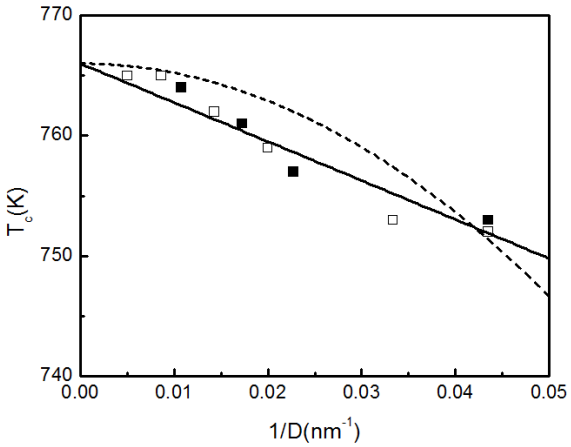

Figure 1: Tc function of PbTiO3 ultra fine particles in terms of equation (4) and experiment results of the specific heat measurements; The solid line is our model and the dash line is a mechanics model.

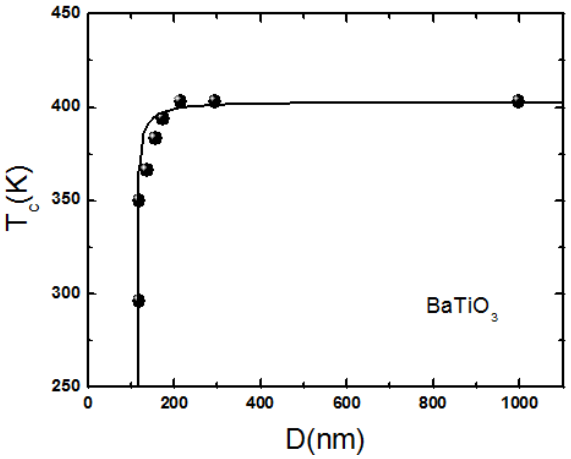

Figure.2: Comparison between theoretical prediction in terms of equation (4) (solid line) and the experimental results ● for Tc of BaTiO3 particles. S0 = 0.1 Jg-atom-1K-1, Tc0 =403 K. D0 has been determined to be 40 nm. However, the value of tetragonality c/a in equation (3) decreases with the decreasing of the particle size. According to this consideration, D0 has been redetermined and resulted D0 = 110 nm.

From Figure 1 and Figure 2, we compare the theoretical models based on mechanics and thermodynamics of Huang with their own models. It is found that the Curie temperature decreases linearly with the reciprocal of particle size but not exponentially. From the above two diagrams and the equations (4), it can be seen that the Curie temperature T_c decreases with the decrease of particle size. The theoretical prediction of $BaTiO_3$ and $PbTiO_3$ particles is in good agreement with the experimental results. Compared with Figure 1 and Figure 2, it is clear that the T_c curves of the two compounds decrease with the particle size D and the amplitude is significantly different. This is because the $BaTiO_3$ has a larger D_0 value and a smaller S_0 relative to the $PbTiO_3$, which makes the T_c of $BaTiO_3$ less than the T_c of the $PbTiO_3$. This difference may be due to the large domain

wall energy density and low four sex c/a of barium titanate compared with lead titanate. So the Curie transformation of barium titanate particles can be easier to take place, and the large size single domain can be easily formed.

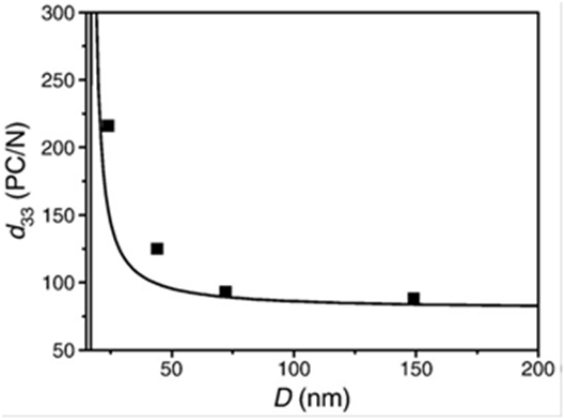

Figure 3: Model predictions of $d_{33}(D)$ at 298K obtained from equation (7) versus experimental results of $PbTiO_3$ particles (Akdogan et al., 2000)

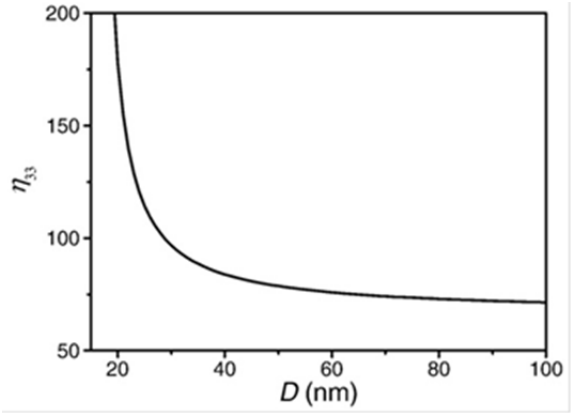

Figure 4: $\eta_{33}(D)$ model prediction results of $PbTiO_3$particles

Figure 3 compares the model predictions of d_{33}(D) at 298K obtained from equation (7) with the experimental results of lead titanate particles, with the relevant parameters listed in Table 1. From the figure, it is clear that the model predictions agree well with the experimental results. As shown in Figure 3, d_{33}(D) increases with the size decreasing, especially when D<100 nm, in which case, its piezoelectric coefficient shows obvious size effect, and as the size decreases, the piezoelectric coefficient shows an obvious size-dependent trend. Conversely, as the nano particle size gradually increases, the piezoelectric coefficient decreases, and when D→∞, d_{33}(D)→d_{33}(∞). In addition, according to the function model for dielectric susceptibility coefficient η_{33}(D) of the equation (7), Figure 4 shows the variation pattern of η_{33}(D) with the size. Due to the lack of necessary experimental data, the model predictions and experimental results cannot be compared. However, the size-dependent trend of η_{33}(D) is consistent with the trend predicted by other theoretical results (Akdogan et al., 2000; Bornand et al., 2004).

According to equation (7), the functions d_{33}(D) and η_{33}(D) are not only size dependent but also temperature dependent. For large blocks of lead titanates, Haun et al. found that d_{33}(∞) and η_{33}(∞) increase with T increasing, which is mainly due to the increasing α1. This also indirectly implies that when T remains constant, d_{33}(D) and η_{33}(D) increase with D decreasing. According to equation (7), the relevant parameters determining the piezoelectric coefficient d_{33}(D) are all determined by the thermodynamic function of the material, and these parameters can be obtained directly from experiment. Therefore, if the relevant parameters are known, the model proposed in this paper can also be applied to other ferroelectric particles, such as barium titanate. In addition, the successful prediction of the piezoelectric coefficient by equation (7) further confirms that the theory and assumptions proposed in this paper are reasonable.

Table 1: Values of the parameters in equation (7) for $PbZr_{1-x}Ti_xO_3$ where T_{c0} and c (Haun et al., 2012) are transformed from Celsius scale to Kelvin temperature

	x =0.6	x=0.7	x=0.8	x=0.9	x=1.0
T_{c0} (K)[81]	691.4	713.2	732.1	750.1	765.1
α_1 ($10^7 mF^{-1}$)[81]	-8.340	-12.47	-14.84	-16.17	-17.08
c ($10^5 K$)[81]	7.107	5.016	4.407	4.212	4.120
Q_{11}($10^{-2} m^4 C^{-2}$)[81]	8.116	7.887	8.142	8.504	8.900
Q_{12}($10^{-2} m^4 C^{-2}$)[81]	-2.950	-2.480	-2.446	-2.507	-2.600
V_m ($cm^3 mol^{-1}$)	43.42	42.83	42.24	41.66	41.07
H_m ($Kjmol^{-1}$)	37.623	35.656	33.689		29.755
T_m (K)	1803.5	1759.8	1716.0		1554.0[80]
S_m ($Jmol^{-1}K^{-1}$)	20.861	20.261	19.632		19.147
S_{vib} ($Jmol^{-1}K^{-1}$)	12.547	11.947	11.318		10.833

Due to the difficulty of finding the melting enthalpy Hm and entropy Sm of lead zirconate titanate PZT, mean values of PbO, TiO_2 and ZrO_2 consisting of the compound are utilized. Tm of PZT (expect $PbTiO_3$) can be obtained by using $H_m=T_mS_m$. Vm is obtained by M/ρ where molar mass M is cited from Ref (Haun et al., 2012) and it is reasonable that we chose the value of density ρ for PZT unanimously to be 7.38 g/cm^3 since compounds in PZT system have similar density (Kanhaiya et al., 2005; Keiko et al., 1996; Breazeale et al., 1992; Maria et al., 2006; Andra et al., 2017; Binsong et al., 2017; Karbassian et al., 2014; KumarManuel et al., 2012; Luca et al., 2016; Alejandro et al., 2013).

4. Conclusion

Based on the thermodynamic parameters measured through experiment, the size dependent models of the lead titanate piezoelectric coefficient d_{33}(D) and dielectric susceptibility coefficient η_{33}(D) proposed in this paper can be used to effectively predict the piezoelectric coefficient and dielectric susceptibility coefficient of the material with different particle sizes, and with the size decreasing, both d_{33}(D) and η_{33}(D) increase. The results of theoretical prediction are consistent with the experimental observations. This work was supported by Engineering Research Center of Geothermal Resources Development Technologies and Equipment, Ministry Education (Grant No. ERCGR201704).

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