

# Theoretical Model Construction of Piezoelectric Coefficient of PbTiO<sub>3</sub> Nanoparticles

Shuai Zhang<sup>a</sup>, Lei Chen<sup>\*b</sup>

<sup>a</sup>College of Materials Science and Engineering, Jilin Jian Zhu University, Changchun 130118, China

<sup>b</sup>College of Municipal and Environmental Engineering, Jilin Jian Zhu University, Changchun 130118, China  
7796549@qq.com

This paper aims to explain the size dependence of piezoelectric coefficient  $d_{33}(D)$  of PbTiO<sub>3</sub> nanoparticles. For this purpose, a theoretical model was created for the size-dependent piezoelectric coefficient, considering the Curie temperature for small ferroelectrics. The research reveals that  $d_{33}(D)$  increased with the decline in the particle size  $D$ . The model prediction agrees well with the experimental results on the piezoelectric coefficient of PbTiO<sub>3</sub> nanoparticles. In addition, the size effect of the dielectric susceptibility coefficient  $\eta_{33}(D)$  was also predicted under the condition of  $\eta_{33}(D) \propto d_{33}(D)$ . Our prediction of  $\eta_{33}(D)$  function was consistent with other theoretical evidences.

## 1. Introduction

The miniaturization and integration of ferroelectrics have placed a high demand on high-strain piezoelectric materials. Essential to micro electromechanical systems (MEMS), these materials are extensively used in microprocessors, pressure sensors and high-frequency transducers (Kim et al., 2006; Tang et al., 2013; Amarin et al. 2014; (Kim et al., 2006; Rarnesh et al., 2002). Among the various high-strain piezoelectric materials, PbTiO<sub>3</sub> nanoparticles, popularly adopted for piezoelectric transducers (Kim et al., 2006; Tang et al., 2013; Amarin et al., 2014; (Kim et al., 2006; Rarnesh et al., 2002), does well in piezoelectricity and fulfills the miniaturization requirement on ferroelectrics. The good performance is attributable to the negative correlation between the piezoelectric coefficient and the size of PbTiO<sub>3</sub>, as well as the relatively large surface-volume ratio of nanoparticles. The varying size of nanoparticles directly bears on the piezoelectricity of the materials. In other words, the piezoelectric coefficient is heavily dependent on size. The dependence plays a significant role in the application of nano-ferroelectrics.

Similar to the structure of perovskite, PbTiO<sub>3</sub> changes from the cubic structure to the stable tetragonal structure as the temperature falls below the Curie temperature. After polarization, PbTiO<sub>3</sub> exhibits a nonzero electric dipole moment, that is,  $P_1 = P_2 = 0$  and  $P_3 = P_s \neq 0$ , where the subscripts are the polarization directions and  $P_s$  is spontaneous polarization. With the strongest effect in the same polarization direction, the spontaneous polarization is the most commonly used polarization mode in designs (Fong et al., 2004; Zembilgotov et al., 2002; Jiang et al., 2004).

Much research has been done on the size dependency of ferroelectrics properties (Zembilgotov et al., 2002; V Sundar and Newnham 2012; Ishikawa et al., 1988; Lang et al., 2007; Haun et al., 1987). For example, it is discovered that the Curie temperature drops with the decrease in size, accompanied by weakening signs of polarization. Akdogan et al. (Ishikawa et al, 1988) found that the electrostriction coefficient tends to increase, sometimes by an order of magnitude, when the size of PbTiO<sub>3</sub> falls to that of nanoparticles, leading to the growth of the piezoelectric coefficient  $d_{33}$ . However, there is few report on the size dependent changes in  $d_{33}$ . To make up for the gap, this paper takes PbTiO<sub>3</sub> nanoparticles as an example, and explores the internal relationship between the piezoelectric coefficient  $d_{33}$  and the diameters ( $D$ ) of the nanoparticles. Following theoretical derivations, a size dependence model was established for the  $d_{33}(D)$  of PbTiO<sub>3</sub> nanoparticles. Then, the theoretically predicted results were compared with the experimental results to verify the effect of the model.

## 2. Modelling

According to the Landau–Ginsburg–Devonshire (LGD) theory for quadratic crystal  $\text{PbTiO}_3$  ferroelectrics, the piezoelectric coefficient  $d_{33}$  can be expressed as:

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

where  $\varepsilon_0$  is space permittivity;  $Q_{11}$  is the piezoelectric coefficient;  $\eta_{33}$  is relative dielectric susceptibility coefficient. The  $\eta_{33}$  can be expressed as:

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

where  $\alpha_1$  is dielectric stiffness;  $\alpha_{11}$  and  $\alpha_{111}$  are high-order stiffness coefficients. The values of these parameters can be derived from thermal dynamic parameters. Here, the values are given directly.

From formula (1), it can be seen that all the parameter values in that formula are needed before determining the value of  $d_{33}$ . The parameter values were obtained as follows. First, the second-order approximation of  $P_s$  and  $Q_{11}$  (Ishikawa et al., 1988; Lang et al., 2007; Haun et al., 1987) was adopted, namely  $x_3=Q_{11}P_s^2$ , where  $x_3$  is the elastic deformation. Both  $x_3$  and  $P_s$  are closely related to the displacement ( $\Delta z$ ) of the atom from the original equilibrium position, i.e.  $P_s$  (or  $x_3$ )  $\sim \Delta z$  (Lang et al., 2007; Newnham et al., 1997). However, the  $Q_{11} \sim \Delta z^{-1}$  is also valid. For simplicity, the product of  $Q_{11}P_s$  in formula (1) was considered as a constant independent of the size. In this way, it is possible to get an approximation from formula (1):  $d_{33} \propto \eta_{33}$ . Here,  $\varepsilon_0$  is assumed to be independent of the size. On the contrary, parameters  $\alpha_1$ ,  $\alpha_{11}$ ,  $\alpha_{111}$  and  $P_s$  in formula (2) are all correlated with the size. According to the Curie-Weiss law,  $\alpha_1$  satisfies the formula below:

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

where  $T$  is the absolute temperature;  $C$  is the Curie constant;  $\theta$  is the Curie temperature.

From the ferroelectric perspective, the change from tetragonal crystals to cubic ones is essentially the transition from the ferromagnetic phase to paramagnetic phase. As its name suggests, the ferromagnetic phase is ferromagnetic, that is, the metal elements carry the features of spontaneous magnetization. At absolute zero, the electron spin ferromagnetic materials are arranged parallel to each other. With the rise of temperature, the orderly arrangement is weakened by thermal agitation, and eventually destroyed at the critical temperature (the Curie point). In this case, the system becomes paramagnetic. The transition is also known as the Curie shift, and the transition temperature is called the Curie temperature.

Taking Ni particles (size: 85nm) for example, there is an obvious peak of on the magnetic susceptibility-temperature curve at the Curie temperature ( $T_c$ ). According to measurement, the Curie temperature of the particles stands at 623K, slightly lower than that of the conventional bulk Ni material (631K).

It has been repeatedly reported that the atomic distance of nanoparticles decreases with the particle size. Using the EXAFS method, Apai et al. directly proved that the atomic distance of Ni and Cu is positively correlated with the particle size. Standuik et al. conducted X-ray diffraction analysis, and concluded that the Ni particles (size: 5nm) are 2.4% shorter in atomic distance than conventional bulk Ni material. According to the theory of ferromagnetism, the atomic distance of Ni tends to decrease with the particle size at the Curie temperature. Despite the extensive empirical research on magnetic nanoparticles, there is still no perfect explanation for the properties of these materials at the Curie temperature.

The important parameters of magnetic nanoparticles, namely atomic distance, also have an impact to the Curie temperature. Theoretical and experimental studies have shown that the thinning of ferromagnetic film can cause a decrease in the Curie temperature; under the small size effect and surface effect, the nanoparticles will be subject to an intrinsic magnetic variation, and thus a lower Curie temperature.

Recently, a thermodynamic model has been developed for first-order phase transition, and applied successfully to metal crystals, finite-size semiconductors, organic compounds and macromolecules. The model has also been extended to second-order phase transition, such as the glass transition of polymers and organic matters. In view of its good performance, the model was modified and applied to explain the Curie transformation of Perovskite ferroelectric nanoparticles, which is a first-order phase transition. In this way, the Curie temperature is linked up with the melting temperature. Then, the solid-liquid phase change size-dependence model was extended to describe the Curie temperature of the ferroelectric nanoparticles. For  $\text{PbTiO}_3$  and  $\text{BaTiO}_3$  particles, the theoretical results were found in good agreement with the experimental results.

In light of the reference, the crystal melting temperature  $T_m(D)$  can be expressed as:

$$\frac{T_m(D)}{T_{m0}} = \exp\left(-\frac{2S_m}{3R} \frac{1}{D/D_0 - 1}\right) \quad (4)$$

where  $D$  is the particle diameter;  $T_{m0}$  is the melting temperature of bulk crystal;  $S_m$  is the melting entropy of bulk crystal;  $R$  is the ideal gas constant;  $D_0$  is the critical particle size. The solid and liquid phases are indistinguishable when the particle size reaches  $D_0$ . Assuming that the particles are spherical and  $h$  is the atomic diameter, the relationship between  $D$  and  $D_0$  is  $D_0 = 2(3-D)h$ . If half of the atoms are on the surface of the nanoparticles, the material still has translational periodicity and crystalline property. The minimum crystal size is  $2r_0$ . In spite of the thin film of the single atomic layer, the material maintains the crystalline structure owing to the translational periodicity. However, if all the atoms are on the surface, the thermal vibration will be entirely different from that of the atoms on the bulk crystal. According to Mitch, the amorphous state disappeared when the  $D$  of Bi films decreased to 0.8nm. Note that the  $h$  is also slightly different if the coordination number of the crystal structure changes. To prevent this from occurring, the  $\Omega$  of a single atom was calculated based on  $h$  as  $\Omega = \pi h^3/6$ . The calculation relies on the principle that the number of atoms always equals the quotient of cell volume and atomic volume, not matter how complex is the crystal structure. To extend the above melting model to the Curie temperature  $T_c$ , the melting entropy  $S_m$  was replaced with the Curie transition entropy  $S_0$ , and the  $D_0$  was redefined. In fact, the ferroelectric Curie shift is a solid phase transition between the ferroelectric and paraelectric phases. The ferroelectric phase contains multiple ordered domains, while the paraelectric phase consists of various disordered domains. Therefore, the transition is also a transformation from the orderly state to disorderly state. As a necessary condition for ferroelectric phase transition, a grain must at least contain two or more domains. If there is only one domain, the Curie shift will not happen because the two phases coexist in the grain. Here,  $D_0$  is redefined as the critical number of orderly domains in ferroelectric particles. The Curie shift only occurs when the number of orderly domains exceeds the critical number.

From the thermodynamic angle, the transition from quadratic crystals to cubic crystals is a first-order phase transition. Hence,  $(T_c - \theta)$  can be regarded as a constant [15], with  $T_c$  being the Curie temperature. Then, size dependenc functions  $T_c(D)$  and  $\theta(D)$  were introduced to get  $T_c(D) - \theta(D) \approx T_c(\infty) - \theta(\infty)$ , with  $\infty$  being the bulk material, and  $T_c(\infty)$  and  $\theta(\infty)$  being the corresponding bulk values. In this case, function  $T_c(D)$  can be expressed as:

$$\frac{T_c(D)}{T_c(\infty)} = \exp\left(-\frac{2S_0}{3R} \frac{1}{D/D_0 - 1}\right) \quad (5)$$

where  $S_0$  is the transformational entropy as ferromagnetic tetragonal crystals change to paramagnetic cubic crystals;  $R$  the ideal gas constant;  $D_0$  is the critical size, at the state of which there is no ferroelectric phase or Curie shift. According to formula (5) and function  $\theta(D)$  at hand, it is possible to deduce  $\alpha_1(D)$ :

$$\alpha_1(D) = [T + T_c(\infty) - \theta(\infty) - T_c(D)] / (2\varepsilon_0 C) \quad (6)$$

The few studies on the size effect of  $\alpha_{11}$  and  $\alpha_{111}$  agree that the effect of temperature on the two parameters is so small as to be negligible, and that the Curie and melting temperatures decrease with the particle size. Therefore, the size decrement can be regarded as the temperature increase. Through these analyses, it is believed that  $\alpha_{11}$  and  $\alpha_{111}$  are parameters independent of particle size.

In addition, the surface layer has a significant impact to  $P_s$  because of the difference of the dipoles on the surface and those inside the material. The smaller the material, the more prominent is the surface effect. In this case, the value of  $P_s$  is changed fundamentally. Hence, the size-dependent spontaneous polarization  $P_s(D)$  is extended as:

$$\frac{P_s(D)}{P_s(\infty)} = \exp\left(-\frac{S_0}{3R} \frac{1}{D/D_0 - 1}\right) \quad (7)$$

where the relevant parameters are the same with those in formula (6). Based on the above considerations, the author determined the expression for size-dependent intrinsic piezoelectric coefficient  $d_{33}(D)$  and the corresponding  $\eta_{33}(D)$ :

$$\frac{d_{33}(D)}{d_{33}(\infty)} = \frac{\eta_{33}(D)}{\eta_{33}(\infty)} = \frac{2\alpha_1(\infty) + 12\alpha_{11}P_s^2(\infty) + 30\alpha_{111}P_s^4(\infty)}{2\alpha_1(D) + 12\alpha_{11}P_s^2(D) + 30\alpha_{111}P_s^4(D)} \quad (8)$$

where  $\alpha_1(D)$  and  $P_s(D)$  can be obtained by formula (5) and formula (6), respectively.

### 3. Results and Discussions

Figure 1 illustrates the predicted and experimental results on the Curie temperature and particle size for  $\text{PbTiO}_3$  nanoparticles. As can be seen from the figure and formula (5), the Curie temperature both decreased with the particle size in the prediction and the experiment.

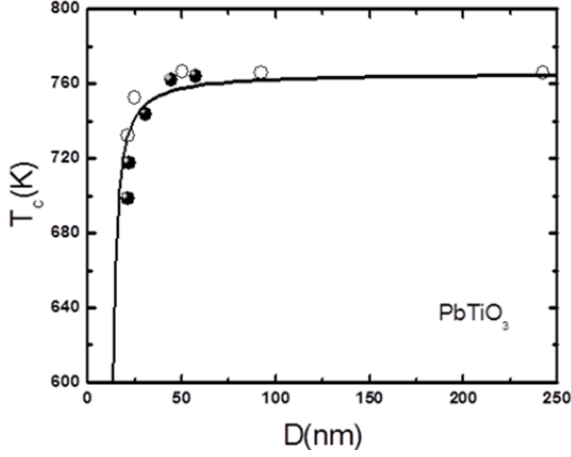


Figure 1: Theoretical estimations and experimental results for  $\text{PbTiO}_3$  particles  $T_c$

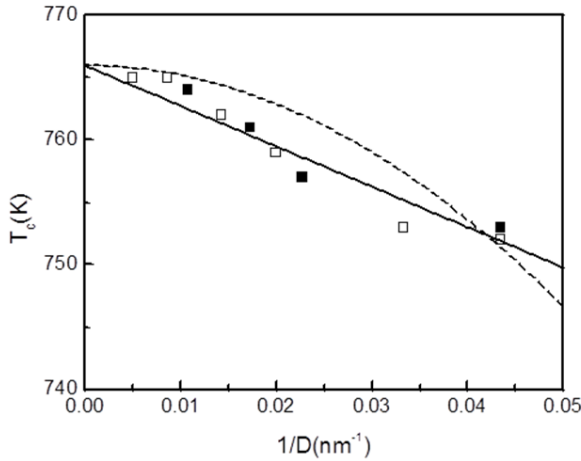


Figure 2: Theoretical estimations and experimental results for  $\text{BaTiO}_3$  particles  $T_c$  function of  $\text{PbTiO}_3$  ultra-fine particles in terms of equation (5) and experiment results of the specific heat measurements, the symbol  $\blacksquare$  and  $\square$  derived from experiment data. The solid line is our model and the dash line is a mechanics model in reference

As shown in Figure 2, the Curie temperature declined with the decrease in particle size and the increase in the Ti content of the  $\text{PbTiO}_3$  solution. Combining the model and Huang's research, the author derived the nonreciprocal linear relationship between Curie temperature increment and particle size decrease.

Figure 3 compares the  $d_{33}(D)$  calculated by formula (8) and the results of  $\text{PbTiO}_3$  particle size dependence experiment. The relevant parameters are listed in Table 1. It is clear that the predicted results agree well with the experimental results. As shown in Figure 1, the  $d_{33}(D)$  increased with the increase in the particle size. In particular, the piezoelectric coefficient was very significant when  $D$  was smaller than 100nm. The coefficient varied more violently with the continued decrease in particle size. The inverse is also true. As  $D \rightarrow \infty$ ,  $d_{33}(D) \rightarrow d_{33}(\infty)$ . Furthermore, Figure 4 shows the variation pattern of  $\eta_{33}(D)$  vs. the particle size obtained by the function model for dielectric susceptibility coefficient  $\eta_{33}(D)$  in formula (7). Due to the lack of statistics, it is impossible to compare the predicted results with the experimental results. However, the variation pattern echoes the predictions in other studies.

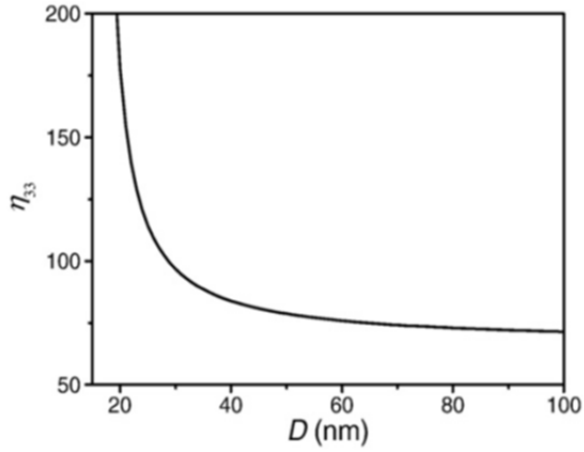


Figure 3:  $d_{33}(D)$  model estimation for  $PbTiO_3$  nanoparticles compared with experimental results at 298K

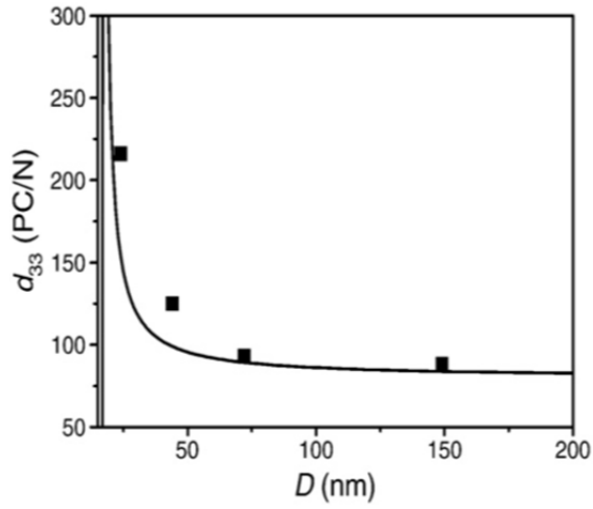


Figure 4: Model estimations for  $PbTiO_3$  particles  $\eta_{33}(D)$

Table 1: The thermodynamic data of  $PbTiO_3$

| Parameters  | Quantity |
|---|----------|
| $T_C(\infty)$ (K)   | 765.4    |
| $\theta(\infty)$ (K)                                      | 752      |
| $T_C - \theta$ (K)  | 13.4     |
| $\alpha_1(\infty)$ ( $10^6$ m F <sup>-1</sup> ) at $T_C$  | 5.045    |
| $\alpha_{11}$ ( $10^7$ m <sup>5</sup> C <sup>-2</sup> F)  | -7.252   |
| $\alpha_{111}$ ( $10^8$ m <sup>9</sup> C <sup>-4</sup> F) | 2.606    |
| $P_s(\infty)$ (C m <sup>-2</sup> ) at 298 K               | 0.75     |
| $d_{33}(\infty)$ (PC N <sup>-1</sup> ) at 298 K           | 79.1     |
| $\eta_{33}(\infty)$ at 298 K                              | 66.6     |
| $S_0$ (J mol <sup>-1</sup> K <sup>-1</sup> )              | 2.3      |
| $D_0$ (nm)  | 13.8     |
| $\epsilon_0 C$ ( $10^{-6}$ K m <sup>-1</sup> F)           | 1.3 a    |

#### 4. Conclusion

In order to explain the size dependence of piezoelectric coefficient  $d_{33}(D)$  of  $\text{PbTiO}_3$  nanoparticles, this paper constructs a theoretical model for the size-dependent piezoelectric coefficient, considering the Curie temperature for small ferroelectrics. The research reveals that  $d_{33}(D)$  increased with the decline in the particle size  $D$ . The model prediction agrees well with the experimental results on the piezoelectric coefficient of  $\text{PbTiO}_3$  nanoparticles. In addition, the size effect of the dielectric susceptibility coefficient  $\eta_{33}(D)$  was also predicted under the condition of  $\eta_{33}(D) \propto d_{33}(D)$ . Our prediction of  $\eta_{33}(D)$  function was consistent with other theoretical evidences (Li et al., 2015; Wang et al., 2013).

#### References

- Akdogan E.K., Rawn C.J., Porter W.D., Payzant E.A., Safari A., 2005, Size effects in  $\text{PbTiO}_3$  nanocrystals: Effect of particle size on spontaneous polarization and strains, *Journal of Applied Physics*, 97, 084305-084308, DOI: 10.1063/1.1872195.
- Amorin H., Jimenez R., Deluca M., Ricote J., Hungria T., Castro A., Alguero M., 2014, Nanostructuring Effects in Piezoelectric  $\text{BiScO}_3$ - $\text{PbTiO}_3$  Ceramics, *Journal Of The American Ceramic Society*, 97(9), 2802-2809, DOI:10.1111/j.1538-7836.2006.02160.x.
- Bornand V., Gautier B., Papet Ph., 2004, Growth and nanoscale ferroelectric investigation of radiofrequency-sputtered  $\text{LiNbO}_3$  thin films, *Materials Chemistry and Physics* 86, 340-346, DOI:10.1016/j.matchemphys.2004.03.018.
- Fong D.D., Stephenson G.B., Streiffer S.K., Eastman J.A., Auciello O., Fuoss P.H., Thompson C., 2004, Ferroelectricity in Ultrathin Perovskite Films, *Science*, 304(5677), 1650-1653, DOI: 10.1126/science.1098252.
- Haun M.J., Furman E., Jang S.J., McKinstry H.A., Cross L.E., 1987, Thermodynamic theory of  $\text{PbTiO}_3$ , *Journal of Applied Physics*, 62, 3331-3334, DOI: 10.1063/1.339293.
- Ishikawa K., Yoshikawa K., Okada N., 1988, Size effect on the ferroelectric phase transition in  $\text{PbTiO}_3$  ultrafine particles, *Physical Review B*, 37, 5852-5856, DOI: 10.1103/PhysRevB.37.5852.
- Jiang Q., Cui X.F., Zhao M., 2004, Size effects on Curie temperature of ferroelectric particles, *Applied Physics A*, 78(5), 78703-78706, DOI: 10.1007/s00339-002-1959-6.
- Kim D.M., Eom C.B., Nagarajan V., Ouyang J., Ramesh R., Vaithyanathan V., Schlom D.G., 2006, Thickness dependence of structural and piezoelectric properties of epitaxial  $\text{Pb}(\text{Zr}_{0.52}, \text{Ti}_{0.48})\text{O}_3$  films on Si and  $\text{SrTiO}_3$  substrates, *Applied Physics Letters*, 88(14), 44, DOI: 10.1063/1.2185614.
- Lang X.Y., Jiang Q., 2007, Size and interface effects on Curie temperature of perovskite ferroelectric nanosolids, *Journal of Nanoparticle Research*, 9(4), 595-598, DOI : 10.1007/s11051-005-9066-1.
- Li H., Xiao H.J., Zhu T.S., Xuan H.C., Li M., 2015, Size Consideration on Shape Factor and Its Determination Role on the Thermodynamic Stability of Quantum Dots, *The Journal of Physical Chemistry C*, 119, 12002-12007, DOI: 10.1021/acs.jpcc.5b02230.
- Newnham R.E., Sundar V., Yimnirun R., Su J., Zhang Q.M., 1997, Electrostriction: Nonlinear Electromechanical Coupling in Solid Dielectrics, *The Journal of Physical Chemistry B*, 101, 10141-10143. DOI: 10.1021/jp971522c.
- Ramesh R., Schlom D.G., 2002, Orienting Ferroelectric Films, *Science*, 296(5575), 1975-1979, DOI: 10.1126/science.1072855.
- Sundar V., Newnham R.E., 2012, Electrostriction and polarization, *Ferroelectrics*, 135(1), 431-446, DOI: 10.1080/00150199208230043
- Tang H., Zhang S.J., Feng Y.J., Li F., Shrout T.R., 2013, Piezoelectric Property and Strain Behavior of  $\text{Pb}(\text{Yb}_{0.5}\text{Nb}_{0.5})\text{O}_3$ - $\text{PbHfO}_3$ - $\text{PbTiO}_3$ , *Journal Of The American Ceramic Society*, 96(9), 2857-2863, DOI: 10.1111/jace.12389.
- Vij J.K., Varaprasad A.M., 1981, Dielectric anomalies in barium strontium niobate, *Ferroelectrics*, 38, 865-868, DOI: 10.1080/00150198108209559.
- Wang H.Z., Gao C.X., Zhang P., Yao S.W., Zhang W.G., 2013, Synthesis and Electrochemical Performance of Graphene/Polyaniline, *Shan Shan Research Office of Surface Technology, College of Chemical Engineering, Tianjin University, Tianjin 300072, China*, 27, 117-122, DOI: 10.3866/PKU.WHXB201210234.
- Zemilgotov A.G., Pertsev N.A., Kohlstedt H., Waser R., 2002, Ultrathin epitaxial ferroelectric films grown on compressive substrates: Competition between the surface and strain effects, *Journal of Applied Physics*, 91(4), 2247-2254, DOI: 10.1063/1.1427406.