SIZE AND TEMPERATURE EFFECT ON $BaTiO_3$ NANOCRYSTALLINES AND POTENTIAL APPLICATIONS IN ENERGY STORAGE

Jackie Li
Department of Mechanical Engineering, the Grove School of Engineering, the City College of New York, New York, New York 10031, USA
email: j.li@ccny.cuny.edu

Summary This paper reports preliminary results for size and temperature effect on $BaTiO_3$ (BT) nanocrystalline materials using Landau-Ginzburg approach to evaluate the polarization distribution and Curie temperature. When the size of BT nanorods or nanoparticles reduces into nanometer, the polarization distribution depends on the external poling conditions and ferroelectric behaviour may diminish at very small size. We also studied the dielectric properties of BT nanoparticles for energy storage applications.

INTRODUCTION

In the past decades, modeling of ferroelectric materials has grown rapidly due to their important applications in smart structures and devices (such as sensors, actuators, transducers, MEMS and NEMS, etc.), and progresses in developing fast and increased computational power. Since the first discovery of ferroelectric behavior in Rochelle salt by Valasek [1] in 1920, the development in ferroelectrics has experienced several different stages. From the early stage of discovery of a greater number of ferroelectric crystals, to the creation of smart devices using ferroelectrics, and to current attempting of nanotechnology associated with nano-scale ferroelectrics. In parallel, the early stage of modeling on ferroelectrics was behind due to the complex microstructures, nonlinear coupling hysteresis loop under an electric field and/or mechanical loading, and the limitation of computational tools. Only in recent years, the modeling of ferroelectrics has been evolved rapidly. In this paper, motivated by recently attempts of using Landau-Devonshire-Ginzburg (LDG) approach [2-7], we first applied LDG model to study the depolarization field and the Curie temperature in terms of the size of BT nanowires. Using different modes, the results show interesting distribution of depolarization fields which agree well with the core-shell theory and the experimental observation on BT nanowires. Then we start to study the dielectric properties of BT nanoparticles for energy storage applications. The preliminary results are shown below.

THEORETICAL MODELING

In LDG models, an appropriate thermodynamic potential should be described in terms of function of temperature, polarization and strain. Then, to determine the equilibrium state, the total energy is minimized at given loading and boundary conditions. The accuracy of the DGL depends on the evaluations of unknown parameters and availability of measurable properties of the materials. It can be very accurate when they are applied to the range where the parameters can be fitted by measurement and less accurate when the results are extrapolated to the range beyond measurable regime. In recent years, LDG theory has been successfully applied to ferroelectric thin-films and bulk materials [8-13]. On the modeling of nano-structured ferroelectrics including ultrathin-films and nanowires using LDG approaches have also gained some momentum [2-7]. Here we also started from LDG theory. Let us consider ferroelectric cylindrical nanowire with radius R, length h and polarization $P_Z(\rho, z)$ oriented along z-axis shown in Figure 1. The external electric field is $E(0, 0, E_0)$.

By minimizing the total LDG free energy of the system and following Euler-Lagrange equations, we can obtain the governing equation as:

$$\alpha_R P_Z(\rho, z) + \beta P_Z^3(\rho, z) + \gamma P_Z^5(\rho, z) - \delta \nabla^2 P = E_0 + E_Z^d(\rho, z) \tag{1}$$

Where,

$$\nabla^2 P = \frac{\partial^2 P_Z(\rho, z)}{\partial z^2} + \frac{1}{\rho}\frac{\partial}{\partial \rho}\rho\frac{\partial}{\partial \rho}P_Z(\rho, z) = \frac{\partial^2 P_Z(\rho, z)}{\partial z^2} + \frac{1}{\rho}\frac{\partial}{\partial \rho}P_Z(\rho, z) + \frac{\partial^2 P_Z(\rho, z)}{\partial \rho^2} \tag{2}$$

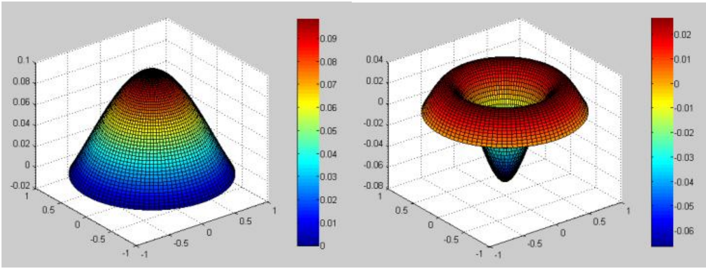
Ignore non-linear terms, move the P_z term to the left, Eq. (1) can be rewritten as:

$$(\alpha_R + \eta(R, h))P_Z(\rho, z) - \delta \nabla^2 P = E_0 + \langle P_Z \rangle \eta(R, h) \tag{3}$$

This is the modified Landau governing equation for $BaTiO_3$ nanowires. With the proper boundary conditions, Eq. (3) can be solved numerically.

RESULTS AND DISCUSSION

Fig. 1 shows the distribution of the depolarization field of a BT nanowire with 1st and 2nd mode solutions. The results indicate that the depolarization of the nanowire can either form a dome-shaped or hat-shaped distribution. Interestingly, our 2nd mode result agrees well with experimental observation [14] which has never been discovered theoretically.



(a) 1st mode (b) 2nd mode

Fig. 1. Depolarization field P_z in terms of radius of a nanowire (a) 1st mode solution and (b) 2nd mode solution.

CONCLUSIONS

Landau theory which is a phenomenological approach was introduced and extended to study the depolarization distribution and the Curie temperature of ferroelectric nanowires. The theoretical results have been compared with experimental observation. During the derivation, a second mode of general solution has been found to be consistent with the existing core-shell theory. The Curie temperature in terms of the size of the nanowire will be presented in the meeting. Finally, we will also deliver our new results on the study of dielectric properties of BT nanoparticles for energy storage applications.

Acknowledgement: This work was supported by NSF CMMI-IDR grant #1014777 and PSC-CUNY award.

References

[1] J. Valasek, *Phys. Rev.* 17, 475 (1921).

[2] Qiu, Q.Y.**;** Nagarajan, V. "Theoretical investigation of polarization scaling in ultrathin epitaxial Pb Zrx Ti1-x O3 films" *Journal of Applied Physics*, v 102, n 10, 104113, 2007.

[3] Liu, Gang**;** Wang, Rui-Hong**;** Sun, Jun "Competitive interactions between the surface effect and the depolarization field effect on the critical size of ferroelectric perovskite ultrathin films," *Scripta Materialia*, v 56, n 5, 337-340, 2007.

[4] A.N. Morozovska, E.A. Eliseev, M.D. Glinchuk, Size effects and depolarization field influence on the phase diagrams of cylindrical ferroelectric nanoparticles, *Physica B* 387, 358-366, 2007.

[5] **J.** Hong and D.N. Fang**,** Size-dependent ferroelectric behaviors of $BaTiO_3$ nanowires, *Applied Physics Letters*, v 92, n 1, 012906, 2008.

[6] Y. Zheng, C.H. Woo and B. Wang, Surface tension and size effect in ferroelectric nanotubes, J. Phys: Condens. Matter 20, 135216, 2008.

[7] E. A. Eliseev and A. N. Morozovska, General approach for the description of size effects in ferroelectric nanosystems, *J. Mat. Sci.* 44, 5149-5160, 2009.

[8] N. A. Pertsev, V. G. Kukhar, H. Kohlstedt, and R. Waser, *Phys. Rev. B* 67, 054107 (2003).

[9] Y.L. Li, S.Y. Hu, Z.K. Liu, L.Q. Chen, "Phase-field model of domain structures in ferroelectric thin-film," *Appl. Phys. Lett*. 78, 3878-3880 (2001).

[10] D. Shilo, G. Ravichandran, and K. Bhattacharya, "Investigation of Twin Wall Structure at the Nanometer Scaleusing Atomic Force Microscopy," *Nature Materials* 3, 453-457 (2004).

[11] Budimir, Marko; Damjanovic, Dragan; Setter, Nava "Qualitative distinction in enhancement of the piezoelectric response in $PbTiO_3$ in proximity of coercive fields: 90° versus 180° switching," *Journal of Applied Physics*, v 101, n 10, 104119 (2007)

[12] Zubko, P.; Jung, D.J.; Scott, J.F. "Space charge effects in ferroelectric thin films," *Journal of Applied Physics*, v 100, n 11, 114112 (2006).

[13] Lu, Xiaoyan; Wang, Biao; Zheng, Yue; Li, Chenliang "Adjustable ferroelectric properties in paraelectric/ferroelectric/ paraelectric trilayers," *Journal of Physics D: Applied Physics*, v 41, n 3, 7, 035303 (2008).

[14] Zhaoyu Wang, Jie Hu, Abhijit P. Suryavanshi, Kyungsuk Yum, and Min-Feng Yu, Voltage Generation from Individual $BaTiO_3$ Nanowires under Periodic Tensile Mechanical Load, Nano Letters, 7, 2966(2007).