

Short Communication

## Influence of Mechanical Alloying on Dielectric Features of Ferroelectric BaTiO<sub>3</sub> Microcrystals

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Dielectric features of BaTiO<sub>3</sub> microcrystals made by mechanical alloying method in the ball mill of SPEX 8000 are studied. Temperature and hysteresis loops are investigated and Curie temperature as well as dielectric constant variation are studied. The obtained results show that, there exists a relationship between the time of milling and the Curie temperature. We have established that with increasing milling time, grain size decrease, as well as Curie temperature. Moreover, with increasing temperature up to the Curie temperature, the hysteresis loop of samples decrease and at the Curie temperature the hysteresis loop disappears.

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**Keywords:** Ferroelectric, Barium Titanate, Curie Temperature, dielectric constant

### 1. INTRODUCTION

Ferroelectric composites with embedded micro- and nanocrystallites present an essential interest with respect to their dielectric and optical features [1-8]. Among the ferroelectrics the family of complex ferroelectric oxides such as BaTiO<sub>3</sub>, Pb(Zr,Ti)O<sub>3</sub> have far reaching applications in the electronics industry as transducers, actuators, and efficient dielectrics[9-14]. There has been growing trend toward preparing nanoferroelectric materials and investigation into the nano and micro-size properties as well as thin films[9,12,15,16]. Barium Titanate is one of the most exhaustively studied materials as well it is one of the materials most widely used in modern electronic and technical devices[16,18-20]. Barium Titanate is used as a ferroelectric material with a high dielectric constant

and it has been widely studied for application in capacitor, varistor and even random access memory (RAM) with developing ultra large scaled integrated circuits (ULSI) and solar cells [21-23]. Ceramics of Barium Titanate also are used for making multilayer capacitors, transformers and temperature sensors [24-26]. The study of ferroelectric transition temperature (Curie temperature) versus nanocrystalline grain size, density, purity [27-28] present one of the central point in the modern materials science of ferroelectrical nanocomposites. The Curie temperature is determined by diagrams of dielectric constants variation via temperature and hysteresis loop.

Coarse-grained ceramics (20–50 $\mu\text{m}$ ) of pure Barium Titanate showed lower dielectric constant at room temperature than fine grained (0.8–1 $\mu\text{m}$ ). It was established that when the grain size decrease below 700 nm, the crystalline lattice of Barium Titanate is changed from tetragonal to pseudo-cubic, and the dielectric constant value is very low. In the doped BaTiO<sub>3</sub> that effect is more complex [29-32]. The main goal of this work is to study of Curie temperature as a function of time milling, its kinetics and different grain sizes of Barium Titanate microcrystallites.

## 2. EXPERIMENTAL PROCEDURE

The studies were performed for BaTiO<sub>3</sub> microcrystalline powders which were fabricated by mechanical alloying at different milling times (3, 6, 10 and 12 hours). The synthesis of BaTiO<sub>3</sub> method includes adding barium acetate to a solution of oxalic acid and titanium oxychloride to form barium titanyl oxalate and then calcining the barium titanyl oxalate to obtain barium titanate powder. The sample tablets were produced by hydraulic press set-up. Then tablets were sintered for two hours at 1200 C. The surfaces of the such-prepared samples were polished and electrodes were connected to the tablets. The thickness of electrodes was varied within the 100...300 nm. The control of absence of the air condensator was controlled by measurements of changes of capacities. The existed ferroelectric domain microcrystalline sizes were controlled by optical phase contrast microscope with the resolution about 0.5  $\mu\text{m}$ . To make a better connection the samples were put in an oven for half an hour at 100 C. The Vetson Bridge was used to measure samples dielectric constants in terms of temperature. Stabilization of temperature was equal to about 0.2 K. It is clear that the hysteresis loop for ferroelectric material is dependent on the temperature at frequency 1 kHz. For thios reason all the measurements were done in the cooling heating regime with rate about 0.2 K/min. The X-ray diffraction method was used for controlling of the such obtained microcrystallites. They show a good agreement with the existed data on the bulk BaTiO<sub>3</sub>. This one mean may indicate on a good quality of the samples.

## 3. RESULTS AND DISCUSSION

The dielectric properties of BaTiO<sub>3</sub> ceramics produced by the described above method of mechanical alloying were studied in several stages. Firstly, the samples were put in a vessel of silicon oil which was on an electrical heater and stirred well by a magnetic force. The principal results are shown in the Fig. 1. One can clearly see that the values and temperature maximum of dielectric

constant strongly depend on the time of milling. As it can be expected, plots of dielectric constant versus temperature show that near the transition, temperature ( $T_c$ ) from ferroelectricity to paraelectricity, there appears its maximum value.

Milling processes have an important influence on the crystal structure and the dielectric properties of BaTiO<sub>3</sub>. With increasing milling time the value of the dielectric constant is increased up to 2.5 times and the corresponding temperature maximum of  $\epsilon$  is shifted from 78 °C up to 98 °C.

It is crucial that increasing milling time the Curie temperature undergoes to the lower value (for example the sample with 3 hours milling time  $T_c=102^\circ\text{C}$  and for the sample with 12 hours milling time is equal to  $T_c=102^\circ\text{C}$ ). All the presented ferroelectric hysteresis loops were obtained at frequency equal to about for 1 kHz.

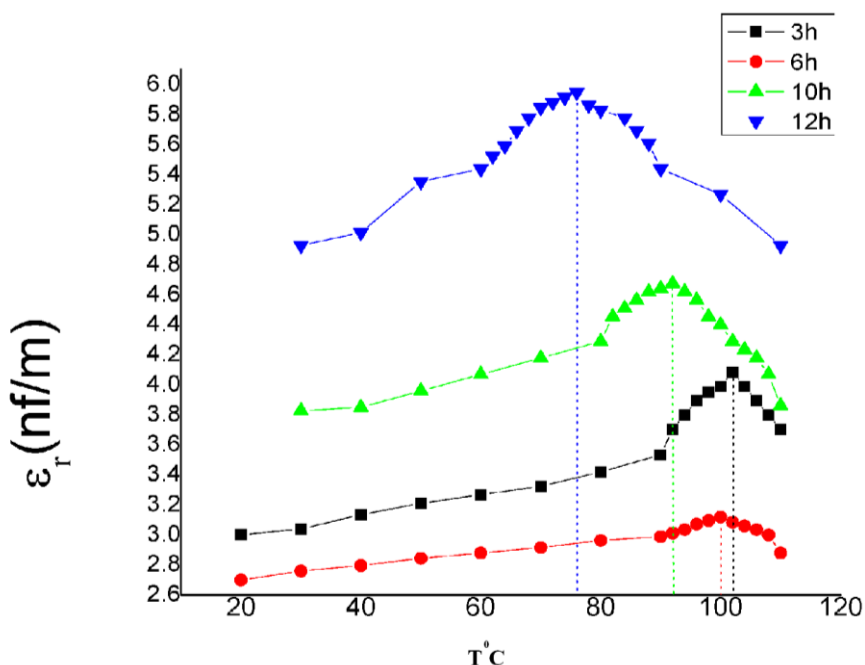


Figure 1. The variation of dielectric constant versus temperature at different milling time.

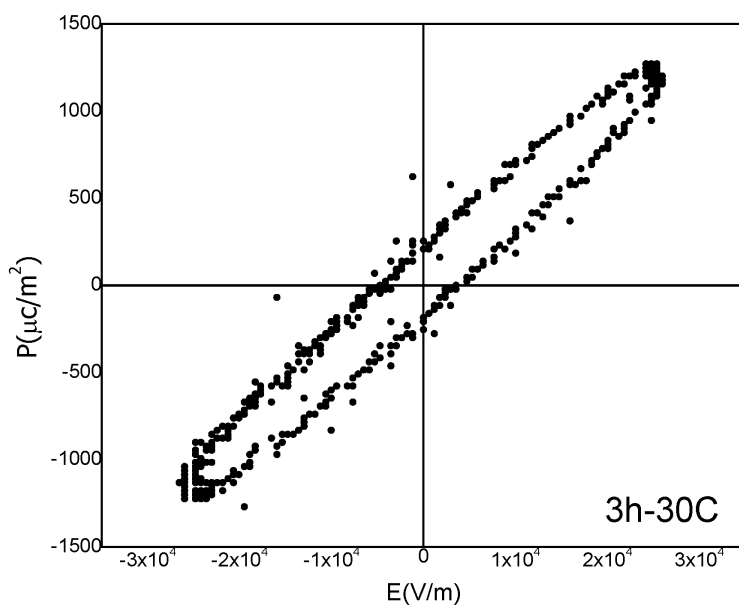


Figure 2. Hysteresis loop for BaTiO<sub>3</sub> with 3 hours alloying, at 30 °C.

The time kinetics of the processes is presented in the figures 4 to 8. With increasing temperature the slope of plots increases and their width decreases. Exactly at the Curie temperature the hysteresis loops are changed to a straight line or it is the same that the ferroelectricity decreases.

Following the Fig. 2-8 one can see a slight asymmetry of hysteresis loops. This asymmetry may be caused by existence of some additional potential on the borders of the ferroelectric microcrystalline grain domain interfaces. This property is due to the decreasing of grain sizes from 11  $\mu\text{m}$  up to 6  $\mu\text{m}$  following the optical microscopy studies. Because with decreasing of grain size, the number of dipoles of every domain decreases. In this case, in order to being parallel with external field, dipoles need a lower electric field. Consequently, Curie temperature also decreases.

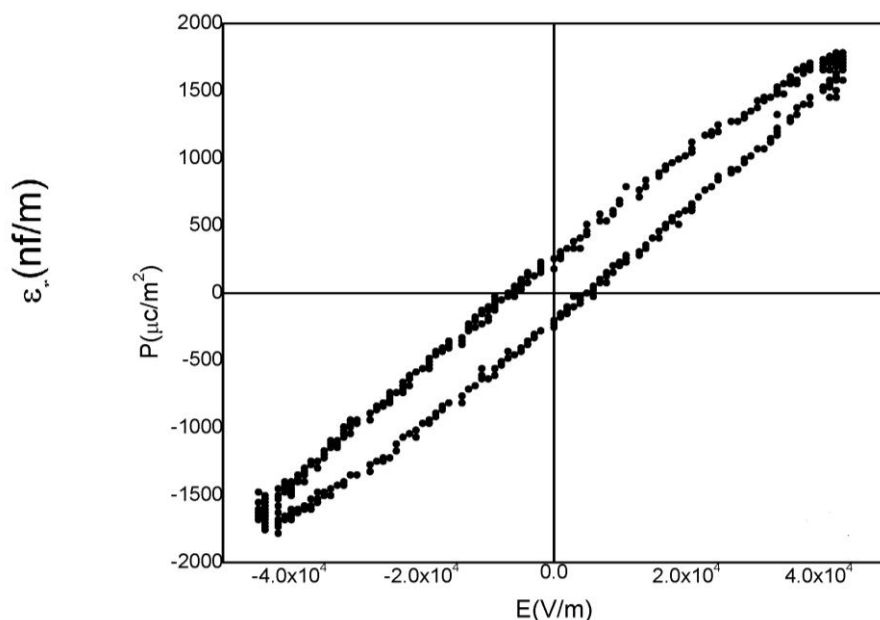


Figure 3 . Hysteresis loop for BaTiO<sub>3</sub> with 6 hours alloying, at 30° C.

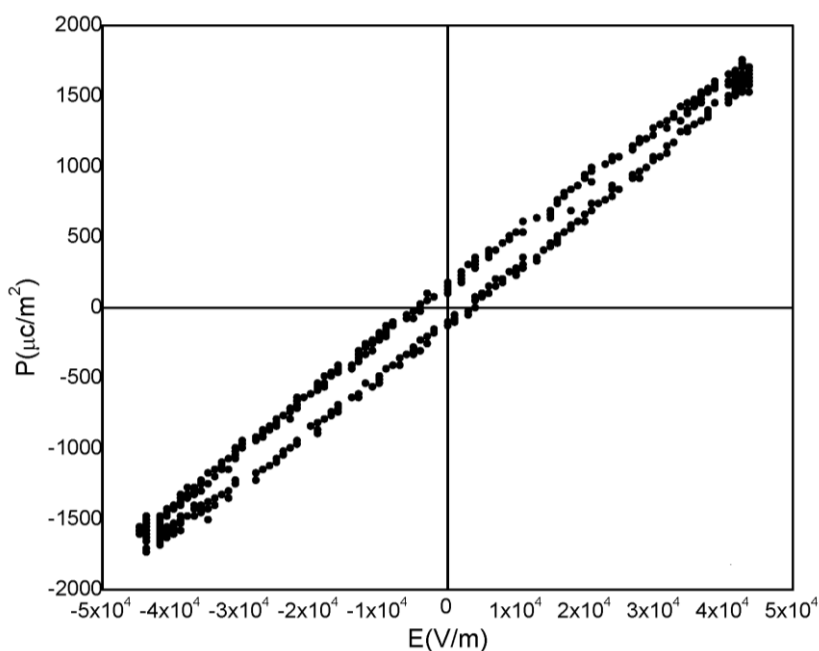
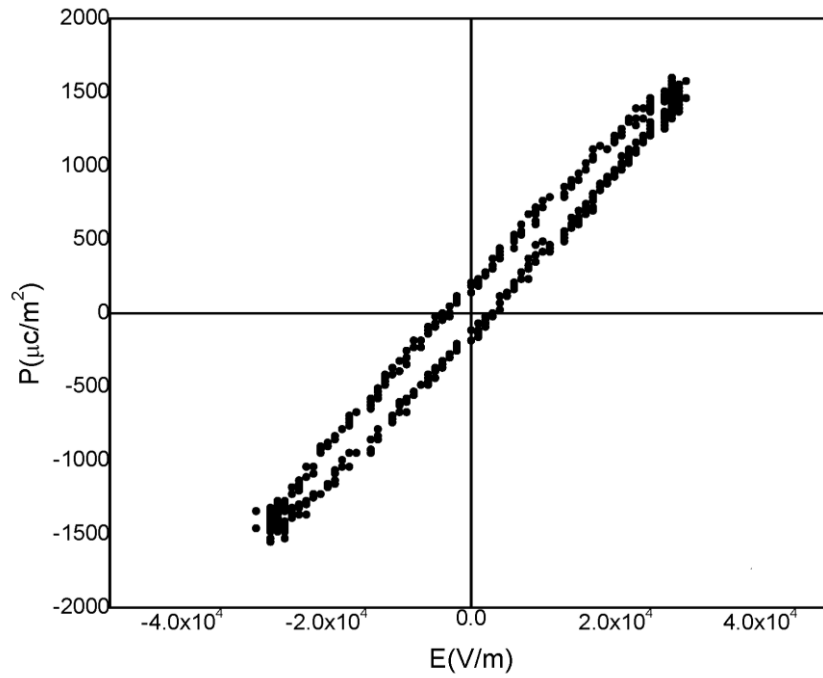
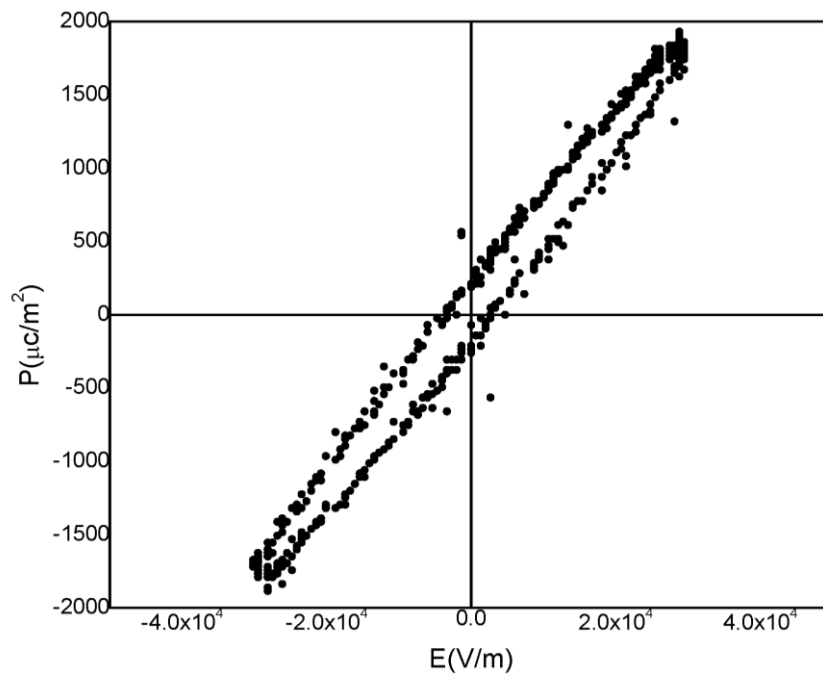


Figure 4. Hysteresis loop for BaTiO<sub>3</sub> with 6 hours alloying, at 100° C.

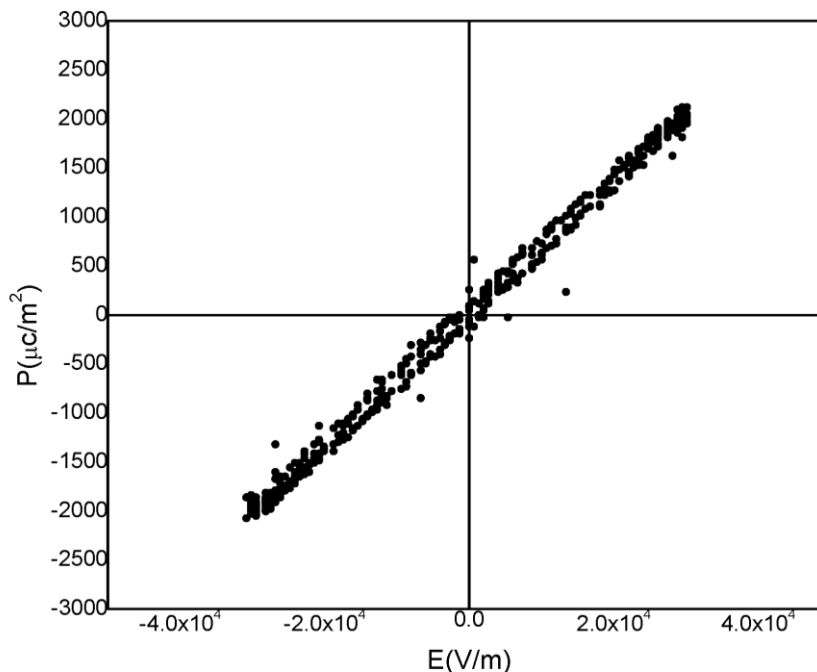


**Figure 5.** Hysteresis loop for BaTiO<sub>3</sub> with 10 hours alloying, at 70 °C.



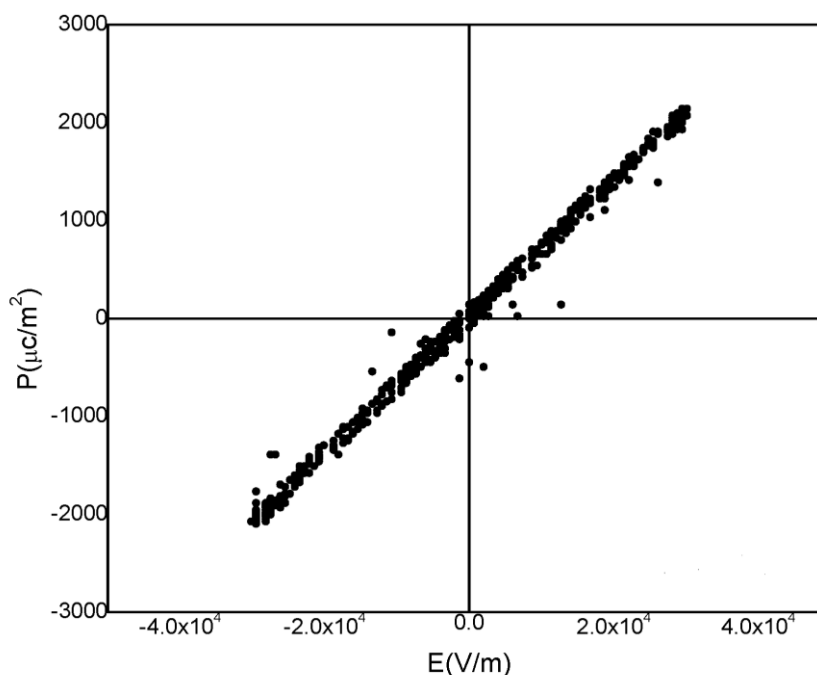
**Figure 6.** Hysteresis loop for BaTiO<sub>3</sub> with 12 hours alloying, at 30 °C.

It is principal that following the kinetics presented in the Fig. 5-8 one can see a substantial decrease of the plane under the hysteresis loop. This one means a successive decrease of spontaneous polarization.



**Figure 7.** Hysteresis loop for BaTiO<sub>3</sub> with 12 hours alloying, at 50 °C.

Another important features of the obtained loops is their nonlinear time-dependent kinetics. Which crucially depend also on the thermoannealing processes. This factor may indicate on additional contribution of the phonon subsystem, which on the borders of the crystallites may give substantial contribution to the corresponding ground state dipole moments [33] defining the spontaneous polarization. The processes observed on the borders due to the changed ground state dipole moments may have a crucial influence on the kinetics of the particular charge states.



**Figure 8.** Hysteresis loop for BaTiO<sub>3</sub> with 12 hours alloying, at 76C.

One of specific of BaTiO<sub>3</sub> crystals is their multi-axis ferroelectrics, which may from some anisotropy in the dielectric feature's behavior. This principally differ these crystals from other ferroelectric crystals. The processes observed may be used for obtaining of the memory devices with the operated values of the coercive field which may be crucial for the such kind of processes.

#### 4. SUMMARY

In this study, we have prepared the tablets of BaTiO<sub>3</sub> microcrystalline powder which was made by mechanical alloying during the time of 3,6,10 and 12 hours, at 1200C sintering temperature. The variation of dielectric constant versus temperature and the hysteresis loop of the samples are measured at different annealing times. Our results show that with increasing milling time, the magnitude of Curie temperature is decreased. It was also shown that the width of hysteresis loops samples are decreased as the temperature is increased and it reaches to zero at Curie temperature. A slight asymmetry of hysteresis loops may reflect some role of the non-homogenous of the domain wall's borders. This asymmetry may be caused by existence of some additional potential on the borders of the ferroelectric microcrystalline grain sizes. This property is due to the decreasing of grain size. Because with decreasing of grain size, the number of dipoles for each domain decreases. In this case, in order to being parallel with external field, dipoles need a lower driving electric field. Consequently, Curie temperature also decreases. Another important property of the obtained loops is their nonlinear time-dependent kinetics. This factor may indicate on additional contribution of the phonon subsystem.

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#### References

1. V.Kapustianyk, M.Partyka, V.Rudyk, M.Piasecki, M.G.Brik, S.Tkaczyk, K.Ozga, K.Plucinski, S.Romanyshyn and I.V.Kityk., *Journal of Alloys and Compounds*, 493 (2010) 26.
2. V.Rudyk, I.Kityk, V.Kapustianyk, and K.Ozga, *Ferroelectrics*. 330 (2006) 19.
3. G. Lach, L. Laskowski, I.V. Kityk, V. Kapustianyk, V. Rudyk, Ya. Shchur, S. Tkaczyk, J. Swiatek and M. Piasecki, *Journ. Non-Crystalline Solids*. 35 (2007) 4342.
4. M.Piasecki, P.Braiel, S.Tkaczyk, I.V.Kityk, J.Ebothe, V.Kapustianyk, M.Partyka, V.Rudyk, K.Nouneh and A.H.Reshak, *Materials Letters*. 62 (2008) 2088.
5. K.Ozga, M.Piasecki, S.Tkaczyk, B.Kapustianyk, P.Bragiel, A.H.Reshak, M.G.Brik and I.V.Kityk. *Physica B*. 403 (2008) 2561.
6. V.Kapustianyk, Ya.Shchur, I.Kityk, V.Rudyk, G.Lach, L.Laskowski, S.Tkaczyk, J.Swiatek and V.Davydov, *J.Phys.:Condens.Matter*. 20, (2008) 365.
7. S.W.Tkaczyk, I.V.Kityk, V.Rudyk and V.Kapustianyk, *Physica E*. 42 (2010) 2124.
8. G.Lakshminarayana, V.Kapustianyk, K.Ozga, V.Rudyk, I.V.Kitykj, M.G.Brik, J.Berdowski, and Z.Tylczynski, *Applied Physics A*. 104 (2011) 721.
9. Wan Soo Yun, Jeffrey J. Urban, Qian Gu, and Hongkun Park, *Nano Letters*. 2 (2002) 447.

10. Yuanqing Cui and Zheng Zhong, *Mechanics of Materials*. 45 (2012) 61; M.C. Kao, H.Z. Chen, S.L. Young, B.N. Chuang, W.W. Jiang, J.S. Song, S.S. Jhan, J.L. Chiang and L.T. Wu, *Journal of crystal growth*. 338 (2012) 139.
11. Stephen O'Brien, Louis Brus, and C. B. Murray, *J. Am. Chem. Soc.* 123 (2001) 12085.
12. M.I.Kolinko, I.V.Kityk, R.Y.Bibikov and J.Kasperczyk. *Journ. Materials Science Letters*.15 (1996) 803.
13. A. H. Reshak, S. Auluck and I. Kityk, *Japanese Journal of Applied Physics*. 47 (2008) 5516.
14. M. Piasecki, I.V. Kityk, P. Bragiel, K. Ozga, V. Kapustianyk and B. Sahraoui, *Chemical Physics Letters*. 433 (2006) 136.
15. M.I.Kolinko, I.V.Kityk and R.V.Bibikov. *Ferroelectrics*. 153 (1994) 127.
16. N. A. Hill, *J. Phys. Chem. B*. 104 (2000) 6694.
17. C. Pitham, D. Hennings, and R. Wases, *Int. J. Appl. Ceram. Technol.* 2 (2005) 1.
18. M. Dawber, K. M. Rabe, and J. F. Scott, *Rev. Mod. Phys.* 77 (2005) 1083.
19. M. Z.-C. Hu, V. Kurian, E. A. Payzant, C. J. Rawn, and R. D. Hunt, *Powder Technology*. 110 (2000) 2.
20. Chen-Feng Kao and Chiao-Ling Yang, *Journal of the European Ceramic Society*. 19 (1999) 1365.
21. M. Yoshimura, S-E. Yoo, M. Hayashi and N. Ishizawa, *Japanese J. Applied Physics*. 28 (1989) 2007.
22. M. Zhong, J. Shi, W. Zhang, H. Han and C. Li, *Materials Science and Engineering B*. 176 (2011) 1115.
23. Z. Wu and M. Yoshimura, *Solid State Ionics*. 122 (1999) 161.
24. G. Vasta, T. J. Jackson and E. Tarte, *Thin Solids film*. 520 (2012) 3071.
25. J. Kim, D. Kim, T. Noh, B. Ahn and H. Lee, *Materials Science and Engineering B*. 176 (2011) 1227.
26. Y. Su and G.J. Weng, *Journal of the Mechanics and Physics of Solids*. 53 (2005) 2071.
27. Yue-Ming Li, Liang Cheng, Xing-Yong Gu, Yu-Ping Zhang and Run-Hua Liao, *Journal of Materials Processing Technology*. 197 (2008) 170.
28. B.D. Stojanovic, C.R. Foschini, M.A. Zaghete, F.O.S. Veira, K.A. Peron, M. Cilense and J.A. Varela, *Journal of Materials Processing Technology*. 143 (2003) 802.
29. B. Jaffe and W.R. Cook, *Piezoelectric Ceramics*, Academic Press, London, New York, 1971.
30. G.H. Heartling, *J. Am. Ceram. Soc.* 82 (1999) 797.
31. G. Bush, *Ferroelectrics*. 4 (1987) 267.
32. K.J.Plucinski, M.Makowska-Janusik, A.Mefleh, I.V.Kityk and V.G.Yushanin. *Materials Science and Engineering*, B64 (1999) 88