CORRELATION OF MICROSTRUCTURE AND DIELECTRICAL PROPERTIES OF BaTIO3 SINTERED FROM MECHANICALLY ACTIVATED POWDERS

B.A. Marinković[1], B.D. Stojanović[1], V.B. Pavlović[2], V.P. Pavlović[3], M.M. Ristić[4]

[1]*Center for Multidisciplinary Studies University of Belgrade, Joint Laboratory for Advanced Materials of SASA, Yugoslavia; e-mail: bojan@rdc.puc-rio.br*[1]

[2]*Faculty of Agriculture, Department of Physics, University of Belgrade, Yugoslavia*

[3]*Faculty of Mechanical Engineering, University of Belgrade, Yugoslavia*

[4]*Serbian Academy of Sciences and Arts, Joint Laboratory for Advanced Materials of SASA, Belgrade, Yugoslavia*

Mechanical activation, as a one of the most outstanding processes in synthesis of advanced materials, is closely related to different structural changes (phase transitions, generation of dislocations and crystal lattice microstrains, decrease of mean crystallite sizes -incoherently diffracting domains) by the influence of mechanical energy.

Investigations of $BaTiO_3$ obtained by reaction sintering at 1200^oC for two hours, from mechanically activated (0, 30 and 180 minutes) equimolar mixture of $BaCO_3$ - TiO_2 (rutile to anatase ratio 1.05:1) were carried out by X-ray powder diffraction (XRPD). Qualitative phase analysis pointed out that reaction in the solid state proceeded entirely to completion with formation of tetragonal (ferroelectric) $BaTiO_3$ modification. Line-broadening analysis for evaluation of microstructural quantities such as mean crystallite sizes (incoherently diffracting domains) and root mean square microstrains was performed by modified variance method on (111) diffraction lines, because of the specific nature of tetragonal $BaTiO_3$ X-ray powder diffraction pattern. Unit-cell constants were evaluated from diffraction patterns obtained in the range 20-80 ° (2θ) using the pattern decomposition method.

Changes of dielectric properties such as Curie point (T_c) and dielectric constant (ε_r) of $BaTiO_3$ as a function of mechanical activation time were correlated with changes of the c/a ratio, mean crystallite sizes and root mean square microstrain.

1.   Introduction

The influence of mean crystallite sizes on the ferroelectric to paraelectric transition temperature (Curie point) and the dielectric constant was recently investigated for different materials [1-7]. However, different intriguing conclusions were made. For example, it was found that the transition temperature of lead lanthanum zirconate titanate increases with decreasing mean crystallite sizes. Also, there is still confusion about the influence of the mean crystallite sizes on ferroelectric to paraelectric transition temperature of $BaTiO_3$. Namely, some authors have found that this property, in $BaTiO_3$, is not sensitive to mean crystallite

size [7]. On the contrary, some other authors have indicated that with decreasing mean crystallite sizes, the transition temperature (Curie point) decrease, too [1, 3, 4]. The relationship between mean crystallite sizes of $BaTiO_3$ and dielectric constant, also, is not well established [3, 6]. It should also be emphasized that $BaTiO_3$ sample in the previously quoted papers were obtained by different preparation routes and, thus, this can be the possible explanation of the different dielectric properties indicated by different authors.

In this paper, the ferroelectric to paraelectric transition temperature and the dielectric constant of $BaTiO_3$ specimens, obtained by reaction sintering of mechanically activated equimolar mixtures of $BaCO_3$-TiO_2, were correlated with the mean crystallite size, root mean square microstrain and the tetragonality ratio, c/a. Pattern decomposition [8] and modified variance method [9] were used for evaluation of the tetragonality ratio, c/a, and microstructural quantities (mean crystallite size and root mean square microstrain), respectively.

2.   Experimental

The mixture of 50 mol% $BaCO_3$ (Merck, p.a. 99%) and 50 mol% TiO_2 (Venton, p.a. 99%) powders were homogenized and mechanically activated in high energy vibromill with rings (CUP Mill, Typ MN 954/3 KHD Humboldt Wedag AG) during 0, 3 and 180 minutes. Mechanically activated mixtures were calcinated for one hour at 800^oC and after that reaction sintered at 1200^oC for two hours, with heating rate of $10^oC/min$. As-prepared specimens were labelled as a $BaTiO_3$-0, $BaTiO_3$-30 and $BaTiO_3$-180.

X-ray diffraction patterns (over the range 20°-80° 2θ) were obtained using PHILIPS PW-1820 diffractometer with $CuK\alpha_{1/2}$ radiation, graphite monochromator and step-scanning mode ($0.02^o/20s$). Additionally, diffraction data were collected over the angular range 38°-40° (2θ) with improved scanning time of 40s, for the line-broadening analysis of the (111) diffraction lines.

The dielectric constant (ε_r) was determined as a function of temperature in the range of 20^oC to 140^oC.

---

1   *Present address of the first author: Pontifícia Universidade Católica do Rio de Janeiro, Departamento di Cięncia dos Materiais e Metalurgia, Brasil*
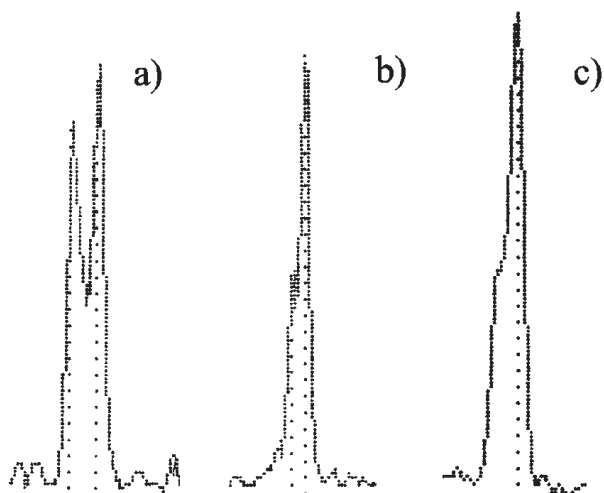
Fig. 1. Characteristic part of the tetragonal BaTiO$_3$ diffraction pattern: (002)-(200) diffraction lines of a) BaTiO$_3$-0 specimen; b) BaTiO$_3$-30 specimen; c) BaTiO$_3$-180 specimen

Fig. 2. Least square fit of the experimental diffraction line (111): a) BaTiO$_3$-0 specimen (due to the small microstructural broadening Kα_2 line is clearly visible); b) BaTiO$_3$-180 specimen; c) BaTiO$_3$-30 specimen
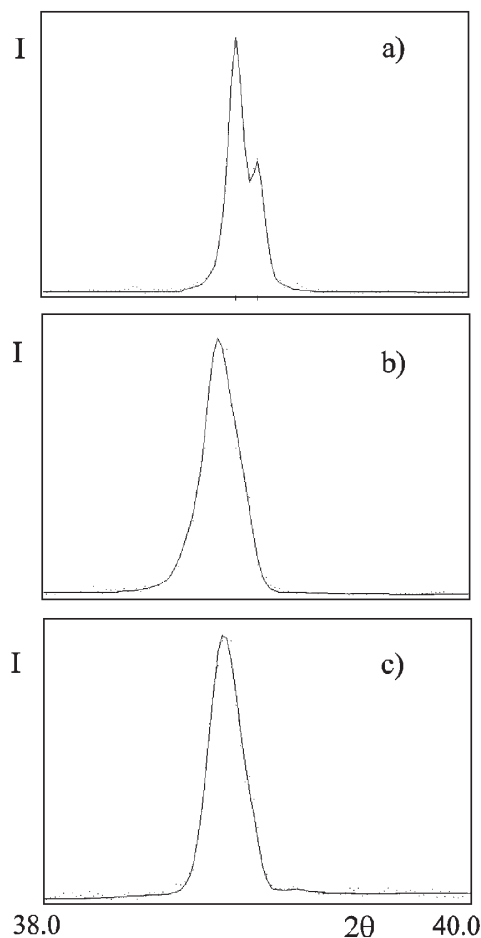
3.   Results and Discussion

The qualitative phase analysis of diffraction patterns (BaTiO$_3$-0, BaTiO$_3$-30 and BaTiO$_3$-180) showed that the solid-state reaction proceeded entirely to the completion with formation of the tetragonal (ferroelectric) BaTiO$_3$ phase. Still, it can be observed that the c/a ratio is dependent on the time of mechanical activation, Fig. 1.

Therefore, the pattern decomposition-pattern matching technique was used as a tool for precise determination of the unit-cell constants (a,c) of as-prepared tetragonal BaTiO$_3$, Table 1. A detailed explanation of the method is presented elsewhere [10]. However, because of severe overlapping of BaTiO$_3$ diffraction lines over the investigated range (20°-80° 2θ), the modified variance method [9] was applied for line-broadening analysis. Thus, the diffraction line (111) was chosen for line-broadening analysis and evaluation of microstructural quantities. As a standard for determining the instrumental profile, a BaF$_2$ sample was used, prepared as described at [11]. Both profiles, instrumental and experimental, were fitted by pseudo-Voigt functions. Least square fit of the (111) experimental diffraction lines are shown in Fig. 2.

Numerical criteria's of fit such as goodness of fit (S$_y$), R$_{wp}$ and R$_e$ factors showed quite satisfactory values.

Microstructural quantities were obtained in a straightforward manner [9] and presented at Table 1.

Mechanical activation [12] of initial mixture obviously have significant influence on the solid-state reaction and, thus, on mean crystallite sizes and crystal lattice microstrains in BaTiO$_3$. Therefore, it can be established that with increasing activation time, the mean crystallite sizes of BaTiO$_3$ are decreased, contrary to the crystal lattice microstrains (expressed as a root mean square values) which are increased. However, one can observe, also, that the tetragonality ratio, c/a, significantly decreases with decreasing

Table 1. Microstructural quantities (mean crystallite size-D, root mean square microstrain - $<e^{1/2}>^2$), unit-cell constants (a,c), c/a ratio and numerical criteria of fit, S$_y$, R$_{wp}$ and R$_e$
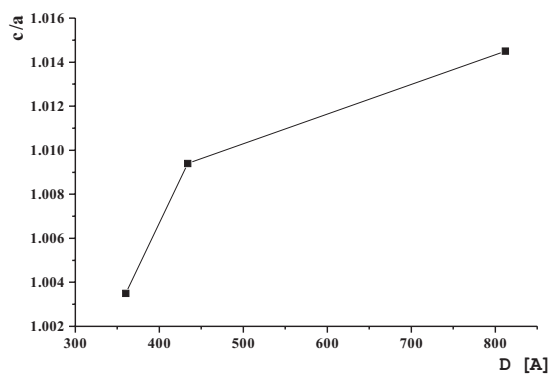
Specimen	D [Å]	$<e^{1/2}>^2$	a [Å]	c [Å]	c/a	S$_y$	R$_{wp}$	R$_e$
BaTiO$_3$-0	812	0.0027	3.9951(12)	4.0531(30)	1.0145	1.31	8.32	6.36
BaTiO$_3$-30	434	0.0049	3.9959(8)	4.0336(8)	1.0094	1.24	10.3	8.30
BaTiO$_3$-180	360	0.0057	4.0032(24)	4.0174(57)	1.0035	1.27	12.4	9.77
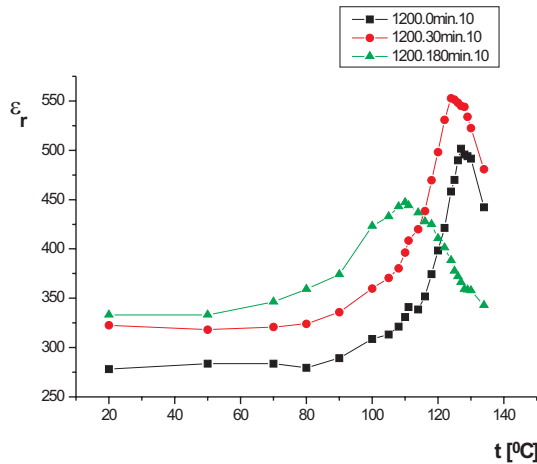
Fig. 3. The dependence of Curie point, T_c, and dielectric constant, ε_r, on time of mechanical activation

Fig. 5. The dependence of Curie point, T_c, on microstructural quantities

mean crystallite size, indicating change of the crystal lattice, which approaches the cubic state, Fig. 1. As the tetragonality ratio is dependent on the mean crystallite size, there is a certain critical mean crystallite size after that $BaTiO_3$ crystal lattice becomes cubic. With increasing of activation time, this values should be reached.
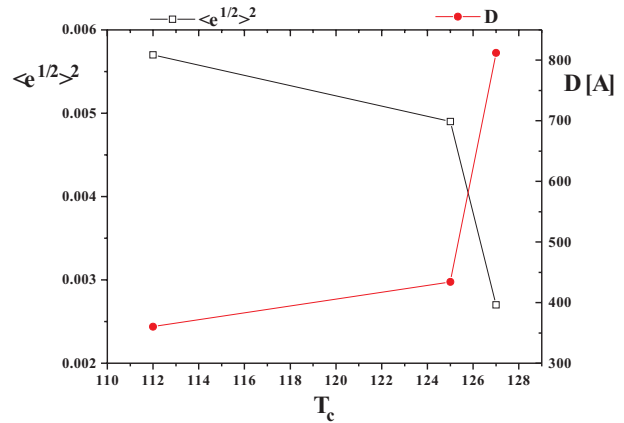
The dielectric measurements, Fig. 3, showed that the ferroelectric to paraelectric transition temperature (Curie point-T_c) decreases as the time of mechanical activation increases.

In other words, Curie point, T_c, is dependent on the tetragonality ratio, c/a, Fig. 4, and microstructural quantities such as mean crystallite sizes and crystal lattice microstrains, Fig. 5. Moreover, this dependence shows that after certain critical values of the tetragonality ratio, the mean crystallite sizes and microstrains, the decrease of Curie point is rather significant.

A possible explanation for this behavior of the $BaTiO_3$ Curie point is based on differences in free energy of the paraelectric and ferroelectric states [3,4]. It is well known that the tetragonal (ferroelectric) state has a lower free energy than the cubic (paraelectric) $BaTiO_3$ state. A recently developed theory [3] concerned with the part of the free energy related to the polarization, shows that small crystallites (mostly single domained) have large depolarization energy, E_d. Because of that, the total free energy has a higher value. The multidomain structure of the larger crystallites, on the other hand, reduce the depolarization energy and, thus, the total free energy has lower value and the tetragonal structure is stable.

Moreover, high concentration of crystal lattice defects, such as dislocations (estimated density in our specimens is about $10^{11} cm^{-2}$), manifested through crystal lattice microstrains, also increased the total free energy, because their contribution to the entropy is small compared with their effect on the internal energy. It can be seen from Fig. 5, that higher microstrain values are associated with smaller crystallites and, thus, additionally increased total free energy.

Therefore, the high total free energy of the smaller $BaTiO_3$ crystallites is a consequence of the increase of two different contributions: a) depolarization energy, E_d, and b) internal energy, U. Accordingly, the increase of the total free energy resulted in a less stable tetragonal $BaTiO_3$ state compared with cubic state.

It should be mentioned that the shape of the crystallites also has a certain influence on the ferroelectric to paraelectric transition temperature. Taking into account our previous investigations [13], we assumed that crystallites have a spherical shape on average.

Further, it can be noticed, Fig. 5, that the dielectric constant (ε_r) increased with an increasing of activation time. More precisely, the decrease of mean crystallite size have a significant effect on the dielectric constant. That is in agreement with conclusion made previously [6]. Thus, the increase of the dielectric constant can be explained by an increased volume fraction of the domain walls with decreasing of mean crystallite size.

4.   Conclusions

The ferroelectric to paraelectric transition temperature (Curie point) is sensitive to the mean crystallite size of $BaTiO_3$. Moreover, the important influence of the crystal lattice microstrains on the behavior of Curie point was established.

Fig. 4. The dependence of the tetragonality ratio, c/a, on mean crystallite sizes of $BaTiO_3$

It can be inferred that microstructural quantities have a profound effect on the free energy of BaTiO$_3$ and through that on dielectric properties.

Acknowledgement

References

1. K. Uchino, E. Sadanaga, T. Hirose, *J. Am. Ceram. Soc.*, **72** [8] (1989) 1555.

2. K. Ishikawa, *Phys. Rev. B: Condens. Matter*, **37** [10] (1988) 5852.

3. W.Y. Shih, W.H. Shih, I.A. Aksay, *Phys. Rev. B: Condens. Matter*, **50** [21] (1994) 15575.

4. X. Li, W.H. Shih, *J. Am. Ceram. Soc.*, **80** [11] (1997) 2844.

5. M.H. Lee, A. Halliyal, R.E. Newnham, *Ferroelectrics*, **87** (1988) 71.

6. G. Arlt, D. Hennings, G. de With, *J. Appl. Phys.*, **58** (1985) 1619.

7. B.D. Begg, E.R. Vance, J. Nowotny, *J. Am. Ceram. Soc.*, **77** [12] (1994) 3186.

8. J.I. Langford, D. Louër, E.J. Sonnveled, J.W. Visser, *Powder Diffr.*, **1**, 3 (1986) 211.

9. F. Sánchez-Bajo, F.L. Cumbrera, *J. Appl. Cryst.*, **30** (1997) 427.

10. B.A. Marinković, Z. Zakula, S. Durić, N. Nikolić, O. Milosević, M.M. Ristić, Line-Profile Analysis of Nanostructured ZnO Powders Obtained by Freeze-Drying Method, *Materials Science Forum*, **321-324** (2000) 1068.

11. D. Louër, J.I. Langford, *J. Appl. Cryst.*, **21** (1988) 430.

12. K. Tkáčová, Mechanical Activation of Minerals, Elsevier, Amsterdam (1989).

13. V.B. Pavlović, B.D. Stojanović, G. Branković, M.M. Ristic, *Sci. Sintering*, **28** Spec. Issue (1996) 143.