Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 27 (2007) 575–579

www.elsevier.com/locate/jeurceramsoc

Microstructural evolution and electric properties of mechanically activated $BaTiO_3$ ceramics

V.P. Pavlović [a,*], M.V. Nikolić [b], Z. Nikolić [c], G. Branković [b], Lj. Živković [d], V.B. Pavlović [e], M.M. Ristić [f]

[a] Faculty of Mechanical Engineering, University of Belgrade, Kraljice Marije 16, 11000 Belgrade, Serbia and Montenegro
[b] Center for Multidisciplinary Studies of the University of Belgrade, Kneza Višeslava 1, 11000 Belgrade, Serbia and Montenegro
[c] Faculty of Physics, University of Belgrade, Serbia and Montenegro
[d] Electronic Faculty, University of Nish, Serbia and Montenegro
[e] Faculty of Agriculture, University of Belgrade, Serbia and Montenegro
[f] Institute of Technical Sciences of Serbian Academy of Sciences and Arts, Belgrade, Serbia and Montenegro

Abstract

Ceramic materials with a perovskite related structures such as non-doped and doped barium titanate ceramics are attracting much interest for their application as capacitor dielectrics, resistors, thermal sensors, etc. Since mechanical activation can be used in order to modify properties of these materials, in this study microstructure evolution and electric properties of mechanically activated $BaTiO_3$ have been analyzed. The sintering process of high purity non-doped mechanically activated $BaTiO_3$ was monitored using a sensitive dilatometer with a heating rate of 10 °C/min. Investigation of the microstructure evolution of mechanically activated $BaTiO_3$ was performed using scanning electron microscope (SEM) and digital pattern recognition (DPR) methods. A dielectric study of the paraelectric–ferroelectric phase transition in the barium titanate ceramics was performed by recording the temperature dependence of dielectric permittivity.

Keywords: Milling; Sintering; Electrical properties; $BaTiO_3$ and titanates

1. Introduction

Microstructure influenced properties are of major interest in many types of electroceramics, especially in materials that undergo phase transitions, such as barium titanate ceramics.[1] Since electrical properties and therefore applications of these materials as capacitors, resistors, thermal sensors, etc. are sensitive to their microstructure, especially pore and grain size distribution and grain boundary conditions, it is very important to understand the nature of these relations. Possible causes for the grain-size dependent behaviour of these materials, according to Frey and Payne could be the existence of depolarization fields, absence of long-range cooperative interactions, internal stresses and structural defects.[2] In the case of dielectric permittivity, numerous investigators have observed that dielectric permittivity of $BaTiO_3$ increases with decreasing grain size, peaks at some critical size, and then decreases with continued size reduction.[3,4] Domain wall and internal stress models could be used to explain these effects.[5] Although size effects may influence changes in the ferroelectric phase transition temperature (Curie temperature), boundary conditions such as formation of compressive and tensile stresses are also expected to decrease or increase the transition temperature. Furthermore, in addition to a simple shift of the transition temperature, stress fields can also influence the order of the phase transition through higher-order elastic coupling coefficients.[6] Since the evolution of the microstructure of barium titanate ceramics is significantly affected by ceramic processing including the initial powder state, forming additive and sintering processes, processing control must be performed carefully. Conventionally, $BaTiO_3$-based materials are manufactured at high temperatures, by solid-state reactions or from chemically derived intermediates.[7,8] Unfortunately, these methods typically produce large, non-uniform and agglomerated particles, which generally limits the ability to fabricate reliable electronic components. One opportunity to influence initial powder microstructure and sintering properties of the material is to mechanically

---

[*] Corresponding author. Tel.: +381 11 637367; fax: +381 11 637239.
E-mail address: vlaver@itn.sanu.ac.yu (V.P. Pavlović).

0955-2219/$ – see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2006.04.074

Table 1
Impurity content of the as-received BaTiO$_3$ powder

Impurities	Concentration (ppm)
Sr	400
Ca	360
Al	12
Sn	35
Cu	4
Zr	51
Pb	54

activate the powder using a high energy milling process.[9] During mechanical activation changes of the free energy lead to the formation of a new surface, diminution of the mean particle size and generation of a stress field. They should result in changes of dielectric permittivity and the dielectric temperature dependence.

Having all this in mind the purpose of our investigations was to study the effects of mechanical activation of BaTiO$_3$ on the evolution of the microstructure during non-isothermal sintering and the influence of mechanical activation on electrical properties of activated BaTiO$_3$.

2. Experimental procedure

The experiments were carried out with a commercial BaTiO$_3$ powder (Merck, 99.8% Ba/Ti ratio of 1:1 grain size ~1 μm) whose impurity levels are summarized in Table 1. Mechanical activation of powders was performed in a planetary-ball mill (Fritsch Pulverissete 5) for 60 and 120 min. The ball/sample mass ratio was 20:1. After mechanical activation the powders were pressed into pellets 6 mm in diameter and average thickness of 4 mm. The green densities of the three different initial BaTiO$_3$ powders were determined as: 3.171 g/cm^3 for the non-activated powder and 3.53 and 3.552 g/cm^3 for the powders activated 60 and 120 min, respectively. Non-isothermal sintering of BaTiO$_3$ was followed by a sensitive dilatometer (Bahr Geratebau GmbH) up to 1300 °C with a heating rate of 10 °C/min. Sample densities were calculated as described in our previous paper.[10] Microstructure investigations of starting powders and sintered samples were performed using a JEOL-JSM-T20 scanning electron microscope. The grain size and morphology were expressed by digital pattern recognition (DPR) microstructure quantity analysis.[11] Dielectric studies of the paraelectric–ferroelectric phase transition in barium titanate ceramics were performed by recording the temperature dependence of dielectric permittivity using a HP 4276A LCZ meter.

3. Results and discussion

Dilatometric analysis showed differences in the densification rate for the non-activated and activated samples (Fig. 1). For all three powders the densification rate reaches a maximum at temperature values between 1200 and 1250 °C, although the curve forms are different for the non-activated and activated powders. The increasing part of the densification curve changes almost linearly for the non-activated powder while several segments can be noted for the activated powder samples. Also, the decreasing part of the densification rate curve is more gradual for the non-activated powder. A more detailed analysis of this phenomenon has been given in our previous work where such behaviour of densification rates was attributed to different activity of microstructure constituents.[10]

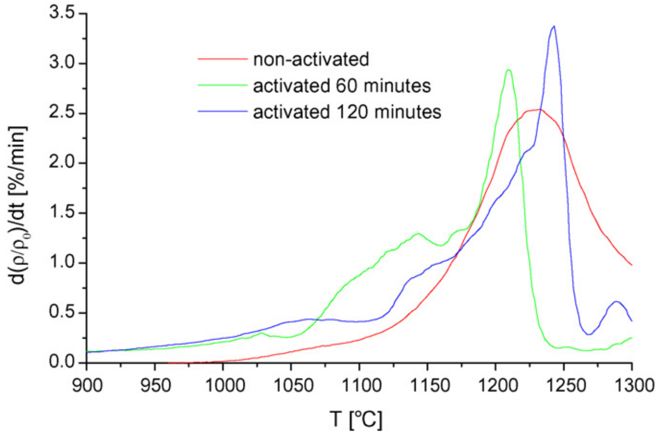

Fig. 1. Change of the densification rate with temperature for the non-activated powder and the powders activated 60 and 120 min.

Changes in the surface activity of grains influenced the microstructure evolution at the temperature of 1300 °C. It was noticed that grains with a higher number of boundaries grow, while grains with a smaller number of boundaries decreased forming microstructures given in Fig. 2. Microstructural analysis showed that the obtained morphology for non-activated samples is characteristic for early stages of sintering, during which, formation of contact necks between grains occurs (Fig. 2(a)). On the other hand, mechanical activation led to intensification of transport processes, resulting in a less porous microstructure characterized by polyhedral grain shapes (Fig. 2(b) and (c)). DPR analysis showed that as a result of internal strain, caused by high pressure applied to the powder particles during mechanical activation, the average grain size for all samples was similar though the grain size distribution was different. Formation of new surfaces and the increase of the concentration of structural defects, which are characteristic result of mechanical activation, increased the surface reactivity, leading to the formation of agglomerates. Our previous investigations emphasized the importance of intra- and inter-agglomerate sintering for the densification process and microstructure development of sintered materials.[10] Agglomeration can influence formation of microstructure defects and microstress thus affecting final properties of materials.

Dielectric measurements have shown that mechanical activation and sintering regime had a significant influence on the dielectric properties of the specimens. The room temperature values of ε_r varied from $\varepsilon_r = 300$ for the non-activated samples, to $\varepsilon_r = 756$ for the 120 min activated samples. The small values of dielectric permittivity, especially for non-activated samples, could be caused by low densification and high porosity of the samples, which is the consequence of the sintering regime. It was also observed that the maximums of $\varepsilon_r = f(T)$ curves, correspond-

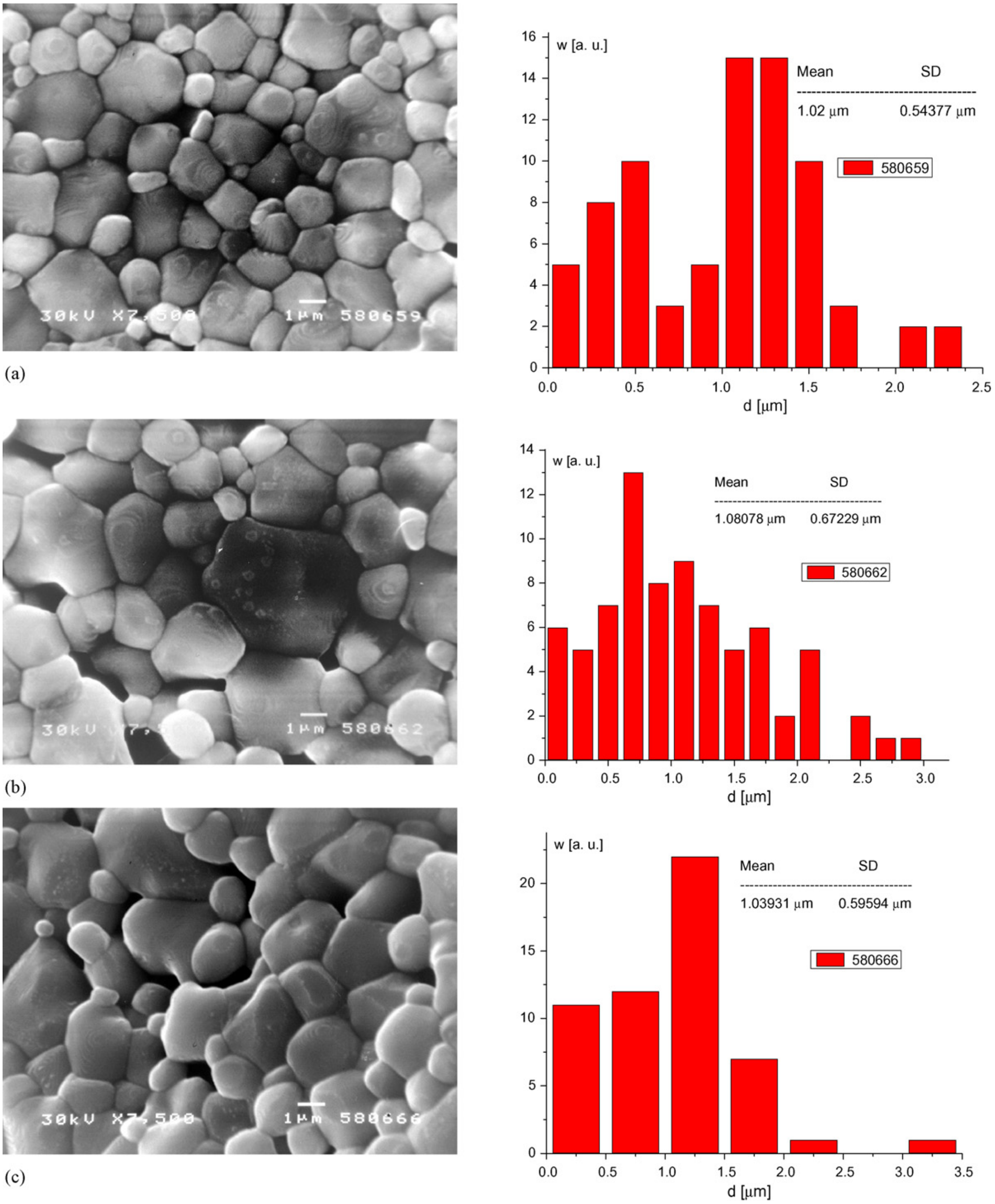

Fig. 2. SEM microstructures and constituent distribution functions for $BaTiO_3$ samples of powders (a) non-activated and activated for (b) 60 min and (c) 120 min sintered at 1300 °C.

ing to the transition from the ferroelectric to the paraelectric states, are displaced towards lower temperatures, as the time of mechanical activation increased (Fig. 3).

It is important to note that the symmetry reduction at the paraelectric–ferroelectric transition depends on size and stress effects and therefore is greatly influenced by the microstructure of the sintered material. Moreover, formation of agglomerates may also play an important role in changes of the transition temperature as shown by Liu's thermal analysis and X-ray investigations of sub-micrometer $BaTiO_3$ particles.[12] In general, size and stress effects may involve shifting of the phase transition to lower temperatures, broadening of the temperature range of paraelectric phase metastability and change of the magnitude of dielectric properties. The manner in which these effects occur is dependent on the order of the phase transition and for barium titanate-based materials the generalized temperature

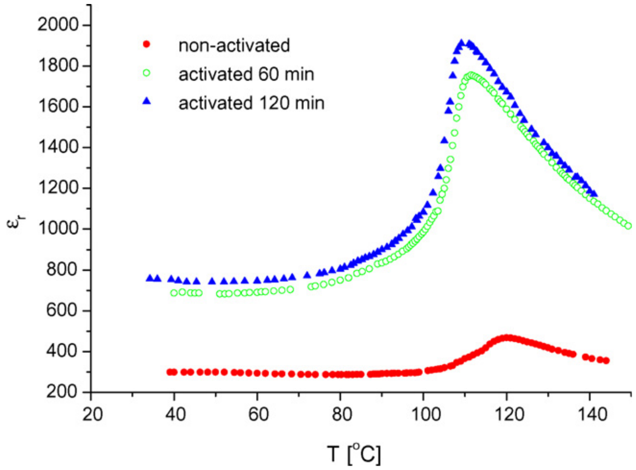

Fig. 3. Temperature dependence of the dielectric permittivity of non-activated and activated $BaTiO_3$.

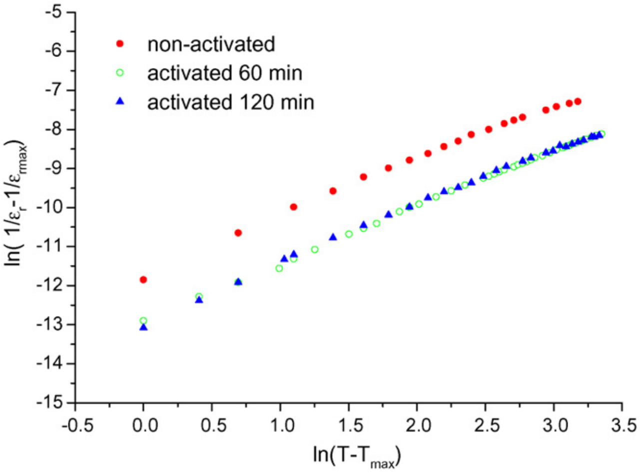

Fig. 4. Plots of $\ln(1/\varepsilon_r - 1/\varepsilon_{rmax})$ vs. $\ln(T - T_{max})$ for non-activated and activated $BaTiO_3$.

dependence (for the temperature range above Curie temperature) may be defined as[13,14] :

$$\frac{1}{\varepsilon_r} - \frac{1}{\varepsilon_{rmax}} = \frac{(T - T_{max})^{\gamma}}{C'} \qquad (1)$$

where C' is a constant, T_{max} is the temperature of dielectric constant maximum, and γ is the critical exponent of the dielectric constant ($\gamma = 1$ for Curie–Weiss conditions and $\gamma \neq 1$ for non-Curie–Weiss conditions). Parameters C' and γ were calculated from linear functional dependence: $\ln(1/\varepsilon_r - 1/\varepsilon_{rmax})$ versus $\ln(T - T_{max})$, at temperatures above T_{max} (Fig. 4) and are given in Table 2. Obtained values for the critical exponent indicate that besides a structural transformation other processes may occur at the Curie temperature, probably connected with porous structure and grain boundary defects.

Table 2
Summary of transition parameters for non-activated and activated $BaTiO_3$

Activation time (min)	T_{max} (K)	$(\varepsilon_r)_{max}$	γ	C' (K)
0	393	468.6	1.41	1.09×10^5
60	384	1756	1.375	3.44×10^5
120	383	1916	1.38	3.41×10^5

Since the influence of the size effects on T_c values in $BaTiO_3$ may become important for the grain size range less than 0.2 μm, it was concluded that in our case the grain size modifications could not significantly affect the change of T_c.[15] Therefore, that phenomena should be interpreted on the basis of the change in lattice defects concentration. Our previous results pointed out that the energy accumulated during mechanical activation lead to plastic deformation of surface layers, forming local stress on grain boundaries, increasing the lattice strains from 5.8% for the non-activated sample to 11.2% and 13.6% for the samples activated 60 and 120 min, respectively.[16] According to that, formation of uncompensated stress during mechanical activation is expected to reduce tetragonal distortion leading to a change of phase transition temperature.

4. Conclusion

In this article the influence of mechanical activation of $BaTiO_3$ on the evolution of the microstructure during non-isothermal sintering and also on dielectric properties and paraelectric–ferroelectric phase transition of $BaTiO_3$ has been investigated. It was concluded that the applied regime of mechanical activation increased structural disorder resulting in changes of microstructure evolution. For non-activated samples the obtained morphology was characteristic for early stages of sintering, while intensification of transport processes due to mechanical activation, led to less porous microstructures characterized by polyhedral grain shapes. Dilatometric investigations also pointed out strong differences in densification rates of the activated samples compared to the non-activated one. For non-activated samples the sintering process took place in one step, while for the activated ones it occurred in three steps. Dielectric measurements have shown that the maxima of the curve $\varepsilon_r = f(T)$ were displaced towards lower temperatures, as the time of mechanical activation increased. Shifting of the phase transition to lower temperatures and dielectric anomaly broadening has been explained by size and stress effects.

Acknowledgements

The authors would like to express their gratitude to N. Labus for dilatometry measurements. This research was performed within the project no. 1832 entitled “Synthesis of functional materials from the ‘synthesis–structure–properties–application’ relationship viewpoint” financed by the Ministry of Science and Environmental Protection of the Republic of Serbia.

References

1. Kretschmer, R. and Binder, K., Surface effects on phase transitions in ferroelectrics and dipolar magnets. *Phys. Rev. B: Condes. Mat.*, 1979, **20**, 1065–1075.
2. Frey, M. H. and Payne, D. A., Grain-size effect on structure and phase transformations for barium titanate. *Phys. Rev. B*, 1996, **54**, 3158–3168.

3. Arlt, G., Henings, D. and de With, G., Dielectric properties of fine-grained barium titanate ceramics. *J. Appl. Phys.*, 1985, **58**, 1619–1625.
4. Kinoshita, K. and Yamaji, A., Grain size effects in $BaTiO_3$ ceramics. *J. Jpn. Phys.*, 1976, **47**, 371–373.
5. Wang, S., Dielectric properties of fine-grained barium titanate-based X7R materials. *J. Am. Ceram. Soc.*, 1999, **82**, 2677–2682.
6. Rosseti Jr., G. A., Cross, L. E. and Kushida, K., Stress induced shift of the Curie point in epitaxial lead titanate films. *Appl. Phys. Lett.*, 1991, **59**, 2524–2526.
7. Pavlović, V. P., Stojanović, B. D., Pavlović, V. B., Živković, Lj. and Ristić, M. M., Low temperature sintering of mechanically activated $BaCO_3$–TiO_2. *Sci. Sint.*, 2002, **34**, 73–77.
8. Zhang, D. L., Processing of advanced materials using high-energy mechanical milling. *Prog. Mater. Sci.*, 2004, **49**, 537–560.
9. Pavlović, V. B., Marinković, Z., Pavlović, V. P., Nikolić, Z., Stojanović, B. and Ristić, M. M., Phase transformations and thermal effects of mechanically activated $BaCO_3$–TiO_2 system. *Ferroelectrics*, 2002, **271**, 391–396.
10. Pavlović, V. P., Nikolić, M. V., Pavlović, V. B., Labus, N., Živković, Lj. and Stojanović, B. D., Correlation between densification rate and microstructure evolution of mechanically activated $BaTiO_3$. *Ferroelectrics*, 2005, **319**, 75–85.
11. Pavlović, V. B., Nikolić, Z., Pavlović, V. P. and Živković, Lj., New digital method of microstructural characterisation of sintered materials. In *Applied physics in Serbia-APS*, *SANU*, *Vol XCVIII Book 2/1*. Belgrade, 2002, pp. 137–143.
12. Liu, X., In *Proceedings of the 98th annual meeting on cluster size effects in $BaTiO_3$ powders*. American Ceramic Society, Indianapolis, USA, 1996.
13. Isupov, I., Some problems of diffuse ferroelectric phase transition. *Ferroelectrics*, 1989, **90**, 113–118.
14. Kuwabara, M. and Kunamoto, K., PTC characteristics in barium titanate ceramics with Curie points between 60 and 360 °C. *J. Am. Ceram. Soc.*, 1983, **65**, C214.
15. Uchino, K., Sadanaga, E. and Hirose, T., Dependence of the crystal structure on the particle size in barium titanate. *J. Am. Ceram. Soc.*, 1989, **72**, 1555–1558.
16. Pavlović, V. P., Nikolić, M. V., Spasojevic, V., Blanusa, J., Živković, Lj., Pavlović, V. B., *et al.*, The influence of tribophysical activation on non-isothermal sintering of $BaTiO_3$ ceramics. In *Book of abstracts*, *Materiais*, *Vol 326*. Portugal, 2005.