Microstructure and Properties of Barium Titanate Ceramics Prepared by Mechanochemical Synthesis

C. MICLEA[1], C. TĂNĂSOIU[1], I. SPÂNULESCU[2], C. F. MICLEA[1], A. GHEORGHIU[2], L. AMARANDE[1], M. CIOANGHER[1], C. T. MICLEA[2]

[1]National Institute for Materials Physics, Bucharest-Măgurele, Romania
[2]Hyperion University, Calea Călăraşilor 169, sector 3, Bucharest, Romania

E-mail: `cmic@infim.ro`

Abstract. The new advanced procedure of mechanochemical synthesis was used to prepare barium titanate from barium and titanium oxides. The X-ray examination of the powders milled for different times showed the phase evolution during synthesis. The perovskite phase was initiated after 5 hours of milling and was completed after 50 hours. Sintered samples from these nanopowders show different dielectric properties depending on their morphostructure. Thus for samples with an average grain size of 2 μm we obtained the highest dielectric constant of 5 800 at room temperature. A sharp maximum of the dielectric constant with values of about 16 000 was recorded at the Curie temperature.

1. Introduction

One of the most studied functional material is barium titanate (BT) especially due to its potential application as multilayer ceramic capacitors, PTC thermistors or electromechanical devices, piezoelectric transducers, actuators, high-ε dielectrics, dynamic RAM or logic circuitry as well as a great variety of electro-optical devices [1, 2]. The characteristics of such electronic ceramic are markedly influenced by the particle size, and morphology of the material [3]. Dielectric constant for example is strongly dependent on the grain size [4–8]. For coarse grained ceramics the dielectric constant at room temperature is lower than for fine grained ones [9, 10]. But if the grain sizes go further down then the dielectric constant decreased again to lower values, so that it has to be assumed that there is an optimum dimension for the

grains where the dielectric constants at room temperature shows a maximum. This peculiar behavior is probably connected with some changes of the lattice of BT from tetragonal to pseudocubic [11]. In order to achieve small grains in fired BT ceramics it is common practice to use additives as grain growth inhibitor, or to control the processes responsible for grain growth such as time-temperature conditions during sintering. In other words the restriction of grain growth can be achieved by establishing the conditions under which mass transport mechanism leading to densification is favored against the mechanism leading to grain boundary migration. BT nanopowders can be obtained via several routes among which: chemical coprecipitations [12,13], hydrothermal synthesis, [14–17], sol-gel technique [18–20] and mechanical synthesis [21–24] are the most important ones. Mechanochemical activation technique is one of the most outstanding process for synthesis of advanced materials and is closely related to different structural changes such as phase transitions, generations of strains, dislocation, crystal lattice deformation or morphostructural modifications, all brought about by mechanical energy involved in the milling process. In the case of conventional solid state reaction the phases formed at the reactant surfaces growth by diffusion of thermally activated atoms through the interfaces and this mass transport needs high temperatures and high energy consumption in order to complete the reaction and formation of the compound. In the case of intensive milling the contact area between the reactant particles increases by continuous particle comminuting, thus creating new fresh surfaces through which the diffusion and mass transport take place easier. Moreover, the particles undergo a mechanical treatment by which the impact energy may become comparable to the energy of the crystal lattice thus allowing an easier movement of the atoms involved in the formation of the new phases. Therefore one can assume that the fine and ultrafine powders become mechanically activated and the chemical reactions between them are stimulated to take place at lower temperature during mechanochemical synthesis without any extra heat. Unfortunately, the nature of this extremely high activity is not yet fully understood and efforts are made by the scientific community to go deeper in the understanding of this phenomenon. Barium titanate could be obtained by mechanosynthesis by mixing either barium carbonate and titanium dioxide [23, 24] or barium and titanium oxides [21, 25]. The BT powders obtained were characterized only from the point of view of powder characteristics. Our paper reports on both powder characteristics and dielectric properties of BT sintered samples obtained from powders synthesized by the new advanced technique of mechanochemical process.

2. Experimental

The starting raw materials used for the preparation of barium titanate were barium oxide and titanium dioxide of p. a. purity. The oxides, with a particle size distribution in the 1–5 μm range were weighted to make batches of 30 g of stoichiometric $BaTiO_3$ and they were loaded into agate jars, of 500 ml together with 100 agate balls of 10 mm diameter corresponding to a ball/oxide powder ratio of 5/1. In order to prevent the ground material from sticking to the jars and balls we added 5 ml of methanol to

allow a better dispersion and to reduce the agglomeration of smaller particles. The jars usually called "the planets" were mounted in their corresponding places on the sun wheel of a Retsch PM 400 planetary mill. The mill operated at a rotation speed of the sun wheel of 350 min^{-1} and a speed ratio of 1:–2, which means that the grinding jar rotates twice for each sun wheel rotation thus providing a high fineness of the powder in a relatively short time. Since the jars rotate about their own axis and in the opposite direction around the common axis of the sun wheel, the grinding balls move with high pulverization energies. Centrifugal forces carry the balls in the direction in which the jar is rotating and the differences between the speeds of the grinding jar and the balls results in strong frictional forces. On the other hand the Coriolis forces act on the balls and displace them from the jar walls and make them fly through the interior of the jar and impact against the sample on the opposite wall of the jar, thus releasing considerable impact energy. The movement and the action of balls within the jars are shown schematically in Fig. 1 [26]. Thus when the ball reaches point A the centrifugal forces created by the sun wheel and jar rotation are summed up and their values are maximum. The friction force is also maximum in this point. The ball moves then along the jar wall where it is kept tight by the centrifugal forces and the friction between the ball and the wall smashes the powder until it reaches point B where centrifugal and Coriolis forces equilibrate and the friction become zero. Further on the ball falls somewhere in point C impacting the wall and smashing again the powder particles and the process repeats itself again and again making the powder finer and finer.
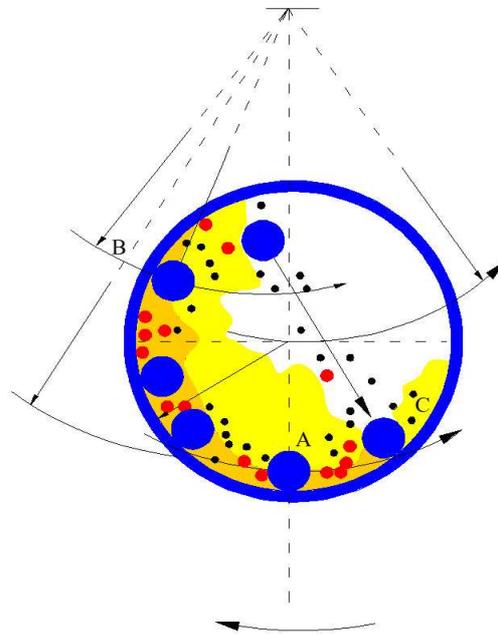

Fig. 1. Schematic view of the balls movement
within the jars of the planetary ball mill.

In this way the impact and frictional forces result in a high degree of pulverization and comminuting of the powders in the nanosize range. The phase development of the milled powders was monitorized by X-ray diffraction (Siemens Kristalloflex IV difractometer). The dielectric properties were measured by an Agilent 4294A Impedance Analyzer.

3. Results and discussions

It is known that the conventional way to synthesize barium titanate by the solid state reaction between barium carbonate and titanium dioxide is a simple and low cost process, but it has the disadvantage to require high temperatures for calcinations and to produce coarse grained powder, unsuitable for a number of applications in which fine grained ceramics are required. Instead the mechanochemical synthesis produces directly fine grained powder of barium titanate without being necessary the calcinations step only as a result of physico-chemical changes of constituent oxides produced by high mechanical energy of the milling process. We started from oxides milled in a planetary ball mill for different times up to 50 hours. Figure 2 shows the XRD patterns of mixed powders mechanically activated for different times. One can see that the XRD for initial mixture of oxides show only the peaks for BaO and TiO_2.

After 5 hours of milling the well-known perovskite structure begin to appear being slightly visible at $2\theta = 31.4°$, $38.7°$ and possible at $45°$. After 20 h the barium titanate seems to be formed in a much higher amount and eventually after 50 h the synthesis of $BaTiO_3$ is completed. No trace of unreacted oxides is present. It is worth noting that no trace of SiO_2, produced by corrosion of the agate balls and jars, was detected. It could be possible that the amount of the corroded SiO_2 to be under the resolution limit of diffractometer. Thus one can conclude that barium titanate was completely synthesized from oxides after 50 h of mechanical activation in a planetary ball mill.
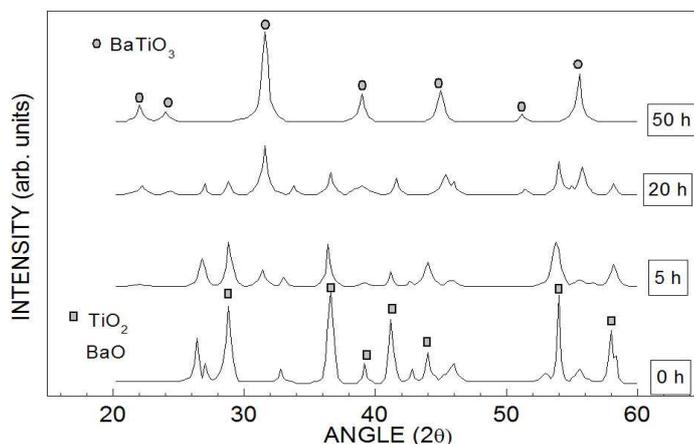

Fig. 2. XRD pattern of mechanically activated oxide powder
for different milling times.

The morphology of the powder milled for 50 h is illustrated in Fig. 3. One may appreciate that the grain sizes are situated around 50 nm, but agglomerates of varying sizes can also be identified. The majority of grains show spherical shapes but some other show faces at different angles. This is probably due to the fact that the grains synthesized in the beginning were much more eroded by milling while the other formed afterwards, were not enough eroded.
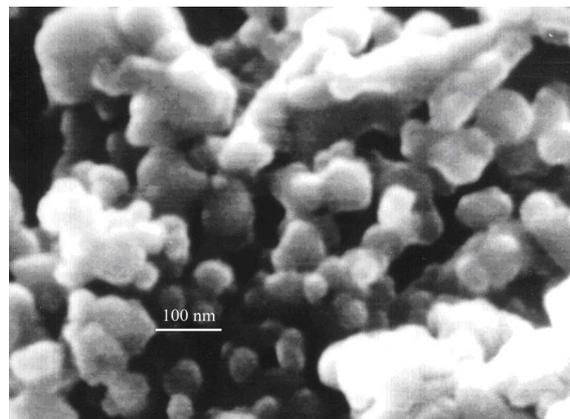

Fig. 3. Morphology of barium titanate powder after 50 hours of milling.

The synthesized powders were uniaxially pressed as discs with 10 mm diameter and about 1 mm thick and were sinterized on platinum boats in air at temperatures between $1\,200°C$ and $1\,450°C$ for 4 h. The densification process is illustrated in Fig. 4 where one can see that between $1\,350°$ and $1\,400°C$ the samples are fully densified and the density reaches maximum values of about 98% of theoretical density. Above $1\,400°C$ the density decreased, probable due to the fact that crystallites increase were rapidly and a greater number of pores are formed.
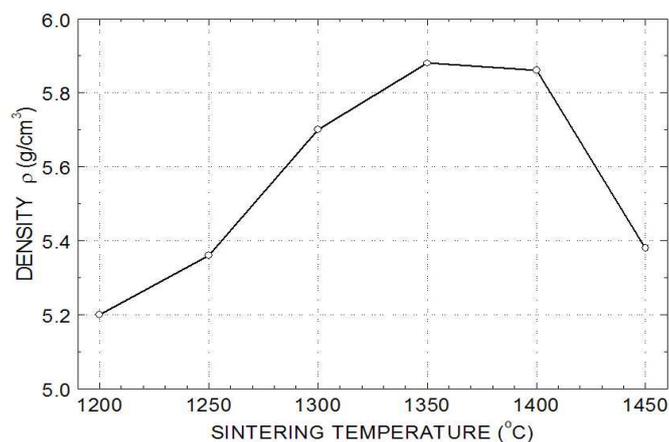

**Fig. 4.** Density vs. sintering temperature for BT.

The average grain size vs sintering temperature is shown in Fig. 5. The grain size increases rather steadily with increasing sintering temperature.
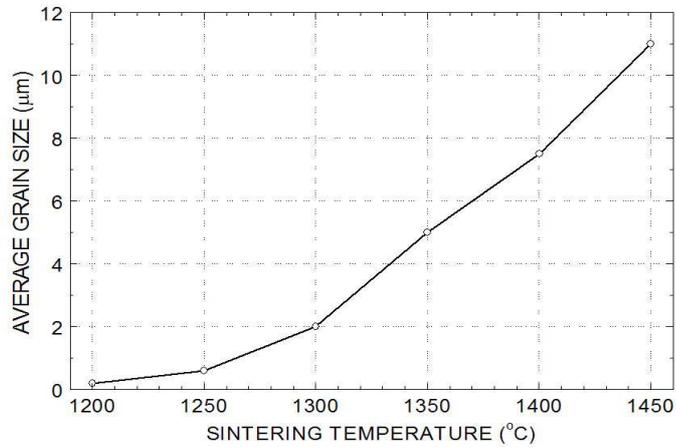
Fig. 5. Grain size behavior of BT powders
as a function of sintering temperature.

Figure 6 shows images of as fired surfaces of samples sintered at different temperatures between 1 300°C and 1 450°C. In Fig. 6a the average grain size is about 2 μm while in Fig. 6e it is about 12 μm.
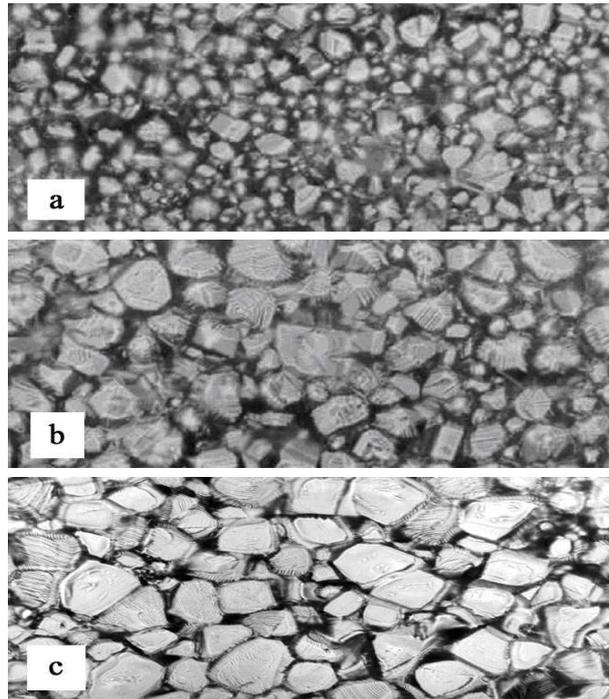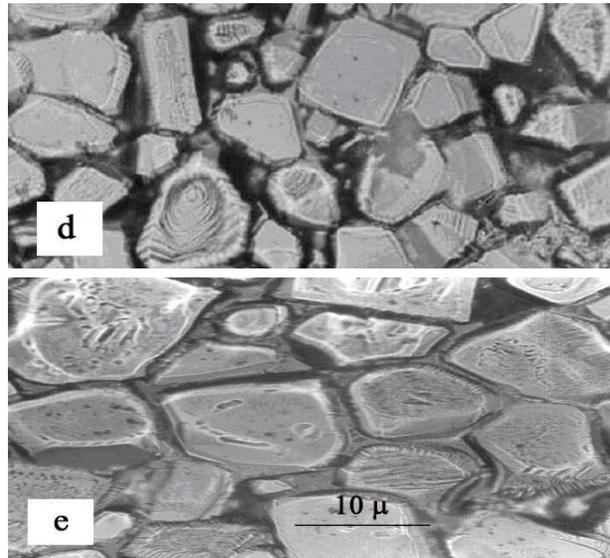
Fig. 6. Images of as fired sample surfaces for BT sintered at:
a) 1 200°C; b) 1 250°C; c) 1 300°C d) 1 400°C and e) 1 450°C respectively.

The dielectric properties of the fine and coarse grains samples of BaTiO$_3$ are shown in Figs. 7 and 8. Figure 7 shows the behavior of the relative dielectric constant as a function of the grain size. One can see that there is an optimum grain size of 2 μm for which the dielectric constant shows a maximum value of 5 800. For samples with smaller or greater grain size the dielectric constant decreases, this process being more pronounced for coarse grained samples. Thus for samples with grains of 12 μm the dielectric constant decreases to 1 000.
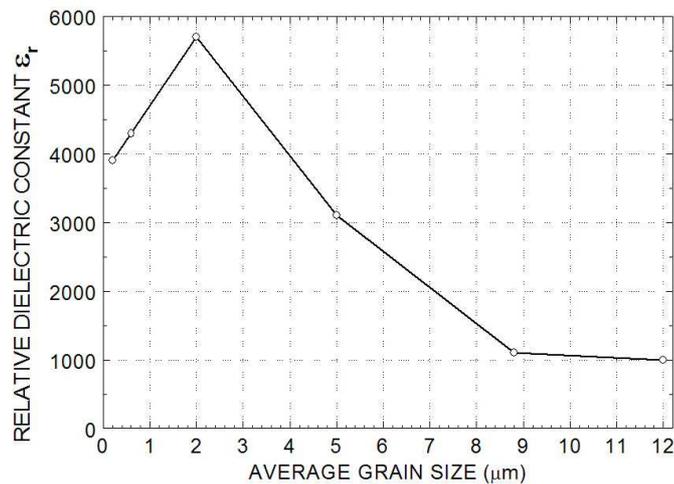
Fig. 7. Dielectric constant for BT sintered samples
with different grain size.

Figure 8 illustrates the behavior of the dielectric constant with temperature. The first observation to be made is that the dielectric constant in the ferroelectric state strongly depends on grain size and very slightly on temperature, being rather constant up to 100°C. In the paraelectric state, above the Curie point, it is almost independent on grain size but strongly on temperature. Such a difference between paraelectric and ferroelectric states implies that the internal stresses may play an important role in the grain size effect because internal stresses do not grow in the cubic phase, above Curie temperature but develops when the ceramic is cooled below T_C. The peak around T_C is sharp for both samples but the maximum value for fine grained sample (nearly 16 000) is higher than that for coarse grained samples (12 500).
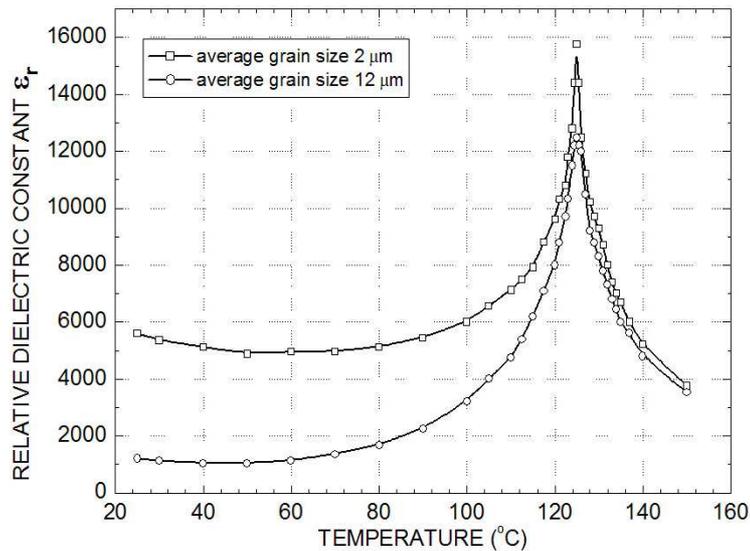
Fig. 8. Dielectric constant as a function of temperature for BT sintered samples with average grain sizes of 2 μm and 12 μm respectively.

Some differences in the piezoelectric properties for fine and coarse grains ceramics were also observed. Thus, for example, the electromechanical planar coupling factor measured on standard sized samples (discs of 10 mm diameter and 1 mm thickness) for fine (12 μm) and coarse (12 μm) grained specimens were different as illustrated in Fig. 9 along the whole temperature interval from room temperature up to the Curie point.

The coupling factor k_p for fine grained samples is greater with about 35% than that of coarse grained ones. The temperature dependence of k_p for the two types of samples is also different. For fine grained one k_p remains constant up to about 80°C and then rapidly decreases while for coarse grained one it decreased rather steadily from the beginning. This behavior could possible be due to the effect of domain alignment. We believe that the poling degree is greater in samples with a smaller number of domains (fine grained sample) than in coarse grained ones.
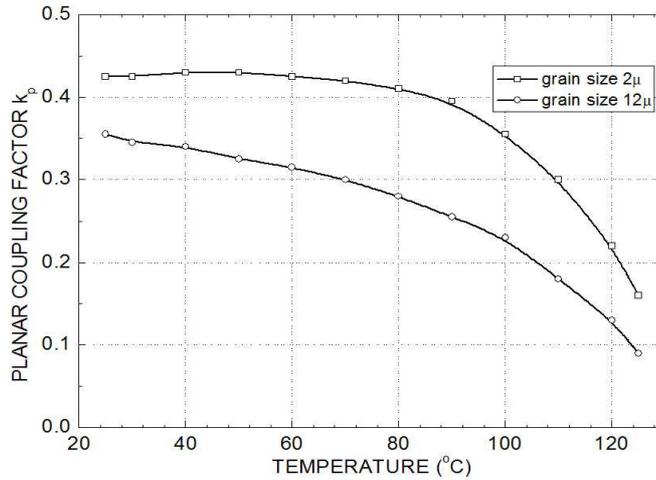
Fig. 9. Electromechanical coupling factor k_p as a function of temperature for BT sintered samples with average grain sizes of 2 μm and 12 μm respectively.

As it was earlier estimated [27] although 180° domains reversal is complete, only about 12% of them switch 90° and that half of these revert back to their original orientation on removing the poling field. In an ideal ceramic only on-sixth of all the domains are favorable oriented to a given field, one-sixth switch by 180° and the other two-thirds switch by 90°. The theoretical maximum polarization for a completely poled ceramic can reach only 80% of the single crystal value so that only about 12% of the misaligned domains remain switched by the 90° due to the inability to remove the local stresses induced during realignment.

4. Conclusion

Single phase $BaTiO_3$ was synthesized by mechanochemical process from BaO and TiO_2, after 50 h of milling in a high energy ball mill. The resulting perovskite phase of $BaTiO_3$ powder exhibited particle size of about 50 nm. The best dielectric properties were obtained in fine grained ceramics with average grain size of 2 μm where the dielectric constant at room temperature was 5 800 compared with only 1 000 for coarse grained ceramics, with average grain size of 12 μm.

References

[1] MOULSON A., HERBERT J., *Electroceramics Material, Properties & Applic.*, Chapman&Hall, 1990.

[2] CALLISTER W., *Mat. Sci. and Eng.: An Introduction*, J. Willey&Sons Inc. Chichester, 1994.

[3] PRASAD V., KUMAR L., *Studies on some* BaTiO₃ *electroceramics*, Ferroelectrics, **102**, p. 141, 1990.

[4] BELL A., MOULSON A., *The effect of grain size on the permitivity of barium titanate ceramics*, Ferroelectrics, **54,** pp. 147–150, 1984.

[5] ARLT G., HENNINGS D., DEWITH G., *Dielectric properties of fine grained BT*, J. Appl. Phys., **58**, pp. 1619–1625, 1985.

[6] WU K., SCHULTZE W., *Aging of the weak field dielectric response in fine and coarse grained BT ceramic*, J. Am. Cer. Soc., **75**, pp. 3390–3395, 1992.

[7] GACHIGI K., KUMAR U., DOUGHERTY J., *Grain size effects in* BaTiO₃, IEEE Sym. Appl. of Ferroelectrics, pp. 492–495, 1992.

[8] LUAN W., GAO L., GUO J., *Size effect on dielectric properties of fine grained* BaTiO₃, Ceramic Int., **25**, pp. 727–729, 1999.

[9] ARLT G., PENSES H., *The dielectric constant of coarse grained BT ceramics*, Ferroelectrics, **48**, pp. 213–214, 1983.

[10] KINOSHITA K., YAMAGI A., *Grain size effects on dielectric properties of* BaTiO₃ *ceramics*, J. Appl. Phys., **47**, pp. 371–373, 1976.

[11] STOIANOVIC B., FOSHINI C., ZAGHETI M., VERRA F., PERON K., CILENSE M., VARELA J., J. Mat. Process. Technology, **143–144**, pp. 802–806, 2003.

[12] TESTINO A., BUSCAGLIA T., VIVIANI M., BUSCAGLIA M., NANI P., *Synthesis of BT particles by precipitation from aqueous solutions*, J. Am. Cer. Soc., **87**, pp. 79–83, 2004.

[13] BUSCAGLIA M. et al., *Ferroelectric properties of dense nanocrystalline BT*, Nanotech., **15**, pp. 1113–1117, 2004.

[14] DUTTA P., GREGG J., *Hydrothermal synthesis of tetragonal BT*, Chem. Mater., **4**, pp. 843–846, 1992.

[15] WU M., LONG J., WANG G., HUANG A., LUO Y., FENG S., XU R., *Hydrothermal synthesis of BT from barium hydroxide* & TiO₂, J. Am. Cer. Soc., **82**, pp. 3254–3256, 1999.

[16] XU H., GAO L., GUO J., *Preparation and characterization of tetragonal BT powders by hydrothermal method*, J. Eur. Cer. Soc., **22**, pp. 1163–1170, 2002.

[17] XUH., GAO L., *Hydrothermal synthesis of high-purity BT powders*, Mat. Lett., **58**, pp. 1582–1586, 2004.

[18] BECK H., EISER W., HABERKORN R., *Influence of different sol-gel preparation methods and characterization of nanoscaled* BaTiO₃, Part I&II, J. Eur. Cer. Soc., **21**, pp. 687–693 and pp. 2319–2323, 2001.

[19] KANG D., HAN M., LEE S., SONG S., *Dielectric and pyroelectric properties of barium titanate ceramics*, J. Eur. Cer. Soc., **23**, pp. 515–518, 2003.

[20] CHO J., KUBAWARA M., *Sintering behavior of partially crystallized BT xerogels with different nanocrystalline structures*, J. Eur. Cer. Soc., **24**, pp. 2959–2968, 2004.

[21] XUO J., WANG J., WAN D., *Nanosized BT powder by mechanoactivation*, J. Am. Cer. Soc., **83**, pp. 121–124, 2000.

[22] ABE O., SUZUKI Y., *Mechanochemically preparation of BT powders*, Mat. Sci. Forum, **225**, pp. 563–568, 1996.

[23] GOMEZ C., BENITEZ C., RAMIREZ H., *Mechanical activation of the synthesis of BT powders*, Ceram. Int., **26**, pp. 271–277, 2000.

[24] MARINKOVIC B., STOJANOVIC B., PAVLOVIC V., RUSTIC M., *Correlation of microstructure of BT sintered from mechanically activated powder*, Mat. Struct., **6**, pp. 96–99, 1999.

[25] STOIANOVICB., SIMOES A., SANTOS C., JAVALEKIC C., MITIC V., VARELA J., *Mechanochemical synthesis of BT*, J. Eur. Cer. Soc., **25**, pp. 1985–1989, 2005.

[26] *Retsch catalog*, 2005.

[27] JAFFE B., COOK W., JAFFE W., *Piezoelectric ceramics*, Acad Press, London, New York, 1971.