

Barium Titanate Dielectric Ceramics Fired by Spark Plasma Sintering with and without Annealing

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ABSTRACT

A series of samples was sintered from nanometric BaTiO₃ powder by spark plasma sintering (SPS). Sintered tablets were polished, sputtered by aluminum to create electrode system and tested in DC and AC electric fields. The results were correlated with the SPS processing parameters and are discussed in connection with other BaTiO₃ samples produced by SPS with or without additional heat treatment. Majority of our SPS fired samples had, even without subsequent thermal treatment, advantageous combination of high permittivity, DC resistivity and low loss factor, seldom reported for SPS technology. Samples were tested also in annealed state and compared with as-sintered ones. Prog. Color Colorants Coat. 13 (2020), 85-92© Institute for Color Science and Technology.

1. Introduction

Spark plasma sintering (SPS) enables extremely rapid fabrication of bulk ceramic materials. It is a novel consolidation technique which combines pulsed electric currents and uniaxial pressure to ensure compaction of the material. Heating rates, applied pressures and pulsed current patterns are the main factors responsible for the densification kinetics and conservation of the submicrometric structure of the materials.

Barium titanate, BaTiO₃, is a multifunctional oxide exhibiting complex phase appearance. Due to its high relative permittivity, BaTiO₃ is used in multilayer ceramic capacitors, dynamic random access memories, piezoelectric sensors, thermistors and resistors with high positive thermal coefficients [1, 2]. Between 120 °C (393 K) and 1457 °C (1730 K) BaTiO₃ has a cubic perovskite structure that consists of corner linked oxygen octahedra containing Ti⁴⁺, with Ba²⁺. Cooling below 120 °C results in small displacements in the

cations positions in the unit cell resulting in polar ferroelectric phase existing in the temperature interval between 5 °C (278 K) and 120 °C [3].

Application of the SPS technique for preparing of ferroelectric ceramic discs was up to now relatively seldom reported. Samples of BaTiO₃ with different grain size ranging from 80 nm to several micrometers were prepared by controlling sintering conditions at the SPS process [4]. Study of the grain size dependence of dielectric properties revealed that the relative permittivity at room temperature decreased with the diminishing grain size – from 4000 for 1 µm grain size to about 1500 for 100 nm grain size. The SPS process, when operated under a reducing atmosphere, allows creating defects as Ti³⁺ associated with oxygen vacancies [5].

We have studied earlier barium titanate sample sintered by SPS at 1300 °C [6]. The difference in both observed sample orientations (i.e. parallel and perpendicular to the pressure direction at SPS) was

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higher relative permittivity and simultaneously lower loss factor in the pressure direction. In our work [6] it was attributed to certain anisotropy of the porosity that should mean more flat pores in the pressure direction and therefore tightly packed structure with easier polarization. Detailed microstructure investigation on this sample was however not performed. The reported “colossal permittivity” [7] values (over 200.000), elsewhere called “supercapacitor features” [5], was confirmed also with our results [6]. The DC volume resistivity of our selected SPS barium titanate sample was relatively low, $5 \times 10^5 \Omega\text{m}$ [6]. Other authors produced BaTiO₃ by SPS at 1200 °C followed by a post-annealing step at 800 °C for 12 hours in air [5]. Such a post-annealing is considered to be necessary to restore the material stoichiometry [8, 9]. Our actual work used an ultra fine powder with a narrow size distribution to lower the SPS temperature even down below 1000 °C.

High porosity has always a detrimental effect on dielectric properties. The body must be in such a case considered as a two-component system, in which the bulk properties and the pore properties are combined via rules of mixing [10]. In the other hand, if the porosity is markedly under 1 %, the influence of the bulk (as grain size, character of grain boundaries) prevails. Using a nanometric powder was tested by us for producing compacts that would be promising dielectrics even without subsequent thermal treatment. However, we applied annealing to our samples and compared the as-sintered and annealed BaTiO₃ from various standpoints.

2. Experimental

An ultrafine powder was used with nominal mean size 100 nm (NO-0041-HP, IoLiTec, Heilbronn, Germany); composed of the cubic BaTiO₃ phase. The size distribution was verified using laser-based dispersive technique (Mastersizer 3000, Malvern, GB). Detected parameters were: $d_{10} = 66 \text{ nm}$; $d_{50} = 126 \text{ nm}$; $d_{90} = 255 \text{ nm}$. Experimental setup of the spark plasma sintering machine (SPS 10-4, Thermal Technology LLC, USA) included variable maximum temperatures 925, 950, 965, and 975 °C, using constant pressure 80 MPa and dwell time 5 minutes. Duration of the whole process including heating and cooling was 30 min. The procedure at 950 °C was repeated for one sample with dwell time doubled (i.e. 10 min; sample labeled 950-10). Tablets with 20 mm in diameter and 3 mm height were produced. For all samples SPS heating rate was 125

°C/min until the temperature was 50 °C lower then the maximum temperature. From that temperature to the maximum temperature the heating rate was 50 °C/min. During the whole SPS process pressure in the chamber reduced to around 10 Pa was used.

The powder X-ray diffraction (PXRD) measurements were carried out on vertical θ - θ diffractometer D8 Discover (Bruker AXS, Germany) using CuK α radiation. Diffracted beam was detected by 1D detector LynxEye. Due to the small size of the irradiated area, parallel beam geometry was applied with polycapillary optics, 1 mm cylindrical collimator and $K\beta$ filter from thin nickel foil inserted into secondary beam. The angular range was from 20 to 95 °2 θ , step size 0.04 °2 θ and the total counting time in each step was 384 s (the 1D detector is composed of 191 point detectors). Quantitative Rietveld refinement [11] was performed in TOPAS V5 software using fundamental parameters approach for evaluation of lattice parameters, average sizes of coherently scattering domains (i.e. the crystallite size) and microstrains.

The surface of specimens was made smooth by grinding to eliminate surface roughness and possible superficial contamination from the carbon foils used at SPS. Wet grinding by SiC papers with decreasing grain size (the finest was #800 grit) was applied. The removed thickness of the material was approx 0.3 mm from each face. Layers of aluminum as thin film electrodes were sputtered in a reduced pressure on both sides of each sample. A three-electrode measurement fixture was used to evaluate dielectric parameters. The electric field was applied parallel to the pressure direction (i.e., perpendicular to the substrate surface).

Capacity at room temperature was measured in the frequency range from 5 to 50 kHz using a programmable impedance analyzer model PM6306 (Fluke, the Netherlands). Applied voltage was 1V AC. Relative permittivity ϵ_r was calculated from measured capacities C_p and specimen dimensions. This same arrangement and equipment was used for the loss tangent measurement at the same frequencies as capacity.

Electric resistance was measured with a special resistivity adapter – Keithley model 6105. The DC electric field was applied from a regulated high-voltage source and the values were read by a multi-purpose electrometer (617C, Keithley Instruments, USA). The magnitude of the applied voltage was $100 \pm 0.05 \text{ V}$. Volume resistivity was calculated from the measured

resistance and specimen dimensions. Vickers microhardness of the samples was measured on polished sections by optical microscope equipped with a Hanemann head and Vickers indenter using 1 N load. The mean value of microhardness was calculated as an average from 20 indentations. Annealing was done at 900 °C for 4 hours in air in a laboratory furnace (Clasic, Czech Rep.). Heating and cooling ramps 8 °C/min were applied. After annealing the samples were tested by the same techniques as all non-annealed samples and compared.

3. Results and Discussion

X-ray diffraction revealed in the barium titanate starting powder besides cubic BaTiO₃ (98.4 %) also witherite BaCO₃ (1.6 %), which is one of the BaTiO₃ production components and was observed also in the

final BaTiO₃ by many other authors. Rietveld analysis showed coherently scattering domain size (crystallite size) about 102 nm, i.e. the crystallite size distribution of the feedstock powder was found comparable to its particle size distribution, Table 1.

XRD patterns of all sintered samples (as well as the powder) were composed solely from tetragonal BaTiO₃ phase. The tetragonality of this phase is always small [12] and in our case it was observed to correlate with the sintering temperature – the higher the temperature, the larger the tetragonality, Table 1. Also the larger dwell time at 950 °C lead to larger tetragonality. The crystallite sizes were only slightly lower than for the starting powder and similar for all SPS parameters. Relative permittivity ϵ_r , Figure 1, and also loss factor $\text{tg } \delta$ were both monotonously decreasing with frequency.

Table 1: Microhardness, XRD and Porosity (annealed samples).

Sample	Microhardness [GPa]	Standard deviation [GPa]	Tetragonality a/c (by XRD)	Crystallite size [nm] (by XRD)	Porosity [%] (water immersion)
925	4.52 / 3.36*	0.84 / 0.61*	1.006636	151	15.64
950	6.04	0.79	1.005688	173	1.75
950**	7.01	0.94	1.007630	76	n.a.
965	7.77	0.77	1.005482	174	1.72
975	7.99	0.98	1.005483	188	2.39
950-10	7.85	0.99	1.005593	176	6.90
Commercial	7.47	2.14	n.a.	n.a.	n.a.

* near surface; ** as-sintered (non-annealed)

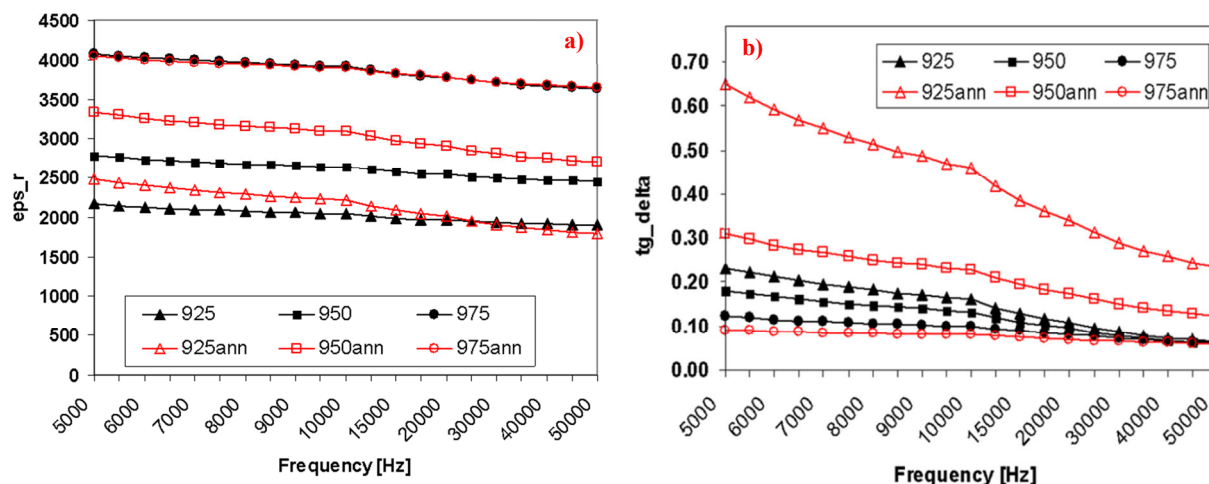


Figure 1: a) Frequency dependence of relative permittivity and b) Frequency dependence of loss factor.

This is usual, because only the small dipoles inside the material can follow the higher frequency of the external field. The sample with the long sintering dwell time (i.e. 950-10) has the highest permittivity, Figure 2, in the as-sintered state. However, the corresponding loss factor was also the highest one, Figure 2. In the annealed state the permittivity dropped to the level of the sample 975 (i.e. 5 min dwell) and the loss factor as well. In the sintered state those two samples were very similar. Surprisingly, worsening of dielectric parameters (particularly the high loss factor) was detected for

annealed samples sintered at 925 and 950 °C.

When we observe the DC resistivity values, Figure 3, the sample 965 has exceptionally low resistivity. It corresponds to its high porosity (not shown), due to conductive part of losses. The sample 950-10 is more resistive, nearly as the samples 925 and 950. But its relative permittivity is much higher than that one of the samples 925 and 950. In the annealed state, the resistivity of samples 975 and 950-10 increased whereas the values of other samples decreased.

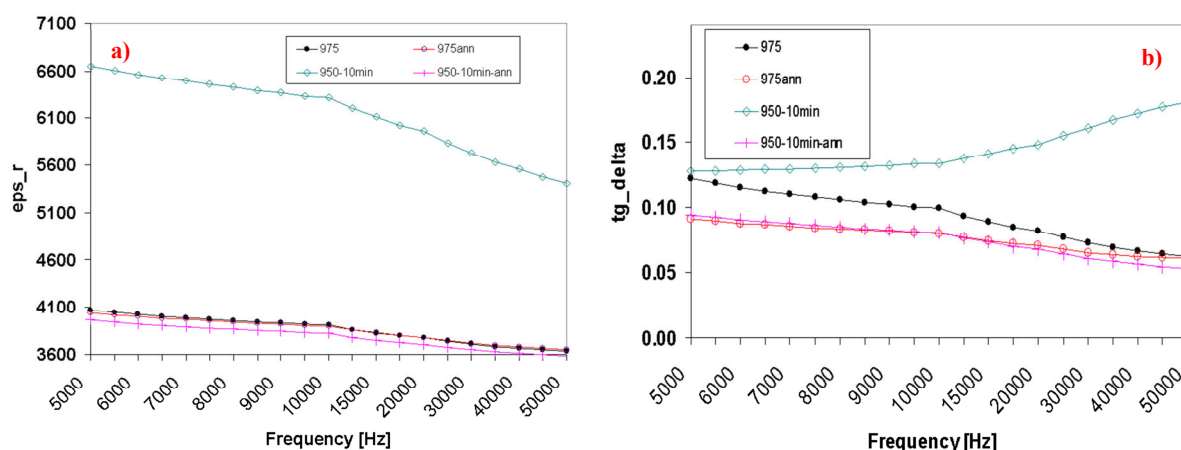


Figure 2: Comparison of the samples 950-10 and 975: a) frequency dependence of relative permittivity and b) frequency dependence of loss factor.

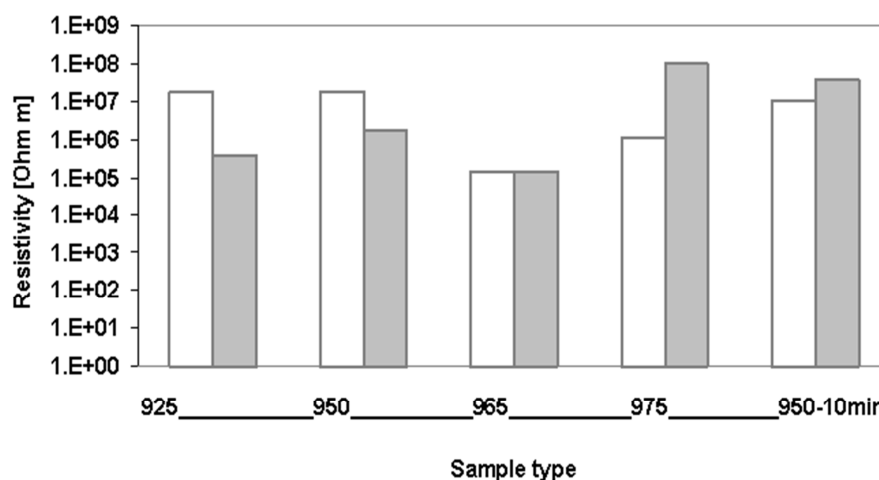


Figure 3: Resistivity of as-sintered (white columns) and annealed (grey columns) samples.

Microhardness measured on the perpendicular cross section, materiallographically polished of the sample 950 (only this sample was measured in the as-sintered form) was 7.01 ± 0.94 GPa. This value is lower compared to BaTiO₃-based multilayer ceramic capacitors with 9.3 GPa (calculated by us from data presented in [13]). We have measured a commercial capacitor dielectric ceramics based of BaTiO₃ bulk, and the value was 7.74 ± 2.14 GPa, Table 1. Our sintered-plus-annealed samples exhibit better homogeneity manifested itself by the lower standard deviation, than this commercial material. The uniformity of the microstructure around microindents was always perfect and the ceramics appear nearly pore-free on the micrometric scale. The sample 925 exhibited lower microhardness near the surfaces (below 40 μ m distance from the surface) than within the bulk. This was most probably because of contamination by carbon at SPS and this effect was not completely removed by annealing. Other samples were homogeneous.

The 925 and 950 samples have high DC electric resistance that was confirmed by the volume resistivity measurement. Their permittivity is rather low and loss factor high, but it drops with the frequency. It indicates insulators with rather limited polarization. Another important factor is that these two samples were rather porous and the quality of the contact between adjacent grains would be therefore worsened, which also contributes to high resistivity.

The dielectric properties of the samples sintered between 925 and 965 °C seem to be due to mixed polarization/conduction mechanisms of the bulk material. For the sample 965 the porosity (not shown, details see elsewhere [14]) is low and due to this the bulk (pore-free) character of the material manifested itself most strongly. As a result, charge transport is easier and the resistivity is lower. The dielectric properties of samples sintered either at higher temperature, i.e. 975, or with longer dwell time, i.e. 950-10, are mostly governed by the true polarization (due to high permittivity). Since BaTiO₃ is a ferroelectric material, it has always relatively high loss factor and low resistivity, about 1.7×10^5 [15]. However, a combination of such a high relative permittivity with correspondingly low loss factor for samples made by SPS (without additional heat-treatment) is absent in the literature. The tetragonality of the as-sintered samples 975 and 950-10 were however the lowest and this is not favorable owing to

the ferroelectric character of BaTiO₃ [16]. Another interpretation of dielectric properties [17] of our samples is that the loss factor decrease at the low frequency results from the DC conductivity while high frequency relaxation (i.e. peak, or better said an increase attributed to a peak at even higher frequency) is to be related to the grain boundaries. Since SPS is a dynamic process, it is possible that our samples exhibit subtle differences from the viewpoint of grain boundary / grain interior oxygen depletion. In such a case, the run of loss factor curves is non-even and non-trivial (however we scanned narrower frequency window than the authors [17] describing the “boundary layer effect”). The color of as-sintered samples was slightly bluish, particularly for sample 950 (i.e. dwell time of 5 min), Figure 4. This is connected with vacancies, as demonstrated in case of BaTiO₃ plasma sprayed coatings [18].

The majority of SPS-related papers [5, 8, 9, 12] reported dielectric measurements on BaTiO₃ undergoing SPS firing plus additional annealing. However, we are looking for maximizing the production potential of the SPS process for direct production of dielectric ceramics with good and stable properties after minimal number of production steps. The occasionally reported “colossal permittivity” of BaTiO₃-based SPS samples [7], also mentioned in connection with our samples in the past [6], is according our experience strictly due to mixed polarization/conductivity mechanism [17].

If the microstructure contains only charged oxygen vacancies and not true sources of space polarization like core/shell grain structure, then the charge is not well confined, to be thermally stable, and the material is not suitable for energy storage. SPS process is probably able to introduce the core/shell structure also into pure (i.e. non-doped BaTiO₃), but the understanding to all involved phenomena remains up to now limited.



Figure 4: Left: Annealed sample “950”, right: as-sintered sample “950”.

The true “giant permittivity” features are attainable preferably by an internal barrier layer capacitor (IBLC) effect introduced extrinsically, for example, by SiO_2 shell applied on individual powder particles prior to sintering [5] or by replacing part of Ba atoms in BaTiO_3 by heterovalent ions [16].

Martinez et al. [19] reported volume resistivity of about $6.3 \times 10^6 \Omega\text{m}$ for SPS produced barium titanate even after annealing at 1000°C for 12h in air which is comparable with the resistivity of our as-sintered 975 sample. Shen and Li [20] reported relative permittivity of over 4300 and loss factor just under 0.03 (at 1 kHz) for BaTiO_3 produced by SPS followed by annealing at 1000°C for 12h in air. Our sample 950-10 had relative permittivity of 7500 and loss factor of 0.15 (at 1 kHz) in the as-sintered state, and 4400 and 0.14 in annealed state (resistivity of $36 \times 10^6 \Omega\text{m}$).

Concerning the grain size, the agreement was reached that the highest relative permittivity is usually obtained for grain size between 0.8 and $1 \mu\text{m}$ [21]. The drop of bulk BaTiO_3 permittivity with a grain size decrease for the nanometric BaTiO_3 is considered to take place due to an increase in grain-boundary density (low-permittivity phase related surface effect) with decreasing grain size [22]. Also, movement of ferroelectric domain walls in the ferroelectric ceramics could be blocked by low-angle grain boundaries (i.e. crystallite boundaries). In the case of our samples, certain oxygen depletion that is not the same at grain boundaries and inside the grain interior seems to be connected with this behavior.

The SPS process decreases the crystallite size of the starting powder, Figure 5, due to the applied pressure combined with the electric pulses during SPS process [23]. After annealing, the crystallite size increased, as expected, but its final size remained below 200 nm.

However, the crystallite size of the annealed samples is ordered according the SPS temperature – higher SPS processing temperature corresponds to higher crystallite size. This manifested itself only very slightly directly after sintering but more pronounced after annealing, Figure 5. Lower tetragonality, cf. Table 1, promotes the crystal growth, which is easier if the lattice is closer to cubic crystal structure, needing lowest energy for the growth [12]. This is because in polycrystalline BaTiO_3 materials with random grain orientation, the cubic arrangement is most efficient for non-blocked growth. In other works focused on SPS processing of nanometric BaTiO_3 [4, 21, 24], the same trend, i.e. larger grains for higher SPS temperature, is reported.

The grains are in general too fine, the boundaries too frequent and the movement of ferroelectric domain walls is therefore partly blocked. For obtaining better dielectric properties probably longer SPS dwell time would be applied (despite the economy disadvantage for the process). At temperatures higher than 1000°C , the grain growth rate is about 10 nm/min [25]. The optimum grain size for dielectric behavior is about $1 \mu\text{m}$ [21, 24]. Already between 100 and 300 nm, which is size window of the grains of our samples, the dependence of tetragonality on grain size it the highest [26] whereas around $1 \mu\text{m}$ is it negligible.

The porosity – as earlier measured by small angle neutron scattering [14] – had such a trend: Lower is it for higher SPS temperature, with a most pronounced “jump” between 950 and 965°C . The porosity of the “high temperature samples” is up to three times lower than for “low temperature samples”. Such a difference should express itself also in dielectric properties, especially at “low frequency” values of relative permittivity- and those are lower for low temperature samples.

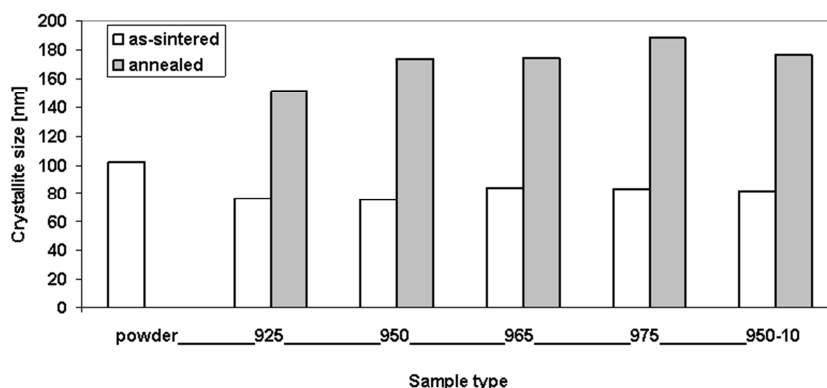


Figure 5: Crystallite size of as-sintered (white columns) and annealed (grey columns) samples.

Also concerning the loss factor the “low temperature” sample 925ann has high values at low frequencies. Species present inside pores, as moisture [27] or OH groups [28], i.e. large molecules with big dipoles polarizable only at low frequencies, used to be mentioned as factors responsible for such a behavior. The dielectric behavior of the 950-10ann sample is connected to its high porosity (Table 1). The high relative permittivity at low frequency and increasing loss factor with the frequency increase are signs of the space charge polarization. The samples 965 qnd 965ann have the lowest resistivity in spite of its lowest porosity.

The cross section of the actual sample 965 is presented in Figures 6 and 7. It emphasizes three aspects of the microstructure – grains (arrow G), coarser pores (arrow P1) and fine pores (arrow P2). Grains are about 15 or 20 μm large (Figure 6). Coarser pores are localized between them. Fine pores are probably results of grain reorientation at the final sintering stage. In a really optimal microstructure both types of pores should be absent, however they were present in all samples. Higher SPS pressure or shorter dwell times are possible solutions for such problems, but a pore free BaTiO_3 is very seldom reported [29].

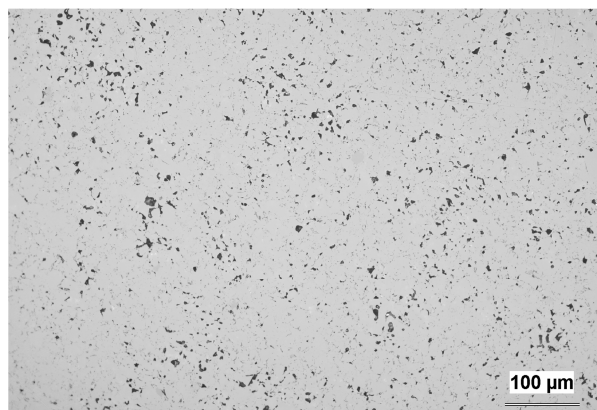


Figure 6: Polished cross section of the sample 965.

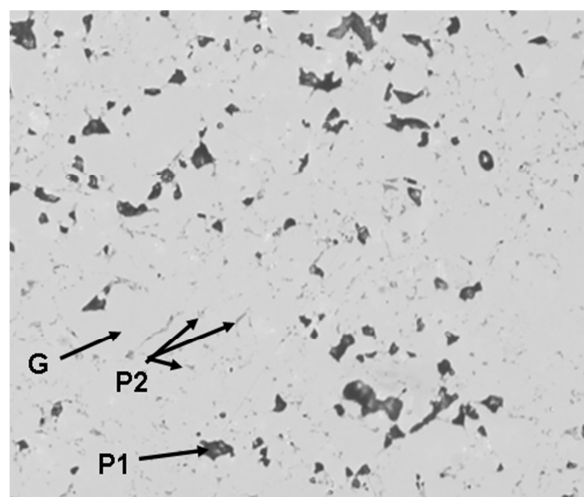


Figure 7: Detail of the polished section with indicated structure features.

4. Conclusions

BaTiO_3 nanometric powder was processed by spark plasma sintering using various process parameters, namely temperature. Dielectric tests in AC electric field revealed a combination of high and rather stable relative permittivity with low loss factor. The size of crystallites in the final compacts was similar to that of the starting powder (about 100 nm). This is mainly due to the use of SPS process. The rapid heating and cooling led to grain size too fine for the optimum dielectric performance of BaTiO_3 , as was discussed above. Increasing the SPS temperature and dwell time can markedly modify the microstructure and electrical properties. The annealing step, however, did not bring very clear improvement of the dielectric behavior. Only the samples completely sintered (i.e. nearly pore-free) by SPS were improved slightly, whereas others were worsened. The interval between 950 and 975 $^{\circ}\text{C}$ is critical for firing of nanometric BaTiO_3 by SPS – the grain growth and reorientation is strongly connected with crystal cell tetragonality and various polarization mechanisms are interlocked together.

5. References

1. P. Ren, H. Fan, X. Wang, K. Liu, A novel approach to prepare tetragonal BaTiO_3 nanopowders, *Mater. Lett.*, 65(2011), 212-214.
2. X. Zhiguo, W. Haidou, Z. Lina, Z. Xinyuan, H. Yanfei, Properties of the BaTiO_3 coating prepared by supersonic plasma spraying, *J. Alloy. Compd.*, 582(2014), 246-252.
3. M. H. Zhao, D. A. Bonnell, J. M. Vohs, Effect of ferroelectric polarization on the adsorption and reaction of ethanol on BaTiO_3 , *Surf. Sci.*, 602(2008), 2849-2855.
4. B. Li, X. Wang, L. Li, H. Zhou, X. Liu, X. Han, Y. Zhang, X. Qi, X. Deng, Dielectric properties of fine-

- grained BaTiO₃ prepared by spark-plasma-sintering, *Mater. Chem. Phys.*, 83(2004), 23-28.
5. U. C. Chung, C. Elissalde, S. Mornet, M. Maglione, Controlling internal barrier in low loss BaTiO₃ supercapacitors, *Appl. Phys. Lett.*, 94(2009), 072903.
 6. P. Ctibor, H. Seiner, J. Sedlacek, Z. Pala, P. Vanek, Phase stabilization in plasma sprayed BaTiO₃, *Ceram. Int.*, 39(2013), 5039-5048.
 7. Z. Valdez-Nava, S. Guillemet-Fritsch, Ch. Tenailleau, T. Lebey, B. Durand, J.Y. Chane-Ching, Colossal dielectric permittivity of BaTiO₃-based nanocrystalline ceramics sintered by spark plasma sintering, *J. Electroceram.*, 22(2009), 238-244.
 8. M. B. Fraga, J. P. Delplanque, N. Yang, E. J. Lavernia, T.C. Monson, High Pressure FAST of Nanocrystalline Barium Titanate, *Ceram. Int.*, 42(2016), 13868-13875.
 9. H. Maiwa, Structure and properties of Ba(Zr_{0.2}Ti_{0.8})O₃ ceramics prepared by spark plasma sintering, *J. Mater. Sci.*, 43(2008), 6385-6390.
 10. P. Ctibor, J. Sedlacek, K. Neufuss, P. Chraska, Dielectric relaxation in calcium titanate-containing ceramics prepared by plasma spraying, *Ceram. Int.*, 29(2003), 955-960.
 11. H. M. Rietveld, A profile refinement method for nuclear and magnetic structures, *J. Appl. Crystallogr.*, 2(1969), 65-71.
 12. M. T. Buscaglia, V. Buscaglia, M. Viviani, P. Nanni, M. Hanuskova, Influence of foreign ions on the crystal structure of BaTiO₃, *J. Eur. Ceram. Soc.*, 20(2000), 1997-2007.
 13. D. H. Park, Y. G. Jung, U. Paik, Crack suppression behavior with post-process parameters in BaTiO₃-based Ni-MLCCs, *Ceram. Int.*, 31(2005), 655-661.
 14. P. Ctibor, J. Sedlacek, V. Ryukhtin, J. Cinert, F. Lukac, Barium titanate nanometric polycrystalline ceramics fired by spark plasma sintering, *Ceram. Int.*, 42(2016), 15989-15993.
 15. D.S.B. Heidary, C.A. Randall, Analysis of the degradation of BaTiO₃ resistivity due to hydrogen ion incorporation: Impedance spectroscopy and diffusion analysis, *Acta Mater.*, 96(2015), 344-351.
 16. A. R. West, T. B. Adams, F. D. Morrison, D. C. Sinclair, Novel high capacitance materials: BaTiO₃:La and CaCu₃Ti₄O₁₂, *J. Eur. Ceram. Soc.*, 24 (2004), 1439-1448.
 17. M. Maglione, M.A. Subramanian, Dielectric and polarization experiments in high loss dielectrics: a word of caution, *Appl. Phys. Lett.*, 93(2008), 032902.
 18. P. Ctibor, J. Čížek, J. Sedláček, F. Lukáč, Dielectric properties and vacancy-like defects in plasma-sprayed barium titanate, *J. Am. Ceram. Soc.*, (2017), 1–12. <https://doi.org/10.1111/jace.14840>
 19. D. Martinez, D. Ghosh, J. Jones, Investigation of annealing condition effects on impedance of barium titanate ferroelectric ceramic, report of the University of Florida, <http://www.phys.ufl.edu/REU/2012/MartinezPaper.pdf>.
 20. Z. Y. Shen, J. F. Li, Enhancement of piezoelectric constant d₃₃ in BaTiO₃ ceramics due to nano-domain structure, *J. Ceram. Soc. Jpn.*, 118(2010), 940943.
 21. H. Ghayour, M. Abdellahi, A brief review of the effect of grain size variation on the electrical properties of BaTiO₃-based ceramics, *Powder Technol.*, 292(2016,) 84-93.
 22. J.C. M'Peko, J.S.C. Francis, R. Raj, Field-assisted sintering of undoped BaTiO₃: Microstructure evolution and dielectric permittivity, *J. Eur. Ceram. Soc.*, 34 (2014), 3655-3660.
 23. K. Chen, X. Zhang, H. Wang, L. Zhang, J. Zhu, F. Yang, L. An, Making nanostructured ceramics from micrometer-sized powders via grain refinement during SPS sintering, *J. Am. Ceram. Soc.*, 91(2008), 2475-2480.
 24. Y. Tan, J. Zhang, Y. Wu, C. Wang, V. Koval, B. Shi, H. Ye, R. McKinnon, G. Viola, H. Yan, Unfolding grain size effects in barium titanate ferroelectric ceramics, *Sci. Reports.*, 5(2015), 9953-9962.
 25. R. Licheri, S. Fadda, R. Orru, G. Cao, V. Buscaglia, Self-propagating high-temperature synthesis of barium titanate and subsequent densification by spark plasma sintering (SPS), *J. Europ. Ceram. Soc.*, 27(2007), 2245–2253.
 26. K. Uchino, E. Sadanaga, T. Hirose, Dependence of the crystal structure on particle size in BaTiO₃, *J. Am. Ceram. Soc.*, 72(1989), 1555–1558.
 27. L. Pawlowski, The relationship between structure and dielectric properties in plasma-sprayed alumina coatings, *Surf. Coat. Technol.*, 35(1988), 285-298.
 28. P. Ctibor, H. Ageorges, V. Stengl, N. Murafa, I. Pis, T. Zahoranova, V. Nehasil, Z. Pala, Structure and properties of plasma sprayed BaTiO₃ coatings: spray parameters versus structure and photocatalytic activity, *Ceram. Intl.*, 37(2011), 2561–2567.
 29. R. Berthelot, B. Basly, S. Buqere, J. Majimel, G. Chevallier, A. Weibel, A. Veillere, L. Etienne, U-Chan Chung, G. Goglio, M. Maglione, C. Estournes, S. Mornet, C. Elissalde, From core – shell BaTiO₃@MgO to nanostructured low dielectric loss ceramics by spark plasma sintering, *J. Mater. Chem. C.*, 2(2014), 683-694.

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