

PREPARATION AND DIELECTRIC PROPERTIES OF THERMO-VAPOROUS BaTiO₃ CERAMICS

PRIPRAVA IN DIELEKTRIČNE LASTNOSTI TERMO-PARNO POROZNE KERAMIKE BaTiO₃

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A crystalline BaTiO₃ powder was synthesized at 350 °C for 0–20 h from TiO₂ (> 99 % purity) and BaO (> 98 % purity) with water vapour acting as the reaction media. According to the XRD and SEM results, the BaTiO₃ synthesized for 3 h proved to be the most adequate raw material for ferroelectric ceramics among the obtained samples as long as it consisted of pure crystalline sphere-shaped BaTiO₃ particles with the average size of 156 nm. Pellets were pressed at (100, 150 and 200) MPa and sintered at 1300 °C for 1 h. The influence of the compacting pressure on the dielectric characteristics of BaTiO₃ ceramics was studied by monitoring the permittivity and loss-tangent values of the pellets at 20 Hz–2 MHz.

Keywords: barium titanate, thermo-vaporious synthesis, microstructure, dielectric ceramics

Kristalni prah BaTiO₃ je bil sintetiziran pri 350 °C od 0 do 20 h iz TiO₂ (čistost: > 99 %) in BaO (čistost: > 98 %) z vodno paro kot reakcijski medij. Iz rentgenogramov in SEM-posnetkov izhaja, da je BaTiO₃, sintetiziran 3 h, najprimernejša surovina med vsemi vzorci za feroelektrično keramiko, dokler sestoji iz čistih kristalnih okroglih delcev BaTiO₃ s povprečno velikostjo 156 nm. Peleti so bili stiskani pri (100, 150 in 200) MPa in sintrani 1 h pri temperaturi 1300 °C. Vpliv tlaka pri stiskanju na dielektrične lastnosti keramike BaTiO₃ je bil preiskovana s spremljanjem permitivnosti in velikosti izgube tg δ peletov pri 20 Hz–2 MHz.

Ključne besede: barijev titanat, termo-parno porozna sinteza, mikrostruktura, dielektrična keramika

1 INTRODUCTION

Since the 1940s barium titanate, BaTiO₃, has been known for its extremely high values of ferroelectric characteristics which make it widely used in the production of multilayer ceramic capacitors (MLCCs), resistors with a positive temperature coefficient of resistivity (PTCR), temperature/humidity/gas sensors, piezoelectric transducers and actuators, ultrasonic and electro-optic devices, IR-detectors, etc.^{1–4} Generally, the BaTiO₃ powder is obtained as the raw material for the bulk-ceramic manufacturing, as well as thin-film and composite-material production.⁴ For this purpose a homogeneous, well-dispersed pure BaTiO₃ powder, consisting of spherical particles up to 200 nm in size, is required.^{1,5,6} Various synthesis routes for the as-characterized powder have been developed over several decades. In addition to the conventional solid-state method, the techniques such as pyrolysis (Pechini, citrate processes), dispersion (catecholate synthesis, spray pyrolysis, sol-gel), precipitation (oxalate, hydrothermal and solvothermal synthesis) are widely used for the fine-crystalline BaTiO₃ processing.^{1,7–14} But, as some of them are multistage and require the use of auxiliary substances, mostly in the solid state, hydrothermal and oxalate techniques are industrially

suitable. The development of a simple and low-cost method for the industrial BaTiO₃ production remains to be a pending problem.

In the present work water vapour at 350 °C was used as the medium for a BaTiO₃ synthesis from simple oxides. A similar technique combined with the treatment in supercritical water fluid was previously successfully used for the production of MgAl₂O₄, ZnAl₂O₄, Y₃Al₅O₁₂, BaFe₁₂O₁₉, LiNbO₃^{15,16} and also BaTiO₃.^{17,18} As ceramic manufacturing is one of the main application areas for the BaTiO₃ powder, steps were taken to develop this technique for obtaining the BaTiO₃ with the thermo-vaporious process. We prepared ceramic samples in the same conditions, but varied the compressing pressure and studied the phase content, the microstructure and dielectric properties of the pellets in order to determine the most appropriate value of the pressure for the ceramic-manufacturing route.

2 EXPERIMENTAL WORK

The synthesis of BaTiO₃ was performed in laboratory stainless-steel autoclaves using BaO (> 98 % purity) and TiO₂ (> 99 % purity) as the starting reagents. As BaO

interacts with CO₂ in the air, forming BaCO₃, in order to avoid a lack of Ba²⁺ ions in the reaction mixture, an amount fraction of excess of BaO 5 % was used. After a thorough mixing by means of grinding in an agate mortar with a pestle, the reagents were placed into a special container inside the autoclave, separated from the distilled water. Hermetically closed autoclaves were heated up to 350 °C (the water-vapour pressure of 16 MPa), kept at this temperature for (0, 0.5, 1, 2, 3, 4, 5, 20) h and then cooled so that the water vapour condensed at the bottom of the autoclaves separated from the product. The product was first washed with acetic acid solution to avoid a BaCO₃ contamination and then with distilled water.

To produce a ceramic powder, the sample synthesized for 3 h (named BT-3h) was mixed with 1 % PVA and uniaxially pressed into pellets at (100, 150 and 200) MPa at room temperature. The pellets were sintered at 1300 °C for 1 h.

The phase contents of the powders and ceramics were identified with an X-ray diffraction analysis (STOE STADI P) using the Cu-K α radiation in a range of $2\theta \leq 80^\circ$. The crystallite size was calculated with the Scherrer equation. The morphologies of the powder and ceramic samples were studied with scanning electron microscopy (JSM-6390 LA). The dielectric permittivity and loss tangent of the pellets were calculated from the capacity and the conductivity, respectively, of the plane condenser, in which each pellet was used as a dielectric layer. Dielectric characteristics were obtained with a precision LCR meter Agilent E4980a with a frequency range of 20 Hz–2 MHz.

3 RESULTS AND DISCUSSION

During the thermo-vaporous BaTiO₃ synthesis, H₂O molecules from the vapour became incorporated into the

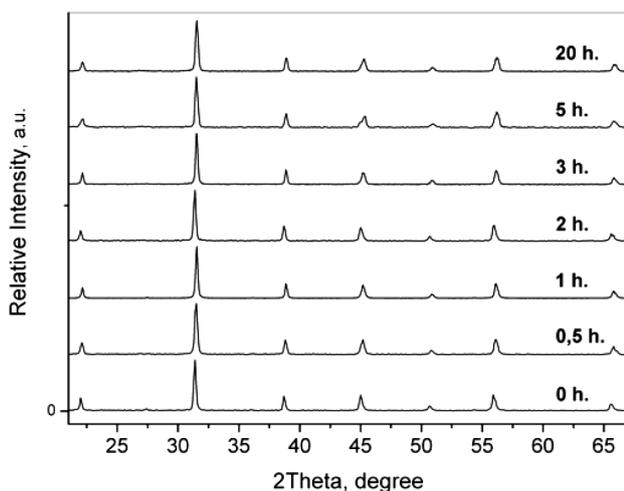


Figure 1: XRD patterns of the BaTiO₃ powders synthesized in water vapour at 350 °C and 16 MPa for 0–20 h

Slika 1: Rentgenogram prahov BaTiO₃ sintetiziranih od 0 do 20 ur, v vodni pari pri 350 °C in 16 MPa

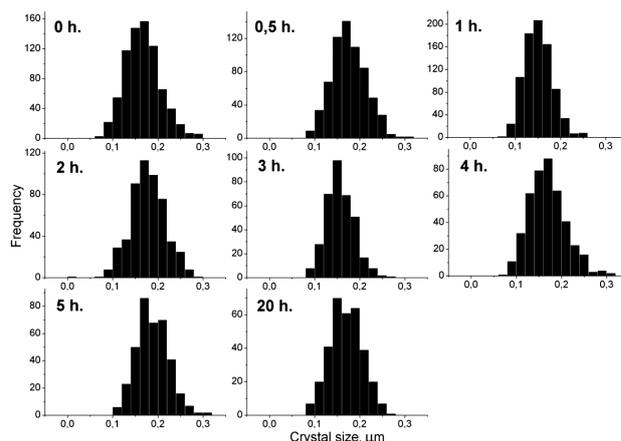


Figure 2: Crystal-size distributions of BaTiO₃ synthesized in water vapour at 350 °C and 16 MPa for 0–20 h

Slika 2: Razporeditev velikosti kristalov BaTiO₃, sintetiziranih od 0 do 20 ur, v vodni pari pri 350 °C in 16 MPa

TiO₂ structure due to the dissociative absorption manifested in the breaking of the Ti-O bonds and the creation of the Ti-OH bonds. In these conditions the TiO₂ structure becomes more flexible, interacting with the Ba²⁺ ions and reorganising into BaTiO₃. The XRD analysis of the powders prepared at 350 °C in the water-vapour atmosphere over the periods of 0–20 h showed that the powders consisted of crystalline BaTiO₃ (**Figure 1**). The formation of BaTiO₃ from TiO₂ and Ba(OH)₂ occurred already during the heating, thus, the sample synthesized for 0 h contained only crystalline BaTiO₃. The interaction of the newly formed BaTiO₃ phase with water vapour led to an elimination of lattice defects and to a perfection of the crystalline structure. **Figure 2** shows the BaTiO₃ crystallite-size dependence on the duration of the thermo-vaporous synthesis, calculated from the Scherrer equation. The crystallite size of the samples synthesized for 0–4 h fluctuates in a range of 35–45 nm, while, in the case of a longer synthesis, the crystallite

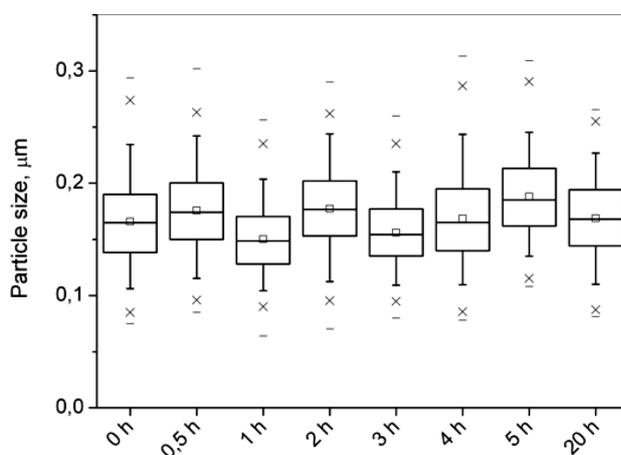


Figure 3: Box charts of the crystal-size distribution of BaTiO₃ synthesized in water vapour at 350 °C and 16 MPa for 0–20 h

Slika 3: Škatlasti diagram razporeditve velikosti kristalnih zrn BaTiO₃, sintetiziranih od 0 do 20 ur, v vodni pari pri 350 °C in 16 MPa

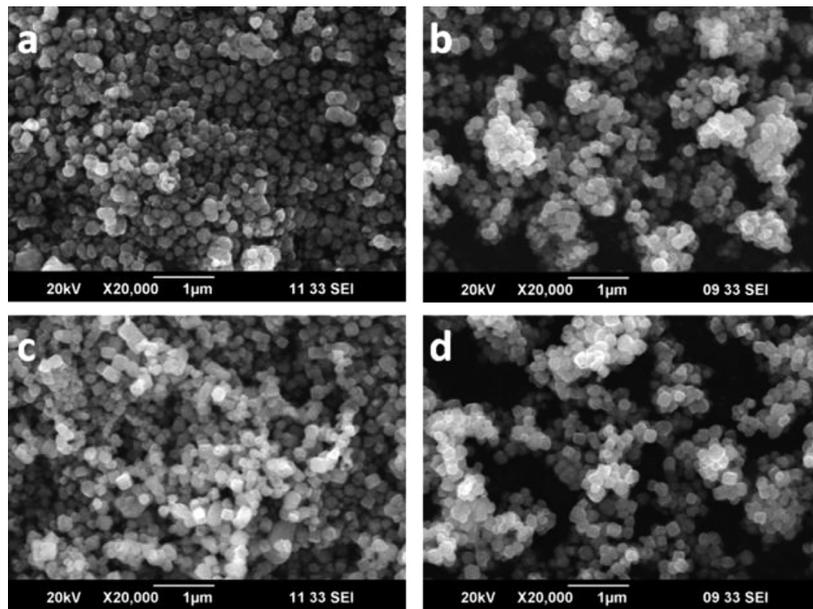


Figure 4: SEM images of BaTiO₃ synthesized in water vapour at 350 °C and 16 MPa for: a) 0 h, b) 3 h, c) 4 h, d) 20 h
Slika 4: SEM posnetki BaTiO₃, sintetiziranega v vodni pari pri 350 °C in 16 MPa po: a) 0 urah, b) 3 urah, c) 4 urah, d) 20 urah

size is reduced. This effect can be explained with the interaction of the excessive amounts of Ba(OH)₂ in the reacting mixture with the already formed BaTiO₃. It is known that the crystallite size from the Scherrer equation is sensitive to phase inhomogeneities.

In the SEM images of the synthesized samples the crystals of BaTiO₃ exhibit a narrow size distribution. The average crystal size slightly varies in a range of 150–188 nm without a distinct relation to the duration of the synthesis (**Figure 3**). There is a clear effect of the reaction time on the shape of the crystals. The samples processed for 0–3 h consist of sphere-shaped particles (**Figures 4a** and **4b**). A longer processing leads to a

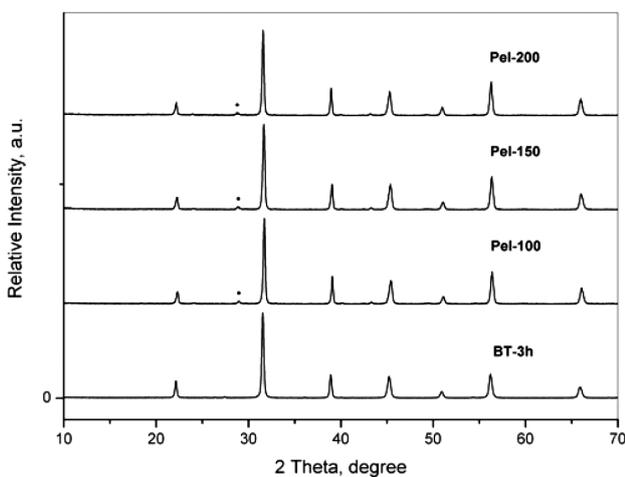


Figure 5: XRD patterns of the BaTiO₃ pellets pressed at 100–200 MPa and sintered at 1300 °C for 1 h and BaTiO₃ powder BT 3 h used as the raw material

Slika 5: Rentgenogram peletov BaTiO₃, stisnjenih pri 100–200 MPa in sintranih 1 uro na 1300 °C in prah BaTiO₃ po 3 urah, uporabljen kot surovina

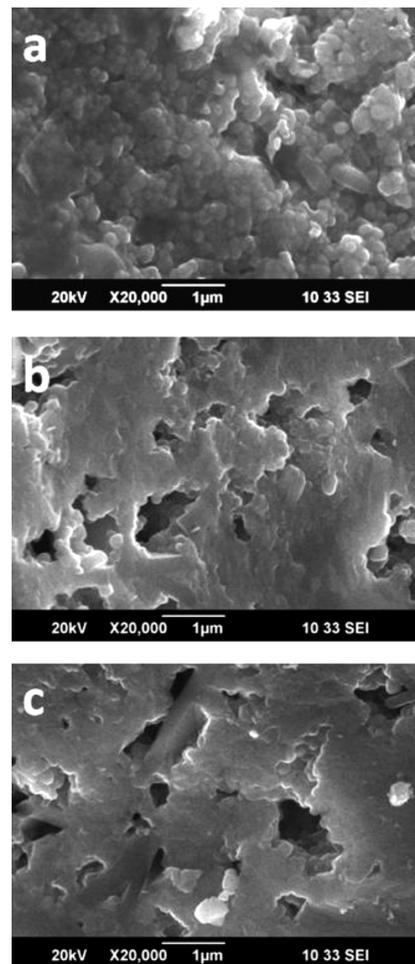


Figure 6: SEM images of the BaTiO₃ pellets pressed at: a) 100 MPa, b) 150 MPa, c) 200 MPa, and sintered at 1300 °C for 1 h

Slika 6: SEM posnetki BaTiO₃ peletov, stisnjenih pri: a) 100 MPa, b) 150 MPa, c) 200 MPa in sintranih 1 uro na 1300 °C

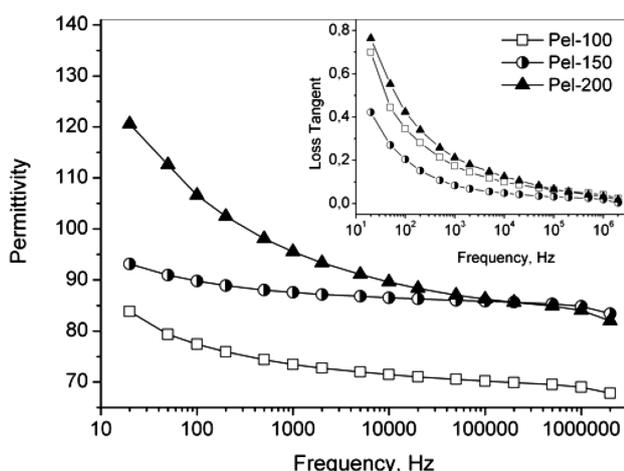


Figure 7: Frequency dependencies of the permittivity and loss tangent of the BaTiO₃ ceramic pellets pressed at 100–200 MPa and sintered at 1300 °C for 1 h

Slika 7: Frekvenčna odvisnost permitivnosti in tangenta izgub BaTiO₃ keramičnih peletov, stisnjenih pri 100–200 MPa in sintranih 1 uro na 1300 °C

formation of crystal facets. In the sample synthesized for 4 h cube-shaped particles could be observed among the sphere-shaped ones and, after 20 h, the sample mainly consisted of faceted crystals (**Figures 4c** and **4d**). The formation of the faceted crystals is related to the BaTiO₃ structure perfection due to its interaction with water vapour.

Ceramic pellets were manufactured from the BaTiO₃ powder sample synthesized in water vapour for 3 h, so that it consisted of pure, crystalline and sphere-shaped BaTiO₃ particles. Three pellets were shaped at different compacting pressures, while the temperature and duration of the sintering were taken from the literature.^{19–23} The geometric density of the pellets was 84–86 % of the theoretical value of 6.01 g/cm³ (**Table 1**) and it naturally rose with the increase in the compaction pressure. In addition to the BaTiO₃, the XRD analysis showed the presence of an impurity phase in every pellet at $2\theta = 29^\circ$ (**Figure 5**), which is a complex barium aluminate titanate originating from the milling process.

Table 1: Ceramic-processing conditions and density of the pellets

Tabela 1: Pogoji pri izdelavi keramike in gostota peletov

Pellet	Compacting pressure, MPa	Sintering temperature, °C	Density, g/cm ³	Relative density, %
Pel-100	100	1300	5.07	84
Pel-150	150		5.14	86
Pel-200	200		5.15	86

In the SEM images the pellets consist of the grains of 160–180 nm in size. Typical features of the pellet microstructure are sub- and micron-sized pores and plates (**Figures 6a** to **6c**). The presence of the plates shows that the recrystallization occurred during the sintering and suggests that the temperature of 1300 °C chosen on the

basis of the reference literature is higher than the appropriate sintering temperature for the thermo-vaporous BaTiO₃ powder.

The frequency dependence of the dielectric permittivity and loss tangent is shown in **Figure 7**. The values of both parameters decrease with the increase in the frequency. This phenomenon is common for all dielectrics. The higher the frequency the less polarization can be realized in a dielectric.²⁴ As the permittivity is a parameter that shows the polarizability of a dielectric,²⁵ it is reduced with a frequency increase. Notably, the permittivity of the pellets shows a strong dependence on the compacting pressure. The permittivity of the pellet manufactured at 150 MPa exhibits the smallest variation in the range of 20 kHz–2 MHz in comparison with the other two pellets. Both the pellets made at 200 MPa and 100 MPa show a more pronounced variation in the permittivity (**Figure 7**). The loss tangent shows a similar tendency as the permittivity, depending on the frequency, and the pellet prepared at 150 MPa exhibits the lowest values of $\text{tg } \delta$ among the three examined pellets. Comparing these results, it can be concluded that 150 MPa is the most appropriate compacting pressure for thermo-vaporous BaTiO₃ ceramics.

4 CONCLUSION

The present work reports on the results of a thermo-vaporous synthesis and ceramic processing of crystalline BaTiO₃. The optimum duration of the synthesis in water vapour at 350 °C and 16 MPa is 3 h in order to obtain a raw material for ceramics. The study of the ceramic microstructure showed that the sintering temperature for the thermo-vaporous BaTiO₃ powder should be lower than 1300 °C. For the ceramics with the permittivity weakly dependent on the frequency in the range of 20 Hz–2 MHz and a low loss tangent, the compacting pressure of 150 MPa involving 1 % PVA as the binder is the most applicable.

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5 REFERENCES

- W. Maison, R. Kleeberg, R. B. Heimann, S. Phanichphant, Phase content, tetragonality and crystallite size of nanoscaled barium titanate synthesized by catecholate process: effect of calcination temperature, *J. Eur. Ceram. Soc.*, 23 (2003) 1, 127–132, doi:10.1016/S0955-2219(02)00071-7
- D. H. Yoon, B. I. Lee, Processing of barium titanate tapes with different binders for MLCC applications – Part I: Optimization using design of experiments, *J. Eur. Ceram. Soc.*, 24 (2004) 5, 739–752, doi:10.1016/S0955-2219(03)00333-9

- ³ U. A. Joshi, S. Yoon, S. Baik, J. S. Lee, Surfactant-free hydrothermal synthesis of highly tetragonal barium titanate nanowires: a structural investigation, *J. Phys. Chem. B.*, 110 (2006), 12249–12256, doi:10.1021/jp0600110
- ⁴ D. Padalia, G. Bisht, U. C. Johri, K. Asokan, Fabrication and characterization of cerium doped barium titanate/PMMA nanocomposites, *Solid State Sciences*, 19 (2013), 122–129, doi:10.1016/j.solidstatesciences.2013.02.002
- ⁵ Ch. Pithan, D. Hennings, R. Waser, Progress in synthesis of nanocrystalline BaTiO₃ powders for MLCC, *Int. J. Appl. Ceram. Technol.*, 2 (2005) 1, 1–14, doi:10.1111/j.1744-7402.2005.02008.x
- ⁶ D. H. Yoon, Tetragonality of barium titanate powder for ceramic capacitor application, *Journal of Ceramic Processing Research*, 7 (2006) 4, 343–354
- ⁷ W. S. Jung, J. H. Kim, H. T. Kim, D. H. Yoon, Effect of temperature schedule on the particle size of barium titanate during solid-state reaction, *Materials Letters*, 64 (2010) 2, 170–172, doi:10.1016/j.matlet.2009.10.035
- ⁸ V. Vinithini, P. Singh, M. Balasubramanian, Synthesis of barium titanate nanopowder using polymeric precursor method, *Ceramics International*, 32 (2006) 2, 99–103, doi:10.1016/j.ceramint.2004.12.012
- ⁹ P. Duran, F. Capel, J. Tartaj, D. Gutierrez, C. Moure, Heating-rate effect on the BaTiO₃ formation by thermal decomposition of metal citrate polymeric precursors, *Solid State Ionics*, 141–142 (2001), 529–539, doi:10.1016/S0167-2738(01)00742-1
- ¹⁰ A. Purwanto, W. N. Wang, I. W. Lenggoro, K. Okuyama, Formation of BaTiO₃ nanoparticles from an aqueous precursor by flame-assisted spray pyrolysis, *J. Eur. Ceram. Soc.*, 27 (2007) 16, 4489–4497, doi:10.1016/j.jeurceramsoc.2007.04.009
- ¹¹ M. R. Mohammadi, D. J. Fray, Sol-gel derived nanocrystalline and mesoporous barium strontium titanate prepared at room temperature, *Particuology*, 9 (2011) 3, 235–242, doi:10.1016/j.partic.2010.08.012
- ¹² Y. B. Kholam, A. S. Deshpande, H. S. Potdar, S. B. Deshpande, S. K. Date, A. J. Patil, A self-sustaining acid-base reaction in semi-aqueous media for synthesis of barium titanyl oxalate leading to BaTiO₃ powders, *Materials Letters*, 55 (2002) 3, 175–181, doi:10.1016/S0167-577X(01)00642-5
- ¹³ K. Y. Chen, Y. W. Chen, Preparation of barium titanate ultrafine particles from rutile titania by a hydrothermal conversion, *Powder Technology*, 141 (2004) 1–2, 69–74, doi:10.1016/j.powtec.2004.03.002
- ¹⁴ S. G. Kwon, K. Choi, B. I. Kim, Solvothermal synthesis of nano-sized tetragonal barium titanate powders, *Materials Letters*, 60 (2006) 7, 979–982, doi:10.1016/j.matlet.2005.10.089
- ¹⁵ M. N. Danchevskaya, Yu. D. Ivakin, S. N. Torbin, G. P. Muravieva, O. G. Ovchinnikova, Thermovaporous synthesis of complicated oxides, *J. Mater. Sci.*, 41 (2006) 5, 1385–1390, doi:10.1007/s10853-006-7411-0
- ¹⁶ Yu. D. Ivakin, M. N. Danchevskaya, G. P. Muravieva, Kinetic model and mechanism of Y₃Al₅O₁₂ formation in hydrothermal and thermovaporous synthesis, *High Pressure Research*, 20 (2001) 1–6, 87–98, doi:10.1080/08957950108206156
- ¹⁷ A. A. Kholodkova, M. N. Danchevskaya, A. S. Fionov, Investigation of fine-crystalline barium titanate synthesized in water fluid, *Abstr. of the XIV Inter. Scientific Conf. High-Tech in Chemical Engineering*, Tula, 2012, 547
- ¹⁸ A. A. Kholodkova, M. N. Danchevskaya, A. S. Fionov, Study of nanocrystalline barium titanate formation in water vapour conditions, *Proc. of the 4th Inter. Conf. NANOCON 2012*, Brno, 2012, 66–71
- ¹⁹ W. Cai, C. Fu, Z. Lin, X. Deng, Vanadium doping effect on micro-structure and dielectric properties of barium titanate ceramics, *Ceramics International*, 37 (2011), 3643–3650, doi:10.1016/j.ceramint.2011.06.024
- ²⁰ M. M. Vijatovic Petrovic, J. D. Bobic, T. Ramoska, B. D. Stojanovic, Electrical properties of lanthanum doped barium titanate ceramics, *Materials Characterization*, 62 (2011), 1000–1006, doi:10.1016/j.matchar.2011.07.013
- ²¹ P. Kumar, S. Singh, M. Spah, J. K. Juneja, Ch. Prakash, K. K. Raina, Synthesis and dielectric properties of substituted barium titanate ceramics, *J. of Alloys and Compounds*, 489 (2010), 59–63, doi:10.1016/j.jallcom.2009.08.024
- ²² S. B. Narang, D. Kaur, Sh. Bahel, Dielectric properties of lanthanum substituted barium titanate microwave ceramics, *Materials Letters*, 60 (2006), 3179–3182, doi:10.1016/j.matlet.2006.02.079
- ²³ L. J. Gao, X. L. Liu, J. Q. Zhang, S. Q. Wang, J. F. Chen, Grain-controlled barium titanate ceramics prepared from high-gravity reactive precipitation process powder, *Materials Chemistry and Physics*, 88 (2004), 27–31, doi:10.1016/j.matchemphys.2004.03.023
- ²⁴ T. Lee, I. A. Aksay, Hierarchical structure-ferroelectricity relationship of barium titanate particles, *Crystal Growth & Design*, 1 (2001) 5, 401–419, doi:10.1021/cg010012b
- ²⁵ B. M. Yavorskiy, A. A. Detlaf, *Spravochnik po fizike*, Nauka, Moscow 1974