Changing of the morphology of crystals $BaTiO_3$, synthesized in supercritical or subcritical water fluid

M.N. Danchevskaya[1, 2], A.A. Kholodkova[1,2] , Yu.D. Ivakin[2], G.P. Muravieva[2], V.V. Rybalchenko[1]

[1]*Moscow Polytech, Avtozavodskaya 16, 115280 Moscow, Russia*
[2]*Chemistry Department, Lomonosov Moscow State University, Leninskie Gory 1-3, 119991 Moscow, Russia*

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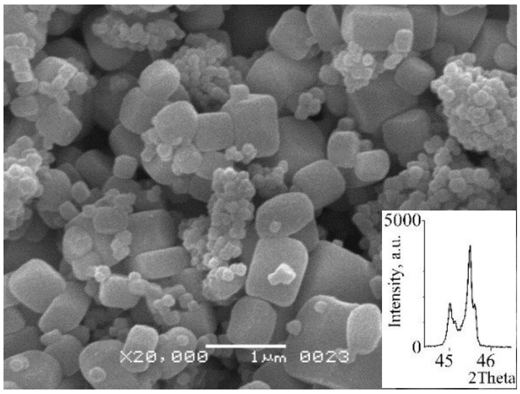
e-mail: mardan@kge.msu.ru

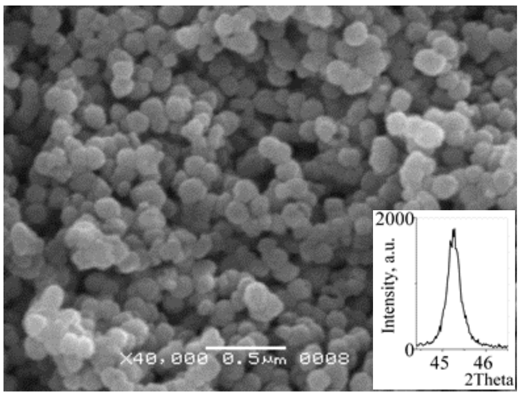
This report presents the results of research the structure and morphology of fine-crystalline barium titanate $BaTiO_3$, synthesized in supercritical and subcritical water fluid, respectively at T=400°C, P=26 MPa and at T=150°C, P=4,76 MPa. Powder synthesis of functional materials in supercritical water fluid recently acquired widespread thanks to the efficiency, availability of technology and environmental safety of production [1]. It has been shown that in to subcritical conditions, at temperature and water vapor pressure below critical values (T=374°C, P=22.4 MPa), also quite intense processes of transformation of the structure and interaction of both simples and complex oxides occur [3, 4]. By this method were synthesized not only simple oxides SiO_2 and Al_2O_3, but also complex oxides: $MgAl_2O_4$, $ZnAl_2O_4$, $LaAlO_3$, $Y_3Al_5O_{12}$ and others [5, 6]. Fine-crystalline $BaTiO_3$ powder use in the production of ferroelectrics and ceramics for capacitors [2]. Requirements for the morphological and structural characteristics of the synthesized $BaTiO_3$ depends on the purpose of its use, therefore technology of barium titanate should allow regulation of the modes of synthesis to obtain product with the desired properties. Synthesis of powder materials in fluid of water allows changing their morphological and structural characteristics, changing state of the reaction medium, namely, of water fluid. Requirements for the morphological and structural characteristics of the synthesized $BaTiO_3$ depends on the purpose of its use, therefore technology of barium titanate should allow regulation of the modes of synthesis to obtain product with the desired properties. Synthesis of powder materials in fluid of water allows changing their morphological and structural characteristics, changing state of the reaction medium, namely, of water fluid.

Synthesis of $BaTiO_3$ was carried out with the use of the following reagents: Barium hydroxide octahydrate $Ba(OH)_2*8H_2O$ and TiO_2 (rutile). The starting substances were mixed in a molar ratio Ba / Ti=1.2. The synthesis was carried out in stainless steel laboratory autoclaves with volume of 17–20 cm^3. The obtained fine-crystalline barium titanate as well as the starting reagents, was studied by X-ray diffraction method (XRD) to determine its phase contents. XRD was carried out by means of Rigaku d/Max-2500 diffractometer with CuKα radiation. The morphology and size of crystals were studied by the methods of scanning (SEM) and transmission (TEM) electron microscopy by means of JSM-6390 LA and JEM-1011). Specific surface area of samples was determining by BET method using automated surface area and pore structure analyzer Auro-sorb-1C/QMS.

The fine crystalline barium titanate, synthesized in supercritical water, was used for to made ceramics with high dielectric permeability (2810) and loss tangent (0.012) respectively at the electromagnetic field of 1 KHz. Ceramics prepared from $BaTiO_3$, synthesized in subcritical water, possessed lower dielectric characteristics, the dielectric permittivity 1619 and loss tangent 0.02. It was explaining that barium titanate crystals were forming at higher process parameter; they have clearly revealed structure of tetragonal modification Figures adduce examples of SEM images of fine-crystalline barium titanate, synthesized in supercritical (Fig. 1) and in subcritical (Fig. 2) conditions.



D = 0,0968 ± 0,0006 μm
Figure1. SEM images of the powder, synthesized in supercritical water at T=400°C, P=26,00 MPa, 20 h.



D= 0,226 ± 0,004 μm
Figure2. SEM images of the powder, synthesized in subcritical water at T=150°C, P=0,48 MPa, 20 h

Increase of pressure and temperature of the fluid upsizes the crystals $BaTiO_3$ and change their shape. In this case, crystals become tetrahedral habitus. On the field of SEM photo also showing the form of reflexes of x-ray in the interval angles 2teta 45-46 for these samples. This cleavage of peak shows that $BaTiO_3$, produced in supercritical conditions consists of mixture of tetragonal phase and impurity of cubic phase.

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[1] Danchevskaya M.N., Ivakin Yu D., Torbin S.N., Panasyuk G.P., Belan V.N., Voroshilov I.L., *J. High Pressure Research*, *Taylor & Francis (United Kingdom),* **2001,** 20, 229.
[2] Biglar M., Gromada M., Stachchowicz F.,Trzepietcinski T., *Akta Mech. Autom*., 2017,11, 275.
[3]Torbin S.N., Danchevskaya M.N., Martynova L.F., Muravieva G.P. *J. High Pressure Research*. 2001, 20, 109.
[4] Khoolodkova A.A., Danchevskaya M.N., Ivakin Yu. D., Muravieva G.P., Ponomarev S.G.,*Russian Journal of Physical Chemistry B*, 2018, 12, 8, 1261.
[5] Kholodkova A. A., Danchevskaya M.N., Ivakin Yu. D., Muravieva G. P., *Journal of* Supercritical *Fluids*, *Elsevier BV (Netherlands)*,2015,105, 201.
[6] Kholodkova A.A., Danchevskaya M.N., Ivakin Yu D., Muravieva G.P., Smirnov A.D., Tarasovskii V.P., Ponomarev S.G., Fionov A.S., Kolesov V.V., *Ceramics International*, PPergamum (United Kingdom),2018, 44, 11,. 13129.