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Crystalline barium titanate synthesized in sub- and supercritical water

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ABSTRACT

The promoting effect of water in different states of aggregation on the transformation processes in oxide mixture was studied in case of $BaTiO_3$ formation. The reaction between barium and titanium oxide was carried out in liquid, in gaseous and in supercritical water. The state of aggregation of the reaction medium had an influence on the degree of transformation of the reagents and on the characteristics of produced $BaTiO_3$ such as the crystal size, the content of volatile impurities and sinterability. On the basis of comparative investigation it was concluded that the synthesis in supercritical water appeared to be the most effective way for production of pure fine-crystalline $BaTiO_3$ for the ceramics preparation.

1. Introduction

Barium titanate is a prominent ferroelectric with high dielectric permittivity [1]. This property ensures for wide industrial applications of $BaTiO_3$ as material for base-metal-electrode capacitors, piezoelectric actuators, thermistors, and electro-optic devices [2,3]. Due to high cost of single crystal, electronic production operates with polycrystalline ceramics. Nowadays $BaTiO_3$ is mostly used for the production of multilayered ceramic capacitors (MLCCs). This direction is intensively developing because of high evolution rate of mobile devices over the world [4,5]. In composition with other oxides (TiO_2, $CaTiO_3$, $Nd_2Ti_2O_7$, $CaZrO_3$, $BaZrO_3$) barium titanate is contained in microcapacitors of NP0, X7R, Z5U, Y5V types [5,6]. A tendency towards miniaturization in electronics demands the use of high-capacitance MLCCs with small dimensions. The dielectric layer thickness in recently developed capacitors does not exceed 2 μm [5]. Further progress in this field requires submicron-grained ceramics produced from fine-crystalline $BaTiO_3$ powders. In this connection strict requirements are proposed to raw materials for ceramics. Perfect powder for MLCC production should be characterized by high purity, homogeneous composition, uniformity of particles, and weak agglomeration of crystals [6]. Further progress in this field requires submicron-grained ceramics produced from fine-crystalline $BaTiO_3$ powders. In this connection strict requirements are proposed to raw materials for ceramics. Perfect powder for MLCC production should be characterized by high purity, homogeneous composition, uniformity of particles, and weak agglomeration of crystals [6]. Low water and hydroxyl groups in raw material are a necessary condition for the removal of pores in ceramics. Besides, the powders of $BaTiO_3$ in tetragonal modification are preferable in ceramics industry [7].

For the moment a plenty of synthesis ways have been developed for preparation of high quality $BaTiO_3$ powder [6]. A conventional route is solid state synthesis which derives $BaTiO_3$ from easily available $BaCO_3$ and TiO_2 at temperatures of 850–1400 °C [2,6,8–12]. The method is simple in operation, and allows large scale production, but however, has important shortcomings. The formation of $BaTiO_3$ occurs by diffusion mechanism through formation of polytitanates, traces of which remain in the final product align with starting reagents [6]. Another problem is almost impossible control of morphology and microstructure of $BaTiO_3$ particles. Preliminary procedures such as milling of reagents and coating of starting $BaCO_3$ by amorphous titania improve the characteristics of product. But these procedures lead to capture of impurities and to increase of synthesis duration and energy consumption. As an alternative to solid state process, various “wet chemical” methods of $BaTiO_3$ synthesis have been developed: sol-gel method [8–11], hydrothermal and solvothermal processing [12–17], microemulsion [18], alkoxide [19], oxalate [20–22], citrate [23], polymeric precursor [24–26] methods etc. These routes yield highly pure, homogeneous, fine $BaTiO_3$ particles with the size down to dozens of nanometers and controlled morphology. Due to operating complication, multistage,

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and comparatively high cost these methods are mostly used at laboratory level with exception to oxalate and hydrothermal methods, which are widely industrialized [6]. Hydrothermal technique utilizes a wide variety of processing conditions for $BaTiO_3$ synthesis from $Ba(OH)_2$ or barium salts ($Ba(NO_3)_2$, $BaCl_2$) and TiO_2 in crystalline or amorphous states. The reaction occurs in water medium at temperature and pressure elevated with respect to the boiling point [27]. The medium is presented either in subcritical or in supercritical state. Below the critical point of water (374 °C, 22.1 MPa) the synthesis is usually carried out in closed batch reactors at temperature above 100 °C under equilibrium pressure and takes several hours [14,15]. Conventionally, water in liquid state with addition of mineralizers (NaOH, KOH) is used as a reaction medium in these processes. Further, it was also shown that water in gaseous state successfully acted as a medium for the formation of simple and complex oxides [28–32], including $BaTiO_3$ [33,34]. Varying the parameters of process in subcritical water (temperature, pressure, duration) it is possible to produce $BaTiO_3$ crystals with sizes in range of 20–1000 nm [6]. Properties of supercritical water (above 374 °C, 22.1 MPa) strongly depend on temperature and pressure and enable the control of $BaTiO_3$ crystal growth [35,36].

The use of flow reactors allows reducing of the processing time from hours to seconds with obtaining of ultrafine particles of 10–50 nm [37–42]. Synthesis in water medium is a high-capacity method providing control of morphology and chemical homogeneity of the crystalline $BaTiO_3$. This method utilizes inexpensive reagents and can easily be scaled up for industrial application. The state of aggregation of water, which acts as a reaction medium, influences the formation rate, morphology, phase contents and other properties of product such as of gahnite and barium hexaferrite [30,43]. Investigations of such kind haven't been provided yet for barium titanate. However, it's supposed that the state of water medium would have an effect on the properties of synthesized $BaTiO_3$. With regards to the requirements for $BaTiO_3$ powder mentioned above, the results would contribute to optimization of synthesis of $BaTiO_3$ and it's applicability for high-quality ceramics production. The purpose of the present work was to study the influence of the state of aggregation of water on the characteristics of $BaTiO_3$ crystals.

2. Materials and methods

Barium titanate was obtained in conventional hydrothermal conditions, in water vapor, and in supercritical water (Table 1). Commercially available barium oxide (BaO, TU 6-09-03-375-74, ≥98% purity), barium hydroxide octahydrate ($Ba(OH)_2{\cdot}8H_2O$, GOST 4107-78, ≥98% purity), and titanium dioxide (TiO_2, STP TU KOMP 2–340-11, ≥99.5% purity) were used as reagents. $Ba(OH)_2{\cdot}8H_2O$ was used as a source of barium ions in case of hydrothermal synthesis. In water vapor and in supercritical water another reagent (BaO) was used instead of $Ba(OH)_2{\cdot}8H_2O$, in order to avoid the influence of crystallization water on the reagents at the initial stage of process. Barium oxide and titanium oxide were thoroughly mixed. Molar ratio Ba/Ti = 1.0. The mixture was placed into stainless steel containers. The masses of reagents utilized to obtain 1.5 g of product were 0.521 g of TiO2 and 1.000 g of BaO. In case of the use of $Ba(OH)_2{\cdot}8H_2O$ the mass of 2.048 g was taken. The containers with the mixture of reagents were placed into laboratory stainless steel autoclaves (volume of 12–15 cm^3). In case of hydrothermal synthesis, distilled water was poured in autoclave inside the container. For the synthesis in water vapor and in supercritical water an amount of distilled water was poured in the autoclaves outside the containers with mixture of oxides. In cases of hydrothermal synthesis and the synthesis in water vapor hermetically closed autoclaves were heated rapidly up to 230 °C with the rate of 200° h^{-1}. To conduct the process in supercritical water, the autoclave was heated with the same rate up to 400 °C. The temperature was maintained for 20 h for each type of conditions. The processes were terminated by rapid cooling of the bottom of autoclaves. The obtained samples were removed from the containers and were dried at 70 °C in air for 12 h.

Table 1
Conditions of synthesis of $BaTiO_3$.

Sample	Conditions of synthesis			
	Reagents	Temperature (°C)	Pressure (MPa)	Duration (h)
HT	$Ba(OH)_2{\cdot}8H_2O$, TiO_2	230	2.9	20
TV	BaO, TiO_2	230	2.9	20
SCF	BaO, TiO_2	400	26.0	20

The synthesized powders were characterized by X-ray diffraction using Rugaku D/Max-2500 diffractometer (Rigaku Corporation, Japan) with CuKα radiation in the range of $10° \geq 2\theta \geq 70°$ with the step of 0.02 °2θ.

IR spectrum of a powder was recorded at EQUINOX 55/S spectrometer. The measurements were performed at a pressed KBr pellet which contained 0.5 mass.% of the analyzed specimen.

Raman spectra of the powders were collected at room temperature using LabRam HR800 UV microscope-spectrometer (Horiba Jobin Yvon Ltd., Japan) with a 632.81 nm wavelength excitation argon laser operating at 5 mW output power in the range of 165–865 cm^{-1}.

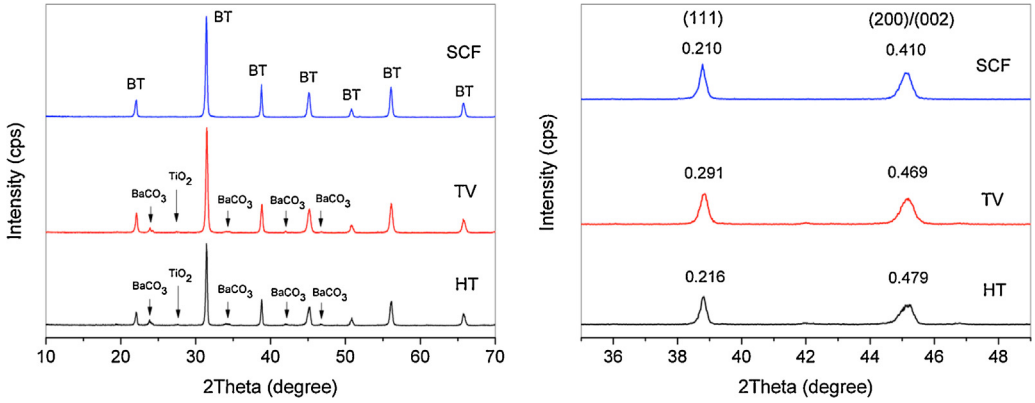

Fig. 1. X-ray diffraction patterns of $BaTiO_3$ samples synthesized at T = 230 °C, p = 2.9 MPa in liquid water (HT) and in water vapor (TV), at T = 400 °C, p = 26.0 MPa in supercritical water fluid (SCF): (a) $10° \leq 2\theta \leq 70°$; (b) $35° \leq 2\theta \leq 49°$, the numbers in brackets identify the indexes of reflections, the numbers without brackets – the values of the full width at half maximum (FWHM) in radians.