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Synthesis of fine-crystalline tetragonal barium titanate in low-density water fluid

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ABSTRACT

Submicron crystals of $BaTiO_3$ were synthesized in mild conditions of low-density water fluid media at $T = 230\,^{\circ}C$, $P_{H2O} = 2.94$ MPa during 20 h. The crystals showed narrow size distribution with the average sizes of 165 and 168 nm. As-synthesized samples of $BaTiO_3$ were annealed in air at 500 °C and washed in acid. It was found that this procedure contributed to the formation of tetragonal $BaTiO_3$. Final $BaTiO_3$ powder contained 0.884 wt.% of water and hydroxyl groups. Ceramics prepared from $BaTiO_3$ powder by SPS technique showed grain-size effect and had dielectric permittivity at room temperature being up to 2320 at 1 MHz. The sequence of annealing and washing of product after synthesis influenced on the phase content of $BaTiO_3$ crystals, but did not affect the properties of sintered ceramics.

1. Introduction

Below the Curie temperature of 120 °C barium titanate ceramics demonstrated high ferroelectric characteristics. Dielectric permittivity of $BaTiO_3$ discs was reported to reach 5000 at ambient temperature and 10,000 at 120 °C [1]. Due to this property $BaTiO_3$ is an important material for microelectronics, e.g., for production of multilayer ceramic capacitors, piezoelectric transducers, positive temperature coefficient resistors and electro–optic devices [2–4]. Physical properties of ceramics such as density, porosity, dielectric permittivity, conductivity, etc. strongly depend not only on sintering conditions, but also on characteristics of the raw material [5]. According to the trend of electronic devices miniaturization, the purpose of the ongoing researches is to obtain fine-grained ferroelectric ceramics. $BaTiO_3$ powder is desired to consist of dispersed, uniform, crystalline particles of submicron size [6]. In contrast to conventional solid-state route [7–9], which leads to coarse inhomogeneous particles of $BaTiO_3$, a plenty of wet chemical methods (sol–gel, hydro- and solvothermal, co-precipitation etc.) allow production of powder that meets the requirements mentioned above [10–13]. But typically, $BaTiO_3$, synthesized by wet chemical methods, contains high amount of water and hydroxyl groups which are unfavorable for ceramics production. In addition, the synthesis of $BaTiO_3$ with tetragonal lattice at room temperature is highly complicated. Though tetragonal modification is thermodynamically stable in these conditions, $BaTiO_3$ crystals obtained by wet chemical routes often retain high-temperature cubic or pseudocubic state below 120 °C. Lattice defects and also high surface tension in case of nano-sized particles obstruct spontaneous polarization [15]. Transition of cubic phase to tetragonal occurs after heating of $BaTiO_3$ crystals up to the temperature higher than 1000 °C, but this operation leads to aggregation of particles. Thus, low water content and tetragonality are desirable characteristics of $BaTiO_3$ powder prepared as raw material for ceramics [16].

Hydrothermal synthesis of $BaTiO_3$ in sub- and supercritical water is attractive and environmentally benign as it requires no expensive auxiliary compounds. In case of supercritical conditions the process is usually carried out in a flow reactor at 400–420 °C and 30–40 MPa and lasts from milliseconds to several seconds [17–20]. TiO_2 aqueous sol, $TiCl_4$ and $Ba(OH)_2$ or barium salts are mostly used as starting reagents. Average crystal size of prepared $BaTiO_3$ is sensitive to the parameters of process and varies in the range of 10–100 nm. Phase modification of the product also shows strong dependence on the reaction conditions: tetragonal $BaTiO_3$ could be obtained at low pressure, while at high fluid pressure cubic $BaTiO_3$ are formed. Tetragonal $BaTiO_3$ samples with average particle sizes in the range of 240–330 nm were produced at 700 °C in 2.5 L/min water vapor flow [21].

The temperature of $BaTiO_3$ synthesis in subcritical water usually does not exceed 300 °C and could be lowered to 80 °C [14,22–24]. The reaction between $TiCl_4$, or titanium alcoholates, or TiO_2 and

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barium salts or hydroxide occurs in solution. Synthesis in liquid media is prolonged in comparison to super critical conditions and lasts for several hours. Produced $BaTiO_3$ crystals have spherical shape and narrow size distribution, the mean sizes vary in the range of 20–120 nm. If well-crystallized TiO_2 was used as a reagent, the size of product particles increases up to 200–700 nm [25]. Tetragonal $BaTiO_3$ formation is observed at temperatures higher than 150 °C [23]. The addition of alkali to the reaction mixture leads to the increase of the tetragonality of product, but this effect has no clear explanation yet [26].

Below the critical point of water (374 °C, 22.1 MPa) liquid–gas phase boundary appears, and mostly the liquid phase is used as media for hydrothermal reactions. However, gaseous phase, or low-density water fluid, is also suitable for this role and successfully acts in the synthesis of crystalline $LaAlO_3$, $Y_3Al_5O_{12}$ and other complex oxides [27]. $BaTiO_3$ nanocrystals (50–80 nm) were obtained in low-density water fluid at 200–280 °C and equilibrium pressure. The crystals had cubic structure at room temperature [28,29].

Hydrothermal method in mild conditions yields crystalline product with controlled morphology. But the necessity of washing and drying of the synthesized powder is a disadvantage of this method [30]. $BaTiO_3$ formation in these conditions occurs in strong alkaline medium [31], and in the presence of air undesired $BaCO_3$ is generated. It was reported [30,32–35] that acid washing of the product for elimination of $BaCO_3$ leads to the leaching of Ba^{2+} ions from the surface of $BaTiO_3$ crystals. Washing resulted nonstoichiometry of $BaTiO_3$ is known to possess pronounced influence on the sinterability of powder, grain growth, and as a result, on dielectric properties of ceramics [34]. According to this research, the effect of post-synthetic treatment on the properties of $BaTiO_3$, obtained in water medium, is of high practical importance. However, the number of research on this subject remains small in comparison to works devoted to developing of new variants of hydrothermal synthesis.

Current work presents the low-density water fluid capability to act as reaction medium for tetragonal $BaTiO_3$ synthesis and includes the optimization of post-synthetic treatment in order to achieve high tetragonality of produced crystals. The comparison of microstructure, phase contents and dielectric characteristics was conducted for ceramics obtained from $BaTiO_3$ powders that underwent different kinds of post-synthetic treatment. The results of the research will reveal the connection between properties of crystals synthesized in low-density water fluid and quality of the produced ceramics.

2. Materials and methods

Synthesis in low-density water fluid was carried out in laboratory stainless steel autoclaves with PTFE inner containers. The volume of the autoclaves was of 80 ml, taking into account inner details. 1.875 g of $Ba(OH)_2{\cdot}8H_2O$, 99% purity, and 0.416 g of TiO_2 (71% rutile and 29% anatase), 99% purity, were thoroughly grinded and mixed in wooden mortar with pestle and put into PTFE container. Distilled water in amount of 0.02 ml was added in the autoclave outside the PTFE container. Ba/Ti molar ratio in prepared mixture amounted to 1.14. As the powders were mixed in air, the interaction between $Ba(OH)_2$ and CO_2 results in $BaCO_3$ and output Ba^{2+} ions from the reaction zone. This lack of Ba^{2+}could be avoided by the use of excessive amount of $Ba(OH)_2{\cdot}8H_2O$ regarding to TiO_2. It is also known that the reaction mixture with molar ratio Ba/Ti > 1 transforms under hydrothermal conditions in $BaTiO_3$, while excessive $Ba(OH)_2$ remains unreacted [31]. Hermetically closed autoclaves were heated up to 230 °C with the rate of 200 °/h and held at this temperature for 20 h. Water vapor pressure inside the autoclave reached 2.94 MPa during the synthesis. The process was stopped by dramatic cooling of the bottoms of autoclaves. Four samples of $BaTiO_3$ were synthesized this way: BT1-1, BT1-2, BT2-1 and BT2-2 (Table B1).

The synthesis of samples BT1-1 and BT2-1 was followed by washing out the residual $Ba(OH)_2$ and $BaCO_3$ with the acetic acid solution, filtration, rinsing with distilled water and drying in air at 70 °C for 24 h. Then BT1-1 and BT2-1 samples were annealed in air at 500 °C for 1 h. Samples BT1-2 and BT2-2 were firstly annealed at 500 °C in air for 1 h and then washed and dried in the same way (Table B1). Thus, the samples within this pairs (BT1-1 and BT2-1, BT1-2 and BT2-2) were obtained in identical conditions. Summarizing, there were two series: BT1 and control one BT2. The difference between samples within each series would be related to the influence of post-synthetic treatment. Control series BT2 was intended for the verification of results obtained for series BT1. Similar observations in both series would show the reliability of obtained result.

Thermal analysis of $BaTiO_3$ powder was carried out in Netzsch STA 449 C Jupiter thermal analyzer. The samples were heated in air with the rate of 10 °/min from 40 to 1150 °C.

Powders BT1-1 and BT1-2 were sintered into ceramic samples by spark plasma sintering technique (SPS) at Labox-625 machine. In order to determine the temperature range, which was the most suitable for the sintering, the shrinkage behavior of powder BT1-1 was investigated. For this purpose the linear shrinkage of BT1-1 and its rate were recorded in SPS conditions on heating up to 1170 °C with the rate of 100 °/min and the pressure of 12 MPa. On the basis of obtained data two sintering conditions were chosen for prepared powders. Disc 1 was sintered from sample BT1-1 at 1140 °C and 50 MPa during 2 min. Disc 2 and Disc 3 were obtained from powders BT1-1 and BT1-2, respectively, at the same conditions of 1170 °C and 50 MPa for 5 min. The conditions of powders sintering are summarized in Table B2. To purify the discs from carbon contaminations after SPS, they were annealed in air at 1100 °C for 8 h.

The capacitance of plane capacitor with round brass electrodes and obtained $BaTiO_3$ ceramic discs as a dielectric layer was measured by LCR meter E7-12 at 1 MHz. Permittivity of the ceramics was calculated from the value of capacitance.

XRD patterns of powders and ceramics were scanned at Rigaku D/Max-2500 diffractometer with CuKα radiation in the range of $10° \leq 2\theta \leq 70°$ with the step of 0.02 °2θ.

The study of morphology and particle size of starting TiO_2 and produced $BaTiO_3$ samples, as well as fractography of ceramic discs were carried out at JEOL JSM-6390 LA scanning electron microscope.

3. Results and discussion

3.1. $BaTiO_3$ powder synthesis and characterization

Fig. A1 shows XRD pattern of as-synthesized sample BT1-1. The sample was prepared in water vapor at 230 °C, 2.94 MPa during 20 h. The pattern contains peaks from $BaTiO_3$ and small signal from $BaCO_3$ and $Ba(OH)_2$ traces. Elimination of admixtures was achieved by washing of the powder with the acetic acid solution (Fig. A2). Final $BaTiO_3$ product obtained at the described conditions had a perfect crystalline structure. According to PDF2 data, the transition from cubic to tetragonal modification of $BaTiO_3$ appears at XRD patterns as a splitting of peaks except to ones related to reflections from (*hhh*) type crystallographic planes. This splitting is mostly pronounced at the range of $44° \leq 2\theta \leq 46°$ in the case of CuKα radiation. According to PDF2 database, cubic modification of $BaTiO_3$ in this range has only one (2 0 0) peak at 44.927° 2θ(card PDF2 [00–031–0174]), while tetragonal modification has two close peaks (0 0 2) at 45.104°2θ and (200) at 45.522 ° 2θ (card PDF2