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Ultrafine powder of barium titanate for production of lead-free ceramic piezomaterials

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Abstract. The paper is aimed to perform and compare the capabilities of the solid state technology and a new method of synthesis in supercritical water for the production of barium titanate powder. This material is of interest for applications such as dense piezoceramics. The new method of synthesis in an aqueous medium allowed obtaining barium titanate of higher phase purity and with a narrow crystal size distribution compared to the solid state method. The ceramics manufactured from the barium titanate powder synthesized in supercritical water possessed a consistently high dielectric constant (2400-2600) and a low loss tangent ($\sim 10^{-2}$) at low and medium frequencies.

1. Introduction

Barium titanate is commonly used in a variety of applications in the microelectronic industry, such as the production of lead-free piezoelectric modules, electro-optic devices, ceramic capacitors, etc. [1]. This material owes its wide utilization to its high dielectric constant: at a temperature below 120 °C, BaTiO₃ exhibits ferroelectric properties. The functional characteristics of barium titanate ceramics depend on the properties of a starting powder. In this regard, it is recommended to use fine powders with high phase purity for the production of dense ceramic materials [2]. For barium titanate powder, it is also important to avoid using the metastable pseudo cubic modification that is paraelectric [3]. Traditionally, BaTiO₃ is synthesized by a simple and convenient solid state route [4]. However, this method is accompanied with high energy consumption and lacks the requirements for purity and morphological homogeneity of the product. A new method of synthesis of fine-crystalline BaTiO₃ in supercritical water was proposed in [5-6]. The method allows obtaining nano- and submicron powders with a low content of impurities, which was successfully applied for the production of dense dielectric ceramics. In this paper, we study the phase and morphological characteristics of BaTiO₃ powders synthesized by the traditional solid state route, and the new method, and compare the structural and functional properties of ceramics based on two kinds of synthesized powder.

2. Experimental

2.1. Materials

BaCO₃ (purity $\geq 99\%$) and TiO₂ (rutile, purity $\geq 99\%$) were used as starting reagents for the synthesis of BaTiO₃ *via* the solid state method. The stoichiometric mixture of reagents was milled in a planetary



mill in isopropyl alcohol for 100 minutes, and then calcinated at 1300 °C in air for 1 hour. The synthesis in supercritical water (SCW) was carried out using BaO (purity $\geq 99\%$) and TiO₂ (rutile, purity $\geq 99\%$) as starting materials. The stoichiometric mixture of oxides was placed into a container in a stainless steel autoclave. The calculated amount of water was poured into the autoclave outside the container. The hermetically sealed autoclave was heated up to 400 °C and held at this temperature for 20 hours. The pressure of the SCW inside the autoclave was 26 MPa. At the end of the process, the autoclave was rapidly cooled down to room temperature, the product was removed from the container and dried in air at 50 °C for 12 hours. To manufacture ceramic samples, 5 mass. % of paraffin were added to the powders as a temporary technological binder, and discs of a diameter of 13 mm and of a thickness of 3-4 mm were pressed uniaxially at 150 MPa. The ceramics were sintered at 1300 °C for 1 hour. The obtained BaTiO₃ powder samples and the manufactured ceramics are listed in table 1. To prepare ceramic samples for electric measurements, their surfaces were polished and painted with silver paste as poles, and fired at 800 °C in for 20 minutes.

Table 1. Conditions of BaTiO₃ synthesis and corresponding ceramics

Sample of powder	Synthesis method	Parameters of synthesis	Conditions of sintering	Sample of ceramics
BT-S	Solid state	t = 1300 °C, 1 h.	t = 1300 °C, 1 h.	BTC-S
BT-F	In SCW medium	t = 400 °C, p = 26 MPa, 20 h.		BTC-F

2.2. Methods

Phase analysis of the synthesized powders was carried out using a STOE STADI P diffractometer with Cu-K α radiation in the range of $20^\circ \leq 2\theta \leq 60^\circ$. The average crystallite size was calculated according to the Scherrer equation [7]. The particle size distribution of the powders was determined on an Analysette 22 NanoTec measuring unit. The morphology of the powders and the microstructure of the ceramic fractures were observed using a JSM-6390 LA scanning electron microscope. The apparent density of the ceramics was determined by the Archimedes method. The porosity of the ceramic samples was measured by the kerosene saturation method. The dielectric characteristics of the ceramics were measured with metallized samples on an Agilent E4980a LCR meter in the frequency range of 20Hz to 2MHz.

3. Results and discussion

XRD analysis of powders synthesized by the solid state method and in a medium of supercritical water (SCW) confirmed the formation of barium titanate in its tetragonal modification (figure 1 a). Along with the peaks corresponding to BaTiO₃, the weak reflections of other phases were presented in the XRD pattern of the BT-S sample in the range $25^\circ \leq 2\theta \leq 30^\circ$. These peaks indicated trace amounts of phases with a Ba:Ti mole ratio different from 1, which originated from the diffusion character of the solid state process. An XRD analysis of the BT-F sample obtained in the SCW medium revealed a pure BaTiO₃ phase within the sensitivity of the method. From the calculation of the average crystallite size, the BT-F sample possessed a well-ordered crystalline structure ($D_{\text{XRD}} = 42$ nm) compared to BT-S ($D_{\text{XRD}} = 33$ nm).

The particle size distribution of the BT-S powder is composed of a minor fraction consisting of submicron particles (0.07-0.2 μm , about 7%) and a major fraction of micron-sized particles (0.9-43 μm , about 93%). Particles of irregular shape and size of 0.5-6.9 μm fell within the SEM sight (figure 1 b). Round-shaped submicron crystals with a diameter from 120 to 740 nm were observed in the BT-F sample (figure 1 c) (mean size $D_{\text{SEM}} = 310 \pm 10$ nm). From a laser diffraction analysis, the crystals in BT-F were considerably agglomerated. The sample exhibited a wide variation of particle sizes from 0.09 to 25 μm , as well as in a range of 107-409 μm (about 23% of the particles). Ultrasonic treatment might improve the dispersion of the powder.

The microstructure of the ceramic samples corresponded to the intermediate stage of sintering [8] (figure 2). On the fracture of BTC-S, the intergrowth of particles in the zones of their contact led to the

formation of a grid of grains (figure 2, a). The size of the visible grains was 0.3-5.1 μm . In the BTC-F sample, the pore space had the shape of communicating channels, which formed isolated regions at the boundaries and in the body of grains (figure 2 b). The size of grains was estimated in the range of 1.2-3.1 μm . For both BaTiO_3 powders, a viscous flow contributed to the sintering mechanism. However, for BT-F this contribution was more significant due to the smaller crystal size and higher surface tension. In the BTC-S sample, the sintering bulk diffusion mechanism was implemented due to the higher defectiveness of the initial BT-S powder (see D_{XRD}).

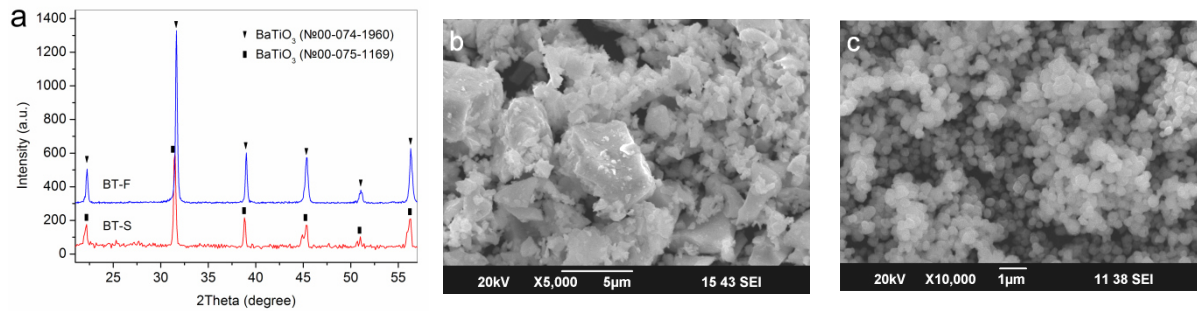


Figure 1. XRD patterns (a) and SEM images of the BaTiO_3 powder samples: b – BT-S; c – BT-F.

Integral structural characteristics, such as density and porosity of the ceramic samples manufactured from BT-S and BT-F powders, possessed close values (table 2).

Table 2. Integral structural characteristics of the BaTiO_3 ceramics

Sample of ceramics	Apparent density (g cm^{-3})	Relative density (%)	Open porosity (%)
BTC-S	5.18	86	4.4
BTC-F	5.24	87	5.6

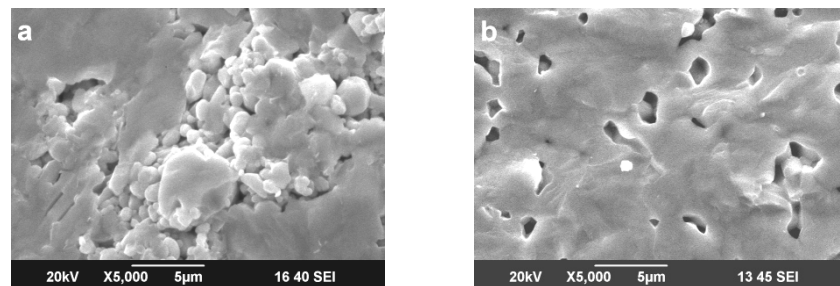


Figure 2. SEM images of BaTiO_3 ceramics: a – BT-S; b – BT-F.

Ceramics based on two types of BaTiO_3 powder possess dielectric characteristics that correspond to the previously reported data and requirements imposed by the electronic industry [9-11]. The BTC-F sample surpassed the BTC-S sample in dielectric properties. The ceramics manufactured from a powder synthesized in the medium of SCW had a higher dielectric constant (2400-2600) and a low loss tangent ($\sim 1\%$), and also showed a higher frequency stability of these characteristics compared to the ceramics from a powder obtained by the traditional solid-state technology (figure 3). This result is ensured by the structural homogeneity of BTC-F at similar density and porosity values of the two types of material.

4. Conclusions

BaTiO_3 powder, synthesized in the medium of SCW, excelled the powder obtained by the traditional solid state technology as a raw material for dense dielectric ceramics. The product of synthesis in an aqueous medium performed the phase purity, a well-ordered crystal structure, a narrow distribution of

crystal sizes, and a regular shape of crystals. As a disadvantage of such a powder, it can be noted that submicron crystals agglomerated and formed micron particles. The phase purity and structural homogeneity of the powder synthesized in SCW contributed to the production of high-quality dielectric ceramics. These ceramics possessed a stably high dielectric permittivity and low dielectric losses in the low and medium frequency range. The method of BaTiO_3 synthesis in the medium of SCW is a promising method for obtaining raw materials for the microelectronic industry.

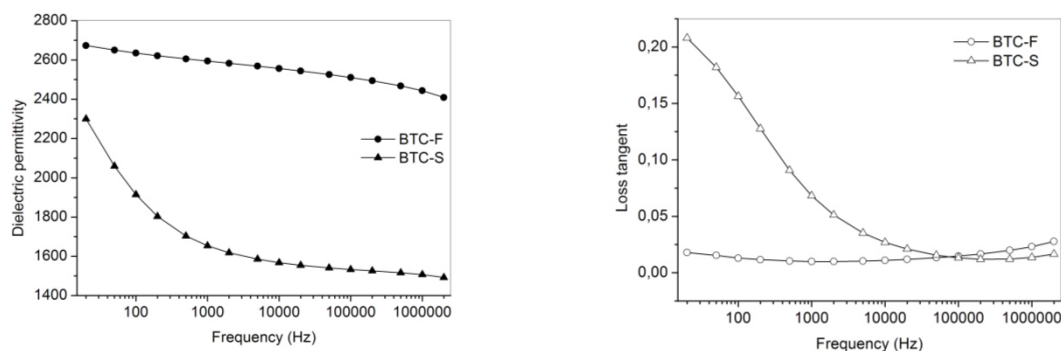


Figure 3. Frequency dependence of dielectric permittivity and loss tangent of BaTiO_3 ceramics.

Acknowledgments

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