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Electrical properties of antimony doped barium titanate ceramics

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ABSTRACT

Antimony doped barium titanate powders were synthesized by polymeric precursors method based on modified Pechini process. Obtained powders were pressed and sintered at 1300 °C for 8 h. XRD analysis showed the formation of tetragonal crystal structure in barium titanate ceramics. The decrease of tetragonality was noticed with antimony concentration increase. The influence of antimony concentration on structure change, grain size reduction and microstructure development was analyzed. Dielectric behavior of pure and antimony doped ceramics showed the change from classical to diffuse ferroelectric material. A modified Curie–Weiss law was used to explore the connection between doping level and the degree of diffuseness of phase transition. The analysis of impedance at higher temperatures showed the presence of both grain interior and grain boundary effects. Modest PTCR jump was observed in the doped barium titanate ceramics.

1. Introduction

Barium titanate (BT) has attracted a considerable attention during the years due to its excellent physical properties and wide practical application. The perovskite structure of barium titanate has capability to host ions of different radii in the crystal lattice. Doping with various ions could enable tailoring of barium titanate structure and electrical properties and widening of its application in electronics.

Different studies have shown that dopants shift transition temperatures of the BT or induce broadening of the ε–T curve and many of them cause diffuseness of the ferroelectric transition [1]. The degree of diffuseness of the transition could show the continuous change from classical ferroelectric to diffuse ferroelectric or to relaxor material, depending on the type of dopant incorporated in the BT lattice. According to literature data, partial substitution of Ba or Ti ions with dopants such as Zn, Y and La cause the formation of diffuse phase transition and Sn, Ce, Zr, Bi, Hf [2] cause the appearance of ferroelectric relaxor behavior.

Pure barium titanate is an electrical insulator at room temperature. Addition of dopants enables the change of barium titanate insulating properties to semiconducting and possibly appearance of PTCR effect in the material [3,4]. To obtain required electrical properties special attention has to be given to the correlation between synthesis method and all processing parameters, obtained structure and final materials properties [5,6].

There is limited number of papers regarding electrical properties of antimony doped barium titanate. However, the literature data mainly reports properties of antimony doped BT obtained by the mixed oxides procedure [7–9]. These researches were based on the study of microstructure formation and appearance of PTCR effect in Sb doped ceramics. The influence of antimony on the grain growth inhibition and formation of more uniform microstructure in doped ceramics in comparison with pure barium titanate was noticed. In the articles written by Brzozowski et al. [7,8], PTCR jump of ~2–3 orders of magnitude was also observed. Tangjuank el al. [10] prepared Sb doped barium titanate by a sol–gel method and the increase of dielectric constant value with Sb doping was prominent in these materials.

In this work, antimony as a donor dopant Sb^{3+} (0.90 Å) that exclusively incorporates at Ba^{2+} (1.35 Å) site was added into barium titanate. The influence of various concentrations of antimony on barium titanate crystal structure formation and microstructure development was monitored. The report on the synthesis, structure and dielectric properties correlations was given. The effect of antimony on the BT ferroelectric phase transition diffuseness was investigated. Impedance analysis was used to determine the presence of grain, grain boundary and electrode contributions to total resistivity.

2. Experimental procedure

The barium titanate powders for this investigation were prepared by polymeric precursor method, modified Pechini process [11]. For preparing titanium citrate and barium citrate solutions as a starting materials titanium tetra-isopropoxide

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($Ti[OCH(CH_3)_2]_4$, Alfa Aesar, 99.995%), barium acetate ($Ba(CH_3COO)_2$, Alfa Aesar, 99.0–102.0%) and antimony acetate salt ($Sb(CH_3COO)_3$, Aldrich, 99.99%) were used. The concentration of added Sb was 0.1, 0.3 and 0.5 mol% Sb (BTS1, BTS3 and BTS5). Ethylene glycol and citric acid were used as solvents for preparation of citrate solutions, where the molar ratio between metal ion, citric acid and ethylene glycol was 1:4:16. Barium citrate and titanium citrate solutions were mixed and heated at 90 °C and then antimony salt was added. Temperature was raised up to 120–140 °C, when transparent yellow solution changed into a solidified dark-brown glassy resin. The decomposition of the most organic part was performed in the oven at 200 °C for 4 h. As soon as the resin incinerated, and became black solid mass, material was pulverized. Thermal treatment of obtained precursor was performed at temperatures ranging from 350 to 850 °C and each step lasted for 4 h. Detailed procedure could be found elsewhere [11,12].

BT powders were pressed into pellets under the pressure of 196 MPa using uniaxial press. According to previous investigations [12], sintering was performed at 1300 °C for 8 h (in tube furnace Lenton, UK) in air atmosphere and the heating rate was 10 °C/min.

The density of barium titanate ceramics was obtained by measuring dimensions and mass of the samples and calculating from equation $\rho = 4m/d^2\,h\,\pi$ (where m is mass, d is average diameter and h is height of the sintered samples). The microstructures of sintered samples were investigated using X-ray diffraction (Model Phillips PW1710 diffractometer) and scanning electron microscope (Tescan VEGA TS 5130MM). The microstructures of sintered samples were analyzed at free and fracture surface and samples were coated with gold before measurement. The electrical measurements were carried out using an LCR meter (model 4284 A, Hewllet-Packard) and samples were prepared by applying Ag electrodes on the polished surfaces of the sintered ceramic disks. Since, from the electrical measurements were obtained values for real (ε') and imaginary (ε'') parts of permittivity, the dielectric loss tangent of barium titanate ceramics was derived calculating from equation $\tan\delta = \varepsilon''/\varepsilon'$.

The impedance measurements were also carried out in the temperature range of 300–550 °C and in the frequency range of 42 Hz–5 MHz using HIOKI 3532-50 LCR HiTester. To obtain continuous metallic contacts, Pt paste was deposed on the polished surfaces of the doped BT ceramics. All collected data were analyzed using the commercial software package *Z-view*.

3. Results and discussion

Cubic barium titanate nanopowders with particles from 40 to 35 nm were obtained by modified Pechini process. The XRD results (Fig. 1) of sintered samples showed formation of barium titanate tetragonal crystal structure identified by the appearance of its characteristic diffraction peaks (JCPDS files no. 05-0626). The lattice parameters confirmed the formation of tetragonal structure in all samples. The change in tetragonality in doped samples was noticed (Fig. 2). The decrease of tetragonality with the increase of dopant concentration indicated the structure change from tetragonal to pseudo-cubic. The tetragonality of pure BT was 1.0053 and it is in agreement with values for BT prepared by other chemical synthesis methods [13,14].

The splitting of diffraction peaks are especially apparent for $2\theta = 45°$. The appearance of new reflections or their splitting at XRD diagrams indicates the change of symmetry in the BT perovskite structure. Therefore, the addition of dopants in the structure leads to this symmetry change due to appearance of irregularities in ions packaging in the BT lattice [7]. In the homogenous and fine-grained materials, the emergence of mechanical stress also leads to stabilization of pseudo-cubic

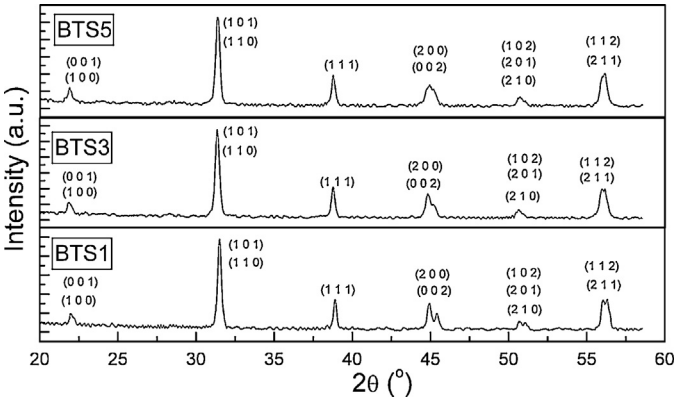

Fig. 1. X-ray diffraction patterns of BTS1, BTS3 and BTS5 ceramics sintered at 1300 °C for 8 h.

structure [15,16]. Buscaglia et al. [13] assumed that XRD peaks symmetry lowering is connected with existing of two structurally different regions, cubic and tetragonal, within doped BT grains. This phenomenon was considered as a connection between dopant incorporation in the BT lattice and transition of material from ferroelectric to paraelectric phase in doped BT ceramics. Wu et al. [16] studied tetragonality change in pure BT samples with different grain size. The highest c/a ratio was found in samples with the biggest grains and this ratio becomes lower as the concentration of smaller grains in the sample increases. Thus, in our study dopants were added in order to reduce the grain size. As a result of grain size lowering, the symmetry was changed and materials crystal structure switched from tetragonal to pseudo-cubic.

Microstructures of barium titanate ceramics sintered at 1300 °C for 8 h are presented in Fig. 3. Microstructure analysis showed polygonal grains but the differences in the grain size, homogeneity and porosity between the doped samples was noticed. The grain size decreased with the Sb concentration increase. Even very low concentration of antimony inhibited grain growth in the BT ceramics significantly. BTS5 ceramic showed the largest grain size reduction up to ~0.45 μm. In the BTS5 and BTS3 samples bimodal grain size distribution was observed, where beside smaller grains, bigger grains with size ~1 μm were noticed, probably associated with non-uniform dopant distribution in the barium titanate.

The sample color was changed after sintering, from pale yellow for the BTS1 sample, to light blue for the BTS3 and dark blue for the

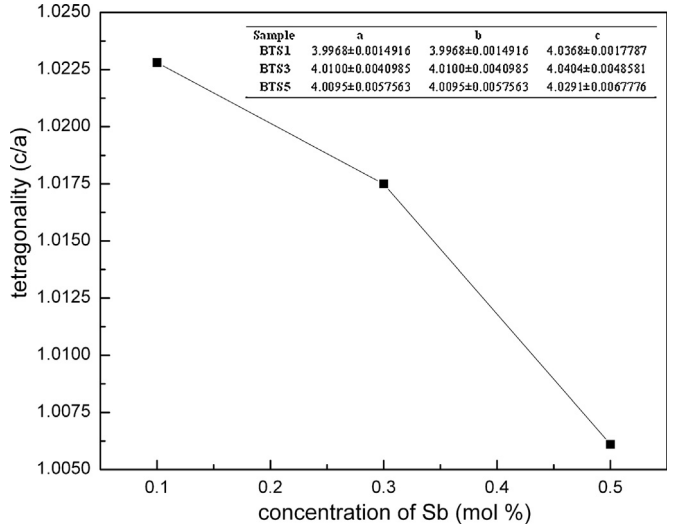

Fig. 2. Tetragonality (c/a) as a function of antimony concentration.