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Characterization of doped $BaTiO_3$ ceramic powders synthesized from polymeric precursors

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In this paper, $BaTiO_3$ doped with Sb and sintered was investigated. Doped barium titanate nanopowder was prepared by doping pure barium titanate starting from citrate solutions of all components: barium, titanium and antimony. Obtained powders were pressed in to pellets calcined at 800 °C for 4 h and sintered at 1300 °C for 8 h in air atmosphere. The formation of phase and crystal structure of $BaTiO_3$ was carried out by XRD analysis and Raman spectroscopy. Microstructural properties such as grain size distribution and morphology of sintered samples were determined using scanning electron microscope. Therefore it was analyzed relation between grain size, structure and properties of obtained ceramics. Influence of Sb doping on barium titanate properties was discussed.

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1. Introduction

Since ferroelectricity was found and due to intensive research in the sphere of polycrystalline ceramics, great technological progress and success in the field of ferroelectric materials was distinguished. Ferroelectric perovskites belong to large group of ferroelectric materials and they have very important role due to its wide application in electronics. Barium titanate has a special place in this group of compounds because it is a first discovered ferroelectric ceramic material and can be formulated in the large number of systems and solid solutions that provide wide range of various applications. The perovskite structure has capability to host ions of different size, so a large number of different dopants can be accommodated in the $BaTiO_3$ lattice that makes $BaTiO_3$ semiconductive. Doping of $BaTiO_3$ (BT) ceramics is very important for obtaining very interesting characteristics for potential applications. For many years, A- and B-site dopants have been used to modify the electrical properties of $BaTiO_3$. It is well known that semiconducting barium titanate can be produced by atmospheric reduction (forming oxygen vacancies) or by donor doping with trivalent ions (lanthanum, yttrium, antimony) on Ba-ion sites, or with heptavalent ions (niobium, antimony, tantalum) on Ti-ion sites [1]. Ionic radius is main parameter that determinates the substitution site. The concentration of donor or acceptor dopants is very low therefore barium titanate purity has to be on the high level as well as the control of each process step. Addition of lanthanum as a donor dopant at a relatively low concentration (< 0.5 at%) leads to room temperature semiconducting ceramics with positive coefficient of resistivity (PTCR) properties, whereas higher dopant concentration lead to insulating materials [2].

In this work the influence of antimony doping on properties of barium titanate powders and ceramics prepared from organometallic complex was studied. Effect of antimony on microstructure and morphology of barium titanate was observed and properties were investigated.

2. Experimental procedures

Barium titanate powders were prepared by the polymeric organometallic precursors method (Pechini process-PPM) using barium and titanium citrates and for doping were used antimony acetate. Firstly, titanium citrate and barium citrate solutions were prepared, using titanium iso-propoxide ($Ti[OCH(CH_3)_2]_4$, Alfa Aesar, 99.995%) and barium acetate ($Ba(CH_3COO)_2$, Alfa Aesar, 99.0-102.0%). The molar ratio of citric acid to ethylene glycol was 4:16, for the citrate solutions. Solutions of titanium citrate and barium citrate were mixed, with constant stirring until it became a clear transparent yellow solution. For doping barium titanate, antimony acetate ($Sb(CH_3COO)_3$) with 0.5 mol% Sb (BTSb). Temperature was raised to 120 - 140 ^oC, to promote polymerization and remove solvents. The solution became more viscous and changed color from yellow to brown and finally solution solidifies into a dark – brown glassy resin. Decomposition of most of the organic carbon residue was performed in an oven at 250 ^oC for 1h and then at 300 ^oC for 4h, the heating rate was 2 $^oC\ min^{-1}$. The resin became a black solid mass and material was pulverized, using Agate Mortar and pestle, before further treatment. Obtained material was sieved and thermaly treated at 800 ^oC for 4h. The agglomerates were broken in agate pulverizer (Fritisch Pulverisette, Type 02.102). After drying at room temperature and passing through sieve (200 mesh), the barium titanate powder was obtained.

The powders were isostatically pressed into pellets 8 mm in diameter and average thickness of about 2.5 mm at pressure of 98.1 MPa. Sintering was performed at 1300 ^oC for 8 h (in a tube furnace "Lenton", UK) and the heating rate was 10 ^oC min^{-1} with nature cooling in an air atmosphere.

Investigation of crystal structure of pure and doped BT ceramic samples was performed using X-ray diffractometer Phillips PW1710.

Room temperature Raman spectra in spectral range from 100 to 1200 cm^{-1}, in back scattering geometry, were obtained by the micro-Raman analyzed using Jobin Yvon T64000 spectrometer, equipped with nitrogen cooled charge-coupled-device detector. As excitation source we used the 514 nm line of an Ar-iron laser. The measurements were performed at 20 mW during 200 s.

The microstructure of BT sintered samples was analyzed by scanning electron microscope Tescan VEGA TS 5130 MM. The microstructure of those samples was obtained by polishing and thermal etching during 30 min at 1200 °C.

3. Results and discussion

The XRD results of all powders indicate the formation of well crystallized cubic phase of $BaTiO_3$ (identified using the JCPDS files no. 31-0174) with crystallite size of about 20-25 nm.

It can be concluded that powders of barium titanate obtained by Pechini process are nanosized, but particle size distribution measurement pointed that the powders are highly agglomerated which can be also seen from calculated agglomeration factor. Densities of all powders have almost the same value 5.71±0.02. The Fig. 1 shows the typical X-ray diffraction (XRD) patterns of pure and Sb- doped $BaTiO_3$ ceramics.

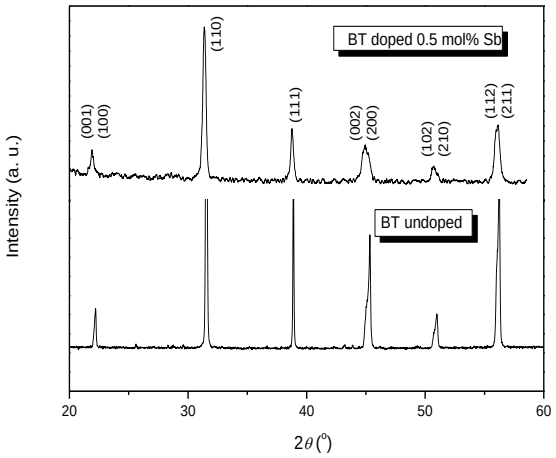


Fig. 1. X-ray diffraction patterns of the $BaTiO_3$ and Sb-doped $BaTiO_3$ ceramics sintered at 1300 ℃ for 8 h.

All the patterns are nearly identical. Comparing obtained patterns with the JCPDS No. 5-0626 standards indicate the formation of tetragonal phase in all samples. The effect of doping on phase formation could not be clearly noted due to small concentration of dopants that are less then sensitivity of used XRD equipment.

The close relationship between ferroelectricity and lattice dynamics makes Raman spectroscopy a valuable technique for the study of ferroelectric materials. Raman scattering spectra can give some information on a local and dynamic symmetry in a much smaller region (correlation length below 2-3 nm) within a much shorter time (< 1ns). Raman spectra obtained at room temperature for $BaTiO_3$ and doped BT with 0.5 mol% Sb are shown in Fig. 2. The first-order Raman spectra of tetragonal BT, similar to those of $BaTiO_3$ doped BT with 0.5 mol% Sb. Also, it is similar to of polycrystalline $BaTiO_3$ samples reported by other authors, show two asymmetric, broad and intense bands associated with $A_1(TO_2)$ and $A_1(TO_3)$ optical modes, a sharp band (i.e., the ``silent`` mode A_1 + E(TO + LO) from cubic F2u) and a week band ($A_1(LO_3)$ + $E(LO_3)$), peaking at 261, 519, 305 and 715 cm^{-1}, respectively. The observed anti-resonance effect at 182 cm^{-1} as an interference feature, is attributed by Scalabrin et al. to a coupling between the sharp $A_1(TO_1)$ and broad $A_1(TO_2)$ modes. Raman spectroscopy confirms that $BaTiO_3$ particles have the tetragonal structure in agreement with the XRD results.

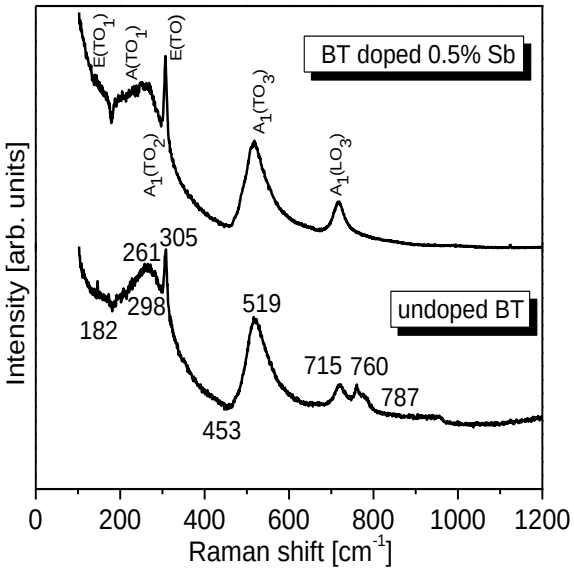
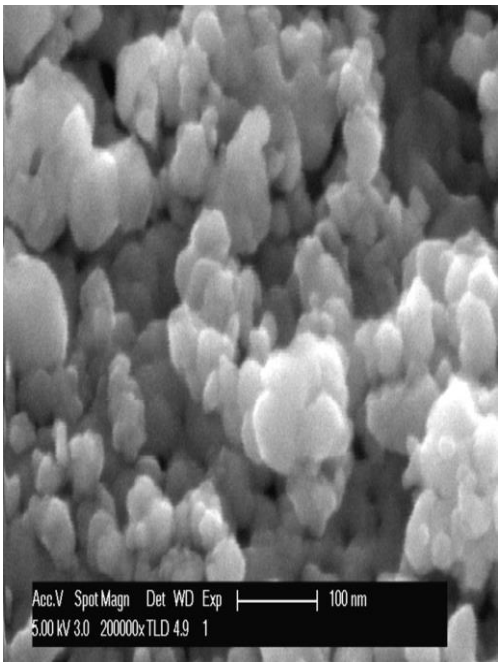


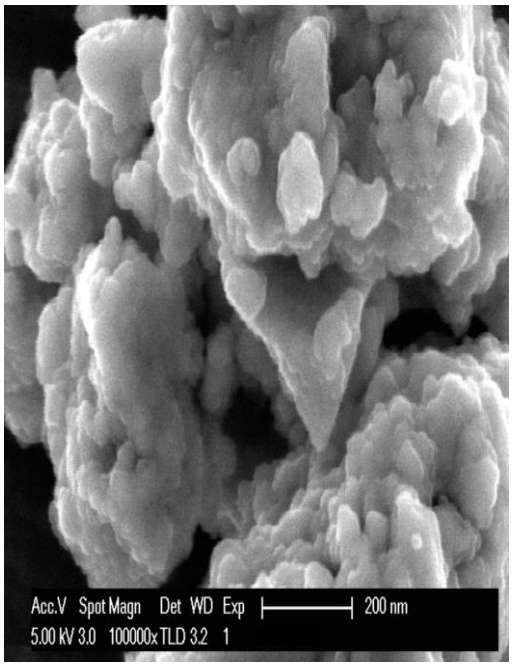
Fig. 2. Raman spectra of the $BaTiO_3$ and Sb-doped $BaTiO_3$ ceramic powders obtained by Pechini method.

Fig. 3 shows the SEM photographs of the $BaTiO_3$ powders. SEM observation indicates that higher percentage of Sb has effect on primary particle size in doped barium titanate. The primary particles were round in shape with uniform size about 40 nm for powders of pure barium titanate and barium titanate doped with 0.1 mol% La. The particle size of about 26 nm was obtained for barium titanate powder doped with 0.3 mol% Sb. It can be assumed that very low concentration of antimony has no

influence on particle size compared with pure BT powders. The particle size becomes smaller with increasing dopant concentration [3].



(a)



(b)

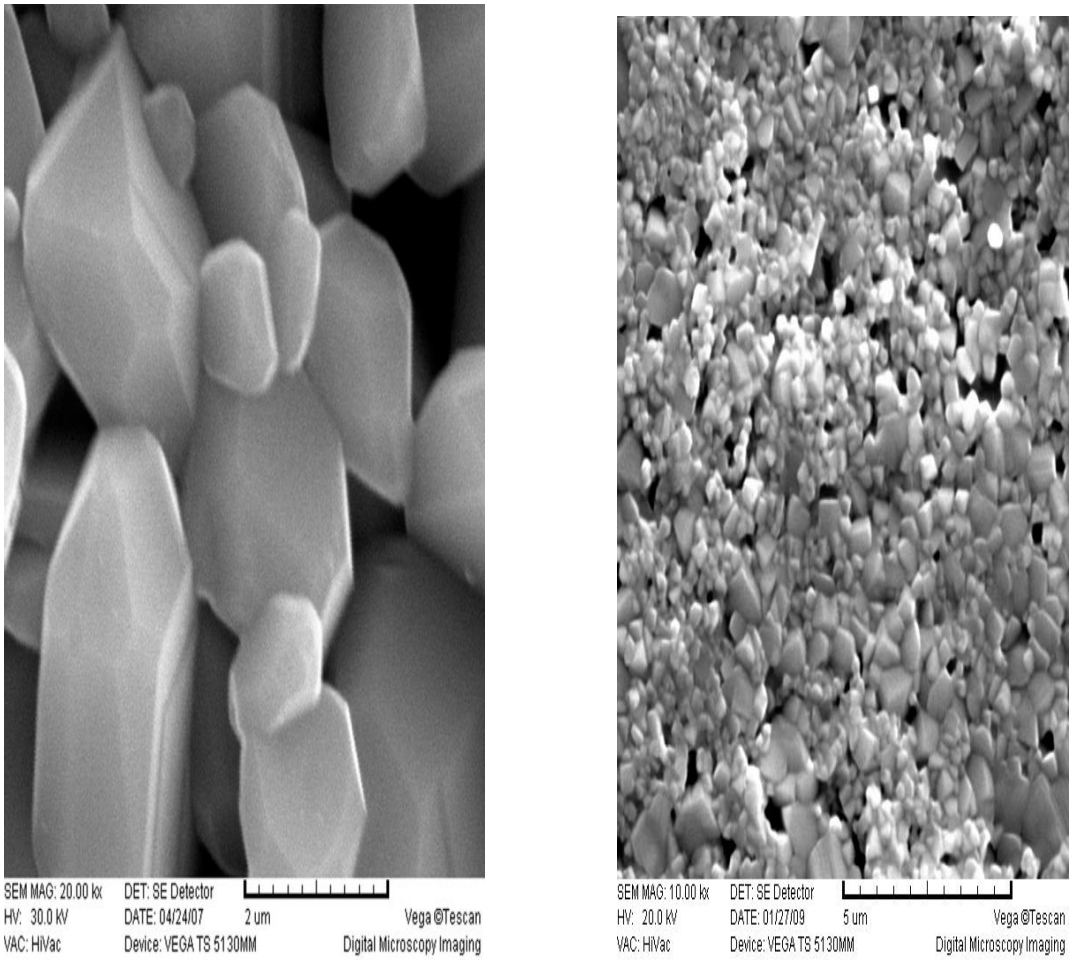
Fig. 3. SEM photographs of a) undoped $BaTiO_3$, b) $BaTiO_3$ doped with 0.5 mol% Sb.

It is well known that it is very difficult to prepare fully dense nanostructured ceramics. There are a lot of factors which can affect on producing fine-grained materials with high density. Strong influence has the powder preparation process, dopant concentration, sintering temperature and time, etc [4]. Having in mind great agglomeration of powders the problems in sintering process were expected.

The dopants have profound effect on the densification and microstructure evaluation of $BaTiO_3$ [5]. Obtained microstructures reveal that the relatively short time of sintering was not enough for significant grain growth, so as the sintering time increase densification (83%/1300/2h – 91%/1300/8h) and grain growth was observed [6]. The difference in grain size for barium titanate doped with 0.1 and 0.3 mol% of antimony were not so evident for 2 hours sintering. The average grain size is about 700 nm with small amount of abnormal grains with grain size of 1 μm. For 0.5 mol% Sb the average grain size is about 0.5 μm, indicating that higher concentration of antimony inhibits grain growth. The grains are rounded or polygonal in shape with large pores among. Those pores could be eliminated by longer sintering times or higher sintering temperature what is in agreement with experimental density.

Increasing sintering time the grain growth intensifies. Therefore average grain size ~1.5 μm was found in samples with 0.1 mol% Sb and sintered for 4h, while samples with 0.3 mol % Sb sintered for the same time show average grain size ~1 μm. BT doped with 0.5 mol% Sb consists of small grains with average grain size of about 0.3 μm, confirming the influence of Sb concentration. The microstructure of samples sintered for 8h and doped with various concentration of antimony follows the same trend as previous. The microstructure consists of polygonal grains, where BT doped with the highest antimony concentration possess small grains from 0.2-0.4 μm. Thus, it can be notified that antimony concentration has significant influence on BT grain growth. As the concentration of antimony in barium titanate increases average grain size decreases.

BT doped with 0.5 mol% Sb consists of small rounded or polygonal grains with average grain size of about 0.5 μm and 0.75 μm (Fig. 4) comparing to pure BT sample in which were found grains of 1.0-2.5 μm. It can be notified that Sb as dopant have significant influence on inhibition of grain growth in BT ceramics. Density of BT samples doped with antimony 96.7 % of theoretical density. Undoped BT sintered samples have density about 90.1 %. Therefore, it can be observed that antimony have profound effect on the densification and microstructure evolution of $BaTiO_3$, and that was also reported by other authors.



(a) *(b)*

Fig. 4. The microstructure of a) the $BaTiO_3$ and b) Sb-doped $BaTiO_3$ ceramics sintered at 1300 ℃ for 8 h.

4. Conclusions

Pure and doped barium titanate with 0.5 mol% Sb was prepared from organometallic complex. The XRD results of BT ceramics obtained by sintering at 1300 °C for 8h show the formation of well crystallized tetragonal phase. The intensity of the Raman bands of Sb doped barium titanate are higher than that of undoped one. The microstructure consists of polygonal grains, where BT doped with Sb possesses small grains around 0.75 μm and undoped sample consists of larger grains of about 1.0-2.5 μm. It can be notified that antimony has great influence on grain growth and densification of $BaTiO_3$ ceramics.

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References

[1] M. Vijatovic, J. D Bobic, B. D. Stojanovic, Sci. Sintering **40**, 235 (2008).
[2] M. T. Biscaglia, V. Buscaglia, M. Viviani, P. Nanni, M. Hanuskova, Journal of the European Ceramic Society **20**, 1997 (2000).
[3] Z. Xinle, M. Zhimei, X. Zoujiang, C. Guang, Jornal of Rare Earths **24**, 82 (2006).
[4] W. Luan, L. Gao, J. Guo, Ceramics International **25**, 27(1999).
[5] B. D. Stojanovic, M. A. Zaghete, C. R. Foschini, F. O. S. Vieira, J. A. Varela, Ferroelectrics **270**, 15 (2002).
[6] H. T. Kim, Y. H. Han, Ceramics International **30**, 1719 (2004).

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