

Study of undoped and donor doped barium titanate prepared by modified Pechini method

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The aim of this study is to investigate the influence of La- doping on the BaTiO₃ synthesized through the Pechini method. La- doped and undoped BaTiO₃ were sintered in air at 1300 °C for 2-8 h. Infrared spectroscopy was used in addition to the XRD, Raman spectroscopy and SEM investigations in order to find evidence of the structural phase in undoped and doped BaTiO₃ ceramics.

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1. Introduction

Barium titanate based ceramics is one of the most investigated ferroelectric ceramics because of its numerous practical applications [1, 2]. The electrical and dielectric properties of ceramics can be modified using various type of additive as well as processing procedures. Among the additive / dopants lanthanum (La) is the most efficient in raising the dielectric permittivity of modified BaTiO₃ ceramics. A small amount of La³⁺ ions, which exclusively replace Ba sites in the perovskite structure of BaTiO₃, leads to the formation of a n-type BaTiO₃ semiconductor, if the samples are heated in a reducing or argon atmosphere. However, samples sintered in air atmosphere are electrically insulating [3, 4]. Taking into consideration the complex structure of polycrystalline ceramics which is composed of grains, grain boundaries, second phases, pores and electrode-ceramics surfaces, it is not possible to distinguish the resistivity or capacitive contributions of each of these elements to the overall resistivity or capacitance of ceramics by simple DC measurements. In this work the influence of lanthanum doping on properties of barium titanate powders and ceramics prepared from organometallic complex was studied. Effect of lanthanum 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 lanthanum nitrate hexahydrate with 0.1-0.5 mol% La (BTLA). Firstly, titanium citrate and barium citrate solutions were prepared, using titanium isopropoxide (Alfa Aesar, 99.995%) and barium acetate (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. Temperature was raised to 120 - 140 °C, 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 °C for 1h and then at 300 °C for 4h, the heating rate was 2 °C 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 thermally treated at 800 °C for 4h. The agglomerates were broken in agate pulverizer (Fritsch Pulverisette, Type 02.102). After drying at room temperature and passing through sieve (200 meshes), 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 °C for 4 h (in a tube furnace "Lenton", UK) and the heating rate was 10 °C 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 900 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.

Far-infrared reflectivity measurements were made in spectral range (50-4000 cm⁻¹) at room temperature with BOMEM DA8 spectrometer.

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 nm. 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 XRD analysis barium titanate powders and sintered samples were referred in more details previously [5].

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 ($< 1\text{ns}$). Raman spectra obtained at room temperature for BaTiO_3 and doped BT with 0.3 mol% La is shown in Fig. 1. The first-order Raman spectra of tetragonal BT, similar to those of BaTiO_3 doped BT with 0.3 mol% La. Also, it is similar to of polycrystalline BaTiO_3 samples reported by other authors, show two asymmetric, broad and intense bands associated with $A_1(\text{TO}_2)$ and $A_1(\text{TO}_3)$ optical modes, a sharp band (i.e., the "silent" mode $A_1 + E(\text{TO} + \text{LO})$ from cubic F_{2u}) and a weak band ($A_1(\text{LO}_3) + E(\text{LO}_3)$), 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 $A_1(\text{TO}_1)$ and broad $A_1(\text{TO}_2)$ modes. Raman spectroscopy confirms that BaTiO_3 particles have the tetragonal structure in agreement with the XRD results.

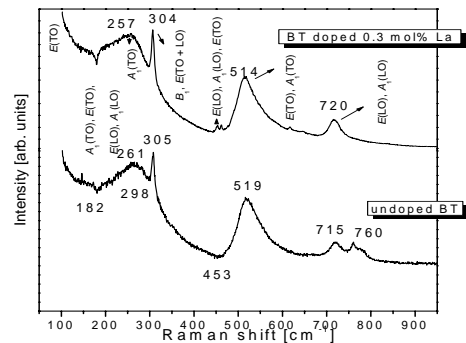


Fig. 1. Raman spectra of the BaTiO_3 and La-doped BaTiO_3 ceramic powders obtained by Pechini method.

The infrared spectra of ABO_3 perovskites have been studied extensively. Factor group analysis for BaTiO_3 with cubic symmetry (space group $\text{Pm}\bar{3}\text{m} = \text{Oh}$) predicts only infrared bands (three triply degenerate infrared active modes of F_{1u} symmetry) and one optically silent (neither infrared nor Raman active) mode of F_{2u} symmetry [6]. The three infrared active modes are commonly called the stretching modes (B-O bond-length modulation), and the external mode in which the BO_6 octahedron vibrates against the A atoms. In tetragonal symmetry (space group $\text{P}4\text{mm} = \text{C}4\text{v}$), 12 fundamental optical modes with the following irreducible representation are expected: $3A_1$, $4E$ and B_1 [7, 8]. 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 BT ceramics is very important for obtaining very interesting characteristics for potential applications.

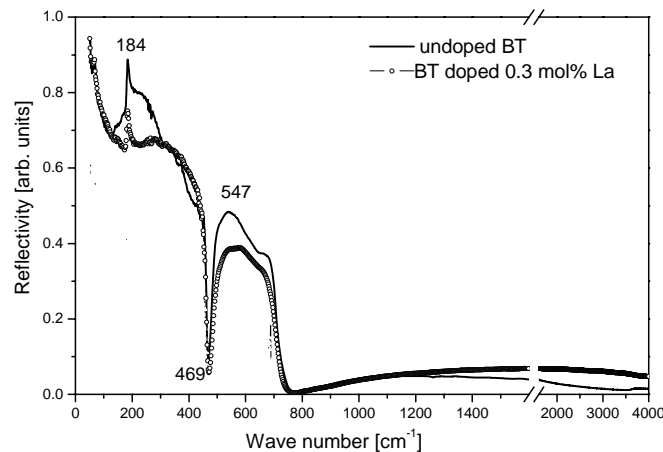


Fig. 2. Infrared spectroscopy of the BaTiO_3 and La-doped BaTiO_3 ceramics sintered at 1300 $^\circ\text{C}$ for 4 h.

Fig. 2 shows the IR spectrum of the BaTiO_3 and La-doped BaTiO_3 ceramics sintered at 1300°C for 4h. The bands in the lower wave number range ($50\text{-}700\text{ cm}^{-1}$) are due to Ti-O vibrations. The characteristic peak is found for all samples. The modes at 180 and 470 cm^{-1} belong to the A1 representation to which the soft phonon mode associated with the ferroelectric phase transition at $T_c = 395\text{ K}$ belongs. The broad band over $50\text{-}180\text{ cm}^{-1}$ is due to soft phonon. Because of the over damped character of the soft phonon, it is difficult to determine the frequency. The intensity of three peaks of the doped BT $0.3\text{ mol}\%$ La and undoped barium titanate appear on 183 and 185 cm^{-1} , respectively. The intensities of the modes at 180 , 250 and 470 cm^{-1} decrease for BaTiO_3 and La-doped BaTiO_3 , respectively. This suggests a change of crystal structure. These results are in agreement with our previous investigations [9]. All observations related to IR indicate the formation of pure single phase of BT and La-doped BT.

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. 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 . Obtained microstructures reveal that the relatively short time of sintering was not enough for significant grain growth, so as the sintering time increase densification and grain growth was observed [10]. The difference in grain size for barium titanate doped with 0.1 and $0.3\text{ mol}\%$ of lanthanum 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 $1\text{ }\mu\text{m}$. For $0.3\text{ mol}\%$ La the average grain size is about $0.5\text{ }\mu\text{m}$, indicating that higher concentration of lanthanum 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 $\sim 1.5\text{ }\mu\text{m}$ was found in samples with $0.1\text{ mol}\%$ La and sintered for 4h, while samples with $0.3\text{ mol}\%$ La sintered for the same time show average grain size $\sim 1\text{ }\mu\text{m}$. The microstructure consists of polygonal grains, where BT doped with the highest lanthanum concentration possess small grains from $0.2\text{-}0.4\text{ }\mu\text{m}$. Thus, it can be notified that lanthanum concentration has significant influence on BT grain growth. As the concentration of lanthanum in barium titanate increases average grain size decreases.

Fig. 3 show fracture surface microstructure of barium titanate ceramics sintered at 1300°C for various sintering times, 2, 4 and 8 h, respectively. BT doped with $0.3\text{ mol}\%$ La consists of small rounded or polygonal grains with average grain size of about 0.6 , 0.8 and $1.0\text{ }\mu\text{m}$ (Fig. 3) comparing to pure BT sample in which were found grains

of $1.0\text{-}4.0\text{ }\mu\text{m}$. It can be notified that La as dopant has significant influence on inhibition of grain growth in BT ceramics. Density of BT samples doped with lanthanum 87% of theoretical density. Undoped BT sintered samples have density about 90.1% . Therefore, it can be observed that lanthanum have profound effect on the densification and microstructure evolution of BaTiO_3 , and that was also reported by other authors.

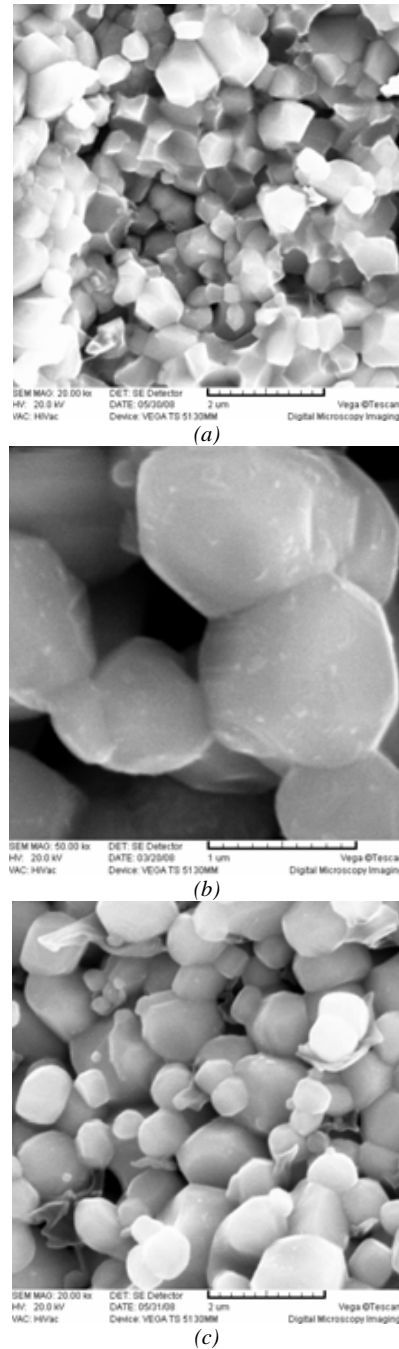


Fig. 3. The microstructure of the BaTiO_3 ceramic doped with $0.3\text{ mol}\%$ La and sintered at 1300°C for various sintering times: a) 2, b) 4 and c) 8 h.

4. Conclusions

Pure and doped barium titanate with 0.3 mol% La was prepared from organometallic complex. The XRD results of BT ceramics obtained by sintering at 1300 °C show the formation of well crystallized tetragonal phase. The intensity of the Raman bands of La- doped barium titanate is higher than that of undoped one. The microstructure consists of polygonal grains, where BT doped with La possesses small grains around 0.6-1.0 μm and undoped sample consists of larger grains of about 1.0-4.0 μm. It can be notified that lanthanum has great influence on grain growth and densification of BaTiO₃ ceramics.

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