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Convectional hydrothermal synthesis of high-purity pesudo-cubic $BaTi_{0.09}Nb_{0.01}O_3$ nanocrystals in rotary autoclave

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ABSTRACT

Nano-sized $BaTiO_3$ powders with particular Nb concentrations were prepared by Rotary- Hydrothermal (RH) method. Hydrothermal method was used at 180 °C for 5 hours with new Ti pressure and the teflon vessel was rotated at a speed of 160 rpm during the hydrothermal reaction. New hydrothermal method was used instead of previous solid state reaction for the system $BaTiO_3 \pm Nb_2O_3$ in high temperature to achieve nano sized particles in lower time and temperature. Synthesis with Rotary-hydrothermal has the advantages of faster crystallization, decreased crystal size, more homogenous distribution of dopants at lower temperature and time in comparison with the solid state method.

In case of the phase evolution studies the X-ray diffraction patterns (XRD) measurements and Raman spectroscopy were performed. The Transmission Electron Microscope (TEM) and the Field Emission Scanning Electron Microscopy (FE-SEM) images were taken for the detailed analysis of the grain size, surface and morphology. Synthesis of Nb doped $BaTiO_3$ with the Rotary- hydrothermal provided advantages of fast crystallization and decreased crystal size.

Keywords: *Ceramics; Chemical synthesis; Convectional -hydrothermal; Pesudo-Cubic; Perovskites.*

INTRODUCTION

Perovskite-type oxides have general formula as ABO_3 in which A is a rare earth or alkaline earth metal and B is a transition metal and these oxides are typically p-type semiconductors. Their composition can be varied in a wide range by partial substitution of lower valent cation in A or B site yielding additional mobile anion vacancies. Perovskite-type oxides are applied in electrochemistry[1-2], oxygen separation membranes[3], chemical sensors for the detection of humidity[4], alcohol sensors [5], gases sensors such as oxygen sensor [6], hydrocarbon sensor [7] and nitric oxide sensor [8] from three decades ago until present.

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Owing to the strong dependence of ferroelectric properties on grain size and compositional aspects, microstructural control has become very important [9].

The understanding of the structural and physical features of the powders in terms of synthesis parameters as well as their size is essential from the practical and theoretical point of views. The use of an advanced rotary step in this work remarkably enhances the grain size distribution, particle reactivity and further sinterability of the ceramic powder. On this matter, the high mechanical energy activates chemical reactions at low temperatures [10].

In this work, we investigated the effect of the incorporating on the properties of $BaTiO_3$ doped with Nb with a new hydrothermal method instead of previous solid state reaction for the system $BaTiO_3$±Nb_2O_3 in high temperature.

EXPERIMENTAL

The RH reactions were performed using a laboratory-made rotary-heating-autoclave system with a PTFE inner vessel with controlled temperature up to the maximum of 220 °C and an auxiliary cooling/heating device is fitted to the system that enables it to operate at a fixed temperature for a long time.

Reagents of $C_{16}H_{36}O_4Ti$, $Ba(OH)_2$*$8H_2O$, $NbCl_5$ and NaOH were used as raw materials. The molar ratio of Ti/Nb was kept at 0.09/0.01. Starting materials of $Ba(OH)_2$*$8H_2O$, $NbCl_5$ and $C_{16}H_{36}O_4Ti$ were mixed in distilled water respectively containing 1M NaOH at 70° C to control the pH under stirring until it turned into a homogeneous solution. The solution was transferred into a sealed PTFE autoclave followed by distilled water until the total volume reached to 100 ml, 80% of the capacity of the autoclave.

The system was heat treated at 180 ˚C for 5 h. The Teflon vessel was rotated at a speed of 160 rpm during the hydrothermal reaction. The resulting powders were centrifuged and washed with distilled water and finally oven dried at 85 °C for 24 h. The obtained powders were characterized by X-ray diffraction patterns (XRD) (X' Pert PRO MPD) with Cu-Kα radiation in the 2θ range from 20 to 60˚ and Raman spectroscopy (BRUKER/ Spectral Range 80-3500 cm^{-1}) Microstructural characterization was performed by the Field Emission Scanning Electron Microscopy (FE-SEM/MIRAII TESCAN) and Transmission Electron Microscopy (TEM, PHILIPS-EM-208).

RESULTS AND DISCUSSION

Figure 1 shows typical X-ray diffraction patterns for the nanoparticles obtained at 180 °C for 5 h. The nanoparticles were pure perovskite Nb-$BaTiO_3$, without some intermediate carbonate phase that usually was observed in the 2θ equals to 24°, 34° and 42° in solid state method (The XRD result compared with known standard JCPDS 01-075-2116) [11]. The presence of $BaCO_3$ can be ascribed either to incomplete reaction or due to the presence of carbonate in Ba alkali source or for the reaction of Co_2 in air. The Nb-$BaTiO_3$ sample crystallized at RH method is carbonate free indicating that Rotary hydrothermal technique was successfully used to produce a pure crystalline nanoparticle [12].

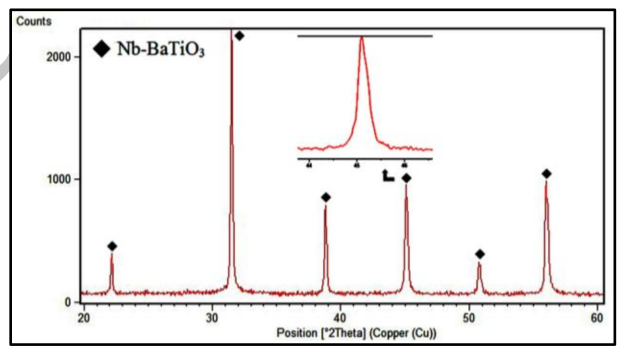

Fig. 1. X-ray diffraction pattern of Nb-$BaTiO_3$ nanoparticles synthesized at 180 °C for 5 h.

All samples could be ascribed as a cubic structure of Nb-$BaTiO_3$, no characteristic separation of the peak at 45° 2θ, which correspond with the tetragonal structure, has been found. An eventual tetragonal peak splitting of the reflections cannot be resolved due to overlapping on the (0 0 2) and (2 0 0) planes. [13, 14].

On the other hand, based on Raman studies particles were tetragonal rather than cubic for the occurrence of asymmetry of TiO_6 octahedral. The Raman spectra, for Nb-

$BaTiO_3$ceramic powders samples obtained are presented in Figure 2. The peak at 518 cm^{-1} is assigned to the TO mode of A1 symmetry, and the sharp peak at 305 cm^{-1} is attributed to the B1 mode, which is the characteristics of tetragonal $BaTiO_3$. The weak peak at 715 cm^{-1} is assigned to the highest-frequency longitudinal optical mode (LO) with A1 symmetry [15-17]. This is contrary to the XRD analysis, because XRD- peaks of the nano particles are wider than the larger one, thus the cubic structure cannot be totally excluded and often makes tetragonal peak splitting difficult to determine. An eventual tetragonal peak splitting of the reflections cannot be resolved due to overlapping of the (0 0 2) and (2 0 0) planes [18].

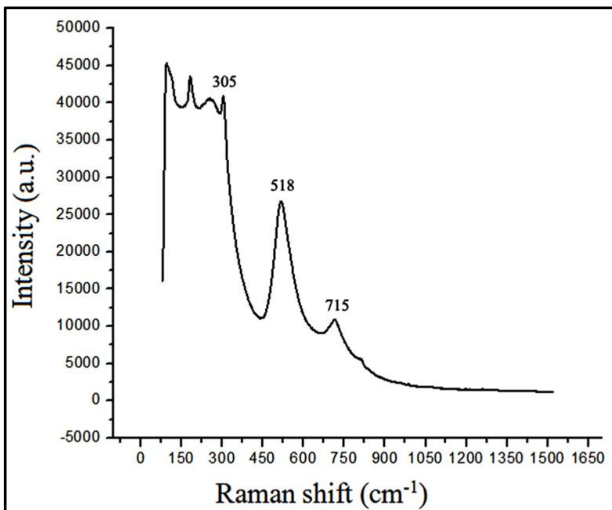

Fig. 2. Raman spectra of the hydrothermal nano-sized Nb-$BaTiO_3$ powders.

The Field Emission Scanning Electron Microscopy (FE-SEM) of the Nb-$BaTiO_3$ powders prepared are shown in Figure 3. The FE-SEM micrographs revealed a spherical morphology for the synthesized powders. Size of the particles are between 50-120 nm and the average size of powder was about 80 nm for samples prepared at 180 °C for 5 h with more uniform spherical shaped crystals. In general, with solid state method the microstructure was not uniform and consisted from region with big particles with size more then 5-6 μm and with region with fine structure with size less than 1-2 μm [19-23].

The Transmission Electron Microscope (TEM) images were taken in order to estimate the size of the grains, also the morphology of the grains of the sample are shown in Figure 4 too. Most particles are spherical shaped crystals with an average size of 80 nm and this result is in good agreement with the XRD and FE-SEM. The decreased crystal size in RH method might be related to the increased nucleation rate and the high mechanical energy which activates chemical reactions at low temperatures.

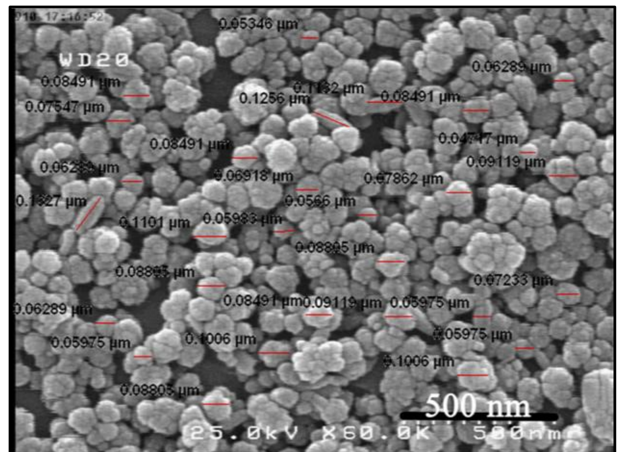

Fig. 3. Nb-$BaTiO_3$ powders prepared at 180 °C for 5 h.

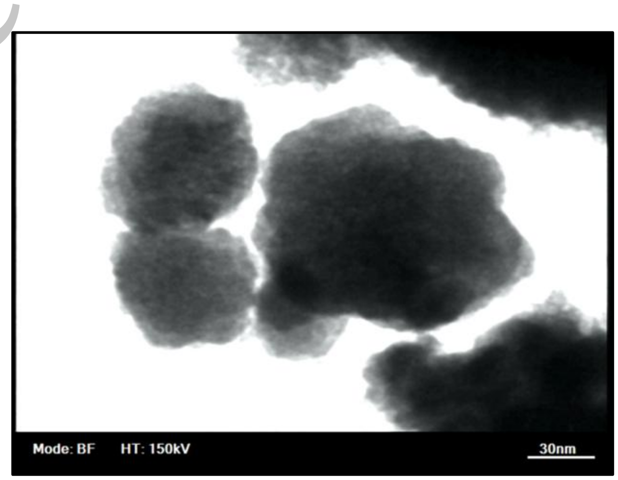

Fig. 4. TEM image of the Nb-$BaTiO_3$ powders.

One should notices that in solid state method a concentration gradient shell that contains most of the dopants surrounding a core are almost chemically pure ferroelectric $BaTiO_3$. Such a material is not in thermodynamic equilibrium and is obtained only under certain sintering conditions. Higher temperature or long sintering may promote a more homogenous distribution of dopants to collapse of the core–shell structure [24-26]. But in this particular case, from TEM image it can be considered that samples are more homogenous with less or without any core-shell structure.

CONCLUSIONS

The present investigation shows that nano particle-sized Nb-$BaTiO_3$ powders can be crystallized with rapid and cost-effective Rotary-assisted hydrothermal process. Synthesis with Rotary-hydrothermal has the advantages of faster crystallization, decreased crystal size, more homogenous distribution of dopants at lower temperature and time in comparison with the solid state method.

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