Functional Materials

MS.3.P065
Influence of the morphology and phase purity of barium titanate nanostructures on phase transition behaviour

A. Gajović[1], M. Plodinec[1], M. Dutour Sikirić[2], J. Šipušić[3], M. Čeh[4]

[1]Rudjer Boskovic Institute, Materials physics, Zagreb, Croatia
[2]Rudjer Boskovic Institute, Physical Chemistry, Zagreb, Croatia
[3]University of Zagreb, Faculty of Chemical Engineering and Technology, Zagreb, Croatia
[4]Institute Jozef Stefan, Nanostructured materials, Ljubljana, Slovenia

gajovic@irb.hr
Keywords: barium titanate nanostructures, TEM, Raman spectroscopy, phase transition

Last years, increasing attention has been dedicated to the synthesis of various $BaTiO_3$ nanostructures, such as nanoparticles, nanorods, nanowires and nanotubes, because dependence of their ferroelectric and piezoelectric properties on their dimension and size [1, 2]. The phase transition from ferroelectric to paraelectric phase in the case of perovskite materials is usually caused by structural phase transition. Typical example is $BaTiO_3$ (BTO) where phase transition from tetragonal to cubic phase induces the transition from ferroelectric to paraelectric state. Expected phase transition temperature is between 110 and 150 °C and depends on the different factors such as doping [3], grain and particle sizes and shapes [4], phase purity [5] etc. In this work the phase purity and morphology of the barium nanostructures were studied by transmission electron microscopy (TEM) techniques as the main method and the influence to the phase transition behavior was monitored by thermo-Raman spectroscopy.

For the synthesis of barium titanate nanostructures we apply hydrothermal method using different starting materials. For the synthesis different aqueous solutions of barium salts and titanium dioxide nanoparticles were hydrothermally treated with NaOH at different temperatures for different reaction times.

Obtained nanostructures were studied in details by high resolution TEM in combination with selected area diffraction (SAED) and energy dispersive X-ray spectroscopy (EDS) measurements. while X-ray powder diffraction (XRD) and Raman spectroscopy (RS) were used for determination of crystal structure and purity of the prepared BTO samples. Scanning electron microscopy (SEM) was used for the preliminary observation of morphology and the agglomeration of the nanostructures, while the size distribution of nanostructures was measured with dynamic light scattering (DLS). The results of DLS measurements were compared with size obtained from TEM images. With the aim to study ferroelectric phase transition in BTO, temperature dependent micro-RS measurements were done *in situ* at different temperature using Linkam heating stage.

Tetragonal phase of BFO, having *4mm* simetry with *c*/*a* axis ratio close to one, is hard or impossible to distinguish from cubic phase by using only XRD technique, so the phase purity and the crystal structure of the samples were determined by the combination of XRD and RS. It was observed that the purity and the structure of the samples depend on the starting salts and synthesis procedure. SEM and TEM measurements indicate that synthesized BTO have morphology of well crystalline nanoparticles and nanocubes of different sizes (Fig. 1), while in some cases nanowires (Fig. 2) were also present in the sample. EDS measurements showed that nanocubes were indeed BTO, while nanowires contained only titanium, oxygen and small amount od sodium indicated possible hydrogen titanete structure. RS was used for study of temperature dependent phase transitions to paralelectric (cubic), structure in BTO having different morphology and phase purity. The shift of phase transition to higher temperature then expected for BTO was observed in synthesized samples. The influence of the BTO nanostructures' morphology, sizes and the phase purity to the temperature of phase transitions will be discussed.

1. T. Yan, X. L. Liu, N.R. Wang and J. F. Chen, J. Cryst. Growth 281 (205) , p. 669.
2. Y. Y. Chen, B.Y. Yu , J. H. Wang, R. E. Cochran, J. J. Shyue, Inorg. Chem. 48 (2009), p. 681.
3. P. S. Dobal, A. Dixit, R. S. Katiyar, D. Garcia, R. Guo, A. S. Bhalla, J. Raman Spectrosc 32 (2001), p. 147.
4. Y. Shiratori, C. Pithan, J. Dornseiffer, R. Waser, J. Raman Spectrosc, 38 (2007), p. 1288 and 1300.
5. A. Gajović, J. Vukajlović Pleština, K. Zagar, M. Plodinec, S. Šturm, M. Čeh, J. Raman Spectrosc (2012), in press, doi: 10.1002/jrs.4206.

6. This work was supported by Croatian Ministry of Science Education and Sport project: 'Physics and applications of nanostructures and bulk matter', 098-0982904-2898, The research leading to part of these results has received funding from the European Union Seventh Framework Programme [FP7/2007-2013] under grant agreement n°312483 (ESTEEM2).

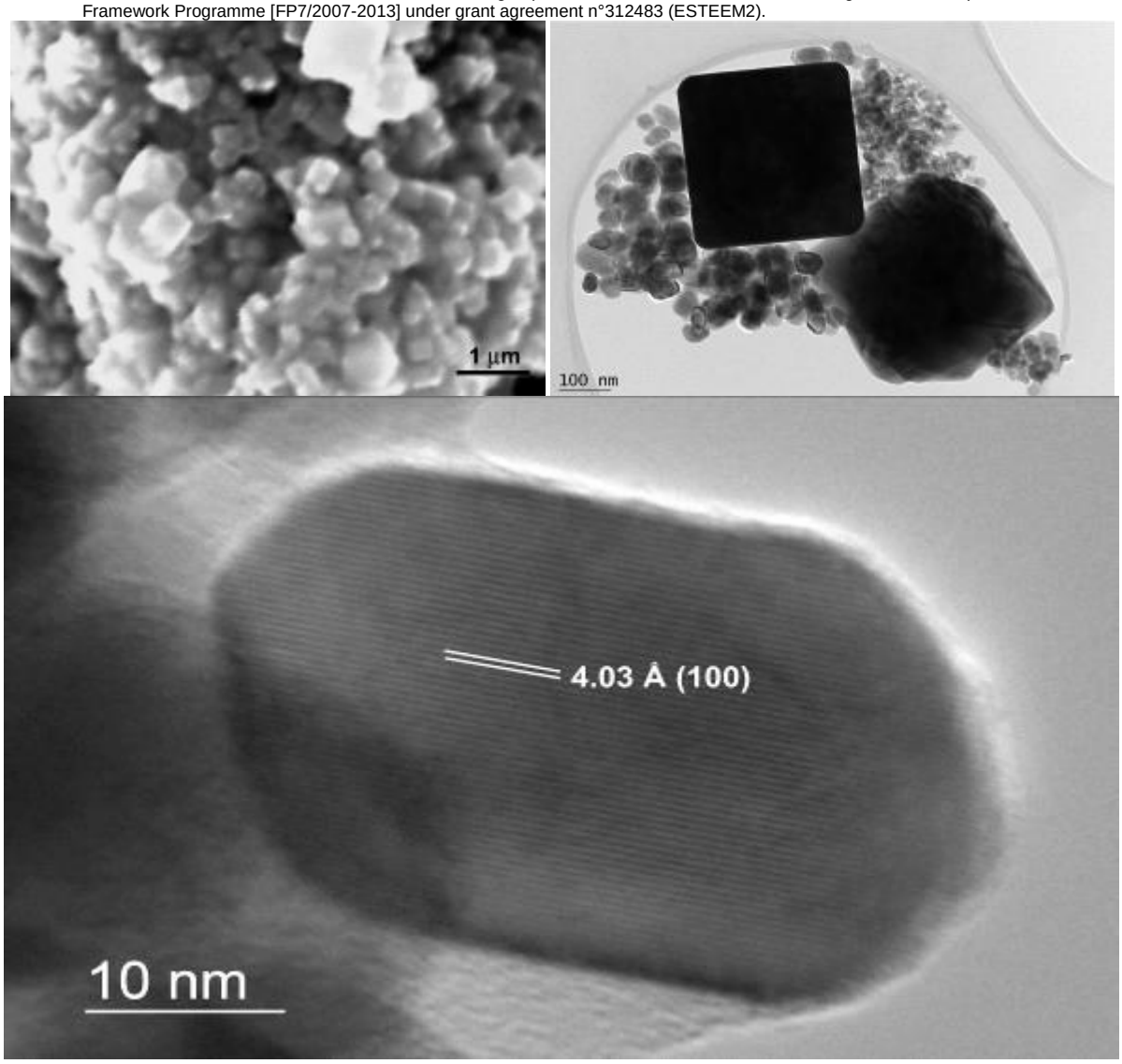

Figure 1. BTO having morphology of nanoparticles and nanocubes; a) SEM image, b) TEM image, c) HRTEM indicated BTO structure of nanoparticles.

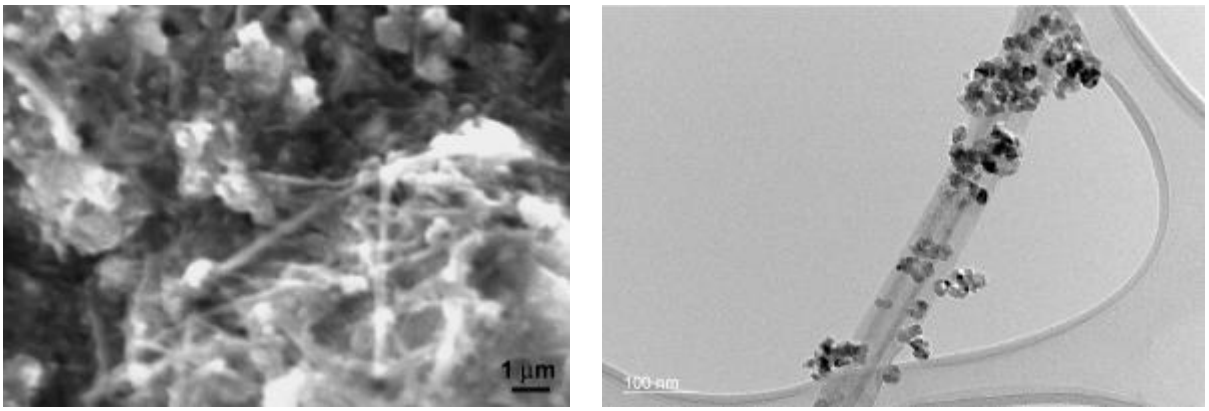

Figure 2. Sample containing nanowires - **a)** SEM image, **b)** TEM image