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Synthesis and investigation of barium titanate nanoparticles covered with silica shell

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Abstract Matrix isolation of ferroelectric $BaTiO_3$ nanoparticles was executed by formation of protective silica shell (via hydrolysis and polycondensation of tetraethyl orthosilicate) on particles of precursor—barium titanyl oxalate. Synthesized $BaTiO_3$–SiO_2 composites have been characterized by IR spectroscopy, XRD, TEM, DTA/DTG methods.

Keywords Barium titanate · Barium titanyl oxalate · Silica

Introduction

Barium titanate is one of the most widespread electroceramic materials for application in multilayer capacitors, infrared detectors, thermistors, transducers, electro-optics devices, sensors of gasses, carriers of catalysts. Microstructure and correspondingly dielectric properties of barium titanate depends on stoichiometry in particular of Ba/Ti ratio. Plenty of different techniques of synthesis of barium titanate in particular sol–gel synthesis [1], oxalate [2], citrate [3], hydrothermal [4] and others were elaborated.

Varieties of theoretical and experimental studies performed with small particles have shown significant changes in their physical properties that occur as their size decrease. One of the approaches of synthesis of small nanoparticles is based on their incorporation in walls of porous matrices. Among them, study of confinement effect of those particles in result of incorporation in nanosized dielectric cell is very important. However, properties of nanosized-ferroelectrics extremely depend on boundary conditions [5]. Temperature of ferroelectric phase transformation in the system of electrically connected particles could be very different from the one for isolated small particles [6].

It is possible to expect that formation of nanoparticles of $BaTiO_3$ as a typical segnetoelectric could lead to phase transformation, paraelectric–ferroelectric. However, experimental confirmations of the confinement effect have not been obtained yet. First data in this direction result their authors in the different conclusions. In particular, impregnation of ordered mesoporous matrices of MCM-41 type with soluble precursors of $BaTiO_3$ results in formation of the composites which did not show any transformation form paraelectric to ferroelectric phase [7].

At the same time an increase of the optical absorption energy (from 3.0 to 3.3 eV), electrons binding energies $Ti2p_{3/2}$ (457.5–458.7 eV in dependence on precursor concentration), and $Ba3d_{5/2}$ electrons binding energies in comparison with the bulk one (456.9 eV and 777.1 eV, respectively) was observed for mesocrystals of barium titanate prepared at the same route by soaking of MCM type silica with soluble precursors of $BaTiO_3$ [8].

The differences in different authors data concerning studies of mesocrystals of barium titanate shown above could be caused by difficulties of inflow of solutions of

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corresponding precursors in mesopores of MCM-41 silica with average pore diameter about 3 nm. Some factors could influence on it, in particular, effects of wetting, the order of introduction of soluble precursors of barium and titanium, conditions of carrying out of synthesis etc.

In this paper, we demonstrate possibility of formation of nanoparticles of $BaTiO_3$ covered with silica shell using sol–gel transformations. Matrix isolation of nanostructures of ferroelectrics can be achieved by formation of protective coating around in advance synthesized nanoparticles of $BaTiO_3$ or directly by synthesis of barium titanate in moment of formation of silica shell due to hydrolysis and polycondensation of tetraalkoxysilane. Thermogravimetric analysis [9–11] in combination with X-ray diffraction and electron microscopy data can be applied for characterization of $BaTiO_3$/silica composites.

Experimental

Barium titanate/silica composites were prepared by sol–gel process in the system tetraethyl orthosilicate (TEOS)–ammonia–ethanol due to processes of hydrolysis and polycondensation accompanied by ultrasonic treatment. Dispersed particles of barium titanyl oxalate (or barium titanate) were introduced into alcohol–ammonia medium and TEOS was added to formed suspensions. As long as rate of hydrolysis and polycondensation of products of hydrolysis of alkoxysilane in alkaline medium are quite high it was expected that dispersed particles of barium titanyl oxalate (or barium titanate) will be covered with silica shell. Obtained suspensions were stirred at room temperature for 2 h and dried at 423 K.

Barium titanyl oxalate (BTO)/silica composites were calcined at 953 K in the air for 2 h with the aim of BTO thermodecomposition and barium titanate formation. Synthesized $BaTiO_3$–SiO_2 samples were characterized using several physicochemical methods. Thermogravimetric analyses were carried out by a Q-1500 derivatograph (Hungary) in the temperature range of 298–973 K at 278 K/min heating rate. IR-spectra of samples of reagents and reaction products were recorded using FTIR spectrometer (Thermo Nicolet Nexus FT-IR, USA). X-ray powder diffraction analysis was carried out with DRON-4-07 X-ray diffractometer (Burevestnik, Russia) using a Ni-filtered CuK_α radiation. Synthesized samples were analyzed using transmission electron microscope JEM-1230 (JEOL, Japan).

Results and discussion

Samples of parent BTO and covered with silica shell (before calcination) were studied by thermogravimetric method. Three main stages of BTO decomposition [12] were detected: dehydration, decompostion of oxalate to carbonate and decomposition of carbonate to barium titanate (Fig. 1).

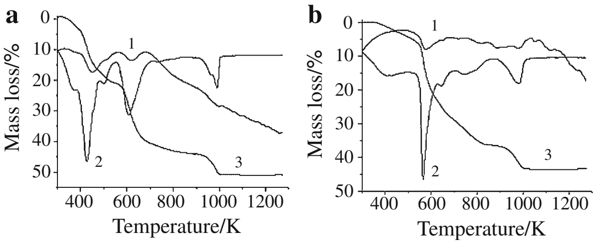

Fig. 1 DTA (*1*), DTG (*2*), and TG-curves (*3*) of barium titanyl oxalate (**a**) and barium titanyl oxalate-silica composite (**b**)

Sample with an excess of water shows the endometric peak below 373 K. Dehydration of tetrahydrate occurred between 393 and 473 K with a maximum near 423 K and loss of weight was 16.64%.

Thermal decomposition of oxalate is a multistage process. First, endothermic peak (evolution of CO) in a temperature range 293–523 K with loss of weight 3.51% is observed. It appeared as a shoulder on the DTA and TG curves and best of all it could be seen at TG curve. Second peak of decomposition of oxalate (evolution of CO and CO_2) is observed at 523–723 K and accompanied by loss of weight 22.55%. This stage of decomposition of oxalate includes complex of reactions: decomposition of oxalate, oxidation and/or disproportionation of carbon oxide and oxidation of carbon as a result of disproportionation of carbon oxide. Following loss of weight between 460 and 600 K is occurred without evident thermal effects.

Intermediate carbonate $Ba_2Ti_2O_5CO_3$ is decomposed between 733 and 1023 K with carbon dioxide evolution and barium titanate formation. Thermal decomposition of carbonate is accompanied by loss of weight up to 7% and appearance of asymmetric peak.

Barium titanyl oxalate covered with silica shell and dried at 423 K (before calcination) was also studied by thermogravimetric method. Endothermic peak of low intensity (DTG curve Fig. 1b) in the temperature range from 373 to 473 K and loss of weight up to 3.29% is observed. Its low intensity could be explained as a result of thermal treatment during process of synthesis.

Endothermic peak with maximum near 563 K and loss of weight up to 18.42% in the temperature range of 523–623 K could be referred to evolution of water adsorbed on the silica surface, carbon oxide and dioxide. Second peak of barium titanyl oxalate decomposition could be observed at 623–723 K and accompanied by loss of weight up to 2.94%. Third peak is appeared at 723–873 K and corresponds to 4.99% loss of weight.

Thermal decomposition of intermediate $Ba_2Ti_2O_5CO_3$ at 873 and 1023 K with carbon dioxide evolution is accompanied by appearing of asymmetric peak and loss of weight up to 6.94%.

Infrared spectra correspond to crystalline structure of BTO and demonstrate lack of isolated Ti=O bonds. Titanyl-containing compounds show Ti=O stretching vibration frequency in the range 1050–950 cm^{-1}. This band is not observes in IR spectrum. A BTO infrared spectrum is shown at Fig. 2, curve 1. BTO vibration bands are observed at 1705 cm^{-1}, ν_{as}(C=O); 1424 cm^{-1}, ν_s(C–O, C–C); 1279 cm^{-1}, ν_s(C–O) + δ(O–C=O); 910 cm^{-1}, ν_s(C–O) + δ(O–C=O); and 824 cm^{-1}, δ(O–C=O) + ν(Ba-O). In IR spectrum of BTO–SiO_2 vibration bands of BTO dried at 150 °C but non-calcined are saved and at 1078 cm^{-1} ν(Si–O) absorption band is appeared [13].

IR spectra of $BaTiO_3/SiO_2$ composite synthesized by sol–gel method from TEOS and $BaTiO_3$ with volumetric ratios of final product $BaTiO_3/SiO_2$ (1:1) and (1:0.5) are shown at Fig. 3. Stretching vibrations ν(Si–O) of frame of silica matrix are appeared in IR spectra of $BaTiO_3/SiO_2$ composite.

All synthesized $BaTiO_3/SiO_2$ samples have shown the presence of bands which correspond to $BaTiO_3$ crystallites formation with the average size near 45 nm in accordance with XRD data. The diffractogram (Fig. 3) contains the (100), (110), (111), (200), (210), (211), and (220) reflections of $BaTiO_3$ typical for formation of tetragonal crystal system. TEM image of $BaTiO_3$ particles is shown at Fig. 3.

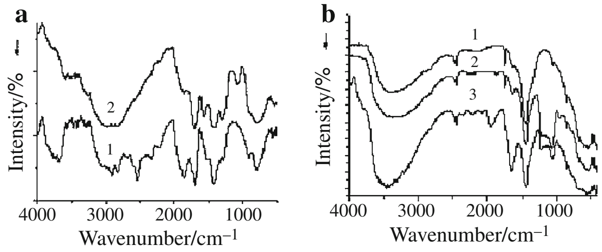

Fig. 2 IR-spectra: **a** (*1*) BTO, (*2*) BTO–SiO_2; **b** (*1*) $BaTiO_3$, (*2*) $BaTiO_3/SiO_2$ (1:1), (*3*) $BaTiO_3/SiO_2$ (1:0.5)

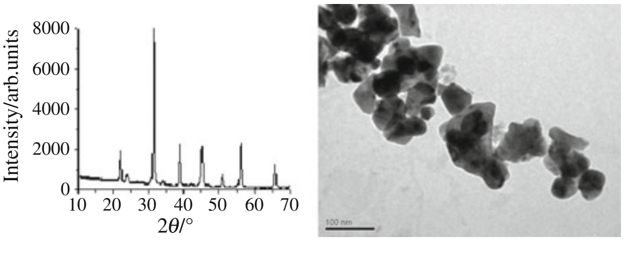

Fig. 3 Large-angle X-ray diffraction patterns and TEM micrograph of initial $BaTiO_3$

Thermal decomposition of BTO results in formation of irregular crystals of $BaTiO_3$ with different shapes. Barium titanate reflections of tetragonal crystals in $BaTiO_3/SiO_2$ composites obtained by sol–gel approach in XRD spectra are saved. $BaTiO_3$ crystals covered with silica shell, spherical shape, with volumetric ratio of final product (1:1) are shown in Fig. 4.

Reflections of parent $BaTiO_3$ are decreased and $BaTiO_3/SiO_2$ (1:1) remained the same after treatment with 10 mL of 1 M HCl solution. It could provide evidence about protective role of the silica shell (Fig. 5).

Decrease of concentration of silica precursor TEOS in 2 times results in formation of $BaTiO_3/SiO_2$ composite with nanoparticles of needle-like shape (Fig. 6). Synthesized composite also shows intensive reflections $BaTiO_3$ crystallites with mean size about 18 nm.

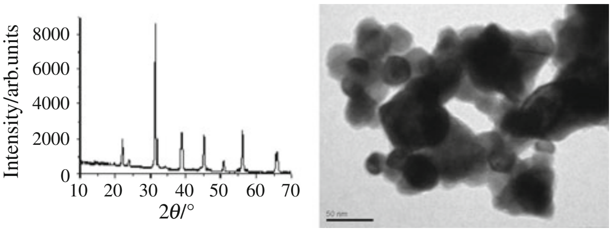

Fig. 4 Large-angle X-ray diffraction patterns and TEM micrograph of $BaTiO_3$–SiO_2 (1:1)

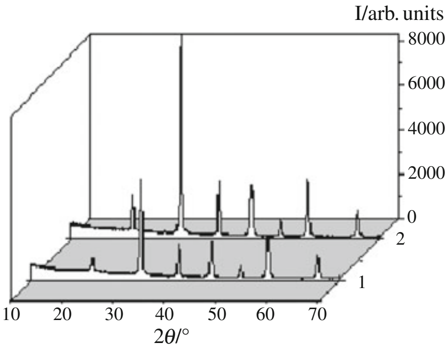

Fig. 5 Large-angle X-ray diffraction patterns of (*1*) parent $BaTiO_3$ and (*2*) $BaTiO_3$–SiO_2 after treatment with 1 M HCl solution

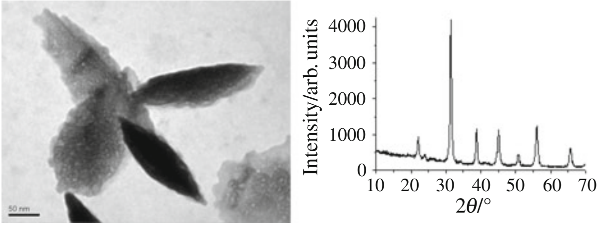

Fig. 6 TEM and large-angle X-ray diffraction patterns of $BaTiO_3$–SiO_2 (1:0.5)

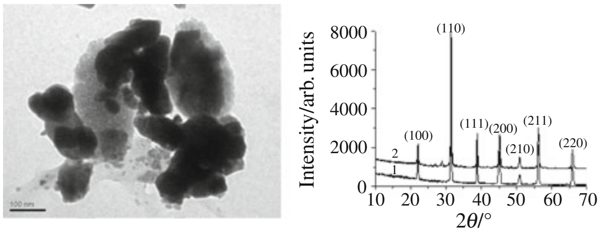

Fig. 7 Large-angle X-ray diffraction patterns and TEM of $BaTiO_3$–SiO_2 synthesized by sol-gel method from TEOS and BTO

Barium titanate crystals and their aggregates in silica array are shown at the image of composition $BaTiO_3/SiO_2$ synthesized by sol–gel method with BTO and TEOS at 423 K and calcined at 953 K. Appearance of new reflections in X-ray spectra of $BaTiO_3/SiO_2$ composite could be referred to formation of crystalline form of silica (Fig. 7).

Thus, techniques of synthesis of $BaTiO_3$–SiO_2 composites from systems of TEOS/$BaTiO_3$ and TEOS/BTO by sol–gel method were elaborated.

Conclusions

Elaborated approaches of sol–gel synthesis of composites barium titanate/silica with use of tetraethoxysilane and previously synthesized $BaTiO_3$ or barium titanyl oxalate in alcohol–ammonia medium allow to obtain nanoparticles of ferroelectric covered with silica shell.

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