

## Preparation and structural stability of ordered nanocomposites: opal matrix – lead titanates

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**Abstract.** The conditions for the formation of nanocomposites based on the basis of lattice packings of SiO<sub>2</sub> nanospheres (opal matrices) with included crystallites of lead titanates (PbTiO<sub>3</sub> and PbTi<sub>3</sub>O<sub>7</sub>) in interspherical nanospacing are considered. For the formation of nanocomposites are used sample opal matrices with dimensions of single-domain regions  $\geq 0,1$  mm.<sup>3</sup> The diameter of SiO<sub>2</sub> nanospheres was  $\sim 260$  nm. Obtained nanocomposites volume  $> 2$  cm<sup>3</sup> in filling  $> 20\%$  of interspherical nanospacing PbTiO<sub>3</sub>, PbTi<sub>3</sub>O<sub>7</sub> crystallites were size of 16–36 nm. Using X-ray diffraction and Raman spectroscopy are studied composition and structural stability when heated nanocomposites to 550°C, which allowed the identification of a local phase transition with change of the space group. The dependence of the composition of synthesized materials on the conditions of their preparation is submitted.

**Keywords:** nanocomposites, opal matrix, lead titanates, X-ray diffractometry, Raman spectroscopy.

### 1. Introduction

Recently there is growing interest to multiferroics - perspective materials for the production of elements of devices for reciprocal conversion of magnetic and electric signals. This property is related to a big magnetoelectric effect observed in series of compounds, for example, in manganese and titanium oxides - the titanates of rare earth elements (REE). In these materials the antiferromagnetic, magnetic and ferroelectric properties coexist at low temperature and they can be used as magnetic carriers and detectors [1-3]. There are reasons to suppose the emergence of construction of devices with tunable phase velocities in the optical, microwave and terahertz range with the use of such materials [4,5].

For massive materials, the frequency restrictions often are associated with the dispersion of dielectric permittivity and magnetic permeability, therefore, it is promising the use of multiferroic materials in the form of ordered 3D nano-lattices of crystals (clusters) of the size 15-50 nm, the use of which will allow to extend the frequency range of their application and to design high operation speed devices controllable by electric and magnetic fields. The ordered 3D nano-lattices of multiferroic crystals can be created with the use of opal matrices, by filling their between spherical cavities with multiferroics [6,7]. The opal matrices are 3-dimensional lattices of close packing of nanospheres of X-ray-amorphous silica (SiO<sub>2</sub>) with the nearly same diameter ( $\Delta d < 5\%$ ), the sizes of which, depending on the production process conditions, may vary within given limits of 200-350 nm. The perspective materials for filling in the between-spherical cavities of the opal matrices are multiferroics such as



REE titanates or metals with the high melting temperature and having segnetoelectric properties. The antiferromagnetic properties are detected for dititanates of REE (frustrated materials –  $\text{Er}_2\text{Ti}_2\text{O}_7$ ,  $\text{Dy}_2\text{Ti}_2\text{O}_7$ ,  $\text{Yb}_2\text{Ti}_2\text{O}_7$  и  $\text{Ho}_2\text{Ti}_2\text{O}_7$ ) [8].

The composition and the structure of the materials in the synthesis in a closed nanosize volume (the process of formation or recrystallization under the conditions of limited geometry of the crystallizer) in the role of which the between spherical cavities of the opal matrices are used, are significantly different from the results of the synthesis of massive samples. The synthesis in a nanosize volume of between-spherical cavities of opal matrices contributes to the stabilization at low temperatures of the high-temperature phase and to the decrease of the formation temperature of the synthesized material [6,9]. Earlier, the construction, the magnetic and dielectric properties of nano-composites on the basis of opal matrices have been obtained and studied, in the between-spherical cavities of which the crystals of REE titanates —oxo-titanates with general formula  $R_2\text{TiO}_5$  and de-titanates  $R_2\text{Ti}_2\text{O}_7$  ( $\text{Er}_2\text{TiO}_5$ ,  $\text{Dy}_2\text{Ti}_2\text{O}_7$ ,  $\text{Gd}_2\text{Ti}_2\text{O}_7$ ,  $\text{La}_2\text{TiO}_5$ ,  $\text{Pr}_2\text{Ti}_2\text{O}_7$ ,  $\text{Tb}_2\text{Ti}_2\text{O}_7$  и  $\text{Yb}_2\text{Ti}_2\text{O}_7$ ) were synthesized [9].

In the present paper, we investigate the influence of the formation conditions on the composition and the structural stability of the nano-composites on the base of the opal matrices in the between-spherical cavities of which the crystals of lead titanates ( $\text{PbTiO}_3$  и  $\text{PbTi}_3\text{O}_7$ ) are obtained.

## 2. Obtaining and the structure of the opal matrices and nano-composites on their basis

The opal matrices were obtained by the hydrolysis reaction of tetra-ether of orthosilicic acid ( $\text{Si}(\text{OC}_2\text{H}_5)_4$ ) with the solution of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) in the presence of ammonium hydroxide ( $\text{NH}_4\text{OH}$ ). The samples of 3D ordered packings of  $\text{SiO}_2$  nano-spheres were manufactured with the diameters of  $\sim 260$  nm, with the volume of  $2\text{--}3$   $\text{cm}^3$  and with the size of mono-domain areas  $>0,1$   $\text{mm}^3$  and  $\Delta d \approx 5\%$ . In Fig. 1a, we demonstrate two layers (1,2) of the densest cubic lattice of  $\text{SiO}_2$  nano-sphere packing (3). Each nano-sphere A with the densest planar layer is surrounded by 6 triangular gaps of different orientations (B and C). The upper layer of the nano-spheres is relatively oriented with respect to the lower one in the positions B or C. Under the conditions, used in the paper, a three-layer (cubic) structure .../ABC/... has been formed. The densest packing of the nano-spheres forms tetrahedron and octahedron between-spherical cavities, the volume of which equals 25,95% of the opal matrix volume [10]. By connecting the centers of the six and four nano-spheres, forming the cavities, we obtain octahedrons (Ok) and tetrahedrons of different orientations (T1 and T2), respectively (Fig. 1,a). The octahedrons and tetrahedrons entirely fill the space (Fig 1,b).

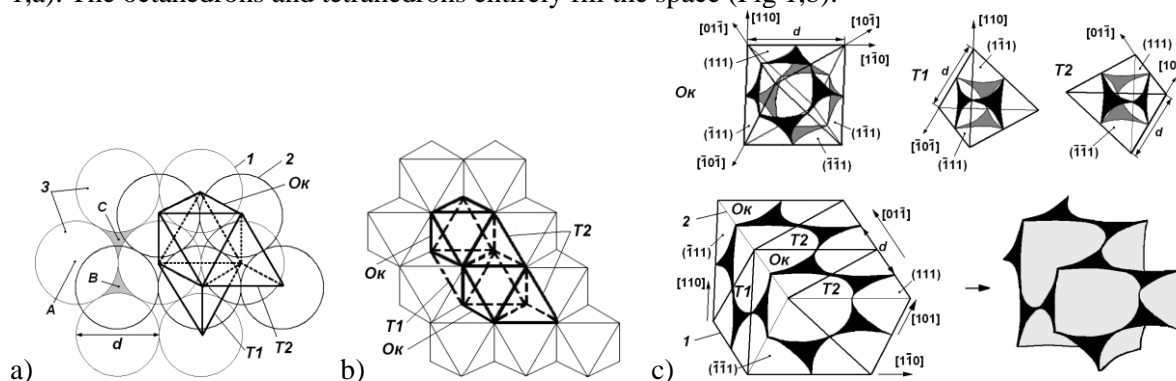


Fig. 1. a) The structure of two densely packed layers of  $\text{SiO}_2$  nano-spheres of diameter  $d$  (projection on the plane  $\{111\}$ ); the centers of  $\text{SiO}_2$  nano-spheres, forming face-centered cubic lattice, form octahedron and tetrahedron cavities. b) The presentation of the opal matrix structure in the form of octahedrons (Ok) and tetrahedrons (T1 and T2) filling the space. c) Octahedrons (Ok) and tetrahedrons (T1 and T2) formed by  $\text{SiO}_2$  nano-spheres and the volume model of the material, filling the between-spherical cavities highlighted in b of two octahedrons and three tetrahedrons.

In Fig 1, c , on the faces of tetrahedrons and octahedrons, the X-cuts of the between-spherical cavities in the region of the contacts of tetrahedrons and octahedrons are shown. The between-spherical tetrahedron and octahedron cavities can be filled with different materials. In Fig. 1,c, we show the volume model of the material, filling five between-spherical cavities, existing in two-layer packing (two octahedron (Ok) and three tetrahedron (one-T1 and two T2)).

The nano-composites on the base of the opal matrices, the between-spherical cavities of which are filled by the crystallites  $\text{PbTiO}_3$ ,  $\text{PbTi}_3\text{O}_7$ , were obtained by the impregnation method including the filling the cavities with the solution of salts of different chemical compound of lead or terbium followed by the thermal treatment, during which the required material is formed. The successful application of the impregnation method is conditioned by the rather wide channels of between-spherical cavities of the opal matrices, which have maximal size  $\sim 0,37d$  on the joint of tetrahedrons and octahedrons (shown in Fig. 1, c).

For obtaining lead titanates, in the between-spherical cavities of the opal matrices, we have introduced by impregnating the lead nitrate, dissolved in the 15% solution of trichloride of titan ( $\text{TiCl}_3$ ) in a weak concentration solution of hydrochloric acid (HCl). The impregnation was conducted up to 8 times with the following low-temperature thermal treatment in the range of temperatures 300–500°C along with a gradual filling the between-spherical cavities of the opal matrices. The concentration of the dissolved lead nitrate was calculated according to the ratio of the components of the synthesized material. The different phase composition and the phase structure of the synthesized material depends on the composition of the impregnation solutions and on the conditions of the thermal treatment of the nano-composites. The synthesized materials filled >20% of the volume of between-spherical cavities of the opal matrices.

### 3. The Phase Composition of Nano-Composites

#### X-ray diffraction

For the identification of crystal phases synthesized in the between-spherical cavities of the opal matrices, the diffractometer *ARL X'tra* (Cu  $k\alpha$  radiation,  $\lambda=0,154178$  nm, an energy dispersion solid detector with Pelette cooler, step size  $0,01^\circ$ , continuous mode  $1^\circ/\text{min}$ ) was used. The X-ray-grams were analyzed by using the automated database *ICDD PDF-2*.

The X-ray diffractograms of the opal matrix samples, the between-spherical cavities of which are filled by lead titanates, are presented in Fig.2. The X-ray-grams are characterized by different sets and relations of the intensities of reflections

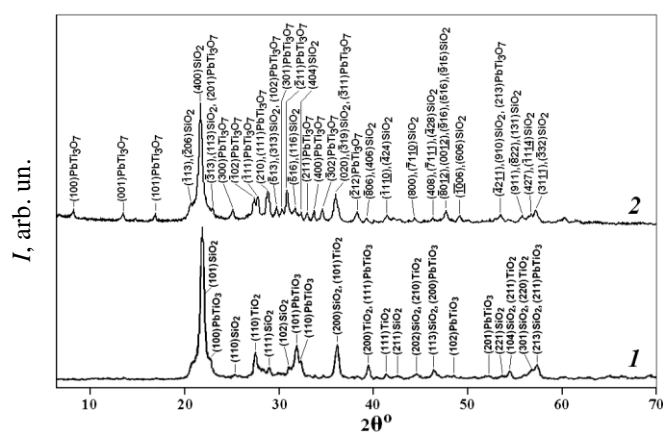


Fig. 2. The X-ray diffractograms of the opal matrix samples, the between-spherical cavities of which are partially filled with  $\text{PbTiO}_3$  (1) and  $\text{PbTi}_3\text{O}_7$  (2) crystals.

and relations of the intensities of reflections (I). The X-ray-phase analysis allowed to confirm the presence of the following crystal phases:  $\text{PbTiO}_3$  (tetragonal crystal system, space group  $P4mm$ ) (Fig. 2, curve 1);  $\text{PbTi}_3\text{O}_7$  (monoclinic crystal system,  $P2_1$ ) (Fig. 2, curve 2). At temperatures higher than 800°C when titan containing salts were inserted, as a rule, polycrystal particles of different titan oxides were formed:  $\text{TiO}_2$  (rutile, tetragonal crystal system  $P4_2/mnm$ );  $\text{Ti}_{0.72}\text{O}_2$  (synthetic anatase, tetragonal crystal system,  $I4_1/amd$ ).

The high temperature thermal treatment in the synthesis of lead titanates is accompanied by the formation of  $\text{SiO}_2$  crystal phases (re-crystallization of X-ray-amorphous silica) (Fig 2):  $\text{SiO}_2$  (cristobalite, tetragonal crystal system,  $P4_12_12$ );  $\text{SiO}_2$  (tridymite, crystal system,  $P6_3/mmc$ );  $\text{SiO}_2$  (monoclinic crystal system,  $I2/a$ ). At temperatures  $\leq 700^\circ\text{C}$ ,  $\text{SiO}_2$

The high temperature thermal treatment in the synthesis of lead titanates is accompanied by the formation of  $\text{SiO}_2$  crystal phases (re-crystallization of X-ray-

crystal phases are not formed. At temperatures  $\geq 1000^\circ\text{C}$  the interaction takes place between the silicon forming materials synthesized in the between-spherical cavities, containing Pb, and silica, during which  $\text{SiO}_2$  nano-spheres are deformed. Under the conditions, used used in this paper, the synthesized titanates of Pb don't interact with  $\text{SiO}_2$ . The crystal size (the areas of coherent scattering of X-rays,  $L_{\text{OKP}}$ ) of the crystal phases  $\text{PbTiO}_3$ ,  $\text{PbTi}_3\text{O}_7$  is determined by the widening of the diffraction maxima on the X-ray diffractograms by the Selyakov-Scherrer formula. The synthesized lead titanates had  $L_{\text{OKP}}$  in the range of 16-36 nm. The synthesized materials present equiaxed crystals. It was established that  $L_{\text{OKP}}$  for  $\text{PbTiO}_3$ ,  $\text{PbTi}_3\text{O}_7$  doesn't depend on the degree of crystallinity.

### ***Spectroscopy of Raman scattering of light***

Besides crystal phases, the studied samples contain X-ray-amorphous phases. The analysis of different materials, including X-ray-amorphous ones, is possible with Raman scattering (RS) spectroscopy of light. The RS spectra were registered by using the RS micro-Raman spectrometer LabRAM HR800 (HORIBA Jobin-Yvon) (line 632,8 nm of a He-Ne laser; the laser power  $< 300$  mWt; diameter of the beam spot  $\sim 4$   $\mu\text{m}^2$ ; the depth of the analyzed layer  $\sim 3$   $\mu\text{m}$ ), equipped with a console THMS600/720 (Linkam Scientific Instruments) for sample heating. The RS spectra for the nanocomposites, containing  $\text{PbTiO}_3$  and  $\text{PbTi}_3\text{O}_7$ , are presented in Fig.3,4. The position (RS shift  $\Delta\nu$ ) and the intensity ( $I$ ) of the stripes on the RS spectra depend on the conditions of their obtaining.

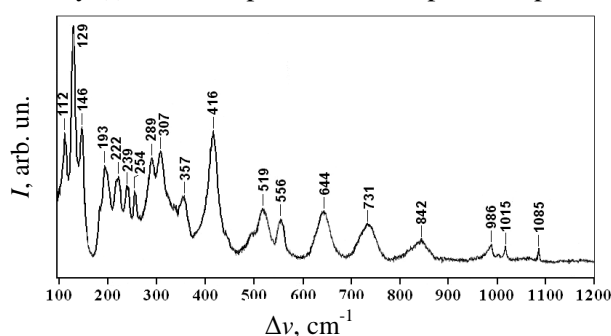


Fig. 3. RS spectra of the opal matrix sample, the between-spherical cavities of which are partially filled with  $\text{PbTi}_3\text{O}_7$  crystals.

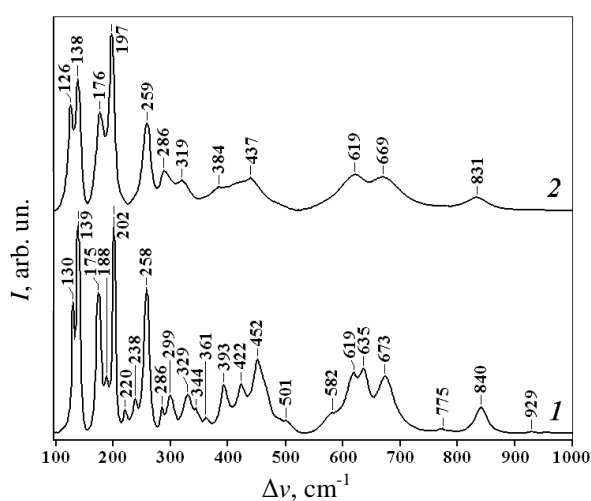


Fig. 4. RS spectra of the opal matrix sample, the between-spherical cavities of which are partially filled with  $\text{PbTiO}_3$  crystallites, the initial (1) and heated to the temperature  $550^\circ\text{C}$  (2).

For the nanocomposites containing  $\text{PbTiO}_3$  we have obtained the RS spectra during the sample heating process (Fig. 4). At room temperatures,  $\text{PbTiO}_3$  has tetragonal crystal system of perovskite type ( $P4mm$ ). When heated to the Curie temperature, equal to  $493^\circ\text{C}$ , a segnetoelectric phase transition takes place from the tetragonal crystal system to the cubic ( $Pm3m$ ) one. The influence of the temperature and other factors leads to the change of phase composition (including the X-ray amorphous phases) of the titanates. The presence and the ratio of the stripe intensities on the RS spectra depend on the conditions of heat treatment. The exposure at high temperatures does not change the features of the RS spectra.

On the RS spectra of the nano-composites containing  $\text{PbTiO}_3$ ,  $\text{PbTi}_3\text{O}_7$  and  $\text{TbMn}_2\text{O}_5$  the stripes of different modes of  $\text{SiO}_2$  are seen. In the presented RS spectra of the nano-composites containing  $\text{PbTiO}_3$  and  $\text{PbTi}_3\text{O}_7$  (Fig. 3,4) the stripes are seen for  $\Delta\nu$  equal to 220–222, 286–289, 299 and  $775$   $\text{cm}^{-1}$ . The derivation of the spatial groups of crystal symmetry is based on the requirement of the translation invariance of its lattice, and also on the finiteness of discrete (point) subgroups of the orthogonal group. The information obtained by the RS spectroscopy, as a rule, in the case of crystals, expresses the peculiarities of the mentioned subgroups (crystal class). Taking into account that such subgroups are

not the crystal movement groups, the RS studies enable to obtain the data on the local phase transformation.

#### 4. Conclusion

In the present we have investigated the influence of the formation process on the composition of the nanocomposites on the basis of opal matrices in the between-spherical cavities of which the crystal titanates of lead ( $\text{PbTiO}_3$ ,  $\text{PbTi}_3\text{O}_7$ ) are synthesized. In obtaining the nanocomposites, the samples of opal matrices (3D lattice packings of nano-spheres of X-ray amorphous silica ( $\text{SiO}_2$ ) with the diameter of  $\sim 260$  nm) having the volume  $>2$  cm<sup>3</sup> and the mono domain area size  $>0,1$  mm<sup>3</sup> were used. The nanocomposites on the basis of the opal matrices, the between-spherical cavities of which are filled with  $\text{PbTiO}_3$ ,  $\text{PbTi}_3\text{O}_7$ , were obtained by the method of impregnation, including the filling up the cavities with the solutions of different chemical compounds with the following thermal treatment. In the synthesis of the lead titanates, the solution of Pb nitrate in the 15% solution of  $\text{TiCl}_3$  in HCl was introduced in the between-spherical cavities. For the crystallization of materials with a given composition, a high-temperature treatment was carried out at temperatures 700–1000°C. The synthesized materials filled  $>20\%$  of the volume of the between-spherical cavities of the opal matrices. The different phase composition and the structure of phases of the synthesized materials depend on the composition of the impregnating solutions and on the conditions of thermal treatment of the nanocomposites.

We have studied the peculiarities of crystallization and phase transitions (when heated to 550°C) of the compounds ( $\text{PbTiO}_3$ ), synthesized in the between-spherical cavities of the opal matrices. The composition of nanocomposites is studied by the methods of X-ray diffraction and RS spectroscopy. It is confirmed that the materials synthesized in the between-spherical cavities are made of crystal (in the form of crystallites) and X-ray-amorphous phases of titanates with the presence of oxides of metals.  $\text{PbTiO}_3$  and  $\text{PbTi}_3\text{O}_7$  synthesized in the between-spherical cavities had the size of crystallites in the range 16-36 nm. The obtained data are results of the synthesis under the limitations with external walls of the between-spherical cavities of crystallite sizes (the process of the formation and re-crystallization under the conditions of limited geometry of a crystallizer).

The understanding of the peculiarities of phase transitions in the between-spherical cavities of opal matrices, in obtaining given materials, will allow to create metamaterials with controllable improved properties of the functional properties and operation characteristics, which is very promising for the future applications of devices. It is assumed that the approach connected with the use of such nanocomposites will be most efficient in the development of different solid state microwave devices: filters, delay lines, phase shifters and other controlling elements.

#### Acknowledgement

The work is partially supported by RFFS (Grant 12-07-00529A) and by the Competitiveness Enhancement Program of Tomsk Polytechnic University.

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