Школа для молодых ученых «Применение золь-гель метода для синтеза функциональных материалов»

A. Lukoviak[1], W. Strek[1], O. Ignatenko[2], D. Karpinsky[2], V. Gaishun[3], D. Kovalenko[3], A. Semchenko[3]

TRANSFERR: THE WAY TO THE SUPERFERROIC MATERIALS

[1]Institute of Low Temperature and Structures Research PAN, Okolna st. 2, Wroclaw, Poland
[2]Scientific-Practical Materials Research Centre of NAS of Belarus, P. Brovki str, 19, 220072, Minsk, Belarus
[3]F. Skorina Gomel State University, Sovetskaya 104, Gomel, 246019, Belarus

At present Francisk Skaryna Gomel State University together with colleagues from other organizations participates in the international project of HORIZON 2020 Maria Sklodowska-Curie Rise. The main goal of the project is development of complex oxides systems with superior functional properties by creating the novel class of materials by introducing structurally metastable states. Controllability of the functional parameters will be achieved using different chemical substituting schemes favoring the superior properties via modification of chemical bond character, variation of the structural parameters and controlling the defectiveness/stoichiometry of the compounds.

A need of efficient materials having outstanding functional properties with controllable characteristics and those which meet demanding ecological restrictions motives researchers to look at complex transition metal oxides with perovskite-like structure [1-3]. It is well known that manganites and ferrites possess several unique properties such as magnetization/magnetotransport and magnetoelectric coupling being enhanced near the structural phase boundaries.

Clarification of the exact structure and magnetic properties of nanoscale clusters is a tough technological and scientific challenge as the size of the nanoscale regions is smaller than the typical spot size for conventional X-ray diffractometers. Therefore, the diffraction patterns of different phases are overlapped making a determination of crystal structure to be extremely complicated. Moreover, local structural defects can significantly modify diffraction patterns and hamper structural analysis.

To overcome the declared difficulties the participants of the Project combine the macroscopic (X-ray, synchrotron and neutron diffraction) and local-scale (scanning probe and transmission electron microscopy, EXAFS/XANES) measurements. Investigations of magnetization, magneto-electric coupling, dielectric and magnetotransport properties are also very important. Analysis of the crystal structure and physical properties under the external stimuli will extent the information about the phase stability and industrial perspectives of the samples. It is very important to bind data about the crystal structure and physicochemical properties of complex oxides with metastable state.

Particularly the three-phase coexistence region has been observed for the Pr-doped bismuth ferrite ceramics upon temperature increase by the participants from Ukraine and Belarus [4-6] using diffraction methods as well as HR-TEM microscopy (Figures 1, 2). The structural data analysis has confirmed the transformation of the anti-polar orthorhombic phase with temperature increase into the non-polar orthorhombic one (space group *Pnma*) via the phase coexistence state. This transformation is accompanied by a decrease of the unit cell volume of about 1%. It should be noted that this transition is in accordance with the group–subgroup relation between the appropriate space groups *Pbam* and *Pnma*. Recently the participants from SPMRC have specified the temperature-driven structural transition in the RE (rare-earth)-doped compounds into the non-polar orthorhombic phase. The structural data obtained for the compounds with single phase rhombohedral structure stable at room testify a revival of the anti-polar orthorhombic phase with increasing temperature prior to the formation of the non-polar orthorhombic phase (Figure 2).

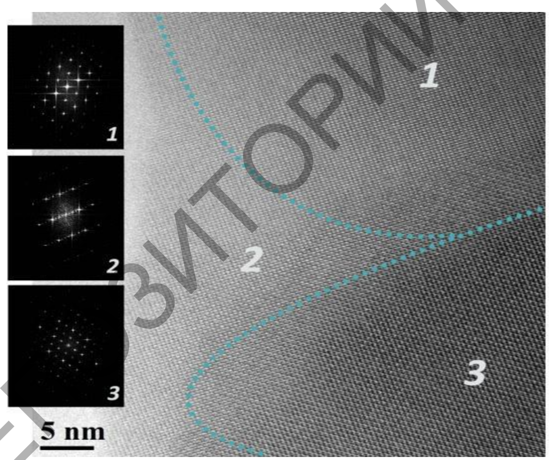

Figure 1 – HRTEM image of the Bi0.875Pr0.125FeO3 at the phase boundary. The regions with different structural symmetry are marked by dot lines. Insets show FFT images of different structural phases

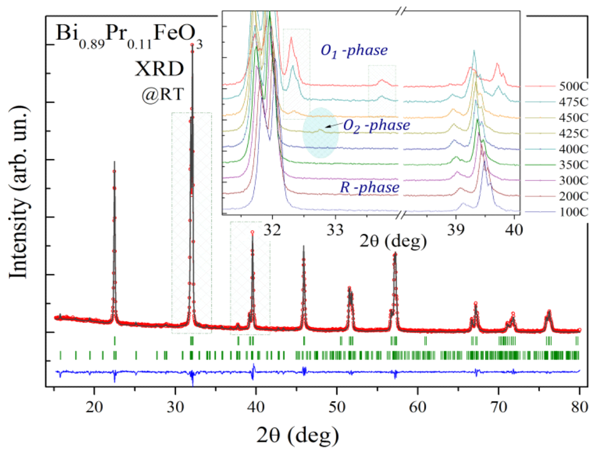

Figure 2 – The XRD pattern of the Bi0.89Pr0.11FeO3 compound obtained at room temperature. The inset shows an evolution of the structural peaks, tiny peak attributed to the anti-polar phase is highlighted

This fact highlights intriguing phase evolution and related physical properties attributed to the compounds near the phase boundary regions. The participants consider a specific role of the anti-polar phase acting as a mediator between the polar rhombohedral and the non-polar orthorhombic phases across the temperature- and composition driven phase transition.

Taking these features into account one can suggest that the ionic size effect is not the only factor influencing the structural transitions. Preliminary investigations of the oxides doped with different rare-earth ions have revealed an ambiguous background underlying the observed phase transitions (chemical bond character, defects, structural peculiarities etc.).

The triple point appearance is a general feature of the Pr-doped compounds and the issues concerning their structural stability near the triple point are of particular interest. It should be noted that the triple-point-type morphotropic phase boundary was recently observed in ferroelectric solid solutions based on $BiFeO_3$ - $PbTiO_3$ and $Ba(Ti_{0.8}Hf_{0.2})O_3$-$(Ba_{0.7}Ca_{0.3})TiO_3$ systems. The detailed study of the structural parameters (unit cell parameters, bond lengths and angles) of the lead-free compounds with compositions near the phase boundary has fundamental significance and practical perspectives and will be implemented during the project realization.

Francisk Skaryna Gomel State University one of the largest scientific research and studying centre in Belarus which has righteously received the recognition of national and international scientific society. High qualified specialists working in the field of technology of processing of materials, optimisation of technological processes, theoretical investigations of materials properties. Francisk Skaryna Gomel State University has accumulated extensive experience in the synthesis of ferroelectric structures by sol-gel method, and the achieved parameters are comparable with the parameters of samples obtained by vacuum methods. The original version of the sol-gel method is patented in the Eurasian Economic Union. The developed techniques can be used to synthesize other systems, such as ferromagnets.

The laboratories of the FSGSU are equipped with unique modern high technology equipment that will be used for powders and thin films preparation and their physical characterization. The staff of the university works in close cooperation with various leading research and educational institutions and has the experience of participation in the mobility and training programs as well as in introduction of the developed products to the internetional market.

The efficient knowledge transfer is a crucial issue for a multidisciplinary consortium (Figure 3) which has been formed in the frames of TRANSFERR project. Within the consortium the teams own the complementary knowledge which can be exchanged in a synergistic way mutually enriching the expertise and consequently the competitive advantages of all the involved partners. Each partner of the consortium will actively contribute to the planned objectives along with knowledge exchange. The contribution of partners to the knowledge, the available experimental facilities, and expertise transfer are specified in other sections. The contributions of different partners will be based on their strongest expertise thus forming complementary competences.

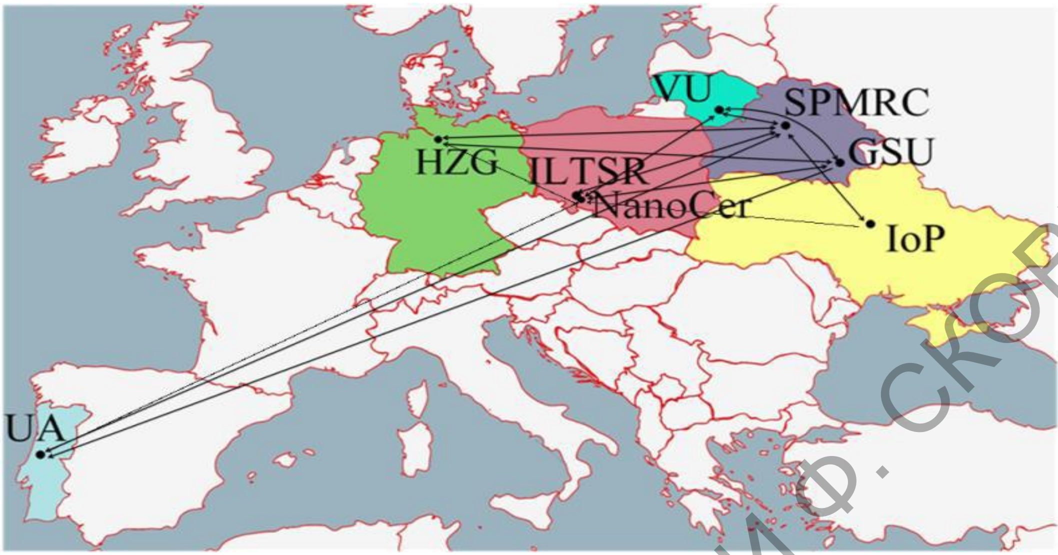

Figure 3 – Scheme of the researchers exchange between the participants

Bibliography

1. D. A. Rusakov, A. M. Abakumov, K. Yamaura, A. A. Belik, G. Van Tendeloo, E. Takayama-Muromachi, Structural Evolution of the BiFeO3−LaFeO3 System, Chem. Mater., 23 (2010) 285.

2. S. Karimi, I. Reaney, Y. Han, J. Pokorny, I. Sterianou, Crystal chemistry and domain structure of rare-earth doped BiFeO3 ceramics, J Mater Sci, 44 (2009) 5102-5112.

3. C. Zhou, W. Liu, D. Xue, X. Ren, H. Bao, J. Gao, L. Zhang, Triple-point-type morphotropic phase boundary based large piezoelectric Pb-free material–Ba(Ti0.8Hf0.2)O3-(Ba0.7Ca0.3)TiO3, Appl. Phys. Lett., 100 (2012) 222910–222915.

4. D.V. Karpinsky, I.O. Troyanchuk, V. Sikolenko, V. Efimov, E. Efimova, M. Willinger, A.N. Salak, A.L. Kholkin, Phase coexistence in Bi1-x Pr x FeO3 ceramics, J Mater Sci, 49 (2014) 6937-6943.

5. D. V. Karpinsky, I. O. Troyanchuk, M. Tovar, V. Sikolenko, V. Efimov, E. Efimova, V.Ya. Shur, A.L. Kholkin, Temperature and Composition-Induced Structural Transitions in Bi1-xLa(Pr)xFeO3 Ceramics, J. Am. Ceram. Soc., 97 (2014) 2631-2638.

6. D.V. Karpinsky, I.O. Troyanchuk, M. Tovar, V. Sikolenko, V. Efimov, A.L. Kholkin, Evolution of crystal structure and ferroic properties of La-doped BiFeO3 ceramics near the rhombohedral-orthorhombic phase boundary, J. Alloys Compd., 555 (2013) 101-107.