Local polarization reversal in polycrystalline BiFeO₃-based solid solutions

<u>A.S. Abramov</u>¹, D.O. Alikin^{1,2}, A.P. Turygin¹, S. Latushko³, A. Zheludkevich³, D. Zheludkevich³, A. Pakalniškis ⁴, R. Skaudžius ⁴, V.Ya. Shur¹, D. Karpinsky^{3,5}, A.L. Kholkin^{1,2}

¹School of Natural Sciences and Mathematics, Ural Federal University, 620000 Ekaterinburg, Russia alexander.abramov@urfu.ru

²Department of Physics & CICECO – Aveiro Institute of Materials, University of Aveiro, Portugal ³Scientific-Practical Materials Research Centre of NAS of Belarus, Minsk, Belarus ⁴Institute of Chemistry, Vilnius University, Vilnius, Lithuania

Institute of Chemistry, Vitnus Oniversity, Vitnus, Elinuar

⁵Nanoceramics Spolka Akcyjna, Wroclaw, Poland

Searching of lead-free materials with the electromechanical characteristics comparable to lead zirconate titanate is an actual topic during recent decades due to the increasing demands of ecology in production and recycling. One of the important materials is bismuth ferrite (BiFeO₃, BFO) possessing large polarization and thereby promising for electromechanical performance [1]. The main problem of BFO is poor phase stability due to existence of secondary phases after synthesis and high leakage current [2]. Different methods are used to improve phase stability and realize morphotropic phase boundary (MPB) conditions, such as doping by rare earth elements leading to formation of coexistence of rhombohedral and orthorhombic phases [3]. The solid solution of BFO with stable perovskites, such as barium titanate (BaTiO₃) allows to achieve phase stabilization.

Here, we implemented this doping strategy and investigated relationship between structural state and local piezoelectric properties. Series of the samples were prepared by conventional solid-state sintering and by sol-gel sintering from liquid phase. Macroscopic X-ray diffraction (XRD) revealed gradual lattice transformation from the rhombohedral symmetry (Bi-rich side) to the pseudocubic and tetragonal symmetry. It was shown that despite trend to develop pseudocubic lattice symmetry BFO-BTO demonstrates large piezoelectric response, which can be attributed to coexistence of nanoscale polar and non-polar phases. We suggested that XRD shows the average symmetry of solid solutions correspondent to the non-polar lattice ordering. Whereas, the local study with high spatial resolution by piezoresponse force microscopy allowed revealing the nanoscale polar phase regions. The change of the domain structure geometry from domain maze to lamellar domains with increasing of BTO content was revealed. Local phase transformation was shown to be part of polarization reversal process. Thus, PFM-based studies of phase composition, domain and phase field-induced dynamics are crucial for comprehensive characterization of BFO-based solid solutions.

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