Ferroelectric Properties of Lead-Free Perovskite Ceramics in Ternary Systems

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During last ten years perovskite structure oxides were intensively studied in order to develop new lead-free piezoelectric materials which could replace widely used PZT-based materials [1 - 3]. We studied ceramic solid solutions in the systems $(Na_{0.5}Bi_{0.5})TiO_3$ – $(K_{0.5}Na_{0.5})NbO_3$ (system I), $BiFeO_3$ - $BaTiO_3$ (system II), and $(Na_{0.5}Bi_{0.5})TiO_3$ - $(K_{0.5}Bi_{0.5})TiO_3$ (system III) with Morphotropic Phase Boundary (MPB) near ~ 7, 25, and 17 mol.% of the second component, correspondingly. As third components, $BiFeO_3$ was added to systems I and III and $Bi(Mg_{0.5}Ti_{0.5})O_3$ to system II. The samples were prepared by the solid-state reaction method at temperatures 700 – 1200oC. The samples were studied using the X-ray Diffraction, DSC/DTA, Scanning Electron Microscopy, Second Harmonic Generation (SHG), and Dielectric Spectroscopy methods. Single phase perovskite structure ceramic solid solutions with varying relative content of tetragonal (orthorhombic) and rhombohedral (pseudocubic) phases were obtained in the systems studied. Monotonous increase in the unit cell volume and decrease in total electroconductivity were observed with increasing $BiFeO_3$ or $Bi(Mg_{0.5}Ti_{0.5})O_3$ content. Ferroelectric phase transitions were revealed at 550 - 610 K (system I) and at 835 – 890 K (system II). Additionally, relaxor-type peaks with strong frequency dependences were observed at lower temperatures. Their origin evidently is related to the presence of oxygen vacancies due to cation deficiency in A-sites and mixed valence of B-type cations. The results obtained proved real prospects for the development of new functional materials for high temperature applications.

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