Processing and characterization of lead-free ferroelectric ceramics on the base of $(Na_{0.5}Bi_{0.5})TiO_3$

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Perovskite structure lead-free oxides on the base of Bismuth-Sodium-Titatane $(Na_{0.5}Bi_{0.5})TiO_3$ (NBT) are being among the most intensively studied [1 – 3] because of ecological problems and demands of the ban of lead. The lead-free NBT-based solid solutions with compositions close to the Morphotropic Phase Boundaries (MPB) are promising for actuator applications. However, preparation of stoichiometric dense ceramics with reproducible characteristics comprises rather difficult task due to the alkaline oxides losses at the stage of sintering, so functional properties of ceramics strongly depend on methods of their preparation.

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), $(Na_{0.5}Bi_{0.5})TiO_3$ - $(K_{0.5}Bi_{0.5})TiO_3$ (system II), and $(Na_{0.5}Bi_{0.5})TiO_3$ - $BaTiO_3$ (system III) close to the Morphotropic Phase Boundary (MPB) near ~ 7, 20 and 7 mol.% of the second component, correspondingly. To regulate properties, the third components were added: $BiFeO_3$ to the systems I and II and $Bi(Mg_{0.5}Ti_{0.5})O_3$ to the system III in amounts up to 10 (I), 20 (III) and 50 (II) mol. %.

Ceramic samples were prepared by the two-step solid-state reaction method at temperatures 700 – 1200°C. To improve sintering, to control stoichiometry by preventing losses of alkaline volatile cations, additives with low melting temperatures, such as Bi_2O_3, KCl, LiF and V_2O_5 were used in amounts up to 15 w. % [4, 5].

The samples were characterized by the X-ray Diffraction, DSC/DTA, Scanning Electron Microscopy (SEM), Second Harmonic Generation (SHG), and Dielectric Spectroscopy methods. Phase formation, crystal structure parameters, microstructure, phase transitions, dielectric and ferroelectric properties were studied.

The formation of perovskite solid solutions with different contents of tetragonal (orthorhombic) and rhombohedral (pseudocubic) phases was observed in compositions I – III. Monotonous increase in the unit cell parameters, while slight decrease in total electroconductivity was observed with increasing $BiFeO_3$ or $Bi(Mg_{0.5}Ti_{0.5})O_3$ content in the systems I - III. Ferro- and antiferroelectric phase transitions were observed near 400 K and at 510 - 560 K (system I); at 550 - 700 K (system II); near 400 K and at 550 – 600 K (system III). The ferroelectric phase transitions near 400 K revealed a relaxor-type behavior, with the origin of the relaxation related to the presence of oxygen vacancies resulting from both the mixed valence of the B-type cations and cation deficiency in A-sites of perovskite structure.

Increase in the spontaneous polarization value was proved for modified ceramics I using the SHG method. The results obtained confirmed prospects of new functional materials development for high temperature applications using the NBT-based ternary compositions.

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References

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