Influence of Additives on Ferroelectric Properties of NBT-based Ceramics

E.D. Politova[1,*], N.V. Golubko[1], D.A. Belkova[2], A.V. Mosunov[1], N.V. Sadovskaya[1], G.M. Kaleva[1], S. Yu. Stefanovich[1,2]

[1]L.Ya.Karpov Institute of Physical Chemistry
Vorontsovo pole, 10, Moscow, Russia, 105064
[2]Lomonosov Moscow State University
Leninskie gory, 1, Moscow, Russia, 119992
*Ekaterina Politova: politova@cc.nifhi.ac.ru

Increasing concern on the environment safety stimulated intensive studies of lead-free piezoelectric materials in order to develop new materials which could replace widely used Pb-based ones. Perovskite structure oxides on the base of bismuth-sodium titanate $(Na_{0.5}Bi_{0.5})TiO_3$ (NBT) are being considered among the most promising ones.

In this work, influence of additives with low melting temperatures (Bi_2O_3, KCl, LiF and V_2O_5) on structure and ferroelectric properties of ceramics with compositions close to the Morphotropic Phase Boundaries in the $(Na_{1/2}Bi_{1/2})TiO_3$ - $BaTiO_3$ (NBT-BT) and $(Na_{1/2}Bi_{1/2})TiO_3$ - $BaTiO_3$ - $Bi(Mg_{1/2}Ti_{1/2})O_3$ (NBT-BT-BMT) systems has been studied.

Ceramic samples were prepared by the two-step solid-state reaction method at temperatures 700 – 1200°C. KCl and LiF were added to composition 0.8NBT - 0.2BT in amounts up to 15 mol. %. Bi_2O_3, KCl, LiF and V_2O_5 were added to composition 0.8(0.8NBT - 0.2BT) - 0.2BMT in amounts of 2 w. %.

The samples were characterized using the X-ray Diffraction, Scanning Electron Microscopy, Second Harmonic Generation (SHG), and Dielectric Spectroscopy methods.

In the BNT-BT compositions the unit cell volume increased in compositions doped by KCl, but did not changed in compositions doped by LiF. In the NBT-BT-BMT system increase in the unit cell volume was observed in compositions doped by the Bi_2O_3 additive, while the unit cell volume decreased in compositions doped by the KCl, LiF and V_2O_5 additives.

Phase transitions were marked by steps near 350-400 K and by peaks at 550 K in dielectric permittivity versus temperature curves. Increase in the spontaneous polarization value was proved for modified ceramics using the SHG method.

At the room temperature, increase in the dielectric permittivity ε_{rt} value was observed in modified compositions BNT-BT with KCl and LiF content 5-7.5 and 2.5-5 mol. %, respectively.

Increase in the dielectric permittivity ε_{rt} was revealed for compositions BNT-BT-BMT doped by the LiF and KCl additives. Dielectric loss $\tan\delta_{rt}$ values decreased in the case of KCl, Bi_2O_3 and V_2O_5 additives. The changes in the electric conductivity observed showed that V_2O_5 and Bi_2O_3 additives enhanced the insulating behavior, while LiF and KCl stimulated increase in total conductivity at the room temperature. At the high temperatures of ~1000 K total conductivity decreased in the Bi_2O_3, LiF and KCl doped samples pointing to decrease in number of vacancies in the A-sites and in the oxygen sublattice. On the other hand, strong increase in the conductivity of the V_2O_5-doped samples is related to increasing number of oxygen vacancies.

Ferroelectric phase transitions near 350-400 K revealed typical relaxor-type behavior. At high temperatures effects of dielectric relaxation related to the presence of oxygen vacancies were revealed in compositions containing B-site cations with mixed valence and deficiency in the A-sites of the perovskite lattice.

The results obtained confirmed prospects of new lead-free piezoelectric materials development by modification of the NBT-based compositions close to MPB by aliovalent additives.

Acknowledgment. The work was supported by the Russian Fund for Basic Research (Project 15-03-03269).