PHASE TRANSITIONS AND TRANSPORT PROPERTIES OF IONIC CONDUCTING BIMEVOX SOLID SOLUTIONS AND COMPOSITES

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Oxides on the base of bismuth vanadate $Bi_4V_2O_{11-y}$ that undergoes phase transitions at ~700 K and 840 K are being intensively studied as promising for applications in portable devices that generate oxygen. They reveal rather high ionic conductivity at temperatures <1000 K though poor thermodynamic stability hinders real applications and comprises main task to be solved.

In this work, the phase formation and properties of solid solutions $Bi_4(V_{1-x}Me_x)_2O_{11-z}$, (BIMEVOX), $(Bi_{1-y}La_y)_4(V_{1-x}Me_x)_2O_{11-z}$ (BILAMEVOX) with Me=Zr, Ga, Cu, Fe, $x, y < 0.3$, have been studied. The introduction of La^{3+} and Me^{n+} cations ensures enhancement of thermodynamic stability of the bismuth vanadate based compositions.

Ceramic samples were prepared by the solid state reaction method at 870 - 1100 K. Phase composition, structure and microstructure parameters of the samples were studied using the X-ray diffraction and atomic force microscopy methods, respectively. Dielectric properties and phase transitions were studied by the DTA/DSC, IR-spectroscopy, and dielectric spectroscopy in the temperature range of 300 – 950 K and frequencies 500 Hz – 1 MHz.

The concentration and temperature stability regions of monoclinic α-, orthorhombic β- and tetragonal γ- and γ'- polymorph modifications have been determined, with α- phase existing at x <0.06 in all the systems studied, while the tetragonal γ'- phase stabilizing at x >0.10. The first order α-β and β-γ phase transitions are marked with anomalies in the heat capacity and dielectric properties. Ferroelectric origin of the α-phase compositions have been proved using the laser second harmonic generation and piezoforce microscopy methods. Peculiarity observed in temperature dependences of dielectric permittivity has been explained by the effect of the ferroelectric domain walls "pinning" caused by the presence of oxygen vacancies in the crystal lattice.

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