

STRUCTURE AND PHASE TRANSITIONS OF OXYGEN CONDUCTING BISMUTH VANADATE-BASED SOLID SOLUTIONS

E.D. Politova^{1*}, I.V. Golosovsky², N.V. Golubko¹, G.M. Kaleva¹, A.V. Mosunov¹, E.A. Fortalnova^{1,3}, V.V. Murasheva³, M.G. Safronenko³, N.U. Venkovskii³, V.S. Rusakov⁴

¹⁾ Karpov Institute of Physical Chemistry, Obukha s.-str., 3-1/12, Moscow, 105064, Russia

²⁾ Petersburg Nuclear Physics Institute RAS, Gatchina, Leningrad district, 188300, Russia

³⁾ Peoples' Friendship University of Russia, Ordzhonikidze st., 3, Moscow, 117198, Russia

⁴⁾ Faculty of Physics, Moscow State University, Leninskie gory, Moscow, 119992, Russia

E-mail: politova@cc.nifhi.ac.ru

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Oxides on the base of bismuth vanadate $\text{Bi}_4\text{V}_2\text{O}_{11-y}$ reveal high ionic conductivity at temperatures <1000 K, so they were intensively studied as membrane materials promising for pure oxygen generation [1-15]. In this work, phase transitions in solid solutions $\text{Bi}_4(\text{V}_{1-x}\text{Me}_x)_2\text{O}_{11-z}$, with Me – Ga, Fe, Cu, Zr, $x<0.3$, have been studied using the X-ray and Neutron diffractions (3T-2, $\lambda=1.22$ Å), Mossbauer technique, DTA/DSC, IR-, and dielectric spectroscopy in the temperature range of 300 – 950 K and frequencies 500 Hz – 1 MHz. Ceramic samples were prepared by the solid state reaction method at temperatures 870 - 1100 K.

In all the systems studied the concentration regions of the α - and β - and tetragonal γ -polymorph modifications were observed, with their width depending of the dopant cations. At room temperature, the monoclinic ferroelectric α -phase exists in compositions with $x<0.06$, while tetragonal ordered γ -polymorph modifications stabilizes at $x>0.10$. At room temperature, in all systems the a and c unit cell parameters and the unit cell volume increase, while b parameter decreases with increasing x in the orthorhombic phase domain. In the tetragonal phase domain, the a and b parameters change rather weakly. Non monotonous behavior of the unit cell volume points to possible changes in valence states of the cations Fe, Cu and V. Using neutron diffraction tetragonal symmetry was determined for composition with high Fe content and monoclinic symmetry for the samples with low Fe content. $\text{Bi}_4(\text{V}_{0.75}\text{Fe}_{0.25})_2\text{O}_{11-z}$ (γ -phase): I 4/mmm, $a=3.9199(1)$, $c=15.5566(6)$ Å. $\text{Bi}_{3.95}(\text{V}_{0.96}\text{Fe}_{0.04})_2\text{O}_{11-z}$ (α -phase): C2/m, $a=5.5838(4)$, $b=15.4381(5)$, $c=16.6853(2)$, $\beta=90.19(4)$.

Slow kinetics of the α - β phase structural phase transition has been revealed in Neutron diffraction experiments. Transformation of peaks at 570 K was observed during 22 hours. It has been proved that presence of oxygen ion vacancies in the crystal lattice and their “pinning” on ferroelectric domain walls are responsible for this effect and large thermal hysteresis of the α - β phase transition as well.

The first order α - β , β - γ and γ - γ phase transitions are marked with anomalies in temperature dependences of

heat capacity and dielectric permittivity. The effects observed in dielectric properties, conductivity, and impedance data confirmed the influence of both intrinsic oxygen vacancies and those “pinned” at ferroelectric domain boundaries on the α - β phase transition temperature hysteresis and their contribution to mechanism of oxygen ion transport.

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