X-ray studies of doped bismuth titanates

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Abstract. X-ray diffraction and NEXAS- and XPS-spectroscopy have been investigated thermostable solid solutions Mn, Cu- doped bismuth titanate with a pyrochlore-type structure. It was shown that manganese and copper in said solid solution of bismuth titanate is present mainly in the oxidation state +2, and titanium - in +4.

1. Introduction and experimental

Doped bismuth titanates, depending on the nature of the dopant and the type of crystal structure, are characterized by wide variability of electrical properties and practical applications as dielectrics, mixed and ionic conductors for solid oxide fuel cells, oxygen permeable membranes and gas sensors, catalysts for oxidative processes.

The pyrochlore Bi₂Ti₂O₇ is thermodynamically unstable at high temperature and decompose at t>650°C [1]. In recent years, there has been a significant structural disordering in the metal-containing bismuth titanates (pyrochlore) and the displacive disorder [2-3]. In a recent studies of manganese and copper–bismuth titanate pyrochlore we have synthesized a broad range of solid solutions by solid state reaction method at the temperatures 900–1150 °C [2-3].

A feature of the pyrochlore structure with the general formula unit A₂B₂O₆O' is independent of the coexistence of two lattices: A₂O' и BО₆. A-positions of large cations, for example bismuth, are surrounded by oxygen atoms О’ and both sublattices (cationic and anionic) can be defective. Cations, which are located in the B-positions (Ti) are in octahedral coordination of oxygen atoms (second anionic sublattice), and these cation and anion positions are completely filled by atoms of metals and oxygen. The M-metal atoms doped in the structure of the pyrochlore-type can be distributed on the two cationic sublattices (positions) [4]. In the present work, we consider the results of an investigation of the antistructural disorder in cation sublattices and the defect structure in the oxygen sublattice of manganese and copper-containing bismuth titanates with pyrochlore structure. For the obtained samples was performed x-ray phase analysis. Also were determined the lattice parameters of the pyrochlore and measured pycnometric density. For individual samples performed a full-profile analysis of diffraction patterns obtained at room temperature using the Fullprof package to specify variable parameters, including the filling of atomic positions. To determine the charge state of atoms of doped metals, all samples were investigated by NEXAS and XPS spectroscopy using the BESSY-II synchrotron source (Berlin) [5]. All of the NEXAS spectra were recorded in total electron yield (TEY) mode.

2. Crystal structure
Diffraction patterns of series of solid solutions are presented in Figure 1. We undertook an attempt to describe the structure of the Bi$_{1.6}$Mn$_{0.4}$Ti$_{1.9}$O$_{6.4}$ sample within the limits of reported models for the pyrochlore Bi$_2$Ti$_2$O$_7$. The ideal high symmetry sites occupied by pyrochlore A$_2$B$_2$O$_6$O’ (Fd3m) are the A cation at the 16c site (0, 0, 0), the B cation at the 16d site (1/2, 1/2, 1/2), the O anion at the 48f site (x, 1/8, 1/8) and the O’ anion at the 8a site (1/8, 1/8, 1/8). We fixed the fractional occupation of the atom sites for the studied sample according to the formulas. The formula of the sample can be presented in two ways: manganese occupies both A (Bi) and B (Ti) sites equally with full occupation of the A position—(Bi$_{1.6}$Mn$_{0.4}$)(Mn$_{0.4}$Ti$_{1.6}$)O$_{6.4}$ (1)—and taking into account the partial deficiency in the bismuth sublattice, the sample formula is (Bi$_{1.54}$ Mn$_{0.31}$)O$_{6.16}$ (2) (A - vacancy). The similar results were obtained for the sample Bi$_{1.9}$Cu$_{0.58}$Ti$_2$O$_7$ – δ. It shows distribution of copper atoms over both A- and B-sites: (Bi$_{1.67}$Cu$_{0.25}$)O$_{6.53}$.

Figure 1. Diffraction pattern of solid solutions of Bi$_{1.6}$Mn$_{0.4}$Ti$_{1.9}$O$_{7.5}$ (left) and Bi$_{1.6}$Cu$_{0.58}$Ti$_2$O$_{7.5}$ (right).

3. XPS-spectroscopy

We have also investigated the XPS-spectra of pyrochlore (Fig.2). All the spectra obtained were decomposed into peaks approximated by Gaussian curves, and the background was approximated by the Sherley-approximation. As can be seen from the XPS spectra of titanium all the atoms in the bismuth titanates are in the same charge positions. This follows from the absence of splitting in the corresponding peaks. At the same time, in the XPS spectrum of oxygen in Bi$_{1.6}$Mn$_{0.4}$Ti$_{1.9}$O$_{6.9}$ shows the splitting of the 1s-state of oxygen - strips A and B (Fig.2, left). The strip C is most likely associated with satellite transitions, so in the spectra of various compounds its position varies greatly. The low-energy strip A corresponds to the more electronegative state of oxygen. Apparently, this is due to atoms from the octahedral environment of titanium (sublattice BO$_6$) with less electronegativity. The higher-energy strip B is associated with non-equivalent oxygen atoms from the bismuth environment (sublattice A$_2$O’). The correctness of this assumption is also indicated by the fact that the ratio of the integral intensities of the peaks A and B is 5:5, which is comparable to the ratio of the number of oxygen atoms O/O’, which is 6 in the pyrochlore structure.

4. NEXAFS spectroscopy

The absorption spectra studied are shown in Fig. 3-4. The NEXAFS Mn2p-spectra analysis points to the following: (i) the spectra of the studied bismuth titanate pyrochlores with various amounts of manganese are similar both in the fine structure, in the shape of the absorption lines and in their energy positions, and (ii) the structure is identical to the spectra of MnO (Fig. 3 left). Based on the above information, we believe that the oxidation states of the manganese atoms in these solid solutions are Mn$^{2+}$. A similar analysis of the absorption spectra of titanium in these compounds indicates their similarity (Fig. 3 right) both to each other and to the structure of the spectra TiO$_2$ in which the titanium atom is in an octahedral cluster of oxygen atoms [TiO$_6$]$^{2-}$. It should be noted that there is a broadening of the B-peak associated with the transition of 2p electrons to the e$_g$-orbitals of titanium in the octahedral field of the oxygen environment. In the spectrum of amorphous titanium oxide (α-TiO$_2$) is
also a noticeable widening of the strip and in the spectrum of anatase and rutile observed splitting of this strip. Apparently, this indicates some distortion in the octahedral environment of titanium. At the same time, we believe that the oxidation states of the studied atoms are Ti$^{4+}$. Similar analysis of the absorption spectra of copper and titanium in Cu-doped bismuth titanate (Fig. 4) led us to the conclusion that their degree of oxidation of Cu is +2 and Ti – +4.

Figure 2. XPS-spectra of titanium (left) and oxygen (right) in Bi$_{1.9}$Mn$_{0.2}$Ti$_{1.9}$O$_{6.9}$. The points are the experimental data, the thin black line is the sum of the approximation curves.

Figure 3. NEXAFS Mn2p- (left) and Ti2p- (right) spectra of manganese doped bismuth titanates.
5. Results

The thermostable bismuth Mn, Cu titanate solid solutions with the pyrochlore structure in a wide range of compositions obtained by the ceramic technique.

The crystal structure of prepared samples and the chemical formula normalized to pyrochlore type ones are simulated and obtained.

The ability of the manganese atoms to be distributed over two cationic crystallographic positions increases the stability of the pyrochore crystal structure of the bismuth titanates, reduces displacive disorder in the bismuth sublattice and causes the formation of solid solutions in a fairly wide range of compositions.

Manganese and cupper in solid solutions of bismuth titanate is present mainly in the oxidation state +2, and titanium +4.

Acknowledgments

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