Spectral studies of bismuth-containing pyrochlores

S V Nekipelov1,2, N A Zhuk2, O V Petrova1, D V Sivkov1,3, K A Bakina1, D V Bogachuk1, R A Skandakov1, V N Sivkov1

1Komi Science Center Ural Division of the RAS, Syktyvkar, 167982, Russia
2Pitirim Sorokin Syktyvkar State University, Syktyvkar, 167001, Russia
3Saint-Petersburg State University, St. Petersburg, 119034, Russia

E-mail: NekipelovSV@mail.ru

Abstract. Thermal stable solid solutions of titanates, niobates, and tantalates of bismuth with a pyrochlore structure doped with 3d-metal atoms were studied using XPS and NEXAFS spectroscopy. Based on spectral studies, it was shown that the manganese, cobalt, nickel and copper atoms in these solid solutions have mainly charge state +2 and iron atoms – charge state +3.

1. Introduction

Compounds with a pyrochlore structure are of great interest due to a wide range of practically useful properties (photocatalytic, dielectric, electrooptical and piezoelectric ones) [1-2]. The cubic structure of pyrochlore (general formula A2B2O7) includes large eight-coordinated A cations (Bi) and relatively small octahedral B cations (Ta, Nb, Ti) [2-3]. The structure contains two interpenetrating weakly interacting sublattices A2O’ and B2O6. The B2O6 sublattice consists of [BO6] octahedra connected at the vertex of the angle; the A2O’ sublattice has an antirstobalite structure and is formed by [O’A4] tetrahedra. Triple pyrochlores containing transition metals are of particular interest [4]. The advantage of bismuth-containing ternary pyrochlores is due to the possibility of replacing Bi3+ cations in A-positions with small C cations (Mg, Cu, Ni, Cr). As a result, the same ions can occupy two nonequivalent positions A and B. They are distinguished by a relatively low synthesis temperature and chemical inertness with respect to Ag electrodes. A useful circumstance is the fact that complex bismuth-containing pyrochlores correspond to wide regions of homogeneity due to the structural flexibility of the pyrochlore crystal lattice. Being within the same structural type and changing the qualitative and quantitative compositions, one can significantly vary the properties of pyrochlore, which makes it possible to study the effect of the chemical composition on its physicochemical characteristics. However, when doping with 3d atoms, the question remains, in which position (A or B) these atoms are implanted, what is their oxidation state (charge state), and whether their states change at different degrees of doping. Since it is known that with different doping parameters, the physicochemical properties of the obtained solid solutions change significantly [1–2, 4].

This work shows the results of spectral studies of the electronic state of 3d-metal atoms in titanates Bi2M,Ti2O7, niobates Bi2MgNb2M3O9 and tantalates Bi3MgTa3M3O13 bismuth with a pyrochlore structure (M = Mn, Fe, Ni, Co, Cu).

2. Experiment details

The synthesis of all solid solutions was carried out by the standard ceramic method from oxides of bismuth, titanium, niobium, tantalum and 3d-metals of special purity grade using stage-by-stage
annealing at temperatures up to 1100°C.

Samples were studied by X-ray absorption (NEXAFS, near-edge X-ray absorption fine structure) and X-ray photoelectron spectroscopy (XPS). The NEXAFS data of this ceramic and oxides were obtained using the synchrotron radiation source (Russian-German Laboratory at BESSY II). Each spectrum was registered in the total electron yield (TEY) mode [5]. XPS studies were carried out at the resource center “Physical methods of surface investigation” (Saint Petersburg University Research park). XPS analysis was performed on a Thermo Scientific ESCALAB 250Xi X-ray spectrometer. The X-ray tube with AlKα radiation (1486.6 eV) was used as a source of ionizing radiation. To neutralize the charge of the sample, an electron-ion charge compensation system was used during the experiments. All peaks were calibrated with respect to the C1s peak at 284.6 eV. The experimental data were processed using the ESCALAB 250 Xi spectrometer software.

**Figure 1.** NEXAFS 2p spectra of bismuth titanates doped with 3d metal atoms. For comparison, the spectra of the corresponding metal oxides are shown.

3. **NEXAFS spectroscopy of bismuth titanates and niobates**

Let us consider the results of X-ray absorption studies of synthesized ceramic samples. Figure 1 shows the absorption spectra of the cobalt atom in bismuth titanates, and for comparison, the obtained spectra of Co3O4 and the spectra of CoO taken from the literature [6]. As can be seen, the spectra of cobalt in bismuth titanates coincide in intensity and energy position of the main peaks with the corresponding details of the Co2p3/2 spectrum of CoO and have significant differences from the spectra of Co3O4. Cobalt atoms in CoO are divalent, i.e. have a charge state Co2+, while in Co3O4, which can be considered as a mixed oxide CoO • Co2O3, there are Co2+ and Co3+. It should be noted that the
spectrum of cobalt in CoO can be considered as a superposition of the spectra of cobalt in the charge state of Co^{2+} and Co^{3+}, while a more intense peak in the region of 782 eV is responsible for the contribution of Co^{3+}, and the low-energy band (779–780 eV) – for the contribution of Co^{2+}, which correlates well with the CoO spectra. Based on the above, it can be concluded that cobalt atoms in cobalt-doped bismuth titanates have a +2 charge state. In this case, a change in the concentration of a doped atom with a constant crystal structure of the corresponding bismuth titanate (pyrochlore structure) does not change the charge state of the cobalt atom. Due to the fact that cobalt cations in CoO oxide occupy octahedral positions, it can be concluded that cobalt ions in bismuth titanate doped with Co also have a coordination equal to six, and indicate the tendency of cobalt (II) ions to occupy octahedral positions B, those replace titanium atoms. A similar analysis of the absorption spectra of nickel and copper in doped bismuth titanates and corresponding oxides shows that the charge state of these atoms is +2, and they are embedded in the titanium position.

Figure 1 also shows the studied spectra of chromium in bismuth titanates and in compounds K₂Cr₂O₇ and Cr₂O₃, in which chromium atoms have valences Cr (IV) and Cr (III), respectively. In this case, all the presented chromium spectra have a different characteristic set of absorption bands, however, the superposition of the spectra of K₂Cr₂O₇ and Cr₂O₃, taken in a 1:1 ratio, makes it possible to obtain a 2p spectrum of the chromium atom, which coincides with the corresponding spectra of chromium in bismuth titanate as in the number of the main features of the spectrum and by their energy position and relative intensity. Based on this, it can be assumed that chromium atoms in bismuth titanates have two nonequivalent positions in the crystal structure with charge states Cr^{3+} and Cr^{6+}.

Let us consider the NEXAFS 2p spectra of 3d metal atoms in bismuth niobates with a pyrochlore-like structure (Figure 2). It can be noted that the spectra of cobalt in doped titanates and niobates practically coincide, which allows us to conclude that their charge state is similar, i.e., they have an effective +2 charge. Similar conclusions about the charge state of copper atoms (+2) in doped bismuth niobates with a pyrochlore structure can be drawn based on a comparison of the spectra of copper in the composites under study and the corresponding copper oxides. As for iron atoms, it can be seen that the main details of the spectra of the studied samples coincide both in the number and energy position of the main absorption bands, and are practically identical to the corresponding features in the Fe₂O₃ oxide spectrum of. Based on this, it can be assumed that the iron atom in the synthesized bismuth niobates is trivalent (has a Fe^{3+} charge state). It should be noted that the incorporation of 3d metal atoms in the case of bismuth niobates is possible when both niobium and magnesium atoms are replaced in the pyrochlore structure, which, however, does not change their charge state.

![Figure 2. NEXAFS 2p spectra of bismuth niobates doped with 3d metal atoms. For comparison, the spectra of the corresponding metal oxides are shown.](image-url)
4. XPS of bismuth tantalates

Let us turn to the consideration of bismuth tantalates doped with cobalt. The studies of these pyrochlores were carried out using XPS spectroscopy methods. The corresponding XPS Co2p spectra are shown in Figure 3. When comparing the spectra of the composites with the spectra of oxide CoO [7] and the spectra of Co3O4 obtained by us, it can be seen that the energy position of the main peaks in all the spectra presented is practically the same. In this case, the spectra of composites and CoO contain pronounced satellite peaks, which is a characteristic feature of almost all XPS 2p spectra of 3d atoms in the bivalent state. This suggests that the cobalt atoms in the samples under study have a +2 charge state. And as in the case of bismuth titanates, cobalt atoms occupy octahedral B positions in the pyrochlore structure, i.e. replace tantalum and magnesium atoms. A similar consideration of the XPS spectra of iron makes it possible to estimate the charge state of these atoms as +3, respectively. Let us turn to the consideration of Ni2p-spectra. When comparing the spectra of the composites with the spectra of NiO obtained by us, one can notice that, as in all the compounds considered above, all nickel atoms are in the same charge state (there is no splitting and distortion of the peaks). In this case, the energy position of the peaks has a characteristic shift towards already higher energies in comparison with the binding energies for these levels in bivalent nickel oxide NiO, which is characteristic of an increase in the effective positive charge. This suggests that all nickel atoms are in the same position in the crystal structure of doped tantalates and have the same effective charge +(2+δ). A similar shift, but towards lower energies, was observed in the spectra of the tantalum atom, which allows, by analogy with nickel atoms, to assert that tantalum atoms have an effective charge of +(5–δ). This indicates the incorporation of nickel atoms into the tantalum positions.

![Figure 3. XPS 2p spectra of bismuth tantalates doped with 3d metal atoms. For comparison, the spectra of the corresponding metal oxides are shown.](image)

A similar comparison of the 2p NEXAFS and XPS spectra of iron, manganese, nickel and copper atoms in synthesized solid solutions of bismuth titanates, niobates and tantalates with a pyrochlore structure and in metal oxides (MnO, MnO2, Mn3O4, MnO2, FeO, Fe2O3, Fe3O4, NiO, CuO, Cu2O) showed that these atoms in the studied bismuth compounds are in the charge state Mn2+, Ni2+, Cu2+ and Fe3+.

5. Conclusions

In this work, spectral studies of a wide class of compounds based on bismuth titanates, niobates and tantalates with a pyrochlore structure, doped with 3d-metal atoms with various degrees of doping, were carried out. Based on the analysis of the XPS and NEXAFS spectra, it was shown that, in these solid solutions, the doping atoms have the charge state Mn2+, Ni2+, Co2+, Cu2+ and Fe3+, and are introduced mainly in position B in the pyrochlore structure, i.e. replace atoms of titanium, niobium or tantalum.
Acknowledgments
The reported study was funded by RFBR, project number 19-32-60018, the Grant of the President of the Russian Federation (MK-3796.2021.1.2), the RFBR and the Komi Republic within the framework of research projects number 20-42-110002 r-a and the bilateral program of the Russian-German laboratory at BESSY II. Scientific research was performed at the Center for Studies in Surface Science of Research park of St. Petersburg State University.

References
[1] Giampaoli G, Siritanon T, Day B, Li J and Subramanian M 2018 *Prog. Sol. St. Chem.* **50** 16-23
[2] Subramanian M, Aravamudan G and Subba Rao G 1983 *Prog. Sol. St. Chem.* **15** 55-143
[3] McCauley R 1980 *J. Appl. Phys.* **51** 290-94
[4] Khaw C, Tan K, Lee C and West A. 2022 *J. Eur. Ceram. Soc.* **32** 671-80
[5] Stöhr J 1992 *NEXAFS Spectroscopy* (Berlin: Springer) p 403
[6] Regan T, Ohldag H, Stamm C, Nolting F, Luning J, Stöhr J and White R 2001 *Phys. Rev. B* **64** 214422
[7] Radtke G, Lazar S and Botton G 2006 *Phys. Rev. B* **74** 155117