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X-ray spectral studies of doped bismuth-magnesium and bismuth-zinc tantalates

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Abstract. Solid solutions of bismuth-magnesium tantalates and bismuth-zinc tantalates doped with 3d-metal atoms were studied by XPS and NEXAFS. It was shown that atoms of bismuth, magnesium and zinc in all the compounds under consideration have the charge states Bi^{3+}, Mg^{2+} and Zn^{2+}, respectively, and the tantalum atoms, in turn, have an effective charge of +(5−δ).

Keywords: bismuth-magnesium, bismuth-zinc, tantalates

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Рентгеноспектральные исследования допированных танталатов висмута-магния и висмута-цинка

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Аннотация. На основе данных XPS- и NEXAFS-спектроскопии твёрдых растворов танталатов висмута-магния и висмута-цинка, допированных атомами меди и никеля, показано, что атомы висмута, магния и цинка во всех исследуемых соединениях обладают зарядовым состоянием Bi^{3+}, Mg^{2+} и Zn^{2+}, соответственно, а атомы тантала имеют эффективный заряд +(5−δ).

Ключевые слова: висмут-магний, висмут-цинк, танталаты

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Introduction

Doping of bismuth tantalates with atoms of various metals can lead to a significant change in their electrophysical properties, which can depend both on the type of doped atoms and on the degree of doping [1–4]. This work shows the results of NEXAFS and XPS studies of the electronic state and nature of interatomic interactions of 3d-metal atoms in bismuth-magnesium and bismuth-zinc tantalates doped with copper and nickel atoms at different degrees of doping $Bi_2Ta_2Mg(Zn)_{1-x}Cu(Ni)_xO_9$ (x = 0.1–0.9). The experimental particularities and the used equipment characteristics are described in detail elsewhere [4].

Results and Discussion

Let us consider the results of spectral studies of bismuth-magnesium tantalates. Figure 1 shows the XPS spectra of bismuth-magnesium tantalates without doping and nickel-doped ones. It is clear that doping with nickel atoms slightly changes the spectral characteristics of bismuth, tantalum, and magnesium atoms. This indicates that the charge state of these atoms in the compounds under consideration is conserved.

Comparison of the XPS Bi 4f and Bi 5d spectra of the samples and Bi_2O_3 oxide (Fig. 1 *a*, *b*) shows that the energy position and width of the peaks in the spectra of all samples almost completely coincide and correlate well with the spectra of Bi_2O_3 oxide. Therefore, the bismuth atom in this compound has the Bi^{3+} charge state. In the case of tantalum atoms (Fig. 1 *a*, *c*), the absence of peak splitting and distortion clearly indicates that all tantalum atoms are in the same charge state. The energy position of the peaks has a shift towards lower energies compared to the binding energy in oxide Ta_2O_5, which is typical for a decrease in the effective positive charge. This evidence may be taken to mean that tantalum atoms have the same effective charge +(5–δ). The energy position of the peaks in the XPS Mg 1s spectra (Fig. 1 *d*) is characteristic of a divalent magnesium atom [5]. Thus, the charge state of these atoms here is Mg^{2+}.

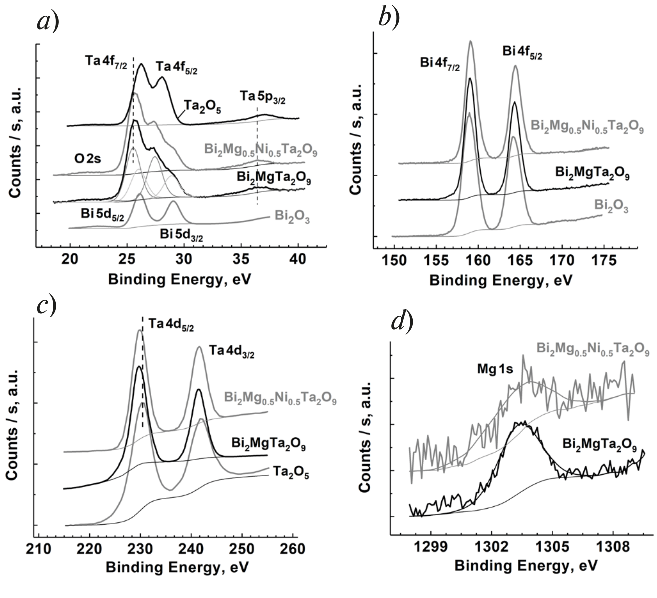

Fig. 1. XPS spectra of bismuth-magnesium tantalates without doping and XPS spectra of bismuth-magnesium tantalates, doped with nickel atoms

Comparison of the XPS and NEXAFS Ni 2p spectra of the samples with the ones of nickel oxide NiO (Fig. 2) shows that nickel atoms have the same charge state, since there is no splitting and distortion of the peaks. The energy positions of the peaks in XPS spectra (Fig. 2 *a*) is shifted towards higher energies compared to the binding energies for the given levels in NiO oxide, which is characteristic of an increase in the effective positive charge. This suggests that nickel atoms have the same effective charge +(2+δ). NEXAFS spectra (Fig. 2 *b*) reflects that the charge state of nickel atoms is preserved when the degree of doping is changed.

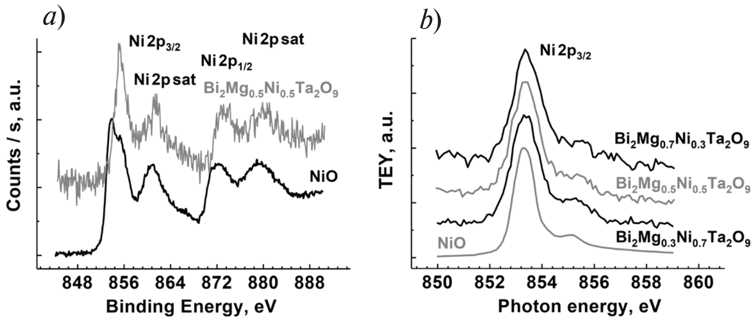

Fig. 2. XPS (*a*) and NEXAFS (*b*) Ni 2p spectra of Ni-doped bismuth-magnesium tantalates

Similar to samples doped with nickel atoms, in the case of doping with copper atoms, the shape of the spectra of bismuth, tantalum, and magnesium atoms remains almost unchanged. Consequently, the charge state of these atoms (Bi^{3+}, $Ta^{(5-\delta)+}$ and Mg^{2+}) in the presented compounds is preserved. In this case, the behaviour of the introduced copper atoms is fundamentally different. Figure 3 shows the XPS and NEXAFS spectra of copper atoms in the samples at various degrees of doping. A comparison of the spectra shows that the samples contain Cu(I) and Cu(II) atoms.

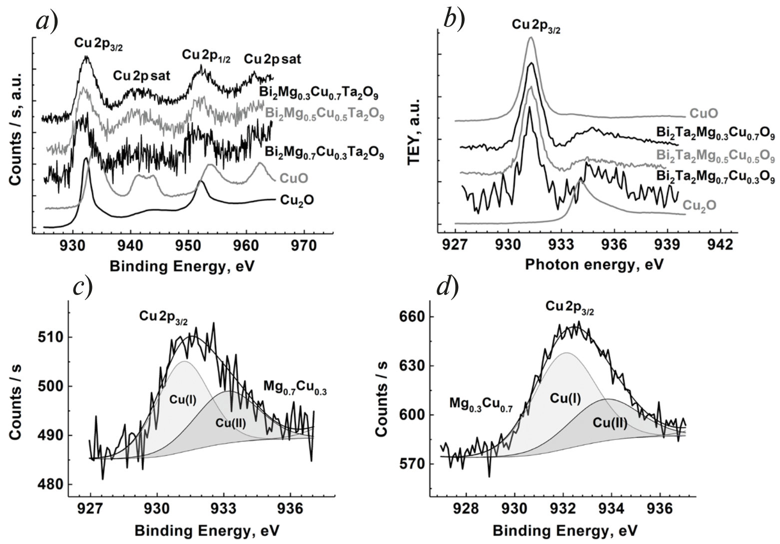

Fig. 3. XPS (*a*) and NEXAFS (*b*) Cu 2p spectra of Cu-doped bismuth-magnesium tantalates and decomposition of XPS Cu 2p spectra at $x = 0.3$ (*c*), at $x = 0.7$ (*d*)

From the analysis of XPS Cu 2p spectra (Fig. 3 *c*, *d*), it is possible to determine the contribution of Cu(I) and Cu(II) atoms to the corresponding spectra. The ratio of integral intensities Cu(I)/Cu(II) is 1.43 at $x = 0.3$ and 2.08 at $x = 0.7$. Thus, the relative contribution of Cu(I) increases with increasing degree of doping with copper atoms, which indicates a change in the position of copper atoms in the structure of pyrochlores. Perhaps, at a low concentration, copper atoms are introduced into the positions of tantalum atoms, and with an increase in their concentration, they are partially introduced into the positions of bismuth atoms. A similar behaviour of all atoms is also observed in the samples of Ni- and Cu-doped bismuth-zinc tantalates.

Conclusions

Thermally stable solid solutions of bismuth-magnesium (zinc) tantalates doped with nickel and copper atoms were obtained in a wide range of compositions. It follows from the NEXAFS and

XPS spectra that the bismuth, magnesium, and zinc atoms in all compounds have the Bi^{3+}, Mg^{2+}, and Zn^{2+} charge state, while the tantalum atoms have an effective charge of +(5–δ). The doped nickel atoms have an effective charge of +(2+δ), and the copper atoms have the charge state Cu^{+} and Cu^{2+}.

REFERENCES

1. **Murugesan S., Huda M.N., Yan Y., Al-Jassim M.M., Subramanian V.,** Band-Engineered Bismuth Titanate Pyrochlores for Visible Light Photocatalysis, J. Phys. Chem. C. 114 (2010) 10598–10605.
2. **Giampaoli G., Siritanon T., Day B., Li J., Subramanian M.A.,** Temperature in-dependent low loss dielectrics based on quaternary pyrochlore oxides, Prog. Solid. State Ch. 50 (2018) 16–23.
3. **Zhuk N.A., Krzhizhanovskaya M.G., Koroleva A.V., Nekipelov S.V., Sivkov D.V., Sivkov V.N., Lebedev A.M., Chumakov R.G., Makeev B.A., Kharton V.V., Panova V.V., Korolev R.I.,** Spectroscopic characterization of cobalt doped bismuth tantalate pyrochlore. Solid State Sciences. 125 (2022) 106820.
4. **Zhuk N.A., Krzhizhanovskaya M.G., Koroleva A.V., Reveguk A.A., Sivkov D.V., Nekipelov S.V.,** Thermal expansion, crystal structure, XPS and NEXAFS spectra of Fe-doped bismuth tantalate pyrochlore, Ceramics International. 48 (2022) 14849–14855.
5. **Khairallah F., Glisenti A.,** XPS study of MgO nanopowders obtained by different preparation procedures, Surface Science Spectra. 13 (1) (2006) 58–71.

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