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02

X-ray spectral studies of manganese-doped bismuth-zinc tantalates

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Thermally stable pyrochlores of bismuth tantalates doped with manganese and zinc atoms were obtained: $Bi_2Zn_xMn_{1-x}Ta_2O_{9.5-\Delta}$ ($x = 0.3$, 0.7). According to XPS and NEXAFS spectroscopy, it was established that the ions in these solid solutions are in the charge states Bi $(+3-\delta)$, Zn $(+2)$, Ta $(+5-\delta)$, and the manganese ions in the samples have predominantly an oxidation state 2^+ and 3^+, while the share of the lat-ter increases with increasing manganese content.

Keywords: bismuth tantalates, pyrochlores, XPS, NEXAFS.

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Introduction

Pyrochlores are an important class of materials in various technological applications due to a wide range of practically useful properties, including metallic and ionic conductivity, superconducting and ferroelectric properties. Pyrochlore-based materials are used in solid-state devices as thin-film resistors, thermistors and communication elements, photocatalysts, and are used as components of ceramic moulds for radioactive waste. Due to excellent dielectric properties, the possibility of dielectric properties control by an electric field, low sintering temperature, oxide pyrochlores are promising as dielectrics for multilayer ceramic capacitors, tunable microwave dielectric components, resonant cavities, devices for VHF applications [1,2]. In this case, additional doping with atoms, in particular 3d-metal atoms, leads to a significant change in the above properties. In this study, a new continuous series of samples of manganese-doped bismuth-zinc tantalates $Bi_2Zn_xMn_{1-x}Ta_2O_{9.5-\Delta}$ was obtained and the influence of manganese ions on their physical properties was observed.

Results and discussion

The $Bi_2Zn_xMn_{1-x}Ta_2O_{9.5-\Delta}$ ($x = 0.3$, 0.7) samples were synthesised from ZnO, Bi_2O_3, Mn_2O_3, Ta_2O_5 oxides by solid-state reaction. The finely ground and homogeneous oxide mixture in stoichiometric amounts was pressed into disc-shaped compacts (diameter — 10 mm, thickness 3–4 mm) using a hand press. High-temperature treatment of the samples was carried out in stages, at temperatures of 650, 850, 950, 1050°C for 15 h at each stage of calcination. Experiments using X-ray photoelectron spectroscopy were carried out on the laboratory unit Escalab 250 Xi of the resource centre „Physical methods of surface research" scientific park of St. Petersburg State University. An X-ray tube with Al Kα-radiation (1486.6 eV) was used as a source of ionising radiation. An ion-electron charge compensation system was used to neutralise the charge of the sample in the experiments. All peaks were calibrated relative to the C1s peak at 284.6 eV. The samples were investigated by NEXAFS spectroscopy at the NanoPES experimental station of the Kurchatov Synchrotron Radiation Source „KISI-Kurchatov" [3]. NEXAFS spectra were obtained by the total electron yield (TEY) method with an energy resolution of 0.5 eV.

XPS spectra for $Bi_2Zn_xMn_{1-x}Ta_2O_{9.5-\Delta}$ ($x = 0.3$ and 0.7) are shown in Fig. 1 and 2,*a*. The spectra of the initial oxides used in the synthesis of the samples are given for comparison. When comparing the XPS Bi4f- spectra of the investigated sample and Bi_2O_3 oxide (Fig. 1,*a*), it can be noted that the energy position and peak widths in the spectra of the samples almost completely match and correlate well with the corresponding spectra of the oxide. A slight relative shift of the absorption bands of Bi4$f_{7/2}$ and Bi4$f_{5/2}$ to lower energies relative to Bi_2O_3 and each other is also observed. For example, the Bi4$f_{5/2}$ band changes its position from 164.10 eV ($x = 0.7$) to 164.13 eV ($x = 0.3$) compared to the oxide spectrum (164.29 eV), which means that the effective charge of bismuth ions decreases as x(Zn) is increased and is associated with the placement of some fraction of divalent ions in the bismuth position. The observed concentration dependence also indicates a possible distribution of zinc ions in the bismuth position compared to manganese ions at higher values x(Zn). The energy position of the peaks in the XPS Zn2p-spectra shown in Fig. 1,*b* is characteristic of the bivalent zinc ion [4]. When considering the spectra of tantalum ions (Fig. 1,*c*), it should be noted that the shape of the peaks

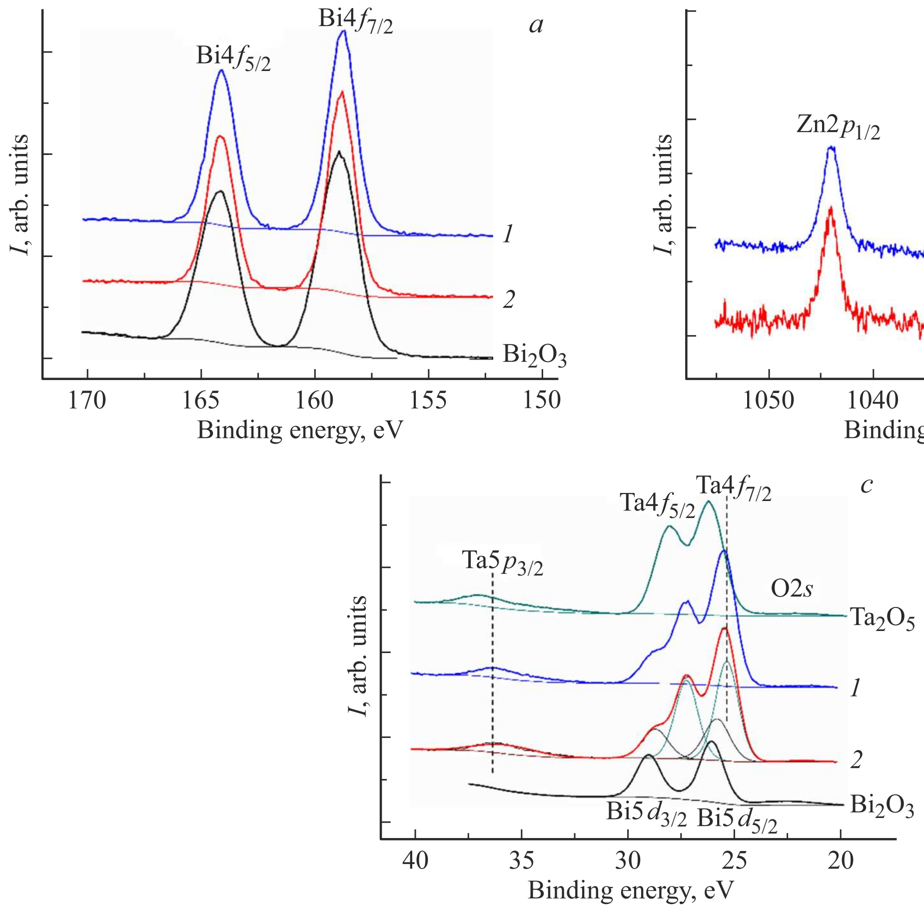

Figure 1. (*a*) XPS Bi4$f_{7/2}$- and Bi4$_{f5/2}$-bismuth spectra; (*b*) XPS Zn2*p*-spectra; (*c*) XPS-tantalum and bismuth spectra in the samples $Bi_2Zn_{0.7}Mn_{0.3}Ta_2O_{9.5-\Delta}$ (*1*) and $Bi_2Zn_{0.3}Mn_{0.7}Ta_2O_{9.5-\Delta}$ (*2*).

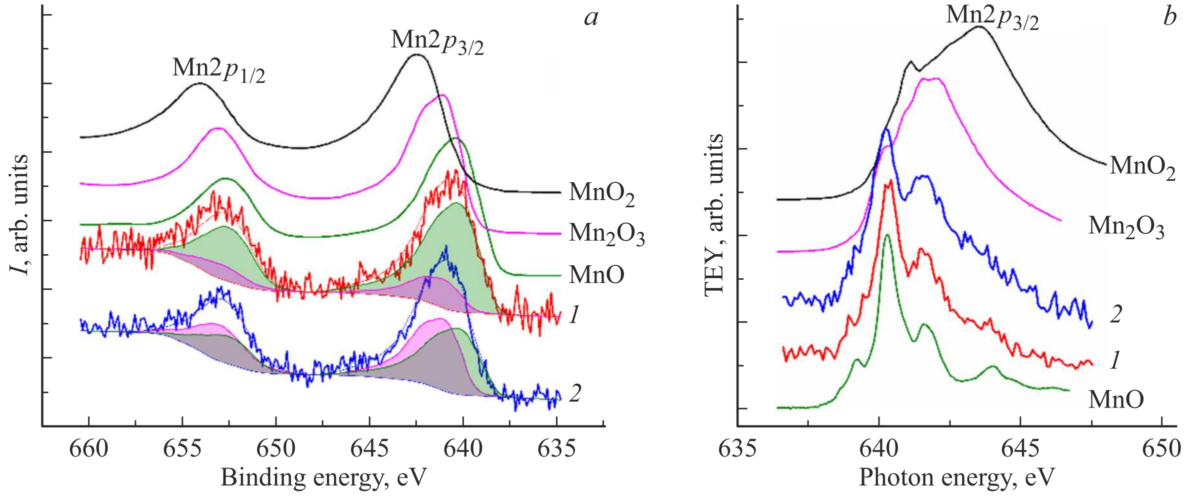

Figure 2. XPS (*a*) and NEXAFS (*b*) Mn2*p*-the spectra in the samples $Bi_2Zn_{0.7}Mn_{0.3}Ta_2O_{9.5-\Delta}$ (*1*) and $Bi_2Zn_{0.3}Mn_{0.7}Ta_2O_{9.5-\Delta}$ (*2*).

unambiguously indicates that all tantalum atoms are in the same charge state (no splitting and distortion of peaks), but the energy position of the peaks has a characteristic shift towards lower energies compared to the bond energy in the pentavalent tantalum oxide Ta_2O_5 [5]. The shift towards lower energies is characteristic of a decrease in the effective positive charge, in particular, for the Ta4*f*- and Ta5*p*-spectra presented by us, this energy shift is $\Delta E = 0.65$ eV. This in turn suggests that the tantalum ions in the studied ceramic samples have the same effective charge $+(5-\delta)$. XPS

Mn2p-spectra of $Bi_2Zn_xMn_{1-x}Ta_2O_{9.5-\Delta}$ ($x = 0.3$ and 0.7) and manganese oxide samples are shown in Fig. 2, a. Comparison of the composite spectra with the spectra of MnO [6], Mn_2O_3 [7] and MnO_2 [8] oxides known from the literature showed that the energy position of the lines correlates most strongly with the MnO spectrum. Based on the above, it was concluded that manganese ions are mostly of oxidation degree (2+). However, as can be seen from Fig. 2, a, there is no complete energy coincidence between the components of the manganese spectrum in composites and MnO, which means that oxidised manganese ions (3+, 4+) are present. To clarify this conclusion, we decomposed the XPS Mn2p-spectra of $Bi_2Zn_{0.3}Mn_{0.7}Ta_2O_{9.5-\Delta}$ and $Bi_2Zn_{0.7}Mn_{0.3}Ta_2O_{9.5-\Delta}$samples into individual components using the oxide spectra presented in Fig. 2, a. The decomposition was carried out in several steps: (1) the background of inelastically scattered photoelectrons was subtracted from the spectra using the Shirley approximation, (2) the resulting „background-free" XPS spectra were normalised by one magnitude in area (in this case 1 was taken), (3) a model spectrum was constructed as the sum of the XPS spectra of MnO, Mn_2O_3 and MnO_2 with the corresponding coefficients α, β and γ ($\alpha + \beta + \gamma = 1$), the value of which was varied to achieve maximum coincidence with the spectrum of the composite. The results of optimal simulation for the sample $Bi_2Zn_{0.7}Mn_{0.3}Ta_2O_{9.5-\Delta}$ ($\alpha = 0.79, \beta = 0.21$ of sample and $\gamma = 0$) and $Bi_2Zn_{0.3}Mn_{0.7}Ta_2O_{9.5-\Delta}$ ($\alpha = 0.48$, $\beta = 0.52$ and $\gamma = 0$) are highlighted in Fig. 2,a. The data thus obtained indicate that there are two non-equivalent states of manganese atoms in the composite structure: +2 and +3. At the same time, as manganese content increases, the proportion of states with +3 increases from 0.21 to 0.52 of the total magnesium content. The oxidation degree of manganese in solid solutions was clarified based on NEXAFS studies. NEXAFS Mn2p-spectra $Bi_2Zn_{0.3}Mn_{0.7}Ta_2O_{9.5-\Delta}$, $Bi_2Zn_{0.7}Mn_{0.3}Ta_2O_{9.5-\Delta}$ and those of manganese oxides are shown in Fig. 2, b. Comparison of the samples spectra with those of the oxides shows that the shape of the spectra and the energy position of the main peaks of the samples (640.3 and 641.5 eV) correlate with the MnO spectra. This suggests that manganese atoms in the studied samples mainly have the charge state +2. At the same time, some features of the spectra indicate the presence of oxidised manganese ions (III, IV) in the samples. This is indicated by the absence of clear absorption lines at 644 and 639 eV, which appear in the MnO spectrum. The ratio of line intensities at 640.3 and 641.5 eV observed in the samples' spectra is less than for the lines in the MnO spectrum. The absorption bands in the samples spectra are delayed and broader and thus differ from the Mn2p-spectrum of MnO, which may be due to the superposition of the manganese ion spectra in different oxidation degrees. Furthermore, the ratio of line intensities at $Bi_2Zn_xMn_{1-x}Ta_2O_{9.5-\Delta}$samples ($x = 0.3$ and 0.7) is not constant. As x(Zn) increases (manganese content decreases), the ratio of line intensities decreases, which may indicate the variable ionic composition of manganese in the samples and the presence of more oxidised manganese ions in the samples with the highest manganese content, which is consistent with the XPS studies. Thus, we can conclude that in XPS-spectra of bismuth and tantalum there is an energy shift of absorption bands depending on the content of dopants towards lower energies (which is typical for bismuth and tantalum ions with effective charge ($+3-\delta$) and ($+5-\delta$)), due to the distribution of some transition element ions in the position of bismuth and tantalum. According to the data obtained by NEXAFS-, XPS-spectroscopy, manganese ions in the samples have mainly +2 and +3, oxidation degrees, and the share of oxidised manganese ions increases as manganese content increases.

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Conflict of interest

The authors declare that they have no conflict of interest.

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