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Effect of doping with iron and magnesium on high-temperature stability and physicochemical properties of bismuth tanalates

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Received May 11, 2023
Revised July 03, 2023
Accepted October 30, 2023.

Bismuth tantalum pyrochlores doped with iron and magnesium atoms were obtained thermally stable up to a temperature of 1140°C: $Bi_2Mg_xFe_{1-x}Ta_2O_{9.5-\Delta}$ $(x = 0 - 1)$. The effect of Fe and Mg codoping on their crystal structure has been studied. The unit cell parameter of solid solutions increases uniformly from 10.4871(2) Å$(x = 0)$ to 10.54607 Å$(x = 1)$. According to the XPS and NEXAFS spectroscopy data, it was found that the ions in these solid solutions are in the charge states Bi(+3), Mg(+2), Fe(+3), Ta$(+5 - \delta)$. The dopant atoms iron and magnesium are introduced into the positions of the tantalum atom without distorting the symmetry of the crystal lattice.

Keywords: bismuth tantalates, pyrochlores, XPS, NEXAFS.

DOI: 10.61011/EOS.2023.11.58022.4917-23

Introduction

Bismuth-containing pyrochlores are promising materials due to their excellent dielectric properties — high dielectric permittivity, low dielectric losses in the megahertz frequency range and adjustable temperature coefficient of capacitance. In this regard, materials based on such pyrochlores can be used in the manufacture of multilayer ceramic capacitors, dielectric resonant cavities, thermistors, thick-film resistors and communication elements, microwave oscillators or filters [1,2].

The cubic structure of pyrochlore (general formula $A_2B_2O_7$) contains large eight-coordinated cations A (Bi) and relatively small octahedral cations B (Ta, Nb, Ti) [2,3]. The structure contains two interpenetrating weakly interacting sublattices: sublattice B_2O_6 consists of octahedra $[BO_6]$ connected at the vertex of the corner; sublattice A_2O' has an anticristobalite structure and is formed by tetrahedra $[O'A_4]$. In this case, bismuth tantalat with an equimolar amount of bismuth (III) and tantalum (V) ions does not form a pyrochlore structure and crystallizes in the $BiTaO_4$ [4] structure type. The structure of pyrochlore can be stabilized with an equal ratio of Bi(III) and Ta(V) atoms by doping with ions whose ionic radius is smaller than that of Bi^{3+}(for example, atoms of 3*d* elements). In this case, as a rule, most of the dopant atoms are located in the octahedral position B, making the bismuth sublattice A_2O' unoccupied, which increases the stability of pyrochlore. Therefore, ternary pyrochlores containing transition metals [5] are of particular interest. The advantage of bismuth-containing ternary pyrochlores is associated with the opportunity of replacing Bi^{3+} cations in the A-positions with small (Mg, Cu, Ni, Cr) cations. As a result, the same ions can occupy two nonequivalent positions A and B. 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, it is possible to significantly vary the properties of pyrochlore, which makes it possible to study the influence of the chemical composition on its physical and chemical characteristics. Meanwhile, the question remains open about the charge state of both the matrix atoms (bismuth and tantalum) and the interstitial (doping) atoms, as well as the position in the crystal structure into which dopant atoms are introduced.

This work demonstrates the opportunity of the formation of pyrochlores of bismuth tantalats doped with magnesium and iron atoms, and notes the influence of magnesium and iron ions on the structure and physical and chemical properties of pyrochlores.

Results and discussion

Solid solutions $Bi_2Mg_xFe_{1-x}Ta_2O_{9.5-\Delta}$ $(x = 0 - 1)$ were synthesized using standard ceramic technology, described in detail in [6] and based on high-temperature treatment of a stoichiometric mixture of oxides MgO, Bi_2O_3, Fe_2O_3, Ta_2O_5. The mixture of precursors was carefully ground to a homogeneous powder and pressed. Then the samples in the form of disks with a diameter of 1 cm were calcined in

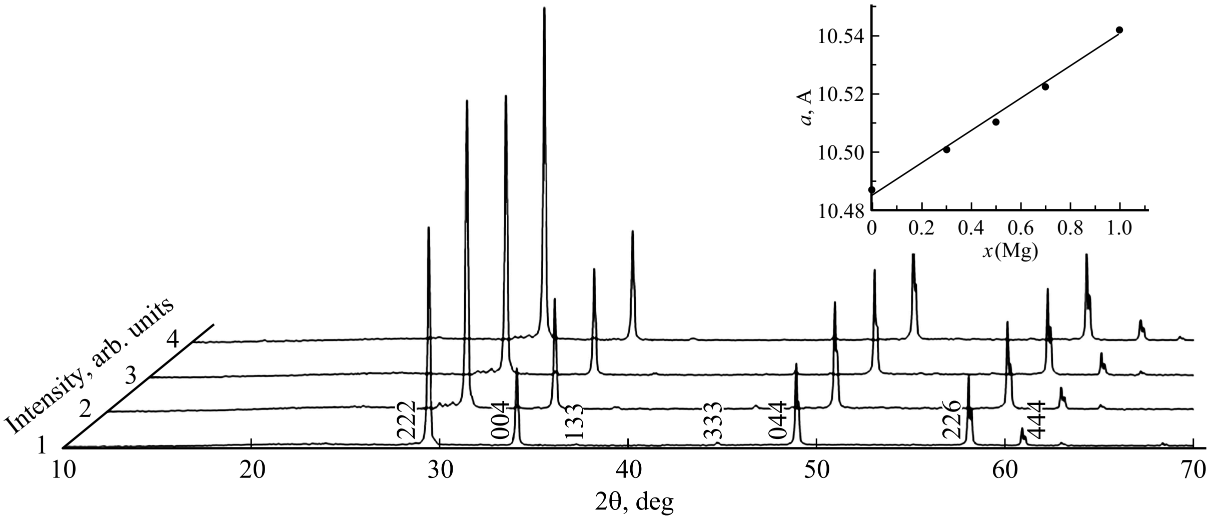

Figure 1. X-ray diffraction patterns and the dependence of the lattice cell parameter on the content of magnesium ions $Bi_2Mg_xFe_{1-x}Ta_2O_{9.5-\Delta}$ ($x = 1$ (*1*), 0.7 (*2*), 0.5 (*3*), 0.3 (*4*)). Inset demonstrates the dependence of lattice constants on the degree of doping with magnesium atoms.

several stages at temperatures of 650 (10 h), 850 (10 h), 950 (10 h) and 1050°C (10 h) for 40 h. After each calcination, the samples were thoroughly ground and pressed again.

Thermal behavior at high temperatures was studied by high-temperature X-ray diffraction (HTXRD) using a RigakuUltima IV X-ray diffractometer (Co Kα radiation). All samples were also studied by X-ray absorption (NEXAFS, near edge X-ray absorption fine structure) spectroscopy in the total electron yield (TEY) mode at the NanoPES beamline of the Kurchatov Synchrotron Radiation Source (NRC Kurchatov Institute) and X-ray photoelectron spectroscopy (XPS) spectroscopy using a Thermo Scientific ESCALAB 250Xi X-ray spectrometer with a sample charging compensation system at the St. Petersburg State University Research Park (Centre for Physical Methods of Surface Investigation).

According to the results of X-ray diffraction analysis, all studied samples crystallize in a cubic system with space group $Fd\bar{3}2$ (Fig. 1). As a result of calculating the unit cell parameter of samples $Bi_2Mg_xFe_{1-x}Ta_2O_{9.5-\Delta}$, it was established that the cell constant with increasing magnesium concentration and decreasing iron content uniformly increases from 10.4871 ($x = 0$) to 10.54607 Å($x = 1$), obeying Vegard law (The dependence of the lattice cell parameter on the magnesium content is shown in the inset of Fig. 1). This fact, firstly, indicates the formation of a continuous series of solid solutions and, secondly, a uniform and same type distribution of iron and magnesium ions in one system of crystallographic positions.

The thermal behavior was studied by the HTXRD method in the range 30–1200°C for the sample $Bi_2Mg_{0.5}Fe_{0.5}Ta_2O_{9.5-\Delta}$ in the range 30–1200°C. The lattice cell parameter a uniformly increases from 10.50183 (30°C) to 10.57607 Å(1110°C). A uniform change in the cell constant indicates the absence of phase transformations and thermal stability of pyrochlore in the temperature range under consideration. Above 1100°C, thermal dissociation of the solid solution probably occurs. It should be noted that the limiting temperature of phase stability $Bi_2Mg_xFe_{1-x}Ta_2O_{9.5-\Delta}$ decreases with increasing magnesium content from 1140 ($x = 0$) to 1050°C ($x = 0.5$), which may be due to a change in the nature of the MeO bond (Me–Fe(III), Mg(II)) in the octahedron from covalent to ionic and the number of oxygen vacancies destabilizing the structure.

In this case, the values of the coefficient of thermal expansion (CTE) $Bi_2Mg_{0.5}Fe_{0.5}Ta_2O_{9.5-\Delta}$ uniformly and slightly increase from $3.6 \cdot 10^{-6}$ to $9.3 \cdot 10^{-6}{}^{\circ}C^{-1}$ in the temperature range 30–1050°C. In connection with this, iron-magnesium pyrochlores can be classified as weakly expanding compounds with isotropic thermal expansion. Taking into account that transition ions are located mainly in octahedral positions, we can talk about the weak influence of the nature of dopant impurities distributed in the three-dimensional cation sublattice B on the thermal expansion of pyrochlores.

Studies of the electronic state of atoms in pyrochlore of bismuth tantalat doped with iron and magnesium atoms were carried out using NEXAFS and XPS spectroscopy. The obtained XPS spectra of bismuth-magnesium tantalats and bismuth-iron tantalats and the corresponding oxides are presented in Fig. 2 and 3, *a*. Let us note only some features of the obtained spectra. Firstly, doping with iron ions does not significantly change the spectral characteristics of bismuth, tantalum and magnesium ions (Fig. 2). Consequently, the electronic state of these ions remains unchanged. Moreover, from comparison with the spectra of the corresponding oxides and with data on bond energies [7,8] known from the literature, the charge state of these atoms in the pyrochlore structure under review

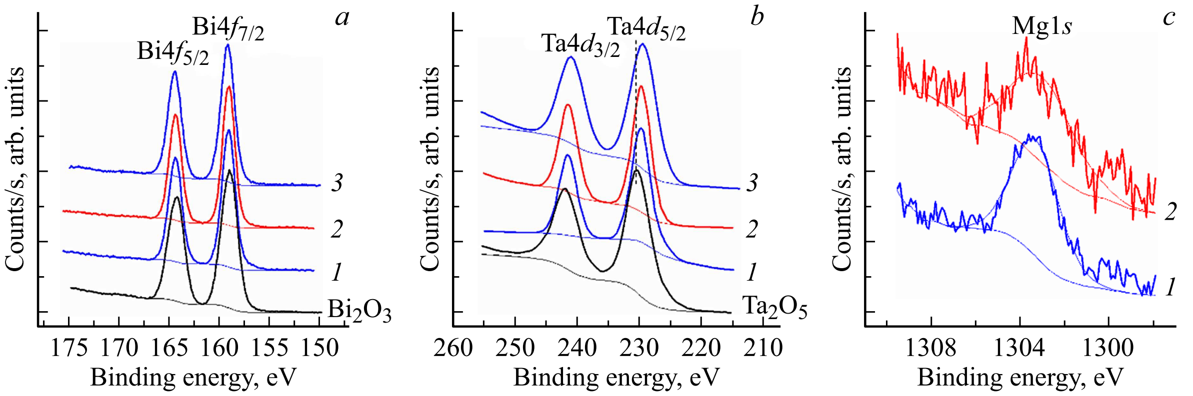

Figure 2. XPS (*a*) Bi_{4f}-, (*b*) Ta4*d*-, (*c*) Mg1*s*-spectra of samples $Bi_2MgTa_2O_9$ (*1*), $Bi_2Mg_{0.5}Fe_{0.5}Ta_2O_{9.5-\Delta}$ (*2*) and $Bi_2FeTa_2O_9$ (*3*).

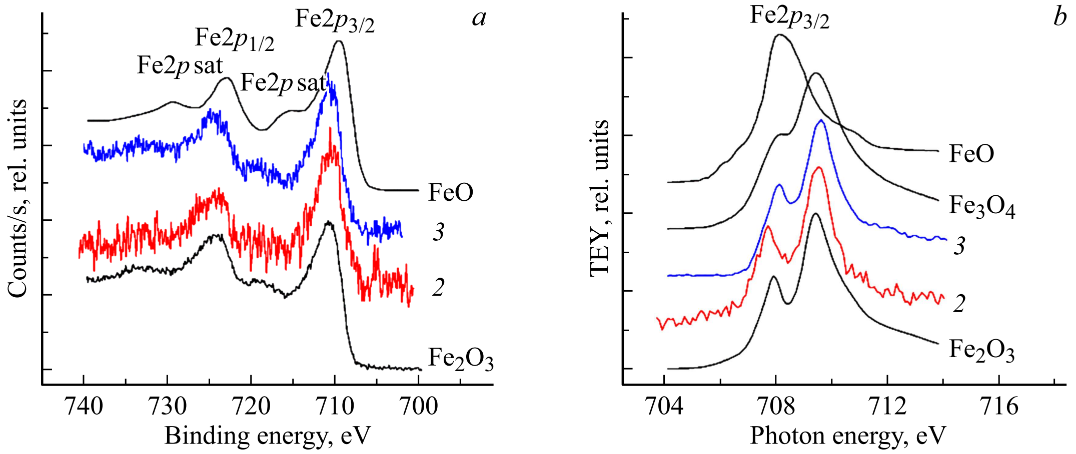

Figure 3. (*a*) XPS- and (*b*) NEXAFS Fe2*p*-spectra of the samples $Bi_2Mg_{0.5}Fe_{0.5}Ta_2O_{9.5-\Delta}$ (*2*) and $Bi_2FeTa_2O_9$ (*3*).

corresponds to Mg(II), Bi(III) ions. At the same time, in the Ta4*d* spectra of tantalum atoms, the energy position of the peaks has a characteristic shift towards lower energies compared to the bond energy in pentavalent tantalum oxide Ta_2O_5, which is typical for the case of a decrease in the effective positive charge. This suggests that tantalum atoms can have the same effective charge of less than five: $+(5-\delta)$. Apparently, the observed shift is due to the replacement of tantalum positions with magnesium (II) and iron (III) ions with a lower effective charge.

XPSFe2*p* spectra of iron (Fig. 3, *a*) in the studied pyrochlore samples demonstrate two broad intense bands corresponding to the bond energies of the Fe2$p_{3/2}$ and Fe2$p_{1/2}$ levels. In addition, there are two low-intensity satellite peaks. Comparison with the spectra of iron oxides in terms of the energy positions of the peaks and especially the satellite bands shows their similarity with the spectra of Fe_2O_3, which suggests that the iron atoms in the pyrochlores under review have an effective charge +3. A similar conclusion on the charge state of iron atoms (Fe^{3+}) follows from the analysis of the NEXAFSFe2$p_{3/2}$ spectra of pyrochlores in comparison with similar spectra of oxides (Fig. 3, *b*). All the results reviewed, based on the analysis of X-ray diffraction and X-ray spectral data, indicate that magnesium and iron atoms are introduced into the positions of the tantalum atom (position B in the structure of pyrochlore).

Thus, samples of bismuth tantalat ceramics doped with magnesium and iron atoms were synthesized, thermally homogeneous and stable up to a temperature of 1140°C. The introduction of magnesium and iron atoms occurs without distortion of the spatial symmetry of pyrochlore and occurs at the position of the tantalum atom (position B in the structure of pyrochlore) .

Funding

The study was carried out with the financial support of the Ministry of Science and Higher Education of Russia as part of agreement N 075-15-2021-1351.

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by E.Potapova