Research Article

Nadezhda A. Zhuk*, Vladimir A. Belyy, Vladimir P. Lutoev, Boris A. Makeev, Sergey V. Nekipelov, Viktor N. Sivkov, Aleksandra V. Koroleva, Dmitriy S. Beznosikov, and Lubov S. Feltsinger

Phase transition of $\text{BiNb}_{1-x}\text{Mn}_x\text{O}_{4-\delta}$: Thermal analyse, NEXAFS, XPS and ESR-study

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Abstract: The manganese-doped polymorphs of bismuth orthoniobate were studied using thermal analysis, ESR, XPS and NEXAFS spectroscopy. It was shown that the phase transition from the orthorhombic (α) to the triclinic (β) modification can be reversible and it can be achieved by prolonged calcination of samples at 750°C. The DSC curves revealed no thermal effects associated with the phase transformation from the triclinic to the orthorhombic modification near 750°C. In the ESR spectra, the absorption band with $g = 3.8$ characterized by sextet structure disappeared during the phase transformation from the β - to the α -form and only the broad component with average intensity was observed at $g = 2.2$. According to NEXAFS spectroscopy data, the content of oxidized Mn(III) atoms increased and the content of Mn(II) decreased in the orthorhombic polymorph obtained at 750°C from the triclinic modification.

Keywords: Phase transitions; Thermal properties; ESR; XPS; NEXAFS

*Corresponding Author: Nadezhda A. Zhuk: Syktyvkar State University, Oktjabrskij prospect, 55, Syktyvkar, Komi Republic, 167001, Russia; Email: nzhuck@mail.ru

Vladimir A. Belyy: Institute of Chemistry of the Komi Science Center UB RAS, Pervomayskaya st. 48, Syktyvkar, 167982, Republic of Komi, Russia

Vladimir P. Lutoev, Boris A. Makeev: Institute of Geology of the Komi Science Center UB RAS, St. Pervomayskaya, 54, Syktyvkar, Komi Republic, 167982, Russia

Sergey V. Nekipelov: Syktyvkar State University, Oktjabrskij prospect, 55, Syktyvkar, Komi Republic, 167001, Russia; Institute of Physics and Mathematics of the Komi Science Center UB RAS, Oplensnina st. 4, Syktyvkar, Republic of Komi, 167982, Russia

Viktor N. Sivkov: Institute of Physics and Mathematics of the Komi Science Center UB RAS, Oplensnina st. 4, Syktyvkar, Republic of Komi, 167982, Russia

Aleksandra V. Koroleva: St. Petersburg State University, Universitetsky pr. 26, St. Petersburg, 198504, Russia

Dmitriy S. Beznosikov, Lubov S. Feltsinger: Syktyvkar State University, Oktjabrskij prospect, 55, Syktyvkar, Komi Republic, 167001, Russia

1 Introduction

For more than half of a century, bismuth orthoniobate remains of great interest to researchers for its useful photocatalytic and microwave dielectric properties [1, 2]. Optimization of the dielectric properties of bismuth orthoniobate usually achieved by substitution of a part of niobium or bismuth atoms with copper [3, 4], iron [5, 6], vanadium [7], or rare-earth elements [8–10]. However, as a result of the iso- and hetero-valent substitution of bismuth orthoniobate, the concentration range for the formation of the solid solutions is limited [6, 11]. It is well known that bismuth orthoniobate has three structural modifications: the orthorhombic modification (α - BiNbO_4 , $a = 4.980 \text{ \AA}$, $b = 11.709 \text{ \AA}$, $c = 5.675 \text{ \AA}$, $Pnna$) [12, 13], the triclinic modification (β - BiNbO_4 , $P-1$, $a = 7.71 \text{ \AA}$, $b = 5.55 \text{ \AA}$, $c = 7.97 \text{ \AA}$, $\alpha = 89^\circ$, $\beta = 77^\circ$, $\gamma = 87^\circ$) [14, 15] and the cubic modification (high pressure phase) [16, 17]. The phase transition from the orthorhombic to triclinic modification is irreversible due to significant structural differences and it occurs at temperature near 1040°C, as it was shown in [12–14]. Recent studies have shown the phase transition from the triclinic modification to the orthorhombic one in powder and compact state of BiNbO_4 [18] and in its solid solutions [19] using the methods of X-ray phase analysis. The consensus on the causes of the reversibility of the phase transition and on the temperature of the process is not found yet. The possible cause of the phase transition is the internal stresses due to defects in BiNbO_4 crystal structure [20].

In the present work, NEXAFS, XPS and ESR spectroscopy techniques, as well as thermal analysis, were used to study the phase transformations of manganese doped solid solutions of bismuth orthoniobate in order to obtain new facts about the reversibility of the phase transformation from the orthorhombic modification to the triclinic one.

2 Experimental

The manganese doped solid solutions $\text{BiNb}_{1-x}\text{Mn}_x\text{O}_{4-\delta}$ ($x \leq 0.06$) of orthorhombic modification were obtained by solid-phase ceramic method of step sintering of a stoichiometric mixture of oxides of bismuth (III), niobium (V) and manganese (III) of purissimum speciale quality at 650°C, 850°C and 950°C for 30 hours. The solid solutions of triclinic modification were obtained from the solid solutions of orthorhombic modification by additional heat treatment of the samples at 1100°C for 30 hours. The phase composition of the samples was controlled with a scanning electron microscope Tescan VEGA 3LMN equipped with an energy dispersion spectrometer INCA Energy 450 and an X-ray diffractometer DRON-4-13 (CuK_α emission). The unit cell parameters of the solid solutions were determined by means of the CSD program package [21].

The thermal behavior of the samples of the manganese doped bismuth orthoniobate solid solutions was carried out using a TG-DSC thermal analyzer Netzsch STA 409 PC Luxx in platinum / rhodium crucibles with perforated lids (an empty crucible was used as an etalon) and dynamic atmosphere (air was a purge gas, the flow was 20 ml/min). The heating and cooling rates were 5°C/min. The rate of 5°/min was chosen for the analysis because it allowed to register well resolved thermal effects and to be closer to the thermodynamic equilibrium in the sample without significant extending of the time of the experiment. The calibration was performed prior to the sample analysis. To calibrate the enthalpy sensitivities and indications of temperature of the TG-DSC analyzer, a DSC/DTA calibration kit (Netzsch 6.223.5–91.2) was used. The following compounds with the corresponding phase transition temperatures from this calibration kit were used for the calibration: BaCO_3 (1081.0 K), K_2CrO_4 (941.0 K), Ag_2SO_4 (699.2 K), KClO_4 (573.8 K), $\text{C}_6\text{H}_5\text{COOH}$ (395.4 K). About 20 mg of a calibration standard weighted with the accuracy of ± 0.001 mg were placed in a Pt/Rh crucible. An empty Pt crucible with a perforated lid was used as a reference. TG and DSC curves were obtained with the heating rate as mentioned above. Each calibration substance was analyzed thrice. The values of enthalpy and onset temperatures of the endothermic effects of the calibration substances were measured in NETZSCH Proteus software and used to obtain the calibration curves. The relative standard deviation of the determination of the temperatures and enthalpy of phase transitions of the calibration substances was 0.5%. During the analysis of the bismuth orthoniobate samples, the temperature program included heating and cooling stages: 298

K $\rightarrow$ 1373 K $\rightarrow$ 973 K. The weight of the samples was 0.0355 ± 0.0002 g.

ESR analysis of the manganese-doped polycrystalline bismuth orthoniobate samples were carried out using an X-diapason spectrometer SE/X2547 RadioPAN with the rectangular resonator RX102 (TE 102 mode). The spectra were obtained in the form of the first derivative at 25°C. The reference sample, anthracite in the quartz ampoule rigidly fixed in the resonator in parallel to the sample tube, had the singlet line with $g_0 = 2.0032$ and $\Delta B_{pp} = 0.5$ mT. This signal was used for the spectrometer calibration and the amplification procedure. 100 MHz HF modulation frequency, 0.25 mT amplitude and 35 mW SHF field power, the magnetic field of 0–700 mT range was used for the measurements. The studied sample (~ 100 mg) was placed into a 4 mm quartz tube, the lines of the sample and the reference were registered one after another using 5 mT scan step. The resulted spectra were normalized to the reference signal intensity and normalized to 100 mg weight.

The near-edge X-ray absorption fine structure (NEXAFS) of the Mn2p-absorption spectra of the Mn-doped solid solutions ($\text{BiNb}_{1-x}\text{Mn}_x\text{O}_{4-\delta}$) and manganese oxides (MnO , Mn_2O_3 and MnO_2) was obtained by means the synchrotron radiation source (Russian-German Laboratory at BESSY II) [22]. The total electron yield (TEY) mode was used to register the spectra [23].

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 AlK_α 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 C 1s peak at 284.4 eV. The experimental data were processed using the ESCALAB 250 Xi spectrometer software.

3 Results and discussion

The formation of the solid solutions $\text{BiNb}_{1-x}\text{Mn}_x\text{O}_{4-\delta}$ of orthorhombic and triclinic modifications was confirmed by X-ray phase analysis (Figure 1) and electron scanning microscopy (Figure 2). The previous study [24] has shown that manganese-doped solid solutions can be formed in a limited concentration range, at $x \leq 0.06$. The unit cell parameters of the solid solutions are slightly different from the parameters of bismuth orthoniobate of triclinic and orthorhombic modifications [24]: $a = 7.60(4)$ Å, $b = 5.53(6)$

Figure 1: X-Ray pattern for $\text{BiNb}_{0.96}\text{Mn}_{0.04}\text{O}_{4-\delta}$ of orthorhombic (α) and triclinic (β) modifications.

Figure 2: Energy dispersion spectrum of $\text{BiNb}_{0.96}\text{Mn}_{0.04}\text{O}_{4-\delta}$ of triclinic (a) and orthorhombic (b) modifications and photomicrography of its surface in the mode of secondary and elastic backscattered electrons.

$\text{\AA}$, $c = 7.92(9) \text{ \AA}$, $\alpha = 90.0(5)^\circ$, $\beta = 77.4(1)^\circ$, $\gamma = 87.1(7)^\circ$ ($x = 0.005$) and $a = 7.60(5) \text{ \AA}$, $b = 5.53(7) \text{ \AA}$, $c = 7.92(5) \text{ \AA}$, $\alpha = 90.1(3)^\circ$, $\beta = 77.4(6)^\circ$, $\gamma = 87.2(3)^\circ$ ($x = 0.06$). The method of microprobe analysis confirmed that the samples of solid solutions did not contain impurity phases (Figure 2). EDS showed that the manganese content in the samples corresponds to the formula composition. The micrographs (Figure 2) revealed significant differences in morphology of the samples of triclinic and orthorhombic modifications. The samples of orthorhombic modification have low-porosity granular microstructure consisting of coalescent grains of elongated shape, the sizes of which vary from 1 to 3 μm . The samples of triclinic modification are pore-free monolithic compacts with weakly manifested grain boundaries.

Thermal behavior and effects associated with the phase transformations of the obtained solid solution samples $\text{BiNb}_{1-x}\text{Mn}_x\text{O}_{4-\delta}$ ($x=0.01$; 0.02; 0.04) of orthorhombic modification were studied by thermal analysis in the heat-

Figure 3: DSC and TG curves of $\alpha\text{-BiNb}_{1-x}\text{Mn}_x\text{O}_{4-\delta}$ at $x=0.04$ (a), 0.02 (b) and 0.01 (c) in the heating-cooling regime in the interval of $25^\circ\text{C} \rightarrow 1100^\circ\text{C} \rightarrow 700^\circ\text{C}$.

ing and cooling modes in the temperature range 25 - 1100 - 700°C . As can be seen from Figure 3, the mass changes in the TG curves of the samples did not exceed 1 mass.% during heating up to 1100°C , which indicated the constancy of the composition of the samples during the phase transformations. In the heating mode, around $1040\text{--}1060^\circ\text{C}$, the DSC curves showed the endothermic effect, the temperature of which decreased with increasing manganese content in the samples, e.g., for $x = 0.01$ the peak temperature of the effect was 1063°C (Figure 3a-c). During the cooling, near the temperature of 997° , all the samples exhibited the exothermic effect associated with the phase transition to the triclinic modification. As we found earlier, the significant difference in the thermal effects of the endothermic and exothermic processes was caused by the existence of fourth high-temperature modification of bismuth orthoniobate ($\gamma\text{-BiNbO}_4$), which was first mentioned in the article of A.W. Sleight *et al.* [25], and by the sequence of the phase transitions from $\alpha\text{-BiNbO}_4 \rightarrow \gamma\text{-BiNbO}_4 \rightarrow \beta\text{-}$

Figure 4: Diffraction patterns of $\text{BiNb}_{1-x}\text{Mn}_x\text{O}_{4-\delta}$ sample in triclinic ($x=0.01$ (1), 0.02 (2)) and orthorhombic ($x=0.03$ (3), 0.04 (4), 0.06 (5); synthesis temperature – 750°C , 120 h) modifications.

Figure 5: Microscope image of the surface in the mode of secondary and elastically reflected electrons, EDX spectrum of $\text{BiNb}_{0.94}\text{Mn}_{0.06}\text{O}_{4-\delta}$ (a) and $\text{BiNb}_{0.98}\text{Mn}_{0.02}\text{O}_{4-\delta}$ (b) with orthorhombic and triclinic structures obtained from triclinic modification at 750°C .

BiNbO_4 . There were no other thermal effects detected in this temperature range. The phase transition observed in bismuth orthoniobate and its solid solutions by the authors of [19, 20] at 750°C was not revealed in the DSC curves in the present work. Thus, it was not possible to obtain indirect confirmation of the reversibility of the phase transition by the method of thermal analysis during cooling the sample of triclinic modification to 700°C . This may indicate either the absence of the phase transformation or its slow and diffusion character.

The works [19, 20] revealed that the orthorhombic modification can be obtained from the triclinic modification by prolonged calcination of a compact sample at the temperature of 750°C . As expected, the continuous calcination of the solid solution samples of triclinic modification for more than 120 hours led to that result. The samples with the maximum manganese content ($x = 0.06$; 0.04 ; 0.03), according to XRD data (Figure 4), had the orthorhombic structure. The samples with $x = 0.01$ and 0.02 remained in the triclinic modification, which indicated the destabilizing effect of manganese atoms on structure of the

Figure 6: NEXAFS $\text{Mn}2p$ -spectra of the manganese-containing solid solutions $\text{BiNb}_{0.94}\text{Mn}_{0.06}\text{O}_{4-\delta}$ synthesized at the temperature of 950°C , 1100°C , 750°C and manganese oxides MnO , Mn_2O_3 and MnO_2 .

solid solutions. The samples of the solid solutions ($x = 0.01$; 0.02 ; 0.03 ; 0.04 ; 0.06) calcined at 750°C were studied by microprobe analysis and EDS. As a result of these analysis, it was shown that the samples were free from impurity phases and manganese atoms were registered in the composition of the solid solutions (Figure 5). The microstructure of the solid solution samples with the orthorhombic structure (synthesized at the temperature of 750°C) did not correspond to the microstructure of the solid solution samples of orthorhombic modification described above, but rather resembled the microstructure of the samples of triclinic modification.

In order to study the electronic state of manganese atoms in the polymorphs of bismuth orthoniobate solid solutions, the samples were analyzed using the NEXAFS, XPS and ESR spectroscopy methods. As can be seen from the $\text{Mn}2p$ -absorption spectra of the manganese doped solid solution $\text{BiNb}_{0.94}\text{Mn}_{0.06}\text{O}_{4-\delta}$ successively calcined at the temperatures of 950°C (the orthorhombic modification), 1100°C (the triclinic modification) and 750°C (the orthorhombic modification), the unambiguous determination of the degree of oxidation of manganese atoms in the solid solutions from these spectra is not possible (Figure 6). Probably, these solid solutions contain manganese atoms of various valence (II), Mn(III) , Mn(IV) . As the tempera-

Figure 7: XPS spectra of $\text{BiNb}_{1-x}\text{Mn}_x\text{O}_{4-\delta}$ ($x=0.03$) solid solution samples of triclinic (BNM3) and of orthorhombic (BNM1) modifications (a); XPS Nb3d spectra of the samples BNM1 and BNM3 (b); XPS Bi 4f spectra of the samples BNM1 and BNM3 (c); XPS O1s spectra (d); XPS Mn2p spectra of the samples BNM1 (e).

ture and duration of the heat treatment increased, the ratio of the absorption lines recorded at 642 and at 640.5 eV changed. This can be related with the increase in the fraction of manganese (III) and in the degree of distortion of the polyhedral surroundings of paramagnetic atoms. It is interesting to note that the solid solutions of orthorhombic modification synthesized at 950 and 750°C had different nature of the surroundings and valence composition of manganese atoms, which may be due to the different distribution of manganese atoms in the structure, as well as due to the amount and composition of clusters of paramagnetic atoms in the solid solutions.

The $\text{BiNb}_{1-x}\text{Mn}_x\text{O}_{4-\delta}$ ($x=0.03$) samples of the orthorhombic (BNM1) and triclinic (BNM3) modifications were studied by XPS-spectroscopy (Figure 7a-e). Figure 7 shows survey scans and the XPS Bi 4f-, Nb 3d-, O 1s- and Mn 2p-spectrums of the $\text{BiNb}_{1-x}\text{Mn}_x\text{O}_{4-\delta}$ samples of the orthorhombic (BNM1) and triclinic (BNM3) modifications. The spectra were fitted with Gaussian-Lorentzian line profiles and a Shirley- or smart-background. Energy positions and the interpretation of the elements of the spectra are presented in Table 1.

The XPS Nb3d spectra of the samples BNM1 and BNM3 (Figure 7b) were characterized by the similarity of the main spectral details in relative intensity and in their energy position, despite the significant differences in the degree of distortion of the coordination polyhedron of niobium

atoms in structures of the orthorhombic and triclinic modifications [12–14]. The identity of the XPS Nb3d spectra allowed us to suggest that the niobium atoms had almost the same charge state, which is determined mainly by the nearest surroundings of these atoms. The similar conclusions can be made by analysis of the spectra of bismuth atoms (Figure 7c), which are also characterized by the change in the shape of the first coordination sphere during the transition from α - to β - BiNbO_4 [26, 27]. In both crystal structures, bismuth atoms are surrounded by six oxygen atoms with a set of nonequivalent Bi-O distances. However, in the orthorhombic modification, the coordination sphere of bismuth had the shape of the distorted octahedron (BiO_6), and, in the triclinic structure, it had the antiprism (BiO_8) shape. The energy position of the peaks in the XPS Bi4f spectrum is characteristic of the trivalent bismuth atom [28]. The similar conclusions were made on the basis of the analysis of XPS spectra of BiNbO_4 doped with silver [29], zinc and lanthanum [30], as well as undoped α - BiNbO_4 [22]. In addition, taking into account the energy shift between the XPS spectra, $\Delta E(\text{O-Bi})=371.1$ eV [28], the peak B in the XPS O1s spectra (Figure 7d) can be associated with the oxygen atoms forming the Bi-O bond ($\Delta E(\text{O-Bi})=371.19$ eV (Table 1)).

This conclusion was supported by the fact that the ratio of the areas of the peaks $B_1(\text{Bi 4f})/B(\text{O 1s})$ was 0.67, which corresponded to the Bi_2O_3 stoichiometry. As a re-

Table 1: The energy positions of components of the XPS spectra.

Peak	Energy (eV)		Interpretation
	BNMI	BNM3	
Nb3d A ₁	206.39	206.44	3d _{5/2}
Nb3d A ₂	209.15	209.21	3d _{3/2}
Bi4f B ₁	158.83	158.79	4f _{7/2}
Bi4f B ₂	164,15	164,16	4f _{5/2}
O1s A	529.35	529.46	O-Nb
O1s B	530.02	529.97	O-Bi
O1s C	531.42	531,17	Adsorbed O/ vacancy V ₀
Mn2p A ₁	640.75	640.80	2p _{3/2} Mn(II)
Mn2p A ₂	651.65	652.60	2p _{1/2} Mn(II)
Mn2p B ₁	641.90	641.88	2p _{3/2} Mn(II)
Mn2p B ₂	653.75	652.85	2p _{1/2} Mn(III)
Mn2p A ₁ /	645.90	645.86	2p _{3/2} Mn(II) satellite
Mn2p A ₂ /	657.18	656.76	2p _{1/2} Mn(II) satellite

sult, the interpretation of the peaks A and C in the oxygen spectrum became easier. The peak C in the spectrum (~531 eV) is usually attributed to oxygen adsorbed on the surface of samples [31, 32] or oxygen found in lattice defects [32, 33]. Taking into account the energy shift $\Delta E(\text{O-Nb})=222.96$ eV characteristic of Nb₂O₅ ($\Delta E(\text{O-Nb})=223.1$ eV [34]), the peak A should be associated with oxygen atoms participating in the Nb-O bond. This conclusion correlates with the interpretation of the XPS Nb3d spectra in [22, 29, 30]; however, the areas of the peaks, $A_1(\text{Nb } 3d)/A(\text{O } 1s)=0.42$ for $\alpha\text{-BiNbO}_4$ and 0.47 for $\beta\text{-BiNbO}_4$, differ from 0.4 (Nb₂O₅). Moreover, in spite of the energy shift between the spectra of niobium and oxygen $\Delta E(\text{O-Nb})$ characteristic of Nb₂O₅ [34], here, as well as in works [22, 29, 30], the whole structure of the Nb3d spectrum was shifted towards lower energies as a result of the doping: the energies of the peak 3d_{3/2} were 206.4 eV (our data), 206.8 [29] and 206.2 [30]; in the absence of doping, this value was 207.1 eV [22]. Additionally, the position of this peak in Nb₂O₅ varies from 207.1 to 207.5 eV according to various literary sources [34, 35]. Taking into account the above, it can be assumed that the doping of BiNbO₄ with manganese atoms decreases the total charge state of niobium atoms, which can be estimated as Nb^{+4.8} in $\alpha\text{-BiNbO}_4$ and Nb^{+4.3} in $\beta\text{-BiNbO}_4$. The similar behavior of niobium spectra was observed and the similar conclusions about the state of niobium atoms were made in [32] during the deposition of lithium atoms on Nb₂O₅ surface. Figure 7e presents the total spectrum of manganese atoms in $\alpha\text{-BiNb}_{0.97}\text{Mn}_{0.03}\text{O}_4$ (BNM1) and the result of its fitting into separate spectral lines, the energy position and identification of which are presented in Table 1. The positions of the peaks A1 and A2 correspond to

the binding energies of the Mn2p_{3/2}- and Mn2p_{1/2}- levels in MnO, i.e. the divalent manganese atom (A₁' and A₂' are the satellites in the spectrum of Mn(II)), and B₁ and B₂ correspond to the trivalent atom in the spectrum of Mn₂O₃ [31, 32, 36]. The ratio of the areas of the peaks A₁/B₁=1.3, i.e. on average, there is one atom of manganese with the effective charge of +3 per 1.3 atoms of Mn²⁺. This makes it possible to estimate the effective charge of manganese atoms as Mn^{+2.43}. The obtained result is very approximate, since the portion of manganese (IV) atoms revealed by ESR and magnetic susceptibility was not taken into account. However, this result satisfactorily correlated with the NEXAFS data regarding the presence of Mn with the oxidation degrees other than Mn(II) in the samples of the solid solutions. It should be noted that the manganese atoms in MnO and Mn₂O₃ had the octahedral coordination, as well as the niobium atoms in BiNbO₄. This led to the suggestion on the distribution of manganese atoms in the cationic positions of niobium in bismuth orthoniobate. This suggestion was experimentally confirmed by the shift of the XPS Nb 3d-spectra toward lower binding energies, associated with the change in the charge state of atoms of niobium (V).

The ESR spectra of the solid solutions BiNb_{1-x}Mn_xO_{4-δ} (x = 0.01; 0.02; 0.04; 0.06) of the triclinic (1100°C) and orthorhombic (750°C) modifications were obtained (Figure 8, 9). The main differences between the ESR spectra of the triclinic and orthorhombic modification (750°C) solid solutions are the absence of the absorption band at g ~ 3.8 with a characteristic sextet structure and the decrease in the integrated intensity of the absorption line. In the spectra of the orthorhombic modification samples (750°C, x = 0.04; 0.06) (Figure 9), a broad component

Figure 8: ESR spectra of $\text{BiNb}_{1-x}\text{Mn}_x\text{O}_{4-\delta}$ ($x=0.04$ and 0.06) solid solution samples of triclinic (red, 1100°C) and of orthorhombic (blue, 750°C) modifications. Reference sample line with $g=2.0032$.

of average intensity was identified at $g \sim 2.0$ - 2.2 , which can be attributed to Mn(II) and Mn(IV) ions or their clusters [37]. The decrease in the integrated intensity of the absorption lines can be associated with oxidation of a part of Mn(II) ions to Mn(III) and Mn(IV) during the prolonged calcination of the samples in the oxidizing environment at 750°C . In the ESR spectra of the samples ($x = 0.01$ and 0.02) calcined at 750°C , but preserved the triclinic structure, according to XRD, changes were also observed (Figure 9) in the low-field part of the spectrum. The weakly manifested low-intensity signal appeared at $g = 3.8$ with the degradation of the sextet structure characteristic of manganese atoms in the triclinic modification. Additionally, the intensity of the wide absorption band with $g = 2.0$ - 2.2 changed. The sextet fine structure attributed to Mn(II) ions in the weak crystal field [38] was observed on the background of this band. The phase transition from the triclinic to the orthorhombic modification triggered by prolonged calcination probably resulted in the following simultaneous processes that affected the shape of the ESR spectra of manganese in the solid solutions: the oxidation of a part of manganese atoms predominantly to Mn(III) and Mn(IV) and the rearrangement of the crystal structure of the solid solutions. In the XPS, ESR and NEXAFS spectra, the differences between the manganese-doped solid solution samples of orthorhombic modifications obtained at 750 and 950°C were due to the difference in the relative content of manganese atoms of different valences in the solutions, namely Mn(III) , as well as due to the distribution and qualitative composition of their clusters.

Thus, the comprehensive study of the phase transitions of bismuth orthoniobate using the example of manganese-doped solid solutions showed that the poly-

Figure 9: ESR spectra of $\text{BiNb}_{1-x}\text{Mn}_x\text{O}_{4-\delta}$ ($x=0.01$ and 0.02) solid solution samples of triclinic (red, 1100°C) and of orthorhombic (blue, 750°C) modifications.

morphs change the qualitative and quantitative characteristics of the NEXAFS, XPS and ESR spectra. The results obtained in this study are important for selection of optimal conditions of production of functional materials (ceramics, thin films, etc.) based on bismuth niobate, as well as for estimation of their performance characteristics.

4 Conclusions

The method of X-ray phase analysis confirmed the reversibility of the phase transition from the orthorhombic modification to the triclinic modification at 750°C for 120 hours. It was established that manganese atoms destabilize the structure of solid solutions, and therefore phase transformations for them occur faster and at lower temperature. The DSC curves revealed no thermal effects near 750°C associated with the phase transformation from the triclinic modification to the orthorhombic one, probably due to the slow process. The characteristic differences in the ESR spectra of the manganese-doped solid solutions of triclinic and orthorhombic modifications were revealed. It was shown that the phase transition from the triclinic modification to the orthorhombic modification led to the disappearance of the absorption band characteristic for the β -phase with $g = 3.8$ and the manifested sextet structure from manganese (II) atoms. The duration of the heat treatment of the samples of triclinic structure in the oxidizing environment was the cause of the partial oxidation of manganese atoms to Mn(III) , according to XPS, NEXAFS and ESR spectra.

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