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# Structural, Magnetic, and Electric Properties of Bismuth Niobates Doped with *d* Elements: X.[1] State of Nickel in $Bi_3Nb_{1-x}Ni_xO_{7-\delta}$ Solid Solutions with a Fluorite-Type Structure

**N. V. Chezhina[a], N. A. Zhuk[b], V. N. Zharenkova[b], and V. P. Lyutoev[c]**

[a] *St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia*
*e-mail: chezhina@nc2490.spb.edu*

[b] *Syktyvkar State University, Oktyabr'skii pr. 55, Syktyvkar, Komi Republic, 167001 Russia*

[c] *Institute of Geology, Komi Scientific Center, Ural Division, Russian Academy of Sciences, ul. Pervomaiskaya 54, Syktyvkar, Komi Republic, 167982 Russia*

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**Abstract**—A magnetic susceptibility study of $Bi_3Nb_{1-x}Ni_xO_{7-\delta}$ solid solutions showed that paramagnetic nickel atoms occur in the solid solutions as Ni(II) monomers, Ni(III) monomers, and exchange-coupled dimers formed by Ni(III) atoms and characterized by the magnetic exchange parameter $J$ of –155 $cm^{-1}$. The distribution of the monomers and dimers of nickel atoms as a function of the solid solution concentration was calculated.

**Keywords:** bismuth niobate, fluorite-type structure, magnetic properties, exchange interactions

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Bismuth oxide-based solid electrolytes have recently been the subject of much research as good oxygen ion conductors with promising applications in fuel cells, oxygen sensors, and oxygen-conducting membranes of catalytic reactors [2–4]. The ionic conductivity in the cubic high-temperature phase of bismuth oxide (δ-$Bi_2O_3$), required for its practical application, is achieved at 730°C (1.0 S/cm [5]).

Highly conducting δ-phase of bismuth oxide is stable in a narrow temperature range of 730–825°C, which significantly limits the scope of its practical application [6]. Stabilization of δ-$Bi_2O_3$ phase can be achieved through partial isovalent substitution of bismuth with trivalent ions (Gd, Y, Er) or via heterovalent substitution (Nb, Ta, W) [7–11]. Substituted solid solutions are mixed electronic-ionic conductors which are promising for application in electrochemical devices [12, 13].

The greatest interest is attracted by substitution of bismuth by niobium atoms due to a high stability of the resulting cubic phase at room temperature. The minimum molar fraction of niobium atoms required for δ-$Bi_2O_3$ phase stabilization was estimated at 6 mol % [11].

Phase diagram studies of the $Bi_2O_3$–$Nb_2O_5$ binary system revealed the formation in the system at the bismuth to niobium molar ratio $1 : 0 \le n(Bi) : n(Nb) \le 5 : 3$ of at least four different types of fluorite-type crystal structures **I–IV** [14, 15].

The cubic structure **II** is formed at 6 to 25 mol % content of niobium atoms [15]; the composition of the solid solution with a quarter of bismuth atoms substituted by niobium atoms is described by the stoichiometric formula $Bi_3NbO_7$. Bismuth niobate $Bi_3NbO_7$ crystallizes in two polymorphic modifications, tetragonal **III** and cubic **II** [14]. The tetragonal phase is formed in the 800–900°C temperature range and is stable down to room temperature; beyond this temperature range (700°C), cubic modification of bismuth niobate is formed [15, 16].

Cubic bismuth niobate $Bi_3NbO_7$ has a defect fluorite-type structure (*Fm*3*m* space group) with the

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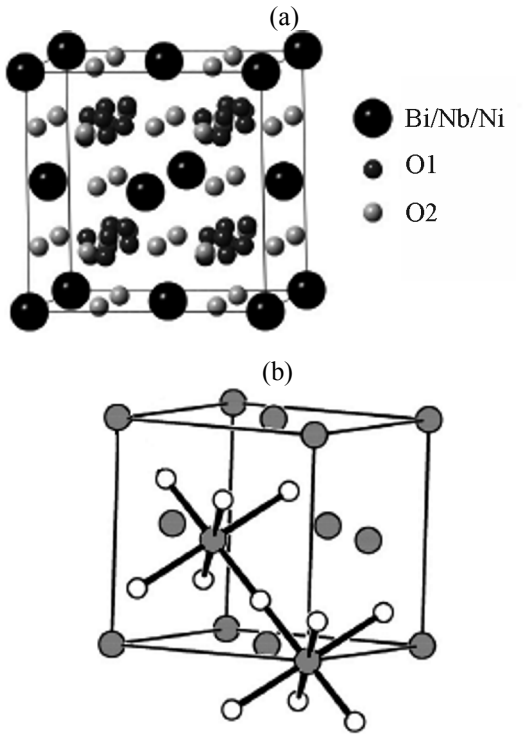


**Fig. 1.** (a) Crystal structure of $Bi_3Nb_{1-x}Ni_xO_{7-\delta}$ [4] and (b) mutual arrangement of paramagnetic atoms in the solid solutions.

unit cell parameter of 0.5479 nm. The bismuth and niobium atoms are distributed over the same system of crystallographic sites in the molar ratio of 3 : 1, with niobium atoms adopting the distorted octahedral coordination geometry [8]. The neutron diffraction data suggest the formation of clusters from niobium-oxygen octahedra in the cubic structure of bismuth niobate [14, 17].

Bismuth niobate is significantly superseded by δ-$Bi_2O_3$ in electrical conductivity [18] because of a twofold lower fraction of oxygen vacancies in its structure (12.5 against 25%). With the view of increasing the electrical conductivity of bismuth niobate, heterovalent substitution of niobium by zirconium [19], yttrium [20], tungsten [21], and erbium [22] atoms was carried out. A neutron diffraction examination of the crystal structure of the resulting solid solutions showed that the dopant atoms adopt an octahedral coordination geometry and undergo clusterization to form chains of octahedra [19–22].

A systematic study of the magnetic properties of isomorphically substituted bismuth niobate solid solutions allows modeling their electronic structure,

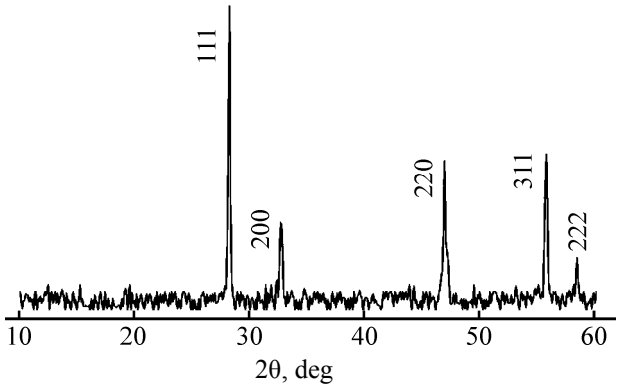


**Fig. 2.** The X-ray diffraction pattern of the $Bi_3Nb_{0.97}Ni_{0.03}O_{7-\delta}$ solid solution.

evaluating the exchange interaction nature and energy, and elucidating the electronic state of paramagnetic atoms and their role in stabilization of vacancies in the crystal structure [23–26].

Our study was concerned with the behavior of paramagnetic nickel atoms in the cubic diamagnetic bismuth niobate $Bi_3NbO_7$ matrix (Fig. 1a).

The $Bi_3Nb_{1-x}Ni_xO_{7-\delta}$ solid solutions were obtained in a narrow nickel concentration range $x < 0.065$ (Fig. 2). The unit cell parameter of the solid solutions remains virtually unchanged and is close to that of bismuth niobate [8].

Basing on the measured magnetic susceptibility of the solid solutions we calculated the paramagnetic components of magnetic susceptibility [$\chi^{para}$(Ni)] and the effective magnetic moment [$\mu_{eff}$(Ni)] of nickel atoms at various temperatures and various concentrations in the solid solutions. The diamagnetic corrections were introduced in the calculated paramagnetic component of magnetic susceptibility with regard to the susceptibility of the cubic bismuth niobate $Bi_3NbO_7$ matrix measured in the same temperature range.

For all solid solutions the temperature dependence of the reciprocal of the molar paramagnetic component of magnetic susceptibility calculated per mole of nickel atoms obeys the Curie–Weiss law over the temperature range examined. The isotherms of the paramagnetic component of magnetic susceptibility of nickel [$\chi^{para}$(Ni)] are typical for antiferromagnetics (Fig. 3). Extrapolation of the concentration dependences of [$\chi^{para}$(Ni)] and [$\mu_{eff}$(Ni)] to infinite dilution of the solid solution gave the effective magnetic moment of single nickel atoms $\mu_{eff}$(Ni) of 2.56 BM on the average

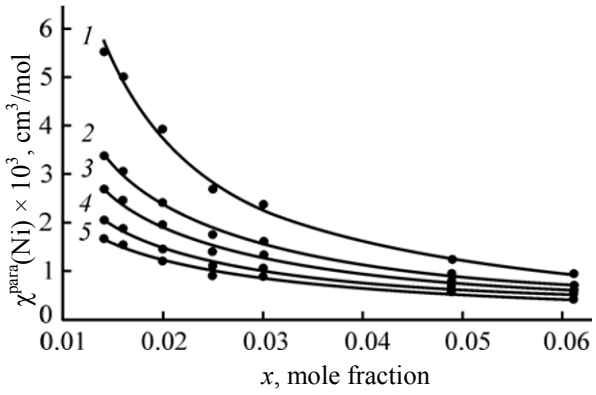


**Fig. 3.** Isotherms of the paramagnetic component of magnetic susceptibility of nickel atoms in the $Bi_3Nb_{1-x}Ni_xO_{7-\delta}$ solid solutions at (*1*) 90, (*2*) 140, (*3*) 180, (*4*) 240, and (*5*) 293 K.

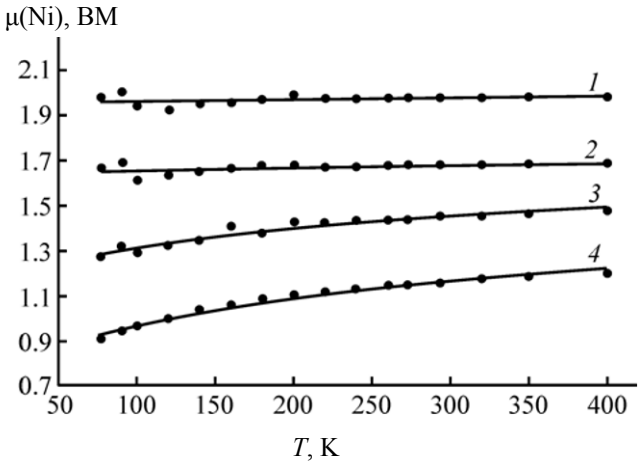


**Fig. 4.** Temperature dependences of the magnetic moment of nickel in the $Bi_3Nb_{1-x}Ni_xO_{7-\delta}$ solid solutions with *x* of (*1*) 0.014, (*2*) 0.02, (*3*) 0.03, and (*4*) 0.049.

independently of temperature, which points to absence of nickel(III) atoms in the high-spin state ($^4T_{2g}$).

| *T*, K | 90 | 140 | 180 | 240 | 293 |
|---|---|---|---|---|---|
| μ, BM | 2.61 | 2.53 | 2.54 | 2.57 | 2.57 |

The value of the magnetic moment is indicative of the occurrence of nickel(II) [$\mu_{eff}$(Ni) ~ 2.83 BM] and nickel(III) [$\mu_{eff}$(Ni) ~ 1.73 BM] atoms in the low-spin state ($^2E_g$). The presence in a dilute solution of exchange-coupled aggregates of paramagnetic nickel atoms Ni(II)–O–Ni(II) with antiferromagnetic exchange is hardly probable, according to the temperature dependences of the magnetic moment of nickel(II) at small *x* values (Fig. 4, curves *1* and *2*).

It can be assumed that, while leaving unaffected the crystal structure, heterovalent substitution of niobium by nickel atoms causes a charge imbalance, whereby a part of nickel atoms is oxidized to Ni(III). As noted in [27], the low-spin state of oxidized atoms results from a significant distortion of their coordination polyhedrons. The fraction of the low-spin Ni(III) atoms in the solid solutions at $x > 0$ was estimated by formula (1).

$$\mu^2_{exp}(Ni) = b\mu^2_{Ni(II)} + (1 - b)\mu^2_{Ni(III)}. \quad (1)$$

Here, *b* is the fraction of nickel(II) atoms and $\mu_{Ni(II)}$ and $\mu_{Ni(III)}$, spin-only magnetic moments of nickel(II) and low-spin Ni(III) atoms, respectively.

The calculation yielded ~30 mol % fraction of Ni(III) atoms in infinitely dilute solid solution. As the concentration of paramagnetic atoms in the solid solutions increases, the magnetic moment of nickel atoms tends to increase with temperature, which is indicative of antiferromagnetic exchange between paramagnetic atoms (Fig. 3).

The ESR spectrum of the solid solution with $x = 0.005$ contains a broad anisotropic signal which is a superposition of an intense line and a weak line with *g*-factors of 2.32 and 2.09, respectively. For the solid solution with $x = 0.015$ the line with the *g*-factor of 2.09 has a higher intensity and can be assigned to Ni(III) atoms [28]. The line with the *g*-factor of 2.32 suggests the presence of nickel(II) atoms assuming a nonoctahedral coordination [29]. This finding may be interpreted as indicating that larger nickel(II) ions {$r_{ion}[Ni(II)]_{cn6}$ 0.70 nm, $r_{ion}[Nb(V)]_{cn6}$ 0.64 nm} easily occupy the vacant bismuth sites available due to volatility of bismuth(III) compounds [6].

It is logical to assume that the number of nickel(II) atoms occupying the vacant bismuth sites will remain unchanged with increasing nickel concentration in the solid solutions. The remaining nickel atoms will occupy the octahedral sites of niobium and undergo oxidation to nickel(III), as is typically the case of complex oxides (so-called forced oxidation in which the electronic balance is preserved to the greatest extent). Obviously, nickel(III) will occur in the low-spin state, because the Nb–O octahedra are significantly distorted in the initial $Bi_3NbO_7$ structure and also due to vacancies arising in the oxygen sublattice [19–22]. In this case, nickel(II) fraction would decrease with increasing concentration, and a decrease in the paramagnetic component of the

magnetic susceptibility could be attributed to formation of clusters with octahedral structure from nickel(III) atoms.

To test this assumption and to determine the exchange parameter for nickel(III) atoms we carried out a model calculation of the magnetic susceptibility of the solid solutions. The experimental dependences of $\chi^{para}$(Ni) on the solid solution concentration were calculated in terms of the dilute solution model which defines the magnetic susceptibility as the sum of the contributions from the single paramagnetic atoms (monomers) and their aggregates M–O–M (dimers). In the first stage of the calculation we restricted ourselves to specifically dimers, since formation of larger clusters in the concentration range of interest is hardly probable. The monomers were Ni(II) and Ni(III) atoms, and the Ni(III)–O–Ni(III) dimers were formed by paramagnetic nickel(III) atoms. Formula (2) defines the paramagnetic component of the magnetic susceptibility of nickel atoms as the sum of the contributions from the magnetic susceptibilities of the monomers and dimers:

$$\chi^{para}_{calc}(\text{Ni}) = (1-b)[a^{dim}_{\text{Ni(III)–Ni(III)}}\chi^{dim}_{\text{Ni(III)–Ni(III)}} + (1 - a^{dim}_{\text{Ni(III)–Ni(III)}}\chi^{mon}_{\text{Ni(III)}}] + b\chi^{mon}_{\text{Ni(II)}}. \quad (2)$$

Here, $b$ is the fraction of nickel(II) atoms, $a^{dim}_{\text{Ni(III)–Ni(III)}}$, fraction of dimers formed by nickel(III) atoms that appear with antiferromagnetic exchange, and $\chi^{mon}_{\text{Ni(II)}}$, $\chi^{mon}_{\text{Ni(III)}}$, and $\chi^{dim}_{\text{Ni(III)–Ni(III)}}$ magnetic susceptibilities of Ni(II) monomers, Ni(III) monomers, and Ni(III)–O–Ni(III) dimers, respectively.

Formula (2) contains three independent parameters: the fractions of isolated Ni(II) and Ni(III) atoms and the parameter of antiferromagnetic exchange between nickel atoms $J_{\text{Ni(III),Ni(III)}}$, implicitly included in the formula.

In terms of Heisenberg–Dirac-Van Vleck theory [23], the magnetic susceptibility of dimers consisting of paramagnetic atoms can be calculated by formula (3).

$$\chi_{dim} = \frac{N\beta^2}{2\cdot 3kT}\frac{\sum_{S'} g^2(S')S'(S'+1)(2S'+1)e^{-E(J,S')/kT}}{\sum_{S'}(2S'+1)e^{-E(J,S')/kT}}. \quad (3)$$

Here, $E(J, S') = \ldots..|S_a - S_b|$; $S_a$, $S_b$ are the spins of the atoms constituting the dimer, in our case $S_a = S_b = S[\text{Ni(III)}] = 1/2$; $g$, $g$-factor of nickel(III) atoms; $J$, exchange parameter; and $T$, absolute temperature.

The magnetic susceptibility of the Ni(III)–O–Ni(III) dimers was calculated by formula:

$$\chi^{dim}_{1/2-1/2} = \frac{N\text{g}^2\beta^2}{2\cdot 3kT}\cdot 2[1 + (1/3)\exp(-2J/kT)]^{-1}. \quad (4)$$

Here, $\chi^{dim}_{1/2-1/2}$ is the paramagnetic component of the magnetic susceptibility of the dimers.

An agreement between the calculated and experimental data was achieved by minimizing the $\Sigma\Sigma_{i\ j}[(\chi^{calc}_{ij})^2 - (\chi^{exp}_{ij})^2]$ function, where $\sum_i$ and $\sum_j$ denote summations over all concentrations and over all temperatures, respectively, and $\chi^{calc}_{ij}$, $\chi^{exp}_{ij}$ (are the calculated and experimental paramagnetic components of magnetic susceptibility of the solid solutions, respectively.

The best agreement between the experimental and calculated data was achieved at the $J_{\text{Ni(III)–O–Ni(III)}}$ exchange parameter of –155 cm$^{-1}$; table compares the experimental and theoretical magnetic susceptibilities of the $Bi_3Nb_{1-x}Ni_xO_{7-\delta}$ solid solutions. The experimental and calculated data agree to within 5%, on the average.

The calculation showed that with increasing concentration of the solid solution the total number of nickel(III) atoms (in the form of monomers and dimers) tends to increase, while the fraction of nickel(II) atoms in the bismuth(III) sites tends to decrease (Fig. 5). With increasing fraction of nickel atoms in the solid solutions the fraction of the Ni(III) monomers tends to decrease due to an increase in the number of the Ni(III)–O–Ni(III) dimers appearing with anti-ferromagnetic exchange.

Noteworthy is the antiferromagnetic, on the whole, exchange between paramagnetic atoms. This type of exchange is possible in cases where indirect exchange interaction occurs between the atoms situated on the face diagonals of the unit cell, e.g., via the $d_{x^2-y^2}||p_x||d_{x^2-y^2}$ exchange channel (Fig. 1b). This conclusion is consistent with clustering of the niobium-oxygen octahedra, assumed on the basis of analysis of the superstructure in cubic bismuth niobate and solid solutions [4, 14, 17, 19–22]. The antiferromagnetic exchange parameter $J$ is –155 cm$^{-1}$, which is smaller in absolute value than the exchange parameter for paramagnetic nickel atoms in layered perovskite-like structures of bismuth niobate [1, 30]. This indirectly evidences the distortion of the

Results of calculation of the distribution of nickel atoms in the $Bi_3Nb_{1-x}Ni_xO_{7-\delta}$ solid solutions[a]

| $x$ | $a^{mon}_{Ni(III)}$ | $a^{mon}_{Ni(II)}$ | $a^{dim}_{Ni(III)-Ni(II)}$ | $\chi_{exp(theor)} \times 10^3$, cm$^3$/mol | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | 90 K | 140 K | 180 K | 240 K | 293 K |
| 0.000 | 0.30 | 0.70 | 0.00 | 9.35(8.95) | 5.66(5.76) | 4.46(4.48) | 3.41(3.36) | 2.80(2.75) |
| 0.014 | 0.21 | 0.40 | 0.39 | 5.52(5.30) | 3.37(3.47) | 2.68(2.74) | 2.02(2.11) | 1.66(1.75) |
| 0.020 | 0.17 | 0.28 | 0.55 | 3.93(3.75) | 2.41(2.50) | 1.94(2.01) | 1.45(1.58) | 1.19(1.33) |
| 0.030 | 0.11 | 0.16 | 0.73 | 2.37(2.31) | 1.60(1.60) | 1.30(1.34) | 1.06(1.09) | 0.89(0.94) |
| 0.049 | 0.04 | 0.09 | 0.87 | 12.2(12.1) | 0.95(0.92) | 0.81(0.82) | 0.66(0.72) | 0.57(0.65) |

[a] $a^{mon}_{Ni(III)}$ is the fraction of the nickel(III) monomers; $a^{mon}_{Ni(II)}$, fraction of the nickel(II) monomers; and $a^{dim}_{Ni(III)-Ni(II)}$, fraction of the nickel(III) dimers.

coordination polyhedra and deviation of the bond angle from 180°. The formation of dimers rather than of more complex aggregates or chains of paramagnetic atoms is due apparently to a low concentration of paramagnetic atoms in the solid solutions.

Thus, heterovalent substitution in bismuth niobate solid solutions results in accumulation of oxygen vacancies destabilizing the crystal structure with increasing nickel fraction, which leads to forced oxidation of paramagnetic nickel atoms, especially pronounced at low nickel concentrations. The stability of the structure upon further heterovalent substitution is obviously determined by the formation of exchange-coupled aggregates localized in the vicinity of the oxygen vacancies.

## EXPERIMENTAL

The solid solutions were prepared by the standard ceramic synthesis route from extra pure grade bismuth(III) and Nb(V) oxides and chemically pure nickel(II) oxide at 650 (10 h) and 950°C (60 h). The phase composition of the compounds was monitored by X-ray diffraction analysis (DRON-4-13, Cu$K_\alpha$ radiation); the unit cell parameters of the solid solutions were calculated using the CSD software package [31].

Nickel in the solid solution samples was quantitatively determined on a SPECTRO CIROS inductively-coupled plasma atomic emission spectrometer accurately to within 5% of $x$ in the solid solution formula.

The magnetic susceptibility of the solid solutions was measured by the Faraday method in the 77–400 K temperature range at 16 fixed temperatures. The accuracy of relative measurements was 2%.

The ESR spectra were obtained with powdered samples placed in a quartz ampule on an SE/X-2547 (RadioPAN, Poland) X-band radiospectrometer at room temperature. The sample weighed portion was 200 mg, the microwave power, 20 mW, and modulation amplitude $B_m$, 0.1 mT.

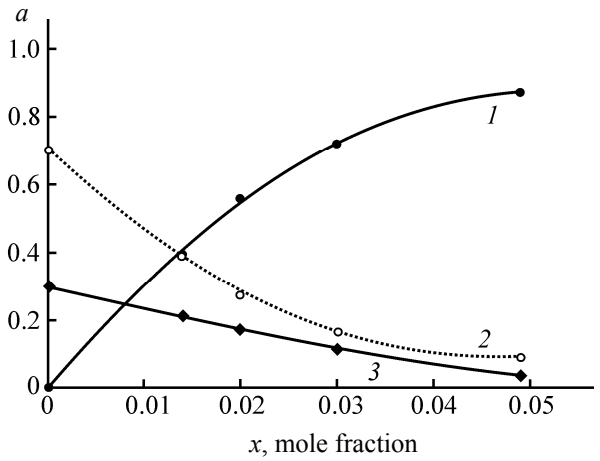


**Fig. 5.** Variation of the fraction of (*1*) Ni(III)–O–Ni(III) dimers, (*2*) Ni(II) monomers, and (*3*) Ni(III) monomers with the concentration of $Bi_3Nb_{1-x}Ni_xO_{7-\delta}$ solid solutions.

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