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Structure, Magnetic, and Electric Properties of Bismuth Niobates Doped with *d*-Elements:

V.[1] Magnetic and Electrophysical Properties of Copper-Containing Solid Solutions with the Structure of Bismuth Niobate, $Bi_5Nb_3O_{15}$

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Abstract—Magnetic susceptibility and electrophysical properties of copper-containing solid solutions with the structure of bismuth niobate, $Bi_5Nb_3O_{15}$, were studied. Paramagnetic aggregates (dimers) of copper atoms are formed in the solid solutions, their fraction substantially exceeding the statistically probable value. The parameters of exchange interactions in the dimer clusters of copper atoms and the distribution of monomers and dimers in the solutions were calculated. The exchange parameter of antiferromagnetic interactions between copper atoms in the dimers is –210 cm^{-1}.

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At present much consideration is given to studying layered perovskite-like compounds for important electrophysical properties have been observed in a number of representatives of this family [2, 3]. These properties are of interest both for fundamental science and for modern materials technology considering their practical application.

This paper presents the results of studying the effect of heterovalent substitution of copper atoms for niobium atoms in $Bi_5Nb_3O_{15}$, bismuth niobate, on the electrophysical properties of the $Bi_5Nb_{3-3x}Cu_{3x}O_{15-\delta}$ solid solutions, and also on the electronic state and distribution of copper atoms in the niobium sublattice.

The crystal structure of bismuth niobate $Bi_5Nb_3O_{15}$ belongs to layered perovskite-like structures, the so-called Aurvillius phases, and is described by the *P*4/*mmm* space group with the unit cell parameters a 0.547, *c* 2.097 nm [4, 5].

Copper-containing $Bi_5Nb_{3-3x}Cu_{3x}O_{15-\delta}$ solid solutions have been obtained with $x < 0.08$. The unit cell parameters of the solid solutions were determined using the CSG program package [6]. The results of calculating the unit cell parameters are given in Table 1.

Solid solutions with $x < 0.02$ were found to have a tetragonal structure, and their unit cell parameters we close to the parameters of bismuth niobate. As the concentration of a solid solution increases ($x \geq 0.02$), a monoclinic distortion of the unit cell occurs that shows itself in a deviation of the α angle from 90° and in the nonequivalence of *a* and *b* unit cell parameters [7]. With regard to this fact we described the X-ray patterns of the solid solutions assuming the space group to be *P*2/*m* [5]. As the concentration of copper atoms in the solid solutions increases, so do the unit cell parameters, and the α angle changes from 90 to 90.6º.

On the basis of measuring the magnetic susceptibility of the solid solutions we calculated the paramagnetic components of magnetic susceptibility [χ^{para}(Cu)] and the effective magnetic moments of copper atoms [μ_{eff}(Cu)] at various temperatures and for various concentrations of the solid solutions. In

[1] For communication IV, see [1].

Table 1. Unit cell parameters of $Bi_5Nb_{3-3x}Cu_{3x}O_{15-\delta}$

Parameters	$Bi_5Nb_3O_{15}$	x 0.005	x 0.01	x 0.02	x 0.03	x 0.04	x 0.06	x 0.08
a, Å	5.472	5.472	5.472	5.475	5.479	5.481	5.484	5.486
b, Å	5.472			5.463	5.464	5.459	5.454	5.449
c, Å	20.97	20.97	20.97	20.97	20.97	21.01	21.04	21.07
α, deg	90			90.28	90.37	90.46	90.53	90.61

calculation of the magnetic susceptibility we introduced the diamagnetic corrections with regard to the susceptibility of $Bi_5Nb_3O_{15}$ matrix measured over the same temperature range. As a result we found that the dependence of the reciprocal of molar paramagnetic component on temperature for all the solid solutions obeyed Curie–Weiss law over the temperature range under study.

The isotherms of paramagnetic component of the magnetic susceptibility for the copper-containing solid solutions are typical for the dilution of antiferromagnetics (Fig. 1). The extrapolation to the infinite dilution ($x \rightarrow 0$) of the isotherms of paramagnetic component of magnetic susceptibility gives the identical effective magnetic moments of copper atoms at any temperature [average μ_{eff}(Cu) 1.55 BM], lower than the spin-only value of the copper(II) magnetic moment, μ(Cu) 1.73 BM. A reduction of the magnetic moment at low concentrations can be accounted for by the presence of diamagnetic Cu(III) atoms in the solid solutions. The fraction of Cu(III) atoms in the solid solutions at $x \rightarrow 0$ can be estimated by formula (1)

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

Here b is the fraction of Cu(II)atoms, μCu(II) is the magnetic moment of Cu(II) atoms, [μCu(III) 0].

The calculated fraction of Cu(III) atoms in the infinitely diluted solid solution is ~40 mol %. In the solid solutions with finite x the magnetic moment of correr atoms increases as temrerature increases indicating the antiferromagnetic exchange between paramagnetic atoms (Fig. 2).

We have carried out a theoretical calculation of the susceptibility to describe the experimental isotherms of magnetic susceptibility of the solid solutions. The calculation was carried out in terms of the diluted solution model. By this model the magnetic susceptibility is determined as a sum of the contributions from single paramagnetic atoms (monomers) and their M–O–M aggregates (dimers) [8]. In our case Cu(II) and Cu(III) copper atoms act as

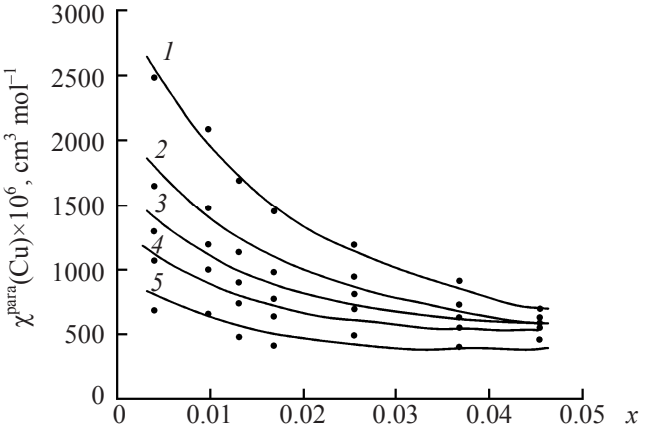

Fig. 1. Isotherms of paramagnetic component of magnetic susceptibility of copper atoms in $Bi_5Nb_{3-3x}Cu_{3x}O_{15-\delta}$ at: (*1*) 90, (*2*) 140, (*3*) 180, (*4*) 220, (*5*) 350 K.

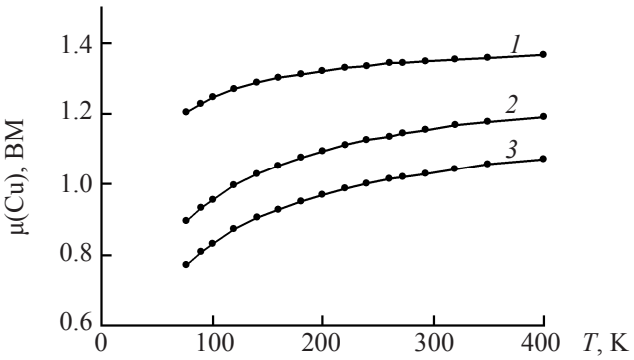

Fig. 2. Plot of magnetic moment of copper atoms in $Bi_5Nb_{3-3x}Cu_{3x}O_{15-\delta}$ vs. temperature at x (*1*) 0.010, (*2*) 0.026, (*3*) 0.040.

Table 2. Results of calculating the distribution of copper atoms in $Bi_5Nb_{3-3x}Cu_{3x}O_{15-\delta}$[a]

x	$b_{Cu(II)}$	$a_{Cu(II)-Cu(II)}$	$\chi_{exp(theor)}\times10^6$, cm^3 mol^{-1}				
			90 K	140 K	180 K	220 K	350 K
0.008	0.69	0.02	2120(2152)	1440(1385)	1140(1079)	960(884)	660(559)
0.01	0.71	0.09	2000(2057)	1400(1329)	1070(1041)	900(859)	630(553)
0.02	0.78	0.44	1380(1396)	955(930)	780(764)	640(665)	470(488)
0.03	0.90	0.64	1040(1040)	770(723)	660(631)	560(583)	430(484)
0.04	1.00	0.74	800(839)	660(610)	590(562)	530(546)	440(494)

[a]Designations: $b_{Cu(II)}$ is the total fraction of Cu(II) atoms, $a_{Cu(II)-Cu(II)}$ in the fraction of dimers in the fraction $b_{Cu(II)}$.

monomers, and the Cu(II)–O–Cu(II) dimers are formed by paramagnetic copper atoms. With regard to the aforesaid, the formula for calculating the paramagnetic component of magnetic susceptibility appears as (2).

$$\chi_{Cu}^{para} = b[a_{Cu(II)-Cu(II)}^{dim}\chi_{Cu(II)-Cu(II)}^{dim} + (1 - a_{Cu(II)-Cu(II)}^{dim})\chi_{Cu(II)}^{mon}] - (1 - b)\chi_{Cu(II)}^{mon}. \quad (2)$$

Here b is the fraction of Cu(II)copper atoms, $a_{Cu(II)-Cu(II)}^{dim}$ is the fraction of dimers of copper(II) atoms with antiferromagnetic type of exchange, $\chi_{Cu(II)}^{mon}$, $\chi_{Cu(III)}^{mon}$, and $\chi_{Cu(II)-Cu(II)}$ are the magnetic susceptibilities of monomers of Cu(II) and Cu(III) atoms and of Cu(II)–O–Cu(II) dimers. In keeping with the diamagnetism of Cu(III) the second addend is zero. The independent calculation parameters are b, $a_{Cu(II)-Cu(II)}^{dim}$, and the exchange parameter $J_{Cu(II)-Cu(II)}$. This latter is a parameter implicitly included to the calculation of magnetic susceptibility of dimers.

According to Heizenberg–Dirack–van Vleck model [8], the magnetic susceptibility of dimers composed of paramagnetic atoms can be calculated by formula (3).

$$\chi_{dim} = \frac{Ng^2\beta^2\sum_S S(S+1)(2S+1)e^{-E(J,S)/kT}}{3kT\sum_S (2S+1)e^{-E(J,S)/kT}}, \quad (3)$$

$E(J,S) = -J[S(S + 1) - S_a(S_a + 1) - S_b(S_b + 1)]$, $S = S_a + S_b, S_a + S_b - 1, \ldots, |S_a - S_b|$.

Here J is the parameter of isotropic exchange, S is the total spin of a dimer, S_a (S_b) are the spins of paramagnetic atoms making up the dimer (S_a, S_b, 1/2), g is g-factor, and T is absolute temperature.

The parameters are accepted as optimal on condition that

$$\Sigma\Sigma(\chi_{ij}^{calc} - \chi_{ij}^{exp}) \to 0.$$

Summing up is performed over all the concentrations and temperatures; χ_{ij}^{calc}, χ_{ij}^{exp} are calculated and experimental magnetic susceptibilities of the solid solutions respectively.

The best agreement between experimental and calculated data was obtained with $J_{Cu(II)-Cu(II)}$ –210 cm^{-1}, the results of calculation are given in Table 2 (Fig. 3).

As a result of the calculation it was found that as the concentration of the solid solution increased the fraction of copper(III) atoms decreased, and at $x \geq 0.04$ it became zero. As the concentration of the solid solution grew the fraction of Cu(II) monomers somewhat decreased due to an increase in the fraction of Cu(II)-O-Cu(II) dimers with antiferromagnetic type of exchange. Note that the obtained fractions of dimers substantially exceed the statistically probable values calculated for various concentrations of the solid solution (Table 3). This points to a tendency of copper atoms in the solid solutions to form exchange-bonded aggregates assisting the stabilization of the crystal structure of the solid solutions. A large exchange

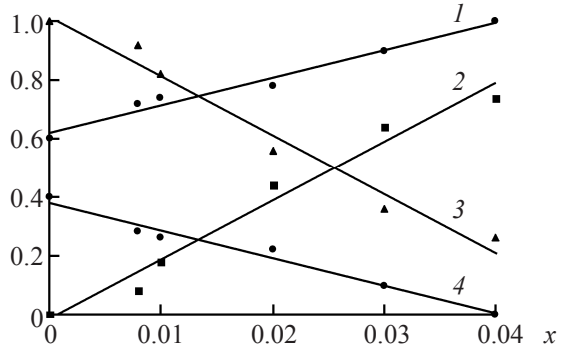

Fig. 3. Plots of the total fraction of (*1*) copper(II) and (*4*) copper(III), (*2*) the fraction of Cu(II)–O–Cu(II) dimers, (*3*) the total fraction of Cu(II) and Cu(III) monomers vs. concentration of $Bi_5Nb_{3-3x}Cu_{3x}O_{15-\delta}$ solid solutions.

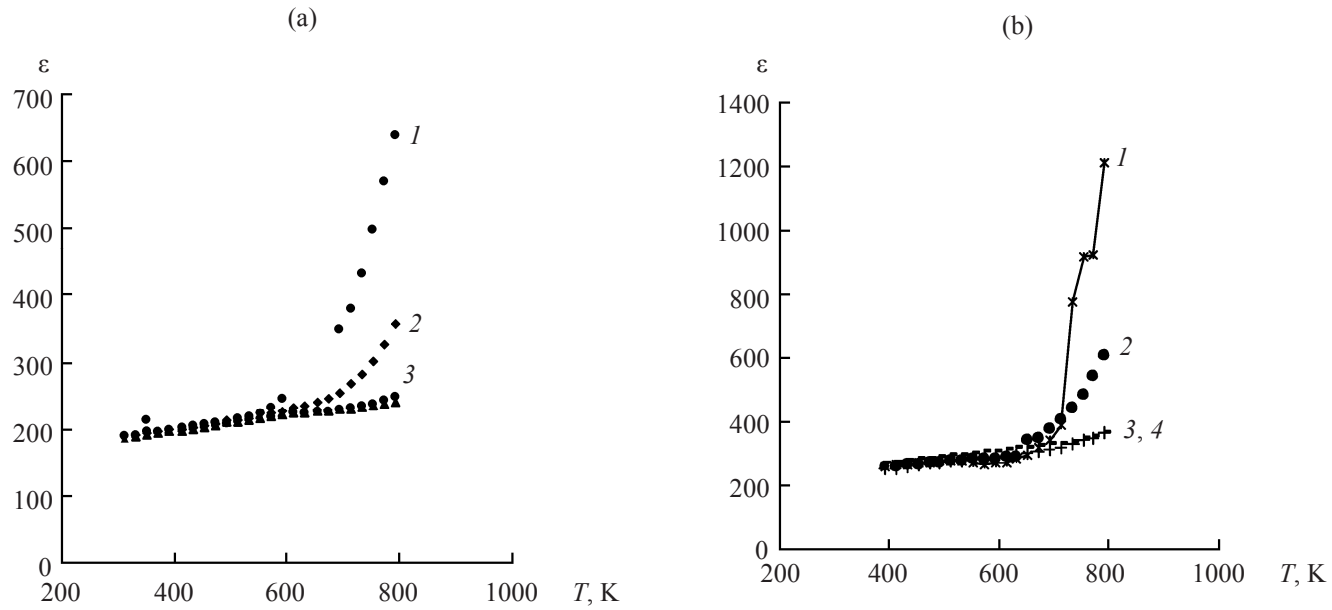

Fig. 4. Temperature dependence of dielectric constant of $Bi_5Nb_{3-3x}Cu_{3x}O_{15-\delta}$ solid solutions [x (a) 0.04, (b) 0.06] at the field frequency ω, kHz: (*1*) 1, (*2*) 10, (*3*) 100, (*4*) 200.

parameter $J_{Cu(II)-Cu(II)}$ of –210 cm^{-1} points to strong antiferromagnetic interactions between Cu(II) atoms.

Therefore, as the concentration of copper atoms in the solid solutions of heterovalent substitution grows, oxygen vacancies are accumulated that destabilize the crystal structure. This shows itself in the distortion of the tetragonal unit cell to monoclinic and in the oxidation of a certain fraction of paramagnetic copper atoms, more pronounced at low concentrations. The oxidation of copper atoms to the trivalent state proves to be possible only within very narrow limits, i.e. their number does not increase with growing x. Consequently, the fraction of Cu(III) decreases to almost zero at x ~0.04. The stability of the structure upon further heterovalent substitution seems to be determined by the formation of exchange-bonded aggregates located near oxygen vacancies.

Table 3. Distribution of copper atoms in the $Bi_5Nb_{3-3x}Cu_{3x}O_{15-\delta}$ solid solutions[a]

x	a_{dim}^{stat}	a_{dim}	$a_{Cu(II)}^{mon}$	$a_{Cu(III)}^{mon}$
0.00	0.00	0.00	0.60	0.40
0.01	0.04	0.09	0.62	0.29
0.02	0.08	0.34	0.44	0.22
0.03	0.11	0.58	0.32	0.10
0.04	0.15	0.74	0.26	0.00

[a] a_{dim}^{stat} is statistically probable fraction of dimers, a_{dim} is the fraction of Cu(II)–O–Cu(II) dimers, $a_{Cu(II)}^{mon}$ and $a_{Cu(III)}^{mon}$ are the fractions of Cu(II) and Cu(III) monomers in the solid solutions.

For the $Bi_5Nb_{3-3x}Cu_{3x}O_{15-\delta}$ solid solutions (x ~0.04, 0.06) we measured the temperature dependences of dielectric constant and specific conductivity in the temperature range 300–750 K at the alternating field frequencies 1–200 kHz (Figs. 4–6).

The dielectric constant of the solid solutions remains almost unchanged up to 650 K (1 kHz). At higher temperatures ε abruptly increases, most pronounced at the frequencies of 1 and 10 kHz (Fig. 4). It may result from polarization phenomena in a sample. The dielectric constant (ε) shows a frequency dependence manifested in an increase in ε as the frequency of the applied field decreases. At the frequencies of 100 and 200 kHz the dielectric constant changes moderately. The temperature of the onset of an abrupt increase in the dielectric constant grows with the frequency. The dependence of the dielectric constant on the concentration of the solid solutions noticeably appears at temperatures over 650 K.

The temperature dependence of the specific conductivity is characterized by two curve pieces. The specific conductivity essentially increases at a temperature higher than a certain value depending on the field frequency (Figs. 5 and 6). The dependence of specific conductivity on the field frequency suggests a mixed electron-ionic type of conductivity in the

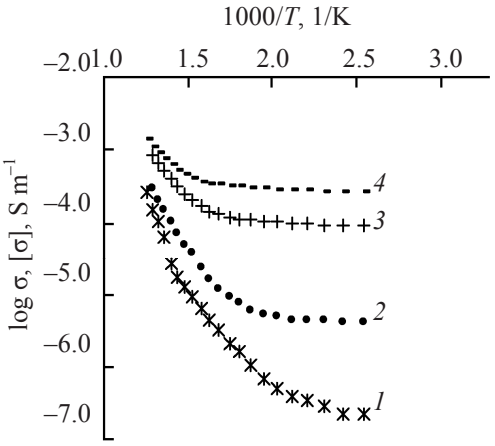

Fig. 5. Temperature dependence of the specific conductivity of the $Bi_5Nb_{3-3x}Cu_{3x}O_{15-\delta}$ solid solution (x 0.04) at the field frequency ω, kHz: (*1*) 1, (*2*) 10, (*3*) 100, (*4*) 200.

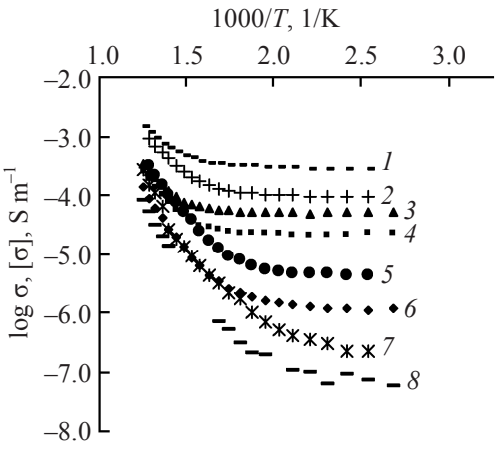

Fig. 6. Temperature dependence of the specific conductivity of the $Bi_5Nb_{3-3x}Cu_{3x}O_{15-\delta}$ solid solutions [x: (*3*), (*4*), (*6*), (*8*) 0.04, (*1*, *2, 5, 7*) 0.06] at the field frequency ω, kHz: (*7*, *8, 1, 5*), (*6*) 10, (*2, 4*) 100, (*1, 3*) 200.

samples. The temperature where the activation energy changes up to E_a 0.15 eV shifts to higher values as the frequency increases. The specific conductivity increases with the concentration of the solid solutions. It can result from an increase in the number of vacancies in the oxygen sublattice owing to the heterovalent substitution and activation of the ion transfer.

Therefore, an increase in the content of heteroatoms with a lower valence in the solid solutions of bismuth niobate results in an increase in the concentration of vacancies. This is seen both in the rates of the increase in the electric conductivity and dielectric constant and in their numerical values that can be traced in the curves of temperature dependences of electrophysical characteristics. In this case the stability of the structure seems to be ensured by copper atom aggregates located near the vacancies; according to magnetic susceptibility data, their number substantially exceeds the statistically probable values.

EXPERIMENTAL

We synthesized the $Bi_5Nb_{3-3x}Cu_{3x}O_{15-\delta}$ solid solutions by multistage sintering of a finely ground stoichiometric mixture of especially pure bismuth, niobium, and copper oxides at 650–950ºC.

The single-phase character of solid solutions was confirmed by the X-ray analysis (DRON-4-13, CuK_α radiation) and electron scanning microscopy (a JSM 6400 electron microscope). We calculated the unit cell parameters of the solid solutions using the CSD program package [6]. The quantitative analysis of copper content in the obtained samples was carried out by the photometric method. The accuracy of the chemical analysis was no worse than 5% of x index in the solid solution formula.

We measured the magnetic susceptibility of the solid solutions over the temperature range 77–400 K by Faraday method, the accuracy of the measurements was 2%.

To measure the electrophysical characteristics, we deposited the conducting layer on the end surfaces of the samples formed as disks by silver paste baked at 600ºC. The capacitance and the tangent of dielectric losses were measured by the two-contact method with the help of an RCL MT-4090 automatic alternating current bridge at the field frequencies 1, 10, 100, and 200 kHz in the temperature range 300–750 K in the heating and cooling mode with the step of 20 deg. The temperature in the operating volume was controlled with Chromel-Alumel thermocouples.

REFERENCES

1. Zhuck, N.A., Piir, I.V., Pimenov, A.L., and Chezhina, N.V., *Zh. Obshch. Khim*., 2007, vol. 77, no. 6, p. 898.
2. Ivanova, L.A. and Venevtsev, Yu.N., *Segneto-elektricheskie, antisegnetoelektricheskie i rodstvennue*

soedineniya (Ferrielectric, Antiferroelectric, and Related Compounds), Moscow: NIITEKhIM, 1983.

3. Voronkova, V.I. and Yanovskii, V.K., *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 1988, vol. 24, no. 12, p. 2062.
4. Gopalakrishnah, J., Ramanan, A., and Rao, N.R., *J. Solid. State Chem*., 1984, vol. 55, p. 101.
5. Yanovskii, V.K., Voronkova, V.I., and Vodolazskaya, I.V., *Neorg. Mater*., 1990, vol. 26, no. 6, p. 1297.
6. Akselrud, L.G., Gryn, Y.N., and Zavalij, P.Yu, Abstracts of Papers, *12th Europ. Crystallogr. Meet*., 1985, p. 55.
7. Sirotinkin, V.P. and Bush, A.A., *Zh. Neorg. Khim.,* 2004, vol. 49, no. 5, p. 840.
8. Kalinnikov, V.T. and Rakitin, Yu.V., *Vvedenie v magnetokhimiyu. Metod staticheskoi magnitnoi vospriimchivosti v khimii* (Introduction to Magnetochemistry. Static Magnetic Susceptibility Method in Chemistry), Moscow: Nauka, 1980.