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Structure and Magnetic and Electric Properties of Bismuth Niobates Doped with *d* Elements: IV.[1] Magnetic Behavior of Chromium-Containing Solid Solutions with the Structure of Bismuth Niobate, $Bi_5Nb_3O_{15}$

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Abstract — The magnetic susceptibility and electrophysical properties of chromium-containing $Bi_5Nb_{3-3x}Cr_{3x}O_{15-\delta}$ solid solutions with the perovskite-like structure were studied. Parameters of exchange interactions in the dimeric clusters of chromium atoms and also the distribution of chromium monomers and dimers in the solid solutions were calculated.
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The majority of bismuth-containing oxide compounds shows nonlinear electrophysical properties, such as ferroelectric and piezoelectric, and in this context they are of great practical and theoretical interest [2–4].

Here we report the electrophysical characteristics of chromium-containing $Bi_5Nb_{3-3x}Cr_{3x}O_{15-\delta}$ solid solutions with the layered perovskite-like structure, prepared by heterovalent substitution of chromium for niobium atoms, and also the results of magnetochemical study of the state of chromium atoms in the solid solutions.

The composition of layered bismuth-containing compounds can be described by the general formula $(Bi_2O_2)\cdot(A_{n-1}B_nO_{3n+1})$, where Bi_2O_2 are bismuth-oxygen layers formed by BiO_4 pyramids and linked with each other through base edges, and $A_{n-1}B_nO_{3n+1}$ are the perovskite-like fragments consisting of BO_6 octahedra linked through their apices, with large A cations located in cubooctahedral voids between them. The coefficient n in this formula corresponds to the number of octahedra along the thickness of the perovskite-like fragment [5]. It was found previously that, along with the conventional layered compounds with the same perovskite fragments, the so-called mixed layered compounds $(Bi_2O_2)(A_{n-1}B_nO_{3n+1})\cdots(Bi_2O_2)(A_{m-1}B_mO_{3m+1})$ with alternating perovskite fragments of various thicknesses can exist in their structure [6].

Bismuth niobate, $Bi_5Nb_3O_{15}$, is among such layered compounds whose structure is characterized by an ordered alternation of the fragments with one and two niobium–oxygen octahedra. Therefore, its structure can be described as $(Bi_2O_2)(NbO_4)(BiNb_2O_7)$ (n 1 and m 2). The niobium–oxygen octahedra share common side apices and are located in the crystallographic ab plane; the Nb–O–Nb bond angle is 180°. The layers of octahedra are separated by bismuth–oxygen layers (Fig. 1).

Chromium-containing $Bi_5Nb_{3-3x}Cr_{3x}O_{15-\delta}$ solid solutions were prepared in the concentration range $0.01 \le x \le 0.1$. We indexed the X-ray patterns of bismuth niobate and of the solid solutions with $x \le 0.04$ assuming space group $P4/mmm$ [7]. The unit cell parameters of the solid solutions with $x \le 0.04$ are close to the parameters of bismuth niobate, $Bi_5Nb_3O_{15}$ (Table 1). As the concentration of the solid solution increases to $x \ge 0.04$, the tetragonal cell undergoes monoclinic distortion. A decrease in the unit cell symmetry is clearly seen in the X-ray patterns (Fig. 2). These X-ray patterns were interpreted assuming space group $P2/m$ [7]. As the concentration of chromium atoms increases, we observe a minor increase in parameter a, a decrease in b, and a change in angle α from 90° to 91.2°. The unit cell parameters were calculated by the least-squares method using the CSD program package [8].

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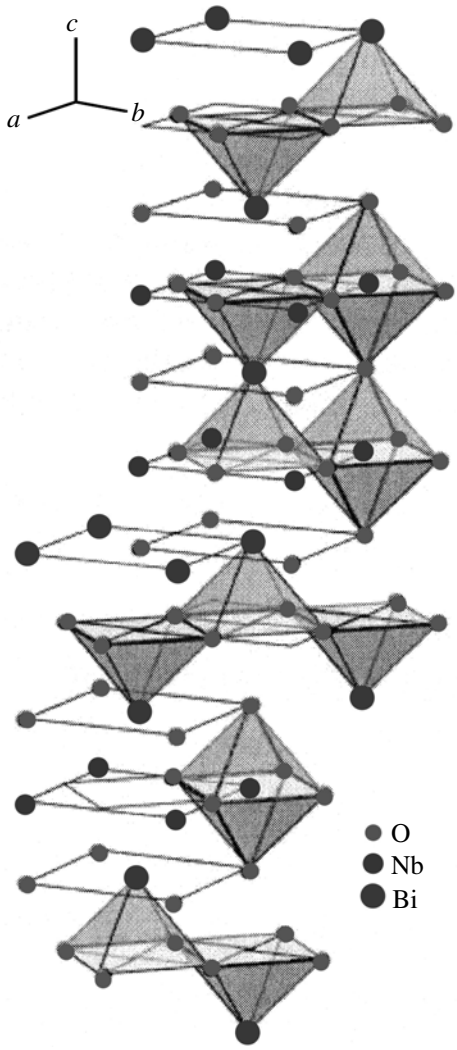

Fig. 1. Crystal structure of bismuth niobate $Bi_5Nb_3O_{15}$.

From the measured magnetic susceptibilities of the solid solutions, we calculated the paramagnetic components of the magnetic susceptibility [χ^{para}(Cr)] and the effective magnetic moments [μ_{eff}(Cr)] of chromium atoms at various temperatures and various concentrations of the solid solution. When calculating the paramagnetic component of the magnetic susceptibility, we introduced the diamagnetic corrections with regard to the susceptibility of the $Bi_5Nb_3O_{15}$ matrix measured over the same temperature range. As a result, we found that the temperature dependence of reciprocal molar paramagnetic susceptibility obeys the Curie–Weiss law in the temperature range under study for all the solid solutions.

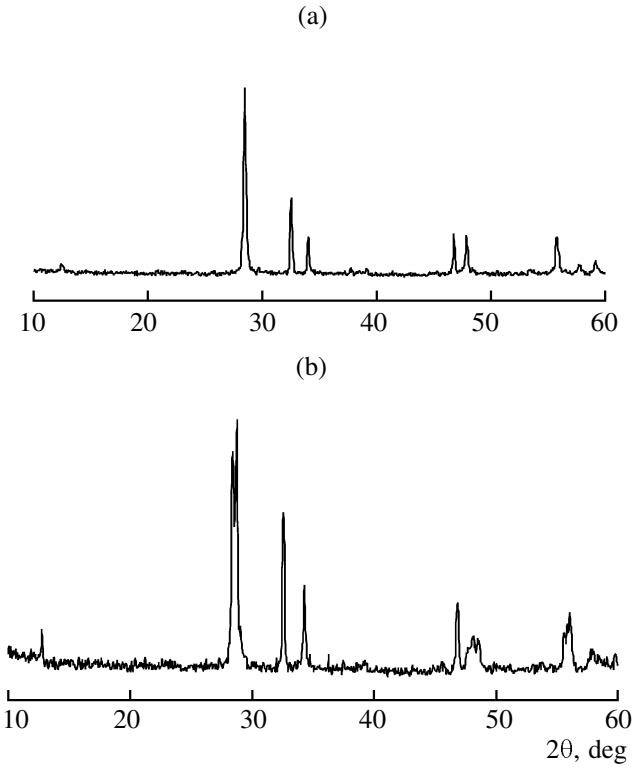

Fig. 2. X-ray patterns of bismuth niobate and of the $Bi_5Nb_{3-3x}Cr_{3x}O_{15-\delta}$ solid solution (x 0.06).

The plots of the paramagnetic component of the chromium magnetic susceptibility in the solid solutions under study vs. the concentration of paramagnetic atoms are shown in Fig. 3. A maximum at x ~0.03 is observed in the isotherms of magnetic susceptibility. The extrapolation of the χ^{para}(Cr) isotherms to the infinitely low concentration ($x \to 0$) results in the values differing from zero, as was the

Table 1. Unit cell parameters of $Bi_5Nb_3O_{15}$ and $Bi_5Nb_{3-3x}Cr_{3x}O_{15-\delta}$ with various x

Parameter	$Bi_5Nb_3O_{15}$	$Bi_5Nb_{3-3x}Cr_{3x}O_{15-\delta}$						
		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	5.469	5.471	5.472	5.473	5.474	5.473	5.473
b, Å	5.472					5.462	5.463	5.460
c, Å	20.97	20.96	20.96	20.97	20.97	21.01	20.99	21.02
α, deg	90					90.33	90.44	90.64

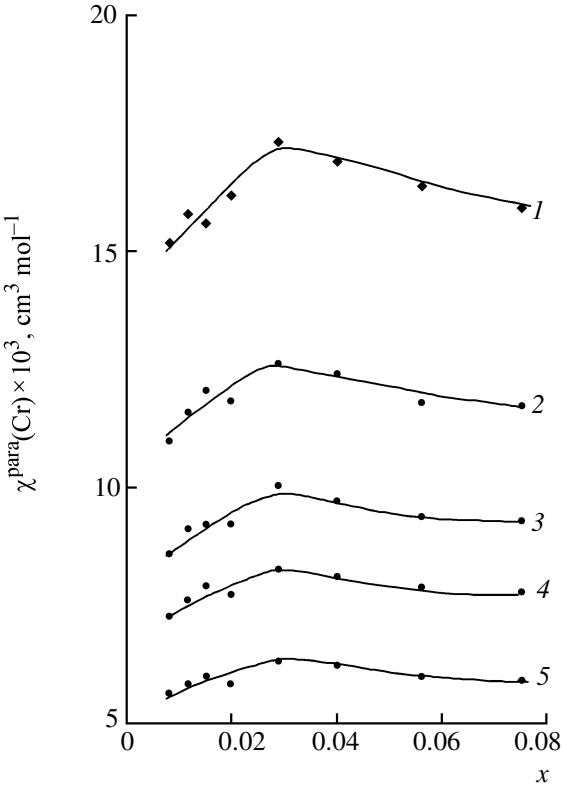

Fig. 3. Isotherms of the paramagnetic component of the magnetic susceptibility of $Bi_5Nb_{3-3x}Cr_{3x}O_{15-\delta}$ at T (*1*) 100 K, (*2*) 140 K, (*3*) 180 K, (*4*) 220 K, and (*5*) 300 K.

case for the $Bi_5Nb_{3-3x}Cr_{3x}O_{15-\delta}$ solid solutions [9]. The obtained effective magnetic moments of chromium atoms given below do not depend on temperature and are ~3.44 BM on the average.

T, K	90	100	120	140	180	220	300	350
$\chi^{para}(Cr)\times10^3$, $cm^3\ mol^{-1}$	16.2	14.7	12.5	10.5	8.0	6.5	4.8	4.2
μ_{eff}, BM	3.45	3.43	3.42	3.45	3.43	3.44	3.40	3.44

This value is less than the spin-only value of magnetic moment for chromium(III) atoms [μ_{eff}(Cr) 3.87 BM] with the $3d^3$ electronic configuration, $^4A_{2g}$ term. A decrease in the effective magnetic moment may be due to a number of reasons, one of them being the presence of Cr(IV) in the infinitely dilute solution, μ_{eff}(Cr) 2.83 BM, $^3T_{1g}$ term. In this case, the magnetic moment of the atoms in the triplet ground state should depend on temperature [10]. However, the experimental data show the lack of any temperature dependence. The second way to account for the experimental magnetic moment of chromium assumes the presence of a certain fraction of diamagnetic chromium atoms, Cr(VI). It is believed that heterovalent substitution of chromium atoms for niobium atoms gives rise to charge unbalance, which is compensated by the partial oxidation of chromium atoms Cr(III) to Cr(VI). Therefore, we suggest that the infinitely dilute solid solution contains chromium atoms in oxidation states 3+ and 6+.

Since the effective magnetic moment is the sum of contributions of the magnetic moments of chromium(III) and (VI) present in the solution, the fraction of Cr(VI) in the infinitely dilute solid solutions can be estimated by the formula

$$\mu^2_{exp} = b\mu^2_{Cr(III)} + (1 - b)\mu^2_{Cr(VI)}, \qquad (1)$$

where $\mu_{Cr(VI)}$ and $\mu_{Cr(III)}$ are the magnetic moments of chromium(VI) and chromium(III) atoms, respectively, and b is the fraction of chromium(III) atoms. The calculated fraction of Cr(VI) is 20 mol%.

A decrease in the paramagnetic component of the magnetic susceptibility of chromium atoms in the solid solutions at $x \geq 0.03$ is attributable to antiferromagnetic interactions between chromium(III) atoms. The temperature dependences of the effective magnetic moment of chromium atoms support this assumption: The magnetic moment of chromium increases with temperature. An increase in the paramagnetic component of magnetic susceptibility of chromium atoms at $x \leq 0.03$ may be due to the competition of two opposite effects: antiferromagnetic interaction between chromium(III) atoms and a decrease in the fraction of Cr(VI) atoms with increasing concentration of the solid solution.

To describe the experimental data, we carried out a theoretical calculation of the magnetic susceptibility within the framework of the model of dilute solutions. According to this model, the magnetic susceptibility is determined as the sum of contributions from single paramagnetic atoms (monomers) and their aggregates (dimers) M–O–M. We used the following approach to the distribution of chromium atoms: in the solution there are isolated chromium(III) and Cr(VI) atoms and also the Cr(III)–O–Cr(III) dimers with the antiferromagnetic type of exchange. The exchange interactions in the dimers were described within the framework of the Heisenberg–Dirac–van Vleck model [10]. In this case, the paramagnetic component of the magnetic susceptibility of chromium atoms can be calculated by formula (2).

$$\chi_{calc} = b(1 - a_{dim})\chi_{mon} + a_{dim}\chi_{mon}. \qquad (2)$$

Here χ_{mon} and $\chi_{di\,m}$ are the magnetic susceptibilities of Cr(III) monomers and of Cr(III)–O–Cr(III) dimers;

Table 2. Calculated distribution of chromium atoms in $Bi_5Nb_{3-3x}Cr_{3x}O_{15-\delta}$[a]

x	b	a	$\chi_{Cr} \times 10^6$, $cm^3\,mol^{-1}$, exp. (theor.)				
			100 K	140 K	180 K	220 K	300 K
0.01	0.885	0.092	15800 (15926)	11400 (11469)	8950 (8943)	7350 (7336)	5430 (5403)
0.02	0.960	0.167	16700 (16824)	12200 (12201)	9550 (9534)	7850 (7838)	5800 (5794)
0.03	1	0.195	17200 (17341)	12600 (12612)	9900 (9864)	8150 (8116)	6000 (6009)
0.04	1	0.234	17000 (17103)	12500 (12486)	9800 (9777)	8100 (8053)	5950 (5974)
0.05	1	0.284	16700 (16789)	12350 (12319)	9700 (9661)	8000 (7970)	5900 (5928)

[a] b is the fraction of Cr(III) atoms; a, fraction of Cr(III)–O–Cr(III) dimers relative to Cr(III) atoms.

b, fraction of chromium(III) atoms; and a_{dim}, fraction of dimers. The susceptibility of chromium(VI) atoms is equal to zero. There are three variables in this formula: b, a_{dim}, and implicitly present exchange parameter J. Since the exchange parameter is constant over the whole temperature range and the fractions of dimers are constant for each x, the number of experimental points is sufficient to find the optimal values of variables.

For each current value of the exchange parameter, we calculated the fractions of the corresponding monomers and dimers for which sum (3) was minimal:

$$\sum_i \sum_j (\chi_{ij}^{calc} - \chi_{ij}^{exp}) \rightarrow 0. \quad (3)$$

Here we are summing up over all the concentrations and temperatures; χ_{ij}^{calc} and χ_{ij}^{exp} are the experimental and calculated magnetic susceptibilities of the solid solutions.

We obtained the best agreement between the experimental and calculated data at J –10 cm^{-1}. The calculation results are given in Table 2 and Fig. 4. The calculation showed that the fraction of Cr(VI) atoms decreases as the concentration of the solid solution increases, and at x 0.03 only Cr(III) exists in the solution. In so doing, the number of dimers of Cr(III) atoms with the antiferromagnetic type of exchange increases, their fraction substantially exceeding the statistically probable value (Table 3).

The antiferromagnetic type of superexchange between chromium atoms and close exchange parameters were obtained on studying chromium-containing solid solutions with the layered K_2NiF_4-type structure (13–18 cm^{-1}) [11–13]. This fact suggests that in perovskite-like structures the interactions between chromium atoms have the same character.

Table 3. Distribution of chromium atoms in $Bi_5Nb_{3-3x}Cr_{3x}O_{15-\delta}$ solid solutions

x	a_{dim}^{random}	a[Cr(VI)]	a[Cr(III)]	a_{dim}Cr(III)–O–Cr(III)
0		0.21	0.79	0
0.01	0.04	0.12	0.80	0.08
0.02	0.08	0.04	0.80	0.16
0.03	0.11	0	0.80	0.20
0.04	0.15	0	0.77	0.23
0.045	0.17	0	0.72	0.28

The observed type of exchange interaction is well described by the theory of exchange channels; within

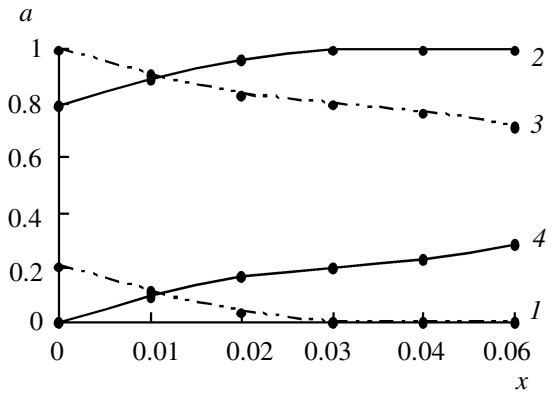

Fig. 4. Plots of the fraction a of (*1*) Cr(VI) and (*2*) Cr(III), and of the total fraction of (*3*) monomers and (*4*) dimers vs. chromium content in the $Bi_5Nb_{3-3x}Cr_{3x}O_{15-\delta}$ solid solutions.

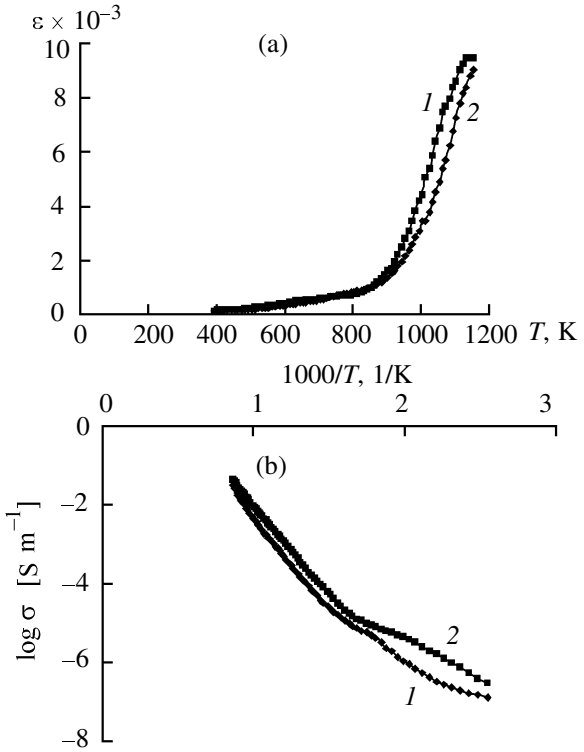

Fig. 5. Temperature dependences of the (a) dielectric constant and (b) specific conductivity of bismuth niobate, $Bi_5Nb_3O_{15}$, recorded in the course of (*2*) heating and (*1*) cooling.

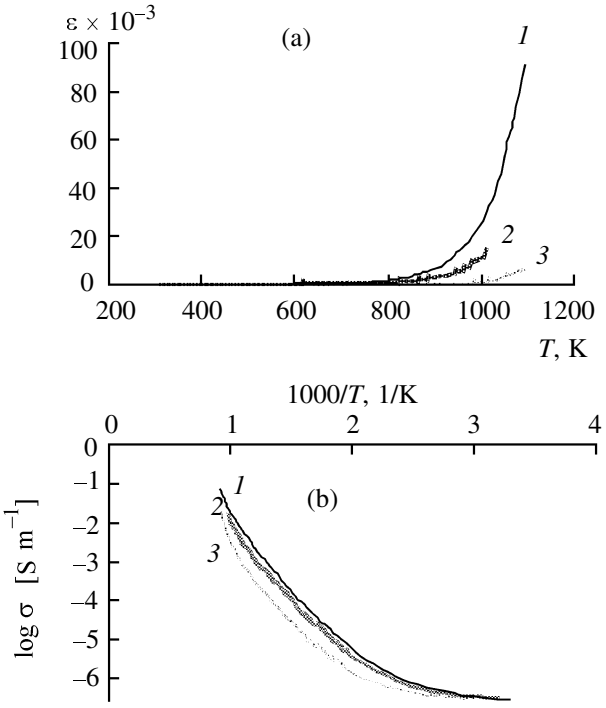

Fig. 6. Temperature dependences of the (a) dielectric constant and (b) specific conductivity of the $Bi_5Nb_{3-3x}Cr_{3x}O_{15-\delta}$ solid solutions at x (*1*) 0.08, (*2*) 0.06, and (*3*) 0.04.

the framework of this theory, the interaction of paramagnetic atoms at an angle of 180° is antiferromagnetic. A small exchange parameter for chromium atoms linked in dimers is due to the fact that the superexchange occurs via overlap of partially filled t_{2g} orbitals of chromium(III) atoms: d_{xy}, d_{xz}, and d_{yz} by the $d_{xz}\|p_z\|d_{xz}$ and $d_{yz}\|p_z\|d_{yz}$ channels, whereas an essentially stronger interaction takes place upon overlap of the $d_{x^2-y^2}\|p_x\|d_{x^2-y^2}$ and $d_{z^2}\|p_z\|d_{z^2}$ orbitals, which are not occupied in chromium(III) atoms. A decrease in the absolute value of the exchange parameter, as compared to the perovskite-like solid solutions studied in [11–13], is attributable to the local distortions of the exchange angles in bismuth niobate if the dimer appears to be located near an oxygen vacancy.

The magnetic characteristics of the solid solutions indicate the following. The heterovalent substitution of chromium for niobium gives rise to vacancies in the oxygen sublattice. At low concentrations, the unbalance of the charge density is compensated by transition of a part of chromium atoms into the Cr(VI) state, though to a lesser extent than it was observed in bismuth orthoniobate [9]. This fact is indicative of higher stability of the perovskite-like structure to formation of vacancies. As the concentration of chromium atoms increases, the fraction of Cr(VI) decreases, and the stability of the structure seems to be provided by the formation of dimeric clusters of the paramagnetic, located in the vicinity of oxygen vacancies. The fraction of such clusters exceeds the statistically probable value. The fact that the increase in the chromium concentration results in monoclinic distortions of the structure also indicates that the dimers are localized near the vacancies. We suggest that this should result in an increase in the ionic conductivity in the solid solutions.

We measured the capacitance and conductivity of bismuth niobate, $Bi_5Nb_3O_{15}$, and of $Bi_5Nb_{3-3x}Cr_{3x}O_{15-\delta}$ solid solutions (x 0.04–0.08) in the range 300–1000 K at an alternating field frequency of 1 kHz. From the results of these measurements, we calculated the dielectric constants and specific conductivities and plotted their temperature dependences (Figs. 5, 6). We have measured these electrophysical characteristics for bismuth niobate and for the $Bi_5Nb_{3-3x}Cr_{3x}O_{15-\delta}$ solid solution (x 0.08) at the frequencies of 10, 100, and 200 kHz (Fig. 7).

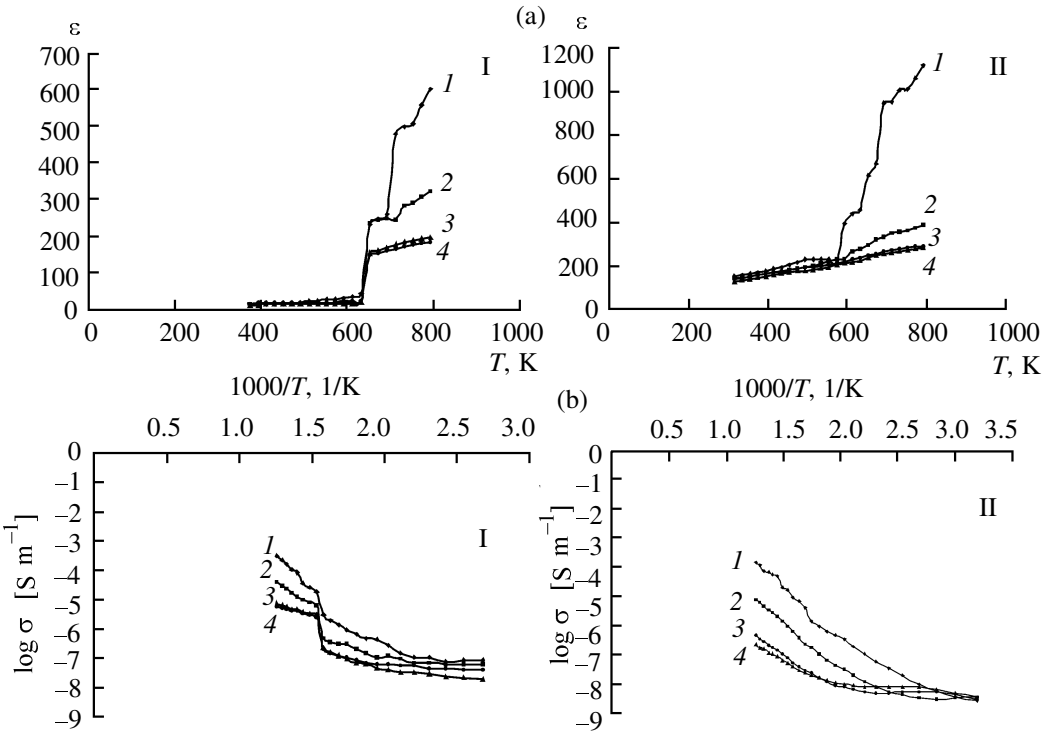

Fig. 7. Temperature dependences of the (a) dielectric constant and (b) specific conductivity of (I) $Bi_5Nb_3O_{15}$ and (II) $Bi_5Nb_{3-3x}Cr_{3x}O_{15-\delta}$ solid solution at a field frequency of (*1*) 1, (*2*) 10, (*3*) 100, and (*4*) 200 kHz.

An abrupt increase in the dielectric constant is observed at the temperatures of 630 and 579 K for bismuth niobate and the solid solution, respectively (Fig. 7a). The value of this increase decreases for bismuth niobate as the frequency of the applied field increases, and the temperature at which it is observed remains unchanged with varying the frequency. This is characteristic for the phenomena associated with the ferroelectric ordering of the ferroelectric–paraelectric type. We emphasize that the ferroelectric properties are typical for the most part of Aurivillius phases to which the bismuth niobate $Bi_5Nb_3O_{15}$ belongs [14, 15]. The Curie temperature found for it does not contradict the data of [16].

The temperature dependences of the dielectric constant (ε) and specific conductivity (σ) for bismuth niobate and for solid solutions at a field frequency of 1 kHz are shown in Figs. 5 and 6. At the temperatures exceeding 650 K, ε increases by several orders of magnitude. This is attributable to the ion polarization and subsequent activation of the ion transfer. At the background of such an abrupt increase in the dielectric constant, its increase observed in Fig. 7a becomes unnoticeable. As the concentration of the solid solution increases, the temperature of the onset of the abrupt increase in the dielectric constant decreases.

In the temperature dependences of $\log\sigma$ of bismuth niobate (I) (Fig. 7b), a discontinuity in the conductivity is observed at all the field frequencies at the temperature corresponding to that of the discontinuity in the dielectric constant (and of a possible phase transition). For the $Bi_5Nb_{2.76}Cr_{0.24}O_{15-\delta}$ solid solution II, the specific conductivity does not depend on temperature at low temperatures, but with raising temperature it increases considerably, especially at low frequencies (Fig. 7b). The values of $\log\sigma$ measured at 1 and 100 kHz and 800 K differ by two orders of magnitude on the average. In the high-frequency plots, we can distinguish two linear portions in the temperature dependence of the conductivity. The frequency-depending conductivity suggests mixed electron-ionic type of conductivity, with the ionic component of the conductivity substantially increasing with temperature. The temperature dependence of $\log\sigma$ of the solid solutions deviates to some extent from the Arrhenius dependence (Fig. 6b). The specific conductivity of the $Bi_5Nb_{3-3x}Cr_{3x}O_{15-\delta}$ solid solutions increases as the content of chromium increases, which can be caused by an increase in the number of vacancies in the oxygen sublattice owing to the heterovalent substitution. Therefore, the electric properties of the solid solutions do not contradict the model of their structure suggested on the basis of the magnetic properties.

EXPERIMENTAL

The $Bi_5Nb_{3-3x}Cr_{3x}O_{15-\delta}$ solid solutions were prepared by prolonged sintering of a finely ground stoichiometric mixture of ultrapure grade bismuth, niobium, and chromium oxides in air at 950°C.

The phase composition of the solid solutions was monitored by X-ray phase analysis (DRON-4-13, CuK_α radiation) and scanning electron microscopy (JSM 6400 electron microscope). The unit cell parameters were calculated using the CSD program package [8]. The chromium content of the samples obtained was determined by atomic emission spectrometry (SPECTRO CIROS ICP spectrometer). The accuracy of the analysis was ~5% of x in the solid solution formula.

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

To measure the electrophysical characteristics of the samples of bismuth niobate and of solid solutions, a conducting silver layer was deposited onto the faces of the pellets obtained. The conductivity and capacitance of the samples were measured by the two-contact method with an RLC automatic ac bridge at a field frequency of 1 kHz in the range 300–1000 K in the course of heating and cooling. The temperature in the working chamber was controlled by a Chromel–Alumel thermocouple.

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