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Structure, Magnetic, and Electric Properties of Bismuth Niobates Doped with *d*-Elements: XI.[1] Magnetic Susceptibility of Bi_3NbO_7 of Cubic and Tetragonal Modifications

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Abstract—Study of magnetic susceptibility and ESR spectra of two modifications of bismuth niobate Bi_3NbO_7, tetragonal and cubic, has shown that a significant difference in the diamagnetic susceptibilities is observed at a reversible phase transition, which is associated with the presence of tetravalent niobium atoms combined in aggregates in the tetragonal modification of the complex oxide.

Keywords: bismuth niobate, phase transition, magnetic susceptibility

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Bismuth niobate Bi_3NbO_7 and solid solutions on its basis are promising as oxygen sensors, electrochemical controllers, cathode materials for solid oxide fuel cells, catalysts for water photolysis or selective oxidation of hydrocarbons [2, 3].

Cubic and tetragonal modifications are known for bismuth niobate Bi_3NbO_7, a reversible transition from cubic to tetragonal phase occurs at 800°C and back to cubic phase, at 900°C [4, 5].

Cubic bismuth niobate has a defective fluorite-like structure (*Fm*3*m, a* = 0.548 nm), where bismuth and niobium atoms are distributed over the same crystallographic sites [6]. Niobium atoms have a distorted octahedral coordination, and niobium-oxygen octahedra in the structure are combined into chains and blocks by oxygen atoms [4, 7]. The crystal structure of tetragonal modification of bismuth niobate is described by the *P*4/*mmm* space group and has a layered structure resembling the structures of pyrochlore and fluorite [8]. In the tetrahedral phase niobium-oxygen octahedra combined by axial apexes form infinite chains and tetrahedral clusters [5, 8].

In this work we studied magnetic susceptibility of bismuth niobate of cubic and tetragonal modifications. A cubic modification sample was obtained by sintering a tetragonal phase sample at 1000ºC for 10 h.

The unit cell parameters of the samples of cubic and tetragonal modifications agree with the published data [6, 9] and are 0.5478 nm (*Fm*3*m*), *a* = 0.5457, *c* = 0.5536 nm (*P*4/*mmm*). The chemical analysis has shown that the number of bismuth and niobium atoms corresponds to the stoichiometric composition of bismuth niobate.

The magnetic susceptibility of both phases depends on temperature, which points to the existence of a paramagnetic component of magnetic susceptibility, the susceptibility of the tetragonal modification exceeding that of the cubic modification (see the figure).

To reveal the nature of bismuth niobate paramagnetism, we studied the same samples by the ESR method. Under identical conditions of recording spectra two types of the signals were found in the ESR spectra for the samples of both modifications. One of them is a wide (ΔB_{pp} = 60–90 mT) asymmetric line of low intensity with *g*-factor 2.0–2.1, which can be

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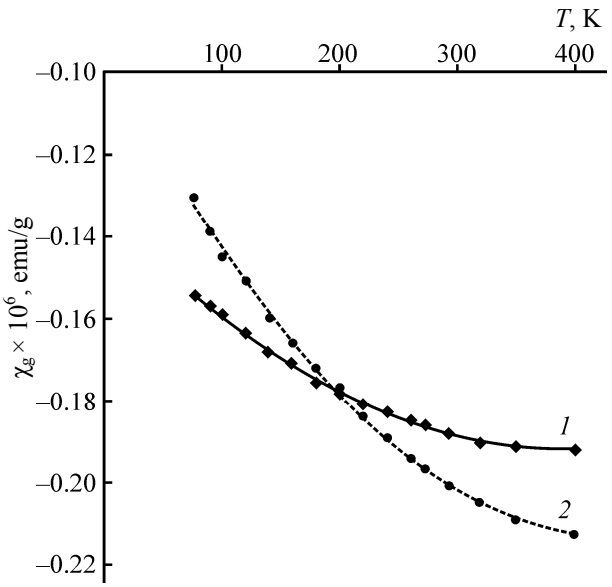

Temperature dependence of specific magnetic susceptibility of Bi_3NbO_7 of (*1*) cubic and (*2*) tetragonal modifications.

assigned to magnetic clusters in a paramagnetic lattice. The integral intensity of this component in the tetragonal phase is twice as large as in the sample of cubic modification. The second type of the signal, most pronounced in the sample of cubic modification, is a series of anisotropic narrow lines, their location changing on rotating the test tube in the resonator. Such signals seem to be associated with large magnetically ordered grains of a substance or with the presence of impurity ions in starting niobium and bismuth oxides. No lines of the ultrafine structure from isolated niobium(IV) ions were observed. It is evident that the absence of a characteristic signal of niobium(IV) in the ESR spectrum is associated with the fact that ESR spectra for the ions with d^1 configuration can be observed only at very low temperatures owing to the presence of low-lying excited states resulting in a short relaxation time and a large width of the absorption line [10].

Summing up the results obtained by the ESR and magnetic susceptibility methods on the samples of bismuth niobate, we can suggest two versions.

The paramagnetism of bismuth niobate results from traces of admixture atoms in starting bismuth(III) and niobium(V) oxides. A lower fraction of paramagnetic component of magnetic susceptibility in the cubic phase (compared to the tetragonal phase) can be associated with a partial oxidation of admixture paramagnetic atoms in air at the temperature of the cubic phase synthesis. However the fact seems contradictory since cubic phases synthesized from the same batch at different temperatures (750 and 1000°C) have identical ESR spectra.

The paramagnetism of the bismuth niobate phases results from admixture atoms of niobium(IV). The differences in the magnetic susceptibilities of samples of tetragonal and cubic phases are determined either by different number of niobium(IV) atoms, or by the presence of magnetic clusters of paramagnetic niobium(IV) ions in the structure of the bismuth niobate tetragonal phase.

A decrease in the fraction of niobium(IV) in the cubic phase can be associated with the oxidation of niobium(IV) to Nb(V) during the high temperature treatment. An approximate calculation based on the data of magnetic susceptibility [11] has given the fraction of niobium(IV) atoms in the tetragonal phase greater by 0.38% than in the cubic phase. The calculation is based on the assumption of a constant fraction of admixture atoms in both phases and a variable fraction of paramagnetic niobium(IV) atoms, and also on the consideration of the tetragonal phase as a solid solution of cubic modification, where a fraction of niobium(V) atoms is replaced by Nb(IV).

The formation of magnetic clusters in the structure of tetragonal phase is also probable and can be associated with special features of its structure, namely with the formation of tetrahedral complexes of niobium-oxygen octahedra [4–7], in which the magnetic susceptibility of paramagnetic atoms can increase at the expense of superexchange interactions [11]. We do not exclude the existence of paramagnetic niobium(IV) atoms even in the cubic phase, but owing to their small number and fragmentary distribution their contribution to the magnetic susceptibility appears to be insignificant.

The assumption about a certain fraction of niobium(IV) atoms in bismuth niobate was proposed earlier [9, 12]. The conductivity of the samples of bismuth niobate was found to be electron-ionic rather than pure ionic. A considerable contribution of electron conductivity to the total conductivity is observed at the temperatures lower than 600°C, and the appearance of electron conductivity is associated with a small fraction of niobium(IV) ions located in chains of niobium-oxygen octahedra.

The last assumptions are supported by the fact that magnetic susceptibilities of samples synthesized at different times at interval of several years coincide with an accuracy of the experimental error, which is 2% for diamagnetic preparations.

EXPERIMENTAL

Samples of bismuth niobate of both modifications were synthesized by a ceramic procedure from specially pure grade bismuth(III) and niobium(V) oxides at 650, 850, and 1000°C. The cubic phase sample of bismuth niobate was obtained by sintering the tetragonal phase sample at 1000°C for 10 h. The single-phase origin of the samples was confirmed by the X-ray analysis (DRON-4-13, CuK_α radiation) and by the electron scanning microscopy (a Link spectrometer). Unit cell parameters were calculated using the CSD program package [13]. Tractions of metal cations in the samples were determined by the atom-emission spectroscopy method (a SPECTRO CIROS spectrometer with inductive coupled plasma). The accuracy of relative measurements was 10%.

The ESR spectra of powdered samples placed into a quartz ampule were recorded on a SE/X-2547 (RadioPAN, Poland) radiospectrometer of X-diapason at room temperature (weighted samples of 300 mg, SHF emission power of 70 mV, the amplitude of HF modulation B_m of 0.2 mT). In the postrecording procedure the spectra were devoid of the ampule signal and normalized to the same weight and amplification of the device.

Magnetic susceptibilities of the samples of cubic and tetragonal modifications were measured by Faraday method in the temperature range 77–400 K at 16 fixed temperatures and at the magnetic field strength of 7240, 6330, 5230, and 3640 Oe. The accuracy of relative measurements was 2%. Specific magnetic susceptibilities of bismuth niobate of tetragonal and cubic modifications were calculated on the basis of the measurements as functions of temperature.

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