ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 1, pp. 1–5. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © N.A. Zhuk, N.V. Rozhkina, 2014, published in Zhurnal Obshchei Khimii, 2014, Vol. 84, No. 1, pp. 3–7.

Structure, Magnetic, and Electrical Properties of Bismuth Niobates Doped with *d*-Elements: VIII.[1] Phase Transitions and Electrophysical Properties of Bismuth Niobate

N. A. Zhuk and N. V. Rozhkina

Syktyvkar State University, Oktyabr'skii pr. 55, Syktyvkar, 167001 Russia
e-mail: nzhuck@mail.ru

Received March 18, 2013

Abstract—Reversible phase transitions of bismuth niobate Bi_3NbO_7 have been observed: from the low-temperature cubic modification to the tetragonal one at 860°C and from the tetragonal modification to the high-temperature cubic one at 950–980°C. With increasing temperature of the cubic modification preparation, the unit cell parameter has been decreasing. Electrophysical properties of the cubic phases have matched at the frequencies below 1 kHz (up to 650 K). The specific conductivity of the tetragonal phase exceeds that of the cubic phase by no more than an order of magnitude (below 1000 K).

DOI: 10.1134/S1070363214010010

Ceramic materials revealing high dielectric permittivity, low dielectric losses, and stable electrophysical characteristics are prospective for creating thin-filmed materials for memory devices and frequency filters consisting of layers of dielectric ceramics and fusible electric conductors [2–5].

Materials based on the cubic modification of bismuth niobate Bi_3NbO_7 reveal low dielectric loss factor, of $\sim 10^{-3}$ at 1 MHz, and high dielectric permittivity [6]. Recently, formation of different polymorphic modifications of bismuth niobate–tetra-gonal and cubic (low- and high-temperature) – has been observed [6–8, 10]. According to the preliminary results, transition of the low-temperature cubic modification to the tetragonal one occurs at 830–850°C, and transition from tetragonal phase to the high-temperature cubic modification is observed at 950°C.

The cubic bismuth niobate possesses a defective fluorite-type structure (*Fm*3*m*) with a unit cell parameter *a* of 0.5479 nm. Bismuth and niobium atoms are statistically distributed over the same system of crystallographic positions in the molar ratio *n*(Bi)/*n*(Nb) = 3 [9].

Assuming the *I*4/*mmm* space group, the unit cell parameters of tetragonal bismuth niobate are of *a* = 0.282 nm and *c* = 0.554 nm [10].

In this work, we studied the phase transitions and electrophysical properties of bismuth niobate polymorphic modifications at the frequency range of 0.1–200 kHz as function of temperature.

According to the X-ray diffraction analysis, the cubic phase of bismuth niobate was formed at above 500°C, and above 700°C the bismuth(III) and niobium(V) oxides admixtures were absent. The transition from the low-temperature cubic bismuth niobate to the tetragonal one was observed at 850–860°C, and the tetragonal phase was transformed into the high-temperature cubic one at ~950°C (Fig. 1).

From the scanning electron microscopy pictures (Fig. 2), surface of the tetragonal and the high-temperature cubic modifications revealed dense, almost nonporous morphology. Surface of the low-temperature cubic modification consisted of loose porous compacts with the grains of 1–3 μm.

The unit cell parameter of the tetragonal bismuth niobate decreased from 0.549 to 0.547 nm with increasing synthesis temperature, as shown in the table below.

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

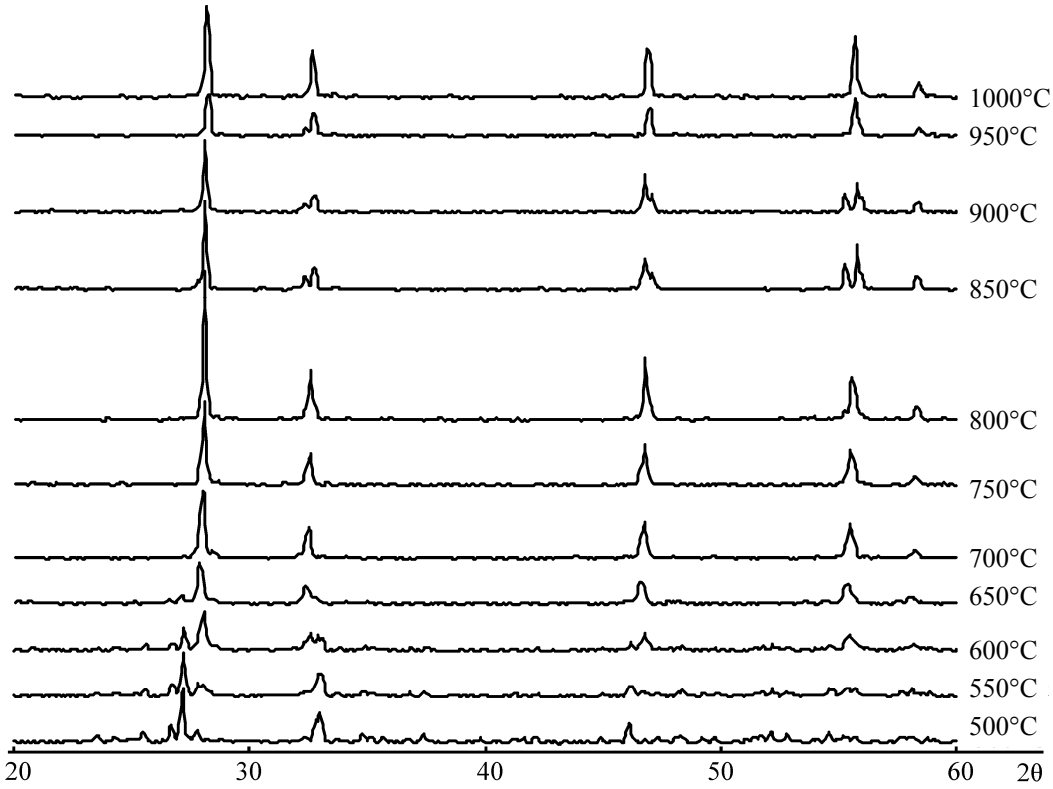

Fig. 1. X-ray diffraction patterns of Bi_3NbO_7 sample after annealing at 500–1000°C.

T, °C	700	750	800	950	1000	1000 (annealing)
a, Å	5.493	5.489	5.480	5.473	5.473	5.473

From the atomic emission spectroscopy results, the stoichiometry of bismuth niobate samples did not change upon prolonged high-temperature annealing.

Reversibility of the observed phase transitions was confirmed by X-ray diffraction analysis. When the high-temperature cubic modification prepared at 950°C was incubated at 850°C during 2 h, the tetragonal modification was formed (Fig. 3). Subsequent incubation of the tetragonal sample at 700°C resulted in its transformation into the cubic phase.

Dielectric permittivity ε of bismuth niobate samples was inversely proportional to the measurement frequency at 300–1000 K (Fig. 4). Below 600–650 K, ε varied moderately, being of 140, 145, and 210 (1 kHz) and of 71, 95, and 140 (10 kHz) in the cases the low-temperature cubic, high-temperature cubic, and tetragonal phases, respectively. Dielectric permittivity of the cubic samples was fairly independent of frequency in the low-temperature region. Above 650 K, the dielectric permittivity was sharply increased, seemingly, due to polarization of ions accompanied with activation of ion transfer. The onset of the abrupt dielectric permittivity increase shifted to higher temperature as the frequency increased: from 600 K (1 kHz) to 700 K (10 kHz).

At low frequencies, below 1 kHz, the dielectric permittivity of the tetragonal modification as function of temperature revealed a maximum. Temperature of the extreme was increased with the measurement frequency, being of 830 K (100 Hz) and 920 K (1 kHz). The observed maximum was likely connected with relaxation processes in the samples activated by the thermal ion polarization.

Dielectric permittivity of the tetragonal phase exceeded that of the cubic modifications at frequencies ω below 10 kHz over the whole studied temperature range. In particular, at 790 K the dielectric permittivity was of 4800 (1 kHz, tetragonal) and of 1120 (1 kHz, high-temperature cubic). At ω of 100–200 kHz, the dielectric permittivities of the phases were comparable: 87 (790 K, 100 kHz, tetragonal) and 85 (790 K, 100 kHz, high-temperature cubic).

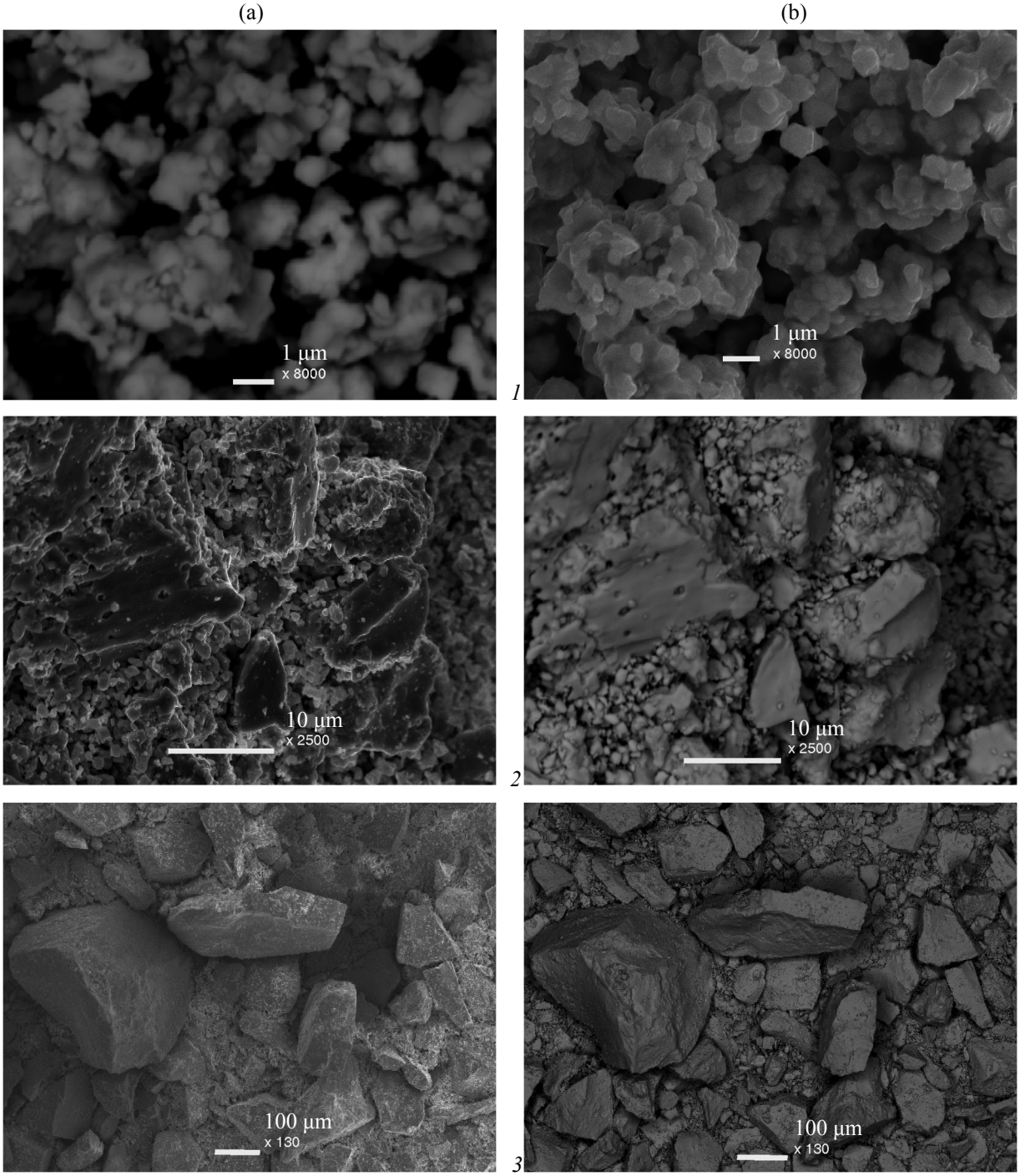

Fig. 2. Surface morphology of Bi_3NbO_7 polycrystalline samples after annealing at (*1*) 800°C, (*2*) 850°C, and (*3*) 900°C in the (a) elastically reflected and (b) secondary electron modes.

Logarithm of total specific conductivity of the studied samples at 1 and 100 kHz is shown in Fig. 5 as function of temperature. The specific conductivity revealed noticeable frequency dependence at below 600–650 K and at $\omega \geq 1$ kHz; under those conditions, the conductivity was proportional to the frequency. For example, in the case of the cubic modification at 450 K, σ equaled $10^{-3.7}$ S/m (200 kHz) and $10^{-5.3}$ S/m (10 kHz). From Fig. 5, conductivities (at 1 kHz) of the both cubic modifications were linear with temperature

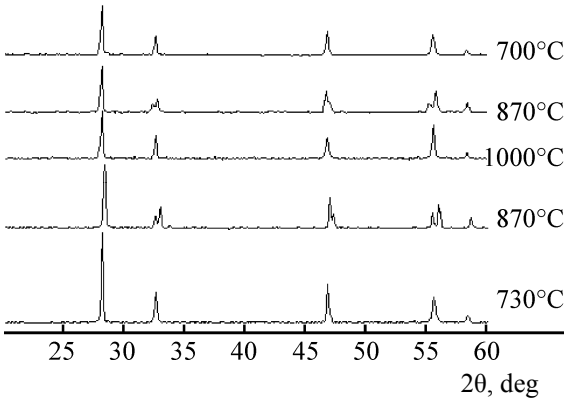

Fig. 3. X-ray diffraction patterns of Bi_3NbO_7 after annealing at 730°C → 870°C → 1000°C → 870°C → 700°C.

and coincided with each other. Above 650 K, the conductivities of all the three modifications were independent of frequency; their temperature dependences obeyed the Arrhenius equation with the activation energy E_a of 0.91 eV (high-temperature cubic), 0.99 eV (low-temperature cubic), and 0.69 eV (tetragonal). The close activation energies in the cases of the both cubic phases pointed to the same mechanism of electronic-ionic conductivity. The half-order of magnitude difference between specific conductivities of the cubic phases in the high-temperature region seemed to be due to insufficiently low density of the low-temperature modification samples. The results of this study suggested that the cubic phases were identical with respect to the crystal structure and electrophysical properties.

Specific conductivity of the tetragonal modification in the high-temperature region exceeded that of the low-temperature cubic phase by an order of magnitude. As seen from the plots (Figs. 4 and 5), the electrophysical parameters of the tetragonal phase exceeded those of the cubic samples over the whole studied temperature range, seemingly, due to distortions of the tetragonal phase crystal structure.

To conclude, bismuth niobate Bi_3NbO_7 underwent reversible phase transitions from the low-temperature cubic modification to the tetragonal and then to the high-temperature cubic ones. With increasing the synthesis temperature of the cubic phases, the unit cell parameter decreased from 0.549 to 0.547 nm. Electrophysical parameters of the both cubic phases were comparable at $\omega \leq 1$ kHz and $T < 650$ K. Likely, the differences in the dielectric permittivity and specific conductivity in the high-temperature region were due to variation of the samples caking degree. The specific conductivity of the tetragonal phase (<1000 K) exceeded that of the cubic phase by less than an order of magnitude.

EXPERIMENTAL

Polymorphic modifications of bismuth niobate were prepared by stepwise annealing of a stoichiometric mixture of bismuth(III) and niobium(V) oxides

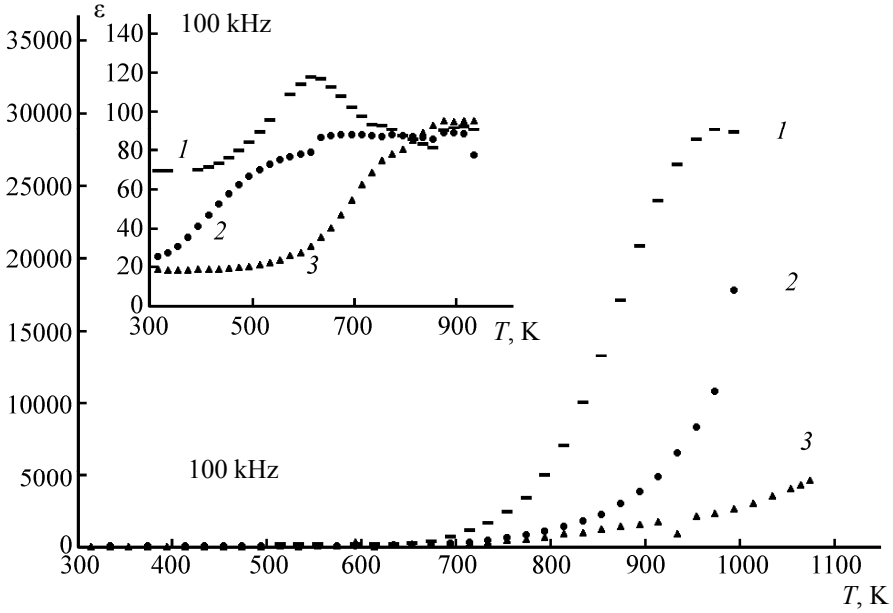

Fig. 4. Dielectric permittivity of (*1*) tetragonal, (*2*) high-temperature cubic, and (*3*) low-temperature cubic modifications of Bi_3NbO_7 as function of temperature at 1 and 100 kHz.

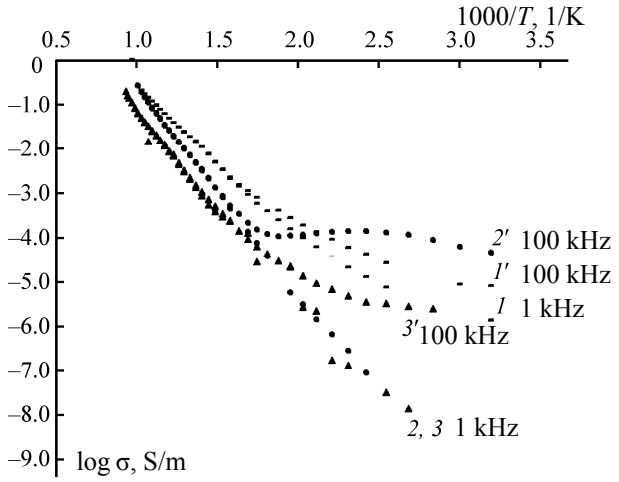

Fig. 5. Logarithm of specific conductivity of (*1*) tetragonal, (*2*) high-temperature cubic, and (*3*) low-temperature cubic modifications of Bi_3NbO_7 as function of temperature at 1 and 100 kHz.

(special pure grade) at 500–1050°C with 50°C steps; at each temperature, the sample was annealed during 10 h, and then the sample was analyzed.

The samples microstructure and phase composition was characterized by scanning electron microscopy (JSM-6400 microscope equipped with Link spectrometer, ISIS-300 software) and X-ray diffraction analysis (DRON-4-13, CuK_α emission). The high-temperature X-ray diffraction analysis was carried out with Shimadzu XRD-6000 X-ray diffractometer equipped with thermal attachment.

The elemental composition of the samples was determined by atom-emission spectroscopy (SPECTRO CIROS spectrometer with inductively coupled plasma); the samples stoichiometry was constant upon prolonged annealing. The error of the analysis was below 5%.

Capacitance and dielectric loss factor of the samples were measured by the double-contact method (ac bridge, LCR MT 4090 meter, dynamic heating and cooling at 300–1000 K). The measurements were performed at the current frequencies of 0.1, 1, 10, 100, and 200 kHz.

In order to measure the electrophysical parameters of the phases, we deposited a current-conducting layer at the faces of pelletized samples by burning in platinum paste at 873 K. The samples inside a quartz tube were placed into a muffle furnace, clamped between platinum electrodes. The muffler temperature was controlled with Chromel-Alumel thermocouples.

ACKNOWLEDGMENTS

The authors are grateful to V.N. Filippov and B.M. Makeev (Institute of Geology of Komi Scientific center, Russian Academy of Sciences, Ural Branch), for scanning electron spectroscopy and high-temperature X-ray analysis studies.

REFERENCES

1. Chezhina, N.V., Piir, I.V., and Zhuk, N.A., *Russ. J. Gen. Chem*., 2008, vol. 78, no. 6, p. 1127.
2. Di Zhou, Hong Wang, and Xi Yao, *J. Am. Ceram. Soc*., 2007, vol. 90, p. 327.
3. Valant, M. and Suvorov, D., *J. Am. Ceram. Soc*., 2004, vol. 87, p. 1056.
4. Yaremchenko, A.A. and Kharton, V.V., *J. Solid State Electrochem*., 1998, vol. 2, p. 146.
5. Ling, C.D. and Wither, R.L., *J. Solid State Chem*., 1998, p. 42.
6. Jong-Hyun Park, Soon-Gil Yoon, Hyung-Dong Kang, and Jeong-Won Lee, *J. Electrochem. Soc*., 2006, vol. 153, p. 236.
7. Wanga, X.P., Corbela, G., Kodjikiana, S., Fangb, Q.F., and Lacorrea, P., *J. Solid State Chem*., 2006, vol. 179, p. 3338.
8. Valant, M. and Suvorov, D., *Chem. Mater*., 2005, vol. 17, p. 5155.
9. Castro, A., Aguado, E., Rojo, J.M., Herrero, P., Enjalbert, R., and Galy, J., *Mat. Res. Bull*., 1998, vol. 33, no. 1, p. 31.
10. Zhuk, N.A., Kozhina, I.I., and Piir, I.V., *Vestnik SPbGU*, 2005, Ser. 4, no. 3, p. 42.