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Ferroelectric Phase Transitions in Non-Stoichiometric Sodium-Bismuth Titanate Ceramics

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Abstract—Features are studied of the phase formation, structural parameters, microstructure, and dielectric and ferroelectric properties of non-stoichiometric $(Na_{0.5+x}Bi_{0.5})TiO_3$ ceramics with $x = 0–0.1$. The investigated samples exhibit ferroelectric phase-transition behavior as anomalies and peaks in dielectric permittivity near 400 and 600 K, respectively. Study of the second harmonic generation shows that phase transitions near 400 K exhibit relaxor-type behavior, indicating there are polar regions in the nonpolar matrix. An increase in the Na/Bi ratio in the initial compositions improves the dielectric and ferroelectric properties of the ceramics.

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INTRODUCTION

Oxides of perovskite-like structure based on the rhombohedral ferroelectric relaxor of sodium-bismuth titanate (NBT), $(Na_{0.5}Bi_{0.5})TiO_3$, are some of most promising lead-free materials intensively studied over the last decade. A feature of these compositions is the notable dependence of functional properties on stoichiometry, which is determined by the conditions of preparation [1–11].

In this work, we studied features of the phase formation, structural parameters, microstructure, dielectric and ferroelectric (SE) properties of ceramics of non-stoichiometric compositions for $(Na_{0.5+x}Bi_{0.5})TiO_3$ ($x = 0–0.1$).

EXPERIMENTAL

Ceramic samples of $(Na_{0.5+x}Bi_{0.5})TiO_3$ ($x = 0–0.1$) were synthesized by double firing at $T_1 = 970–1070$ K (for 6 h) and $T_2 = 1270–1470$ K (for 1–2 h). Na_2CO_3 (98%) and Bi_2O_3 and TiO_2 (>99.9%) were used as the initial reagents.

The phase composition and parameters of the crystal structure were investigated at room temperature via X-ray diffraction (XRD) (DRON-3M diffractometer, CuK_α radiation). The second harmonic of laser radiation (SHG) (Nd:YAG laser, $\lambda = 1.064$ μm) was used to estimate the magnitude of spontaneous polarization. Dielectric properties of the ceramics were studied via dielectric spectroscopy (Agilent 4284A LCR meter, 1 V) at 300–1000 K and 100 Hz–1 MHz.

RESULTS AND DISCUSSION

According to the XRD data, our samples of perovskite-like structure were formed at $T_1 = 973–1173$ K. Dense single-phase samples with $x < 0.075$ were prepared by sintering the ceramics at $T_2 = 1450–1470$ K (2 h). The compositions with $x \geq 0.075$ contained $Na_2Ti_6O_{13}$ impurities (Fig. 1). Figure 2 shows parts of the diffractograms with diffraction peaks $N = h^2 + k^2 + l^2 = 4$ ($hkl = 200$) for $(Na_{0.5+x}Bi_{0.5})TiO_3$ with $x = 0, 0.0, 0.02, 0.03, 0.04, 0.05, 0.075, 0.10$. The displacement of the peak position toward the region of smaller angles at $x = 0–0.03$ indicates a volume increase in the pseudocubic perovskite cell as a result of the substitution of vacancies in sublattice A, due to the loss of low-melting cations A at high temperatures. The widening and change in the shape of the peak at $x > 0.04$ indicates a transition from pseudocubic lattice symmetry to rhombohedral symmetry, which corresponds to the literature [6–9].

The microstructure of the samples with $x < 0.04$ is characterized by isometric grains ~(1 ± 5) μm in size (Fig. 3). The microstructure of the samples with $x \geq 0.04$ is characterized by an increase in the average grain size to ~10 μm. On the samples' surfaces, we were also able to observe grains of elongated shape corresponding to the formation of the $Na_2Ti_6O_{13}$ phase (Fig. 3).

Upon an increase in the Na/Bi ratio in the initial compositions, an rise in the spontaneous polarization value was confirmed by SHG measurements. The change in the SHG signal, $q = I_{2w}/I_{2w}(SiO_2)$, from $q \sim 10$ at Na/Bi < 1.05 to $q \sim 130$ at Na/Bi > 1.2, improved

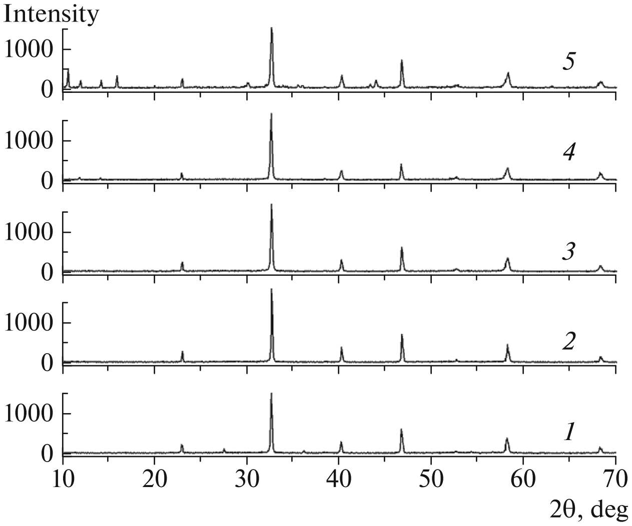

Fig. 1. Diffractograms of $(Na_{0.5+x}Bi_{0.5})TiO_3$ with x = (*1*) 0.0, (*2*) 0.02, (*3*) 0.03, (*4*) 0.075, (*5*) 0.10.

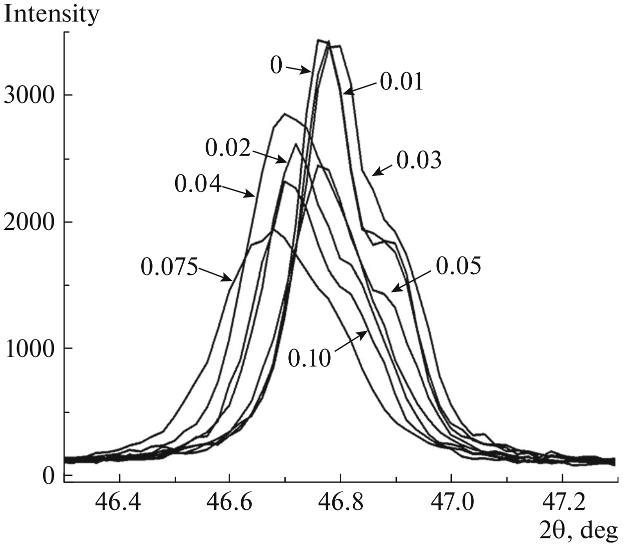

Fig. 2. Parts of diffractograms of $(Na_{0.5+x}Bi_{0.5})TiO_3$ with x = 0–0.1. The numbers on the curves correspond to the x-value.

the dielectric and SE properties of the ceramics (Fig. 4).

The samples were characterized by SE phase transitions observed as anomalies in dielectric permittivity at ~400 K and peaks at T_m ~ 600 K (Fig. 5). The phase transitions at 390–420 K show pronounced relaxor behavior, indicating there were polar regions in the nonpolar matrix [12, 13]. This is supported by the SHG data and agrees with the studied NBT compositions consisting of SE clusters embedded in a nonpolar matrix. Charge disorder in A-positions occupied by randomly arranged Bi^{3+} and Na^+ cations determines the formation of random electric fields affecting the local balance between the displacements from the central positions of Ti^{4+} cations in positions B and of cations in positions A of the perovskite lattice in opposite directions, facilitating local correlations of dipoles and the relaxational properties of NBT compounds [14]. At high temperatures, the effects of dielectric relaxation associated with the presence of vacancies in the oxygen sublattice are also revealed.

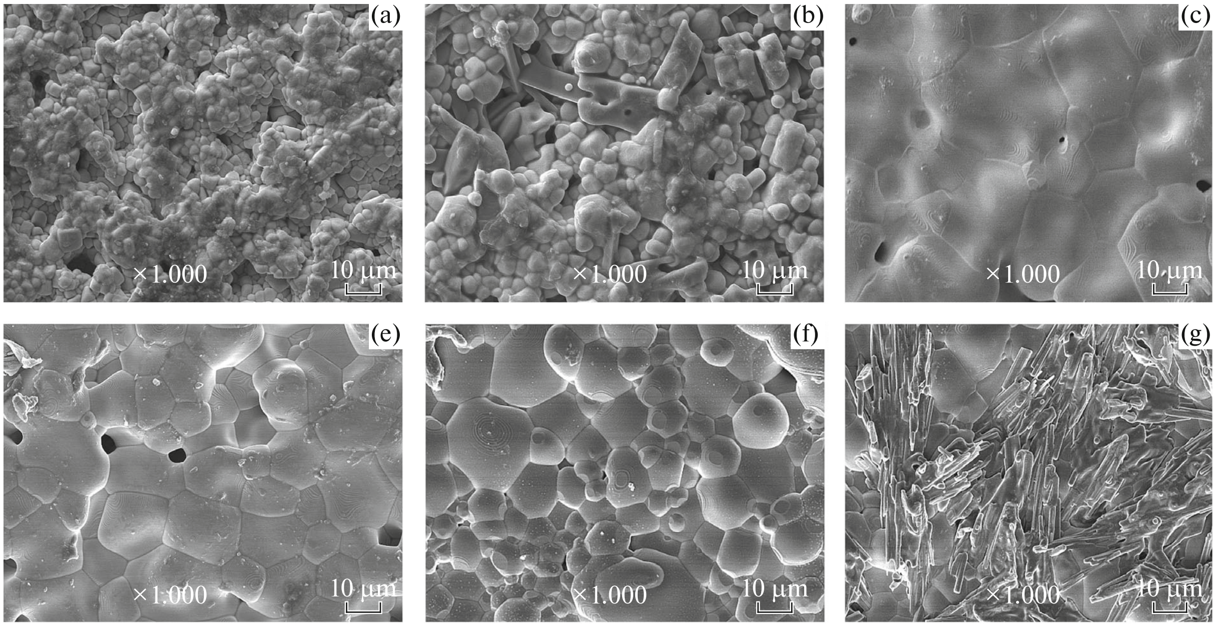

Fig. 3. Microstructure of $(Na_{0.5+x}Bi_{0.5})TiO_3$ with x = (a) 0, (b) 0.02, (c) 0.04, (d) 0.075, and (e, f) 0.10.

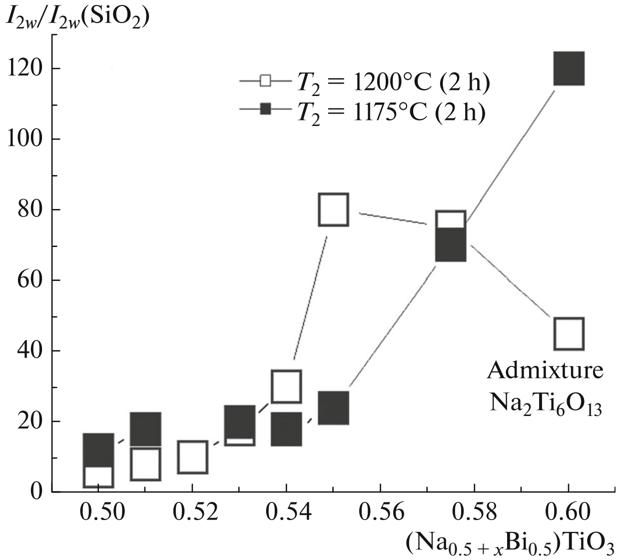

Fig. 4. Dependence of SHG signal intensity on the initial concentration of Na^{1+} cations.

CONCLUSIONS

The change in the parameters of the structure and dielectric properties of the investigated ceramics confirms the effect of the cation deficit in sublattice *A* on their functional properties. Upon an increase in the Na/Bi ratio in the initial compositions, a rise in spontaneous polarization was observed through SHG measurements, indicating improvement in the dielectric and SE properties of the ceramics. The observed increase in the dielectric permittivity at room temperature in compositions with $x = 0.01–0.04$ also testifies to the potential for improving the piezoelectric properties of the investigated ceramics.

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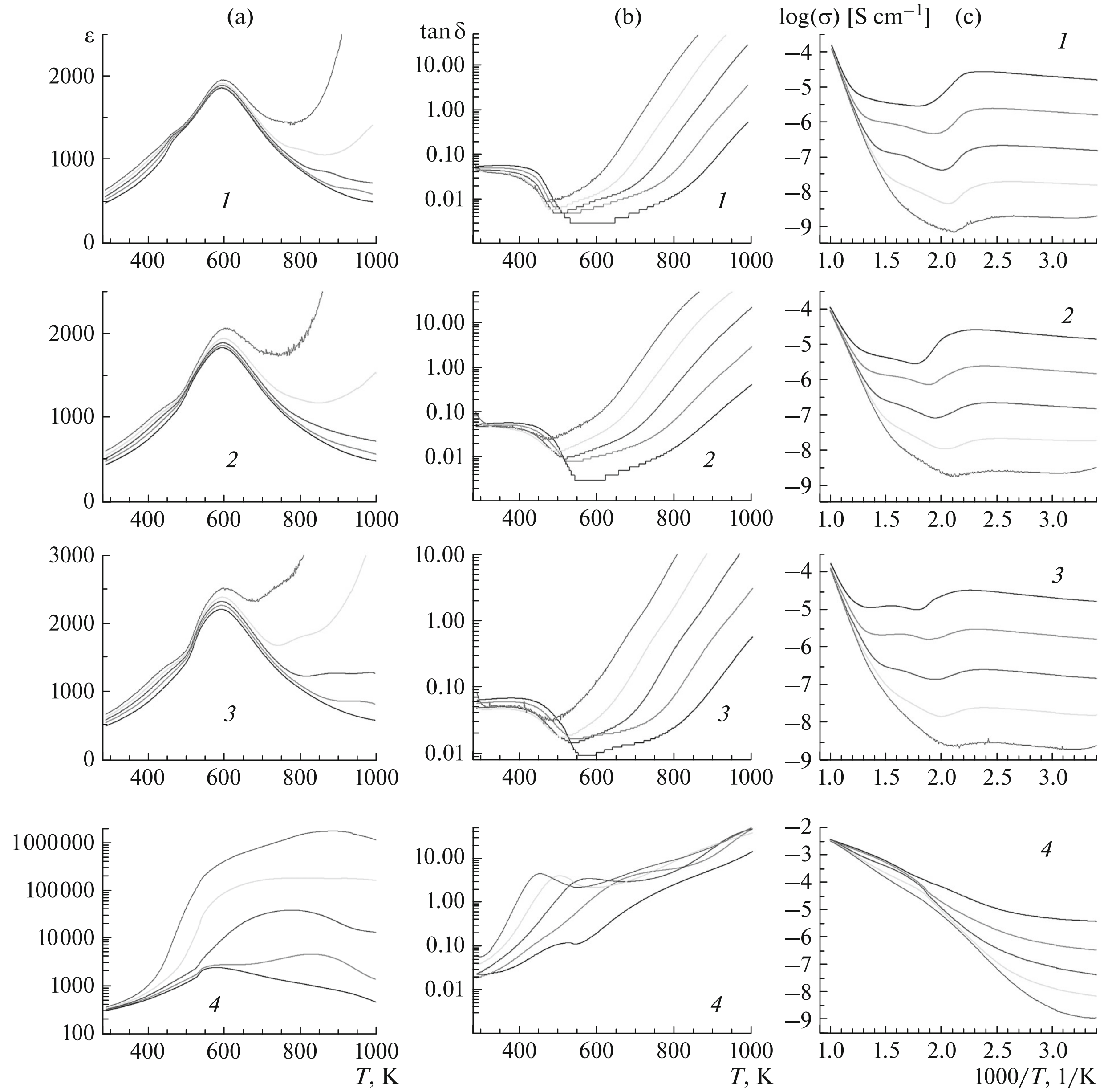

Fig. 5. Temperature dependences of (a) dielectric constant $\varepsilon(T)$, (b) tangent of the dielectric loss angle $\tan\delta(T)$, and (c) electric conductivity $\log\sigma(1000/T)$ of $(Na_{0.5+x}Bi_{0.5})TiO_3$ with x = (*1*) 0.0, (*2*) 0.03, (*3*) 0.05, (*4*) 0.075, measured at 100 Hz–1 MHz.

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