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Ferroelectric Phase Transitions of Modified $[(Na_{0.5}Bi_{0.5})_{1-x}La_x]TiO_3$ ($x = 0$–0.1) Sodium Bismuth Titanate-Based Ceramics

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Abstract—We have studied the effect of A-site cation substitutions in sodium bismuth titanate on the structural parameters, microstructure, and dielectric and ferroelectric properties of $[(Na_{0.5}Bi_{0.5})_{1-x}A_x]TiO_3$ (A = La^{3+}, $x = 0$–0.1) ceramics, including those modified with KCl additions. The samples have been shown to undergo phase transitions, which show up as anomalies in dielectric permittivity near ~400 K and peaks at ~600 K. The phase transitions near 400 K exhibit well-defined relaxor behavior, indicative of the presence of polar regions in a nonpolar matrix, as supported by laser second harmonic generation measurements.

Keywords: perovskite structure, sodium bismuth titanate, dielectric, relaxor

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INTRODUCTION

Lead-free materials have been the subject of intense studies in the past decade [1–5]. The most promising of them include perovskite oxides based on sodium bismuth titanate, $(Na_{0.5}Bi_{0.5})TiO_3$ (NBT), a rhombohedral ferroelectric relaxor [6, 7]. The presence of polar clusters, responsible for the high mobility of “domain wall/polar cluster” boundaries, is an important advantage of NBT-based materials, which are characterized by a high remanent polarization, ($P_r = 38\ \mu C/cm^2$) and high Curie temperature ($t_C = 320°C$).

Uncontrolled sodium oxide and bismuth oxide losses during high-temperature sintering lead to poor reproducibility of results. Accordingly, an inherent feature of NBT is that its functional properties depend significantly on its stoichiometry, which in turn depends on preparation conditions [8–14].

One drawback to this material is its high electrical conductivity, which causes polarization problems. Moreover, in the case of A-cation deficiency, lattice charge neutrality is maintained via the formation of oxygen vacancies, which hinder the motion of domain walls during poling and lead to a considerable increase in the ionic conductivity of the material [15–18].

The purpose of this work was to study the effect of A-site cation substitutions on the structure, microstructure, and dielectric and ferroelectric (FE) properties of $[(Na_{0.5}Bi_{0.5})_{1-x}A_x]TiO_3$ (A = La^{3+}, $x = 0$–0.1) ceramics. The substitutions were expected to suppress the formation of oxygen vacancies. To improve the sintering behavior of the ceramics, we added 10 wt % potassium chloride (KCl), a compound with a low melting point: $t_m = 776°C$ [19–24].

EXPERIMENTAL

$[(Na_{0.5}Bi_{0.5})_{1-x}A_x]TiO_3$ (A = La^{3+}, $x = 0$–0.1) ceramic samples with the addition of 10 wt % KCl were prepared by solid-state reactions via two-step annealing at temperatures $T_1 = 1020$–1070 K (6 h) and $T_2 = 1440$–1470 K (1–4 h), using the Na_2CO_3 carbonate (analytical grade), the Bi_2O_3, La_2O_3, and TiO_2 oxides (extrapure grade), and KCl (pure grade) as starting chemicals.

The phase composition and lattice parameters of the ceramics were determined by X-ray diffraction (DRON-3M diffractometer, CuK_α radiation) at room temperature.

The microstructure of the samples was examined on an SMM-2000 scanning probe microscope (Proton Works, Zelenograd, Russia) by atomic force microscopy using MSNL silicon nitride cantilever probes (Bruker, the United States) with a tip radius (determining the resolving power of the instrument) of

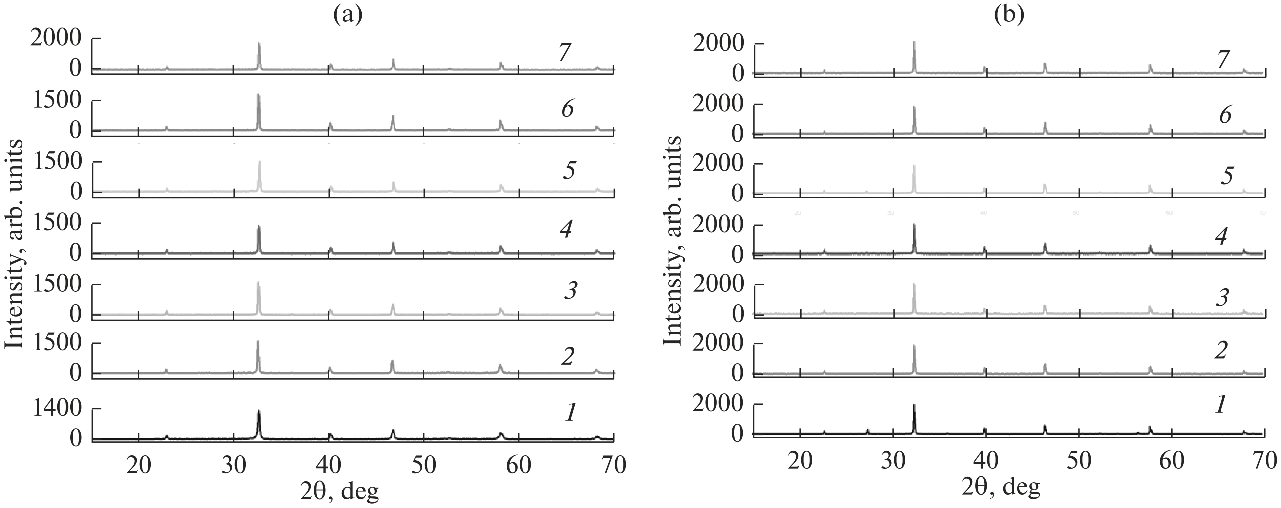

Fig. 1. X-ray diffraction patterns of (a) the $[(Na_{0.5}Bi_{0.5})_{1-x}La_x]TiO_3$ ceramics and (b) the samples modified with 10 wt % KCl: x = (*1*) 0, (*2*) 0.01, (*3*) 0.02, (*4*) 0.03, (*5*) 0.04, (*6*) 0.05, and (*7*) 0.06; T_2 = (a) 1470 and (b) 1420 K (2 h).

2 nm (horizontal and vertical resolving powers of 1 and 0.2 nm, respectively). To evaluate the average horizontal grain size of the samples, which was up to 2–3 μm, we obtained micrographs of regions 8.632 × 9.151 × (1.153–1.786) μm in dimensions. The average grain size S and mean surface roughness R_a were evaluated according to the ISO 4287 international standard.

Spontaneous polarization P_s of the samples was estimated using second harmonic generation (SHG) of laser radiation (Nd:YAG laser, λ = 1.064 μm), whose measured signal, $q = I_{2\omega}/I_{2\omega}(SiO_2)$, was proportional to the square of P_s: $q \sim P_s^2$. The dielectric properties of the ceramics were studied by dielectric spectroscopy (Agilent 4284 A meter, 1 V) at temperatures from 300 to 1000 K and frequencies from 100 Hz to 1 MHz.

RESULTS AND DISCUSSION

According to X-ray diffraction data, single-phase $[(Na_{0.5}Bi_{0.5})_{1-x}La_x]TiO_3$ (x = 0–0.1) samples with the perovskite structure, with and without KCl additions, were obtained at temperatures in the range T_1 = 1020–1070 K, with subsequent sintering at T_2 = 1440–1470 K (Fig. 1).

At the x values indicated above, the pseudocubic lattice parameters of the samples are essentially constant in both systems.

The microstructure of the samples is formed by isometric grains ~1–5 μm in size (Fig. 2). With increasing x, the average grain size of the ceramics decreases slightly.

Measurements of dielectric characteristics revealed FE phase transitions, which showed up as anomalies in dielectric permittivity near ~400 K and peaks at T_{max} ~ 600 K (Figs. 3–5). The phase transitions in the range 390–420 K demonstrate well-defined relaxor behavior, characteristic of NBT and due to the presence of polar FE regions in a nonpolar matrix [25, 26]. SHG measurements confirm that the ceramics have FE properties. The decrease in the SHG signal intensity for $x > 0.01$ correlates with the characteristic feature of the ceramics: better defined relaxor properties. Distributed at random over the A site of the perovskite structure, the Bi^{3+} and Na^+ cations determine the formation of random electric fields, favoring the formation of relaxor properties of the NBT-based materials.

The addition of lanthanum cations was found to suppress relaxor properties, which showed up in the presence of oxygen vacancies in the undoped samples, but in the KCl-modified samples high-temperature (>700 K) dielectric relaxation effects, indicating the presence of oxygen vacancies, were detected (Figs. 4b, 4d, 4f).

Figure 5 shows composition dependences of room-temperature dielectric parameters for the samples studied. Increasing the concentration of lanthanum cations leads to a rise in dielectric permittivity, accompanied by a considerable reduction in electrical conductivity and, accordingly, in dielectric loss (Figs. 5a, 5b, curves *1*). SHG measurements demonstrate that the spontaneous polarization of the $[(Na_{0.5}Bi_{0.5})_{1-x}La_x]TiO_3$ samples with $x > 0.01$ decreases, which points to poorer FE properties (better defined relaxor properties) of the ceramics, presumably as a result of a reduction in the size of polar regions.

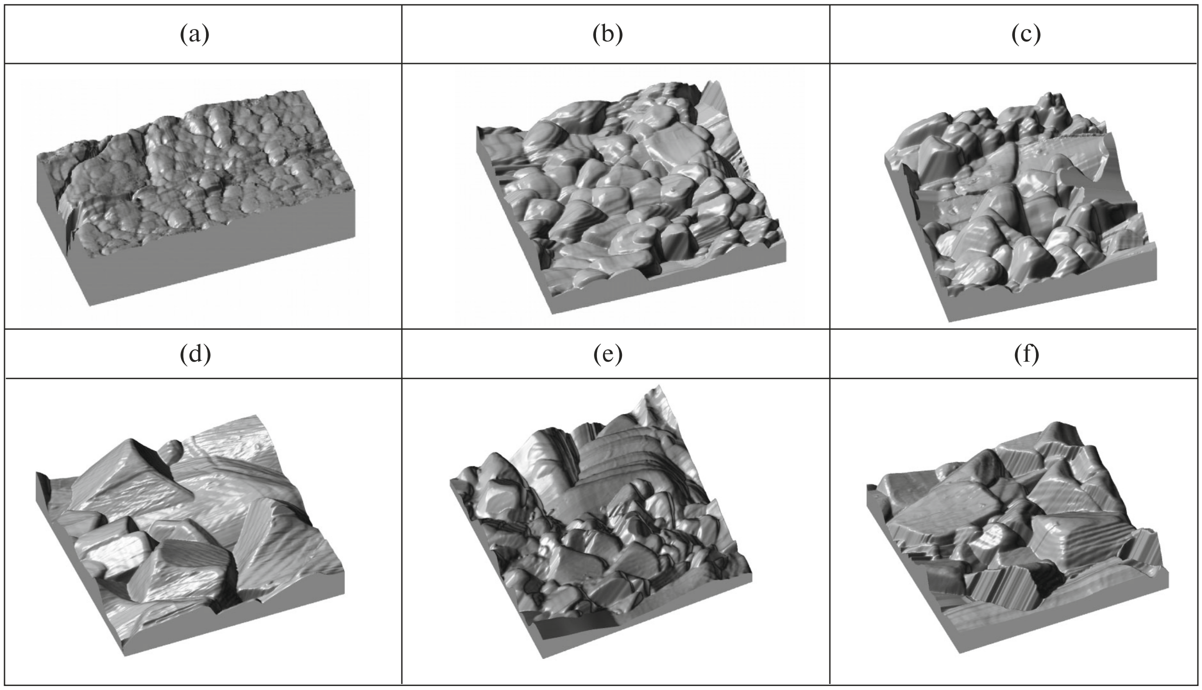

Fig. 2. Microstructures of the $[(Na_{0.5}Bi_{0.5})_{1-x}La_x]TiO_3$ ceramics with x = (a) 0, (b) 0.03, and (c) 0.06 and the KCl-modified ceramics with x = (d) 0, (e) 0.03, and (f) 0.06.

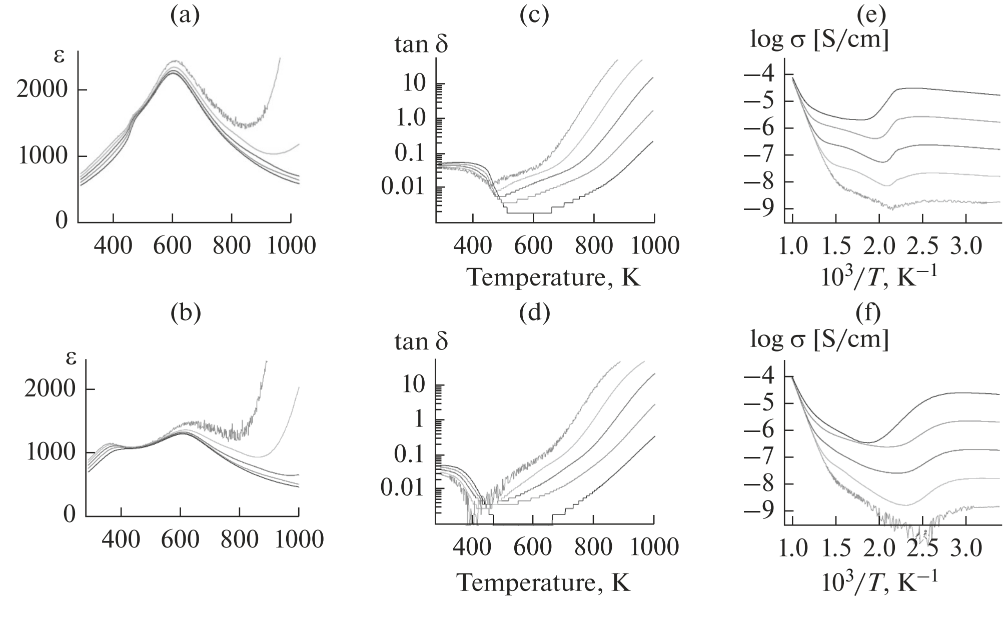

Fig. 3. Temperature dependences of (a, b) dielectric permittivity ε, (c, d) dielectric loss tan δ, and (e, f) electrical conductivity logσ for the $[(Na_{0.5}Bi_{0.5})_{1-x}La_x]TiO_3$ samples with x = (a, c, e) 0 and (b, d, f) 0.06 prepared at T_2 = 1470 K (2 h). The curves were obtained at frequencies f = 100 Hz, 1 kHz, 10 kHz, 100 kHz, and 1 MHz.

CONCLUSIONS

A-site cation substitutions have been shown to influence the properties of $[(Na_{0.5}Bi_{0.5})_{1-x}A_x]TiO_3$ ($A = La^{3+}$, x = 0–0.1) ceramics with the perovskite structure, including those modified with 10 wt % KCl. The observed variations in the dielectric properties of the ceramics confirm that the stoichiometry of the A cation sublattice influences their functional properties. The spon-

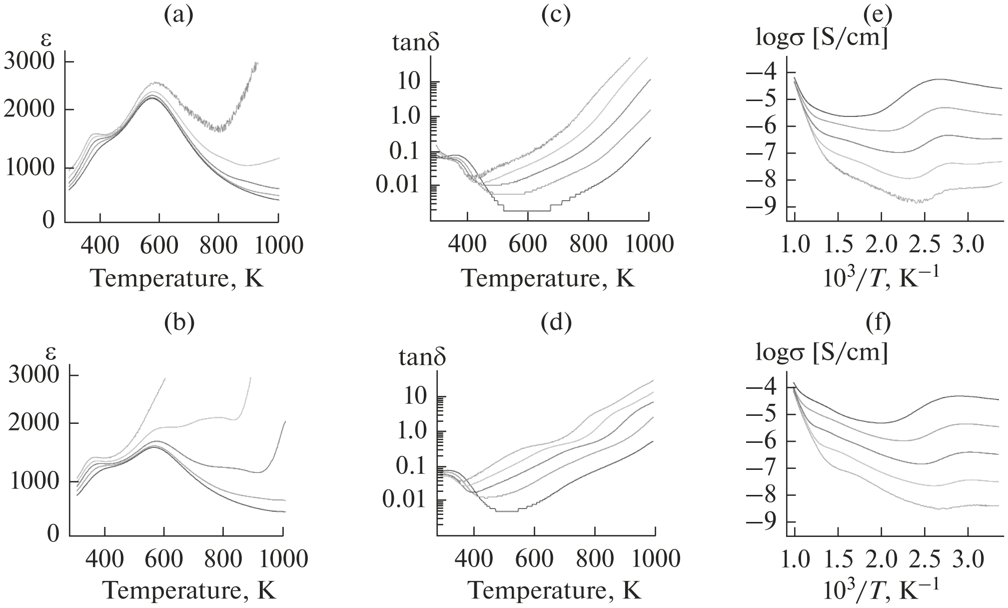

Fig. 4. Temperature dependences of (a, b) dielectric permittivity ε, (c, d) dielectric loss tan δ, and (e, f) electrical conductivity logσ for the KCl-modified $[(Na_{0.5}Bi_{0.5})_{1-x}La_x]TiO_3$ samples with x = (a, c, e) 0 and (b, d, f) 0.06 prepared at T_2 = 1420 K (2 h). The curves were obtained at frequencies f = 100 Hz, 1 kHz, 10 kHz, 100 kHz, and 1 MHz.

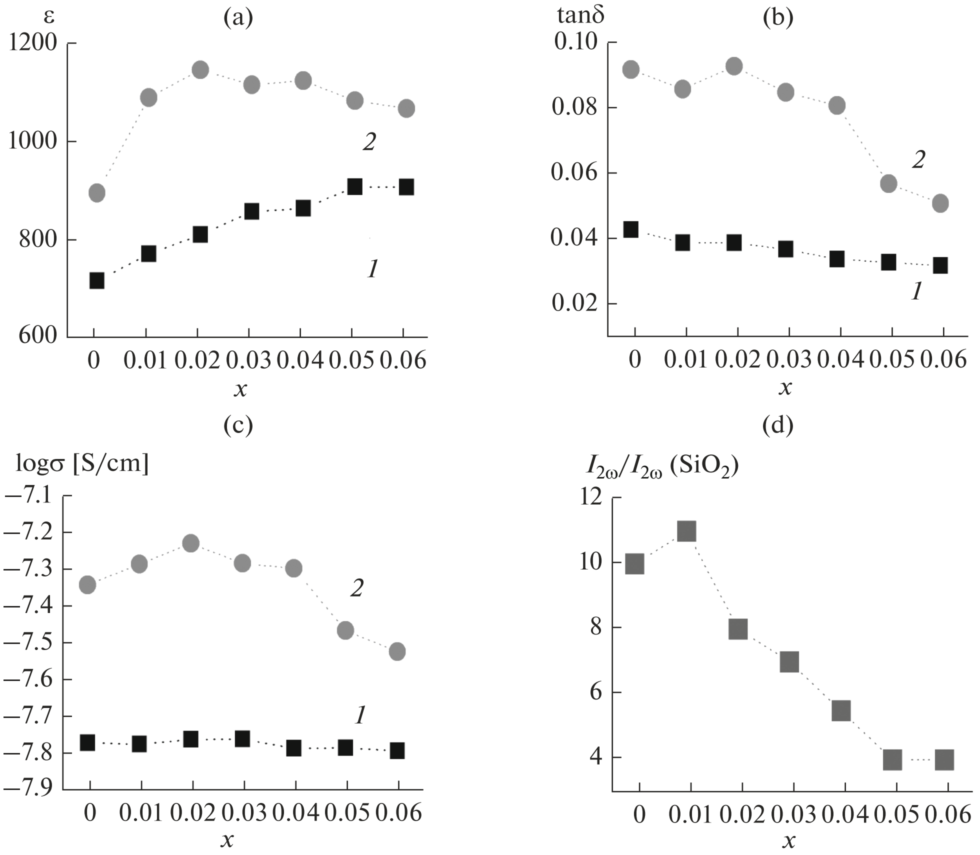

Fig. 5. Composition dependences of room-temperature (a) dielectric permittivity, (b) dielectric loss, (c) electrical conductivity, and (d) SHG signal intensity $I_{2\omega}/I_{2\omega}(SiO_2)$ for the (*1*) $[(Na_{0.5}Bi_{0.5})_{1-x}La_x]TiO_3$ and (*2*) KCl-modified samples prepared at T_2 = (*1*) 1470 and (*2*) 1420 K (2 h).

taneous polarization of the $[(Na_{0.5}Bi_{0.5})_{1-x}La_x]TiO_3$ samples with $x > 0.01$ decreases, which points to better defined relaxor properties of the ceramics, presumably as a result of a reduction in the size of polar regions. At the same time, the increase in dielectric permittivity with increasing x, accompanied by a reduction in dielectric loss, suggests that the piezoelectric properties of ceramics in the system studied here can be improved.

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