

Synthesis, Microstructure, Dielectric and Ferroelectric Properties of (Na,Bi,K)TiO₃ Ceramics

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Abstract—Single-phase ceramic samples with the perovskite structure [(Na_{0.5}Bi_{0.5})_{1-x}K_x]TiO₃ ($x = 0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06$) are prepared by the method of solid-state synthesis and their structure, microstructure and dielectric and ferroelectric properties are studied. An increase in the unit-cell parameters of the perovskite lattice as a result of an increase in the K-cation content in accordance with the ratio of the radii of cations in the *A* sublattice of the perovskite structure is proved. The method of second-harmonic generation confirms that the introduction of potassium cations in the *A* positions of the perovskite lattice promotes enhancement of the ferroelectric properties of the studied samples. Dielectric-relaxation effects are revealed, which indicate the presence of vacancies in the oxygen sublattice.

Keywords: sodium bismuth titanate, ceramics, perovskite structure, microstructure, ferroelectrics, dielectric properties

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INTRODUCTION

Oxide-ion conductors are widely used in many important technological instruments and devices, such as solid oxide fuel cells, oxygen sensors, pumps, and oxygen-permeable membranes [1–5]. The last decade has been marked by extraordinary progress in the study of new oxide-ion conductors that meet the requirements of creating environmentally friendly energy sources, sensors and other devices. Scientists are faced with the task of finding lead-free technological materials in the field of creating eco-friendly ceramic piezoelectric materials for applications in sensors, actuators and transducers in view of the current acute need to replace lead zirconate titanate PbZr_{1-x}Ti_xO₃ (LZT), which has been most widely used for several decades. The toxicity of lead as an element that is part of almost all widely used piezoelectrics, which causes significant harm to the environment, has motivated the search and development of lead-free materials over the last decade. Therefore, a new family of oxide-ion conductors based on a ferroelectric with the perovskite structure, i.e., sodium bismuth titanate Na_{0.5}Bi_{0.5}TiO₃ (SBT), is one of the most promising candidates for the substitution of PZT and the formation of solid solu-

tions with other ferroelectric materials, such as BaTiO₃ and K_{1-x}Na_xNbO₃, and piezoelectric and high-temperature dielectric capacitor applications [6–8].

High ion conductivity was found in the non-stoichiometric compound Na_{0.5}Bi_{0.49}TiO_{2.985} [9]. Weak Bi–O bonds ensure the migration of oxygen ions along paths with low diffusion barriers (ion transport number $t_i > 0.9$ at temperatures of 600–700°C). There are two types of SBT compound formulations that dramatically differ in nature of their electrical properties. The first type includes compounds close to stoichiometric Na_{0.5}Bi_{0.5}TiO₃. Compounds of these compositions are characterized by electronic conductivity with an activation energy of $E_a \sim 1.7$ eV and are excellent dielectrics. Another type is Bi-deficient compositions. Such SBT compounds exhibit high ion conductivity. In the temperature range below 600°C, the activation energy decreases to values of $E_a < 0.9$ eV, and the conductivity increases significantly (by more than three orders of magnitude). The effect of switching between electronic and ion conductivity in SBT is induced by non-stoichiometry at a level of ≤ 2 at % in the *A* positions of the perovskite structure (Na and/or Bi cat-

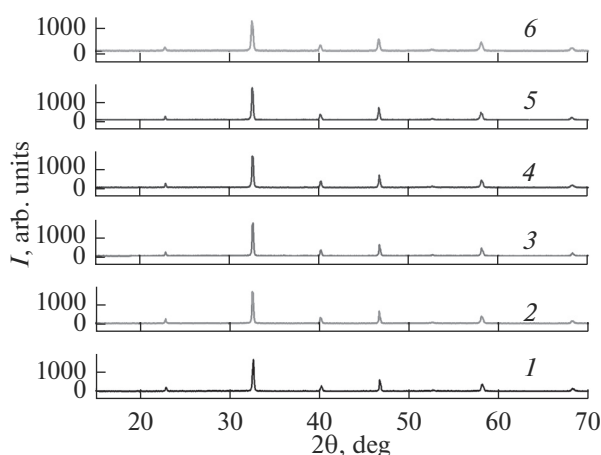


Fig. 1. Diffraction patterns of the surface of ceramic samples $[(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{K}_x]\text{TiO}_3$ from $x = 0$ (1), 0.01 (2), 0.02 (3), 0.03 (4), 0.04 (5), 0.05 (6), 0.06 (7) obtained for $T_1 = 1073$ K (6 h), $T_2 = 1423$ K (2 h).

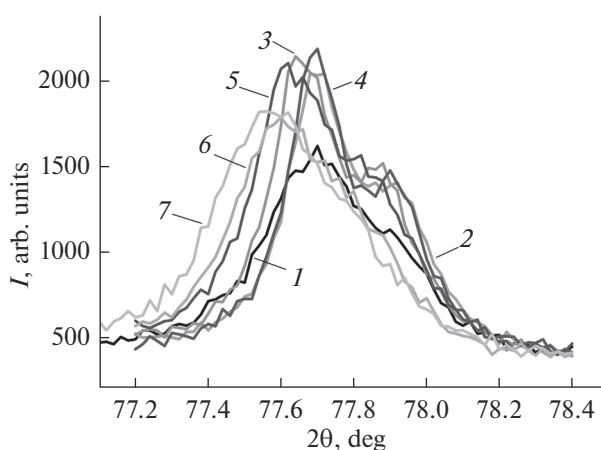


Fig. 2. Plots of diffraction patterns of the surface of ceramic samples $[(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{K}_x]\text{TiO}_3$ from $x = 0$ (1), 0.01 (2), 0.02 (3), 0.03 (4), 0.04 (5), 0.05 (6), 0.06 (7) obtained for $T_1 = 1073$ K (6 h), $T_2 = 1423$ K (2 h).

ions). The effect of non-stoichiometry for cations in the A positions on the electrical and piezoelectric properties of SBT were studied in a number of works [10–18]. However, due to the uncontrollable losses of bismuth oxide during high-temperature synthesis, the reproducible production of single-phase samples remains a challenge. In addition, despite intensive research on SBT-based ceramics, it seems appropriate to more thoroughly study and systematize the effects of donor and acceptor doping in SBT-based solid solutions.

The aim of this study is a comprehensive investigation into the effects of acceptor additives, namely potassium cations, in the A position of perovskite

structures on the structural parameters, microstructure and functional properties of ceramics.

EXPERIMENTAL

Ceramic compositions $[(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{K}_x]\text{TiO}_3$ ($x = 0, 0.01, 0.02, 0.03, 0.04, 0.05$ and 0.06) were obtained by solid-phase synthesis during double annealing. Homogenized stoichiometric mixtures were pressed and annealed at temperatures of $T_1 = 1073$ K (8 h) and $T_2 = 1423$ K (2 h) with intermediate grinding in ethanol. The optimal synthesis mode was determined by varying the temperature and duration of heat treatment. Bismuth oxides were used as the initial reagents ultra-high purity Bi_2O_3 and ultra-high purity titanium TiO_2 , and sodium carbonate Na_2CO_3 (analytic grade) and potassium carbonate K_2CO_3 (analytic grade). The phase composition and parameters of the crystal structure were studied at room temperature by X-ray phase analysis (DRON-3M diffractometer, CuK_α -radiation).

The microstructure of the samples was studied by atomic-force microscopy on an SMM-2000 scanning probe microscope (PROTON Plant, Zelenograd, Russia) using cantilever probes of the MSNL type made of silicon nitride from Bruker (USA) with a probe radius of 2 nm, which determines the resolution (1 nm horizontally and 0.2 nm vertically). To calculate the average horizontal grain sizes of the studied samples, reaching 2–3 microns, frames with a size of $8.632 \times 9.151 \times (1.153\text{--}1.786)$ μm were taken, and the average grain size S and average surface roughness R_a are calculated according to the methods of the international standard ISO 4287.

To estimate the value of spontaneous polarization P_s the samples used the method of the second-harmonic generation (SHG) of laser radiation (Nd: YAG laser, $\lambda = 1.064$ μm), given that the measured signal $q = I_{2\omega}/I_{2\omega}(\text{SiO}_2)$ is proportional to the value of spontaneous polarization P_s : $q \sim P_s^2$. The dielectric properties of ceramics were studied by dielectric spectroscopy (Agilent 4284 A meter, 1 V) in the temperature range 300–1000 K and frequencies of 100 Hz–1 MHz.

RESULTS AND THEIR DISCUSSION

According to X-ray phase analysis, a phase with the perovskite structure is formed during annealing at a temperature of $T_1 = 1073$ K (8 h). As a result of sintering at $T_2 = 1423$ K (2 h), single-phase samples were obtained in the entire studied region of the partial substitution of sodium and bismuth cations with potassium cations. The samples are characterized by a pseudocubic structure (Fig. 1). Figure 2 shows frag-

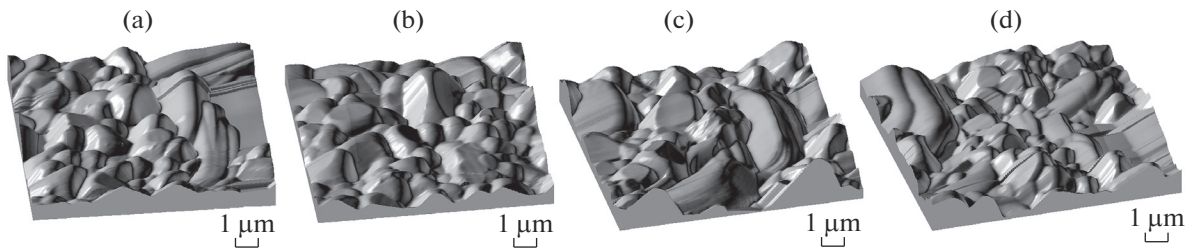


Fig. 3. Microstructure of the ceramic surface $[(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{K}_x]\text{TiO}_3$ from $x = 0.01$ (a), 0.02 (b), 0.04 (c), 0.06 (d).

ments of the diffraction patterns of samples with replacement of a part of the sodium and bismuth cations by potassium cations, demonstrating the successive shift of the diffraction peaks with $h^2 + k^2 + l^2 = 14$ to the region of smaller angles, which indicates an increase in the unit-cell parameter as a result of the replacement of Na^+ and Bi^{3+} cations with K^+ cations in accordance with the ratio of the radii of cations in the sublattice A (Na^+ is 1.39, Bi^{3+} is 1.17, K^+ is 1.64 Å).

The microstructure of the modified ceramics was studied by atomic-force microscopy. The surface of the samples is characterized by a homogeneous microstructure with isometric grains $\sim 2\text{--}5\ \mu\text{m}$ in size (Fig. 3). The effect of grain-boundary melting, which reflects the fact of the liquid-phase sintering mechanism during high-temperature processing, should be noted. The microstructure of such ceramics is characterized by the dense packing of grains. The average grain size is $\sim 3\ \mu\text{m}$ in samples with a low content of potassium cations ($x = 0.01\text{--}0.02$) and $\sim 2.5\ \mu\text{m}$ in samples with higher content of potassium cations ($x = 0.04\text{--}0.06$).

In order to confirm the ferroelectric properties of the samples, the SHG method of laser radiation was used. As expected, all synthesized samples belong to the polar class of substances. The results obtained indicate an increase in the ferroelectric properties of SBT ceramics with the introduction of potassium cations in the A position of the perovskite lattice (Fig. 4). With an increase in the content of potassium cations in the samples (values x) there is an increase in the SHG signal $q = I_{2\omega}/I_{2\omega}(\text{SiO}_2)$, proportional to the value of the spontaneous polarization, from $q = 10$ to $q = 50$ in the samples with $x = 0.0$ and 0.06 , respectively.

As a result of dielectric measurements, ferroelectric-phase transitions of the first kind were revealed: pronounced maxima are observed in the temperature dependences of the dielectric constant ϵ near 600 K and corresponding minima are observed in the temperature dependences of the dielectric losses (Fig. 5). The dielectric constant of the potassium-modified

samples at room temperature decreases as the content of potassium cations in the ceramics increases. Near T_C they also decline with the growth of x by more than twice when doubling the content of potassium cations in the samples. In the potassium-modified ceramics, a decrease in the total electrical conductivity σ is observed near the phase-transition temperature (Fig. 5). At high temperatures at $\sim 1000\ \text{K}$, the synthesized samples are characterized by an increase in electrical conductivity to $\sigma \sim 10^{-4}\ \text{S/cm}$.

At temperatures above 700 K, dielectric-relaxation effects were also revealed in the samples modified with potassium cations, which indicate the presence of vacancies in the oxygen sublattice, caused, among other things, by the loss of bismuth oxide during high-temperature synthesis (Figs. 5c, 5d). During the transport of oxygen ions in ferroelectric ceramics, dipoles are formed that relax in an alternating electric field [19–21].

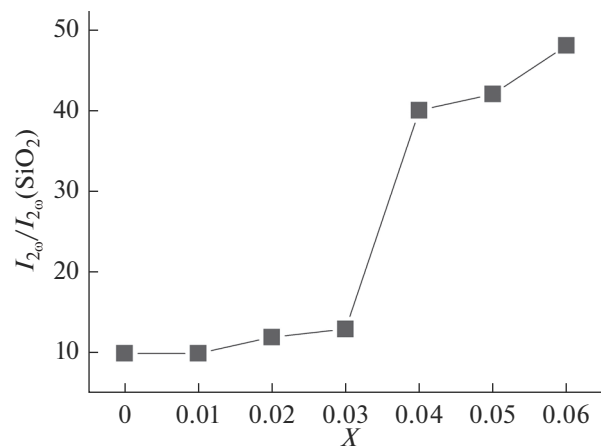


Fig. 4. Concentration dependence of the SHG signal intensity $q = I_{2\omega}/I_{2\omega}(\text{SiO}_2)$ samples $[(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{K}_x]\text{TiO}_3$ obtained for $T_1 = 1073\ \text{K}$ (6 h), $T_2 = 1423\ \text{K}$ (2 h).

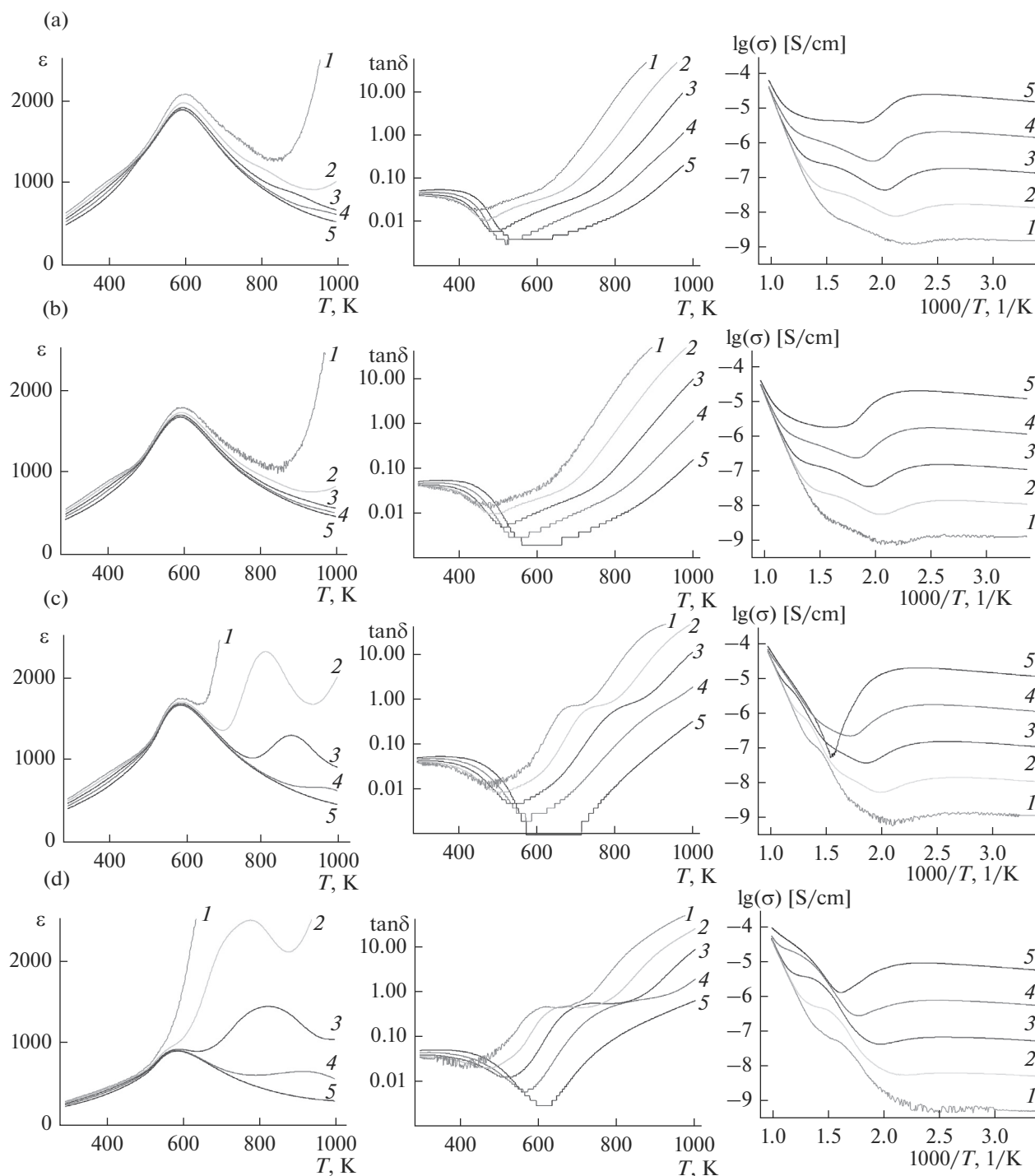


Fig. 5. Temperature dependences of the dielectric constant ϵ , dielectric loss $\tan \delta$ and electrical conductivity $\log \sigma$ of the ceramic samples $[(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{K}_x]\text{TiO}_3$ with $x = 0.03$ (a), 0.04 (b), 0.05 (c), 0.06 (d), measured at frequencies of: f : 100 Hz (1); 1 (2); 10 (3); 100 kHz (4); 1 MHz (5).

CONCLUSIONS

Single-phase ceramic samples of new compositions based on sodium bismuth titanate $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ modified with potassium cations, and their structure,

microstructure, dielectric and ferroelectric properties were studied. The effect of expansion of the unit cell of samples modified by potassium cations with the partial substitution of A sublattice cations of the per-

ovskite structure with cations with a large ionic radius is established.

First-order ferroelectric phase transitions near 600 K are confirmed by dielectric spectroscopy and the second-harmonic generation of laser radiation. The results of measuring the samples by the SHG method indicate an increase in the ferroelectric properties of SBT ceramics with the introduction of potassium cations in the *A* positions of the perovskite lattice. The effects of dielectric relaxation are revealed, indicating the presence of vacancies in the oxygen sublattice.

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REFERENCES

1. T. Ishihara, M. Honda, T. Shibayama, H. Minami, H. Nishiguchi, and Y. Takita, *J. Electrochem. Soc.* **145**, 3177 (1998).
2. K. Huang, R. S. Tichy, and J. B. Goodenough, *J. Am. Ceram. Soc.* **81**, 2576 (1998).
3. S. P. S. Badwal, S. Giddey, C. Munnings, and A. Kulkarni, *J. Austral. Ceram. Soc.* **50**, 23 (2014).
4. R. Biswal and K. Biswas, *Int. J. Hydrogen Energy* **40**, 509 (2015).
5. P. Majewski, M. Rozumek, C. A. Tas, and F. Aldinger, *J. Electroceram.* **8**, 65 (2002).
6. P. K. Panda, *J. Mater. Sci.* **44**, 5049 (2009).
7. V. V. Shvartsman and D. C. Lupascu, *J. Am. Ceram. Soc.* **95**, 1 (2012).
8. J. Rödel, K. G. Webber, R. Dittmer, Jo. Wook, M. Kimura, and D. Damjanovic, *J. Eur. Ceram. Soc.* **35**, 1659 (2015).
9. L. Ming, H. Zhang, S. N. Cook, L. Linhao, J. A. Kilner, J. M. Reaney, and D. C. Sinclair, *Chem. Mater.* **27**, 629 (2015).
10. S. B. Vakhrushev, V. A. Isupov, B. E. Kvyatkovsky, N. M. Okuneva, I. P. Pronin, G. A. Smolensky, and P. P. Syrnikov, *Ferroelectrics* **63**, 153 (1985).
11. G. O. Jones and P. A. Thomas, *Acta Crystallogr., Sect. B: Struct. Sci.* **58**, 168 (2002).
12. V. Dorcet, G. Trolliard, and P. Boullay, *Chem. Mater.* **20**, 5061 (2008).
13. X. Tan, M. Cheng, J. Frederick, S. Beckman, and K. Webber, *J. Am. Ceram. Soc.* **94**, 4091 (2011).
14. E. D. Politova, D. A. Strebkov, A. V. Mosunov, N. V. Golubko, G. M. Kaleva, N. V. Sadovskaya, and S. Yu. Stefanovich, *Bull. Russ. Acad. Sci.: Phys.* **82**, 269 (2018).
15. E. D. Politova, A. V. Mosunov, D. A. Strebkov, N. V. Golubko, G. M. Kaleva, B. A. Loginov, A. B. Loginov, and S. Yu. Stefanovich, *Inorg. Mater.* **54**, 744 (2018).
16. E. D. Politova, N. V. Golubko, G. M. Kaleva, A. V. Mosunov, N. V. Sadovskaya, D. A. Belkova, and S. Yu. Stefanovich, *Phys. Solid State* **60**, 428 (2018).
17. E. D. Politova, N. V. Golubko, A. V. Mosunov, N. V. Sadovskaya, G. M. Kaleva, D. A. Kiselev, and A. M. Kislyuk, *Ferroelectrics* **531**, 22 (2018).
18. E. D. Politova, G. M. Kaleva, N. V. Golubko, A. V. Mosunov, N. V. Sadovskaya, D. A. Belkova, and S. Yu. Stefanovich, *Crystallogr. Rep.* **63**, 266 (2018).
19. A. V. Mosunov, N. U. Venskovskii, and G. M. Kaleva, *Ferroelectrics* **299**, 149 (2004).
20. W. Li, C. Wang, J. Zhu, and Y. Wang, *J. Phys.: Condens. Matter* **16**, 9201 (2004).
21. E. D. Politova, E. A. Fortalnova, G. M. Kaleva, A. V. Mosunov, M. G. Safronenko, N. U. Venskovskii, V. V. Shvartsman, and W. Kleemann, *Ferroelectrics* **391**, 3 (2009).

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