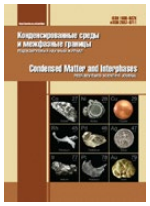

ISSN 1606-867X (Print)
ISSN 2687-0711 (Online)
Condensed Matter and Interphases
Kondensirovannye Sredy i Mezhfaznye Granitsy
https://journals.vsu.ru/kcmf/

Original articles

Research article
https://doi.org/10.17308/kcmf.2025.27/13015

Dielectric and piezoelectric properties of ceramic material based on modified lead zirconate titanate

L. N. Korotkov, N. A. Tolstykh, I. I. Popov✉, A. I. Bocharov, M. A. Kashirin

Voronezh State Technical University,
20 let Oktyabrya st., 84, Voronezh 394006, Russian Federation

Abstract

Objective: A new high-entropy ferroelectric material $0.9Pb_{0.95}Sr_{0.05}(Zr_{0.52}Ti_{0.48})O_3$-$0.05Pb(Zn_{1/3}Nb_{2/3})O_3$-$0.05Pb(Mn_{1/3}Sb_{2/3})O_3$ was synthesized. At room temperature, it has a tetragonal perovskite-like crystal lattice and is characterized by a high electromechanical quality factor.

Experimental: The dielectric properties were studied in the temperature range of 20–500 °C at frequencies of 0.5–500 kHz. A noticeable decrease in the temperature of the ferroelectric phase transition (T_m) in comparison with the base composition $Pb_{0.95}Sr_{0.05}(Zr_{0.52}Ti_{0.48})O_3$ and its diffusion were revealed.

Conclusions: Analysis of experimental data suggests that the material under study is an "intermediate link" between conventional and relaxor ferroelectrics.

Keywords: High-entropy ferroelectrics, Electromechanical quality factor, Permittivity, Diffuse phase transition, Dielectric relaxation

Funding: This work was funded by Russian Science Foundation according to the research project No. 24-22-20054.

For citation: Korotkov L. N., Tolstykh N. A., Popov I. I., Bocharov A. I., Kashirin M. A. Dielectric and piezoelectric properties of ceramic material based on modified lead zirconate titanate. *Condensed Matter and Interphases*. 2024;25(1): 000-000. *Condensed Matter and Interphases*. 2025;27(3): 391–397. https://doi.org/10.17308/kcmf.2025.27/13015

Для цитирования: Коротков Л. Н., Толстых Н. А., Попов И. И., Бочаров А. И., Каширин М. А. Диэлектрические и пьезоэлектрические свойства керамического материала на основе модифицированного цирконата-титаната свинца. *Конденсированные среды и межфазные границы*. 2024;26(1): 391–397. https://doi.org/10.17308/kcmf.2025.27/13015

✉ Ivan I. Popov, e-mail: popovich_vano@mail.ru

1. Introduction

To create some electronic devices (piezoelectric resonators, filters), materials with a high electromechanical quality factor are required. They are produced on the basis of hard ferroelectric ceramics with a homogeneous fine-grained structure and small dissipation of elastic and electric energy over a wide frequency range. Despite the fairly wide range of piezoelectric materials with a high quality factor at present, research aimed at improving their technical characteristics continues.

In recent years, the interest of researchers in the so-called high-entropy materials and, in particular, in high-entropy ferroelectrics has noticeably increased [1]. These materials are distinguished by the fact that in their crystal lattice a certain position can be randomly occupied by various ions with different ionic radii and charge states. For example, in the .9$Pb_{0.95}Sr_{0.05}(Zr_{0.52}Ti_{0.48})O_3-0.05Pb(Zn_{1/3}Nb_{2/3})O_3-0.05Pb(Mn_{1/3}Sb_{2/3})O_3$ perovskite solid solution studied in this work, the "A" sublattice is randomly occupied by Pb^{2+} and Sr^{2+} cations, and the "B" sublattice is randomly occupied by Zr^{4+}, Ti^{4+}, Zn^{2+}, Nb^{5+}, Mn^{2+}, Sb^{5+} cations. High configurational entropy can lead to the following effects [1]: stabilization of new materials, causing significant lattice distortions, preventing grain coarsening, etc. High-entropy ferroelectric materials are widely used in energy storage devices [2, 3], electronic memory devices [1], and piezoelectric transducers [4–7] due to their unique physical properties.

It was shown [7] that the introduction of several cations with different valences and ionic radii can lower the local crystallographic symmetry and, thus, increase the misorientation of the polarization vector relative to the crystal axes. A high-entropy crystal structure can exhibit the so-called flexible polarization, when the crystallographic symmetry restrictions are violated and some rotation of the polarization relative to the "allowed" directions under an electric field becomes possible. Despite the fact that a fairly wide range of high-entropy piezoelectric ceramics currently exists [4–7], including ceramics with a high electromechanical quality factor, a detailed analysis of the dielectric properties in the vicinity of the ferroelectric phase transition has not been carried out.

In this regard, the aim of this work was to synthesize and to investigate the dielectric response of a new high-entropy ferroelectric ceramic material in the vicinity of the ferroelectric phase transition and to study its piezoelectric properties.

2. Experimental

High-entropy ferroelectric ceramics PMZN–PZT [4], PZTM [5], and PZT–PMS–PZN [6] with high electromechanical quality factors were chosen as prototypes of the material synthesized in this work. The synthesized compound has the general formula 0.9$Pb_{0.95}Sr_{0.05}(Zr_{0.52}Ti_{0.48})O_3-0.05Pb(Zn_{1/3}Nb_{2/3})O_3-0.05Pb(Mn_{1/3}Sb_{2/3})O_3$ + 0.1 mol. % CeO_2 (PSZT-PZN-PMS). It is evident from the general formula that the main component of the studied ceramics is a lead zirconate – titanate solid solution, and its composition corresponds to the morphotropic phase boundary. Cerium dioxide localized predominantly at grain boundaries [8] was added to prevent grain growth.

The studied samples were obtained using standard two-stage ceramic technology. Powders of PbO, ZrO_2, TiO_2, MnO_2, MgO, Nb_2O_5, ZnO, Sb_2O_3, and $SrCO_3$ taken in a given stoichiometric ratio were used as initial components in the synthesis. The material was synthesized at a temperature of 850 °C. The powder of the synthesized material was ground in a solution of polyvinyl alcohol in a mortar until the alcohol solution was completely dry. The samples were sintered in an air atmosphere at a temperature of 1100 °C.

X-ray phase analysis (Fig. 1) performed on a Bruker D2 Phaser X-ray diffractometer with CuKα radiation showed that the obtained samples have a slightly distorted tetragonal lattice of perovskite *P4mm* with parameters $a \approx 4.068$ Å and $c \approx 4.086$ Å. Another phase with an undefined structure is present in an insignificant volume along with the tetragonal phase.

The samples for studying the dielectric and piezoelectric properties had the shape of a disk with a diameter of 11 mm and a thickness of 1 mm. Silver conductive paste was applied to the flat surfaces of the samples, then dried and fired at a temperature of 770 °C. Dielectric measurements were carried out on an E7-20 immittance meter at frequencies of 500 Hz – 500 kHz in the temperature range of 20–500 °C

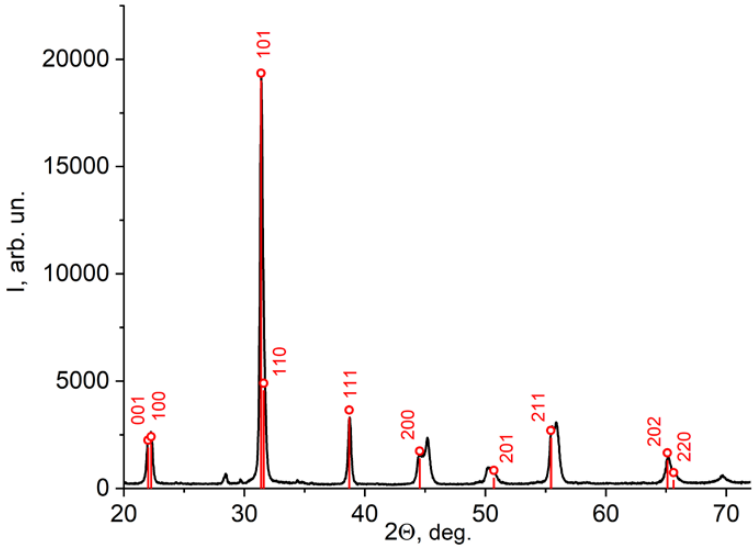

Fig. 1. X-ray diffraction pattern of the studied material

during slow heating (cooling) of the sample at a rate of about 2 °C/min. The temperature was controlled by an alumel – chromel thermocouple with an error of no more than ± 0.5 °C.

The samples for measuring the piezoelectric response were polarized at 120 °C in a DC electric field of 3 kV/mm for 30 minutes. The piezoelectric modulus d_{31}, the electromechanical coupling coefficient K_p, and the mechanical quality factor Q_m were measured at room temperature using the resonance-antiresonance method described in [9].

The microstructure of the samples was examined using a Tescan MIRA 3 scanning electron microscope. The fracture morphology of the sample is shown in Fig. 2. It can be seen that the material has a uniform microstructure with grain sizes of about 2 μm.

3. Results and discussion

Studies of the piezoelectric properties of the material showed that at $T \approx 23$ °C it had a relatively high mechanical quality factor of $Q_m \approx 1095$. The electromechanical coupling coefficient $K_p \approx 0.29$ and the piezoelectric modulus $d_{31} \approx 55$ pC/N had relatively low values, which is typical for ferroelectric ceramics with an increased electromechanical quality factor [9].

Let us discuss the dielectric properties of the synthesized material, which largely determine its piezoelectric activity. The temperature dependences of the permittivity (ε′) obtained by heating the unpolarized sample passed through an almost symmetrical maximum in the vicinity of the temperature $T_{mh} \approx 260$ °C (Fig. 3). This temperature is noticeably lower than in the base composition $Pb_{0.95}Sr_{0.05}(Zr_{0.52}Ti_{0.48})O_3$, where it is about 320 °C [9].

On the cooling curve, the maximum e' was observed at a temperature of $T_{mc} \approx 257$ °C (insert on the right in Fig. 3). The existence of a

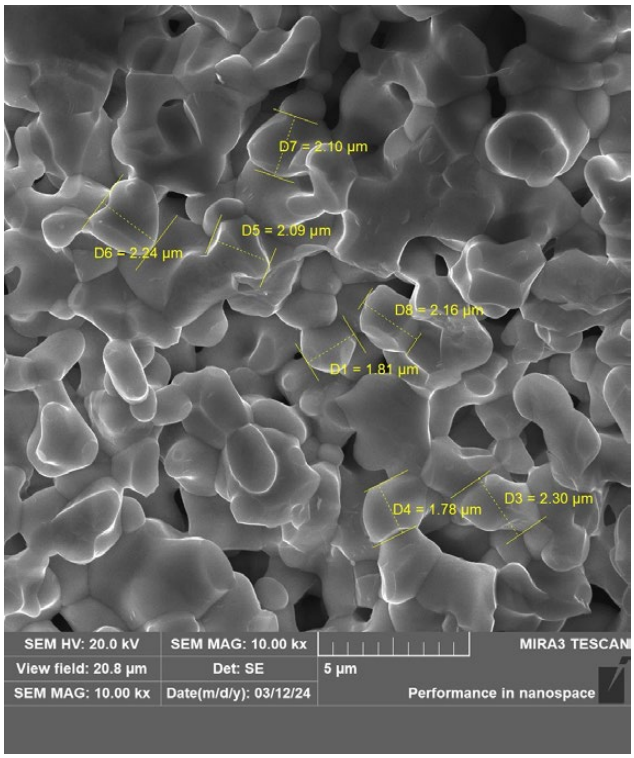

Fig. 2. SEM image of sintered ceramics

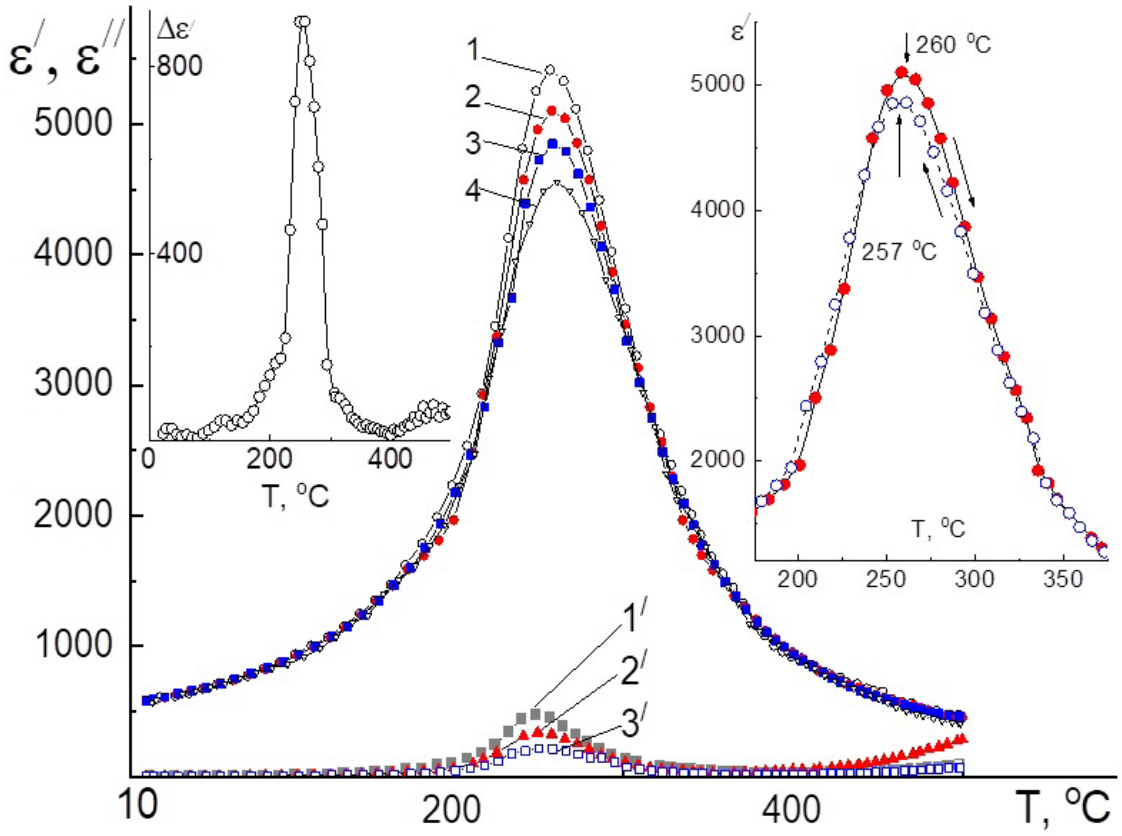

Fig. 3. Temperature dependences of real (*1* – *4*) and imagery (*1′*–*3′*) parts of dielectric permittivity obtained at frequencies 0.5 (*1* and *1′*), 2 (*2* and *2′*), 10 (*3* and *3′*) and 500 (4) kHz during sample heating. The inset on the left shows the $\Delta\varepsilon'(T)$ dependence. The inset on the right shows the $\varepsilon'(T)$ dependences obtained during heating and cooling at a frequency of 2 kHz

temperature hysteresis of the permittivity in the material under study indicates that it underwent a first-order phase transition.

Note, however, that the detected temperature hysteresis e' differed from the characteristic hysteresis of permittivity observed for canonical ferroelectrics, such as $BaTiO_3$, $KNbO_3$, and others, in which hysteresis phenomena are localized in the region of the phase transition and in the polar phase [9, 10]. In this case, $e'(T_{mh}) < \varepsilon'(T_{mc})$. In the case under consideration, the hysteresis e' extended by more than 50 °C into the paraelectric phase. In this case, $\varepsilon'(T_{mh}) > \varepsilon'(T_{mc})$.

Further analysis of the experimental data showed that the $\varepsilon'(T)$ dependences follow the Curie–Weiss law in the vicinity of the phase transition [10]:

$$\varepsilon'(T) = \varepsilon_\infty + \frac{C_1}{T - \theta_1}, \text{ at } T > T_m \quad (1a)$$

and

$$\varepsilon'(T) = \varepsilon_\infty + \frac{C_2}{\theta_2 - T}, \text{ at } T < T_m. \quad (1b)$$

Here $e_¥$ is the temperature-independent component of the permittivity, C_i is the Curie-Weiss constant, q_i is the Curie–Weiss temperature.

The linear dependencies $1/\varepsilon'(T)$ shown in Fig. 4a confirm the applicability of relations (1a) and (1b) to describe the temperature dependences of permittivity in both ferroelectric and paraelectric phases. The best approximation of the experimental results by the Curie–Weiss law was achieved with following parameter values: $C_1 \approx 86555$ K, $\theta_1 \approx 310$ °C, $C_2 \approx 146263$ K, $\theta_2 \approx 260$ °C. The values of the constants C_1 and C_2 are of the order of ~ 10^5 K, which is typical for a ferroelectric phase transition of the displacement type.

Note that the temperature $\theta_1 \approx 310$ °C is higher than $T_{mh} \approx 260$ °C and the ratio of constants $C_1/C_2 \approx 0.59$ in the studied material. This contradicts the phenomenological theory of first-order

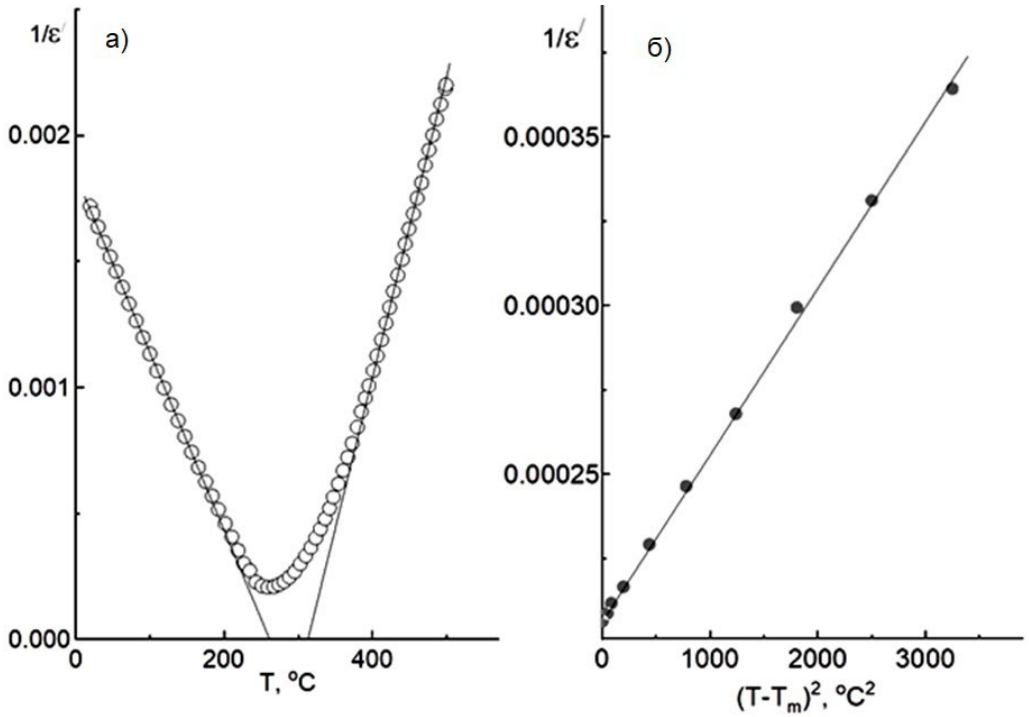

Fig. 4. Temperature dependences of the permittivity, plotted at the coordinates 1/e'(*T*) (a) and at the coordinates 1/e'$(T\text{-}T_m)^2$ (b)

ferroelectric phase transitions [10], according to which $C_1/C_2 \approx 4$ and $\theta_1 < T_m$. This is probably due to the high degree of phase transition diffusion. Indeed, ferroelectrics with a diffuse phase transition are characterized by a bell-shaped maximum of the permittivity [10] and the fulfillment of the inequality $\theta_1 \geq T_m$. It is interesting to note that in the case under consideration θ_1 differs slightly from the Curie temperature of the base composition $Pb_{0.95}Sr_{0.05}(Zr_{0.52}Ti_{0.48})O_3$.

The study of the causes of phase transition diffusion is one of the main areas in the research of disordered ferroelectrics. Currently, a number of models explain this phenomenon [10–14]. The most obvious is the model proposed by V. A. Isupov and G. A. Smolensky, where the ferroelectric phase transition diffusion is associated with composition fluctuations [10]. The phase transformation in different microregions of the crystal occurs at different temperatures due to the microscopic inhomogeneity of the material and is accompanied by a broadening of the maximum e'. According to the fluctuation model, the temperature dependence of the permittivity near T_m is determined by the expression [10]:

$$\frac{1}{\varepsilon'} = \frac{1}{\varepsilon'_m} + \frac{(T_m - T)^2}{2\varepsilon'_m \sigma^2}, \quad (2)$$

where ε_m is the dielectric permittivity value at temperature T_m, s is the transition diffusion parameter meaning the standard deviation of the local Curie temperature. The dependence $1/\varepsilon'(T-T_m)^2$ should be linear according to expression (2), which is indeed observed in the temperature range $T_m \leq T \leq T_d$ (Fig. 4b). Here T_d is the Burns temperature, where the dependence e'(*T*) begins to deviate from the Curie-Weiss law upon cooling from the paraelectric phase. The estimate of the dependence ε′(T) made according to expression (2) yielded s ≈ 64 °C and $T_d \approx 400$ °C.

A characteristic feature of ferroelectrics with a diffuse phase transition is a strong dispersion of the permittivity in the vicinity of T_m and the dependence of the temperature T_m on the frequency of the measuring field. Studies of the dielectric response at different frequencies revealed a strong dispersion of ε′ (Fig. 3), the depth of which was determined as Δε′ ≈ ε′(500 Hz) – ε′(500 kHz). It was found that the maximum of De' is observed in the region of the diffuse ferroelectric phase transition at a temperature of approximately 7 °C below

T_m. The width of the $\Delta\varepsilon'(T)$ dependence at half height is about 55 °C and is close in value to the diffusion parameter $\sigma \approx 64$ °C. This suggests that the experimentally observed e' dispersion may be due to the dynamics of polar microregions in accordance with the approaches proposed for relaxor ferroelectrics [10, 11, 13, 14].

Above T_m, the value of De' decreases rapidly as the Burns temperature $T_d \approx 400$ °C is approached, where it reaches a minimum. The growth of $\Delta\varepsilon$ observed at $T > T_d$ is apparently associated with an increase in electrical conductivity. The small depth of the permittivity dispersion at temperatures significantly below T_m indicates a low mobility of ferroelectric domain boundaries.

The temperature dependence of the imaginary part of the dielectric permittivity $\Delta\varepsilon''$ slightly below T_m passes through a maximum (Fig. 3), which shifts toward higher temperatures with increasing measurement frequency, as in the case of relaxor ferroelectrics. However, unlike the latter, the maximum of ε'' noticeably decreases with increasing frequency of the measurement field *f*.

The temperature dependence of the characteristic time of dielectric relaxation near T_m, determined from the frequency shift of the maximum ε'', was approximated by both the Arrhenius equation and the empirical Vogel–Fulcher–Tammann equation [15], but in both cases the obtained values of the parameters (pre-exponential factor and activation energy) go beyond the physically reasonable values.

Thus, the observed dielectric relaxation requires further study. However, it is assumed that the experimentally observed dispersion of the dielectric response near T_m is due to several dielectric relaxation mechanisms, as in the case considered in [16].

4. Conclusions

A hard ferroelectric high-entropy ceramic $0.9Pb_{0.95}Sr_{0.05}(Zr_{0.52}Ti_{0.48})O_3$-$0.05Pb(Zn_{1/3}Nb_{2/3})O_3$-$0.05Pb(Mn_{1/3}Sb_{2/3})O_3$ + 0.1 mol. % CeO_2 with a comparatively high electromechanical quality factor $Q_m \approx 1095$ was synthesized. It was found that the introduction of complex additives, $Pb(Zn_{1/3}Nb_{2/3})O_3$ and $Pb(Mn_{1/3}Sb_{2/3})O_3$, into a solid solution based on the base composition, $Pb_{0.95}Sr_{0.05}(Zr_{0.52}Ti_{0.48})O_3$, leads to a noticeable decrease in the ferroelectric phase transition temperature (T_m) and its diffusion. With cyclic temperature changes in the vicinity of T_m, an anomalously wide temperature hysteresis of the permittivity was observed, which extended into both the ferroelectric and paraelectric phases.

Near *T*m, the $\varepsilon'(T)$ dependences are satisfactorily described by the so-called quadratic Curie–Weiss law with a phase transition diffusion parameter of $\sigma \approx 64$ °C. Analysis of the dispersion of the dielectric response showed that the dispersion depth $\Delta\varepsilon'$ reaches its greatest values near the permittivity maximum in the temperature range of the s order. The nature of the ε' and ε'' dispersion near T_m differs qualitatively from that observed for relaxor ferroelectrics and is apparently due to the action of several mechanisms.

Based on the totality of the results obtained, it can be stated that the studied material is an "intermediate link" between conventional and relaxor ferroelectrics. Its composition can be considered as a base for the development of piezoceramics with increased electromechanical quality factor.

Contribution of the authors

The authors contributed equally to this article.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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** Translated by author of the article*

Information about the authors

Leonid N. Korotkov, Dr. Sci. (Phys.–Math), Professor at the Department of Solid-State Electronics, Voronezh State Technical University (Voronezh, Russian Federation).
https://orcid.org/0000-0002-5350-5841
l_korotkov@mail.ru

Nikita A. Tolstykh, Cand. Sci. (Phys.–Math.), Head of the Scientific and Educational Laboratory «Functional Materials», Voronezh State Technical University (Voronezh, Russian Federation).
https://orcid.org/0000-0001-5994-9331
mad_nik@bk.ru

Ivan I. Popov, Cand. Sci. (Phys.–Math.), Senior Lecturer at the Department of Solid-State Electronics, Voronezh State Technical University (Voronezh, Russian Federation).
https://orcid.org/0000-0002-1183-0662
popovich_vano@mail.ru

Alexey I. Bocharov, Leading Engineer of the BREC «Thermoelectric Phenomena», Voronezh State Technical University (Voronezh, Russian Federation).
https://orcid.org/0000-0003-4812-9586
lekha.bocharoff@yandex.ru

Maxim A. Kashirin, Engineer of the Scientific and Educational Laboratory «Functional Materials, Voronezh State Technical University (Voronezh, Russian Federation).
https://orcid.org/0000-0003-0150-0317
mnitro@yandex.ru

Received September 10, 2024; approved after reviewing October 7, 2024; accepted for publication October 15, 2024; published online September 25, 2025.