

Article

Phase Formation and Properties of Multicomponent Solid Solutions Based on $\text{Ba}(\text{Ti}, \text{Zr})\text{O}_3$ and AgNbO_3 for Environmentally Friendly High-Efficiency Energy Storage

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Abstract: This paper investigates the processes of phase formation of solid solutions of $(1 - x)\text{BaTi}_{0.85}\text{Zr}_{0.15}\text{O}_3 - x\text{AgNbO}_3$ where $x = 0, 0.03, 0.06, 0.09$. The optimal temperatures of synthesis and sintering are determined. From the results of X-ray diffraction analysis, it follows that all solid solutions have a perovskite-type structure. Analysis of the microstructure showed that the average grain size decreases at concentrations $x = 0.03$ and 0.06 . Correlations between the cationic composition and dielectric characteristics of the studied solid solutions have been established. The values of the total stored energy and efficiency are determined. The maximum stored energy was found for a solid solution with $x = 0.03$ and amounted to $0.074 \text{ J} \cdot \text{cm}^{-3}$ with an efficiency of 76.5%.

Keywords: barium titanate; microstructure; ferroelectrics; ceramics; energy storage



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1. Introduction

Currently, there is an increasing number of research papers devoted to the study of media that combine several different ordered charge subsystems: ferroelectric or antiferroelectric [1–9]. Such systems of solid solutions are investigated in search of morphotropic phase boundaries, which demonstrate high values of the dielectric constant and piezoelectric parameters. By increasing the number of solid solutions components, we usually improve the manufacturability of the systems. This is probably because heterovalent substitutions, with an increase in the set of ions included in solid solutions, lead to the formation of an additional concentration of point defects that provide an intensive course of diffusion processes and, consequently, the sintering process and the formation of the optimal microstructure and physical properties of ceramics. In addition, the dimensionality of the morphotropic phase boundaries, as well as the adjacent regions of the phase diagram, increases, which significantly expands the possibilities of choosing solid solutions with desired properties. The production of such media is often complicated by a large difference in the sintering temperatures of the initial components, as well as by the problem of chemical decomposition of solid solutions both at the boundaries of different phases and throughout the volume of the material. Solving these problems would create a promising basis for reliable and highly efficient energy storage devices. Such devices could compete with regular ceramic capacitors due to their high energy intensity, high efficiency, and wide range of operating temperatures [10–15].

A promising basis for the creation of such materials is the lead-free systems of solid solutions $\text{BaTi}_{1-x}\text{Zr}_x\text{O}_3$, which have a wide variety of phases, providing a higher dielectric constant than in BaTiO_3 . However, it is difficult to obtain high-quality ceramics based on them using conventional ceramic technology due to the relatively low reactivity of the components during the synthesis and diffusion activity during sintering [16]. To

overcome these difficulties, mechanoactivation and modification by AgNbO_3 were used. Silver niobate is a well-studied antiferroelectric [17–20], capable of accumulating twice as much electric charge as BaTiO_3 [21], and demonstrates a high breakdown voltage of up to 200 kV/cm [22,23] and the P-E double loop characteristic of antiferroelectrics, which is important for energy storage. In addition, heterovalent substitutions, especially with highly charged substituents (Nb^{5+}), contribute to an increase in the diffusion rate, a decrease in temperature, and an increase in sintering efficiency [24].

Thus, the aim of this study was to establish the influence of cationic composition and thermodynamic history on the production, structure, and microstructure of solid solutions $(1-x)\text{BaTi}_{0.85}\text{Zr}_{0.15}\text{O}_3 - x\text{AgNbO}_3$ where $x = 0, 0.03, 0.06, 0.09$.

2. Materials and Methods

$\text{BaTi}_{0.85}\text{Zr}_{0.15}\text{O}_3$ was obtained in air by two-stage solid-phase synthesis at $T = 1593$ K, $t = 4$ h, and $T_2 = 1723$ K, $t = 6$ h. Before sintering, the mechanoactivation was performed for 20 min (1800 rpm). Subsequent sintering was carried out at $T_{\text{sint.}} = 1733$ K, $t = 2$ h. [25].

$(1-x)\text{BaTi}_{0.85}\text{Zr}_{0.15}\text{O}_3 + x\text{AgNbO}_3$ ceramics were obtained in air by two-stage solid-state synthesis, using precursors at $T_1 = 1593$ K, $t = 4$ h and $T_2 = 1623$ K, $t = 6$ h. The precursors $\text{BaTi}_{0.85}\text{Zr}_{0.15}\text{O}_3$ and AgNbO_3 were obtained in air at $T_1 = 1593$ K, $t = 4$ h, $T_2 = 1723$ K, $t = 6$ h, and $T_1 = 1173$ K, $t = 4$ h, respectively. Before sintering, the mechanoactivation procedure was performed for 20 min (1800 rpm). Subsequent sintering was carried out at $T_{\text{sint.}} = 1643$ K, $t = 2$ h.

Raw materials: BaCO_3 (99.9%), ZrO_2 (99.9%), TiO_2 (99.9%), Ag_2CO_3 (99.9%), Nb_2O_5 (99.9%).

X-ray studies were carried out on a diffractometer DRON-3, $\text{CoK}\alpha$ radiation (Bragg–Brentano focusing scheme). The powder ceramics were studied, which made it possible to exclude the influence of surface effects, stresses, and textures arising in the process of its manufacture. The parameters of the unit cell were calculated from the diffraction reflections 111 and $11\bar{1}$, which are most sensitive to changes in the angular parameter of the unit cell in the studied interval of diffraction angles $2\theta = 20\text{--}60^\circ$. At large angles of 2θ , diffuse scattering is enhanced, especially near diffraction peaks, which, with small distortions of the cubic cell, does not allow the calculation of parameters with greater accuracy. The approximation of the X-ray peaks was carried out by the Lorentz function. Measurement errors of structural parameters have the following values: linear, $\Delta a = \Delta c = \pm(0.002\text{--}0.004)$ Å, angular, $\Delta\alpha = \pm 0.05^\circ$, volume, $\Delta V = \pm(0.07\text{--}0.10)$ Å³. At each stage of the technological process, a step-by-step optimization of the conditions for the formation of solid solutions was carried out. The experimental density of the samples was determined by hydrostatic weighing, and n-octane was used as a liquid medium. The density was calculated using Formula (1):

$$\rho = \frac{\rho_{\text{oct}} \cdot m_1}{m_2 - m_3 + m_4} \quad (1)$$

where ρ_{oct} is the density of octane, m_1 is the mass of the dry workpiece, m_2 is the mass of the workpiece saturated with octane, m_3 is the mass of the saturated billet suspended in octane with a suspension, and m_4 is the mass of the suspension for the workpiece. X-ray density was calculated by Formula (2):

$$\rho_{\text{X-ray}} = \frac{M \cdot Z}{N_A \cdot V} \quad (2)$$

where M is the molecular mass, Z is the number of formula units per unit cell, N_A is Avogadro's number, and V is the unit cell volume. The relative density was found by Formula (3):

$$\rho_{\text{rel}} = \frac{\rho}{\rho_{\text{X-ray}}} \cdot 100\% \quad (3)$$

The study of the microstructure was carried out using the equipment of the Center for Collective Use of the SSC RAS. Photographs of the microstructure were obtained using a

scanning electron microscope Carl Zeiss EVO 40. The study was carried out on transverse chips of ceramics without a conductive layer. The shooting was carried out in the mode of high accelerating voltage of 20 kV.

For further measurements, samples in the form of a disk with a diameter of 11 mm and a thickness of 1 mm were used. The electrodes were applied by firing a silver-containing paste. The study of dielectric characteristics was carried out in temperature ranges 80–300 K using a filler nitrogen cryostat, and at 300–750 K in a high-temperature furnace in the frequency range $10^2 \dots 10^6$ Hz with the Agilent E4980A. The study of hysteresis loops P - E (P -polarization, E -electric field strength) was carried out on an installation assembled according to the Sawyer–Tower scheme at a frequency of 50 Hz and at room temperature. The values of W , W_{rec} , and η were quantitatively calculated using the Formulas (4)–(6)

$$W_{rec} = \int_{P_r}^{P_{max}} EdP \quad (4)$$

$$W = \int_0^{P_{max}} EdP \quad (5)$$

$$\eta = \frac{W_{rec}}{W} \cdot 100\% \quad (6)$$

where W represents the total energy storage density, W_{rec} is the recoverable energy storage density, P_{max} and P_r are, respectively, the maximum and remnant polarizations, and η represents the energy storage efficiency.

3. Result and Discussion

X-ray diffraction patterns of solid solutions are shown in Figure 1. All solid solutions crystallized in the perovskite structure; traces of the impurity compound $\text{Ba}_2\text{Ti}_5\text{O}_{12}$ (4%) (PDF set 17, card 661 [26]) are visible only in samples with an AgNbO_3 content of 6 mol% and 9 mol%

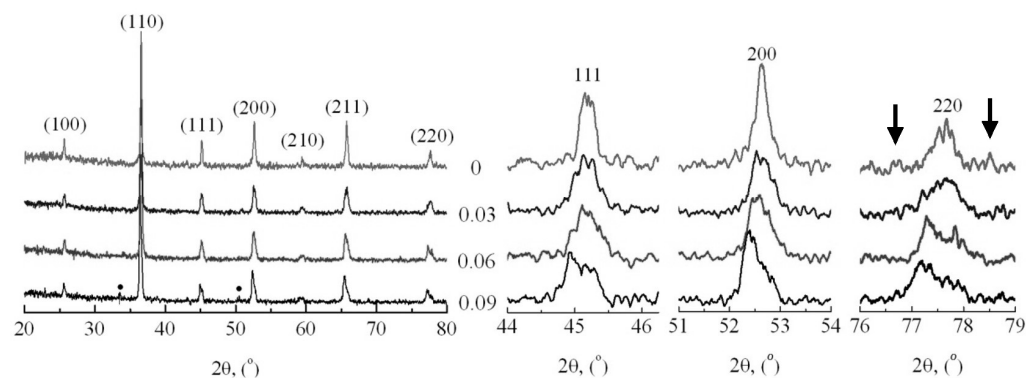


Figure 1. Radiographs of solid solutions $(1-x)\text{BaTi}_{0.85}\text{Zr}_{0.15}\text{O}_3 - x\text{AgNbO}_3$ in the range $2\theta = (20 - 80)$ and diffraction peaks 111, 200, 220 on an enlarged scale. The dots mark the $\text{Ba}_2\text{Ti}_5\text{O}_{12}$ lines.

The symmetry of the original (unmodified) solid solution due to the small distortion of the perovskite cell and the ambiguous cleavage of diffraction peaks is designated as pseudocubic with the cell parameter $a = 4.044$ Å. 220 diffraction reflection satellites (arrows in Figure 1), indicate short-range order and modulation in the direction $\langle 110 \rangle$. Figure 1 shows that the introduction of only 3 mol% AgNbO_3 leads to the decomposition of the solid solution into a series of solid solutions with similar cell parameters. At 9 mol% AgNbO_3 , two inhomogeneous solid solutions with cell parameters $a_1 = 4.04$ Å and $a_2 = 4.06$ Å are distinguished, and the volume of the last fraction is greater.

Figure 2 shows the dependences of the cell parameter, the half-width (FWHM) of the diffraction peak 200, and the density of solid solutions $(1-x)\text{BaTi}_{0.85}\text{Zr}_{0.15}\text{O}_3 - x\text{AgNbO}_3$ on the concentration of AgNbO_3 .

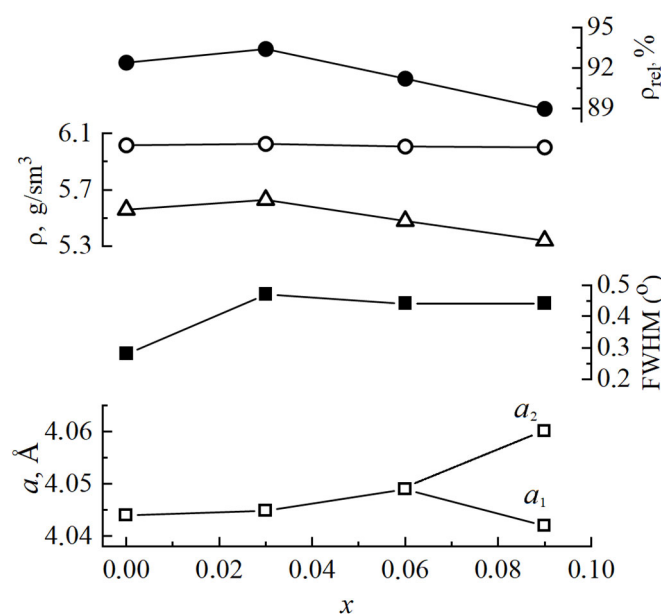


Figure 2. The cell parameter a (empty squares), a_1 , and a_2 parameters of two phases, FWHM (squares) of the diffraction peak 200, experimental (triangles), X-ray (empty circles), and relative p_{rel} (circles) density of solid solutions $(1 - x)\text{BaTi}_{0.85}\text{Zr}_{0.15}\text{O}_3 - x\text{AgNbO}_3$.

A slight increase in the cell parameter cannot be a consequence of the substitution of $\text{Ag}^{1+} \rightarrow \text{Ba}^{2+}$ since the ionic radius of Ag^{1+} is much smaller than the ionic radius of Ba^{2+} (1.13 Å and 1.38 Å for the coordination number 6 [27]), respectively. According to the empirical rules of isomorphism, the difference in ionic radii interchangeable ions should not exceed 15% of the smaller value; in this case, it is 22%. The electronegativity (EN) difference of these ions also prevents the formation of solid solutions substitution [28]: EN Ba = 0.89, EN Ag = 1.93, $\Delta\text{EN} = 1.04$ with a permissible value of 0.4. With a general heterogeneity of solid solution with 3 mol% AgNbO_3 , ceramic density increased.

The results of the study of the microstructure showed that the landscape of all solid solutions is fine-grained, pores are present, and fragments of chips are shown in Figure 3.

The chip of ceramics equally passes along the border and volume of grain, which indicates a comparable strength of grains and intergrain layers. The chip, in some places, forms steps, which testify in favor of the layer-by-layer mechanism of growth from the liquid phase, probably associated with the formation of eutectic mixtures. In all solid solutions, the heterogeneity of the grain landscape can be noted: diameter D of large and small grains differ by an order of magnitude; near the pores, the packaging of grains becomes looser, and there are more small grains. The reason for this growth may be the pores themselves, which play the role of “drains” of vacancies and dislocations that stimulate the growth of crystallites and their conglomerates. Similar structures were previously observed in [24]. The shape of small grains is close to spherical, which may be due to their partial melting. For solid solutions containing AgNbO_3 in their composition, another concomitant mechanism for the growth of small grains of irregular shape can be implemented. At the same time, AgNbO_3 particles themselves can act as crystallization centers. Such a process, on the one hand, can lead to a decrease in the average D of grains and, on the other hand, to destabilization of the grain structure and greater heterogeneity. The obtained density values indicate the high role of the second mechanism: the introduction of a small fraction of AgNbO_3 (3 mol%) leads to an increase in the total density of solid solution from 92% to 93.4% due to the formation of new crystallization centers. But a further increase in the proportion of AgNbO_3 up to 6 mol% and 9 mol.% leads to a decrease in the density of solid solutions $93.4\% \rightarrow 91.2\% \rightarrow 88.9\%$. The average D of grains for solid solutions with $x = 0, 0.03, 0.06, 0.09$ were $D = 2.54 \mu\text{m}, D = 1.71 \mu\text{m}, D = 1.67 \mu\text{m}, D = 1.66 \mu\text{m}$.

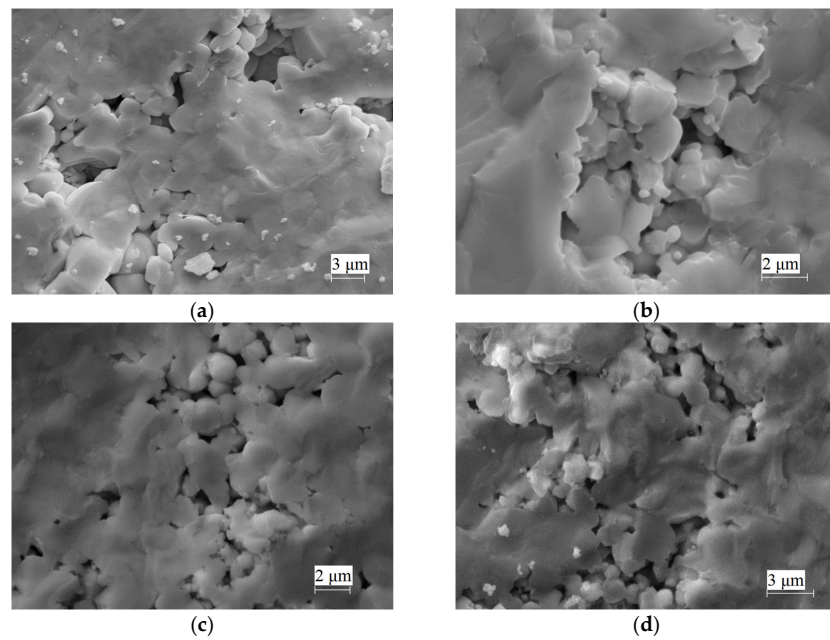


Figure 3. Microstructure of the ceramic chipped surface area at different magnifications. (a) $x = 0$, (b) $x = 0.03$, (c) $x = 0.06$, (d) $x = 0.09$.

Figures 4–7 show the dependences of the real and imaginary parts of the dielectric constant on temperature, obtained at the frequencies of the measuring field $f = 10^2 - 10^6$ Hz.

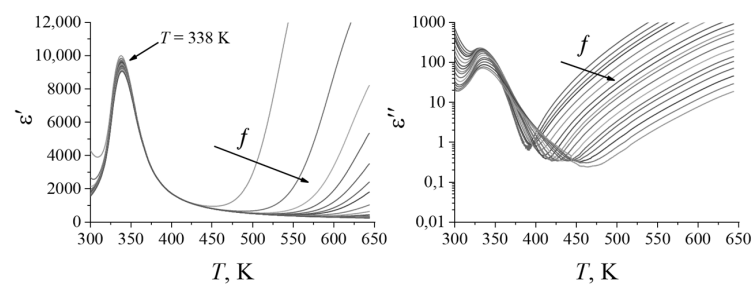


Figure 4. Dependence of the dielectric constant of solid solution on temperature at $x = 0$. The concentration x is shown in the figures.

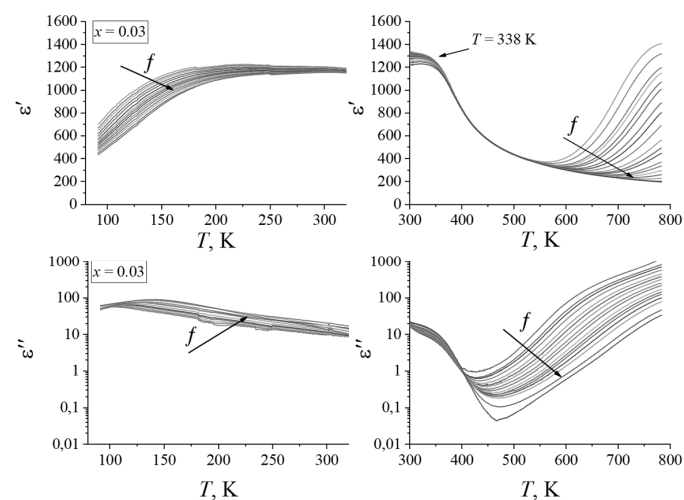


Figure 5. Dependence of the dielectric constant of solid solution on temperature at $x = 0.03$. The concentration x is shown in the figure.

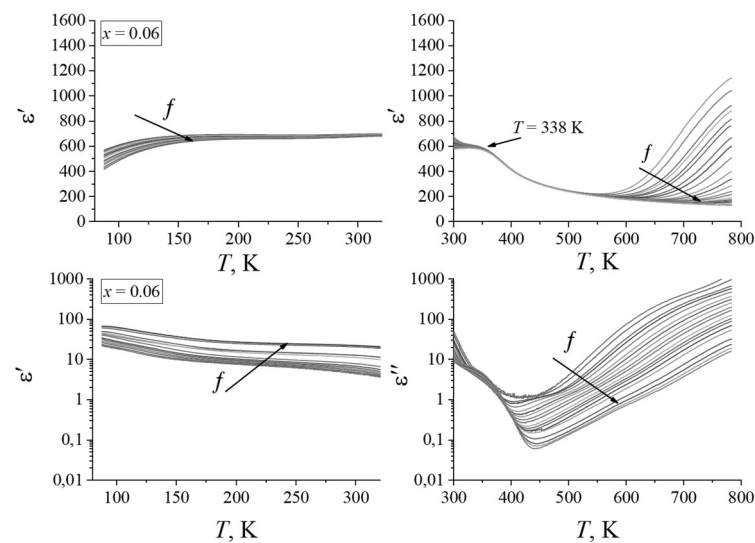


Figure 6. Dependence of the dielectric constant of solid solutions on temperature at $x = 0.06$. The concentration x is shown in the figure.

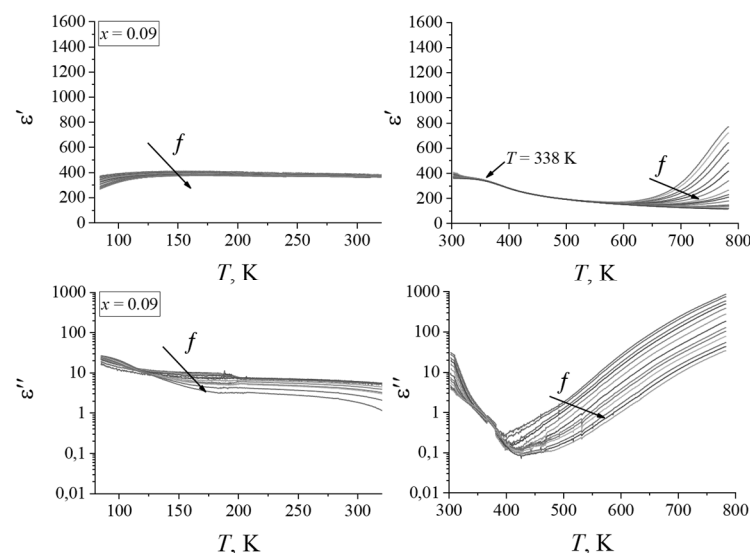


Figure 7. Dependence of the dielectric constant of solid solutions on temperature at $x = 0.09$. The concentration x is shown in the figure.

In Figure 4, the maximum ϵ' is observed at $T = 338$ K and associated with the transition from the ferroelectric to the paraelectric state. The temperature of the maximum of the dielectric constant shifts to the region of higher values with an increase in the frequency of the measuring field, which is typical for relaxors and dipole glasses. The imaginary part of the dielectric constant in the above temperature range also corresponds to that characteristic behavior in the phase transition region [29,30]. In solid solutions with $x \neq 0$, the formation of a wide maximum is observed. The height of this maximum decreases with increasing concentration x . At concentrations $x \neq 0$ (Figures 5–7), the formation of this maximum occurs at $T = 338$ K, which coincides with the temperature of the phase transition from the ferroelectric phase to the antiferroelectric phase in AgNbO_3 [31]. From this, we assume that the formation of this maximum with a decrease in temperature is initiated by a phase transition in AgNbO_3 . A comparison of the dielectric constant for solid solutions with $x \neq 0$ at $f = 10^3$ Hz is shown in Figure 8.

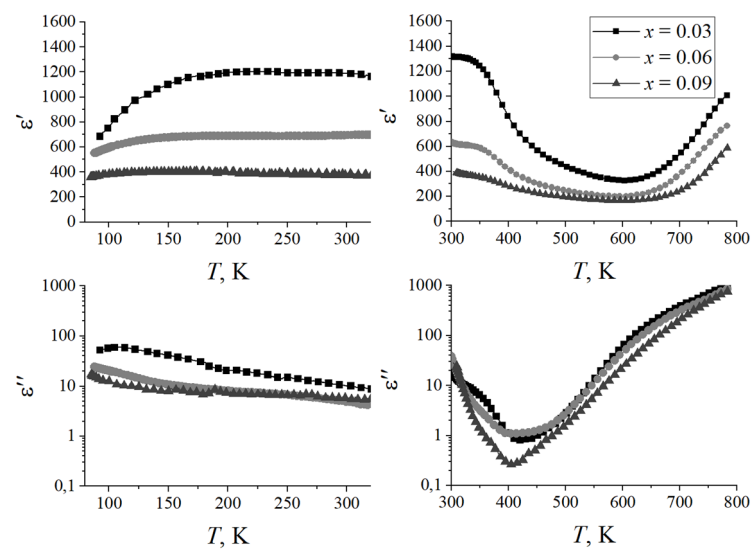


Figure 8. Dependence of the dielectric constant solid solutions on temperature at $f = 10^3$ Hz. Concentrations x are shown in the figure.

As the concentration x increases, the blurred maximum experiences broadening, and its low-temperature section shifts to the region of even lower temperatures. Further, an increase in frequency dispersion is observed, which may indicate the transition of the solid solution to the state of a frozen dipole glass. A similar behavior can be observed in solid solutions $\text{BaTi}_{1-x}\text{Zr}_x\text{O}_3$ at $x > 0.15$, where at such concentrations, in accordance with the phase diagram [32], a transition from the ferroelectric phase to the mixed phase occurs.

The loops of dielectric hysteresis are shown in Figure 9.

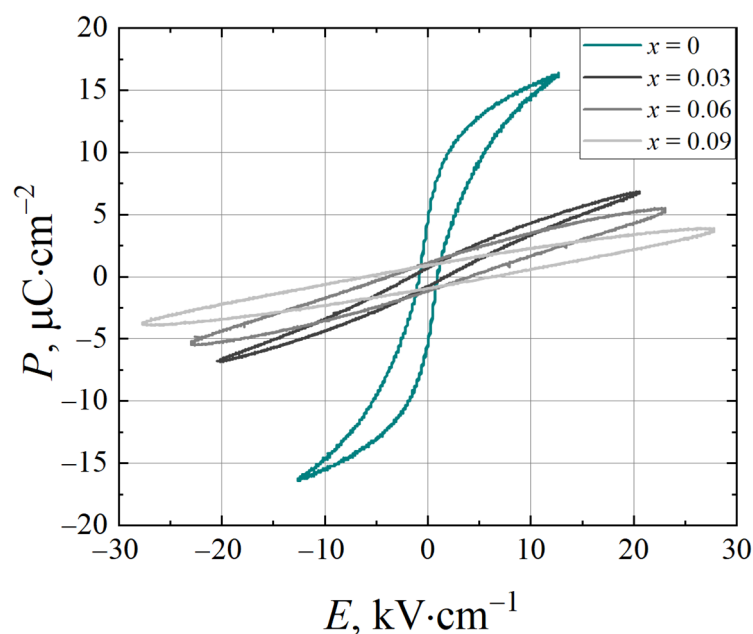


Figure 9. Loops P - E of solid solutions. The concentration x is shown in the figure.

At $x = 0$, the dielectric hysteresis loops cease to experience saturation at the same fields as $\text{BaTi}_{0.85}\text{Zr}_{0.15}\text{O}_3$. A further increase in the electric field strength for the solid solution with $x = 0$ led to a dielectric breakdown. The energy values calculated by Formulas (4)–(6) are presented in Table 1.

Table 1. Summary of energy storage properties and related parameters of solid solutions.

Composition	$W, \text{J} \cdot \text{cm}^{-3}$	$W_{\text{rec}}, \text{J} \cdot \text{cm}^{-3}$	$\eta, \%$
$x = 0$	0.081	0.043	53.1
$x = 0.03$	0.074	0.053	76.5
$x = 0.06$	0.067	0.037	54.9
$x = 0.09$	0.063	0.031	48.6

From the calculations, it can be seen that the additive 3 mol. % AgNbO_3 significantly increases η with a slight decrease in W . A further increase in the concentration x reduces both η and W . From the above, we can conclude that despite the fact that the optimal density values are achieved in the concentration range of $0.03 < x \leq 0.06$, the best indicators for stored energy are achieved at concentrations $0 < x \leq 0.03$. It is advisable to use the obtained data in the production process of multicomponent lead-free ceramics based on $\text{BaTi}_{1-x}\text{Zr}_x\text{O}_3$ with other antiferroelectric modifiers, such as LiNbO_3 , NaNbO_3 , etc. Further work will be aimed at studying the dielectric characteristics of solid solutions and searching for correlations between the mole fractions of Zr^{2+} in $\text{BaTi}_{1-x}\text{Zr}_x\text{O}_3$ and the AgNbO_3 modifier.

4. Conclusions

This paper demonstrates the possibility of obtaining impurity-free solid solutions $(1 - x)\text{BaTi}_{0.85}\text{Zr}_{0.15}\text{O}_3 + x\text{AgNbO}_3$ with a perovskite-type structure by two-stage solid-phase synthesis from precursors. From the results of X-ray diffraction analysis, it follows that the obtained solid solutions are impurity-free and show signs of coexistence of several phases with similar unit cell parameters. It has been shown that AgNbO_3 can be used in order to reduce the sintering temperature of solid solutions in the absence of impurities and high density for 3 mol% and 6 mol%; however, for 9 mol%, density decreased. Thus, from the point of view of structural characteristics, the optimal concentration is 6 mol% or less. A finer-grained and more uniform structure should have a positive effect on the service life of ceramic energy storage devices. From the results of the study of dielectric parameters, it follows that the addition of AgNbO_3 leads to a decrease in the actual part of the dielectric constant. In solid solutions with $x \neq 0$, a transition to the state of a dipole glass is observed at $T \leq 338 \text{ K}$, a further decrease in temperature leads the solid solutions to the state of a frozen dipole glass. An increase in the concentration of AgNbO_3 leads to a broadening of the maximum, which passes into the state of a frozen dipole glass at $T < 200 \text{ K}$. The study of dielectric hysteresis loops showed solid solutions with an AgNbO_3 content of 3 mol% and less because they demonstrate the highest value of η and W from the entire series of modified solid solutions. It is advisable to use the obtained data in the production process of multicomponent lead-free ceramics based on $\text{BaTi}_{1-x}\text{Zr}_x\text{O}_3$ with other antiferroelectrics modifiers, such as NaNbO_3 and PbZrO_3 .

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