Physics of the Solid State, 2025, Vol. 67, No. 9

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Effect of electrical and temperature conditions on the thermal expansion of $Ba_{0.97}Bi_{0.02}TiO_3$ ceramics in the $Pm\bar{3}m \leftrightarrow P4mm$ phase transition region

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Received August 1, 2025
Revised September 2, 2025
Accepted September 17, 2025

The influence of various combinations and conditions of the electric field and temperature on the thermal expansion of $Ba_{0.97}Bi_{0.02}TiO_3$ ceramics in the region of the ferroelectric phase transition $Pm\bar{3}m \leftrightarrow P4mm$ was studied. The sequence of thermal/electrical processes required to obtain reliably reproducible results during thermal cycling has been established. The possibility of targeted variation within the limits of $\sim (20-30)\,\%$ of the values both of the anomalous thermal expansion coefficient and deformation near and far from the transition temperature, respectively, is shown, which can undoubtedly be used at the stage of developing ceramic elements for miniature electromechanical devices.

Keywords: phase transitions, ferroelectrics, thermal expansion, electric field.

DOI: 10.61011/PSS.2025.09.62356.220-25

1. Introduction

When searching for and designing new ferroelectric materials that are promising, in particular, for use as functional elements in electromechanical devices, it is necessary to study not only their properties, but a nature and a degree of their sensitivity to external effects: the temperature T, the electric field E, hydrostatic p and uniaxial σ pressure, etc., which can be regarded as tools that allow purposefully varying the physical properties. Since in certain conditions materials can often demonstrate relaxation and hysteresis phenomena that are different in nature, it is also necessary to specify a dependence of the properties on a sequence of thermal/electric processes, which result in brining the sample to an equilibrium thermodynamic state, which precedes a specific subsequent experimental study. Such a property in ferroelectrics is polarization, the behavior and magnitude of which also significantly depend on the physicochemical quality of the samples and the size factor (single crystal, ceramics, thin film) [1–3].

When applying the external electric field, even in a paraelectric phase symmetry of the ferroelectric crystal is forcedly changed according to a Curie principle: only symmetry elements of a crystal lattice, which are common with effect symmetry elements, are preserved. Thus, the crystal distortion type depends on a direction of the field vector. For example, when applying the electric field along the direction [110] of the cubic phase $Pm\bar{3}m$ near a temperature of transition to the tetragonal phase $P4mm$, T_1, the $BaTiO_3$ single crystal exhibited a mixture of tetragonal and rhombic domains, whereas at the higher temperature the field-induced single-phase state was characterized by rhombic symmetry that coincided with effect symmetry [4].

A more complicated response of the physical properties to the effect of the external electric field is observed in ceramic materials, in particular, based on barium titanate, which are more and more widely used. Indeed, in the phase $Pm\bar{3}m$ each crystallite has arbitrary orientation of the crystal lattice and without a texture the ceramic sample is an isotropic system. The external field induces individual distortions in the crystallites in accordance with a degree of mismatch of directions of the lattice axes and the field vector. When being cooled under the field into the tetragonal phase $P4mm$, each crystallite forms domains with predominant orientation of spontaneous polarization along the field-predefined direction, thereby resulting in origination of anisotropy.

Information about conditions and reversibility of the transition between isotropic and anisotropic states in the ceramics can be obtained not only by quite complicated studies of polarization. According to a thermodynamic theory of phase transitions, a value and behavior of anomalous linear spontaneous deformation and a coefficient of thermal linear expansion are determined by spontaneous polarization, namely, $\Delta(\Delta L/L) \propto P^2$ and $\Delta\alpha \propto (\partial P^2/\partial T)_E$ [1]. Thus, thermal expansion is an indirect, but important and reliable characteristic of behavior of polarization both directly around the temperature of the phase transition, where the function $\Delta\alpha(T)$ has a extremum, and in a distorted phase away from the temperature of the transition, where the function $\Delta(\Delta L/L)(T)$ tends to saturation. Moreover, investigation of deformation makes it possible to obtain precious information about a possibility and degree of variation of linear/volume sizes of the ceramics in electric fields at various temperatures.

Due to the fact that in ceramic solid solutions based on barium titanate the parameter of the phase transitions is polarization, studies of various physical effects in these materials under conditions of effect of the electric field are quite informative and actively performed for many years [1,2,5–10]. However, by virtue of various circumstances, as far as we know, the influence of the electric field on thermal expansion has not been studied.

Only recently, we performed the studies of this kind for the $Ba_{1-x}Bi_{2x/3}TiO_3 (x = 0.03) \equiv Ba_{0.97}Bi_{0.02}TiO_3$ ceramic sample (BBT) to show that chemical pressure and the electric field caused an increase of the temperature of the phase transition $Pm\bar{3}m \leftrightarrow P4mm$ and a decrease of an anomalous part of the coefficient of thermal expansion [11]. These results agree with data of the previous studies of thermal expansion and permittivity of a system of the $Ba_{1-x}Bi_{2x/3}TiO_3$ solid solutions ($x = 0-0.05$) when $E = 0$ [12]. At the same time, it was found in the last study that when $x > 0.02$ instead of the three phase transitions $Pm\bar{3}m \leftrightarrow P4mm \leftrightarrow C2mm \leftrightarrow R3m$ that are typical for $BaTiO_3$ a phase diagram $T-x$ exhibits only two transformations $Pm\bar{3}m \leftrightarrow P4mm \leftrightarrow R3m$. According to analysis carried out in the study [13], with heterovalent substitution $Bi^{3+} \to Ba^{2+}$ a charge is compensated due to formation of vacancies in positions occupied by barium. Charged defects create in the crystal lattice random electric fields, which increase with an increasing of the bismuth concentration and result in origination of heterogeneous ferroelectric states and wedging of an intermediate rhombic phase $C2mm$.

The present study continues experiments of studying the influence of an electric and thermal history of the sample as well as various combinations of external effects on deformation and the coefficient of thermal expansion of BBT in order to determine conditions both for obtaining reliably reproducible results during thermal cycling between the phases tetragonal ↔ cubic ↔ tetragonal as well as for purposefully varying linear sizes of the ceramic sample.

2. Samples and experimental methods

The BBT solid solution was prepared as a result of a solid-state reaction $0.97BaCO_3 + 0.01Bi_2O_3 + TiO_2 \to Ba_{0.97}Bi_{0.02}TiO_3 + 0.97CO_2$ according to a methodology described in the study [6]. After thorough trituration for one hour, a mixture of initial materials was pressed under the pressure of 100 MPa as discs ($d = 7$ mm, $h = 1.1$ mm). A paste OPTAPIX (Zschimmer et Schwarz) was added as a binder. After synthesis with a duration of 2 h at 1100 ° C, the samples were annealed in an oxygen atmosphere for 15 h at 850 °C. The samples were coated with electrodes by spraying gold in vacuum.

The structure and quality of the ceramic samples were characterized by X-ray diffraction studies at the room temperature using a Haoyuan diffractometer with Cu-K_α radiation and a linear detector. A detector step 2θ was $0.01°$ with 0.2 s exposure at each point. Analysis of the experimental diffraction pattern by the Rietveld method using the TOPAS 4.2 program [14] showed that, firstly, the refinement is stable with low R-factors ($R_{wp} = 6.45$, $R_p = 4.53$, $\chi^2 = 3.61$), secondly, as expected, the samples are characterized by tetragonal symmetry ($P4mm$, $Z = 1$), thirdly, any foreign phases, as well as texture, are absent, at least on the surfaces perpendicular to the axis of the ceramic disk.

Parameters of a lattice cell ($a = 3.99612(17)$ Å; $c = 4.02771(17)$ Å, $V = 64.318(6)$ Å^3) are close to the parameters of $BaTiO_3$ ($a = 3.99117(40)$ Å; $c = 4.03015(49)$ Å, $V = 64.198(15)$ Å^3) [11]. But, as it is clear, heterovalent substitution $Bi^{3+} \to Ba^{2+}$ resulted, first of all, in an increase and a decrease of the parameters a and c, respectively, secondly, an increase of the lattice cell volume and, thirdly, to a decrease of the tetragonality parameter c/a: 1.010 (BT) → 1.008 (BBT). The crystallite size in the ceramic varies within the range 300−800 nm.

Temperature dependences of linear deformation $\Delta L/L(T)$ and the coefficient of thermal linear expansion $\alpha(T)$ were studied in an induction dilatometer DIL-402C manufactured by Netzsch, whose design was modified so as to energize the sample electrodes with voltage within the range $U \leq 600$ V. A standard made of fused quartz was used to calibrate and account for expansion of a measuring system. The contents of successive measurement cycles were to perform experiments in variable conditions: heating-cooling without ($E = 0$) and when applying ($E_1 = 2.72$ kV/cm and $E_2 = 5.45$ kV/cm) the electric field as well as at the short-circuited electrodes of the sample (SC).

Results of X-ray diffraction studies indicate no texture in the studied ceramic sample, thereby making it possible to consider the BBT as an isotropic medium despite tetragonal symmetry at the room temperature. However, applying the external electric field shall inevitable result in anisotropy in the sample. Therefore, in the present study thermal expansion was measured along two mutually perpendicular directions with a fixed direction of applying the electric field: along a sample diameter, i. e. orthogonal to the direction E (Option A) and along a pill thickness, i. e. parallel to the field direction (Option B) (Figure 1).

In order to clarify a degree of the dependence of deformation $\Delta L/L(T)$ and the coefficient of thermal expansion $\alpha(T)$ on the thermal and electric history, each stage of measurements included various combinations of boundary conditions and processes in the heating−cooling cycles:

1) ZFH (zero field heating) — heating in the conditions $E = 0$ or at SC (short-circuited electrodes);

2) ZFC (zero field cooling) — cooling when $E = 0$ or at SC;

3) FH (field heating) — heating, $E \neq 0$;

4) FC (field cooling) — cooling, $E \neq 0$;

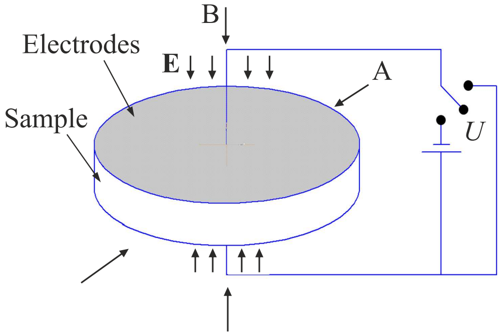

Figure 1. Schematic representation of the options of A- and B-measurement of linear thermal expansion at the fixed direction of the electric field vector **E**.

5) FHaFC (field heating after field cooling) — heating when $E \neq 0$ in 3 hours after FC;

6) ZFHaFC (zero field heating after field cooling) — heating when $E = 0$ or at SC in 3 hours after FC.

It was found during the studies that a chronological sequence of the measurement cycles (see Table) played a significant role for correctly representing a mechanism of formation of anomalous thermal expansion related to the phase transition.

3. Results and discussion

Results of measurement of thermal expansion of the BBT sample without the external electric field are shown in Figure 2 as the temperature dependences of the coefficient of linear thermal expansion $\alpha(T)$. Despite that the goal of the study was to investigate the influence of the boundary electric and thermal conditions on thermal expansion only within the region of the transition $Pm\bar{3}m \leftrightarrow P4mm$, correct determination of the anomalous and lattice contributions to $\Delta L/L(T)$ and $\alpha(T)$, which are related and unrelated to polarization, respectively, required experiments within a large interval of the temperatures (Figure 2, *a*). It is clear that in the $Ba_{0.97}Bi_{0.02}TiO_3$ solid solution with a low concentration of Bi^{3+} that substitutes Ba^{2+} only the transition between the cubic and tetragonal phases is accompanied by a significant anomaly of $\alpha(T)$. Variation of the coefficient of expansion at a low-temperature transformation $P4mm \leftrightarrow R3m$ observed in the study [12] is almost unrecorded. The lattice contribution $\alpha_{\text{latt}}(T)$ to the total thermal expansion, which is shown by a dashed line in Figure 2, *a* was determined by a previously developed methodology. It showed that the behavior of the lattice part of the coefficient of linear thermal expansion was most correctly described by a relationship [15]

$$A_{\text{latt}}(T) = aT + bC_D(T, \Theta_D),$$

where a, b, Θ_D are fitting parameters and $C_D(T, \Theta_D)$ is heat capacity in a Debye model. A value of the Debye temperature for BBT $\Theta_D \approx 500$ K is somewhat different from the parameter that is typical for pure barium titanate $\Theta_D \approx 430$ K [16]. It was analyzed to show that the anomalous contribution to thermal expansion, which is determined as $\Delta\alpha(T) = \alpha(T) - \alpha_{\text{latt}}(T)$, is present considerably lower than the temperature of the phase transition T_1 (Figure 2, *a*).

In all the subsequent experiments, the heating-cooling cycles were performed within the temperature intervals (320−450) K – (450−395) K. It was impossible to control the measurement process of cooling below ~ 395 K due to design specific features of a dilatometer thermal control system.

Figure 2, *b* shows temperature dependences of the coefficient of linear thermal expansion $\alpha(T)$ (Option A, No. of cycle 1, 2 in Table), which are determined in the heating and cooling modes within the region of the transition from the cubic phase into the tetragonal one. Repeated thermal cycling exhibited high reproducibility of results both relative to a form of the peak of $\alpha(T)$ and its depth as well as the temperature of the phase transformation, which corresponded to a minimum of the anomaly of $\alpha(T)$, and a value of hysteresis, which were $T_1 = 404.7 \pm 0.2$ K and $\delta T_1 = 2.5 \pm 0.4$ K, respectively.

In Figure 2, *c*, you can see the temperature dependences of the anomalous part of the coefficient of thermal expansion $\Delta\alpha^{\text{A}}(T)$ and $\Delta\alpha^{\text{B}}(T)$, which are determined for the case when $E = 0$. The measurement option B showed a considerably higher spread of experimental points due to a significantly smaller size of the ceramic cylindrical sample along the height than along the diameter. Despite this, the results of measurements of thermal expansion in two different directions turned out to be close (within an

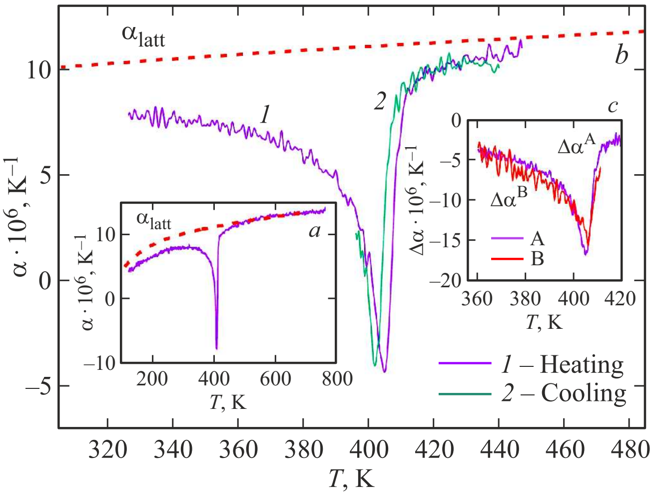

Figure 2. Temperature dependences of the coefficient of linear thermal expansion $\alpha(T)$ when $E = 0$ (Option A): *a* — within the wide temperature interval, *b* — around T_1 in the modes of heating (*1*) and cooling (*2*). A dashed line means a lattice contribution $\alpha_{\text{latt}}(T)$. *c* is the temperature behavior of the anomalous coefficients of linear thermal expansion $\Delta\alpha^{\text{A}}(T)$ and $\Delta\alpha^{\text{B}}(T)$, which are determined when $E = 0$ in the measurement options A and B, respectively.

Table. Chronological sequence and the contents of the cycles for the options A and B for measuring thermal expansion

Option A			Option B		
No. of cycle	Process	E, kV/cm	No. of cycle	Process	E, kV/cm
1	ZFH	0	1	ZFH	SC
	ZFC	0		ZFC	SC
$\tau = 15$ h			$\tau = 3$ h		
2	ZFH	0	2	ZFH	SC
	ZFC	0		ZFC	SC
$\tau = 15$ h			$\tau = 15$ h		
3	FH	2.72	3	ZFH	SC
	FC	2.72		ZFC	SC
$\tau = 3$ h			$\tau = 3$ h		
4	FHaFC	2.72	4	ZFH	SC
	FC	2.72		ZFC	SC
$\tau = 15$ h			$\tau = 15$ h		
5	FH	5.45	5	FH	5.45
	FC	5.45		FC	5.45
$\tau = 3$ h			$\tau = 3$ h		
6	FHaFC	5.45	6	FHaFC	5.45
	FC	5.45		FC	5.45
$\tau = 15$ h			$\tau = 15$ h		
7	ZFH	0	7	FH	5.45
	ZFC	0		FC	5.45
$\tau = 70$ h			$\tau = 3$ h		
8	ZFH	0	8	FHaFC	5.45
	ZFC	0		FC	5.45
$\tau = 15$ h			$\tau = 15$ h		
9	ZFH	SC	9	FH	5.45
	ZFC	SC		ZFC	SC
$\tau = 15$ h			$\tau = 3$ h		
10	FH	5.45	10	ZFH	SC
	FC	5.45		ZFC	SC
$\tau = 3$ h			$\tau = 70$ h		
11	FHaFC	5.45	11	ZFH	SC
	FC	5.45		ZFC	SC
$\tau = 15$ h					
12	ZFH	SC			
	ZFC	SC			

Table (*continued*).

Option A			Option B		
№ of cycle	Process	E, kV/cm	№ of cycle	Process	E, kV/cm
$\tau = 3$ h					
13	ZFH	SC			
	ZFC	SC			
$\tau = 15$ h					
14	FH	5.45			
	FC	5.45			
$\tau = 3$ h					
15	ZFHaFC	0			
	ZFC	0			

error of determination), which complies with results of structure studies that specified no texture in the sample at the room temperature. Thus, without the external electric field the studied ceramic sample is indeed isotropic: $\Delta\alpha^{A}_{T_1} = \Delta\alpha^{B}_{T_1} = -16 \cdot 10^{-6}\,\mathrm{K}^{-1}$.

A nature and a degree of the influence of the thermal and electric history of the sample on the temperature behavior and the values of $\Delta\alpha$ determined in the measurement options A (Figure 3, *a* and 3, *b*) and B (Figure 3, *c* and 3, *d*) turned out to be significantly different. In the first stage (Option A), the influence of the electric field on thermal expansion was studied in conditions when $E_1 = 2.72$ kV/cm. The cycle 3 (see Table) exhibited an insignificant, but still noticeable decrease of the value of the anomaly of the coefficient of thermal expansion at T_1, $\Delta\alpha^{A}_{T_1}$ during the measurements in the heating mode as compared to results obtained in the cycles 1 and 2 when $E = 0$ (Figure 3, *b*). With repeated heating (the cycle 4), a further decrease of $\Delta\alpha^{A}_{T_1}$ was detected. At the same time, this behavior was not observed in the cooling mode — the anomaly was reproduced from series to series without variation.

Since the value of the field strength $E_1 = 2.72$ kV/cm is quite small as compared to fields that are usually used for perovskite-like compounds and, therefore, does not make it possible to generate a definite representation about the nature of the influence of the electric field on a process of undergoing of the phase transformation, then all the subsequent measurements were performed at the field strength $E_2 = 5.45$ kV/cm, which corresponded to voltage at plates of a ceramic capacitor ($U = 600$ V), which is maximum allowable with a used combination of elements in the updated dilatometer installation.

As a result, during the heating process in the cycle 5 the anomaly $\Delta\alpha$ was not considerably changed as compared to the cycle 4, whereas with further thermal cycling under the field (the cycle 6) its significant decrease was observed (Figure 3, *a*). The measurement that followed without the field (the cycle 7) did not reveal restoration of the initial results observed in the cycles 1 and 2 when $E = 0$. A depth of the anomaly $\Delta\alpha$ was still reduced (Figure 3, *b*).

It was found as a result of the studies in the cooling processes that at the same electric conditions $E = 0$ or $E \neq 0$, which were realized in the phase $Pm\bar{3}m$, the values of $\Delta\alpha^{A}_{T_1}$, i.e. in the transition point, are well reproduced in all the cycles (Figure 3, *b*). Despite an increasing spread of the experimental points during the anomaly decrease, it is clear that when $E \neq 0$ as compared to the conditions when $E = 0$ no considerable change of hysteresis was observed, $\delta T_1 = 2.2 \pm 0.4$ K (Figure 3, *a*). This fact indicates that the electric field of 5.45 kV/cm practically does not change a degree of proximity of the first-order phase transition $Fm\bar{3}m \leftrightarrow P4mm$ to a tricritical point, whichth is characteriesed by tendency to zero both of the δT_1 value and a polarization jump.

Further measurements both in the field E_2 and without the field (the cycles 8–15, Option A) showed that the value of and the temperature behavior of $\Delta\alpha^{A}$ that were realized in the heating mode were significantly affected by the boundary thermal and electric conditions, in particular, by a mode included the transition from the cubic into tetragonal phase, which had preceded the measurements. During the FHaFC process (the cycles 6, 11) and the ZFHaFC process (the cycles 7, 12, 15), the values of the anomalous coefficient of expansion turned out to be close to each other, $\Delta\alpha^{A}_{T_1} = -11 \cdot 10^{-6}\,\mathrm{K}^{-1}$ (Figure 3, *b*). In case of cooling in the conditions when $E = 0$ the anomalies in the subsequent heating processes (the cycles 8–10, 13, 14) were $\Delta\alpha^{A}_{T_1} = -16 \cdot 10^{-6}\,\mathrm{K}^{-1}$, i.e. corresponded to the values observed in the cycles 1 and 2 (Figure 3, *b*). Thus, it was found for the case of measurements of thermal expansion along a direction perpendicular to a direction of the applied electric field $E_2 = 5.45$ kV/cm that there was an interval of the limit values of $\Delta\alpha^{A}_{T_1}$, which corresponded to

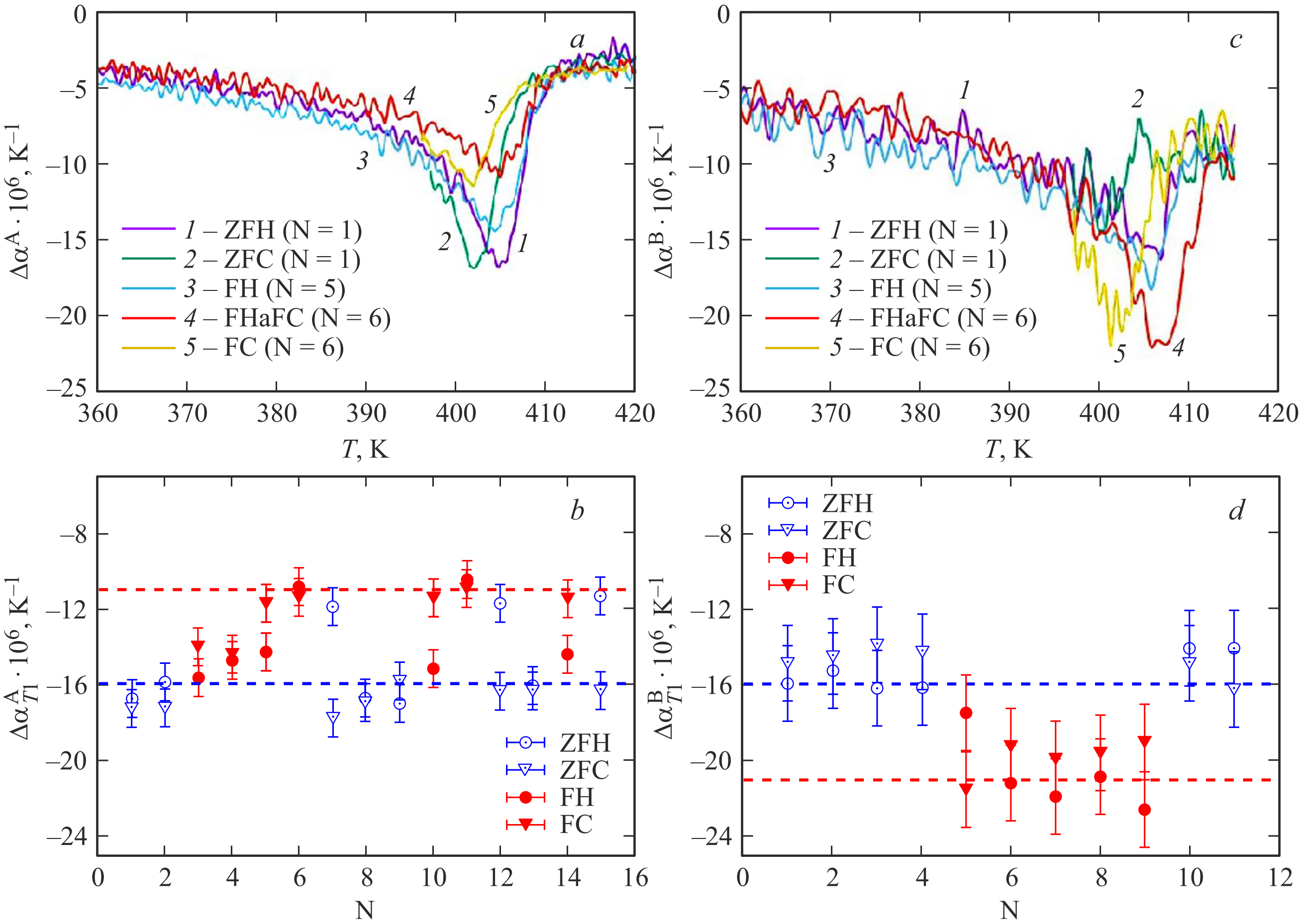

Figure 3. Above: the temperature dependences of the anomalous coefficients of linear expansion $\Delta\alpha(T)$, which are determined in the different electric/thermal modes: a — along the field, c — perpendicular to the field. Below: the values of the anomalous coefficients of linear expansion when $T = T_1$ according to the cycle number N: b — along the field, c — perpendicular to the field. The dashed lines correspond to values of $\Delta\alpha$ for the isotropic ($\Delta\alpha^{A}_{T_1} = \Delta\alpha^{B}_{T_1} = -16\cdot10^{-6}\,\mathrm{K}^{-1}$) and limit values for the anisotropic ($\Delta\alpha^{A}_{T_1} = -11\cdot10^{-6}\,\mathrm{K}^{-1}$; $\Delta\alpha^{B}_{[T_1} = -21\cdot10^{-6}\,\mathrm{K}^{-1}$) states of the BBT ceramic in the field of 5.45 kV/cm.

the isotropic and anisotropic states of the BBT ceramic. It should be noted that the values of the anomalous coefficient of thermal expansion, which are determined during the cooling processes, also correspond to this interval.

Taking into account that after the cycle of measurements under the field the residual uncompensated charge can exist on the plates of the ceramic capacitor, the measurements were taken not only when $E = 0$ (the cycle 12), but with the pre-short-circuited electrodes in a ferroelectric phase in order to depolarize the sample (Figure 1). It is clear from Figure 3, b that it did not result in the significant change of the value of $\Delta\alpha^{A}_{T_1}$ as compared to the results obtained in the cycles 7 and 15 with the open electrodes. Thus, the described SC procedure did not contribute to transferring the studied sample into the initial isotropic state.

The following phenomena were detected when measuring the coefficient of thermal expansion according to the option B (Figure 1), i.e. along a direction coinciding with the direction of the electric field. As said above, when $E = 0$ the dependences and the values of the $\Delta\alpha^{A}(T)$ and $\Delta\alpha^{B}(T)$ are almost the same (Figure 2, c). However, the character of the influence of the electric field on the anomalies determined in the different directions of the measurements turned out to be considerably different — when $E \neq 0$ the option A has the anomalies decreased, while the option B has them increases (Figure 3, a and 3, c). The multiple measurements of $\alpha^{B}(T)$ at a various combination of the processes in the cycles (see Table) showed that in the same way as in the case A, for the field $E_2 = 5.45$ kV/cm a difference of the limit values of $\Delta\alpha^{B}_{T_1}$, which corresponded to the isotropic and anisotropic states of the BBT ceramic, was $\sim 5\cdot10^{-6}\,\mathrm{K}^{-1}$ (Figure 3, d).

In the cubic phase $Pm\bar{3}m$ of the ceramic sample the crystallites are randomly oriented and, therefore, as a result of the transition into the phase $P4mm$ when $E = 0$ a direction of origination of spontaneous polarization in each crystallite is also random and it determines the isotropic state of the sample (Figure 2, c). However, when cooling in the conditions when $E \neq 0$, there is a predominant polarization direction that coincides with the

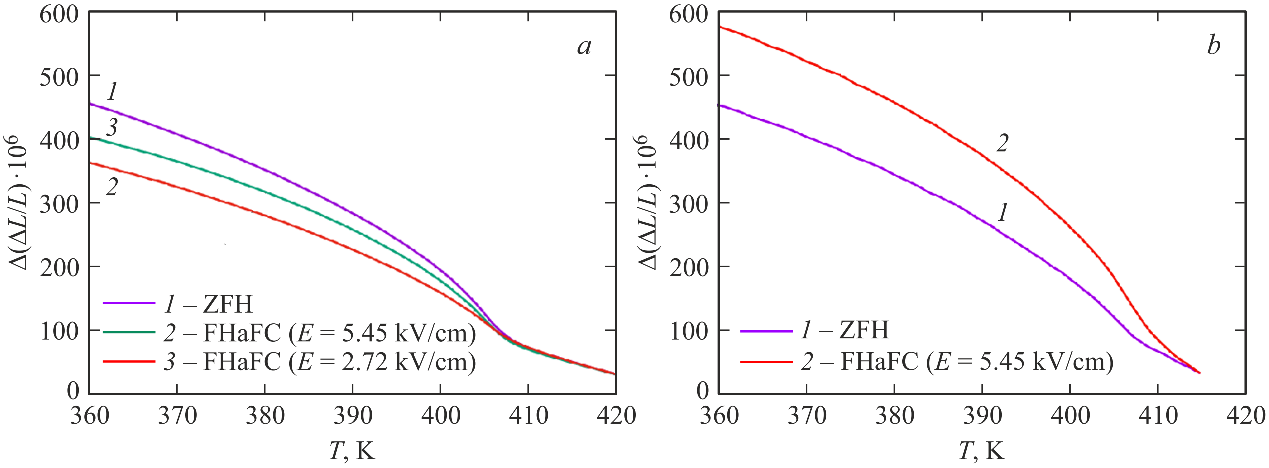

Figure 4. Temperature dependences of anomalous deformation, which are determined in the various modes of measurements: *a* — along the field, *b* — perpendicular to the field.

vector of the external electric field, which is manifested in observed anisotropy of anomalous thermal expansion, which is characterized by considerably different limit parameters: $\Delta\alpha_{T_1}^{A} = -11\cdot 10^{-6}\,\mathrm{K}^{-1}$ and $\Delta\alpha_{T_1}^{B} = -21\cdot 10^{-6}\,\mathrm{K}^{-1}$ (Figure 3, *b* and 3, *d*). The foregoing considerations are supported by analysis of the sequence of the cycles 9 and 10 (Table, Option B), when the external field was switched off and the electrodes were short-circuited in a high-temperature (paraelectric) phase after completion of the FH process. After this, as a result of cooling in the SC conditions, the sample returned to the initial isotropic state — the value of the anomaly $\Delta\alpha_{T_1}^{B}$ in the cycle 10 coincided with the results of the first measurements when $E = 0$ (the cycles 1–4) (Figure 3, *b*).

Despite the noticeable spread of the experimental points (Figure 3, *b* and 3, *d*), both the measurement options have revealed process sequences that result in implementation of the values of $\Delta\alpha_{T_1}$ within the interval of the limit values: A — FH in the cycles 10 and 14 after ZFC, correspondingly in the cycles 9 and 13; B — FH in the cycle 5 after ZFC in the cycle 4. This phenomenon is caused by variation of the degree of polarization of the ceramic sample in various directions due to the fact that the phase $P4mm$ originated induced polarization that was coaxial with the vector of the external electric field.

Up to now, we have considered specific features of the influence of the electric and thermal conditions on the values of the coefficients of thermal expansion mainly around the phase transition $Pm\bar{3}m \leftrightarrow P4mm$. A set of the obtained experimental data indicates that thermal expansion is not noticeably affected by a time of holding the sample in the tetragonal phase between the measurement cycles, which is confirmed by results of measurements in the successive cycles 5–6–7–8–9, which are realized in the option B (see Table and Figure 3, *d*).

In order to obtain information about thermal expansion within the wide temperature range, it is more informative to analyze the behavior of anomalous deformation that is related to structural transformation and is determined as follows: $\Delta(\Delta L/L)(T) = \int \Delta\alpha(T)\mathrm{d}T$ (Figure 4).

It follows from Figure 4 that in the same way as for $\Delta\alpha$ deformations in the two studied directions of the sample are characterized by existence of individual value intervals that expand as the temperature moves away from the phase transition point. For the isotropic state of the sample, the values and the temperature behavior of $\Delta(\Delta L/L)(T)$, which are determined in the ZFH processes, coincide within the measurement error (the curves *1* in Figure 4 *a* and 4 *b*). The curves *2* demonstrate an increase of anisotropy when $T < T_1$, which is characterized by a difference of deformations measured along the directions A and B, and at 360 K it is $\sim 200\cdot 10^{-6}$. Reliability of the obtained and discussed data for the field of 5.45 kV/cm is also supported by results of measurements during the FHaFC process of the cycle 4 at field strength of 2.72 kV/cm: the curve *3* in Figure 4, *a* is within the interval of the limit values of $\Delta(\Delta L/L)(T)$. It is clear that the increase of the field in two times is accompanied by an almost proportional decrease of deformation.

The dependences of deformation during the cooling processes were not analyzed, since for the above-explained technical reasons these data were obtained within a very narrow interval of the tetragonal phase temperatures ($T_1 - 10\,\mathrm{K}$).

The study neither discusses a nature and a value of the negative coefficient of thermal expansion and their relation to the tetragonality degree of the crystal lattice c/a, which in the studied solid solution has turned out to be by $\sim 0.2\,\%$ less as compared to $\mathrm{BaTiO_3}$. This analysis requires availability of at least information about the dependences $\Delta(\Delta L/L)(T, E)$ and $\Delta\alpha(T, E)$ as well as structure data for some BBT substituted compounds with a various concentration of bismuth. The respective studies will be performed by us in the nearest future.

Thus, varying the conditions of the heating/cooling cycles even in low-strength electric fields makes it possible to considerably affect the behavior of thermal expansion of the BBT ceramic both around the phase transition $Pm\bar{3}m \leftrightarrow P4mm$ as well as deep in the tetragonal phase. Due to the direct relation of linear deformation and the coefficient of linear thermal expansion to polarization, $\Delta(\Delta L/L) \propto P^2$ and $\Delta\alpha \propto (\partial P^2/\partial T)_E$ [1], it is possible to vary both the nature of the behavior of polarization (i. e. a variation rate) and its value.

On the one hand, undoubtedly, the obtained results can be considered to be typical not only for perovskite-like ferroelectrics, but for any other ceramic ferroelectrics. On the other hand, they are of a practical interest as well, for example, when designing electromechanical devices with controllable linear dimensions of a functional element: working bodies in waste energy harvesting schemes, thermal keys in miniature electrocaloric refrigerators, etc.

4. Conclusion

Thermal expansion of the $Ba_{0.97}Bi_{0.02}TiO_3$ ferroelectric ceramic was studied within the region of the phase transition $Pm\bar{3}m \leftrightarrow P4mm$ and in the tetragonal phase at the various boundary thermal and electric conditions. The experiments are performed for the two options of the ratio of directions of elongation measurement and the electric field vector: orthogonal (Option A) and parallel (Option B). We have determined the conditions of implementation of thermal cycling, which allow realizing the isotropic and anisotropic states of the sample, which are determined from the temperature dependences of anomalous linear deformation and the coefficient of linear thermal expansion.

The heterovalent substitution $Bi^{3+} \rightarrow Ba^{2+}$ caused variation of the cell parameters in the phase $P4mm$, which was accompanied by reduction of the tetragonality degree c/a as compared to $BaTiO_3$.

No reliably-recorded variation of the coefficient of thermal expansion is detected in the region of the low-temperature phase transition $P4mm \leftrightarrow R3m$, which was observed within the temperature range $\sim (210-220)$ K when studying permittivity of BBT [12], which, in particular, can be caused by heavy smearing of the anomaly $\Delta\alpha$ in the ceramic sample.

The electric field does not significantly affect the degree of proximity to the tricritical point of the transition $Fm\bar{3}m \leftrightarrow P4mm$ in BBT, which is indicated by an almost unchanged value of temperature hysteresis $\delta T_1 \approx 2.5$ K recorded during thermal cycling in the conditions when $E = 0$ and $E = 5.45$ kV/cm.

Equality of the values of the anomalous coefficients of thermal expansion, $\Delta\alpha^{A}_{T_1} = \Delta\alpha^{B}_{T_1} = -16 \cdot 10^{-6}\,K^{-1}$, which are determined according to the measurement geometry options A and B, indicates isotropicity of the BBT ceramic sample when $E = 0$ and corresponds to the results of the structure studies, which showed no texture. Anisotropy of anomalous thermal expansion, which occurs in the sample when cooling from the cubic phase at $E \neq 0$ and is recorded during subsequent heating is characterized by significantly different values (which are limit ones for $E = 5.45$ kV/cm) $\Delta\alpha^{A}_{T_1} = -11 \cdot 10^{-6}\,K^{-1}$ and $\Delta\alpha^{B}_{T_1} = -21 \cdot 10^{-6}\,K^{-1}$. Considerable variation of both the anomalous coefficients $\Delta\alpha^{A}_{T1}$ and $\Delta\alpha^{B}_{T_1}$ relative to the value that is typical for the sample in the isotropic state is caused by the ceramic nature of the sample: when being cooled in the conditions when $E \neq 0$ each crystallite has the predominant polarization direction that coincides with the electric field vector, whereas when $E = 0$ the direction of origination of spontaneous polarization is random.

The similar situation is also typical for the behavior of deformation in the tetragonal phase, but away from the temperature of the transition $Fm\bar{3}m \leftrightarrow P4mm$, wherein when $T_1 - 50$ K and $E_2 = 5.45$ kV/cm the difference of the limit values of deformations that occur in the isotropic and anisotropic state of BBT can be up to $\sim (20-30)$ %.

The decrease of field strength is accompanied by proportional narrowing of the interval of the limit values of $\Delta\alpha_{T_1}$ and $\Delta(\Delta L/L)$.

Acknowledgments

X-ray and dilatometric data were obtained using the equipment of the Krasnoyarsk Regional Common Use Center of the Federal Research Center Krasnoyarsk Scientific Center of the Siberian Branch of the Russian Academy of Sciences.

Funding

The study was carried out within the framework of the research topic of the State Assignment of the Institute of Physics of the Siberian Branch of the Russian Academy of Sciences.

Conflict of interest

The author declares that he has no conflict of interest.

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Translated by M.Shevelev