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Microstructure, domain structure, ferroelectric and piezoelectric properties of textured bismuth-containing ceramics

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In this report, the processes of texture formation in grain-oriented ferroelectric ceramics based on layer-structured ferroelectric $Bi_4Ti_3O_{12}$ (LSBT) prepared by hot forging method are considered. The microstructural and X-ray methods revealed the axial textured formation in ferroelectric ceramic that are used to estimate the orientation factor of ceramics. For the first time, the domain structure changes when poling the anisotropic ferroelectric ceramics are investigated. The anisotropy of electromechanical, piezoelectric and ferroelectric properties of ferroelectric ceramics due to the crystal texture existence in it is studied. The aim of this study is to study the processes of crystalline texture formation in polycrystalline BLSF and to establish the dependence of the electrophysical properties of ceramics on the degree of texturing. Ceramics were textured using the hot stamping (HS) method developed at the Research Institute of Physics. The mechanism of the method is that the workpiece is subjected to uniaxial pressure and free radial deformation occurs due to the plastic flow of the material until the workpiece fills the free volume of the mold, which is created by placing the workpiece in the mold with a gap. The study of the microstructure of ceramics showed that an increase in the firing temperature in the range 950–1050°C causes a sharp decrease in porosity and increases the density to 7.95 g/cm^3, which is 98% of theoretical. An X-ray analysis was performed and microstructural studies were carried out, which revealed the formation of an axial texture in ceramics. The features of the switching processes of textured ceramics are revealed. The characteristics of the polarization switching of ceramics in the directions parallel and perpendicular (⊥) of the pressure axis during hot processing were obtained from the dielectric hysteresis $P(E)$ loops, i.e., axis axial texture. The ⊥-cut ceramics are characterized by a more complete polarization switching, which is associated with the additional orientation of the (001) crystallographic planes in the textured material, as well as the presence of a threshold switching field. In the temperature range from -196 to + 600°C, the anisotropy of the electro physical properties of ceramics due to the presence of a crystalline texture in it was studied. The dielectric constant, electrical conductivity, piezoelectric and elastic coefficients were measured for sections of ceramics of different orientations relative to the axis of the texture. The anisotropy of the dielectric constant and electrical conductivity manifests itself weakly at room temperature and increases sharply when approaching the Curie temperature. In the temperature range +20–400°C, the high thermal stability of the piezoelectric module d_{33}, measured by the quasistatic method, was established.

Keywords: Textured ceramics; microstructure; domain structure; permittivity; piezoelectric modules; elastic coefficients.

1. Introduction

Most modern piezoelectric materials used in the operating temperature range from 100°C to 300°C are chemical compositions based on the lead titanate–zirconate system. Another group of materials works on the basis of bismuth and sodium-bismuth titanates in the temperature range up to 650°C. Currently, bismuth-containing layered ferroelectrics (BLSF), due to the high temperature of the ferroelectric phase transition, attract special attention, having the stability of piezoelectric parameters over a wide temperature range, good thermal stability and excellent fatigue characteristics.[1] Layered perovskite-like bismuth titanate ($Bi_4Ti_3O_{12}$) one of the classic BLSF, has generated great interest for high temperature piezoelectric sensor applications due to its high Curie temperature (T_C) of 675°C and strong ferroelectric polarization.[1]

The anisotropic grain-oriented ceramics based on layer-structured ferroelectric $Bi_4Ti_3O_{12}$ (LSBT) differs substantially from PZT-based ferroelectric ceramics. First, it exhibits enhanced temperature stability of electro physical parameters. Second, the presence of the texture (anisotropy) allows one to realize in the same material both ferroelectric soft and ferroelectric hard properties, depending on the direction of the external electrical field. Relatively low values of the dielectric constant and fairly high values of the remanent polarization ensure stable operation of functional elements made from this ferroelectric ceramics under severe conditions (mechanical stresses, electric field, temperature etc.).

Bismuth titanate with a layered perovskite-like structure ($Bi_4Ti_3O_{12}$, BLSF) was of great interest for use in piezoelectric sensors at high temperature due to its high Curie temperature (T_C = 675°C) and strong ferroelectric polarization.[1]

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Ferroelectrics of the $Bi_4Ti_3O_{12}$ type with a layered perovskite-like structure are used as the basis for the development of high-temperature applications polycrystalline piezomaterials of various practical applications. They have a number of significant advantages over ferroelectric representatives of the perovskite family: A higher Curie temperature (up to 950°C), a relatively low permittivity value (100–200), a small temperature coefficient of the resonant frequency and a low rate of aging of properties and a high mechanical Q-factor ($>10^3$). This makes it possible to create high-quality and stable piezo materials based on them for high-frequency converters operating in a wide temperature range.

It was found that the highest values of ferroelectric and piezoelectric properties, comparable in magnitude to the properties of a single crystal, are achieved in textured (anisotropic) ceramics of layered ferroelectrics obtained in the hot processing mode.[2–4] This is due to the fact that the spontaneous polarization vector P_s in ferroelectrics of the $Bi_4Ti_3O_{12}$ type is inclined at a small angle to the (001) plane, which causes limited possibilities for changing its spatial orientation in ceramics.[5] The additional orientation of the planes (001) in the textured material provides a more complete switching during subsequent polarization (a higher value of the residual polarization and related properties).

The most studied member of the layered ferroelectric family is bismuth titanate $Bi_4Ti_3O_{12}$. Below the Curie temperature (675°C), bismuth titanate has monoclinic symmetry, the spontaneous polarization vector P_s is inclined at an angle of 5–7° to the (001) plane, and is characterized by two switching components. On the a-axis, the magnitude of the coercive field is 50 kV•cm^{-1}, spontaneous polarization-P_s = 50 ±10 μC/cm^2, along the c axis-approximately 12 times less.[4]

Accordingly, in layered bismuth titanate, the existence of domains with opposite "a" and "c" components was established[6] along with true 180°and 90°domain structures, which determines the uniqueness of the domain structure of these compounds. Domain structure research in $Bi_4Ti_3O_{12}$ was carried out exclusively on single crystals, while ceramics in this respect remained completely unexplored. The first data on the domain structure of polycrystalline layered bismuth titanate were presented in Ref. 7.

The results of a comprehensive study presented in this paper were obtained on samples of high-density (density not less than 95% of the theoretical value, ρ_{theor} = 8.04 g/cm^3) ceramics of layered bismuth titanate modified with neodymium and niobium additives (TB-2), sintered using conventional ceramic technology and in the hot-pressing mode. The need for modification is due to the fact that these additives significantly reduce the electrical conductivity of pure $Bi_4Ti_3O_{12}$.[8]

Polycrystalline powder was used as the starting material after two-fold synthesis of the stoichiometric mixture $2Bi_2O_3$+$3TiO_2$ in the air atmosphere T_{max} = 950°C. Previously, the influence of synthesis conditions (single and double firing, temperature and time regimes, in the air atmosphere and in vapors Bi_2O_3), the purity of the initial oxides, modifying additives and other factors in order to obtain ceramics with improved electro physical properties. It is established that in all cases, the lamellar shape and particle size of the initial powder are essential for obtaining texture in samples, which are also controlled by the conditions of material synthesis.

To obtain textured ceramics with a controlled degree of preferential orientation of crystallites, the modernized method of forming products by pressure at high temperature (MHS), proposed in Ref. 9 was applied. The technique used combines the best aspects of two well-known methods: Hot pressing (HP) and hot stamping (HS). It allows us to adjust the spreading limits of the sintered material using a special mold, which makes it possible to control the pressing process and get a denser and stronger textured ceramic. The technological parameters of the method used for TB-2 are shown in Fig. 1. The degree of texture of ceramics was estimated by calculating X-ray images and micrographs.

The analysis of TB-2 ceramic samples was performed on a DRON-2.0 diffractometer on filtered Cu-Kα radiation. Powder diagram of compound $Bi_4Ti_3O_{12}$ indicated based on the parameters of the pseudo-tetragonal cell a = 3.841 Å, with=32.84 Å listed in ASTM. A fine synthesized powder that was not processed under pressure was used as a reference textless sample.

The obtained X-ray images were used to evaluate the degree of ceramic texturing according to the method and formula[10]:

$$f = \frac{P - P_0}{1 - P_0}, \quad (1)$$

where f is the degree of orientation of the crystallites; $P = \Sigma I_{00c}/\Sigma I_{hkl}$ for ceramics; P_0 - the same for the reference powder. ΣI_{hkl} includes all reflexes present on the X-ray image (including m 00l) in the widest possible angle range 2Θ. The value of f varies from 0 for powder to 1 for the case of a "perfect" texture.

Studies of the microstructure and domain structure of TB-2 ceramics were performed using a Nu-2E microscope in

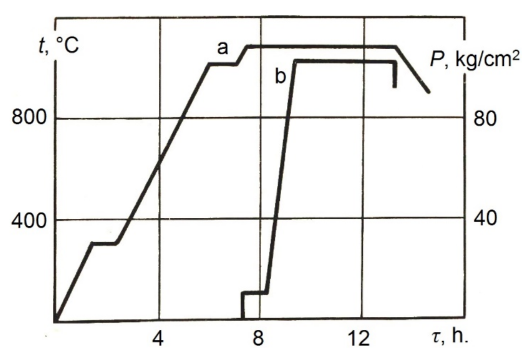


Fig. 1. Technological mode of the MHS method: (a) Dependence of temperature (t) on time (τ); (b) Dependence of pressure (P) on time (τ).

the reflected light mode and an EVM-100B electron microscope using single-stage platinumo-carbon replicas. Polished surfaces and chipped samples previously etched with concentrated HNO_3 with the addition of HF at room temperature were studied. In addition, we used the method of thermal etching (temperatures T_{max} = 1000°C, etching time τ - 30 min), which is effective for identifying grain boundaries.

When interpreting the domain structure from the etching relief, we proceeded from general crystallographic considerations regarding the possibility of developing domain twins in monoclinic layered bismuth titanate, taking into account the main and substructural elements, the nature of the boundaries (charged and uncharged), and their spatial orientation relative to cleavage (001). Elements of overlaying etching reliefs of the blast furnace, grain boundary, growth layers, and cleavage reliefs were also taken into account.

2. Experimental Methods

Analysis of the obtained X-ray images indicates the formation of an axial texture with a predominant orientation of the crystallite axes parallel to the pressure axis during hot processing. It is also obvious that the degree of orientation of crystallites in all the studied samples is small, the maximum values of did not exceed 0.3.

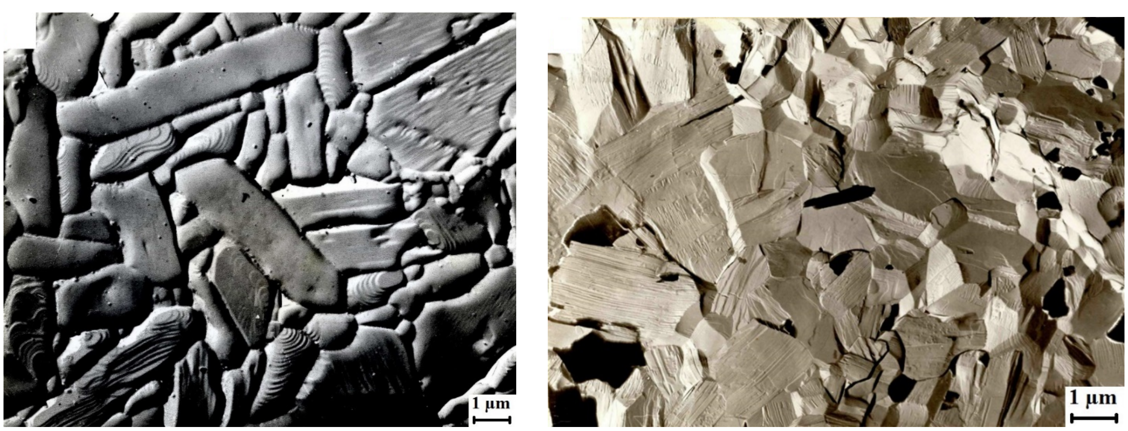
The ceramics examined is characterized by thin-grained structure. The grains are of tabular habitus with perfect sealing along (001) and well-developed domain structure. Under hot forging, the grains are oriented with their surface most develops along (001) across the forging axis. The grains are 0.5–3.0 μm thick, the linear dimensions along the well-developed surface are 5–20 μm. The dense packing of the grains when the surface (001) of one grain is laid on the corresponding surface of another gives rise to a monolithic structure.

The microstructure of TB-2 ceramics is characterized by an elongated tabular grain shape with perfect cleavage according to (001) and a different degree of packing — with mostly dense boundaries in HP and MHS ceramics and the presence of pores (up to 5%) in ceramics of conventional sintering. The linear grain sizes along the most developed plane (001) reach a maximum of 20 microns, while the grain thicknesseis 5–10 times smaller. In addition, the presence of large (up to 50 microns or more) xenomorphic grains of the nonferroelectric phase that do not respond to chemical etching, corresponding, according to X-ray spectral analysis, to the $Bi_2Ti_2O_7$ compound, is widely observed. Thermal etching reveals a finer grain substructure in these grains. The grain distribution in ceramics is completely dependent on the sintering modes; under normal sintering conditions, it is chaotic, sometimes poorly ordered, and more or less textured in HP and MHS ceramics (Fig. 2).

The domain structure studies performed made it possible to identify almost all the suggested types of domain walls, establishing a wide variety of domain structures in polycrystalline TB-2, which is to a certain extent determined by the initial conditions of formation at a high-temperature phase transition due to the high electrical conductivity of the medium. Apparently, this explains the stability of the domain structure known for layered bismuth titanate to external influences.

Figure 3 shows some types of domains in TB-2 ceramics. 90°domains are plate-shaped and wedge-shaped. In the section, excluding (001), a distinct etching relief is found (see Fig. 3) these domains. If their walls are charged, then a series of wedges moves away from them. 90°domains are most resistant to the electric field. It is known[11] that even in constant electric fields of 40–60 kV•cm^{-1} nonswitched 90°volumes may remain. Usually, 90° domains dissect the lamellar grain transversely to the cleavage, their width is l–3 microns, and sometimes there are cylindrical domains with a diameter of 2–5 microns, cutting the main structure at a small angle to the cleavage.

In ceramics with a grain size of less than a micrometer, 90° twinning is rare. In its pure form, 90° structures are not



(a) (b)

Fig. 2. (a) Microstructure (grain structure) of TB-2 ceramics (magnification × 3500). (b) Microstructure of nontextured ferroelectric ceramics of the BLSF-type.

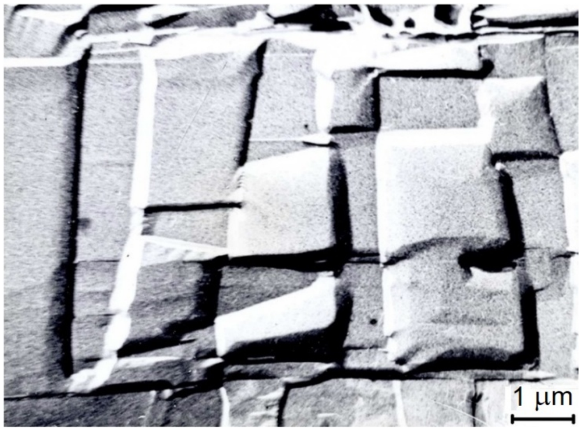


Fig. 3. Real domain structure in TB-2 ceramics: 90°structure with a substructure along the a-component, wall along (001).

observed. As a rule, they have a substructure with an antiparallel a component in the form of wedge-shaped domains oriented parallel to the cleavage. In oblique sections relative to the 90° wall, the cell structure can be revealed, which is formed solely due to etching of differently charged outputs of domains with an inversion of the sign when passing through the 90° boundary (Fig. 3).

Domains with an antiparallel a component are often found in the studied material, regardless of 90° twinning. These are wedge-shaped structures with a wall according to (001) with a clear etching relief in all oblique sections relative to the P_s vector, or with a charged zigzag wall according to (010), locally developed in the grain volume. When studying the repolarization processes in bismuth titanate single crystals, it was found in Ref. 11 that in fields up to 10 kV•cm^{-1} by direction [001] switching by a-component is not allowed occurs, i.e., domains with an antiparallel a-component are quite stable.

As shown by our studies, bismuth titanate is generally characterized by the presence of charged domain walls - zigzag, sawtooth and wedge-shaped. Such walls also occur at the (001) domain boundary with the antiparallel c component, the latter being rare in the studied material. Domains with an antiparallel c component with an uncharged wall according to (010) are poorly detected by etching and therefore poorly identified. According to Refs. 2–4, this type of wall is the most cstable, and c-component switching starts from the 300 V•cm^{-1} field when the [001] field 300 V•cm^{-1} is applied and ends completely in the field 10 kV•cm^{-1}.

True 180° structures in bismuth titanate ceramics are wedge-shaped, can be arbitrarily shaped in cross-sections, usually include a substructure with an antiparallel a-component and exhibit an inversion of the etching relief at the 180° boundary.

The domain structure of the unpoled grain-oriented ceramics is represented by a variety of domain configurations that correspond to domains with antiparallel a- and c-components, to genuinely 180° – and 90° – domains. Specific features of the domain structure of the LSBT ceramics have been described by us in Ref. 7.

Fig. 4. Domain structure of the anisotropic ferroelectric LSBT ceramics: Poled ceramics 90° – domain structure and crossing of grain boundaries are seen.

The dc electric field of E_o = 60 kV/cm causes a domain restructuring E_o is perpendicular to the forging axis). The structure grows coarser and the area of the domain walls is, accordingly, diminished. The number of 180°-domain walls is reduced considerably a sharp reduction occurs in the number of domains having the antiparallel a-component with the uncharged wall (001). Small wedge-shaped domains with a charged wall along the a-component (010) combine into larger ones with the length of the charged wall directed across the tabular grain.

A good number of charged 90°-walls are retained. In this case, the principal type of the domain structure of the polarized ferroelectric ceramics is represented by the 90°-domains with domain walls oriented roughly perpendicular to the direction of the field (Fig. 4).

The presence of the texture and the dense packing of grains provides conditions for the development of unidirectional 90°–domain groups going across the grain boundaries, which makes the domain structure of the polarized ferroelectric ceramics in the certain sense similar to that of the single crystal $Bi_4Ti_3O_{12}$.

Samples in the form of disks with a diameter of 10 mm and a thickness of 1 mm with silver and platinum electrodes were used to measure the electrophysical properties of TB-2 ferroceramics. The samples were polarized in silicone oil at a temperature of 200°C by an electric field of up to 60 kV•cm^{-1}. The exposure time under the field is 30 min.

Piezoelectric and elastic coefficients were determined by the dynamic method[4] when thickness vibrations are excited in a thin disk, since in all samples of the studied blocks, the radial vibrations of the disk are extremely weakly expressed. Piezo module value d_{33} it was also determined by the quasi-static method using the direct piezoelectric effect. It should

Table 1. Electrophysical properties ferroelectric ceramics TB-2.

Technology of obtaining	OS	HP		MH	
Slice orientation		**P||F**	**P⊥F**	**P||F**	**P⊥F**
ρ, g/cm^3	7.72	7.88	7.88	7.88	7.88
$\varepsilon^*/\varepsilon_0$, Unpolarized sample	147	163	165	154	152
$\varepsilon_{33}^T/\varepsilon_0$	146	162	159	152	149
K_ρ	0.04	0.04	0.04	0.03	0.03
$d_{31}\cdot 10^{12}$ C/N	2.4	2.3	2.2	1.7	3.1
Poisson's ratio, σ	0.24	0.24	0.25	0.23	0.25
Quasistatic $d_{33}\cdot 10^{12}$ C/N	15.9	15.7	19.0	9.0	19.5
C_{33}^D 10^{-11} Pa	1.47 [13]	1.43	1.50	1.35	1.53

be noted that the samples of TB-2 ceramics obtained by conventional sintering (OS) technology almost all had a non-monofrequency spectrum of thickness vibrations, which is obviously due to the inhomogeneous distribution of the elastic modulus in the disk.

Table 1 shows some electroelastic properties of TB-2 ferroelectric ceramics obtained by various technological methods. For HP and MHS ceramics, the properties were measured at different orientations of the polarization axis relative to the direction of pressure action during pressing: ***P***||***F*** - the axis of polarization coincides with the direction of pressure action and ***P***⊥***F*** - the axis of polarization is perpendicular to the direction of pressure action.

It follows from the obtained data that the hot processing technology leads to an increase in the dielectric permittivity, piezoelectric modulus d_{33} and elastic modulus in comparison with conventional sintering C_{33}^D (for ceramic sections of orientation ***P***⊥***F***). At the same time, the ceramic preparation technology does not significantly affect the value of the electroelastic constants determined from the radial mode of vibrations (K_p, d_{31}, σ).

A comparison of the above results shows that the TB-2 ceramic obtained by hot processing methods has a pronounced anisotropy of piezoelectric and elastic properties, indicating the texturing of the ceramic during its sintering. Moreover, the MHS method leads to a higher degree of anisotropy compared to pressing, which is confirmed by X-ray and microstructural studies. It should also be noted that there is almost no anisotropy of the dielectric properties, which is obviously due to the low anisotropy of the permittivity of the single crystal $Bi_4Ti_3O_{12}$ ($\varepsilon_a = 120$, $\varepsilon_b = 205$ and $\varepsilon_c = 140$)[13] and a low degree of ceramic texturing. In addition, the sintering method also affects the absolute values of piezoelectric and elastic coefficients, and in all cases, with the mutually orthogonal direction of the axes, higher values of piezoelectric coefficients K_t, d_{33} and elastic modulus. These values exceed the values of the corresponding coefficients measured for TB-2 ceramics obtained by the conventional technology.[13]

The temperature dependences of the electro-elastic constants $\varepsilon_{33}^T/\varepsilon_0$, K_t, C_{33}^D and d_{33} of TB-2 ceramics obtained by HP and MHS methods in the temperature range 180–+600°C. From the above data, it can be seen that the anisotropy of properties is preserved over the entire temperature range studied. Values of piezoelectric and elastic coefficients of ceramics HP lie between the values of the corresponding values measured for the orientation sections ***P***⊥***F*** and ***P***||***F*** for MHS ceramics.

It can be noted that the elastic modulus decreases almost linearly with increasing temperature. Lower values in the direction of ***P***||***F*** apparently are related to the layered structure of bismuth titanate crystallites and the weak bond between the layers. Maximum permittivity at temperature ~ 540°C is obviously at a relaxation nature. Similar maxima is found in the temperature dependence of the permittivity of a single crystal $Bi_4Ti_3O_{12}$.[12] In the entire studied temperature range piezo module d_{33}, measured by the resonance method, increases with increasing temperature by ~ 20%.

Thus, the technology of hot processing (HP and MHS) leads to anisotropy of piezoelectric and elastic properties of TB-2 ferroelectric ceramics associated with the texturing of the material, which is consistent with the data of calculations based on X-ray diffraction patterns and the results of the studied microstructure.

Over the temperature range of (–196 ÷ 550)°C it is ascertained that the modulus of elasticity $c_{33}{}^D$ is, in practice, linearly temperature-dependent. Within a temperature range from 20 to 400°C, the piezoelectric modulus d_{33} measured using the quasistatic method is found to have the high thermal stability. The estimate of the piezoelectric constant g_{33} at 20 °C (for the permittivity $\varepsilon_{33}{}^T \sim 130$) shows that its value is close to the corresponding constants of PZT-ceramics or even exceeds them.

The features of switching processes in textured ceramics are revealed from the dielectric hysteresis loops. The

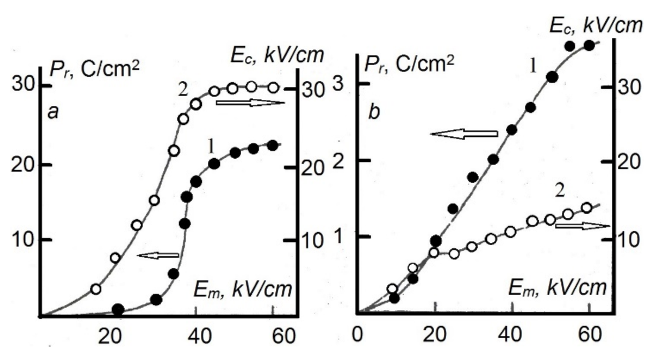


Fig. 5. Dependence of parameters of the dielectric hysteresis loop for the anisotropic LSBT ceramics on the amplitude of the field (50 Hz): (a) Field perpendicular to the forging axis; (b) field parallel to it. 1 - Remnant polarization P_r; 2 - coercive field, E_c.

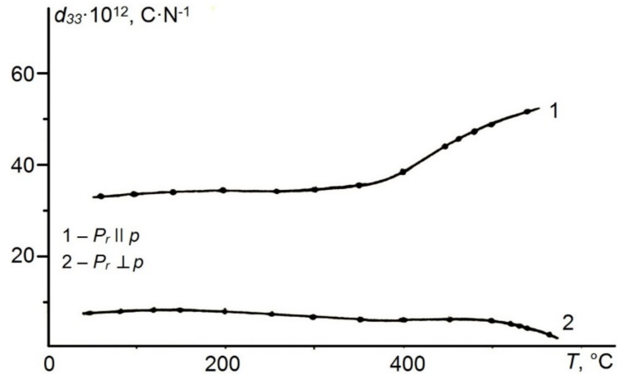


Fig. 6. Temperature dependence of the piezoelectric modulus d_{33} of textured STB ferroelectric ceramics.

anisotropic characteristic of ceramic switching in the direction parallel and perpendicular to the forging axis for hot forging case are obtained (Fig. 5). A higher switching and the present of switching threshold field as well are characteristic of perpendicular cut ferroelectric ceramics (Fig. 5(a)).

The textured piezoceramic STB also has a characteristic "anisotropy" of piezoelectric parameters (Fig. 6). For $E_p \perp p$, the piezoelectric modulus d_{33} is significantly higher than for $E_p \parallel p$; the temperature dependence of the piezoelectric modulus d_{33} also turns out to be different: In the first case, starting from $T = 350°C$, an increase in d_{33} is observed with an increase in T, in the second, starting from $T = 200°C$, d_{33} decreases. Hence, we can conclude that the stability of the polarized state to thermal effects in the first case is higher than in the second.

3. Conclusions

Based on the conducted research, the following conclusions can be drawn:

It has been established that the technology of HP and HS leads to anisotropy of the piezoelectric and elastic properties of STV ceramics associated with the texturing of the material.

The degree of texturing is higher for hot-forged ceramics than for hot-pressed ones.

Higher piezoelectric and elastic properties are possessed by sections $P_r \perp p$, when the direction of the polarization axis is orthogonal to the direction of the force during ceramic sintering.

The conducted studies allow us to conclude that the study of anisotropic ferroelectric ceramics based on layered bismuth titanate is promising both for solving the fundamental scientific problem of a ferroelectric polycrystal and for creating sensors for various purposes operating under extreme conditions.

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