ANOMALOUS CHANGE IN THE MATERIAL MODULI
OF THIN FILMS OF BARIUM TITANATE

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Abstract: A method is proposed to determine the moduli of thin ferroelectric films subjected to forced deformation due to the mismatch between the crystal lattice sizes of the film and substrate materials and the difference of their thermal expansion coefficients. Models of single-crystal films of barium titanate are studied using the eighth-degree Landau thermodynamic potential. It is shown that in the considered range of forced strain of the barium titanate film, three main states exist: a tetragonal phase (c phase) of 4mm symmetry with spontaneous polarization directed along the normal to the film plane; an orthorhombic phase (aa phase) of 2 mm symmetry with polarization oriented along the diagonal plane of the film; monoclinic phase (r phase) of C_m symmetry with the intermediate direction of polarization. All phases are separated by the lines of transitions of the second kind. Dependences of the elastic, electric and piezoelectric moduli on the magnitude of forced strain are plotted. It is shown that at the phase boundaries there is an anomalous change in the constants of the ferroelectric film and in the region of existence of the r phase, some moduli reach extreme values.

Keywords: ferroelectrics, thin films, forced strain, material constants, piezoelectric moduli, elastic moduli.

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INTRODUCTION

An anomalous ferroelectric state in thin films is caused by high mechanical stresses that occur at the film–substrate interface due to the mismatch between the crystal lattice parameters of the film and substrate materials, the difference of their thermal expansion coefficients, and the occurrence of spontaneous deformation in the phase transition if the film is deposited at a temperature exceeding the phase transition temperature. Thermal stress can lead to a shift in the temperature of the ferroelectric phase transition in the film and a change in the structure of the low-symmetry phases, which should be considered when designing acoustoelectronic devices for various purposes. Typically, the operating parameters of ferroelectric structures are optimized using linear piezoelectric equations [1, 2] which define the linear relationship between state variables and external parameters. Large deformation in thin films leads to a change in the material constants, which necessitates using nonlinear thermodynamic models [3]. In this work, a method of sequential linearization and determination of constant linear piezoelectric equations for thin ferroelectric films was developed using the phenomenological theory of phase transitions. The behavior of the constants as a function of forced strain was studied for single-crystal films of barium titanate as an example. The

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study of the material equations using the eighth-degree Landau potential revealed an anomalous change in the constants at the boundaries of the regions of existence of the phases and their extremal change in the region of existence of the r phase.

1. CALCULATION OF MATERIAL CONSTANTS OF FERROELECTRIC THIN FILMS

As the basic relation, we use the thermodynamic potential of the phenomenological theory of the phase transitions

$$\Phi = F_1(p_1, p_2, p_3) + F_2(\sigma_k, p_n) + F_3(\sigma_k), \tag{1}$$

where

$$F_2(\sigma_k, p_n) = -q_{11} \sum_{k=1}^{3} \sigma_k p_k^2 - q_{44}(\sigma_4 p_2 p_3 + \sigma_5 p_1 p_3 + \sigma_6 p_1 p_2)$$

$$- q_{12}(\sigma_1(p_2^2 + p_3^2) + \sigma_2(p_1^2 + p_3^2) + \sigma_3(p_1^2 + p_2^2)),$$

$$F_3(\sigma_k) = -\frac{1}{2} s_{11} \sum_{k=1}^{3} \sigma_{kk}^2 - \frac{1}{2} s_{44}(\sigma_{23}^2 + \sigma_{13}^2 + \sigma_{12}^2) - s_{12}(\sigma_{11}\sigma_{22} + \sigma_{11}\sigma_{33} + \sigma_{22}\sigma_{33}).$$

Here $F_1(p_1, p_2, p_3)$ is the Landau potential, p_k are the components of the polarization vector, q_{kn} are the electrostrictive constant, and σ_k and s_k are the components of the stress and ductility tensors, respectively, in the Voigt matrix notation. For many materials, in particular, for barium titanate BaTiO$_3$, the function F_1 is the potential of the eighth degree for the components of the polarization vector [4]. The equilibrium state of the material is defined by the system of equations

$$E_n = \frac{\partial \Phi}{\partial p_n}, \quad n = 1, 2, 3, \qquad u_k = -\frac{\partial \Phi}{\partial \sigma_k}, \quad k = 1, 2, \ldots, 6. \tag{2}$$

Here E_n are the components of the electric field and u_k are the components of the strain tensor. For the material of a three-dimensional object in the absence of external forces, the problem reduces to solving the first three equations of system (2). In this case, the remaining six equations define spontaneous strains. The material constants of the piezoelectric equations are found by linearization of the equations of state (2) under fixed external conditions.

For a thin film, the problem is solved in two steps. Initially, the mechanical problem is solved for the following initial strain conditions [5] [film at the (001) section of a cubic substrate]: $u_1 = u_m$, $u_2 = u_m$, $\sigma_3 = 0$, $\sigma_4 = 0$, and $\sigma_5 = 0$ (u_m is the forced strain). Then, the possible basic states are studied based on the constructed u_m–temperature T phase diagram, which depends on the elastic [6] and electroelastic [7] constants.

The form of the potential (1) corresponds to the linear system of piezoelectric equations in the form

$$u_k = s_{km}^D \sigma_m + g_{mk} p_m, \qquad E_i = -g_{ik}\sigma_k + \beta_{ij}^T p_j, \tag{3}$$

where the mechanical stresses and polarization are chosen as independent variables. In the general case, from system (3) and potential (1), for the film phase of trivial symmetry, we obtain the constants

$$s_{kk}^D = s_{11}, \quad k = 1, 2, \ldots, 6, \qquad s_{12}^D = s_{13}^D = s_{23}^D = s_{12}; \tag{4}$$

$$g_{kk} = 2q_{11}P_k, \quad k = 1, 2, 3, \qquad g_{12} = g_{13} = 2q_{12}P_1,$$

$$g_{21} = g_{23} = 2q_{12}P_2, \qquad g_{31} = g_{32} = 2q_{12}P_3, \tag{5}$$

$$g_{26} = g_{35} = q_{44}P_1, \qquad g_{16} = g_{34} = q_{44}P_2, \qquad g_{15} = g_{24} = q_{44}P_3;$$

$$\beta_{11}^T = q_1 P_1^2 + q_2 P_2^2 + D_{11}, \qquad \beta_{22}^T = q_2 P_1^2 + q_1 P_2^2 + D_{22},$$

$$\beta_{33}^T = q_{12}B(P_1^2 + P_2^2) + 4Aq_{12}^2 P_3^2 - 4Aq_{12}u_m + F_{1,33}, \tag{6}$$

$$\beta_{12}^T = q_{44}^2 s_{44}^{-1} P_1 P_2 + F_{1,12}, \qquad \beta_{m3}^T = F_{1,m3}, \quad m = 1, 2.$$

Here

$$D_{kk} = q_{12}BP_3^2 - Bu_m + F_{1,kk}, \quad k = 1, 2, \qquad A = (s_{11} + s_{12})^{-1}, \qquad B = 2A(q_{11} + q_{12}),$$

the subscript after the comma marks the derivatives of the Landau potential with respect to the polarization components.

Remark 1. Equations (3) contains components of the induction vector D [8]. However, for ferroelectrics, the permittivity is virtually identical to the receptivity, and, therefore, the difference between polarization and induction can be neglected.

From relations (4)–(6), it follows that the elastic constants (4) and electroelastic constants (5) do not provide symmetry of the trivial phase. This implies that if Eqs. (3) is used as the constitutive relations, the representation of the potential (1) should include additional terms. At the same time, the dielectric tensor (6) is low-symmetry and therefore, as the main constants we can choose other ones that are more adequate to problems of mechanics and switch from the linear piezoelectric equations in the form (3) to the equations [8]

$$\sigma_m = c_{mk}^E u_k - e_{im} E_i, \qquad p_i = e_{ik} u_k + \varepsilon_{ij}^S E_j, \tag{7}$$

in which the strain is the initial parameter, along with the electric field intensity. Transition from constants (4) and (6) to these constants is based on the relations [8]

$$g_{mi} = \beta_{nm}^T d_{ni} = h_{mj} s_{ji}^D, \quad d_{mi} = \varepsilon_{nm}^T g_{ni} = e_{mj} s_{ji}^E, \quad e_{mi} = \varepsilon_{nm}^S h_{ni} = d_{mj} c_{ji}^E. \tag{8}$$

Next, system (7) is used to determine the total set of material constants of a thin ferroelectric film.

2. MATERIAL CONSTANTS OF THIN FILMS OF BARIUM TITANATE

As an example, we consider a single crystal of BaTiO$_3$, for which the spontaneous polarization at $T = 300$ K is 0.26 K/m^2. When using the experimental values of the constants g from [9], the coefficients in the representation of the Landau potential are, respectively, $q_{11} = 0.1106$ m^4/K^2, $q_{12} = -0.0442$ m^4/K^2, and $q_{44} = 0.0585$ m^4/K^2. For the subsequent calculations, we use high-temperature compliances $s_{11} = 8.33 \cdot 10^{-12}$ m^2/N, $s_{12} = -2.68 \cdot 10^{-12}$ m^2/N, and $s_{44} = 9.24 \cdot 10^{-12}$ m^2/N [9]. In this paper, the eighth-degree potential $F_1(p_1, p_2, p_3)$ from [4] is used. Analysis of the problem shows that for a thin film of BaTiO$_3$ at room temperature and adopted parameters of the potential (1), three main states are possible:

(1) a c phase of 4mm tetragonal symmetry with spontaneous polarization directed along the normal to the film plane ($p_x = 0$, $p_y = 0$, and $p_z \neq 0$);

(2) a rhombic aa phase of 2mm symmetry with polarization oriented diagonally in the film plane $p_x = p_y \neq 0$ and $p_z = 0$);

(3) amonoclinic r phase of C_m symmetry with polarization directed along the diagonal of the crystal lattice of the film material ($p_x = p_y \neq 0$ and $p_z \neq 0$).

All phases are separated by the lines of transitions of the second kind. Calculation of the material constants based on the solution of system (7) for the BaTiO$_3$ film is performed for a state close to the main one, which depends on the value of u_m. It has been found [10] that at $T = 300$ K, the phases of the BaTiO$_3$ film exist in the following ranges:

—the c phase exists at $u_m < -1.80 \cdot 10^{-3}$;

—the r phase at $-1.80 \cdot 10^{-3} < u_m < 1.45 \cdot 10^{-3}$;

—the aa phase at $u_m > 1.45 \cdot 10^{-3}$.

In Eqs. (7), different material constants are used for different phases [11]. In the calculation of these constants, we will use a single coordinate system with the axes lying along the cubic directions of the high-symmetry phase. In the c phase, the set of constants of the film from Eqs. (7) is the same as that for the three-dimensional sample of barium titanate and includes two dielectric constants, three piezoelectric constants, and six elastic constants. In this case, the elastic and electrical characteristics are related as

$$\boldsymbol{\sigma} = A\boldsymbol{u}, \qquad \boldsymbol{\sigma} = (\sigma_1, \sigma_2, \sigma_3, \sigma_4, \sigma_5, \sigma_6, p_1, p_2, p_3)^{\mathrm{t}},$$

$$A = \begin{bmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 & 0 & 0 & -e_{31} \\ c_{12} & c_{11} & c_{13} & 0 & 0 & 0 & 0 & 0 & -e_{31} \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 & 0 & 0 & -e_{33} \\ 0 & 0 & 0 & c_{44} & 0 & 0 & 0 & -e_{15} & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 & -e_{15} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{66} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & e_{15} & 0 & \varepsilon_{11} & 0 & 0 \\ 0 & 0 & 0 & e_{15} & 0 & 0 & 0 & \varepsilon_{11} & 0 \\ e_{31} & e_{31} & e_{33} & 0 & 0 & 0 & 0 & 0 & \varepsilon_{33} \end{bmatrix}, \tag{9}$$

$$\boldsymbol{u} = (u_1, u_2, u_3, u_4, u_5, u_6, E_1, E_2, E_3)^{\mathrm{t}}.$$

In the aa phase, the film has three dielectric constants, five piezoelectric constants, and nine elastic constants. In this case, the elastic and electrical characteristics are related as

$$\boldsymbol{\sigma} = A\boldsymbol{u}, \qquad \boldsymbol{\sigma} = (\sigma_1, \sigma_2, \sigma_3, \sigma_4, \sigma_5, \sigma_6, p_1, p_2, p_3)^{\mathrm{t}},$$

$$A = \begin{bmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & c_{16} & -e_{11} & -e_{12} & 0 \\ c_{12} & c_{11} & c_{13} & 0 & 0 & c_{16} & -e_{12} & -e_{11} & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & c_{36} & -e_{13} & -e_{13} & 0 \\ 0 & 0 & 0 & c_{44} & c_{45} & 0 & 0 & 0 & -e_{34} \\ 0 & 0 & 0 & c_{45} & c_{44} & 0 & 0 & 0 & -e_{34} \\ c_{16} & c_{16} & c_{36} & 0 & 0 & c_{66} & -e_{16} & -e_{16} & 0 \\ e_{11} & e_{12} & e_{13} & 0 & 0 & e_{16} & \varepsilon_{11} & \varepsilon_{12} & 0 \\ e_{12} & e_{11} & e_{13} & 0 & 0 & e_{16} & \varepsilon_{12} & \varepsilon_{11} & 0 \\ 0 & 0 & 0 & e_{34} & e_{34} & 0 & 0 & 0 & \varepsilon_{33} \end{bmatrix}, \tag{10}$$

$$\boldsymbol{u} = (u_1, u_2, u_3, u_4, u_5, u_6, E_1, E_2, E_3)^{\mathrm{t}}.$$

In the r phase, the ferroelectric has four dielectric constants, ten piezoelectric constants, and thirteen elastic constants. In this case, the relationship between its elastic and electrical characteristics is represented as

$$\boldsymbol{\sigma} = A\boldsymbol{u}, \qquad \boldsymbol{\sigma} = (\sigma_1, \sigma_2, \sigma_3, \sigma_4, \sigma_5, \sigma_6, p_1, p_2, p_3)^{\mathrm{t}},$$

$$A = \begin{bmatrix} c_{11} & c_{12} & c_{13} & c_{14} & c_{15} & c_{16} & -e_{11} & -e_{12} & -e_{31} \\ c_{12} & c_{11} & c_{13} & c_{15} & c_{14} & c_{16} & -e_{12} & -e_{11} & -e_{31} \\ c_{13} & c_{13} & c_{33} & c_{34} & c_{34} & c_{36} & -e_{13} & -e_{13} & -e_{33} \\ c_{14} & c_{15} & c_{34} & c_{44} & c_{45} & c_{46} & -e_{14} & -e_{15} & -e_{34} \\ c_{15} & c_{14} & c_{34} & c_{45} & c_{46} & c_{46} & -e_{15} & -e_{14} & -e_{34} \\ c_{16} & c_{16} & c_{36} & c_{46} & c_{46} & c_{66} & -e_{16} & -e_{16} & -e_{36} \\ e_{11} & e_{12} & e_{13} & e_{14} & e_{15} & e_{16} & \varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\ e_{12} & e_{11} & e_{13} & e_{15} & e_{14} & e_{16} & \varepsilon_{12} & \varepsilon_{11} & \varepsilon_{13} \\ e_{31} & e_{31} & e_{33} & e_{34} & e_{34} & e_{36} & \varepsilon_{13} & \varepsilon_{13} & \varepsilon_{33} \end{bmatrix}, \tag{11}$$

$$\boldsymbol{u} = (u_1, u_2, u_3, u_4, u_5, u_6, E_1, E_2, E_3)^{\mathrm{t}}.$$

Remark 2. Matrices (9)–(11) are written in a coordinate system associated with the cubic substrate: the coordinate axes are directed along fourth-order axes. Matrix (9) has the standard form [8], and the form of matrices (10) and (11) differs from it. To reduce matrice (10) and (11) to the standard form, it is necessary to make a transformation that corresponds to the rotation of the matrices around the [001] axis at an angle of 45°.

Figures 1–5 show the results of calculations of the material constants of the $\mathrm{BaTiO_3}$ film at $T = 300$ K. These results shows that phase transitions occur at $u_m^0 = -1.80 \cdot 10^{-3}$ and $u_m^1 = 1.45 \cdot 10^{-3}$. Figure 1 shows curves of the dielectric permittivity versus forced strain. (Vertical thin lines in Figs. 1–5 mark the boundaries of the regions of existence of the phases.) It is evident that the transition from the c phase to the r phase leads to a sharp increase in ε_{11}^S due to the appearance of planar polarization components. The sharp increase in ε_{33}^S in the transition from

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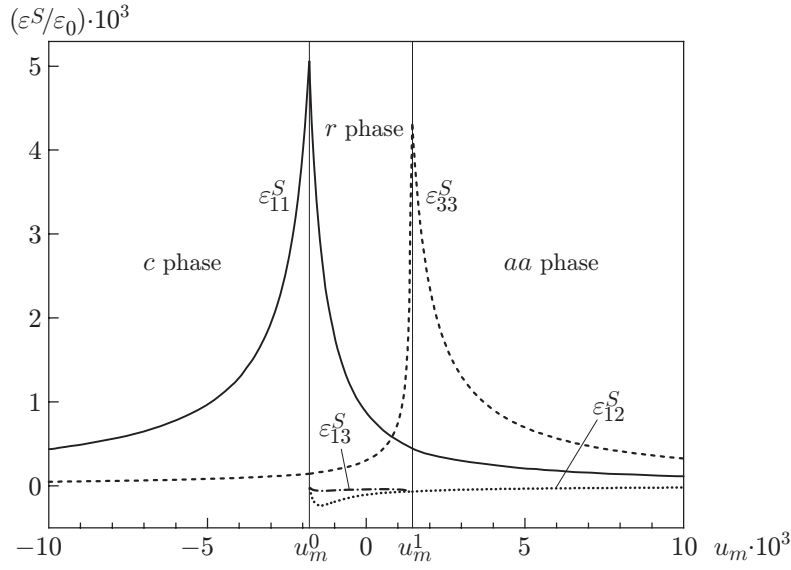
Fig. 1. Permittivity components of the BaTiO$_3$ film versus forced strain.

the r phase to the aa phase can be explained by the disappearance of the normal polarization component. It should be noted that the extreme values of the permittivity components at the phase boundaries are finite.

Figures 2 and 3 show the effect of forced strain on elastic moduli. Curves of the moduli of the initial material (constants of the three-dimensional sample) versus forced strain are presented in Fig. 2. Curved of the moduli that occur after the transition of the film from the tetragonal phase to the monoclinic and rhombic phases versus forced strain are presented in Fig. 3. From Figs. 2 and 3, it follows that the change in the elastic constants is due mostly to phase transitions. With increasing forced strain at the boundary of the region of existence of the c and r phases, the modulus c_{44}^E decreases to zero, and then in the region of existence of the r phase, it increases, reaching a maximum at $u_m = 0.74 \cdot 10^{-3}$. In the c phase and after the transition from it to the r phase, the modulus c_{33}^E decreases, reaching a minimum in approaching from the left to the boundary of the regions of existence of the r and aa phases. However, having reached this boundary, it increases suddenly. In the region of existence of the aa phase, the modulus c_{33}^E does not change.

Figures 4 and 5 show curves of the electroelastic constants of the initial three-dimensional sample and the constants occurring after the transition of the film from the tetragonal phase to the monoclinic and rhombic phases versus forced strain. From Figs. 4 and 5, it follows that the change in the constants is also due mainly to the phase transitions. As the forced strain increases, the modulus e_{15} increases, reaching a maximum at the boundary between the regions of existence of the c and r phases. With further increase in the forced strain, the value of e_{15} decreases sharply, reaching zero at the boundary of the regions of existence of the r and aa phases, in which the modulus e_{33} has the main effect on the electroelastic properties of the film.

The piezoelectric modulus e_{34} has a maximum at the boundary between the regions of existence of the r and aa phases. In the region of existence of the r phase in approaching the boundary with the c phase, the constants e_{11}, e_{16}, e_{14}, e_{13}, and e_{12} increase monotonically in absolute value and then sharply decrease to zero. All these moduli reach extreme values in the region of existence of the r phase. The piezomoduli e_{33} and e_{31} change similarly. In approaching the boundary of the regions of existence of the r and aa phases, the moduli reach a maximum and then rapidly tend to zero.

CONCLUSIONS

A method was proposed to determine the moduli of ferroelectric thin films under conditions of forced deformation due to the mismatch between the crystal lattice sizes of the film and substrate materials and the difference
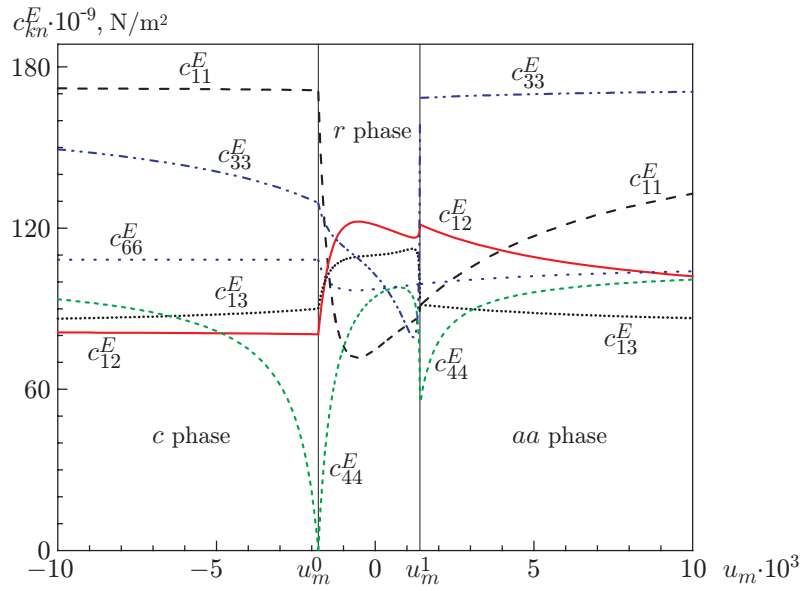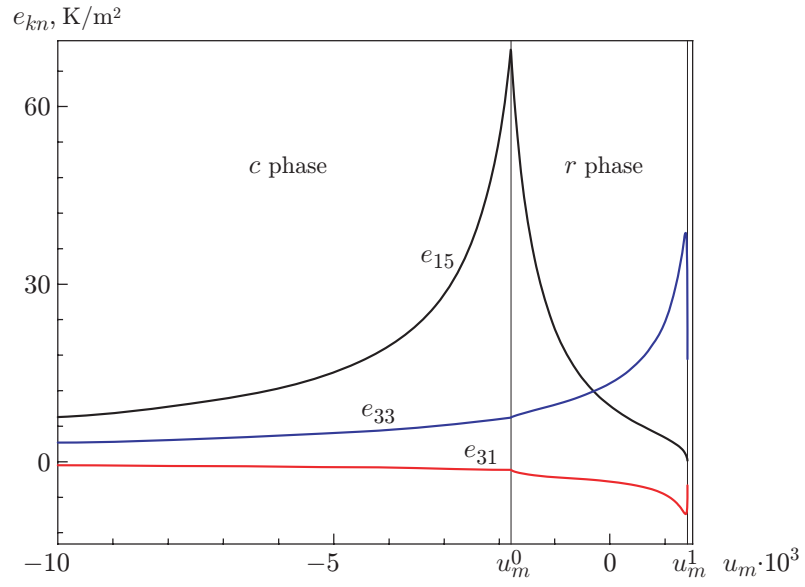
Fig. 2. Elastic moduli of the initial $BaTiO_3$ film versus forced strain at $T = 300$ K.
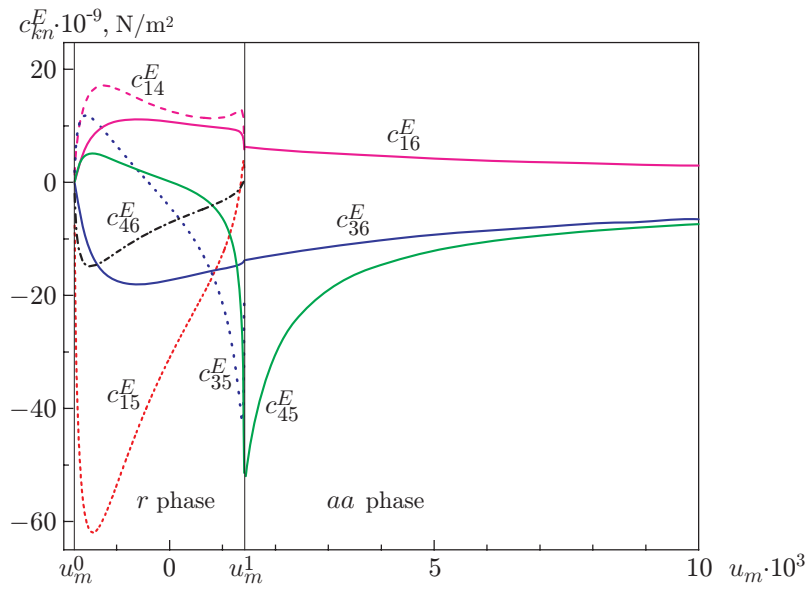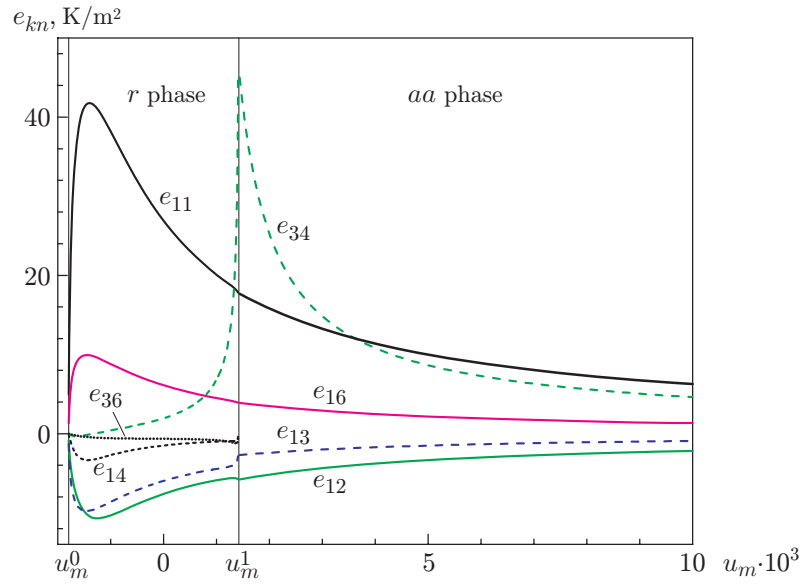

Fig. 3. Elastic moduli of the $BaTiO_3$, film in the orthorhombic and monoclinic phases versus forced strain.

between their thermal expansion coefficients. It has been shown on the example of single-crystal barium titanate films that the elastic and electrical properties of thin films change more significantly than the material properties of three-dimensional objects, particularly, in the vicinity of the phase transition boundaries, where the forced strain of the film is close to the critical value. A region of small strain (region of existence of the r phase) was determined in which material moduli change most significantly. Thus, the elastic and electrical properties of films can be varied by changing forced strain. This can be done by selecting the substrate material, film thickness, and deposition techniques as the forced strain is a process parameter and depends primarily on the thermal expansion coefficients of the substrate and the film.

Fig. 4. Piezomoduli of the initial BaTiO₃ film versus forced strain.

Fig. 5. Piezomoduli of the BaTiO₃ film in the orthorhombic and monoclinic phases versus forced strain.

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