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Using of mechanical deformations to control for phase transformations in multilayer ferroelectric structures

© A.S. Sidorkin[1], B.M. Darinskii[1], Y. Gagou[2], P. Saint-Gregoire[3],
A.V. Kalgin[1,4,¶], L.P. Nesterenko[1]

[1] Voronezh State University,
Voronezh, Russia
[2] Universite de Picardie Jules Verne,
Amiens, France
[3] University of Nimes,
Nimes, France
[4] Voronezh State Technical University,
Voronezh, Russia
¶ E-mail: kalgin_alexandr@mail.ru

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Based on the results of studies of the temperature dependences of dielectric constant, polarization and coercive field, the Curie points and the type of phase transition for three-layer ferroelectric structures barium titanate — strontium titanate $SrTiO_3/BaTiO_3/SrTiO_3$ and lead titanate — strontium titanate $SrTiO_3/PbTiO_3/SrTiO_3$ were determined. It is shown that in a multilayer with barium titanate there is a significant (about two hundred degrees) increase in the Curie temperature of the created structure compared to homogeneous barium titanate, and the type of ferroelectric phase transition changes from first order to second order. In a multilayer with lead titanate, the Curie point and the type of transition practically do not change in comparison with homogeneous lead titanate, which is associated primarily with the practical coincidence of the cell sizes of lead titanate and strontium titanate in the plane of contact.

Keywords: ferroelectric superlattices, multilayer structures, permittivity, polarization, mechanical strains, phase transition, phase transition order, incompatibility strains.

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1. Introduction

The well known factor is recognition of the potential of using ferroelectrics having practically useful electrophysical characteristics in displacement sensors, electrical memory, piezoelectric generators to convert sun energy into the electric energy, in pyroelectric devices, implanted medical devices etc. [1] This sets the objective to control the electrical characteristics of ferroelectrics, for its solution different methods were developed and partially used to control the properties and characteristics of the ferroelectric and rete materials [2–4].

The possible methods changing the properties of ferroelectric materials comprise creation of the ferroelectric composite structures where size and chemical composition of components is possible [5–7].

Nature of said factors effect, in particular, in multilayer compositions, is based on the possibility to vary their properties by changing the acting in these structures long-range elastic or electric fields, as well as short-range chemical interactions of compositions in contact in such structures [8–10].

Among the artificially created for practical purposes ferroelectric structures the so called ferroelectric superlattices being multilayer componds of related materials with close structural characteristics occupy one of the first places due to beneficial properties. Such superlattices are, in particular, ferroelectric superlattices with layers made of crystal components of materials of perovskite group [11,12].

For this there are obvious groundings. These materials have rather simple chemical formula and known methods of individual compositions used for their making. There is a group of materials of perovskite group with close parameters of lattice cells,ensuring to implement in practice based on this the set doped change of cell dimensions of mating materials, and expect, finally, the controllable change of properties of synthesized materials.

2. Experimental features of behavior of multilayer ferroelectric structures

The present paper relates to relative study of dielectric properties of three-layer structures $SrTiO_3/BaTiO_3/SrTiO_3$ [13] and $SrTiO_3/PbTiO_3/SrTiO_3$ on doped by Nb single-crystal substrate $SrTiO_3$ with conductive sublayer of $LaSrCoO_3$, obtained by method of laser sputtering. For dielectric measurements for such

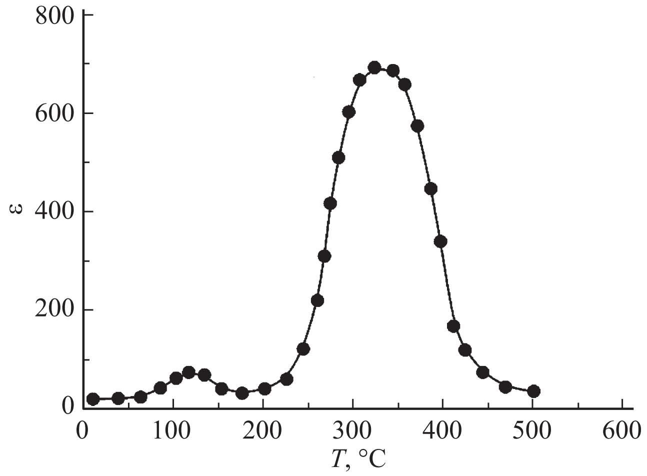

Figure 1. Dielectric permittivity vs. temperature for laminar structure $SrTiO_3/BaTiO_3/SrTiO_3$.

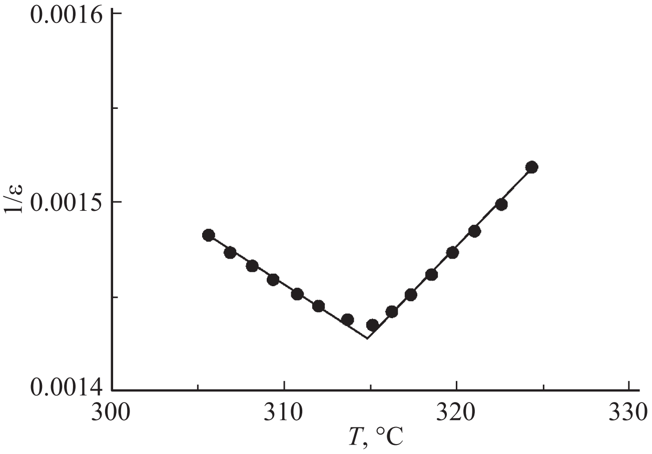

Figure 2. Reverse dielectric permittivity vs. temperature for structure $SrTiO_3/BaTiO_3/SrTiO_3$.

structures the platinum electrodes were used. The dielectric properties of described structures were studied using LCR-meter and Sawyer–Tower diagram with conductivity compensation at the frequency of the measuring external field 100 Hz.

Study of temperature dependence of dielectric permittivity $\varepsilon(T)$ for the three-layer structures $SrTiO_3/BaTiO_3/SrTiO_3$ (Figure 1) identified main a somewhat smeared maximum in the temperature range of 310 to 320°C with value of dielectric permittivity about 700 in maximum, and second small maximum with value ε about 40 at temperatures about 115°C, its value is only 6% of first maximum.

Relative smallness of the second maximum ensures the conclusion that the ferroelectric phase transition in studied three-layer structures occurs in temperature range $310-320$°C, which exceeds the transition temperature in ferroelectric films of barium titanate by practically 200°C.

Said conclusion is confirmed also by studies of reverse dielectric permittivity of these materials. Figure 2 presents reverse dielectric permittivity of structure $SrTiO_3/BaTiO_3/SrTiO_3$ vs. temperature, it shows that this three-layer structure acts as material with phase transition of second kind [9].

First of all this is confirmed by absence of temperature hysteresis of Curie point [13]. Besides, the change in the order of the phase transition is also indicated by the regularities of temperature changes in the dielectric permittivity: the linear dependence of the inverse dielectric permittivity in the vicinity of the Curie point and the fulfillment of the law of „two“: the ratio of the tangents of the angles of inverse dependences $1/\varepsilon$ as functions of temperature above and below Curie point (~ 2.4) differs hear by about two times.

Studies of switching characteristics of these structures identified significant changes if said parameters as compared to homogeneous barium titanate: for three-layer structures with barium titanate the coercive field $E_c = 392$ kV/cm was registered. Value of spontaneous polarization here is also large — about $P_s = 24\,\mu$C/cm^2 (Figure 3).

Three-layer structures with lead titanate, studied in present paper are laminar formations made of three consequently deposited layers of strontium titanate $SrTiO_3$, lead titanate $PbTiO_3$ and again strontium titanate $SrTiO_3$ on doped with Nb single-crystal substrate $SrTiO_3$ with underlayer of conductive oxide $La_{1/2}Sr_{1/2}CoO_3$ (LSCO) as bottom electrode and platinum top electrodes. Layer thickness of ferroelectric lead titanate $PbTiO_3$ in this structure is about 4 nm, and thickness of $SrTiO_3$ — 3.5 nm.

Results of study of temperature dependence of dielectric permittivity of said three-layer structures strontium titanate — lead titanate — strontium titanate $SrTiO_3/PbTiO_3/SrTiO_3$ show presence of maximum of said dependence at temperature about 544°C.

Above said temperature the dielectric permittivity in this structure follows the Curie–Weiss law with Curie constant

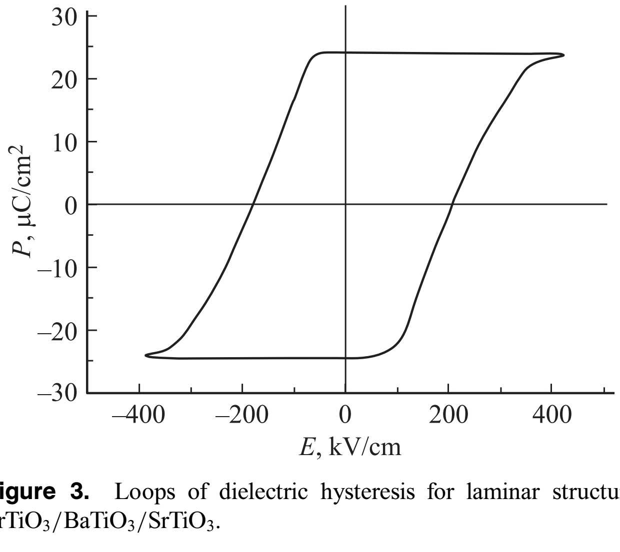

Figure 3. Loops of dielectric hysteresis for laminar structure $SrTiO_3/BaTiO_3/SrTiO_3$.

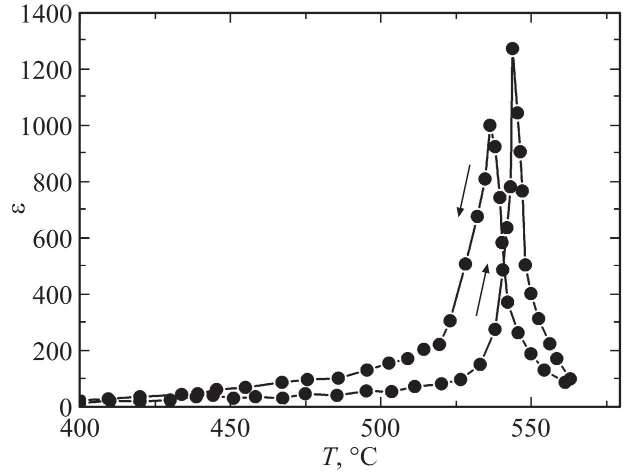

Figure 4. Dielectric permittivity vs. temperature for laminar structure $SrTiO_3/PbTiO_3/SrTiO_3$, subjected to heating and further cooling. Amplitude and frequency of measuring field are 100 mV and 1 kHz respectively.

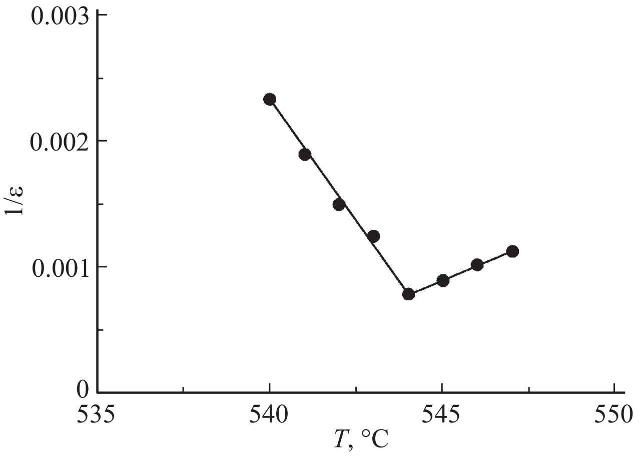

Figure 5. Reverse dielectric permittivity vs. temperature near phase transition temperature (Curie–Weiss law) for laminar structure $SrTiO_3/PbTiO_3/SrTiO_3$.

$C = 4.7 \cdot 10^4$ K and Curie–Weiss temperature 530°C. Besides, during heating and cooling of these structures the temperature hysteresis of Curie point near 15°C (Figure 4) is observed, this together with values of Curie constant indicates the phase transition of first kind in this structure.

The observed ratio of inclinations of dependence of reverse dielectric permittivity on temperature (Figure 5) above and under Curie temperature is about 4.5, i. e. is close to four, this also confirms that the phase transition in studied laminar structure relates to the first kind.

Layers of strontium titanate are initially supposed to be dielectrics, so it is difficult to expect their electrical effect on materials of the ferroelectric layers. At same time the mechanical effect due to parameters difference of mating structures are obvious. Presumably, they can be accounted during thermodynamic consideration.

3. Theoretical description of behavior features of ferroelectric multilayer structures

It is natural to ensure theoretical description of mechanical stresses effect on the phase transitions in considered structures on the basis of thermodynamic potential of materials with perovskite structure. The thermodynamic potential of such compositions, taking into account the mechanical stresses acting on the material, has the form [14,15]:

$$\begin{aligned} G &= a_1(P_1^2+P_2^2) + a_3P_3^2 + a_{11}(P_1^4+P_2^4) + a_{33}P_3^4 \\ &+ a_{13}(P_1^2P_3^2+P_2^2P_3^2) + a_{12}P_1^2P_2^2 + a_{111}(P_1^6+P_2^6+P_3^6) \\ &+ a_{112}\left[P_1^4(P_2^2+P_3^2) + P_3^4(P_1^2+P_2^2) + P_2^4(P_1^2+P_3^2)\right] \\ &+ a_{123}P_1^2P_2^2P_3^2 + \frac{u_m^2}{s_{11}+s_{12}}; \end{aligned} \qquad (1)$$

Here

$$a_1^* = a_1 - u_m\frac{Q_{11}+Q_{12}}{s_{11}+s_{12}}, \quad a_3 = a_1 - u_m\frac{2Q_{12}}{s_{11}+s_{12}},$$

$$a_{11}^* = a_{11} + \frac{1}{2}\,\frac{1}{s_{11}^2+s_{12}^2}\left[(Q_{11}^2+Q_{12}^2)s_{11} - 2Q_{11}Q_{12}s_{12}\right],$$

$$a_{33} = a_{11} + \frac{Q_{12}^2}{s_{11}+s_{12}},$$

$$a_{12}^* = a_{12} - \frac{1}{s_{11}^2-s_{12}^2}\left[(Q_{11}^2+Q_{12}^2)s_{12} - 2Q_{11}Q_{12}s_{11}\right] + \frac{Q_{44}^2}{2s_{44}},$$

$$a_{13} = a_{12} + \frac{Q_{12}(Q_{11}+Q_{12})}{s_{11}+s_{12}}. \qquad (2)$$

In recorded expressions a^* — coefficients of the thermodynamic potential decompositions renormalized taking into account the elastic effects, P_i — components of spontaneous polarization vector, Q_{11} and Q_{12} — striction coefficients, s_{ij} — components of elastic compliance tensor, u_m — incompatibility strain of lattice layers.

Stability loss of structures, described by this thermodynamic potential, is determined by conversion to zero of coefficients at quadratic polynomial terms (1). It is obvious that due to size difference of lattice cells the layers of barium titanate in the considered structures are under compression conditions, and of strontium titanate — under extension conditions in plate plane. In this case for it (at electrostrictive constant qualitatively unchanged with regard to signs) the relative incompatibility strain is negative: $u_\mathrm{m} < 0$. Expansion coefficients at polarization components in contact plane P_1 and P_2 are positive, but coefficient at quadratic term of expansion in polarizations at P_3 change sign, and, consequently, the polarization occurs perpendicular to contact surface of layers of multilayer structure. This is confirmed also by evaluations made based on the registered potential.

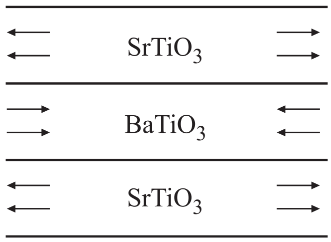

Figure 6. Directions of deformations in layers of barium titanate and strontium titanate of three-layer structure $SrTiO_3/BaTiO_3/SrTiO_3$.

Let's evaluate the temperature of stability loss of structures described by thermodynamic potential (1). In our structures for layers of barium titanate $Q_{11} > 0$, $Q_{12} < 0$, at that $Q_{11} > -Q_{12}$. In free state dimensions of lattice cells comprising this multilayer structure of single-crystal films are 3.992 Å for barium titanate and 3.904 Å for strontium titanate. In this case the barium titanate layer is characterised by negative incompatibility strain (relative difference of cell dimensions) $u_m = 0.025 < 0$ (Figure 6).

So, associated with mechanical deformations addition to renormalized coefficient a_3 for compression strains $u_m < 0$ for the layer of barium titanate leads to increase in temperature of stability loss of paraelectric phase with respect to polarization $P_3 = 0$. As a result of action of said strains in layers of the barium titanate of considered multilayer structures the vector of spontaneous polarization occurs perpendicular to layers plane.

The obtained changes in coefficients at quadratic terms of polynome (1) ensure evaluation of caused by them offsets of Curie point of considered three-layer structure relative to T_C homogeneous infinite barium titanate.

From (1) and (2) we can see that said offset is described by expression

$$T_C = T_0 + \frac{(Q_{11} + Q_{12})u_m}{a_0(s_{11} + s_{12})}, \tag{3}$$

where $a_0 = 4\pi/C = \partial a_1/\partial T$ — derivative of coefficient at quadratic term in expansion (1) in polarization in plain of lattice layers in temperature for layer of barium titanate, C — Curie–Weiss constant. Substituting in (3) $Q_{11} = 0.7 \cdot 10^{-12}$, $Q_{12} = -0.2 \cdot 10^{-12}$, of incompatibility strain $u_m = 0.025$ calculated based on known dimensions of lattice cells, Curie–Weiss constant for barium titanate equal to $1.2 \cdot 10^5$ K, $s_{11} = 8.3 \cdot 10^{-13}$, $s_{12} = -2.78 \cdot 10^{-13}$ (all in el. stat. units), we obtain positive offset of Curie point, equal to about 200°C, retaining the polar state in the considered multilayer structure at high temperatures. Thus, mechanical stresses occurred due to difference of parameters of layers of considered three-layer structure actually act as some internal bias field.

During analysis of dielectric properties of the laminar structures with lead titanate we pay attention to the fact that in these three-layer structures we observe practical equality of parameter $a = 3.904$ Å of crystal cell of tetragonal $PbTiO_3$ with parameter $a = 3.905$ Å strontium titanate, in contact with layer of lead titanate. This explains minimum effect of strontium titanate layer on dielectric properties of lead titanate layer in three-layer structure, including basic characteristic inherent to individual single-crystal of lead titanate, such as first kind of phase transition into ferroelectric state, practical absence of Curie point offset in considered three-layer structure with temperature as compared to thin film lead titanate, etc.

So, behavior of three-layer structure with lead titanate in its basic dielectric characteristics coincide with behavior of lead titanate. Together with behavior of multilayer structure with barium titanate (large offset of the Curie point for three-layer structure with barium titanate and its absence in multilayer structure with lead itanate) confirms the importance of mechanical deformations in control the position of Curie point, and thus does not require separate review under study in this paper.

4. Conclusion

By our opinion, the key factor of changing progress of phase transformations in considered ferroelectric multilayer structures is mechanical strains varying structure of individual layers, they occur in them due to difference in dimensions of lattice cells comprising the crystal layers. Said effect changes not only size of interval where flowing ferroelectric properties of multilayer structures occur, but also their basic characteristics including kind o phase transition.

Associated mechanical stresses cause not only quantitative changes of structural state of ferroelectric layer in the multilayer structure (in particular, in layer of barium titanate), but also radical change (phase transition) in multilyer structure.

Together with change of the dielectric response, the mechanical deformations occurred in layer of three-layer structures with barium titanate, due to difference of dimensions of lattice cells comprising their crystal layers, significantly (by several hundreds of degrees) extend into the region of high temperatures the temperature range of polar state existence in them. Upon absence of structural differences of mated layers of multilayer structures in form of difference of dimensions of lattice cells (example is structures with lead titanate) no significant change of temperature of phase transition into the ferroelectric state occurs as compared to behavior of single-component ferroelectric films.

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Conflict of interest

The authors declare that they have no conflict of interest.

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