RESEARCH ARTICLE

Influence of misfit stresses on the dielectric permeability of ferroelectric superlattices BaTiO$_3$/BaZrO$_3$

Boris M. Darinskii$^a$, Alexander S. Sidorkin$^a$ and Alexander S. Sigov$^b$

$^a$Voronezh State University, Voronezh, Russian Federation; $^b$Moscow Technological University (MIREA), Moscow, Russian Federation

ABSTRACT
The mechanisms of increasing the dielectric response of the BaTiO$_3$/BaZrO$_3$ ferroelectric superlattices in comparison with the characteristics of the bulk materials of the lattice are discussed. It is assumed that changes in the dielectric response in superlattices are caused by mechanical stresses arising in layers of the superlattice due to the mismatch of the sizes of the unit cells that make up the lattice of single-crystal layers. These stresses lead to the formation of longitudinal polarization in the layers of barium titanate and to the related contribution of the transverse component of the dielectric tensor to the effective permeability of the superlattice in the direction normal to the plane of the layers. The misfit stresses cause the appearance of a ferroelectric phase transition in the barium zirconate the lattice layers with an increase in the dielectric constant of these layers in the direction normal to the plane of the lattice layers.

Highlights: Mismatch stresses in ferroelectric superlattices

1. Introduction
Currently, ferroelectric materials are widely used in microelectronics, micromechanics and other applications [1–9]. In the case of using homogeneous crystalline or ceramic materials in working devices, the elemental composition, crystal structure (mono- or polycrystalline), device geometry, for example, the thickness of the films of the used composition and the material of the electrodes, are usually changed to change the characteristics of the materials used in the desired direction. Multilayer working materials [10,11] have a wider list of parameters controlling their characteristics. The characteristics of such structures used in practice can change significantly as a result of the strong mutual influence of individual layers of a multilayer system. This is achieved by changing, for example, the thickness of the homogeneous layers that make up the multilayer structure, using various combinations of the composition of two or more crystalline phases, changing the ratios between the fractions of each of them, etc.

The nature of the influence of the layers of a multilayer material on each other, providing the possibility of changing its properties in the practically necessary direction, is based on the possibility of varying the properties of this material by
changing the long-range elastic or electric fields acting in such structures, as well as short-range chemical interactions of the components contacting in such structures [12–14]. Among the indicated factors, the influence of elastic deformations for obtaining the required characteristics of multilayer materials is currently used, apparently, most often.

As a rule, elastically deformed multilayer heterostructures or superlattices are used in the absence of mechanical stresses acting along the normal to the contact planes of their constituent layers, and, conversely, undergoing compression-tension deformations along these surfaces. The characteristics of multilayer heterostructures depend on the degree of the elastically deformed state of the superlattices, the value of which can be varied by choosing the ratio between the periods of the atomic structure of individual layers of the superlattice with each other and with the substrate. A variation of this choice is most convenient for materials of superlattice layers with a related structure. First of all, such a variation can be carried out for materials with a perovskite structure, for which a large amount of experimental and practically important material has been accumulated.

2. Object of research

The present work is devoted to assessing the influence of mechanical stresses of mismatch of unit cells of layers on the magnitude of the change in the dielectric constant in ferroelectric superlattices of barium titanate/barium zirconate in comparison with the dielectric characteristics of their constituent components in a homogeneous state.

The influence of misfit stresses on the polarization of barium titanate/barium zirconate superlattices caused by differences in the size of elementary cells of the connected layers were studied in [15]. The studies of the dielectric response of this superlattice (Figure 1a,b) was carried out in [16]. Experimental studies of the temperature dependence of the dielectric constant of barium titanate/barium zirconate superlattices (Figure 1a) show the presence in them of a maximum corresponding to a ferroelectric phase transition at temperatures of ~393°C [16] significantly exceeding the transition temperature for bulk (120°C) and film barium titanate samples. Thus, a huge excess of the transition temperature to a ferroelectric state compared to one of the parent materials - the titanate of barium. I.e., there is a huge exceeding of the transition temperature to a ferroelectric state compared to one of the parent materials - the titanate of barium. The dielectric constant for the superlattice under study reaches a maximum of about 11 thousand units.

It is also easy to see that the values of the dielectric constant actually observed in the considered superlattice differ significantly from its value obtained by determining the effective dielectric constant of layered structures by the formula

\[ \frac{1}{\varepsilon_{\text{eff}}} = c_1/\varepsilon_1 + c_2/\varepsilon_2, \]

where \( \varepsilon_1, \varepsilon_2 \) are the dielectric constants of the components of the lattice, measured along the normal to the plane of the superlattice, \( c_1, c_2 \) are the fractions of the volume occupied by layers of different materials in the superlattice.

Indeed, for bulk crystals of barium titanate, the longitudinal component of the permittivity is approximately 150, and the transverse component is 4000 [17]. Similar measurements for individual barium zirconate [18], which in the free state is not ferroelectric at all, show that the dielectric constant of bulk samples of this material lies in the range 8–55. Substitution of the indicated individual

![Figure 1. (a,b). Temperature dependence of the dielectric constant and the dielectric loss tangent of the BaZrO3/BaTiO3 ferroelectric superlattice [16].](image)
contributes to the effective dielectric constant \((1)\) of the \(\text{BaTiO}_3/\text{BaZrO}_3\) superlattice shows that the use of their values obtained for isolated layers that do not interact with neighboring layers cannot explain the experimentally observed effective dielectric constant \(\varepsilon_{\text{eff}}\) of the superlattice.

The results of measurements of the tangent of the dielectric loss angle, which characterizes the relaxation processes occurring when an alternating electric field is applied perpendicular to the plane of the superlattice, are shown in Figure 1b. They show that the main feature of the temperature dependence of \(\tan \delta\) is a step that appears at a temperature close to the temperature of the peak of the dielectric permittivity and continues into the region of relatively low temperatures [16].

Such a temperature dependence of \(\tan \delta\) cannot be associated only with the phase transition from the para- to the homogeneous ferroelectric phase, since in this case a sharp loss peak should be observed only in the vicinity of \(T_c\). The presence in our case of dielectric losses below \(T_c\) obviously indicates the presence of dissipative processes in this region as well.

The nature of these losses is indicated by the study of switching processes in the investigated superlattice using the Merz method [19], which revealed the activation character of switching in it. According to estimates [19], this type of switching can be associated only with the presence of a domain structure [20], which requires an order of magnitude smaller field compared to switching material as a whole.

3. Theoretical description of the influence of mechanical stresses on the increase in the dielectric constant of ferroelectric superlattices

3.1. Stabilization of the longitudinal direction of polarization in barium titanate layers by mechanical stresses associated with the difference in the sizes of the unit cells of the contacting layers

Theoretical description of the influence and contribution of interacting layers of the considered superlattice to its characteristics as a whole is natural to execute on the basis of an analysis of the thermodynamic potential of materials with a perovskite structure. The thermodynamic potential of single-crystal single-domain materials of this type, taking into account the mechanical stresses acting on the material, has the form [21,22]:

\[
G = a_1^*\left(P_1^2 + P_2^2\right) + a_2^*P_3^2 + a_3^*\left(P_1^2 + P_2^2\right) + a_4^*\left(P_1^2 + P_2^2\right) + a_5^*\left(P_1^2 + P_2^2\right) + a_6^*\left(P_1^2 + P_2^2\right) + a_7^*\left(P_1^2 + P_2^2\right) + a_8^*\left(P_1^2 + P_2^2\right) + a_9^*\left(P_1^2 + P_2^2\right) + a_{10}^*\left(P_1^2 + P_2^2\right)
\]

\(a_1^* = a_1 - u_m\frac{Q_{11} + Q_{12}}{s_{11} + s_{12}}, a_2^* = a_1 - u_m\frac{2Q_{12}}{s_{11} + s_{12}}, a_3^* = a_1 - u_m\frac{Q_{12}}{s_{11} + s_{12}}, a_4^* = a_1 - u_m\frac{Q_{11}}{s_{11} + s_{12}}, a_5^* = a_1 - u_m\frac{Q_{12}}{s_{11} + s_{12}}, a_6^* = a_1 - u_m\frac{Q_{11}}{s_{11} + s_{12}}, a_7^* = a_1 - u_m\frac{Q_{12}}{s_{11} + s_{12}}, a_8^* = a_1 - u_m\frac{Q_{11}}{s_{11} + s_{12}}, a_9^* = a_1 - u_m\frac{Q_{12}}{s_{11} + s_{12}}, a_{10}^* = a_1 - u_m\frac{Q_{11}}{s_{11} + s_{12}}\)

\(a_1 = a_{12} - \frac{1}{s_{12}}\left[Q_{11} + 2Q_{12}s_{12} - 2Q_{12}Q_{11}s_{12}\right] + \frac{Q_{14}^2}{2s_{12}}, a_{13} = a_{12} + \frac{Q_{12}(Q_{11} + Q_{12})}{s_{11} + s_{12}}\)

In the written expressions (2) and (3), \(a^*\) are the expansion coefficients of the thermodynamic potential renormalized taking into account elastic effects, \(P_i\) are the components of the spontaneous polarization vector, \(Q_{ij}\) and \(Q_{ij}\) are the strict coefficients, \(s_{ij}\) are the components of the elastic compliance tensor, \(u_m = u_1 = u_2\) - deformation of the lattice layers mismatch.

The loss of stability of structures described by a given thermodynamic potential is determined by the vanishing of the coefficients at the quadratic terms of polynomial (2). For barium titanate layers \(Q_{11} > 0, Q_{12} < 0,\) while \(Q_{11} > -Q_{12}.\) In the free state, the sizes of the unit cells of the monocrystalline films composing the superlattice are 4.011 Å for barium titanate and 4.233 Å for barium zirconate. The barium titanate layer is characterized by misfit deformation (relative difference in cell sizes) \(u_m = 0.0539 > 0\) (Figure 2). Therefore, the addition to the renormalized coefficient \(a_1\) for tensile deformations \(u_m > 0\) for barium titanate, associated with mechanical deformations, leads to an increase in the temperature of the loss of stability of the paraelectric phase relative to the polarizations \(P_1 = P_2\) and \(P_3 = 0.\) As a result of the action of the indicated deformations in the barium titanate layers of the considered superlattices, a vector of spontaneous polarization arises in the plane of the layers.

As noted above, in barium titanate crystals, the permittivity along the polar axis is much lower than the permittivity in the perpendicular direction. Since, due to mechanical deformations in the superlattices under consideration, the polar axis of the barium titanate layer is parallel to the surface of the superlattice layers, the dielectric constant of the stretched barium titanate layer along the normal in the superlattice planes is determined by the transverse component of the dielectric constant tensor. This component is more than an order of magnitude larger than the longitudinal component; therefore, it can be assumed that the replacement of the longitudinal component of the dielectric constant by the transverse one in the barium titanate layer caused by the action of mechanical stresses is one of
the mechanisms for increasing the effective dielectric constant of the superlattice.

3.2. The emergence of a mechanical stress-induced ferroelectric phase transition in a layer of barium zirconate

Another mechanism for increasing the dielectric constant of the superlattice is the processes occurring in the layers of barium zirconate. The action of mechanical deformations on it, as in the case of barium titanate, is described by decomposition (2). In this case, taking into account their sign, under the action of the indicated deformations, qualitatively different changes occur in barium zirconate. As can be seen from Figure 2, the layers of barium zirconate in the superlattice are under conditions of elastic longitudinal compression in the plane of the plate. In this case \( u_m < 0 \) (with the electrostriction coefficients not qualitatively changing in terms of signs), therefore the expansion coefficient at \( P_1 \) and \( P_3 \) remains positive and, on the contrary, the coefficient at the quadratic term of the polarization expansion at \( P_2 \) changes its sign. Thus, the action of the indicated (compressive for barium zirconate) deformations causes the appearance of polarization in it along the normal to the plane of the superlattice layers, which naturally leads to the appearance of a large dielectric response of barium zirconate along this direction.

The onset of a phase transition to the ferroelectric phase in deformed barium zirconate has also been demonstrated by other calculations. It was indeed shown with the help of ab initio calculations in [23,24] that the action of mechanical compression leads to the loss of stability of the initial unstressed phase for barium zirconate. In particular, according to [23–25], with an increase in the uniform pressure in these crystals, a phase transition occurs from the cubic phase to the tetragonal phase at a pressure of 17.2 GPa. Under conditions of compression in the plane of the plate and the absence of normal stress perpendicular to the plane of the plate, Poisson expansion of the crystal occurs in this direction. At sufficiently high mechanical stresses, this effect along with the rotation of the oxygen octahedra ZrO\(_6\) around a normal to the plane of the layers can lead to the loss of stability of the zirconium ion in the symmetric position of the cell of the crystal lattice of barium zirconate and to its displacement in the normal direction.

Changes in the structure of the barium zirconate layers, stimulated by the phase transformation, naturally lead to an increase in their permittivity in accordance with its relationship with the coefficients at the quadratic terms of the polynomial (2)

\[
4\pi/(\varepsilon_2 - 1) = a^s_3,
\]

and specific expressions \(a^s_3\).

In addition to changes associated with deformation contributions to the dielectric response of the superlattice, changes in the coefficients at the quadratic terms of polynomial (2) stimulated by mechanical deformations make it possible to estimate the induced displacements of the Curie point of the superlattice under consideration relative to \( T_c \) of homogeneous infinite barium titanate.

From (3) it is easy to see that the indicated displacement is described by the formula:

\[
T_C = T_0 + \frac{(Q_{11} + Q_{12})u_m}{a_0(s_{11} + s_{12})},
\]

where \( a_0 = 4\pi/C = \partial a_1/\partial T \) is derivative of the coefficient at the quadratic term in expansion (2) in polarization in the plane of the lattice layers in temperature for the barium titanate layer, \( C \) is the Curie-Weiss constant. Substituting in (5) \( Q_{11} = 0.7 \times 10^{-12}, Q_{12} = -0.2 \times 10^{-12}, u_m = 0.057 \), the Curie-Weiss constant for barium titanate, equal to 1.2 \( \times 10^5 \) K, \( s_{11} = 8.3 \times 10^{-13}, s_{12} = -2.78 \times 10^{-13} \) (all in electronic stat. units), we get a positive shift of Curie melancholy equal to several hundred degrees, which retards the polar state at high temperatures. Thus, the mechanical stresses arising from the mismatch of the lattice parameters of adjacent layers act as a certain internal displacement field.

4. Conclusion

In conclusion, let us summarize the ideas expressed about the possible mechanisms for increasing the dielectric response in ferroelectric gratings of the type under consideration. In our opinion, the key factor in the increase in the dielectric constant of the considered perovskite-like ferroelectric superlattices is mechanical deformations that change the structure of individual superlattice layers, arising in them due to
the difference in the sizes of unit cells that make up the lattice of crystal layers. A sufficiently large deformation associated with this can lead not only to a quantitative change in the structural state of the barium titanate layer, but also to a radical change (phase transition) in the barium zirconate layer, leading to an increase in the dielectric response of individual layers and the superlattice as a whole.

The indicated elastic deformations in the BaTiO$_3$/BaZrO$_3$ ferroelectric superlattice lead to stabilization of the longitudinal (along the surface of the contacting lattice layers) direction of the spontaneous polarization vector in the barium titanate layers. The indicated direction of polarization provides the contribution of the transverse component of the dielectric permittivity tensor of barium titanate to the effective permittivity of the superlattice in the direction normal to its layers, which significantly exceeds the longitudinal (along the direction of polarization) component of the dielectric response of free barium titanate.

Another significant contribution to the effective permittivity of the BaTiO$_3$/BaZrO$_3$ superlattice is the mechanical stress-induced transition of the non-ferroelectric barium zirconate layers in the superlattice to the polar ferroelectric state, and the contribution of the crystalline component of this material to the total dielectric constant of the superlattice associated with softening near the phase transition.

Far from the point of the ferroelectric phase transition, the domain structure of the material makes a significant contribution to the dielectric constant of the studied lattice through a change in polarization due to the movement of domain walls, which is indicated by the presence of a plateau in the temperature dependence of $\tan \delta$.

In the barium zirconate layers, the polarization direction is oriented perpendicular to the plane of the superlattice layers. Consequently, their contribution to the polarization-reversal processes is provided by the usual motion of domain walls perpendicular to the polarization vector.

In a strained barium titanate layer existing in the lattice, the polarization vector, in contrast to the polarization direction in barium zirconate, lies in the plane of the layer. To ensure a smooth rotation of polarization at the boundaries between these layers with perpendicular directions of polarization, a stepwise rotation of polarization occurs. This rotation creates an interface similar to the observed distribution of polarization near the surface of ferroelectric films using TEM microscopy [26]. This turning layer also obviously involved in polarization reversal. While in a typical situation, the width of this layer is less than the thicknesses of individual layers of the superlattice; therefore, its presence cannot radically change the above effects.

Along with the dielectric response, deformations arising in the layers of the BaTiO$_3$/BaZrO$_3$ ferroelectric superlattice due to the difference in the sizes of the unit cells of their constituent crystalline layers, significantly (by several hundred degrees) extend the temperature interval for the existence of a polar state in them.

**Disclosure statement**

The authors declare no conflict of interest.

**Funding**

The work was supported by Russian Science Foundation (project no. 17-72-20105).

**Notes on contributors**

*Boris M. Darinskii*, Doctor of Phys.-Math. sciences, professor, founder and head of the scientific and pedagogical school in the field of condensed matter physics ‘Relaxation phenomena in condensed matter’. The main scientific results are: theoretical concepts of the physical mechanisms of relaxation phenomena in crystalline and amorphous materials, an atomic model of intercrystalline and interphase boundaries of a general type, a physical model of relaxation phenomena in a highly nonequilibrium state of matter, patterns of wave propagation in crystals, classification and specific features of possible structural phase transitions in crystals.

*Alexander S. Sidorkin*, Doctor of Physical and Mathematical Sciences, Professor, Author of three monographs, member of the RAS Scientific Council on the physics of ferroelectrics and dielectrics, member of the European Physical Society. Main research interests lie in the physics of phase transformations and critical phenomena, physics of nonlinear polar dielectrics (ferroelectrics) and multiferroics, physics of nanoscale materials and structures, physics of emission phenomena in solids, etc. As a visiting researcher he worked at J. Vern, University of Nimes (France), etc., took part in numerous Russian and international conferences, seminars, symposia.

*Alexander S. Sigov*, President of the Russian Technological University (MIREA), Academician of the Russian Academy of Sciences. Specialist in the field of solid state physics, solid-state electronics and physical materials science. The field of scientific activity is the study of the physical properties of systems with a reduced dimension and/or structural disorder and the creation on their basis of functional devices of nano- and microelectronics. A.S.Sigov - Honored Scientist of the Russian Federation, laureate of the State Prize of the Russian Federation, the Prize of the Government of the Russian Federation in the field of education and two prizes of the Government of the Russian Federation in the field of science and technology; Chairman of the Scientific Council of the Russian Academy of Sciences on the physics of ferroelectrics and dielectrics, a member of the European Physical Society. Editor-in-chief of the scientific journals ‘Electronics’, ‘Nanomaterials and nanostructures’, deputy editor-in-chief of the journal ‘Integrated Ferroelectrics’. 
References

1. Li F, Lin D, Chen Z, et al. Ultra high piezoelectricity in ferroelectric ceramics by design. Nat Mater. 2018;17(4):349–354.
2. Zheng Y, Cai MQ, Woo CH. Critical properties of symmetric nanoscale metal-ferroelectric-metal capacitors. Acta Mater. 2010;58(8):3050–3058.
3. Scholm DG, Chen L-Q, Eom C-B, et al. Strain tuning of ferroelectric thin films. Annu Rev Mater Res. 2007;37(1):589–626.
4. Sharma P, Zhang Q, Sando D, et al. Nonvolatile ferroelectric domain wall memory. Sci Adv. 2017;3(6):e1700512.
5. Scott JF. Electrocaloric materials. Annu Rev Mater Res. 2011;41(1):229–240.
6. Wu HH, Cohen RE. Electric-field-induced phase transition and electrocaloric effect in PMN-PT. Phys. Rev. 2017; B 96:054116.
7. Ma RJ, et al. Nonvolatile ferroelectric domain wall memory. Science. 2017; 357:130–134.
8. Catalan G, Seidel J, Ramesh R, et al. Domain wall nanoelectronics. Rev Mod Phys. 2012;84(1):119–156.
9. Shaw TM, Trolier-Mckinstry S, McIntyre PC. The properties of ferroelectric films at small dimensions. Annu Rev Mater Sci. 2000;30(1):263–298.
10. Dawber M, Rabe K, Scott J. Physics of thin-film ferroelectric oxides. Rev Mod Phys. 2005;77(4):1083–1130.
11. Rajnders G, Blank DH. Materials science: Build your own superlattice. Nature. 2005;433(7024):369–370.
12. Shen J, Yu-Qiang M. Long-range coupling interactions in ferroelectric superlattices. Phys. Rev. 2000; B61:14279.
13. Kok-Geng L, Khian-Hooi C, Lye-Hock O, et al. Recent advances in application of Landau-Ginzburg theory for ferroelectric superlattices. SSP. 2015;232:169–195.
14. Sepliarsky M, Phillpot S, Wolf D, et al. Long-ranged ferroelectric interactions in perovskite superlattices. Phys Rev. 2001;B64:060101.
15. Marssi ME, Gagou Y, Belhadi J, et al. Ferroelectric BaTiO3/BaZrO3 superlattices: X-ray diffraction, raman spectroscopy, and polarization hysteresis loops. J Appl Phys. 2010;108(8):084104.
16. Sidorkin A, Nesterenko L, Gagou Y, et al. Dielectric properties and switching processes of barium titanate–barium zirconate ferroelectric superlattices. Materials. 2018; 11:1436.
17. Iona F, Shirane D. Segnetoelektricheskie kristally (ferroelectric crystals). In: Shuvalov LA, editor. Moscow: Mir; 1965.
18. Azad A-M, Subramaniam S. Temperature dependence of the dielectric response of BaZrO3 by impedance spectroscopy. Mater Res Bull. 2002;37(1):11–21.
19. Sidorkin AS, Nesterenko LP, Gagou Y, et al. Repolarization of ferroelectric superlattices BaZrO3/ BaTiO3. Sci Rep. 2019;9(1):18948.
20. Darinsky BM, Lazarev AP, Sidorkin AS. Domain structure formation in ferroelectric films with free charge carriers. Crystalllogr Rep. 1991;36:757–758.
21. Pertsev NA, Koukhar VG. Polarization instability in polydomain ferroelectric epitaxial thin films and the formation of heterophase structures. Phys Rev Lett. 2000;84(16):3722–3725.
22. Koukhar VG, Pertsev NA, Waser R. Thermodynamic theory of epitaxial ferroelectric thin films with dense domain structures. Phys Rev. 2001; B64:214103.
23. Lebedev AI. Ground state and properties of ferroelectric superlattices based on crystals of the perovskite family. Phys Solid State. 2010;52(7):1448–1364.
24. Zhang Y, Liu M, Wang J, et al. Strain tunable ferroelectric and dielectric properties of BaZrO3. J. Appl. Phys. 2014;115(22):224107.
25. Yang X, Wang Y, Song Q, et al. Pressure effects on structural, electronic, elastic, and optical properties of cubic and tetragonal phases of BaZrO3. Acta Phys Polon. 2018; A133, 5:1138–1143.
26. Nelson CT, Winchester B, Zhang Y, et al. Spontaneous vortex nanodomain arrays at ferroelectric heterointerfaces. Nano Lett. 2011;11(2):828–834.