Piezoelectric properties of ferroelectric perovskite superlattices with polar discontinuity

Alexander I. Lebedev

Physics Department, Moscow State University, 119991 Moscow, Russia
(Dated: December 17, 2020)

The stability of a high-symmetry $P4mm$ polar phase in seventeen short-period ferroelectric perovskite superlattices with polar discontinuity is studied from first principles within the density-functional theory. It is shown that in most superlattices this phase exhibits either the ferroelectric instability or the antiferrodistortive one, or both of them. For each superlattice, the ground-state structure, the structure of possible metastable phases, the spontaneous polarization, and piezoelectric properties are calculated. The properties of superlattices with the polar discontinuity are compared with those of superlattices with broken symmetry and of ordinary superlattices, which have no the polar discontinuity. It is shown that high piezoelectric coefficients (up to 150–270 pC/N) in some superlattices with the polar discontinuity are due to the appearance of strong lattice distortions, whose symmetry follows that of a low-lying polar phonon mode of the ground-state structure, under the influence of external strain.

DOI: 10.1016/j.commatsci.2020.110113

Keywords: ferroelectric superlattices, piezoelectricity, phase transitions, polar discontinuity, perovskites

I. INTRODUCTION

In recent years, much attention has been paid to studies of low-dimensional structures in which new physical phenomena that have no analogues in bulk materials have been discovered. Due to these new functional properties, these materials are considered as very promising for their use in electronics. Ferroelectric superlattices (SLs)—quasi-two-dimensional artificial periodic structures whose properties can be tailored to obtain the necessary functionality—belong to this interesting class of materials.

Most of the earlier experimental [1–23] and theoretical [24–48] studies of ferroelectric superlattices with the perovskite structure were performed on II-IV/II-IV or I-V/I-V type superlattices (here, the numbers indicate the valence of atoms entering the A and B sites of the ABO$_3$ perovskite structure). In such superlattices, there are no double electric layers at the interface between two dielectric materials, and therefore both the bulk and interfaces of these superlattices remain macroscopically electrically neutral.

Studies of the SrTiO$_3$/LaAlO$_3$ heterostructures have revealed new interesting phenomena that appear in these structures as a result of so-called polar discontinuity—of a polarization jump induced by effective $\pm e/2$ charges per unit cell which appear at the interface between SrTiO$_3$ and LaAlO$_3$ because the charged character of LaO$^+$ and AlO$_2^-$ layers [49]. These phenomena include the appearance of a conducting layer near the interface (a two-dimensional electron gas), its magnetism, and even superconductivity [49–51]. These phenomena can be controlled using an external electric field [52]. The divergence of the electrostatic potential in such heterostructures, which can result in the appearance of conductive layers at the interface between two dielectrics, is called a polar catastrophe. The possibility of the appearance of the two-dimensional electron gas at the interface between a ferroelectric and a nonpolar dielectric in perovskites was systematically studied in [53]. Later it was realized that conductive layers can also be obtained in ferroelectric structures without the polar discontinuity [54]. This made it possible to create new types of electronic devices—ferroelectric structures with switchable giant tunneling conductivity [55–56]; the idea of such devices was proposed earlier in [57, 58]. Note that the appearance of similar phenomena can also be anticipated in epitaxial films of II-IV and I-V perovskites, which are grown on DyScO$_3$, GdScO$_3$, NdScO$_3$, NdGaO$_3$, and LaGaO$_3$ substrates to create a biaxial strain in them, since the polar discontinuity is possible in these structures [59].

Until now, theoretical studies of superlattices with the polar discontinuity have focused on studying the distribution of polarization and electric field in these structures and on finding the conditions for the appearance of a two-dimensional electron gas at the interface [50–70]. The questions of the stability of the high-symmetry polar structure in such SLs, possible phase transitions in them, and the physical properties of low-symmetry phases were not analyzed. At the same time, the ferroelectric and antiferrodistortive (AFD) instabilities characteristic of many perovskites can result in strong distortions of the structure of SLs. This means that the earlier predictions of their physical properties obtained without taking these distortions into account may be incorrect.

One of the questions that remains insufficiently studied is the question about the piezoelectric properties of superlattices with the polar discontinuity. The calculations of these properties are limited to the calculations for the high-symmetry tetragonal $P4mm$ phase of such...
First-principles calculations were performed within the density functional theory using the ABINIT program and norm-conserving pseudopotentials constructed according to the RRKJ scheme in the local density approximation (LDA), like in \cite{77}. The cutoff energy was 30 Ha (816 eV) with the exception of Ta-containing systems in which it was 40 Ha (1088 eV). Integration over the Brillouin zone was carried out using a $8 \times 8 \times 4$ Monkhorst–Pack mesh for high-symmetry structures and meshes with equivalent density of k-points for low-symmetry phases. The equilibrium lattice parameters and atomic positions were calculated by relaxing forces acting on the atoms to values less than $2 \times 10^{-6}$ Ha/Bohr (0.1 meV/Å). The phonon spectra, the tensors of piezoelectric stress coefficients $e_{i\mu}$, and the elastic compliance tensors $S_{\mu\nu}$ were calculated using the density-functional perturbation theory. The $e_{i\mu}$ values were then converted to the piezoelectric strain coefficients $d_{i\mu}$ using the formula $d_{i\mu} = e_{i\mu}S_{\mu\nu}$, and for monoclinic structures the tensor components were transformed to the standard setting of the monoclinic unit cell, in which the polarization vector lies in the $xz$ plane.

\section{RESULTS AND DISCUSSION}

\subsection{Search for the ground-state structure}

It is known that the electrical conductivity of materials is usually a factor that prevents the practical use of their ferroelectric properties. Since the experiments on structures with the polar discontinuity often revealed metallic conductivity at the interface, it was necessary first to ensure that the superlattices under study are insulating. The calculations confirmed that in all superlattices studied in the work, the conduction band is separated from the valence band by a sufficiently large energy gap (see Table S1 in the Supplementary data), and therefore all studied SLs are dielectrics.

Since the layer sequence in considered superlattices does not admit the reversal of $z \to -z$ (Fig. 1), the superlattices are always polar and their high-symmetry phase is described by the $P4mm$ space group. However, this structure can exhibit various instabilities characteristic of crystals with the perovskite structure: either the ferroelectric instability or the antiferrodistortive one, or both of them simultaneously. In this work, the ground state of superlattices was searched in the traditional way. First, the structures resulting from the condensation of all unstable phonons found in the phonon spectrum of the $P4mm$ phase were calculated taking into account a possible degeneracy of phonon modes. Then, by calculating the phonon frequencies at all high-symmetry points of the Brillouin zone and the elastic tensor for these distorted structures, the stability of the obtained solutions was checked. In the case when an instability was found in any of these structures, the search for the ground state was continued until a structure whose phonon spectrum has no unstable modes and whose matrix composed of the elastic tensor components in the Voigt notation is positive definite is found. In this case, the conclusion that a
stable phase which can be a possible ground-state structure can be made. The problem here is that in chains of phases generated by different octahedra rotations, several stable phases can be found, as was recently demonstrated for SrTiO$_3$ [78]. In this case, the ground state is the stable phase with the lowest total energy; other stable phases should be considered as metastable. If the energy of such metastable solutions differs little from the energy of the ground state, then these solutions should be considered as phases that can be observed in experiment. For them, as well as for the ground state, an analysis of their physical properties should also be carried out.

Calculations of the phonon spectra show that in most studied superlattices with the polar discontinuity (except for BaTiO$_3$/LaAlO$_3$, SrTiO$_3$/LaAlO$_3$, PbTiO$_3$/KTaO$_3$, PbTiO$_3$/LaAlO$_3$, and KTaO$_3$/LaAlO$_3$) the high-symmetry $P4mm$ phase exhibits the ferroelectric instability with respect to the in-plane distortion of the structure or, in other words, to the inclination of the polarization vector. The phonon spectrum of one of such superlattices, KNbO$_3$/BaTiO$_3$, is shown in Fig. 2. It is seen that in addition to the instability at the Γ point, the instabilities also appear at the $X$, $R$, and $Z$ points of the Brillouin zone. We have already encountered a similar situation in KNbO$_3$/KTaO$_3$ [42] and BaTiO$_3$/BaZrO$_3$ [44] SLs.

An instability zone, which is observed as a band of imaginary phonon frequencies on the $\Gamma-Z-R-X-\Gamma$ line (imaginary frequencies are represented in the figure by negative values), is a consequence of the ferroelectric instability in the $\ldots$–Ti–O–$\ldots$ chains propagating in the plane of the SL—the so-called chain instability [79]. Indeed, an analysis of the eigenvectors of these modes shows that at all the above-mentioned points of the Brillouin zone the out-of-phase, transverse, $xy$-polarized displacements of Ti and O atoms in chains propagating in the [100] and [010] directions dominate in the atomic motion. In Ba(Sr)TiO$_3$/KNb(Ta)O$_3$ superlattices, the displacements of the Nb(Ta) atoms are small, whereas in superlattices containing no Ti atoms as well as in the PbTiO$_3$/KNbO$_3$ SL the chain instability is observed mainly in $\ldots$–Nb–O–$\ldots$ chains. In BiScO$_3$/LaAlO$_3$ and PbTiO$_3$/BiScO$_3$ superlattices, additional out-of-phase, $xy$-polarized displacements of Bi and oxygen atoms lying in the same $xy$ plane are stronger; this displacement pattern is characteristic of BiScO$_3$. A similar displacement pattern is also typical for unstable modes at the $Z$ point in these superlattices. At the $\Gamma$ point, the described displacement pattern corresponds to a doubly degenerate ferroelectric $E$ mode ($\Gamma_5$) [80].

Of two possible polar phases resulting from the condensation of the unstable ferroelectric $E$ mode,
TABLE I. Energies (per 10-atom supercell) of different low-symmetry phases resulting from the condensation of unstable phonons in the high-symmetry $P4nm$ phase of short-period KNbO$_3$/BaTiO$_3$ and KNbO$_3$/SrZrO$_3$ superlattices.

| Phase    | Unstable phonon | Energy (meV) | Phase    | Unstable phonon | Energy (meV) |
|----------|-----------------|--------------|----------|-----------------|--------------|
| $P4mm$   | —               | 0            | $P4mm$   | $Pm$            | $Z_5(\eta,0)$ | $\Gamma_5(\eta,0)$ | $-27.8$ |
| $Abm_2$  | $R_4$           | $-13.8$      | $Pm$     | $Z_5(\eta,\eta)$| $13.7$       |
| $Pma_2$  | $X_4$           | $-14.8$      | $Cm$     | $M_5(\eta,0)$  | $-39.4$      |
| $Pmc_2_1$| $Z_5(\eta,0)$  | $-21.3$      | $Pmc_2_1$| $M_5(\eta,\eta)$| $-40.2$      |

The $Cm$ phase with atomic displacements along the [110] direction has the lowest energy in all systems except for KNbO$_3$/LaAlO$_3$, PbTiO$_3$/LaGaO$_3$, and SrTiO$_3$/BiScO$_3$. The predominant [111] displacements correlate with the fact that at normal conditions, bulk BaTiO$_3$ and KNbO$_3$ are polarized along the [111] direction. The same polarization direction is also characteristic of BiScO$_3$ when the octahedral rotations are turned off. As an example, the energies of different low-symmetry phases for the KNbO$_3$/BaTiO$_3$ superlattice are given in Table I. It is seen that the structures obtained from the condensation of $Z_5$, $R_4$, and $X_4$ unstable phonons have a higher energy as compared to the energy of the $Cm$ phase. The lattice parameters and atomic positions in ground-state structures of this and other superlattices studied in this work are given in Tables S2–S26 of the Supplementary data.

The absence of the ferroelectric instability in the $P4mm$ phase of PbTiO$_3$/KTaO$_3$ and PbTiO$_3$/LaAlO$_3$ SLs can be explained by a tendency of bulk PbTiO$_3$ to be polarized along the [001] axis. This instability was also absent in SrTiO$_3$/LaAlO$_3$ and KTaO$_3$/LaAlO$_3$ superlattices, in which both constituents are nonpolar. In addition, the ferroelectric instability did not appear in the BaTiO$_3$/LaAlO$_3$ superlattice, in which its absence is a result of the strong (by 2.3%) in-plane compression of the BaTiO$_3$ layers. Our calculations of the influence of strain on the ground-state structure of BaTiO$_3$ showed that the biaxial compression of 1% is already sufficient for the $P4mm$ phase to become the most stable polar

FIG. 4. Phonon spectrum of the KNbO$_3$/SrZrO$_3$ superlattice (a) in the high-symmetry $P4mm$ phase and (b) in the ground-state $Pc$ phase. The numbers near the curves indicate the symmetry of unstable modes.
phase in this material, in agreement with \[S1\] \[S2\].

Along with the ferroelectric instability, in the high-symmetry \(P4mm\) phase of twelve superlattices with the polar discontinuity (except for \(\text{KNbO}_3/\text{PbTiO}_3\), \(\text{KNbO}_3/\text{BaTiO}_3\), \(\text{KNbO}_3/\text{BaZrO}_3\), \(\text{BaTiO}_3/\text{KTaO}_3\), and \(\text{KTaO}_3/\text{PbTiO}_3\)), an antiferrodistortive instability with octahedra rotations around the \(z\) axis is observed. This is clearly seen by the appearance of unstable phonons on the \(M-A\) line (Fig. 3). The appearance of the AFD instability in a superlattice clearly correlates with its existence in one or both components of the SL (\(\text{SrTiO}_3\), \(\text{SrZrO}_3\), \(\text{LaAlO}_3\), \(\text{BiScO}_3\)). A comparison of the energies of phases resulting from the condensation of phonons at \(M\) and \(A\) points of the Brillouin zone shows that of two phases resulting from the \(M\) phonon condensation (space group \(P4bm\)) and from the \(A\) phonon condensation (space group \(I4cm\)), the \(P4bm\) phase was energetically more favorable in all cases except for the \(\text{PbTiO}_3/\text{BiScO}_3\) superlattice.

The most complex picture is observed in superlattices, in which both the ferroelectric and AFD instabilities are simultaneously present in the \(P4mm\) phase. Since the energy difference between the \(P4bm\) and \(I4cm\) phases is small and both phases can exhibit the ferroelectric instability, it was necessary to consider all polar subgroups of these phases when searching for the ground state. The \(\text{KNbO}_3/\text{SrZrO}_3\) superlattice is an example of such a system. Its phonon spectrum is shown in Fig. 4 and the energies of different phases are given in Table II.

The calculations show that the ferroelectric instability of the \(P4bm\) and \(I4cm\) phases is characteristic of \(\text{KNbO}_3/\text{SrTiO}_3\), \(\text{KNbO}_3/\text{SrZrO}_3\), \(\text{SrTiO}_3/\text{KTaO}_3\) superlattices and all SLs containing \(\text{BiScO}_3\). Of two phases, \(Cm(2)\) and \(Pc\), into which the \(P4bm\) structure can transform upon the polar distortion, the \(Pc\) phase with polarization along the \([110]\) direction of the pseudocubic cell had lower energy in all SLs except for \(\text{PbTiO}_3/\text{LaGaO}_3\). Of two phases, \(Cc\) and one more phase of the \(Cm\) symmetry, \(Cm(3)\), into which the \(I4cm\) structure can transform upon the polar distortion, the \(Cc\) phase whose polarization is also directed along the \([110]\) direction of the pseudocubic cell usually had a lower energy. In \(\text{BiScO}_3/\text{LaAlO}_3\) and \(\text{KNbO}_3/\text{BiScO}_3\) superlattices, it was the \(Cm(3)\) phase which had a lower energy, but this phase has never become the ground state. In \(\text{KNbO}_3/\text{SrTiO}_3\) and \(\text{SrTiO}_3/\text{KTaO}_3\) superlattices, the energy difference between the \(Cc\) and \(Pc\) phases was only 0.5–0.7 meV, whereas in other systems it was within 8–80 meV. Since the calculations proved the stability of both \(Cc\) and \(Pc\) phases in the two superlattices, the \(Cc\) phase should be considered as a metastable one. As the energy difference between the two phases is very small, there is a real possibility that both structures can occur in an experiment simultaneously. That is why the properties of these superlattices were calculated below for both phases, \(Pc\) and \(Cc\).

The \(\text{PbTiO}_3/\text{LaGaO}_3\) superlattice is the only one in which the \(Cm(2)\) phase is the ground state. It originates from the \(P4bm\) phase and has the polarization directed along the \([x0z]\) direction of the pseudocubic cell.

In addition to the unstable \(M_4\) mode discussed above, in phonon spectra of the \(P4mm\) phase of nine SLs (\(\text{KNbO}_3/\text{SrTiO}_3\), \(\text{KNbO}_3/\text{SrZrO}_3\), \(\text{SrTiO}_3/\text{LaAlO}_3\), \(\text{PbTiO}_3/\text{LaAlO}_3\), \(\text{PbTiO}_3/\text{LaGaO}_3\), and all SLs containing \(\text{BiScO}_3\)) one more doubly degenerate unstable \(M_5\) mode is observed (Fig. 5). This mode describes the octahedra rotations around one or both of the \(x\) and \(y\) axes. The distortions described by this mode in the order parameters of \((\eta, 0)\) and \((\eta, \eta)\) result in the \(Pma2\) and \(Cmm2\) phases whose energies are usually higher than that of the \(P4bm\) phase (except for \(\text{PbTiO}_3/\text{LaGaO}_3\), \(\text{SrTiO}_3/\text{BiScO}_3\), \(\text{KNbO}_3/\text{BiScO}_3\), and \(\text{KNbO}_3/\text{SrZrO}_3\) SLs). Both the \(Pma2\) and \(Cmm2\) phases are characterized by the ferroelectric instability. An analysis of the polar subgroups of these phases (with \(Pc, Cm\), and \(Pm\) space groups) shows that the \(Pc\) phase has the lowest energy among them. It should be noted, however, that in the \(\text{BiScO}_3/\text{LaAlO}_3\) and \(\text{PbTiO}_3/\text{LaAlO}_3\) superlattices, the structure of this phase differs from that of the \(Pc\) phase, which originates from the \(P4bm\) phase. In the \(\text{BiScO}_3/\text{LaAlO}_3\) superlattice, this new \(Pc(2)\) phase becomes the ground-state structure because its energy is lower than that of the \(Pc\) phase originating from the \(P4bm\) phase. In the \(\text{PbTiO}_3/\text{LaAlO}_3\) superlattice, the energy of the \(Pc(2)\) phase is intermediate between those of the \(Pc\) phase and ground-state \(Cm(2)\) structure. As the \(Pc(2)\) phase demonstrates its stability with respect to all acoustic and optical distortions, we conclude that this is a metastable phase.

In two latter superlattices, \(\text{BiScO}_3/\text{LaAlO}_3\) and \(\text{PbTiO}_3/\text{LaAlO}_3\), we encounter a situation when the metastable solutions appear. The cause of this metastability is that the relaxation paths of the \(P4bm\) and \(Pma2\) (\(Cmm2\)) phases, in which the rotations are described by the \(M_4\) and \(M_5\) irreducible representations, are separated by a potential barrier. In other superlattices, these barriers are absent, and the structures, regardless of the initial rotation pattern, relax to the same ground-state \(Pc\) structure. It may seem strange why the same phase appears as a result of condensation of distortions described by two different irreducible representations. However, it should be taken into account that the vertical axis of the octahedra in the \(Pc\) phase is slightly inclined, which means that, in fact, this phase is described by two non-zero rotations around the coordinate axes. This explains why two structures, in which rotational distortions are described by different irreducible representations, relax to the same phase when the polar distortions are turned on.

In \(\text{SrTiO}_3/\text{LaAlO}_3\) and \(\text{PbTiO}_3/\text{LaAlO}_3\) superlattices, both the \(Pma2\) and \(Cmm2\) phases relax to the \(P4bm\) structure when the polar distortions are turned on. Here, as in the case of the \(\text{KNbO}_3/\text{LaAlO}_3\) SL, the strong AFD instability of \(\text{LaAlO}_3\) results in a complete suppression of the ferroelectric instability which was present in the high-symmetry \(P4mm\) phase.
the ground-state structure is \( Cm(2) \). The discrepancy between our results and those obtained for the KNbO\(_3\)/BaTiO\(_3\) SL in \cite{67} stems from the fact that the calculations in Ref. \cite{67} were performed for the superlattice clamped on the SrTiO\(_3\) substrate; at these boundary conditions, the \( P4mm \) phase is indeed the ground state.

Table III also presents the energy gain \( \Delta E \) per 10-atom formula unit, which results from the in-plane ferroelectric distortion. The obtained values show that, at room temperature, the predicted ground-state structures are likely to be observed in the KNbO\(_3\)/BaTiO\(_3\), KNbO\(_3\)/BaZrO\(_3\), KNbO\(_3\)/SrZrO\(_3\), SrTiO\(_3\)/BiScO\(_3\), PbTiO\(_3\)/BiScO\(_3\), and KNbO\(_3\)/BiScO\(_3\) superlattices. For the ground-state structures of all superlattices, the calculated spontaneous polarization and components of the piezoelectric tensor are presented in the following sections.

### 2. Calculation of polarization

Classical electrostatics of an electrically neutral interface between two dielectrics requires that the electric displacement field components normal to this interface are equal in two materials. If the materials are ferroelectrics and have different spontaneous polarizations, a bound electric charge appears at the interface, and the electric field generated by it makes the electric displacement fields equal in two materials.

In superlattices with the polar discontinuity, a violation of the order of charged AO and BO\(_2\) planes generates an additional electrostatic perturbation at the interfaces and creates a polarization jump of \( \Delta P = e/2a^2 \) in superlattices with a change in ionic charges of components by \( e \) and \( \Delta P = e/a^2 \) in superlattices with a change in the ionic charges by \( 2e \) (here \( a \) is the in-plane lattice parameter of the superlattice) \cite{60}. An elegant solution to this problem within the modern theory of polarization, which is valid in the general case, was proposed in \cite{64}.

An application of this approach to our superlattices enables us to calculate the electric displacement field in them and to use it to determine the average polarization in the SLs. In this work, we are interested precisely in this property. The polarization values in individual layers of a SL can be calculated by correcting the obtained average polarization taking into account the jump in the ionic contribution to the Berry phase at the interface and dielectric constants of individual components \cite{83}.

When calculating the polarization by the Berry phase method, it should be borne in mind that the ionic contributions to the Berry phase are different in nonpolar \( Pm\overline{3}m \) phases of I-V, II-IV, and III-III perovskites \cite{84}. That is why for each SL with the polar discontinuity it is necessary first to find the Berry phase for the nonpolar structure before calculating the polarization. Unfortunately, in our case, the calculation of the \( z \) component of the Berry phase becomes a problem because it is impossible to reverse the polarization or construct a non-polar structure for the high-symmetry \( P4mm \) phase, which

| Superlattice     | Space group | \( P_x \) | \( P_y \) | \( P_z \) | \( \Delta E \) |
|------------------|-------------|----------|----------|----------|-------------|
| KNbO\(_3\)/PbTiO\(_3\) | \( Cm \)    | 0.181    | 0        | 0.567    | 3.3         |
| KNbO\(_3\)/BaTiO\(_3\) | \( Cm \)    | 0.338    | 0        | –0.033   | 38.6        |
| KNbO\(_3\)/BaZrO\(_3\) | \( Cm \)    | 0.229    | 0        | 0.181    | 33.8        |
| KNbO\(_3\)/SrTiO\(_3\) | \( Pc \)    | 0.281    | 0        | 0.066    | 53.3; 9.0*  |
| KNbO\(_3\)/SrZrO\(_3\) | \( Pc \)    | 0.268    | 0        | 0.187    | 51.9; 49.8* |
| BaTiO\(_3\)/KTaO\(_3\) | \( Cm \)    | 0.180    | 0        | 0.130    | 9.7         |
| BaTiO\(_3\)/LaAlO\(_3\) | \( P4bm \)  | 0        | 0        | 0.057    |             |
| SrTiO\(_3\)/KTaO\(_3\) | \( Pc \)    | 0.105    | 0        | 0.141    | 11.9; 0.8*  |
| SrTiO\(_3\)/LaAlO\(_3\) | \( P4bm \)  | 0        | 0        | 0.012    |             |
| SrTiO\(_3\)/BiScO\(_3\) | \( Pc \)    | 0.501    | 0        | 0.329    | 671.1; 331.1 |
| PbTiO\(_3\)/KTaO\(_3\) | \( P4mm \)  | 0        | 0        | 0.454    |             |
| PbTiO\(_3\)/LaAlO\(_3\) | \( P4bm \)  | 0        | 0        | 0.119    |             |
| PbTiO\(_3\)/LaGaO\(_3\) | \( Cm(2) \) | 0.073    | 0        | 0.192    | 24.0*       |
| PbTiO\(_3\)/BiScO\(_3\) | \( Pc \)    | 0.710    | 0        | 0.330    | 865.5; 349.3 |
| KNbO\(_3\)/LaAlO\(_3\) | \( P4bm \)  | 0        | 0        | 0.061    |             |
| KTaO\(_3\)/LaAlO\(_3\) | \( P4bm \)  | 0        | 0        | 0.109    |             |
| KNbO\(_3\)/BiScO\(_3\) | \( Pc \)    | 0.558    | 0        | 0.241    | 381.3; 281.5 |
| KNbO\(_3\)/NaTaO\(_3\) | \( Pc \)    | 0.302    | 0        | 0.119    | 26.5; 26.4* |
| BaTiO\(_3\)/SrZrO\(_3\) | \( Pc \)    | 0.234    | 0        | 0.072    | 186.8       |
| BaTiO\(_3\)/SrSnO\(_3\) | \( Pc \)    | 0.189    | 0        | 0.072    | 275.9       |
| BiScO\(_3\)/LaAlO\(_3\) | \( Pc(2) \) | 0.493    | 0        | -0.116   | 535.1; 189.3 |
| BaTiO\(_3\)/SrTiO\(_3\) | \( Cm \)    | 0.233    | 0        | 0.061    | 4.8         |
| KNbO\(_3\)/KTaO\(_3\) | \( Cm \)    | 0.223    | 0        | 0.119    | 11.7        |
| PbTiO\(_3\)/PbZrO\(_3\) | \( Pc \)    | 0.586    | 0        | 0.314    | 488.2; 147.4 |
| KNbO\(_3\)/NaNbO\(_3\) | \( Pmc2_1 \) | 0.502    | 0        | 0        | 104.5; 98.6* |

*a* As compared to the non-polar \( P4bm \) phase.

*b* As compared to the non-polar \( P4/mmb \) phase.

In all BiScO\(_3\)-containing superlattices with the polar discontinuity, one more unstable mode, \( A_5 \), appears in the phonon spectrum at the \( A \) point. An analysis of chains of phases induced by the corresponding distortions showed that all obtained phases have the energy much higher than that of the ground-state structure.

The space groups of the energetically most favorable phases obtained for all studied superlattices are given in Table III. It is seen that in superlattices exhibiting only the ferroelectric instability in the high-symmetry \( P4mm \) phase, the \( Cm \) phase is the ground state. In superlattices exhibiting only the AFD instability, the \( P4bm \) phase is the ground state. And, finally, in superlattices in which both instabilities are present, the \( Pc \) phase is the ground state, with the exception of the KNbO\(_3\)/LaAlO\(_3\) and PbTiO\(_3\)/LaGaO\(_3\) superlattices. In the first of these exceptions, the AFD instability suppresses the ferroelectric one, and the \( P4bm \) phase becomes the ground state. In the second of them,
does not have \( \sigma_z \) mirror plane. To estimate \( P_z \), we considered unrelaxed structures with ideal atomic positions corresponding to the cubic perovskite structure in both layers. In this structure, the electron contribution to the Berry phase is nonzero because of the redistribution of the electron density between the layers, and the ionic contribution reflects the difference in the Berry phases of individual perovskites. The average polarization in a superlattice was calculated using standard formulas from a change in the Berry phase upon the transition from the above-described unrelaxed structure to the ground-state one. To correctly determine the polarization from the change in the Berry phase, which is well-defined modulo \( 2\pi \), for all superlattices the calculations were also performed for at least one intermediate point at which the atoms are halfway between the ground-state and unrelaxed structures.

The calculated polarizations are given in Table III. The components of the polarization vector are given relative to the axes of the standard crystallographic settings for tetragonal and monoclinic unit cells (their axes are often rotated in the \( xy \) plane relative to each other by \( 45^\circ \)). A comparison of polarizations calculated for structures with and without octahedral rotations shows that in SLs with the \( Pc \) ground-state structure, the neglect of these rotations can result in an error in determining \( P_z \) up to 30% and, in some cases, even an error in the sign of this quantity. For the \( P4mm \) phase, our values reasonably agree with the published values of \( P_z = 0.532 \) C/m\(^2\) for \( \text{PbTiO}_3/\text{KNbO}_3 \) \([72]\), \( P_z = 0.202 \) C/m\(^2\) for \( \text{PbTiO}_3/\text{LaAlO}_3 \) \([72]\), and \( P_z = 0.38 \) C/m\(^2\) for \( \text{PbTiO}_3/\text{KTaO}_3 \) \([85]\) SLs.

3. Piezoelectric properties

The reason for our interest to ferroelectric instability in superlattices with the polar discontinuity is that in such SLs it is possible to obtain rather high piezoelectric coefficients resulting from the in-plane ferroelectric phase transitions appearing in them. The literature data on the piezoelectric properties of such superlattices are limited to calculations for the high-symmetry \( P4mm \) phase of \( \text{PbTiO}_3/\text{LaAlO}_3 \) and \( \text{KNbO}_3/\text{PbTiO}_3 \) SLs \([71, 72]\) and of the \( \text{PbTiO}_3/\text{KTaO}_3 \) one \([85]\). As the ground-state structure of the first two superlattices differs from \( P4mm \), more correct calculations for these SLs are needed. For other superlattices considered in this work, data on their piezoelectric properties are absent.

In superlattices with a tetragonal ground-state structure, in which the polarization is directed along the \( z \) axis, five components of the piezoelectric tensor \( d_{i\nu} \) are nonzero. Among them, the highest values of \( d_{i\nu} \) are obtained for \( \text{PbTiO}_3/\text{KTaO}_3 \) and \( \text{PbTiO}_3/\text{LaAlO}_3 \) SLs (Table III). Interestingly, among these coefficients, the \( d_{15} \) values turned out to be the largest. This coefficient characterizes the polarization \( P_z \) that appears as a result of the inclination of the polarization vector. However, no clear correlation between \( d_{15} \) and \( P_z \) was observed in tetragonal SLs. Moreover, in the related system, \( \text{BaTiO}_3/\text{LaAlO}_3 \), the piezoelectric coefficients were unexpectedly low (Table III). This means that the inclination of the polarization vector is not an effective way for obtaining high piezoelectric coefficients.

In superlattices with a monoclinic ground-state structure, in which the polarization vector lies in the \( xz \) plane, the piezoelectric tensor is characterized by ten nonzero components. In these SLs, the highest values of \( d_{i\nu} \) are the \( d_{24} \) and \( d_{26} \) coefficients, which describe the appearance of polarization in the \( y \) direction normal to the \( xz \) plane under the \( yz \) and \( xy \) shear strain. An analysis of the obtained data also does not find a clear correlation between the piezoelectric coefficients and the average polarization. Stretching the unit cells of these superlattices in the \( xz \) plane changes the polarization, but the corresponding piezoelectric coefficients \( (d_{11} \) and \( d_{33} \) in Table III) are not the largest.

To understand the mechanism of the appearance of high piezoelectric coefficients in some superlattices with the polar discontinuity, we analyzed the third-rank tensors \( \partial u_i / \partial \sigma_{\mu\nu} \). This tensor characterizes the displacement of the \( i \)th atom in the unit cell in the \( \alpha \) direction produced by strain \( \sigma_{\mu\nu} \). It turned out that in SLs exhibiting strong piezoelectricity, the values of some components of these tensors for some atoms reach 10–15 Å (that is, the unit cell strain of 1% generates atomic displacements exceeding 0.1 Å). For example, in the \( \text{PbTiO}_3/\text{LaAlO}_3 \) superlattice, such atoms are \( \text{Pb}(1), \text{La}(6), \) and two oxygen atoms \( O(4) \) and \( O(14) \) located in the \( \text{TiO}_2 \) layer (Table IV); the contributions of \( O(8) \) and \( O(9) \) oxygen atoms located in the \( \text{AlO}_2 \) layer are 25 times smaller.

The fact that strong distortions in the \( \text{PbTiO}_3/\text{LaAlO}_3 \) SL are observed in the \( \text{TiO}_2 \) layer suggests that the \( \text{Ti}(2) \) atom also actively participates in the appearance of polarization. Indeed, the displacement pattern of the \( \text{Pb}, \text{Ti}, \) and \( \text{O} \) atoms in the \( \text{PbO} \) and \( \text{TiO}_2 \) layers resembles that of the polar mode in \( \text{PbTiO}_3 \). A more detailed analysis of atomic displacements in monoclincally strained SL, whose deformation is described by a nonzero component \( \sigma_{xz} = 0.005 \), simultaneously finds two types of distortions: the rotations of corner-linked \( \text{TiO}_6 \) and \( \text{AlO}_6 \) octahedra around the \( x \) axis, resembling rotations described by an unstable phonon at the \( R \) point of the cubic perovskite structure, and out-of-phase (polar) displacements of \( \text{Pb}(1), \text{La}(6), \text{Ti}(2), \text{O}(4), \) and \( \text{O}(14) \) atoms along the \( x \) axis, like in the polar mode in \( \text{PbTiO}_3 \). The observed displacement pattern is very close (with the correlation coefficient of 0.902) to the eigenvector of the soft \( E \) mode with a surprisingly low frequency of 27 cm\(^{-1}\) in the phonon spectrum of the \( P4mm \) phase of this SL. Under the influence of strain, the irreducible representation \( E \) reduces to a sum of \( A' + A'' \) irreducible representations of the low-symmetry \( Cm \) phase, and the structure distorts according to the eigenvector of the full-symmetry \( A' \) mode. In other SLs
with lower piezoelectric properties, the frequencies of the corresponding modes were higher (40–120 cm⁻¹), but we didn’t find simple correlations between the frequencies and effective charges of these modes and the piezoelectric properties. This question needs more detailed investigation.

A comparison of the piezoelectric properties of the metastable \( Cc \) phase and the ground-state \( Pc \) phase in \( \text{KNbO}_3/\text{SrTiO}_3 \) and \( \text{SrTiO}_3/\text{KTaO}_3 \) superlattices, in which the energy difference between the two structures is very small, shows that their piezoelectric tensors are quite close to each other (Table II). This means that a change in the character of the octahedra rotations weakly affects the piezoelectric properties of SLs.

According to our calculations, the piezoelectric coefficients in studied superlattices can reach 150–270 pC/N. A comparison of the obtained results with the published data in some cases finds their good agreement. For example, for the \( P4mm \) phase of \( \text{PbTiO}_3/\text{LaAlO}_3 \) SL our result \( e_{33} = -3.52 \) C/m² is quite close to the value \( e_{33} = -2.85 \) C/m² obtained in [21]. However, our value of \( d_{33} = -18.9 \) pC/N for the same phase of the same SL differs from the value \( d_{33} = 13.9 \) pC/N obtained in [72]: these values are close in magnitude, but have a different sign. An additional reason for the stronger discrepancies here may be a neglect of the difference in the displacements and effective charges of the O atoms in Ref. [22] (according to our data, the effective charges varies from \(-2.07 \) to \(-5.84 \)). As for the \( \text{PbTiO}_3/\text{KTaO}_3 \) SL studied in [85], the \( e_{33} \) and \( e_{15} \) piezoelectric coefficients obtained there are almost 100 times less than our data, and the \( e_{33} \) value is close to our result in magnitude, but differs in sign.

In conclusion, it was interesting to compare the piezoelectric properties of superlattices with the polar discontinuity with those of “isoelectronic” superlattices: (1) SLs without the polar discontinuity, in which the broken symmetry and high-symmetry \( P4mm \) structure are formed, by analogy with [21], as a result of the absence of the mirror symmetry in the sequence of layers (\( \text{BaTiO}_3/\text{SrZrO}_3, \text{BaTiO}_3/\text{SrSnO}_3, \text{KNbO}_3/\text{NaTaO}_3, \) and \( \text{BiScO}_3/\text{LaAlO}_3 \)), and (2) ordinary SLs with one substituted atom (\( \text{BaTiO}_3/\text{SrTiO}_3, \text{KNbO}_3/\text{KTaO}_3, \) and two famous systems known for their high piezoelectric properties, \( \text{PbTiO}_3/\text{PbZrO}_3 \) and “lead-free” \( \text{KNbO}_3/\text{NaNbO}_3 \)).

### Table III. Nonzero components of the piezoelectric tensor \( d_{ij} \) (in pC/N) for the ground-state structures of all studied short-period superlattices.

| Superlattice       | \( d_{11} \) | \( d_{12} \) | \( d_{13} \) | \( d_{15} \) | \( d_{24} \) | \( d_{26} \) | \( d_{31} \) | \( d_{32} \) | \( d_{33} \) | \( d_{35} \) |
|--------------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| \( \text{KNbO}_3/\text{PbTiO}_3 \) | 13.4 | 3.7 | -13.9 | 158.3 | 273.3 | 137.3 | -3.0 | -2.9 | -10.9 | -0.8 |
| \( \text{KNbO}_3/\text{BaTiO}_3 \) | 23.5 | 9.6 | -12.7 | 3.8 | -2.8 | 106.4 | 10.7 | 7.9 | -16.3 | 17.4 |
| \( \text{KNbO}_3/\text{BaZrO}_3 \) | 16.3 | 4.7 | -11.7 | 5.6 | 7.9 | 20.8 | -8.9 | -7.3 | 16.7 | 1.8 |
| \( \text{KNbO}_3/\text{SrTiO}_3 \) | 35.9 | 15.3 | -19.1 | 8.3 | 41.7 | 151.0 | -22.0 | -12.1 | 16.1 | 9.4 |
| \( \text{KNbO}_3/\text{SrZrO}_3 \) | 30.8 | 10.1 | -18.8 | 9.1 | 11.0 | 85.5 | -18.1 | -9.8 | 17.7 | 12.9 |
| \( \text{BaTiO}_3/\text{KTaO}_3 \) | 19.2 | 9.5 | -18.5 | 2.5 | 7.9 | 25.3 | -18.1 | -11.6 | 43.4 | 10.1 |
| \( \text{BaTiO}_3/\text{LaAlO}_3 \) | - | - | - | 1.4 | 1.4 | - | 3.0 | 3.0 | -4.6 | - |
| \( \text{SrTiO}_3/\text{KTaO}_3 \) | 39.7 | 22.8 | -27.6 | 28.2 | 46.9 | 41.2 | -18.4 | -13.0 | 26.1 | -4.2 |
| \( \text{SrTiO}_3/\text{LaAlO}_3 \) | - | - | - | 2.0 | 2.0 | - | 1.0 | 1.0 | -1.6 | - |
| \( \text{SrTiO}_3/\text{BiScO}_3 \) | 23.6 | 5.4 | -6.0 | 14.3 | 17.9 | 24.6 | -4.7 | 0.6 | 11.8 | 12.2 |
| \( \text{PbTiO}_3/\text{KTaO}_3 \) | - | - | - | 91.4 | 91.4 | - | -8.8 | 8.8 | 41.2 | - |
| \( \text{PbTiO}_3/\text{LaAlO}_3 \) | - | - | - | 158.6 | 158.6 | - | -4.3 | 4.3 | 2.8 | - |
| \( \text{PbTiO}_3/\text{LaGaO}_3 \) | 19.1 | -5.8 | -3.0 | -29.6 | 15.1 | -35.1 | 7.8 | -2.9 | -18.5 | 4.3 |
| \( \text{PbTiO}_3/\text{BiScO}_3 \) | 31.1 | 2.7 | -7.4 | 5.1 | 1.5 | 47.0 | -2.3 | -4.0 | 18.5 | 13.6 |
| \( \text{KNbO}_3/\text{LaAlO}_3 \) | - | - | - | 5.7 | 5.7 | - | 1.1 | 1.1 | -0.8 | - |
| \( \text{KTaO}_3/\text{LaAlO}_3 \) | - | - | - | 5.3 | 5.3 | - | -0.8 | -0.8 | 3.7 | - |
| \( \text{KNbO}_3/\text{BiScO}_3 \) | 19.2 | 9.2 | -5.9 | 10.0 | 23.2 | 51.2 | -0.5 | 3.9 | 2.1 | 6.9 |
| \( \text{KNbO}_3/\text{NaTaO}_3 \) | 90.2 | 19.8 | -97.1 | 24.3 | -16.0 | 70.2 | 154.6 | 43.1 | -209.2 | 73.5 |
| \( \text{BaTiO}_3/\text{SrZrO}_3 \) | 23.3 | 4.9 | -12.8 | 1.2 | 2.6 | 19.3 | 3.9 | 4.0 | -7.8 | 5.1 |
| \( \text{BaTiO}_3/\text{SrSnO}_3 \) | 23.9 | 6.6 | -12.7 | -7.1 | -6.4 | 23.2 | -1.0 | -2.2 | 3.2 | 2.1 |
| \( \text{BiScO}_3/\text{LaAlO}_3 \) | 30.2 | -1.1 | -5.9 | -5.7 | 8.3 | 23.1 | 0.3 | 1.3 | -3.5 | 10.5 |
| \( \text{BaTiO}_3/\text{SrTiO}_3 \) | 103.5 | 37.4 | -117.1 | -59.5 | 21.1 | 187.9 | -287.3 | -131.5 | 460.5 | 288.1 |
| \( \text{KNbO}_3/\text{KTaO}_3 \) | 108.3 | 60.4 | -157.1 | -15.9 | 18.7 | 123.9 | -181.6 | -111.3 | 315.5 | 45.4 |
| \( \text{PbTiO}_3/\text{PbZrO}_3 \) | 62.1 | 12.5 | -38.8 | 3.2 | 29.9 | 132.7 | -45.8 | -19.5 | 70.4 | 26.6 |
| \( \text{KNbO}_3/\text{NaNbO}_3 \) | 17.9 | 5.3 | -9.2 | - | - | - | 133.0 | - | - | 60.1 |
TABLE IV. The values of the $\partial u_i^\alpha / \partial \sigma_{15}$ component of the $\partial u_i^\alpha / \partial \sigma_{\mu \nu}$ tensor (in Å) for all atoms in the ground-state structure of PbTiO$_3$/LaAlO$_3$ and BaTiO$_3$/LaAlO$_3$ superlattices ($P4bm$ phase) and in ordinary superlattices, PbTiO$_3$/PbZrO$_3$ ($Pc$ phase) and KNbO$_3$/NaNbO$_3$ ($Pmnc2$ phase), of systems known for their piezoelectric properties. Atoms 1–10 are numbered according to Fig. 1; atoms 11–20 are located in the second part of the doubled unit cell of the high-temperature phase and are shifted from atoms 1–10 along the $x$ axis. For atomic positions of all atoms see tables in the Supplementary data.

| Atom $i$ | PbTiO$_3$/LaAlO$_3$ | BaTiO$_3$/LaAlO$_3$ | PbTiO$_3$/PbZrO$_3$ | KNbO$_3$/NaNbO$_3$ |
|----------|---------------------|---------------------|---------------------|---------------------|
| 1        | +5.18               | +0.09               | +0.35               | +0.00               |
| 2        | +2.37               | −0.08               | +0.03               | −0.58               |
| 3        | −1.19               | +0.24               | +0.14               | −0.31               |
| 4        | −5.61               | +0.10               | +0.17               | −0.51               |
| 5        | −1.02               | −0.11               | +0.49               | +0.00               |
| 6        | +4.56               | +0.73               | +0.44               | +0.00               |
| 7        | +0.76               | +0.02               | −0.23               | +0.58               |
| 8        | −0.21               | −0.31               | −0.31               | +0.31               |
| 9        | −0.22               | −0.15               | −0.83               | +0.51               |
| 10       | −0.84               | −0.10               | −0.42               | +0.00               |
| 11       | +1.71               | −0.38               | +0.01               | +0.00               |
| 12       | +2.37               | −0.08               | +0.08               | −0.41               |
| 13       | −1.19               | +0.24               | −0.11               | −0.51               |
| 14       | −5.61               | +0.10               | −0.43               | −1.15               |
| 15       | −1.02               | −0.11               | +0.47               | +0.00               |
| 16       | +0.48               | +0.37               | +0.76               | +0.00               |
| 17       | +0.76               | +0.02               | −0.19               | +0.41               |
| 18       | −0.21               | −0.31               | −0.06               | +0.51               |
| 19       | −0.22               | −0.15               | −0.26               | +1.15               |
| 20       | −0.84               | −0.10               | −0.12               | +0.00               |

TABLE V. Nonzero components of the piezoelectric tensor $d_{\mu \nu}$ (in pC/N) in the ground and metastable states of two short-period superlattices with the polar discontinuity.

| Phase   | $d_{11}$ | $d_{12}$ | $d_{13}$ | $d_{15}$ | $d_{24}$ | $d_{26}$ | $d_{31}$ | $d_{32}$ | $d_{33}$ | $d_{35}$ |
|---------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| KNbO$_3$/SrTiO$_3$ superlattice |          |          |          |          |          |          |          |          |          |          |
| $Pc$    | 35.9     | 15.3     | −19.1    | 8.3      | 41.7     | 151.0    | −22.0    | −12.1    | 16.1     | 9.4      |
| $Cc$    | 35.0     | 14.8     | −18.3    | 7.7      | 41.4     | 154.0    | −21.4    | −11.6    | 15.7     | 11.1     |
| SrTiO$_3$/KTaO$_3$ superlattice |          |          |          |          |          |          |          |          |          |          |
| $Pc$    | 39.7     | 22.8     | −27.6    | 28.2     | 46.9     | 41.2     | −18.4    | −13.0    | 26.1     | −4.2     |
| $Cc$    | 39.2     | 22.3     | −27.4    | 27.1     | 45.7     | 41.1     | −18.6    | −13.1    | 26.3     | −3.7     |

It is seen that in spite of a large scatter of the data, superlattices with the polar discontinuity are not much different in their piezoelectric properties from other superlattices (high piezoelectric properties of BaTiO$_3$/SrTiO$_3$ and KNbO$_3$/KTaO$_3$ SLs, as follows from the corresponding values of $\Delta E$ (Table II), can be realized only at low temperatures). Thus, the only advantage of superlattices with the polar discontinuity as well as of SLs with broken symmetry is that one component of polarization in them is not switchable.

IV. CONCLUSIONS

First-principles calculations have been used to study the stability of a high-symmetry $P4mm$ polar phase in seventeen ferroelectric perovskite superlattices with the polar discontinuity. In most superlattices, this phase exhibits either the ferroelectric instability or the antiferrodistortive one, or both of them simultaneously. For each superlattice, the ground-state structure, the structure of possible metastable phases, spontaneous polarization, and piezoelectric properties were calculated. A comparison of the piezoelectric properties of superlattices with the polar discontinuity and those without the polar discontinuity (superlattices with broken symmetry
and ordinary superlattices) showed that these properties are not much different. It was demonstrated that high piezoelectric coefficients (up to 150–270 pC/N) in some superlattices with the polar discontinuity are due to the appearance of strong lattice distortions, whose symmetry follows that of a low-lying polar phonon mode of the ground-state structure under the influence of external strain.

Data availability statement

All data included in this study are available upon request from the author.

Declaration of competing interests

The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

ACKNOWLEDGMENTS

This work was partially supported by the Russian Foundation for Basic Research under Grant 17-02-01068.

Appendix A: Supplementary data

Supplementary data associated with this article can be found in the online version at https://doi.org/10.1016/j.commatsci.2020.110113.

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