

## Effect of Epitaxial Strain on the Spontaneous Polarization of Thin Film Ferroelectrics

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Epitaxial strain can substantially enhance the spontaneous polarizations and Curie temperatures of ferroelectric thin films compared to the corresponding bulk materials. In this Letter we use first principles calculations to calculate the effect of epitaxial strain on the spontaneous polarization of the ferroelectrics BaTiO<sub>3</sub>, PbTiO<sub>3</sub>, and LiNbO<sub>3</sub>, and the multiferroic material BiFeO<sub>3</sub>. We show that the epitaxial strain dependence of the polarization varies considerably for the different systems, and in some cases is, in fact, very small. We discuss possible reasons for this different behavior and show that the effect of epitaxial strain can easily be understood in terms of the piezoelectric and elastic constants of the unstrained materials. Our results provide a computational tool for the quantitative prediction of strain behavior in ferroelectric thin films.

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The possible application of ferroelectric materials in microelectronic devices has led to strong interest in the properties of thin film ferroelectrics [1]. One important question in this context is how epitaxial strain, which is incorporated in the ferroelectric material due to the lattice mismatch with the substrate, affects the ferroelectric characteristics of the thin film. It has been demonstrated that epitaxial strain can have drastic effects, such as inducing ferroelectricity at room temperature in otherwise paraelectric SrTiO<sub>3</sub> [2] or increasing the ferroelectric Curie temperature of BaTiO<sub>3</sub> by nearly 500 °C and the remanent polarization by 250% compared with the corresponding bulk values [3]. Based on these observations, it is often assumed that the strong sensitivity to epitaxial strain is a common feature of all ferroelectrics.

Indeed, this assumption has been supported by first principles calculations for several simple ABO<sub>3</sub> perovskite ferroelectrics [4–7]. Strain is introduced in these calculations by fixing the lattice constants corresponding to the lateral directions of the substrate while relaxing all remaining structural parameters, according to the minimum of the total energy under the epitaxial constraint. This makes it possible to isolate the pure strain effect from other effects present in real thin film samples such as structural defects, chemical inhomogeneities, and interface effects. For example, in Refs. [6,7] the change in phase stability due to epitaxial strain was investigated by first principles techniques for several simple perovskite systems including the prototype ferroelectrics BaTiO<sub>3</sub> and PbTiO<sub>3</sub>. It was shown that for these systems a series of consecutive phase transitions occur that effectively rotate the polarization from “out-of-plane” for compressive epitaxial strain to “in-plane” for tensile epitaxial strain. Also, the magnitude of the spontaneous polarization within the different phases was shown to be strongly strain dependent. In contrast, we have recently shown that in BiFeO<sub>3</sub>, a multiferroic system where ferroelectricity coexists with magnetic order, the magnitude of the polarization barely changes even for relatively large strain values of ±3% [8].

In this Letter we investigate the factors that lead to a strong strain dependence of the spontaneous polarization in some materials and to a relative inertness to epitaxial strain in other materials. To do this, we compare the spontaneous polarization as a function of epitaxial strain (in a fixed phase) for a variety of different perovskite-derived ferroelectrics with different structural symmetries and different mechanisms causing the ferroelectric displacements. We show that the sensitivity to epitaxial strain varies considerably for different materials and that strong strain dependence is not a universal feature of all ferroelectrics. Furthermore, we show that the strain dependence of the polarization for experimentally relevant strain values in all systems can be understood in terms of the piezoelectric and elastic constants of the unstrained materials, and we discuss the factors determining the sensitivity to epitaxial strain of a certain material.

In general, the total change of the spontaneous polarization  $P$  to linear order in the strain components  $\epsilon_i$  is given by the improper piezoelectric tensor,  $c_{\alpha i}$  [9]:

$$\frac{\partial P_\alpha}{\partial \epsilon_i} = c_{\alpha i}. \quad (1)$$

Here,  $\alpha = 1, 2, 3$  stands for the usual Cartesian components  $x, y,$  and  $z$ , whereas  $i = 1, \dots, 6$  denotes the components of the strain tensor in Voigt notation (see, e.g., Ref. [10]). For epitaxial strain,  $\epsilon_4 = \epsilon_5 = \epsilon_6 = 0$  and  $\epsilon_1 = \epsilon_2 \neq 0$ . Furthermore, the ratio between in-plane and out-of-plane strain is given by the *Poisson ratio*  $n = -\epsilon_1/\epsilon_3$ . In the following we consider only the situation where the spontaneous polarization is directed perpendicular to the orientation of the substrate plane, and we use this as the  $z$  direction of our coordinate system. The substrate surface is then oriented parallel to the  $x$ - $y$  plane. In this case, the change in polarization (to linear order in the strain) is given by

$$\Delta P_3 = \left( 2c_{31} - \frac{c_{33}}{n} \right) \epsilon_1 = c_{\text{eff}} \epsilon_1. \quad (2)$$

Here we have further assumed that the symmetry is such that  $c_{31} = c_{32}$ .

We now investigate the validity of Eq. (2) for experimentally relevant strain values by comparing directly calculated values of the spontaneous polarization as a function of epitaxial strain with values calculated using Eq. (2) and the piezoelectric constants and Poisson ratios of the corresponding unstrained structure. We also investigate how the effective piezoelectric constant  $c_{\text{eff}}$ , which describes the change in polarization due to epitaxial strain, varies for different materials.

In Ref. [8] several possible explanations for the different strain behavior in BiFeO<sub>3</sub> compared to systems like BaTiO<sub>3</sub>/PbTiO<sub>3</sub> were suggested: (i) different structural symmetry: BiFeO<sub>3</sub> crystallizes in the rhombohedral  $R3c$  structure with a doubled unit cell compared to the ideal perovskite structure and shows rotated oxygen octahedra in addition to the polar displacements (see Ref. [11]), whereas the relevant phases [12] for BaTiO<sub>3</sub>/PbTiO<sub>3</sub> are simple tetragonally distorted perovskite structures (space group  $P4mm$ ) [6,7]; (ii) different displacement mechanisms: in BaTiO<sub>3</sub>/PbTiO<sub>3</sub> the  $d^0$  configuration of the Ti cation plays a crucial role for the ferroelectric instability, whereas in the multiferroic system BiFeO<sub>3</sub> the ferroelectricity is caused solely by the Bi 6s lone electron pair [14]; (iii) a general high stability of the ferroelectric state in BiFeO<sub>3</sub>, indicated by rather large ionic displacements and a high ferroelectric Curie temperature of 1123 K (BaTiO<sub>3</sub> : 400 K, PbTiO<sub>3</sub> : 763 K) [13].

In order to systematically address the possible explanations (i) to (iii), we study the following systems: the prototypical ferroelectrics BaTiO<sub>3</sub> and PbTiO<sub>3</sub>; the multiferroic system BiFeO<sub>3</sub>, both in its ground state  $R3c$  structure and in a hypothetical  $P4mm$  structure, i.e., isostructural to BaTiO<sub>3</sub>/PbTiO<sub>3</sub>; LiNbO<sub>3</sub>, which is isostructural to BiFeO<sub>3</sub>, with large ionic displacements and a very high Curie temperature of 1480 K [13], but where, in contrast to the multiferroic system BiFeO<sub>3</sub>, the transition metal cation plays an active role in the ferroelectric instability, similar to the case of BaTiO<sub>3</sub>/PbTiO<sub>3</sub> [15,16].

Values for the spontaneous polarization obtained in this work are calculated using the Berry phase approach for determining the electronic contribution to the polarization [17,18]. The piezoelectric constants are obtained using the Berry phase approach and a finite difference method analogous to Ref. [19]. The Poisson ratios are estimated from the change in the out-of-plane lattice constant when fixing the in-plane lattice constant and relaxing all ionic positions. For all calculations we use the *Vienna Ab initio Simulation Package* (VASP) [20], which employs the projector augmented wave method within the density functional theory [21,22]. Except where otherwise noted, we use the local spin-density approximation (LSDA); see Ref. [23]. All calculational parameters are tested to result in good convergence of all quantities under consideration.

The structural parameters calculated in this work corresponding to the unstrained systems are listed in Table I for

TABLE I. Structural parameters calculated for LiNbO<sub>3</sub>.  $a$  and  $c$  are the lattice parameters of the corresponding hexagonal unit cell.  $z$ ,  $u$ ,  $v$ ,  $w$  are internal structural parameters defined in Ref. [16].

$a$ [Å]	$c$ [Å]	$z$	$u$	$v$	$w$
5.073	13.702	0.0337	0.01257	0.0426	0.0178

LiNbO<sub>3</sub> and in Table II for the tetragonal systems. All structural parameters are in good agreement with previous calculations; see Refs. [15,16] for LiNbO<sub>3</sub>, Ref. [4] for BaTiO<sub>3</sub>, and Ref. [24] for PbTiO<sub>3</sub>. For  $R3c$  BiFeO<sub>3</sub> the structural parameters are listed in Table II of Ref. [11] ( $U_{\text{eff}} = 0$ ). All systems except  $P4mm$  BiFeO<sub>3</sub> are fully relaxed using the LSDA. For  $P4mm$  BiFeO<sub>3</sub> calculations are performed using the LSDA +  $U$  method [25] with a small  $U_{\text{eff}} = 2$  eV in order to ensure the insulating character. The Poisson ratios and the spontaneous polarization as a function of epitaxial strain were extracted from Ref. [4] for BaTiO<sub>3</sub> and from Ref. [6] for PbTiO<sub>3</sub>. All other quantities are calculated in this Letter.

Since BiFeO<sub>3</sub> in the  $P4mm$  structure has not been discussed in the literature before, we give a few more details obtained by our structural relaxation of this system. The energy minimum of the relaxed  $P4mm$  structure of BiFeO<sub>3</sub> is 0.26 eV/(formula unit) higher than for the ground state  $R3c$  structure (calculated with the same  $U_{\text{eff}}$ ). The relaxed  $P4mm$  structure is strongly distorted compared to the ideal perovskite structure, with a  $c/a$  ratio of 1.27 and a very large polarization of 151  $\mu\text{C}/\text{cm}^2$ . These values are similar to those found for the recently predicted isostructural ferroelectric BiGaO<sub>3</sub> [26].

Before presenting our main results, we clarify two technical points. First, since the polarization of a periodic solid is only well defined modulo  $eR/V$ , where  $e$  is the electronic charge,  $R$  is a lattice vector, and  $V$  is the unit cell volume, the calculation of the polarization for a certain bulk structure leads to a lattice of values [17,18]. The spontaneous polarization  $P$  can be obtained by monitoring the change in polarization  $\Delta P$  of an arbitrary chosen “branch” of the polarization lattice, when the structure is deformed from the original structure into a state with inverted polarization. It has been shown by King-Smith and Vanderbilt [17,18] that this change is independent of the chosen “path” leading from the initial to the final state,

TABLE II. Structural parameters calculated for  $P4mm$  BaTiO<sub>3</sub>, PbTiO<sub>3</sub>, and BiFeO<sub>3</sub>.  $a$  and  $c/a$  describe the tetragonal unit cell, and  $\Delta_i$  is the displacement of ion  $i$  along the  $c$  axis (in units of  $c$ ). The notation is the same as used in Ref. [4].

	$a$ [Å]	$c/a$	$\Delta_B$	$\Delta_{O_i}$	$\Delta_{O_{ii}}$
BaTiO <sub>3</sub>	3.945	1.011	0.012	-0.019	-0.013
PbTiO <sub>3</sub>	3.870	1.040	0.034	0.087	0.101
BiFeO <sub>3</sub>	3.665	1.270	0.064	0.170	0.203

as long as the system stays insulating for all intermediate states along the path. The spontaneous polarization is then given by  $P = \Delta P/2$  and is also independent of the chosen branch.

Second, it has been pointed out in the literature that the improper piezoelectric response depends on the specific branch used to calculate this quantity [27]. The distinction between *proper* and *improper* piezoelectric response is a consequence of the definition of the polarization as the dipole moment per volume, which causes the polarization to vary as a function of strain even when the dipole moment does not change (see Fig. 1) [9,27]. This pure volume effect is included in the improper but not in the proper piezoelectric response. However, the two are trivially related by the spontaneous polarization (in the case of  $c_{33}$  the proper is equal to the improper piezoelectric response; for  $c_{31}$  the proper piezoelectric response is given by the improper value plus the spontaneous polarization) [9,27]. Here we report the improper piezoelectric response, which is used in Eqs. (1) and (2), since they refer to the total change in spontaneous polarization. We point out that the improper piezoelectric constant corresponding to the *spontaneous* polarization is well defined and does not depend on the specific branch used in the evaluation of this quantity.

The improper piezoelectric constants and Poisson ratios for the five systems are given in Table III. Note that for the tetragonal systems the fourfold axis is used as the  $z$  direction of our coordinate system, whereas for the rhombohedral systems the threefold axis is used. It is evident that the effective piezoelectric constants  $c_{\text{eff}}$  describing the effect of epitaxial strain (to linear order) on the spontaneous polarization are much larger for BaTiO<sub>3</sub> and PbTiO<sub>3</sub> than for the other three systems. This is mainly due to the larger  $c_{33}$  in BaTiO<sub>3</sub>/PbTiO<sub>3</sub> but also due to the smaller Poisson ratio of the  $P4mm$  structures [28]. The Poisson ratios are comparable for systems with the same structural symmetry. In  $P4mm$  BiFeO<sub>3</sub> the smaller Poisson ratio leads to a slightly increased  $c_{\text{eff}}$  compared to  $R3c$  BiFeO<sub>3</sub> although the piezoelectric constant  $c_{33}$  is similar for both symmetries. Another observation is that, although  $c_{33}$  is smaller in  $R3c$  BiFeO<sub>3</sub> than in LiNbO<sub>3</sub>,  $c_{\text{eff}}$  is larger due to the different sign of  $c_{31}$ .

Figure 2 compares the directly calculated change in spontaneous polarization caused by epitaxial strain with

TABLE III. Improper piezoelectric constants  $c_{33}$ ,  $c_{31}$ , and  $c_{\text{eff}}$  (in  $\mu\text{C}/\text{cm}^2$ ) as well as the Poisson ratio  $n$  for the various systems. References are given for values not calculated in this work.

	$c_{33}$	$c_{31}$	$n$	$c_{\text{eff}}$
BaTiO <sub>3</sub>	670	30	0.65 [4]	-971
PbTiO <sub>3</sub>	586	103	0.58 [6]	-804
BiFeO <sub>3</sub> ( $R3c$ )	213	50	1.15	-85
LiNbO <sub>3</sub>	124	-75	1.5	-233
BiFeO <sub>3</sub> ( $P4mm$ )	203	-15	0.65	-342

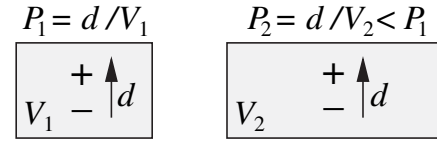


FIG. 1. Reason for the difference between proper and improper piezoelectric response: the polarization  $P_2$  is smaller than  $P_1$  although the dipole moment  $d$  is unchanged.

the corresponding change calculated using  $c_{\text{eff}}$  from Table III for all five systems. One can see that the linear approximation of Eq. (2) works well for all systems up to strains of  $\pm 3\%$ . Even in the case of BaTiO<sub>3</sub> and PbTiO<sub>3</sub>, where we have used data from two different sources, the agreement between the polarization calculated using Eq. (2) and the directly calculated values is remarkably good. For the systems where all values are calculated in the present work the agreement is extremely good.

The present study shows that the polarization response to epitaxial strain for experimentally relevant strain values can be described in terms of the piezoelectric and elastic constants of the unstrained system. Two further observations can be made. First, the appearance of two different terms in Eq. (2) with potentially opposite signs makes it possible that a system can in principle have rather large piezoelectric constants, but that due to partial cancellation  $c_{\text{eff}}$  is rather small. Second, a large value of  $c_{33}$  can eventually be suppressed by a large Poisson ratio. Otherwise, if no partial cancellation occurs, a system with a large piezoelectric response will in general also show a strong response of the spontaneous polarization to epitaxial strain.

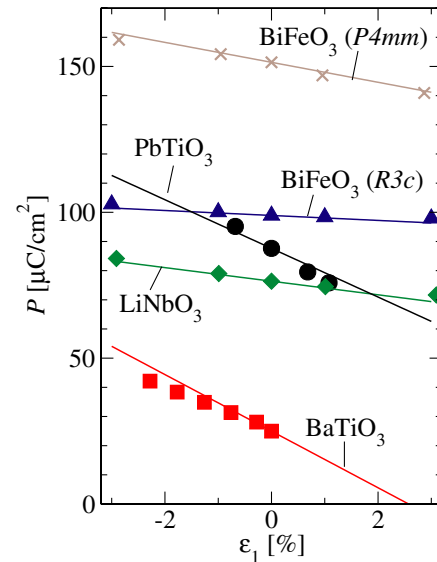


FIG. 2 (color online). Spontaneous polarization  $P$  for several ferroelectrics as a function of epitaxial strain  $\epsilon_1$ . Symbols represent directly calculated values, lines are calculated using Eq. (2), and the effective piezoelectric constants are from Table III. Directly calculated values for BaTiO<sub>3</sub> and PbTiO<sub>3</sub> are taken from Refs. [4,6], respectively.

The question of whether epitaxial strain enhances the polarization in ferroelectric thin films therefore leads to the more general problem of what determines the piezoelectric (and elastic) response of a certain material. An overview of recent first principles research on piezoelectricity is given in Ref. [29]. Some insight can be gained by separating the piezoelectric response into a “clamped ion” part and an “internal strain” part. The first measures the strain-induced change in polarization for fixed internal ionic coordinates, whereas the latter gives the contribution resulting from the relaxation of the ions. It can be shown that the internal strain part of the piezoelectric tensor contains the inverse of the force constant matrix [30]. Therefore, if the force constant matrix has rather small eigenvalues, i.e., low energy phonon modes, and these modes couple to a certain strain component, the piezoelectric response can be very large and is then dominated by the internal strain part. In a soft mode system at least one phonon energy goes to zero at the ferroelectric transition temperature and the piezoelectric response diverges [10]. Far away from the transition temperature the energy of this soft phonon mode increases again. This can in principle explain the decrease of the (zero temperature) value of  $c_{33}$  in the series BaTiO<sub>3</sub>, PbTiO<sub>3</sub>, BiFeO<sub>3</sub>, and LiNbO<sub>3</sub>, i.e., for increasing Curie temperatures. For  $c_{31}$  both contributions to the piezoelectric constant are comparable and of opposite sign, leading to no clear trend in magnitude or sign for the different materials.

In summary, regarding the three possible explanations (i) to (iii) given in Ref. [8] for the different strain behavior in different systems, we can now conclude that the structural symmetry (i) mainly affects the value of the Poisson ratio, whereas the “general stability” of the ferroelectric state (iii) determines the order of magnitude of  $c_{33}$ . No clear influence of the different displacement mechanisms (ii) or of the “multiferroicity” of BiFeO<sub>3</sub> can be identified from our results, although the displacement mechanism can, of course, influence the stability of the ferroelectric state. It seems that in most cases a large  $c_{33}$  leads to a strong dependence of the polarization on epitaxial strain, and conversely a strong epitaxial strain dependence is usually connected with a large  $c_{33}$ . Nevertheless, a small (large) Poisson ratio can enhance (suppress) this effect and the same is true for the sign and magnitude of  $c_{31}$ . It also becomes clear from our results that not every ferroelectric necessarily shows a strong sensitivity to epitaxial strain, and that the response for a certain material can be calculated from its piezoelectric tensor and Poisson ratio using Eq. (2) for all experimentally accessible epitaxial strains.

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