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Flexoelectricity in ATiO₃ (A = Sr, Ba, Pb) perovskite oxide superlattices from density functional theory

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Flexoelectric coefficients for several bulk and superlattice perovskite systems are determined using a direct approach from first principles density functional theory calculations. A strong enhancement in the longitudinal flexoelectric coefficient has been observed in the 1SrTiO₃/1PbTiO₃ superlattice with alternating single atomic layers of SrTiO₃ and PbTiO₃. It was found that atomistic displacement, charge response under strain, and interfaces affect the flexoelectric properties of perovskite superlattice systems. These factors can be used to tune this effect in dielectrics. It was further found that the calculated Born effective charge for an ion under the influence of strain can differ significantly from the bulk value. These insights can be used to help search for more effective flexoelectric materials to be implemented in electromechanical devices. Published by AIP Publishing.

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I. INTRODUCTION

The polarization of a dielectric material due to a strain gradient, known as flexoelectricity, has drawn interest in recent years for possible implementation in functional devices. Because the strain gradient breaks the symmetry that constrains piezoelectricity to a limited set of crystal symmetries, flexoelectricity can exist in insulators of any symmetry class. Flexoelectricity enables some electromechanical functionality that is otherwise not possible, such as the mechanical polarization switching of ferroelectrics and generation of voltage in non-piezoelectric materials. In addition, novel flexoelectric material systems hold promise for numerous modern technologies, such as sensors, actuators, and energy harvesters. For instance, Bhaskar et al. demonstrated that a nanoscale flexoelectric electromechanical actuator could perform at the same level of a micron scale piezoelectric PZT actuator. Moreover, flexoelectricity can be used to enhance the electromechanical response in lead-free piezoelectrics. In macroscale material systems explored to date, flexoelectricity has a relatively weak effect compared with piezoelectricity. However, flexoelectric effects can be substantial at the nanoscale due to the possibility of much larger strain gradients. Significant progress has been made recently in understanding flexoelectric effects in materials. In particular, high permittivity materials have been of primary interest as the flexoelectric effect is thought to scale with the dielectric constant. However, the influence from interfaces, which are ubiquitous in nanoscale devices, is poorly understood.

Oxide superlattices contain a large number of interfaces in a small volume, amplifying the potential for large interfacial effects. In addition, oxide superlattices exhibit many novel properties and functionalities that their bulk counterparts do not. These properties have been used to improve specific functionality of the materials, such as the strong polarization enhancement observed in CaTiO₃/SrTiO₃/BaTiO₃ superlattices. Furthermore, due to advances in fabrication technology, high quality oxide superlattices and epitaxial heterostructures can be obtained, paving the way for next generation electronics and photonics. Interfaces in superlattices break the rotation and the translation symmetry of the crystal and modify the bond distance and angles, consequently inducing changes in atomic and electronic structures. Furthermore, the mismatches of spin, charge, orbital, or lattice symmetry at the interfaces of superlattices provide a powerful means to tune the interfacial properties. The variations in charge and valence states at the interfacial region change both the electronic structure and the charge response under strain, which may profoundly affect the flexoelectric response.

Experimentally, the static flexoelectric response of a material is measured by bending a material in a particular geometry and measuring the displacement current. It has been shown that these experiments alone cannot determine the full flexoelectric tensor. Even in the case of simple cubic systems, at least one of the three flexoelectric coefficients must be independently measured by a different method. In particular, it is difficult to measure the longitudinal flexoelectric coefficient due to challenges of creating a uniform longitudinal strain gradient. Theoretical methods have the capacity to mitigate this problem as well-defined strain gradients can be applied to a system, such as in the direct calculation method developed by Hong et al.

In this study, first principles density functional theory (DFT) calculations are employed to evaluate the longitudinal flexoelectric response of 1/1 layered superlattices consisting of SrTiO₃ (STO), BaTiO₃ (BTO), and PbTiO₃ (PTO). The approach developed by Hong et al. is used to examine the effect of the A-site (A = Sr, Ba, Pb) and interfaces on the flexoelectric response of the 1SrTiO₃/1PbTiO₃ (SPT) and 1BaTiO₃/1SrTiO₃ (BST) superlattices. Additionally, the variation of the Born effective charge tensor across the supercell is examined.
II. METHODOLOGY

Flexoelectricity is described as the polarization response due to a strain gradient related by a fourth rank tensor according to

\[ P_z = \frac{1}{\Omega} \sum_{\beta,k} Z_{\kappa,\beta} f_{\kappa,\beta}, \]

where \( P_z \) is the spontaneous polarization in the z direction, \( \Omega \) is the unit cell volume, \( Z_{\kappa,\beta} \) is the Born effective charge for the atom in the bulk material, and \( f_{\kappa,\beta} \) is the displacement of the atom along the direction relative to the centrosymmetric structure. Calculations performed here were used to determine the \( f_{3333} \) flexoelectric coefficient.

Calculations based on DFT within the generalized-gradient approximation (GGA) were performed using VASP (Vienna \textit{ab initio} Simulation Program).\textsuperscript{31,32} The ion-electron interactions were treated by a projected-augmented wave (PAW) method with local-density approximation (LDA) and generalized gradient approximation (GGA) functionals. Particularly for GGA, we employed PBEsol\textsuperscript{33} functionals including the valence electrons of 5d, 6s, and 6p for Pb, 5s, 5p, and 6p for Ba, 4s, 4p, and 5s for Sr, 3d and 4s for Ti, and 2s and 4p for O. A cut-off energy of 600 eV was used based on convergence tests. Brillouin zone integration was sampled using 4x4x2 Monkhorst-Pack k-point grids. To satisfy the periodic boundary condition, supercells with periodically repeating geometries of atoms were constructed, as shown in Fig. 1. A sinusoidal strain gradient was applied in these supercells, which has an equal magnitude at the beginning and ending of the cells. This continuity maintains the periodic boundary condition. The supercell size required for the calculation of the flexoelectric coefficient was found through convergence tests. The static ion-clamped dielectric matrix was found for each system using the density functional perturbation theory within VASP in order to determine the Born effective charge tensor. For ferroelectric systems, the initial spontaneous polarization is subtracted from the final system polarization in the coefficient calculations to determine the net polarization only from the flexoelectric effect.

A summary of the structural calculations is detailed in Table I in comparison with previous results.\textsuperscript{34–37} Initial calculations of parent bulk oxides showed that smaller supercells were not able to maintain strain gradients, leading to lower polarizations, and thus smaller calculated flexoelectric coefficients. This effect was seen to dissipate as the supercell size increased, approximately at a size of 14 unit cells. For this reason, all calculations were performed on supercells with 14 unit cells. Additionally, calculations were performed at several magnitudes of max strain, which reveals the variation that can be expected from these calculations. The magnitudes of strain were chosen to be within the range physically allowed without fracture. This convergence at 14 unit cells and variation across different strains can be seen in Fig. 2. The results were similar between the LDA and GGA potentials (PBEsol), with PBEsol potentials typically resulting in slightly smaller calculated flexoelectric coefficients. Superlattice systems were modeled to be epitaxially deposited on an STO substrate resulting in the lattice constants in the a and b direction equal to that of STO. The superlattice systems STP and BST were tetragonal in structure, layered 1/1, and assumed to be grown in the (001) direction on a SrTiO\textsubscript{3} substrate. Therefore, the in-plane lattice constant of SrTiO\textsubscript{3} was used for the superlattices and the c/a ratio of the superlattices was systemically optimized.

### Table I. Structure of structural properties using PBEsol in this study.

<table>
<thead>
<tr>
<th>System</th>
<th>a (Å)</th>
<th>Reference a (Å)</th>
<th>c/a</th>
<th>( P_z ) (µC/cm\textsuperscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>STO</td>
<td>3.898</td>
<td>3.90 (Ref. 34)</td>
<td>1</td>
<td>...</td>
</tr>
<tr>
<td>BTO</td>
<td>3.985</td>
<td>3.985 (Ref. 35)</td>
<td>1</td>
<td>...</td>
</tr>
<tr>
<td>PTO</td>
<td>3.971</td>
<td>3.937 (Ref. 36)</td>
<td>1</td>
<td>...</td>
</tr>
<tr>
<td>SPT</td>
<td>3.898</td>
<td>1.019</td>
<td>36.26 (Ref. 37)</td>
<td>...</td>
</tr>
<tr>
<td>BST</td>
<td>3.898</td>
<td>1.035</td>
<td>30.98</td>
<td>...</td>
</tr>
</tbody>
</table>

The resulting ground state of the \(^1\text{BaTiO}_3/\text{SrTiO}_3\) (BST) system is found to be ferroelectric, while the \(^1\text{BaTiO}_3/\text{STO}\) (STP) system is found to be paraelectric.
The $^{1}$SrTiO$_3$/PbTiO$_3$ (SPT) system is antiferrodistortive (AFD)/ferroelectric with rotations of oxygen octahedra in the $xy$ plane of $+7.3^\circ$ and $-1.1^\circ$ in alternating layers. This is similar to the result of Bousquet et al. who found rotations of $+6.2^\circ$ and $-1.8^\circ$.

In comparing the calculations of the flexoelectric coefficients for the three bulk oxides, we see the BTO bulk system has a larger longitudinal flexoelectric coefficient than STO and PTO, which both have similar coefficients to each other (Fig. 3). These values agree reasonably well with previous results. Both superlattice systems have substantially higher flexoelectric coefficients, with SPT having the highest magnitude of the systems examined. The flexoelectric constant of SPT is over five times greater than the parent oxide STO.

The underlying cause for the enhanced flexoelectric coefficient in the SPT superlattice system can be seen by analyzing the individual polarization contributions for each atom in the system. As can be seen in Fig. 4, the overall enhancement in the polarization of the SPT system over its bulk constituents lies largely in a decrease in magnitude of polarization from the oxygen atoms. This leads to the net positive polarization being significantly greater even without an enhancement in the polarization from the positive ions. While the charge changed slightly between these systems, the primary difference in the polarization lies with the displacement of the atoms, particularly the oxygen atoms in these superlattices with strong interfacial effects.

The BST system B-site has polarization contributions between those of the bulk constituents and the A-site polarization contributions are greater than STO and of about equal magnitude with BTO. This shows that the atomic site contributing the most to the flexoelectric polarization enhancement in the superlattice systems can differ based on which atoms are in the system. The BST system also does not have as much of an increase in the polarization as the SPT system, which accounts for its relatively smaller flexoelectric coefficient compared with SPT.

One final observation in this study is that the calculated Born effective charges vary throughout the system, depending on the magnitude of displacement at any given point in

![Fig. 2](image-url)  Calculated longitudinal flexoelectric coefficients for tetragonal strontium titanate across different strains and supercell sizes using LDA and GGA potentials showing convergence with increasing supercell size.

![Fig. 3](image-url)  Comparison of the magnitudes of the calculated longitudinal flexoelectric coefficients.

![Fig. 4](image-url)  Volume normalized polarization contribution from each atom type in the strained supercell at the position where the strain gradient is at a maximum.
FIG. 5. Relationship between displacement from the centrosymmetric position in the z-direction and Born effective charges in the z-direction for the titanium atoms in strontium titanate across different system sizes.

the supercell. This magnitude of change was also correlated with the system size as is shown in Fig. 5. These variations of calculated Born effective charge can be significant (~0.1 e) suggesting that this difference can have an impact on the calculated local polarization in the supercell, and thus impact the flexoelectric calculation. This is significant as many calculations of the flexoelectric effects in materials involve assuming the bulk Born effective charges,\textsuperscript{24} instead of calculating them for the strained system.

**IV. CONCLUSION**

In conclusion, this study has demonstrated that perovskite oxide superlattices, such as SPT, have a strong enhancement in the longitudinal flexoelectric coefficient compared with its constituent compounds. Many factors affect the magnitude of the flexoelectric effect, particularly the displacement of atoms in the strained system. The Born effective charge values differ locally within a strained unit cell from the bulk values, indicating that this should be considered for future flexoelectric calculations using this direct method. This study suggests a possible means to tune the flexoelectric response of materials for flexoelectric devices through composition and interfacial effects. These insights can be used to aid in the search for more effective flexoelectric materials.

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