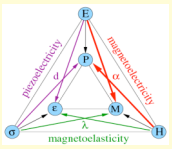
Inducing multiferroic behavior in tri-layer superlattices: A first principles study

Alison J. Hatt and Nicola A. Spaldin
Materials Department, University of California, Santa Barbara, CA 93106

Magnetoelectric Multiferroics

- Combine ferromagnetism and ferroelectricity
- Exhibit coupling between the ferroic properties
- Promise great technological advantages

But…
Magnetism and ferroelectricity are *contraindicated*

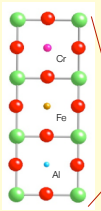


- Ferroelectrics generally have d^0 e^- configuration
- Ferromagnets need d electrons
- Thus, difficult to combine in a single material

Heterostructures may potentially circumvent this incompatibility

In a heterostructure, we can manipulate material properties via:
- Interface effects
- Internal fields
- Imposed symmetry

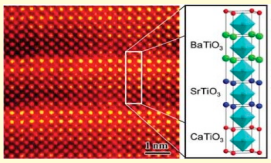
Tri-layered $LaAlO_3/LaFeO_3/LaCrO_3$



- A-B-C-A-B-C… stacking
- Two magnetic layers
- No ferroelectric layers
- Broken inversion symmetry may constrain ions in polar, ferroelectric state

Motivation for approach

- New growth techniques allow epitaxial growth with atomic level precision
- Studies show enhanced ferroelectricity in layered perovskites [1,2,3]
- May be induced/enhanced by
  - strain
  - electrostatics
  - inversion symmetry breaking

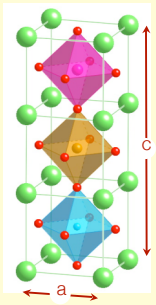


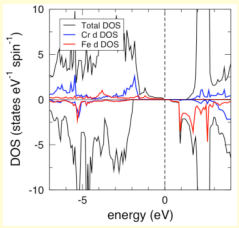
Epitaxially grown tri-layer superlattice of $BaTiO_3/SrTiO_3/CaTiO_3$, from Lee, et al. Nature, 2005

References
[1] H. N. Lee et al., Nature **433,** 395 (2005).
[2] N. Sai et al., Phys. Rev. Lett. **84,** 5636 (2000).
[3] J. Neaton and K. Rabe, Appl. Phys. Lett. **82,** 1586 (2003).
[4] G. Kresse and J. Furthmuller, Phys. Rev. B **54,** 11169 (1996).
[5] G. Kresse and D. Joubert, Phys. Rev. B **59,** 1758 (1999).
[6] R. D. King-Smith and D. Vanderbilt, Phys. Rev. B **47,** 1651 (1993).

Methodology

- Density functional theory (as implemented in VASP) [4]
- LDA+U
  - U/J_{Fe} = 6.0/0.6 eV
  - U/J_{Cr} = 5.0/0.5 eV
- PAW potentials [5]
- 6x6x2 Monkhorst-Pack k-point mesh
- Plane wave energy cut off = 450 eV
- Berry phase method polarization calculations [6]





Left: Unit cell of La(Al,Fe,Cr)O_3.
Right: Density of states for the reference structure showing a band gap of 0.32 eV.

Reference structure

- Constrain in-plane lattice constant a=3.85 Å
  - simulates growth on SrTiO3 substrate
  - $LaAlO_3$ (a=3.75 Å) is under tensile strain
  - $LaFeO_3/LaCrO_3$ (a=3.85/3.84 Å) are unstrained
- Adjust out of plane lattice constant, c, to minimize stress
- Constrain atoms to high-symmetry positions
- Ferromagnetic ordering, magnetization=440 emu cm^{-3}

Reference structure has unswitchable polarization of 0.21 μC/cm²

(Polarization given relative to the non-polar single-component material at same lattice parameters)

Structural optimization

- Again, constrain a=3.85 Å
- Use optimized c=11.43
- Move atoms to minimize Hellmann-Feynman forces
- Maintain tetragonal symmetry
- Results in a relaxed ground state, 0.14 eV lower in energy than reference structure

Optimized structure has relaxed ground state, but no further polarization

Epitaxial strain

- Constrain in-plane lattice parameter, a
- Adjust out-of-plane parameter to conserve volume of fully-optimized cell
- Relax atomic positions
- Polar transition occurs at strain=-0.016 (compressive), a=3.76 Å

strain = $(a - a_0)/a_0$
a_0=equilibrium value

Epitaxially strained structure has strong, switchable polarization

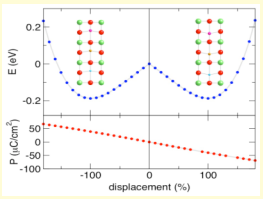
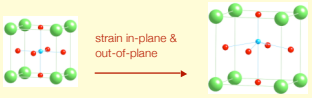


Figure: Energy and polarization as a function of distortion for epitaxially strained La(Al,Fe,Cr)O_3 with a=3.95 Å. The minima correspond to the relaxed structures with off-centered cations. The central energy maximum corresponds to the centrosymmetric structure.

Negative pressure

- Create "negative pressure" by expanding all lattice parameters equally, constraining c=3a
- Relax atomic positions
- Polar transition occurs at strain=0.001, a=3.85 Å



Negative pressure structure has strong, switchable polarization

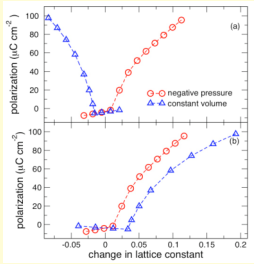
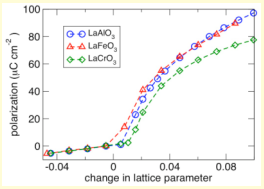


Figure: Calculated polarizations of negative pressure and epitaxially strained La(Al,Fe,Cr)O_3 as a function of the change in (a) in-plane and (b) out-of-plane lattice constants relative to the lattice constants of the fully relaxed structure.

Parent compounds

- Illuminate the role of tri-layering by looking at parent compounds in bulk form, $LaAlO_3$, $LaFeO_3$,and $LaCrO_3$
- All become polar under epitaxial strain and negative pressure
- Average polarization:
  $(P_{LAO}+P_{LFO}+P_{LC})/3$ = 47.0 μC cm^{-2}
- Tri-layered polarization:
  P= 38.9 μC cm^{-2}

→ Tri-layering is not required for ferroelectricity



Polarization as a function of the change in lattice parameter for the parent compounds under negative pressure. All three demonstrate the same behavior as the tri-layered heterostructure, becoming polar at small values of tensile strain.

$LaAlO_3$, $LaFeO_3$,and $LaCrO_3$ all polar under 2D and 3D epitaxial strain

Conclusions

- Tri-layering alone does not induce ferroelectricity
- The parent compounds all become polar under epitaxial strain and negative pressure
- Tri-layering modifies the polarization, providing greater control of material properties

Acknowledgements
Funding provided by NSF IGERT program, grant no. DGE-9987618 and NSF Division of Materials Research, grant no. DMR-0605852