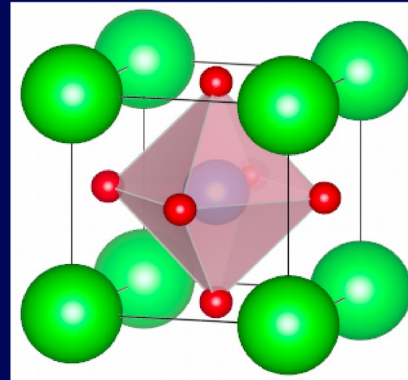


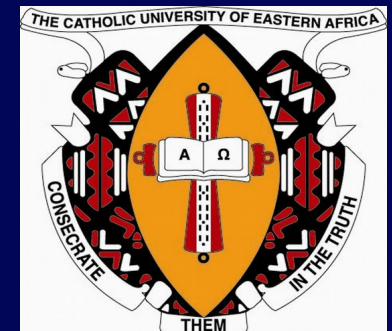
The Interplay of Lattice Distortion and Bands near the Fermi Level in $ATiO_3$ (A=Ca, Sr, Ba)



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and George Amolo**



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Most important paper that we followed in this work

PHYSICAL REVIEW B

VOLUME 8, NUMBER 12

15 DECEMBER 1973

Empirical Relation between Energy Gap and Lattice Constant in Cubic Semiconductors

Richard Dalven

Department of Physics, University of California, Berkeley, California 94720

(Received 25 June 1973)

<https://doi.org/10.1103/PhysRevB.8.6033>

Introduction

Perovskites

```
graph TD; A[Perovskites] --> B[Inorganic Oxide perovskites]; A --> C[Halide perovskites]; B --> D[Intrinsic perovskites]; B --> E[Doped perovskites]; C --> F[Alkali perovskites]; C --> G[Organo metal perovskites];
```

Inorganic Oxide perovskites

Halide perovskites

Intrinsic perovskites

Doped perovskites

Alkali perovskites

Organo metal perovskites

In this work, we focus on ABO_3 perovskites.

$CaTiO_3$
 $SrTiO_3$
 $BaTiO_3$

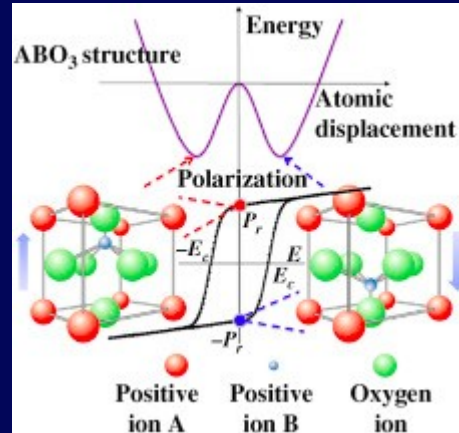
Why are Perovskites popular?

The research of transition metal oxides is today in a momentous stage.

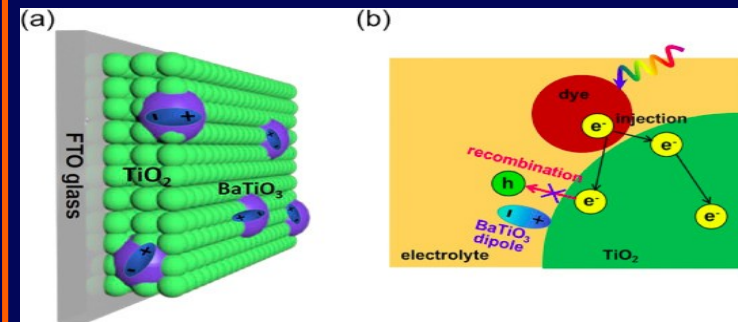
This can be equated to the evolution of the semiconductor field many years ago.

<https://doi.org/10.1126/science.1151094>

- Electronics
- Photovoltaics
- Ferroelectrics
- Spintronics
- Superconductivity
- Multiferroics



<https://doi.org/10.1016/B978-0-12-811180-2.00002-5>



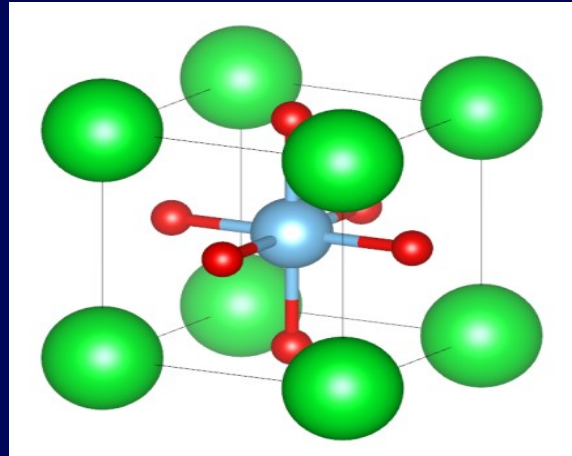
<https://doi.org/10.1016/j.jpowsour.2017.03.049>

PHYSICAL REVIEW B **101**, 174114 (2020)

First-principles study of two-dimensional electron and hole gases at the head-to-head and tail-to-tail 180° domain walls in PbTiO₃ ferroelectric thin films

James Sifuna^{1,2,3,*}, Pablo García-Fernández,¹ George S. Manyali⁴, George Amolo³, and Javier Junquera^{1,†}

Why the titanate class in this study?



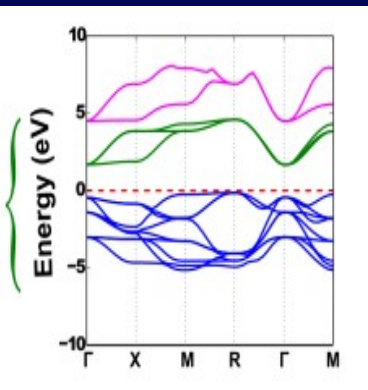
Here we consider the ABO_3 as follows:

- The **A** cation is considered to be chemically inactive
- The **B-metal** is an interconnected transition metal complex
- The **O** anion is not in anyway isolated

This implies that the behavior of the $ATiO_3$ materials in this study will highly depend on the complex behavior of Ti 3d.

The valence band will mainly be comprised of oxygen and the conduction is mainly comprised of Ti.

We expect this scheme in all transition metal perovskites.



Problem statement

- Bandgap engineering in materials has become a norm in many studies. Scientists have managed to employ both volatile and non-volatile approaches in tuning the bandgaps.
- A study done by **Richard Dalven** decades ago seems interesting. He employed a non-volatile approach in tuning the bandgap of cubic semiconductors. He found out that the bandgap (E_g) varied inversely proportional as the square of the lattice parameter (a_0).
- We employed the same technique to ascertain if the same relationship can be seen in the $ATiO_3$ ($A=Ca, Sr, Ba$) materials.
- Literature reports the same in these chosen materials. The bandgap varies with the lattice but it is not yet clear if the bandgap changes as a result of **electrostatic**, or **covalency** or **both**.
- We sought to find out why and how the the bandgap varies in our selected insulators.

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Objectives of this study

This work employs *ab initio* methods to study the interplay between the lattice distortion and the bands near the Fermi level in cubic CaTiO_3 , SrTiO_3 and BaTiO_3 .

Specifics

- To study the relationship between lattice parameter a_0 and band gap in ATiO_3 ($A = \text{Ca}, \text{Sr}$ and Ba).
- To elucidate the origin of lattice-band gap relationship.

Scope of this study

All the calculations were done at 0K and 0Gpa.

The LCAO method as implemented in the SIESTA code was used as the basis sets.

The study focused only on the cubic structures.

The distortions were mild so as to remain in the elastic regime.

Literature review

In 1973, Dalven showed that through non-volatile methods, the band gap E_{gap} of cubic semiconductors varied inversely proportionately as the square of the lattice parameter a_0 .

<https://doi.org/10.1103/PhysRevB.8.6033>

Bousquet *et al* showed that under given conditions of epitaxial strain, BaO could undergo phase transition from paraelectric BaO to ferroelectric BaO.

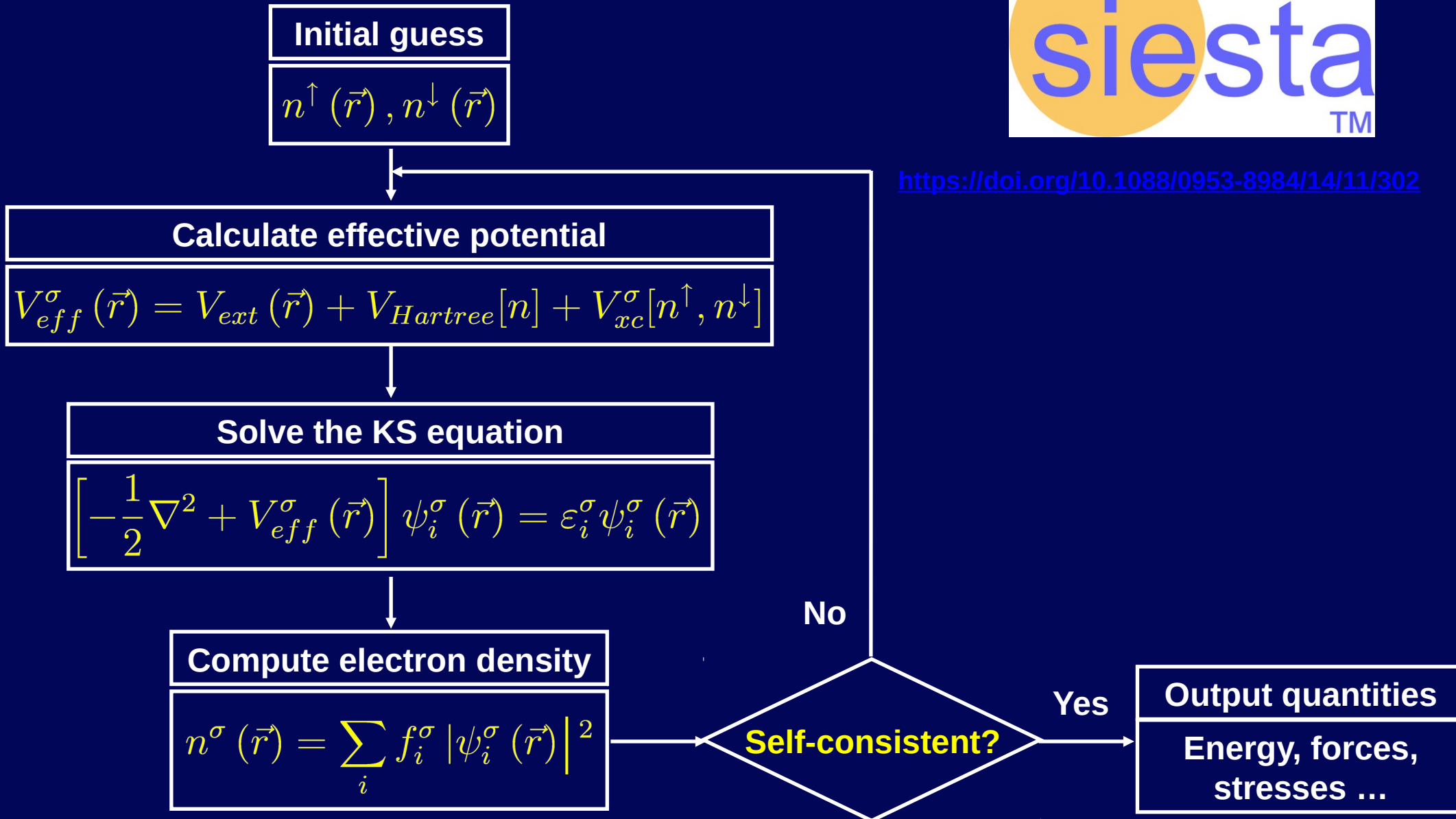
<http://dx.doi.org/10.1103/PhysRevLett.104.037601>

In both studies, no explanation was provided for the relationship between the lattice distortion and changes in the electronic structure of the compounds.

The approach



<https://doi.org/10.1088/0953-8984/14/11/302>



Computational details

We replaced the core electrons with ab-initio norm-conserving pseudopotentials that followed the Troullier-Martins scheme in the Kleinman-Bylander fully non-local separable representation.

Exchange and correlation functions were treated by the generalized gradient approximation (PBE).

We expanded the one-electron eigen states in a set of strictly localized numerical atomic orbitals.

Using plane-wave cutoff of 600 Ry in the representation of charge density, we were able to calculate the corresponding matrix elements between the orbitals, the electronic charge density, the Hartree potentials together with the exchange-correlation potential.

In this calculation, the atomic coordinates were relaxed until the forces were smaller than 0.01 eV/\AA and we ensured that the stress tensor components were below 0.0001 eV/\AA^3 .

Results and discussion

Structural Properties.

	Exp(Ang)	Theoretical (Ang)
CaTiO ₃	3.83	3.89
SrTiO ₃	3.90	3.93
BaTiO ₃	4.00	4.02

It can be noted that the calculated values of the lattice parameter lie slightly above the experimental ones for the three titanates.

This in principle should not raise an alarm since it's a well known problem, in that the GGA-PBE approximation will tend to overestimate the lattice parameters.

<https://doi.org/10.1103/PhysRevLett.77.3865>

In the three titanates, CaTiO₃ has the smallest lattice parameter. Again, this is intentional in that there is a huge relationship in the ionic radius of Ca, Sr, Ba and the lattice parameter.

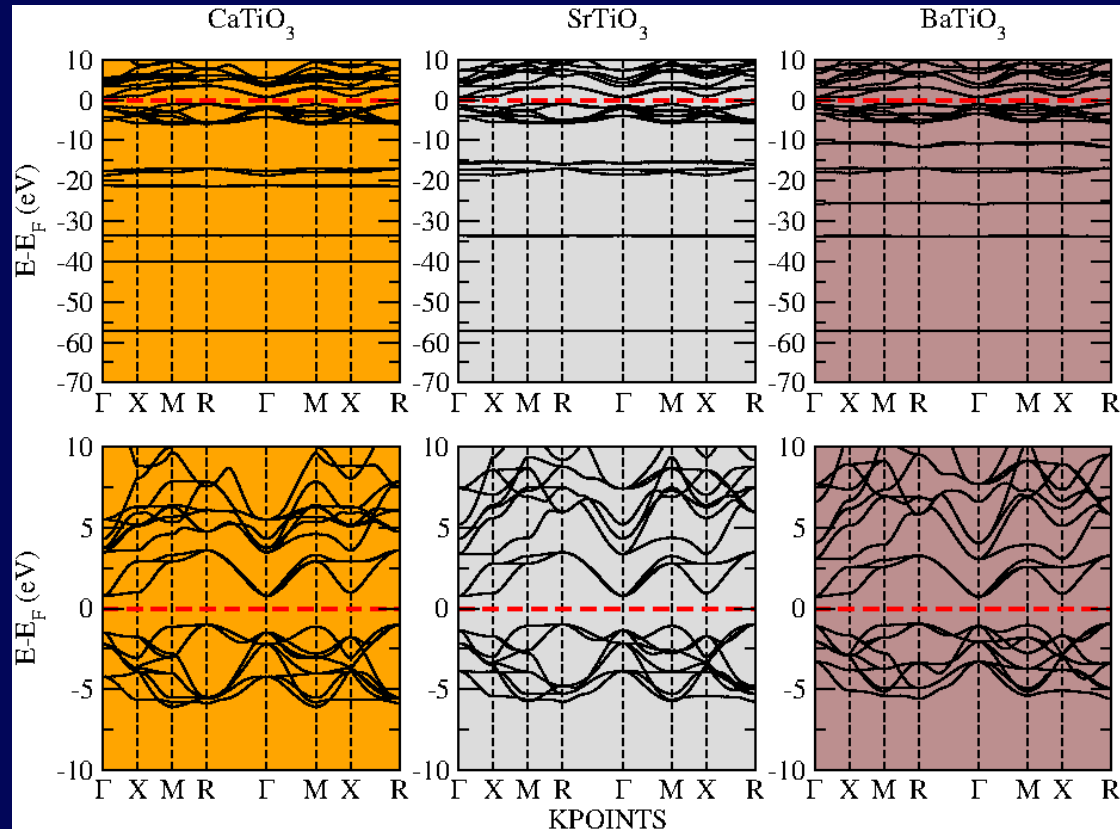
In the three cubic crystal structures of ABO₃, the lattice parameter (*a*) and the ionic radii will tend to obey the relationship in the Equation below.

$$a = \sqrt{2}(r_A + r_O) = 2(R_B + r_O)$$

Where *r_A*, *R_B* and *r_O* are the radii of ions A, B and O in that order.

Results and discussion

Band structure of the three titanates.



Top row, the full band structure is shown, including the bands coming from the semi-core states.

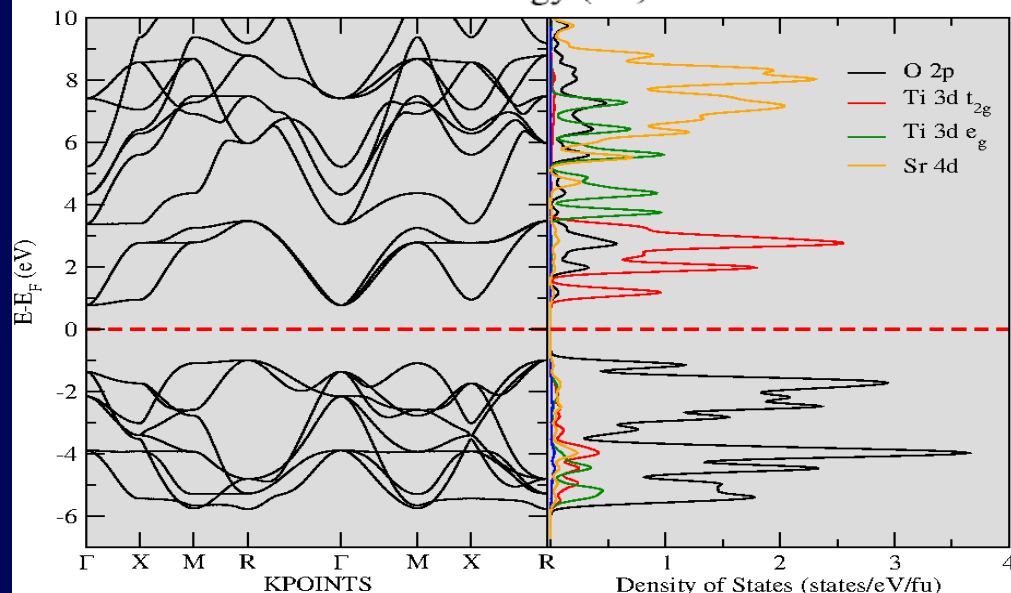
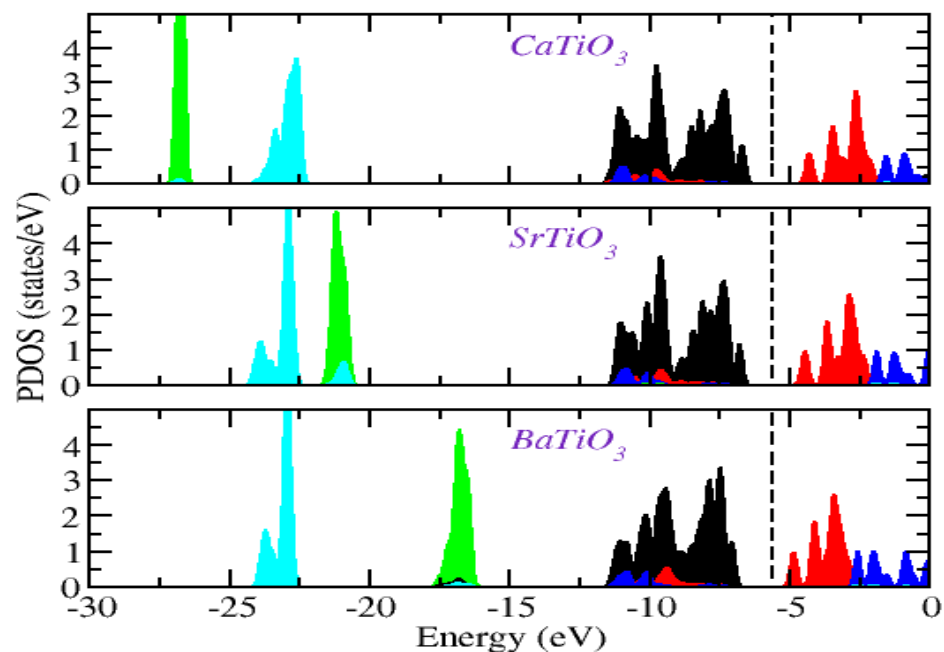
Bottom row displays a zoom highlighting the top of the valence bands (O-2p orbitals) and the bottom of the conduction bands (Ti-3d in character).

The top layer indicates that the three materials have an ionic character between the ranges of -30 eV to -60 eV arising from the well separation of the flat bands. The bottom layer however, shows the covalency character due to the dispersive signatures in the bands at energies between approximately -6 eV to -1 eV.

Apart from the electrostatic couplings, the ions also communicate due to the overlap of their electron wavefunctions. This trait causes hybridization between the p and d orbitals and the formation of covalent bonds between the B-cation and the O-anions at energies ranging between -6 eV to -1 eV.

Results and discussion

Orbital contributions of the the three titanates.



Here, we note that the order in which different orbitals are filled in within a given species of a material plays a role in terms of binding strengths.

From all the aforementioned similarities, we can see a sharp contrast on the A-cation (green) peak with respect to the O 2s states (cyan).

In terms of bonding, ionicity and covalency are depicted in these three titanates. Covalency tends to be more significant if at all we have B-site occupied by a transition element as it is in this case. It is split into both sigma (A/B-O) and pi (B-O) bonding.

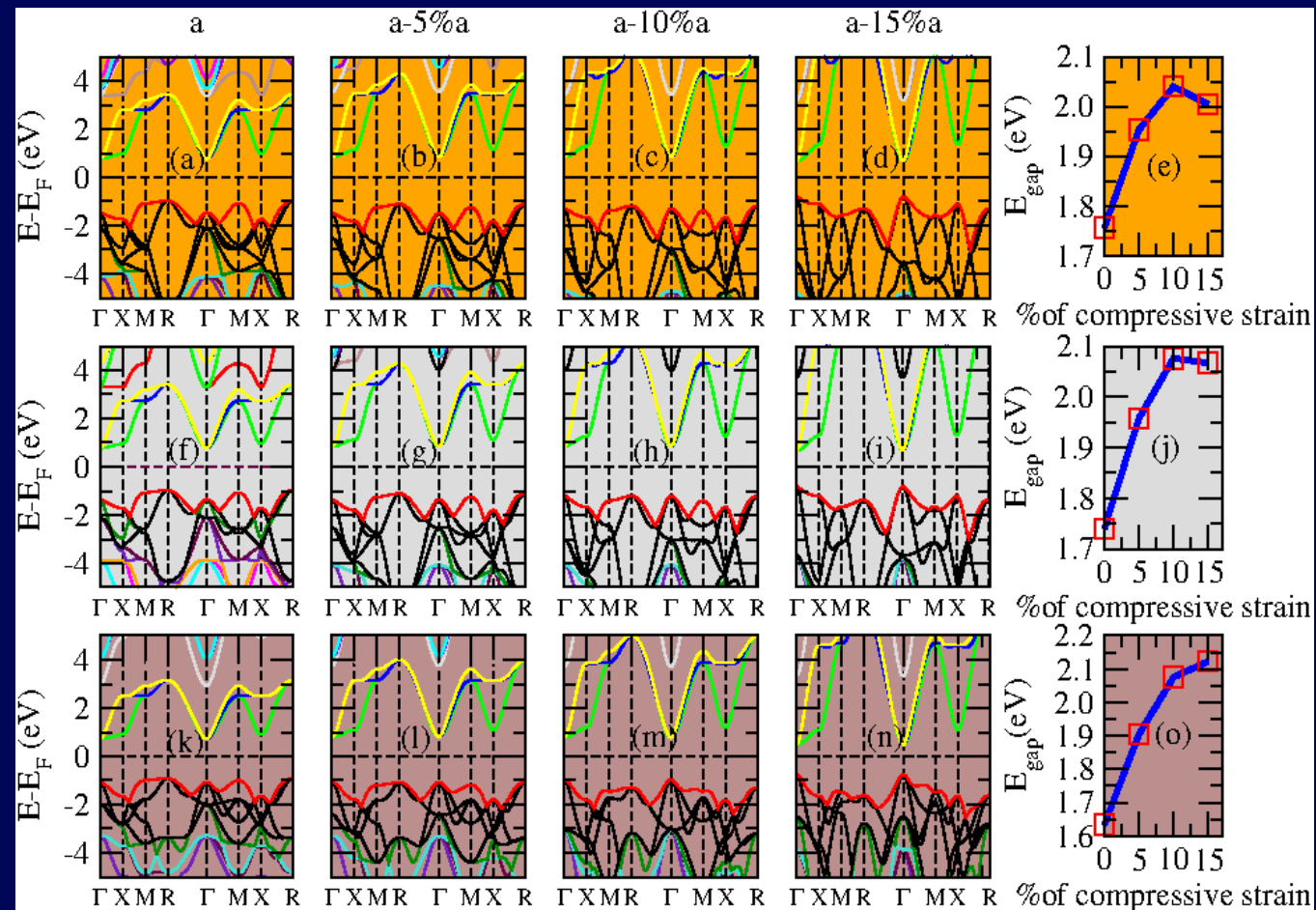
The bottom image shows the composition of the valence band is made mostly of O-2p character while the bottom of the conduction band is populated by the Ti-3d orbitals (t_{2g})

We can see from the PDOS that hybridization occurs between O 2p and Ti 3-d at energies between 1 and 3 eV as well as energies between -6 and -1 eV thus conforming to covalency.

Results and discussion

Interplay of lattice distortion and bandgap in the titanates.

On compression



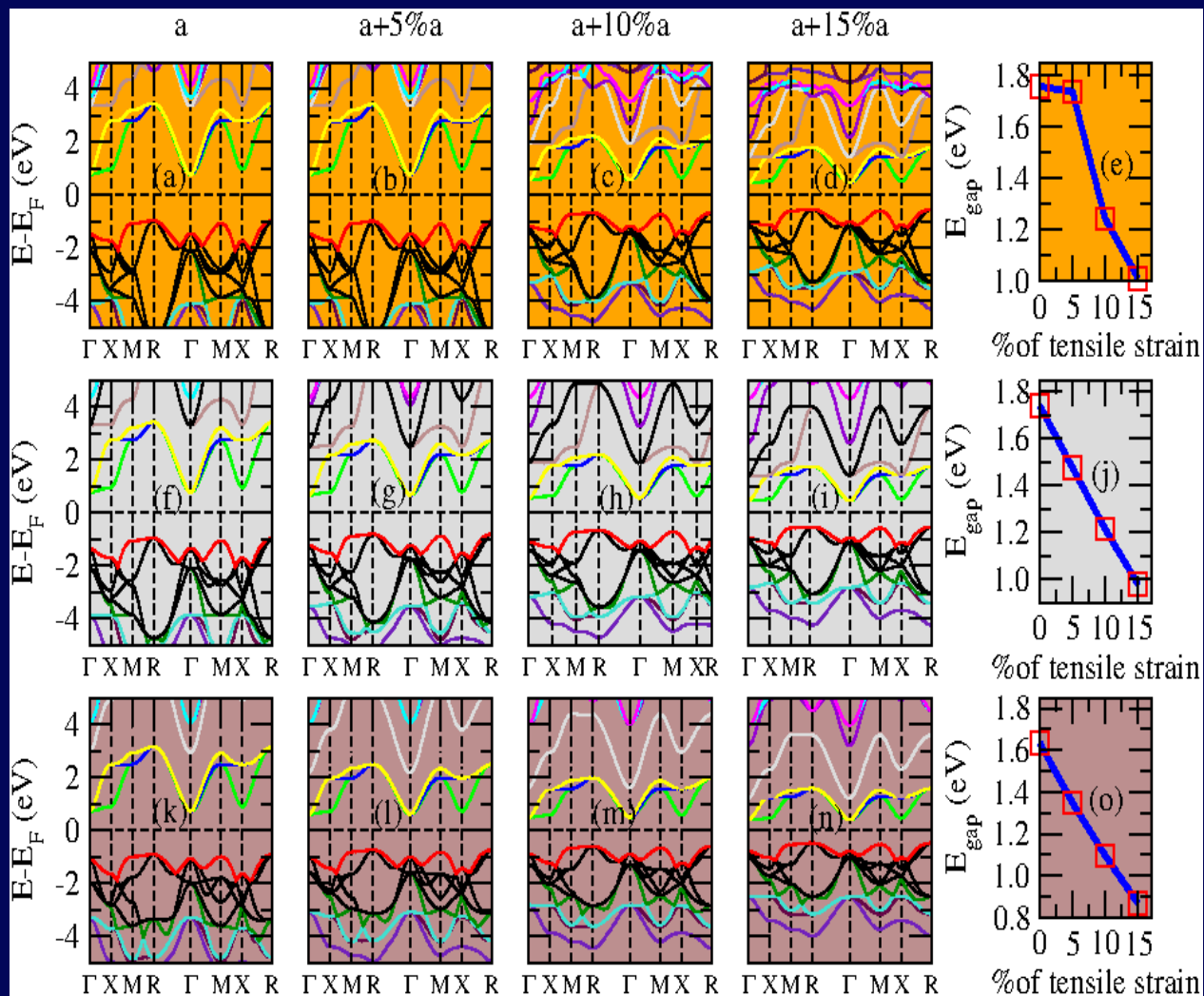
Variation of bandgap with compressive strains in the three titanates. Top row (Orange) represents CaTiO₃, middle row (gray) represents SrTiO₃, while the bottom row (brown) illustrates BaTiO₃.

a – d illustrates the changes in the bandstructure of CaTiO₃ with respective strains. f – i show a similar trend as well as k – n in SrTiO₃ and BaTiO₃ respectively. e, j and o give a schematic variation of the gaps with the values of the strain in the three titanates. It is prudent enough to say that as the lattice is slightly decreased, it is possible to tune the bandgap of these titanates to larger values.

Results and discussion

Interplay of lattice distortion and bandgap in the titanates.

On tensile strain



Variation of bandgap with tensile strain in the three titanates. Top row (Orange) represents CaTiO₃, middle row (grey) represents SrTiO₃, while the bottom row (brown) illustrates BaTiO₃.

a – d illustrates the changes in the bandstructure of CaTiO₃ with respective strains. f – i show a similar trend as well as k – n. e, j and o give a schematic variation of the gaps with the values of the strain. It is prudent enough to say that as the lattice is slightly increased, it is possible to tune the bandgap of these titanates to smaller values.

Conclusion

From this research:

Both covalent and ionic bonds play a crucial role in the bonding of $ATiO_3$.

Band gap of the cubic titanates is highly sensitive to lattice perturbations.

The relationship between the band gap of cubic titanates and their lattice parameter can be

expressed as: $E_{gap} \propto \frac{1}{a^x}$ with x ranging between 2.19 and 3.1.

The origin of the relationship between the band gap of the cubic titanates and lattice distortions has been found to be due to electrostatic and covalent interactions between orbitals at the valence band and the parent atoms of the titanates.

Many thanks to:



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