Lanthanide titanates : A new family of oxide materials for photovoltaic applications

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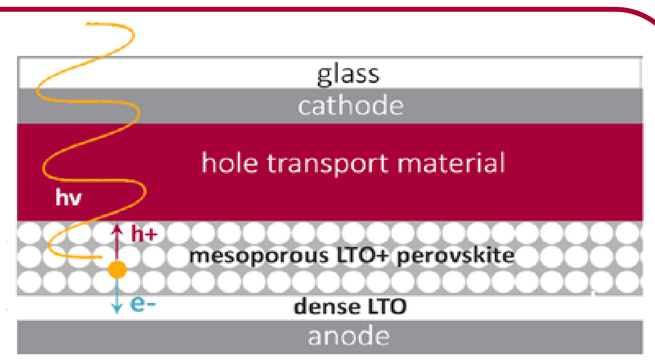
INTRODUCTION

In the context of the energy crisis we are facing, extensive studies have been dedicated to the identification of new materials to efficiently convert solar light into electricity thanks to the photovoltaic effect. Various approaches based on different architectures and implementing a wide choice of materials have been pursued. In this work, we focus on third-generation dye sensitized solar cells (DSSC). These solar cells are composed of several layers, one of which is dedicated to electron transport and is typically a n-type oxide, e.g. titanium dioxide. In the context of a collaboration with the Solid State Catalysis and Chemistry Unit of the University of Artois, a new family of oxides has been envisaged as an electron carrier material: lanthanide titanates ($Ln_2Ti_2O_7$), and more specifically lanthanum titanate ($La_2Ti_2O_7$ or **LTO**).

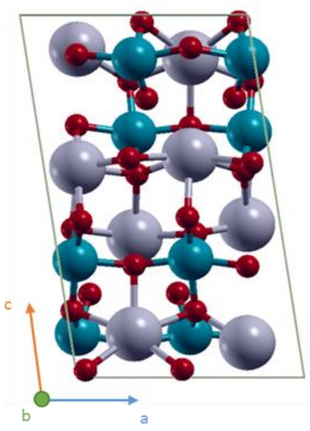


METHODOLOGY

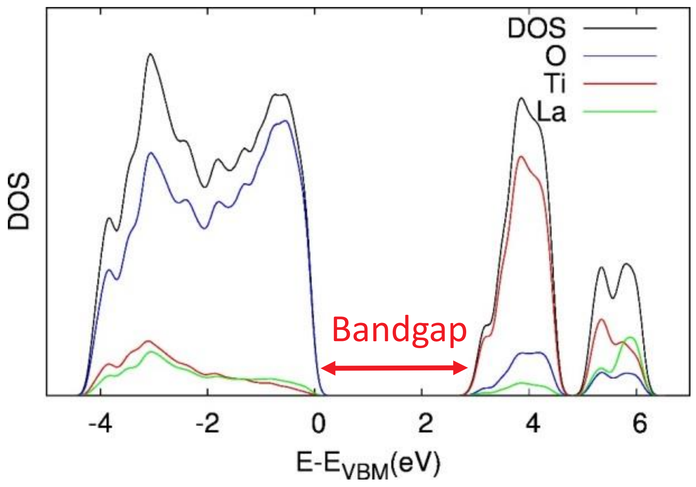
Density Functional Theory (DFT) method (PW/PP).
All calculations were performed at the DFT level with the PBE functional and Ultra soft pseudo-potential, as implemented in Quantum Espresso. First, we studied the bulk material in order too validate the methodology against experiment and other theoretical results. Then, we investigated surface electronic and adsorption properties in a slab configuration. Cut-off = 25/200Ry, 3x4x2 of k-points mesh for bulk and 3x4x1 for surface.

RESULTS

1. $La_2Ti_2O_7$ in Bulk



Lanthanum
Titanium
Oxygen

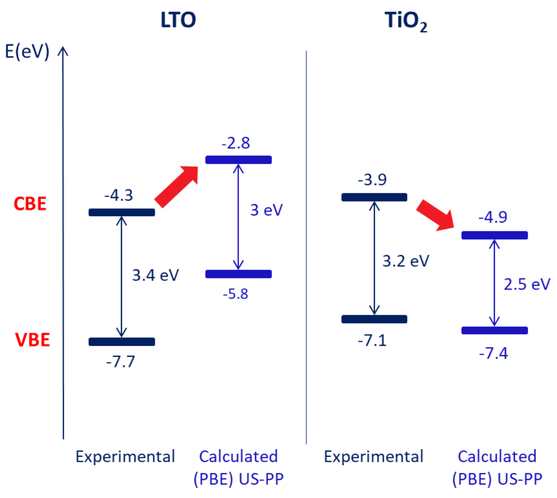


- **LTO electronic properties comparable to TiO_2,** see density of states (VB composed mainly of oxygen, CB composed mainly of titanium and lanthanum negligible).
- **The electronic bandgap is 2.9 eV** vs 3.4 eV experimentally (GGA functional underestimates bandgaps).
- **Promising charge transport properties,** as anticipated from the effective masses

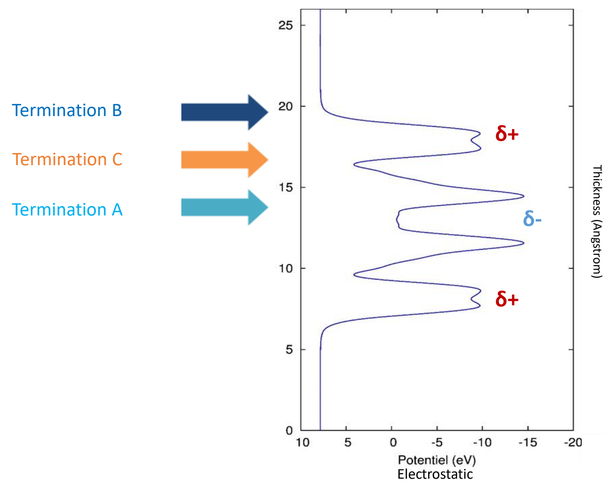
Material	Direction	m^*_e	m^*_h
TiO_2	Γ → X	**0.46**	**-0.77**
$La_2Ti_2O_7$	Γ → Z	**1.12**	-1.92
$La_2Ti_2O_7$	Γ → Y	6.59	**-1.11**

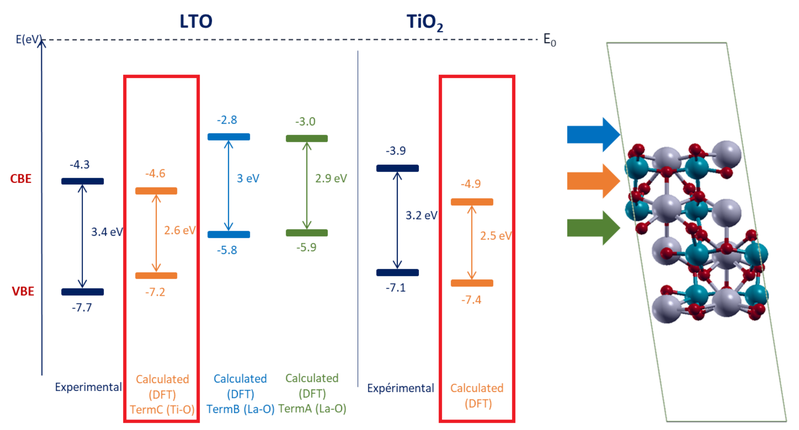
m^* ↘ Charge mobility ↗ bands dispersion ↗

2. $La_2Ti_2O_7$ surface (electronic properties)



- Construction of the LTO surface in the (100) axis
- The zero of the energy scale is fixed at the vacuum in the cell.
- Unexpected result: for **2 very similar n-type oxides, DFT predictions of energy levels shifted in opposite directions with respect to experiment**.
  Why is that?





- Issues with models and/or methods? No (e.g. same picture @ DFT+U level).
- Focus on the material surface, and more precisely, it's **electrostatic potential**:

  ➔ For LTO, **variations of the electrostatic potential according to the surface termination** (in contrast to TiO_2)

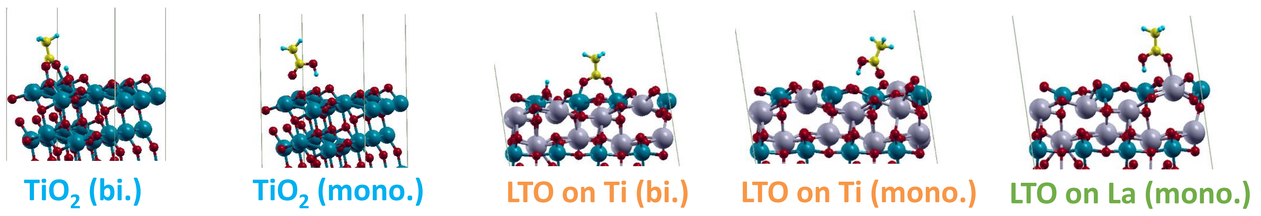
- **What are the effects of surface dipoles on the energy of the electronic levels?** If the interface dipole is negative, the vacuum level shifts up in energy, hence the work function increases. For a positive dipole, it's the opposite.

  ➔ **The energetic position of the band edges respective to the vacuum level shifts according to surface termination.**

➔ **Modulation of the electronic properties of the material with the termination**
➔ The surface with similar electronic properties than TiO_2 is the most stable in energy.
(Termination C = 532.8 mJ/m² **vs** Termination B = 550,7 mJ/m²)

3. $La_2Ti_2O_7$ surface (adsorption properties with acetic acid molecule)

Anchor Geometry	Adsorption energy (eV) on Ti of TiO_2	Adsorption energy (eV) on Ti of LTO	Adsorption energy (eV) on La of LTO
Dissociated bidentate	-0.29	**-1.73**	/
Molecular monodentate	-0.85	-0.92	**-1.01**



TiO_2 (bi.) | TiO_2 (mono.) | LTO on Ti (bi.) | LTO on Ti (mono.) | LTO on La (mono.)

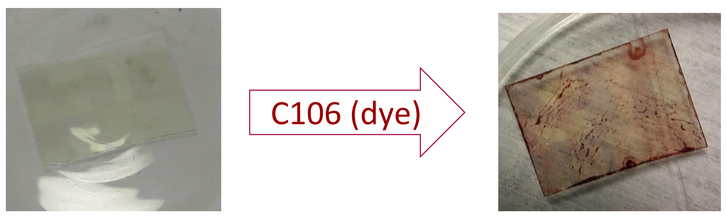
➔ **Carboxylic groups promote large adsorption binding energies on LTO**

CONCLUSIONS

- Promising charge transport properties of bulk LTO
- Modulation of the electronic properties according to the surface
- Favorable energetics for dye adsorption using carboxylic anchoring groups

PERSPECTIVES

- Thin films of LTO (~ 50 nm of grain size)
- Adsorption tests on thin films of LTO vs TiO_2 in progress…



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