FLANDERS INNOVATION & ENTREPRENEURSHIP SIM

Clusters for Growth

How first-principles calculations can help the development of new transparent conductive oxides

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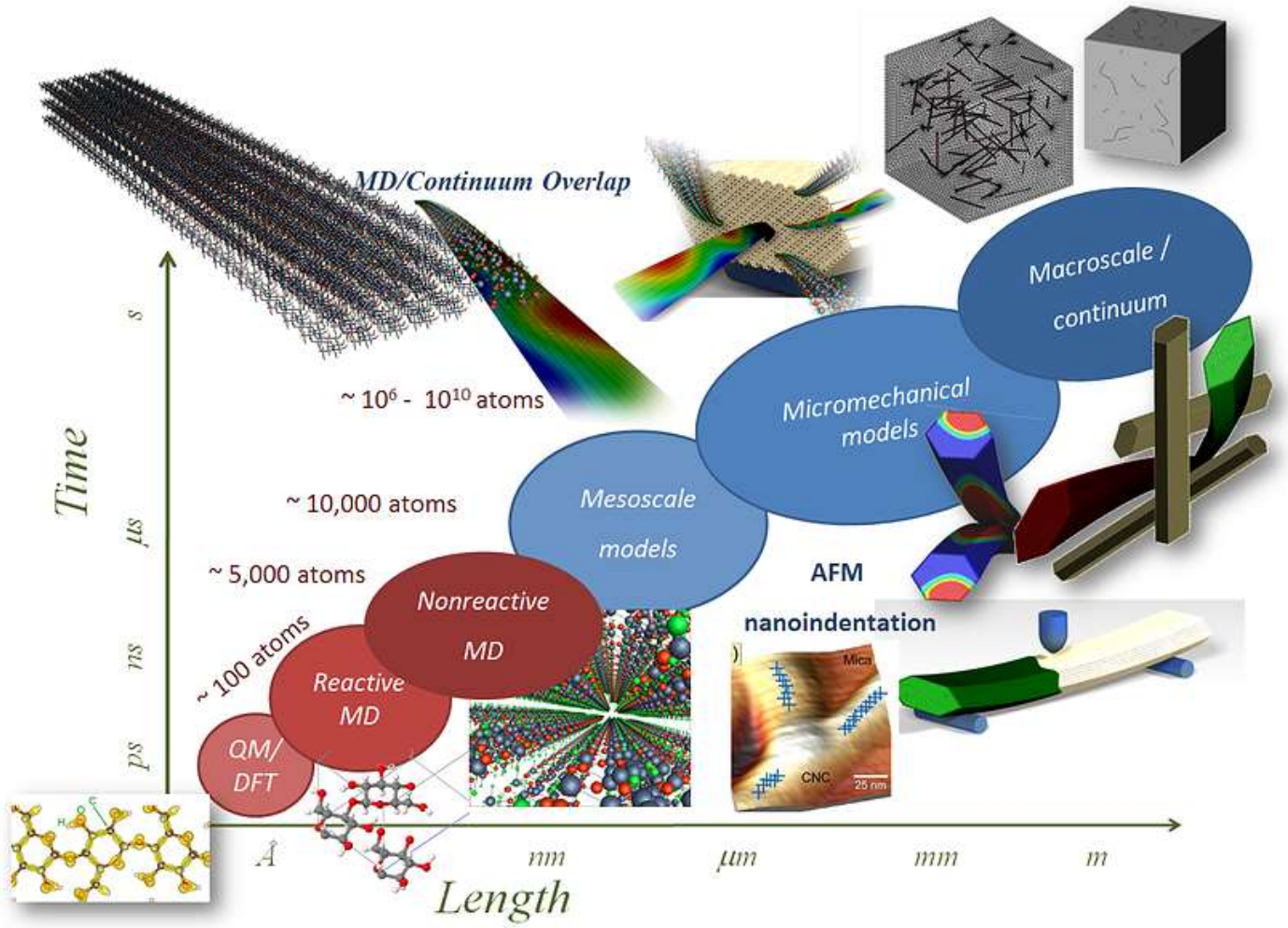
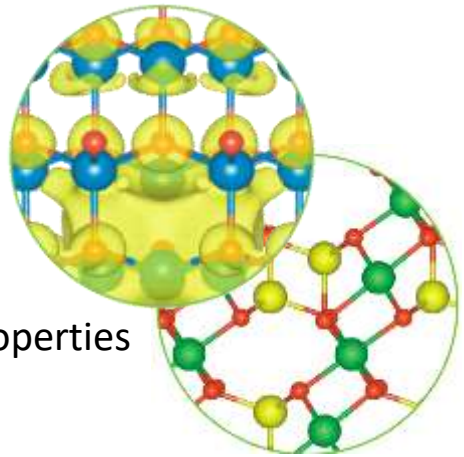
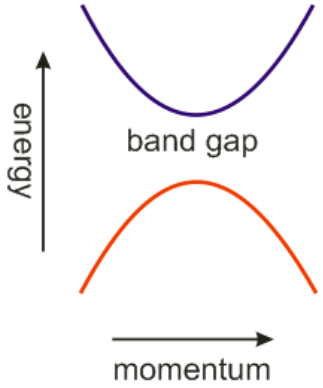
Computational hierarchy



Density functional theory

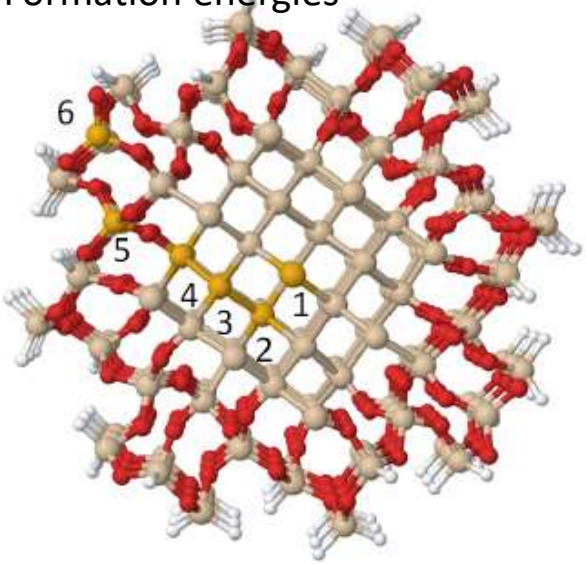


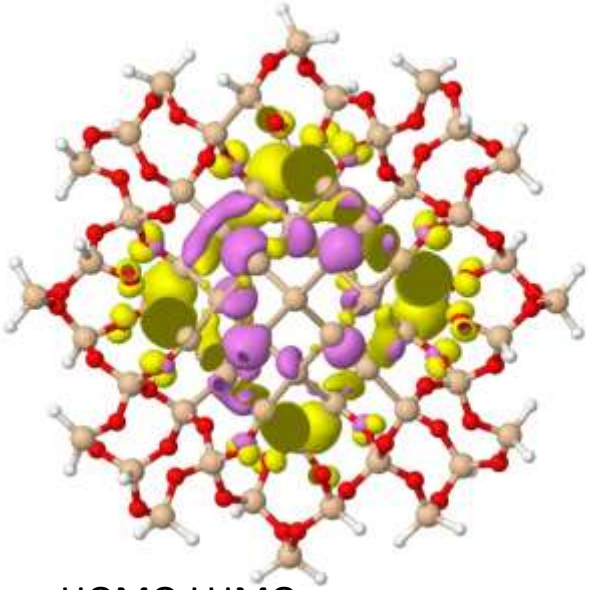
Structural properties



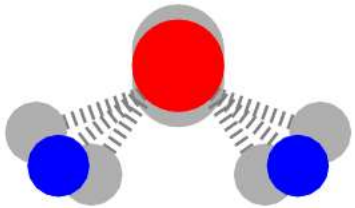
Band structure

Formation energies





HOMO LUMO



Vibrational frequencies

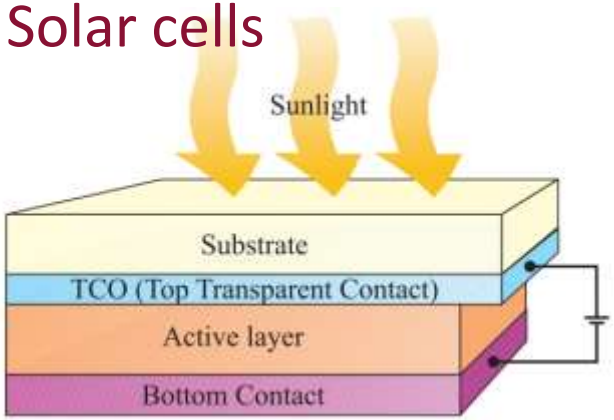
Transparent conductive oxides

Optically transparent

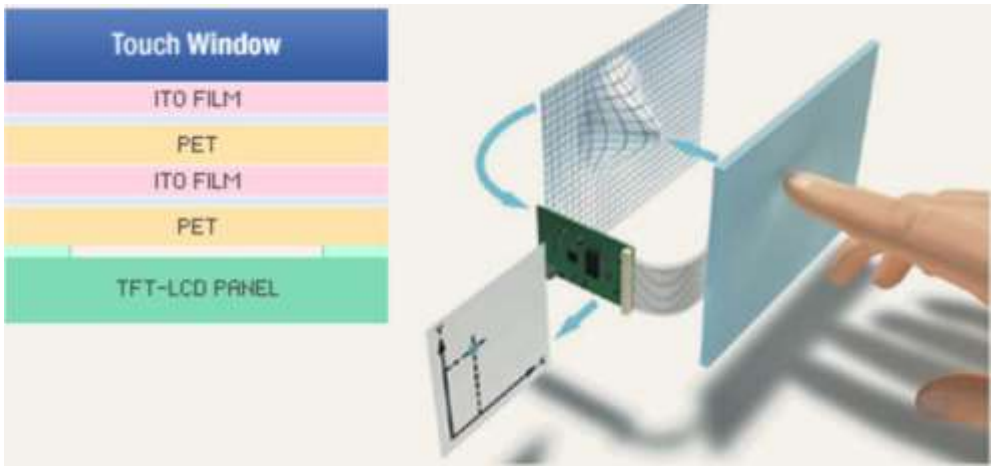
Electrically conductive

Applications

Solar cells



Touch screens



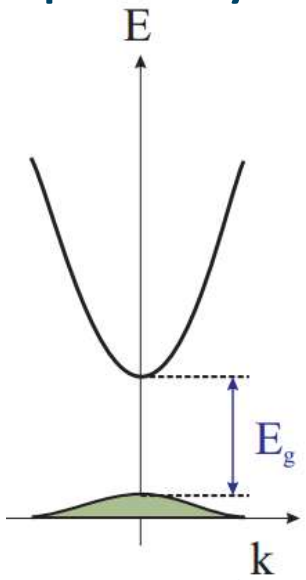
Transparent electronics

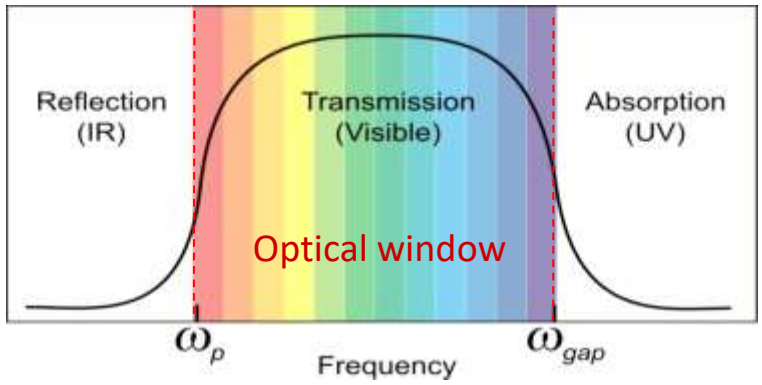
TCO materials: Sn-doped In_2O_3 (ITO), ZnO, SnO_2, CdO, …

Challenges: cost, good p-type TCO's

Transparent conductive oxides

Optically transparent

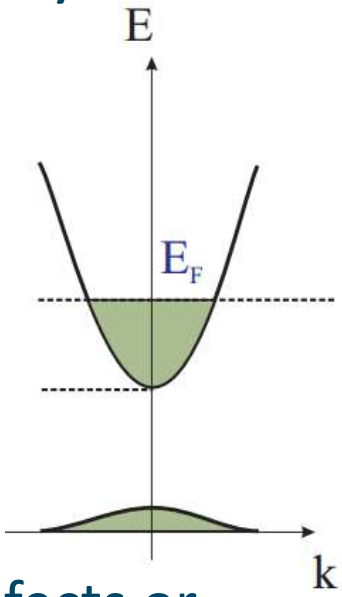




Semiconductors with

band gaps > 3 eV $\Rightarrow$ oxides

Electrically conductive



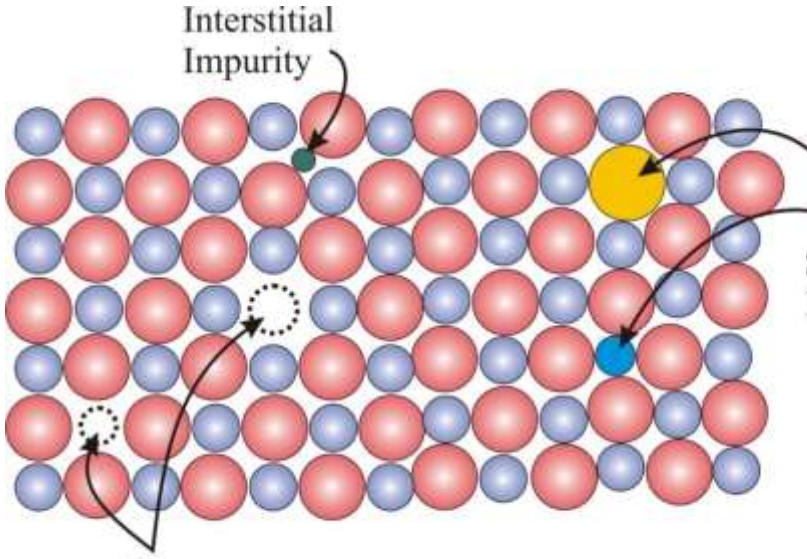
Native defects or

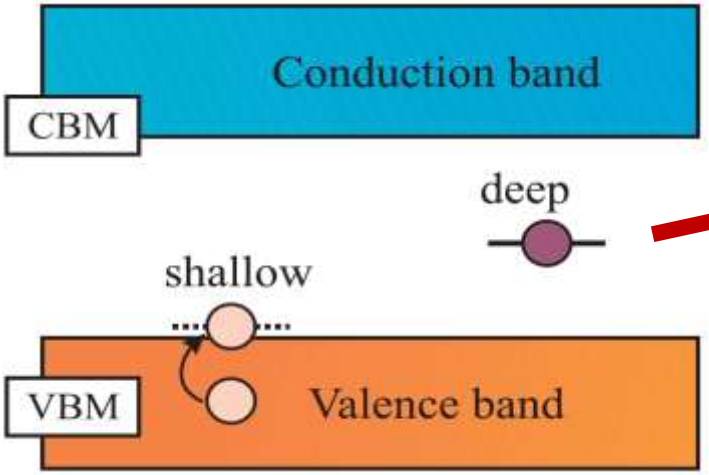
doping with impurities

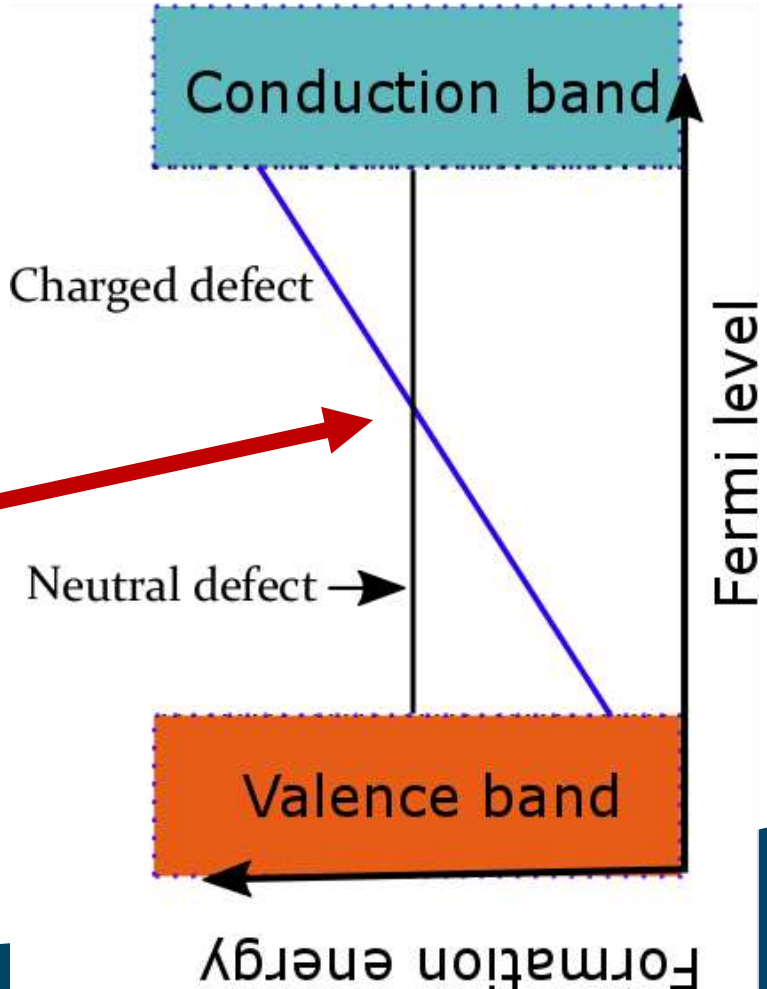
Key physical properties: Band gap, Effective mass of charge carriers, Sign of charge carriers, Characteristics of impurities

Defects in crystals

- Does the native defect/impurity lead to a shallow or deep level? What is its charge state?
- What is its formation energy? What is the effect of the growth conditions?
- Is it a donor or acceptor?





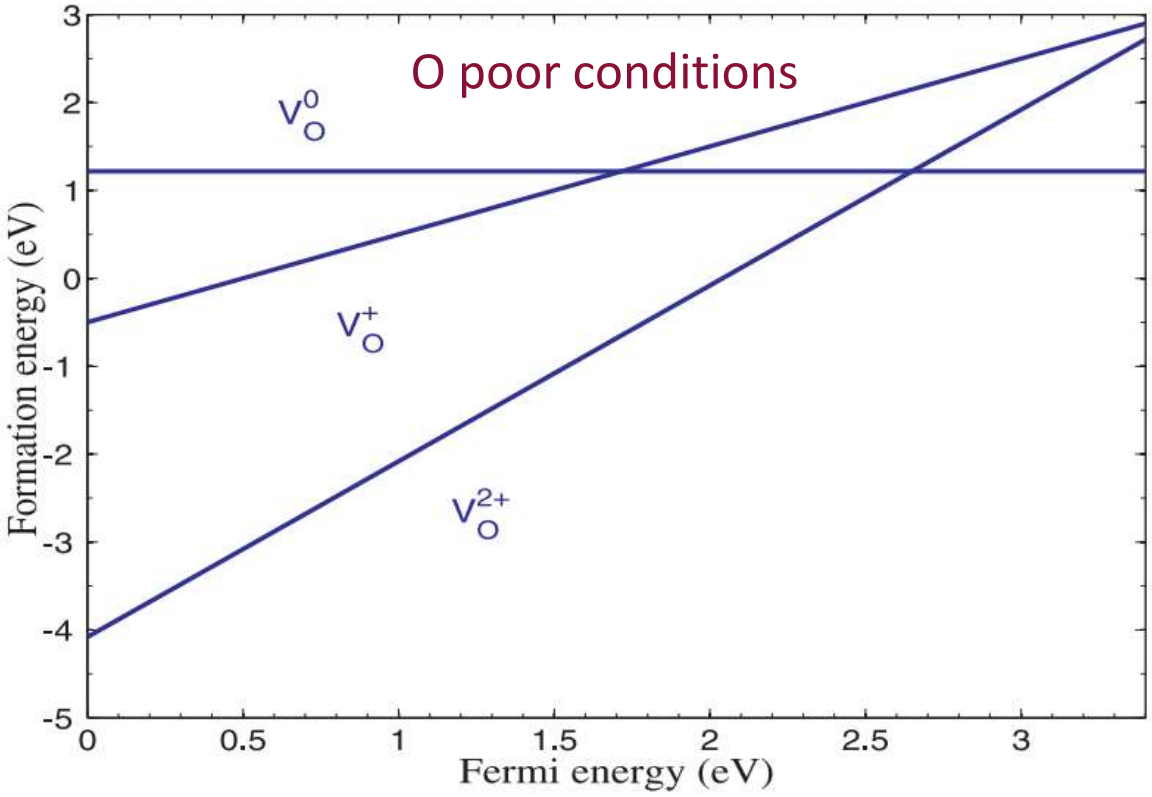


Deep : localized states in the band gap

Shallow : extended states in the CB (VB)

Native defects in ZnO

V_O: oxygen vacancy ➞ deep donor!



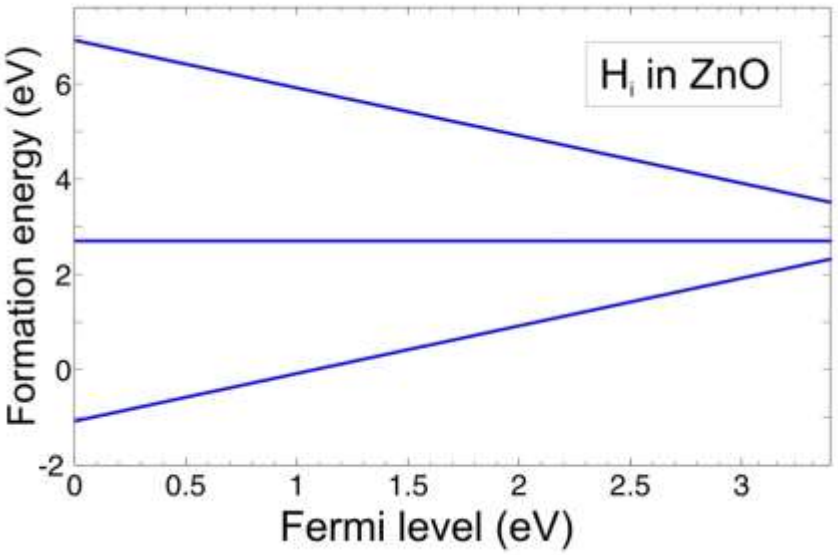
In O rich conditions:
Formation energies
increase by 3.12 eV

Transition levels independent
of growth conditions

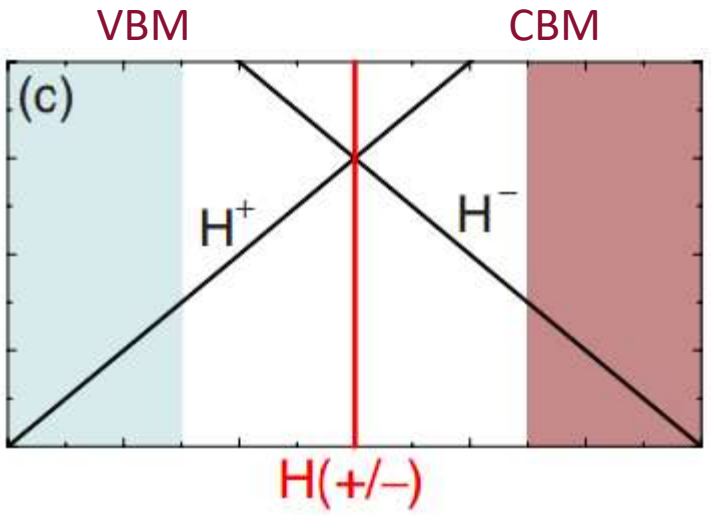
Impurities/dopants in ZnO

Interstitial H ➞ shallow donor!

C. G. Van de Walle, Phys. Rev. Lett. 85, 1012 (2000)



H$_i$ in typical semiconductor



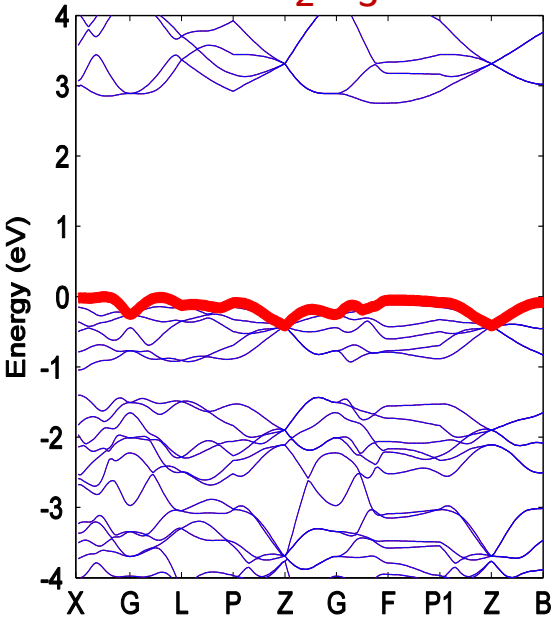
In other semiconductors, H is amphoteric and reduces conductivity

Al_{Zn}, Ga_{Zn}, In_{Zn} , Al_i, Ga_i are all shallow donors ⇒ ZnO is n-type TCO

Cr_2O_3 alloyed with sulfur: a new p-type TCO host

Experimental observation: Li and Mg doped Cr_2O_3 is p-type TCO, but bad conductivity

Cr_2O_3

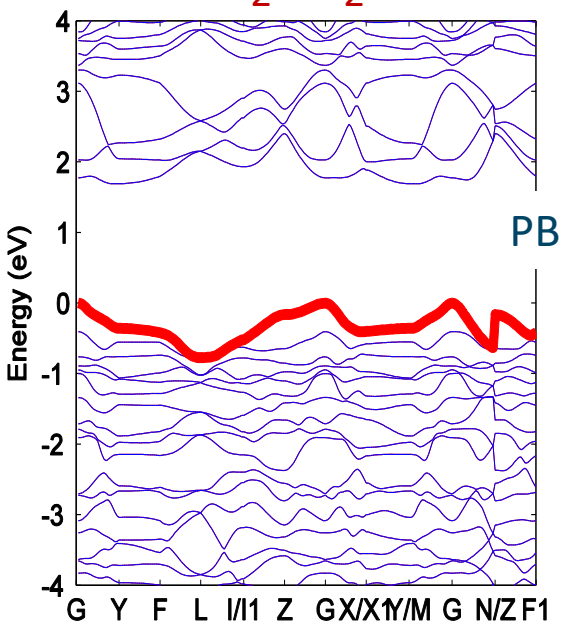


add Sulfur

$$\sigma = ne\mu$$

$$\mu = \frac{e\tau}{m^*}$$

Cr_2SO_2



PBE+U

Hole effective mass = 13.3 m_e

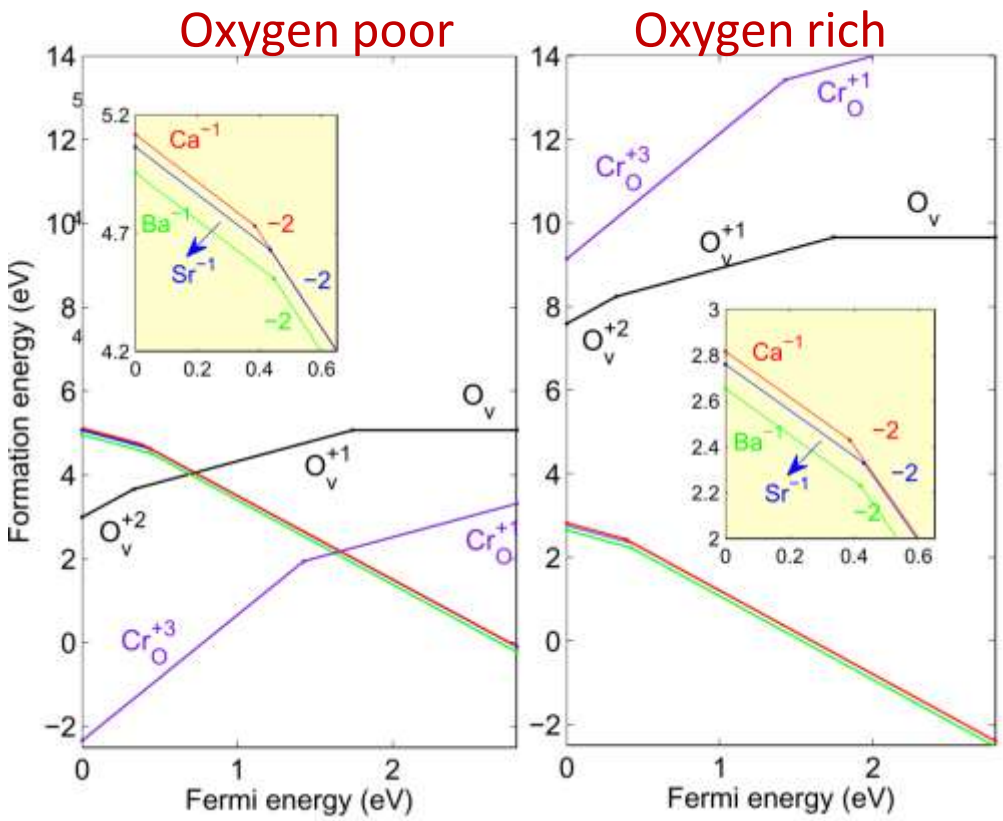
Band gap 3.4 eV

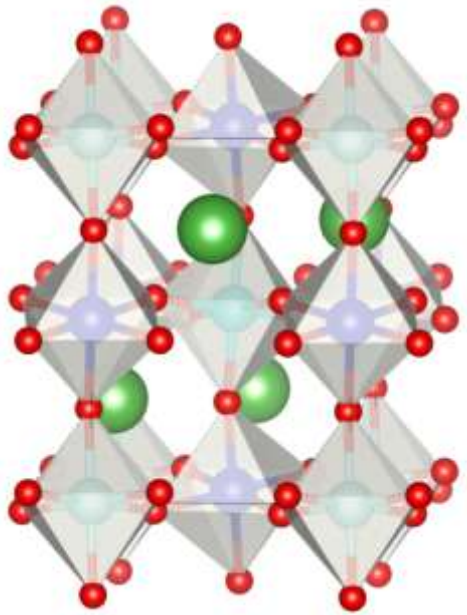
Predicted hole effective mass=1.8 m_e

Predicted band gap 3.08 eV (scGW0)

Doped $LaCrO_3$ as new p-type TCO

Experimental observation: Sr_{La} doping of $LaCrO_3$ leads to p-type conductivity (K. Zhang *et all*, Adv. Mater. 2015, 27, 5191-5195)





Not only Sr, also Ba and Ca act as shallow acceptors

No killer defects in oxygen rich growth conditions

First-principles based high-throughput search for new p-type TCOs

Large class of materials
(virtual or from database)

Binary and ternary oxides in
ICSD/AFLOWLIB databases

Screening criteria

Hole effective mass < 1 m_e
Band gap > 2.5 eV
p-type dopability based on band alignment
Thermodynamic stability

Promising candidates

La_2SeO_2

Afterwards more detailed calculations can be performed:

Na_{La} is indeed a shallow acceptor in La_2SeO_2

Summary

First-principles calculations can help

- to understand known TCOs
- to improve TCOs
- to design new TCOs

Similar first-principles studies can be performed for other technologically important materials like photovoltaic absorber layers, photo-catalytic materials

Computational expertise also useful in other fields