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DTU

Computational Screening of Materials for Water Splitting

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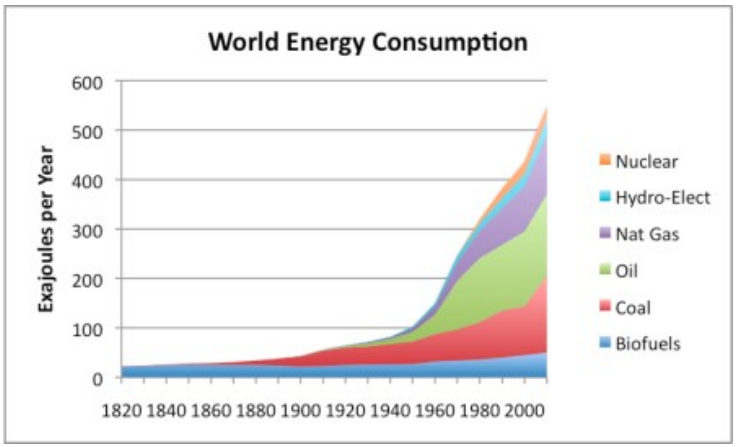
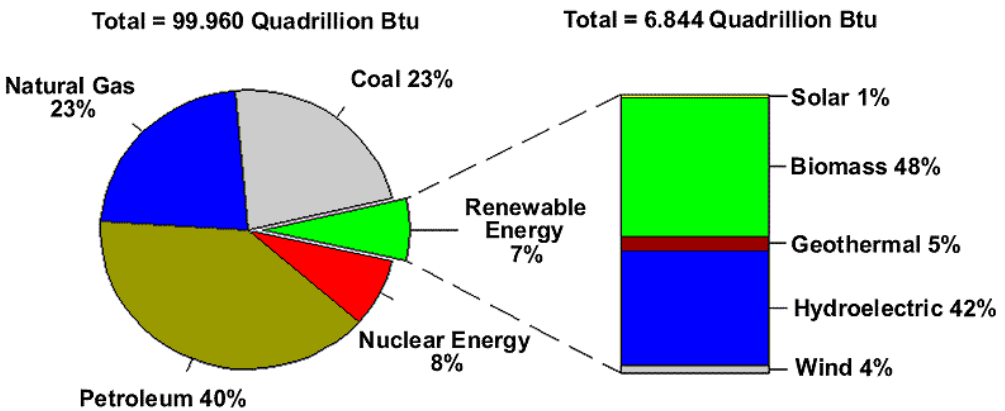
GPAW Workshop
22 May 2013

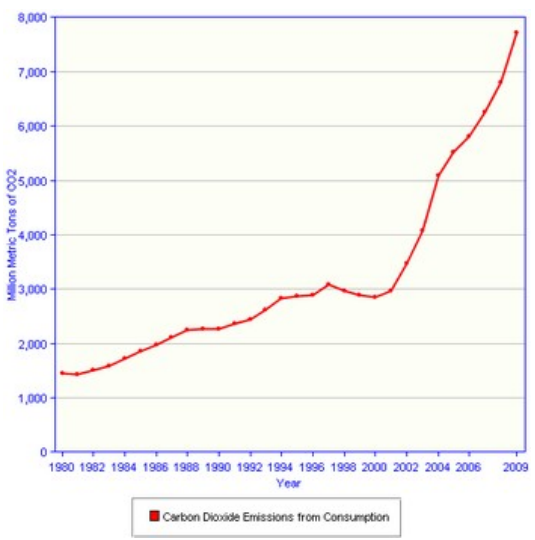
The World Needs Clean Energy

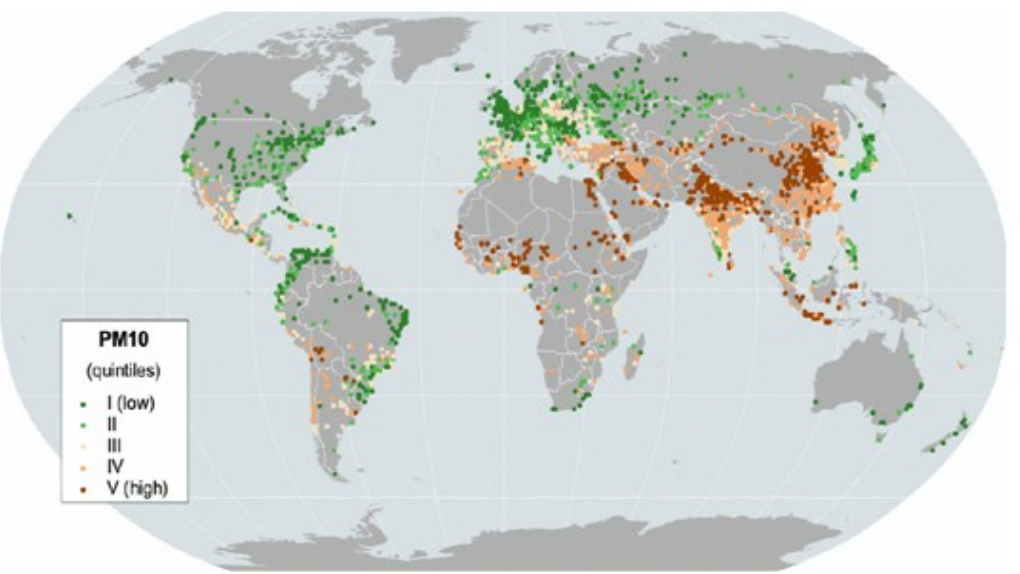
More/cheap energy





Less pollutants (CO_2, NO_x, PM10)



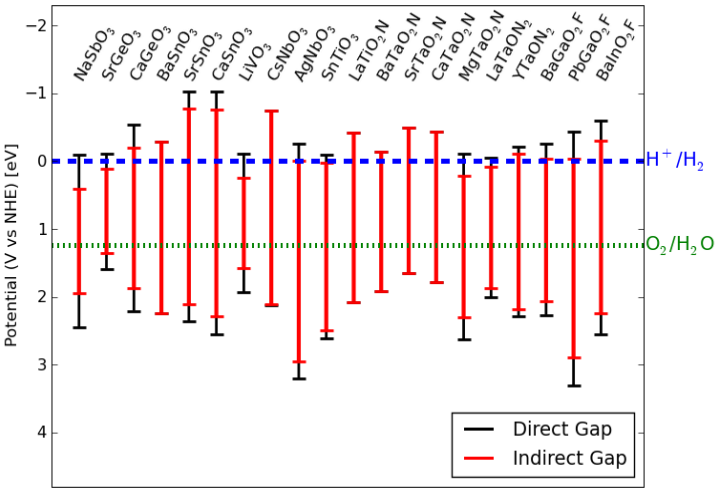


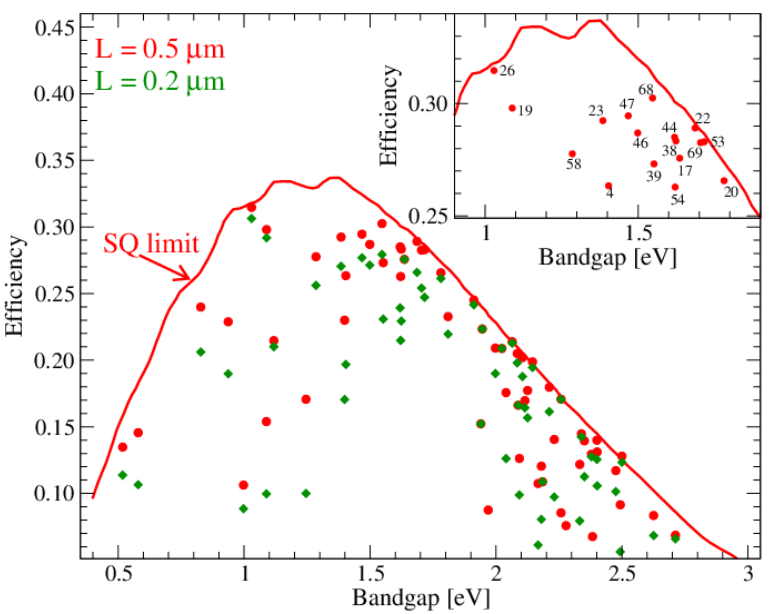
Conclusions

Few materials (40) identified for one- and two-photon water splitting;

The GLLB-SC potential works well for bandgap calculations;

17 materials proposed for single-layer thin film solar cell.





Photoelectrochemical Cell

Computational search for materials able to collect the visible part of the solar spectrum and to split water in oxygen and hydrogen.

Complicated process:

- Light absorption;
- Electron-hole mobility;
- Induce reactions.

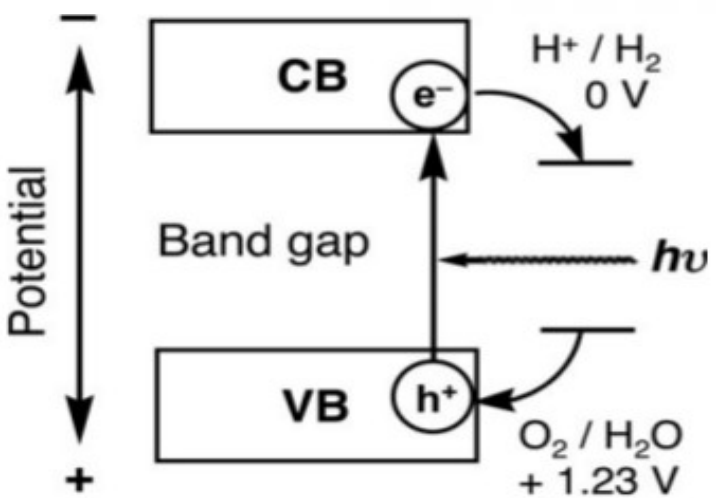
Few examples: TiO_2, GaN:ZnO, $ZnGeN_2$:ZnO

Fujishima and Honda, *Nature* **238**, 37 (1972).

Maeda *et al.*, *JACS* **127**, 8286 (2005).

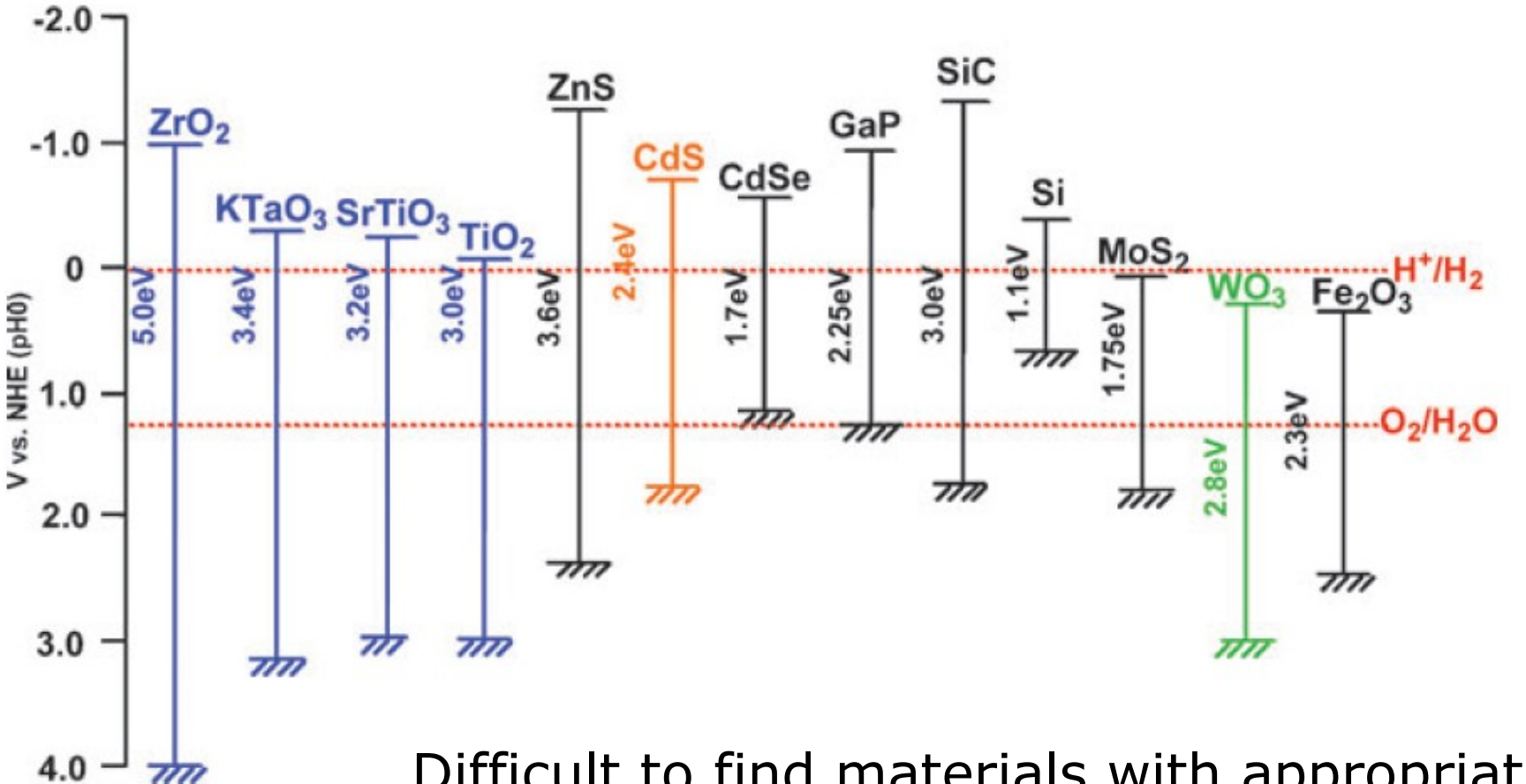
Materials for Water Splitting

1) **Chemical/structural stability**;
2) **Bandgap in the visible range** (1.5 - 3 eV);
3) **Band edge positions straddle the water red-ox potentials**;
4) Good electron/hole mobility;
5) Good catalytic properties;
6) Low cost and non-toxicity.



Principle of water splitting using semiconductor photocatalysts.

Possible Solutions

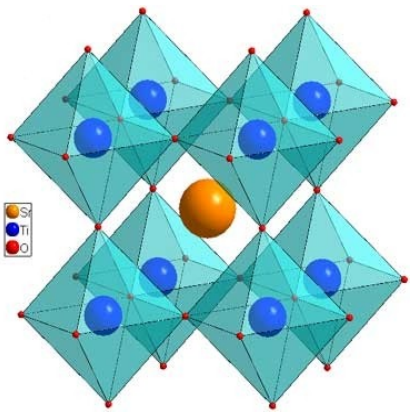


Difficult to find materials with appropriate bandgap and band edge positions!

Kudo and Miseki, *Chem. Soc. Rev*. **38**, 253 (2009).

Cubic Perovskite

- Common structure, several chemical elements can be used;
- High stability;
- Variety of properties: ferroelectricity, magnetism, superconductivity and (photo)catalytic activity;
- Computationally cheap (5 atoms)
- 52 metals from the periodic table;
- Different anions (O, N, S, F, Cl, …).



																	He
Li	Be					H						B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

Excluded elements:

- Non Metals;
- Radioactive, toxic.

Computational Method:

1) Stability Analysis

Perovskite compared with a pool of reference systems (400 compounds, from the ICSD experimental database):

- Single metal bulk: A(s) and B(s);
- Single metal oxides (nitrides, …): $A_xO_y(s)$;
- Bi-metal oxides (nitrides, …): $A_xB_yO_z(s)$;
- Single and bi-metal oxinitrides (oxyfluorides, …): $A_xO_yN_z(s)$ and $A_xB_yO_zN_k(s)$.

Energies calculated from DFT: RPBE xc-functional.

Formation energy (solved by linear programming):

$$\Delta E = \mathrm{ABO_3(s)} - \min_{c_i} \left(c_1 \mathrm{A\,(s)} + c_2 \mathrm{B\,(s)} + c_3 \mathrm{A_xO_y\,(s)} + c_4 \mathrm{B_xO_y\,(s)} + c_5 \mathrm{O} \right)$$

$$c_1 + c_3 = 1\,, \qquad c_2 + c_4 = 1\,, \qquad c_3 + c_4 + c_5 = 3$$

Computational Method:

2) Calculation of the bandgaps: GLLB-SC

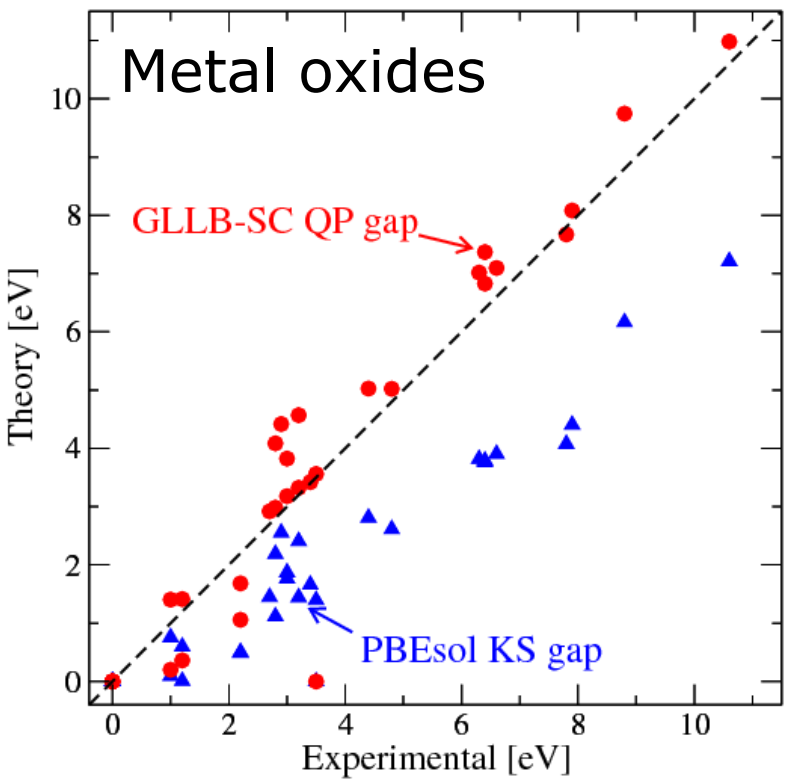
First description: Gritsenko *et al.*, *Phys. Rev. A* **51**, 1944 (1995).

Implemented in GPAW: Kuisma *et al.*, *Phys. Rev. B* **82**, 115106 (2010).

$$E_g^{QP} = E_g^{KS} + \Delta_{xc}$$

Minimal computational cost.

Gap within an error 0.5 eV.

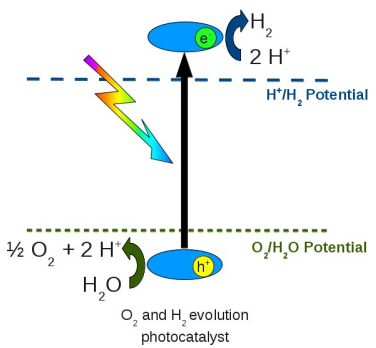


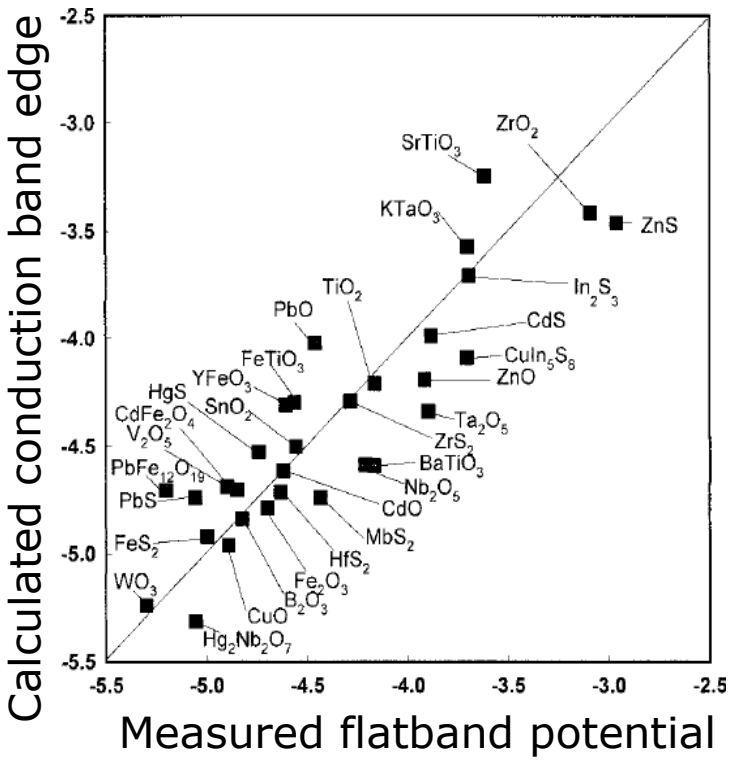
I. E. Castelli, T. Olsen, S. Datta, D. D. Landis, S. Dahl, K. S. Thygesen, and K. W. Jacobsen, *Energy & Environmental Science*, **5**, 5814 (2012).

Computational Method:

3) Evaluation of the band edges

Empirical formula: $E_C = (\chi_A \chi_B \chi_O{}^3)^{1/5} - 1/2 E_{gap} + E_0$





$\chi = 1/2\left(A + I_1\right)$

= Absolute electronegativity (Mulliken scale).
A = electron affinity
I_1 = first ionization energy

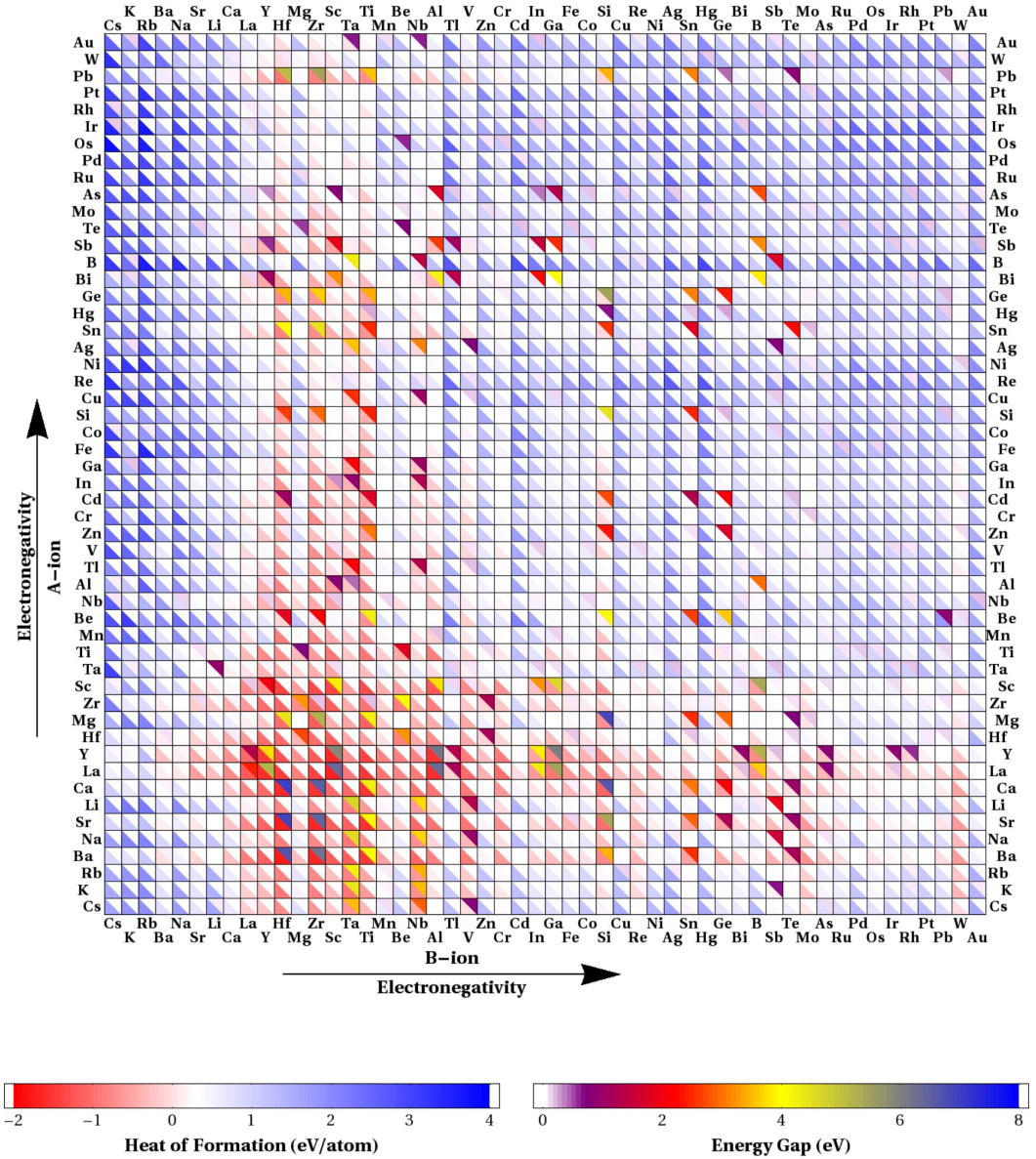
E_{gap} = Bandgap.

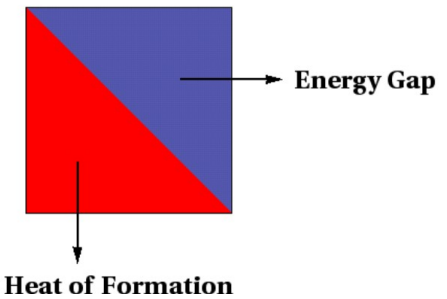
E_0 = Reference electrode redox level to the vacuum.

Butler and Ginley, *J. Electrochem. Soc.* **125**, 228 (1978).

Xu and Schoonen, A*m. Mineral.* **85**, 543 (2000).

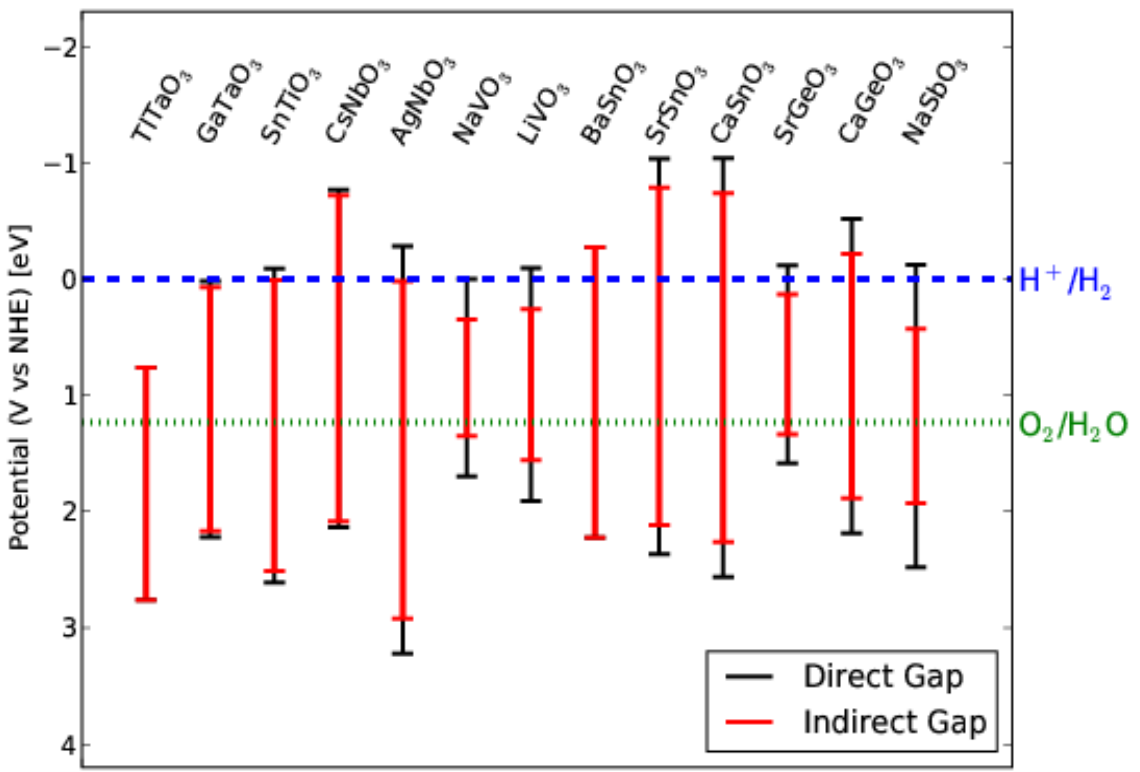
ABO_3 Perovskite





Chemical-based rules for stability and bandgap:
- Goldsmith's tolerance factor;
- even number of electrons in the unit cell;
- sum of the possible oxidation states = 6.

Candidates for One-photon WS - Oxides



$AgNbO_3$ and $BaSnO_3$ are known:

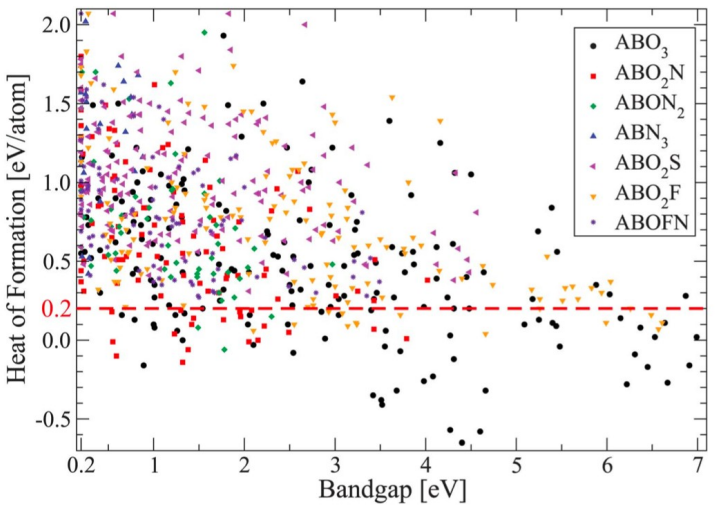
$AgNbO_3$: works!

$BaSnO_3$: defect induced recombination.

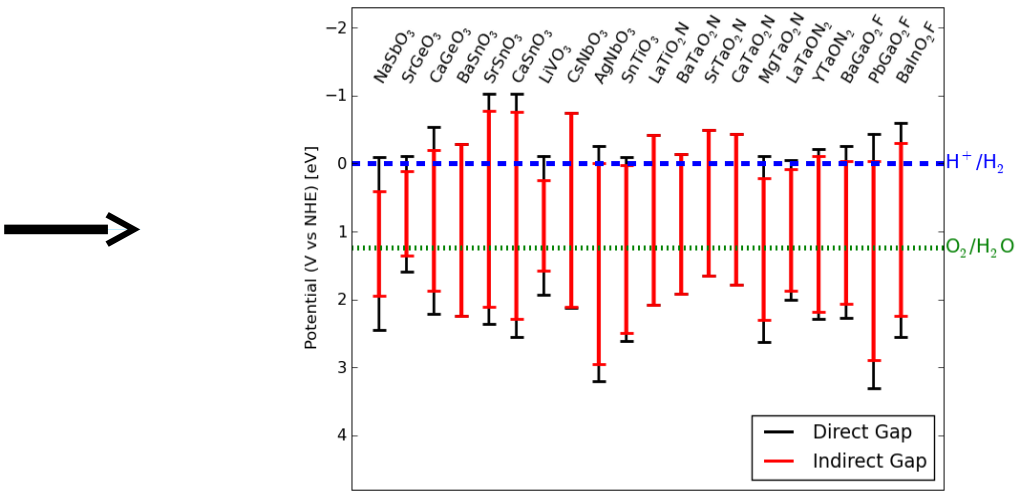
$SrSnO_3$ and $CaSnO_3$: orthorhombic perovskite (too large bandgap).

None of the others is known.

Candidates for One-photon WS



~19000 materials



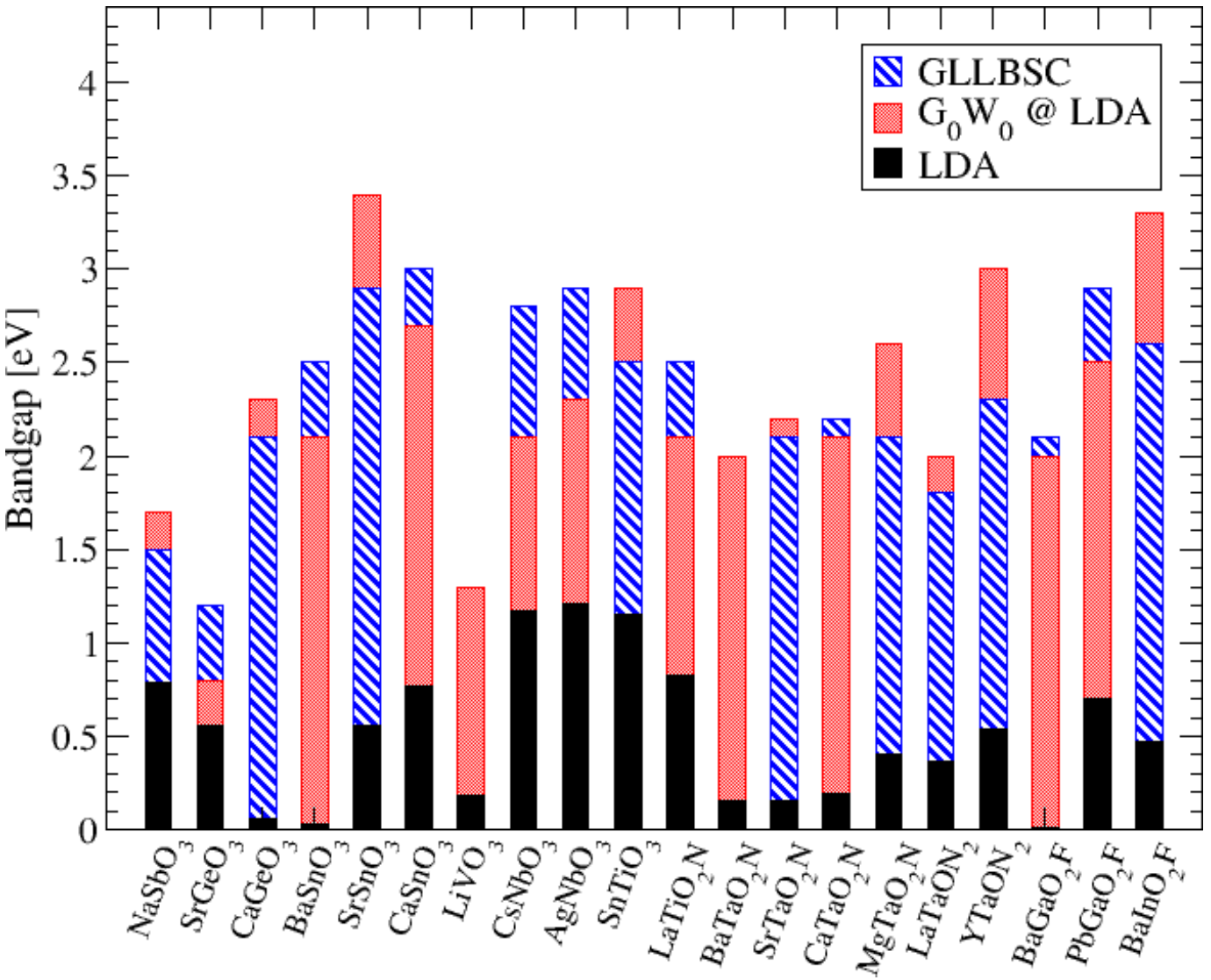
20 candidates

Screening parameters	One-photon WS
Chemical/structural stability (ΔE)	$\Delta E \leq 0.2$ eV
Bandgap (E_{gap})	$1.5 \leq E_{gap} \leq 3$ eV
Band edges (VB_{edge}, CB_{edge})	$VB_{edge} > 1.23$ eV $CB_{edge} < 0$ eV

- ABO_3: 10 ($AgNbO_3$)
- ABO_2N: 5 ($BaTaO_2N$, $SrTaO_2N$, $CaTaO_2N$, $LaTiO_2N$)
- $ABON_2$: 2 ($LaTaON_2$)
- ABO_2F: 3

I. E. Castelli, D. D. Landis, K. S. Thygesen, S. Dahl, I. Chorkendorff, T. F. Jaramillo, and K. W. Jacobsen, *Energy & Environmental Science,* **5**, 9034 (2012).

GLLB-SC and G_0W_0@LDA



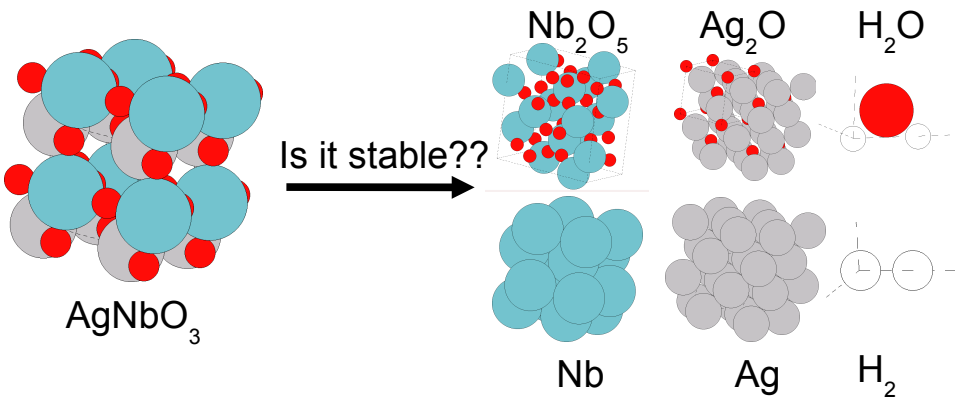
Good agreement between GLLB-SC and G_0W_0@LDA within the plasmon-pole approx.

MAE = 0.345

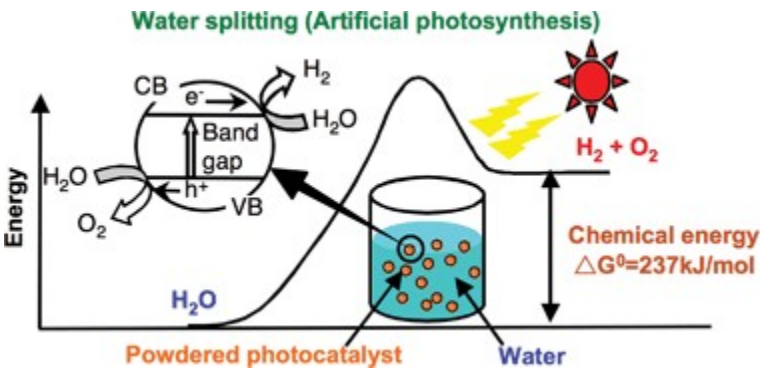
Pourbaix Diagrams

Evaluation of the stability

So far: stability w.r.t. solid substances.



In a photocatalytic cell, the light harvester material is in touch with water.



Are our candidates stable also in water?

Evaluate the stability also w.r.t. dissolved substances and at various pH/potential. → **Pourbaix diagram**

Pourbaix Diagram for Zinc

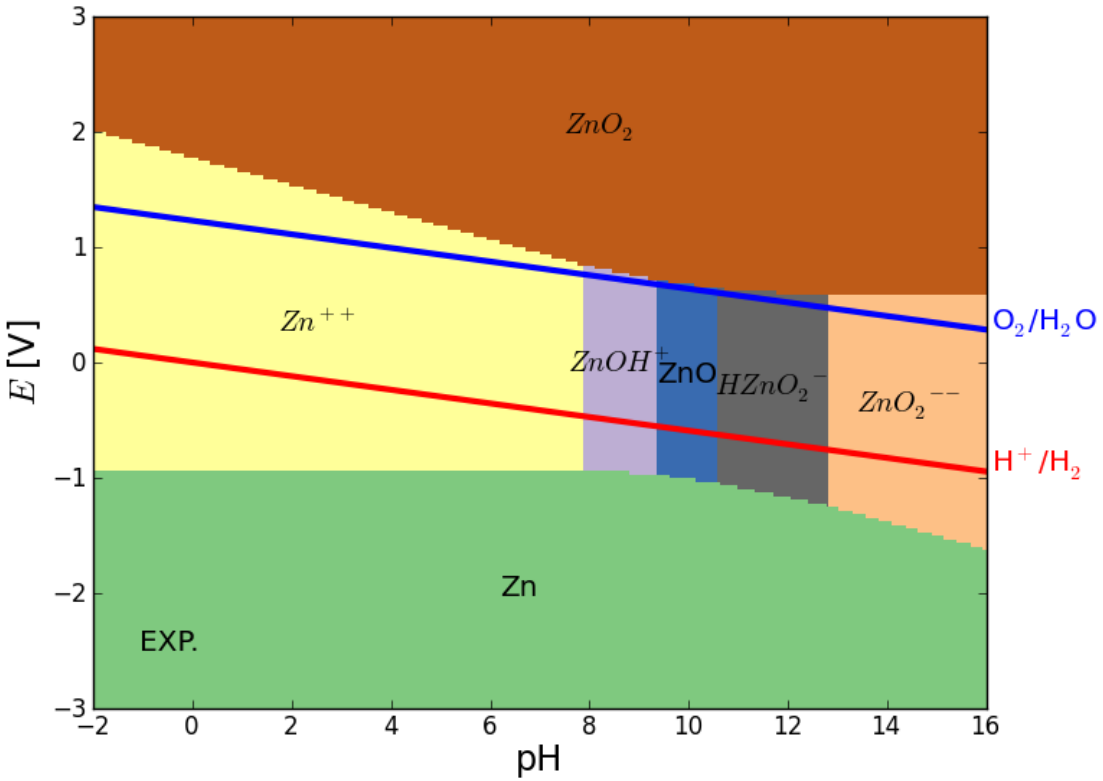
General reaction:

$$rR + wH_2O = pP + hH^+ + ne^-$$

Nernst equation at room temperature:

$$nE = \Delta G + 0.0591 \log \frac{(a_P)^p}{(a_R)^r} - 0.0591h\ pH$$

Solids: DFT
Dissolved substances:
Experiments



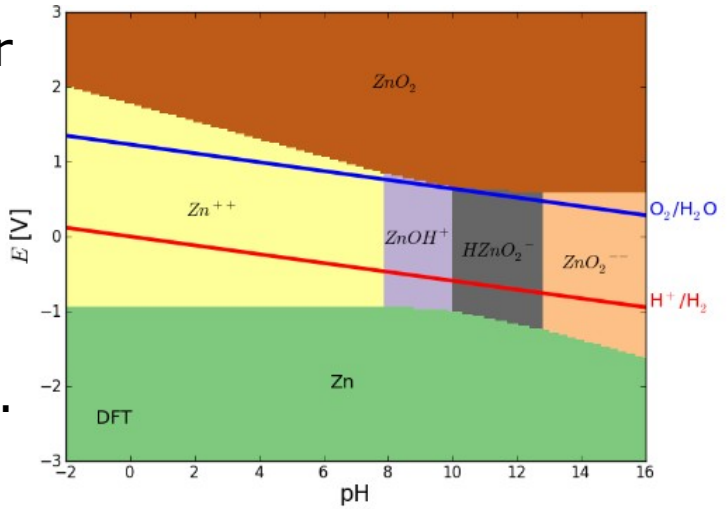
Three different lines:
- vertical: solid, dissolved substances and hydrogen ions. $ZnOH^+_{(aq)} = ZnO + H^+$
– horizontal: solid, dissolved substances with free electrons. $Zn^{++}_{(aq)} = Zn + 2e^-$
– straight with a slope equal to 0.0591h/n: solid and dissolved substances with free electrons and hydrogen ions. $Zn + H_2O = ZnO + 2H^+ + 2e^-$

DFT vs Experiments

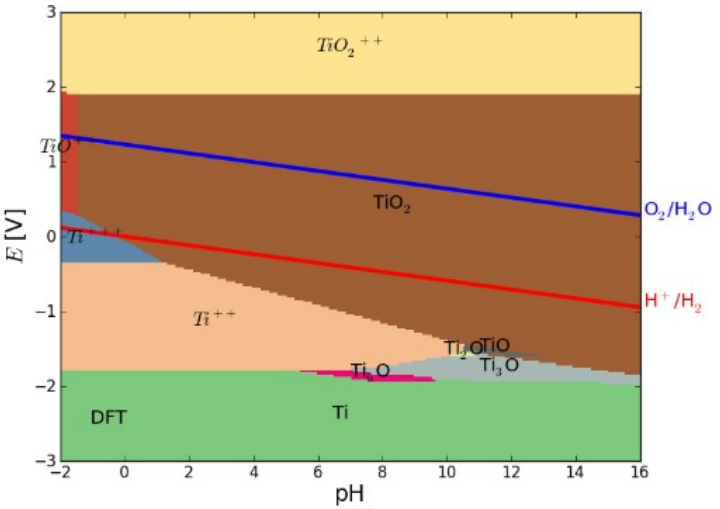
Pourbaix diagrams for Zn and Ti.

DFT and Experiments give similar diagrams.

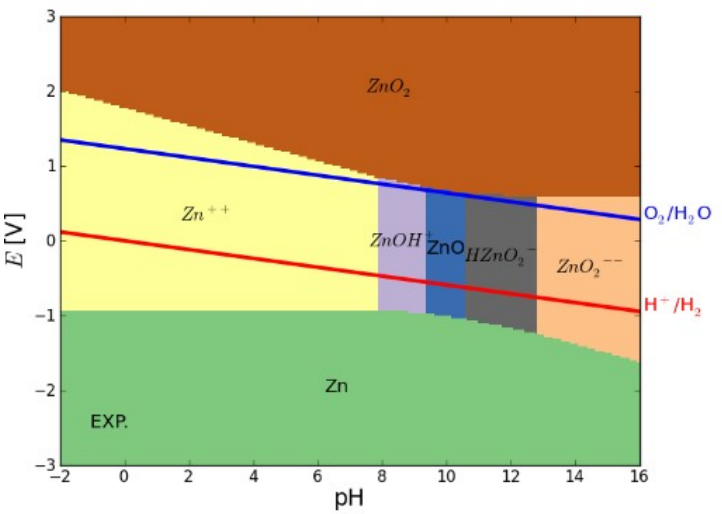
Differences:
- inaccuracy in the data;
- more data available for DFT calculations.



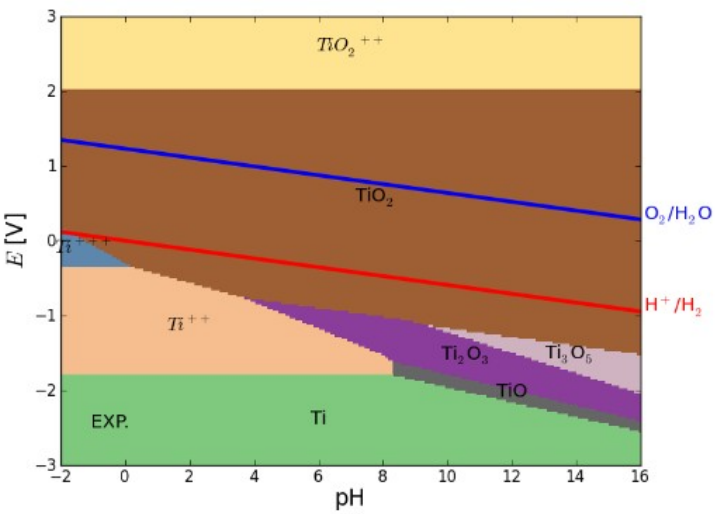
(a) ZnO - DFT



(b) TiO_2 - DFT

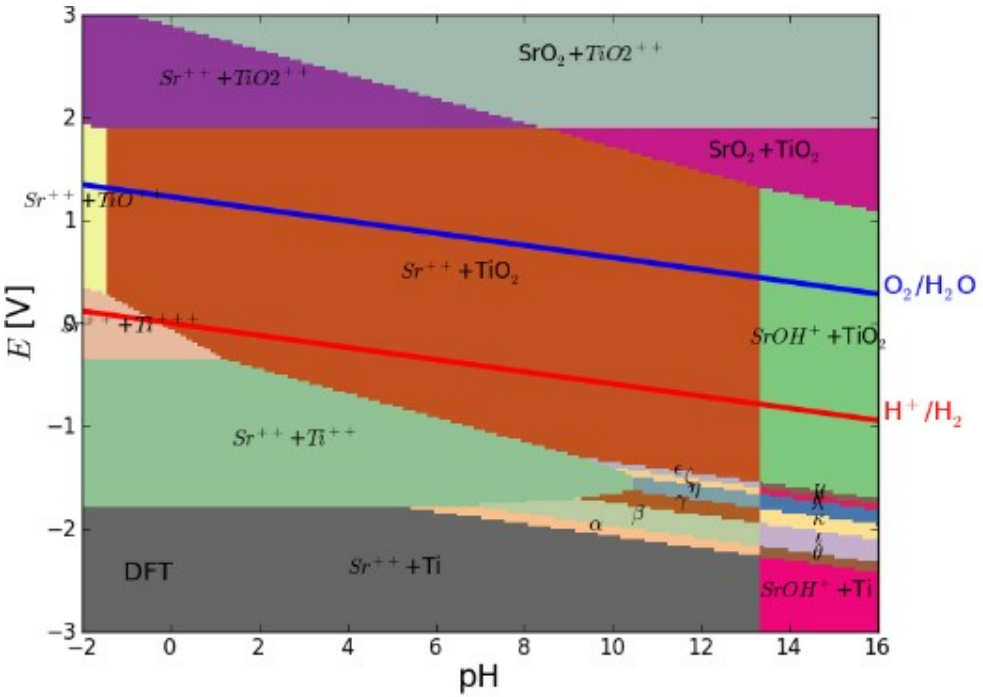


(c) ZnO - Experiments

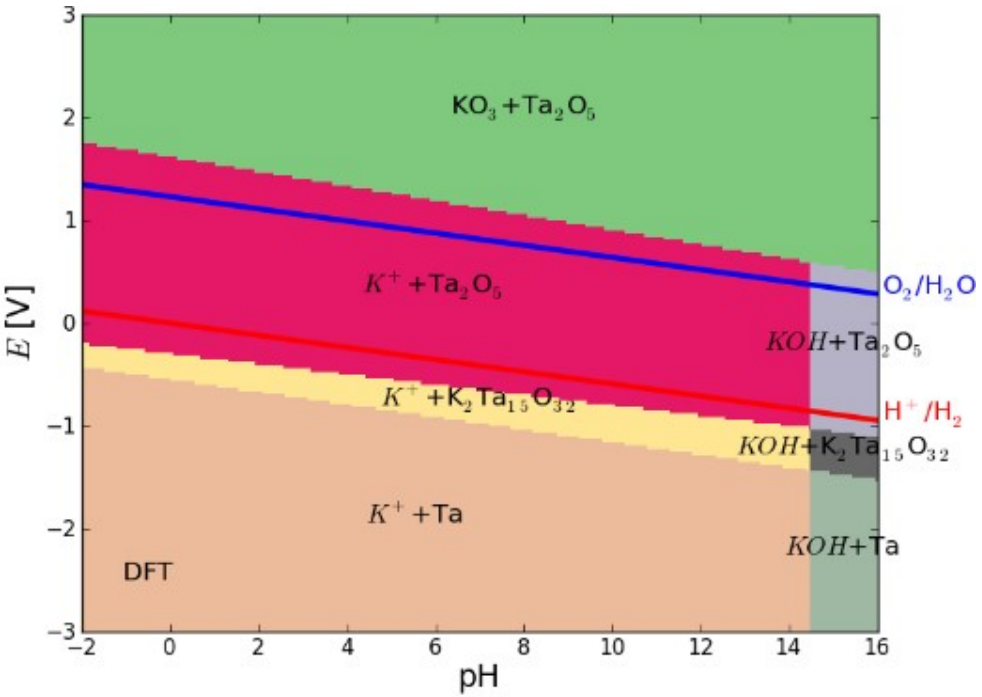


(d) TiO_2 - Experiments

$SrTiO_3$ and $KTaO_3$



(a) $SrTiO_3$ - DFT



(b) $KTaO_3$ - DFT

The cubic perovskite phase is **never** the most stable phase ($\Delta E < 0\, eV/atom$).

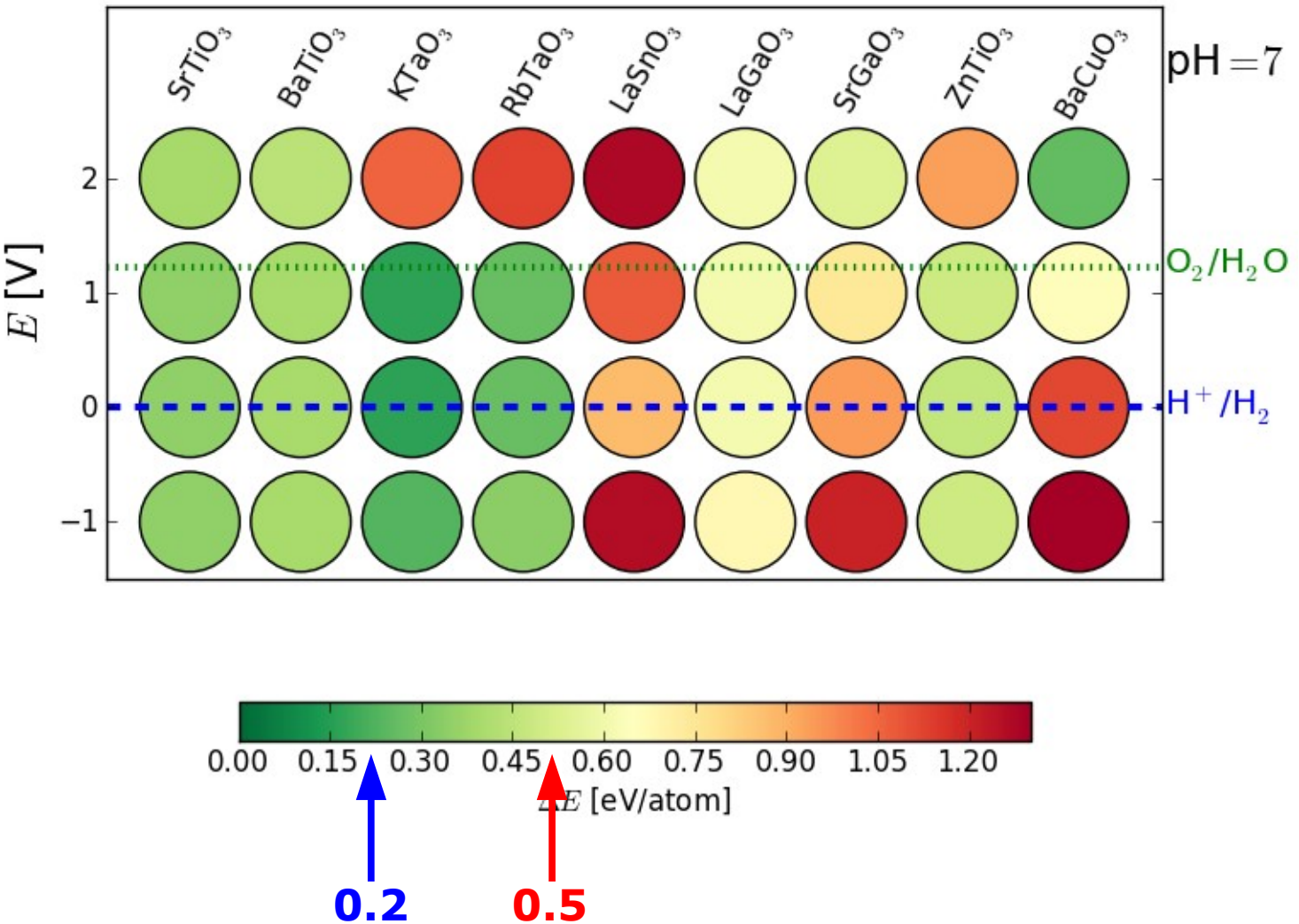
But they are experimentally known to be stable.
The reaction <u>kinetics</u> (not included in the Pourbaix diagrams) is important to find stable materials!
We can increase the energy threshold to take into account the kinetic term.

Stability of Known Perovskites

Stability analysis of selected cubic perovskites at pH=7 and potential equal to -1, 0, 1, and 2 V.

Only $KTaO_3$ is stable with a threshold of 0.2 eV/atom.

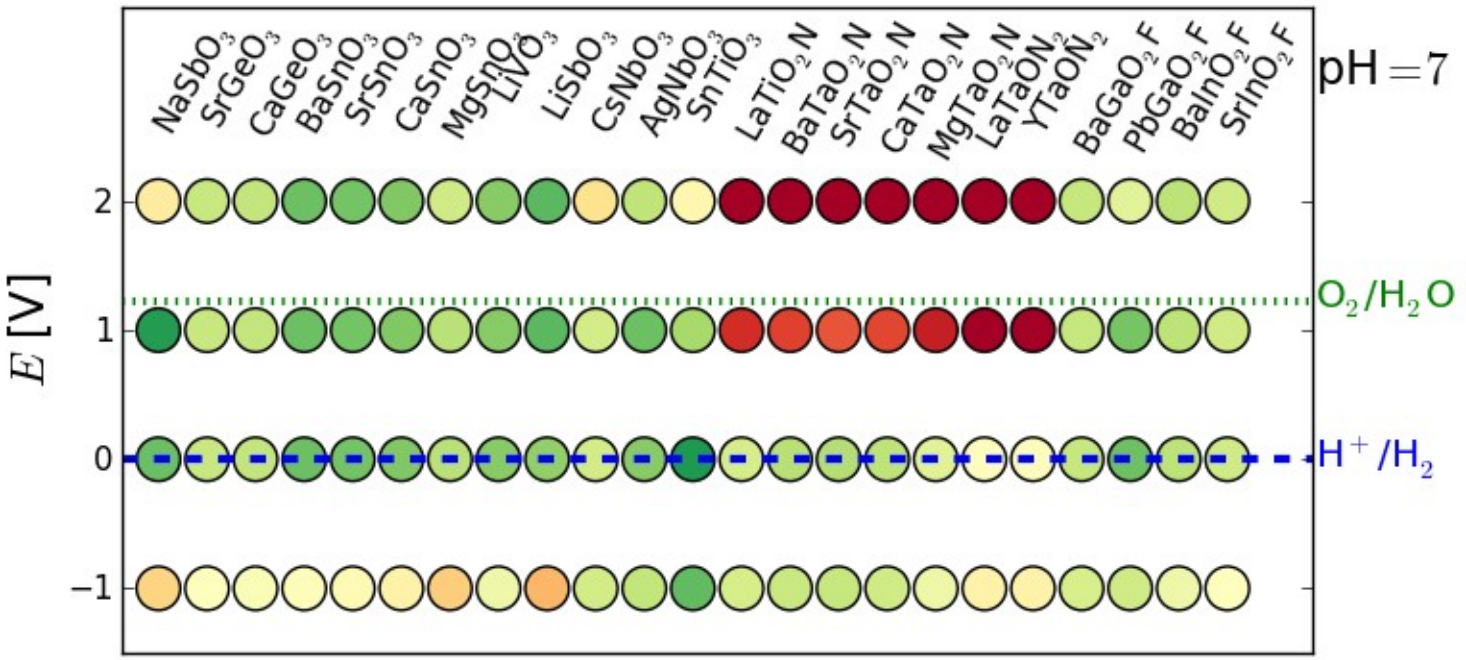
Few more are stable for a larger threshold (0.5 eV/atom).



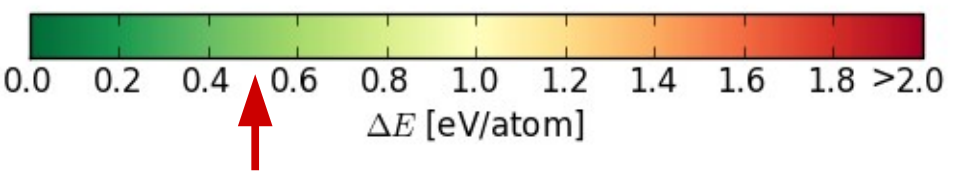
Water Splitting Candidates

Oxides and oxyfluorides have a region where they are stable ($\Delta E < 0.5\,eV/atom$).

Oxynitrides are less stable, especially at high potential.

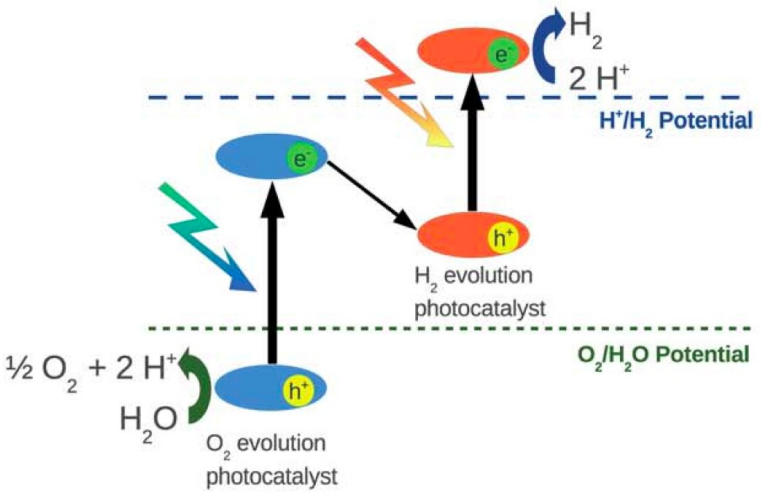


I. E. Castelli, K. S. Thygesen, and K. W. Jacobsen, *Submitted* (2013).



New stability threshold to account some metastability, inaccuracy in the calculations, and kinetic of the reactions.

Two-photon WS



Two semiconductors – two photons

- SC 1: Hole for oxygen evolution
- SC 2: Electron for hydrogen evolution

H_2 photocatalyst: Si

O_2 photocatalyst: screening

Requirements:

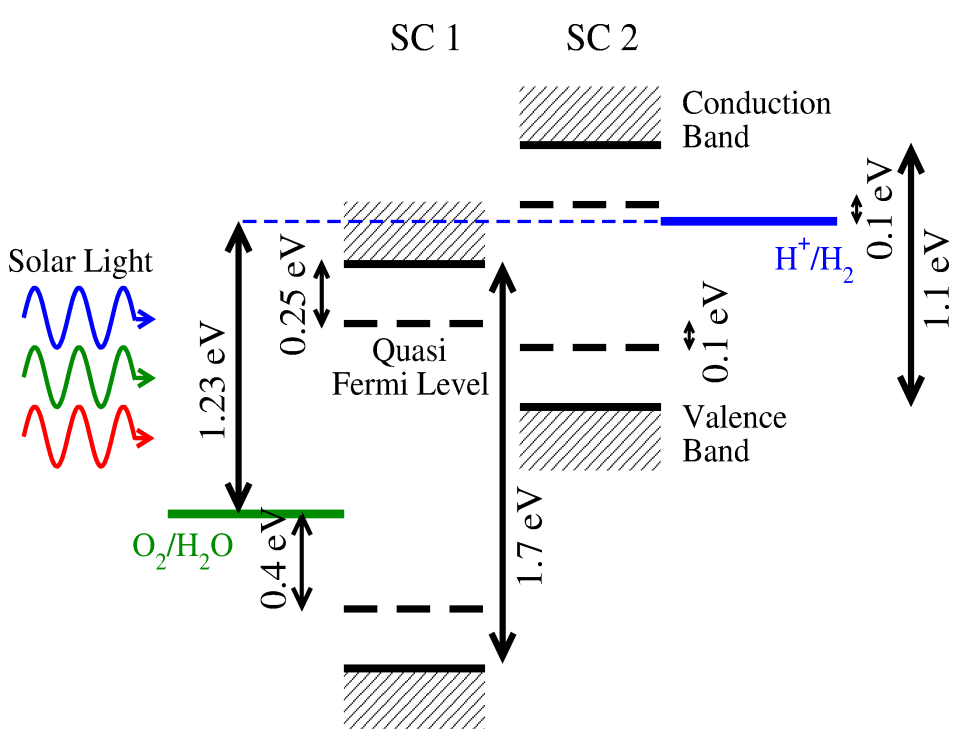
- structural/chemical stability;

- two visible light harvesters (optimal gaps: 1.1 eV and 1.7 eV);

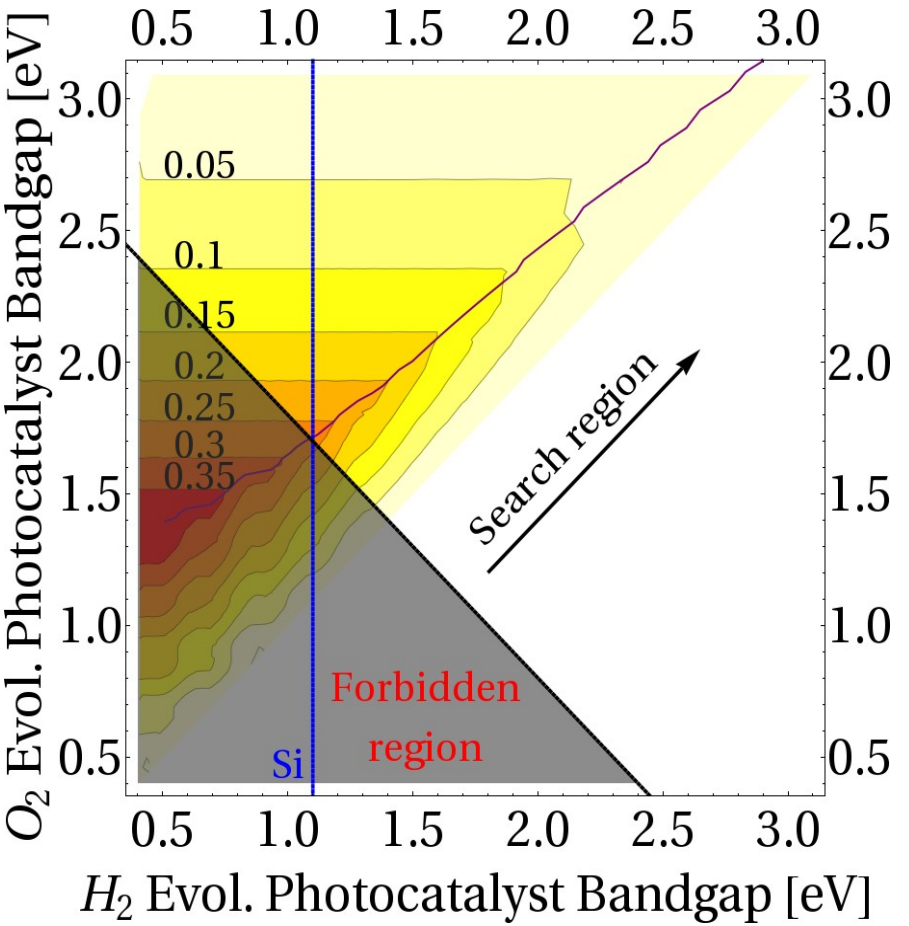
- band edges that match with oxygen and hydrogen potentials;

- Small overlap between the semiconductors band edges for the electron transfer reaction.

Tandem Cell Efficiency



Solar-to-hydrogen energy conversion efficiency

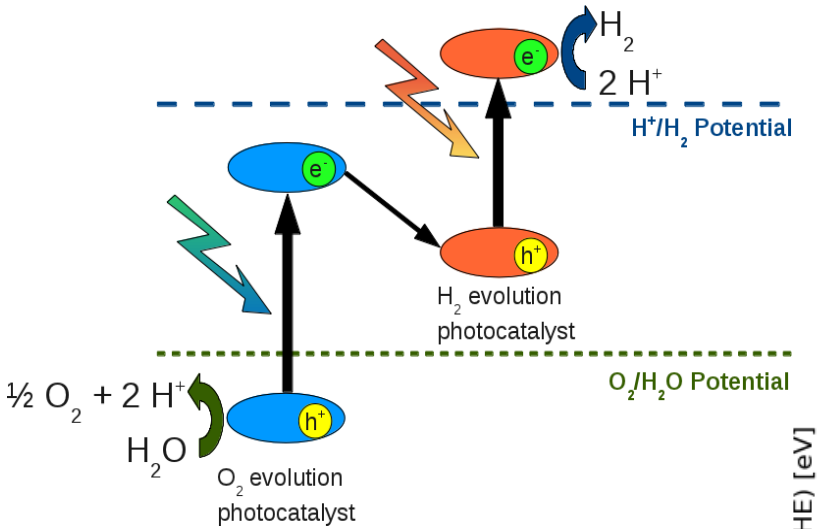


J. R. Bolton et al., *Nature* 1985.

M. G. Walter et al., *Chem Rev* **110**, 6446, 2010.

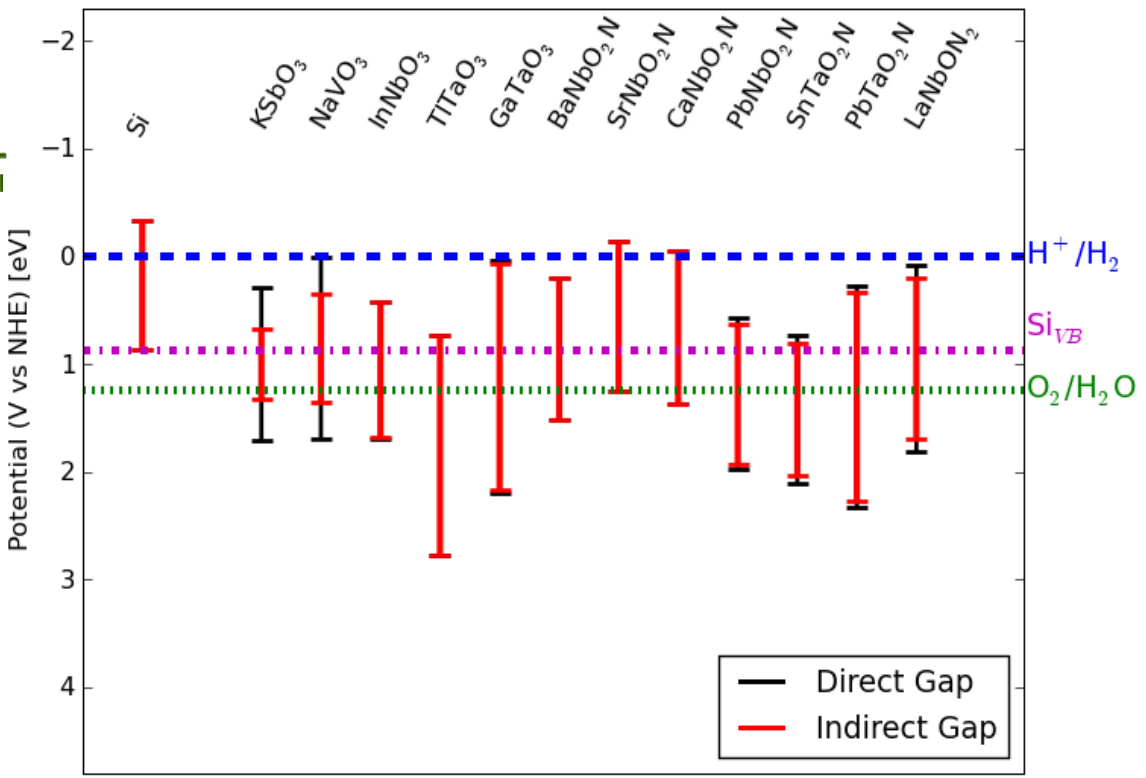
I. E. Castelli et al., *Energy & Environmental Science,* **5**, 9034 (2012).

Two-photon WS: Candidates



Eform < 0.2

1.3 < Egap < 3 eV



12 candidates

+ 20 from overall WS

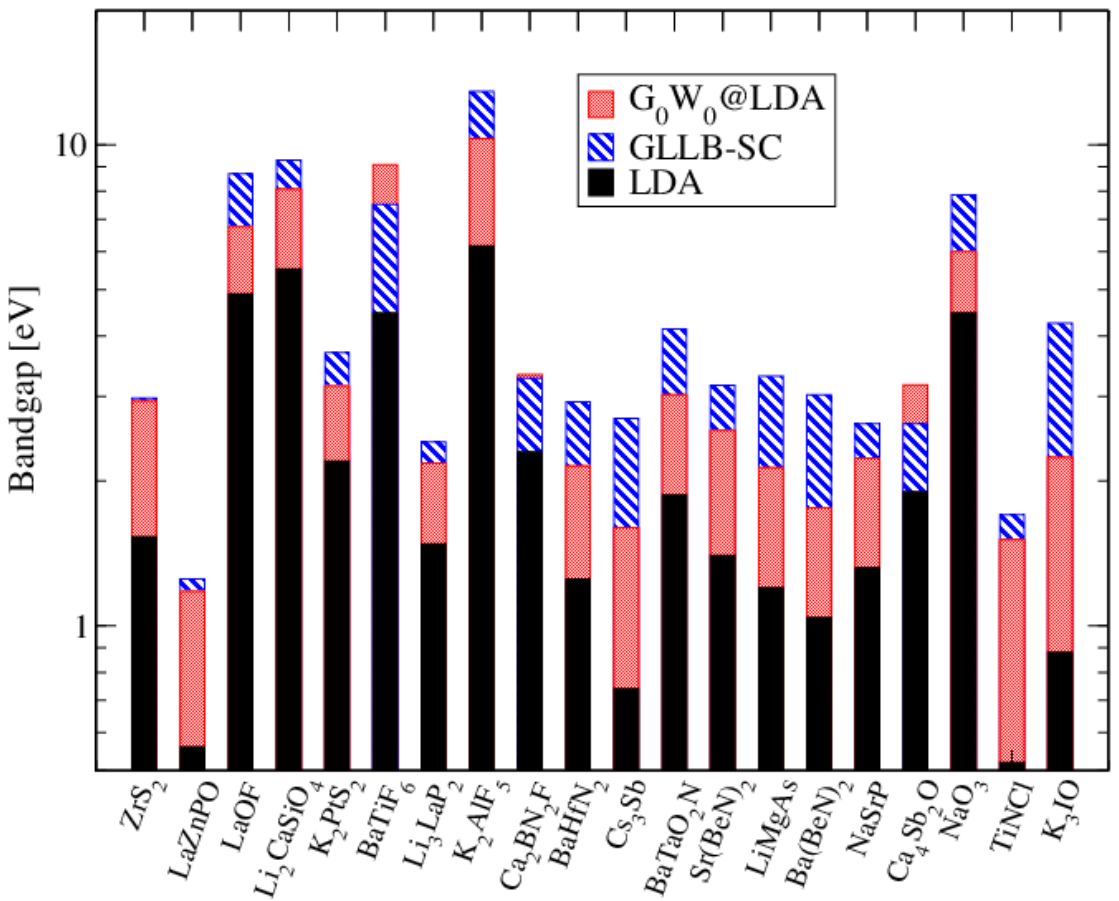
Materials Project Database

Calculation of the bandgaps of 6000 known structures from the Materials Project database.

(in collaboration with: A. Jain and K. Persson, LBNL; G. Ceder, MIT).

MATERIALS PROJECT

A Materials Genome Approach



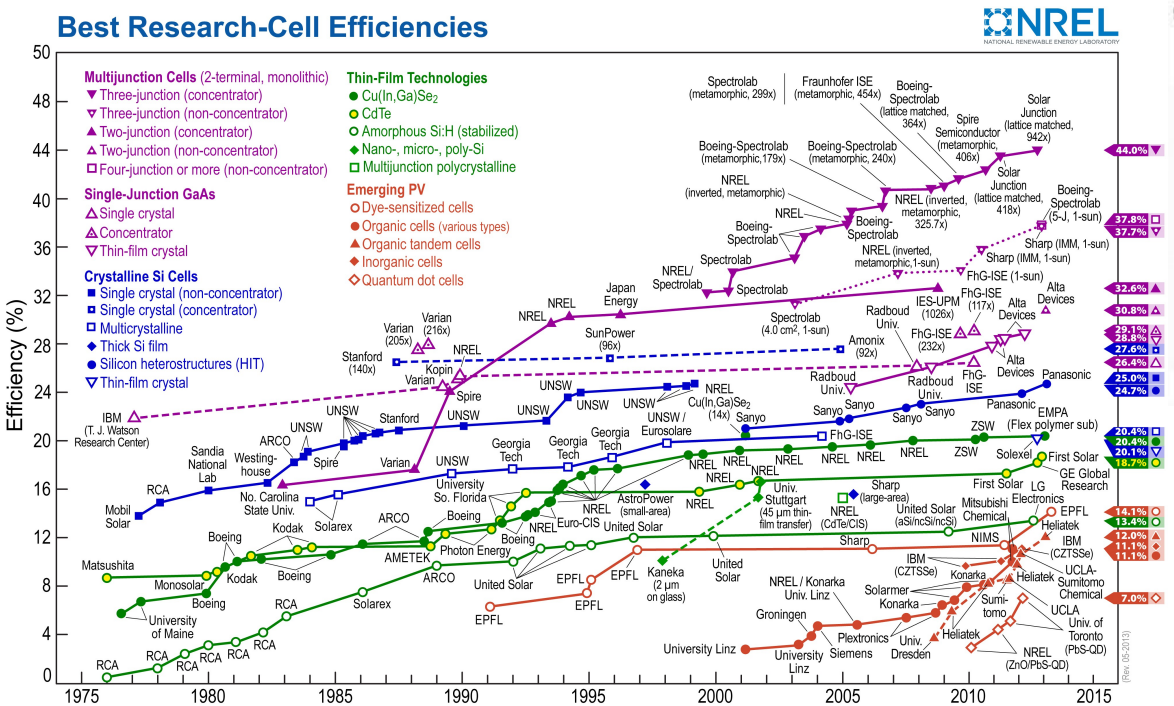
Reasonable agreement between GLLB-SC and G_0W_0.

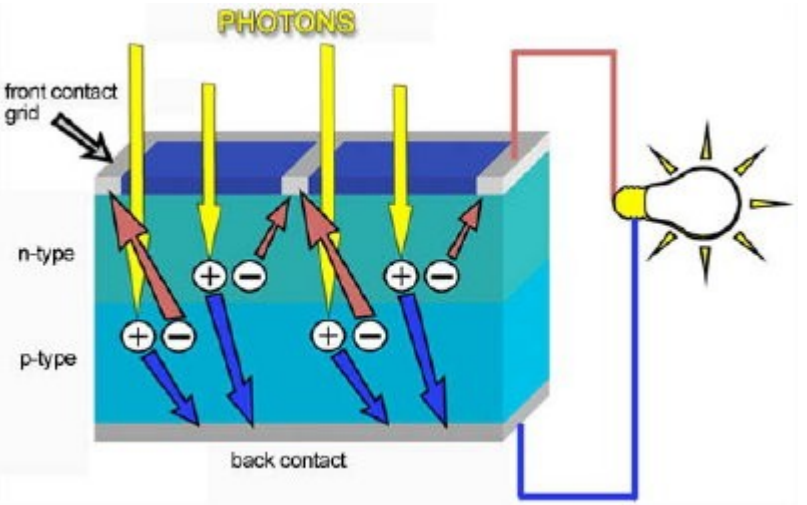
(Calculations from Falco Huser).

Applications: water splitting; photovoltaics; ...

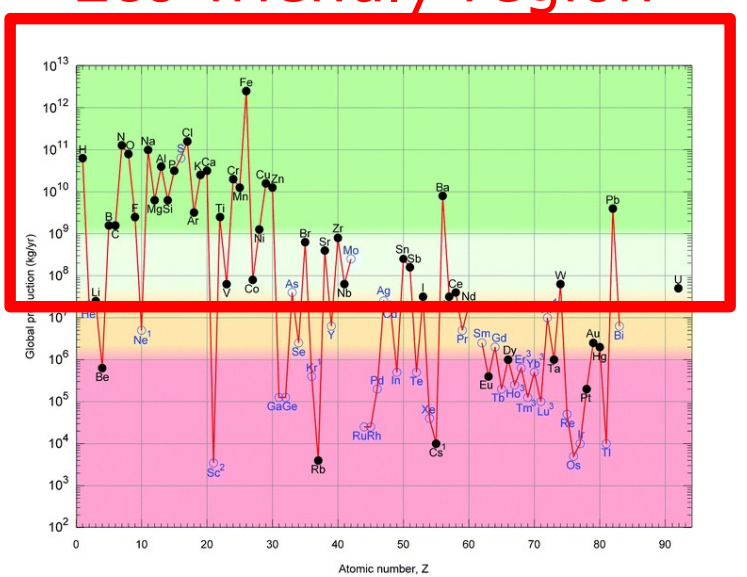
Thin Film Solar Cell

Photons are used to create current.





Eco-friendly region

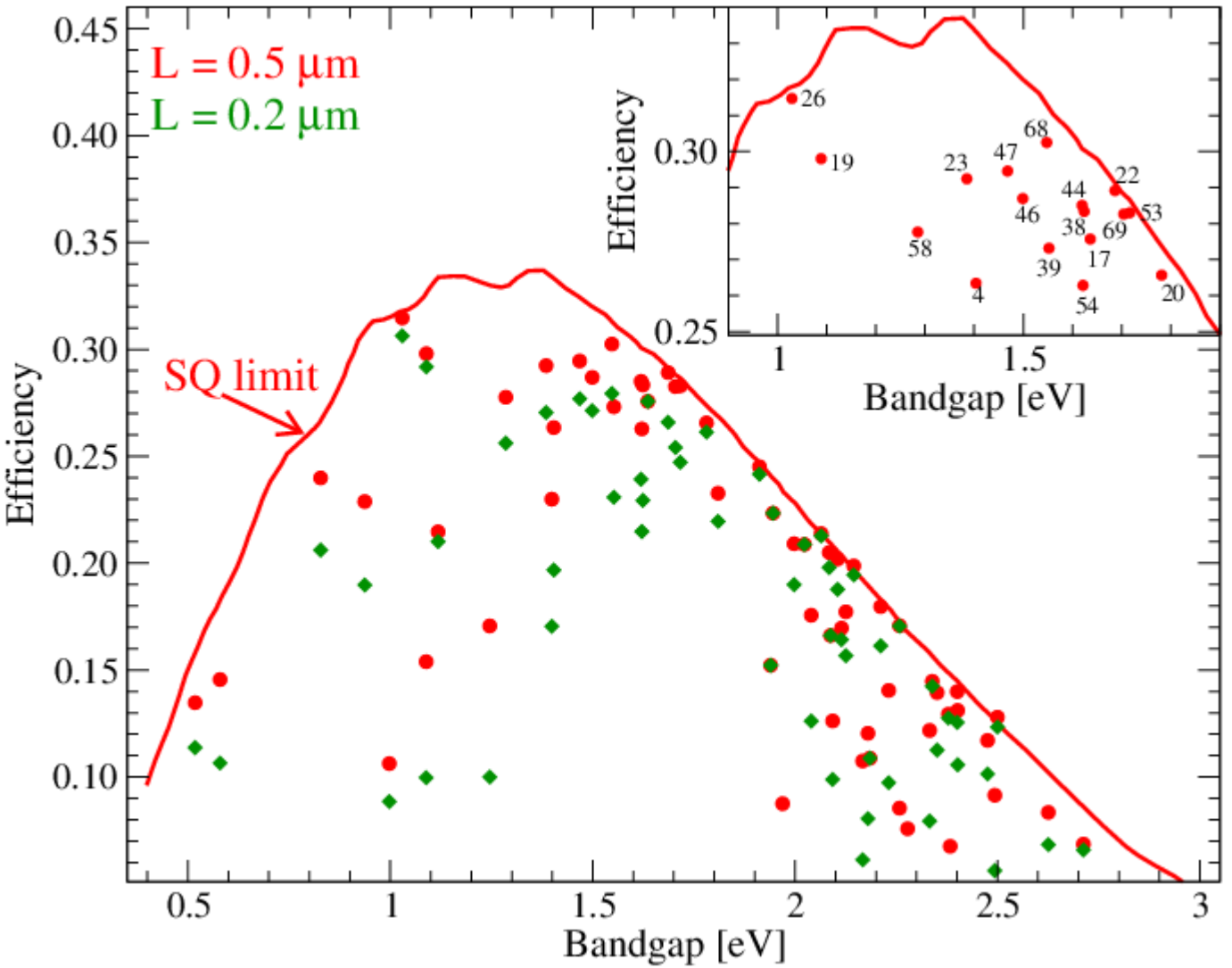


Calculation of the absorption spectra of 70 interesting known materials to use in a thin film SC.

Single-layer Thin Film SC

17 materials have a theoretical efficiency larger than 25 %.

4 have been already used in a SC.



The Computational Materials Repository

Computational Materials Repository

Hide search box

Link to image

Do not forget to press **update matrix** after changing the selection!
If there is an error - it means that the dataset is already being calculated! Please wait a moments and try again.

Chose a data set:	ABO3 (2704)
Width:	800
Height:	1200
X axis ticks:	B
Y axis ticks:	automatically selected
X sort order:	Electronegativity (Paulin
Y sort order:	Electronegativity (Paulin
Action on Click:	show band edges

References:
- ABN (3)
- ABO (20)
- AN (50)
- AO (52)
- AON (35)
- default (3)
- mbulk (52)

	Value field:	Colors:
Triangle 1: (top-right)	gllbsc_ind-gap (eV)	0->white,0.7->purple,2.2->re
Triangle 2: (bottom-left)	heat_of_formation (eV)	min->red,0.3->white,4->blue
Triangle 3:		
Triangle 4:		

Examples for the color choice:

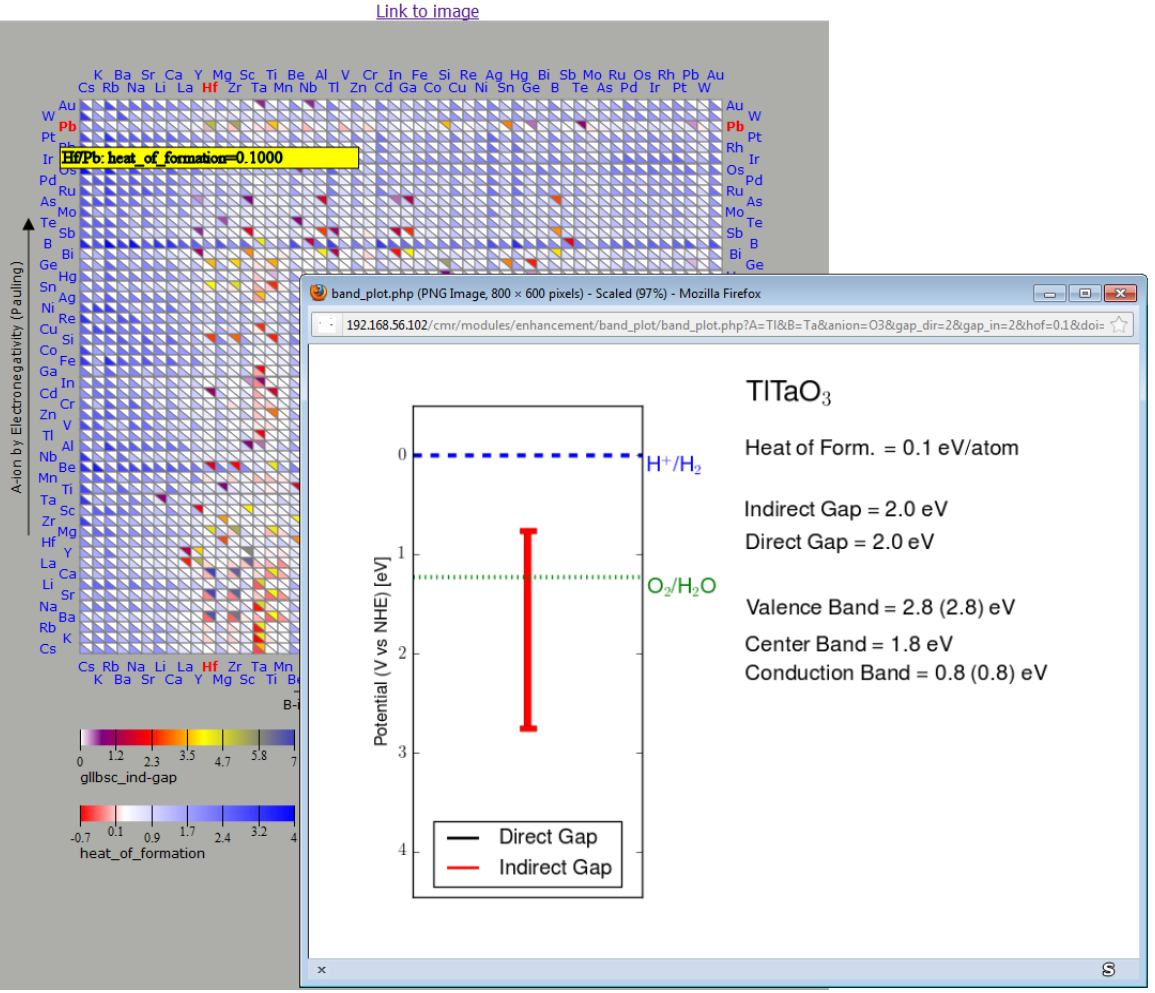
```
0->white,1->red,7->blue

0->white,0.9->red,2.2->green,4->yellow,8->blue

-100->blue,100->red
```

Valid color names are black, blue, cyan, green, gray, green, lightblue, pink, red, purple, white, yellow. Please note that the values must be in **increasing** order.

Update matrix



http://cmr.fysik.dtu.dk - the database

http://wiki.fysik.dtu.dk/cmr - the software

Conclusions

- Few materials (40) have been identified for one- and two-photon water splitting;
- The GLLB-SC potential works well for bandgap calculations;
- 17 materials have been proposed for single-layer thin film solar cell;
- A database has been developed for an easy access to the data.

Acknowledgment

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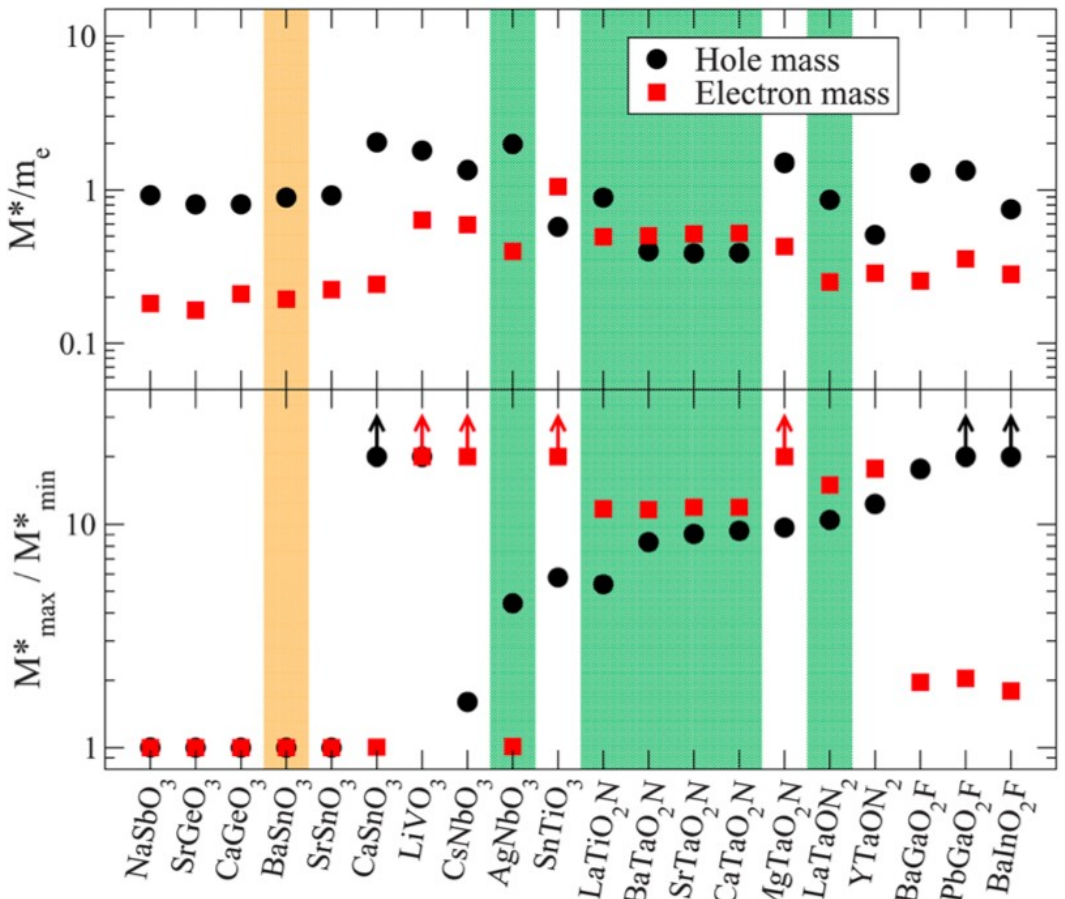
David D. Landis
Thomas Olsen
Falco Huser

CAMd
Center for Atomic-scale Materials Design

CASE
Catalysis for Sustainable Energy

e-h Masses and Mobility



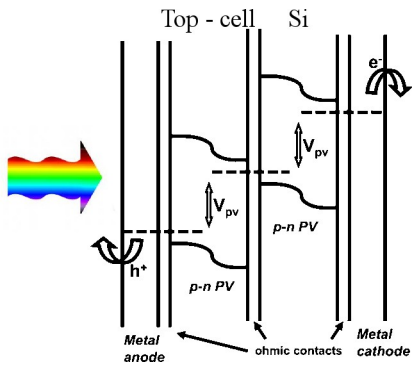
$$\frac{1}{M^*} = \frac{1}{3}\left(\frac{1}{m_x^*} + \frac{1}{m_y^*} + \frac{1}{m_z^*}\right)$$

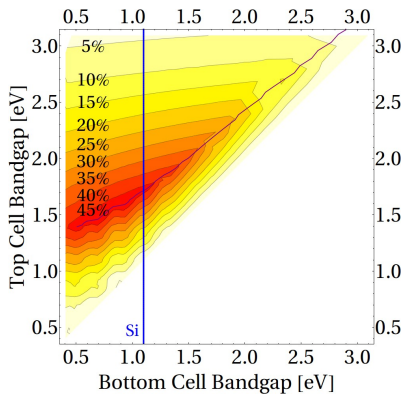
Green systems: known to split water (with sacrificial reagents).

Orange system: BaSnO3 known not to work (probably defect-assisted recombination).

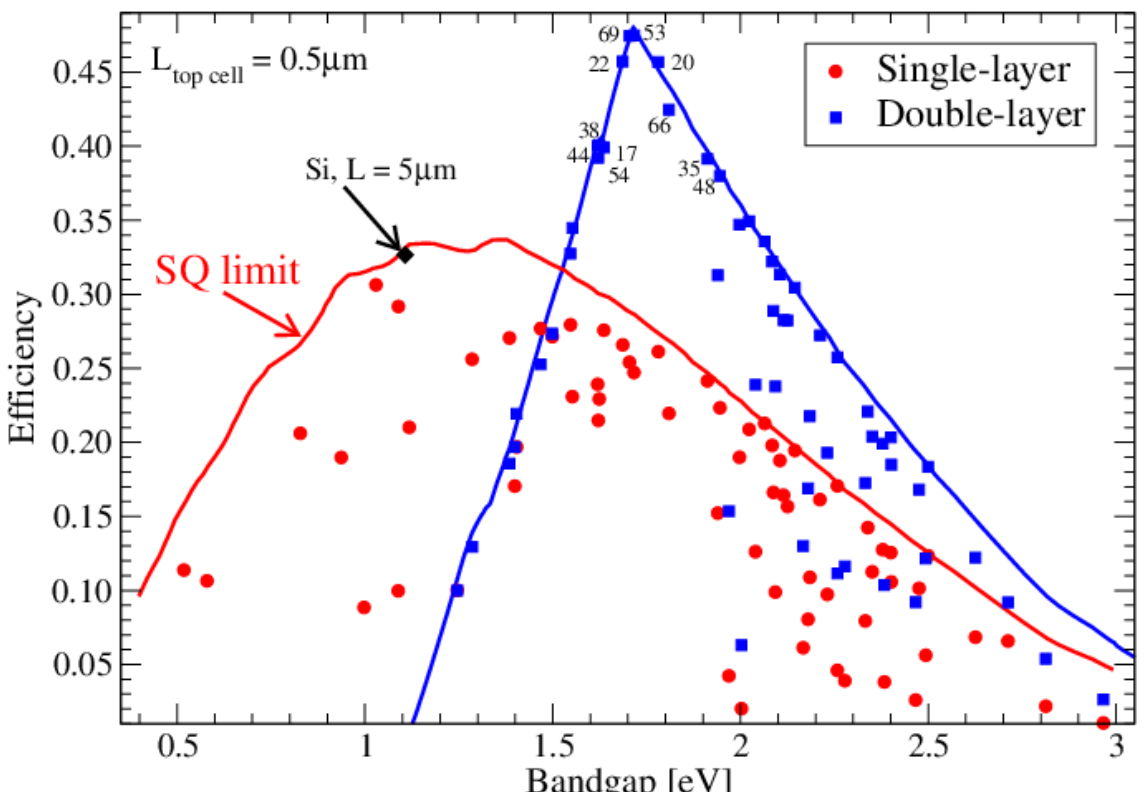
Systems observed to work seems fairly isotropic.

Double-layer Thin Film SC





Top-cell: ???
Bottom-cell: silicon



11 materials have an efficiency of more than 35 %.

3 of them have been used so far in a SC.

Background

Design