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CASE
Catalysis for Sustainable Energy

DTU

Computational Screening of Materials for Water Splitting Applications

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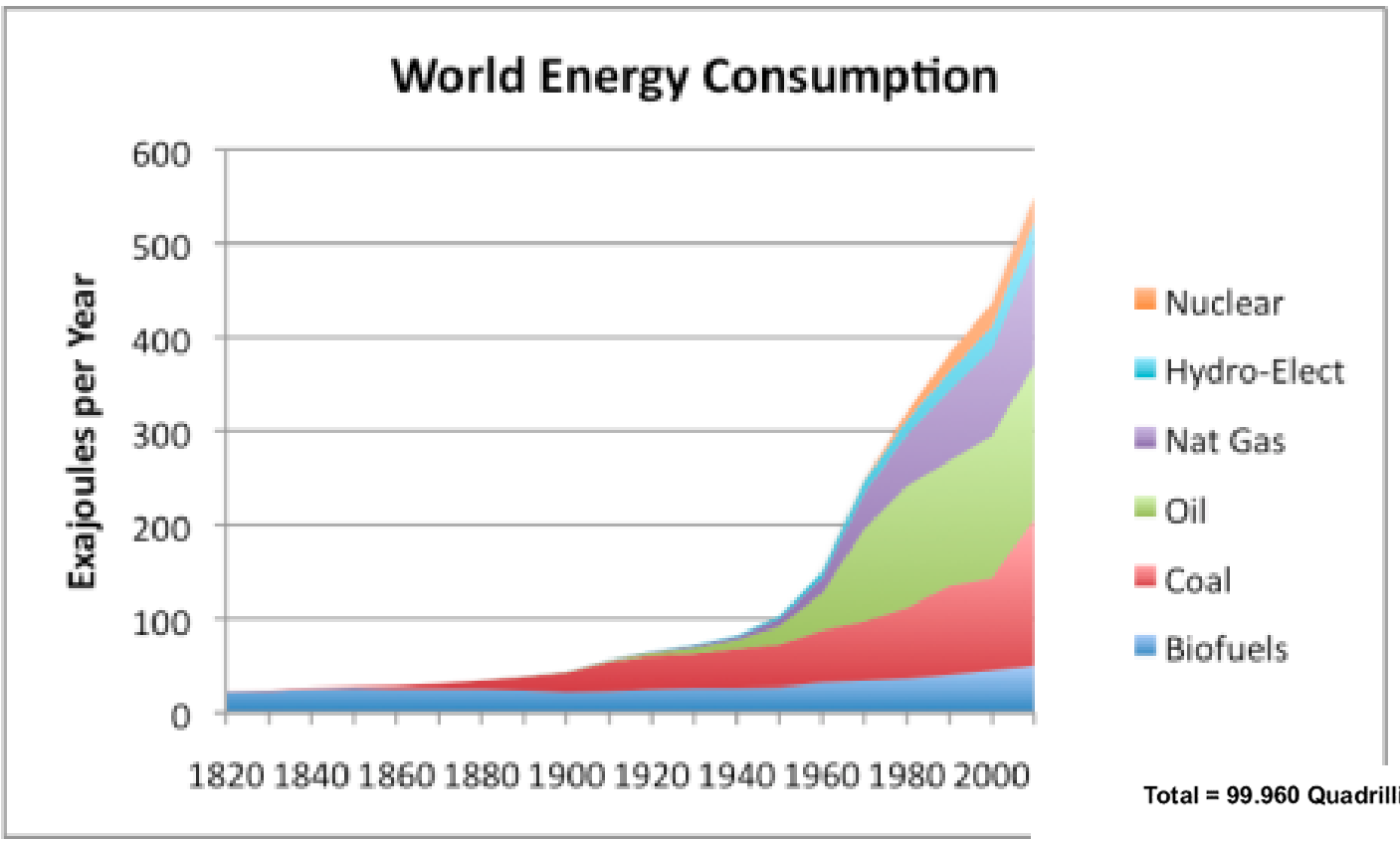
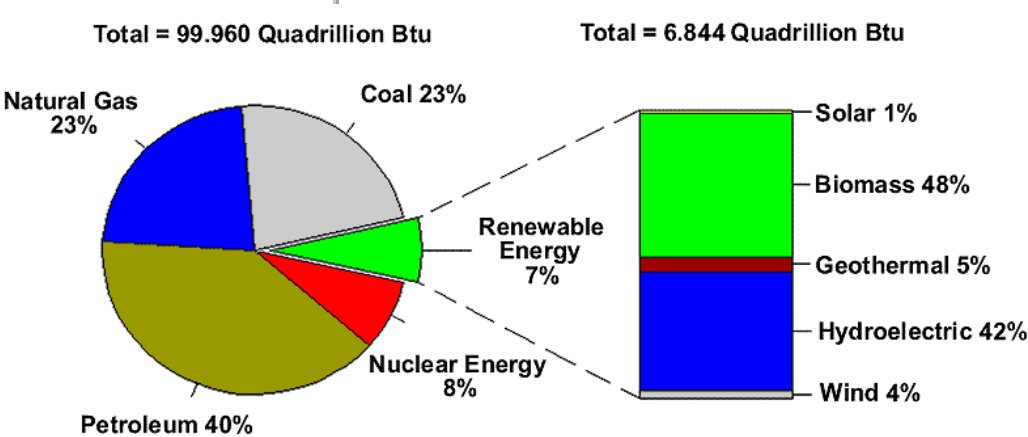
Ph.D. Defense
24 June 2013

The World Needs Clean Energy



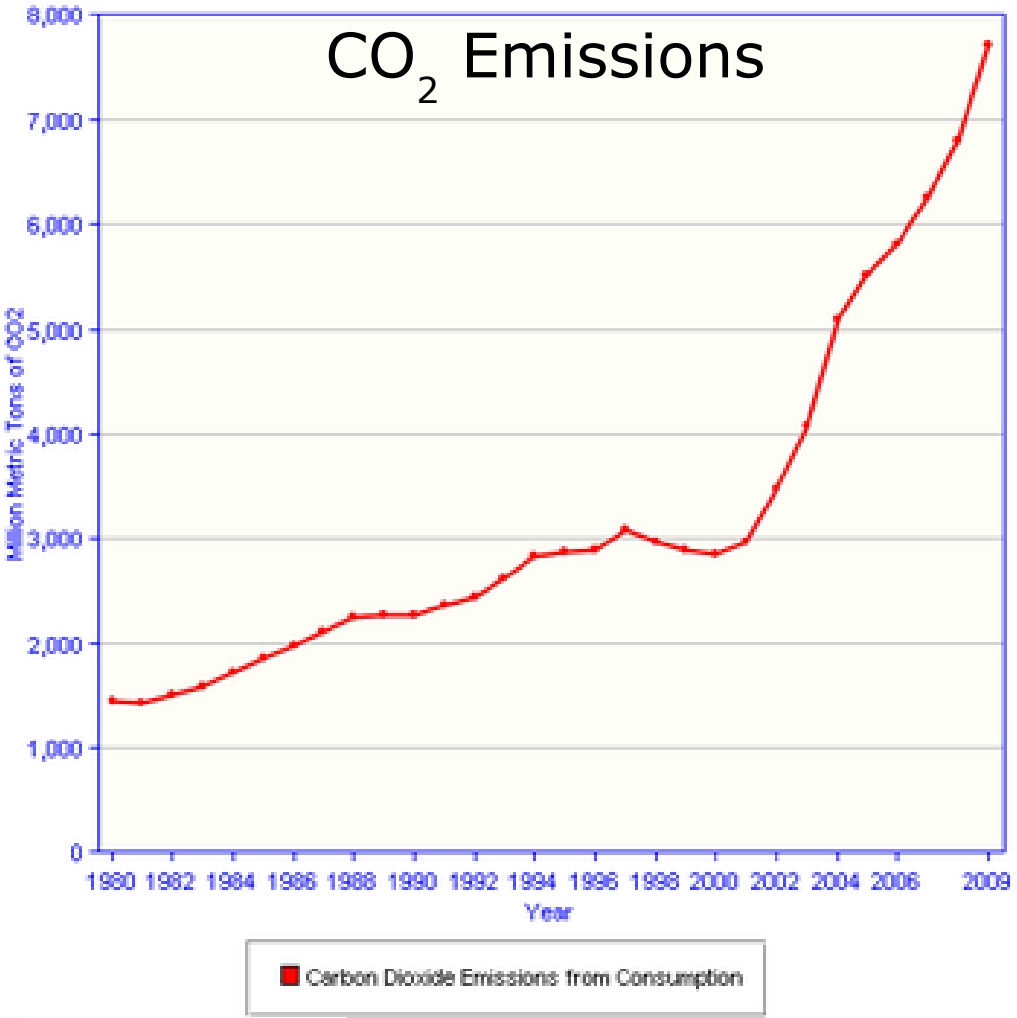
Energy consumption increases of 4 times in 50 years!



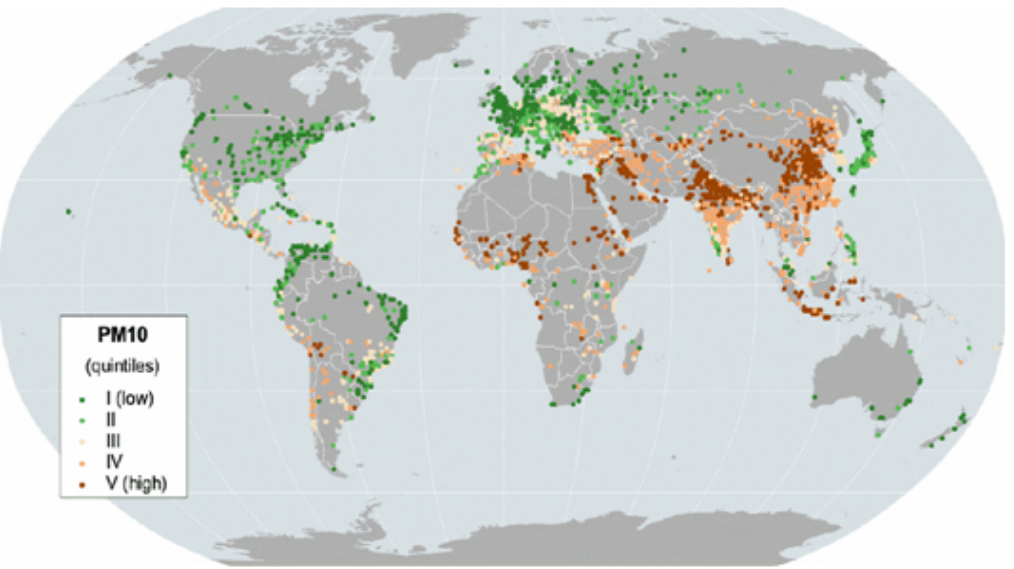
The World Needs Less Pollutants

Pollutants are direct consequence of combustion of fossil fuels

CO_2 Emissions

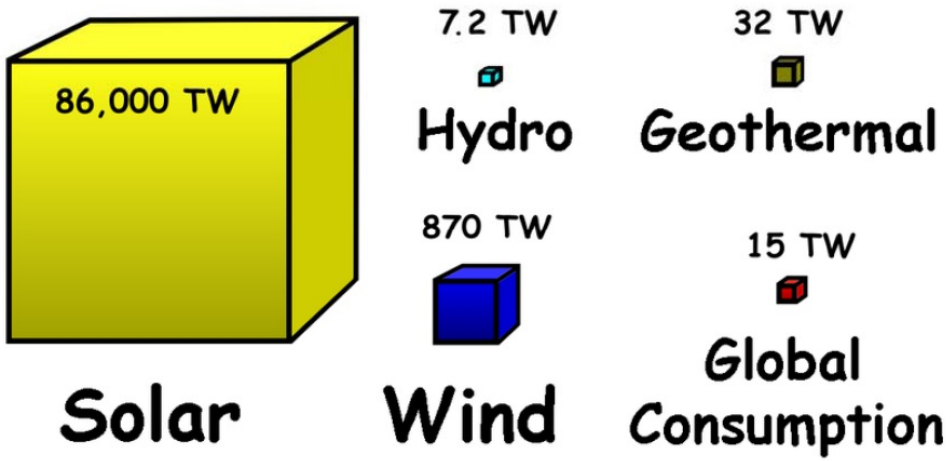


PM_{10} Concentration



Solar Energy and Hydrogen Production

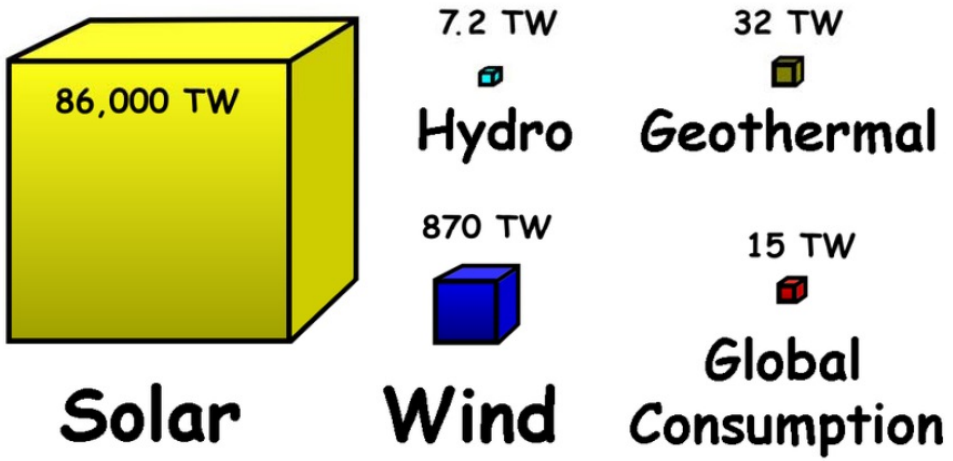
Available energy:



Natural to look at clean renewable energy: **solar**, wind, hydroelectric, biomass, ...

Solar Energy and Hydrogen Production

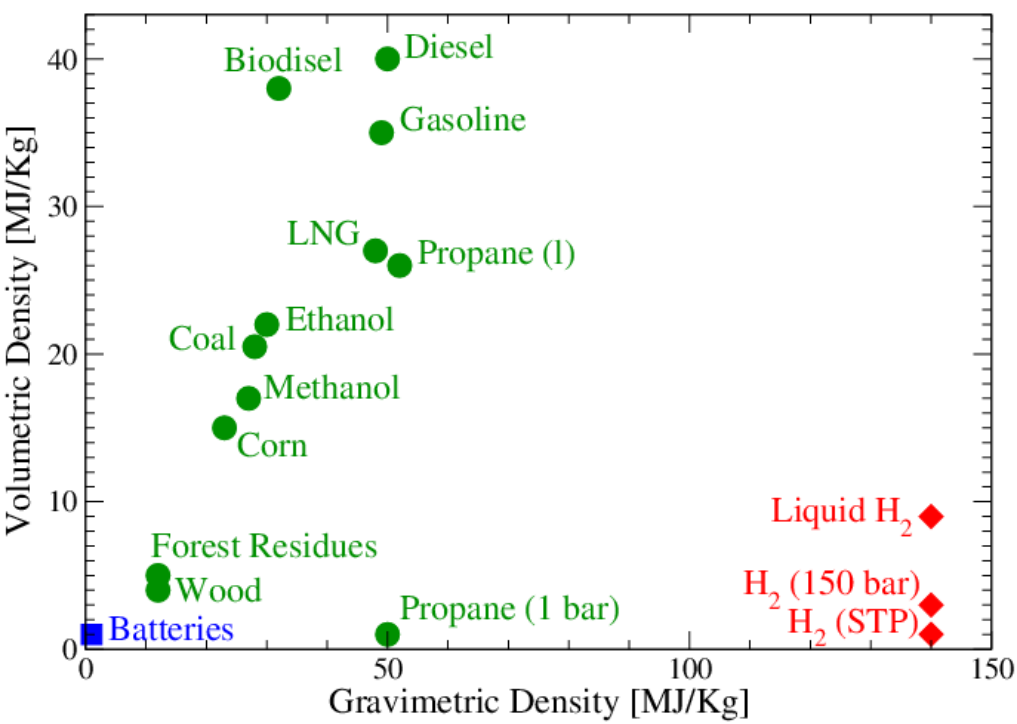
Available energy:



Natural to look at clean renewable energy: **solar**, wind, hydroelectric, biomass, ...

Energy storage and transport:

- Battery;
- Chemical energy: **H_2**, CH_4, ...



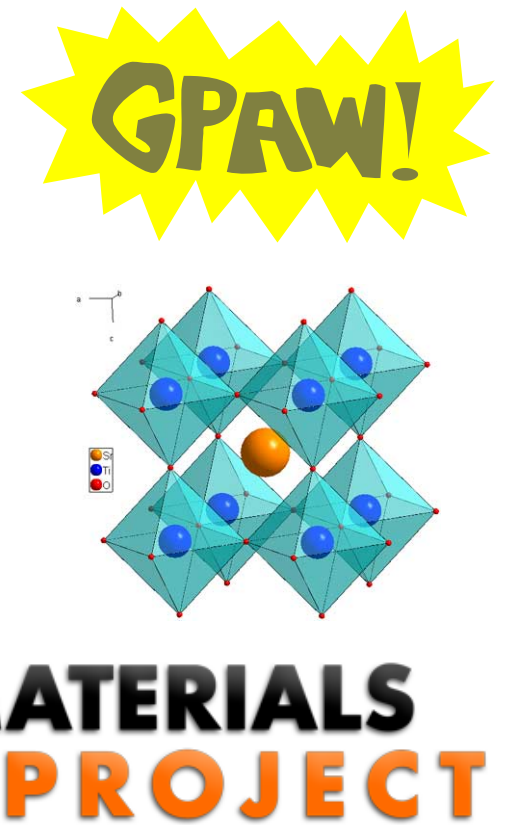
What Is This Talk About?

New materials for solar light conversion into hydrogen and oxygen.

1) Computational Method: Density Functional Theory and screening approach;

2) Water Splitting Applications:
   a) One-photon WS
   b) Two-photon WS
   c) Transparent protective shield

3) Thin Film Solar Cell (photovoltaic):
   a) Single-layer
   b) Double-layer

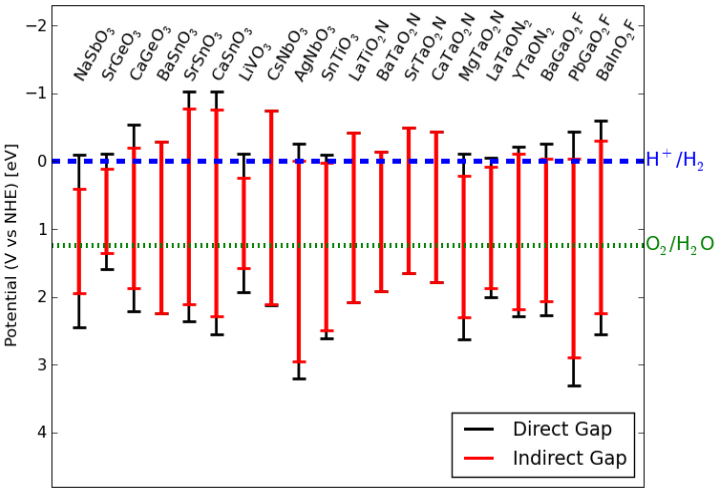


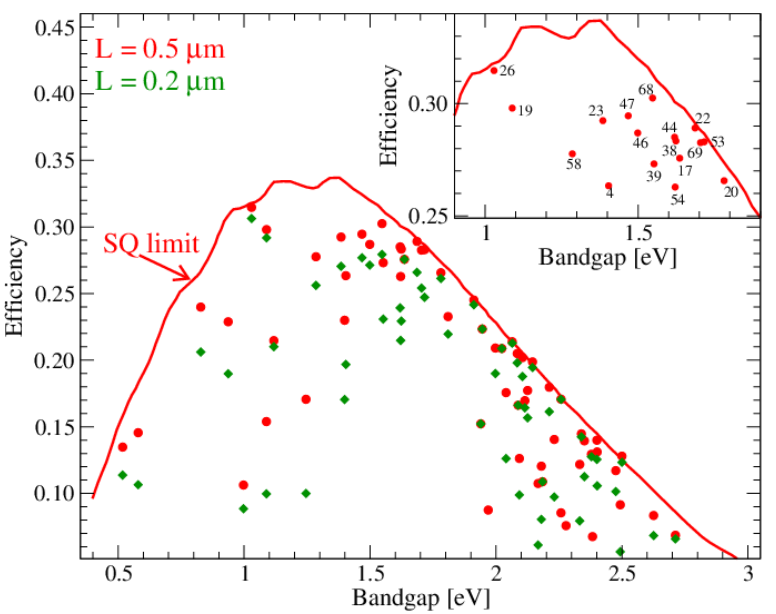
Conclusions

Few materials 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 and 11 for double-layer.



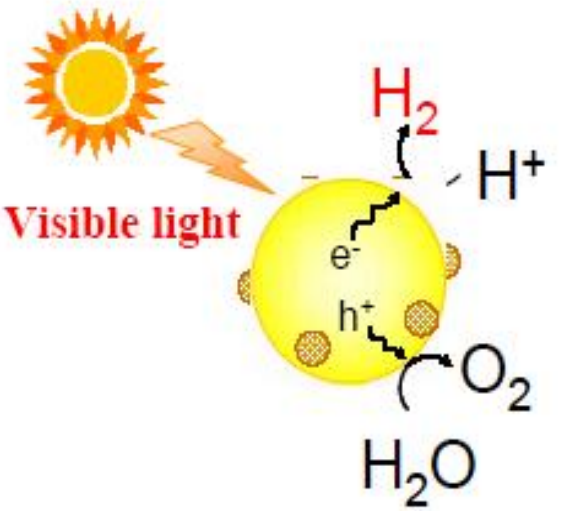


Photoelectrochemical Cell

A material collects the visible part of the solar spectrum and splits water in oxygen and hydrogen.

Complicated process:

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



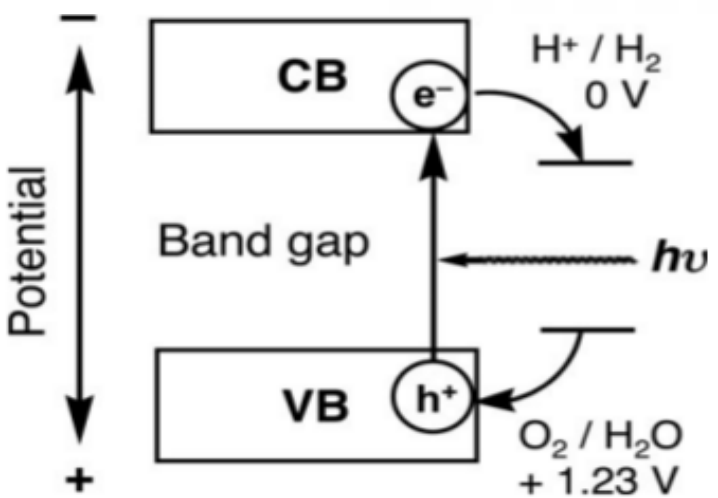
Few examples: TiO_2, GaN:ZnO

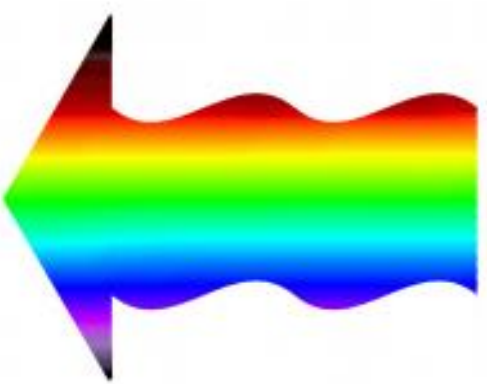
Fujishima and Honda, *Nature* **238**, 37 (1972).

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

Properties for Water Splitting Materials

1) Chemical/structural stability;
2) Bandgap in the visible range;
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.

Properties for Water Splitting Materials

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2) **Bandgap in the visible range**;
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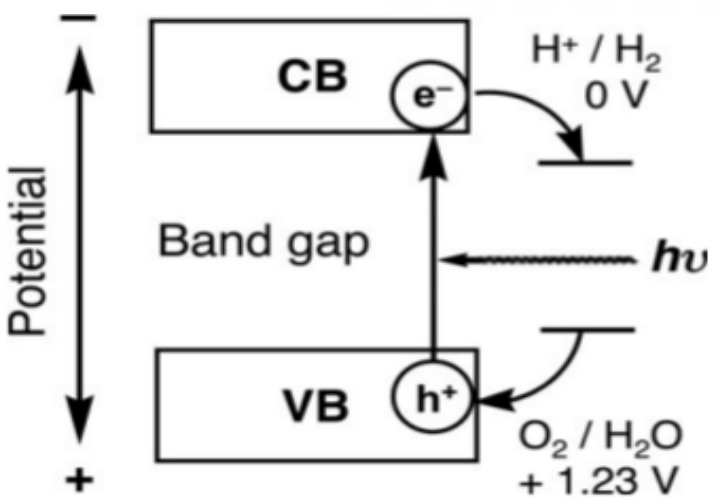
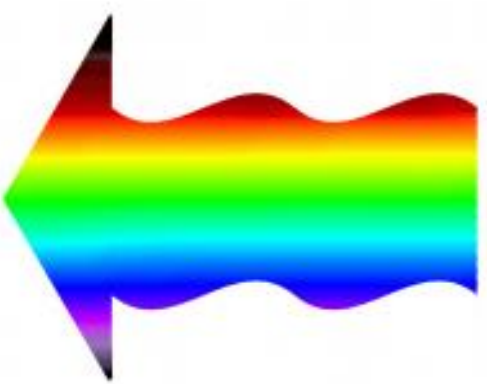
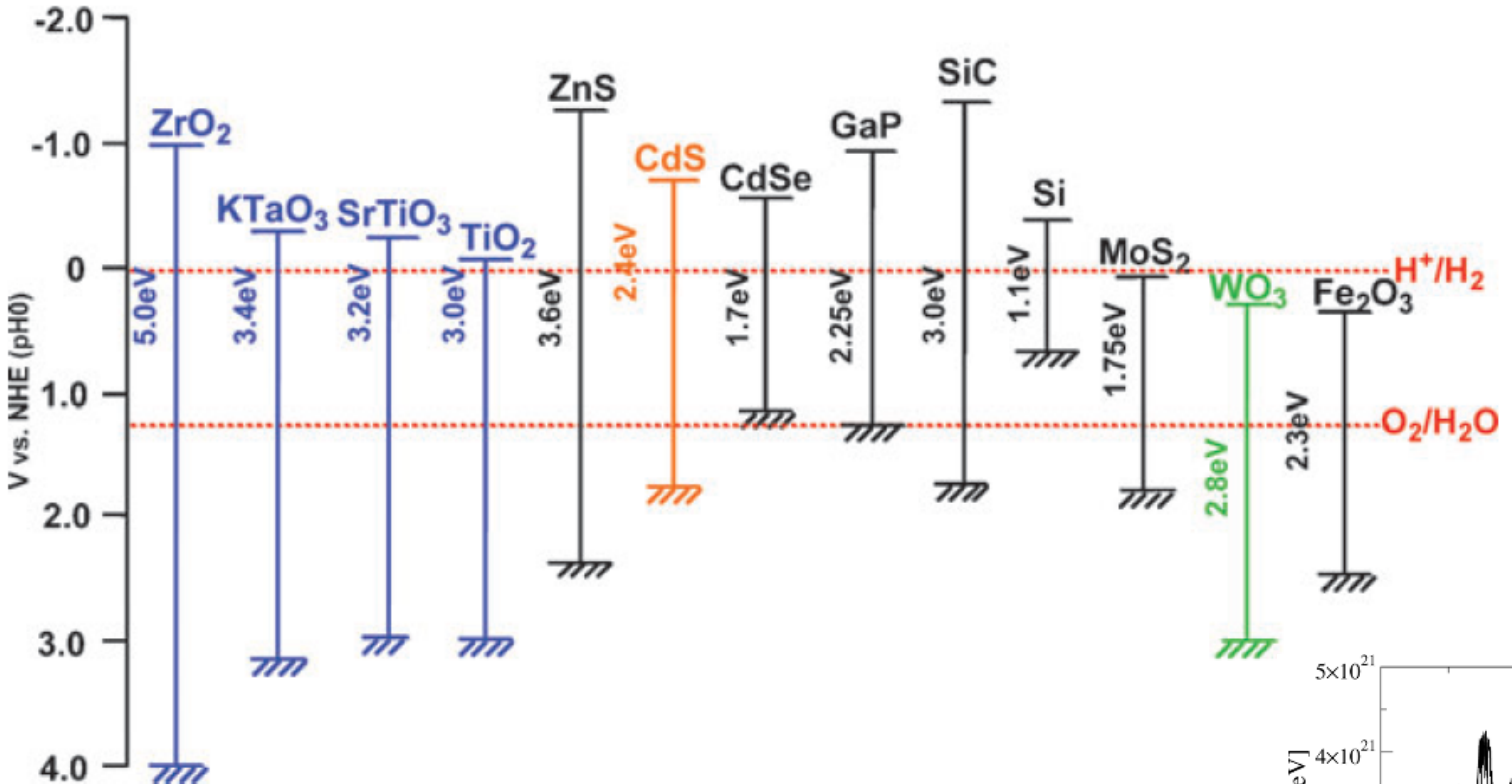
Used in the screening

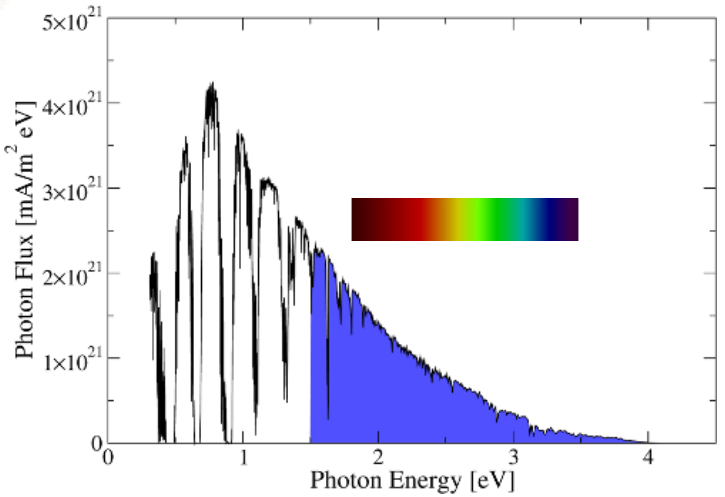




Principle of water splitting using semiconductor photocatalysts.

The Optimal Material Has Not Been Found





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

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

Computational Method:

1) Stability Analysis

Candidates compared with a pool of reference systems (2000 compounds, from the ICSD experimental database):

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

Energies calculated from DFT-GGA: RPBE xc-functional.

Formation energy (solved by linear programming):

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

$$c_i \geq 0, \qquad c_1 + c_3 = 1\,, \qquad c_2 + c_4 = 1\,, \qquad c_3 + c_4 + c_5 = 3$$

Candidate **stable** if: $\Delta E \leqslant 0.2 \;\; eV/atom$

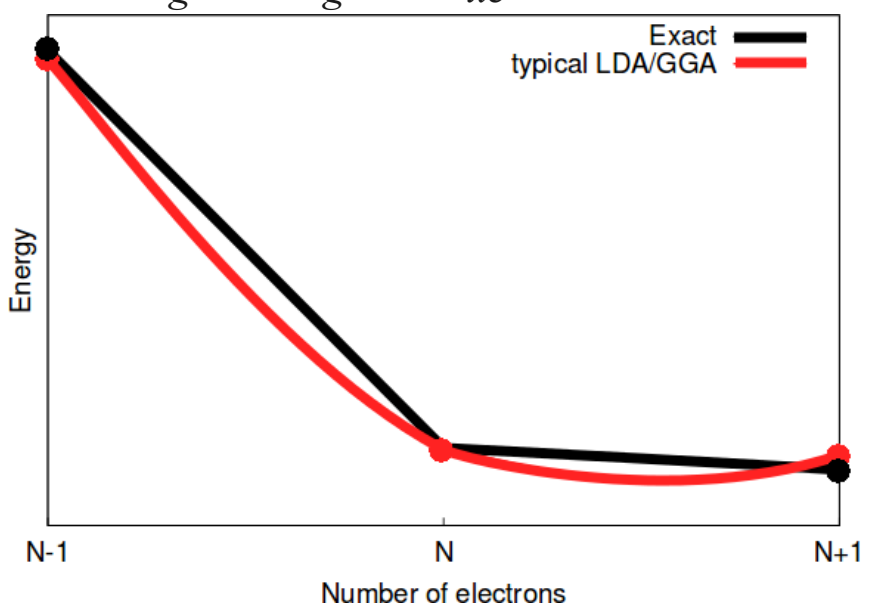
Computational Method:

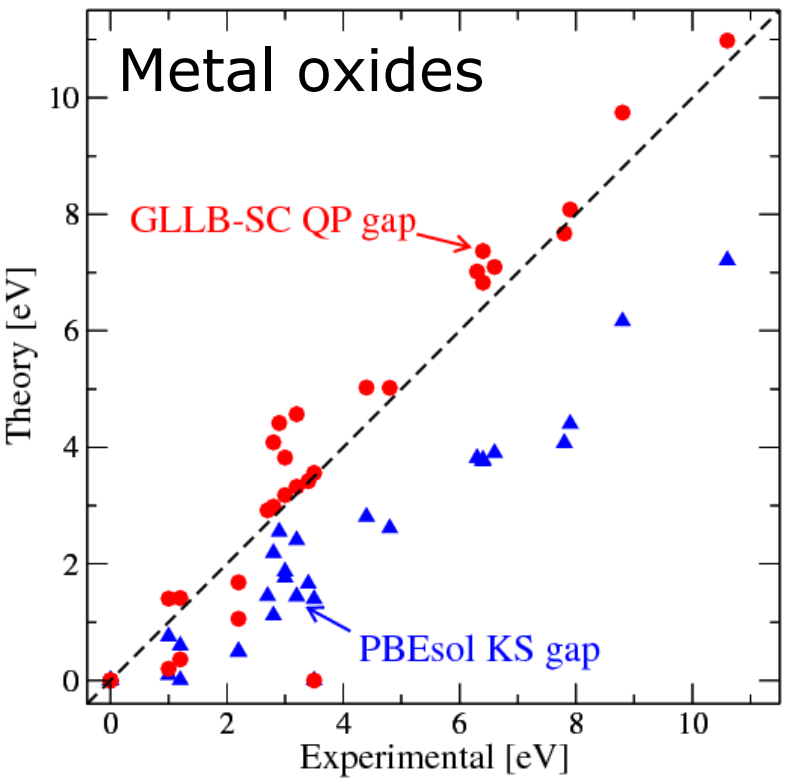
2) Calculation of the bandgaps: GLLB-SC

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

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

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





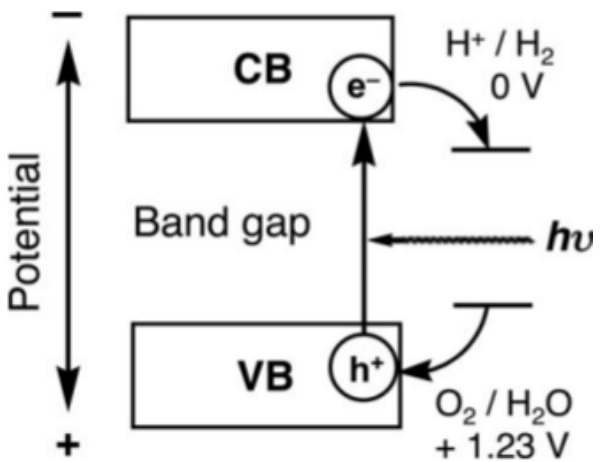
Gap within an error 0.5 eV.
Minimal computational cost.

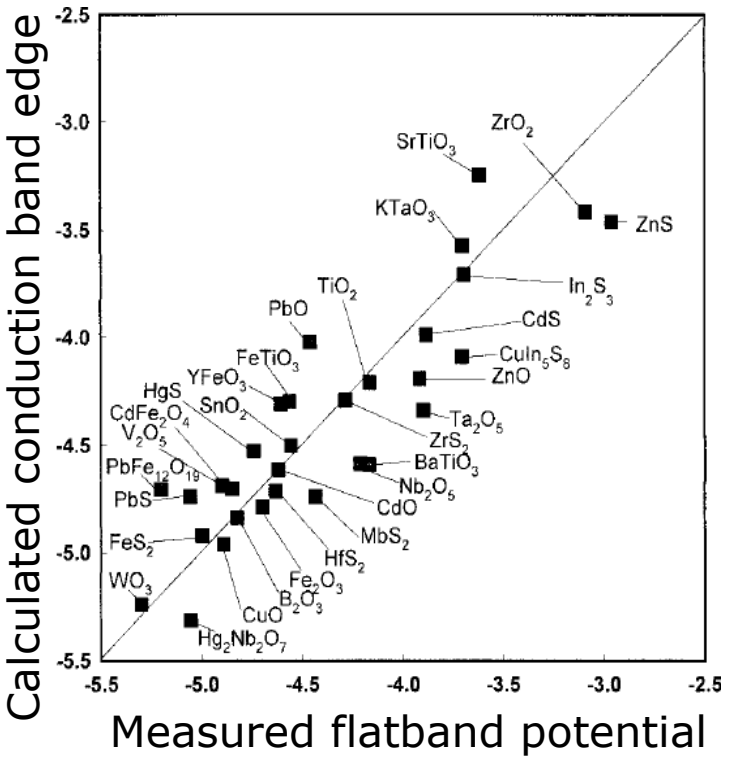
I. E. Castelli, T. Olsen, S. Datta, D. D. Landis, S. Dahl, K. S. Thygesen, and K. W. Jacobsen, *Energy & Environmental Science*, **5**, 5814 (2012).

Computational Method:

3) Evaluation of the band edges

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





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

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

E_{gap} = Bandgap

E_0 = Reference electrode potential vs vacuum

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

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

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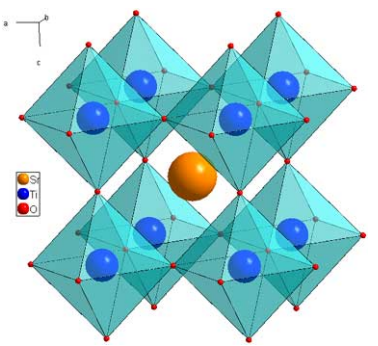
GPAW!

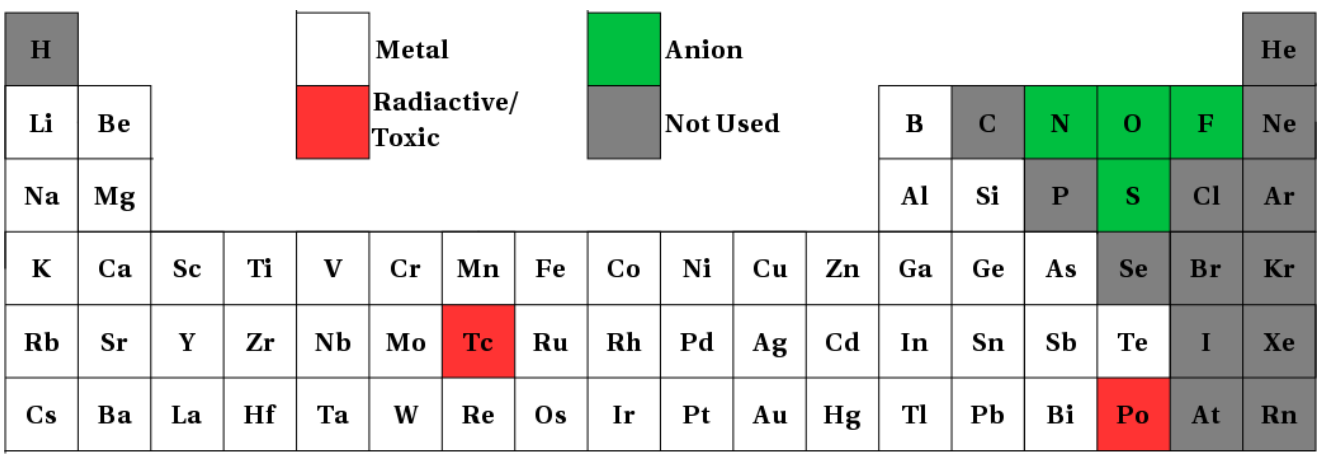


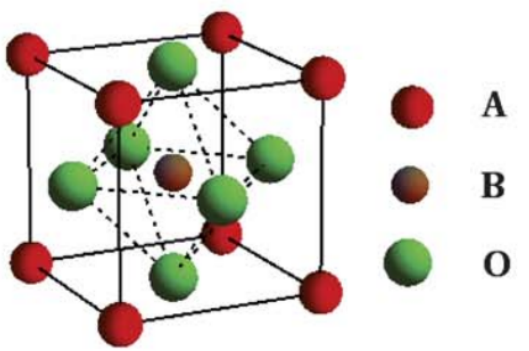
MATERIALS PROJECT

A Materials Genome Approach

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: 2 metals and 3 anions)
- 52 metals from the periodic table;
- Different anions (O, N, S, F, Cl, …).

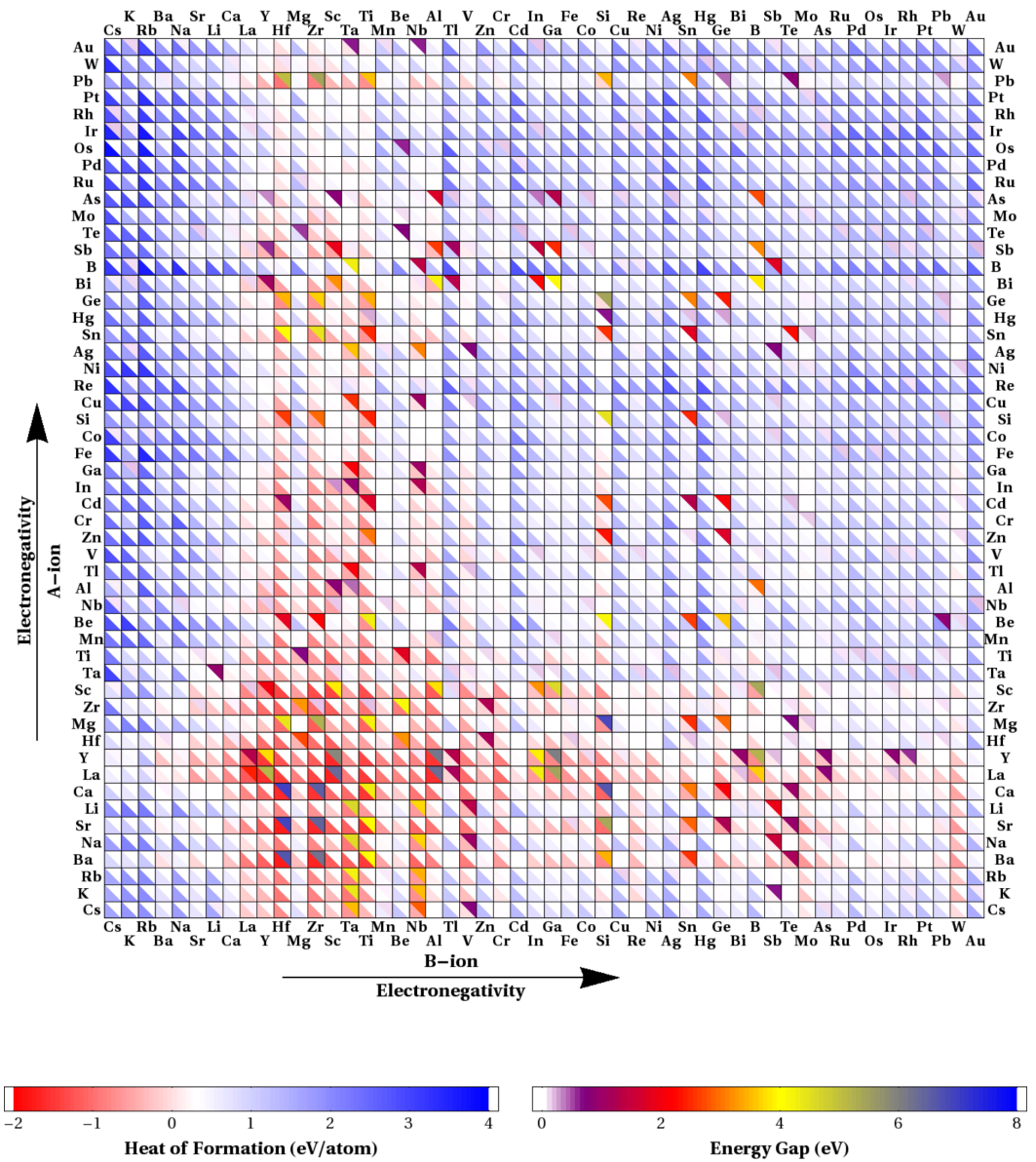


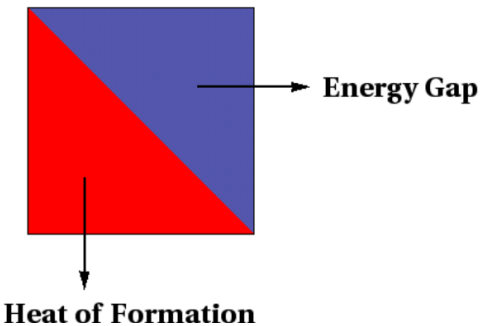


Excluded elements:

- Non Metals;
- Radioactive, toxic.

ABO_3 Perovskite



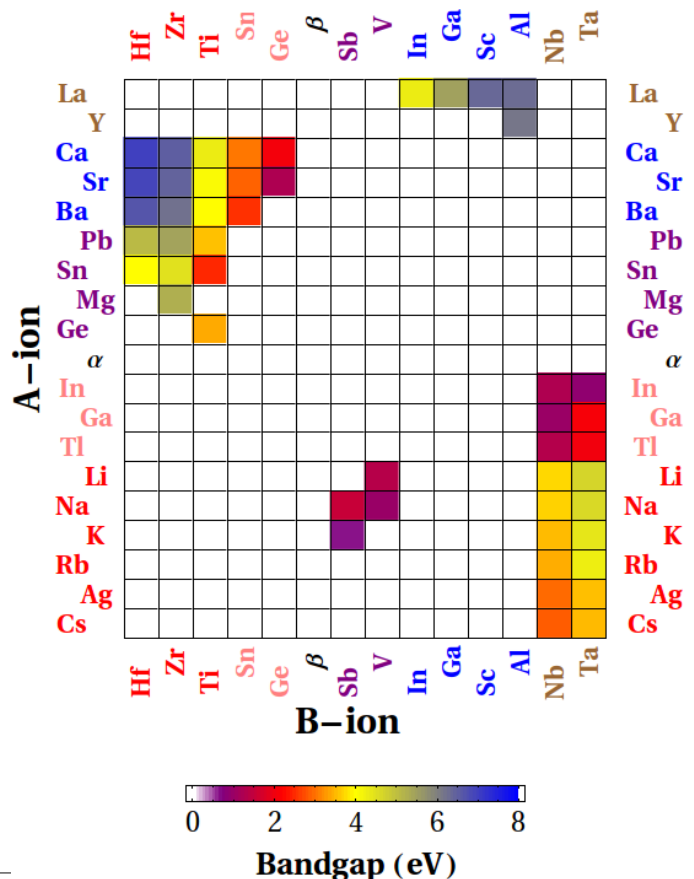


Trends for stability and bandgap:
- Goldsmith's tolerance factor:

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \qquad 0.8 < t < 1.05$$

- even number of electrons in the unit cell;
- sum of the possible oxidation states of the two metals = 6 (2 electrons per oxygen atom).

Trends on Bandgaps



Similar elements generate perovskites with similar bandgaps.

Chemical elements grouped depending on the valence and on the position on the periodic table.

Bandgap engineering!

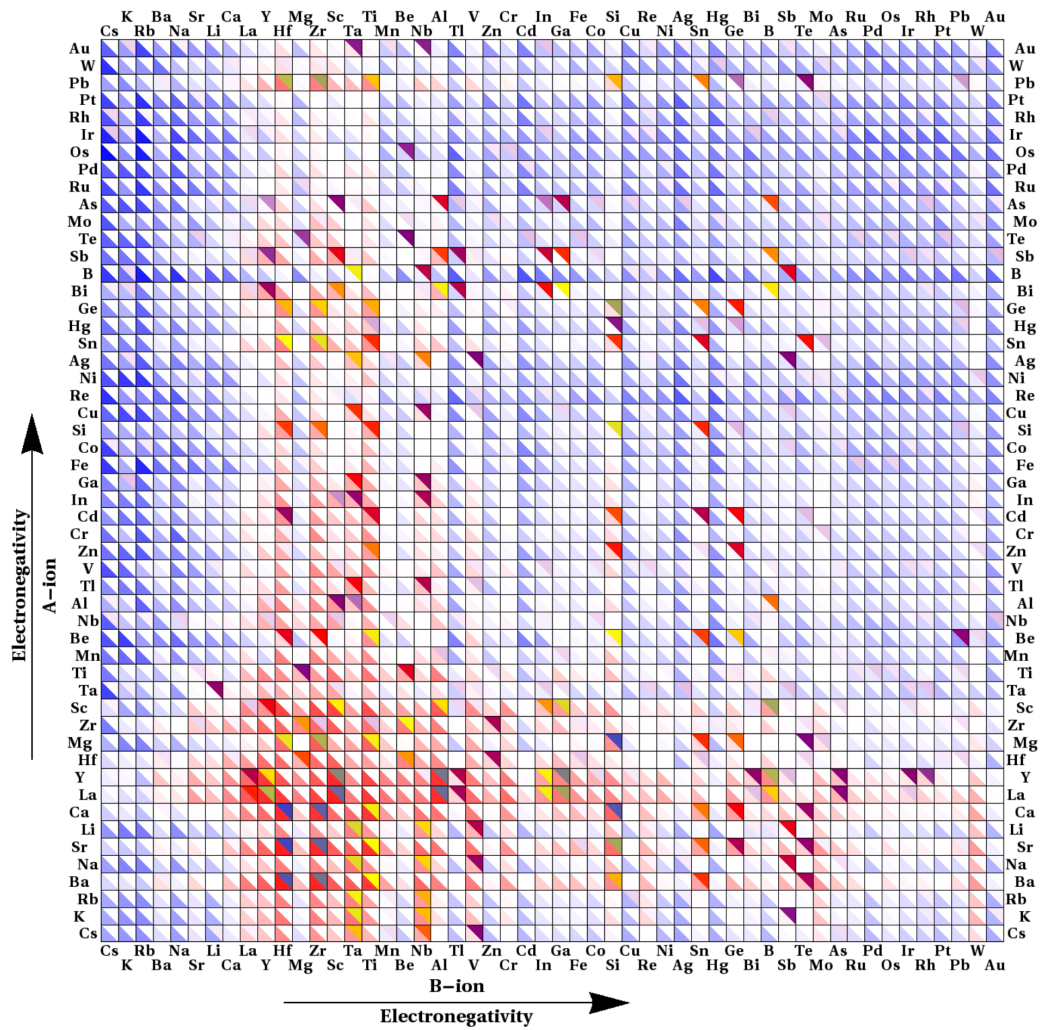
A-ion

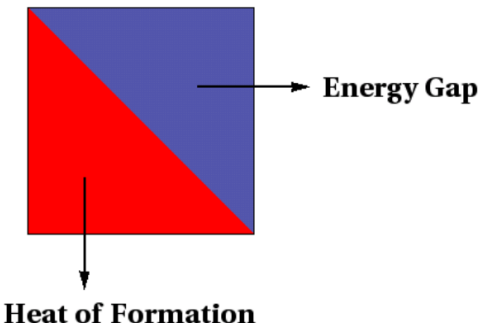
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

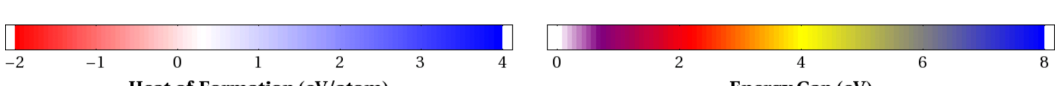
B-ion

H																	He
Li	Be											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

ABO_3 Perovskite







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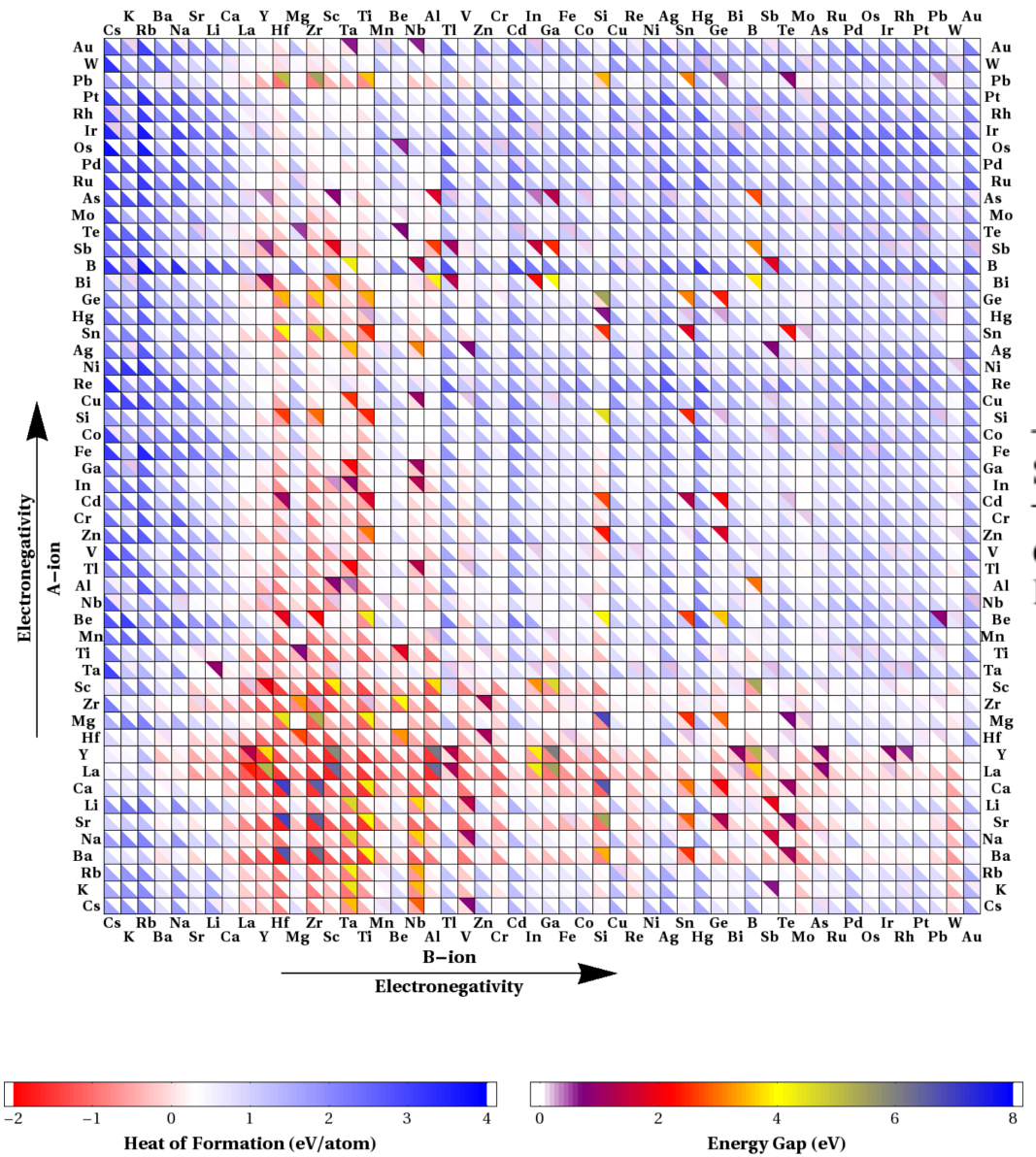
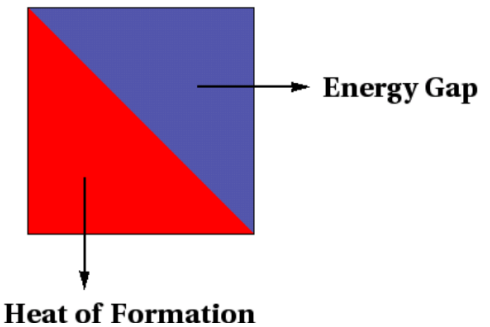


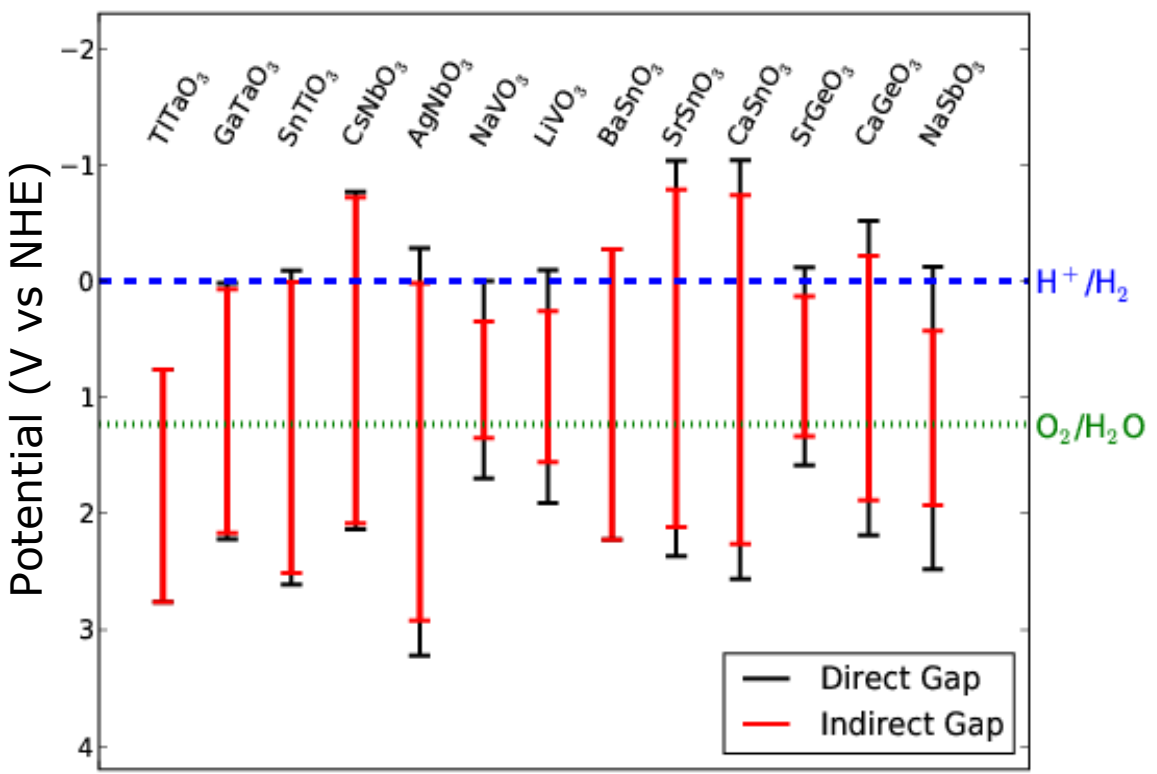


Screening parameters	One-photon WS
Chemical/structural stability (ΔE)	$\Delta E \leq 0.2$ eV
Bandgap (E_{gap})	$1.5 \leq E_{gap} \leq 3$ eV

13 materials fulfill the criteria on stability and bandgap.

Candidates for One-photon WS - Oxides

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



$AgNbO_3$ and $BaSnO_3$ are known:

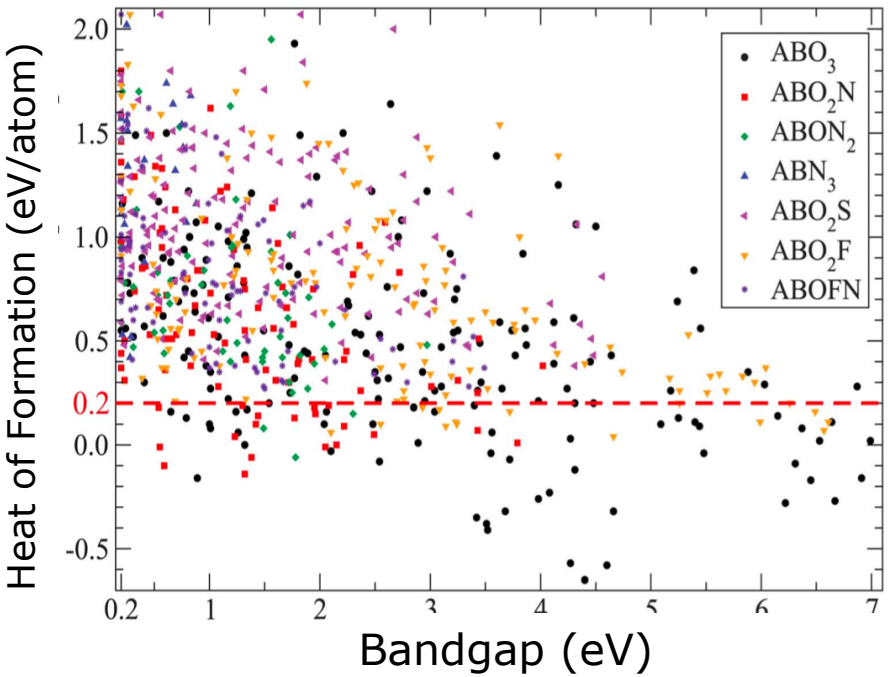
$AgNbO_3$: works!

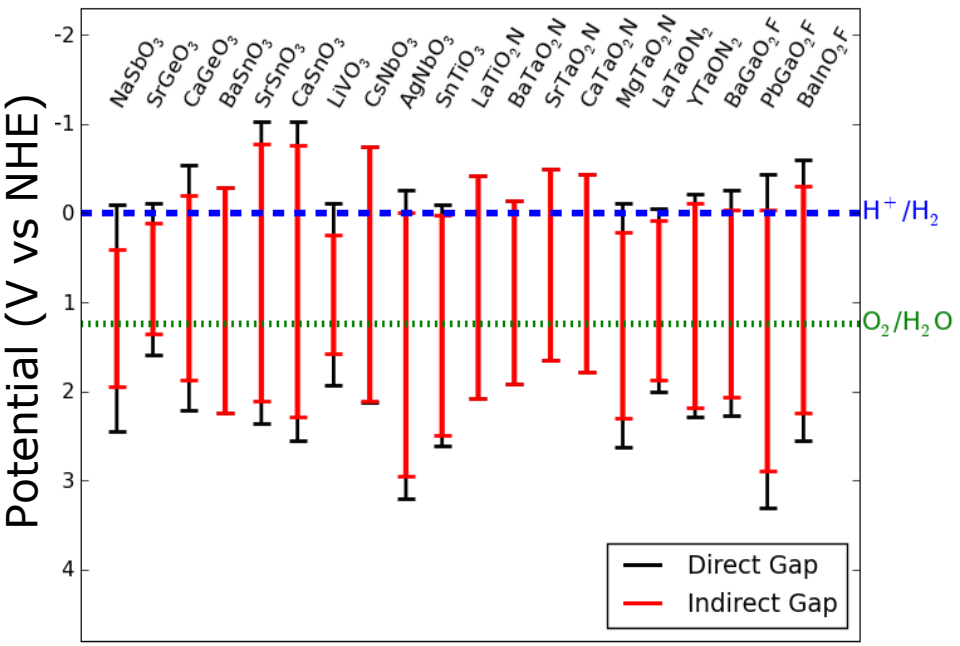
$BaSnO_3$: defect induced recombination.

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

None of the others is known.

Candidates for One-photon WS





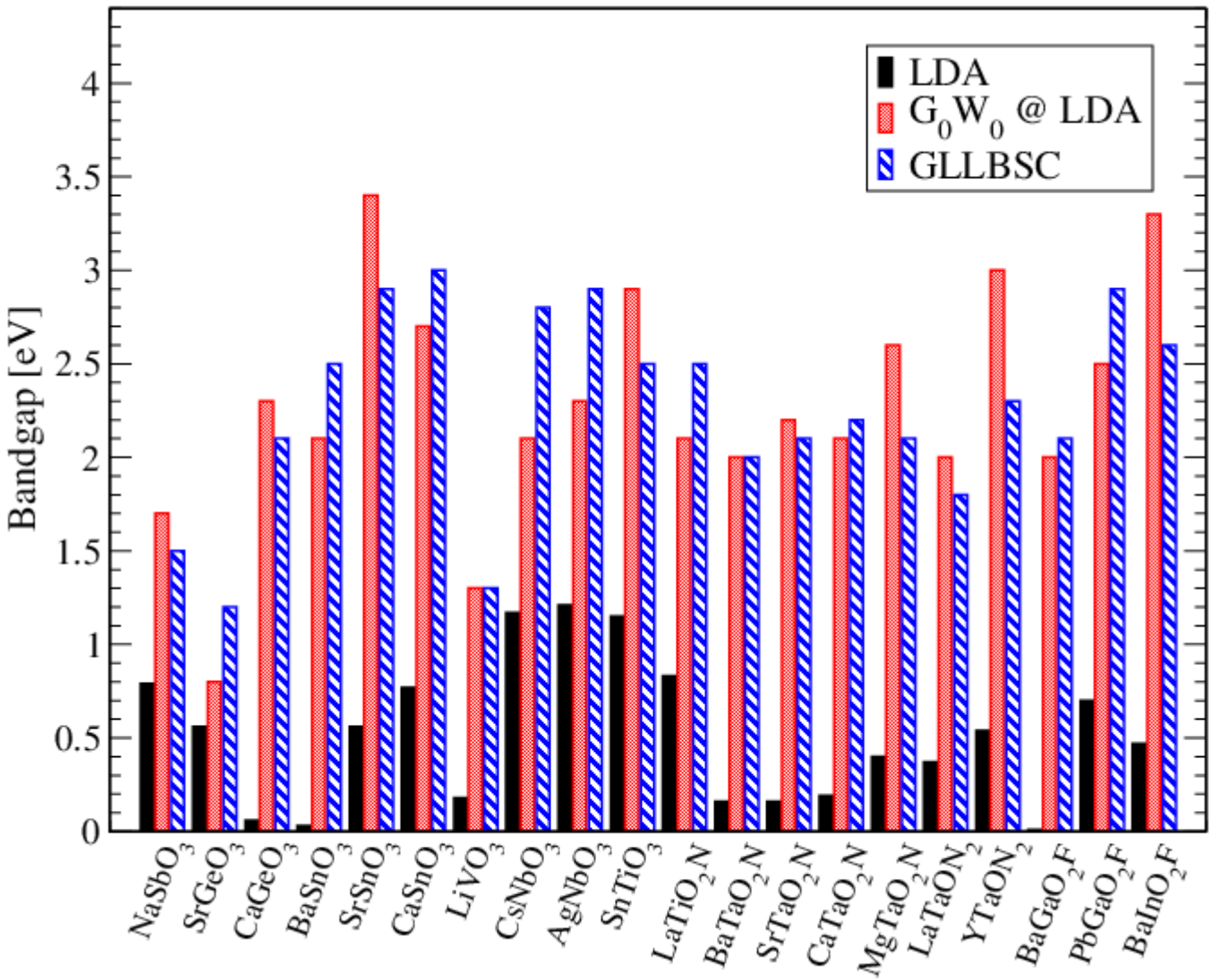
~19000 materials → 20 candidates

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



LDA: underestimate
PBE0: overestimate

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

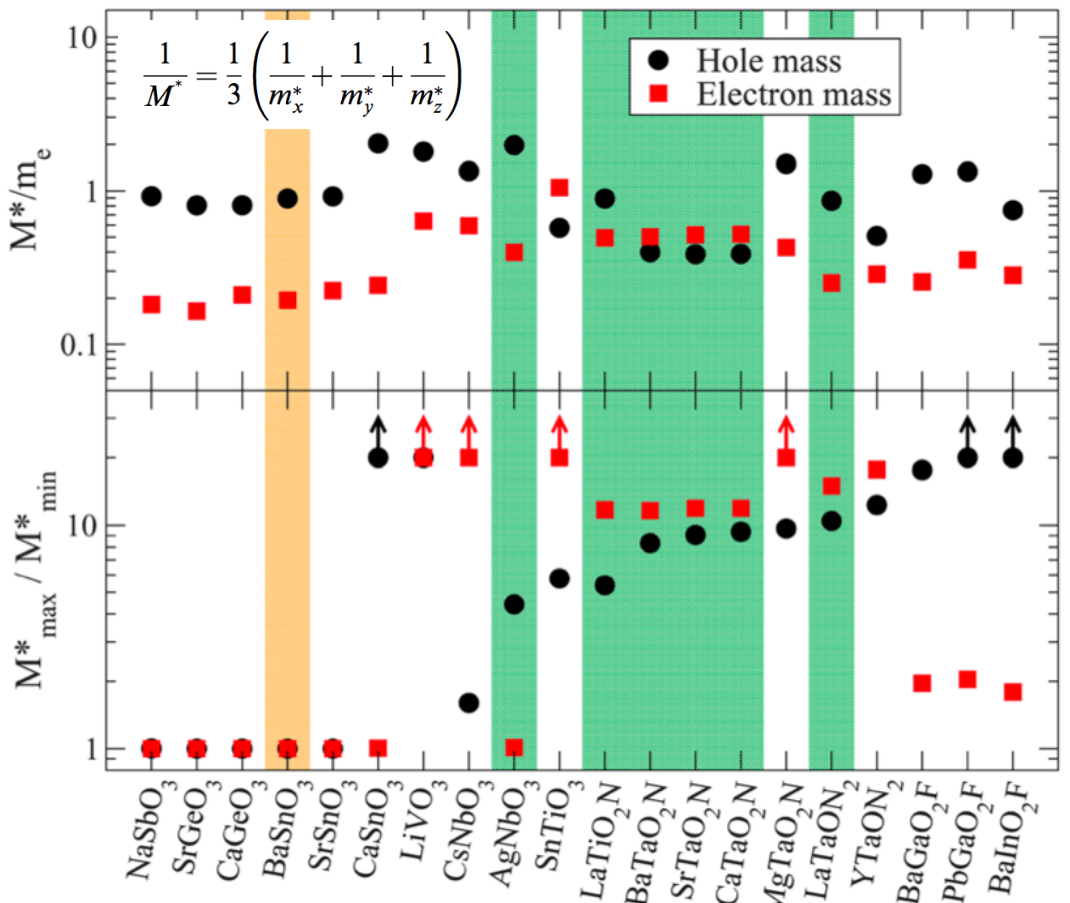
MAE = 0.35 eV

I. E. Castelli, J. M. Garcia-Lastra, F. Huser, K. S. Thygesen, and K. W. Jacobsen, *Submitted* (2013).

e-h Mobility and Effective Masses

Mobility goes with the inverse of the effective mass:

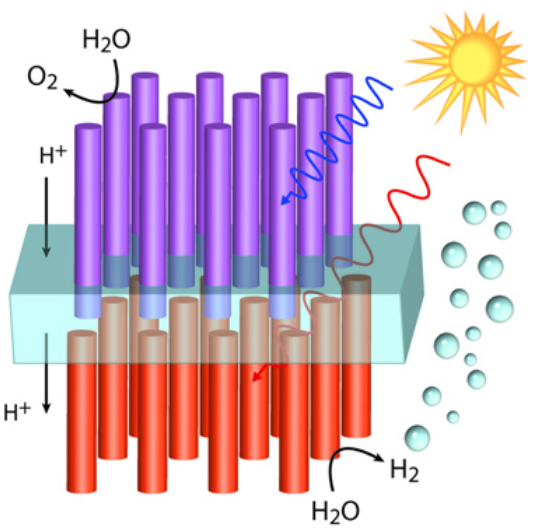
$$\mu = \frac{q}{m^*}\overline{\tau} \qquad m^* = \hbar^2 \left(\frac{\partial^2 \epsilon}{\partial k_i \partial k_j} \right)^{-1}$$



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

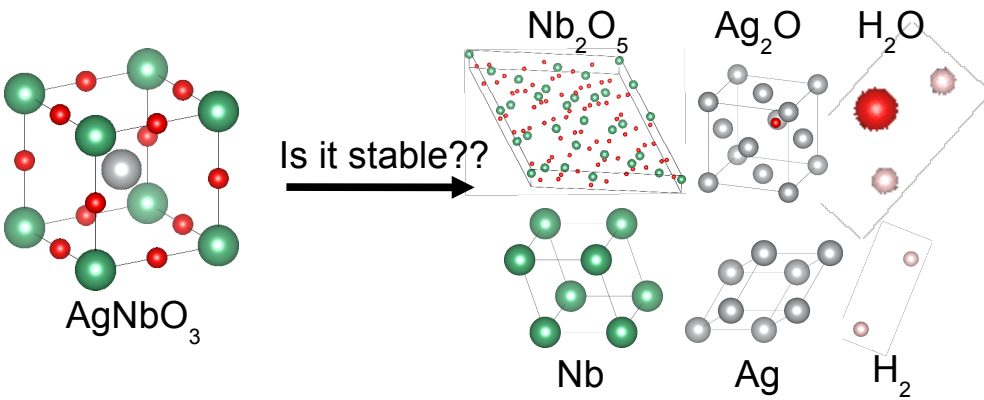
Orange system: $BaSnO_3$ known not to work (defect-assisted recombination).

Systems observed to work seems to have similar e-h masses.

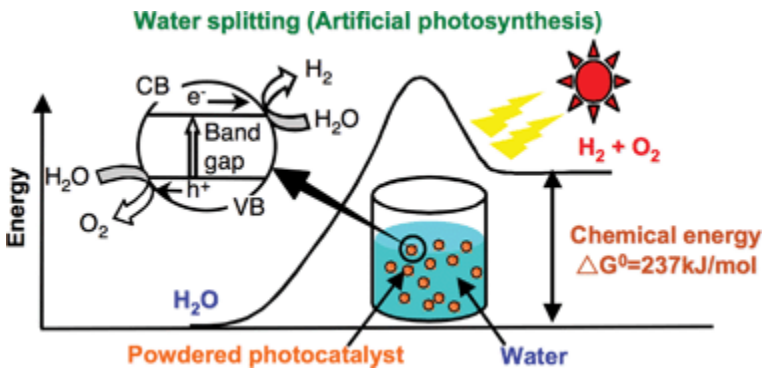


Calculation of the Stability in Water

So far: stability against solid phases.



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



Are our candidates stable also in water?

Evaluate the stability also versus dissolved phases and at various pH/potential.

→ **Pourbaix diagrams**

Pourbaix Diagram for Zinc

General reaction:

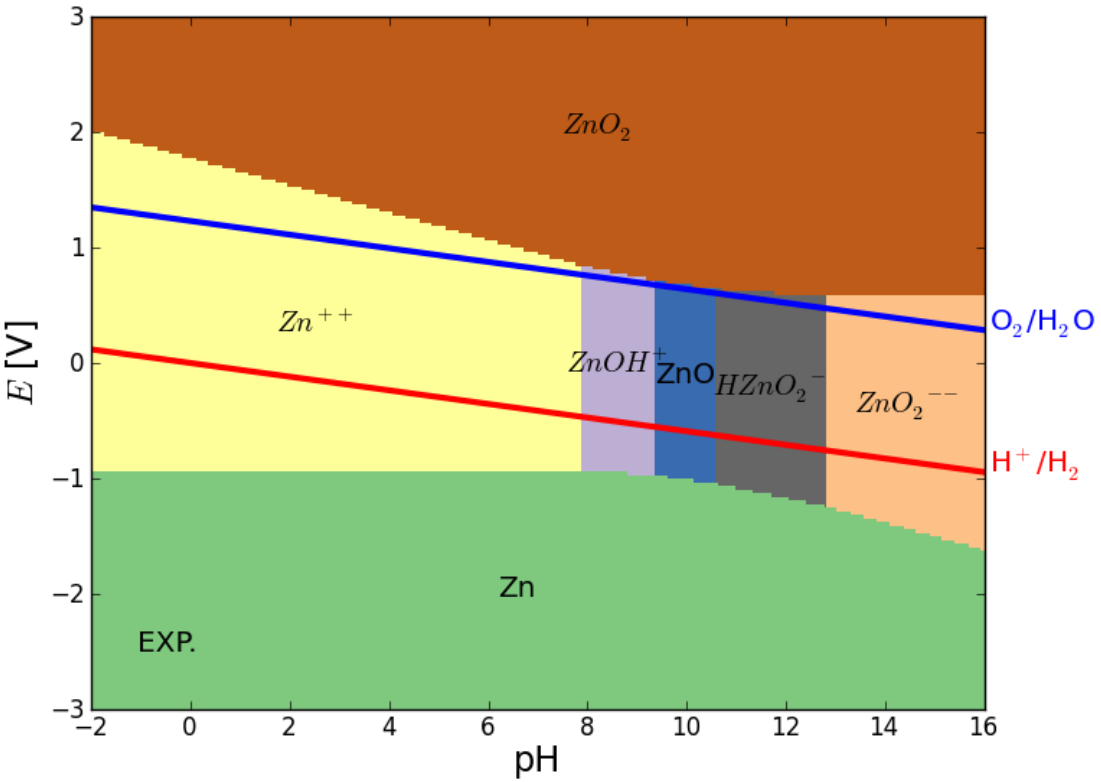
$$rR + wH_2O = pP + hH^+ + ne^-$$

Nernst equation at room temperature:

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

Solids: DFT

Dissolved phases: Experiments



Three different lines:

– vertical: solid, dissolved phases and hydrogen ions. $ZnOH^+_{(aq)} = ZnO + H^+$

– horizontal: solid, dissolved phases with free electrons. $Zn^{++}_{(aq)} = Zn + 2e^-$

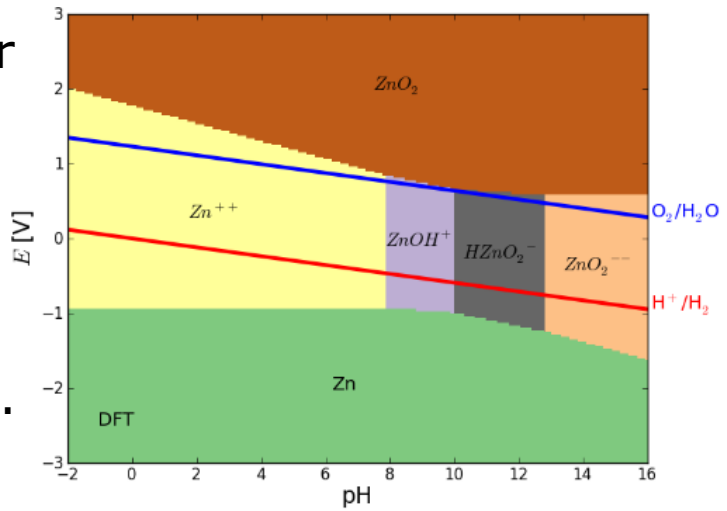
– straight with a slope equal to 0.0591h/n: solid and dissolved phases with free electrons and hydrogen ions. $Zn + H_2O = ZnO + 2H^+ + 2e^-$

DFT vs Experiments

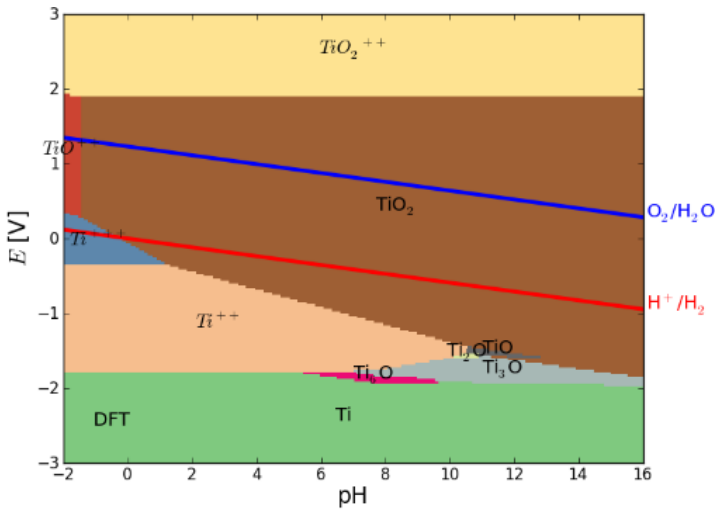
Pourbaix diagrams for Zn and Ti.

DFT and Experiments give similar diagrams.

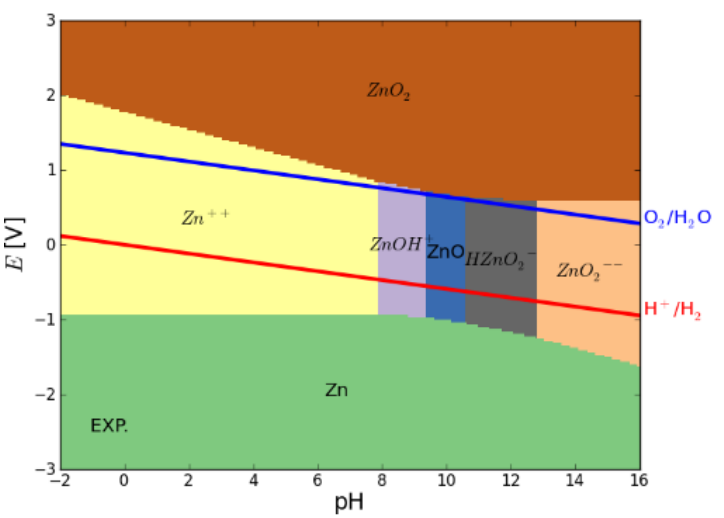
Discrepancies:
- inaccuracy in the data/calculations;
- metastability and reaction kinetics;
- role of surfaces and their passivation;
- more data available for DFT calculations.



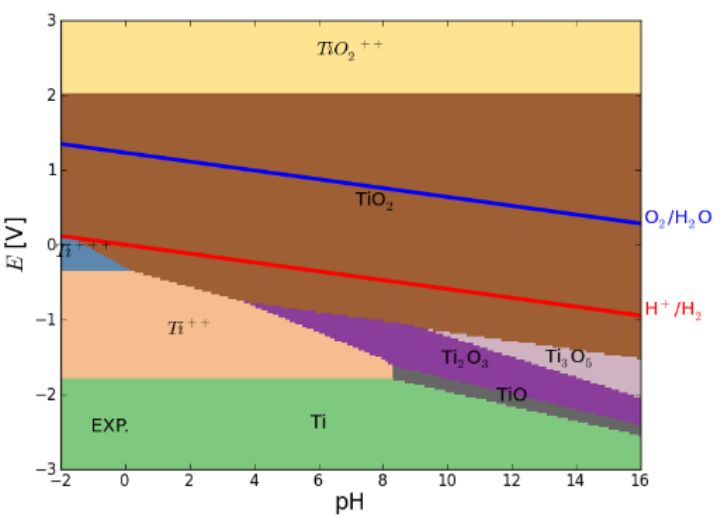
(a) ZnO - DFT



(b) TiO_2 - DFT

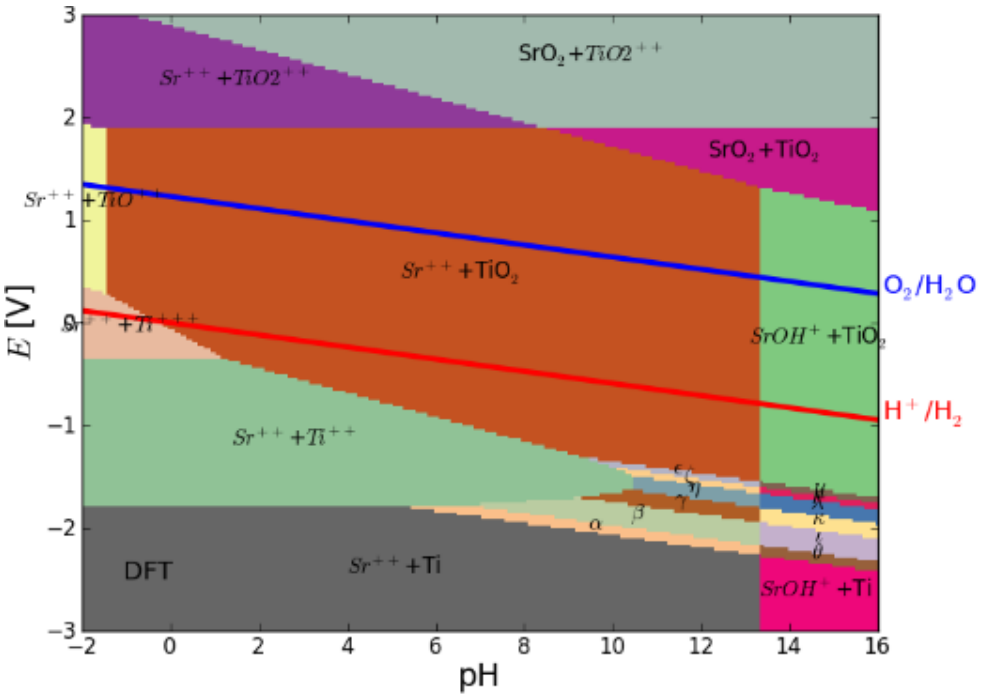


(c) ZnO - Experiments

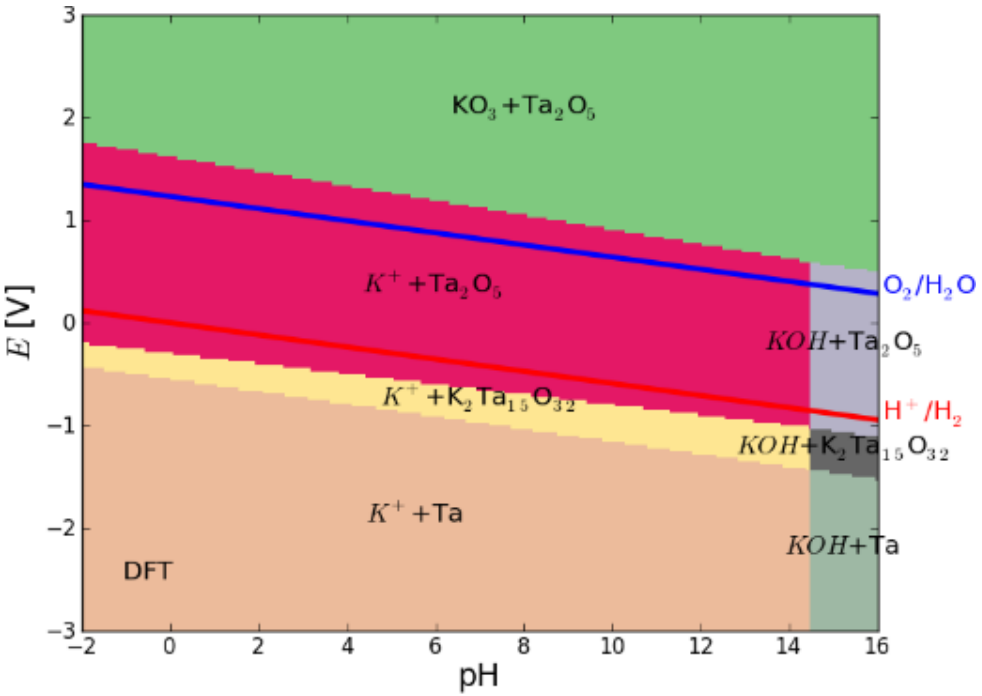


(d) TiO_2 - Experiments

$SrTiO_3$ and $KTaO_3$



(a) $SrTiO_3$ - DFT



(b) $KTaO_3$ - DFT

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

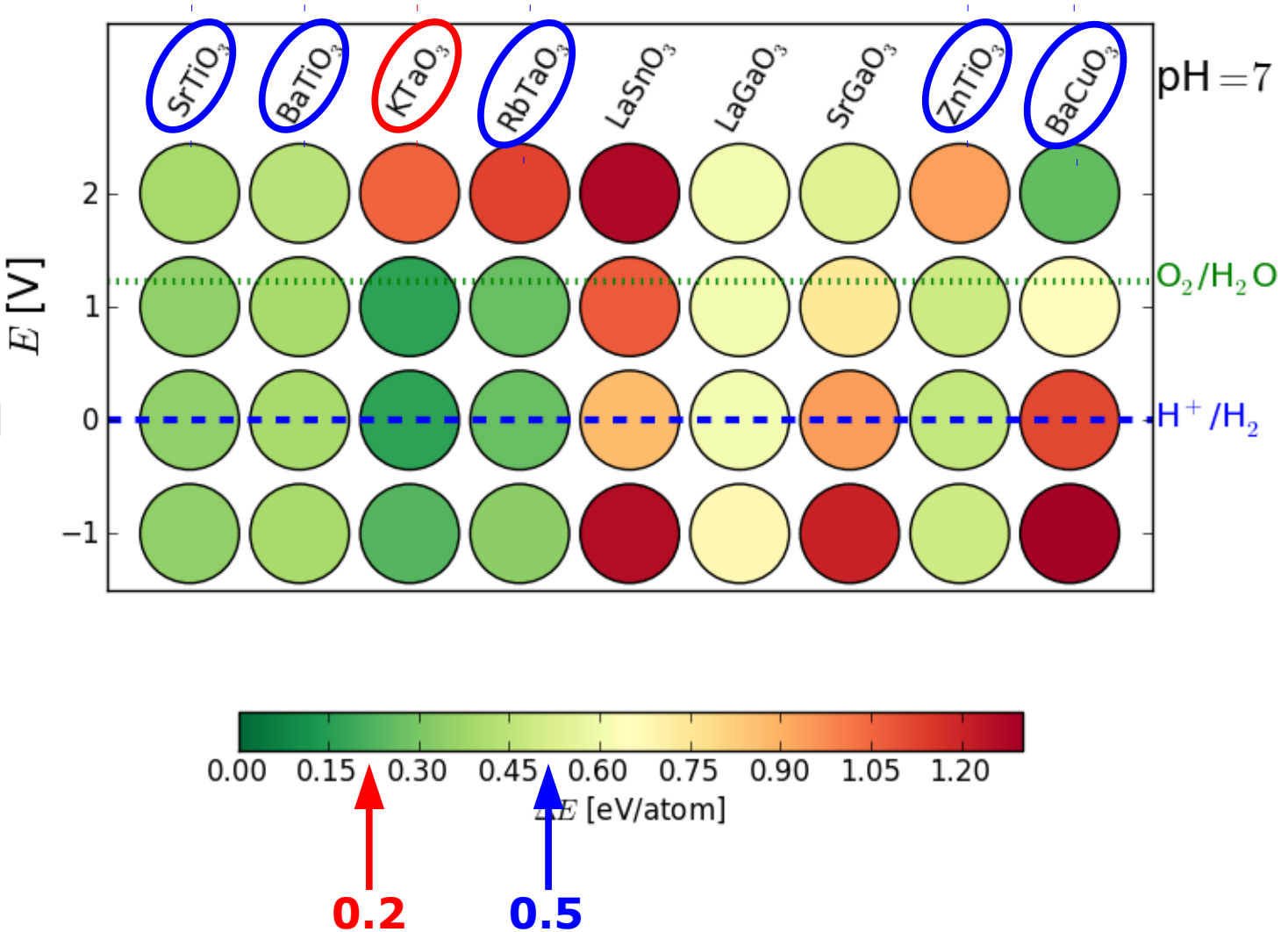
But they are experimentally known to be stable and used for water splitting.
The reaction kinetics (not included in the Pourbaix diagrams) and metastability are important to define stable materials!
We can increase the energy threshold to take into account these effects.

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 energy threshold of **0.2 eV/atom**.

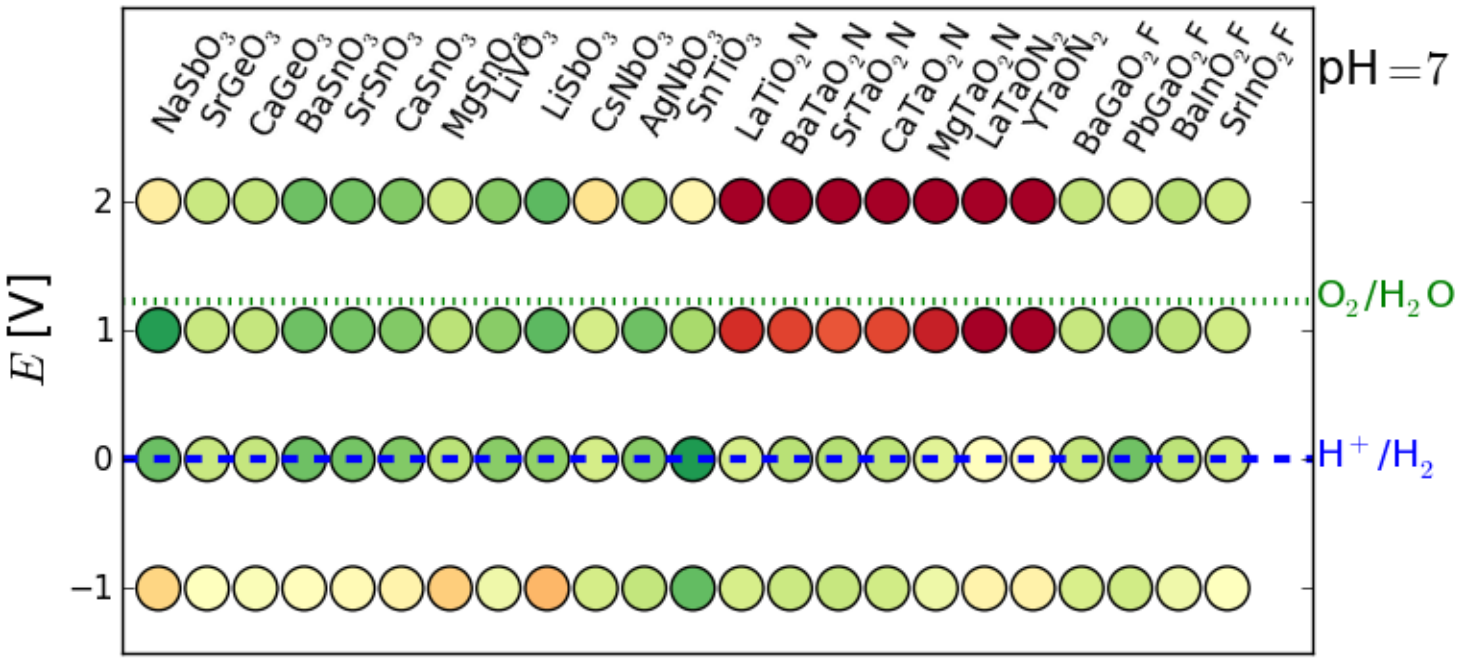
Few more are stable with a larger threshold (**0.5 eV/atom**).



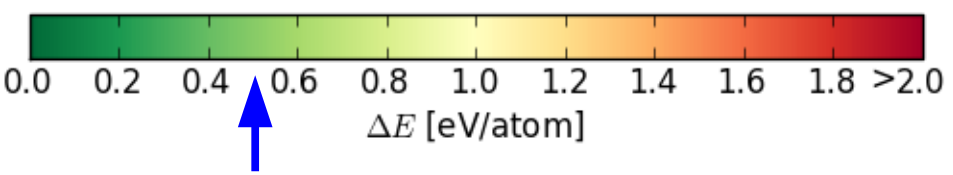
Water Splitting Candidates

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

Oxynitrides are less stable, especially at high potential.

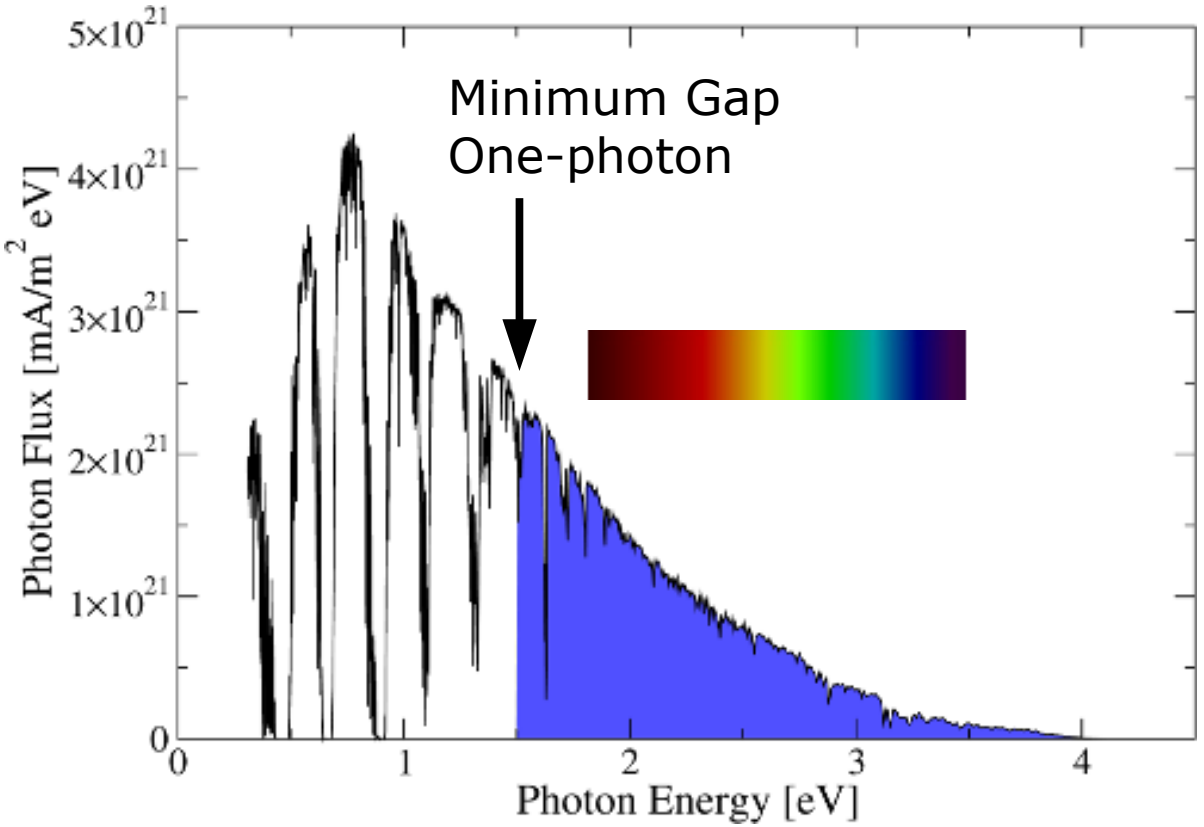


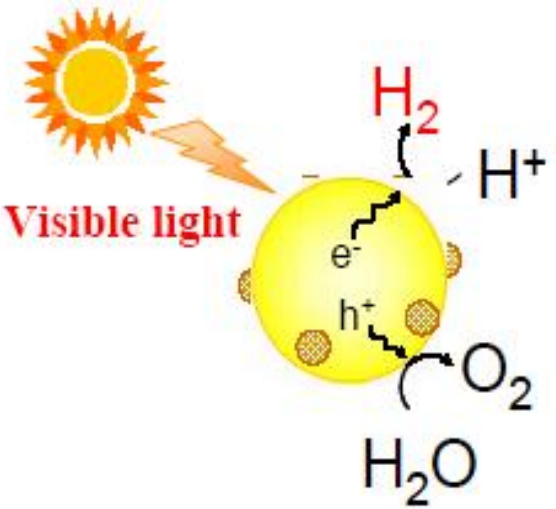
I. E. Castelli, K. S. Thygesen, and K. W. Jacobsen, *Topic in Catalysis* (2013).



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

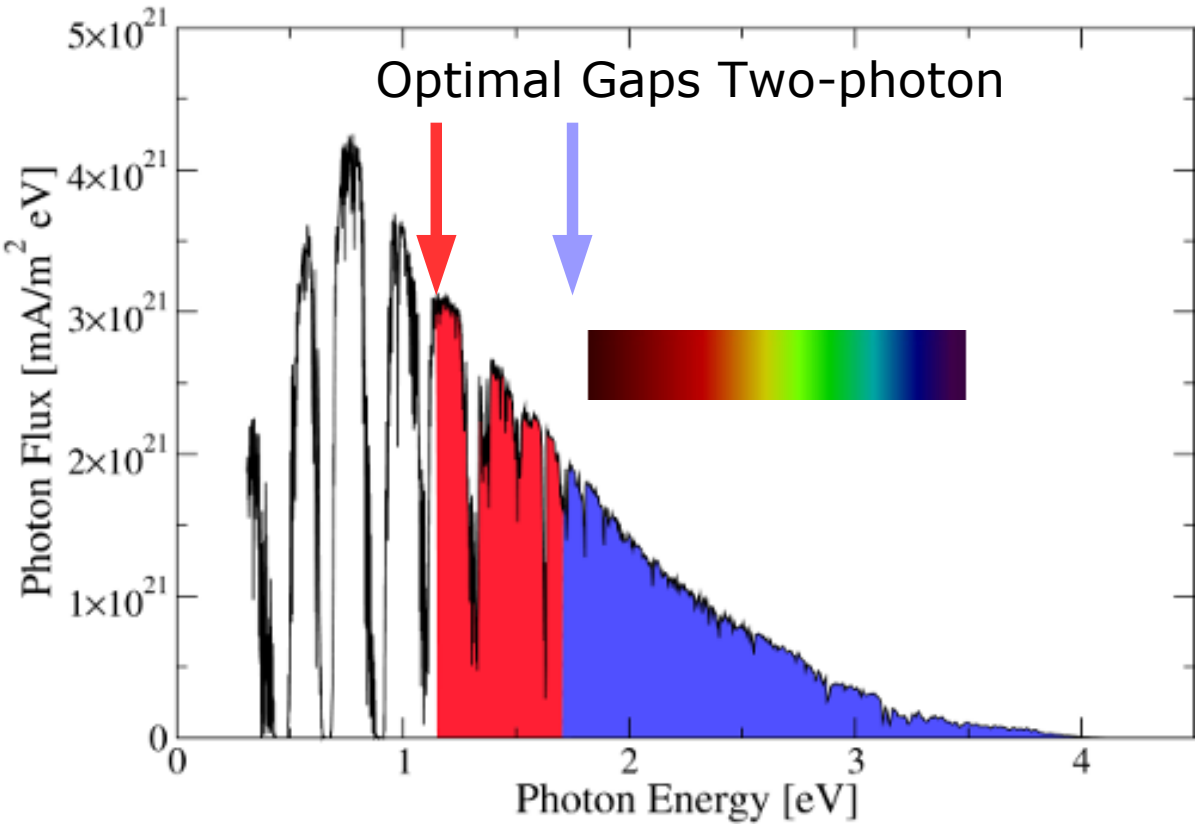
One- vs Two-photon WS

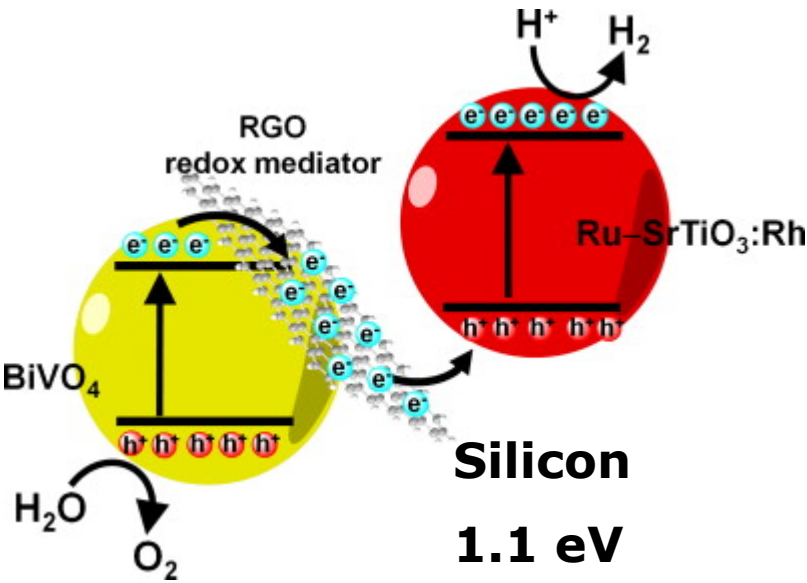




One-photon WS Efficiency: 7 %

One- vs Two-photon WS

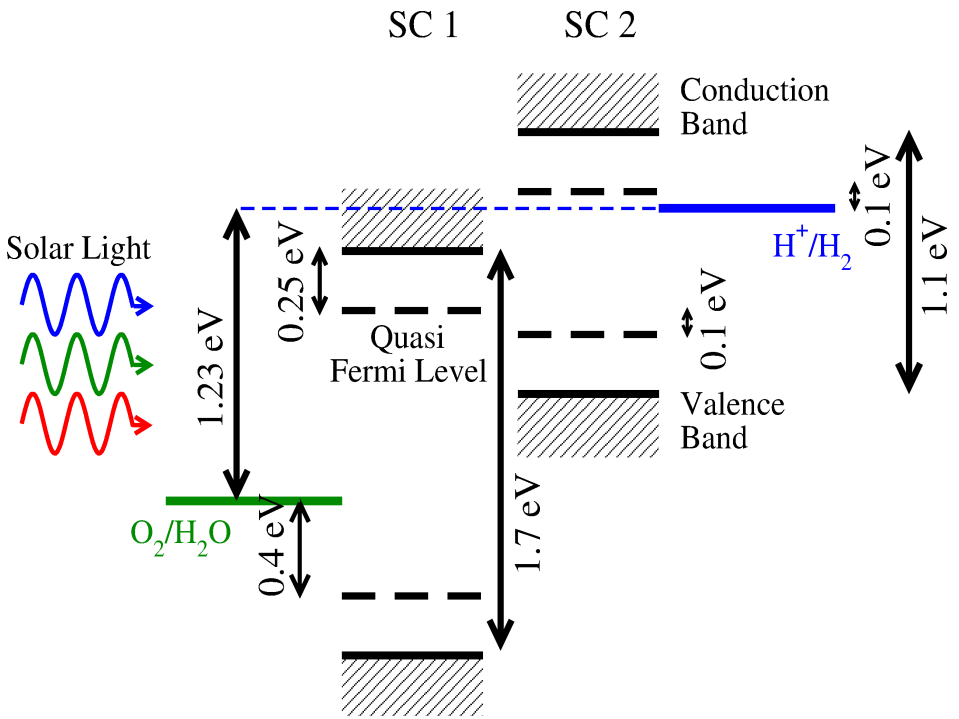




One-photon WS Efficiency: 7 %

Two-photon WS Efficiency: 28 %

Tandem Cell Efficiency



Minimum energy gaps: 2.8 eV

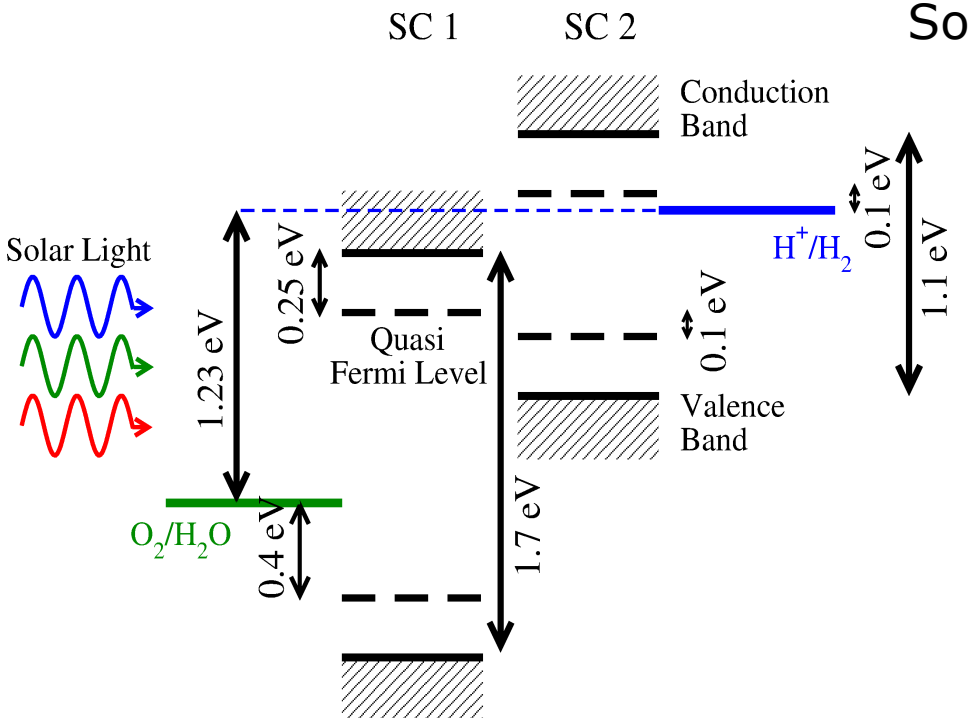
1.23 eV bare water splitting

4 * 0.25 eV Quasi Fermi Level

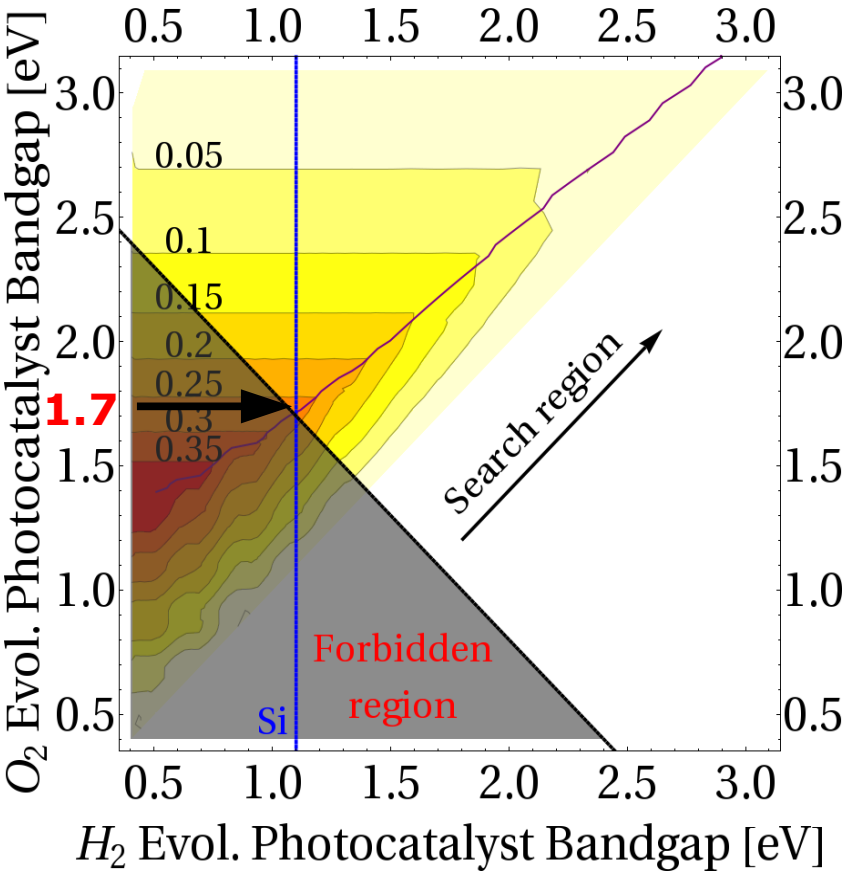
0.4 + 0.1 eV Overpotentials

0.1 eV e-h recombination SC1-SC2

Tandem Cell Efficiency



Solar-to-hydrogen energy conversion efficiency



Minimum energy gaps: 2.8 eV

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0.4 + 0.1 eV Overpotentials

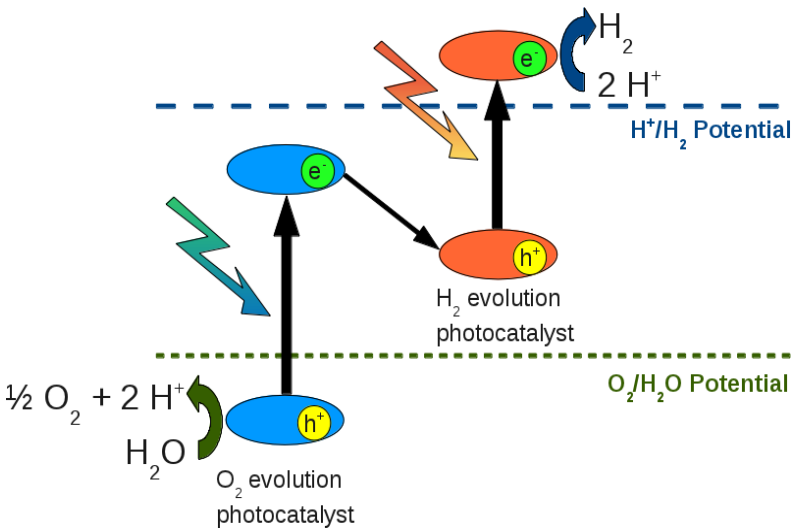
0.1 eV e-h recombination SC1-SC2

J. R. Bolton et al., *Nature* **316**, 495, 1985.

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

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

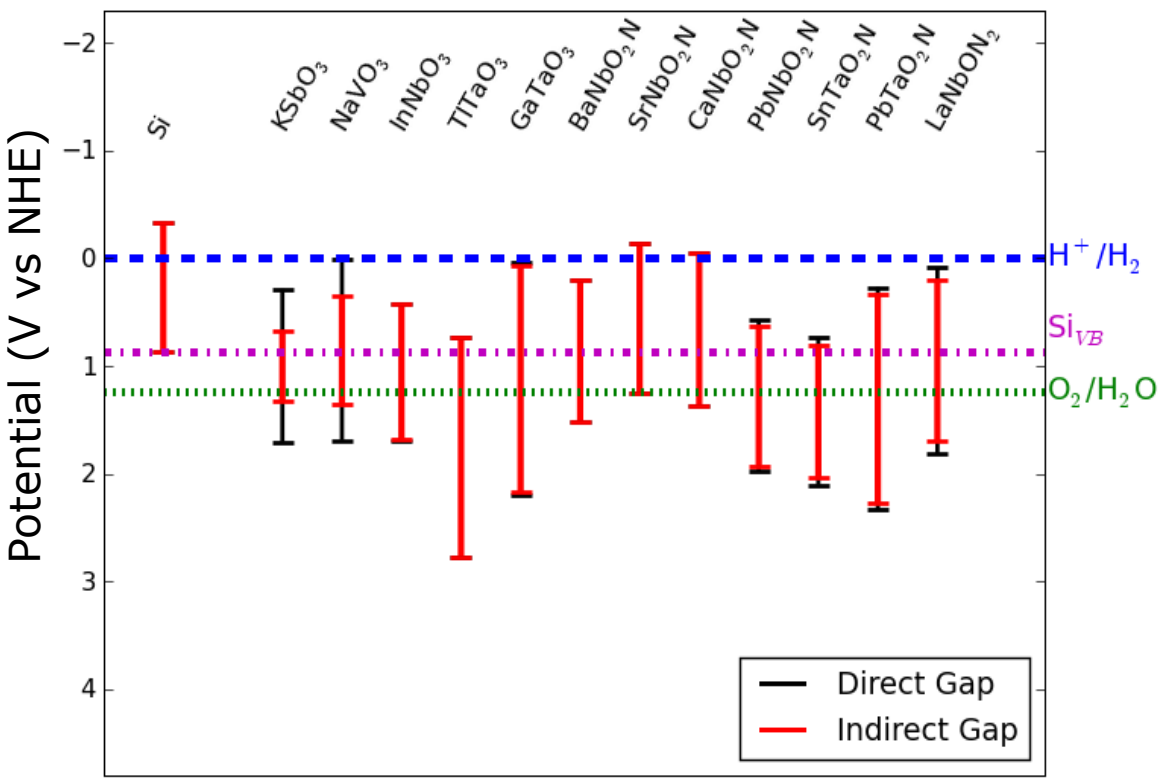
Two-photon WS: Candidates



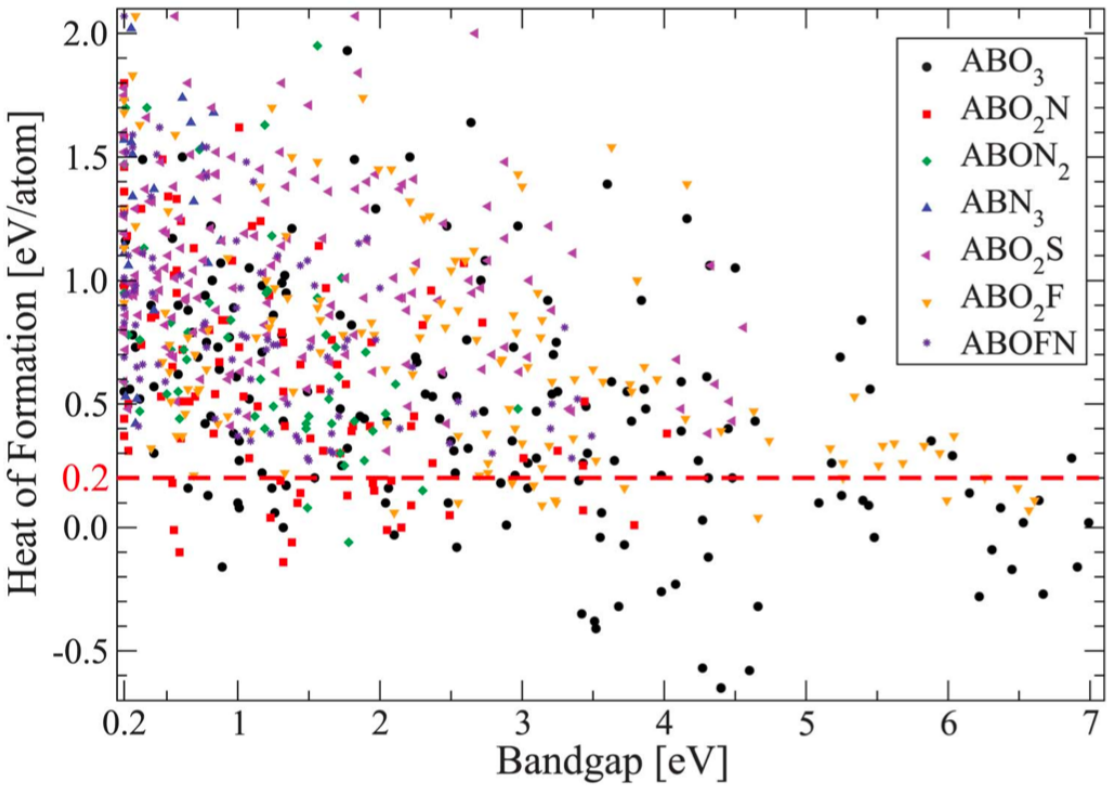
Screening parameters	Two-photon WS
Chemical/structural stability (ΔE)	$\Delta E \leq 0.2$ eV
Bandgap (E_{gap})	$1.3 \leq E_{gap} \leq 3$ eV
Band edges (VB_{edge}, CB_{edge})	$VB_{edge}^{anode} > 1.23$ eV $CB_{edge}^{cathode} < 0$ eV $VB_{edge}^{cathode} > CB_{edge}^{anode}$

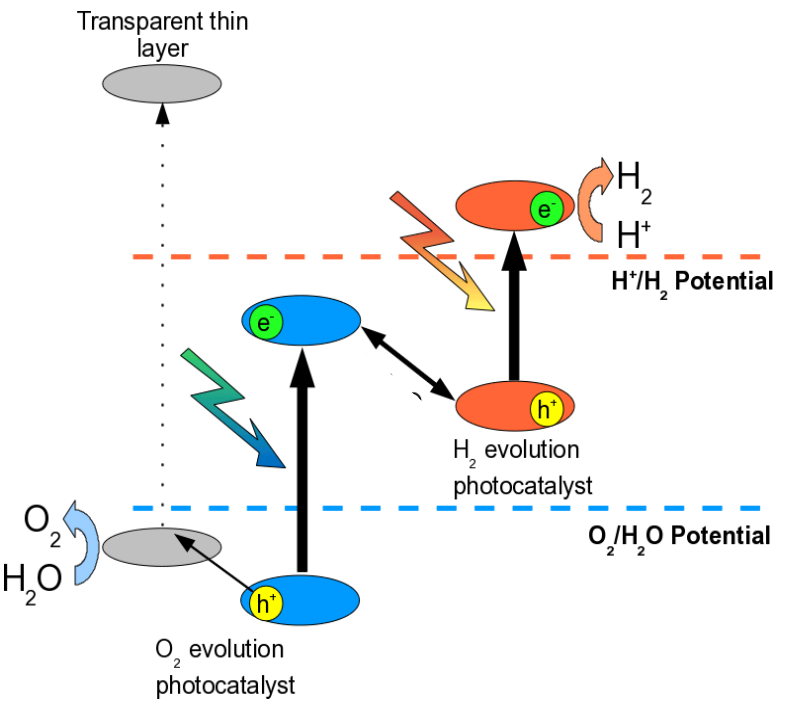
12 candidates (+ 20 one-photon WS)

$BaNbO_2N$, $SrNbO_2N$, $CaNbO_2N$, and $LaNbON_2$ are known as water splitters.



Transparent Protective Shield





Large Bandgap ⟶ High Stability

Transparent Shield - Photoanode

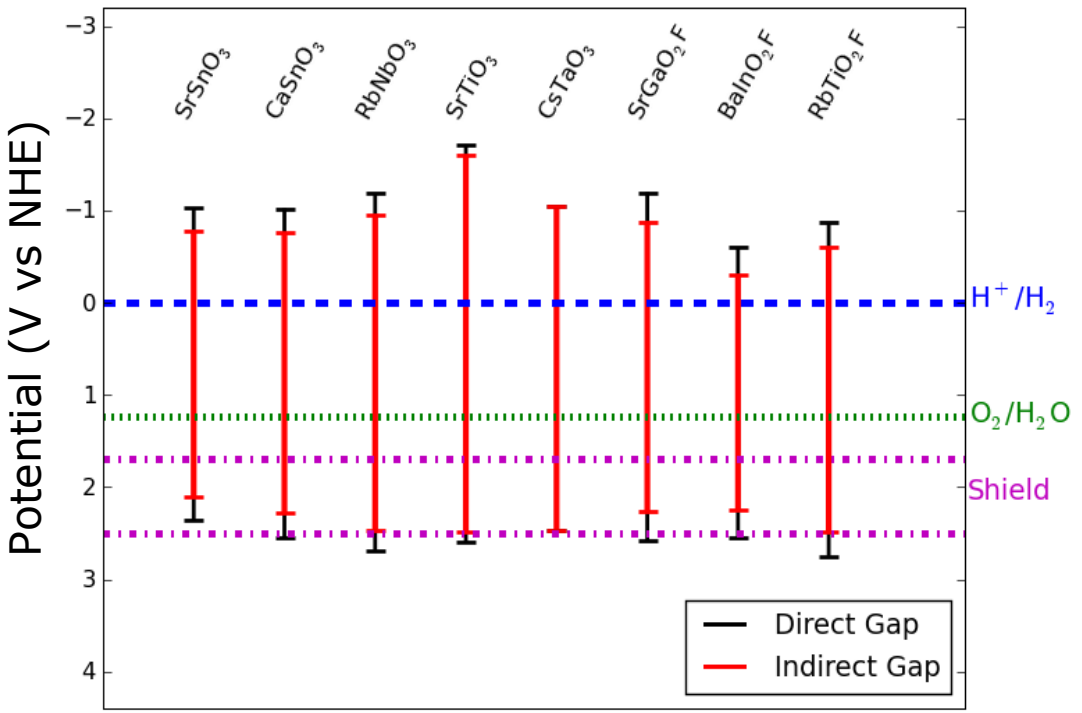
Screening parameters	Transparent Shield (TS)
Chemical/structural stability (ΔE)	$\Delta E \leq 0.2$ eV
Bandgap (E_{gap})	$E_{\mathrm{gap}}^{\mathrm{dir}} > 3$ eV
Band edges ($\mathrm{VB_{edge}}$, $\mathrm{CB_{edge}}$)	Photoanode TS: $1.7 < \mathrm{VB_{edge}} < 2.5$ eV vs NHE Photocathode TS: $-0.7 < \mathrm{CB_{edge}} < 0$ eV vs NHE

8 materials (5 new).

$SrTiO_3$ known for water splitting in UV light.

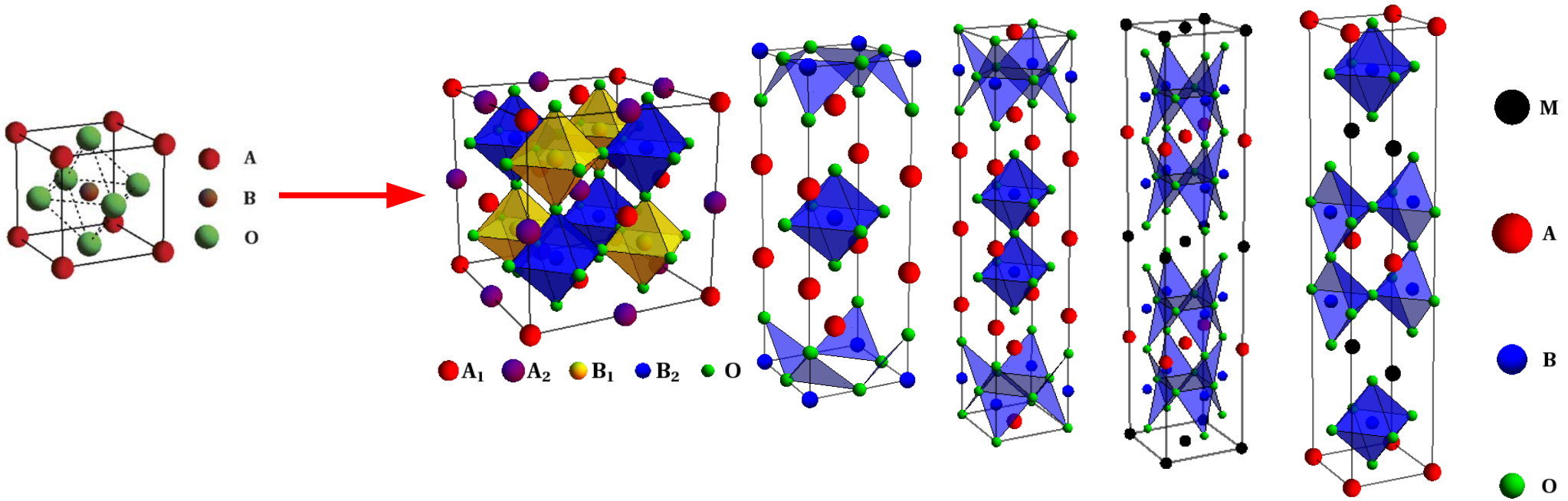
$SrSnO_3$ and $CaSnO_3$ known in the orthorhombic phase.

Similar analysis for the photocathode.



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

Towards Low Symmetry Perovskites

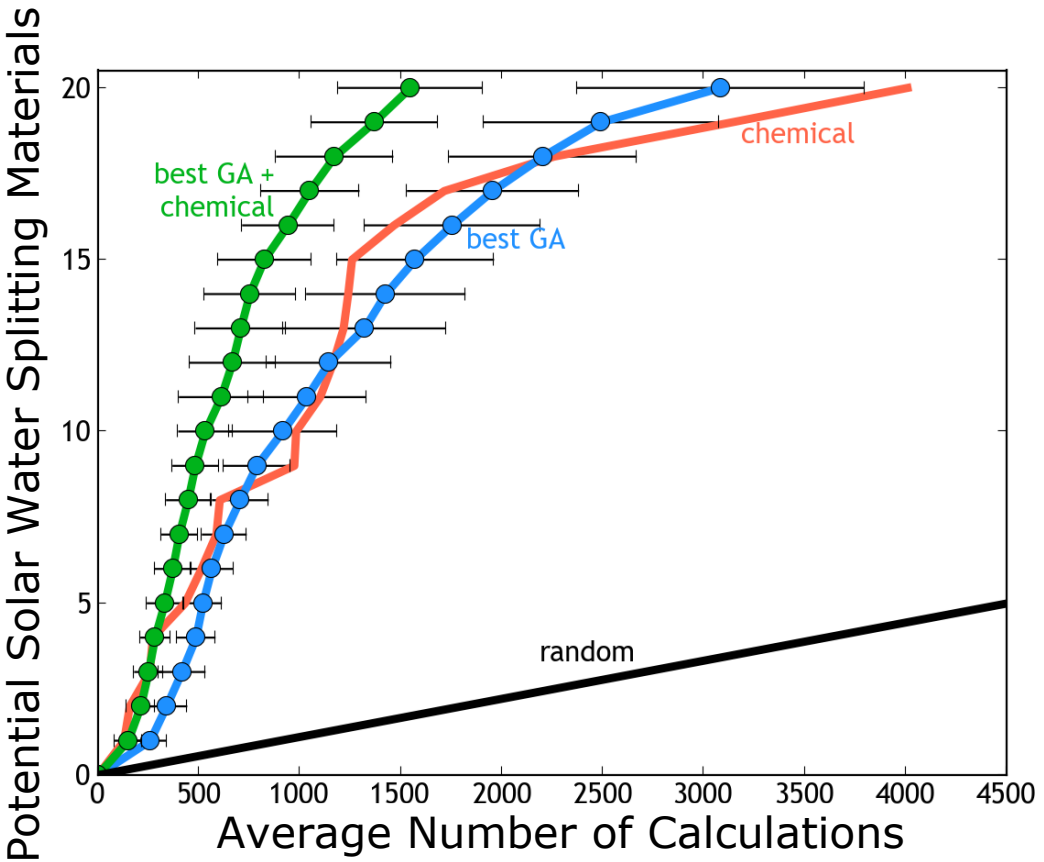


Cubic (5) → Double (20) Ruddlesden-Popper (14-24) Dion-Jacobson (24-44)

Too expensive to run the "brute force" screening for low symmetry structures.

We can use few chemical-based rules to reduce the search space:
- Goldsmith's tolerance factor;
- even number of electrons in the unit cell;
- sum of the possible oxidation states of elements = 0.

Evolutionary Algorithm



An evolutionary algorithm performs as good as a chemical-based search!

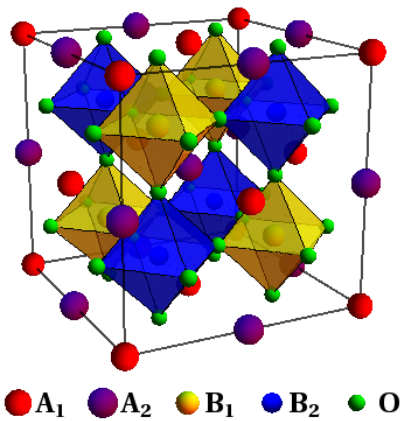
From now on we use these rules.

60 % less calculations!

A. Jain, I. E. Castelli, G. Hautier, D. H. Bailey, and K. W. Jacobsen, *Journal of Materials Science,* Printed Online (2013).

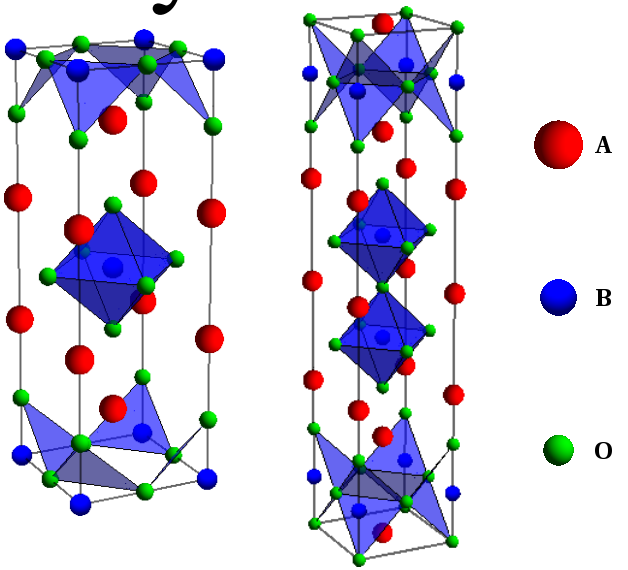
Low Symmetry Perovskite

Double



New Candidates, Bandgap Engineering!

Layered



Bandgap increases when p- and d-metals are combined in the B-ion position.

Bandgap decreases with the thickness of the octahedron when p-metals are in the B-ion position. Opposite for d-metals.

I. E. Castelli, K. S. Thygesen, and K. W. Jacobsen, *MRS Online Proceedings Library* **1523** (2013).

I. E. Castelli, J. M. Garcia-Lastra, F. Huser, K. S. Thygesen, and K. W. Jacobsen, *Submitted* (2013).

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:

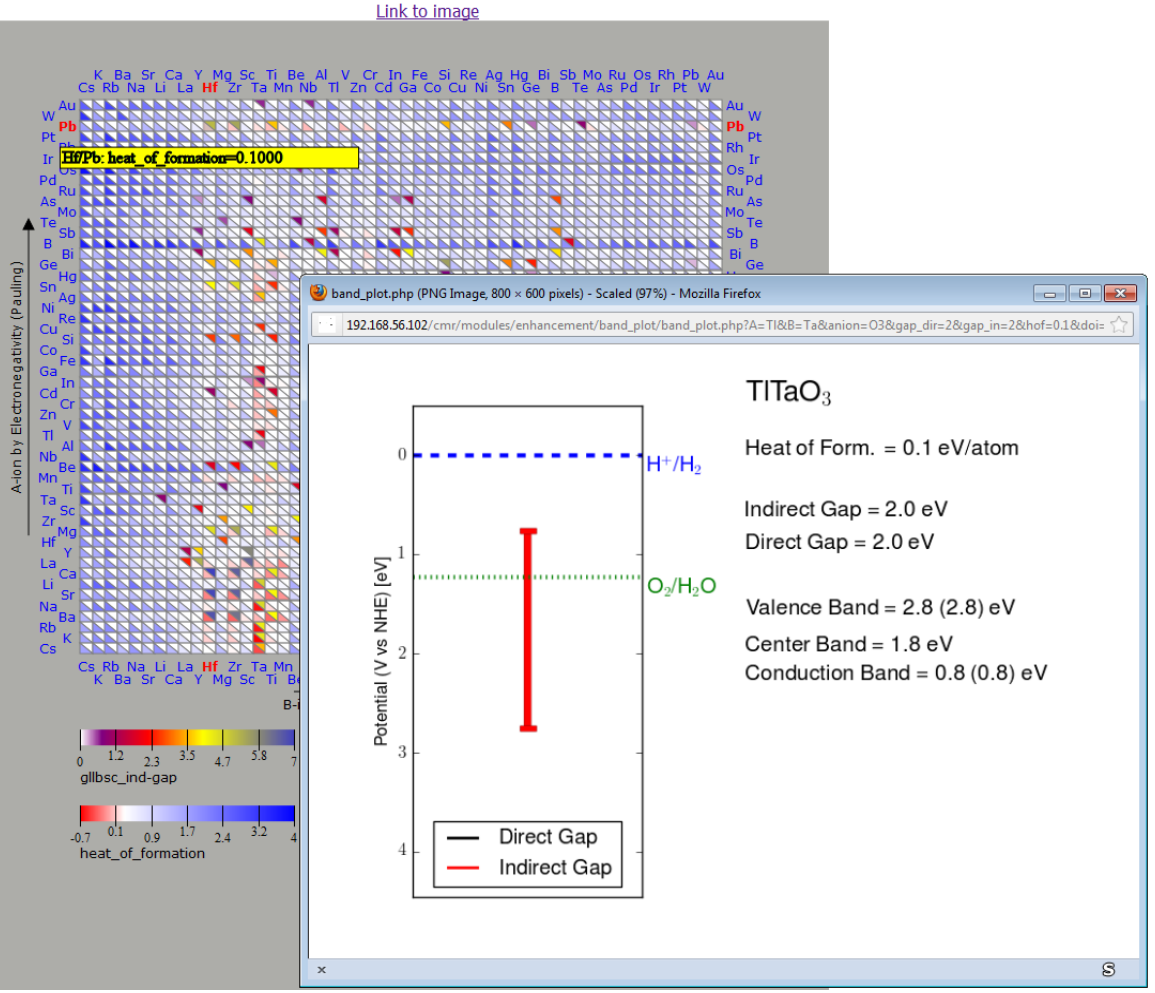
```
0->white,1->red,7->blue

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



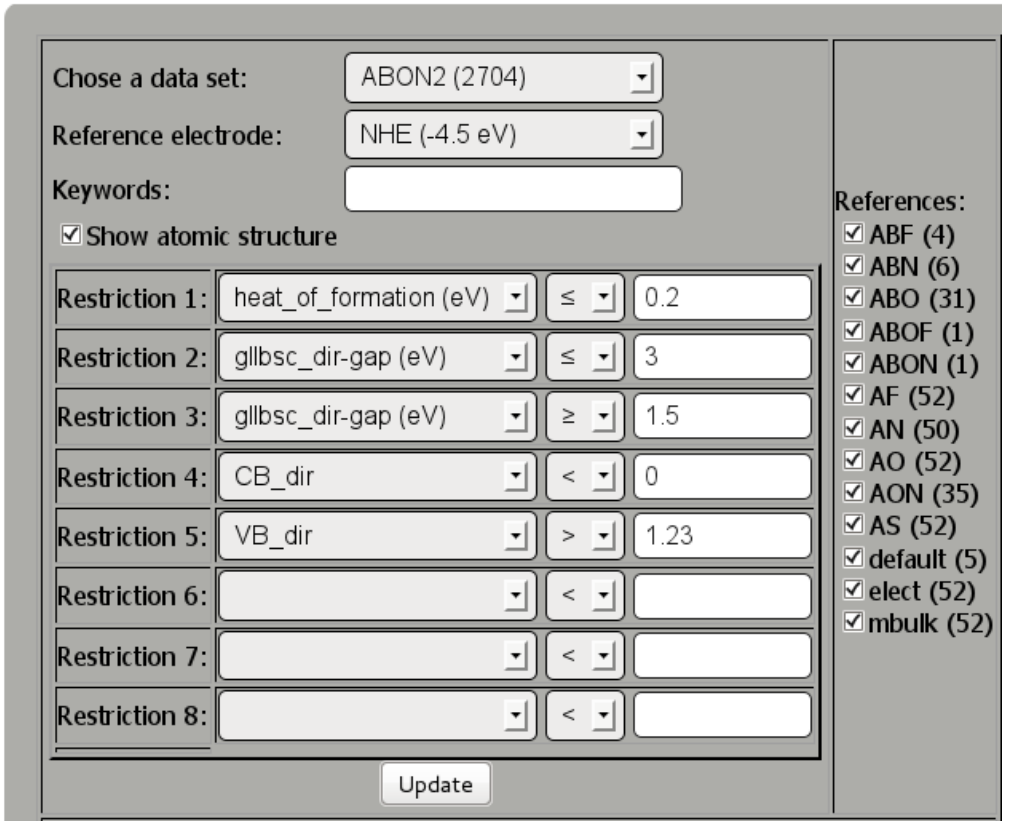
http://cmr.fysik.dtu.dk - the database

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

(Thanks to David Landis).

How to Search in CMR

Computational Materials Repository



Freely available

(Almost) ALL the calculated structures are included

jmol	id_ref	A	B	anion	heat_of_formation	gllbsc_dir-gap	gllbsc_ind-gap	CB_dir	CB_ind	VB_dir	VB_ind	atoms	db_keywords	doi	ingredients	db_description	downloads
Jmol	802207	Y	Ta	ON2	0.1500	2.5000	2.3000	-0.2128	-0.1128	2.2872	2.1872	Ta Y O N (1Ta, 1Y, 1O, 2N)	ABON2 moxn N O ON2 perovskite Ta tandem Y YTaN2O	11.0000/b000000x	0.02 O48Y32 + 0.08 N4Y4 + 0.33 N3Ta3 + 0.33 N2	Screening cubic perovskite structures, metal oxynitrides	ASE CMR json XYZ
Jmol	805242	La	Ta	ON2	-0.0200	2.1000	1.8000	-0.0731	0.0769	2.0269	1.8769	Ta La O N (1Ta, 1La, 1O, 2N)	ABON2 La LaTaN2O moxn N O ON2 perovskite Ta tandem	11.0000/b000000x	0.06 La6N12Ta4 + 0.26 N3Ta3 + 0.28 N2 + 0.33 La2O3	Screening cubic perovskite structures, metal oxynitrides	ASE CMR json XYZ

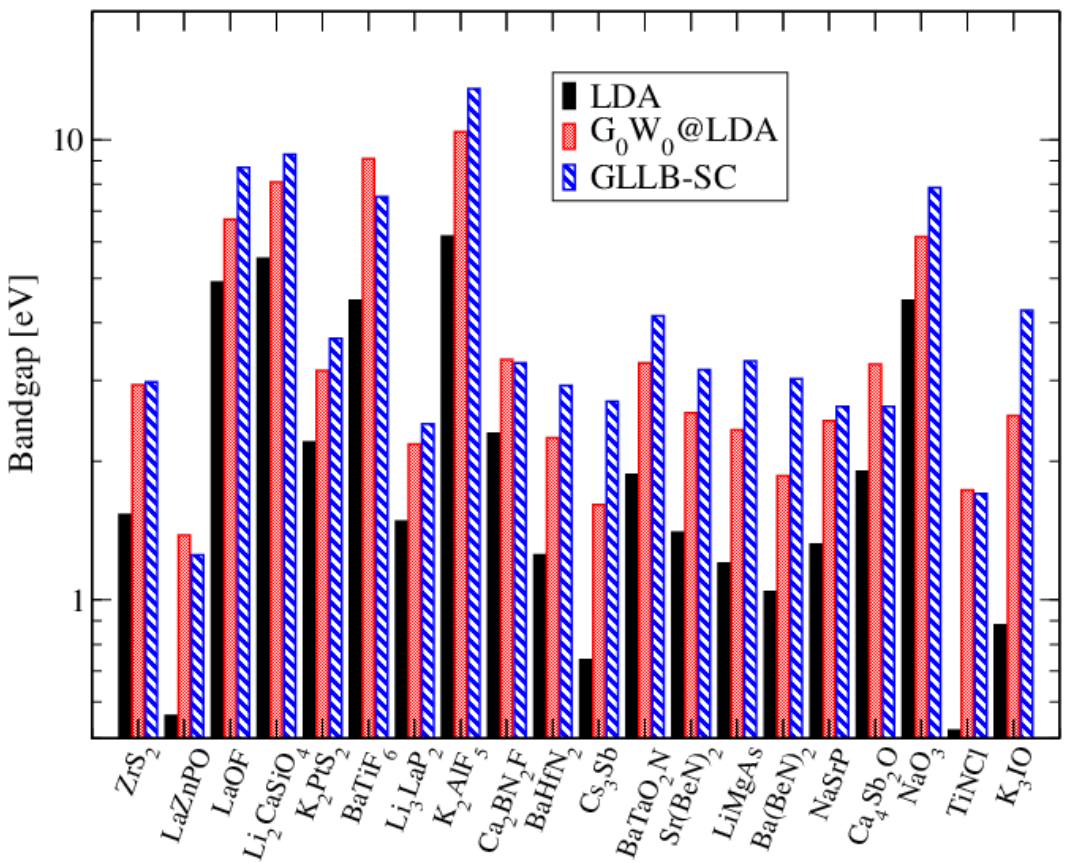
Materials Project Database

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

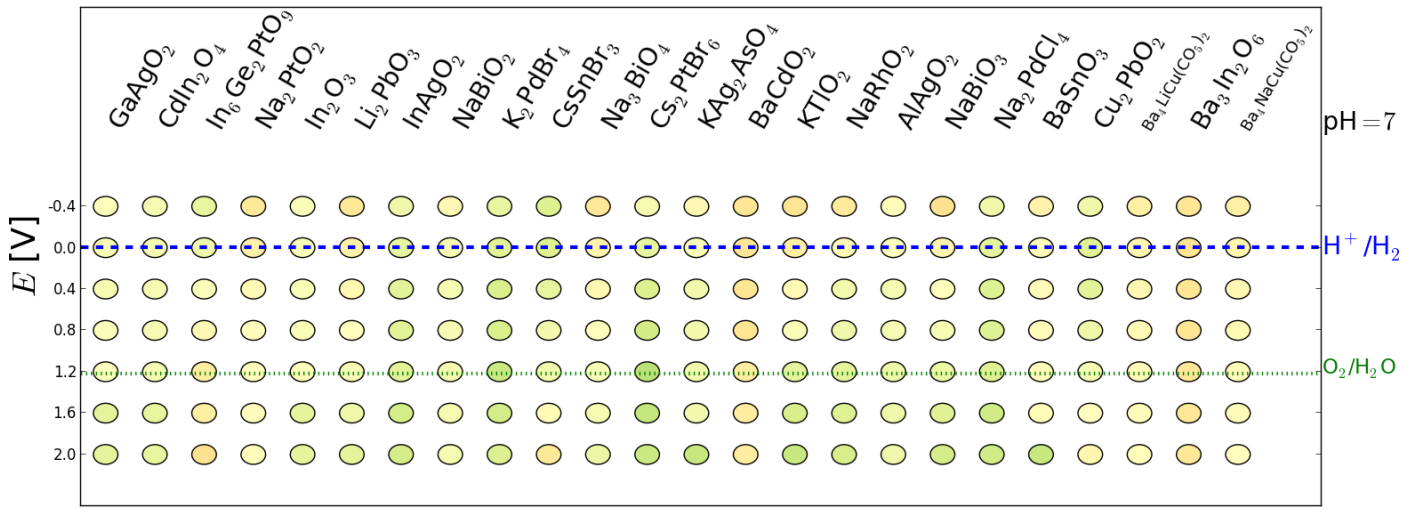


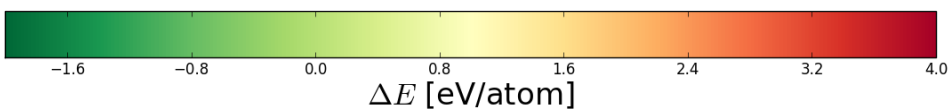
Reasonable agreement between GLLB-SC and G_0W_0 (Relative Error = 0.2).

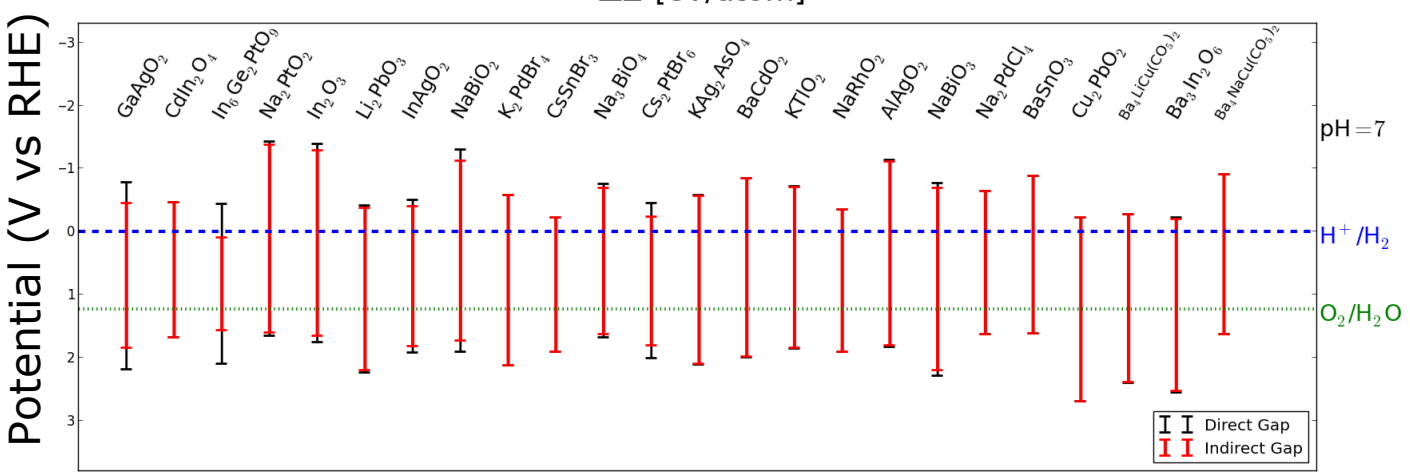
(Calculations from Falco Huser).

Applications: water splitting; photovoltaics; ...

One-photon Water Splitting







Descriptors:
- Stability against corrosion;
- Bandgap;
- Band edge positions.

24 known materials for one-photon water splitting.

More materials for the other applications.

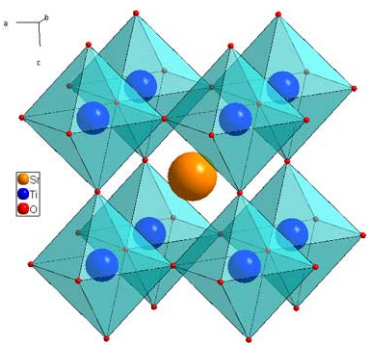
What Is This Talk About?

New materials for solar light conversion into hydrogen and oxygen.

1) Computational Method: Density Functional Theory and screening approach;

2) Water Splitting Applications:
   a) One-photon WS
   b) Two-photon WS
   c) Transparent protective shield

3) Thin-Film Solar Cell (photovoltaic):
   a) Single-layer
   b) Double-layer

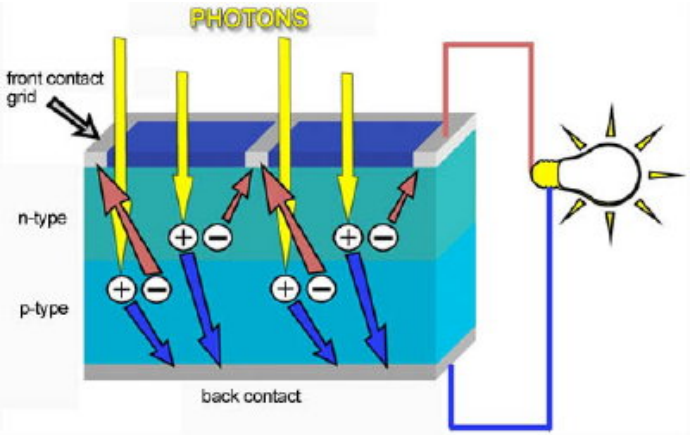


MATERIALS PROJECT

A Materials Genome Approach

Solar Cell

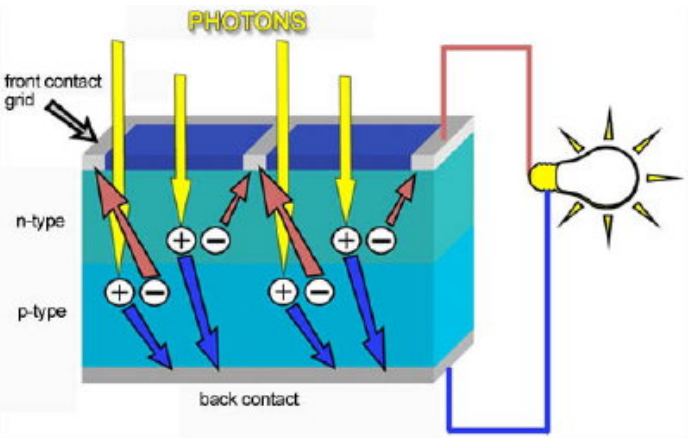
Photons are used to generate electricity.



	Solar Cell	Water Splitting
Efficiency	44 %	5%
Transport	Batteries	Hydrogen
Current Technology	Advanced	Beginners

Solar Cell

Photons are used to generate electricity.

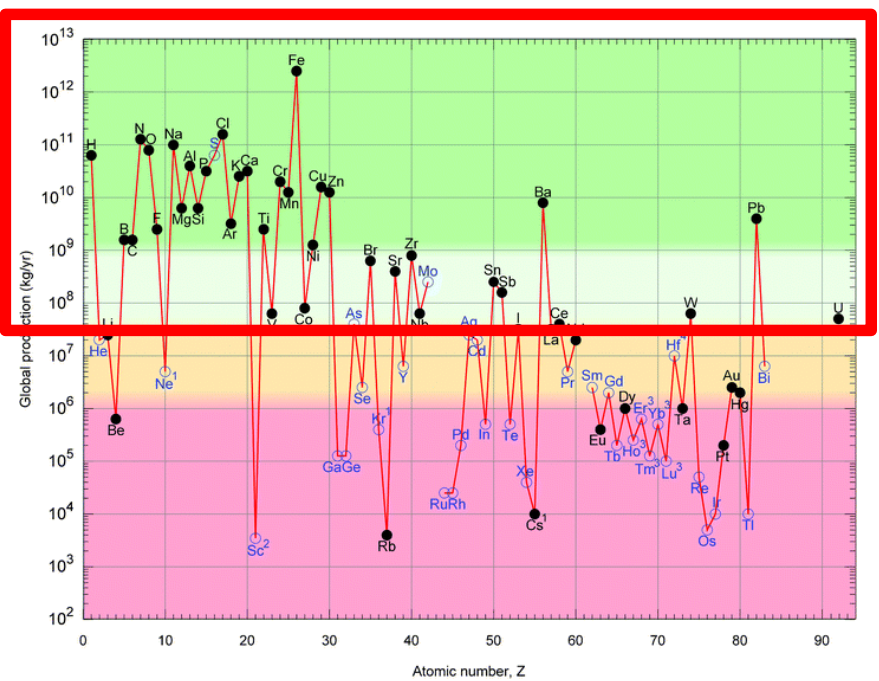


	Solar Cell	Water Splitting
Efficiency	44 %	5%
Transport	Batteries	Hydrogen
Current Technology	Advanced	Beginners

Thin Film SC: save materials (cheap).

Screening for cheap elements (global production > 33kton/year).

Eco-friendly region



P.C.K. Vesborg and T.F. Jaramillo, *RSC Adv.* **2**, 7933, 2012.

Thin Film Solar Cell

Requirements:
- Direct bandgap between 0.5 – 2.5 eV.

MATERIALS PROJECT
A Materials Genome Approach

Absorption spectra of 70 compounds.

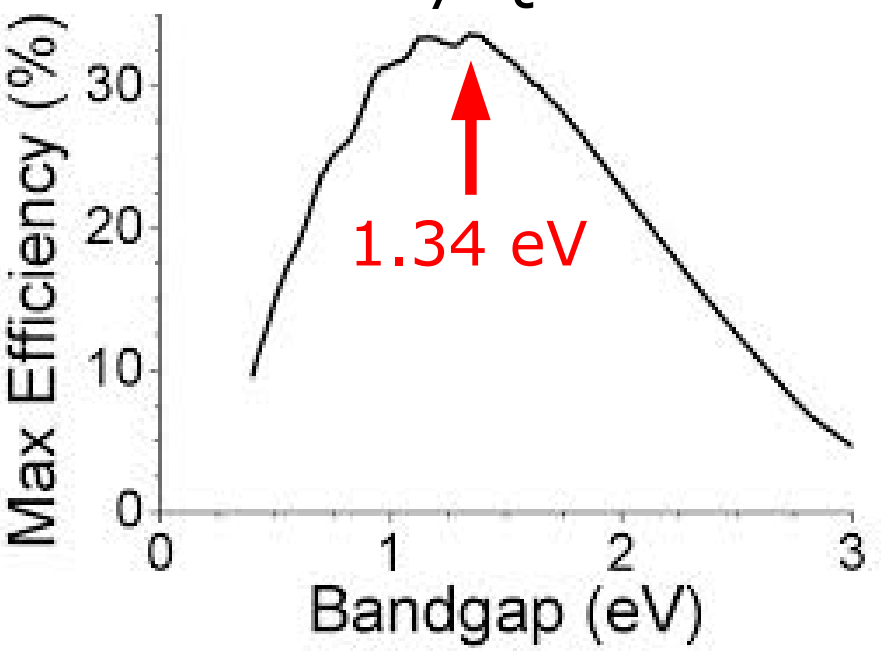
Efficiency of a cell:

$$\eta = \frac{P_{\text{out}}}{P_{\text{in}}}$$

$$P_{out} = J_{sc} V_{sc} = J_{sc} E_{gap}$$

Losses: recombination, photons below the bandgap

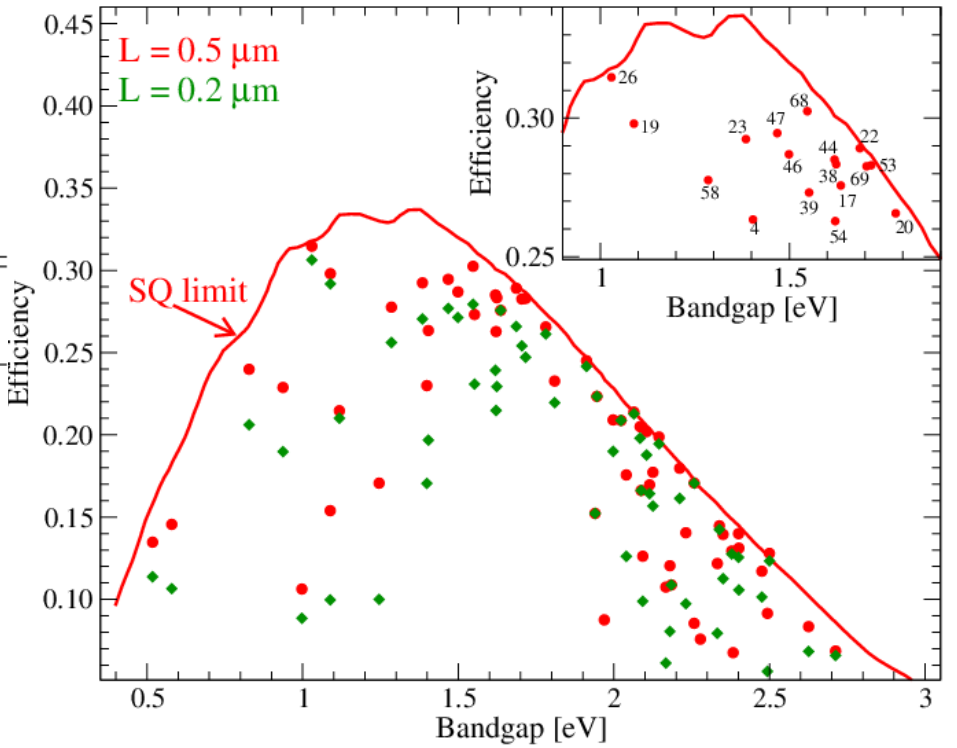
Shockley-Queisser Limit



Single-layer Thin Film SC

Efficiency depends on the thickness.
Silicon not suited for thin film SC.

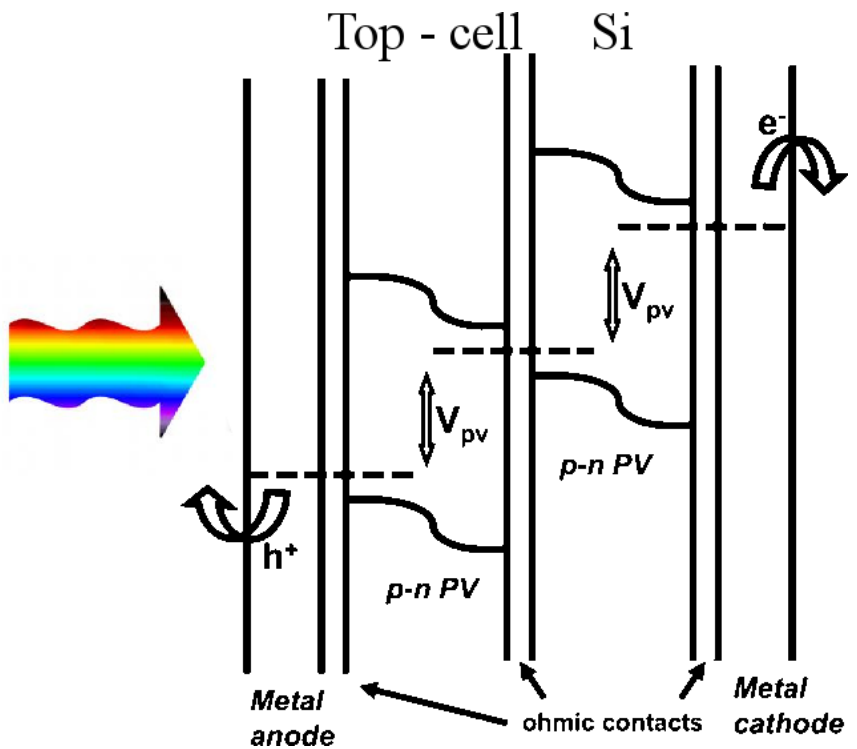
Id	Formula	Materials Project Id	Bandgap [eV]	Efficiency
4	$Sr(ZnP)_2$	8276	1.4	26.3%
17	$ZrCl_2$	23162	1.6	27.6%
19	MnP_4	487	1.1	29.8%
20	WBr_6	504993	1.8	26.6%
22	TiBrN	27849	1.7	28.9%
23	MgP_4	384	1.4	29.2%
26	Cu_2O	361	1.0	31.5%
38	Sr_3SbN	7752	1.6	28.3%
39	CuP_2	927	1.6	27.3%
44	$ZnSiAs_2$	3595	1.6	28.5%
46	$K(MoS)_3$	8116	1.5	28.7%
47	$Ba_2Cu(PO_4)_2$	9372	1.5	29.5%
53	$KZrCuS_3$	9317	1.7	28.3%
54	BaP_3	7808	1.6	26.3%
58	$TiNb_3O_6$	29699	1.3	27.8%
68	K_2NiAs_2	9673	1.5	30.2%
69	TiNCl	27850	1.7	28.3%

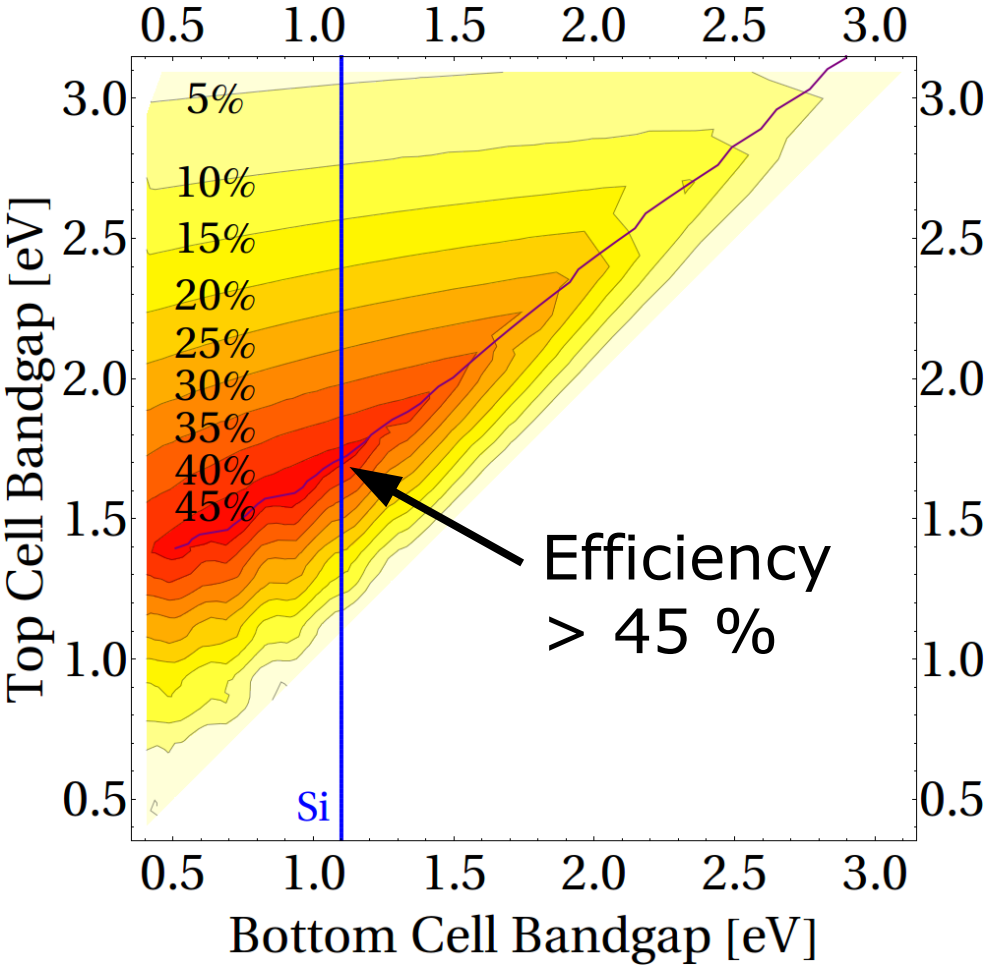


17 materials have a theoretical efficiency larger than 25 %.

4 have been already used in a SC.

Double-layer Thin Film SC

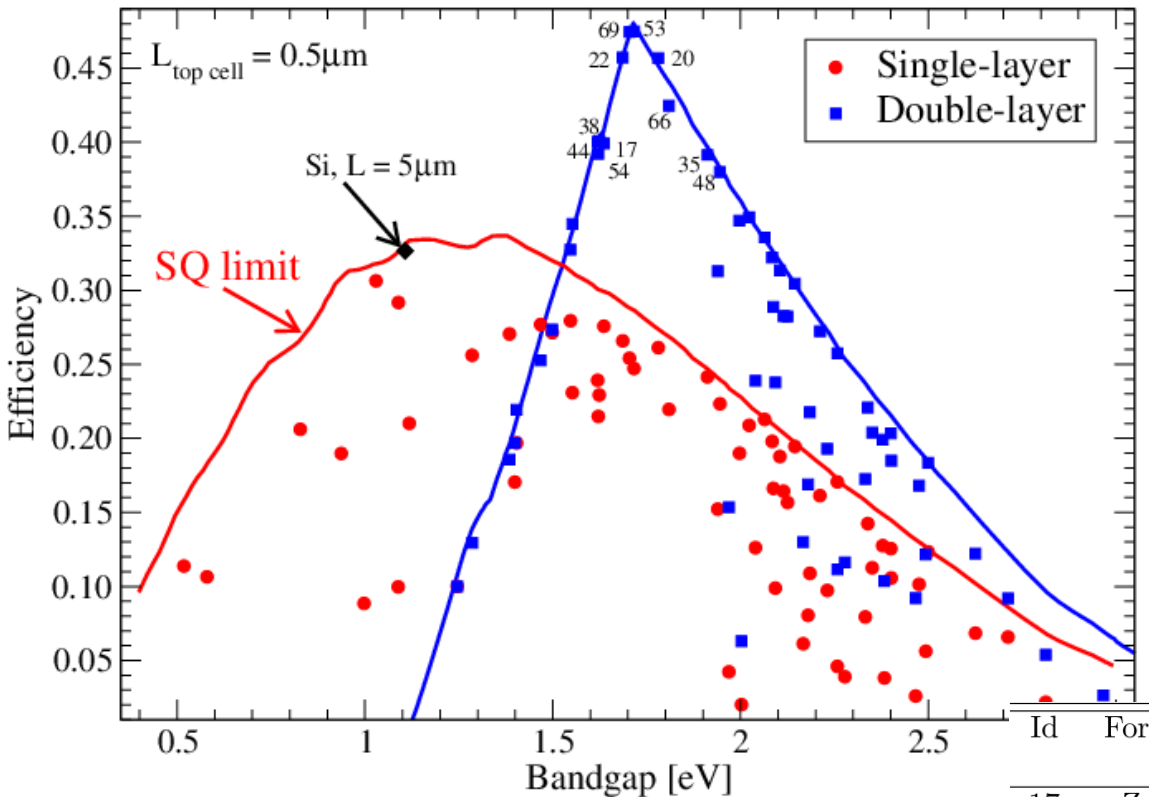




Top-cell: Screening

Bottom-cell: thick-enough silicon
(absorbs everything above its gap)

Double-layer Thin Film SC



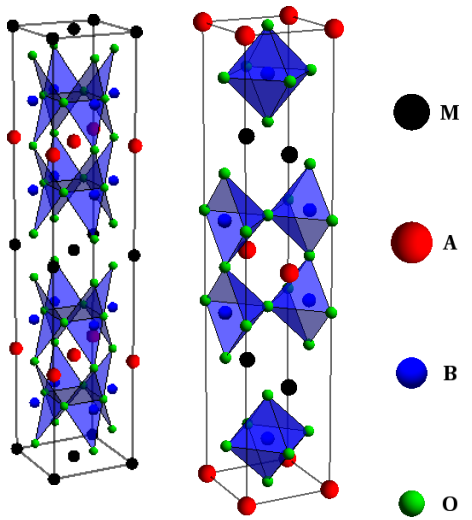
11 materials have an efficiency of more than 35 %.

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

Id	Formula	Materials Project Id	Bandgap [eV]	Efficiency Single-layer	Efficiency Double-layer
17	$ZrCl_2$	23162	1.6	27.6%	39.9%
20	WBr_6	504993	1.8	26.6%	45.7%
22	TiBrN	27849	1.7	28.9%	45.7%
35	K_2P_3	8262	1.9	24.5%	39.1%
38	Sr_3SbN	7752	1.6	28.3%	40.1%
44	$ZnSiAs_2$	3595	1.6	28.5%	40.0%
48	$NaSbS_2$	5414	1.9	15.4%	38.0%
53	$KZrCuS_3$	9317	1.7	28.3%	47.5%
54	BaP_3	7808	1.6	26.3%	39.2%
66	SnS	2231	1.8	23.3%	42.5%
69	TiNCl	27850	1.7	28.3%	47.5%

What's Next?

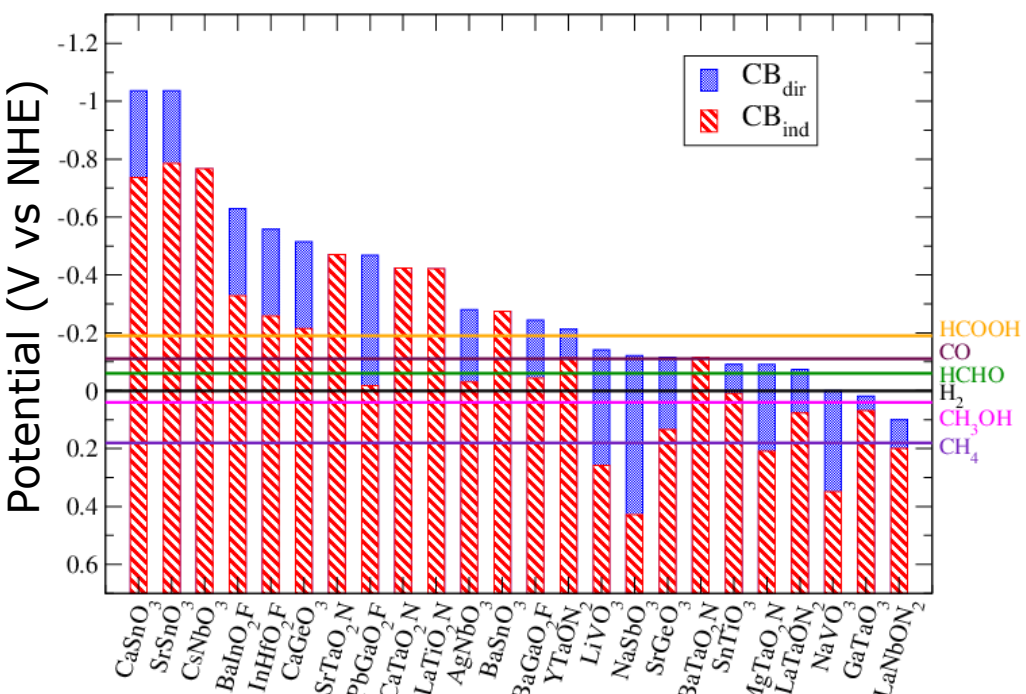
Screen for new structures-cell: more complex layered perovskites, new stoichiometries, ...



Calculate the bandgaps of known structures.

Look at new application:
- Fuel production using photocatalysis.

- Photovoltaics (three-layers)
- Fuel cells.



Conclusions

- Few materials 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 and 11 for double-layer mechanism;
- A database has been developed for an easy access to the data.

Acknowledgment

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David D. Landis
Thomas Olsen
Falco Huser
Juan Maria Garcia-Lastra

CAMd
Center for Atomic-scale Materials Design

CINF
Center for Individual Nanoparticle Functionality

CASE
Catalysis for Sustainable Energy

Last Suggestion!

Lyngby Games 03/06/2012. 800m: 1:56.10

NEVER run if you have a broken arm!

Thanks to all the people that help me when a broke first the harm and then the leg!

Thank you for your attention!

Conclusions

- Few materials 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 and 11 for double-layer mechanism;
- A database has been developed for an easy access to the data.

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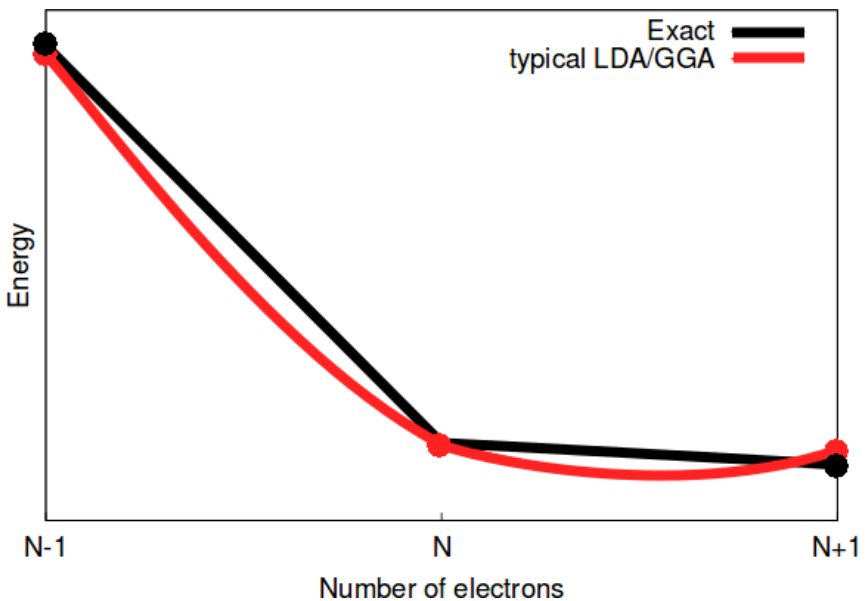
The GLLB Potential

$E_g^{QP} = E_g^{KS} + \Delta_{xc}$ Kohn-Sham bandgap + Derivative discontinuity

$$E_{\text{gap}}^{\text{deriv}} = \varepsilon_{\text{LUMO}}^{\text{KS}} - \varepsilon_{\text{HOMO}}^{\text{KS}} + \Delta_{xc} = E_{\text{gap}}^{\text{KS}} + \Delta_{xc}$$

$$\Delta_{\text{xc}} = \Delta_{\text{xc}}(\mathbf{r}) = v_{\text{xc}}(\mathbf{r}; J + \delta) - v_{\text{xc}}(\mathbf{r}; J - \delta)$$



Methods to solve the problem:
- LDA+U
- OEP
- …

Approximations for the GLLBSC:
- OEP (way too expensive)
- KLI (still too expensive).

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

The GLLB(-SC) Potential

$$E_g^{QP} = E_g^{KS} + \Delta_{xc}$$ Kohn-Sham bandgap + Derivative discontinuity

$$v_{\mathrm{x}}(\mathbf{r}) = v_{\mathrm{S}}(\mathbf{r}) + v_{\mathrm{resp}}(\mathbf{r})$$ Screening + Response

$$v_{\mathrm{S}}(\mathbf{r}) = \frac{2\epsilon_x^{\mathrm{GGA}}(\mathbf{r};n)}{n(\mathbf{r})}$$ GGA exchange: B88, PBEsol, ...

$$v_{\mathrm{resp}}(\mathbf{r}) = \sum_i^{\mathrm{occ}} w_i \frac{|\psi_i(\mathbf{r})|^2}{n(\mathbf{r})}, \qquad w_i = \langle i|\, v_{\mathrm{x}}(\mathbf{r}) - \hat{V}_{\mathrm{x}}^{(HF)}\, |i\rangle$$ Approx. OEP, KLI.

$$v_{\mathrm{resp}}(\mathbf{r}) = \sum_i^{\mathrm{occ}} K[n]\sqrt{\varepsilon_{\mathrm{r}} - \varepsilon_i}\frac{|\psi_i(\mathbf{r})|^2}{n(\mathbf{r})}$$ Contains the discontinuity through ε_r

$$\epsilon_r = \begin{cases} \epsilon_J & , N \leq J \\ \epsilon_{J+1} & , N > J, \end{cases}$$

$$\Delta_{x,\mathrm{resp}}(\mathbf{r}) = \sum_i^N K\left(\sqrt{\varepsilon_{N+1} - \varepsilon_i} - \sqrt{\varepsilon_N - \varepsilon_i}\right)\frac{|\psi_i(\mathbf{r})|^2}{n(\mathbf{r})}$$

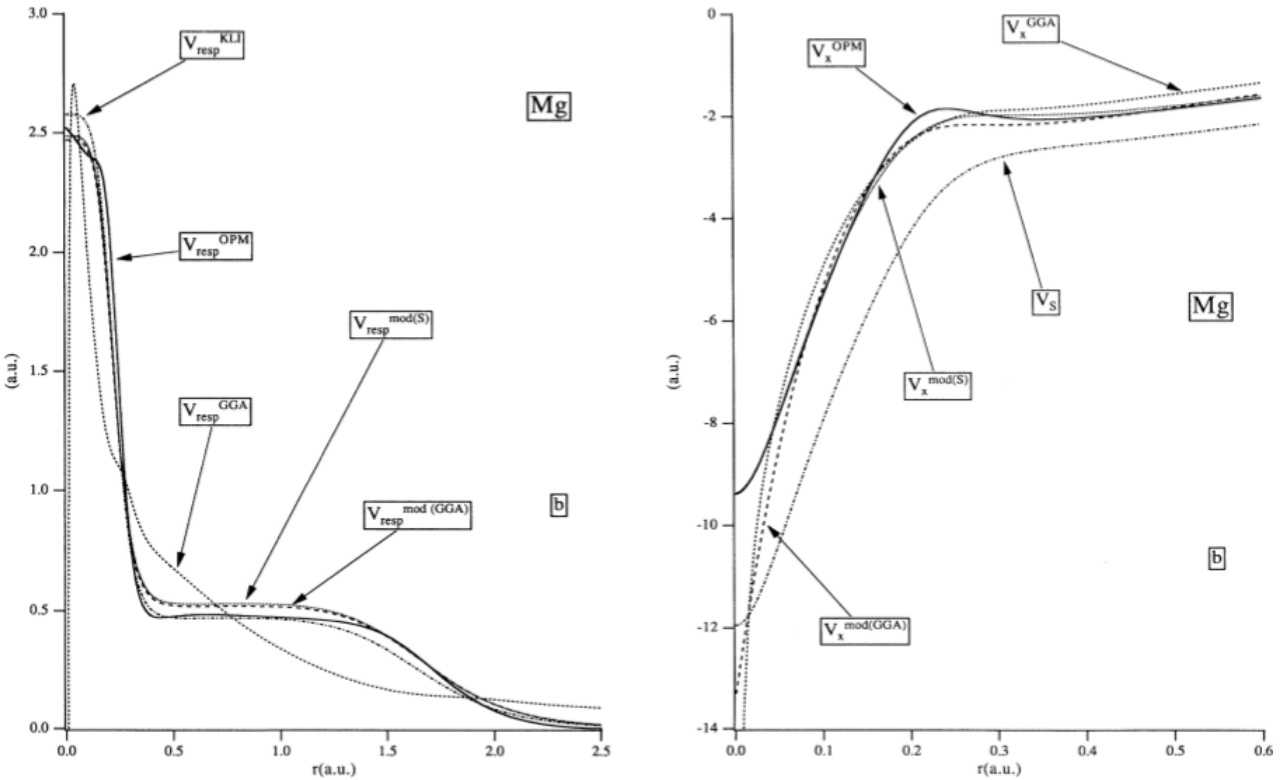
Correlation from PBEsol:

$$\tilde{v}_{\mathrm{GLLB-SC}}(\mathbf{r}) = 2\epsilon_x^{\mathrm{PBEsol}}[\tilde{n}(\mathbf{r}), |\nabla\tilde{n}(\mathbf{r})|^2](\mathbf{r}) + \sum_i^{val.} K_G\sqrt{\epsilon_r - \epsilon_i}\frac{|\tilde{\psi}_i(\mathbf{r})|^2}{\sum_i^{val.}|\tilde{\psi}_i(\mathbf{r})|^2} + v_{\mathrm{c}}^{PBEsol}[\tilde{n}(\mathbf{r}), |\nabla\tilde{n}(\mathbf{r})|^2](\mathbf{r})$$

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

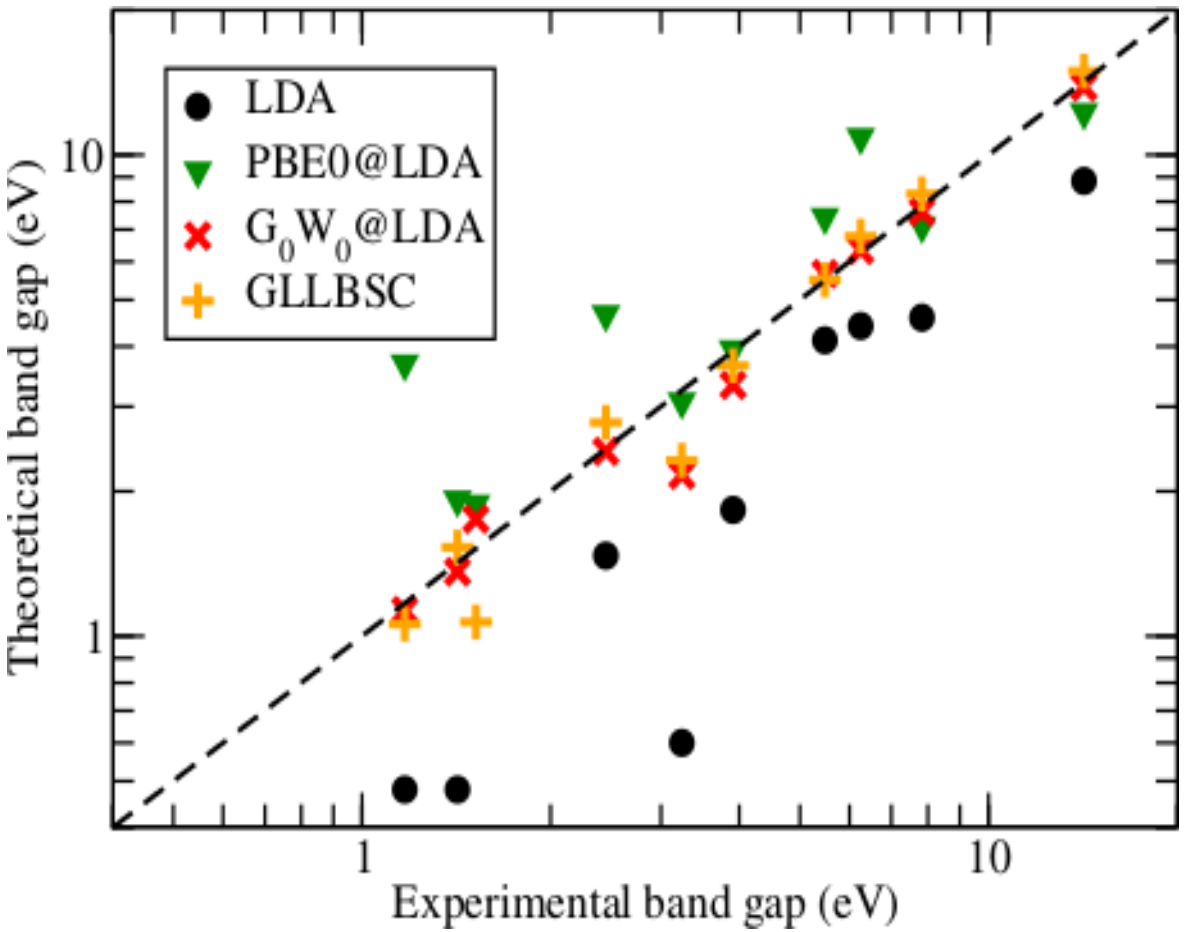
Kuisma *et al.*, *Phys. Rev. B* **82**, 115106 (2010).

The GLLB(-SC) Potential



- Correct decay as $-e^2/r$ at long distances;
- XC discontinuous for integer number of electrons;
- **good bandgaps!**
- not easy to calculate the energies;
- a bit more expensive than GGA.

The GLLB(-SC) Potential



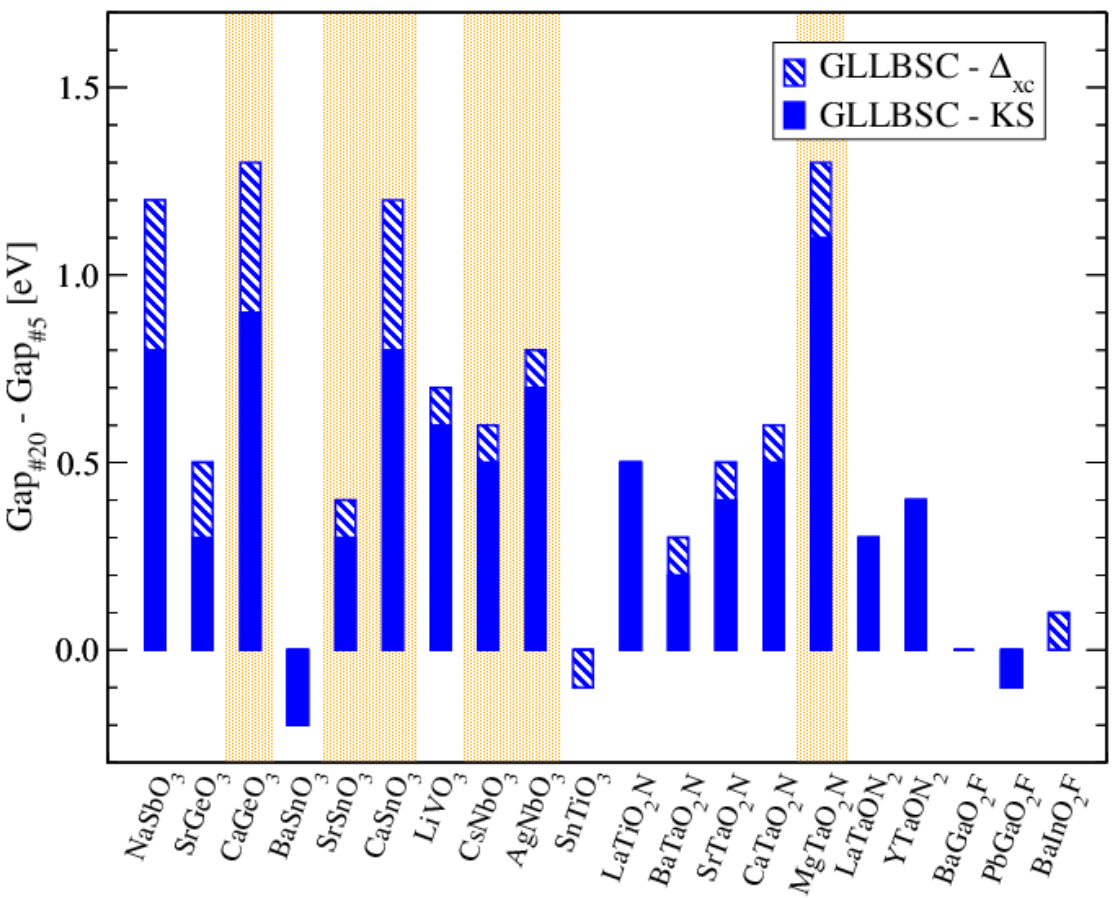
GLLB-SC and G_0W_0@LDA give similar results.

MAE GLLB-SC = 0.4
MAE G_0W_0@LDA = 0.3

Included materials: Si, InP, GaAs, AlP, ZnO, ZnS, C, BN, MgO, and LiF.

Huser *et al.*, Accepted *Phys. Rev. B* (2013).

20 Atoms Unit Cell



20 atoms unit cell allows for distortions (orthorhombic perovskite).

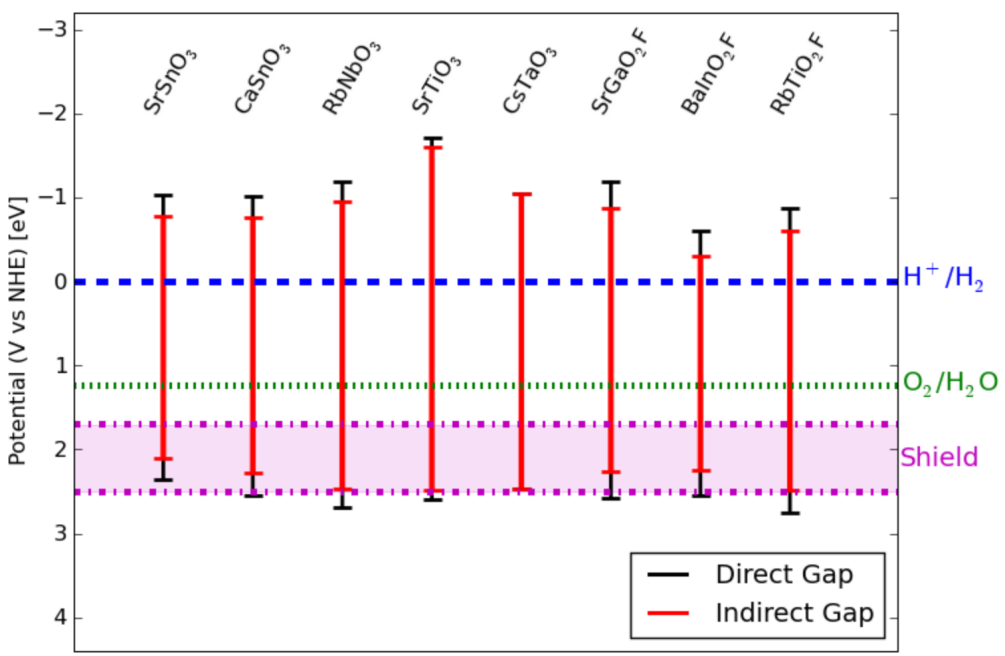
Increase in the gap is mainly due to the KS gap.

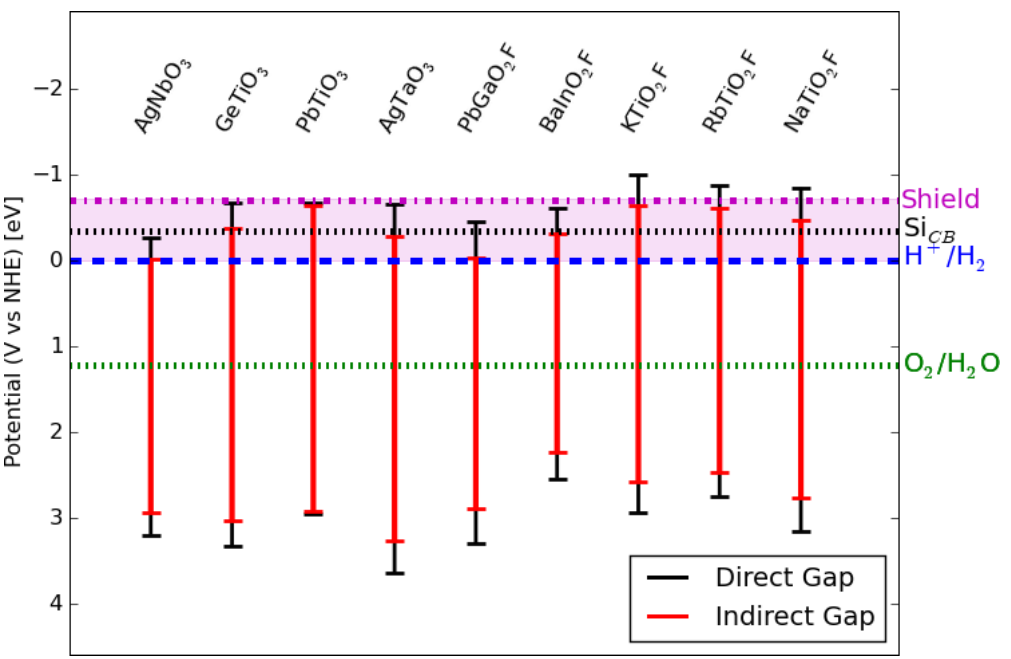
Smaller changes in the discontinuity.

6 materials (in orange) fall out from the visible light window.

Transparent Shield

Screening parameters	Transparent Shield (TS)
Chemical/structural stability (ΔE)	$\Delta E \leq 0.2$ eV
Bandgap (E_{gap})	$E_{\text{gap}}^{\text{dir}} > 3$ eV
Band edges (VB_{edge}, CB_{edge})	Photoanode TS: $1.7 < \text{VB}_{\text{edge}} < 2.5$ eV vs NHE Photocathode TS: $-0.7 < \text{CB}_{\text{edge}} < 0$ eV vs NHE





Nernst Equation

$$S \stackrel{\text{def}}{=} k \ln \Omega,$$

$$\Delta S = S_2 - S_1 = -k \ln \frac{c_2}{c_1},$$

$$aA + bB \rightarrow yY + zZ$$

$$\Delta G = \Delta H - T\Delta S = \Delta G^0 + kT \ln Q,$$

$$\Delta G = -nFE$$

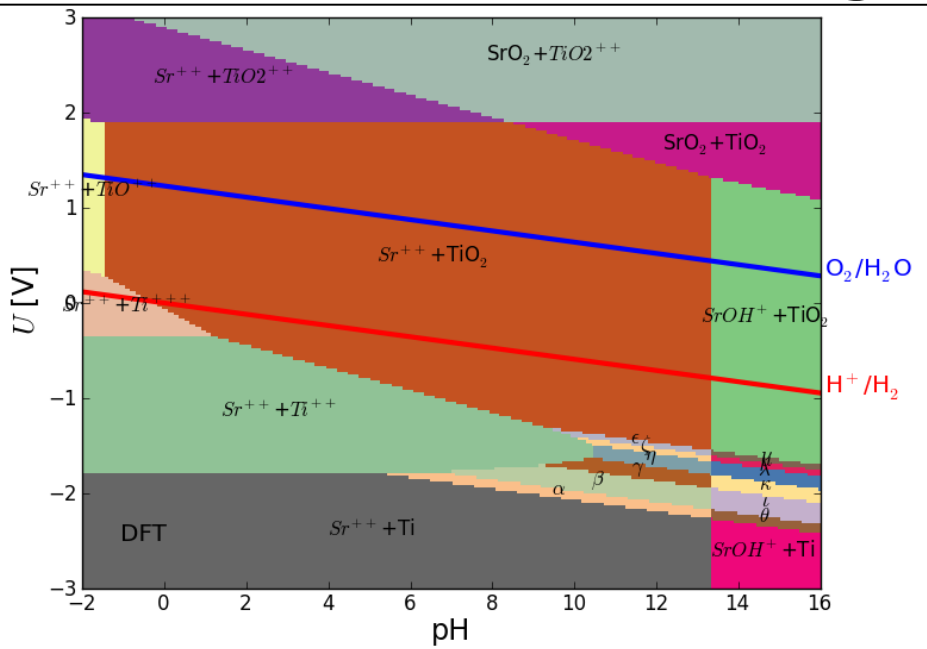
$$E = E^0 - \frac{kT}{ne} \ln Q.$$

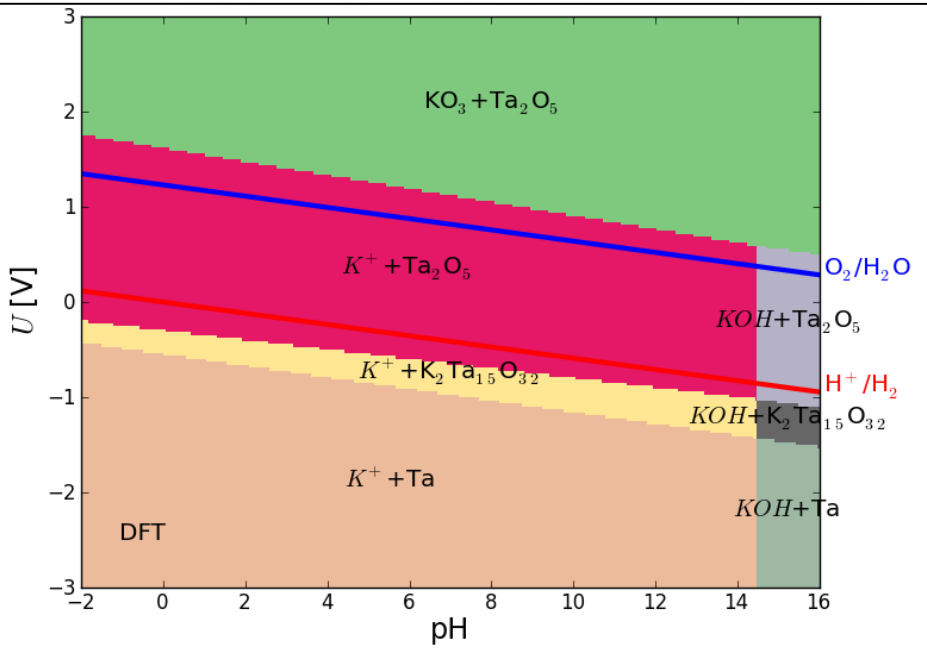
$$E = E^0 - \frac{kT}{ne} \ln \frac{[\text{Red}]}{[\text{Ox}]} = E^0 - \frac{RT}{nF} \ln \frac{[\text{Red}]}{[\text{Ox}]} = E^0 - \frac{RT}{nF} \ln Q.$$

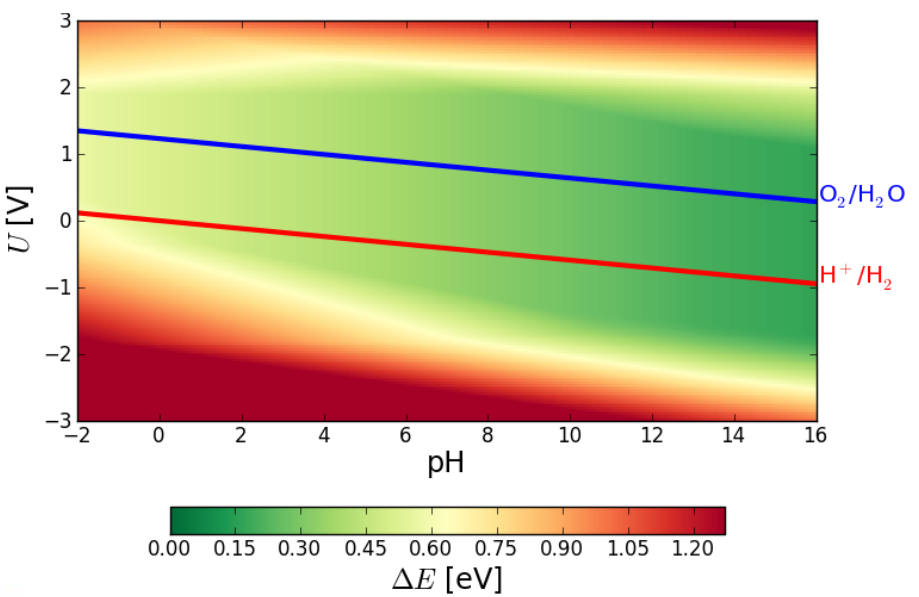
Limitations:

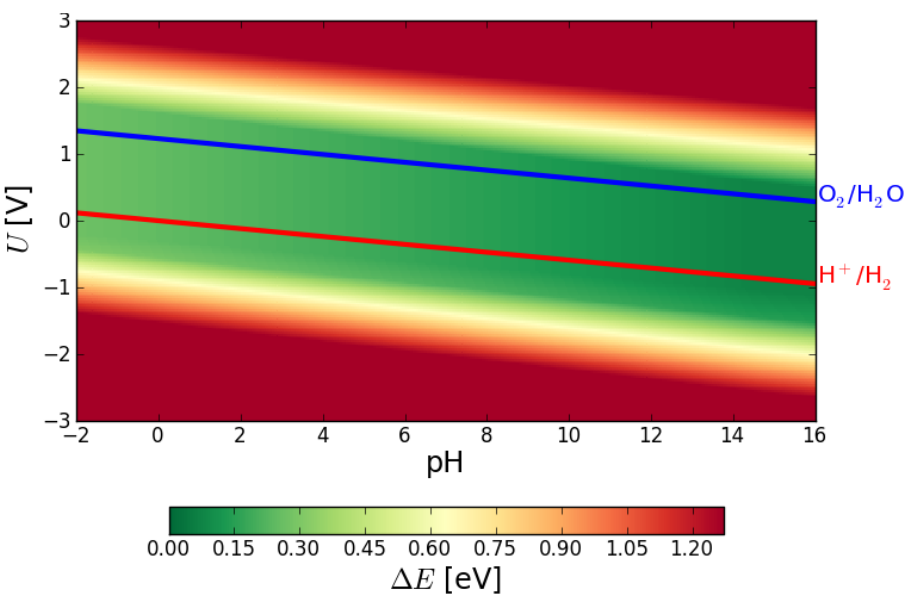
- at high concentration, [Red/Ox] needs to be replaced by the activity of the species;
- no current flows between the electrodes that might change the activity of the ions.

Pourbaix Diagrams of Perovskites









Absorption Spectrum

$$\delta n(\mathbf{r},\omega) = \int d\mathbf{r}\chi(\mathbf{r},\mathbf{r}',\omega)\delta V_{\rm ext}(\mathbf{r}',\omega)$$

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \frac{1}{N_q\Omega}\sum_{\mathbf{q}}^{\rm BZ}\sum_{\mathbf{GG'}} e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}\chi_{\mathbf{GG'}}(\mathbf{q},\omega)e^{-i(\mathbf{q}+\mathbf{G'})\cdot\mathbf{r}'}$$

$$\chi_{\mathbf{GG'}}(\mathbf{q},\omega) = \chi^0_{\mathbf{GG'}}(\mathbf{q},\omega) + \sum_{\mathbf{G_1G_2}} \chi^0_{\mathbf{GG_1}}(\mathbf{q},\omega)K_{\mathbf{G_1G_2}}(\mathbf{q})\chi_{\mathbf{G_2G'}}(\mathbf{q},\omega)$$

$$K^C_{\mathbf{G_1G_2}}(\mathbf{q}) = \frac{4\pi}{|\mathbf{q}+\mathbf{G_1}|^2}\delta_{\mathbf{G_1G_2}}$$

$$K^{\rm xc-ALDA}_{\mathbf{G_1G_2}}(\mathbf{q}) = \frac{1}{\Omega}\int d\mathrm{r}\, f_{xc}[n(\mathrm{r})]e^{-i(\mathbf{G_1}-\mathbf{G_2})\cdot\mathrm{r}} \qquad f_{xc}[n(\mathrm{r})] = \left.\frac{\partial^2 E_{xc}[n]}{\partial n^2}\right|_{n_0(\mathrm{r})}$$

$$\epsilon^{-1}_{\mathbf{GG'}}(\mathbf{q},\omega) = \delta_{\mathbf{GG'}} + \frac{4\pi}{|\mathbf{q}+\mathbf{G}|^2}\chi_{\mathbf{GG'}}(\mathbf{q},\omega)$$

$$\epsilon_M(\mathbf{q},\omega) = \frac{1}{\epsilon^{-1}_{00}(\mathbf{q},\omega)}$$

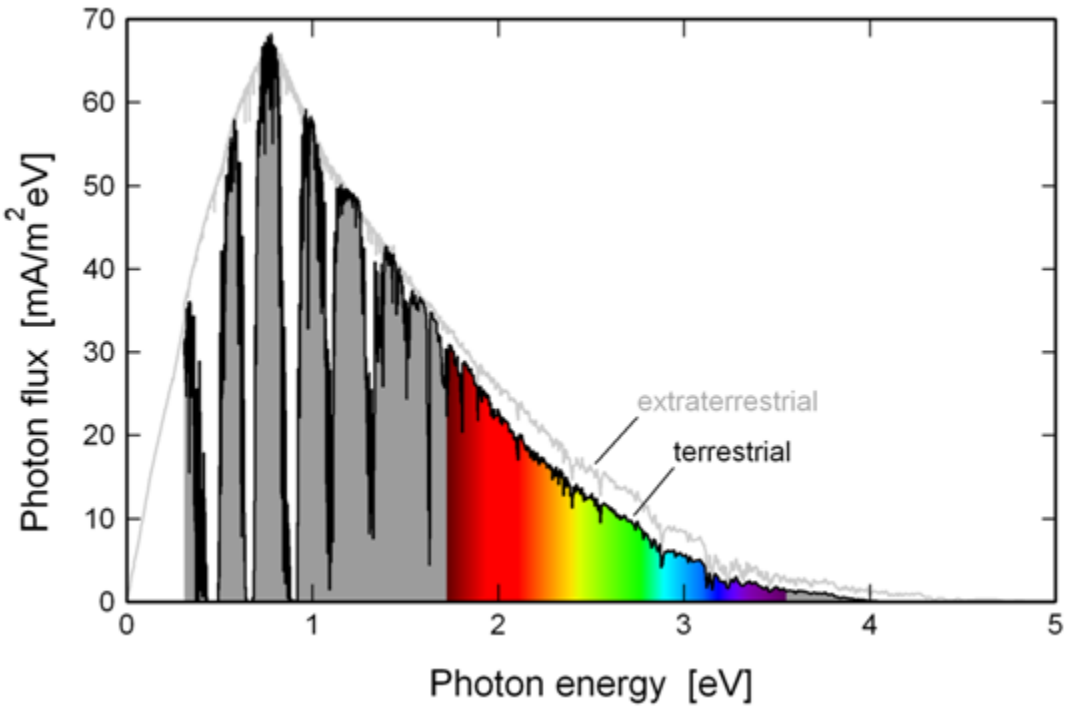
Absorption Spectrum: $\mathrm{Im}\ \epsilon_M(\mathbf{q}\to 0,\omega)$

Thin Film Solar Cell: Efficiency

$$\eta = \frac{P_{\text{out}}}{P_{\text{in}}}$$

$$P_{out} = J_{sc} V_{sc} = J_{sc} E_{gap}$$

$$J_{\text{sc}} = e \int_{E_{\text{gap}}}^{\infty} a(E) I_{\text{sun}}(E) \mathrm{d}E$$

$$a(E) = 1 - e^{-2\alpha(E)L}$$

$$\alpha(E) = \frac{2E}{\hbar c} k(E) \qquad k^2 = \frac{-\epsilon_1 + \sqrt{\epsilon_1^2 + \epsilon_2^2}}{2}$$