High-throughput Screening of New Materials for Water Splitting Applications

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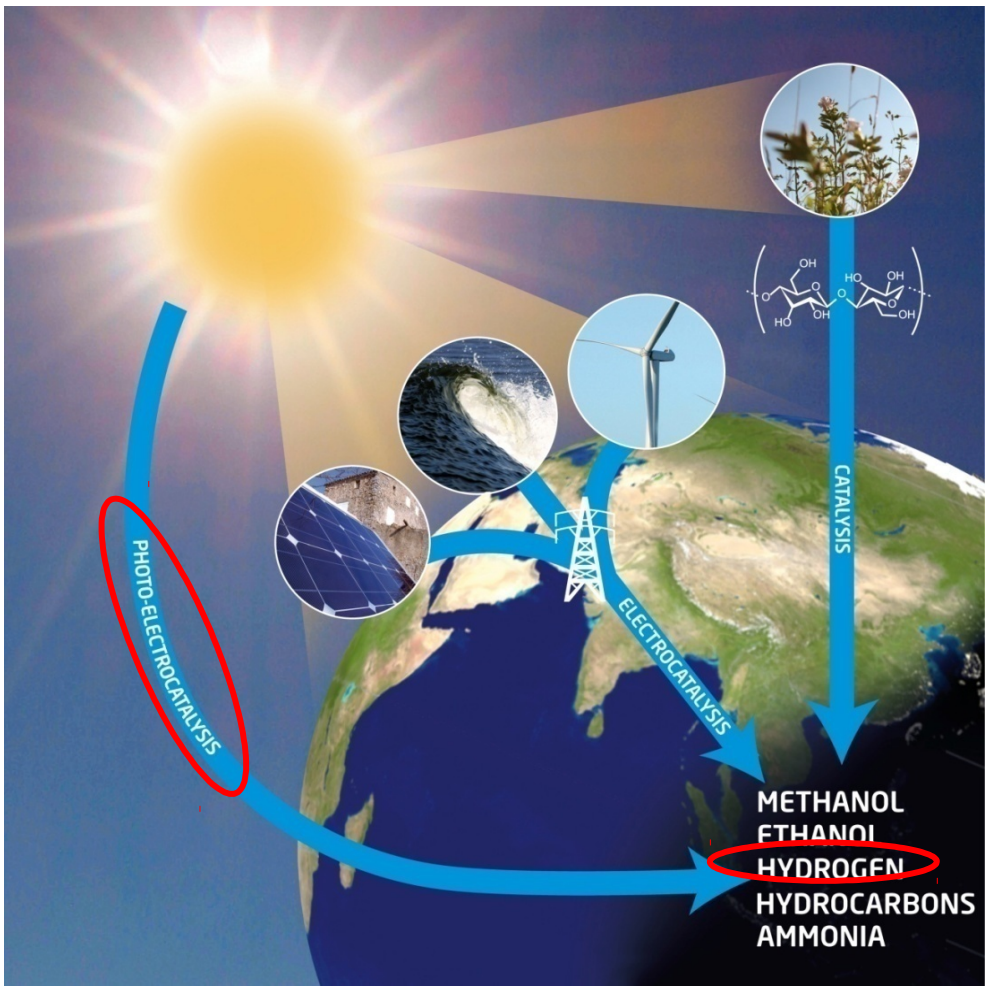
Materials for Sustainable Energy Future
Workshop II: Fuels from Sunlight
17 October 2013

From Sun Light into Fuels



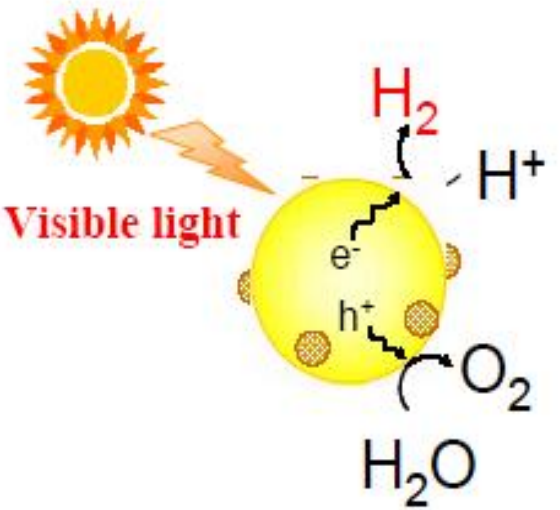
Direct production of energy by generating hydrogen from sun light.

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.



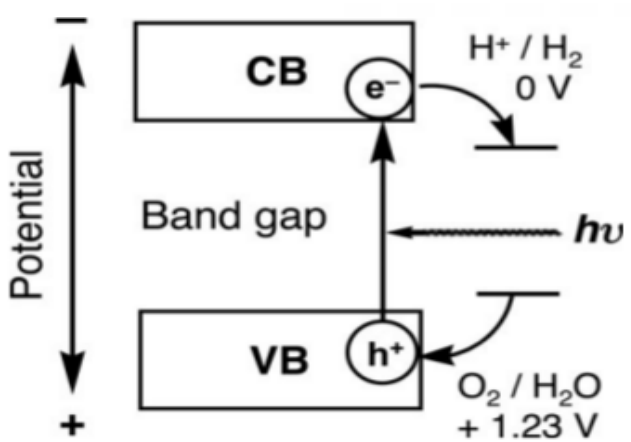
Few examples: TiO_2, GaN:ZnO

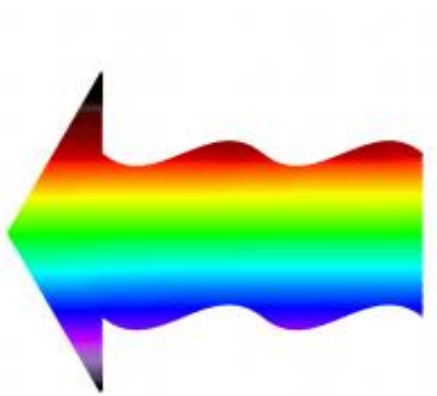
Fujishima and Honda, *Nature* **238**, 37 (1972).

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

Properties for Water Splitting Materials

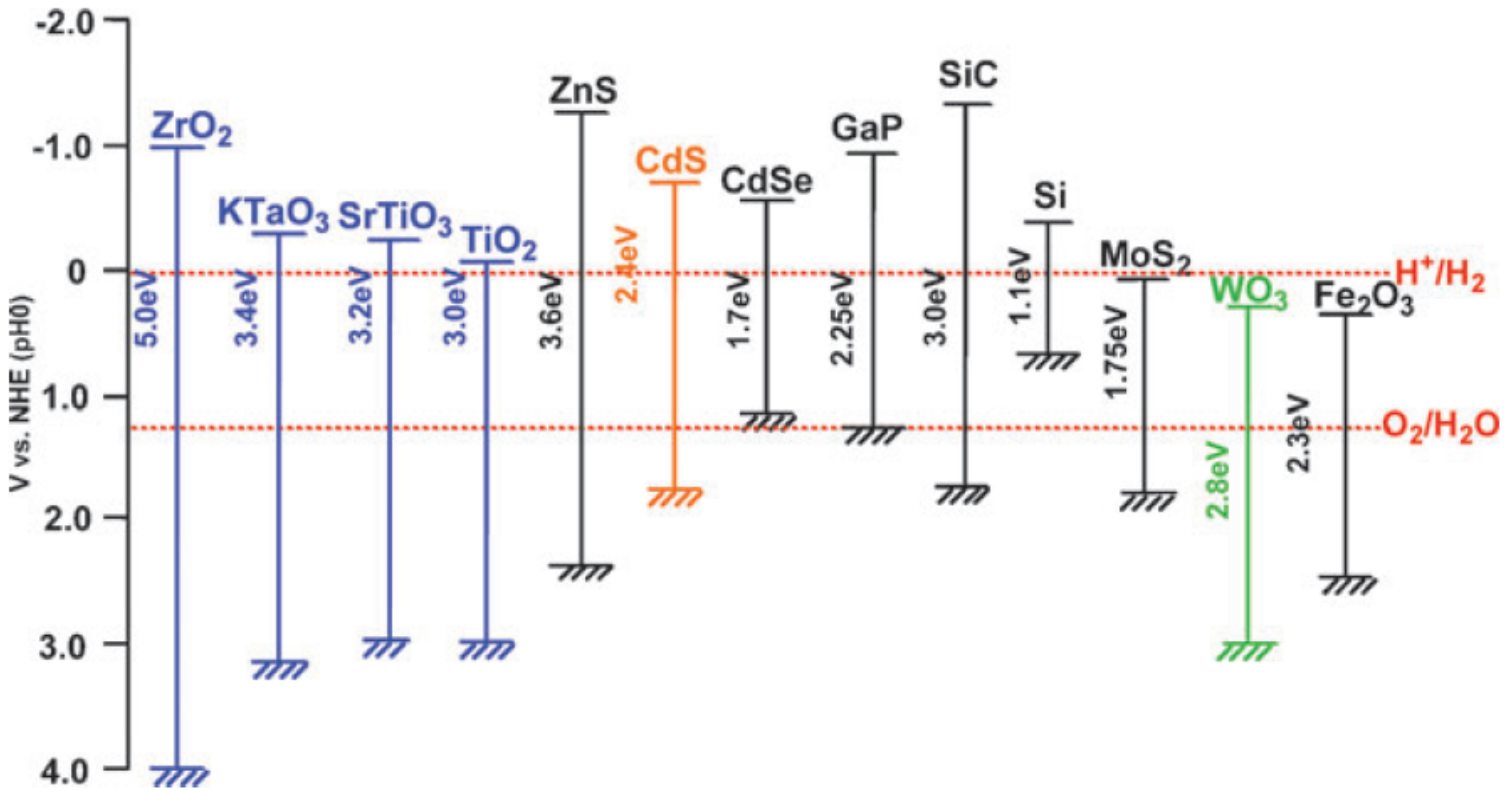
1) Chemical/structural stability;
2) Good light absorption;
3) Photogenerated charges at correct potentials;
4) Good electron/hole mobility;
5) Good catalytic properties;
6) Eco-friendly: low cost and non-toxicity.





Principle of water splitting using semiconductor photocatalysts.

The Optimal Material Has Not Been Found



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

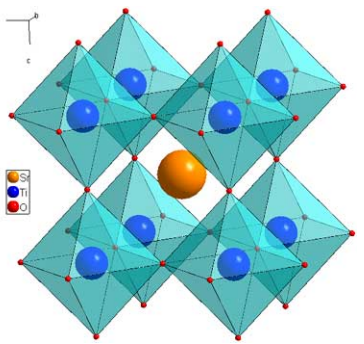
Kudo and Miseki, *Chem. Soc. Rev*. **38**, 253 (2009).

Agenda

New materials for solar light conversion into hydrogen and oxygen.

1) Computational method: DFT and screening approach;

2) Water splitting applications:
   a) Cubic perovskites:
      One-photon WS
      Two-photon WS
      Transparent protective shield
   b) Low symmetry perovskites
   c) Pourbaix diagrams for corrosion analysis



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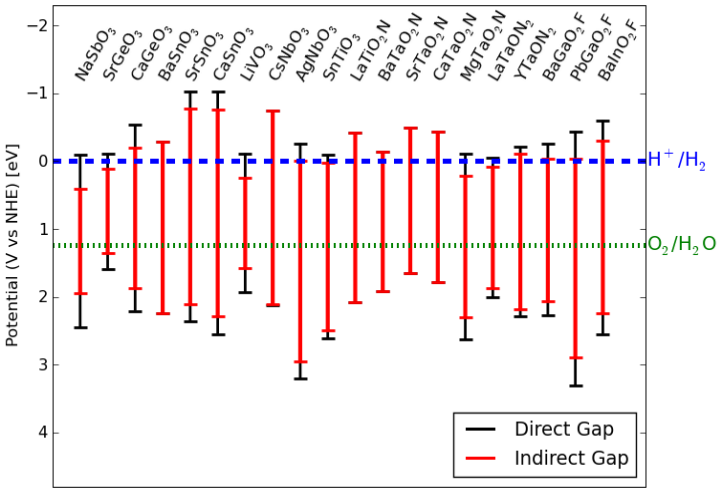
3) Bandgap calculations for energy applications.

Conclusions

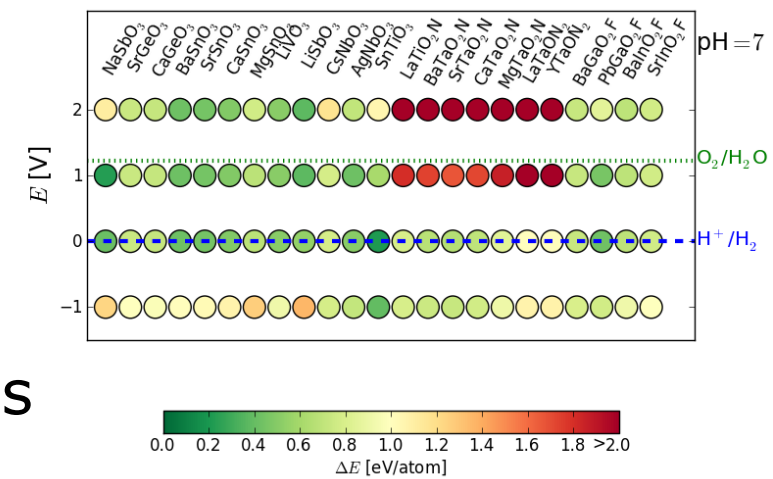
Handful materials identified for one- and two-photon water splitting:

- Cubic perovskite
- Double and layered perovskite
- Known materials from the Materials Project database



Use of simple statistic to reduce the simulations to perform

Pourbaix diagrams to evaluate the stability in water



The bandgaps of 2200 known materials have been calculated (energy related applications)

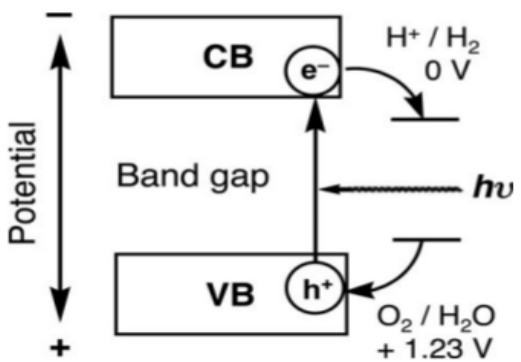
Descriptors for the Screening

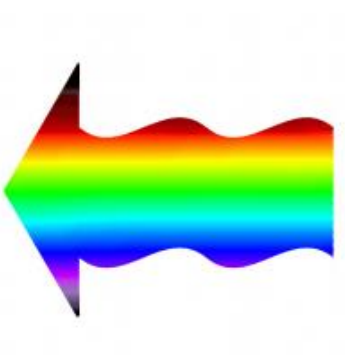
1) Chemical/structural stability;

2) Good light absorption;

3) Photogenerated charges at correct potentials;

4) Good electron/hole mobility;
5) Good catalytic properties;
6) Low cost and non-toxicity.

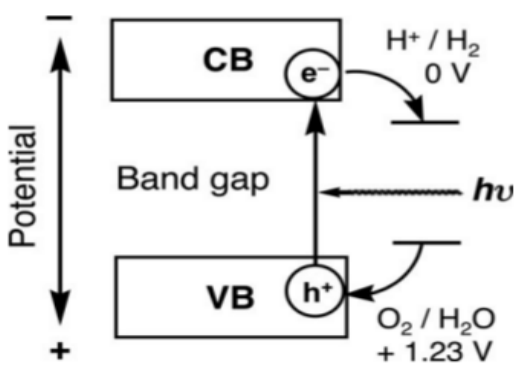




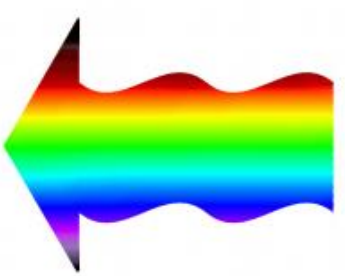
Principle of water splitting using semiconductor photocatalysts.

Descriptors for the Screening

1) **Chemical/structural stability**;
   Heat of Formation
2) **Good light absorption**;
   Bandgap in the visible range
3) **Photogenerated charges at correct potentials**;
   Band edges 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.



J. Enkovaara *et al.* J. Phys.:Cond. Mat. **22** (2010)

https://wiki.fysik.dtu.dk/gpaw/

Descriptor: Stability

1) Heat of Formation

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: $\Delta E \leqslant 0.2 \ eV/atom$

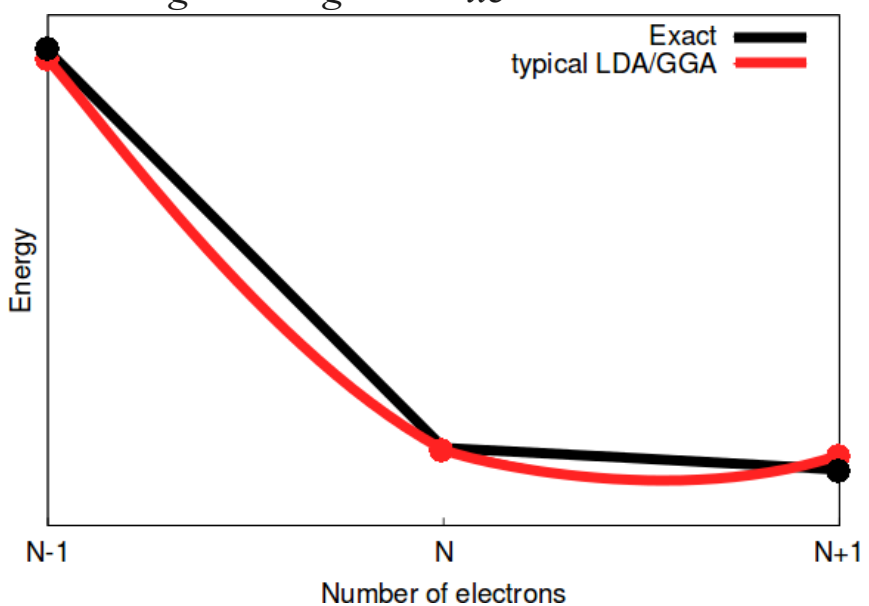
Descriptor: Light Absorption

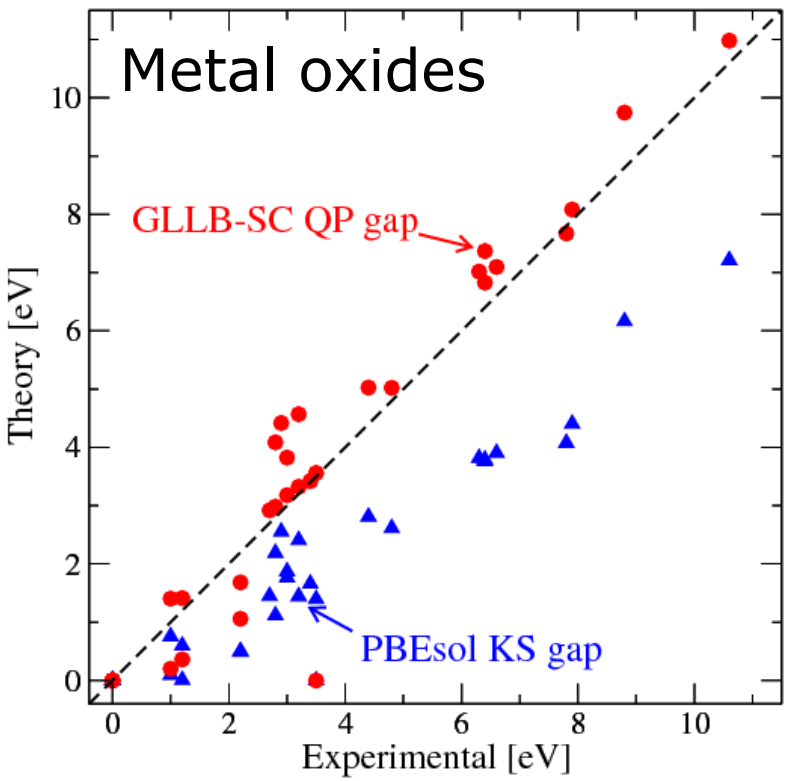
2) Calculation of the bandgaps: GLLB-SC

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).

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

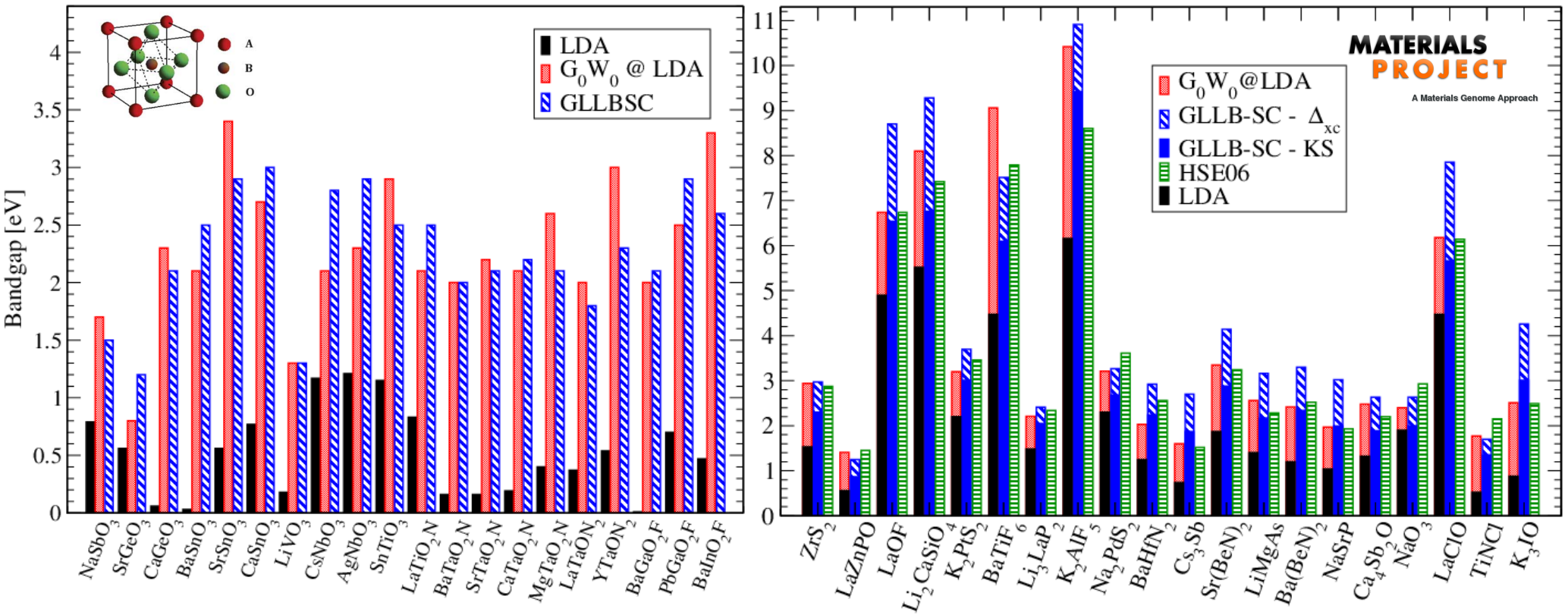




Gap within an error 0.5 eV.
Minimal computational cost.

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).

GLLB-SC and G_0W_0@LDA



Good agreement between GLLB-SC and G_0W_0@LDA (MRE = 0.2).

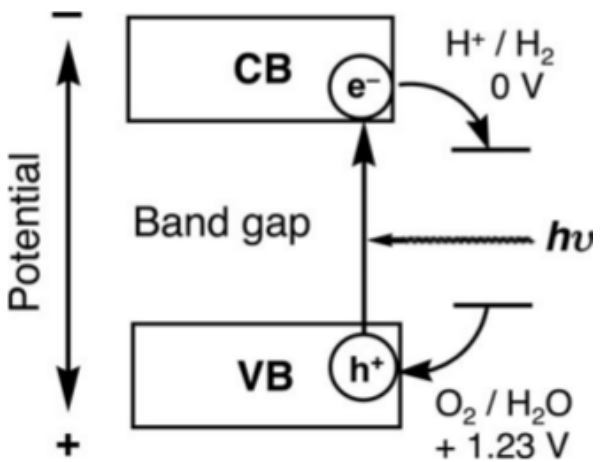
I. E. Castelli, J. M. Garcia-Lastra, F. Huser, K. S. Thygesen, and K. W. Jacobsen, *New J. Phys.* (2013).

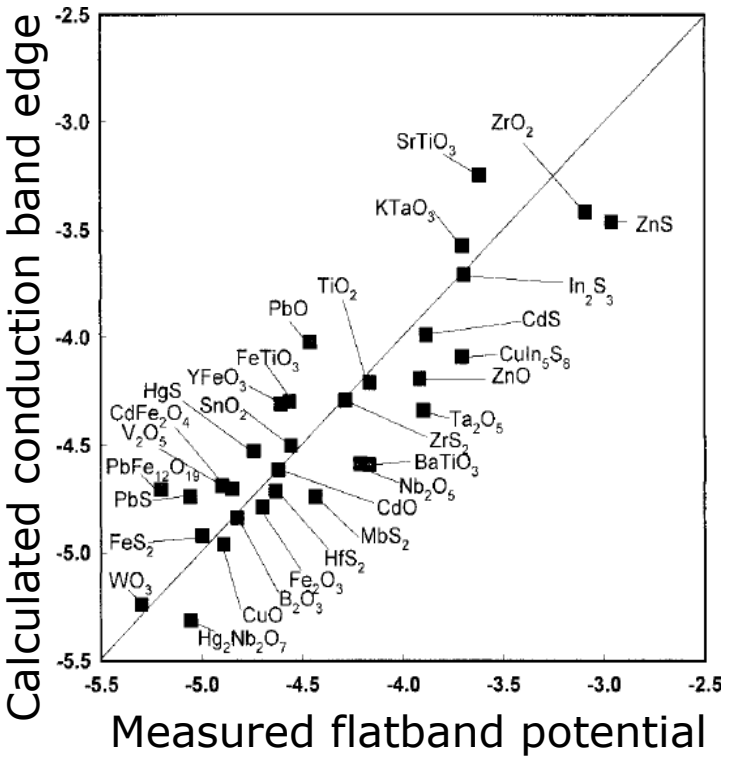
In collaboration with A. Jain, and K. Persson (LBL); G. Ceder (MIT).

Descriptor: Potential of the Charges

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!

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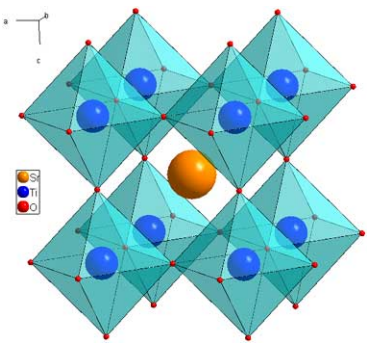

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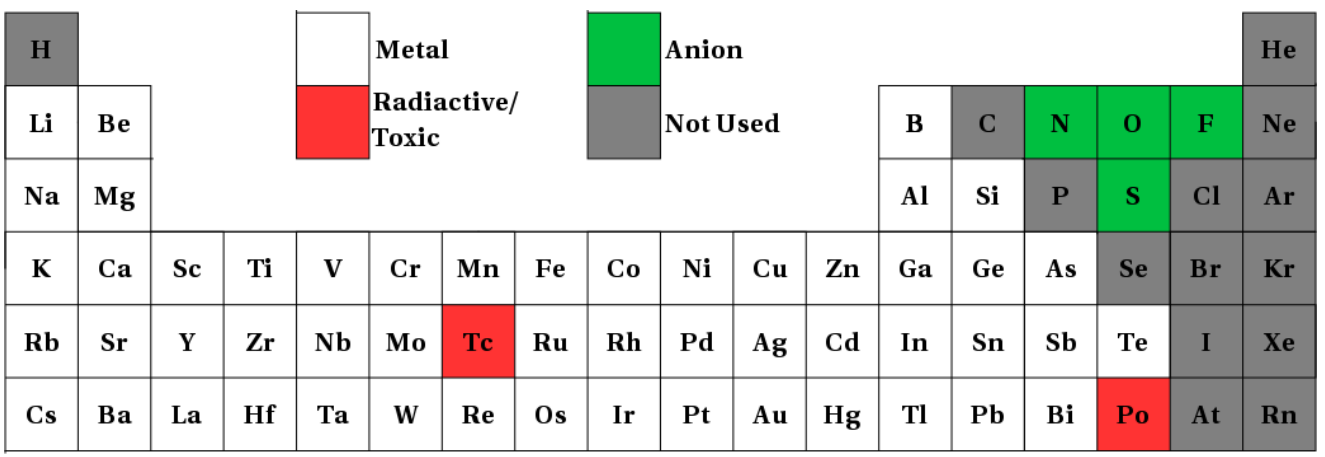
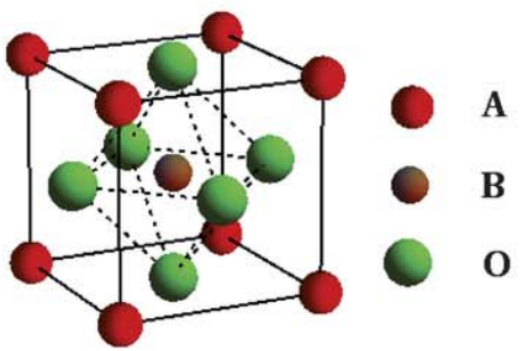
3) Bandgap calculations for energy applications.

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, …).

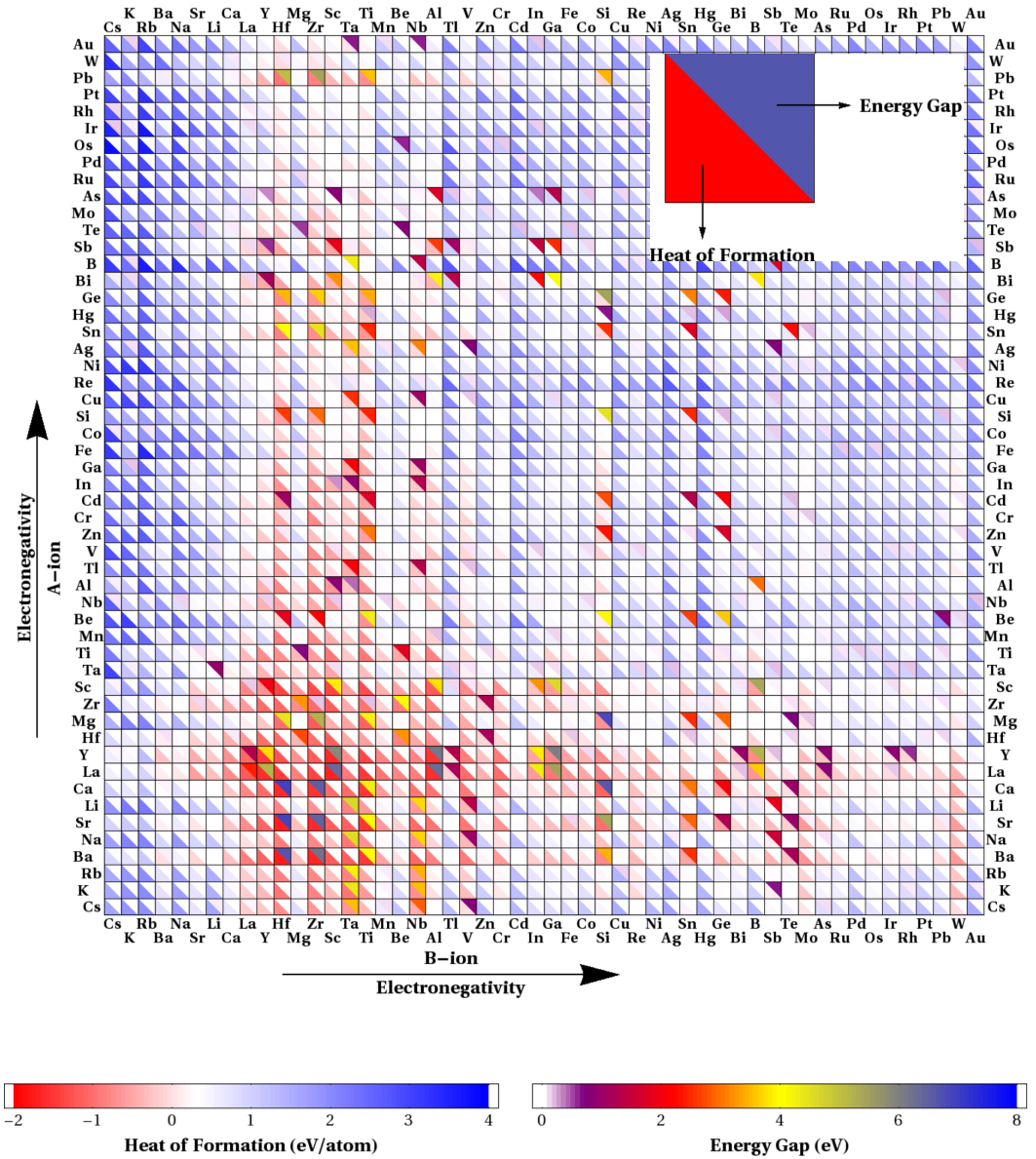




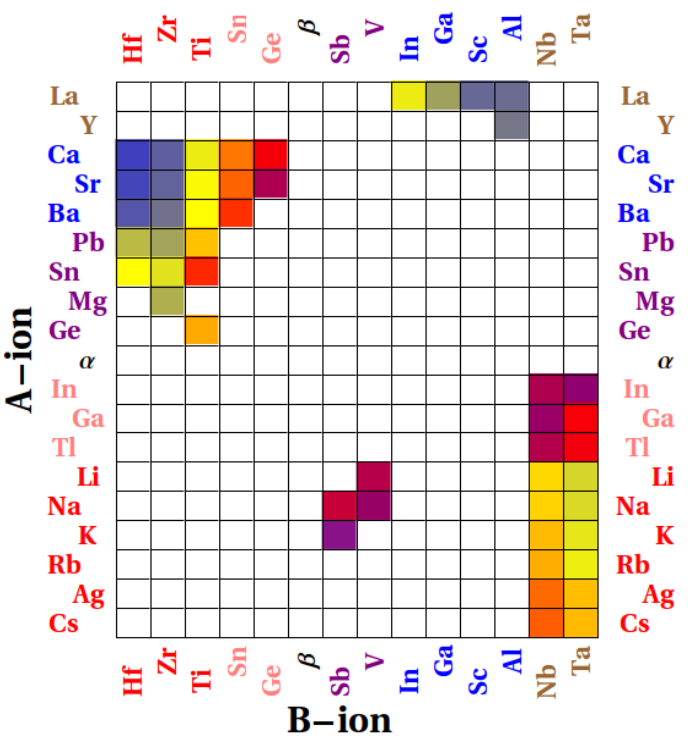
Excluded elements:

- Non Metals;
- Radioactive, toxic.

ABO_3 Perovskite



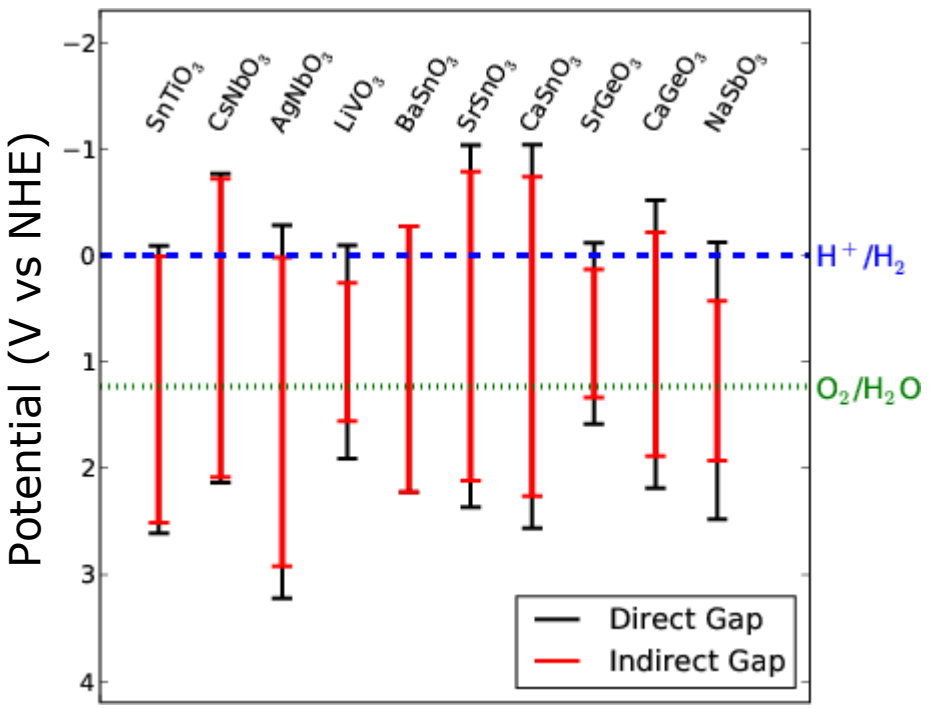
Trends for stability and bandgap:
- ionic radii;
- even number of electrons in the unit cell;
- sum of the possible oxidation states of the two metals = 6 (2 electrons per oxygen atom).



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

10 oxides fulfill the criteria



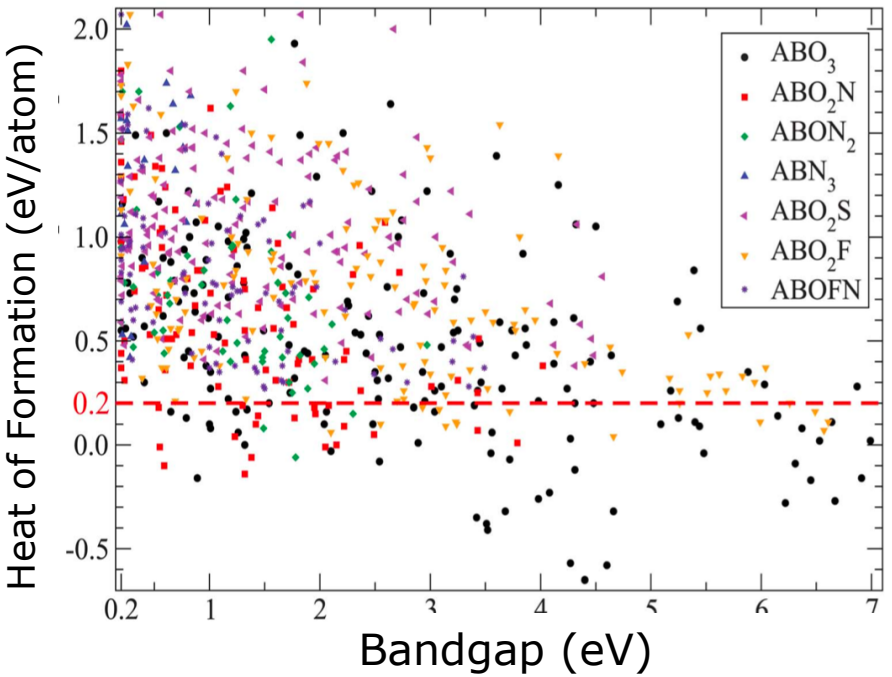
$AgNbO_3$ and $BaSnO_3$ are known:
$AgNbO_3$: works!
$BaSnO_3$: defect induced recombination.

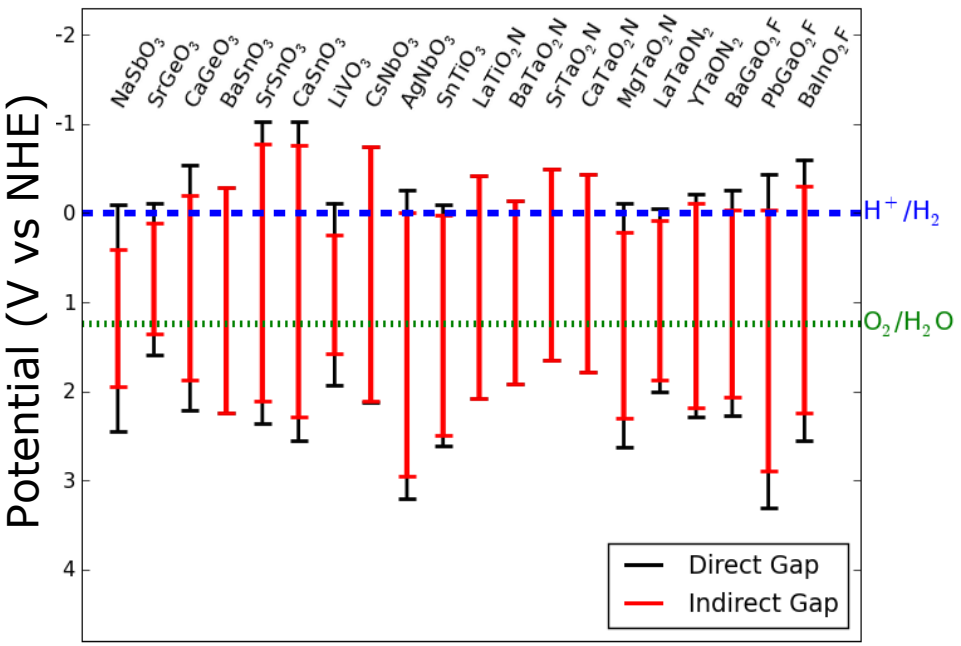
$SrSnO_3$ and $CaSnO_3$: orthorhombic perovskite (too large bandgap).

None of the others is known.

$LiVO_3$ under investigation at CINF/DTU.

Candidates for One-photon WS





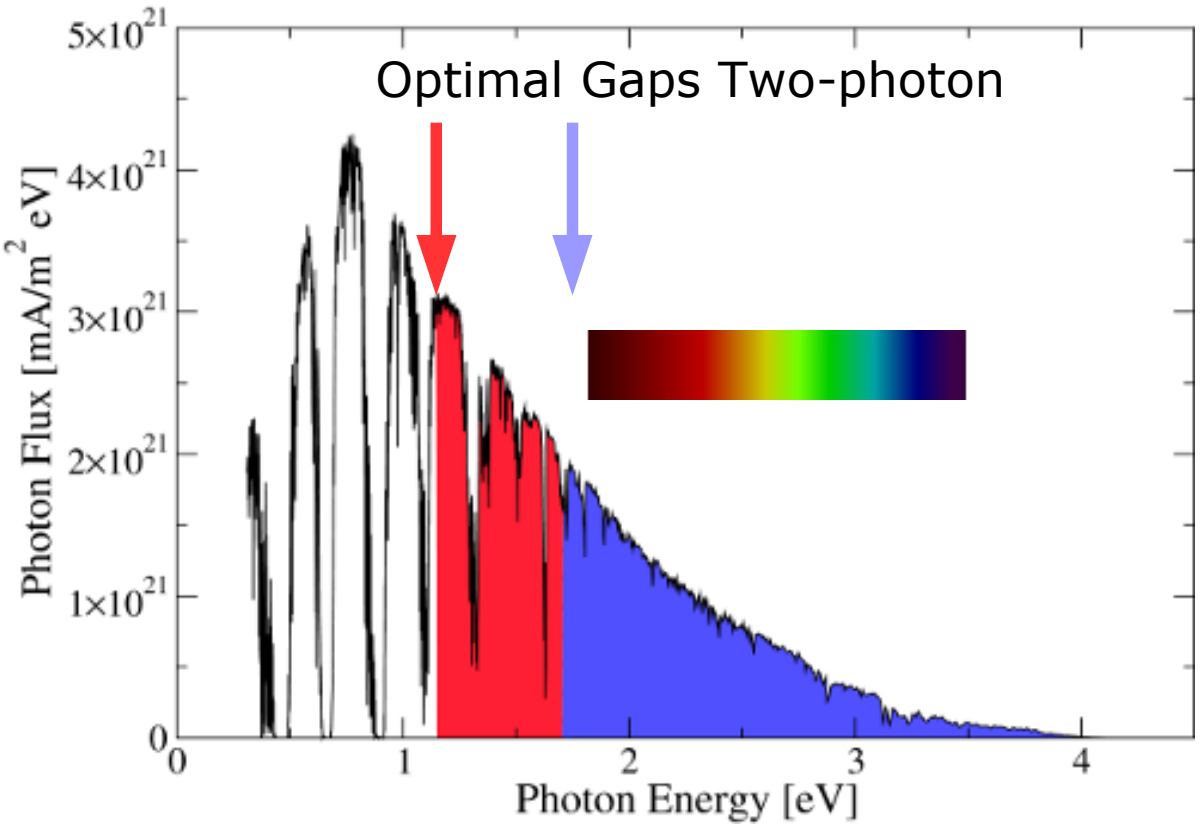
~19000 materials → 20 candidates

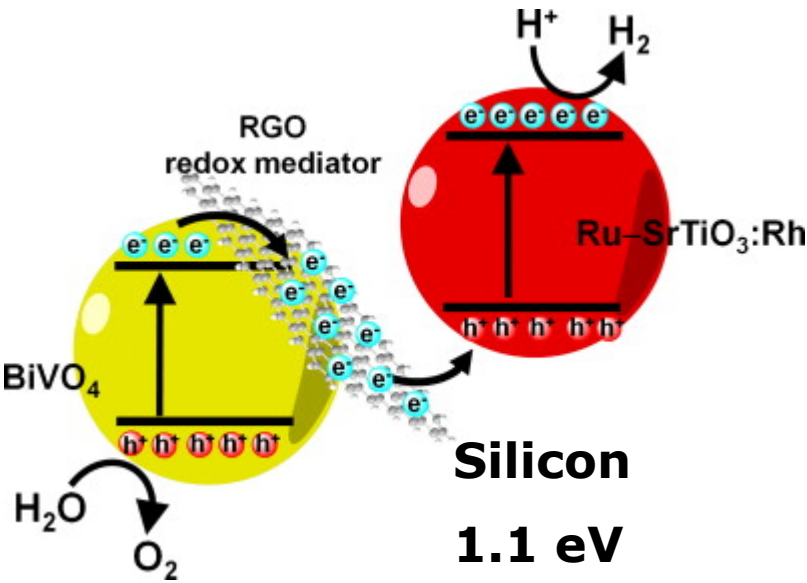
Screening parameters	One-photon WS
Chemical/structural stability (ΔE)	$\Delta E \leq 0.2$ eV
Bandgap (E_{gap})	$1.5 \leq E_{gap} \leq 3$ eV
Band edges (VB_{edge}, CB_{edge})	$VB_{edge} > 1.23$ eV $CB_{edge} < 0$ eV

- 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).

One- vs Two-photon WS

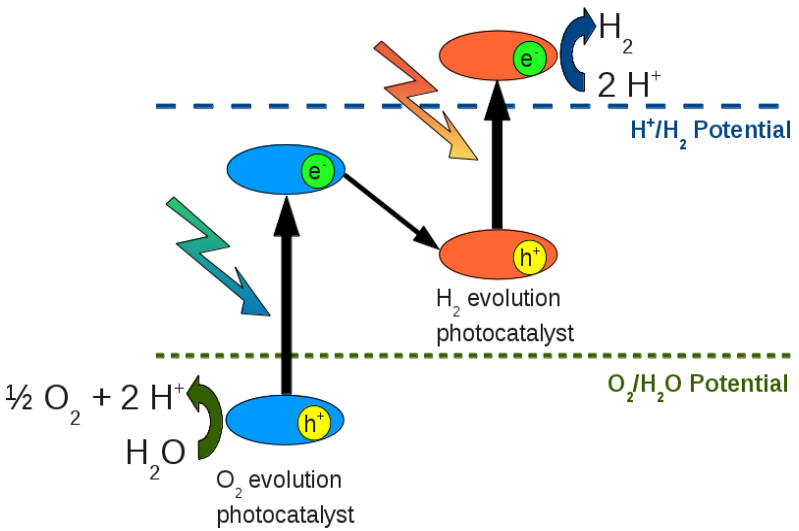




One-photon WS Efficiency: 7 %

Two-photon WS Efficiency: 28 %

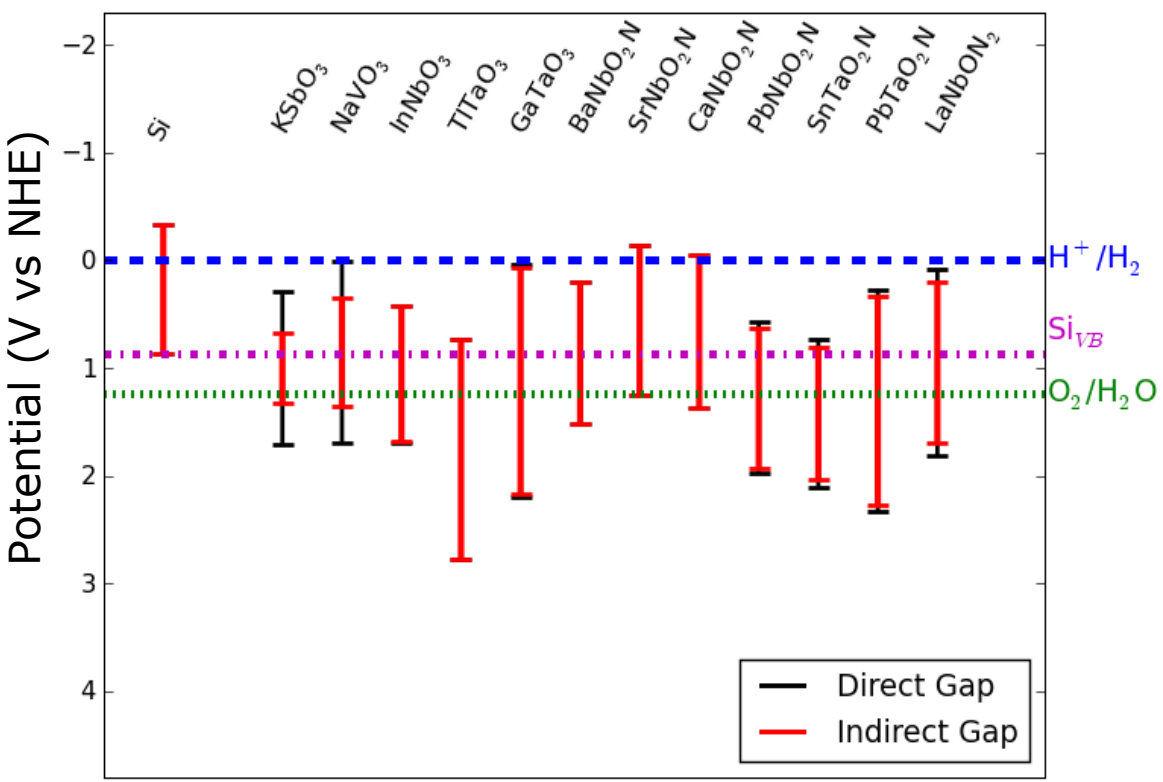
Two-photon WS: Candidates



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 $VB_{edge}^{cathode} > CB_{edge}^{anode}$

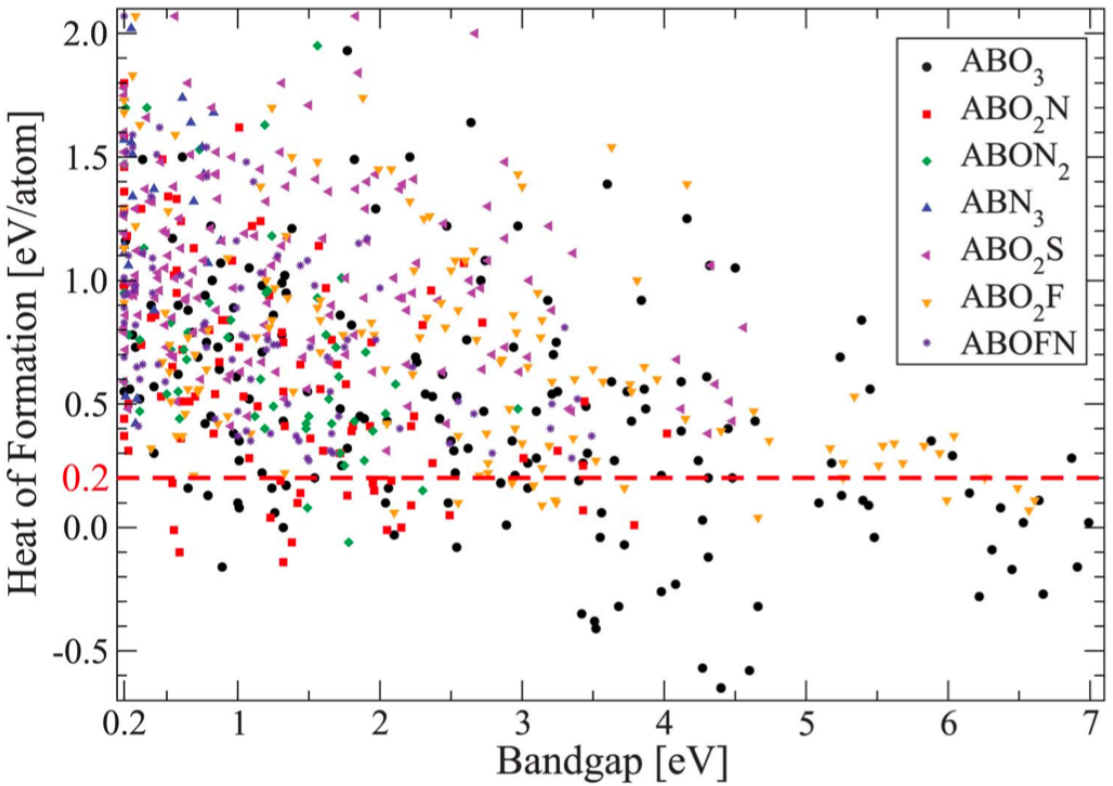
12 candidates (+ 20 one-photon WS)

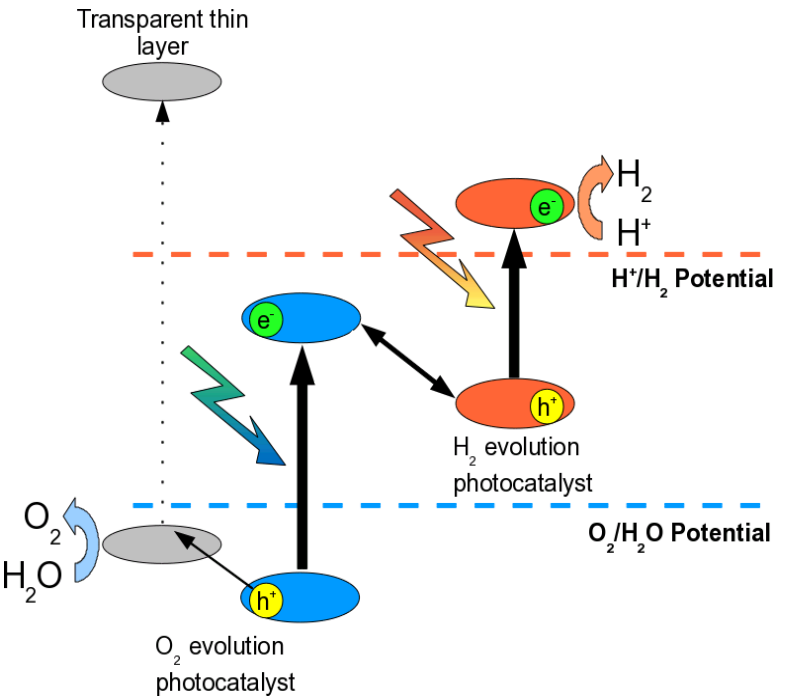
$BaNbO_2N$, $SrNbO_2N$, $CaNbO_2N$, and $LaNbON_2$ are known as water splitters.



Transparent Protective Shield

Large Bandgap ⟶ High Stability





Example: TiO_2 protects MoS_2 for H_2 production.

Seger et al., *Angewandte Chemie* **51**, 9128 (2012).

Transparent Shield - Photoanode

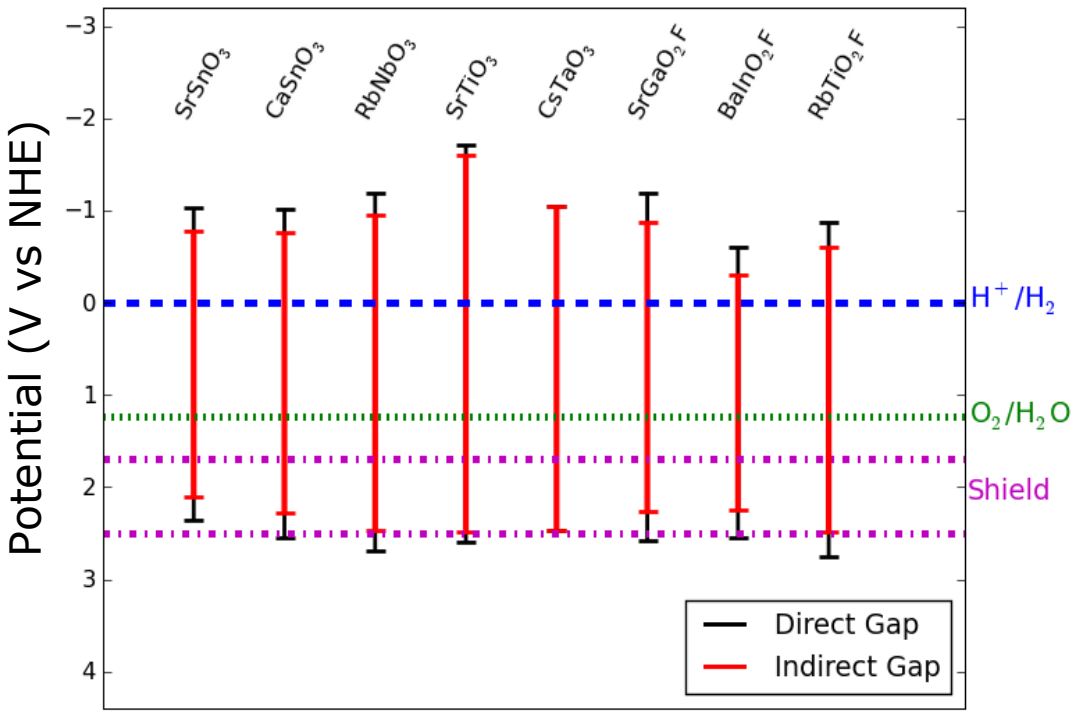
Screening parameters	Transparent Shield (TS)
Chemical/structural stability (ΔE)	$\Delta E \leq 0.2$ eV
Bandgap (E_{gap})	$E_{\mathrm{gap}}^{\mathrm{dir}} > 3$ eV
Band edges ($\mathrm{VB_{edge}}$, $\mathrm{CB_{edge}}$)	Photoanode TS: $1.7 < \mathrm{VB_{edge}} < 2.5$ eV vs NHE Photocathode TS: $-0.7 <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

8 materials (5 new).

$SrTiO_3$ known for water splitting in UV light.

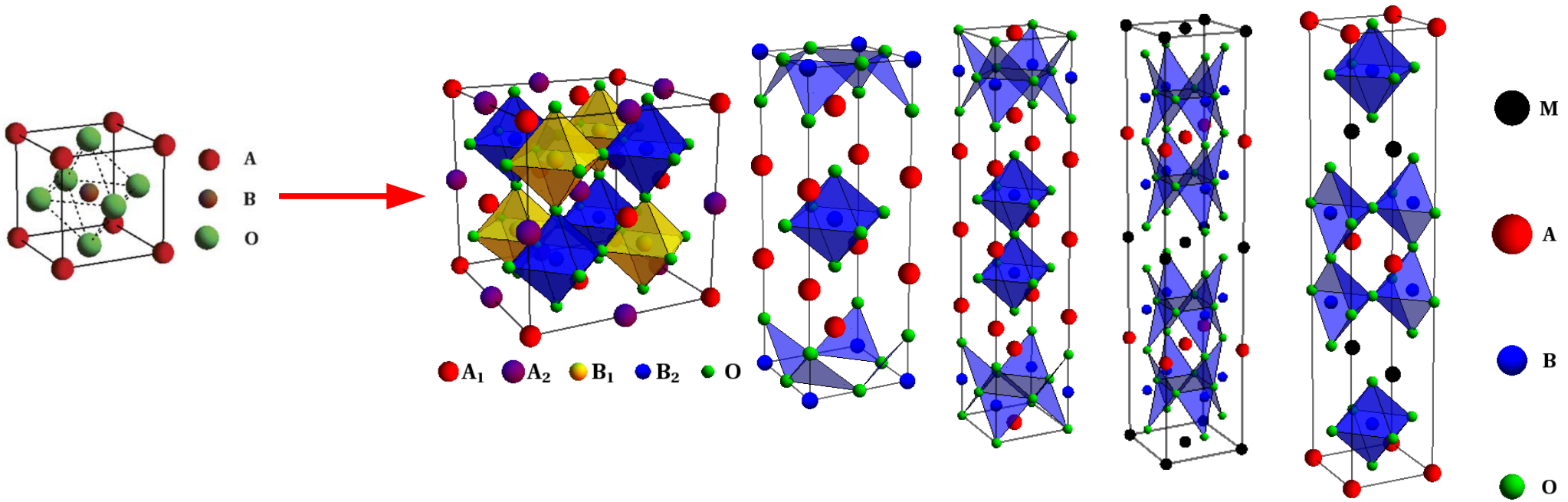
$SrSnO_3$ and $CaSnO_3$ known in the orthorhombic phase.

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:

1) even number of electrons in the unit cell;
2) sum of the possible oxidation states of elements = 0.
3) size of the ionic radii;

Chemical-based Rules

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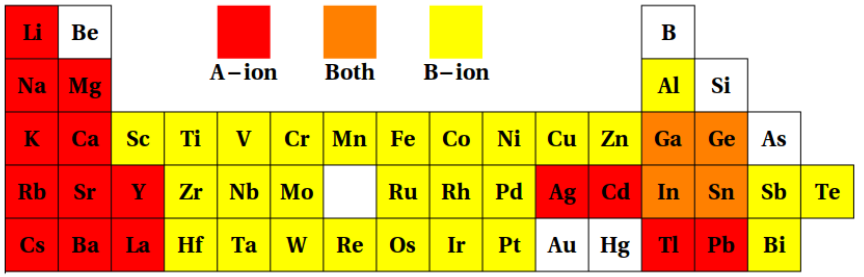

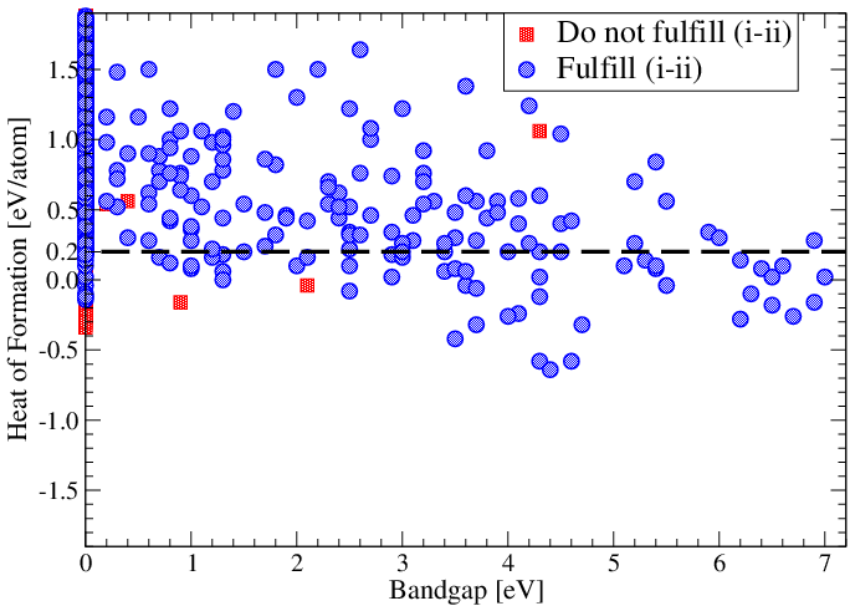

1 and 2 are important to design semiconductors.
2700 → 800 combinations

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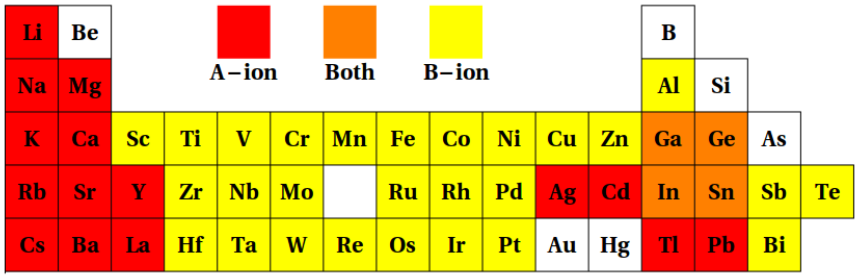

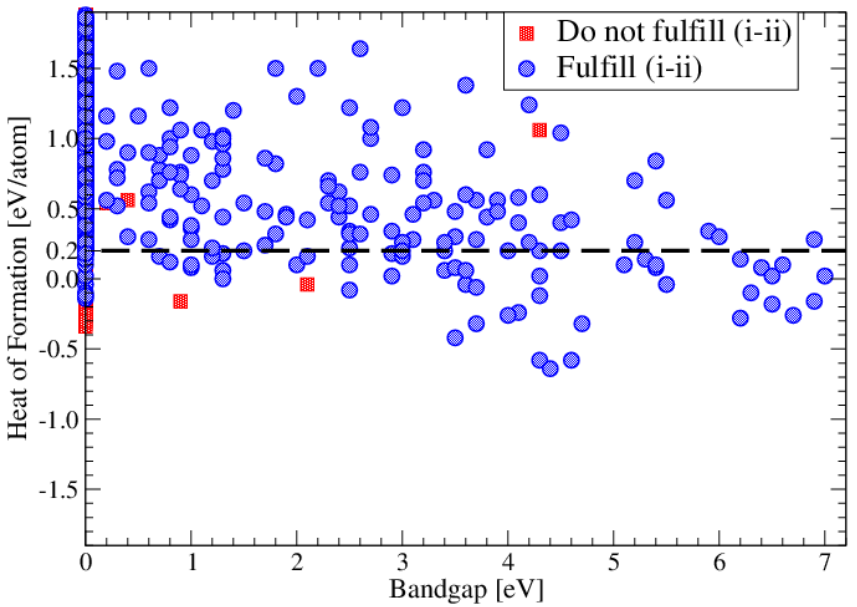

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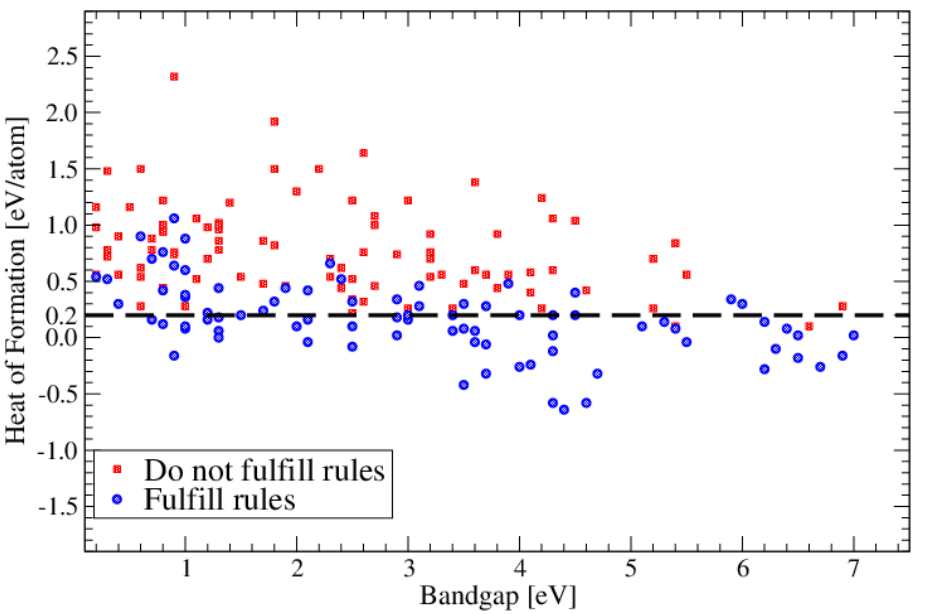
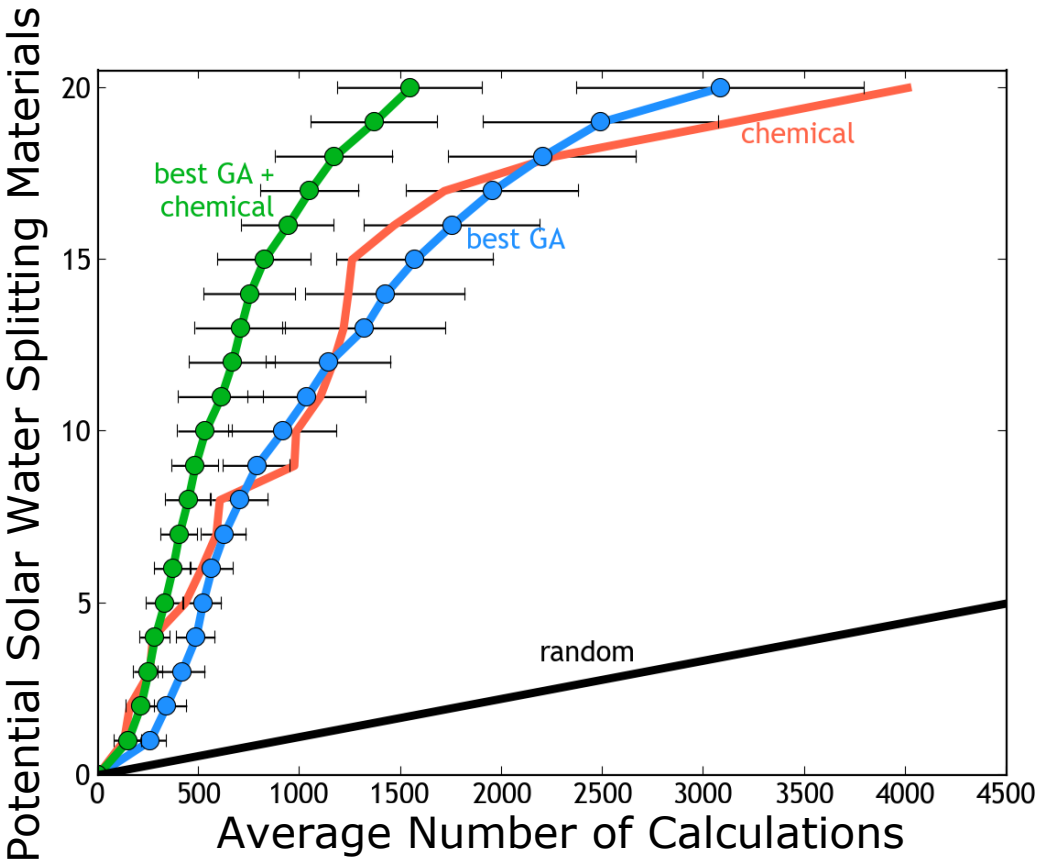


3 works on the stability.
2700 ⟶ 300 combinations

Evolutionary Algorithm



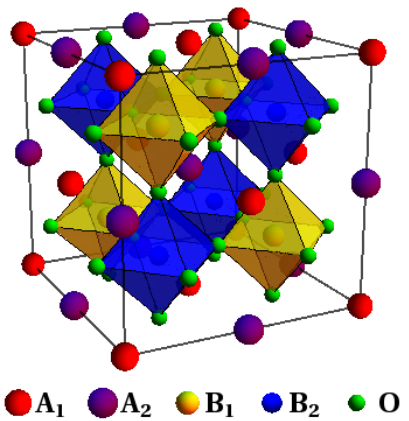
An evolutionary algorithm performs as good as a chemical-based search!

80 % less calculations!

A. Jain, I. E. Castelli, G. Hautier, D. H. Bailey, and K. W. Jacobsen, *Journal of Materials Science* **48**, 6519 (2013).

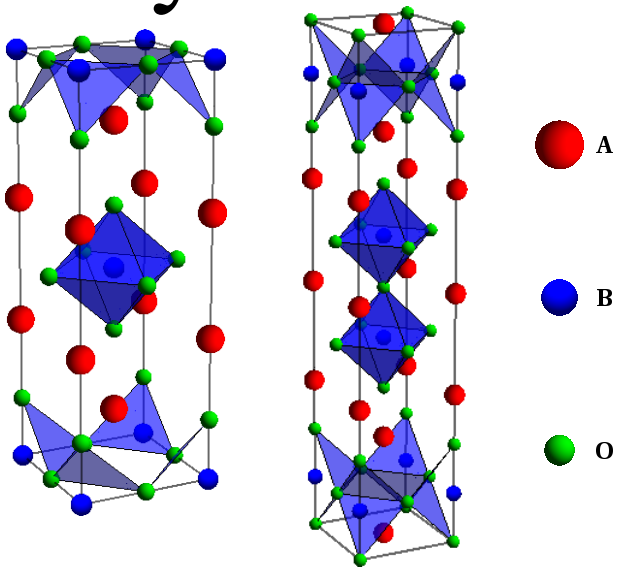
Low Symmetry Perovskite

Double



New candidates, bandgap engineering!

Layered



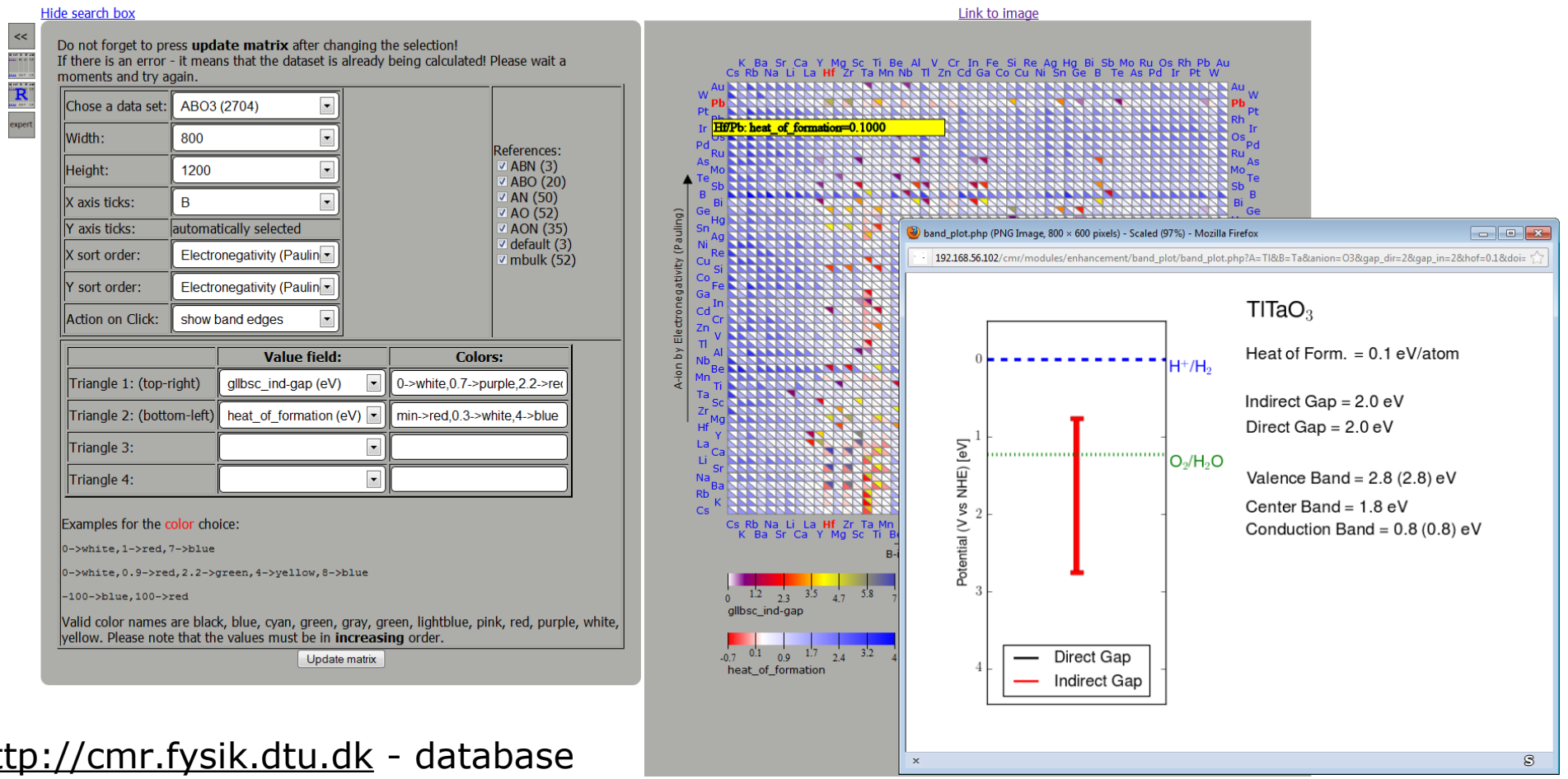
Bandgap increases when p- and d-metals are combined in the B-ion position.

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, *New J. Phys.* (2013).

The Computational Materials Repository



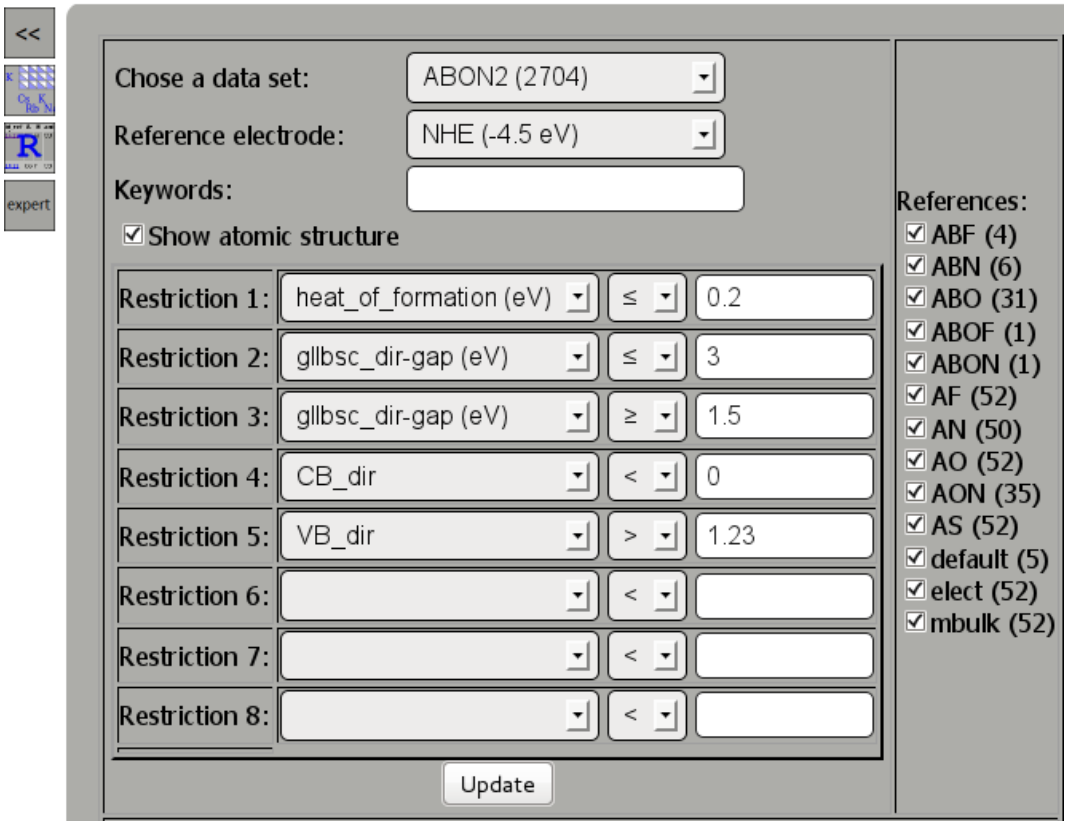
http://cmr.fysik.dtu.dk - database

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

Landis et. al, *Computing in Science and Engineering* **14**, 51 (2012).

How to Search in CMR

Computational Materials Repository



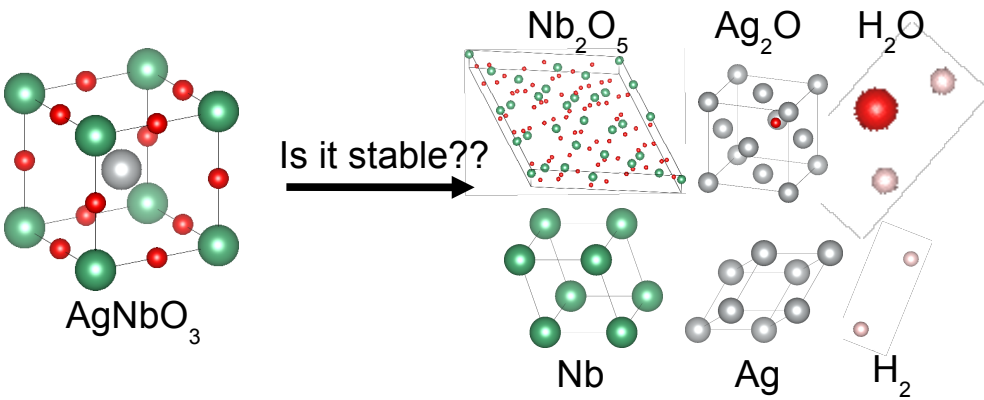
Freely available

(Almost) ALL the calculated structures are included

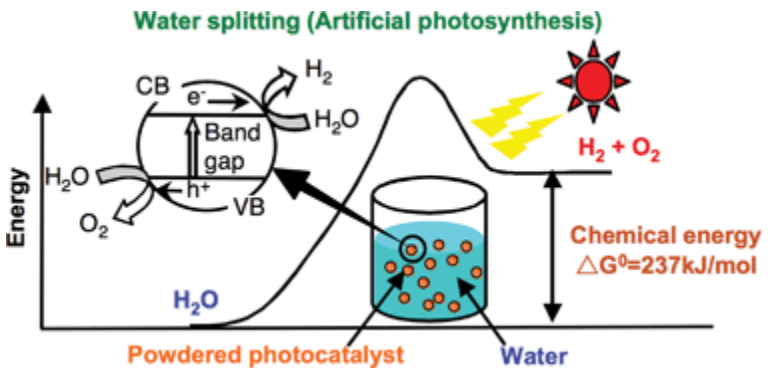
jmol	id_ref	A	B	anion	heat_of_formation	gllbsc_dir-gap	gllbsc_ind-gap	CB_dir	CB_ind	VB_dir	VB_ind	atoms	db_keywords	doi	ingredients	db_description	downloads
Jmol	802207	Y	Ta	ON2	0.1500	2.5000	2.3000	-0.2128	-0.1128	2.2872	2.1872	Ta Y O N (1Ta, 1Y, 1O, 2N)	ABON2 moxn N O ON2 perovskite Ta tandem Y YTaN2O	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

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:

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

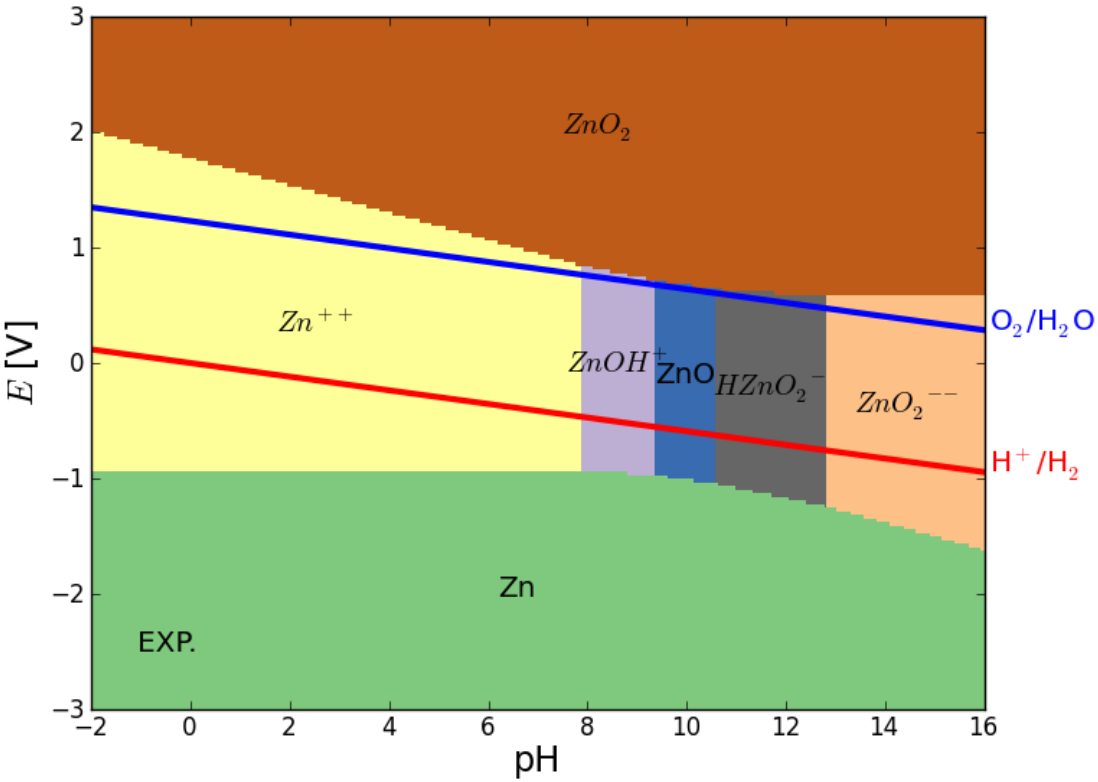
Nernst equation at room temperature:

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

Solids: DFT

Dissolved phases: Experiments

Persson et. al, Phys. Rev. B **85**, 235438 (2012).



Three different lines:

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

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

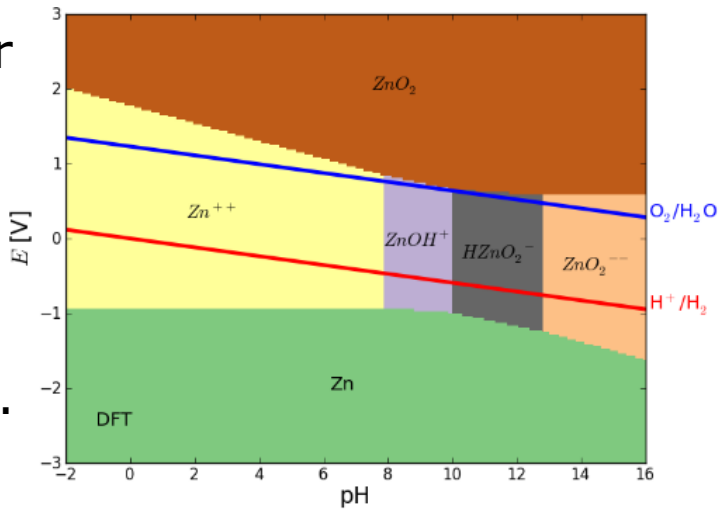
– straight with a slope equal to 0.0591h/n: solid and dissolved phases with free electrons and hydrogen ions. $Zn + H_2O = ZnO + 2H^+ + 2e^-$

DFT vs Experiments

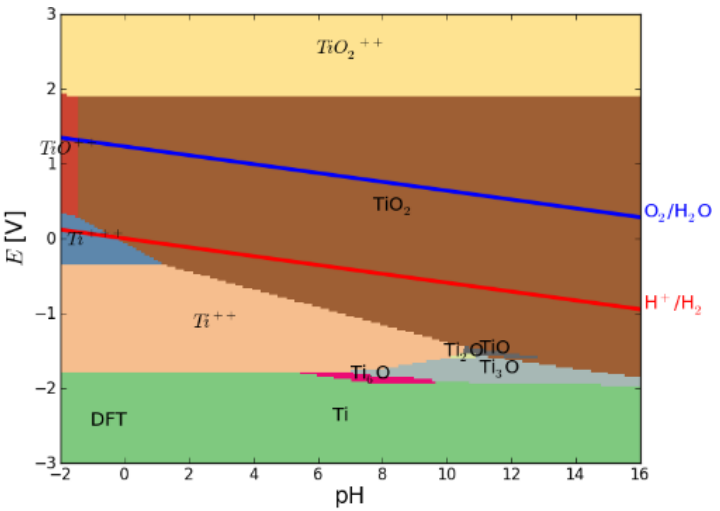
Pourbaix diagrams for Zn and Ti.

DFT and Experiments give similar diagrams.

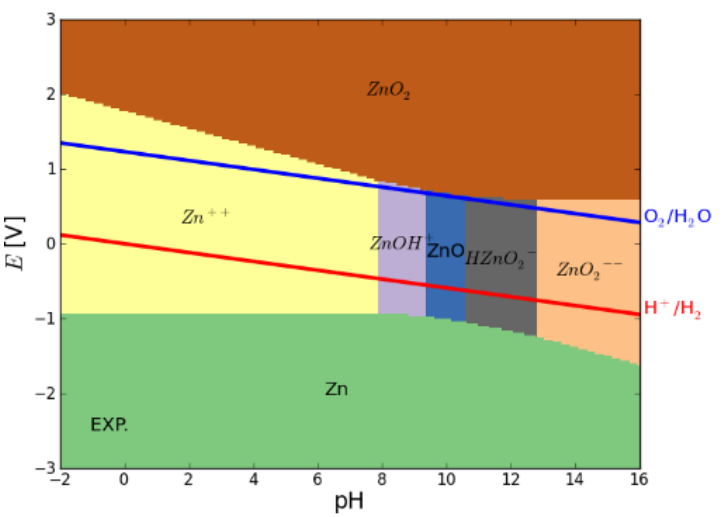
Discrepancies:
- inaccuracy in the data/calculations;
- metastability and reaction kinetics;
- role of surfaces and their passivation;
- more data available for DFT calculations.



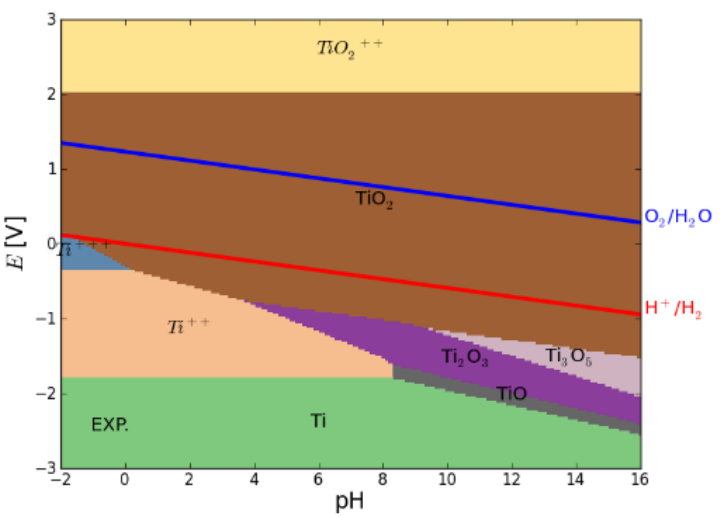
(a) ZnO - DFT



(b) TiO_2 - DFT

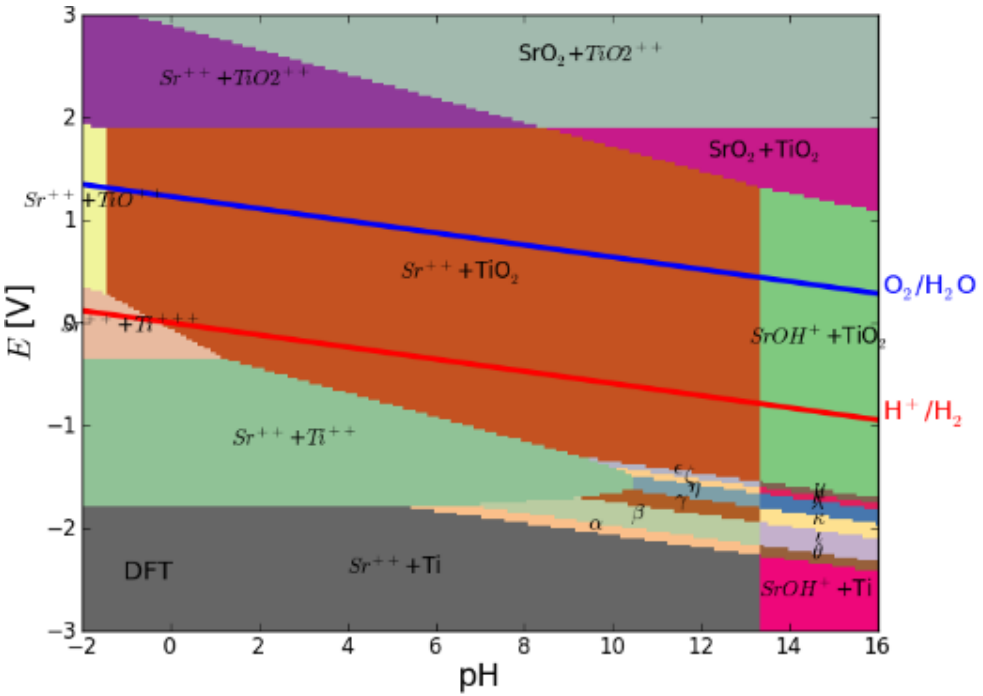


(c) ZnO - Experiments

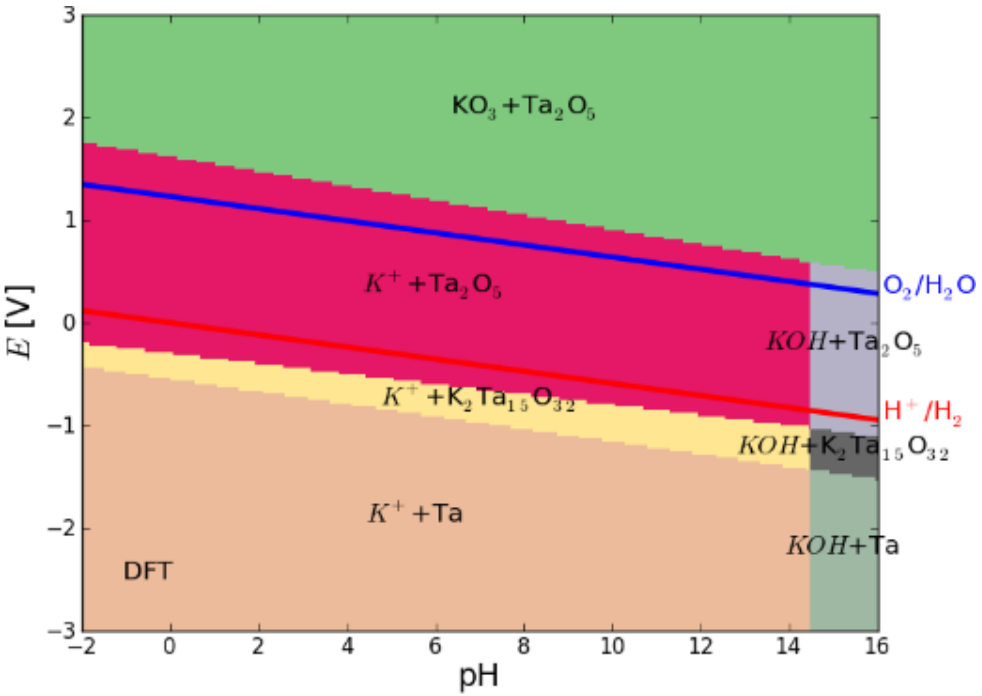


(d) TiO_2 - Experiments

$SrTiO_3$ and $KTaO_3$



(a) $SrTiO_3$ - DFT



(b) $KTaO_3$ - DFT

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

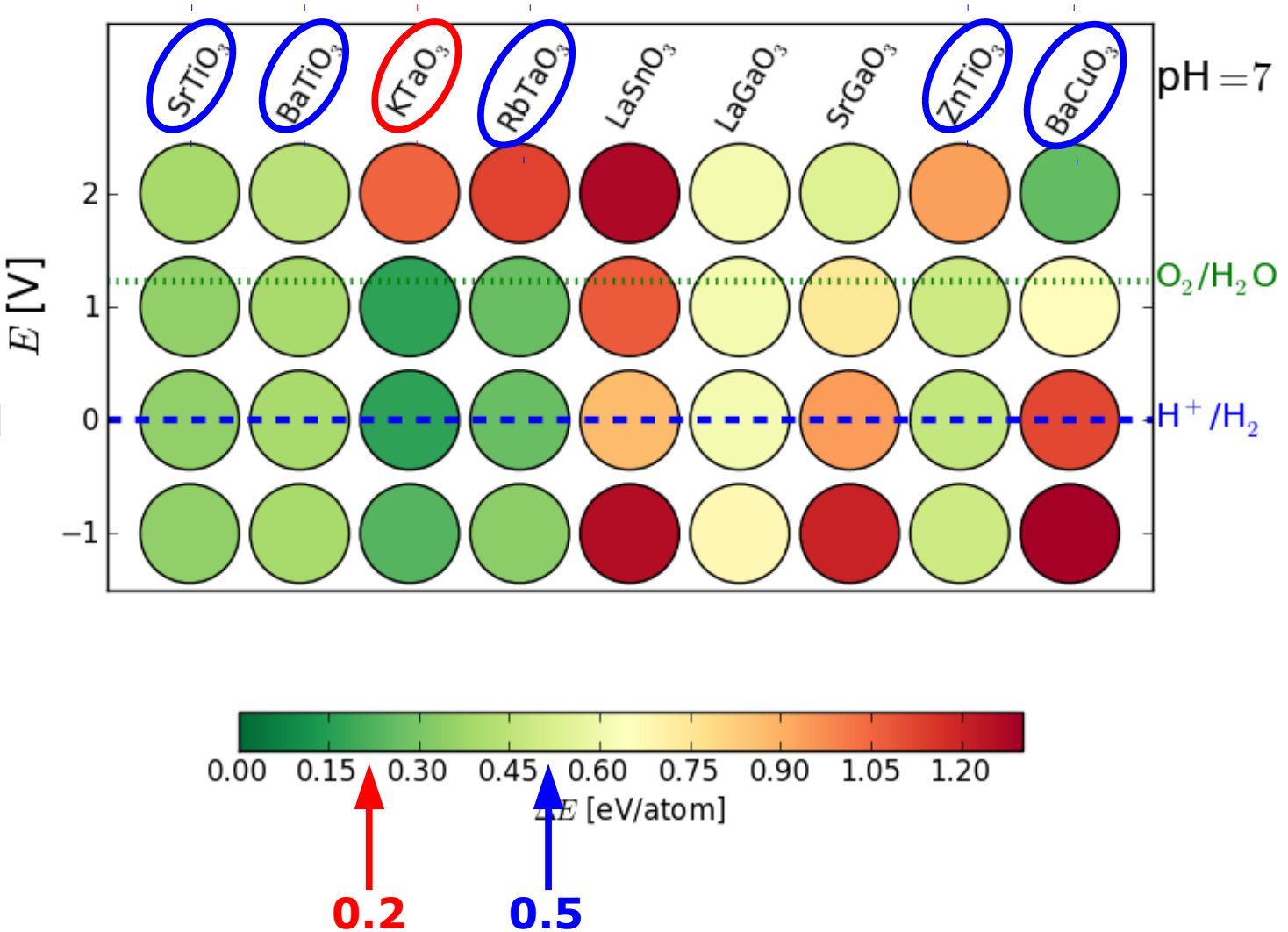
But they are experimentally known to be stable and used for water splitting.
The reaction kinetics (not included in the Pourbaix diagrams) and metastability are important to define stable materials!
We can increase the energy threshold to take into account these effects.

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**).

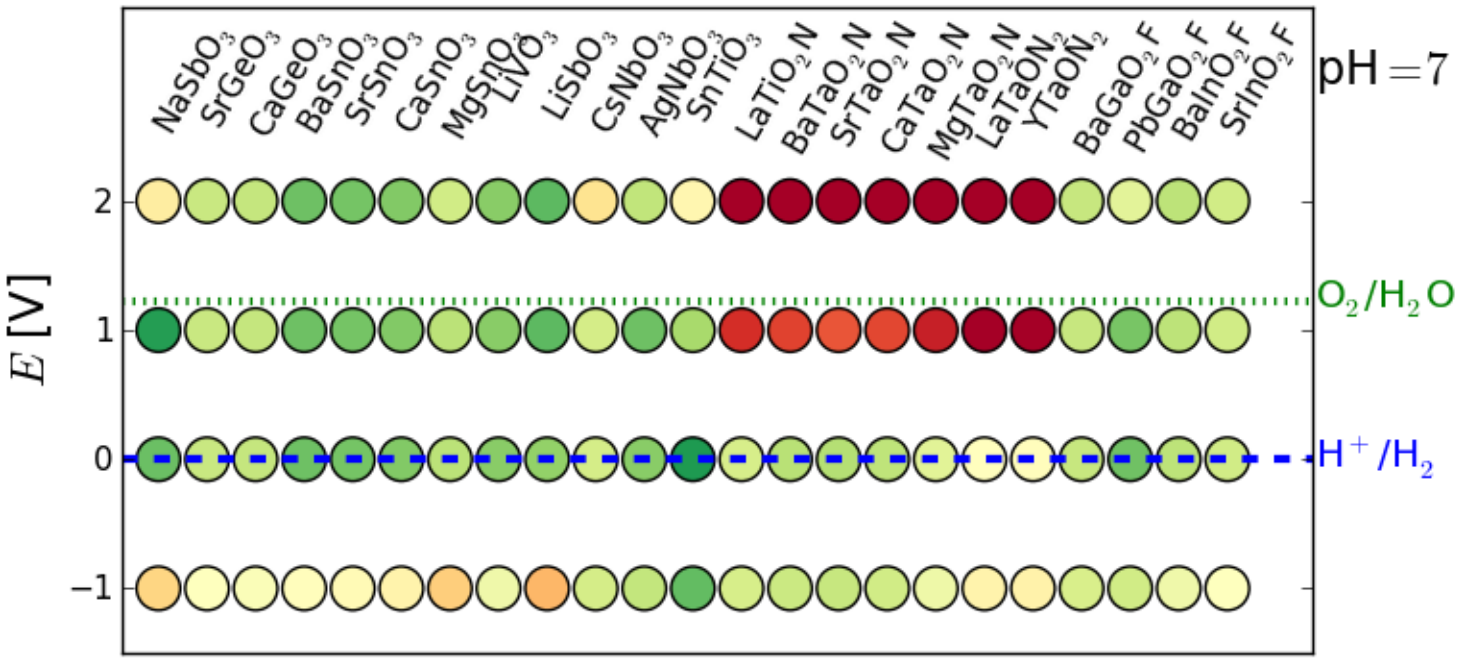


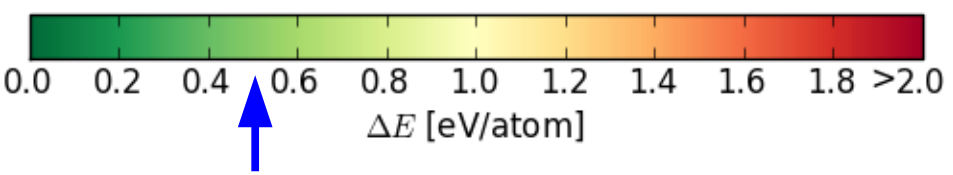
Water Splitting Candidates

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

Oxynitrides are less stable, especially at high potential.

?? Role of the kinetics for the stability in water





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

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

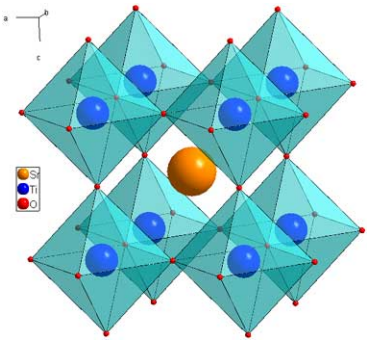
Agenda

New materials for solar light conversion into hydrogen and oxygen.

1) Computational method: DFT and screening approach;

GPAW!

2) Water splitting applications:
   a) Cubic perovskites:
      One-photon WS
      Two-photon WS
      Transparent protective shield
   b) Lower symmetry perovskites
   c) Pourbaix diagrams for corrosion analysis



MATERIALS PROJECT
A Materials Genome Approach

3) Bandgap calculations for energy applications.

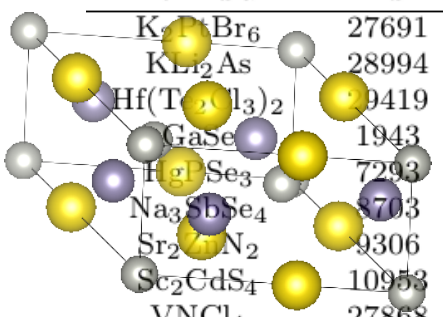
Materials Project Database

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

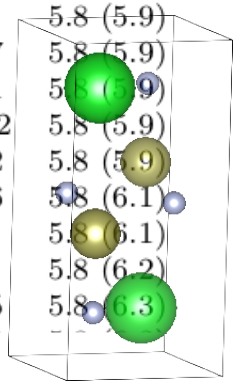
(in collaboration with: A. Jain and K. Persson, LBL; G. Ceder, MIT).

MATERIALS PROJECT

A Materials Genome Approach



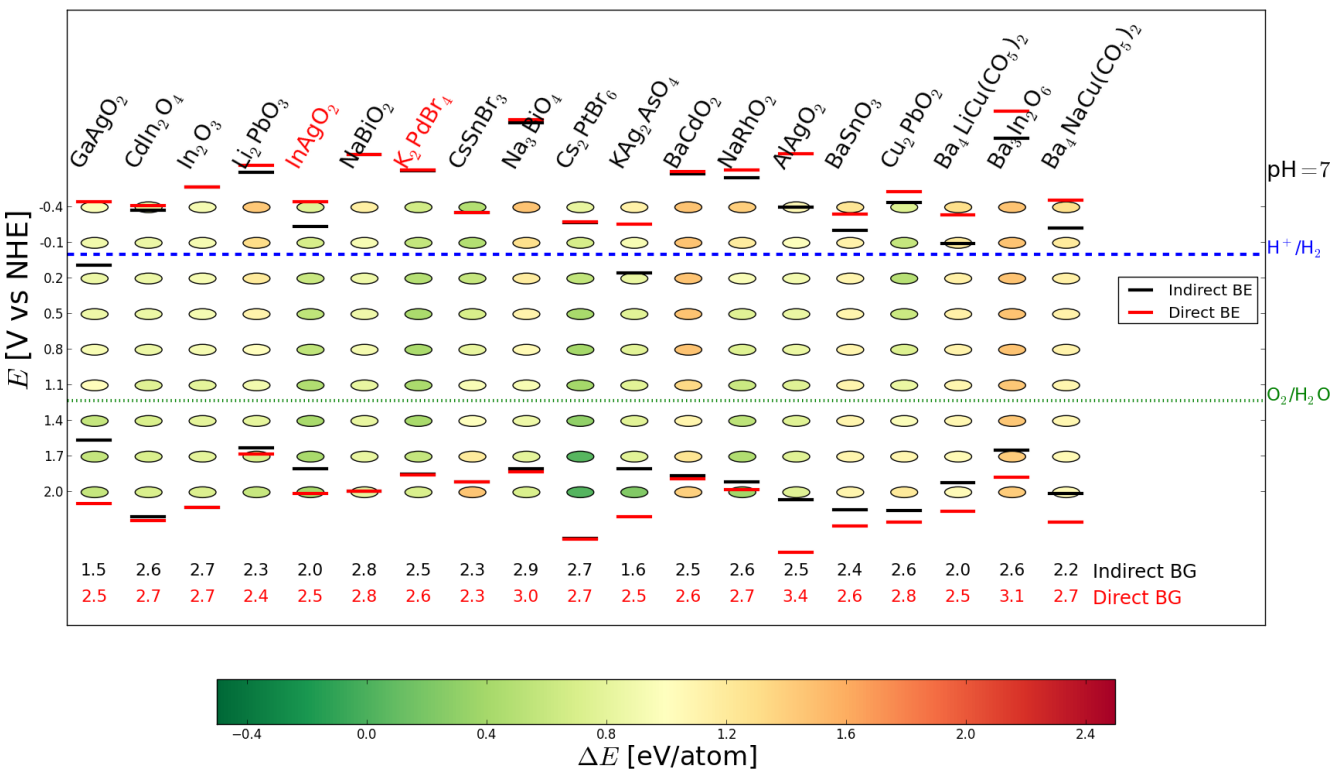
Formula	Id	Gap	Formula	Id	Gap	Formula	Id	Gap
K_2PbBr_6	27691	2.2 (2.2)	$KInP_2S_7$	22583	3.7 (3.7)	Li_2ZnGeO_4	8184	5.8 (5.8)
KLi_2As	28994	2.2 (2.2)	$NbAlCl_8$	28358	3.7 (3.7)	$BaPbF_6$	19799	5.8 (5.8)
$Hf(TeCl_3)_2$	29419	2.2 (2.2)	Rb_2CdO_2	28364	3.7 (3.7)	K_2NaAlH_6	24412	5.8 (5.8)
GaSe	1943	2.2 (2.2)	$K_2Zn_3O_4$	504936	3.7 (3.7)	AlI_3	30930	5.8 (5.8)
HgI_2Se_3	7293	2.2 (2.2)	Ba_2SnS_4	541832	3.7 (3.7)	KNaS	504938	5.8 (5.8)
Na_3SbSe_4	8703	2.2 (2.2)	$Cd(GaS_2)_2$	4452	3.7 (3.7)	$RbTaO_3$	3033	5.8 (5.8)
Sr_2ZnN_2	9306	2.2 (2.2)	$AlAgS_2$	5782	3.7 (3.7)	$BaMoO_4$	19276	5.8 (5.8)
Sc_2CdS_4	10953	2.2 (2.2)	$SrPSe_3$	7198	3.7 (3.7)	$RbIn(MoO_4)_2$	504506	5.8 (5.8)
$VNCl_4$	27868	2.2 (2.2)	$CsYCdSe_3$	11116	3.7 (3.7)	ScBrO	546279	5.8 (5.8)
$BaHgS_2$	28007	2.2 (2.2)	K_2NaRhF_6	14039	3.7 (3.7)	TlF	720	5.8 (5.9)
$Sr_5Mo_2N_7$	31231	2.2 (2.2)	Sr_3ScRhO_6	18247	3.7 (3.7)	PbBrCl	22997	5.8 (5.9)
KPt_2S_3	510130	2.2 (2.2)	$KAlTe_2$	18347	3.7 (3.7)	$Ba(IO_3)_2$	30991	5.8 (5.9)
WS_2	224	2.2 (2.3)	PCl_5	23228	3.7 (3.7)	Pb_2CO_4	505702	5.8 (5.9)
$NaTlO_2$	3056	2.2 (2.3)	$NClO_6$	27774	3.7 (3.7)	$TiTl_2F_6$	10402	5.8 (5.9)
Sr_3GaN_3	7191	2.2 (2.3)	$CsPS_3$	504838	3.7 (3.7)	$ZnCN_2$	29826	5.8 (6.1)
Ca_2ZnN_2	8818	2.2 (2.3)	$Ba_4Li(SbO_4)_3$	7971	3.7 (3.8)	$Ca(AsO_3)_2$	4555	5.8 (6.1)
K_2VAgS_4	8900	2.2 (2.3)	$BaPSe_3$	11008	3.7 (3.8)	LiN_3	2659	5.8 (6.2)
$NaSe_2$	15514	2.2 (2.3)	LaI_3	27979	3.7 (3.8)	BaH_2	23715	5.8 (6.3)



Applications: **water splitting**; photovoltaics; ...

Known Materials for One-photon WS

Descriptors:
- Stability against corrosion in water (using Pourbaix diagrams);
- Bandgap;
- Band edge positions.

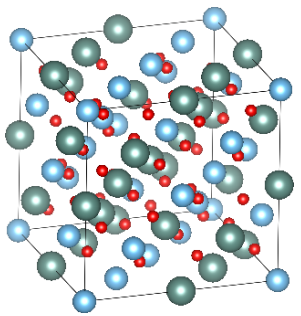


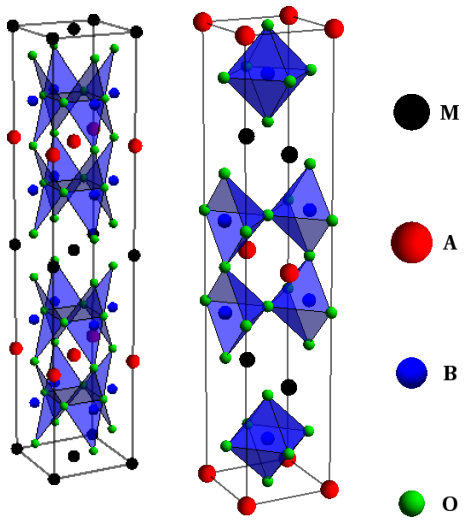
20 known materials for one-photon water splitting.

Few of them are already known in the community: In_2O_3, $BaSnO_3$, $CsSnBr_3$, ...

What's Next?

Screen for new structures-cell: more complex layered perovskites (Dion-Jacobson phase), new stoichiometries (pyrochlore), ...

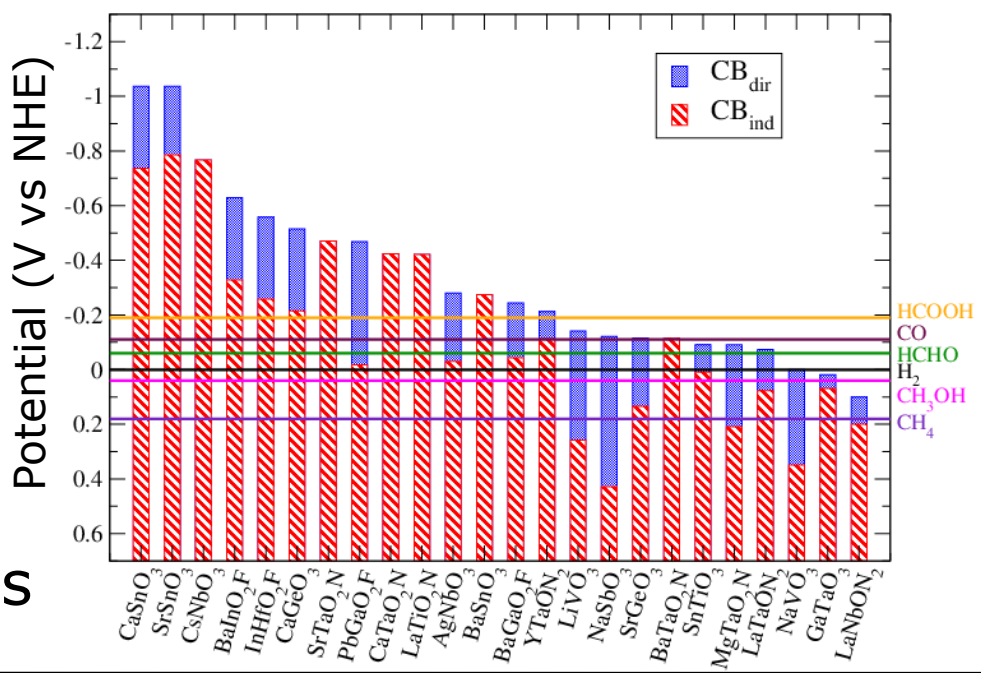




Calculate the bandgaps of known structures.

Look at new application:
- Fuel production using photoelectrocatalysis
- Photovoltaics

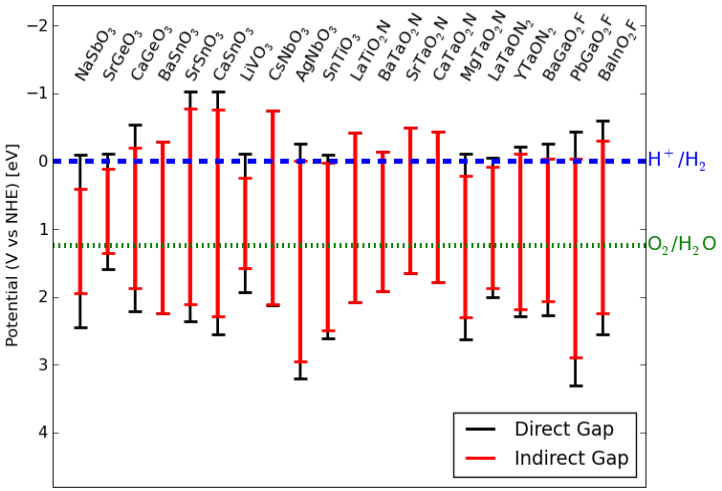
?? Corrosion, band edges positions



Conclusions

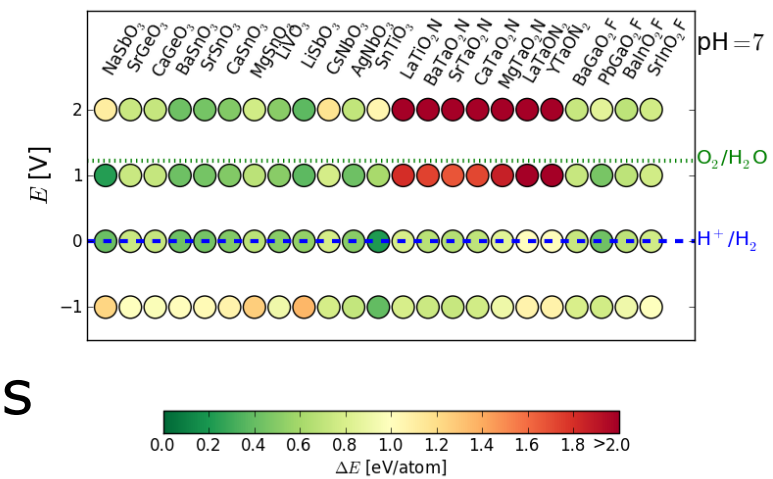
Handful materials identified for one- and two-photon water splitting:

- Cubic perovskite
- Double and layered perovskite
- Known materials from the Materials Project database



Use of simple statistic to reduce the simulations to perform

Pourbaix diagrams to evaluate the stability in water



The bandgaps of 2200 known materials have been calculated (energy related applications)

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LBL
Anubhav Jain
Kristin Persson

CINF/DTU
Ib Chorkendorff
Soren Dahl (now at Topsoe A/S)
Brian Seger
Peter Vesborg
Fabio Dionigi

Stanford University
Tom Jaramillo

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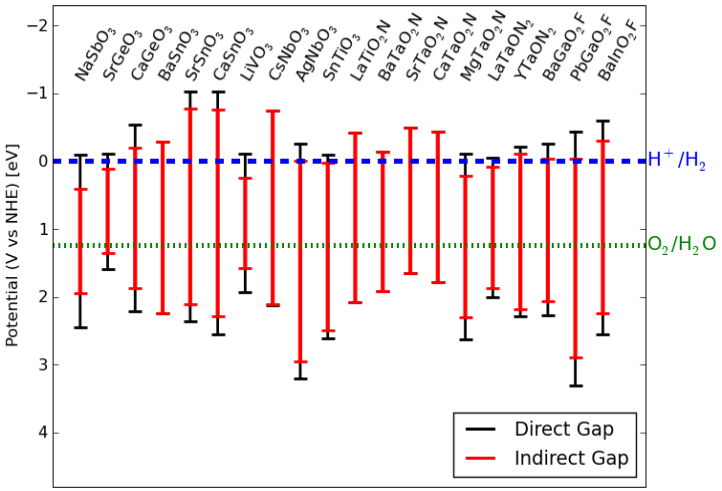

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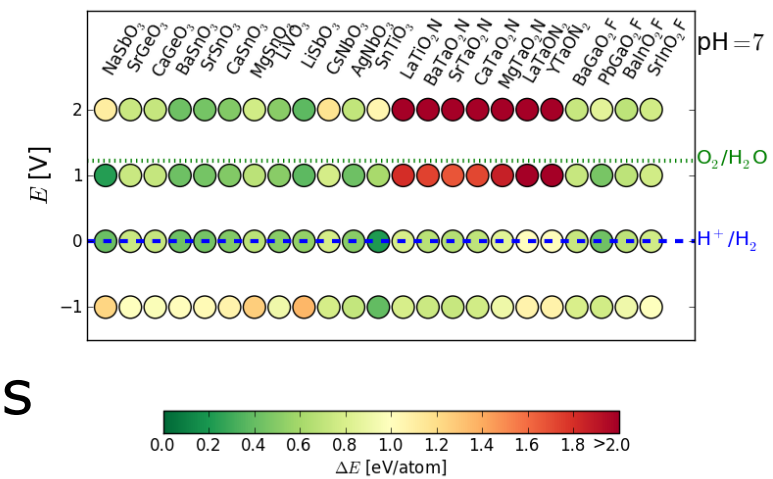

The bandgaps of 2200 known materials have been calculated (energy related applications)