Atomic-scale design of light-absorbing materials (or can computing compete with chemical intuition?)

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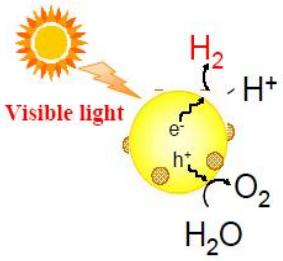
CASE Catalysis for Sustainable Energy

Overview

- Intro about water splitting
- Methodology (DFT and friends)
  - Material stabilities vs standard states and beyond
  - Pourbaix diagrams
  - Bandgaps and light absorption
- One-photon water splitting
- Tandem cells
- Water protection layers
- Materials
  - Perovskites
    - Oxides, oxynitrides, oxysulfides, oxyfluorides, OFN
    - Double perovskites
    - Layered perovskites (Ruddlesden-Popper)
    - Organic halide perovskites
  - Inorganic crystal structure database (ICSD)
- Outlook

Light absorption and water splitting

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



Complicated process:

- Light absorption
- Electron-hole motion
- Induce reactions

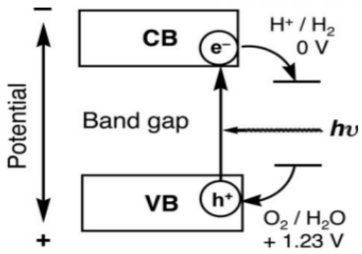
Examples: TiO_2, GaN:ZnO, $ZnGeN_2$:ZnO

(Fujishima and Honda, Nature 1972)

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

Materials for water splitting

- Chemical/structural stability
- Band gap of 1.5-3 eV (overpotentials, losses)
- Band edge positions straddle the water redox potentials
- Good electron/hole mobilities
- Good catalytic properties
- Low cost, non-toxicity



Principle of water splitting using semiconductor photocatalysts.

Materials for water splitting

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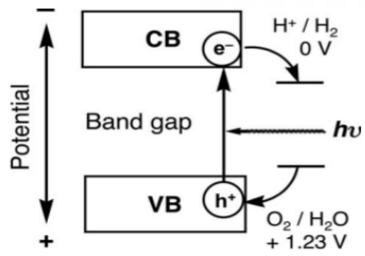
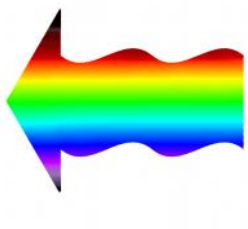




Principle of water splitting using semiconductor photocatalysts.

Methodology – density functional theory + friends

GPAW – projector augmented wave method in real space

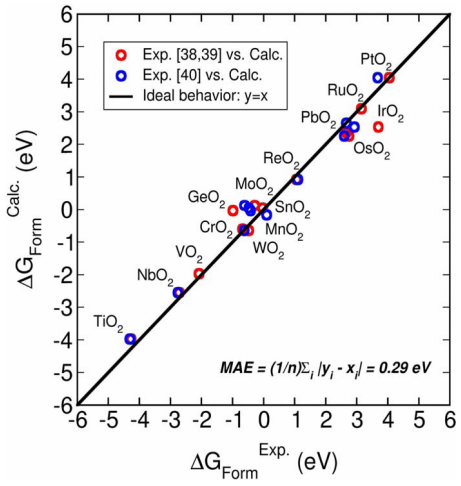
J. Enkovaara *et al.* J. Phys.:Cond. Mat. **22** (2010) ← **Review article**

https://wiki.fysik.dtu.dk/gpaw/ ← **Free download, GPL**

- High accuracy: Wave functions expanded on real space grids or plane waves
- High efficiency: Wave functions expanded in atomic-like orbitals (LCAO)
- Efficient parallelization (good scalability up to > 32.000 CPUs)
- Xc-functionals: LDA, GGAs, meta-GGA, LDA+U, EXX, vdWDF, GLLB, BEEF
- Time-dependent DFT (including “Bootstrap”)
- Many-body perturbation theory (GW and Bethe-Salpeter equation)
- Phonons and electron-phonon coupling
- Quantum electron transport
- Atomic Simulation Environment (ASE) python scripting interface

Predicting stability of oxides

- Oxides highly relevant because of high stability (towards oxidation!)
- DFT-RPBE calculated formation energy for rutile dioxides.
- Similar results obtained for perovskite structures.

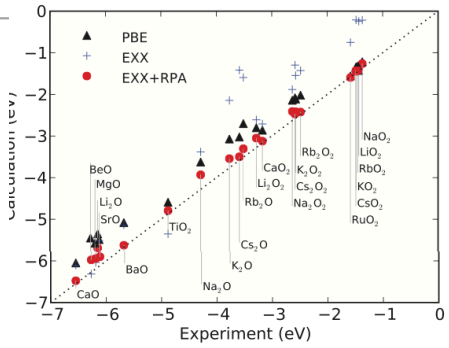


J. I. Martínez *et al.* , Phys. Rev B 2009

Predicting stability of oxides (II)

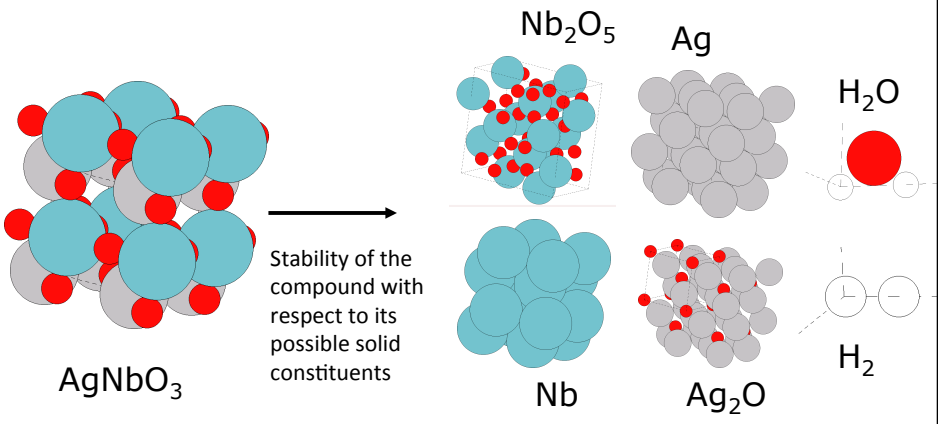
	PBE	EXX	EXX + RPA@PBE
Li_2O	−5.35	−5.72	−5.69
Li_2O_2	−2.80	−2.61	−3.05
LiO_2	−1.42	−0.24	−1.38
Na_2O	−3.62	−3.38	−3.93
Na_2O_2	−2.14	−1.88	−2.41
NaO_2	−1.22	−0.22	−1.26
K_2O	−3.07	−2.14	−3.54
K_2O_2	−2.11	−1.55	−2.42
KO_2	−1.34	−0.21	−1.45
Rb_2O	−2.70	−1.59	−3.30
Rb_2O_2	−2.02	−1.43	−2.42
RbO_2	−1.31	0.12	−1.43
Cs_2O	−3.02	−1.42	−3.50
Cs_2O_2	−2.08	−1.30	−2.47
CsO_2	−1.36	0.15	−1.43
BeO	−5.45	−6.31	−5.89
MgO	−5.57	−6.04	−5.94
CaO	−6.05	−6.10	−6.48
CaO_2	−2.86	−2.71	−3.12
SrO	−5.49	−5.51	−5.90
BaO	−5.08	−5.14	−5.62
TiO_2	−4.59	−5.35	−4.79
RuO_2	−1.56	−0.75	−1.59
MAE	0.44	0.96	0.15
MAE-s	0.21		0.10

Shifted O reference



Yan, Hummelshøj, and Nørskov, PRB **87**, 075207 (2013)

Stability vs other solid phases



Stability vs other solid phases

Example: Stability of perovskite ABO_3

Pool of reference systems:

- ❑ Single metal bulk: A(s) and B(s)
- ❑ Single metal oxides: A_xO_y(s) (and later nitrides, sulfides, …)
- ❑ Bimetallic oxides $A_xB_yO_z$(s) — Obtained from ICSD
  - Composition and structure available experimentally
  - Energy calculated

Oxygen is taken from water (and hydrogen molecule)

Formation energy:

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

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

→ Solved by linear programming.

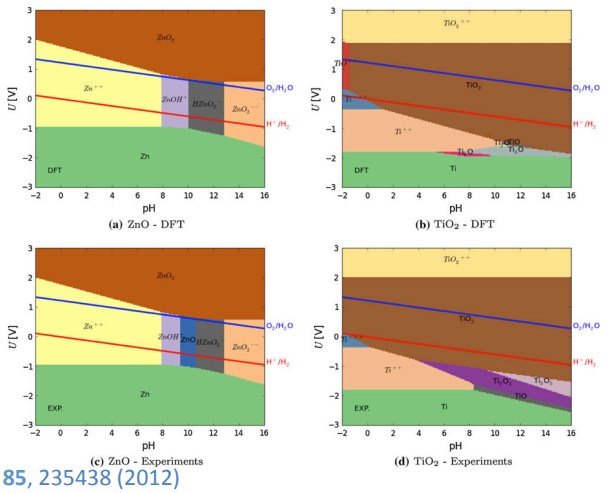
Stability vs dissolution in water – Pourbaix diagrams

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

- Using the Nernst equation

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

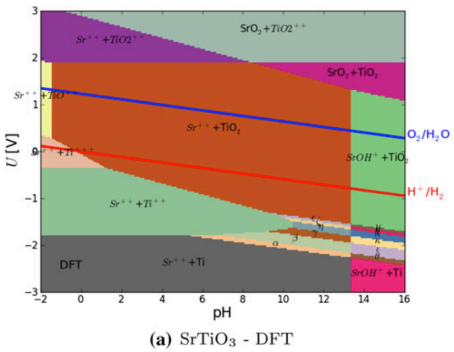
- Free energies of dissolved species taken from expt.

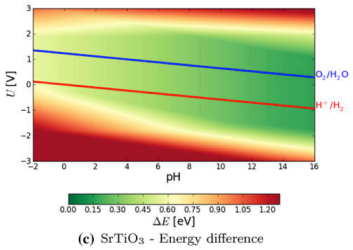


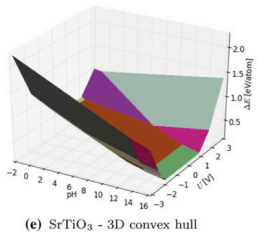
K. A. Persson et al. Phys Rev B **85**, 235438 (2012)
I. E. Castelli, K. S. Thygesen, K. W. Jacobsen, Top Catal **57**, 265 (2013)

Stability vs dissolution in water – Pourbaix diagrams (II)

$SrTiO_2$







The cubic perovskite phase never most stable.
Known to exist experimentally -> metastability, kinetics

I. E. Castelli, K. S. Thygesen, K. W. Jacobsen, Top Catal **57**, 265 (2013)

The bandgap in density functional theory

- DFT is aimed at calculating ground state total energies
- Kohn-Sham states describe the density of a non-interacting electron gas
- But the quasiparticle gap can be determined as a total energy difference for different number of particles
  - Works well with LDA/GGA for molecules
  - Does not work with LDA/GGA for semiconductors

Calculated ionization potentials for small molecules

Molecule	Expt.[a]	PBE-eig	PBE0-eig	HF-eig	GW	G_0W_0(HF)	G_0W_0(PBE)-QP	MP2[a]	PBE-tot
LiH	7.90	4.34	5.81	8.14	8.0[b]	8.2[b]	8.0	8.20	8.02
Li_2	5.11	2.96	3.62	4.62	4.6	4.7	4.4	4.91	5.09
LiF	11.30	6.00	8.62	13.26	11.7	11.2	12.0	12.64	11.87
Na_2	4.89	2.81	3.38	4.16	4.1	4.3	4.7	4.48	4.97
					34 molecules				
P_2	10.62	7.09	8.21	9.65	9.2	9.8	9.0	10.09	10.37
SiH_4	12.30	8.50	10.13	12.93	12.3	12.6	12.4[c]	13.25	11.95
Si_2H_6	10.53	7.27	8.54	10.82	10.2	10.6	9.9	11.03	10.36
SiO	11.49	7.46	9.14	11.78	10.9	11.2	11.3	11.82	11.27
MAE		4.35	2.55	0.81	0.5	0.4	0.5	0.82	0.24

DFT Kohn-Sham spectrum

Many-body perturbation theory

DFT total energies

However, DFT-LDA/PBE total energies cannot be used for semiconductor bandgaps.

KS gap + derivative discontinuity!

(C. Rostgaard, K. W. Jacobsen, and K. S. Thygesen, PRB 2010)

Bandgap calculations with GLLB

The GLLB xc-functional (Gritsenko, van Leeuwen, van Lenthe and Baerends):

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

Derivative discontinuity

Screening + response

$$v_x(\mathbf{r}) = v_S(\mathbf{r}) + v_{resp}(\mathbf{r})$$

$$v_S(\mathbf{r}) = \frac{2\epsilon_x^{GGA}(\mathbf{r}; n)}{n(\mathbf{r})}$$

$$v_{resp}(\mathbf{r}) = \sum_{i}^{occ} K[n]\sqrt{\varepsilon_r - \varepsilon_i}\frac{|\psi_i(\mathbf{r})|^2}{n(\mathbf{r})}$$

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

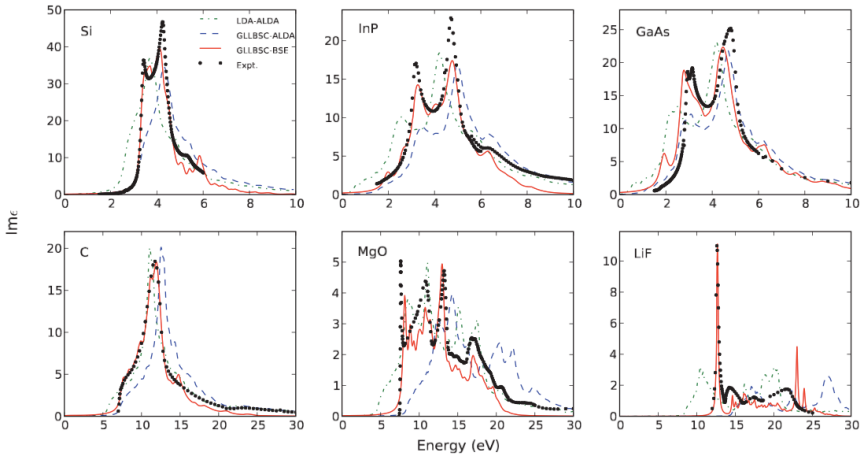
Material	E_g^{KS} (LDA)	E_g^{KS}	Δ_{xc}	E_g^{QP}	Exp.
C	4.09	4.14	1.27	5.41	5.48
Si	0.443	0.68	0.32	1.00	1.17
GaAs	0.36	0.79	0.25	1.04	1.63
AlAs	1.34	1.67	0.82	2.49	2.32
LiF	8.775	10.87	4.09	14.96	14.2
Ar	8.18	10.28	4.69	14.97	14.2

GLLB-SC: Screening exchange-correlation from PBEsol

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

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

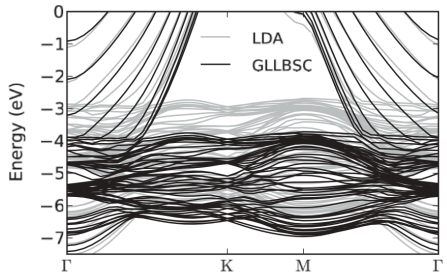
Optical absorption spectra with GLLB-SC

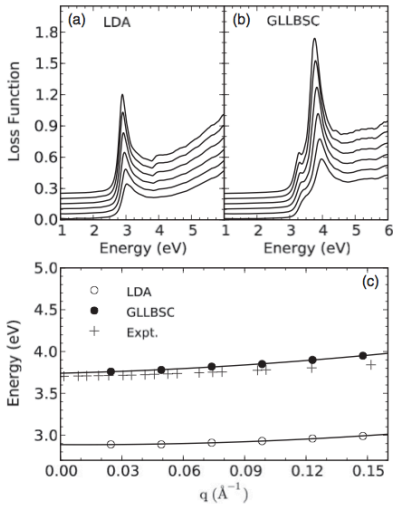


Derivative discontinuity used in spectrum for TDDFT, but not for W in BSE.

J. Yan, K. W. Jacobsen, and K. S. Thygesen, PRB **86**, 45208 (2012)

Ag surface plasmon with GLLB-SC





J. Yan, K. W. Jacobsen, and K. S. Thygesen, PRB **84**, 235430 (2011)

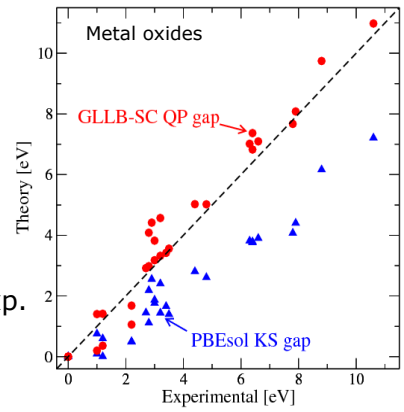
Predicting bandgaps of oxides with GLLB-SC

The GLLB-SC (solid-correlation) xc-functional:

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

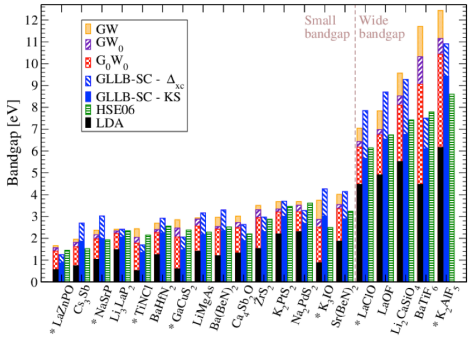
Derivative discontinuity

- ❑ Bandgaps within ~0.5 eV of exp.
- ❑ Minimal computational cost
- ❑ Neglect of electron-hole interaction



Bandgaps for a selection of systems from Inorganic Crystal Structure Database

20 “randomly” selected systems



xc \ xc$_{ref}$	LDA	GLLB-SC	HSE06	G_0W_0	GW_0	GW
LDA	—	1.64 (−1.64)	1.21 (−1.21)	1.14 (−1.14)	1.37 (−1.37)	1.67 (−1.67)
GLLB-SC	1.64 (1.64)	—	0.61 (0.43)	0.53 (0.50)	0.50 (0.27)	0.41 (0.03)
HSE06	1.21 (1.21)	0.61 (−0.43)	—	0.19 (0.07)	0.23 (−0.16)	0.46 (−0.46)
G_0W_0	1.14 (1.14)	0.53 (−0.50)	0.19 (−0.07)	—	0.24 (−0.24)	0.53 (−0.53)
GW_0	1.37 (1.37)	0.50 (−0.27)	0.23 (0.16)	0.24 (0.24)	—	0.30 (−0.30)
GW	1.67 (1.67)	0.41 (−0.03)	0.46 (0.46)	0.53 (0.53)	0.30 (0.30)	—

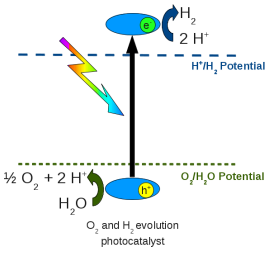
Small bandgap systems

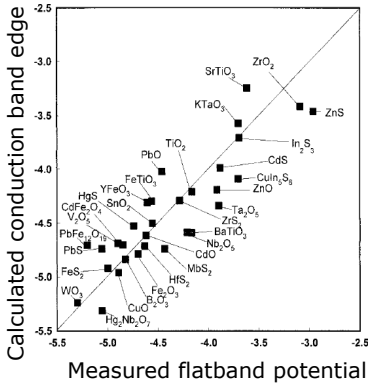
(Collaboration with Materials Project)

Castelli, Hüser, Pandey, Li, Seger, Thygesen, Jain, Persson, Ceder, Jacobsen, in preparation.

Band edge positions

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





X = 1/2(A+I_1) = Absolute electronegativity (Mulliken scale)

A=Affinity level

I_1=Ionization level

E_{gap}= Band gap

E_0 = Difference between NHE and vacuum ~ -4.5 eV

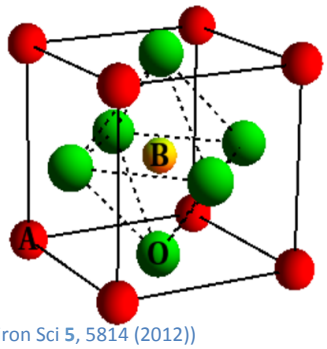
M. A. Butler and D. S. Ginley, Journal of The Electrochemical Society (1978)

Y Xu and MAA Schoonen, American Mineralogist (2000)

Screening of oxides in the cubic perovskite structure

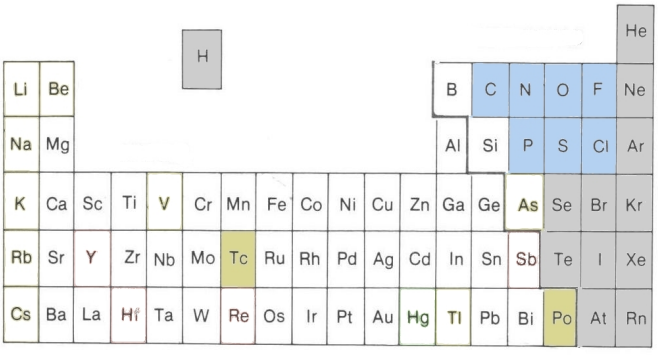
- Very common (50 % of all perovskites are quasi-cubic)
- High stability
- Variety of properties: ferroelectricity, magnetism, superconductivity and (photo)catalytic activity
- Easy and computationally cheap to represent

- Oxygen (3 atoms)
- Metals (2 atoms)
  - A-ion (12 coordinated cation)
  - B-ion (6 coordinated cation)



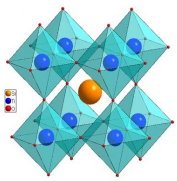
(Castelli, Olsen, Datta, Landis, Dahl, Thygesen, Jacobsen, Energy Environ Sci **5**, 5814 (2012))

Metal elements in alloy oxides



Excluded elements:

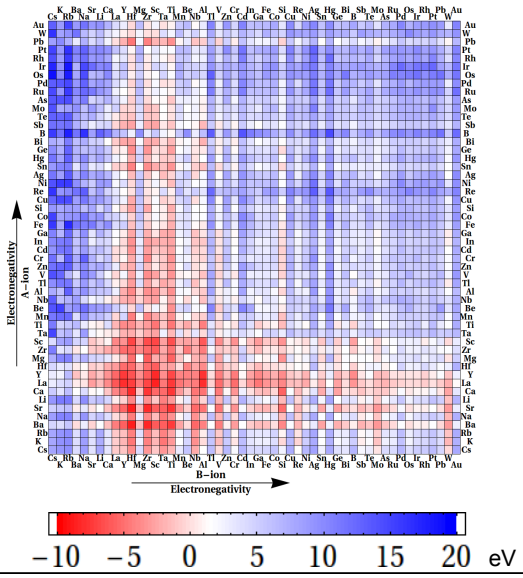
- Non Metals;
- Radioactive, toxic.



- ❑ 52 different metallic elements
- ❑ Different anions (O, N, S, F, Cl, ...)
- ❑ Different periodic structures (**perovskite**, rutile, spinel)

(Castelli, Olsen, Datta, Landis, Dahl, Thygesen, Jacobsen, Energy Environ Sci **5**, 5814 (2012))

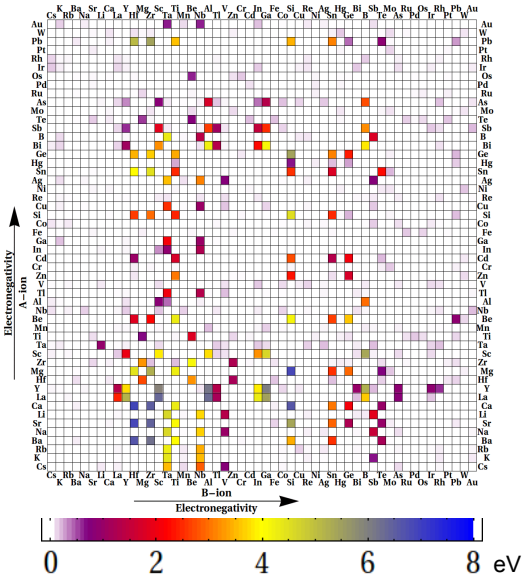
Perovskites: Heat of formation



Stable materials:

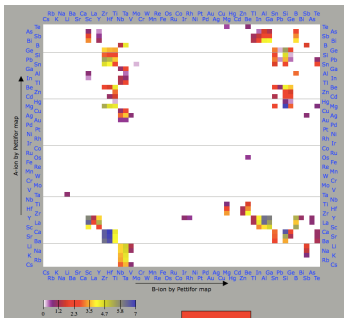
- Low electronegativity
- Sum of oxidation numbers = 6
- Geometric tolerance factor ~1

Perovskites: Band gaps

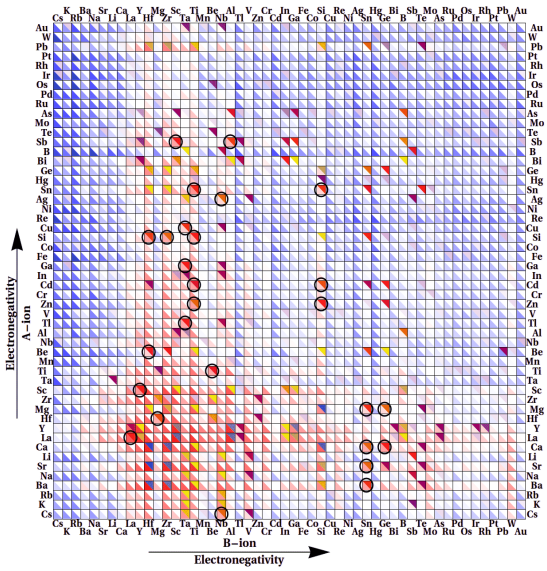


Most perovskites are metallic or low-gap semiconductors

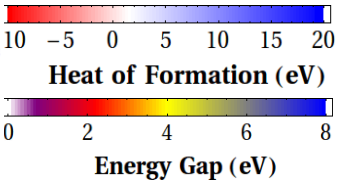
Using “Pettifor-stringing” of periodic table



Perovskites: ABO_3 candidates



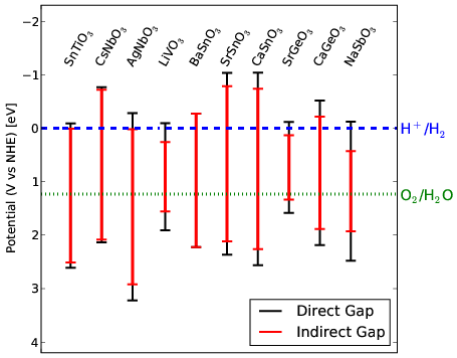
Stability:
std. formation energy < 0.2 eV;
Light absorption:
1.5 eV < bandgap < 3 eV.
-> **43 oxides**
Stability vs pool of reference systems
-> **13 oxides**
Bandgap straddling redox levels
-> **10 oxides**



Perovskites: ABO_3 WS candidates (II)

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 (with low efficiency)

$BaSnO_3$: defect induced recombination.

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

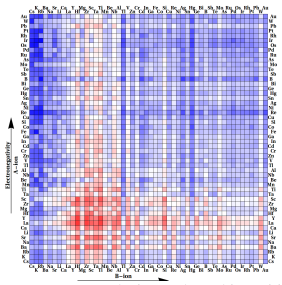
None of the others are known.

Attempts to investigate $LiVO_3$ at CINF/DTU

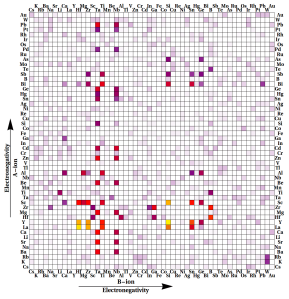
(Castelli, Olsen, Datta, Landis, Dahl, Thygesen, Jacobsen, Energy Environ Sci **5**, 5814 (2012))

Perovskite oxynitrides

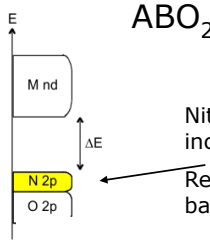
Stability



Bandgap

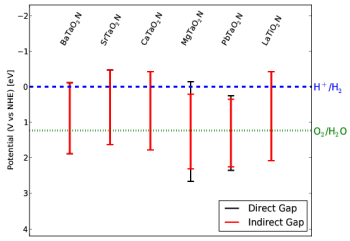


ABO_2N



Nitrogen 2p states increase VB edge

Reduction of bandgap



5 materials for water splitting

Known: $BaTaO_2N$, $SrTaO_2N$, $CaTaO_2N$, $LaTiO_2N$

Unknown: $MgTaO_2N$

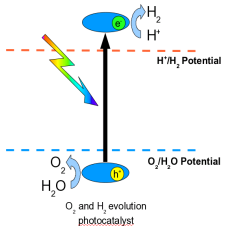
Oxides, oxynitrides, oxysulfides, oxyfluorides, oxyfluornitrides

Materials candidates:

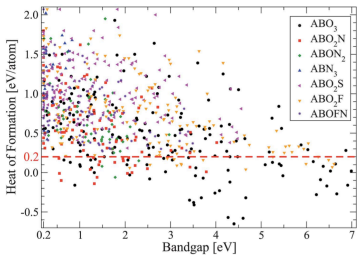
- ABO_3 :10
- ABO_2N :5
- $ABON_2$:2 — $LaTaON_2$ (known), $YTaON_2$ (unknown)
- ABN_3 :0
- ABO_2S :0
- ABO_2F :3
- ABOFN :0

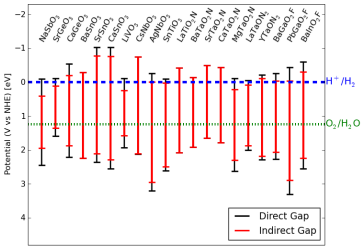
~19000 materials

One-photon water splitting



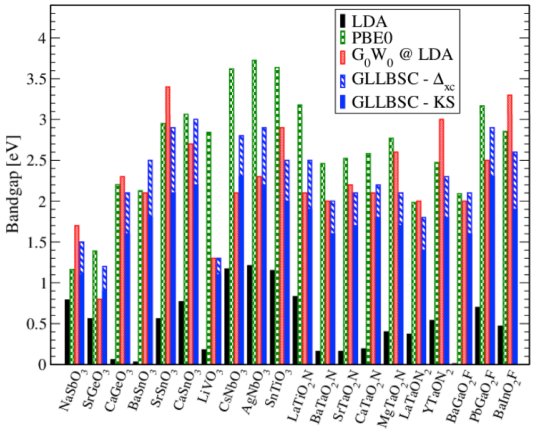
20 candidate materials





(Castelli, Landis, Thygesen, Dahl, Chorkendorff, Jaramillo, Jacobsen, Energy Environ Sci **5**, 9034 (2012))

Further analysis of candidate materials: bandgap calculations

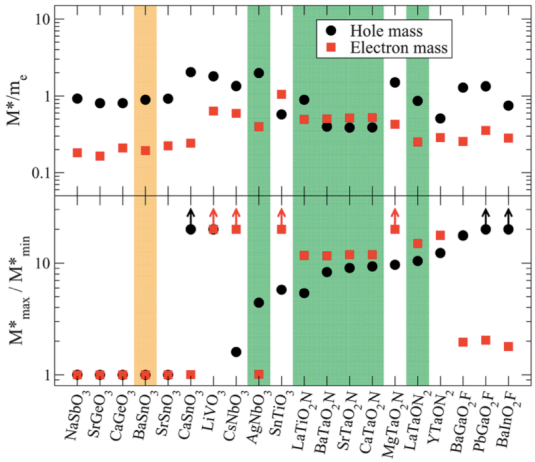


G_0W_0 on top of LDA using plasmon pole approximation

GLLBSC – G_0W_0 mean absolute deviation 0.3 eV

Castelli, Garcia-Lastra, Hüser, Thygesen, Jacobsen, New Journal of Physics **15**, 105026 (2013)

Further analysis of candidate materials: mobilities – e/h band-masses



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

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

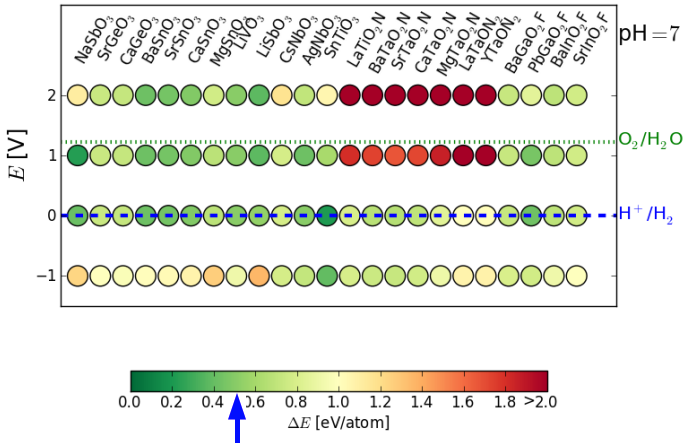
Orange system: $BaSnO_3$ known not to work (probably defect-assisted recombination)

Systems observed to work so far seems fairly isotropic

Further analysis of candidate materials: stability in water

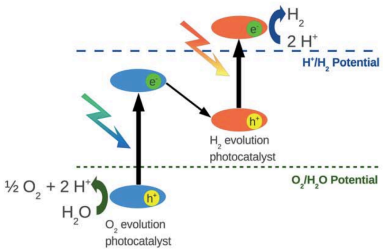
Oxides and oxyfluorides have a region where they are stable (with 0.5 eV threshold).

Oxynitrides are less stable, especially at high potential.



New stability threshold to include some metastability/kinetics and perhaps inaccuracies in the calculations.

Tandem cell principle



Two semiconductors – two photons

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

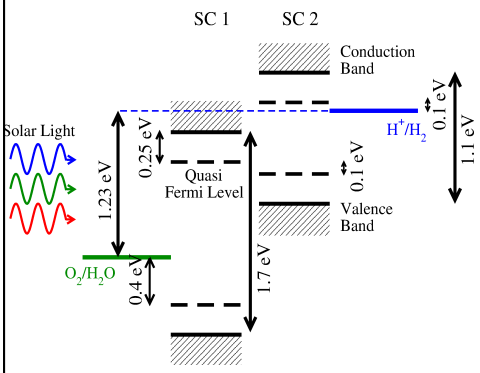
Requirements:

- structural/chemical stability;
- two visible light harvests (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.

H_2 photocatalyst: Si

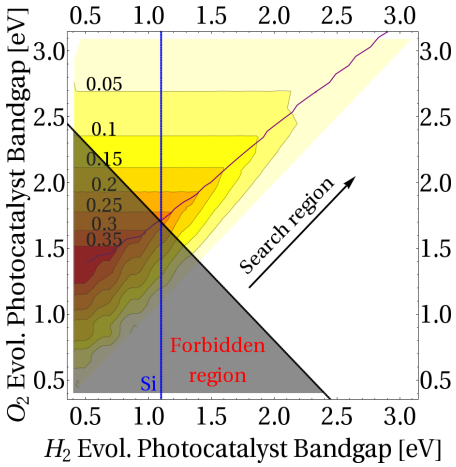
O_2 photocatalyst: screening

Tandem cell efficiency



Max efficiency ~28% (vs 7% for one-photon)

Solar-to-hydrogen energy conversion efficiency

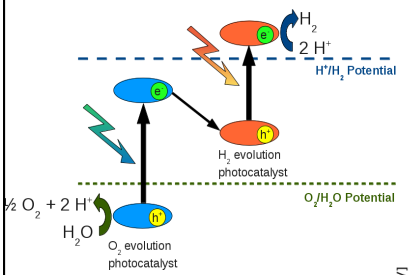


(J. R. Bolton et al., *Nature* 1985.)

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

(I.E. Castelli, D.D. Landis, K.S. Thygesen, S. Dahl, I. Chorkendorff, T.F. Jaramillo, and K.W. Jacobsen, *Energy & Environmental Science*, doi: 10.1039/c2ee22341d)

Tandem cell water splitting: Screening results

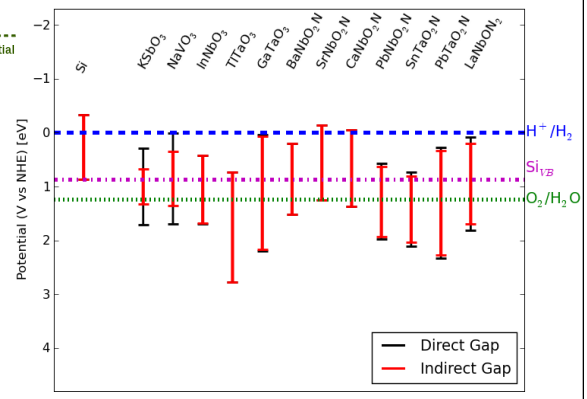


Screening parameters	Two-photon WS
Chemical/structural stability (ΔE)	$\Delta E \leq 0.2$ eV
Bandgap (E_{gap})	$1.3 \leq E_{gap} \leq 3$ eV
Band edges (VB_{edge}, CB_{edge})	$VB_{edge}^{anode} > 1.23$ eV $CB_{edge}^{cathode} < 0$ eV $VB_{edge}^{cathode} > CB_{edge}^{anode}$

12 candidates

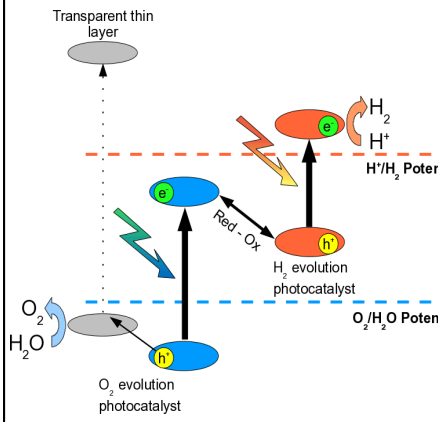
+ 20 from overall WS

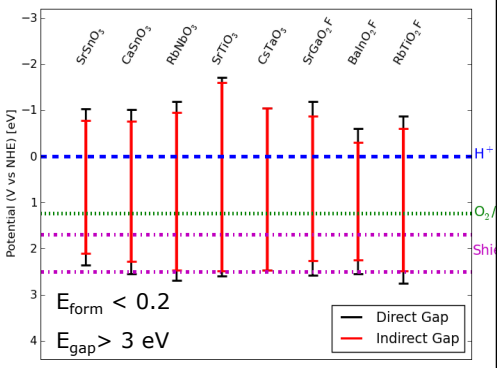
$BaNbO_2N$, $SrNbO_2N$, $CaNbO_2N$, and $LaNbON_2$ are known as water splitters.



(Castelli, Olsen, Datta, Landis, Dahl, Thygesen, Jacobsen, Energy Environ Sci **5**, 5814 (2012))

Transparent protecting shield – photoanode

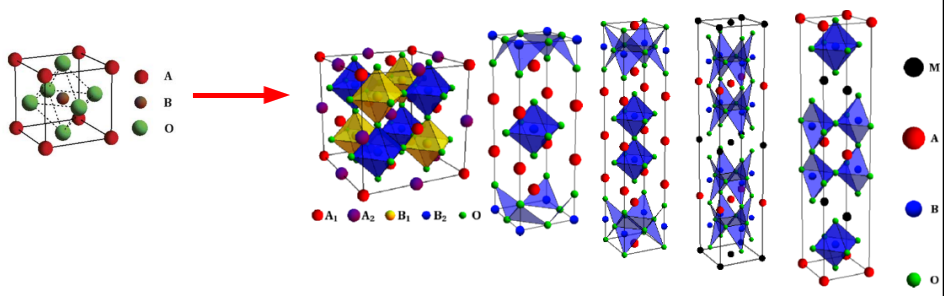




$SrTiO_3$ known for water splitting in UV light.
$SrSnO_3$ and $CaSnO_3$ known in the orthorhombic phase.

Example: TiO_2 can be used to protect MoS_2 for hydrogen evolution (Seger et al., JACS, **135**, 1057 (2013).

Towards low-symmetry perovskites



Cubic (5 atom/cell) | Double (20) | Ruddlesden-Popper (14-24) | Dion-Jacobson (22-44)

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

Use three chemical-based rules derived from cubic perovskites:

1) Even-odd rule: Even number of electrons in unit cell to have a bandgap
2) Valence rule: Sum of possible valences should add up to zero.
3) Radius rule: Radius(A) > Radius(B)

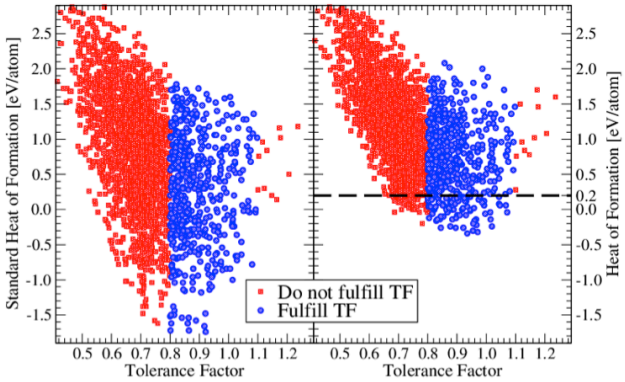
Castelli and Jacobsen, Modelling Simul. Mater. Sci. Eng. **22**, 055007 (2014)

"Traditional" rules not good enough
Example: tolerance factor

Tolerance factor:

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$

Traditional rule:
$0.8 < t < 1.1$

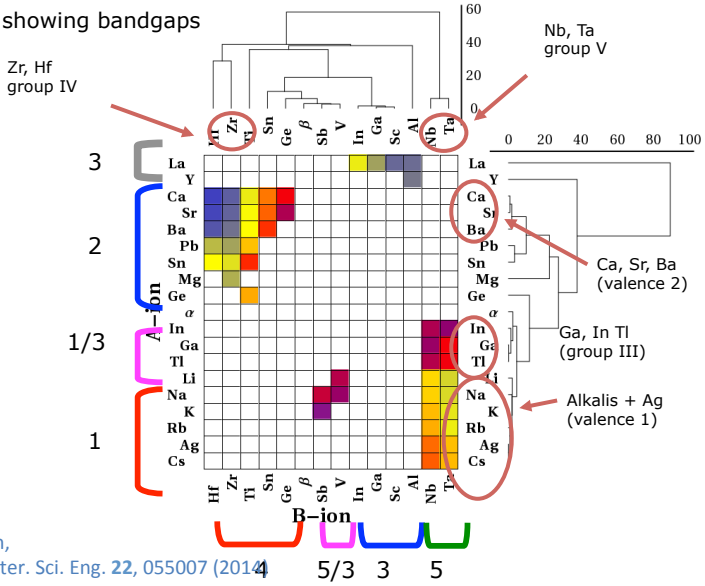


Example: $AgNbO_3$ has t outside [0.8, 1.1]

Castelli and Jacobsen, Modelling Simul. Mater. Sci. Eng. **22**, 055007 (2014)

Cluster analysis based on bandgap for ABO_3: Valence rules!

46 stable ABO_3 showing bandgaps



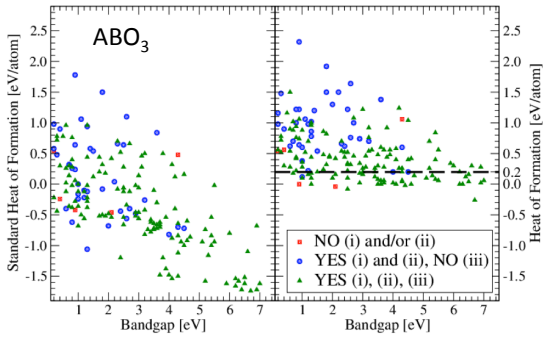
Clusters follow the valences of the elements.

Castelli and Jacobsen, Modelling Simul. Mater. Sci. Eng. **22**, 055007 (2014)

Fulfillment of chemical rules

Use three chemical-based rules derived from cubic perovskites:

1) Even-odd rule: Even number of electrons in unit cell to have a bandgap
2) Valence rule: Sum of possible valences should add up to zero.
3) Radius rule: Radius(A) > Radius(B)



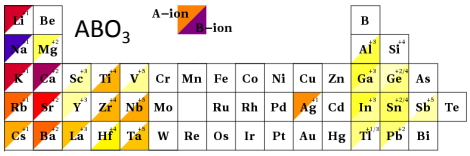
Simulations to run:
- No rules: 2704;
- With i and ii: 778;
- With all rules: 547.

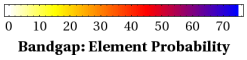
Only three combinations are interesting but do not fulfill the rules

Rules transferable to oxynitrides -> only 16% satisfy rules

Castelli and Jacobsen, Modelling Simul. Mater. Sci. Eng. **22**, 055007 (2014)

Propensity and chemical rules





Probability for an element to generate a stable semiconductor for the ABO_3 stoichiometry

Probabilities and rules transferable to oxynitrides:

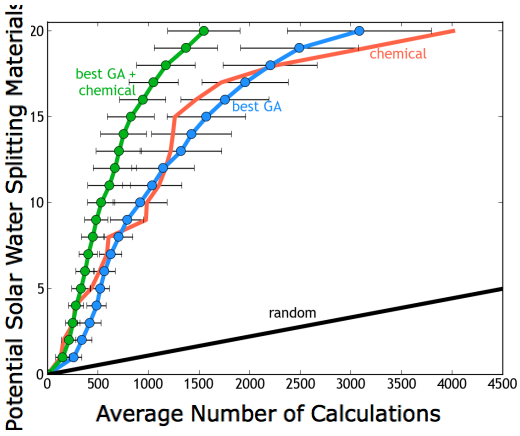
$$\tilde{P}(\mathrm{ABO_2N}) = P_A(\mathrm{A})P_B(\mathrm{B})P_{\mathrm{rules}}(\mathrm{ABO_2N})$$

A-ion	B-ion	Stable?	Gap [eV]
Ca	Ta	✓	2.2
Sr	Ta	✓	2.1
Ca	Nb	✓	1.4
Sr	Nb	✓	1.4
Ba	Ta	✓	2.0
Ba	Nb	✓	1.3
La	Zr	✓	3.4
La	Hf	✓	3.8
La	Ti	✓	2.5
Sn	Ta	✓	1.2
Sn	Nb	✓	0.5
Pb	Ta	✓	2.0
Pb	Nb	✓	1.3
Sr	Sb		0
Ca	Sb		0
Sr	V		0
Ca	V		0
In	Zr		0
Mg	Ta	✓	2.1
Mg	Nb		1.5
Ba	Sb		0
Ba	V		0

A-ion	B-ion	Stable?	Gap [eV]
(cont.)			
In	Hf		0
La	Sn		1.8
In	Ti		0
La	Ge		0
Y	Zr		3.3
Ge	Ta		1.8
Ge	Nb		1.1
Y	Hf		3.4
In	Sn		0
Y	Ti		2.4
Sn	Sb		0
Pb	Sb		0
Sn	V		0
Pb	V		0
In	Ge		0
Mg	Sb		0
Mg	V		0
Y	Sn		2.7
Y	Ge		1.3
Ge	Sb		0
Ge	V		0

Castelli and Jacobsen,
Modelling Simul. Mater. Sci. Eng. **22**, 055007 (2014)

Evolutionary algorithm

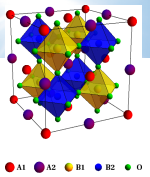


An evolutionary algorithm performs as good as a chemical-based search (rules i and ii).

Applying the chemical rules, the evolutionary algorithm shows a significant improvement.

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

Bandgap engineering: Double perovskites

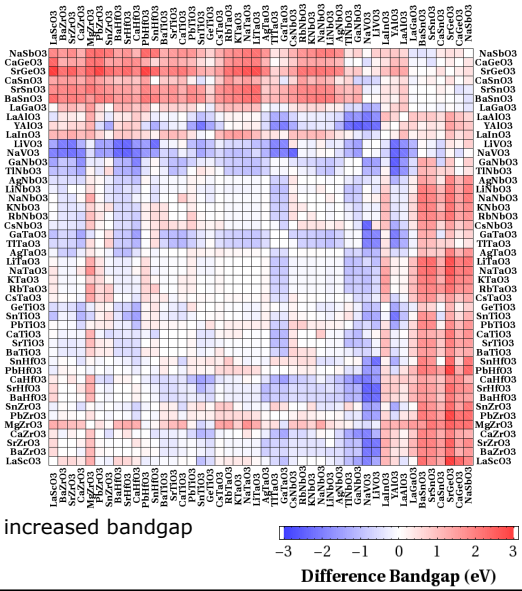


Difference between the double perovskite bandgap and the average gap coming from the two constituent cubic perovskites

New "design rules":

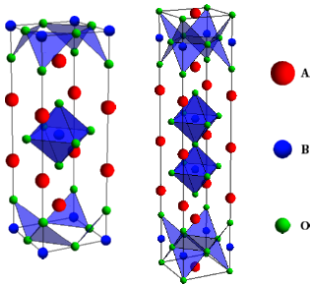
- Double perovskite has average of perovskite gaps
- But, for B1 p-metal and B2 d-metal gap is significantly increased

•B1-ion(d) - B2-ion(p) hybridization -> increased bandgap



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

Bandgap engineering: Layered perovskites (Ruddlesden-Popper)

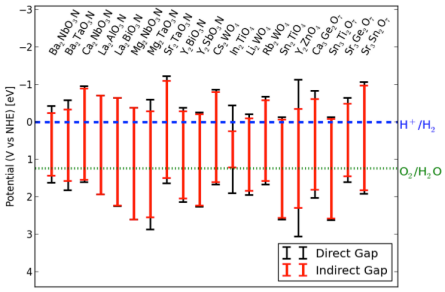


Bandgap decreases with the thickness of the octahedron layer when p-metals are in the B-ion position. Opposite for d-metals.

Criterion	One-photon WS	Two-photon WS
Stability (ΔE)	$0.2\,\mathrm{eV\,atom^{-1}}$	$0.2\,\mathrm{eV\,atoms^{-1}}$
Bandgap (E_{gap})	$1.7 \leqslant E_{gap} \leqslant 3$	$1.3 \leqslant E_{gap} \leqslant 3$
Band edges (VB_{edge}, CB_{edge})	$VB_{edge} > 1.6$	$VB_{edge}^{anode} > 1.6$
	$CB_{edge} < -0.1$	$CB_{edge}^{cathode} < -0.1$
		$CB_{edge}^{anode} < VB_{edge}^{cathode}$

I. E. Castelli, J. M. Garcia-Lastra, F. Huser, K. S. Thygesen, and K. W. Jacobsen, *New J. Phys.* **15**, 105026 (2013).

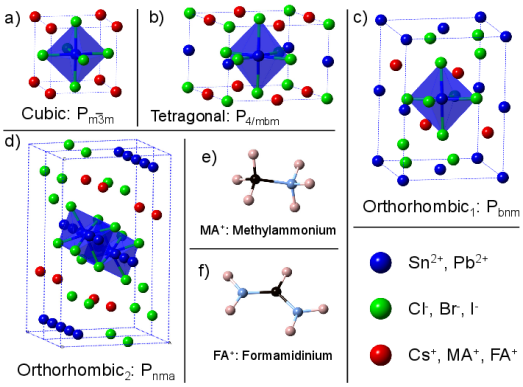
More candidates for water splitting:



Organic halide perovskites

CH_3NH_3PbI based solar cells show up to 15% power conversion efficiency

(Burschka et al. Nature **499**, 316 (2013))



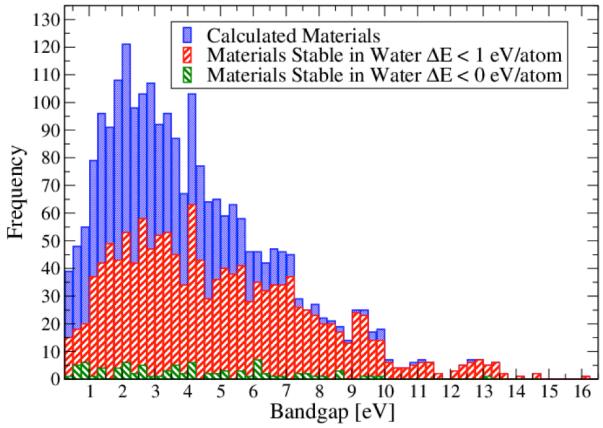
Properties:

- Direct bandgaps
- Large absorption coefficients
- High carrier mobilities

240 possible combinations

Screening for WS materials based on Inorganic Crystal Structure Database (ICSD)

Bandgaps of 2400 materials from ICSD

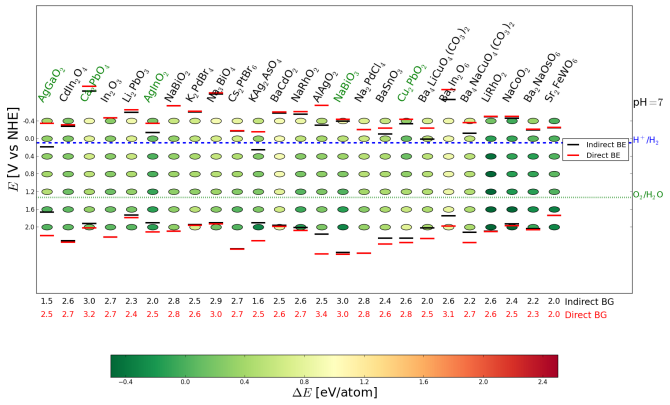


(Collaboration with Materials Project)

Castelli, Hüser, Pandey, Li, Seger, Thygesen, Jain, Persson, Ceder, Jacobsen, in preparation.

Screening for one-photon water splitting based on ICSD

Stability in water at -0.4<V<2.0
Bandgap: 1.7 eV < E_{gap} < 3.0 eV
Band edge positions:
CB_{edge} < -0.1 vs NHE
Vb_{edge} > 1.6 eV vs NHE



Some do not work: Ba_2NaOsO_6 Mott insulator, $BaSnO_3$ has a bandgap ~3.1-3.3 eV
Some are known in other contexts: Ca_2PbO_4, E_{gap}~1.8 eV steel primer
Interesting candidates noted in green.

(Collaboration with Materials Project)

(Castelli, Hüser, Pandey, Li, Seger, Thygesen, Jain, Persson, Ceder, Jacobsen, in preparation)

Computational Materials Repository

A system for storing/uploading, analyzing, retrieving, and sharing computational data.

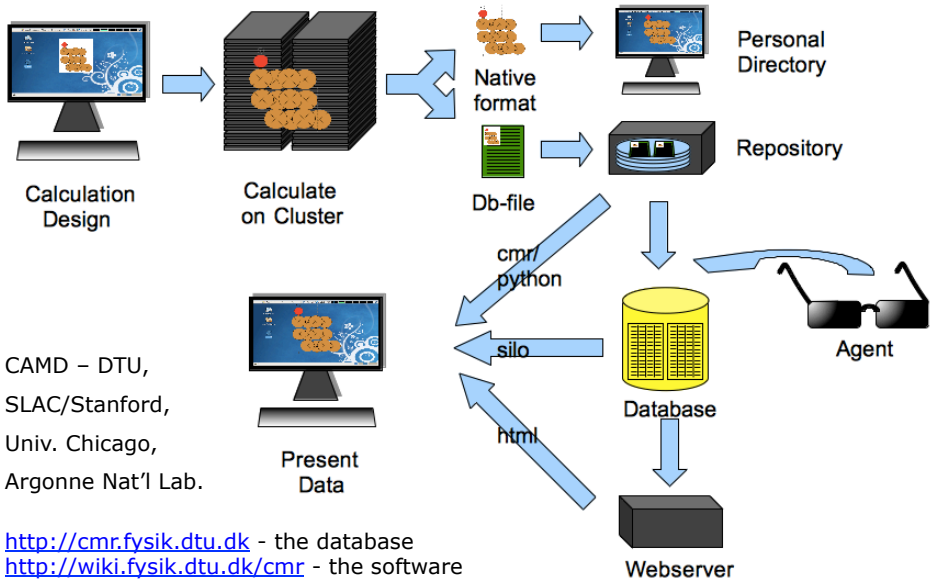
Some ideas:

- Many interfaces (sql, python, web, ”silo”)
- Agents – small pieces of code automatically performing calculations in the database
- Taxonomy/folksonomy

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

(Landis, Hummelshøj, Nestorov, Greeley, Dulak, Bligaard, Nørskov, Jacobsen, Comp. Sci. Eng. **14**, 51 (2012))

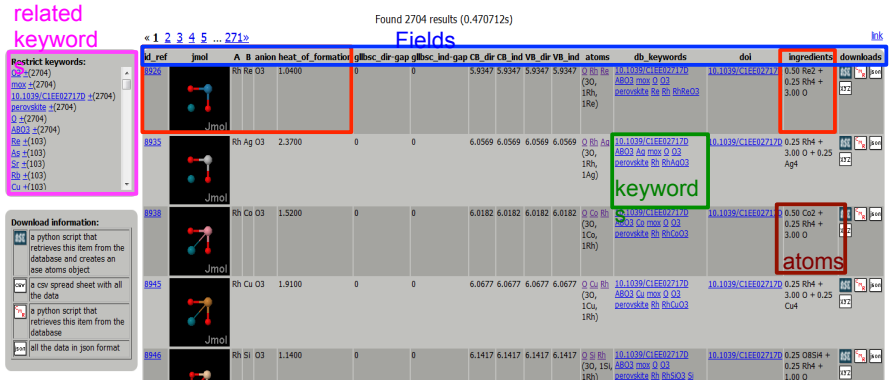
Computational Materials Repository



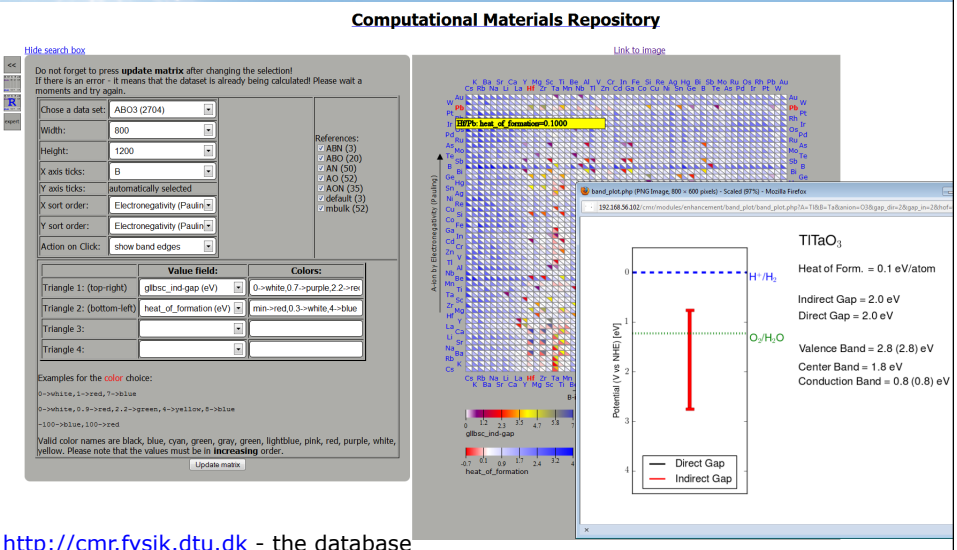
CAMD – DTU,
SLAC/Stanford,
Univ. Chicago,
Argonne Nat’l Lab.

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

Generic data view



Computational Materials Repository
Project-specific web-interface



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

http://wiki.fysik.dtu.dk/cmr - the software, Publication to appear in Comp. Sci. Eng.

Outlook

- Material screenings (stability and bandgap)
  - Learn trends and new chemical rules, info transfer
  - Build up useful (hopefully) materials databases
  - Find specific materials
- Challenges
  - Absorption spectra
    - Matrix elements
    - Excitonic effects
  - Mobilities (so far only band masses)
  - Defects
  - Surfaces/level alignments (so far empirical formula)
  - Nanostructuring
  - Catalysis (SC surface or co-catalysts?)

Acknowledgements

CAMD/DTU:
Ivano E. Castelli
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Falco Hüser
Mohnish Pandey
Hong Li
Kristian S. Thygesen

MIT:
Gebrand Ceder

LBL:
Anbhav Jain
Kristin Persson

CINF/DTU:
Brian Seger
Søren Dahl
Peter Vesborg
Ib Chorkendorff

Stanford:
Tom Jaramillo

CASE
Catalysis for Sustainable Energy

neec
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