ICTP Caribbean School on Materials for Clean Energy

30 May - 5 June 2019, Cartagena, Colombia

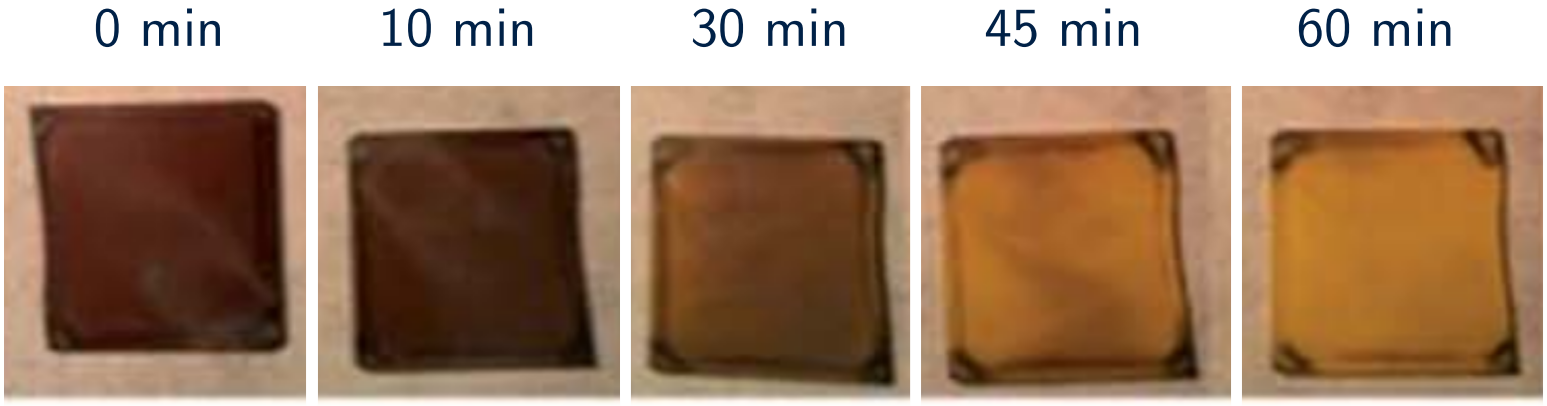
Perovskite Photovoltaics: Computational Design

Feliciano Giustino
Department of Materials, University of Oxford

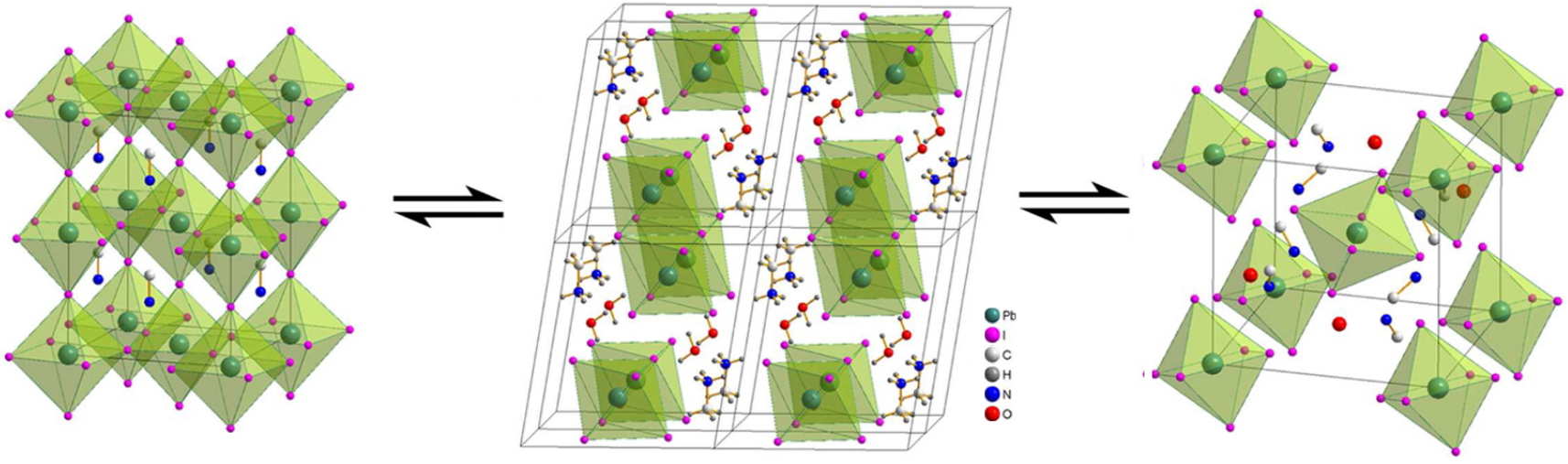
1 Understanding electron transport

2 Finding non-toxic alternatives to Pb

Stability of lead halide perovskites

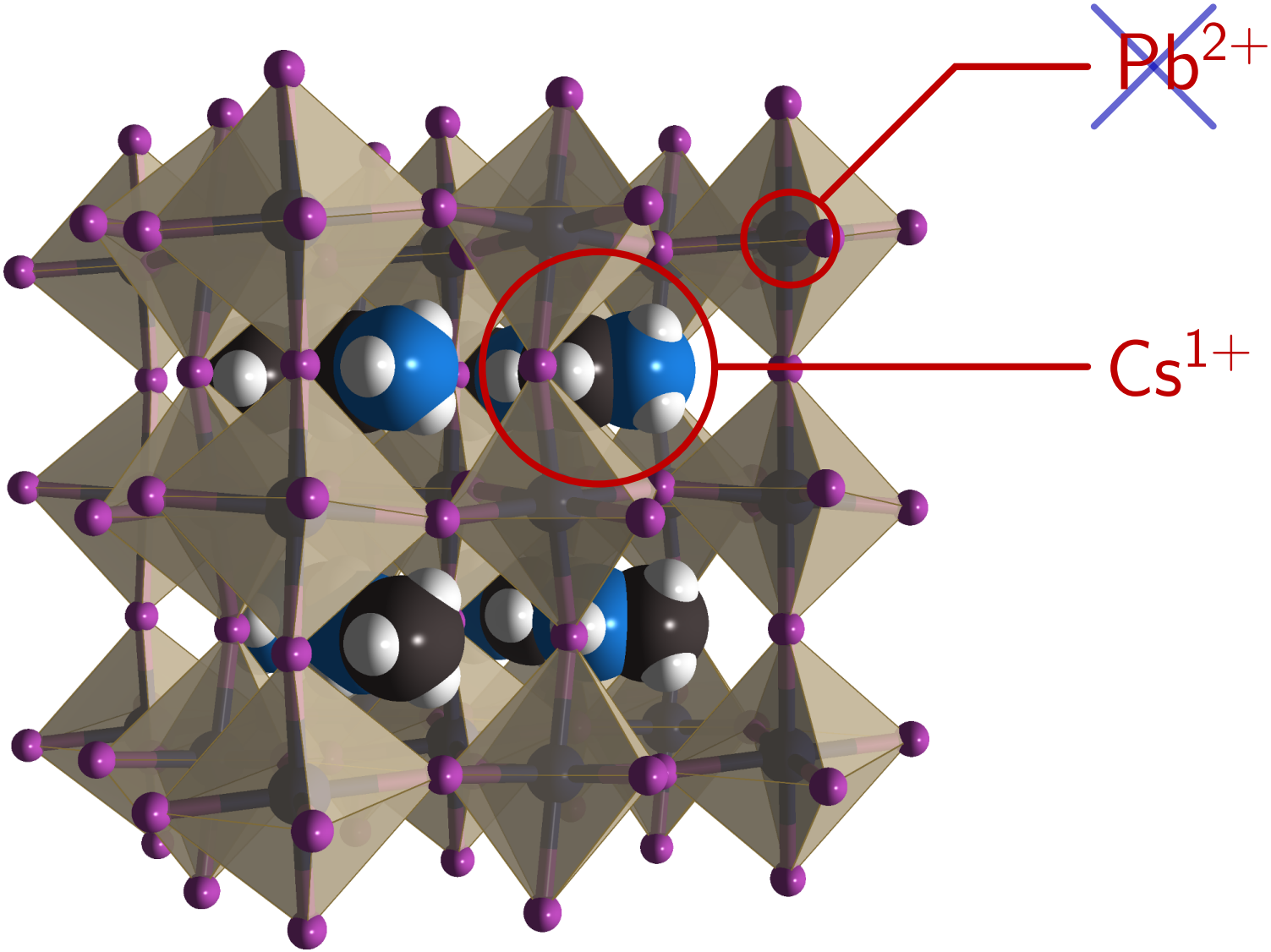


Leijtens et al., J. Mater. Chem. A 5, 11483 (2017)

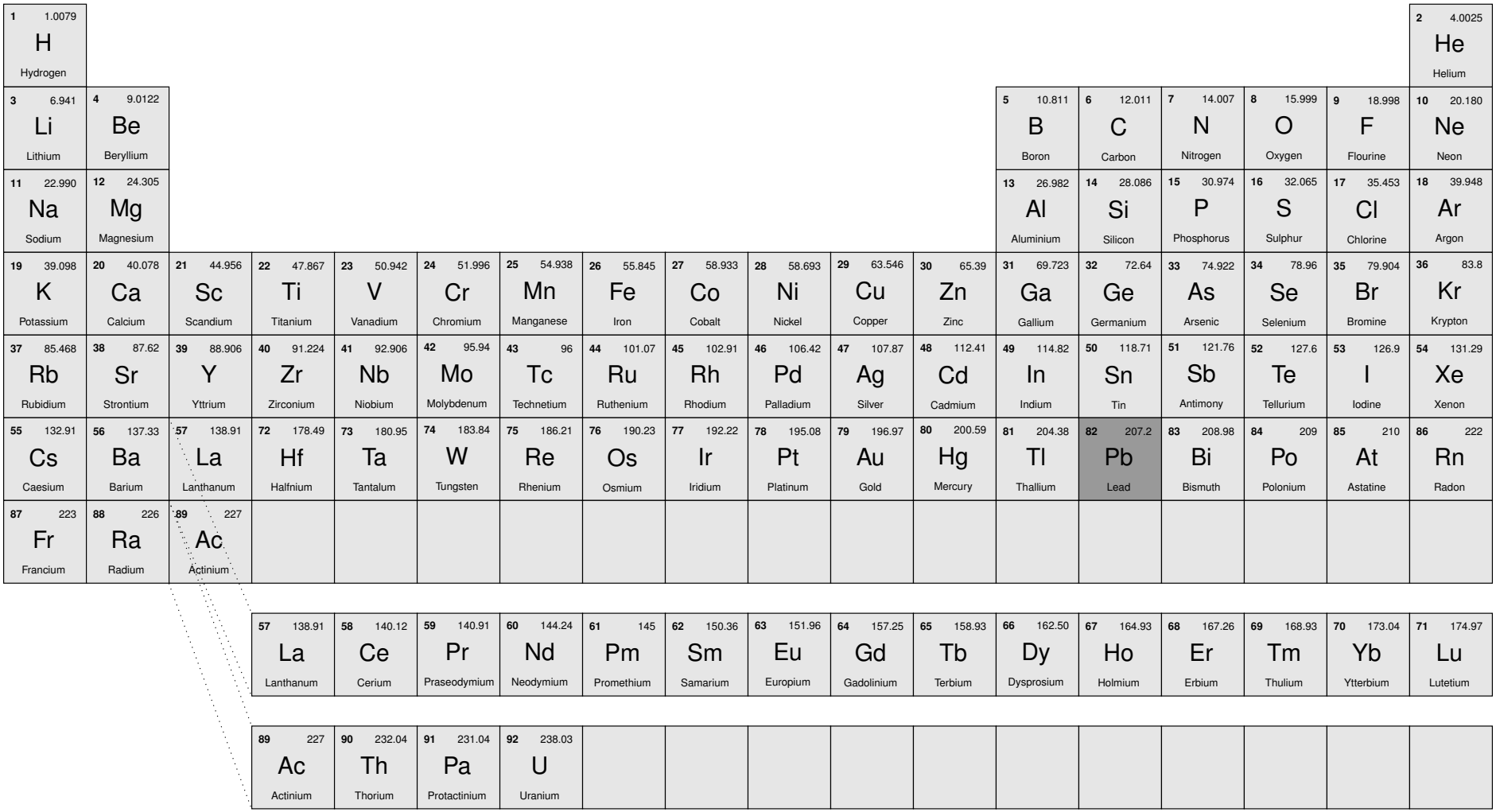


Leguy et al., Chem. Mater. 27, 3397 (2015)

Computational cation exchange

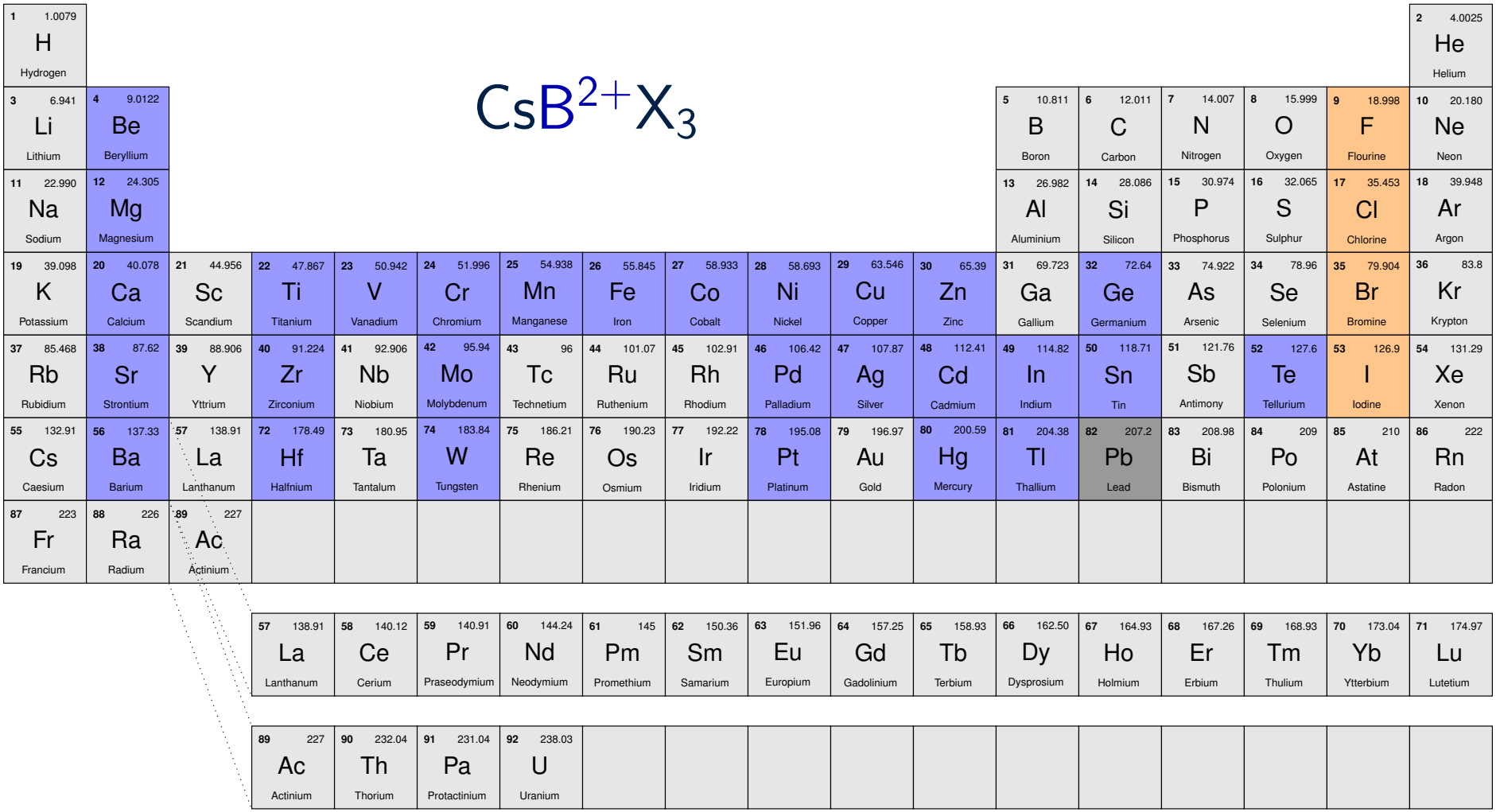


Homovalent Pb replacement



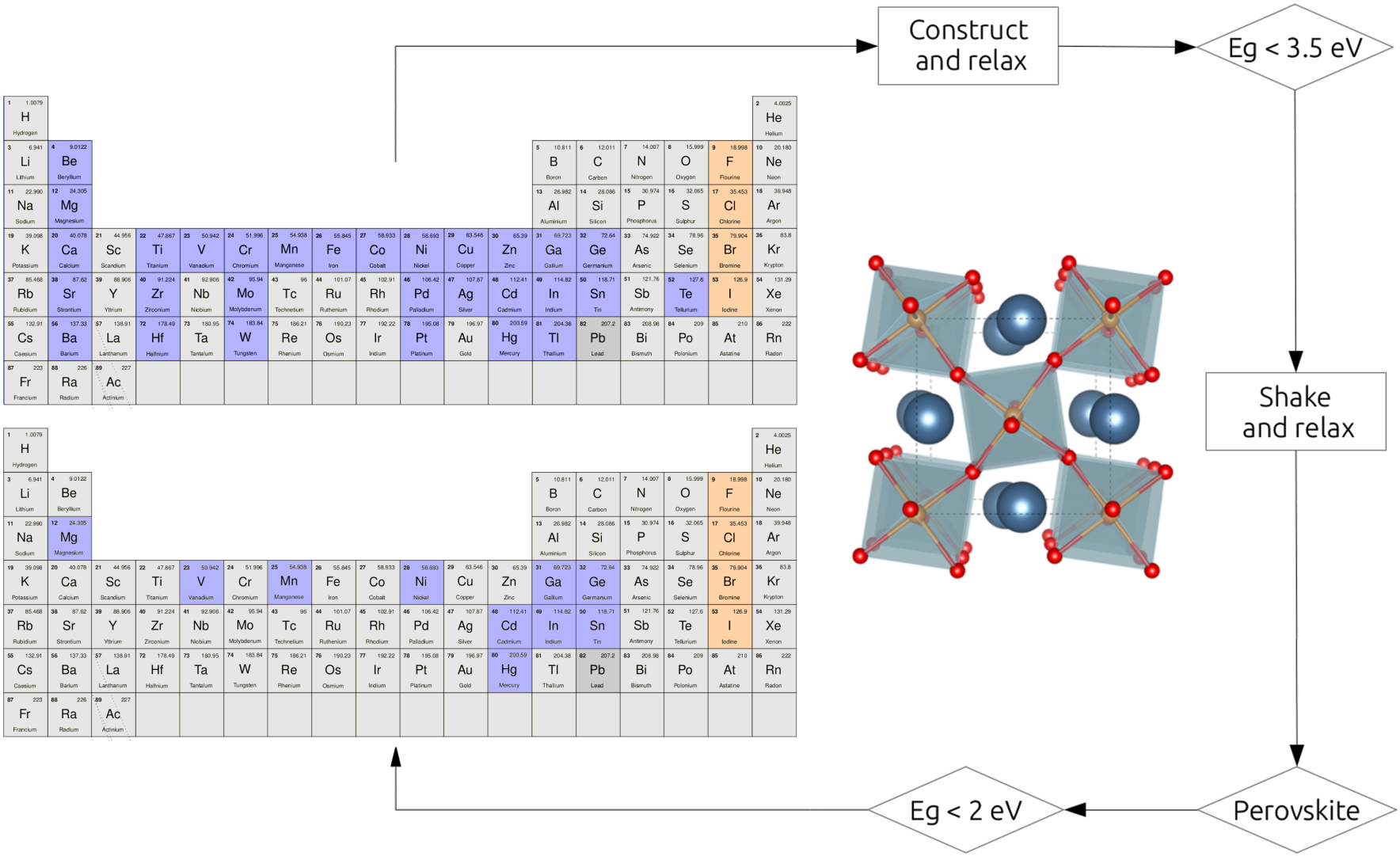
Filip & Giustino, J. Phys. Chem. C 120, 166 (2016)

Homovalent Pb replacement



Filip & Giustino, J. Phys. Chem. C 120, 166 (2016)

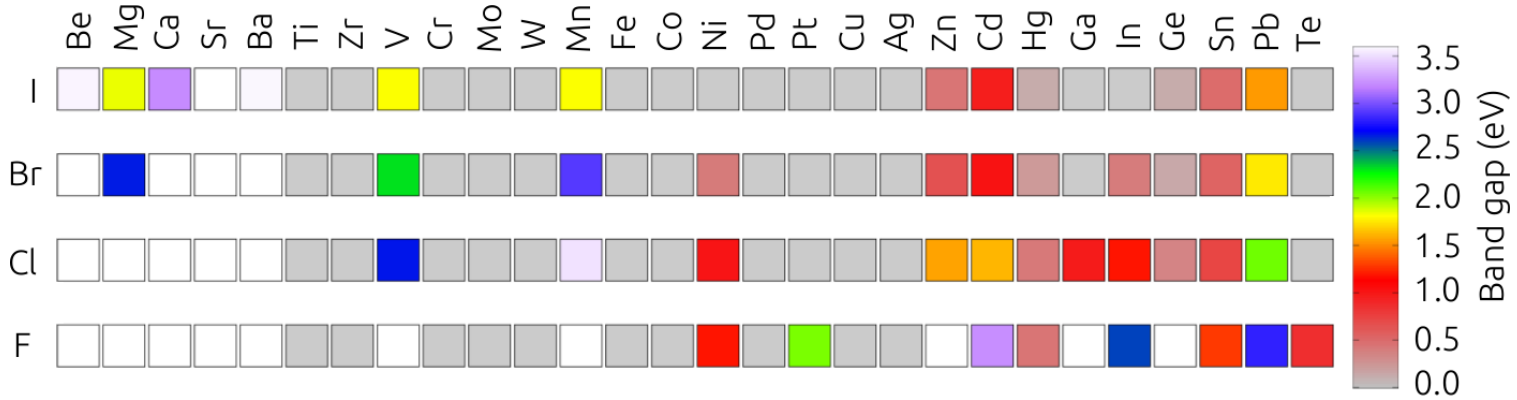
Screening by successive refinements



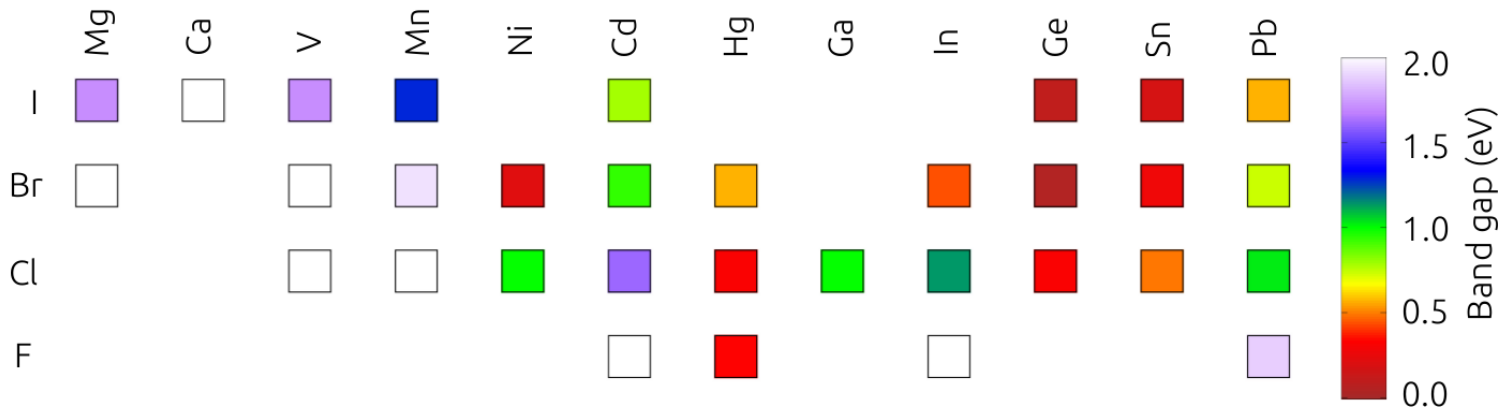
Filip & Giustino, J. Phys. Chem. C 120, 166 (2016)

Screening by successive refinements

w/o spin-orbit coupling



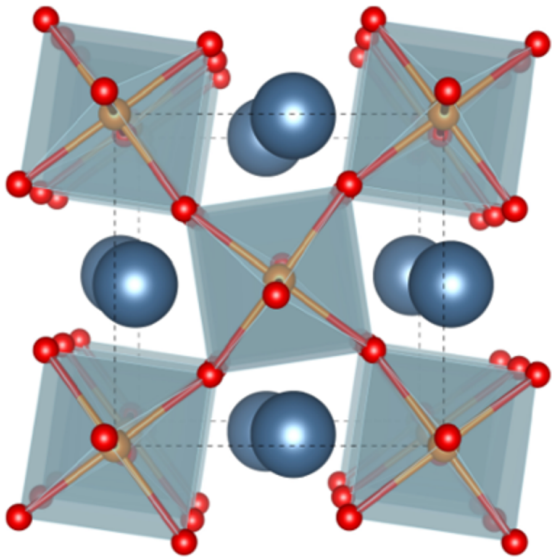
with spin-orbit coupling



Filip & Giustino, J. Phys. Chem. C 120, 166 (2016)

Screening by successive refinements

Example: Hyphothetical $CsMgI_3$ perovskite

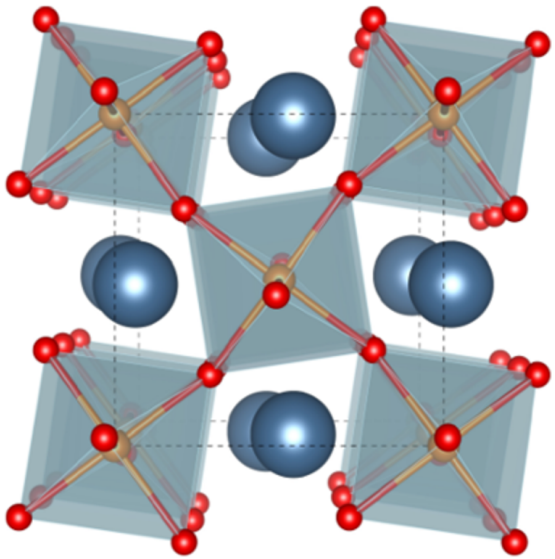


Our working hypothesis

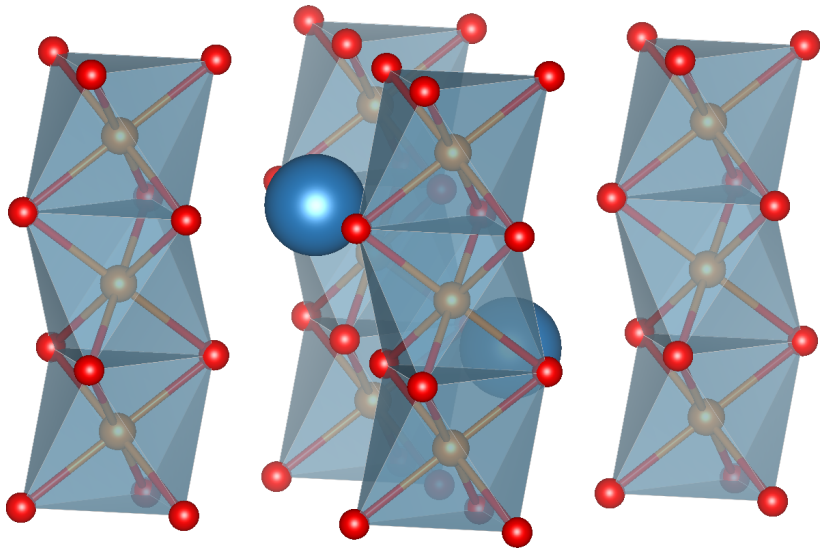
Filip & Giustino, J. Phys. Chem. C 120, 166 (2016)

Screening by successive refinements

Example: Hyphothetical $CsMgI_3$ perovskite



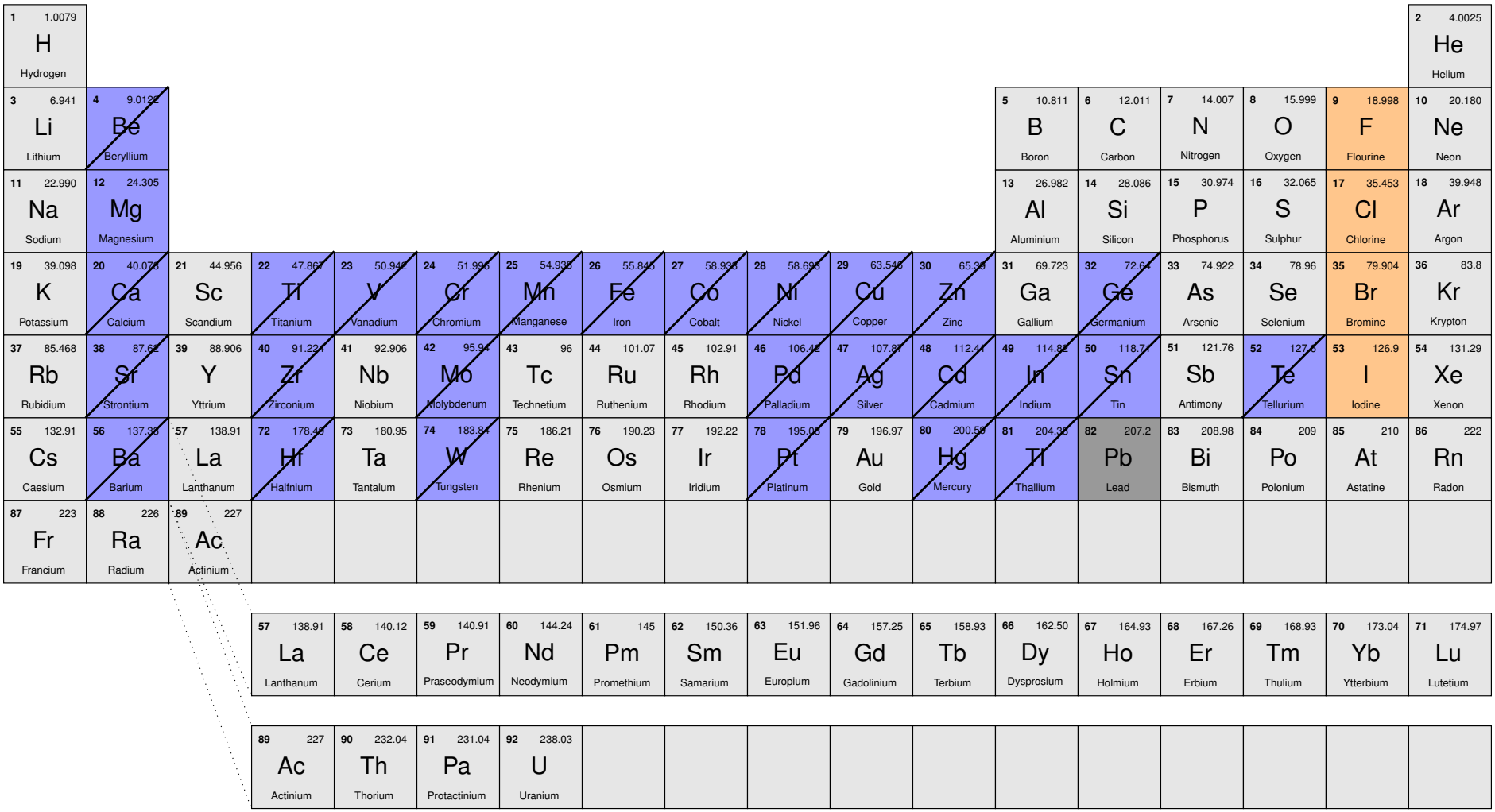
Our working hypothesis



The real structure from the Inorganic Crystal Structure Database (ICSD)

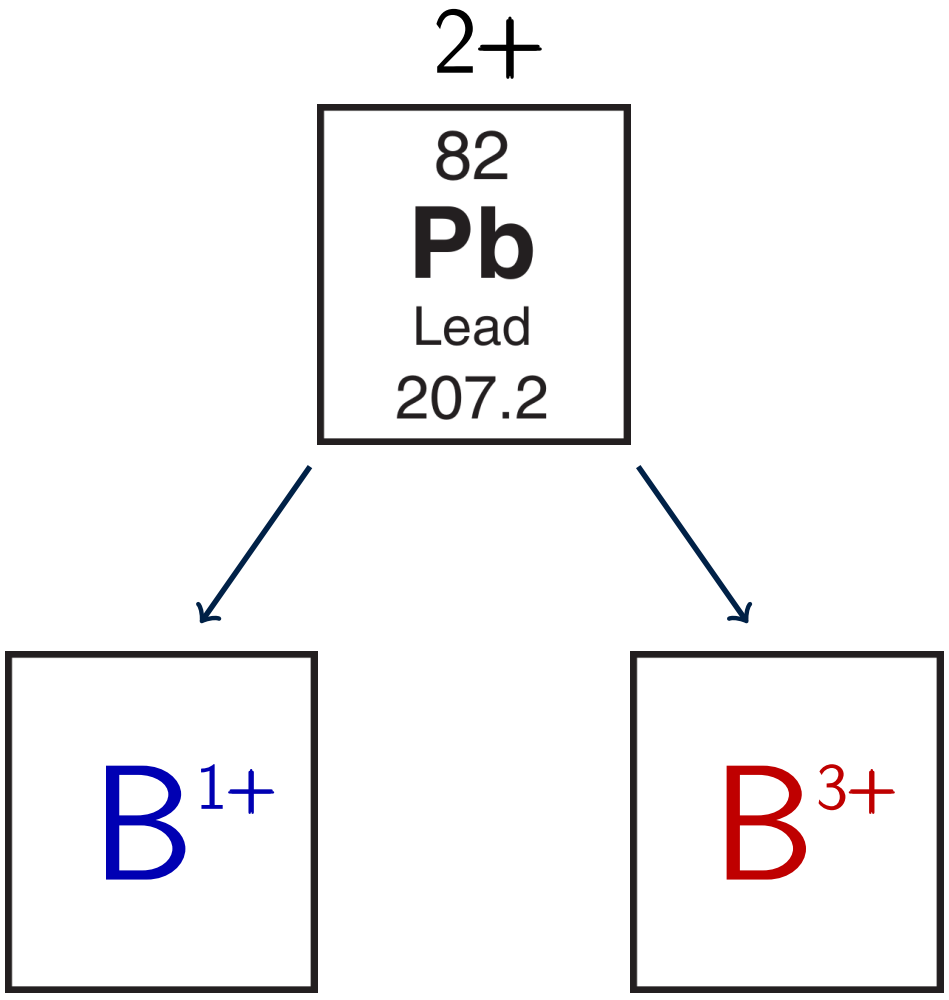
Filip & Giustino, J. Phys. Chem. C 120, 166 (2016)

Homovalent Pb replacement



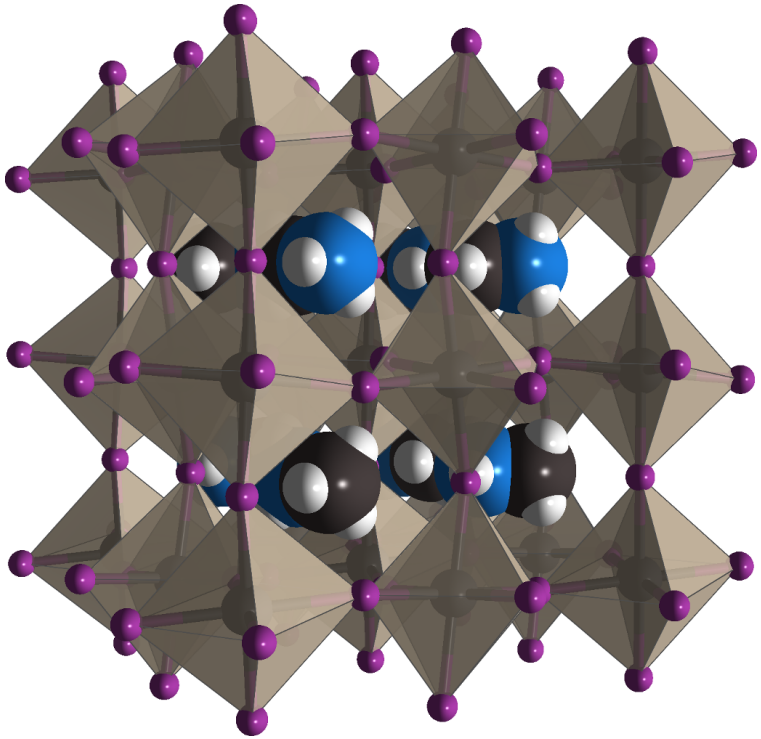
Filip & Giustino, J. Phys. Chem. C 120, 166 (2016)

Heterovalent Pb replacement



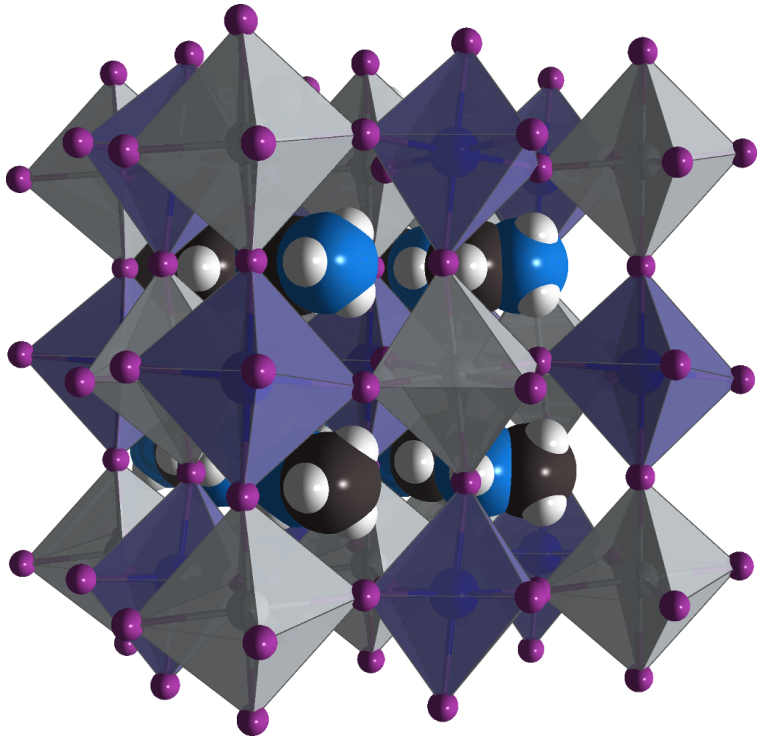
Double perovskites

$MAB^{2+}X_3$



perovskite

$MA_2B^{1+}B^{3+}X_6$



double perovskite

(elpasolite)

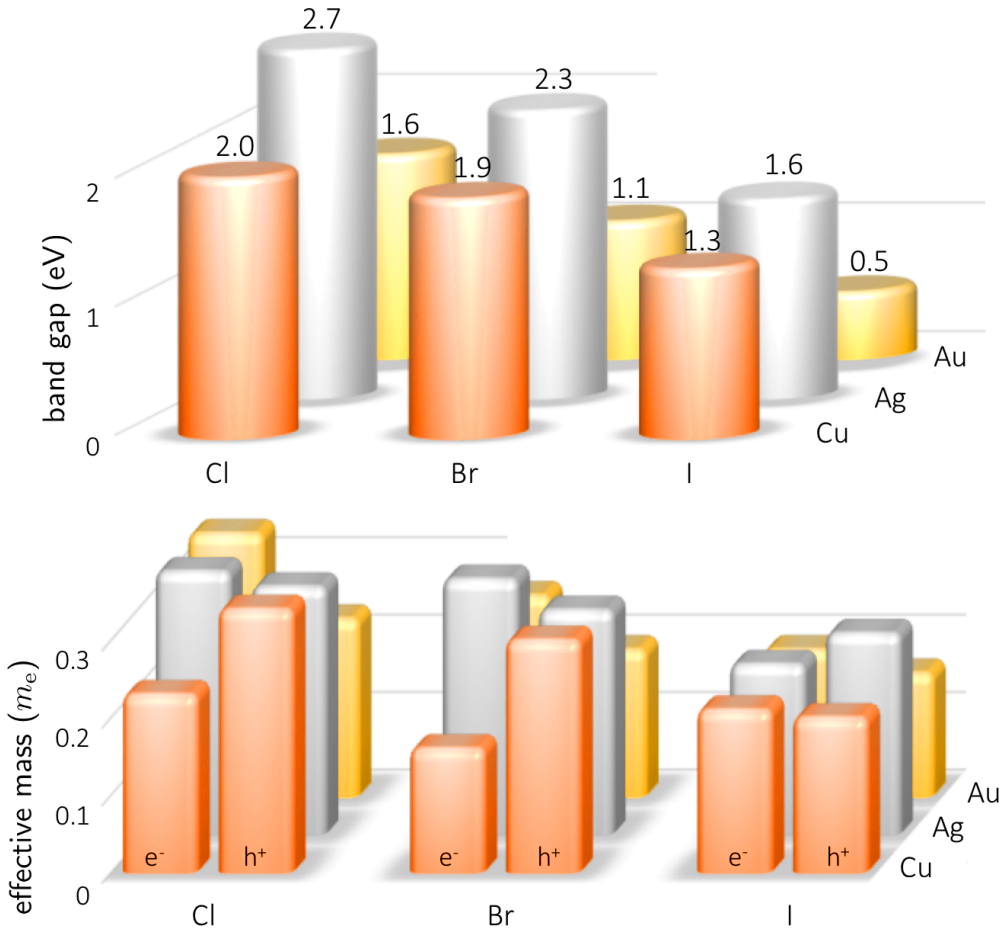
Heterovalent Pb replacement

$$Cs_2B^{3+}B^{1+}X_6$$

1 1.0079 H Hydrogen																	2 4.0025 He Helium
3 6.941 Li Lithium	4 9.0122 Be Beryllium											5 10.811 B Boron	6 12.011 C Carbon	7 14.007 N Nitrogen	8 15.999 O Oxygen	9 18.998 F Flourine	10 20.180 Ne Neon
11 22.990 Na Sodium	12 24.305 Mg Magnesium											13 26.982 Al Aluminium	14 28.086 Si Silicon	15 30.974 P Phosphorus	16 32.065 S Sulphur	17 35.453 Cl Chlorine	18 39.948 Ar Argon
19 39.098 K Potassium	20 40.078 Ca Calcium	21 44.956 Sc Scandium	22 47.867 Ti Titanium	23 50.942 V Vanadium	24 51.996 Cr Chromium	25 54.938 Mn Manganese	26 55.845 Fe Iron	27 58.933 Co Cobalt	28 58.693 Ni Nickel	29 63.546 Cu Copper	30 65.39 Zn Zinc	31 69.723 Ga Gallium	32 72.64 Ge Germanium	33 74.922 As Arsenic	34 78.96 Se Selenium	35 79.904 Br Bromine	36 83.8 Kr Krypton
37 85.468 Rb Rubidium	38 87.62 Sr Strontium	39 88.906 Y Yttrium	40 91.224 Zr Zirconium	41 92.906 Nb Niobium	42 95.94 Mo Molybdenum	43 96 Tc Technetium	44 101.07 Ru Ruthenium	45 102.91 Rh Rhodium	46 106.42 Pd Palladium	47 107.87 Ag Silver	48 112.41 Cd Cadmium	49 114.82 In Indium	50 118.71 Sn Tin	51 121.76 Sb Antimony	52 127.6 Te Tellurium	53 126.9 I Iodine	54 131.29 Xe Xenon
55 132.91 Cs Caesium	56 137.33 Ba Barium	57 138.91 La Lanthanum	72 178.49 Hf Halfnium	73 180.95 Ta Tantalum	74 183.84 W Tungsten	75 186.21 Re Rhenium	76 190.23 Os Osmium	77 192.22 Ir Iridium	78 195.08 Pt Platinum	79 196.97 Au Gold	80 200.59 Hg Mercury	81 204.38 Tl Thallium	82 207.2 Pb Lead	83 208.98 Bi Bismuth	84 209 Po Polonium	85 210 At Astatine	86 222 Rn Radon
87 223 Fr Francium	88 226 Ra Radium	89 227 Ac Actinium															

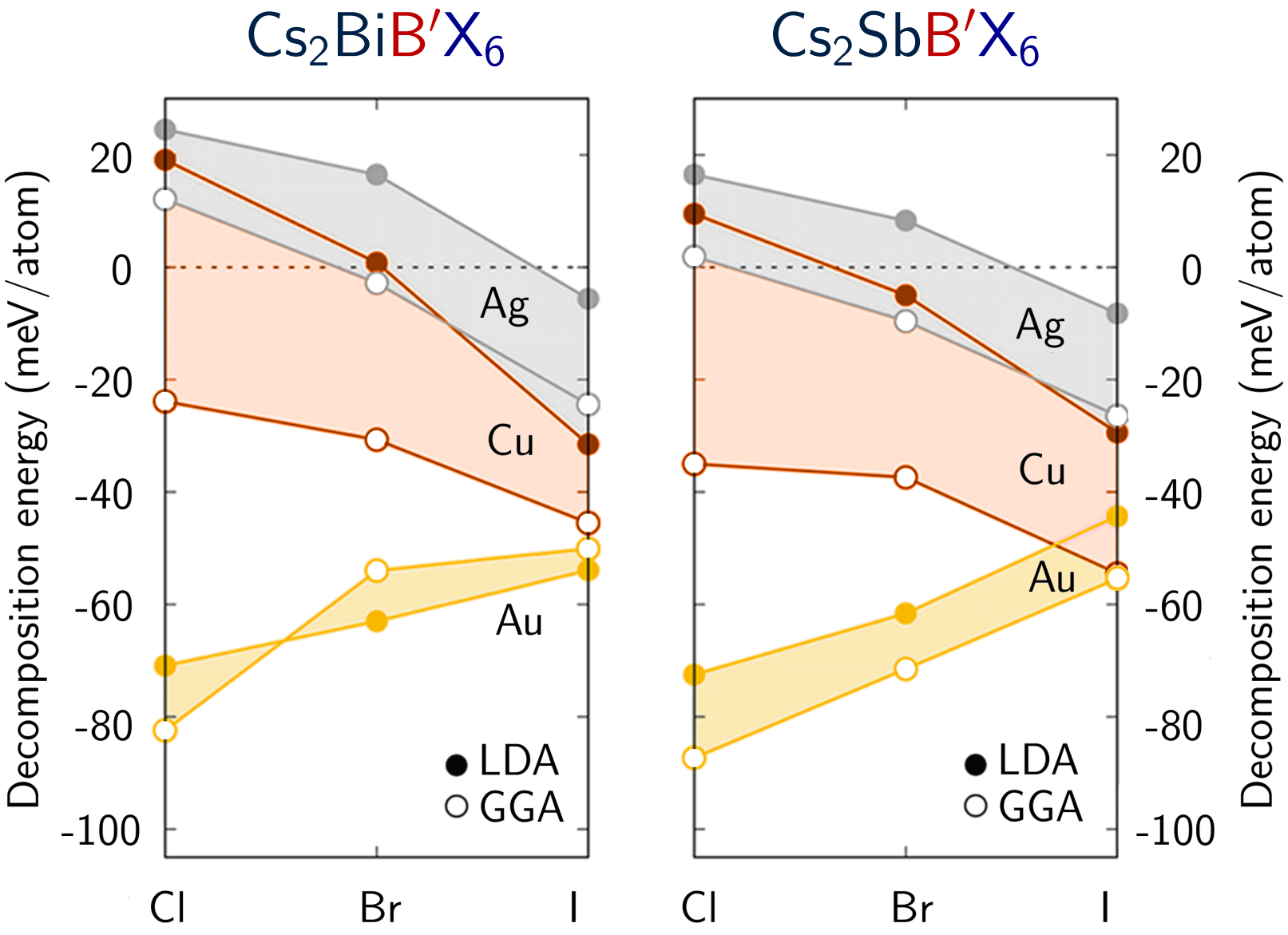
57 138.91 La Lanthanum	58 140.12 Ce Cerium	59 140.91 Pr Praseodymium	60 144.24 Nd Neodymium	61 145 Pm Promethium	62 150.36 Sm Samarium	63 151.96 Eu Europium	64 157.25 Gd Gadolinium	65 158.93 Tb Terbium	66 162.50 Dy Dysprosium	67 164.93 Ho Holmium	68 167.26 Er Erbium	69 168.93 Tm Thulium	70 173.04 Yb Ytterbium	71 174.97 Lu Lutetium
89 227 Ac Actinium	90 232.04 Th Thorium	91 231.04 Pa Protactinium	92 238.03 U Uranium											

$Cs_2BiB'X_6$, $B' = Cu, Ag, Au$



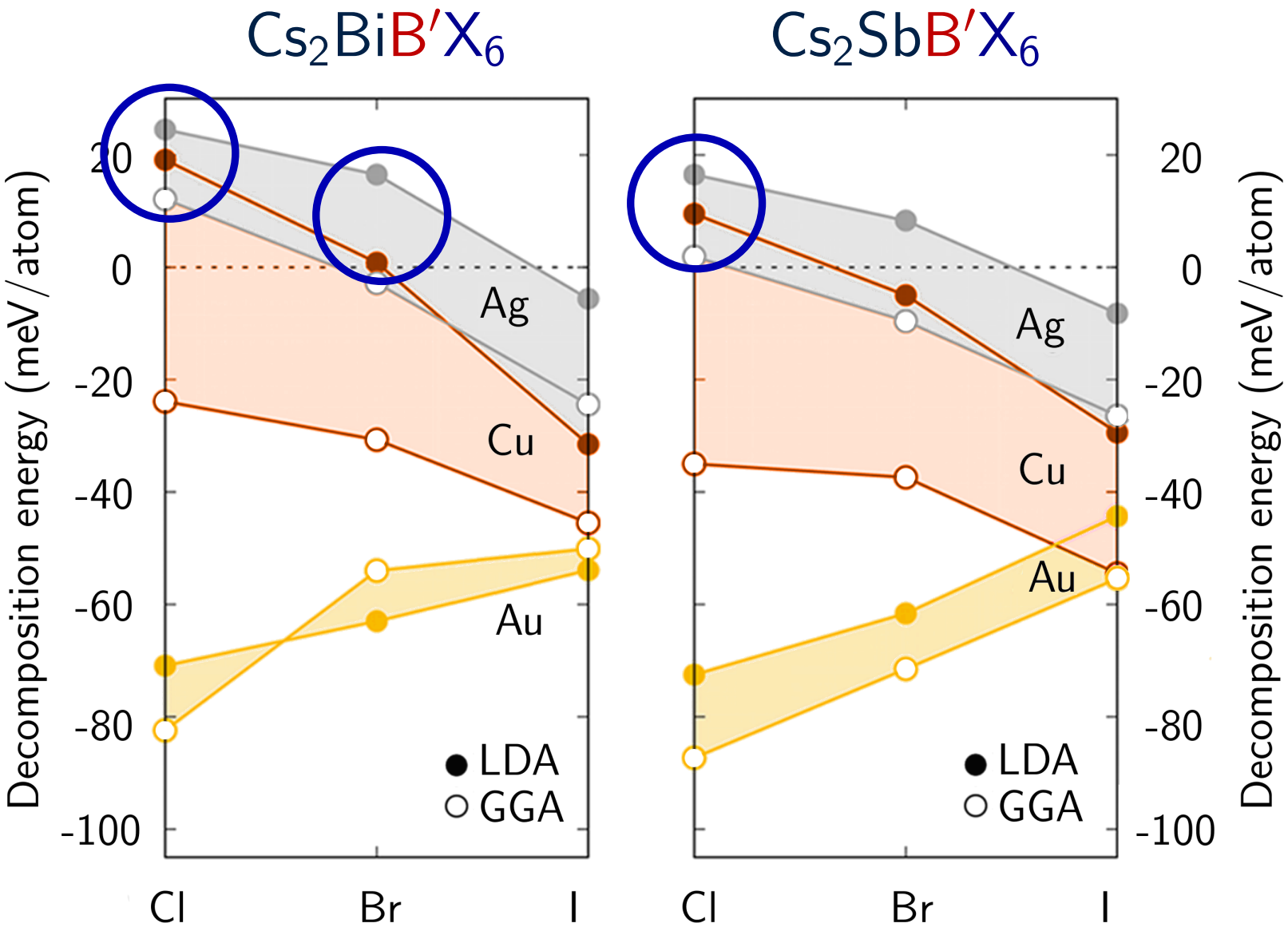
Volonakis et. al, J. Phys. Chem. Lett. 7, 1254 (2016)

Stability analysis of double perovskites



Filip et al., J. Phys. Chem. C 122, 158 (2018)

Stability analysis of double perovskites



Filip et al., J. Phys. Chem. C 122, 158 (2018)

Double perovskites predicted by DFT

$Cs_2BiAgCl_6$

$Cs_2BiAgBr_6$

$Cs_2SbAgCl_6$

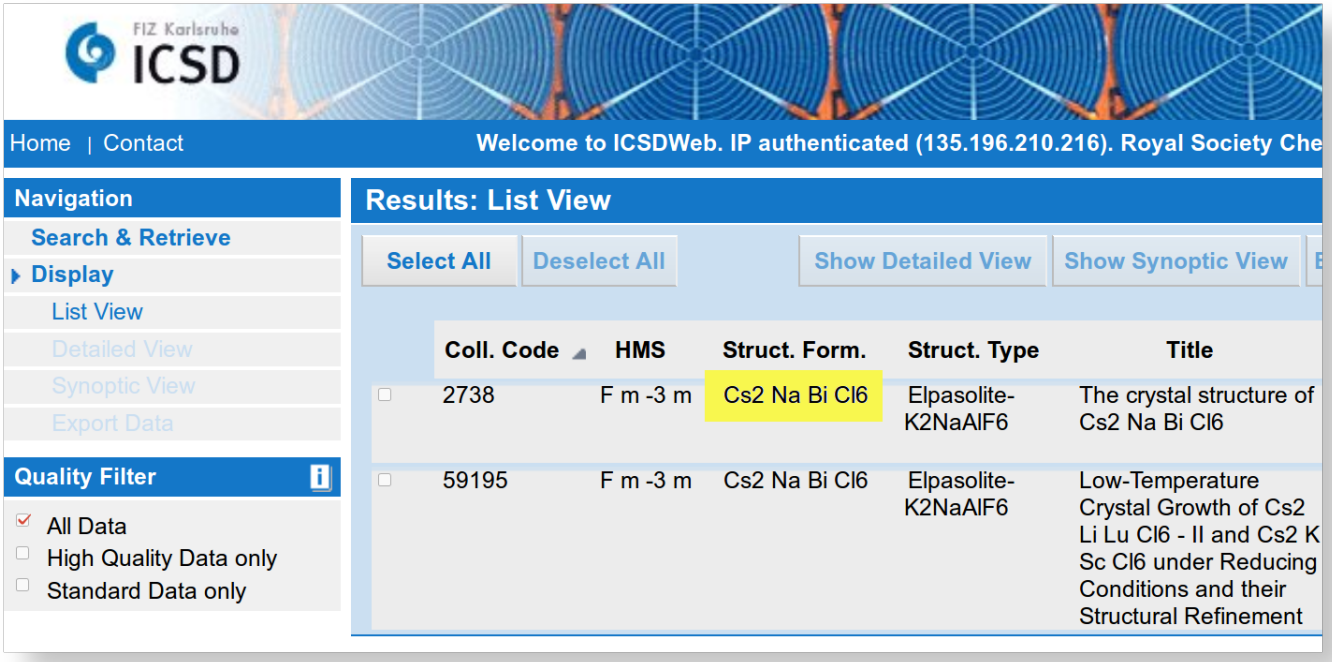
Double perovskites predicted by DFT

$Cs_2BiAgCl_6$

$Cs_2BiAgBr_6$

$Cs_2SbAgCl_6$

Where do we start with experiments?

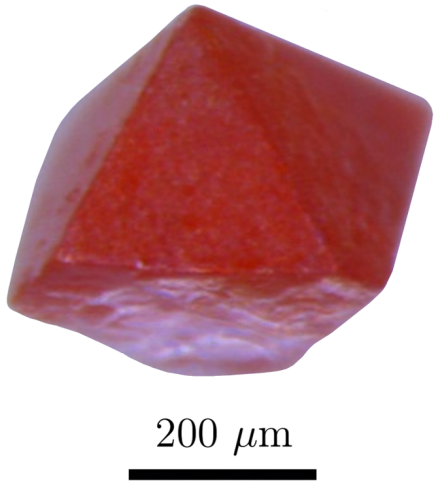


Experimental synthesis of predicted compounds

$Cs_2AgBiCl_6$

solid-state reaction

$Cs_2AgBiBr_6$

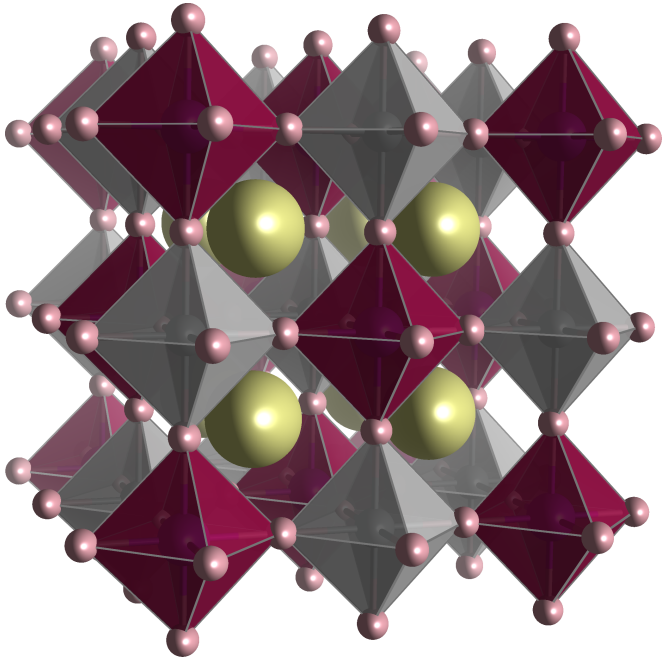


solution process

Amir Haghighirad

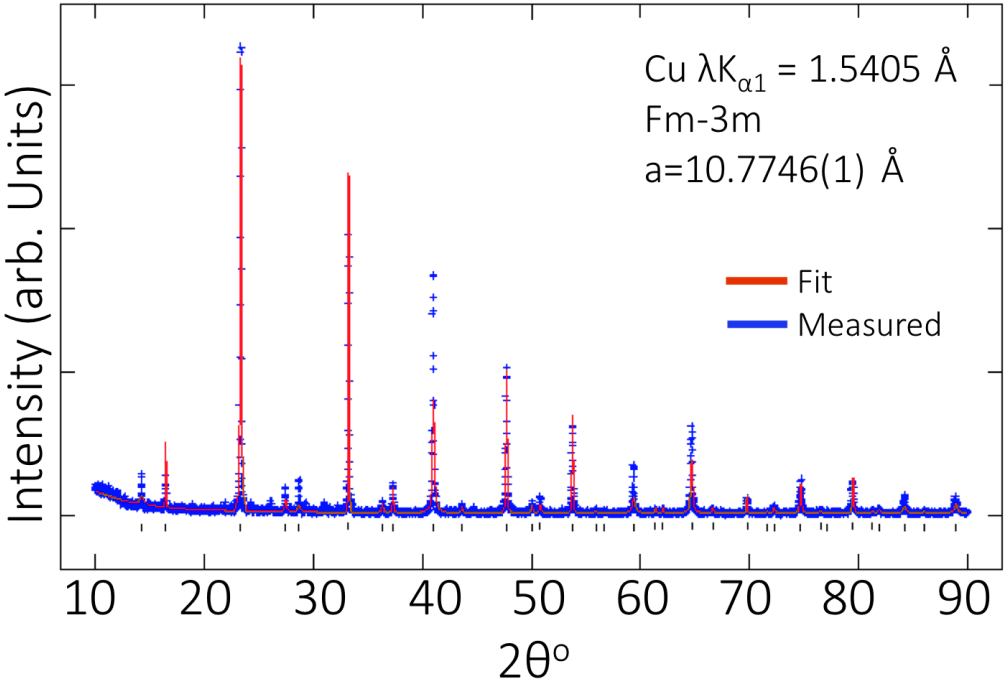
Volonakis et al., J. Phys. Chem. Lett. 7, 1254 (2016); Filip et al., JPCL 7, 2579 (2016)
Slavney et al., J. Am. Chem. Soc. 128, 2138 (2016)
McClure et al., Chem. Mater. 28, 1348 (2016)

Characterization of new compounds



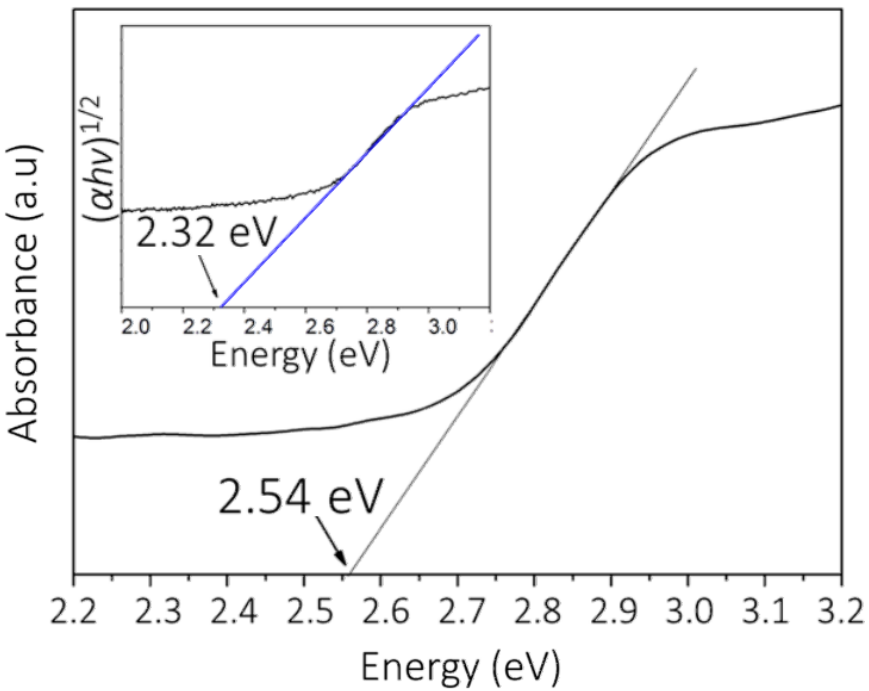
$Cs_2BiAgCl_6$, cubic $Fm\bar{3}m$

Powder X-ray diffraction

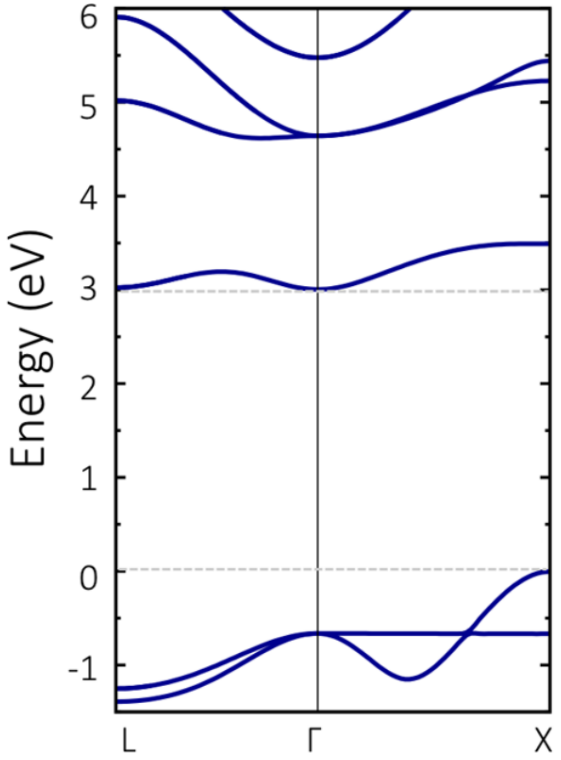


$Cs_2BiAgCl_6$

Absorption spectrum for visible/UV light



Band structure (PBE0)



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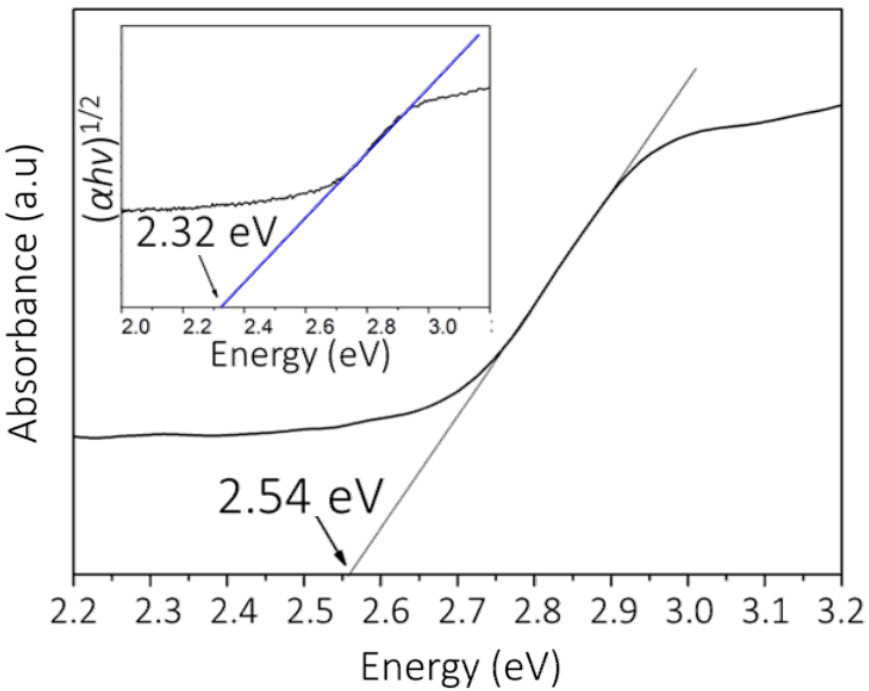

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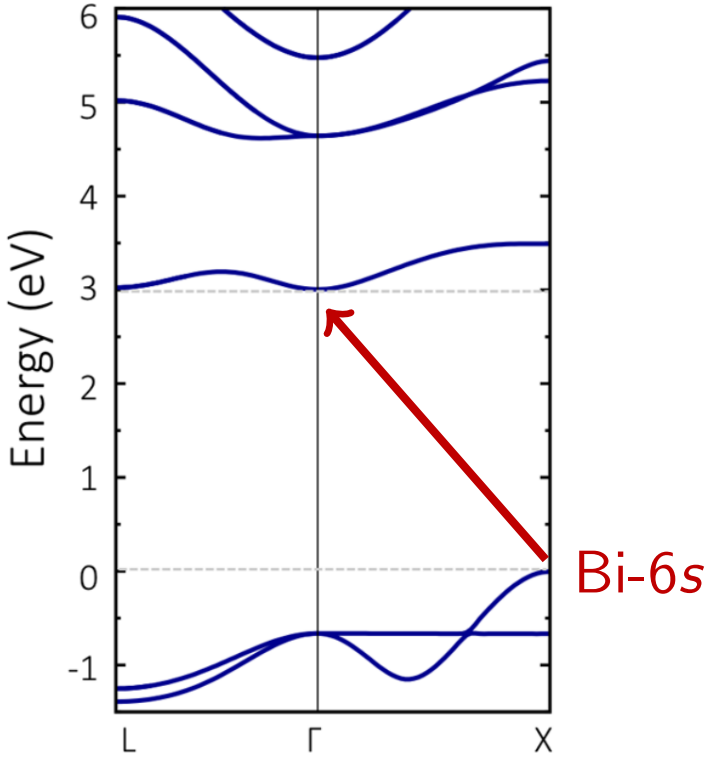
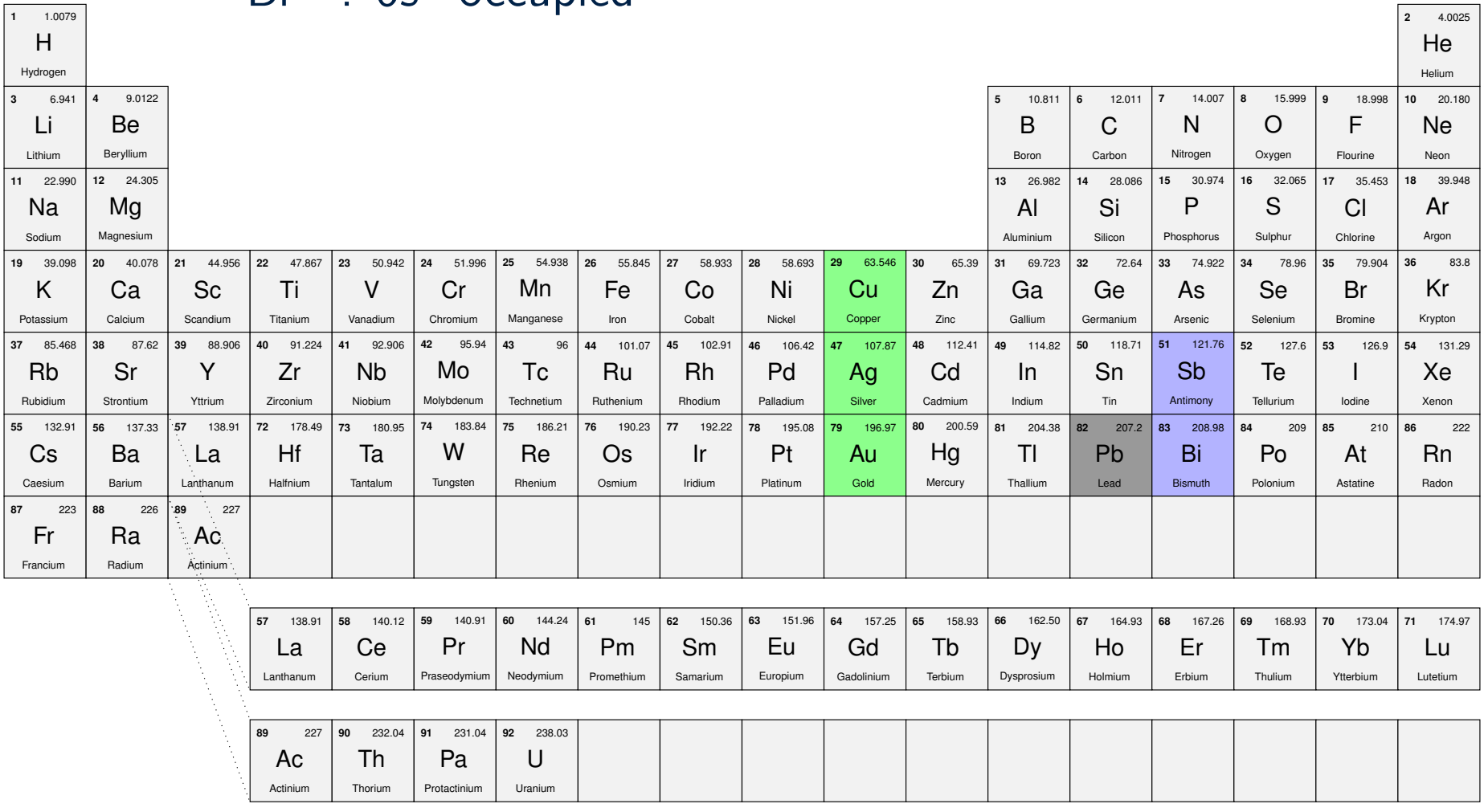


Indirect band gap

Double perovskites with direct band gap

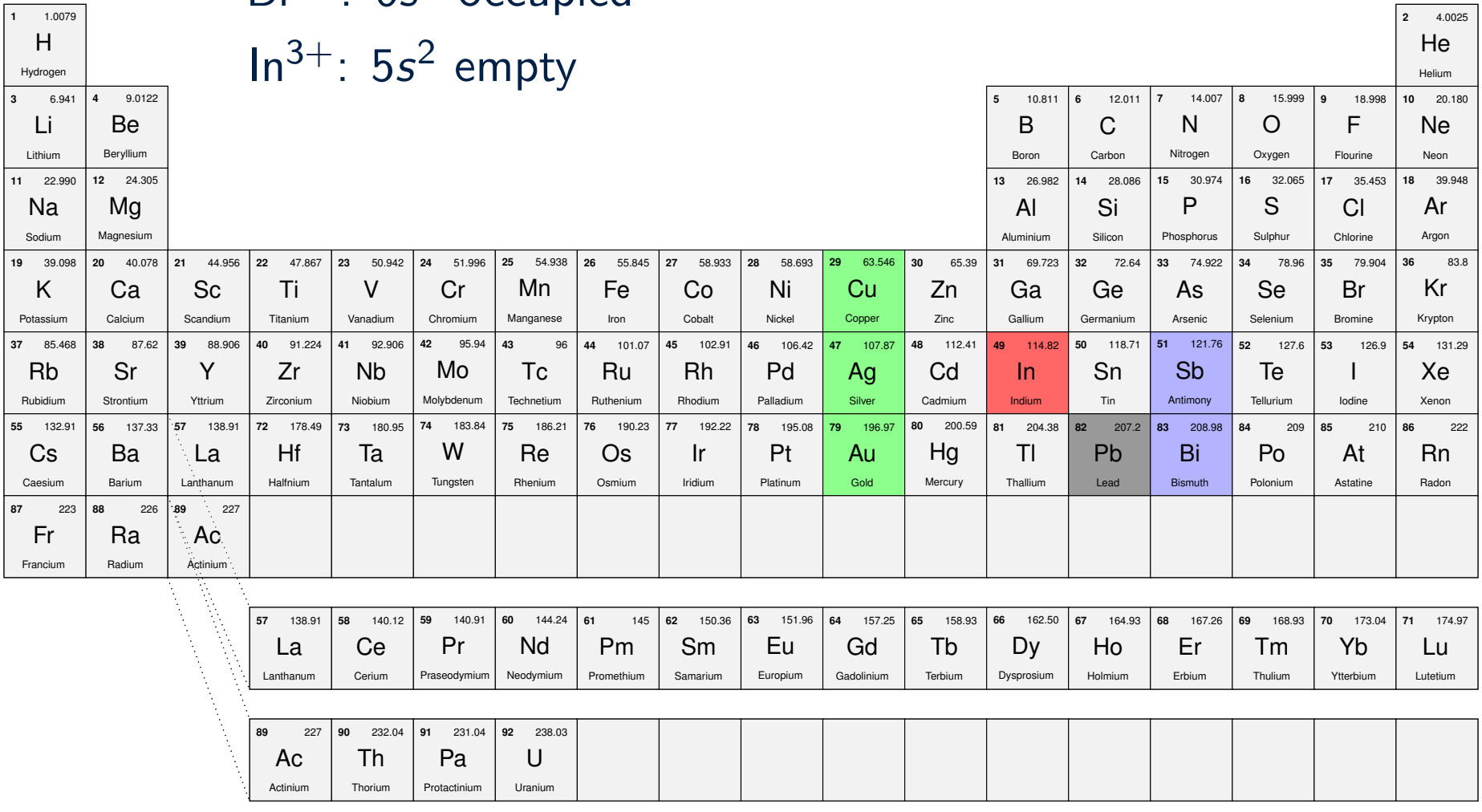
Bi^{3+}: $6s^2$ occupied



Double perovskites with direct band gap

Bi^{3+}: $6s^2$ occupied

In^{3+}: $5s^2$ empty

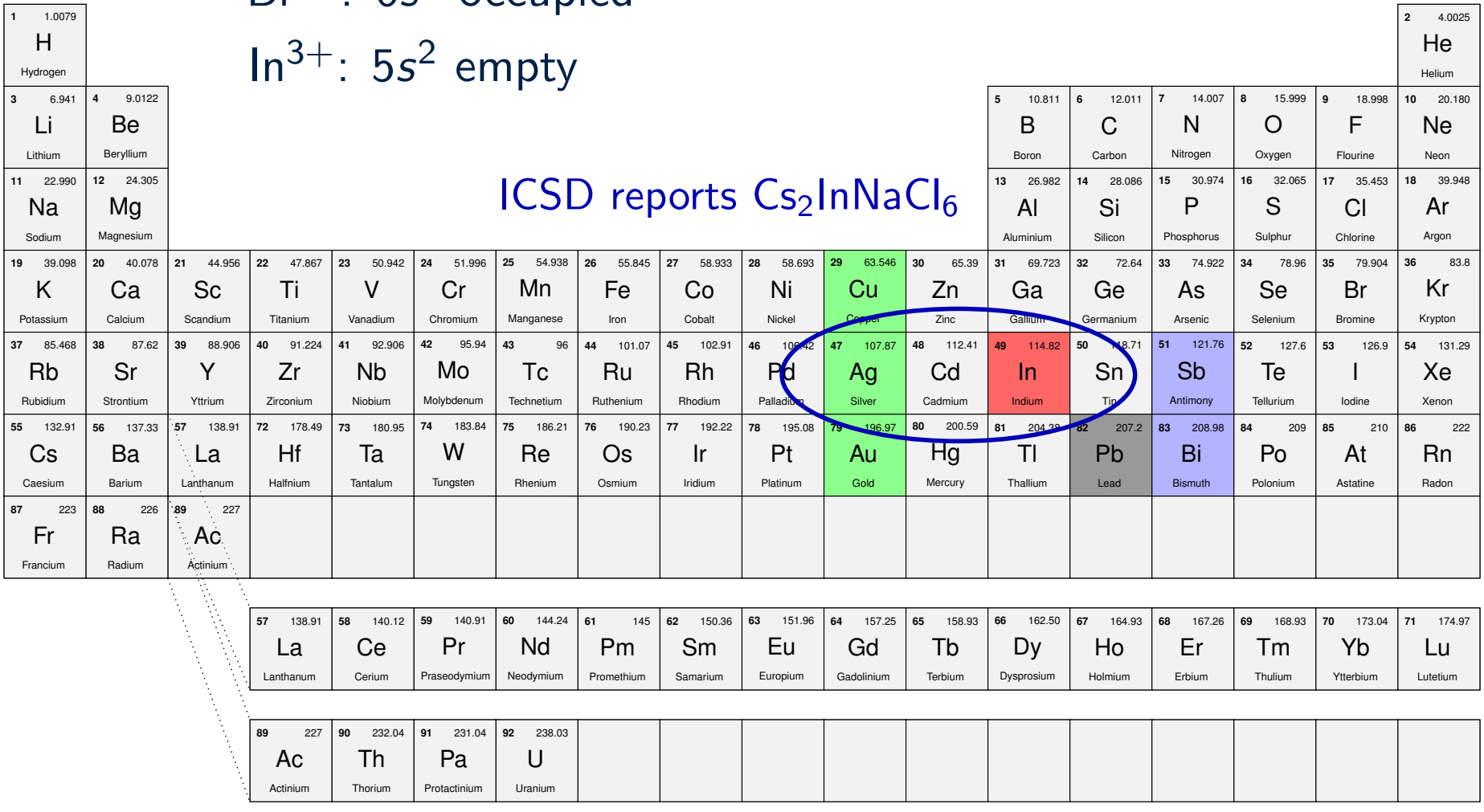


Double perovskites with direct band gap

Bi^{3+}: $6s^2$ occupied

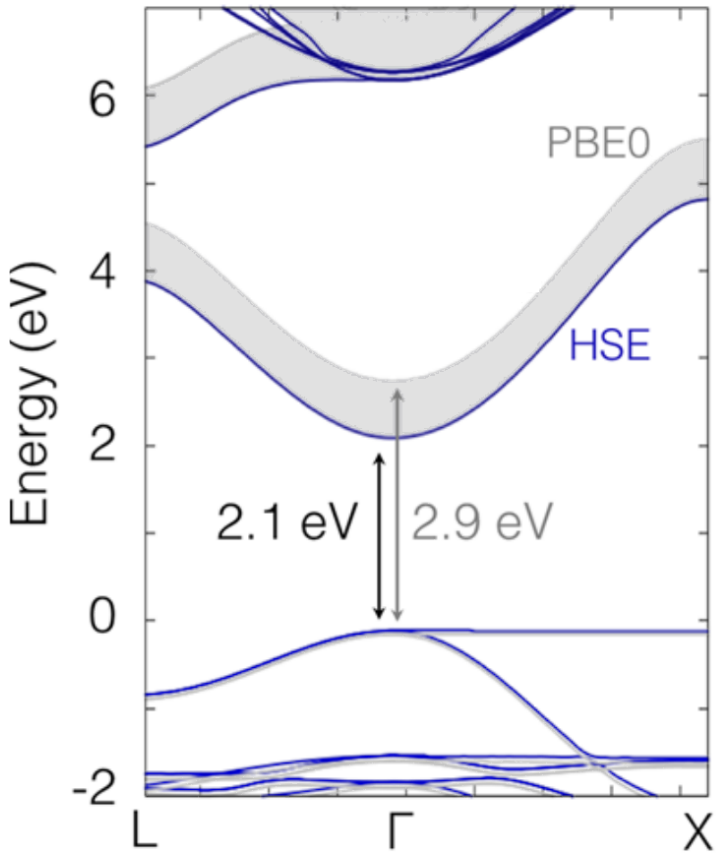
In^{3+}: $5s^2$ empty

ICSD reports $Cs_2InNaCl_6$

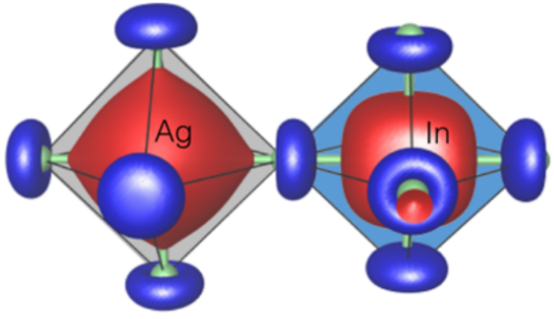


Double perovskites with direct band gap

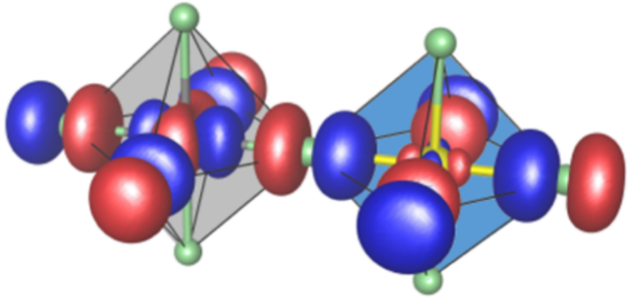
$Cs_2InAgCl_6$



Conduction band



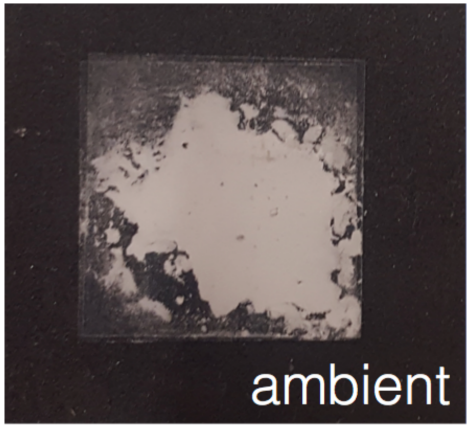
Valence band



Direct band gap as anticipated

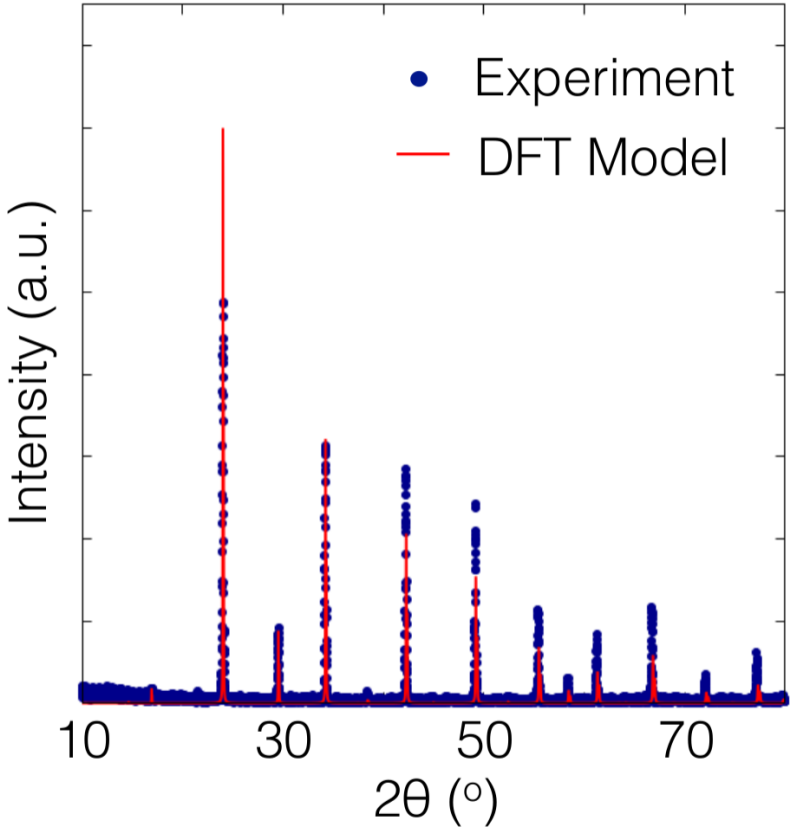
Double perovskites with direct band gap

$Cs_2InAgCl_6$



Amir Haghighirad

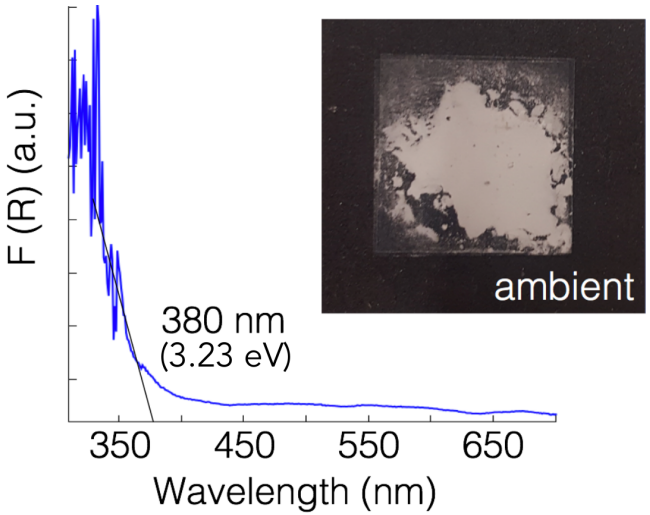
Powder X-ray diffraction

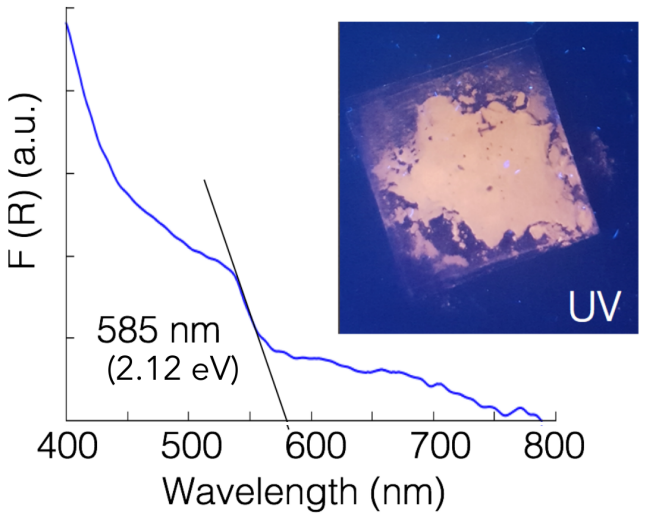


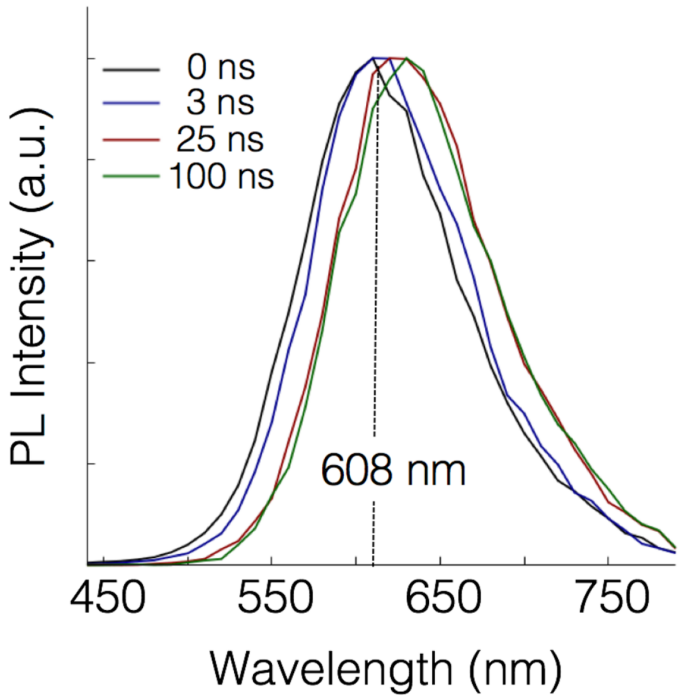
DFT lattice parameter
set to experimental value

Double perovskites with direct band gap

Optical absorption and photoluminescence of $Cs_2InAgCl_6$







Volonakis et al., J. Phys. Chem. Lett. 8, 772 (2017)

nature
International journal of science

Letter | Published: 07 November 2018

Efficient and stable emission of warm-white light from lead-free halide double perovskites

Jiajun Luo, Xiaoming Wang, Shunran Li, Jing Liu, Yueming Guo, Guangda Niu, Li Yao, Yuhao Fu, Liang Gao, Qingshun Dong, Chunyi Zhao, Meiying Leng, Fusheng Ma, Wenxi Liang, Liduo Wang, Shengye Jin, Junbo Han, Lijun Zhang, Joanne Etheridge, Jianbo Wang, Yanfa Yan ✉, Edward H. Sargent & Jiang Tang ✉

Nature **563**, 541–545 (2018) | Download Citation ⬇

The optimally alloyed $Cs_2(Ag_{0.60}Na_{0.40})InCl_6$ with 0.04 per cent bismuth doping emits warm-white light with 86 ± 5 per cent quantum efficiency and works for over 1,000 hours. We anticipate that these results will stimulate research on single-emitter-based white-light-emitting phosphors and diodes for next-generation lighting and display technologies.

New perovskites designed and synthesized

Compound	Band Gap	Character	First reported
$Cs_2BiAgCl_6$	2.4 eV	indirect	Slavney et al., JACS 128, 2138 (2016)
$Cs_2BiAgBr_6$	1.9 eV	indirect	McClure et al., Chem Mater 28, 1348 (2016)
$Cs_2SbAgCl_6$	2.5 eV	indirect	Tran et al., Mater Horiz 4, 688 (2017)
$Cs_2InAgCl_6$	3.3 eV	direct	Volonakis et al., JPCL 8, 772 (2017)
Ba_2AgIO_6	1.9 eV	direct	Volonakis et al., JPCL 10, 1722 (2019)

New perovskites designed and synthesized

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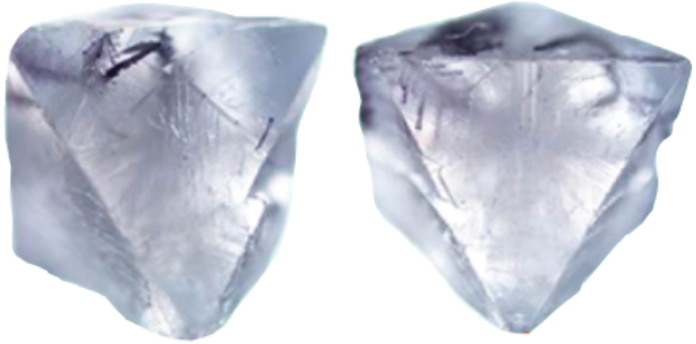
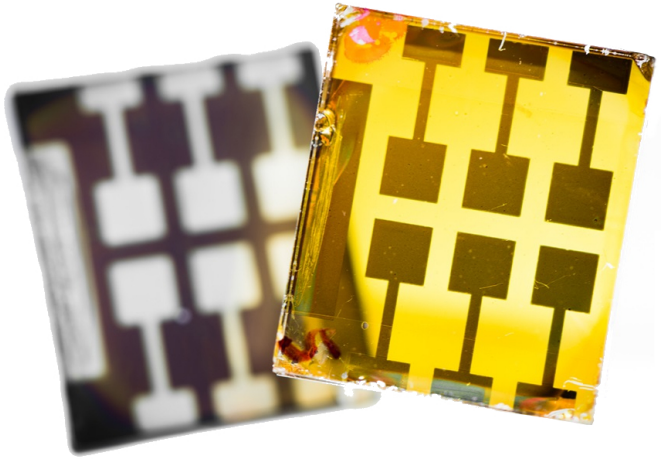


Zhuo et al,
J Mater Chem A 5, 15031 (2017)



Ning et al,
Adv Mater 30, 1706246 (2018)

Broadening the search space

History [edit]

The mineral was discovered in the Ural Mountains of Russia by Gustav Rose in 1839 and is named after Russian mineralogist Lev Perovski (1792–1856).[2] Perovskite's notable crystal structure was first described by Victor Goldschmidt in 1926, in his work on tolerance factors.[7] The crystal structure was later published in 1945 from X-ray diffraction data on barium titanate by Helen Dick Megaw.[8]

en.wikipedia.org/wiki/Perovskite

Other perovskites for photovoltaics?

Examples from the Materials Project

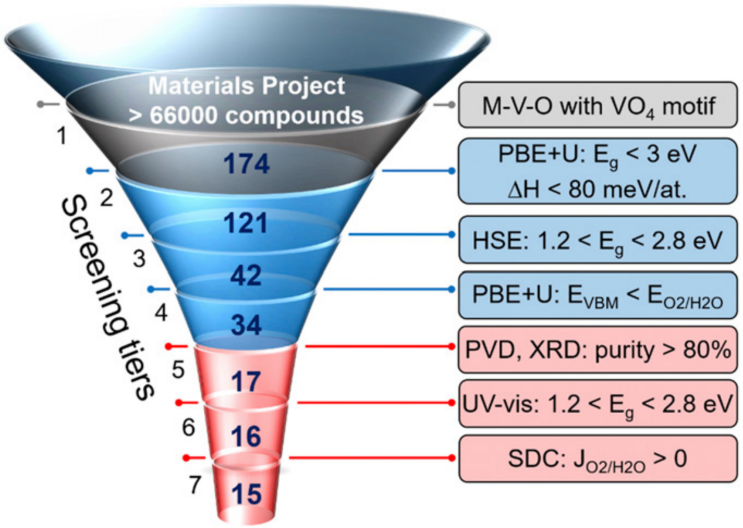


Fig. 1. Tiered screening pipeline for accelerated discovery of solar fuels photoanodes. The number of compounds (bold) and screening criteria used in this study for the seven-tier pipeline that integrates database mining (gray), high-throughput computational screening (blue), and high-throughput experimental screening (red).

Yan et al., PNAS 114, 3040 (2017)

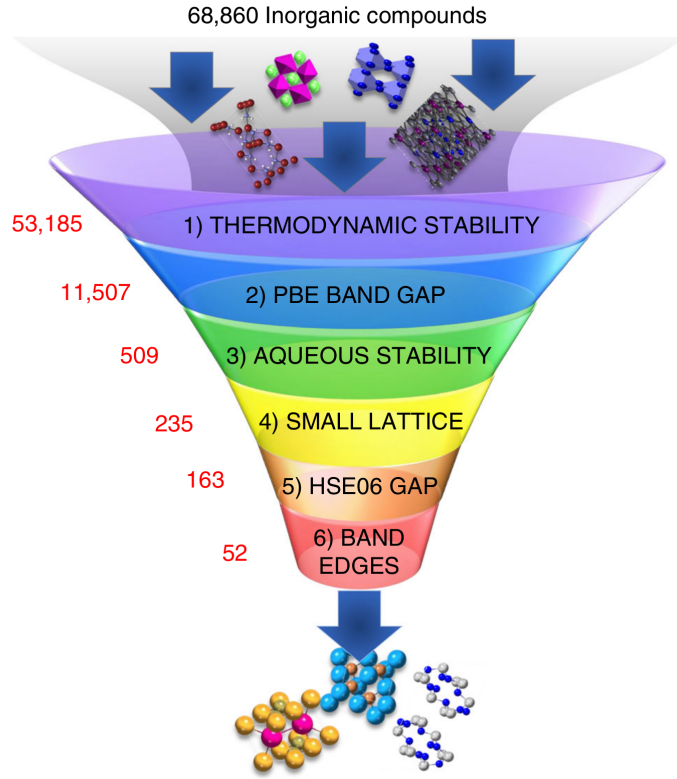


Fig. 2 The selection criteria, as well as the number of materials which satisfy the criterion, are shown for each tier. Note that less than 5% of the semiconductors from tier 2 make it through tier 3, highlighting that very few semiconductors are water-stable at the reducing conditions needed for CO_2 reduction

Singh et al., Nat. Commun. 10, 443 (2019)

Known perovskites and double perovskites
from ICSD and literature

1,622

Counting perovskites

Known perovskites and double perovskites
from ICSD and literature

1,622

Possible quaternary compounds
ABX_3 or $A_2BB'X_6$

3,658,527

Counting perovskites

Known perovskites and double perovskites
from ICSD and literature

1,622

Possible quaternary compounds
ABX_3 or $A_2BB'X_6$

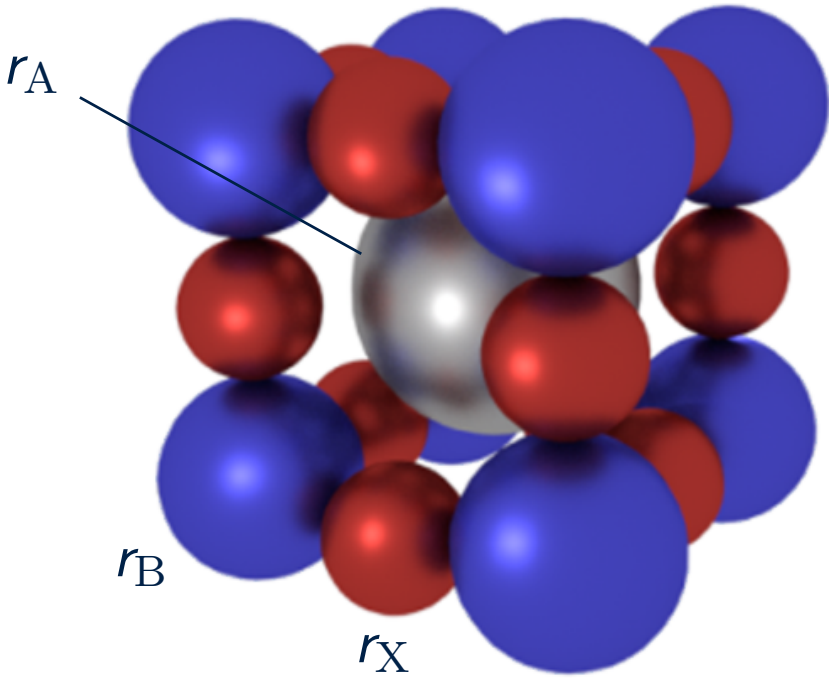
3,658,527

Assuming 1h of HPC per calculation,
screening this database would require

160 years

No-rattling principle

ABX_3



tolerance factor

$$t = \frac{1}{\sqrt{2}} \frac{r_A + r_X}{r_B + r_X}$$

octahedral factor

$$\mu = \frac{r_B}{r_X}$$

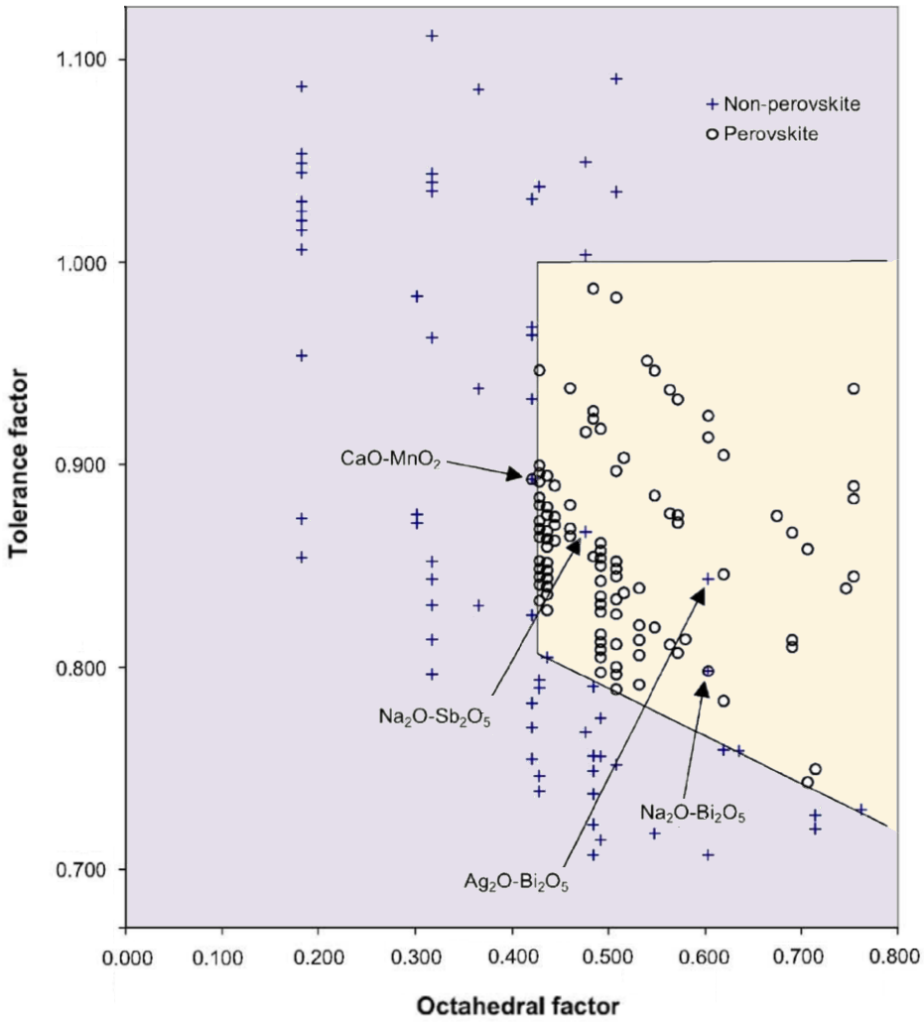
V. M. Goldschmidt, *The laws of crystal chemistry*, Naturwissenschaften 14, 477 (1926)

A. Magnus, *The chemistry of complex compounds*, Z. Anorg. Allg. Chem. 124, 289 (1922)

H. Megaw, *Crystal Structures. A Working Approach* (Saunders, Philadelphia, 1973)

Classification using Goldschmidt descriptors

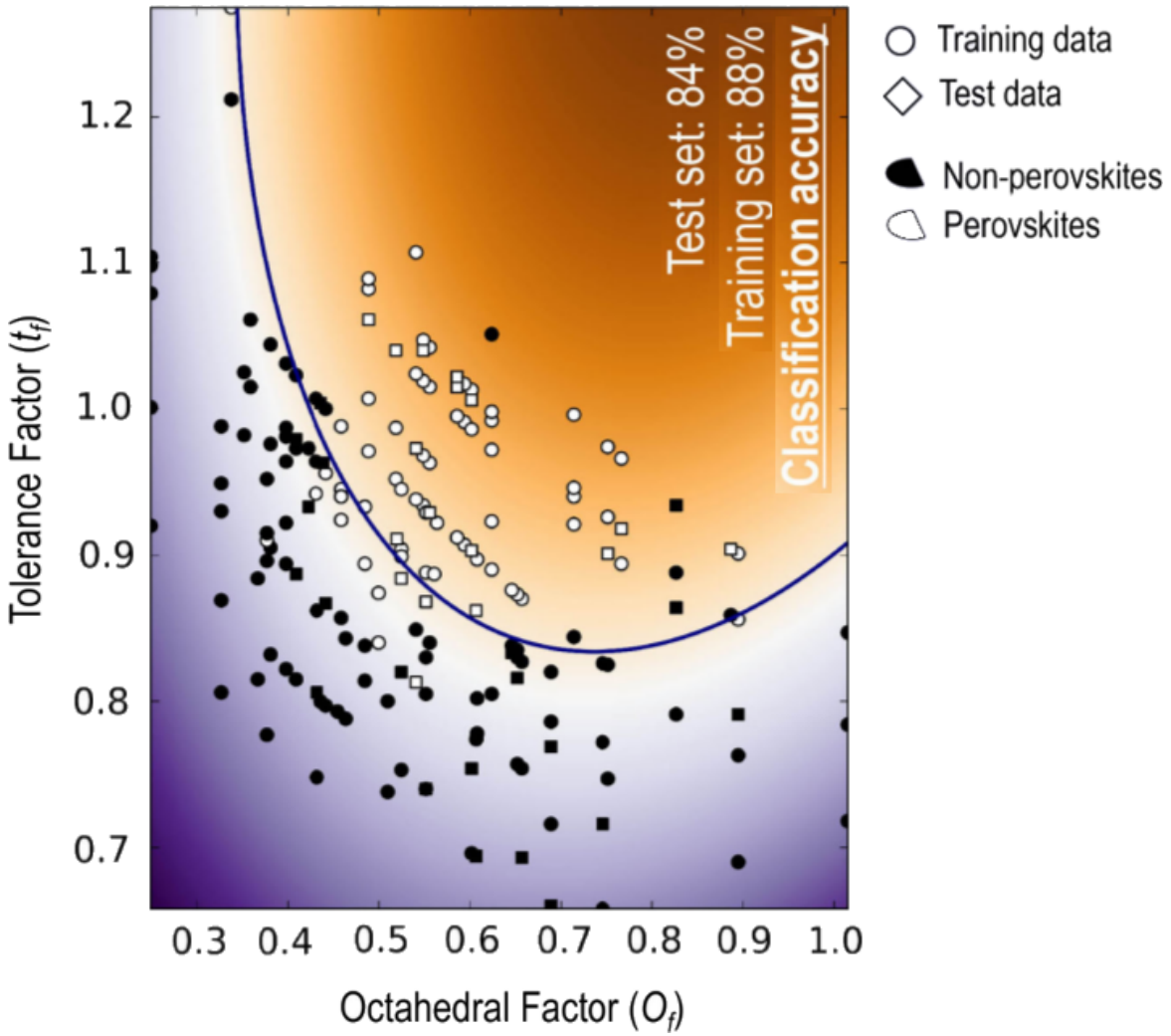
171 oxides



Li, Soh & Wu, J. Alloys Cmpd. 372, 40 (2004)

Classification using Goldschmidt descriptors

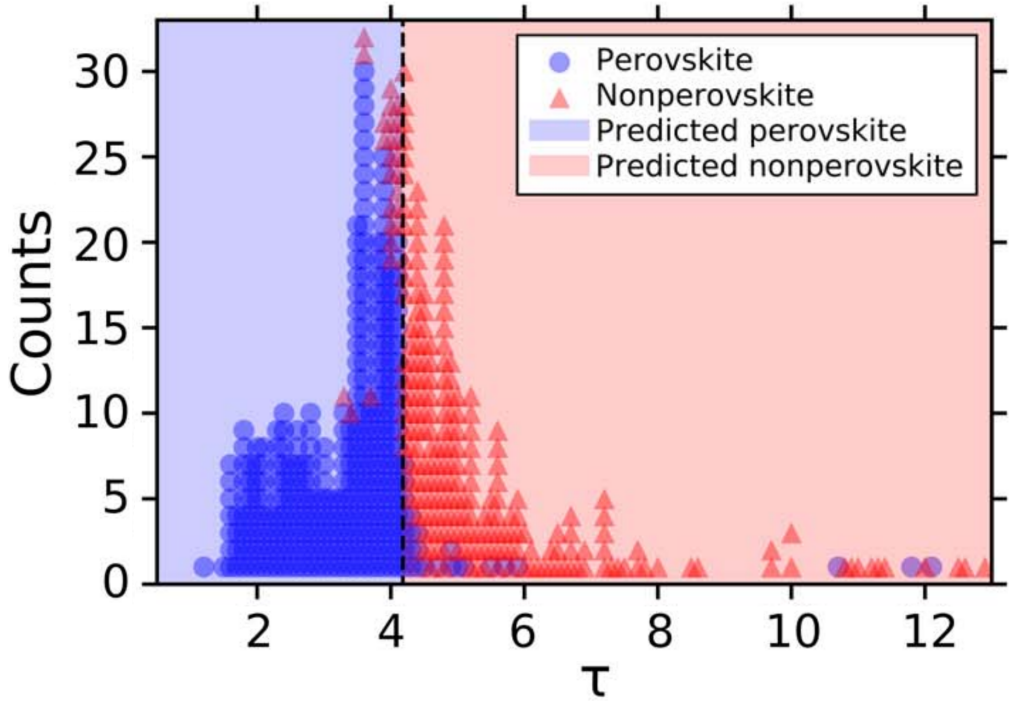
183 halides



Pilania, Balachandran, Kim & Lookman, Front. Mater. 3, 19 (2016)

Classification using Goldschmidt descriptors

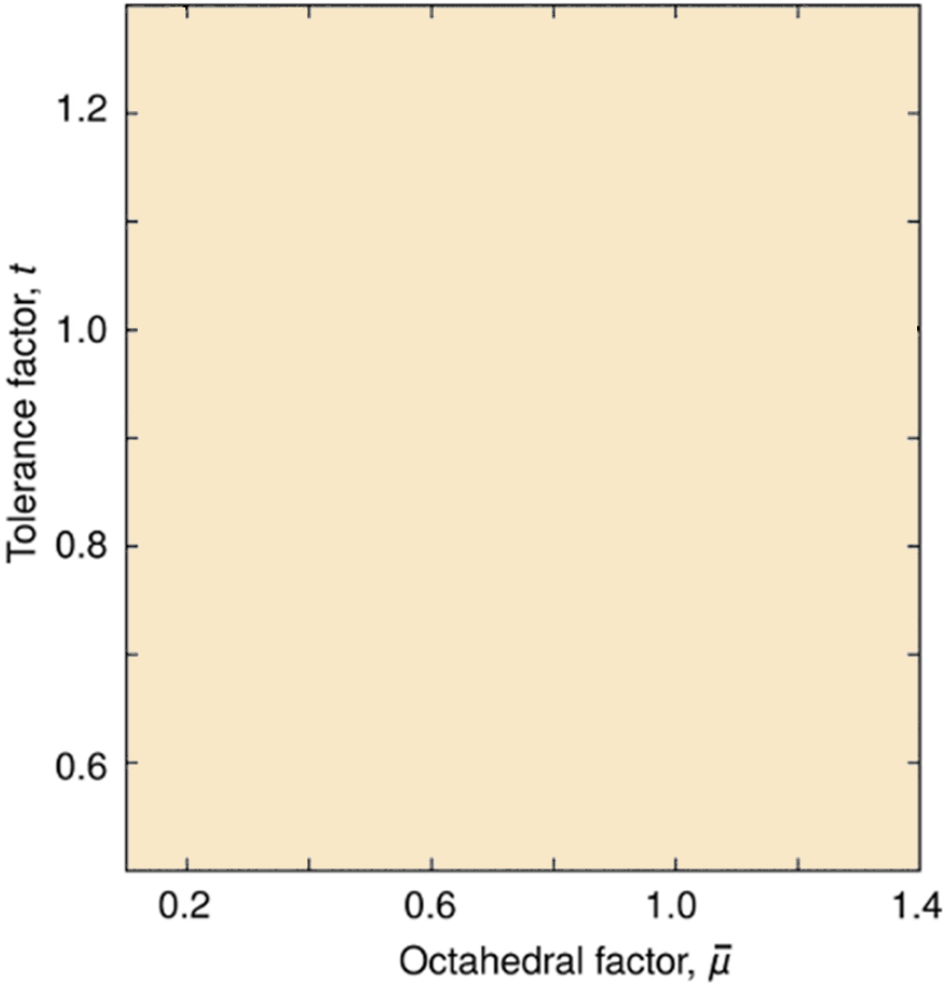
576 ABX_3 compounds, Machine learning using SISSO
(sure independence screening and sparsifying operator)



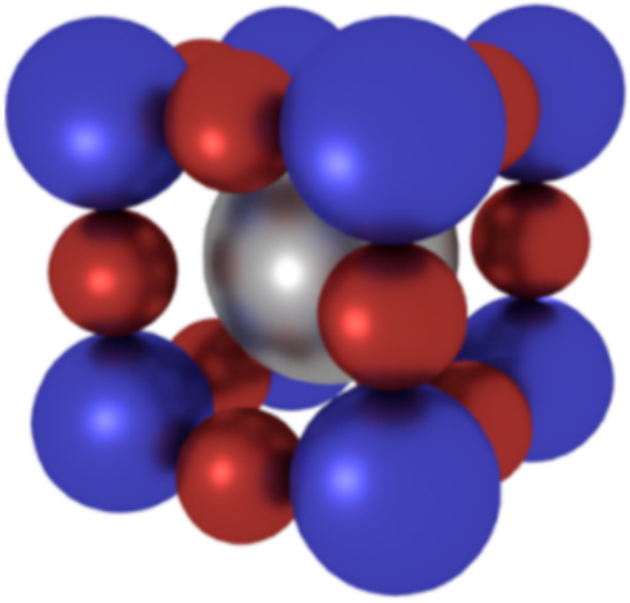
$$\tau = \frac{r_{\mathrm{X}}}{r_{\mathrm{B}}} - n_{\mathrm{A}}\left(n_{\mathrm{A}} - \frac{r_{\mathrm{A}}/r_{\mathrm{B}}}{\log r_{\mathrm{A}}/r_{\mathrm{B}}}\right)$$

Bartel et al., Sci. Adv. 5, eaav0693 (2019)

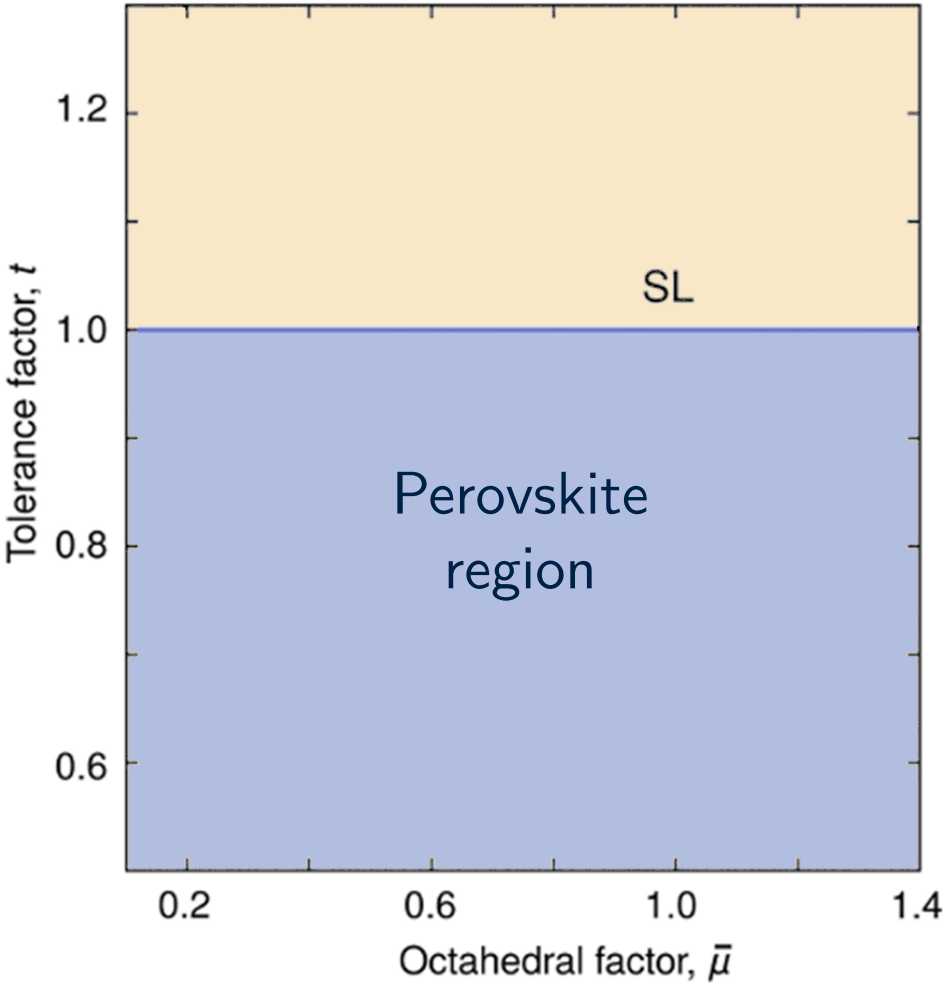
No-rattling principle in equations



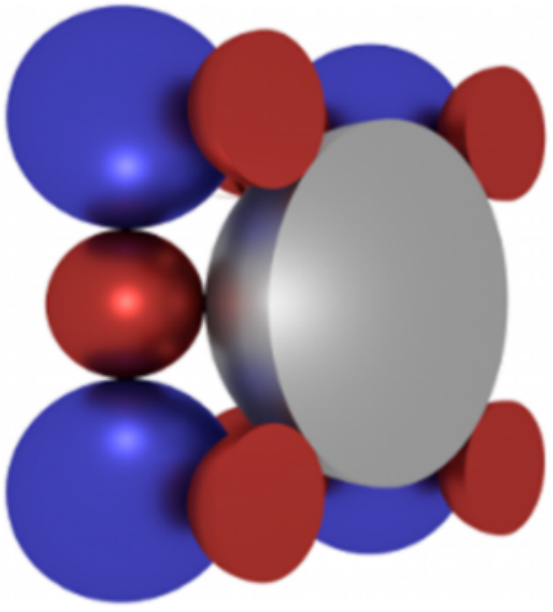
Cubic perovskite



No-rattling principle in equations



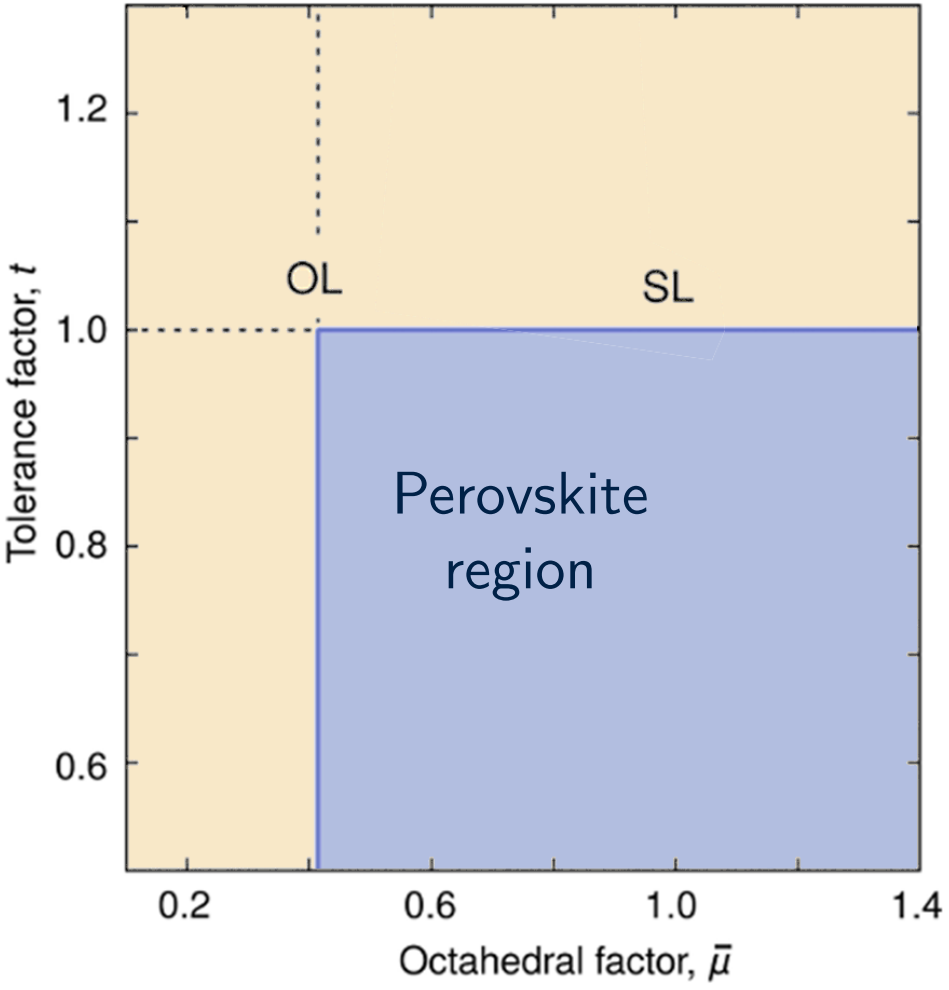
Stretch limit



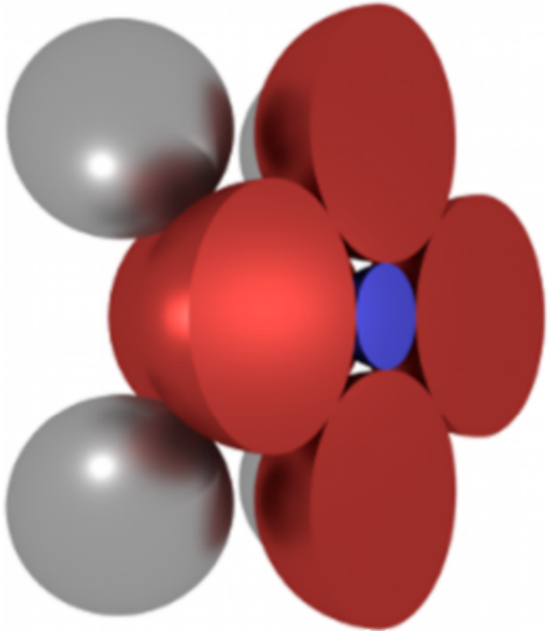
$$r_{\mathrm{A}} + r_{\mathrm{X}} = \sqrt{2}\,(r_{\mathrm{B}} + r_{\mathrm{X}})$$

$$t = 1$$

No-rattling principle in equations



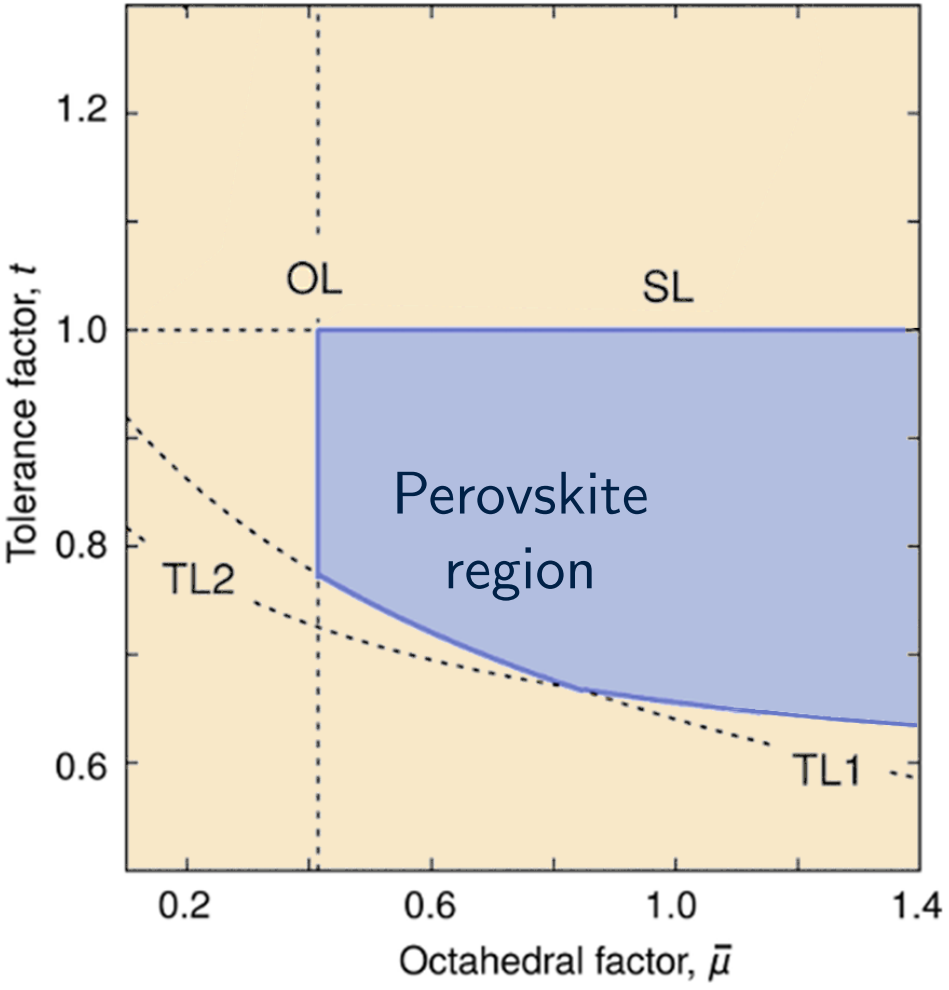
Octahedral limit



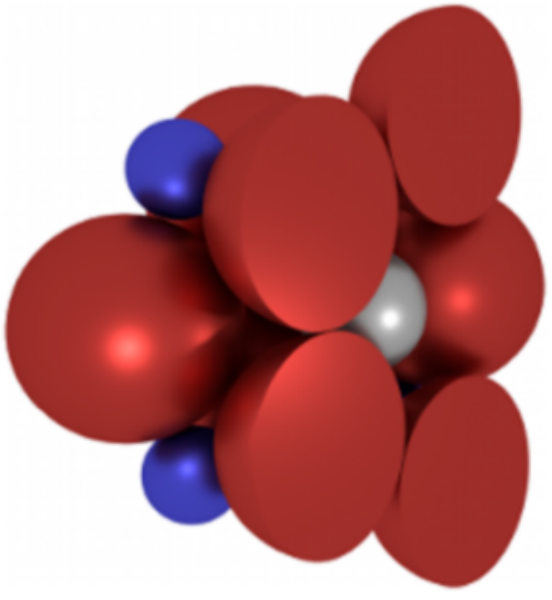
$$\sqrt{2}\,(r_{\mathrm{B}} + r_{\mathrm{X}}) = 2\,r_{\mathrm{X}}$$

$$\mu = \sqrt{2} - 1$$

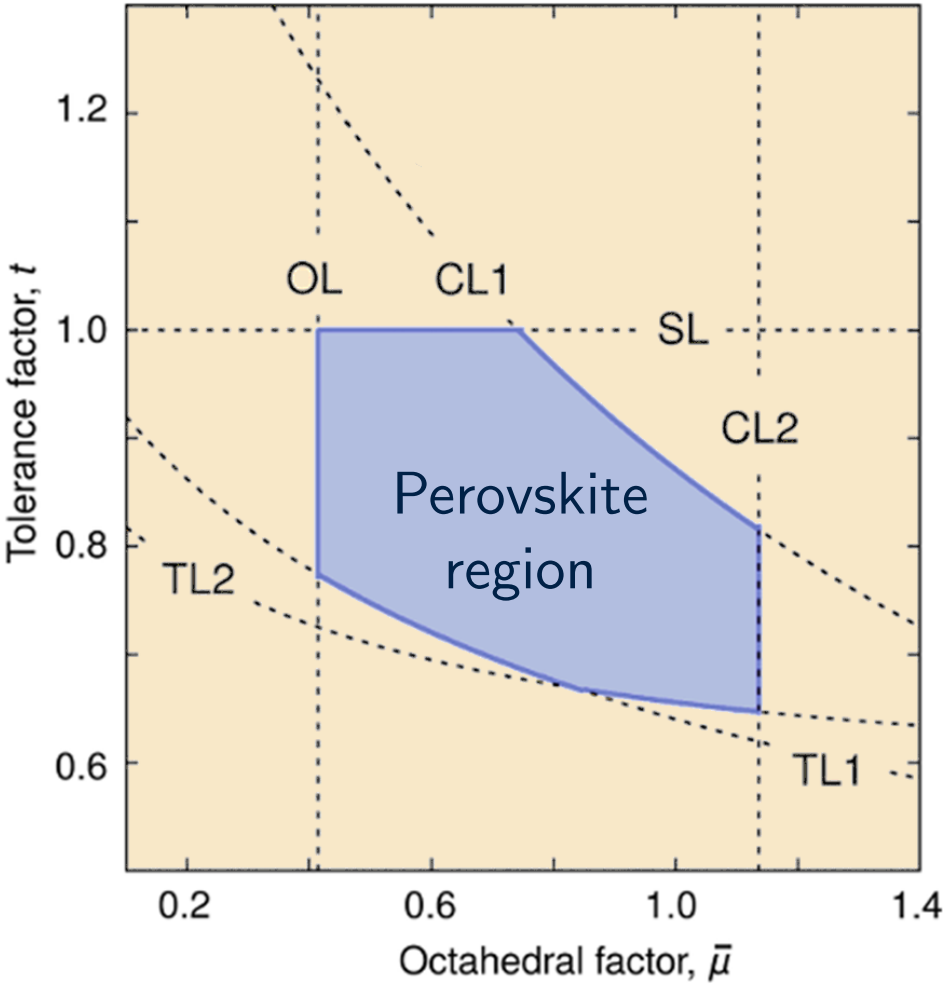
No-rattling principle in equations



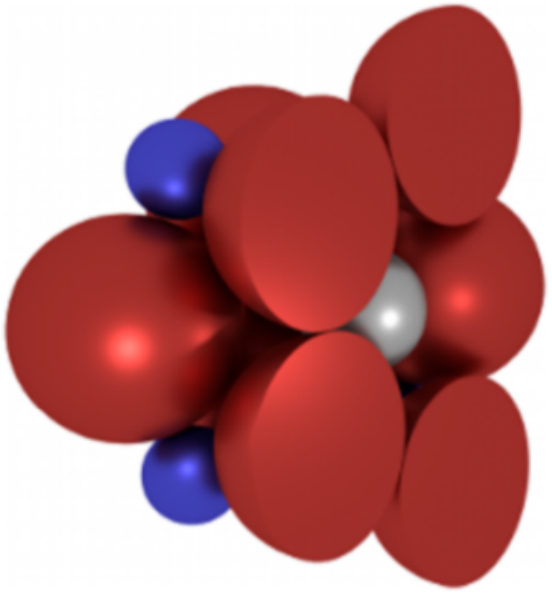
Tilt limit



No-rattling principle in equations



Tilt limit



No-rattling principle in equations

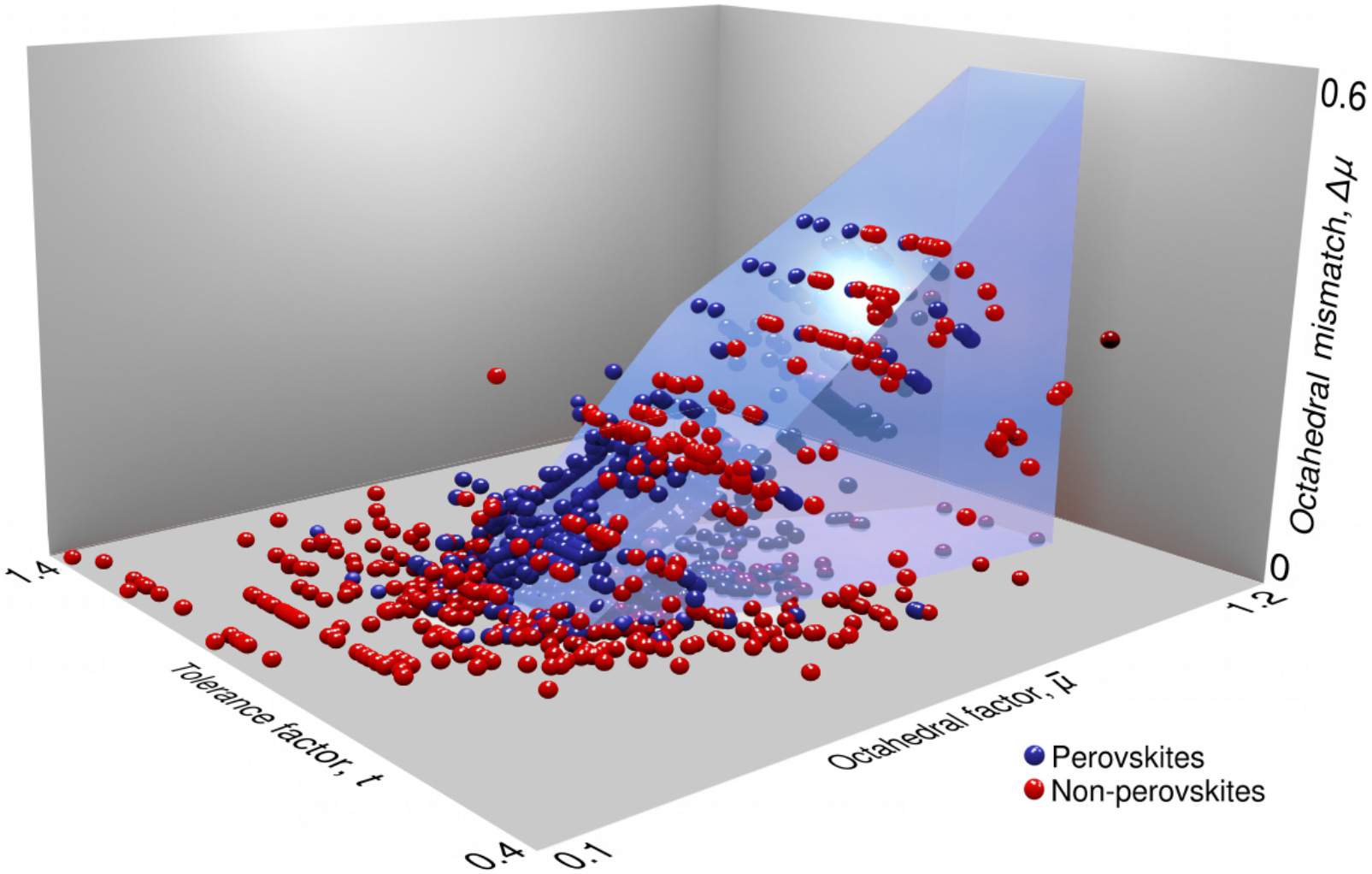
Bound type	Abbreviation	Inequality
Stretch limit	SL	$t \leq 1$
Octahedral limit	OL	$\bar{\mu} \geq \sqrt{2} - 1 + \Delta\mu$
Tilt limit	TL1	$t \geq (0.44\ \bar{\mu} + 1.37)/\sqrt{2}(\bar{\mu} + 1)$
	TL2	$t \geq (0.73\ \bar{\mu} + 1.13)/\sqrt{2}(\bar{\mu} + 1)$
Chemical limit	CL1	$t \leq 2.46/[2(\bar{\mu} + 1)^2 + \Delta\mu^2]^{1/2}$
	CL2	$\bar{\mu} \leq 1.05$

$$t = \frac{1}{\sqrt{2}} \frac{r_A + r_X}{r_B + r_X} \qquad \mu = \frac{r_B}{r_X}$$

Filip & FG, Proc Natl Acad Sci USA 115, 5397 (2018)

Classification accuracy of Goldschmidt's rules

1,622 perovskites and 669 non-perovskites



Filip & Giustino, Proc Natl Acad Sci USA 115, 5397 (2018)

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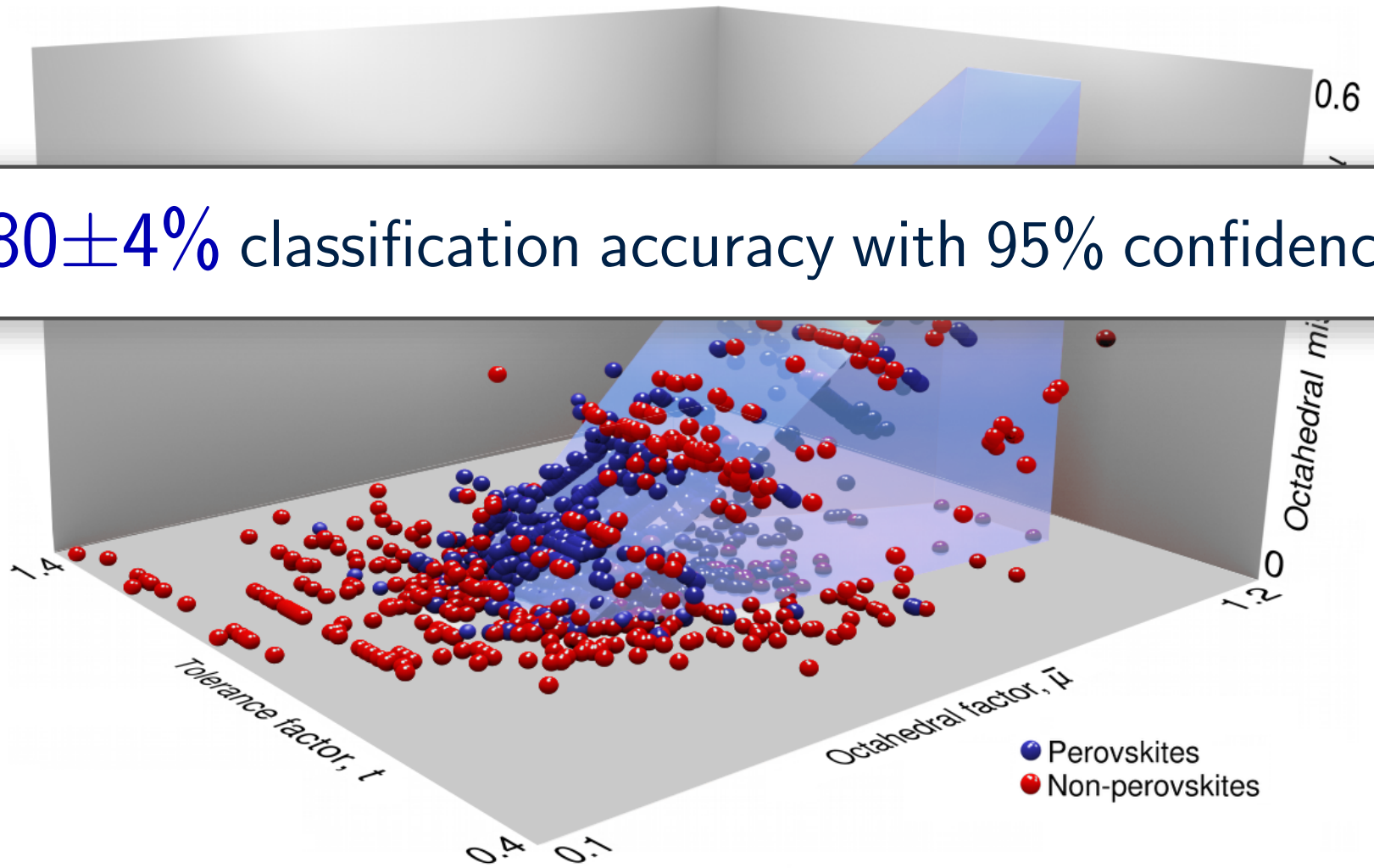

80±4% classification accuracy with 95% confidence

Filip & Giustino, Proc Natl Acad Sci USA 115, 5397 (2018)

Classification accuracy of Goldschmidt's rules

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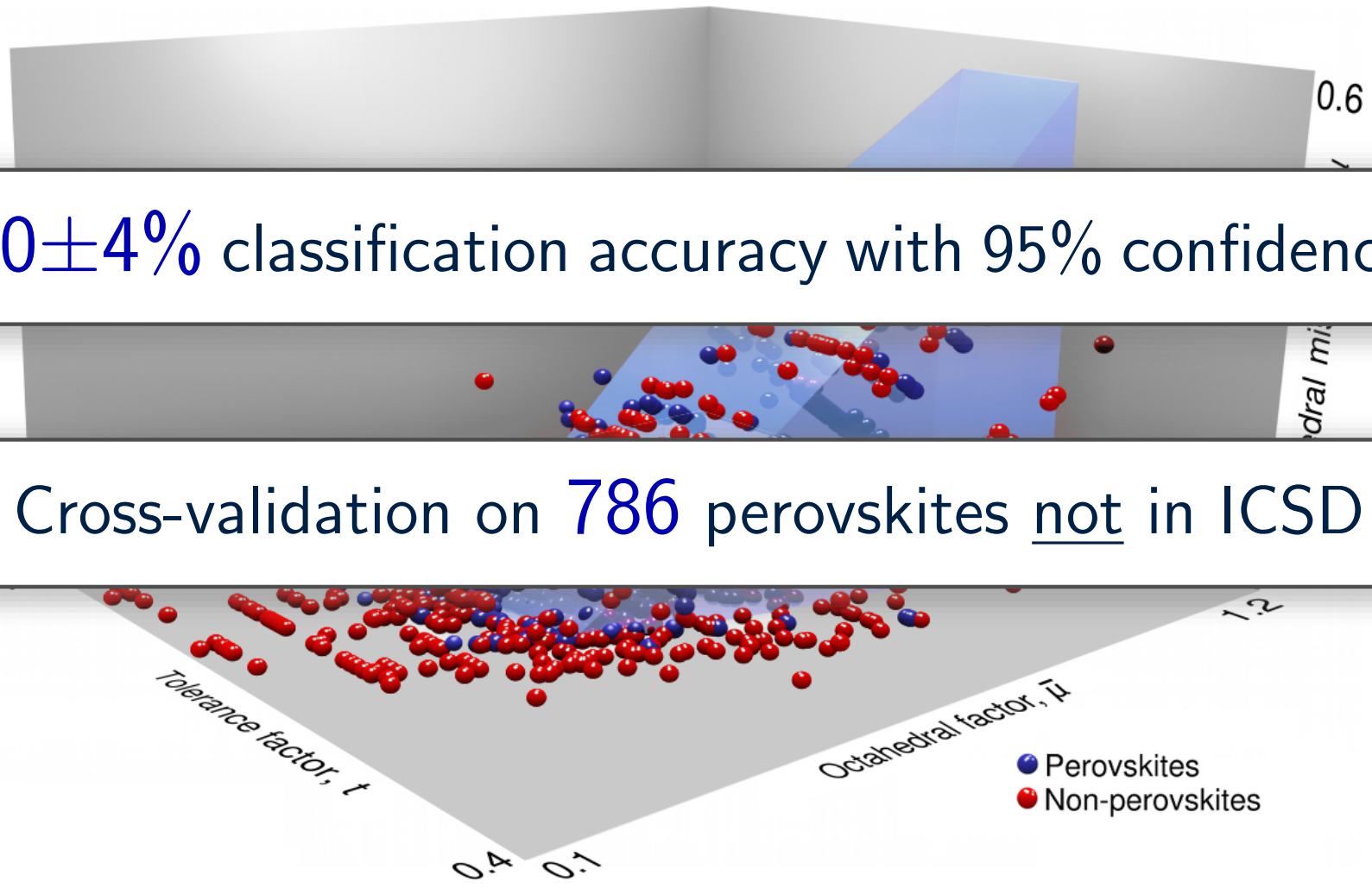


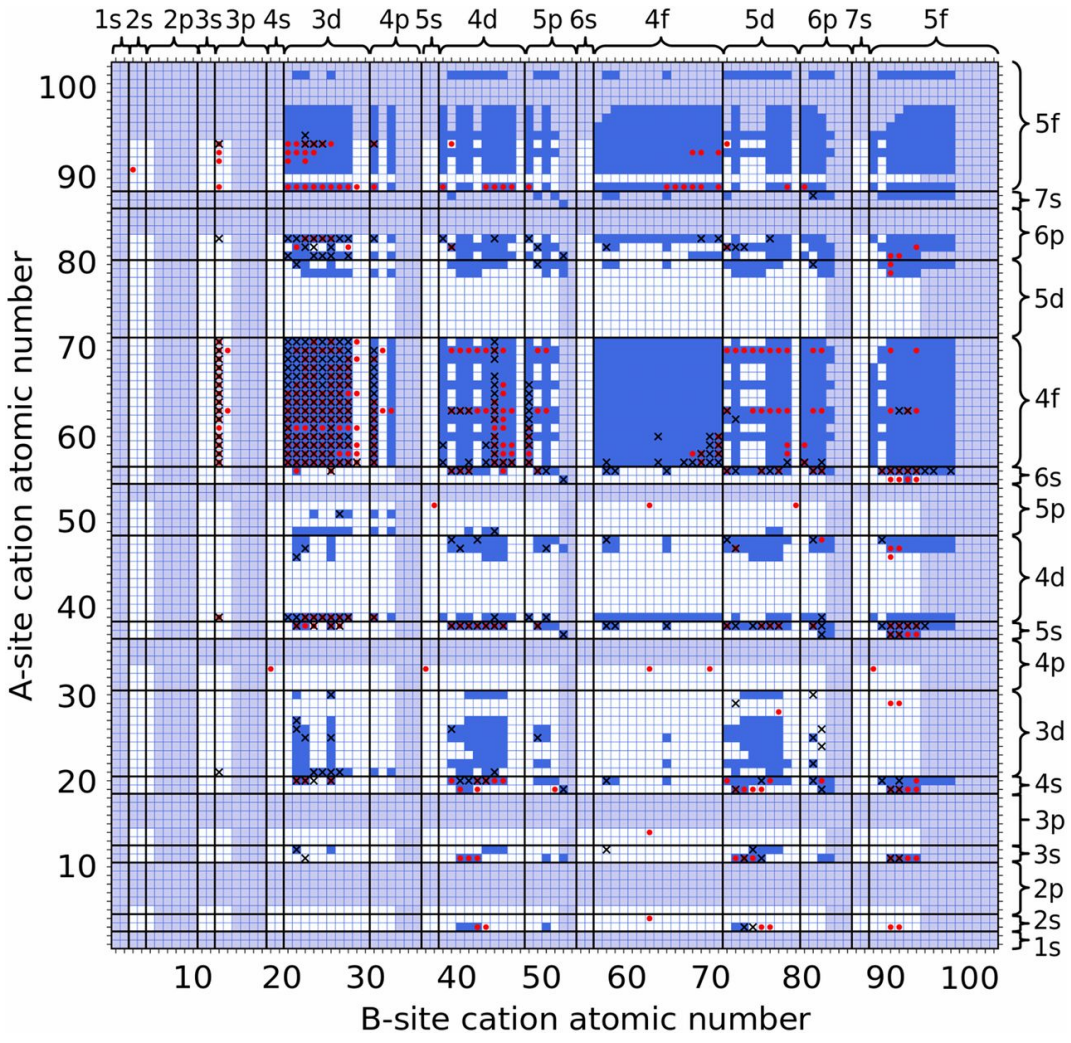
80±4% classification accuracy with 95% confidence

Cross-validation on 786 perovskites not in ICSD

Filip & Giustino, Proc Natl Acad Sci USA 115, 5397 (2018)

Comparison with DFT screening

DFT calculations from Emery et al, Chem Mater 28, 5621 (2016), ABO_3 compounds



× experiment (382 perovskites)

■ geometric model (92%)

● DFT (59%)

Screening of 4M compounds yields

94,232

perovskites

Data mining the internet

```
> w3m "http://duckduckgo.com/?q=Cs2BiAgCl6" -dump
DuckDuckGo

[Cs2BiAgCl6                              ] [Search]

1.    Band Gaps of the Lead-Free Halide Double Perovskites ...
      The recent discovery of lead-free halide double perovskites with band gaps
      in the visible represents an important ... Cs2BiAgCl6 and Cs2BiAgBr6 are
      stable compounds ...
      pubs.acs.org/doi/abs/10.1021/acs.jpclett.6b01041

2.    PDF Band Gaps of the Lead-Free Halide Double Perovskites ...
      Band Gaps of the Lead-Free Halide Double Perovskites Cs 2BiAgCl 6 and Cs
      2BiAgBr 6 from Theory and Experiment Supporting Information Marina R.
      Filip,ySamuel Hillman, zAmir Abbas Haghighirad,zHenry J. Snaith,
      pubs.acs.org/doi/suppl/10.1021/acs.jpclett.6b01041/sup...

3.    APS March Meeting 2017 - American Physical Society
      APS March Meeting 2017 Volume 62 ... In this talk we will present the
      electronic and optical properties of Cs2BiAgCl6 and Cs2BiAgBr6 calculated
      within DFT ...
      meetings.aps.org/Meeting/MAR17/Session/K34.5
```

DuckDuckGo

93,499 perovskites never reported

Data mining the internet

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DuckDuckGo

[Cs2BiAgCl6                              ] [Search]

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      meetings.aps
```

DuckDuckGo

93,499 perovskites never reported

mmdg-oxford / papers

Branch: master ▾ papers / Filip-PNAS-2018 / databases-arxiv / Database_S2.1.txt

93500 lines (93499 sloc) | 888 KB

```
1   Ac2O3
2   Ac3AmO6
3   Ac3BkO6
4   Ac3CfO6
5   Ac3CmO6
6   Ac3NpO6
7   Ac3PaO6
```

giustino.materials.ox.ac.uk

22 days left

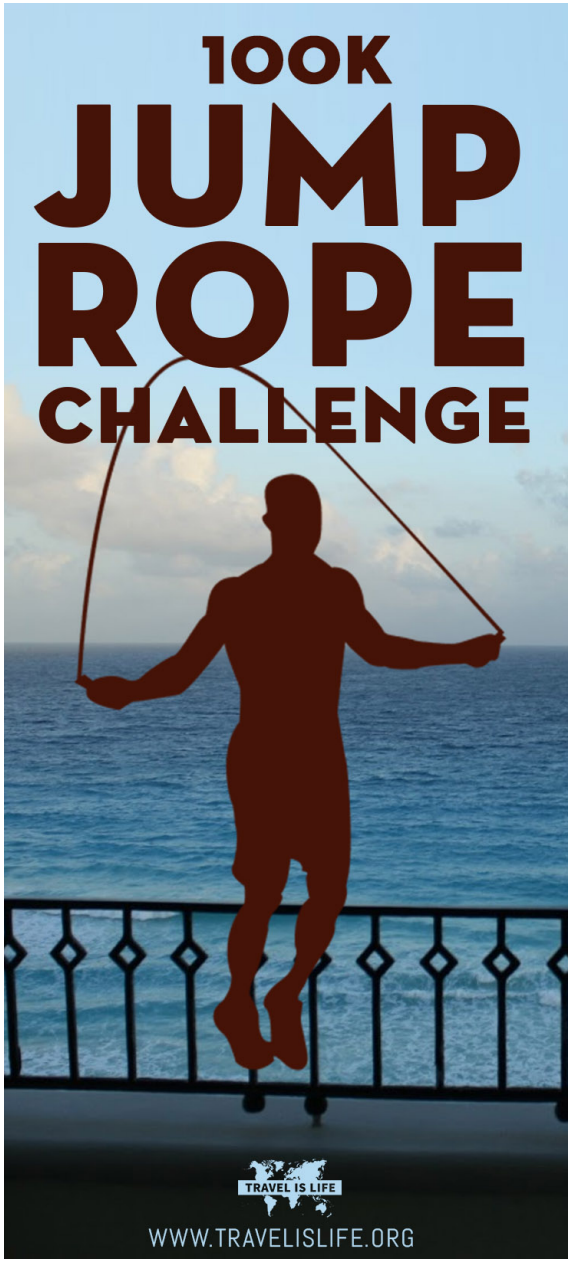
June 100K Challenge

13.24 / 62.13 MI

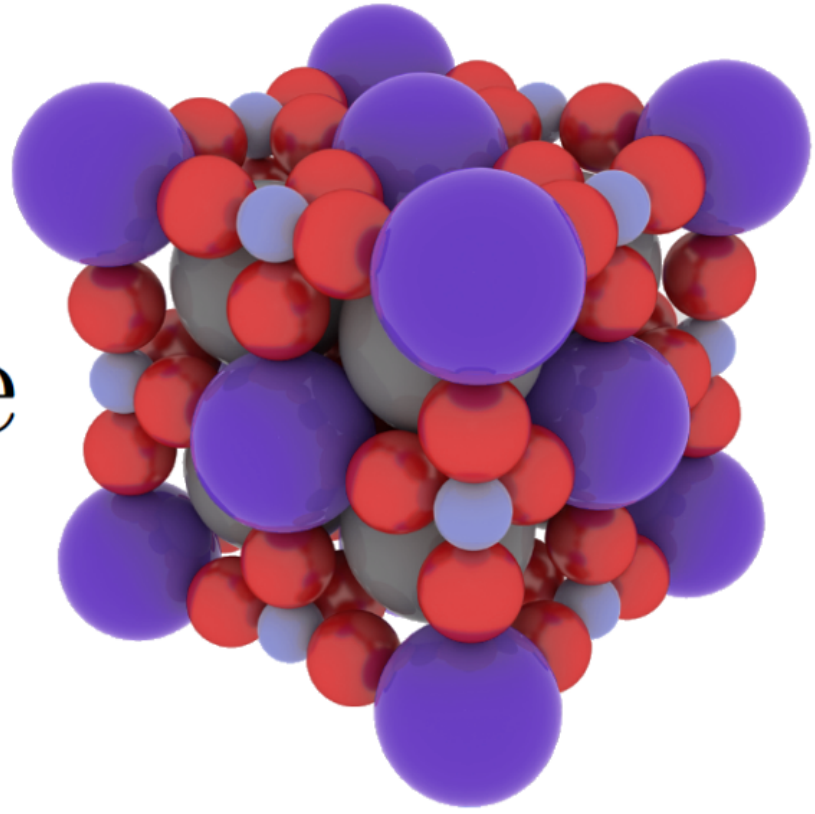
22 days left

June 100K Challenge

13.24 / 62.13 MI



100K Perovskite Challenge



Take-home messages

- The new lead-free perovskites are promising for photovoltaics and lighting
- By combining DFT and experiments we can truly make new materials for energy
- Simple concepts such as ionic radii can go a long way in materials discovery

Recommended reading

The high-throughput highway to computational materials design

S. Curtarolo, G. L. W. Hart, M. Buongiorno Nardelli, N. Mingo, S. Sanvito, O. Levy, Nature Mater. 12, 191 (2013)

https://www.nature.com/articles/nmat3568

Toward Lead-Free Perovskite Solar Cells

F. Giustino and H. J. Snaith, ACS Energy Lett. 1, 1233 (2016)

http://pubs.acs.org/doi/10.1021/acsenergylett.6b00499

Acknowledgments

Oxford Theory

George Volonakis
Marina Filip
Miguel Angel Pérez
Xinlei Liu
Samuel Poncé
Martin Schlipf
Carla Verdi

Oxford Experiments

Amir Haghighirad
Nobuya Sakai
Rebecca Milot
Jay Patel
Laura Herz
Mike Johnston
Adam Wright
Giles Eperon
Henry Snaith

Louvain Theory

Aurélie Champagne
Gian Marco Rignanese

Cambridge Experiments

Richard Phillips