Inorganic Electride from First-principles Crystal Structure Prediction and High-throughput Data Mining

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Workshop on Crystal Structure Prediction: Exploring the Mendeleev Table As a Palette to Design New Materials, 14-18, January 2019

Crystal structure prediction from the First-principles

- Define the system
- Exhaustive structure navigation
    - Evolutionary algorithm (USPEX)
    - Random search (AIRSS)
    - Minima hopping
    - Some others ……
- Intelligent analysis

The ultimate goal to do suggest new materials.
CSP solves the structure searching problem, assuming the chemistry is known!
We relies on the experts tell us which system to look at!

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How to define the chemical system?

Helium based compounds under high pressure? He-F/O or He-Na/Li

Crystal structure prediction from the First-principles

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    - Evolutionary algorithm (USPEX)
    - Random search (AIRSS)
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    - Some others ……
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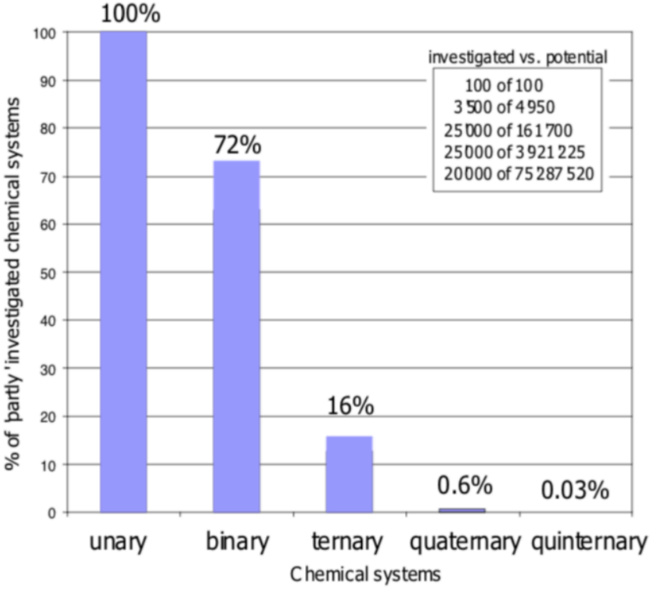
The ultimate goal to do suggest new materials.
CSP solves the structure searching problem, assuming the chemistry is known!
We relies on the experts tell us which system to look at!

If no clue about it?
Two many systems ahead of us !

Mendeleev CSP search?
Perhaps too expensive to do so in reality.

Pierre Villars
(PaulingFile)



How to suggest new materials without the help of expert?

High-throughput screening on the known materials as many as possible.

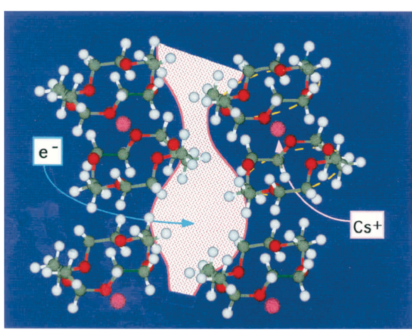
Data mining: chemical substitution to generate new materials.

CSP: generate complete new structures

Conceptually, these three important ingredients are complementary to each other. Mixing them at different levels can be useful.

Outline

I. The fundamentals of Electrides
II. The Rule for Design & Analysis
III. Binary Electrides from CSP + DM
IV. Full Database Screening from HT



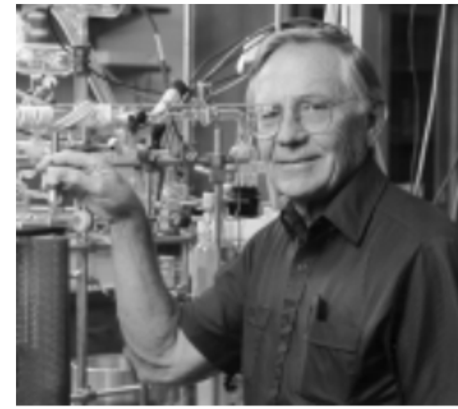
CSP+DM+HT

Many new materials in a wide chemical space.

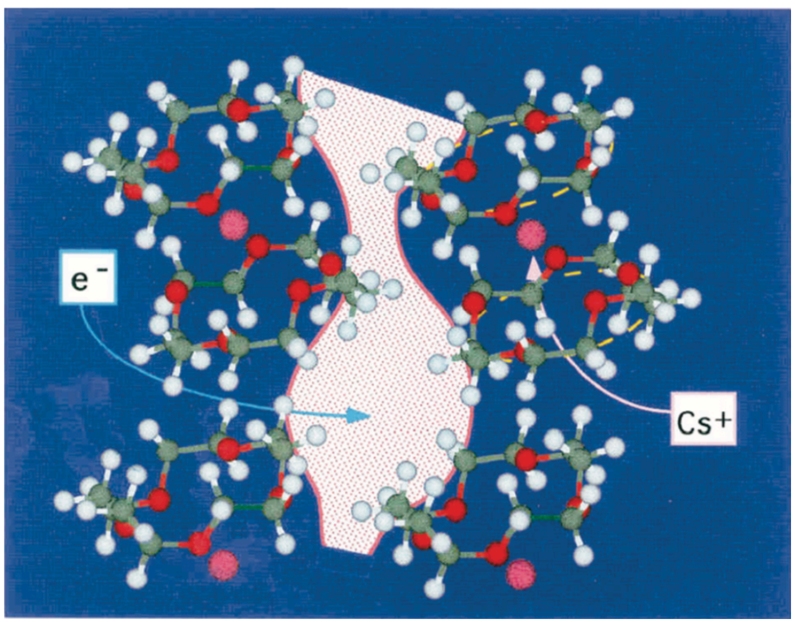
I. The Fundamentals of Electride

Electride (1983-present)

- Ionic solids
- Interstitial electrons
- Stoichiometric



J. L. Dye, MSU



encapsulation of the alkali *cation* within a complex matrix

Pros:
Low work function
Reducing agents
Catalytic

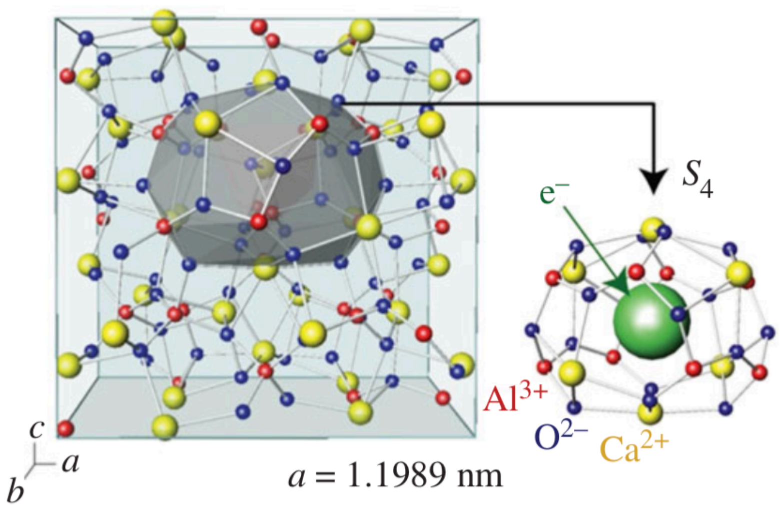
Cons:
Thermal instability
Air/water sensible

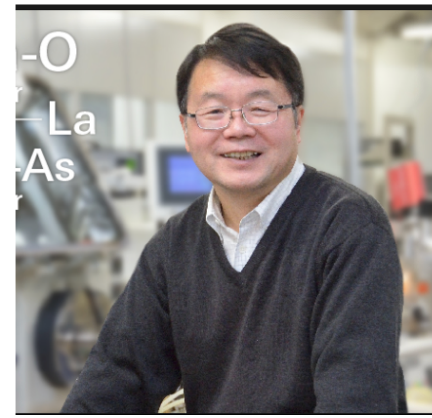
Ellaboudy & Dye, JACS, 1983,
Dye, Acc. Chem. Res. 2009

Inorganic Electride (2003-present)

- Ionic solids
- Interstitial electrons
- Stoichiometric

$12CaO.7Al_2O_3$





Hiedo Hosono

Pros:
Low work function
Reducing agents
Catalytic

Cons:
Thermal stability
Air/water sensitivity

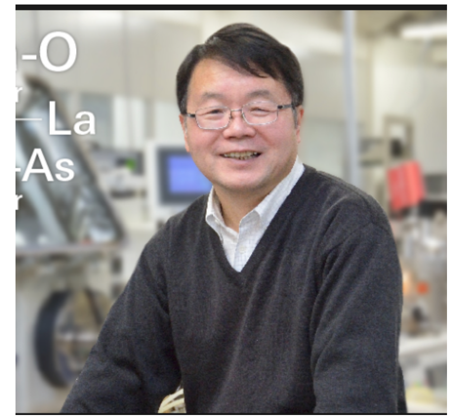
Reductive replacement of cavity-trapped O^{2-} ion by electrons,

Through high temperature reduction with Ca

Matsuishi, et al, Science, 2003
Kitano, et al, Nat. Chem, 2012

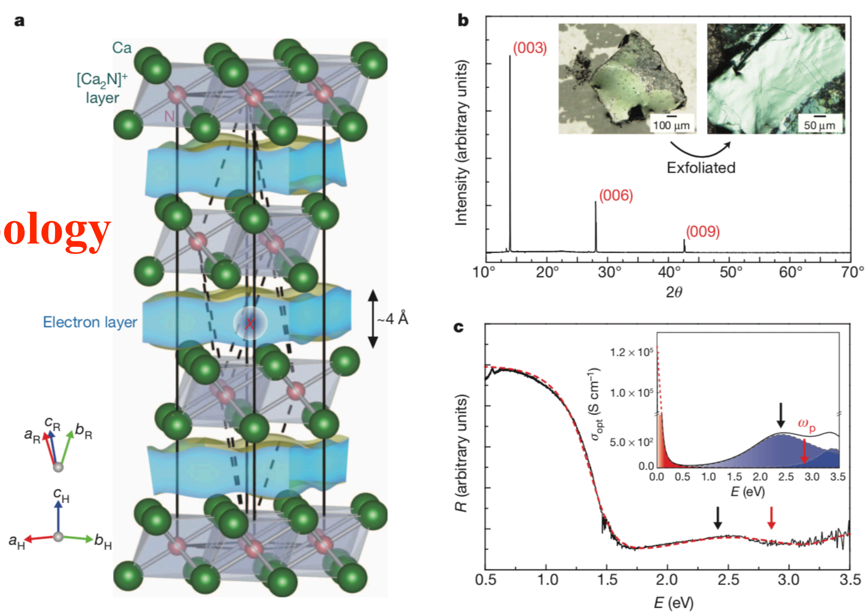
Inorganic Electride (2003-present)

- Ionic solids
- Interstitial electrons
- Stoichiometric



Hiedo Hosono

new topology



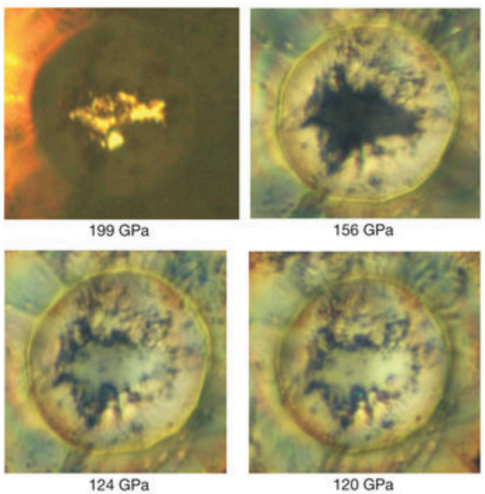
Ca_2N

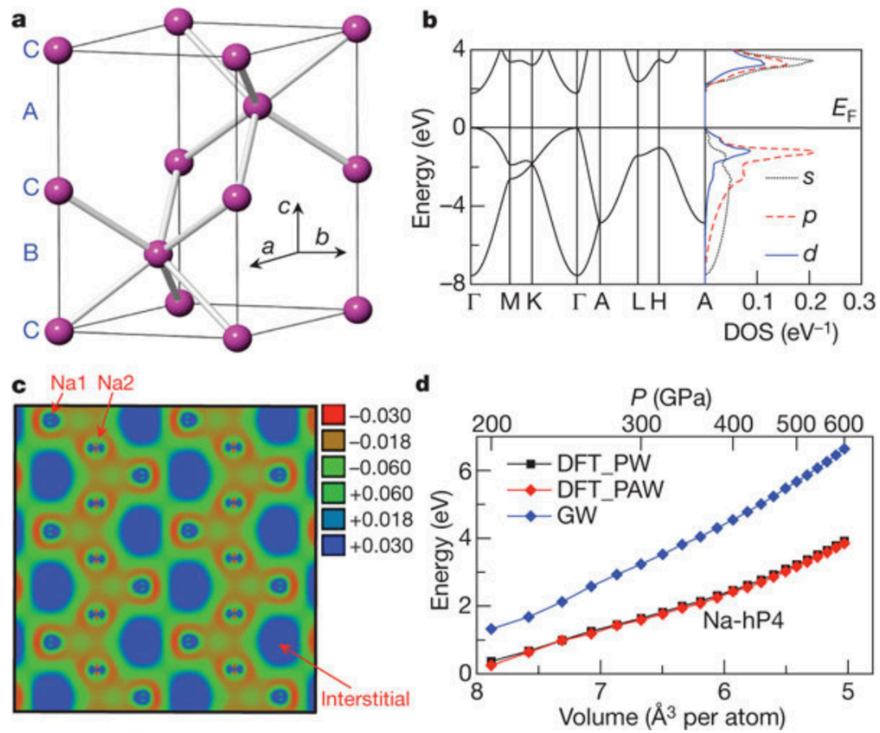
- First electride with 2D interstitial electrons
- Lower work function
- High electron mobility
- 2D electronic device

Lee, et al, Nature, 2012

High Pressure Electrides (2001-present)

- Firstly found on several simple metals (Li, Ca, K, Mg, .etc)
- Also in some compounds (Mg_3O_2, $NaHe_2$, .etc)
- Ambient electride phases (Ca_2N) also have recent structural behavior under pressure
- viable behaviors (metal, semiconductor, insulator, superconductor, magnet)



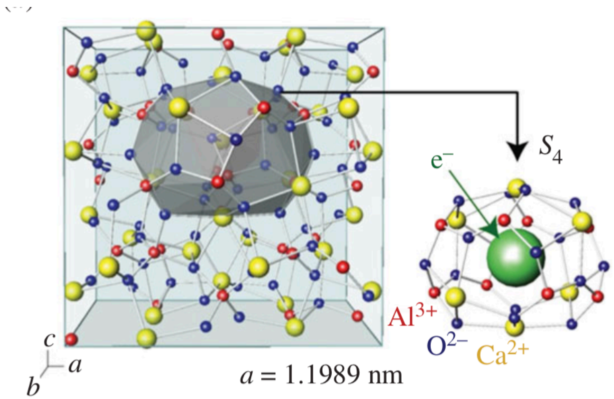


Rousseau & Ashcroft, PRL, 2008
Ma, Eremet, Oganov, Nature, 2009
Pickard, PRL, 2011
Zhu & Oganov, PCCP, 2013
Miao & Hoffman, Acc. Chem. Res., 2014
Dong, et al, Nat. Chem, 2017
Zhang et al, JACS, 2017

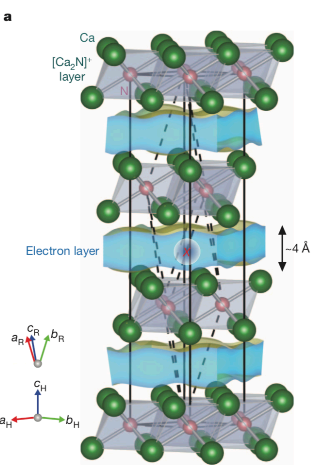
II. The Design Rules & Analysis

Synergy between Expt. & Theory

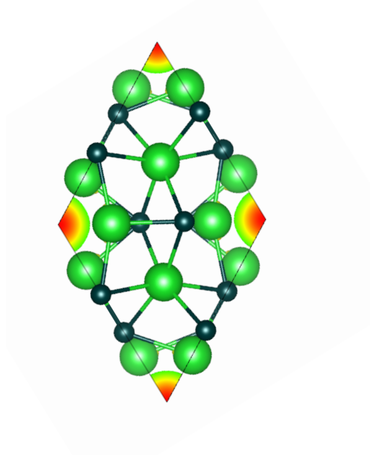
C12A7

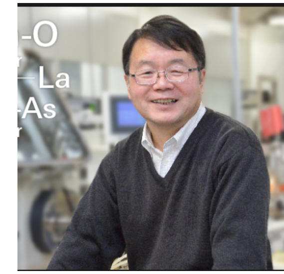


Ca_2N

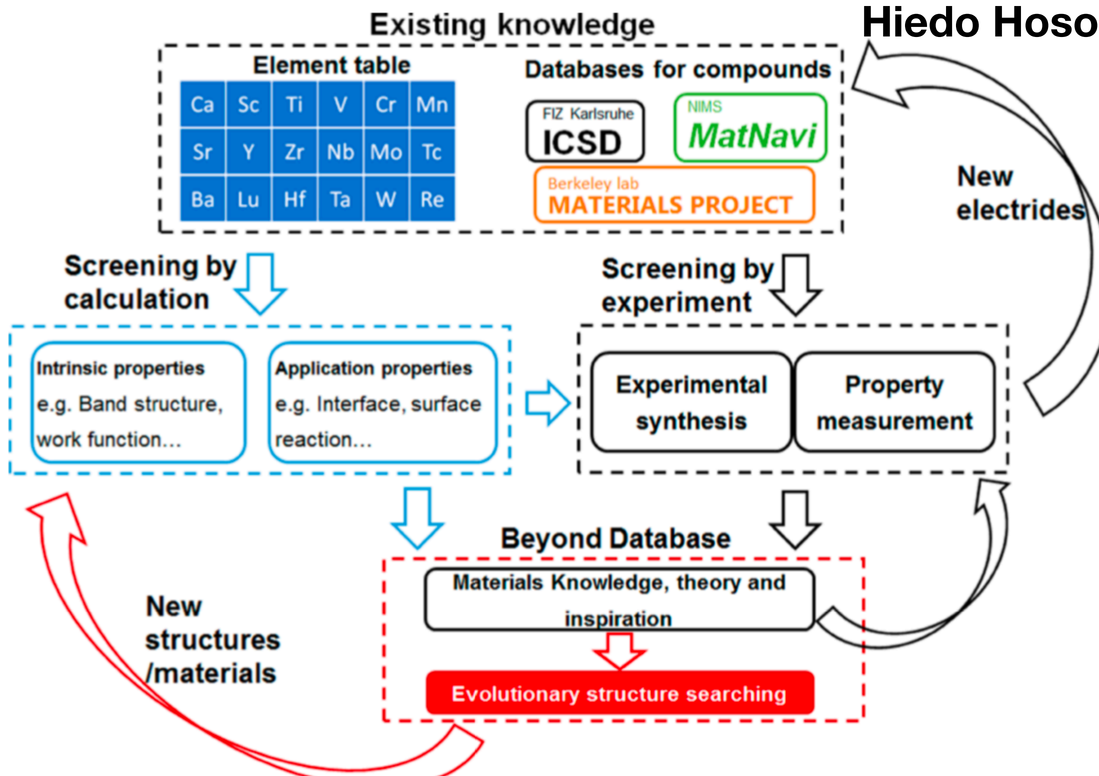


Y_5Si_3





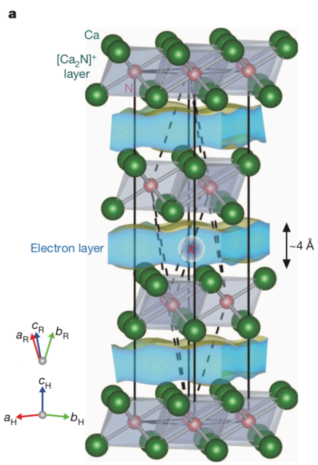
Hiedo Hosono



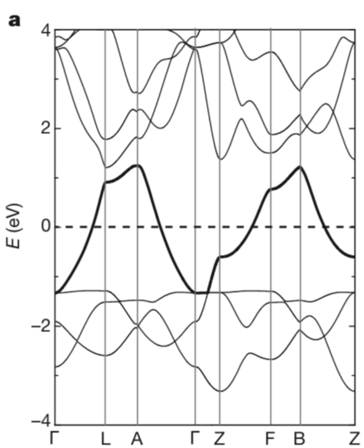
Matsushi, et al, Science, 2003
Lee, et al, Nat. Chem, 2013
Lu, et al, JACS, 2016

Others include: LaScSi, La(Ce, Y)H_2, $La_8Sr_2(SiO_4)_6$

Synergy between Expt. & Theory



Ca_2N



Existing knowledge

Element table

Ca	Sc	Ti	V	Cr	Mn
Sr	Y	Zr	Nb	Mo	Tc
Ba	Lu	Hf	Ta	W	Re

Databases for compounds

FIZ Karlsruhe ICSD

NIMS MatNavi

Berkeley lab MATERIALS PROJECT

Known Materials with same structures → HT screening → *Inoshita, PRX, 2014* $(Sr/Ba)_2N$, $(Y/Tb/Ho/Dy)_2C$,

unknown Materials with same structures → Substitution → *Tada, Inorg Chem., 2014* $(Sr/Ba)_2N$, $(K/Rb)_2(Br/Cl)$

unknown Materials with similar chemistries → CSP on many binaries → *Weng, JACS, 2017* *Wang, JACS, 2017*

Select the candidate structures, and then analyze each !

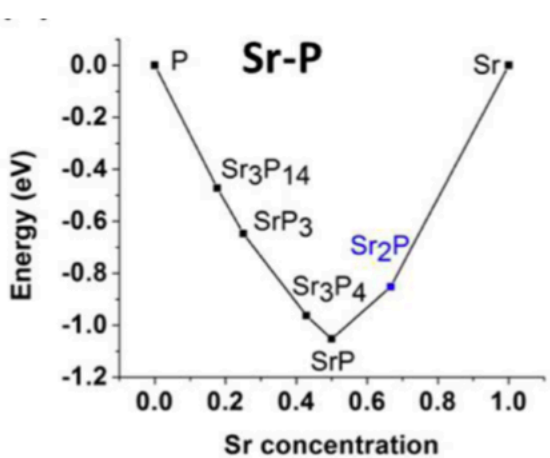
CSPs: Fixed or Variable composition

Weng et al, JACS, 2017
(CALYPSO)

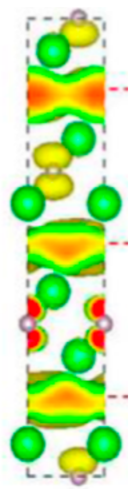
Wang et al, JACS, 2017
(USPEX)

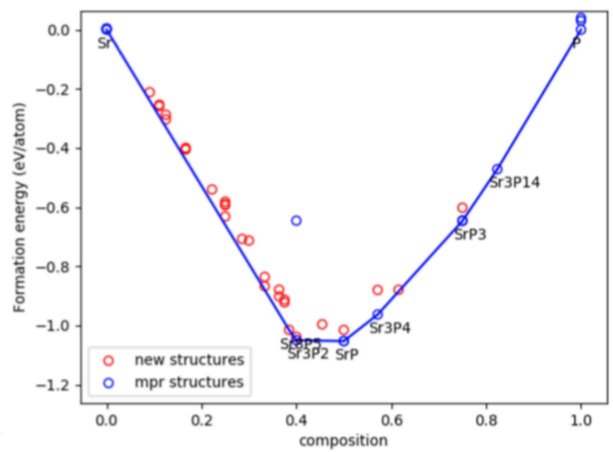
Fixed composition CSP search on Sr_2P (and other binaries)

Fixed composition CSP search on Sr-P

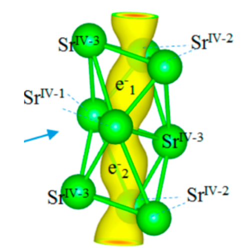


Sr_2P

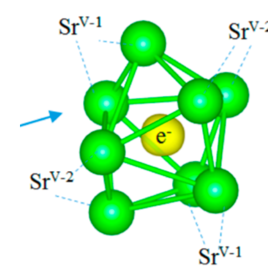




Sr_5P_3



Sr_8P_5



Sr_2P is slightly unstable relative to the convex hull.
Shall we consider it?

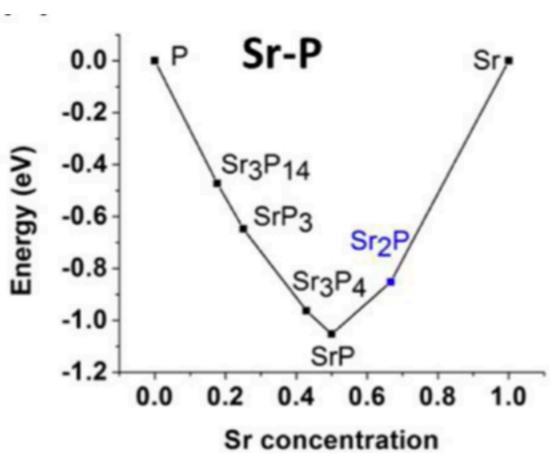
CSPs: Fixed or Variable composition

Weng et al, JACS, 2017
(CALYPSO)

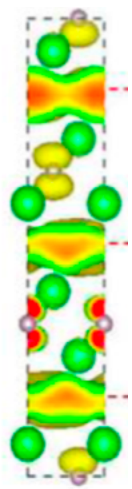
Fixed composition CSP search on Sr_2P (and other binaries)

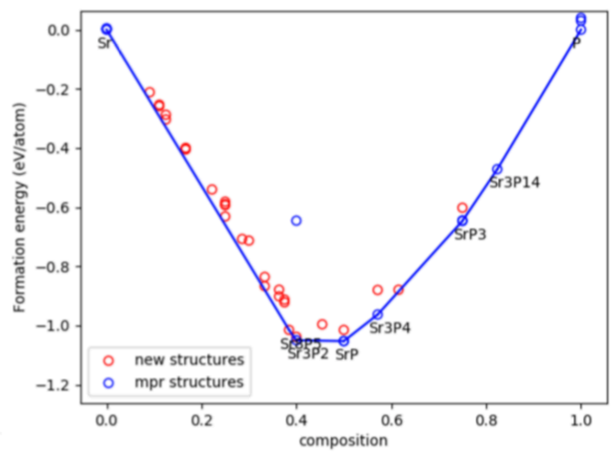
Wang et al, JACS, 2017
(USPEX)

Fixed composition CSP search on Sr-P

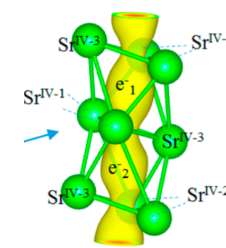


Sr_2P

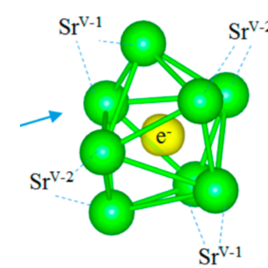




Sr_5P_3



Sr_8P_5



If we are also interested in the metastable structures,
We need to check many structures if they are electrides.

Identify the Electrides for Many structures

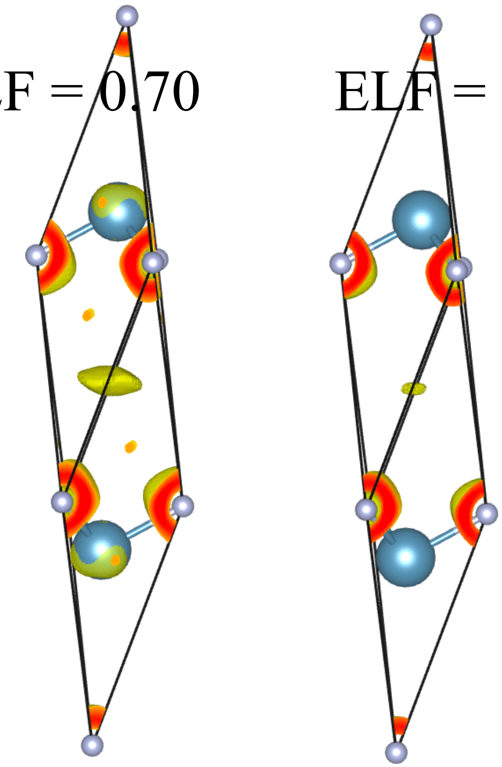
Describe the interstitial electrons occupying DOS close (across) E_F

1, ELF analysis

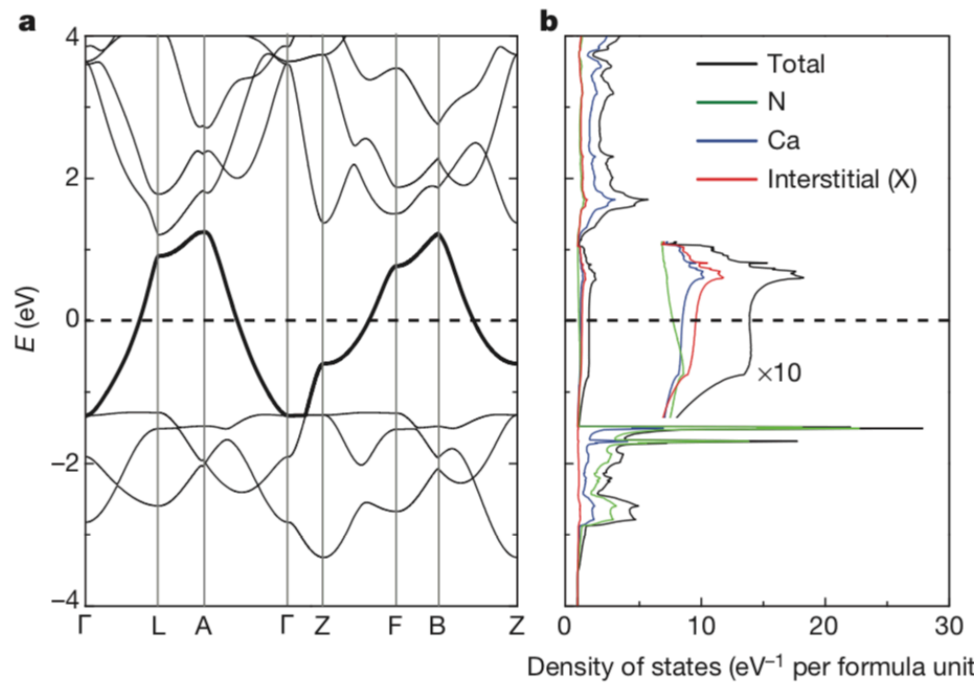
2, PDOS analysis

ELF = 0.70

ELF = 0.75



Ca_2N



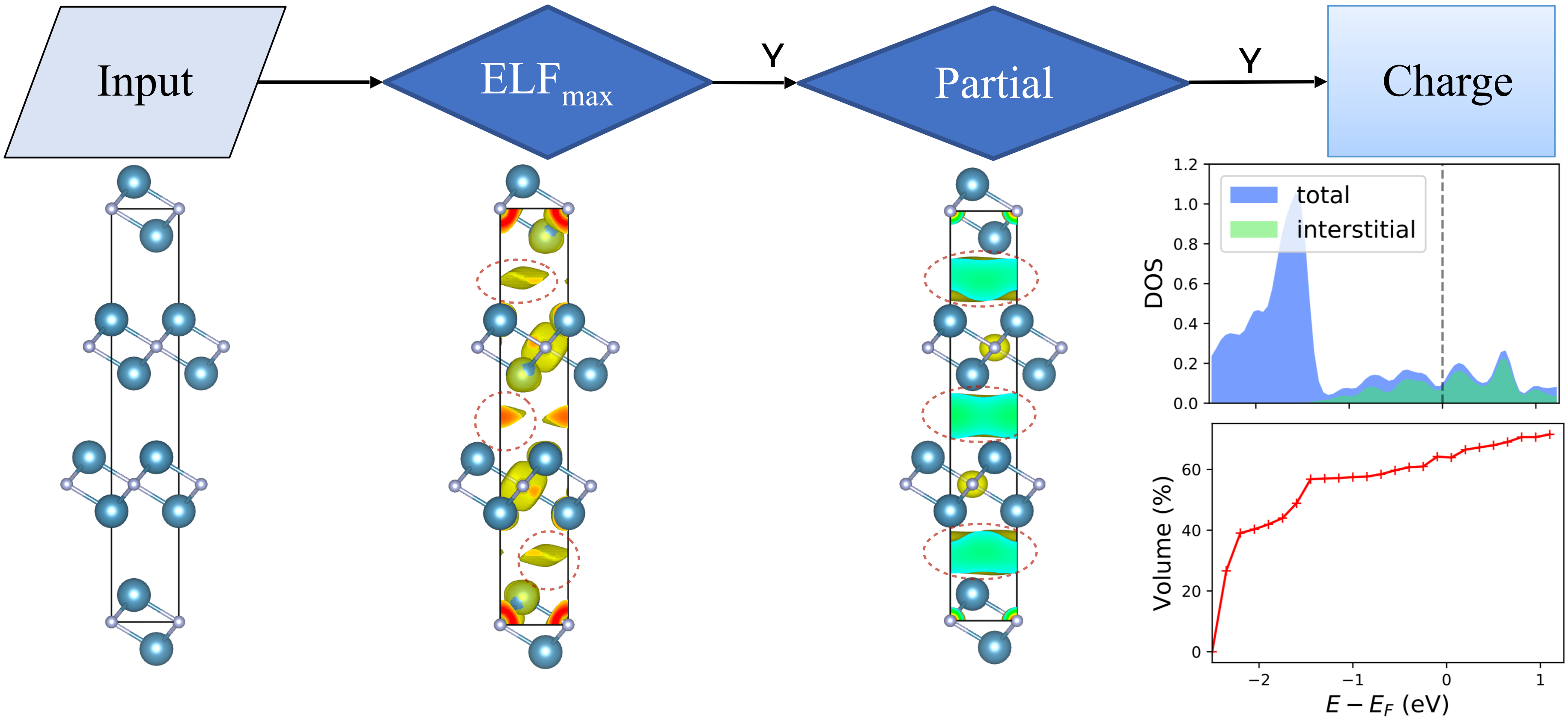
$\Omega(\mathrm{ELF}_{0.75})$

DOS_X (E_F) > 50%

Zhang et al, PRX, 2017

Burton et al, Chem. Mater, 2018

We develop a new descriptor



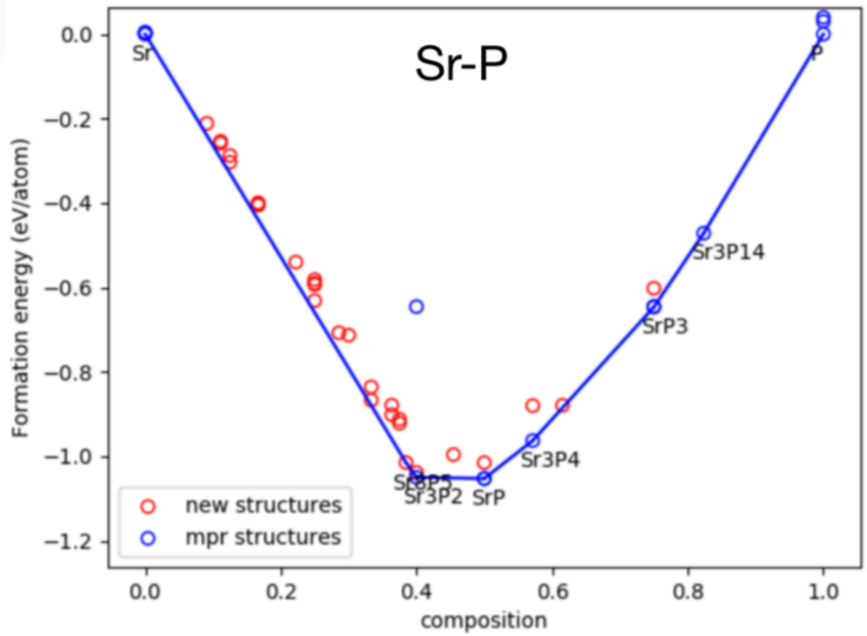
- Simultaneous analysis on ELF/charge info
- Computationally affordable
- More robust than the previous approaches

Zhu & Frolov, arXiv, 2018

III. Binary Electrides from CSP + DM

A trial CSP on Sr-P by USPEX

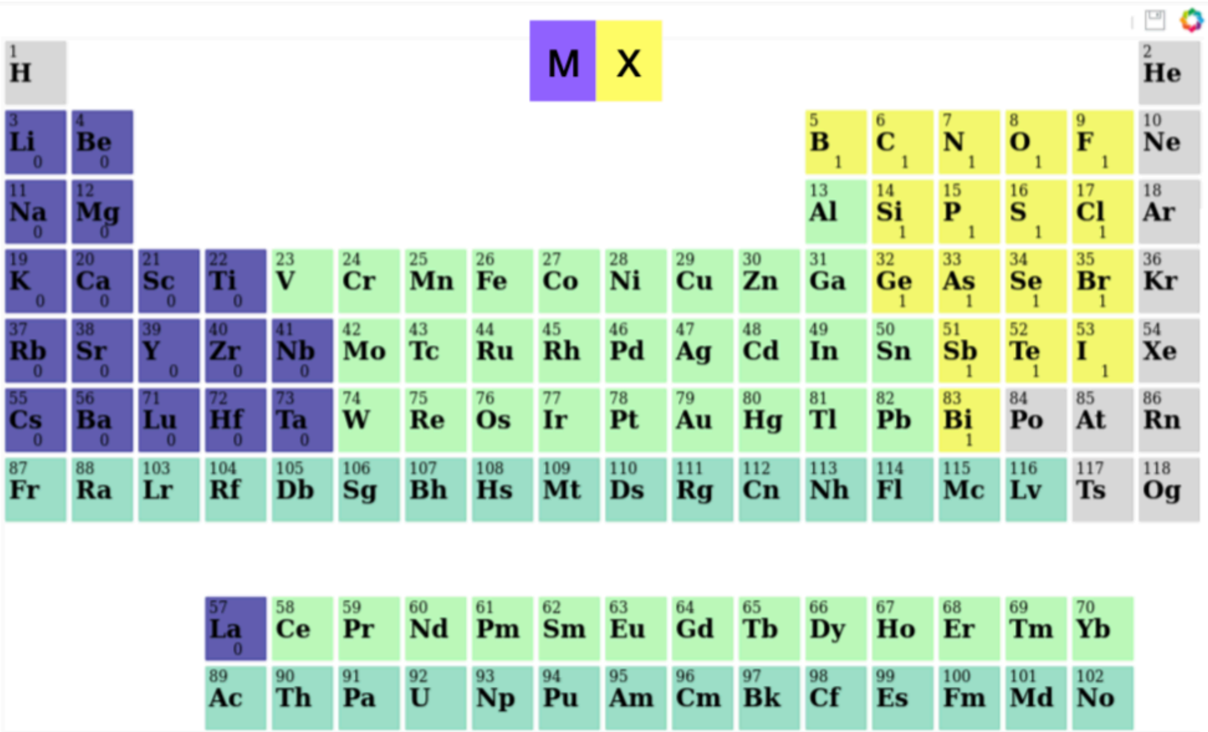
	Formula	Space group	Prototype	Source	Composition	Formation energy (eV/atom)	e_above_hull (eV/atom)
0	Sr5P8	C2/m	Ca5P8	own	0.615385	-0.879451	0.005801
1	Sr8P5	I-4	new	own	0.384615	-1.015240	0.000000
2	SrP	P-62m	EuAs	mpr	0.500000	-1.052954	0.000000
3	Sr2P	Fdd2	new	own	0.333333	-0.867195	0.012680
4	Sr10P	C2/m	new	own	0.090909	-0.211559	0.028407
5	Sr6P5	Cm	new	own	0.454545	-0.996288	0.055424
6	Sr7P4	C2/m	new	own	0.363636	-0.901736	0.058127
7	Sr7P4	Cm	new	own	0.363636	-0.879277	0.080587
8	Sr7P3	Cm	new	own	0.300000	-0.713190	0.078697
9	Sr8P	P4/mmm	new	own	0.111111	-0.253788	0.039503
10	Sr8P	C2/m	new	own	0.111111	-0.258493	0.034799
11	Sr3P	C2/m	MoCl3	own	0.250000	-0.631493	0.028413
12	SrP3	P-1	new	own	0.750000	-0.602179	0.044731
13	SrP	P6_3/mmc	NaS	own	0.500000	-1.015396	0.037558
14	Sr7P	Cm	new	own	0.125000	-0.303570	0.026383
15	Sr5P3	Cm	new	own	0.375000	-0.922124	0.067735
16	Sr3P	R32	new	own	0.250000	-0.593473	0.066433
17	Sr3P	I4/mmm	new	own	0.250000	-0.590381	0.069525
18	Sr5P3	C2/m	new	own	0.375000	-0.912738	0.077121
19	Sr7P	R-3	new	own	0.125000	-0.287604	0.042349
20	Sr5P	Cm	new	own	0.166667	-0.399585	0.040352
21	Sr2P	P2_1/m	new	own	0.333333	-0.836071	0.043804
22	Sr5P	C2/m	new	own	0.166667	-0.405096	0.034841
23	Sr5P	I4/m	UF5	own	0.166667	-0.402246	0.037691
24	Sr7P2	C2/m	new	own	0.222222	-0.540275	0.046308
25	Sr5P2	C2/m	new	own	0.285714	-0.707654	0.046524
26	Sr3P4	Cm	new	own	0.571429	-0.880164	0.082914
27	Sr3P2	P-3m1	La2O3	own	0.400000	-1.038737	0.011483
28	Sr3P	C2/m	new	own	0.250000	-0.581662	0.078244



A lot of low energy structures are not counted by the existing database

Search in an extended chemical space

- From Materials Project, we search for all MX
- We take the advantage of both structures from CSP and MP



19*16 = 304 binaries

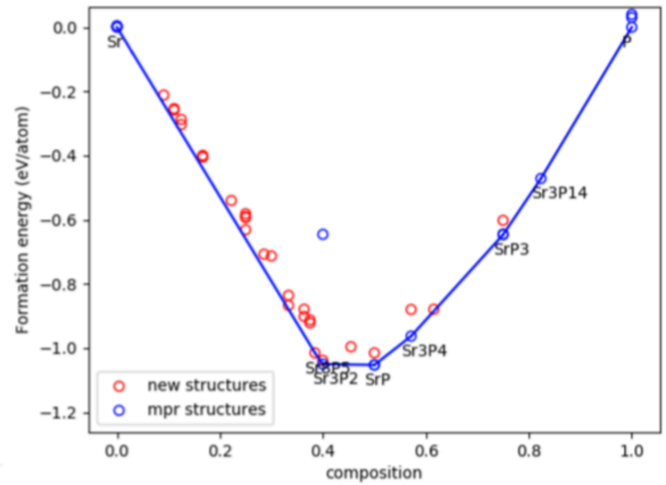
CSP + Data Mining

Crystal Structure Search

USPEX

Li-O
Sr-N
Sc-C
Cs-F
Hf-N
....

20 binaries, from Junjie Wang



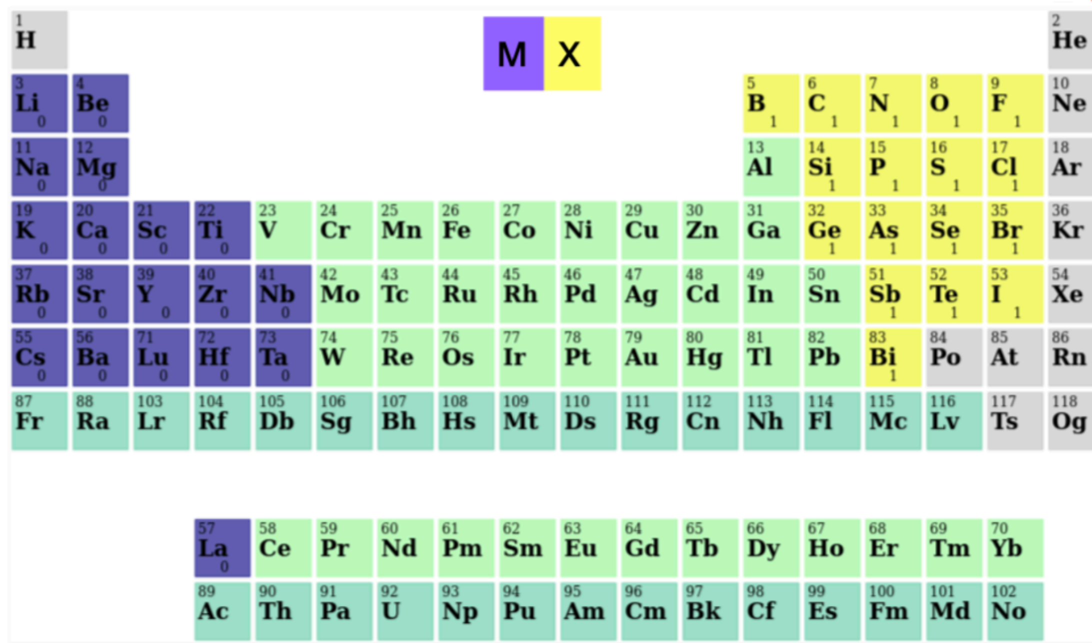
Low energy structures

< 0.1 eV/atom

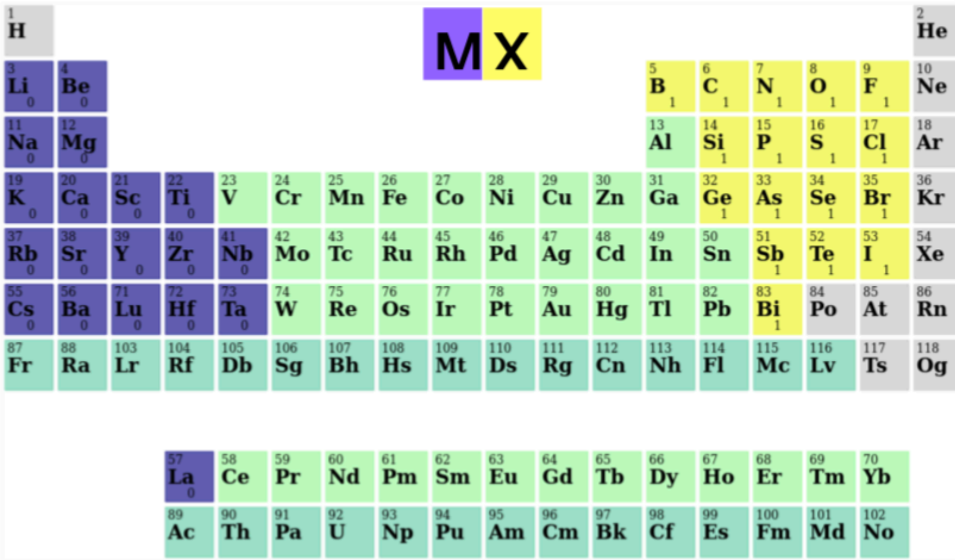
"Data mining"

< 0.15 eV/atom

~6000 structures



The Binary Electride Database



- Combining first principles crystal structure predictions and data mining, we obtained ~6000 structures, of which about ~2000 are energetically favorable
- Of ~2000 low energy structures, we found 147 new stable compounds and 753 low energy compounds
- A certain fraction of structures resembles new prototypes which haven't been found in ICSD database.

The Binary Electride Database

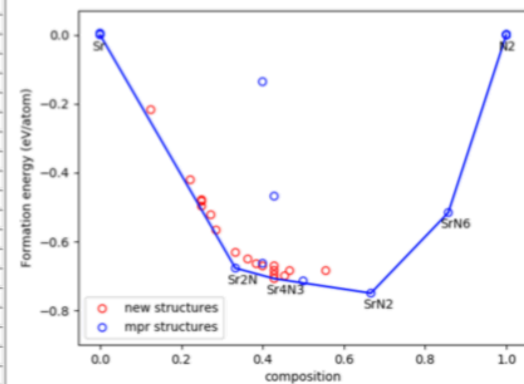
UNLV_db.py

```
$ python UNLV_db.py -h
Usage: UNLV_db.py [options]

Options:
  -h, --help show this help message and exit
  -s system, -system=system, quick search by
system, e.g., Sc-N
  -i materials id, --id=materials id, quick
search by id
```

python UNLV_db.py -s Sr-N

Formula	Space group	Prototype	Source	Composition	Formation energy (eV/atom)	e_above_hull (eV/atom)	Electride
Sr2N	R-3m	Ca2N	mpr	0.3333	-0.6771	0.0000e+00	True
Sr5N2	C2/m	new	USPEX	0.2857	-0.5666	1.3780e-02	True
Sr3N	P-1	new	USPEX	0.2500	-0.4820	2.5828e-02	True
Sr8N5	C2/m	new	USPEX	0.3846	-0.6641	2.9259e-02	True
Sr3N	C2/m	MoCl3	USPEX	0.2500	-0.4785	2.9304e-02	True
Sr7N2	P-1	new	USPEX	0.2222	-0.4207	3.0707e-02	True
Sr8N3	C2/m	new	USPEX	0.2727	-0.5222	3.1818e-02	True
Sr4N3	P-1	new	USPEX	0.4286	-0.6704	3.7035e-02	True
Sr4N3	P-1	new	USPEX	0.4286	-0.7074	0.0000e+00	False
SrN6	Fddd	SrN6	mpr	0.8571	-0.5159	0.0000e+00	False
Sr	Fm-3m	Fe	mpr	0.0000	0.0000	0.0000e+00	False
N2	P2_13	Li	mpr	1.0000	0.0000	0.0000e+00	False
N2	Pa3	N2	mpr	1.0000	0.0000	0.0000e+00	False
N2	R-3c	N2	mpr	1.0000	0.0000	0.0000e+00	False
N2	P6_3/mmc	Ti	mpr	1.0000	0.0000	0.0000e+00	False
N2	P4_2/mnm	N2	mpr	1.0000	0.0000	0.0000e+00	False
N2	I2_13	C	mpr	1.0000	0.0000	0.0000e+00	False
N2	P6_3/mmc	Br	mpr	1.0000	0.0000	0.0000e+00	False
N2	C2/m	new	mpr	1.0000	0.0000	0.0000e+00	False
SrN2	I4/mmm	CaC2	mpr	0.6667	-0.7496	2.7756e-17	False
Sr	P6_3/mmc	Ti	mpr	0.0000	0.0012	1.2480e-03	False
Sr	P6_3/mmc	Nd	mpr	0.0000	0.0033	3.2781e-03	False
Sr	Im-3m	Sn	mpr	0.0000	0.0044	4.4475e-03	False
SrN	C2/m	SrN	mpr	0.5000	-0.7141	5.9403e-03	False
Sr3N	P6_3/mcm	RuCl3	USPEX	0.2500	-0.4971	1.0681e-02	False
Sr4N3	P2/m	new	USPEX	0.4286	-0.6960	1.1431e-02	False
Sr6N5	P-1	new	USPEX	0.4545	-0.6991	1.2873e-02	False

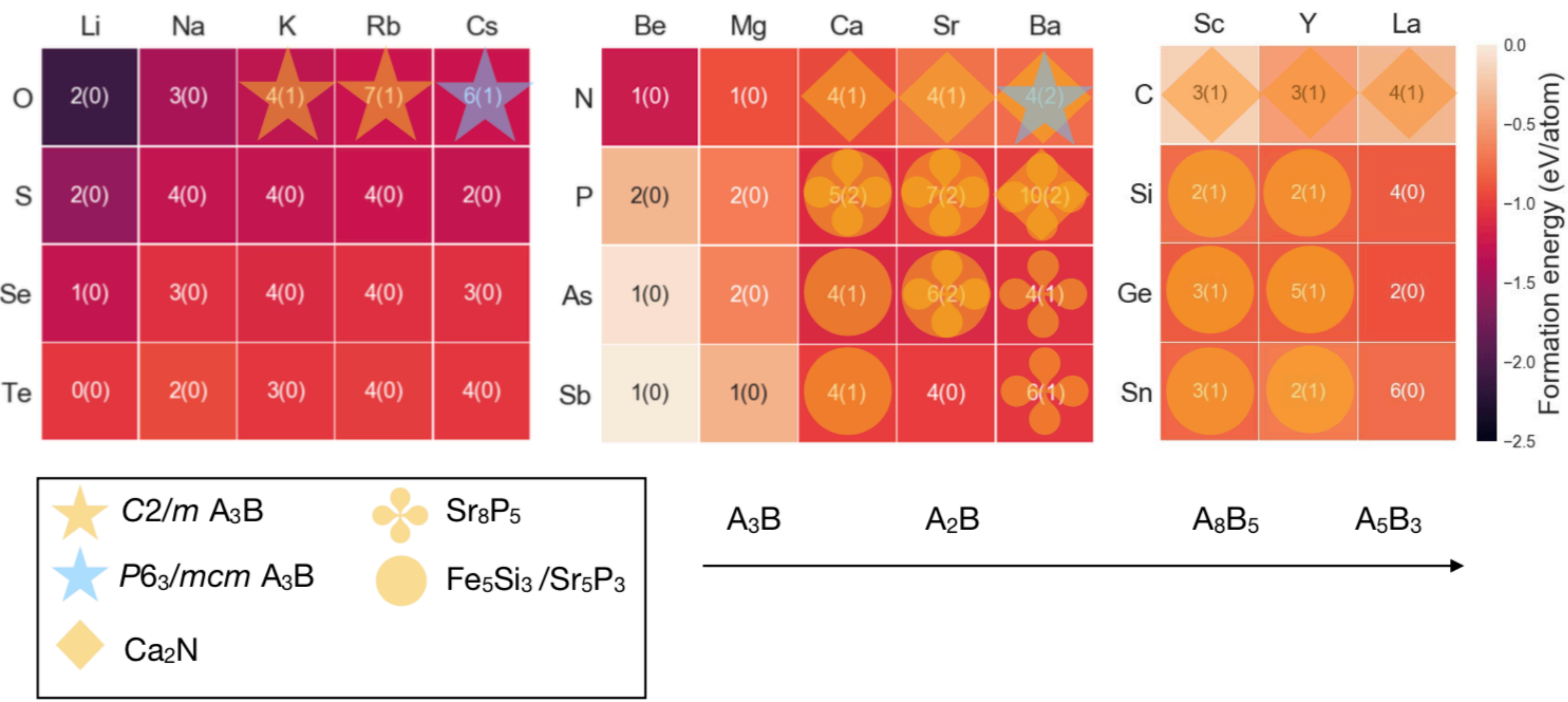


python UNLV_db.py -i [materials_id]

- Cif file
- Vasp POSCAR file
- Vasp INCAR file for PARCHG analysis

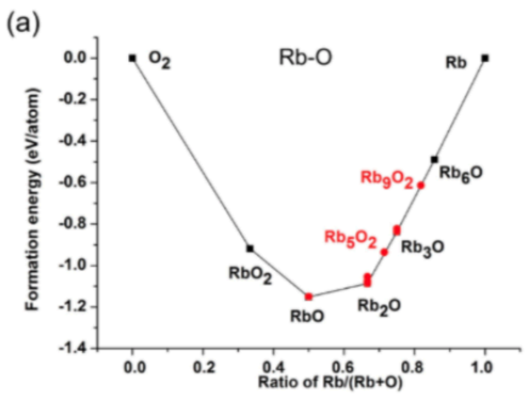
Among the short list of ~2000 low energy structures, we identified 364 potential electrides (35 from materials project, 329 from prediction)

Distribution of stable electrodes

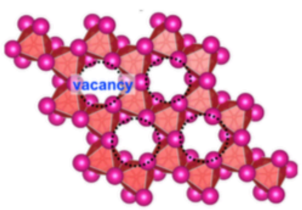


Zhu, Wang, Chen & Zhu, arXiv, 2018

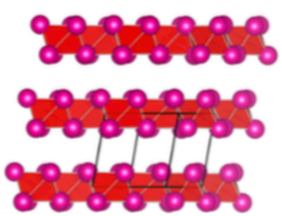
Example 1: Flexible Electride Rb_3O

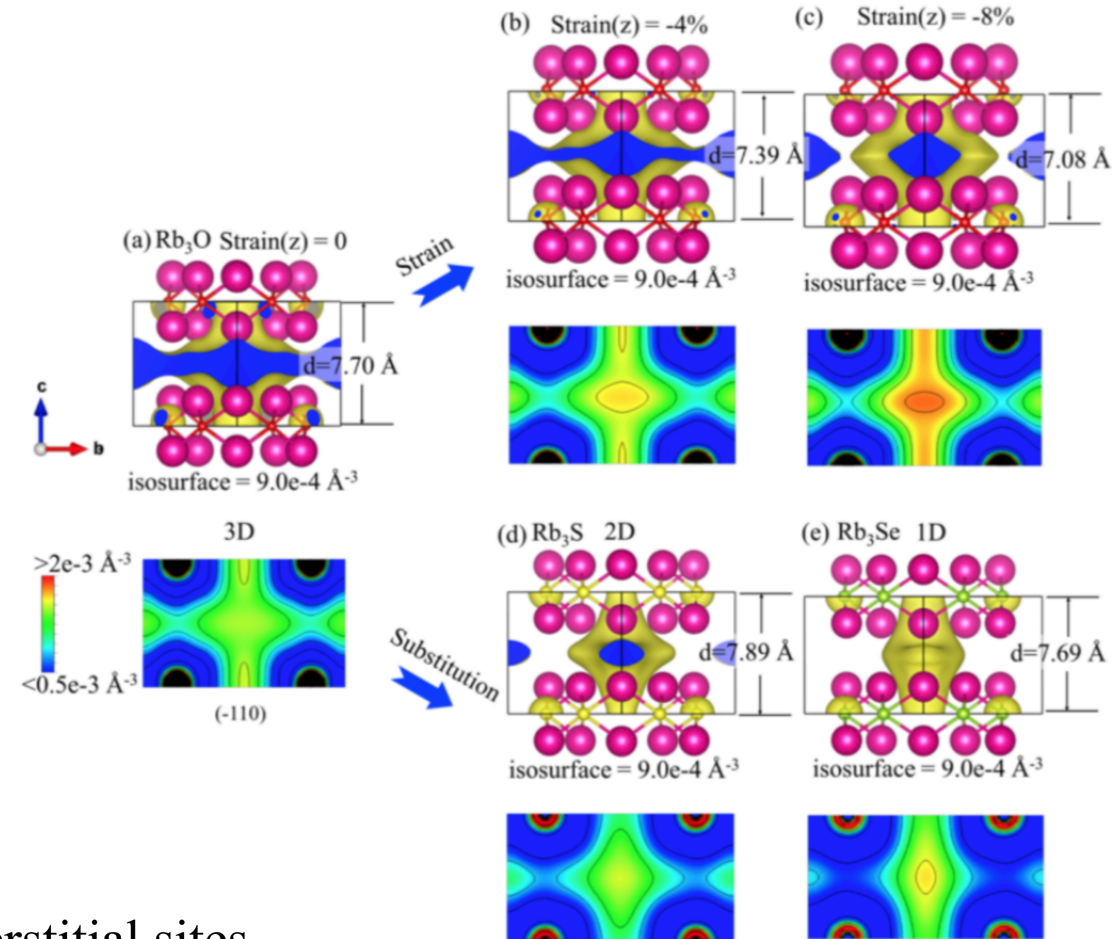


Top view



Side view





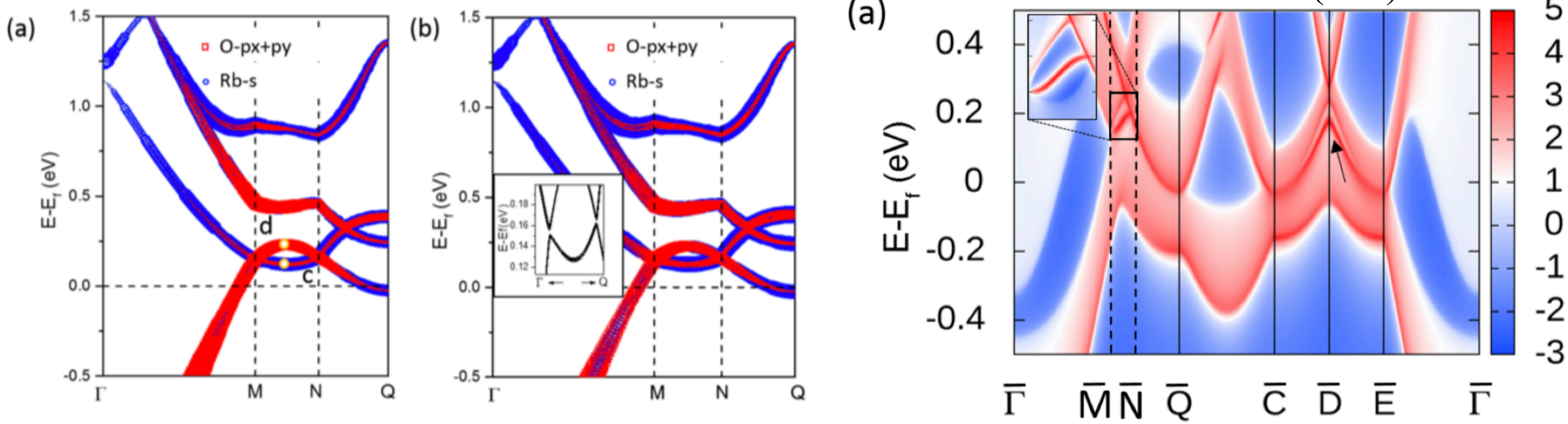
Rb_3O

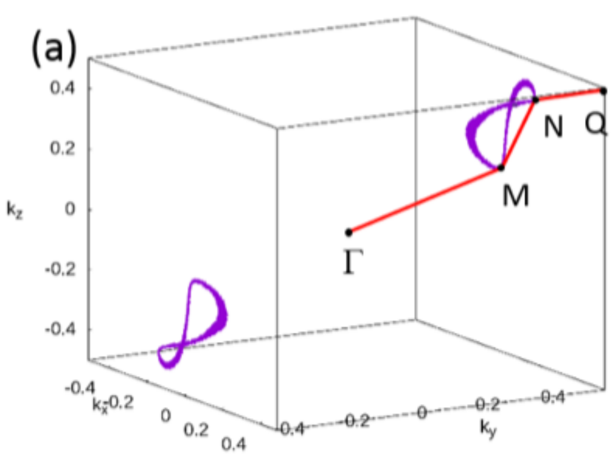
- Two interstitial sites
- tunable electron topology under strain or dopping
- Such characteristics only exist in a few electrides

Zhu, Wang, Chen & Zhu, arXiv, 2018

Example 1: Topological Electride Rb_3O

No SOC　　SOC　　Surface band at (001)





Topological Electrides were proposed recently.
The combination of two properties are interesting

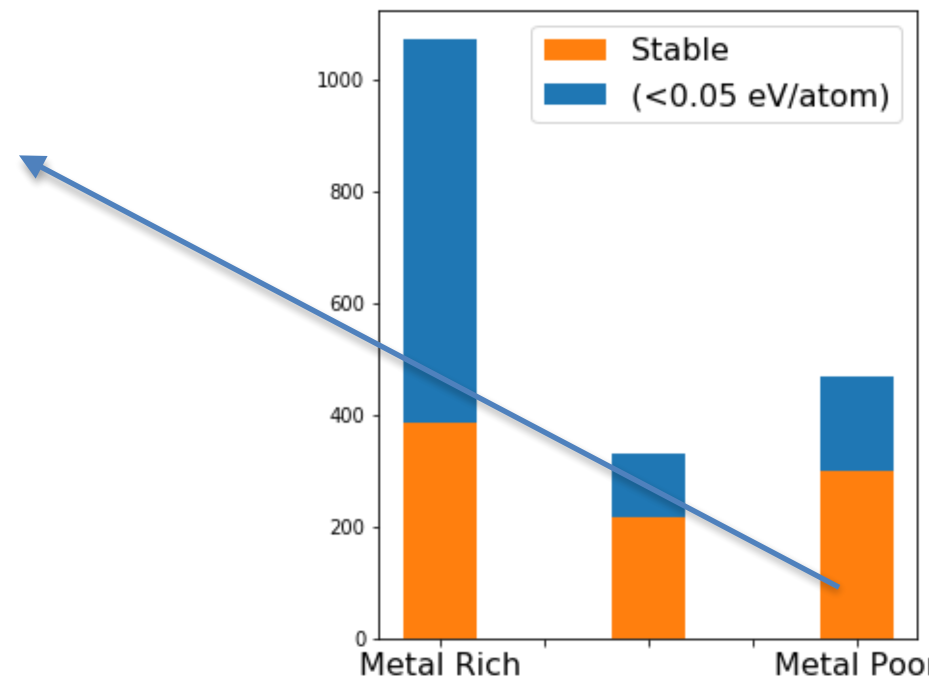
Rb_3O

- a topological Dirac nodal line semimetal
- induced by the interstitial electric charges
- Band inversion not at the high-symmetry point & high-symmetry line

Zhu, Wang, Chen & Zhu, arXiv, 2018

Example 2: Electrides with Pernitride Anions

CSP+DM database
Classification by stoichiometry

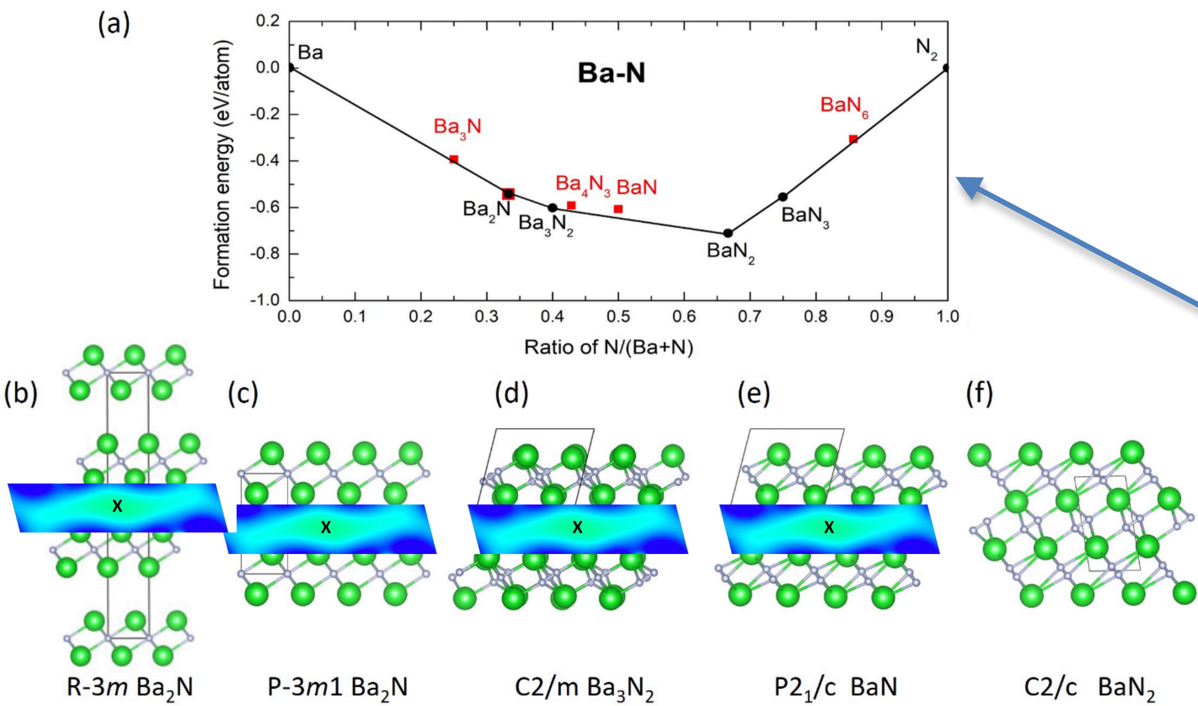


Several metal-poor compounds are electrides !

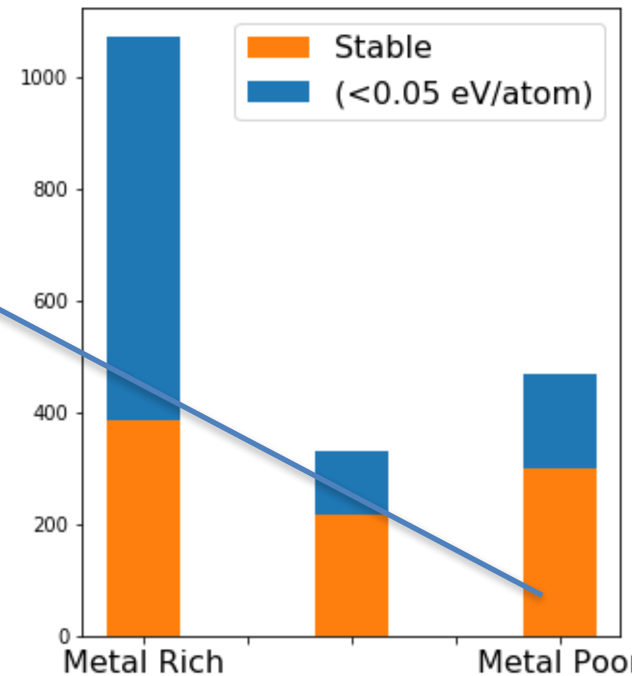
Qu & Zhu, ACS Appl. Mater. Interface, 2018

Example 2: Electrides with Pernitride Anions

Ba-N



CSP+DM database
Classification by stoichiometry

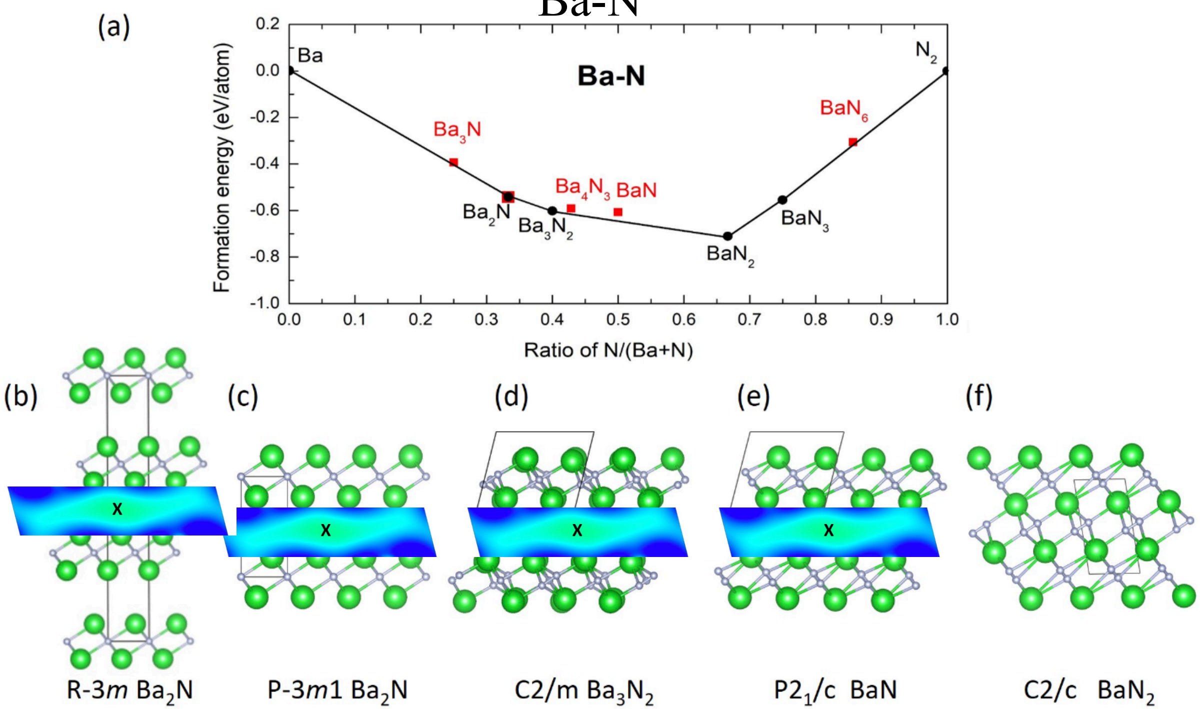


BaN and Ba_3N_2 are also electrides.
maybe overlooked if one just look at the chemical formula unit

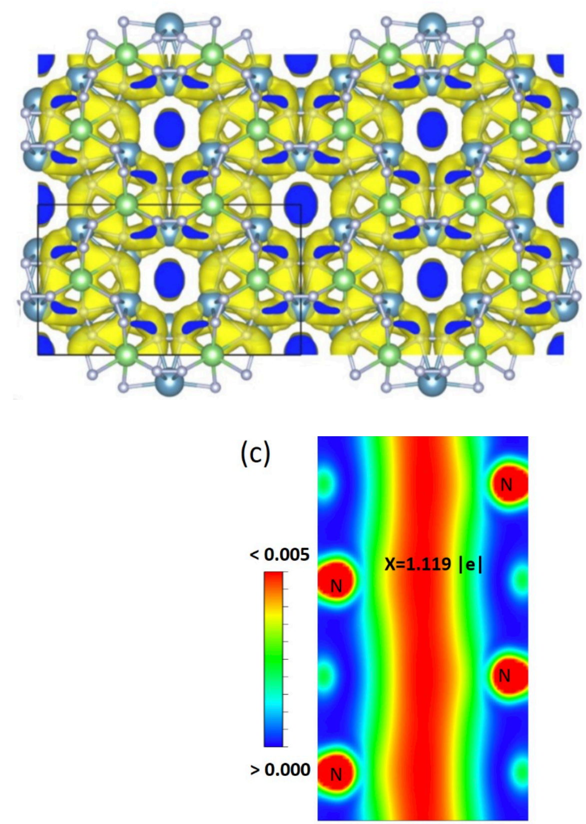
Qu & Zhu, ACS Appl. Mater. Interface, 2018

Example 2: Electrides with Pernitride Anions

CSP+DM database
Ba-N



HT on the ICSD materials:
$Li_2Ca_3N_6$



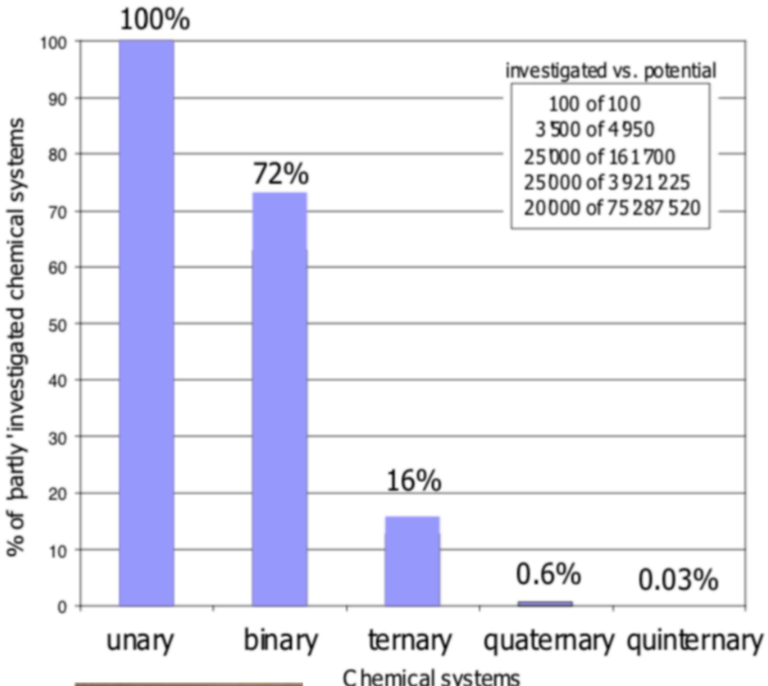
BaN and Ba_3N_2 are also electrides.
maybe overlooked if one just look at the chemical formula unit

$Li_2Ca_3N_6$ is another electride with [N_2] from our high throughput search

Qu & Zhu, ACS Appl. Mater. Interface, 2018

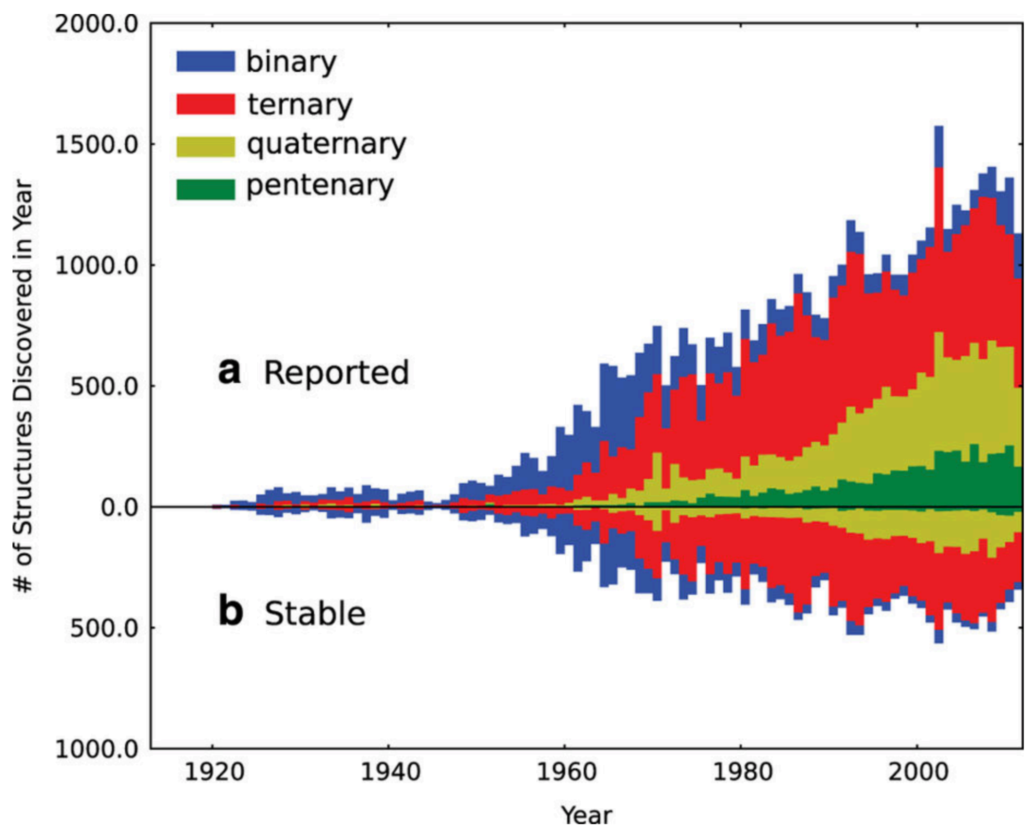
IV. Beyond Binary Systems

The unary/binary systems may have been largely explored in both expt. & theory



Explored systems

Pierre Villars
(PaulingFile)



Increasing materials in the ICSD by year

Kirklin, NPJ Comput. Mater., 2018

Search for more complex electrides?

Stable Ternary Electrides Made of Main Group Elements

Materials Project

69640

↓ stable *ABX* compounds

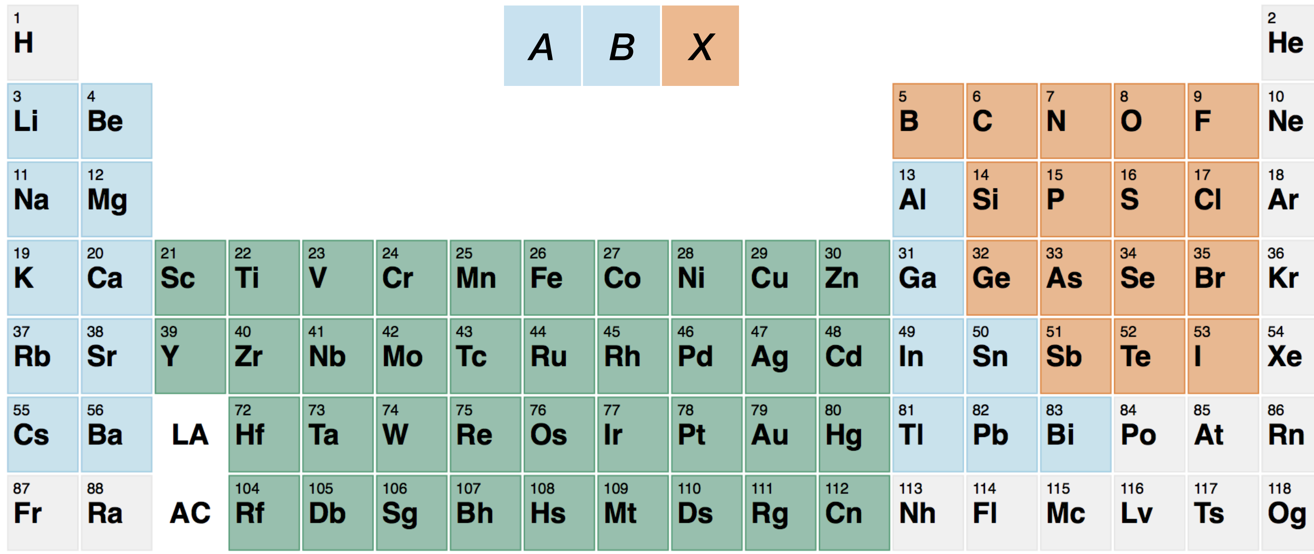
827

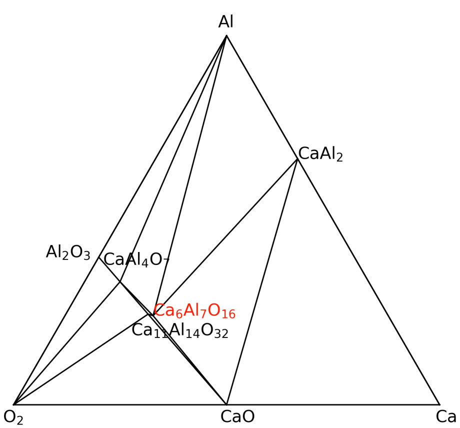
↓ positive formal charge
<120 atoms in the cell

59

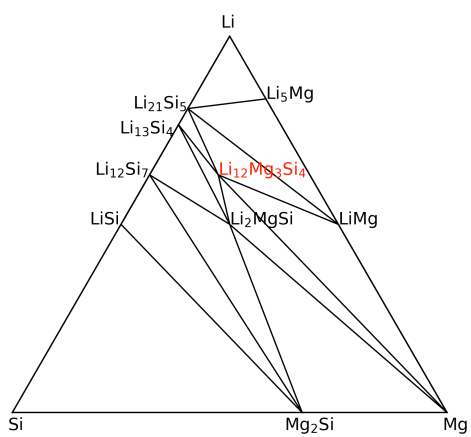
↓ electride analysis

4

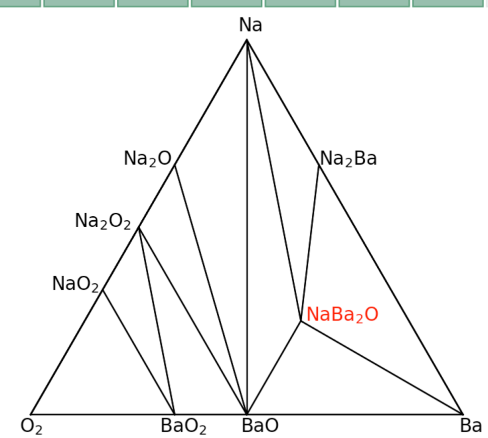




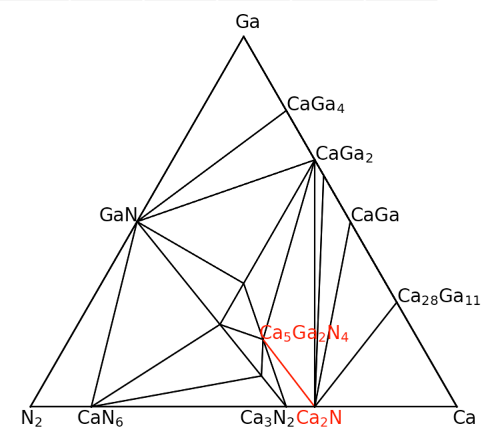
$Ca_6Al_7O_{16}$



$Li_{12}Mg_3Si_4$



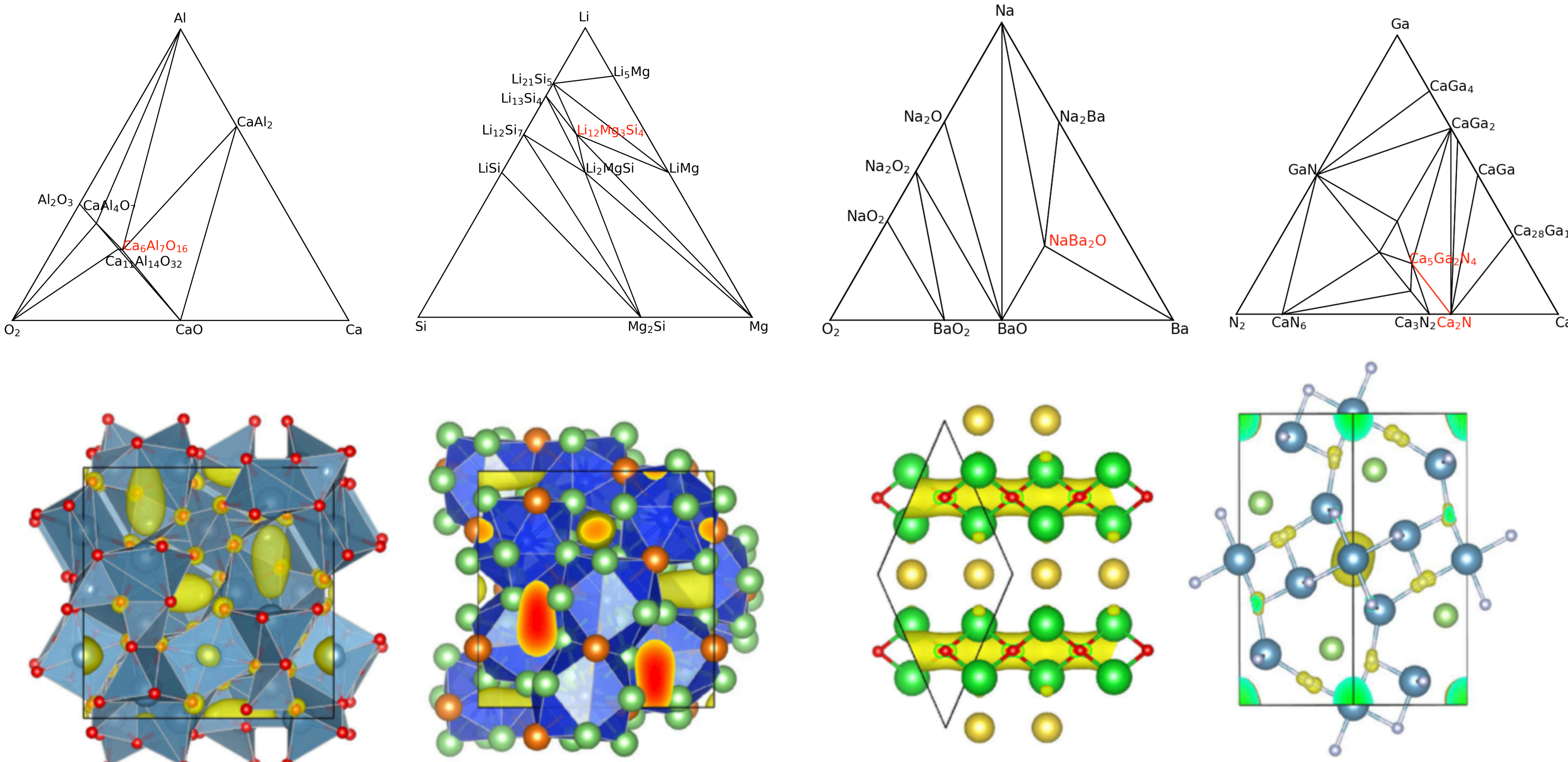
$NaBa_2O$



$Ca_5Ga_2N_4$

Wang & Zhu, arXiv, 2018

Stable Ternary Electrides Made of Main Group Elements



$Ca_6Al_7O_{16}$ $Li_{12}Mg_3Si_4$ $NaBa_2O$ $Ca_5Ga_2N_4$

Wang & Zhu, arXiv, 2018

An extended search from the entire ICSD

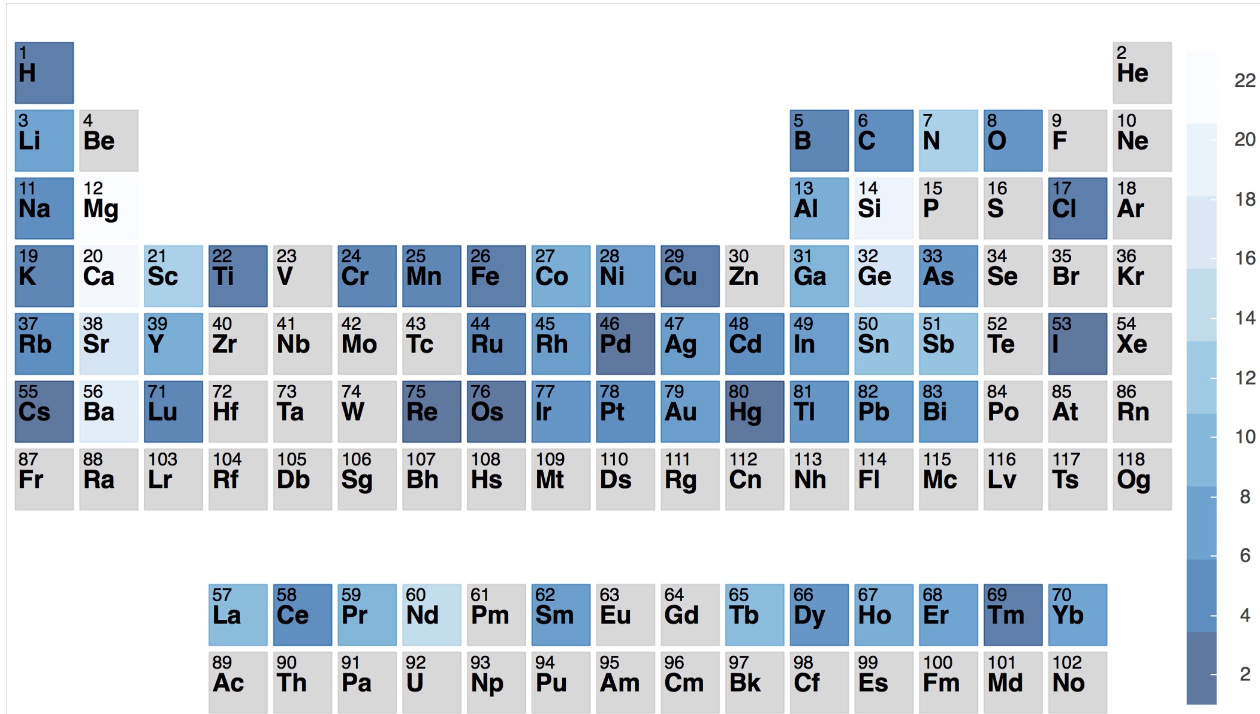
Materials Project
69640

- *ICSD exists*
- *gap < 0.25 eV*
- *# of element > 1*
- *# of atoms < 100*

17756

electride analysis

169



Zhu & Frolov, arXiv, 2018

An extended search from the entire ICSD

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69640

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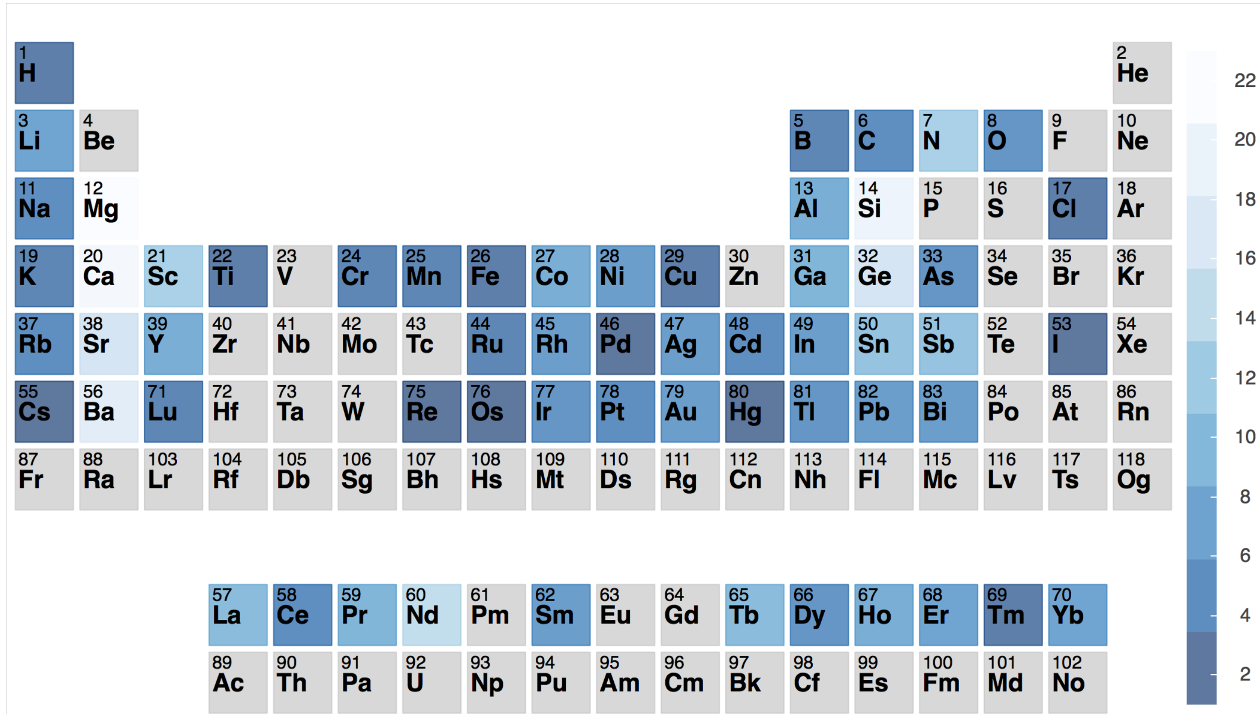

Burton et al (Chem. Mater., 2018) did a similar screening on the same data set, found 65 electrides. Among 10 experimentally recognized electrides, only 3 were found.

Here we found 169 electrides, and 7 out of 10 experimental electrides were identified in this work. All structure prototypes were identified.

Zhu & Frolov, arXiv, 2018

An extended search from the entire ICSD

Materials Project
69640

- *ICSD exists*
- *gap < 0.25 eV*
- *# of element > 1*
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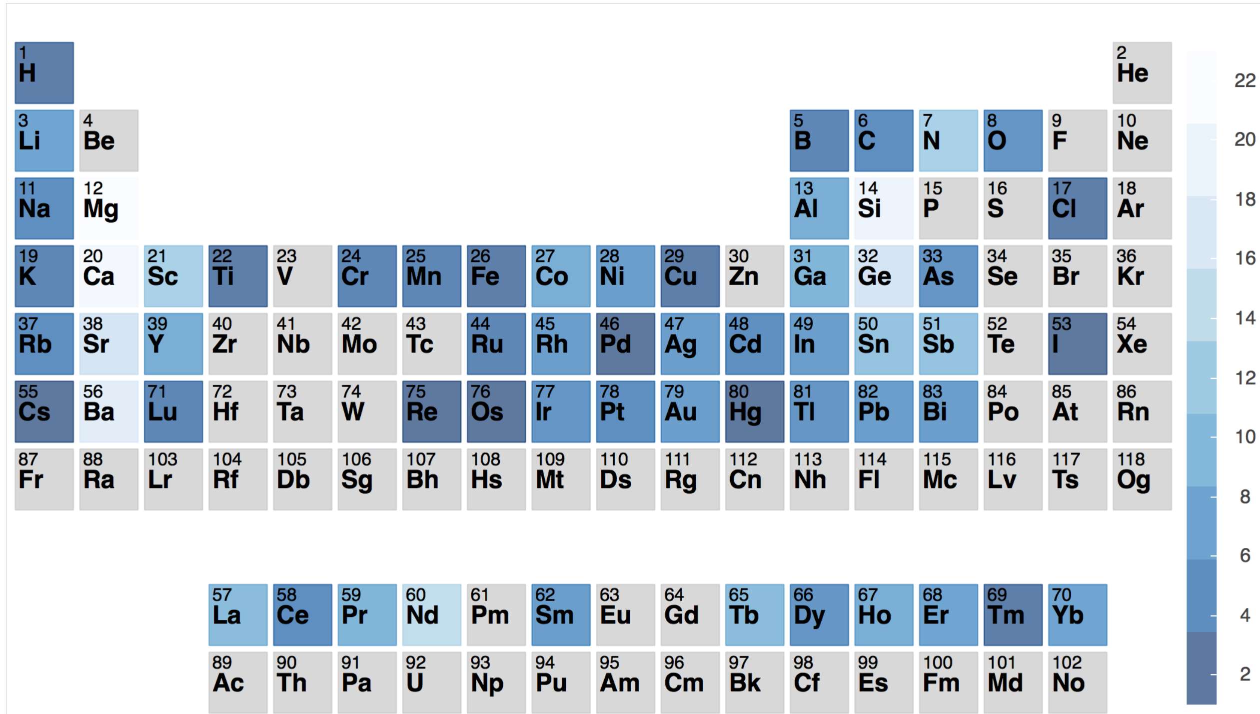
17756

electride analysis

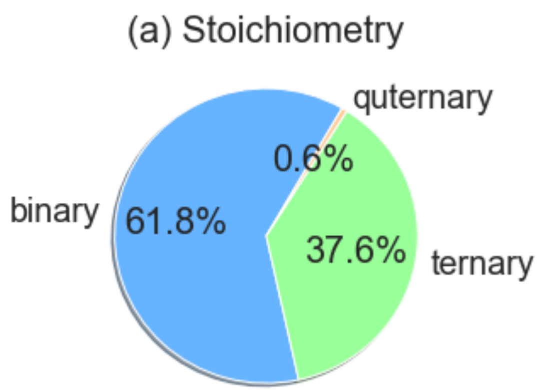
169

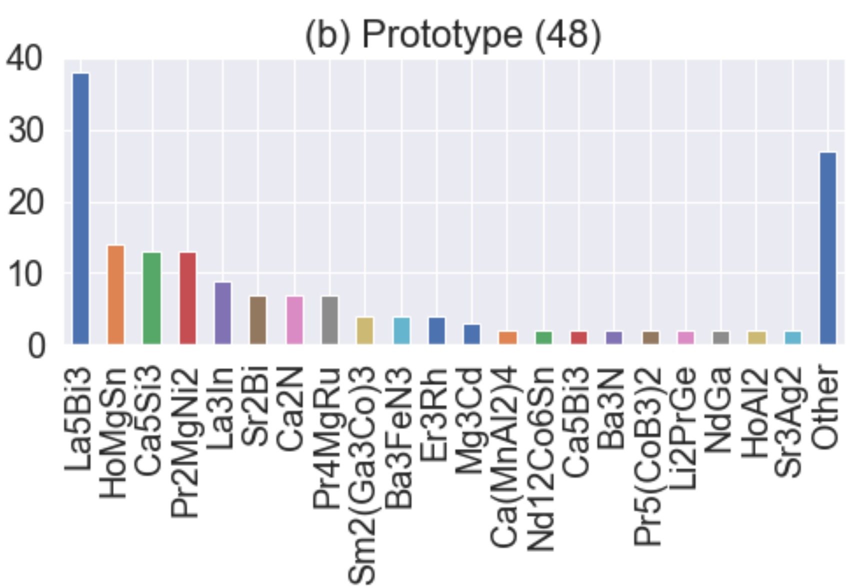


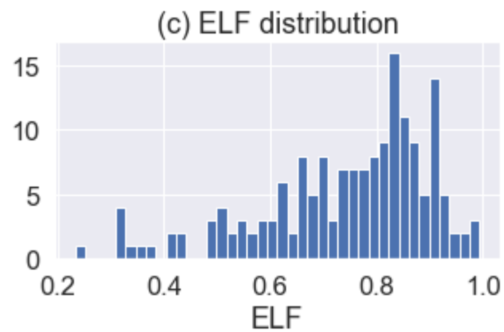
We learn
- 59 elements are involved (previous researches were focusing on only a small space)
- Group II elements (Mg/Ca/Sr/Ba) are most frequent electron providers.
- Many transition metals (mostly forming intermetallics) are found, which are rarely studied in the past

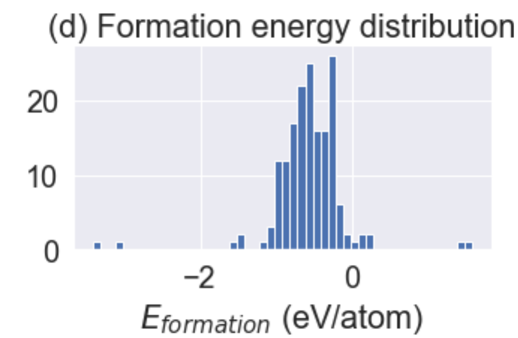
Zhu & Frolov, arXiv, 2018

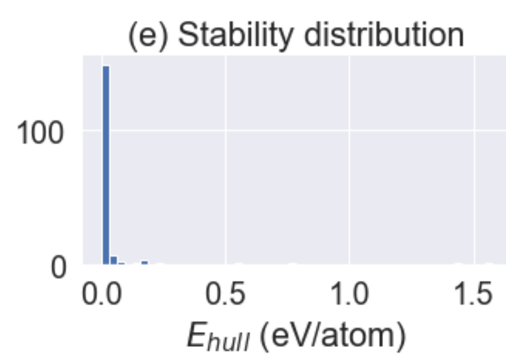
Various Statistics



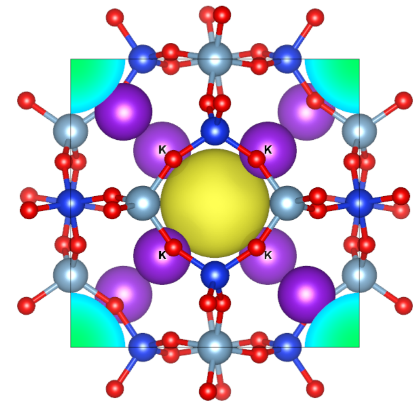


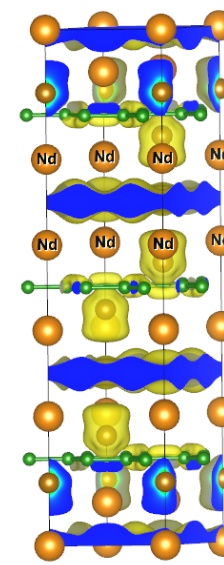






0D $K_4Al_3(SiO_4)_3$

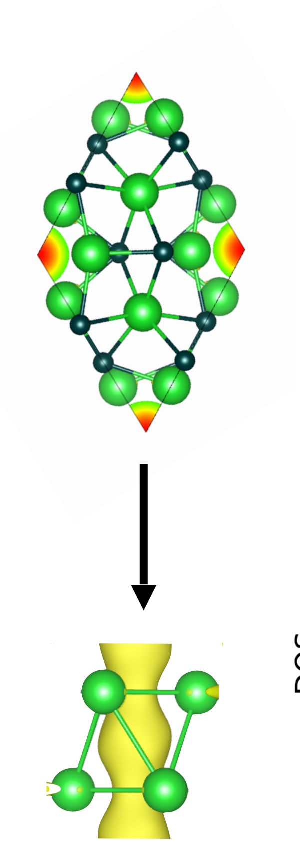


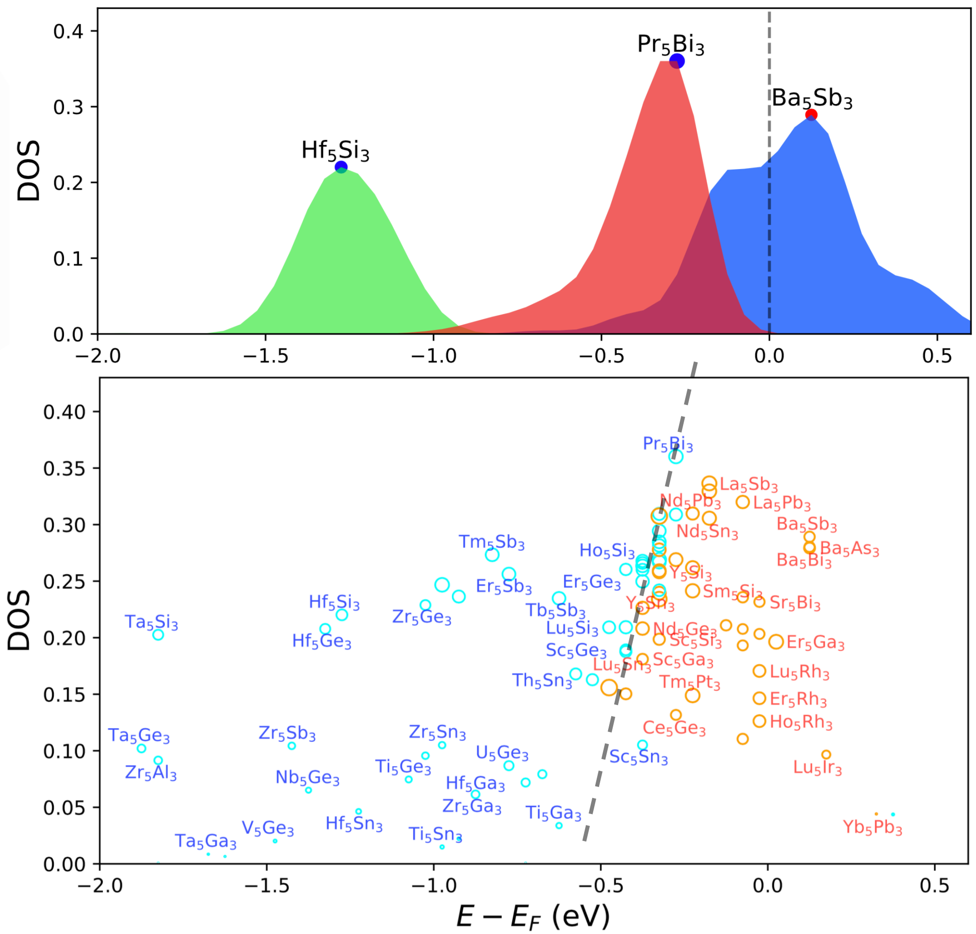


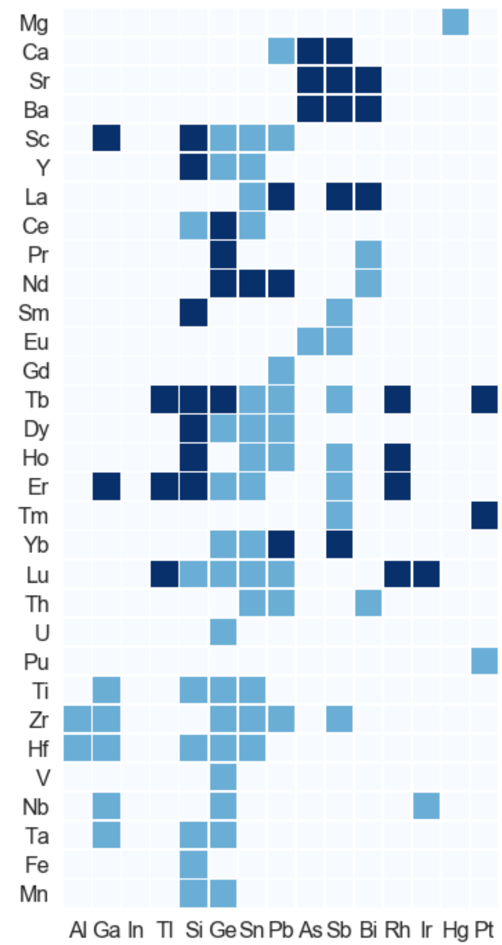
2D $Nd_5(FeB_3)_2$

Zhu & Frolov, arXiv, 2018

Chemistry-Structure dependence







There exist 105 different Fe_5Si_3 type compounds, but not all of them are electrides!

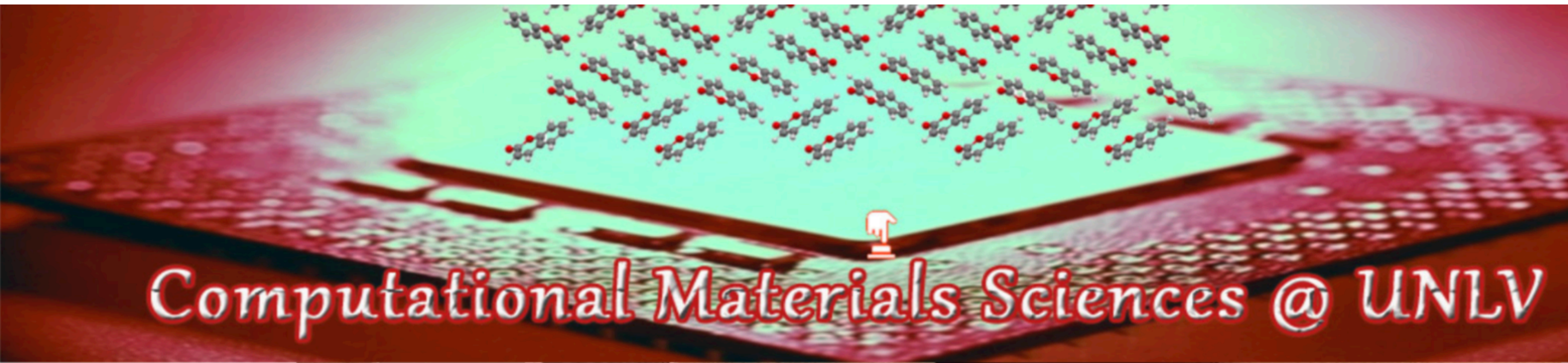
Zhu & Frolov, arXiv, 2018

Summary

- **Technical implementation**
  - Hybrid CSP + DM + HT method used for the search and design of functional electrides
  - A new descriptor for identifying interstitial electrons

- **Important results**
  - A growing library for many (>364) low-energy binary electrides from CSP + HT + DM
  - 169 electrides from HT screening on the ICSD

- **Related Articles from this work**
  - Zhu Q*, Frolov T (2018) Inorganic Electrides from High-throughput Screening, arxiv 1812.06222
  - Zhu S-C, Wang L, Qu, J-Y, Wang, J-J, Frolov T, Chen X-Q and Zhu, Q*. (2018) Computational Design of Flexible Electrides with Non-trivial Band Topology, arXiv 1811.11334
  - Wang J-J, Zhu, Q*, Wang Z-H, Hosono H. (2018) Ternary Inorganic Electrides with mixed bonding, arXiv 1811.10682
  - Qu J-Y, Zhu S-C, Zhang W-W, Zhu, Q* (2018) Electrides with Pernitride Anions, ACS Applied Materials & Interfaces, just accepted
  - Zhu, Q*, Wang, J-J, in preparation.



Merci
谢谢
Спасибо
Grazie
Thank You
ありがとう

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X-Q, Chen, L Wang, IMR, China
Hiedo Hosono, Tokyo Inst. of Tech.
J. Wang, NWPU, China