Searching for functional oxides using high-throughput *ab initio* screening

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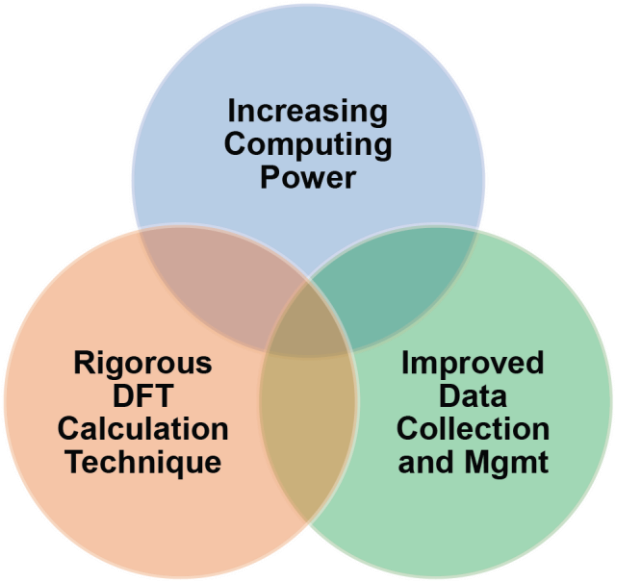
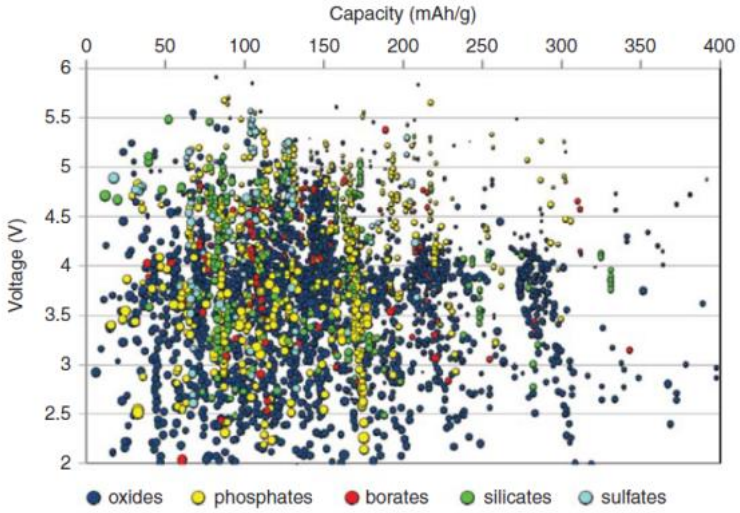
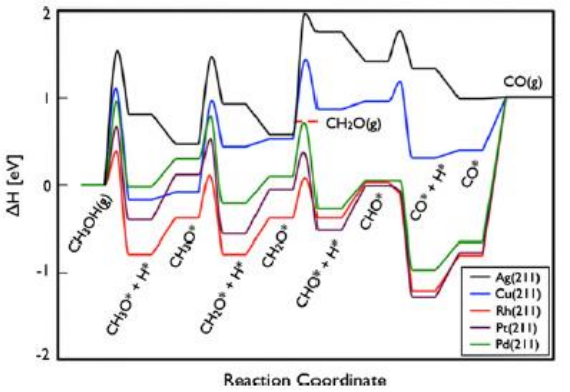
Introduction

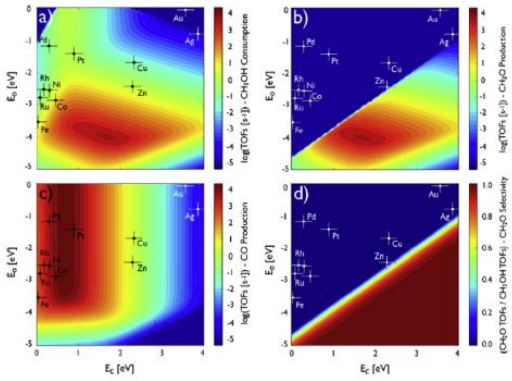


- Battery (Ceder group)



- Catalyst (Norskov group)





Automatic computation of material properties

Complexity level of modeling	Property
I	Lattice parameter, band structure (energy gap, effective mass), elastic constant, phonon, dielectric constant, absorption coefficient,..
II	Point defect (formation energy, transition level, migration energy), surface (exposed to vacuum),
III	Defect complex, doping,
IV	Interface (band alignment)

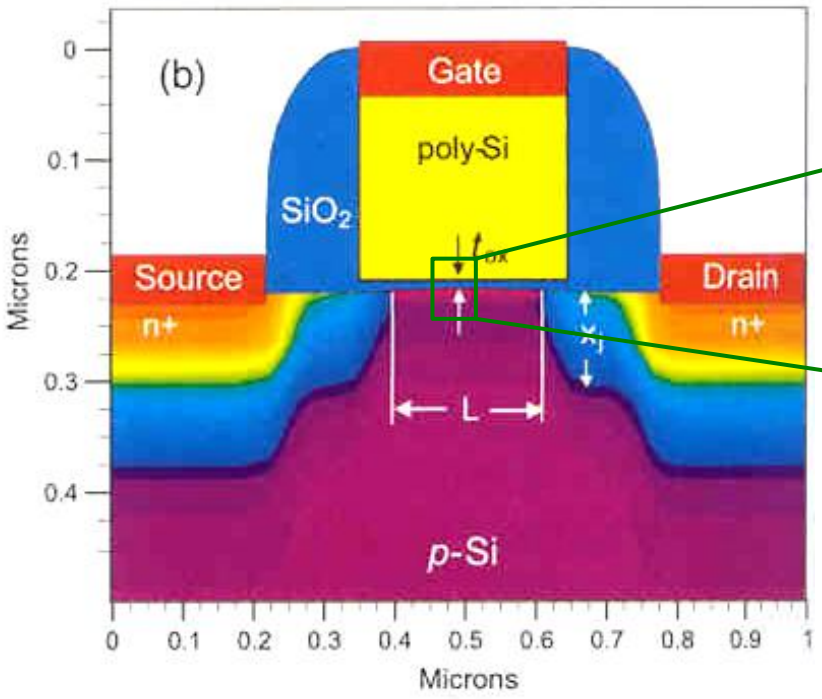
Automation package

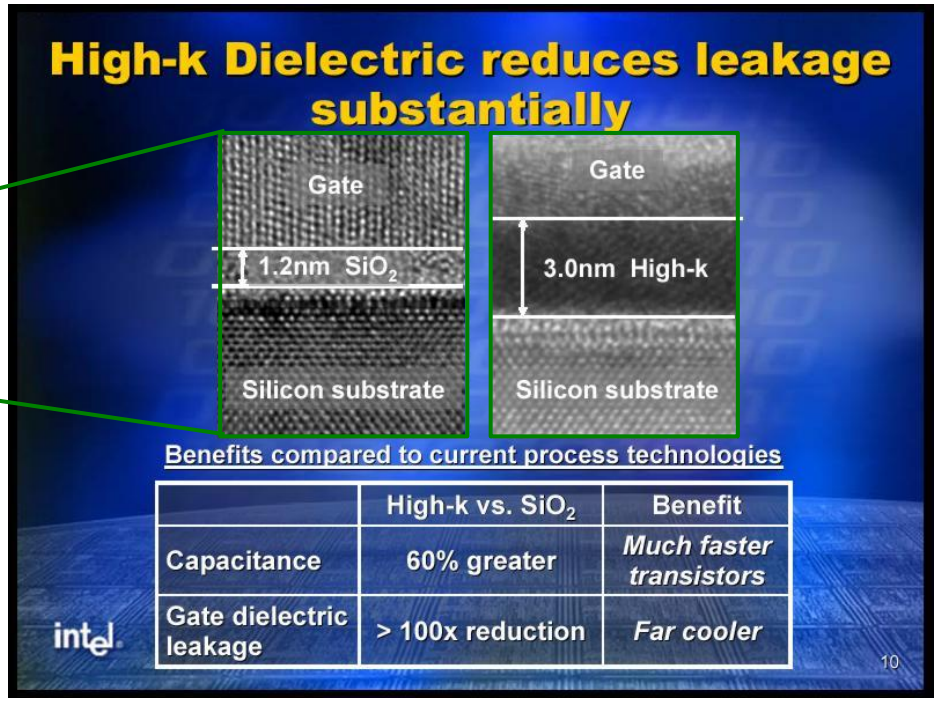
- Automation script module (compatible with VASP)

Program	Input	Output
icsd.py	ICSD# or elements (valid ICSD account)	POSCARs
param.py	Crystal structure	E_{cut} or PREC, k-point set for convergence of total energy, stress, force
relax.py	Crystal structure Parameter set	(Fully) relaxed structure
band.py	Crystal structure Parameter set	-Band structure (plotting) -Band gap (line or full 3-d search, one-point hybrid)
epsilon.py	Crystal structure Parameter set	Optical and/or static dielectric tensor

to be open at http://mtcg.snu.ac.kr

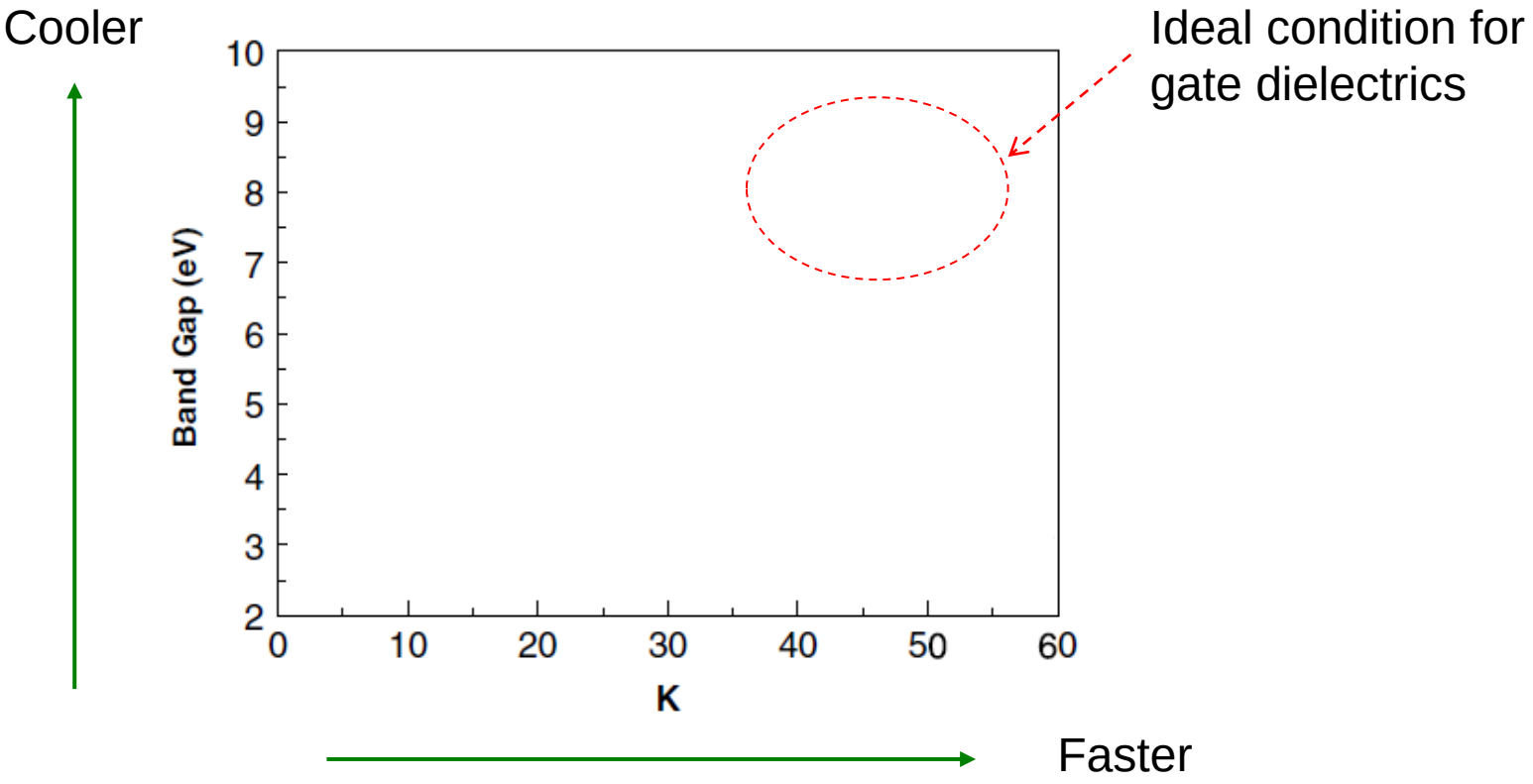
High-throughput ab initio screening I: high-k dielectrics





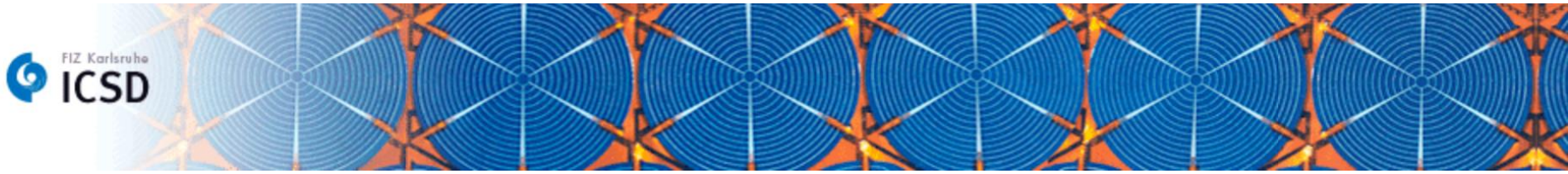
- HfO_2 and ZrO_2 are already being used as high-k dielectrics in transistors and capacitors of recent CPUs and DRAMs

Ideal gate dielectrics



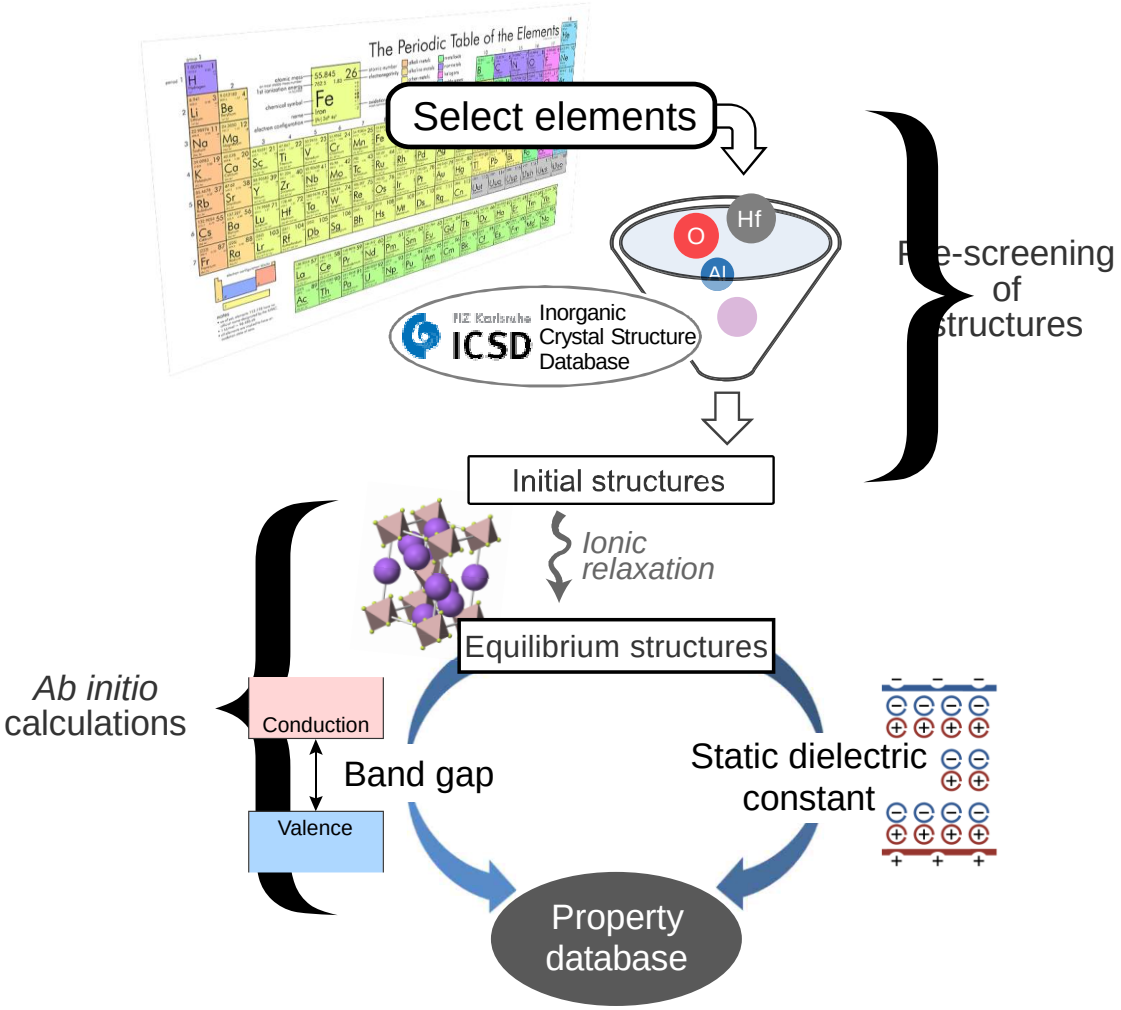
- If we search over a larger material database, possibly all oxides, is there any material that possess both large band gap and high K?
- Only dozens of oxides are experimentally known for both band gap and K values.
- Modern ab initio codes and computing environment may enable collection of a much larger database.

ICSD (Inorganic Crystal Structure Database)



- Abundant inorganic crystal structure data (161,000 structures) are easily accessible. (as of 2013)
  - 1,716 crystal structures of the elements
  - 30,968 records for binary compounds
  - 60,640 records for ternary compounds
  - 56,730 records for quarternary and quintenary compounds
- Number of oxides
  - binary oxides: 2,830 records
  - ternary oxides: 16,270 records
- Due to the large number of candidate structures, we need to automatize the computational procedure.

Computational strategy



VASP was used for the ab initio calculations.

Computational cost

- Calculated data from more than 1,500 structures are collected over effectively 1 year or so. (~500 structures are metallic within GGA)
- Computational resources

  - Quadcore Intel Xeon 2.50 GHz (E5420)

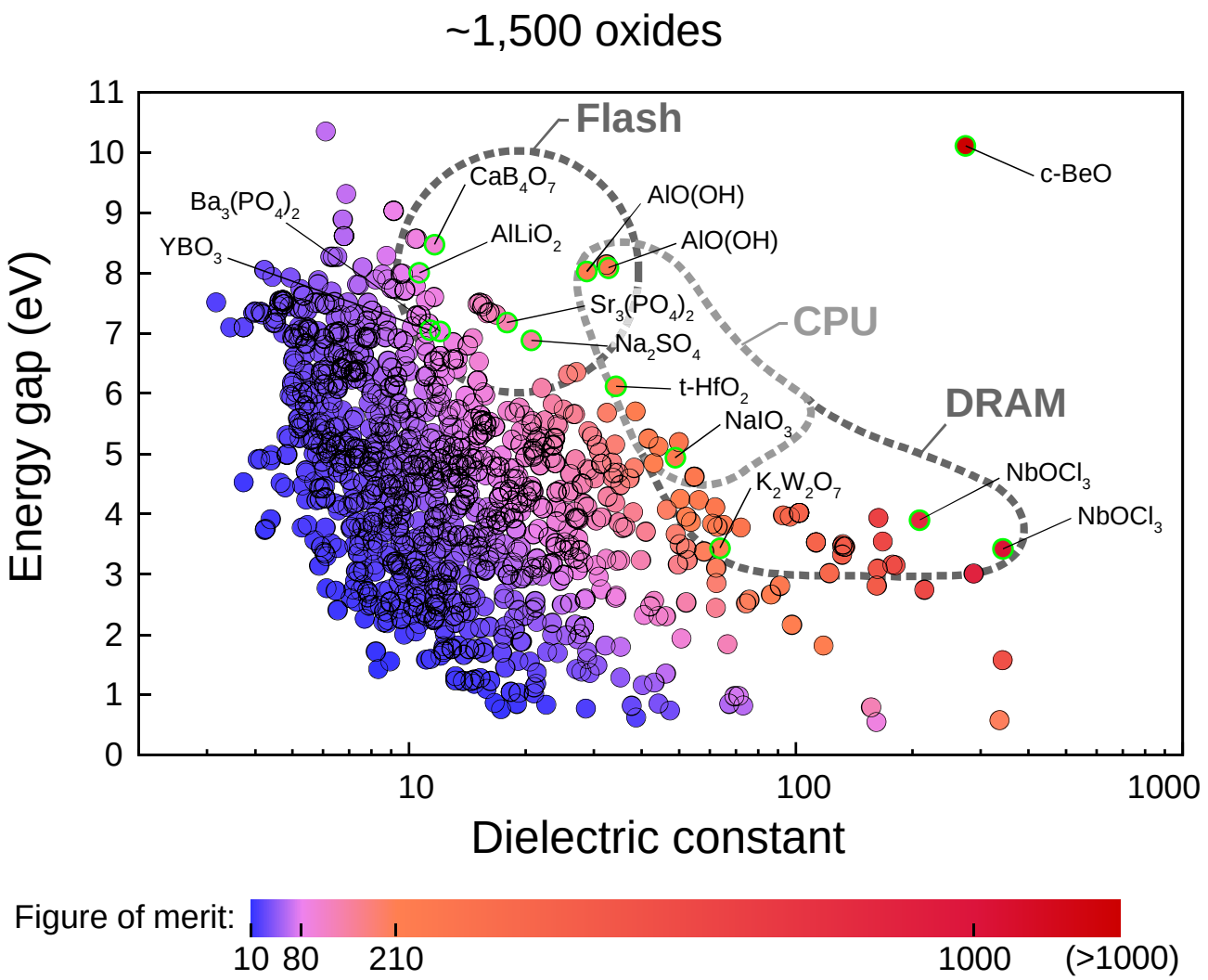
  - 8 nodes (64 cores)
- Average computational costs

  ~ 130 CPU hours per structure

  or ~ 8 structures per day

Time cost	Structure relaxation	Band gap (GGA)	Band gap (HSE)	Dielectric constant
%	6	21	43	30

Results



[DRAM]
- f_{FOM} > 210
- E_g > 3 eV and κ > 30

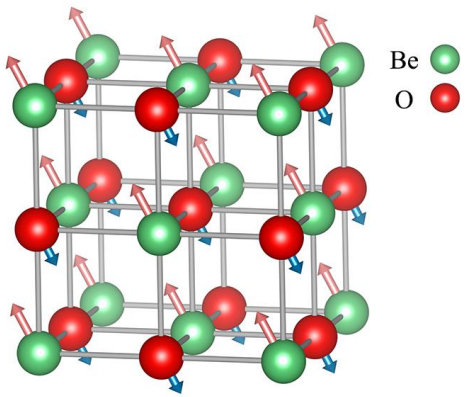
[CPU]
- f_{FOM} > 210
- E_g > 4 eV
- E_{vac} > 5.6 eV

[Flash]
- f_{FOM} > 80
- E_g > 6 eV

FOM = (band gap)x(dielectric constant)

[Binary oxide]

- c-BeO (rocksalt)



Be-O bond length is 0.16 Å longer than w-BeO

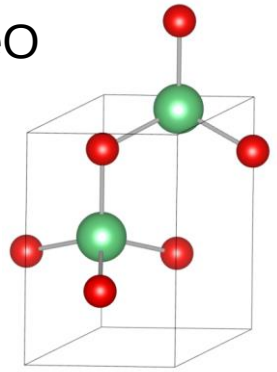
ε^0 : 276

E_g : 10.0 eV

Phase transition at P > 137 GPa[2]

ΔE/atom = 480 meV at 0K

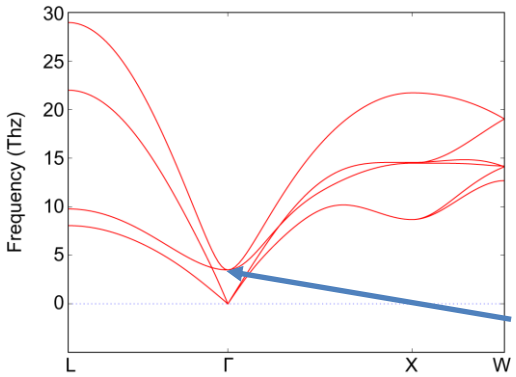
- w-BeO



ε^0 : 6.9

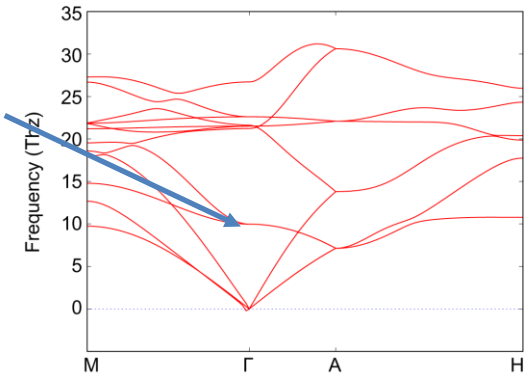
E_g : 9.3 eV

Phonon dispersion curve



f = 9.96 THz

f = 3.48 THz



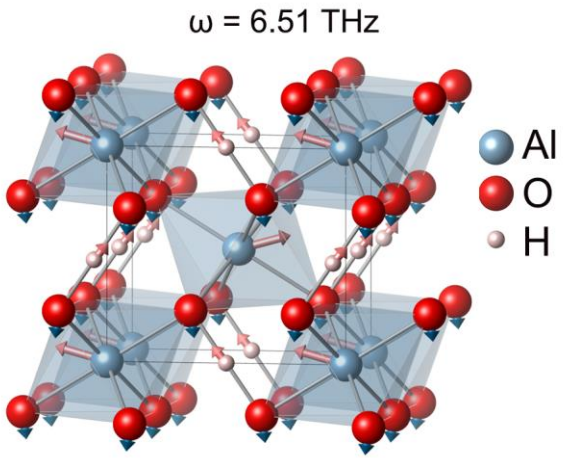
[Ternary oxides]

- AlO(OH)

ε^{∞} : 4.7

ε^{0} : 18.4

E_g : 5.7 eV

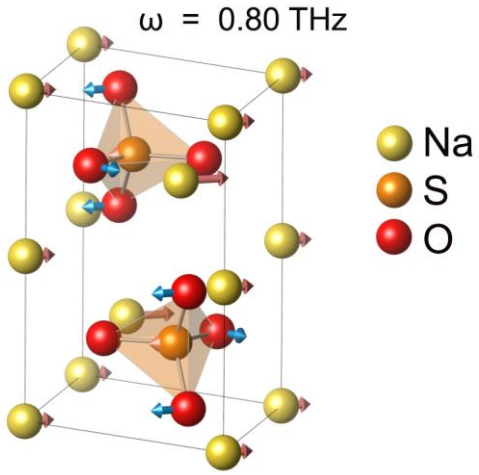


- Na_2SO_4

ε^{∞} : 2.3

ε^{0} : 20.7

E_g : 6.9 eV



- **Two common features for ternary higher-k candidates**

① **Cations in edge-shared octahedra cage**

- ✓ Edge-shared anion octahedra form loose cages.
- ✓ Cations in the cages vibrate with soft phonon frequency.

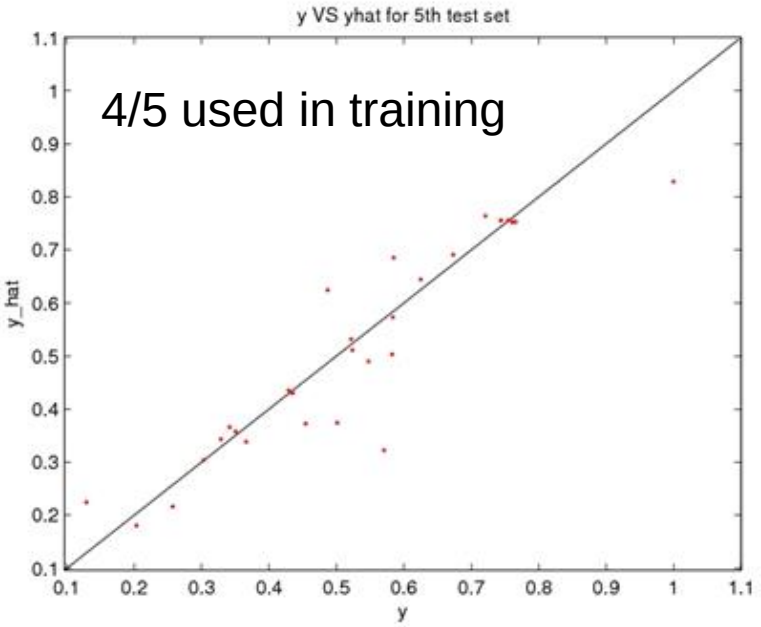
② **Channeled structure by strong covalent oxide unit**

- ✓ Strong covalent oxide unit + loosely bound cation
- ✓ Channeled structure : ions easily vibrate along the channel that is not blocked by other ions.

Support vector regression

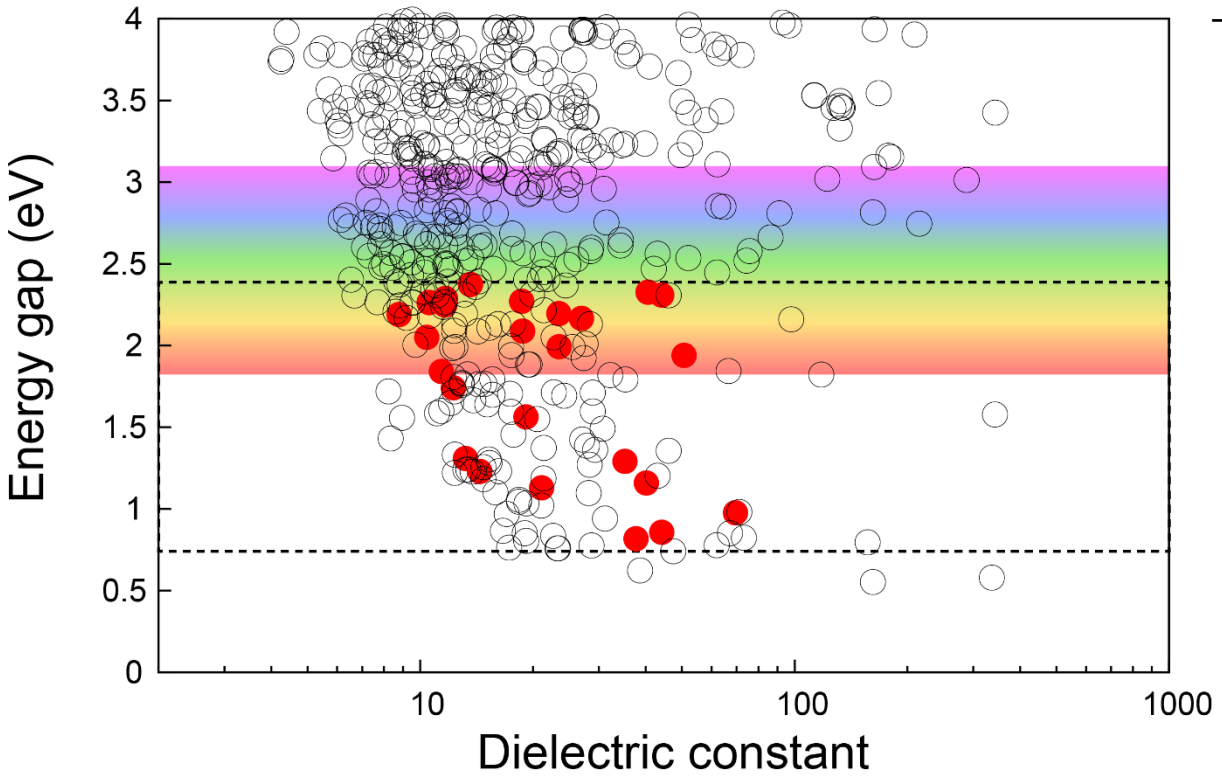
- Support vector regression on 152 binary oxides over a wide range of band gap.
- Four properties (Z, NN distance, effective CN, Bader charge) are selected for the Gaussian-type regression model.

$$E_g(\{X\}) = \sum_{i=1}^{N} a_i \exp\left[- \frac{1}{2s^2} \left| X - X_i \right|^2 \right]$$



✓ In collaboration with Samsung Advanced Institute of Technology

Photoabsorber for solar cell



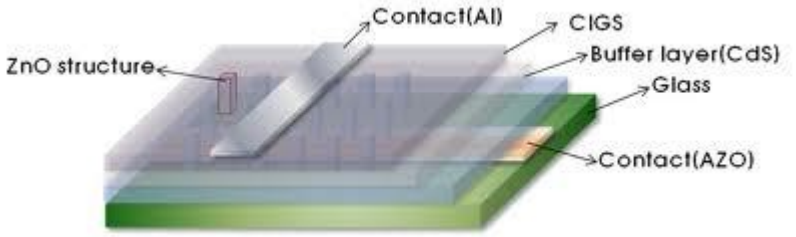
● direct band gap, 0.8 eV < E_g < 2.4 eV

name	E_g (eV)	name	E_g (eV)
Sr_3GeO	0.82	Cd_3TeO_6	1.99
Sr_3SiO	0.86	K_4OBr_2	2.05
$WOCl_3$	0.98	Cd_2Sb_2O7	2.09
Ag_2BiO_3	1.13	MoO_3	2.17
Tl_2O	1.16	K_3OCl	2.19
$Hg_3O_2Cl_2$	1.23	MoO_3	2.20
Ag_2HgO_2	1.31	$Hg_4O_2(NO_3)_2$	2.26
Rb_4Br_2O	1.56	$CdGeO_3$	2.27
$Rb_2Sn_2O_3$	1.74	SnO_2	2.29
$LiAg_3O_2$	1.84	WO_3	2.31
Sb_2OS_2	1.94	$LiNbO_2$	2.37

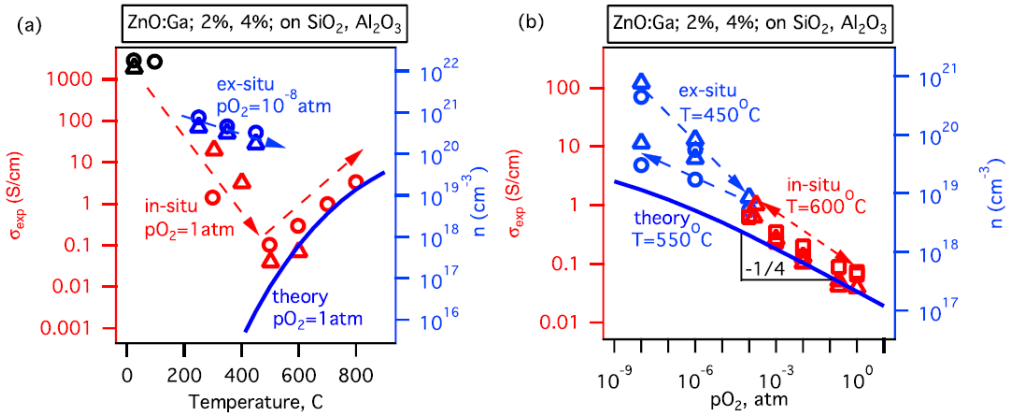
High-throughput ab initio screening II: dopants in ZnO

- Carrier concentration control for electrode applications

<Transparent conductor>



Conventional dopant: Al, Ga, In, Mn, Co, B, rare earth

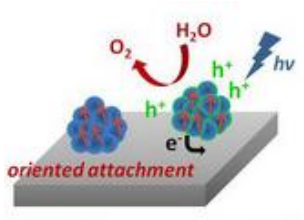


A. Zakutayev et al., *Appl. Phys. Lett.* **103**, 232106 (2013)

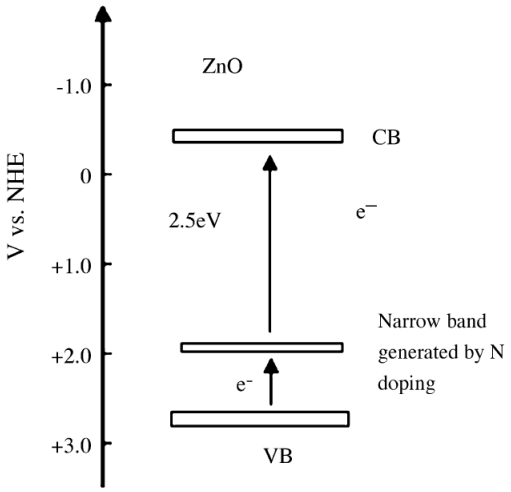
: Heavily doped-ZnO has High conductivity (ρ ~ 10^{-4} Ωcm) comparable to ITO (0.72×10^{-4} Ωcm)

Dopant in ZnO

- Band gap engineering and facilitate absorption of visible light

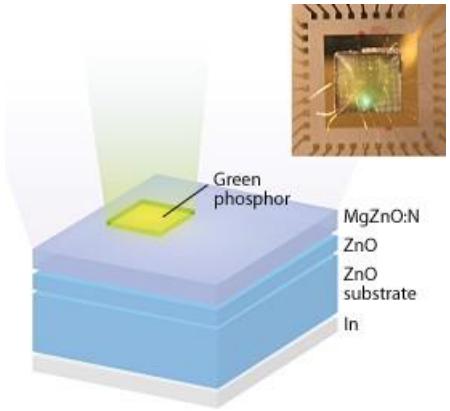


Conventional dopant
: N, C, F, transition metal

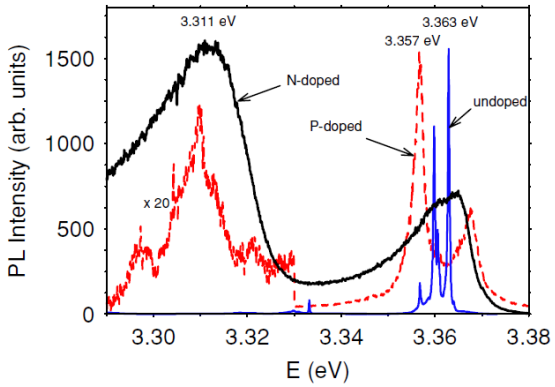


S. Rehman et al., J. Hazard. Mater. 170 (2009)

- Reliable and reproducible p-type doping

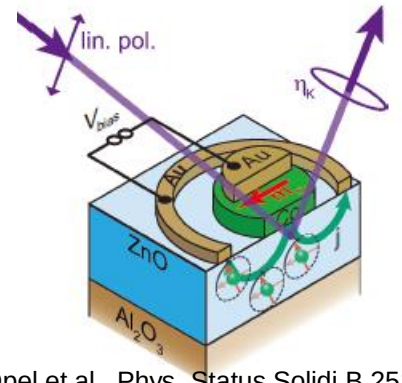


Conventional dopant
: N, P, Mg, Cd, transition metal



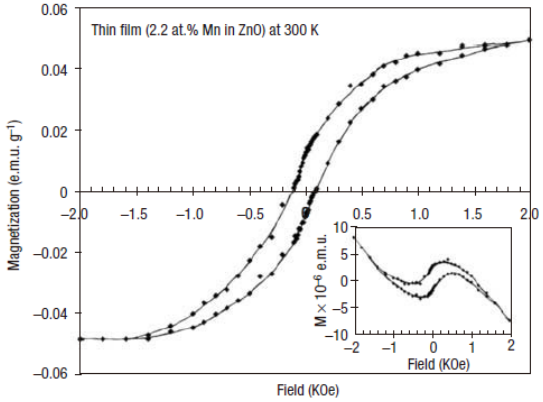
D.C. Look et al., Semicond. Sci. Technol. 20 (2005)

- Diluted magnetic semi-conductor of transition-metal doped ZnO



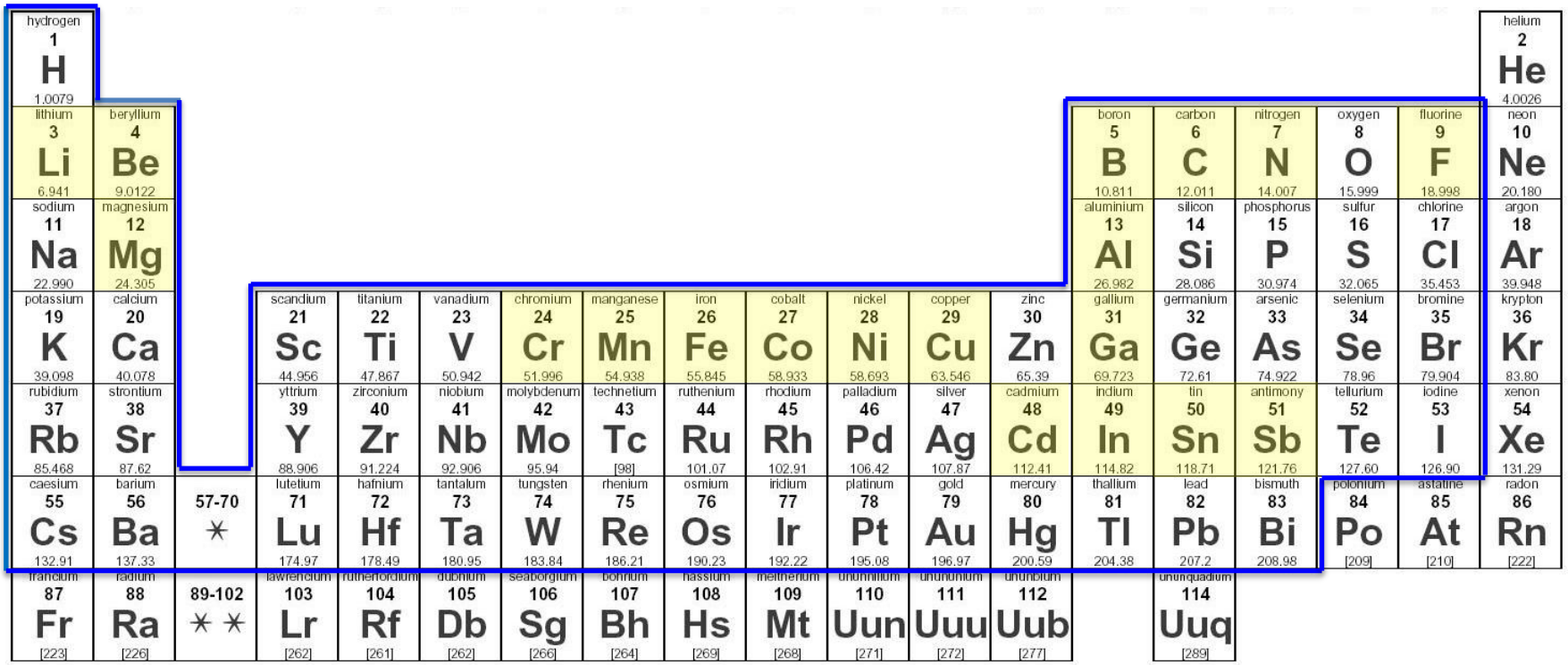
M. Opel et al., Phys. Status Solidi B 251 (2014)

Conventional dopant
: transition metal, Li



P. Sharma et al., Nat. Mater. 2 (2003)

Dopants in ZnO

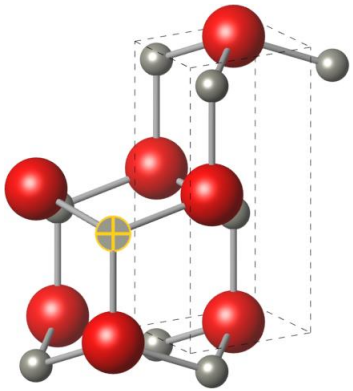


We wish to calculate:

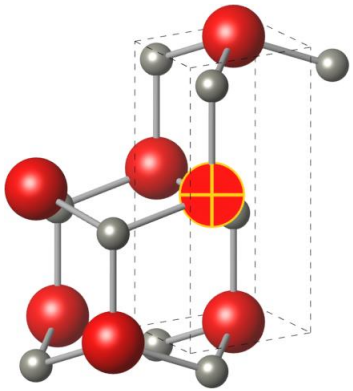
- Stable dopant site
- Solubility limit
- Band gap and carrier density

Possible doping sites

- Substitutional sites

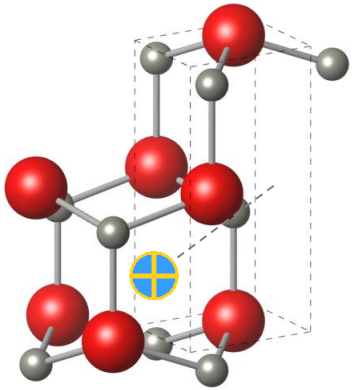


- Cation site

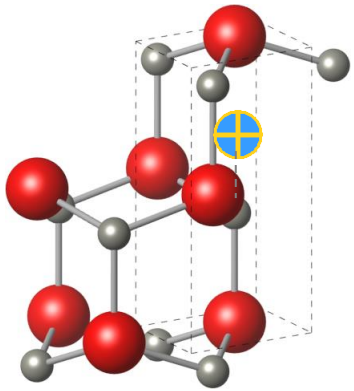


- Anion site

- Interstitial sites

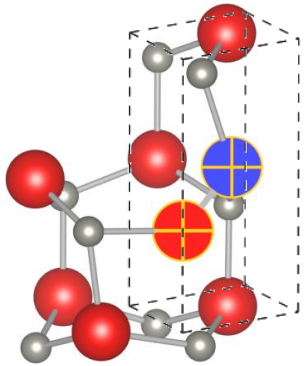


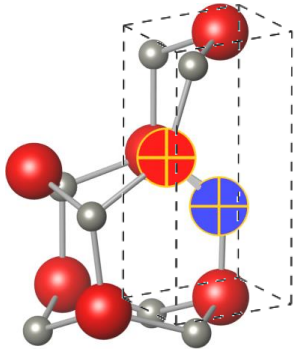
- Octahedral site ($AB_{||}$)



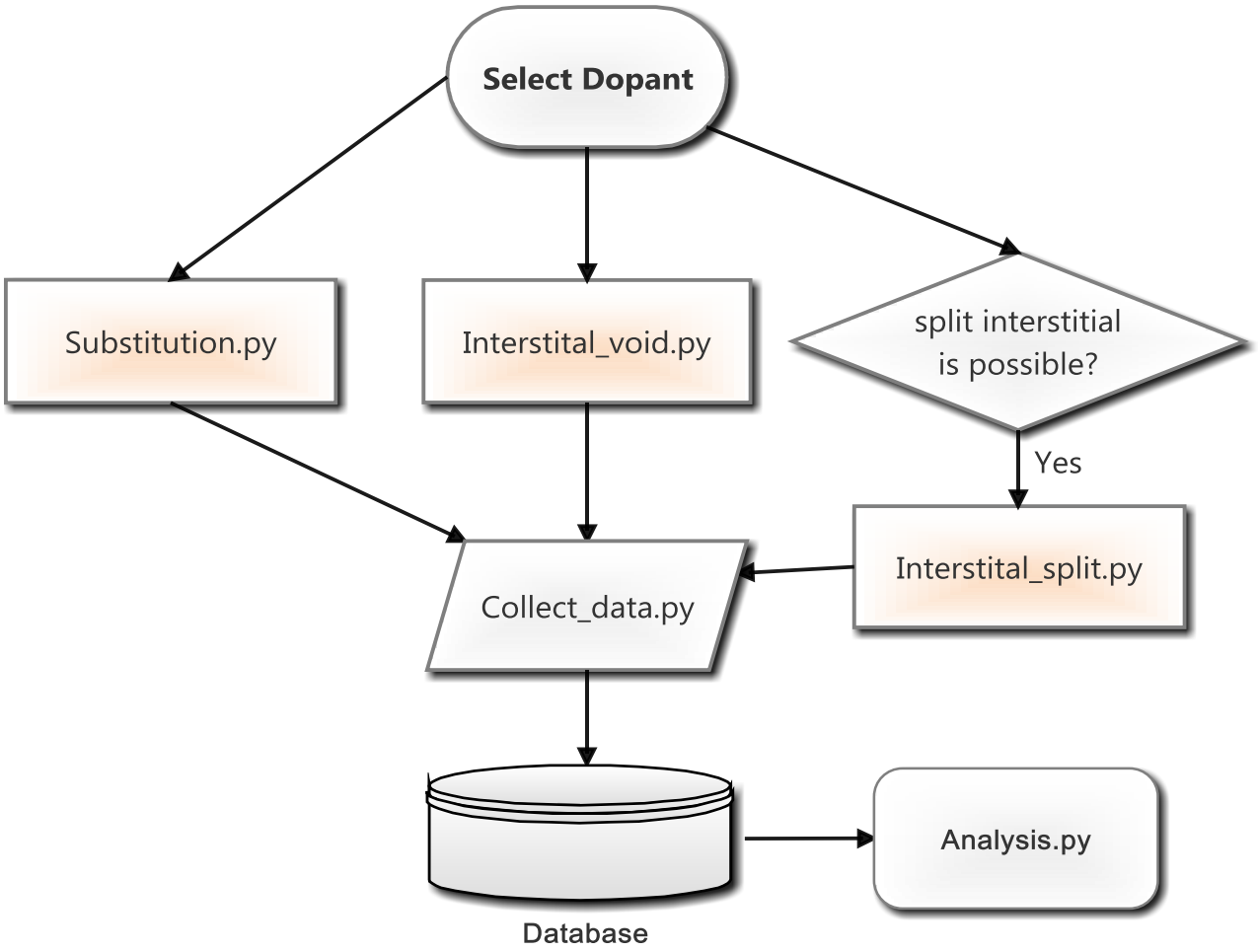
- Tetrahedral site ($AB_{\perp}$)

- Split-interstitial

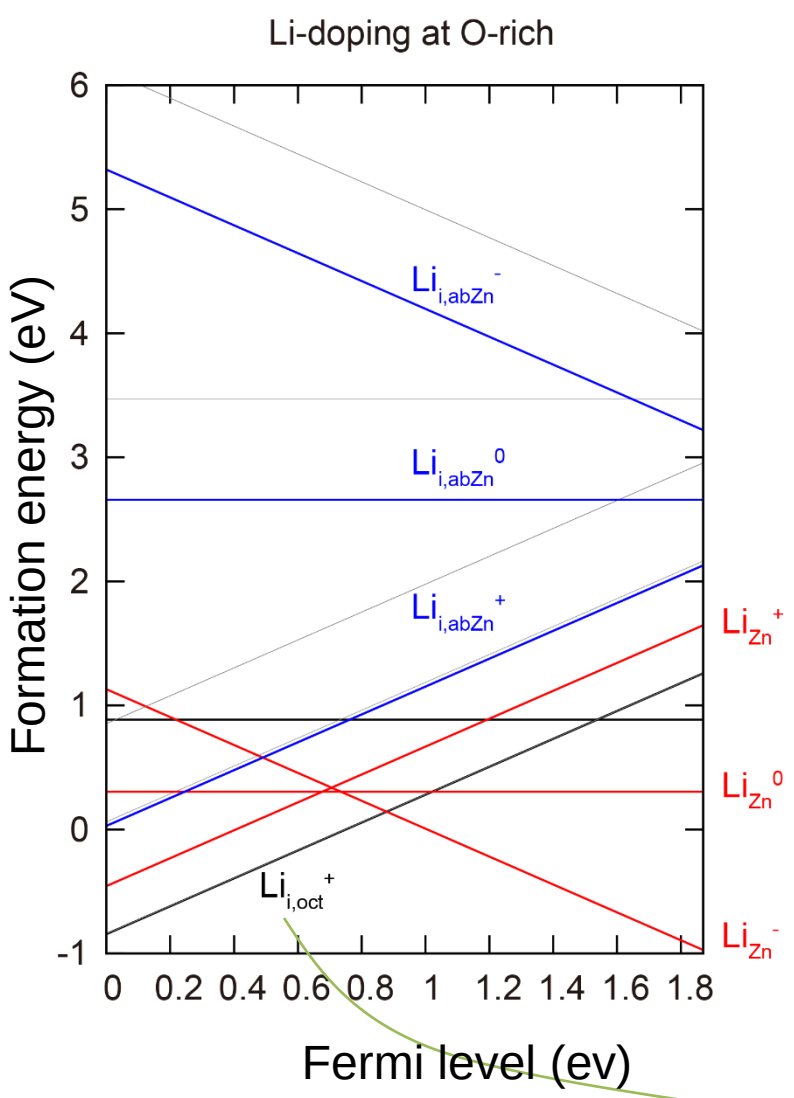


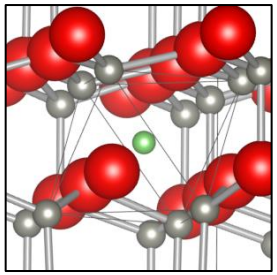


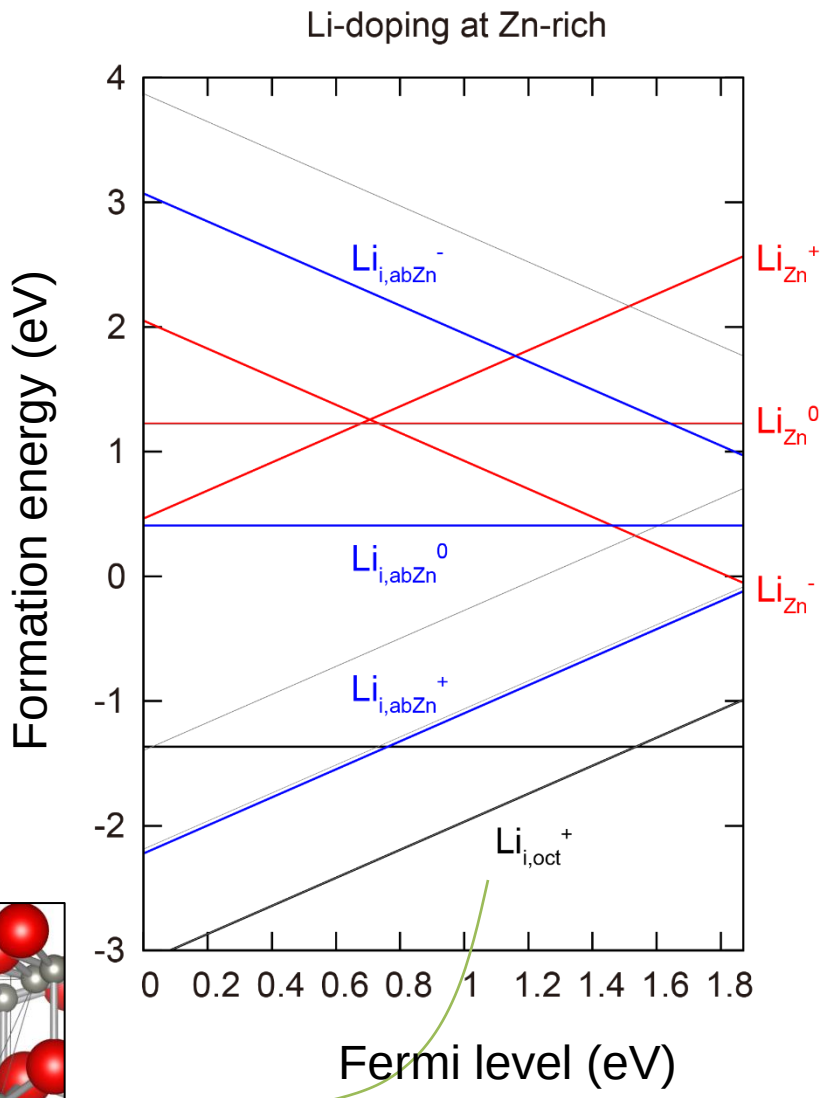
Work flow to find stable doping sites



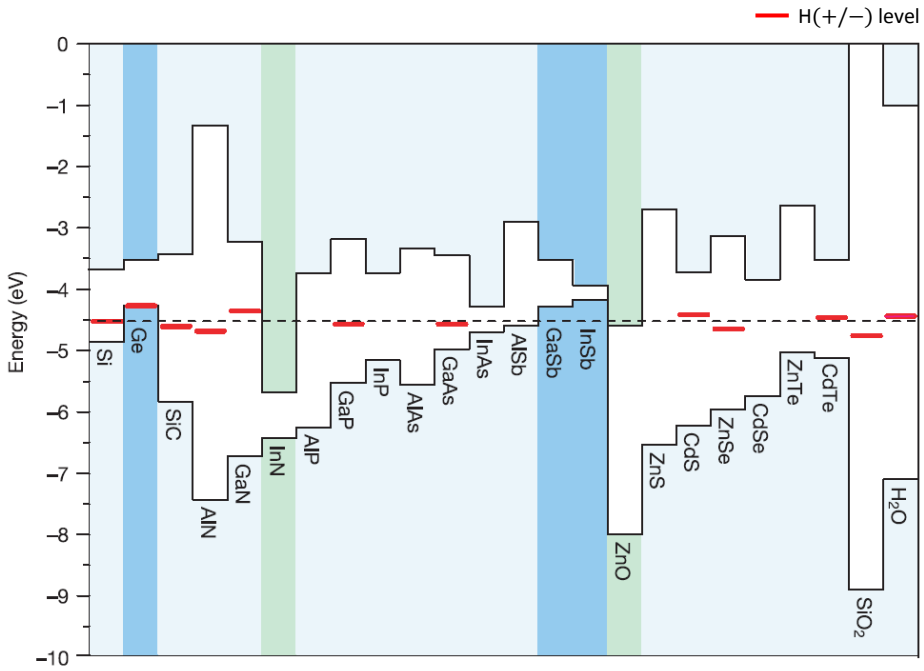
Preliminary results on Li dopant







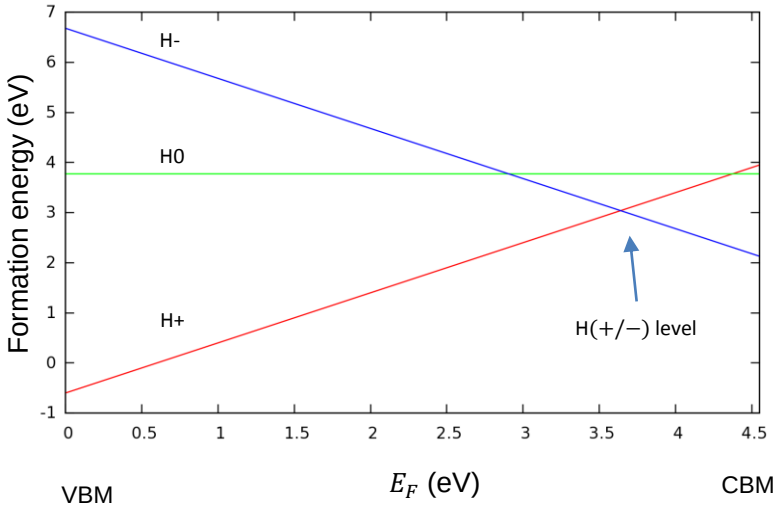
High-throughput ab initio screening III: band alignment of oxides



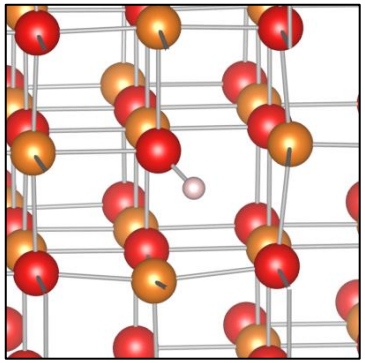
C. G. Van de Walle et al, Nature **423**, 626 (2003)

- H(+/-) level as the charge neutrality level (CNL) can be a reference level to align relative band positions of solids.

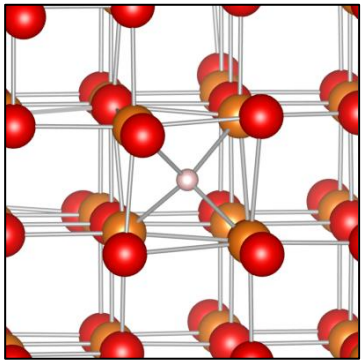
- Formation Energy of MgO:H (GGA)



H^+ stable configuration



H^- stable configuration



Summary

- We are developing programs for automatic high-throughput ab initio computations
- With decent computational resources, it is possible to compute a certain bulk property with the speed of ~500 structures per month.
- We built a materials map related to band gap and dielectric constants and found several candidate high-k dielectrics that worth experimental investigation.
- We are expanding the automated ab initio screening to find suitable dopants in ZnO and band alignment of various oxides.