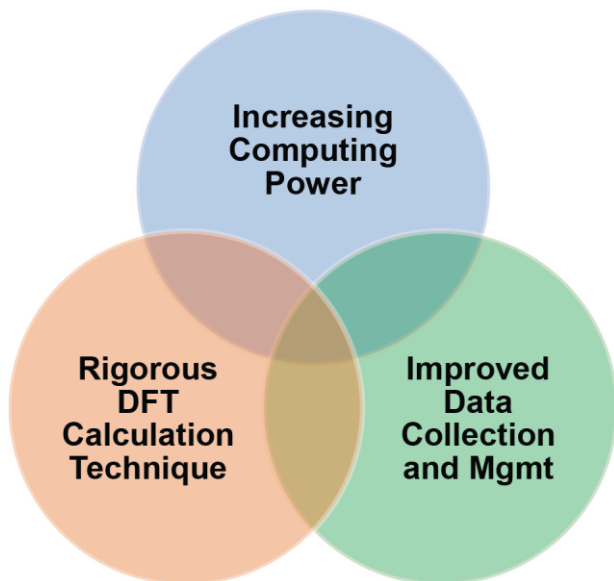


Searching for functional oxides using high-throughput *ab initio* screening

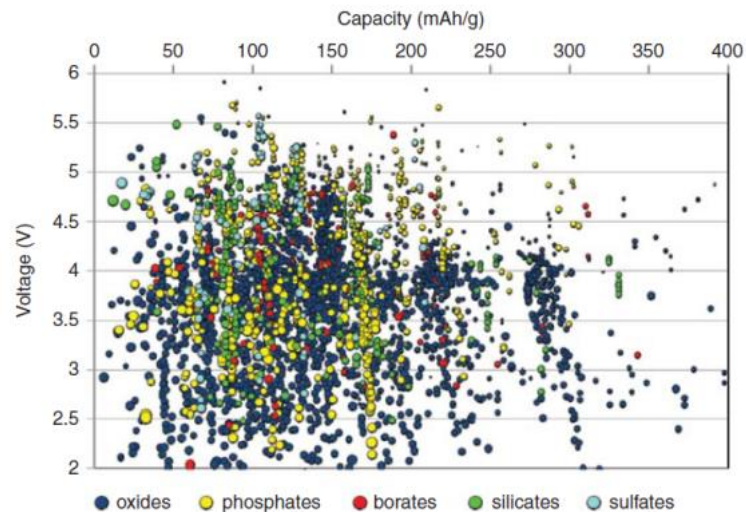
Kanghoon Yim, Joohee Lee, Yong Youn, Kyu-hyun Lee, and
Seungwu Han

Materials Theory and Computation Group
Department of Materials Science and Engineering
Seoul National University

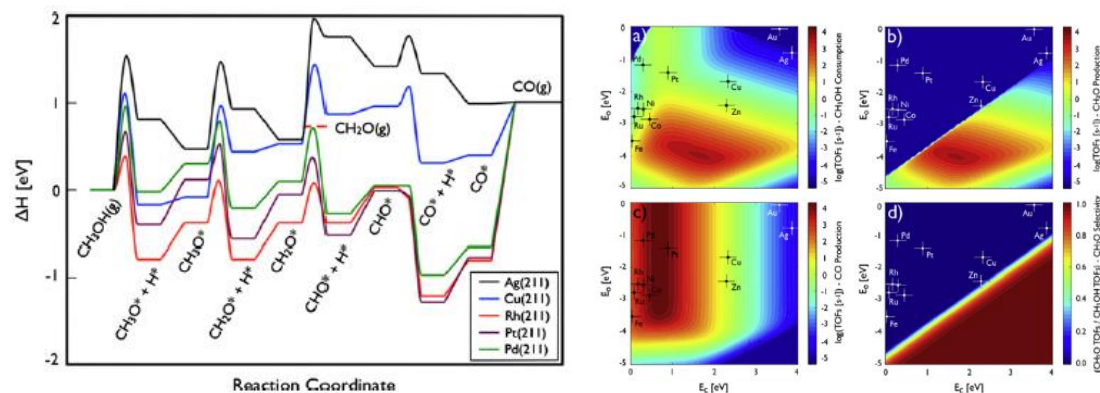




- Battery (Ceder group)



- Catalyst (Norskov group)



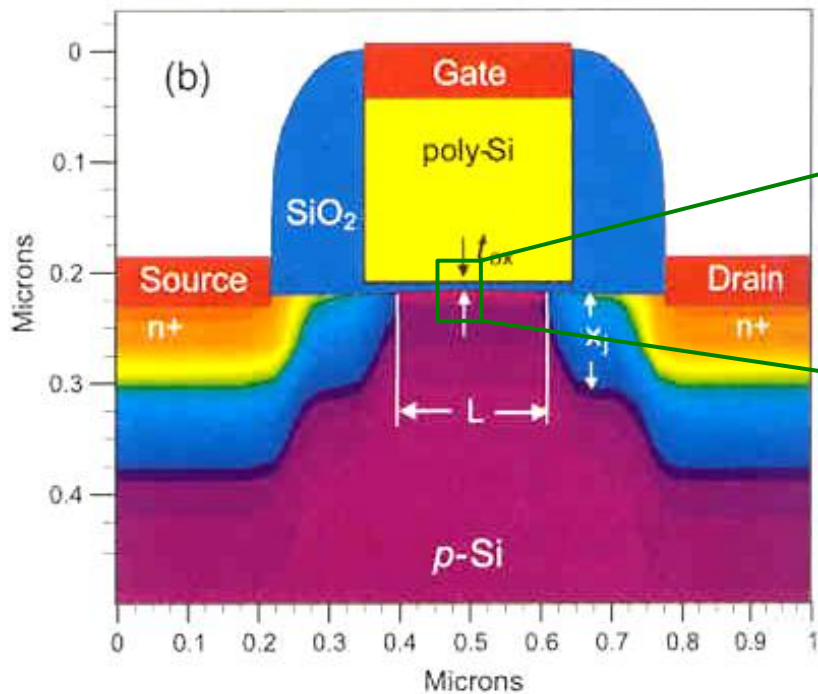
Complexity level of modeling	Property
I	Lattice parameter, band structure (energy gap, effective mass), elastic constant, phonon, dielectric constant, absorption coefficient,..
II	Point defect (formation energy, transition level, migration energy), surface (exposed to vacuum),
III	Defect complex, doping,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

- Automation 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-k Dielectric reduces leakage substantially

Gate

1.2nm SiO₂

Silicon substrate

Gate

3.0nm High-k

Silicon substrate

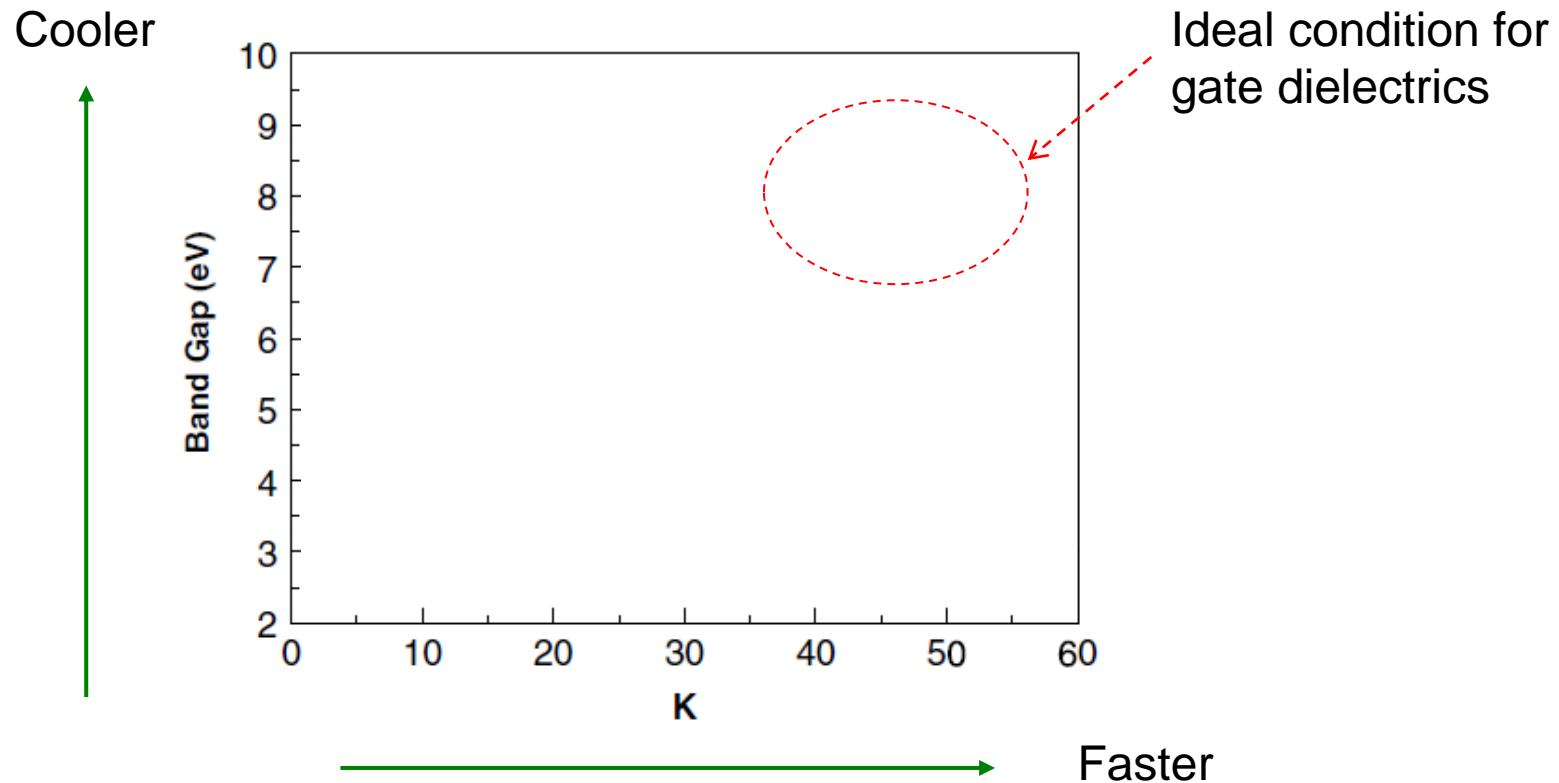
Benefits compared to current process technologies

	High-k vs. SiO ₂	Benefit
Capacitance	60% greater	<i>Much faster transistors</i>
Gate dielectric leakage	> 100x reduction	<i>Far cooler</i>

intel.

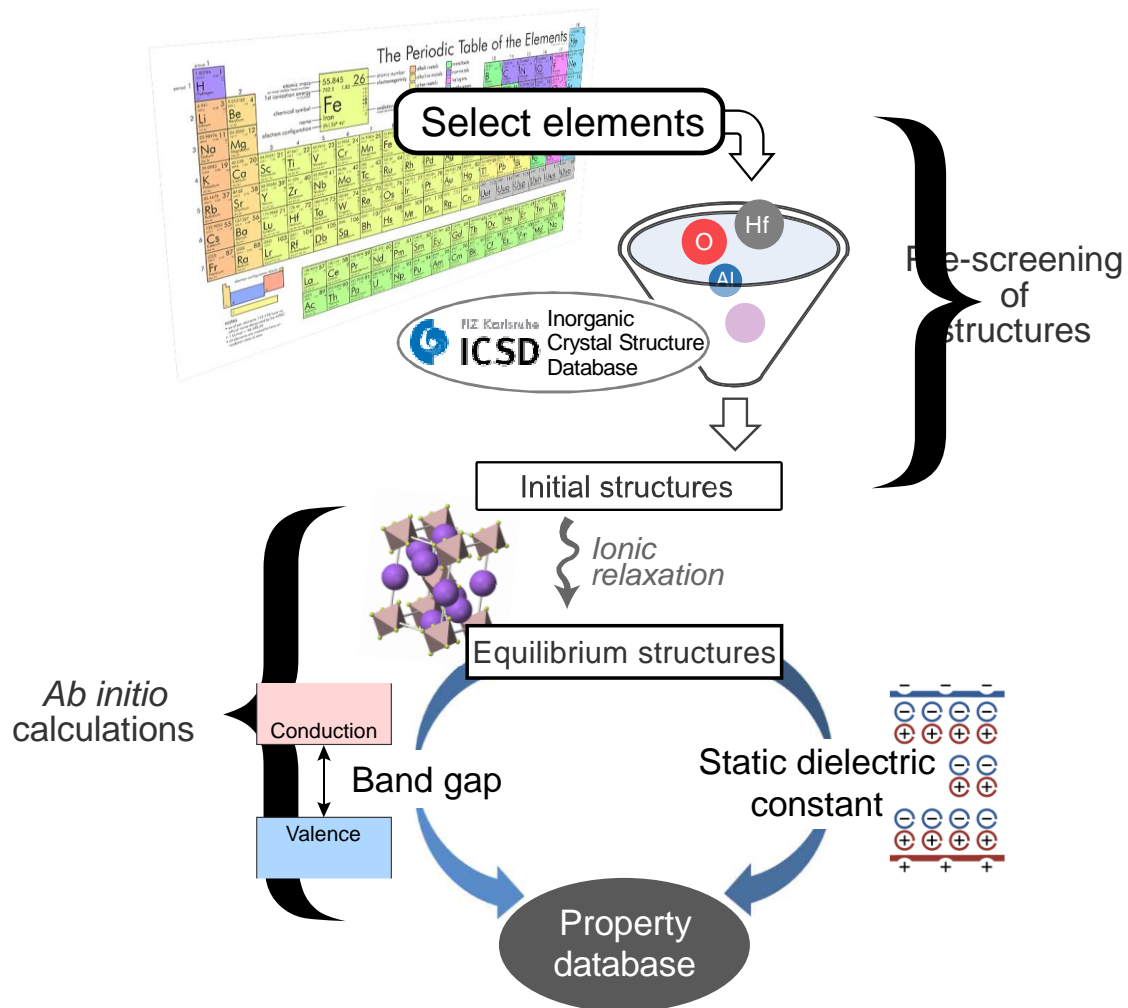
10

- HfO₂ and ZrO₂ are already being used as high-k dielectrics in transistors and capacitors of recent CPUs and DRAMs



- 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.

- 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 quinary 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.



VASP was used for the ab initio calculations.

Computational cost

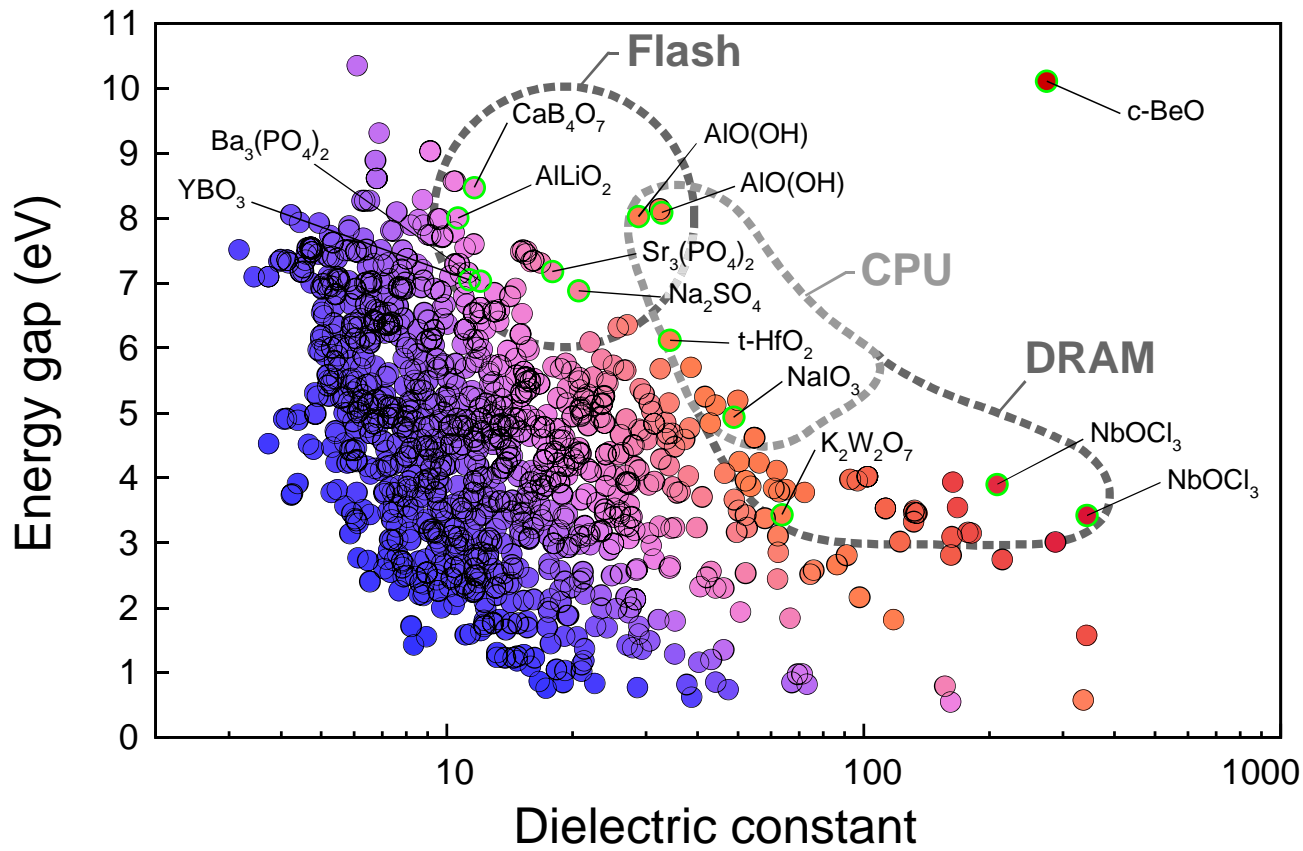
- Calculated data from more than 1,500 structures are collected over effectively 1 year or so. (~500 structures are metallic within GGA)
- Computational resources
 - Quadcore Intel Xeon 2.50 GHz (E5420)
 - 8 nodes (64 cores)
- Average computational costs
 - ~ 130 CPU hours per structure
 - or ~ 8 structures per day



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



~1,500 oxides



[DRAM]

- $f_{FOM} > 210$
- $E_g > 3 \text{ eV}$ and $\kappa > 30$

[CPU]

- $f_{FOM} > 210$
- $E_g > 4 \text{ eV}$
- $E_{vac} > 5.6 \text{ eV}$

[Flash]

- $f_{FOM} > 80$
- $E_g > 6 \text{ eV}$



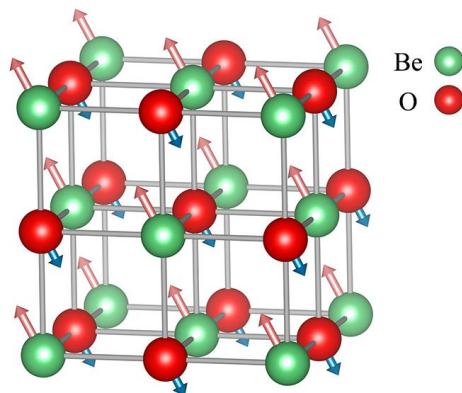
$$FOM = (\text{band gap}) \times (\text{dielectric constant})$$



[Binary oxide]

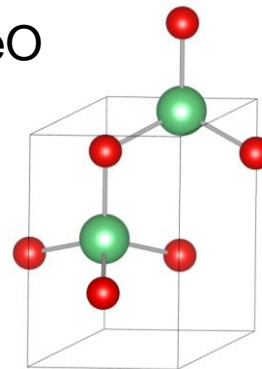
- c-BeO (rocksalt)

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



ϵ^0 : 276
 E_g : 10.0 eV

- w-BeO

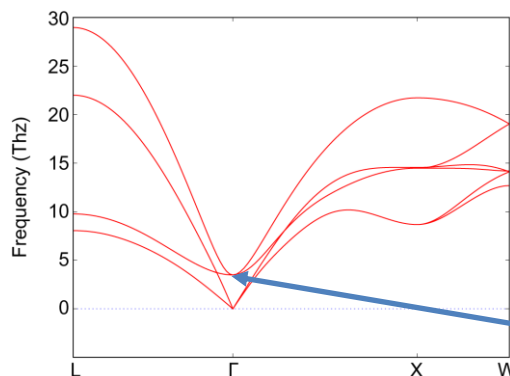


ϵ^0 : 6.9
 E_g : 9.3 eV

Phase transition at $P > 137 \text{ GPa}^2$

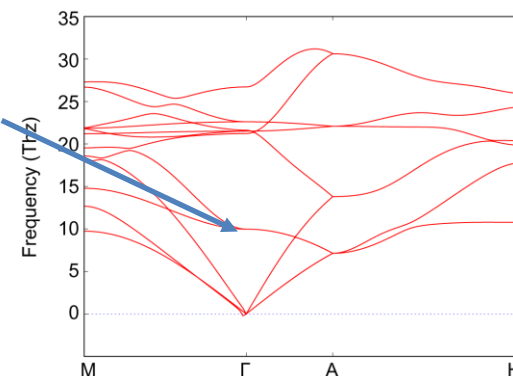
$\Delta E/\text{atom} = 480 \text{ meV}$ at 0K

Phonon dispersion curve



$f = 9.96 \text{ THz}$

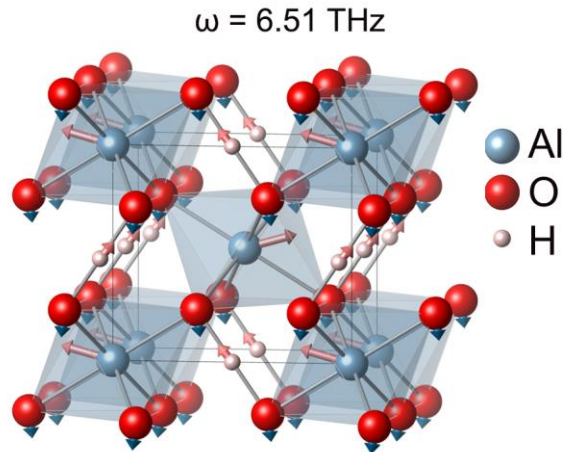
$f = 3.48 \text{ THz}$



[Ternary oxides]

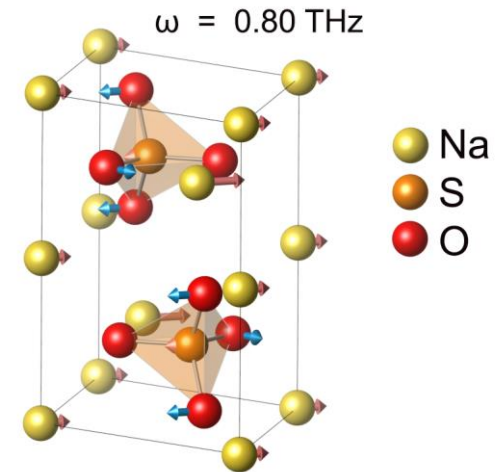
- $\text{AlO}(\text{OH})$

$$\begin{aligned}\epsilon^\infty &: 4.7 \\ \epsilon^0 &: 18.4 \\ E_g &: 5.7 \text{ eV}\end{aligned}$$



- Na_2SO_4

$$\begin{aligned}\epsilon^\infty &: 2.3 \\ \epsilon^0 &: 20.7 \\ E_g &: 6.9 \text{ eV}\end{aligned}$$



- **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.

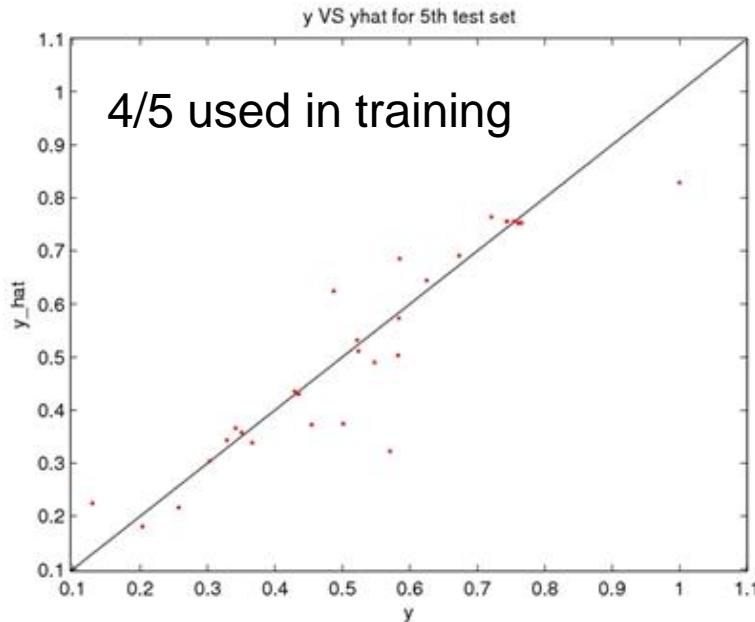
- ② **Channeled structure by strong covalent oxide unit**

- ✓ 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

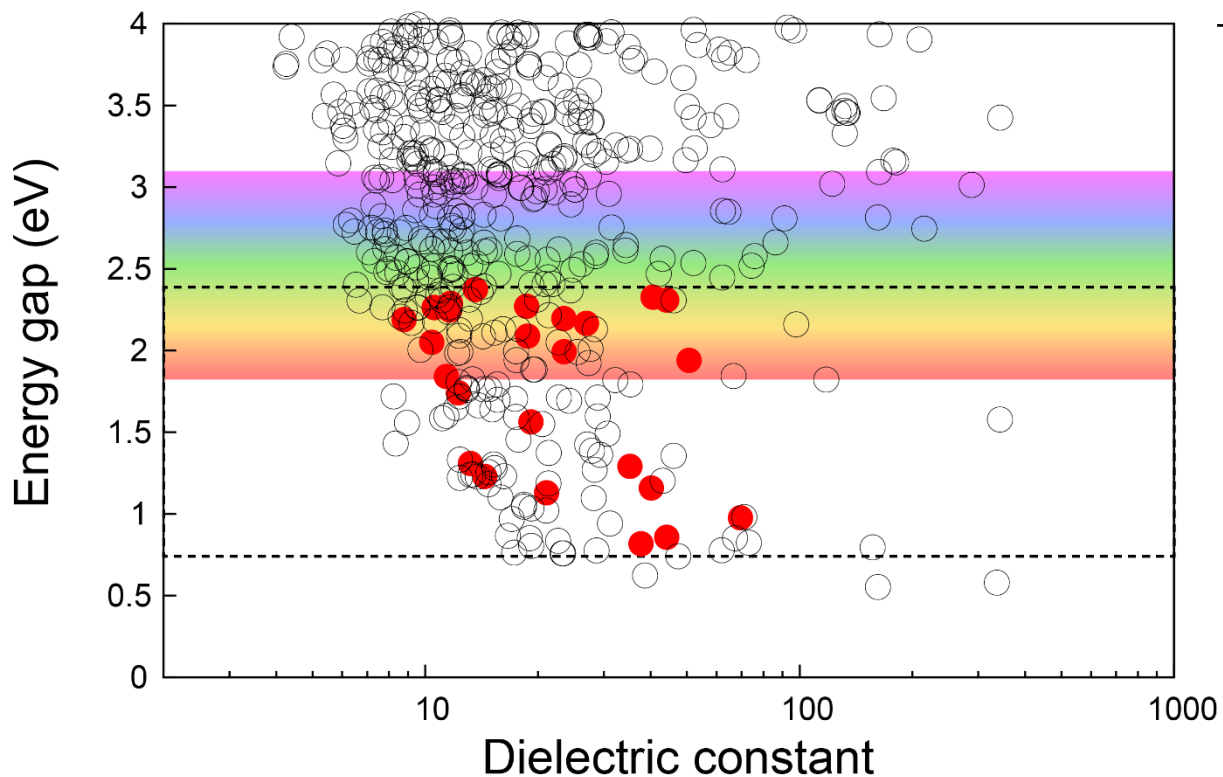
- Support vector regression on 152 binary oxides over a wide range of band gap.
- Four properties (Z, NN distance, effective CN, Bader charge) are selected for the Gaussian-type regression model.

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



✓ In collaboration with Samsung Advanced Institute of Technology

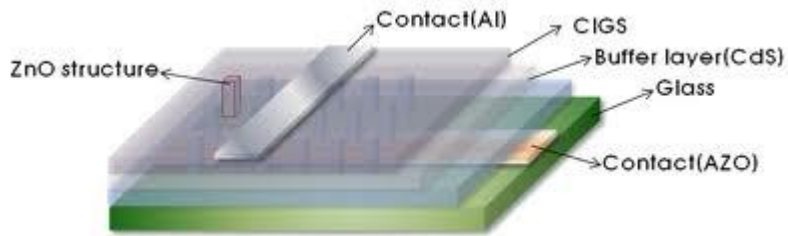




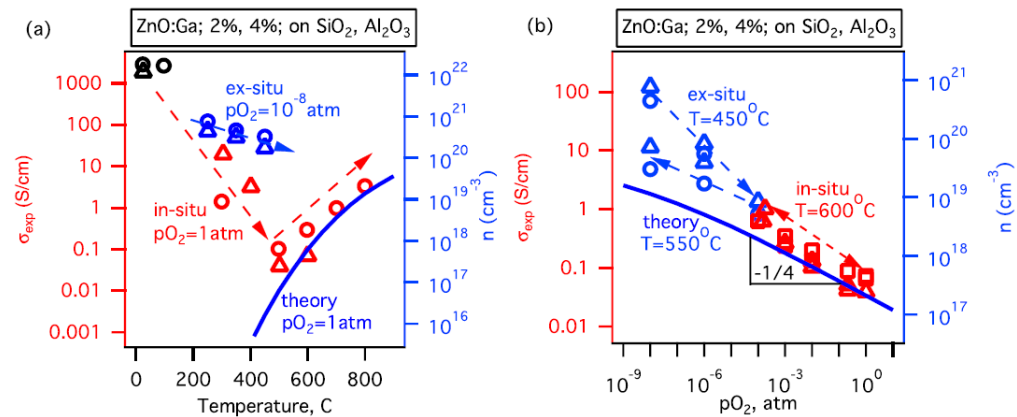
name	E_g (eV)	name	E_g (eV)
Sr_3GeO	0.82	Cd_3TeO_6	1.99
Sr_3SiO	0.86	K_4OBr_2	2.05
WOCl_3	0.98	$\text{Cd}_2\text{Sb}_2\text{O}_7$	2.09
Ag_2BiO_3	1.13	MoO_3	2.17
Tl_2O	1.16	K_3OCl	2.19
$\text{Hg}_3\text{O}_2\text{Cl}_2$	1.23	MoO_3	2.20
Ag_2HgO_2	1.31	Hg_4O_2 $(\text{NO}_3)_2$	2.26
$\text{Rb}_4\text{Br}_2\text{O}$	1.56	CdGeO_3	2.27
$\text{Rb}_2\text{Sn}_2\text{O}_3$	1.74	SnO_2	2.29
LiAg_3O_2	1.84	WO_3	2.31
Sb_2OS_2	1.94	LiNbO_2	2.37

- Carrier concentration control for electrode applications

<Transparent conductor>



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

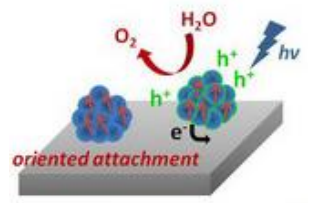


A. Zakutayev et al., *Appl. Phys. Lett.* **103**, 232106 (2013)

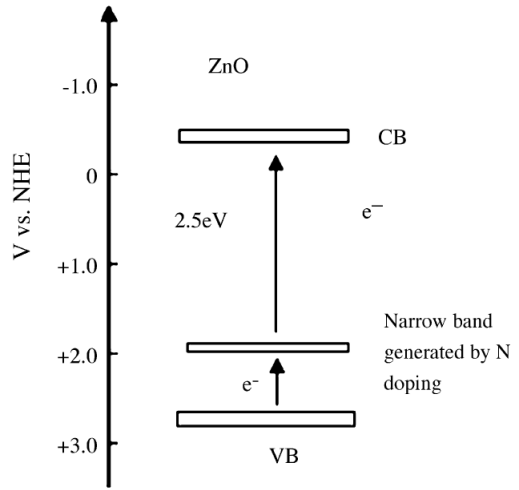
: Heavily doped-ZnO has High conductivity ($\rho \sim 10^{-4} \Omega\text{cm}$) comparable to ITO ($0.72 \times 10^{-4} \Omega\text{cm}$)

Dopant in ZnO

- Band gap engineering and facilitate absorption of visible light

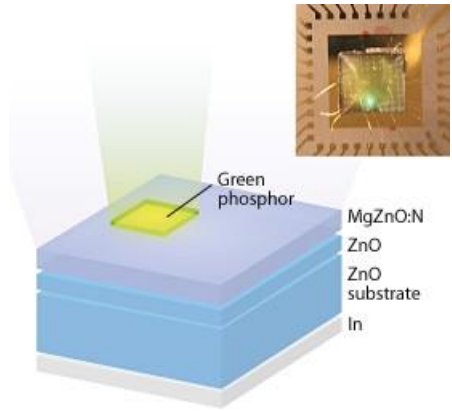


Conventional dopant : N, C, F, transition metal

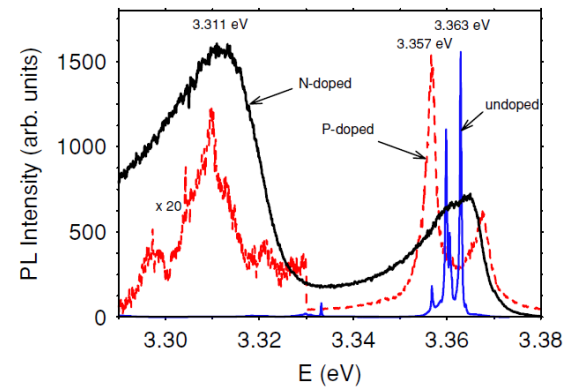


S. Rehman et al., J. Hazard. Mater. 170 (2009)

- Reliable and reproducible p-type doping

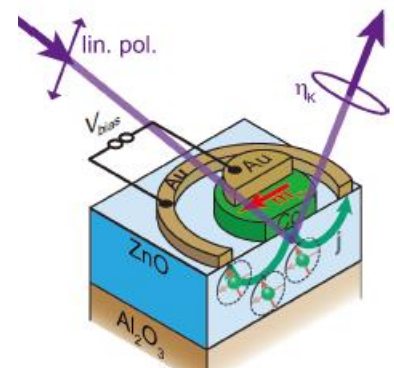


Conventional dopant : N, P, Mg, Cd, transition metal



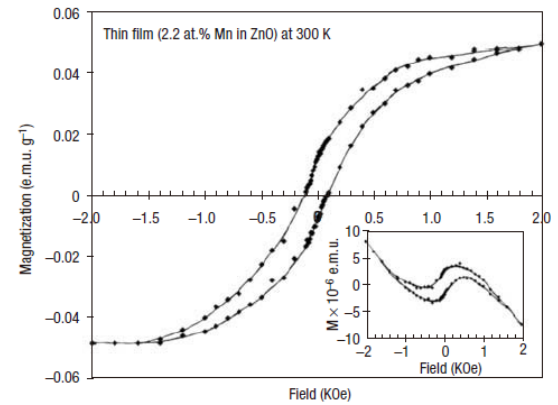
D.C. Look et al., Semicond. Sci. Technol. 20 (2005)

- Diluted magnetic semiconductor 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)

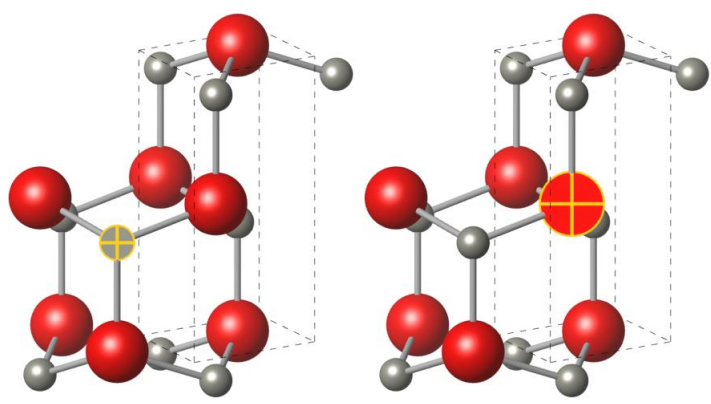


hydrogen 1 H 1.0079																		helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122											boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180	
sodium 11 Na 22.990	magnesium 12 Mg 24.305											aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948	
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80	
rubidium 37 Rb 85.468	strontium 38 Sr 87.62											indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29	
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	89-102 * *	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	unnilium 110 Uun [271]	ununium 111 Uuu [272]	unbibium 112 Uub [277]		ununquadium 114 Uuq [289]				

We wish to calculate:

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

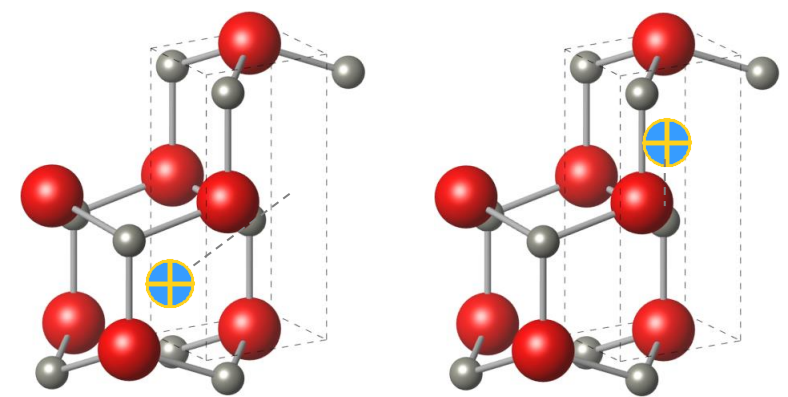
- Substitutional sites



- Cation site

- Anion site

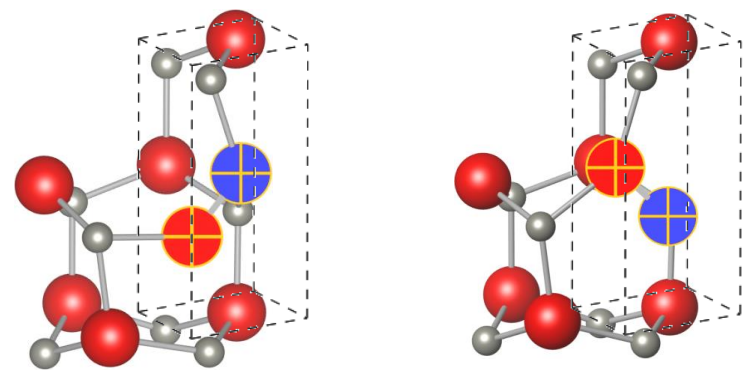
- Interstitial sites



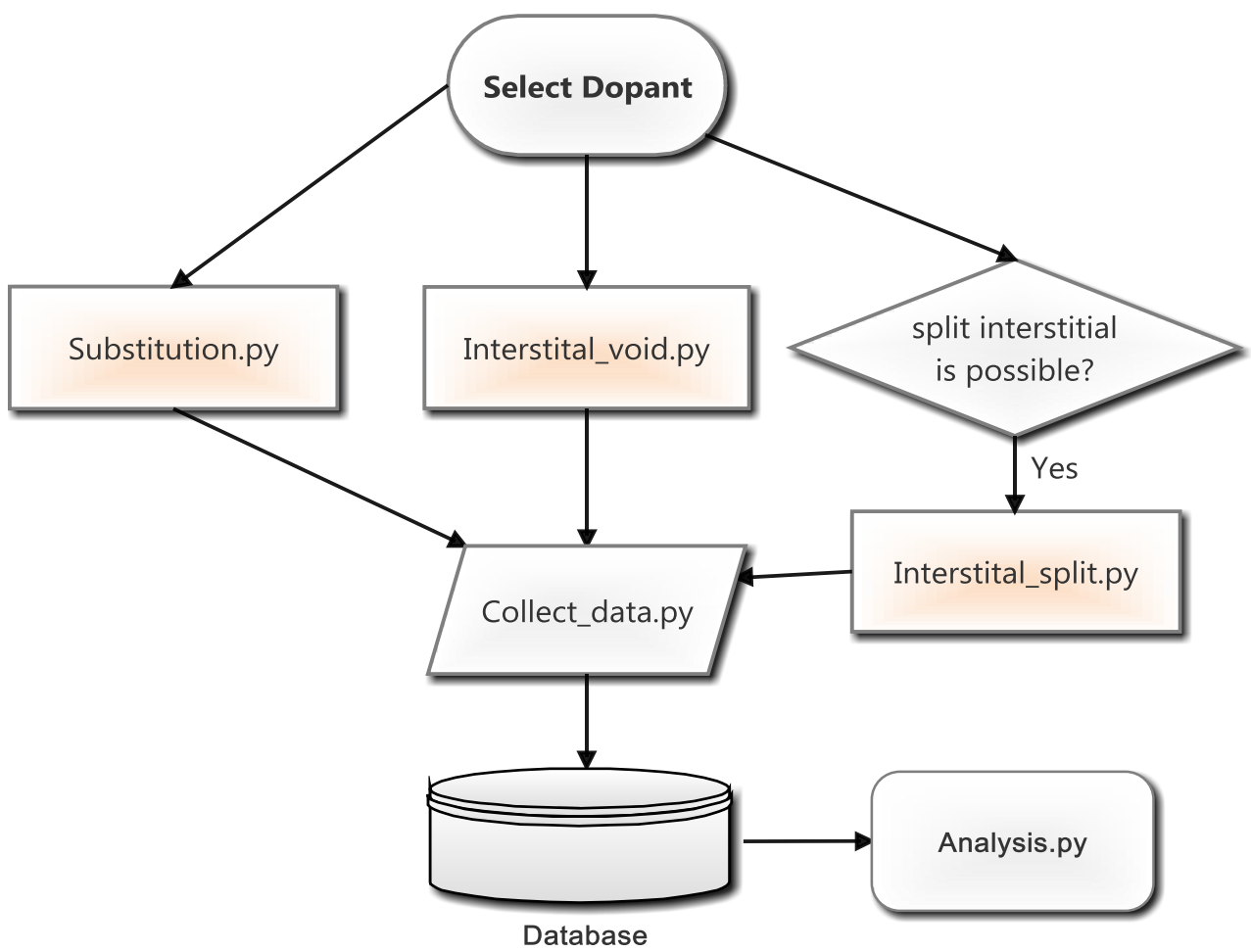
- Octahedral site ($AB_{||}$)

- Tetrahedral site (AB_{\perp})

- Split-interstitial

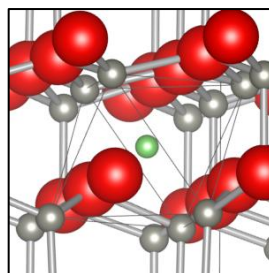
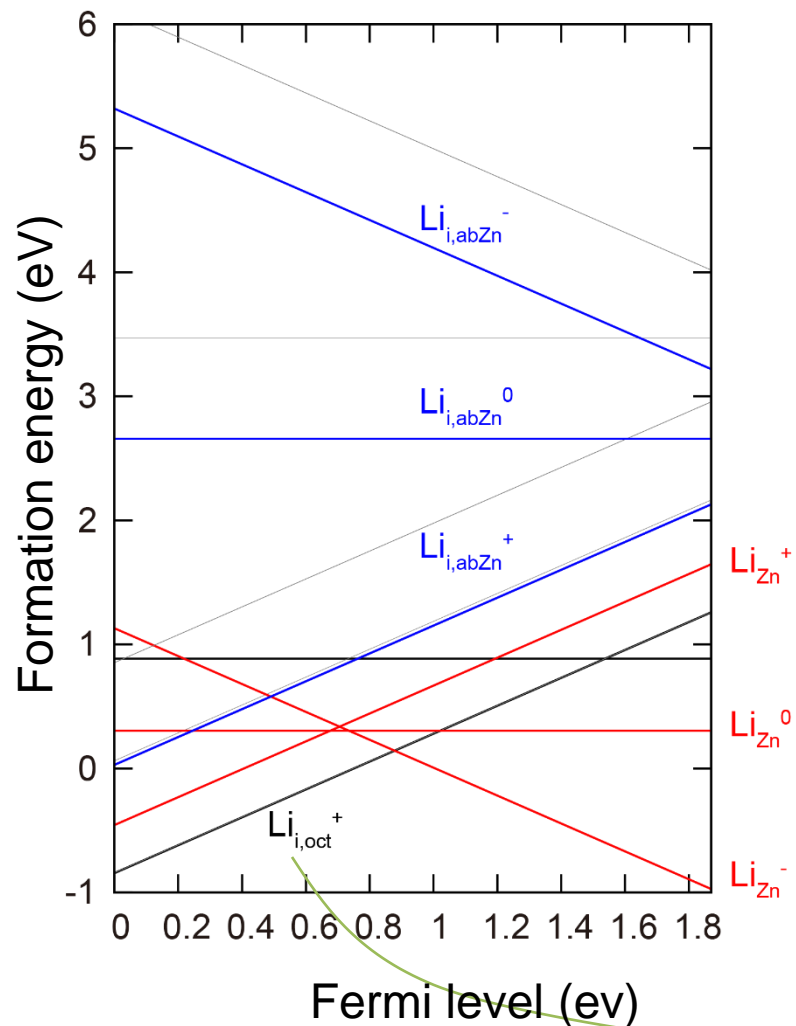


Work flow to find stable doping sites

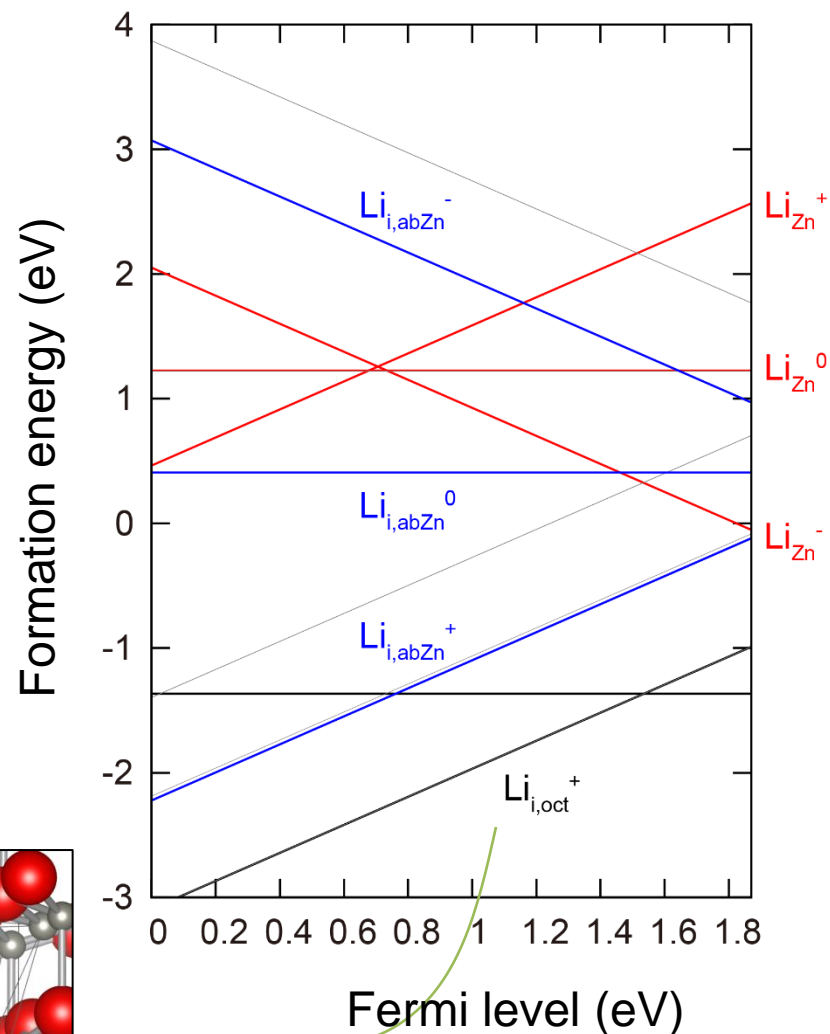


Preliminary results on Li dopant

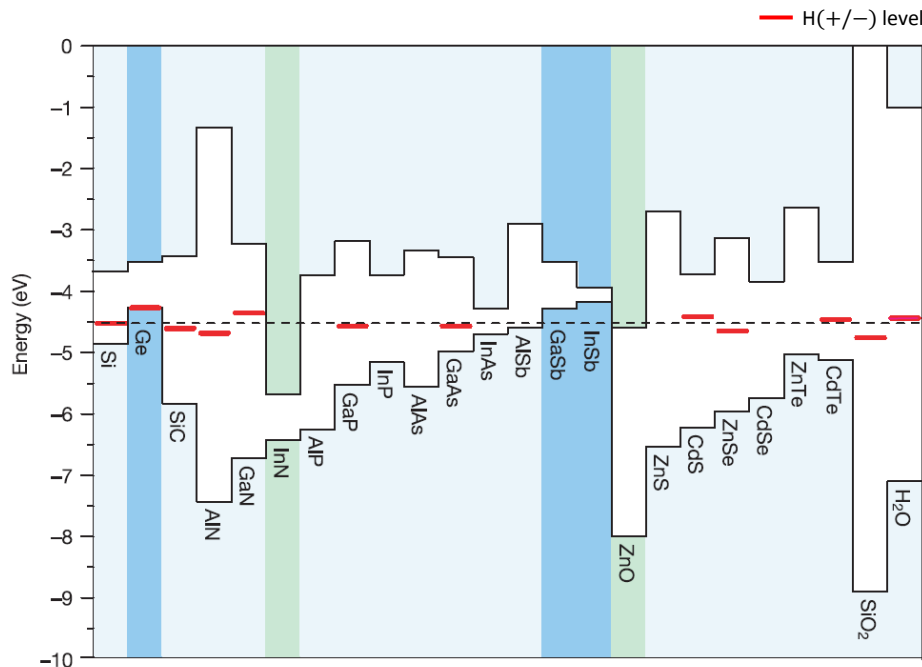
Li-doping at O-rich



Li-doping at Zn-rich



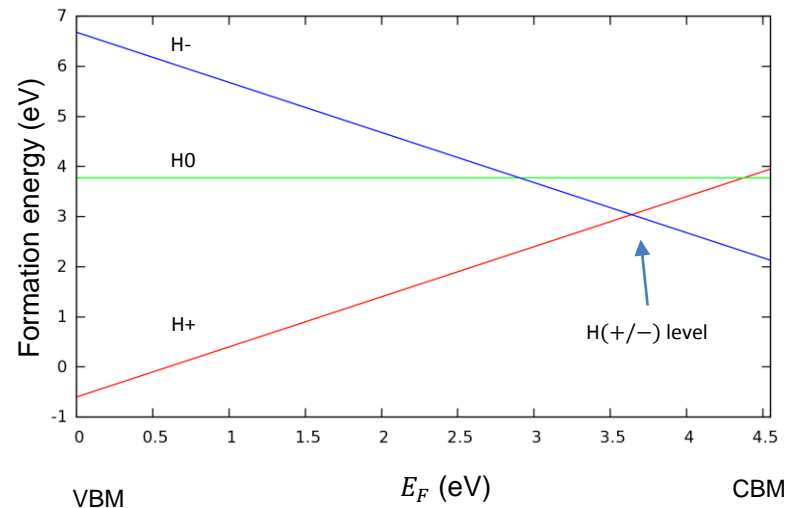
High-throughput ab initio screening III: band alignment of oxides



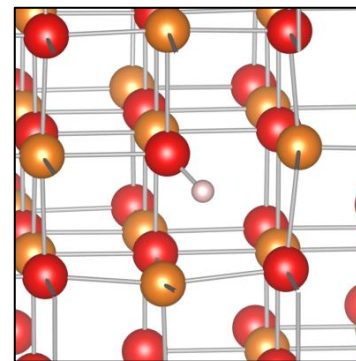
C. G. Van de Walle et al, Nature **423**, 626 (2003)

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

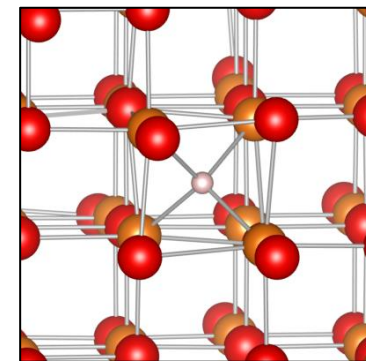
- Formation Energy of MgO:H (GGA)



H⁺ stable configuration



H⁻ stable configuration



- 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.

