Searching for functional oxides using high-throughput \textit{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
Introduction

- Battery (Ceder group)

- Catalyst (Norskov group)
## Automatic computation of material properties

<table>
<thead>
<tr>
<th>Complexity level of modeling</th>
<th>Property</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Lattice parameter, band structure (energy gap, effective mass), elastic constant, phonon, dielectric constant, absorption coefficient,..</td>
</tr>
<tr>
<td>II</td>
<td>Point defect (formation energy, transition level, migration energy), surface (exposed to vacuum),</td>
</tr>
<tr>
<td>III</td>
<td>Defect complex, doping,</td>
</tr>
<tr>
<td>IV</td>
<td>Interface (band alignment)</td>
</tr>
</tbody>
</table>
- Automation script module (compatible with VASP)

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

to be open at http://mtcg.snu.ac.kr
- HfO$_2$ and ZrO$_2$ 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.
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.
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

<table>
<thead>
<tr>
<th>Time cost</th>
<th>Structure relaxation</th>
<th>Band gap (GGA)</th>
<th>Band gap (HSE)</th>
<th>Dielectric constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>6</td>
<td>21</td>
<td>43</td>
<td>30</td>
</tr>
</tbody>
</table>
Results

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

\[ \begin{align*}
\text{[DRAM]} & \quad - f_{\text{FOM}} > 210 \\
& \quad - E_g > 3 \text{ eV and } \kappa > 30
\end{align*} \]

\[ \begin{align*}
\text{[CPU]} & \quad - f_{\text{FOM}} > 210 \\
& \quad - E_g > 4 \text{ eV} \\
& \quad - E_{\text{vac}} > 5.6 \text{ eV}
\end{align*} \]

\[ \begin{align*}
\text{[Flash]} & \quad - f_{\text{FOM}} > 80 \\
& \quad - E_g > 6 \text{ eV}
\end{align*} \]
[Binary oxide]

- **c-BeO**
  - rocksalt
  - Be-O bond length is 0.16 Å longer than w-BeO
  - $\varepsilon^0 : 276$
  - $E_g : 10.0$ eV

- **w-BeO**
  - Phase transition at $P > 137$ GPa
  - $\Delta E/\text{atom} = 480$ meV at 0K
  - $\varepsilon^0 : 6.9$
  - $E_g : 9.3$ eV

Phonon dispersion curve:
- $f = 9.96$ THz
- $f = 3.48$ THz
[Ternary oxides]

- **AlO(OH)**
  - $\varepsilon^\infty$: 4.7
  - $\varepsilon^0$: 18.4
  - $E_g$: 5.7 eV

- **$\ce{Na2SO4}$**
  - $\varepsilon^\infty$: 2.3
  - $\varepsilon^0$: 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.

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

4/5 used in training

✓ In collaboration with Samsung Advanced Institute of Technology
Photoabsorber for solar cell

direct band gap, $0.8 \text{ eV} < E_g < 2.4 \text{ eV}$

<table>
<thead>
<tr>
<th>name</th>
<th>$E_g$ (eV)</th>
<th>name</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr$_3$GeO</td>
<td>0.82</td>
<td>Cd$_3$TeO$_6$</td>
<td>1.99</td>
</tr>
<tr>
<td>Sr$_3$SiO</td>
<td>0.86</td>
<td>K$_4$OBr$_2$</td>
<td>2.05</td>
</tr>
<tr>
<td>WOCl$_3$</td>
<td>0.98</td>
<td>Cd$_2$Sb$_2$O$_7$</td>
<td>2.09</td>
</tr>
<tr>
<td>Ag$_2$BiO$_3$</td>
<td>1.13</td>
<td>MoO$_3$</td>
<td>2.17</td>
</tr>
<tr>
<td>Tl$_2$O</td>
<td>1.16</td>
<td>K$_3$OCl</td>
<td>2.19</td>
</tr>
<tr>
<td>Hg$_3$O$_2$Cl$_2$</td>
<td>1.23</td>
<td>MoO$_3$</td>
<td>2.20</td>
</tr>
<tr>
<td>Ag$_2$HgO$_2$</td>
<td>1.31</td>
<td>Hg$_4$O$_2$(NO$_3$)$_2$</td>
<td>2.26</td>
</tr>
<tr>
<td>Rb$_4$Br$_2$O</td>
<td>1.56</td>
<td>CdGeO$_3$</td>
<td>2.27</td>
</tr>
<tr>
<td>Rb$_2$Sn$_2$O$_3$</td>
<td>1.74</td>
<td>SnO$_2$</td>
<td>2.29</td>
</tr>
<tr>
<td>LiAg$_3$O$_2$</td>
<td>1.84</td>
<td>WO$_3$</td>
<td>2.31</td>
</tr>
<tr>
<td>Sb$_2$OS$_2$</td>
<td>1.94</td>
<td>LiNbO$_2$</td>
<td>2.37</td>
</tr>
</tbody>
</table>
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


: 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**
  
  ![Diagram of oriented attachment](image)

  Conventional dopant: N, C, F, transition metal


- **Reliable and reproducible p-type doping**

  ![Diagram of MgZnO:N](image)

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


- **Diluted magnetic semiconductor of transition-metal doped ZnO**

  ![Diagram of diluted magnetic semiconductor](image)

  Conventional dopant: transition metal, Li


  P. Sharma et al., Nat. Mater. 2 (2003)
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 \( (\text{AB}_{||}) \)
  
  - Tetrahedral site \( (\text{AB}_{\perp}) \)

- **Split-interstitial**
Work flow to find stable doping sites

1. Select Dopant
   - Substitution.py
   - Interstital_void.py
2. Check if split interstital is possible?
   - Yes: Interstital_split.py
   - No: Collect_data.py
3. Database
4. Analysis.py
Preliminary results on Li dopant

Li-doping at O-rich

Li-doping at Zn-rich

Formation energy (eV)

Fermi level (eV)
High-throughput ab initio screening III: band alignment of oxides

- 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)
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.