PEC Materials: Theory and Modeling

Database Driven Novel Photo-catalysts by Alloying

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Overview

Timeline

- Project start date: Sept, 2009
- Project end date: Dec, 2012
- Percent complete: 100% 
  \textit{(completion of the previous project)}

Barriers

- Barriers addressed
  - Materials efficiency
  - Materials durability

Budget

- Total project funding $244,739
- Funding received in FY12: $83,867
- Funding for FY13: $00

Partners

- Interactions/ collaborations:
- Project lead:

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Approach 1:
Stabilization of High Efficiency Crystalline Material Systems

Approach 2:
Enhanced Efficiency in Thin-Film Material Systems

DOE Targets:
>1000h @STH > 8% (2013)
Projected PEC Cost: $2 - 4/kg H₂
PV-Electrolysis: >$10/kg H₂

Approach 3:
Development of 3rd Generation Materials and Structures

Efficiency

Durability

 DOE PEC Working Group
National/International Collaborations

MVSystmes
NREL
UNLV
TU Delft
HNEI

UT, University of Toledo
National Renewable Energy Laboratory
University of Nevada, Las Vegas
TUDelft
Empa
Questions:

• How to discover a material with a desired set of properties?
• What would be the crystal structure for that material?
• Is that material stable?
• What are electronic and optical properties of that material?
The goal is to theoretically/computationally predict semiconductor photo-catalysts which will satisfy the following criteria to produce hydrogen by water splitting:

1. Stable in an aqueous electrolyte
2. The band gap in the range 1.7eV ~ 2.2eV
3. Right band edge positions
4. Efficient optical absorptions properties
5. Good charge carrier transport
Either band gaps are too large
Or, band edges are not at the right position

Question: How do we get the right materials?
How do we tune band properties?

1. By isovalent doping.

2. By passive co-doping.

3. By predicting novel alloys

4. By reducing the dimensions.

Nanostructures: Nanocrystal, etc.

Challenging!
•Why not doping (light or heavy)?

In doping, the overall crystal structure of the host materials remains same, but crystallinity usually deteriorate.

In alloy a new crystal structure emerges, and stoichiometric relationship may change.
We first consider WO$_3$ as our example:

To improve let us dope $\text{WO}_3$ with nitrogen:

After N-doping:


A general feature: Crystalinity is poor after doping.
Mineral database search to design efficient energy-conversion materials

• There are thousands of naturally occurring minerals available, which are inherently stable.

• We plan to follow a “natural selection” process followed by a selective band-engineering approach.

• These new materials will have better crystalline properties than the doped materials.
Oxides those need to be avoided:

In selecting oxides we have avoided the oxides which are Mott insulators due to the following reasons:

• They have very poor transport properties for both electrons and holes.
• Doping does not improve the conduction properties significantly.
• Photo-current will be very insignificant.
Predicting new alloy:

Modify band structure of WO$_3$, but not by doping.

The **first step** is to identify what to alloy with WO$_3$:

(We do a lot of reading and testing!)

- In Bi$_2$W$_2$O$_9$, uplift of VB due to hybridization of O-2p and Bi-6s.

- In Ag$_2$WO$_4$, hybridization of O-2p and Ag-4d was found favorable for water splitting.
Instead of doping Ag and Bi in WO$_3$, we search for a mineral structure which can accommodate all of these in W-oxide.

Need to define proper search descriptors:

Question:
What kind of atomic coordination we are looking for?
What are the charge states?
What symmetries?

...
Goal: Instead of doping, we are looking for a mineral structure which will have both Ag and Bi in W-oxides, and a stable multi-cation oxide.
Mineral database search for AgBiW$_2$O$_8$:  

**Possible Structures**

- **Scheelite**
  - **Derivatives**
    - **Monoclinic**
      - $AlWO_4$ (S.G. 12 $C2/m$)
      - Wolframite (S.G. 13 $P2/c$)
      - Raspite (S.G. 14 $P2_1/a$)
      - Fergusonite (S.G. 15 $I2/a$)
    - **Orthorhombic**
      - $BaUO_4$ (S.G. 57 $Pbcm$)
      - Alumotantite (S.G. 60 $Pbcn$)
Computation Details:

• Density functional theory (DFT) has been used to calculate the total energies and other electronic properties of the minerals.

• Vienna *Ab-initio* Simulation Package (VASP) was used.

• Crystal structure relaxations were performed without any symmetry constraint.
Three most probable mineral structures for $\text{AgBiW}_2\text{O}_9$:

- **Scheelite**
  - $\Delta E = 0.69\text{eV}$

- **Wolframite**
  - $\Delta E = 0.00\text{eV}$

- **Fergusonite**
  - $\Delta E = 0.28\text{eV}$
Wolframite structure with different layer arrangements:

Experimental (SCS and SSR)
By Rajeshwar’s group at UTA

Figure 5: Partial DOS and band structure of wolframite $AgBiW_2O_8$. 
Second alloy structure
CuBiW$_2$O$_8$
Optical Properties of CuBiW$_2$O$_8$:
Third alloy structure
Summary

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cohesive Energy (eV/atom)</th>
<th>Optical Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgBiW$_2$O$_8$</td>
<td>-2.476</td>
<td>2.06</td>
</tr>
<tr>
<td>CuBiW$_2$O$_8$</td>
<td>-2.547</td>
<td>1.48</td>
</tr>
<tr>
<td>CuSnW$_2$O$_8$</td>
<td>-3.296</td>
<td>0.96</td>
</tr>
<tr>
<td>CuWO$_4$</td>
<td>-2.721</td>
<td>2.26</td>
</tr>
</tbody>
</table>
Collaborators:

- Muhammad N. Huda (Lead Investigator, UTA)
- Pranab Sarker (graduate student, UTA)
- Nicolas Gaillard (HNEI)
- Krishnan Rajeswar (UTA)
- Todd Deutsch (NREL)
- Mowafak M. Al-Jassim (NREL)
- John A. Turner (NREL)
Conclusions:

We have shown that new functional materials can be designed by predicting new alloy crystal structures.

In general, multi-cation oxides (more than 2 cations) are very challenging to synthesize.

This new modeling will guide the experimental scientists by providing “what to look for” to tune the synthesize process for multi-cation oxides.
Future work:

• A robust mineral database search descriptors based on desired functionality will be developed.

• Crystal structure optimizations need to be done at a higher flexibility.

• Collaboration with synthesis groups and feedback from them will be integrated more closely.

• Nano-crystals for selected structures will be considered.