UNIVERSITY OF TEXAS ARLINGTON

PEC Materials: Theory and Modeling

Database Driven Novel Photo-catalysts by Alloying

Muhammad N. Huda

University of Texas at Arlington

May, 2013

Project ID # PD052

Timeline

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

Barriers

- Barriers addressed
  - Materials efficiency
  - Materials durability

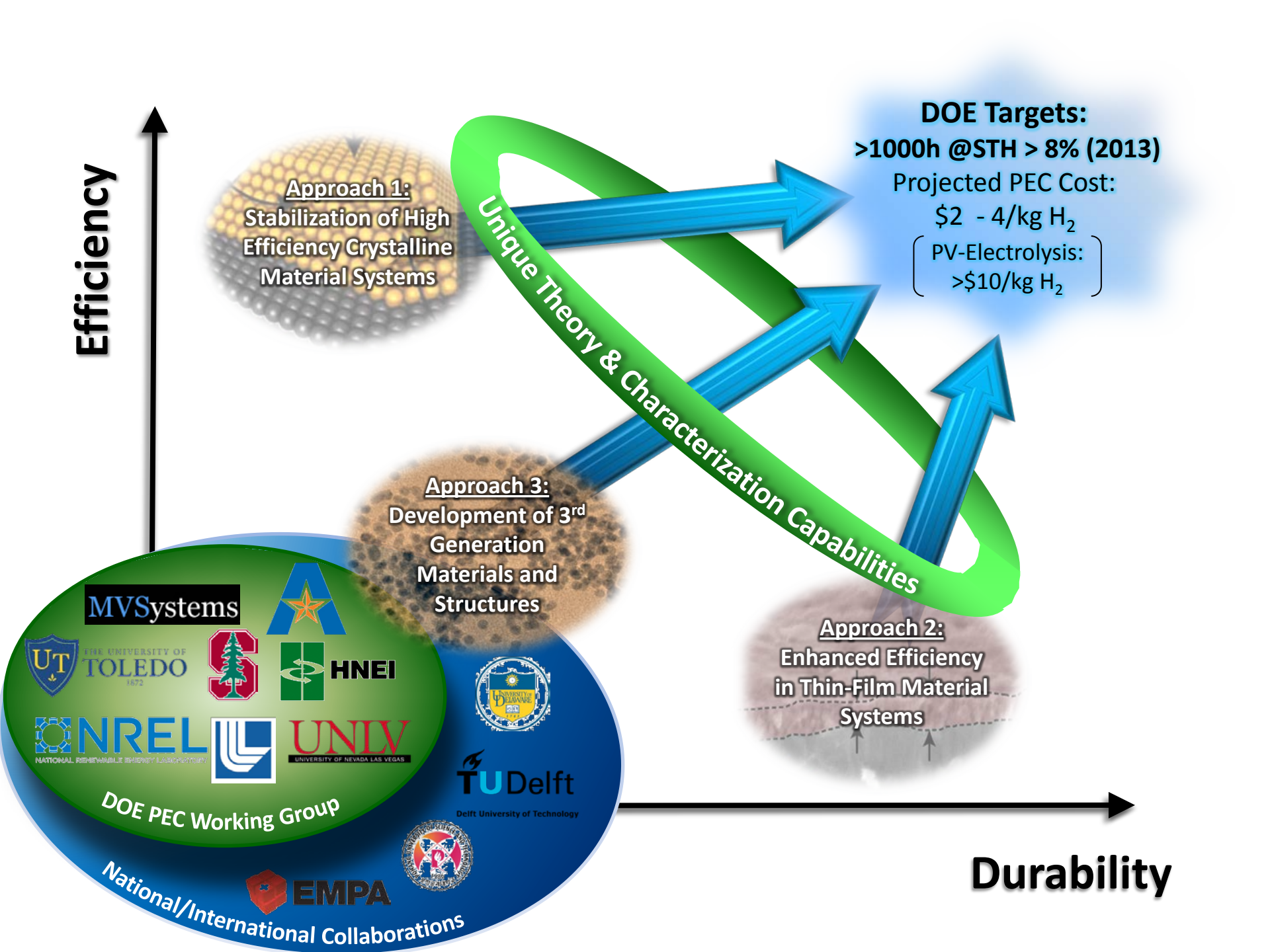
Budget

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

Partners

- Interactions/ collaborations:

- Project lead:


Efficiency
Durability
Approach 1:
Stabilization of High Efficiency Crystalline Material Systems
Approach 2:
Enhanced Efficiency in Thin-Film Material Systems
Approach 3:
Development of 3rd Generation Materials and Structures
Unique Theory & Characterization Capabilities
DOE Targets:
>1000h @STH > 8% (2013)
Projected PEC Cost:
$2 - 4/kg H2
PV-Electrolysis:
>$10/kg H2
MVSystems
THE UNIVERSITY OF TOLEDO
HNEI
NREL
NATIONAL RENEWABLE ENERGY LABORATORY
UNLV
UNIVERSITY OF NEVADA LAS VEGAS
DOE PEC Working Group
TU Delft
Delft University of Technology
EMPA
National/International Collaborations

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?

Introduction to the problem:

The goal is to theoretically/computationally predict semiconductor photo-catalysts which will satisfy the following criteria to produce hydrogen by water splitting:

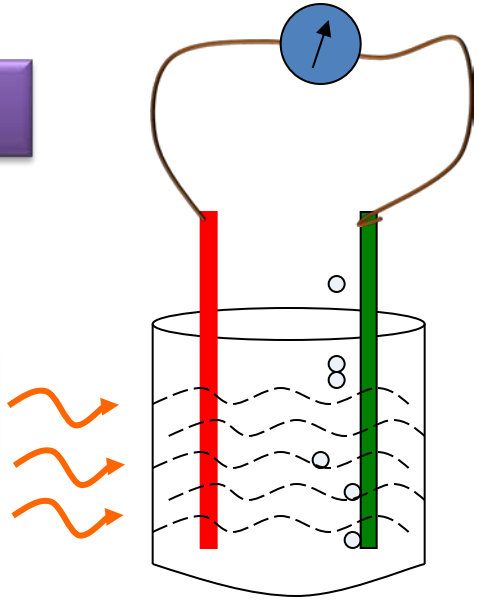
1 – Stable in an aqueous electrolyte

2 – The band gap in the range 1.7eV ~ 2.2eV

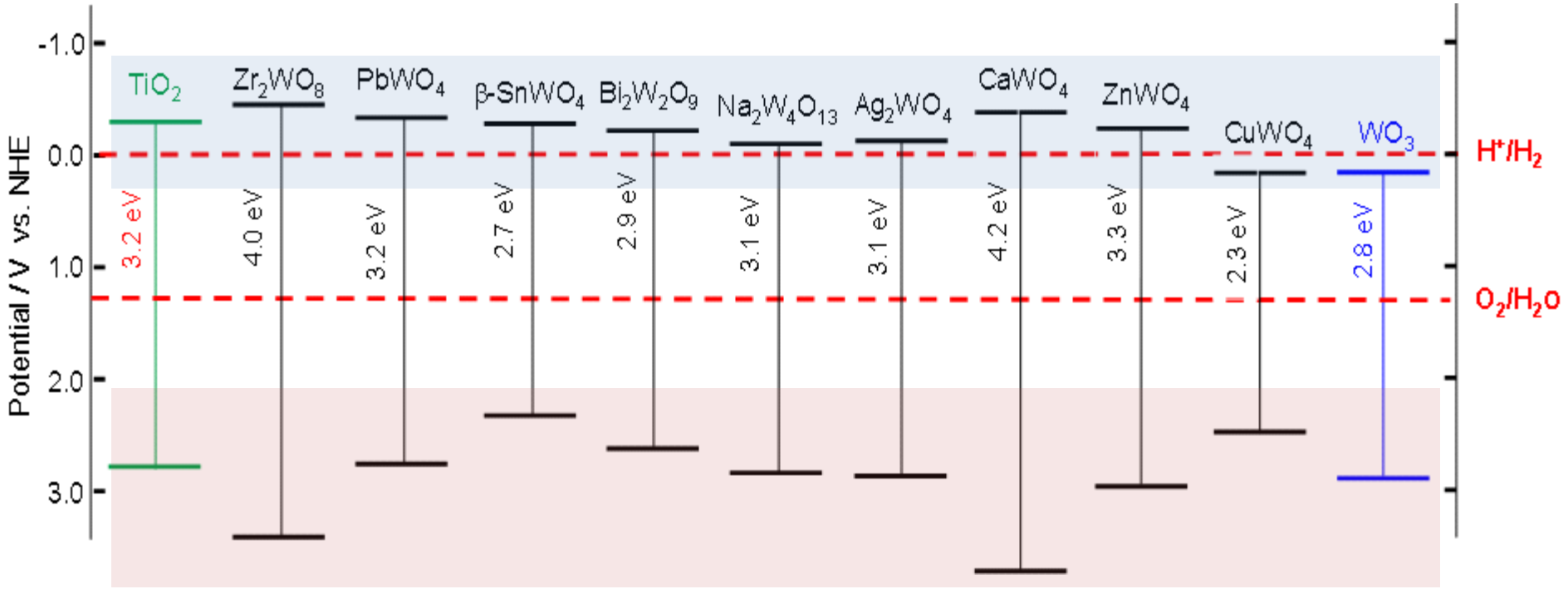
3 – Right band edge positions

4 – Efficient optical absorptions properties

5 – Good charge carrier transport



Introduction to the problem:



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?

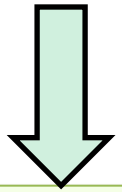
1. By isovalent doping. → GaN ↑ $Al_xGa_{1-x}N$

2. By passive co-doping. → GaN ↑ $Zn_xGa_{1-x}N_{1-x}O_x$

3. By predicting novel alloys → Challenging !

4. By reducing the dimensions. → Nanostructures: Nanocrystal, etc.

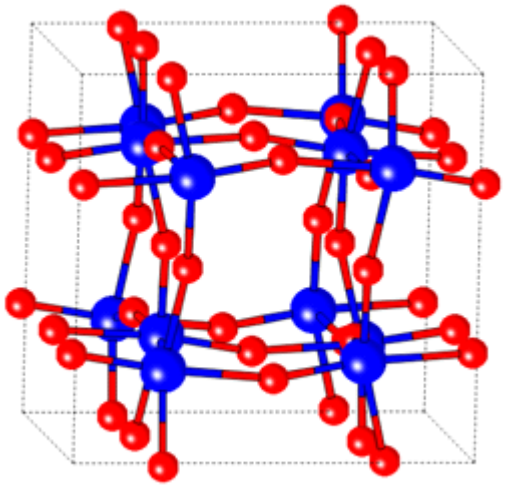
•Why not doping (light or heavy)?

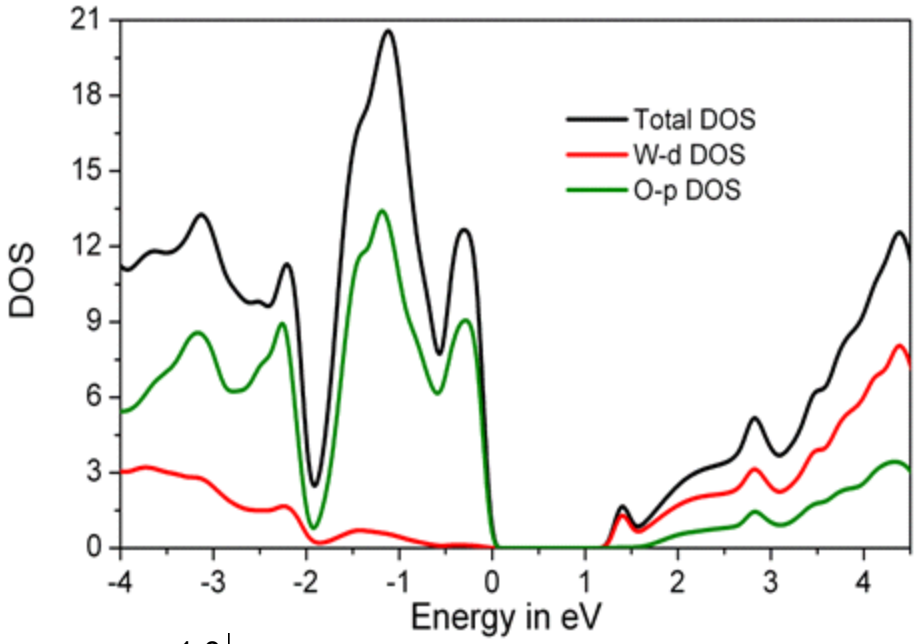


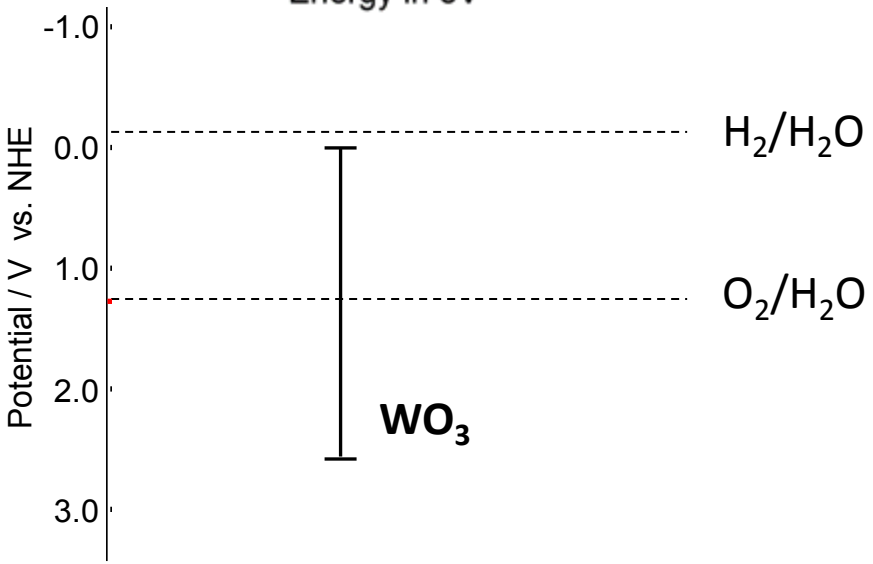
In doping, the overall crystal structure of the host materials remains same, but crystallinity usually deteriorate.

In alloy a new crystal structure emerges, and stoichiometric relationship may change.

We first consider WO_3 as our example:



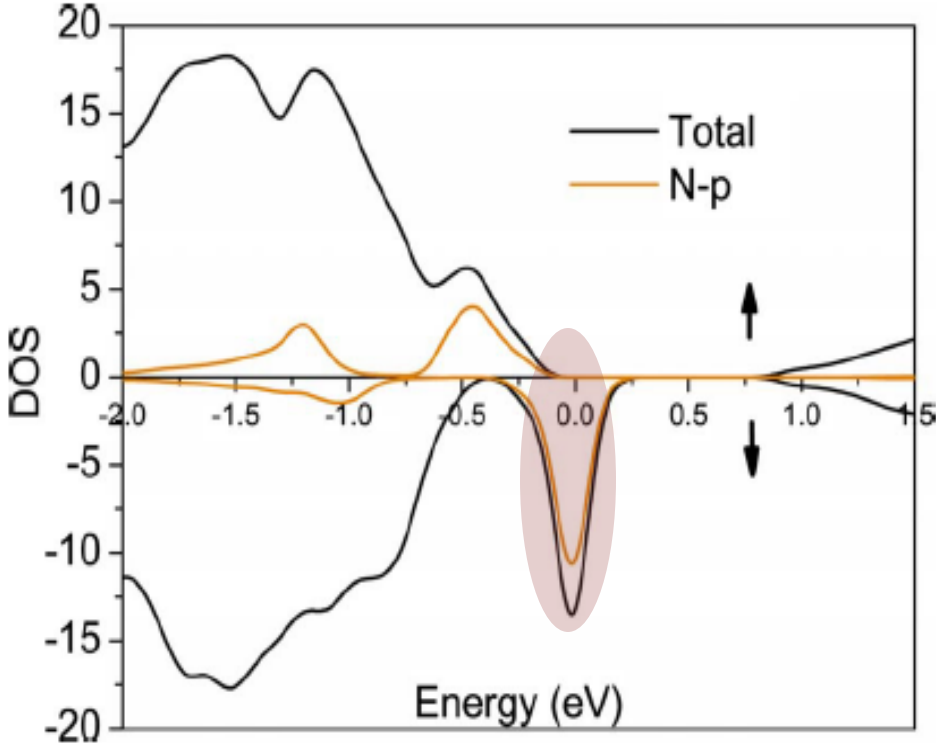




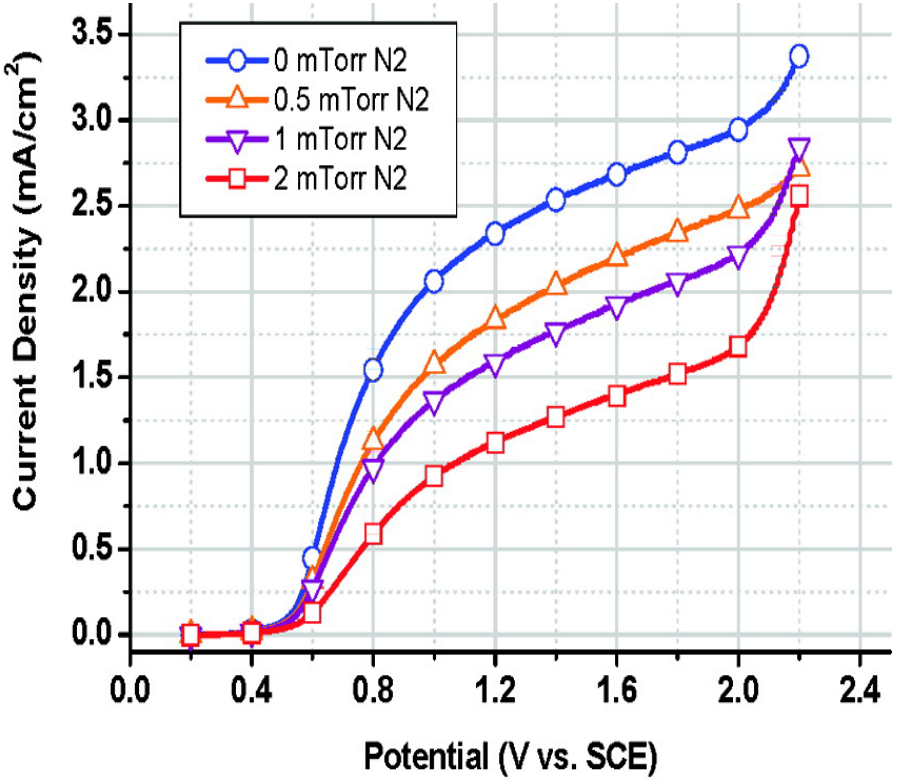
Physical Review B, **77**, 195102 (2008);
Physical Review B, **80**, 115118 (2009);
Catalysis Today, **199**, 53-64 (2013).

To improve let us dope WO_3 with nitrogen:

After N-doping:



Huda et al. Physical Review B, **77**, 195102 (2008).



Cole et al. Journal of Physical Chemistry C, 112, 5213 (2008).

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.

Journal of Renewable and Sustainable Energy, **3**, 053101 (2011).

Predicting new alloy:

Modify band structure of WO_3, <u>but not by doping</u>.

The **first step** is to identify what to alloy with WO_3 :

(We do a lot of reading and testing!)

- In $Bi_2W_2O_9$, uplift of VB due to hybridization of O-2p and Bi-6s.

- In Ag_2WO_4, hybridization of O-2p and Ag-4d was found favorable for water splitting.

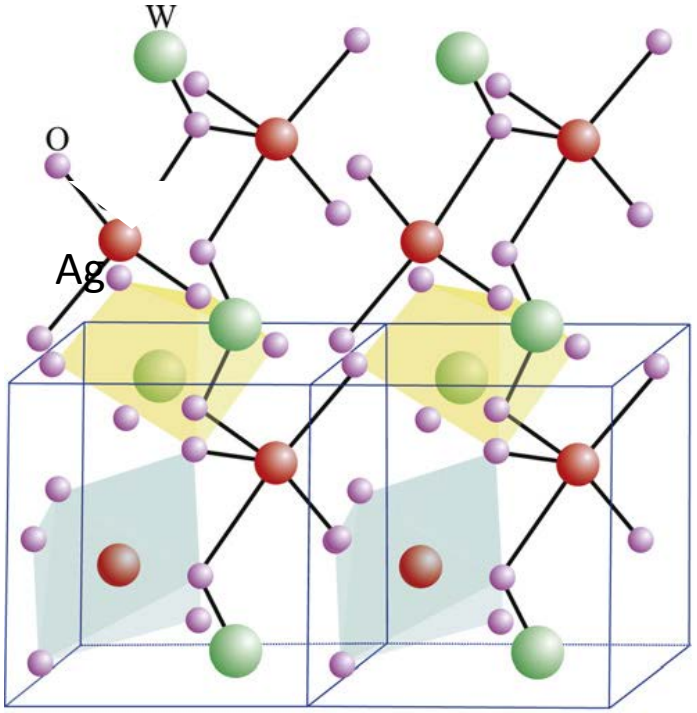
Instead of doping Ag and Bi in WO_3, we search for a mineral structure which can accommodate all of these in W-oxide.

Need to define proper search descriptors:

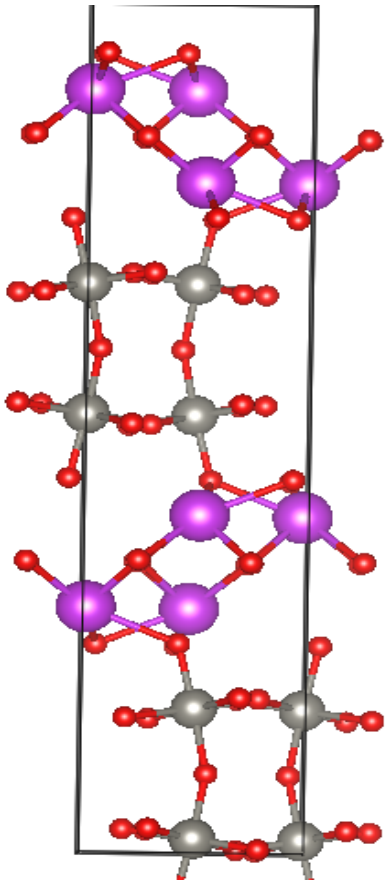
Question:
What kind of atomic coordination we are looking for?
What are the charge states?
What symmetries?
…

What type of bond coordination they prefer:

$AgWO_4$



$Bi_2W_2O_9$



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 $AgBiW_2O_8$:

Possible Structures

↓

Scheelite

↓

Derivatives

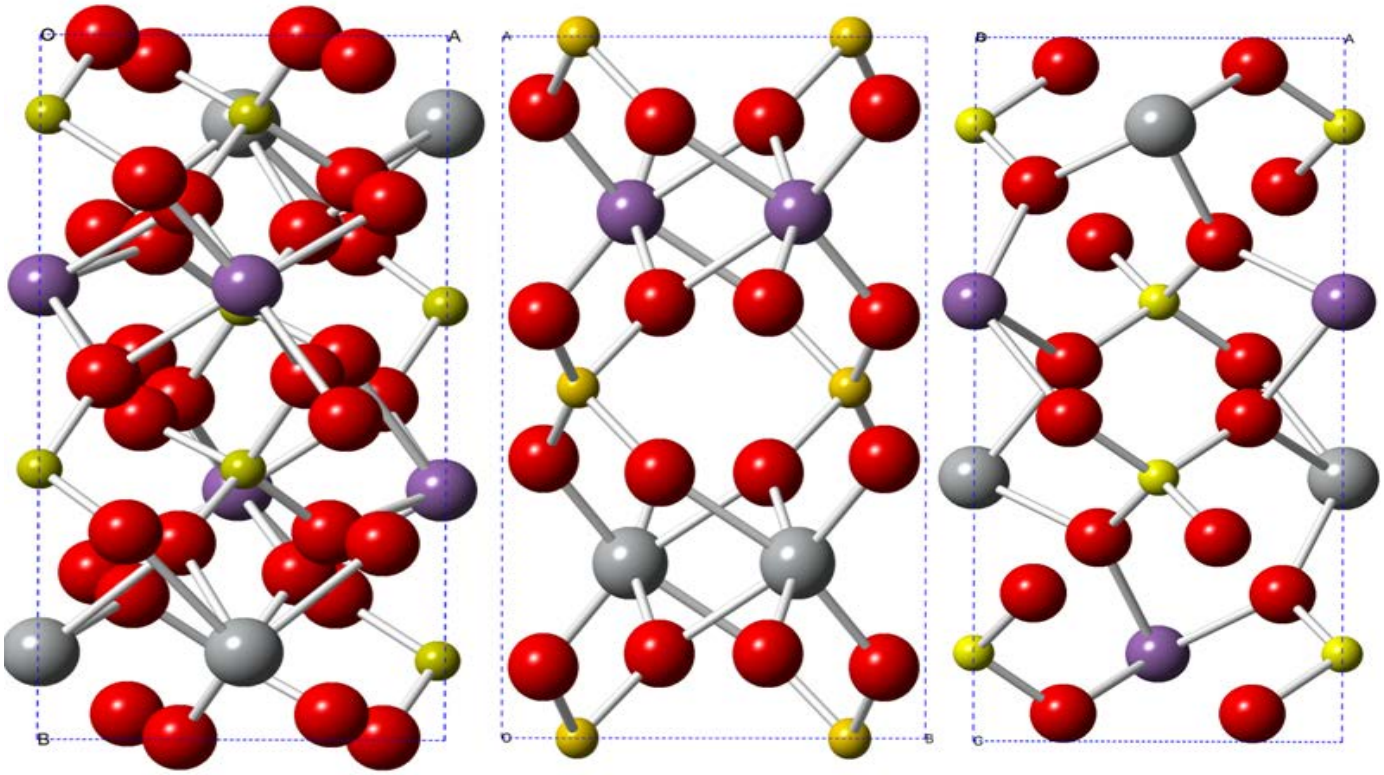
↓

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

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 $AgBiW_2O_9$:



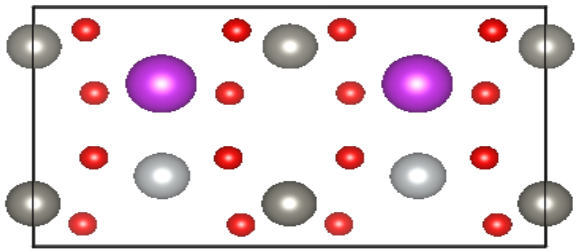
Scheelite
ΔE=0.69eV

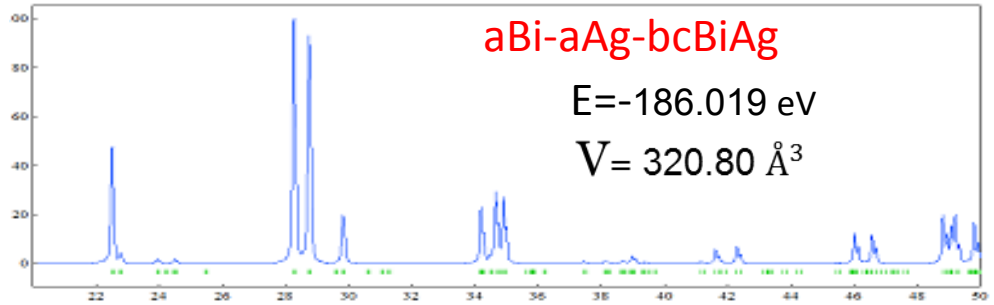
Wolframite
ΔE=0.00eV

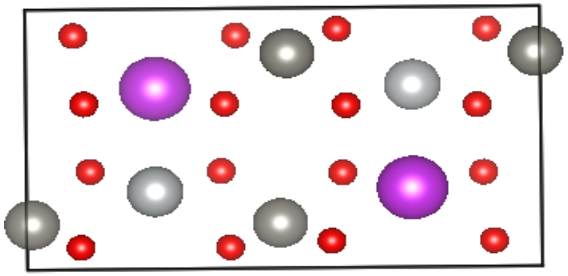
Fergusonite
ΔE=0.28eV

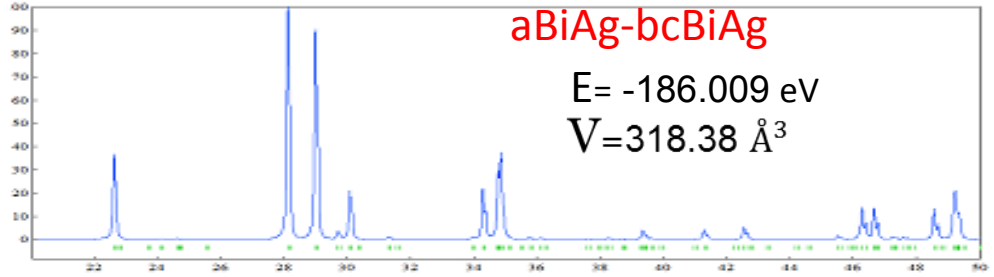
Wolframite structure with different layer arrangements:

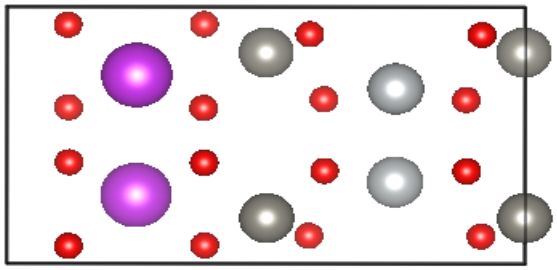
XRD:

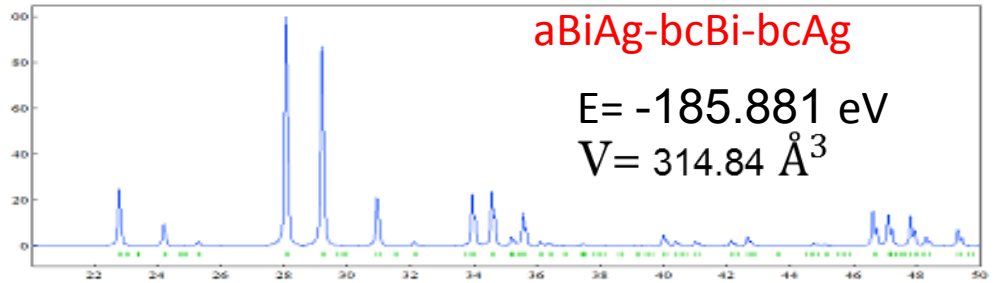


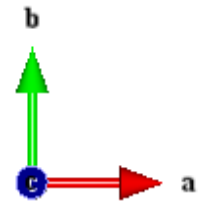




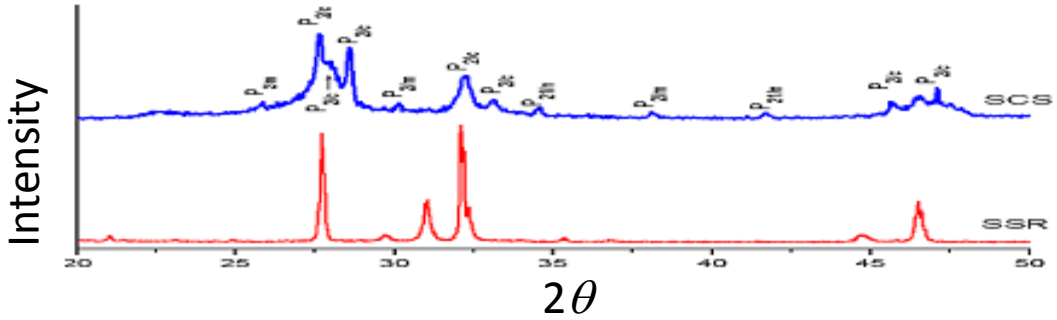








Experimental (SCS and SSR)
By Rajeshwar's group at UTA ⟶



ChemPhysChem, **13**, 2945 (2012)

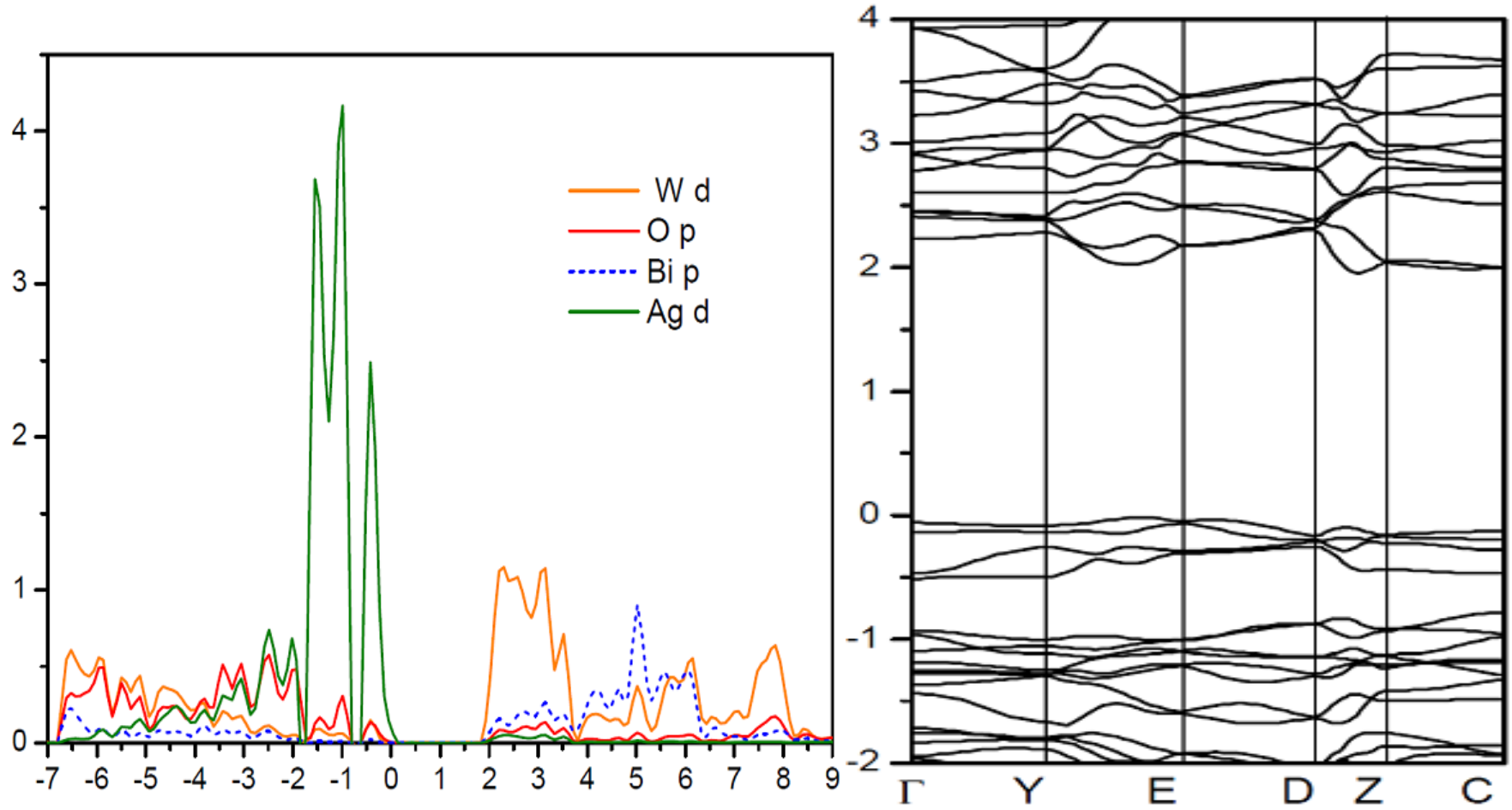
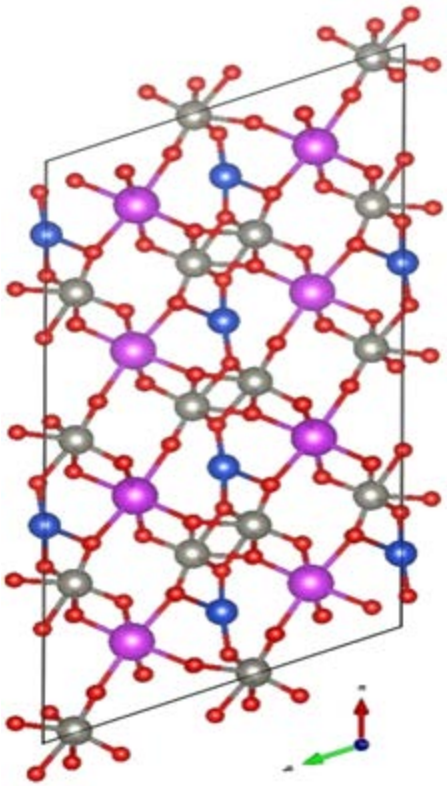
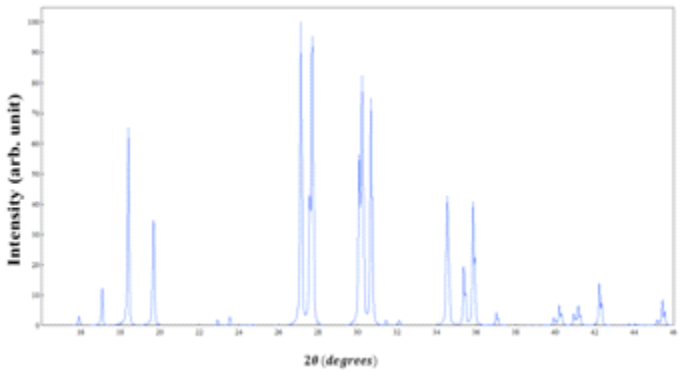


Figure 5: Partial DOS and band structure of wolframite $AgBiW_2O_8$.

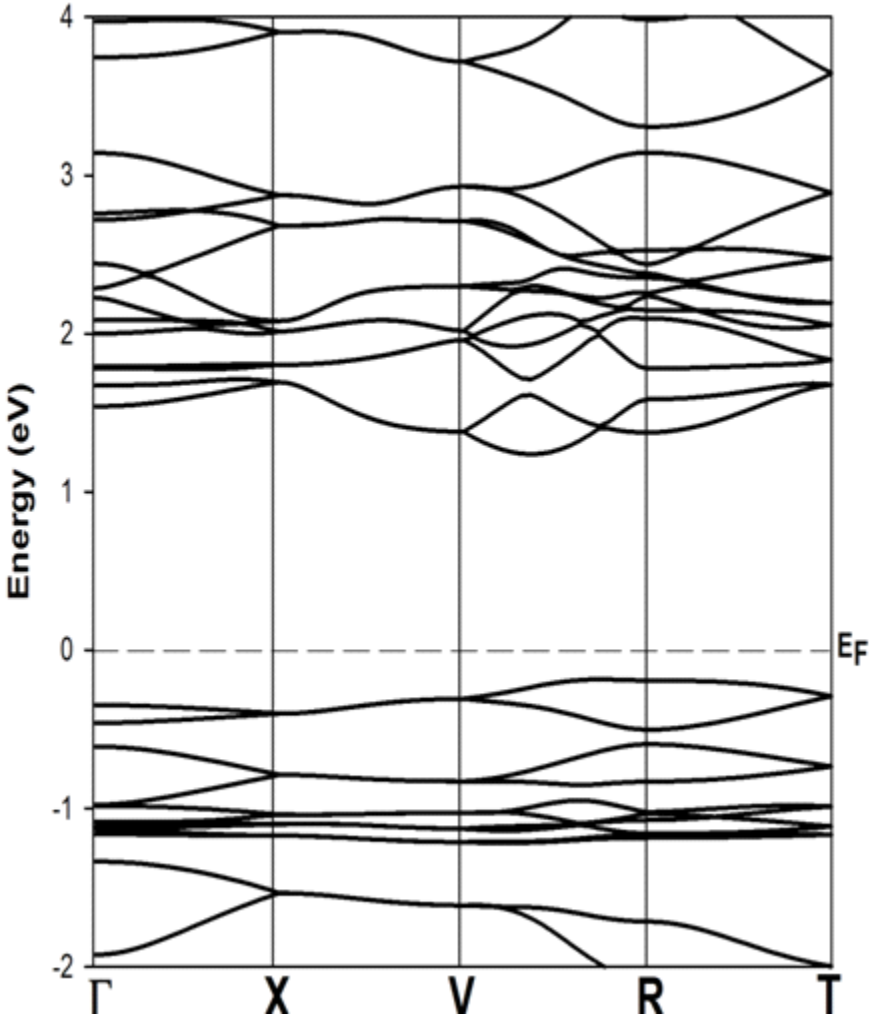
Second alloy structure

$CuBiW_2O_8$

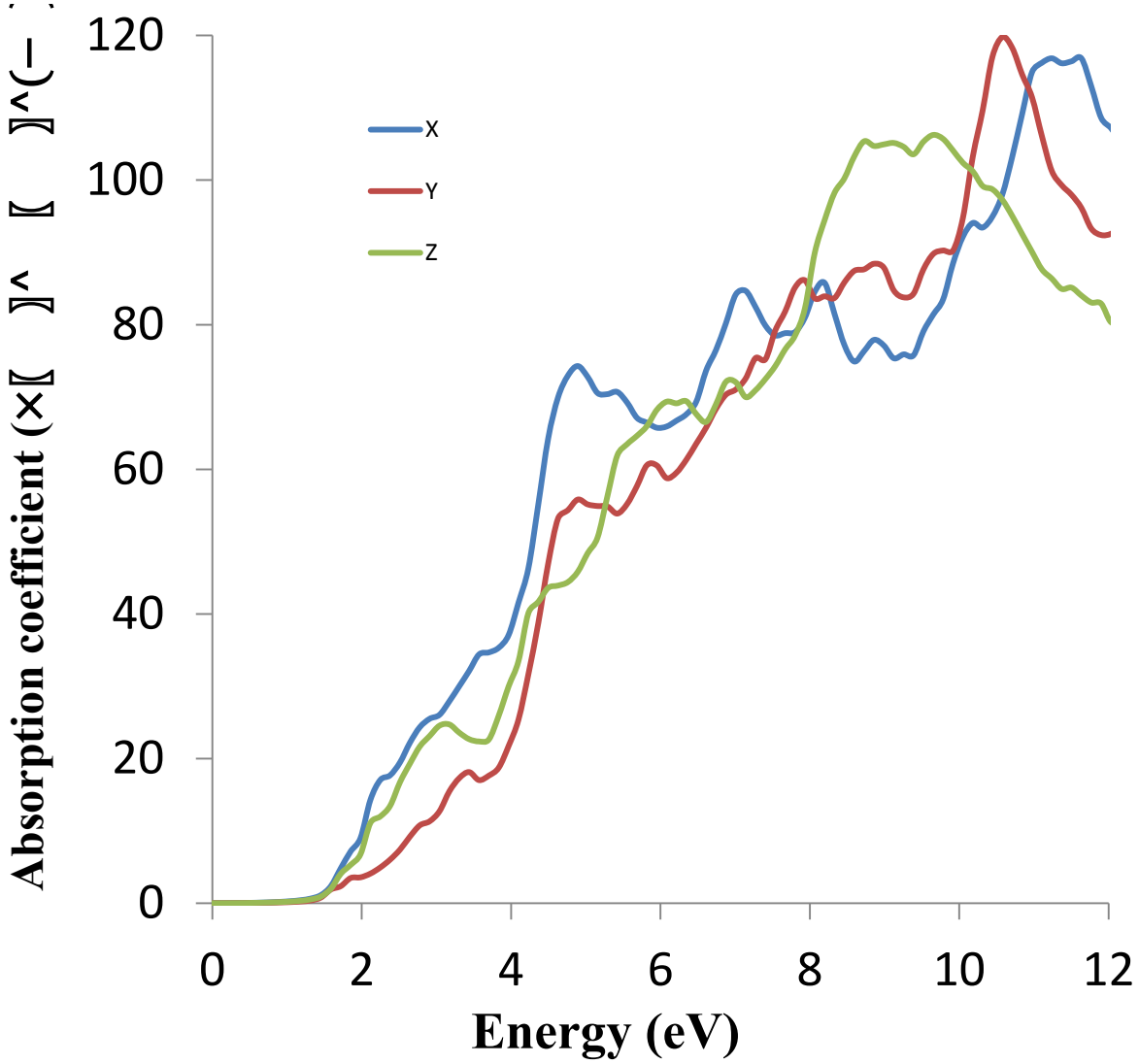




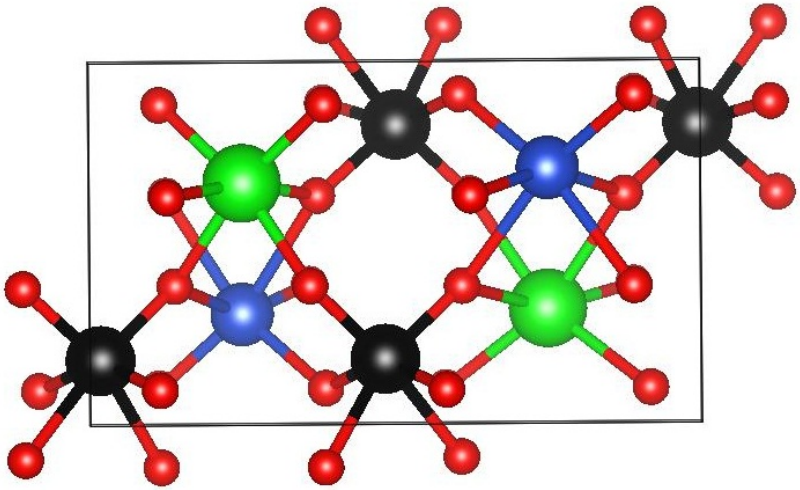
Band structures

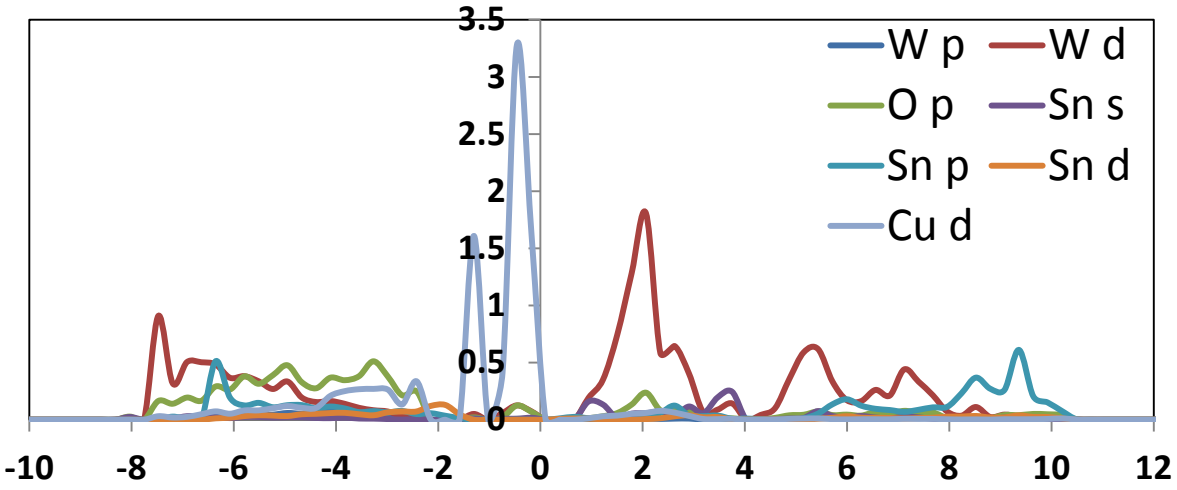


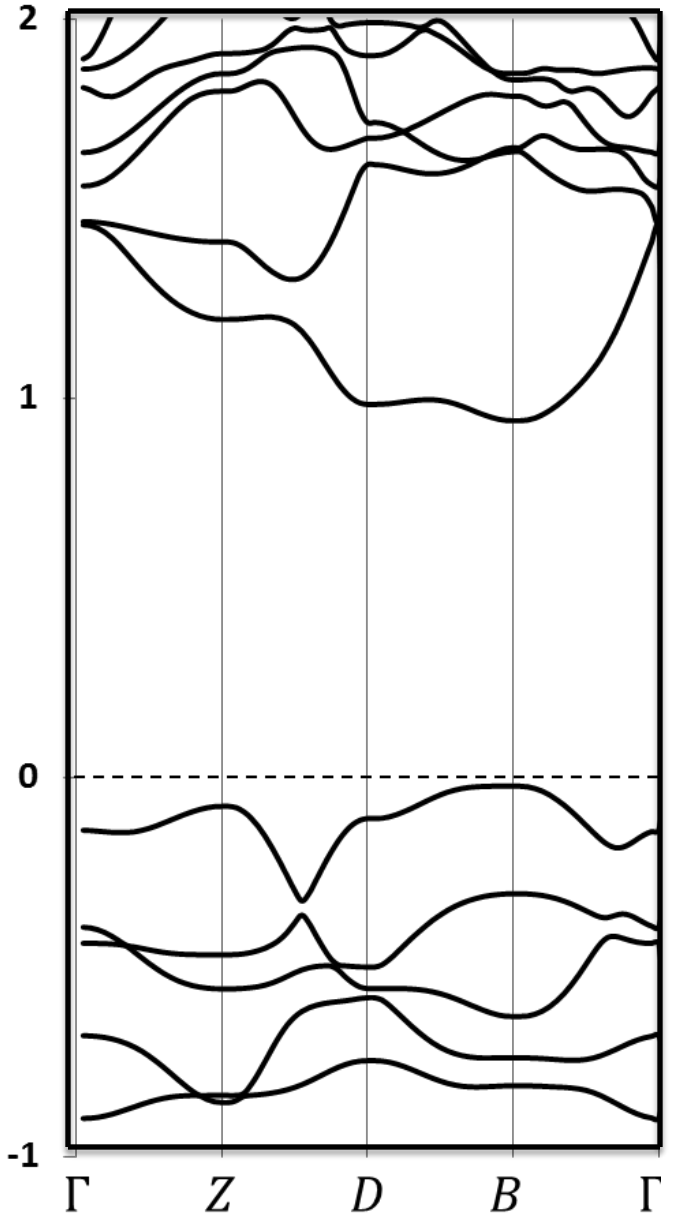
Optical Properties of $CuBiW_2O_8$:



Third alloy structure


W
Bi
O
Cu


W p
W d
O p
Sn s
Sn p
Sn d
Cu d
3.5
3
2.5
2
1.5
1
0.5
0
-10
-8
-6
-4
-2
0
2
4
6
8
10
12


2
1
0
-1
Γ
Z
D
B
Γ

Summary

	Cohesive Energy (eV/atom)	Optical Band gap (eV)
$AgBiW_2O_8$	-2.476	2.06
$CuBiW_2O_8$	-2.547	1.48
$CuSnW_2O_8$	-3.296	0.96
$CuWO_4$	-2.721	2.26

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.