



PEC Materials: Theory and Modeling

Database Driven Novel Photocatalysts by Alloying

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Project ID #
PD052

Timeline

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

Budget

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

Barriers

- Barriers addressed
 - Materials efficiency
 - Materials durability

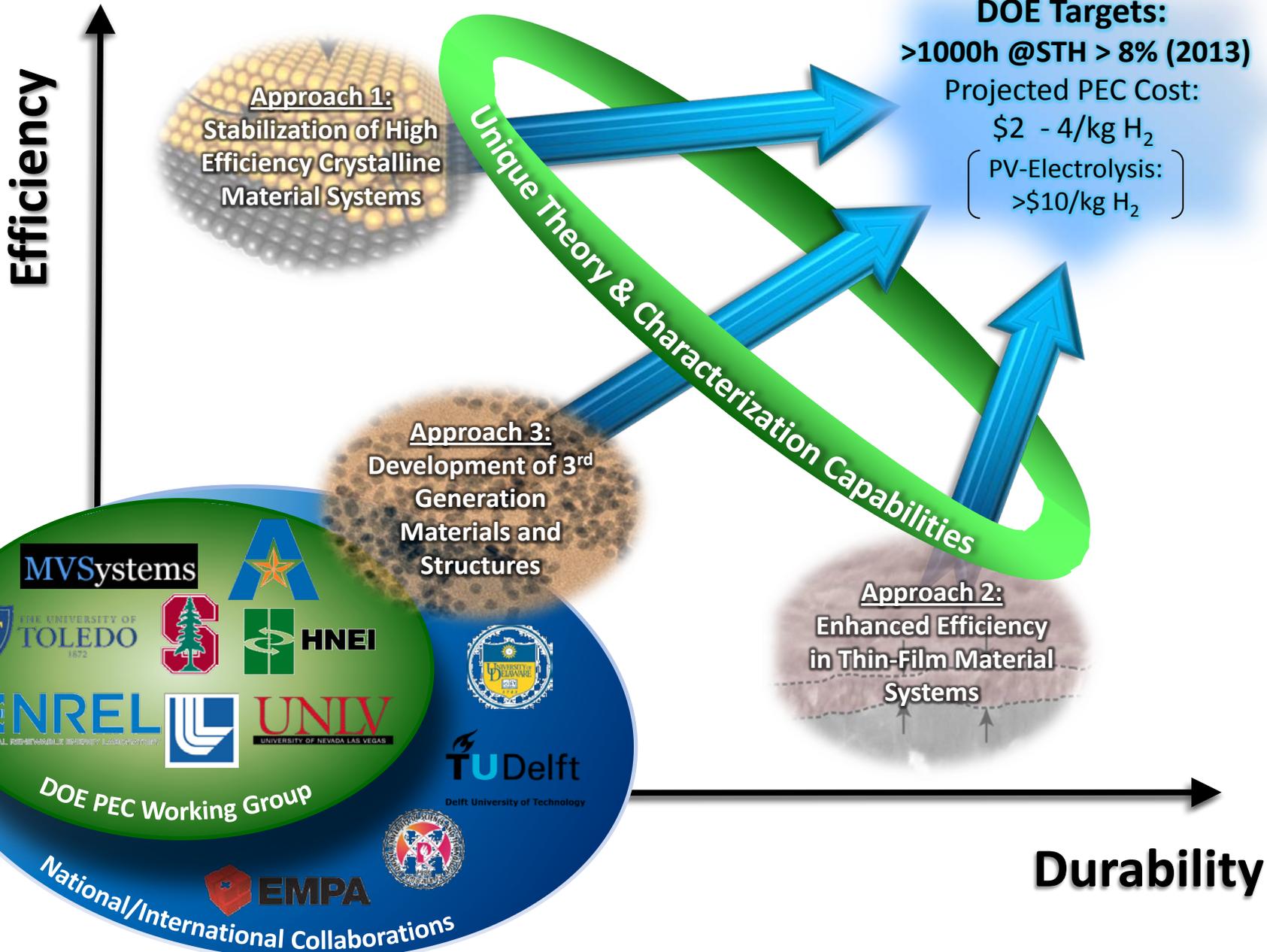
Partners

- Interactions/ collaborations:



- Project lead:





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:

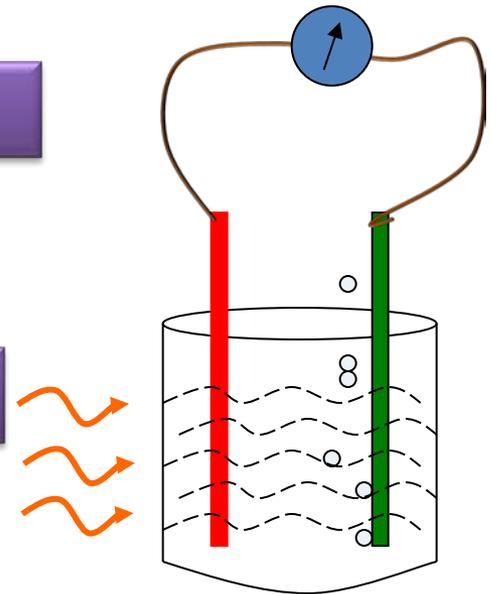
1 – Stable in an aqueous electrolyte

2 – The band gap in the range $1.7\text{eV} \sim 2.2\text{eV}$

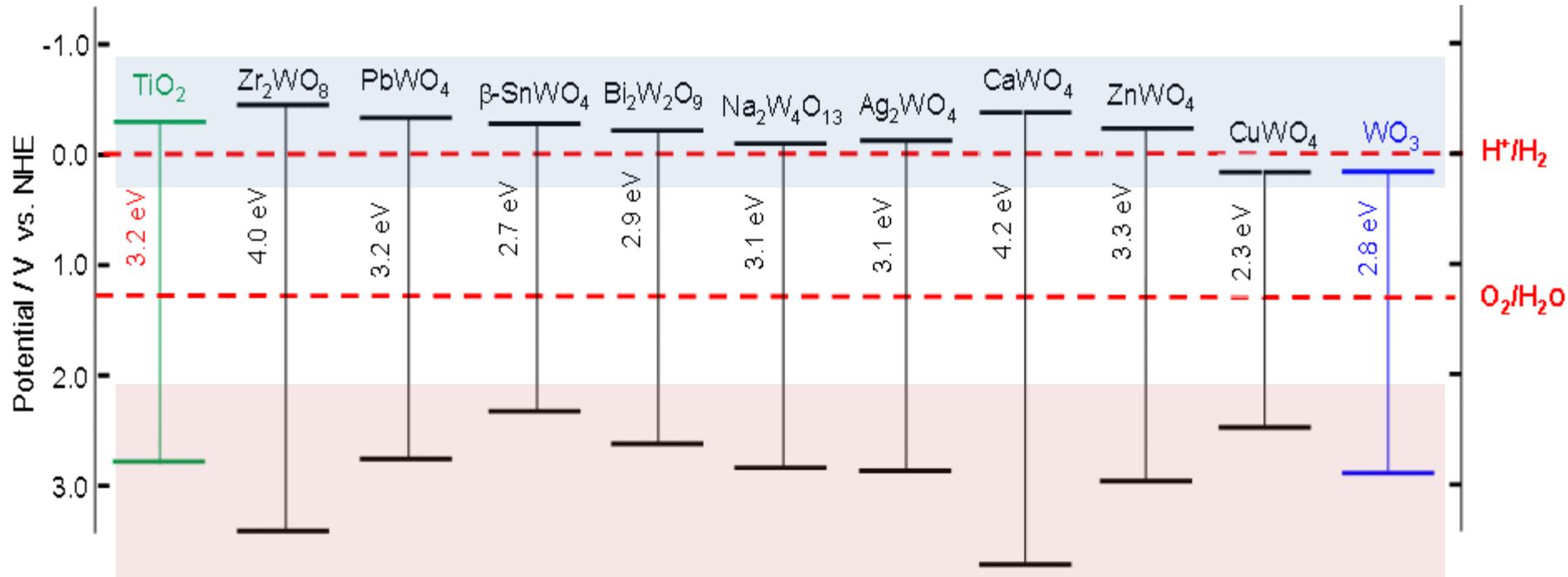
3 – Right band edge positions

4 – Efficient optical absorptions properties

5 – Good charge carrier transport



Introduction to the problem:

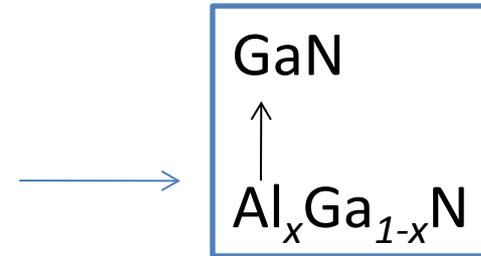


Either band gaps are too large
Or, band edges are not at the right position

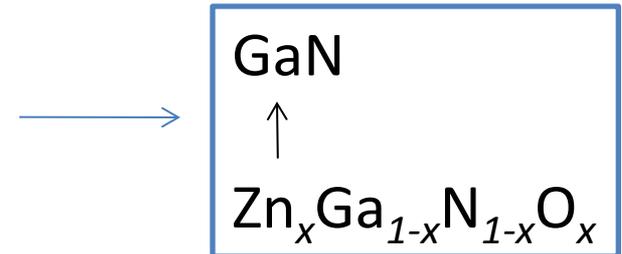
Question: How do we get the right materials?

How do we tune band properties?

1. By isovalent doping.



2. By passive co-doping.



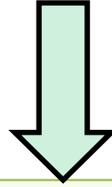
3. By predicting novel alloys

→ Challenging !

4. By reducing the dimensions.

→ Nanostructures:
Nanocrystal, etc.

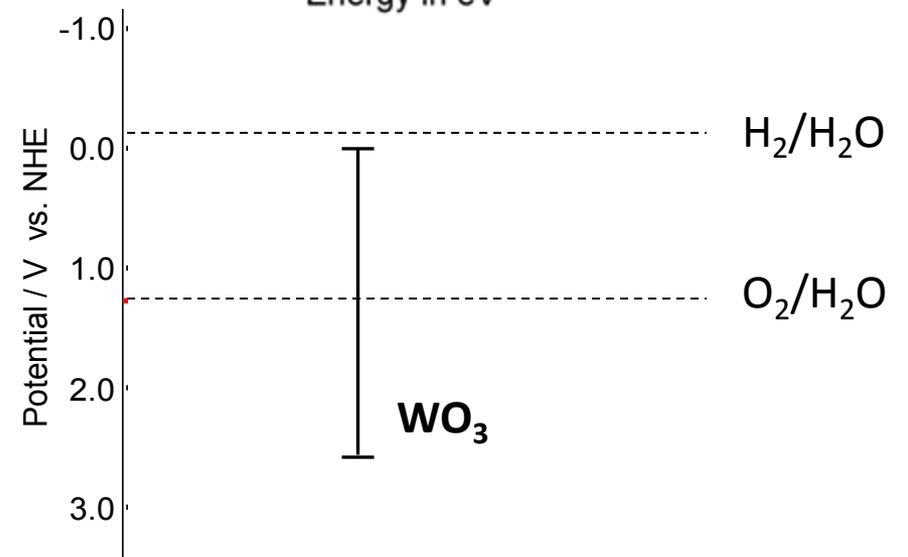
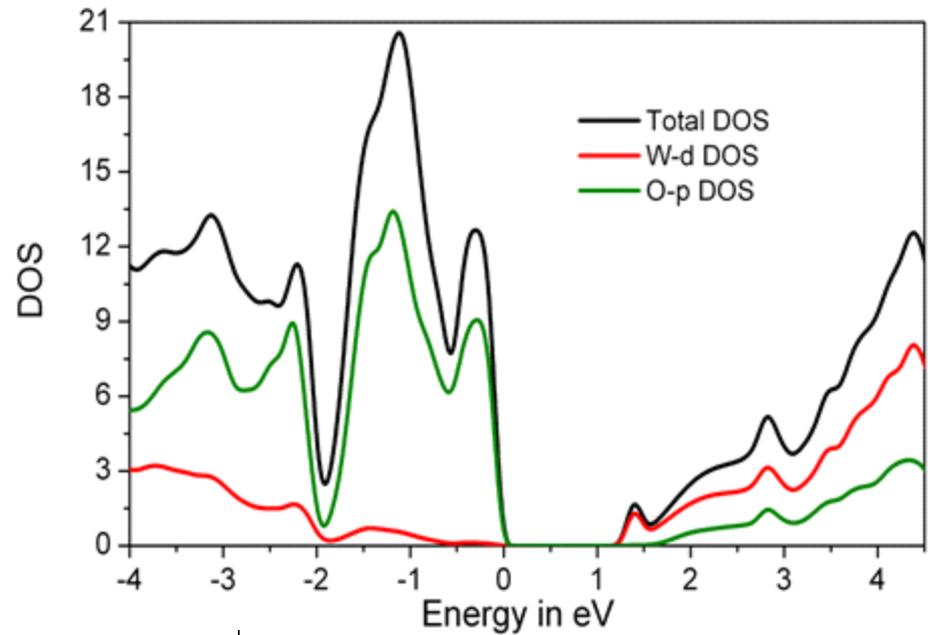
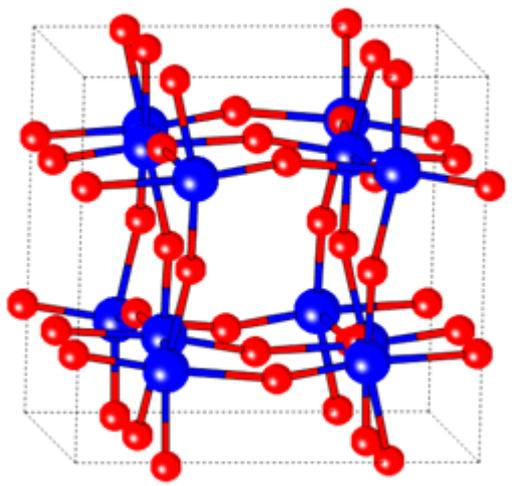
•Why not doping (light or heavy)?



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.

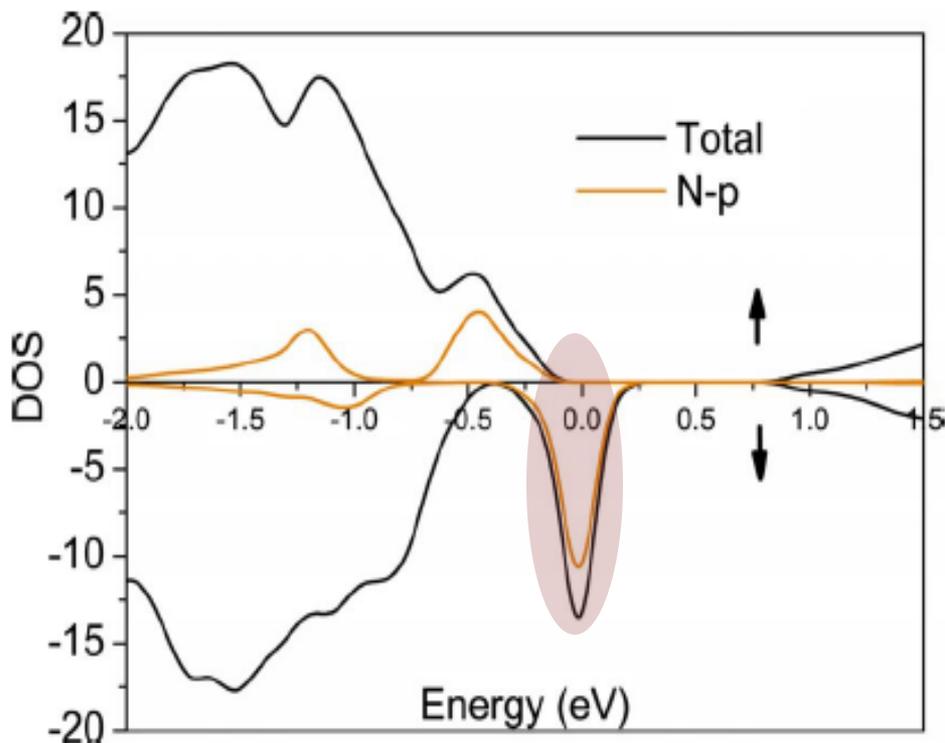
We first consider WO_3 as our example:



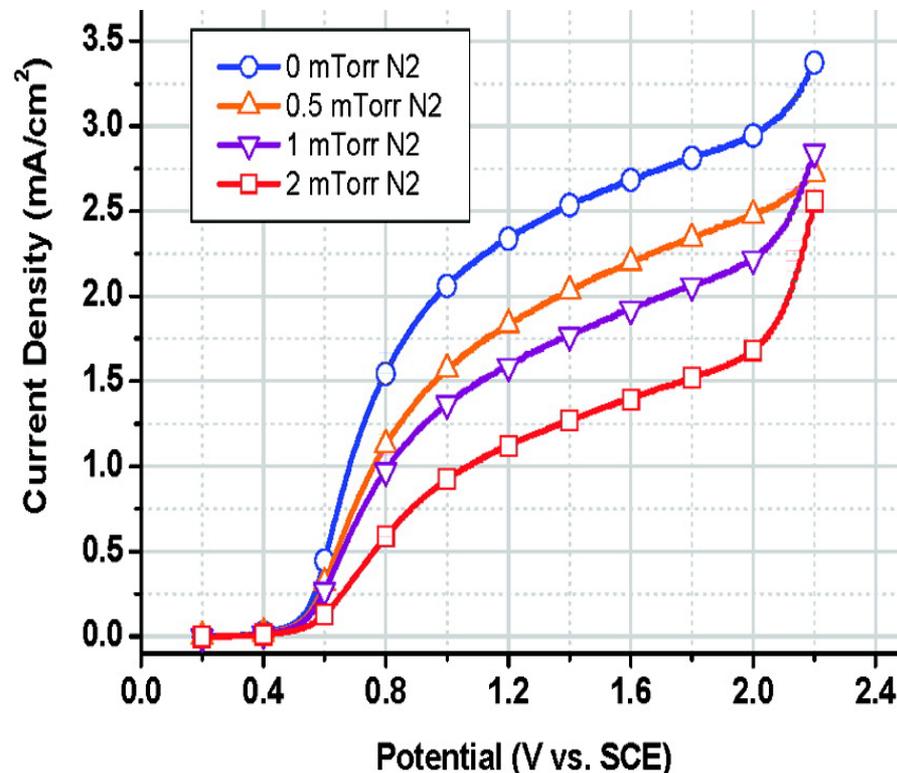
Physical Review B, **77**, 195102 (2008);
Physical Review B, **80**, 115118 (2009);
Catalysis Today, **199**, 53-64 (2013).

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: Crystallinity 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 $\text{Bi}_2\text{W}_2\text{O}_9$, 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:

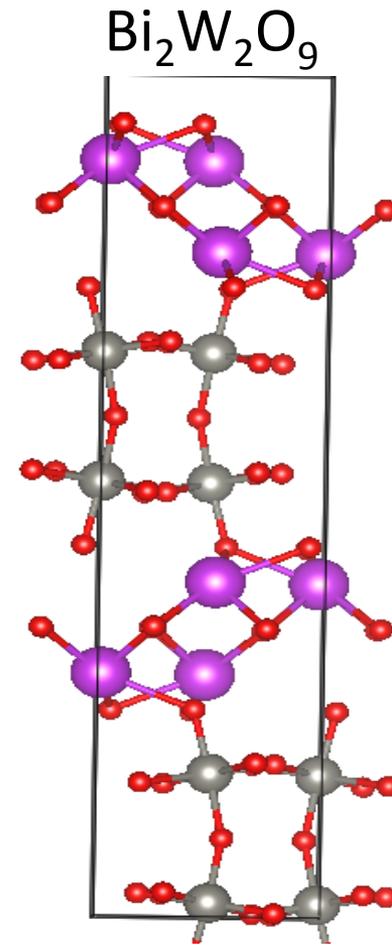
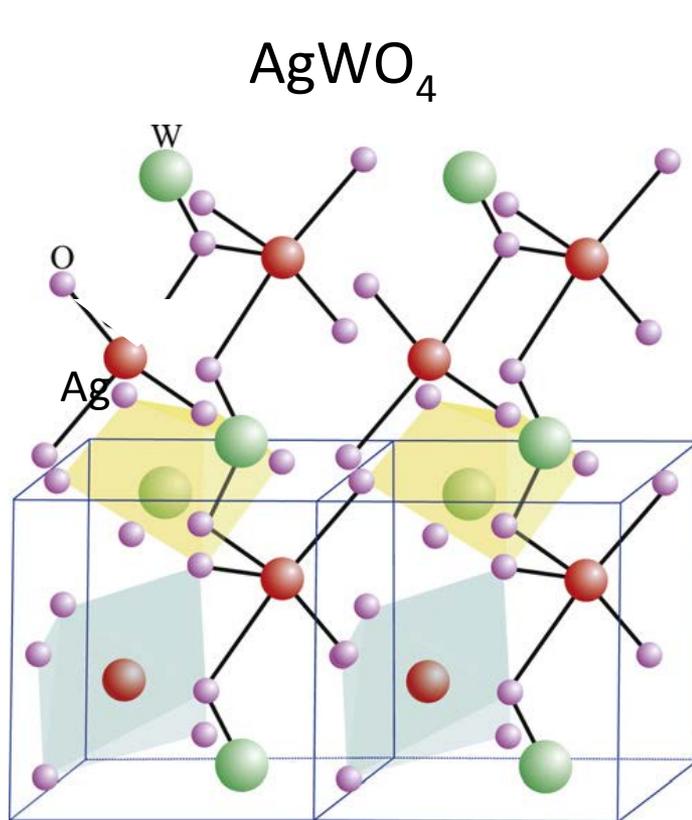
What kind of atomic coordination we are looking for?

What are the charge states?

What symmetries?

...

What type of bond coordination they prefer:



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

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

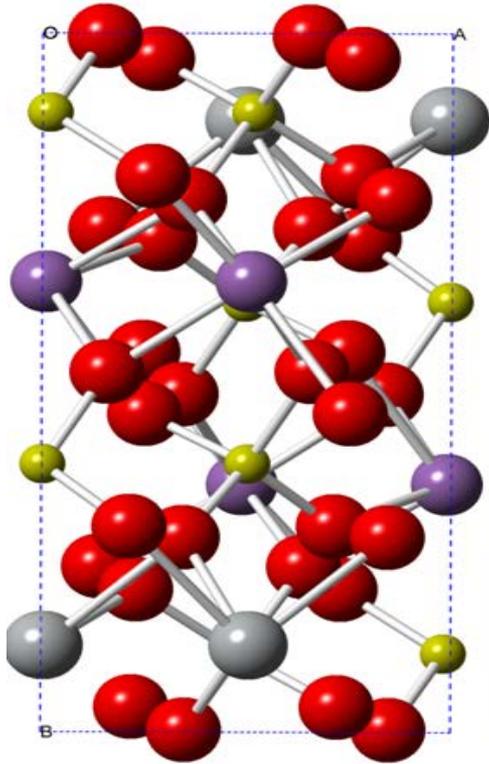
BaUO_4 (S. G. 57 $Pbcm$)

Alumotantite (S.G. 60 $Pbcn$)

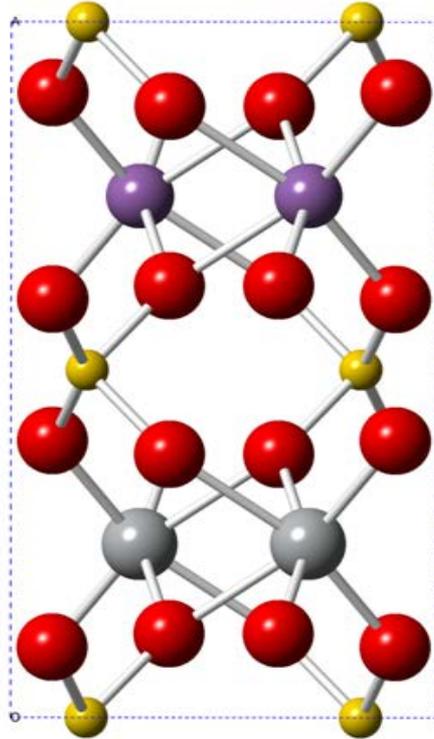
Computation Details:

- 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.

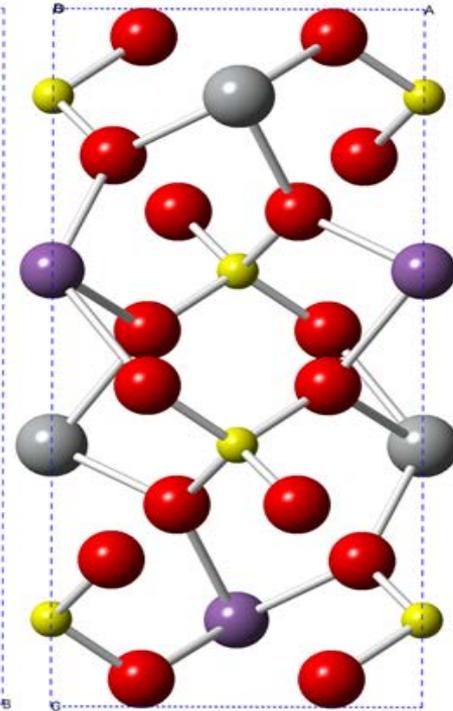
Three most probable mineral structures for AgBiW_2O_9 :



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



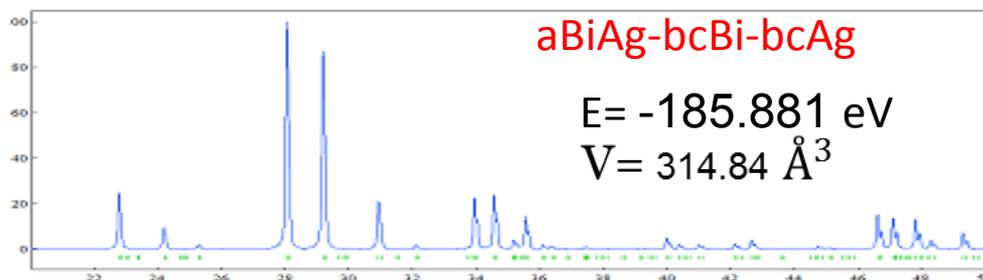
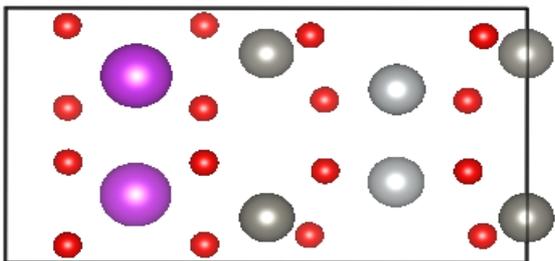
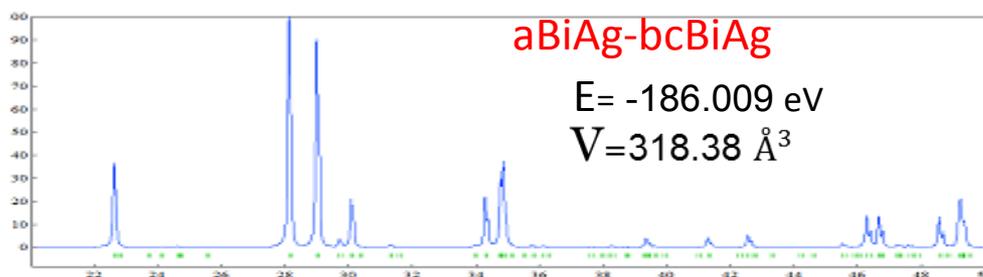
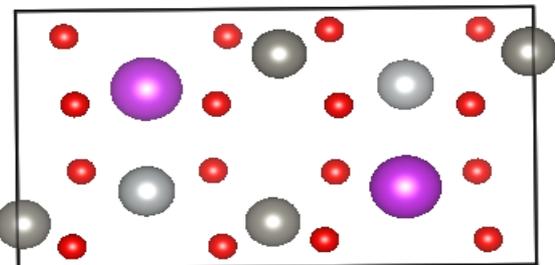
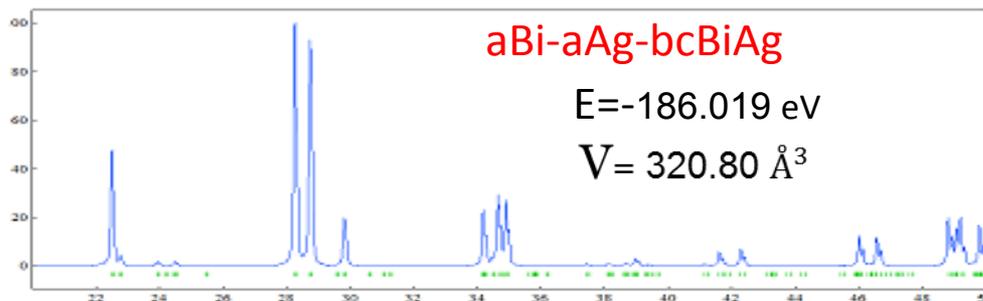
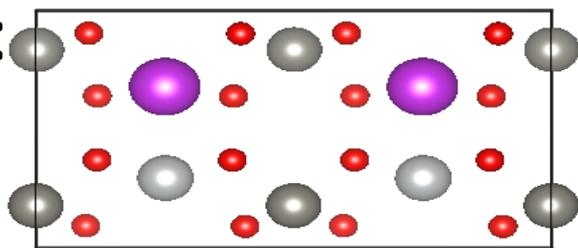
Wolframite
 $\Delta E=0.00\text{eV}$



Fergusonite
 $\Delta E=0.28\text{eV}$

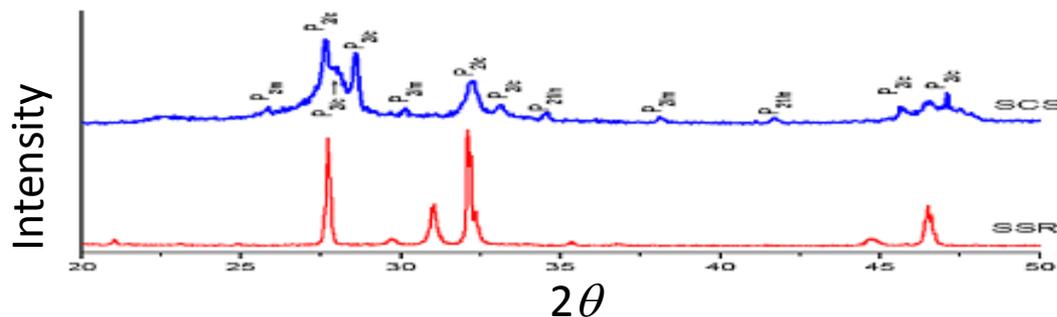
Wolframite structure with different layer arrangements:

XRD:



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

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



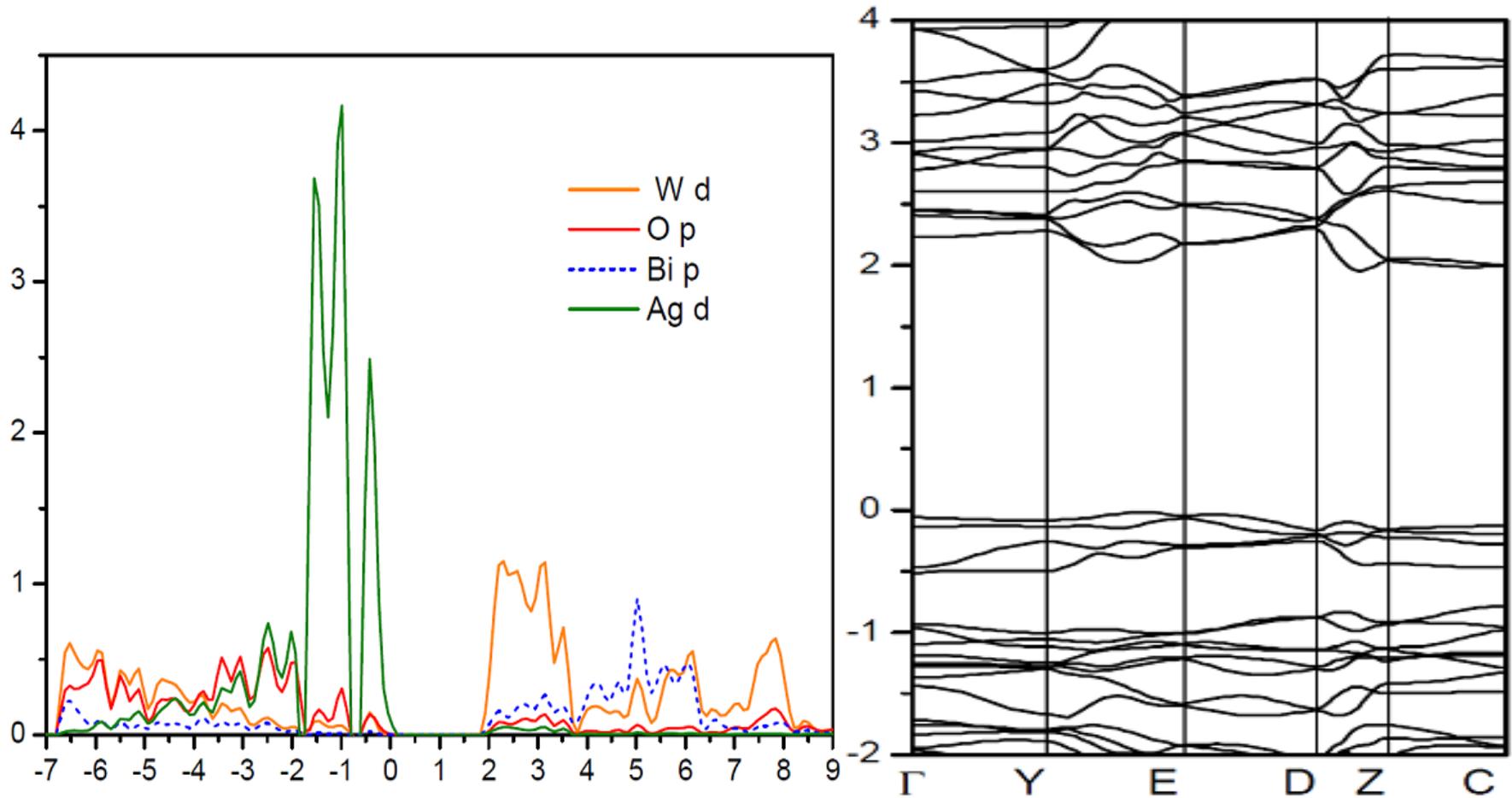
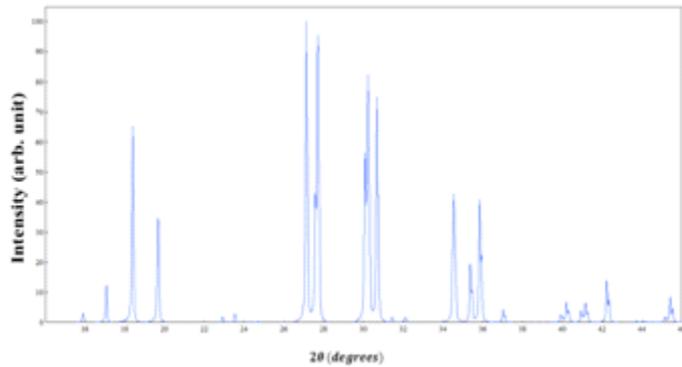
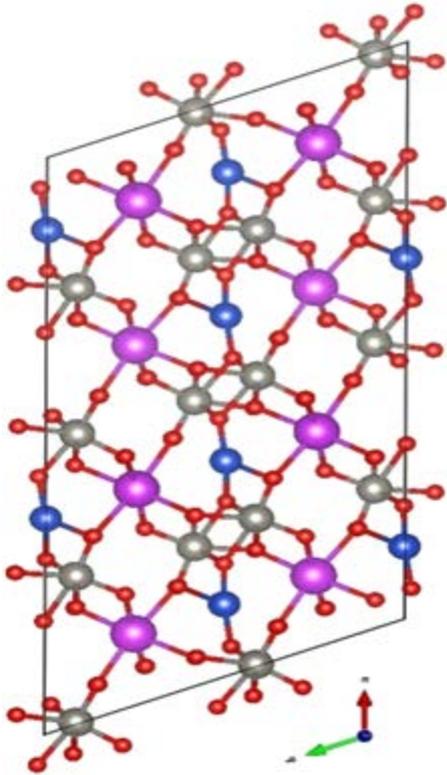


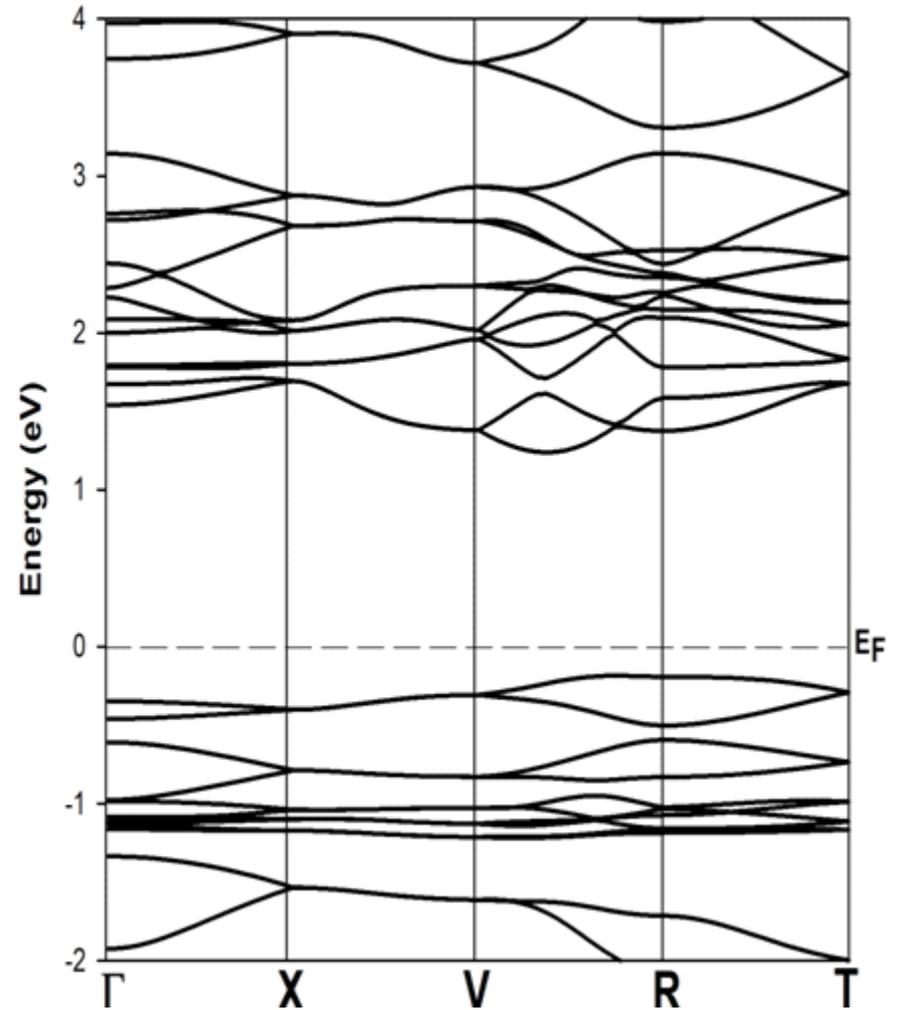
Figure 5: Partial DOS and band structure of wolframite $AgBiW_2O_8$.

Second alloy structure

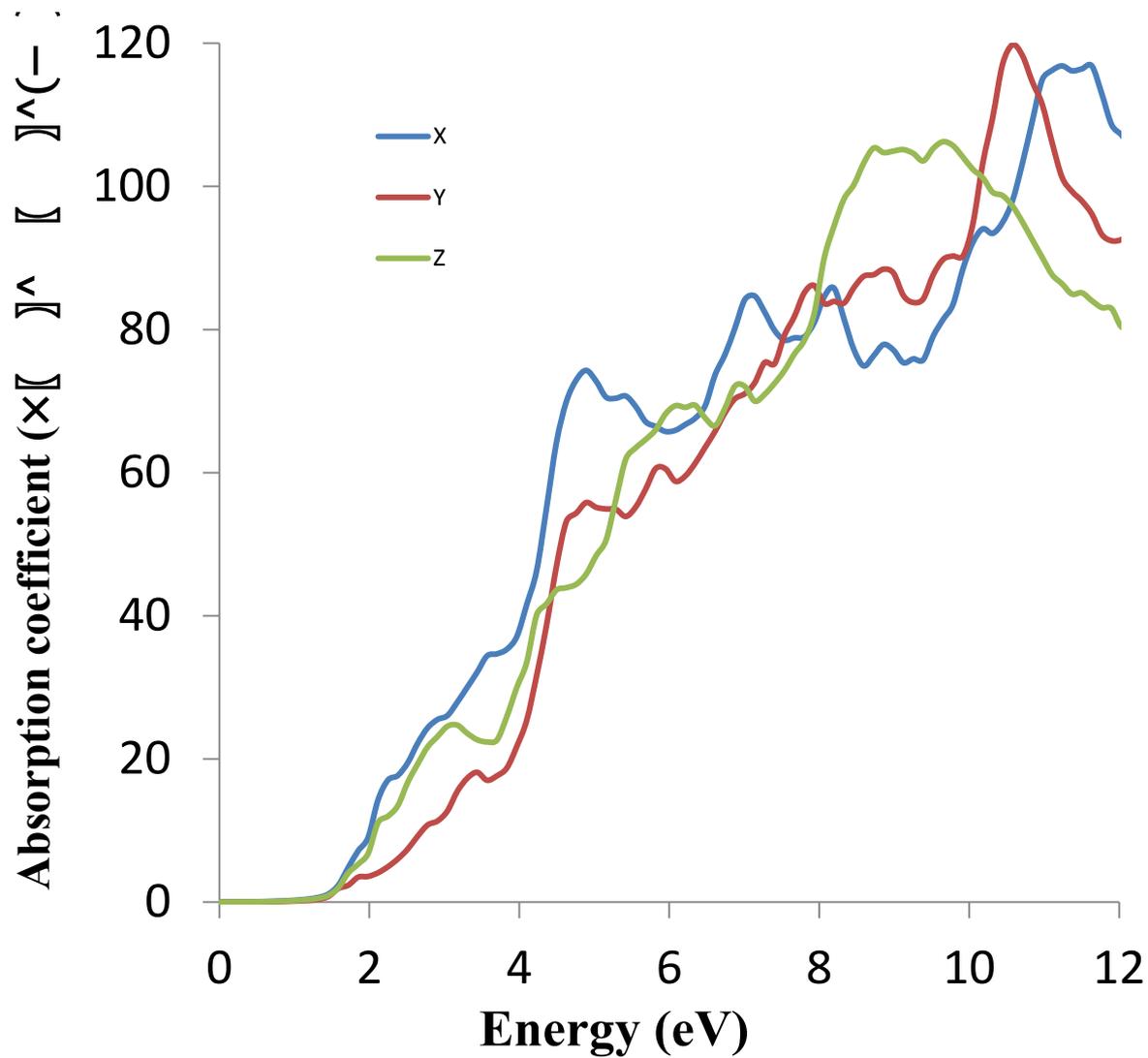
CuBiW₂O₈



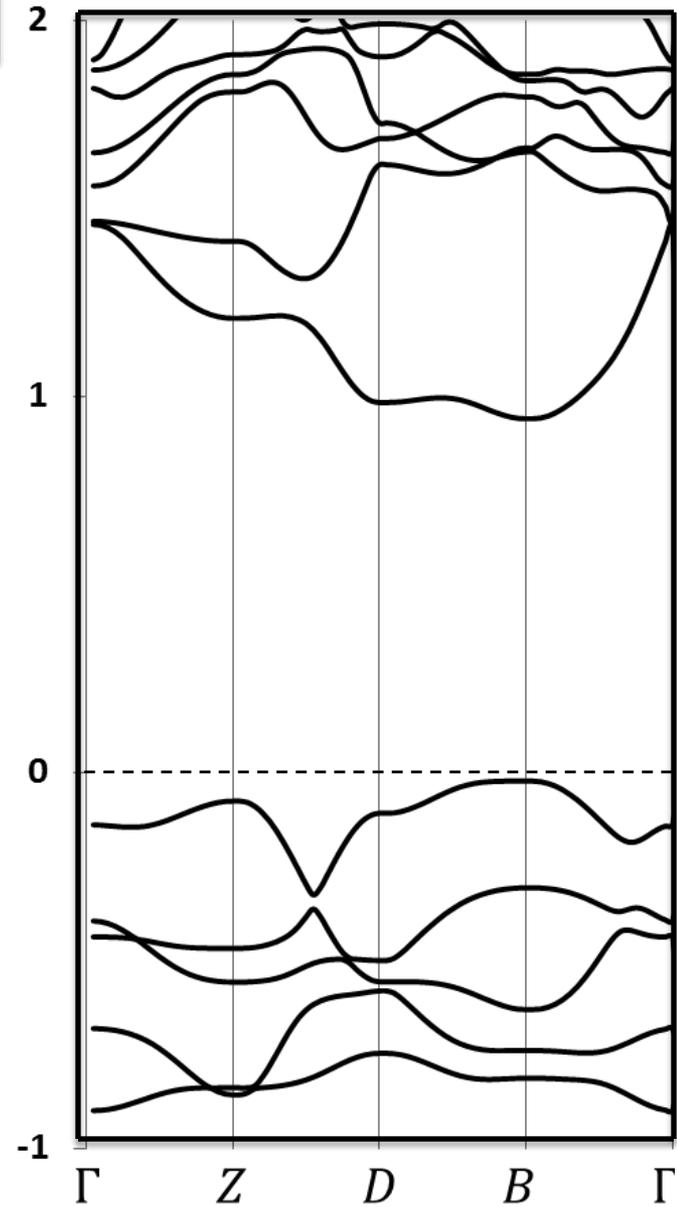
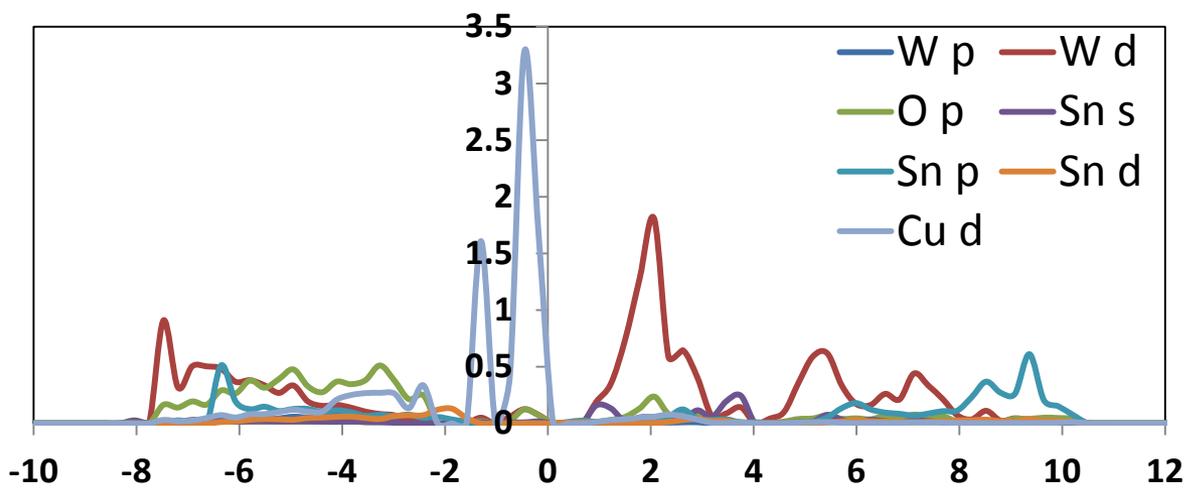
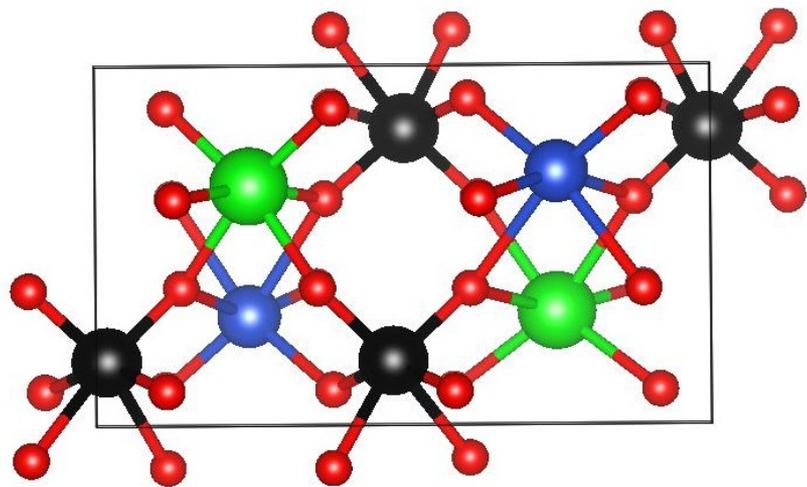
Band structures



Optical Properties of CuBiW_2O_8 :



Third alloy structure



Summary

	Cohesive Energy (eV/atom)	Optical Band gap (eV)
AgBiW₂O₈	-2.476	2.06
CuBiW₂O₈	-2.547	1.48
CuSnW₂O₈	-3.296	0.96
CuWO₄	-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.