PEC Materials: Theory and Modeling

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Project ID # PD052

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Overview

Timeline

- Project start date: Sept, 2009
- Project end date: Aug, 2012
- Percent complete: 70%

Partners

National Renewable Energy Laboratory

University of Texas at Arlington

Budget

- Total project funding:
  $244,739
- Funding received in FY11:
  $81,561
- Funding for FY12: $
  $83,867

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Relevance

Technical Barriers

This project addresses the following technical barriers from the Production section of the Fuel Cells Technologies Program Multi-Year Research, Development and Demonstration Plan (MYP):

- (Y) Materials Efficiency
- (Z) Materials Durability

For the year 2011, the main goal of this project was to improve materials efficiency by understanding and hence tuning the conduction properties, optical gaps and absorption probabilities by theoretical modeling.

This allows us to devise materials selection criteria for photoelectrodes for photoelectrochemical (PEC) energy conversion.

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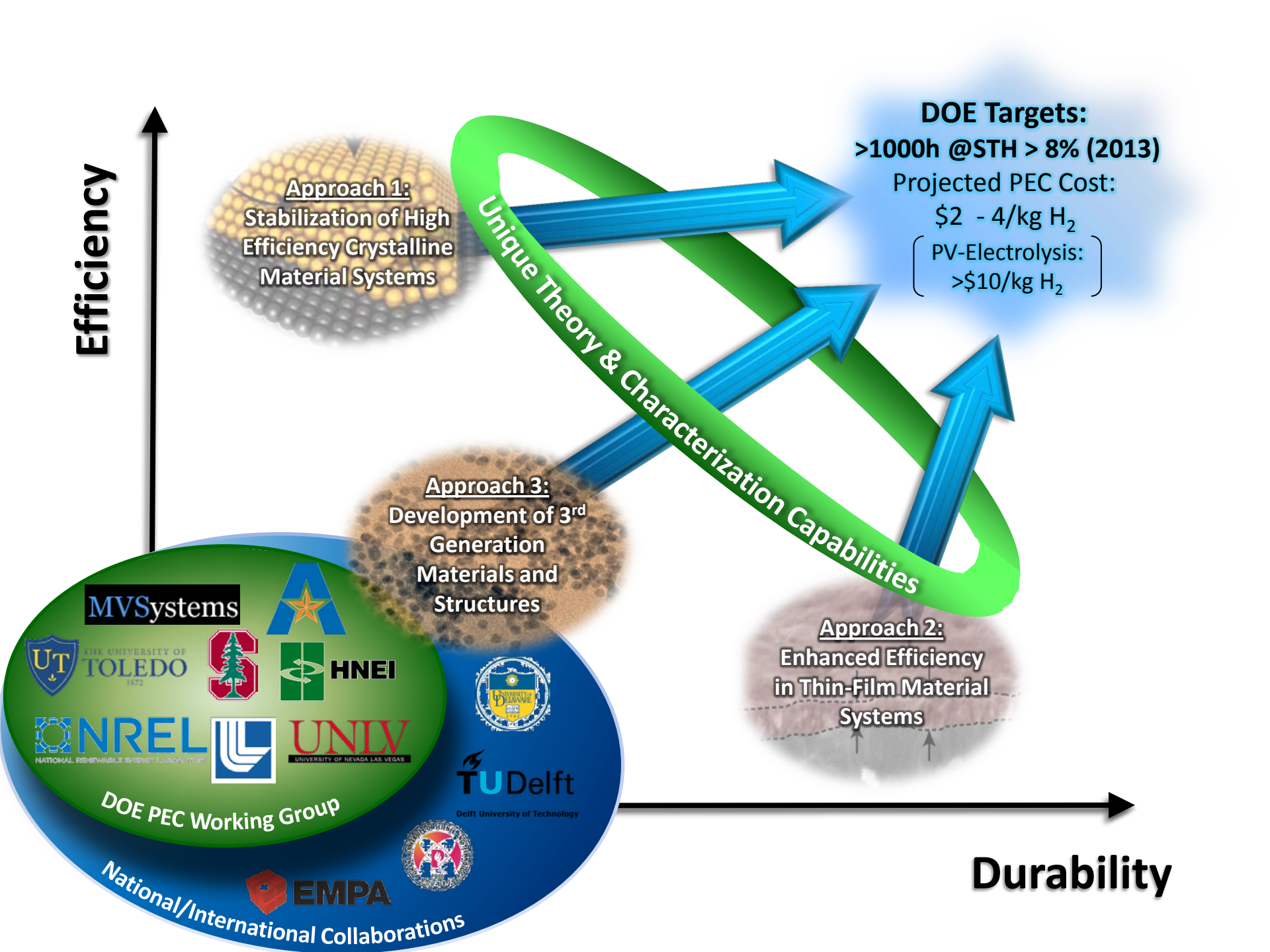

Efficiency
Approach 1:
Stabilization of High Efficiency Crystalline Material Systems
Unique Theory & Characterization Capabilities
DOE Targets:
>1000h @STH > 8% (2013)
Projected PEC Cost:
$2 - 4/kg H2
PV-Electrolysis:
>$10/kg H2
Approach 3:
Development of 3rd Generation Materials and Structures
Approach 2:
Enhanced Efficiency in Thin-Film Material Systems
MVSystems
UT
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
Durability

Approach

The goal is to theoretically/computationally predict semiconductor photo-catalysts which will satisfy the following criteria:

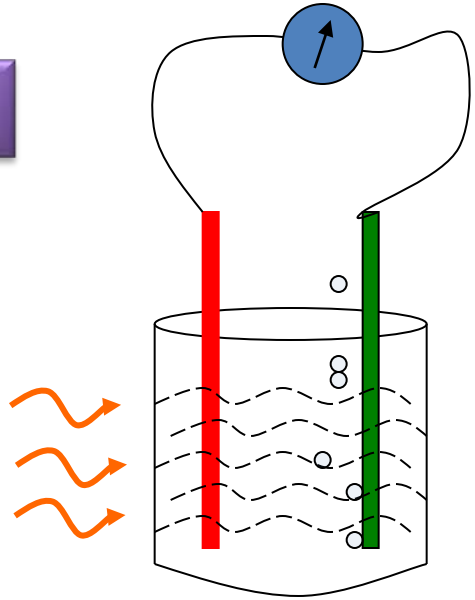
1 – Stable in an aqueous electrolyte

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



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Approach

Theoretical modeling of PEC water splitting

(i) Bulk properties:

Band engineering
for tuning
band gap,
band edges,
optical properties,
carrier mobility, etc.

(ii) Surface properties:

Basic understanding
of molecular
absorption/dissociation
on the surface;
simple catalytic activity,
surface doping.

(ii) Interface properties
(semiconductor/electrolyte):

Reaction mechanism,
reaction energetic,
material stability in solution, etc.

We use density functional theory (DFT) and its variants (hybrid, DFT+U, etc.) to calculate the electronic properties of materials.

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How do we tune optical (band) gaps?

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 random alloying. → Challenging for ab initio modeling!

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

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Oxides that need to be avoided:

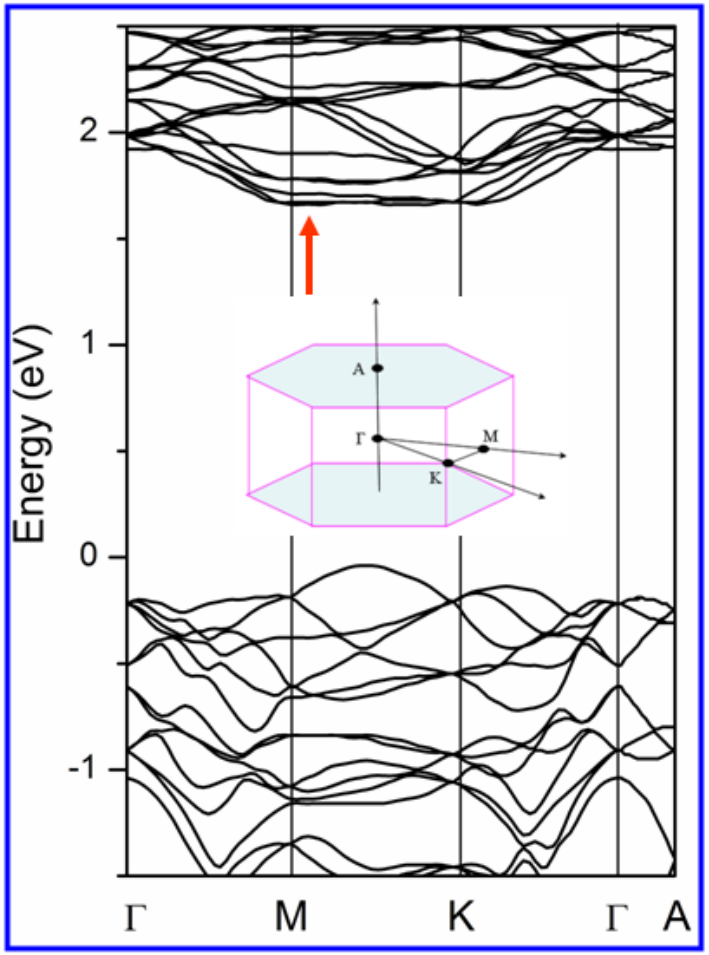
In selecting oxides we have avoided the oxides which are Mott insulators due to the following reasons:

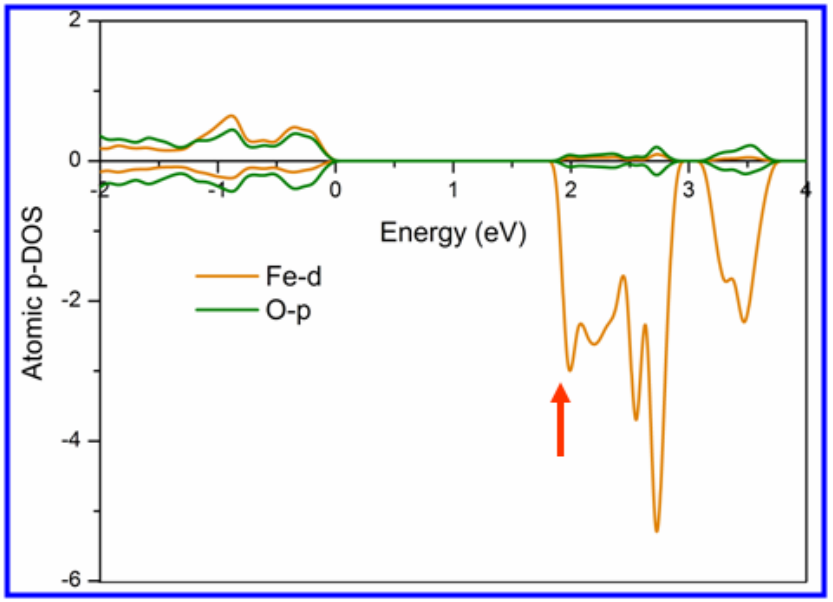
- They have very poor transport properties for both electrons and holes.
- Doping does not improve the conduction properties significantly.
- Photo-current will be very insignificant.

Ref: Huda et al., *Journal of Renewable and Sustainable Energy*, **3**, 053101 (2011).

A common feature in a Mott insulator :

The electronic structure of α-Fe_2O_3





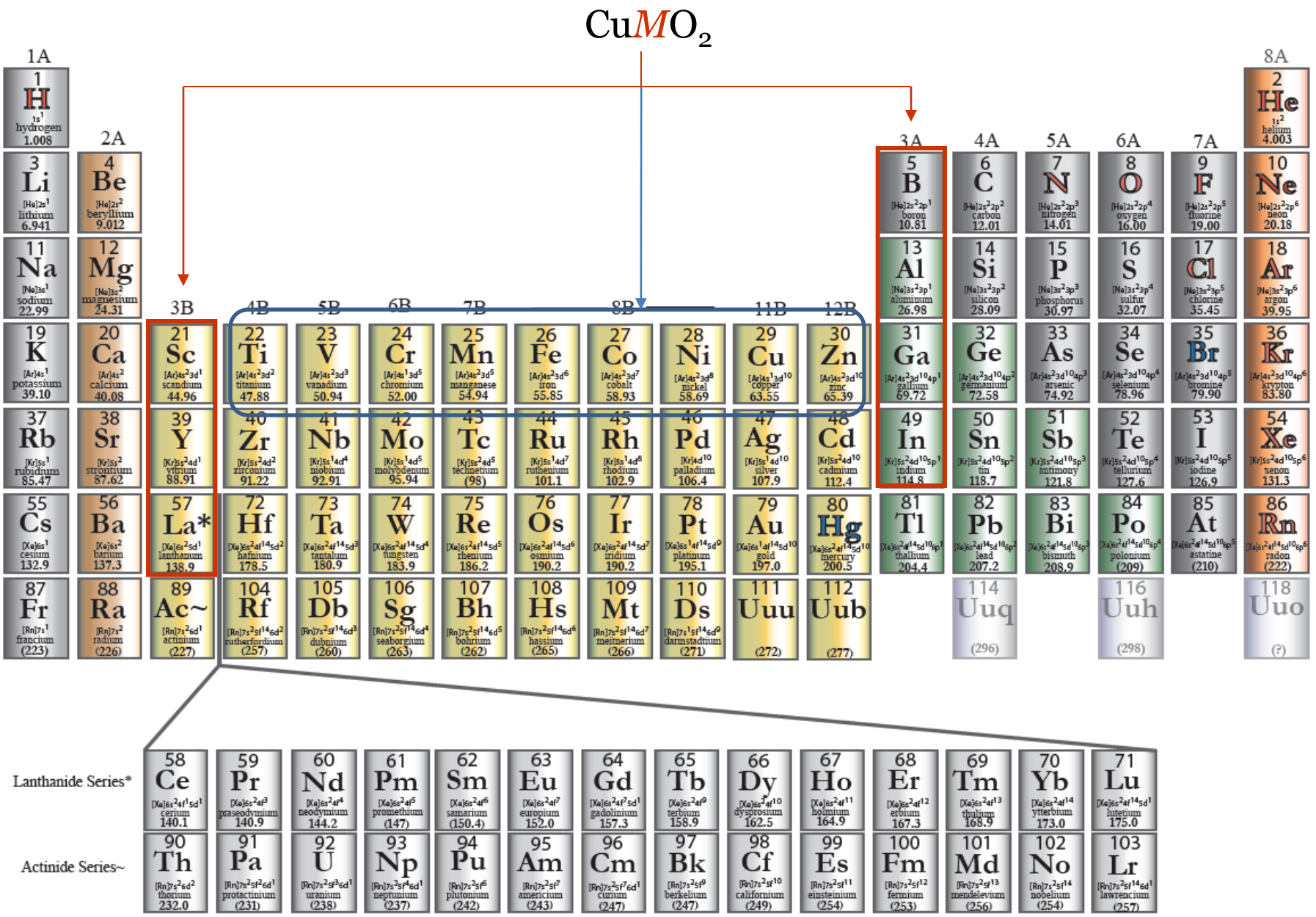
Band gap = 1.72 eV

p-d transition is possible, but the CBM is flat

⇓

Huge electron effective mass

Materials considered for present project: Cu-delafossites

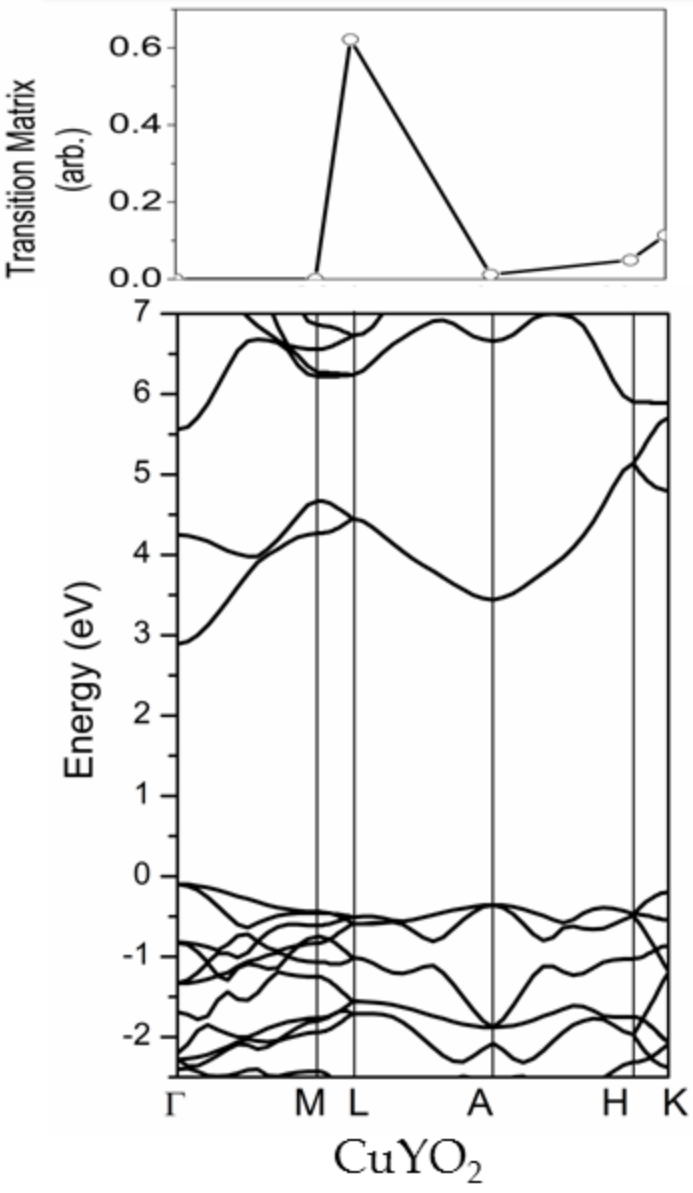


Why Cu-delafossites, $CuMO_2$:

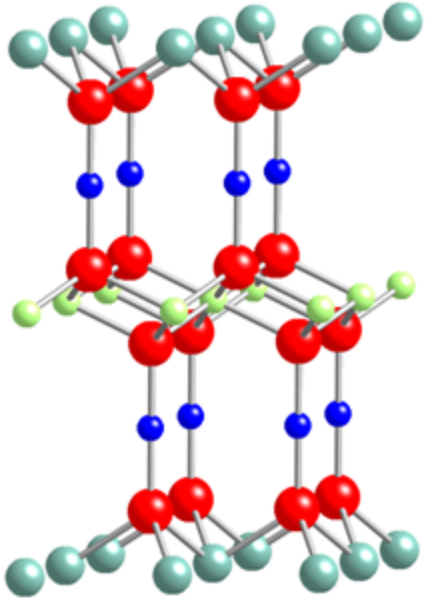
- A prototype multi-cation oxide.
- Due to Cu-d band, the valence band maximum is relatively less electro-negative compared to other oxides.
- Group IIIA delafossites has direct band gaps.
- Band gap: $CuScO_2 > CuYO_2 > CuLaO_2$.
- Stable in solution
- Available

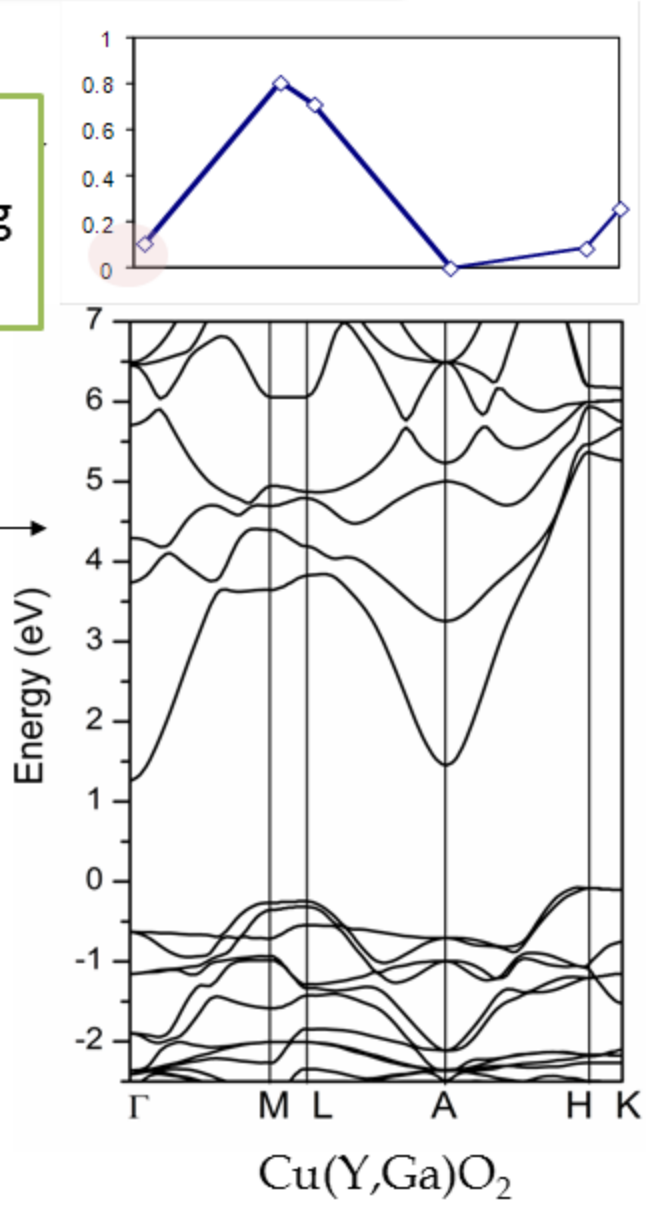
Ref: Huda et al., *Physical Review B*, **80**, 035205 (2009);
Applied Physics Letters, **94**, 251907 (2009);
Proc. Of SPIE, **7770**, 77700F-1 (2010).

Problem with optical absorptions in delafossites:

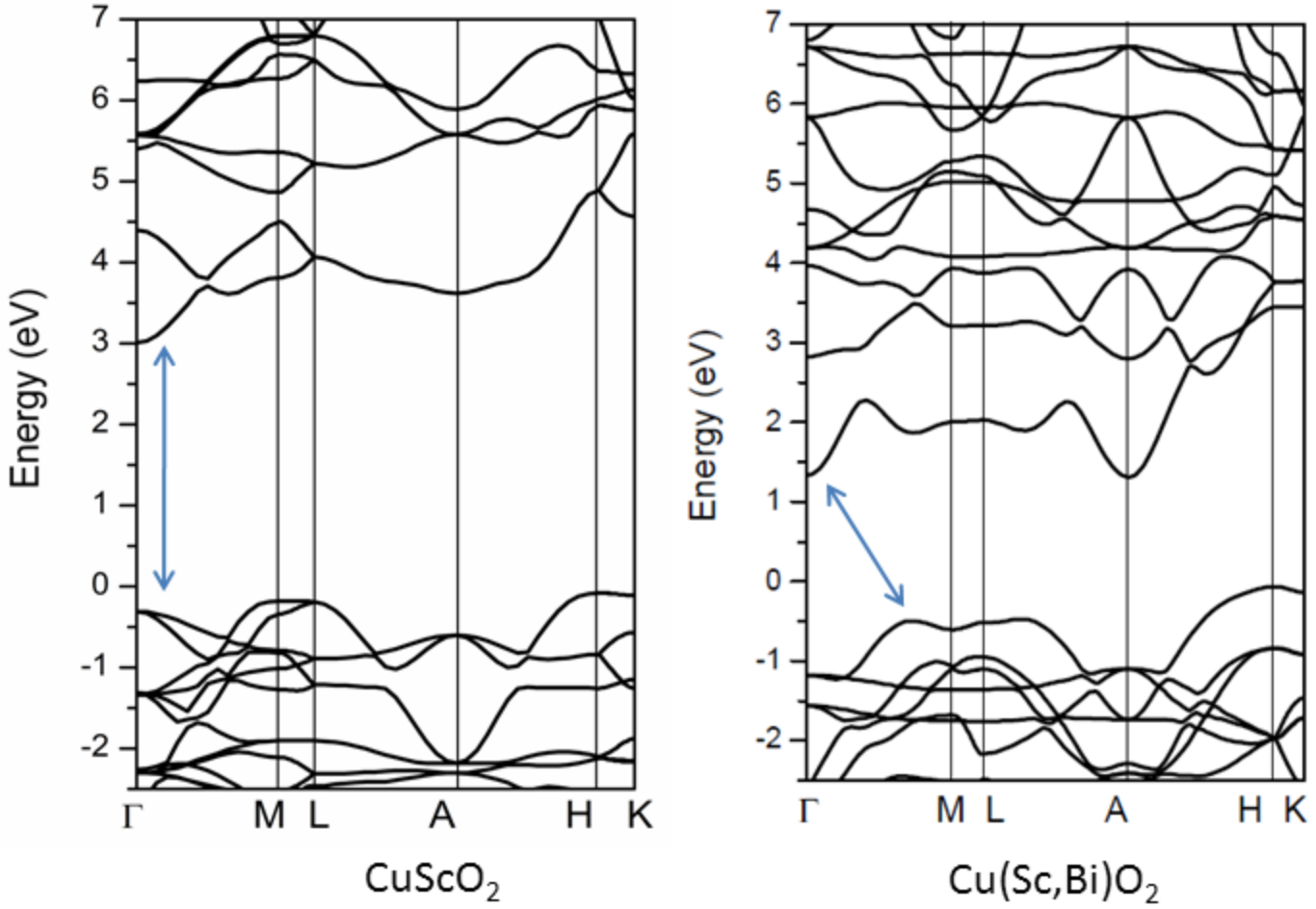


Solution:
Symmetry breaking by alloying.





We have tried other delafossite-alloys to band engineer the optical gap:

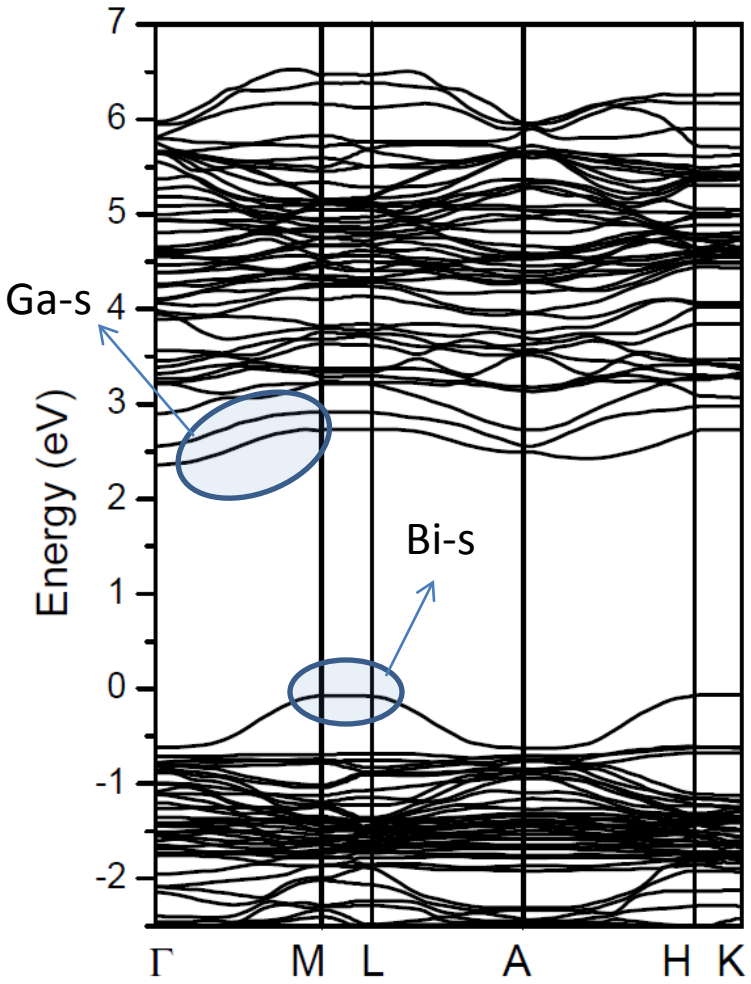


$CuScO_2$ $Cu(Sc,Bi)O_2$

In spite of the s-contribution in the valence band (which is good for low electron effective mass – meaning higher carrier mobility), Bi doping changes delafossites into indirect gap materials, and optical absorption did not improve much either.

Ref: Huda et al., *Journal of Applied Physics,* **109**, 113710 (2011).

We tried more complicated alloys: **$Cu(Sc,Ga,Bi)O_2$**



Important feature here is that all Bi-doped Cu*A*O_2 delafossites has always(!) indirect gap

Two structures have been tried:

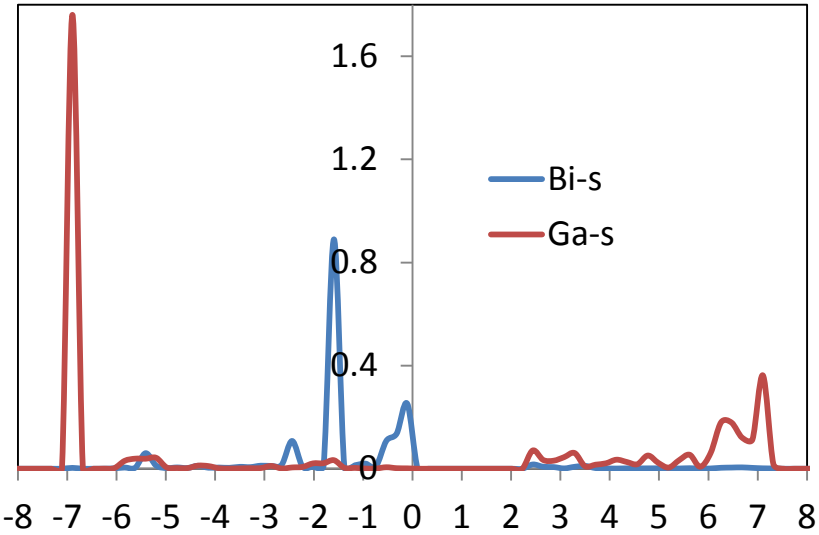
(i) Ga and Bi are on the same layer,
(ii) Ga and Bi are on different layer.

First one being the most stable by 0.32 eV

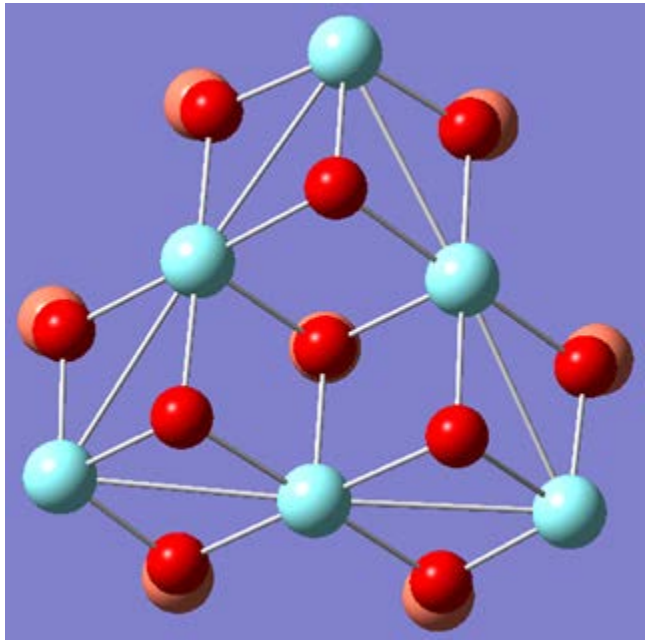
The relative ratio of Sc:Bi:Ga is 10:1:1.

The band gap is still indirect (Γ to M point), and is 2.35eV.

Optical properties did not improve.



Delafossite nano-structures



In parallel to the bulk structure study, we have started considering nano-crystalline phase of delafossite materials.

The purpose is to examine if these nano-structures have improved optical absorption properties, so that these can be used as photo-catalysts.

Computational methods:

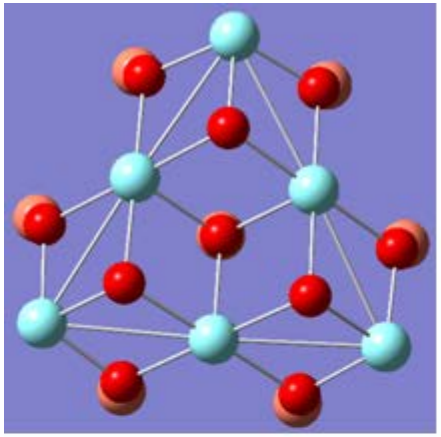
- Density functional theory (DFT) has been used as implemented in Gaussian03/09.
- Both hybrid (B3LYP) and GGA (PW91) has been tried. (The results shown here are with hybrid functional).
- Different multiplicities (spin-states) were tested.
- Smaller nanocrystals were tested to as the basic building blocks.
- Time dependent DFT (TDDFT) has been used to calculate the excited states of the nano-crystals.

Delafossite nano-structures

- We have considered here several $CuYO_2$ delafossite nano-crystal structures;
- Nano-crystals are modeled here by cutting a portion of the bulk delafossite structure by keeping the basic delafossite structural blocks.
- Finding charge compensated nano-structure (i.e. for $Cu_mY_nO_l$, $m+3n-2l=0$) is a challenging task.
- Thermodynamically competing clusters were not considered here, as the main goal was to study the behavior of the nano-crystalline delafossite.

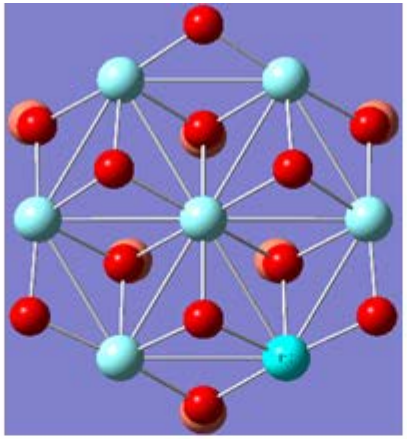
Some selected structures:

$Cu_7O_{20}Y_{12}$ (39 atoms)



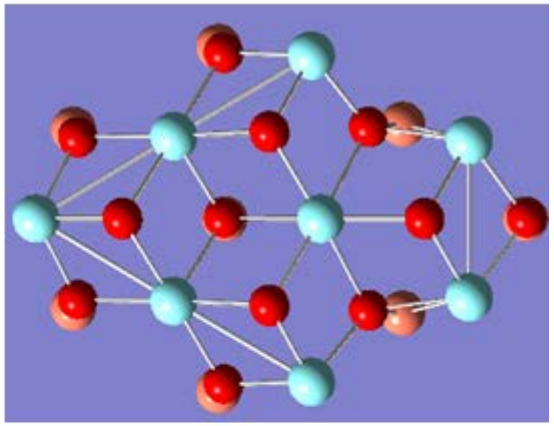
B.E. = 5.173 eV/atom

$Cu_6O_{24}Y_{14}$ (44 atoms)



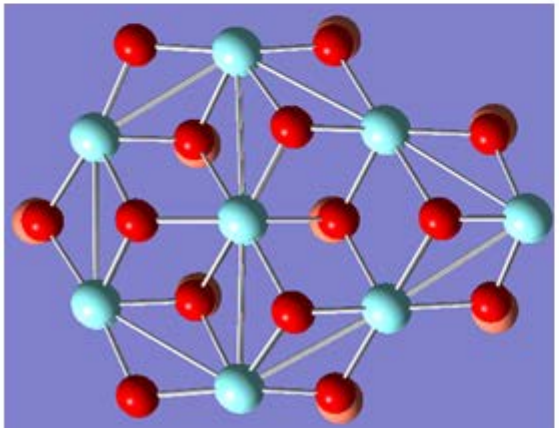
B.E. = 5.408 eV/atom

$Cu_8O_{24}Y_{16}$ (48 atoms)



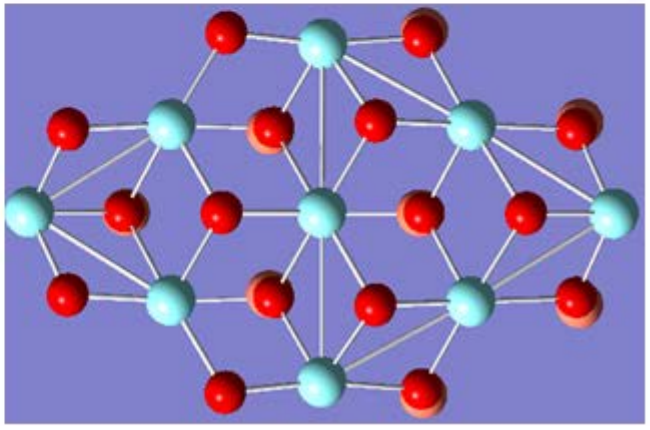
B.E. = 5.165 eV/atom

$Cu_8O_{28}Y_{16}$ (52 atoms)



B.E. = 5.390 eV/atom

$Cu_8O_{32}Y_{18}$ (58 atoms)

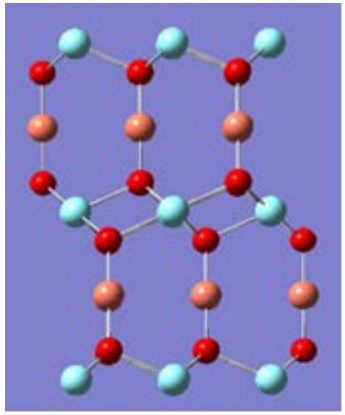


B.E. = 5.351 eV/atom

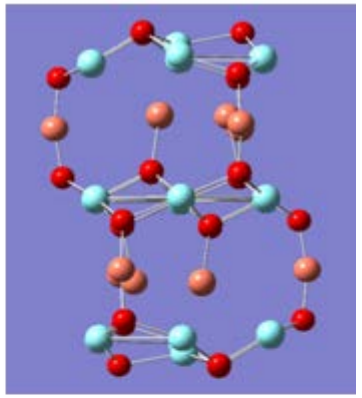
$$\text{B.E./atom} = [m\text{E(Cu)}+n\text{E(Y)}+l\text{E(O)} - \text{E}(\text{Cu}_m\text{Y}_n\text{O}_l\text{-cluster})]/(m+n+l)$$

Role of oxygen termination:

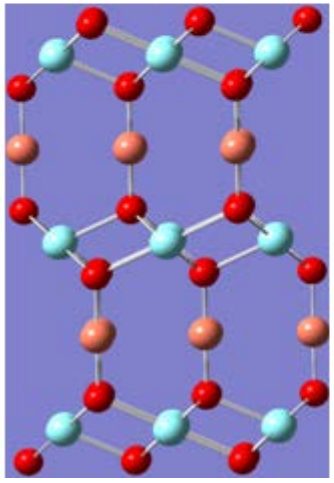
Previously without O-termination:
high distortion



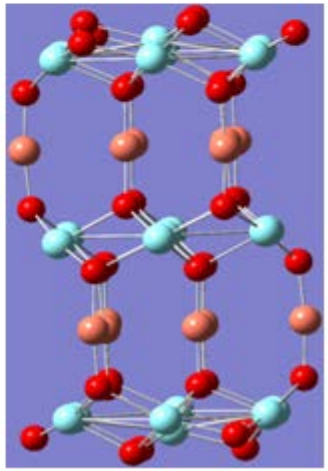
Relaxed to



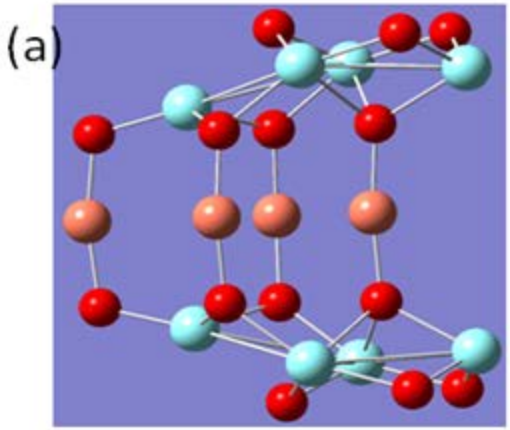
Previously with O-termination:
Little distortion
Keeping the "delafossite" structure



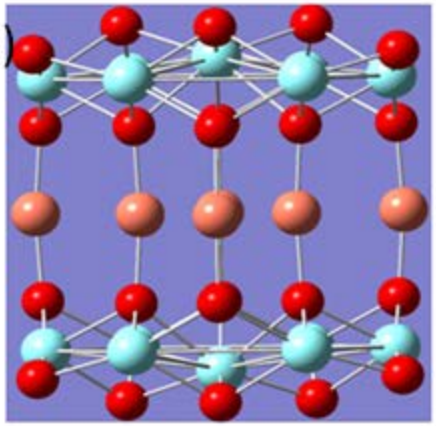
Relaxed to



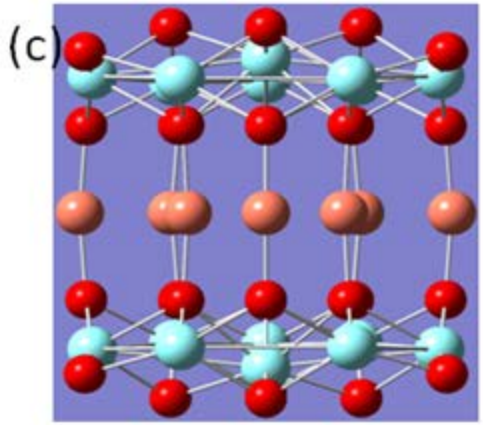
Few selected structures (side view) for detail study:



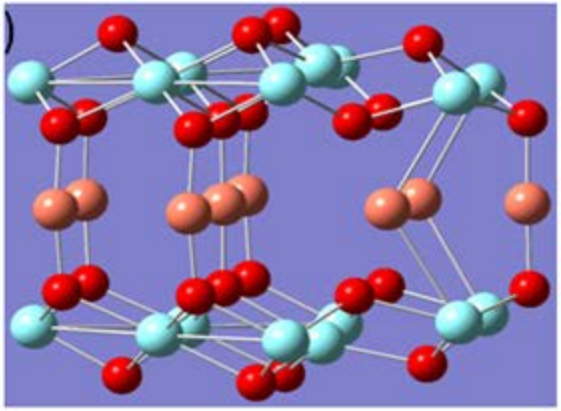
$Cu_4Y_8O_{14}$



$Cu_6Y_{14}O_{24}$



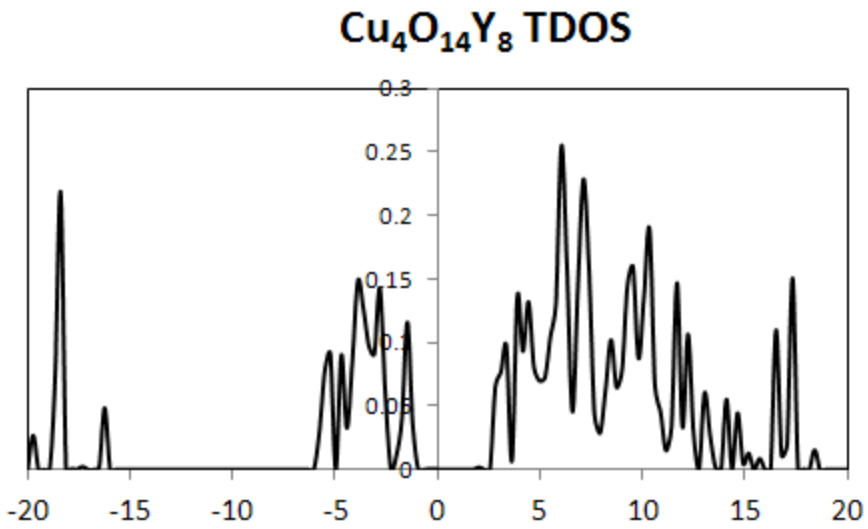
$Cu_8Y_{16}O_{28}$

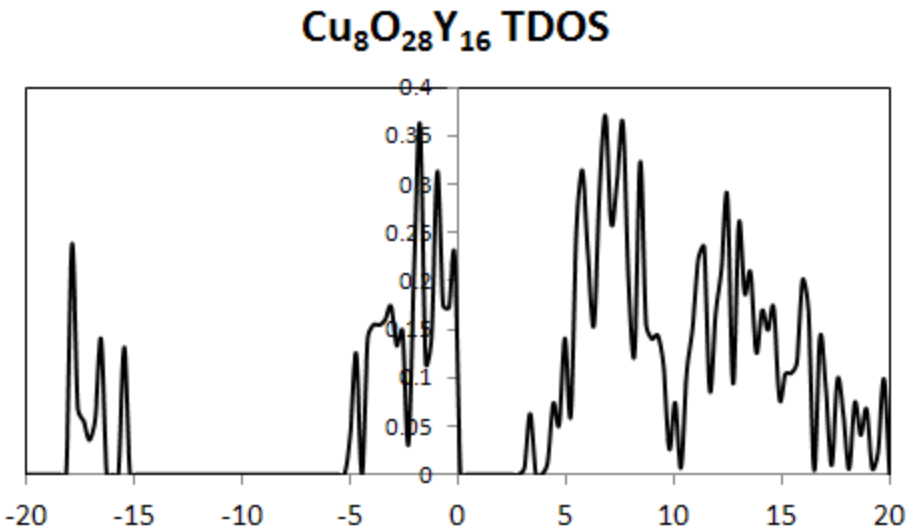


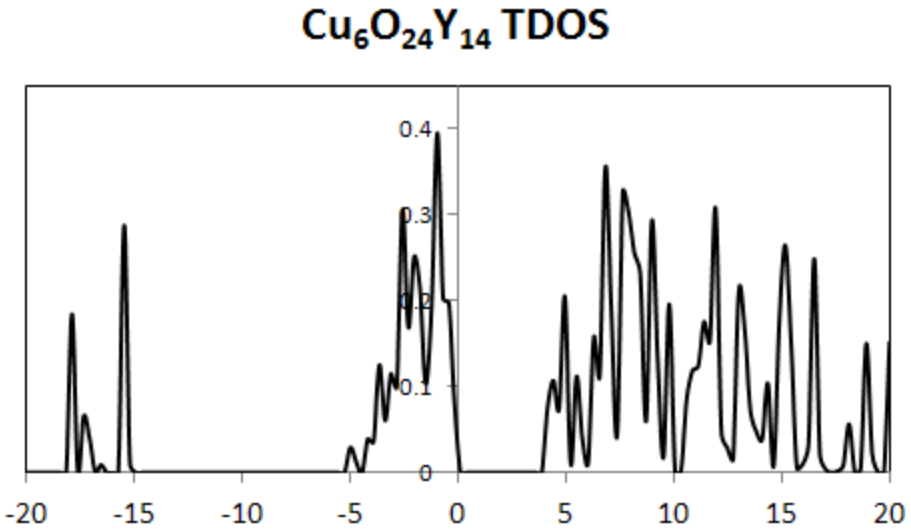
$Cu_8Y_{16}O_{24}$

Structures shown in figures (a), (b) and (c) are charge compensated

Density of states (DOS) for charge compensated nano-crystals:

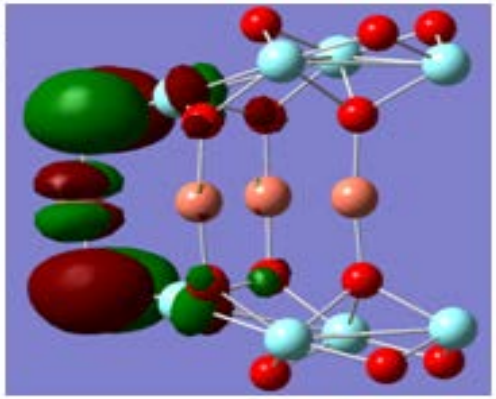






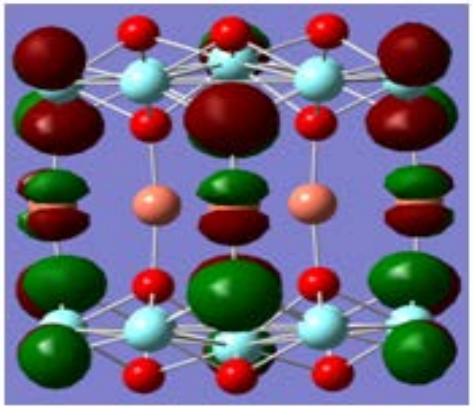
Highest occupied molecular orbital (HOMO):

(a)



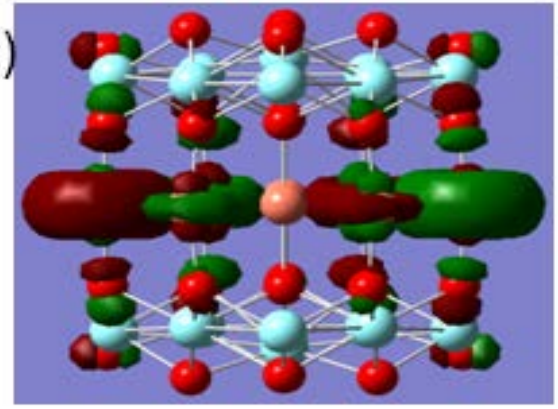
$Cu_4Y_8O_{14}$

(b)



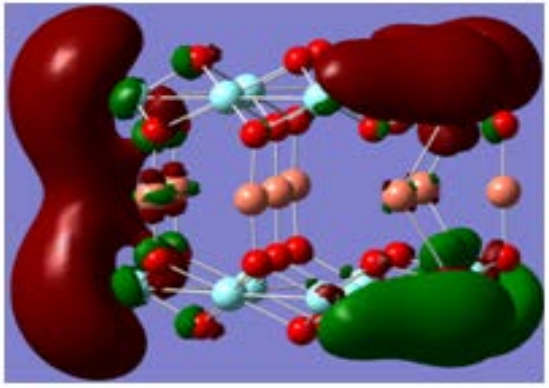
$Cu_6Y_{14}O_{24}$

(c)



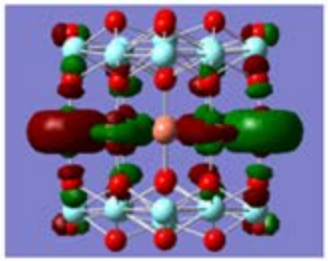
$Cu_8Y_{16}O_{28}$

(d)

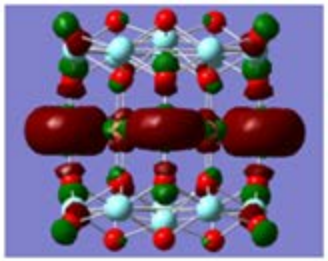


$Cu_8Y_{16}O_{24}$

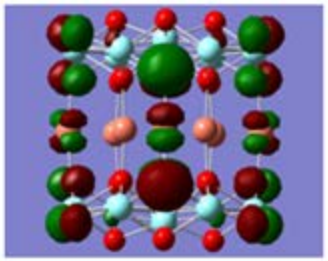
$Cu_8Y_{16}O_{28}$:



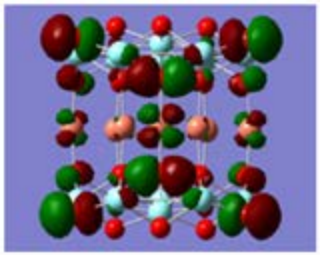
HOMO



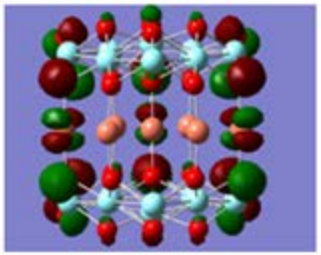
HOMO – 1
(ΔE=0.035eV)



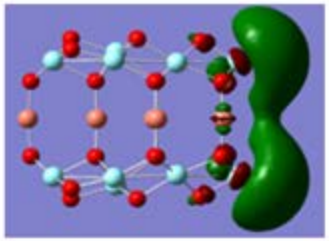
HOMO – 2
(ΔE=0.037eV)



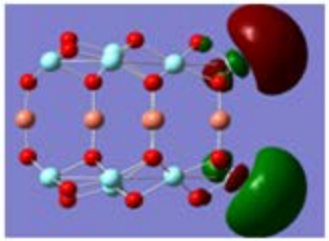
HOMO – 3
(ΔE=0.064eV)



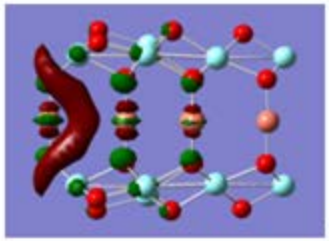
HOMO – 4
(ΔE=0.114eV)



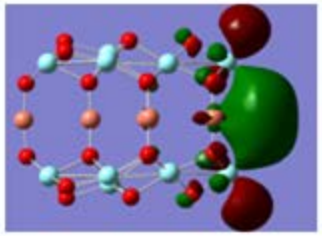
LUMO



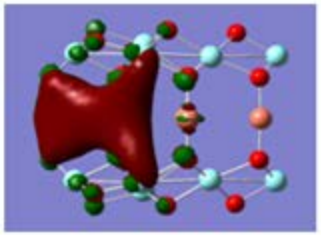
LUMO+1
(ΔE=0.170eV)



LUMO+2
(ΔE=1.064eV)



LUMO+3
(ΔE=1.217eV)

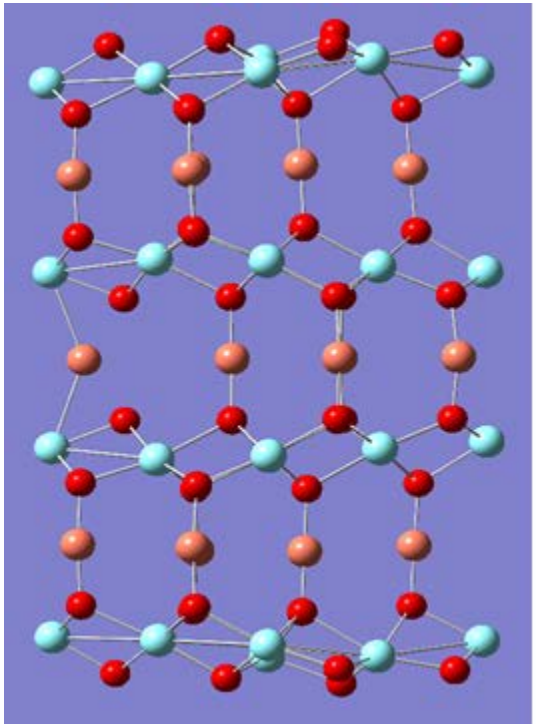


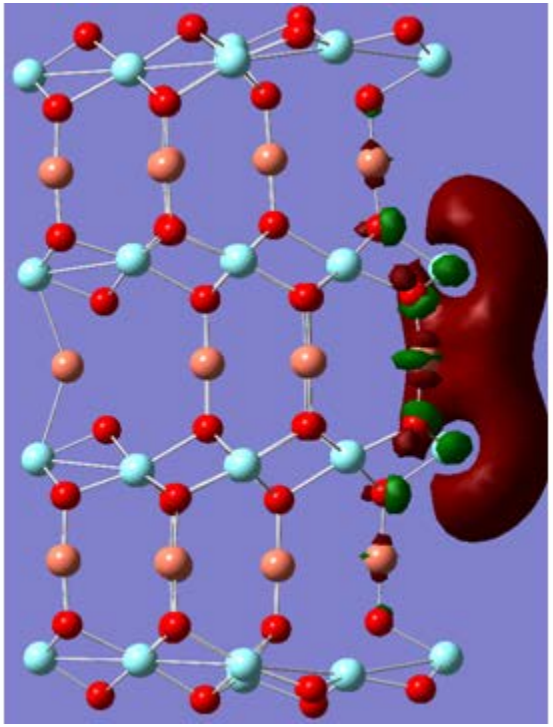
LUMO+4
(ΔE=1.302eV)

Structures	B.E./atom (eV)	HOMO-LUMO Gap (eV)	TDDFT gap (eV)	Oscillator strength	Dipole moment (Debye)
$Cu_4 Y_8O_{14}$	5.087	1.359 (s)	1.026	0.000	19.795
$Cu_6Y_{14}O_{24}$	5.408	4.159 (s)	3.371	0.000	0.000
$Cu_8Y_{16}O_{24}$	5.165	0.582	1.155	0.003	9.786
$Cu_8Y_{16}O_{28}$	5.390	3.165 (s)	2.734	0.000	14.820
$Cu_8Y_{18}O_{32}$	5.351	0.293	0.174	0.000	15.245

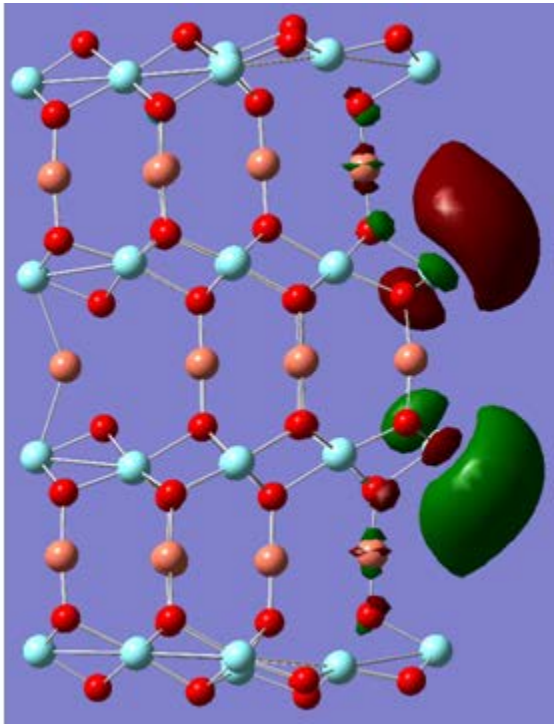
Optical absorption is not possible at the lowest gap.
In fact first few transitions are not allowed for all of these structures.

Multi-layered structure:





HOMO



LUMO

The top and bottom layer has Y-Y bonds to saturate the surfaces.
The middle two Y-O octahedron layers do not have Y-Y bonds, except at the left end.

Summary:

- It has been found that the $C_mY_nO_l$ nano-crystals have, in general, high binding energies which are more than 5eV/ atom.
- The stability of these nano-crystals is ensured by the Y-Y bonds to saturate the Y-O octahedrons on the terminating surfaces.
- We have also observed that Y-terminated surfaces are not stable.
- M-O octahedrons sites are not chemically active
- For both the larger charge-compensated structures, the hybrid-DFT HOMO-LUMO gaps are higher than 3eV, and the TDDFT gaps for the same structures are more than 2.7eV.
- Despite the low band gap of some of these delafossite nano-crystals, the extremely low oscillator strength precludes the absorption of photons in the visible portion of the electromagnetic spectrum.

Future plan:

- Transport properties calculation. (SIESTA code has already been installed to do this type of calculations).
- Electron hopping to the surface, and transfer of electrons from the surface will be studied.
- Doped nano-crystals will be considered.
- Detail orbital analysis will be performed to understand and predict other nano-structures for photo-catalysts.