

PEC Materials: Theory and Modeling

Muhammad N. Huda¹, Yanfa Yan², Todd Deutsch²,
Mowafak M. Al-Jassim² and John A. Turner²

¹University of Texas at Arlington

²National Renewable Energy Laboratory

March 20, 2012

Project ID #
PD052

Overview

Timeline

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

Budget

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

Partners

National Renewable Energy Laboratory
University of Texas at Arlington



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.

Efficiency

Approach 1:
Stabilization of High Efficiency Crystalline Material Systems

Approach 3:
Development of 3rd Generation Materials and Structures

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

Unique Theory & Characterization Capabilities

MVSystems

UT THE UNIVERSITY OF TOLEDO 1872

NREL NATIONAL RENEWABLE ENERGY LABORATORY

HNEI

UNIV UNIVERSITY OF NEVADA LAS VEGAS

TU Delft Delft University of Technology

EMPA

DOE PEC Working Group

National/International Collaborations

Durability

Approach

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

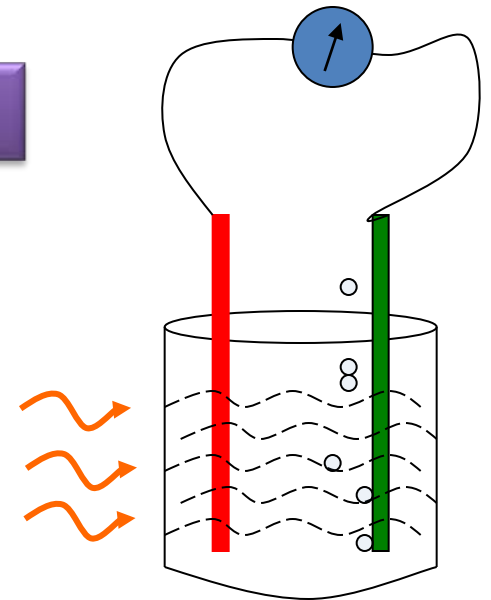
1 – Stable in an aqueous electrolyte

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

3 – Right band edge positions

4 – efficient optical absorptions properties

5 – Good charge carrier transport



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

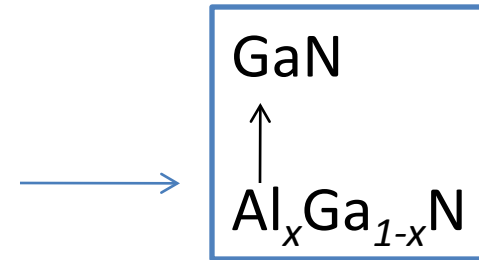
(semiconductor/electrolyte):

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

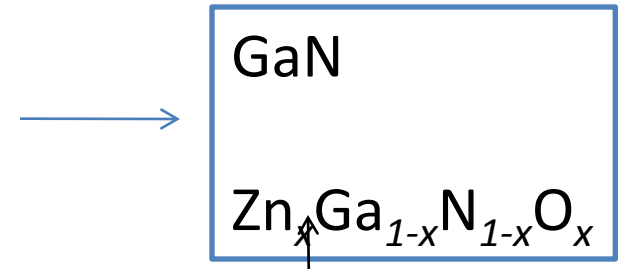
We use density functional theory (DFT) and its variants (hybrid, DFT+U, etc.) to calculate the electronic properties of materials.

How do we tune optical (band) gaps?

1. By isovalent doping.



2. By passive co-doping.



3. By random alloying.

→

Challenging
for ab initio
modeling!

4. By reducing the dimensions.

→

Nanostructures:
Nanocrystal, etc.

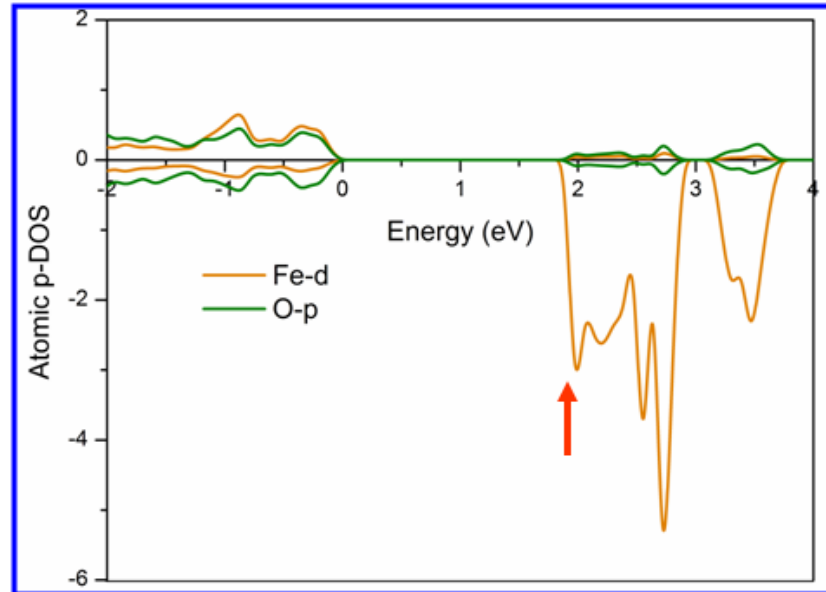
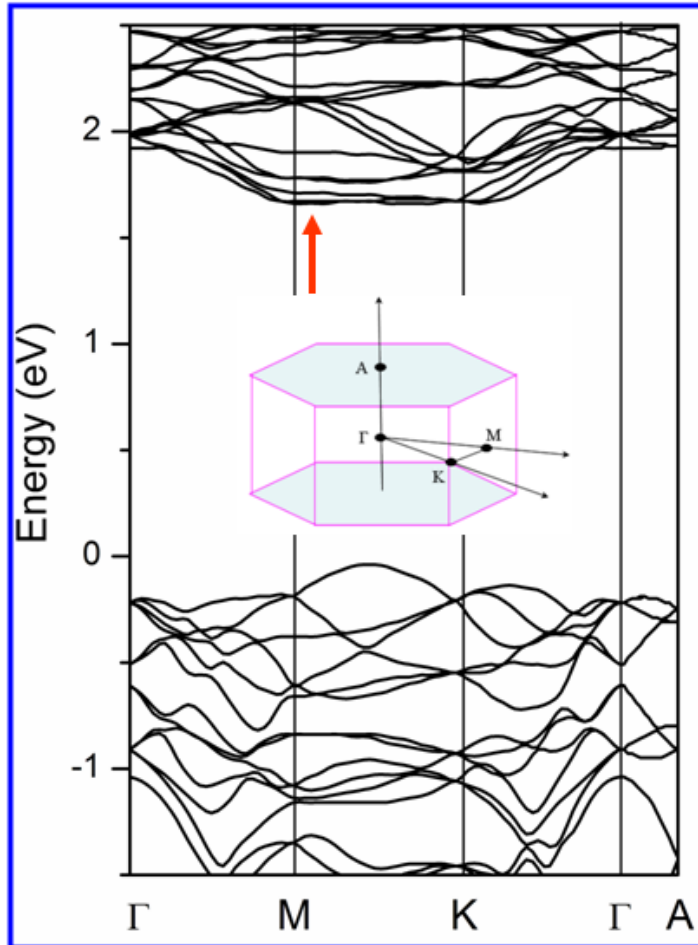
Oxides that need to be avoided:

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.

A common feature in a Mott insulator :

The electronic structure of $\alpha\text{-Fe}_2\text{O}_3$



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-delafoffsites



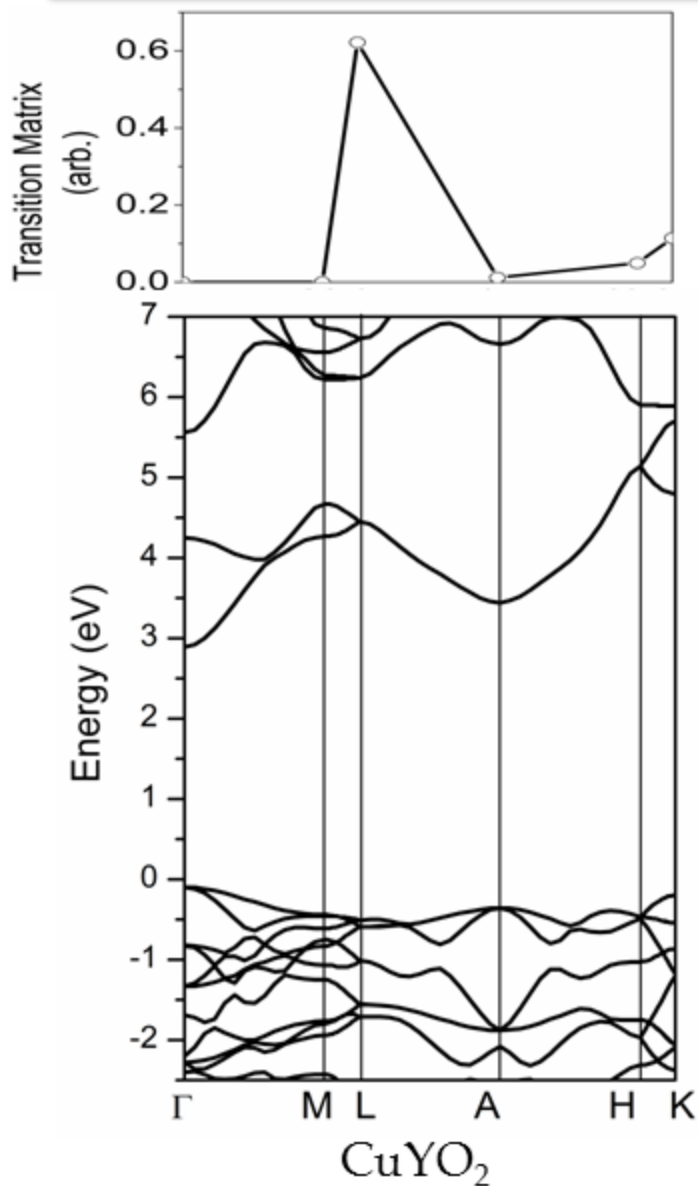
| | | | | | | | | | | | | | | | | | | | | | |
|--------------------------------------|--|--|--|--|---|--|---------------------------------------|---|---|--------------------------------------|--|---------------------------------------|---|--------------------------------------|---------------------------------------|--------------------------------------|-------------------------------------|------------------------------------|----------------------------------|------------------------------------|----------------------------------|
| CuMO_2 | | | | | | | | | | | | | | | | | | | | | |
| 1A | | | | | | | | | | | | | | | | | 8A | | | | |
| 1 H hydrogen 1.008 | | | | | | | | | | | | | | | | | 2 He helium 4.003 | | | | |
| 2A | | | | | | | | | | | | | | | 3A | | 4A | 5A | 6A | 7A | 10 |
| 3 Li lithium 6.941 | 4 Be beryllium 9.012 | | | | | | | | | | | | | | | 5 B boron 10.81 | 6 C carbon 12.01 | 7 N nitrogen 14.01 | 8 O oxygen 16.00 | 9 F fluorine 19.00 | 10 Ne neon 20.18 |
| 3B | 4B | 5B | 6B | 7B | 8B | 9B | 10B | 11B | 12B | 13B | 14B | 15B | 16B | 17B | 18B | 19B | 20B | | | | |
| 11 Na sodium 22.99 | 12 Mg magnesium 24.31 | 21 Sc scandium 44.96 | 22 Ti titanium 47.88 | 23 V vanadium 50.94 | 24 Cr chromium 52.00 | 25 Mn manganese 54.94 | 26 Fe iron 55.85 | 27 Co cobalt 58.93 | 28 Ni nickel 58.69 | 29 Cu copper 63.55 | 30 Zn zinc 65.39 | 31 Ga gallium 69.72 | 32 Ge germanium 72.58 | 33 As arsenic 74.92 | 34 Se selenium 78.96 | 35 Br bromine 79.90 | 36 Kr krypton 83.80 | | | | |
| 37 Rb rubidium 85.47 | 38 Sr strontium 87.62 | 39 Y yttrium 88.91 | 40 Zr zirconium 91.22 | 41 Nb niobium 92.91 | 42 Mo molybdenum 95.94 | 43 Tc technetium (98) | 44 Ru ruthenium 101.1 | 45 Rh rhodium 102.9 | 46 Pd palladium 106.4 | 47 Ag silver 107.9 | 48 Cd cadmium 112.4 | 49 In indium 114.8 | 50 Sn tin 118.7 | 51 Sb antimony 121.8 | 52 Te tellurium 127.6 | 53 I iodine 126.9 | 54 Xe xenon 131.3 | | | | |
| 55 Cs cesium 132.9 | 56 Ba barium 137.3 | 57 La* lanthanum 138.9 | 72 Hf hafnium 178.5 | 73 Ta tantalum 180.9 | 74 W tungsten 183.9 | 75 Re rhenium 186.2 | 76 Os osmium 190.2 | 77 Ir iridium 190.2 | 78 Pt platinum 195.1 | 79 Au gold 197.0 | 80 Hg mercury 200.5 | 81 Tl thallium 204.4 | 82 Pb lead 207.2 | 83 Bi bismuth 208.9 | 84 Po polonium (209) | 85 At astatine (210) | 86 Rn radon (222) | | | | |
| 87 Fr francium (223) | 88 Ra radium (226) | 89 Ac~ actinium (227) | 104 Rf rutherfordium (257) | 105 Db dubnium (260) | 106 Sg seaborgium (263) | 107 Bh bohrium (262) | 108 Hs hassium (265) | 109 Mt meitnerium (266) | 110 Ds darmstadtium (271) | 111 Uuu (272) | 112 Uub (277) | 114 Uuq (296) | | 116 Uuh (298) | | 118 Uuo (?) | | | | | |
| Lanthanide Series* | | | | | | | | | | | | | | | | | | | | | |
| 58 Ce cerium 140.1 | 59 Pr praseodymium 140.9 | 60 Nd neodymium 144.2 | 61 Pm promethium (147) | 62 Sm samarium (150.4) | 63 Eu europium 152.0 | 64 Gd gadolinium 157.3 | 65 Tb terbium 158.9 | 66 Dy dysprosium 162.5 | 67 Ho holmium 164.9 | 68 Er erbium 167.3 | 69 Tm thulium 168.9 | 70 Yb ytterbium 173.0 | 71 Lu lutetium 175.0 | | | | | | | | |
| Actinide Series~ | | | | | | | | | | | | | | | | | | | | | |
| 90 Th thorium 232.0 | 91 Pa protactinium (231) | 92 U uranium (238) | 93 Np neptunium (237) | 94 Pu plutonium (242) | 95 Am americium (243) | 96 Cm curium (247) | 97 Bk berkelium (247) | 98 Cf californium (249) | 99 Es einsteinium (254) | 100 Fm fermium (253) | 101 Md mendelevium (256) | 102 No nobelium (254) | 103 Lr lawrencium (257) | | | | | | | | |

Why Cu-delafofossites, CuMO_2 :

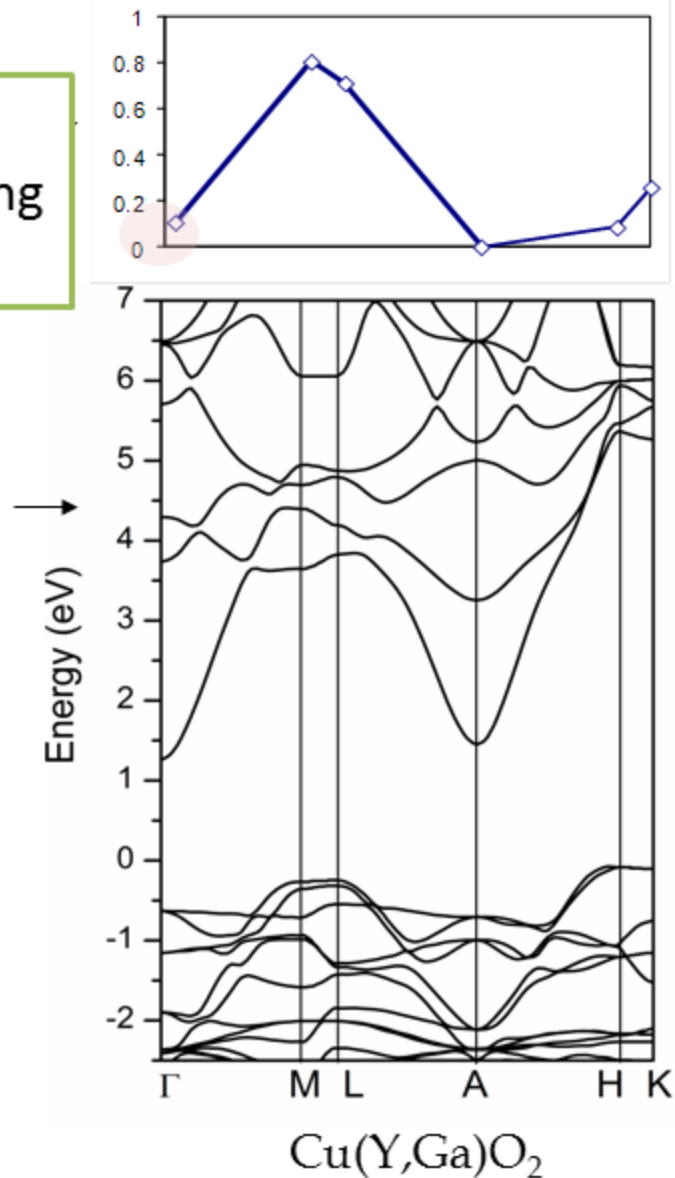
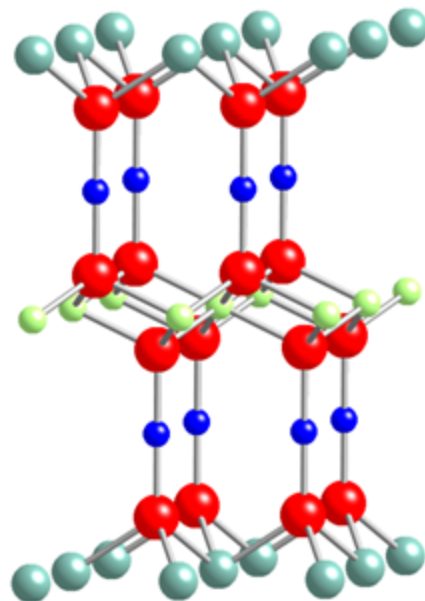
- A prototype multi-cation oxide.
- Due to Cu-d band, the valence band maximum is relatively less electro-negative compared to other oxides.
- Group IIIA delafossites has direct band gaps.
- Band gap: $\text{CuScO}_2 > \text{CuYO}_2 > \text{CuLaO}_2$.
- Stable in solution
- Available

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

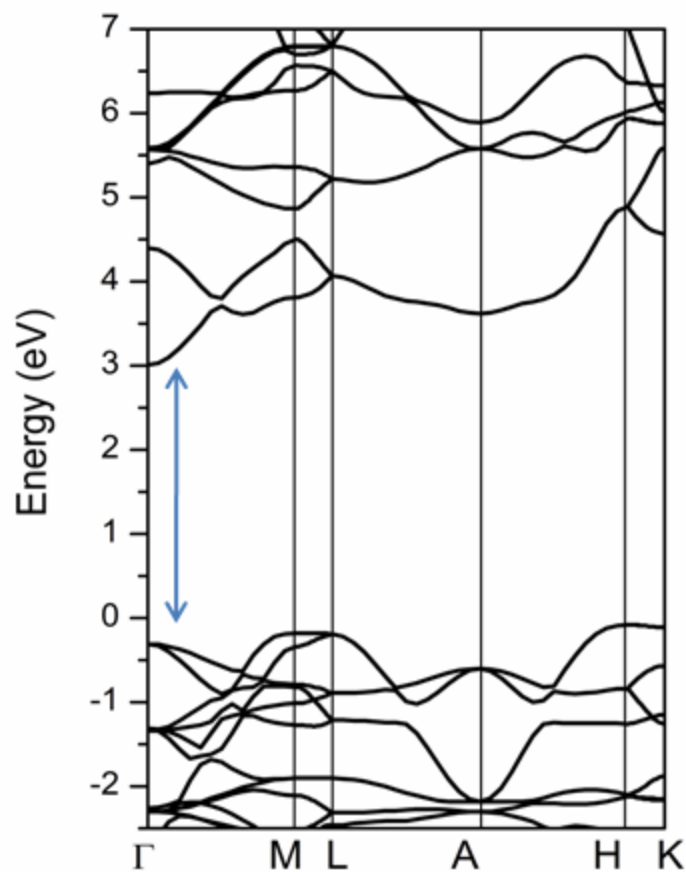
Problem with optical absorptions in delafossites:



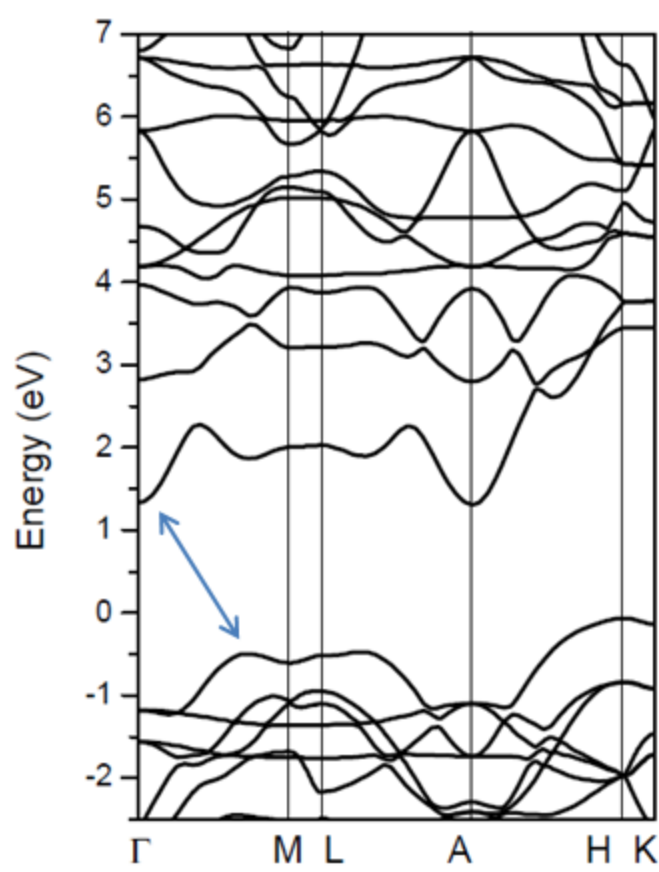
Solution:
Symmetry breaking
by alloying.



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



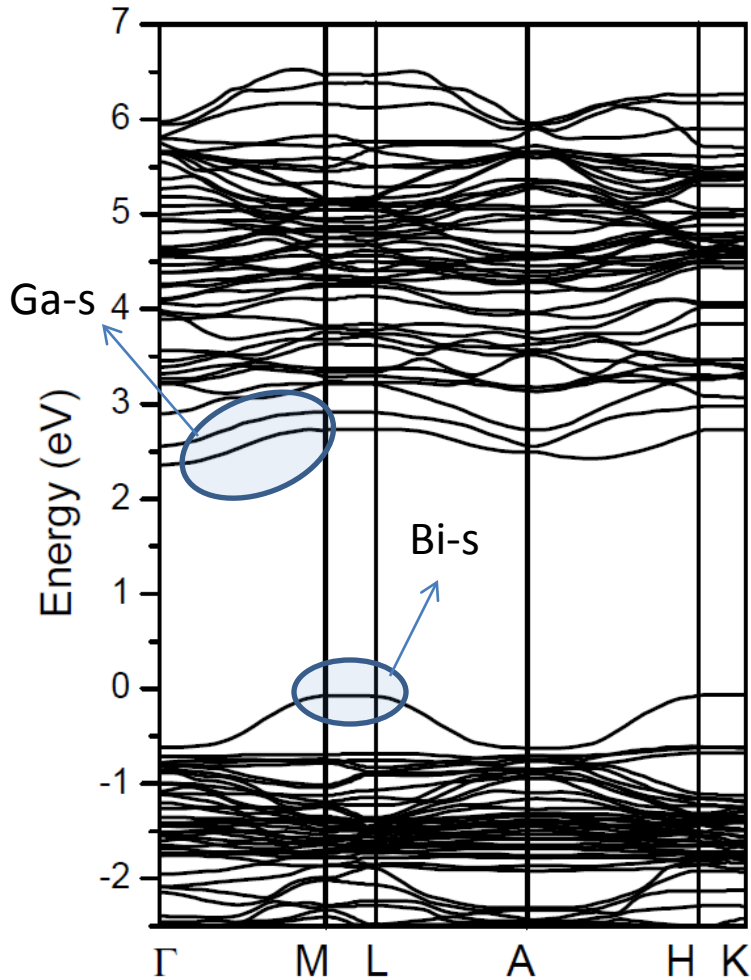
CuScO_2



$\text{Cu}(\text{Sc,Bi})\text{O}_2$

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.

We tried more complicated alloys:



Important feature here is that all Bi-doped CuAO₂ delafossites has always(!) indirect gap

Two structures have been tried:

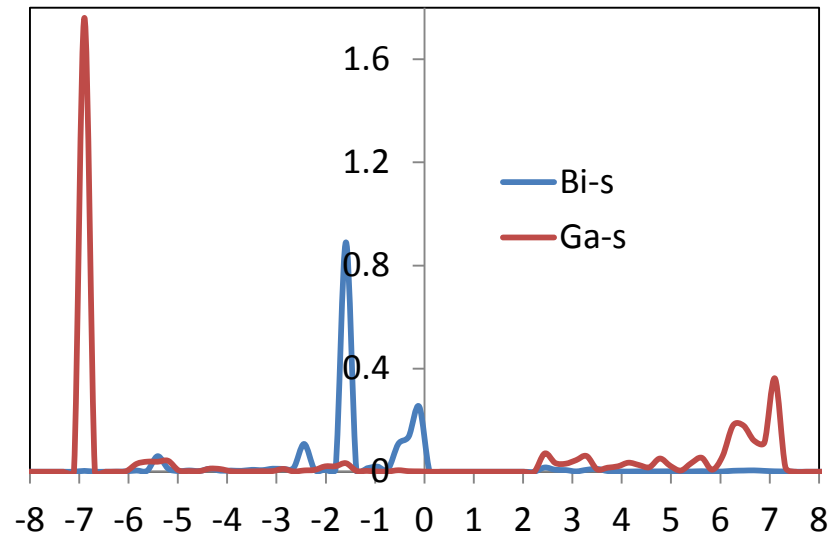
- (i) Ga and Bi are on the same layer,
- (ii) Ga and Bi are on different layer.

First one being the most stable by 0.32 eV

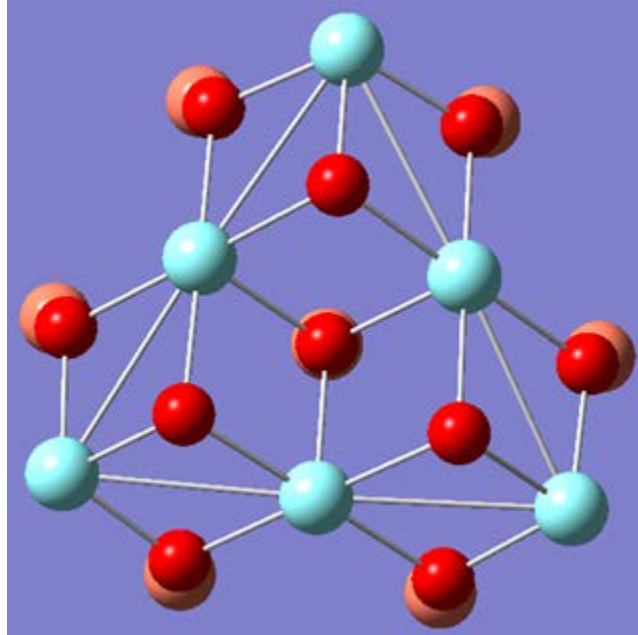
The relative ratio of Sc:Bi:Ga is 10:1:1.

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:

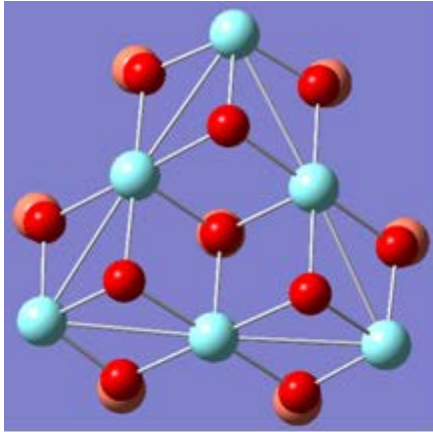
- Density functional theory (DFT) has been used as implemented in Gaussian03/09.
- Both hybrid (B3LYP) and GGA (PW91) has been tried. (The results shown here are with hybrid functional).
- Different multiplicities (spin-states) were tested.
- Smaller nanocrystals were tested to as the basic building 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 $\text{Cu}_m\text{Y}_n\text{O}_l$, $m+3n-2l=0$) 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.

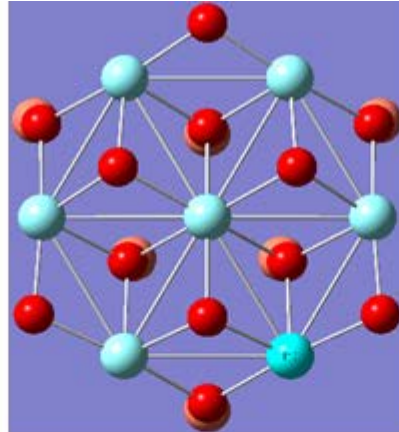
Some selected structures:

$\text{Cu}_7\text{O}_{20}\text{Y}_{12}$ (39 atoms)



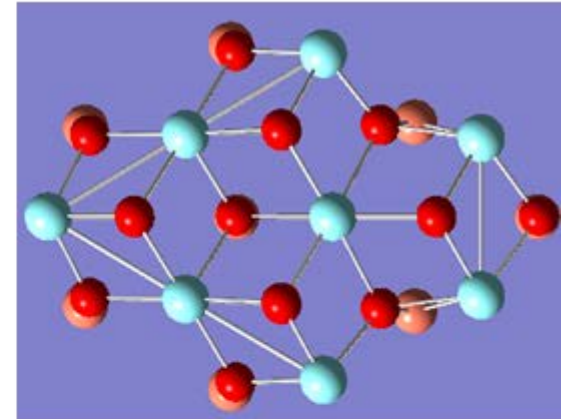
B.E. = 5.173 eV/atom

$\text{Cu}_6\text{O}_{24}\text{Y}_{14}$ (44 atoms)



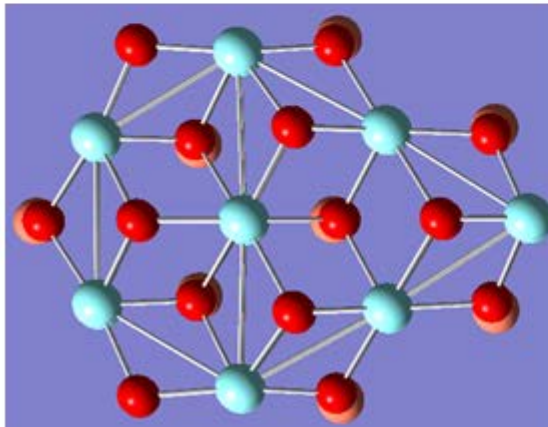
B.E. = 5.408 eV/atom

$\text{Cu}_8\text{O}_{24}\text{Y}_{16}$ (48 atoms)



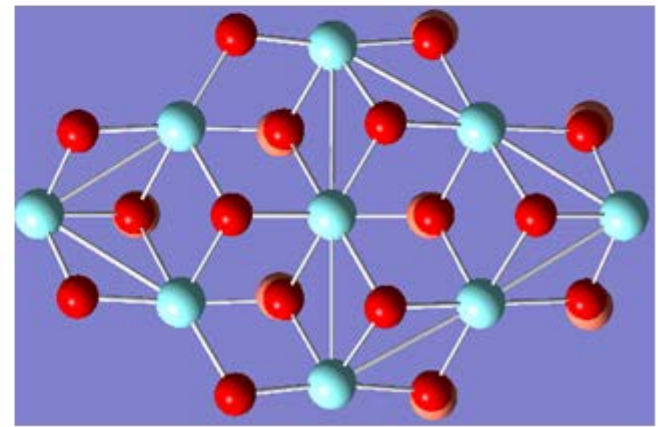
B.E. = 5.165 eV/atom

$\text{Cu}_8\text{O}_{28}\text{Y}_{16}$ (52 atoms)



B.E. = 5.390 eV/atom

$\text{Cu}_8\text{O}_{32}\text{Y}_{18}$ (58 atoms)

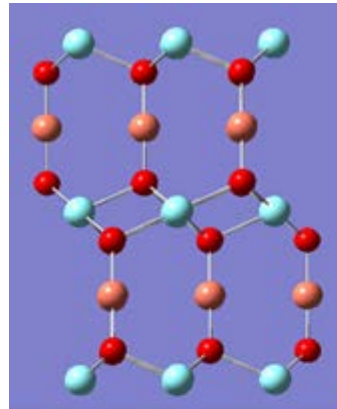


B.E. = 5.351 eV/atom

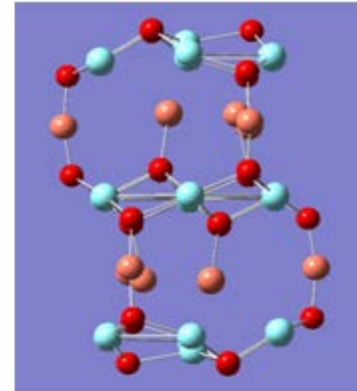
$$\text{B.E./atom} = [mE(\text{Cu}) + nE(\text{Y}) + lE(\text{O}) - E(\text{Cu}_m\text{Y}_n\text{O}_l\text{-cluster})] / (m+n+l)$$

Role of oxygen termination:

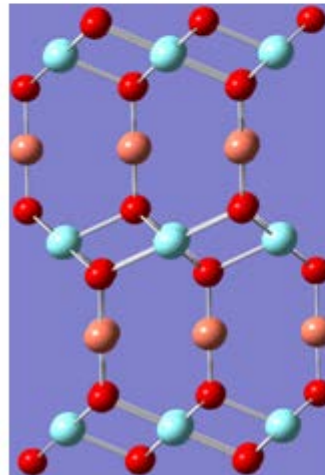
Previously without
O-termination:
high distortion



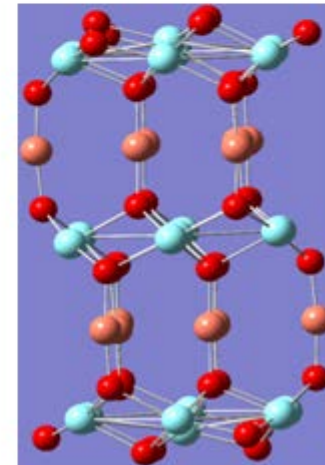
Relaxed to →



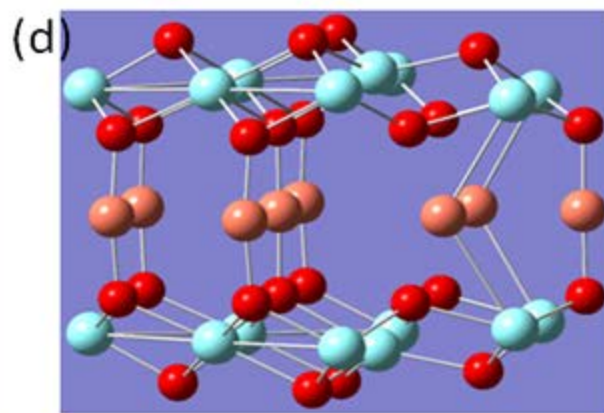
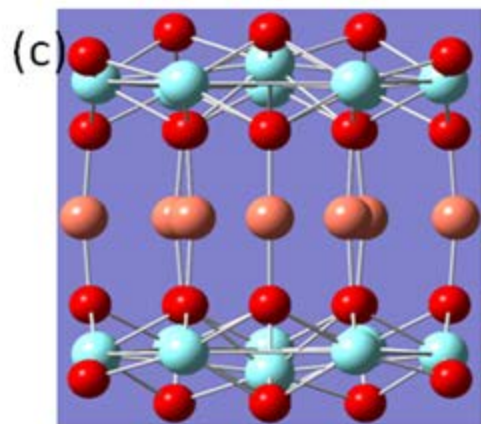
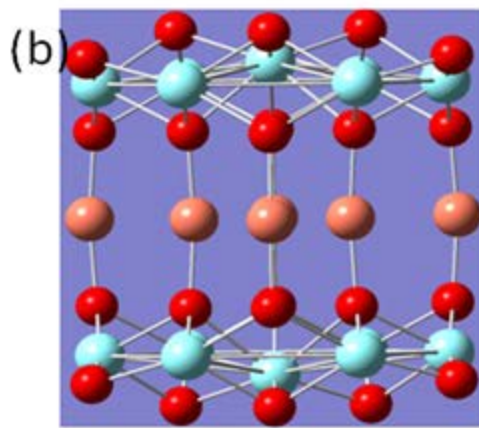
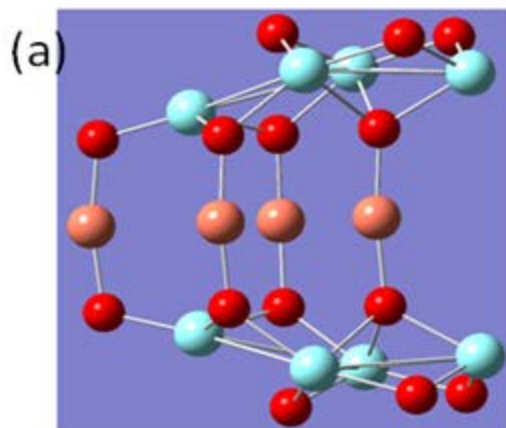
Previously with
O-termination:
Little distortion
Keeping the
“delafossite” structure



Relaxed to →



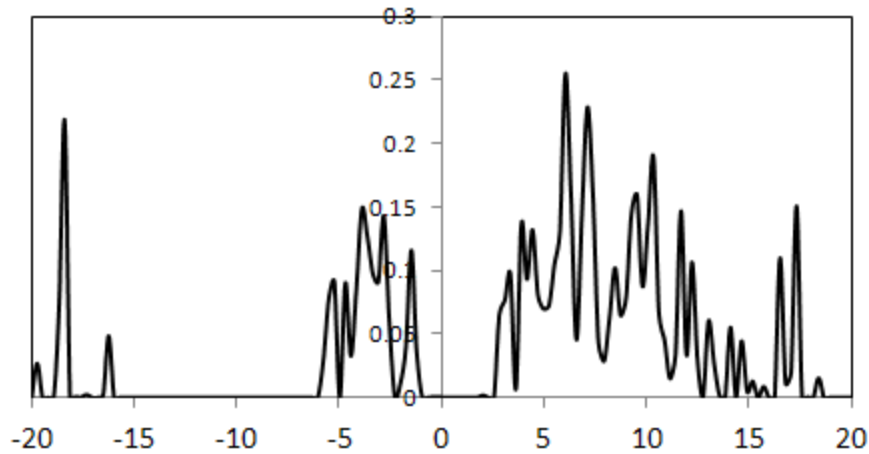
Few selected structures (side view) for detail study:



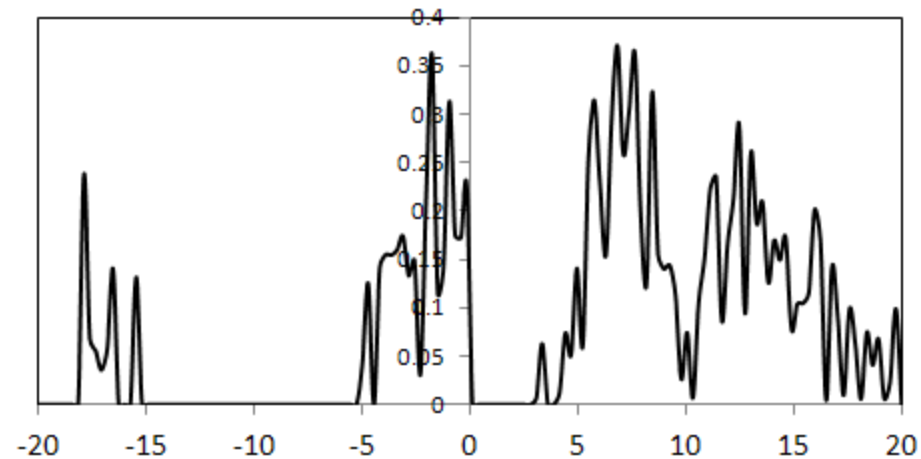
Structures shown in figures (a), (b) and (c) are charge compensated

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

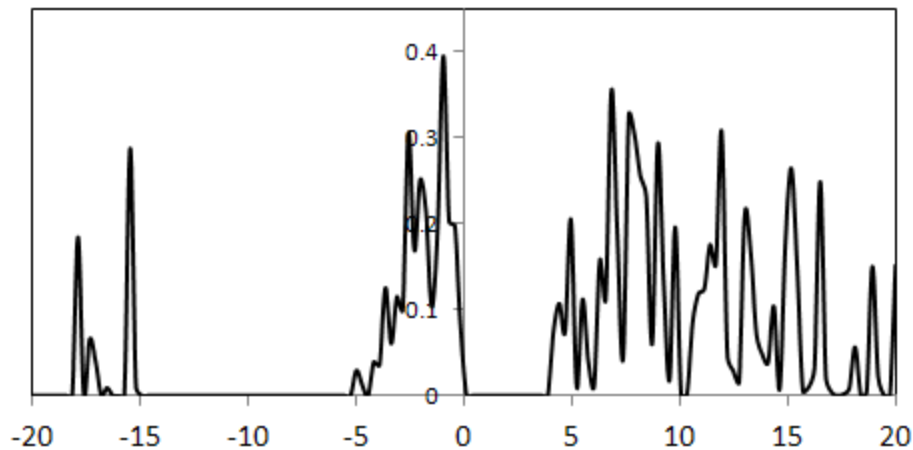
$\text{Cu}_4\text{O}_{14}\text{Y}_8$ TDOS



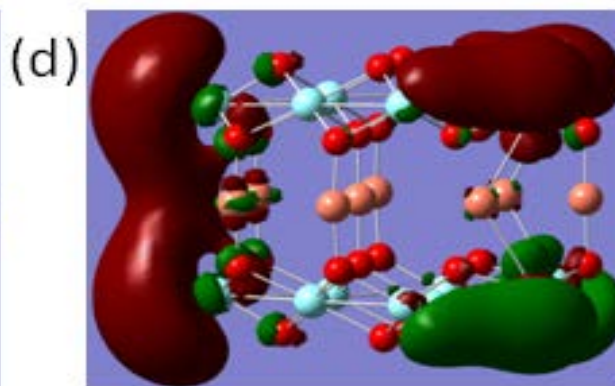
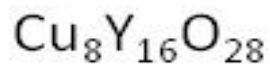
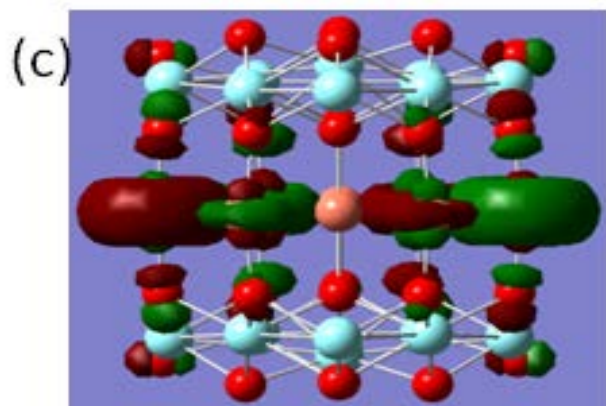
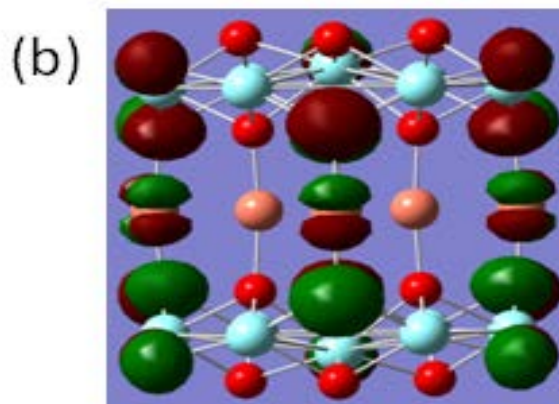
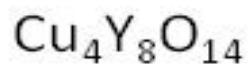
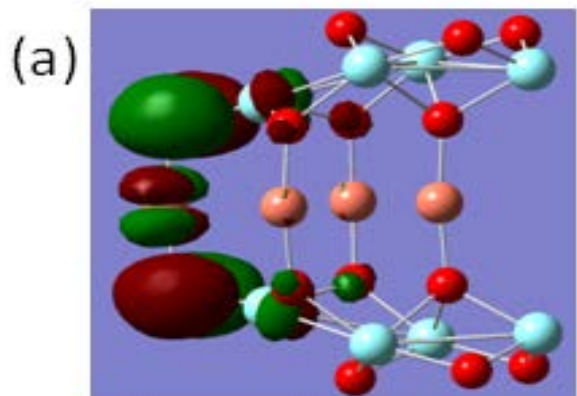
$\text{Cu}_8\text{O}_{28}\text{Y}_{16}$ TDOS

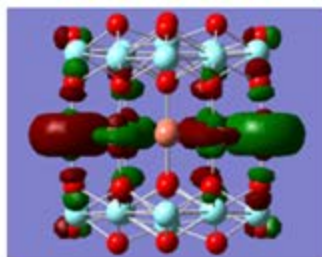
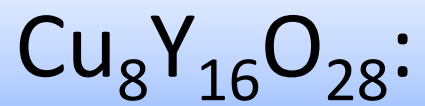


$\text{Cu}_6\text{O}_{24}\text{Y}_{14}$ TDOS

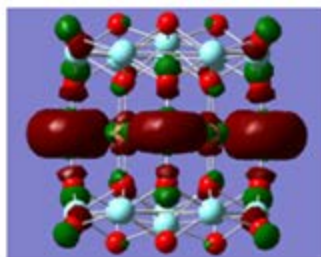
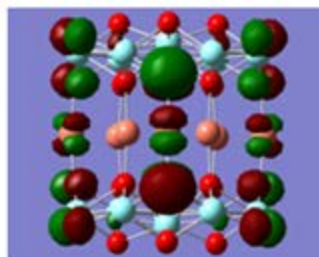
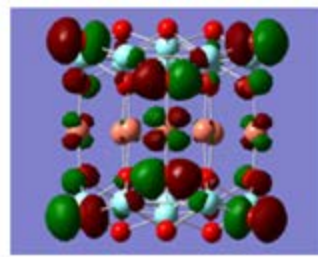
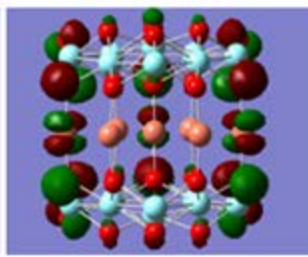
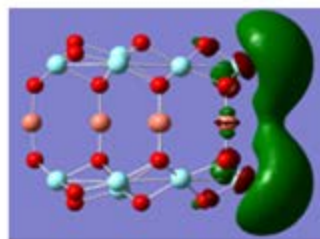


Highest occupied molecular orbital (HOMO):

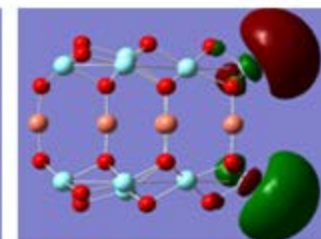
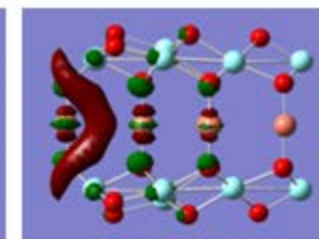
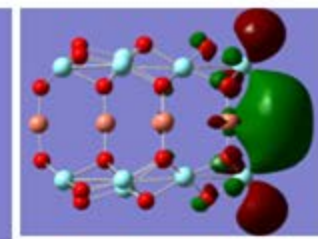
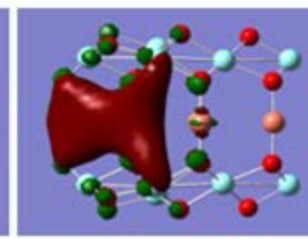




HOMO

HOMO-1
($\Delta E=0.035\text{eV}$)HOMO-2
($\Delta E=0.037\text{eV}$)HOMO-3
($\Delta E=0.064\text{eV}$)HOMO-4
($\Delta E=0.114\text{eV}$)

LUMO

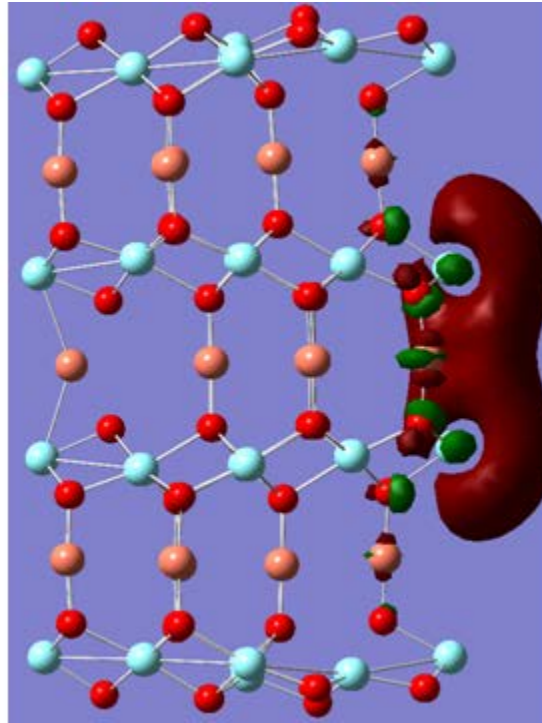
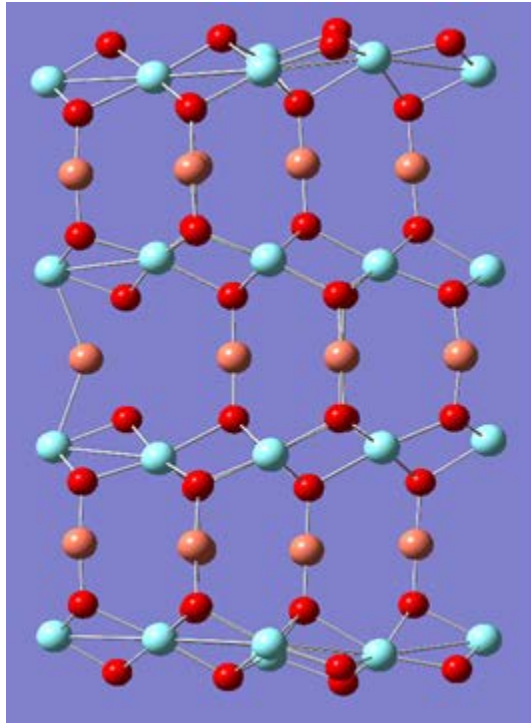
LUMO+1
($\Delta E=0.170\text{eV}$)LUMO+2
($\Delta E=1.064\text{eV}$)LUMO+3
($\Delta E=1.217\text{eV}$)LUMO+4
($\Delta E=1.302\text{eV}$)

| Structures | B.E./atom (eV) | HOMO-LUMO Gap (eV) | TDDFT gap (eV) | Oscillator strength | Dipole moment (Debye) |
|---|-------------------|-----------------------|-------------------|------------------------|-----------------------------|
| $\text{Cu}_4\text{Y}_8\text{O}_{14}$ | 5.087 | 1.359 (s) | 1.026 | 0.000 | 19.795 |
| $\text{Cu}_6\text{Y}_{14}\text{O}_{24}$ | 5.408 | 4.159 (s) | 3.371 | 0.000 | 0.000 |
| $\text{Cu}_8\text{Y}_{16}\text{O}_{24}$ | 5.165 | 0.582 | 1.155 | 0.003 | 9.786 |
| $\text{Cu}_8\text{Y}_{16}\text{O}_{28}$ | 5.390 | 3.165 (s) | 2.734 | 0.000 | 14.820 |
| $\text{Cu}_8\text{Y}_{18}\text{O}_{32}$ | 5.351 | 0.293 | 0.174 | 0.000 | 15.245 |

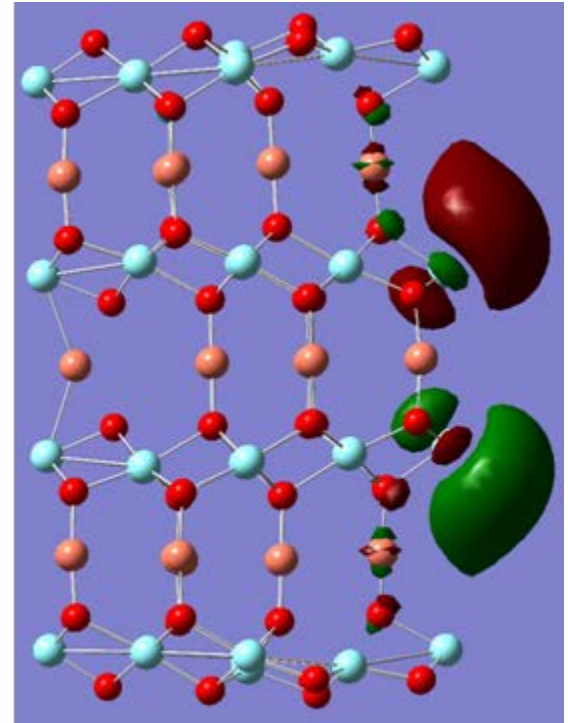


**Optical absorption is not possible at the lowest gap.
In fact first few transitions are not allowed for all of these structures.**

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 $C_m Y_n O_l$ 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.