National Renewable Energy Laboratory
Innovation for Our Energy Future

PEC Materials: Theory and Modeling

DOE AMR

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PEC Materials: Theory and Modeling

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National Renewable Energy Laboratory, Golden, Colorado

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Project ID # pd052

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Overview

Timeline

- Start date: 1991 (2007 for this task)
- Project end date: 2012
- Percent complete: NA

Barriers

- Barriers addressed
  - Y. Materials efficiency
  - Z. Materials durability
  - AB. Materials synthesis

Budget

- Total project funding
  - Part of NREL PEC Program
- Funding received in FY09 ~$120K
- Funding for FY10: ~$100K
- Note: Task with pd035 by John Turner

Partners

- University of Hawaii – Eric Miller
- University of California – Eric McFarland
- University of Nevada – Clemens Heske

Objectives - Relevance

The **main focus** of the project is to:

- Understand the performance of current PEC materials
- Provide guidance and solution for performance improvement
- Design and discover new materials

and

- Provide theoretical basis for go/no-go decisions to DOE PEC H_2 projects.

Approach

1. Work closely with other DOE H_2 projects

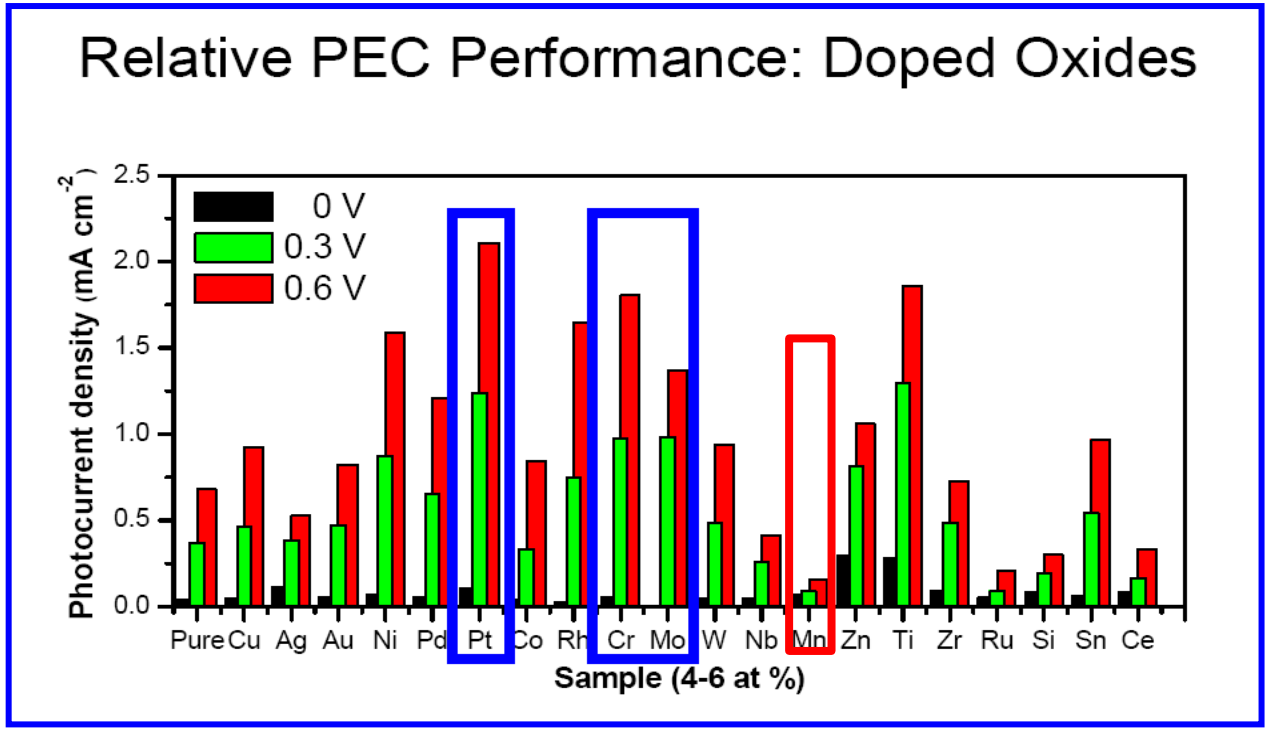
2. Follow the PEC R&D feedback loop

3. Use state-of-the-art, first-principles, density-functional theory calculation, which can calculate important properties:
    - Band structure
    - Optical absorption
    - Defect and doping effects
    - Surface chemistry
    - Structural stability

R&D feedback loop

Previous Technical Accomplishments and Progress

Understood the performance improvement for α-Fe_2O_3 observed by UC–Santa Barbara.



Doping of Pt, Cr, Mo, and Ti enhanced significantly the PEC performance, while doping of Mn decreased the performance – No theoretical explanation available

Previous Technical Accomplishments and Progress

Understood the performance improvement for α-Fe_2O_3 observed by UC–Santa Barbara.

Our density-function theory calculation of electronic band structure explained very well the results observed by UC–Santa Barbara.

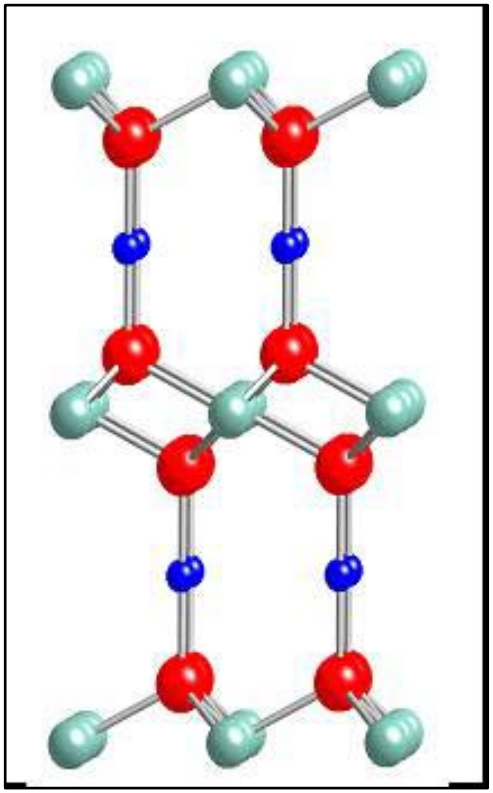
1. Doping of Pt, Ti, Cr, and Mo reduces significantly the electron effective mass – leading to improved electron mobility and thus enhanced PEC performance.

2. Doping of Mn does not alter electron effective mass, but introduces detrimental harmful deep levels, leading to decreased PEC performance

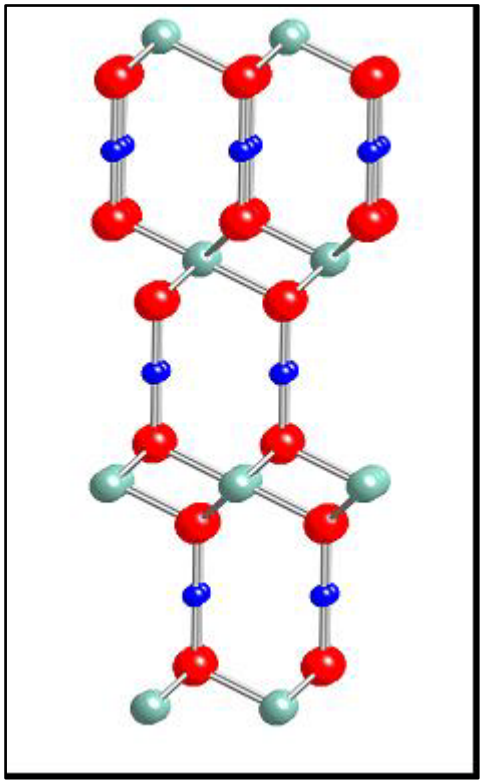
New Technical Accomplishments and Progress

Understanding the property of Cu delafossite ($CuXO_2$, *X*= group-IIIA, or IIIB) materials for PEC water splitting
Experimental collaboration: University of California

Structures of Cu delafossites



Hexagonal



Rhombohedral

New Technical Accomplishments and Progress (Cont.)

Properties of Cu delafossites

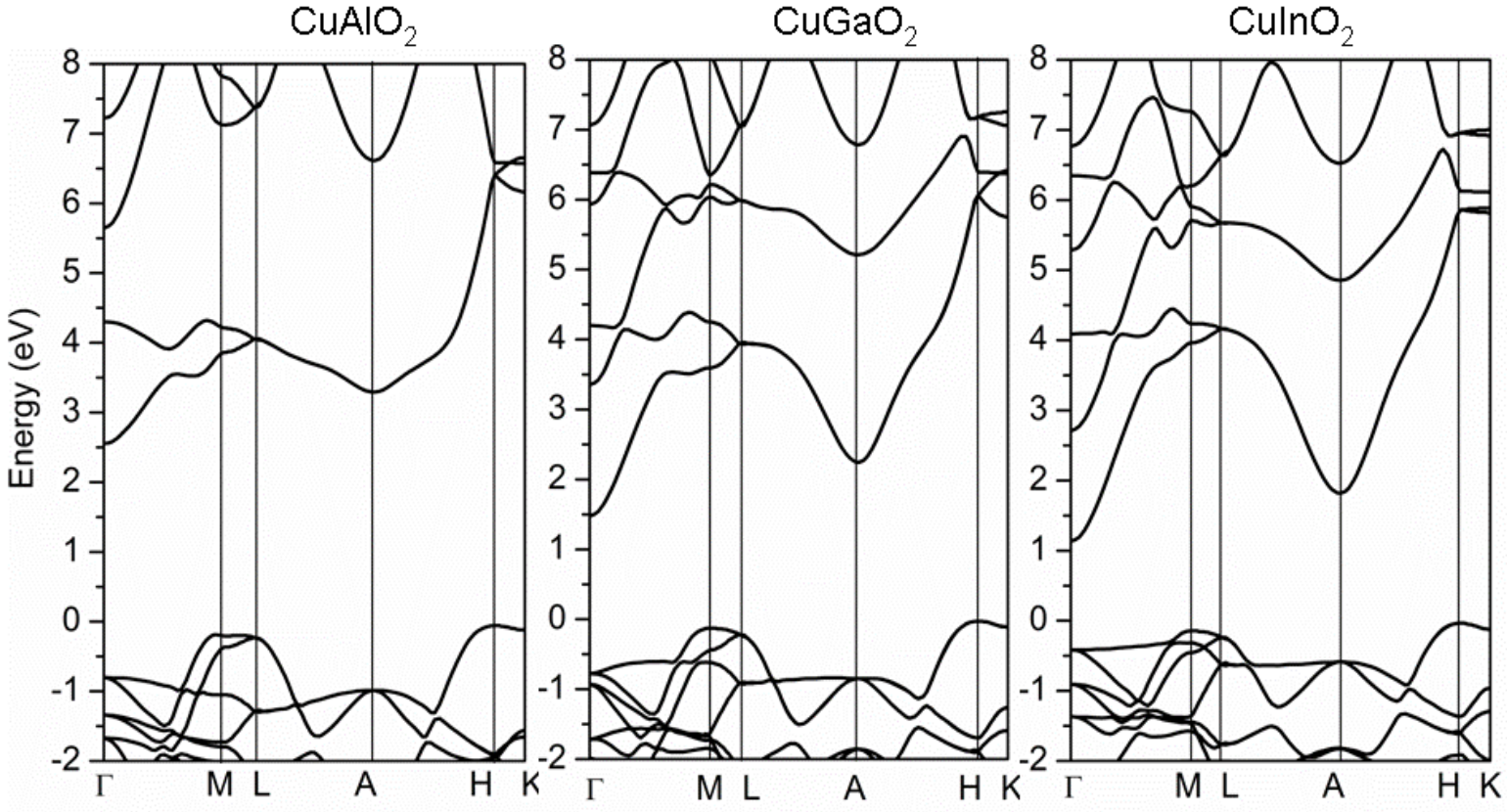
Good: Excellent electron mobility
Stable in aqueous solutions
Various band edge positions
Low cost

Bad: Low optical absorption
Low hole mobility

Our goal: Understand the properties
and find ways to improve the properties

New Technical Accomplishments and Progress (Cont.)

$CuXO_2$; X=group-IIIA , Hexagonal

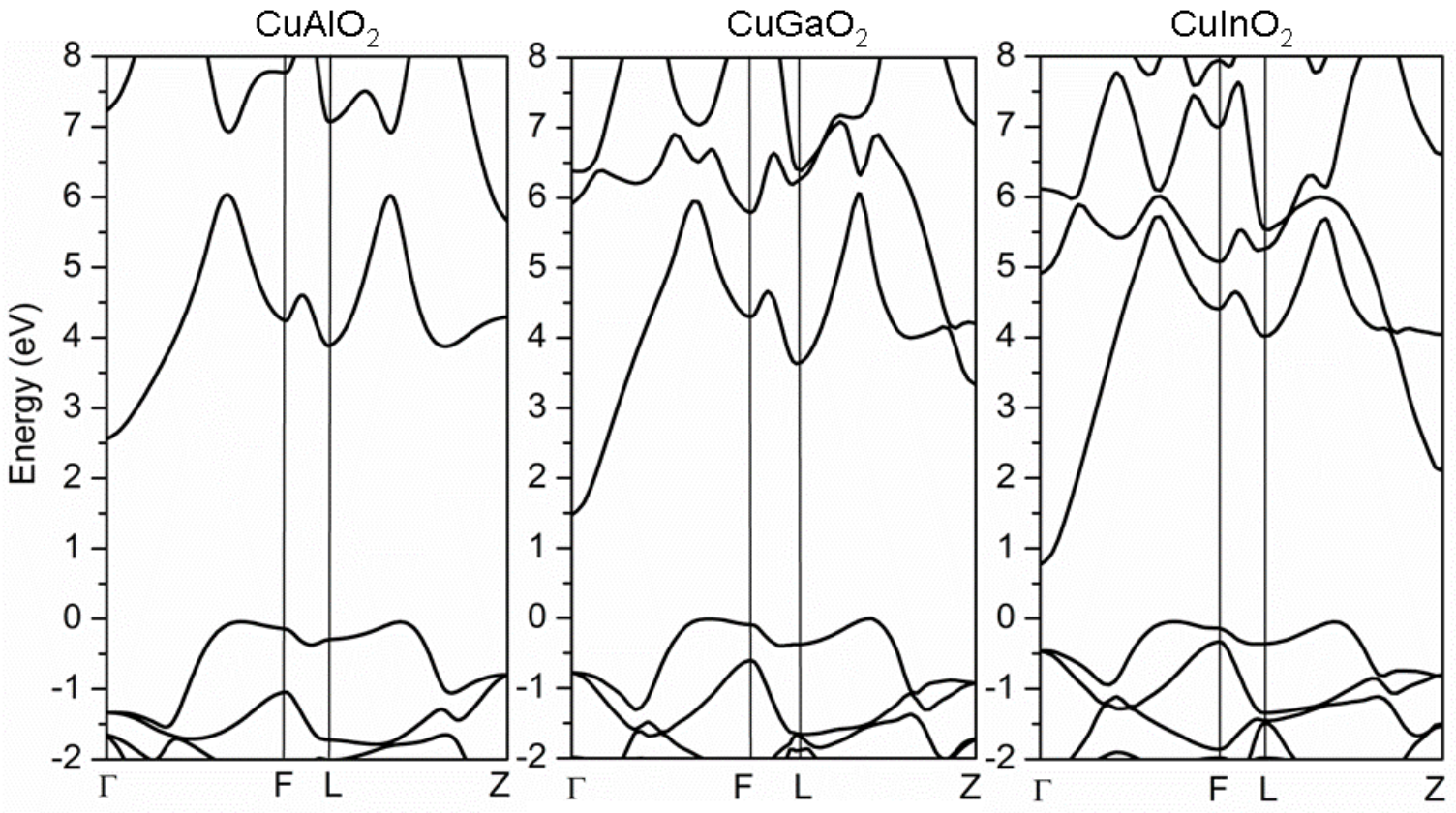


Calculated Band Structure

The excellent electron mobility due to very delocalized group IIIA *s* states

New Technical Accomplishments and Progress (Cont.)

$CuXO_2$; X=group-IIIA, rhombohedral

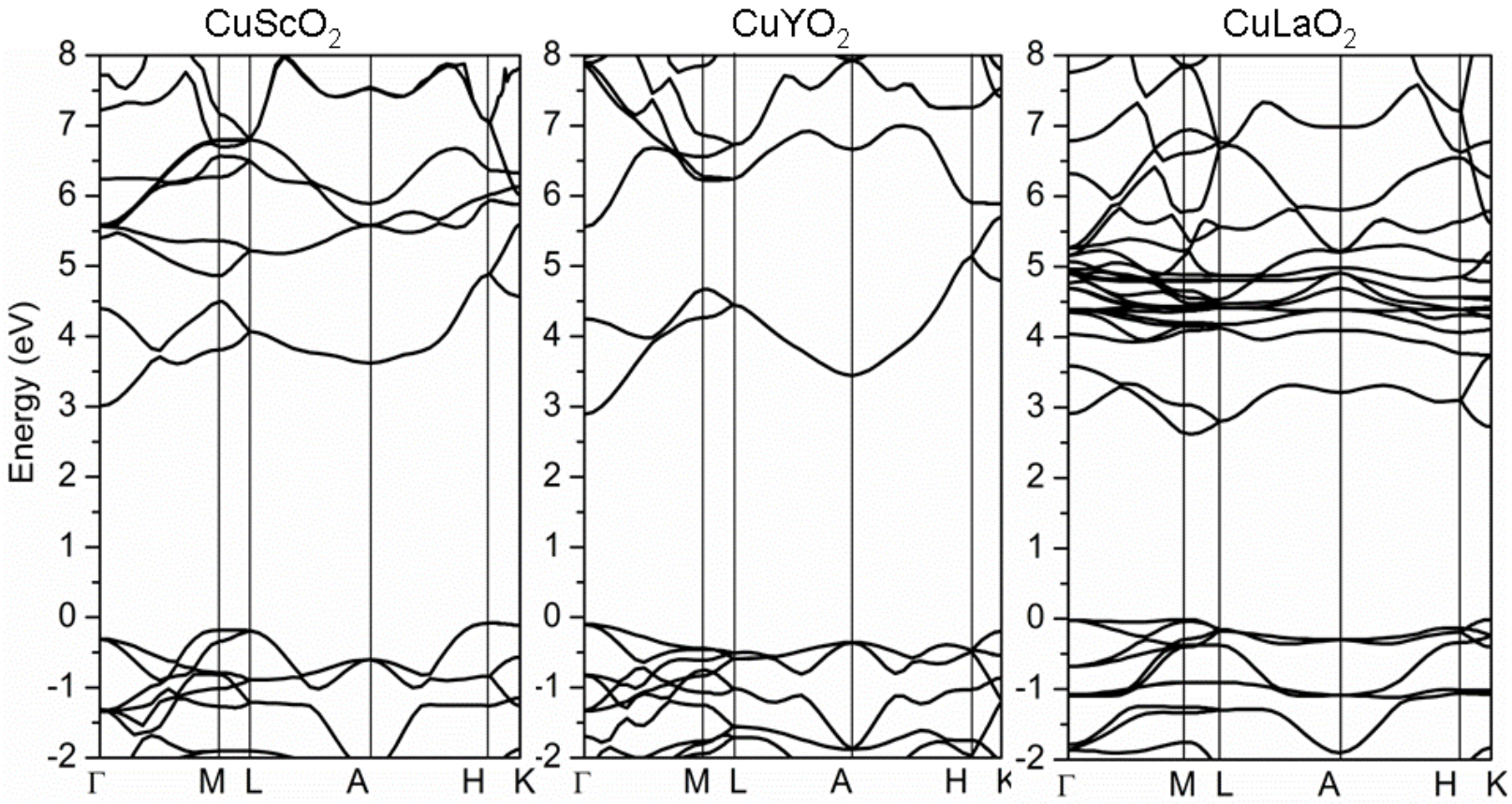


Calculated Band Structure

The bad hole mobility due to localized Cu 3*d* states

New Technical Accomplishments and Progress (Cont.)

$CuXO_2$; X=group-IIIB , Hexagonal

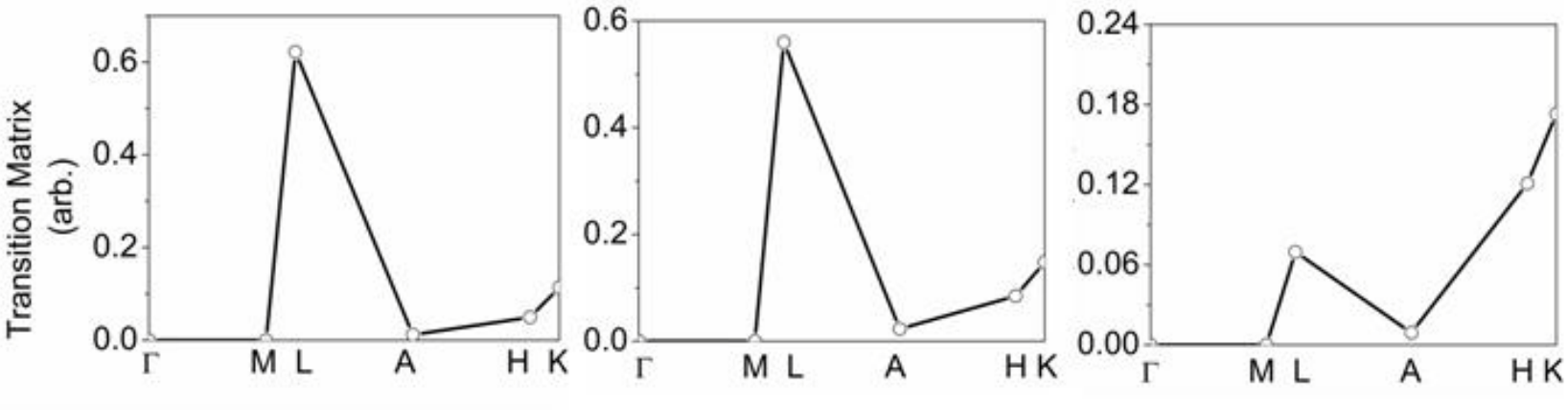


Calculated Band Structure

The difference between fundamental gap and optical gap for group-III B is smaller than that for group-IIIA

New Technical Accomplishments and Progress (Cont.)

$CuXO_2$; X=group-IIIB



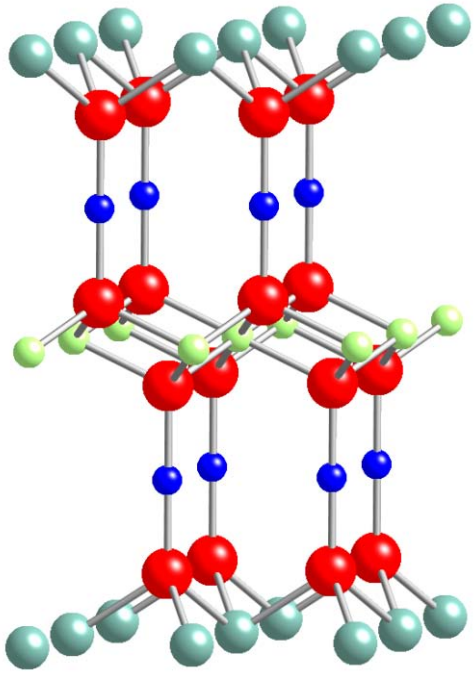
Calculated optical transition probabilities from the highest valence band to the lowest conduction band

All Cu delafossites have indirect band gaps due to the inversion symmetry of delafossite structure.

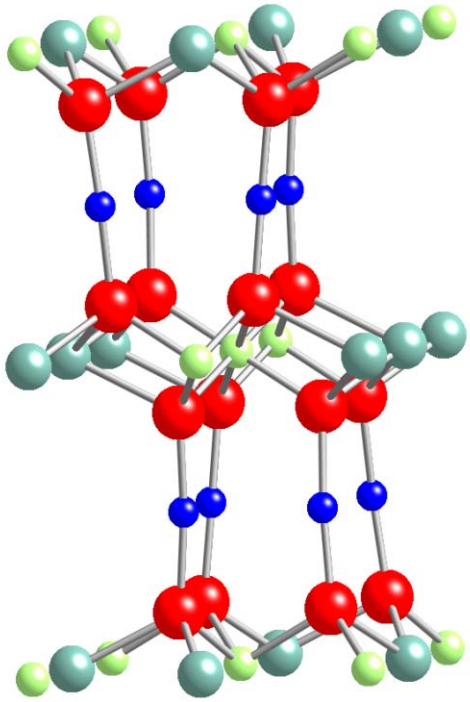
$CuYO_2$, and $CuLaO_2$ better than $CuAlO_2$, $CuInO_2$

New Technical Accomplishments and Progress (Cont.)

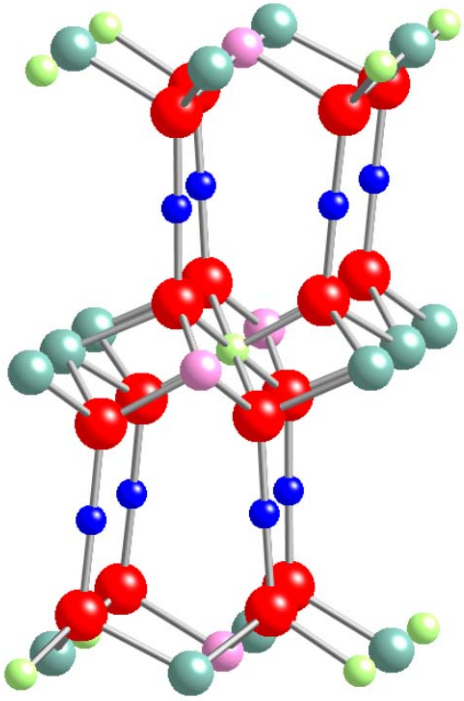
Breaking symmetry by group-IIIA and group-IIIB alloys to enhance optical absorption



(Ga,Y) -I



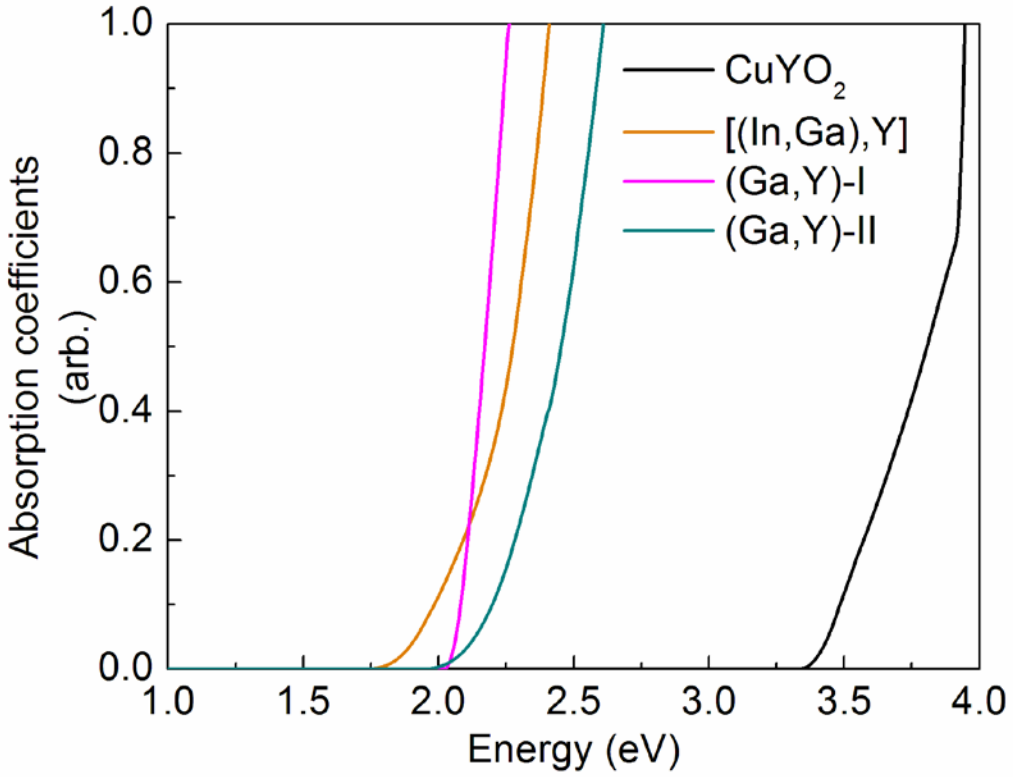
(Ga,Y) -II



(In,Ga, Y)

New Technical Accomplishments and Progress (Cont.)

Breaking symmetry by group-IIIA and group-IIIB alloys to enhance optical absorption

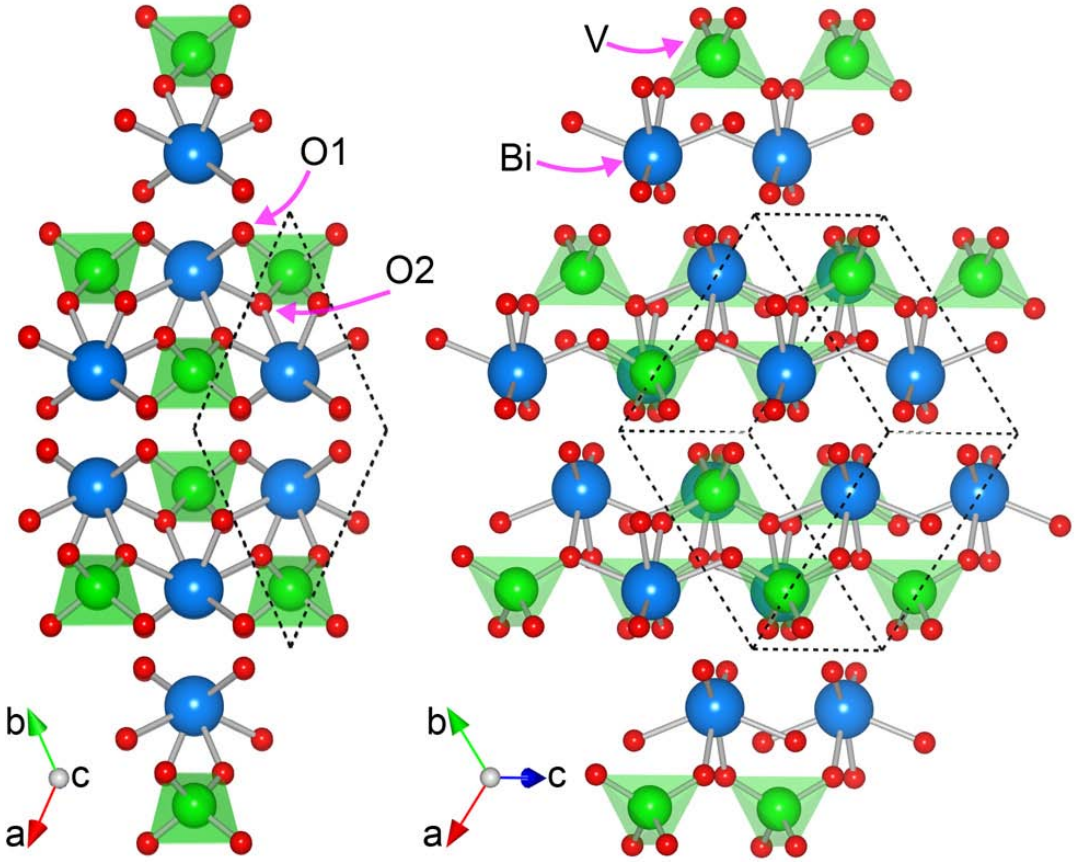


Optical Absorption Coefficient

Optical absorption is enhanced by alloying Ga and In with Y

New Technical Accomplishments and Progress (Cont.)

Doping of $BiVO_4$, an attractive and promising oxide



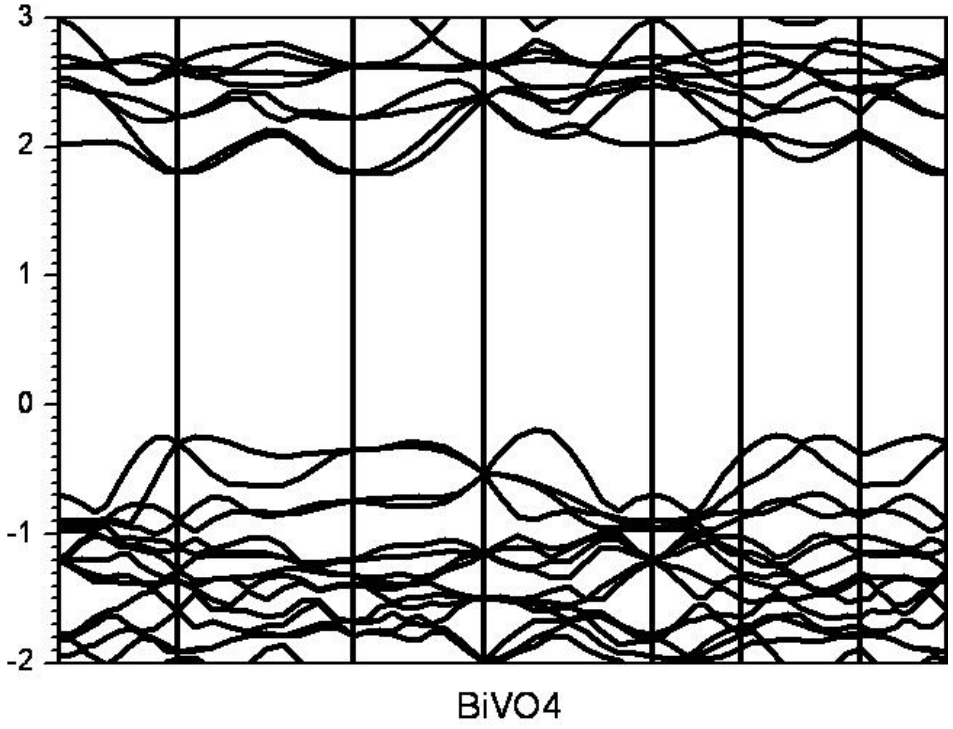
Atomic Structure of $BiVO_4$

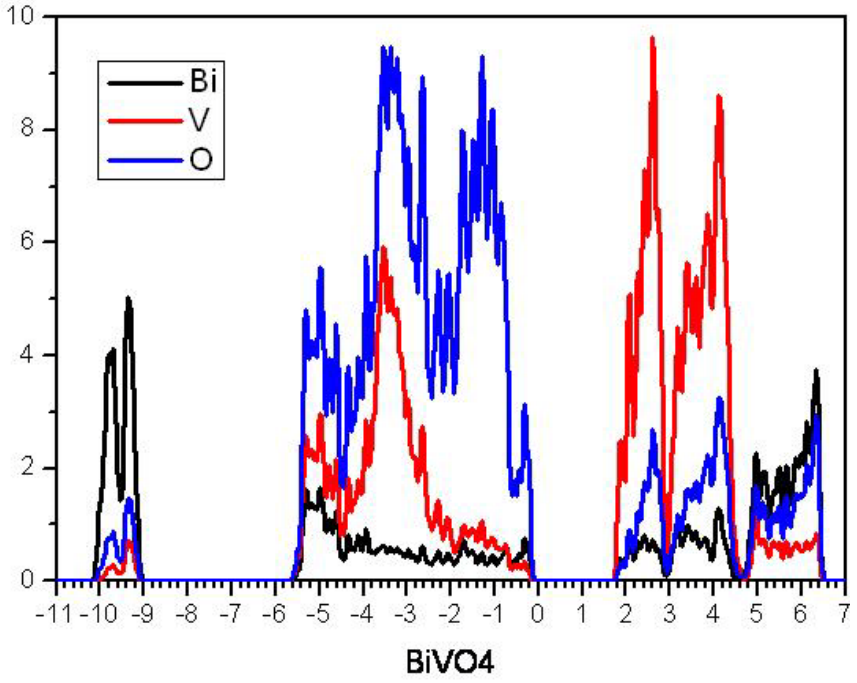
PEC properties of $BiVO_4$

- Excellent optical absorption coefficient
- Good Valence band edge position
- Good carrier mobility

New Technical Accomplishments and Progress (Cont.)

Pure $BiVO_4$



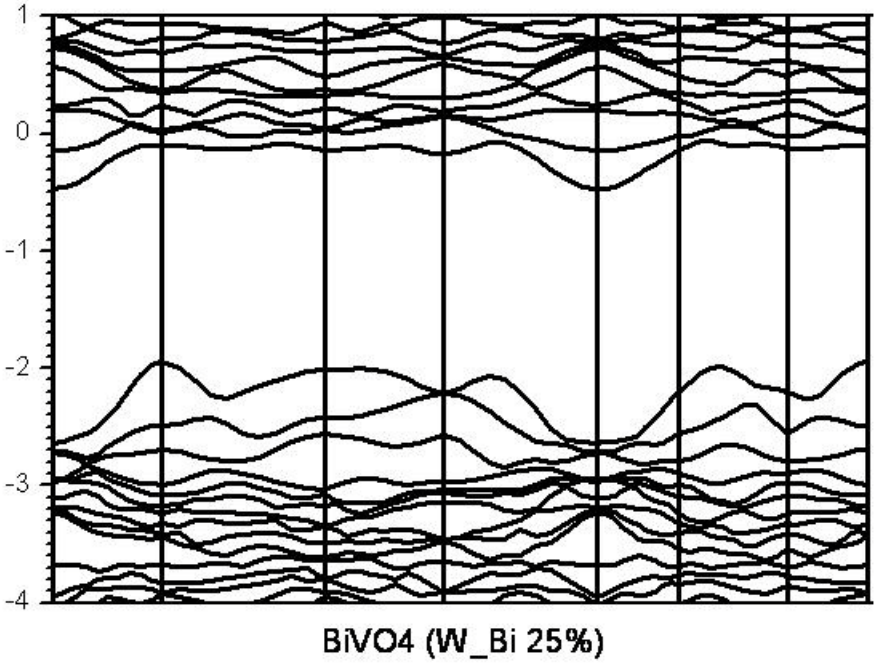


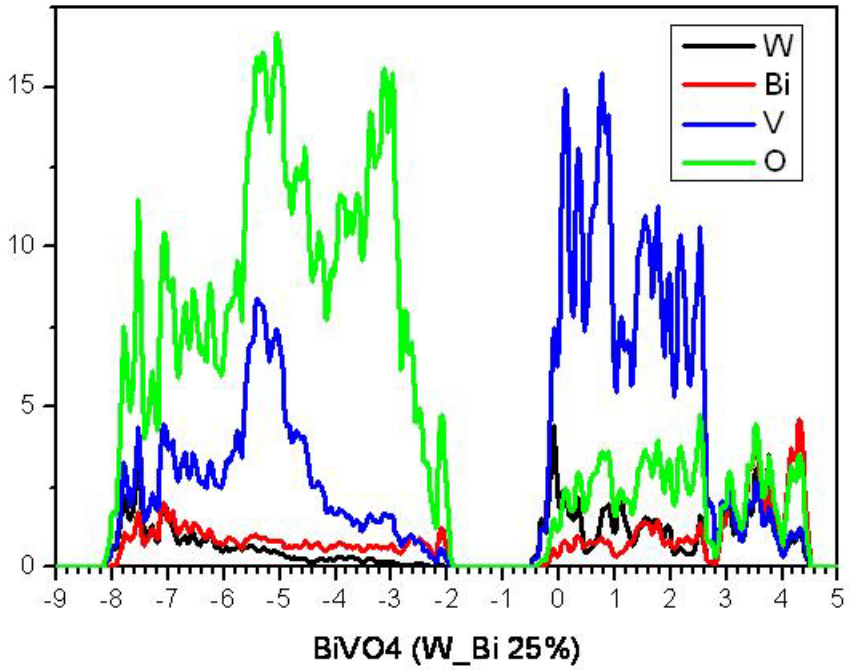
Band Structure and DOS of $BiVO_4$

The good hole mobility is due to the Bi 6s and O 2p antibonding nature

New Technical Accomplishments and Progress (Cont.)

Doping of $BiVO_4$,W on Bi site – shallow donor



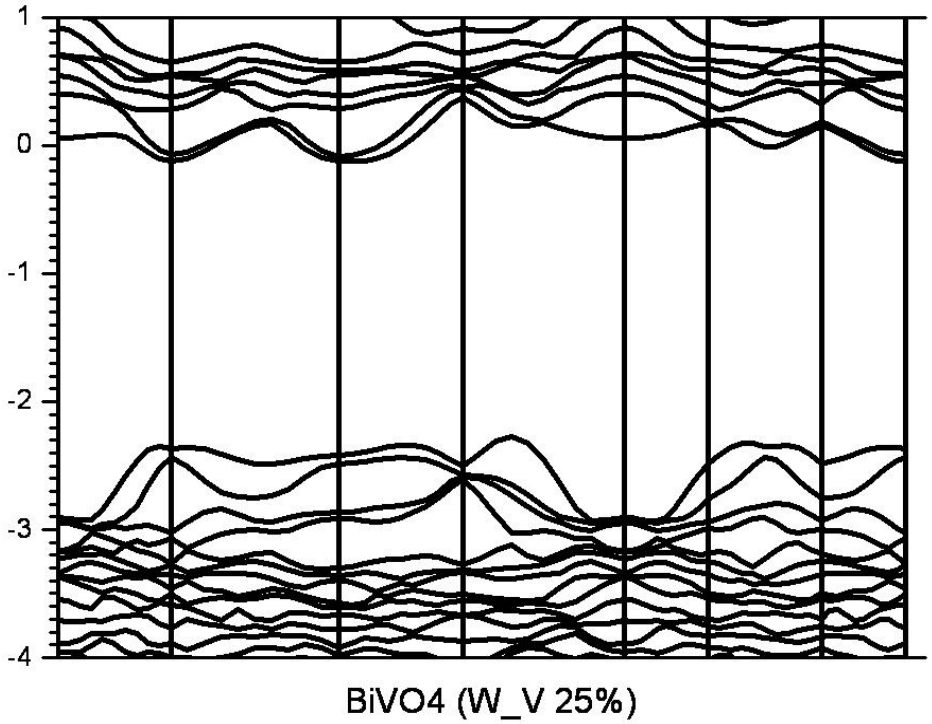


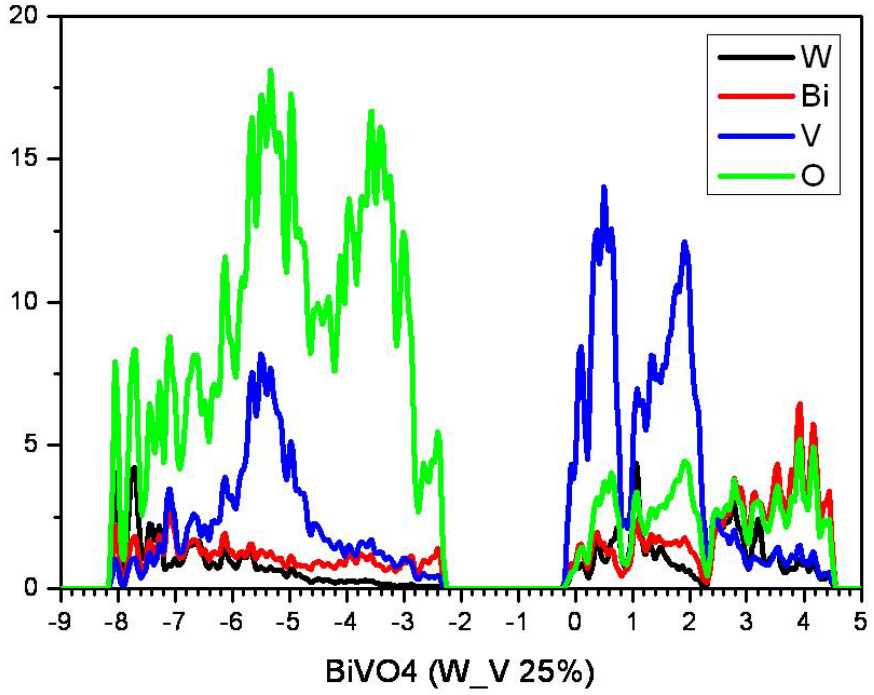
Band Structure and DOS

Realizing required carrier concentration with least dopants – leading to high carrier mobility

New Technical Accomplishments and Progress (Cont.)

Doping of $BiVO_4$,W on V site – shallow donor





Band Structure and DOS

Realizing required carrier concentration with least dopants – leading to high carrier mobility

Collaborations

- University of Hawaii: improving the performance of WO_3 and CGS PEC materials
- University of California: understanding the performance of Fe_2O_3
- University of Nevada: determining electronic structures of oxides
- MV System: understanding amorphous SiC materials.

Active collaborations continued via frequent conference calls and meetings during DOE quarterly working group meetings.

Proposed Future Work

- Continue to support the DOE Fuel Cell Technologies Program.
- Continue to provide understanding and direction to DOE PEC H_2 projects.
- Explore Cu-containing oxides as PEC material candidates that may lead to promising performance.
- Perform detailed study of $BiVO_4$ as a PEC candidate.
- Develop strategies for engineering existing popular oxides.
- Explore electronic and optical properties of non-oxide PEC materials, such as nitrides and carbides.

Project Summary

Relevance: Provide advice to other DOE PEC H_2 projects and assist with understanding of performance.

Approach: Use first-principles, density-functional theory.

Technical Accomplishments and Progress: Gained an understanding of the performance of Cu delafossite oxide materials and provided suggestions. Developed preliminary results on doping of $BiVO_4$.

Collaborations: Active partner of University of Hawaii, University of California, University of Nevada, and MVSystems.

Future Work: Continue to support the DOE H_2 Program by exploring new materials.

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