PEC Materials: Theory and Modeling

Yanfa Yan, Muhammad Huda, Aron Walsh, Su-Huai Wei, Mowafak Al-Jassim, and John Turner

National Renewable Energy Laboratory, Golden, Colorado

May 19, 2009

Project ID # pdp_03_yan

Overview

Timeline

- Start date: 1991 (2007 for this task)
- Project end date: 2018
- Percent complete: NA

Barriers

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

Budget

- Total project funding
  - DOE share: $7.8M
- Funding received in FY08

  $2000K
- Funding for FY09: -0-
- Note: Task with pdp_02_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 programs

Approach

1. Work closely with other DOE H_2 projects

2. Follow the PEC R&D feedback loop

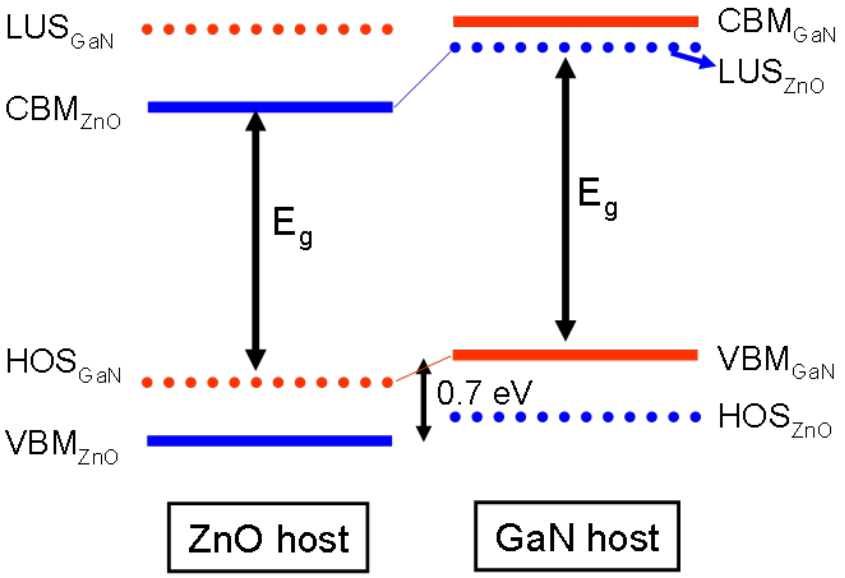
R&D feedback loop

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

4. Planned milestone: understand some key PEC materials

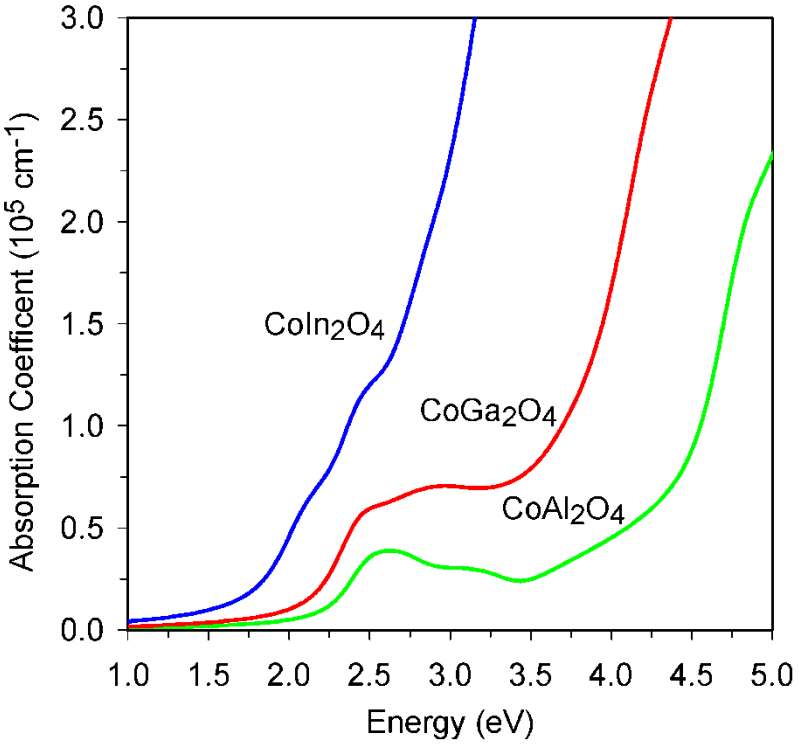
Previous Technical Accomplishments and Progress

1. Bandgap reduction of ZnO – Ga, N passive co-incorporation



The asymmetric reduction was explained by confinement effects

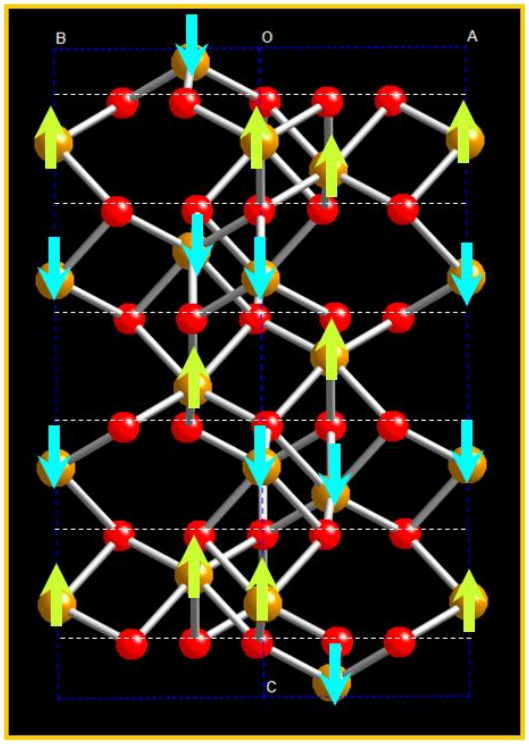
2. Absorption of Co-Fe-Al oxides



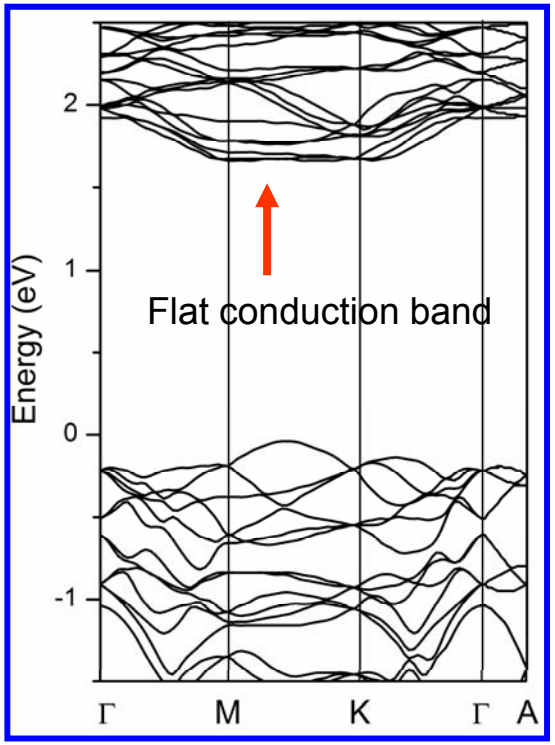
The bad performance was understood

New Technical Accomplishments and Progress

Identifying the problems for α-Fe_2O_3 (Hematite)



Atomic structure



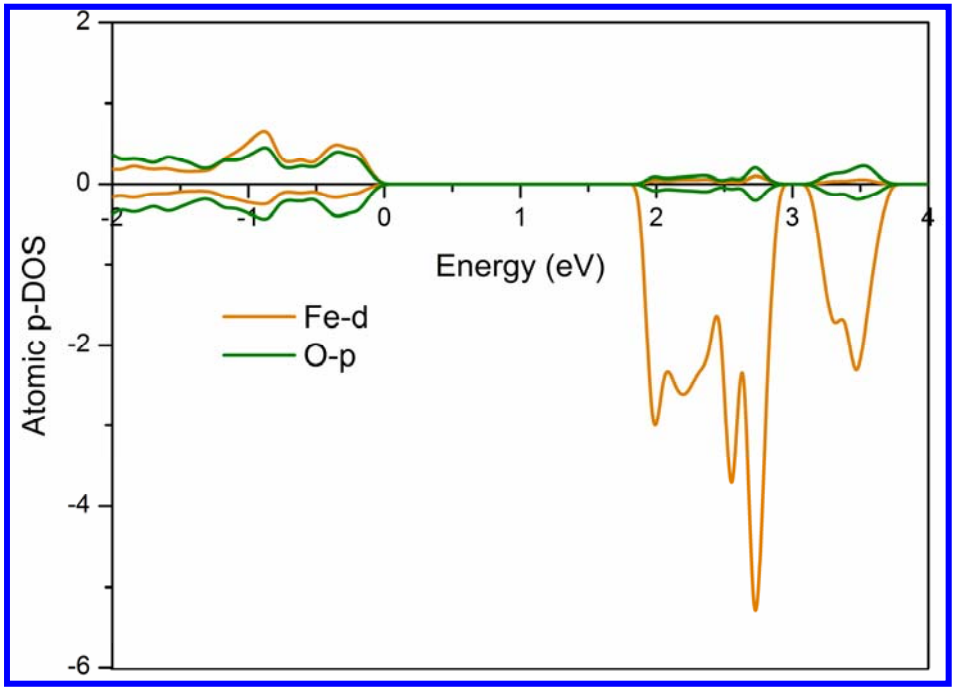
Calculated band structure

Problem I:

Huge electron effective mass –
short carrier life time

New Technical Accomplishments and Progress (Cont.)

Identifying the problems of α-Fe_2O_3 (Hematite) (Cont.)



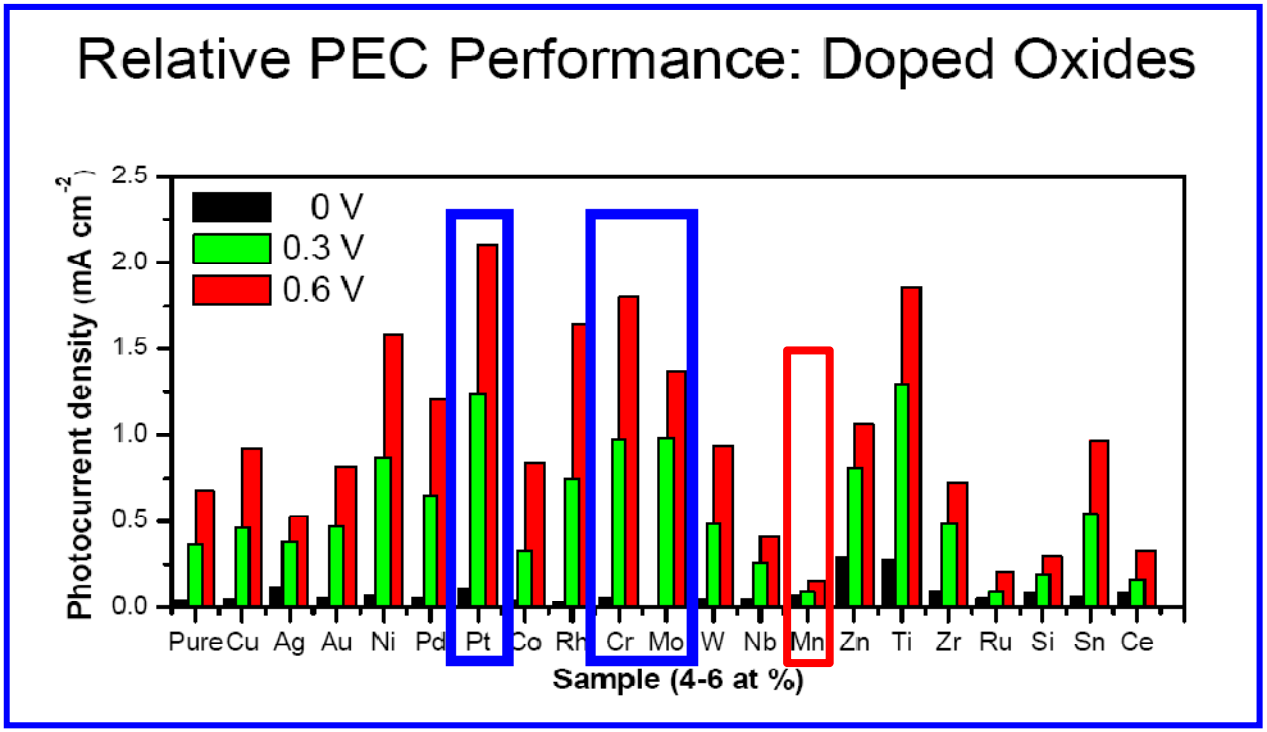
Calculated density of states

Problem II:

Low absorption coefficient for visible light due to Fe *d-d* transition

New Technical Accomplishments and Progress (Cont.)

Performance improvement for α-Fe_2O_3 observed by UC –Santa Barbara



High PEC performance: dopant, microstructure, etc…

- ➔ Impurities (dopants) matter!
- ➔ Synthesis matters!

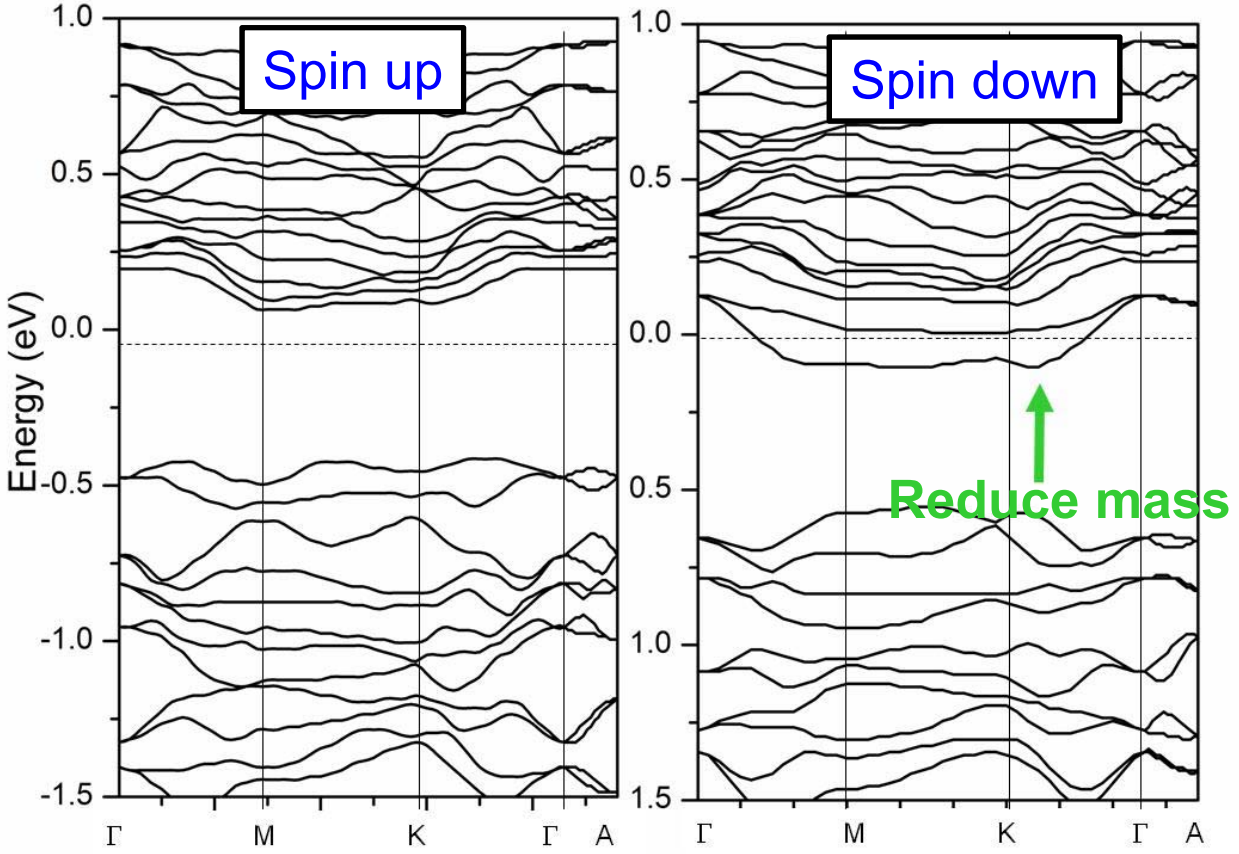
Pt, Ti, Cr

Mn

Why & How?

New Technical Accomplishments and Progress (Cont.)

Performance improvement for α-Fe_2O_3 observed by UC –Santa Barbara



Calculated band structure of Pt doped α-Fe_2O_3

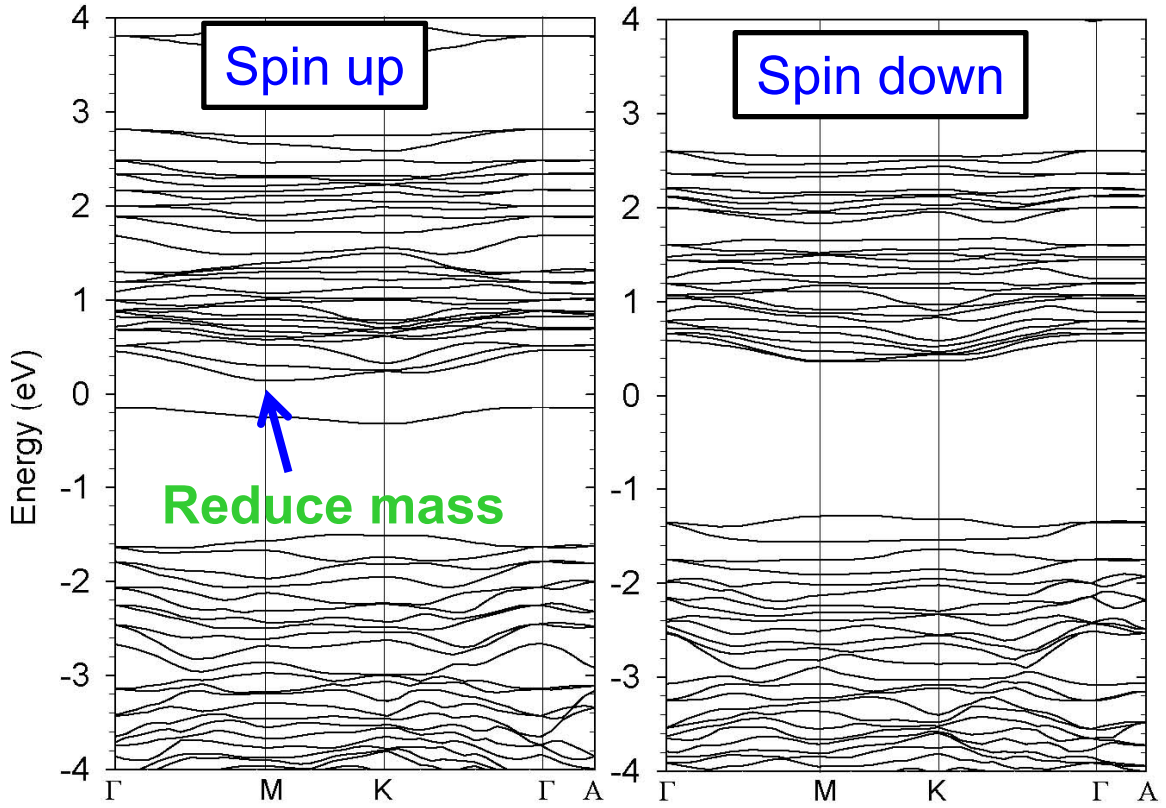
1. Improved conductivity
2. Reduced recombination

⇩

Better performance

New Technical Accomplishments and Progress (Cont.)

Performance improvement for α-Fe_2O_3 observed by UC –Santa Barbara



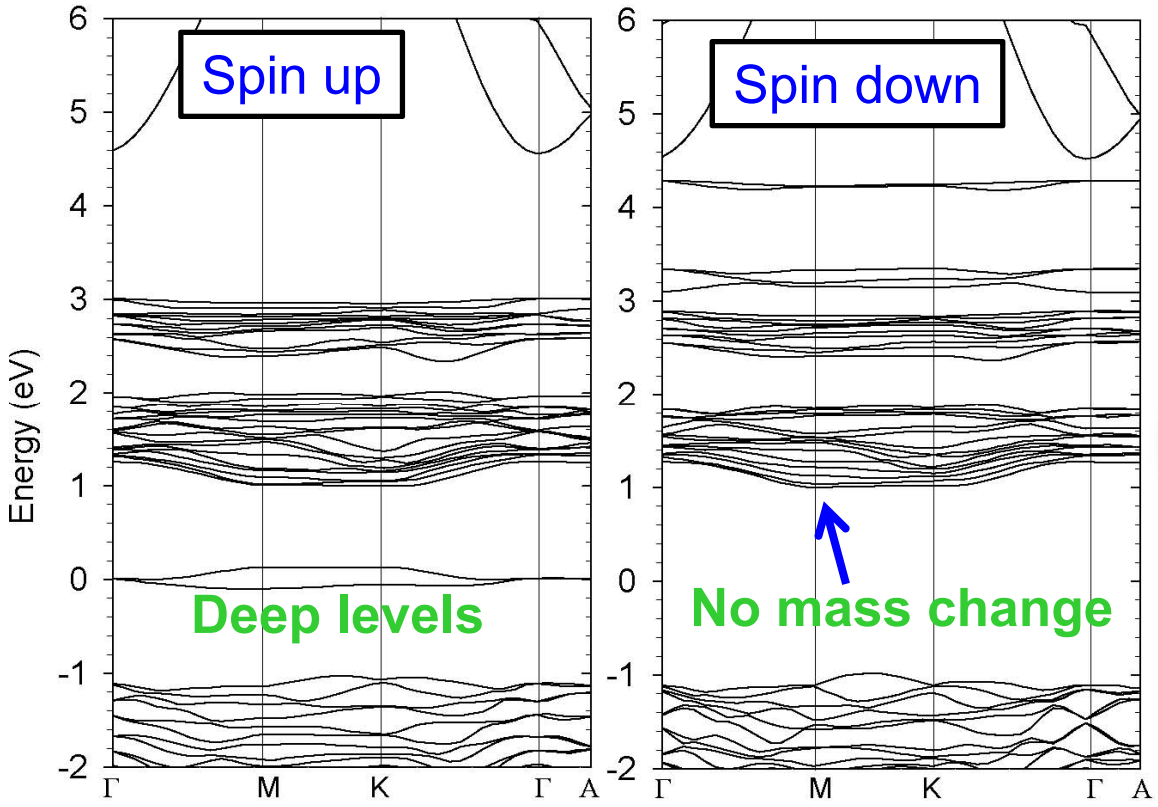
1. Improved conductivity
2. Reduced recombination

Better performance

Calculated band structure of Ti doped α-Fe_2O_3

New Technical Accomplishments and Progress (Cont.)

Performance improvement for α-Fe_2O_3 observed by UC –Santa Barbara



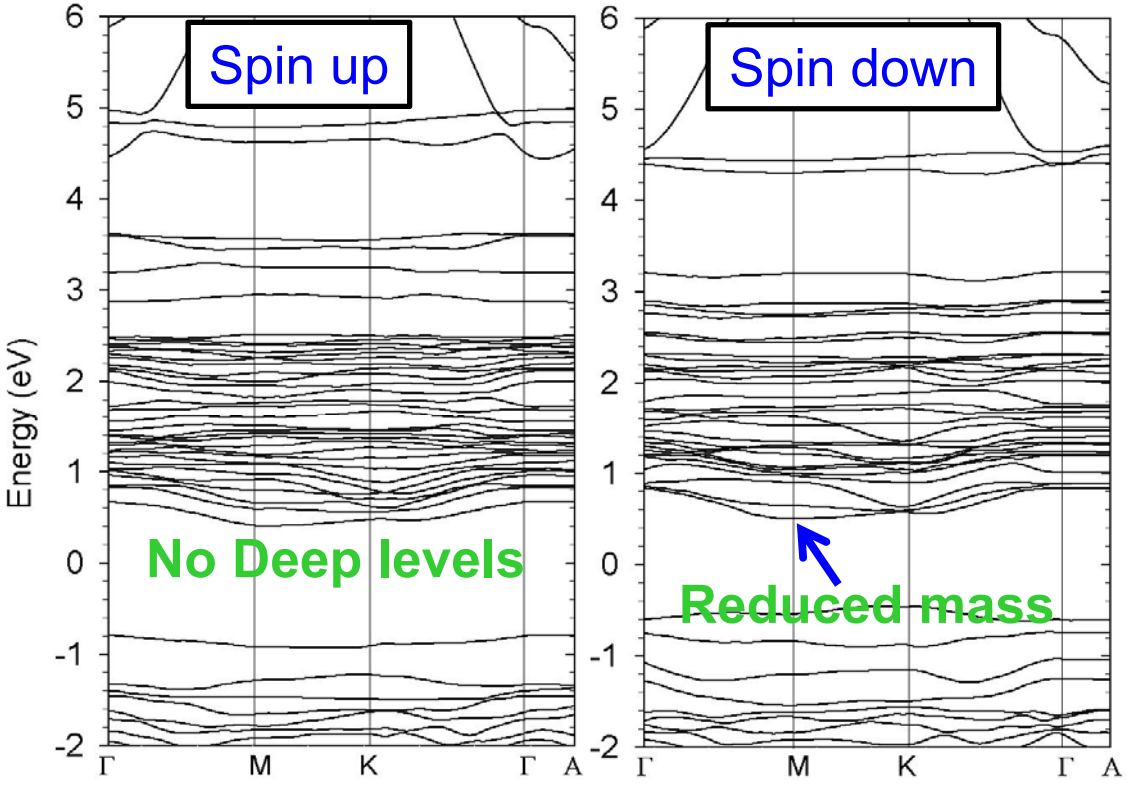
1. No Improved conductivity
2. Increased recombination

Worse performance

Calculated band structure of Mn doped α-Fe_2O_3

New Technical Accomplishments and Progress (Cont.)

Suggestion for further improvement of α-Fe_2O_3 – passive (Ti, N) co-doping



Enhanced conductivity

Less charged defects

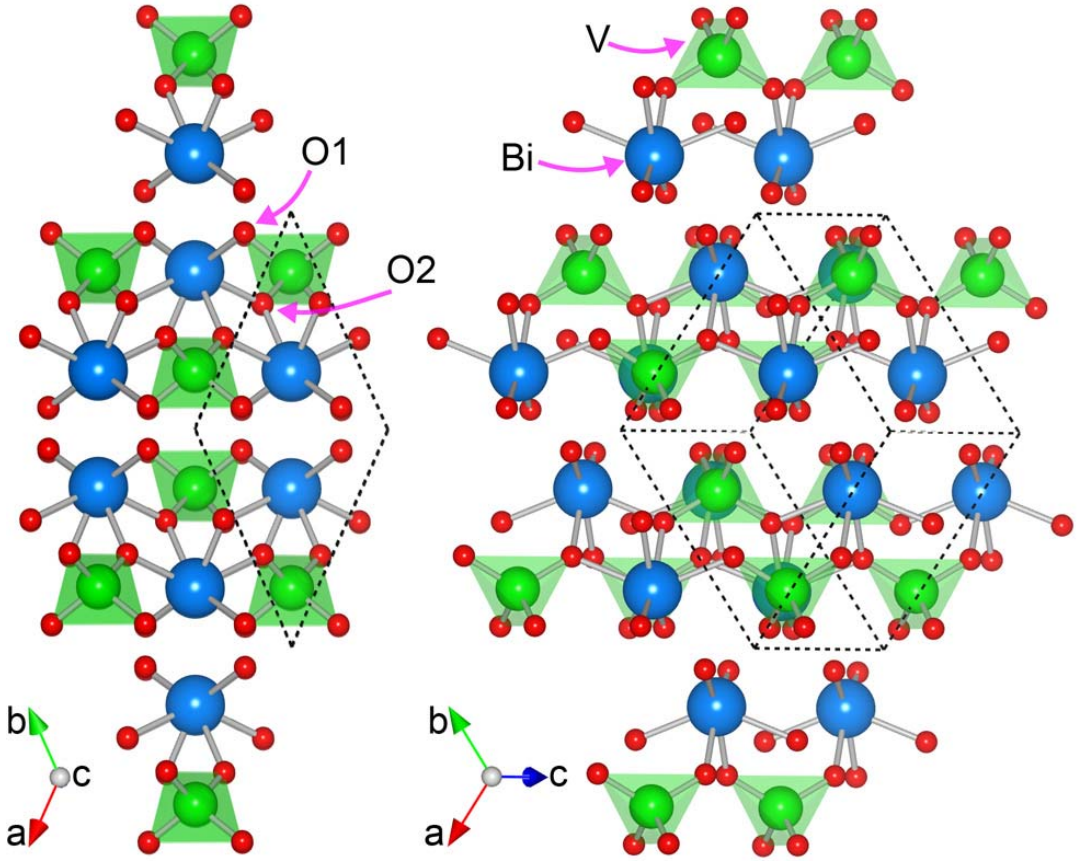
better band gap

More improved performance

Calculated band structure of (Ti, N) co-doped α-Fe_2O_3

New Technical Accomplishments and Progress (Cont.)

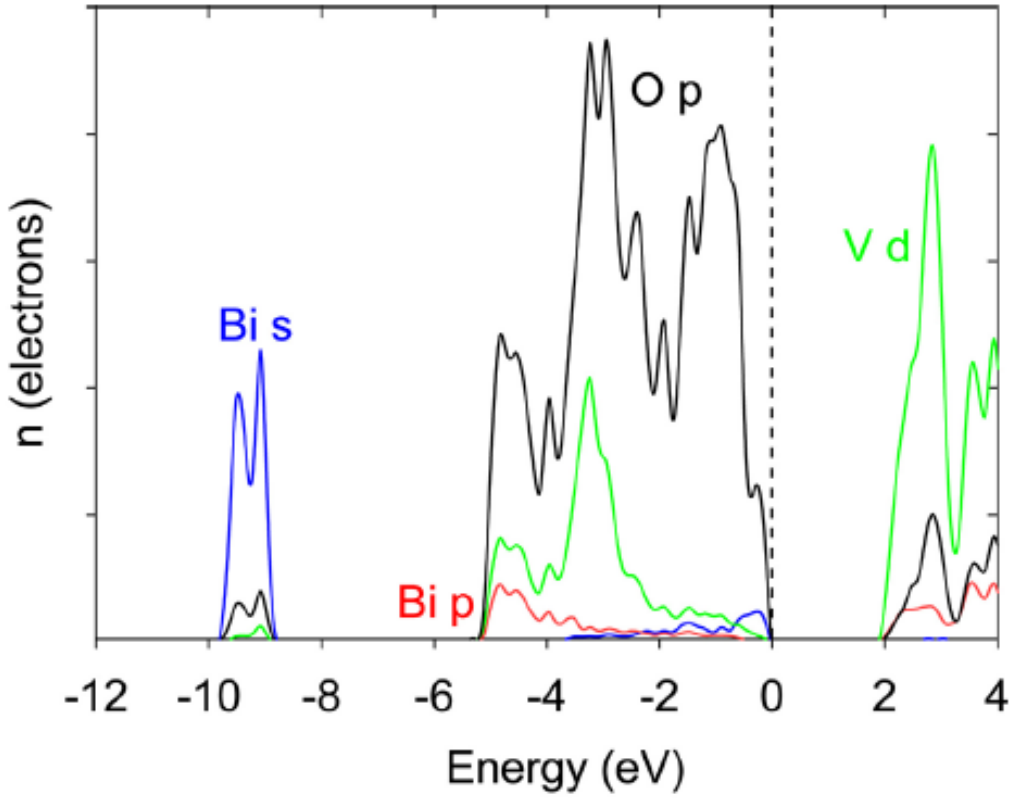
Understanding the performance of $BiVO_4$
an attractive promising oxide



Atomic structure of $BiVO_4$

New Technical Accomplishments and Progress (Cont.)

Understanding the performance of $BiVO_4$
an attractive promising oxide

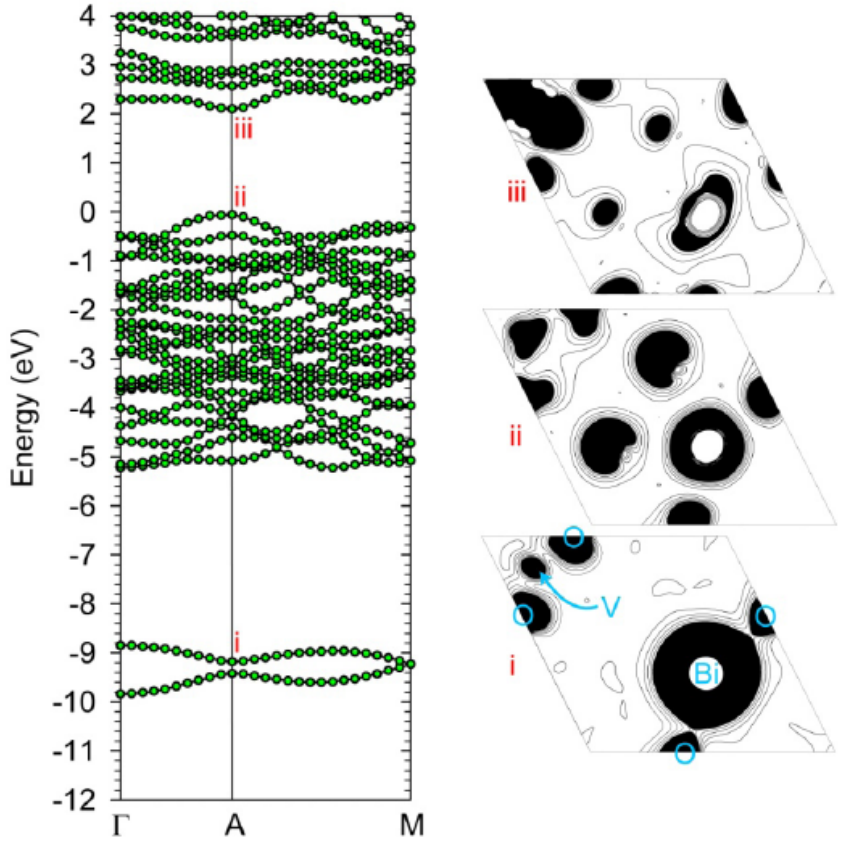


Non pair Bi S
upshift O p band
leading to
optimal band gap

Calculated density of states of $BiVO_4$

New Technical Accomplishments and Progress (Cont.)

Understanding the performance of $BiVO_4$
an attractive promising oxide

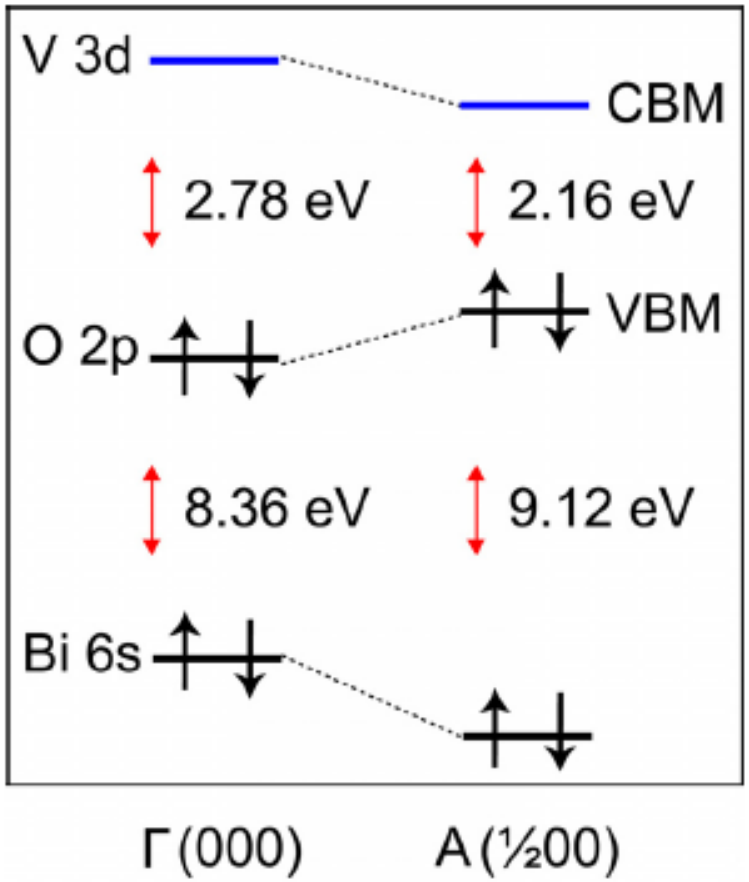


Direct band gap indicating possible good optical absorption

Calculated band structure of $BiVO_4$

New Technical Accomplishments and Progress (Cont.)

Understanding the performance of $BiVO_4$
an attractive promising oxide

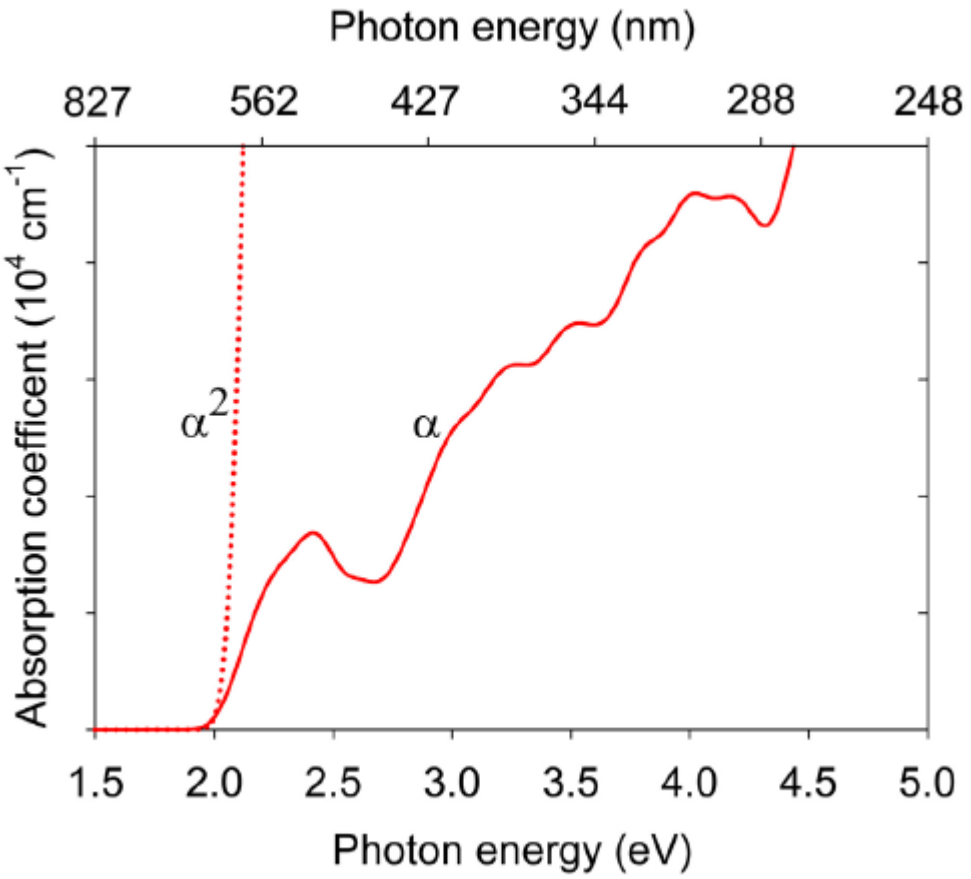


Orbital level interactions

Understanding why a direct band gap is obtained

New Technical Accomplishments and Progress (Cont.)

Understanding the performance of $BiVO_4$
an attractive promising oxide

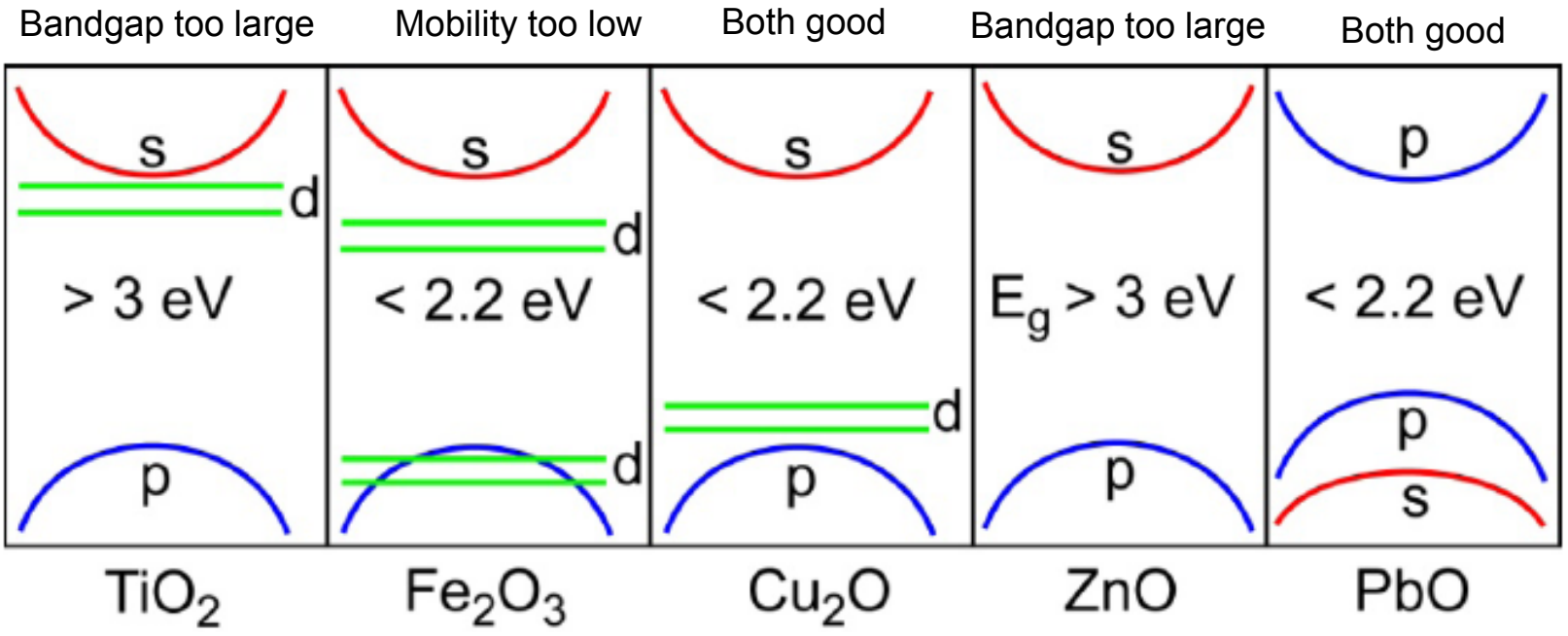


Indeed good optical absorption α^2

Calculated optical absorption spectrum

New Technical Accomplishments and Progress (Cont.)

Identifying groups of oxides for PEC application



Analysis suggests Cu-,Pb-, Bi-,or Sn- containing oxides as promising PEC candidates

Collaborations

Partner

- University of Hawaii (university, DOE H_2 Program): collaborations on improving the performance of WO_3 and CGS PEC materials
- University of California (university, DOE H_2 Program): collaborations on understanding the performance of Fe_2O_3
- University of Nevada (university, DOE H_2 Program): collaborations on electronic structures of oxides
- MV System (industry, DOE H_2 Program): collaborations on understanding amorphous SiC materials

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

Proposed Future Work

- Continue to provide understanding and advise to other DOE PEC H2 projects.
- Explore Cu-containing oxides as PEC material candidates which may lead to promising performance
- Detailed study of Cu delafossites as PEC candidates.
- Propose more methods to improve the performance of F_2O_3 and Co-Al-oxides.
- Explore electronic and optical properties of non-oxide PEC materials, such as nitrides, carbides, …

Project Summary

Relevance: Help DOE PECH2 projects to understand the performance and provide advises

Approach: Use first-principles density functional theory

Technical Accomplishments and Progress: Understood the performance of Fe2O3 and provided suggestion. Explored the electronic and optical properties of $BiVO_4$

Collaborations: Active partner of University of Hawaii, University of California, University of Nevada, MVsystem

Future work: Continue to support DOE H2 program by explore new materials

Yanfa Yan
303-384-6456
yanfa.yan@nrel.gov