

PEC Materials: Theory and Modeling

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Project ID #
pdp_03_yan

Overview

Timeline

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

Budget

- Total project funding
 - DOE share: \$7.8M
- Funding received in FY08
\$2000K
- Funding for FY09: -0-
- Note: Task with pdp_02_turner

Barriers

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

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 H₂ programs

Approach

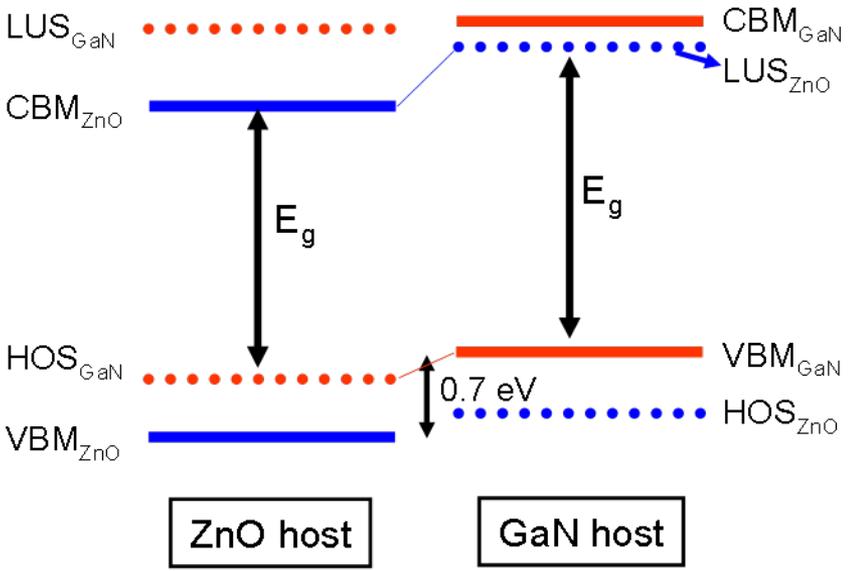
1. Work closely with other DOE H₂ projects
2. Follow the PEC R&D feedback loop
3. Use state-of-the-art first principle density-functional theory calculation which can calculate important properties:
 - Band structure.
 - Optical absorption.
 - Defect and doping effects.
 - Surface chemistry.
 - Structural stability.
4. Planned milestone: understand some key PEC materials



R&D feedback loop

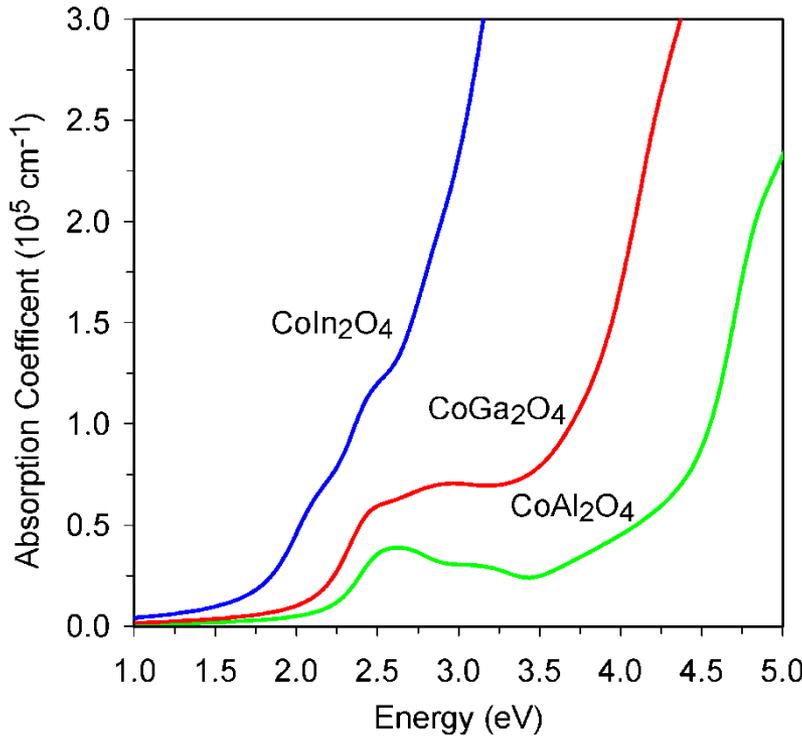
Previous Technical Accomplishments and Progress

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



The asymmetric reduction was explained by confinement effects

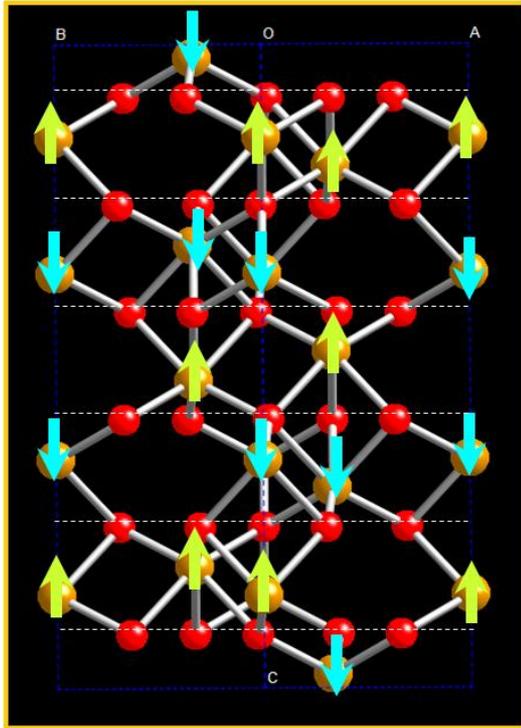
2. Absorption of Co-Fe-Al oxides



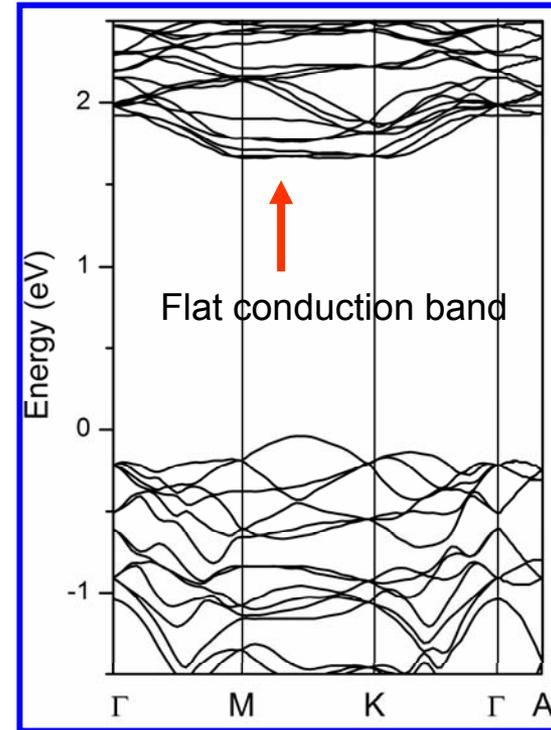
The bad performance was understood

New Technical Accomplishments and Progress

Identifying the problems for $\alpha\text{-Fe}_2\text{O}_3$ (Hematite)



Atomic structure



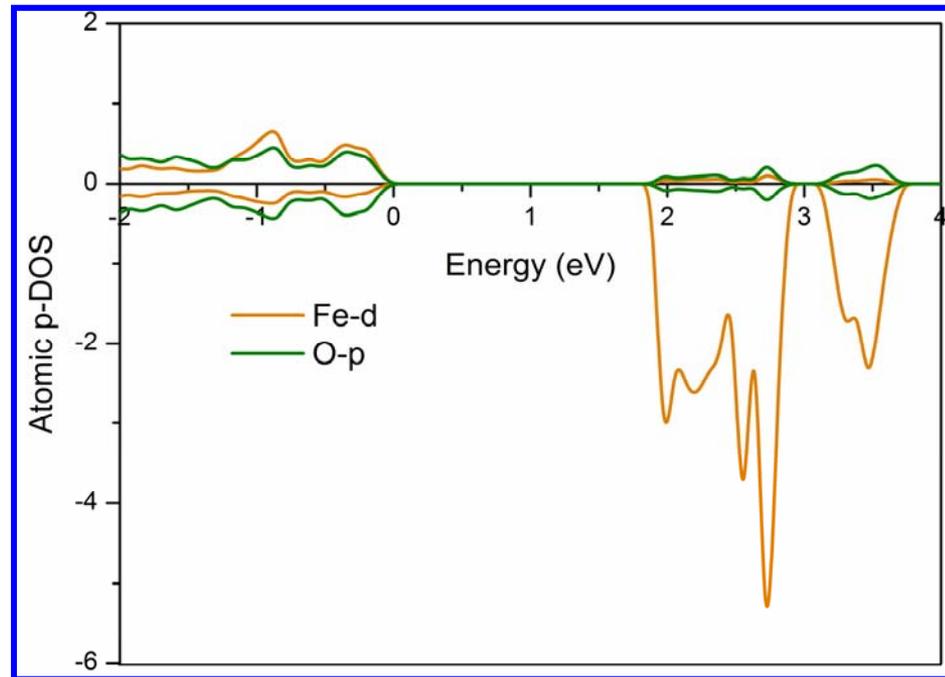
Calculated band structure

Problem I:

Huge electron effective mass –
short carrier life time

New Technical Accomplishments and Progress (Cont.)

Identifying the problems of $\alpha\text{-Fe}_2\text{O}_3$ (Hematite) (Cont.)



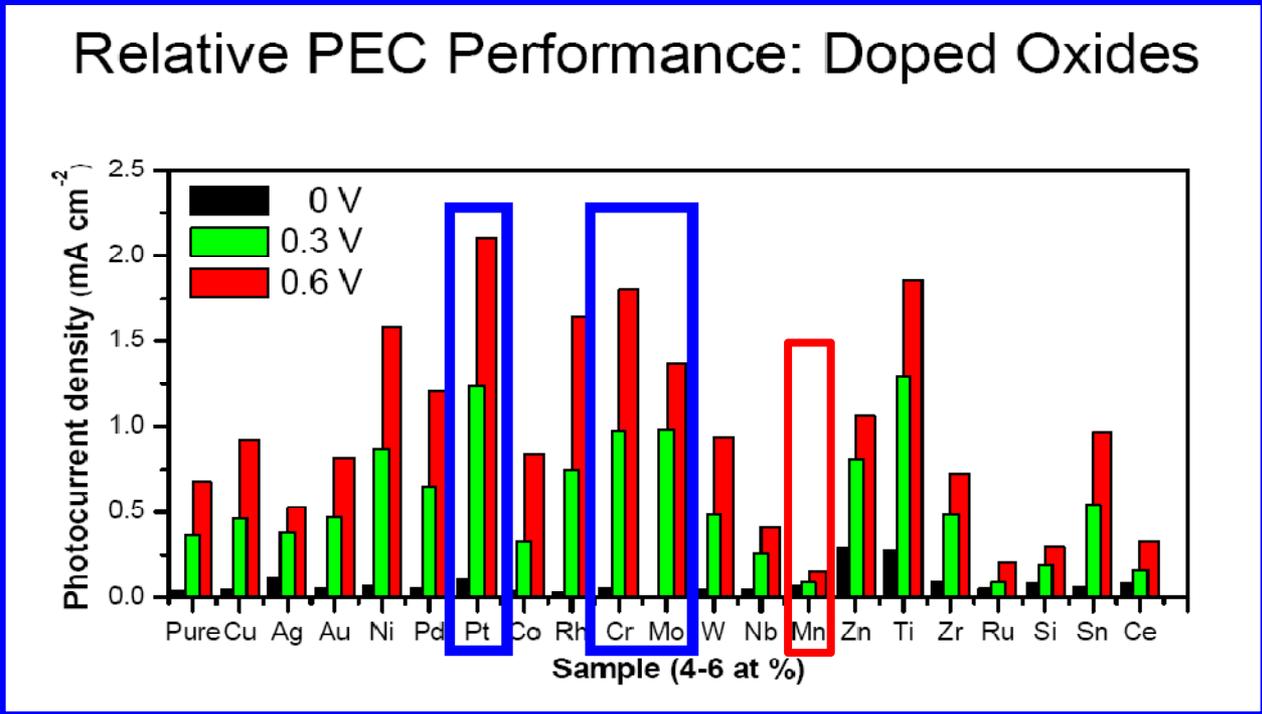
Calculated density of states

Problem II:

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

New Technical Accomplishments and Progress (Cont.)

Performance improvement for $\alpha\text{-Fe}_2\text{O}_3$ observed by UC –Santa Barbara



High PEC performance: dopant, microstructure, etc...
→ Impurities (dopants) matter!
→ Synthesis matters!



Pt, Ti, Cr

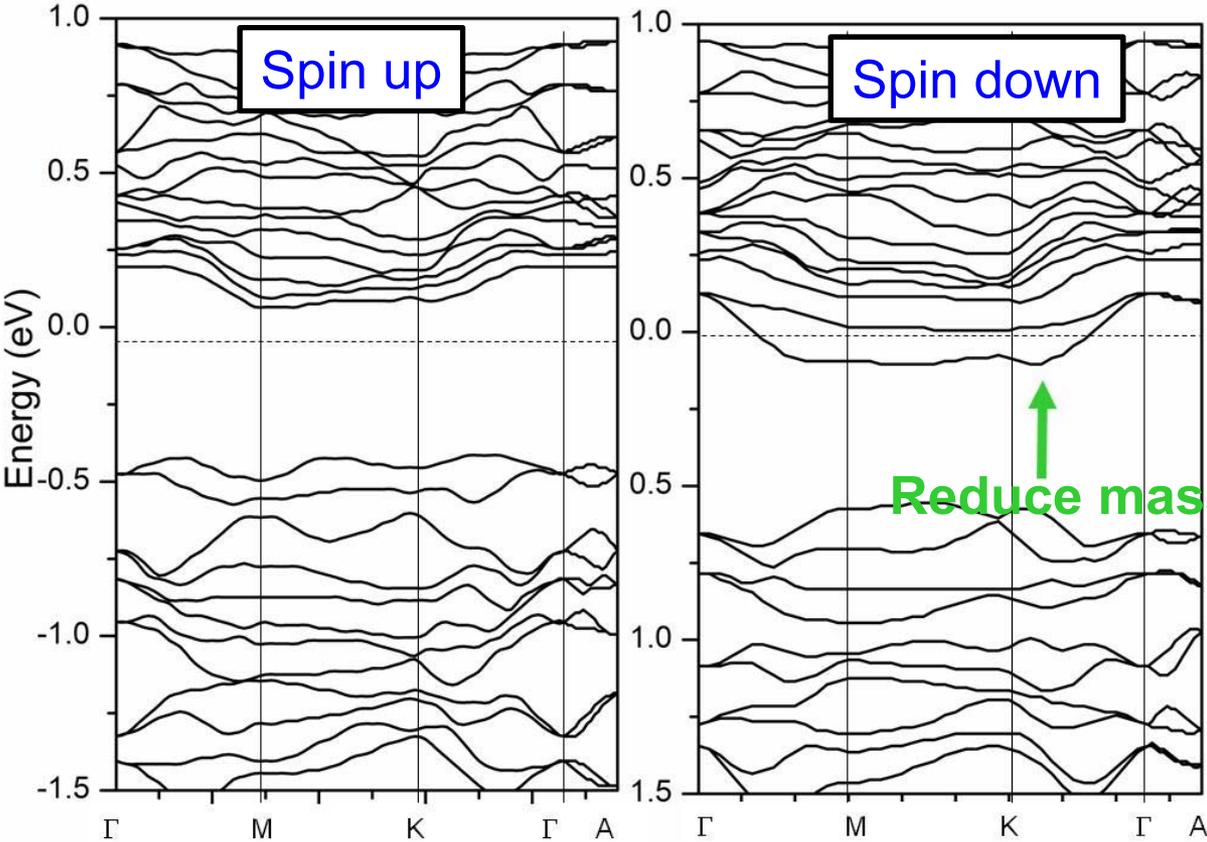


Mn

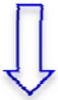
Why & How?

New Technical Accomplishments and Progress (Cont.)

Performance improvement for $\alpha\text{-Fe}_2\text{O}_3$ observed by UC –Santa Barbara



- 1. Improved conductivity
- 2. Reduced recombination

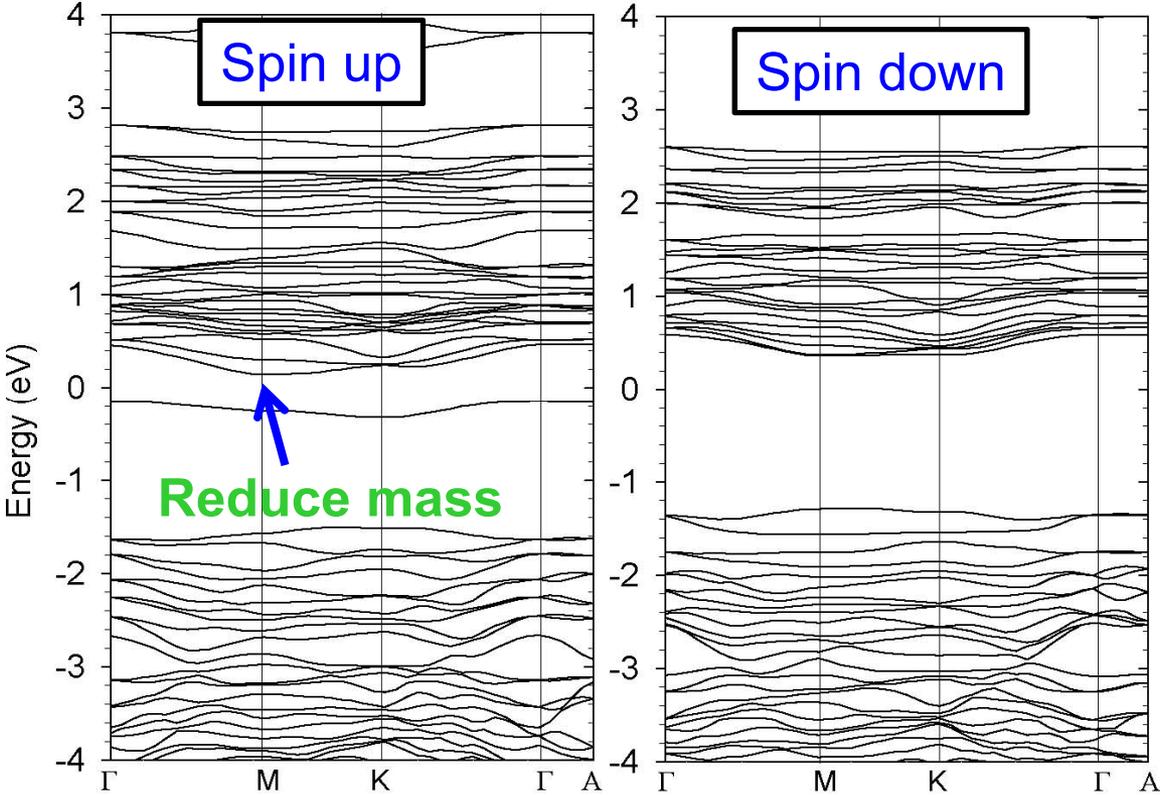


Better performance

Calculated band structure of Pt doped $\alpha\text{-Fe}_2\text{O}_3$

New Technical Accomplishments and Progress (Cont.)

Performance improvement for $\alpha\text{-Fe}_2\text{O}_3$ observed by UC –Santa Barbara

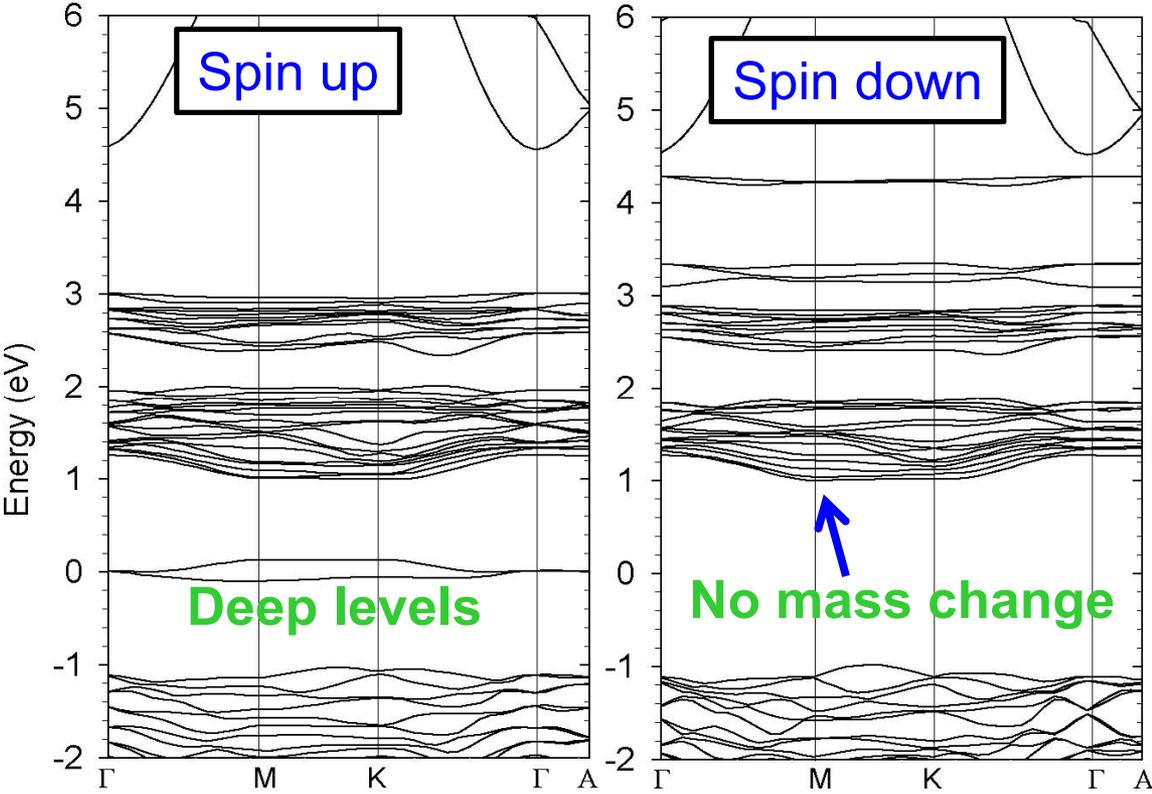


- ⇒
- 1. Improved conductivity
 - 2. Reduced recombination
- ↓
- 👍 Better performance

Calculated band structure of Ti doped $\alpha\text{-Fe}_2\text{O}_3$

New Technical Accomplishments and Progress (Cont.)

Performance improvement for $\alpha\text{-Fe}_2\text{O}_3$ observed by UC –Santa Barbara



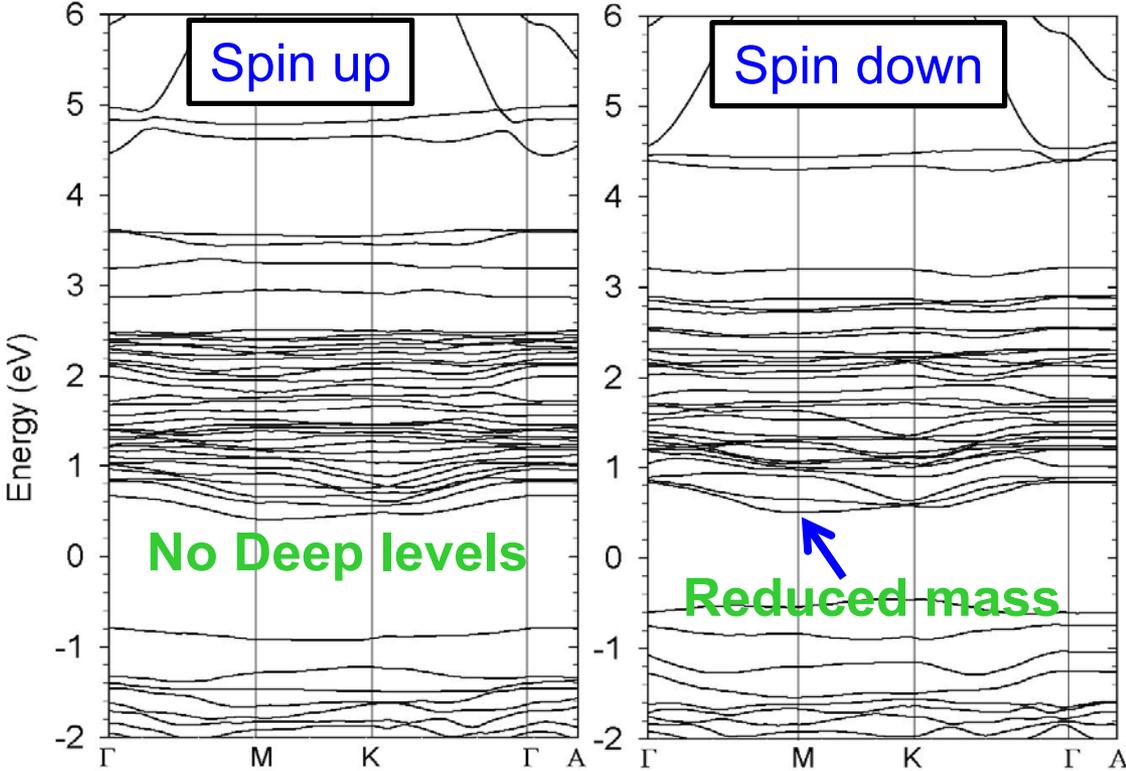
- 1. No Improved conductivity
- 2. Increased recombination

↓
👎 Worse performance

Calculated band structure of Mn doped $\alpha\text{-Fe}_2\text{O}_3$

New Technical Accomplishments and Progress (Cont.)

Suggestion for further improvement of $\alpha\text{-Fe}_2\text{O}_3$ – passive (Ti, N) co-doping

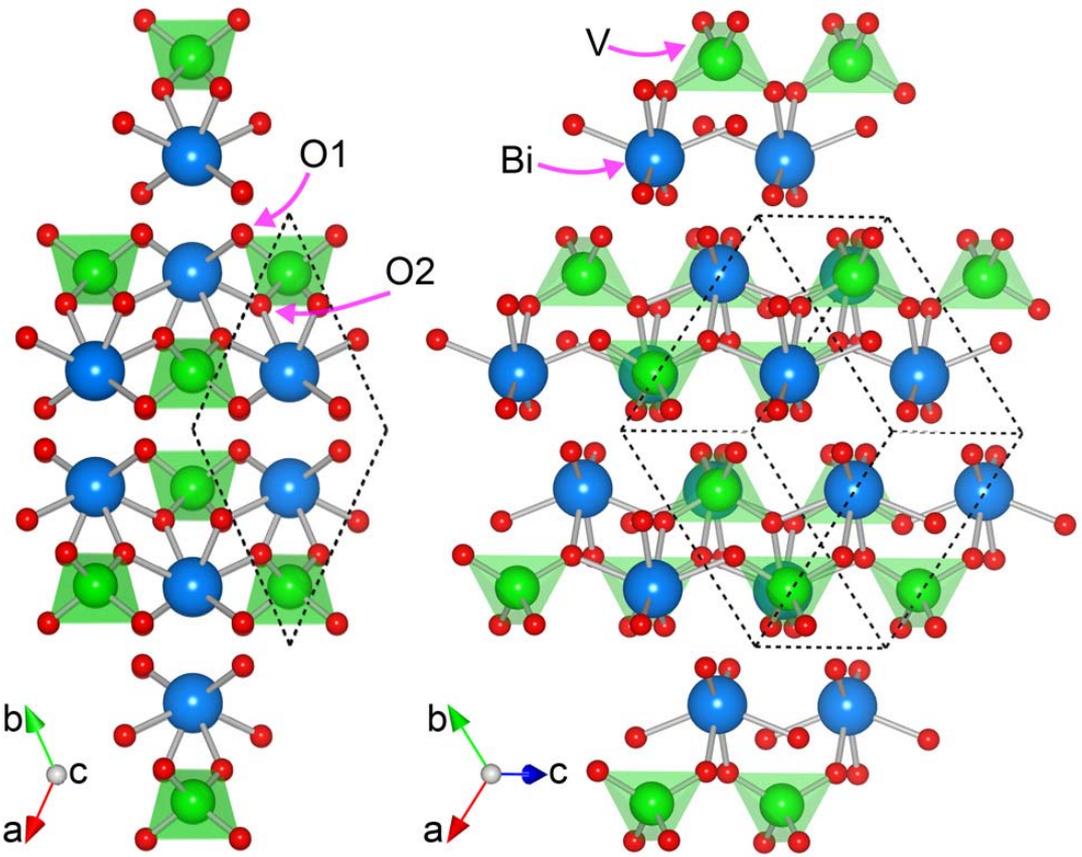


Enhanced conductivity
Less charged defects
better band gap
More improved performance

Calculated band structure of (Ti, N) co-doped $\alpha\text{-Fe}_2\text{O}_3$

New Technical Accomplishments and Progress (Cont.)

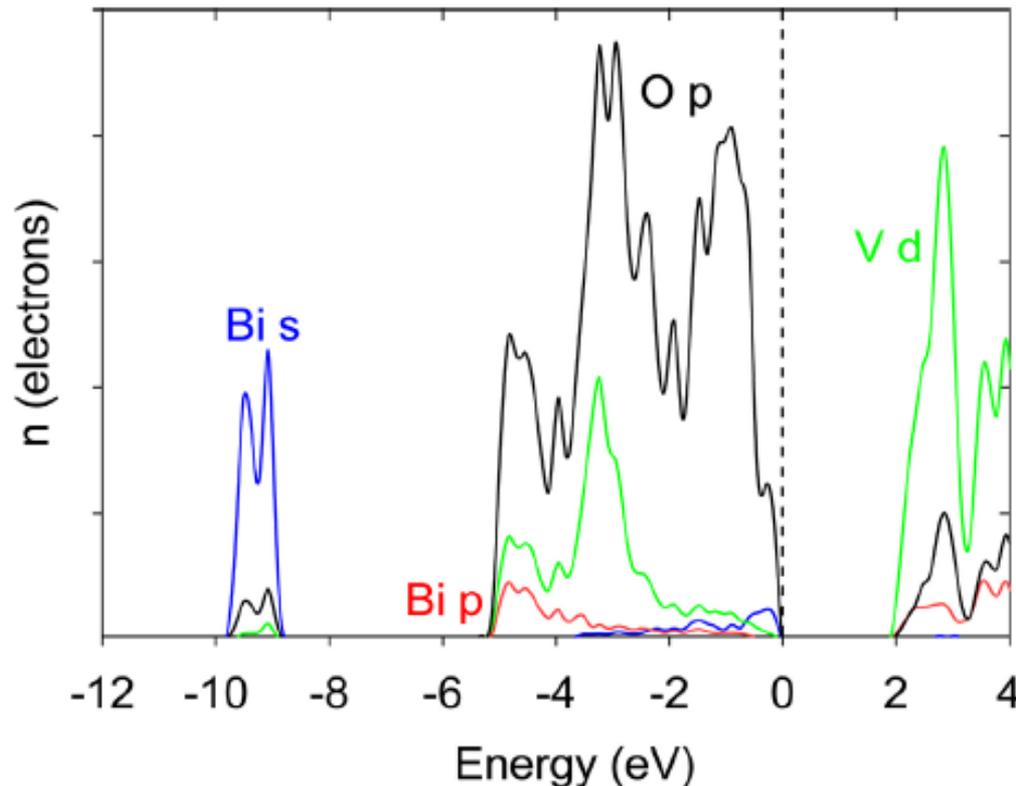
Understanding the performance of BiVO_4
an attractive promising oxide



Atomic structure of BiVO_4

New Technical Accomplishments and Progress (Cont.)

Understanding the performance of BiVO_4
an attractive promising oxide



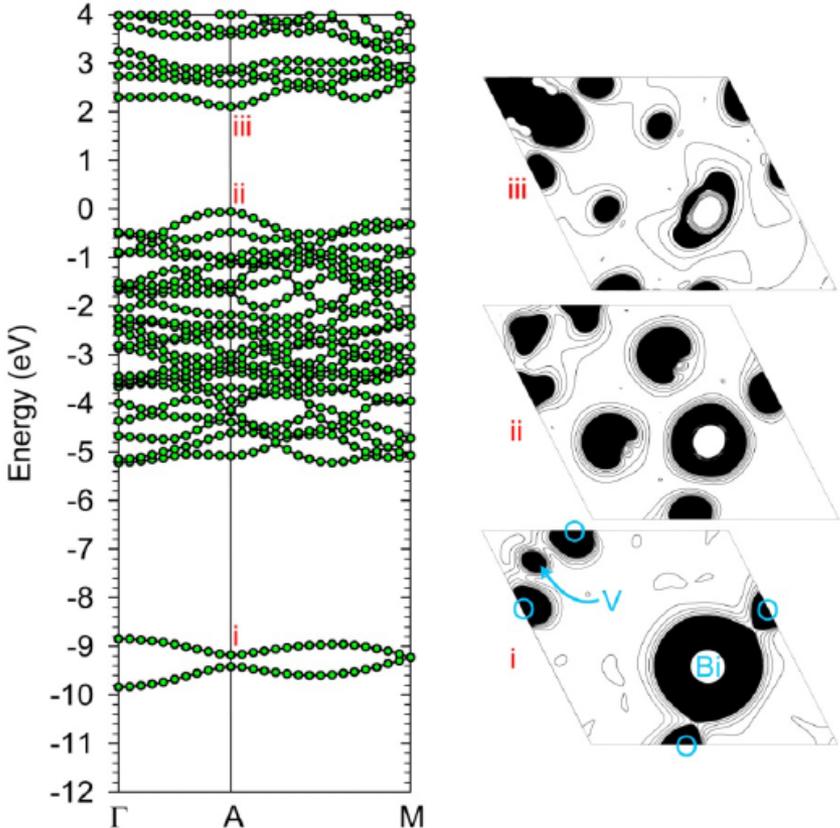
Non pair Bi S
upshift O p band
leading to
optimal band gap



Calculated density of states of BiVO_4

New Technical Accomplishments and Progress (Cont.)

Understanding the performance of BiVO_4
an attractive promising oxide



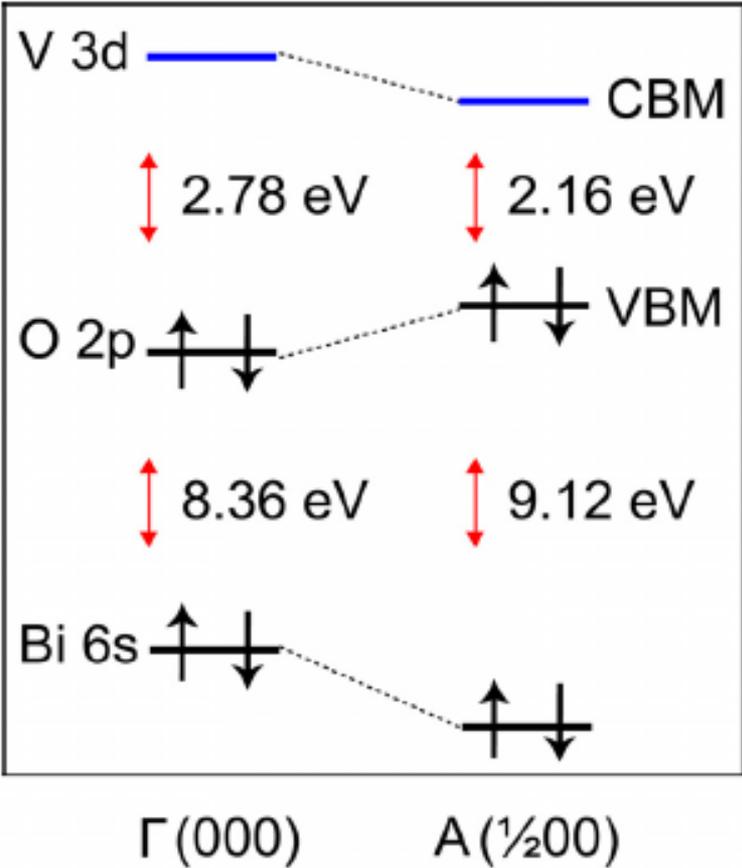
Direct band gap
indicating possible
good optical
absorption



Calculated band structure of BiVO_4

New Technical Accomplishments and Progress (Cont.)

Understanding the performance of BiVO_4
an attractive promising oxide



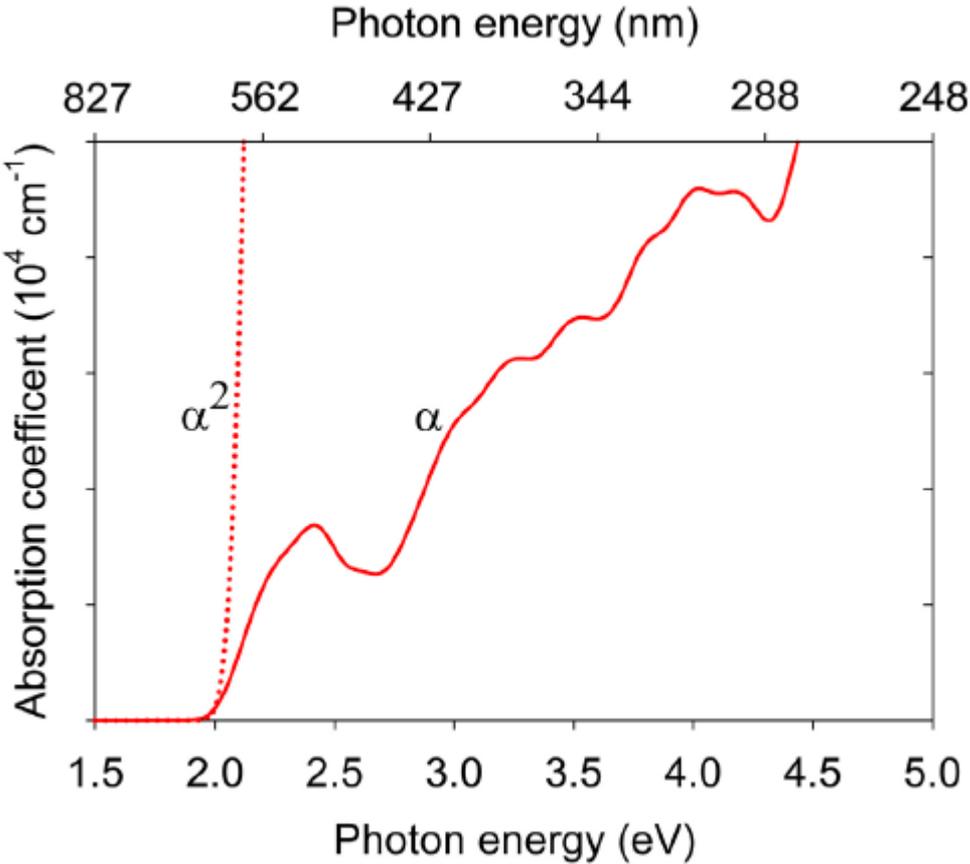
Understanding why a direct band gap is obtained



Orbital level interactions

New Technical Accomplishments and Progress (Cont.)

Understanding the performance of BiVO_4
an attractive promising oxide



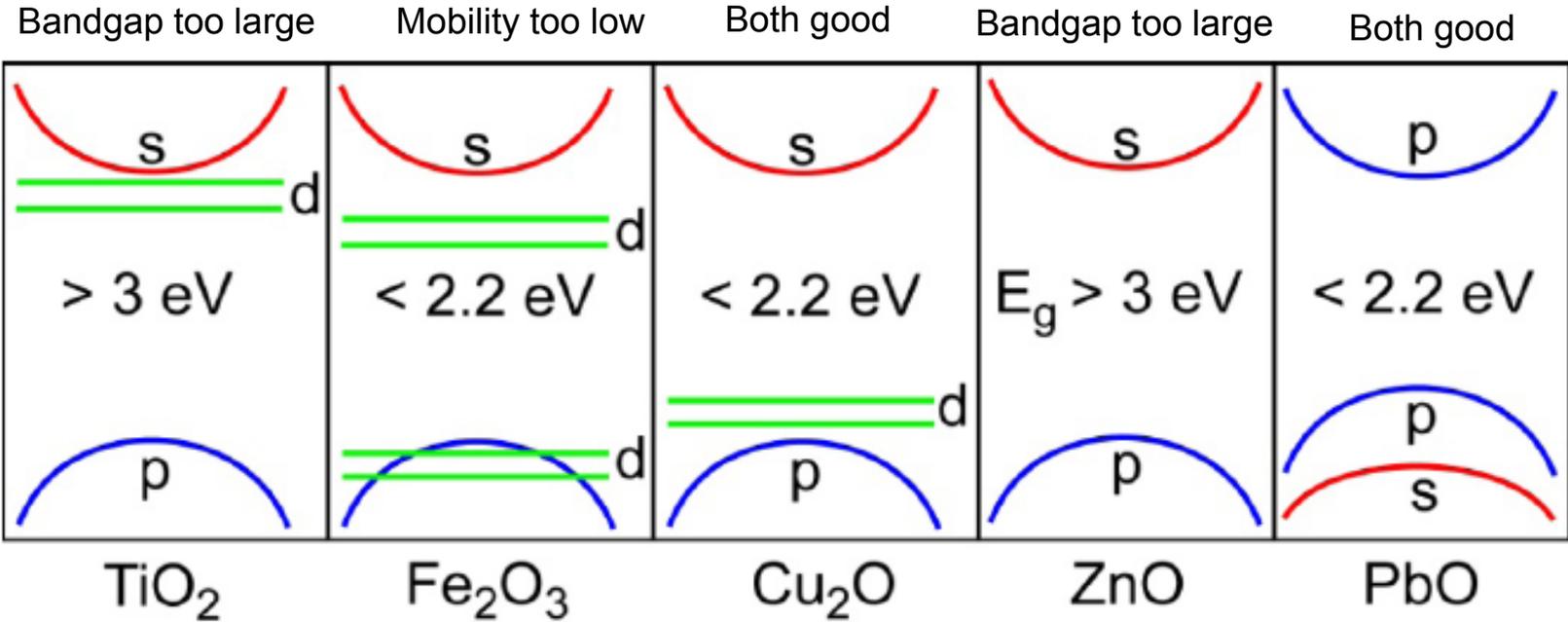
Indeed good optical absorption α^2



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 H₂ Program): collaborations on improving the performance of WO₃ and CGS PEC materials
- University of California (university, DOE H₂ Program): collaborations on understanding the performance of Fe₂O₃
- University of Nevada (university, DOE H₂ Program): collaborations on electronic structures of oxides
- MV System (industry, DOE H₂ 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 BiVO₄

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

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