National Renewable Energy Laboratory
*Innovation for Our Energy Future*

# PEC Materials: Theory and Modeling

DOE AMR

Yanfa Yan

May 10, 2011

Project ID #
PD052

# PEC Materials: Theory and Modeling

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Golden, Colorado

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# Overview

## Timeline

- Start date: 2007 for this task
- Project end date: Oct. 2011*
- Percent complete: 75%*

## Barriers

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

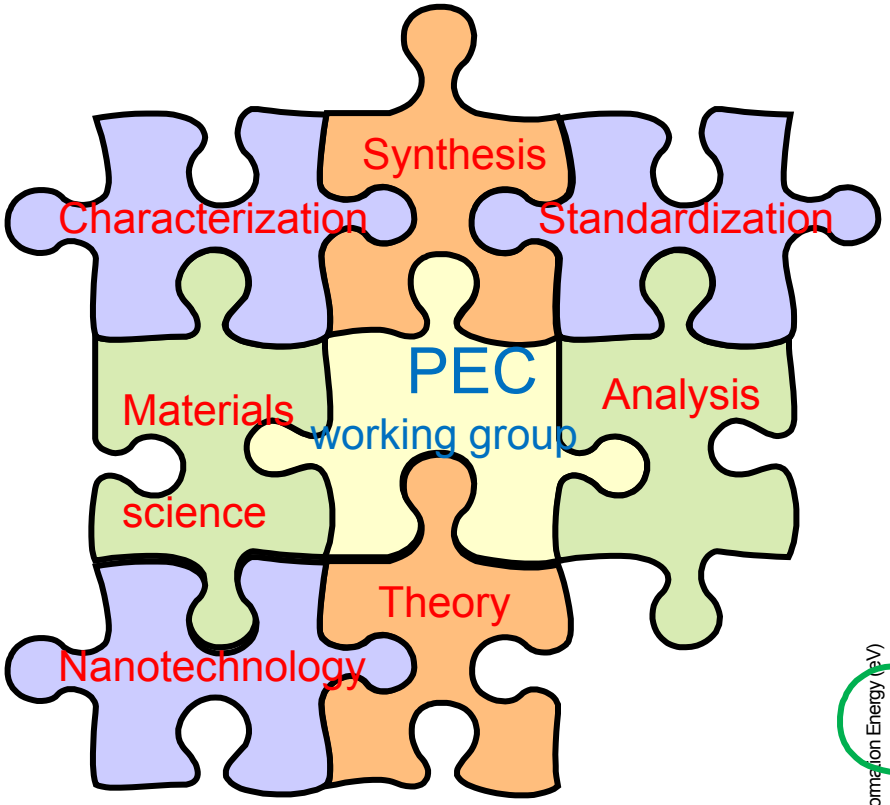
## Budget

- Total project funding
  - Part of NREL PEC Program
- Funding received in FY10

  ~ $ 120K
- Funding for FY11: ~ $ 100K
  - *Project continuation and direction determined annually by DOE
- Note: Task with PD035- Turner

## Partners

- University of Hawaii – Nicolas Gaillard
- University of California – Eric McFarland
- University of Nevada – Clemens Heske

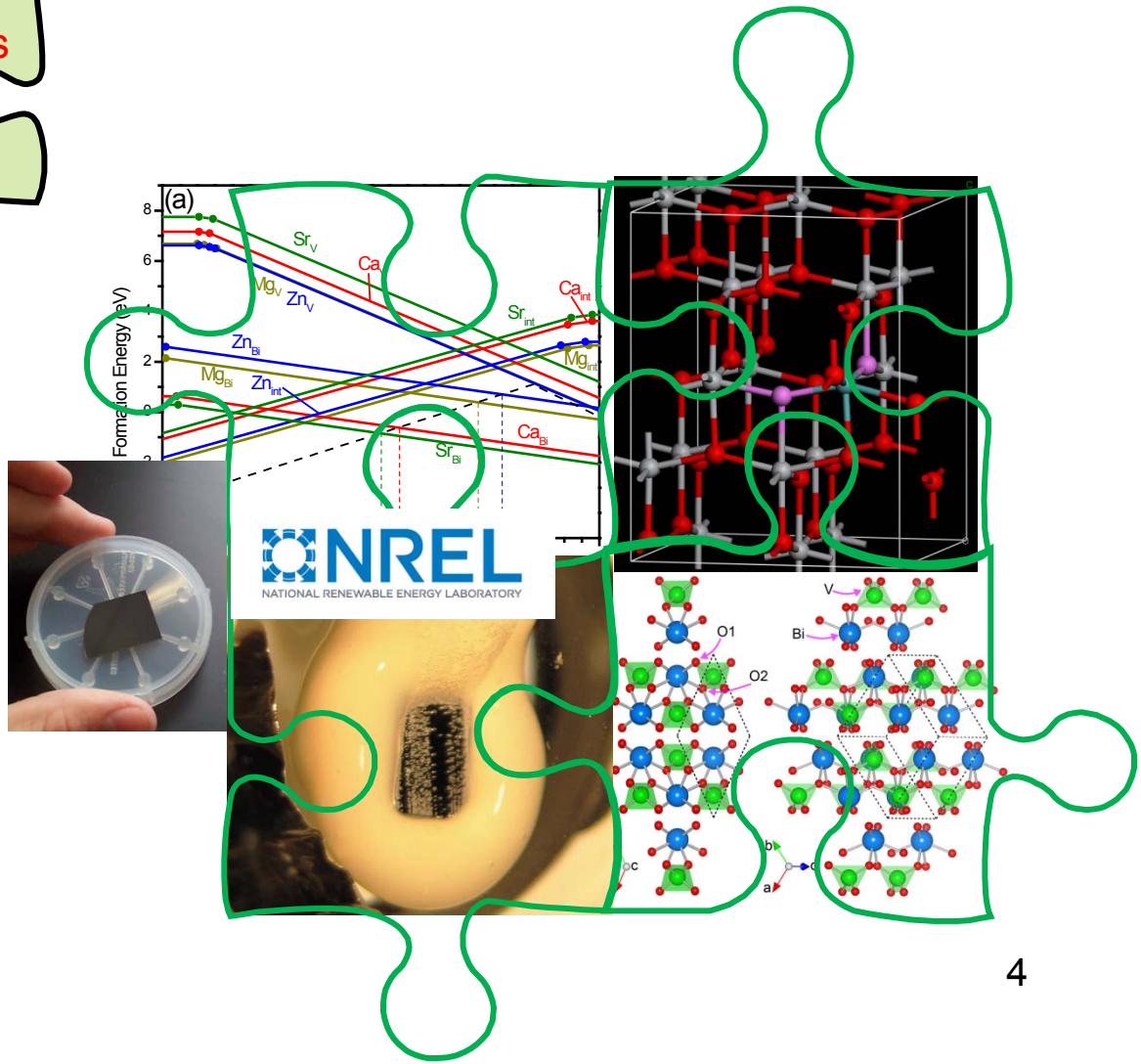



## PEC Working Group:

Evaluating working directions
Sharing and building-up knowledge
Accelerating research progress

- **Theoretical discovery of new PEC materials**

**DOE Goal:**
**1000h @STH > 8% (2013)**
Projected PV electrolysis cost: $10 ~ 15/kg $H_2$



# 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

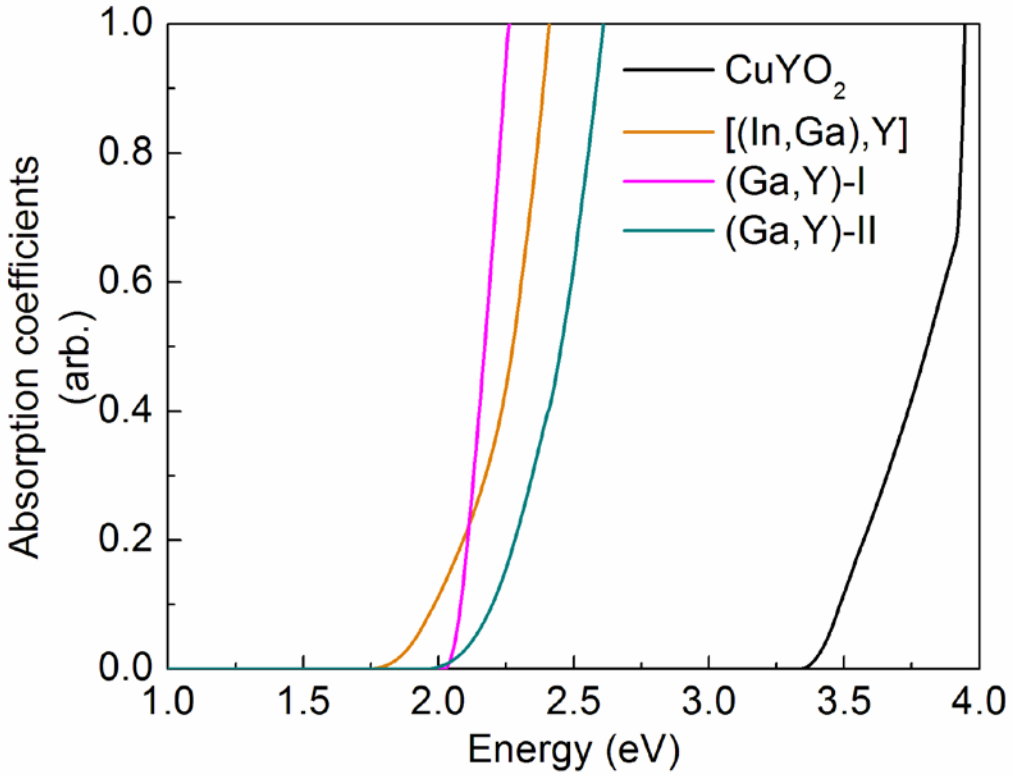
2. Follow the PEC R&D feedback loop

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

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




Optical Absorption Coefficient

Optical absorption is enhanced by alloying Ga and In with Y

# New Technical Accomplishments and Progress

## 1. Rational band structure engineering of $TiO_2$ for improved PEC water splitting

**Strategies**

**1. Charge balanced donor-acceptor alloying**

**Overcome solubility limit, reduce charged defects, improve materials quality**

**2. Using 4*d*, 5*d* TM acceptor**

**Lift up the conduction band**

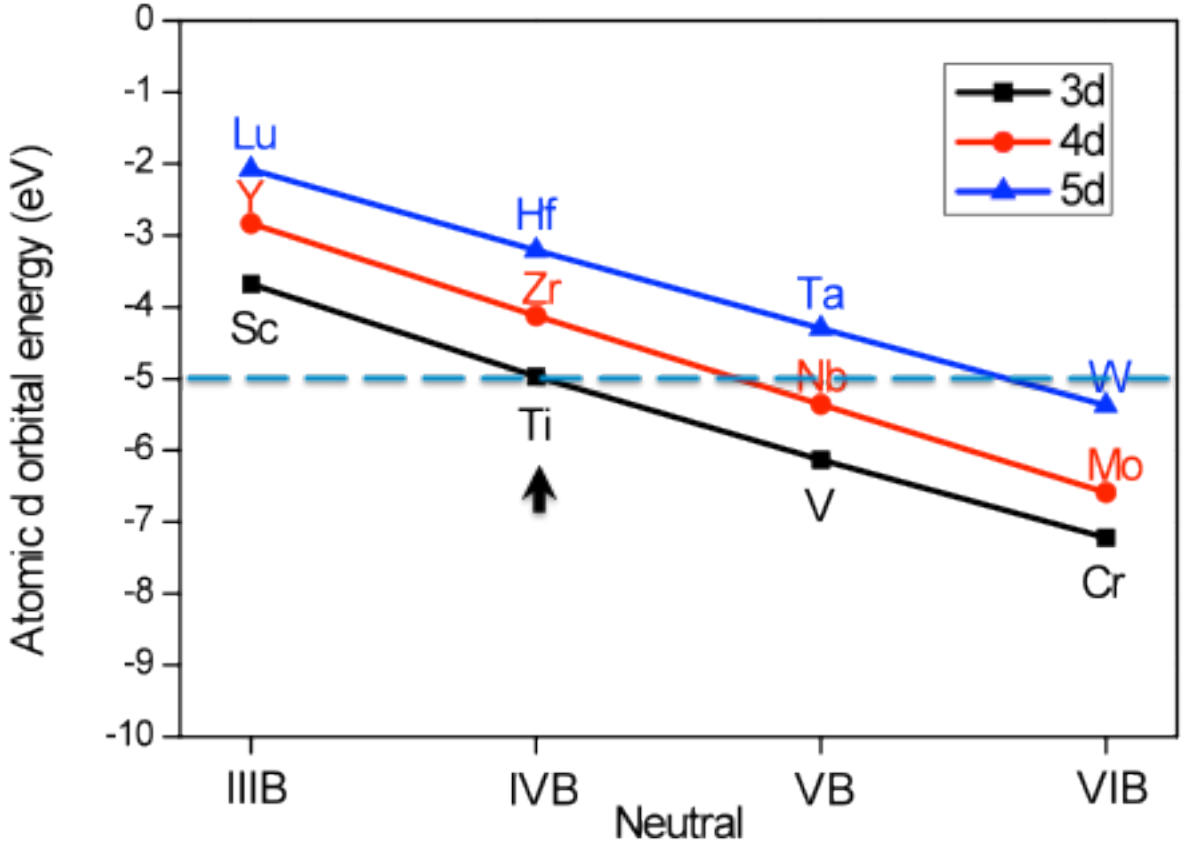
**3. Using higher *p*-orbital donors**

**Raise the valence band**

**4. High concentration of the alloying elements**

**Enhance optical absorption, improve hole mobility**

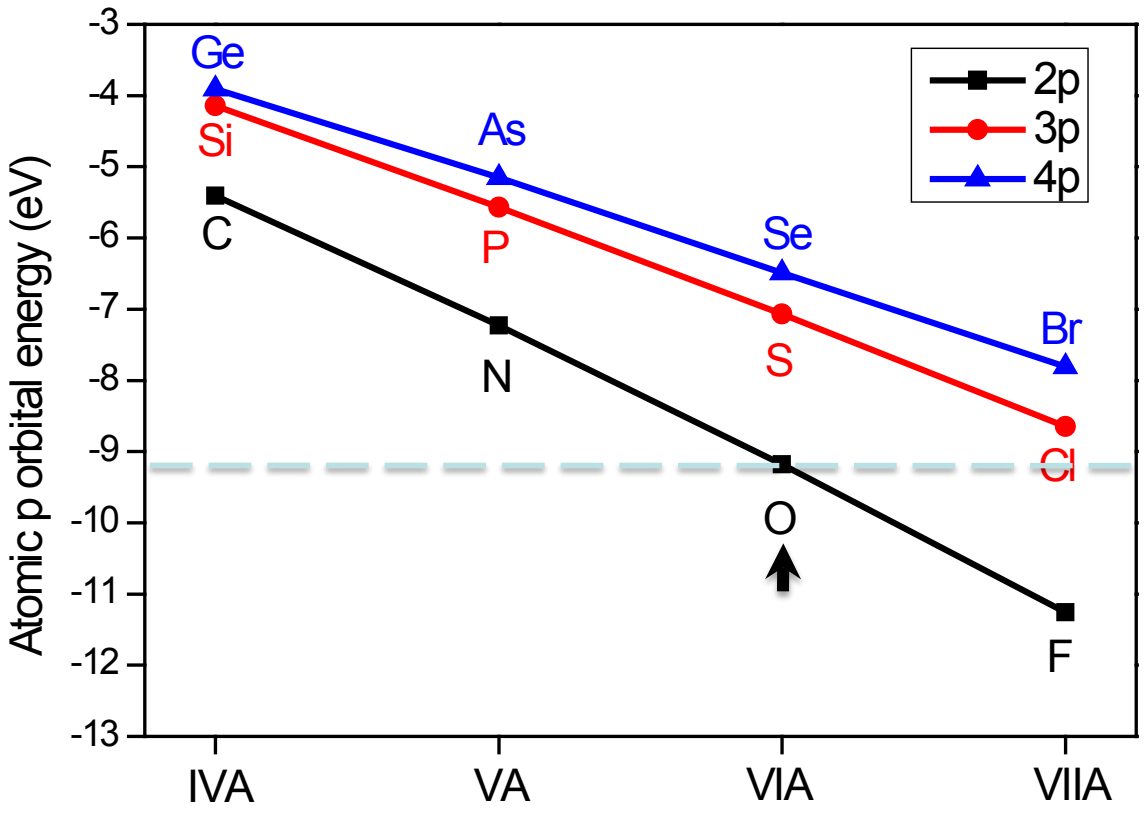
# New Technical Accomplishments and Progress (Cont.)




**Potential candidates as donor: Ta, Nb, W, Mo**

**Isovalent impurities: Zr, Hf**

# New Technical Accomplishments and Progress (Cont.)

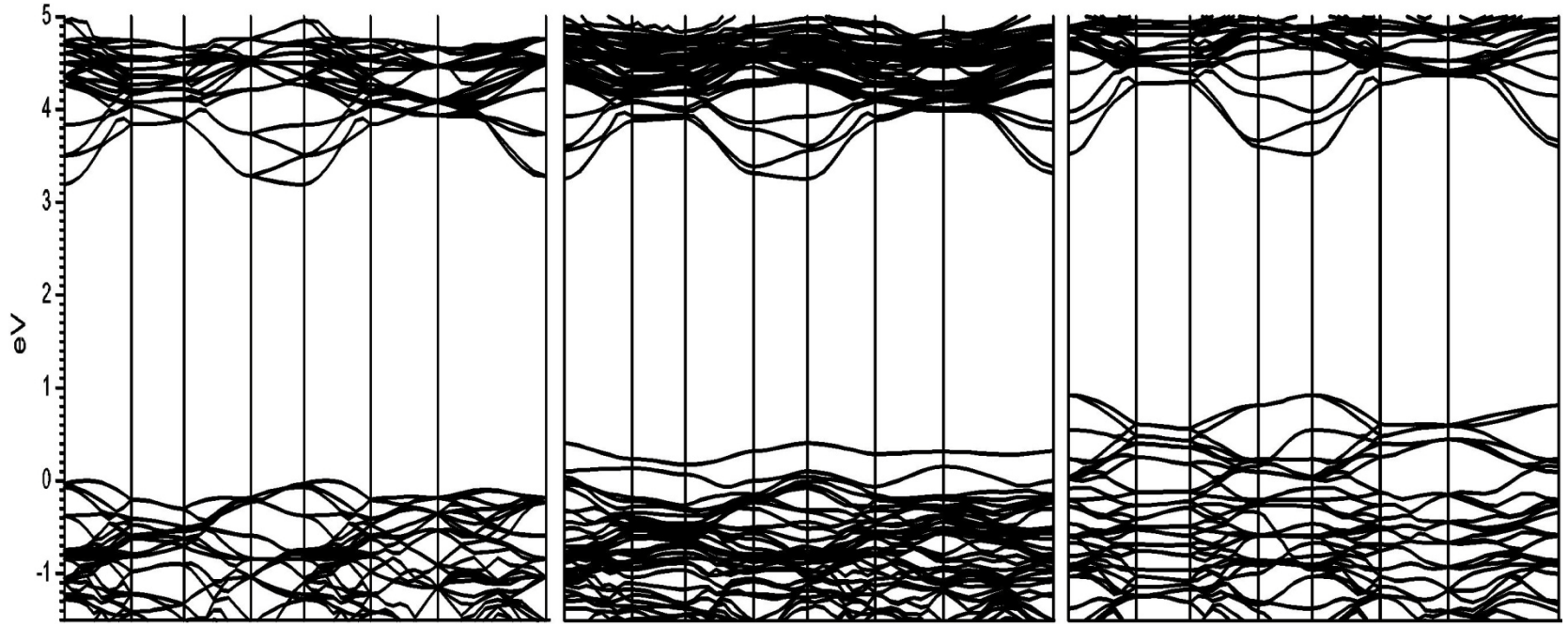



**Potential candidates as acceptor: N, C, P, Si, As**

**Isovalent impurities: S, Se**

# New Technical Accomplishments and Progress (Cont.)

**Calculated (GGA) band structure**

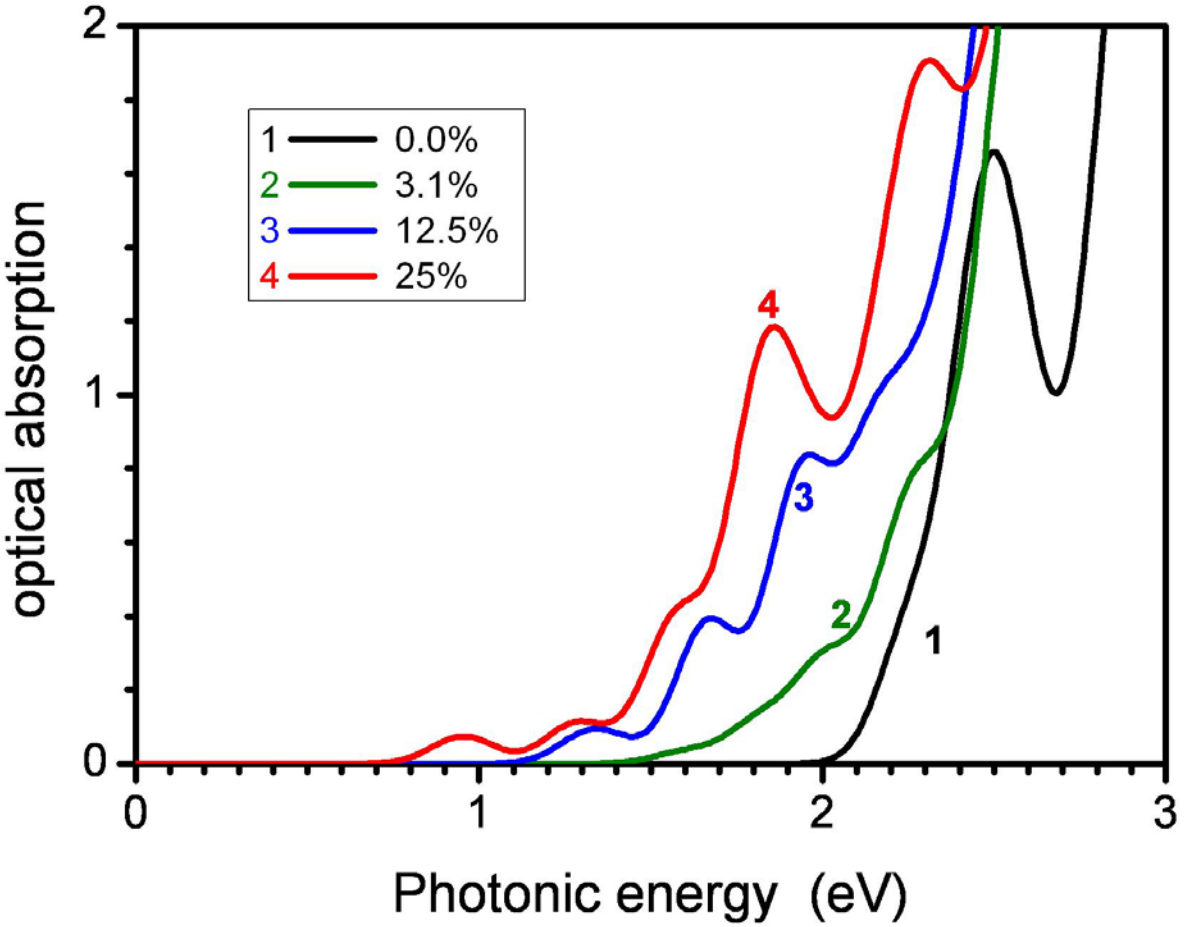



**Pure $TiO_2$** **(Ta, N) 3.1%(O)** **(Ta, N) 12.5%(O)**

Sufficient foreign elements must be incorporated to enhance carrier mobilities

# New Technical Accomplishments and Progress (Cont.)

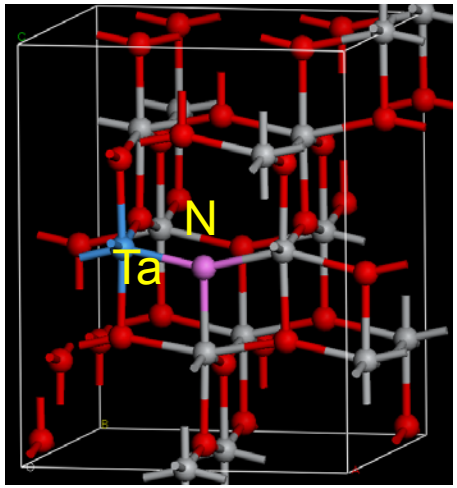
**Calculated (GGA) absorption coefficient**

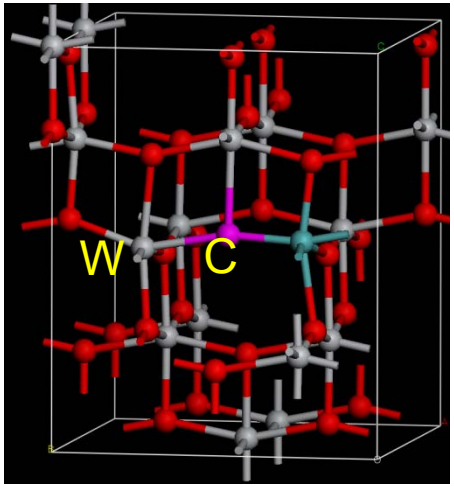


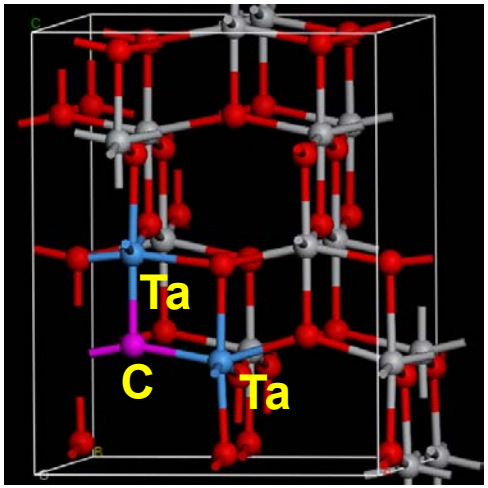

Sufficient foreign elements must be incorporated to obtain good optical absorption

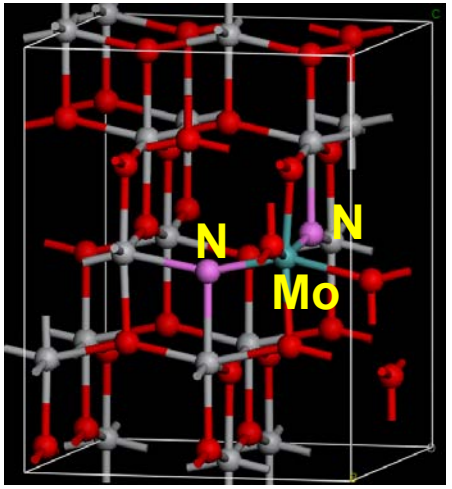
# New Technical Accomplishments and Progress (Cont.)

**Possible donor-acceptor combinations**



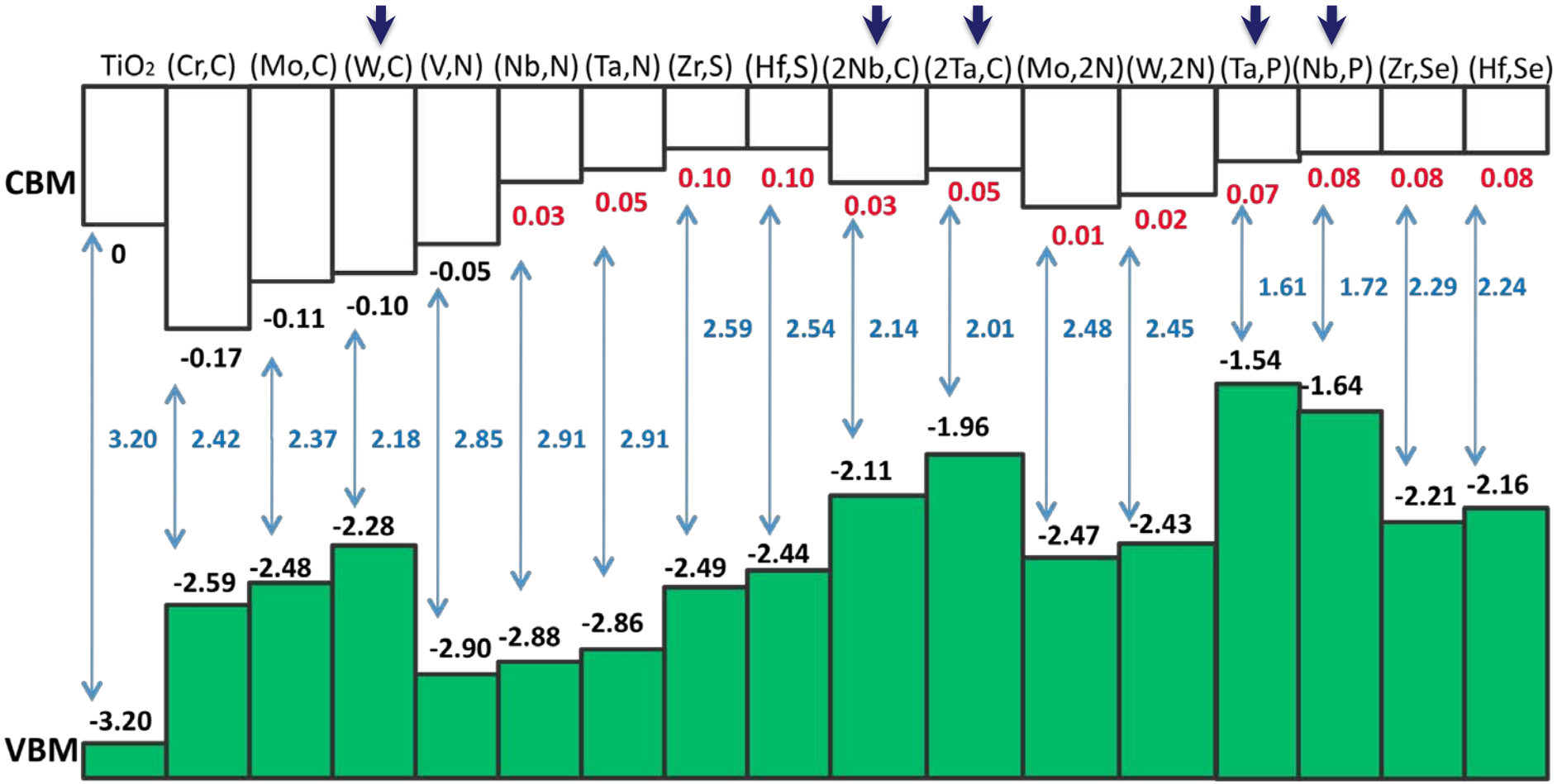



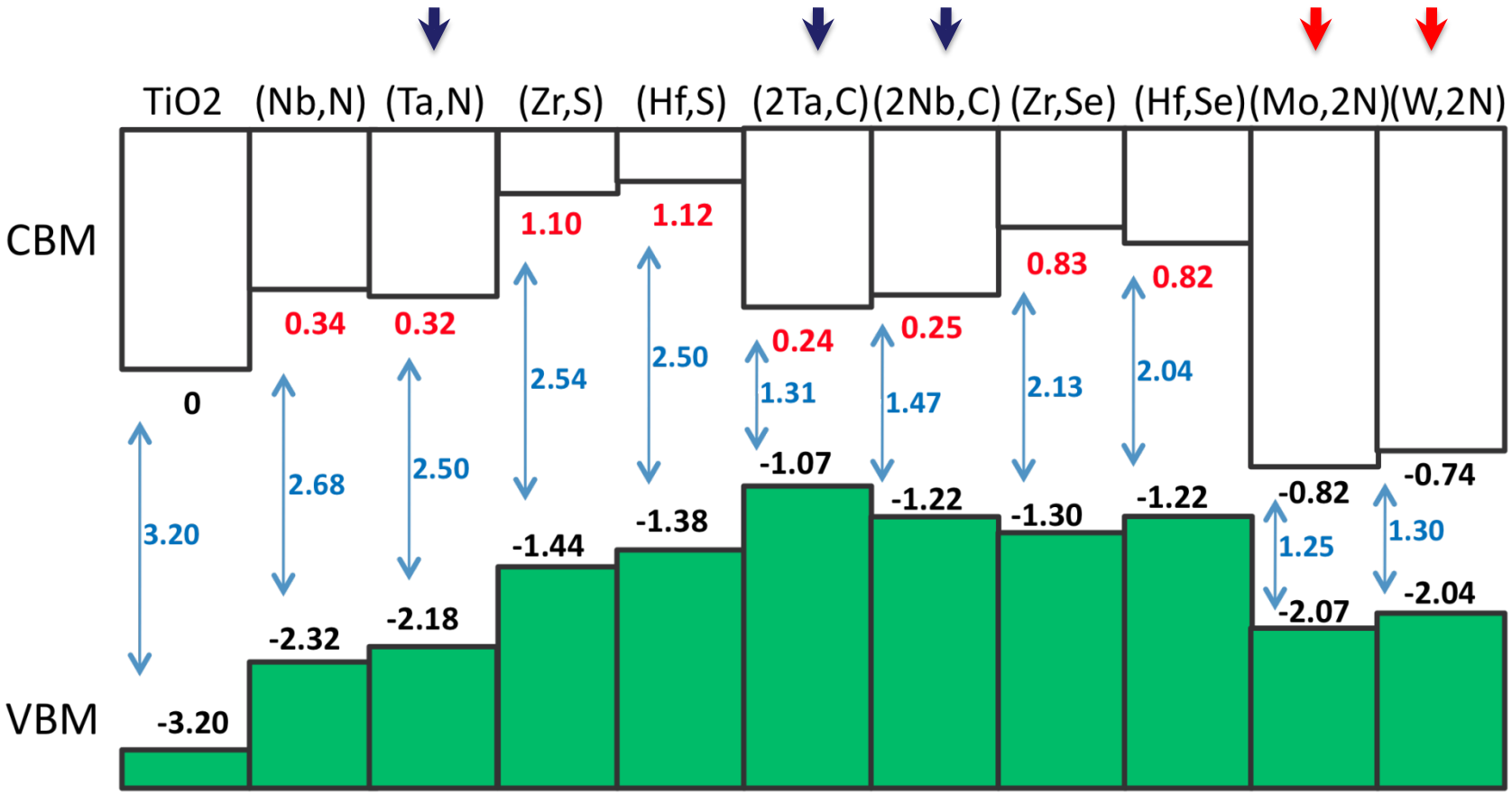

**(donor, acceptor)** **(2 donors, acceptor)** **(donor, 2 acceptors)**

# New Technical Accomplishments and Progress (Cont.)




GGA + band gap correction at Γ point: low concentration

# New Technical Accomplishments and Progress (Cont.)




GGA + band gap correction at Γ point: high concentration

# New Technical Accomplishments and Progress (Cont.)

## Good combinations

**Low concentration:**

**(Mo, 2N), (W, 2N)**

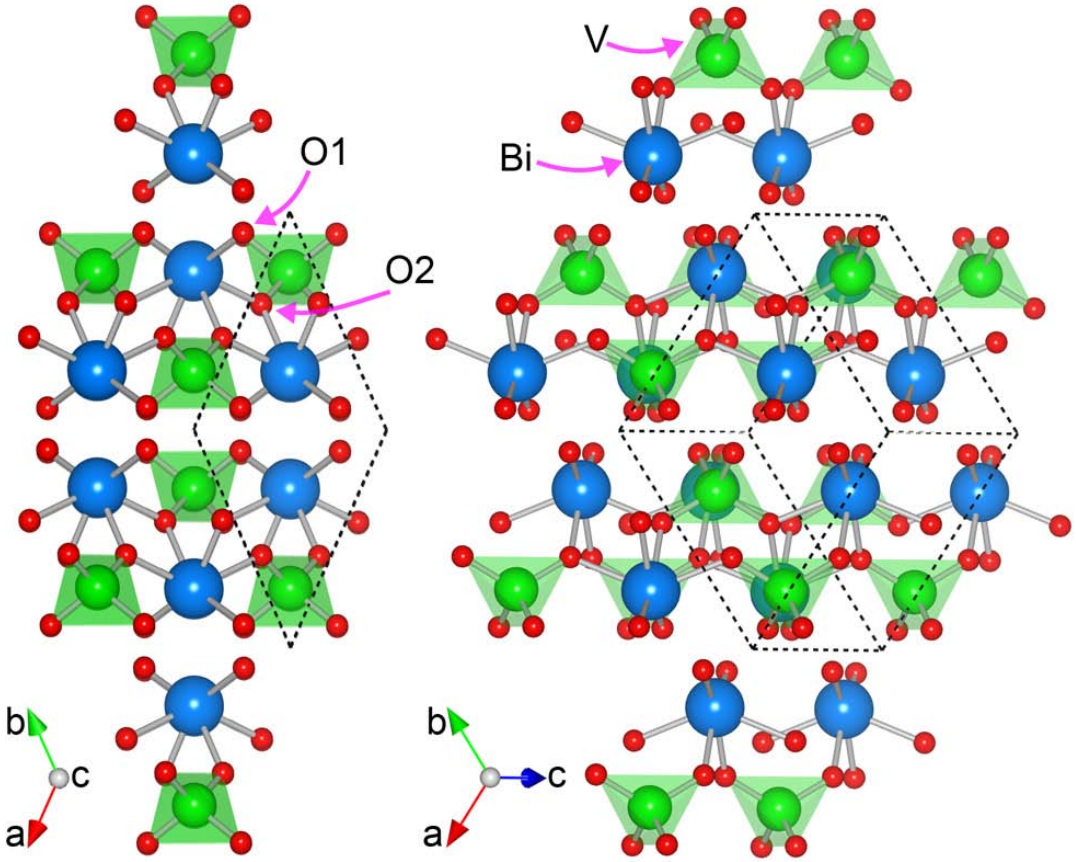
**High concentration:**

**(Ta, N), (Nb, N), (2Ta, C), (2Nb, C)**

Phys. Rev. B **82**, 045106 (2010)

# New Technical Accomplishments and Progress (Cont.)

## 2. Superior doping properties of $BiVO_4$

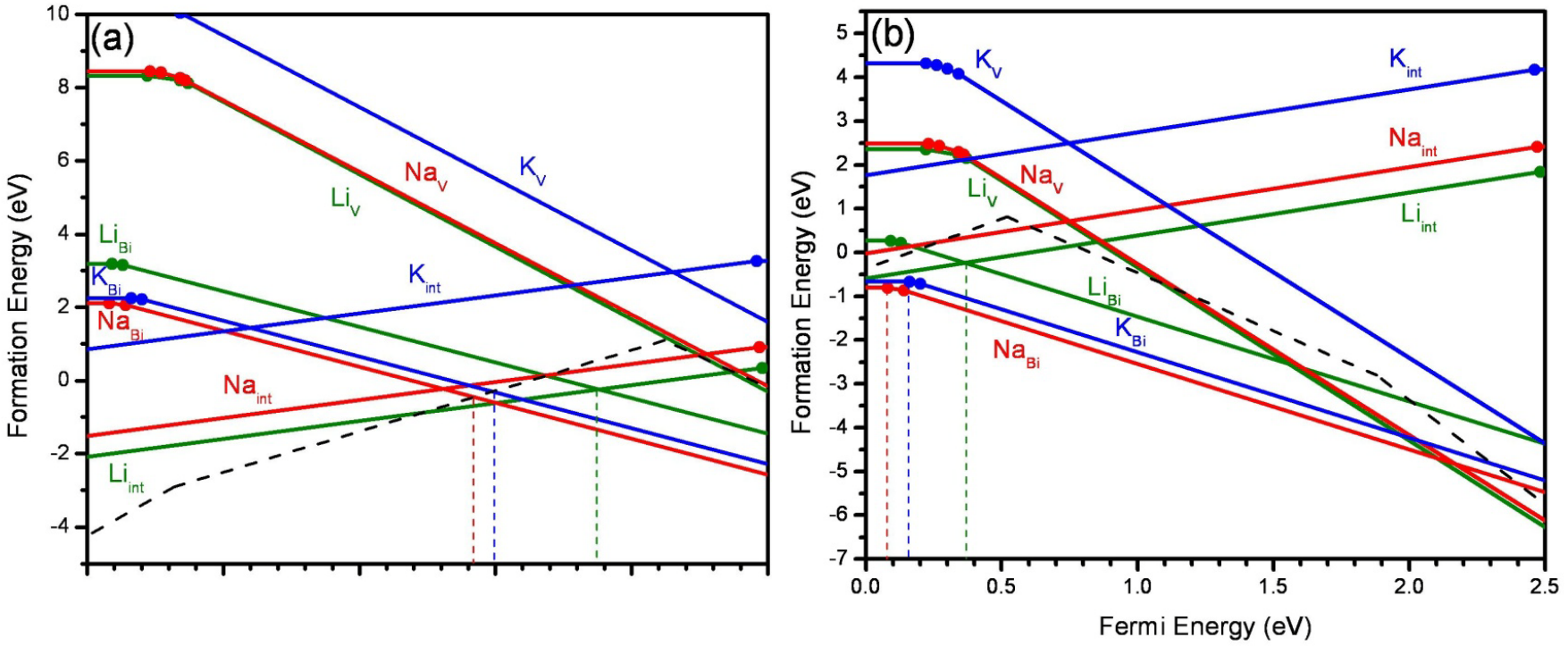



Atomic Structure of $BiVO_4$

PEC properties of $BiVO_4$

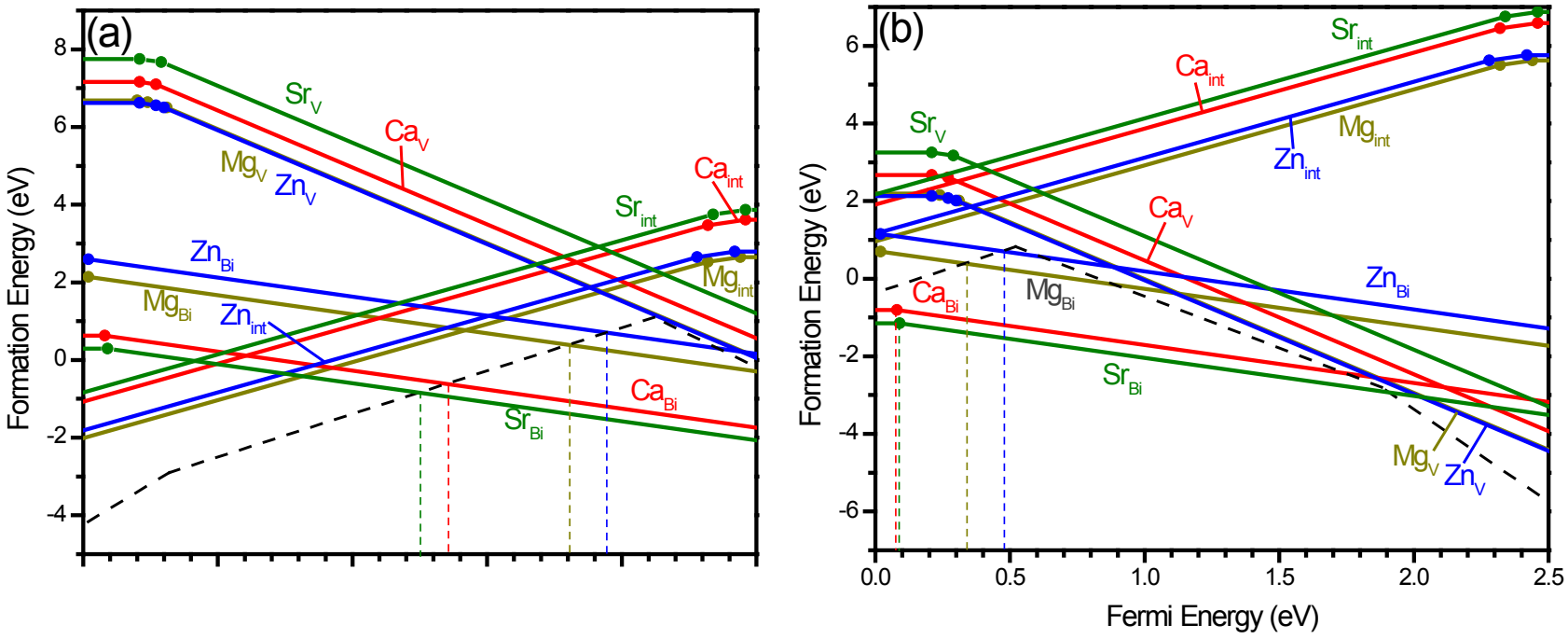
- Excellent optical absorption coefficient
- Good Valence band edge position
- Good carrier mobility

# New Technical Accomplishments and Progress (Cont.)



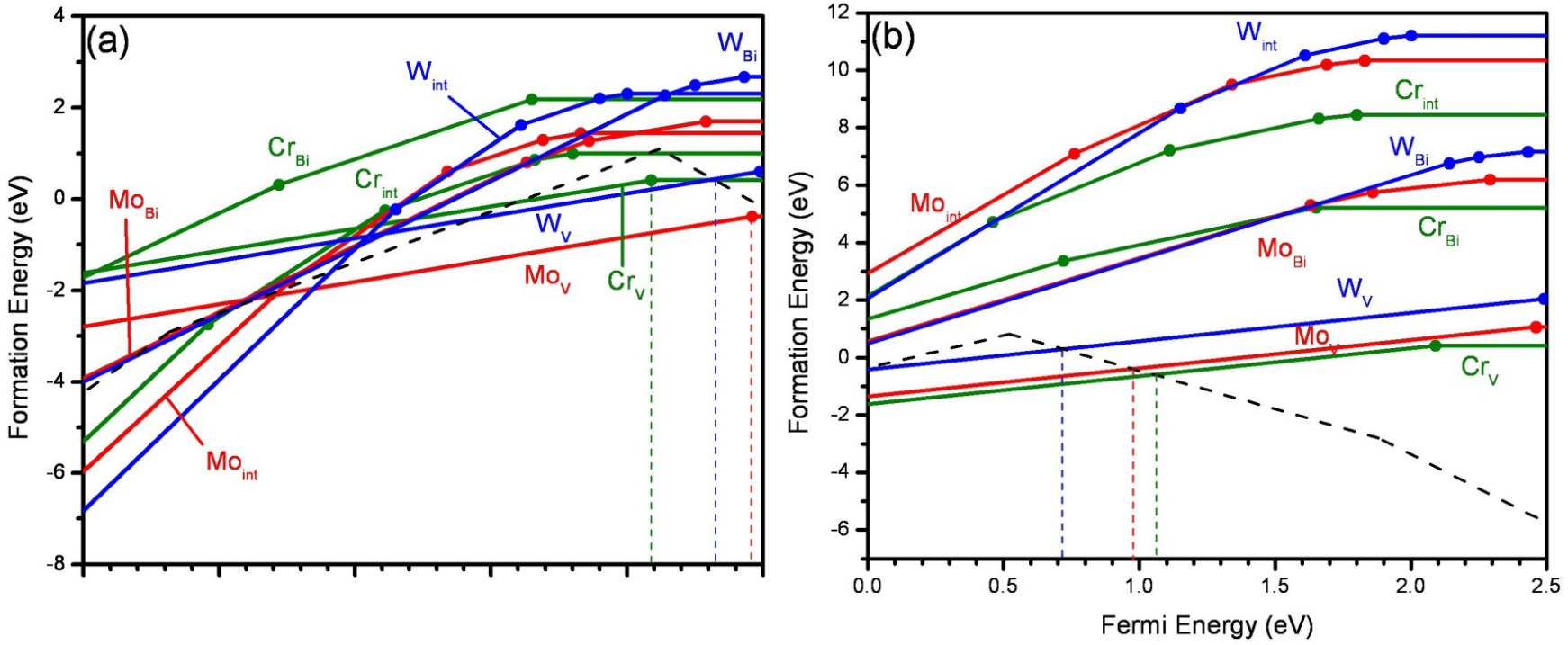

Na on Bi can lead to good p-type of $BiVO_4$

# New Technical Accomplishments and Progress (Cont.)




Ca and Sr doping can lead to good p-type of $BiVO_4$

# New Technical Accomplishments and Progress (Cont.)




Mo and W doping can lead to good n-type of $BiVO_4$

# New Technical Accomplishments and Progress (Cont.)

BiVO4 has superior doping properties -

It can be doped both good n-type and p-type

These excellent doping properties are required for PEC $H_2$ production application

# 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.
- Band structure engineering of $BiVO_4$ for PEC application.
- 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-principle density-functional theory.

Technical Accomplishments and Progress: Proposed strategies for band structure engineering of $TiO_2$ for improved PEC water splitting performance. Demonstrated superior doping properties 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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