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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National Renewable Energy Laboratory,
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

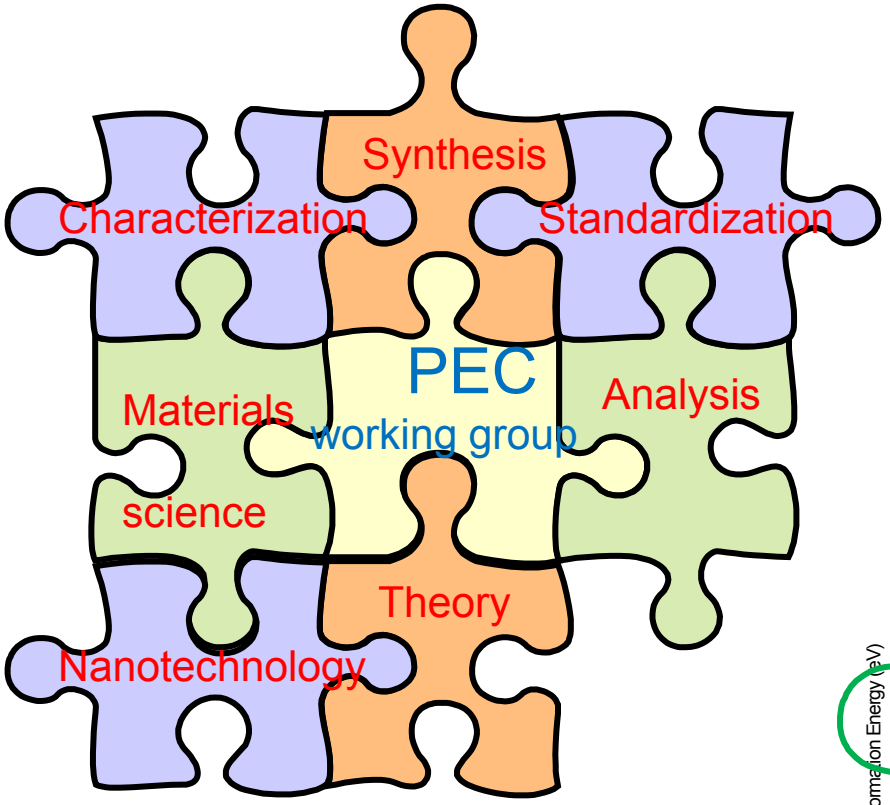
Budget

- 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

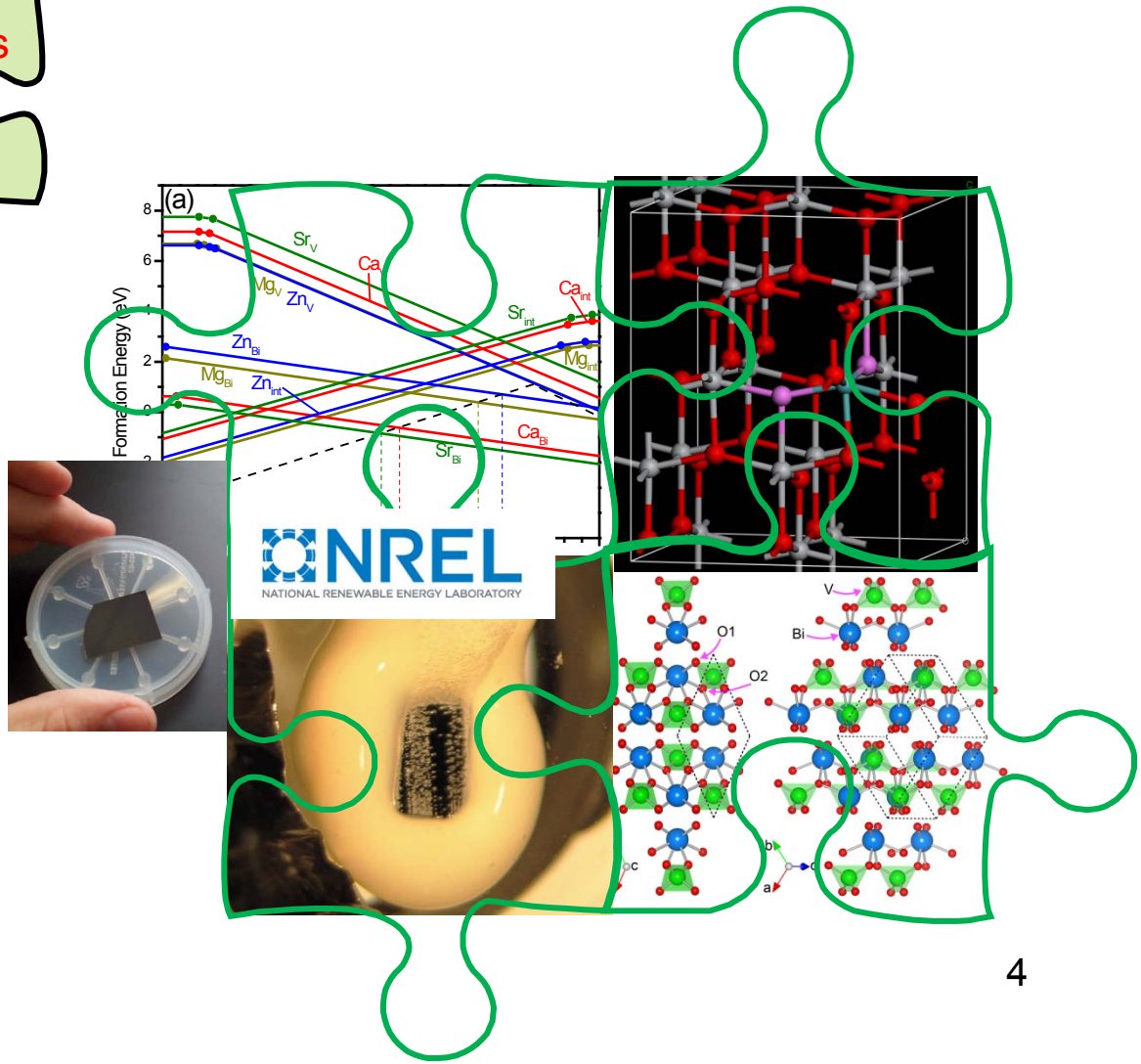


PEC Working Group:

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

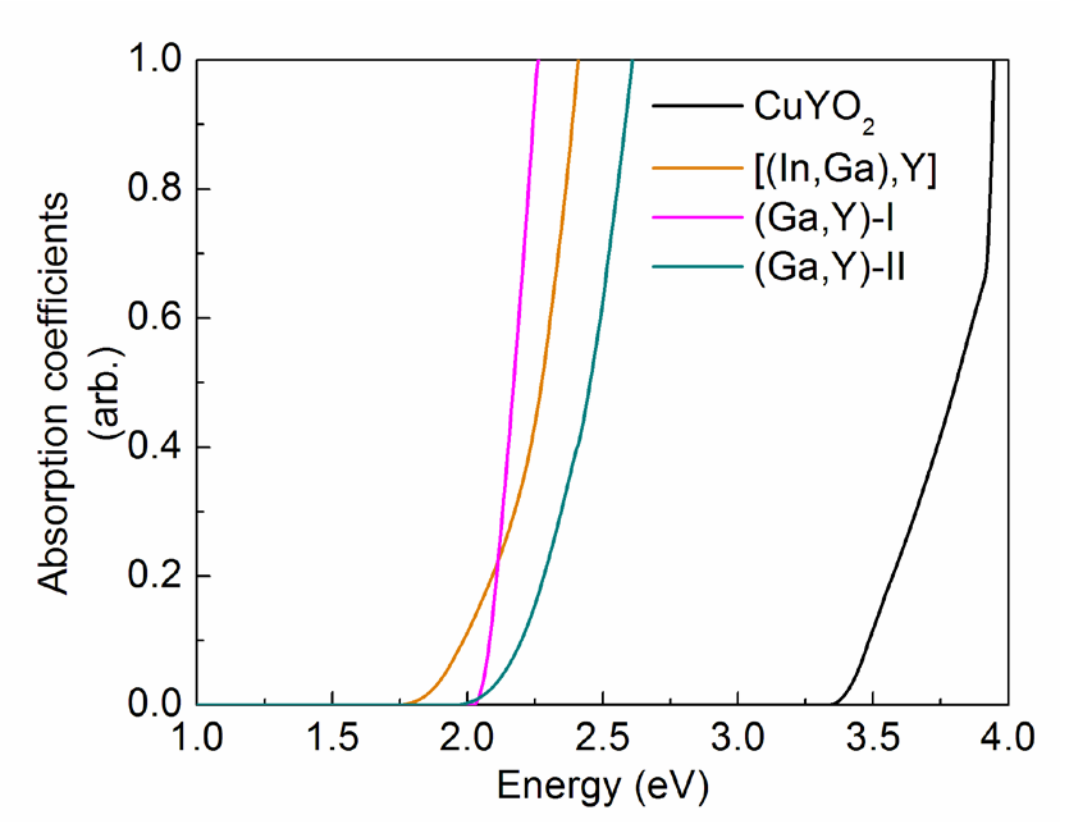
2. Follow the PEC R&D feedback loop

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

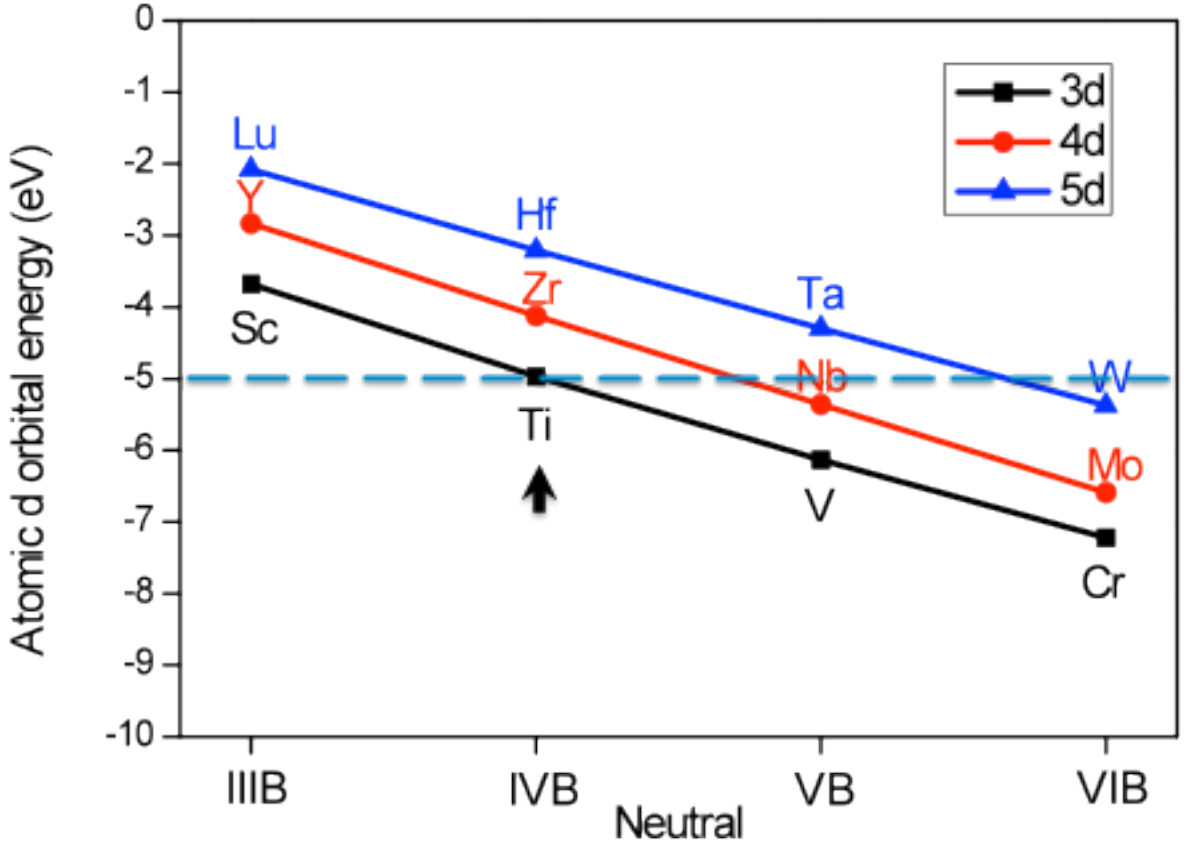
3. Using higher *p*-orbital donors

Raise the valence band

4. High concentration of the alloying elements

Enhance optical absorption, improve hole mobility

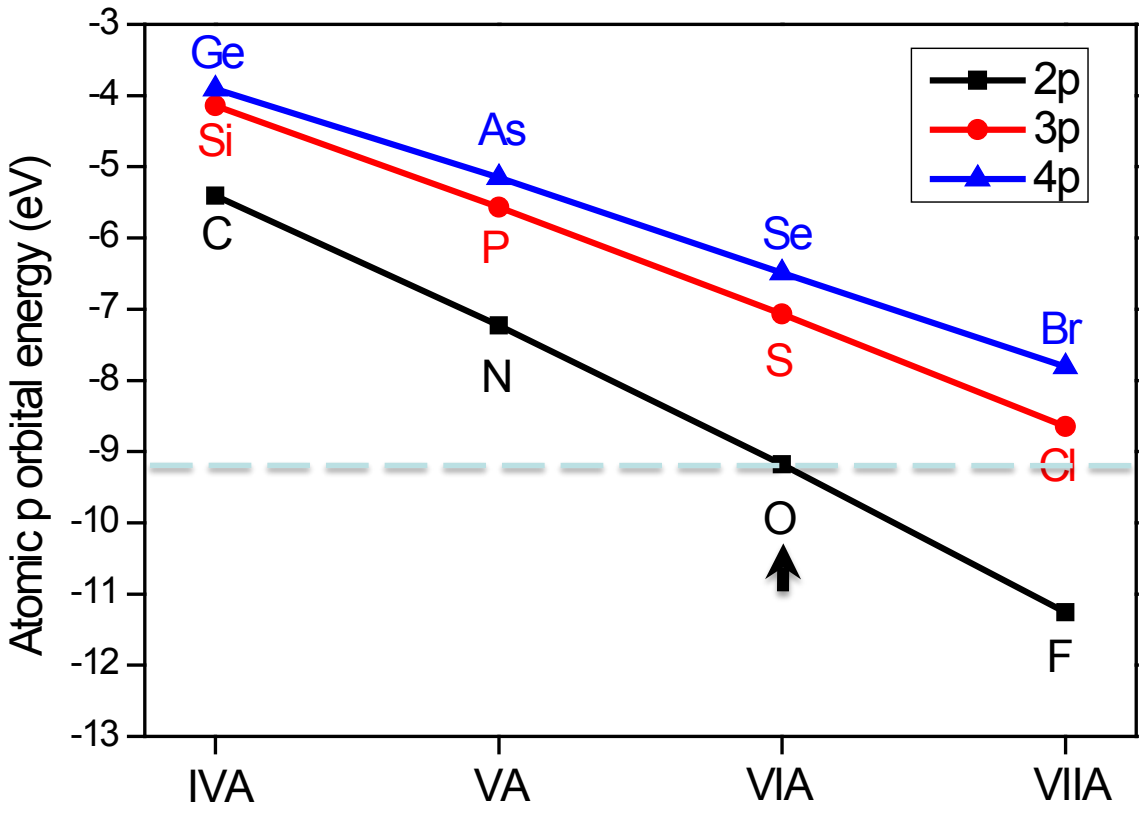
New Technical Accomplishments and Progress (Cont.)



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

Isovalent impurities: Zr, Hf

New Technical Accomplishments and Progress (Cont.)

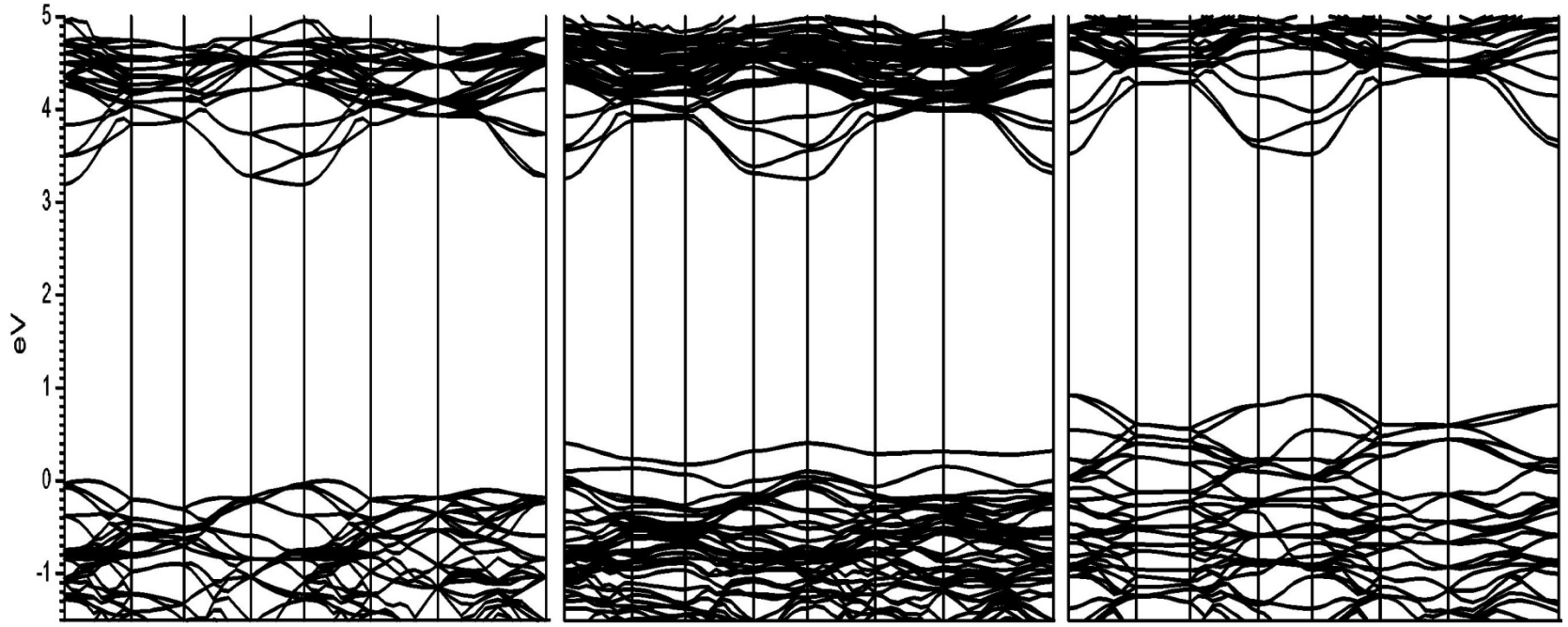


Potential candidates as acceptor: N, C, P, Si, As

Isovalent impurities: S, Se

New Technical Accomplishments and Progress (Cont.)

Calculated (GGA) band structure

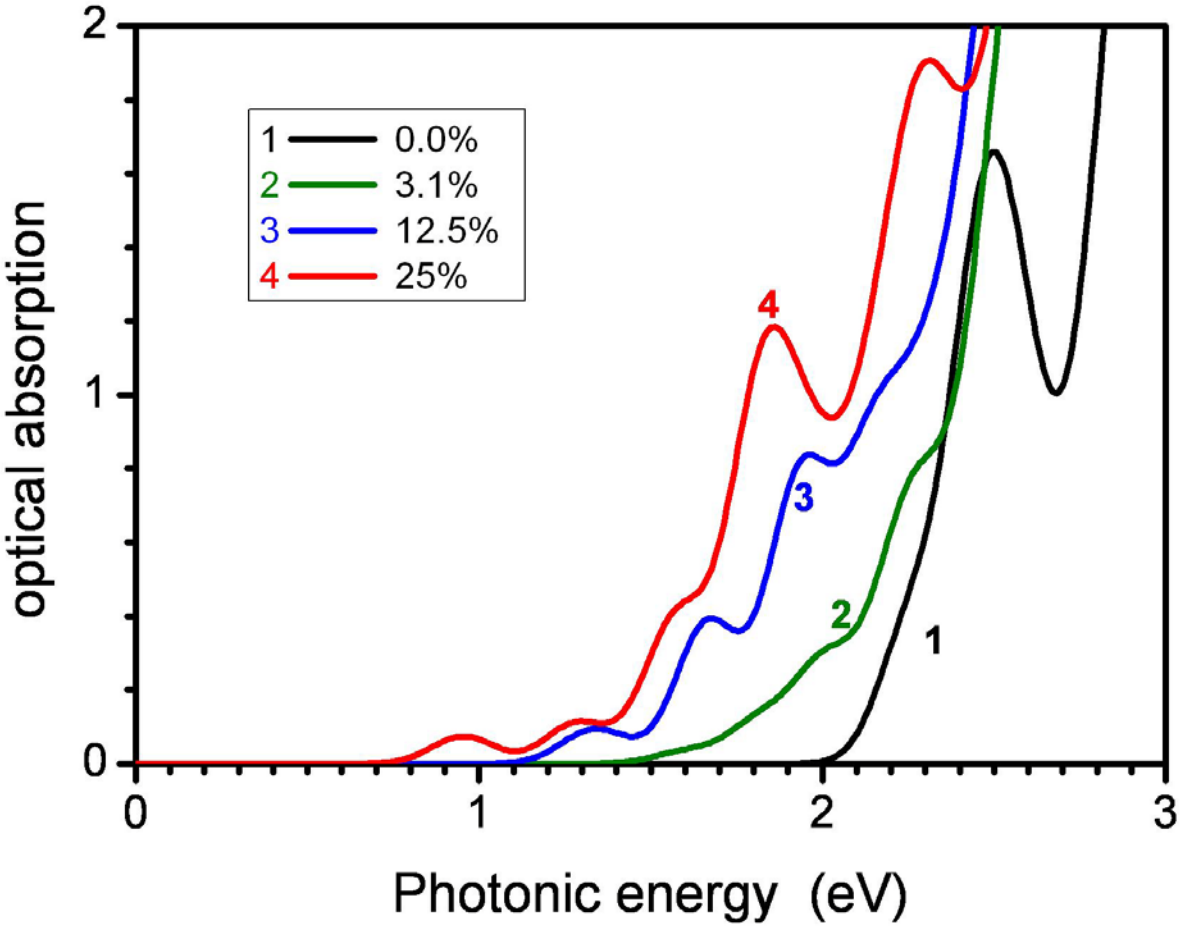


Pure TiO_2 **(Ta, N) 3.1%(O)** **(Ta, N) 12.5%(O)**

Sufficient foreign elements must be incorporated to enhance carrier mobilities

New Technical Accomplishments and Progress (Cont.)

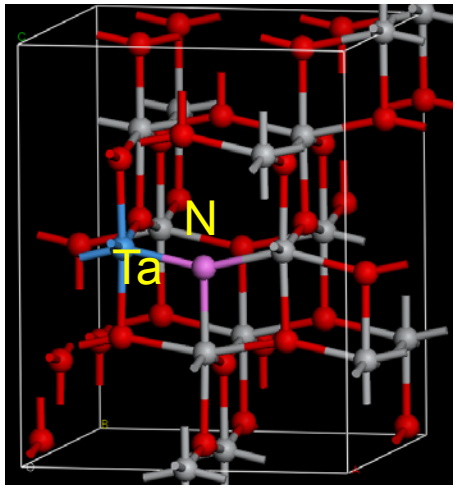
Calculated (GGA) absorption coefficient

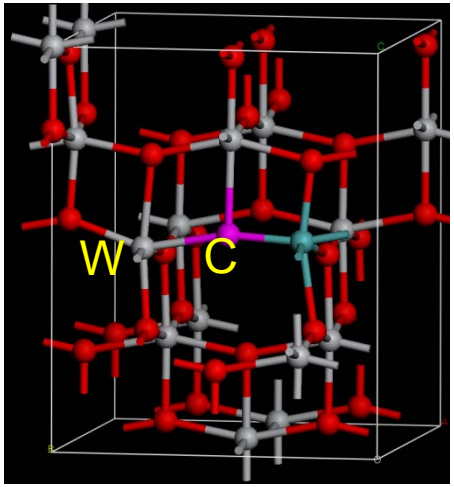


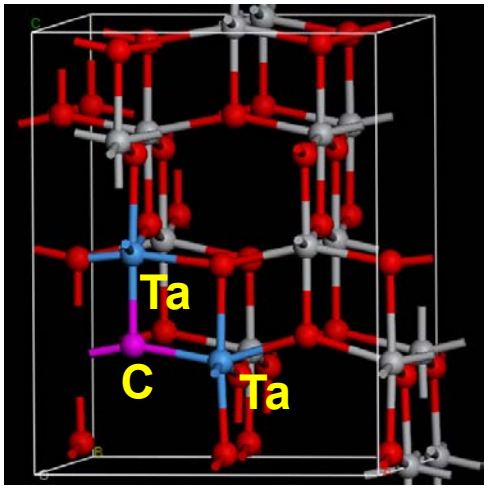
Sufficient foreign elements must be incorporated to obtain good optical absorption

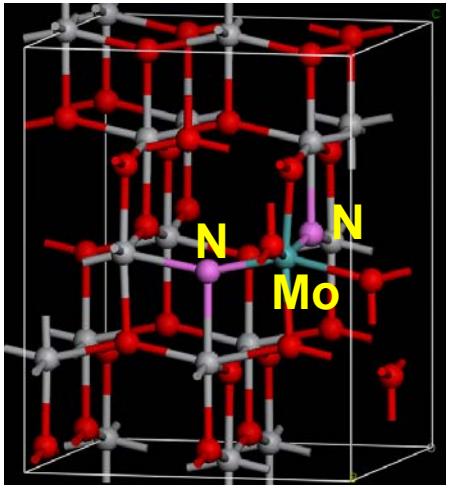
New Technical Accomplishments and Progress (Cont.)

Possible donor-acceptor combinations



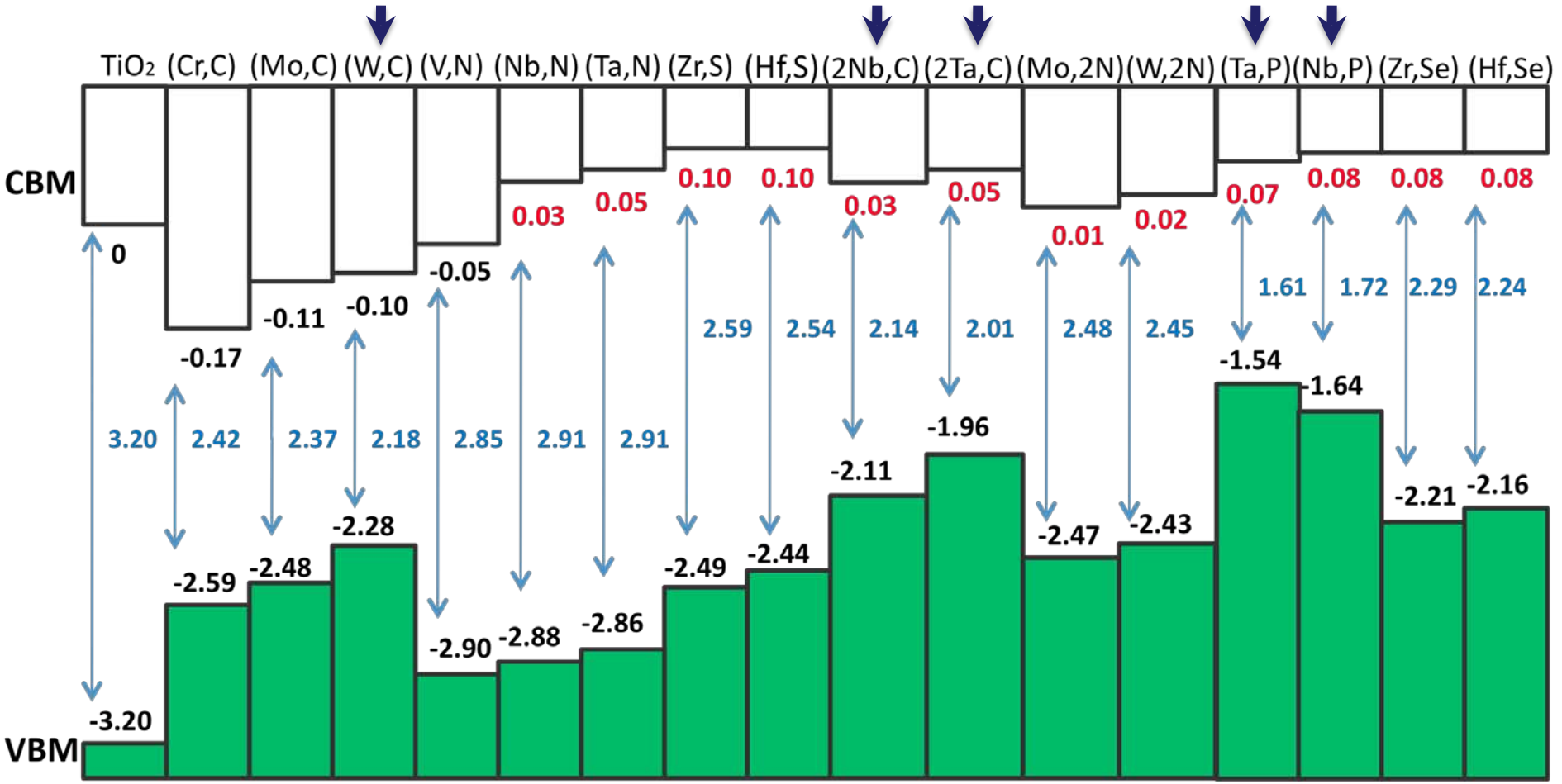






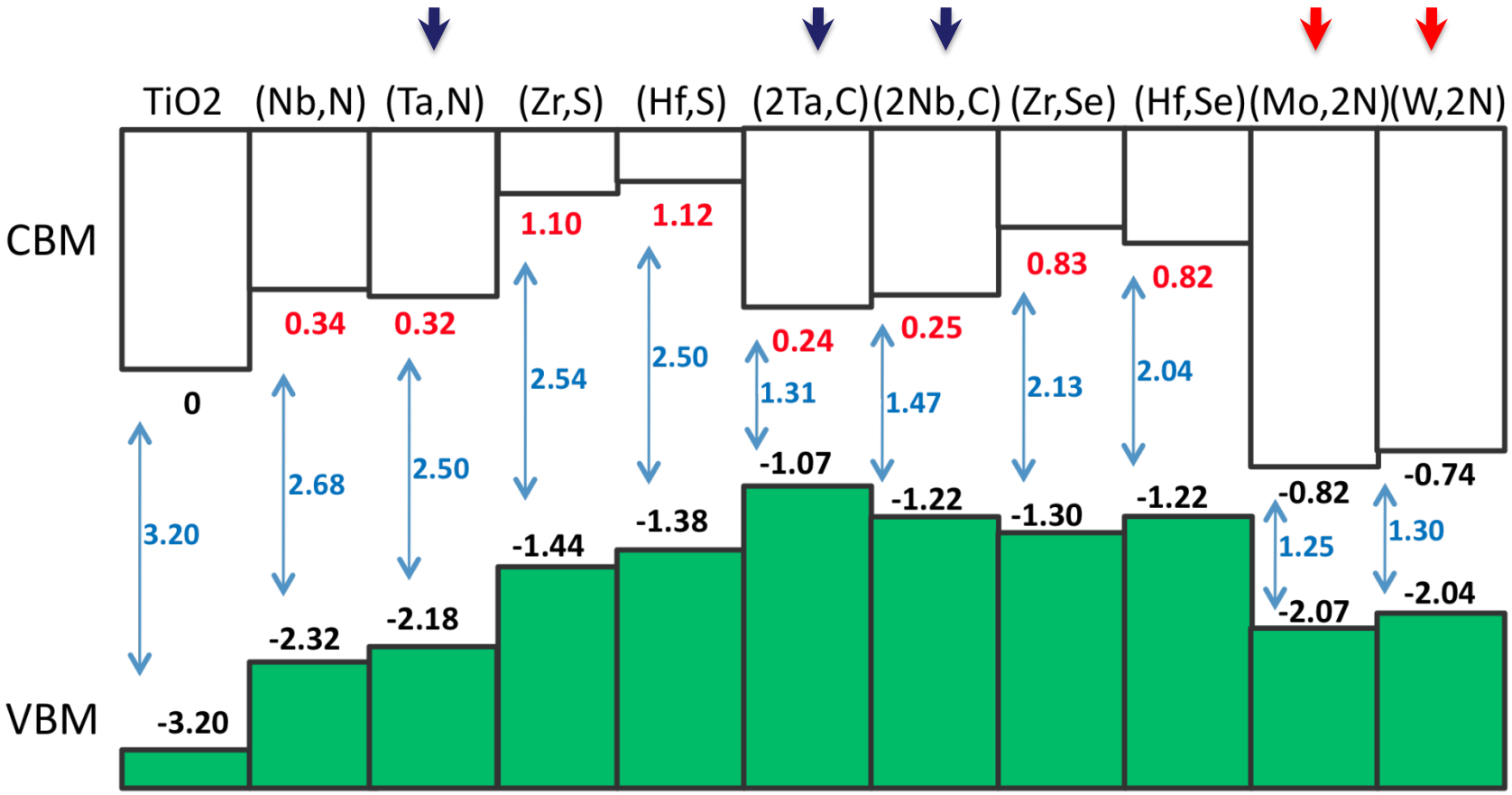
(donor, acceptor) **(2 donors, acceptor)** **(donor, 2 acceptors)**

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)

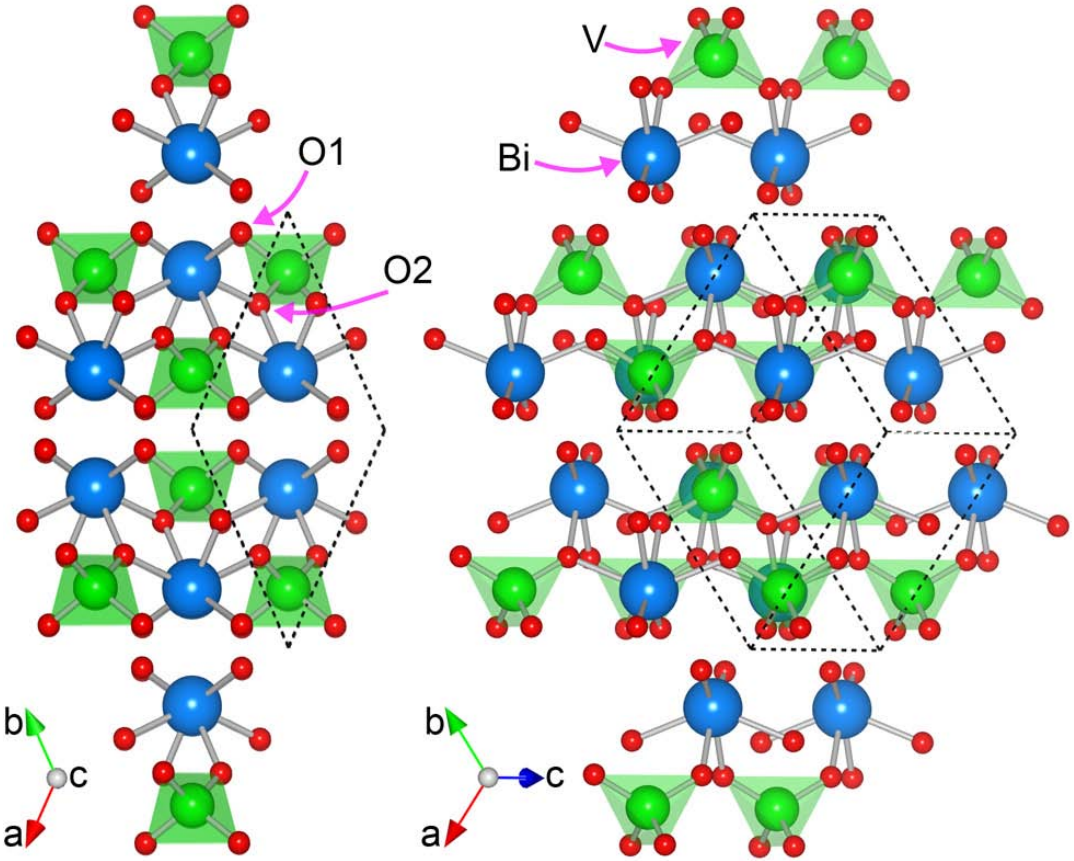
High concentration:

(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 $BiVO_4$

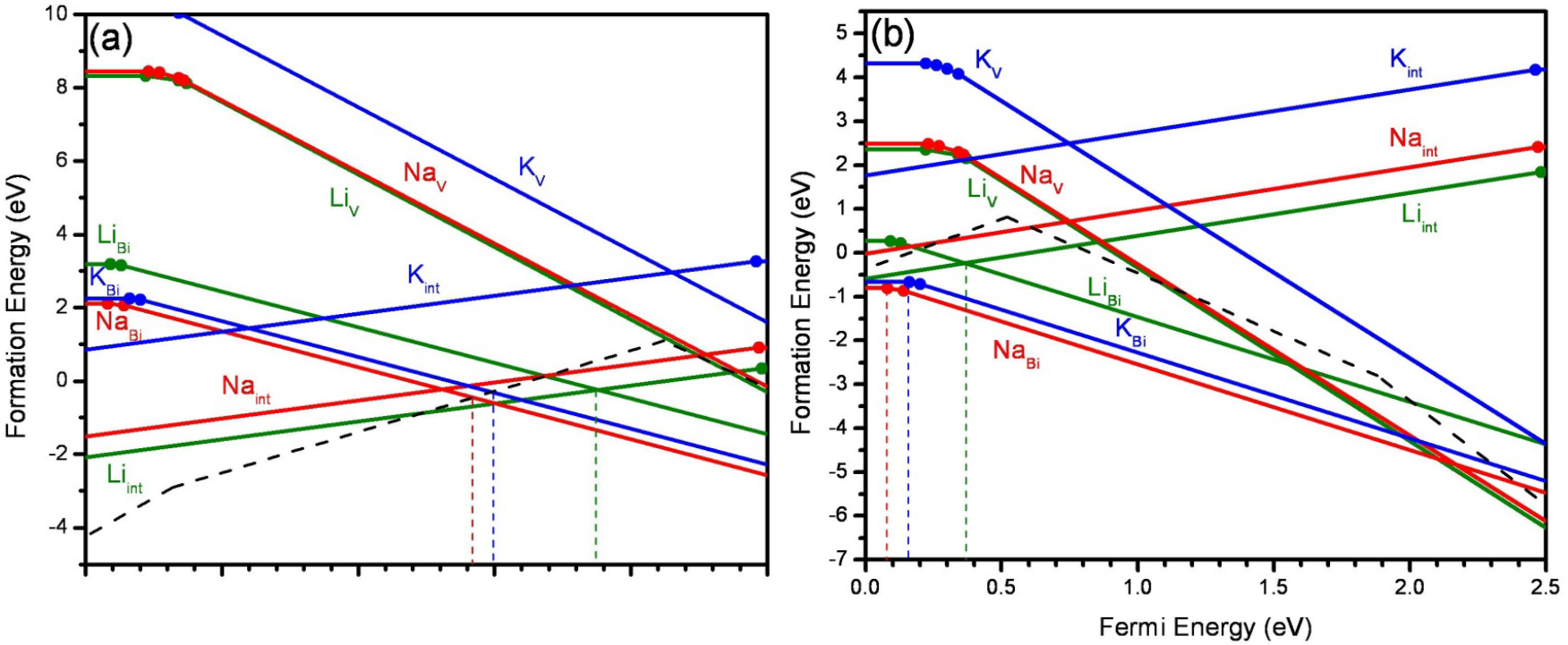


Atomic Structure of $BiVO_4$

PEC properties of $BiVO_4$

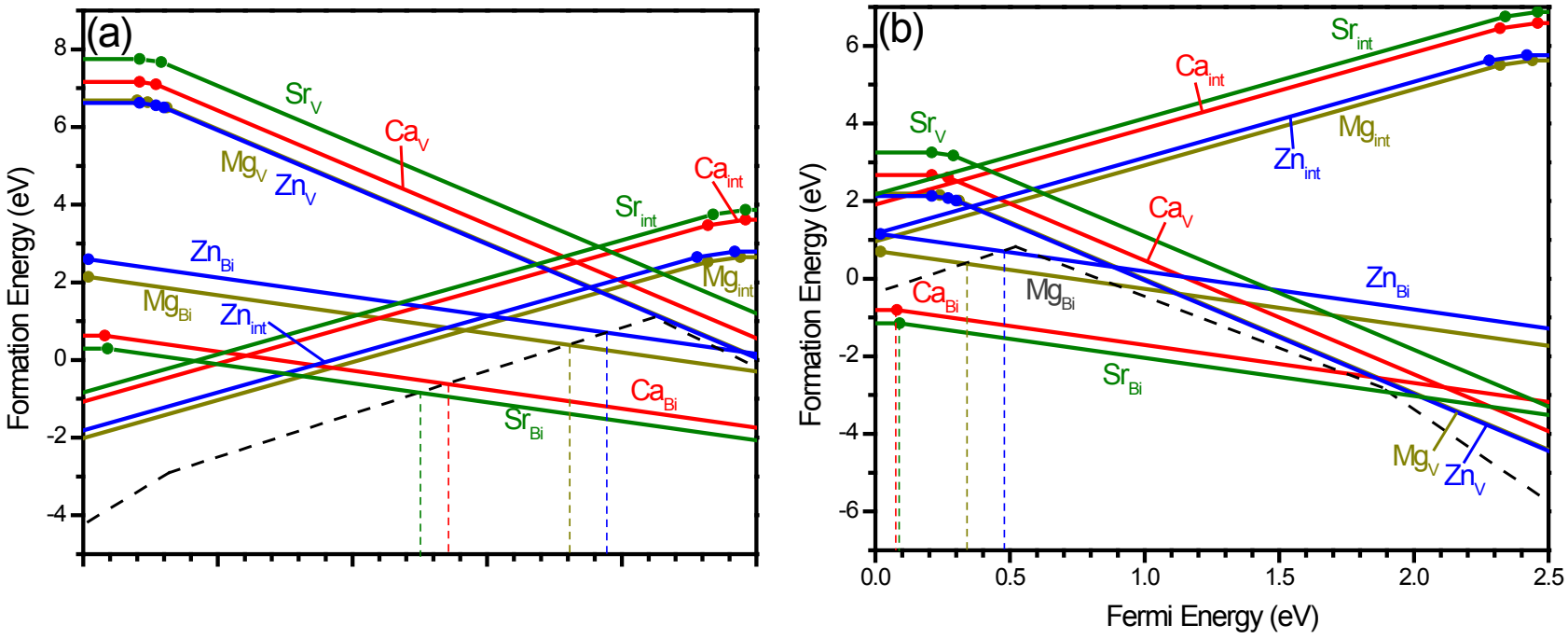
- Excellent optical absorption coefficient
- Good Valence band edge position
- Good carrier mobility

New Technical Accomplishments and Progress (Cont.)



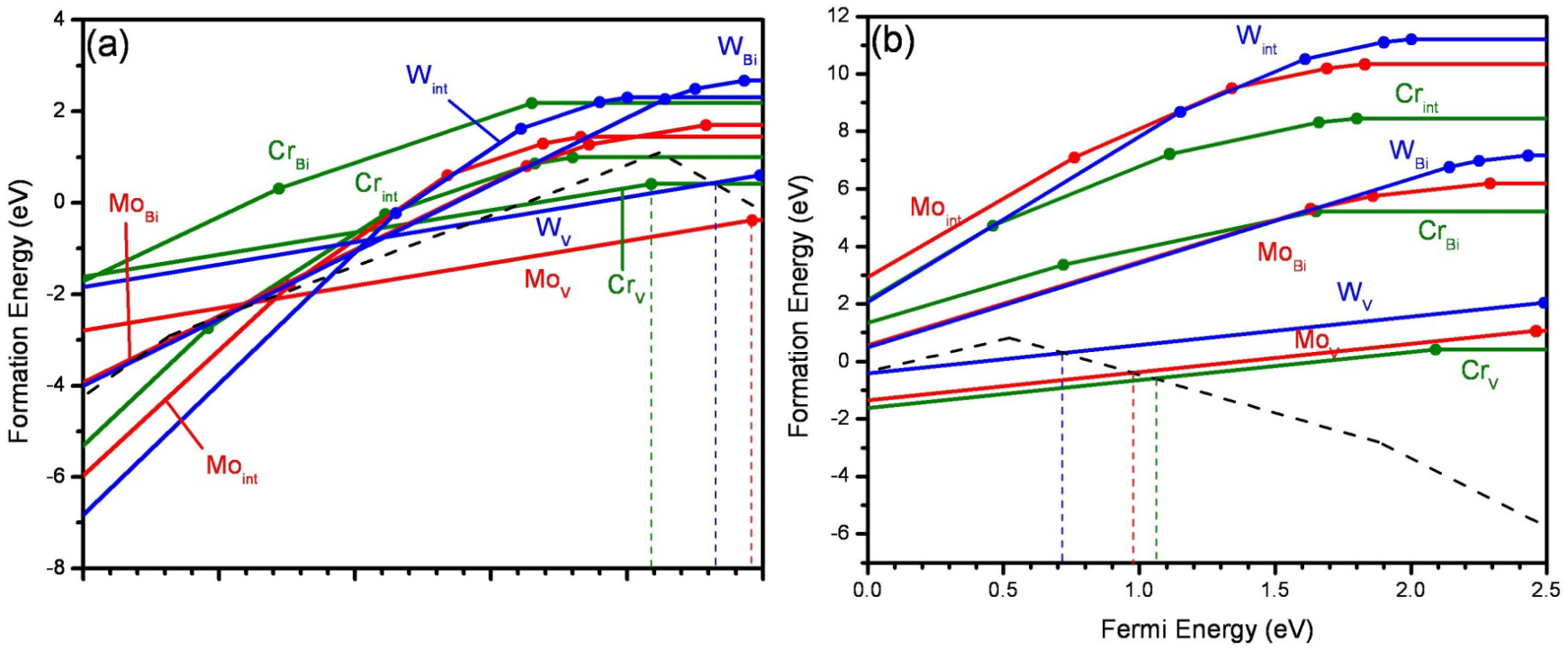
Na on Bi can lead to good p-type of $BiVO_4$

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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