Materials by Design and Advances in Photovoltaic R&D

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UNSW Seminar

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NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Photovoltaics Summary

Rapid progress has been made in PV but we aren't done yet

Solar energy can deliver low-carbon energy to mitigate Climate Change BUT further advances are needed for TWs

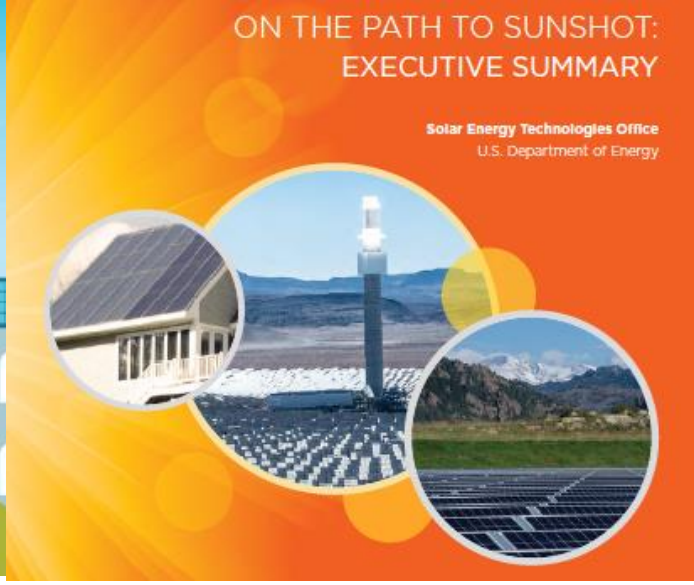
- Grid parity ≤ 2020
- Systems approach (module, BOS/soft costs, reliability, grid integration)
- Policy/markets; Utility models, Financing

Beyond Grid Parity with signficant further cost reductions (2-3¢/kW-hr)

- Next-Gen technologies: new materials, concepts and processes for high efficiency, low cost, AND manufacturability
- Novel processing technologies (low CAP-EX mfg)
- Mitigate devaluation of solar at high penetration
- Grid flexibility, energy mix, and low cost energy storage

Solar energy can also provide power to the underserved

- Multi-scale approaches to energy systems
- Distributed and dispatchable energy, microgrids, storage



- Since 2011, costs down 65% and 70% towards **grid parity goals**
- 8 reports DOE and 4 National Labs (NREL, Berkeley, Argonne, Sandia)
  - Lessons Learned; Challenges/Opportunities

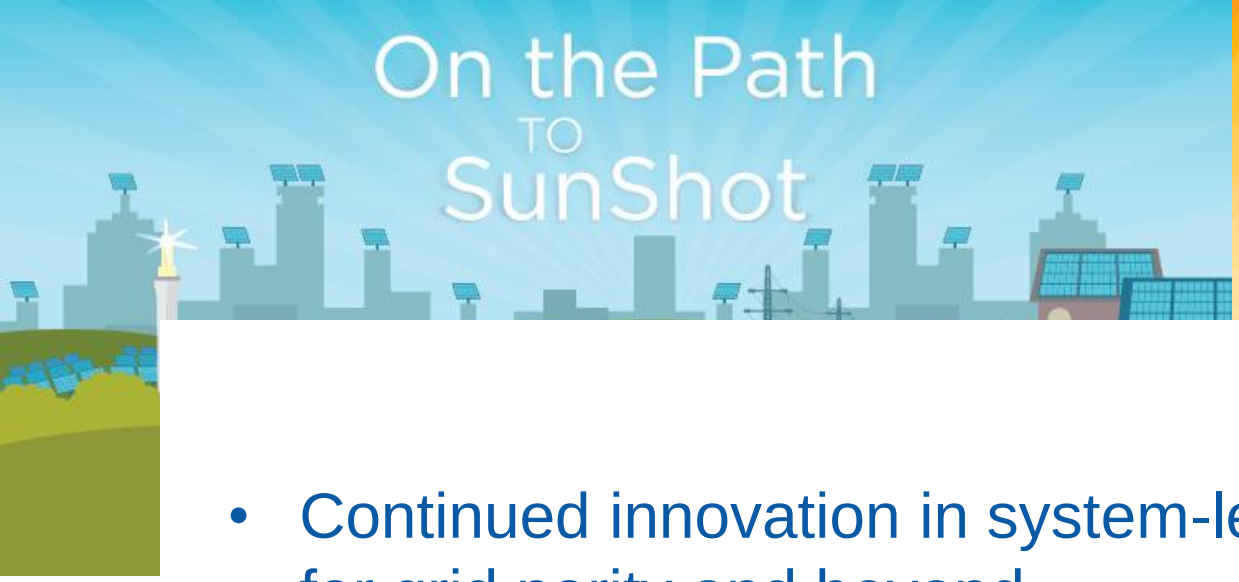
PHOTOVOLTAIC EFFICIENCY, RELIABILITY, AND COSTS
ADVANCING CONCENTRATING SOLAR POWER TECHNOLOGY

U.S. SOLAR MANUFACTURING

INTEGRATING HIGH LEVELS OF SOLAR INTO TRANSMISSION
INTEGRATING HIGH LEVELS OF SOLAR INTO THE DISTRIBUTION SYSTEM
FINANCING SOLAR
UTILITY REGULATION AND BUSINESS MODEL FOR FINANCIAL IMPACTS

ENVIRONMENTAL AND PUBLIC HEALTH BENEFITS

http://energy.gov/eere/sunshot/path-sunshot



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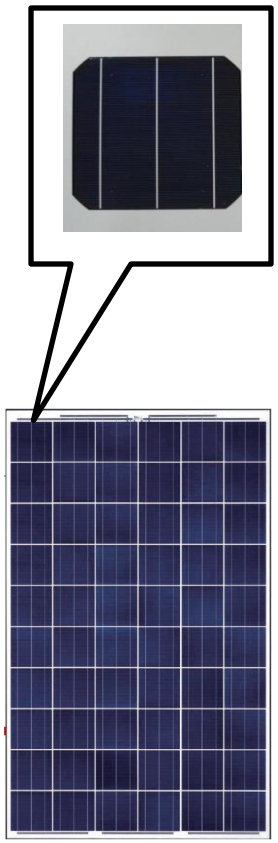
- Continued innovation in system-level S&T critical for grid parity and beyond
- Need to pursue multiple strategies to maintain the value (costs + benefits) of solar
- Increasing grid flexibility, next-gen power electronics and other strategies could enable 25% solar
- Monetizing environmental benefits could add ~3.5¢/kWh to the value of solar energy

http://energy.gov/eere/sunshot/path-sunshot

NREL Solar R&D: Materials, Cells, Modules, Systems



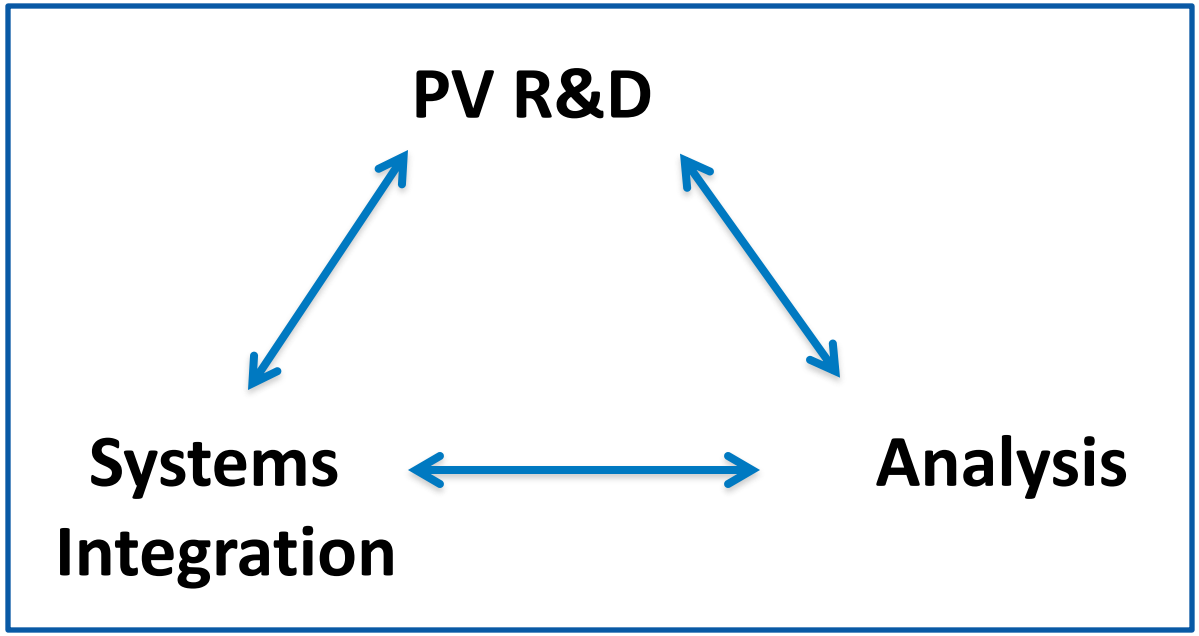
- Cost, Performance
- Manufacturability
- PV and System Reliability
- Analysis
- Balance of System & Soft Costs
- Grid Integration
- Energy Storage

NREL Solar R&D: Materials, Cells, Modules, Systems

Understand limitations and enhance performance in current systems

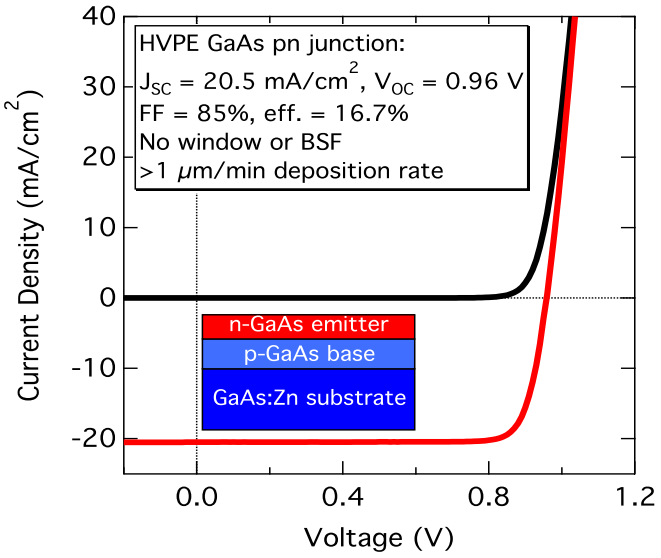
Accelerate emerging concepts

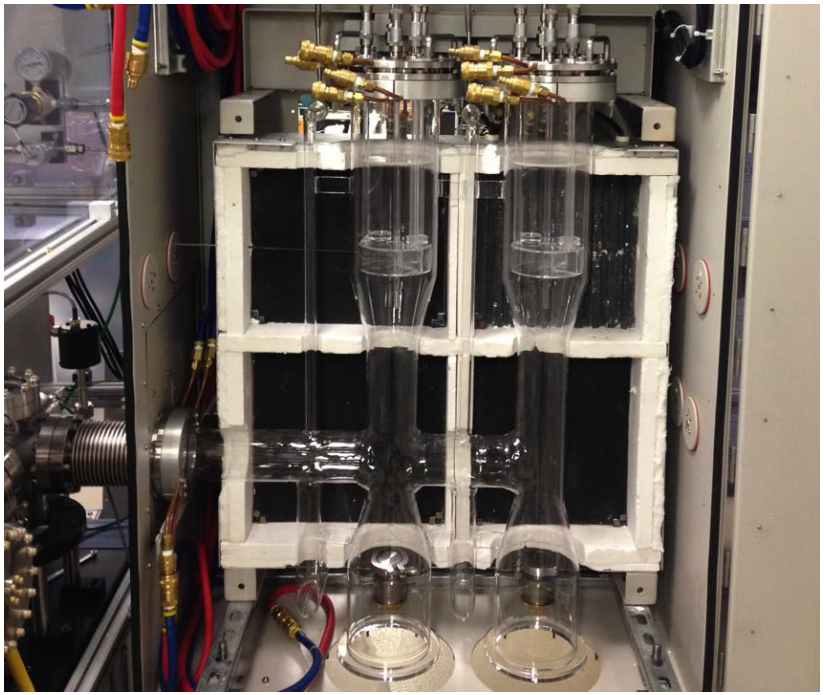
Develop next generation concepts and materials



Hydride Vapor Phase Epitaxy for GaAs

Now >23% GaAs homojunction cell (no cladding layers) :

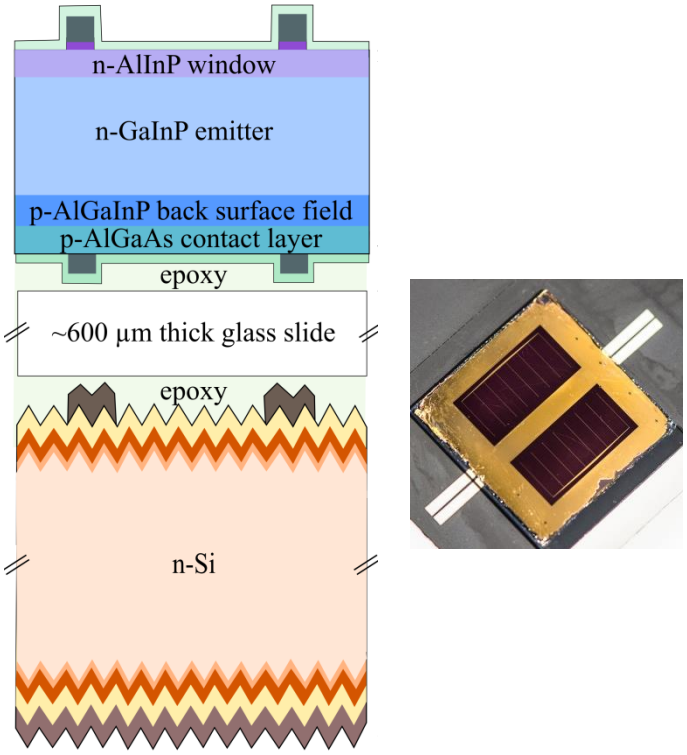




- Dual chamber HVPE reactor for Ga, In, As, P alloys
  - full 3D computational fluid dynamics (CFD) modeling
- Produced epitaxial GaAs materials at growth rates exceeding 1.8 μm/min
- Can produce flat, parallel, low-defect homo- and hetero-interfaces
- Demonstrated very high metal utilization (~70% for Ga)

A. Ptak, J. Simon, NREL

Development of World Record GaInP/Si Dual-Junction, One-Sun Solar Cell



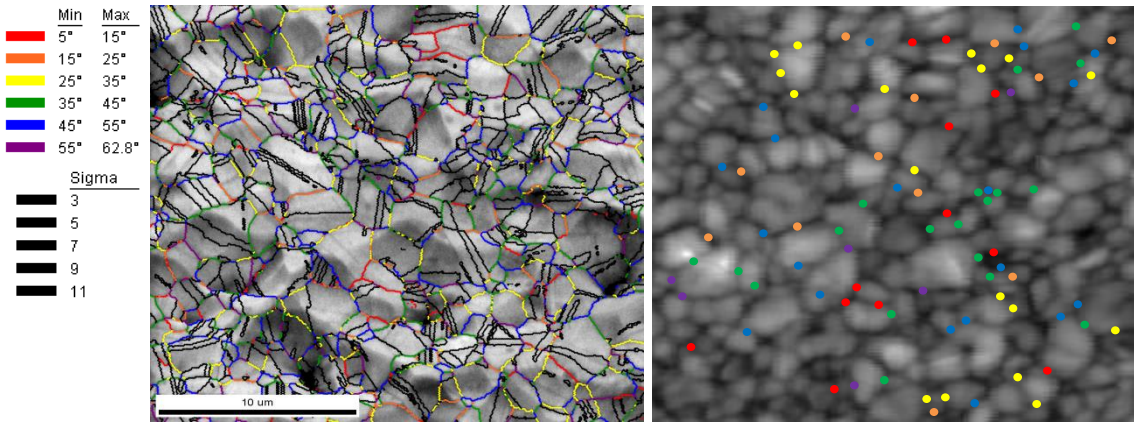
1.8-eV GaInP top junction with a silicon bottom junction, with a four-terminal interconnection

- A two-junction structure with a silicon bottom junction
- New device structure combining a III-V GaInP top junction and a silicon bottom junction,
- Demonstrated a world record 29.8% efficiency – significantly exceeding the best conventional silicon efficiency of 25.6%.
- Four-terminal structure allows ease of construction, and optimal energy production under real-world operating conditions.
- Developing an improved, manufacturable bonding

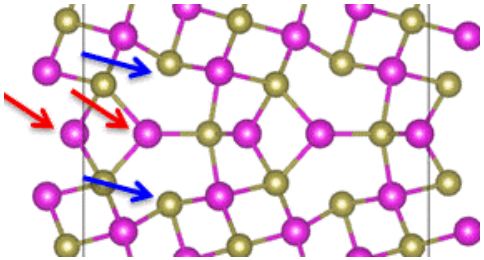
S. Essig et al., Energy Procedia 77, p. 464 (2015).

CdTe Technology

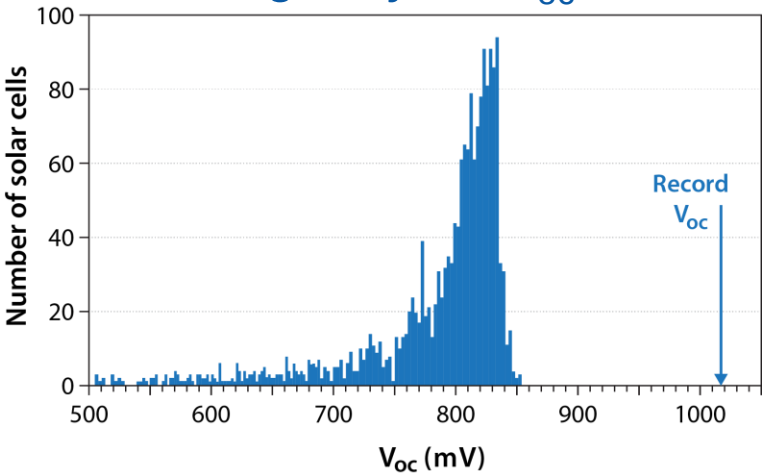
Cataloging the role of GBs, surfaces and bulk defects



Σ5 gran boundary



Overcoming 20-year V_{oc} barriers

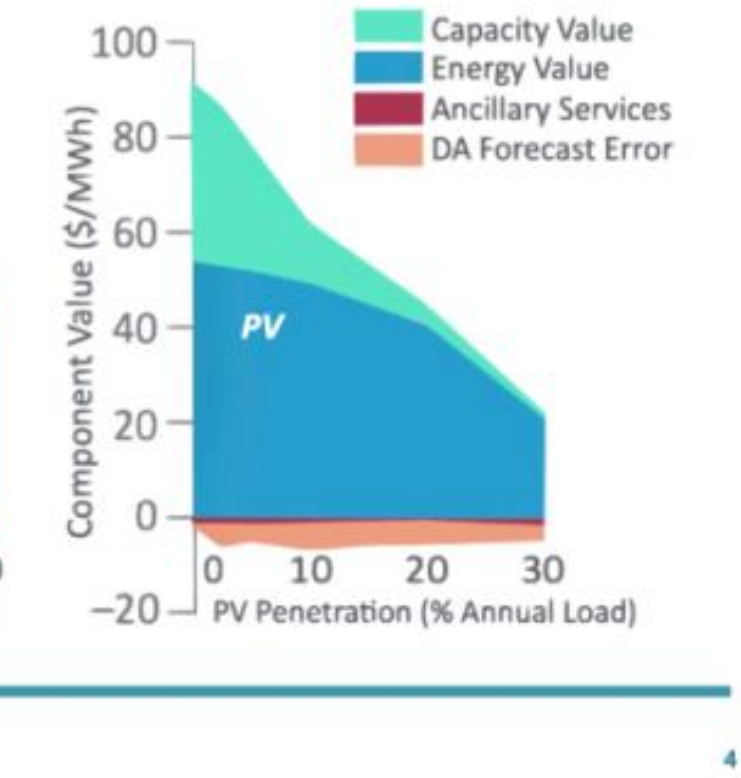


Histogram of V_{oc} values for about 2200 polycrystalline CdTe devices

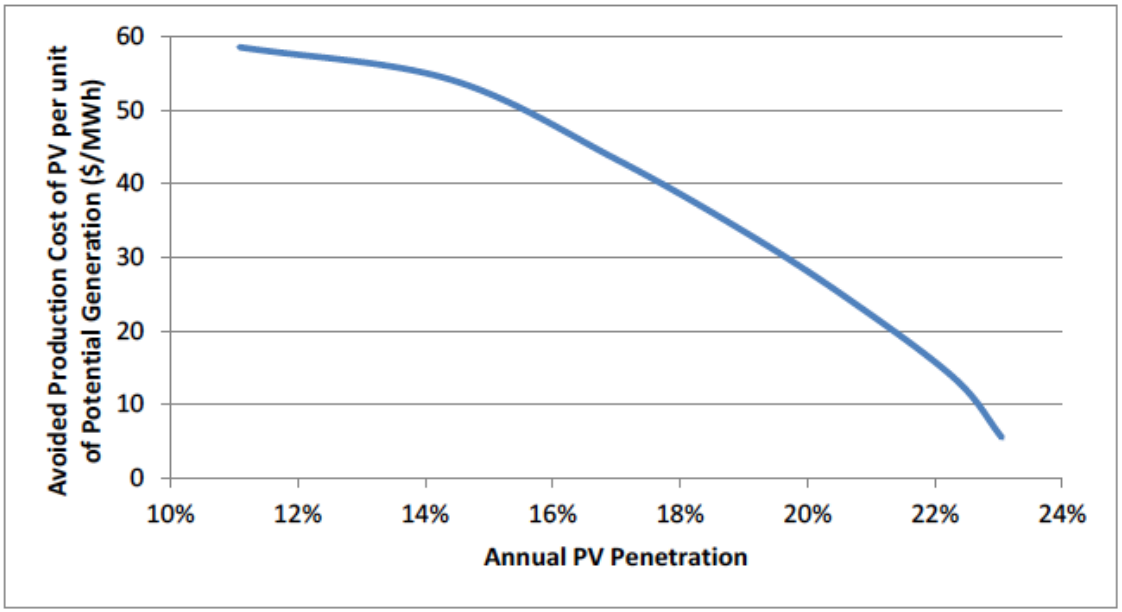
- Worked w/o universal $CdCl_2$ treatment
- Switched to anion Group V doping
- Shifted to Cd-rich stoichiometry to Improve lifetime by removing Te_{Cd} antisites, and hole density by placing P on Te sites.

T. Barnes, W. Metzger et al.
Burst et al Nature Energy, 2016

Solar Devaluation with Increasing Deployment



Mills, Wiser, LBNL, 2012

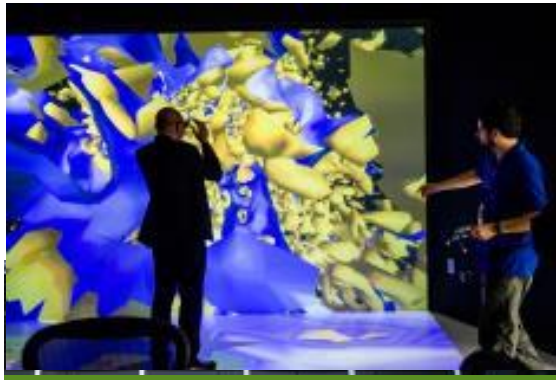


Denholm, NREL, 20126

Grid Modernization Lab Consortium

- Grid Modernization Laboratory Consortium involves 14 DOE national laboratories and industry, academia, and state and local government partner
- Energy Systems Integration Facility

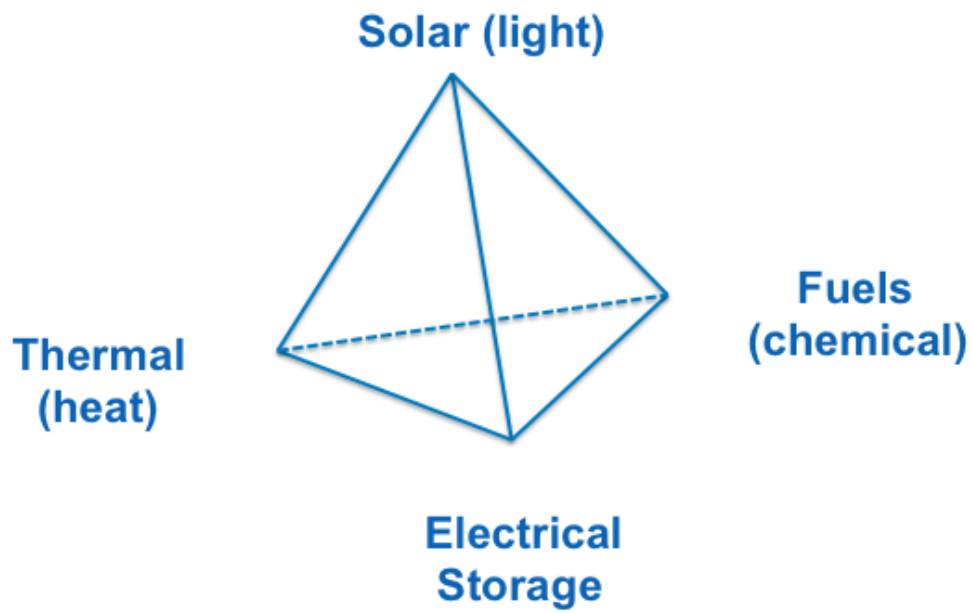
- Multiple parallel AC and DC experimental busses (MW power level) with grid simulation
- “Hardware-in-the-loop” simulation capability to test grid scenarios with high penetration of renewables
- Peta-scale high-performance computing and data management system
- Virtual utility operations center and visualization rooms



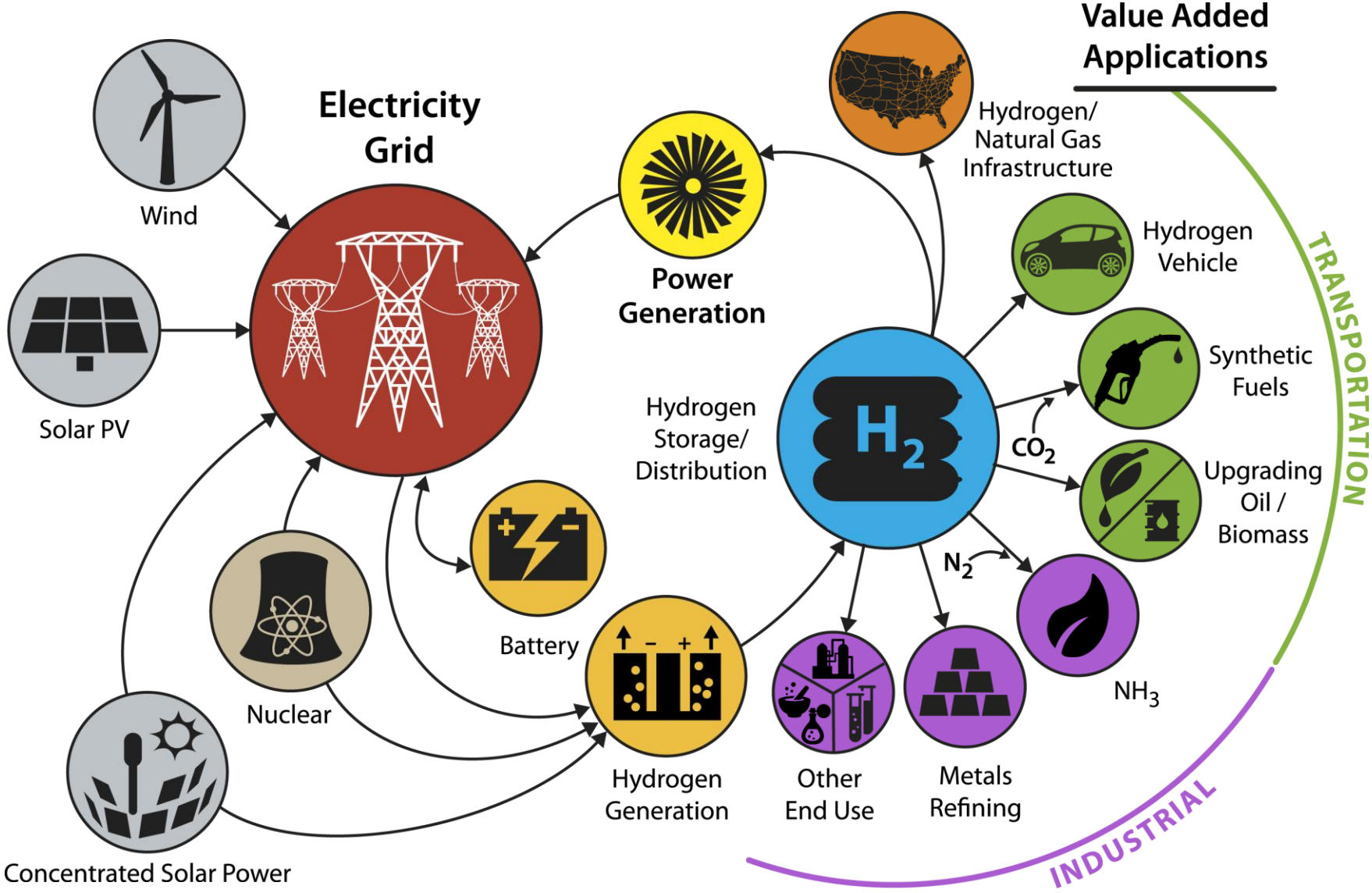
NREL Energy Systems Integration Facility (ESIF)
Research and Testing

Grid Modernization Lab Consortium

- Flexible Grid
- Vehicles to Grid, Buildings
- Water purification/desalination
- Fuels, Chemicals
  - CO_2 reduction; $N_2 \rightarrow NH_3$; C



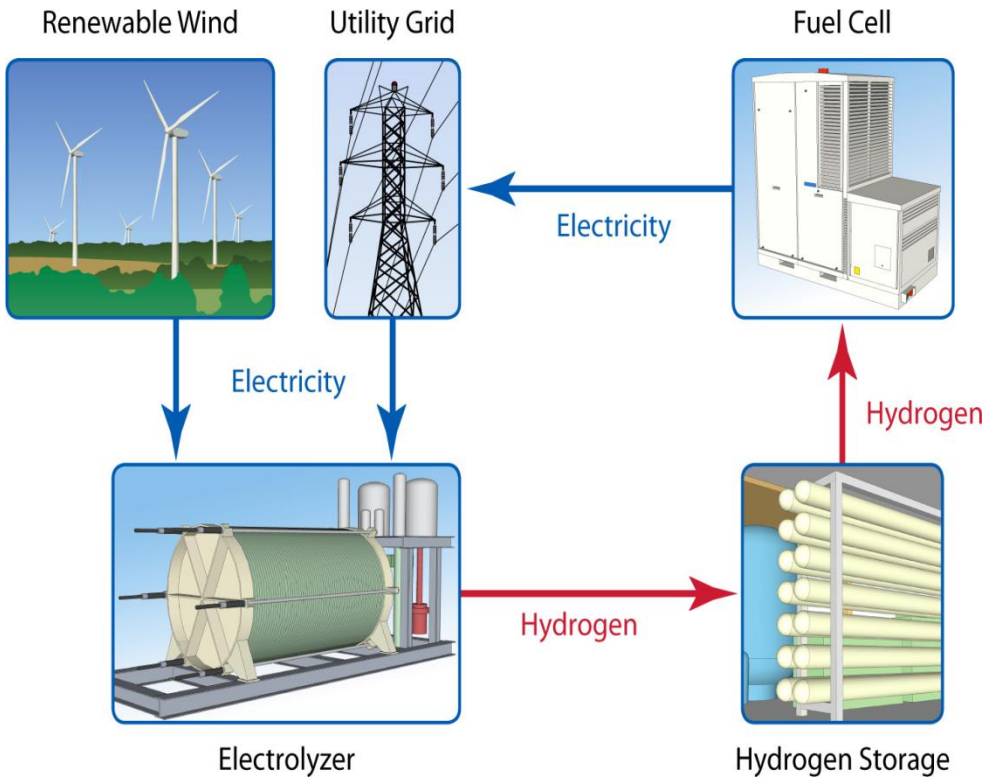
Conceptual H_2@Scale Energy System



*Illustrative example, not comprehensive

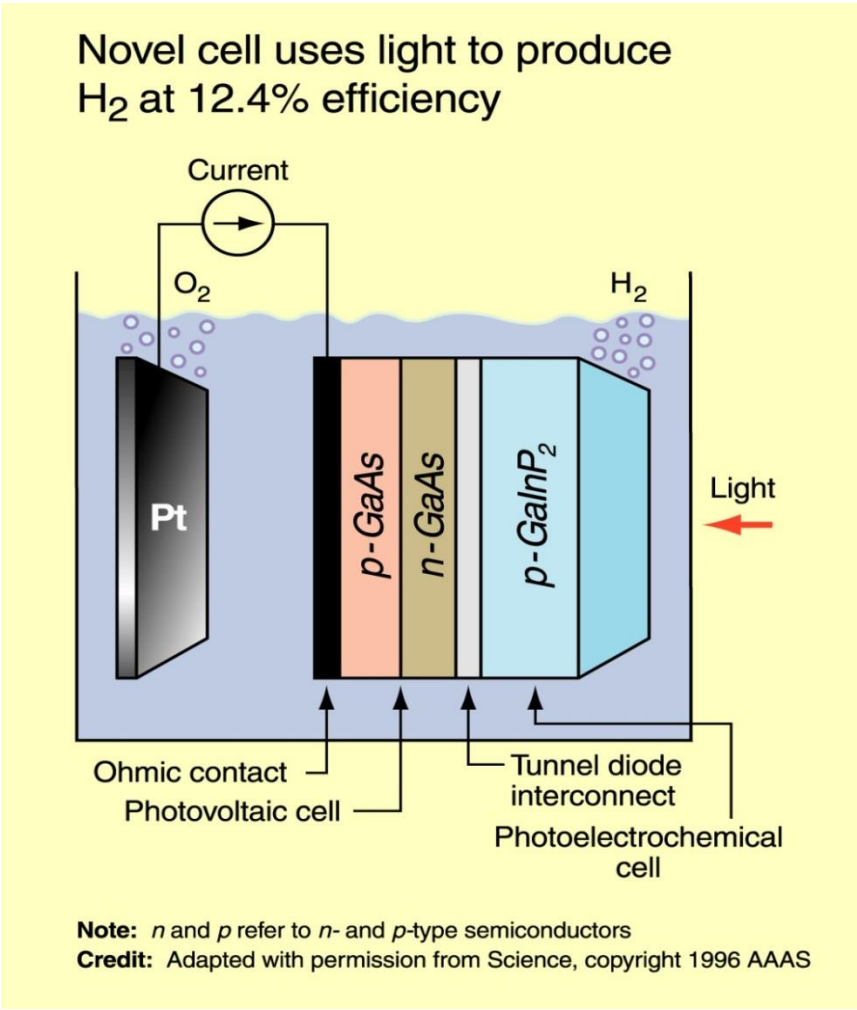
Solar Hydrogen Generation for Energy Storage

PV-Electrolysis



K. Harrison *et al*.

Photoelectrochemical Water Splitting



J. Turner *et al*.

World Record: Photoelectrochemical (PEC): $H_2O \rightarrow H_2 + \frac{1}{2}O_2$

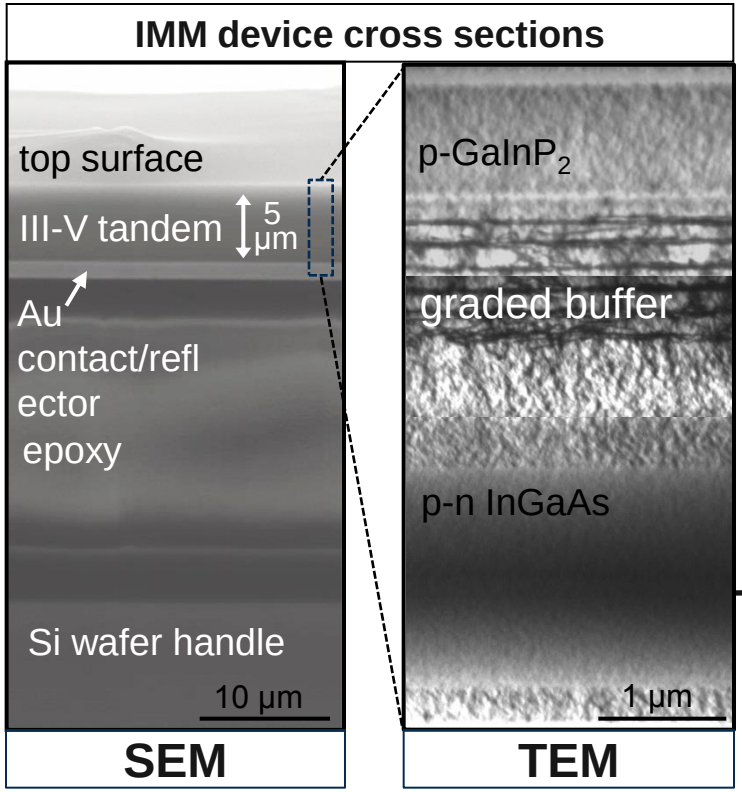
Technology

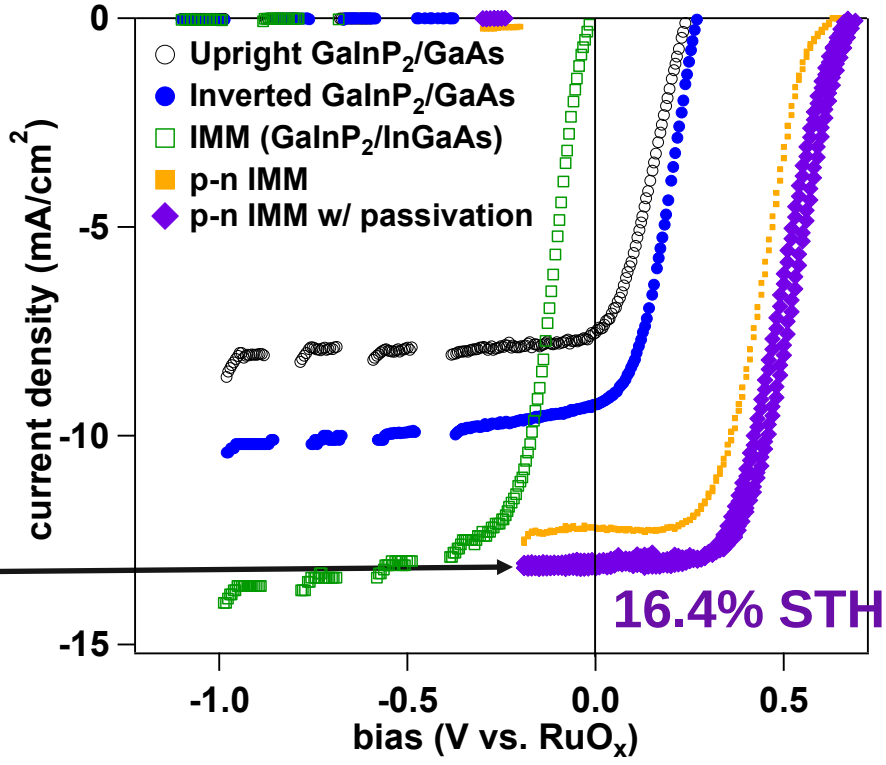
- **Inverted metamorphic multijunction (IMM) PEC** device enables more ideal bandgaps
- Grown by **organometallic vapor phase epitaxy**
- Incorporates **buried p/n $GaInP_2$ junction** and **AlInP passivation layer**

Solar-to-hydrogen Efficiency

16.4%

Benchmarked under outdoor sunlight at NREL





Credit: NREL

New ultrafast laser spectroscopy technique uncovers how photoelectrodes produce solar hydrogen from water

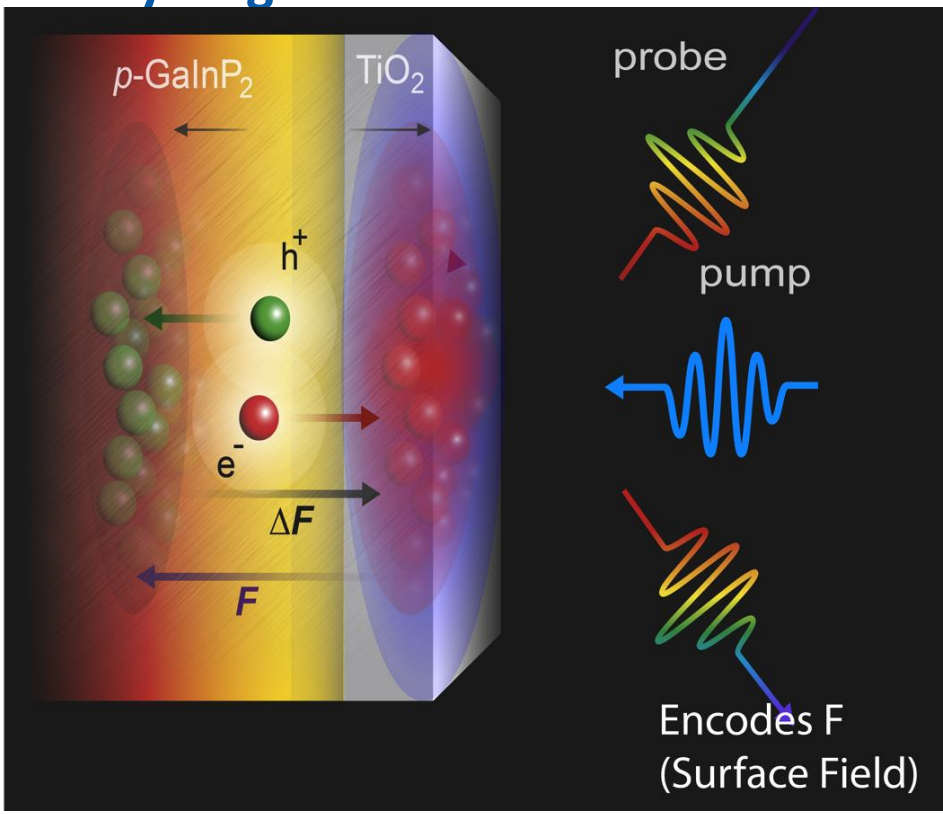
Semiconductor photoelectrodes convert solar energy directly into chemical fuels

NREL's new probe measures transient electrical fields and shows how semiconductor junctions convert sunlight to fuels

The field formed by the TiO_2 layer drives electrons to the surface where they reduce water to form hydrogen.

The oxide prevents photocorrosion by keeping holes away from the surface

This new understanding will lead to more stable and efficient solar fuel generators

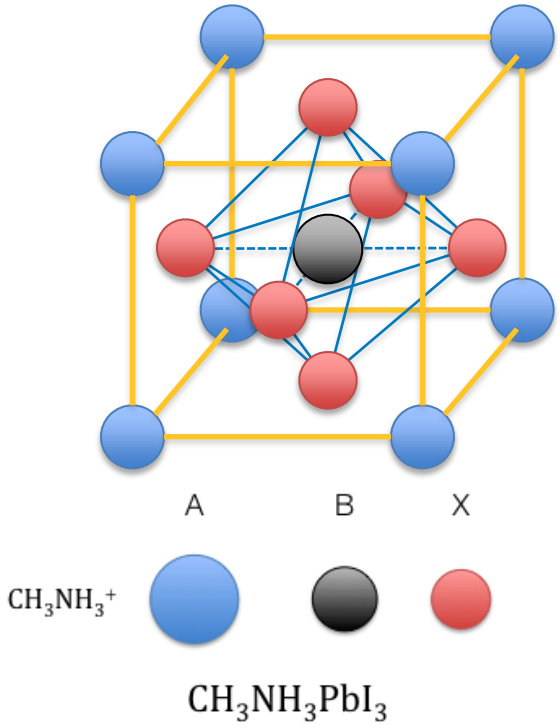


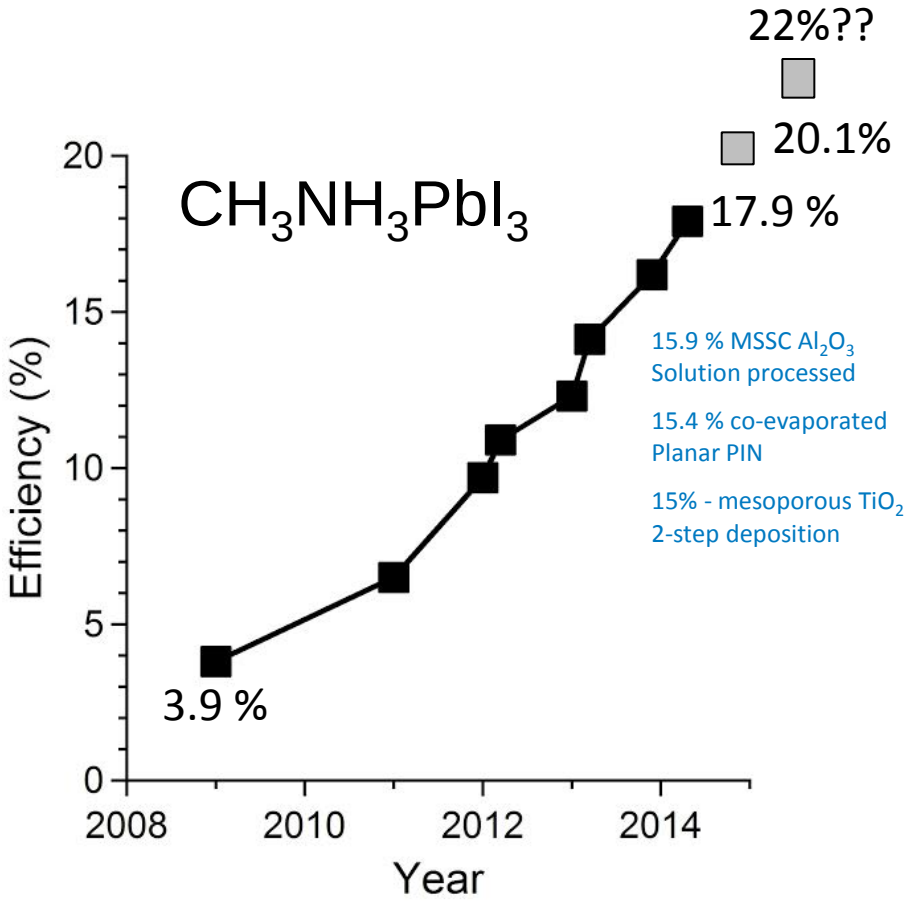
The transient photoreflectance (TPR) technique technique measures short-lived electrical fields that arise due to charges generated by light that are driven in opposite directions by the properties of the interface.

Ye Yang et al, Science **350**, 1061-1065, (2015)

Perovskites

ABX_3



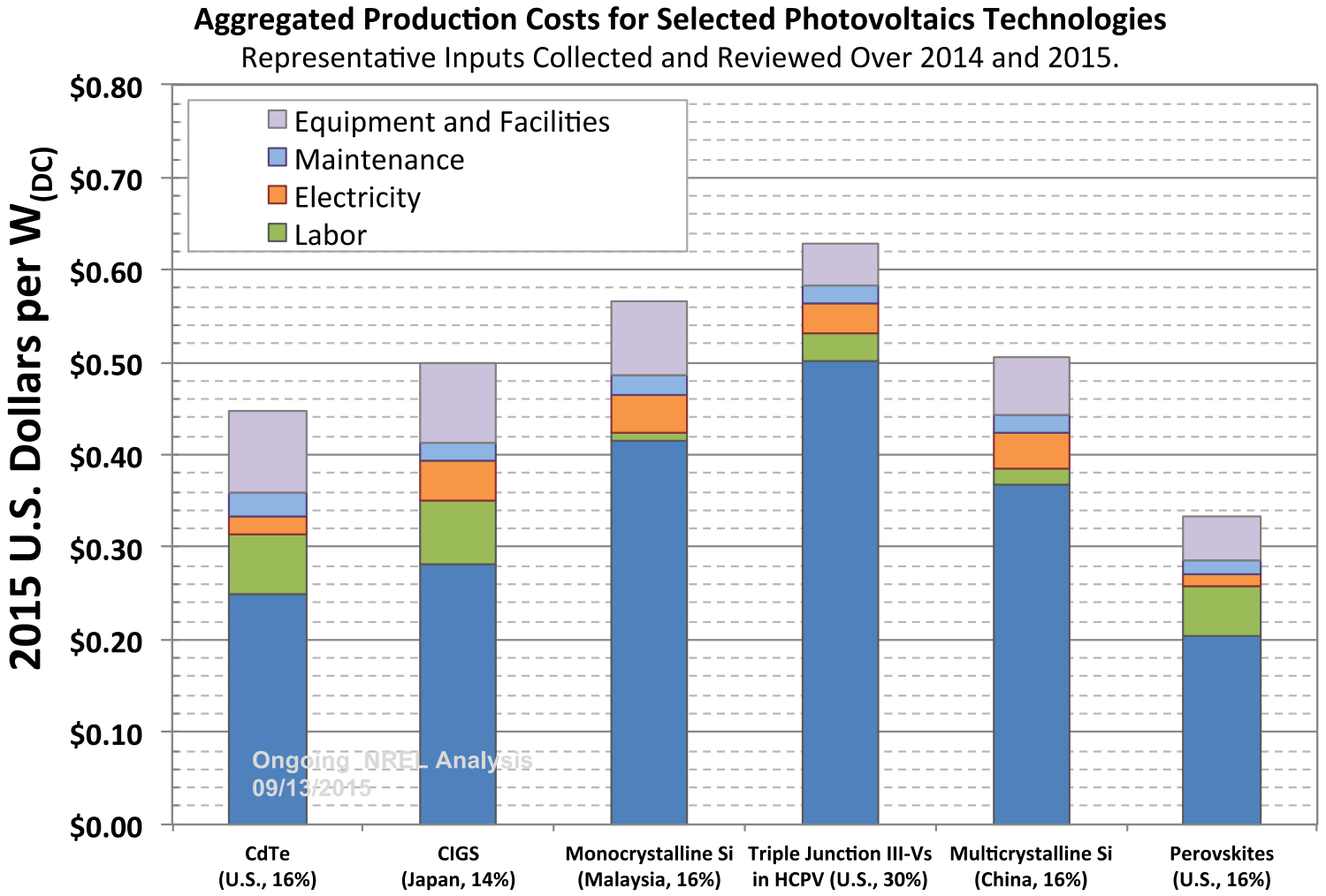


- Minority carrier diffusion lengths > 1μm in thin films, 175μm in single xtal c
- Monomolecular recombination lifetimes of 280 ns
- Minority carrier mobilities ~ 10 $cm^2/V/s$ are reasonable
- High ε_r = 60-70; Low m^* = 0.1, 0.16

Molecular approaches to solution-processable, defect-tolerant GaAs

Potential Costs

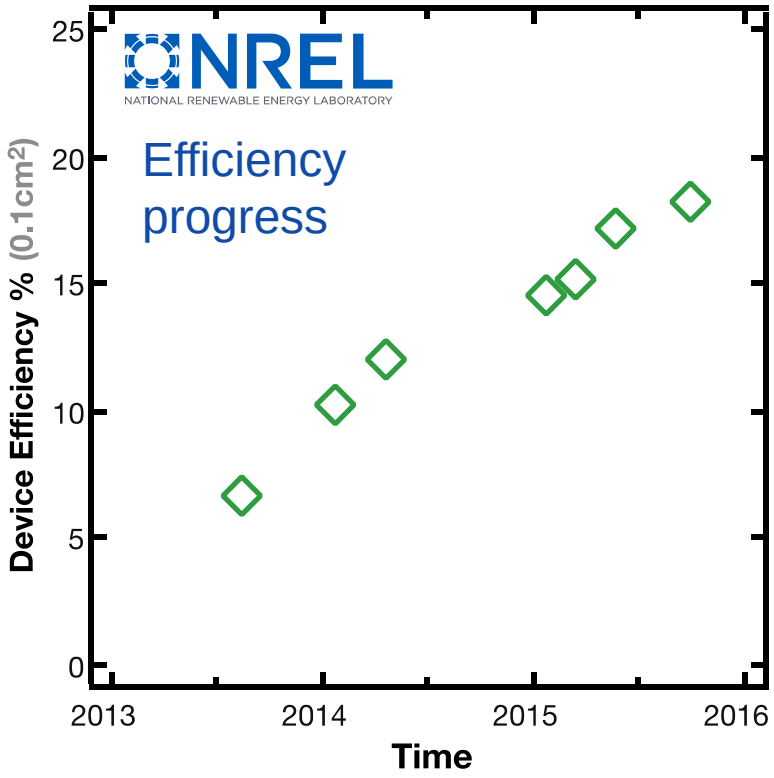
16% Perovskite compared to other PV



Stable perovskite PV meets 2020 targets (Woodhouse/NREL)

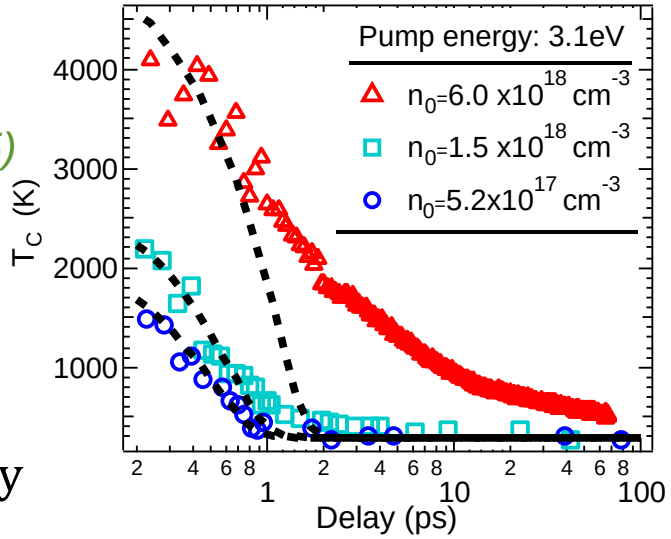
NREL R&D Themes

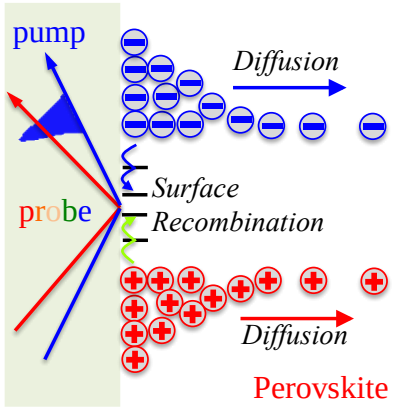
- Basic understanding of photophysics & transport
- Theory and modeling
- Discovery
- Device fabrication and characterization
- Synthesis & processing
- Interfaces
- Device operation & physics
- Stability and degradation mechanisms



Fundamental Perovskite work at NREL

- **Hot carrier dynamics**
  - Phonon bottle neck carrier cooling rate (~3x more efficient than GaAs) - *Nature Photonics (2015)*
- **Role of excitons**
  - Excitons enhance absorption and modify recombination *J. Phys. Chem. Lett.*,6, 4688-4692, **2015**
- **Surface recombination**
  - Intrinsic surface recombination velocity is very low *Nature Comm*, **2015**, 6, 7961
  - Difference in single crystal and thin film surface recombination velocities
  - Grain boundaries impact on recombination
- **Interface charge transport**
  - Substrate controlled electronics (Kahn/Princeton)
  - SAM layer for enhanced charge separation (Snaith/Oxford, Ginger & Jen/UW, Friend/Cambridge)

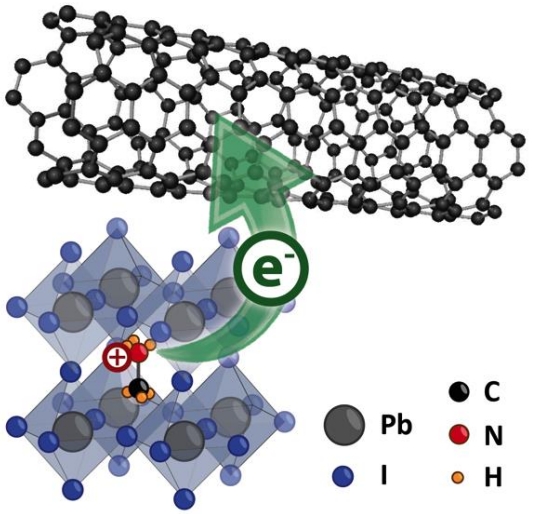




Some Perovskite Advances

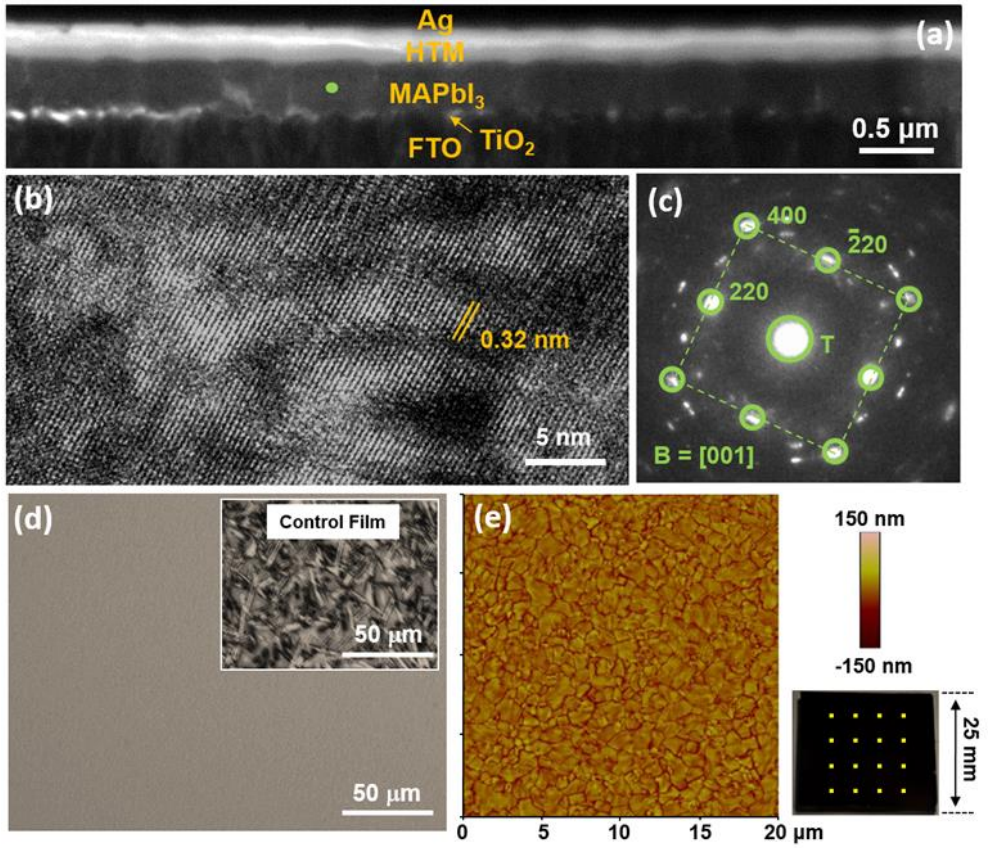
- Band bending at model SWCNT:perovskite interface using PES. Ultrafast spectroscopy shows efficient photoexcited hole extraction

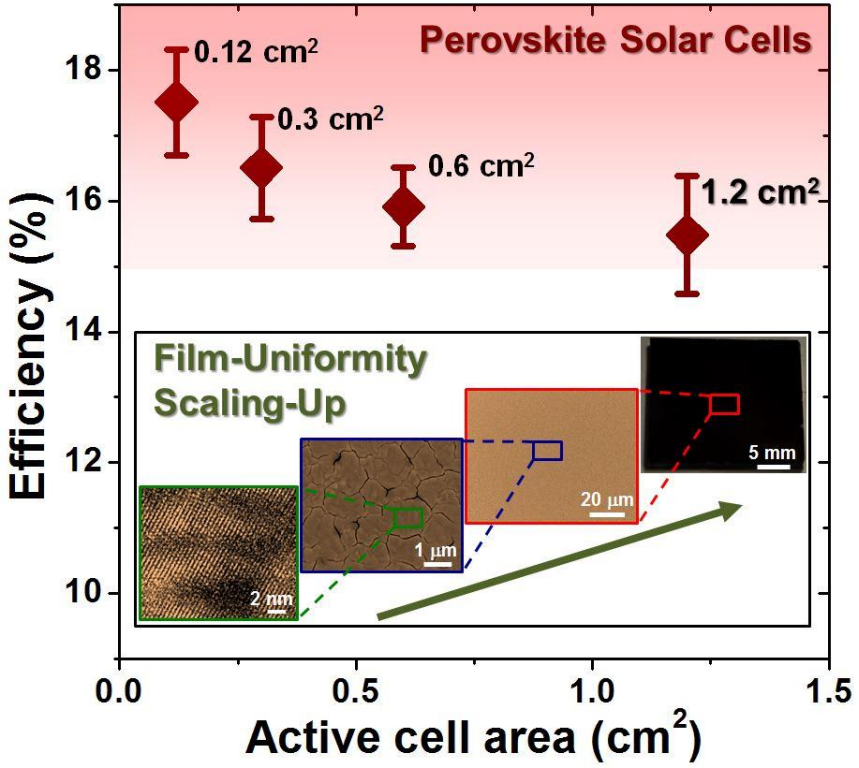
  - J.Phys. Chem. Lett (2016)



- Developed new tools and techniques to evaluate absorber structure as function of processing. Using quantitative x-ray diffraction at SLAC showed that high efficiency device structures have a large amount of material in amorphous phase.

Square-Centimeter Solution-Processed Planar $MAPbI_3$ PSC with PCE >15%





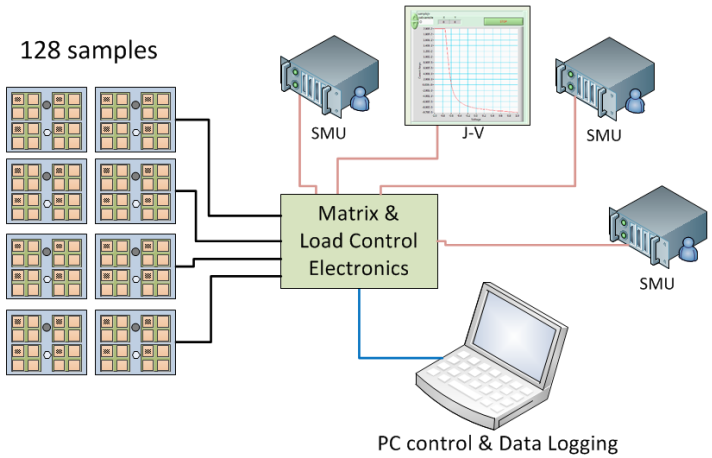
Novel solution chemistry for uniform, high-crystallinity, planar perovskite films with high-aspect-ratio grains over a square-inch area; and >15% efficiency PSC with 1.2 cm^2 active area

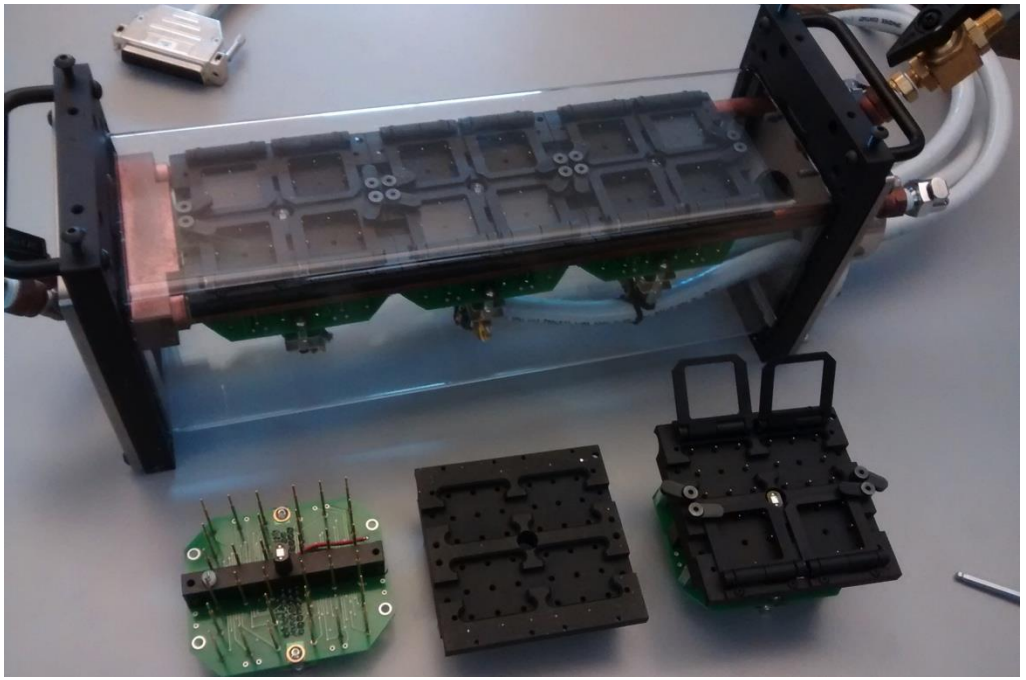
Yang, et al. Adv. Mater. 2015, DOI:10.1002/adma.201502586.

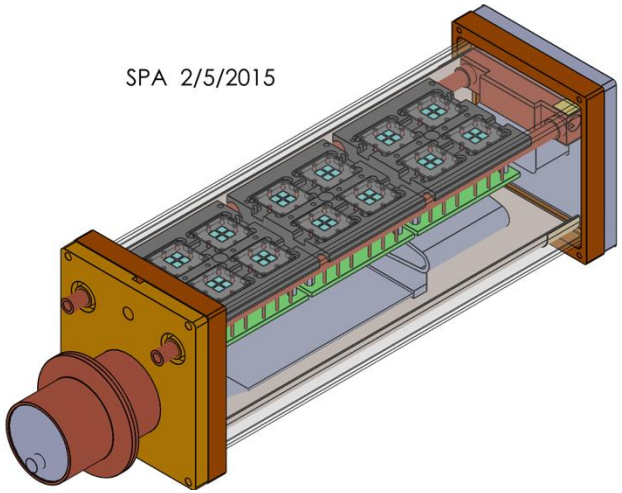
New Device Level Stability Capabilities

Functional device studies using combinatorial device testing rig

New stability parameter analysis systems







- **Flow cell geometry, controlled temperature, humidity and atmosphere**

Clean Energy Materials Challenges

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Structural Materials

lightweight alloys & composites
cars, buses, wind turbines, fuel tanks...

Optical Materials

advanced optical absorbers
PV, solar fuels, solar purifiers..

efficient solid-state converters
thermoelectrics, LED lighting..

high temp materials
CSP, combustion, geothermal...

advanced membranes
batteries, fuel cells, purifiers...

WBG semiconductors
power electronics, grid integration..

electrode materials
batteries, fuel cells, electrolyzers…

Thermal Materials

energy storage materials
thermal, thermochemical.

Electronic Materials

alternative fuels
advanced combustion, bio/synthetic fuels…

non precious catalysts
fuel cells, electrolyzers, reformers...

Chemical Materials

Numerous materials classes are vital to "Clean Energy Technologies"

From E. Miller, DOE-EERE, Dec 2014

Center for Next Generation of Materials by Design
Energy Frontier Research Center

CNGMD
Incorporating Metastability

1. Design and discover new energy-relevant materials with targeted functionalities.
2. Develop foundational theoretical, synthesis, characterization tools.
3. Incorporate functional metastable materials into MbD.
4. Develop a systematic theory-driven approach to guide synthesis.

Address four Critical Gaps limiting Materials by Design

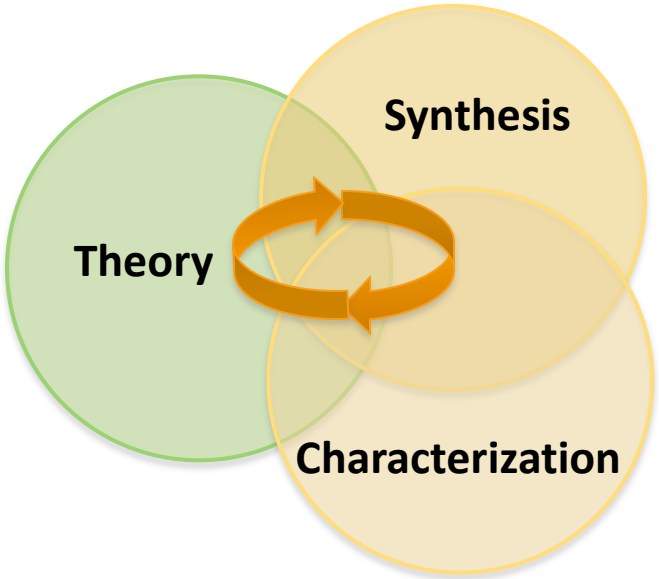
1. Multiple-Property Design
2. Accuracy and Relevance
3. Metastability
4. Synthesizability

www.cngmd-efrc.org

U.S. DEPARTMENT OF ENERGY | Office of Science

NREL NATIONAL RENEWABLE ENERGY LABORATORY | MIT Massachusetts Institute of Technology | HARVARD UNIVERSITY | SLAC NATIONAL ACCELERATOR LABORATORY | OSU Oregon State University | BERKELEY LAB

CNGMD Team Integrates Theory, Experiment, Data



LBL-Berkeley – Gerd Ceder (Chief Theorist)
Kristin Persson
NREL – Stephan Lany
CSM – Vladan Stevanovic
MIT – Alexie Kolpak

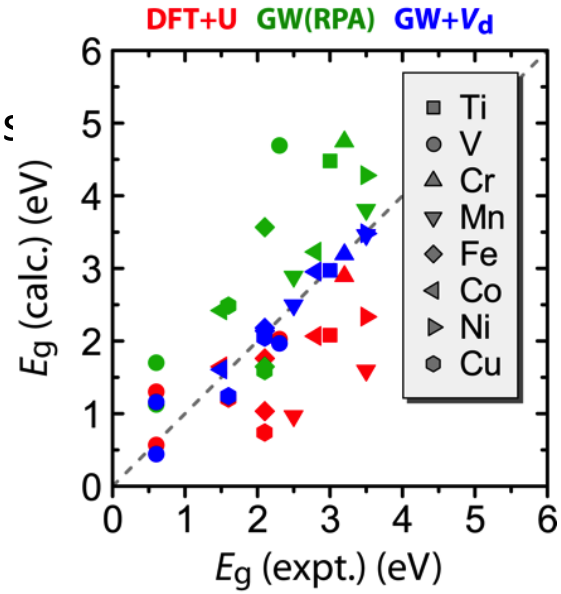
NREL – David Ginley (Chief Experimentalist)
Andriy Zakutayev
CSM – Brian Gorman
MIT – Tonio Buonassisi
Harvard – Dan Nocera
Roy Gordon
OSU – Janet Tate
SLAC – Mike Toney

NREL – Bill Tumas (Director), John Perkins (Program Integrator)

Theory Tools Development: DFT Improvements

- GW Corrections for bandgaps
  - One empirical parameter per TM atom, good trans to ternaries

    S. Lany, Phys. Rev. B **87**, 085112 (2013)



- Fitted Elemental Reference Energies (FERE) for heats of formation
  - μ^0 (FERE) = μ^0 (GGA+U) + $\delta\mu^0$ (FERE)
  - FERE reduces the mean average error (MAE) to 0.054 eV/atom ≈ 1 kcal/mol

    Stevanovic et al. Phys. Rev. B **85**, 115104 (2012)

- SCAN functional to reproduce basic MnO_2 properties
  - First functional to simultaneously reproduce strong covalent-like bonds and weaker long-range interactions
  - J. Perdew (Temple), CCDM EFRC

    Kitchaev et al. Phys. Rev. **93,** 045132 (2016)

- Neural Networks for large-scale Defects

  A. Kolpak et al., in progress

Materials.NREL.gov

High-throughput calculations

DFT level (atomic structure and total energy)

ca. 20,000 crystalline ordered materials

- Repository of atomic structures
- Thermochemistry and stability

GW level (electronic structure)

ca. 250 semiconducting and insulating materials

- So far: Mostly oxides, chalcogenides, nitrides
- Direct and indirect band gaps
- Band-edge shifts wrt DFT (defects, IP/EA, band offsets)
- Effective masses, density of states
- Optical properties, dielectric function, absorption spectra

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

High Performance Computing Center
Materials Database

HOME QUERY HELP

NREL MatDB Query

Disclaimer

Required elements subset: ○ **At most** these elements ○ **Exactly** these elements ◉ **At least** all these elements ○ **Formula:** exactly this formula

Required elements: **Forbidden Elements:**

Restrictions:

(Restriction info: energy (total energy, per atom, eV/Atom), **gap** (bandgap, eV), **gapd** (direct bandgap, eV), **netcharge** (net charge), **pressure** (final pressure, Kbar), **stable** (qhull stability)
Example: gap > 0.2 and gap < 0.8 and netcharge = 0 and stable = true

Standards: gwvd **(Examples:** fere, gwvd, post-lopt) Standards help

Keywords: **(Examples:** bandgap, enthalpy, ggau, ggauwf, gwvd, hse, hsefere, hsewf, vexp)

View: ○ General ○ Thermochemistry ◉ GW_Bandgap (Changing the **View** and clicking **Submit** will reset the standards and columns.)

Show columns: ☑ id ☑ sorted formula ☐ ΔH_f (eV/atom) ☐ Stb ☐ Stb ☐ ΔH_{Gnd} ☐ ΔH_{Decomp}
☐ ICSD SG ☑ final SG ☐ E_{tot} (eV/Atom) ☐ minID ☑ ΔEcbm ☑ ΔEvbm ☐ ε_e(IP) ☑ ε_e(TDDFT)
☐ ε_e(post-lopt) ☑ E_g (eV) ☑ $E_{g,d}$ (eV) ☐ netCharge ☐ pressure ☐ mag mom ☑ numSpin ☐ icsdId
☐ lastName ☐ standards ☐ keywords ☑ parents

Sort order: sorted chemical formula, increasing

Hide dups: ☑ (Hide duplicate FERE entries for each formula and ICSD space group.)

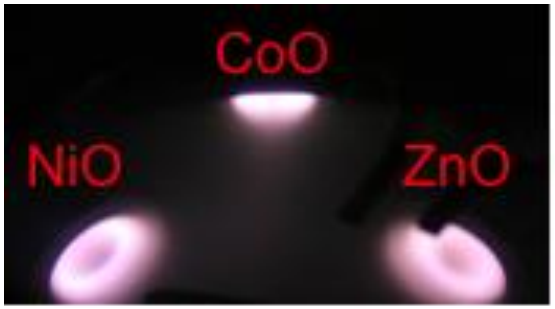
Output format: ◉ HTML ○ CSV **Submit Query**

Total matches: 238 **Page length: 100** **Page:** 0 1 2

id	sorted formula	final SG	ΔEcbm	ΔEvbm	ε_e(TDDFT)	E_g (eV)	$E_{g,d}$ (eV)	numSpin	parents	Family
8298	Al2 Cd O4	227	1.138	-1.420	2.960	5.716	5.716	1	[8982]	family 8027
9404	Al2 Co O4	227	1.602	-1.455	2.913	6.240	6.334	2	[7725]	family 8595
8686	Al2 Cu O4	141	-0.297	-1.422	3.308	2.291	2.810	2	[8699]	family 6992
7915	Al2 Mg O4	227	1.404	-2.004	2.530	8.896	8.905	1	[8837]	family 8983
8048	Al2 Mn O4	227	1.259	-1.719	2.831	6.157	6.157	2	[8622]	family 9022
8404	Al2 Ni O4	74	1.840	-1.205	3.047	5.676	5.676	2	[9310]	family 8217
9497	Al2 O3	167	1.619	-1.883	2.681	9.753	9.753	1	[7984]	family 8682
8146	Al2 O4 Zn	227	1.393	-1.696	2.767	7.554	7.554	1	[8767]	family 9110
8783	Al2 S3	167	0.248	-1.317	5.836	4.042	4.392	1	[8923]	family 7153
8038	Al2 Se3	9	0.504	-1.141	4.821	3.720	3.733	1	[9181]	family 9146
8192	Al As	216	-0.080	-0.674	7.764	2.029	3.237	1	[8876]	family 7982
9008	Al Cu O2	166	0.993	-1.079	3.898	4.385	5.077	1	[10357]	family 8973
7829	Al N	186	0.834	-1.269	3.694	6.345	6.345	1	[8714]	family 8898
8581	Al N	216	0.566	-1.262	3.752	5.152	6.268	1	[8471]	family 6936
9322	Al N	225	1.021	-1.092	4.267	6.731	7.909	1	[7518]	family 8536
7942	Al P	216	-0.004	-1.092	6.599	2.659	4.519	1	[8441]	family 8899
10491	As Ga	216	0.538	-0.528	10.607	1.625	1.625	1	[10444]	family 9770
10824	As In	216	0.268	-0.400	16.819	0.484	0.484	1	[11172]	family 10144
10728	B2 O3	144	1.701	-2.168	2.364	10.349	10.662	1	[13405]	family 10914
8515	Ba O	225	0.588	-0.859	3.569	3.369	3.369	1	[8425]	family 8229

NREL High-Throughput Experimental Tools

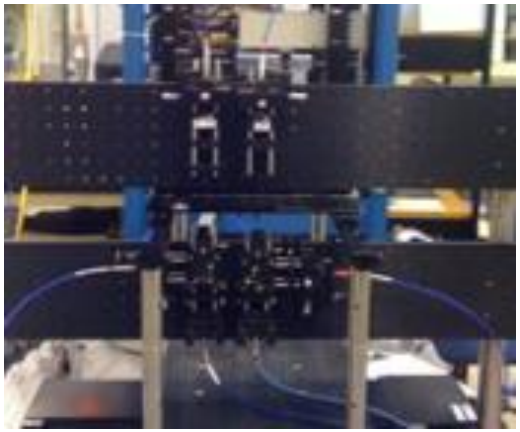
Thin Film Deposition



4 Dedicated PVD System
- 3 RF sputtering
- 1 PLD

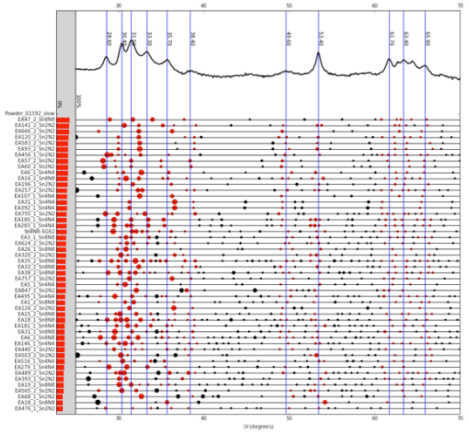
- Composition Gradients
- Thickness Gradients
- Temperature Gradients
- Ar, N, O, Ar/H_2S gasses
- Atomic S & N sources

Property Mapping



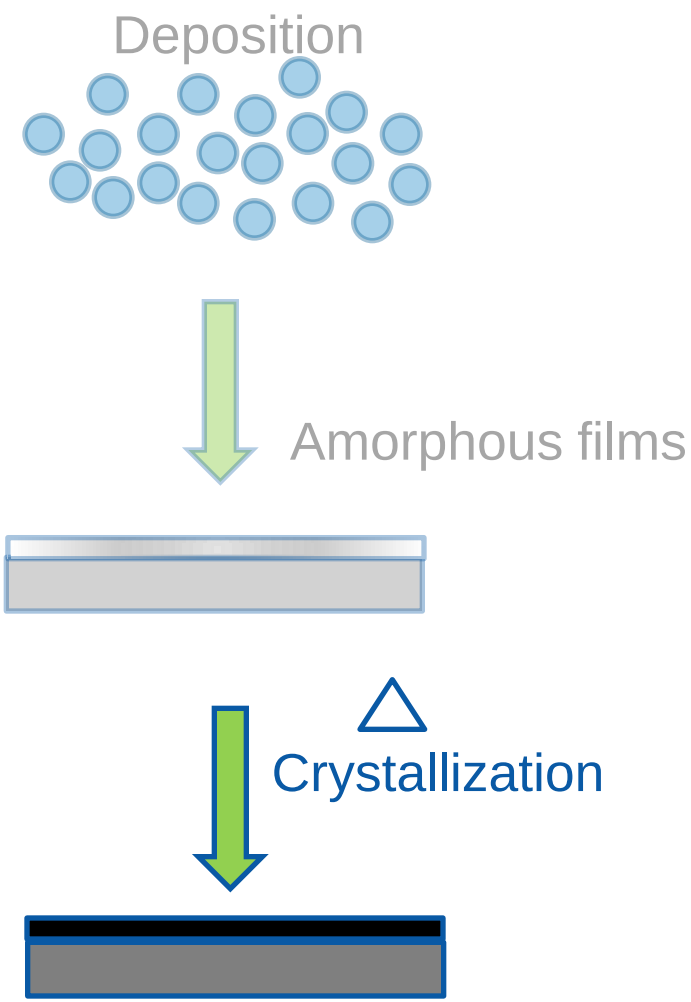
15 Mapping Tools
- Composition (XRF,RBS)
- Structure (XRD, Raman)
- Transport (4pp, Seebeck)
- Optical (UV-Vis, IR,PL)
- Surface (KP, XPS/UPS)
- Microscopy (SEM, AFM)

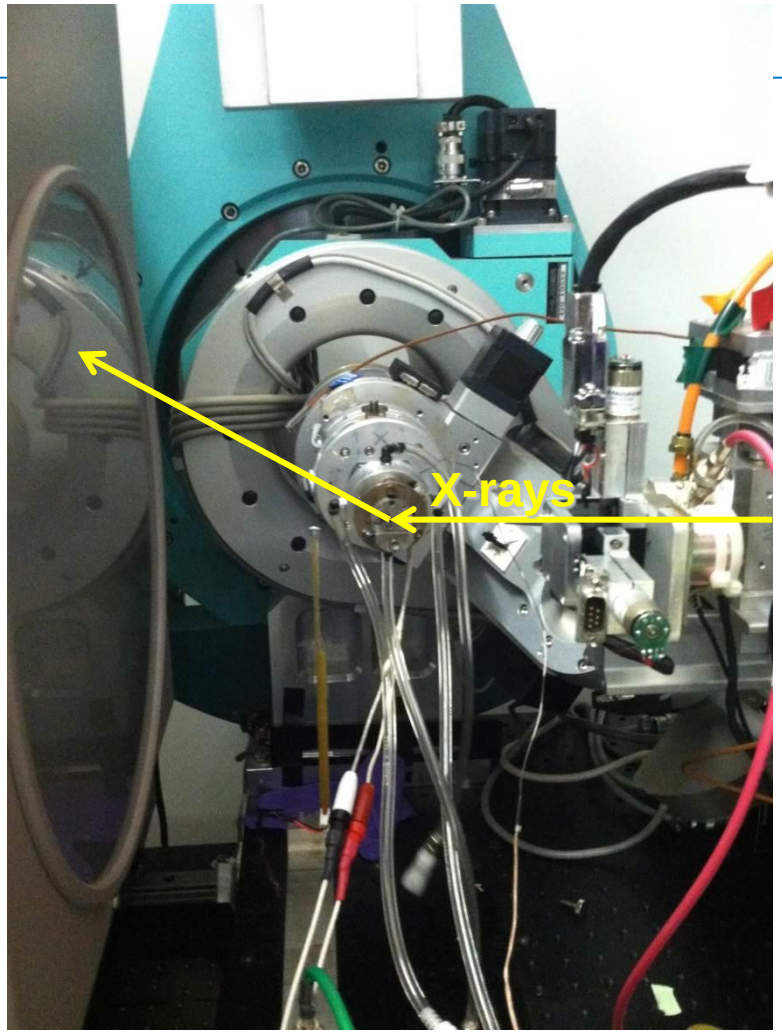
Analysis & Visualization



Advanced Data Tools
- NREL Data Network
- Igor PRO framework
- Extensible
- User-assisted analysis
- Data mining/analysis

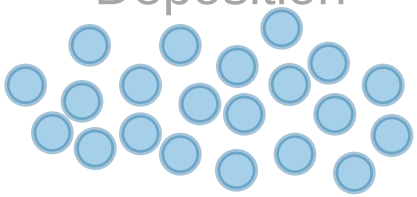
In-Situ Tools at SLAC: In-situ crystallization of amorphous films



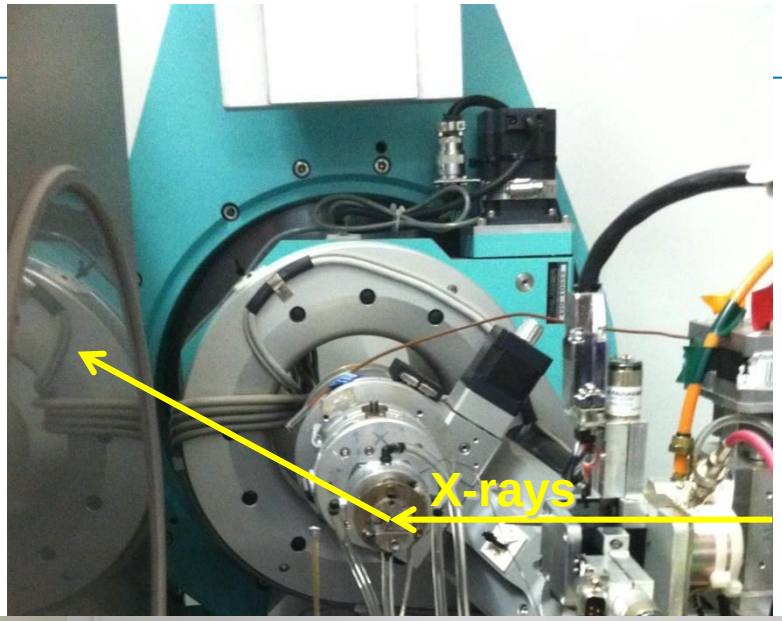


In-Situ Tools at SLAC: In-situ crystallization of amorphous films

Deposition



Amorphous films



Some of the CNGMD team with various SLAC tools

Two Main Approaches to Materials by Design

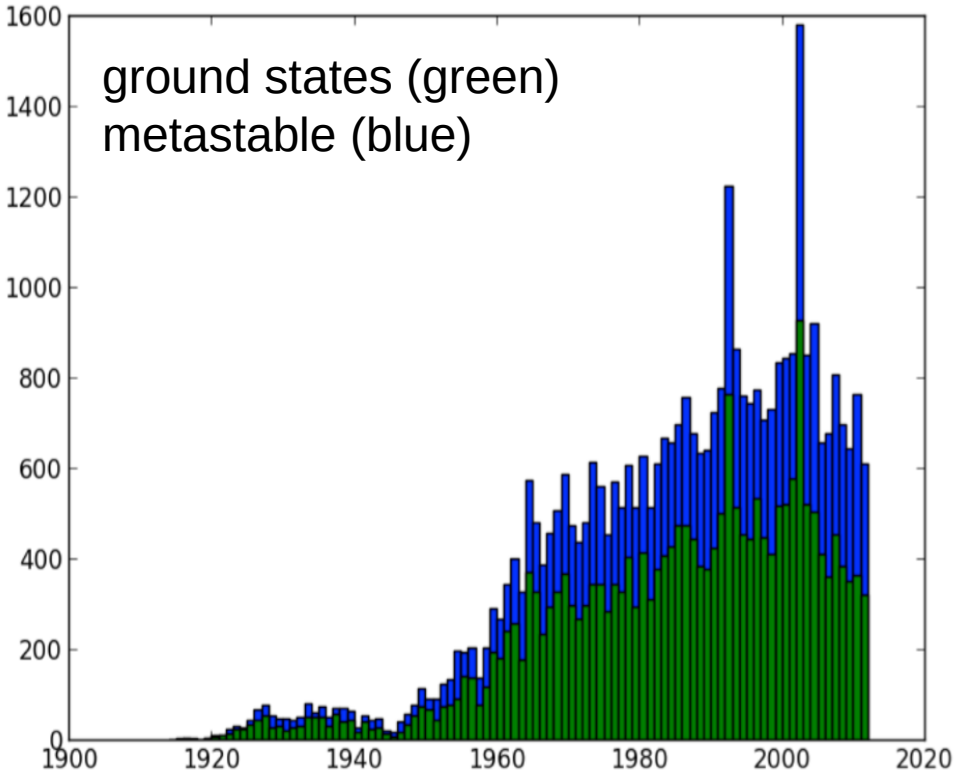
Design by Design Principles

- Many material systems with known structure and composition (e.g. ICSD)
- Functionality unknown
- Search via design principles for targeted functionalities

Missing Materials

- Many material systems, but structure unknown
- Many (~ 50–100) possible configurations, requiring energy minimization and stability analysis
- Target properties: first existence, then other properties

Metastable Compounds



G. Ceder, and K.A. Persson
C. Wolverton, et al. Journ of Mater, 65, 1501 (2013).

Two Main Approaches to Materials by Design

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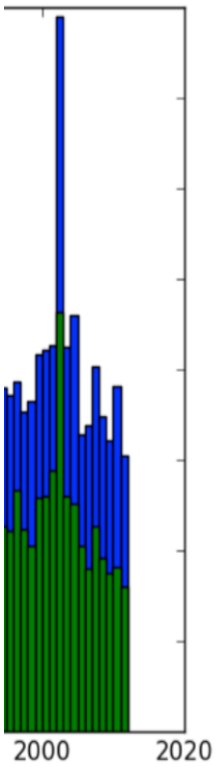
define search goals
and search space

High-throughput
materials search

Focused studies,
theory and experiment

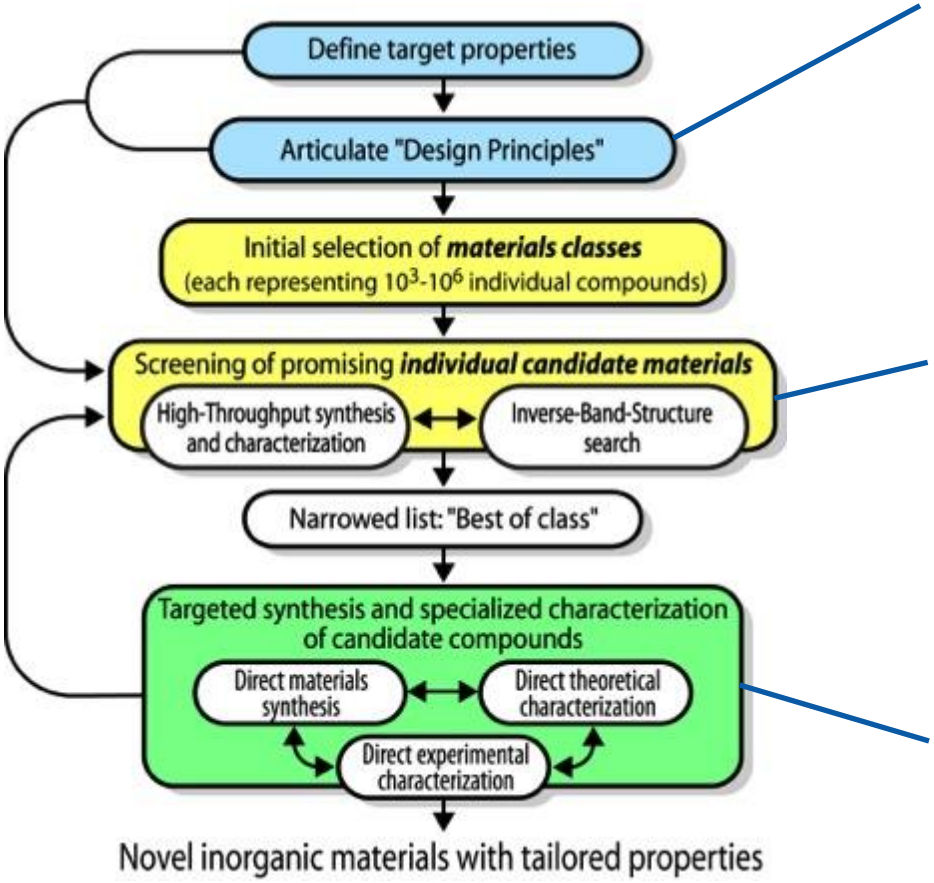
nds



501 (2013).

Implementing Inverse Design

Designing p-Type Ternary Oxides

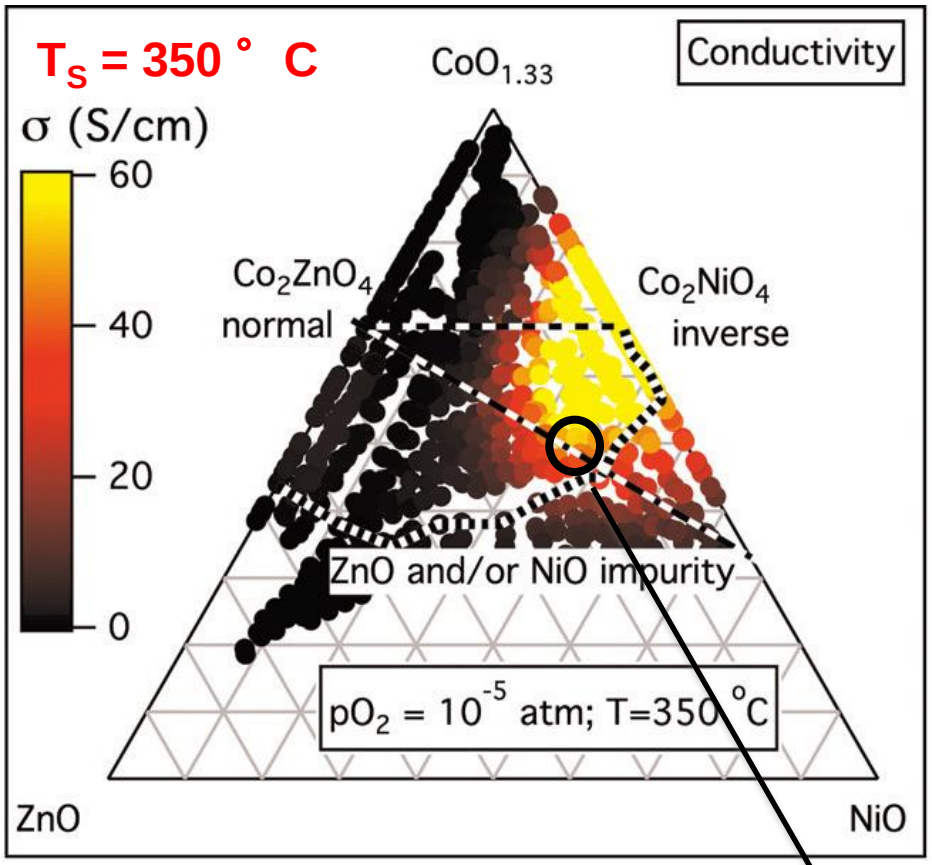


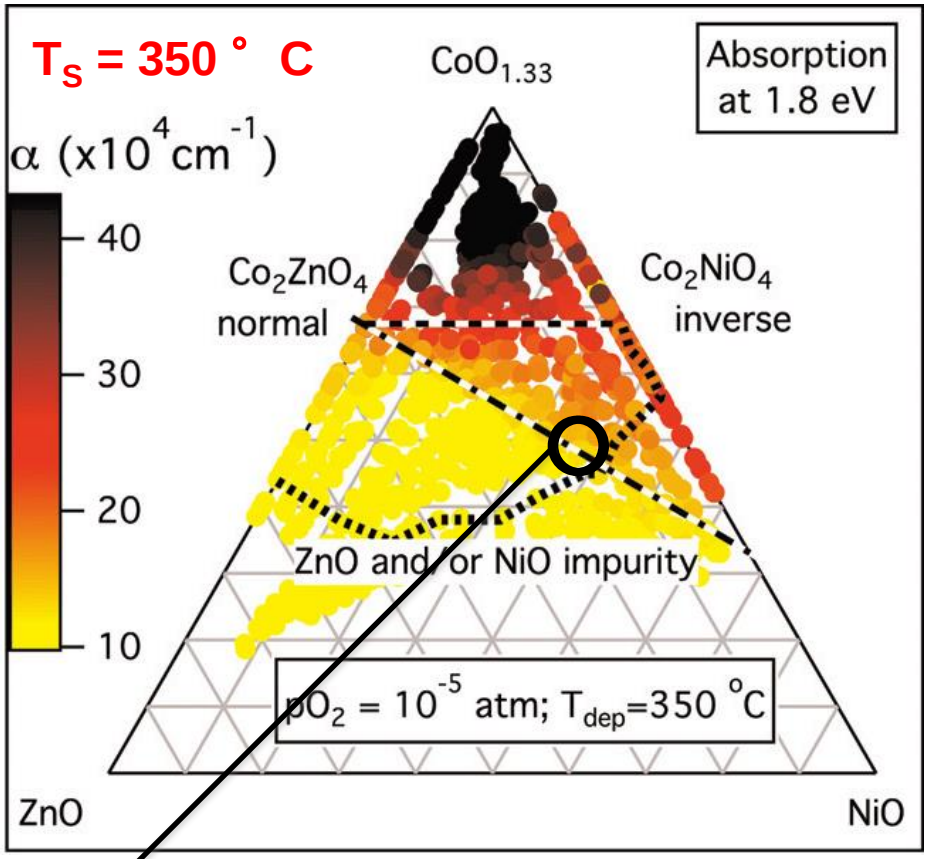
DEVELOP p-type TCO design principles

SEARCH A_2BO_4 w.r.t. design principles

IMPROVE Co_2ZnO_4 based on design principles

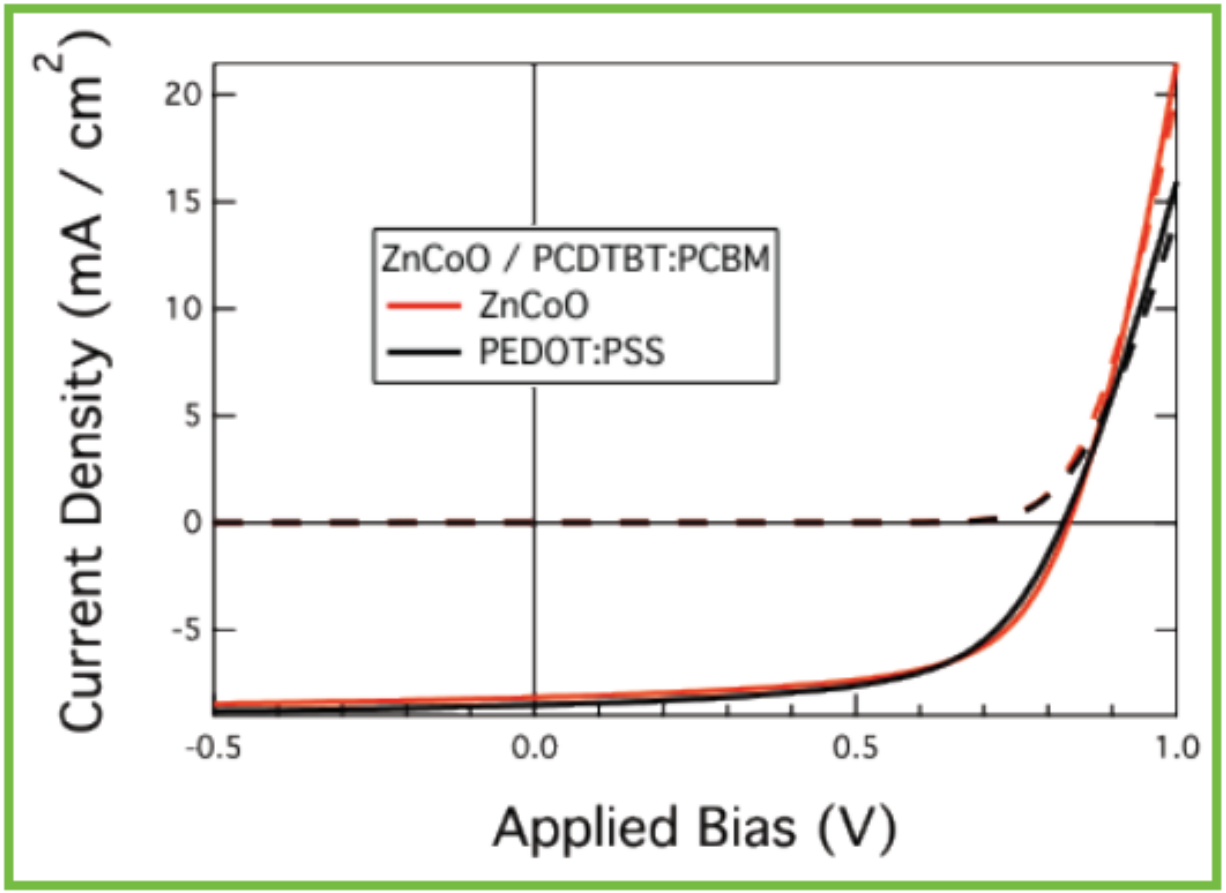
Optical and Electrical: Region of Interest

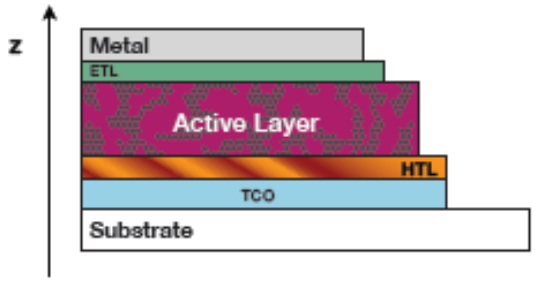


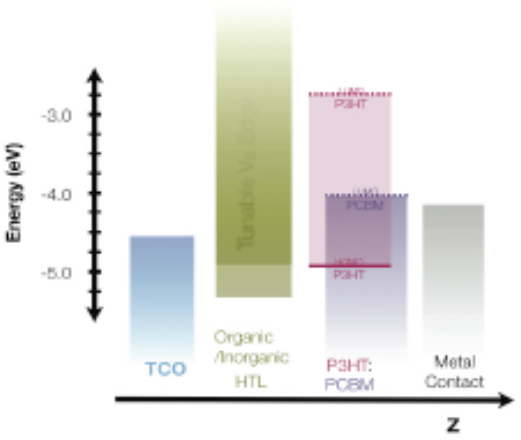


Optical **and** Electrical properties optimized in composition region

Zn-Co-O as a hole transport layer (HTL) for OPV



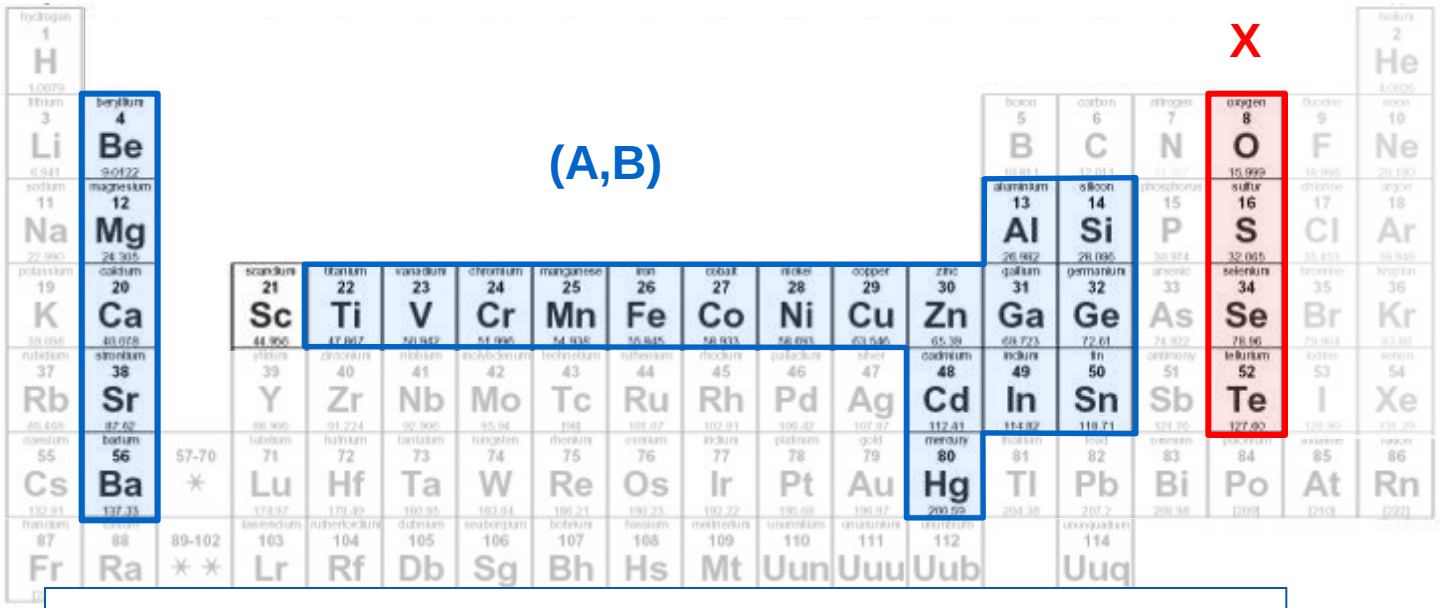




- Performance comparable to PEDOT:PSS **on the first try**

"Zn-Ni-Co-O wide-bandgap p-type conductive oxides with high work functions"
A. Zakutayev, J. D. Perkins, P. A. Parilla, N. E. Widjonarko, A. K.Sigdel, J. J. Berry and D. S. Ginley, MRS Communications (2011)

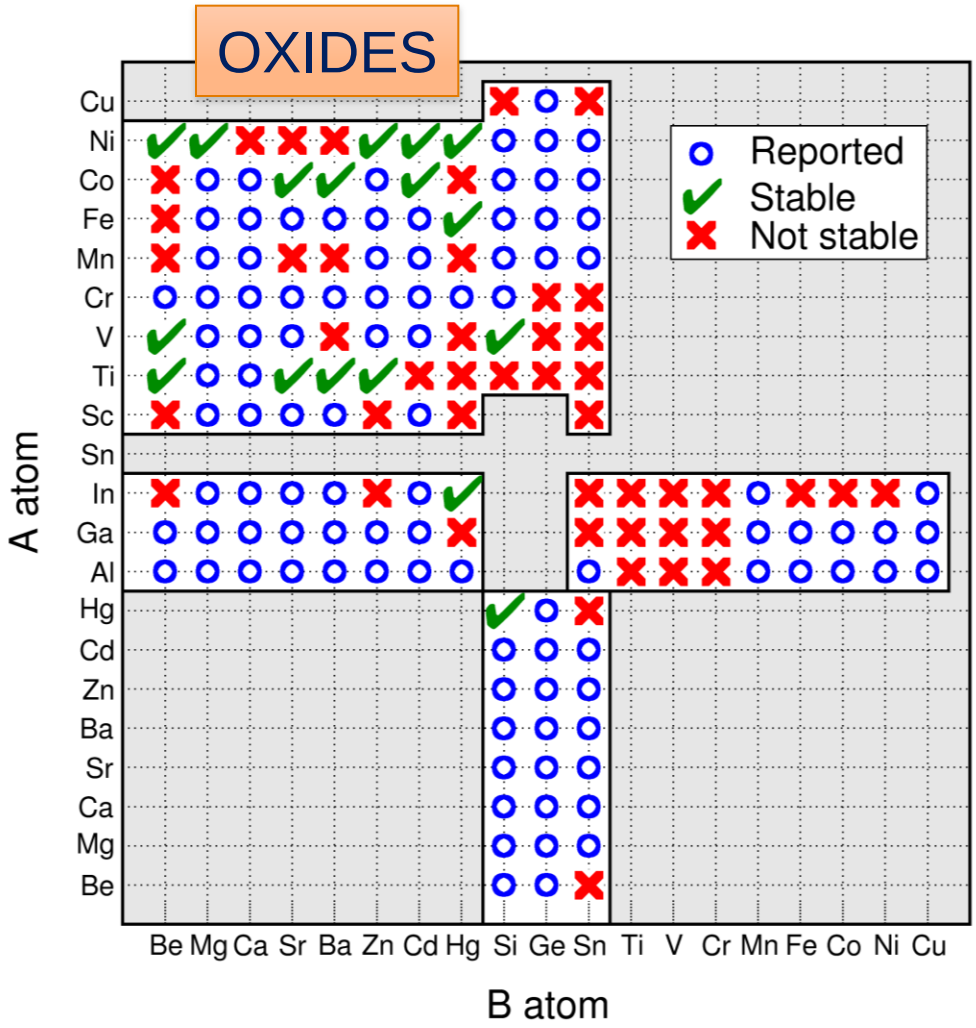
High-throughput Discovery of New A_2BX_4 Compounds



Rules:(1) only one transition metal at a time
(2) respect possible oxidation states

Total 656 possible combinations
250 are reported
406 are not reported (“missing compounds”)

Predicted New A_2BO_4



7 already predicted by Hautier *et al.*, Chem. Mater., 2010

Out of 63 missing oxides
46 not stable
17 stable

Newly predicted:

Hg_2SiO_4 In_2HgO_4
Ti_2BeO_4 Ti_2SrO_4
Ti_2BaO_4 Ti_2ZnO_4
V_2BeO_4 V_2SiO_4

A_2BX_4 search:
~80000 individual total-energy calculations
(incl. structures and magnetic configurations)

CID Predicted Ternary Materials

A_2BX_4 materials main group and 3d elements:

Out of 684 variations, 429 are unreported

100 predicted stable, 11 undetermined, and 318 predicted not stable

X. Zhang, V. Stevanovic, M. d'Avezac, S. Lany, and A. Zunger, Phys. Rev. B, 86, 014109 (2012)

ABX materials with 8 electrons:

Out of 714 variations, 488 are unreported

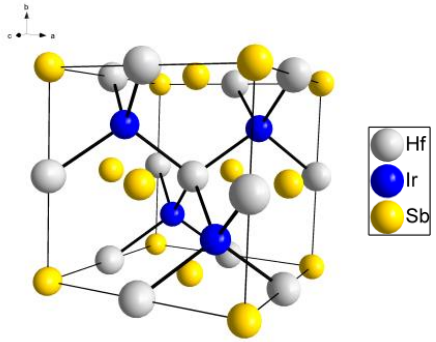
235 predicted stable, 18 undetermined, and 235 predicted not stable

*X. Zhang et al., Adv. Funct. Mater. **22**, 1425–1435 (2013).*

Identification of ABX ternary materials

HfIrSb, ZrRhBi, ScRhTe, TaCoSn, TaIrGe, VIrSi, VRhSi and HfRhP have been shown to crystallize in their predicted crystal structure.

Example:
HfIrSb
F-43m



Predicted crystal structure

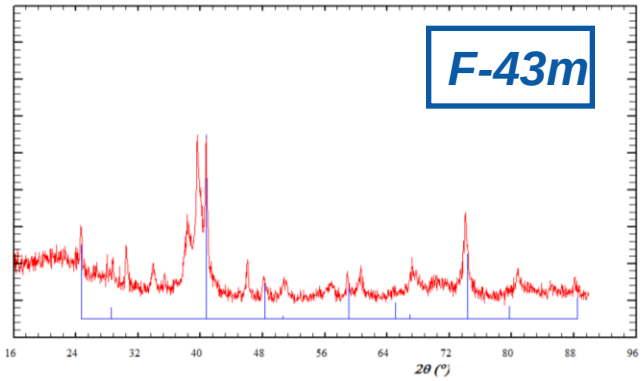
The symmetry of a predicted stable compound makes possible:

↓

1) Simulation of diffraction pattern

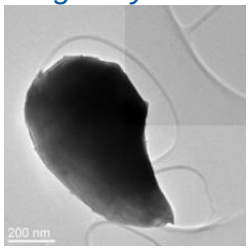
↓

2) Fast identification in the experimental pattern

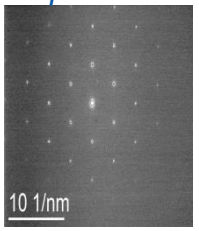


With Confirmation By Electron diffraction

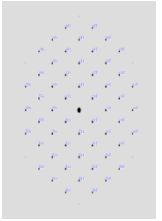
Single crystallite



Experiment



Simulation



(110) zone

Fast identification in multiphasic sample

X. Zhang et al. Nature Materials

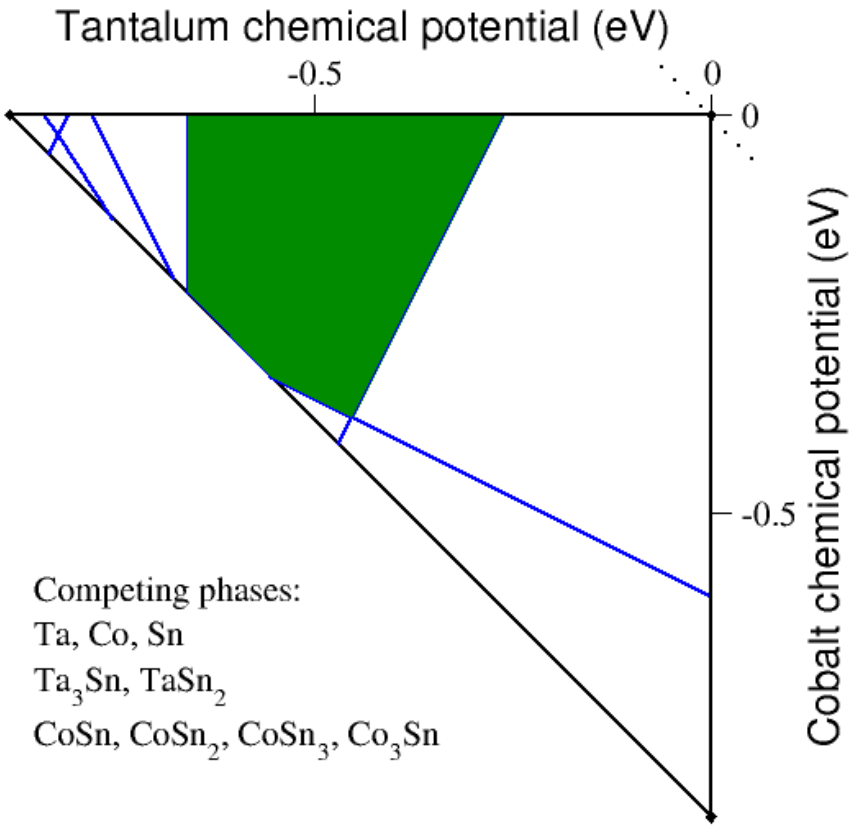
Missing TaCoSn Compound

Not known in ICSD or ICDD

Large stability range

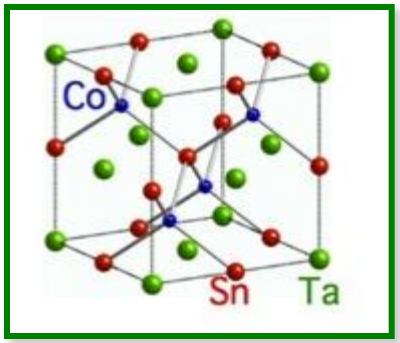
Predicted to have semi-conducting gap ~ 1.3 eV

(GGA + U)

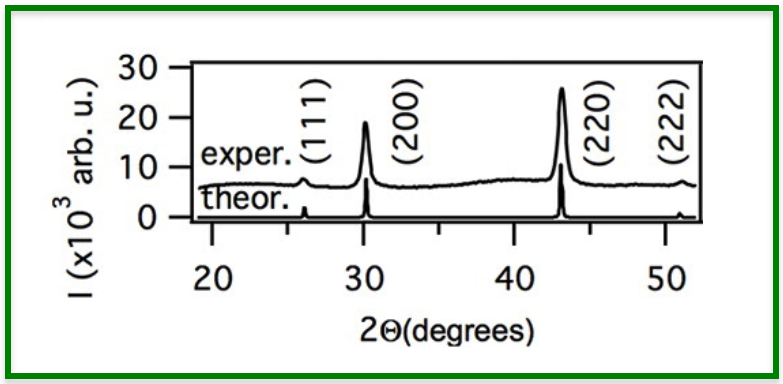


Validation: growth of new TaCoSn

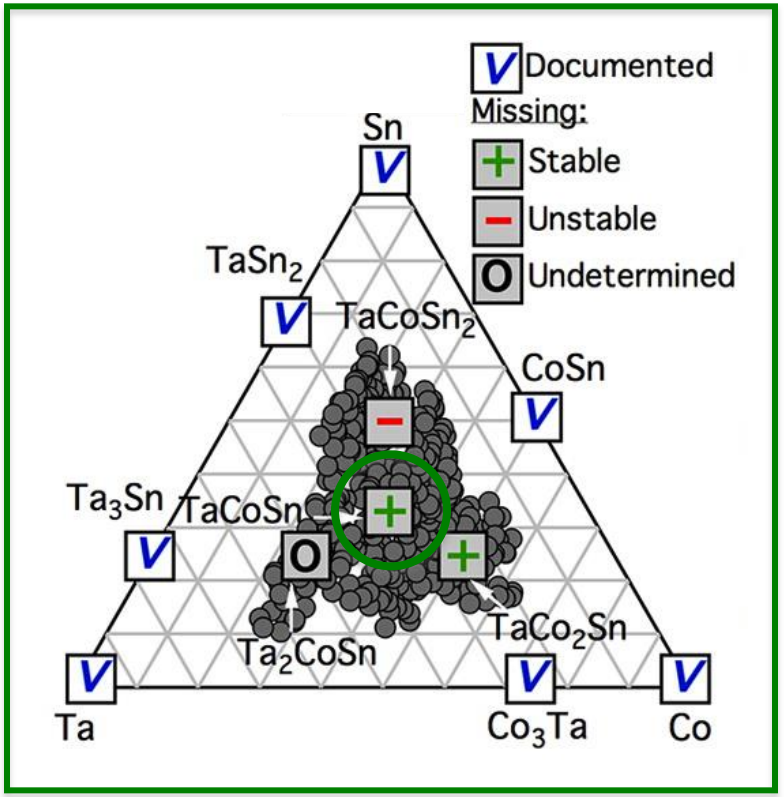
Predicted Structure



XRD: Predicted & Measured



TaCoSn Grown

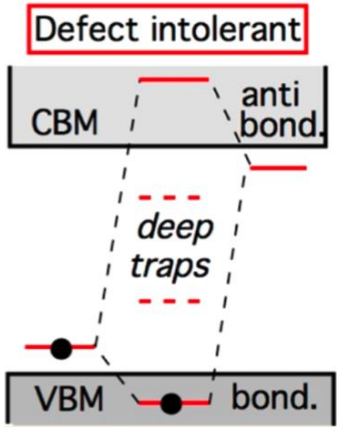


Zakutayev et al. J. Am. Chem. Soc., ***2013****, 135, 10048*

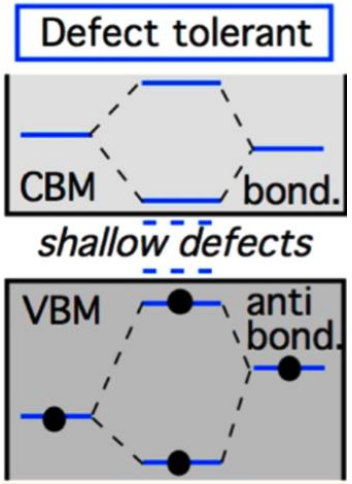
Perovskite Search: Proxy for Transport/Defect Tolerance

- Minority carrier lifetimes challenging for both computation and experiment
- The concept of defect tolerance can used as a proxy (qualitative)
- Defect tolerance is a consequence of the electronic structure

Classic III-Vs and II-Vis are defect intolerant: GaAs, InP, GaN, ZnO,…



Electronic structure of a defect tolerant material

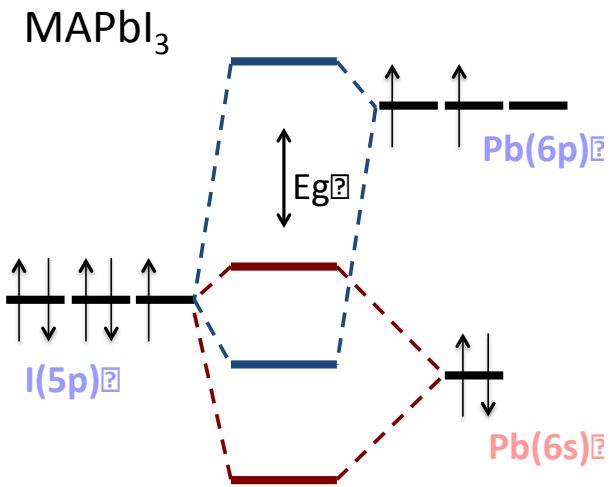


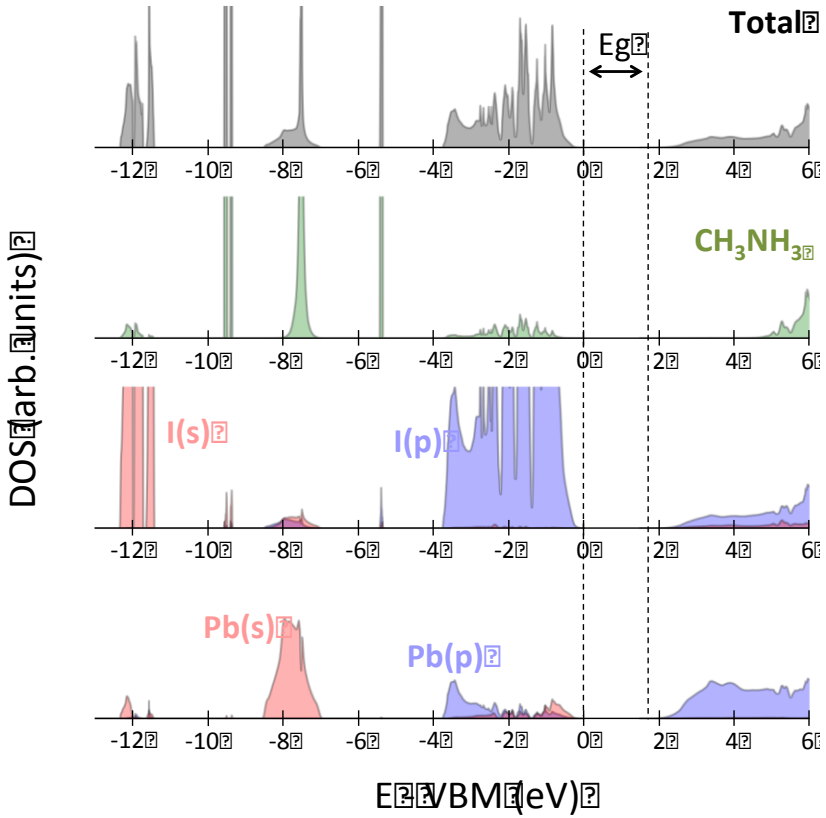
Zakutayev *et al. J. Phys. Chem. Lett.* 5 (2014)
Brandt et al.*MRS Communications* **5**, 265–275 (2015)
S.B. Zhang, *et al., Phys. Rev. B* 57, 9642 (1998)

Electronic structure of $MAPbI_3$

In $MAPbI_3$:

- Pb 6s orbitals provide antibonding character to the VBM (s-p repulsion)
- With spin-orbit coupling, conduction band is more disperse





R.E. Brandt, V. Stevanović, D.S. Ginley, T. Buonassisi,
MRS Communications **5**, 265–275 (2015)

Electronic structure of $MAPbI_3$

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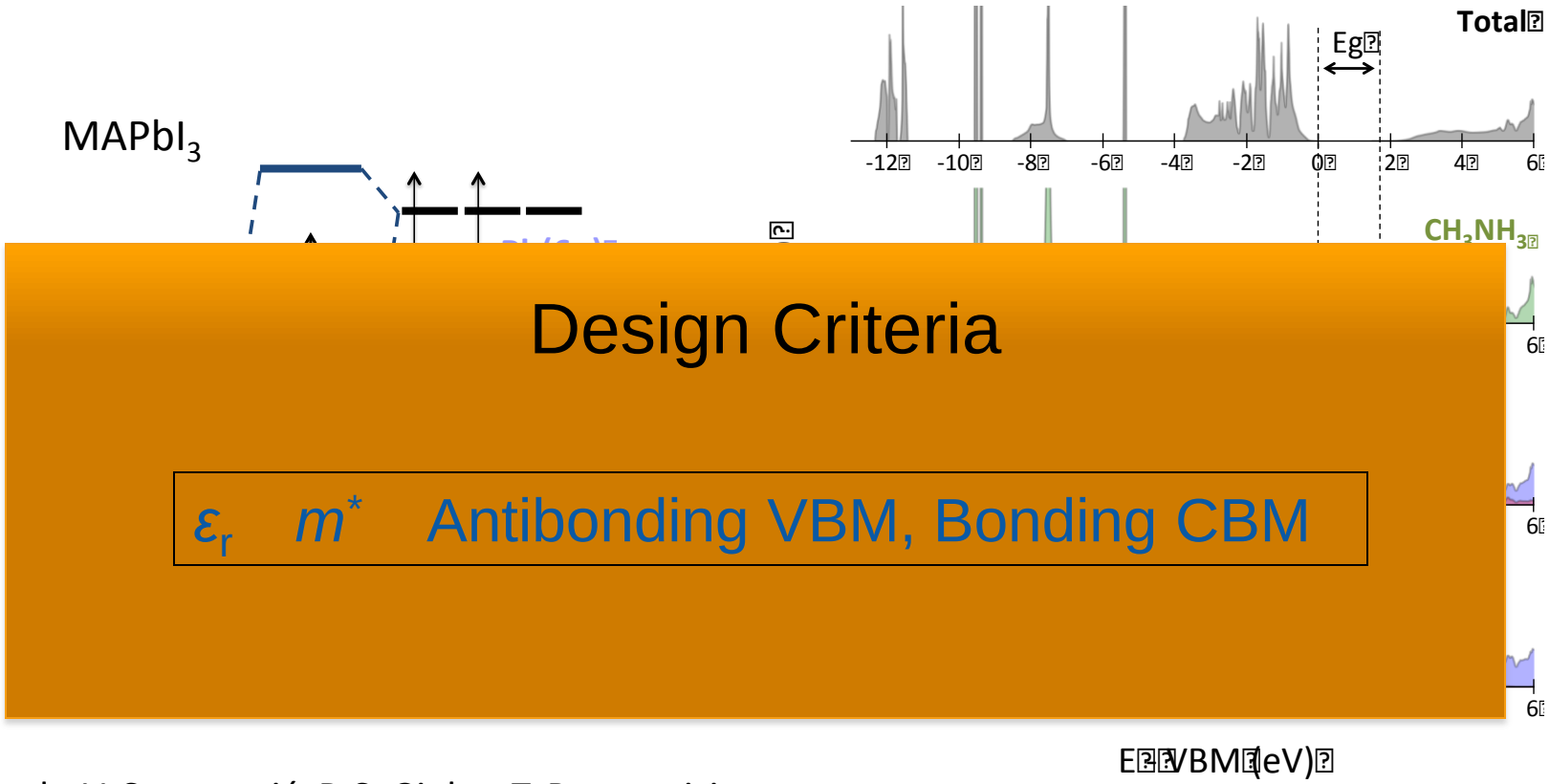
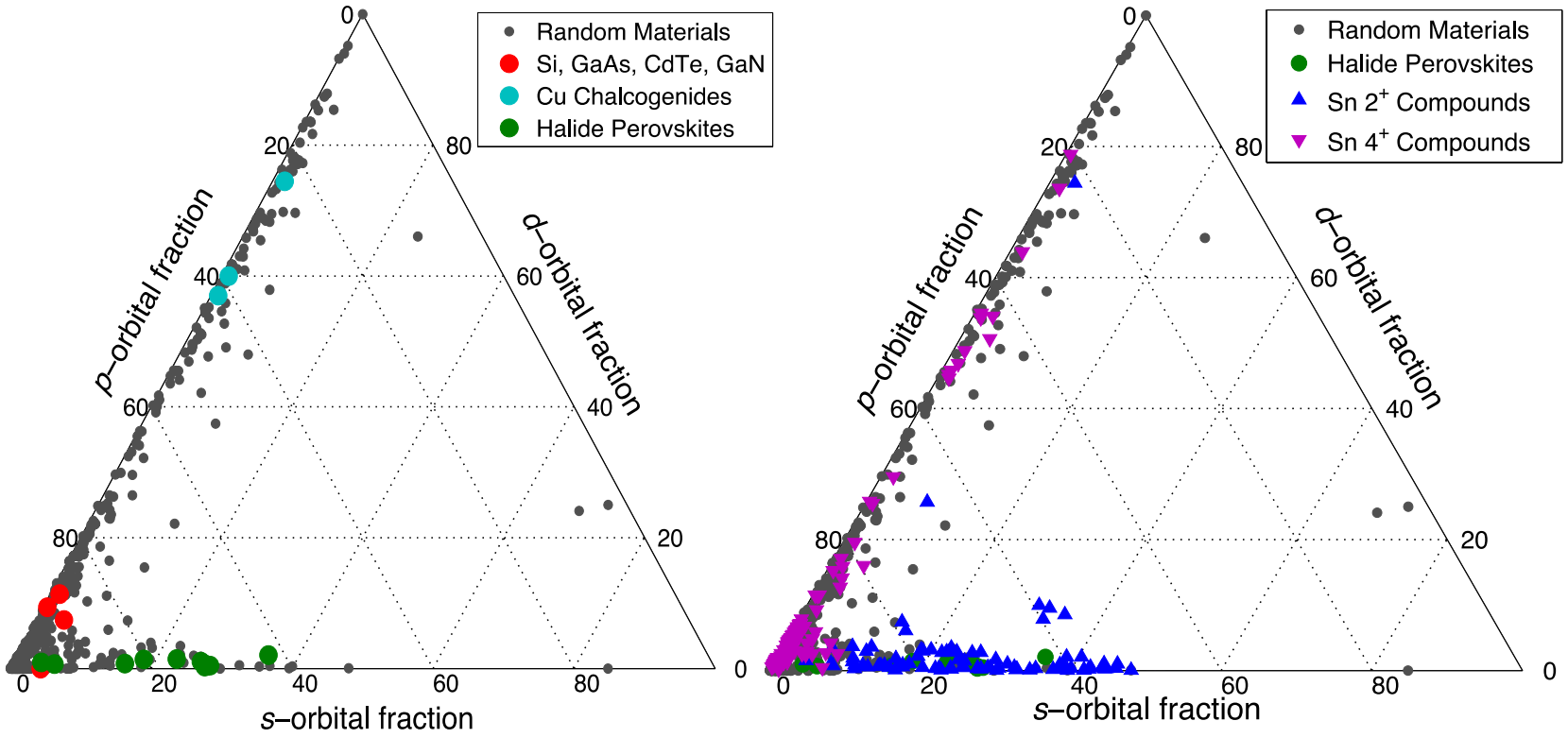


R.E. Brandt, V. Stevanović, D.S. Ginley, T. Buonassisi,
MRS Communications **5**, 265–275 (2015)

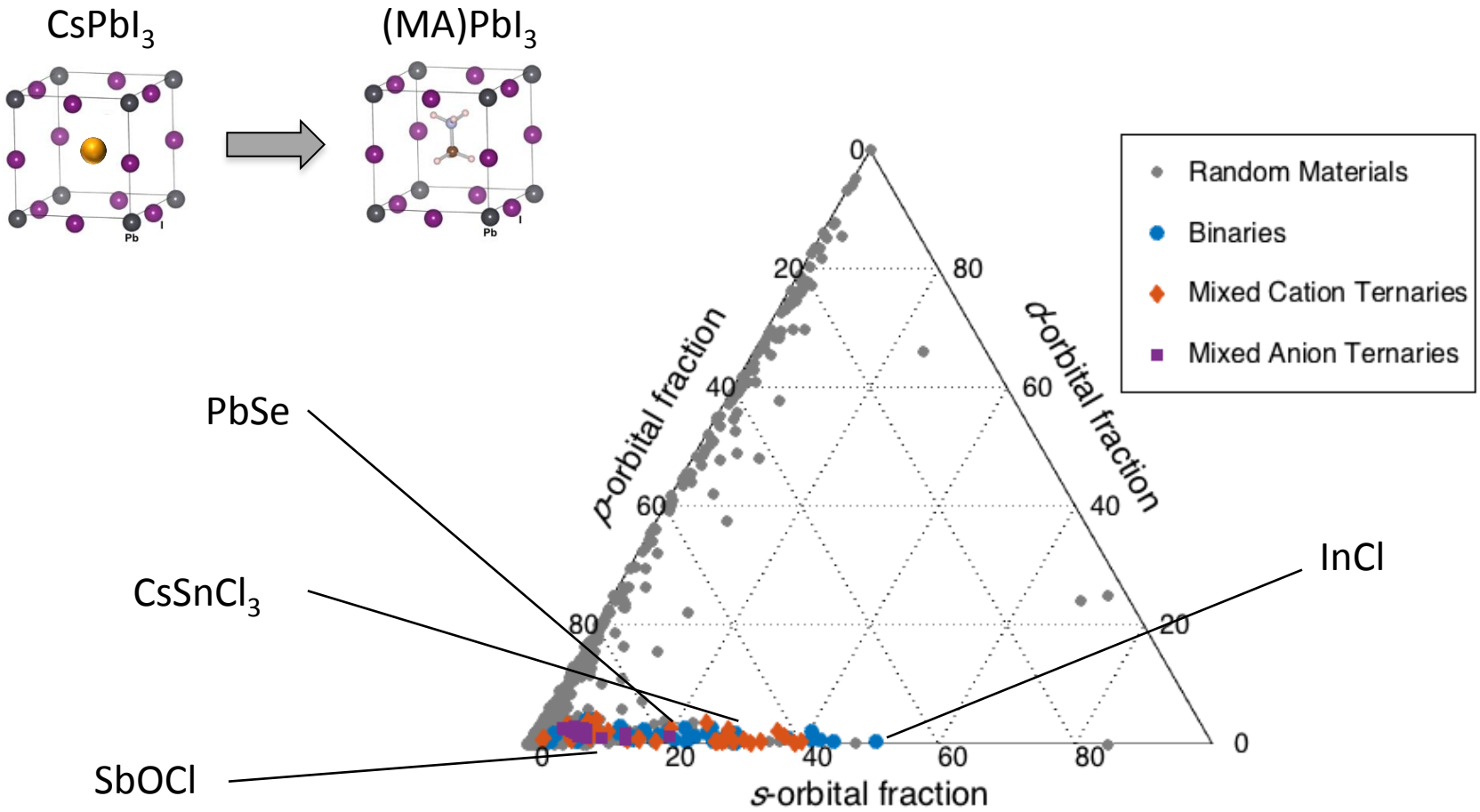
Search 27,000 Inorganic Materials for *s*-VBM



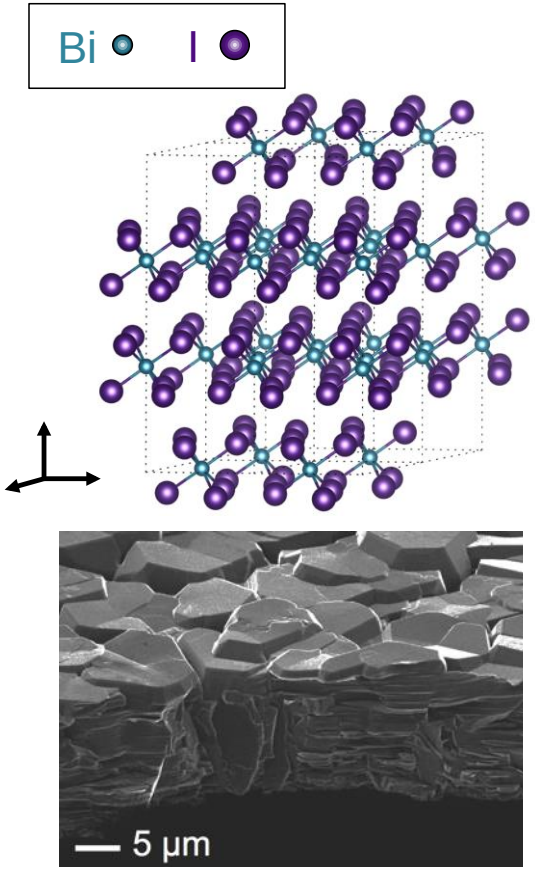
R.E. Brandt, V. Stevanović, D.S. Ginley, T. Buonassisi, *MRS Comm.* **5**, 265 (2015)
A. Jain, S.P. Ong, G. Hautier, *et al. APL Materials* **1**, 011002 (2013)
www.materialsproject.org

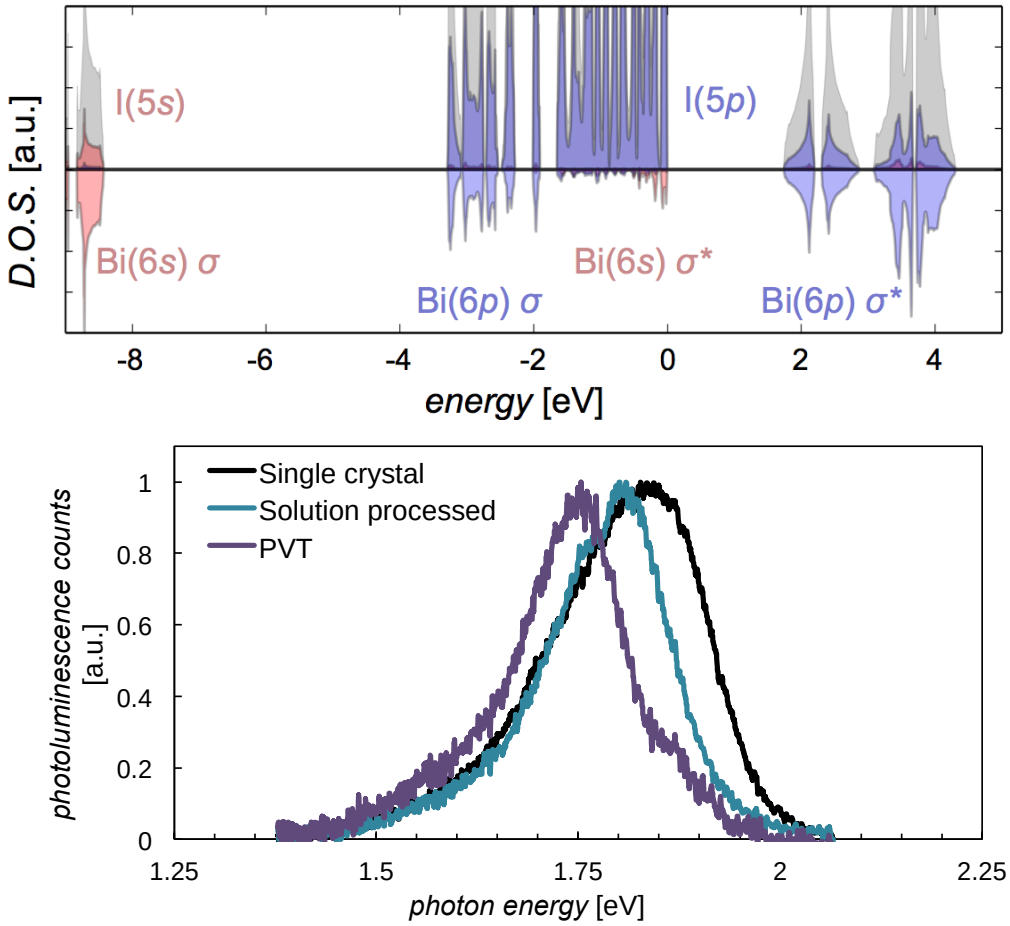
Multiple Material Classes Identified

- Compounds with “lone-pair” cations: **In^{+}, Sn^{2+}, Sb^{3+}, Tl^{+}, Pb^{2+}, Bi^{3+}**
- Building libraries of hybrid materials through inorganic analogues



Bismuth Triiodide (BiI_3)

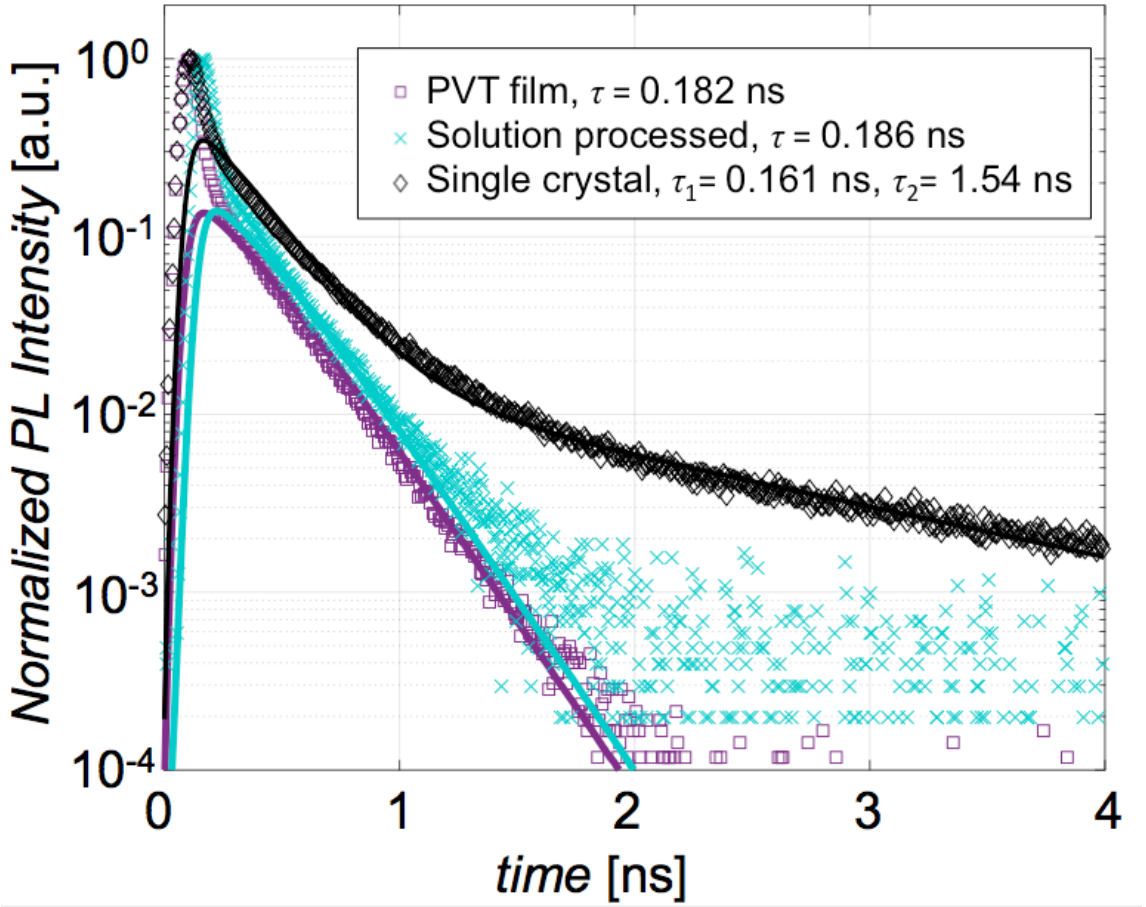




- First films synthesized exhibited room-temperature photoluminescence

R.E. Brandt *et al.*, *J. Phys. Chem. Lett.* **6**, 4297 (2015).

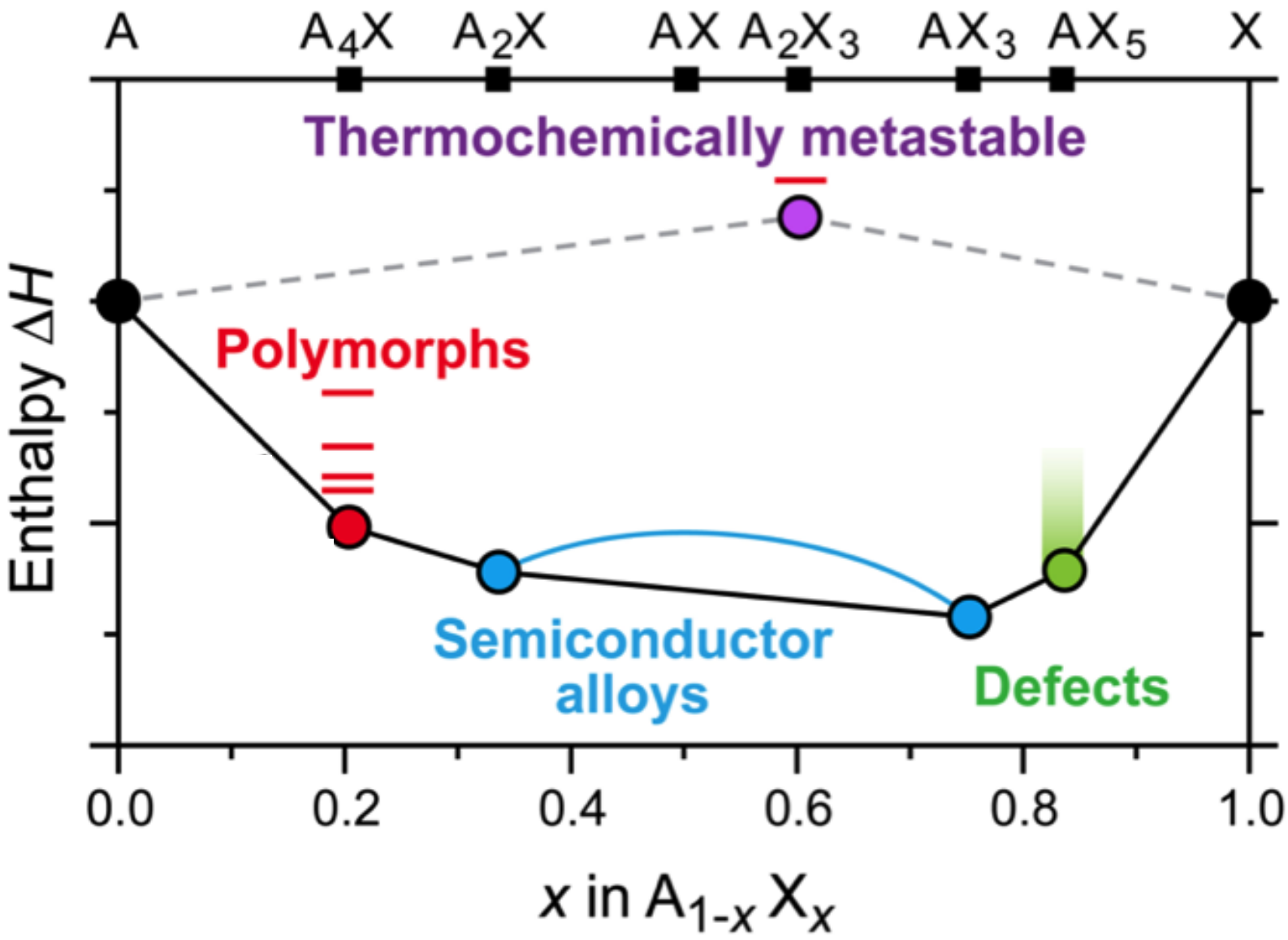
BiI_3 – Carrier Lifetime Measurements



- Informed new design criterion – purity of materials and growth environments

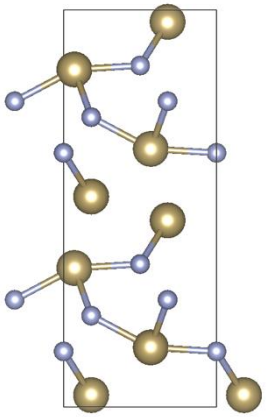
R.E. Brandt *et al.*, *J. Phys. Chem. Lett.* **6**, 4297 (2015).

Incorporating Metastability



Search for New Nitrides

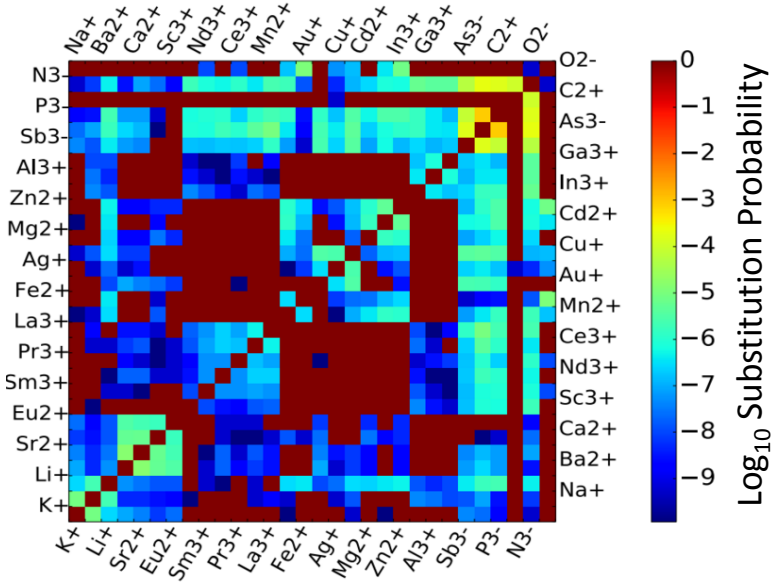
Known Compounds



OsN

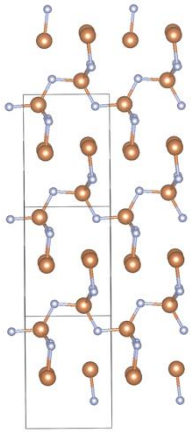
ICSD #167514

Data-Mined Ionic Substitution



Hautier, G, et al. *Inorganic Chemistry* (2010)

Suggested Compounds



SbN

Predicted Structure

Train data-mining algorithm on known Oxides+Pnictides

Cross-validated by "predicting" known nitrides. ~80% chance of recovery

492 suggested binary nitrides

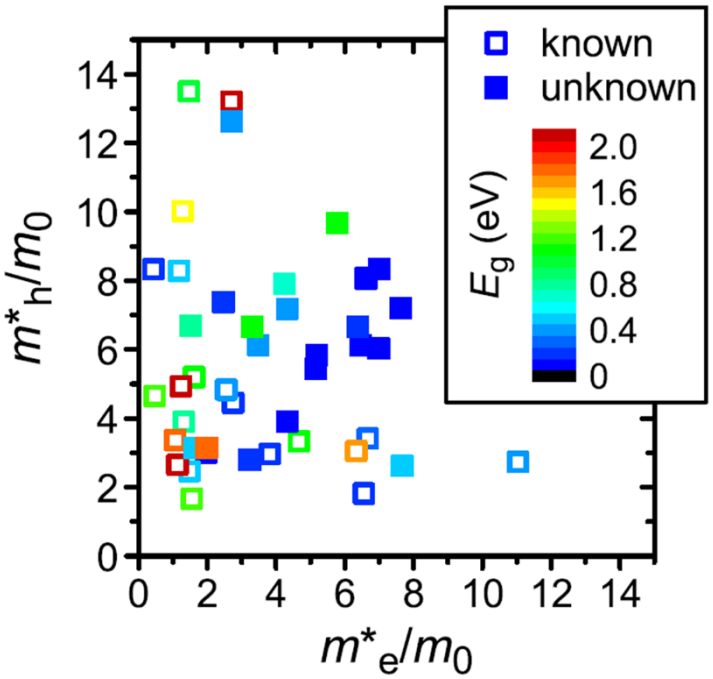
(Alkali, Transition, Main Group)

Candidate Stable Phases

Co_2N, CoN, Cr_3N_2, Cr_3N_4, CrN, Hf_3N_4, Nb_2N, SbN, Sr_2N, Ta_2N, TeN_2, V_2N, V_3N_2, VN, Zn_3N_2

Optoelectronic properties *(Work in progress)*

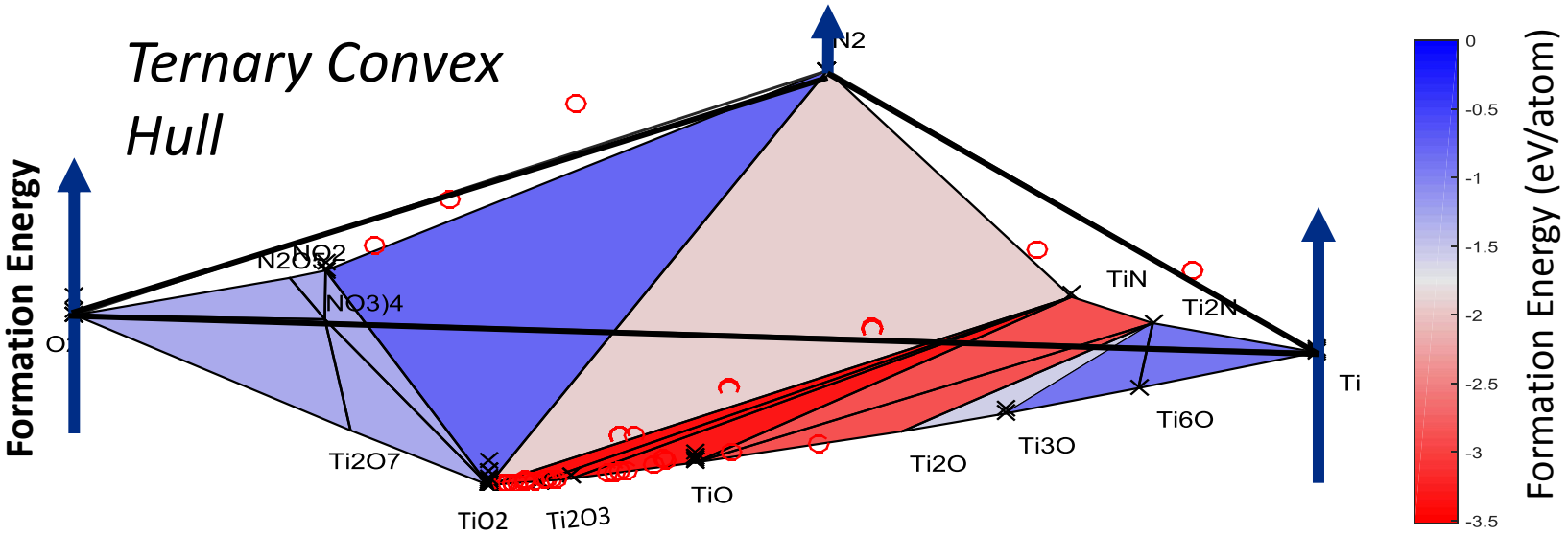
Pathway to new nitrides – from search to application



From design & discovery to properties search

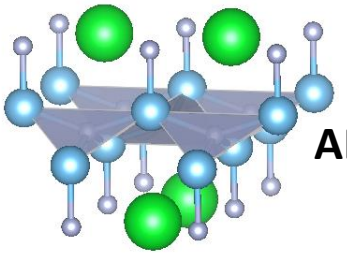
- We calculate optoelectronic properties of newly predicted nitrides.
- Promising semiconductor nitrides *accessible via sputtering* will be further screened using higher levels of theory (G_0W_0)
- **Down-selection** for experimental synthesis and characterization

In progress: Ternary Nitride Search



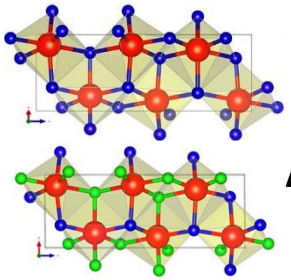
4000 potential ternary nitrides

Ternary Nitride Phases



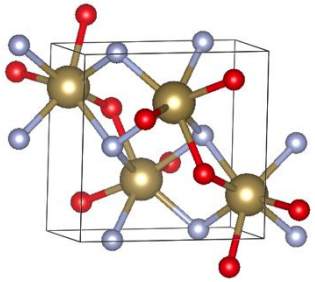
ABN_2

Alloyed Binary Nitrides



$A_xB_{1-x}N$

Metal Oxynitrides

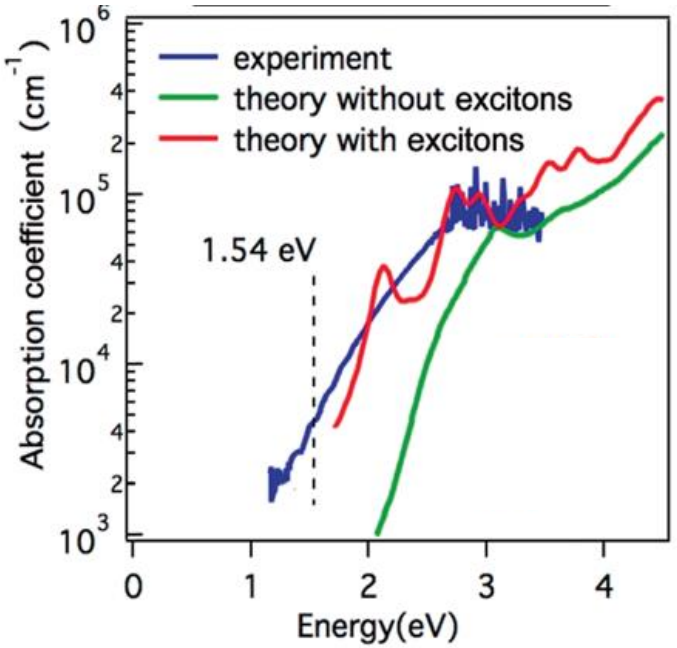


Me-O-N

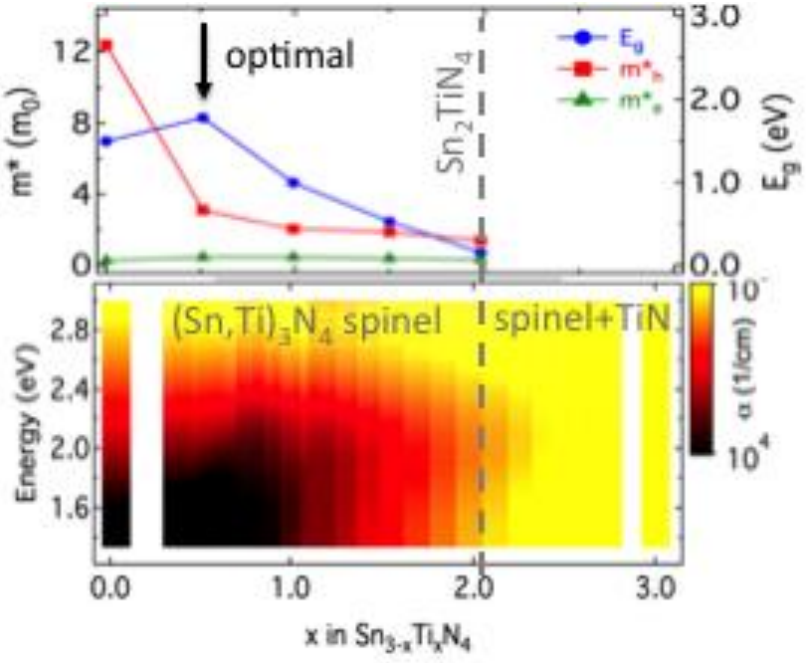
Enormous exploration and design space for new nitrides!

Sn Nitride Thin Films

Entry point material: metastable Sn_3N_4



Improved material: metastable $Sn_{3-x}Ti_xN_4$



- **Sn_3N_4 is a potential PEC material:**
  - good optical absorption (E_g=1.6 eV)
  - suitable VB position for H_2O oxidation
  - n-type conductivity (light electrons)
- However: large hole effective masses

- **$Sn_{3-x}Ti_xN_4$ has better properties than Sn_3N_4**
  - Theory: lighter m_h, same m_e, and lower E_g
  - Experiment: strong optical absorption
  - Also: $SnTi_2N_4$ is a new spinel nitride!!!
  - Structure: pure by XRD, spinodal by TEM

C. Caskey et al, J. Mater. Chem. C, 3, 1389(2015)

Realization of tetrahedral MnO by alloying with ZnO

ZnO has tetrahedral wurtzite structure similar to zinc-blende

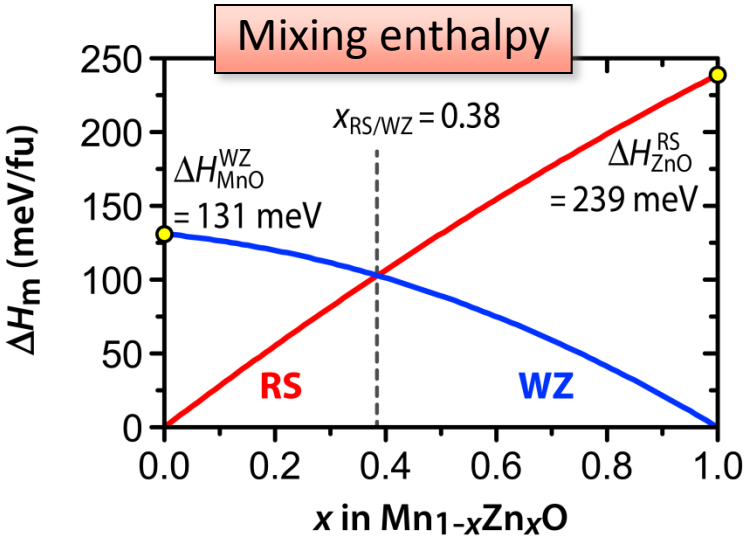
Mixing enthalpy

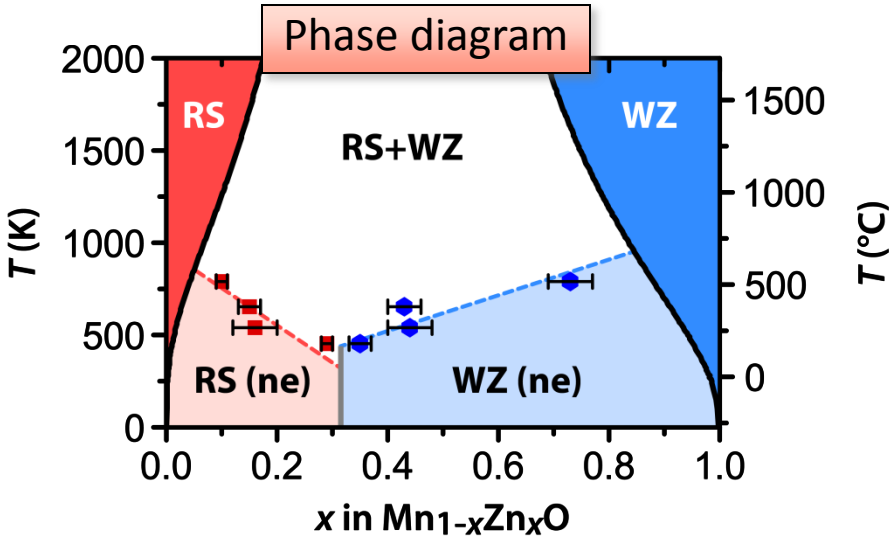
$$\Delta H_{mix}(x) = (1-x)\cdot H_{\mathrm{MnO}} + x\cdot H_{\mathrm{ZnO}} + \beta\cdot x(1-x)$$

- β = **46** meV (RS), β = **94** meV (WZ)

_T-x_ phase diagram

- Common tangent construction
- Ideal solution model for entropy





Theory

Phase transition predicted at x = 0.38

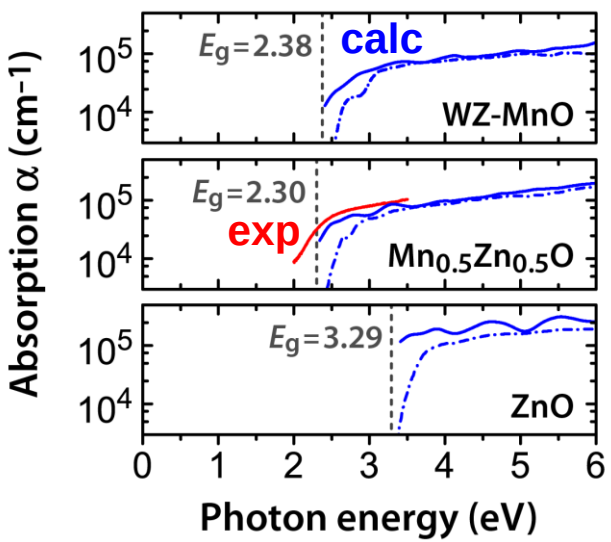
However, desired alloy composition is deep inside miscibility gap

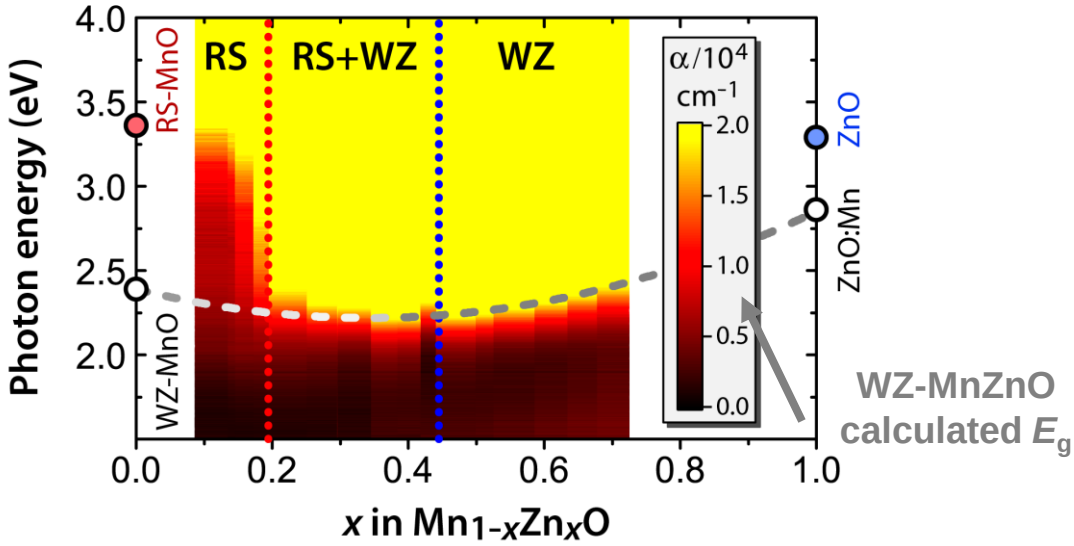
Experiment

Realization of single-phase WZ MnZnO by non-equilibrium PLD growth

Predicted phase transition confirmed

Optical absorption: Theory vs experiment





Measured absorption coefficient α (contour plot) and calculated band gaps (dashed line)

Metastable transition metal oxide alloy with unique semiconducting properties

- Band gap control through alloying
- Non-equilibrium growth via PLD
- PEC measurements
  - Band alignment, carrier transport

MOx Polymorphs

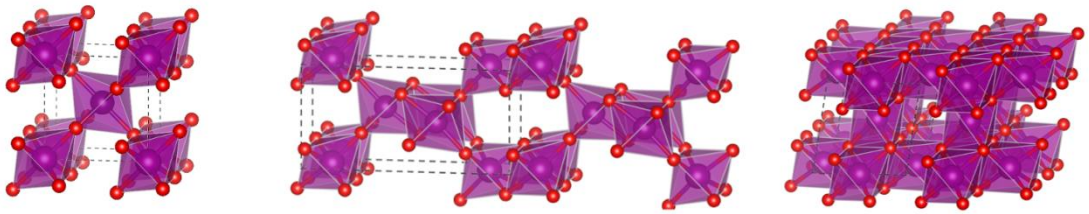
Manganese Oxides

- Over 30 known polymorphs
- Energy storage, catalysis, pigments

Vanadium Oxides

- Highly complex phase diagram
- Batteries, reagents, coatings

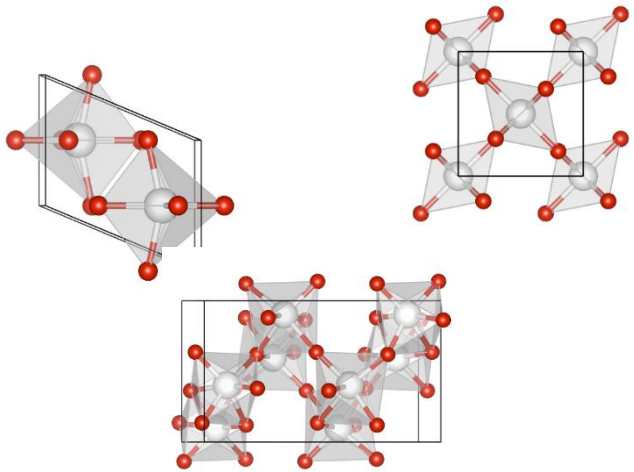
MnO_2 Polymorphs



Pyrolusite | Ramsdellite | Spinel

Titanium Oxides

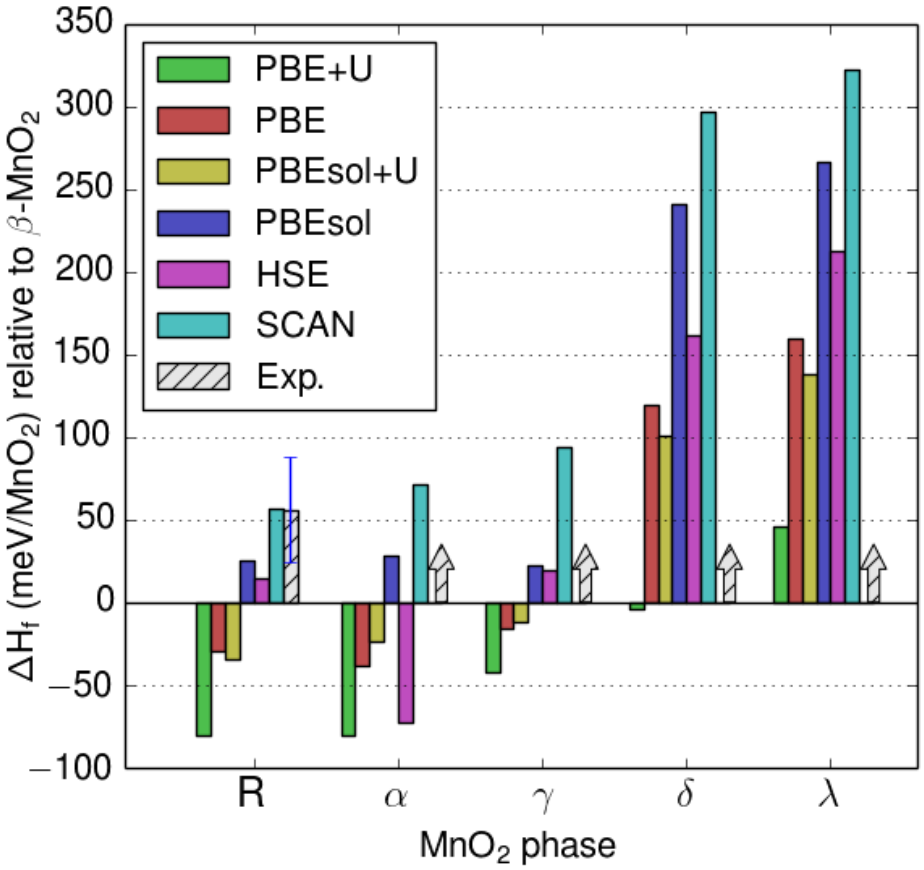
- Poorly understood nanoscale transformations, polymorphs
- Widely studied photocatalyst

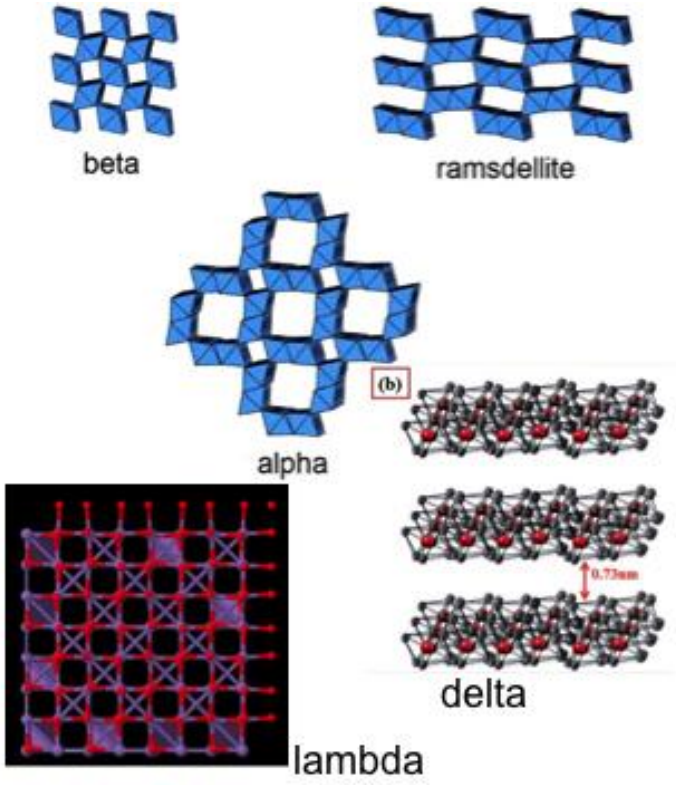


Challenging Energetics for MnO_2

SCAN: new meta GGA (Perdew et al.)

- **All known DFT methods fail to reproduce basic MnO_2 properties**
- First functional to simultaneously reproduce strong covalent-like bonds and weaker long-range interactions
- **Formation energies of MnO_2 polymorphs are reproduced in SCAN**



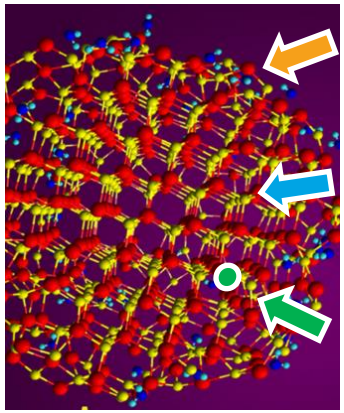


Kitchaev et al. Phys. Rev B. ***93,*** *045132 (2016)*

Understanding of synthesis paths is required to rationally and effectively design metastable compounds

Controlled synthesis

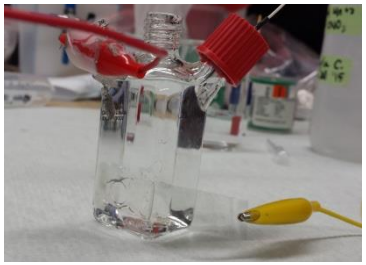
Nucleation



Surface Energy

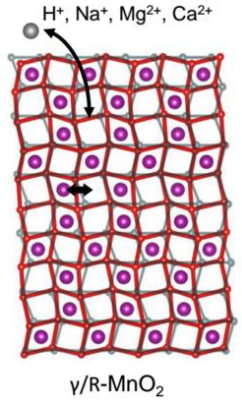
Bulk Energy

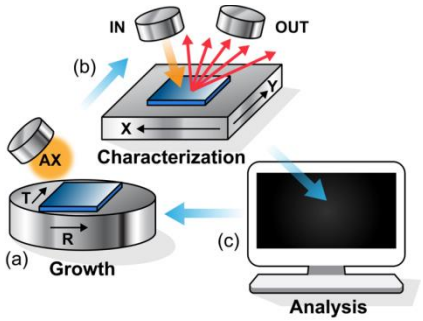
Defect Energy

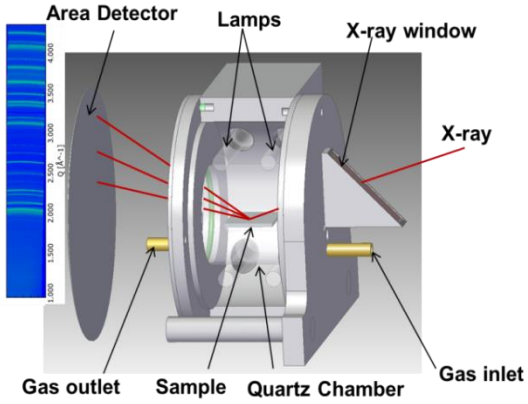


Atomic → Nanoscale → Bulk

Bulk solid







In-situ experiments

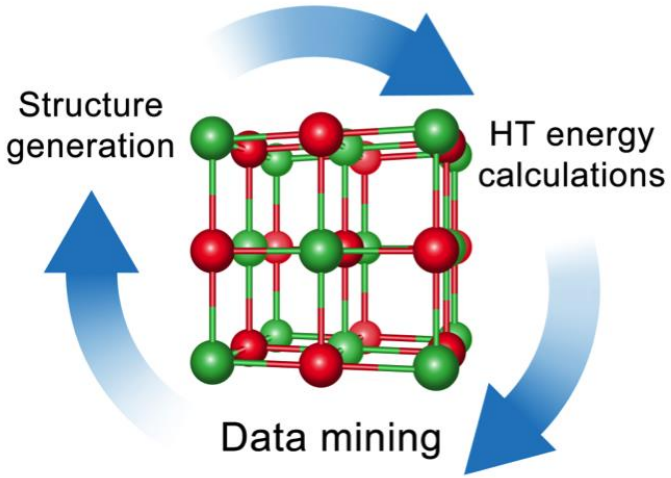
Apply the same fundamental science used to understand properties to understand synthesis

Polymorph selection

Need to understand thermodynamics in all relevant environments

1. **Bulk energy of polymorphs**
2. **Intercalation of ions from solution**
3. **Surface energies in solution**
   - **Predicting nucleation behavior**
4. **Electrochemical transformations**
5. **Modeling solid-solid transformations**
   - **Kinetics of polymorph conversion**
6. **Substrate-controlled depositions**

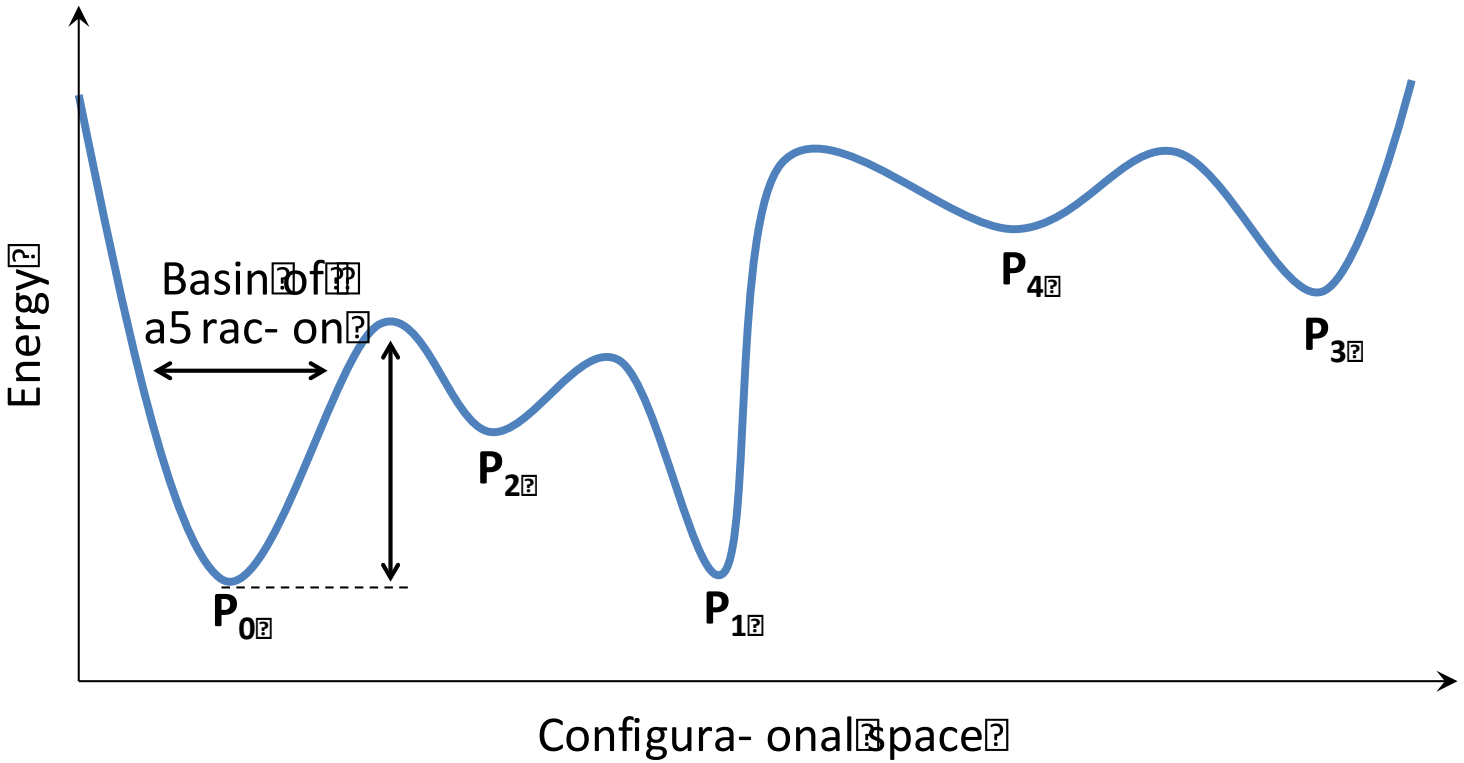
Polymorph Sampler



- Volume of configuration space (“width”) of local minima shown to correlate with realization of different polymorphs
- Random structure sampling followed by local DFT relaxations used to estimate the “width”
- All experimentally realized polymorphs appear as high frequency structures in random sampling
- Translates into a simple and elegant approach for predicting polymorphism - Polymorph sampler
- Easy to apply in a high-throughput fashion

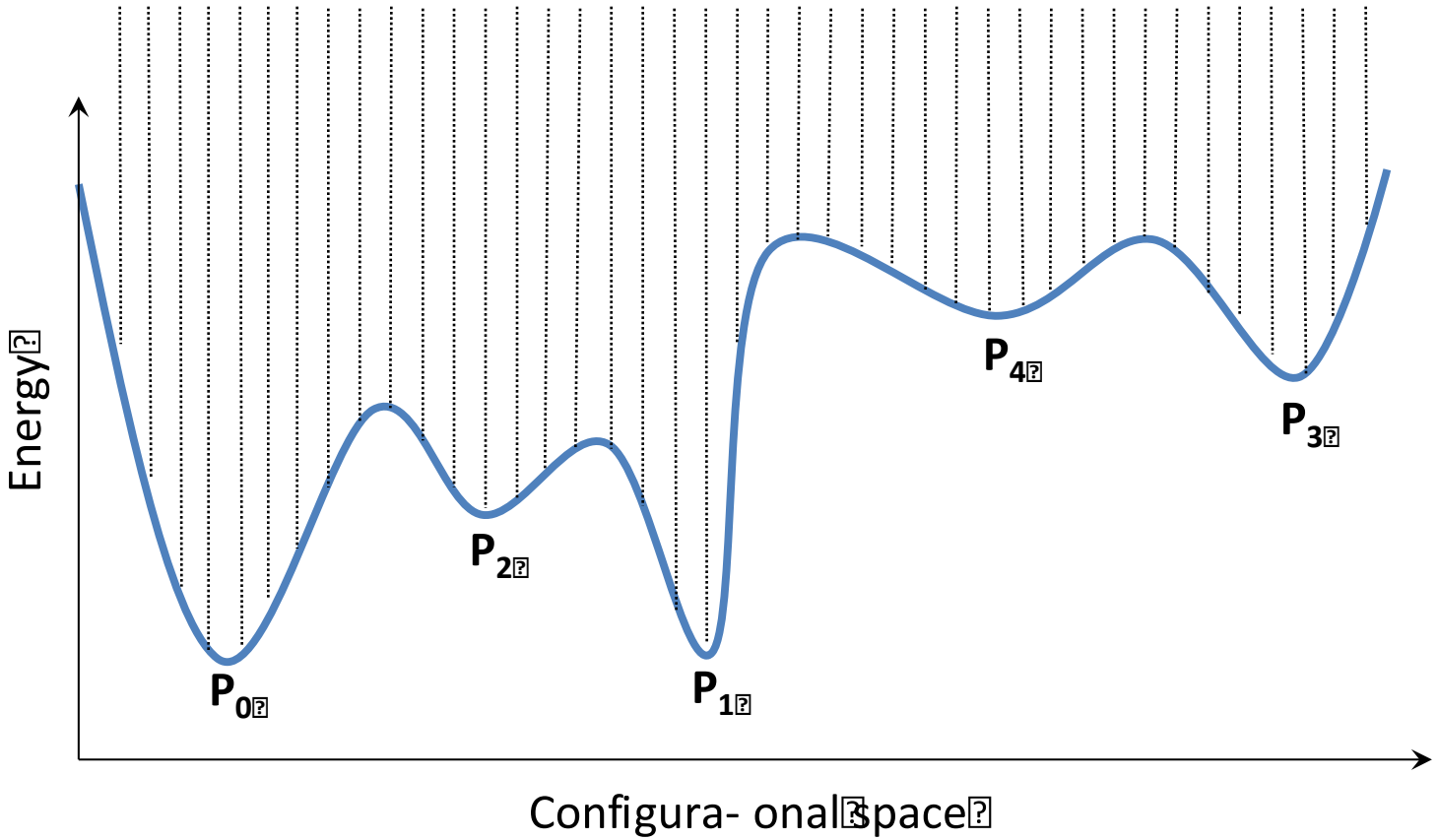
V. Stevanovic, Phys. Rev. Lett. 116, 075503 (2016)

Realizability from the “width” of local minima



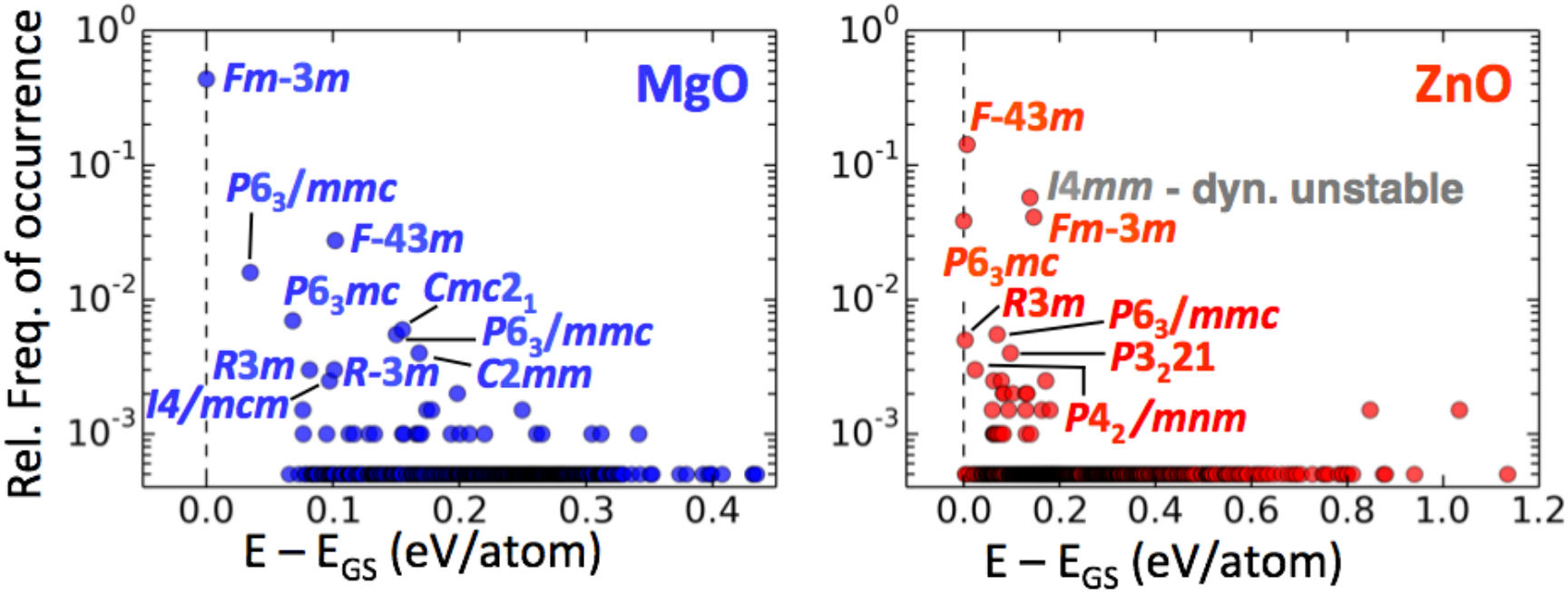
- For majority of systems, even well studied, only a relatively small number of polymorphs is known (experimentally realized)
- Theoretical predictions usually suggest a large number of low energy structures
- Our approach: “Width” of local minima matters, i.e. it is more probable to create exp. conditions that will prepare the system nearby larger (“wider”) minima

Random sampling to measure the “width”



- Random structure sampling followed by DFT relaxations can be used to measure/estimate the “width” of local minima
- Frequencies of occurrence in random sampling to assess the “width” of individual basins

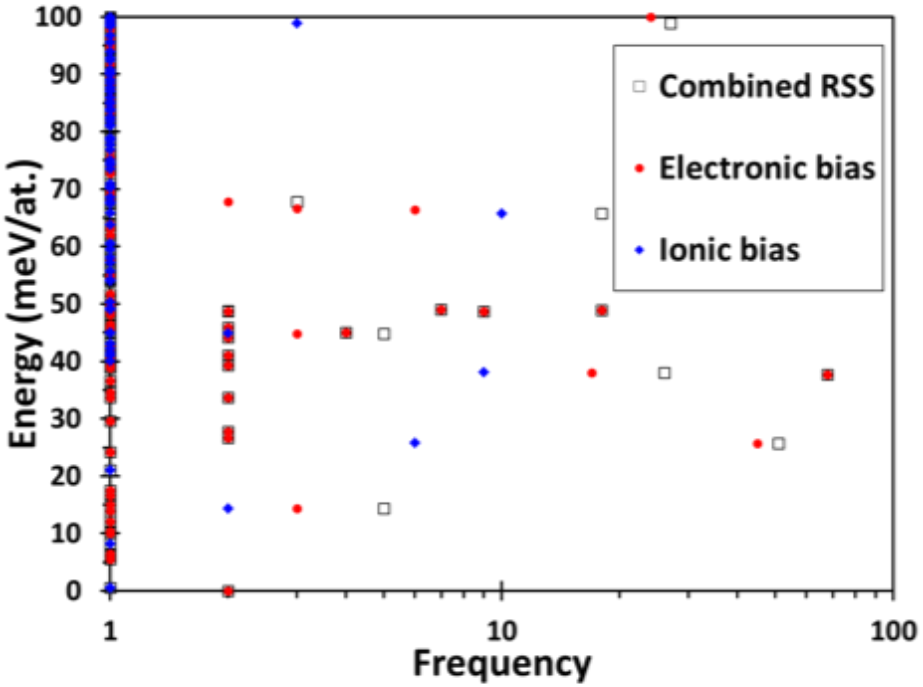
Validation of the hypothesis - MgO and ZnO



- 2,000 random structures per system
- All experimentally realized polymorphs appear as high freq. structures in random sampling
- RS MgO about 25 times more frequent than any other structure, indicates why is RS the only exp. realized MgO structure
- Experimentally realized ZnO structures are three top occurring in random sampling

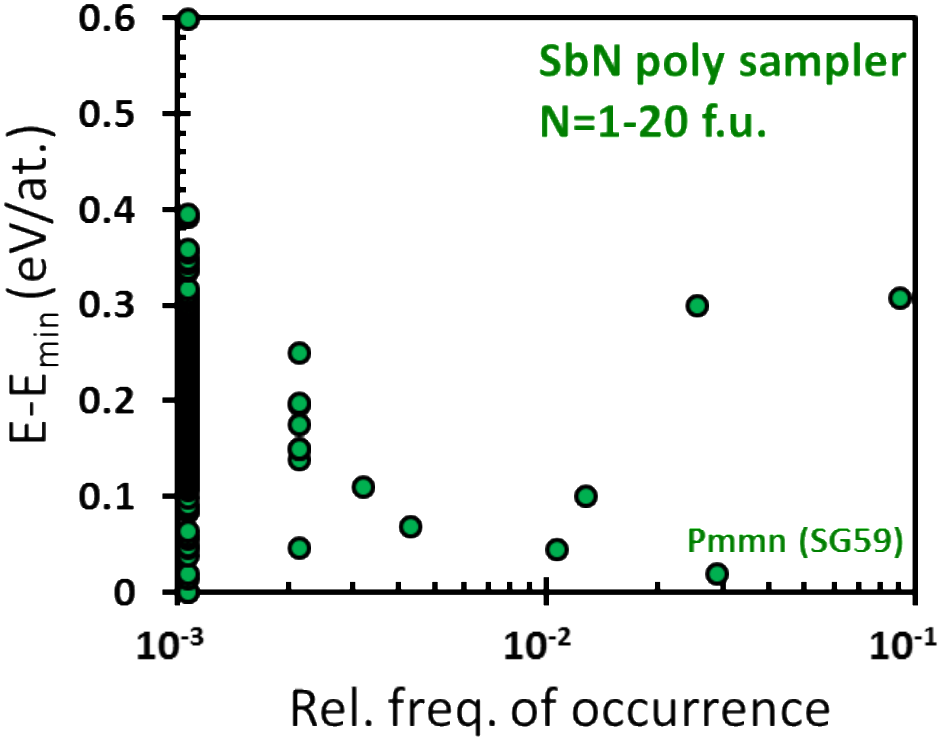
CNGMD - Poly sampler applied in nitrides search

SnN



Paper submitted
(NREL/CSM/SLAC/LBNL/MIT)

Sb(III) "Nitride" (SbN) "structures"



Nitride search

Brief Summary: Materials by Design

Materials by Design has advanced considerably

- Increasing number of active centers
- Structural and functional materials
- Tools being developed, databases being developed

Integration (and iteration) of theory and experiment is critical

- Tool development
- Validation, accuracy

Materials Properties for have been predicted and confirmed

New materials have been predicted and synthesized

oxides, charge transport layers, absorbers, perovskite-analogs

Computational databases are becoming readily available, applied research can be built on top of these more basic science efforts

Theory and experiment can provide information on metastable systems, e.g. new nitrides, alloys, polymorphs

Predicting synthesis constitutes a grand challenge for materials science

Acknowledgements

NREL Slides and Content for PV:

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Paul Denholm, Kristen Ardani, Jim Cale, Sarah Truitt

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Eicke Weber F-ISE), Martin Green (UNSW)
TW Challenge Workshop (Freiburg, March 2016)

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OSU: Janet Tate, James Haggerty, Bethany Matthews, Chiyuki Sato

NREL: Dave Ginley, John Perkins, Stephan Lany, Andriy Zakutayev, Kristen Kennedy, Paul Ndione, Peter Graf, Azure Avery, Andre Bikowski, Sebastian Siol, Lauren Garten, Aaron Holder, Pawel Zawadzki