Computational approaches for clean energy materials

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- Defect graph neural networks
- Equilibria with interacting defects
- Interface structure prediction

Collaborations

Anuj Goyal (NREL, IITH)

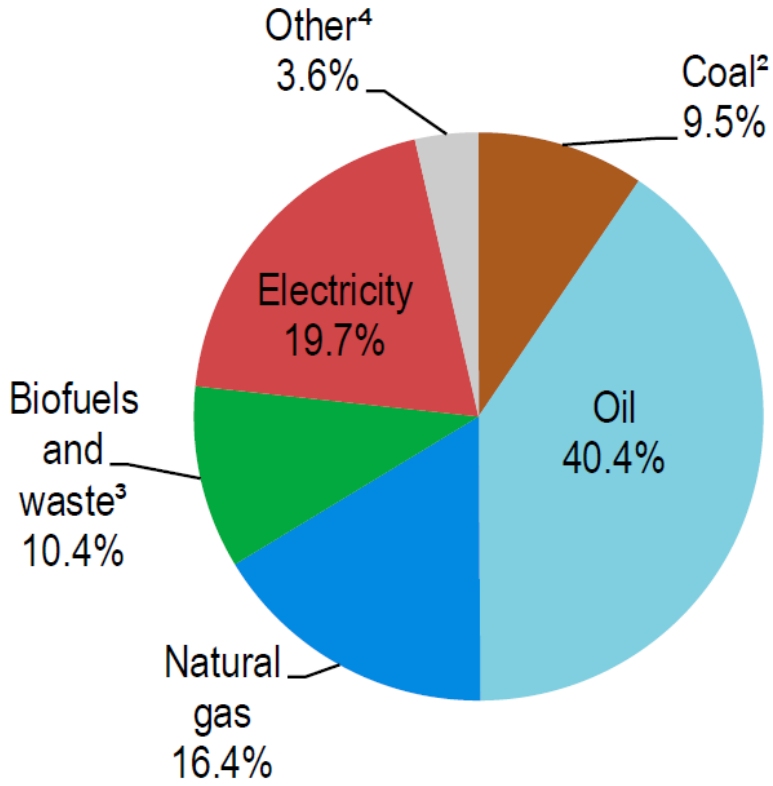
Matt Witman, Tony McDaniel (SNL), Tadashi Ogitsu (LLNL)

Michael Sanders, Ryan O'Hayre (Mines)

Abhishek Sharan (NREL, KU), N. Singh, D. Krasikov (First Solar), Marco Nardone (BGSU)

Energy transition

2019 world final energy consumption by source



20% electricity / 80% fuels

Key World Energy Statistics 2021, IEA report

2050 Energy Needs (average power)

- Current infrastructure 58,000 GW
- Trend extrapolation **32,000** GW
- Total electrification 12,000 GW

Kurtz *et al*, Revisiting the Terawatt Challenge, MRS Bulletin 2020

2022	P_{cap} (GW)	f_{cap} (%)	P_{av} (GW)
Hydro	1400	40	560
Wind	900	35	320
Solar (PV)	1000	15	150
Total	3400		1,030

Renewable Capacity Statistics 2023, IRENA report

add/yr	P_{cap} (GW)	f_{cap} (%)	P_{av} (GW)
Hydro	30	40	12
Wind	80	35	28
Solar (PV)	220	15	33
Total	340		63

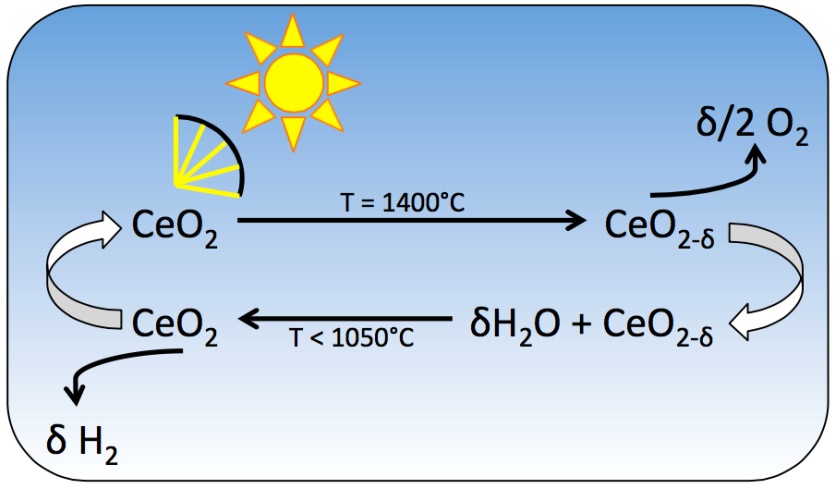
Renewables 2022, IEA report

Non-electricity solar fuels: Thermochemical Hydrogen

$$M_xO \rightarrow M_xO_{1-\delta} + \frac{\delta}{2} \cdot O_2$$ Reduction (solar heat)

$$M_xO_{1-\delta} + \delta \cdot H_2O \rightarrow M_xO + \delta \cdot H_2$$ Oxidation (H_2 production)

$$H_2 + \tfrac{1}{2}\, O_2 \leftrightarrow H_2O$$ Ideal gas law (H_2, O_2, H_2O)



(1) Materials Discovery
- Down-selection of candidate materials
- Broad screening of materials databases

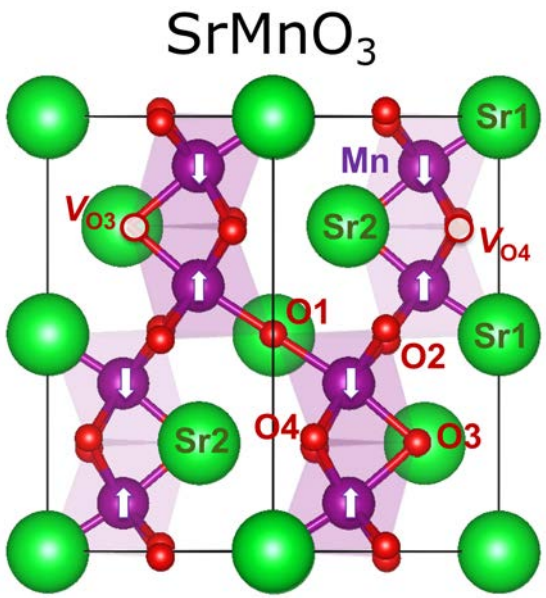
(2) Quantitative and mechanistic models
- Specific materials systems
- Understand the underlying physics
- Assess potential and limitations

(1) Screening and discovery ML models for defects

Supercell calculations

- O vacancy formation energy

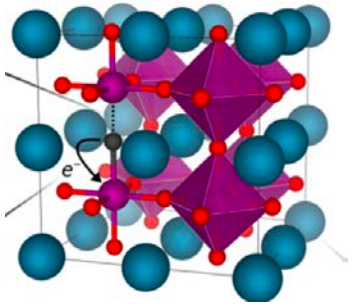
$$\Delta H_D^{ref} = E_D - E_H + \mu_O^{ref}$$



	Mn-O-Mn (°)	ΔH_D^{ref} (eV)
O1	174.3	3.27
O2	171.1	3.27
O3	82.0	2.33
O4	82.1	2.35

Phenomenological models can be quite successful

Deml *et al*, JPCL **2015**
Wexler *et al*, JACS **2021**



Linear Model works well for ABO3 perovskites:

$$0.1\Sigma E_b - 1.5V_r + 0.4E_g - 55.8E_{hull} + 0.4 \text{ (eV)}$$

Crystal bond dissociation | Crystal reduction | Band gap | Stability | features

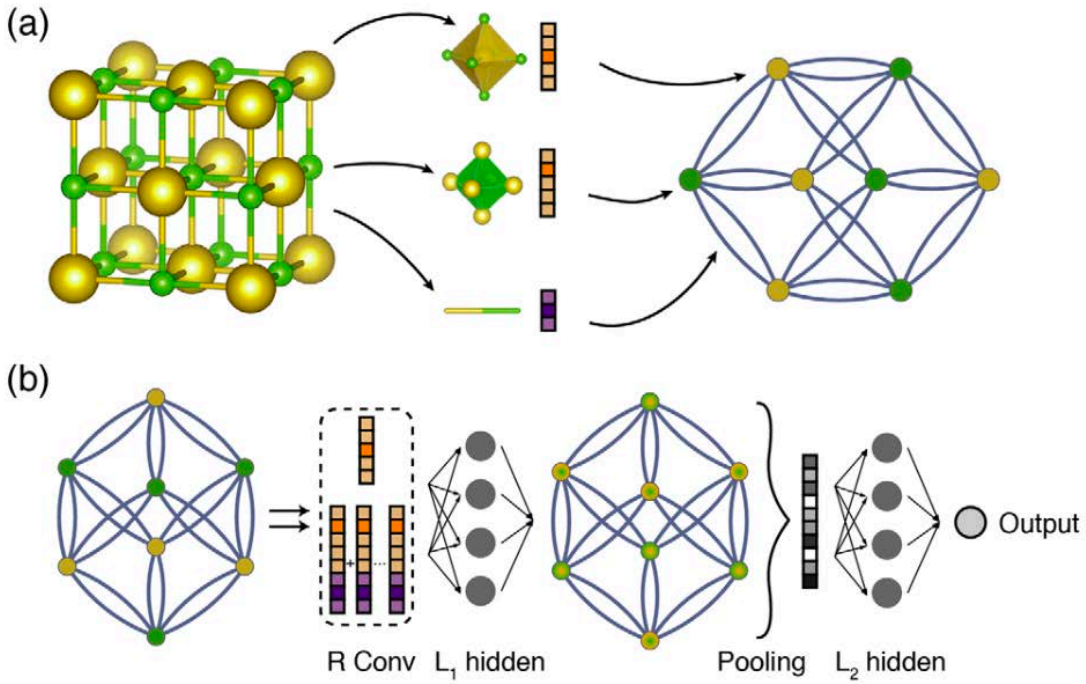
- Model limitations to specific chemistries and/or structure types
- Limited scaling of accuracy of regression-based approaches
- Explicit structure dependence needed to differentiate symmetry sites

Defect Graph Neural Network

Explicit structure dependence via graph neural networks

- Crystal Graph Convolutional Neural Networks
- Automated feature extraction

Xie and Grossman, PRL (2018)

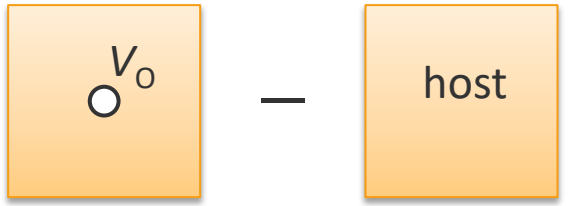


Crystal structure -> energy

- Need defect structure
- Accuracy of energy differences?

DFT: $\Delta H_{\mathrm{D}} = E_{\mathrm{DFT}}(\boldsymbol{X}_{\mathrm{D}}) - E_{\mathrm{DFT}}(\boldsymbol{X}_{\mathrm{H}}) + \mu_{\mathrm{O}}^{\mathrm{ref}}$

supercells
~100 atoms



ML using only host structure: $\Delta\widehat{H}_{\mathrm{D}} = f_{\mathrm{GNN}}(\boldsymbol{X}_h, i'; \theta)$

➢ Example graph: $\boldsymbol{v}_1$ O $\boldsymbol{e}_{12}$ Mn $\boldsymbol{v}_2$

➢ Encode the graph (step $t = 0$):

$\boldsymbol{v}_1^{t=0} = \{r_{\mathrm{O}}, \chi_{\mathrm{O}}, \ldots, s_1\}$

Accuracy boosting, site-specific inputs (i.e. oxidation state)

➢ Convolutions ($t = 1 \ldots T$)

$$\boldsymbol{v}_i^{(t+1)} = g\left(\boldsymbol{v}_i^{(t)} + \sum_j \sigma\left(\boldsymbol{z}_{ij}^{(t)}\boldsymbol{W}_1^{(t)} + \boldsymbol{b}_1^{(t)}\right) \odot g\left(\boldsymbol{z}_{ij}^{(t)}\boldsymbol{W}_2^{(t)} + \boldsymbol{b}_2^{(t)}\right)\right)$$

➢ Node-level pooling

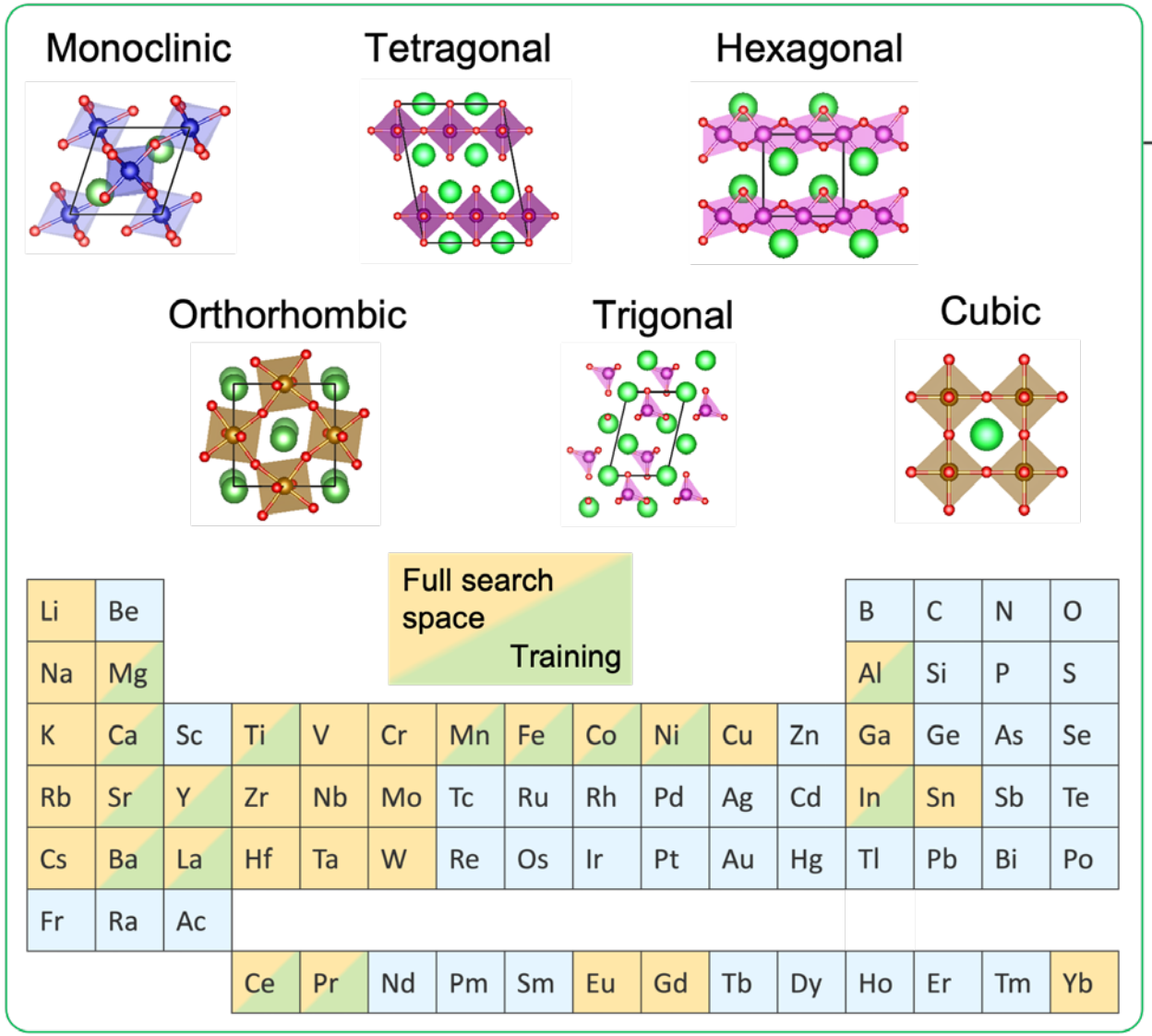
$$\boldsymbol{v}_d = g\left(\left(\boldsymbol{v}_{i'}^{(T)} \oplus \boldsymbol{v}_g\right) \cdot \boldsymbol{W} + \boldsymbol{b}\right)$$

M. Witman *et al.*, Nat Comp Sci (2023)

- Extract defect feature vector
- Use host's global properties, $\boldsymbol{v}_g = \{E_g, m^*, \Delta H_f\}$

Structurally and compositionally diverse training data

First-principles DFT workflow is robust but time consuming (using NRELMatDB hosts)



DFT workflow

A. Material Space

Diversity in Training:
40 unique crystal structures and
38 unique compositions

B. Host Calculations

Relaxed structure,
Atomic spin and oxidation state,
Enthalpy of formation,
Bandgap, Electron effective mass

C. Defect Calculations

Calculated oxide space:
~200 host structures
~1500 defect relaxations

Existing oxide space:
~10,000s host structures
~1Ms defect relaxations

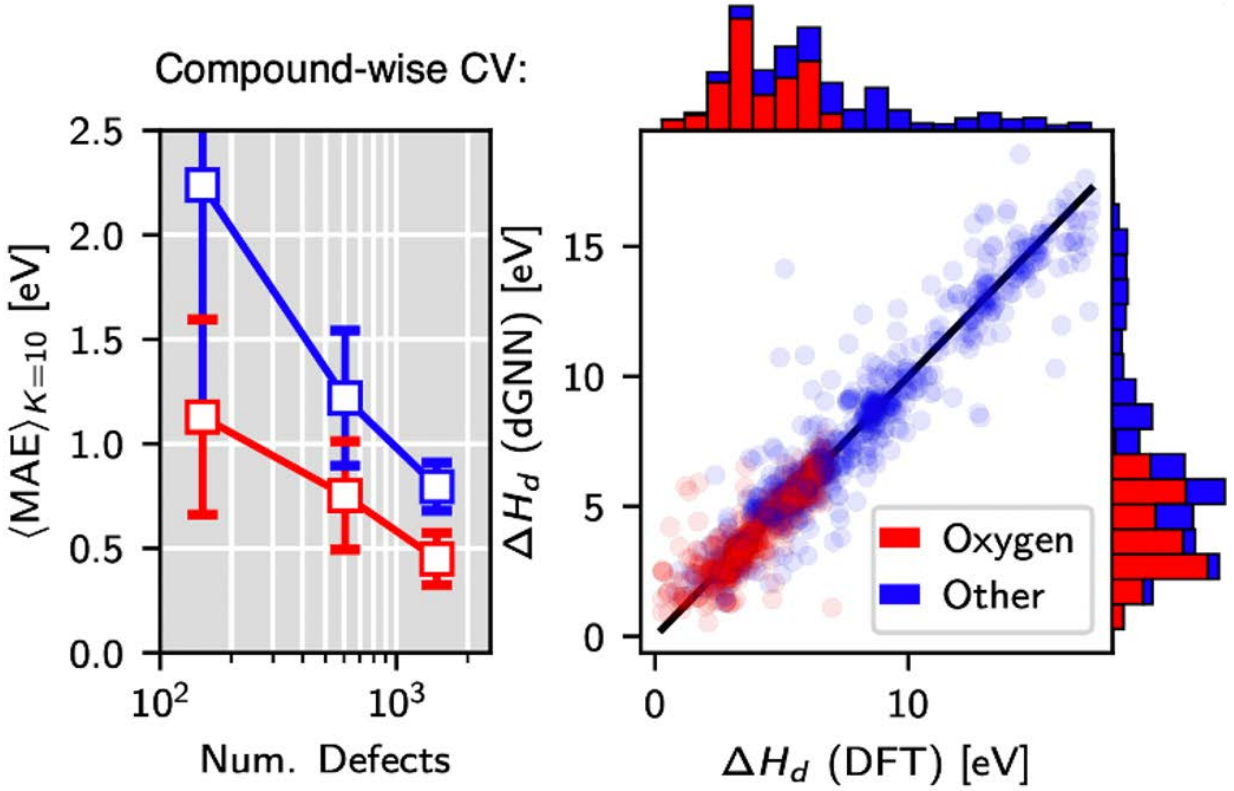
Benchmarking

Encoding strategies

- Element only: Crystal structure and atomic type
- Full: Additional local (s_i) and global (v_g) properties

Cross-validation

- Defect-wise vs compound-wise

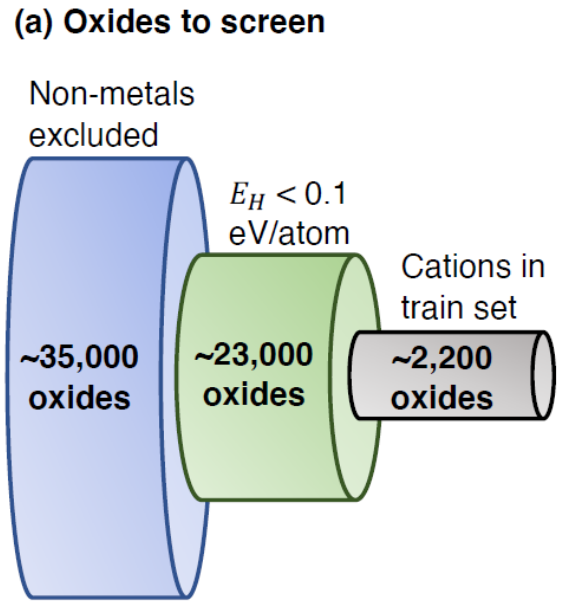


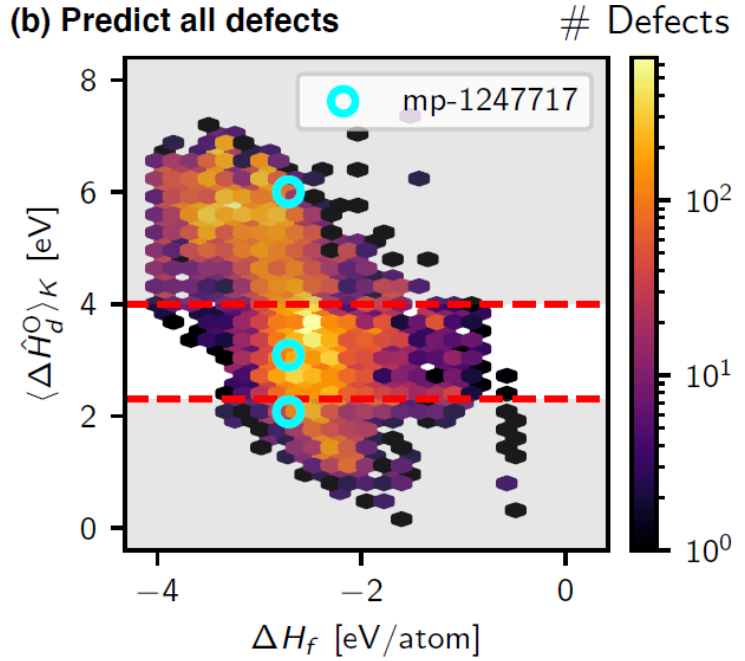
Model Encoding Type		Element only (v_e)		DFT only (s_i, v_g)		Full (v_e, s_i, v_g)		Continuous (v_e', s_i', v_g)	
Defect type		ΔH_d^{O}	ΔH_d^{Other}	ΔH_d^{O}	ΔH_d^{Other}	ΔH_d^{O}	ΔH_d^{Other}	ΔH_d^{O}	ΔH_d^{Other}
Defect-wise CV:	$\langle MAE^Y \rangle_K$ $\sigma_K(MAE^Y)$	0.37 (0.08)	0.85 (0.11)	0.44 (0.06)	0.82 (0.12)	**0.30** **(0.03)**	**0.65** **(0.08)**	0.31 (0.03)	0.66 (0.05)
Compound-wise CV:	$\langle MAE^Y \rangle_K$ $\sigma_K(MAE^Y)$	0.52 (0.16)	0.96 (0.18)	0.58 (0.17)	1.13 (0.20)	**0.45** **(0.12)**	0.79 (0.12)	0.49 (0.19)	**0.78** **(0.19)**

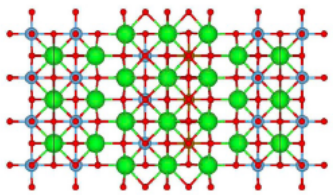
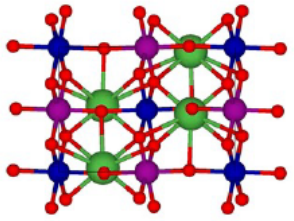
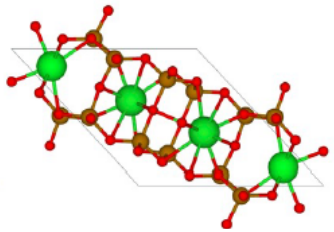
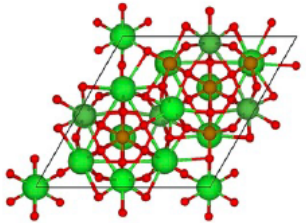
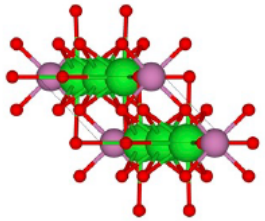
Materials Project screening

Co-design of defects and stability for water-splitting

Metric	Requirement
Frac. of defects w/ΔH_d^O > 2.3 eV	$x_{\min} = 1$
Frac. of defects w/$\Delta H_d^O \in$ [2.3, 4.0] eV	$x_{\text{rng}} > 0$
P_{O_2} operating conditions for STCH	$\Delta\mu'_{O_2}$
P_{O_2} where host's GC energy above hull < X	$\Delta\mu_{O_2}^{\phi_H<X}$
Host stability criteria (ranges intersect)	$\Delta\mu_{O_2}^{\phi_H<X} \cap \Delta\mu'_{O_2}$





753 formulas (80 training)	197 formulas (48 training)	114 formulas (33 training)	34 formulas (17 training)	16 formulas (11 training)	9 formulas (9 training)
➢ $x_{\text{min},1} = 1$ ➢ $x_{\text{rng},1} > 0$ ➢ $E_H < 0.1$	➢ $x_{\text{min},1} = 1$ ➢ $x_{\text{rng},1} > 0$ ➢ $\Delta\mu_O^{\phi_H<0.1}$	➢ $x_{\text{min},2} = 1$ ➢ $x_{\text{rng},2} > 0$ ➢ $\Delta\mu_O^{\phi_H<0.1}$	➢ $x_{\text{min},3} = 1$ ➢ $x_{\text{rng},3} > 0$ ➢ $\Delta\mu_O^{\phi_H<0.05}$	➢ $x_{\text{min},3} = 1$ ➢ $x_{\text{rng},3} > 0$ ➢ $\Delta\mu_O^{\phi_H=0}$	➢ $x_{\text{min},3} = 1$ ➢ $x_{\text{rng},3} = 1$ ➢ $\Delta\mu_O^{\phi_H=0}$
	$Sr_6Ti_3FeO_{14}$ (mp-1645141)	La_2MnCoO_6 (mp-19208)	$BaSr(FeO_2)_4$ (mp-1228024)	$Ba_5SrLa_2Fe_4O_{15}$ (mp-698793)	$Ba_3In_2O_6$ (mp-20352)
					

High-throughput thermodynamics

Witman, Goyal, Ogitsu, McDaniel, Lany
Nat Comp Sci (2023)

Thermodynamic analysis

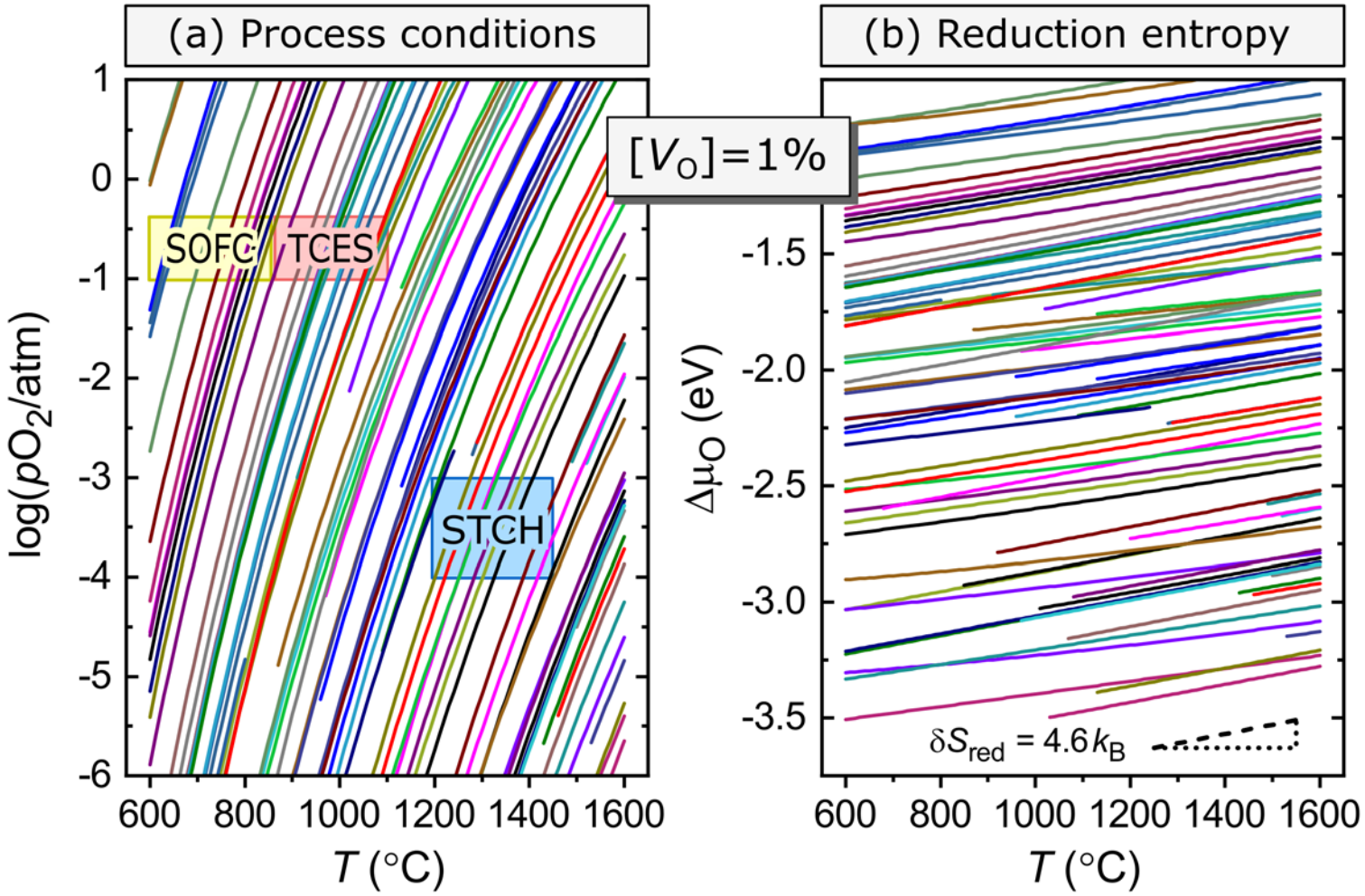
- Sum over non-equivalent sites

$$[V_O] = \sum_i g_i \frac{\exp[-(\Delta H_{V_O,i} + \Delta\mu_O)/k_B T]}{1 + \exp[-(\Delta H_{V_O,i} + \Delta\mu_O)/k_B T]}$$

- Inversion of $\Delta\mu_O$ –> $[V_O]$ relationship
- Ideal gas law for (pO_2,T) diagrams
- Entropy analysis

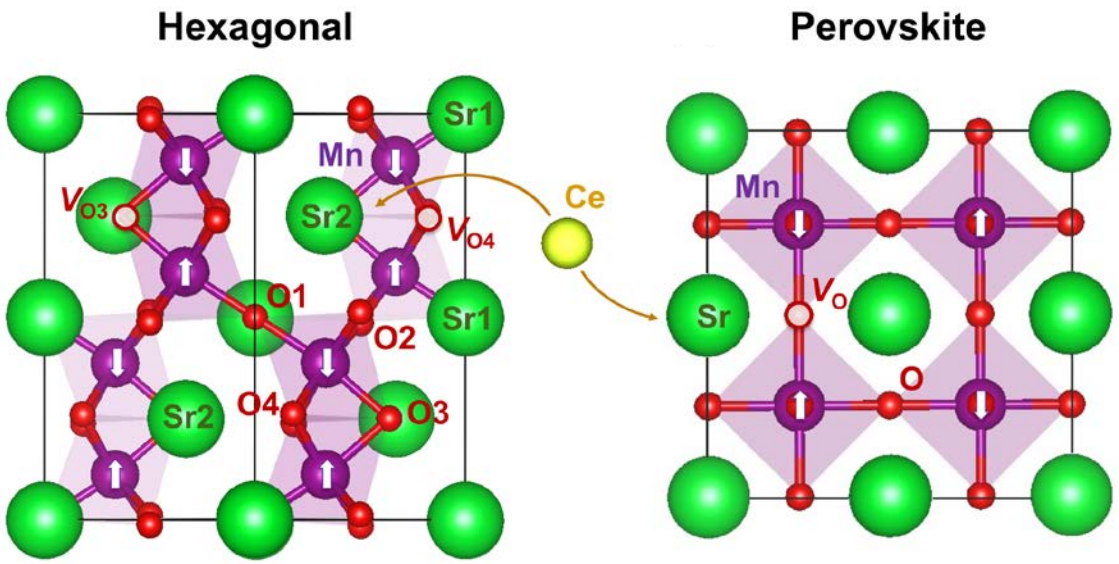
$$\frac{\partial}{\partial T}\Delta\mu_O(T) = \frac{\partial}{\partial \delta}\Delta S^{red}$$

SL, JCP **2018**



Quantitative and mechanistic models

VASP-SCAN+U
$U_{\text{Mn-}d}$ = 2 eV
$U_{\text{Ce-}f}$ = 1 eV



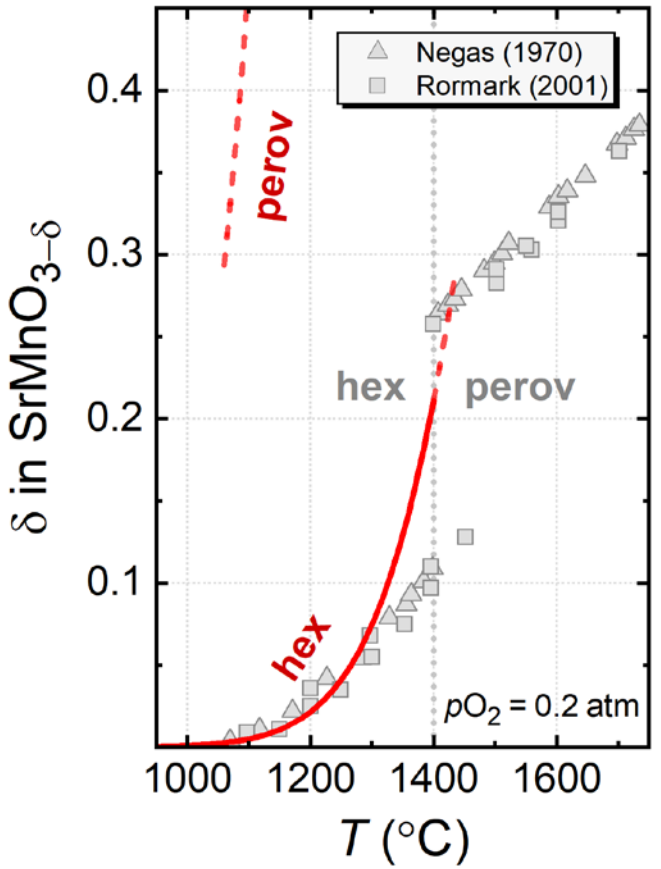
hex	$d_{\text{Mn-O}}$ (Å)	Mn-O-Mn (°)	ΔH_D^{ref} (eV)
O1/O2	1.89-1.92	82	2.37
O3/O4	1.87-1.89	171-174	3.30
perov			
O1	1.90	180	2.04

$Sr_{1-x}Ce_xMnO_{3-\delta}$
HydroGEN seedling
School of Mines

R. O'Hayre
M. Sanders

Role of repulsive defect interactions?

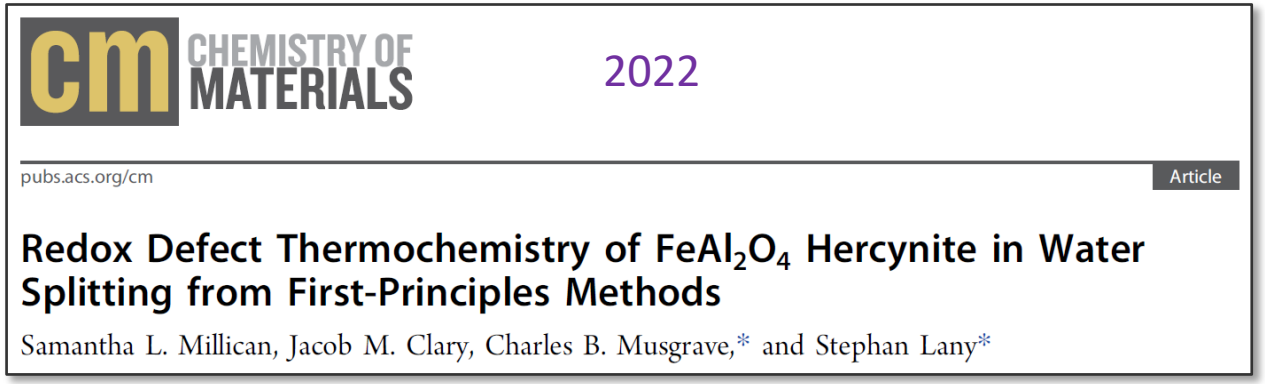
δ = 2.4 @ 1400 °C



$$\Delta H_D = \Delta H_D^{\text{ref}} + \Delta\mu_O$$

$$[V_O] = \frac{\exp(-\Delta H_D / k_B T)}{1 + \exp(-\Delta H_D / k_B T)}$$

Modeling interacting defects



CHEMISTRY OF MATERIALS 2022

pubs.acs.org/cm Article

Redox Defect Thermochemistry of $FeAl_2O_4$ Hercynite in Water Splitting from First-Principles Methods

Samantha L. Millican, Jacob M. Clary, Charles B. Musgrave,* and Stephan Lany*

CHEMISTRY OF MATERIALS 2022

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pubs.acs.org/cm Article

Predicting Oxygen Off-Stoichiometry and Hydrogen Incorporation in Complex Perovskite Oxides

Samantha L. Millican, Ann M. Deml, Meagan Papac, Andriy Zakutayev, Ryan O'Hayre, Aaron M. Holder, Charles B. Musgrave,* and Vladan Stevanović*

npj computational materials 2023 www.nature.com/npjcompumats

ARTICLE OPEN Check for updates

Accurate prediction of oxygen vacancy concentration with disordered A-site cations in high-entropy perovskite oxides

Jiyun Park[1], Boyuan Xu[2], Jie Pan[3], Dawei Zhang[4], Stephan Lany[5], Xingbo Liu[6], Jian Luo[4,7] and Yue Qi[1]✉

Attractive defect interactions

- Electrostatic or strain energies
- Defect pair/complex binding energy
- Law-of-mass-action

Disorder and solid solutions

- Distribution of defect energies

Repulsive defect interactions

- Concentration-dependent formation energy

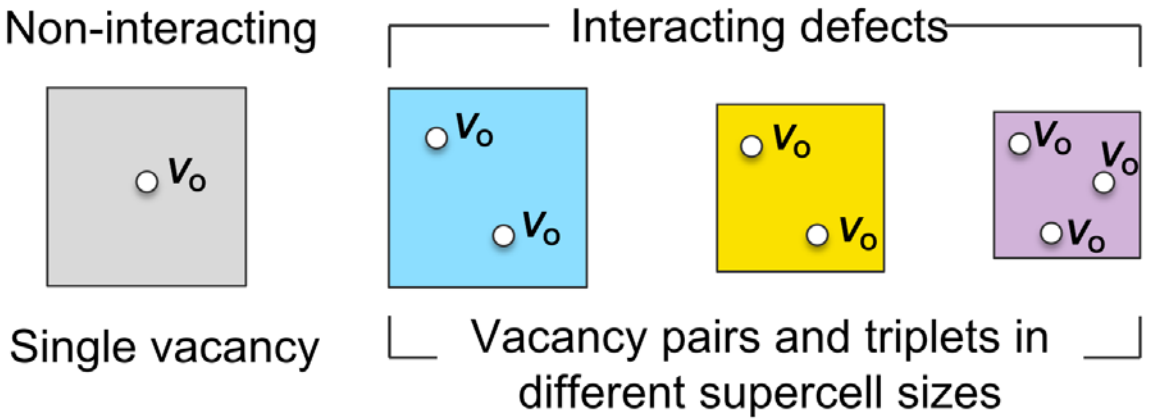
Defect model

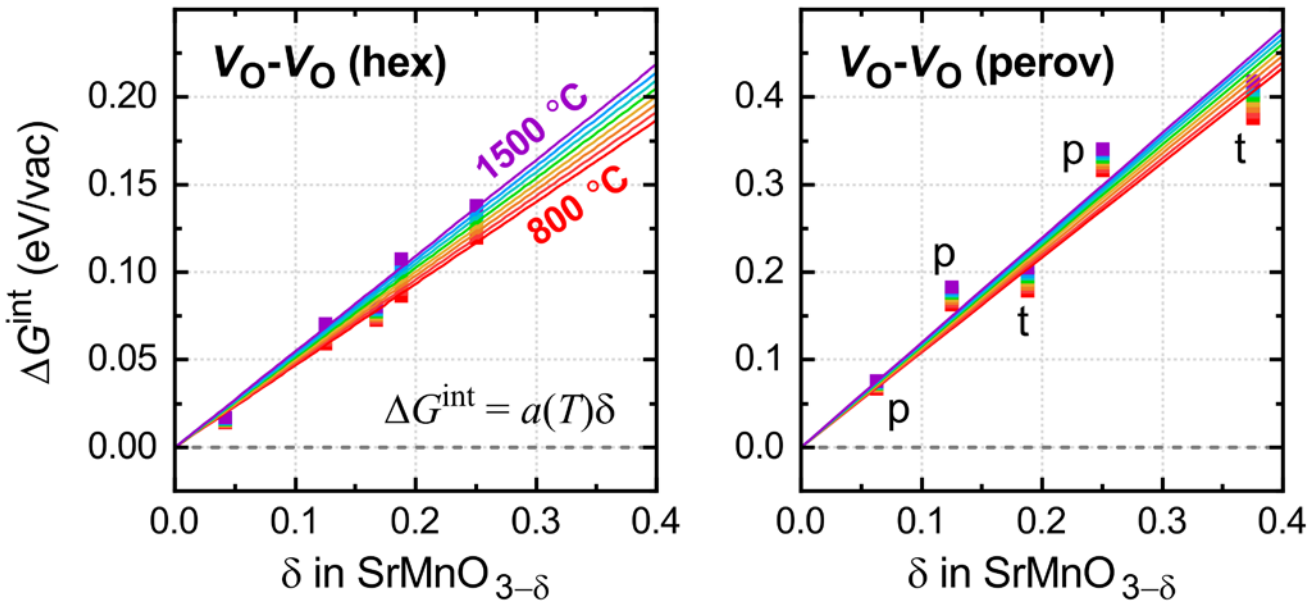
Free energy of defect interaction

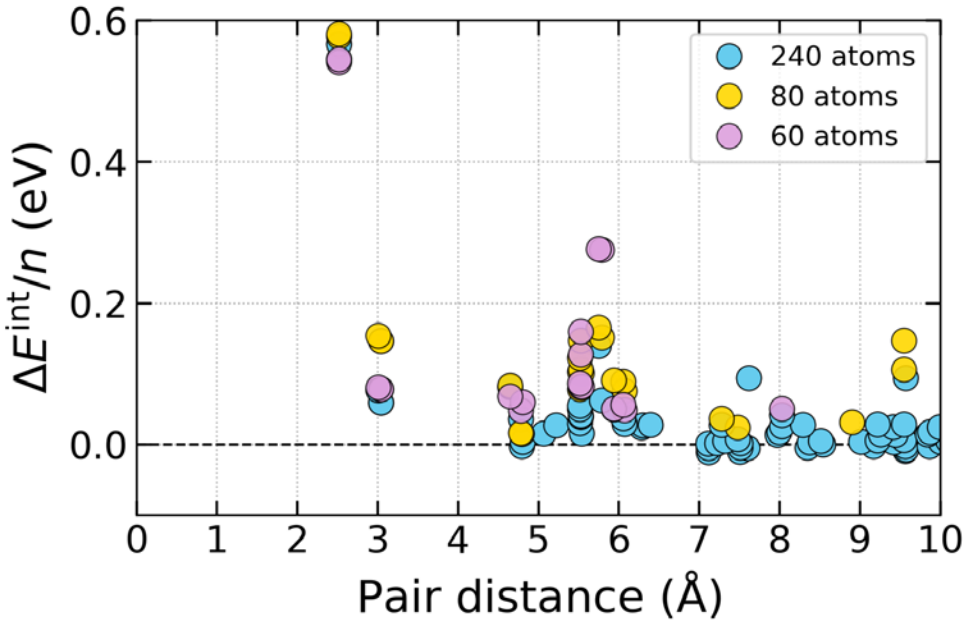
$$\Delta E_i^{\text{int}} = \Delta H_{\text{D},i}(nV_{\text{O}}) - n \times \Delta H_{\text{D}}(V_{\text{O}})$$

$$\Delta G^{\text{int}} = -\frac{k_{\text{B}}T}{n} \ln \sum_i \left(g_i \exp\left(-\Delta E_i^{\text{int}} / k_{\text{B}}T \right) \right)$$

$$\Delta G^{\text{int}}(T) = (a_0 + a_1 T)\delta$$ parameterization







$SrMnO_3$ reduction

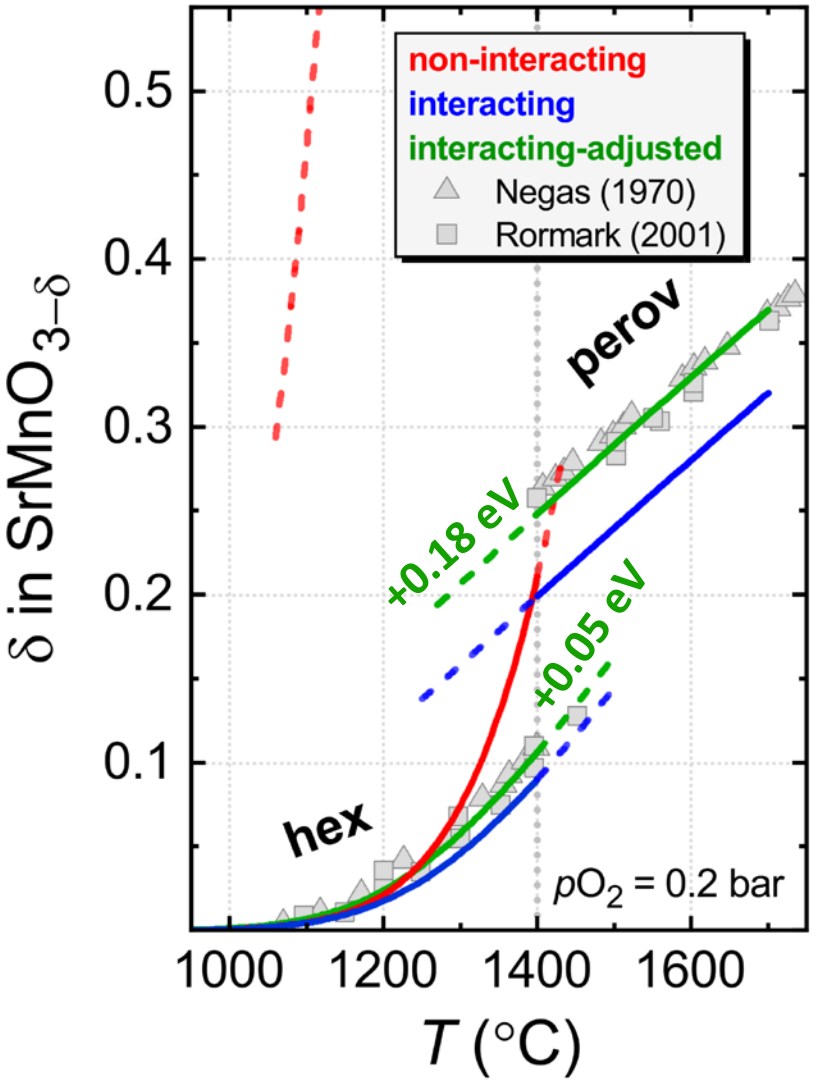
$$\Delta G^{\mathrm{tot}} = f_{\mathrm{d}}\left(x_{\mathrm{V}}\left(\Delta H_{\mathrm{D}} + \Delta G_{\mathrm{D}}^{\mathrm{int}}\right) + k_{\mathrm{B}}T\left(x_{\mathrm{V}}\ln(x_{\mathrm{V}}) + (1-x_{\mathrm{V}})\ln(1-x_{\mathrm{V}})\right)\right)$$

Interacting defect model

- δ moderately underestimated in both phases
- Very good description of *T*-dependence
- Slight adjustment of ΔH_D yields perfect agreement for all *T*

Hexagonal-perovskite phase transition

- ΔE_{poly} = 0.16 eV/fu in SCAN+U
  ΔG^{tot} = 0.13 eV/fu
- Possible additional contributions:
  - vibrational free energies and ZPE
  - polymorph energies beyond DFT



Ce alloying in $Sr_{1-x}Ce_xMnO_{3-\delta}$

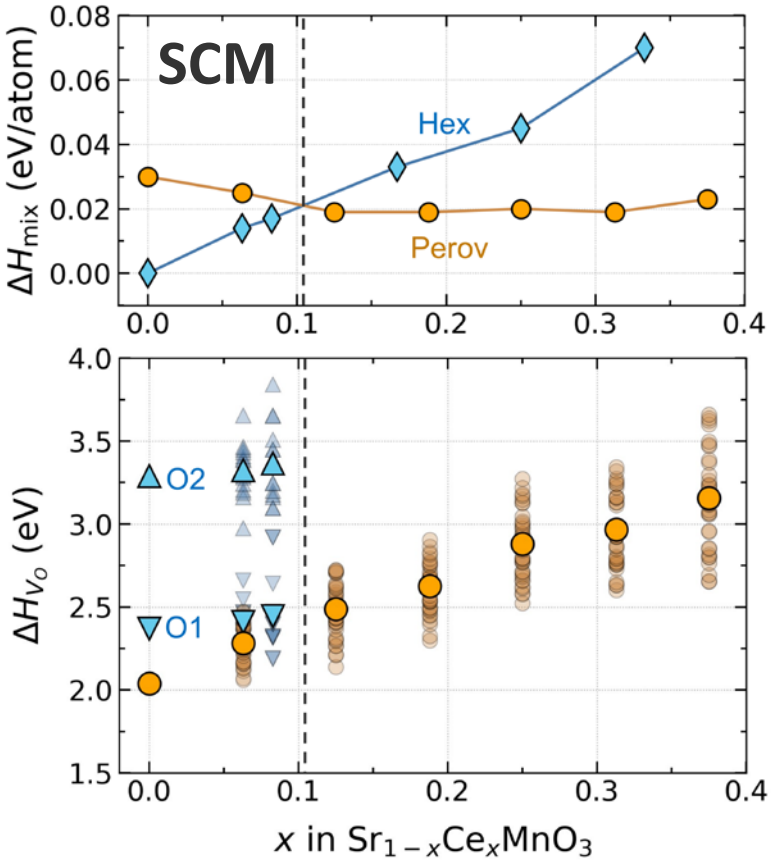
Mixing enthalpy

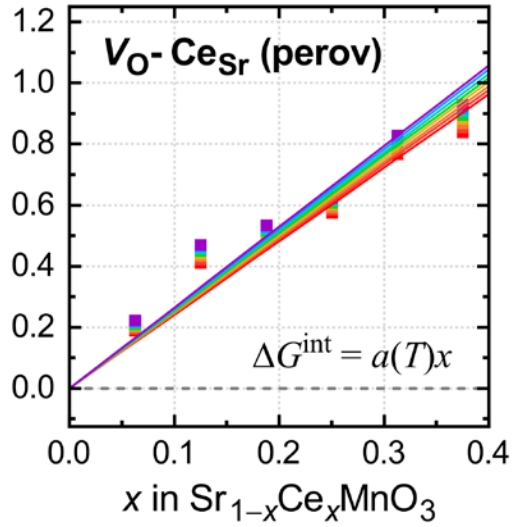
- Positive ΔH_{mix} as expected for solid solution
- x = 1: $CeMnO_3$ is unstable wrt CeO_2+MnO
- Hexagonal-Perovskite transition at x = 0.1 (experimentally at x = 0.05)

O vacancy formation energies

- Strong x dependence
- Superposition of defect interactions:

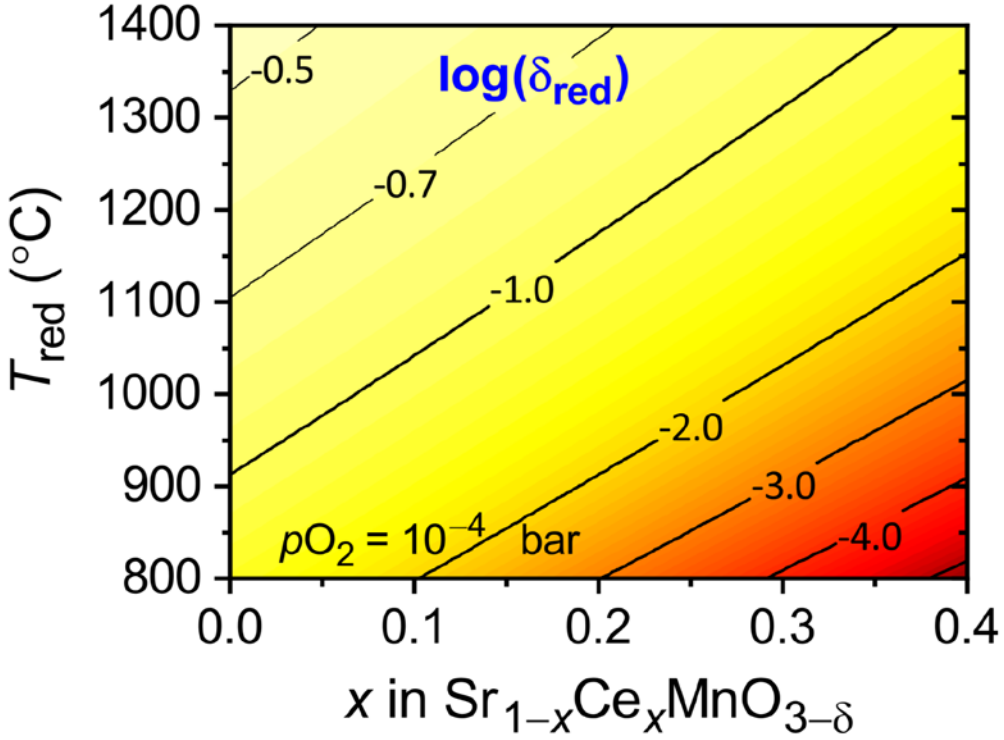
$$\Delta G^{\mathrm{int}}(T) = (a_0 + a_1 T)\,\delta + (a_0' + a_1' T)\,x_{\mathrm{Ce}}$$



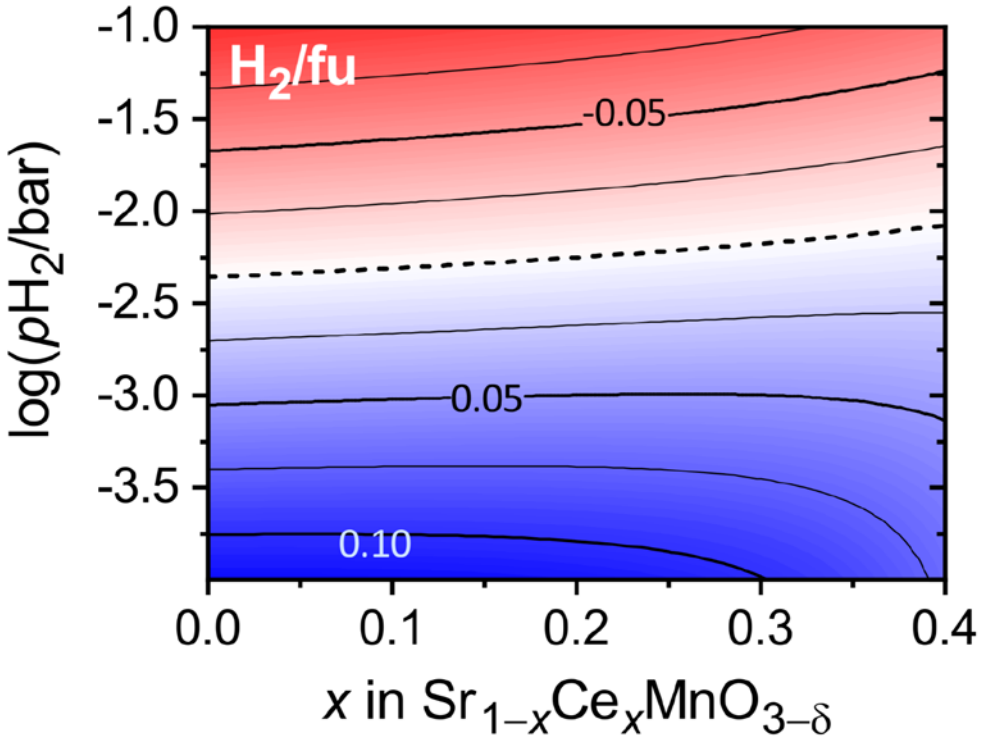


SCM reduction and H_2

- δ decreases with Ce fraction
- Near quantitative agreement with experiment Bergeson-Keller *et al*, Ene. Tech. (2022)



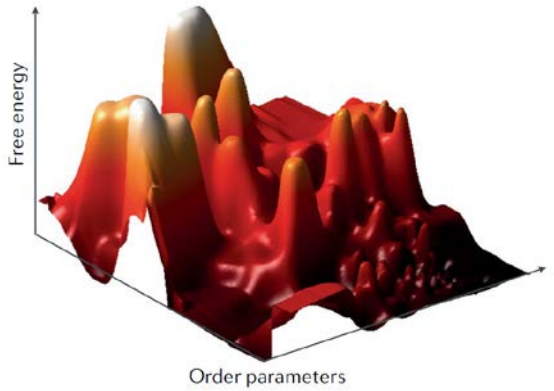
- Reduction: T = 1400 °C, $pO_2 = 10^{-4}$ atm
  Oxidation: T = 850 °C, pH_2O = 1 atm
- Ideal gas law: $H_2 + O_2 \leftrightarrow H_2O$
- Water splitting only under dilute H_2:H_2O
  $pH_2 < 10^{-2}$ atm
- Increasing pH_2 threshold with x_{Ce}



A. Goyal, M.D. Sanders, R.P. O'Hayre, S. Lany, PRX Energy **3**, 013008 (2024)

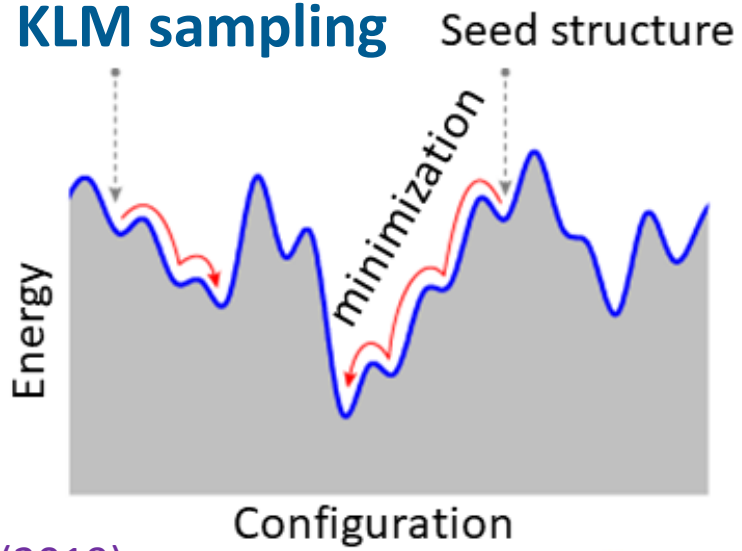
Materials Discovery – structure prediction

New metastable binary nitrides



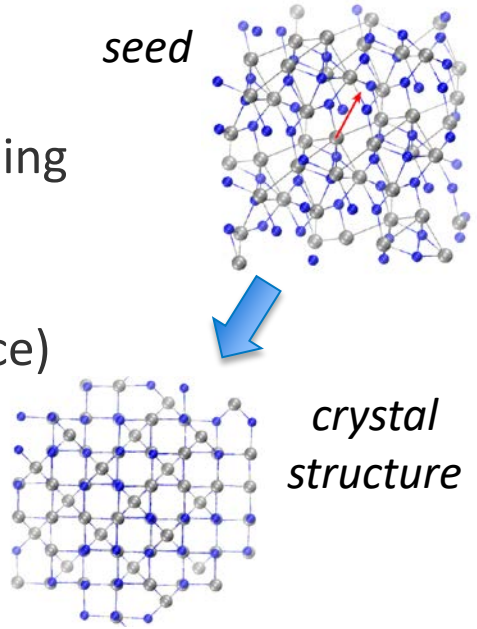
Oganov, Pickard, Zhu, Needs,
Nature Reviews Materials 4, 331 (2019)

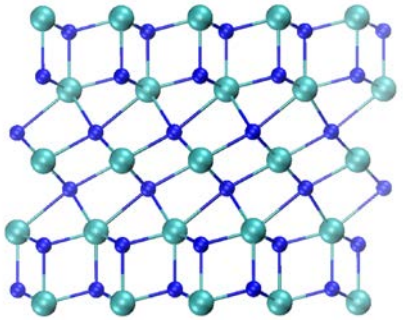
KLM sampling



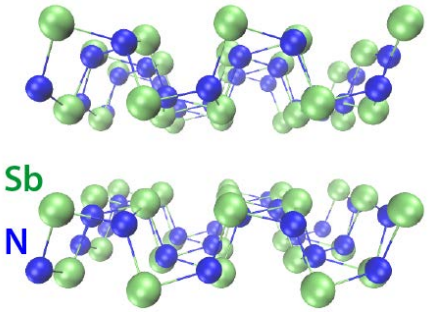
Kinetically limited minimization (KLM)

- Hybrid random search and basin hopping
- DFT total energy (VASP-PAW)
- Metastable materials
- Reduction of phase space (min distance)
- Applications
  - ternary nitrides
  - oxynitrides





Ce_3N_4 (sg 166)
E_g = 2.15 eV

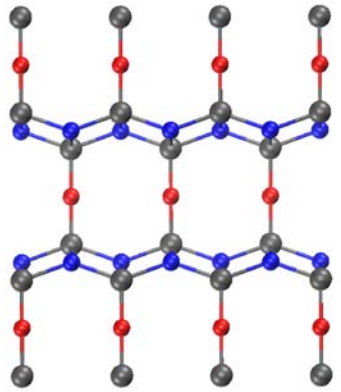


SbN (sg 29)
E_g = 2.21 eV

Sharan, SL, JCP (2021)

Chen, SL, *et al*, Cell Reports (2022)

Oxynitrides



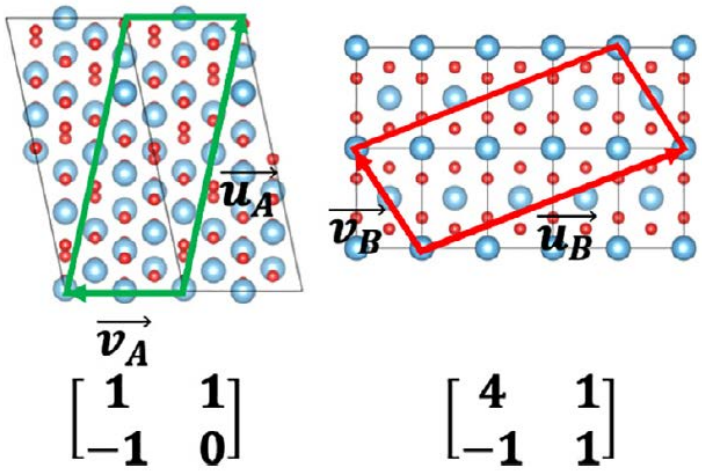
Ti_2ON_2 (sg 139)
E_g = 1.74 eV

Structure prediction for interfaces?

Construction of interfaces structures (literature)

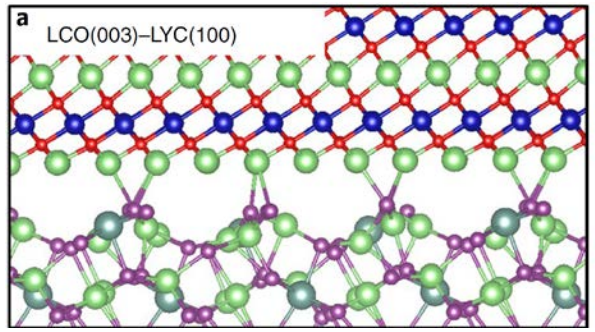
coincidence site lattice (CSL)

Zur, McGill, JAP (1984)

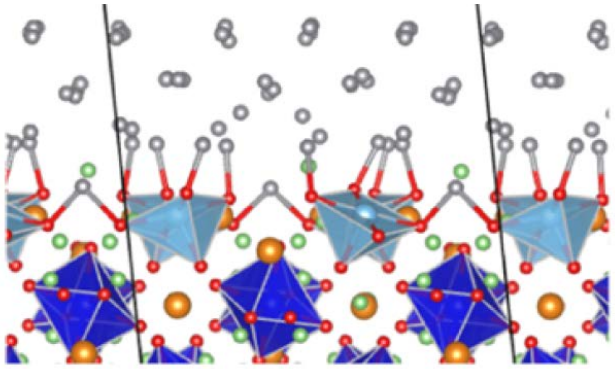


Gao *et al*, Sci Bull (2019)

free-surface joint (free surfaces, translation)



Zahiri *et al*, Nat Mater (2021)

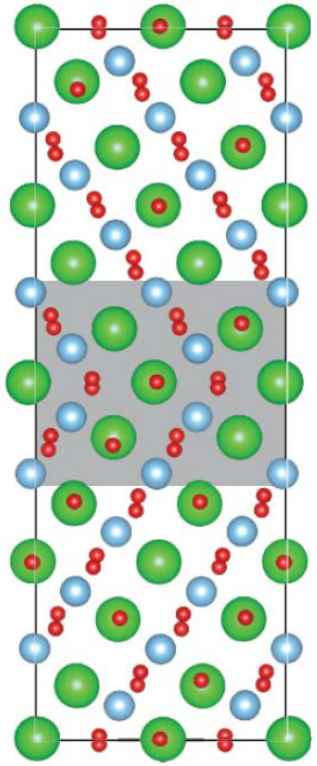


Gao *et al*, ACS Appl Mat Int (2020)

structure sampling

$SrTiO_3$ grain boundary

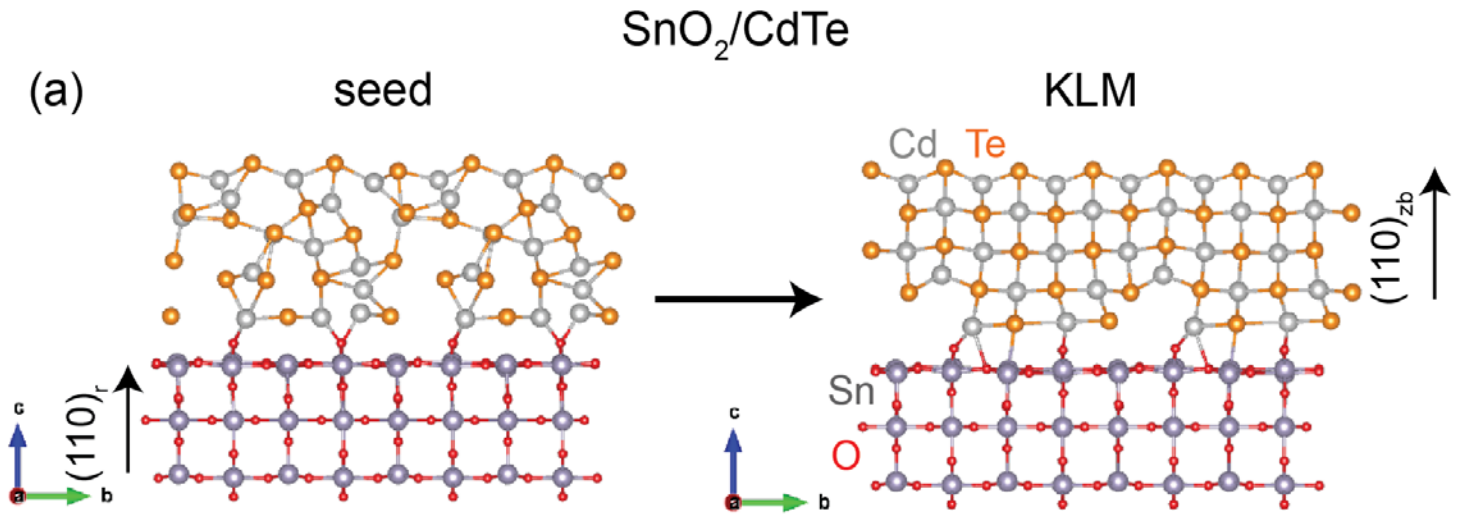
randomization region

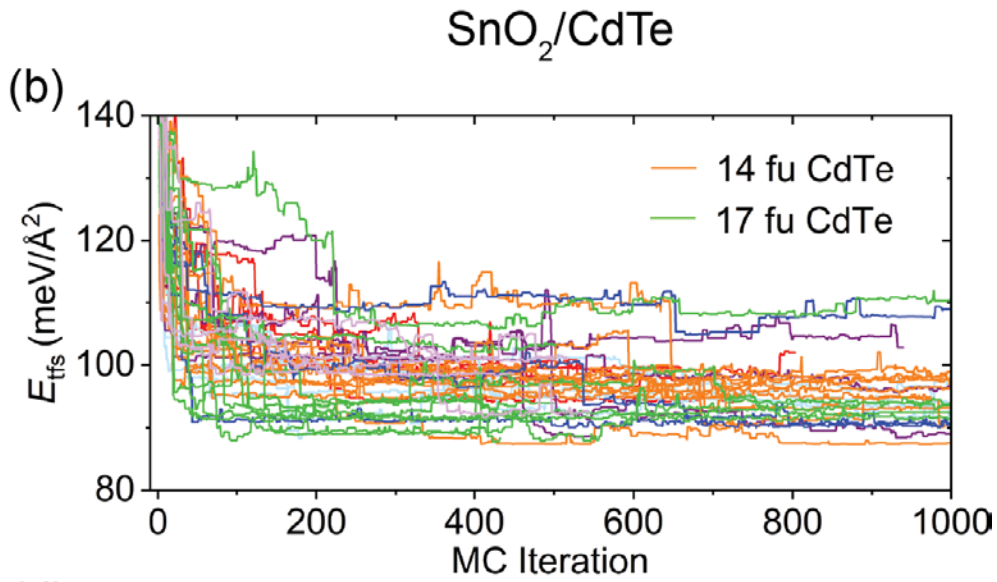


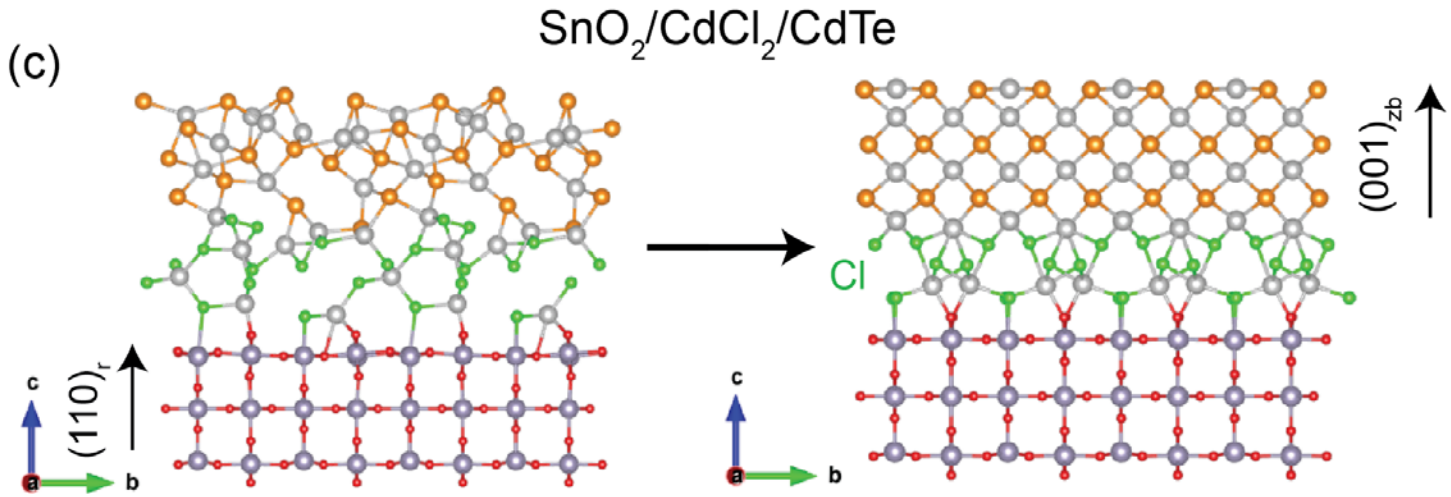
Schusteritsch, Pickard, PRB (2014)

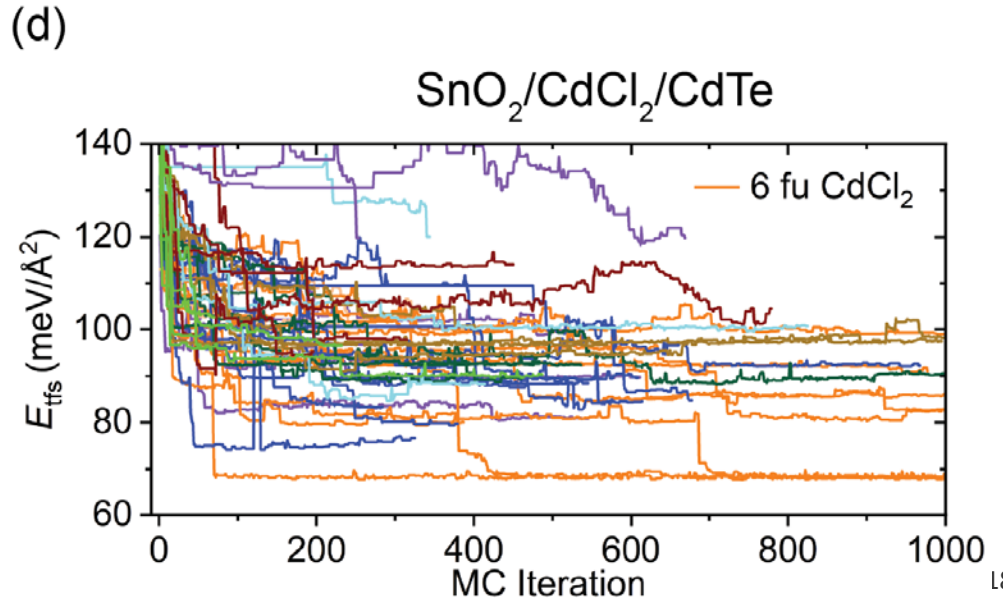
Interface structure prediction: SnO_2/CdTe

Sharan *et al*, SL, Appl Phys Rev (2022)



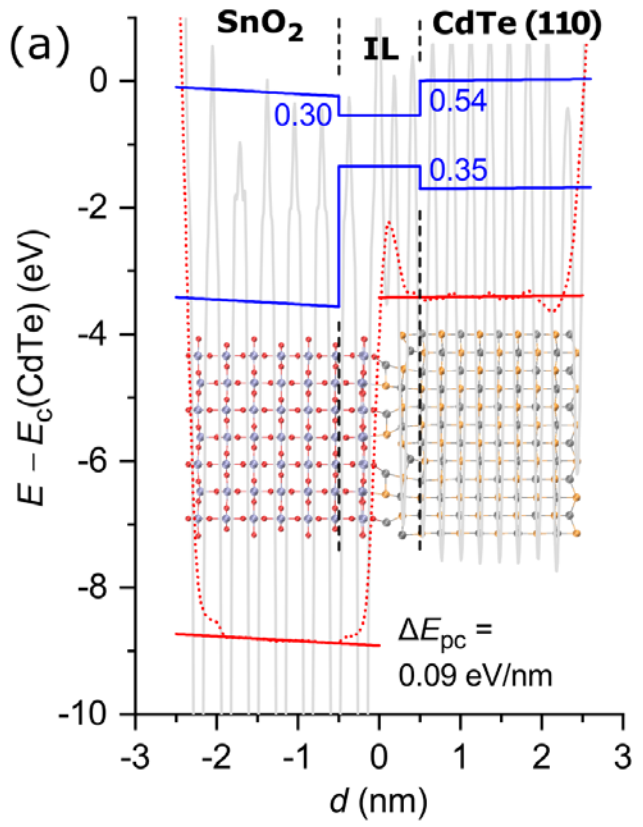


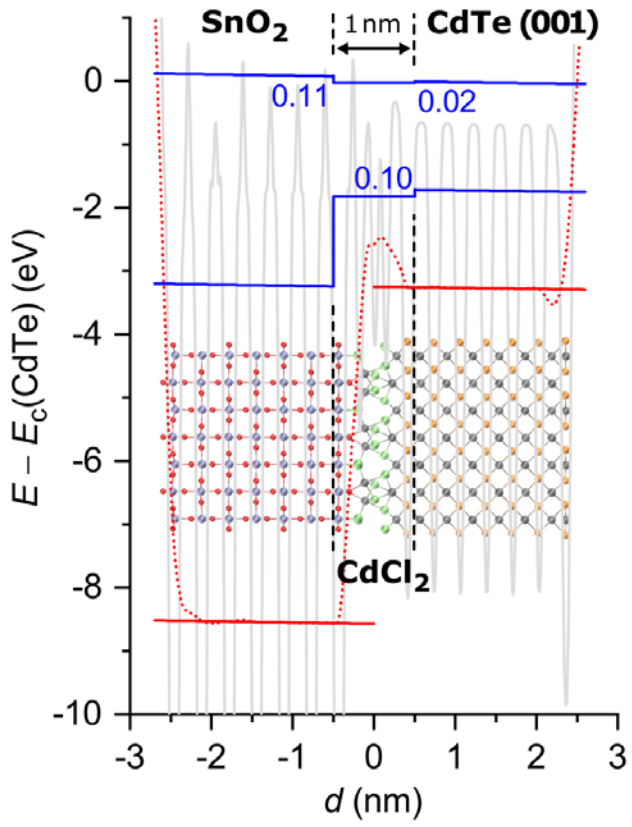


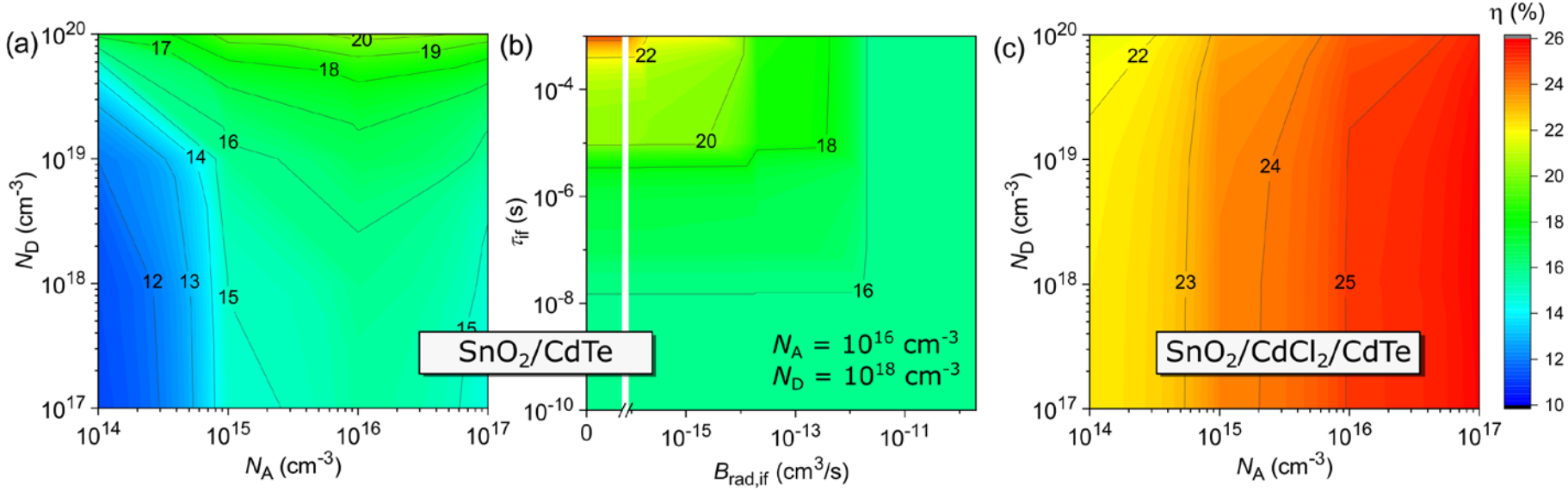


From first-principles to device modeling

- Band gap corrected calculation
- Definition of 1 nm interface layer
- Band alignment data enters device modeling
- $CdCl_2$ interlayer changes device behavior
- η approaches SQ limit







Sharan *et al*, SL, Appl Phys Rev (2022)

Conclusions

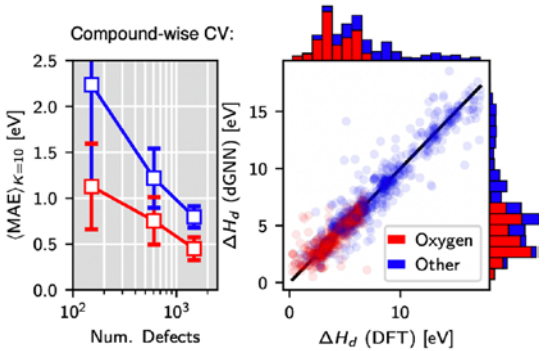
Energy Transition

- Need for direct, non-electricity renewable fuels (H_2)

Machine learning of defect formation energies

- dGNN approach uses crystal structure of defect-free system
- Database screening and targeted experimental and theoretical studies for STCH (NREL, Sandia, LLNL)

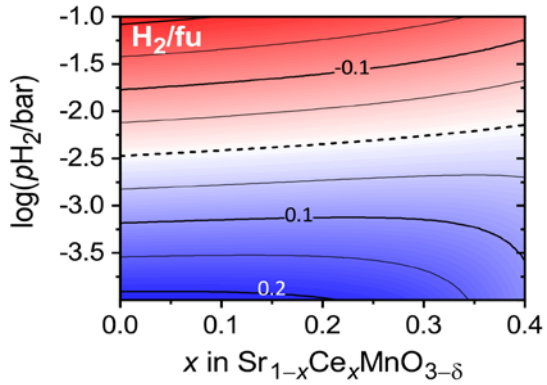
M.D. Witman, A. Goyal, T. Ogitsu, A.H. McDaniel, S. Lany,
Nature Comp. Sci. 3, 675 (2023)



Thermochemical equilibria with interacting defects

- Free energy of defect interaction $\Delta G_D^{int}(\delta,x,T)$ for $Sr_{1-x}Ce_xMnO_{3-\delta}$
- Thermodynamic modeling of H_2 yield vs pH_2

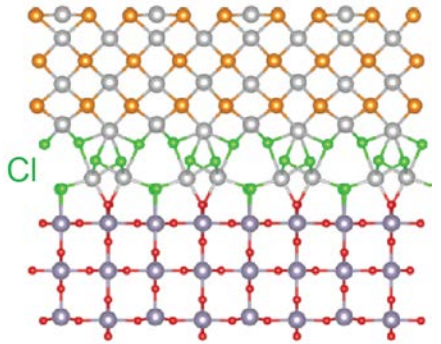
A. Goyal, M.D. Sanders, R.P. O'Hayre, S. Lany,
PRX Energy **3**, 013008 (2024)



Interface structure predictions

- Opportunities in "Interface Discovery"
- Atomically thin interlayers to connect otherwise incompatible materials

A. Sharan, M. Nardone, D. Krasikov, N. Singh, S. Lany,
Appl. Phys. Rev. **9**, 041411 (2022)



Thank you

www.nrel.gov

NREL/PR-5K00-89707

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