Machine Learning-Guided Design of Perovskite Oxides for High-Temperature Oxygen Sensing

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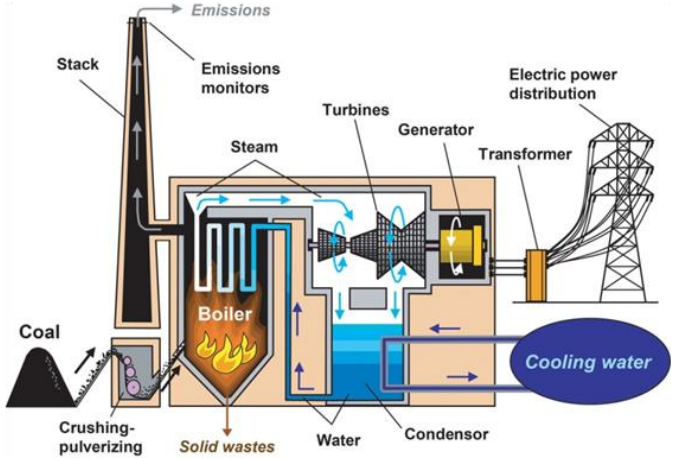
Introduction

- Real-time gas monitoring in harsh combustion environments requires robust high-temperature sensors
- Perovskite oxides (ABO_3) offer superior thermal stability and tunable properties through A/B-site doping
- Machine learning combined with first-principles calculations accelerates materials discovery

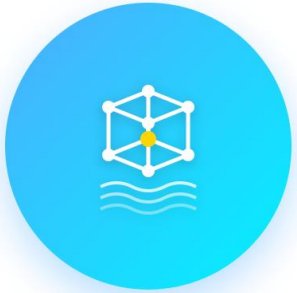
Fossil-/Nuclear-based power plants



Harsh Environment

High-temperature combustion conditions require robust materials

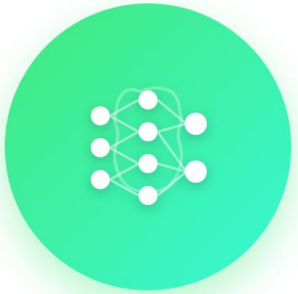
300-1000°C



Material Stability + High Sensitivity

Perovskite oxides with tunable properties and thermal resilience

ABO_3 Structure



ML Discovery

Machine learning screens millions of candidates to accelerate materials design

187M → Top Candidates

ML-driven Discovery Pipeline

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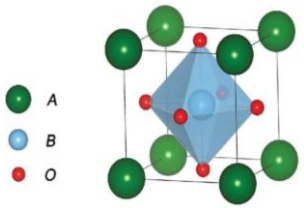


Composition Generation

~187M

13 A-site × 36 B-site combinations

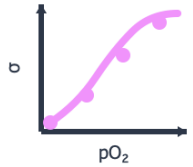
2

Stability Prediction

~39M

Gradient Boosting
F1 = 0.95

3



Conductivity Prediction

XGBoost

R^2 = 0.99
RMSE = 0.18

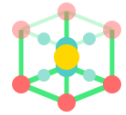
4

Ranking Top Materials

Top 10

By O_2 sensitivity (conductivity gradient)

5



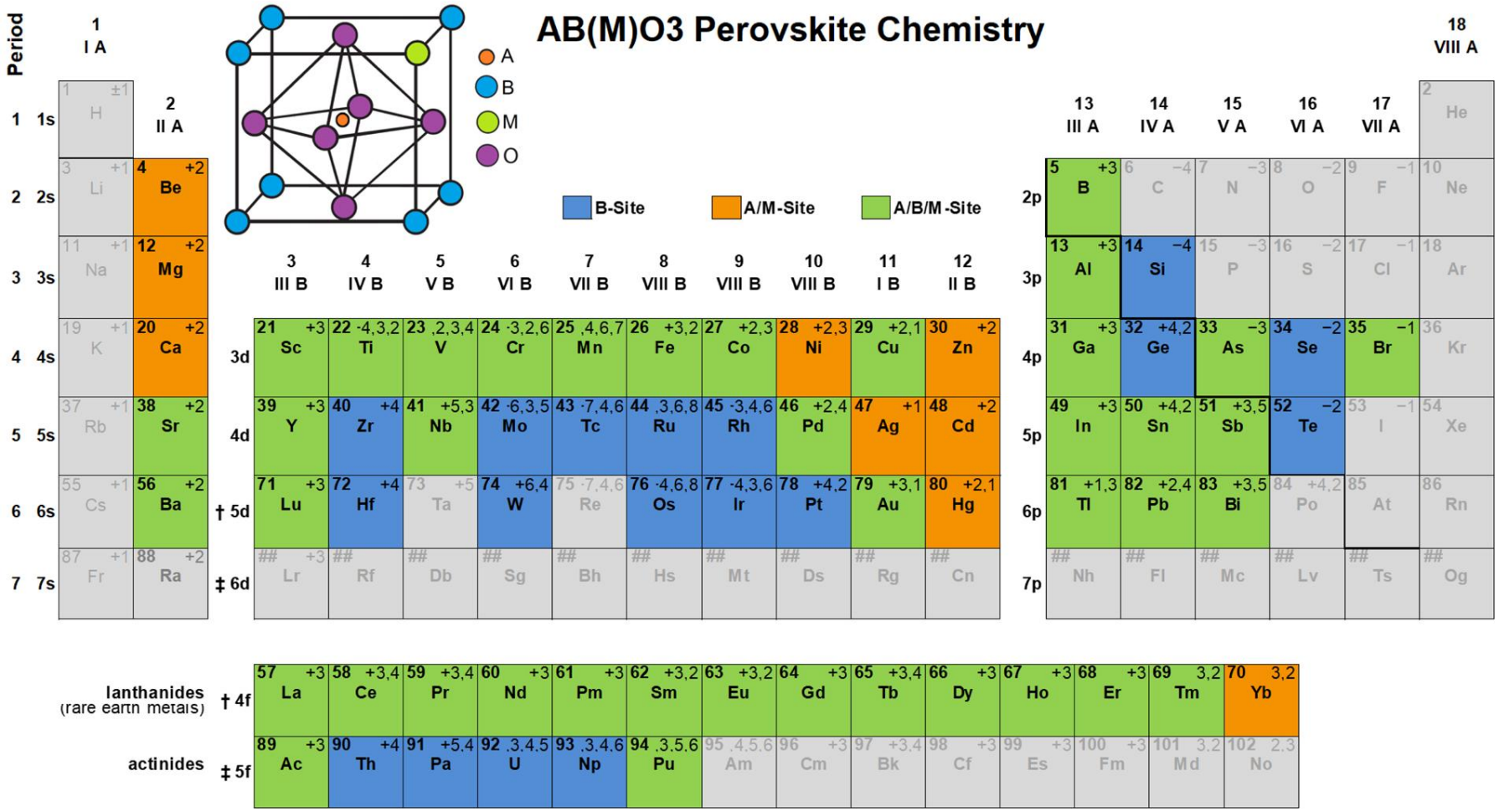
DFT Validation

Selected

Structure, Band, DOS, Optical properties

- **Generated 187 million ABO_3 combinations from 13 A-site (Sr, La, Ca, Ba...) and 36 B-site (Ti, Nb, Dy...) elements with varied ratios**

Initial Composition Generation



187 million compositions

$A_xA'_{1-x}B_yB'_{1-y}O_{3-\delta}$

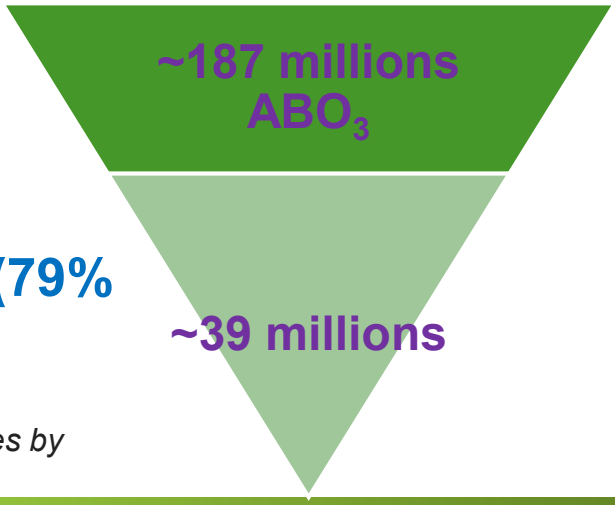
A site	Ba	Bi	Ca	Ce	Gd	La	Mg
	Nd	Pr	Sm	Sr	Y	Yb	
B site	Al	Be	Ca	Ce	Co	Cr	
	In	La	Lu	Mg	Mn	Mo	
	Sn	Tb	Th	Ti	V	W	
	Cu	Dy	Er	Fe	Ga	Gd	
	Nb	Nd	Ni	Pr	Sc	Si	
	Y	Yb	Zn	Zr	Hf	Sm	

Priya, Pikee, and Narayana R. Aluru. "Accelerated design and discovery of perovskites with high conductivity for energy applications through machine learning." npj Computational Materials 7, no. 1 (2021): 90.

Stability Prediction

Database	Features	Target
1120 ABO3 from the ICSD database by Zhai et al. and literature by Priya et al.	Site-specific elemental features, including cation-oxygen bond distance, Mendeleev number, oxidation states, and ionic radius	**946 Perovskite/** **174 not Perovskite**

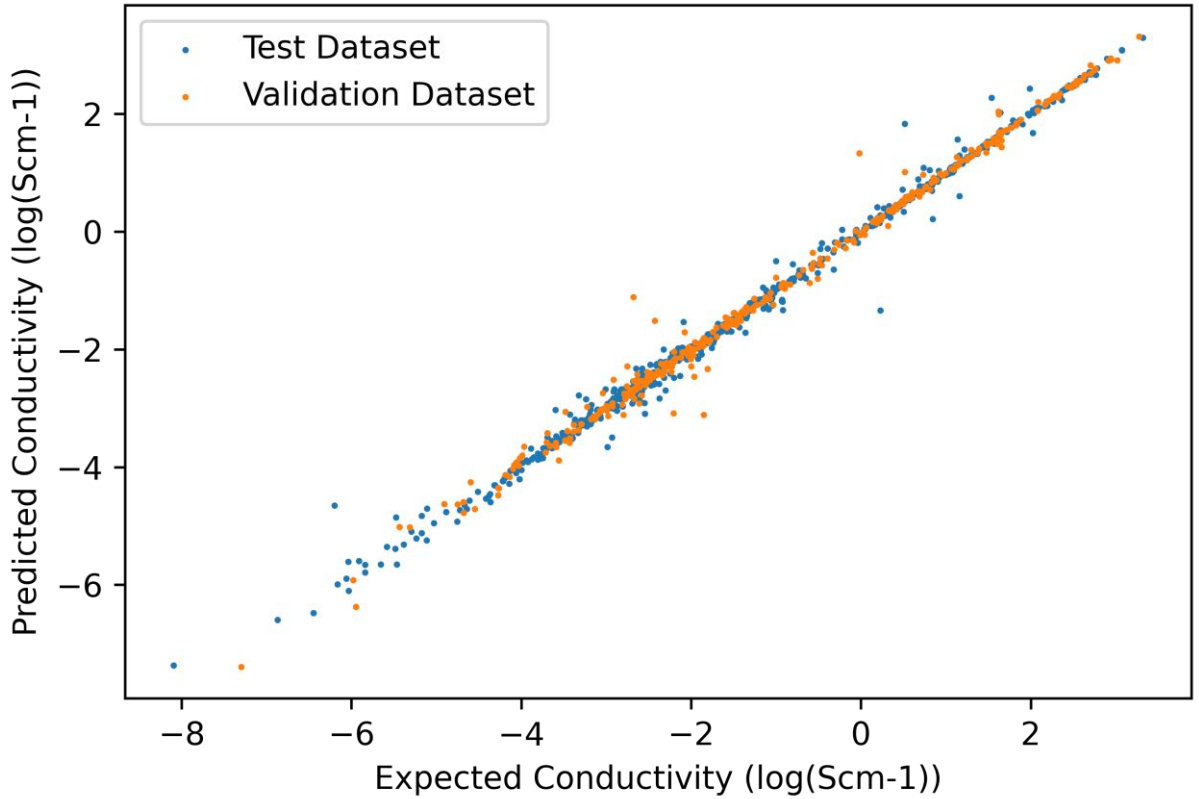
- **A gradient boosting classification model predicted perovskite stability**
- **Mean F1 score of 0.95 ± 0.02 on 5-fold cross-validation**
- **Reduced candidates from ~187M to ~39M stable compositions (79% reduction)**



Zhai, X., Ding, F., Zhao, Z., Santomauro, A., Luo, F. and Tong, J., 2022. Predicting the formation of fractionally doped perovskite oxides by a function-confined machine learning method. Communications Materials, 3(1), p.42.

Conductivity Prediction

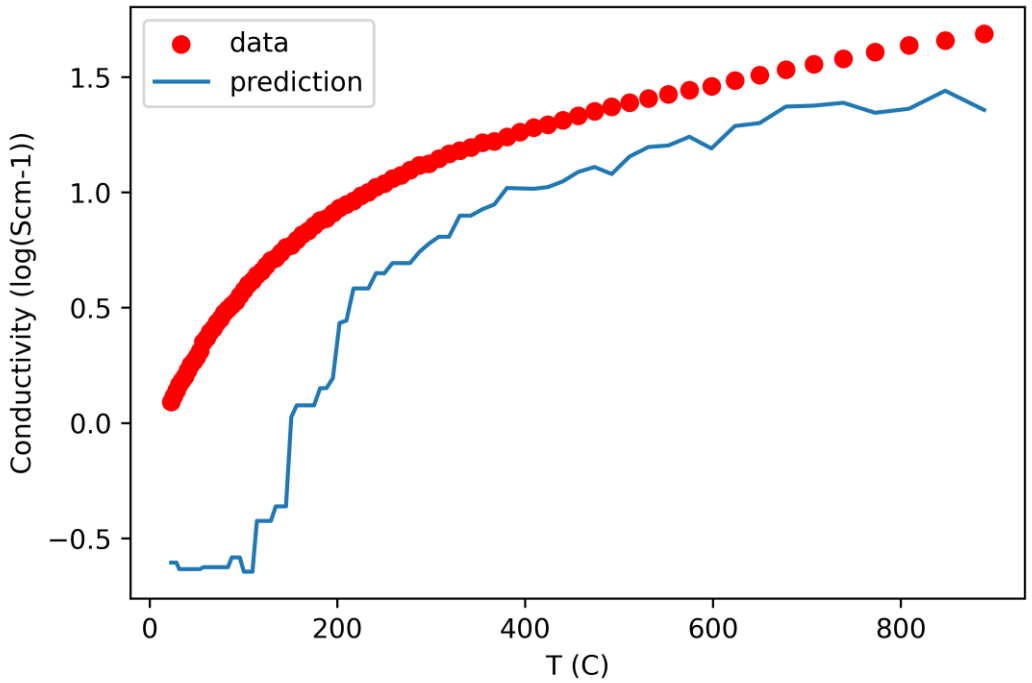
- XGBoost regression model: 600 estimators, max depth 10, trained on the dataset reported by Priya et al.
- 100 features derived from Materials Project database (oxide properties) and Shannon tables (elemental properties)
- Top predictors: ionic radius, electronegativity, atomic mass, oxide formation energy
- Performance: $R^2 = 0.99$, RMSE = 0.18



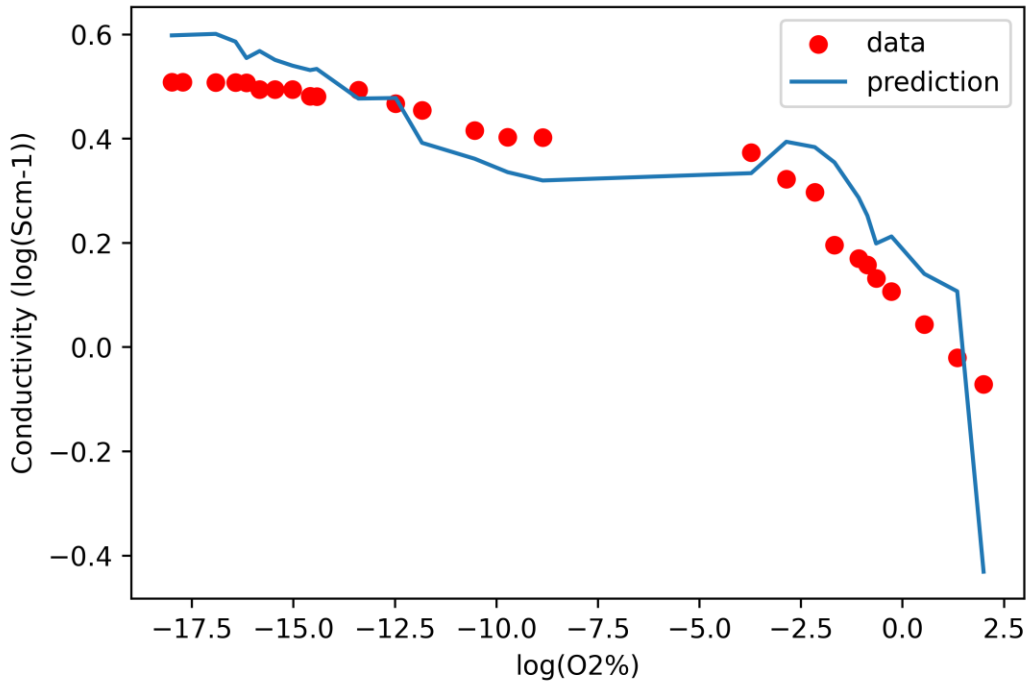
Priya, Pikee, and Narayana R. Aluru. "Accelerated design and discovery of perovskites with high conductivity for energy applications through machine learning." npj Computational Materials 7, no. 1 (2021): 90.

Conductivity Prediction

- Predicted conductivity trends match experimental ground truth for a given perovskite across temperature and oxygen partial pressure
- Validated model fitness enables oxygen sensitivity quantification



$La_{0.7}Sr_{0.3}Cr_{0.5}Mn_{0.5}O_3$



$La_{0.2}Sr_{0.575}Ti_{0.75}Nb_{0.25}O_3$

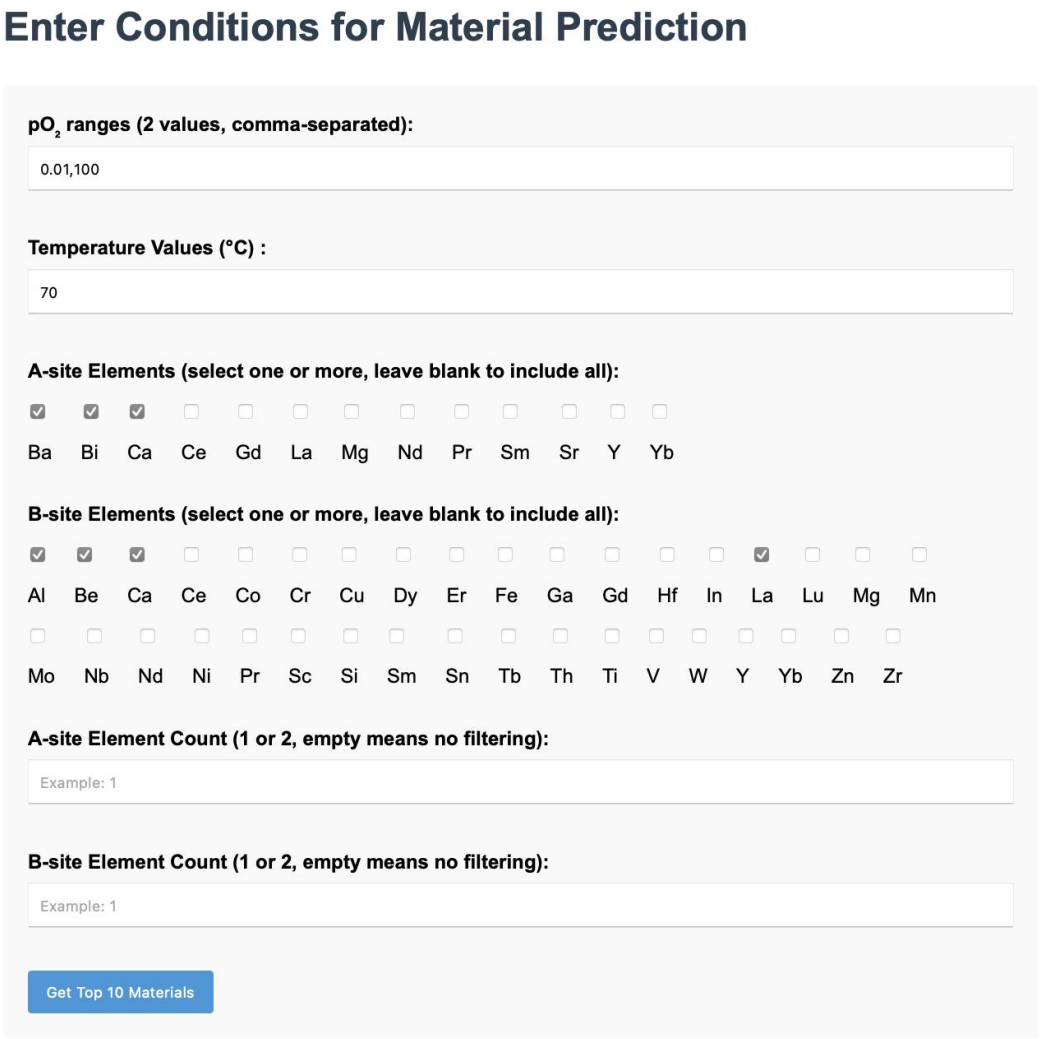
Top Oxygen Sensing Candidates

- 39M candidates screened with full Temperature-pO_2 conductivity profiles
- Materials ranked by oxygen-conductivity gradient (sensitivity metric)
- Top candidates show 3-order-magnitude conductivity change across pO_2 range
- Literature validation confirms model predictions

#	Composition	pO2 (%)	Temp (°C)	$\Delta\log_{10}$(Conductivity)	Experimental reported
1	$La_{0.4},Sr_{0.4}\ TiO_3$	1e-18 - 100	930	3.0789201	$La_{0.4}S_{r0.4}\ TiO_3$
2	$La_{0.6}Sr_{0.1}TiO_3$	1e-18 - 100	930	2.9785082	
3	$La_{0.45}Sr_{0.25}\ TiO_3$	1e-18 - 100	930	2.924773	
4	$La_{0.55}Sr_{0.15}TiO_3$	1e-18 - 100	930	2.9047394	
5	$La_{0.5}Sr_{0.2}TiO_3$	1e-18 - 100	930	2.887693	
6	$La_{0.3}Sr_{0.5}TiO_3$	1e-18 - 100	930	2.7824388	
7	$Ba_{0.25}Y_{0.45}TiO_3$	1e-18 - 100	930	2.7820268	
8	$La_{0.4}Sr_{0.3}Nb_{0.05}Ti_{0.95}O_3$	1e-18 - 100	930	2.7802086	
9	$Ba_{0.25}Y_{0.45}Nb_{0.05}Ti_{0.95}O_3$	1e-18 - 100	930	2.7801607	
10	$La_{0.25}Sr_{0.55}Nb_{0.05}Ti_{0.95}O_3$	1e-18 - 100	930	2.7787879	

Interactive Web Tool

- An interactive web tool has been developed to enable researchers to leverage the predictive power of the ML model
- The web tool allows users to input perovskite compositions and obtain ranking of promising candidates with conductivity profiles, and O_2-conductivity gradients

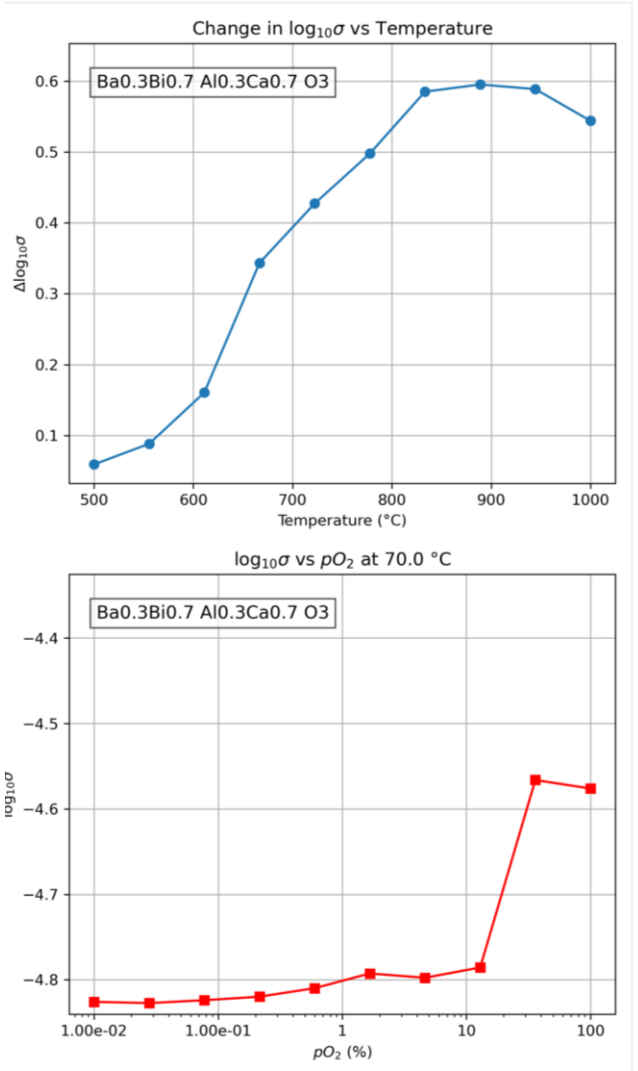


Interactive Web Tool

- **Output of the web tool:**

Top 10 Materials for Selected Conditions

Rank	ABO_3 Composition	Temperature (°C)	pO_2 Range (%)	Conductivity Change Δσ (log10(S/cm))
1	Ba0.3Bi0.7 Al0.3Ca0.7 O3	70.0	1e-02 - 100	0.24959039688110352
2	Ba0.3Bi0.7 Be0.1Ca0.9 O3	70.0	1e-02 - 100	0.24631690979003906
3	Ba0.3Bi0.7 Al0.2Ca0.8 O3	70.0	1e-02 - 100	0.2430119514465332
4	Ba0.3Bi0.7 Al0.4Ca0.6 O3	70.0	1e-02 - 100	0.23980045318603516
5	Ba0.3Bi0.7 Al0.1Ca0.9 O3	70.0	1e-02 - 100	0.23726129531860352
6	Ba0.3Bi0.7 Be0.2Ca0.8 O3	70.0	1e-02 - 100	0.2346029281616211
7	Ba0.3Bi0.7 Be0.3Ca0.7 O3	70.0	1e-02 - 100	0.21727752685546875
8	Ba0.3Bi0.7 Ca O3	70.0	1e-02 - 100	0.1578836441040039
9	Ba0.6Bi0.4 Be0.7Ca0.3 O3	70.0	1e-02 - 100	0.1559600830078125
10	Ba0.4Bi0.6 Be0.6Ca0.4 O3	70.0	1e-02 - 100	0.1464672088623047



Density Functional Theory Analysis

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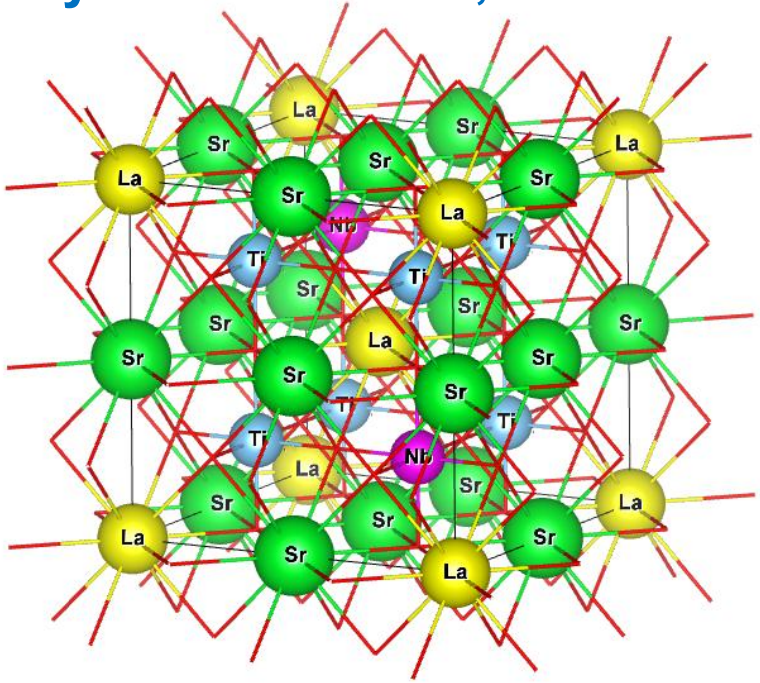
- **ML predictions at 700°C with 1-20% O_2 range guide DFT analysis**

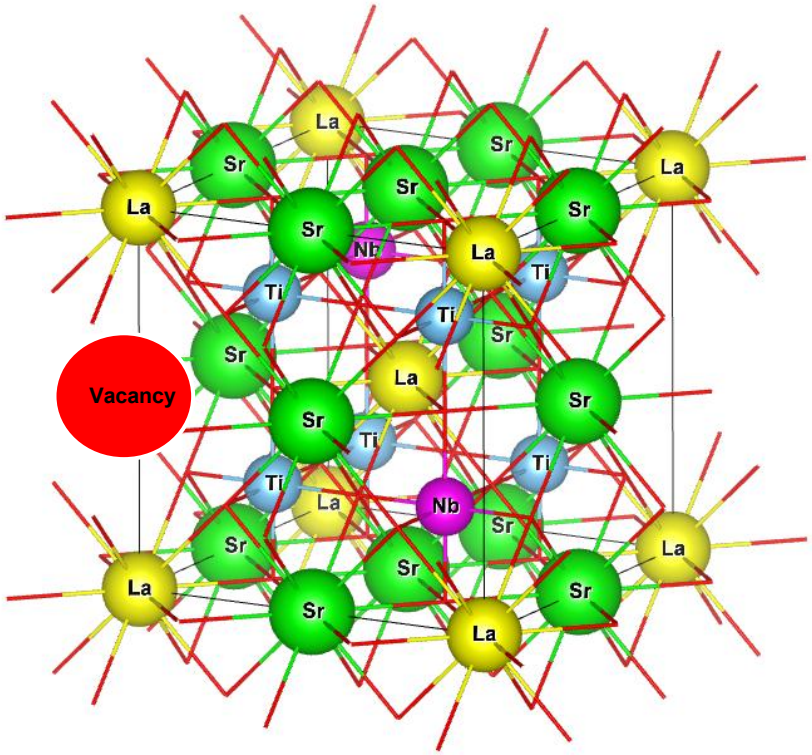
#	Conductivity change	PO2 Range (%)	Temperature (oC)	Material
1	0.8612474	1-20	700	La0.2Sr0.6 Nb0.2Ti0.8 O3
2	0.6170686	1-20	700	La0.2Sr0.6 Nb0.15Ti0.85 O3
3	0.615512	1-20	700	La0.4Sr0.3 Nb0.15Ti0.85 O3
4	0.6091372	1-20	700	La0.2Sr0.6 Nb0.1Ti0.9 O3
5	0.5975531	1-20	700	Nd0.2Sr0.6 Nb0.15Ti0.85 O3
6	0.5874653	1-20	700	Ba0.45Ca0.45 Nb0.2Ti0.8 O3
7	0.56509346	1-20	700	Gd0.2Sr0.6 Nb0.1Ti0.9 O3
8	0.5614067	1-20	700	Sm0.2Sr0.6 Nb0.15Ti0.85 O3
9	0.56001383	1-20	700	La0.2Sr0.6 Nb0.05Ti0.95 O3
10	0.53898513	1-20	700	Pr0.4Sr0.3 Nb0.15Ti0.85 O3

- **$La_{0.2}Sr_{0.6}Ti_yNb_{(1-y)}O_3$ series (y = 0.8, 0.85, 0.9, 0.95) selected for validation**
- **Predicted that higher y values show decreased sensitivity (inverse correlation)**

DFT Structural Analysis

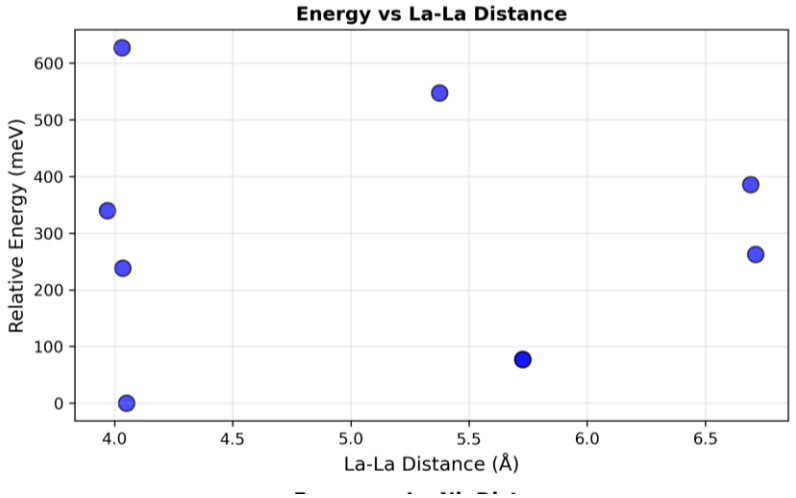
- PAW-PBE+U functional in generalized gradient approximation
- $La_{0.2}Sr_{0.6}Ti_{0.8}Nb_{0.2}O_3$ supercell: 7.8 Å cubic lattice
- Dopant separations: La-La = 6.76 Å, Nb-Nb = 6.76 Å, La-Nb = 3.38 Å
- Sr vacancy proximity: Sr/La = 3.91 Å, Ti/Nb = 3.38 Å

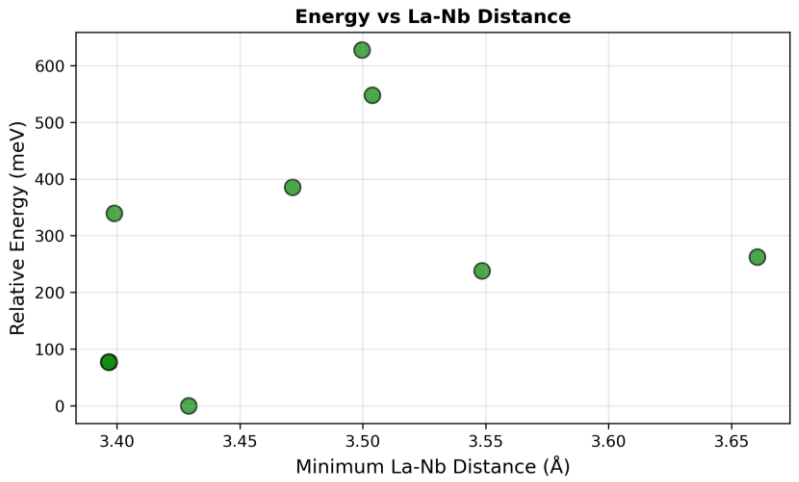


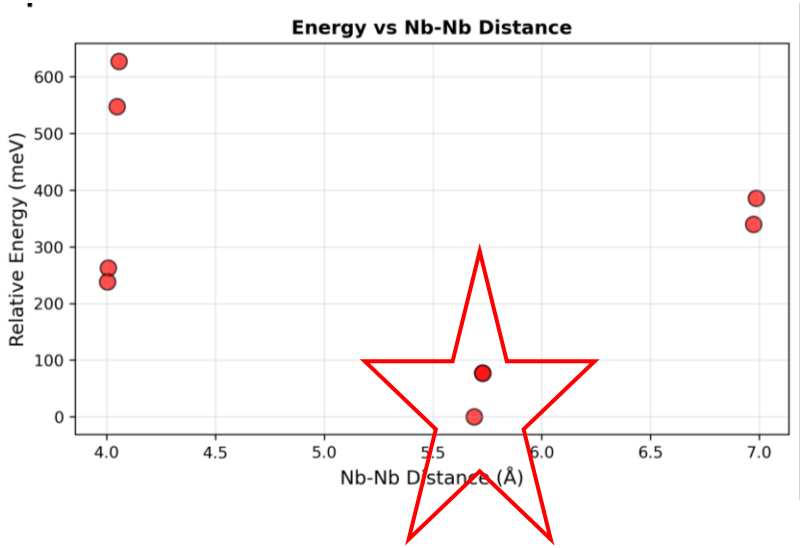


Dopant Configuration Optimization

- 8 structural models tested for non-vacancy $La_{0.2}Sr_{0.8}Ti_{0.8}Nb_{0.2}O_3$
- Ground state energy vs. dopant distances (La-La, Nb-Nb, La-Nb)
- Lowest energy configuration identified



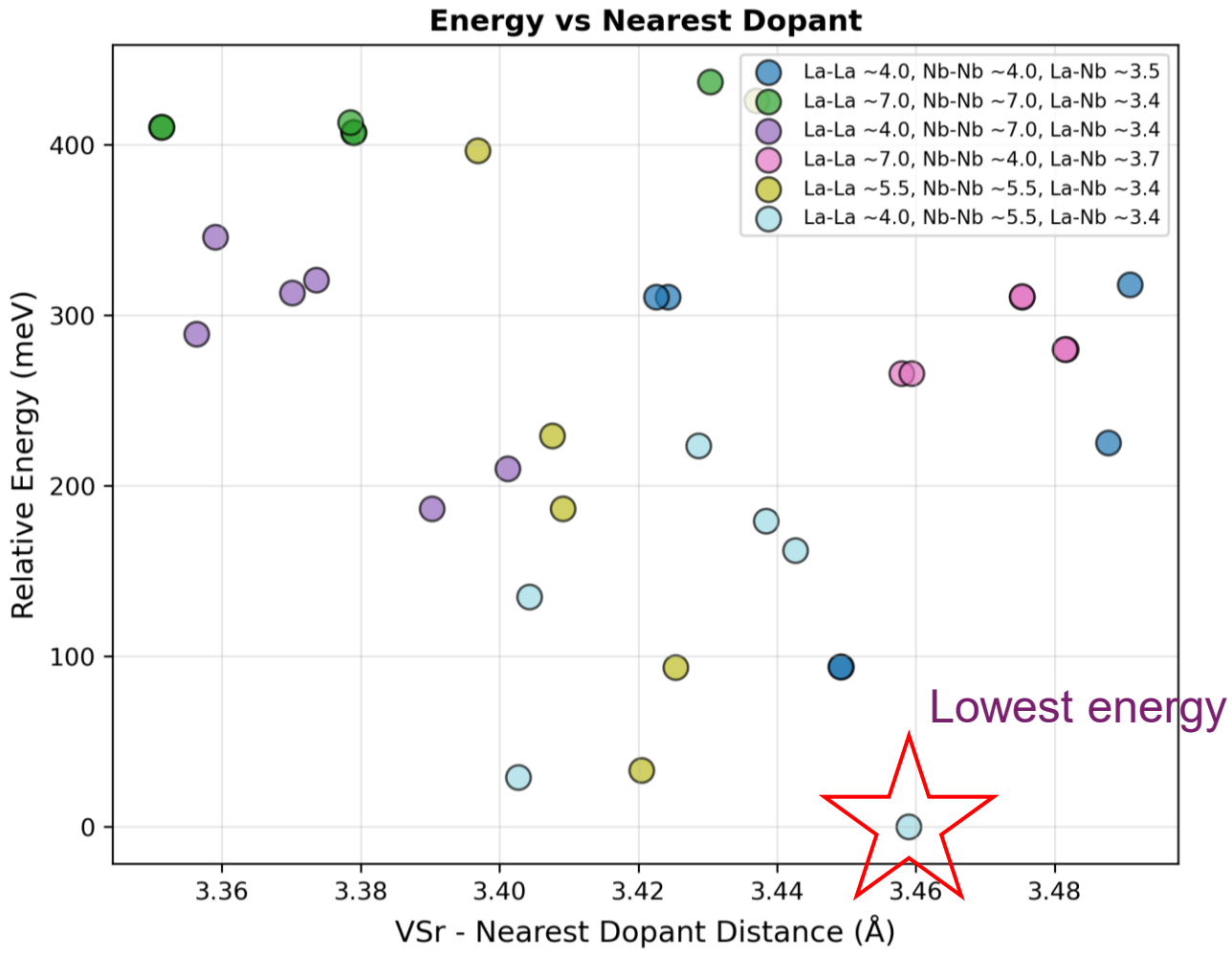




Lowest energy

Vacancy Configuration Optimization

- 42 structural models with Sr vacancy for $La_{0.2}Sr_{0.6}Ti_{0.8}Nb_{0.2}O_3$
- Energy landscape mapped across Sr vacancy-dopant separations
- Lowest-energy configuration selected for property calculations



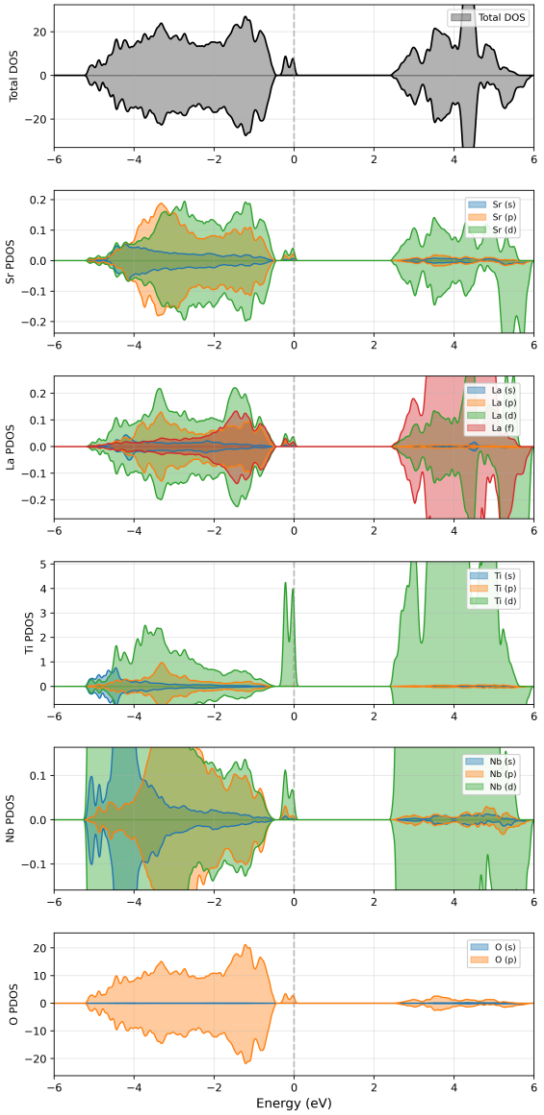
Formation Energy

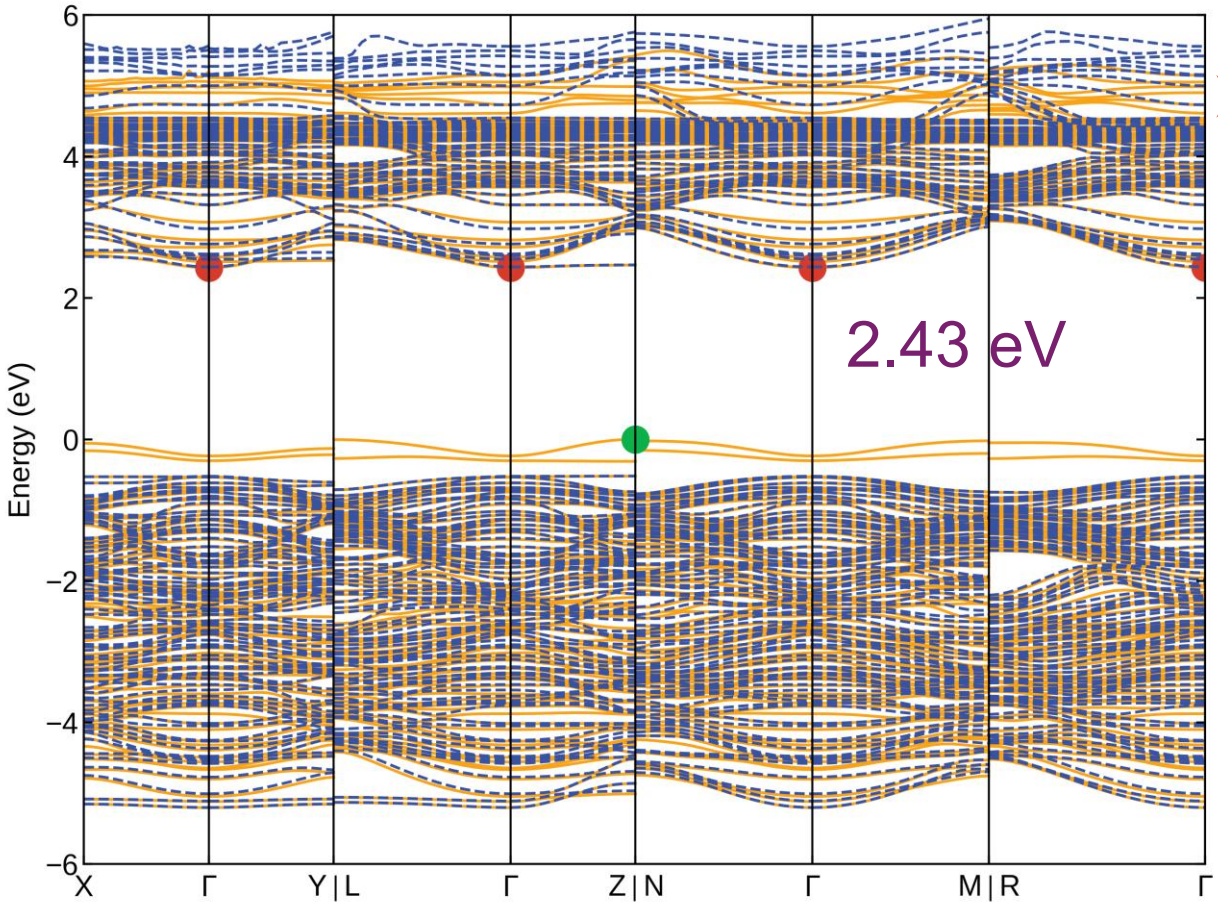
- Formation energy of optimized $Sr_{0.6}La_{0.2}Ti_{0.8}Nb_{0.2}O_3$ structure
- Thermodynamic stability confirmed through DFT calculations

$$\Delta E_f = E_{\text{bulk}} - n_{\text{Sr}}E_{\text{Sr}} - n_{\text{Ti}}E_{Ti} - n_{\text{La}}E_{La} - n_{\text{Nb}}E_{Nb} - n_{\text{O}}\frac{1}{2}E_{O2}$$

Formation energy (eV)	DFT	G(300K)	G(700k)
$SrTiO_3$	-16.82	-16.05	
$Sr_{0.6}La_{0.2}Ti_{0.8}Nb_{0.2}O_3$	-16.38	-15.54	-14.52

Electronic Structure



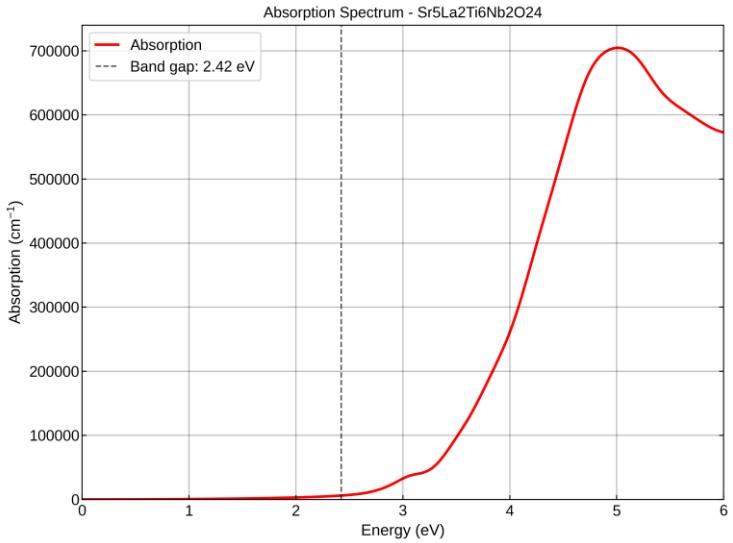


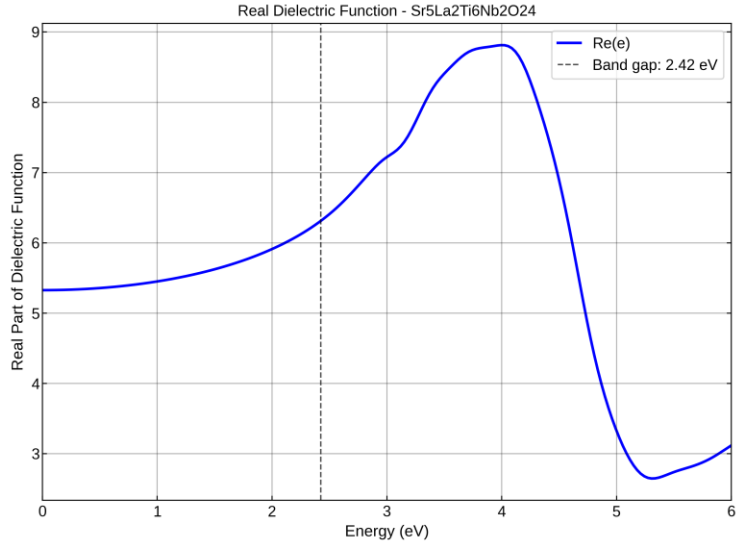
- Band structure reveals semiconductor behavior
- Density of states shows contributions from Sr, La, Ti, Nb, and oxygen orbitals

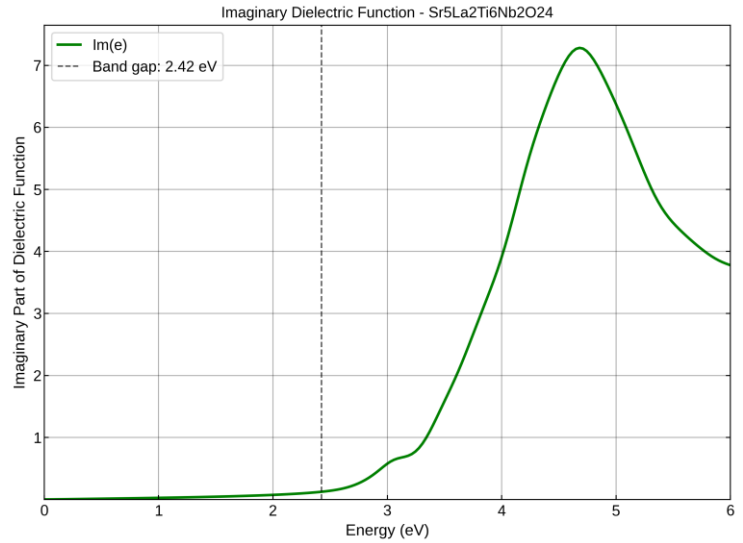
Optical Properties

- Optical properties calculated from frequency-dependent dielectric function
  - Real/imaginary dielectric components characterize optical response

$$\varepsilon(\omega) = \varepsilon_1(\omega) + \mathrm{i}\varepsilon_2(\omega) = (n + \mathrm{i}k)^2 = \frac{4\pi\mathrm{i}}{\omega}\sigma(\omega)$$







Conclusion

- Developed ML-DFT pipeline to screen 187M perovskite compositions for O_2 sensing
- Identified high-sensitivity candidates (3-order conductivity change)
- Validated $Sr_{0.6}$ $La_{0.2}Ti_{0.8}Nb_{0.2}O_3$ as promising material through DFT
- Accelerated materials discovery for harsh-environment sensors for combustion monitoring, aerospace propulsion, industrial process control
- Future Work: Experimental synthesis and sensor device fabrication

Acknowledgement

We thank the computational resource at NETL

THANK YOU!