Computational Screening and Design of Sensing Materials for Harsh Environment Applications

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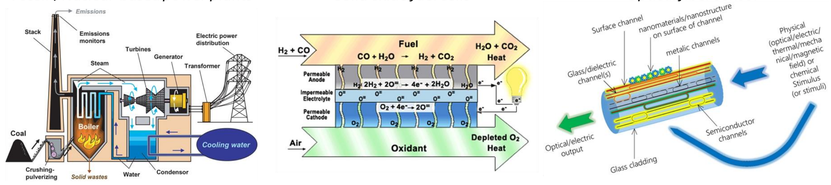
Introduction

- **For advanced real-time monitoring and control of gas species in combustion environments,** development of efficient sensing platforms and new sensor materials able to work under **harsh environments** are required.
- **Semiconducting optical-based sensor platforms** show promise. MO_x metal-oxides and ABO_3 perovskite-oxides can be attractive for high-temperature applications due to their high decomposition temperatures and structural stability; ABO_3 allows tunable electronic and optical properties owing to flexible choices of A, B dopants and forming oxygen non-stoichiometric point-defects

Fossil-/Nuclear-based power plants | *Solid oxide fuel cells* | *Optical fiber sensor*



- Combining first-principles modeling with machine learning is a powerful tool to screen and design functional materials for sensing application under harsh environments. It can be also used to determine the sensing mechanisms and the performance of the high-temperature sensors.

Methods

- **Density functional theory (DFT):** PAW-PBE(+*U*) XC in GGA
  - ➢ Energies of formation of point defects (La and Mg dopants, O vacancies)

$$\Delta H(SrTiO_{3,def}) = E(SrTiO_{3,def}) - E(SrTiO_3) - \sum_i n_i\mu_i$$

  - ➢ Optical properties calculated from frequency-dependent dielectric function

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

- **Allen-Heine-Cardona (AHC) theory**
  - ➢ Lattice thermal expansion and, most dominantly, electron-phonon coupling contribute to renormalization of the band gaps
  - ➢ Prediction of electron-phonon coupling effect on eigenstate energy level shifts $\Delta\epsilon_{nk}(T)$, in harmonic phonon approximation

$$\Delta\epsilon_{nk}(T) = \frac{1}{N_q}\sum_{q,\nu}\frac{a^{(2)}_{qv;qv}}{\omega_{qv}}\left[\frac{1}{2} + n_B(\omega_{qv}, T)\right]$$

- P. B. Allen, V. Heine, **J. Phys. C 9**(1976)2305-12;
- P. B. Allen, M. Cardona, **Phys. Rev. B 23**(1981)1495-1505

- **Fit to empirical O'Donnell model**

$$E_g = E_0 - S < \hbar\omega > \left[\coth\left(\frac{< \hbar\omega >}{2k_BT}\right) - 1\right]$$

- K.P. O'Donnell, X. Chen, **Appl. Phys. Lett. 58**(1991)2924-26.

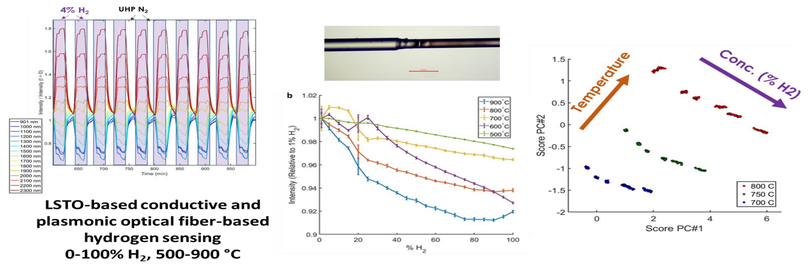
- **Machine Learning**
  - ➢ Principal component analysis applied to combine 37 features into one reduced feature for each parameter in the O'Donnell model

E_0	S	$< \hbar\omega >$
Formation energy, molar density, melting point	Atomic mass, **Electron-Phonon Debye temperature**, thermal conductivity, heat of vaporization, speed of sound, boiling point, melting point	**Entropy of formation**, heat capacity, volume, density

  - ➢ Bolded features were found to have the highest absolute value of the eigenvector (high relative importance in their respective principal component)
  - ➢ Gaussian process (GP) regression models were trained separately for each of the three parameters

Doped Perovskite Sensing Layers on Optical Fiber

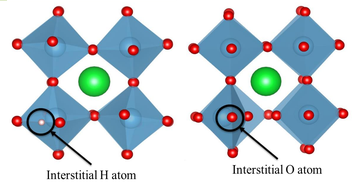
- As a functional sensing layer on evanescent-field based optical fiber sensors, A- or B-site doped can operate as a versatile, high-T sensor for reducing or oxidizing gas streams.
- La-doped $SrTiO_3$ acts like an ***n***-type doped semiconductor under reducing conditions – demonstrating **an effective high-T sensing material for H_2.**



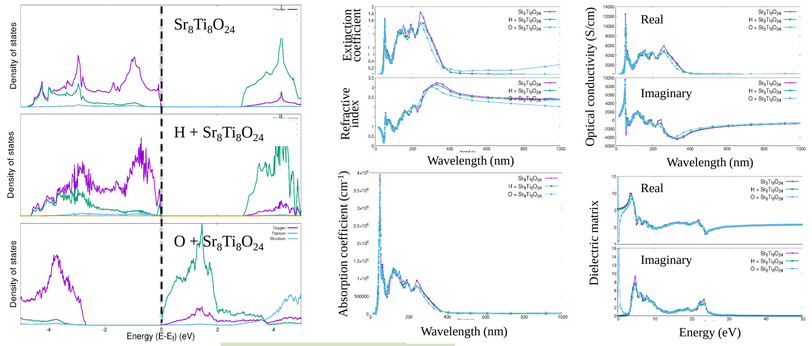
- Other $SrTiO_3$-based systems such as $SrFe_xTi_{1-x}O_3$ (**SFTO**) and **Mg-doped $SrTiO_3$ can act as *p*-type doped semiconductors** under oxidizing conditions and show promise for **high-T stable oxygen sensing**.

Interstitial Hydrogen and Oxygen Impurities

- Interstitial H atom preferably binds to O atom in STO leading to breaking of octahedral symmetry
- Interstitial O atom bonds to apical O causing distortion of Ti octahedral but does not break symmetry of the crystal



- Incorporation of H, O interstitials alters $SrTiO_3$ electronic, optical properties as both can act as electron donors to system
- H introduces defect states at VBM above Fermi level without significant changes to bandgap, optical absorption, or the dielectric matrix
- O induces *n*-type conductivity, evident in DOS and Drude peak in imaginary component of dielectric matrix; causes peak shift in optical conductivity to lower wavelength (higher photon energy)

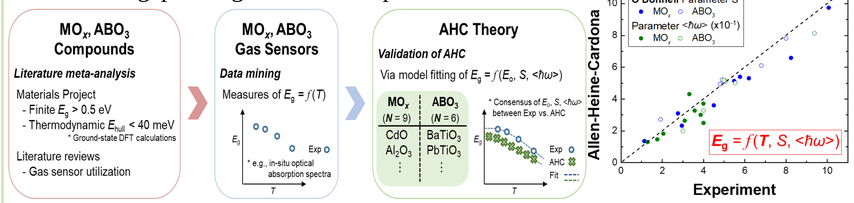


Publications

- J. Park *et al.*, **Phys. Chem. Chem. Phys. 22**(2020) 27163-72; **ACS Appl. Mater. Interfaces 13**(2021) 17717-25; **J. Phys. Chem. C 125**(2021) 22231-38; **126**(2022)8832-38; **Chem. Mater. 34**(2022)6108-15
- Y.-N. Wu *et al.*, **J. Phys. Chem. C 122**(2018) 22642-49; **J. Phys. Chem. Lett. 11**(2020) 2518-23; **J. Phys. Condens. Matter 32**(2020) 405705.
- T. Jia *et al.*, **RSC Adv. 7**(2017) 38798-804; **Phys. Chem. Chem. Phys. 22**(2020) 16721-26; **Applied Energy 281** (2021)116040; **J. Phys. Chem. C 125**(2021) 12374-81; **126**(2022)11421-25
- Y. Duan *et al.*, **J. Solid State Chem. 256**(2017) 239-251.
- S. Nations, *et al.*, **RSC Adv. 11**(2021) 22264-72; **Mater. Adv. 3**(2022)3897-3905; **Nanomaterials 13**(2023)276
- T. Nandi, L. Chong, J. Park, W. A. Saidi, B. Chorpening, S. Bayham, Y. Duan, **AIP Advances 14**(3)(2024)035231.

Applicability of AHC Theory via Machine Learning

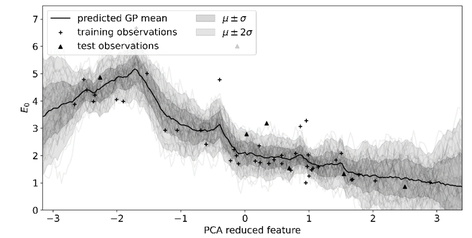
- Assess the consensus between the AHC theory and the measurements on temperature dependence of the band gaps in MO_x and ABO_3
  - In conjunction with O'Donnell model to quantify the temperature dependence of band gaps using well-defined parameters

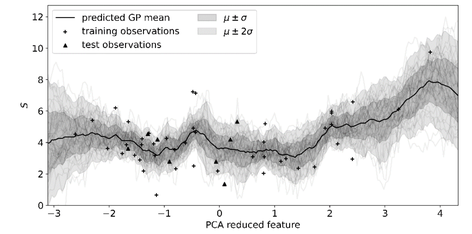


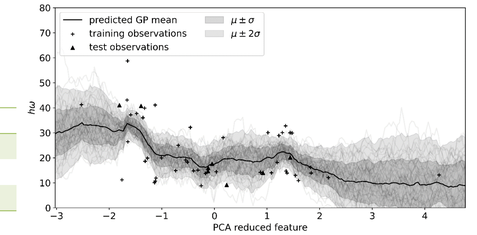
- Machine learning (ML) for predicting O'Donnell model parameters in MO_x
  - Ultimately enables ML prediction of the temperature dependence of band gaps

Machine Learning

- O'Donnell parameters have been calculated by DFT for 54 metal oxides and are accepted as ground truth for the development of the ML models
- Most of the training data as well as the test predictions fall within the predicted mean $\mu \pm 2\sigma$ region
- Region of uncertainty is observed to be larger where the training points are sparsely populated and increases significantly for regions outside of the training dataset







	RMSE	MAE
E_o (eV)	0.8863	0.6729
S	1.142	0.8881
ħω (meV)	6.943	5.414

- SnO_2 used as an example test data point for the combined prediction of parameters to calculate band gap

SnO_2	Predicted	Observation
E_o (eV)	2.8101 ± 0.8618	1.9978
S	3.8541 ± 2.1652	2.35
ħω (meV)	30.2017 ± 6.3966	40.77
E_g (eV) @ 1000 K	2.2555	1.681

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