UPISC UNIVERSITY OF PITTSBURGH INFRASTRUCTURE SENSING COLLABORATION WORKSHOP

NATIONAL ENERGY TECHNOLOGY LABORATORY

# Theoretical Study of Temperature Dependence and Optical properties of Gas Sensor Materials

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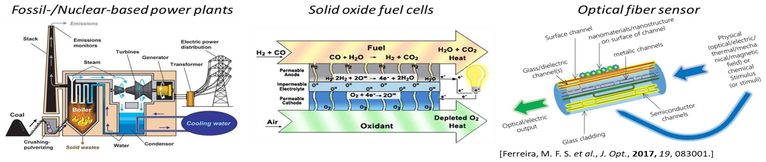
## Introduction

- **For advanced real-time monitoring, control of gas species in combustion environments**, developing efficient sensing platforms and materials under **harsh environments** are required
- **Semiconducting optical-based sensor platform** can be promising; however, examining impact of operating conditions on functional sensor properties (e.g., band gaps, optical properties) has been limited

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




[Ferreira, M. F. S. *et al.*, *J. Opt.*, **2017**, *19*, 083001.]

- **For high-temperature gas sensor materials**, understanding temperature dependence of relevant features is valued; temperature effect on electronic and optical properties originates from the electron-phonon coupling which perturbs the atomic motions
- **$MO_x$ metal-oxides and $ABO_3$ perovskite-oxides** can be attractive for high-temperature applications due to high decomposition temperatures and structural stability; $ABO_3$ allows tunable electronic and optical properties owing to flexible design space by choices of A, B, and forming oxygen non-stoichiometry point-defects
- First-principles modeling assesses the **temperature dependence of band gap renormalizations and optical properties**, of which are vital for determining performance of the high-temperature sensors

## Methods

- **Density functional theory (DFT)**
  - PAW-PBE(+*U*) exchange-correlation in GGA (e.g., electronic structures)
  - Optical properties from the frequency dependent dielectric function

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

  - Formation energy of oxygen vacancy $v_O^q$ in $ABO_{3-\delta}$ ($q$: charge states)

$$\Delta H^q(ABO_3, v_O^q) = E^q(ABO_3, v_O^q) - E(ABO_3) + \mu_O(T,P) + qE_F + E_{corr} + \Delta F^q(T)$$

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

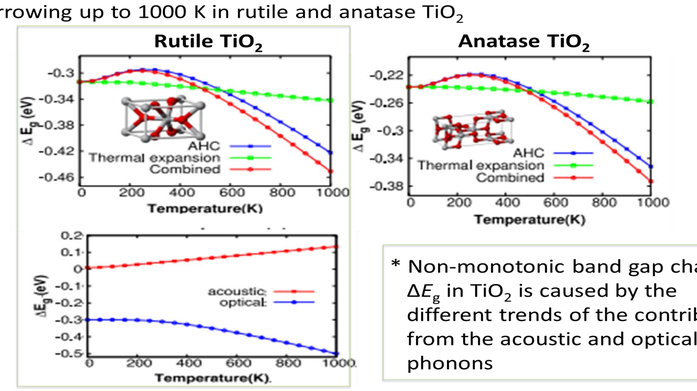
$$\Delta\epsilon_{nk}(T) = \frac{1}{N_q}\sum_{q,\nu}\frac{a^{(2)}_{qv;qv}}{\omega_{qv}}\left[\frac{1}{2} + n_B(\omega_{qv}, T)\right]$$

- **Frozen-phonon method**
  - Optical properties calculation at finite temperatures
  - Configurational averaging of optical properties using temperature-dependent configurations incorporating the atomic displacements $u_n$ by phonons

$$u_n = \sum_{q,\nu} u_{n,qv} = \sqrt{\frac{\hbar}{m_n}}\sum_{q,\nu}\frac{\hat{n}_{qv}\mathrm{e}^{\mathrm{i}(q\cdot R_n + \phi_{qv})}}{\sqrt{(\mathrm{e}^{\hbar\omega_{qv}/k_BT} - 1)\omega_{qv}}}$$

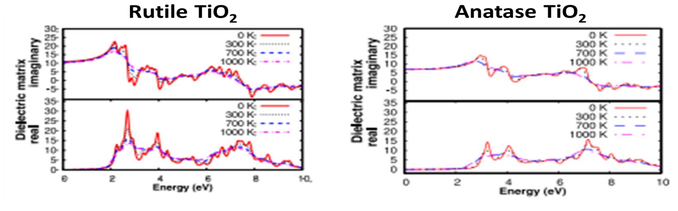
## Metal-Oxides: $TiO_2$ and $SnO_x$

- Au/**$TiO_2$** (Au-nanoparticle incorporated plasmonic oxides) have shown the potential for robust and reliable optical gas sensing properties at high working temperatures
  - AHC calculations show the band gap widening up to ~ 300 K, followed by narrowing up to 1000 K in rutile and anatase $TiO_2$

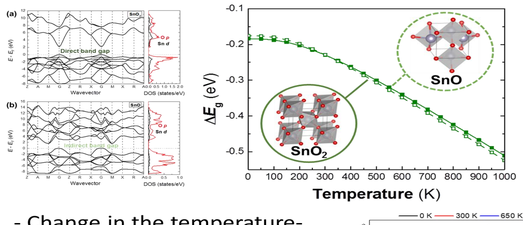



* Non-monotonic band gap change $\Delta E_g$ in $TiO_2$ is caused by the different trends of the contribution from the acoustic and optical phonons

  - Due to thermal smearing effect, the dielectric matrix (and resulting refraction index, extinction coefficient, and optical conductivity) spectra are greatly smoothened and broadened in rutile and anatase $TiO_2$

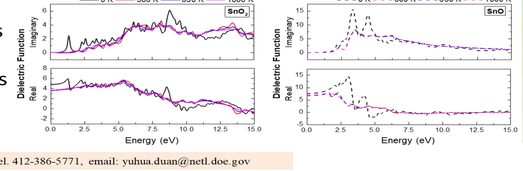



- **$SnO_x$** (x = 2, 1) are applied in many energy applications including catalysts, photovoltaics, and gas sensors
  - AHC predictions show downshifts of the direct and indirect band gaps in $SnO_x$



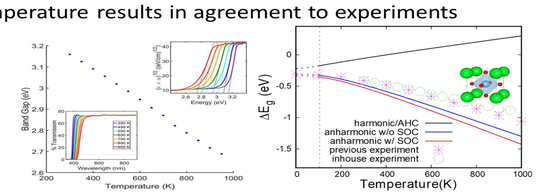

* Despite different electronic structure depending on *x* stoichiometry, resulted in very similar monotonic band gap change $\Delta E_g$

  - Change in the temperature-dependent optical properties is relevant to the above electronic structure variances

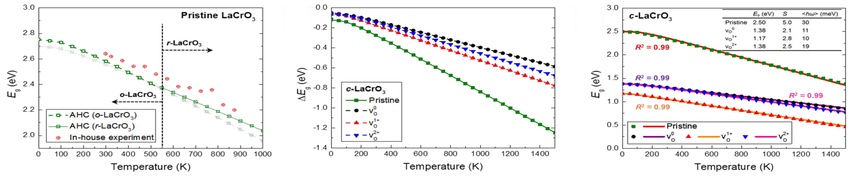



## Perovskite-Oxides: $SrTiO_3$ and $LaCrO_{3-\delta}$

- In **$SrTiO_3$**, conventional harmonic phonons show soft modes, which leads AHC theory to predict incorrect trends of band gap change with temperature
  - Self-consistent phonon approach to obtain the soft-mode-free phonons at finite temperature results in agreement to experiments

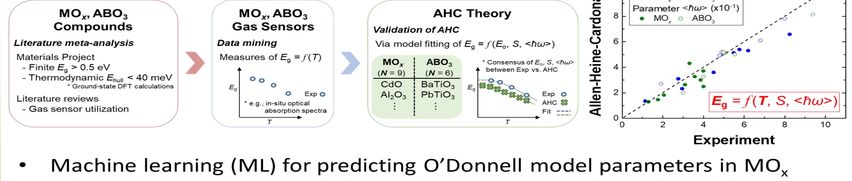



- Antiferromagnetic ordered, strongly-correlated **$LaCrO_3$** undergoes structural phase transitions with temperature; **cubic** $LaCrO_3$ exists as a single phase at temperature relevant to the high-temperature application > 1000 K
  - Quantitative agreement between AHC prediction and in-house experiment in temperature-dependent band gaps, with mild anomaly at phase transition *T*
  - Band gap closure by 1.13 eV up to 1500 K in pristine **cubic**; analogous narrowing, but at lower magnitude by ~ 0.62 eV for oxygen-vacant $v_O^q$ states
  - O'Donnell model rationalizes the band gap shifts: $E_g = E_O - S < \hbar\omega > \left[\coth\left(\frac{< \hbar\omega >}{2k_BT}\right) - 1\right]$




## Applicability of AHC Theory Towards 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

## 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) 16721-16726; **Appl. 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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