UPISC UNIVERSITY OF PITTSBURGH INFRASTRUCTURE SENSING COLLABORATION WORKSHOP

NATIONAL ENERGY TECHNOLOGY LABORATORY

Modeling and Experimental Testing of High-temperature Stable Sensor Materials for Gas Monitoring

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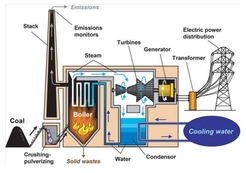
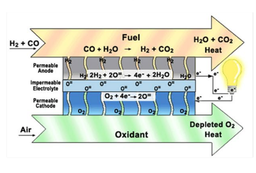
Introduction

- **For advanced real-time monitoring and control of gas species in combustion environments**, development of efficient sensing platforms and materials under **harsh environments** are required
- **Semiconducting optical-based sensor platform** based on strontium titanate ($SrTiO_3$) shows promise; cubic ABO_3 structure has tunable electronic, optical properties dependent on A- or B-site doping and density oxygen vacancies
- **Hydrogen (H) and oxygen (O) impurities** are thought to contribute to room temperature, long lasting photoconductivity in $SrTiO_3$, indicating the potential use of $SrTiO_3$ in H and O gas sensing applications
- Understanding how **lanthanum (La) and magnesium (Mg) doping of $SrTiO_3$ and oxygen vacancy defects** affect electronic, optical properties of $SrTiO_3$ is required to tailor $SrTiO_3$-based materials for development of sensitive, selective gas sensors
- First-principles modeling assesses the **tunability of $SrTiO_3$ material properties via incorporation of La, Mg impurities and emergence of oxygen vacancies**

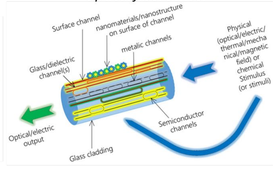
Fossil-/Nuclear-based power plants



Solid oxide fuel cells



Optical fiber sensor

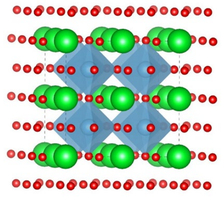


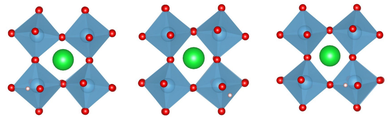
Methods

- **Density functional theory (DFT):** PAW-PBE(+*U*) exchange-correlation in generalized gradient approximation (GGA)
  - Energies of formation of point defects (La and Mg dopants, O vacancies)

$$\Delta H(SrTiO_{3,\,def}) = E(SrTiO_{3,\,def}) - E(SrTiO3) - \sum_i n_i \mu_i$$

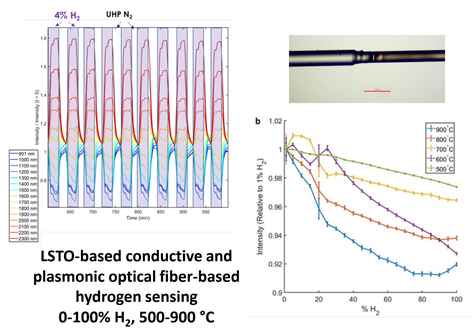
  - Optical properties calculated from frequency-dependent dielectric functior
- **Incorporation of H and O impurities**
  - Probing energetics of interstitial H and O atoms in $SrTiO_3$
  - Locate local energy minima (binding sites) of H and O
  - Elucidate electronic, optical properties of $SrTiO_3$ with interstitial H and O atoms
  - Nudged elastic band calculations to determine relevant diffusion and associated energetic barriers





Doped Perovskite Sensing Layers on Optical Fiber

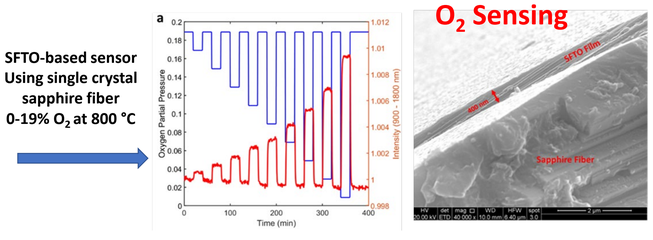
- As a functional sensing layer on evanescent-field based optical fiber sensors, A- or B-site doped can operate as a versatile, high-temperature sensor for reducing or oxidizing gas streams
- La-doped $SrTiO_3$ acts like an n-type doped semiconductor under reducing conditions – demonstrated as **an effective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



LSTO-based conductive and plasmonic optical fiber-based hydrogen sensing 0-100% H_2, 500-900 °C

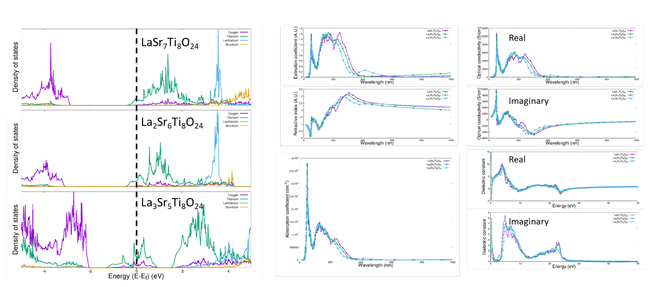
- Other $SrTiO_3$-based systems such as $SrFe_xTi_{1-x}O_3$ (**SFTO**) and **Mg-doped $SrTiO_3$ can act as p-type doped semiconductors** under oxidizing conditions and show promise for **high-temperature stable oxygen sensing**

SFTO-based sensor Using single crystal sapphire fiber 0-19% O_2 at 800 °C

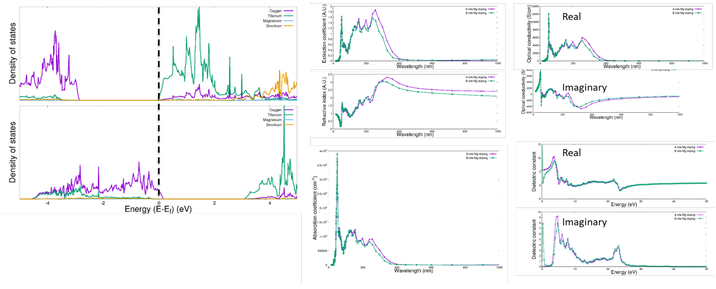


Perovskite Oxides: La- and Mg-doped $SrTiO_3$

- La-doped $SrTiO_3$ shows n type behavior for all La doping levels studied ranging from 12.5 to 37.5 at.%; La doping impacts the free carrier concentration
- Imaginary component of dielectric matrix at sub-bandgap energy of $SrTiO_3$ confirms metallicity; La doping causes shift in dielectric matrix to higher photon energy above 4 eV
- La doping causes drop in NUV absorption due to shifting of band edge



- Mg-doped $SrTiO_3$ exhibits changes of electronic, optical properties dependent on site of Mg substitution; neither show absorption in visible light range
- B-site doped $SrTiO_3$ has occurrence of Drude peak in imaginary component of dielectric matrix, confirming the presence of free carriers



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