First-principles DFT study of the electronic and optical properties of lanthanum and magnesium-doped strontium titanates for advanced gas sensing applications

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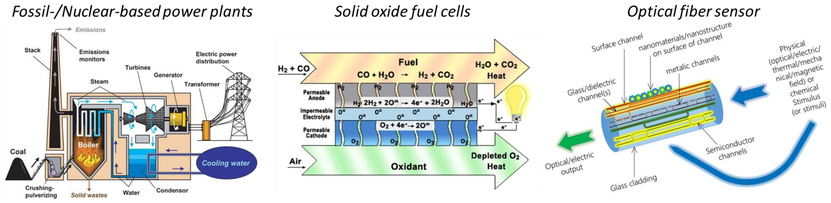
Introduction

- **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 platform** based on strontium titanate ($SrTiO_3$, STO) shows promise; cubic ABO_3 structure has tunable electronic, optical properties dependent on A-site, B-site doping, oxygen vacancies

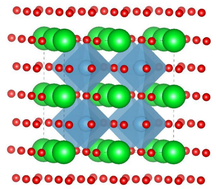
Fossil-/Nuclear-based power plants | *Solid oxide fuel cells* | *Optical fiber sensor*



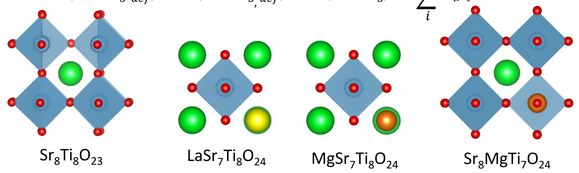
- **Hydrogen (H) and oxygen (O) impurities** are ubiquitous to metal oxide perovskites; both H and O are thought to contribute to room temperature, long lasting photoconductivity in STO, indicating the potential use of STO in H, O gas sensing applications
- Understanding how **lanthanum (La) and magnesium (Mg) doping of STO and oxygen vacancy defects** affect electronic and optical properties of $SrTiO_3$ is required to tailor STO-based materials for development of sensitive, selective gas sensors
- First-principles modeling assesses the **tunability of STO material properties via incorporation of La, Mg impurities and emergence of oxygen vacancies**

Methods

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



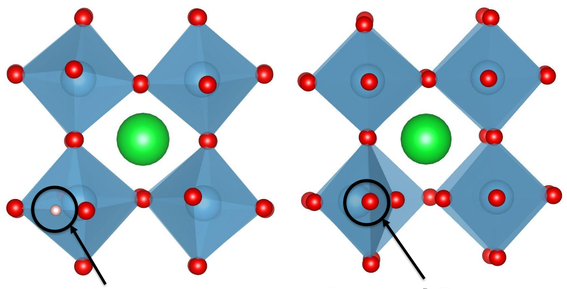
$$\Delta H(SrTiO_{3\ def}) = E(SrTiO_{3\ def}) - E(SrTiO_3) - \sum_i n_i\mu_i$$



  - Optical properties calculated from frequency-dependent dielectric function

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

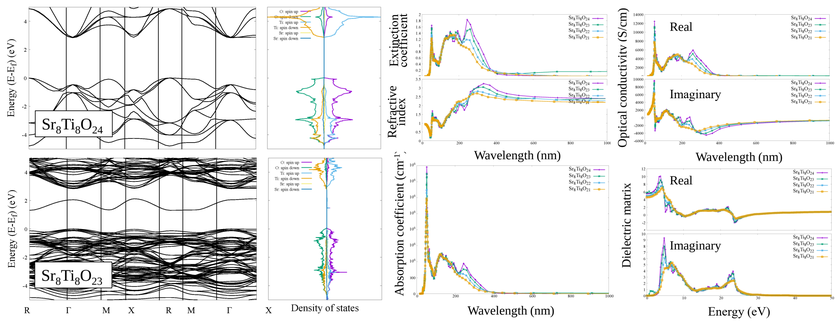
- **Incorporation of H and O interstitial atoms**



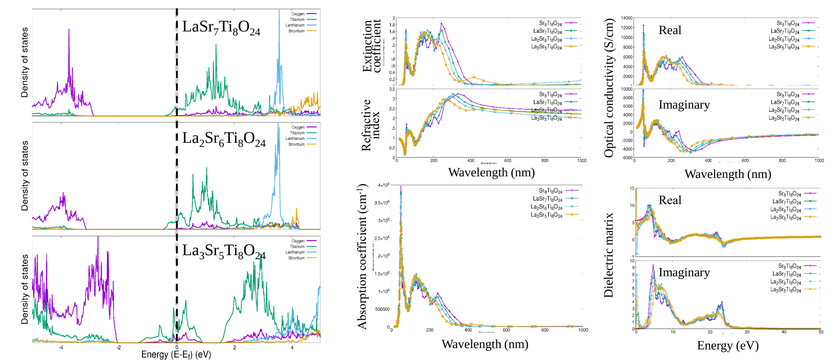
- Determine local energy minima of adsorbate H, O atom binding sites
- Elucidate electronic, optical properties of STO with interstitial H, O atoms
- Nudged elastic band calculations to determine relevant diffusion barriers

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

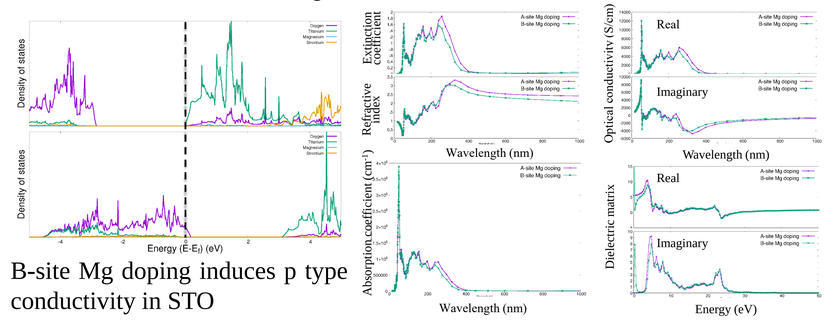
- Electronic structure of $SrTiO_3$ shows a bandgap of 2.98 eV; optical calculations indicate $SrTiO_3$ has absorption peak in the IR spectrum at 55 nm
- Incorporation of O vacancy creates an occupied defect state within the bandgap. Its location is sensitive to Hubbard parameter U; contributions to defect state are shown to be due to O 2*p*, Ti 3*d* hybridization
- Incorporation of O vacancies to $SrTiO_3$ due not cause peaks in the absorption coefficient within the range of visible light; increase in O vacancies causes lower-wavelength peak in optical conductivity below 200 nm



- La-doped STO shows n type behavior for all doping levels of La studied ranging from 12.5 to 37.5 at. %; La doping impacts free carrier concentration
- La doping causes shift in dielectric matrix to higher photon energy above 4 eV
- La doping causes loss in optical transparency at lower range of visible light



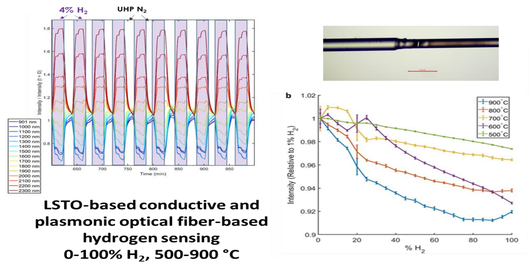
- Mg-doped STO exhibits varied electronic, optical properties dependent on site of Mg substitution; neither show absorption in visible light range
- B-site doped STO has occurrence of Drude peak in imaginary component of dielectric matrix, confirming the presence of free carriers



B-site Mg doping induces p type conductivity in STO

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.**

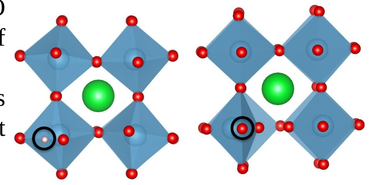


LSTO-based conductive and plasmonic optical fiber-based hydrogen sensing 0-100% H_2, 500-900 °C

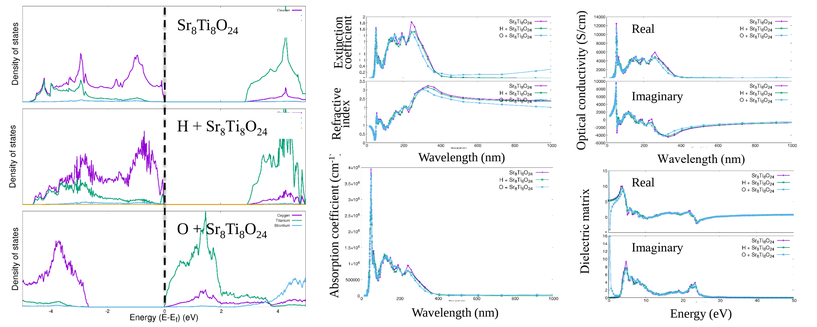
- Other $SrTiO_3$-based systems such as $SrFe_xTi_{1-x}O_3$ (**SFTO**) and **Mg-doped $SrTiO_3$ can act as p-type doped semiconductors** under oxidizing conditions and show promise for **high-T stable oxygen sensing**.

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 causes distortion of Ti octahedral but does not break symmetry of crystal



- Incorporation of H, O interstitials alters $SrTiO_3$ electronic, optical properties as both can act as electron donors to system
- H introduces defect state at VBM below Fermi level without significant change to bandgap, absorption, or 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)



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