



# The Role of Fe Charge State on the Defect and Crystal Structure of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ ( $0 \leq x \leq 1$ ) under SOFC Operating Conditions: A Combined Density Functional Theory and Thermodynamics Approach

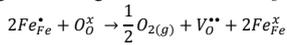


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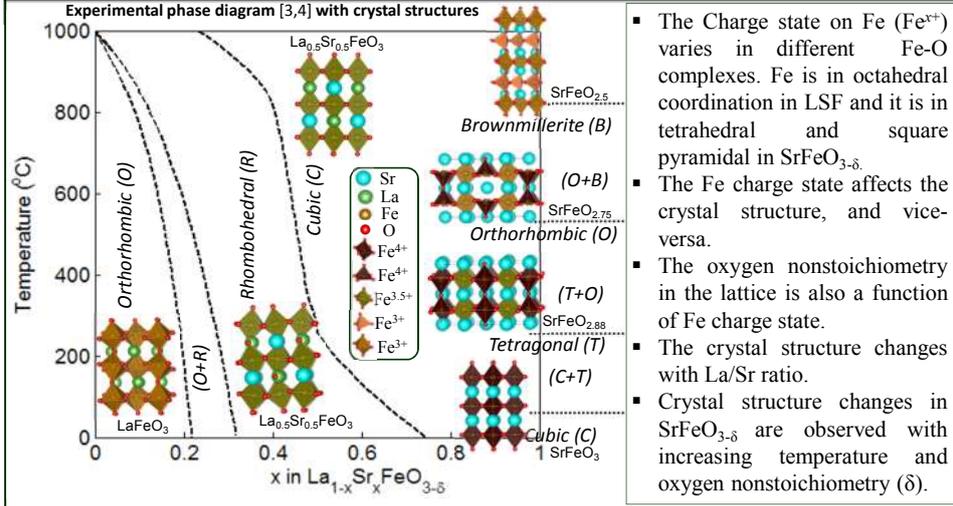
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## 1. Motivation

- Ultimate Goal: Computationally design new materials with high oxygen vacancy concentration ( $c_{V_{O^{\bullet\bullet}}}$ ), i.e. a high oxygen nonstoichiometry ( $\delta$ ), at SOFC operating conditions.
- Focus of this study: Establish a method to accurately calculate the oxygen vacancy concentration of a known perovskite system, LSF ( $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ ), and compare with experimental results [1].
- The main challenge is to predict the free energy of oxygen vacancy formation ( $\Delta G_{f,vac}$ ) at SOFC operating conditions.
  - For non interacting vacancies,  $\Delta G_{f,vac} = f(T, p)$  only
  - For interacting vacancies,  $\Delta G_{f,vac} = f(T, p, \delta)$
- $\delta$  depends on the:
  - Crystal structure, ▪ La/Sr ratio in LSF,
  - Oxygen chemical potential,  $\Delta\mu_O = f(T, p)$ ,
  - Charge state/ magnetic moment of Fe [2]



## 2. Fe Charge State Calculation for $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ ( $0 \leq x \leq 1$ )

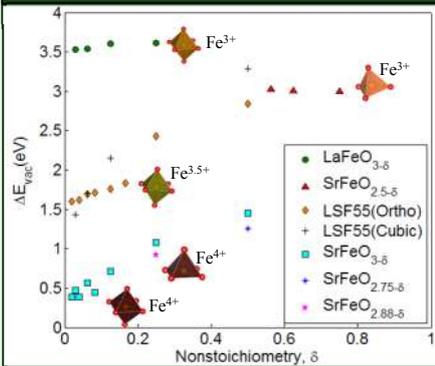


- The Charge state on Fe ( $\text{Fe}^{x+}$ ) varies in different Fe-O complexes. Fe is in octahedral coordination in LSF and it is in tetrahedral and square pyramidal in  $\text{SrFeO}_{3-\delta}$ .
- The Fe charge state affects the crystal structure, and vice-versa.
- The oxygen nonstoichiometry in the lattice is also a function of Fe charge state.
- The crystal structure changes with La/Sr ratio.
- Crystal structure changes in  $\text{SrFeO}_{3-\delta}$  are observed with increasing temperature and oxygen nonstoichiometry ( $\delta$ ).

## 3. Computational Approach

- Computational studies were performed using Density Functional Theory and Thermodynamics.
- $U = 3$  was selected to give Fe magnetic moment and lattice parameters comparable with experimental results for  $\text{LaFeO}_3$  and  $\text{SrFeO}_3$ .
- DFT+U was used to minimize all the crystal structure energies and predict the magnetic moment on Fe.
- DFT+U was used to calculate the oxygen vacancy formation energy in supercells with varying size and a single oxygen vacancy, mimicking a broad range of oxygen nonstoichiometry.

## 4. $\Delta E_{vac} \downarrow$ with $\uparrow x$ on $\text{Fe}^{x+}$



## 5. $V_{O^{\bullet\bullet}}$ is Generated Near Higher $\text{Fe}^{x+}$

- The magnetic moment on Fe is used to describe classical charge state on Fe in Fe-O complexes.
- The magnetic moment on Fe in  $\text{SrFeO}_3$  (3.61  $\mu_B$ ) is assigned with a classical charge state of 4+. The magnetic moment on Fe in  $\text{LaFeO}_3$  (4.23  $\mu_B$ ) is assigned with charge state of 3+. Then a linear interpolation gives the intermediate charge states.
- DFT calculation show that the vacancy formation energy increases with decreasing charge on Fe in different Fe-O complexes.
- Oxygen vacancies are preferentially formed near high oxidation state Fe cations, if the LSF structure has mixed Fe charge states.

## 6. Thermodynamic Extension

- To account for SOFC operating conditions, we used [6,7]:

$$\Delta G_{f,vac} = \Delta E_{f,vac} + \frac{1}{2}\Delta\mu_{O_2}(T, p)$$

$$\Delta G_{f,vac} = E_{defective} - E_{perfect} + \frac{1}{2}\mu_{O_2}$$

$E_{perfect}$  = Perfect crystal structure

$E_{defective}$  = Crystal structure with one oxygen vacancy.

Chemical potential of oxygen at SOFC operating conditions [8,9],

$$\mu_{O_2}(T, p) = E_{O_2}^{DFT} + \Delta\mu_{O_2}^0(T_r) + \int_{T_r}^T C_p dT - T \int_{T_r}^T \frac{C_p}{T} dT - (T - T_r)S_r + kT \ln p_{O_2}$$

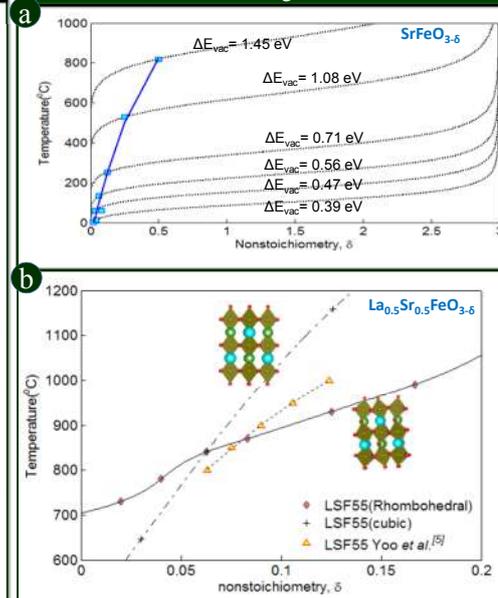
$E_{O_2}^{DFT}$  = DFT calculated energy of a single oxygen molecule.

$\Delta\mu_{O_2}^0(T_r)$  = Connection energy of oxygen from 0 K, isolated molecule to standard state (298.15 K, 1atm). Where  $T_r$  is the standard state temperature (298.15K).  $S_r$  is the entropy of oxygen molecule at standard state.

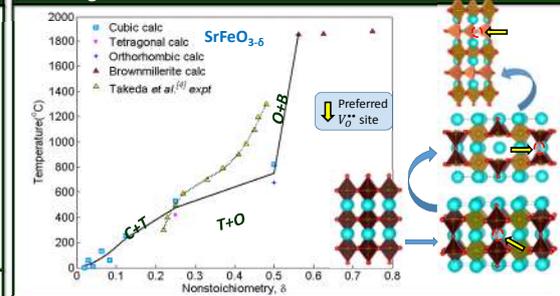
- The interactive vacancy concentration ( $c$ ) was calculated as a function of vacancy formation energy via [10]:

$$\frac{\delta}{3-\delta} = \frac{c}{1-c} = \exp\left(-\frac{\Delta G_{f,vac}(T, p, \delta)}{RT}\right)$$

## 7. $\Delta G_{f,vac}$ is $c_{V_{O^{\bullet\bullet}}}$ Dependent



## 8. $c_{V_{O^{\bullet\bullet}}}$ Induces Phase Transformations



## 9. Conclusions

- In this work a combined thermodynamics and DFT approach was used to predict oxygen vacancy concentrations and crystal structures at SOFC operating conditions.
- In LSF, the oxygen vacancies are formed near the Fe site, especially in structures with a high Fe charge state.
- Recommendations:
  - Stabilize the rhombohedral structure instead of the cubic structure (Fig 7b).
  - Stabilize  $\text{Fe}^{4+}$  in octahedral not square pyramidal coordination (Fig 8).