



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

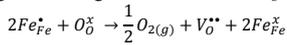


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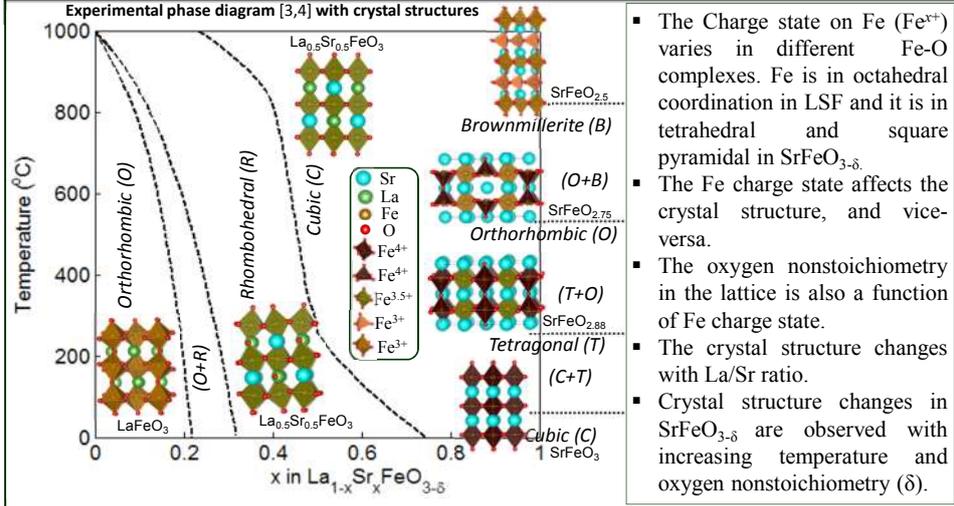
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1. Motivation

- Ultimate Goal: Computationally design new materials with high oxygen vacancy concentration ($c_{V_{O^{\bullet\bullet}}}$), i.e. a high oxygen nonstoichiometry (δ), 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, $\Delta G_{f,vac} = f(T, p, \delta)$
- δ 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 $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ ($0 \leq x \leq 1$)

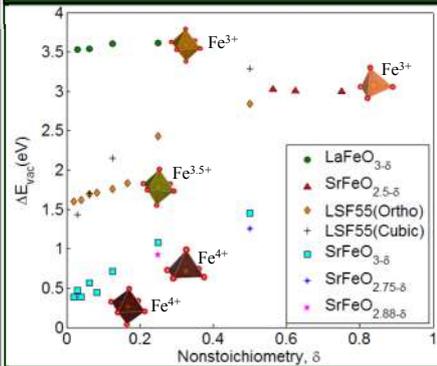


- The Charge state on Fe (Fe^{x+}) varies in different Fe-O complexes. Fe is in octahedral coordination in LSF and it is in tetrahedral and square pyramidal in $\text{SrFeO}_{3-\delta}$.
- The Fe charge state affects the crystal structure, and vice-versa.
- The oxygen nonstoichiometry in the lattice 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 (δ).

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 LaFeO_3 and 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 Fe^{x+}



5. $V_{O^{\bullet\bullet}}$ is Generated Near Higher 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 SrFeO_3 (3.61 μ_B) is assigned with a classical charge state of 4+. The magnetic moment on Fe in LaFeO_3 (4.23 μ_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],

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

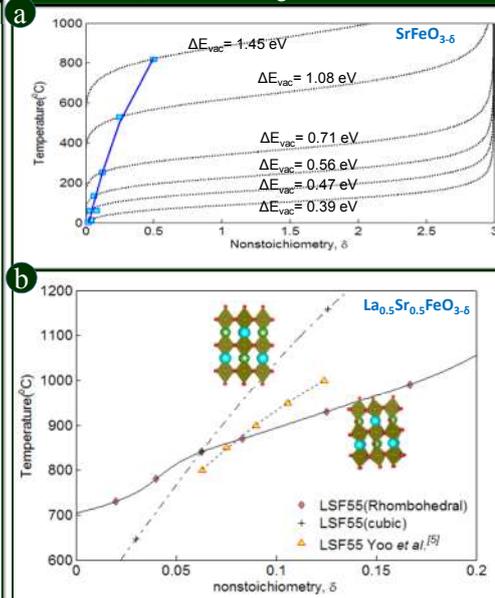
$E_{O_2}^{DFT}$ = DFT calculated energy of a single oxygen molecule.

$\Delta\mu_{O_2}^0(T_r)$ = 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.

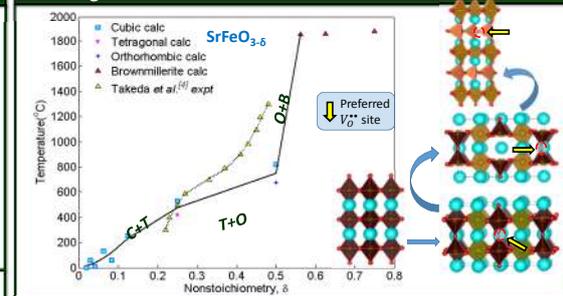
- The interactive vacancy concentration (c) was calculated as a function of vacancy formation energy via [10]:

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

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 Fe^{4+} in octahedral not square pyramidal coordination (Fig 8).

References: [1] Mizusaki et al., *J. Solid State Chem.*, **58**, 257-266 (1985) [2] Yang et al., *Solid State Ionics*, **249**, 123 (2013) [3] Fossdal et al., *J. Am. Ceram. Soc.*, **87** (10), 1952-1958 (2004) [4] Takeda et al., *J. Solid State Chem.*, **63**, 237-249 (1986) [5] Yoo et al., *Solid State Ionics*, **175**, 55-58 (2004) [6] Lee et al., *Phys. Rev. B*, **80**, 224101 (2009) [7] Sholl et al., *Density Functional Theory: A Practical Introduction*, p. 169, Wiley, New Jersey (2009) [8] Zhang et al., *Phys. Rev. B*, **70**, 024103 (2004) [9] Guo et al., *Appl. Phys. Lett.* **92**, 241921 (2008) [10] C. Kittel, *Introduction to Solid State Physics*, p. 541, Wiley, New York (1996)