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Modeling Perovskite Oxide Thermodynamics via the Compound Energy Formalism for Solar Thermochemistry

H. Evan Bush, N. Ty Nguyen, Tyler Farr, Ellen B. Stechel, Peter Loutzenhiser, Andrea Ambrosini

Sandia National Laboratories

Georgia Institute of Technology

Arizona State University

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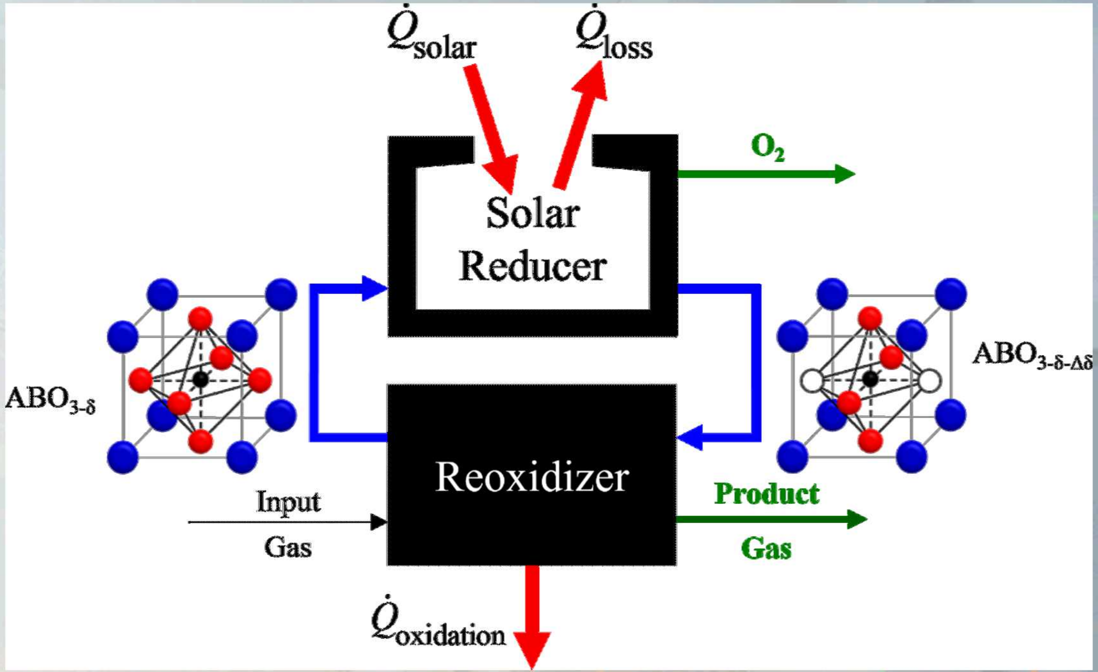
Motivation

- Mixed ion-electron conducting perovskites $ABO_{3-\delta}$ are appealing for two-step thermochemical cycles
  - Continuous reducibility
  - Structural stability
  - Rapid kinetics
  - Large thermodynamic space via A/B-site substitution
- Thermodynamic modeling permits cycle performance prediction
  - Reduction-oxidation (redox) enthalpy and entropy
  - Predictions of $\delta = f(T, p_{O_2})$
  - Fitting terms for substituents would allow mapping solution space



Partial Substitution:

→ $(A'_xA_{1-x})BO_{3-\delta}$

$A(B'_xB_{1-x})O_{3-\delta}$

$(A'_xA_{1-x})(B'_xB_{1-x})O_{3-\delta}$

Strontium Ferrite ($SrFeO_{3-\delta}$)

- Promising candidate for thermochemistry
  - Thermodynamically stable
  - Low enthalpy of reduction
  - High reducibility
- Relevant applications:
  - Chemical looping CH_4 combustion
  - Solid oxide fuel cells
  - Air separation
- Screening identified A' = La, Ba for air separation:
  - Improved reducibility
  - Similarly rapid kinetics

- Previous methods: lattice defect models

$$2Fe_{Fe}^{\times} + O_O^{\times} \rightleftharpoons 2Fe_{Fe}^{'} + V_O^{\cdot\cdot} + \frac{1}{2}O_{2(g)}$$

$$2Fe_{Fe}^{\times} + O_O^{\times} \rightleftharpoons \langle Fe_{Fe}^{'} - V_O^{\cdot\cdot} - Fe_{Fe}^{'} \rangle + \frac{1}{2}O_{2(g)}$$

  - Model fidelity varies with δ, T, p_{O_2}
  - Doesn't readily capture multiple lattice phenomena
  - Not readily extended to capture varying substitution

Goal: Model thermodynamics as a function of T, p_{O_2} and quantitatively capture substituent type and fraction influences

Compound Energy Formalism (CEF)

- $(Sr^{2+}, Ba^{2+}, La^{3+})(Fe^{4+}, Fe^{3+})(O^{2-}, V_O)_3$
  - Three sublattices
- Semi-empirical: fitted, weighted by site fractions y_k
- Captures redox without assuming single defect reactions
- Three components:
  1. Weighted sum of end members with T fit

     $°G_i$ represented as solid solution of materials with known thermodynamics, *e.g.* Fe_2O_3, SrO, O_2
  2. Ideal mixing entropy, weighted by stoichiometry v_m
  3. Excess terms (sublattice interactions) using Redlich-Kister polynomials

1 2 3

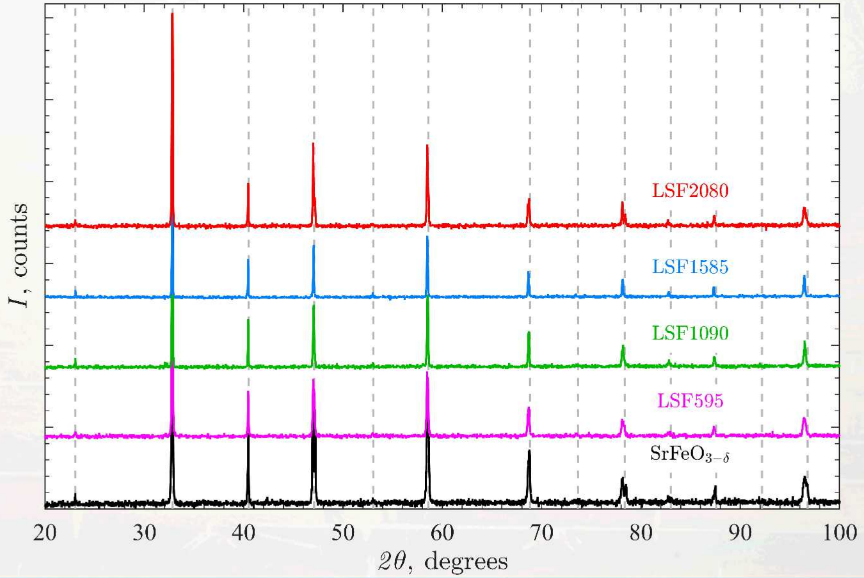
$$G^P = \sum_i \left({}^{\circ}G_i \prod_{k \in S_i} y_k \right) + RT \sum_m \left(v_m \sum_{k \in S_m} y_k \ln y_k \right) + {}^{E}G^P$$

$$°G_{oxide} = °G_{end} + °G_{mix} + °G_{exs}$$

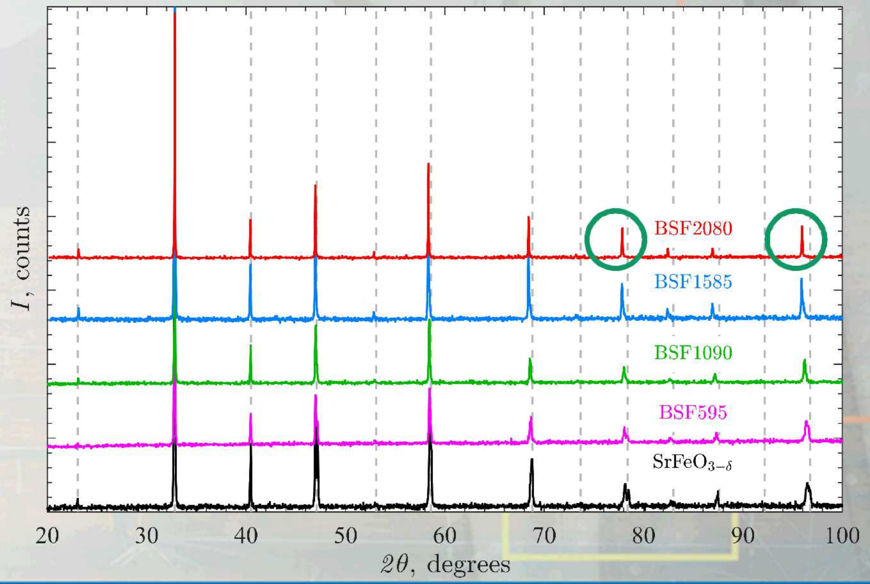
$$^{E}G^P = \sum_m \left(\prod_{k \in S_i} y_k \sum_n y_{k' \in S_m} \, {}^{\circ}L_i^n \left[y_{k' \in S_m} - y_{k \in S_m} \right]^n \right)$$

Synthesis & Characterization

- Sol-gel method
  - Metal nitrate precursors
  - Calcination at 1250-1350 °C



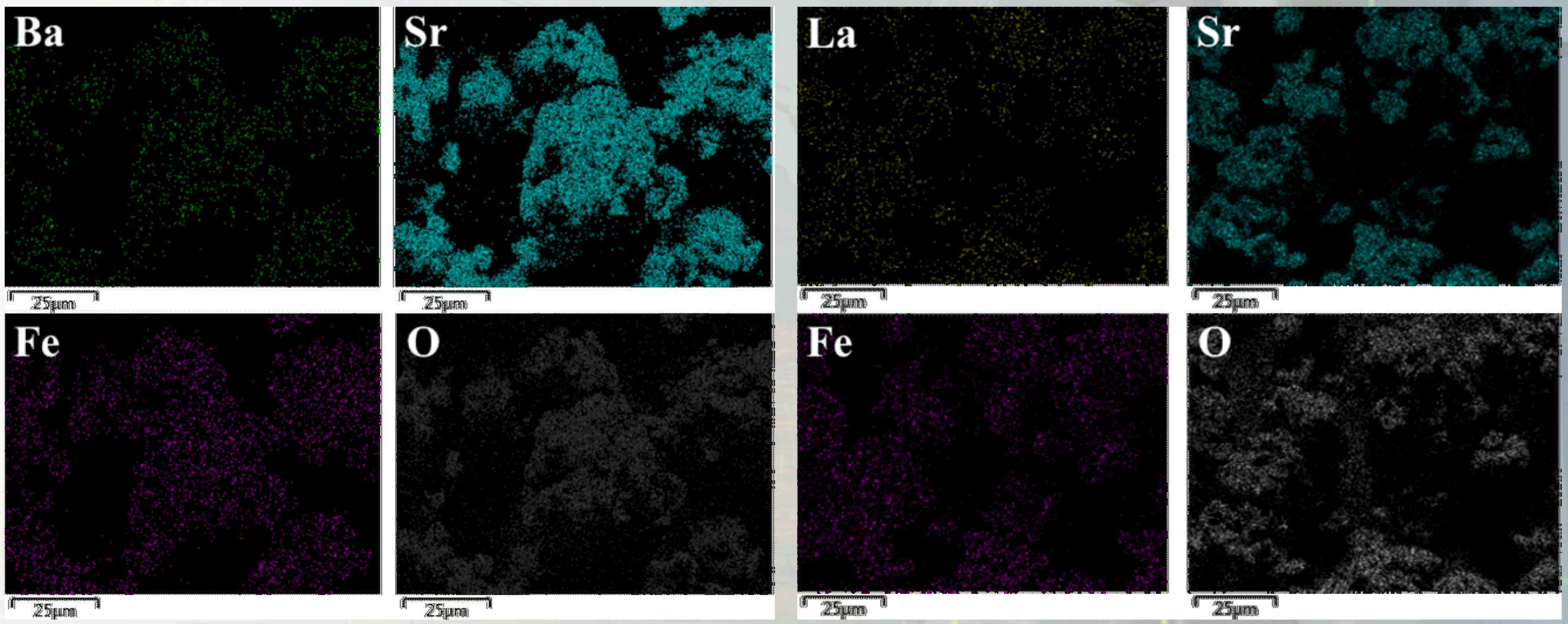
- XRD
  - Single phase, cubic or tetragonal $SrFeO_{3-\delta}$
  - Peak shifting from Ba^{2+} ionic radii



Synthesis & Characterization

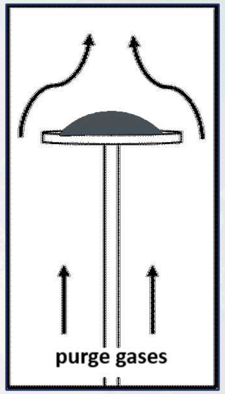
- SEM/EDS
  - Identified Sr, Fe, O, Ba, and La ions
  - Homogenous cationic distributions
  - No detected impurities
  - No evidence of phase segregation

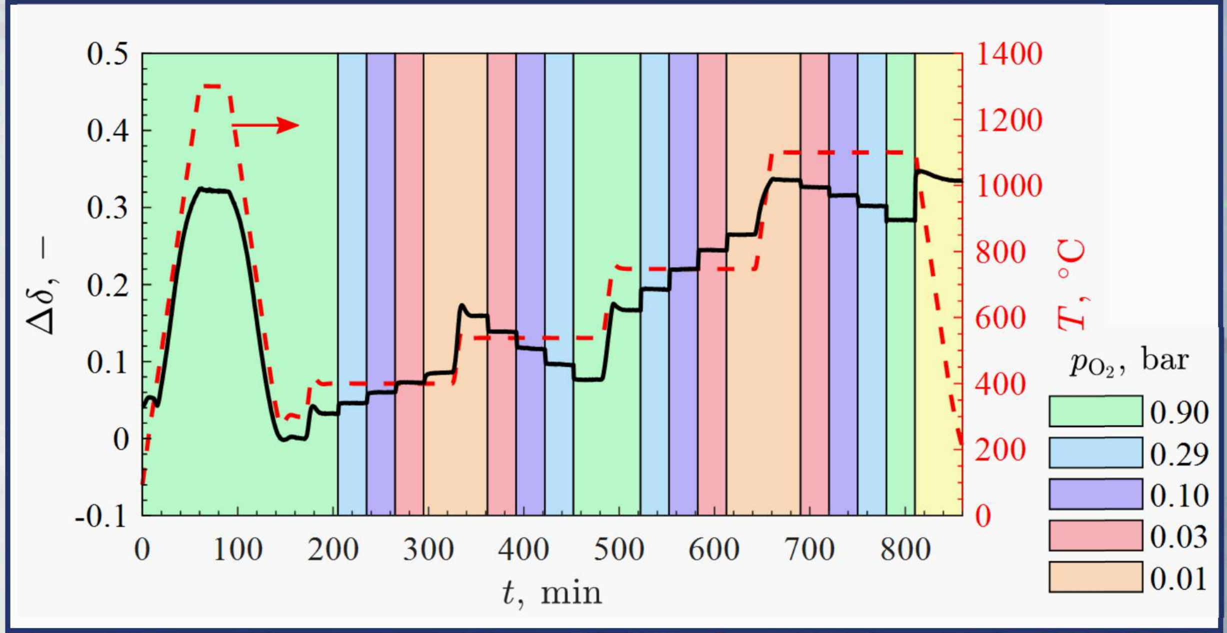
BSF LSF



TGA Equilibria

- Thermogravimetric analysis to measure equilibrium nonstoichiometry
  - 30 min (p_{O_2} , T) steps
- Confidence intervals calculated via error propagation of experimental variability
  - Two replicates performed per sample
  - Ten replicates performed for blank run
- $\delta_0 = \delta$ at $p_{O_2} = 0.9$ bar, $T = 300$ °C





Naming convention:

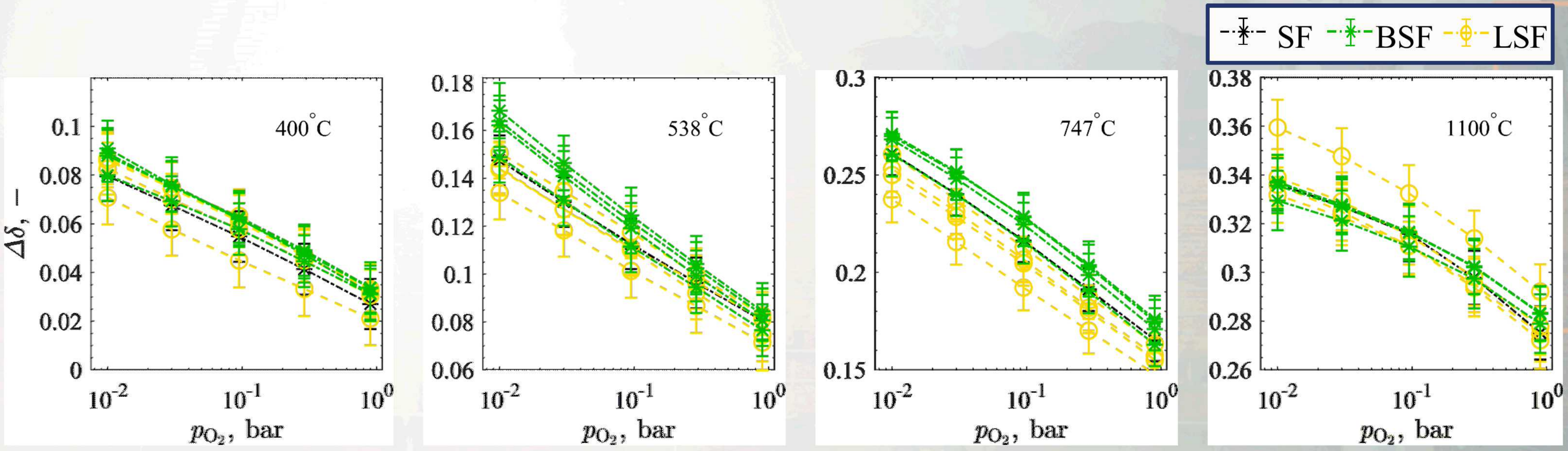
SF = $SrFeO_{3-\delta}$

BSF595 = $Ba_{0.05}Sr_{0.95}FeO_{3-\delta}$
BSF1090 = $Ba_{0.1}Sr_{0.9}FeO_{3-\delta}$
BSF1585 = $Ba_{0.15}Sr_{0.85}FeO_{3-\delta}$
BSF2080 = $Ba_{0.2}Sr_{0.8}FeO_{3-\delta}$

LSF595 = $La_{0.05}Sr_{0.95}FeO_{3-\delta}$
LSF1090 = $La_{0.1}Sr_{0.9}FeO_{3-\delta}$
LSF1585 = $La_{0.15}Sr_{0.85}FeO_{3-\delta}$
LSF2080 = $La_{0.2}Sr_{0.8}FeO_{3-\delta}$

Experimental Results

- LSF generally less reducible than SF/BSF, but trend changed at high T
- "Best" composition highly dependent upon cycle conditions
- Modeling necessary to optimize composition to application



Compound Energy Model

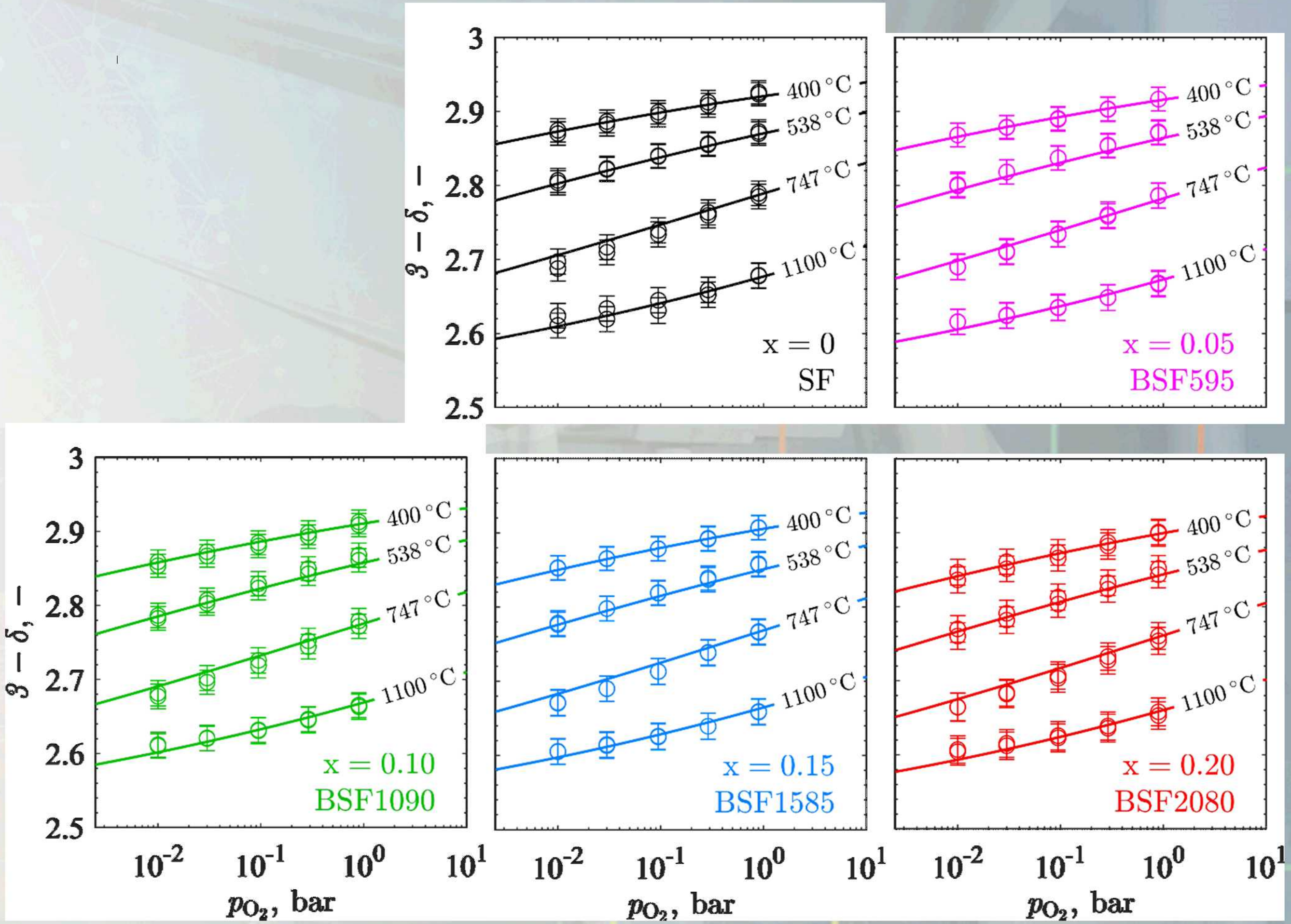
- Simultaneously fit to improve model statistics
- End member terms ($°G_{end}$):
  - Linear fits with T sufficient
  - Similar T-dependence for La, Ba terms
- Mixing entropy terms ($°G_{mix}$):
  - Ideal intra-sublattice mixing
  - No fitted parameters
- Excess terms ($°G_{exs}$):
  - A-site interactions insignificant
  - 2nd order terms important at high T
  - Fe^{4+}-Fe^{3+}, O^{2-}-V_O terms capture vacancy ordering

End Members	
$Sr^{2+} : Fe^{4+} : O^{2-}$	$Sr^{2+} : Fe^{3+} : O^{2-}$
$Ba^{2+} : Fe^{4+} : O^{2-}$	$Ba^{2+} : Fe^{3+} : O^{2-}$
$La^{3+} : Fe^{4+} : O^{2-}$	$La^{3+} : Fe^{3+} : O^{2-}$
A : B : Vo (six terms)	
$°G_{A:B:Vo} = °G_{A:B:O} - 3/2°G_{O2(g)}$ (reciprocal relationship)	

Interaction	Gibbs Free Energy ($°G_{exs}$) Definition	
	0th Order	1st Order
$Fe^{3+} - Fe^{4+}$	$(7.67 \pm 0.09)E{-2}\ T - (1.15 \pm 0.71)E{-6}\ T^2$	$(4.99 \pm 0.07)E{-1}\ T + (9.77 \pm 0.60)E{-5}\ T^2$
$O^{2-} - V_O$	$-(2.24 \pm 0.14)E{-2}\ T + (9.06 \pm 1.32)E{-6}\ T^2$	–

CEF Model: BSF

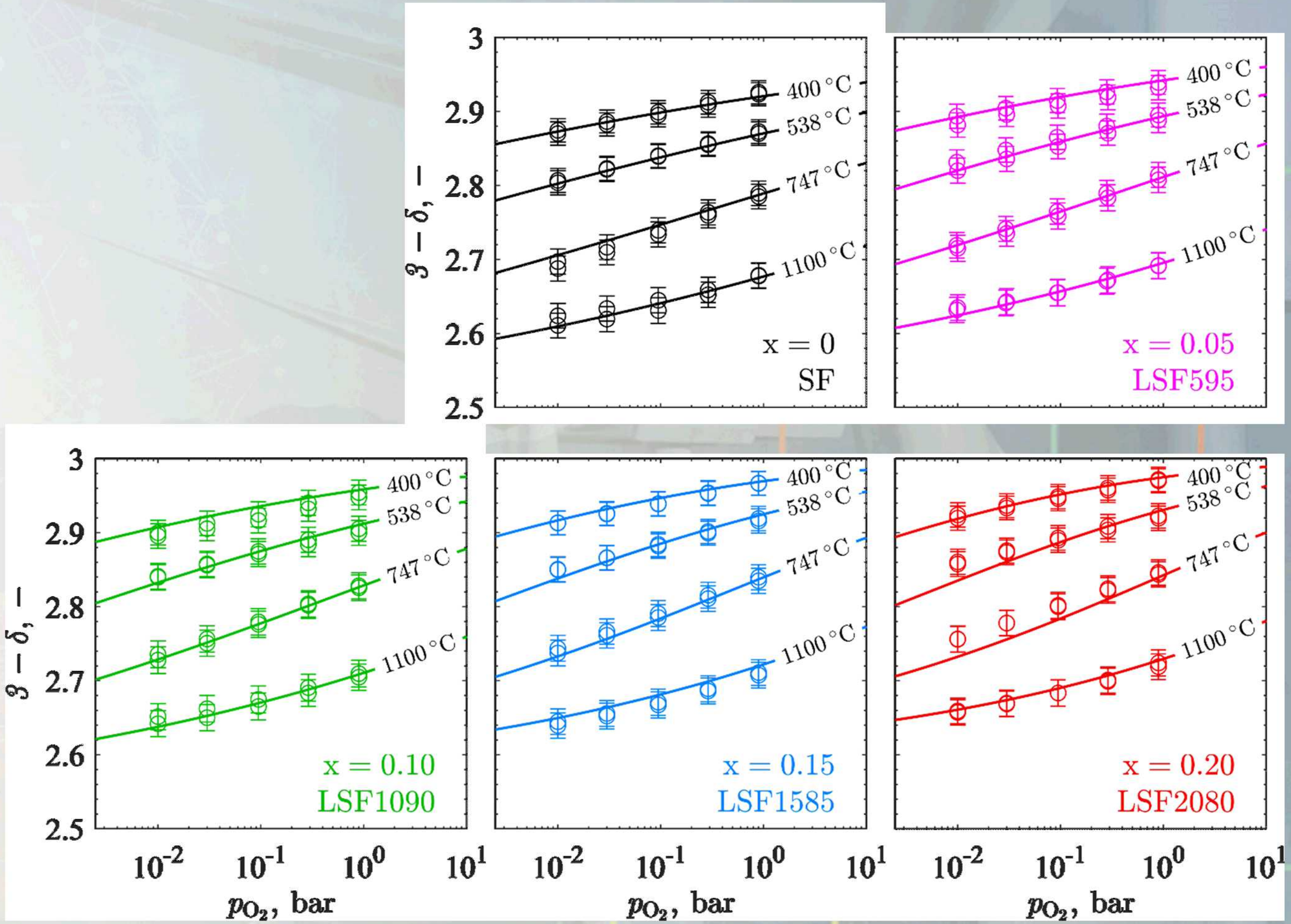
- High experimental repeatability
  - Large overlap of marker error bounds
- All compositions within error bounds
- Interactions important at high T
  - T^2 terms necessary at 1100 °C



CEF Model: LSF

- High experimental/model fidelity
  - LSF2080 largest error: low p_{O_2}, mid T
- Interactions important at high T
- Smaller δ_0 for LSF compared to BSF

x	BSF	LSF
0	0.05 ± 0.01	
0.05	0.05 ± 0.01	0.04 ± 0.02
0.10	0.06 ± 0.01	0.02 ± 0.01
0.15	0.06 ± 0.01	0.00 ± 0.00
0.20	0.07 ± 0.01	0.01 ± 0.01



Thermodynamics

- Van't Hoff estimates of ΔH_δ and ΔS_δ from CEF fits
- Ba and La-substitution decreased ΔH_δ
- Small (insignificant) ΔS_δ difference for BSF
- Larger LSF ΔS_δ difference: La^{3+}/Fe^{3+} charge compensation
  - Diminished reduction favorability ($G = H - TS$)

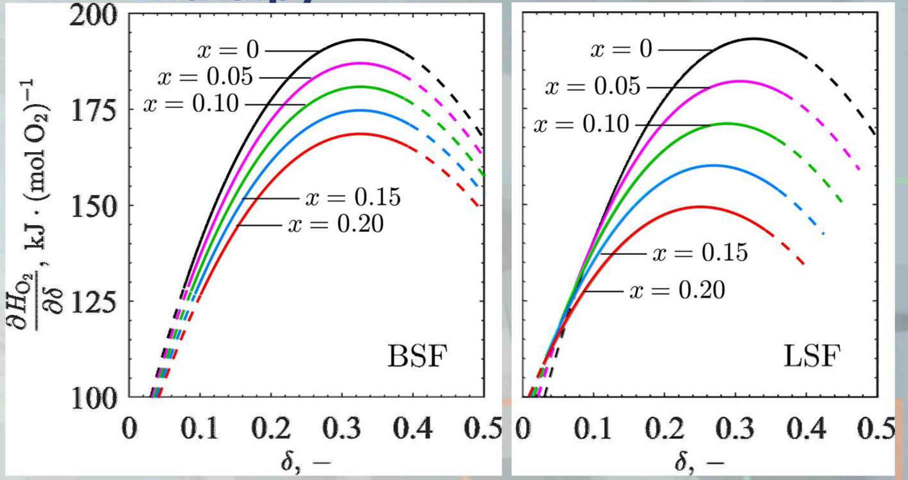
BSF

Sample	ΔH_δ kJ/mol O_2	ΔS_δ J/mol O_2-K
$SrFeO_3$	166 ± 1	145 ± 6
BSF595	161 ± 2	144 ± 7
BSF1090	156 ± 1	143 ± 7
BSF1585	152 ± 1	141 ± 7
BSF2080	147 ± 1	140 ± 7

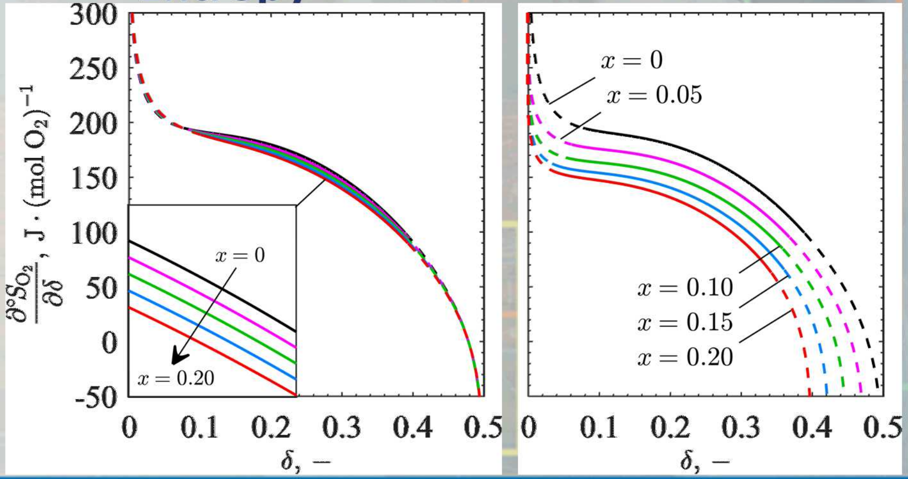
LSF

Sample	ΔH_δ kJ/mol O_2	ΔS_δ J/mol O_2-K
$SrFeO_3$	166 ± 1	145 ± 6
LSF595	159 ± 1	133 ± 5
LSF1090	151 ± 1	124 ± 4
LSF1585	142 ± 1	118 ± 6
LSF2080	133 ± 0	114 ± 3

Enthalpy



Entropy



Summary

- CEF captured substituted strontium ferrite redox behavior as a function of temperature, O_2 pressure, and Ba/La substituent fraction
  - Ba substitution more appealing for lower temperature cycles
  - La substation more appealing for higher temperature cycles
- Provides framework for comparing substituents with general model
- Thermodynamics may be coupled to cycle model for process optimization

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Georgia Tech Solar Fuels and Technology Lab

ASU LightWorks ARIZONA STATE UNIVERSITY

For More Information:

H. Evan Bush
Postdoctoral Appointee
Sandia National Labs

hebush@sandia.gov