Investigation of $\text{La}_x\text{Sr}_{1-x}\text{Co}_y\text{M}_{1-y}\text{O}_{3-\delta}$ (M = Mn, Fe) perovskite materials as thermochemical energy storage media

Sean M. Babiniec¹, Eric N. Coker², James E. Miller², Andrea Ambrosini^{1,*}

1. Sandia National Laboratories – Materials, Devices, & Energy Technology

2. Sandia National Laboratories – Advanced Materials Laboratory

ABSTRACT

Materials in the $\text{La}_x\text{Sr}_{1-x}\text{Co}_y\text{Mn}_{1-y}\text{O}_{3-\delta}$ (LSCM) and $\text{La}_x\text{Sr}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ (LSCF) families are candidates for high-temperature thermochemical energy storage due to their facility for cyclic endothermic reduction and exothermic oxidation. A set of 16 LSCM and 21 LSCF compositions were synthesized by a modified Pechini method and characterized by powder X-ray diffraction and thermogravimetric analysis. All materials were found to be various symmetries of the perovskite phase. LSCM was indexed as tetragonal, cubic, rhombohedral, or orthorhombic as a function of increased lanthanum content. For LSCF, compositions containing low lanthanum content were indexed as cubic while materials with high lanthanum content were indexed as rhombohedral. An initial screening of redox activity was completed by thermogravimetric analysis for each composition. The top three compositions with the greatest recoverable redox capacity for each family were further characterized in equilibrium thermogravimetric experiments over a range of temperatures and oxygen partial pressures. These equilibrium experiments allowed the extraction of thermodynamic parameters for LSCM and LSCF compositions operated in thermochemical energy storage conditions.

* P.O. Box 5800, MS 0734, Albuquerque, NM 87185, United States
aambros@sandia.gov, +1-505-284-1340

1. INTRODUCTION

In the face of ever increasing worldwide energy demand occurring in the context of increasing global climate concerns, several renewable energy technologies are under development. One such technology is concentrating solar power (CSP) for generation of electricity. However, the inherent intermittent availability of solar energy complicates the delivery of on-demand electricity. Energy storage technologies can mitigate this limitation provided they can be implemented in a cost effective manner. In the case of CSP, thermal energy can be stored while the system is on-sun, and released at other times to mitigate transients and extend or shift the hours of continuous power generation. Such an approach is currently implemented with molten salts wherein the energy is stored in the form of sensible heat.

In order to realize widespread use of CSP plants, the U.S. Department of Energy (DOE) estimates electricity should be generated at a cost of 6 ¢/kWh (NREL 2012). This target can be approached in part by maximizing the efficiency at which heat is converted to power by utilizing high-temperature ($> 1000\text{ }^{\circ}\text{C}$), high-efficiency power cycles, such as Brayton cycles (Stekli, 2013). Likewise, the cost of thermal storage must be minimized by reducing the storage volume, which requires materials with high energy storage density (Stekli, 2013). The energy density of molten salts ($\sim 410\text{ kJ/kg}$ (Stekli, 2013; Wu, 2011)) is insufficient in minimizing such storage volume. In addition, molten salts tend to decompose at temperatures of $\sim 800\text{ }^{\circ}\text{C}$ (Wu, 2011), precluding high-temperature storage and delivery. Thus, new methods and materials are under investigation in an effort to increase the stored energy density and to deliver stored heat at higher temperatures. One option under investigation is materials which undergo a reversible chemical reaction, thus storing heat indefinitely in the form of chemical bonds in addition to storing sensible heat. This option is termed thermochemical energy storage (TCES) (Tescari, 2014; Pardo, 2014; Steinfeld; 2001).

Current state-of-the-art high-temperature TCES research is focused on metal oxide reduction/oxidation (redox) materials due to their redox reversibility, higher temperature of operation as compared to molten salts, and absence of product gasses that require separation and/or storage (Pardo2014). Two families of metal oxides are the targets of current scrutiny: metal oxide redox pairs which undergo a stoichiometric reduction to a new crystal phase, and mixed-ionic/electronic conducting (MIEC) materials that are capable of supporting a large number of oxygen vacancies without undergoing a crystallographic phase change. Manganese and cobalt oxides have been extensively studied as metal oxide redox pairs (Agrafiotis, 2014; Carrillo, 2014; Hutchings, 2006; Pardo, 2014; Tescari, 2014). In the case of manganese oxide, the redox reaction of interest is (Carrillo, 2014):

The reduction of MnO_2 to Mn_2O_3 occurs at a low temperature, 530 °C in air, and tends to be kinetically limited and irreversible in practice at standard pressure. Further reduction to MnO is only favorable in air at 1700 °C, which is higher than the melting point of Mn_3O_4 (1567 °C) (Hutchings, 2006; Stobbe, 1999).

For cobalt oxide, the redox reaction is (Carillo, 2014):

Although manganese is significantly less expensive than cobalt, the higher energy density of cobalt oxide in the reactions listed above makes cobalt oxide a technologically more attractive choice

(Carrillo, 2014; Pardo, 2014). Reduction of Co_3O_4 to CoO is observed to occur rapidly at temperatures near 885 °C. However, oxidation proceeds at a much slower pace (Agrafiotis, 2014). Slow re-oxidation kinetics could cause limits in outlet air temperature and hinder efficient integration with power generation (General Atomics, 2011). Attempts to increase kinetics and/or energy density by doping certain transition metals (Mn, Mg, Ni, Cu) onto the cation site failed to improve the performance of the redox reaction (Agrafiotis, 2014; Carrillo, 2014). However, doping Fe into cobalt oxide was shown to increase reaction kinetics at the expense of a decrease in reaction enthalpy (Block, 2014; General Atomics, 2011).

The MIEC ceramic alternatives differ from the more conventional metal oxides by the fact that the material maintains its crystal structure over a large range of oxygen non-stoichiometry (Eq. 3). Also, the high ionic and electronic conductivities of these compounds facilitate the reaction within the bulk of the material thus increasing reaction extent and kinetics, and they tend to exhibit stability at high temperatures (Ambrosini, 2006; Mueller, 2010; Scott, 2002). MIEC ceramics of the perovskite family, ABO_3 , exhibit remarkable flexibility for doping in the A and B metal cation sites, enabling the tuning of many materials properties (Pena, 2001). These include the capacity for oxygen non-stoichiometry and ionic/electronic conductivity, both important for maximizing extent of reaction and kinetics in TCES operation.

As the perovskite reduction does not necessitate a discrete structural phase change (Eq. 3), latent heat stored in the system is continuously increased as oxygen non-stoichiometry (δ) is increased. This feature potentially allows greater flexibility in operating temperatures. Furthermore, changes in oxygen partial pressure, however small, will shift the chemical equilibrium of the continuous reaction resulting in high tuneability through manipulation of gas environments (Pishahang, 2013; Scott, 2002).

Existing materials of interest for TCES include $\text{La}_x\text{Sr}_{1-x}\text{Co}_y\text{Mn}_{1-y}\text{O}_{3-\delta}$ (LSCM) and $\text{La}_x\text{Sr}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ (LSCF). Members of these materials families have a large reduction capacity (Ambrosini, 2006; Demont, 2014; Klande, 2013; Stevenson, 1996; Tai, 1995). Although LSCM and LSCF perovskites have been widely studied as mixed-conductors for oxygen separation and fuel cell cathode applications (Chen, 2008; De Souza, 1998; Doshi, 1999; Jiang, 2002; Klande, 2013; Murata, 2005; Wang, 2005), a characterization of redox activity and thermodynamics in TCES operating conditions across a broad range of compositions is missing. This study aims to fill that gap thereby providing insight on the applicability of LSCM and LSCF as TCES materials.

2. Experimental Approach

2.1 Synthesis

LSCM and LSCF perovskites were synthesized using a modified Pechini method (Pechini, 1967).

Stoichiometric amounts of nitrate salts ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.999% Alfa-Aesar), $\text{Sr}(\text{NO}_3)_2$ (99.9965% Alfa-Aesar), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.9% Acros Organics), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.999% Alfa-Aesar), $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (98%, Alfa-Aesar)) were dissolved in water, then citric acid was added to the solution in a 1:1 molar cation: citric acid ratio. The solution was dried and combusted, and the resulting ash was pre-calcined at 850 °C for 2 hours in air. These powders were mixed with 1.5 wt.% polyvinyl butyral (PVB) and pressed in a $\varnothing$ 13 mm die at 35 MPa. Pressed pellets were calcined at 1250 °C for 48 hours in air. To aid in simplified discussion, the formula for each composition is abbreviated as such: $\text{La}_{0,a}\text{Sr}_{0,b}\text{Co}_{0,x}\text{Mn}_{0,y}\text{O}_{3-\delta}$ is noted as LSCMabxy, e.g. $\text{La}_{0.1}\text{Sr}_{0.9}\text{Co}_{0.9}\text{Mn}_{0.1}\text{O}_{3-\delta}$ is noted as LSCM1991.

2.2 Structural Characterization

Crystallographic structure of the calcined pellets was examined using PANalytical X'Pert and Bruker AXS D8 Advance X-ray diffractometers (XRDs) with Cu K α radiation. Crystal structure was determined by analyzing XRD patterns using Jade 9 software (Materials Data Inc. Jade+, Livermore, CA). Materials with a calculated impurity of > 5% were not considered single-phase.

2.3 Thermal Analysis

Two thermogravimetric analysis (TGA) procedures were adopted for this study. The first was a simple evaluation of the redox capacity for each member of the composition set. This analysis was used to identify the best candidates for more-detailed study. The second involved obtaining equilibrium measurements over a range of temperatures and oxygen partial pressures to verify the initial results and to provide a measure of the redox thermodynamics and reproducibility.

The initial reduction/oxidation (redox) characterization was performed using pellet fragments (~ 15 mg) in a TA Instruments Q600 TG/DSC. Figure 1a shows the programmed temperature and gas composition profile for the pre-screen TGA cycle. The purpose of this experiment was not to determine absolute equilibrium values of δ , but to provide an efficient method for comparing the redox performance between different compositions under reasonable operating parameters (time and temperature). An initial break-in cycle was performed in air, followed by reduction in air to 1250 °C, further reduction in argon, and then re-oxidation in air while cooling to 200 °C. Argon is used to examine how each material reacts to a large change in oxygen partial pressure, i.e. how deeply the reduction can be driven, and if deep reduction leads to an irreversible change in the material. The break-in cycle serves to eliminate any adsorbed species on the surface of the sample and to ensure that each material is equilibrated under a common set of conditions (Ambrosini, 2010; Ksepko, 2014).

Figure 1b illustrates the notation representing oxygen non-stoichiometry (δ) for the redox measurements using a representative sample. A change in oxygen non-stoichiometry due to reduction in air from 200 °C to 1250 °C is termed δ_1 , further reduction at 1250 °C due to a gas switch from air to argon is termed δ_2 , and reoxidation due to a gas switch from argon to air, followed by cooling from 1250 °C to 200 °C, is termed δ_3 . While $\Delta\delta_3$ is not a measure of the full recovery possible at equilibrium, principally due to slow kinetics at the lowest temperatures, it nonetheless provides an effective metric for comparing and identifying materials for further study, particularly when the importance of reaction kinetics to achievable systems is considered. Note that in practice the final temperature did not quite reach 200 °C due to a lag in the furnace cooling rate at low temperatures (Fig 1b.). δ was calculated as:

$$\delta = (m / m_{\text{init}}) \cdot (MW_{\text{ABO}_3} / MW_{\text{O}}) \quad (4)$$

where m is the mass change measured by TGA, m_{init} is the initial mass, MW_{ABO_3} is the molecular weight of the perovskite assuming that the initial state of the material is the ABO_3 stoichiometry ($\delta = 0$), and MW_{O} is the molecular weight of monatomic oxygen.

Instrumental drift was measured by heating a known mass of stable material to 1250 °C, cooling, and then comparing the initial and final weights. Three measurements yielded an average mass change of $0.022\% \pm 0.008\%$. Error owing to sample inhomogeneity, such as sample weight or fragment surface area, was characterized by measuring a select composition three times using different pellet fragments for each measurement. Standard deviations of 2.97%, 5.49%, and 2.56% were measured for δ_1 , δ_2 , and δ_3 , respectively. These errors are small relative to the differences in measured values of δ for different compositions, indicating that meaningful comparisons can be made.

Further analyses of the three candidates with the largest measured δ_3 values in each materials family were performed using a Netzsch STA449F3 Jupiter TGA loaded with ~100 mg of sample powder.

170 Following a single break-in cycle and an initial mass measurement at a temperature of 200 °C and pO_2
171 of 0.9 atm, samples were given adequate time to equilibrate at temperatures of 600, 800, 950, 1100,
172 and 1250 °C repeated at oxygen partial pressures of 0.9, 0.1, 0.01, and 0.001 atm. Oxygen
173 concentration was established by mixing UHP oxygen and argon using calibrated mass flow controllers.
174 The corresponding TGA profile for this experiment can be found in the supplemental material
175 (Supplemental Figure A).

176 The data collected identifies the δ vs. temperature at each pO_2 , assuming that the oxygen non-
177 stoichiometry at the starting condition of the experiment is $\delta = 0$. A linear regression was performed to
178 characterize the data in van't Hoff form as $\ln(pO_2)$ vs. $1/T$ for each value of δ . A second linear
179 regression was performed to extract the enthalpy and entropy at each value of δ from the slope and
180 intercept of the regression, respectively (Miller, 2014; Mizusaki, 1991).

181 3. Results and Discussion

182 While the ideal perovskite phase is cubic in nature, perovskite materials often crystallize in a
183 number of crystal structures as a result of distortions within the lattice (Pena, 2001). LSCM
184 compositions synthesized in this work adopted the perovskite phase, crystallizing in tetragonal, cubic,
185 rhombohedral, and orthorhombic structures. LSCF compositions were perovskite phase, indexed to
186 either a cubic or rhombohedral structures. Figure 2 illustrates characteristic examples of LSCM (a) and
187 LSCF (b) XRD patterns. The rhombohedral and orthorhombic distortions were identified at higher 2θ
188 angles, where distortions from the cubic structure result in peak-broadening or splitting. For several
189 compositions, peak intensity ratios corresponded more closely to tetragonal structures instead of cubic
190 structures. These compositions were indexed as tetragonal. In addition, the positions and intensities of
191 peak splitting were not commensurate with those calculated for $K_{\alpha 2}$ radiation. For both materials sets,
192 increasing La concentrations resulted in a lattice distortion away from the ideal cubic structure. For

example, LSCF8228 is rhombohedral, while LSCF2828 is cubic, despite having an identical B-site composition. In contrast, LSCF2882 and LSCF2828, which have identical La content but varying B site compositions, are both cubic. The structure of each composition is reported in Tables 1 and 2. Predictions of perovskite lattice distortions based on the Goldschmidt tolerance factor (Goldschmidt, 1926) were largely inaccurate, likely due to ionic radii ambiguities caused by doping on both the A- and B-sites. A more detailed description of the analysis is provided in the supplemental information.

Data from the preliminary TGA experiments are shown in Tables 1 and 2. The crystallographic structure appears to correlate highly with redox capacity. For both material families, the cubic structure results in the highest redox capacities, with LSCM3791 ($\delta_3=0.39$) and LSCF3773 ($\delta_3=0.40$) being the highest performers for each material family. LSCM displays a wider variety of lattice distortions than LSCF, crystallizing in tetragonal (low [La]) and orthorhombic (high [La]) structures in addition to the cubic and rhombohedral crystal structures adopted by both families. The tetragonal structure in LSCM displays redox properties similar to the cubic structure, while the orthorhombic structure behavior is similar to that of the rhombohedral structure. These findings are consistent, as the tetragonal structure is closely related to the cubic structure, while orthorhombic and rhombohedral generally display a larger a degree of distortion from the cubic structure.

A closer look at the performance of both material families reveals values of δ_{1-3} that are relatively constant as a function of La content for small concentrations of La. Delta reaches a maximum at a La A-site content of 0.3, then decreases sharply as La content is increased (Figure 3). The data points in Figure 3 represent varying B-site ratios for each La concentration. The tight grouping of δ in the LSCF family at each lanthanum fraction indicates that the ratio of Co:Fe not only has little impact on the crystal structure, but relatively little impact on the redox behavior as well. This is further illustrated by plotting the reoxidation non-stoichiometry as a function of B-site Co:Mn/Fe ratio, as seen

216 in Figure 4. In both materials sets, different crystallographic structures were identified for many
217 compounds sharing the same B-site composition. LSCF shows no clear trend between reoxidation
218 performance and cobalt content, while the LSCM compositions show a weak trend of increasing
219 reoxidation performance with increasing cobalt content. This suggests that the Co:Mn ratio has a more
220 significant role in the redox mechanism for LSCM than does the Co:Fe ratio for LSCF, but both materials
221 show stronger trends as a function of crystallographic structure.

222 The three compositions from each family exhibiting the highest values for δ_3 measured in the
223 preliminary TGA evaluation were LSCM1991, LSCM3791, LSCM3782, and LSCF2882, LSCF3791, and
224 LSCF3773. These compositions were analyzed in greater detail as described above (Section 2.3). Figure
225 5a illustrates equilibrium data collected for LSCM3791. Mass equilibrium is reached at each
226 temperature/oxygen partial pressure (Figure 5b). Mass equilibrium times varied between ~40 minutes
227 to nearly instantaneous depending on the temperature, oxygen partial pressure, and reaction extent.
228 The need for the break-in cycle is also illustrated by the increase in mass after the break-in cycle
229 relative to the initial mass. The observation that the material equilibrates to the same mass at the end
230 of the experiment as to that measured immediately after the break-in cycle (under identical
231 conditions) is indicative that the materials is tolerant to redox cycling. Furthermore, Figure 5a
232 illustrates the effectiveness of a single break-in cycle for our purposes. Preliminary cycling
233 measurements in air indicate that the redox activity is reversible (see supplemental material Figure B);
234 more rigorous evaluation is underway and will be reported in a future publication. Representative data
235 obtained by the procedure are shown in Figure 6. Figure 6a illustrates the range of equilibrium data
236 acquired and the application of a linear fit to the data. The linear fits can be used to transform the data
237 into van't Hoff form, Figure 6b. A linear regression of the van't Hoff plot yields an estimation of the
238 enthalpy (slope) and entropy (intercept) of the reduction reaction.

The enthalpies extracted from the van't Hoff data for the LSCM and LSCF compounds are shown in Figure 6. Each extracted enthalpy is representative of removing a mole of O₂ from the lattice at a specific δ (left axis). In other words, each data point extracted from the van't Hoff analysis represents a discrete reaction at a specific composition, and a series of these reactions describes the continuous reduction. Therefore, the curve must be integrated to calculate the total enthalpy required to remove all oxygen atoms up to a specific δ :

$$\Delta H_{\text{red}} = \int_{\delta_0}^{\delta} \frac{dH_{\text{red}}}{d\delta} d\delta \quad (5)$$

Note that Equation 5 converts the enthalpy units to kJ/mol-perovskite. Dividing by the molecular weight of the perovskite yields a result in units of the weight-specific enthalpy, kJ/kg-perovskite (right axis of Figure 6).

The enthalpy data plotted in Figure 7 are truncated to represent the maximum extent of reduction observed for each composition, measured by the equilibrium TGA experiment. From Figure 7, it is clear that LSCF requires less energy to extract oxygen at low δ , making it easier to reduce, thus storing less heat at lower extent of reduction. However, as δ increases, LSCF becomes increasingly difficult to reduce and eventually exhibits a higher enthalpy of reduction per mole of oxygen than LSCM. Yet, the larger enthalpy (and thus larger thermal storage potential) of LSCM at low extents of reduction is of benefit when the enthalpy is summed (integrated) with increasing reduction. When comparing the total enthalpy of the two families (integrated curve, right axis), it becomes apparent that LSCF must reach a higher δ to store as much latent heat as LSCM. The integrated enthalpy for each composition at its maximum observed δ (δ_{max}) is listed in Table 3.

The total heat available for storage, and subsequently delivery, is the summation of the reduction enthalpy and the sensible enthalpy. The contribution of sensible enthalpy is to be discussed in future studies. However, the sensible enthalpy for each composition within a materials family is

expected to be similar, thus the reaction enthalpy is a valid way to qualitatively compare the energy storage performance of a materials family.

4. Conclusions

$\text{La}_x\text{Sr}_{1-x}\text{Co}_y\text{Mn}_{1-y}\text{O}_{3-\delta}$ and $\text{La}_x\text{Sr}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ compositions were synthesized and their structures characterized by XRD. Preliminary TGA revealed that both families show the highest redox activity at compositions of low [La], which adopt a cubic structure (and in LSCM, the closely-related tetragonal structure). At higher [La], the perovskite structure shows greater distortion and redox activity decreases accordingly. The maximum redox activity was determined to occur at lanthanum contents of $x = 0.3$ for both families. There appears to be less of a correlation between B-site composition (Co:Mn/Fe) and redox activity. The reason for this is unknown at this time and is under investigation. One hypothesis is the occurrence of cation or vacancy ordering within the structure. More detailed structural analysis is underway to more clearly elucidate the structure-property relationships in these materials, utilizing such techniques as in-situ XRD and microscopy.

The three compositions of each materials family with the highest values of δ_3 were analyzed in-depth as potential TCES candidates. Equilibrium TGA measurements were taken to extract thermodynamic data using van't Hoff plots. Although the LSCF candidates reach a higher maximum δ , LSCM candidates show a higher integrated enthalpy due to the higher enthalpy per mole O_2 at low δ . LSCM3791 demonstrates the largest perovskite weight-specific reaction enthalpy of 250 kJ/kg- ABO_3 .

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Figure Captions List

- Fig. 1 Preliminary TGA (a) profile, and (b) terminology of measured changes in oxygen non-stoichiometry during the second cycle following the break-in
- Fig. 2 XRD patterns for (a) LSCM and (b) LSCF with varying crystallographic symmetry
- Fig. 3 Oxygen non-stoichiometry of (a) LSCM and (b) LSCF for air (top) and argon reduction (middle), and reoxidation (bottom) as a function of A-site lanthanum content. T, C, R, and O denote tetragonal, cubic, rhombohedral, and orthogonal phases, respectively.
- Fig. 4 Oxygen non-stoichiometry of (a) LSCM and (b) LSCF for reoxidation as a function of B-site cobalt content. Orange, green, red, and grey symbols correspond to tetragonal, cubic, rhombohedral, and orthogonal phases, respectively.
- Fig. 5 Equilibrium TGA data for LSCM3791, a) complete data set, b) detail of select range illustrating equilibrium times. Oxygen partial pressures are in atm.
- Fig. 6 Equilibrium measurements of changes in oxygen stoichiometry in LSCF3773 a) as a function of temperature for lines of constant oxygen partial pressure, b) as a function of reciprocal temperature for lines of constant δ . Linear regressions are shown to demonstrate the linearity of the data.

Fig. 7 Enthalpy as a function of oxygen non-stoichiometry for LSCM (top) and
LSCF (bottom)

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403 **Table Caption List**

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Table 1	Crystallography and pre-screen redox properties of LSCM compositions
Table 2	Crystallography and pre-screen redox properties of LSCF compositions
Table 3	Enthalpy values at maximum reduction of each composition

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Fig. 1. Preliminary TGA (a) profile, and (b) terminology of measured changes in oxygen non-stoichiometry during the second cycle following the break-in.

Fig. 2. XRD patterns for (a) LSCM and (b) LSCF with varying crystallographic symmetry

Fig. 3. Oxygen non-stoichiometry of (a) LSCM and (b) LSCF for air (top) and argon reduction (middle), and reoxidation (bottom) as a function of A-site lanthanum content. T, C, R, and O denote tetragonal, cubic, rhombohedral, and orthogonal phases, respectively.

Fig. 4. Oxygen non-stoichiometry of (a) LSCM and (b) LSCF for reoxidation as a function of B-site cobalt content. Orange, green, red, and grey symbols correspond to tetragonal, cubic, rhombohedral, and orthogonal phases, respectively.

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Fig. 5. Equilibrium TGA data for LSCM3791, a) complete data set, b) detail of select range illustrating equilibrium times. Oxygen partial pressures are in atm.

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Fig. 6. Equilibrium measurements of changes in oxygen stoichiometry in LSCF3773 a) as a function of temperature for lines of constant oxygen partial pressure, b) as a function of reciprocal temperature for lines of constant δ . Linear regressions are shown to demonstrate the linearity of the data.

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Fig. 7. Enthalpy as a function of oxygen non-stoichiometry for LSCM (top) and LSCF (bottom).

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Table 1
Crystallography and pre-screen redox properties of LSCM compositions

Nominal Composition	>95% single-phase?	Crystal structure	δ_1	δ_2	δ_3
$\text{La}_{0.1}\text{Sr}_{0.9}\text{Co}_{0.9}\text{Mn}_{0.1}\text{O}_{3-\delta}$ (LSCM1991)	Yes	Tetragonal	0.25	0.12	0.32
$\text{La}_{0.1}\text{Sr}_{0.9}\text{Co}_{0.8}\text{Mn}_{0.2}\text{O}_{3-\delta}$ (LSCM1982)	Yes	Tetragonal	0.24	0.12	0.31
$\text{La}_{0.1}\text{Sr}_{0.9}\text{Co}_{0.7}\text{Mn}_{0.3}\text{O}_{3-\delta}$ (LSCM1973)	Yes	Tetragonal	0.21	0.11	0.28
$\text{La}_{0.2}\text{Sr}_{0.8}\text{Co}_{0.9}\text{Mn}_{0.1}\text{O}_{3-\delta}$ (LSCM2891)	Yes	Tetragonal	0.25	0.11	0.33
$\text{La}_{0.2}\text{Sr}_{0.8}\text{Co}_{0.8}\text{Mn}_{0.2}\text{O}_{3-\delta}$ (LSCM2882)	No	Tetragonal	0.21	0.11	0.28
$\text{La}_{0.2}\text{Sr}_{0.8}\text{Co}_{0.7}\text{Mn}_{0.3}\text{O}_{3-\delta}$ (LSCM2873)	Yes	Tetragonal	0.23	0.12	0.31
$\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.9}\text{Mn}_{0.1}\text{O}_{3-\delta}$ (LSCM3791)	No	Cubic	0.31	0.12	0.39
$\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.8}\text{Mn}_{0.2}\text{O}_{3-\delta}$ (LSCM3782)	Yes	Cubic	0.28	0.12	0.36
$\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.7}\text{Mn}_{0.3}\text{O}_{3-\delta}$ (LSCM3773)	Yes	Cubic	0.23	0.12	0.31
$\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.6}\text{Mn}_{0.4}\text{O}_{3-\delta}$ (LSCM4664)	Yes	Cubic	0.17	0.11	0.24
$\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.3}\text{Mn}_{0.7}\text{O}_{3-\delta}$ (LSCM7337)	Yes	Rhombohedral	0.03	0.07	0.01
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.8}\text{O}_{3-\delta}$ (LSCM8228)	Yes	Rhombohedral	0.02	0.05	-0.007
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.3}\text{Mn}_{0.7}\text{O}_{3-\delta}$ (LSCM8237)	Yes	Rhombohedral	0.02	0.05	-0.003
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Co}_{0.1}\text{Mn}_{0.9}\text{O}_{3-\delta}$ (LSCM9119)	Yes	Orthorhombic	0.04	0.06	0.020
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Co}_{0.2}\text{Mn}_{0.8}\text{O}_{3-\delta}$ (LSCM9128)	Yes	Orthorhombic	0.02	0.05	-0.002
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Co}_{0.3}\text{Mn}_{0.7}\text{O}_{3-\delta}$ (LSCM9137)	Yes	Orthorhombic	0.03	0.06	-0.005

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Table 2
Crystallography and pre-screen redox properties of LSCF compositions

Nominal Composition	>95% single-phase?	Crystal structure	δ_1	δ_2	δ_3
$\text{La}_{0.1}\text{Sr}_{0.9}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ (LSCF1991)	No	Cubic	0.23	0.09	0.31
$\text{La}_{0.1}\text{Sr}_{0.9}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (LSCF1982)	Yes	Cubic	0.30	0.11	0.37
$\text{La}_{0.1}\text{Sr}_{0.9}\text{Co}_{0.7}\text{Fe}_{0.3}\text{O}_{3-\delta}$ (LSCF1973)	Yes	Cubic	0.29	0.10	0.36
$\text{La}_{0.2}\text{Sr}_{0.8}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ (LSCF2891)	Yes	Cubic	0.31	0.11	0.38
$\text{La}_{0.2}\text{Sr}_{0.8}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (LSCF2882)	Yes	Cubic	0.32	0.11	0.38
$\text{La}_{0.2}\text{Sr}_{0.8}\text{Co}_{0.7}\text{Fe}_{0.3}\text{O}_{3-\delta}$ (LSCF2873)	No	Cubic	0.30	0.11	0.38
$\text{La}_{0.2}\text{Sr}_{0.8}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF2828)	Yes	Cubic	0.30	0.09	0.35
$\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ (LSCF3791)	Yes	Cubic	0.30	0.12	0.38
$\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.7}\text{Fe}_{0.3}\text{O}_{3-\delta}$ (LSCF3773)	Yes	Cubic	0.32	0.11	0.40
$\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ (LSCF4691)	Yes	Cubic	0.27	0.12	0.35
$\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (LSCF4682)	Yes	Cubic	0.28	0.12	0.36
$\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.7}\text{Fe}_{0.3}\text{O}_{3-\delta}$ (LSCF4673)	Yes	Cubic	0.26	0.11	0.35
$\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.4}\text{Fe}_{0.6}\text{O}_{3-\delta}$ (LSCF4646)	Yes	Cubic	0.25	0.10	0.30
$\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$ (LSCF4664)	Yes	Rhombohedral	0.26	0.11	0.32
$\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$ (LSCF5555)	Yes	Rhombohedral	0.22	0.11	0.29
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.4}\text{Fe}_{0.6}\text{O}_{3-\delta}$ (LSCF6446)	Yes	Rhombohedral	0.17	0.11	0.22
$\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.3}\text{Fe}_{0.7}\text{O}_{3-\delta}$ (LSCF7337)	Yes	Rhombohedral	0.10	0.10	0.19
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF8228)	Yes	Rhombohedral	0.06	0.09	0.06
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.3}\text{Fe}_{0.7}\text{O}_{3-\delta}$ (LSCF8237)	Yes	Rhombohedral	0.07	0.10	0.08
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF9128)	Yes	Rhombohedral	0.03	0.07	0.01
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Co}_{0.3}\text{Fe}_{0.7}\text{O}_{3-\delta}$ (LSCF9137)	Yes	Rhombohedral	0.04	0.08	0.03

Table 3
Enthalpy values at maximum reduction of each composition

Composition	$\delta_{\max}$	H (kJ/kg-ABO ₃)
LSCM1991	0.43	220
LSCM3791	0.46	250
LSCM3782	0.41	230
LSCF2882	0.49	210
LSCF3791	0.46	220
LSCF3773	0.45	220