Revisiting the thermal and chemical expansion and stability of La$_{0.6}$Sr$_{0.4}$FeO$_3$–δ

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ABSTRACT

The thermal and chemical expansivity of La$_{1-x}$Sr$_x$FeO$_{3-δ}$ ($x = 0.4$) was measured using in situ powder neutron and synchrotron X-ray diffraction at temperatures between 932 K and 1170 K and oxygen partial pressures, $P_{O_2}$, between $10^{-19}$ bar and 0.1 bar, giving a wide range of oxygen non-stoichiometry from $δ = 0.05$ to 0.22. Changes in $δ$ were measured independently using gas analysis. This $P_{O_2}$ and temperature range covers the material’s use as a chemical looping oxygen carrier, a sensor material and in solid oxide fuel cells. Thermal and chemical expansivities were found to be dependent on the oxygen non-stoichiometry, $δ$. For $δ < 0.2$ and $T = 932–1050$ K, the linear thermal expansivity was $5.72(4) × 10^{-5}$ Å/K and the linear chemical expansivity was $0.144(9)$ Å per unit change in $δ$. For $δ > 0.2$ and $T = 973–1173$ K, the linear thermal expansivity increases to $6.18(8) × 10^{-5}$ Å/K. For $δ > 0.2$, the linear chemical expansivity varies with both $δ$ and temperature.

1. Introduction

Perovskite oxides such as strontium-doped lanthanum ferrite, La$_{1-x}$Sr$_x$FeO$_{3-δ}$, have been investigated for use in various functional devices such as solid oxide fuel cell (SOFC) cathodes [1–4], oxygen permeation membranes [5], and chemical sensors [6–8] due to their high conductivity of both electrons and oxide ions. More recently, these materials have been studied as oxygen carriers for chemical looping combustion (CLC) and chemical looping H$_2$ production [9–11]. Both CLC and chemical-looping H$_2$ production have the potential to reduce the cost of separating CO$_2$ from gaseous product streams, negating the need for energy intensive processes like CO$_2$ removal using amine columns (for CO$_2$ capture from power plants) or pressure swing adsorption (for CO$_2$ separation from H$_2$ product streams) [12].

Repeated oxidation and reduction of a crystalline oxygen carrier material (OCM) can cause relatively large changes in its unit cell parameters and can lead to decreased operational lifetime owing to decreased mechanical integrity. Bishop et al. [13] reviewed the effect of structural changes of a material based on changing chemical conditions. They found that the chemical expansivity can have a direct effect on the elastic modulus of the material and its ionic and electronic conductivity. Understanding the magnitude of the shifts in unit cell parameter due to chemical changes of the material is, therefore, important for the design of functional devices. Thermal stresses have a similar effect to chemical stresses, compromising the mechanical integrity of a material and causing cracks [14]. Therefore, knowledge of the phase stability and the chemical and thermal expansivities, under relevant operation conditions underpins the appropriate design and implementation of functional devices.

The thermal and chemical expansivities of a material describe how the unit cell parameter changes as a function of temperature and the material’s composition. For a cubic ABO$_3$–δ structure, the expansivities are defined by Equations (1) and (2).

\[
\text{Thermal expansivity} = \left( \frac{\partial a}{\partial T} \right)_\delta
\]

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Chemical expansivity = $\frac{\Delta h}{\Delta \delta}$, where $a$ is the cubic unit cell parameter, $T$ is the temperature and $\delta$ represents the deviation from stoichiometry in moles of oxygen per mole of perovskite.

This study focused on the $x = 0.4$ member of the series La$_1-x$Sr$_x$FeO$_3$,$\delta$. La$_{0.6}$Sr$_{0.4}$FeO$_3$,$\delta$ is of particular interest as it remains single phase at the oxygen partial pressures ($P_{O2}$) and temperatures of interest to chemical looping and sensor technologies (10$^{-4}$ to 10$^1$ bar and 500–1200 K). La$_{0.6}$Sr$_{0.4}$FeO$_3$,$\delta$ has a rhombohedrally distorted perovskite structure at room temperature. As the temperature increases, it transforms to a cubic structure, with the exact temperature of the transition depending on $\delta$.

La$_{0.6}$Sr$_{0.4}$FeO$_3$,$\delta$ is well studied in the literature, and this includes the investigation of the oxygen non-stoichiometry over a wide range of temperatures and $P_{O2}$, and the thermal and chemical expansivity over a smaller range of temperatures and $P_{O2}$ [1,2,16–20]. The expansivity studies concentrated on SOFC cathode applications so that the range of $P_{O2}$ where the thermal and chemical expansivity was investigated was limited to $10^{-7}$ bar, as shown in Fig. 1.

The oxygen non-stoichiometry of strontium-doped lanthanum ferrite has been explained using a point defect model [1,2,20], and the acceptor (Sr$^{2+}$ in Kröger-Vink notation) compensation mechanism is known to change as a function of $P_{O2}$. In the stoichiometric state (i.e. $\delta = 0$), Sr$^{2+}$ is compensated by holes in the form of Fe$^{4+}$ (Fe$^{4+}_\delta$). As $P_{O2}$ is lowered, oxygen vacancies form and the proportion of Fe$^{4+}$ content decreases (i.e. an increasing amount of oxygen vacancies, $V_{O2}^\delta$, offset by a decreasing amount of Fe$^{4+}_\delta$ are present). This is followed by a plateau at $\delta = x/2$ (i.e. $\delta = 0.2$ for La$_{0.6}$Sr$_{0.4}$FeO$_3$,$\delta$) where vacancy compensation dominates over a wide $P_{O2}$ range. Finally, at low $P_{O2}$ further reduction creates additional oxygen vacancies and electrons in the form of reduced Fe$^{2+}$ (Fe$^{2+}_\delta$).

Taylor et al. [11] used synchrotron XRD and neutron diffraction to study how the structure of different strontium-doped lanthanum ferrites changes during chemical looping combustion using CH$_4$ as the reducing agent and O$_2$ as the oxidising agent. This shows these materials’ ability to regenerate when cycled and how they might change under these specific conditions. However, the lack of a well-defined $P_{O2}$ for the reduction step makes extraction of chemical and thermal expansivities impossible, limiting the insight this work can give to the other uses of La$_{0.6}$Sr$_{0.4}$FeO$_3$,$\delta$.

Chen and Grande [16] reported how the unit cell parameter of La$_{0.6}$Sr$_{0.4}$FeO$_3$,$\delta$ and other perovskites in the La–Sr series changed under two different gas environments, O$_2$ and N$_2$ (assumed to be a $P_{O2}$ of 5 × 10$^{-5}$ bar). These experiments defined $\delta$ based on thermogravimetric (TG) data and an understanding of the relationship between $P_{O2}$ and $\delta$. With only two $P_{O2}$’s at a given temperature, extraction of both chemical and thermal expansion for a range of $\delta$ and temperatures is problematic. Additionally, the system was limited to a minimum $P_{O2}$ of 5 × 10$^{-5}$ bar, significantly higher than that required for chemical looping combustion or hydrogen production (down to 10$^{-22}$ bar). Kuhn et al. [20] conducted studies at a slightly less reducing condition (10$^{-6}$) using N$_2$/O$_2$ mixtures. The exact $P_{O2}$ was determined using zirconia sensors. This allowed them to separate the chemical and thermal expansivities of the material between 1 bar and 10$^{-4}$ bar and up to a temperature of 1173 K. Both expansivities were found to be constant and independent of each other. The chemical expansivity was found to be 0.07773 Å per $\delta$ and the thermal expansivity was found to be 4.307 × 10$^{-3}$ Å/K in the range of temperatures and $P_{O2}$ they studied. These values are used as the benchmark for comparison in this work.

While both the thermal and chemical expansivity of La$_{0.6}$Sr$_{0.4}$FeO$_3$,$\delta$ were found to be constant when $\delta > 0.2$ (where the transformation from Fe$^{4+}$ to Fe$^{3+}$ dominates) [20], it is expected that, due to the different oxidation states of Fe species present, the expansivities will be different when $\delta < 0.2$, where the transformation from Fe$^{4+}$/Fe$^{3+}$ to Fe$^{2+}$/Fe$^{3+}$ dominates [2].

In this work, in situ neutron and synchrotron X-ray powder diffraction studies were performed at temperatures between 932 K and 1170 K and $P_{O2}$ between 10$^{-10}$ bar and 0.1 bar under continuous gas flow, to determine the thermal and chemical expansivity of La$_{0.6}$Sr$_{0.4}$FeO$_3$,$\delta$ over a wide range of oxygen non-stoichiometry from $\delta = 0.05$–0.22. The $P_{O2}$ range extends to much lower oxygen partial pressures than previously studied. This was coupled with analysis of the gas composition at the outlet of the system to determine the changes in $\delta$ caused by the different $P_{O2}$ and temperature conditions. The use of gas analysis also ensured that steady state was reached and that $\delta$ was well defined and corroborated by independent methods.

1. Experimental

1.1. Sample preparation

La$_{0.6}$Sr$_{0.4}$FeO$_3$,$\delta$ was synthesised using a Pechini-type method [22]. In order to produce 20 g of La$_{0.6}$Sr$_{0.4}$FeO$_3$,$\delta$, 23.38 g of La(NO$_3$)$_3$·6H$_2$O (Sigma Aldrich, 61520), 7.62 g of Sr(NO$_3$)$_2$ (Sigma Aldrich, 243426), 36.36 g of Fe(NO$_3$)$_3$·9H$_2$O (Sigma Aldrich, 216828) and 34.58 g of citric acid (Sigma Aldrich, 791725) were dissolved in 90 ml of deionised H$_2$O. 13.10 g of ethylene glycol (Sigma Aldrich, 243426) was then added. The mixture was mixed for 5 min before drying at 333 K for 48 h. The resulting orange cake was lightly crushed and placed in an alumina crucible and heated to 1323 K at 1 K min$^{-1}$ and held for 18 h. The resulting powder was then sieved to select particles between 80 and 160 µm in size.

The sample was analysed via synchrotron X-ray powder diffraction at room temperature and atmospheric pressure and found to be a perovskite in the space group R$ar{3}$c. The comparison between the observed and calculated diffraction patterns can be found in Supplementary Information Fig. S2.

1.2. Flow systems and gas analysis

A schematic diagram of the reactor systems used in this work are shown in Fig. 2. Gas flow was controlled using Brooks flow meters which give a flowrate controllable from 0 to 100 ml/min (STP) with an accuracy of 1% of the set point. A manifold was used to allow rapid switching between gas sources. The gases attached to the system were from premixed cylinders supplied by BOC, a complete list of the gas compositions used is given in Table 1. Throughout the paper CO$_2$, CO and Ar gas mixtures are referred to by the CO$_2$:CO ratio without reference to the inert Ar.

Two different reactors were used for the in situ diffraction
The experiments for the neutron experiments we used a double-walled reactor made from 2 mm wall thickness silica tubing. This allowed gas flow down through a central 10 mm internal diameter (id) tube holding the reactor bed supported on sintered silica, and exit via an 18 mm id outer tube to the top of the reactor. This design fits inside the Riso furnace [23] supplied by ISIS Neutron and Muon Source and allows both inlet and outlet gases to be fed to the top of the reactor. 2.95 g of La$_{0.6}$Sr$_{0.4}$FeO$_3$-δ, sieved to 80–160 μm, was placed in the reactor giving a bed height of 30 mm. Temperature was measured with a K-type thermocouple placed inside the reactor, 10 mm above the sample.

The silica reactor used for the X-ray diffraction experiments had an id of 4 mm. 0.44 g of La$_{0.6}$Sr$_{0.4}$FeO$_3$ (sieved to 80–160 μm) was intimately mixed with 0.09 g of Y$_2$O$_3$ (sieved to 10–20 μm) and placed in the reactor. The sample had a bed height of 25 mm and was held in place using silica wool. The furnace detailed by Metcalfe et al. [24] was used to heat the sample. Y$_2$O$_3$ was used as an internal temperature reference due to its inertness to the CO, CO$_2$ and O$_2$ [25], and the fact that its Bragg peaks do not overlap with major peaks of La$_{0.6}$Sr$_{0.4}$FeO$_3$-δ.

The temperature could only be derived from the internal standard during analysis, so thermocouple measurements outside the reactor were used during experiments to ensure thermal equilibrium had been achieved.

Outlet gas analysis was carried out using a quadrupole mass spectrometer (QGA, Hiden Analytical). This measured the mole fraction of O$_2$, CO, CO$_2$ and Ar present in the outlet gas. The outlet gas composition was used to determine when equilibrium between the gas and solid had been reached after a change in the inlet gas composition or in reactor temperature. Equilibrium was defined as when the outlet gas mole fractions for all reactive gases were within 0.05 mol% of the inlet values for over 180 s and when the temperature variation was less than 1 K over 60 s based on thermocouple readings.

By integrating the difference between the inlet and outlet gas composition between the initiation of a change and when the sample reached a new equilibrium state, it is possible to calculate the change in oxygen content of the solid and therefore the change in δ associated with that change in temperature or gas composition. A full description of the steps involved in the gas analysis can be found in SI Section 3.

1.3. High temperature in situ neutron diffraction under different P$_{O_2}$

Neutron powder diffraction data were collected using the High Resolution Powder Diffractometer (HRPD) at the ISIS time-of-flight (tof) neutron source of the Rutherford Appleton laboratory. A tof range of 10–110 ms was chosen (d-spacing ranges approx. 0.4–3.3 and 0.3–2.2 Å for the 90° and backscattering detectors, respectively).

Data were collected on an as-prepared sample of La$_{0.6}$Sr$_{0.4}$FeO$_3$-δ as it was heated from 298 K to 1098 K in 25 K steps under a gas environment of 1:1 CO$_2$:CO in Ar at atmospheric pressure (P$_{O_2}$ = 1.23 × 10$^{-16}$ bar at 1093 K if equilibrium is achieved). Each scan was for a duration of 5 min to maximise the number of temperatures that could be measured.

Following these measurements, data were collected on the same sample at different temperatures between 973 K and 1173 K in five different flowing gas environments at atmospheric pressure (4 CO$_2$/CO mixtures in Ar and 5% O$_2$ in Ar), corresponding to the P$_{O_2}$ detailed in Table 1. The system was given 30 min to equilibrate at each temperature and gas environment. Data were recorded in five 20 μAh (~30 min) blocks once equilibrium was achieved. Rietveld fitting of separate 20 μAh blocks recorded under the same conditions gave consistent results within experimental uncertainty, confirming the sample had fully equilibrated. Individual data sets were therefore summed for use in the final analysis.

1.4. High temperature in situ X-ray diffraction

High temperature synchrotron X-ray diffraction (XRD) was used to determine expansivities to compare with those reported in previous work and our neutron diffraction experiments. This was done to check for systematic errors in either experiment. Experiments were carried out on ID22 at the European Synchrotron Radiation Facility (ESRF) using the multi-analyser detector [26]. Diffraction patterns were recorded from 9° to 17° in 2θ at a scan speed of 2° per minute with a wavelength of 0.3542 Å (35 keV), calibrated using a silicon standard. The sample temperature was extracted using the cell parameter data of Y$_2$O$_3$ published by Swamy et al. [27] and Taylor et al. [28] via the expression:

\[ T = -B + (B' - 4 \times A(1 - a_{Y_2O_3}))^{0.5} \]

\[ A = 1.29340 \times 10^{-8} \text{Å}^2/K, \quad B = 6.46011 \times 10^{-5} \text{Å}^2/K, \quad C = 10.58733218 \text{Å}, \quad B \text{ and } C \text{ are empirical constants, } T \text{ is the temperature of the sample and } a_{Y_2O_3} \text{ is the measured unit cell parameter.} \]

The dependence of the unit cell parameter of La$_{0.6}$Sr$_{0.4}$FeO$_3$-δ on thermal and chemical changes was studied between 920 K and 1060 K for P$_{O_2}$ of 0.2–0.01 bar using 20%, 5% and 1% O$_2$ in Ar. Experiments were also conducted for P$_{O_2}$ in the range 10$^{-13}$–10$^{-19}$ bar using CO$_2$:CO ratios of 10:1, 1:1 and 1:10 at temperatures from 1065 K to 1090 K.

1.5. Rietveld fitting strategy

Rietveld fitting of the diffraction data was performed using TOPAS v7 [29,30]. Unit cell parameters, oxygen site occupancy, atomic displacement parameters (anisotropic for oxygen) and sample contributions to the peak shape were refined. The neutron background was fitted by including a function describing the measured background of the empty sample container, along with additional terms of a Chebyshev polynomial. Sample peak shape contributions were described by convolving terms describing isotropic size and strain broadening onto an instrumental peak shape determined empirically from a Si (neutron) or LaB$_6$ (synchrotron) standard. The site occupancies of La, Sr and Fe were kept constant at 0.6, 0.4 and 1.0 respectively.

For the neutron diffraction data collected on warming from 298 to 1098 K under a reducing 1:1 CO$_2$:CO atmosphere, a rhombohedral model (R3c) was used to fit experimental data at all temperatures, and cell parameters converted to pseudo-cubic values for plotting. Various structural models were investigated to determine the oxygen content.
allowing the oxygen site occupancy to vary led to an overall content of 2.957(6) per formula unit at temperatures below 623 K. Here and later in this paragraph the value in parentheses is the standard deviation of the mean of the Rietveld determined oxygen content at different temperatures. This value decreased on heating in a 1:1 CO\textsubscript{2}:CO atmosphere to an average of 2.721(8) between 873 and 1093 K. This apparent oxygen loss is greater than indicated by the gas analysis (which showed the expected oxygen content of 2.793(3)). This difference between neutron scattering results and other methods for oxygen determination has been seen in other perovskite structures [31]. Given the significant number of oxygen vacancies in the reduced material, it is probable that there is local short-range ordering of vacancies, despite the average structure remaining perovskite like. It is well known, for example, that several materials that form ordered bimillerite structures at composition \( \text{ABO}_3 \) have perovskite average structures at higher oxygen content or when quenched from high temperature [15]. To model short-range order, an additional oxygen site close to that expected for local tetrahedral Fe coordination was introduced. This site remained unpopulated below 623 K but became partially populated at the higher temperatures where oxygen disorder is expected. Using this treatment, total refined oxygen contents became 2.794(7) above 743 K. The corresponding oxygen loss is closer to that measured by gas analysis. Values based on this model are reported in Fig. 3.

Neutron and synchrotron data sets at high temperature under different atmospheres were analysed using a \( \text{Pm}3\text{m} \) model. Additional details of both structural models are given in the SI Section 1.

1.6. Thermogravimetric analysis

Thermogravimetric analysis was carried out on the as-synthesised material using a Rubotherm dynamic THERM unit. Gas composition was controlled using Brooks flow meters. The sample consisted of 0.25 g of \( \text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3 \) sieved to 80–160 \( \mu \)m and placed in the sample holder. The sample was exposed to 5\% O\textsubscript{2} in Ar with a gas flow rate of 1.47 \( \times 10^{-4} \) mol/s at 973 K, 1013 K, 1053 K, 1093 K, 1133 K, and 1173 K, with a heating rate of 1 K min\(^{-1}\) between each temperature.

To ensure that the sample had reached equilibrium with the gas environment, the temperature was held constant until the mass change was less than 5 \( \times 10^{-5} \) g/min. The gas buoyancy effect on the sample was negligible, when compared with the mass changes resulting from oxygen release, so was omitted from the calculations.

2. Results

2.1. Crystal structure as a function of temperature

The rhombohedral to cubic transition of \( \text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3 \) on heating was investigated in a reducing environment (of 1:1 CO\textsubscript{2}:CO in Ar at atmospheric pressure, corresponding to \( P_{\text{\text{O}}2} = 1.23 \times 10^{-18} \) bar at 1093 K). The sample was heated from 298 K to 1098 K and neutron diffraction patterns collected every 25 K. Unit cell parameters as a function of temperature are shown in Fig. 3, based on a rhombohedral cell with \( a = b = c = \sqrt{2}a_{\text{r} \text{m}}, \) and \( \alpha = \beta = \gamma \approx 60\)° converted to pseudo-cubic values. The phase transition to cubic is signified by \( a_{\text{c} \text{u} \text{b} \text{b}} = c_{\text{c} \text{u} \text{b} \text{b}} \) and \( \alpha = \beta = \gamma = 60\)°. Fig. 3 shows that under this atmosphere, the rhombohedral to cubic transition occurred at approximately 750 K. The phase transition is associated with the reduction of \( \text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3 \) and the Rietveld-refined oxygen content per formula unit at each temperature is shown in Fig. 3c. The relatively high degree of scatter is due to the short data collection times used.

2.2. Relationship between oxygen content and \( P_{\text{\text{O}}2} \) for \( \text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3 \)

The oxygen non-stoichiometry of \( \text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3 \) as a function of temperature in a \( P_{\text{\text{O}}2} \) of 0.05 bar was investigated using three different methods: thermogravimetric analysis (TGA), Rietveld fitting of oxygen content from \textit{in situ} neutron diffraction patterns, and oxygen balance calculated from the outlet gas composition measured in the same neutron diffraction experiment. These results are shown in Fig. 4 and compared to literature values [1,2,20].

The outlet gas analysis from the neutron diffraction experiment and TGA results only measure the change in \( \delta \) between two states. In order to compare these results with those obtained through neutron diffraction, they are plotted relative to the degree of non-stoichiometry at 973 K of \( \delta = 0.02 \). This is the value derived from the \( \delta/P_{\text{\text{O}}2} \)/temperature relationship determined by Kuhn et al. [20] under the same conditions. It is worth noting that, with this assumption, the starting stoichiometry of oxygen of the as-synthesised material used in the TGA experiment was found to be 3.001 at room temperature, consistent with the expected value of 3.0 within experimental uncertainty [1,2,20].

Fig. 4 shows that the values of \( \delta \) determined from the TGA, gas analysis from the neutron diffraction experiments and the predictions based on the work of Kuhn et al. [20] agree to within one standard deviation. Mizusaki et al. [1] and Segarra et al. [2] both predict a higher value of \( \delta \) than measured by the TGA or determined by Rietveld analysis. Individual values of the oxygen content from the Rietveld fitting agree with the gas analysis and TGA results, as well as the \( \delta/P_{\text{\text{O}}2} \)/temperature relationship of Kuhn et al. [20] to within the estimated uncertainty from the Rietveld fitting. However, the Rietveld values have a steeper gradient compared to other methods. This is perhaps unsurprising given the short-range order likely at higher defect levels which will affect the Rietveld results.

Fig. 5 compares \( \delta \) from the three techniques with literature predictions as a function of \( P_{\text{\text{O}}2} \) at 1093 K. The changes in \( \delta \) measured from the difference between the inlet and outlet gas concentrations during the neutron diffraction studies are plotted relative to the value predicted by Kuhn et al. [20] at a \( P_{\text{\text{O}}2} \) of 0.05 bar. The gas analysis and model results agree well with literature [20], but the values of \( \delta \) from the Rietveld fits are higher by around two standard deviations. Based on these observations, the \( \delta/P_{\text{\text{O}}2} \)/temperature relationship of Kuhn et al. [20] will be used to determine the oxygen content of the material at a given temperature and \( P_{\text{\text{O}}2} \) in all subsequent analysis.

2.3. Thermal and chemical expansivity for \( \delta < 0.2 \)

In order to provide information on the thermal and chemical expansivity of \( \text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3 \) in the region where \( \delta < 0.2 \), synchrotron XRD data were collected covering a range of \( P_{\text{\text{O}}2} \) from 0.01 bar to 0.2 bar. This is of interest to chemical looping and chemical sensor applications [20].

Fig. 6a shows our measured unit cell parameters as a function of \( \delta \) (calculated using the \( \delta/P_{\text{\text{O}}2} \)/temperature relationship detailed by Kuhn et al. [20]) at four different temperatures. The uncertainties in \( \delta \) are dominated by the uncertainty in the pressure measurement, \( \pm 0.1 \) bar. As the relationship between \( \delta \) and \( P_{\text{\text{O}}2} \) is non-linear, the error bars are asymmetric. These data were used to estimate the chemical and thermal expansivity of \( \text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3 \). The average chemical expansivity in the temperature range 930–1050 K was found to be 0.144(5) Å per unit change in \( \delta \) as defined in Equation (2). This was largely independent of temperature (i.e., the lines in Fig. 6a are parallel).

In order to extract the underlying thermal expansivity, the chemical expansion was removed to obtain a pure thermal expansivity plot, Fig. 6b. This was performed by extrapolating each line in Fig. 6a to \( \delta = \)
0 and gave the linear thermal expansivity as 5.70(5) \times 10^{-5} \, \text{Å/K}. The extrapolated unit cell parameter at 0 K and \( \delta = 0 \) using this method was found to be 3.8741(5) Å, smaller than the value of 3.8846 Å reported by Kuhn et al. [20]. Cell parameters derived from neutron diffraction in 5% \( \text{O}_2 \) at 1 bar were used to validate the chemical and thermal expansivity; these data are shown in SI Fig. S4.

2.4. Thermal and chemical expansivity for \( \delta > 0.2 \)

It is expected that the chemical and thermal expansivities of \( \text{La}_0.6\text{Sr}_0.4\text{FeO}_{3-\delta} \) will be different for \( \delta > 0.2 \) compared to for \( \delta < 0.2 \), due to the presence of \( \text{Fe}^{2+}/\text{Fe}^{3+} \) ions instead of \( \text{Fe}^{4+}/\text{Fe}^{3+} \) at these lower oxygen contents [2].

As illustrated in Fig. 1, low \( P_{\text{O}_2} \) values are required to obtain \( \delta > 0.2 \) and redox buffers such as \( \text{CO}_2: \text{CO} \) couples or \( \text{H}_2\text{O}:\text{H}_2 \) couples are needed to maintain such low \( P_{\text{O}_2} \). In this work, \( \text{CO}_2: \text{CO} \) redox couples were used because the reaction

\[
\epsilon \text{CO} + \text{La}_0.6\text{Sr}_0.4\text{FeO}_{3-\gamma} \rightarrow \epsilon \text{CO}_2 + \text{La}_0.6\text{Sr}_0.4\text{FeO}_{3-\delta} \quad \text{Reaction 1}
\]

has a \( \Delta H \) close to zero and consequently the equilibrium constant will not change with temperature [20,21]. As a result, the oxygen content of the perovskite should not change significantly between 973 and 1173 K for a given \( \text{CO}_2: \text{CO} \) buffer. The thermal expansivity can then be measured without the influence of the chemical expansion. This differs to the work in Section 3.3 where the \( P_{\text{O}_2} \) remains constant, leading to different \( \delta \) at different temperatures. The cell parameters of \( \text{La}_0.6\text{Sr}_0.4\text{FeO}_{3-\delta} \) derived from neutron diffraction data under various \( \text{CO}_2: \text{CO} \) buffers are shown in Fig. 7 (also see Table S3 from the SI). Similar to the case of \( \delta < 0.2 \), the thermal expansivity of \( \text{La}_0.6\text{Sr}_0.4\text{FeO}_{3-\delta} \) is essentially independent of \( \delta \) (Table 2). The average thermal expansivity using the data collected for all the buffer gasses was 6.18(8) \times 10^{-5} \, \text{Å/K}, larger than the value of 5.72(4) \times 10^{-5} \, \text{Å/K} found for \( \delta < 0.2 \). This indicates that two regimes of thermal expansivity exist.

The small change in unit cell parameter on switching from a 100:1 to 1:10 \( \text{CO}_2: \text{CO} \) buffer (i.e. to a more reducing atmosphere) is plotted as a function of calculated \( \delta \) in Fig. 8a at six different temperatures, using the data of Fig. 7. It shows that the chemical expansivity is non-linear for \( \delta > 0.2 \), decreasing with increasing \( \delta \). The chemical expansivity also becomes dependent on temperature, with higher temperatures resulting in larger changes in unit cell parameter for the same change in \( \delta \). Furthermore, the chemical expansivity is approximately a tenth of the values found for \( \delta < 0.2 \). As such, for \( \delta > 0.2 \), the effect of the thermal expansivity is much larger than the effect of chemical expansivity in these experiments; this results in the change in unit cell parameter between the different experiments being dominated by the effect of temperature in Fig. 7.

Fitting a straight line through the curves in Fig. 8a gives an indicative linear chemical expansivity at each temperature. Using the 1093 K chemical expansivity, unit cell parameters were predicted for the small range of \( P_{\text{O}_2} \) which was studied using X-ray diffraction experiments to provide a consistency check. The comparison can be seen in SI Fig. S5.

3. Discussion

It is clear from the results presented in Section 3 that the chemical expansivity of \( \text{La}_0.6\text{Sr}_0.4\text{FeO}_{3-\delta} \) changes significantly at \( \delta \approx 0.2 \). This gives insight into the main structural influences on the cell parameter. Assuming fixed oxidation states for La, Sr and O, the principal charge compensation on reduction is via a changing ratio of \( \text{Fe}^{4+}/\text{Fe}^{3+} \) for \( 0 \leq \delta \leq 0.2 \).
Given that the sample retains, at least on average, the cubic perovskite structure at the high temperatures studied, one might assume that the chemical expansivity would be influenced by the increasing average ionic radius of Fe on reduction (high spin radii for Fe\(^{4+}\), Fe\(^{3+}\) and Fe\(^{2+}\) are 0.58, 0.645 and 0.78 Å, respectively [32]). Under this assumption, one might expect the chemical expansivity in the Fe\(^{3+}\) to Fe\(^{2+}\) region (δ > 0.2) to be larger than in the Fe\(^{4+}\) to Fe\(^{3+}\) (δ < 0.2) region, due to the larger change in ionic radii in the former case. However, the change in oxidation state of Fe occurs alongside a change in its average coordination number from 6 at δ = 0.0 to 5.5 at δ = 0.25. Even though the average structure remains perovskite, locally there will be a

\[ \delta/C_2O_0.2 \text{ and Fe}^{3+} \text{ to Fe}^{2+} \]
mixture of square pyramidal (as found in Sr$_8$Fe$_{23}$O$_{39}$ and Sr$_4$Fe$_{11}$O$_{23}$; $\delta$ = 0.125 and 0.25 respectively) or tetrahedral (as found in Sr$_2$Fe$_2$O$_5$; $\delta$ = 0.5) or some other coordination environment present [33].

As shown in Fig. 9, the ionic radius of a four-coordinate Fe$^{2+}$ is comparable to six-coordinate Fe$^{3+}$. One would therefore see little change in local bond lengths, and therefore unit cell parameters, if this transformation occurs. We therefore conclude that the cell parameter of La$_{0.6}$Sr$_{0.4}$FeO$_{3-\delta}$ depends more on the local coordination environment than on the average oxidation state of Fe, which results in the strong non-linearity seen in Fig. 8. While Fig. 9 is based on room temperature data, similar arguments are likely to hold at high temperature. Similar observations have been made for related perovskites such as (La,Sr)FeO$_3$ [16], (La,Sr)CoO$_3$ [34], and (La,Sr)Co$_2$Fe$_{1.5}$O$_{4.5}$ [35]. Studies on Cr and Co based perovskites also showed strong non-linear dependence on oxygen content but for these materials the expansivity was still dominated by the cation size [36,37].

4. Conclusions

In this work, the variation of the chemical and thermal expansivities of La$_{0.6}$Sr$_{0.4}$FeO$_{3-\delta}$ over the important operating $P_{O_2}$ ranges for chemical looping and sensor applications was obtained through neutron and X-ray diffraction experiments combined with in situ measurement of oxygen content changes through simultaneous gas analysis. This approach provides an independent check that equilibrium conditions are reached and allows confirmation of the true change in oxygen content of samples during diffraction experiments.

The change in equilibrium $\delta$ between different conditions was determined experimentally, and calculated using literature values of the $\delta/P_{O_2}$/temperature relationship [20]. It was found that:

![Graph showing the change in unit cell parameter relative to a $\delta$ of 0.201 calculated from in situ neutron diffraction as a function of calculated $\delta$ in different atmospheres. This was carried out at 973 K, 1013 K, 1053 K, 1093 K, 1133 K and 1173 K using gas atmospheres of CO$_2$:CO = 1:10 ($\delta = 0.240$), 1:1 ($\delta = 0.214$), 10:1 ($\delta = 0.205$) and 100:1 ($\delta = 0.201$). B) unit cell parameter at 1093 K using gas atmospheres of 1%, 5% and 20% O$_2$ in Ar at a total pressure of 1 bar and CO$_2$:CO buffers with ratio of 1:10, 1:1, 10:1 and 100:1.](image)
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Appendix A. Supplementary data

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