

In-situ Compatibility Studies of Lanthanum Nickelate with a Ceria-based Electrolyte for SOFC Composite Cathodes

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Keywords

Lanthanum nickelate; Mixed conducting oxides; SOFCs, synchrotron X-ray diffraction, compatibility

Abstract

The phase stability and compatibility of intermediate temperature solid oxide fuel cell (IT-SOFC) composite cathodes of lanthanum nickelate, $\text{La}_2\text{NiO}_{4+\delta}$ (LNO), and ceria-gadolinium oxide, $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$ (CGO10), have been investigated by high resolution synchrotron X-ray diffraction (XRD). No reaction was observed between LNO and CGO10 at temperatures of up to 900°C when the composite is open to an ambient air environment. However, in a sealed capillary environment the 50:50 wt% LNO:CGO10 composite undergoes a partially reversible reaction at temperatures of 750°C and above, whereby LNO decomposes to La_2O_3 and Ni. Changes in the CGO10 Bragg peaks indicate that this component is actively involved in this process. This study shows that the phase stability of LNO:CGO10 composites is highly dependent on oxygen partial pressure. In addition, it is observed that *ex-situ* XRD is insufficient to determine the presence of reactivity in composite cathodes and that high resolution *in-situ* XRD measurements are required to obtain details of the complexity of phase stability in SOFC composite cathodes.

1.0 Introduction

Intermediate temperature solid oxide fuel cells (IT-SOFC) cathode materials are required to display high oxide ion transport, good electronic conductivity, excellent thermal stability and a lack of reactivity with electrolytes. Lanthanum nickelate, $\text{La}_2\text{NiO}_{4+\delta}$ (LNO), is a promising cathode material for IT-SOFCs and displays excellent oxygen ion transport properties with a diffusion coefficient of $2 \times 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$ reported at 700°C ^{1, 2} and an area specific resistance (ASR) of $1.0 \text{ } \Omega \cdot \text{cm}^2$ at 700°C (and $0.2 \text{ } \Omega \cdot \text{cm}^2$ at 800°C) showing promising electrode performance^{3, 4}. LNO is a K_2NiF_4 -type material and belongs to the Ruddlesden-Popper series of general formula $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$ where $n = 1$ and n refers to the number of perovskite blocks in a formula unit. The structure consists of ABO_3 perovskite layers separated by AO rocksalt layers⁵. The increase in the number of perovskite blocks with increasing n leads to the formation of oxygen deficient higher order phases $\text{La}_3\text{Ni}_2\text{O}_{7-\delta}$ and $\text{La}_4\text{Ni}_3\text{O}_{10-\delta}$ ⁶⁻⁹. The stoichiometric compound $\text{La}_2\text{NiO}_{4.0}$ has a network of unoccupied interstitial sites that, upon oxidation of the material, allow for the accommodation of excess oxygen¹⁰. $\text{La}_2\text{NiO}_{4+\delta}$, has shown relatively high solubility for oxygen excess, with values of δ as high as 0.3 being reported¹¹. Atomistic simulations have indicated that the incorporated oxygen excess is charge compensated by creation of nickel holes^{12, 13} whereby the oxygen interstitial concentration is accommodated by the presence of $\text{Ni}^{2+}/\text{Ni}^{3+}$. The ideal A_2BO_4 structure is tetragonal, however the addition of oxygen interstitials leads to distortion from the ideal structure and is accommodated by tilting of the NiO_6 octahedra, which leads to an orthorhombic structure^{14, 15}.

The room temperature structure of oxygen excess LNO is generally reported to be orthorhombic with either an Fmmm or Bmab crystallographic structure^{5, 10, 16, 17}. Through *in-situ* high resolution neutron powder diffraction in a vacuum environment, Skinner¹⁶ finds

that at room temperature $\text{La}_2\text{NiO}_{4.18}$ is orthorhombic with space group Fmmm, however at temperatures greater than 150°C there is a structural transformation to the tetragonal phase with space group I4/mmm and a δ value of 0.13 is determined by Rietveld refinement. Skinner¹⁶ observes that there are no further structural transformations up to 800°C. In agreement, Aguadero et al.¹¹ undertook *in-situ* neutron diffraction measurements in air on $\text{La}_2\text{NiO}_{4+\delta}$ ($\delta=0.3$) and found there to be a structural transition at approximately 150°C from the orthorhombic Fmmm phase to the tetragonal F4/mmm which was stable up to 700°C. The structure of LNO in the orthorhombic Bmab and tetragonal I4/mmm spacegroups is shown in Figure 1 oriented with the b axis in the long direction; a slight tilting of the nickel octahedra can be seen in the Bmab structure shown in Figure 1(a).

The performance of composite LNO cathodes has previously been reported and shows promising performance, with Laberty et al.¹⁸ and Pérez-Coll et al.¹⁹ investigating composite cathodes based on LNO and ceria-samarium oxide, $\text{Ce}_{1-x}\text{Sm}_x\text{O}_{2-\delta}$ (CSO) and Gong et al.²⁰ reporting the performance of strontium doped LNO and CSO composites. The lowest ASR of these LNO based composite cathodes is $0.11 \text{ } \Omega\cdot\text{cm}^2$ at 800°C for a 50:50 wt% composite cathode of LNO: $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ with an yttria-stabilised zirconia electrolyte, reported by Laberty et al.¹⁸. The reactivity of LNO in composite cathodes has been studied by *ex-situ* ambient temperature XRD and Pérez-Coll et al.¹⁹ observe a reaction between LNO and $\text{Ce}_{1-x}\text{Sm}_x\text{O}_{2-\delta}$ in composite cathodes, forming the $\text{La}_3\text{Ni}_2\text{O}_7$ phase. Gong et al.²⁰ do not observe any additional diffraction peaks from X-ray diffraction of calcined $\text{La}_{1.6}\text{Sr}_{0.4}\text{NiO}_{4+\delta}$ /CSO composites, however they do observe a change in peak position and intensity, which suggests there may some interdiffusion of cations in the composite. Previously the stability of LNO in composites with $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ (CGO20) and

La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-δ} (LSGM8282) determined by *ex-situ* ambient temperature XRD²¹ has been reported. A significant reaction was observed between LNO and CGO20 after 24 hours at 900°C with the formation of the higher order Ruddlesden-Popper phases La₃Ni₂O_{7-δ} and La₄Ni₃O_{10-δ}; however no reaction was identified between LNO and LSGM8282 up to 1000°C. The formation of higher order Ruddlesden-Popper phases when LNO is in contact with ceria-based IT-SOFC electrolytes has been reported and Amow et al.⁷ observed degradation of cobalt doped LNO deposited on CGO10 into higher order Ruddlesden-Popper phases after heating at 950°C in air. The characteristics of LNO as an IT-SOFC cathode are dependent on its compatibility with electrolyte materials as the reactivity of SOFC component materials can lead to the formation of performance limiting intermediate phases at the electrode/electrolyte interface as well as in composite electrodes. It is therefore important to investigate the reactivity of LNO with the common IT-SOFC electrolyte Ce_{0.9}Gd_{0.1}O_{2-δ} (CGO10) to be able to better understand the electrode performance of LNO deposited on CGO10 and the phase stability of composite cathodes of these materials.

From the studies discussed above^{7, 18-21} it appears that LNO reacts with fluorite structured ceria based electrolytes and is apparently stable in contact with perovskite-type lanthanum gallate. However, all of these studies were performed using *ex-situ* XRD, that is, XRD was performed at room temperature after the composite had been annealed. With this method it is not possible to monitor any reactions as they develop, as either a function of temperature or time, nor is it possible to identify whether there is any degree of reversibility. This study differs from those previously undertaken through the use of *in-situ* synchrotron XRD, enabling a detailed probing of the reaction mechanisms as a function of temperature, time and environment. Whilst it is apparent from the *ex-situ* XRD studies, that there is ready formation of higher order Ruddlesden-Popper phases under certain conditions, it is likely that LNO phase stability is sensitive to oxygen partial pressure and temperature and there is a need to

investigate the reaction as it develops; for this reason, we have undertaken *in-situ* studies of LNO:CGO10 composites using high resolution synchrotron X-ray powder diffraction.

2.0 Experimental

A 50:50 wt% composite of LNO:CGO10 was created from LNO powder (Cerpotech) and CGO10 powder (Praxair), which were calcined separately at 1400°C for 5 hours. The relative weight percentage of each powder was measured for the desired composition and the mixture was ballmilled with zirconia mixing balls for 24 hours in ethanol. The resultant composite powder was dried at 100°C for 16 hours. All synchrotron X-ray diffraction patterns were obtained on beamline I11 at the Diamond Light Source, UK. Technical descriptions of the I11 instrument can be found in the paper by Thompson et al.²². Data were collected from 3 to 140 °2 θ using the MAC detectors and subsequently rebinned to a step size of 0.004°, a heating and cooling ramp rate of 2°C/ minute was used for the hot air blower (Cyberstar) and a dwell time of 10 minutes was programmed on reaching temperature to allow thermal equilibration of the sample, prior to commencement of the diffraction measurement. Powders were loaded into quartz capillaries with 0.5 mm inner diameter. The synchrotron wavelength, capillary sealing and temperature regimes for each of the three sets of experiments performed, referred to as IS1, IS2 and IS3, are given in Table 1; the aim of IS1 was to study low temperature (< 500°C) phase changes in LNO in a sealed capillary environment, the aims of IS2 and IS3 were to investigate the high temperature reactivity between LNO and CGO in different ambient environments (unsealed and sealed capillaries, respectively). Rietveld refinements were performed using GSAS²³ and EXPGUI²⁴; in all cases the background was modelled using a Shifted Chebyshev function.

3.0 Results and Discussion

3.1 IS-1: Low temperature phase change in LNO

Synchrotron X-ray diffraction confirmed the presence of LNO and CGO in the composite, with no impurity phases detected at room temperature. The composite was heated in a sealed capillary *in-situ* according to the thermal regime described in Table 1 for IS-1 and XRD patterns were obtained. A phase transition was observed in LNO, which was manifested as splitting of the orthorhombic (200) peak at 350°C, shown in Figure 2; there is no reaction observed in the composite below 500°C. We have previously determined the oxygen stoichiometry of LNO powder to be $\delta = 0.15^1$ and based on Rietveld refinement of synchrotron XRD patterns the room temperature structure of LNO in the composite was found to be orthorhombic, however the structure which obtained the lowest goodness of fit parameters was bi-phasic Fmmm-Bmab. This structure has previously been reported from Rietveld refinement of neutron powder diffraction data by Jorgensen et al.¹⁰ at room temperature for $\text{La}_2\text{NiO}_{4.07}$, however we observe this structure in LNO powder of a higher oxygen stoichiometry.

Rietveld refinements indicated an orthorhombic bi-phasic (Fmmm-Bmab) structure for LNO at 25°C and 250°C. An orthorhombic to tetragonal (I4/mmm) phase transition in LNO was observed above 250°C over a broad temperature range (250°C to 500°C shown in Figure 2), with the phase fraction of tetragonal phase increasing with increasing temperature. The fitting for the three LNO phases at 350°C can be seen in Figure 3 between, showing that the most appropriate fitting for these peaks is a mixed bi-phasic orthorhombic and tetragonal structure. The goodness of fit parameters indicated good fits for the structural model over the temperature range 25°C to 500°C, obtaining R_{wp} values less than 8.8% and R_p values less than 6.9%. The low R_{wp} and R_p values indicate good fitting between the observed and calculated data and the values indicate that the optimum collection time has been used for

Beamline I11²⁵. Further details of the model selection and refinement for this complex composite material are given as supplementary information (Figs S1-S4).

We observe a complex phase transition in LNO, which involves a room temperature two-phase orthorhombic system (Fmmm and Bmab) undergoing a transition to a 3-phase orthorhombic (Fmmm and Bmab) and tetragonal (I4/mmm) system, with increasing temperature. As the temperature increases above 400°C the tetragonal phase begins to dominate and the fraction of orthorhombic phase decreases, with the Fmmm phase no longer present and a decreasing phase fraction of Bmab. This agrees well with previous observations from thermogravimetric analysis²⁶ (TGA) whereby above 400°C there is a rapid decrease in oxygen stoichiometry, which is associated with the transition to the tetragonal phase. On heating, LNO is reduced and the oxygen interstitial content decreases, leading to the phase changes observed here.

The refined phase fractions are given in Figure 4; the phase fractions of LNO and CGO at room temperature are 51% and 49% respectively, which correlates very well with the expected values of the composite. The refined phase fraction of CGO is $52\% \pm 1\%$ over the entire temperature range, which also correlates well with the expected values. It would be anticipated that the phase fraction of CGO would remain the same as it does not undergo any phase changes, which agrees with the results from Rietveld refinements. In Figure 4, it can be seen that on heating the phase fraction of orthorhombic LNO decreases and that of tetragonal LNO increases.

It is interesting to note there is a slight deviation from this trend at 400°C, where the phase fraction of orthorhombic LNO increases and tetragonal LNO decreases. This correlates well with observations made by thermogravimetric analysis and differential scanning calorimetry, where deviation from the decrease in oxygen content on heating is observed at 380°C on an

initial heating cycle of the composite ²⁷. The phase transition behaviour of LNO has been seen to be dependent on the thermal history of the sample ²⁷ and Aguadero et al. ¹¹ observe a dependency between the reversibility of LNO phase transitions and the oxygen environment from neutron powder diffraction of $\text{La}_2\text{NiO}_{4.30}$.

3.2 IS-2: Open to atmosphere

The *in-situ* synchrotron X-ray powder diffraction patterns of LNO:CGO10 50:50wt% composite heated in an open ended capillary are shown in Figure 5. There are no visible diffraction peaks belonging to possible reaction phases over the entire temperature range indicating that there is no reaction between LNO and CGO up to 900°C in an environment which is open to ambient air. There are, however, some changes to the LNO and CGO peak heights and shifts in peak positions, which are worthy of further examination. The LNO diffraction pattern in Figure 5 displays no splitting of the orthorhombic (200) peak, indicating that there is no transition from the room temperature orthorhombic phase to a tetragonal phase. In addition, no evidence for any of the tetragonal peaks present on heating up to 900°C is observed and the orthorhombic phase is retained on cooling. As the phase changes observed in LNO in IS-1 are associated with oxygen loss, it is likely that when exposed to ambient air (IS-2), the reduction and oxidation processes in LNO will differ and result in structural differences to the LNO phases. As expected, the structure of LNO is clearly very sensitive to the oxygen stoichiometry and environment.

In addition, the diffraction patterns in Figure 5 display changes to the CGO phase on heating, which require further comment. Close inspection of the CGO peaks in Figure 6 indicates a reduction in peak intensity and a broadening of the diffraction peaks to higher 2θ values on heating, suggesting structural changes in CGO, which are reversible on cooling to 25°C. It

can be seen that with increasing temperature, the major CGO peak begins to broaden and a clear shoulder is visible at 900°C. It is worth noting that the structural change is apparent at relatively low temperatures, with a decrease in intensity and increase in peak width visible at 350°C, suggesting that it is not associated with cation diffusion between the composite phases. The cause of these changes is reversible as the CGO peak position and intensity at 25°C prior to heating is the same as that after heating to 900°C and cooling back to 25°C. Attempts to refine the CGO peak splitting as a cubic phase undergoing a tetragonal transition were unsuccessful with Rietveld refinement of CGO with a tetragonal phase giving an unrealistic fit to the observed diffraction pattern.

There are two alternative possibilities regarding the likely cause of this observation, namely, formation of two CGO phases of different stoichiometries either by gadolinium dissolution from the solid solution or gadolinium enrichment by segregation to the surface or the formation of two phases with differing cerium charges. Microdomains have been reported in doped CeO₂, where the structure varies on a local scale (~ nm) as a result of oxygen vacancy ordering^{28, 29}. Scanlon et al.³⁰ investigated the surface composition of 20% doped CGO at room temperature and determined a gadolinium enriched surface of up to 50%, which maintained the fluorite structure. It is possible that on heating the CGO powder, there is reduction of Ce⁴⁺ to Ce³⁺ and as a result of this there is a bi-phasic mixture, which is observed as peak splitting in the XRD patterns.

3.3 IS-3: Sealed capillary

In IS-3, the open end of the capillary was sealed using commercial vacuum grease and a heating and cooling regime applied to the composite. The synchrotron X-ray powder diffraction patterns obtained on heating from 650°C to 900°C are shown in Figure 7. No reaction between LNO and CGO10 in the 50:50wt% composite was observed below 650°C,

however at 750°C and above it is clear that a reaction occurs upon heating in a sealed capillary whereby new peaks grow in intensity on increasing the temperature. At these temperatures the LNO phase is tetragonal with the spacegroup I4/mmm, and there are evident changes in the LNO diffraction pattern, namely a reduction in the intensity of the LNO reflections on increasing temperature, indicating structural changes to this phase. The structural changes to LNO in this composite are at a lower temperature than those previously reported in LNO:CGO20 composites determined from *ex-situ* XRD studies (750°C here compared with 900°C in reference 21) highlighting the additional information that can be acquired using *in-situ* XRD.

In an effort to understand the phase changes Rietveld refinements were performed on the synchrotron powder diffraction patterns. The diffraction patterns recorded on heating to temperatures of 750°C and above were refined with multiple phases; the CGO phase was refined to two cubic Fm3m phases with different Gd contents indicating that there is a non-uniform distribution of gadolinium in the CGO10 phase on heating, in agreement with the observations of CGO peak splitting in IS-2 shown in Figure 6. The nickelate phase is refined to $\text{La}_2\text{NiO}_{4+\delta}$ (I4/mmm), La_2O_3 (P3m1) and Ni (Fm3m), identifying that LNO decomposes into the constituent oxide La_2O_3 and metallic nickel. A typical fitted pattern for the composite on heating to 900°C is shown in Figure 8 and the 2θ range 20° to 24.5° is shown in the inset, highlighting the numerous phases present. The best fit to the observed data was achieved by fitting the diffraction peaks belonging to the doped ceria to two fluorite phases with cubic lattice parameters of 5.47040(2) Å and 5.45285(2) Å, indicating that the ceria phase may consist of a range of compositions resulting in the difference plot shown in Figure 8.

From these observations, it is proposed that heating a LNO:CGO10 50:50wt% composite in a sealed capillary results in partial decomposition of LNO to La_2O_3 and Ni. Given that LNO does not decompose in a capillary with one end open to the atmosphere (IS-2), it is proposed

that the decomposition is associated with the oxygen atmosphere that the composite is exposed to. It has previously been observed ²⁶ that with a barrier layer of alumina between LNO and platinum, LNO displays no decomposition up to 1000°C and previous authors have reported phase stability of LNO up to 800°C in vacuum ¹⁶. Therefore, it can be concluded that the observations made here are associated with the nature of the composite and not the constituent LNO and CGO phases independently.

The phase fractions from Rietveld refinement of the composite in IS-3 are given in Figure 9 and the change in the lattice parameters of the phases originating from lanthanum nickelate are shown in Figure 10. At 350°C the refined phase fractions of CGO and LNO are 53% and 47%, respectively, which is in good agreement with the room temperature values and corresponds well with the expected ratios of the starting composite, the CGO phase fraction has been determined from summing the two cubic gadolinium doped ceria phases in the Rietveld refinements. As the temperature increased to 750°C the reaction phases have formed by decomposition of LNO and there is a linear decrease in the phase fraction of LNO with increasing temperature. This correlates to a linear increase in La_2O_3 from 5% at 750°C to 22% at 900°C, indicating continuing decomposition of LNO with increasing temperature. The nickel phase fraction shows a small linear increase between 850°C and 900°C and is approximately 5% in this temperature range.

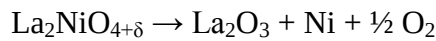
The trends in the lattice parameters indicate a significant decrease in the a and c lattice parameters of the LNO tetragonal cell on decomposition on heating. Between 650 °C and 750 °C there is an increase in the a and c lattice parameters of LNO, as expected from thermal expansion, however above 750 °C both lattice parameters decrease, leading to an overall decrease in the unit cell volume. This may be understood by considering the increase in the phase fraction of the decomposition products, La_2O_3 and Ni on heating, leading to a reduction in the unit cell volume of LNO. However, there appears to be a complex set of changes also

occurring in the La_2O_3 unit cell, whereby the c lattice parameter increases with increasing temperature and the a parameter decreases. As the phase fraction of nickel is 5% or below, the errors on the unit cell size from Rietveld refinement here are relatively large, however this does appear to follow a linear trend with temperature. To gain a clear insight into the different mechanisms occurring in the composite on heating it would be necessary to measure diffraction patterns over a temperature range with narrow intervals, say 25 °C,.

Having identified the phases formed on heating of the composite in a sealed capillary, examination of the diffraction patterns on cooling, leads to further interesting observations. Figure 11 shows the synchrotron X-ray powder diffraction patterns of the composite after heating to 900°C and on cooling to room temperature. At room temperature the CGO peaks no longer appear broadened confirming that the structural changes in CGO are reversible on cooling, as seen in IS-2. The intensity of the major La_2O_3 peak at $\sim 15.9^\circ 2\theta$ reduces with decreasing temperature indicating a degree of reversibility to the reaction, however the reaction phase diffraction peaks are still clearly visible at room temperature. It can be seen that at 350°C and at room temperature the intensity of the tetragonal (110) LNO peak at $17.4^\circ 2\theta$ reduces and there is a new peak at $\sim 17.2^\circ 2\theta$. Initial consideration of the position of the new peak indicated a higher order Ruddlesden-Popper phase however attempts to perform Rietveld refinement including the $\text{La}_3\text{Ni}_2\text{O}_{7-\delta}$ and $\text{La}_4\text{Ni}_3\text{O}_{10-\delta}$ phases led to unsatisfactory matches. The most appropriate match to the peak splitting at $\sim 17.2^\circ 2\theta$ was obtained by refining with an orthorhombic LNO phase, with spacegroup Bmab. Based on this observation, it appears that after a degree of decomposition in tetragonal LNO, a phase transition is observed to the orthorhombic phase on cooling in a sealed capillary. This confirms that the phase formation in LNO is highly dependent on the oxygen atmosphere as well as the cation stoichiometry of the phase.

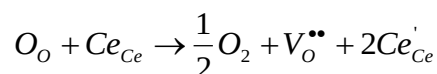
The long term stability of LNO is an important consideration for operation in an SOFC. Odier et al.³¹ find the A_2BO_4 structure of LNO to be stable in air up to 1200°C and Skinner¹⁶ finds LNO to be stable up to 800°C in vacuum. However Odier et al. comment that the maximum stability temperature is likely to be dependent on oxygen partial pressure and above 1200°C, for compositions where La/Ni is less than two, La_2NiO_4 and NiO form. Rice and Buttrey³² investigated the oxygen stoichiometry range over which $La_2NiO_{4+\delta}$ is stable using powder X-ray diffraction. The authors find that LNO displays phase stability over the approximate regime 1×10^{-10} Pa to 1×10^{-7} Pa between 800°C and 1000°C. Yaremchenko and co-authors³³ comment on thermodynamic predictions by Yokokawa et al.³⁴ which show that minor deviations from the nominal La:Ni ratio should have a strong effect on the stability limit. This stability limit may vary from an upper oxygen partial pressure value for a slight excess of nickel ($Ni + \frac{1}{2}O_2 \leftrightarrow NiO$) to a lower limit for a slight excess of lanthanum oxide ($La_2O_3 + Ni + \frac{1}{2}O_2 \leftrightarrow La_2NiO_4$).

It is proposed that the decomposition process occurs by reduction of LNO, outlined in the reaction below;



In IS-3, the capillary is sealed and it would therefore be expected that the oxygen pressure in the capillary would increase on heating, however from Rietveld refinement of the XRD data under these conditions it is apparent that LNO is reduced to form La_2O_3 and Ni. This indicates that the reduction of LNO is not due to the ambient oxygen pressure in the capillary but is related to the nature of the composite material and the presence of the CGO.

Ceria is a well known redox catalyst with its activity attributed to its variable oxidation states, and fast oxide ion transport properties^{28, 29, 35-38}. Reduction of ceria results in the formation of oxygen vacancies and occurs by the process outlined below,



In the LNO:CGO composite studied here, we observe the formation of multiple phases composed of gadolinium doped ceria and it is feasible that ceria is present as a result of gadolinium dissolution from CGO which is acting as a catalyst for the decomposition of LNO. This may have a significant effect on the performance of these materials combined in an SOFC device.

4.0 Conclusions

In-situ high resolution synchrotron X-ray powder diffraction studies of LNO:CGO10 50:50wt% composites indicated that there was no phase reaction in an unsealed capillary. Changes to the CGO structure are, however, observed and it is believed that these are associated with changes in the gadolinium content of the sample resulting in the formation of multiple gadolinium deficient CGO phases of slightly differing compositions. This is reversible on cooling and at room temperature CGO is single phase. Diffraction patterns from the same composite in a sealed capillary show a reaction between LNO and CGO on heating which results in the decomposition of LNO and formation of La_2O_3 and Ni phases. On cooling to room temperature, the reaction displays a degree of reversibility, with limited reformation of LNO and a decrease in the phase fraction of La_2O_3 and nickel.

It should be noted however, that the role of CGO in the reactions may involve direct participation in a reaction with LNO by rare earth cation diffusion or may be as a redox catalyst in the form of CeO_2 formed by gadolinium dissolution. CeO_2 is a known redox catalyst and its presence may promote reduction of LNO to La_2O_3 and Ni, depending on the environmental and experimental conditions.

The behaviour and stability of LNO with IT-SOFC electrolytes²² has shown by *ex-situ* XRD of heated compacted pellets, that no reaction occurred between LNO and LSGM8282,

however there was significant reaction in LNO:CGO20 50:50wt% composites after heating to 900°C for 24 hours. The main reaction phase was assigned to a higher order Ruddlesden-Popper phase of lanthanum nickelate. This clearly differs from the observations made here using high resolution synchrotron diffraction during *in-situ* heating and cooling in capillaries exposed to different atmospheric environments. From this we can surmise that that there are a complex set of reactions which occur in LNO-based composites, which are not only temperature, time and oxygen partial pressure dependent but also appear to be dependent on the composite state (compacted pellet or loose powder).

Acknowledgements

The authors would like to thank EPSRC Supergen Fuel Cells for funding of a studentship (RS). This work was carried out with the support of the Diamond Light Source.

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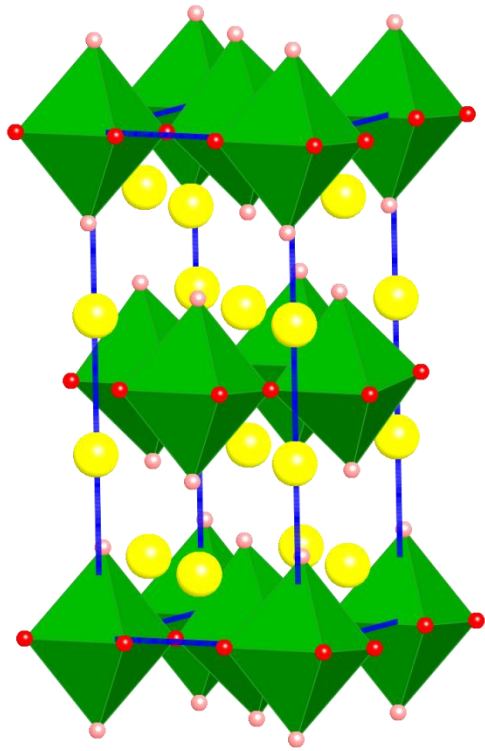
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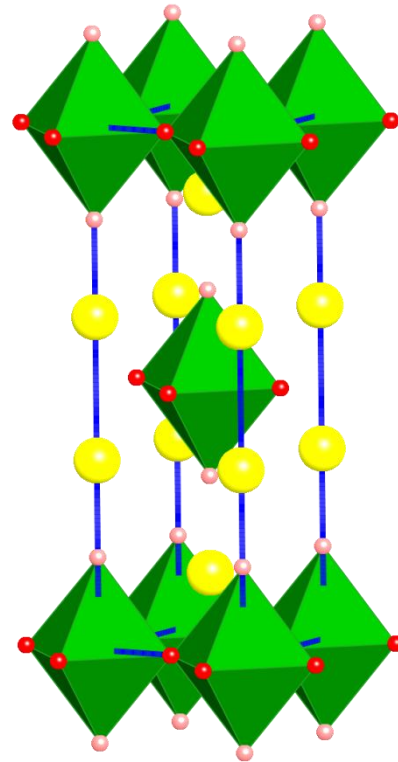
Tables

Expt.	Wavelength (Å)	Capillary Sealing	Experiment description
IS-1	0.82712	Open end sealed with commercial superglue	Heat from 250°C to 500°C
IS-2	0.826471	Open end unsealed	Heat to 900°C collecting data at RT, 350°C, 650°C, 900°C Cool to RT collecting data at 800°C, 750°C, 700°C, 650°C, 350°C, RT
IS-3	0.826471	Open end sealed with commercial vacuum grease	Heat to 900°C collecting data at 350°C, 650°C, 750°C, 850°C, 900°C Cool to RT collecting data at 800°C, 750°C, 700°C, 650°C, 350°C, RT

Table 1 – Experimental conditions for X-ray synchrotron experiments on LNO:CGO10 composites conducted in air.



(a)



(b)

Figure 1 : LNO structures with spacegroups (a) Bmab and (b) I4/mmm; lanthanum atoms are in yellow, the NiO₆ octahedra are shown in green and oxygen (equatorial position) in red and (apical position) in pink.

Figures

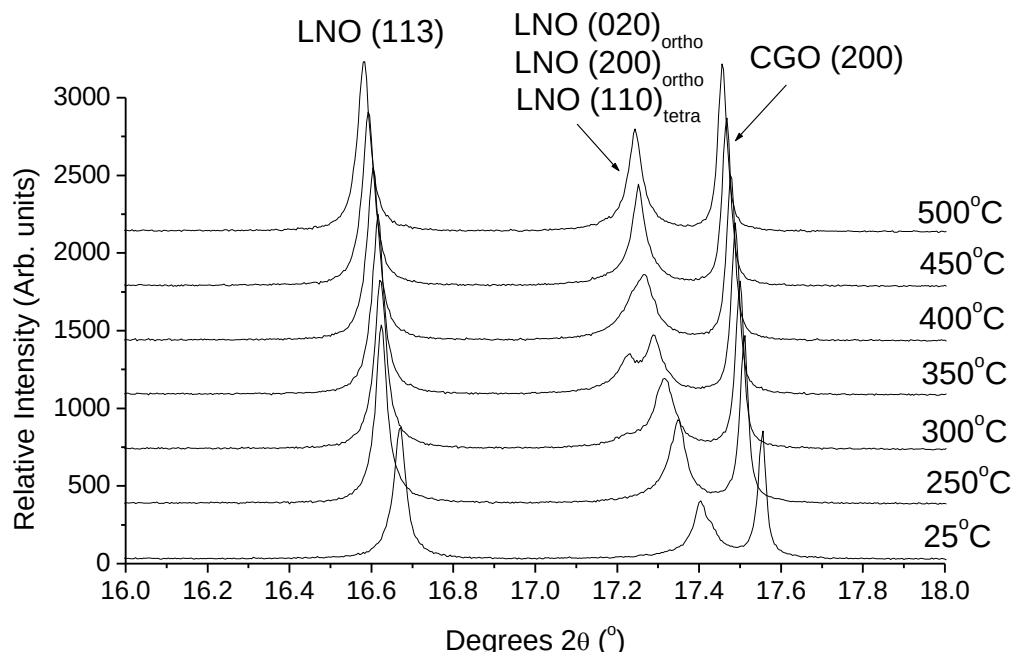


Figure 2: Synchrotron X-ray diffraction patterns of LNO:CGO10 50:50 wt% composite on heating in a sealed capillary, showing overlapping peaks at 17.4 °2θ, composed of the orthorhombic (020) and (200) and the tetragonal (110) LNO peaks at 350°C ($\lambda = 0.82712 \text{ \AA}$), note that no offset has been applied to the x-axis.

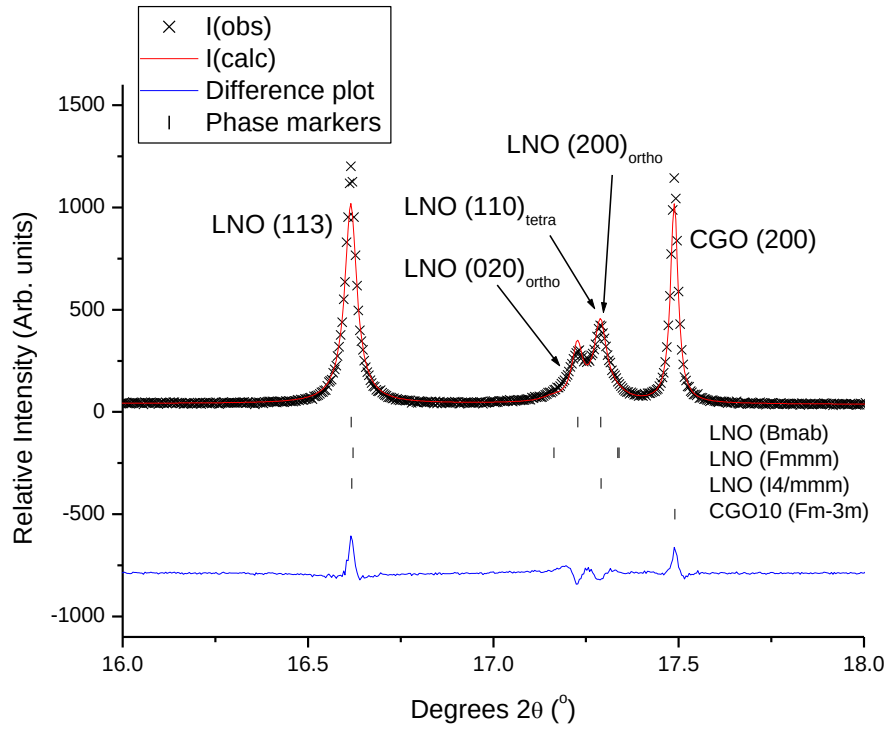


Figure 3: Selected region (16 to 18° 2 θ) of the refined LNO:CGO10 composite at 350°C, showing the observed (symbols) and calculated (line) diffraction patterns with difference plot and the phase markers ($\lambda = 0.82712 \text{ \AA}$), $R_{wp} = 7.35\%$, $R_p = 5.77\%$. The LNO peaks at 17.2° 2 θ are composed of the (020) and (200) orthorhombic reflections and the (110) tetragonal reflection, as LNO undergoes an orthorhombic to tetragonal phase transition on heating.

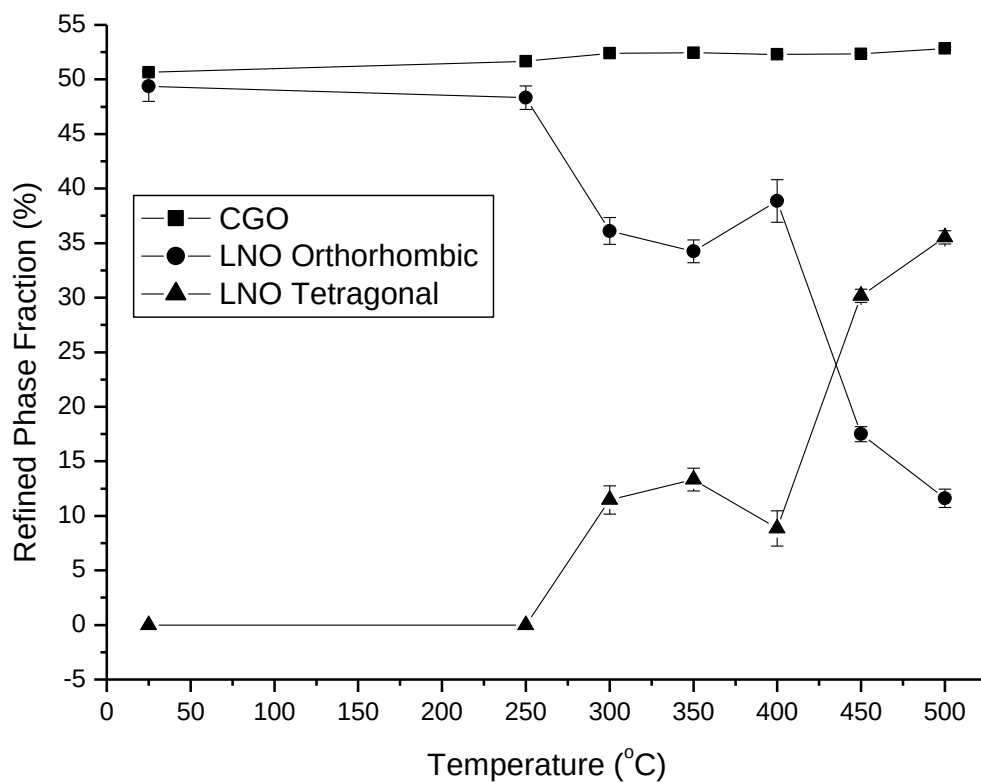


Figure 4: Refined phase fractions of LNO:CGO 50:50 wt% composite on heating; the errors are twice the standard deviation from the refinement, however in some places they are sufficiently small that they lie beneath the data symbols.

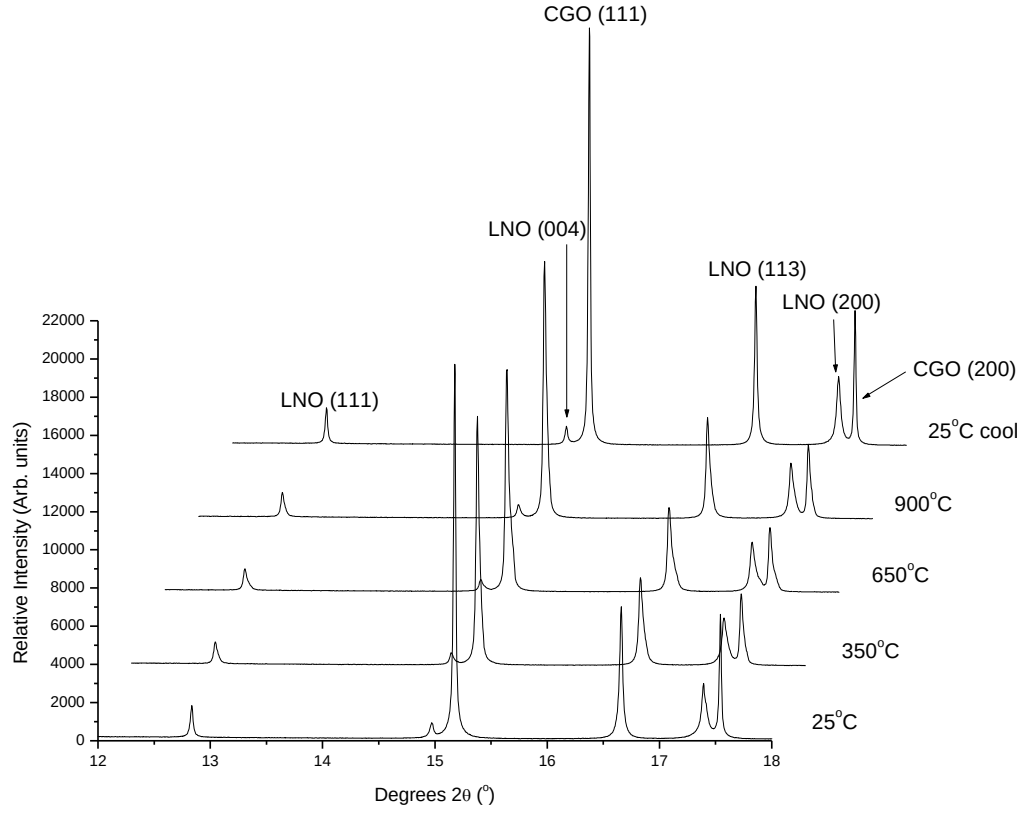


Figure 5: Synchrotron powder diffraction patterns of LNO:CGO10 50:50wt% composite in an open ended capillary on heating from 25 °C to 900°C and on cooling to 25°C ($\lambda = 0.826471 \text{ \AA}$), indicating the orthorhombic LNO and CGO10 (hkl) reflections. LNO retains the orthorhombic phase on heating up to 900°C in an open ended capillary.

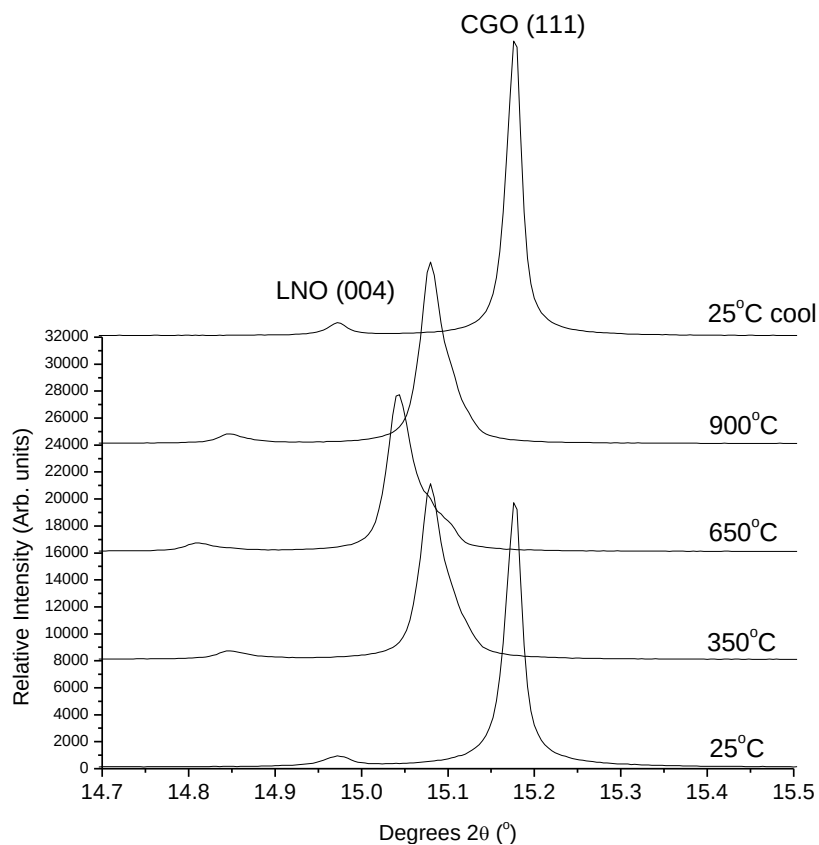


Figure 6: Synchrotron powder diffraction patterns of LNO:CGO10 50:50wt% composite in an open ended capillary ($\lambda = 0.826471 \text{ \AA}$), showing the broadening of the CGO (111) peak on heating and the reversible nature of this effect on returning to room temperature; note that no offset has been applied to the x-axis.

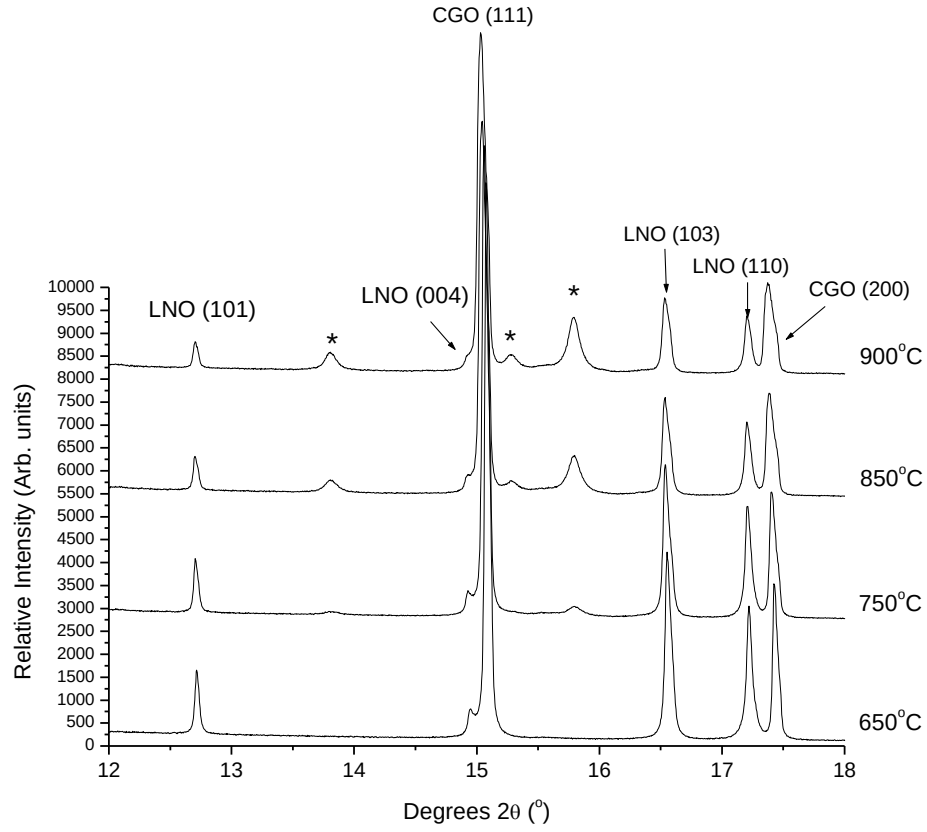
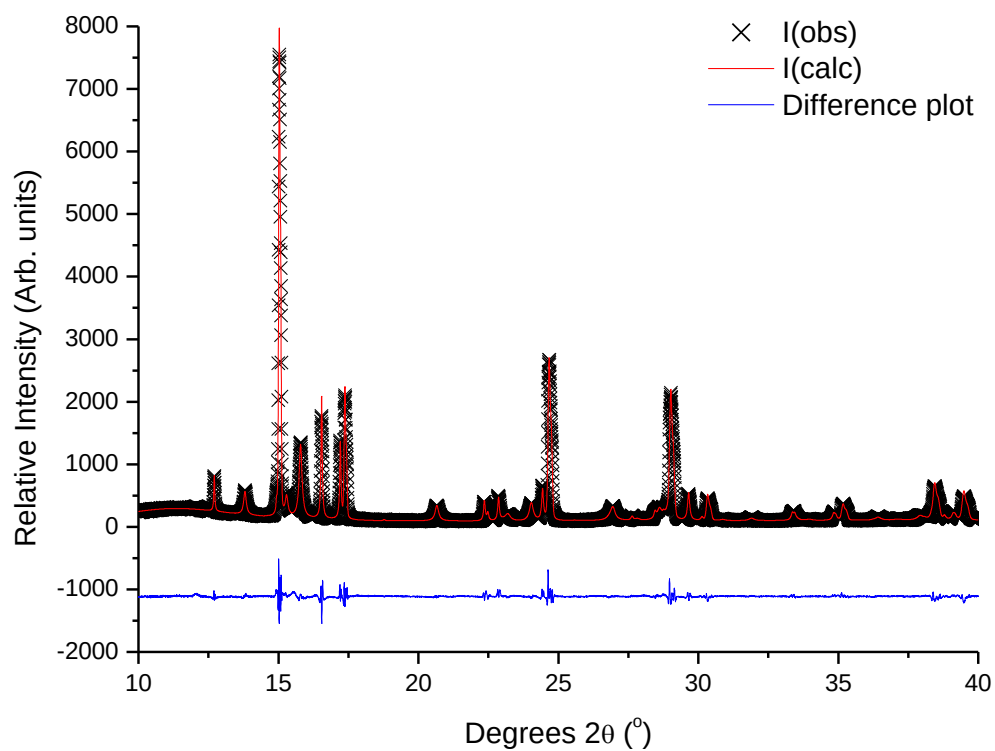


Figure 7: Synchrotron powder diffraction patterns of LNO:CGO10 50:50wt% composite in sealed capillary on heating from 650°C to 900°C ($\lambda = 0.826471 \text{ \AA}$), indicating the tetragonal LNO and CGO10 (hkl) reflections and the peaks associated with new phase formation are marked with *, note that no offset has been applied to the x-axis.



Inset:

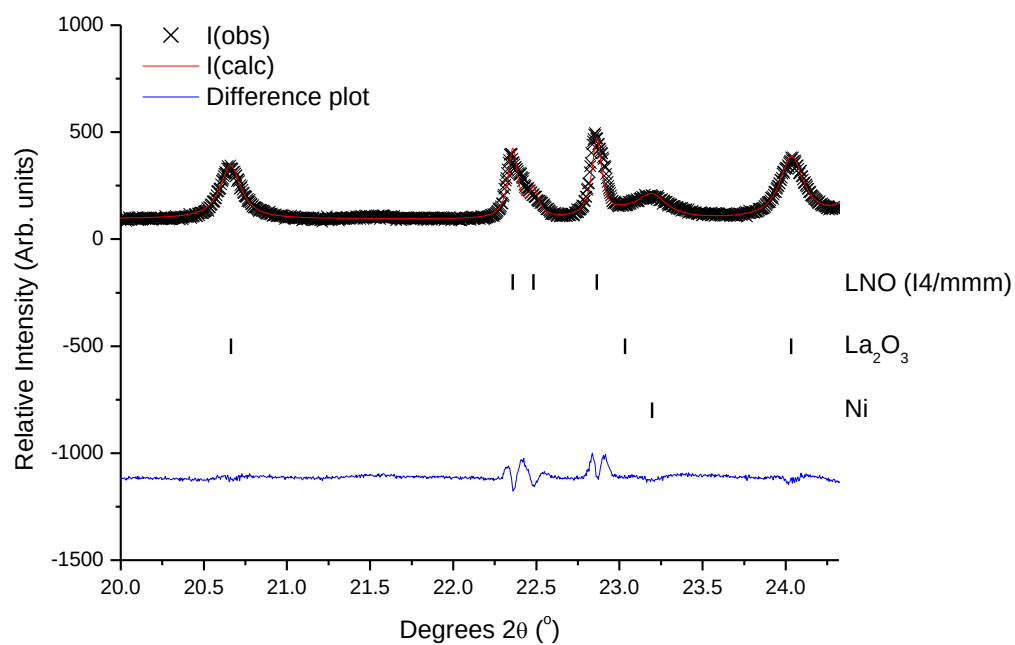


Figure 8: Rietveld refinement of LNO:CGO10 composite at 900°C in a sealed capillary, showing the observed (symbols) and calculated (line) diffraction patterns with difference plot ($\lambda = 0.826471 \text{ \AA}$), $R_{wp} = 11.66\%$, $R_p = 7.87\%$. Inset shows the region 20 to 24.5 °2 θ with phase markers for La_2NiO_4 (LNO), La_2O_3 and Ni.

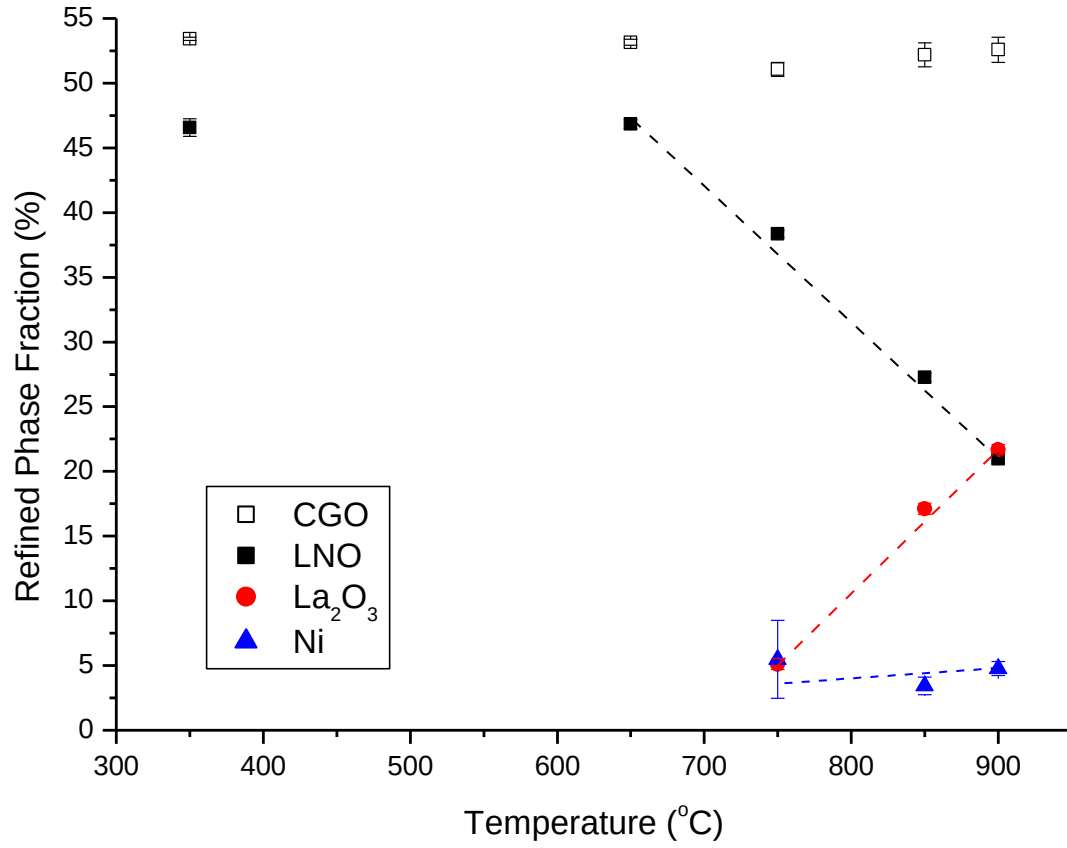
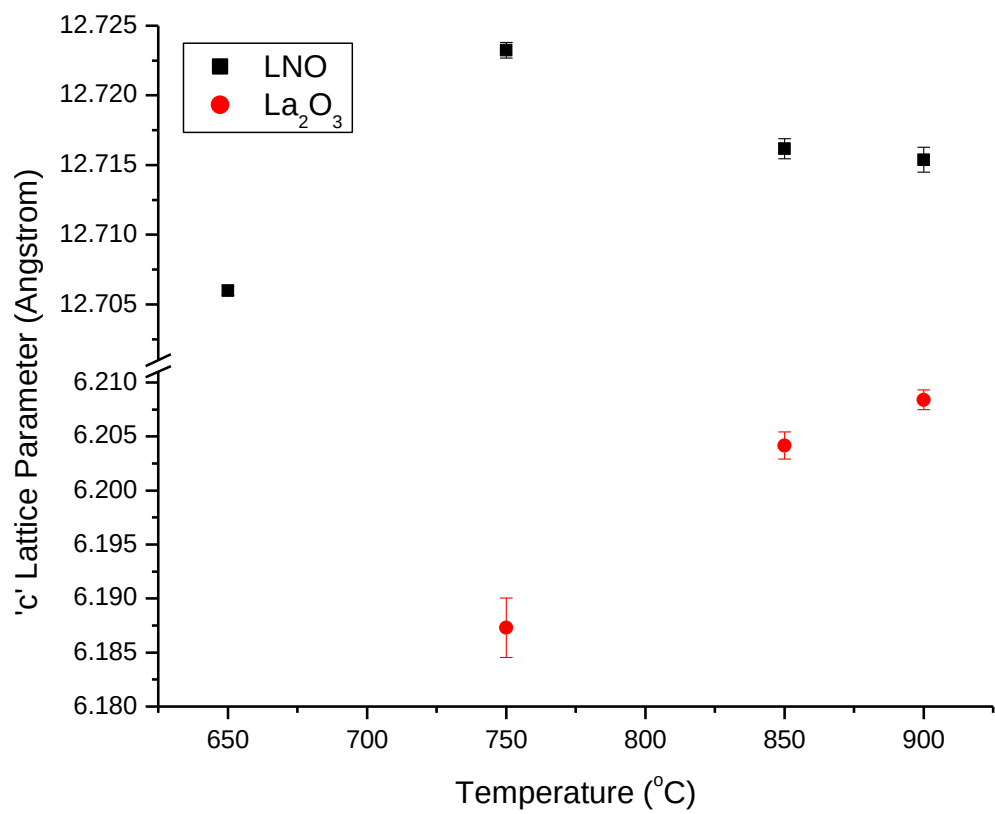
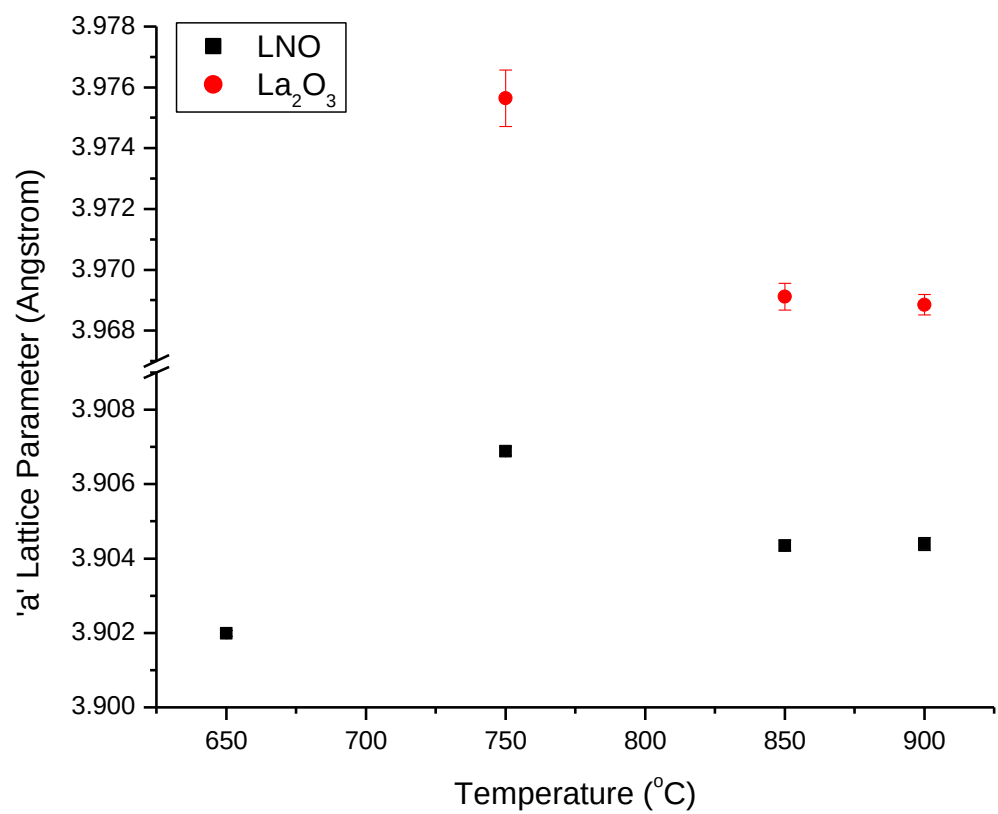


Figure 9: Refined phase fractions of LNO:CGO 50:50 wt% composite on heating in a sealed capillary; the errors are twice the standard deviation from the refinement, however in some places they are sufficiently small that they lie beneath the data symbols, note that lines are a guide for the eye only.



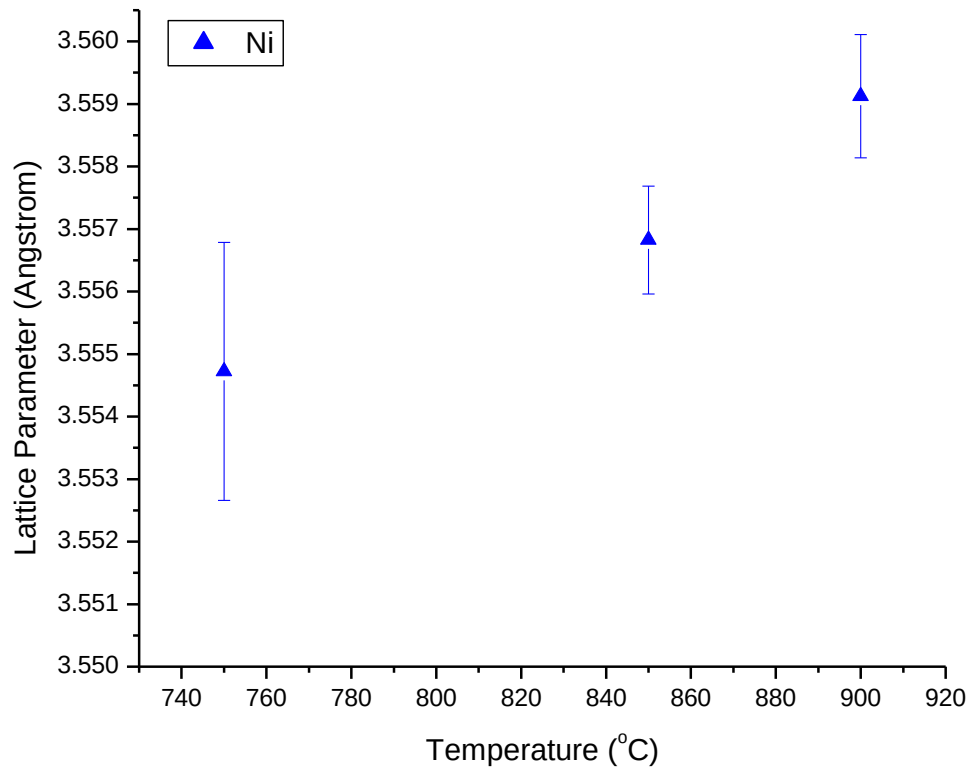


Figure 10: Refined lattice parameters for (a) and (b) LNO and La_2O_3 and (c) nickel from Rietveld refinement of heating LNO:CGO10 50:50wt% composite in a sealed capillary; errors are twice the standard deviation from Rietveld refinement.

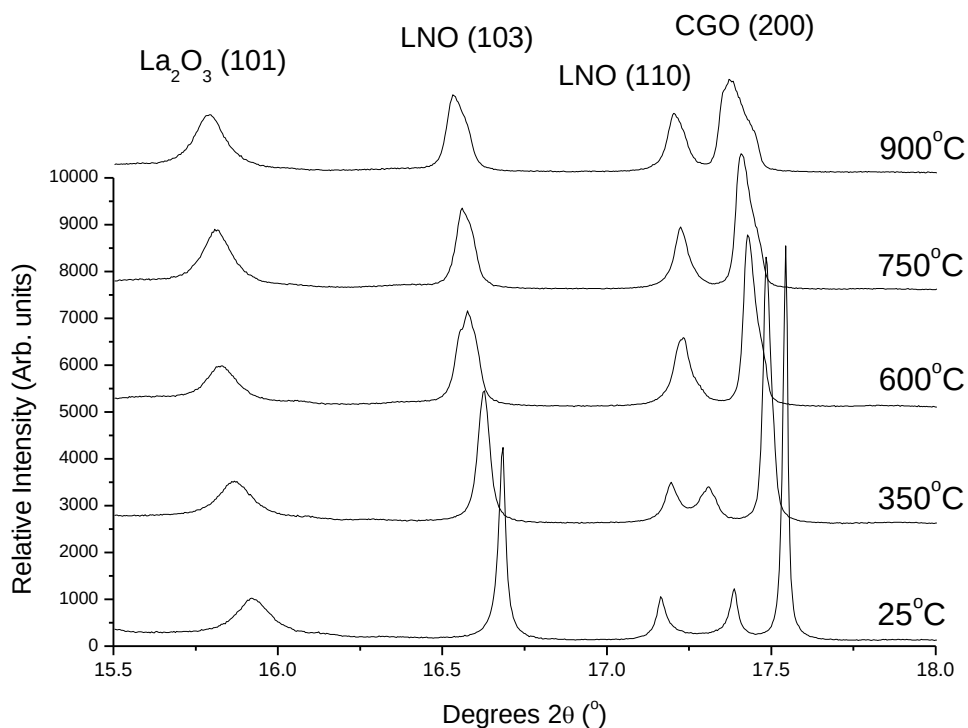


Figure 11: Synchrotron powder diffraction patterns of LNO:CGO10 50:50wt% composite in sealed capillary on cooling from 900°C to 25°C ($\lambda = 0.826471 \text{ \AA}$), indicating the tetragonal LNO and CGO10 and La_2O_3 (hkl) reflections. The splitting of the tetragonal LNO (110) indicative of a transition to the orthorhombic phase can be seen at 350°C and below; note that no offset has been applied to the x-axis.