Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Supplementary Information

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

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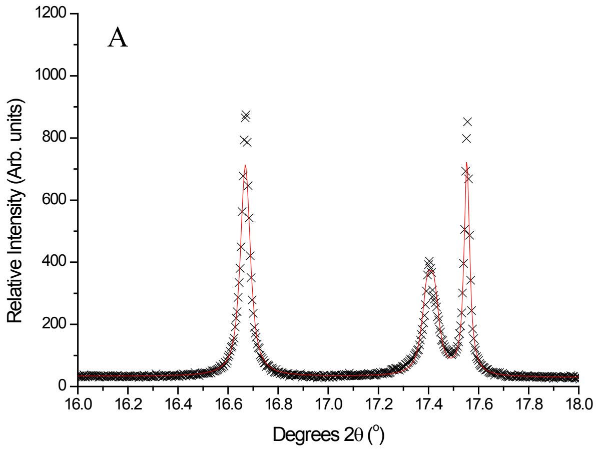
Assignment of LNO phases

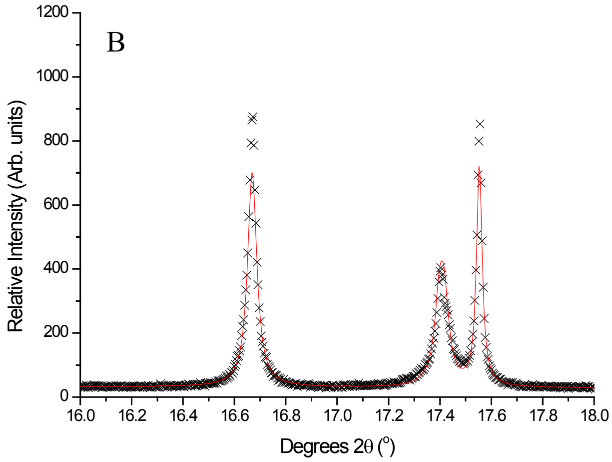
The assignment of two orthorhombic phases to room temperature LNO is shown in Figure S1, where Rietveld refinements for each individual orthorhombic phase (Fmmm and Bmab) is compared with the Rietveld refinement for the dual phase system. The goodness of fit parameters (wRp and Rp) decrease for the dual phase system and the fit is visibly improved.

The assignment of three phases to LNO on heating above 250°C (the dual phase orthorhombic system with the addition of a tetragonal phase (space group I4/mmm)) is demonstrated in Figures S2, S3 and S4 for XRD data collected at 300°C, 350°C and 400°C (these are representative temperatures). It can be seen that individual orthorhombic or tetragonal phases result in a poor fit for the LNO peaks at 17.5° 2theta, however a mixed dual orthorhombic phase (Fmmm and Bmab) with tetragonal phase (I4/mmm) yields low goodness of fit parameters and a visibly improved fit to the measured data.

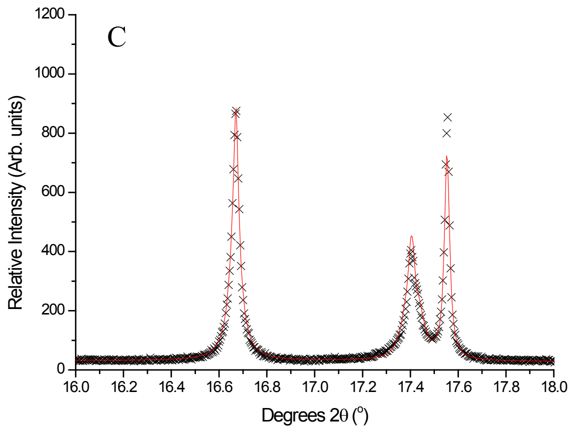
In the orthorhombic spacegroups Fmmm and Bmab the (200) reflection and (020) reflection are observed at very close 2 theta values, which can be observed as an apparent splitting of the (200) peak. Here, the Fmmm and Bmab models used both display reflections which can independently be assigned to the (200) and (020) reflections; this can be seen in the phase markers for Fmmm and Bmab in Figure 3 in the main text – both space groups have two phase markers in the 2theta region between 17° and 17.5°, the marker at lower 2theta values belongs to the (020) reflection and the marker at higher 2theta belongs to the (200) reflection. However, Figures S2, S3 and S4 show that the LNO peaks in the region of 17.5° 2theta are not adequately fitted by the (020) and (200) reflections in the orthorhombic spacegroups alone. The peak in the region of 17.5° 2theta belongs to the (110) reflection of the I4/mmm spacegroup. As an orthorhombic to tetragonal phase transition has been previously reported in LNO (see references 11 and 16 in the main text), a tetragonal phase was added to the Rietveld refinements with the aim of improving the fit. The gradual phase transition from orthorhombic to tetragonal on heating of LNO, makes chemical sense as it would be unusual for an abrupt change in unit cell lattice positions and lattice parameters to occur. On the basis of this it therefore seems reasonable to conclude that on heating from 250°C to 500°C, there is mixed phase region of orthorhombic and tetragonal phases, with an increasing amount of tetragonal phase as heating continues above 400°C.



wRp = 9.45%, Rp = 7.30%

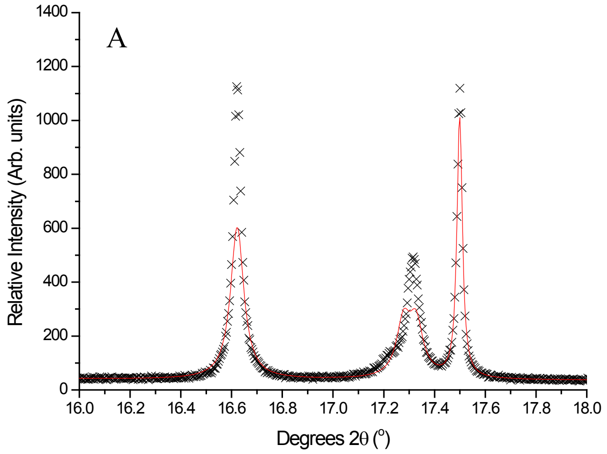


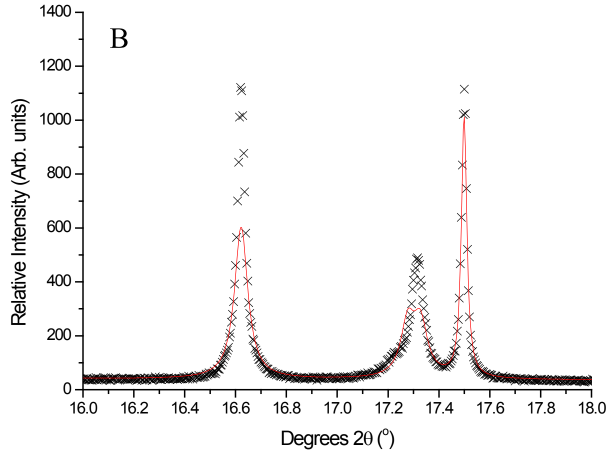
wRp = 10.16%, Rp = 7.89%



wRp = 8.79%, Rp = 6.82%

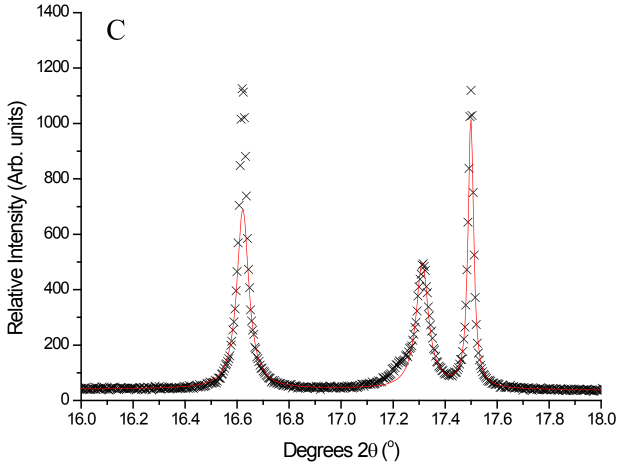
Figure S1: Selected region (16 to 18° 2θ) of the refined LNO:CGO10 composite at 25°C, showing the observed (symbols) and calculated (line) diffraction patterns (λ = 0.82712 Å) for (A) Fmmm orthorhombic model, (B) Bmab orthorhombic phase and (C) dual phase Fmmm and Bmab (refined to 35.4(4)% Fmmm, 13.9(6)% Bmab).

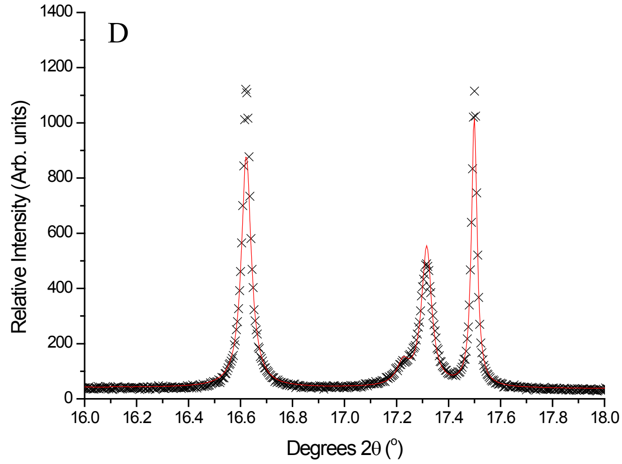




wRp = 11.09%, Rp = 7.70%

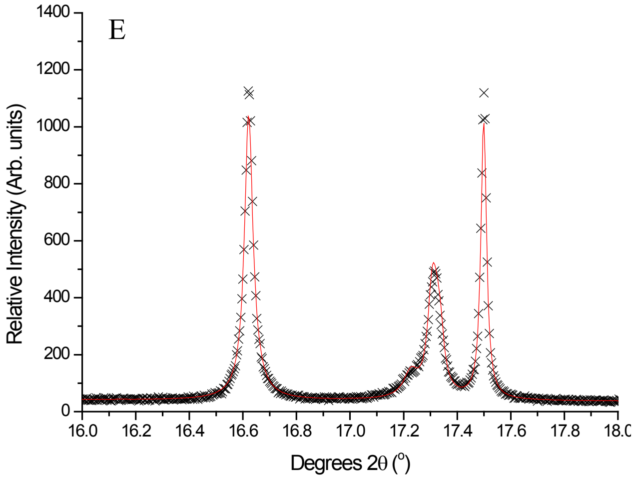
wRp = 11.09%, Rp = 7.70%





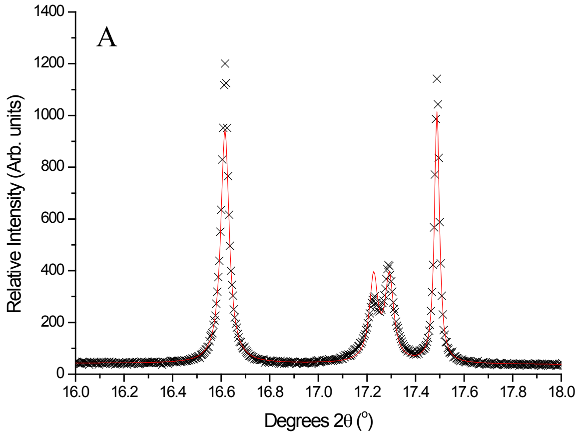
wRp = 9.51%, Rp = 6.93%

wRp = 7.84%, Rp = 6.09%

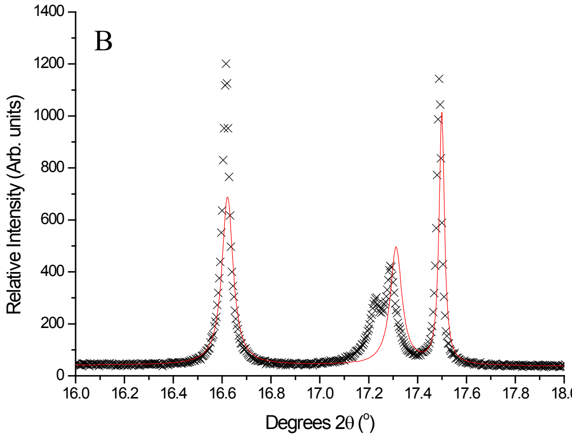


wRp = 7.30%, Rp = 5.69%

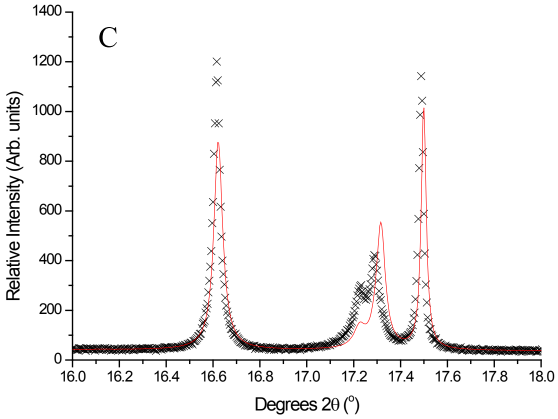
Figure S2: Selected region (16 to 18° 2θ) of the refined LNO:CGO10 composite at 300°C, showing the observed (symbols) and calculated (line) diffraction patterns (λ = 0.82712 Å) for (A) Fmmm orthorhombic model, (B) Bmab orthorhombic phase, (C) I4/mmm tetragonal phase, (D) mixed phase Fmmm orthorhombic and tetragonal I4/mmm, and (E) mixed phase composed of dual phase orthorhombic Fmmm, Bmab and tetragonal I4/mmm.



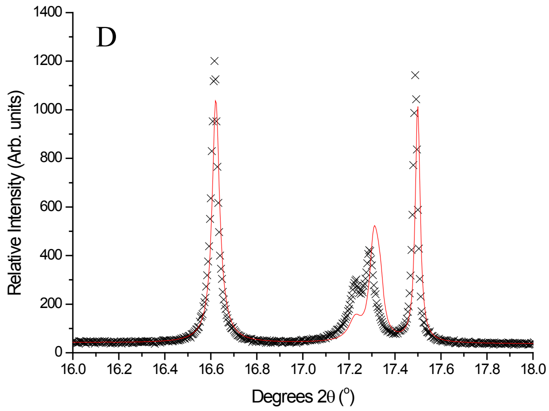
wRp = 8.07%, Rp = 6.23%



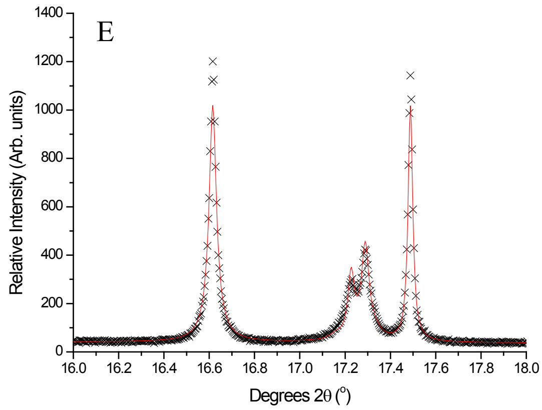
wRp = 14.81%, Rp = 9.79%



wRp = 10.98%, Rp = 7.56%

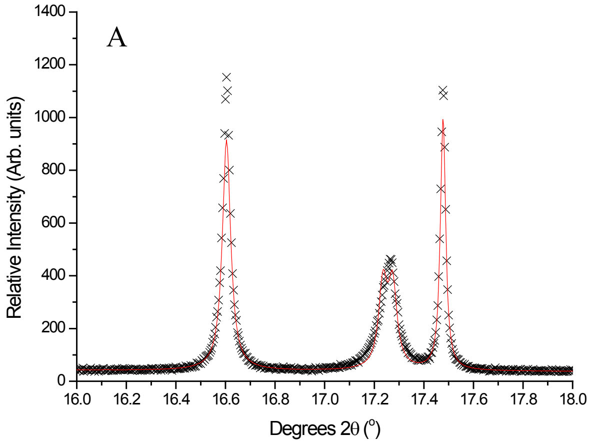


wRp = 7.70%, Rp = 6.00%

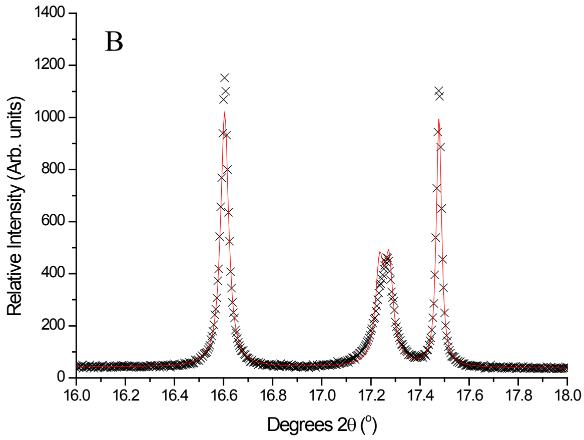


wRp = 7.35%, Rp = 5.77%

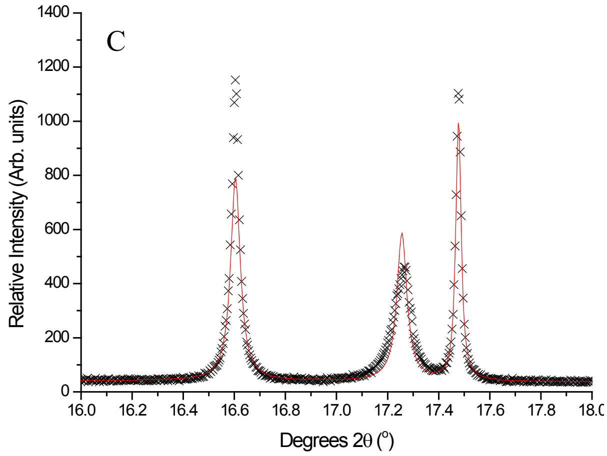
Figure S3: Selected region (16 to 18° 2θ) of the refined LNO:CGO10 composite at 350°C, showing the observed (symbols) and calculated (line) diffraction patterns (λ = 0.82712Å) for (A) Fmmm orthorhombic model, (B) Bmab orthorhombic phase, (C) I4/mmm tetragonal phase, (D) mixed phase Fmmm orthorhombic and tetragonal I4/mmm, and (E) mixed phase composed of dual phase orthorhombic Fmmm, Bmab and tetragonal I4/mmm.



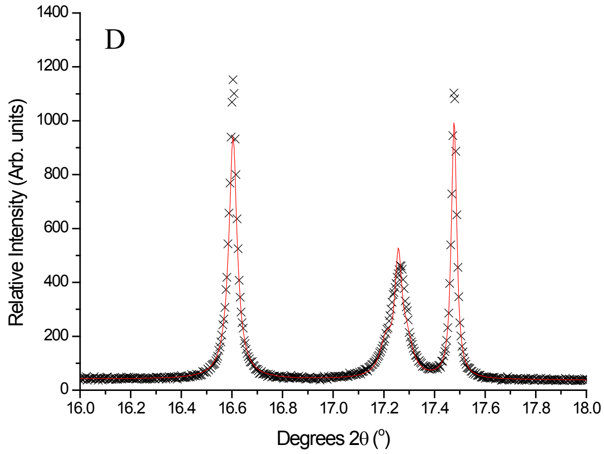
wRp = 8.07%, Rp = 6.23%



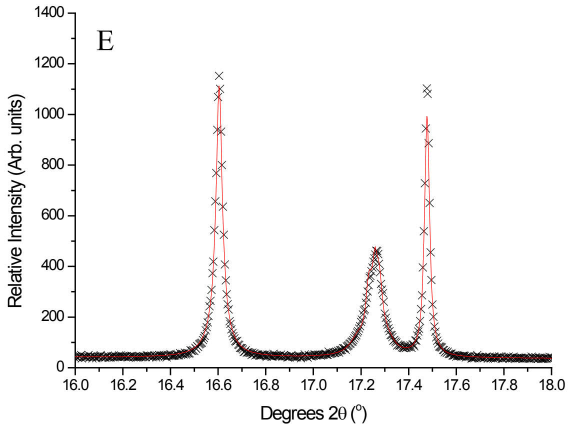
wRp = 14.81%, Rp = 9.79%



wRp = 10.98%, Rp = 7.56%



wRp = 7.70%, Rp = 6.00%



wRp = 7.35%, Rp = 5.77%

Figure S4: Selected region (16 to 18° 2θ) of the refined LNO:CGO10 composite at 400°C, showing the observed (symbols) and calculated (line) diffraction patterns (λ = 0.82712Å) for (A) Fmmm orthorhombic model, (B) Bmab orthorhombic phase, (C) I4/mmm tetragonal phase, (D) mixed phase Fmmm orthorhombic and tetragonal I4/mmm, and (E) mixed phase composed of dual phase orthorhombic Fmmm, Bmab and tetragonal I4/mmm.

Effect of capillary sealant

In IS1 the capillary was sealed with commercial superglue and in IS2 the capillary was sealed with commercially available grease. The aim of these experiments was to isolate the sample in the capillary from the ambient environment. The capillaries were heated using a hot-air blower (described in the Experimental section of the main text, Section 2.0), and the I11 instrument arrangement is such that the X-ray beam is incident on the region of capillary which is under direct heating i.e. the diffraction patterns obtained are from a region of sample that is at controlled temperature, however there will be a temperature gradient across the capillary. The sealed ends of the capillary will therefore be at a lower temperature to that of the sample.

From experiments IS1 and IS2 it is possible to conclude that the low temperature (< 500°C) orthorhombic to tetragonal phase transition in LNO is dependent on the nature of the ambient environment. The phase transition proceeds in IS1, which is sealed to the environment, whereas the orthorhombic phase is maintained in IS2, where the capillary is open to the environment. As the orthorhombic to tetragonal phase transition in LNO is associated with loss of oxygen, it seems that the structure is sensitive to the oxygen stoichiometry and environment.

The phases present in LNO at 350°C in capillaries sealed by different means (i.e. IS1 and IS3) were compared; the obtained diffraction patterns are shown in Figure S5.

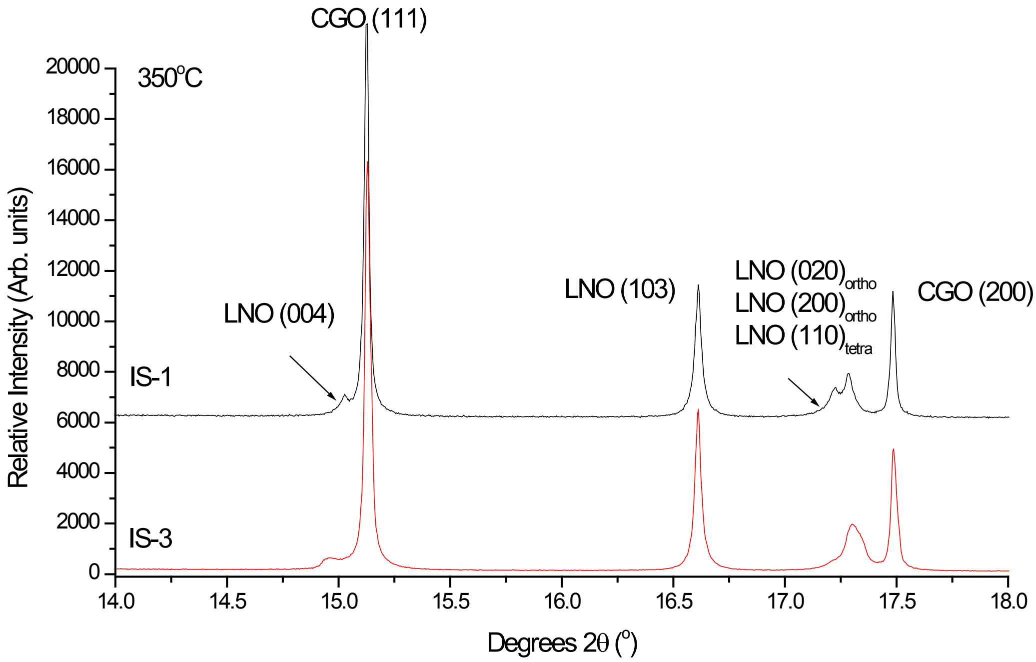


Figure S5 – Low temperature phase transition in LNO, patterns from IS1 and IS3 at 350°C, showing the same LNO diffraction peaks, each capillary was sealed (IS1 with superglue, IS3 with grease; the agreement in diffraction patterns indicates the different sealants did not affect the observed phase change).

It can be seen in Figure S5, that the diffraction patterns differ depending on the sealant type used. From Rietveld refinement of the XRD patterns, the best fit is achieved with a phase mixture of dual orthorhombic phase (Fmmm and Bmab) and tetragonal (I4/mmm) phase, however there are differences in the phase fractions, shown in Table S1.

Table S1: Phase fractions of LNO from Rietveld refinements of LNO:CGO10 composite at 350°C in sealed capillaries; IS-1 sealed with commercial superglue and IS-2 sealed with commercially available vacuum grease

Experiment and obtained goodness of fit parameters	**Relative phase fractions of LNO phases in LNO: CGO composite**		
	Fmmm	**Bmab**	**I4/mmm**
IS1 wRp = 7.35%, Rp = 5.77%	29.1(4)%	5.2(3)%	13.3(5)%
IS3 wRp = 8.55%, Rp = 6.11%	10.4(5)%	26.8(8)%	9.9(6)%

This indicates that the different sealants used for the capillaries are air-tight to differing degrees, which affects the observed LNO phases.