**Supplemental data**

**Cation reducibility of LaNi0.5Ti0.5O3, LaNi0.5Ti0.45Co0.05O3, and LaNi0.45Co0.05Ti0.5O3 perovskites from X-ray powder diffraction data using the Rietveld Method**

Mayra Guamán-Ayala1, Pablo V. Tuza1\* and Mariana M.V.M. Souza2

1 Departamento de Energía y Mecánica, Carrera de Petroquímica, Universidad de las Fuerzas Armadas ‒ ESPE, EC170501 Sangolquí, Ecuador.

2 Escola de Química, Universidade Federal do Rio de Janeiro (UFRJ), Centro de Tecnologia, Bloco E, Sala 206, CEP 21941‒909, Rio de Janeiro/RJ, Brazil.

­­\* Corresponding author (Tel: +593‒32810206 ex 4303, Email: pvtuza@espe.edu.ec).

Table SI.Atomic coordinates, unit-cell parameters, isotropic displacement parameter, the fraction of site occupancy, and the peak and asymmetry parameters for LN0.5T0.5O-1.8, LN0.5T0.5O-10, LN0.5T0.45C0.05O-10, and LN0.45C0.05T0.5O-10.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Parameter | LN0.5T0.5O-1.8 | LN0.5T0.5O-10 | LN0.5T0.45C0.05O-10 | LN0.45C0.05T0.5O-10 | ICSD (2017) |
| **Ni0 *a,b*** |  |  |  |  |  |
| *a* | 3.51919(152) | 3.52492(3) | 3.52364(6) | 3.52509(5) | 3.54 |
| *b* | 3.51919(152) | 3.52492(3) | 3.52364(6) | 3.52509(5) | 3.54 |
| *c* | 3.51919(152) | 3.52492(3) | 3.52364(6) | 3.52509(5) | 3.54 |
| Ni: *x*  *y*  *z* | 0  0  0 | 0  0  0 | 0  0  0 | 0  0  0 | 0  0  0 |
| B(Å2) | 0.1 | 0.1 | 0.1 | 0.1 |  |
| Occ | 0.02083 | 0.02083 | 0.01894 | 0.01875 | 0.02083 |
| Co: *x*  *y*  *z* |  |  | 0  0  0 | 0  0  0 |  |
| B(Å2) |  |  | 0.1 | 0.1 |  |
| Occ |  |  | 0.00189 | 0.00208 |  |
| Peak parameters | 1 | 2 | 2 | 2 |  |
| Asymmetry parameters | 0 | 0 | 0 | 0 |  |
| **La2O3 *c*** |  |  |  |  |  |
| *a* | 3.937 | 3.937 | 3.92557(64) | 3.937 | 3.937 |
| *b* | 3.937 | 3.937 | 3.92557(64) | 3.937 | 3.937 |
| *c* | 6.13 | 6.13 | 6.16366(1) | 6.13 | 6.13 |
| La: *x*  *y*  *z* | 0.333  0.667  0.247 | 0.333  0.667  0.247 | 0.333  0.667  0.26277(368) | 0.333  0.667  0.247 | 0.333  0.667  0.247 |
| B(Å2) | 1 | 1.5 | 0.5 | 1.5 |  |
| Occ | 0.16667 | 0.16667 | 0.16667 | 0.08333 | 0.16667 |
| O1: *x*  *y*  *z* | 0  0  0 | 0  0  0 | 0  0  0 | 0  0  0 | 0  0  0 |
| B(Å2) | 1 | 0.5 | 0.5 | 0.5 |  |
| Occ | 0.08333 | 0.08333 | 0.08333 | 0.04167 | 0.08333 |
| O2: *x*  *y*  *z* | 0.333  0.667  0.645 | 0.333  0.667  0.645 | 0.333  0.667  0.64640(1500) | 0.333  0.667  0.645 | 0.333  0.667  0.645 |
| B(Å2) | 1 | 0.5 | 0.5 | 0.5 |  |
| Occ | 0.16667 | 0.16667 | 0.16667 | 0.08333 | 0.16667 |
| Peak parameters | 1 | 0 | 0 | 1 |  |
| Asymmetry parameters | 0 | 0 | 0 | 0 |  |
| **La2TiO5 *d*** |  |  |  |  |  |
| *a* |  | 10.98210(98) | 10.96218(169) | 10.97962(138) | 11.00739 |
| *b* |  | 11.35177(84) | 11.34196(145) | 11.34726(117) | 11.40036 |
| *c* |  | 3.95336(28) | 3.95193(43) | 3.95187(41) | 3.943832 |
| La1: *x*  *y*  *z* |  | 0.13916(89)  0.06420(80)  0.25 | 0.12998(185)  0.06594(204)  0.25 | 0.13871(120)  0.06478(117)  0.25 | 0.13582  0.06179  0.25 |
| B(Å2) |  | 0.5 | 0.5 | 1.5 | 0.419 |
| Occ |  | 0.5 | 0.5 | 0.5 | 0.5 |
| La2: *x*  *y*  *z* |  | 0.40157(86)  0.21246(86)  0.75 | 0.40991(226)  0.20959(235)  0.75 | 0.40310(121)  0.20963(137)  0.75 | 0.40445  0.21386  0.75 |
| B(Å2) |  | 0.5 | 0.5 | 1.5 | 0.419 |
| Occ |  | 0.5 | 0.5 | 0.5 | 0.5 |
| Ti: *x*  *y*  *z* |  | 0.19374 0.37379  0.25 | 0.19374 0.37379  0.25 | 0.18922(291)  0.36882(400)  0.25 | 0.19374  0.37379  0.25 |
| B(Å2) |  | 0.5 | 0.5 | 1 | 0.241 |
| Occ |  | 0.5 | 0.5 | 0.5 | 0.5 |
| O1: *x*  *y*  *z* |  | 0.01570(663)  0.09636(600)  0.75 | 0.01694(1404)  0.08767(1660)  0.75 | 0.01224(914)  0.09949(753)  0.75 | 0.009  0.1002  0.75 |
| B(Å2) |  | 0.5 | 0.5 | 1 | 0.273 |
| Occ |  | 0.5 | 0.5 | 0.5 | 0.5 |
| O2: *x*  *y*  *z* |  | 0.26440(600)  0.01526(666)  0.75 | 0.48234(1468)  0.05707(1613)  0.75 | 0.26705(843)  0.02137(950)  0.75 | 0.2755  0.0307  0.75 |
| B(Å2) |  | 0.5 | 0.5 | 1 | 0.273 |
| Occ |  | 0.5 | 0.5 | 0.5 | 0.5 |
| O3: *x*  *y*  *z* |  | 0.24309(559)  0.39610(714)  0.75 | 0.31876(1557)  0.37698(1814)  0.75 | 0.25928(694)  0.35408(833)  0.75 | 0.2384  0.3698  0.75 |
| B(Å2) |  | 0.5 | 0.5 | 1 | 0.273 |
| Occ |  | 0.5 | 0.5 | 0.5 | 0.5 |
| O4: *x*  *y*  *z* |  | 0.27538(642)  0.21778(677)  0.25 | 0.27558(1573)  0.20598(1526)  0.25 | 0.28489(872)  0.24038(800)  0.25 | 0.2769  0.2267  0.25 |
| B(Å2) |  | 0.5 | 0.5 | 1 | 0.273 |
| Occ |  | 0.5 | 0.5 | 0.5 | 0.5 |
| O5: *x*  *y*  *z* |  | 0.04838(635)  0.35003(636)  0.25 | 0.04990(1506)  0.34954(1611)  0.25 | 0.05132(873)  0.37115(836)  0.25 | 0.0378  0.3297  0.25 |
| B(Å2) |  | 0.5 | 0.5 | 1 | 0.273 |
| Occ |  | 0.5 | 0.5 | 0.5 | 0.5 |
| Peak parameters |  | 2 | 0 | 2 |  |
| Asymmetry parameters |  | 0 | 0 | 2 |  |
| **Non-stoichiometric precursor*e*** |  |  |  |  |  |
| *a* | 3.91924(196) | 3.92613 | 3.92699(43) | 3.92613 |  |
| *b* | 3.91924(196) | 3.92613 | 3.92699(43) | 3.92613 |  |
| *c* | 3.91924(196) | 3.92613 | 3.92699(43) | 3.92613 |  |
| La: *x*  *y*  *z* | 0  0  0 | 0  0  0 | 0  0  0 | 0  0  0 |  |
| B(Å2) | 1.5 | 1.5 | 1.5 | 1.5 |  |
| Occ | 0.01042 | 0.01042 | 0.01042 | 0.01042 |  |
| Ni: *x*  *y*  *z* | 0.5  0.5  0.5 | 0.5  0.5  0.5 | 0.5  0.5  0.5 | 0.5  0.5  0.5 |  |
| B(Å2) | 1 | 1 | 1 | 1 |  |
| Occ | 0.00521 | 0.00521 | 0.00521 | 0.00469 |  |
| Ti: *x*  *y*  *z* | 0.5  0.5  0.5 | 0.5  0.5  0.5 | 0.5  0.5  0.5 | 0.5  0.5  0.5 |  |
| B(Å2) | 1 | 1 | 1 | 1 |  |
| Occ | 0.00521 | 0.00521 | 0.00469 | 0.00521 |  |
| Co: *x*  *y*  *z* |  |  | 0.5  0.5  0.5 | 0.5  0.5  0.5 |  |
| B(Å2) |  |  | 1 | 1 |  |
| Occ |  |  | 0.00052 | 0.00052 |  |
| O1: *x*  *y*  *z* | 0.5  0.5  0 | 0.5  0.5  0 | 0.5  0.5  0 | 0.5  0.5  0 |  |
| B(Å2) | 1 | 1 | 1 | 1 |  |
| Occ | 0.03125 | 0.03125 | 0.03125 | 0.03125 |  |
| Peak parameters | 2 | 1 | 2 | 1 |  |
| Asymmetry parameters | 4 | 0 | 4 | 4 |  |
| **Non-stoichiometric**  **La2NiO4*f*** |  |  |  |  |  |
| *a* |  | 3.9103 | 3.9103 | 3.9103 | 3.9103 |
| *b* |  | 3.9103 | 3.9103 | 3.9103 | 3.9103 |
| *c* |  | 12.7843 | 12.7843 | 12.7843 | 12.7843 |
| La: *x*  *y*  *z* |  | 0  0  0.3631 | 0  0  0.3631 | 0  0  0.3631 | 0  0  0.3631 |
| B(Å2) |  | 0.5 | 0.5 | 0.5 | 0 |
| Occ |  | 0.0625 | 0.0625 | 0.0625 | 0.125 |
| Ni: *x*  *y*  *z* |  | 0  0  0 | 0  0  0 | 0  0  0 | 0  0  0 |
| B(Å2) |  | 0.5 | 0.5 | 0.5 | 0 |
| Occ |  | 0.03125 | 0.03125 | 0.03125 | 0.0625 |
| O1: *x*  *y*  *z* |  | 0  0.5  0 | 0  0.5  0 | 0  0.5  0 | 0  0.5  0 |
| B(Å2) |  | 0.5 | 0.5 | 0.5 | 0 |
| Occ |  | 0.0625 | 0.0625 | 0.0625 | 0.125 |
| O2: *x*  *y*  *z* |  | 0  0  0.178 | 0  0  0.178 | 0  0  0.178 | 0  0  0.178 |
| B(Å2) |  | 0.5 | 0.5 | 0.5 | 0 |
| Occ |  | 0.0625 | 0.0625 | 0.0625 | 0.125 |
| Peak parameters |  | 1 | 1 | 1 |  |
| Asymmetry parameters |  | 0 | 0 | 0 |  |

The refined parameters are those with the corresponding standard uncertainties and both the peak and asymmetry parameters.

*a*: For cobalt containing perovskites: Ni0-Co0.

*b*: Ni0(ICSD: 53807).

*c*: La2O3(ICSD: 641603).

*d*: La2TiO5(ICSD: 261167).

*e*: Non-stoichiometric precursor for LN0.5T0.5O-1.8 is the same for the case of LN0.5T0.5O-10. On the other hand, Non-stoichiometric precursor for LN0.5T0.5O-10/LN0.5T0.45C0.05O-10/ LN0.45C0.05T0.5O-10 is Non-stoichiometric LN0.5T0.5O/ Non-stoichiometric LN0.5T0.45C0.05O-10/ Non-stoichiometric LN0.45C0.05T0.5O.

*f*: La2NiO4(ICSD: 98562).

Gráfico, Histograma

Descripción generada automáticamenteFigure S1. XRD profile of LN0.5T0.5O-1.8 after TPR at 625 °C.

Table SII. Atomic coordinates, unit-cell parameters, isotropic displacement parameter, the fraction of site occupancy, and the peak and asymmetry parameters for LN0.5T0.5O after reaction.

|  |  |  |
| --- | --- | --- |
| Parameter | LN0.5T0.5O-1.8 | ICSD (2017) |
| **Ni0 *a*** |  |  |
| *a* | 3.51664(314) | 3.54 |
| *b* | 3.51664(314) | 3.54 |
| *c* | 3.51664(314) | 3.54 |
| Ni: *x*  *y*  *z* | 0  0  0 | 0  0  0 |
| B(Å2) | 0.1 |  |
| Occ | 0.02083 | 0.02083 |
| Peak parameters | 1 |  |
| Asymmetry parameters | 0 |  |
| **La2O3 *b*** |  |  |
| *a* | 3.937 | 3.937 |
| *b* | 3.937 | 3.937 |
| *c* | 6.13 | 6.13 |
| La: *x*  *y*  *z* | 0.333  0.667  0.247 | 0.333  0.667  0.247 |
| B(Å2) | 1 |  |
| Occ | 0.16667 | 0.16667 |
| O1: *x*  *y*  *z* | 0  0  0 | 0  0  0 |
| B(Å2) | 1 |  |
| Occ | 0.08333 | 0.08333 |
| O2: *x*  *y*  *z* | 0.333  0.667  0.645 | 0.333  0.667  0.645 |
| B(Å2) | 1 |  |
| Occ | 0.16667 | 0.16667 |
| Peak parameters | 1 |  |
| Asymmetry parameters | 0 |  |
| **Non-stoichiometric LN0.5T0.5O** |  |  |
| *a* | 3.92274(345) |  |
| *b* | 3.92274(345) |  |
| *c* | 3.92274(345) |  |
| La: *x*  *y*  *z* | 0  0  0 |  |
| B(Å2) | 1.5 |  |
| Occ | 0.01042 |  |
| Ni: *x*  *y*  *z* | 0.5  0.5  0.5 |  |
| B(Å2) | 1 |  |
| Occ | 0.00521 |  |
| Ti: *x*  *y*  *z* | 0.5  0.5  0.5 |  |
| B(Å2) | 1 |  |
| Occ | 0.00521 |  |
| O1: *x*  *y*  *z* | 0.5  0.5  0 |  |
| B(Å2) | 1 |  |
| Occ | 0.03125 |  |
| Peak parameters | 2 |  |
| Asymmetry parameters | 4 |  |

The refined parameters are those with the corresponding standard uncertainties and both the peak and asymmetry parameters.

a: Ni0(ICSD: 53807).

b: La2O3(ICSD: 641603).

Table SIII. Phase analysis results, conventional discrepancy factors from Rietveld refinement of powder XRD data, H2 uptake, and RD calculated using Rietveld Refinement (RDRR) for LN0.5T0.5O after reaction.

|  |  |
| --- | --- |
|  | LN0.5T0.5O |
| **Ni0** |  |
| Scale factor (1 x 104) | 0.40466(8457) |
| Composition (wt.%) | 3.22(0.69) |
| *R*bragg (%) | 4.15 |
| **La2O3** |  |
| Scale factor (1 x 105) | 25.3512(2.3626) |
| Composition (wt.%) | 53.02(5.62) |
| *R*bragg (%) | 8.47 |
| **Non-stoichiometric LN0.5T0.5O** |  |
| Scale factor  (1 x 103) | 1.546965(31423) |
| Composition (wt.%) | 43.76(2.39) |
| *R*bragg (%) | 4.15 |
| *R*p (%)  *R*wp (%)  *χ*2 | 23.2  29  1.3 |
| RDRR | 26.35 |

Thestandard uncertainty refers only to the mantissa and not to the exponent of the value.

**Reference**

ICSD (**2017**). “Inorganic Crystal Structure Database”. Available at <https://bdec.dotlib.com.br/>.