

Supporting Information

Table 1

A- Ceramic Electrolytes

| LLTO (LeBail) Cmmm | | | | | | |
|--------------------|--------|----------|----------|----------|-----------|----------|
| Temperature /°C | Rwp /% | a /Å | b /Å | c /Å | Mustrain | Size /nm |
| 30 | 8.10 | 7.753(1) | 7.803(1) | 7.706(1) | 2147(172) | 219(22) |
| 100 | 8.57 | 7.758(1) | 7.803(1) | 7.714(1) | 1962(173) | 206(20) |
| 200 | 8.87 | 7.764(1) | 7.808(1) | 7.723(1) | 2014(176) | 216(22) |
| 300 | 9.14 | 7.771(1) | 7.816(1) | 7.728(1) | 2035(173) | 227(24) |
| 400 | 9.48 | 7.778(1) | 7.819(1) | 7.739(1) | 2086(176) | 244(28) |
| 500 | 9.62 | 7.786(1) | 7.828(1) | 7.747(1) | 2118(172) | 256(30) |
| 600 | 9.85 | 7.794(1) | 7.835(1) | 7.756(1) | 1658(164) | 218(21) |
| 700 | 10.14 | 7.802(1) | 7.844(1) | 7.764(1) | 1762(172) | 223(23) |
| 800 | 10.45 | 7.810(1) | 7.851(1) | 7.773(1) | 2112(177) | 303(42) |
| 900 | 10.58 | 7.818(1) | 7.864(1) | 7.778(1) | 2577(53) | 427(96) |
| 1000 | 9.69 | 7.827(1) | 7.840(1) | 7.821(1) | 872(107) | 392(39) |
| 30 (retour) | 7.72 | 7.742(1) | 7.768(1) | 7.756(1) | 1883(106) | 630(101) |

| Al-LLZO (Le Bail) <i>I-43d</i> | | | | | La2Zr2O7 (Le Bail) <i>Fd-3m</i> | | |
|--------------------------------|--------|-----------|-----------|----------|---------------------------------|----------|----------|
| Temperature /°C | Rwp /% | a /Å | Mustrain | Size /nm | a /Å | Mustrain | Size /nm |
| 30 | 12.74 | 12.970(1) | 2626(136) | 84(1) | | | |
| 100 | 14.74 | 13.003(1) | 4400(263) | 53(1) | | | |
| 200 | 12.04 | 13.036(1) | 841(167) | 52(1) | | | |
| 300 | 12.60 | 13.045(1) | 481(150) | 55(1) | | | |
| 400 | 11.71 | 13.047(1) | 114(131) | 57(1) | | | |
| 500 | 11.34 | 13.056(1) | -201(139) | 63(1) | 10.897(1) | | 53(2) |
| 600 | 11.24 | 13.076(1) | 905(62) | 124(2) | 10.910(1) | | 51(1) |
| 700 | 12.24 | 13.099(1) | 1001(47) | 171(3) | 10.912(1) | | 69(2) |
| 800 | 12.56 | 13.123(1) | 896(49) | 200(5) | 10.898(1) | | 73(3) |
| 900 | 12.68 | 13.144(1) | 718(49) | 228(7) | 10.905(1) | | 57(3) |
| 1000 | 11.97 | 13.164(1) | 900(49) | 303(11) | 10.913(1) | | 117(5) |
| 30 (retour) | 10.79 | 12.962(1) | 1001(58) | 244(9) | 10.810(1) | | 78(2) |

| LATP (Le Bail) R-3c | | | | | |
|----------------------------|---------------|-------------|-------------|-----------------|-----------------|
| Temperature /°C | Rwp /% | a /Å | c /Å | Mustrain | Size /nm |
| 30 | 8.29 | 8.505(1) | 20.800(1) | 1063(78) | 201(6) |
| 100 | 8.85 | 8.501(1) | 20.850(1) | 1108(82) | 206(7) |
| 200 | 8.91 | 8.501(1) | 20.909(1) | 1280(81) | 219(8) |
| 300 | 10.44 | 8.501(1) | 20.970(1) | 1242(90) | 224(9) |
| 400 | 11.49 | 8.502(1) | 21.034(1) | 1243(95) | 229(10) |
| 500 | 9.29 | 8.504(1) | 21.099(1) | 856(67) | 199(5) |
| 600 | 10.76 | 8.503(1) | 21.159(1) | 1079(70) | 254(9) |
| 700 | 10.17 | 8.504(1) | 21.225(1) | 593(53) | 253(7) |
| 800 | 12.40 | 8.504(1) | 21.297(1) | 934(103) | 219(12) |
| 900 | 13.23 | 8.505(1) | 21.365(1) | 660(144) | 158(9) |
| 1000 | 15.24 | 8.506(1) | 21.430(1) | 715(198) | 139(9) |
| 30 (retour) | 10.39 | 8.507(2) | 20.800(3) | 1388(272) | 106(8) |

B- Active material

| NMC111 (Rietveld) R-3m | | | | | |
|-------------------------------|---------------|-------------|-------------|-----------------|-----------------|
| Temperature /°C | Rwp /% | a /Å | c /Å | Mustrain | Size /nm |
| 30 | 3.29 | 2.859(1) | 14.231(1) | 2383(62) | 275(10) |
| 100 | 3.67 | 2.862(1) | 14.249(1) | 2289(67) | 270(10) |
| 200 | 3.68 | 2.865(1) | 14.277(1) | 2115(65) | 268(10) |
| 300 | 3.58 | 2.869(1) | 14.306(1) | 1948(61) | 262(9) |
| 400 | 3.54 | 2.874(1) | 14.337(1) | 1660(59) | 239(7) |
| 500 | 3.33 | 2.878(1) | 14.368(1) | 1617(56) | 247(7) |
| 600 | 3.44 | 2.883(1) | 14.401(1) | 1575(57) | 256(8) |
| 700 | 4.22 | 2.889(1) | 14.436(1) | 41723(113) | 357(25) |
| 800 | 4.41 | 2.899(1) | 14.483(1) | 5284(134) | 493(55) |
| 900 | 3.71 | 2.909(1) | 14.523(1) | 999(62) | 221(7) |
| 1000 | 3.89 | 2.923(1) | 14.564(1) | 343(58) | 207(6) |
| 30 (retour) | 3.54 | 2.860(1) | 14.231(1) | 1791(38) | 529(20) |

| NMC532 (Rietveld) R-3m | | | | | |
|---|--------|----------|-----------|-----------|----------|
| Temperature /°C | Rwp /% | a /Å | c /Å | Mustrain | Size /nm |
| 30 | 3.78 | 2.870(1) | 14.239(1) | 1754(59) | 298(11) |
| 100 | 3.82 | 2.873(1) | 14.259(1) | 1986(63) | 322(13) |
| 200 | 3.84 | 2.876(1) | 14.288(1) | 1753(61) | 303(12) |
| 300 | 3.81 | 2.881(1) | 14.316(1) | 1631(59) | 297(11) |
| 400 | 3.71 | 2.885(1) | 14.347(1) | 1332(55) | 264(8) |
| 500 | 3.66 | 2.889(1) | 14.378(1) | 1204(52) | 263(8) |
| 600 | 3.68 | 2.894(1) | 14.410(1) | 1129(53) | 259(8) |
| 700 | 4.37 | 2.899(1) | 14.440(1) | 3290(97) | 375(25) |
| 800 | 4.77 | 2.907(1) | 14.472(1) | 4309(122) | 585(73) |
| 900 | 5.12 | 2.917(1) | 14.516(1) | 4305(140) | 521(67) |
| 1000 | 5.50 | 2.929(1) | 14.546(1) | 132(81) | 206(8) |
| 30 (retour) | 4.95 | 2.877 | 14.262 | 1133 | 220 |
| 30 (retour dans un four ex-situ) | 5.40 | 2.880(1) | 14.273(1) | | |

| NCA (Le Bail) R-3m | | | | | |
|---|--------|-----------|-----------|----------|----------|
| Temperature /°C | Rwp /% | a /Å | c /Å | Mustrain | Size /nm |
| 30 | 2.75 | 2.866(1) | 14.190(1) | 2129(51) | 213(5) |
| 100 | 2.75 | 2.867 (1) | 14.213(1) | 2212(52) | 212(5) |
| 200 | 2.68 | 2.870 (1) | 14.242(1) | 2485(52) | 238(6) |
| 300 | 2.53 | 2.875 (1) | 14.263(1) | 2414(49) | 244(6) |
| 400 | 2.43 | 2.879 (1) | 14.295(1) | 2203(46) | 237(5) |
| 500 | 2.49 | 2.884(1) | 14.327(1) | 1946(46) | 230(5) |
| 600 | 2.57 | 2.888(1) | 14.360(1) | 2007(48) | 242(6) |
| 700 | 2.81 | 2.895 (1) | 14.394(1) | 2899(61) | 297(10) |
| 800 | 2.69 | 2.904(1) | 14.424(1) | 1976(52) | 273(8) |
| 900 | 3.00 | 2.917 (1) | 14.450(1) | 869(51) | 298(11) |
| 30 (retour dans un four ex-situ) | 2.56 | 2.873(1) | 14.192(1) | 2319(34) | 663(27) |

| LFP (Rietveld) <i>Pnma</i> | | | | | | |
|----------------------------|--------|------------|----------|----------|-----------|----------|
| Temperature /°C | Rwp /% | a /Å | b /Å | c /Å | Mustrain | Size /nm |
| 30 | 8.78 | 10.321(1) | 6.001(1) | 4.693(1) | 1693(259) | 114(7) |
| 100 | 7.70 | 10.330(1) | 6.006(1) | 4.698(1) | 2088(210) | 118(6) |
| 200 | 7.43 | 10.345 (1) | 6.015(1) | 4.707(1) | 2090(189) | 118(6) |
| 300 | 7.32 | 10.359(1) | 6.025(1) | 4.716(1) | 2133(184) | 118(5) |
| 400 | 7.31 | 10.373(1) | 6.037(1) | 4.727(1) | 2110(182) | 113(5) |
| 500 | 7.38 | 10.387(1) | 6.049(1) | 4.738(1) | 1816(181) | 106(4) |
| 600 | 7.63 | 10.402(1) | 6.062(1) | 4.749(1) | 1829(191) | 104(4) |
| 700 | 8.32 | 10.417(1) | 6.075(1) | 4.760(1) | 4557(319) | 99(6) |
| 800 | 9.05 | 10.434(1) | 6.089(1) | 4.772(1) | 4552(295) | 198(22) |
| 30 (retour) | 8.63 | 10.346(1) | 6.003(1) | 4.693(1) | 732(218) | 146(11) |

| LFMP (Rietveld) <i>Pnma</i> | | | | | | |
|-----------------------------|--------|-----------|----------|----------|-----------|----------|
| Temperature /°C | Rwp /% | a /Å | b /Å | c /Å | Mustrain | Size /nm |
| 30 | 9.07 | 10.414(1) | 6.074(1) | 4.728(1) | -957(279) | 53(2) |
| 100 | 7.75 | 10.423(1) | 6.079(1) | 4.733(1) | -653(219) | 53(1) |
| 200 | 7.42 | 10.439(1) | 6.087(1) | 4.742(1) | -501(193) | 55(1) |
| 300 | 7.33 | 10.455(1) | 6.097(1) | 4.751(1) | -222(187) | 57(1) |
| 400 | 7.11 | 10.470(1) | 6.107(1) | 4.761(1) | -268(177) | 57(1) |
| 500 | 7.23 | 10.486(1) | 6.118(1) | 4.771(1) | -195(178) | 58(1) |
| 600 | 7.17 | 10.502(1) | 6.129(1) | 4.781(1) | 12(171) | 60(1) |
| 700 | 8.15 | 10.517(1) | 6.140(1) | 4.791(1) | 3004(201) | 126(6) |
| 800 | 9.46 | 10.537(1) | 6.155(1) | 4.803(1) | 2626(199) | 170(12) |
| 30 (retour) | 7.66 | 10.412(1) | 6.073(1) | 4.727(1) | 15(142) | 123(5) |

| FP (Rietveld) <i>Pnma</i> | | | | | | |
|---------------------------|--------|----------|----------|----------|-----------|----------|
| Temperature /°C | Rwp /% | a /Å | b /Å | c /Å | Mustrain | Size /nm |
| 30 | 8.35 | 9.818(1) | 5.790(1) | 4.781(1) | 1130(198) | 130(8) |
| 100 | 7.80 | 9.819(1) | 5.796(1) | 4.784(1) | 809(155) | 123(6) |
| 200 | 7.64 | 9.825(1) | 5.807(1) | 4.789(1) | 891(147) | 119(5) |
| 300 | 7.66 | 9.831(1) | 5.819(1) | 4.795(1) | 1128(142) | 129(5) |
| 400 | 7.68 | 9.836(1) | 5.831(1) | 4.801(1) | 1000(139) | 128(5) |
| 500 | 7.32 | 9.840(1) | 5.841(1) | 4.807(1) | 793(140) | 130(5) |
| 600 | | | | | | |
| 700 | | | | | | |
| 800 | | | | | | |
| 30 (retour) | | | | | | |

| LNMO | | Spinel (LeBail) <i>Fd-3m</i> | | Rock salt (Le Bail) <i>Fm-3m</i> | | |
|--------|----------|------------------------------|----------|----------------------------------|----------|----------|
| Rwp /% | a /Å | Mustrain | Size /nm | a /Å | Mustrain | Size /nm |
| 5.23 | 8.174(1) | 1961(196) | 41.4(8) | | | |
| 5.22 | 8.179(1) | 2362(195) | 42.5(8) | | | |
| 5.20 | 8.187(1) | 1740(194) | 40.1(7) | | | |
| 5.09 | 8.196(1) | 2077(188) | 41.9(7) | | | |
| 5.03 | 8.207(1) | 1614(184) | 41.1(7) | | | |
| 4.91 | 8.220(1) | 2379(183) | 42.9(7) | | | |
| 4.79 | 8.236(1) | 1345(169) | 42.7(7) | | | |
| 6.94 | 8.268(1) | 4567(154) | 157(7) | 4.1884(3) | | |
| 9.88 | 8.299(1) | | 46.6(7) | 4.1885(3) | | |
| 9.65 | 8.405(1) | | 30.9(5) | 4.2106(3) | | |
| 6.46 | 8.504(2) | | | 4.23546(7) | | |
| 6.42 | 8.206(1) | 1133 | 117 | | | |

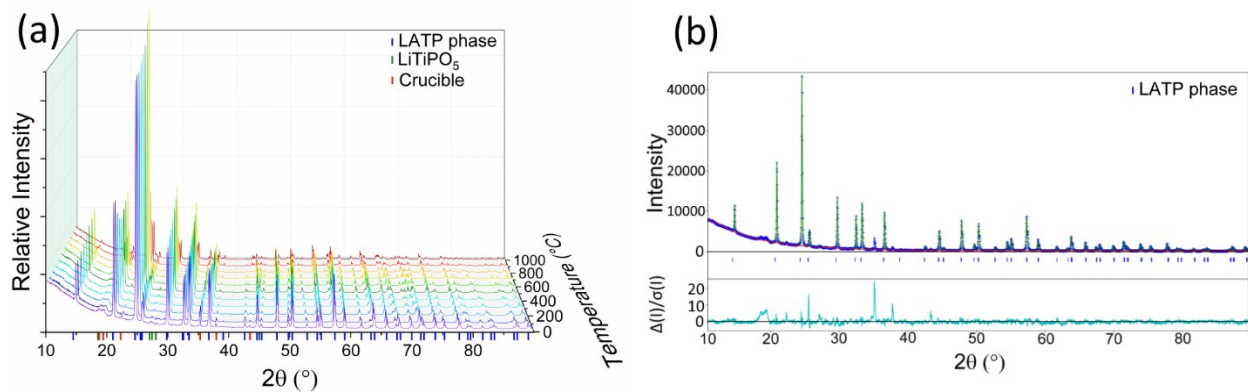


Fig. SI-1: (a) Diffractograms of LATP between 30 and 1000°C and (b) Fit of diffractogram of LATP at 30°C using Le Bail refinement.

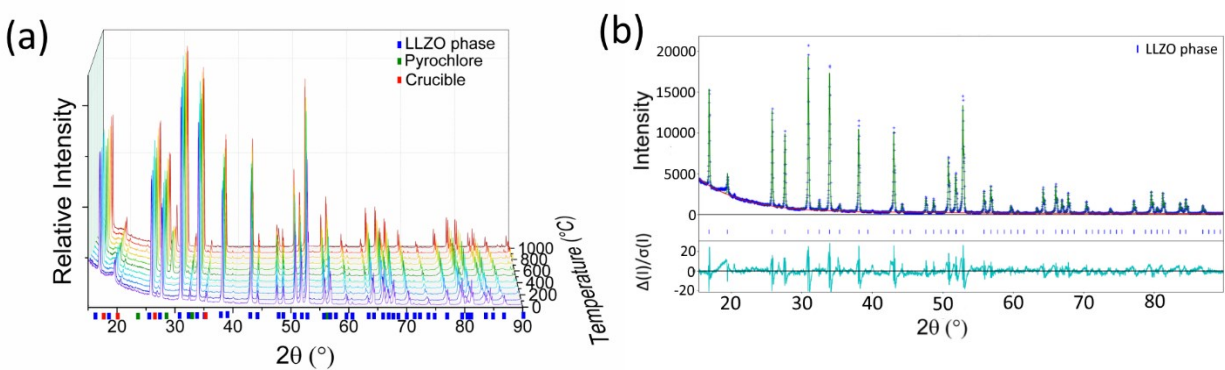


Fig. SI-2: (a) Diffractograms of LLZO between 30 and 1000°C and (b) Fit of diffractogram of LLZO at 30°C using Le Bail refinement.

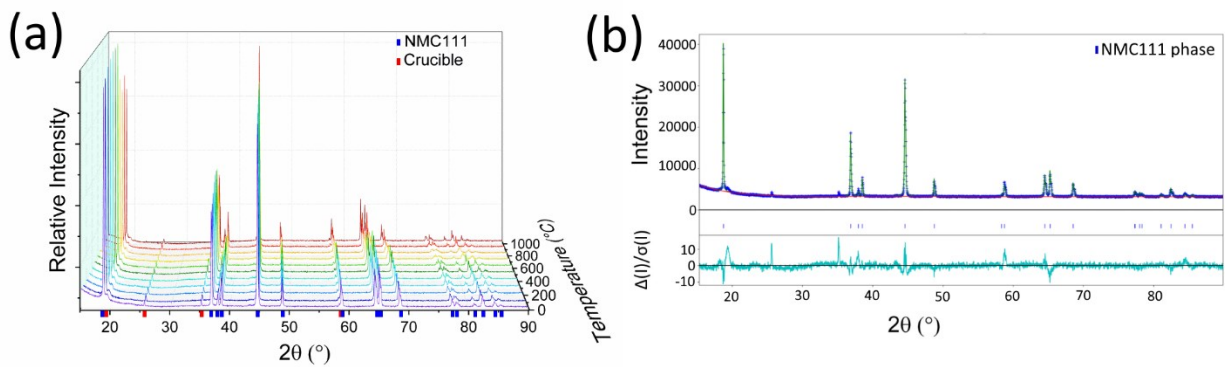


Fig. SI-3: (a) Diffractograms of NMC111 between 30 and 1000°C and (b) Fit of diffractogram of NMC111 at 30°C using Rietveld refinement.

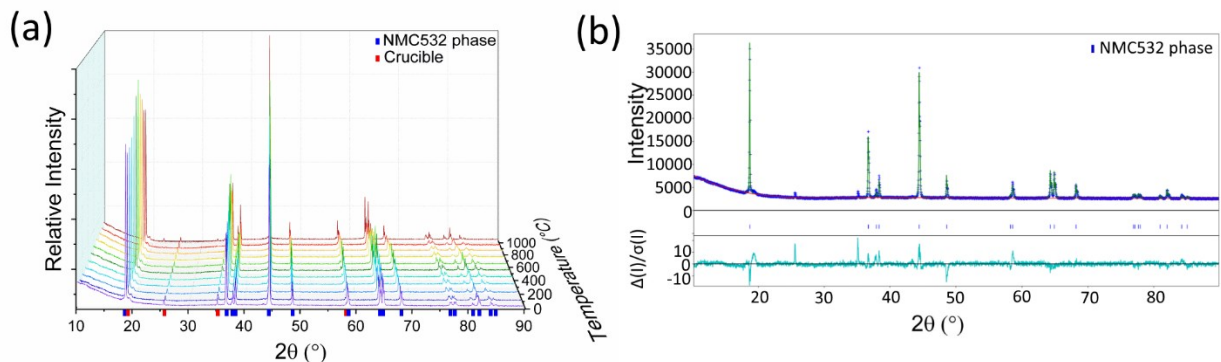


Fig. SI-4: (a) Diffractograms of NMC532 between 30 and 1000°C and (b) Fit of diffractogram of NMC532 at 30°C using Rietveld refinement.

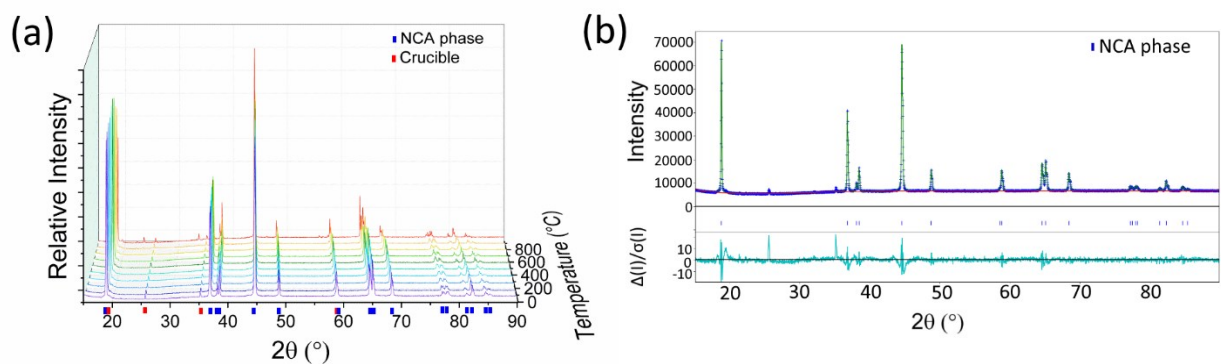


Fig. SI-5: (a) Diffractograms of NCA between 30 and 900°C and (b) Fit of diffractogram of NCA at 30°C using Le Bail refinement.

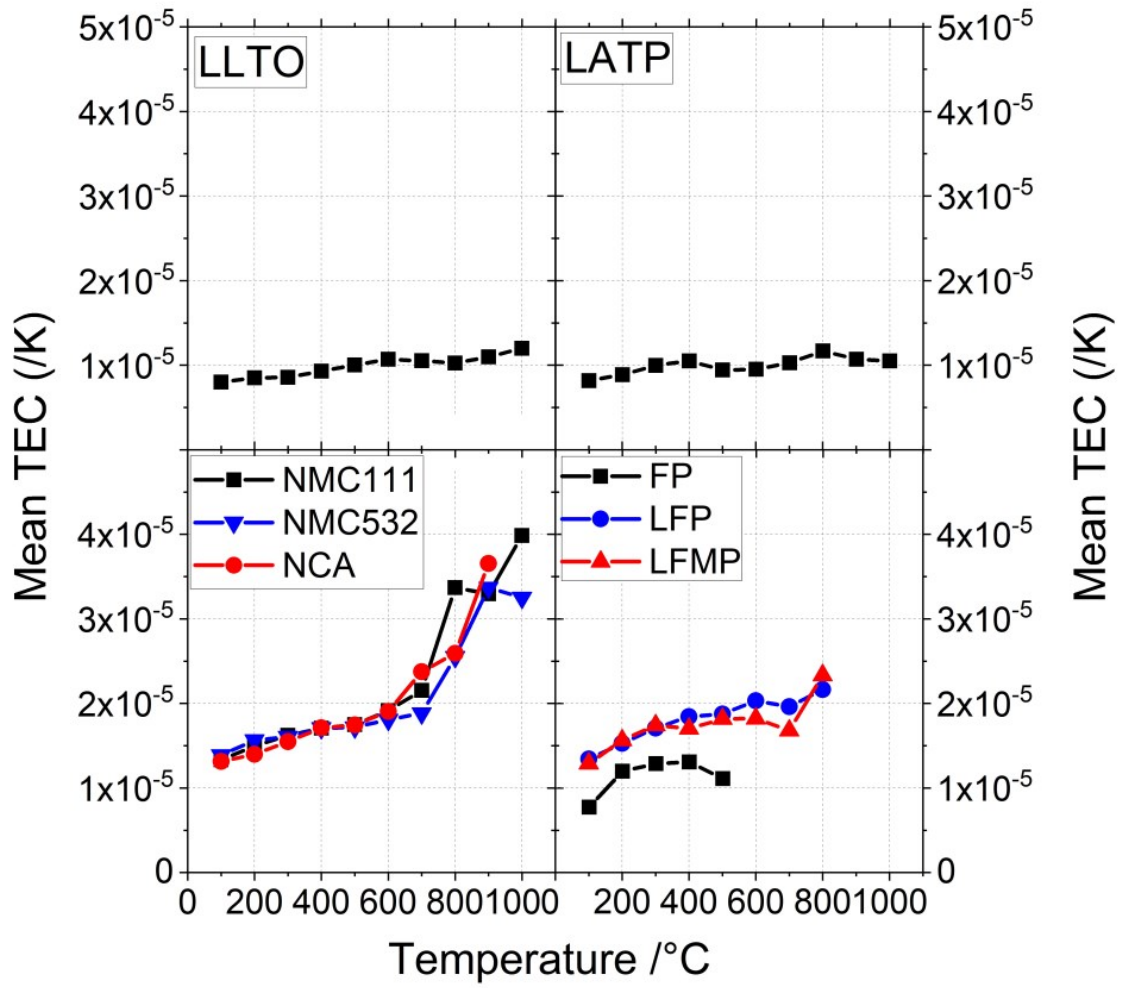


Fig. SI-6

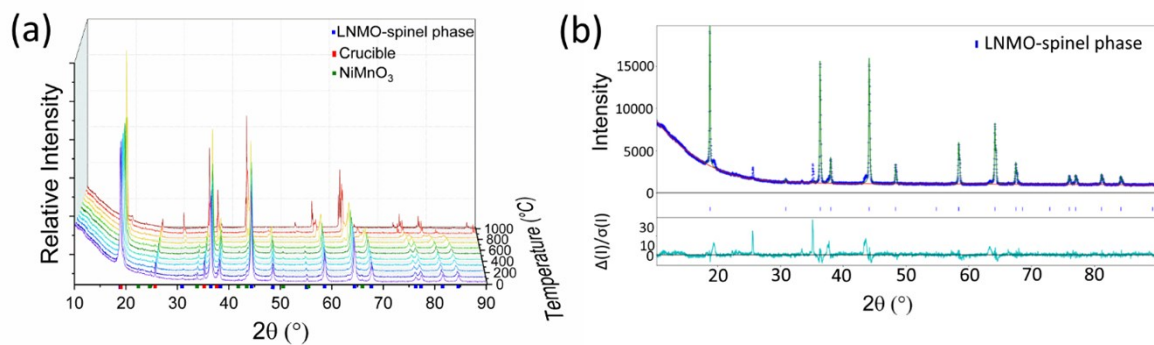


Fig. SI-7: (a) Diffractograms of LNMO between 30 and 1000°C and (b) Fit of diffractogram of LNMO at 30°C using Le Bail refinement.

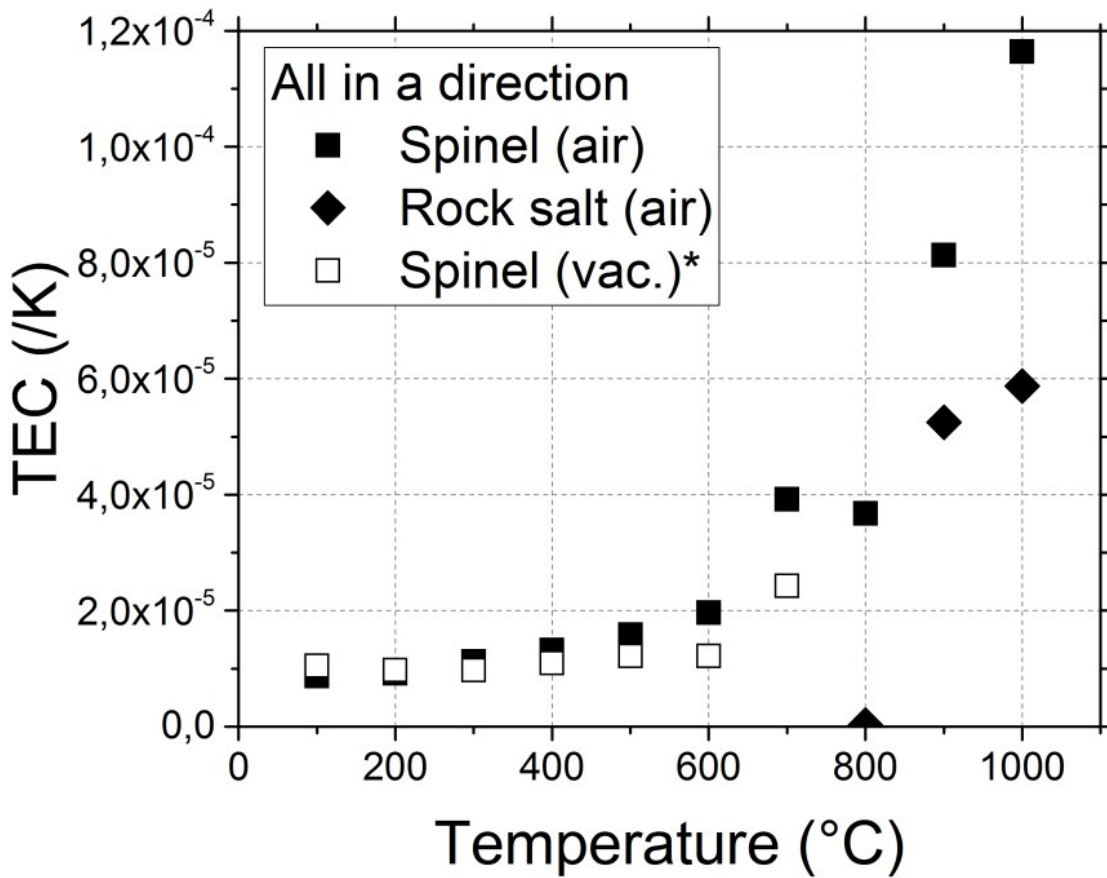


Fig. SI-8

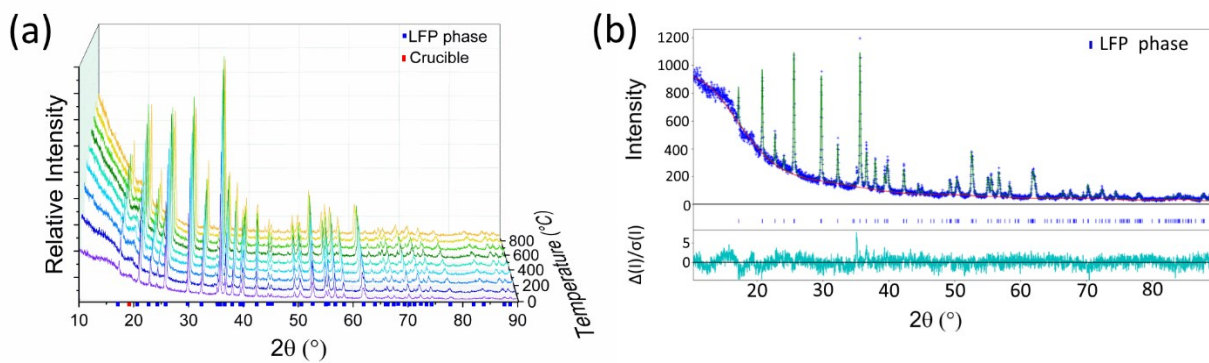


Fig. SI-9: (a) Diffractograms of LFP between 30 and 800°C and (b) Fit of diffractogram of LFP at 30°C using Rietveld refinement.

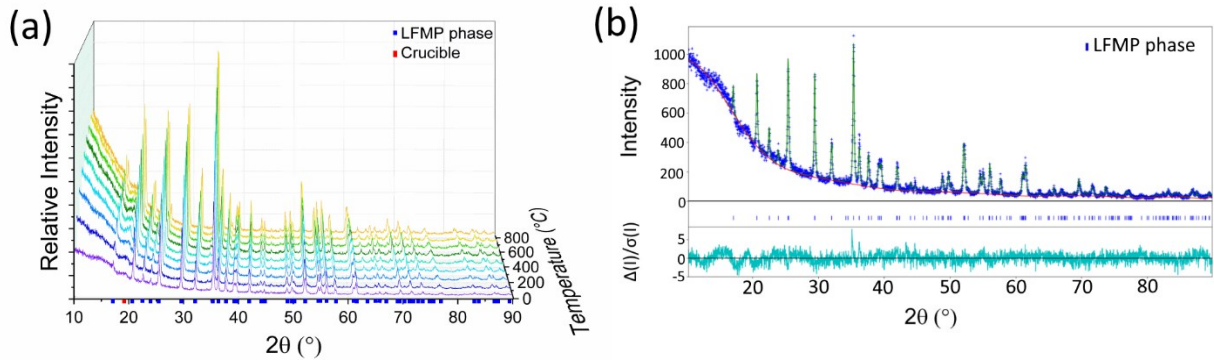


Fig. SI-10: (a) Diffractograms of LFMP between 30 and 1000°C and (b) Fit of diffractogram of LFMP at 30°C using Rietveld refinement.

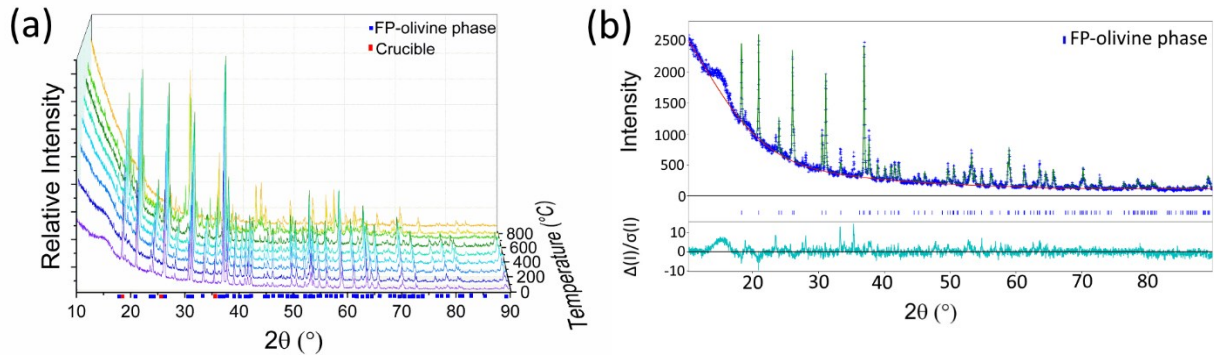


Fig. SI-11: (a) Diffractograms of FP between 30 and 1000°C and (b) Fit of diffractogram of FP at 30°C using Rietveld refinement.