Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary information

In situ powder X-ray diffraction study of the hydro-thermal formation of $LiMn_2O_4$ nanocrystallites

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Table of Contents

Disordered and ordered δ-MnO_2

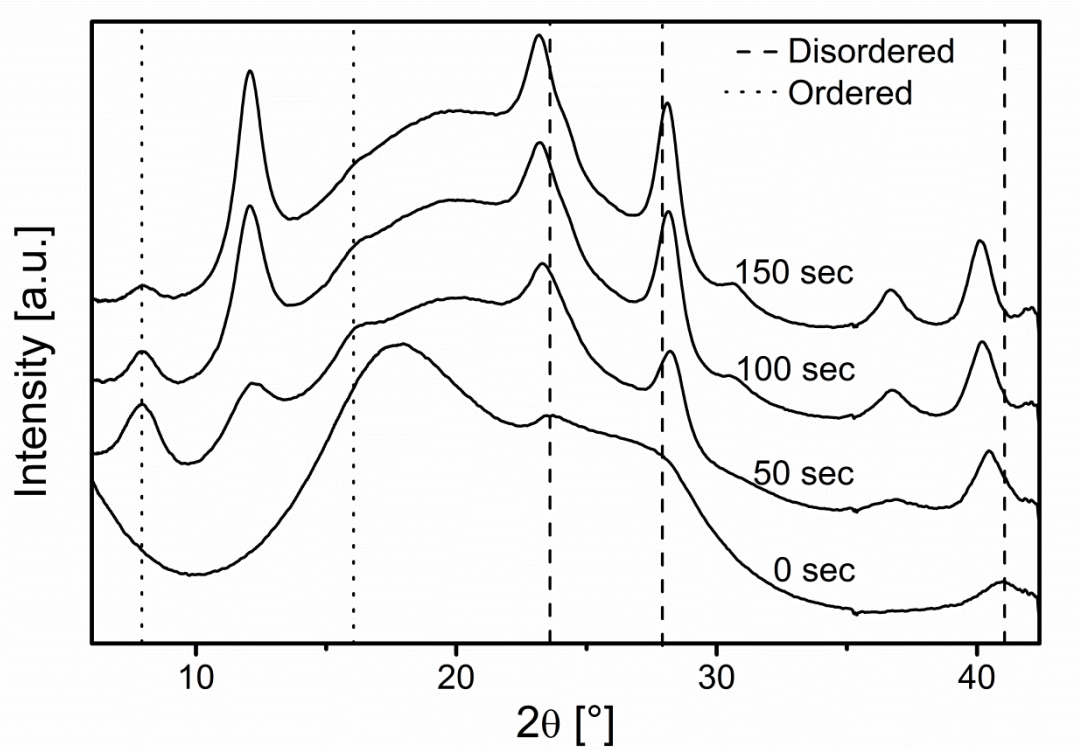

Fig. S1 Appearance and disappearance of ordered δ-MnO_2 shortly after reaction initiation at 220°C. Note that unmarked Bragg reflections in the PXRD frames after reaction initiation stem from LMO that coexists with the ordered δ-MnO2-phase.

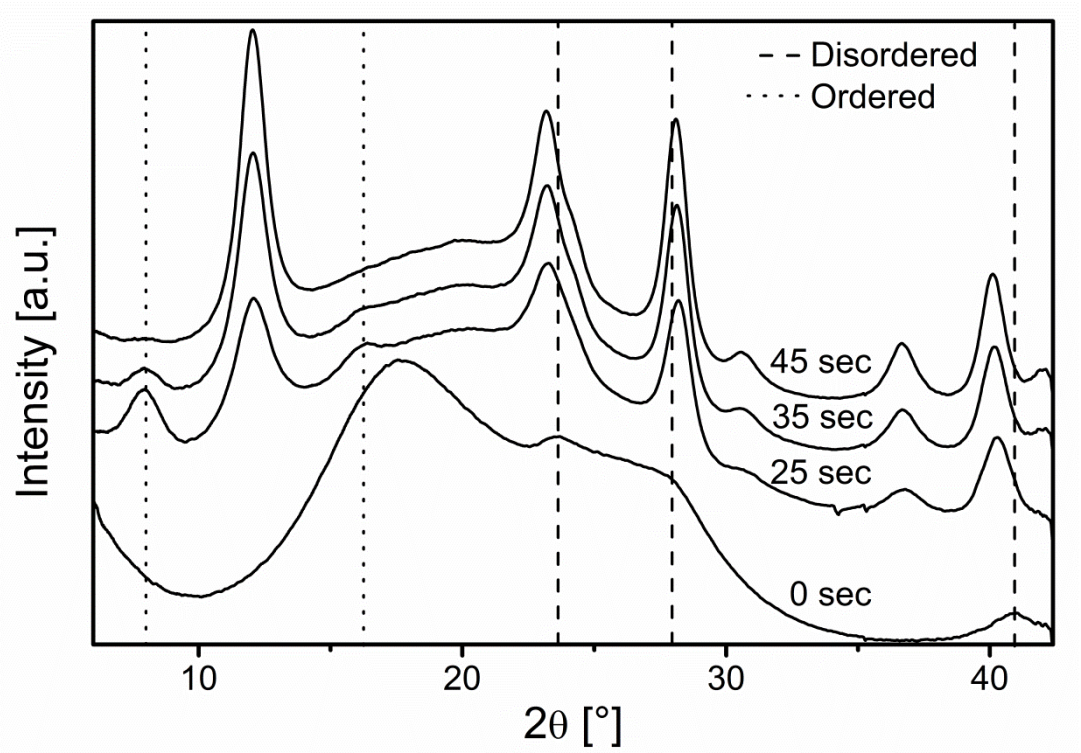

Fig. S2 Appearance and disappearance of ordered δ-MnO_2 shortly after reaction initiation at 260°C. Note that unmarked Bragg reflections in the PXRD frames after reaction initiation stem from LMO that coexists with the ordered δ-MnO2-phase.

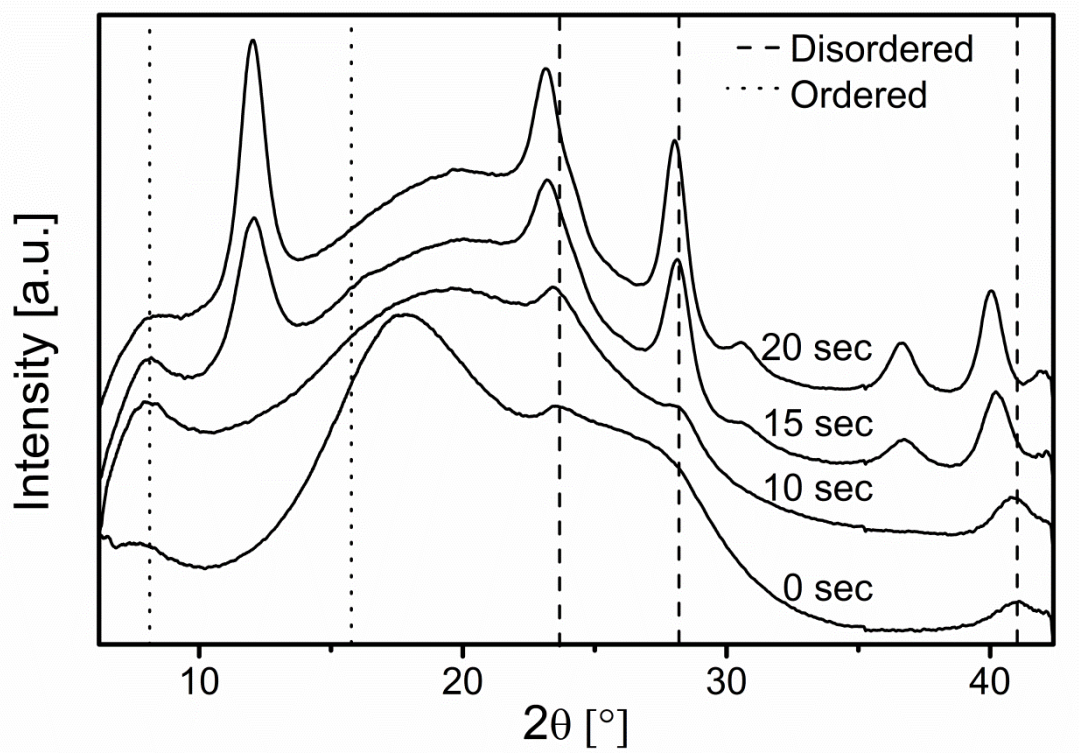

Fig. S3 Appearance and disappearance of ordered δ-MnO_2 shortly after reaction initiation at 300°C. Note that unmarked Bragg reflections in the PXRD frames after reaction initiation stem from LMO that coexists with the ordered δ-MnO2-phase.

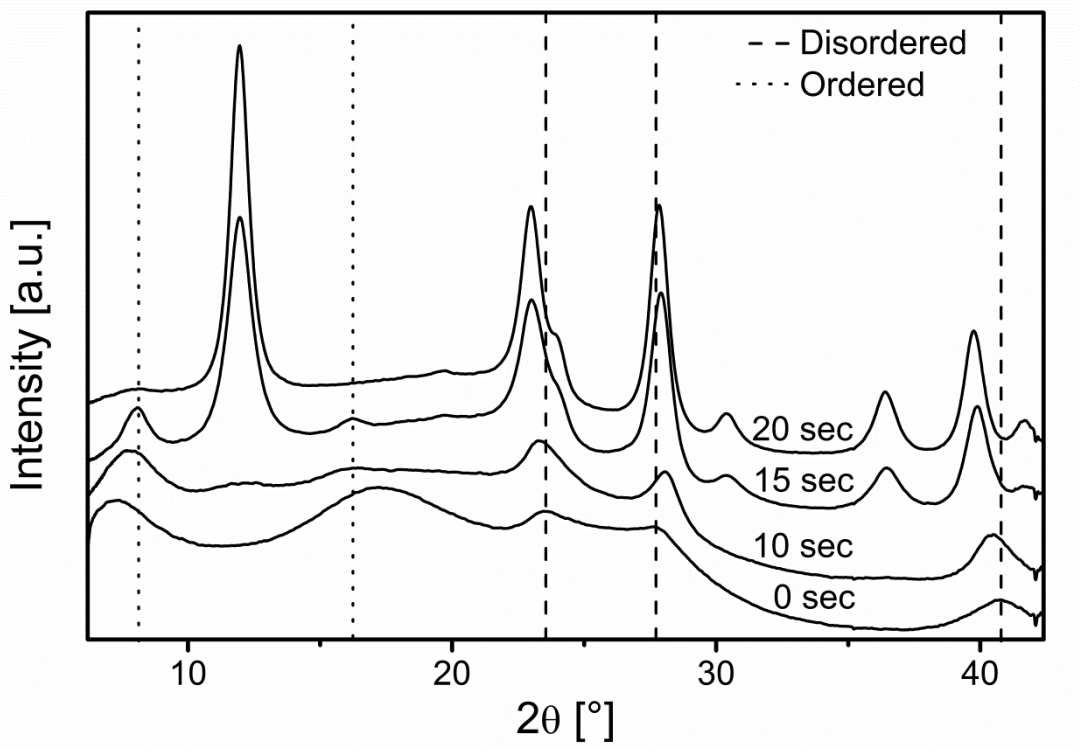

Fig. S4 Appearance and disappearance of ordered δ-MnO_2 shortly after reaction initiation at 350°C. Note that unmarked Bragg reflections in the PXRD frames after reaction initiation stem from LMO that coexists with the ordered δ-MnO2-phase.

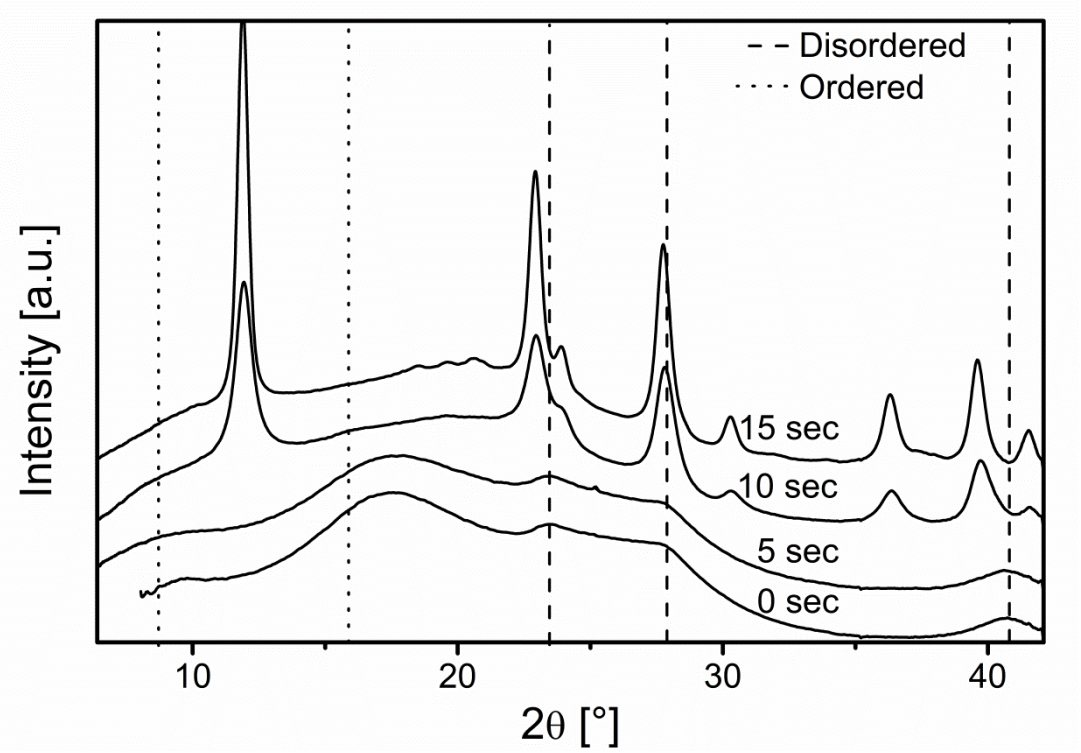

Fig. S5 No appearance of ordered δ-MnO_2 shortly after reaction initiation at 400°C. Note that unmarked Bragg reflections in the PXRD frames after reaction initiation stem from LMO that coexists with the ordered δ-MnO2-phase.

Time resolved PXRD

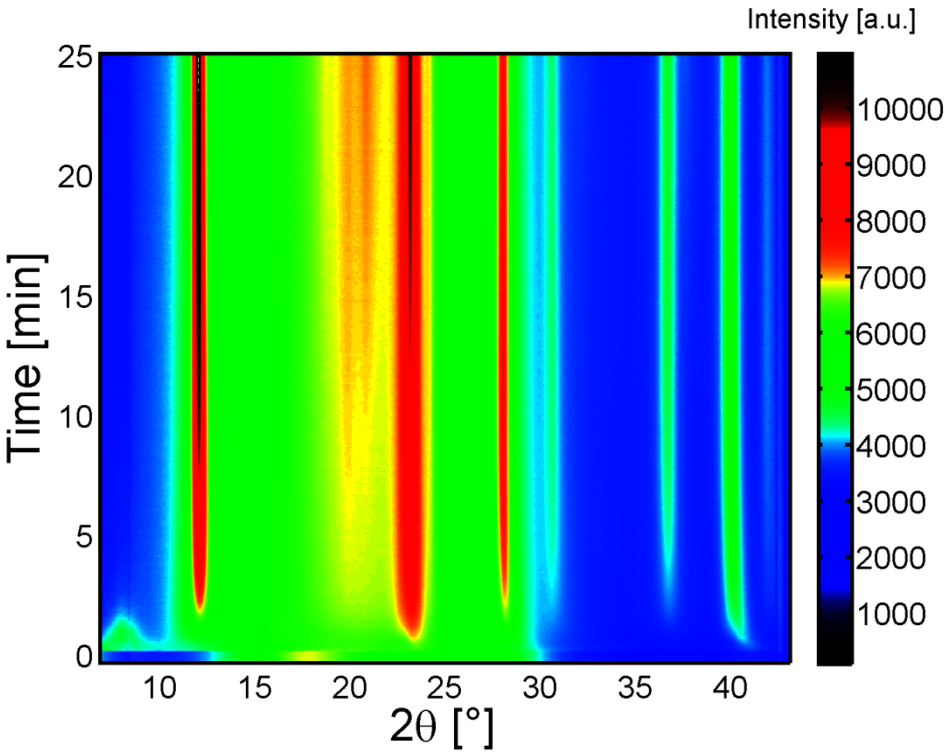

Fig. S6 Time resolved PXRD for reaction at 220°C.

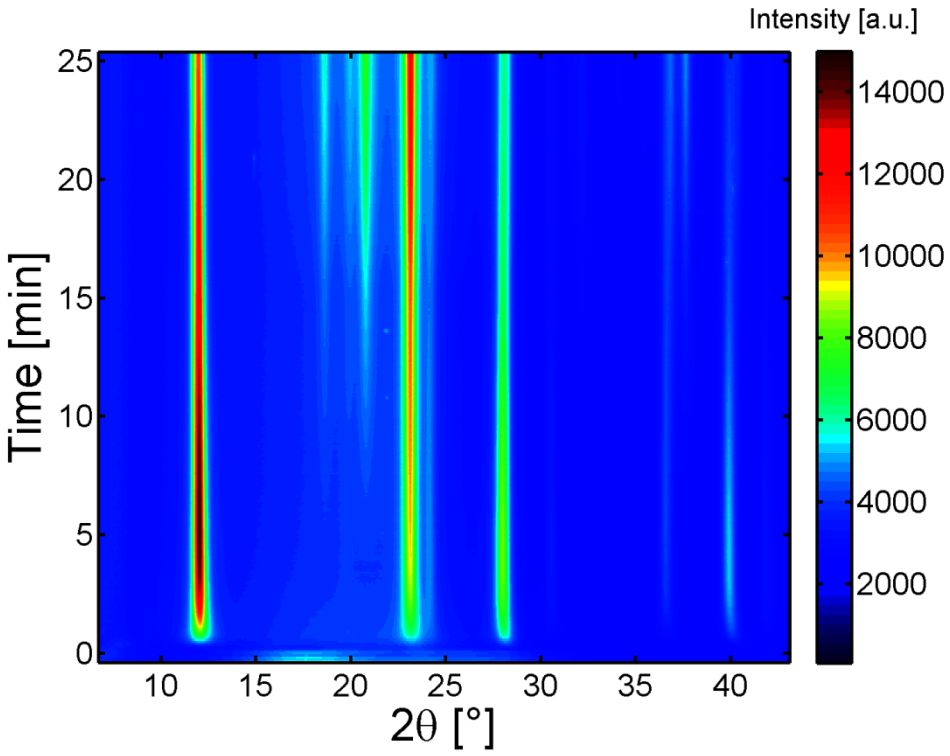

Fig. S7 Time resolved PXRD for reaction at 260°C.

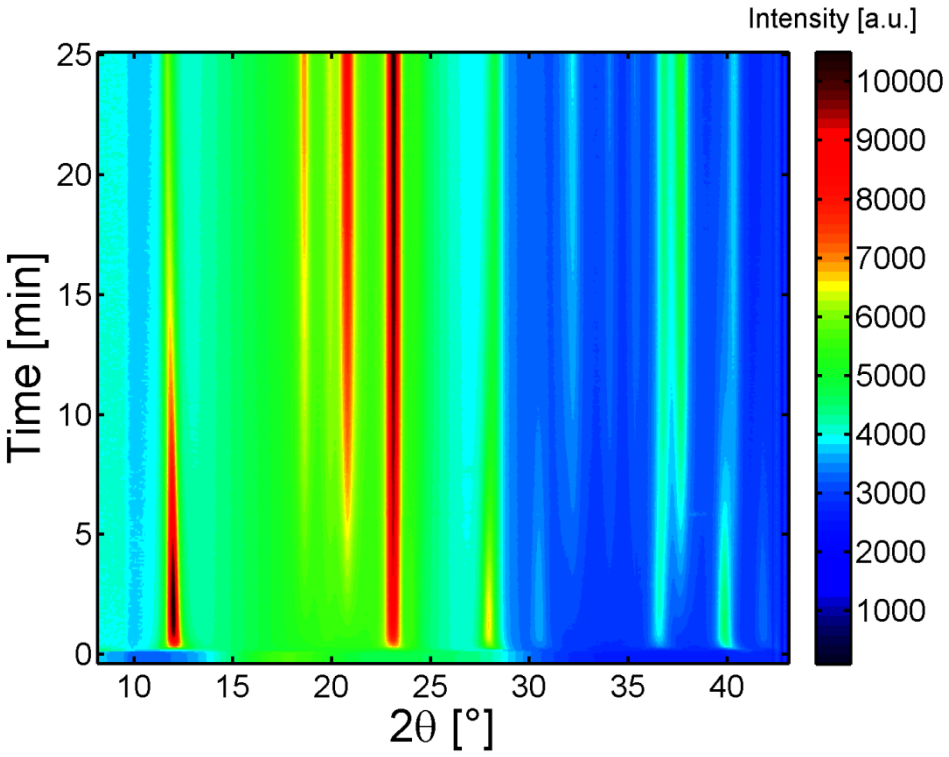

Fig. S8 Time resolved PXRD for reaction at 300°C.

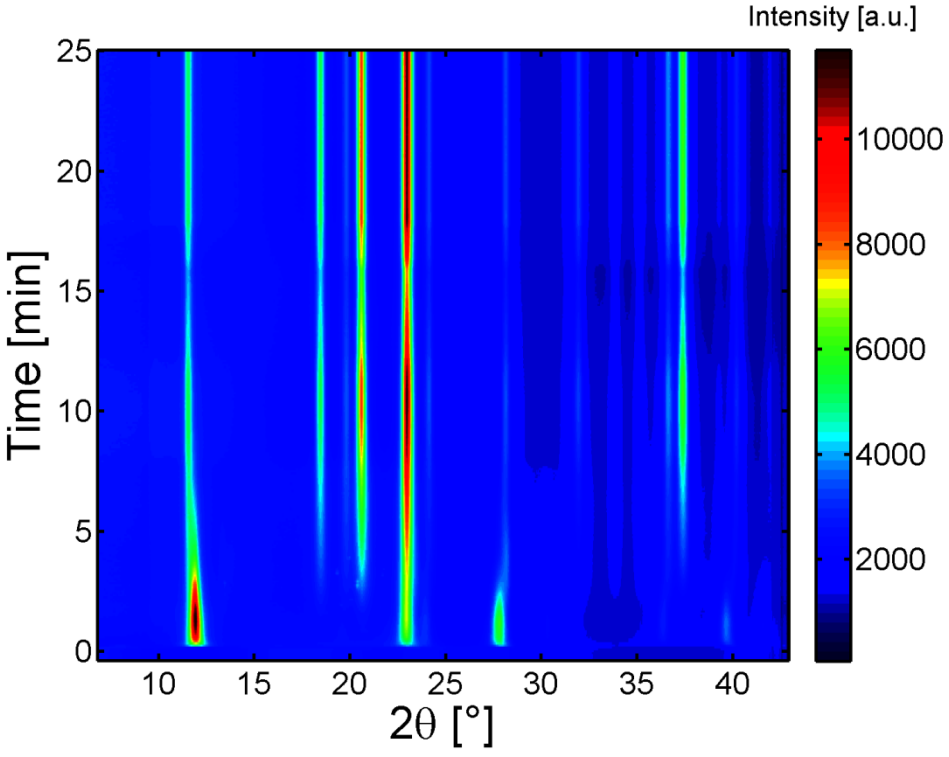

Fig. S9 Time resolved PXRD for reaction at 350°C.

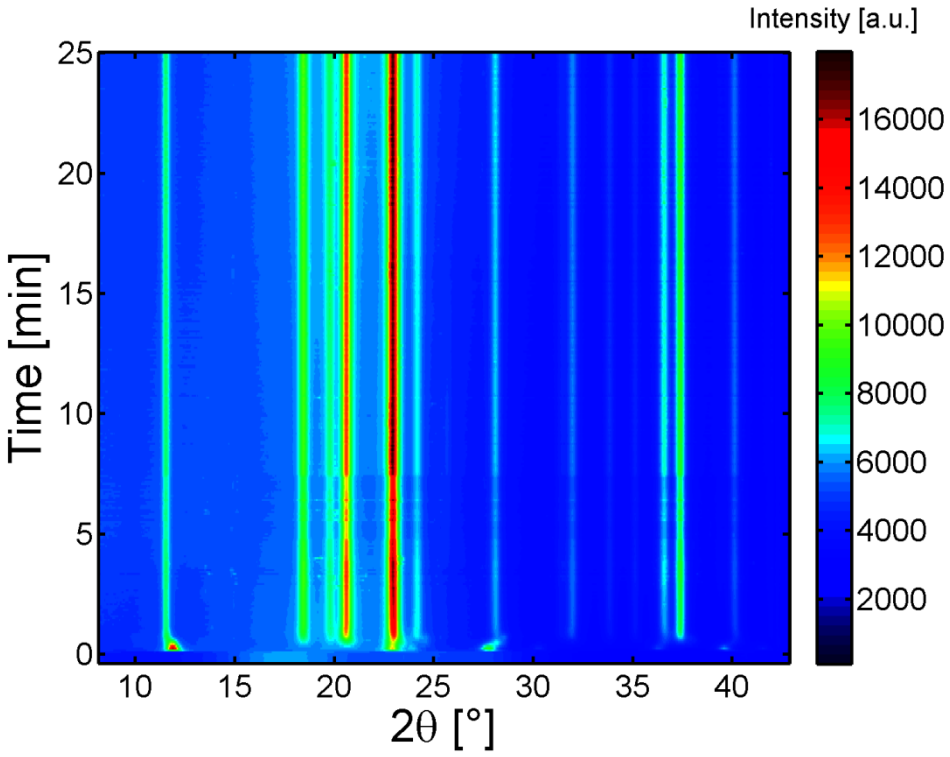

Fig. S10 Time resolved PXRD for reaction at 400°C.

Balanced chemical reactions

(1) $2LiOH_{(aq)} + 4KMnO_{4(aq)} + 3CH_3CH_2OH_{(l)} + 4xH_2O_{(l)} \xrightarrow{\Delta} 4\,\delta - MnO_2 \cdot (^1/_2\,LiOH, KOH, xH_2O)_{(s)} + 3CH_3COOH_{(l)} + H_2O_{(l)}$

(2) $8\delta - MnO_2 \cdot (^1/_2\,LiOH, KOH, xH_2O)_{(s)} + CH_3CH_2OH_{(l)} \xrightarrow{\Delta} 4LiMn_2O_{4(s)} + 8KOH_{(aq)} + CH_3COOH_{(l)} + 3H_2O_{(l)} + 8xH_2O_{(l)}$

(3) $4LiMn_2O_{4(s)} + CH_3CH_2OH_{(l)} + H_2O_{(l)} \xrightarrow{\Delta} 4\,\gamma - Mn_2O_{3(s)} + 4LiOH_{(aq)} + CH_3COOH_{(l)}$

(4) $6\,\gamma - Mn_2O_{3(s)} + CH_3CH_2OH_{(l)} \xrightarrow{\Delta} 4Mn_3O_{4(s)} + CH_3COOH_{(l)} + H_2O_{(l)}$

Time resolved PXRD for stoichiometric reactions

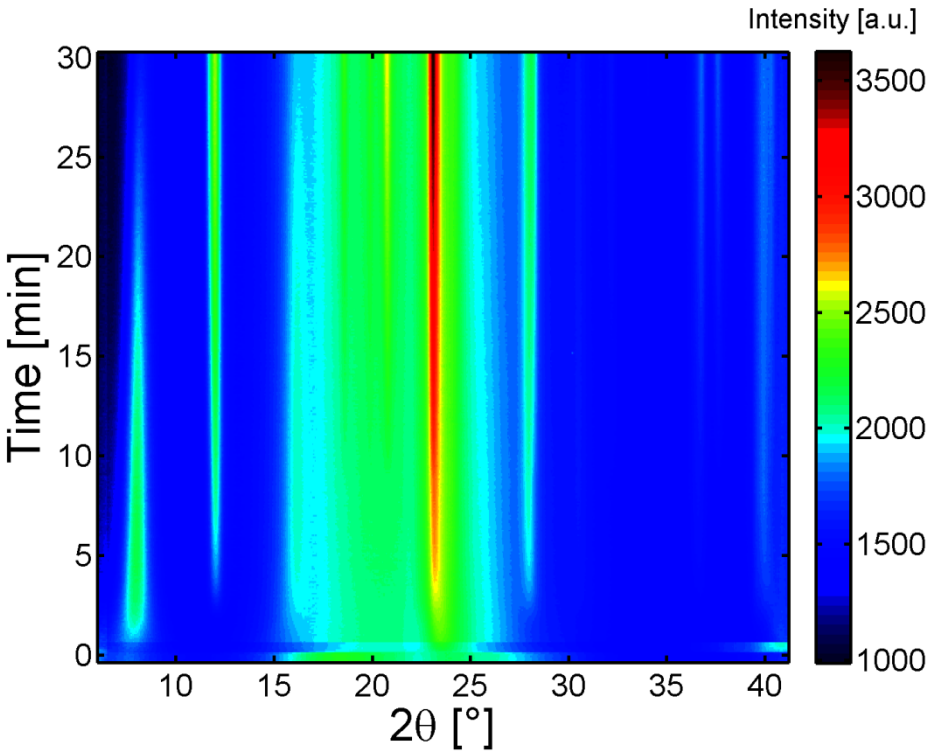

Fig. S11 Time resolved PXRD for stoichiometric reaction at 220°C.

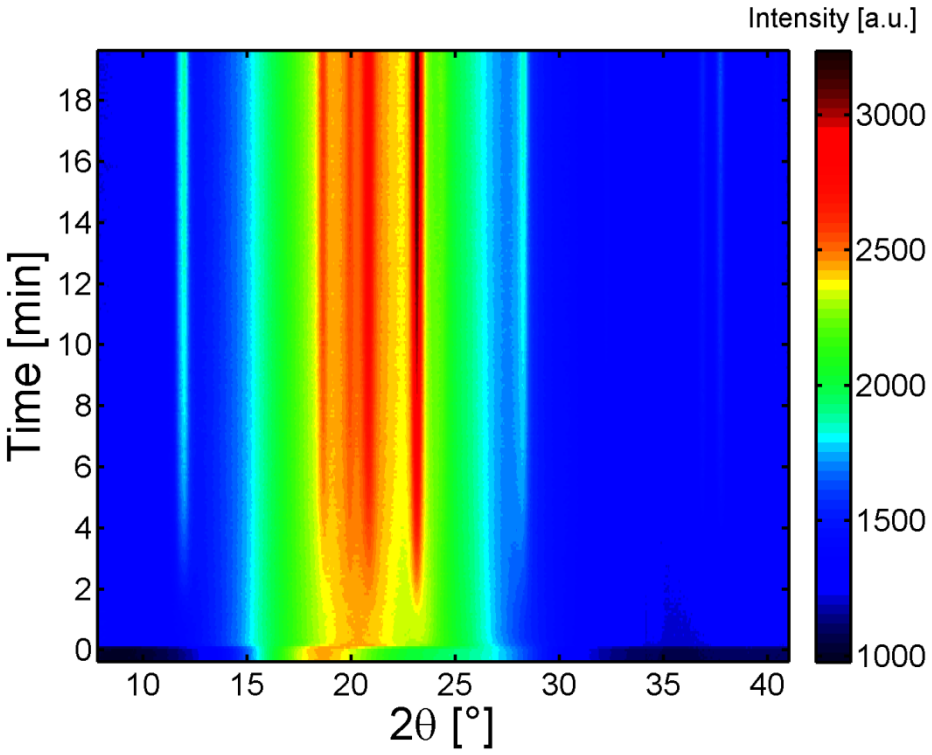

Fig. S12 Time resolved PXRD for stoichiometric reaction at 260°C.

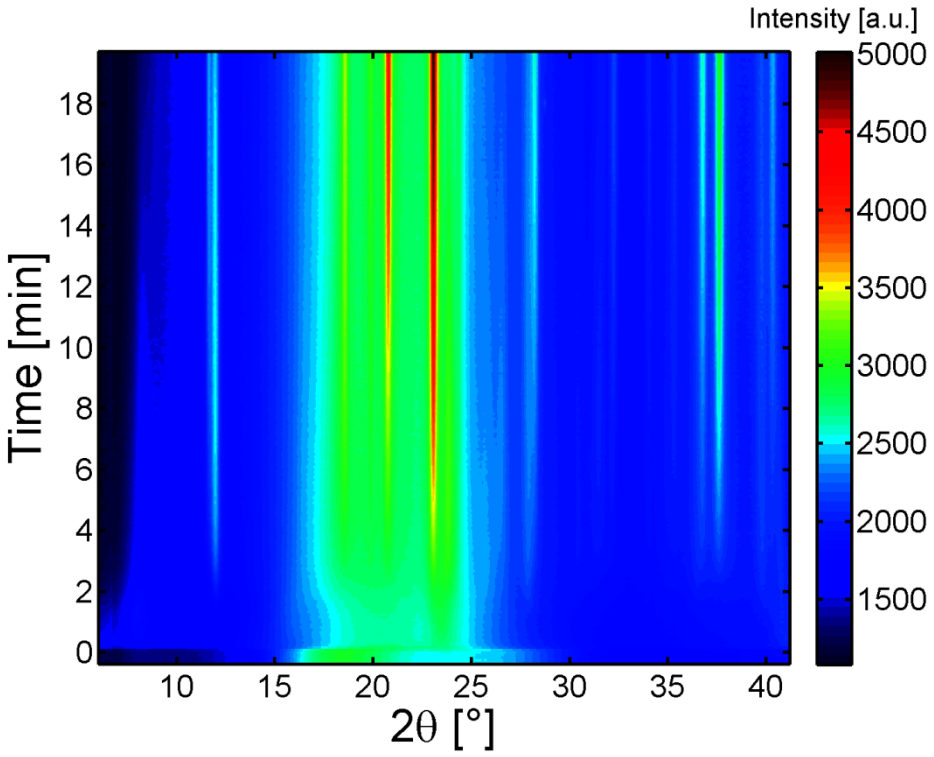

Fig. S13 Time resolved PXRD for stoichiometric reaction at 300°C.

Changes in unit cell vs crystallite size

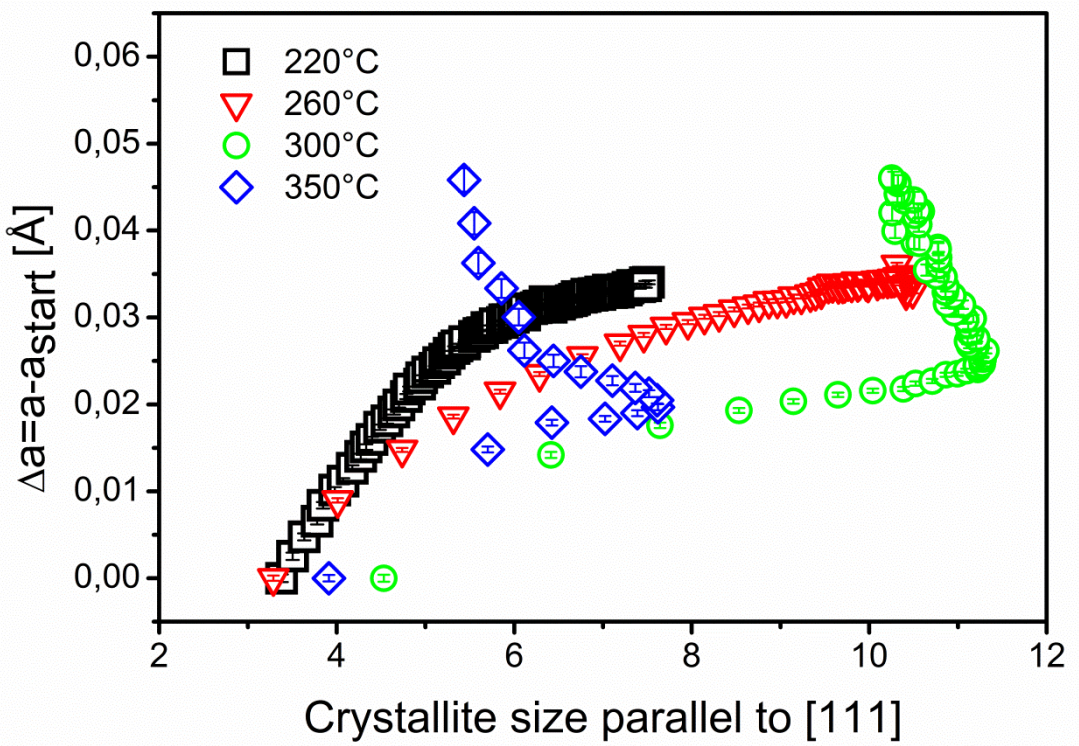

Fig. S14 Changes in unit cell vs crystallite size parallel to [111]. For clarity every third data point is shown.

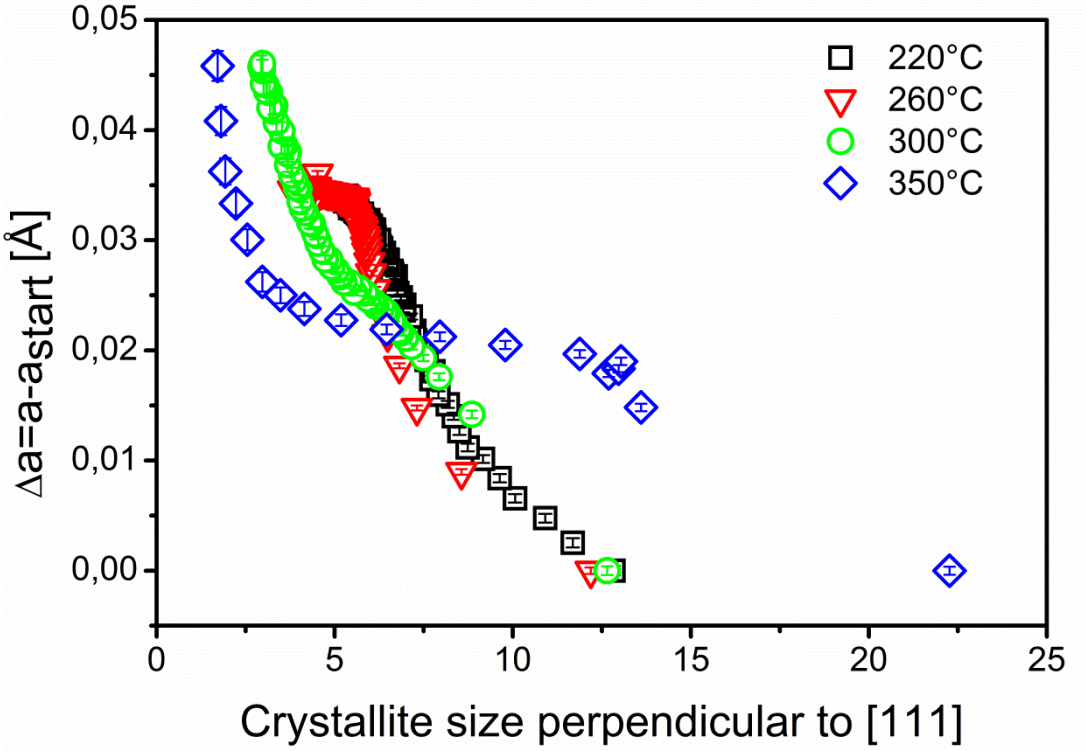

Fig. S15 Changes in unit cell vs crystallite size perpendicular to [111]. . For clarity every third data point is shown.

Crystallite sizes

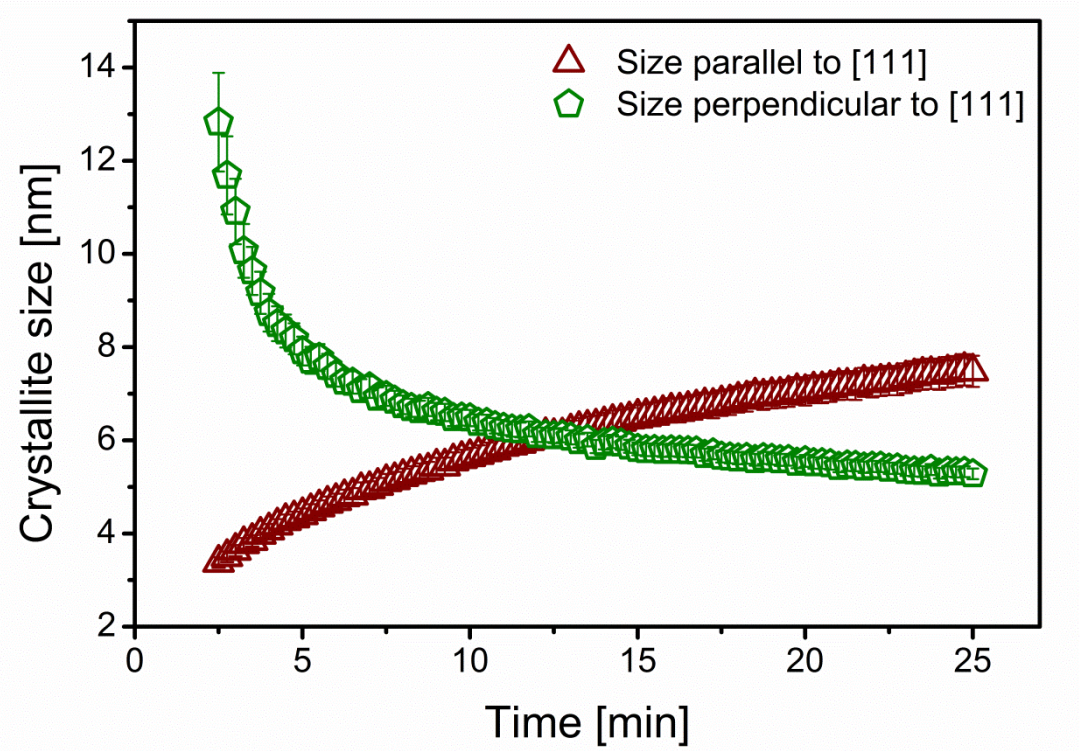

Fig. S16 LMO crystallite sizes at 220°C. For clarity every third data point is shown.

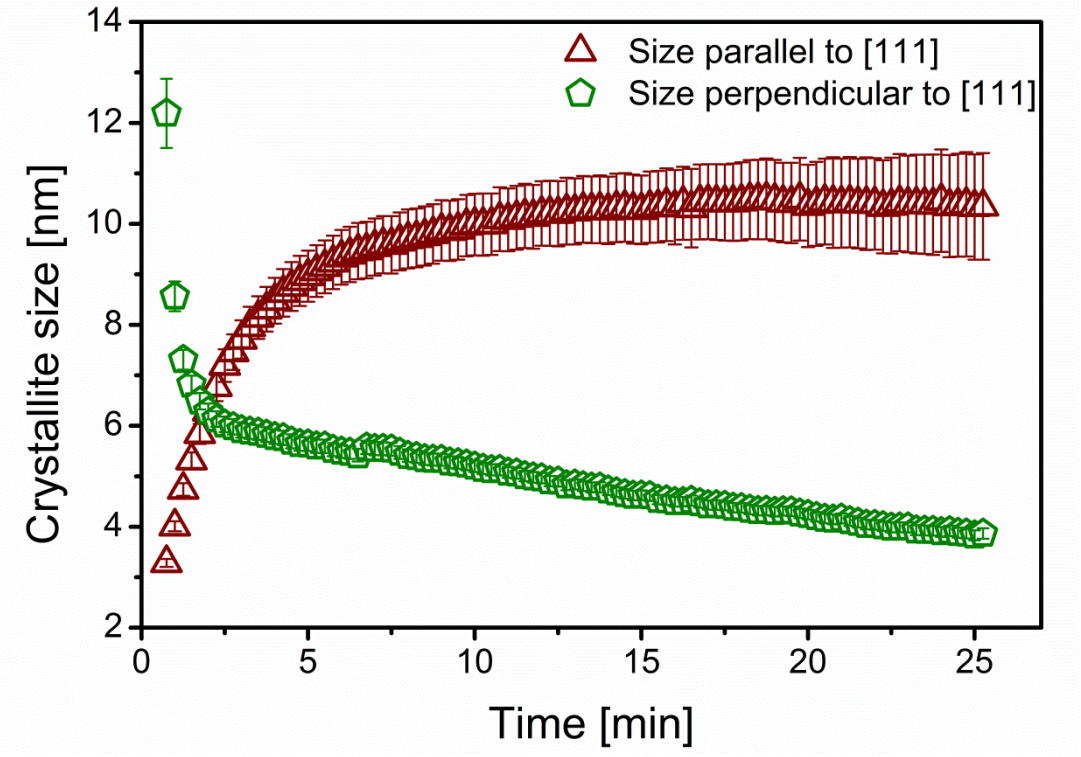

Fig. S17 LMO crystallite sizes at 260°C. For clarity every third data point is shown.

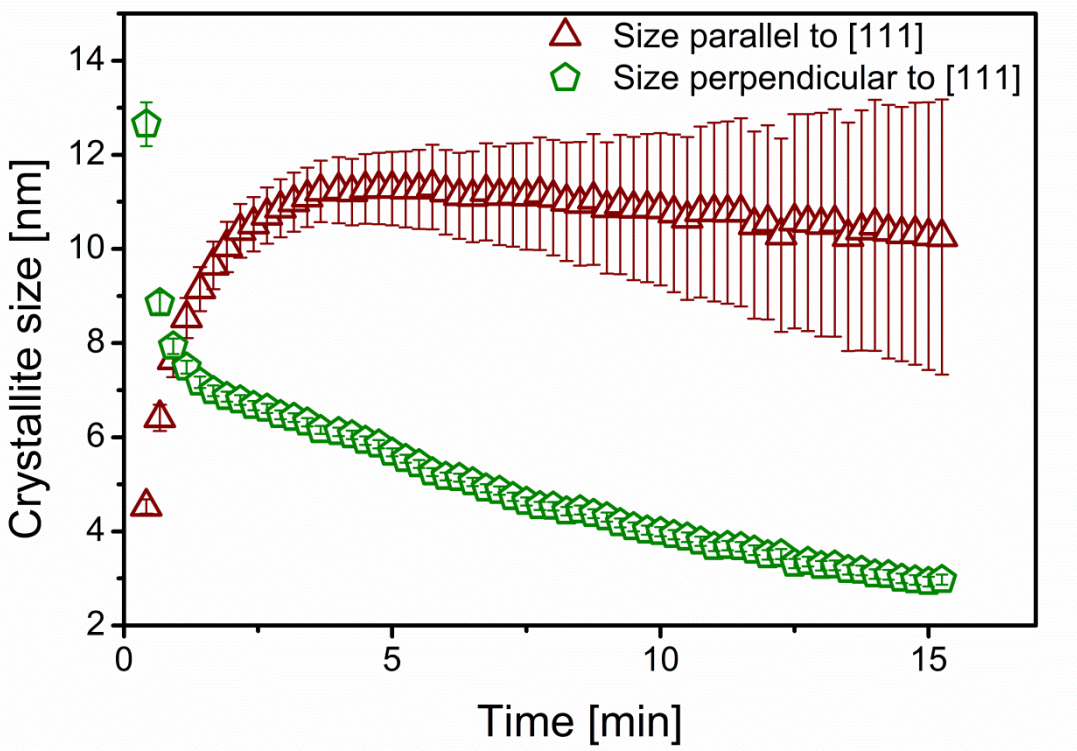

Fig. S18 LMO crystallite sizes at 300°C. For clarity every third data point is shown.

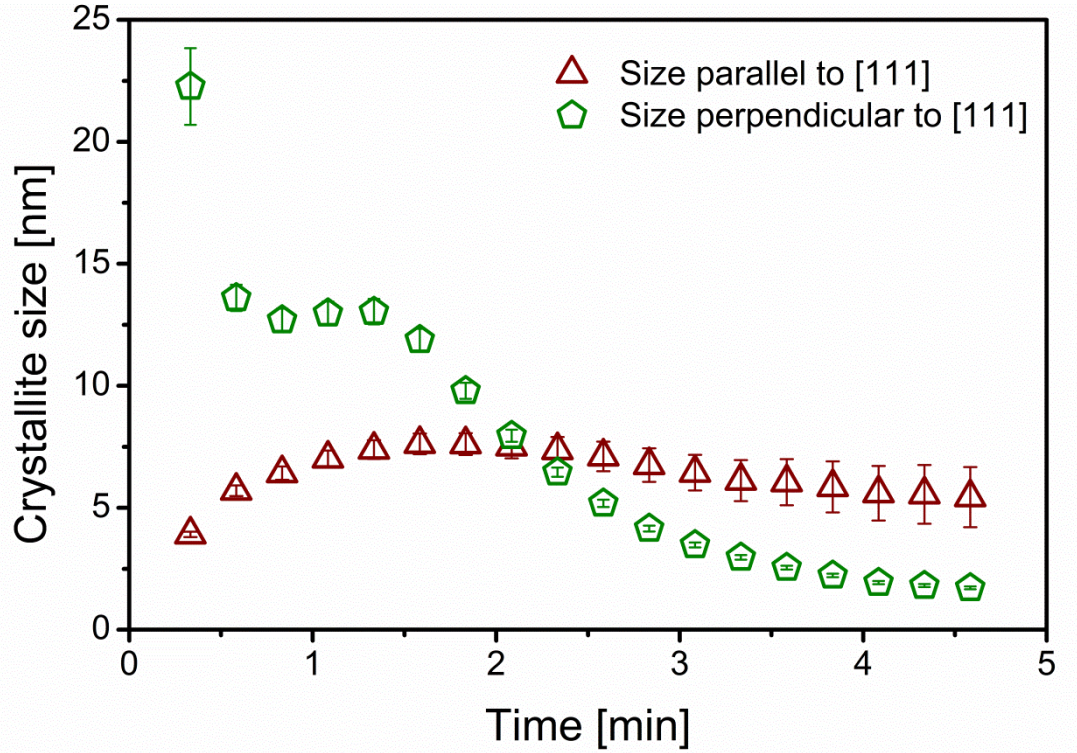

Fig. S19 LMO crystallite sizes at 350°C. For clarity every third data point is shown.

Details about Rietveld refinements and representative fits

220°C

Good fit was obtained for the last PXRD data frame, i.e. frame 306. A sequential refinement using these starting values was conducted from frame 306 to frame 35. This corresponds to the reaction time 2:30-25:05. Fitted parameters were:

- LMO
    - Scale factor
    - Unit cell parameters
    - 2 profile parameters (cylindrical shape)
- Mn_3O_4
    - Scale factor

Fit to data frame 305 (after 25 minutes)

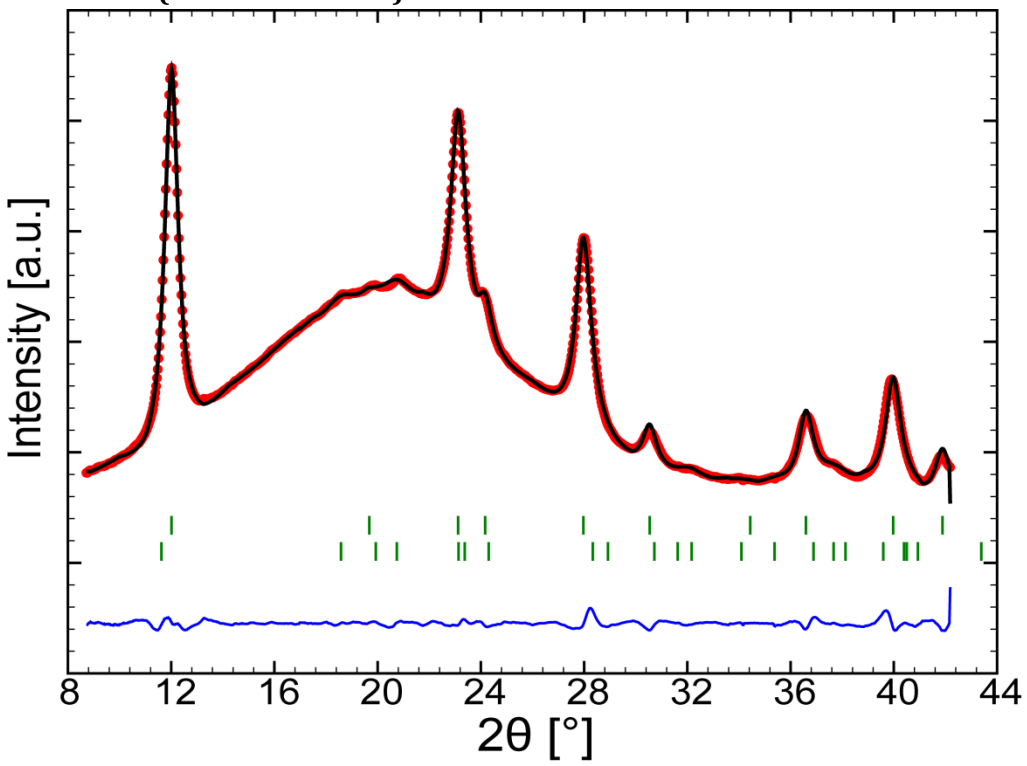

Fig. S20 Rietveld fit for reaction at 220°C after 25 minutes of reaction.

Number of data points	1440
Number of background parameters	25
Total number of refined parameters	30
R_{wp}	5.34
LMO	
Number of Bragg peaks	10
R_F	0.467
Wt%	85.16(96)
***a* [Å]**	8.2059(2)
Y [°]	0.6(1)
SZ [$Å^{-1}$]	-5.5(4)
Mn_3O_4	
Number of Bragg peaks	21
R_F	1.02
Wt%	14.84(57)

260°C

Good fit was obtained for the last PXRD data frame, i.e. frame 309. A sequential refinement using these starting values was conducted from frame 309 to frame 86. This corresponds to the reaction time 6:45-25:20. Fitted parameters were:

- LMO
  - Scale factor
  - Unit cell parameters
  - 2 profile parameters (cylindrical shape)
- Mn_3O_4
  - Scale factor
  - Unit cell parameters
  - 2 profile parameters (cylindrical shape)

Fit to data frame 305 (after 25 minutes)

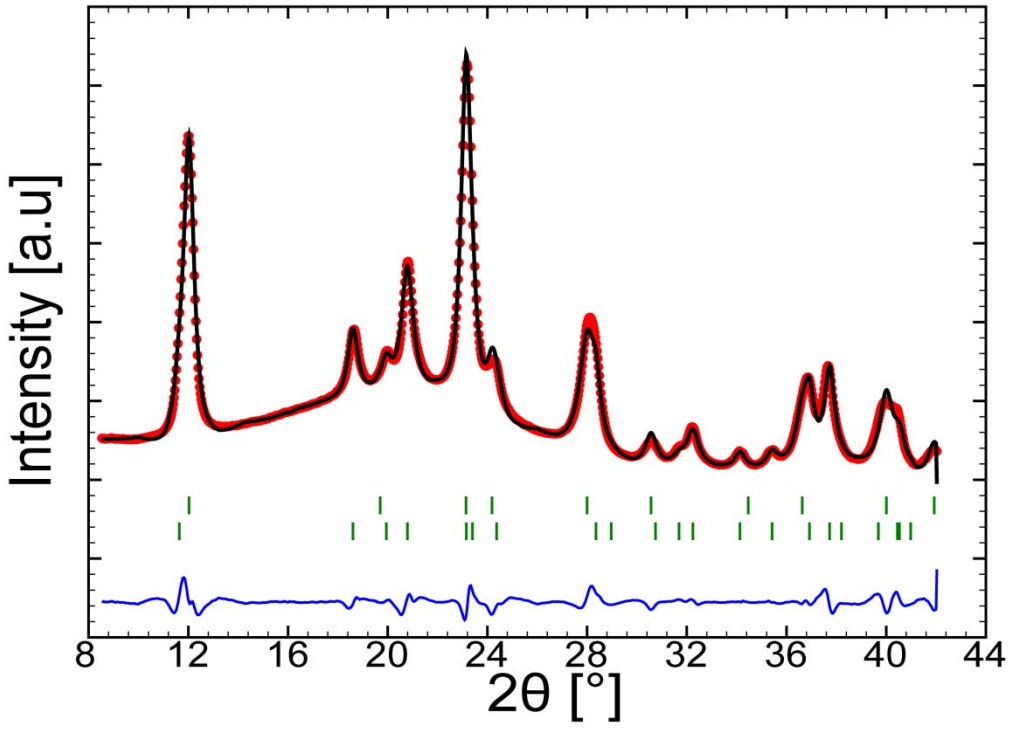

Fig. S21 Rietveld fit for reaction at 260°C after 25 minutes of reaction.

Number of data points	1440
Number of background parameters	22
Total number of refined parameters	31
R_{wp}	8.02
LMO	
Number of Bragg peaks	10
R_F	0.888
Wt%	45.16(57)
***a* [Å]**	8.1984(3)
Y [°]	0.95(2)
SZ [$Å^{-1}$]	-16.5(7)
Mn_3O_4	
Number of Bragg peaks	21
R_F	0.812
Wt%	54.84(78)
***a* [Å]**	5.7252(3)
***c* [Å]**	9.3961(8)
Y [°]	0.49(1)
SZ [$Å^{-1}$]	-5.6(4)

At frame 86 the fit became unstable for Mn_3O_4 since only small amount of it is present in the reaction solution. For that reason unit cell and profile parameters for Mn_3O_4 were fixed and the sequential refinement continued from frame 85 to 14. This corresponds to the reaction time 6:45-25:20. Fitted parameters were:

- LMO
    - Scale factor
    - Unit cell parameters
    - 2 profile parameters (cylindrical shape)
- Mn_3O_4
    - Scale factor

Fit to data frame 125 (after 10 minutes)

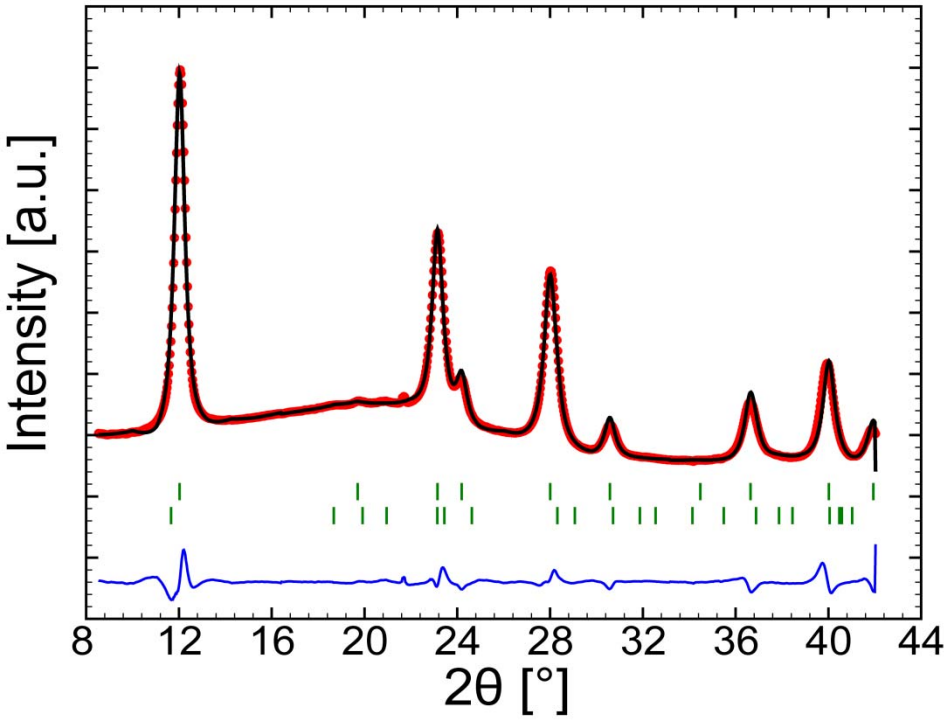

Fig. S22 Rietveld fit for reaction at 260°C after 10 minutes of reaction.

Number of data points	1440
Number of background parameters	22
Total number of refined parameters	27
R_{wp}	8.97
LMO	
Number of Bragg peaks	10
R_F	1.208
Wt%	91(1)
***a* [Å]**	8.1957(2)
Y [°]	0.64(2)
SZ [$Å^{-1}$]	-6.5(5)
Mn_3O_4	
Number of Bragg peaks	21
R_F	1.362
Wt%	8.9(8)

300°C

Good fit was obtained for an intermediate PXRD data frame, i.e. frame 51. This frame was chosen because in this frame the amount of Mn_3O_4 is just enough to refine on unit cell and morphology. A sequential refinement using the starting values from frame 51 was conducted from frame 50 to frame 10. This corresponds to the reaction time 0:25-3:45. Fitted parameters were:

- LMO
    - Scale factor
    - Unit cell parameters
    - 2 profile parameters (cylindrical shape)
- Mn_3O_4
    - Scale factor

Fit to data frame 41 (after 3 minutes)

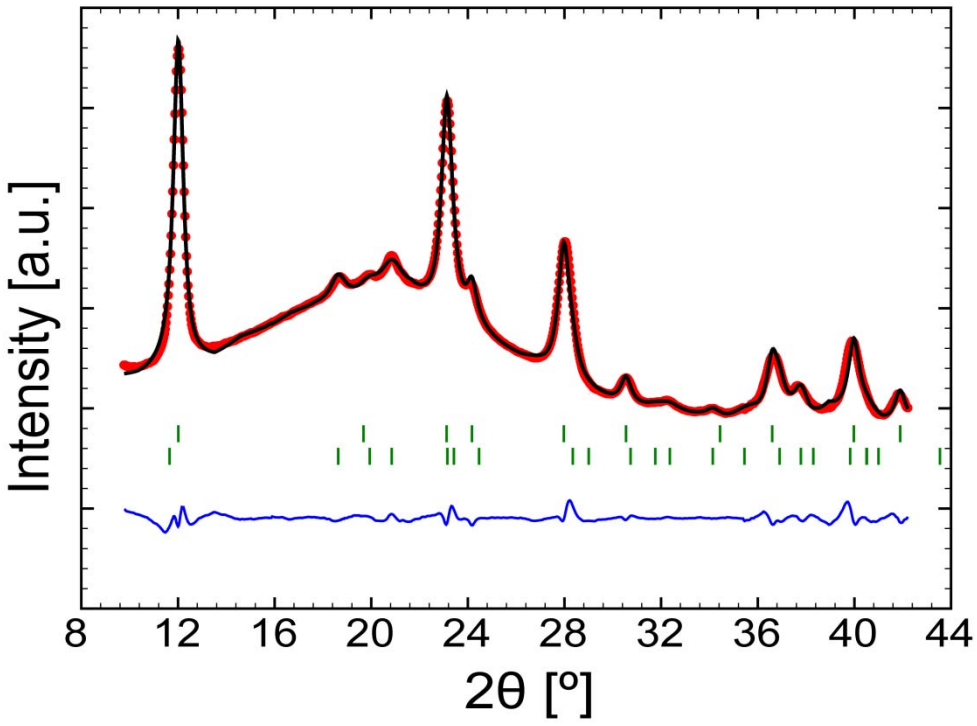

Fig. S23 Rietveld fit for reaction at 300°C after 3 minutes of reaction.

Number of data points	1440
Number of background parameters	22
Total number of refined parameters	27
R_{wp}	8.57
LMO	
Number of Bragg peaks	10
R_F	0.934
Wt%	61.75(67)
***a* [Å]**	8.2041(2)
Y [°]	0.562(8)
SZ [$Å^{-1}$]	-6.3(5)
Mn_3O_4	
Number of Bragg peaks	21
R_F	1.002
Wt%	38.25(74)

A sequential refinement using the starting values from frame 51 was conducted from frame 51 to frame 189. This corresponds to the reaction time 3:50-15:20. Fitted parameters were:

- LMO
  - Scale factor
  - Unit cell parameters
  - 2 profile parameters (cylindrical shape)
- Mn_3O_4
  - Scale factor
  - Unit cell parameters
  - 2 profile parameters (cylindrical shape)

Fit to data frame 65 (after 5 minutes)

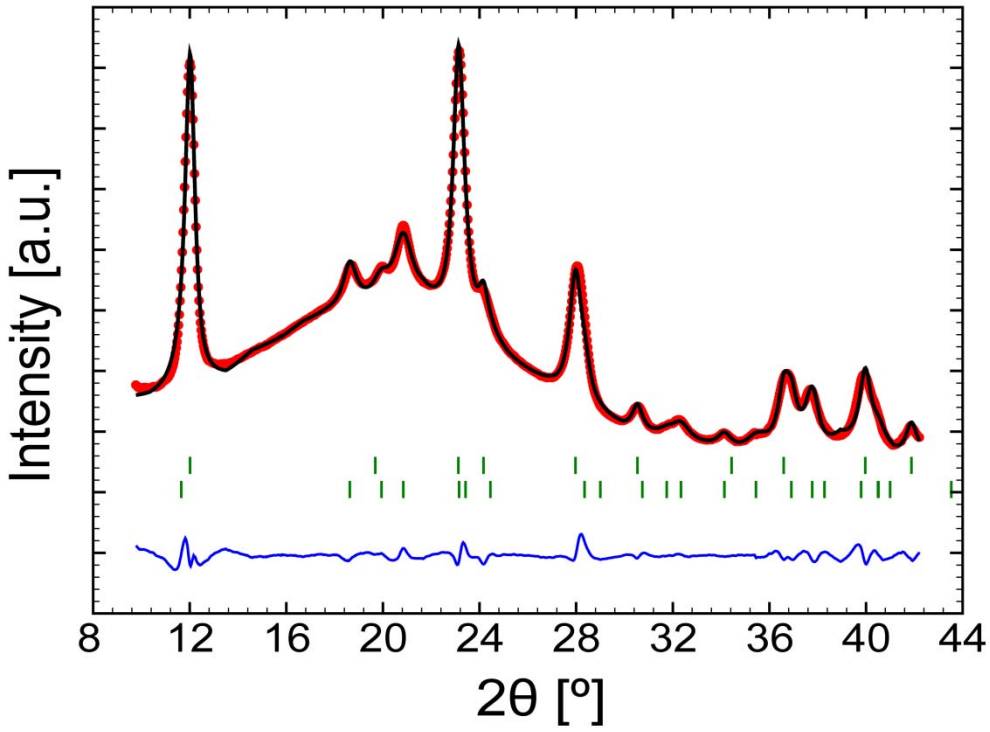

Fig. S24 Rietveld fit for reaction at 300°C after 5 minutes of reaction.

Number of data points	1440
Number of background parameters	22
Total number of refined parameters	31
R_{wp}	8.04
LMO	
Number of Bragg peaks	10
R_F	0.664
Wt%	49.36(73)
***a* [Å]**	8.2062(3)
Y [°]	0.636(9)
SZ [$Å^{-1}$]	-8.7(6)
Mn_3O_4	
Number of Bragg peaks	21
R_F	0.6089
Wt%	51(1)
***a* [Å]**	5.7274(4)
***c* [Å]**	9.366(2)
Y [°]	1.00(3)
SZ [$Å^{-1}$]	-16.8(9)

At frame 190 the fit became unstable for LMO since only small amount of it is present in the reaction solution. For that reason profile parameters for LMO were fixed and the sequential refinement continued from frame 190 to 306. This corresponds to the reaction time 15:25-25:05. Fitted parameters were:

- LMO
    - Scale factor
    - Unit cell parameters
- Mn_3O_4
    - Scale factor
    - Unit cell parameters
    - 2 profile parameters (cylindrical shape)

Fit to data frame 245 (after 20 minutes)

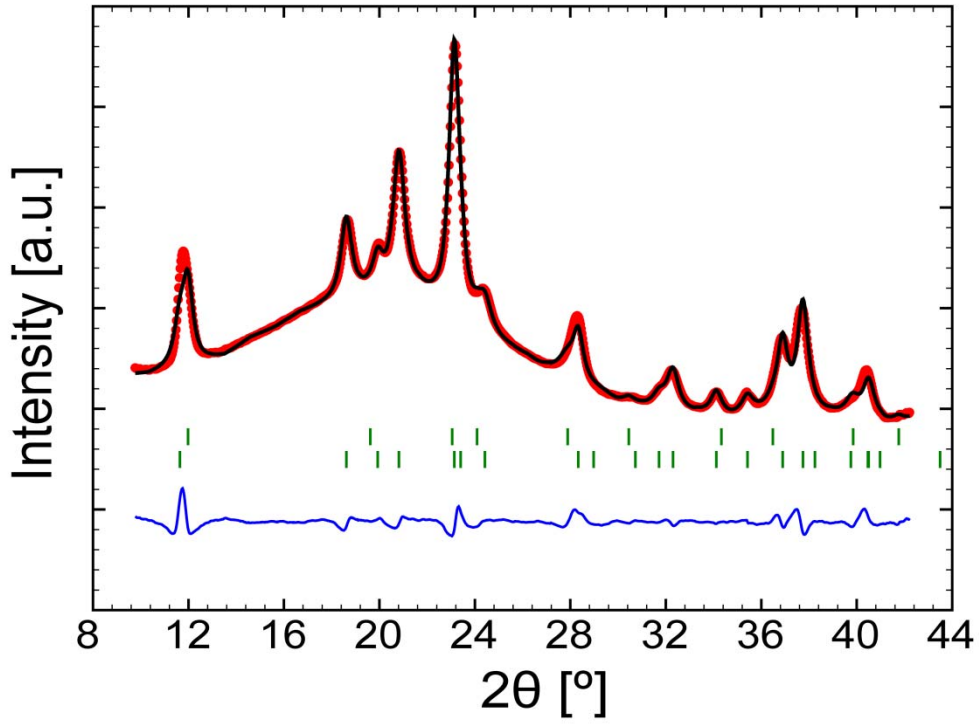

Fig. S25 Rietveld fit for reaction at 300°C after 20 minutes of reaction.

Number of data points	1440
Number of background parameters	22
Total number of refined parameters	29
R_{wp}	11.0
LMO	
Number of Bragg peaks	10
R_F	1.131
Wt%	14.91(35)
***a* [Å]**	8.230(1)
Mn_3O_4	
Number of Bragg peaks	21
R_F	1.079
Wt%	85(2)
***a* [Å]**	5.7298(3)
***c* [Å]**	9.3776(9)
Y [°]	0.53(1)
SZ [$Å^{-1}$]	-4.9(4)

350°C

Good fit was obtained for an intermediate PXRD data frame, i.e. frame 20. This frame was chosen because in this frame the amount of Mn_3O_4 is just enough to refine on unit cell and morphology. A sequential refinement using the starting values from frame 20 was conducted from frame 19 to frame 9. This corresponds to the reaction time 0:20-1:10. Fitted parameters were:

- LMO
    - Scale factor
    - Unit cell parameters
    - 2 profile parameters (cylindrical shape)
- Mn_3O_4
    - Scale factor

Fit to data frame 17 (after 1 minute)

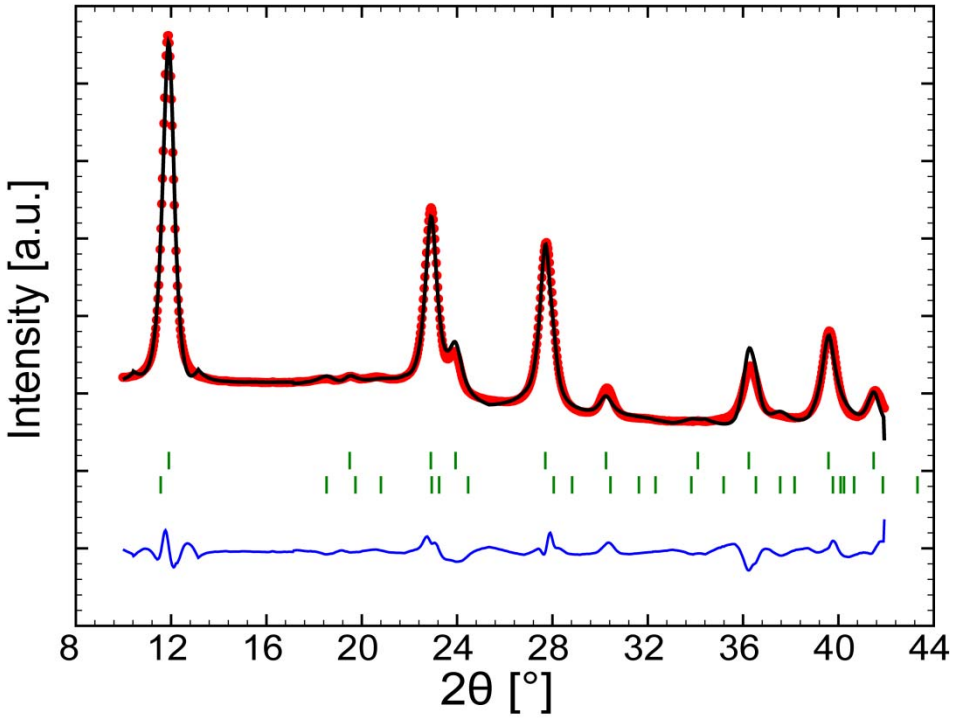

Fig. S26 Rietveld fit for reaction at 300°C after 3 minute of reaction.

Number of data points	1440
Number of background parameters	21
Total number of refined parameters	26
R_{wp}	10.1
LMO	
Number of Bragg peaks	10
R_F	2.013
Wt%	78(2)
***a* [Å]**	8.2885(3)
Y [°]	0.27(1)
SZ [$Å^{-1}$]	7.0(6)
Mn_3O_4	
Number of Bragg peaks	21
R_F	1.978
Wt%	22.3(9)

A sequential refinement using the starting values from frame 20 was conducted from frame 20 to frame 60. This corresponds to the reaction time 1:15-4:35. Fitted parameters were:

- LMO
  - Scale factor
  - Unit cell parameters
  - 2 profile parameters (cylindrical shape)
- Mn_3O_4
  - Scale factor
  - Unit cell parameters
  - 2 profile parameters (cylindrical shape)

Fit to data frame 41 (after 3 minutes)

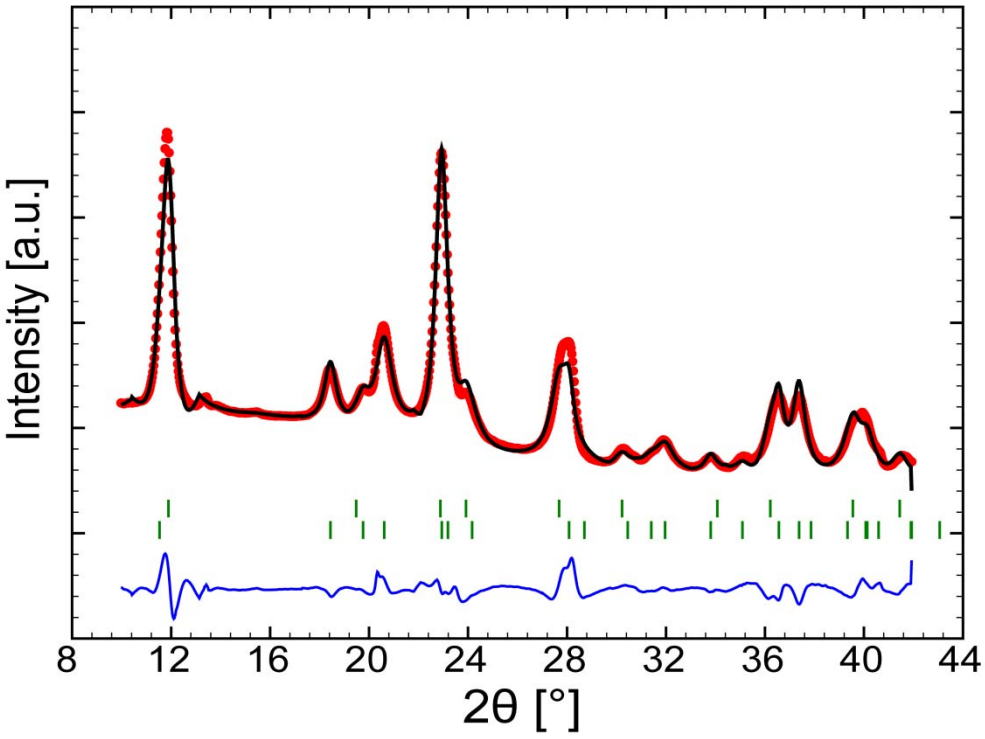

Fig. S27 Rietveld fit for reaction at 350°C after 3 minutes of reaction.

Number of data points	1440
Number of background parameters	21
Total number of refined parameters	30
R_{wp}	10.9
LMO	
Number of Bragg peaks	10
R_F	1.229
Wt%	45(2)
***a* [Å]**	8.2947(7)
Y [°]	0.98(6)
SZ [$Å^{-1}$]	-11(1)
Mn_3O_4	
Number of Bragg peaks	21
R_F	2.166
Wt%	55(1)
***a* [Å]**	5.7833(4)
***c* [Å]**	9.481(2)
Y [°]	0.88(3)
SZ [$Å^{-1}$]	-15.6(9)

At frame 61 the fit became unstable for LMO since only small amount of it is present in the reaction solution. For that reason unit cell and profile parameters for LMO were fixed and the sequential refinement continued from frame 61 to 117. This corresponds to the reaction time 4:40-9:20. Fitted parameters were:

- LMO
    - Scale factor
- Mn_3O_4
    - Scale factor
    - Unit cell parameters
    - 2 profile parameters (cylindrical shape)

Longer reaction time at 350°C only contained Mn_3O_4 so these PXRD frames were not included in this study.

Fit to data frame 65 (after 5 minutes)

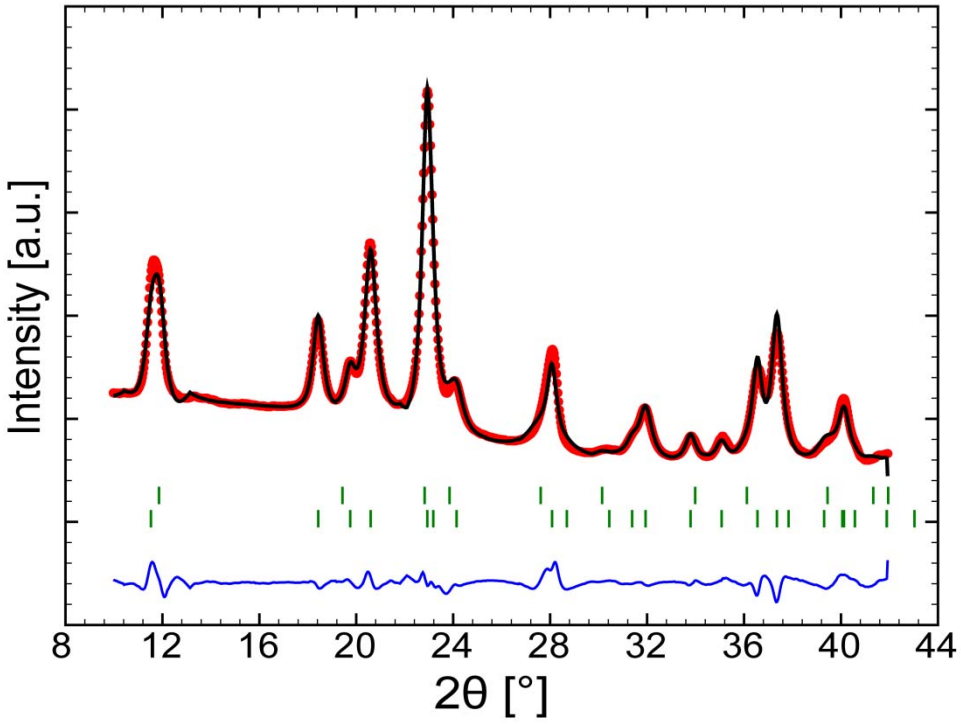

Fig. S28 Rietveld fit for reaction at 350°C after 5 minutes of reaction.

Number of data points	1440
Number of background parameters	21
Total number of refined parameters	27
R_{wp}	8.55
LMO	
Number of Bragg peaks	10
R_F	0.9256
Wt%	24.4(5)
Mn_3O_4	
Number of Bragg peaks	21
R_F	1.712
Wt%	75.6(9)
***a* [Å]**	5.7845(2)
***c* [Å]**	9.4892(6)
Y [°]	0.55(1)
SZ [$Å^{-1}$]	-6.8(3)