

SUPPORTING INFORMATION

Mechanistic Studies on the Formation of Ternary Oxides by Thermal Oxidation of the Cubic Laves Phase CaAl_2

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Table S1. Summary of the Rietveld fit results of the powder X-ray diffraction data collected from the samples oxidized in a muffle furnace in air. Five samples were simultaneously heated to 1273 K ($\sim 15 \text{ K min}^{-1}$) with a dwell time of 1 h.

dwelling time (h)	phase contributions obtained by PXRD (mass%)				
	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	CaAl_2O_4	CaO	Al_2O_3	Al
5	67.1	13.0	1.8	6.8	11.3
5	63.1	20.7	1.9	7.5	6.8
5	67.5	14.5	2.1	7.7	8.2
5	65.0	17.6	1.7	7.4	8.3
5	67.9	15.7	2.4	7.2	6.8
average	66.1	16.3	2.0	7.3	8.3

Table S2. Summary of the Rietveld fit results of the powder X-ray diffraction data collected from the sample repeatedly oxidized in a muffle furnace in air for 5 h. The sample was heated to 1273 K ($\sim 15 \text{ K min}^{-1}$) with a dwelling time of 5h over the course of 100 h.

dwelling time (h)	phase contributions obtained by PXRD (mass%)				
	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	CaAl_2O_4	CaO	Al_2O_3	Al
5	70	12	1	10	7
10	65	16	1	13	5
15	59	20	1	16	4
20	57	25	0	16	2
25	51	31	0	16	2
30	43	39	0	17	1
35	39	44	0	16	1
40	35	49	0	15	1
45	31	54	0	14	1
50	27	59	0	13	1
55	23	64	0	13	0
60	20	69	0	11	0
65	16	74	0	10	0
70	13	78	0	9	0
75	11	80	0	9	0
80	8	83	0	9	0
85	6	87	0	7	0
90	4	89	0	7	0
95	2	91	0	7	0
100	2	92	0	6	0

Table S3. Summary of the quantum-chemical calculations on the DFT Level. The compounds are sorted by increasing Ca content.

Compound	space group	Z	E/unit cell (eV)	E/atom (eV)
Al ₂ O ₃	<i>R</i> $\bar{3}c$	6	-236.03	-7.87
CaAl ₁₂ O ₁₉	<i>P6</i> ₃ / <i>mmc</i>	2	-498.75	-7.79
CaAl ₄ O ₇	<i>C2</i> ₁ / <i>c</i>	4	-367.80	-7.66
CaAl ₂ O ₄	<i>P2</i> ₁ / <i>c</i>	12	-632.88	-7.53
Ca ₅ Al ₆ O ₁₄	<i>Cmc2</i> ₁	4	-741.48	-7.41
Ca ₁₂ Al ₁₄ O ₃₃	<i>I</i> $\bar{4}3d$	4	-853.76	-7.36
Ca ₃ Al ₂ O ₆	<i>Pa</i> $\bar{3}$	24	-1908.38	-7.23
CaO	<i>Fm</i> $\bar{3}m$	4	-53.64	-6.71

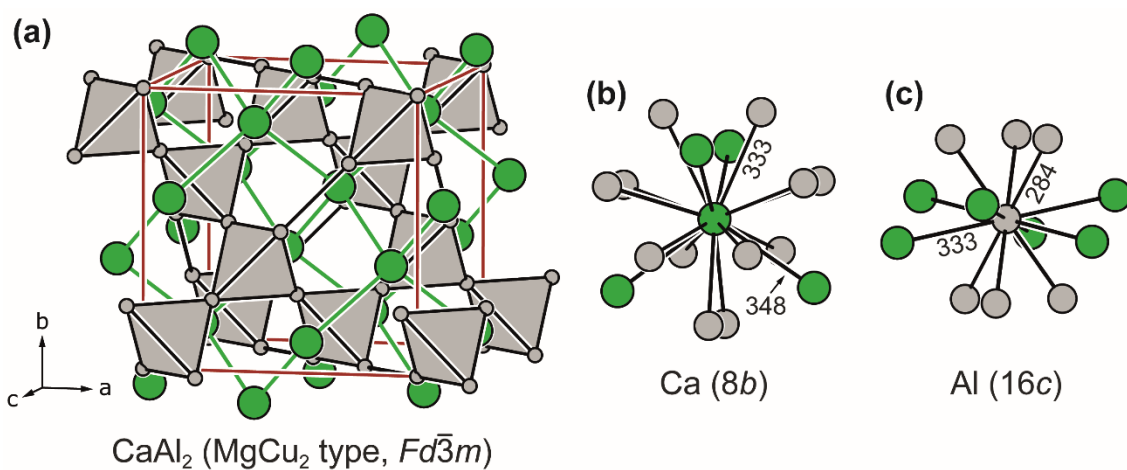


Figure S1. (a) Unit cell and coordination polyhedra of the (b) Ca and (c) Al atoms in cubic CaAl_2 ($Fd\bar{3}m$, MgCu_2 type). Ca atoms are depicted in green, Al atoms as grey circles. Wyckoff positions and site symmetries are given.

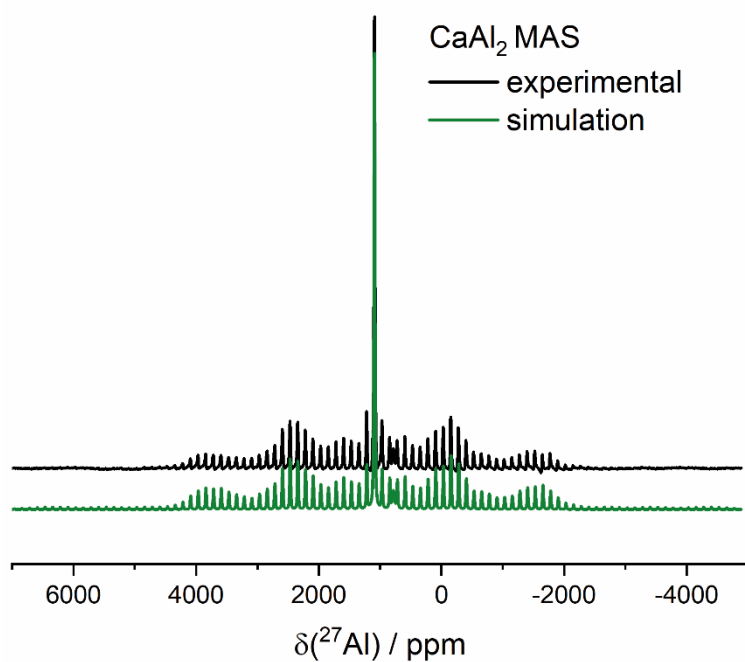


Figure S2. ^{27}Al solid state MAS NMR for cubic CaAl_2 (MgCu_2 type). The experimental data is shown in black, the fit in green.

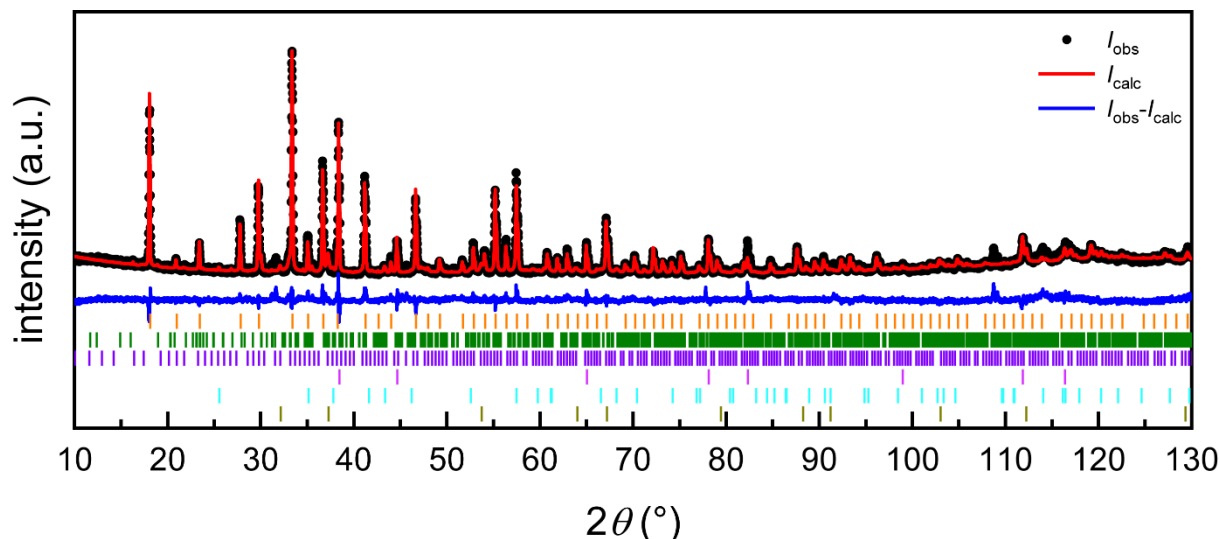


Figure S3. Rietveld fit of the powder X-ray diffraction pattern of CaAl_2 oxidized by the following conditions: STA; heating rate: 20 K min^{-1} ; dwelling time: 0 h; gas flow: $40 \text{ mL min}^{-1} \text{ Ar} : 10 \text{ mL min}^{-1} \text{ O}_2$. The ticks indicate the Bragg positions for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (orange), CaAl_2O_4 (green), $\text{Ca}_3\text{Al}_2\text{O}_6$ (purple), elemental Al (pink), Al_2O_3 (cyan), CaO (olive).

Refinement details for the data shown in Figure S3						
Source	Bruker D8 ADVANCE (laboratory X-ray)					
Temperature	RT					
Pressure	ambient					
Wavelengths	Cu $K\alpha_1$ and Cu $K\alpha_2$: 154.0596 and 154.4308 pm					
Chemical formula	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	CaAl_2O_4	$\text{Ca}_3\text{Al}_2\text{O}_6$	Al	Al_2O_3	CaO
Abbreviation	C12A7	CA	C3A1	–	–	–
Space group	$I\bar{4}3d$	$P2_1/c$	$Pa\bar{3}$	$Fm\bar{3}m$	$R\bar{3}c$	$Fm\bar{3}m$
a / pm	1197.86(2)	875.0(10)	1527.0(6)	405.27(1)	475.65(11)	482.04(6)
b / pm	A	809.2(4)	a	A	a	a
c / pm	A	1748.2(18)	a	A	1300.6(6)	a
$\beta / ^\circ$	90	120.00(14)	90	90	90	90
V / nm^3	1.7189	1.0720	3.5600	0.0666	0.2548	0.1120
Z	4	12	24	4	6	4
d -space range	0.85–14.35 Å (6–130° 2θ)					
χ^2	3.30					
R_p	6.89					
R_{wp}	9.32					
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2}$					

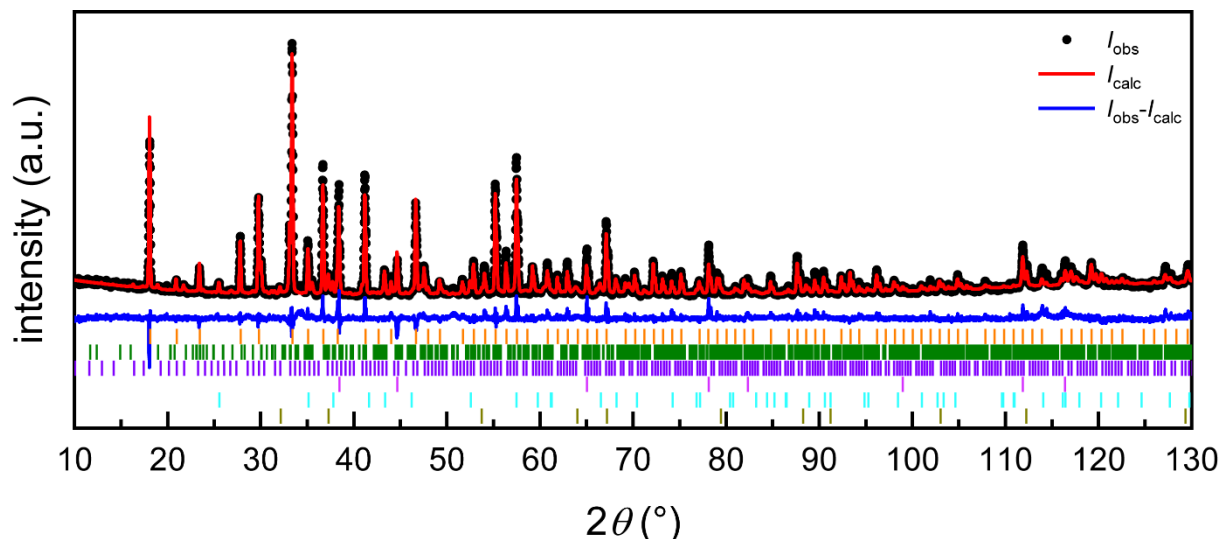


Figure S4. Rietveld fit of the powder X-ray diffraction pattern of CaAl_2 oxidized by the following conditions: STA; heating rate: 20 K min^{-1} ; dwelling time: 5 h; gas flow: $40 \text{ mL min}^{-1} \text{ Ar} : 10 \text{ mL min}^{-1} \text{ O}_2$. The ticks indicate the Bragg positions for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (orange), CaAl_2O_4 (green), $\text{Ca}_3\text{Al}_2\text{O}_6$ (purple), elemental Al (pink), Al_2O_3 (cyan), CaO (olive).

Refinement details for the data shown in Figure S4						
Source	Bruker D8 ADVANCE (laboratory X-ray)					
Temperature	RT					
Pressure	ambient					
Wavelengths	Cu $K\alpha_1$ and Cu $K\alpha_2$: 154.0596 and 154.4308 pm					
Chemical formula	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	CaAl_2O_4	$\text{Ca}_3\text{Al}_2\text{O}_6$	Al	Al_2O_3	CaO
Abbreviation	C12A7	CA	C3A1	–	–	–
Space group	$\bar{I}43d$	$P2_1/c$	$Pa\bar{3}$	$Fm\bar{3}m$	$R\bar{3}c$	$Fm\bar{3}m$
a / pm	1197.79(1)	875.7(3)	1526.78(4)	405.20(7)	476.01(3)	481.50(7)
b / pm	a	809.05(18)	a	a	a	a
c / pm	a	1745.4(6)	a	a	1299.66(14)	a
$\beta / ^\circ$	90	119.99(4)	90	90	90	90
V / nm^3	1.7184	1.0710	3.5590	0.0665	0.2550	0.1116
Z	4	12	24	4	6	4
d -space range	0.85–14.35 Å (6–130° 2θ)					
χ^2	3.92					
R_p	7.08					
R_{wp}	9.60					
Definition of R factors	$R_p = \frac{\sum w I_o - I_c ^2}{\sum w I_o^2}$					

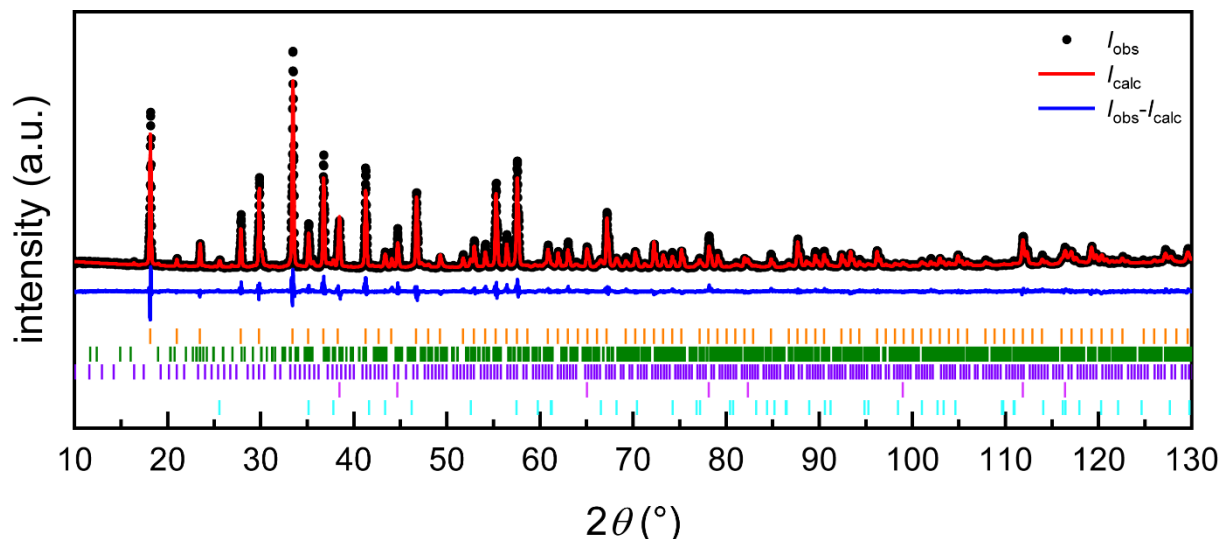


Figure S5. Rietveld fit of the powder X-ray diffraction pattern of CaAl_2 oxidized by the following conditions: STA; heating rate: 5 K min^{-1} ; dwelling time: 0 h; gas flow: $40 \text{ mL min}^{-1} \text{ Ar} : 40 \text{ mL min}^{-1} \text{ O}_2$. The ticks indicate the Bragg positions for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (orange), CaAl_2O_4 (green), $\text{Ca}_3\text{Al}_2\text{O}_6$ (purple), elemental Al (pink), Al_2O_3 (cyan), CaO (olive).

Refinement details for the data shown in Figure S5					
Source	Bruker D8 ADVANCE (laboratory X-ray)				
Temperature	RT				
Pressure	ambient				
Wavelengths	Cu $K\alpha_1$ and Cu $K\alpha_2$: 154.0596 and 154.4308 pm				
Chemical formula	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	CaAl_2O_4	$\text{Ca}_3\text{Al}_2\text{O}_6$	Al	Al_2O_3
Abbreviation	C12A7	CA	C3A1	–	–
Space group	$I\bar{4}3d$	$P2_1/c$	$Pa\bar{3}$	$Fm\bar{3}m$	$R\bar{3}c$
a / pm	1197.87(11)	874.7(9)	1522.5(3)	405.32(8)	476.00(3)
b / pm	a	809.9(3)	a	a	a
c / pm	a	1746.8(19)	a	a	1300.27(18)
$\beta / ^\circ$	90	120.00(13)	90	90	90
V / nm^3	1.7188	1.0720	3.5290	0.0666	0.2551
Z	4	12	24	4	6
d -space range	0.85-14.35 Å (6-130° 2θ)				
χ^2	6.39				
R_p	8.28				
R_{wp}	11.20				
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2 }$				

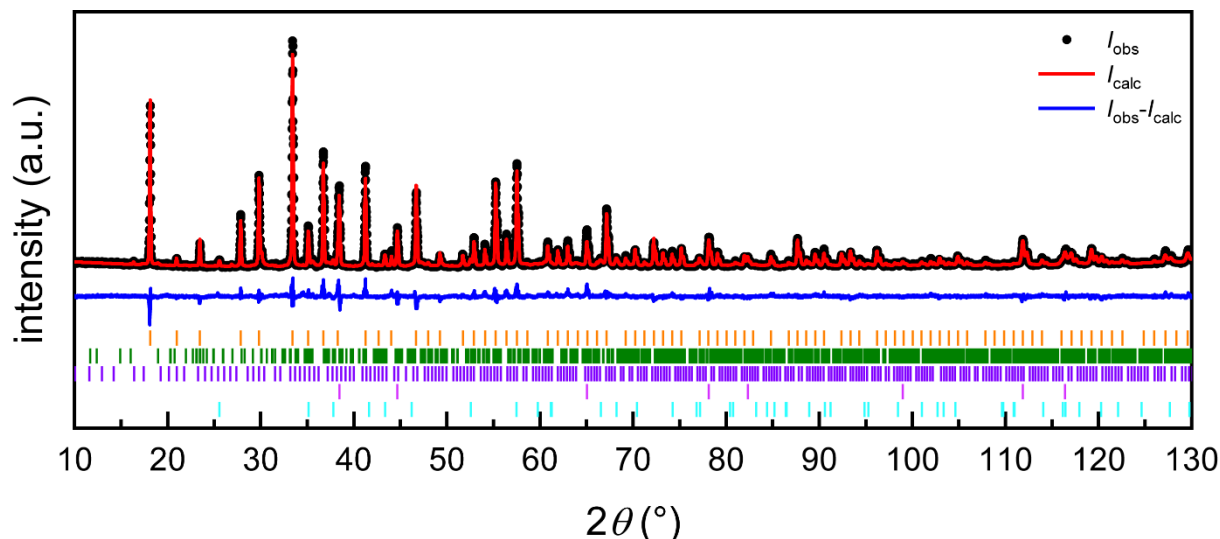


Figure S6. Rietveld fit of the powder X-ray diffraction pattern of CaAl₂ oxidized by the following conditions: STA; heating rate: 10 K min⁻¹; dwelling time: 0 h; gas flow: 40 mL min⁻¹ Ar : 40 mL min⁻¹ O₂. The ticks indicate the Bragg positions for Ca₁₂Al₁₄O₃₃ (orange), CaAl₂O₄ (green), Ca₃Al₂O₆ (purple), elemental Al (pink), Al₂O₃ (cyan), CaO (olive).

Refinement details for the data shown in Figure S6					
Source	Bruker D8 ADVANCE (laboratory X-ray)				
Temperature	RT				
Pressure	ambient				
Wavelengths	Cu K α ₁ and Cu K α ₂ : 154.0596 and 154.4308 pm				
Chemical formula	Ca ₁₂ Al ₁₄ O ₃₃	CaAl ₂ O ₄	Ca ₃ Al ₂ O ₆	Al	Al ₂ O ₃
Abbreviation	C12A7	CA	C3A1	–	–
Space group	$I\bar{4}3d$	$P2_1/c$	$Pa\bar{3}$	$Fm\bar{3}m$	$R\bar{3}c$
<i>a</i> / pm	1197.86(1)	874.5(13)	1522.0(6)	405.33(6)	476.01(3)
<i>b</i> / pm	<i>a</i>	810.5(4)	<i>a</i>	<i>a</i>	<i>a</i>
<i>c</i> / pm	<i>a</i>	1747(3)	<i>a</i>	<i>a</i>	1300.28(18)
β / °	90	119.99(16)	90	90	90
<i>V</i> / nm ³	1.7187	1.0730	3.5260	0.0666	0.2552
<i>Z</i>	4	12	24	4	6
<i>d</i> -space range	0.85–14.35 Å (6–130° 2 θ)				
χ^2	4.24				
<i>R</i> _p	6.75				
<i>R</i> _{wp}	8.94				
Definition of <i>R</i> factors	$R_p = \frac{\sum w I_o - I_c ^2}{\sum w I_o^2}^{1/2}$				

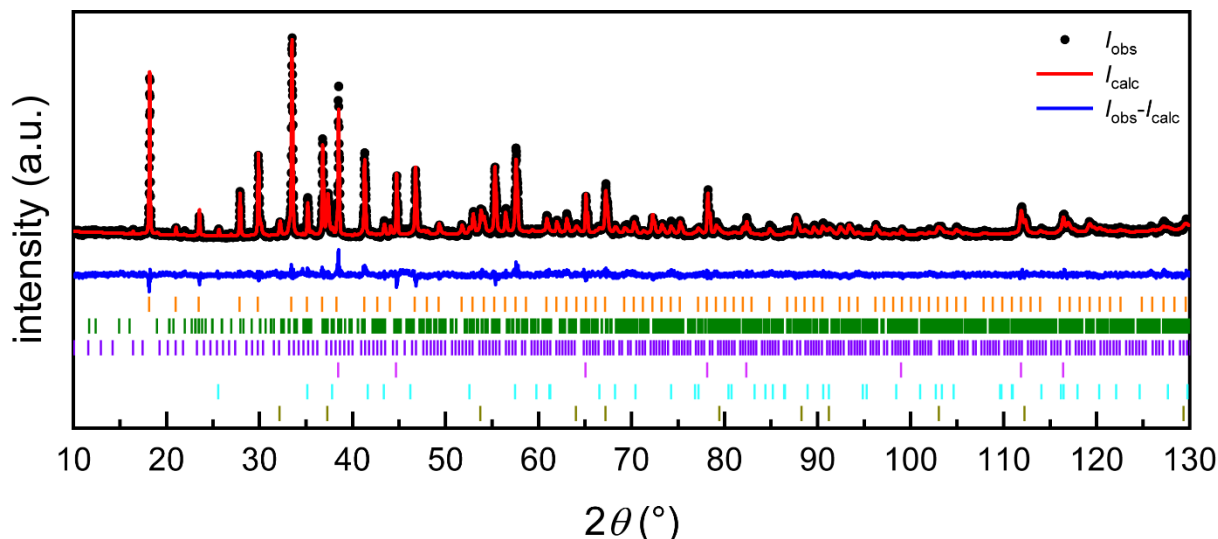


Figure S7. Rietveld fit of the powder X-ray diffraction pattern of CaAl_2 oxidized by the following conditions: STA; heating rate: 20 K min^{-1} ; dwelling time: 0 h; gas flow: $40 \text{ mL min}^{-1} \text{ Ar} : 40 \text{ mL min}^{-1} \text{ O}_2$. The ticks indicate the Bragg positions for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (orange), CaAl_2O_4 (green), $\text{Ca}_3\text{Al}_2\text{O}_6$ (purple), elemental Al (pink), Al_2O_3 (cyan), CaO (olive).

Refinement details for the data shown in Figure S7						
Source	Bruker D8 ADVANCE (laboratory X-ray)					
Temperature	RT					
Pressure	ambient					
Wavelengths	Cu $K\alpha_1$ and Cu $K\alpha_2$: 154.0596 and 154.4308 pm					
Chemical formula	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	CaAl_2O_4	$\text{Ca}_3\text{Al}_2\text{O}_6$	Al	Al_2O_3	CaO
Abbreviation	C12A7	CA	C3A1	–	–	–
Space group	$\bar{I}43d$	$P2_1/c$	$Pa\bar{3}$	$Fm\bar{3}m$	$R\bar{3}c$	$Fm\bar{3}m$
a / pm	1198.00(2)	874(2)	1526.5(4)	405.31(1)	1300.7(3)	482.01(2)
b / pm	a	811.8(6)	a	a	a	a
c / pm	a	1750(6)	a	a	475.93(5)	a
$\beta / ^\circ$	90	120.0(4)	90	90	90	90
V / nm^3	1.7194	1.0756	3.5570	0.0666	0.2552	0.1120
Z	4	12	24	4	6	4
d -space range	0.85-14.35 Å (6-130° 2θ)					
χ^2	1.85					
R_p	7.15					
R_{wp}	9.10					
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2};$ $R_{wp} = \left(\frac{\sum w I_0 - I_c ^2}{\sum w I_0^2} \right)^{\frac{1}{2}}$					

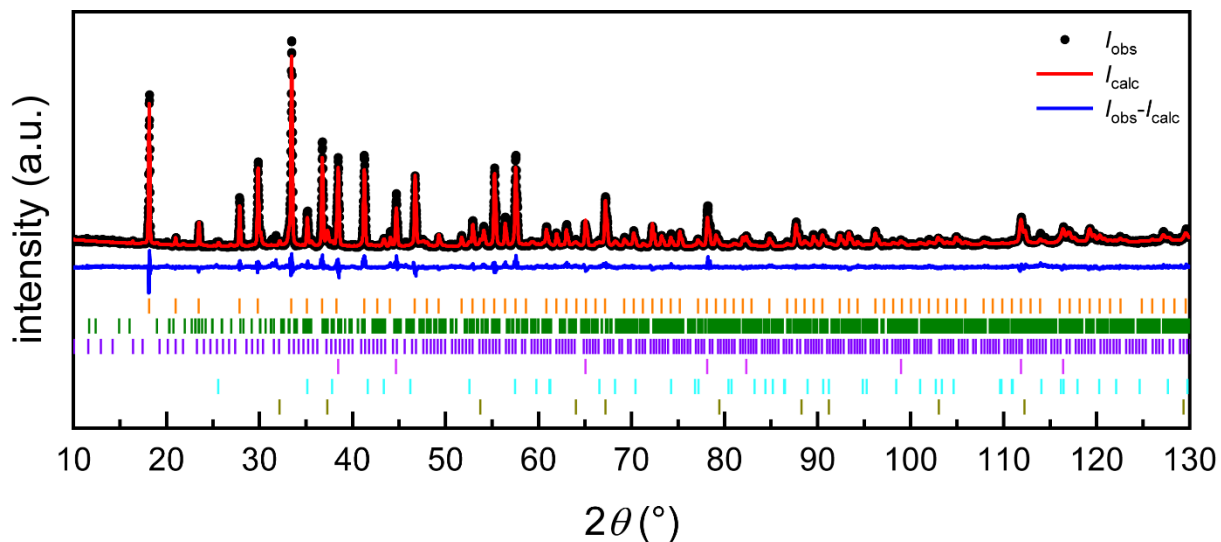


Figure S8. Rietveld fit of the powder X-ray diffraction pattern of CaAl_2 oxidized by the following conditions: STA; heating rate: 40 K min^{-1} ; dwelling time: 0 h; gas flow: $40 \text{ mL min}^{-1} \text{ Ar} : 40 \text{ mL min}^{-1} \text{ O}_2$. The ticks indicate the Bragg positions for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (orange), CaAl_2O_4 (green), $\text{Ca}_3\text{Al}_2\text{O}_6$ (purple), elemental Al (pink), Al_2O_3 (cyan), CaO (olive).

Refinement details for the data shown in Figure S8						
Source	Bruker D8 ADVANCE (laboratory X-ray)					
Temperature	RT					
Pressure	ambient					
Wavelengths	Cu $K\alpha_1$ and Cu $K\alpha_2$: 154.0596 and 154.4308 pm					
Chemical formula	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	CaAl_2O_4	$\text{Ca}_3\text{Al}_2\text{O}_6$	Al	Al_2O_3	CaO
Abbreviation	C12A7	CA	C3A1	–	–	–
Space group	$\bar{I}43d$	$P2_1/c$	$Pa\bar{3}$	$Fm\bar{3}m$	$R\bar{3}c$	$Fm\bar{3}m$
a / pm	1197.92(1)	874.8(12)	1526.2(2)	405.35(1)	475.90(6)	481.96(5)
b / pm	a	809.9(4)	a	a	a	a
c / pm	a	1748(3)	a	a	1300.9(4)	a
$\beta / ^\circ$	90	120.00(16)	90	90	90	90
V / nm^3	1.7190	1.0720	3.5552	0.0666	0.2552	0.1120
Z	4	12	24	4	6	4
d -space range	0.85-14.35 Å (6-130° 2θ)					
χ^2	5.00					
R_p	7.50					
R_{wp}	10.06					
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2 }^{1/2}$					

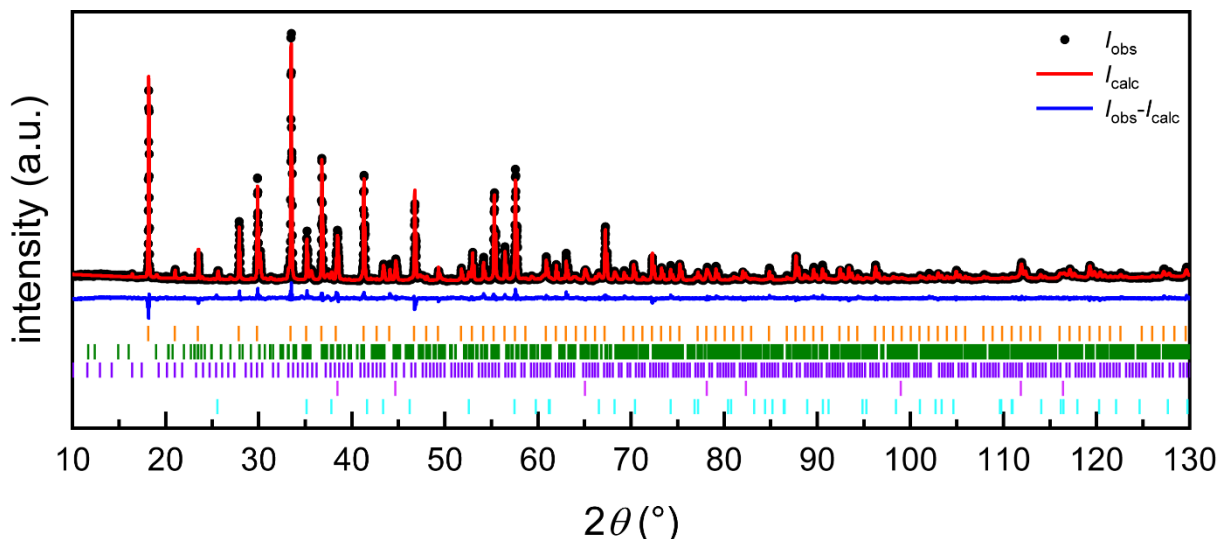


Figure S9. Rietveld fit of the powder X-ray diffraction pattern of CaAl_2 oxidized by the following conditions: STA; heating rate: 5 K min^{-1} ; dwelling time: 5 h; gas flow: $40 \text{ mL min}^{-1} \text{ Ar} : 40 \text{ mL min}^{-1} \text{ O}_2$. The ticks indicate the Bragg positions for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (orange), CaAl_2O_4 (green), $\text{Ca}_3\text{Al}_2\text{O}_6$ (purple), elemental Al (pink), Al_2O_3 (cyan).

Refinement details for the data shown in Figure S9					
Source	Bruker D8 ADVANCE (laboratory X-ray)				
Temperature	RT				
Pressure	ambient				
Wavelengths	Cu $K\alpha_1$ and Cu $K\alpha_2$: 154.0596 and 154.4308 pm				
Chemical formula	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	CaAl_2O_4	$\text{Ca}_3\text{Al}_2\text{O}_6$	Al	Al_2O_3
Abbreviation	C12A7	CA	C3A1	–	–
Space group	$I\bar{4}3d$	$P2_1/c$	$Pa\bar{3}$	$Fm\bar{3}m$	$R\bar{3}c$
a / pm	1197.72(1)	874.49(15)	1526.69(12)	405.43(1)	475.85(2)
b / pm	a	809.09(9)	a	a	a
c / pm	a	1743.6(2)	a	a	1299.77(10)
$\beta / ^\circ$	90	119.80(1)	90	90	90
V / nm^3	1.7182	1.0705	3.5583	0.0666	0.2550
Z	4	12	24	4	6
d -space range	0.85–14.35 Å (6–130° 2θ)				
χ^2	3.75				
R_p	6.72				
R_{wp}	8.79				
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2}$				

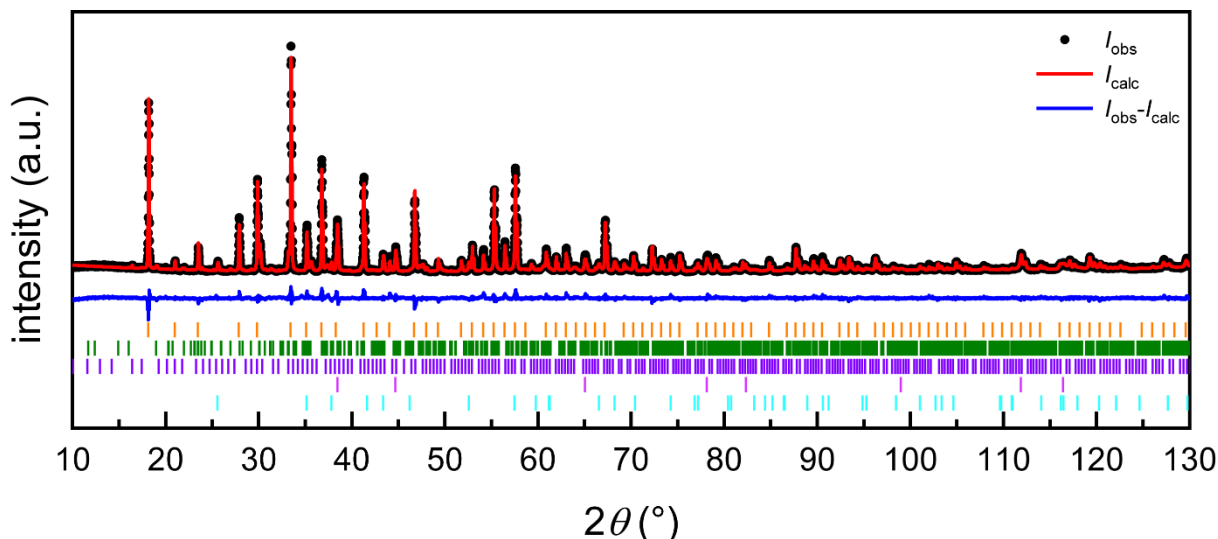


Figure S10. Rietveld fit of the powder X-ray diffraction pattern of CaAl_2 oxidized by the following conditions: STA; heating rate: 10 K min^{-1} ; dwelling time: 5 h; gas flow: $40 \text{ mL min}^{-1} \text{ Ar} : 40 \text{ mL min}^{-1} \text{ O}_2$. The ticks indicate the Bragg positions for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (orange), CaAl_2O_4 (green), $\text{Ca}_3\text{Al}_2\text{O}_6$ (purple), elemental Al (pink), Al_2O_3 (cyan).

Refinement details for the data shown in Figure S10					
Source	Bruker D8 ADVANCE (laboratory X-ray)				
Temperature	RT				
Pressure	ambient				
Wavelengths	Cu $K\alpha_1$ and Cu $K\alpha_2$: 154.0596 and 154.4308 pm				
Chemical formula	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	CaAl_2O_4	$\text{Ca}_3\text{Al}_2\text{O}_6$	Al	Al_2O_3
Abbreviation	C12A7	CA	C3A1	–	–
Space group	$I\bar{4}3d$	$P2_1/c$	$Pa\bar{3}$	$Fm\bar{3}m$	$R\bar{3}c$
a / pm	1197.77(1)	874.38(19)	1527.04(7)	405.47(1)	475.99(2)
b / pm	a	809.21(10)	a	a	a
c / pm	a	1743.9(3)	a	a	1299.72(9)
$\beta / ^\circ$	90	119.82(2)	90	90	90
V / nm^3	1.7183	1.0705	3.5609	0.0666	0.2550
Z	4	12	24	4	6
d -space range	0.85–14.35 Å (6–130° 2θ)				
χ^2	3.91				
R_p	6.85				
R_{wp}	8.92				
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2 }$				

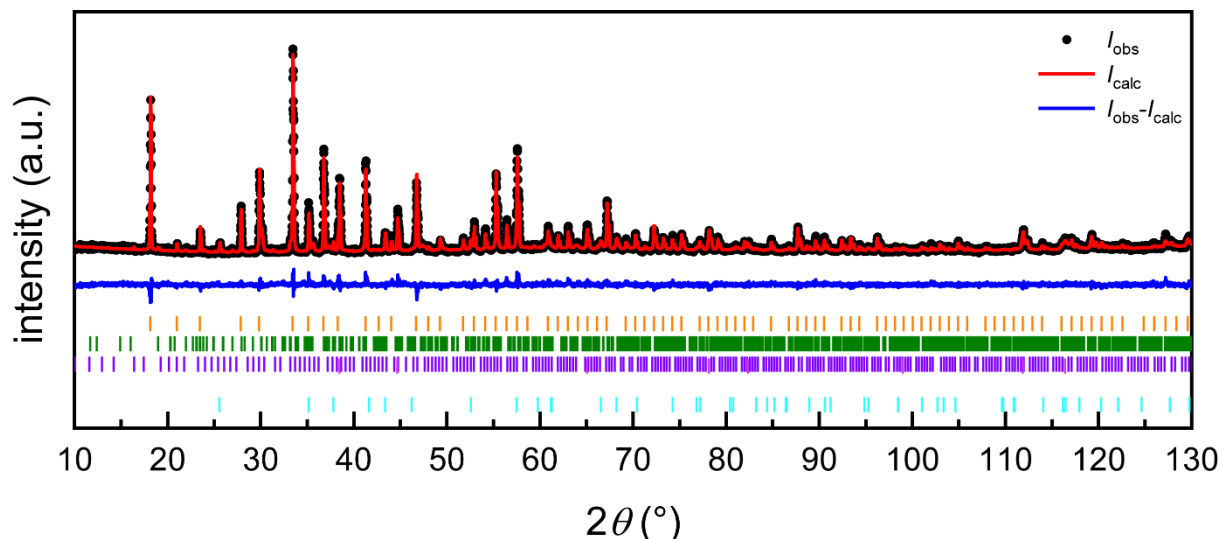


Figure S11. Rietveld fit of the powder X-ray diffraction pattern of CaAl_2 oxidized by the following conditions: STA; heating rate: 20 K min^{-1} ; dwelling time: 5 h; gas flow: $40 \text{ mL min}^{-1} \text{ Ar} : 40 \text{ mL min}^{-1} \text{ O}_2$. The ticks indicate the Bragg positions for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (orange), CaAl_2O_4 (green), $\text{Ca}_3\text{Al}_2\text{O}_6$ (purple), elemental Al (pink), Al_2O_3 (cyan).

Refinement details for the data shown in Figure S11					
Source	Bruker D8 ADVANCE (laboratory X-ray)				
Temperature	RT				
Pressure	ambient				
Wavelengths	Cu $K\alpha_1$ and Cu $K\alpha_2$: 154.0596 and 154.4308 pm				
Chemical formula	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	CaAl_2O_4	$\text{Ca}_3\text{Al}_2\text{O}_6$	Al	Al_2O_3
Abbreviation	C12A7	CA	C3A1	–	–
Space group	$I\bar{4}3d$	$P2_1/c$	$Pa\bar{3}$	$Fm\bar{3}m$	$R\bar{3}c$
a / pm	1197.86(1)	875.1(5)	1527.1(3)	405.35(1)	476.01(2)
b / pm	a	809.49(17)	a	a	a
c / pm	a	1744.8(6)	a	a	1299.83(13)
$\beta / ^\circ$	90	199.92(6)	90	90	90
V / nm^3	1.7188	1.0713	3.5610	0.0666	0.2551
Z	4	12	24	4	6
d -space range	0.85–14.35 Å (6–130° 2θ)				
χ^2	1.78				
R_p	7.08				
R_{wp}	8.99				
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2}$				

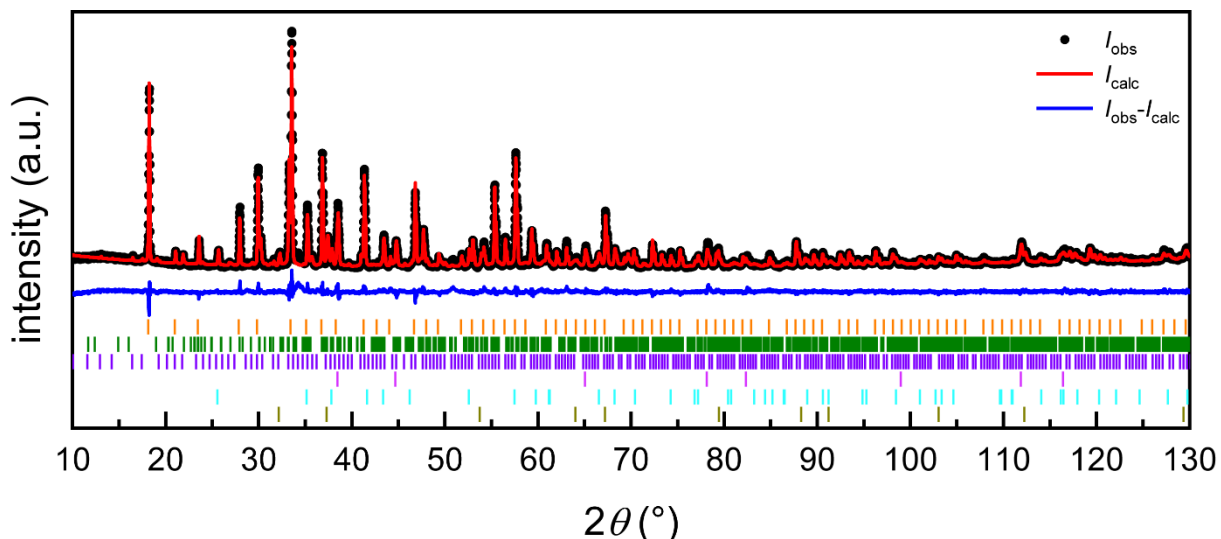


Figure S12. Rietveld fit of the powder X-ray diffraction pattern of CaAl_2 oxidized by the following conditions: STA; heating rate: 40 K min^{-1} ; dwelling time: 5 h; gas flow: $40 \text{ mL min}^{-1} \text{ Ar} : 40 \text{ mL min}^{-1} \text{ O}_2$. The ticks indicate the Bragg positions for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (orange), CaAl_2O_4 (green), $\text{Ca}_3\text{Al}_2\text{O}_6$ (purple), elemental Al (pink), Al_2O_3 (cyan), CaO (olive).

Refinement details for the data shown in Figure S12						
Source	Bruker D8 ADVANCE (laboratory X-ray)					
Temperature	RT					
Pressure	ambient					
Wavelengths	Cu $K\alpha_1$ and Cu $K\alpha_2$: 154.0596 and 154.4308 pm					
Chemical formula	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	CaAl_2O_4	$\text{Ca}_3\text{Al}_2\text{O}_6$	Al	Al_2O_3	CaO
Abbreviation	C12A7	CA	C3A1	–	–	–
Space group	$I\bar{4}3d$	$P2_1/c$	$Pa\bar{3}$	$Fm\bar{3}m$	$R\bar{3}c$	$Fm\bar{3}m$
a / pm	1197.84(1)	876.4(2)	1527.13(3)	405.43(1)	476.05(2)	481.41(3)
b / pm	a	808.89(16)	a	a	a	a
c / pm	a	1744.1(4)	a	a	1299.89(9)	a
$\beta / ^\circ$	90	119.97(3)	90	90	90	90
V / nm^3	1.7187	1.0711	3.5615	0.0666	0.2551	0.1116
Z	4	12	24	4	6	4
d -space range	0.85–14.35 Å (6–130° 2θ)					
χ^2	3.85					
R_p	7.01					
R_{wp}	9.42					
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2 }$					

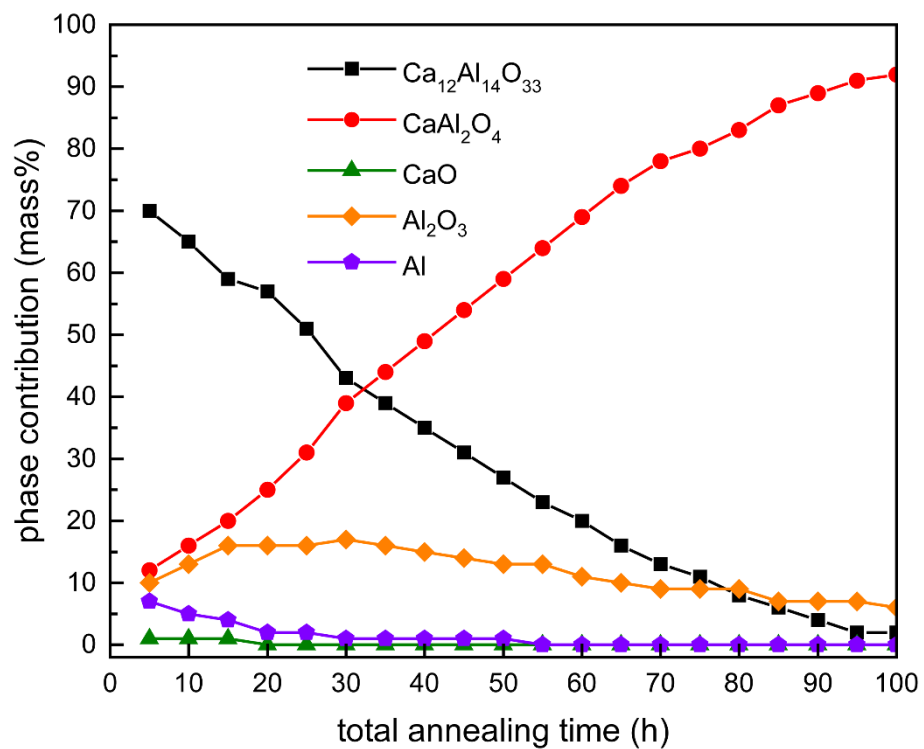


Figure S13. Results of the Rietveld refinements of the oxidation approach of CaAl_2 with repeated heating to 1273 K for 5 h each followed by grinding.

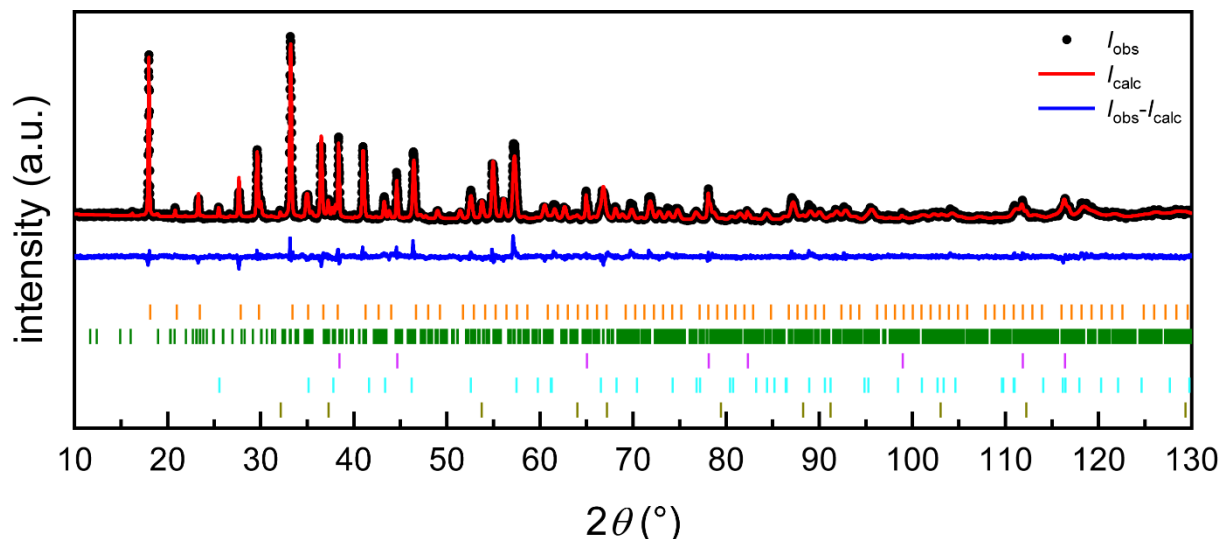


Figure S14. Rietveld fit of the powder X-ray diffraction pattern of CaAl_2 oxidized by the following conditions: muffle furnace; heating rate: 15 K min^{-1} ; dwelling time: 1 h; air. The ticks indicate the Bragg positions for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (orange), CaAl_2O_4 (green), $\text{Ca}_3\text{Al}_2\text{O}_6$ (purple), elemental Al (pink), Al_2O_3 (cyan), CaO (olive).

Refinement details for the data shown in Figure S14					
Source	Bruker D8 ADVANCE (laboratory X-ray)				
Temperature	RT				
Pressure	ambient				
Wavelengths	Cu $K\alpha_1$ and Cu $K\alpha_2$: 154.0596 and 154.4308 pm				
Chemical formula	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	CaAl_2O_4	Al	Al_2O_3	CaO
Abbreviation	C12A7	CA	–	–	–
Space group	$I\bar{4}3d$	$P2_1/c$	$Fm\bar{3}m$	$R\bar{3}c$	$Fm\bar{3}m$
a / pm	1203.25(2)	877.6(6)	405.40(1)	476.32(3)	481.71(4)
b / pm	a	809.0(3)	a	a	a
c / pm	a	1747.3(11)	a	1300.48(16)	a
$\beta / ^\circ$	90	120.00(8)	90	90	90
V / nm^3	1.7421	1.0743	0.0666	0.2555	0.1118
Z	4	12	4	6	4
d -space range	0.85–14.35 Å (6–130° 2θ)				
χ^2	3.85				
R_p	8.73				
R_{wp}	11.12				
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2}$				

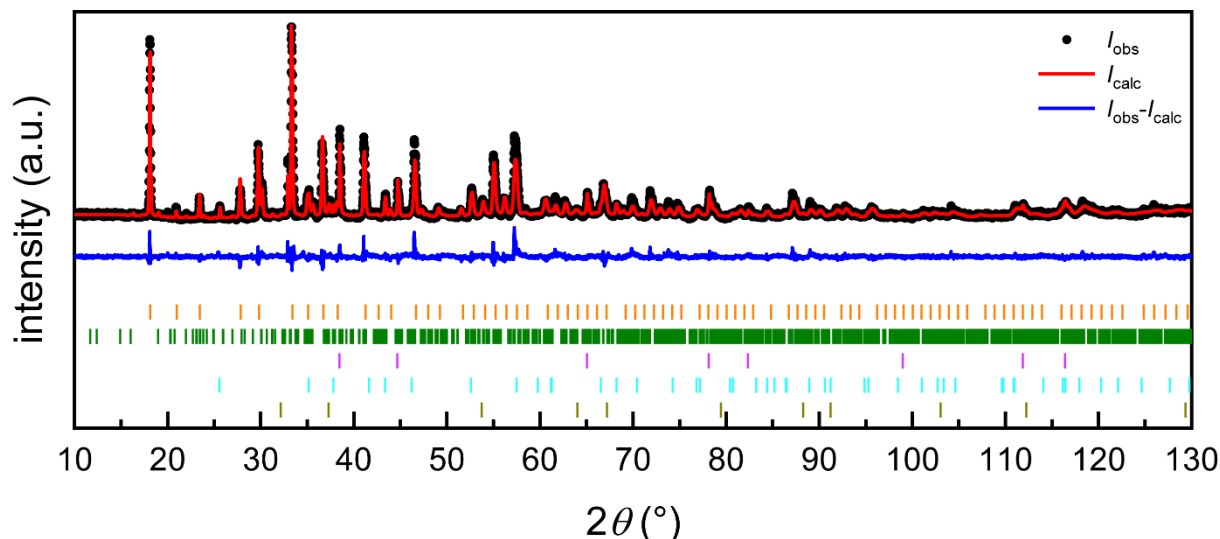


Figure S15. Rietveld fit of the powder X-ray diffraction pattern of CaAl_2 oxidized by the following conditions: muffle furnace; heating rate: 15 K min^{-1} ; dwelling time: 5 h; air. The ticks indicate the Bragg positions for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (orange), CaAl_2O_4 (green), elemental Al (pink), Al_2O_3 (cyan), CaO (olive).

Refinement details for the data shown in Figure S15					
Source	Bruker D8 ADVANCE (laboratory X-ray)				
Temperature	RT				
Pressure	ambient				
Wavelengths	Cu $K\alpha_1$ and Cu $K\alpha_2$: 154.0596 and 154.4308 pm				
Chemical formula	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	CaAl_2O_4	Al	Al_2O_3	CaO
Abbreviation	C12A7	CA	–	–	–
Space group	$I\bar{4}3d$	$P2_1/c$	$Fm\bar{3}m$	$R\bar{3}c$	$Fm\bar{3}m$
a / pm	1203.13(3)	876.2(5)	405.29(1)	476.25(3)	481.71(15)
b / pm	a	809.35(18)	a	a	a
c / pm	a	1745.9(8)	a	1299.42(17)	a
β / °	90	119.93(17)	90	90	90
V / nm^3	1.7416	1.0730	0.0666	0.2552	0.1118
Z	4	12	4	6	4
d -space range	0.85-14.35 Å (6-130° 2θ)				
χ^2	2.97				
R_p	9.15				
R_{wp}	11.77				
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2}$ $R_{wp} = \left(\frac{\sum w I_0 - I_c ^2}{\sum w I_0^2} \right)^{\frac{1}{2}}$				

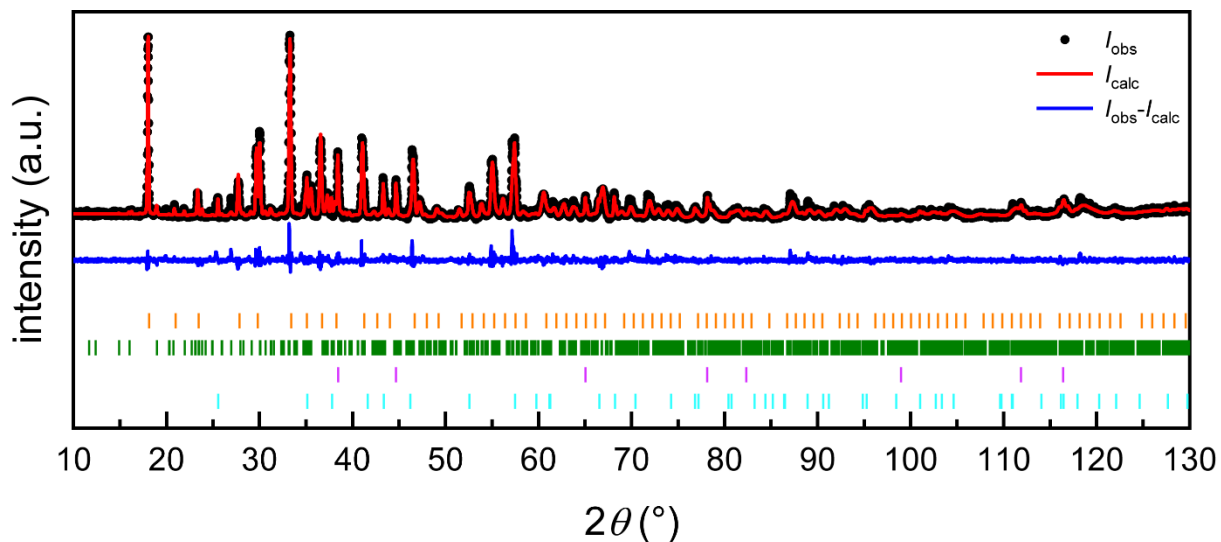


Figure S16. Rietveld fit of the powder X-ray diffraction pattern of CaAl_2 oxidized by the following conditions: muffle furnace; heating rate: 15 K min^{-1} ; dwelling time: 48 h; air. The ticks indicate the Bragg positions for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (orange), CaAl_2O_4 (green), elemental Al (pink), Al_2O_3 (cyan).

Refinement details for the data shown in Figure S16				
Source	Bruker D8 ADVANCE (laboratory X-ray)			
Temperature	RT			
Pressure	ambient			
Wavelengths	Cu $K\alpha_1$ and Cu $K\alpha_2$: 154.0596 and 154.4308 pm			
Chemical formula	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	CaAl_2O_4	Al	Al_2O_3
Abbreviation	C12A7	CA	–	–
Space group	$I\bar{4}3d$	$P2_1/c$	$Fm\bar{3}m$	$R\bar{3}c$
a / pm	1201.92(3)	875.02(13)	405.19(1)	476.08(2)
b / pm	a	809.69(9)	a	a
c / pm	a	1744.4(2)	a	1299.84(10)
β / °	90	119.76(1)	90	90
V / nm^3	1.7363	1.0729	0.0665	0.2551
Z	4	12	4	6
d -space range	0.85–14.35 Å (6–130° 2θ)			
χ^2	2.92			
R_p	8.57			
R_{wp}	11.12			
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2}$			

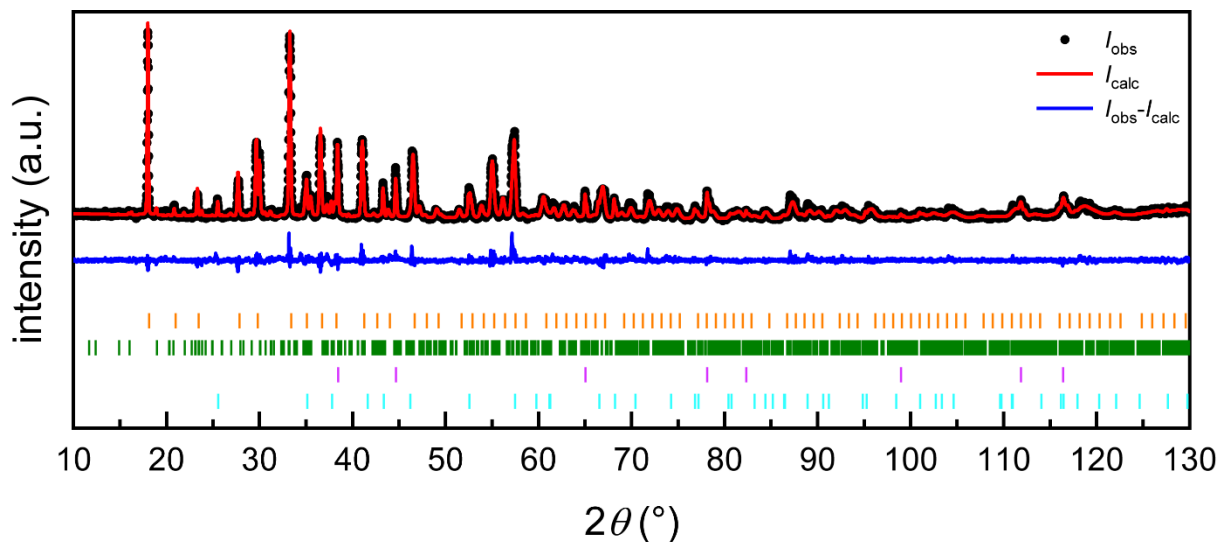


Figure S17. Rietveld fit of the powder X-ray diffraction pattern of CaAl_2 oxidized by the following conditions: muffle furnace; heating rate: 15 K min^{-1} ; dwelling time: 96 h; air. The ticks indicate the Bragg positions for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (orange), CaAl_2O_4 (green), elemental Al (pink), Al_2O_3 (cyan).

Refinement details for the data shown in Figure S17				
Source	Bruker D8 ADVANCE (laboratory X-ray)			
Temperature	RT			
Pressure	ambient			
Wavelengths	Cu $K\alpha_1$ and Cu $K\alpha_2$: 154.0596 and 154.4308 pm			
Chemical formula	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	CaAl_2O_4	Al	Al_2O_3
Abbreviation	C12A7	CA	–	–
Space group	$I\bar{4}3d$	$P2_1/c$	$Fm\bar{3}m$	$R\bar{3}c$
a / pm	1202.26(3)	875.20(15)	405.13(1)	476.12(2)
b / pm	a	809.60(8)	a	a
c / pm	a	1743.86(17)	a	1299.74(9)
$\beta / ^\circ$	90	119.77(2)	90	90
V / nm^3	1.7378	1.0726	0.0665	0.2552
Z	4	12	4	6
d -space range	0.85–14.35 Å (6–130° 2θ)			
χ^2	3.10			
R_p	8.47			
R_{wp}	11.22			
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2}$			

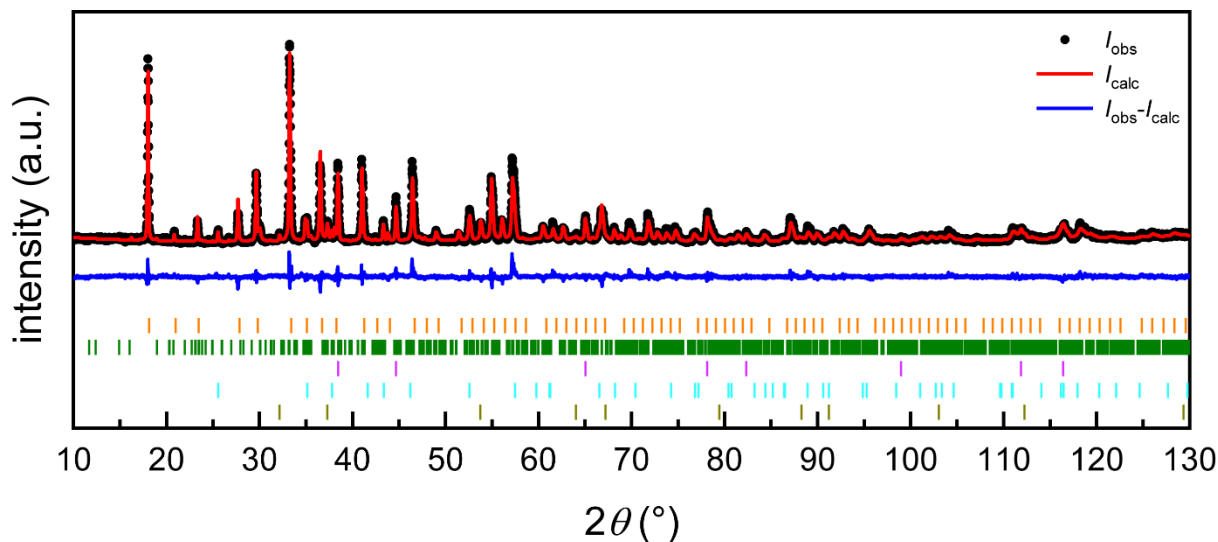


Figure S18. Rietveld fit of the powder X-ray diffraction pattern of CaAl_2 oxidized by the following conditions: muffle furnace; heating rate: 15 K min^{-1} ; dwelling time: 1 h; total dwelling time: 1 h; air. The ticks indicate the Bragg positions for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (orange), CaAl_2O_4 (green), elemental Al (pink), Al_2O_3 (cyan), CaO (olive).

Refinement details for the data shown in Figure S18					
Source	Bruker D8 ADVANCE (laboratory X-ray)				
Temperature	RT				
Pressure	ambient				
Wavelengths	Cu $K\alpha_1$ and Cu $K\alpha_2$: 154.0596 and 154.4308 pm				
Chemical formula	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	CaAl_2O_4	Al	Al_2O_3	CaO
Abbreviation	C12A7	CA	–	–	–
Space group	$\bar{I}43d$	$P2_1/c$	$Fm\bar{3}m$	$R\bar{3}c$	$Fm\bar{3}m$
a / pm	1203.72(2)	877.5(4)	405.20(1)	475.24(3)	481.61(4)
b / pm	a	808.5(4)	a	a	a
c / pm	a	1749(2)	a	1300.15(16)	a
β / °	90	120.00(17)	90	90	90
V / nm^3	1.7441	1.0750	0.0665	0.2554	0.1117
Z	4	12	4	6	4
d -space range	0.85–14.35 Å (6–130° 2θ)				
χ^2	2.97				
R_p	8.30				
R_{wp}	10.59				
Definition of R factors	$R_p = \frac{\sum w I_o - I_c ^2}{\sum w I_o^2}^{1/2}$				

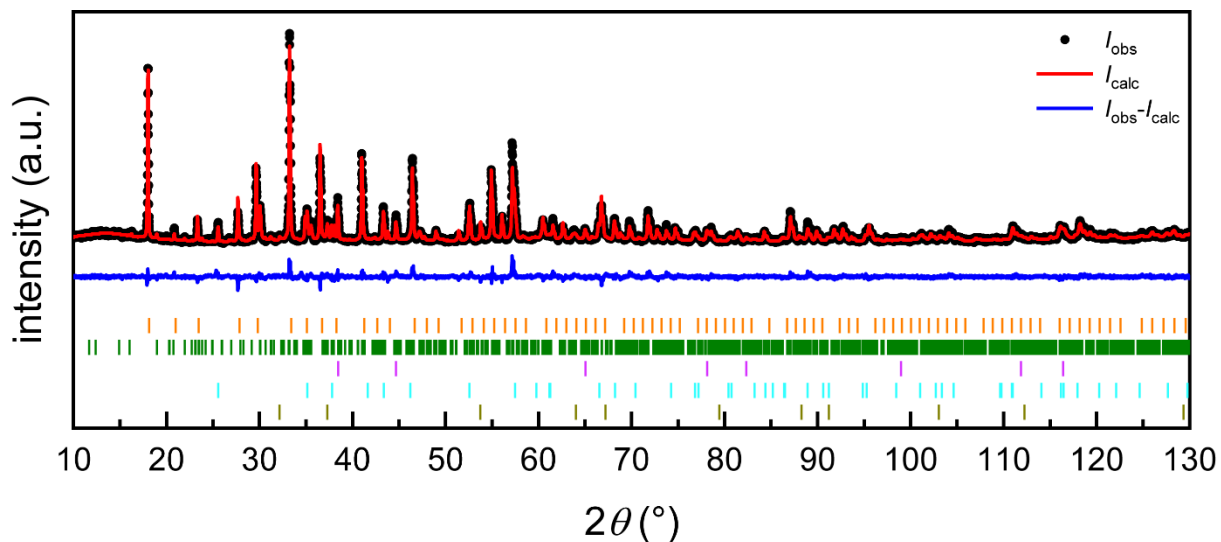


Figure S19. Rietveld fit of the powder X-ray diffraction pattern of CaAl_2 oxidized by the following conditions: muffle furnace; heating rate: 15 K min^{-1} ; dwelling time: 1 h; total dwelling time: 2 h; air. The ticks indicate the Bragg positions for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (orange), CaAl_2O_4 (green), elemental Al (pink), Al_2O_3 (cyan), CaO (olive).

Refinement details for the data shown in Figure S19					
Source	Bruker D8 ADVANCE (laboratory X-ray)				
Temperature	RT				
Pressure	ambient				
Wavelengths	Cu $K\alpha_1$ and Cu $K\alpha_2$: 154.0596 and 154.4308 pm				
Chemical formula	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	CaAl_2O_4	Al	Al_2O_3	CaO
Abbreviation	C12A7	CA	–	–	–
Space group	$I\bar{4}3d$	$P2_1/c$	$Fm\bar{3}m$	$R\bar{3}c$	$Fm\bar{3}m$
a / pm	1204.10(2)	876.1(3)	405.38(1)	476.13(2)	481.50(7)
b / pm	a	809.22(14)	a	a	a
c / pm	a	1746.8(6)	a	1299.98(9)	a
β / °	90	119.98(5)	90	90	90
V / nm^3	1.7458	1.0728	0.0666	0.2552	0.1116
Z	4	12	4	6	4
d -space range	0.85-14.35 Å (6-130° 2θ)				
χ^2	3.12				
R_p	8.43				
R_{wp}	6.08				
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2}$				

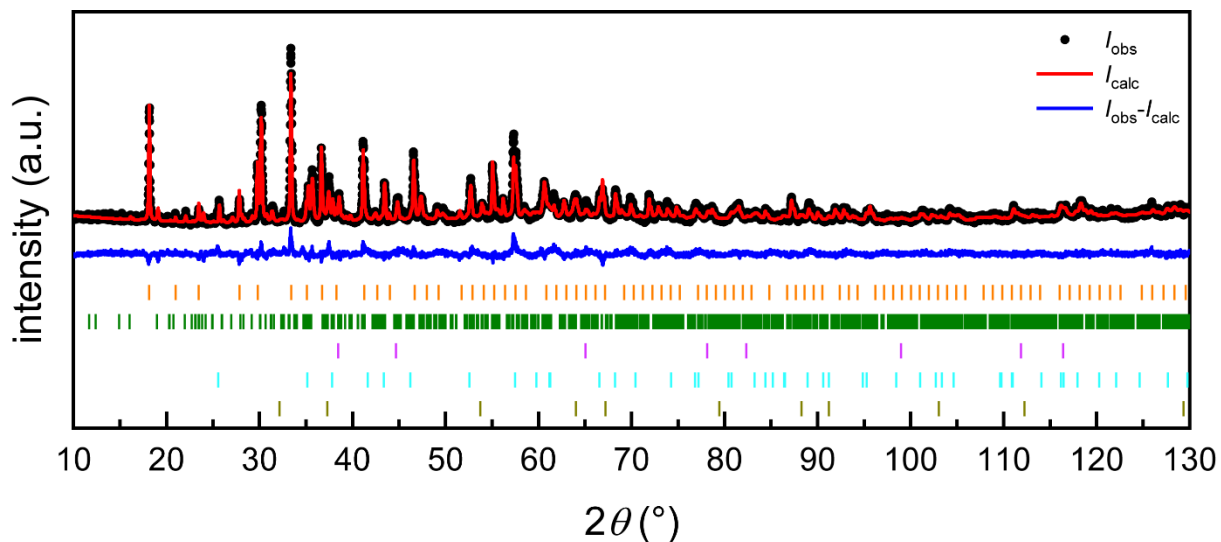


Figure S20. Rietveld fit of the powder X-ray diffraction pattern of CaAl_2 oxidized by the following conditions: muffle furnace; heating rate: 15 K min^{-1} ; dwelling time: 5 h; total dwelling time: 7 h; air. The ticks indicate the Bragg positions for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (orange), CaAl_2O_4 (green), elemental Al (pink), Al_2O_3 (cyan), CaO (olive).

Refinement details for the data shown in Figure S20					
Source	Bruker D8 ADVANCE (laboratory X-ray)				
Temperature	RT				
Pressure	ambient				
Wavelengths	Cu $K\alpha_1$ and Cu $K\alpha_2$: 154.0596 and 154.4308 pm				
Chemical formula	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	CaAl_2O_4	Al	Al_2O_3	CaO
Abbreviation	C12A7	CA	–	–	–
Space group	$\bar{I}43d$	$P2_1/c$	$Fm\bar{3}m$	$R\bar{3}c$	$Fm\bar{3}m$
a / pm	1203.96(3)	874.57(12)	405.46(4)	476.11(2)	482.4(3)
b / pm	a	809.64(7)	a	a	a
c / pm	a	1744.39(18)	a	1299.91(11)	a
β / °	90	119.791(11)	90	90	90
V / nm^3	1.74515(11)	1.0719(2)	0.066656(18)	0.25519(3)	0.1122(2)
Z	4	12	4	6	4
d -space range	0.85–14.35 Å (6–130° 2θ)				
χ^2	2.80				
R_p	8.82				
R_{wp}	11.27				
Definition of R factors	$R_p = \frac{\sum w I_o - I_c ^2}{\sum w I_o^2};$ $R_{wp} = \left(\frac{\sum w I_o - I_c ^2}{\sum w I_o^2} \right)^{\frac{1}{2}}$				

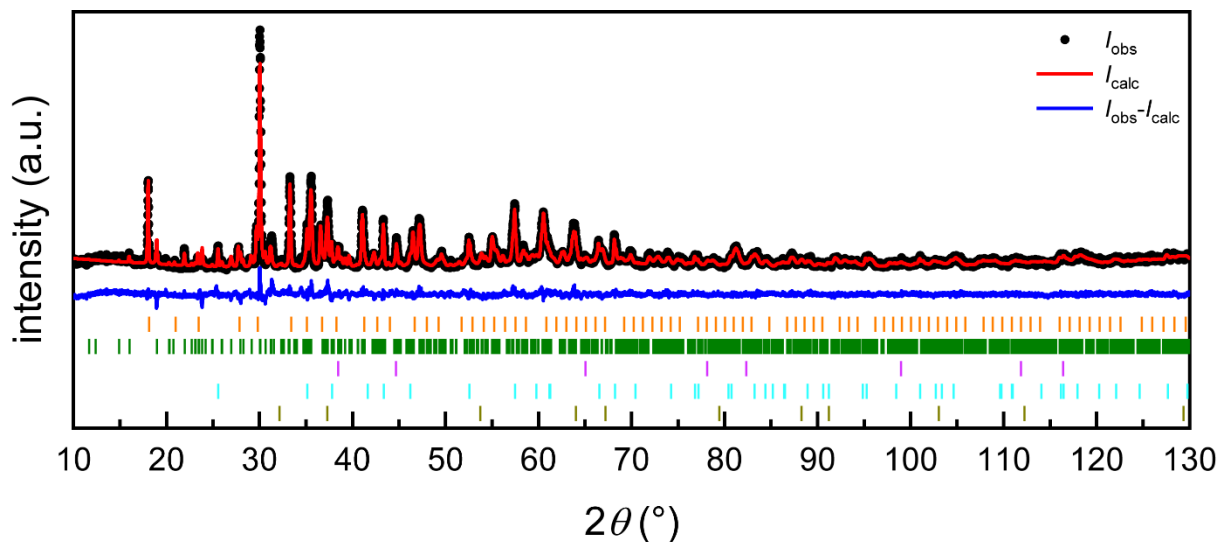


Figure S21. Rietveld fit of the powder X-ray diffraction pattern of CaAl_2 oxidized by the following conditions: muffle furnace; heating rate: 15 K min^{-1} ; dwelling time: 10 h; total dwelling time: 17 h; air. The ticks indicate the Bragg positions for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (orange), CaAl_2O_4 (green), elemental Al (pink), Al_2O_3 (cyan), CaO (olive).

Refinement details for the data shown in Figure S21					
Source	Bruker D8 ADVANCE (laboratory X-ray)				
Temperature	RT				
Pressure	ambient				
Wavelengths	Cu $K\alpha_1$ and Cu $K\alpha_2$: 154.0596 and 154.4308 pm				
Chemical formula	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	CaAl_2O_4	Al	Al_2O_3	CaO
Abbreviation	C12A7	CA	–	–	–
Space group	$\bar{I}43d$	$P2_1/c$	$Fm\bar{3}m$	$R\bar{3}c$	$Fm\bar{3}m$
a / pm	1202.55(4)	874.57(12)	405.39(7)	476.12(2)	482.0(2)
b / pm	a	809.64(7)	a	a	a
c / pm	a	1744.39(18)	a	1300.05(10)	a
β / °	90	119.79(1)	90	90	90
V / nm^3	1.7390	1.0719	0.0666	0.2552	0.1120
Z	4	12	4	6	4
d -space range	0.85–14.35 Å (6–130° 2θ)				
χ^2	3.05				
R_p	7.69				
R_{wp}	10.41				
Definition of R factors	$R_p = \frac{\sum w I_o - I_c ^2}{\sum w I_o^2};$ $R_{wp} = \left(\frac{\sum w I_o - I_c ^2}{\sum w I_o^2} \right)^{\frac{1}{2}}$				

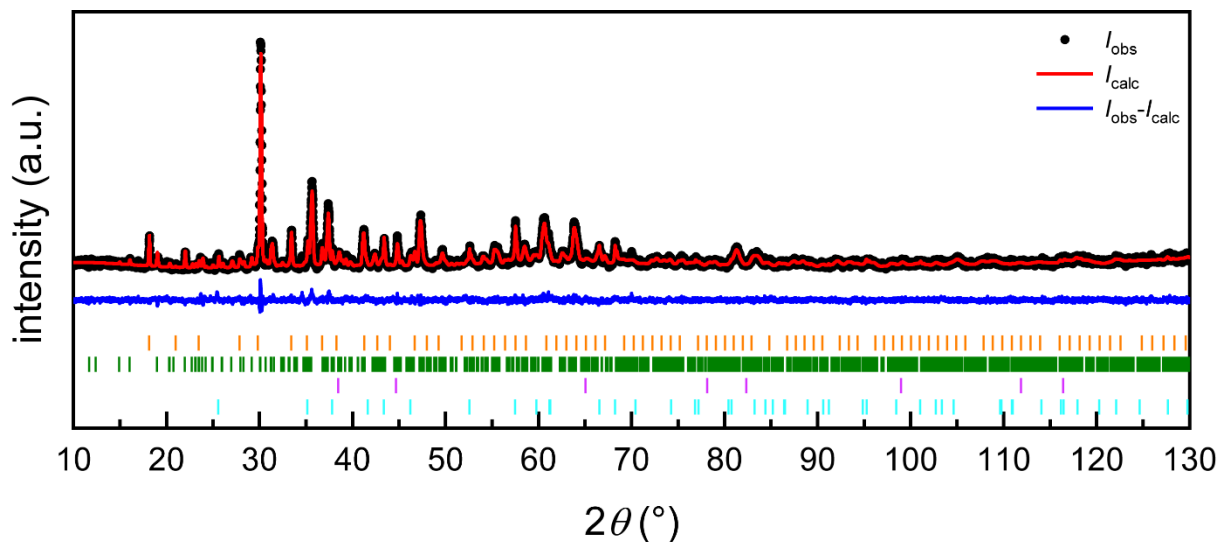


Figure S22. Rietveld fit of the powder X-ray diffraction pattern of CaAl_2 oxidized by the following conditions: muffle furnace; heating rate: 15 K min^{-1} ; dwelling time: 20 h; total dwelling time: 37 h; air. The ticks indicate the Bragg positions for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (orange), CaAl_2O_4 (green), elemental Al (pink), Al_2O_3 (cyan).

Refinement details for the data shown in Figure S22				
Source	Bruker D8 ADVANCE (laboratory X-ray)			
Temperature	RT			
Pressure	ambient			
Wavelengths	Cu $K\alpha_1$ and Cu $K\alpha_2$: 154.0596 and 154.4308 pm			
Chemical formula	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	CaAl_2O_4	Al	Al_2O_3
Abbreviation	C12A7	CA	–	–
Space group	$I\bar{4}3d$	$P2_1/c$	$Fm\bar{3}m$	$R\bar{3}c$
a / pm	1200.12(7)	874.65(8)	405.17(11)	476.05(3)
b / pm	a	809.29(5)	a	a
c / pm	a	1743.83(11)	a	1299.86(12)
β / °	90	119.77(1)	90	90
V / nm^3	1.7285	1.0714	0.0665	0.2551
Z	4	12	4	6
d -space range	0.85–14.35 Å (6–130° 2θ)			
χ^2	2.08			
R_p	8.33			
R_{wp}	10.95			
Definition of R factors	$R_p = \frac{\sum w I_o - I_c ^2}{\sum w I_o^2 }^{1/2}$			

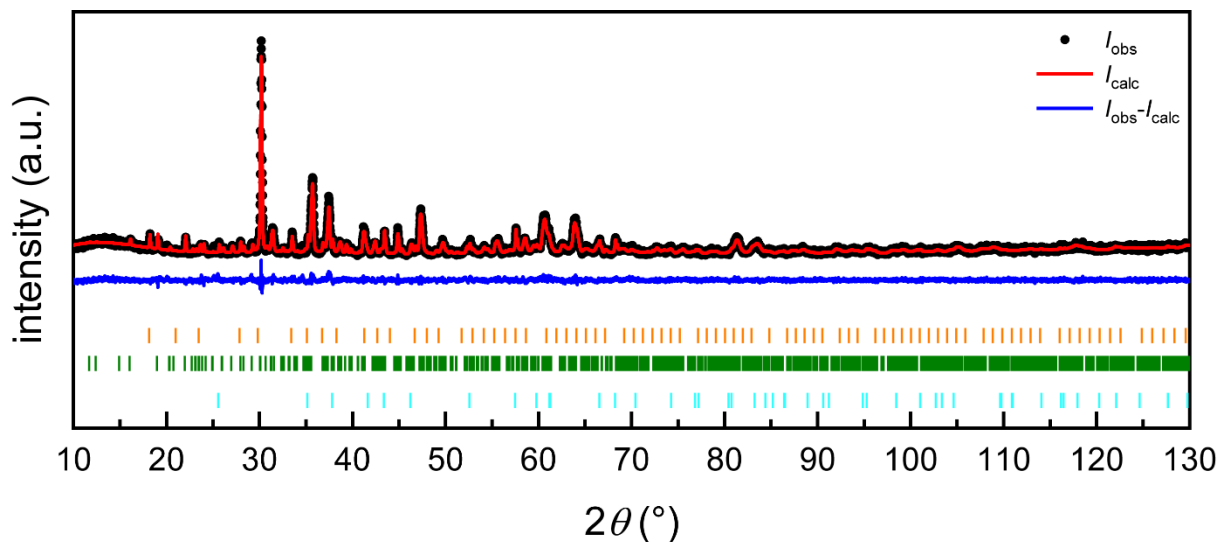


Figure S23. Rietveld fit of the powder X-ray diffraction pattern of CaAl_2 oxidized by the following conditions: muffle furnace; heating rate: 15 K min^{-1} ; dwelling time: 20 h; total dwelling time: 57 h; air. The ticks indicate the Bragg positions for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (orange), CaAl_2O_4 (green), Al_2O_3 (cyan).

Refinement details for the data shown in Figure S23			
Source	Bruker D8 ADVANCE (laboratory X-ray)		
Temperature	RT		
Pressure	ambient		
Wavelengths	Cu $K\alpha_1$ and Cu $K\alpha_2$: 154.0596 and 154.4308 pm		
Chemical formula	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	CaAl_2O_4	Al_2O_3
Abbreviation	C12A7	CA	–
Space group	$I\bar{4}3d$	$P2_1/c$	$R\bar{3}c$
a / pm	1198.58(9)	871.48(5)	476.12(3)
b / pm	a	809.26(4)	a
c / pm	a	1749.41(14)	1299.51(13)
$\beta / ^\circ$	90	119.78(1)	90
V / nm^3	1.7219	1.0709	0.2551
Z	4	12	6
d -space range	0.85-14.35 Å (6-130° 2θ)		
χ^2	2.22		
R_p	8.42		
R_{wp}	12.18		
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2 }^{1/2}$		

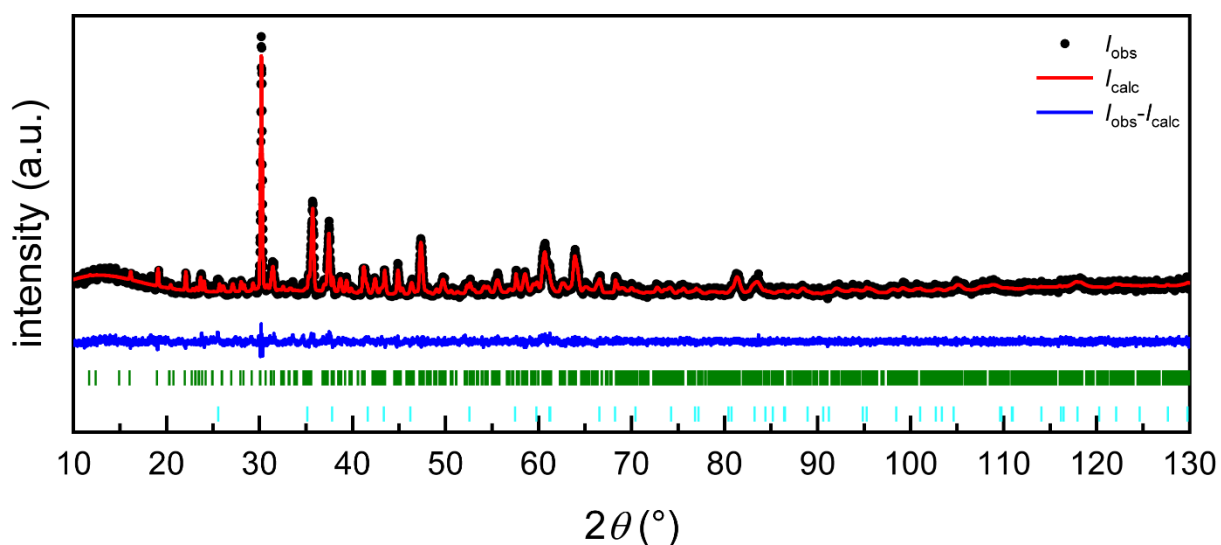


Figure S24. Rietveld fit of the powder X-ray diffraction pattern of CaAl_2 oxidized by the following conditions: muffle furnace; heating rate: 15 K min^{-1} ; dwelling time: 20 h; total dwelling time: 77 h; air. The ticks indicate the Bragg positions for CaAl_2O_4 (green), Al_2O_3 (cyan).

Refinement details for the data shown in Figure S24		
Source	Bruker D8 ADVANCE (laboratory X-ray)	
Temperature	RT	
Pressure	ambient	
Wavelengths	Cu $K\alpha_1$ and Cu $K\alpha_2$: 154.0596 and 154.4308 pm	
Chemical formula	CaAl_2O_4	Al_2O_3
Abbreviation	CA	–
Space group	$P2_1/c$	$R\bar{3}c$
a / pm	871.49(6)	476.21(4)
b / pm	809.41(6)	a
c / pm	1749.67(18)	1299.3(2)
β / °	119.78(1)	90
V / nm ³	1.0712	0.2552
Z	12	6
d -space range	0.85-14.35 Å (6-130° 2θ)	
χ^2	1.74	
R_p	9.77	
R_{wp}	12.71	
Definition of R factors	$R_p = \frac{\sum w I_o - I_c ^2}{\sum w I_o^2}$ $R_{wp} = \left(\frac{\sum w I_o - I_c ^2}{\sum w I_o^2} \right)^{\frac{1}{2}}$	

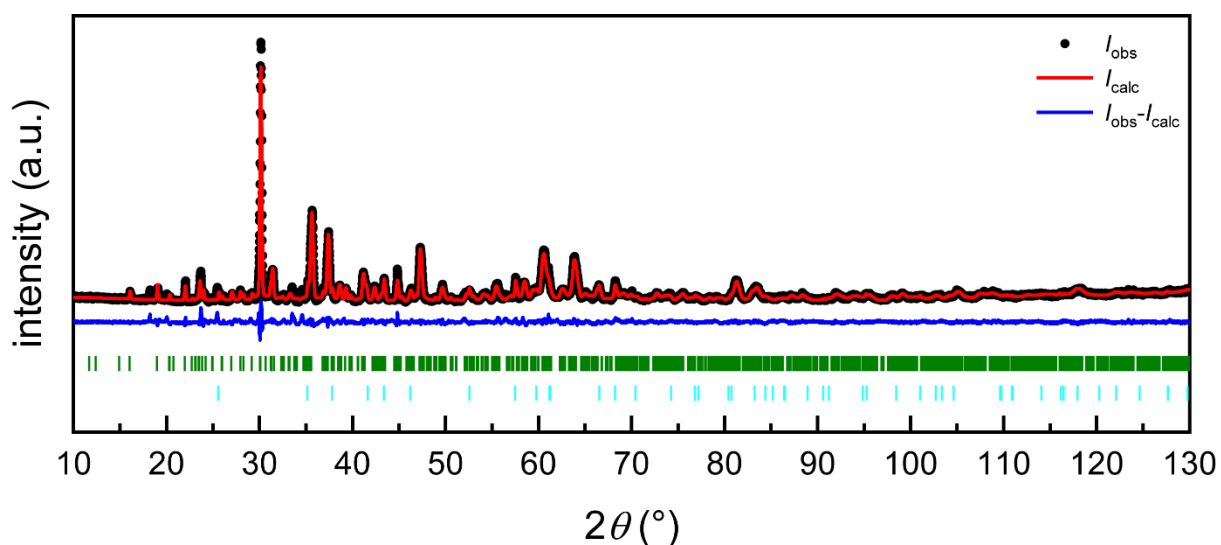


Figure S25. Rietveld fit of the powder X-ray diffraction pattern of CaAl_2 oxidized by the following conditions: muffle furnace; heating rate: 15 K min^{-1} ; dwelling time: 20 h; total dwelling time: 97 h; air. The ticks indicate the Bragg positions for CaAl_2O_4 (green), and Al_2O_3 (cyan).

Refinement details for the data shown in Figure S25		
Source	Bruker D8 ADVANCE (laboratory X-ray)	
Temperature	RT	
Pressure	ambient	
Wavelengths	Cu $K\alpha_1$ and Cu $K\alpha_2$: 154.0596 and 154.4308 pm	
Chemical formula	CaAl_2O_4	Al_2O_3
Abbreviation	CA	–
Space group	$P2_1/c$	$R\bar{3}c$
a / pm	871.45(5)	476.13(4)
b / pm	809.38(4)	a
c / pm	1749.77(15)	1299.27(17)
β / °	119.78(1)	90
V / nm^3	1.0712	0.2551
Z	12	6
d -space range	0.85-14.35 Å (6-130° 2θ)	
χ^2	3.08	
R_p	8.16	
R_{wp}	12.22	
Definition of R factors	$R_p = \frac{\sum w I_o - I_c ^2}{\sum w I_o^2}$ $R_{wp} = \left(\frac{\sum w I_o - I_c ^2}{\sum w I_o^2} \right)^{\frac{1}{2}}$	

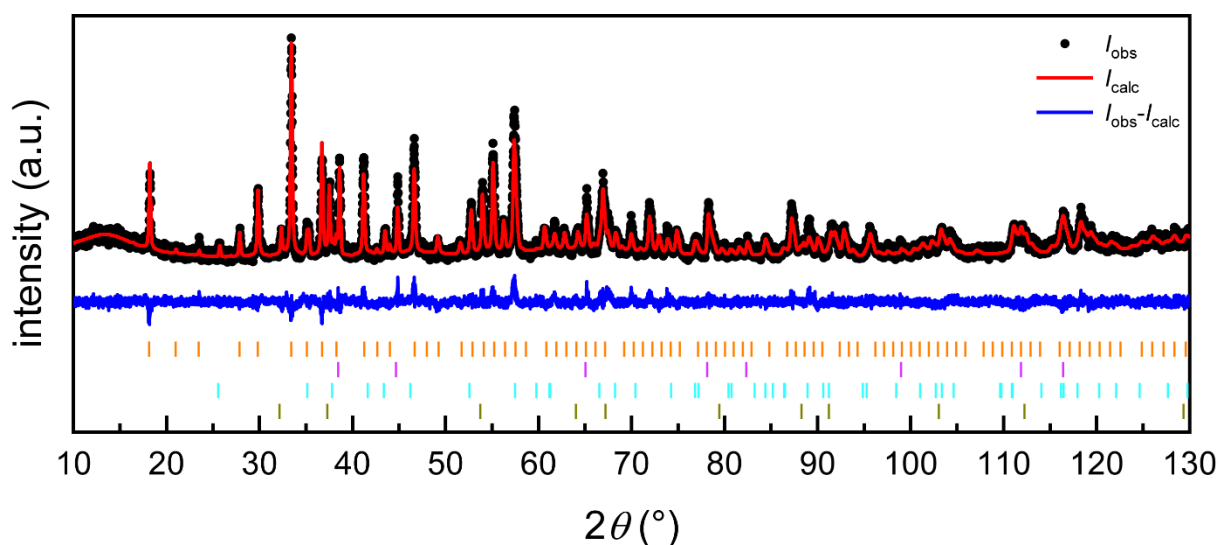


Figure S26. Rietveld fit of the powder X-ray diffraction pattern of CaAl_2 oxidized by the following conditions: muffle furnace; heating rate: 15 K min^{-1} ; dwelling time: 0 h; number of cycle: 1; air. The ticks indicate the Bragg positions for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (orange), elemental Al (pink), Al_2O_3 (cyan), CaO (olive).

Refinement details for the data shown in Figure S26				
Source	Bruker D8 ADVANCE (laboratory X-ray)			
Temperature	RT			
Pressure	ambient			
Wavelengths	Cu $K\alpha_1$ and Cu $K\alpha_2$: 154.0596 and 154.4308 pm			
Chemical formula	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	Al	Al_2O_3	CaO
Abbreviation	C12A7	–	–	–
Space group	$I\bar{4}3d$	$Fm\bar{3}m$	$R\bar{3}c$	$Fm\bar{3}m$
a / pm	1204.28(3)	405.43(1)	476.43(6)	481.65(2)
b / pm	a	a	a	a
c / pm	a	a	1301.5(3)	a
β / °	90	90	90	90
V / nm^3	1.7466	0.0666	0.2559	0.1117
Z	4	4	6	4
d -space range	0.85-14.35 Å (6-130° 2θ)			
χ^2	2.04			
R_p	9.74			
R_{wp}	12.65			
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2}$			

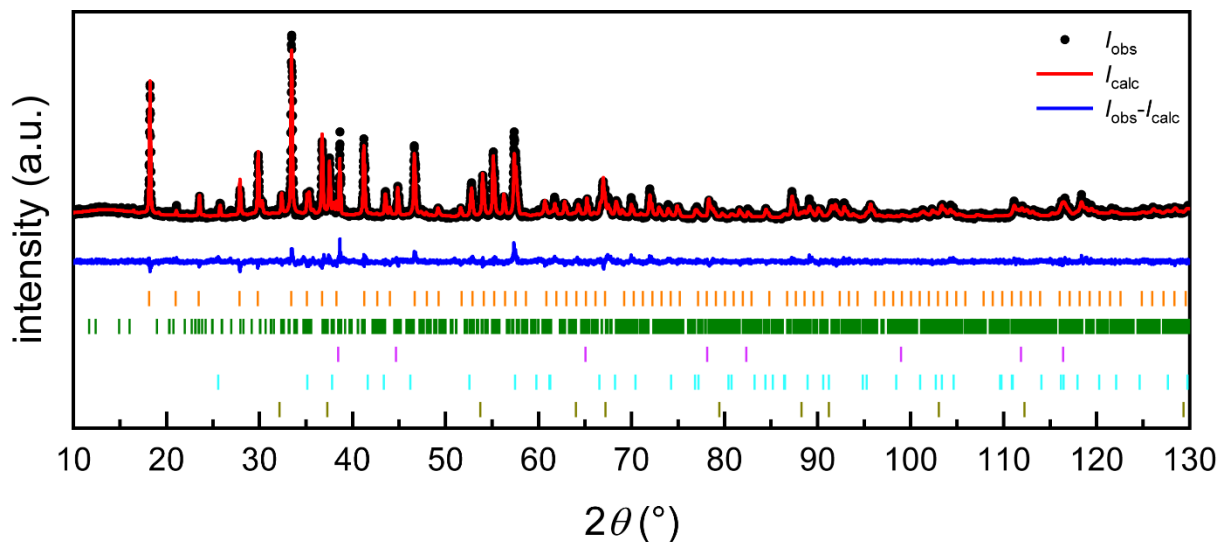


Figure S27. Rietveld fit of the powder X-ray diffraction pattern of CaAl_2 oxidized by the following conditions: muffle furnace; heating rate: 15 K min^{-1} ; dwelling time: 0 h; number of cycle: 2; air. The ticks indicate the Bragg positions for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (orange), CaAl_2O_4 (green), elemental Al (pink), Al_2O_3 (cyan), CaO (olive).

Refinement details for the data shown in Figure S27					
Source	Bruker D8 ADVANCE (laboratory X-ray)				
Temperature	RT				
Pressure	ambient				
Wavelengths	Cu $K\alpha_1$ and Cu $K\alpha_2$: 154.0596 and 154.4308 pm				
Chemical formula	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	CaAl_2O_4	Al	Al_2O_3	CaO
Abbreviation	C12A7	CA	–	–	–
Space group	$\bar{I}43d$	$P2_1/c$	$Fm\bar{3}m$	$R\bar{3}c$	$Fm\bar{3}m$
a / pm	1203.84(2)	877.2(14)	405.30(1)	476.11(3)	481.39(2)
b / pm	a	808.0(5)	a	a	a
c / pm	a	1749(3)	a	1300.03(14)	a
β / °	90	120.0(2)	90	90	90
V / nm^3	1.7447	1.0740	0.0666	0.2552	0.1116
Z	4	12	4	6	4
d -space range	0.85-14.35 Å (6-130° 2θ)				
χ^2	2.33				
R_p	9.89				
R_{wp}	12.44				
Definition of R factors	$R_p = \frac{\sum w I_o - I_c ^2}{\sum w I_o^2};$ $R_{wp} = \left(\frac{\sum w I_o - I_c ^2}{\sum w I_o^2} \right)^{\frac{1}{2}}$				

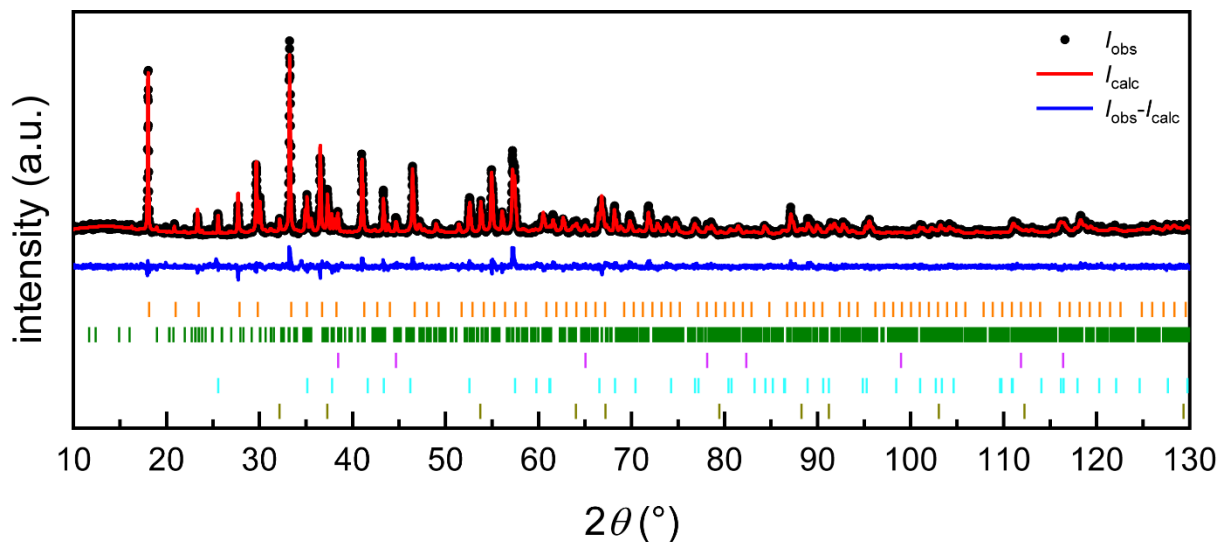


Figure S28. Rietveld fit of the powder X-ray diffraction pattern of CaAl_2 oxidized by the following conditions: muffle furnace; heating rate: 15 K min^{-1} ; dwelling time: 0 h; number of cycle: 9; air. The ticks indicate the Bragg positions for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (orange), CaAl_2O_4 (green), elemental Al (pink), Al_2O_3 (cyan), CaO (olive).

Refinement details for the data shown in Figure S28					
Source	Bruker D8 ADVANCE (laboratory X-ray)				
Temperature	RT				
Pressure	ambient				
Wavelengths	Cu $K\alpha_1$ and Cu $K\alpha_2$: 154.0596 and 154.4308 pm				
Chemical formula	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	CaAl_2O_4	Al	Al_2O_3	CaO
Abbreviation	C12A7	CA	–	–	–
Space group	$I\bar{4}3d$	$P2_1/c$	$Fm\bar{3}m$	$R\bar{3}c$	$Fm\bar{3}m$
a / pm	1203.65(2)	876.0(3)	405.37(2)	476.10(1)	481.41(2)
b / pm	a	809.46(14)	a	a	a
c / pm	a	1746.0(4)	a	1299.91(7)	a
β / °	90	119.93(4)	90	90	90
V / nm ³	1.7438	1.0729	0.0666	0.2552	0.1116
Z	4	12	4	6	4
d -space range	0.85-14.35 Å (6-130° 2θ)				
χ^2	2.10				
R_p	8.89				
R_{wp}	11.41				
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2}$				

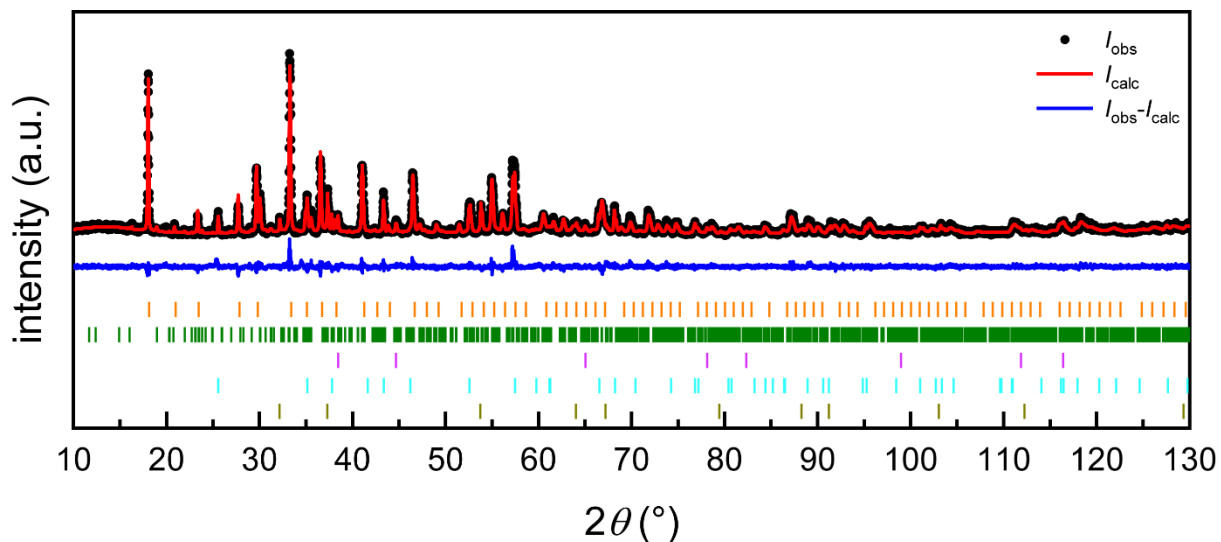


Figure S29. Rietveld fit of the powder X-ray diffraction pattern of CaAl_2 oxidized by the following conditions: muffle furnace; heating rate: 15 K min^{-1} ; dwelling time: 0 h; number of cycle: 10; air. The ticks indicate the Bragg positions for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (orange), CaAl_2O_4 (green), elemental Al (pink), Al_2O_3 (cyan), CaO (olive).

Refinement details for the data shown in Figure S29					
Source	Bruker D8 ADVANCE (laboratory X-ray)				
Temperature	RT				
Pressure	ambient				
Wavelengths	Cu $K\alpha_1$ and Cu $K\alpha_2$: 154.0596 and 154.4308 pm				
Chemical formula	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	CaAl_2O_4	Al	Al_2O_3	CaO
Abbreviation	C12A7	CA	–	–	–
Space group	$\bar{I}43d$	$P2_1/c$	$Fm\bar{3}m$	$R\bar{3}c$	$Fm\bar{3}m$
a / pm	1203.24(2)	876.3(2)	405.42(3)	476.13(1)	481.43(2)
b / pm	a	809.39(13)	a	a	a
c / pm	a	1746.3(4)	a	1299.80(7)	a
β / °	90	119.96(3)	90	90	90
V / nm^3	1.7421	1.0731	0.0666	0.2552	0.1116
Z	4	12	4	6	4
d -space range	0.85–14.35 Å (6–130° 2θ)				
χ^2	2.08				
R_p	8.84				
R_{wp}	11.35				
Definition of R factors	$R_p = \frac{\sum w I_o - I_c ^2}{\sum w I_o^2};$ $R_{wp} = \left(\frac{\sum w I_o - I_c ^2}{\sum w I_o^2} \right)^{\frac{1}{2}}$				

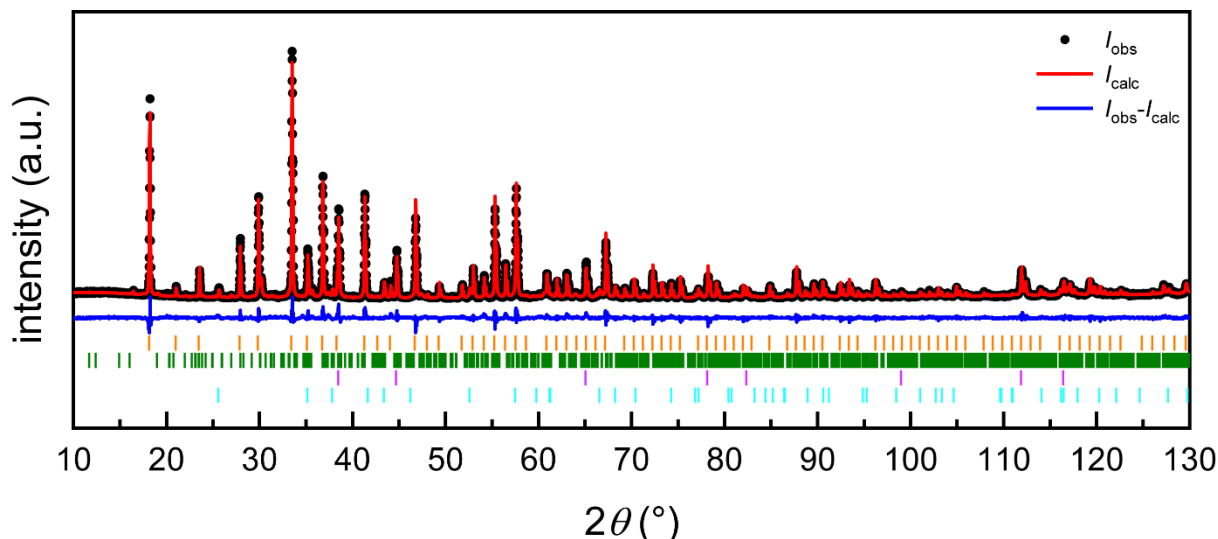


Figure S30. Rietveld fit of the powder X-ray diffraction pattern of CaAl_2 oxidized by the following conditions: tube furnace; heating rate: 4 K min^{-1} ; dwelling time: 0 h; gas flow: 20 mL min^{-1} dried Ar : 20 mL min^{-1} O_2 . The ticks indicate the Bragg positions for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (orange), CaAl_2O_4 (green), elemental Al (pink), Al_2O_3 (cyan).

Refinement details for the data shown in Figure S30				
Source	Bruker D8 ADVANCE (laboratory X-ray)			
Temperature	RT			
Pressure	ambient			
Wavelengths	Cu $K\alpha_1$ and Cu $K\alpha_2$: 154.0596 and 154.4308 pm			
Chemical formula	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	CaAl_2O_4	Al	Al_2O_3
Abbreviation	C12A7	CA	–	–
Space group	$I\bar{4}3d$	$P2_1/c$	$Fm\bar{3}m$	$R\bar{3}c$
a / pm	1197.77(1)	874.7(3)	405.23(1)	475.97(2)
b / pm	a	808.36(17)	a	a
c / pm	a	1746.5(9)	a	1299.60(9)
β / °	90	120.03(6)	90	90
V / nm^3	1.7184	1.0691	0.0665	0.2550
Z	4	12	4	6
d -space range	0.85-14.35 Å (6-130° 2θ)			
χ^2	5.67			
R_p	7.97			
R_{wp}	10.6			
Definition of R factors	$R_p = \frac{\sum w I_o - I_c ^2}{\sum w I_o^2};$ $R_{wp} = \left(\frac{\sum w I_o - I_c ^2}{\sum w I_o^2} \right)^{\frac{1}{2}}$			

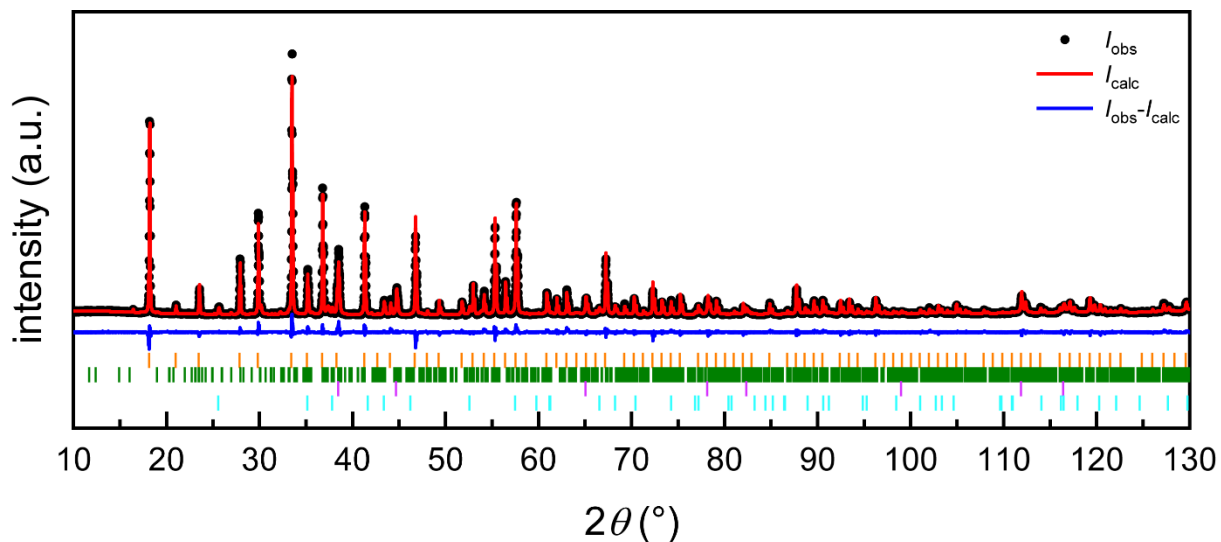


Figure S31. Rietveld fit of the powder X-ray diffraction pattern of CaAl_2 oxidized by the following conditions: tube furnace; heating rate: 4 K min^{-1} ; dwelling time: 0 h; gas flow: $20 \text{ mL min}^{-1} \text{ O}_2$. The ticks indicate the Bragg positions for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (orange), CaAl_2O_4 (green), elemental Al (pink), Al_2O_3 (cyan), CaO (olive).

Refinement details for the data shown in Figure S31				
Source	Bruker D8 ADVANCE (laboratory X-ray)			
Temperature	RT			
Pressure	ambient			
Wavelengths	Cu $K\alpha_1$ and Cu $K\alpha_2$: 154.0596 and 154.4308 pm			
Chemical formula	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	CaAl_2O_4	Al	Al_2O_3
Abbreviation	C12A7	CA	–	–
Space group	$I\bar{4}3d$	$P2_1/c$	$Fm\bar{3}m$	$R\bar{3}c$
a / pm	1197.73(1)	874.8(8)	405.18(1)	475.96(1)
b / pm	a	808.4(4)	a	a
c / pm	a	1746(3)	a	1299.43(8)
$\beta / ^\circ$	90	120.1(2)	90	90
V / nm^3	1.7182	1.0690	0.0665	0.2549
Z	4	12	4	6
d -space range	0.85–14.35 Å (6–130° 2θ)			
χ^2	4.90			
R_p	7.09			
R_{wp}	9.41			
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2 }^{1/2}$			

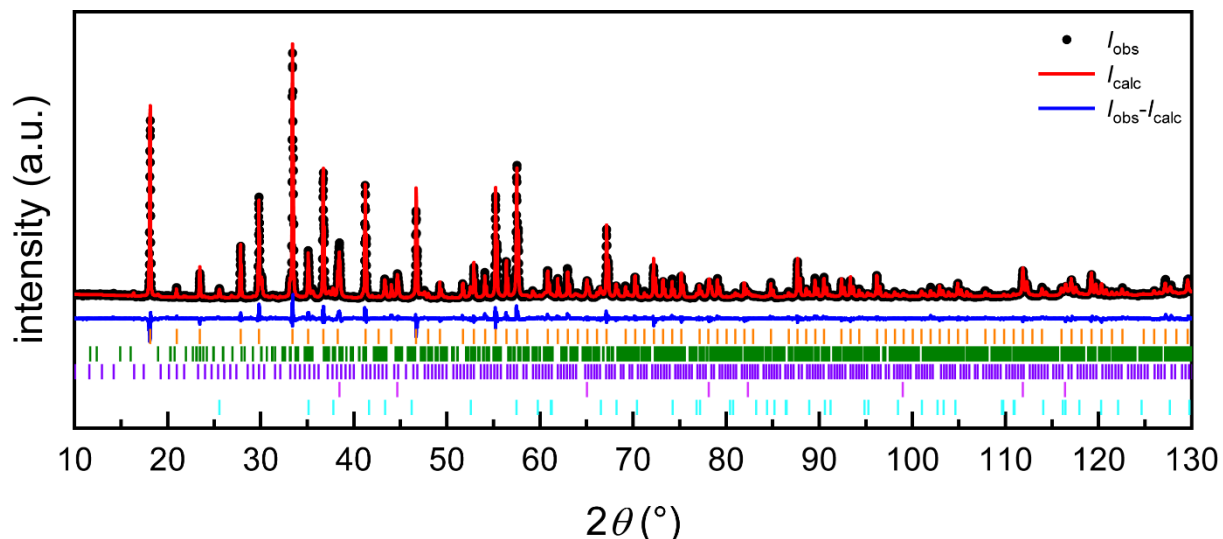


Figure S32. Rietveld fit of the powder X-ray diffraction pattern of CaAl_2 oxidized by the following conditions: tube furnace; heating rate: 4 K min^{-1} ; dwelling time: 5 h; gas flow: $20 \text{ mL min}^{-1} \text{ O}_2$. The ticks indicate the Bragg positions for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (orange), CaAl_2O_4 (green), $\text{Ca}_3\text{Al}_2\text{O}_6$ (purple), elemental Al (pink), Al_2O_3 (cyan).

Refinement details for the data shown in Figure S32					
Source	Bruker D8 ADVANCE (laboratory X-ray)				
Temperature	RT				
Pressure	ambient				
Wavelengths	Cu $K\alpha_1$ and Cu $K\alpha_2$: 154.0596 and 154.4308 pm				
Chemical formula	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	CaAl_2O_4	$\text{Ca}_3\text{Al}_2\text{O}_6$	Al	Al_2O_3
Abbreviation	C12A7	CA	C3A1	–	–
Space group	$I\bar{4}3d$	$P2_1/c$	$Pa\bar{3}$	$Fm\bar{3}m$	$R\bar{3}c$
a / pm	1197.93(1)	871.82(17)	1527.08(8)	405.18(1)	476.03(1)
b / pm	a	809.08(14)	a	a	a
c / pm	a	1748.7(4)	a	a	1299.55(7)
$\beta / ^\circ$	90	119.81(2)	90	90	90
V / nm^3	1.7191	1.0703	3.5611	0.0665	0.2550
Z	4	12	24	4	6
d -space range	0.85–14.35 Å (6–130° 2θ)				
χ^2	5.36				
R_p	7.12				
R_{wp}	9.4				
Definition of R factors	$R_p = \frac{\sum w I_o - I_c ^2}{\sum w I_o^2};$ $R_{wp} = \left(\frac{\sum w I_o - I_c ^2}{\sum w I_o^2} \right)^{\frac{1}{2}}$				

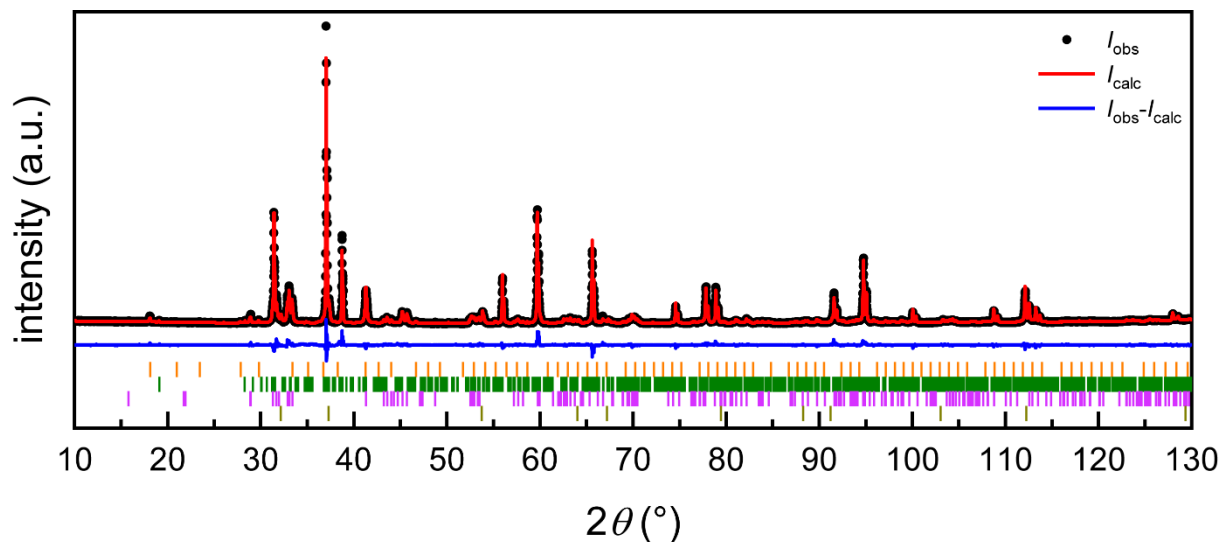


Figure S33. Rietveld fit of the powder X-ray diffraction pattern of CaAl_2 oxidized by the following conditions: induction furnace; The ticks indicate the Bragg positions for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (orange), CaAl_2 (green), CaAl_4 (pink), CaO (olive).

Refinement details for the data shown in Figure S33				
Source	Bruker D8 ADVANCE (laboratory X-ray)			
Temperature	RT			
Pressure	ambient			
Wavelengths	Cu $K\alpha_1$ and Cu $K\alpha_2$: 154.0596 and 154.4308 pm			
Chemical formula	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	CaAl_2	CaAl_4	CaO
Abbreviation	C12A7	–	–	–
Space group	$I\bar{4}3d$	$Fd\bar{3}m$	$C2/m$	$Fm\bar{3}m$
a / pm	1198.89(6)	803.98(1)	616.83(2)	481.156(9)
b / pm	a	a	618.83(2)	a
c / pm	a	a	634.48(2)	a
β / °	90	90	118.06(1)	90
V / nm ³	1.7232	0.5197	0.2135	0.1114
Z	4	8	2	4
d -space range	0.85-14.35 Å (6-130° 2θ)			
χ^2	5.12			
R_p	7.43			
R_{wp}	9.84			
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2}$ $R_{wp} = \left(\frac{\sum w I_0 - I_c ^2}{\sum w I_0^2} \right)^{\frac{1}{2}}$			

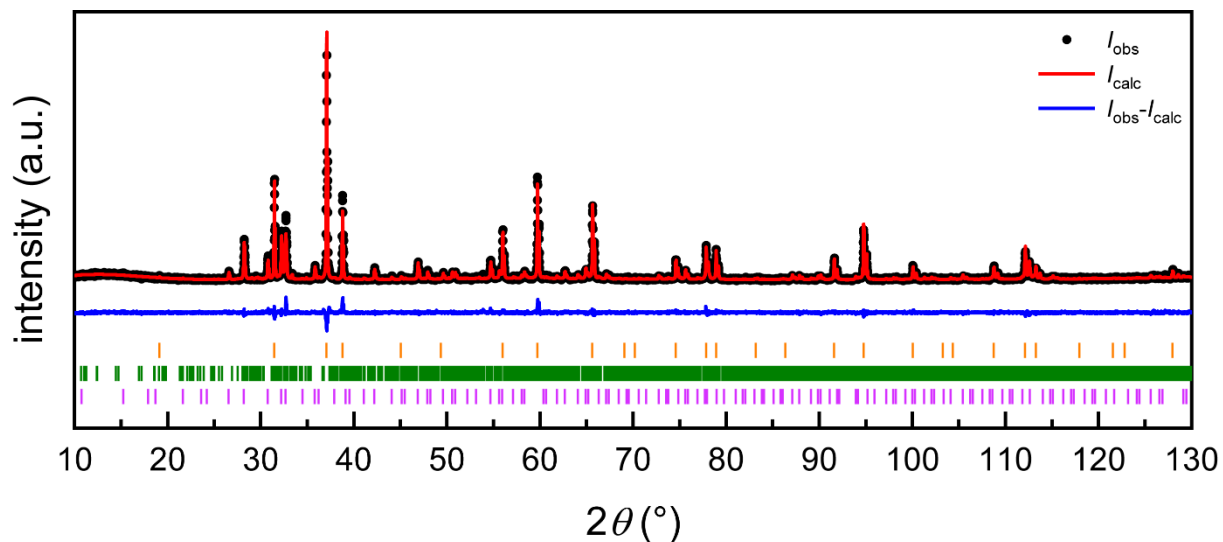


Figure S34. Rietveld fit of the powder X-ray diffraction pattern taken from nominal ‘Ca₆Al₇’. The ticks indicate the Bragg positions for CaAl₂ (orange), Ca₈Al₃ (green), Ca₁₁Al₇ (purple).

Refinement details for the data shown in Figure S34			
Source	Bruker D8 ADVANCE (laboratory X-ray)		
Temperature	RT		
Pressure	ambient		
Wavelengths	Cu K α_1 and Cu K α_2 : 154.0596 and 154.4308 pm		
Chemical formula	CaAl ₂	Ca ₈ Al ₃	Ca ₁₁ Al ₇
Space group	<i>Fd</i> $\bar{3}m$	<i>P</i> $\bar{1}$	<i>Fm</i> $\bar{3}m$
<i>a</i> / pm	804.03(1)	948.5(2)	1642.92(1)
<i>b</i> / pm	<i>a</i>	966.6(2)	<i>a</i>
<i>c</i> / pm	<i>a</i>	957.4(3)	<i>a</i>
α / °	90	99.57(2)	90
β / °	90	100.99(2)	90
γ / °	90	119.32(2)	90
<i>V</i> / nm ³	0.5198	0.7159	4.4346
<i>Z</i>	8	2	8
<i>d</i> -space range	0.85-14.35 Å (6-130° 2 θ)		
χ^2	1.58		
<i>R</i> _p	8.77		
<i>R</i> _{wp}	11.48		
Definition of <i>R</i> factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2};$ $R_{wp} = \left(\frac{\sum w I_0 - I_c ^2}{\sum w I_0^2} \right)^{\frac{1}{2}}$		

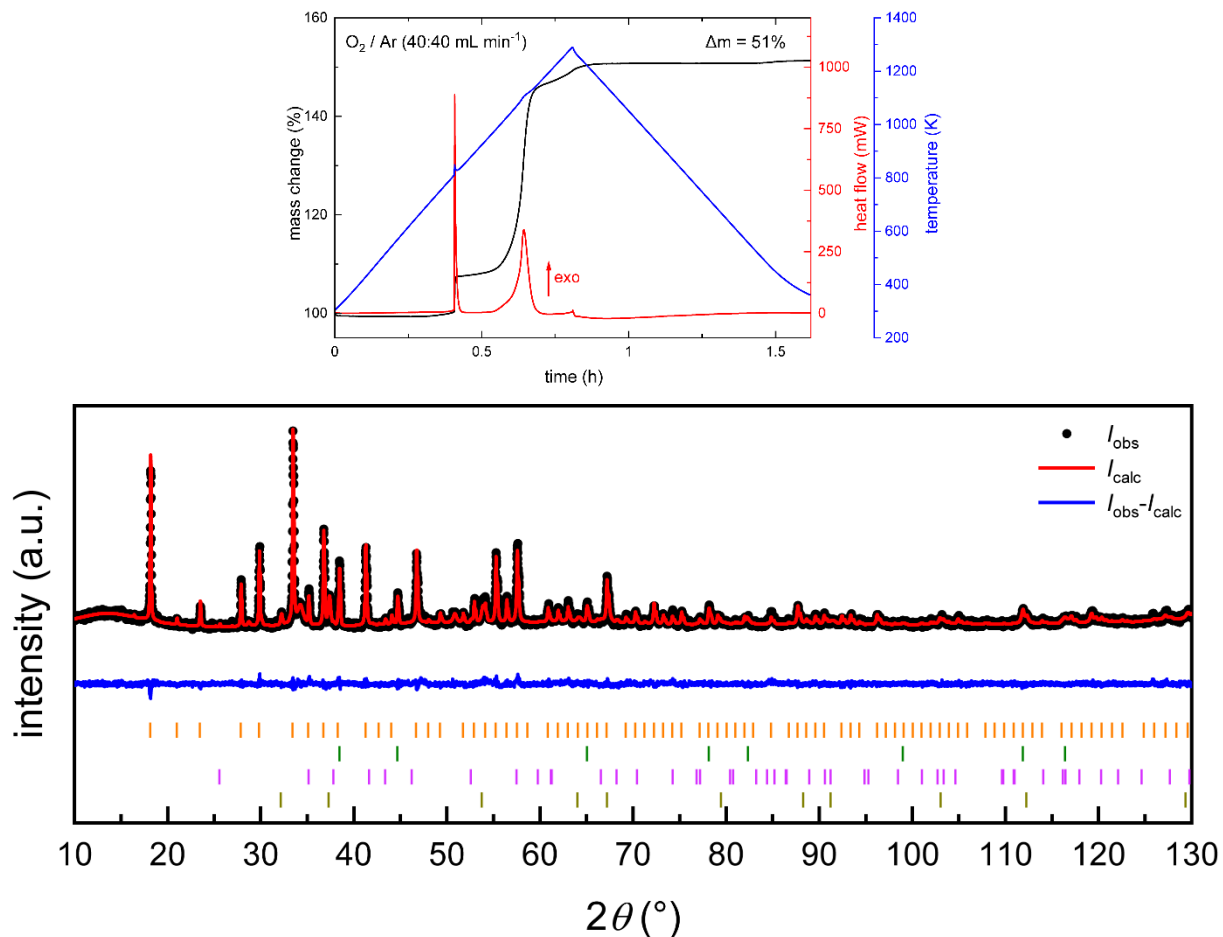


Figure S35. STA experiment (top) and the corresponding Rietveld refinements of the collected powder X-ray diffraction data (bottom) of the oxidation of nominal ‘Ca₆Al₇’. The ticks indicate the Bragg positions for Ca₁₂Al₁₄O₃₃ (orange), Al (green), Al₂O₃ (pink), CaO (olive).

Refinement details for the data shown in Figure S35				
Source	Bruker D8 ADVANCE (laboratory X-ray)			
Temperature	RT			
Pressure	ambient			
Wavelengths	Cu K α_1 and Cu K α_2 : 154.0596 and 154.4308 pm			
Chemical formula	Ca ₁₂ Al ₁₄ O ₃₃	Al	Al ₂ O ₃	CaO
Abbreviation	C12A7	–	–	–
Space group	<i>I</i> $\bar{4}3d$	<i>Fm</i> $\bar{3}m$	<i>R</i> $\bar{3}c$	<i>Fm</i> $\bar{3}m$
<i>a</i> / pm	1198.00(2)	405.43(2)	475.65(11)	481.58(4)
<i>b</i> / pm	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>
<i>c</i> / pm	<i>a</i>	<i>a</i>	1301.4(8)	<i>a</i>
β / °	90	90	90	90
<i>V</i> / nm ³	1.7194	0.0666	0.2552	0.1117
<i>Z</i>	4	4	6	4
<i>d</i> -space range	0.85-14.35 Å (6-130° 2 θ)			
χ^2	2.87			
<i>R</i> _p	8.77			
<i>R</i> _{wp}	11.95			
Definition of <i>R</i> factors	$R_p = \frac{\sum w I_o - I_c ^2}{\sum w I_o^2};$ $R_{wp} = \left(\frac{\sum w I_o - I_c ^2}{\sum w I_o^2} \right)^{\frac{1}{2}}$			

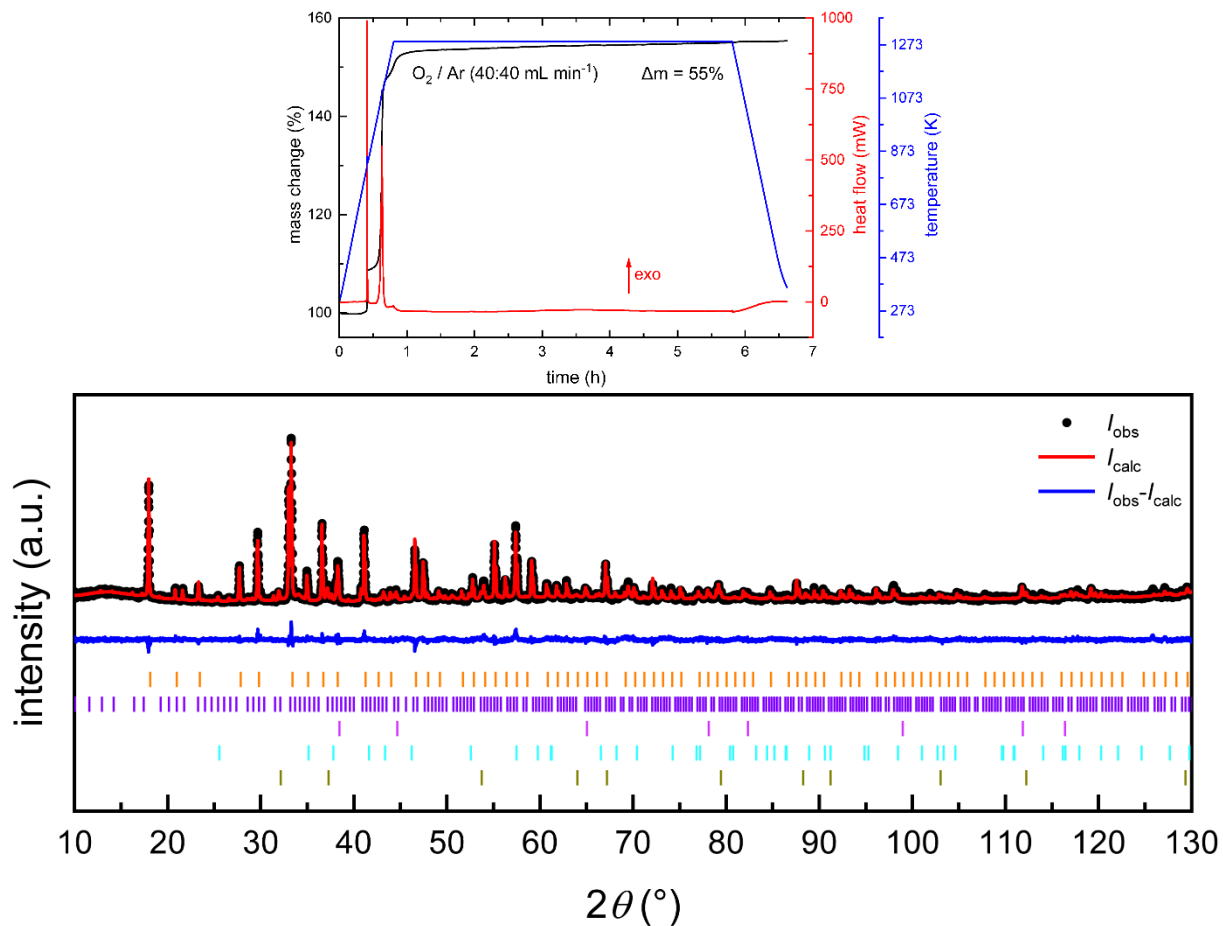


Figure S36. STA experiment (top) and the corresponding Rietveld refinements of the collected powder X-ray diffraction data (bottom) of the oxidation of nominal ‘Ca₆Al₇’. The ticks indicate the Bragg positions for Ca₁₂Al₁₄O₃₃ (orange), Al (green), Al₂O₃ (pink), CaO (olive).

Refinement details for the data shown in Figure S36					
Source	Bruker D8 ADVANCE (laboratory X-ray)				
Temperature	RT				
Pressure	ambient				
Wavelengths	Cu K α_1 and Cu K α_2 : 154.0596 and 154.4308 pm				
Chemical formula	Ca ₁₂ Al ₁₄ O ₃₃	Ca ₃ Al ₂ O ₆	Al	Al ₂ O ₃	CaO
Abbreviation	C12A7	C3A1	–	–	–
Space group	$I\bar{4}3d$	$Pa\bar{3}$	$Fm\bar{3}m$	$R\bar{3}c$	$Fm\bar{3}m$
a / pm	1197.77(1)	1526.96(3)	405.34(2)	476.00(4)	481.48(5)
b / pm	a	a	a	a	a
c / pm	a	a	a	1300.1(2)	a
β / °	90	90	90	90	90
V / nm ³	1.7184	3.5602	0.0666	0.2551	0.1112
Z	4	24	4	6	4
d -space range	0.85-14.35 Å (6-130° 2 θ)				
χ^2	2.67				
R_p	8.52				
R_{wp}	10.86				
Definition of R factors	$R_p = \frac{\sum w I_o - I_c ^2}{\sum w I_o^2}$				

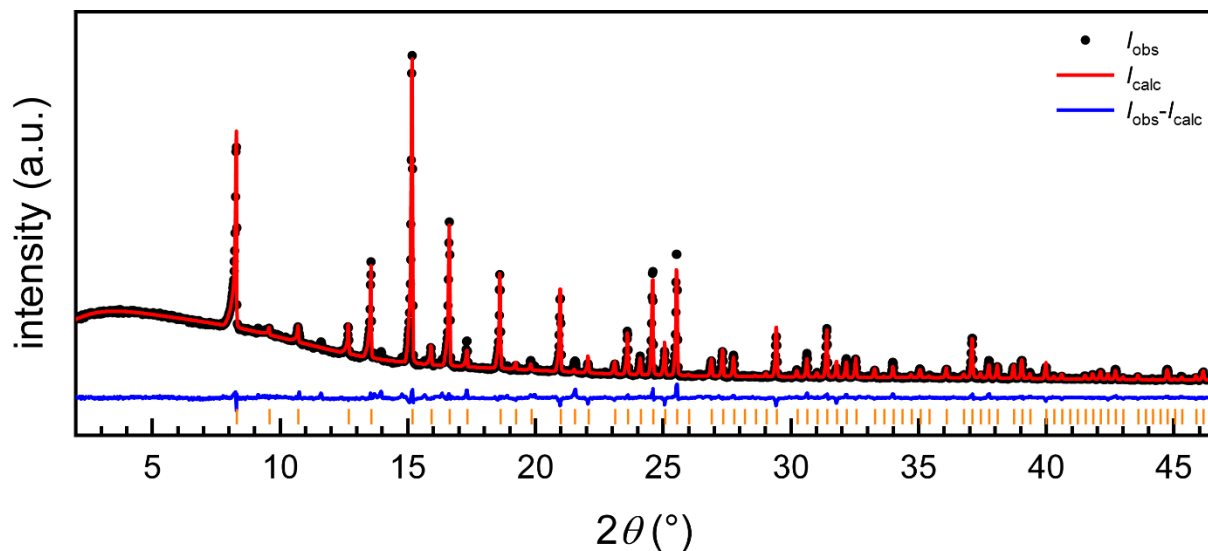


Figure S37. Rietveld refinements of the collected powder X-ray diffraction data for the result of the solid-state reaction between $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$. The ticks indicate the Bragg positions for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (orange).

Refinement details for the data shown in Figure S37	
Source	Stoe Stadi P diffractometer (laboratory X-ray)
Temperature	RT
Pressure	ambient
Wavelengths	Mo $K\alpha_1$: 70.93 pm
Chemical formula	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$
Abbreviation	C12A7
Space group	$I\bar{4}3d$
a / pm	1200.20(3)
b / pm	a
c / pm	a
β / °	90
V / nm ³	1.7289
Z	4
d -space range	0.91-20.08 Å (2-46° 2θ)
χ^2	7.53
R_p	3.07
R_{wp}	4.94
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2};$ $R_{wp} = \left(\frac{\sum w I_0 - I_c ^2}{\sum w I_0^2} \right)^{\frac{1}{2}}$

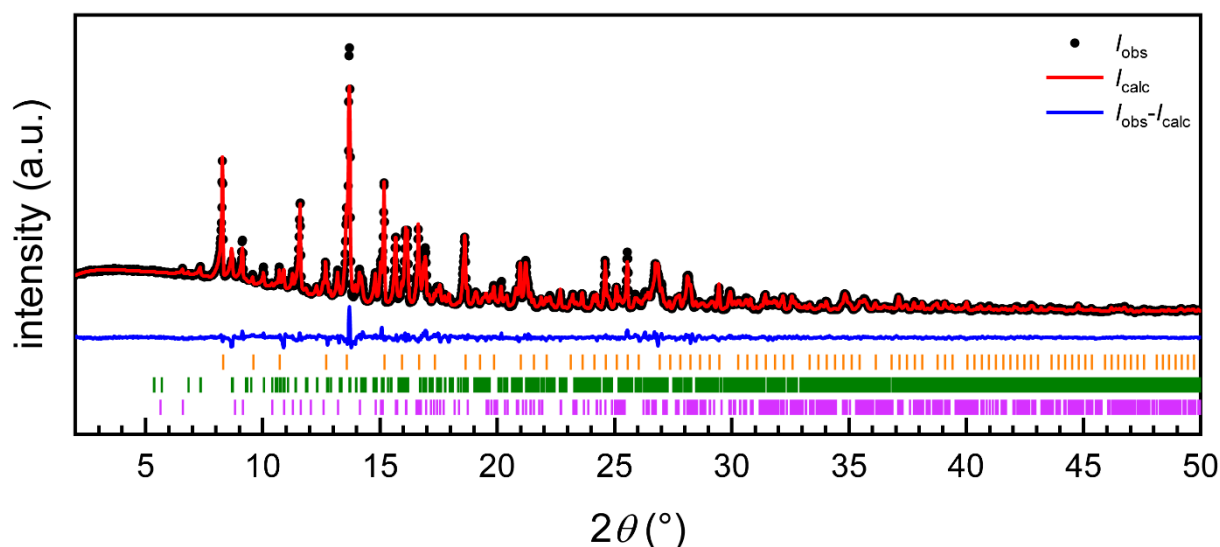


Figure S38. Rietveld refinements of the collected powder X-ray diffraction data for the result of the solid-state reaction between $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ and $2 \text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$. The ticks indicate the Bragg positions for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (orange), CaAl_2O_4 (green) and CaAl_4O_7 (purple).

Refinement details for the data shown in Figure S38			
Source	Stoe Stadi P diffractometer (laboratory X-ray)		
Temperature	RT		
Pressure	ambient		
Wavelengths	Mo $K\alpha_1$: 70.93 pm		
Chemical formula	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	CaAl_2O_4	CaAl_4O_7
Abbreviation	C12A7	CA	CA2
Space group	$I\bar{4}3d$	$P2_1/c$	$C2_1/c$
a / pm	1198.99(7)	874.16(8)	1289.14(10)
b / pm	a	809.14(6)	888.33(7)
c / pm	a	1741.93(13)	543.70(4)
β / °	90	119.76(1)	107.03(1)
V / nm ³	1.7236	1.8965	0.5953
Z	4	12	4
d -space range	0.91-20.08 Å (2-46° 2θ)		
χ^2	14.35		
R_p	3.76		
R_{wp}	5.53		
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2};$ $R_{wp} = \left(\frac{\sum w I_0 - I_c ^2}{\sum w I_0^2} \right)^{\frac{1}{2}}$		