

SUPPORTING INFORMATION

Changing the reaction pathway of the CaAl_2 oxidation using ball milling

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Powder X-ray diffraction

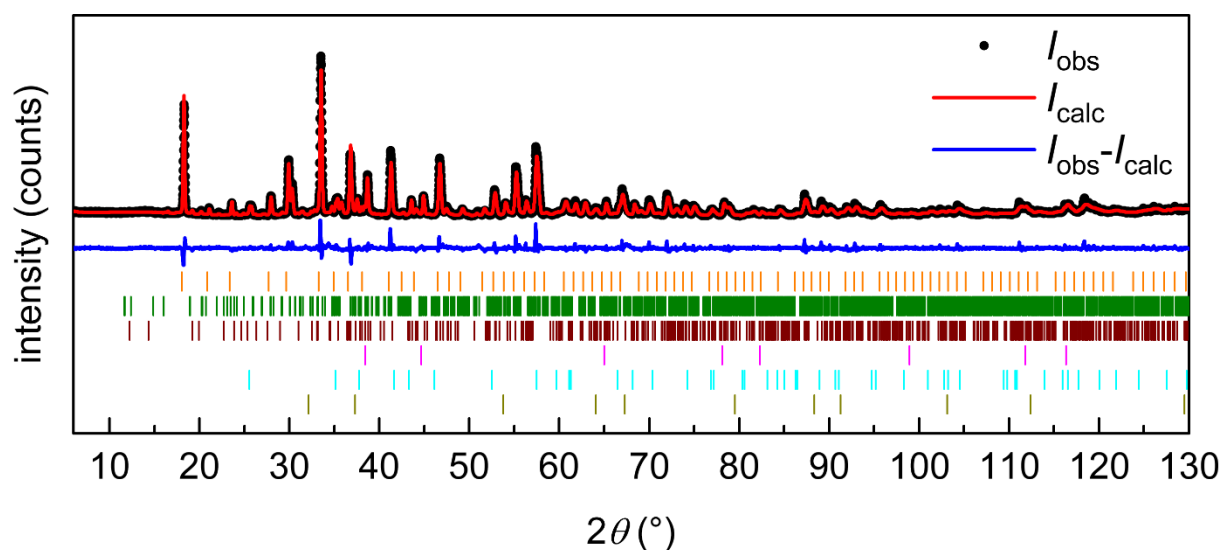


Figure S1. Powder X-ray diffraction pattern of CaAl_2 oxidized with wet argon. Black circles represent the collected data, the red line is the fit, the blue line the difference curve and the ticks represent the Bragg positions of the refined phases. The following color code applies: orange – $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ ($\bar{I}43d$); green – CaAl_2O_4 ($P2_1/c$); dark red – CaAl_4O_7 ($C2/c$); pink – Al ($Fm\bar{3}m$); cyan – Al_2O_3 ($R\bar{3}c$); olive – CaO ($Fm\bar{3}m$).

Refinement details for the data shown in Figure S1	
Source	Bruker D8 ADVANCE (laboratory X-ray)
Temperature	RT
Pressure	ambient
Wavelengths	$\text{Cu } K\alpha_1$ and $\text{Cu } K\alpha_2$: 154.0596 and 154.4308 pm
d -space range	0.85-14.35 Å (6-130° 2θ)
χ^2	6.36
R_p / %	8.13
R_{wp} / %	10.64
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2};$ $R_{wp} = \left(\frac{\sum w I_0 - I_c ^2}{\sum w I_0^2} \right)^{\frac{1}{2}}$

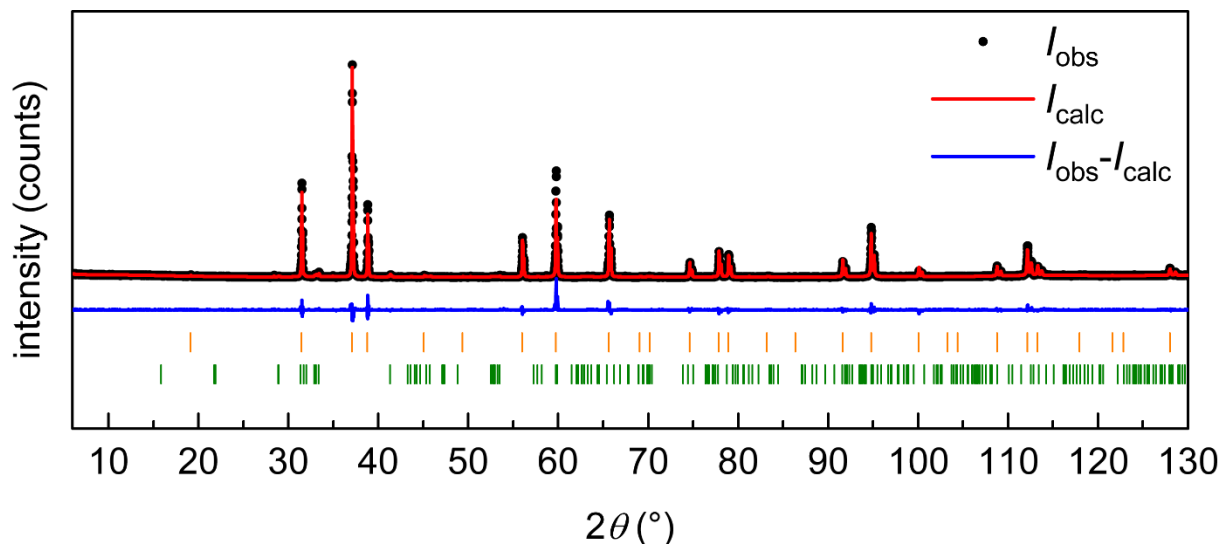


Figure S2. Powder X-ray diffraction pattern of as synthesized CaAl_2 . Black circles represent the collected data, the red line is the fit, the blue line the difference curve and the ticks represent the Bragg positions of the refined phases. The following color code applies: orange – CaAl_2 ($Fd\bar{3}m$); green – CaAl_4 ($C2/m$).

Refinement details for the data shown in Figure S2	
Source	Bruker D8 ADVANCE (laboratory X-ray)
Temperature	RT
Pressure	ambient
Wavelengths	$\text{Cu } K\alpha_1$ and $\text{Cu } K\alpha_2$: 154.0596 and 154.4308 pm
d -space range	0.85-14.35 Å (6-130° 2θ)
χ^2	4.11
R_p / %	7.10
R_{wp} / %	10.04
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2};$ $R_{wp} = \left(\frac{\sum w I_0 - I_c ^2}{\sum w I_0^2} \right)^{\frac{1}{2}}$

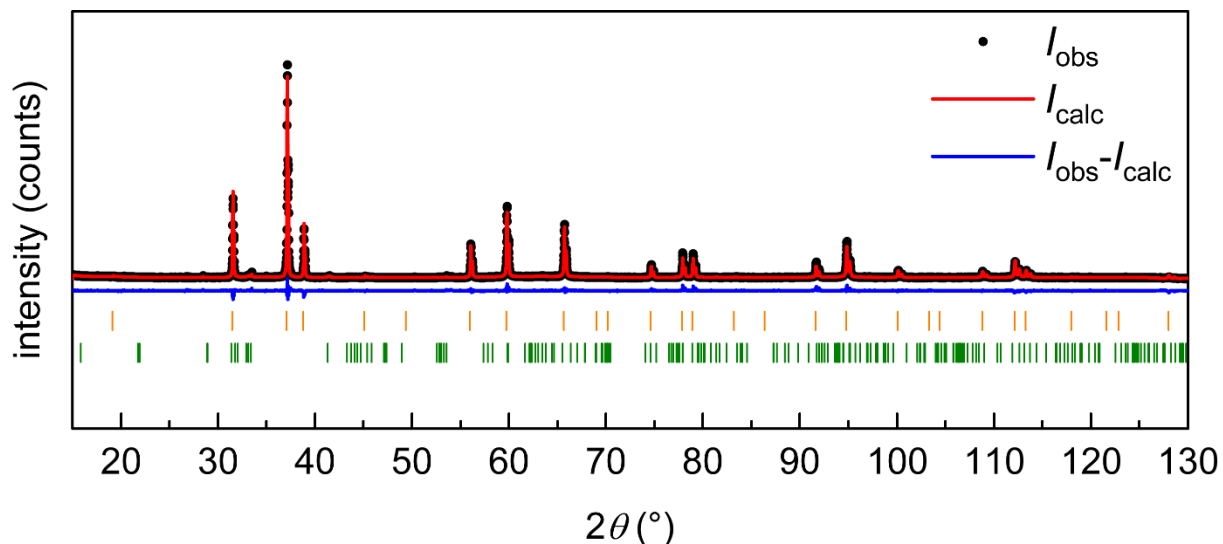


Figure S3. Powder X-ray diffraction pattern of CaAl₂ ball milled for 5 min. Black circles represent the collected data, the red line is the fit, the blue line the difference curve and the ticks represent the Bragg positions of the refined phases. The following color code applies: orange – CaAl₂ (*Fd* $\bar{3}$ *m*); green – CaAl₄ (*C2/m*).

Refinement details for the data shown in Figure S3	
Source	Bruker D8 ADVANCE (laboratory X-ray)
Temperature	RT
Pressure	ambient
Wavelengths	Cu <i>K</i> α ₁ and Cu <i>K</i> α ₂ : 154.0596 and 154.4308 pm
<i>d</i> -space range	0.85-14.35 Å (6-130° 2 θ)
χ^2	2.41
<i>R</i> _p / %	8.11
<i>R</i> _{wp} / %	10.77
Definition of <i>R</i> factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2};$ $R_{wp} = \left(\frac{\sum w I_0 - I_c ^2}{\sum w I_0^2} \right)^{\frac{1}{2}}$

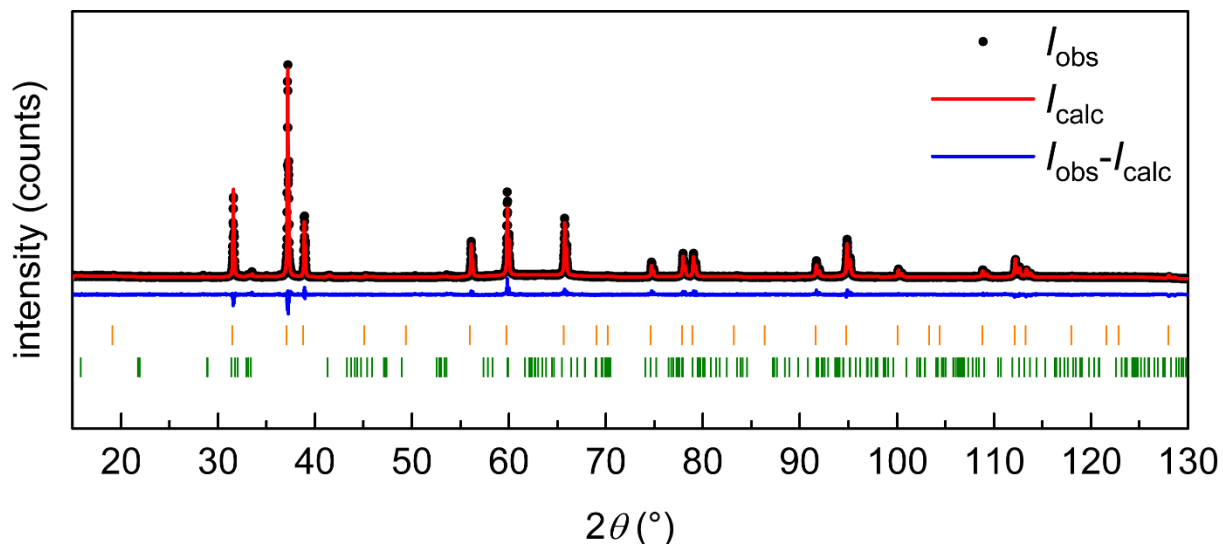


Figure S4. Powder X-ray diffraction pattern of CaAl_2 ball milled for 10 min. Black circles represent the collected data, the red line is the fit, the blue line the difference curve and the ticks represent the Bragg positions of the refined phases. The following color code applies: orange – CaAl_2 ($Fd\bar{3}m$); green – CaAl_4 ($C2/m$).

Refinement details for the data shown in Figure S4	
Source	Bruker D8 ADVANCE (laboratory X-ray)
Temperature	RT
Pressure	ambient
Wavelengths	$\text{Cu } K\alpha_1$ and $\text{Cu } K\alpha_2$: 154.0596 and 154.4308 pm
d -space range	0.85-14.35 Å (6-130° 2θ)
χ^2	2.23
R_p / %	8.81
R_{wp} / %	11.37
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2};$ $R_{wp} = \left(\frac{\sum w I_0 - I_c ^2}{\sum w I_0^2} \right)^{\frac{1}{2}}$

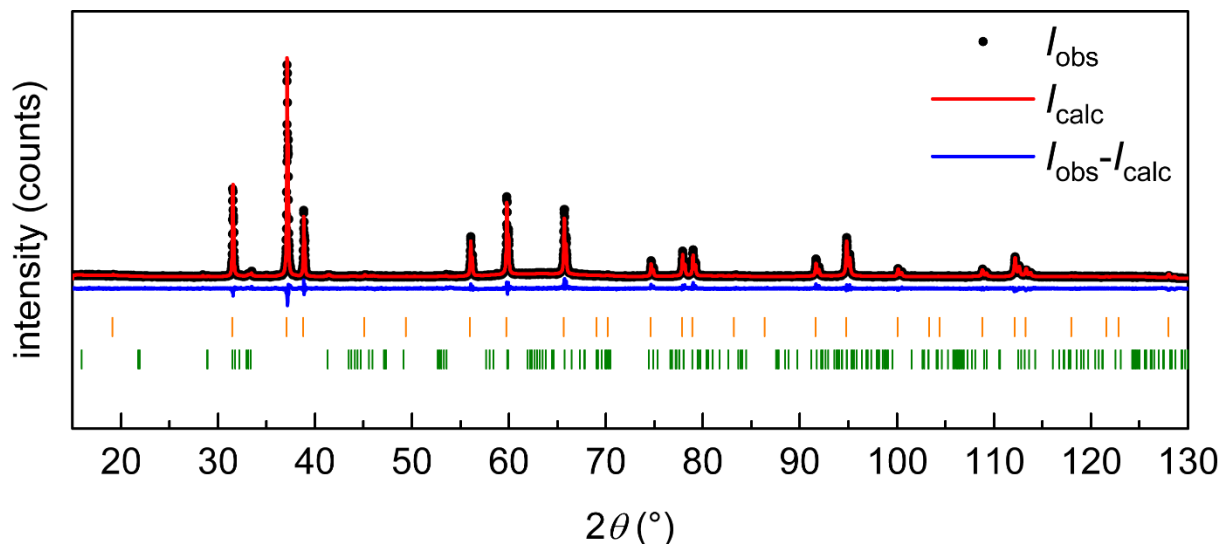


Figure S5. Powder X-ray diffraction pattern of CaAl₂ ball milled for 15 min. Black circles represent the collected data, the red line is the fit, the blue line the difference curve and the ticks represent the Bragg positions of the refined phases. The following color code applies: orange – CaAl₂ (*Fd* $\bar{3}$ *m*); green – CaAl₄ (*C2/m*).

Refinement details for the data shown in Figure S5	
Source	Bruker D8 ADVANCE (laboratory X-ray)
Temperature	RT
Pressure	ambient
Wavelengths	Cu <i>K</i> α_1 and Cu <i>K</i> α_2 : 154.0596 and 154.4308 pm
<i>d</i> -space range	0.85-14.35 Å (6-130° 2 θ)
χ^2	1.89
R_p / %	8.24
R_{wp} / %	10.50
Definition of <i>R</i> factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2};$ $R_{wp} = \left(\frac{\sum w I_0 - I_c ^2}{\sum w I_0^2} \right)^{\frac{1}{2}}$

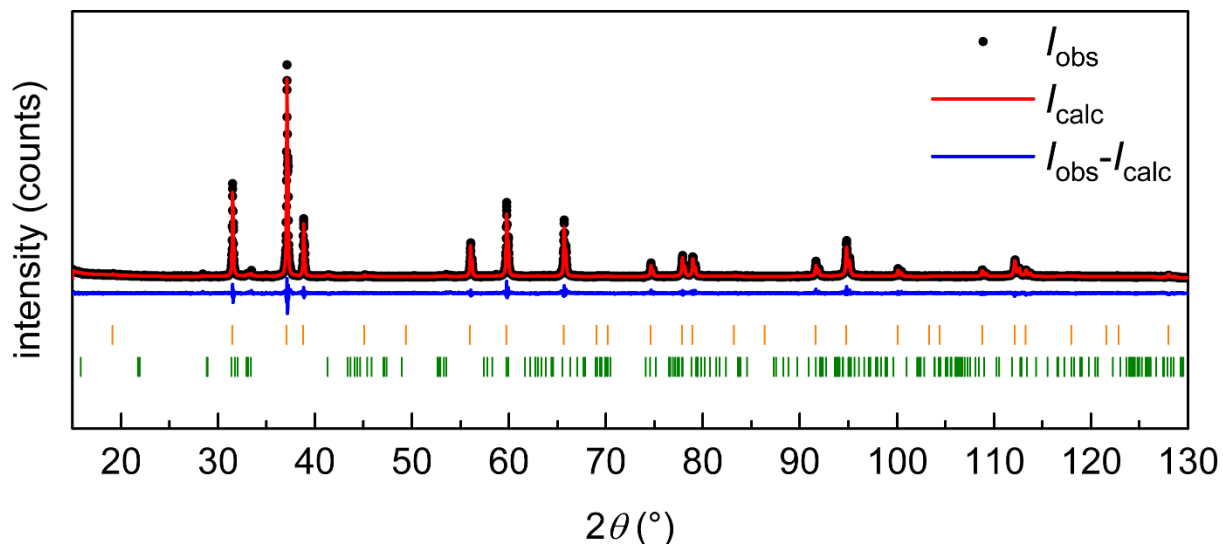


Figure S6. Powder X-ray diffraction pattern of CaAl₂ ball milled for 20 min. Black circles represent the collected data, the red line is the fit, the blue line the difference curve and the ticks represent the Bragg positions of the refined phases. The following color code applies: orange – CaAl₂ (*Fd* $\bar{3}$ *m*); green – CaAl₄ (*C2/m*).

Refinement details for the data shown in Figure S6	
Source	Bruker D8 ADVANCE (laboratory X-ray)
Temperature	RT
Pressure	ambient
Wavelengths	Cu <i>K</i> α ₁ and Cu <i>K</i> α ₂ : 154.0596 and 154.4308 pm
<i>d</i> -space range	0.85-14.35 Å (6-130° 2 θ)
χ^2	1.77
<i>R</i> _p / %	7.94
<i>R</i> _{wp} / %	9.92
Definition of <i>R</i> factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2};$ $R_{wp} = \left(\frac{\sum w I_0 - I_c ^2}{\sum w I_0^2} \right)^{\frac{1}{2}}$

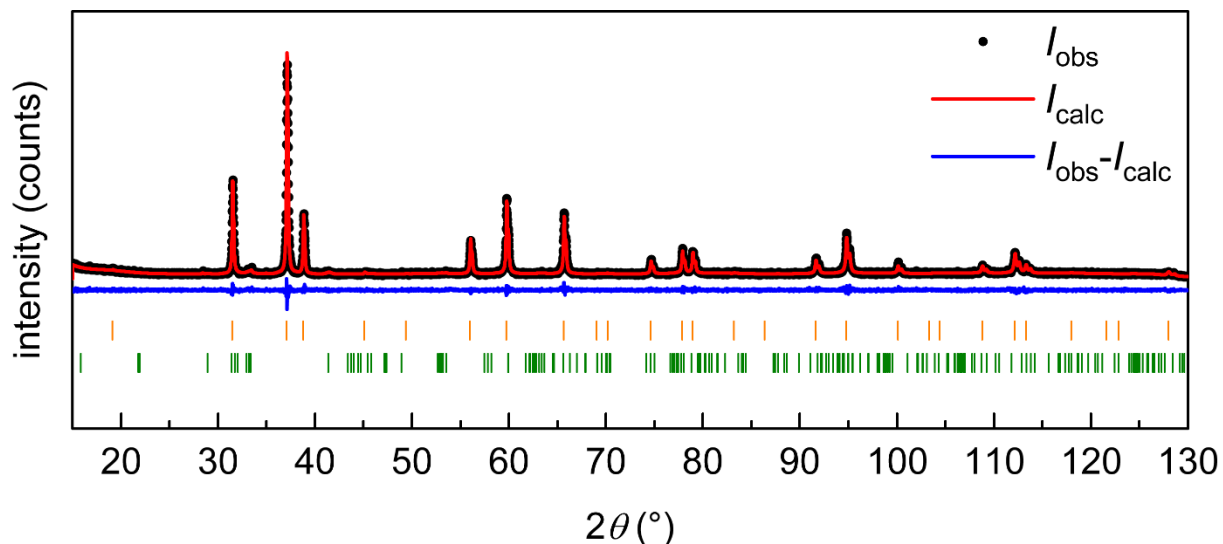


Figure S7. Powder X-ray diffraction pattern of CaAl₂ ball milled for 30 min. Black circles represent the collected data, the red line is the fit, the blue line the difference curve and the ticks represent the Bragg positions of the refined phases. The following color code applies: orange – CaAl₂ (*Fd* $\bar{3}$ *m*); green – CaAl₄ (*C2*/*m*).

Refinement details for the data shown in Figure S7	
Source	Bruker D8 ADVANCE (laboratory X-ray)
Temperature	RT
Pressure	ambient
Wavelengths	Cu <i>K</i> α ₁ and Cu <i>K</i> α ₂ : 154.0596 and 154.4308 pm
<i>d</i> -space range	0.85-14.35 Å (6-130° 2 θ)
χ^2	1.18
<i>R</i> _p / %	7.00
<i>R</i> _{wp} / %	8.99
Definition of <i>R</i> factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2};$ $R_{wp} = \left(\frac{\sum w I_0 - I_c ^2}{\sum w I_0^2} \right)^{\frac{1}{2}}$

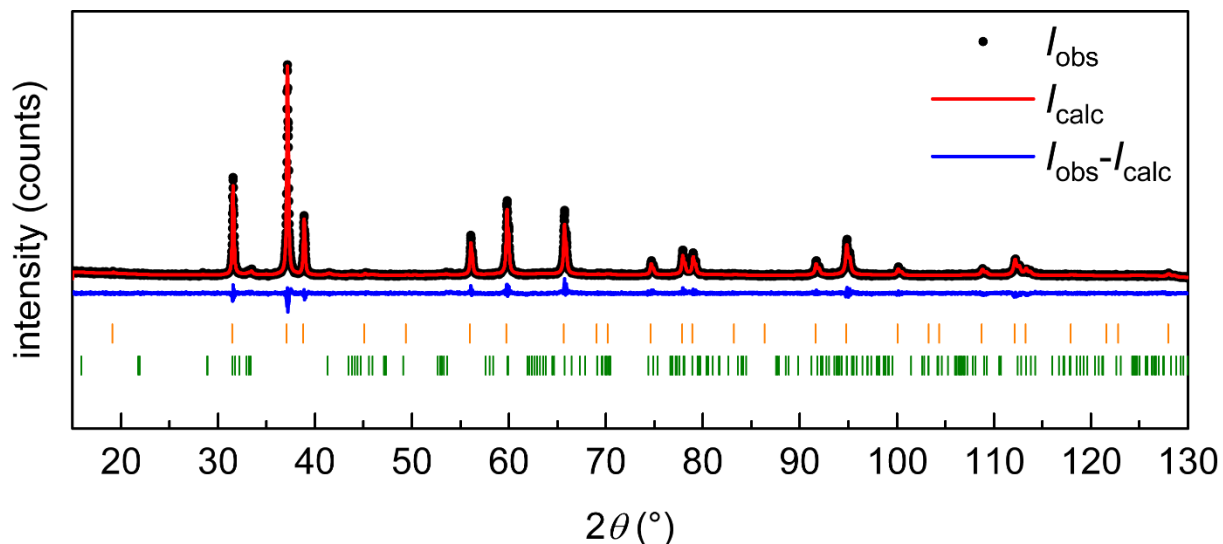


Figure S8. Powder X-ray diffraction pattern of CaAl₂ ball milled for 45 min. Black circles represent the collected data, the red line is the fit, the blue line the difference curve and the ticks represent the Bragg positions of the refined phases. The following color code applies: orange – CaAl₂ (*Fd* $\bar{3}$ *m*); green – CaAl₄ (*C2*/*m*).

Refinement details for the data shown in Figure S8	
Source	Bruker D8 ADVANCE (laboratory X-ray)
Temperature	RT
Pressure	ambient
Wavelengths	Cu <i>K</i> α ₁ and Cu <i>K</i> α ₂ : 154.0596 and 154.4308 pm
<i>d</i> -space range	0.85-14.35 Å (6-130° 2 θ)
χ^2	1.57
<i>R</i> _p / %	8.07
<i>R</i> _{wp} / %	10.09
Definition of <i>R</i> factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2};$ $R_{wp} = \left(\frac{\sum w I_0 - I_c ^2}{\sum w I_0^2} \right)^{\frac{1}{2}}$

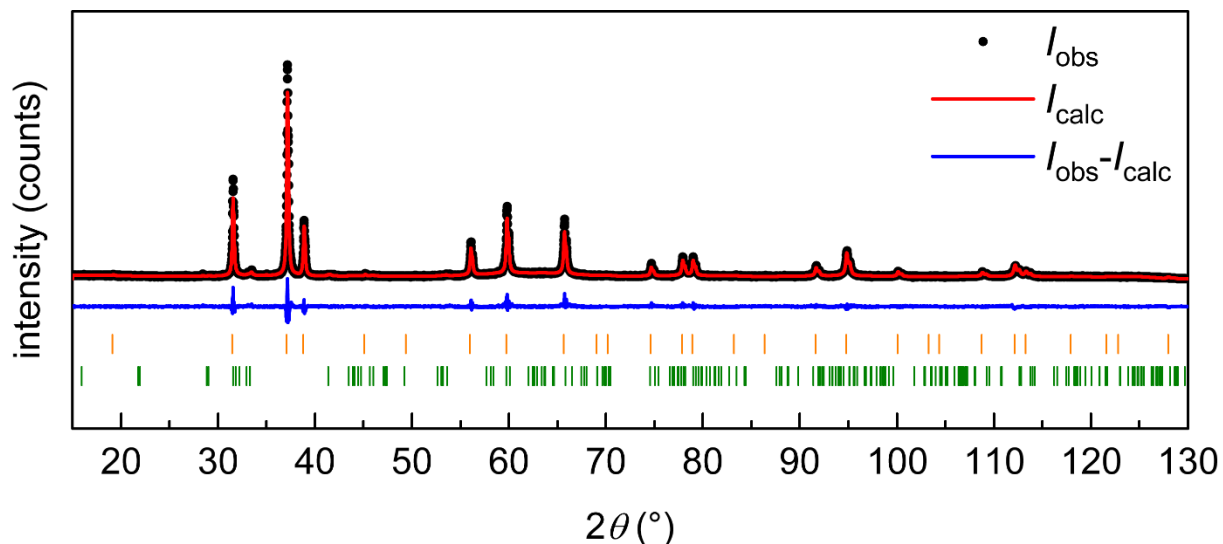


Figure S9. Powder X-ray diffraction pattern of CaAl₂ ball milled for 60 min. Black circles represent the collected data, the red line is the fit, the blue line the difference curve and the ticks represent the Bragg positions of the refined phases. The following color code applies: orange – CaAl₂ (*Fd* $\bar{3}$ *m*); green – CaAl₄ (*C2/m*).

Refinement details for the data shown in Figure S9	
Source	Bruker D8 ADVANCE (laboratory X-ray)
Temperature	RT
Pressure	ambient
Wavelengths	Cu <i>K</i> α ₁ and Cu <i>K</i> α ₂ : 154.0596 and 154.4308 pm
<i>d</i> -space range	0.85-14.35 Å (6-130° 2 θ)
χ^2	2.10
<i>R</i> _p / %	8.43
<i>R</i> _{wp} / %	10.72
Definition of <i>R</i> factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2};$ $R_{wp} = \left(\frac{\sum w I_0 - I_c ^2}{\sum w I_0^2} \right)^{\frac{1}{2}}$

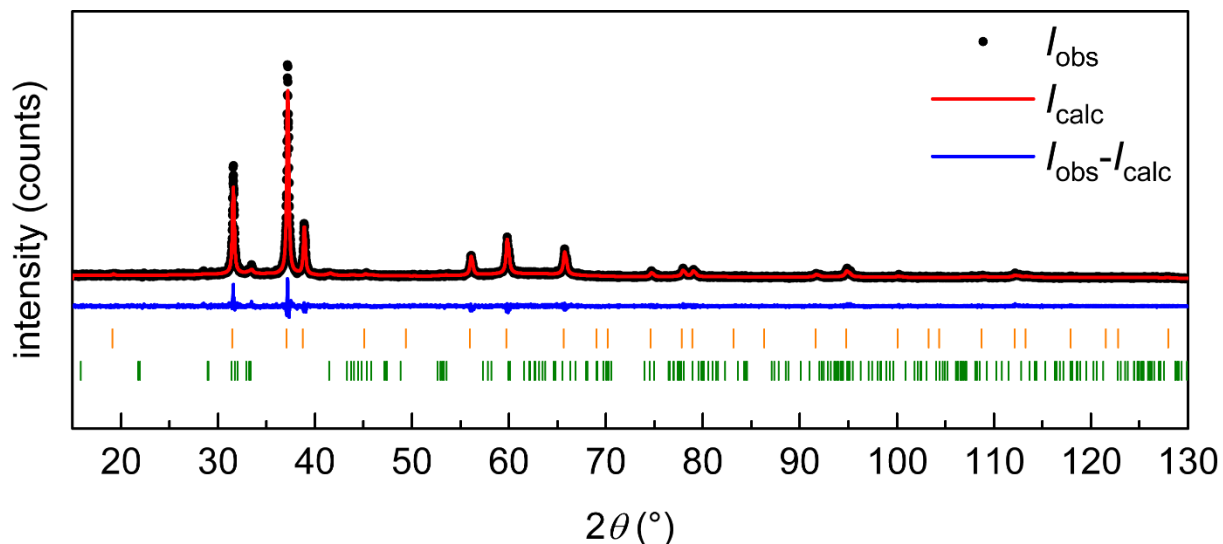


Figure S10. Powder X-ray diffraction pattern of CaAl₂ ball milled for 90 min. Black circles represent the collected data, the red line is the fit, the blue line the difference curve and the ticks represent the Bragg positions of the refined phases. The following color code applies: orange – CaAl₂ (*Fd* $\bar{3}$ *m*); green – CaAl₄ (*C2*/*m*).

Refinement details for the data shown in Figure S10	
Source	Bruker D8 ADVANCE (laboratory X-ray)
Temperature	RT
Pressure	ambient
Wavelengths	Cu <i>K</i> α ₁ and Cu <i>K</i> α ₂ : 154.0596 and 154.4308 pm
<i>d</i> -space range	0.85-14.35 Å (6-130° 2 θ)
χ^2	1.27
<i>R</i> _p / %	10.62
<i>R</i> _{wp} / %	13.89
Definition of <i>R</i> factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2};$ $R_{wp} = \left(\frac{\sum w I_0 - I_c ^2}{\sum w I_0^2} \right)^{\frac{1}{2}}$

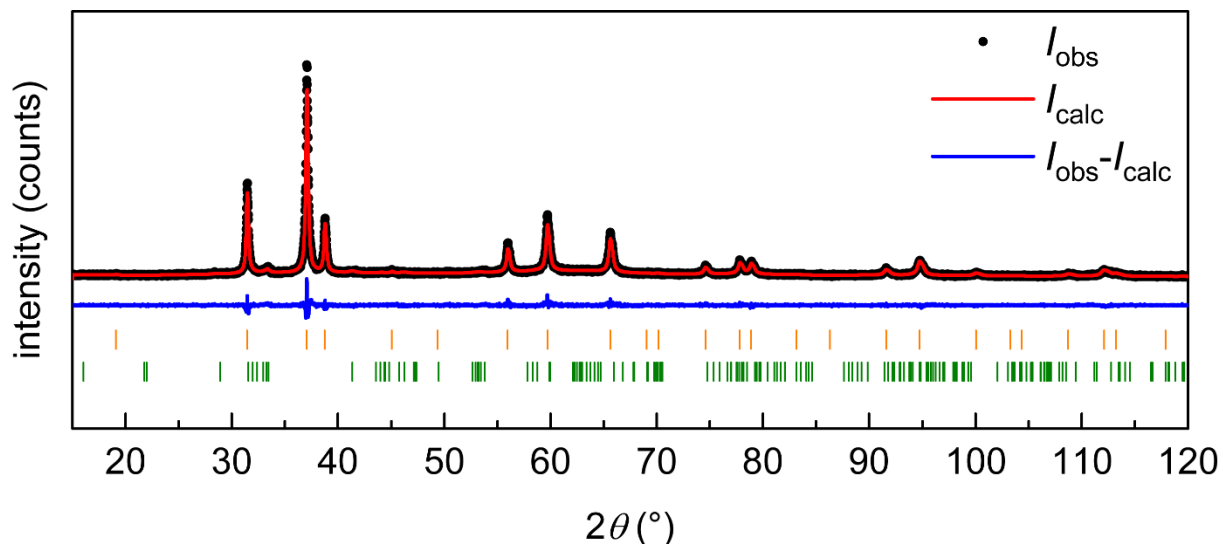


Figure S11. Powder X-ray diffraction pattern of CaAl₂ ball milled for 180 min. Black circles represent the collected data, the red line is the fit, the blue line the difference curve and the ticks represent the Bragg positions of the refined phases. The following color code applies: orange – CaAl₂ (*Fd* $\bar{3}$ *m*); green – CaAl₄ (*C2/m*).

Refinement details for the data shown in Figure S11	
Source	Bruker D8 ADVANCE (laboratory X-ray)
Temperature	RT
Pressure	ambient
Wavelengths	Cu <i>K</i> α_1 and Cu <i>K</i> α_2 : 154.0596 and 154.4308 pm
<i>d</i> -space range	0.85-14.35 Å (6-130° 2 θ)
χ^2	1.34
<i>R</i> _p / %	7.25
<i>R</i> _{wp} / %	9.14
Definition of <i>R</i> factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2};$ $R_{wp} = \left(\frac{\sum w I_0 - I_c ^2}{\sum w I_0^2} \right)^{\frac{1}{2}}$

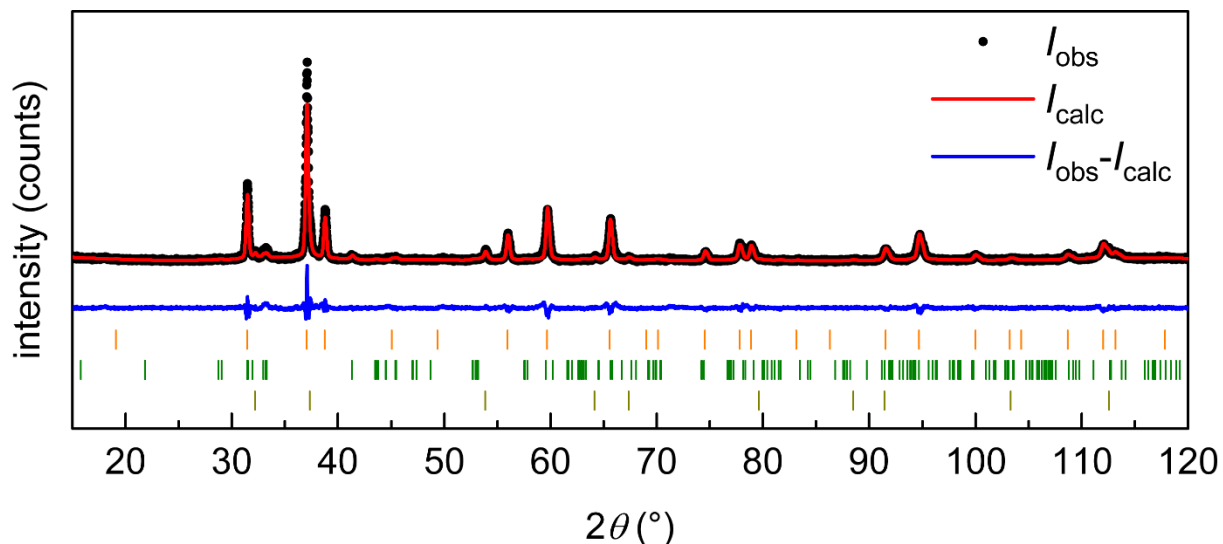


Figure S12. Powder X-ray diffraction pattern of CaAl_2 ball milled for 180 min after the pyrolytic reaction. Black circles represent the collected data, the red line is the fit, the blue line the difference curve and the ticks represent the Bragg positions of the refined phases. The following color code applies: orange – CaAl_2 ($Fd\bar{3}m$); green – CaAl_4 ($C2/m$); olive – CaO ($Fm\bar{3}m$).

Refinement details for the data shown in Figure S12	
Source	Bruker D8 ADVANCE (laboratory X-ray)
Temperature	RT
Pressure	ambient
Wavelengths	$\text{Cu } K\alpha_1$ and $\text{Cu } K\alpha_2$: 154.0596 and 154.4308 pm
d -space range	0.85-14.35 Å (6-130° 2θ)
χ^2	1.62
R_p / %	6.58
R_{wp} / %	8.44
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2};$ $R_{wp} = \left(\frac{\sum w I_0 - I_c ^2}{\sum w I_0^2} \right)^{\frac{1}{2}}$

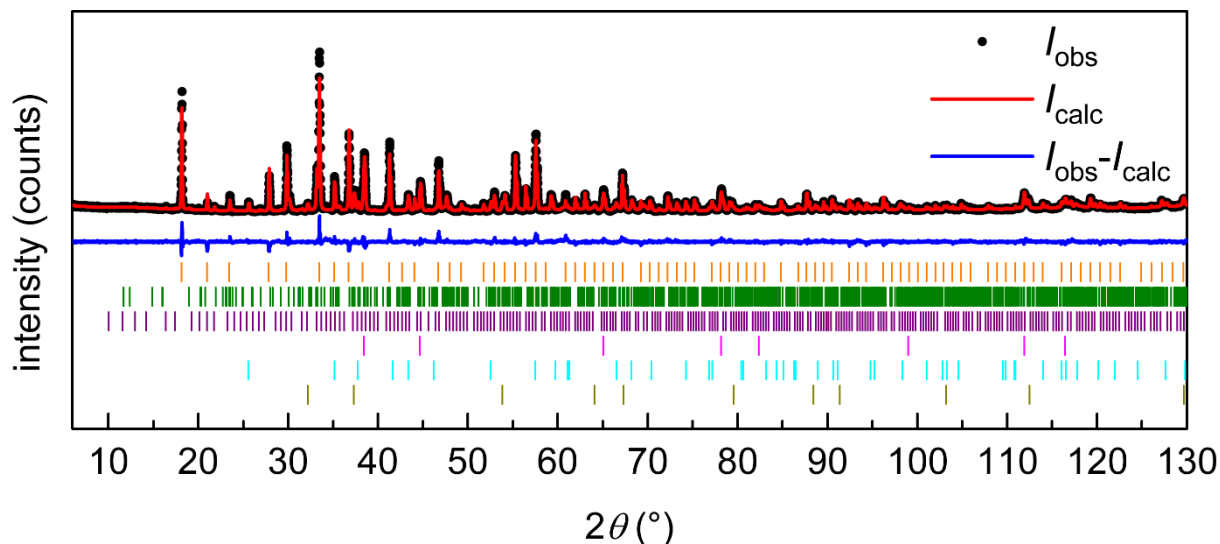


Figure S13. Powder X-ray diffraction pattern of pristine CaAl_2 and oxidized during thermal analysis. Black circles represent the collected data, the red line is the fit, the blue line the difference curve and the ticks represent the Bragg positions of the refined phases. The following color code applies: orange – $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ ($I\bar{4}3d$); green – CaAl_2O_4 ($P2_1/c$); purple – $\text{Ca}_3\text{Al}_2\text{O}_6$ ($Pa\bar{3}$); pink – Al ($Fm\bar{3}m$); cyan – Al_2O_3 ($R\bar{3}c$); olive – CaO ($Fm\bar{3}m$).

Refinement details for the data shown in Figure S13	
Source	Bruker D8 ADVANCE (laboratory X-ray)
Temperature	RT
Pressure	ambient
Wavelengths	$\text{Cu } K\alpha_1$ and $\text{Cu } K\alpha_2$: 154.0596 and 154.4308 pm
d -space range	0.85-14.35 Å (6-130° 2θ)
χ^2	4.34
R_p / %	6.67
R_{wp} / %	9.06
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2 }$ $R_{wp} = \left(\frac{\sum w I_0 - I_c ^2}{\sum w I_0^2 } \right)^{\frac{1}{2}}$

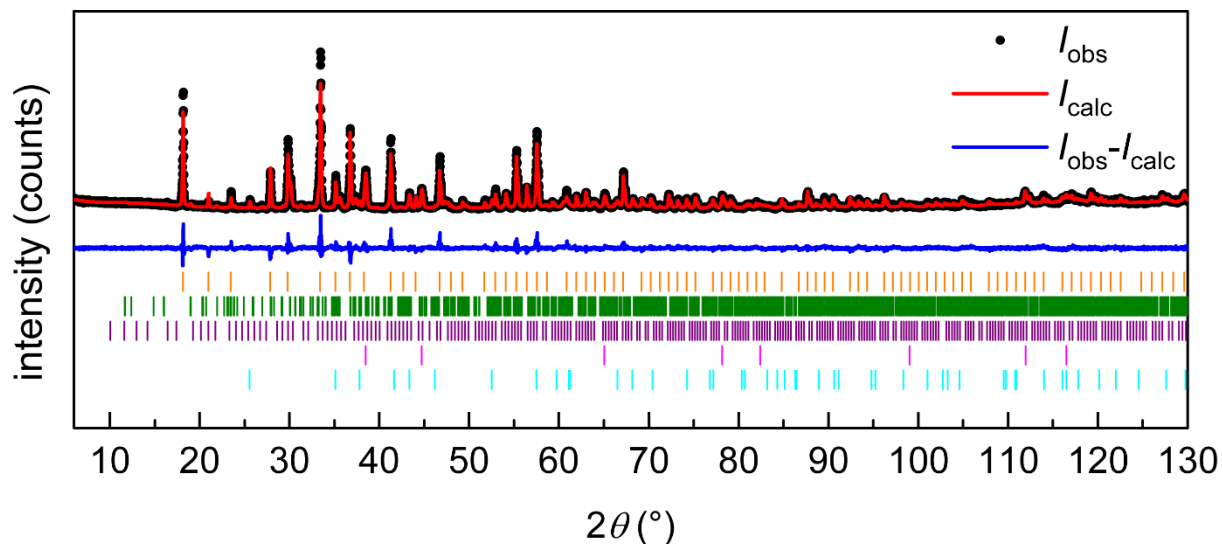


Figure S14. Powder X-ray diffraction pattern of CaAl₂ ball milled for 5 min and oxidized during thermal analysis. Black circles represent the collected data, the red line is the fit, the blue line the difference curve and the ticks represent the Bragg positions of the refined phases. The following color code applies: orange – Ca₁₂Al₁₄O₃₃ ($I\bar{4}3d$); green – CaAl₂O₄ ($P2_1/c$); purple – Ca₃Al₂O₆ ($Pa\bar{3}$); pink – Al ($Fm\bar{3}m$); cyan – Al₂O₃ ($R\bar{3}c$); olive – CaO ($Fm\bar{3}m$).

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
d -space range	0.85-14.35 Å (6-130° 2θ)
χ^2	3.59
R_p / %	6.56
R_{wp} / %	8.81
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2 }$ $R_{wp} = \left(\frac{\sum w I_0 - I_c ^2}{\sum w I_0^2 } \right)^{\frac{1}{2}}$

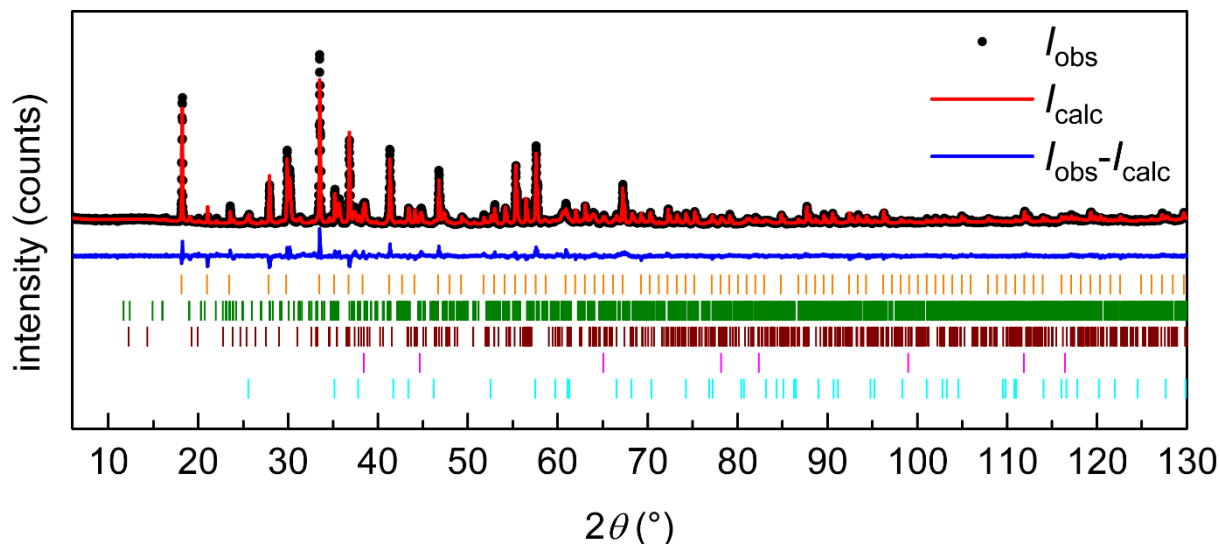


Figure S15. Powder X-ray diffraction pattern of CaAl₂ ball milled for 10 min and oxidized during thermal analysis. Black circles represent the collected data, the red line is the fit, the blue line the difference curve and the ticks represent the Bragg positions of the refined phases. The following color code applies: orange – Ca₁₂Al₁₄O₃₃ ($I\bar{4}3d$); green – CaAl₂O₄ ($P2_1/c$); purple – Ca₃Al₂O₆ ($Pa\bar{3}$); pink – Al ($Fm\bar{3}m$); cyan – Al₂O₃ ($R\bar{3}c$); olive – CaO ($Fm\bar{3}m$).

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
d -space range	0.85-14.35 Å (6-130° 2 θ)
χ^2	4.40
R_p / %	6.88
R_{wp} / %	9.29
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2};$ $R_{wp} = \left(\frac{\sum w I_0 - I_c ^2}{\sum w I_0^2} \right)^{\frac{1}{2}}$

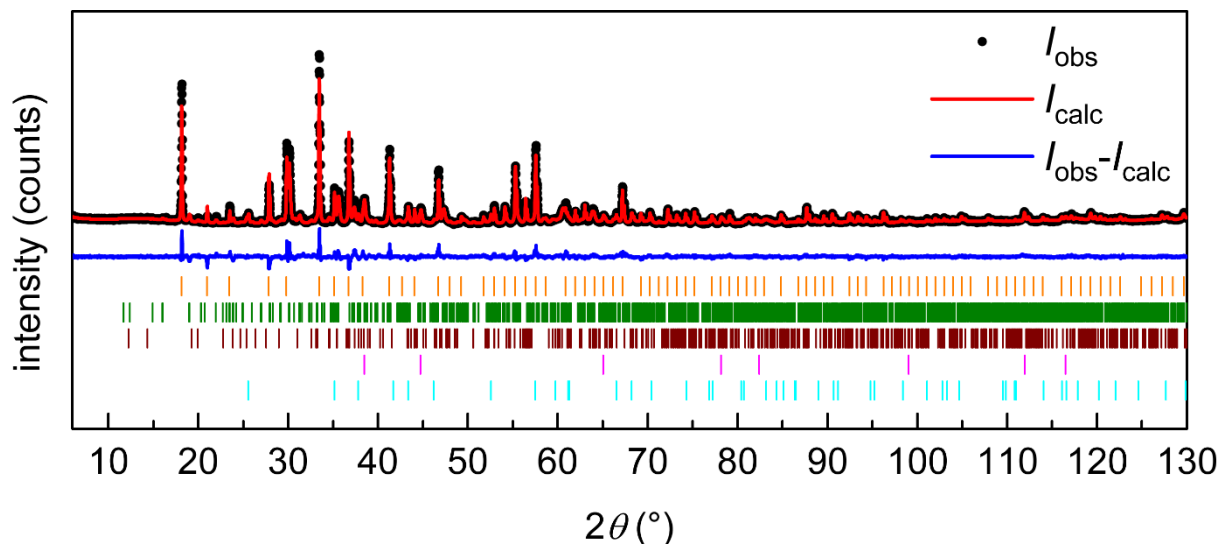


Figure S16. Powder X-ray diffraction pattern of CaAl₂ ball milled for 15 min and oxidized during thermal analysis. Black circles represent the collected data, the red line is the fit, the blue line the difference curve and the ticks represent the Bragg positions of the refined phases. The following color code applies: orange – Ca₁₂Al₁₄O₃₃ ($I\bar{4}3d$); green – CaAl₂O₄ ($P2_1/c$); purple – Ca₃Al₂O₆ ($Pa\bar{3}$); pink – Al ($Fm\bar{3}m$); cyan – Al₂O₃ ($R\bar{3}c$); olive – CaO ($Fm\bar{3}m$).

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
d -space range	0.85-14.35 Å (6-130° 2 θ)
χ^2	5.12
R_p / %	7.18
R_{wp} / %	9.73
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2};$ $R_{wp} = \left(\frac{\sum w I_0 - I_c ^2}{\sum w I_0^2} \right)^{\frac{1}{2}}$

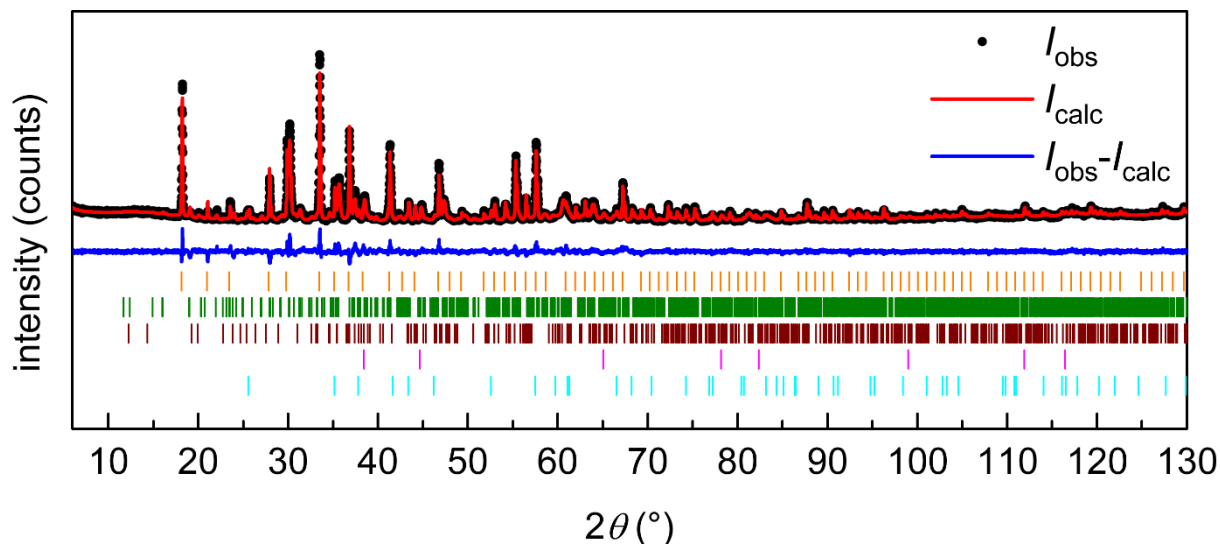


Figure S17. Powder X-ray diffraction pattern of CaAl₂ ball milled for 20 min and oxidized during thermal analysis. Black circles represent the collected data, the red line is the fit, the blue line the difference curve and the ticks represent the Bragg positions of the refined phases. The following color code applies: orange – Ca₁₂Al₁₄O₃₃ ($I\bar{4}3d$); green – CaAl₂O₄ ($P2_1/c$); purple – Ca₃Al₂O₆ ($Pa\bar{3}$); pink – Al ($Fm\bar{3}m$); cyan – Al₂O₃ ($R\bar{3}c$); olive – CaO ($Fm\bar{3}m$).

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
d -space range	0.85-14.35 Å (6-130° 2θ)
χ^2	3.10
R_p / %	6.37
R_{wp} / %	8.49
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2};$ $R_{wp} = \left(\frac{\sum w I_0 - I_c ^2}{\sum w I_0^2} \right)^{\frac{1}{2}}$

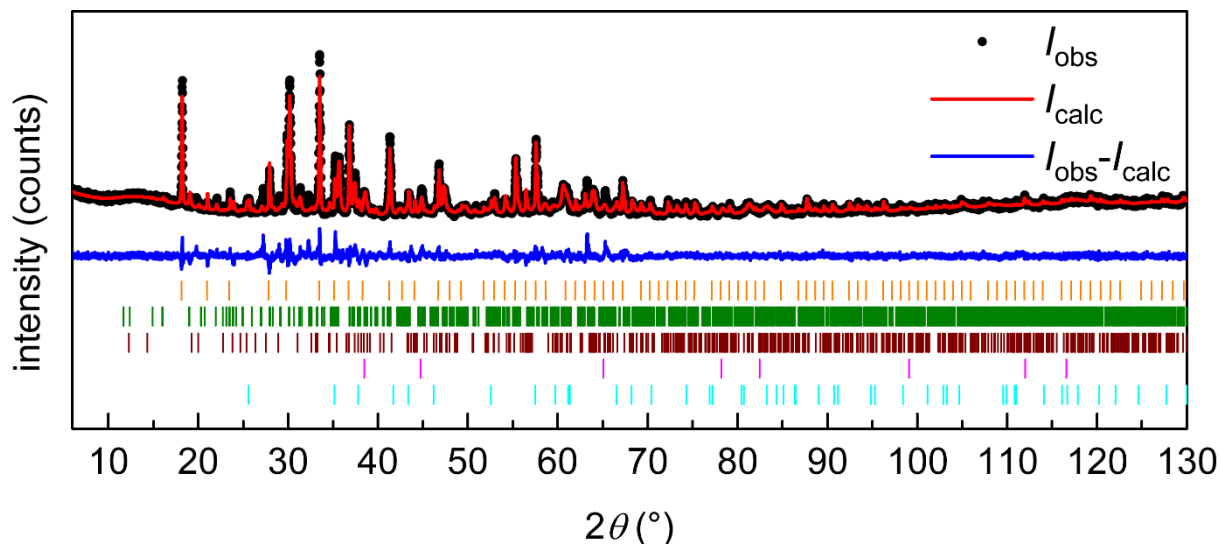


Figure S18. Powder X-ray diffraction pattern of CaAl₂ ball milled for 30 min and oxidized during thermal analysis. Black circles represent the collected data, the red line is the fit, the blue line the difference curve and the ticks represent the Bragg positions of the refined phases. The following color code applies: orange – Ca₁₂Al₁₄O₃₃ ($I\bar{4}3d$); green – CaAl₂O₄ ($P2_1/c$); purple – Ca₃Al₂O₆ ($Pa\bar{3}$); pink – Al ($Fm\bar{3}m$); cyan – Al₂O₃ ($R\bar{3}c$); olive – CaO ($Fm\bar{3}m$).

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
d -space range	0.85-14.35 Å (6-130° 2θ)
χ^2	3.08
R_p / %	6.57
R_{wp} / %	9.06
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2};$ $R_{wp} = \left(\frac{\sum w I_0 - I_c ^2}{\sum w I_0^2} \right)^{\frac{1}{2}}$

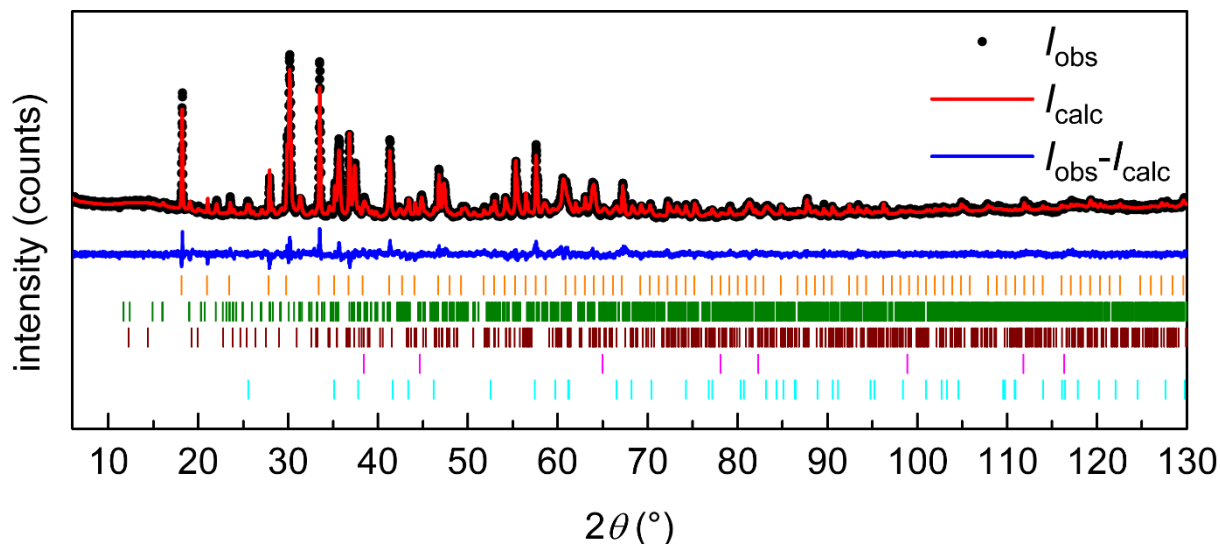


Figure S19. Powder X-ray diffraction pattern of CaAl₂ ball milled for 45 min and oxidized during thermal analysis. Black circles represent the collected data, the red line is the fit, the blue line the difference curve and the ticks represent the Bragg positions of the refined phases. The following color code applies: orange – Ca₁₂Al₁₄O₃₃ ($I\bar{4}3d$); green – CaAl₂O₄ ($P2_1/c$); purple – Ca₃Al₂O₆ ($Pa\bar{3}$); pink – Al ($Fm\bar{3}m$); cyan – Al₂O₃ ($R\bar{3}c$); olive – CaO ($Fm\bar{3}m$).

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
d -space range	0.85-14.35 Å (6-130° 2θ)
χ^2	2.46
R_p / %	5.93
R_{wp} / %	7.73
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2 }^{1/2}$

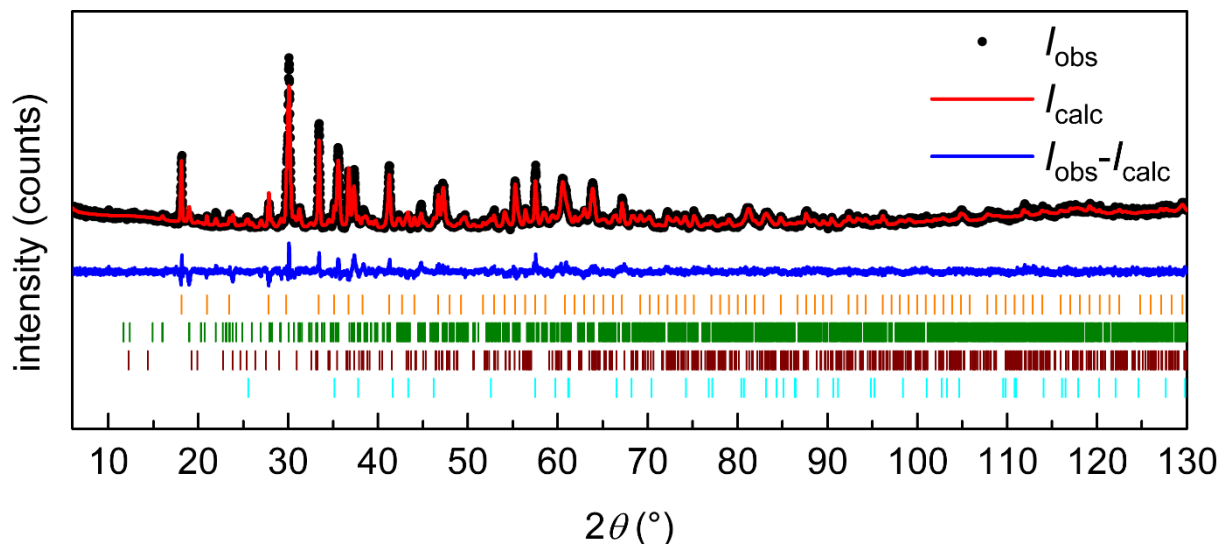


Figure S20. Powder X-ray diffraction pattern of CaAl₂ ball milled for 60 min and oxidized during thermal analysis. Black circles represent the collected data, the red line is the fit, the blue line the difference curve and the ticks represent the Bragg positions of the refined phases. The following color code applies: orange – Ca₁₂Al₁₄O₃₃ ($I\bar{4}3d$); green – CaAl₂O₄ ($P2_1/c$); purple – Ca₃Al₂O₆ ($Pa\bar{3}$); pink – Al ($Fm\bar{3}m$); cyan – Al₂O₃ ($R\bar{3}c$); olive – CaO ($Fm\bar{3}m$).

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
d -space range	0.85-14.35 Å (6-130° 2θ)
χ^2	2.68
R_p / %	6.02
R_{wp} / %	7.91
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2}$ $R_{wp} = \left(\frac{\sum w I_0 - I_c ^2}{\sum w I_0^2} \right)^{\frac{1}{2}}$

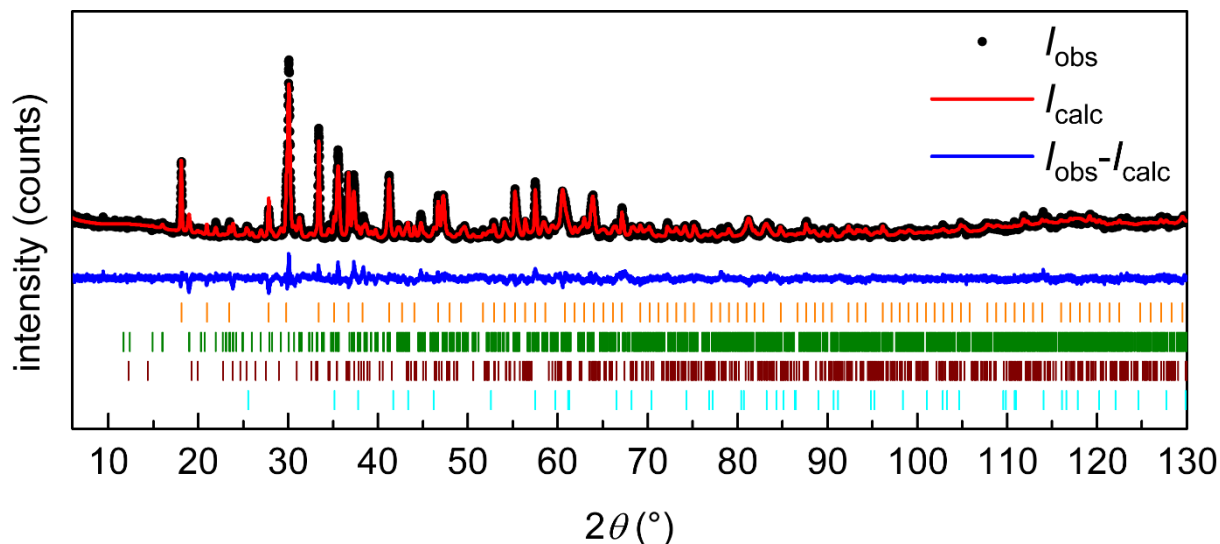


Figure S21. Powder X-ray diffraction pattern of CaAl₂ ball milled for 90 min and oxidized during thermal analysis. Black circles represent the collected data, the red line is the fit, the blue line the difference curve and the ticks represent the Bragg positions of the refined phases. The following color code applies: orange – Ca₁₂Al₁₄O₃₃ ($I\bar{4}3d$); green – CaAl₂O₄ ($P2_1/c$); dark red – CaAl₄O₇ ($C2/c$); cyan – Al₂O₃ ($R\bar{3}c$).

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
d -space range	0.85-14.35 Å (6-130° 2θ)
χ^2	2.71
R_p / %	6.26
R_{wp} / %	8.26
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2};$ $R_{wp} = \left(\frac{\sum w I_0 - I_c ^2}{\sum w I_0^2} \right)^{\frac{1}{2}}$

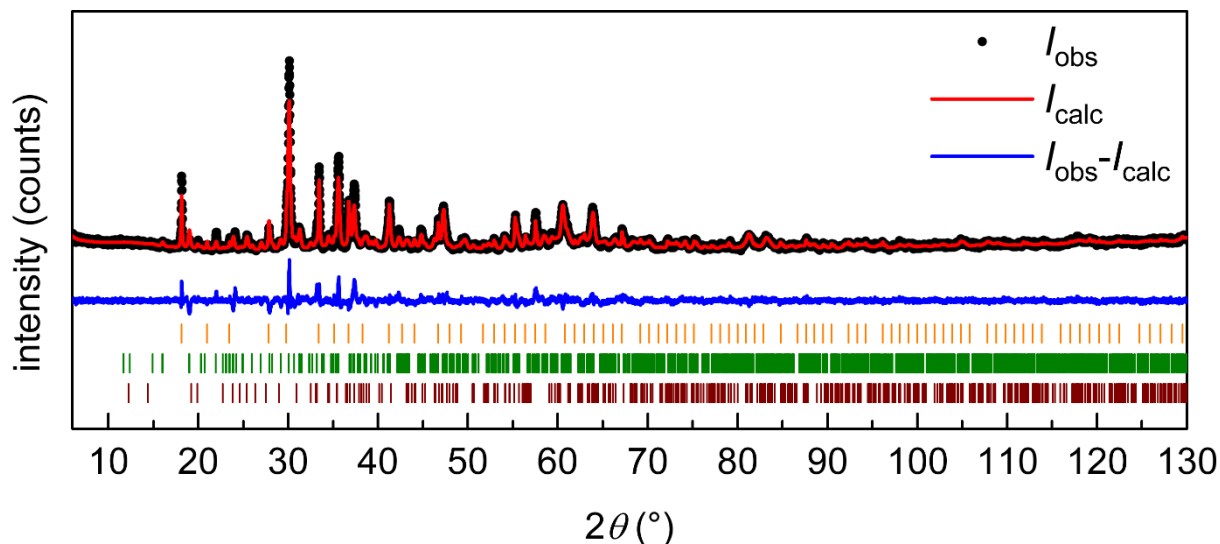


Figure S22. Powder X-ray diffraction pattern of CaAl₂ ball milled for 180 min and oxidized during thermal analysis. Black circles represent the collected data, the red line is the fit, the blue line the difference curve and the ticks represent the Bragg positions of the refined phases. The following color code applies: orange – Ca₁₂Al₁₄O₃₃ ($I\bar{4}3d$); green – CaAl₂O₄ ($P2_1/c$); dark red – CaAl₄O₇ ($C2/c$).

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
d -space range	0.85-14.35 Å (6-130° 2θ)
χ^2	3.06
R_p / %	8.03
R_{wp} / %	10.84
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2 };$ $R_{wp} = \left(\frac{\sum w I_0 - I_c ^2}{\sum w I_0^2 } \right)^{\frac{1}{2}}$

Thermal analysis

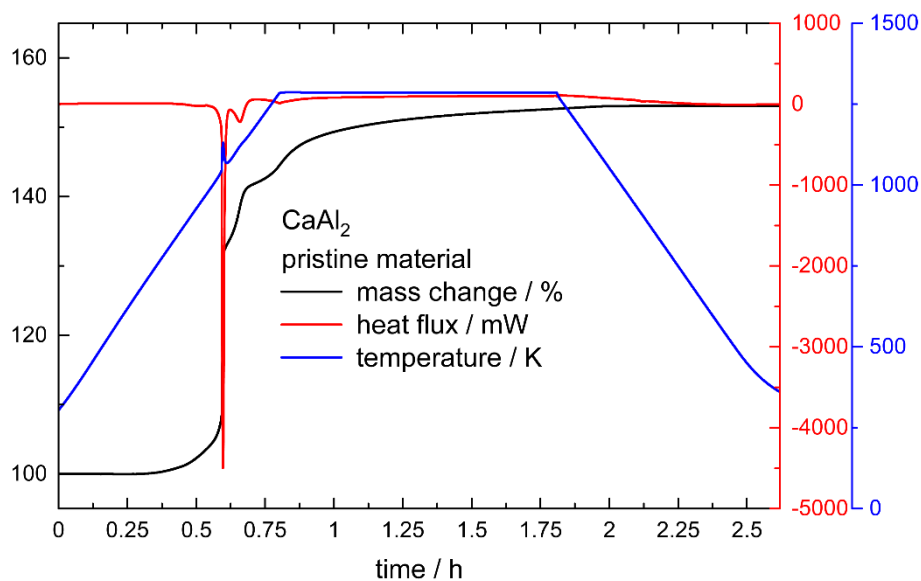


Figure S23. STA measurements of pristine CaAl_2 under a 50:50 flow of $\text{Ar}:\text{O}_2$. The black curve indicates the mass trace, blue the temperature change and red the heat flux.

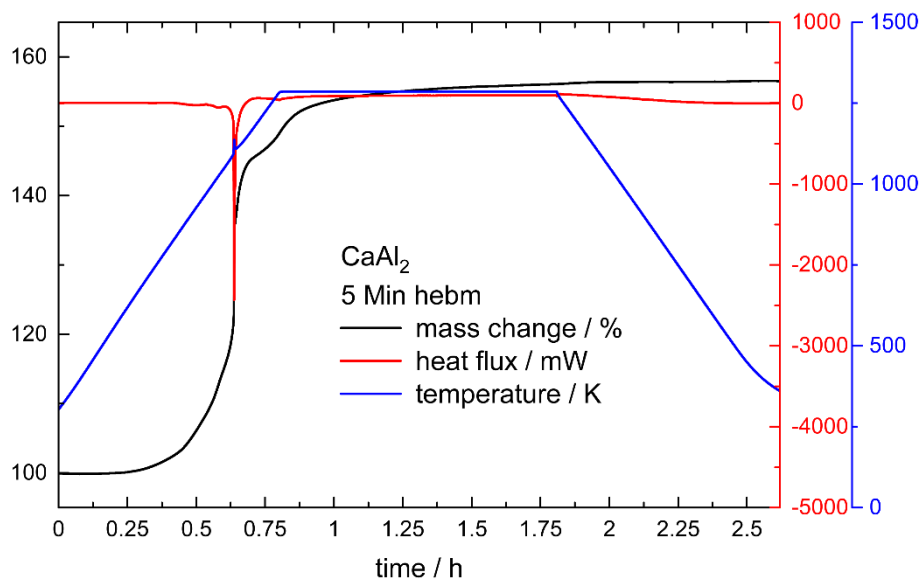


Figure S24. STA measurements of CaAl_2 ball milled for 5 min under a 50:50 flow of $\text{Ar}:\text{O}_2$. The black curve indicates the mass trace, blue the temperature change and red the heat flux.

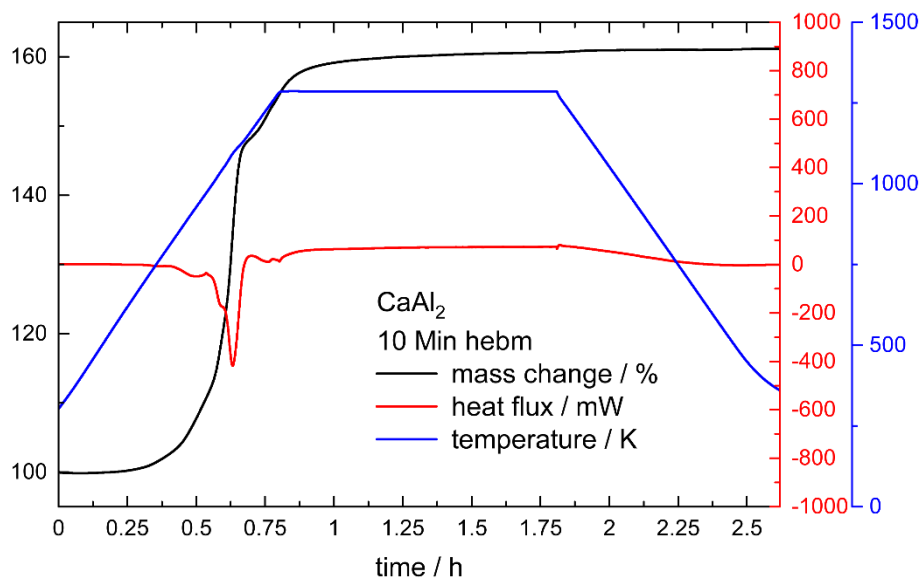


Figure S25. STA measurements of CaAl₂ ball milled for 10 min under a 50:50 flow of Ar:O₂. The black curve indicates the mass trace, blue the temperature change and red the heat flux.

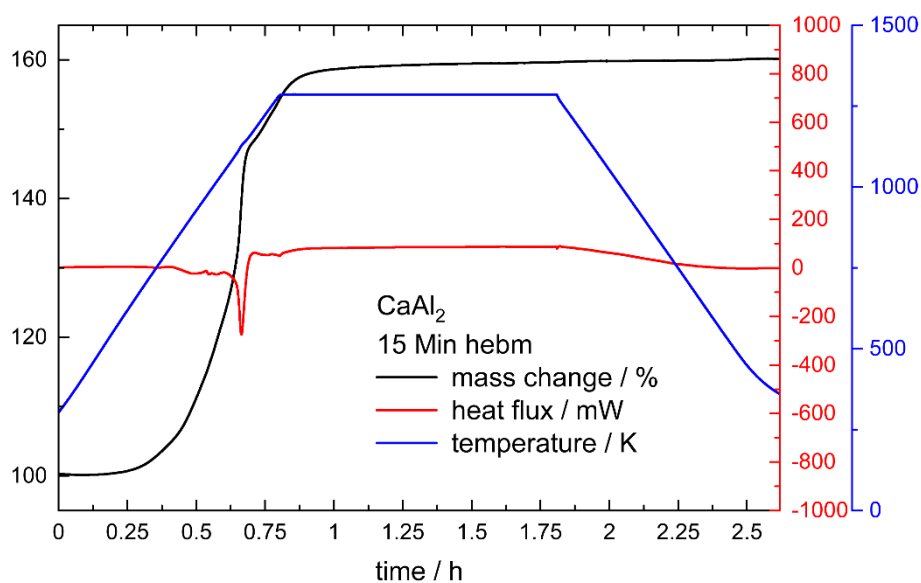


Figure S26. STA measurements of CaAl₂ ball milled for 15 min under a 50:50 flow of Ar:O₂. The black curve indicates the mass trace, blue the temperature change and red the heat flux.

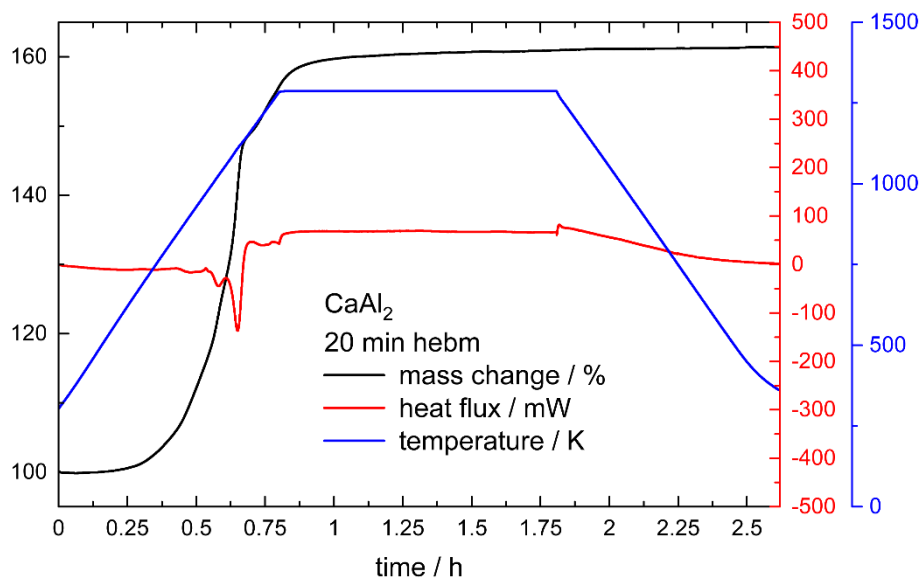


Figure S27. STA measurements of CaAl₂ ball milled for 20 min under a 50:50 flow of Ar:O₂. The black curve indicates the mass trace, blue the temperature change and red the heat flux.

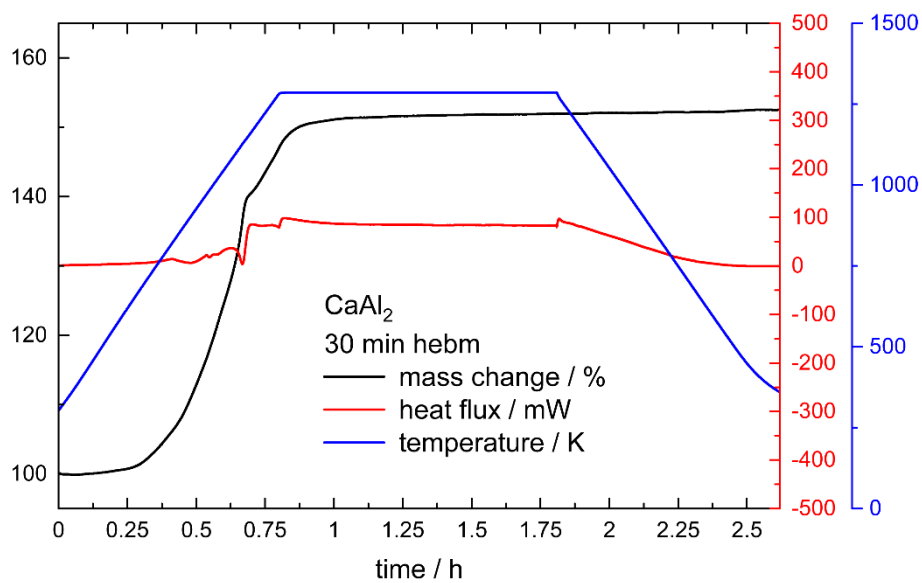


Figure S28. STA measurements of CaAl₂ ball milled for 30 min under a 50:50 flow of Ar:O₂. The black curve indicates the mass trace, blue the temperature change and red the heat flux.

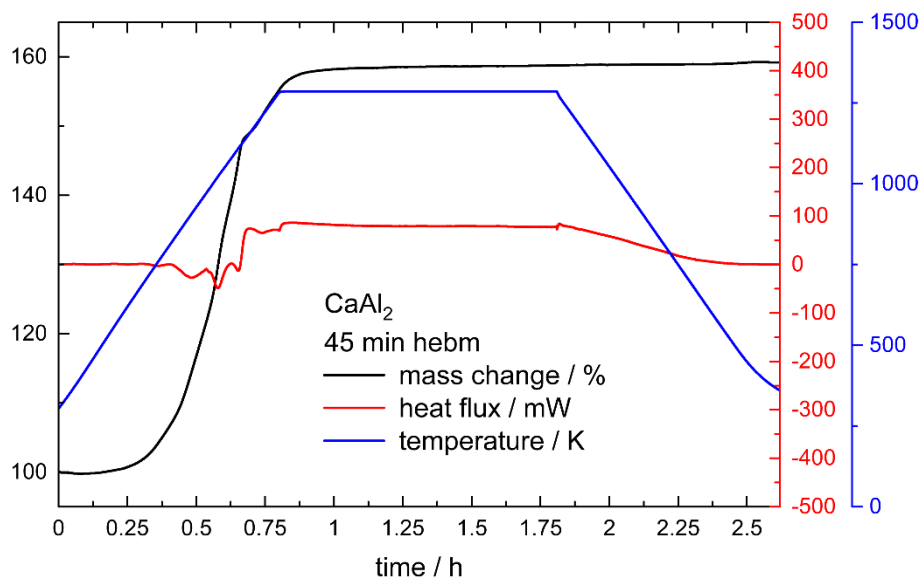


Figure S29. STA measurements of CaAl₂ ball milled for 45 min under a 50:50 flow of Ar:O₂. The black curve indicates the mass trace, blue the temperature change and red the heat flux.

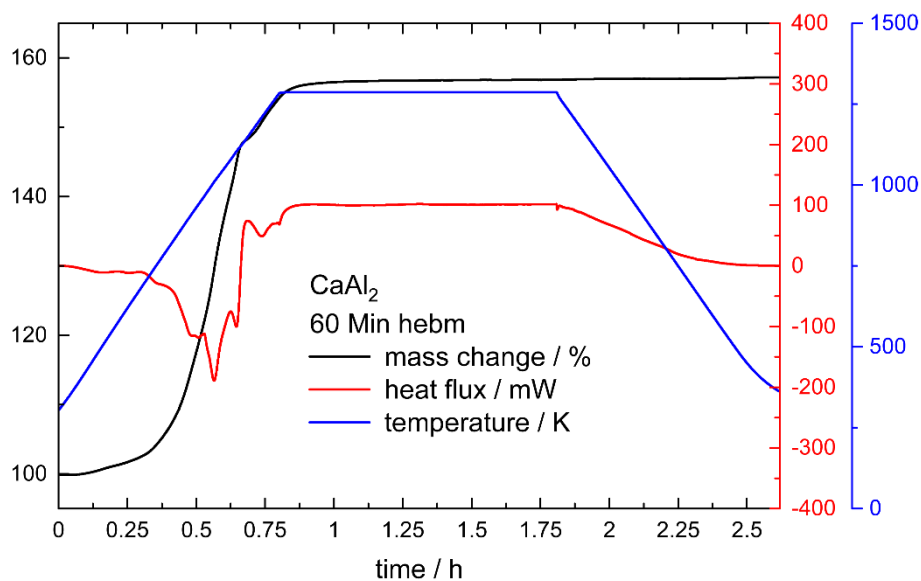


Figure S30. STA measurements of CaAl₂ ball milled for 60 min under a 50:50 flow of Ar:O₂. The black curve indicates the mass trace, blue the temperature change and red the heat flux.

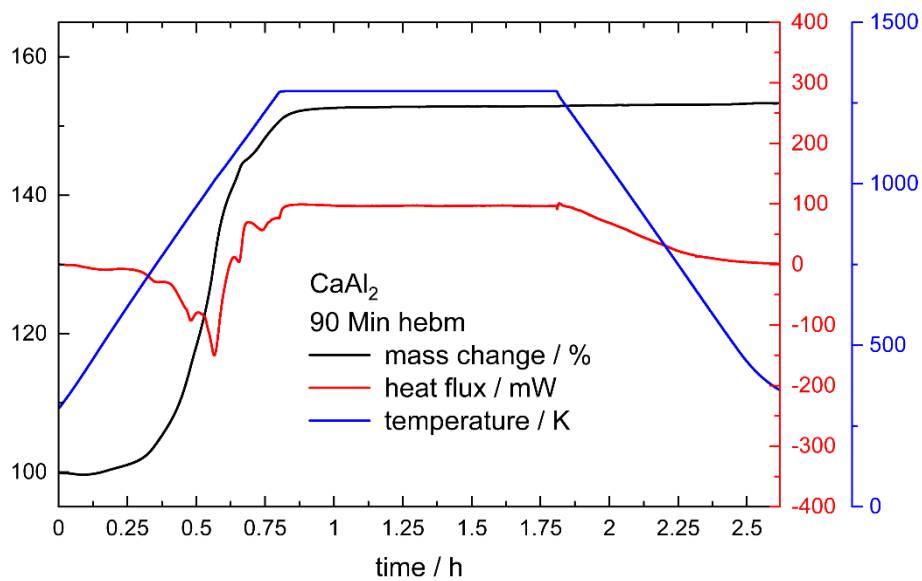


Figure S31. STA measurements of CaAl₂ ball milled for 90 min under a 50:50 flow of Ar:O₂. The black curve indicates the mass trace, blue the temperature change and red the heat flux.

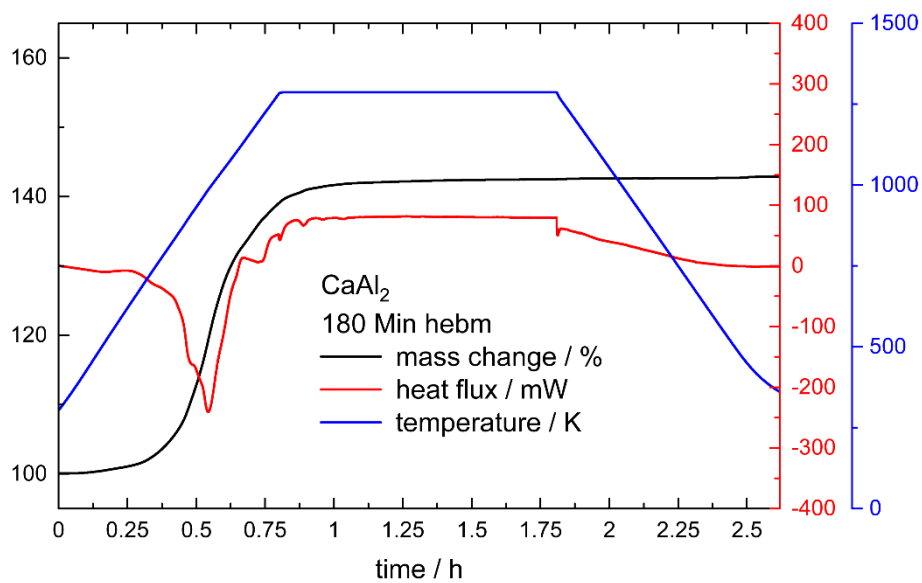


Figure S32. STA measurements of CaAl₂ ball milled for 180 min under a 50:50 flow of Ar:O₂. The black curve indicates the mass trace, blue the temperature change and red the heat flux.

^{27}Al solid state MAS NMR

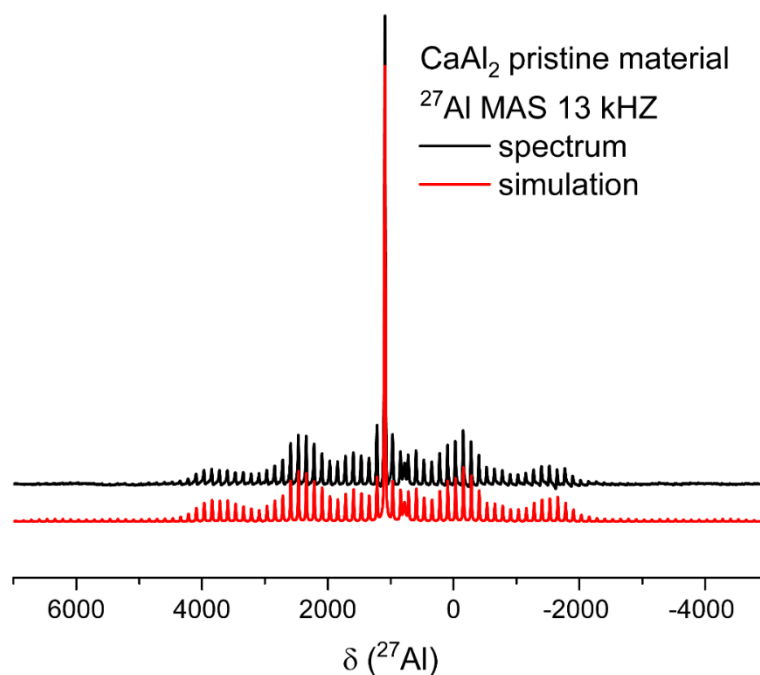


Figure S33. ^{27}Al solid-state MAS NMR spectrum of pristine CaAl₂ recorded at a spinning frequency of 13 kHz. The black line shows the experimental data, the red line the simulation.

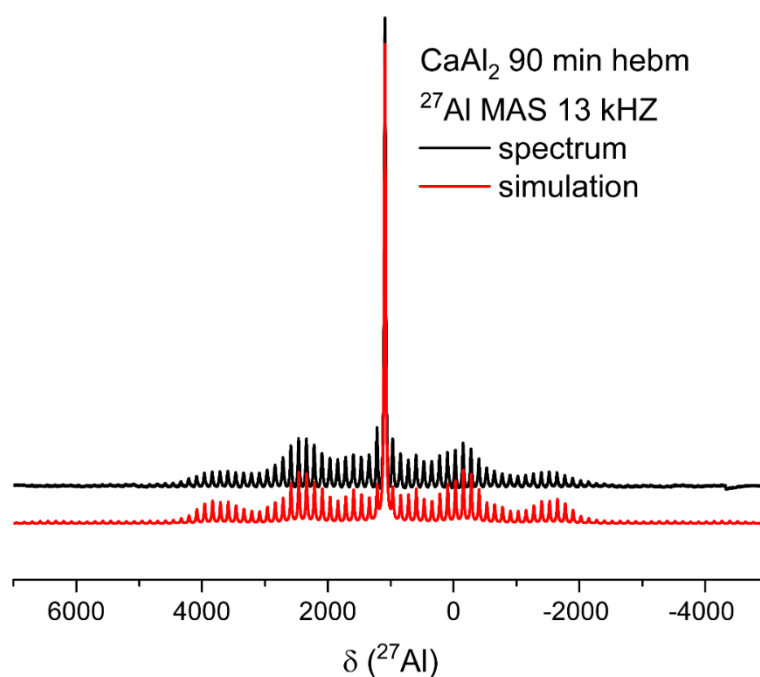


Figure S34. ^{27}Al solid-state MAS NMR spectrum of CaAl₂ ball milled for 90 min recorded at a spinning frequency of 13 kHz. The black line shows the experimental data, the red line the simulation.

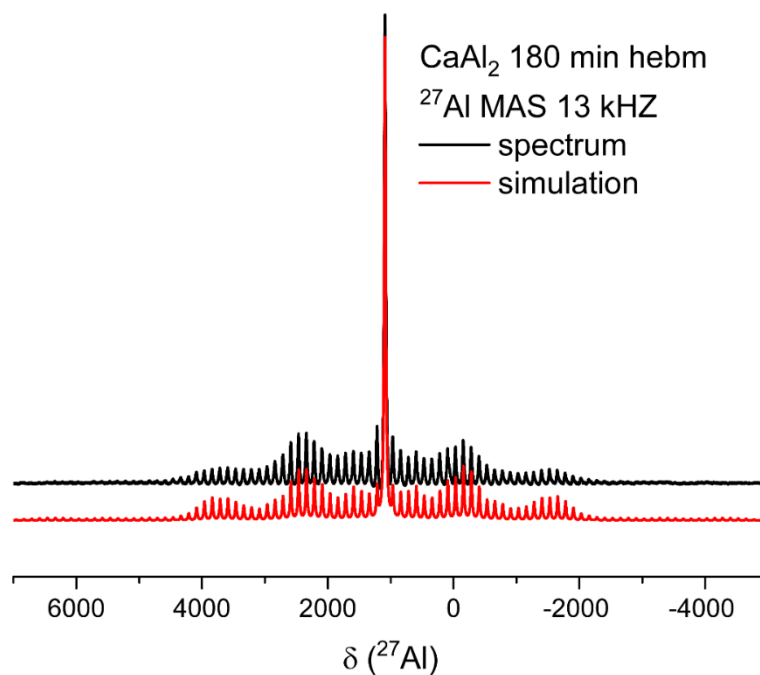


Figure S35. ²⁷Al solid-state MAS NMR spectrum of CaAl₂ ball milled for 180 min recorded at a spinning frequency of 13 kHz. The black line shows the experimental data, the red line the simulation.

Product spectrum determined from PXRD

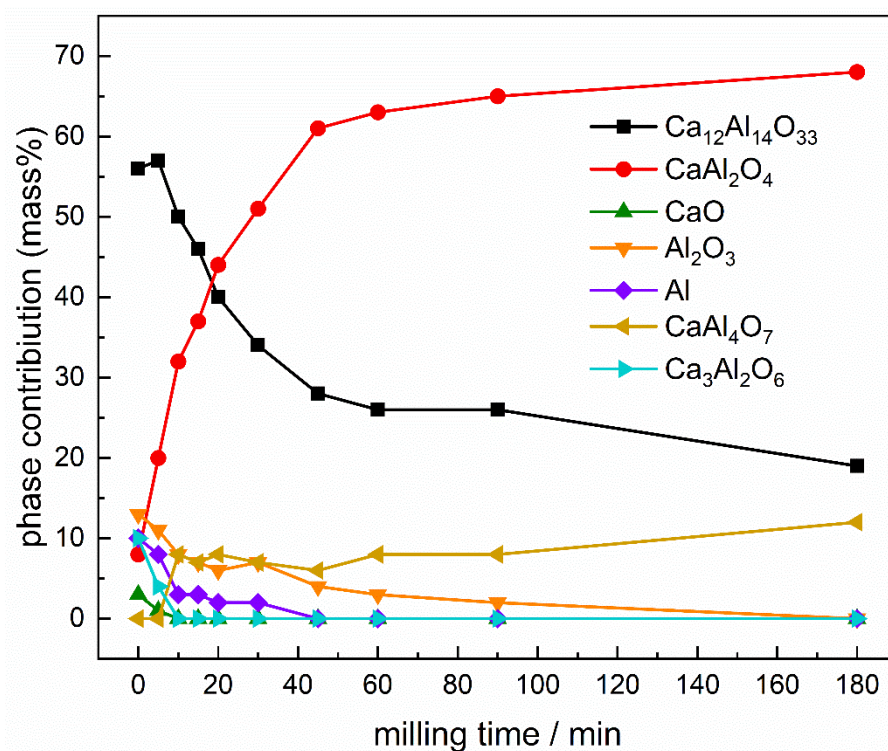


Figure S36. Phase contributions in mass-% for the oxidation reactions of ball milled CaAl_2 plotted against the milling time.

Powder X-ray diffraction with internal standard

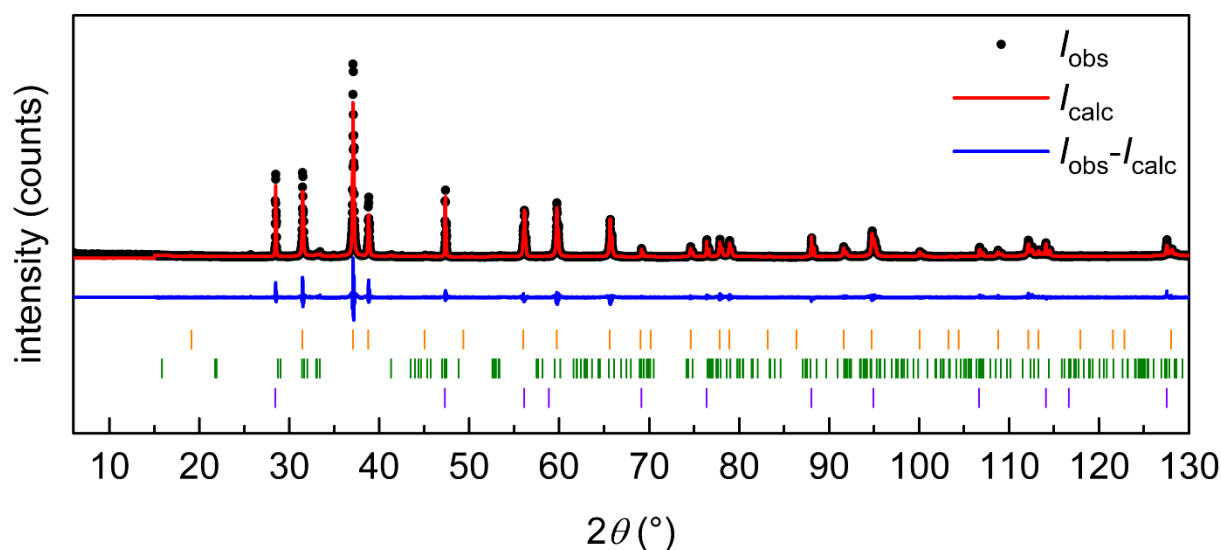


Figure S37. Powder X-ray diffraction pattern of CaAl₂ ball milled for 30 min, mixed with elemental Si as internal standard. Black circles represent the collected data, the red line is the fit, the blue line the difference curve and the ticks represent the Bragg positions of the refined phases. The following color code applies: orange – CaAl₂ (*Fd* $\bar{3}$ *m*); green – CaAl₄ (*C*2/*m*); purple – Si (*Fd* $\bar{3}$ *m*).

Refinement details for the data shown in Figure S37	
Source	Bruker D8 ADVANCE (laboratory X-ray)
Temperature	RT
Pressure	ambient
Wavelengths	Cu <i>K</i> α ₁ and Cu <i>K</i> α ₂ : 154.0596 and 154.4308 pm
<i>d</i> -space range	0.85-14.35 Å (6-130° 2θ)
χ ²	1.28
<i>R</i> _p / %	8.32
<i>R</i> _{wp} / %	10.55
Definition of <i>R</i> factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2};$ $R_{wp} = \left(\frac{\sum w I_0 - I_c ^2}{\sum w I_0^2} \right)^{\frac{1}{2}}$

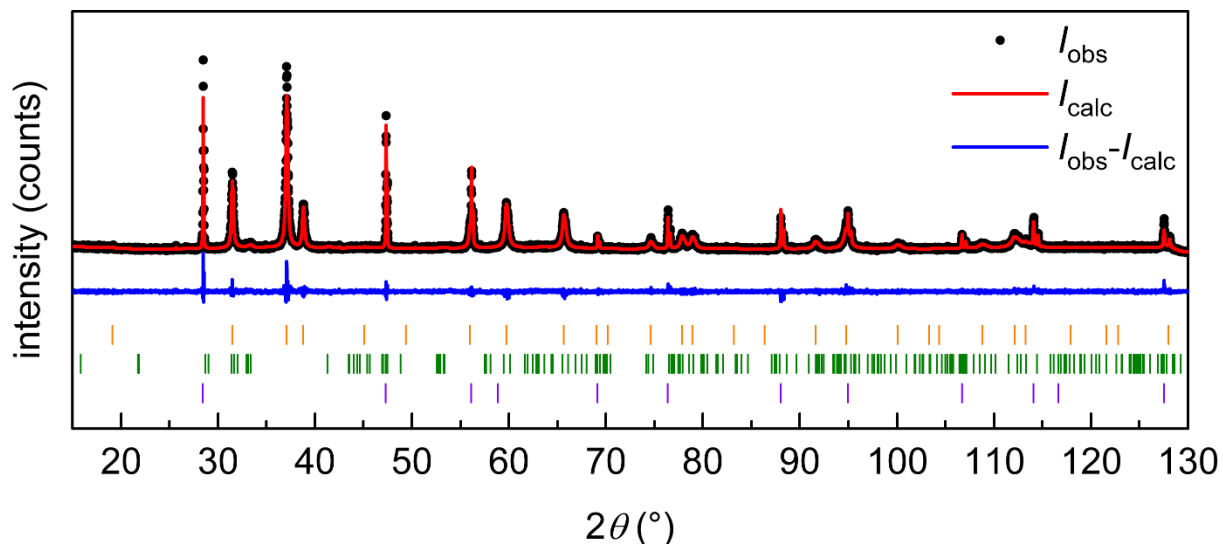


Figure S38. Powder X-ray diffraction pattern of CaAl_2 ball milled for 180 min, mixed with elemental Si as internal standard. Black circles represent the collected data, the red line is the fit, the blue line the difference curve and the ticks represent the Bragg positions of the refined phases. The following color code applies: orange – CaAl_2 ($Fd\bar{3}m$); green – CaAl_4 ($C2/m$); purple – Si ($Fd\bar{3}m$).

Refinement details for the data shown in Figure S38	
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
d -space range	0.85-14.35 Å (6-130° 2θ)
χ^2	3.43
R_p / %	9.41
R_{wp} / %	11.80
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2}$ $R_{wp} = \left(\frac{\sum w I_0 - I_c ^2}{\sum w I_0^2} \right)^{\frac{1}{2}}$

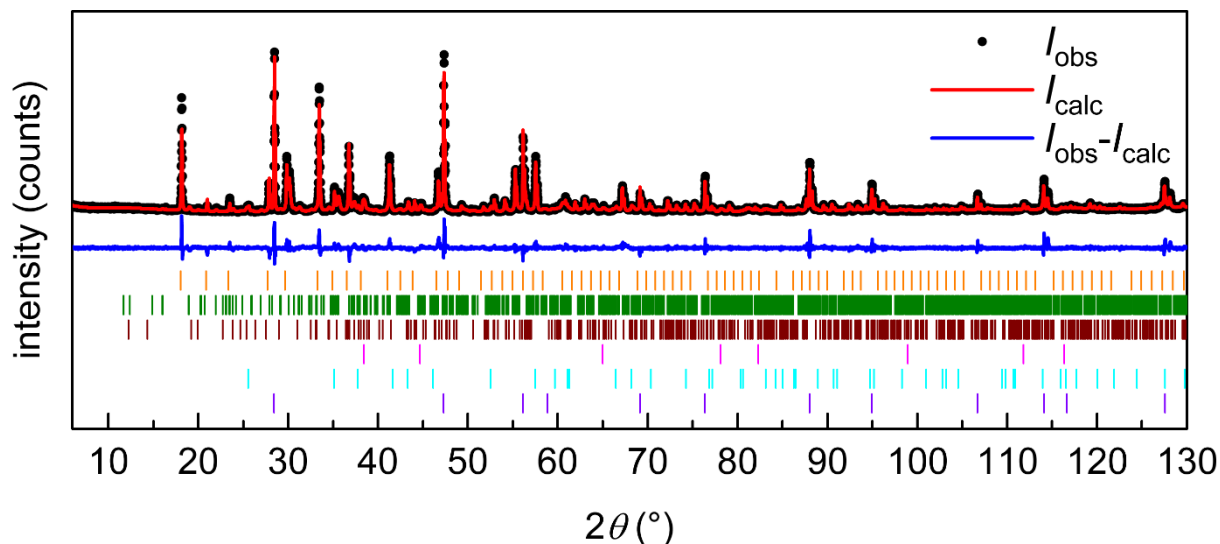


Figure S39. Powder X-ray diffraction pattern of CaAl₂ ball milled for 30 min and oxidized using pure O₂ in a tube furnace. Elemental Si was added as internal standard. Black circles represent the collected data, the red line is the fit, the blue line the difference curve and the ticks represent the Bragg positions of the refined phases. The following color code applies: orange – Ca₁₂Al₁₄O₃₃ ($I\bar{4}3d$); green – CaAl₂O₄ ($P2_1/c$); dark red – CaAl₄O₇ ($C2/c$); pink – Al ($Fm\bar{3}m$); cyan – Al₂O₃ ($R\bar{3}c$); purple – Si ($Fd\bar{3}m$).

Refinement details for the data shown in Figure S39	
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
d -space range	0.85-14.35 Å (6-130° 2 θ)
χ^2	4.01
R_p / %	9.04
R_{wp} / %	11.96
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2}$ $R_{wp} = \left(\frac{\sum w I_0 - I_c ^2}{\sum w I_0^2} \right)^{\frac{1}{2}}$

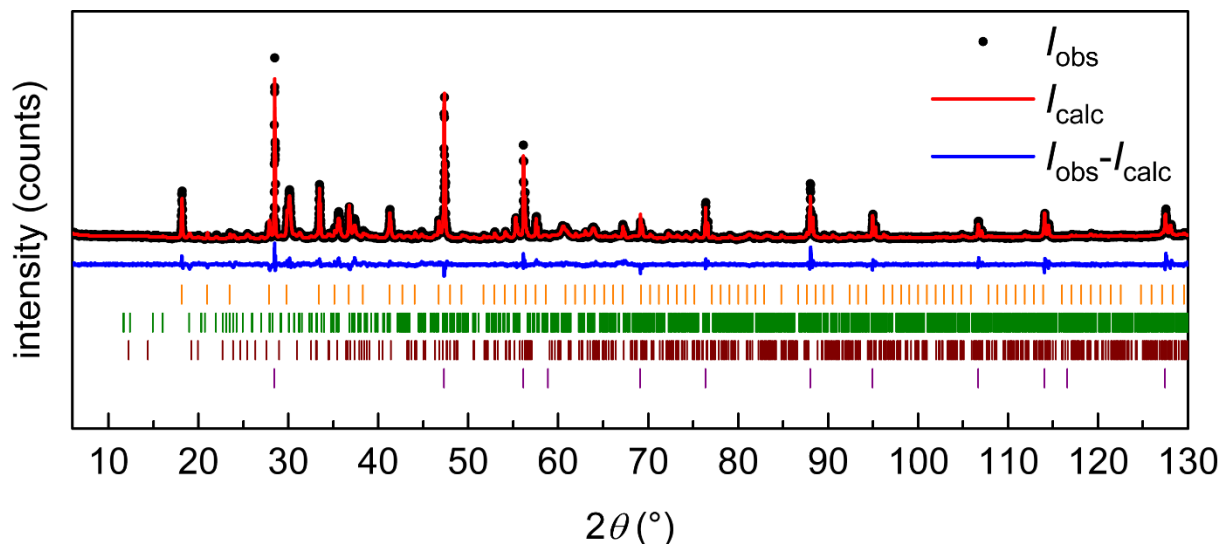


Figure S40. Powder X-ray diffraction pattern of CaAl₂ ball milled for 180 min and oxidized using pure O₂ in a tube furnace. Elemental Si was added as internal standard. Black circles represent the collected data, the red line is the fit, the blue line the difference curve and the ticks represent the Bragg positions of the refined phases. The following color code applies: orange – Ca₁₂Al₁₄O₃₃ ($I\bar{4}3d$); green – CaAl₂O₄ ($P2_1/c$); dark red – CaAl₄O₇ ($C2/c$); purple – Si ($Fd\bar{3}m$).

Refinement details for the data shown in Figure S40	
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
d -space range	0.85-14.35 Å (6-130° 2θ)
χ^2	3.12
R_p / %	8.02
R_{wp} / %	10.57
Definition of R factors	$R_p = \frac{\sum w I_0 - I_c ^2}{\sum w I_0^2};$ $R_{wp} = \left(\frac{\sum w I_0 - I_c ^2}{\sum w I_0^2} \right)^{\frac{1}{2}}$

Crystallite sizes of the STA oxidized samples

Table S1. Crystallite size (LVol-IB) of the via STA oxidized and previously milled CaAl_2 samples at different milling times.

Milling time / min	CaAl_2O_4 crystallite size / nm	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ crystallite size / nm	Fig.
5	36(3)	84(2)	S14
10	37(2)	121(2)	S15
15	38(2)	119(3)	S16
20	37(1)	116(3)	S17
30	44(2)	99(5)	S18
45	37(1)	79(2)	S19
60	29(1)	47(1)	S20
90	30(1)	56(2)	S21
180	31(1)	84(7)	S22