Electronic Supplementary Material (ESI) for Nanoscale.

In situ X-ray diffraction study of the solvothermal formation mechanism of gallium oxide nanoparticles

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Temperature calibrations

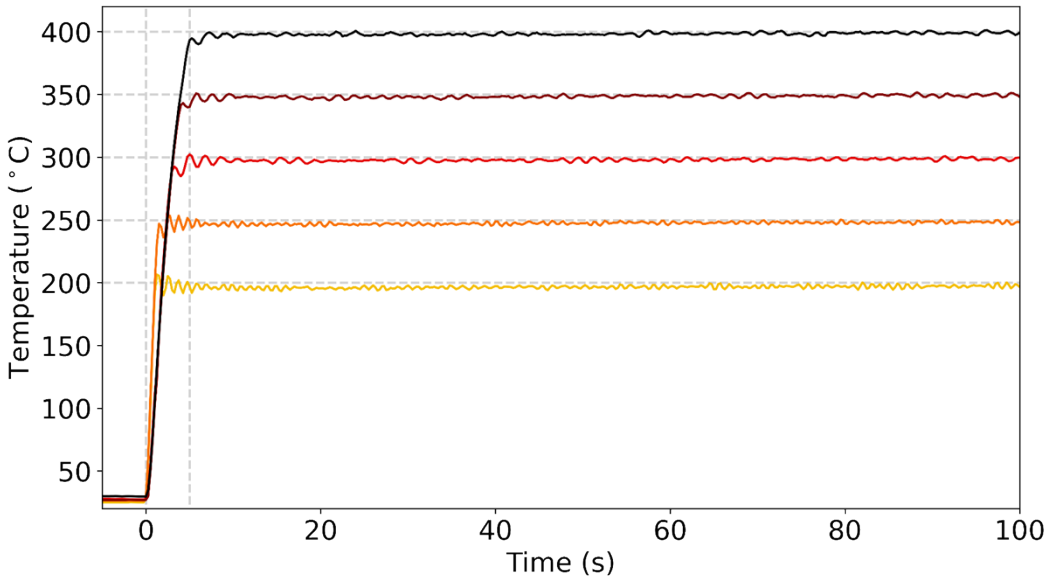


Figure S1. Temperature calibration and heating profile for the *in situ* solvothermal setup for the experiments with fast heating and water or ethanol as solvent. All three experiments with slow heating used this temperature calibration, but slower heating profile, aiming for 10°C/min as illustrated along with the data in Figure S8, S14 and S20.

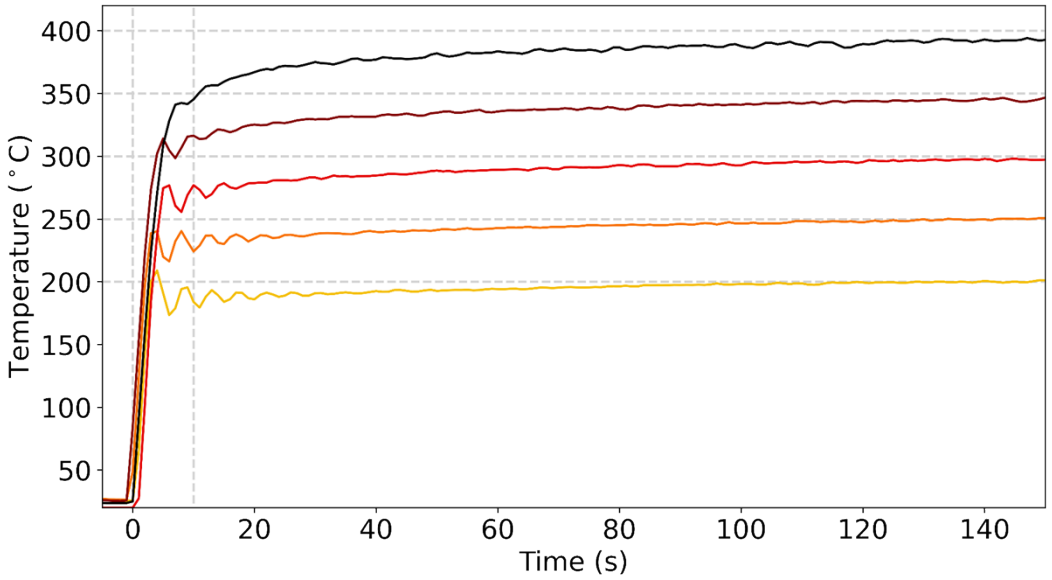


Figure S2. Temperature calibration and heating profile for the *in situ* solvothermal setup for experiments with fast heating and aqueous NaOH as solvent.

Time resolved data of the solvothermal gallium oxide synthesis

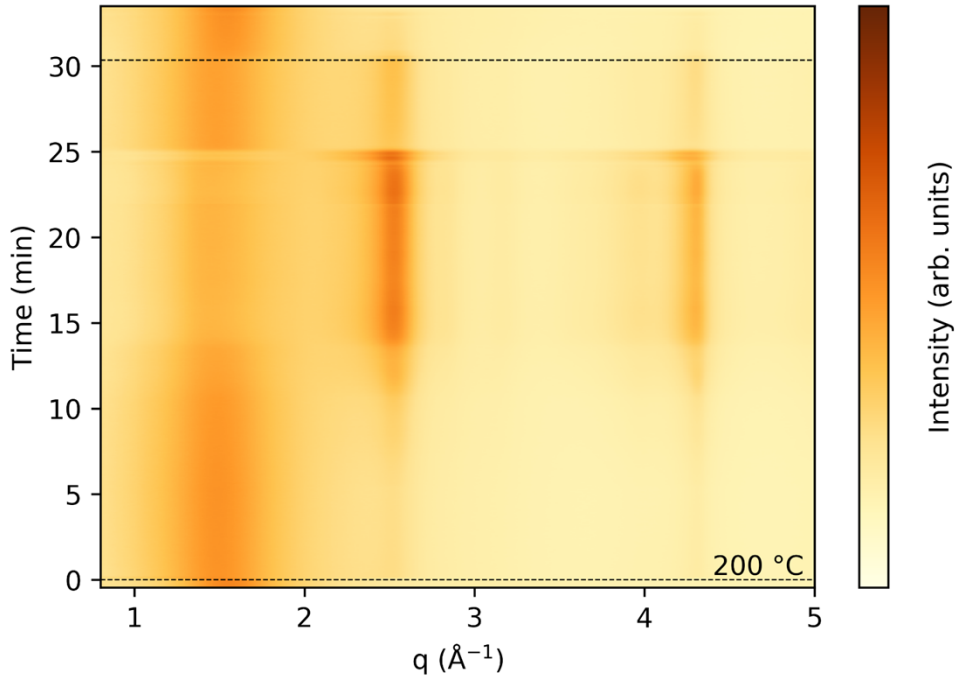


Figure S3. Time-resolved scattering data for the direct heating of $Ga(NO_3)_3$ in ethanol to 200°C.

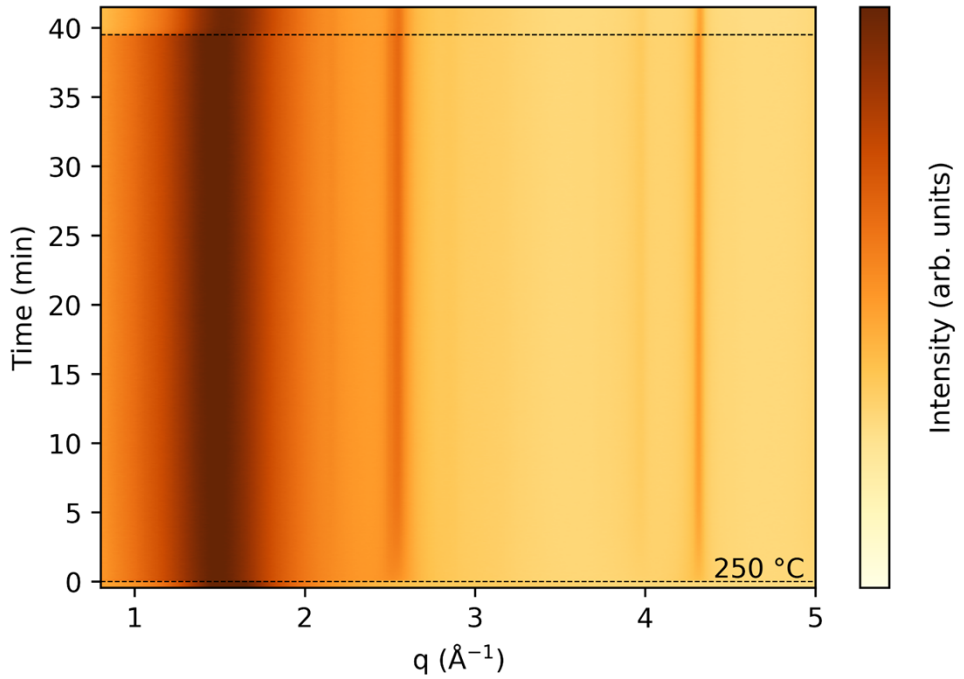


Figure S4. Time-resolved scattering data for the direct heating of $Ga(NO_3)_3$ in ethanol to 250°C.

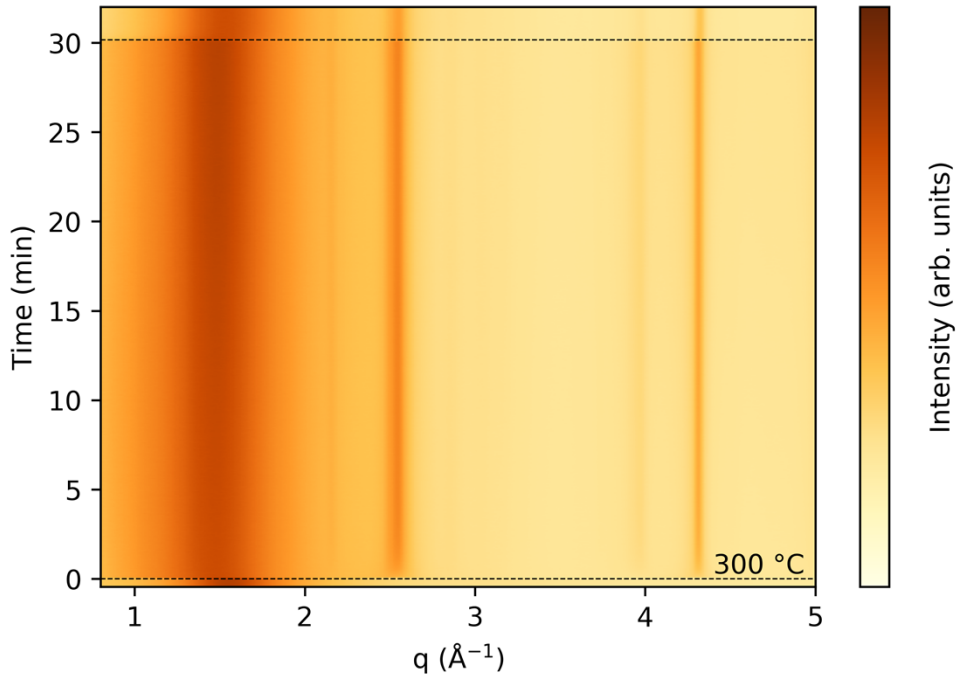


Figure S5. Time-resolved scattering data for the direct heating of $Ga(NO_3)_3$ in ethanol to 300°C.

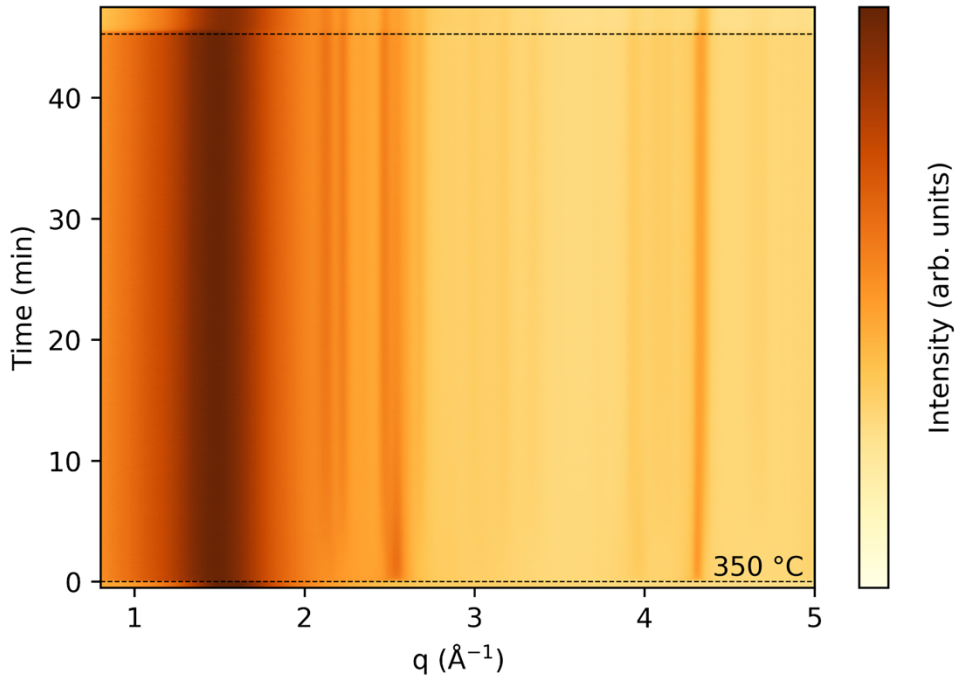


Figure S6. Time-resolved scattering data for the direct heating of $Ga(NO_3)_3$ in ethanol to 350°C (EtOH_350).

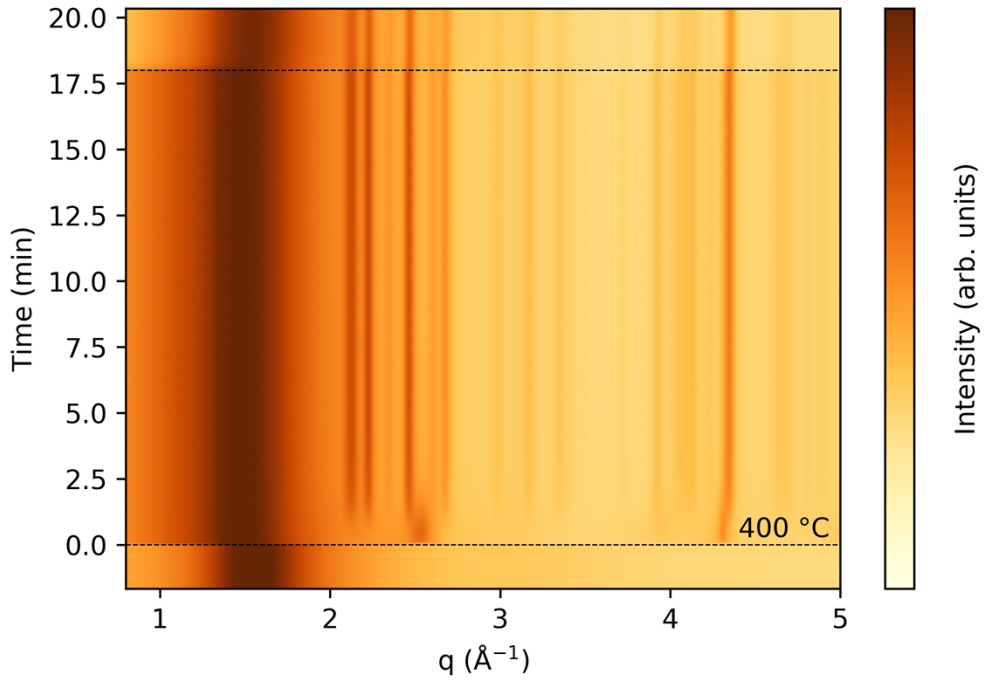


Figure S7. Time-resolved scattering data for the direct heating of $Ga(NO_3)_3$ in ethanol to 400°C (EtOH_400).

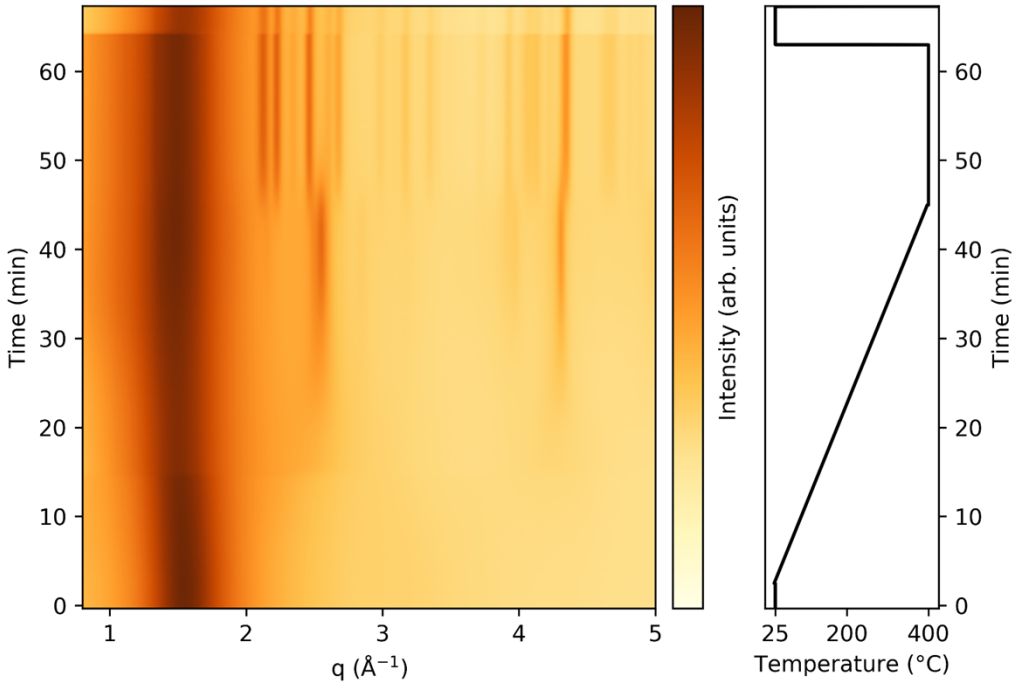
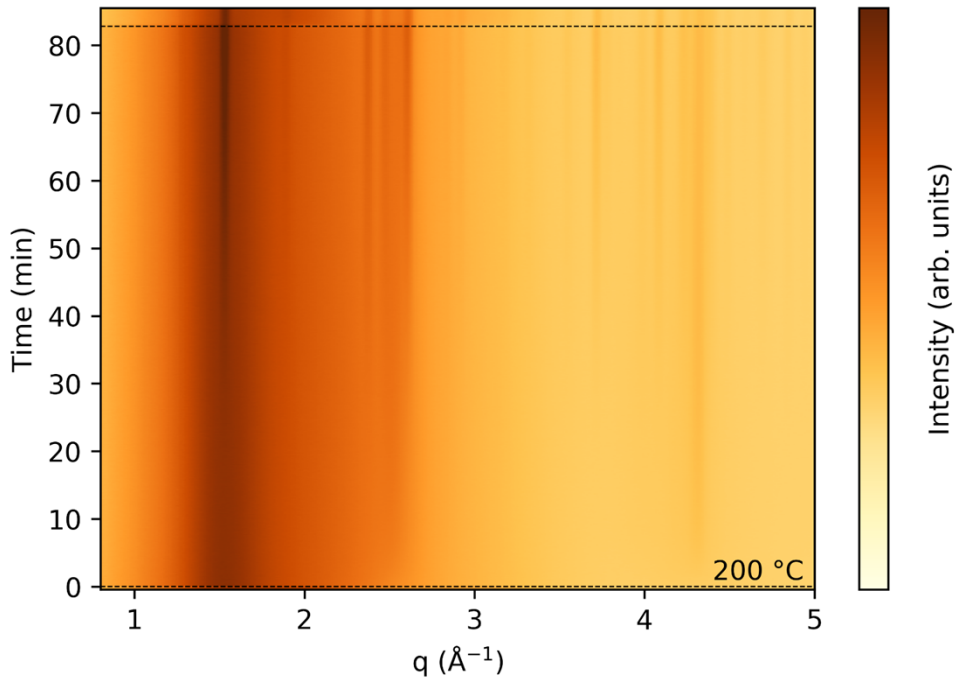


Figure S8. Time-resolved scattering data for the ramp heating of $Ga(NO_3)_3$ in ethanol to 400°C with the used heating profile.



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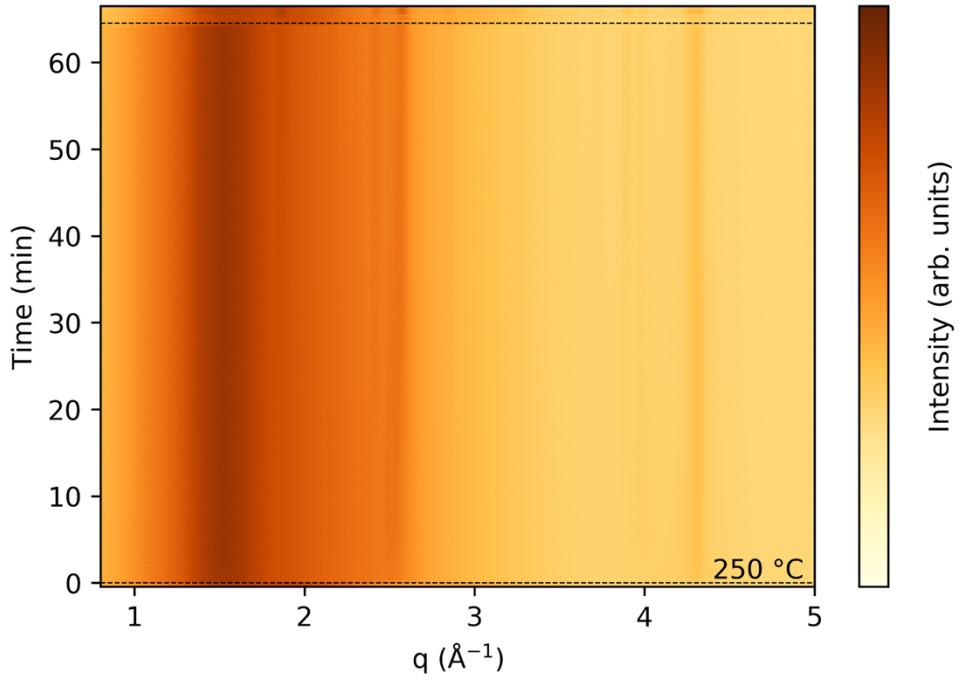
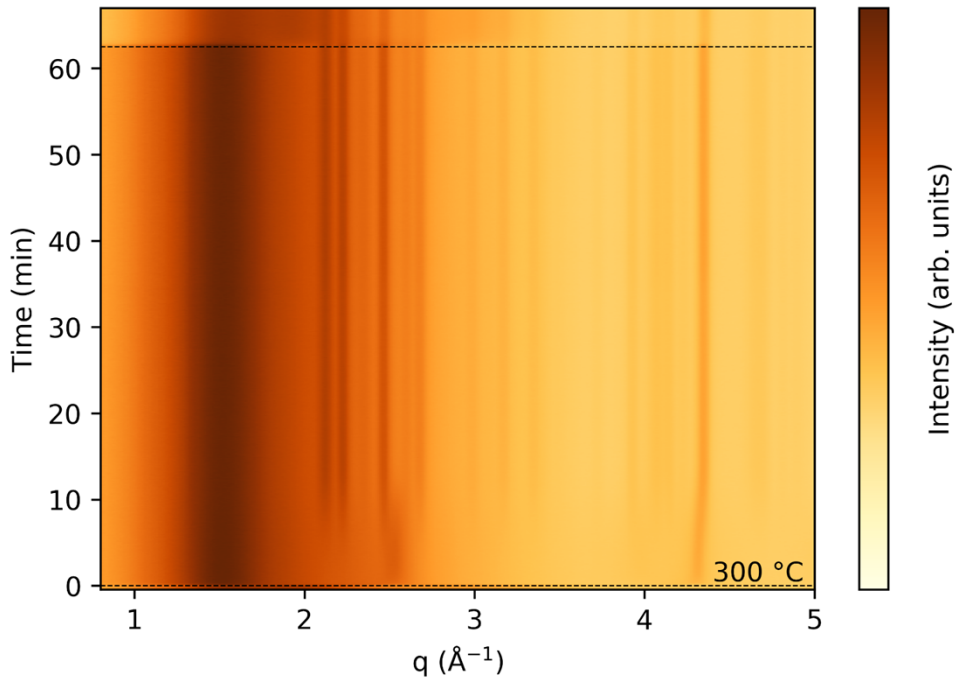


Figure S10. Time-resolved scattering data for the direct heating of $Ga(NO_3)_3$ in water to 250°C.



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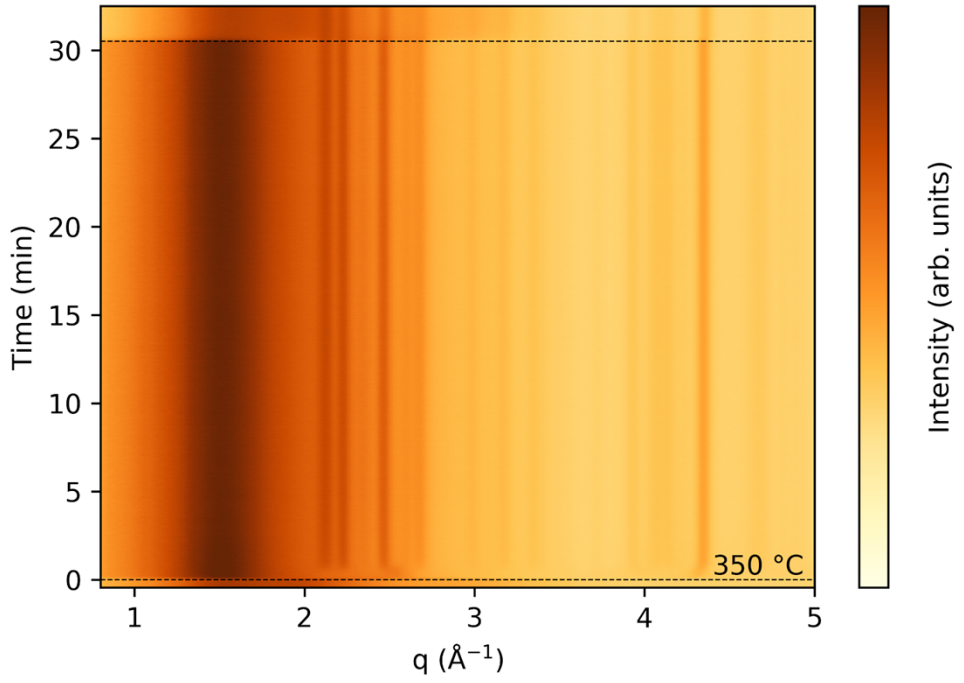

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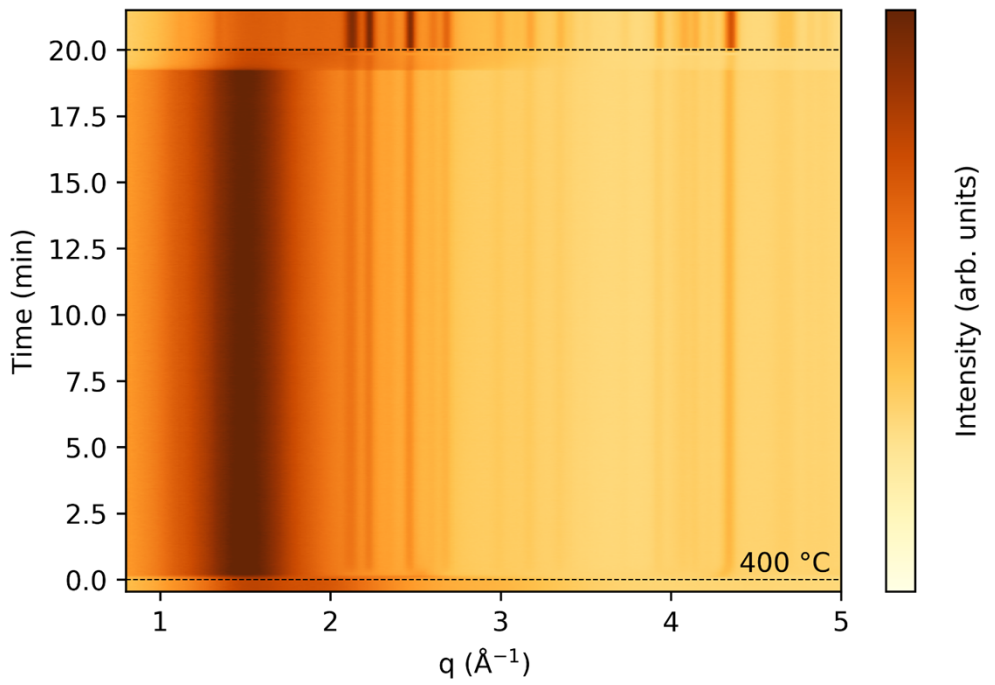

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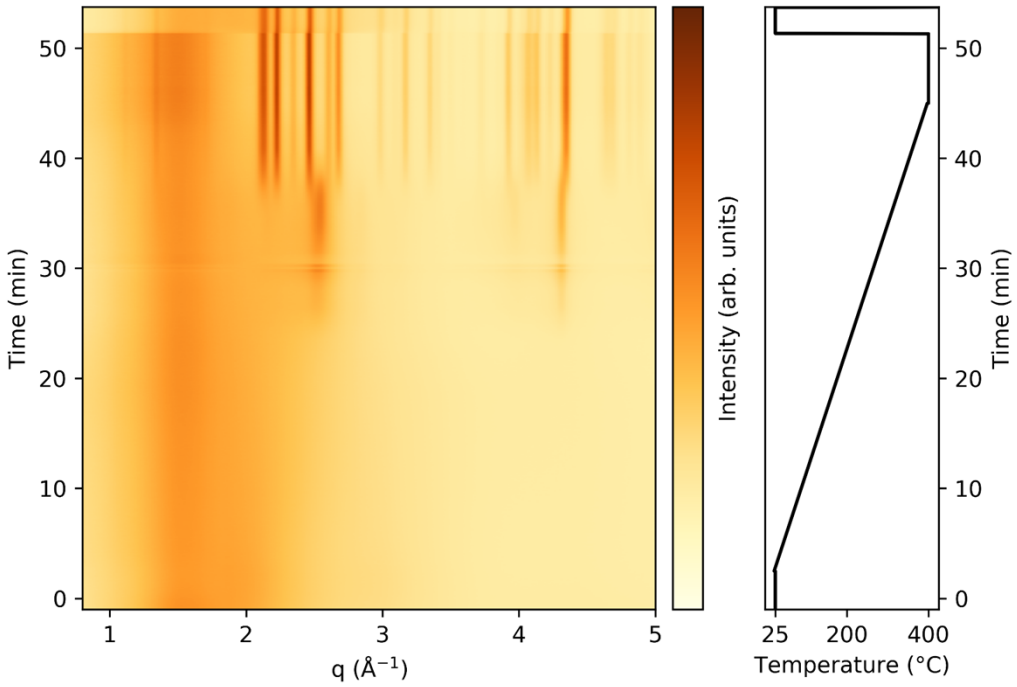

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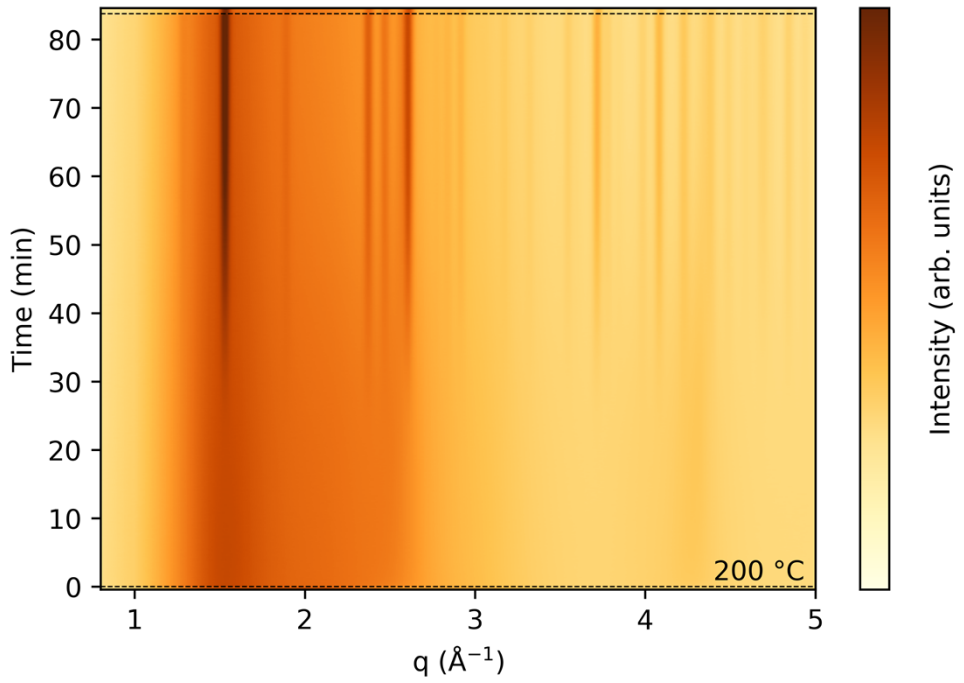

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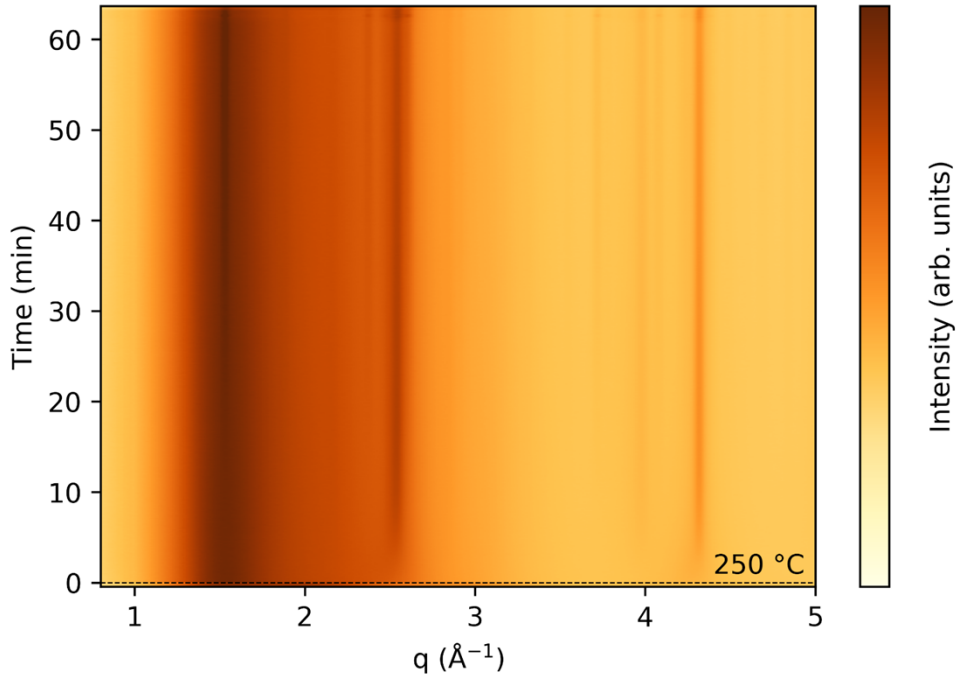

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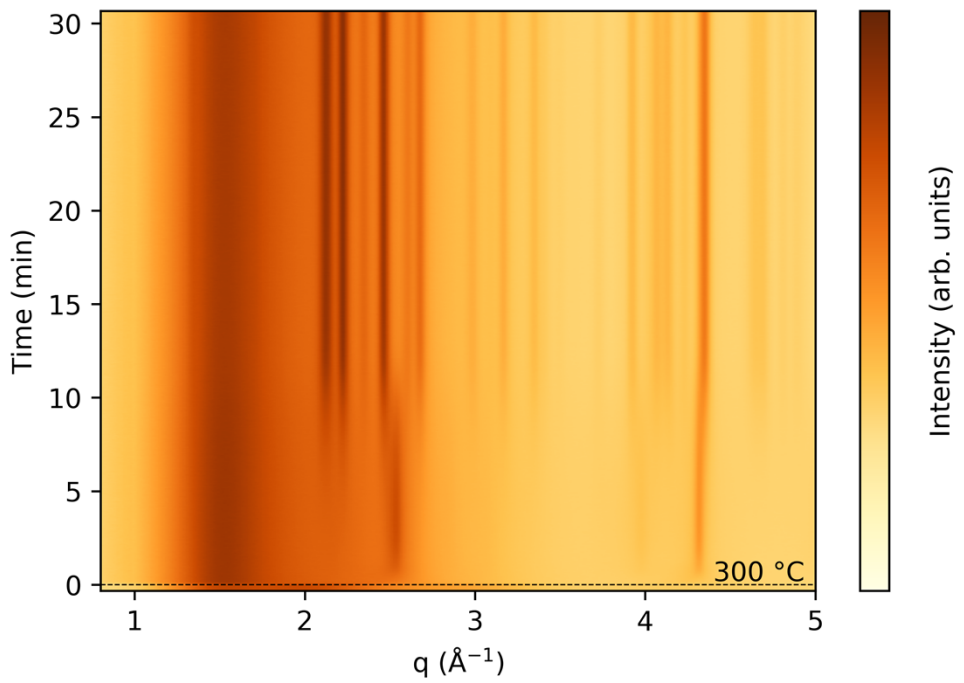

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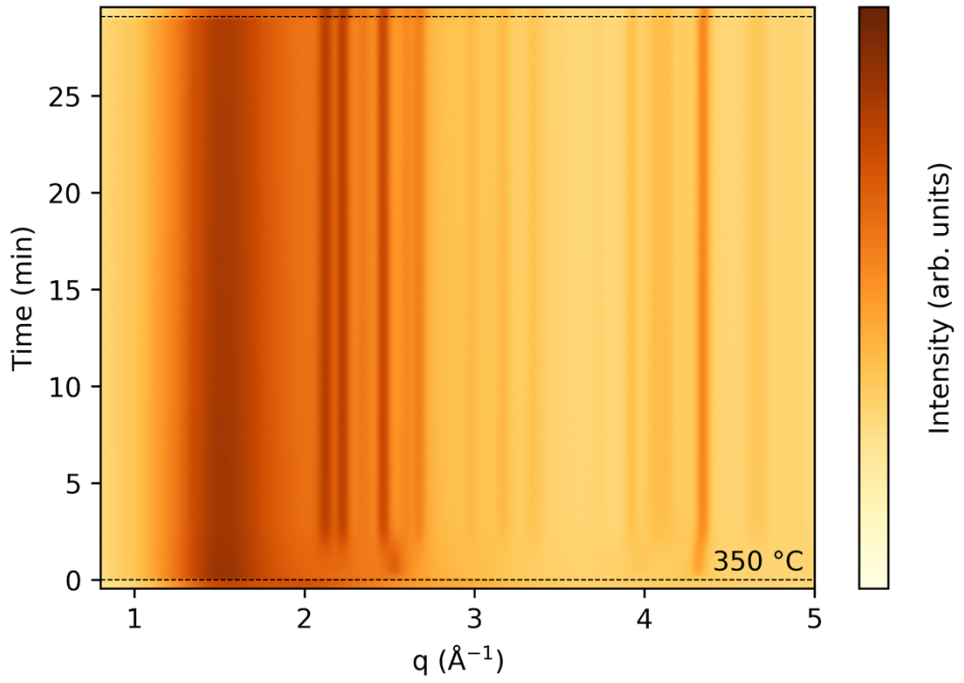

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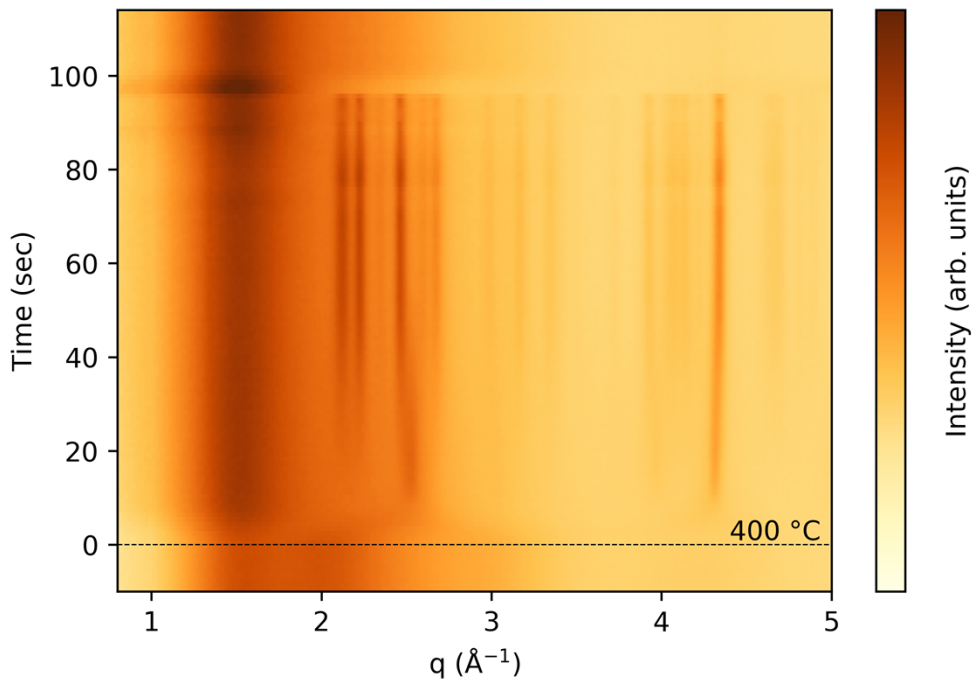

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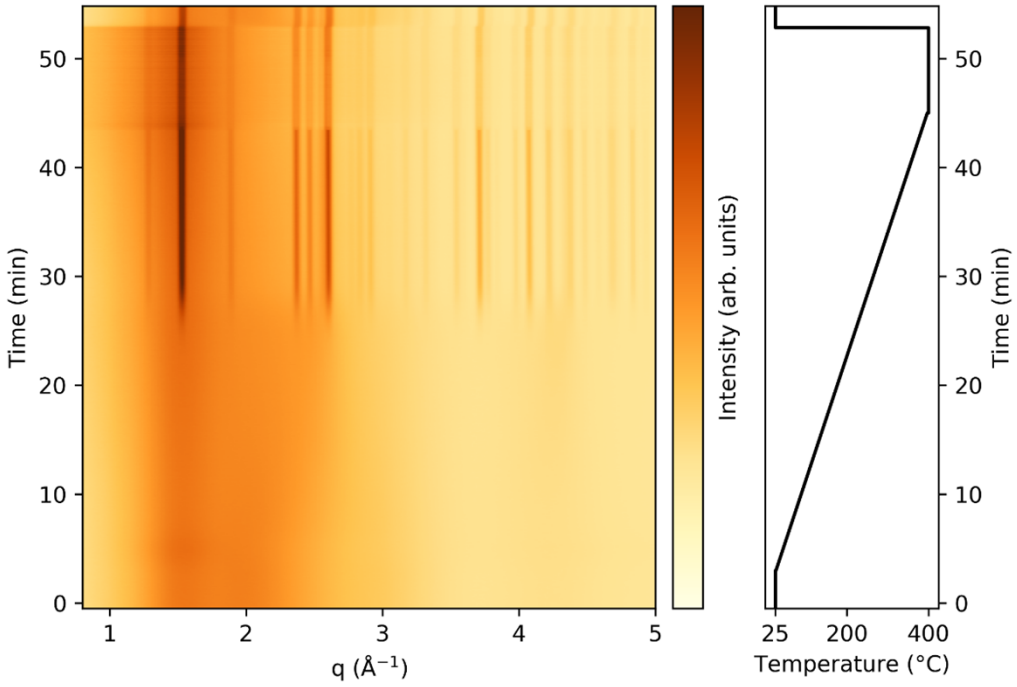


Figure S20. Time-resolved scattering data for the ramp heating of $Ga(NO_3)_3$ in water with added NaOH to 400°C with the used heating profile.

Examples of Rietveld fits

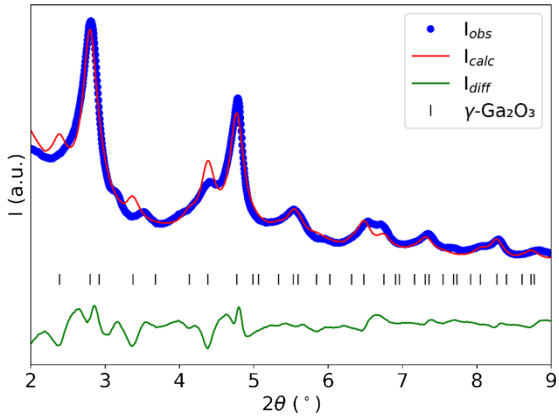


Figure S21. Rietveld refinement of the last frame of heating for $Ga(NO_3)_3$ in ethanol at 200°C. The refinement show γ-Ga_2O_3

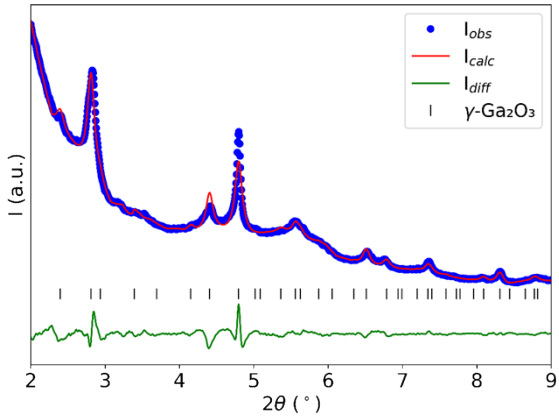
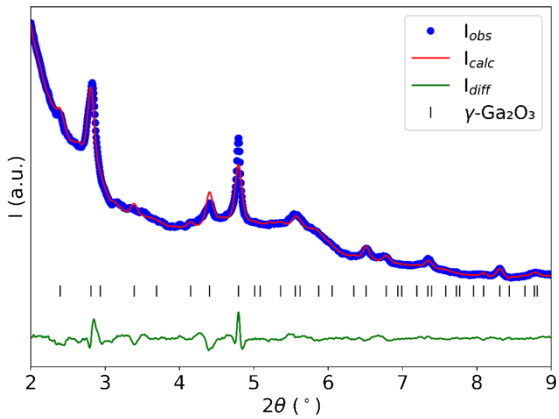


Figure S22. Rietveld refinement of the last frame of heating for $Ga(NO_3)_3$ in ethanol at 250°C. The refinement show γ-Ga_2O_3



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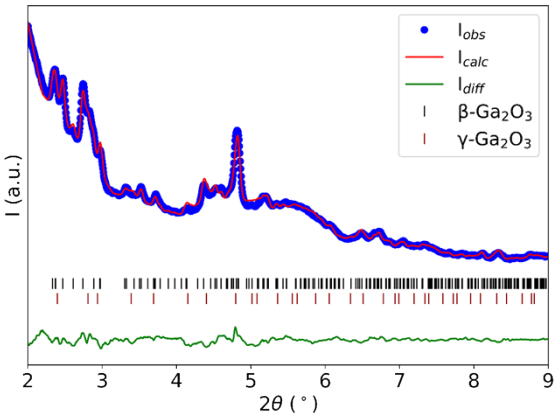

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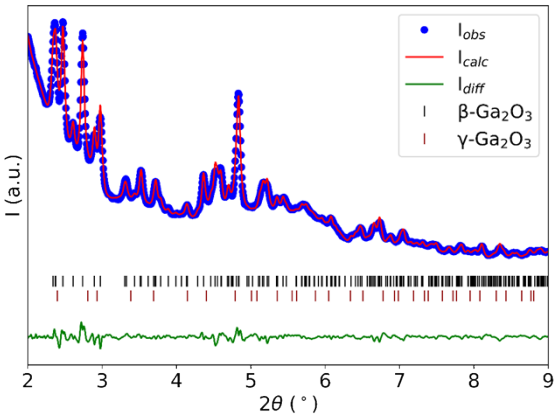


Figure S25. Rietveld refinement of the last frame of heating for $Ga(NO_3)_3$ in ethanol at 400°C. The refinement show phase pure β-Ga_2O_3.

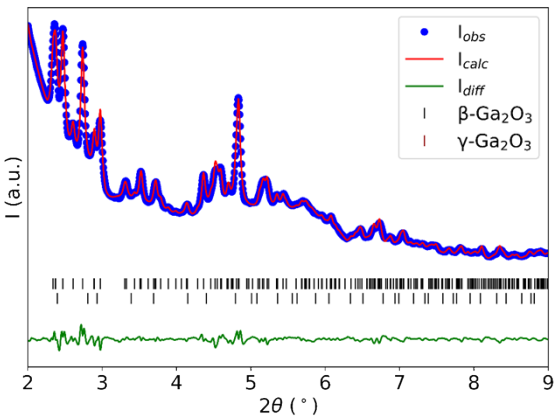


Figure S26. Rietveld refinement of the last frame of heating after ramp heating for $Ga(NO_3)_3$ in ethanol at 400°C. The refinement show phase pure β-Ga_2O_3.

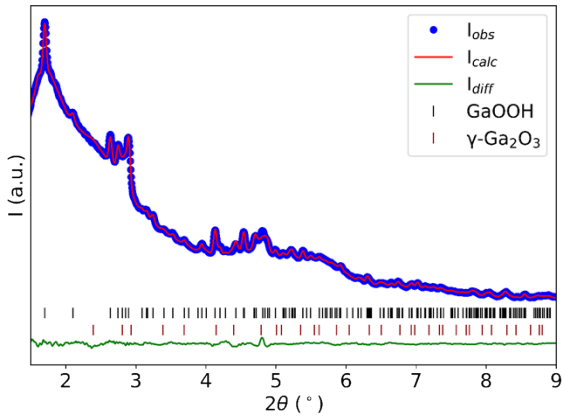


Figure S27. Rietveld refinement of the last frame of heating for $Ga(NO_3)_3$ in water at 200°C. The refinement show a mixture of GaOOH and γ-Ga_2O_3.

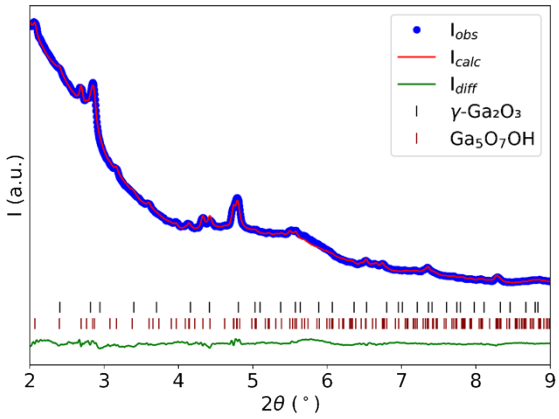


Figure S28. Rietveld refinement of the last frame of heating for $Ga(NO_3)_3$ in water at 250°C. The refinement show a mixture of Ga_5O_7OH and γ-Ga_2O_3.

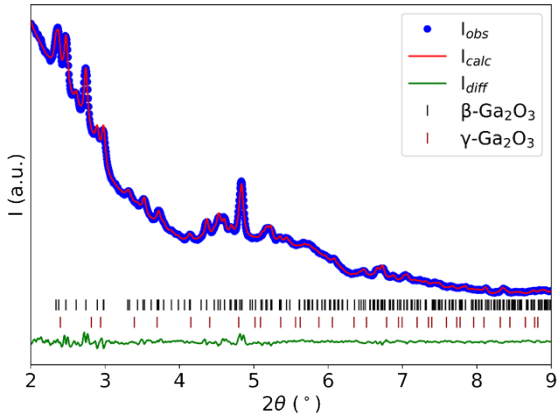
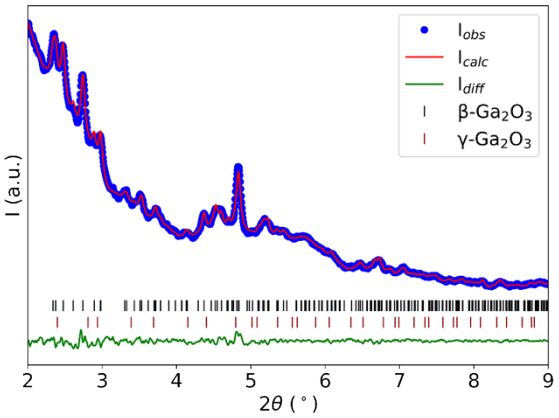


Figure S29. Rietveld refinement of the last frame of heating for $Ga(NO_3)_3$ in water at 300°C. The refinement show phase pure β-Ga_2O_3.



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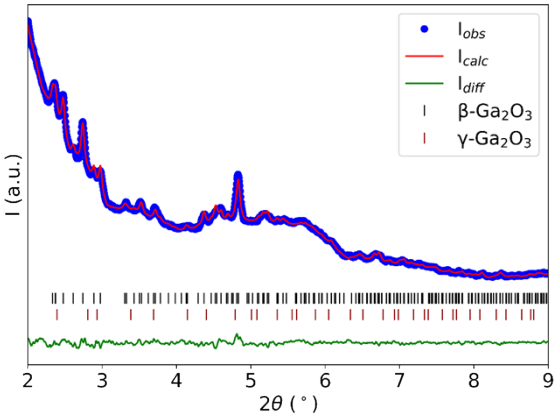

Figure S31. Rietveld refinement of the last frame of heating for $Ga(NO_3)_3$ in water at 400°C. The refinement show phase pure β-Ga_2O_3.

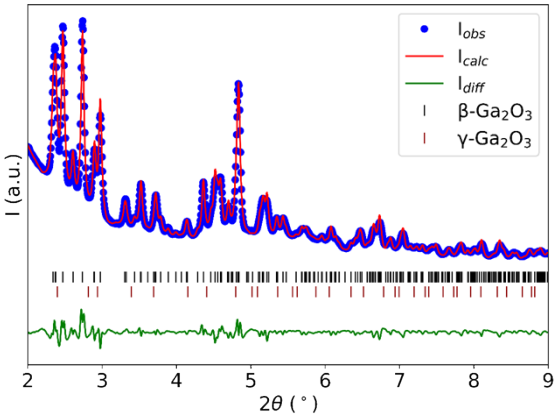

Figure S32. Rietveld refinement of the last frame of heating after ramp heating for $Ga(NO_3)_3$ in water at 400°C. The refinement show phase pure β-Ga_2O_3.

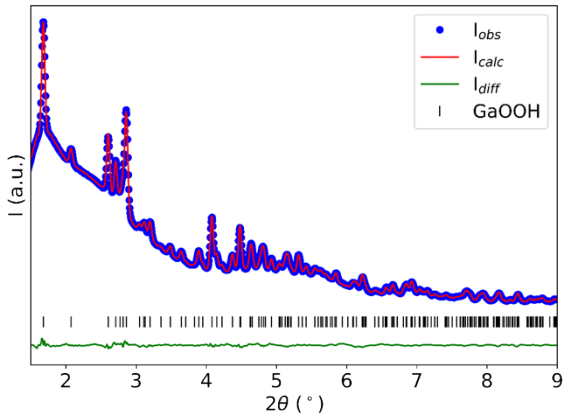

Figure S33. Rietveld refinement of the last frame of heating for $Ga(NO_3)_3$ in water with added NaOH at 200°C. The refinement show phase pure GaOOH.

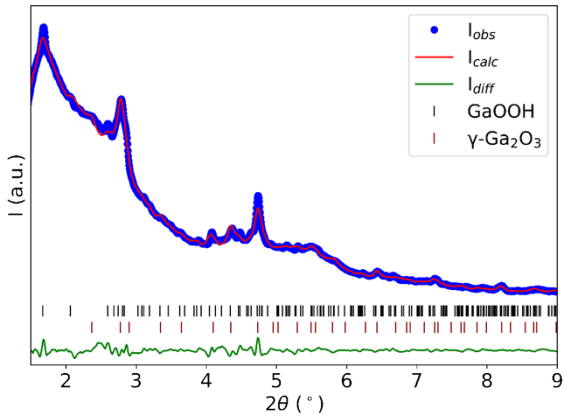

Figure S34. Rietveld refinement of the last frame of heating for $Ga(NO_3)_3$ in water with added NaOH at 250°C. The refinement show a mixture of GaOOH and γ-Ga_2O_3.

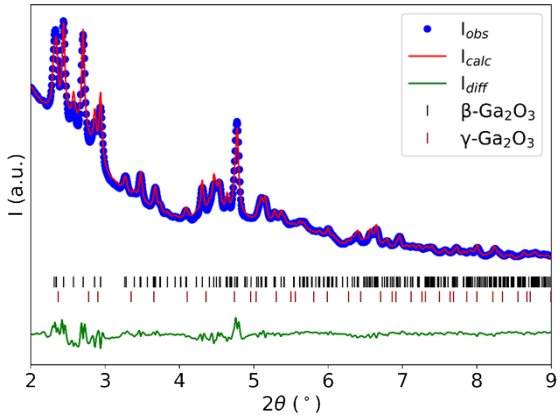

Figure S35. Rietveld refinement of the last frame of heating for $Ga(NO_3)_3$ in water with added NaOH at 300°C. The refinement show phase pure β-Ga_2O_3.

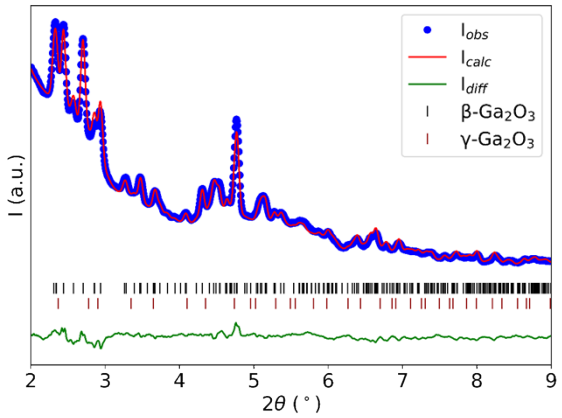

Figure S36. Rietveld refinement of the last frame of heating for $Ga(NO_3)_3$ in water with added NaOH at 350°C. The refinement show phase pure β-Ga_2O_3.

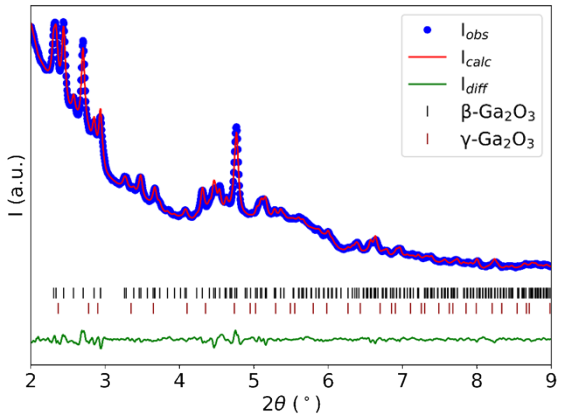

Figure S37. Rietveld refinement of the last frame of heating for $Ga(NO_3)_3$ in water with added NaOH at 400°C. The refinement show phase pure β-Ga_2O_3.

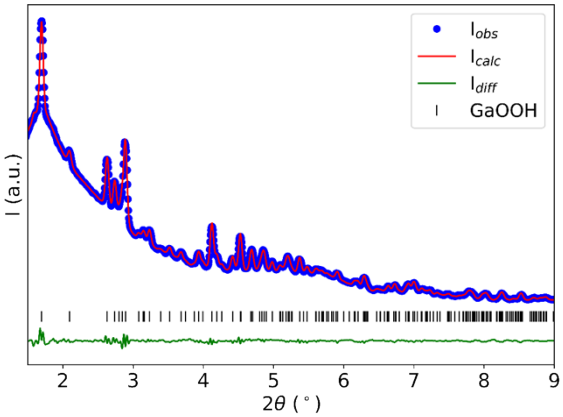

Figure S38. Rietveld refinement of the last frame of heating after ramp heating for $Ga(NO_3)_3$ in water with added NaOH at 400°C. The refinement show phase pure GaOOH.

Extracted values from Rietveld refinements

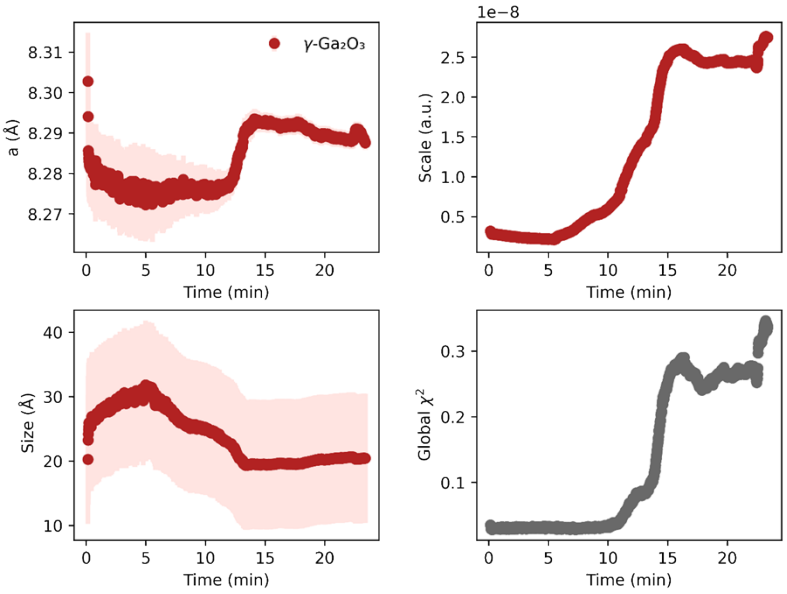

Figure S39. Extracted values for the sequential Rietveld refinement of the experiment with fast heating for $Ga(NO_3)_3$ in ethanol at 200°C. The sudden shifts in parameters are most likely caused by movement of the particles in the capillary. The shaded area represent the estimated standard deviations.

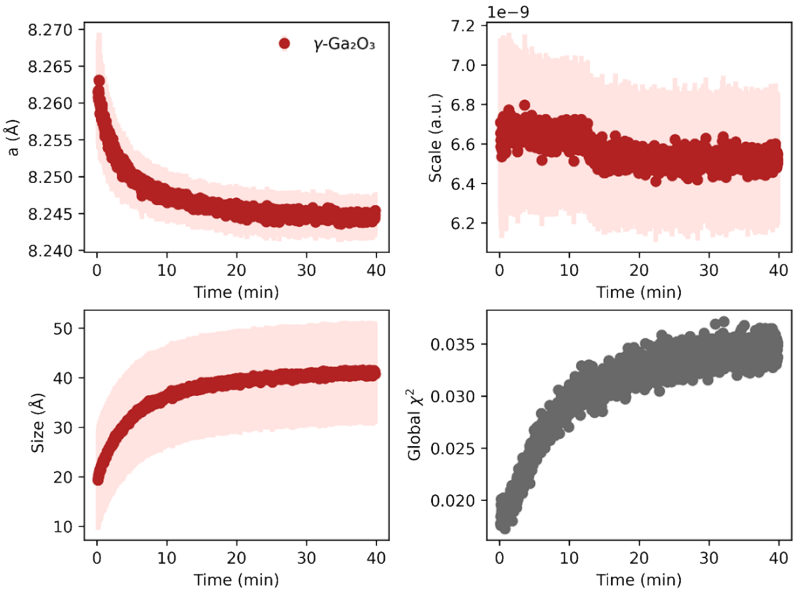

Figure S40. Extracted values for the sequential Rietveld refinement of the experiment with fast heating for $Ga(NO_3)_3$ in ethanol at 250°C.

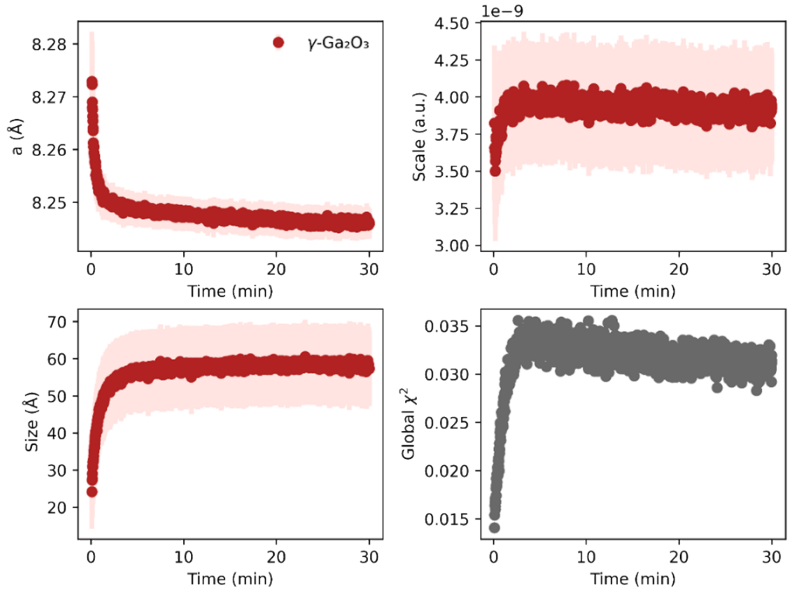

Figure S41. Extracted values for the sequential Rietveld refinement of the experiment with fast heating for $Ga(NO_3)_3$ in ethanol at 300°C.

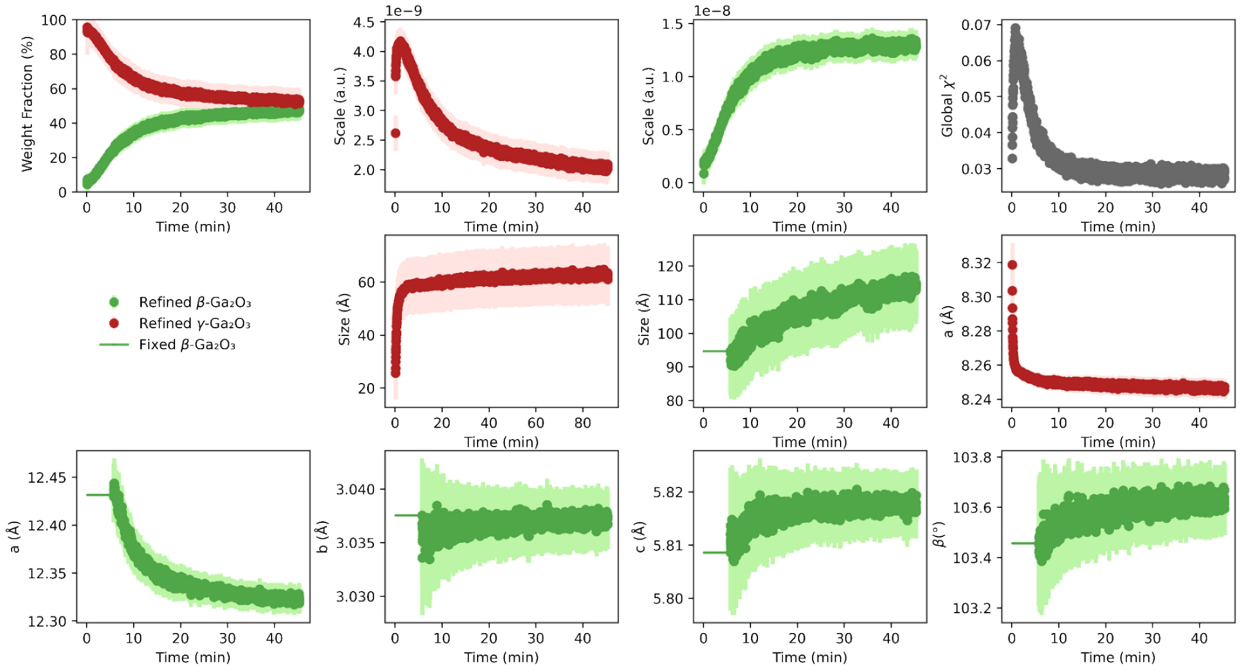

Figure S42. Extracted values for the sequential Rietveld refinement of the experiment with fast heating for $Ga(NO_3)_3$ in ethanol at 350°C.

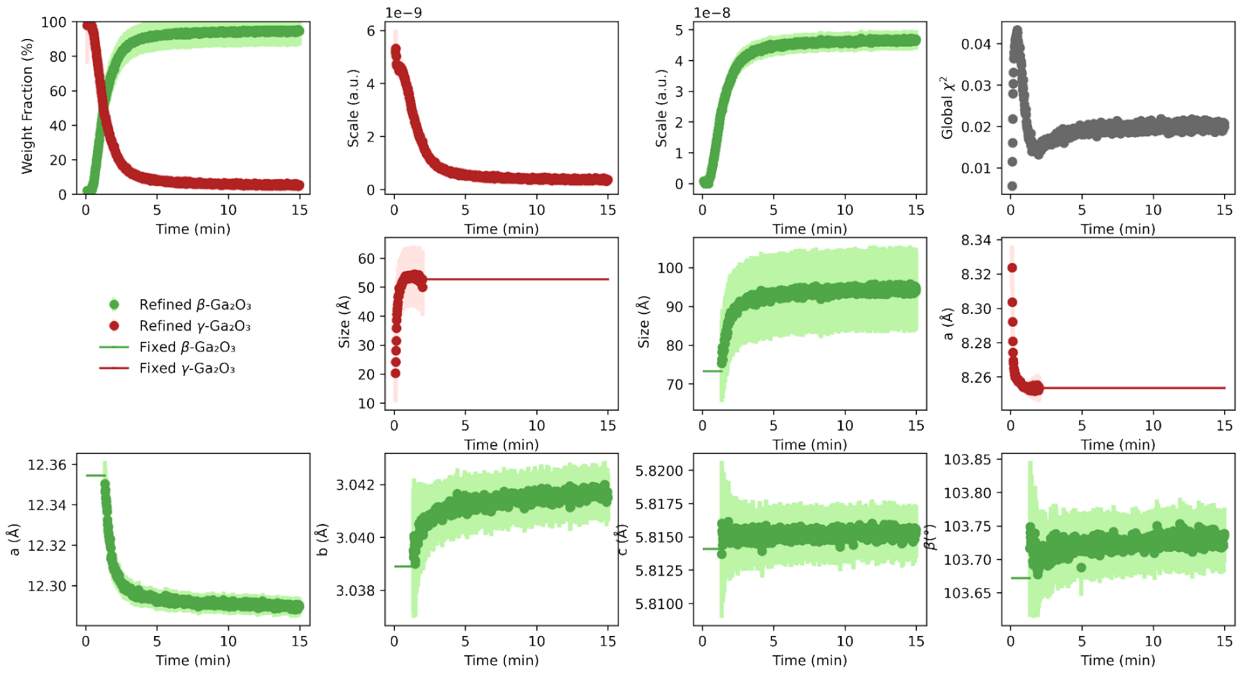

Figure S43. Extracted values for the sequential Rietveld refinement of the experiment with fast heating for $Ga(NO_3)_3$ in ethanol at 400°C.

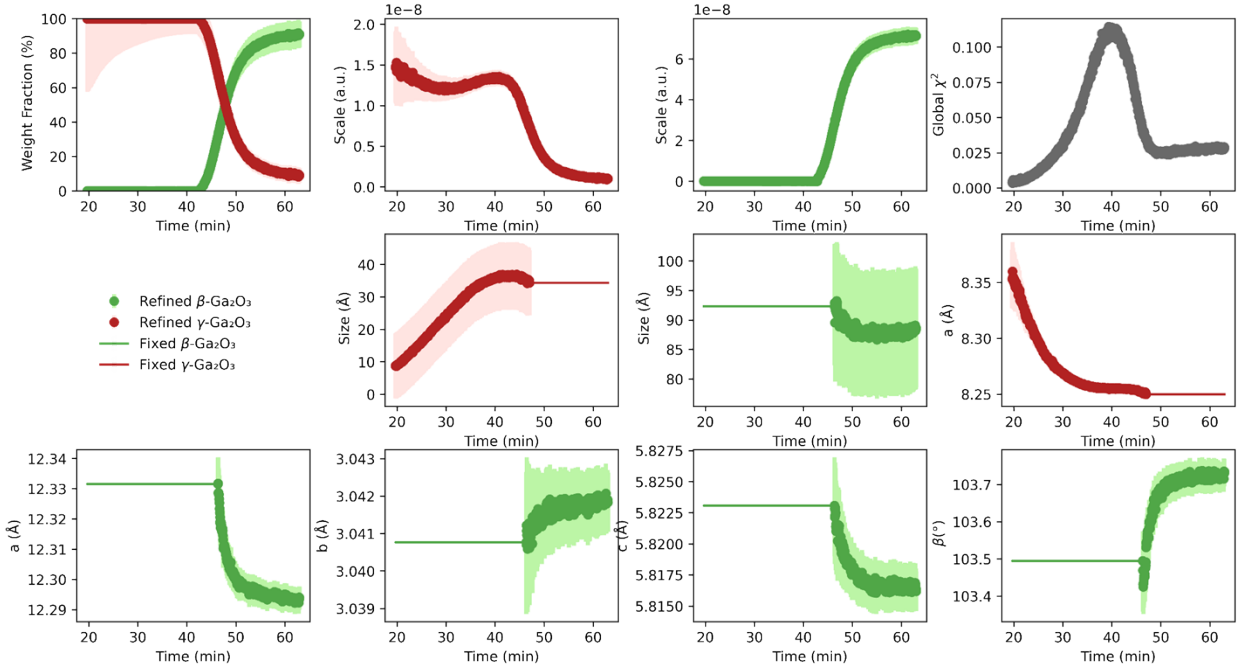

Figure S44. Extracted values for the sequential Rietveld refinement of the experiment with slow heating for $Ga(NO_3)_3$ in ethanol to 400°C.

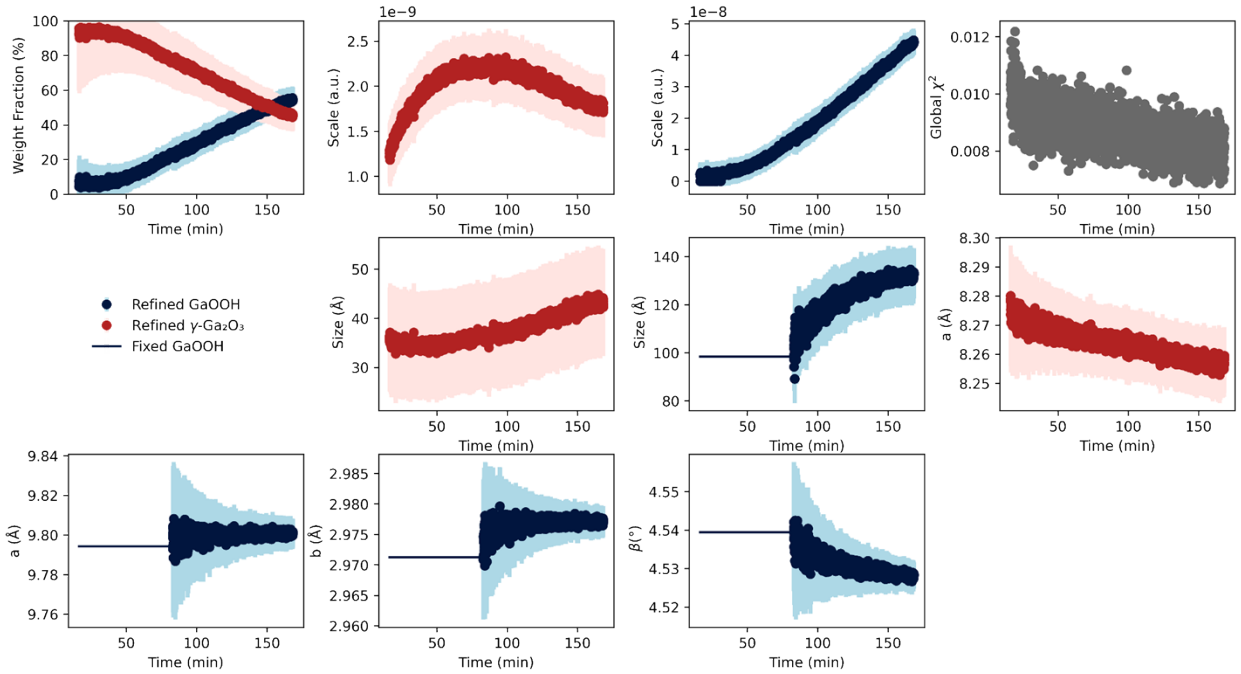

Figure S45. Extracted values for the sequential Rietveld refinement of the experiment with fast heating for $Ga(NO_3)_3$ in water at 200°C.

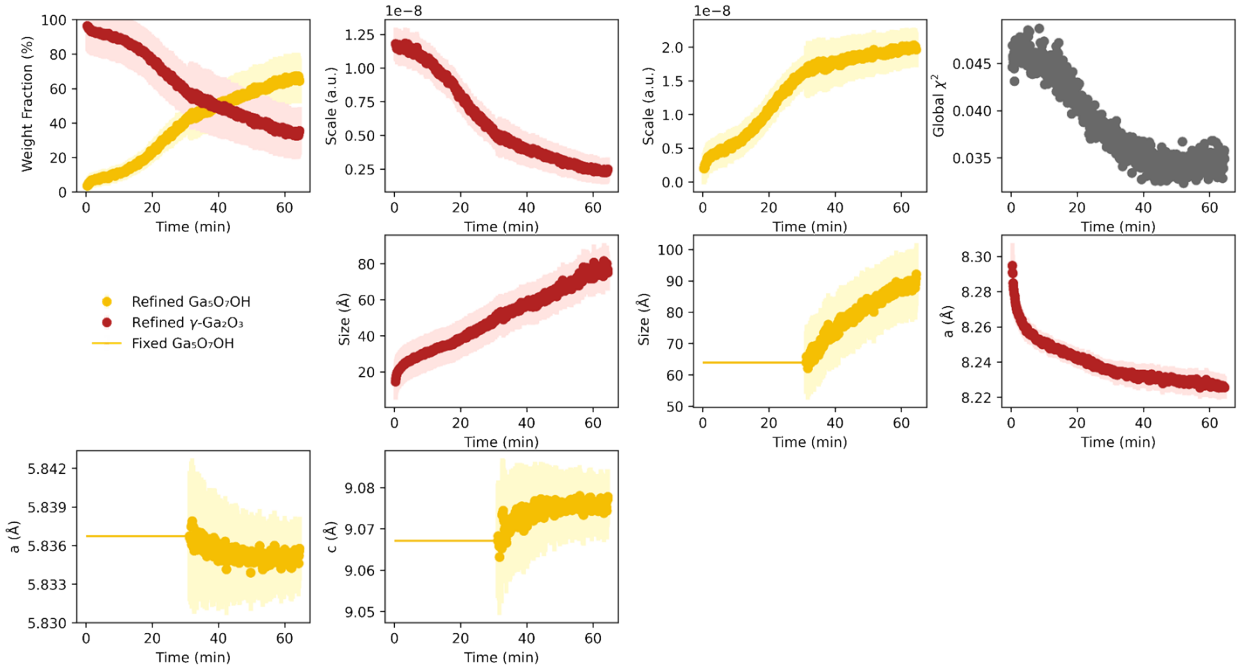

Figure S46. Extracted values for the sequential Rietveld refinement of the experiment with fast heating for $Ga(NO_3)_3$ in water at 250°C.

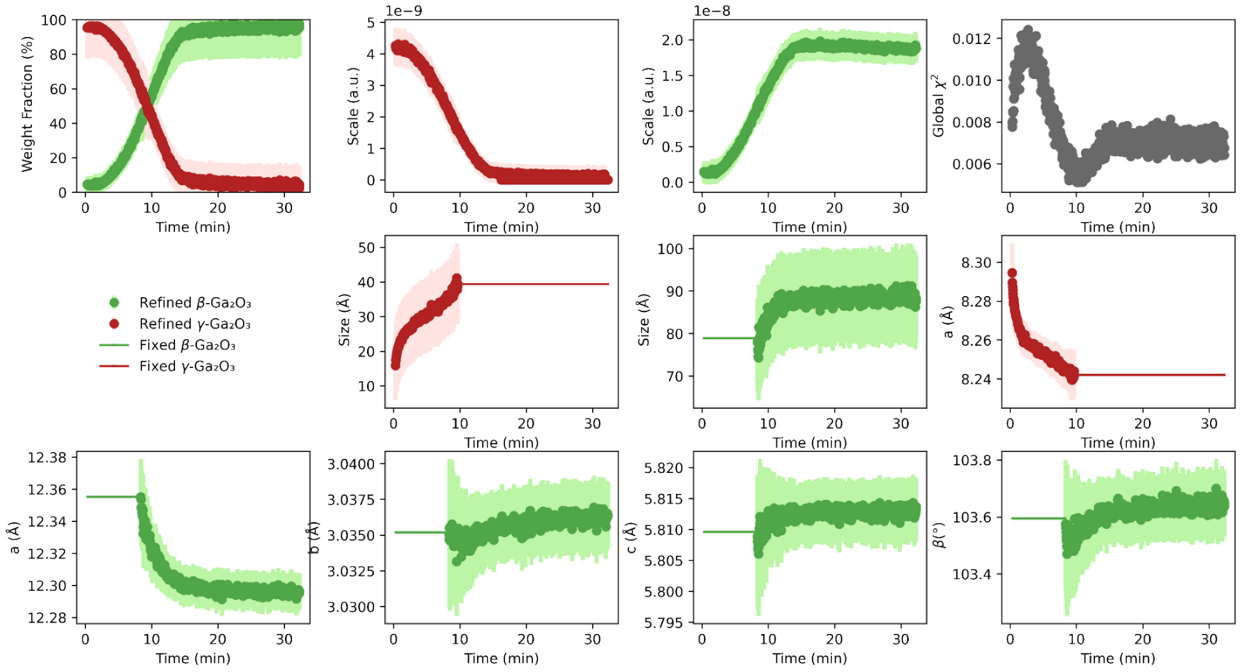

Figure S47. Extracted values for the sequential Rietveld refinement of the experiment with fast heating for $Ga(NO_3)_3$ in water at 300°C.

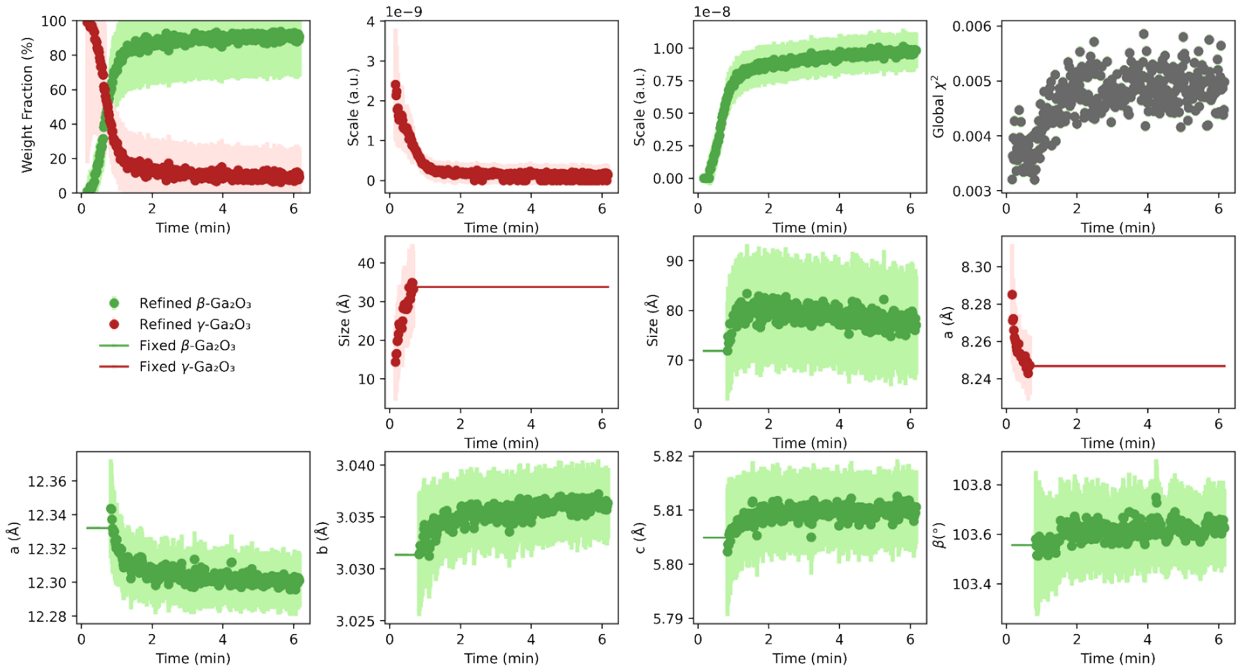

Figure S48. Extracted values for the sequential Rietveld refinement of the experiment with fast heating for $Ga(NO_3)_3$ in water at 350°C.

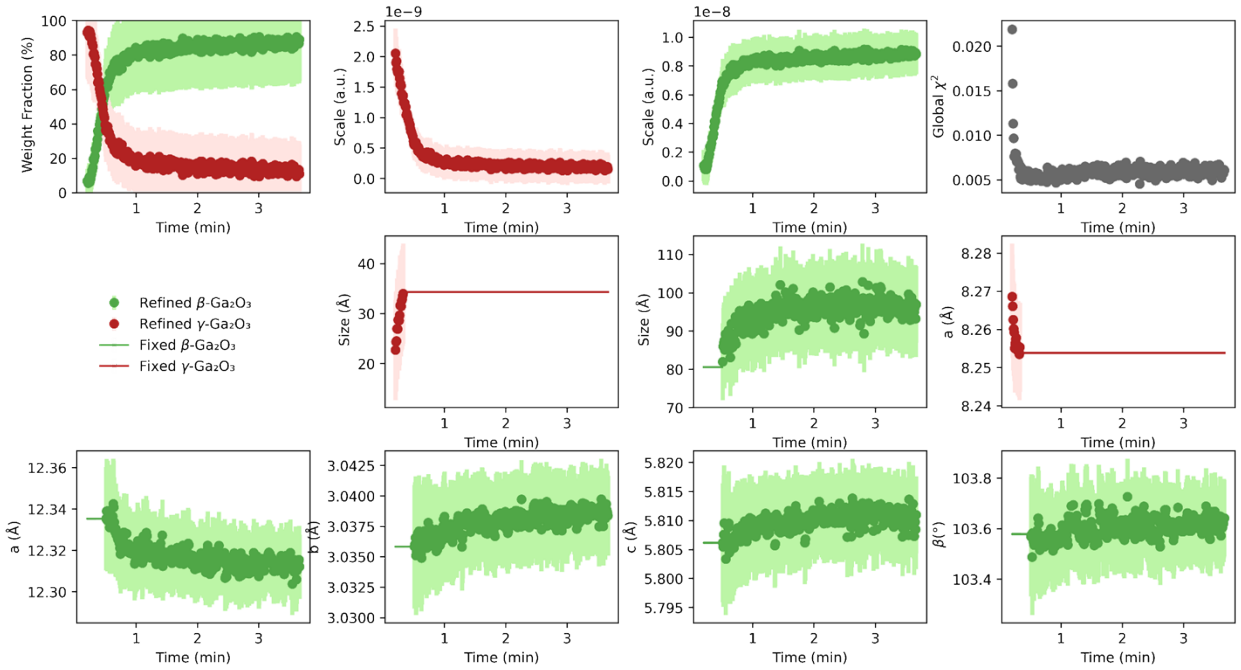

Figure S49. Extracted values for the sequential Rietveld refinement of the experiment with fast heating for $Ga(NO_3)_3$ in water at 400°C.

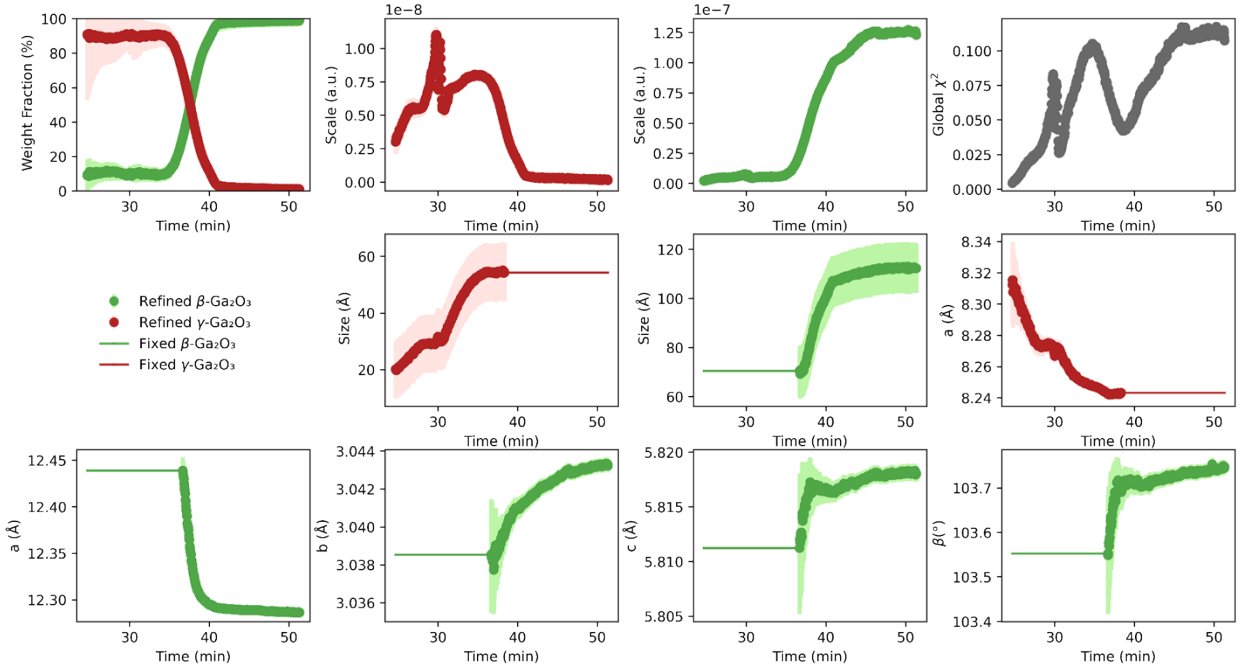

Figure S50. Extracted values for the sequential Rietveld refinement of the experiment with slow heating for $Ga(NO_3)_3$ in water to 400°C.

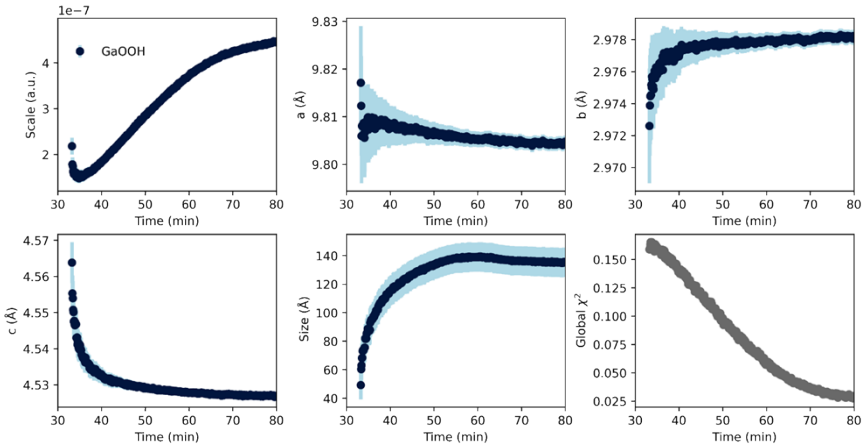

Figure S51. Extracted values for the sequential Rietveld refinement of the experiment with fast heating for $Ga(NO_3)_3$ in water with added NaOH at 200°C.

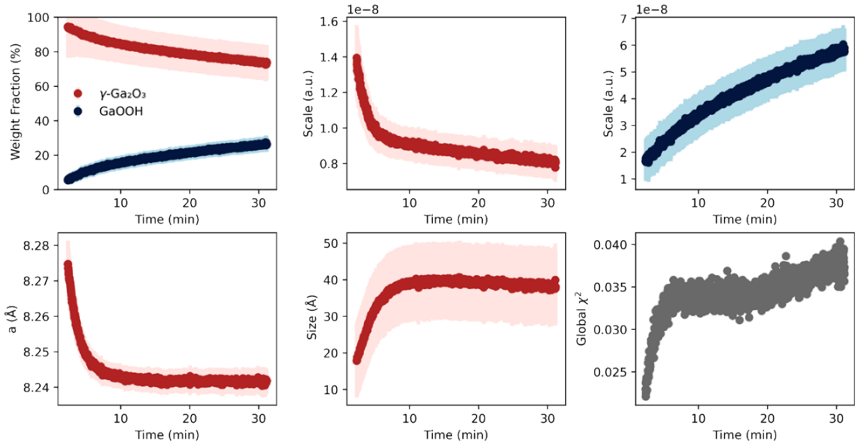

Figure S52. Extracted values for the sequential Rietveld refinement of the experiment with fast heating for $Ga(NO_3)_3$ in water with added NaOH at 250°C.

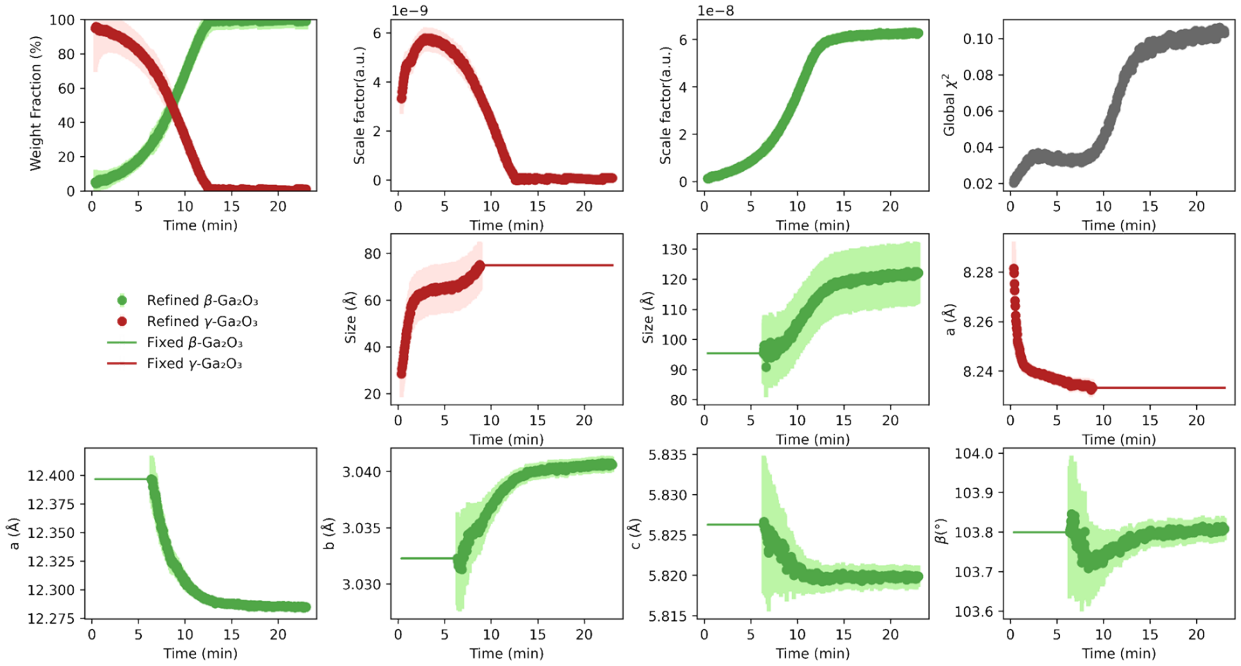

Figure S53. Extracted values for the sequential Rietveld refinement of the experiment with fast heating for $Ga(NO_3)_3$ in water with added NaOH at 300°C.

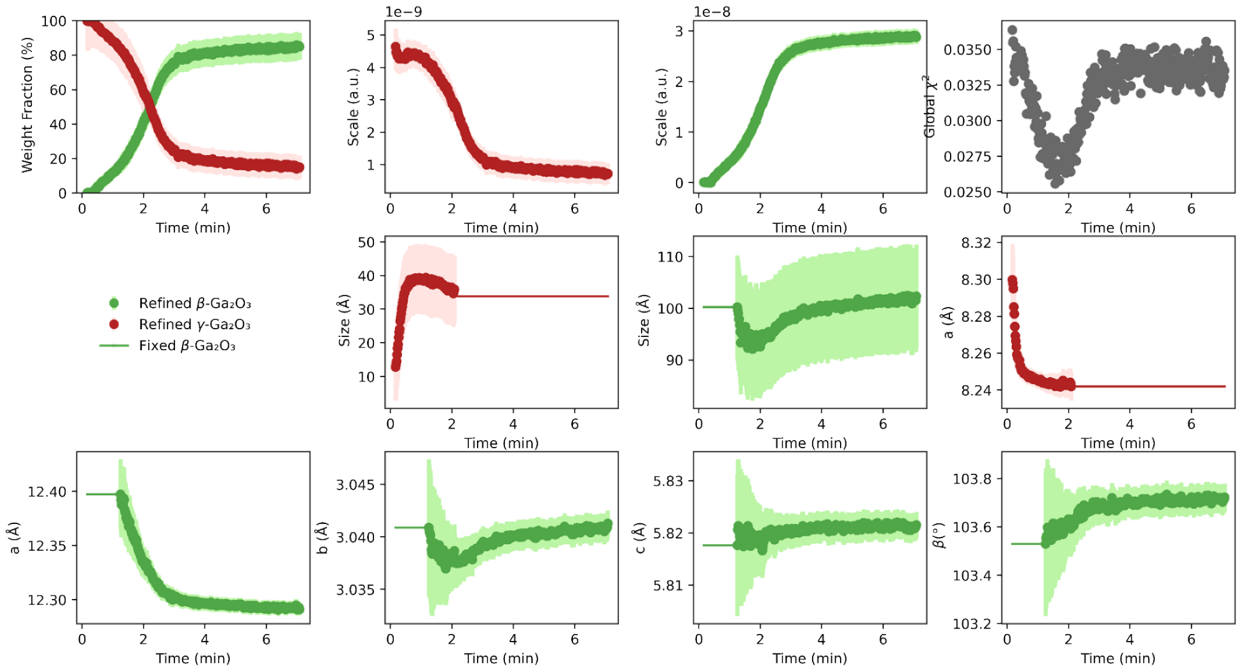

Figure S54. Extracted values for the sequential Rietveld refinement of the experiment with fast heating for $Ga(NO_3)_3$ in water with added NaOH at 350°C.

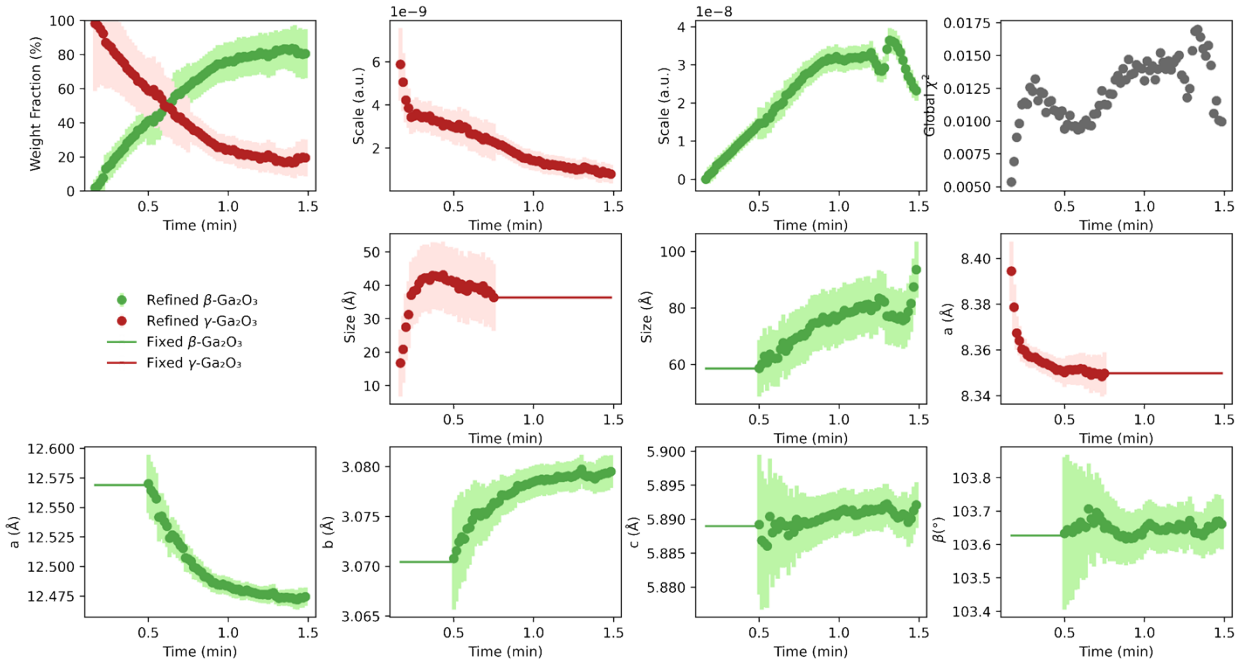

Figure S55. Extracted values for the sequential Rietveld refinement of the experiment with fast heating for $Ga(NO_3)_3$ in water with added NaOH at 400°C.

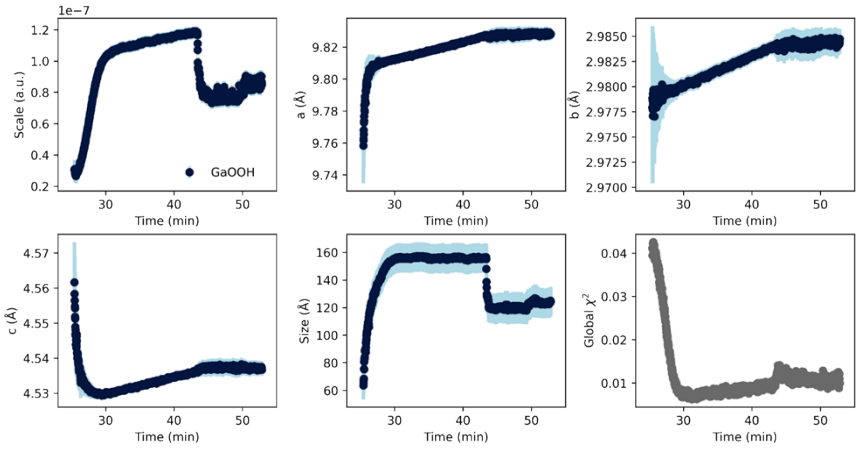

Figure S56. Extracted values for the sequential Rietveld refinement of the experiment with slow heating for $Ga(NO_3)_3$ in water with added NaOH to 400°C.

Refinement of the γ-Ga_2O_3 phase

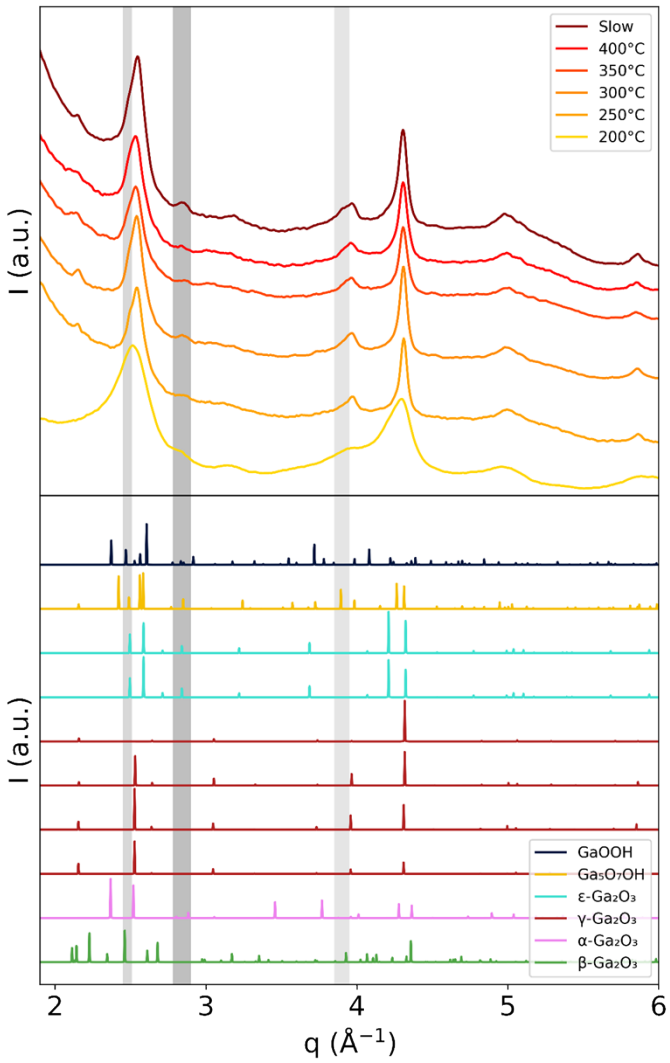

Figure S57. Comparison of XRD data for several experiments to reference XRD patterns of GaOOH, Ga_5O_7OH, ε-Ga_2O_3, γ-Ga_2O_3, α-Ga_2O_3 and β-Ga_2O_3.[1–6] The grey markings highlights areas, where γ-Ga_2O_3 show no peaks. For the light grey the signal is present as shoulders, while a peak not matching γ-Ga_2O_3 is a shade darker. The different reference patterns illustrate the difference in intensity induced by altering occupancies for γ-Ga_2O_3, which do not explain the discrepancies to the recorded patterns.

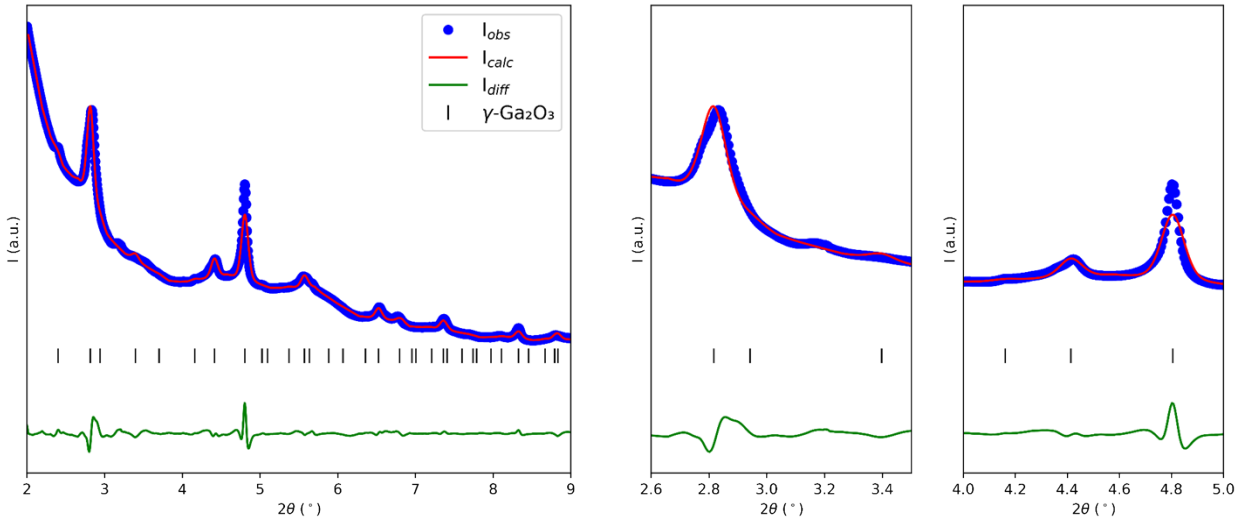

Figure S58. Le Bail fit of data from the experiment with fast heating to 250°C and ethanol as solvent. Fit using γ-Ga_2O_3, space group $Fd\bar{3}m$, a=8.2285 Å, size=6.0 nm, χ^2=1.54

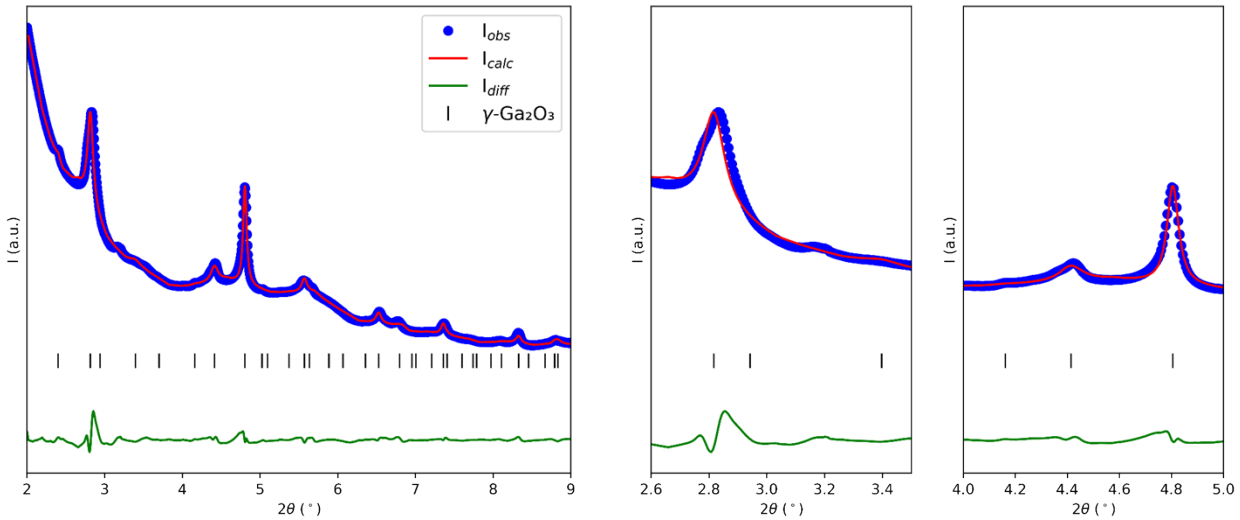

Figure S59. Le Bail fit of data from the experiment with fast heating to 250°C and ethanol as solvent. Fit using γ-Ga_2O_3, space group $Fd\bar{3}m$ and four anisotropic size broadening parameters, a=8.2282 Å, size=3.2-10 nm, χ^2=1.27

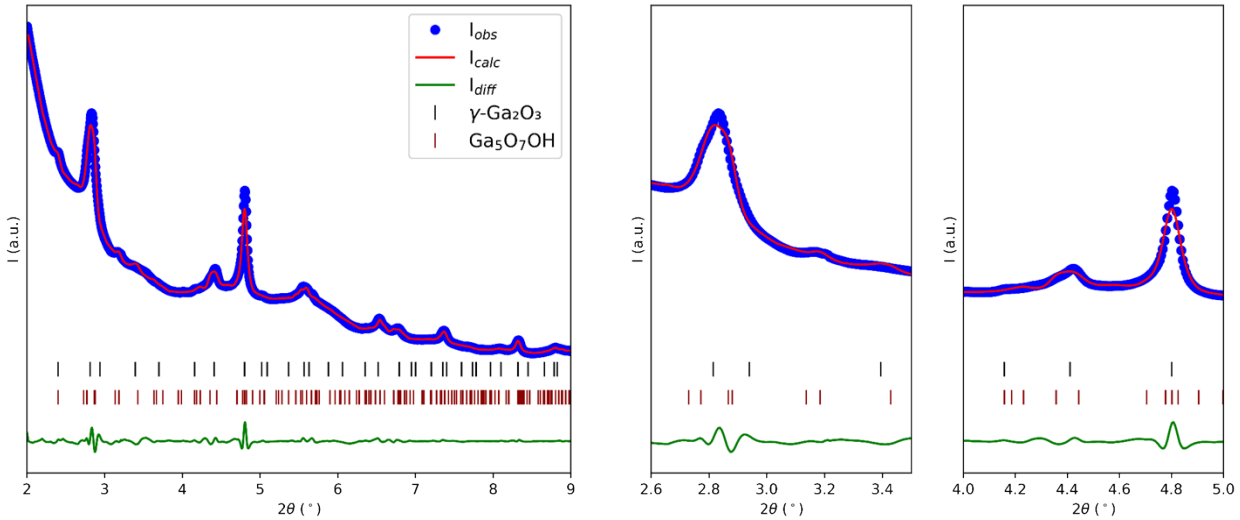

Figure S60. Le Bail fit of data from the experiment with fast heating to 250°C and ethanol as solvent. Fit using phase 1 (γ-Ga_2O_3): space group $Fd\bar{3}m$, a=8.235 Å, size=6.0 nm and phase2 (Ga_5O_7OH): space group $P6_3mc$, a=b=5.823 Å, c=8.915 Å, size=12 nm, χ^2=0.550

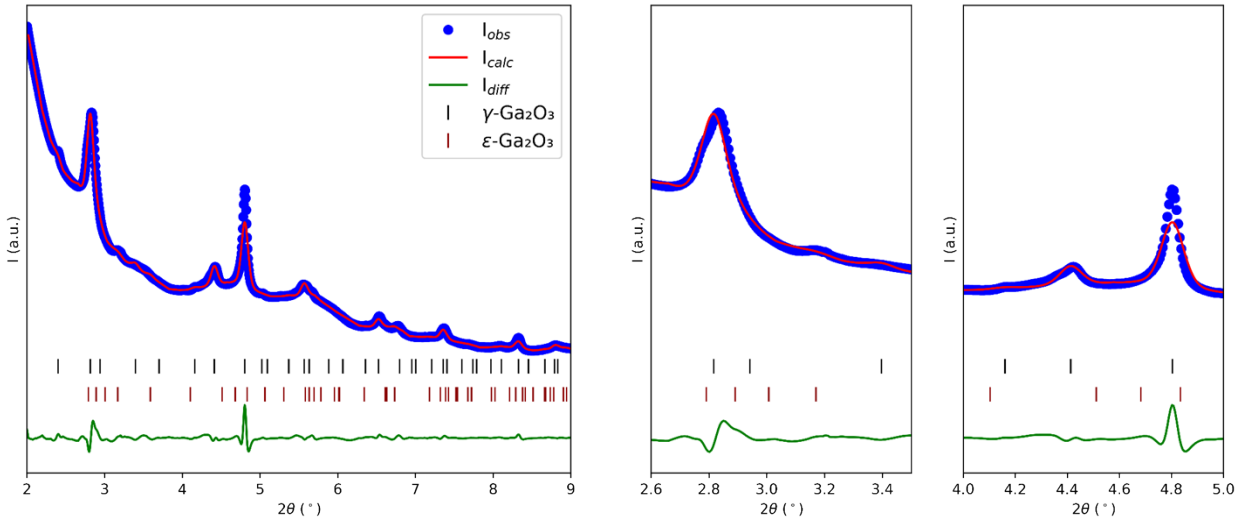

Figure S61. Le Bail fit of data from the experiment with fast heating to 250°C and ethanol as solvent. Fit using phase 1 (γ-Ga_2O_3): space group $Fd\bar{3}m$, a=8.231 Å, size=6.0 nm and phase2 (ε-Ga_2O_3): space group $P6_3mc$, a=b=2.911 Å, c=9.241 Å, size=22 nm, χ^2=0.736

Kinetic analysis of the β-Ga_2O_3 formation

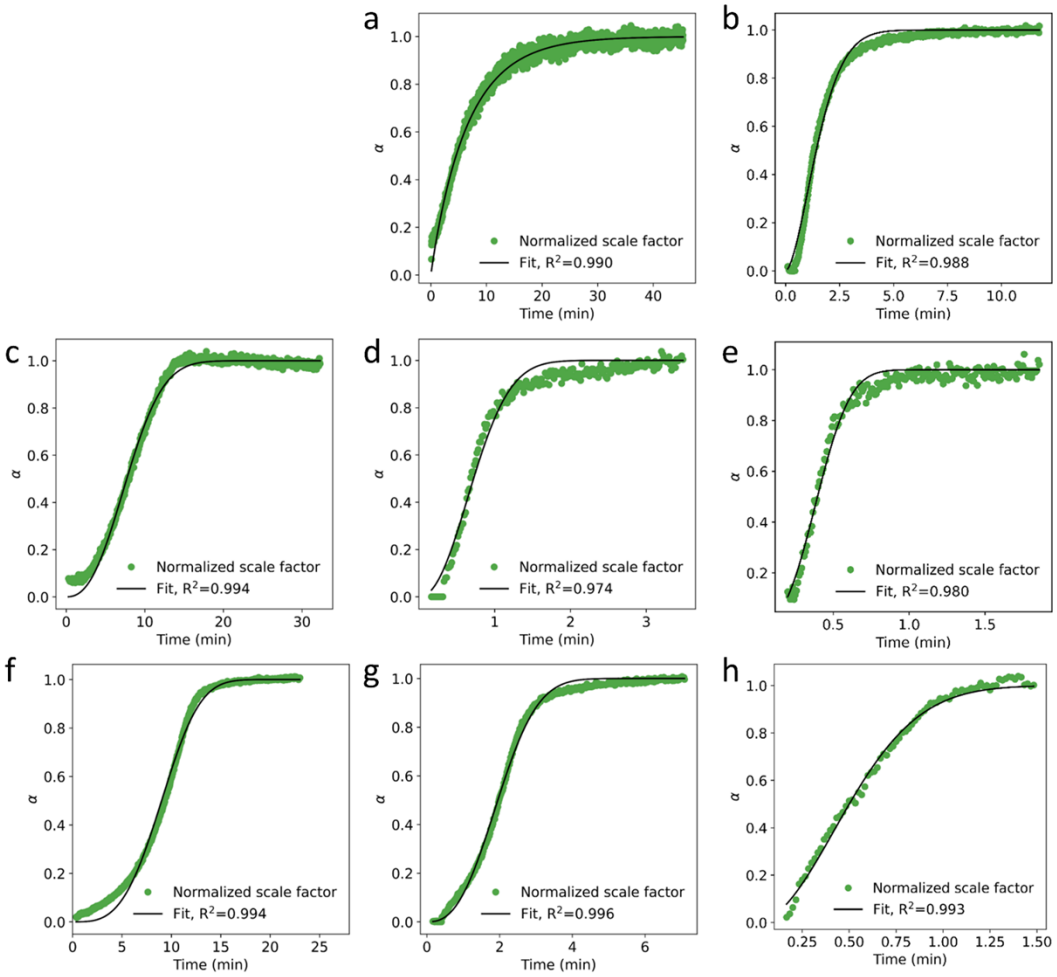

Figure S62. Johnson-Mehl-Avrami-Kolmogorov fits using $\alpha=1-\exp(-(k\cdot t)^n)$ of the normalized scale factors for the experiments fast heating to a) 350 in ethanol, b) 400 in ethanol, c) 300 in water, d) 350 in water, e) 400 in water, f) 300 in water with added NaOH, g) 350 in water with added NaOH and h) 400 in water with added NaOH. The induction time, which is sometimes included as t_0 ($\alpha=1-\exp(-(k\cdot(t-t_0))^n)$, have not been necessary to describe the data. Thus, the induction time is negligible for the reaction.

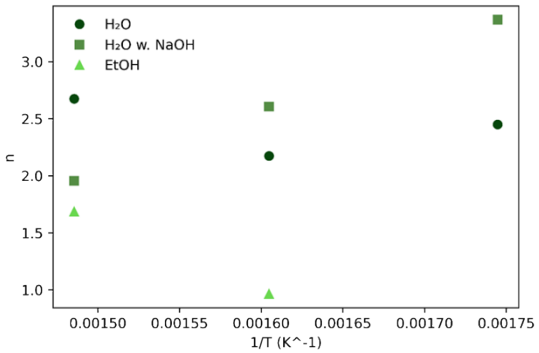

Figure S63. Extracted n-values from the Johnson-Mehl-Avrami-Kolmogorov fits

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