Electronic Supplementary Material (ESI) for Nanoscale.

SUPPORTING INFORMATION for

Formation and growth mechanism for niobium oxide nanoparticles: Atomistic insight from *in situ* X-ray total scattering

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Niobium oxide structures

Table S1 Overview of reported niobium oxides

Name	Crystal system	Space group	ReO_3 block sizes	Formed at T (°C) from NbO_2[1]
H-Nb_2O_5	Monoclinic	P 1 2/m 1	(3x5) + (3x4)	>900
M-Nb_2O_5	Tetragonal	I 4/m m m	(4x4)	850
T-Nb_2O5	Orthorhombic	P b a m	-	600 - 800
TT-Nb_2O_5	Monoclinic/Pseudo hexagonal	-	-	500 - 600
R-Nb_2O_5	Monoclinic	A 1 2/m 1	-	
B-Nb_2O_5	Monoclinic	B 1 1 2/b	-	
N-Nb_2O_5	Monoclinic	C 1 2/m 1	(4x4)	
P-Nb_2O_5	Tetragonal	I 4 1 2 2	-	600 - 750
$Nb_{22}O_{54}$	Monoclinic	P 1 2/m 1	(3x4) + (3x3)	
$Nb_{12}O_{29}$	Monoclinic	A 1 m 1	(3x4)	

Background scattering signal and subtraction

The *in situ* experiments were initiated upon applied heating. Figure S1 shows how the scattering signal from the solvent used in the experiment changes upon heating. The rapid change in the scattering pattern of the benzyl alcohol followed by a stabilization reflect that after 10 s of heating, the temperature stabilizes.

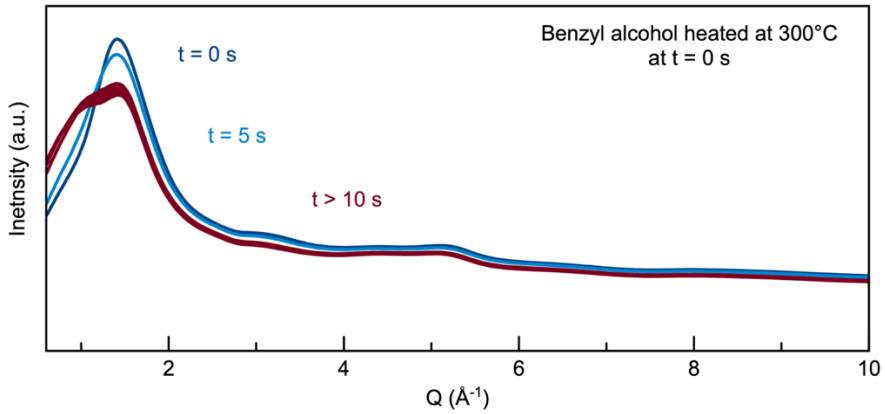

Fig. S1 Heating of benzyl alcohol to 300 °C.

Figure S2 shows the scattering pattern obtained from the reaction solution (benzyl alcohol and $NbCl_5$) together with the background, i.e. the scattering pattern measured from the pure solvent (benzyl alcohol) in the fused silica capillary at the appropriate temperature and pressure. The scattering patterns measured from the background and precursor were first normalized to have the same intensity at the Q-max value of 14.5 $Å^{-1}$, after which a background scaling factor was determined by identifying the scaling value, where no peaks from the solvent and glass could be identified in the final PDF after background subtraction and Fourier transformation. Figure S2 shows the signal and background data obtained for frames at room temperature and after heating to 300 °C along with the final background subtracted data.

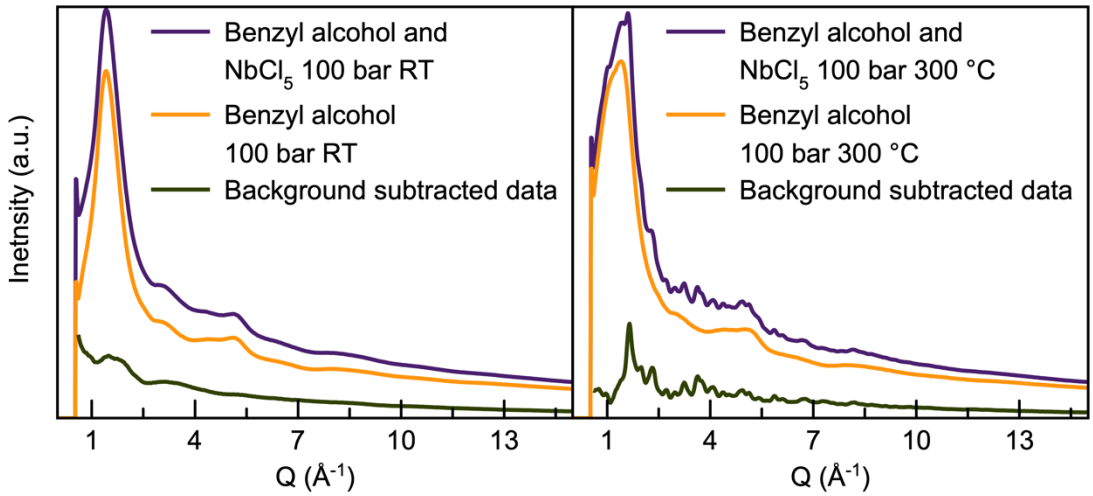

Fig. S2 Background subtraction for the room temperature data and the data collected after 24 min of heating at 300 °C.

Total scattering data and PDF analysis of Nb_2O_5 growth

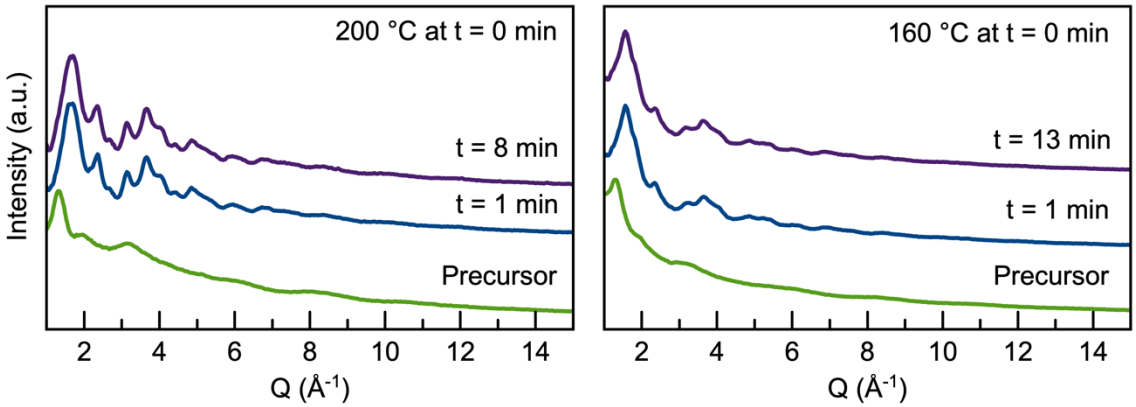

Fig. S3 Scattering patterns collected for the experiments conducted at 160 °C and 200 °C (precursor, 1 min and 8/13 min of reaction).

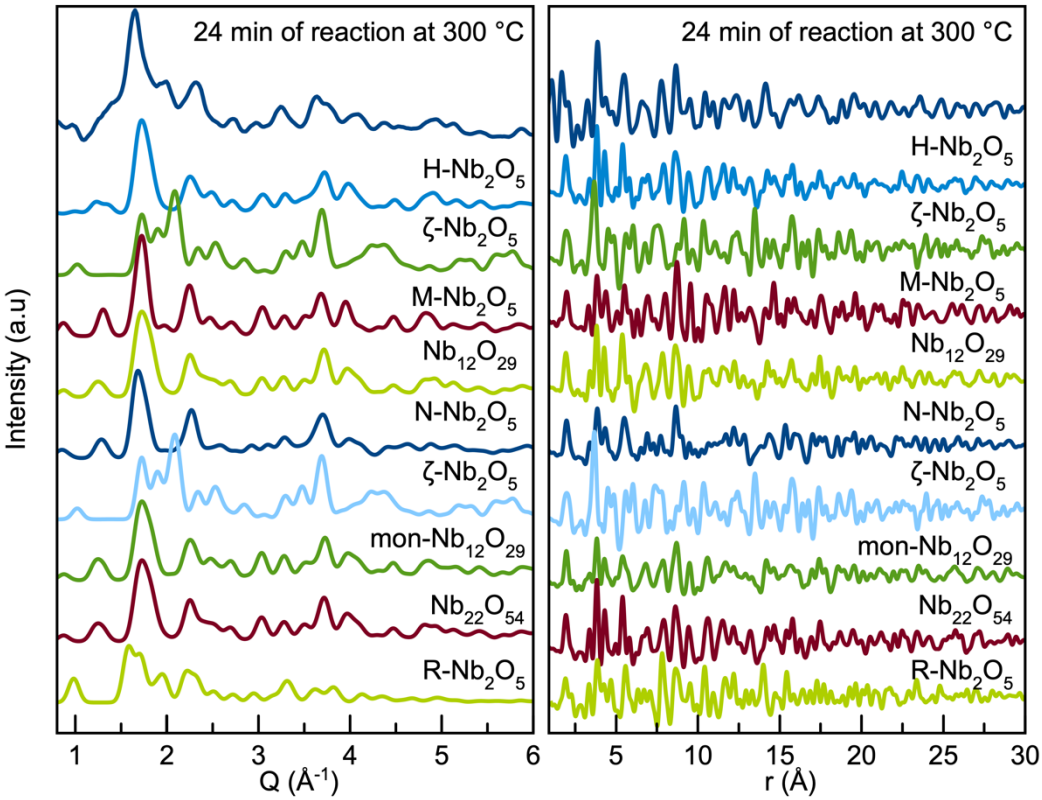

Fig. S4 Scattering pattern and PDF collected after 24 min of reaction at 300 °C compared with calculated scattering patterns of selected niobium oxide structures. It shows that many of the niobium oxides have the same structural motif, however, none of the reported structures can fully describe the data collected.

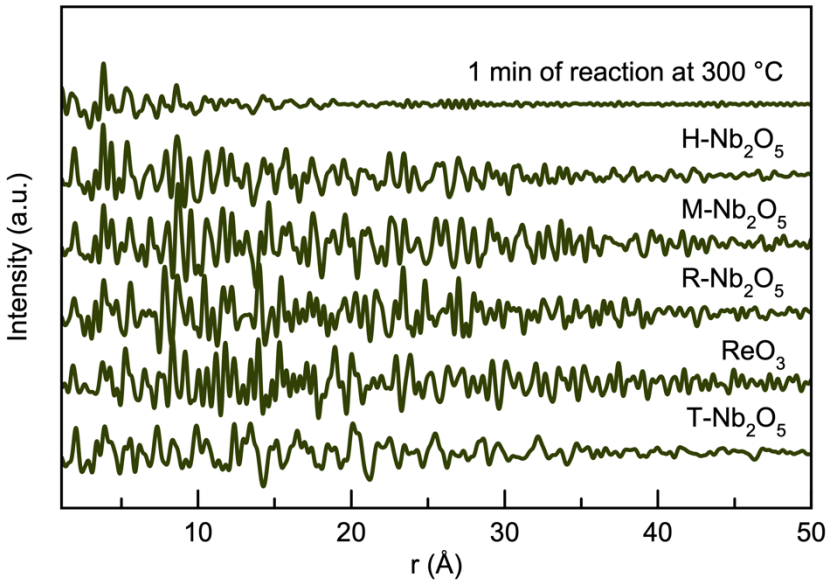

Fig. S5 PDF collected after 1 min of reaction time at 300 °C compared with calculated PDFs of selected Nb_2O_5 structures and the ReO_3. Many of the reported structures have locally very similar PDFs.

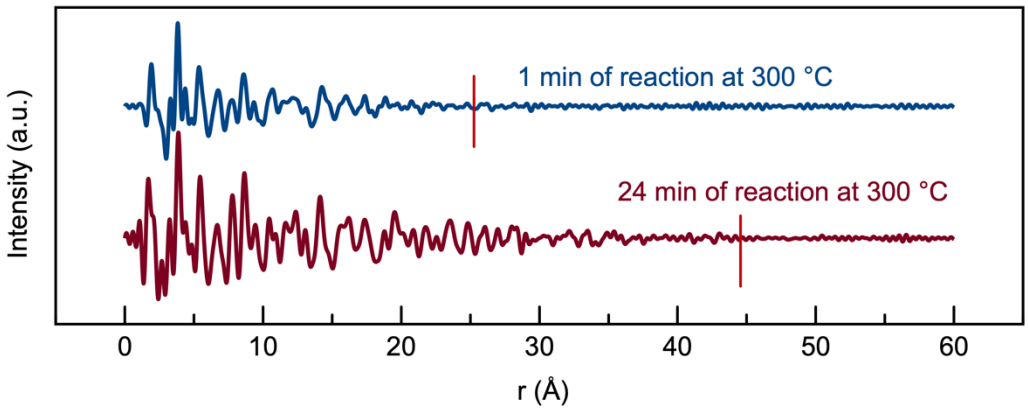

Fig. S6 PDFs collected after 1 min and 24 min of reaction time at 300 °C showing particle growth. The PDF oscillations extend to 24 Å and 45 Å for the 1 min and 24 min data respectively.

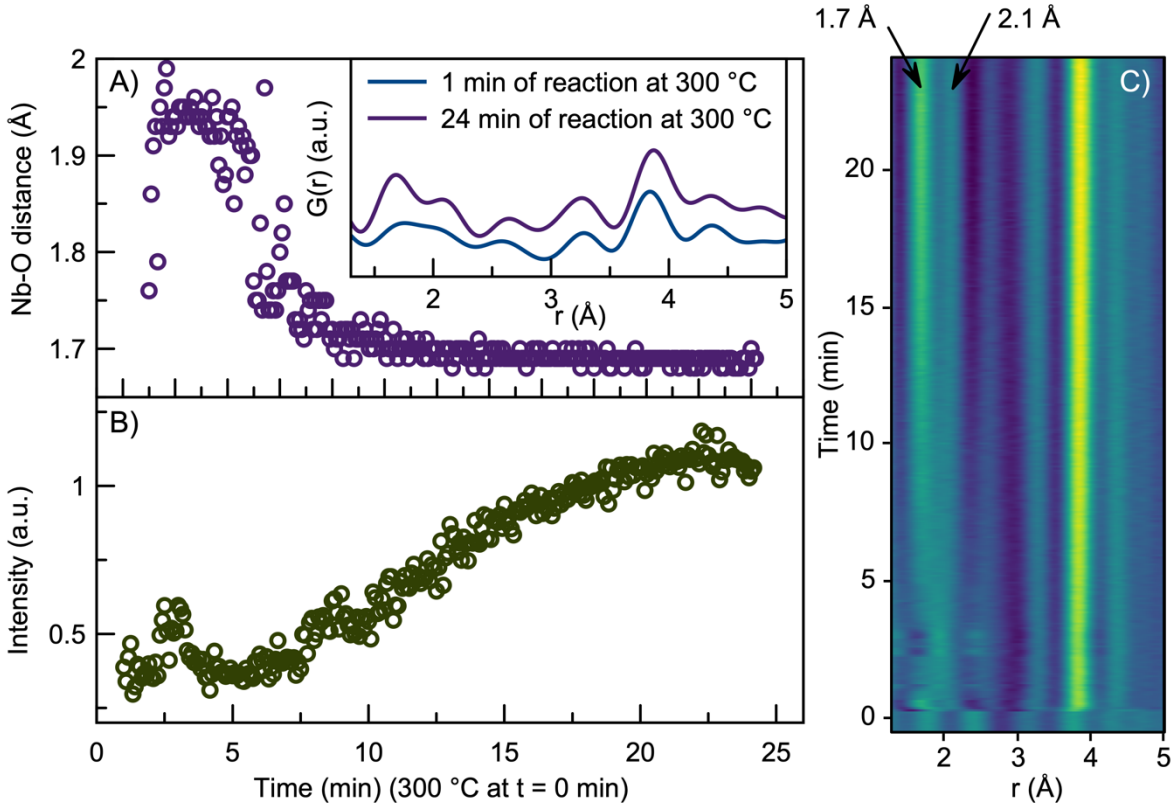

Fig. S7 (A) First PDF peak position (Nb-O distance) plotted as a function of time. As shown from the inset there is a splitting of this peak (1.7 Å and 2.1Å). (B) The intensity of the first Nb-O distance as a function of time. The splitting is indicated by an increase in the intensity of the peak at 1.7 Å with time. (C) Contour plot showing the low *r*-range, where the peak splitting with time is clearly observed.

PDF refinements

One phase sequential refinement, H-Nb_2O_5 model

Table S2-S4 show the refinement values for datasets collected at 300 °C, 200 °C and 160 °C using the H-Nb_2O_5 as the structural starting model. The first frame in the sequential refinement (1 min of reaction) and the last frame were refined using all data points in the PDF. The sequential refinement of the rest of the frames was performed on the Nyquist data sampling.
The scale factor, lattice parameters a, b, c and β, U_{iso} for oxygen and the sp-diameter were refined in the sequential refinement. The atomic positions of oxygen were kept fixed at the initial values obtained from the cif-file. U_{iso} for niobium was furthermore fixed to a value of 0.005 Å^2. δ_2 was kept at a value of 3 Å^2 which was determined from a refinement including the very low r-range. Fixed parameters were chosen in order to be able to perform a stabilized sequential refinement and keep parameters at physically reasonable values. The atomic positions of niobium were refined for the first frame in the sequential refinement (1 min of reaction) but kept fixed throughout the sequential refinement.

Table S2 Refined values for the data collected 1 min and 24 min into the reaction at 300 °C using the H-Nb_2O_5 model (Fits shown in Figure 3A + B).

	H-Nb_2O_5		
	Initial values	**300 °C , 1 min**	**300 °C , 24 min (last frame)**
Space group	*P* 1 2/m 1		
Lattice par., a (Å)	21.153(7)	20.84	20.76
Lattice par., b (Å)	3.8233(5)	3.86	3.90
Lattice par., c (Å)	19.3560(50)	19.30	19.29
Lattice par., β (°)	119.80(2)	120.61	120.31
Number of refined parameters		7 + 28	7 + 28
Data range		3 Å – 30 Å	3 Å – 30 Å
R_w		0.35	0.56
Scale factor		0.38	0.52
U_{iso} Nb (Å^2)		0.005	0.005
U_{iso} O (Å^2)		0.044	0.040
δ_2 (Å^2)		3.00	3.00
Sp-diameter (Å)		25.58	28.26

Atomic positions for H-Nb_2O_5						
	Initial values			**Refined values**		
Label	x (Å)	y (Å)	z (Å)	x (Å)	y (Å)	z (Å)
Nb1	0	0.2285(3)	0	0.000000	0.190820	0.000000
Nb2	0.5	0	0.5	0.500000	0.000000	0.500000
Nb3	0.16430(3)	0	0.00353(3)	0.156992	0.000000	0.000249
Nb4	0.23623(3)	0	0.23134(3)	0.241400	0.000000	0.231220
Nb5	0.30284(3)	0	0.45456(3)	0.299751	0.000000	0.457878
Nb6	0.36087(3)	0	0.04553(3)	0.360465	0.000000	0.056640
Nb7	0.43325(3)	0	0.27741(4)	0.445501	0.000000	0.280925
Nb8	0.56270(3)	0	0.09346(3)	0.555657	0.000000	0.086263
Nb9	0.62943(3)	0	0.32219(3)	0.640662	0.000000	0.313702
Nb10	0.09353(3)	0.5	0.20187(3)	0.101029	0.500000	0.205564
Nb11	0.15921(3)	0.5	0.42410(3)	0.152594	0.500000	0.420687
Nb12	0.70330(3)	0.5	0.12414(3)	0.698531	0.500000	0.129695
Nb13	0.77056(3)	0.5	0.35151(3)	0.778609	0.500000	0.350835
Nb14	0.89895(3)	0.5	0.16353(3)	0.901519	0.500000	0.151909
Nb15	0.96461(3)	0.5	0.38928(4)	0.982518	0.500000	0.405926

Table S3 Refined values for the data collected 1 min and 5 min into the reaction at 200 °C using the H-Nb_2O_5 model (Fit shown in Figure 6D).

	H-Nb_2O_5		
	Initial values	**200 °C, 1 min**	**200 °C, 5 min (last frame)**
Space group	*P* 1 2/m 1		
Lattice par., a (Å)	21.153(7)	20.83	20.89
Lattice par., b (Å)	3.8233(5)	3.87	3.87
Lattice par., c (Å)	19.3560(50)	19.77	19.67
Lattice par., β (°)	119.80(2)	118.75	118.67
Number of refined parameters		7 + 28	7 + 28
Data range		3 Å – 30 Å	3 Å – 30 Å
R_w		0.35	0.40
Scale factor		0.42	0.47
U_{iso} Nb (Å^2)		0.005	0.005
U_{iso} O (Å^2)		0.070	0.077
δ_2 (Å^2)		3.00	3.00
Sp-diameter (Å)		20.67	20.28

Atomic positions for H-Nb_2O_5						
	Initial values			**Refined values**		
Label	x (Å)	y (Å)	z (Å)	x (Å)	y (Å)	z (Å)
Nb1	0	0.2285(3)	0	0.000000	0.012848	0.000000
Nb2	0.5	0	0.5	0.500000	0.000000	0.500000
Nb3	0.16430(3)	0	0.00353(3)	0.164827	0.000000	0.011097
Nb4	0.23623(3)	0	0.23134(3)	0.212939	0.000000	0.197181
Nb5	0.30284(3)	0	0.45456(3)	0.304924	0.000000	0.450204
Nb6	0.36087(3)	0	0.04553(3)	0.365570	0.000000	0.049181
Nb7	0.43325(3)	0	0.27741(4)	0.440342	0.000000	0.279791
Nb8	0.56270(3)	0	0.09346(3)	0.556894	0.000000	0.092212
Nb9	0.62943(3)	0	0.32219(3)	0.642206	0.000000	0.338850
Nb10	0.09353(3)	0.5	0.20187(3)	0.085348	0.500000	0.192639
Nb11	0.15921(3)	0.5	0.42410(3)	0.145172	0.500000	0.414201
Nb12	0.70330(3)	0.5	0.12414(3)	0.693303	0.500000	0.132323
Nb13	0.77056(3)	0.5	0.35151(3)	0.757023	0.500000	0.321090
Nb14	0.89895(3)	0.5	0.16353(3)	0.890187	0.500000	0.137560
Nb15	0.96461(3)	0.5	0.38928(4)	0.963236	0.500000	0.403199

Table S4 Refined values for the data collected 1 min and 13 min into the reaction at 1600 °C using the H-Nb_2O_5 model (Fit shown in Figure 6C).

	H-Nb_2O_5		
	Initial values	**160 °C, 1 min**	**160 °C, 13 min (last frame)**
Space group	*P* 1 2/m 1		
Lattice par., a (Å)	21.153(7)	20.77	20.97
Lattice par., b (Å)	3.8233(5)	3.77	3.78
Lattice par., c (Å)	19.3560(50)	19.76	19.86
Lattice par., β (°)	119.80(2)	121.85	121.89
Number of refined parameters		7 + 28	7 + 28
Data range		3 Å – 20 Å	3 Å – 20 Å
R_w		0.42	0.40
Scale factor		0.21	0.17
U_{iso} Nb (Å^2)		0.005	0.005
U_{iso} O (Å^2)		0.0029	0.0022
δ_2 (Å^2)		3.00	3.00
Sp-diameter (Å)		12.86	14.63

Atomic positions for H-Nb_2O_5						
	Initial values			**Refined values**		
Label	x (Å)	y (Å)	z (Å)	x (Å)	y (Å)	z (Å)
Nb1	0	0.2285(3)	0	0.000000	0.117279	0.000000
Nb2	0.5	0	0.5	0.500000	0.000000	0.500000
Nb3	0.16430(3)	0	0.00353(3)	0.162612	0.000000	0.017641
Nb4	0.23623(3)	0	0.23134(3)	0.239352	0.000000	0.235610
Nb5	0.30284(3)	0	0.45456(3)	0.310369	0.000000	0.460093
Nb6	0.36087(3)	0	0.04553(3)	0.353042	0.000000	0.051398
Nb7	0.43325(3)	0	0.27741(4)	0.439332	0.000000	0.279767
Nb8	0.56270(3)	0	0.09346(3)	0.550582	0.000000	0.102557
Nb9	0.62943(3)	0	0.32219(3)	0.646236	0.000000	0.327372
Nb10	0.09353(3)	0.5	0.20187(3)	0.095710	0.500000	0.198541
Nb11	0.15921(3)	0.5	0.42410(3)	0.143072	0.500000	0.413255
Nb12	0.70330(3)	0.5	0.12414(3)	0.689860	0.500000	0.135442
Nb13	0.77056(3)	0.5	0.35151(3)	0.763397	0.500000	0.365031
Nb14	0.89895(3)	0.5	0.16353(3)	0.901001	0.500000	0.176405
Nb15	0.96461(3)	0.5	0.38928(4)	0.955898	0.500000	0.387857

One-phase sequential refinement, $Nb_{12}O_{29}$ and $Nb_{22}O_{54}$ model

Sequential refinements using other niobium oxides show how other structures with the same local motifs give highly similar results compared to the refinements using the H-Nb_2O_5 model.
In the refinement using $Nb_{12}O_{29}$ as the starting model a scale factor, lattice parameters a, b, c and β, U_{iso} for oxygen and niobium and the sp-diameter were refined in the sequential refinement. The niobium positions were refined for the first frame (1 min of reaction) and kept fixed in the sequential refinement.
In the refinement using $Nb_{22}O_{29}$ as the structural starting model a scale factor, lattice parameters a, b, c and β, U_{iso} for oxygen and niobium and the sp-diameter were refined in the sequential refinement.

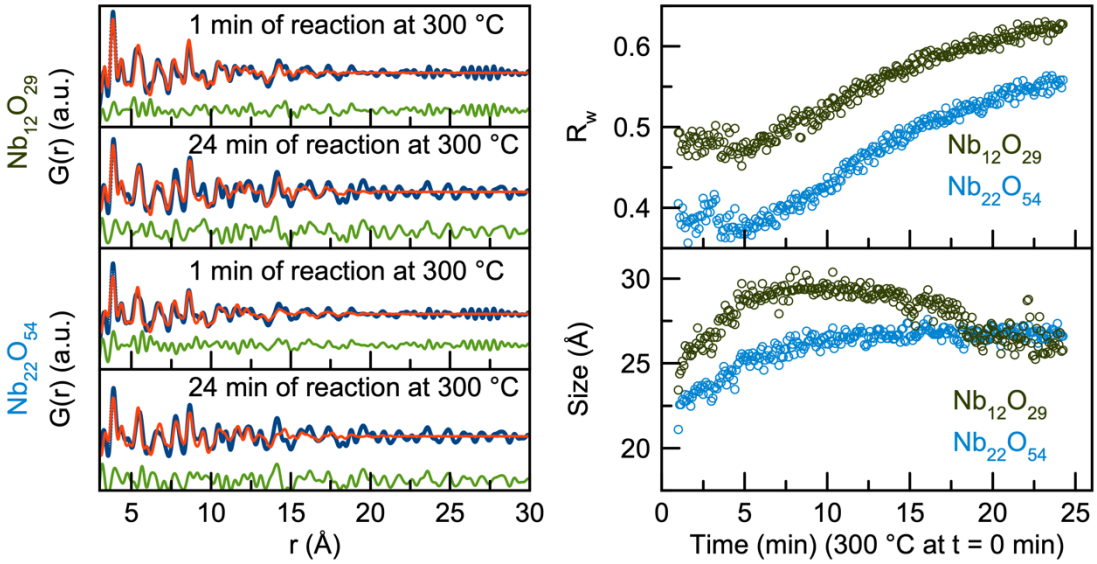

Fig. S8 Sequential refinement of data collected at 300 °C using $Nb_{12}O_{29}$ and $Nb_{22}O_{54}$ respectively as the structure model. The changes in both R_w and sp-diameter with time look highly similar to those observed in the refinement using the H-Nb_2O_5 model

Table S5 Refined values for data collected 1 min and 24 min of reaction at 300 °C using $Nb_{12}O_{29}$ as the structural starting model (Figure S8).

	$Nb_{12}O_{29}$		
	Initial values	**300 °C , 1min**	**300 °C , 24 min (last frame)**
Space group	*P* 1 2/m 1		
Lattice par., a (Å)	15.6856	15.56	15.50
Lattice par., b (Å)	3.8307	3.85	3.87
Lattice par., c (Å)	20.71	20.52	20.59
Lattice par., β (°)	113.056	113.49	113.78
Cell vol., V (Å^3)			
Number of refined parameters		20	8 + 12
Data range		3 Å – 30 Å	3 Å – 30 Å
R_w		0.41	0.56
Scale factor		0.39	0.51
U_{iso} Nb (Å^{-2})		0.0032	0.0042
U_{iso} O (Å^{-2})		0.015	0.016
Sp-diameter (Å)		21.10	25.58

Atomic positions for $Nb_{12}O_{29}$						
	Initial values			Refined values		
Label	x (Å)	y (Å)	z (Å)	x (Å)	y (Å)	z (Å)
Nb1	0.1004(9)	0	0.0689(7)	0.092171	0.000000	0.071936
Nb2	0.0997(9)	0	0.6996(7)	0.097270	0.000000	0.699624
Nb3	0.0985(9)	0	0.8822(6)	0.103033	0.000000	0.887738
Nb4	0.373(1)	0	0.1455(7)	0.366071	0.000000	0.141586
Nb5	0.367(1)	0	0.7746(7)	0.375591	0.000000	0.775090
Nb6	0.365(1)	0	0.958(1)	0.369910	0.000000	0.958615

Table S6 Refined values for data collected 1 min and 24 min of reaction at 300 °C using $Nb_{22}O_{54}$ as the structural starting model (Figure S8).

	$Nb_{22}O_{54}$		
	Initial values	**300 °C, 1 min**	**300 °C, 24 min (last frame)**
Space group	*P* 1 2/m 1		
Lattice par., a (Å)	15.7491	15.45	15.81
Lattice par., b (Å)	3.8236	3.85	3.88
Lattice par., c (Å)	17.8521	17.95	17.69
Lattice par., β (°)	102.029	103.62	102.75
Cell vol., V (Å^3)			
Number of refined parameters		8	8
Data range		3 Å – 30 Å	3 Å – 30 Å
R_w		0.49	0.63
Scale factor		0.35	0.46
U_{iso} Nb (Å^{-2})		0.0082	0.0075
U_{iso} O (Å^{-2})		0.033	0.034
Sp-diameter (Å)		23.38	25.54

Refinement of the data collected 24 min of reaction at 300 °C, ReO_3 and R-Nb_2O_5 model

Table S7 Refined values for data collected 24 min into the reaction at 300 °C using ReO_3 as the structural model (Figure 5A).

	Initial values	**300 °C, 24 min (last frame)**
	ReO_3	
Space group	*I* m -3	
Lattice par., a = b = c (Å)	7.4456(2)	7.74
Number of refined parameters		5
Data range		3 Å – 30 Å
R_w		0.68
Scale factor		0.25
U_{iso} Nb (Å^{-2})		0.012
U_{iso} O (Å^{-2})		0.11
δ_2 (Å^2)		3.00
Sp-diameter (Å)		23.64

Table S8 Refined values with data collected 24 min into the reaction at 300 °C using ReO_3 and R-Nb_2O_5 as the structural models (Figure 5B).

	Initial values	**300 °C, 24 min (last frame)**
	ReO_3	
Space group	*I* m -3	
Lattice par., a = b = c (Å)	7.4456(2)	7.68
Number of refined parameters		10
Data range		3 Å – 30 Å
R_w		0.47
Scale factor		0.069
U_{iso} Nb (Å^{-2})		0.010
U_{iso} O (Å^{-2})		0.12
δ_2 (Å^2)		3.00
Sp-diameter (Å)		42.01
	R-Nb_2O_5	
Space group	A 1 2/m 1	
Lattice par., a (Å)	3.983(4)	3.89
Lattice par., b (Å)	3.826(4)	3.89
Lattice par., c (Å)	12.79(1)	12.90
Lattice par., β (°)	90.75(5)	92.04
Scale		0.28

Two-phase sequential refinement with R-Nb_2O_5 and H-Nb_2O_5

The data collected at 300 °C were refined using a two-phase refinement with H-Nb_2O_5 and R-Nb_2O_5. Both U_{iso} for niobium and oxygen along with the sp-diameter were constrained to the same values for both phases throughout the sequential refinement.

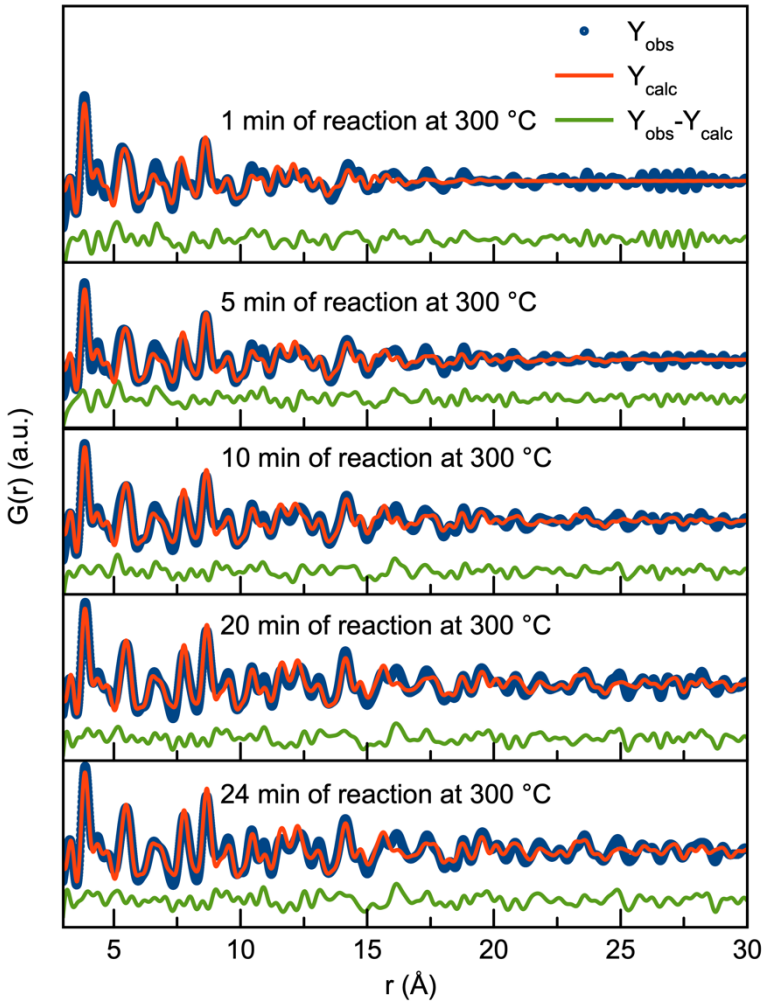

Fig. S9 Selected fits from the sequential refinement of the data collected at 300 °C using H- and R-Nb_2O_5 as the structural starting models.

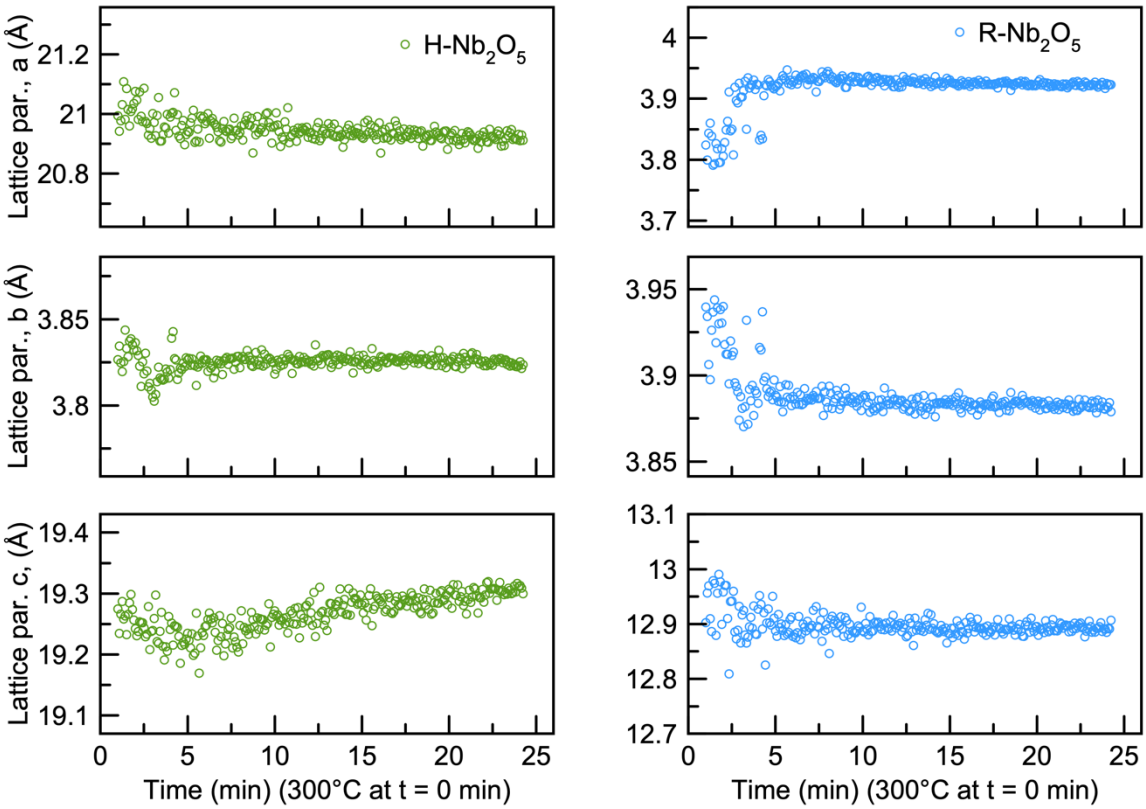

Fig. S10 Lattice parameters as a function of time from the two-phase refinement of the data collected at 300 °C using H- and R-Nb_2O_5 as models.

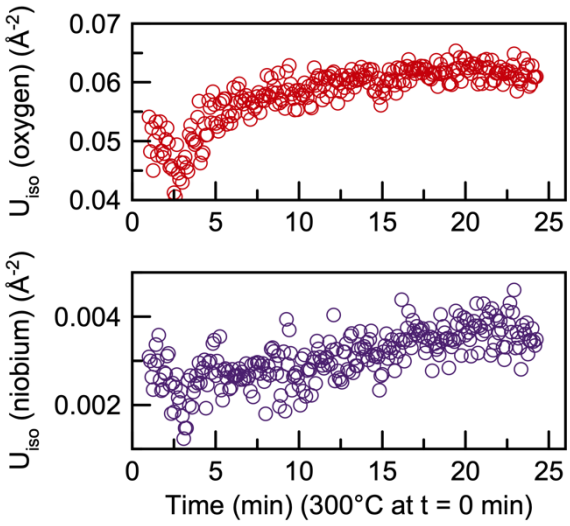

Fig. S11 U_{iso} for niobium and oxygen as a function of time from the two-phase refinement of the data collected at 300 °C using H- and R-Nb_2O_5 as models.

Table S9 Refined values with data collected at different time-points in the synthesis 300 °C using H-Nb_2O_5 and R-Nb_2O_5 as the structural starting models (Figure 5C + S9).

	Initial values	**1 min**	**5 min**	**10 min**	**20 min**	**24 min**
	H-Nb_2O_5					
Space group	*P* 1 2/m 1					
Lattice par., a (Å)	21.153(7)	20.99	20.94	20.96	20.91	20.91
Lattice par., b (Å)	3.8233(5)	3.83	3.83	3.82	3.83	3.82
Lattice par., c (Å)	19.3560(50)	19.27	19.23	19.27	19.31	19.30
Lattice par., β (°)	119.80(2)	120.44	120.22	120.33	120.33	120.29
	R-Nb_2O_5					
Space group	A 1 2/m 1					
Lattice par., a (Å)	3.983(4)	3.82	3.92	3.93	3.92	3.92
Lattice par., b (Å)	3.826(4)	3.94	3.89	3.89	3.88	3.88
Lattice par., c (Å)	12.79(1)	12.90	12.89	12.89	12.90	12.91
Lattice par., β (°)	90.75(5)	92.89	91.52	91.66	91.53	91.59
Number of refined parameters		13 + 29	13 + 29	13 + 29	13 + 29	13 + 29
Data range		3 Å – 30 Å	3 Å – 30 Å	3 Å – 30 Å	3 Å – 30 Å	3 Å – 30 Å
R_w		0.45	0.40	0.36	0.35	0.35
Scale factor (H)		0.42	0.35	0.31	0.29	0.29
Scale factor (R)		0.062	0.091	0.13	0.17	0.18
U_{iso} Nb ($Å^{-2}$)		0.0031	0.0027	0.0024	0.0036	0.0035
U_{iso} O ($Å^{-2}$)		0.062	0.053	0.059	0.064	0.061
Sp-diameter (Å)		22.70	31.74	40.28	53.66	53.50

Atomic positions for H-Nb_2O_5						
	Initial values			**Refined values**		
	x (Å)	y (Å)	z (Å)	x (Å)	y (Å)	z (Å)
Nb1	0	0.2285(3)	0	0.000000	0.181599	0.000000
Nb2	0.5	0	0.5	0.500000	0.000000	0.500000
Nb3	0.16430(3)	0	0.00353(3)	0.155071	0.000000	-0.011129
Nb4	0.23623(3)	0	0.23134(3)	0.241870	0.000000	0.236585
Nb5	0.30284(3)	0	0.45456(3)	0.293222	0.000000	0.463501
Nb6	0.36087(3)	0	0.04553(3)	0.379844	0.000000	0.047979
Nb7	0.43325(3)	0	0.27741(4)	0.438832	0.000000	0.283428
Nb8	0.56270(3)	0	0.09346(3)	0.567540	0.000000	0.083822
Nb9	0.62943(3)	0	0.32219(3)	0.637105	0.000000	0.307446
Nb10	0.09353(3)	0.5	0.20187(3)	0.109324	0.500000	0.189915
Nb11	0.15921(3)	0.5	0.42410(3)	0.158402	0.500000	0.421711
Nb12	0.70330(3)	0.5	0.12414(3)	0.694720	0.500000	0.119776
Nb13	0.77056(3)	0.5	0.35151(3)	0.771249	0.500000	0.351663
Nb14	0.89895(3)	0.5	0.16353(3)	0.880633	0.500000	0.164061
Nb15	0.96461(3)	0.5	0.38928(4)	0.968163	0.500000	0.387467
Atomic positions for R-Nb_2O_5						
Nb1	0.07(1)	0	0.146(2)	0.051956	0.00000	0.146677

One-phase sequential refinement of 160 °C and 200 °C with H-Nb_2O_5

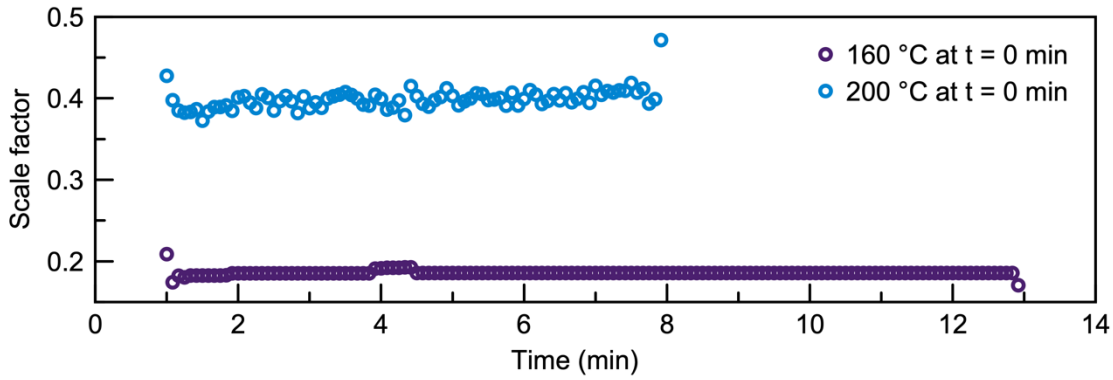

Fig. S12 From sequential refinement of the data collected at 160 °C and 200 °C with H-Nb_2O_5 we observe no significant changes in the scale factors.

Cluster refinement of precursor PDFs

For the refinement of the precursor PDFs we apply *Diffpy-CMI*[2] and perform a least-square optimization between a theoretical calculated PDF (calculated with the Debye equation) and the experimental PDF. The cluster models used for the calculated PDF were all obtained as cutouts from the $Cs_2[Nb_3O_5Cl_7]$ crystal structure shown in Figure S12. Clusters with different sizes and different Cl/O ratios were extracted in order to get the best structural starting models for the refinements. Figures S12 also shows such a cut-out.
In all refinements, the scale factor and Nb atomic positions were refined. The isotropic ADP values of Cl, Nb and O were all fixed to 0.03 Å^2. For the refinement with single octahedra, a wavefunction was implemented in order to describe the solvent-cluster interaction.[3]

$$w(r) = A \cdot sin\left(2\pi\left(\frac{r}{\lambda} - \varphi\right)\right) e^{-\left(\frac{(r-r_0)}{2\sigma_{eff}}\right)^2}$$

Figure S13 shows the refinement of the precursor data for the 200ºC experiment both with a without implementing the wave function.

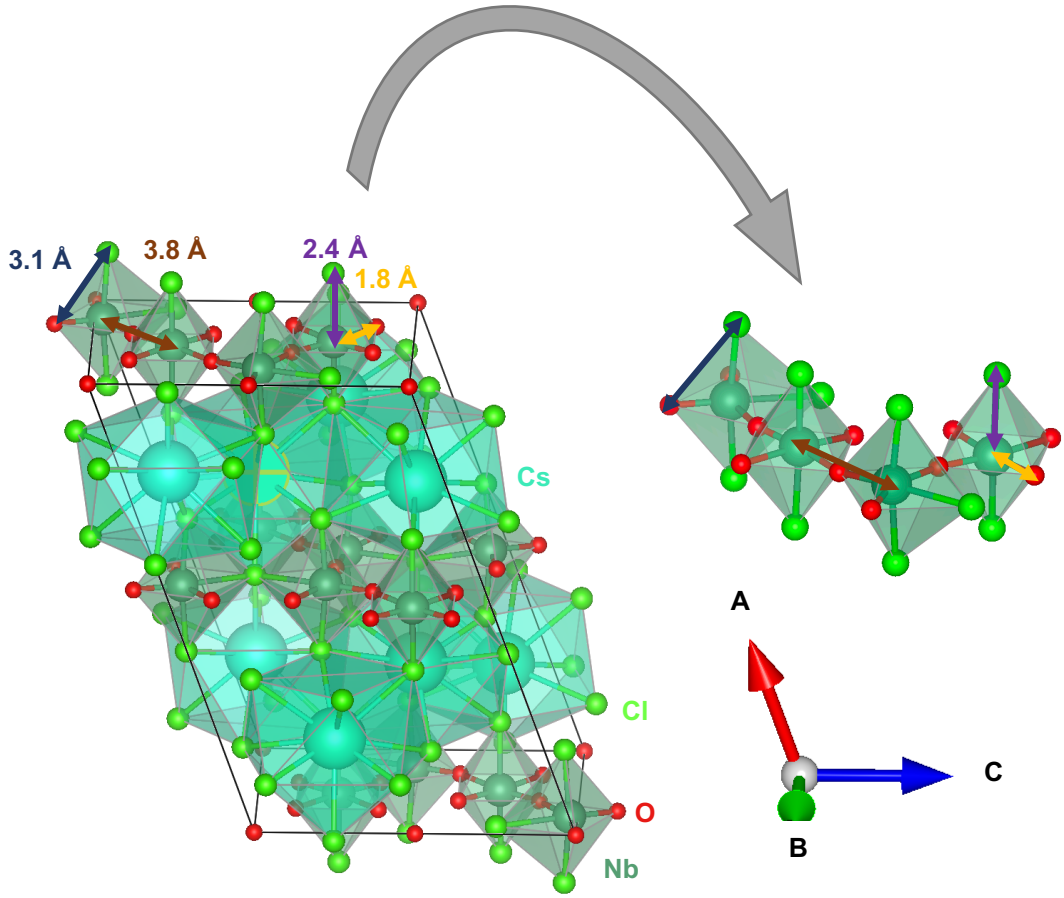

Fig. S13 Crystal structure of $Cs_2[Nb_3O_5Cl_7]$ to the left. Bright green: Cl, dark green: Nb, turquoise: Cs and red: O. A cut-out illustrating how the models for the refinement were extracted.

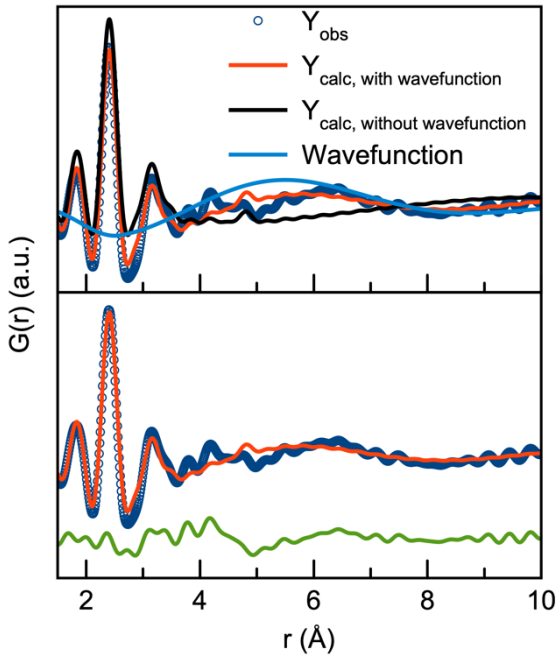

Fig. S14 Refinement of the precursor PDF collected for the 160 °C experiment using a single $[NbCl_{6-x}O_x]$ octahedra showing the contribution from the wavefunction.

Table S10 Refined values of the precursor collected for the experiment conducted at 300 °C (Figure 7B). Here, a chain of four [$NbCl_{6-x}O_x$] was used in the structural refinement.

	Initial values	Precursor for the 300 °C experiment
Nb0 position (x,y,z)	(-7.22, 7.05, 2.07)	(-7.10, 7.00, 2.06)
Nb1 position (x,y,z)	(-5.38, 1.88, 1.54)	(-5.43, 1.89, 1.54)
Nb2 position (x,y,z)	(-6.43, 4.18, 1.83)	(-6.33, 4.28, 1.83)
Nb3 position (x,y,z)	(-4.74, 4.74, 1.31)	(-4.70, 4.60, 1.30)
Data range		1.5 Å – 10 Å
Data summation number		1 frame (5 s)
Number of refined parameters		13
Scale		0.25
R_w		0.55

Table S11 Refined values of the precursor collected for the experiment conducted at 200 °C and 160 °C. Here single [$NbCl_{6-x}O_x$] octahedra were used in the structural refinements (Figure 7C + D)

	Initial values	Precursor for the 200 °C experiment	Precursor for the 160 °C experiment
Nb0 position (x,y,z)	(1.45, 4.22, 7.83)	(1.45, 4.28, 7.89)	(1.46, 4.20, 7.87)
Data range		1.5 Å – 10 Å	1.5 Å – 10 Å
Data summation number		6 frames (30 s)	58 frames (290 s)
Number of refined parameters		10	10
Scale		0.346	0.207
R_w		0.349	0.324
wA		-0.28	110
wasym		3.73	2.50
wlam		7.03	5.92
wphi		1.03	7.15
wr0		-4.08	-8.94
wsig		-1.02	7.10

Data analysis of experiment conducted at 100 °C with ambient pressure

In order to slow down the reaction an experiment at 100 °C and ambient pressure was conducted.

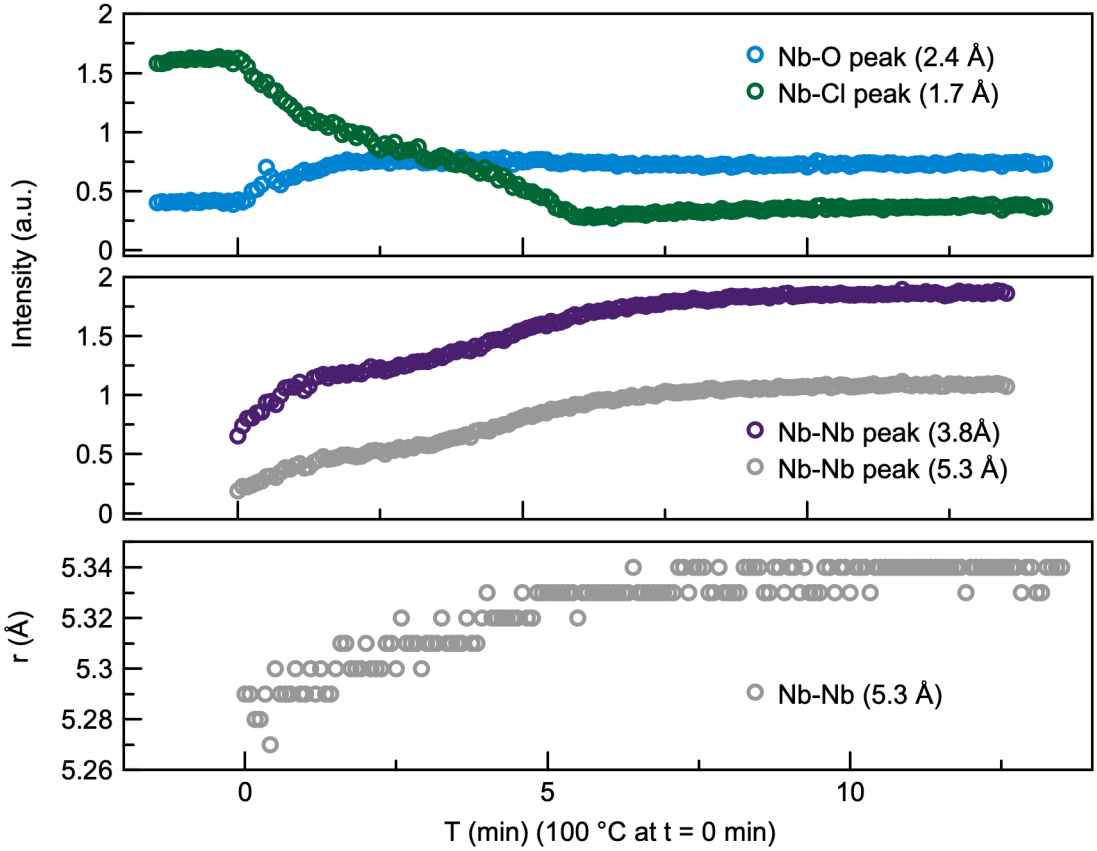

Fig. S15 Changes in intensity and peak positions of selected structural peaks plotted as a function of time of the reaction in the experiment conducted at 100 °C.

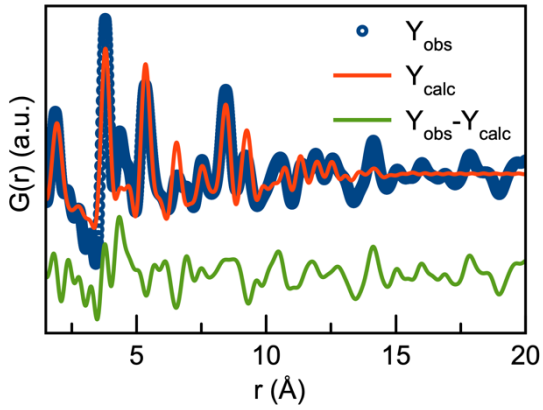

Fig. S16 Structural refinement of data collected after 13 min of reaction at 100 °C using the structural model of $HNbO_3$.

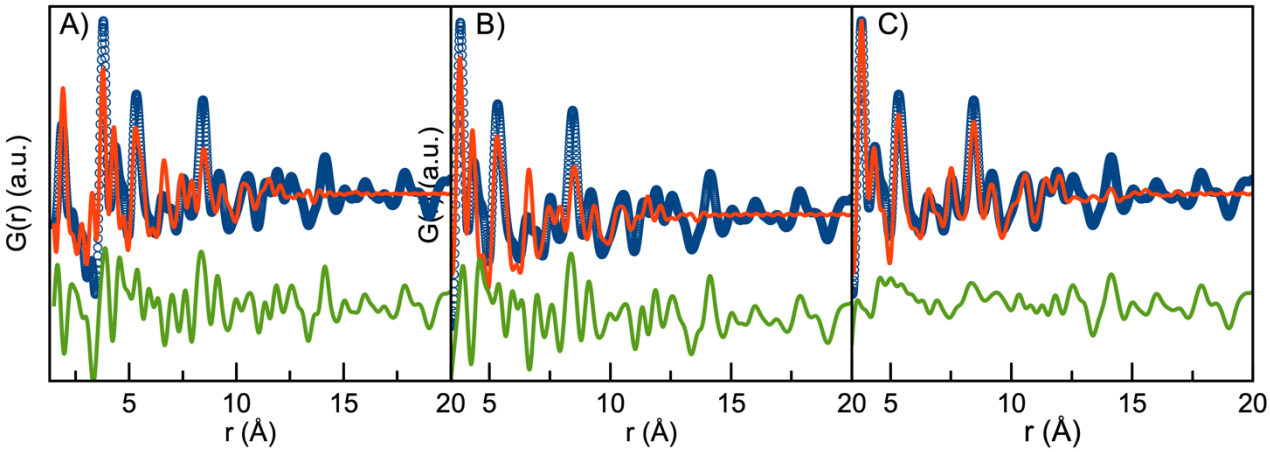

Fig. S17 PDF refinement of data collected at 13 min of reaction 100 °C and ambient pressure using H-Nb_2O_5 as the structural starting model. (A) Without refining niobium atomic positions including the first Nb-O peak. (B) Without the refinement of niobium atomic positions. (C) With the refinement of the niobium atomic positions.

Table S12 Refined values for data collected at 100 °C using a single [$NbCl_{6-x}O_x$] octahedra for the precursor data and a chain of two [$NbCl_{6-x}O_x$] octahedra for the data collected after 1 min of reaction (Figure 8B + C).

	Initial values	Precursor	Initial values	100 °C , 1 min
Nb0 position (x,y,z)	(1.45, 4.18, 7.85)	(1.44, 4.19, 7.92)	(15.3, 7.08, 5.47)	(15.3, 6.99, 5.45)
Nb1 position (x,y,z)			(14.5, 4.20, 7.79)	(14.5, 4.20, 7.83)
Data range		1.5 Å – 10 Å		1.5 Å – 10 Å
Data summation number		1 frame (5 s)		1 frame (5 s)
Number of refined parameters		10		7
Scale		0.49		0.32
R_w		0.27		0.52
wA		0.13		
wasym		15.0		
wlam		5.30		
wphi		0.76		
wr0		2.15		
wsig		0.53		

Table S13 Refined values for data collected after 13 min of reaction at 100 °C using ReO_3 as the structural starting model (Figure 8D).

	ReO_3	
	Initial values	**100 °C, 13 min**
Space group	*I* m -3	
Lattice par., a=b=c (Å)	7.4456(2)	7.5574(8)
Number of refined parameters		6
Data range		1.5 Å – 20 Å
R_w		0.57
Scale factor		0.32
U_{iso} Nb ($Å^{-2}$)		0.0089
U_{iso} O ($Å^{-2}$)		0.097
δ_2 ($Å^2$)		2.68
Sp-diameter (Å)		16.09

Table S14 Refined values for data collected after 13 min of reaction at 100 °C using $HNbO_3$ as the structural starting model (Figure S15).

	$HNbO_3$	
	Initial values	**100 °C , 13 min**
Space group	*I* m -3	
Lattice par., a=b=c (Å)	7.645(2)	7.56
Cell vol., V ($Å^3$)	446.82	
Number of refined parameters		6
Data range		1.5 Å – 20 Å
R_w		0.48
Scale factor		0.32
U_{iso} Nb ($Å^{-2}$)		0.0094
U_{iso} O ($Å^{-2}$)		0.041
δ_2 ($Å^2$)		1.20
Sp-diameter (Å)		16.50

Table S15 Refined values for data collected after 13 min of reaction at 100 °C using H-Nb_2O_5 as the structural starting model (Figure S16 A-C).

	H-Nb_2O_5			
	Initial values	**100 °C , 13 min (C)**	**100 °C , 13 min (C)**	**100 °C , 13 min (D)**
Space group	*P* 1 2/m 1			
Lattice par., a (Å)	21.153(7)	20.74	20.64	20.58
Lattice par., b (Å)	3.8233(5)	3.77	3.78	3.79
Lattice par., c (Å)	19.3560(50)	20.10	20.029	19.90
Lattice par., β (°)	119.80(2)	120.94	120.44	119.99
Cell vol., V (Å^3)	1358.4			
Number of refined parameters		8	8	35
Data range		1.5 Å – 20 Å	3.4 Å – 20 Å	3.4 Å – 20 Å
R_w		0.61	0.60	0.39
Scale factor		0.38	0.50	0.54
U_{iso} Nb (Å^{-2})		0.0009	0.0024	0.0017
U_{iso} O (Å^{-2})		0.0046	0.0029	0.0033
Sp-diameter (Å)		17.56	16.070	18.84

Atomic positions for H-Nb_2O_5						
	Initial values			**Refined values**		
Label	x (Å)	y (Å)	z (Å)	x (Å)	y (Å)	z (Å)
Nb1	0	0.2285(3)	0	0.000000	0.179043	0.000000
Nb2	0.5	0	0.5	0.500000	0.000000	0.500000
Nb3	0.16430(3)	0	0.00353(3)	0.165001	0.000000	0.017419
Nb4	0.23623(3)	0	0.23134(3)	0.248426	0.000000	0.232997
Nb5	0.30284(3)	0	0.45456(3)	0.292427	0.000000	0.483580
Nb6	0.36087(3)	0	0.04553(3)	0.357421	0.000000	0.050262
Nb7	0.43325(3)	0	0.27741(4)	0.451415	0.000000	0.271137
Nb8	0.56270(3)	0	0.09346(3)	0.532910	0.000000	0.092918
Nb9	0.62943(3)	0	0.32219(3)	0.636956	0.000000	0.307538
Nb10	0.09353(3)	0.5	0.20187(3)	0.105737	0.500000	0.210789
Nb11	0.15921(3)	0.5	0.42410(3)	0.168956	0.500000	0.440706
Nb12	0.70330(3)	0.5	0.12414(3)	0.705899	0.500000	0.141844
Nb13	0.77056(3)	0.5	0.35151(3)	0.770681	0.500000	0.349591
Nb14	0.89895(3)	0.5	0.16353(3)	0.905035	0.500000	0.181087
Nb15	0.96461(3)	0.5	0.38928(4)	0.961990	0.500000	0.390516

Ex situ experiment: Synthesis of niobium oxide nanoparticles ambient pressure and 100 °C

A synthesis similar to the *in situ* experiment was done in our home laboratory to produce particles for TEM and SAXS characterization, as well as *ex situ* PDF analysis.
Total scattering data of the as-prepared solution was measured for 50 hours on a Panalytical Empyrean Series 3 with an Ag-source (wavelength of 0.56 Å), equipped with a Galipix detector. Background scattering was collected in the same way with a capillary filled with pure benzyl alcohol. The total scattering data was Fourier Transformed to obtain the PDF using PDFgetX3.[4] The following parameters were used for the data reduction: : Q_{min}=1.3 Å^{-1}, Q_{max}=13.5 Å^{-1}, $Q_{maxinst}$=18.4 Å^{-1} and rpoly=0.9.
TEM images were collected on a Tecnai T20 G2 200 kV TEM at the National Center for Micro-and Nanofabrication at the Technical University of Denmark.
SAXS and WAXS data were measured on a SAXSLab instrument (JJ-X-ray, Denmark) at the Niels Bohr Institute, University of Copenhagen. The instrument is equipped with a 100XL + microfocus sealed X-ray tube from Rigaku that produces a photon beam with a wavelength of 1.54 Å and a 2D 300 K Pilatus detector from Dectris. The 2D scattering patterns were azimuthally averaged, normalised for sample transmission, primary beam intensity and exposure time and corrected for detector inhomogeneities using Saxsgui. Scattering patterns from an empty quartz capillary and a capillary with benzyl alcohol were measured as backgrounds. The background subtraction was done in a Python script. The scattering angles 2θ were converted to a Q-scale: $Q = \frac{4\pi}{\lambda}\sin\left(\frac{2\theta}{2}\right)$. Simulated SAXS formfactor models were calculated in Diffpy-CMI, which uses SASVIEW functions, with a monodisperse sphere model.

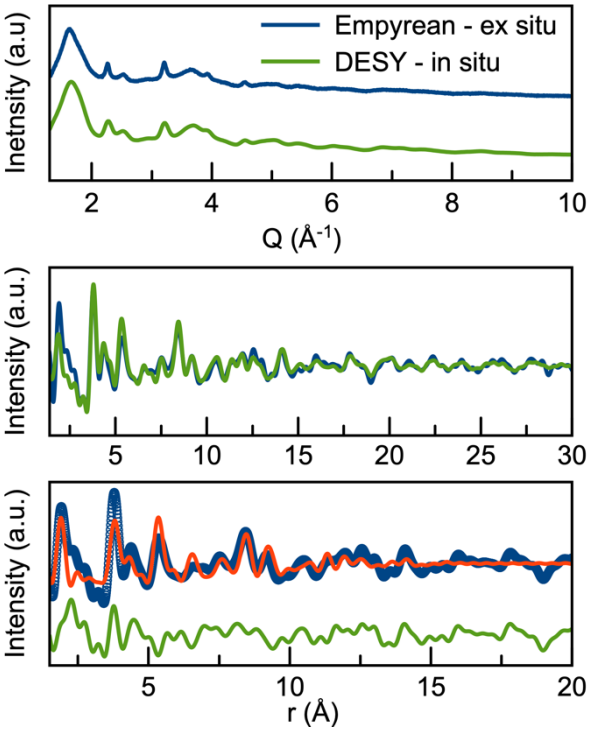

Fig. S18 Top: Total scattering data collected after 13 min of reaction at 100 °C and ambient pressure at the Beamline P.01. DESY (in-situ) compared an experiment performed in our home laboratory. Middle: PDFs obtained for the two datasets. Bottom: Structural refinement on PDF collected for the ex situ experiment using ReO_3 as the structural starting model.

Table S16 Refined values obtained for data collected on Panalytical Empyrean using ReO_3 as the structural starting model (Figure S17).

	ReO_3	
	Initial values	**100 °C, 13 min *ex situ***
Space group	*I* m -3	
Lattice par., a=b=c (Å)	7.4456(2)	7.56
Number of refined parameters		6
Data range		1.5 Å – 20 Å
Q_{damp}, Q_{max}, Q_{min}		0.011, 1.3 Å, 13.5 Å
R_w		0.61
Scale factor		0.019
U_{iso} Nb ($Å^{-2}$)		0.0096
U_{iso} O ($Å^{-2}$)		0.11
Sp-diameter (Å)		17.21
δ_2 ($Å^2$)		3.46

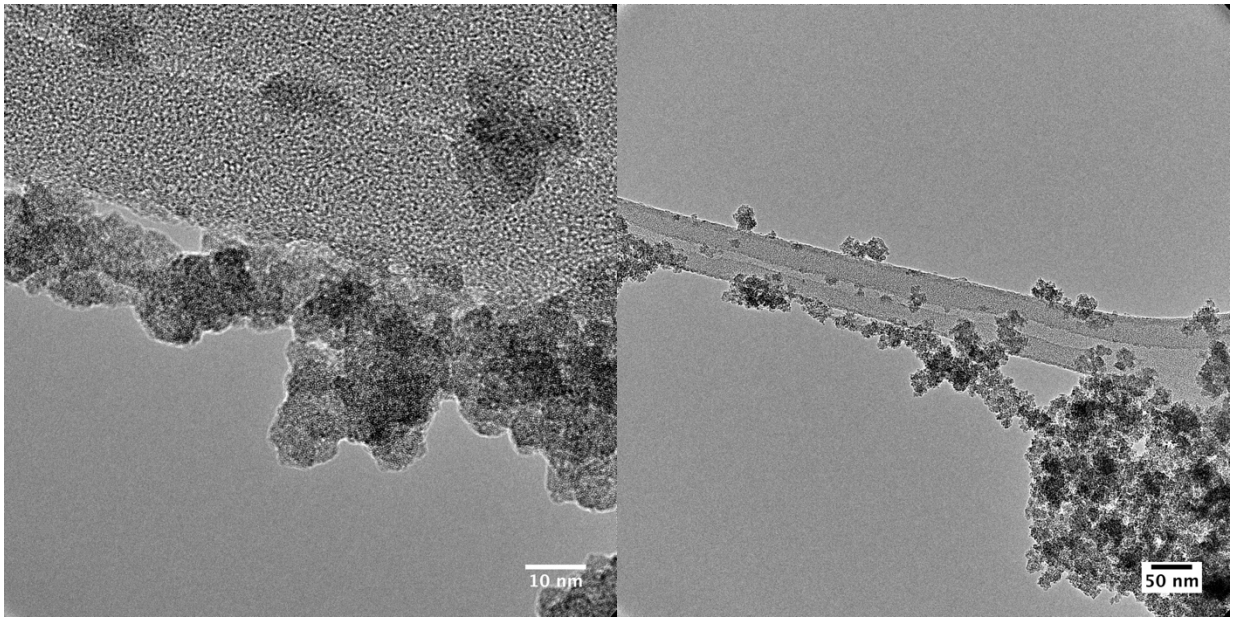

Fig. S19 TEM of particles formed in the *ex situ* set-up at 100 °C.

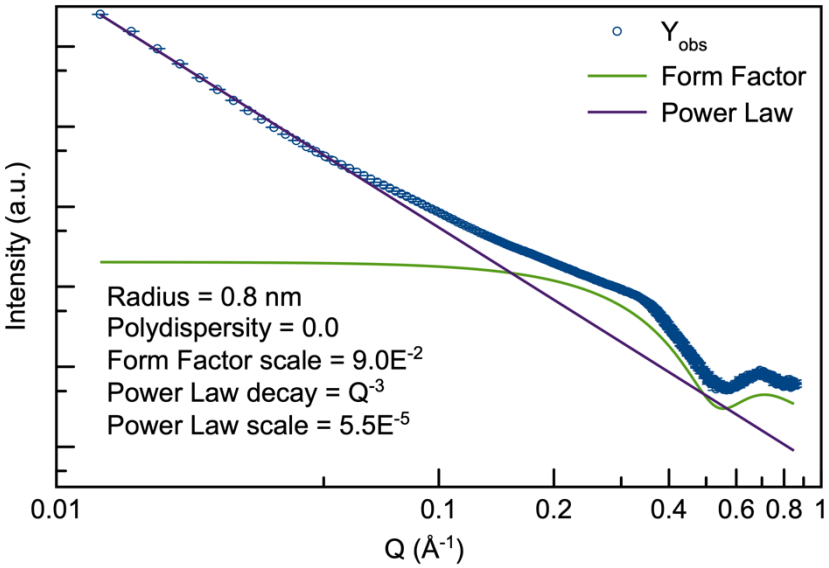

Fig. S20 SAXS data obtained for the as-synthesized niobium oxide nanoparticles. A calculated SAXS form factor assuming a spherical shape and a particle radius of 0.8 nm gives a good description of the data in the high Q-regime of the data. A power law can describe the aggregation of particles into a two-dimensional network, seen in the low Q-regime.

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2. P. Juhas, C. L. Farrow, X. H. Yang, K. R. Knox and S. J. L. Billinge, *Acta Cryst.*, 2015, **71**, 562-568.
3. M. Zobel, R. B. Neder and S. A. J. Kimber, *Science*, 2015, **347**, 292-294.
4. P. Juhas, T. Davis, C. L. Farrow and S. J. L. Billinge, *J. Appl. Cryst.*, 2013, **46**, 560-566.