Stabilizing tetragonal ZrO_2 nanocrystallites in solvothermal synthesis

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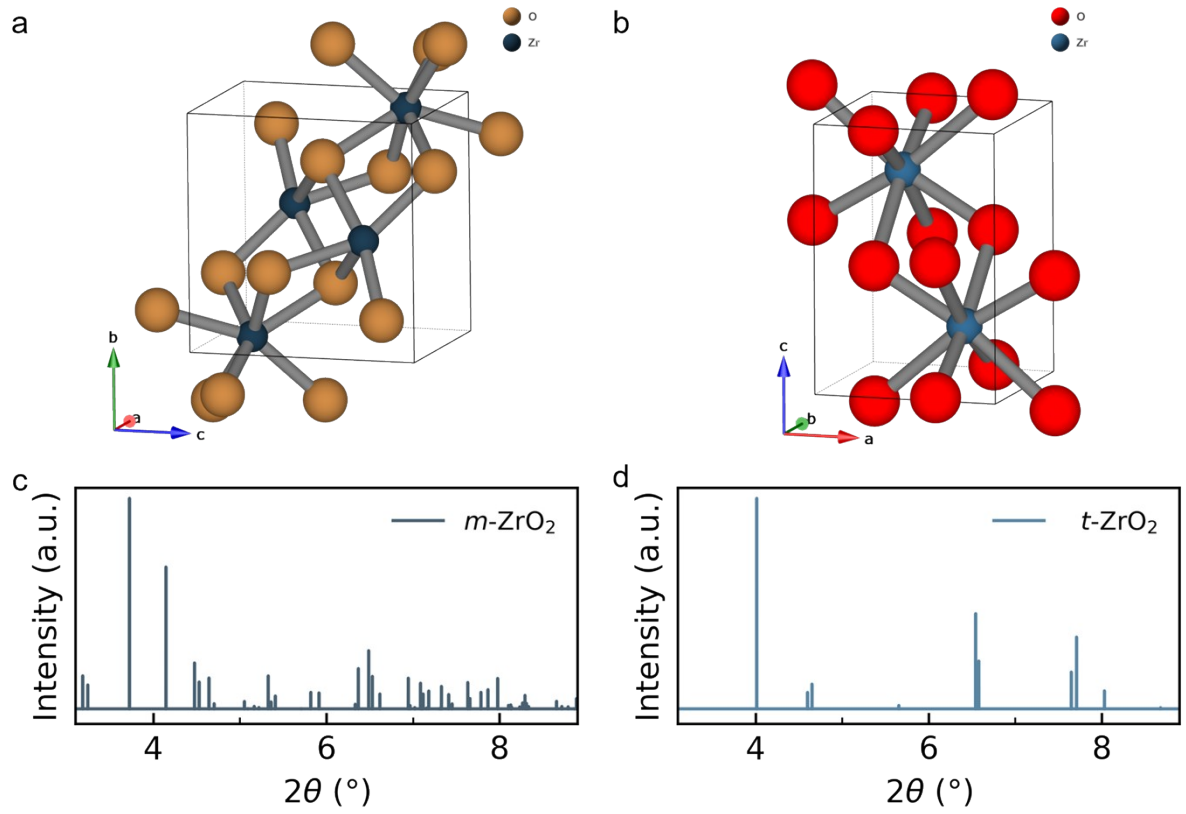

Figure S1. Illustration of a) monoclinic ZrO_2 (*m*-ZrO_2) and b) tetragonal ZrO_2 (*t*-ZrO_2) crystal structures and c,d) their calculated PXRDs.

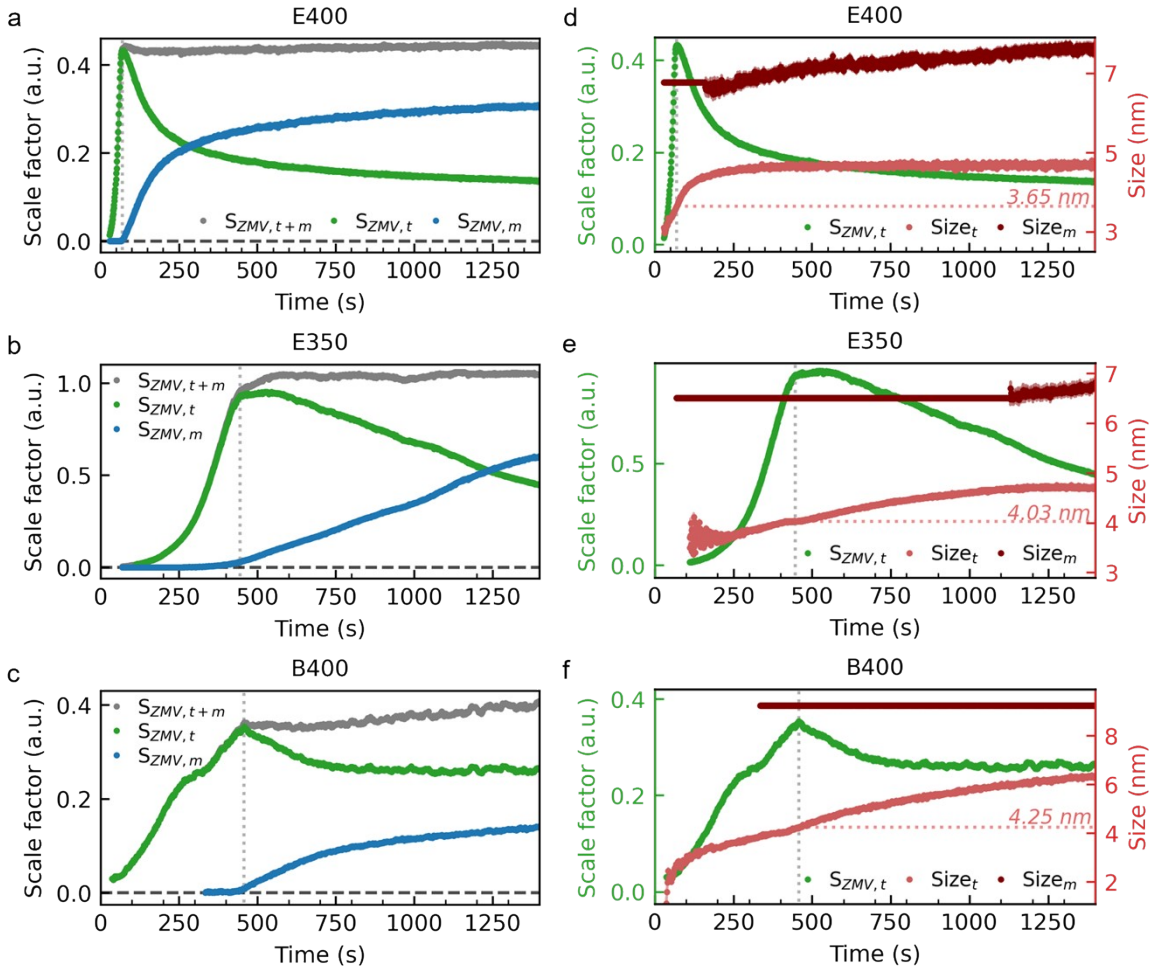

Figure S2. a,b,c) Refined scale factors weighted with mass and unit cell volume (ZMV) from PXRD refinements of *t*-ZrO_2, *m*-ZrO_2 and *t*-ZrO_2+*m*-ZrO_2 for a) E400, b) E350 and c) B400. c,d) ZMV scale factor and crystallite size of *t*-ZrO_2 for d) E400, e) E350 and f) B400. Note that the crystallite size of *m*-ZrO_2 was fixed in the initial part of each experiment as indicated by the constant sizes, when *m*-ZrO_2 phase contribution is low, to ensure robust refinement. Gray dashed lines mark the maximum of the tetragonal scale factor and onset of *t*→*m* transformation.

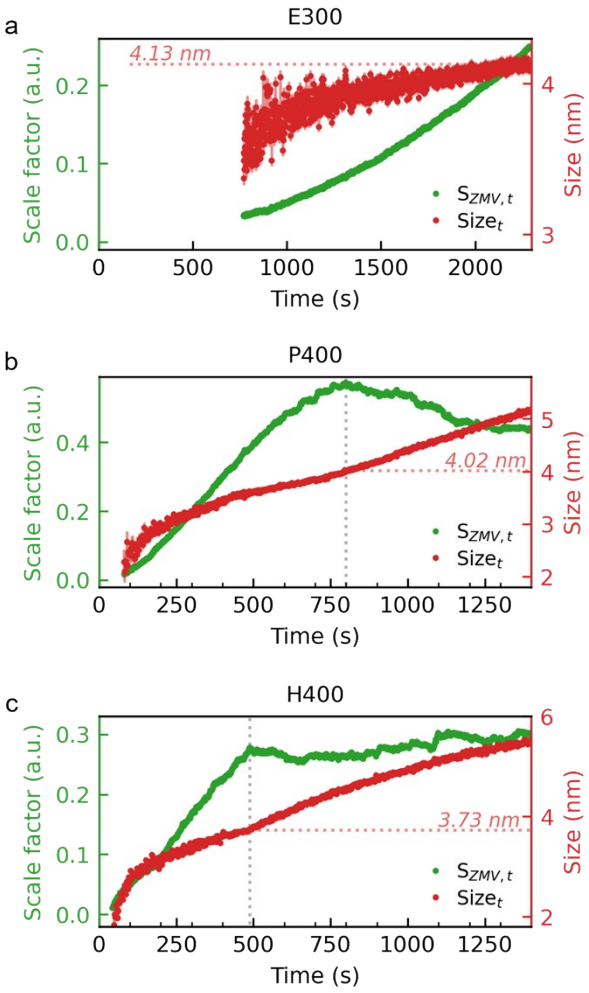

Figure S3. Refined scale factors weighted with mass and unit cell volume (ZMV) and crystallite size from PXRD refinements of *t*-ZrO_2 for a) E300, b) P400 and c) H400.

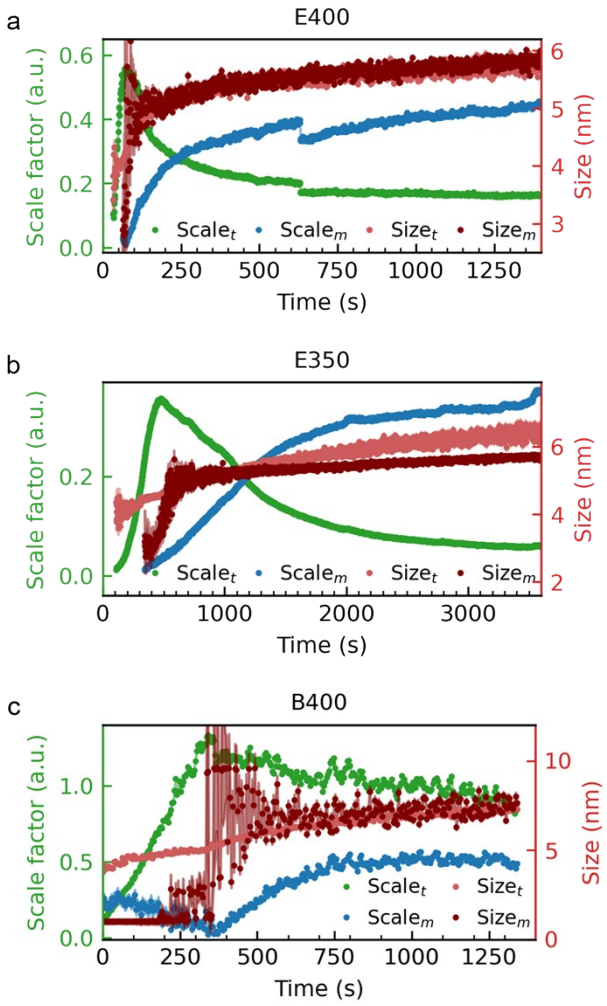

Figure S4. Refined scale factors and coherent domain sizes from PDF refinement of *t*-ZrO_2 and *m*-ZrO_2 for a) E400, b) E350 and c) B400. Note that because of very little phase contribution of *m*-ZrO_2, two frames were summed for B400, thus giving 4 s exposure per frame for B400 compared to 2 s for E400 and E350.

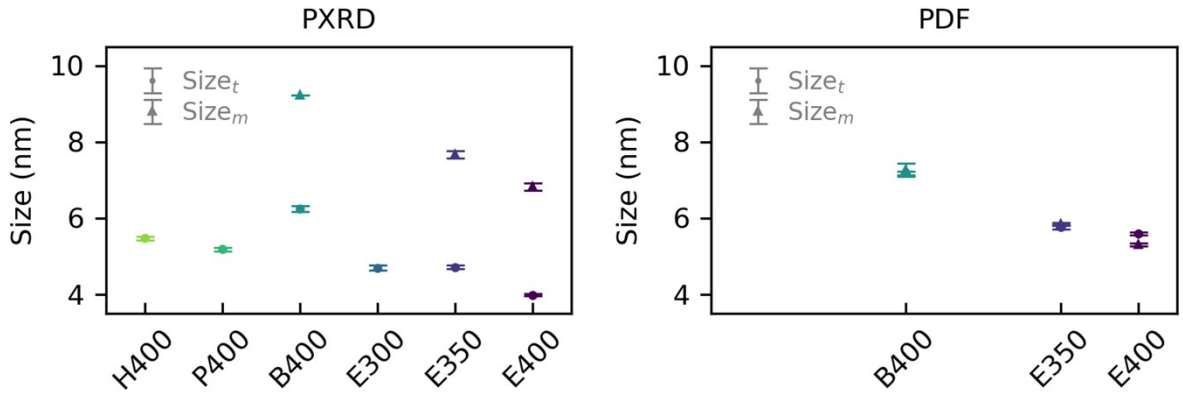

Figure S5. a) Refined crystallite sizes from PXRD and b) refined coherent domain sizes from PDF after 1400 s of synthesis time. Dots and triangles indicate crystallite sizes of *t*-ZrO_2 and *m*-ZrO_2 phases, respectively.

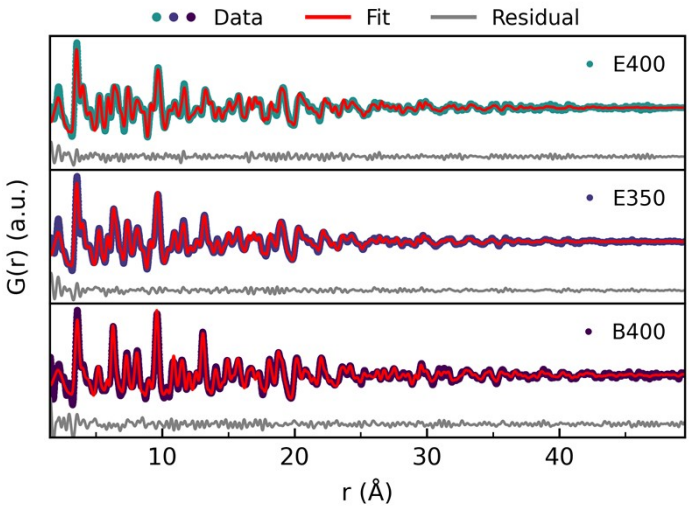

Figure S6. Refined PDFs of E400, E350 and B400 with both *t*-ZrO_2 and *m*-ZrO_2 phases. Note that because of very little phase contribution of *m*-ZrO_2, two 2 s frames were summed for B400, thus giving a 4 s exposure per refined frame for B400.

Note S1. Generally, the sizes estimated from PDF analysis are larger than those from PXRD analysis (Figure S5). This is not too surprising, and it is often seen in studies directly comparing sizes obtained from Rietveld refinements on PXRD data and PDF refinements on the same, but Fourier transformed real-space data.[1,2] From the refinement results, the two methods seem to disagree on the relative crystallite sizes of *t*-ZrO_2 and *m*-ZrO_2. From PXRD refinement, the sizes of *m*-ZrO_2 are more than two nanometers larger than of *t*-ZrO_2, whereas PDF refinements yield similar sizes for the two phases after 1400 s. The crystallite sizes from PXRD refinements are determined from Bragg-peak broadening, and since the data for this study were collected in total scattering geometry, the non-ideal Q-space resolution, $\frac{dQ}{Q}$, dictates a significant instrumental broadening. This coupled with low symmetry of the *m*-ZrO_2 crystal structure and thus unresolved peak overlap and low phase contribution of *m*-ZrO_2, can all be contributing factors to why PXRD refinements yield much larger sizes than PDF. Evidently, the structural signal in the PDFs of B400, E400 and E350 do not extend out to 70-90 Å, as the PXRD sizes suggest they should.

Table S1. List of refined parameters from Rietveld refinements after 1400 s (~23 min) for all datasets. Note that some parameters have been refined at specific frames and fixed during sequential refinements. These are marked with symbols and explanation given below table.

Experiment ID	**E300**	**E350**		**E400**		**B400**		**P400**	**H400**
Solvent	Ethanol	Ethanol		Ethanol		Butan-1-ol		Pentan-1-ol	Hexan-1-ol
Temperature	300 °C	350 °C		400 °C		400 °C		400 °C	400 °C
Pressure	25 MPa	25 MPa		25 MPa		25 MPa		25 MPa	25 MPa
$[Zr^{4+}]$	1.0 M	1.0 M		1.0 M		1.0 M		1.0 M	1.0 M
Exposure	1 s	1 s		1 s		2 s		2 s	2 s
Time after heating	1400 s	1400 s		1400 s		1400 s		1400 s	1400 s
Frame	1076	1459		1469		699		744	759
Zero displacement	-0.0136(7)*	-0.0108(8)*		-0.0221(7)*		-0.0100(10)*		-0.0124(8)*	-0.0133(8)*
Crystal structure	*t*-ZrO_2	*t*-ZrO_2	*m*-ZrO_2	*t*-ZrO_2	*m*-ZrO_2	*t*-ZrO_2	*m*-ZrO_2	*t*-ZrO_2	*t*-ZrO_2
Scale factor (a.u.)	$5.60(2)\cdot10^{-6}$	$2.645(16)\cdot10^{-5}$	$8.46(7)\cdot10^{-6}$	$8.02(6)\cdot10^{-6}$	$4.29(3)\cdot10^{-6}$	$1.61(10)\cdot10^{-5}$	$2.05(2)\cdot10^{-6}$	$2.640(12)\cdot10^{-5}$	$1.750(7)\cdot10^{-5}$
Weight fractions (%)	100	42.8(2)	57.2(2)	31.0(2)	69.0(2)	34.8(3)	65.2(3)	100	100
a (Å)	3.6216(4)	3.625(5)	5.1884(6)*	3.638(6)	5.2035(7)*	3.6006(4)	5.153(2)	3.609(4)	3.642(4)
b (Å)	3.6216(4)	3.625(5)	5.2229(6)*	3.638(6)	5.2406(7)*	3.6006(4)	5.172(3)	3.609(4)	3.642(4)
c (Å)	5.2131(12)	5.2265(14)	5.3646(6)*	5.2491(18)	5.3813(7)*	5.1847(13)	5.338(2)	5.1876(13)	5.2360(13)
α (°)	90	90	90	90	90	90	90	90	90
β (°)	90	90	99.156(14)*	90	99.14(11)*	90	99.27(4)*	90	90
γ (°)	90	90	90	90	90	90	90	90	90
$z_{O,Zr}$	0.0569(6)*	0.0524(7)$^{\phi}$	-	0.0548(6)‡	-	0.0500(12)*	-	0.0507(10)*	0.0506(9)*
$B_{iso,Zr}$ (Å^2)	1.087(13)*	0.920(14)$^{\phi}$	0.458(14)*	1.012(12)‡	0.491(16)*	0.66(2)*	0.39(6)*	0.696(16)*	0.736(16)*
$B_{iso,O}$ (Å^2)	0.5$^{\#}$	0.5$^{\#}$	0.5$^{\#}$	0.5$^{\#}$	0.5$^{\#}$	0.5$^{\#}$	0.5$^{\#}$	0.5$^{\#}$	0.5$^{\#}$
Crystallite size (nm)	3.98(3)	4.71(5)	6.82(10)$^{+}$	4.69(6)	7.67(9)$^{\natural}$	6.24(8)	9.2(5)*	5.18(5)	5.47(5)

$^{\#}$ Fixed in all refinements.

* Refined at final frame and fixed in sequential refinement.

$^{\phi}$ Refined at frame 600 (most *t*-ZrO_2 phase) and fixed in sequential refinement.

$^{+}$ Fixed below frame 1190 to ensure robust sequential refinement. Refined freely above frame 1190.

‡ Refined at frame 140 (most *t*-ZrO_2 phase) and fixed in sequential refinement.

$^{\natural}$ Fixed below frame 280 to ensure robust sequential refinement. Refined freely above frame 280.

Table S2. List of refined parameters from PDF refinements after 1400 s (~23 min) for all datasets. Note that some parameters have been refined at specific frames and fixed during sequential refinements. These are marked with symbols and explanation given below table.

Experiment ID	**E350**		**E400**		**B400**	
Solvent	Ethanol		Ethanol		Butan-1-ol	
Temperature	350 °C		400 °C		400 °C	
Pressure	25 MPa		25 MPa		25 MPa	
$[Zr^{4+}]$	1.0 M		1.0 M		1.0 M	
Exposure	1 s		1 s		24 s	
Time after heating	1400 s		1400 s		1400 s	
Frame	1459		1469		699	
Crystal structure	*t*-ZrO_2	*m*-ZrO_2	*t*-ZrO_2	*m*-ZrO_2	*t*-ZrO_2	*m*-ZrO_2
Scale factor (a.u.)	$1.460(8)\cdot10^{-1}$	$2.477(16)\cdot10^{-1}$	$1.6276(14)\cdot10^{-1}$	$4.451(3)\cdot10^{-1}$	$9.63(7)\cdot10^{-2}$	$4.23(12)\cdot10^{-2}$
Weight fractions (%)	37.1(2)	62.9(2)	26.8(2)	73.2(2)	68.2(6)	31.8(6)
a (Å)	3.6268(3)	5.1921(6)*	3.6465(5)	5.2138(7)*	3.6045(3)	5.162(2)
b (Å)	3.6268(3)	5.2316(6)*	3.6465(5)	5.2579(7)*	3.6045(3)	5.198(2)
c (Å)	5.2355(10)	5.3684(5)*	5.2550(17)	5.3961(7)*	5.1992(11)	5.332(2)
α (°)	90	90	90	90	90	90
β (°)	90	99.297(10)*	90	99.30(4)*	90	99.30(4)*
γ (°)	90	90	90	90	90	90
$z_{O,Zr}$	0.0539(12)*	-	0.0548(6)*	-	0.0622(17) *	-
$B_{iso,Zr}$ ($Å^2$)	0.819(12)*	0.404(9)*	1.0*	0.422(13)*	0.63(2)*	0.28(4)*
$B_{iso,O}$ ($Å^2$)	3.58(11)*	3.58(11)*	3.58(11)*	3.58(11)*	3.58(11)*	3.58(11)*
Coherent domain size (nm)	5.60(4)	5.284(19)[+]	5.77(6)	5.841(19)[¤]	7.27(7)	8.7(4) *

* Refined at final frame and fixed in sequential refinement.

Table S3. Input parameters and R_w for fit of dimer model to the room temperature PDF of Zr propoxide in ethanol. Hydrogen atoms have not included in the model, and oxygen atoms are a proxy of RO^-/ROH molecules.

Dimer model			
Parameter	Value		
Q_{damp}	0.0316		
R_w	0.661		
Atom	x coordinate	y coordinate	z coordinate
Zr(1)	5.744	2.944	2.095
Zr(2)	6.573	-0.404	1.133
O(1)	4.961	1.096	1.184
O(2)	4.134	4.443	2.139
O(3)	5.194	2.297	3.884
O(4)	6.295	3.590	0.307
O(5)	7.358	1.439	2.048
O(6)	6.532	4.789	3.009
O(7)	6.024	-1.059	2.919
O(8)	8.203	-1.524	1.223
O(9)	5.592	-1.899	0.284
O(10)	7.122	0.249	-0.654

Table S4. Input parameters and R_w for fit of trimer model to the room temperature PDF of Zr propoxide in ethanol. Hydrogen atoms have not included in the model, and oxygen atoms are a proxy of RO^-/ROH molecules.

Trimer model			
Parameter	Value		
Q_{damp}	0.0316		
R_w	0.672		
Atom	x coordinate	y coordinate	z coordinate
Zr(1)	5.744	2.944	2.095
Zr(2)	6.573	-0.404	1.133
Zr(3)	4.920	6.295	3.046
O(1)	3.292	7.418	2.946
O(2)	5.471	6.937	1.256
O(3)	5.194	2.297	3.884
O(4)	5.903	7.794	3.886
O(5)	4.961	1.096	1.184
O(6)	4.134	4.443	2.139
O(7)	6.295	3.590	0.307
O(8)	7.358	1.439	2.048
O(9)	6.532	4.789	3.009
O(10)	4.367	5.656	4.837
O(11)	6.024	-1.059	2.919
O(12)	8.203	-1.524	1.223
O(13)	5.592	-1.899	0.284
O(14)	7.122	0.249	-0.654

S2 References

1 R. S. Christensen, M. Kløve, M. Roelsgaard, S. Sommer and B. B. Iversen, *Nanoscale*, 2021, **13**, 12711–12719.

2 M. Roelsgaard, M. Kløve, R. S. Christensen, A. D. Bertelsen, N. L. N. Broge, I. Kantor, D. R. Sørensen, A.-C. Dippel, S. Banerjee, M. v. Zimmermann, P. Glaevecke, O. Gutowski, M. R. V. Jørgensen and B. B. Iversen, *J. Appl. Crystallogr.*