

# Stabilizing tetragonal ZrO<sub>2</sub> nanocrystallites in solvothermal synthesis

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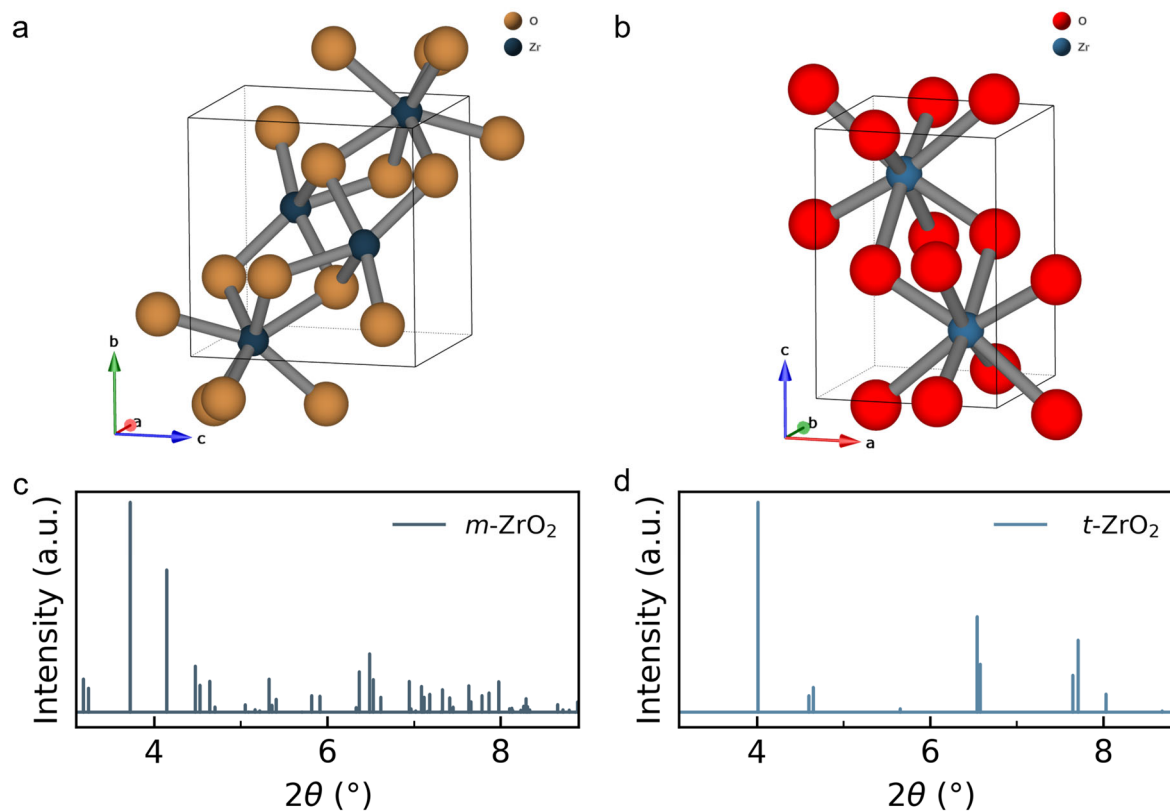
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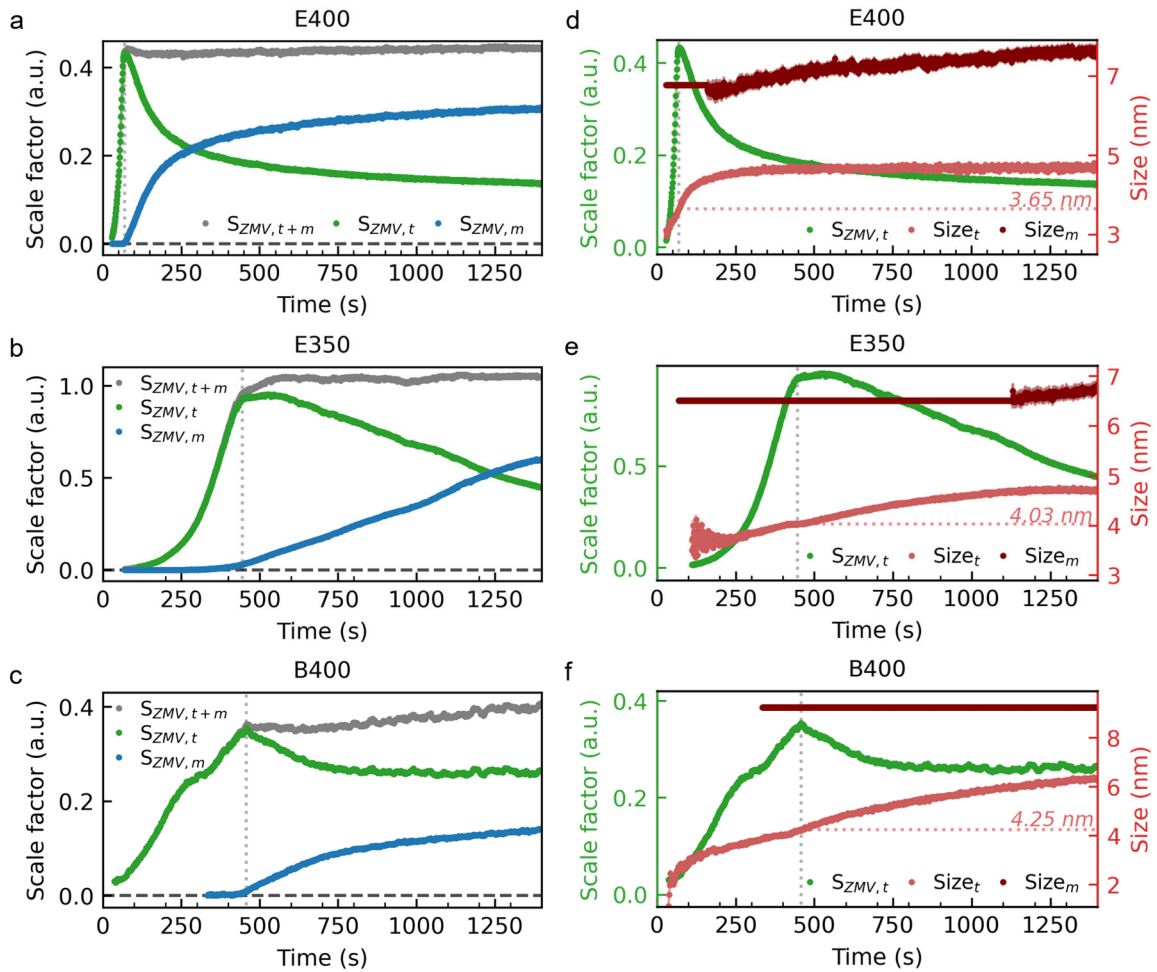
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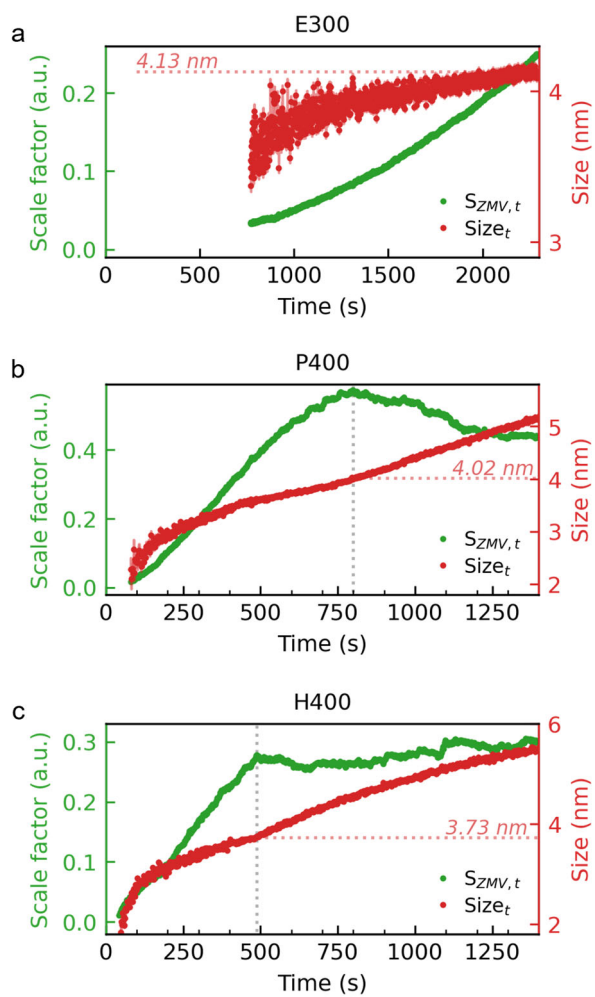
## S1 Supporting figures and text



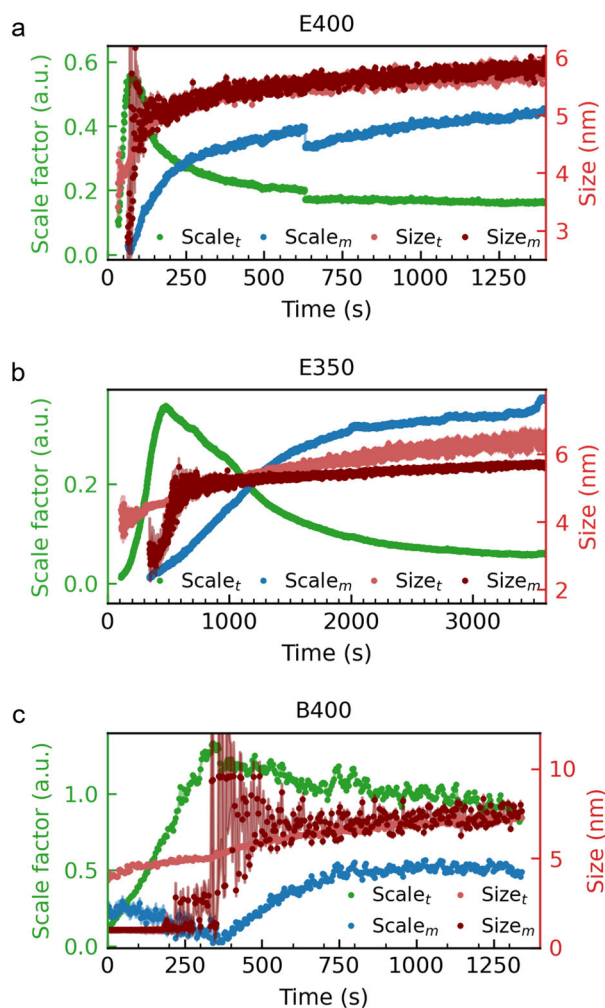
**Figure S1.** Illustration of a) monoclinic ZrO<sub>2</sub> (*m*-ZrO<sub>2</sub>) and b) tetragonal ZrO<sub>2</sub> (*t*-ZrO<sub>2</sub>) crystal structures and c,d) their calculated PXRDs.



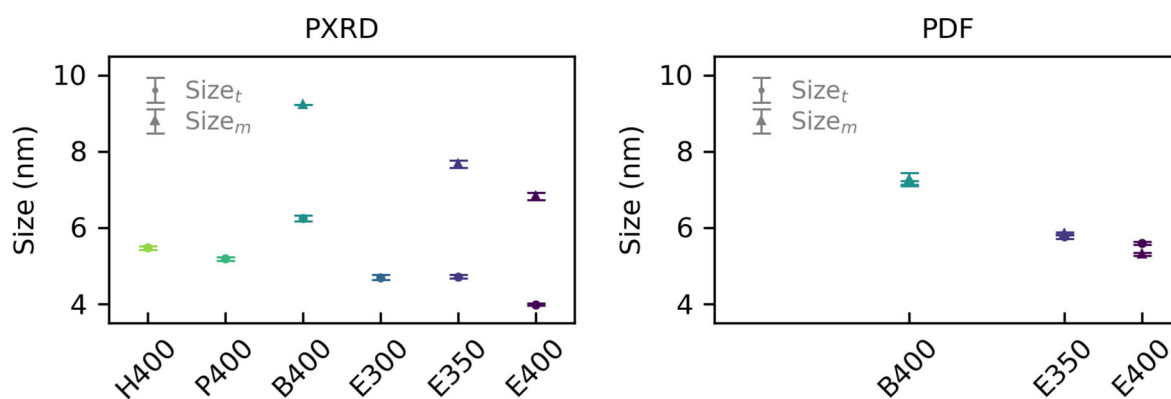
**Figure S2.** a,b,c) Refined scale factors weighted with mass and unit cell volume (ZMV) from PXRD refinements of  $t$ -ZrO<sub>2</sub>,  $m$ -ZrO<sub>2</sub> and  $t$ -ZrO<sub>2</sub>+ $m$ -ZrO<sub>2</sub> for a) E400, b) E350 and c) B400. c,d) ZMV scale factor and crystallite size of  $t$ -ZrO<sub>2</sub> for d) E400, e) E350 and f) B400. Note that the crystallite size of  $m$ -ZrO<sub>2</sub> was fixed in the initial part of each experiment as indicated by the constant sizes, when  $m$ -ZrO<sub>2</sub> phase contribution is low, to ensure robust refinement. Gray dashed lines mark the maximum of the tetragonal scale factor and onset of  $t \rightarrow m$  transformation.



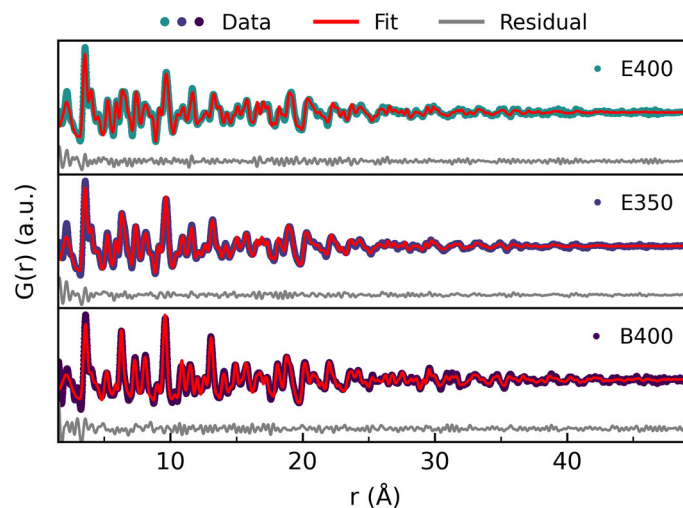
**Figure S3.** Refined scale factors weighted with mass and unit cell volume (ZMV) and crystallite size from PXRD refinements of  $t\text{-ZrO}_2$  for a) E300, b) P400 and c) H400.



**Figure S4.** Refined scale factors and coherent domain sizes from PDF refinement of *t*-ZrO<sub>2</sub> and *m*-ZrO<sub>2</sub> for a) E400, b) E350 and c) B400. Note that because of very little phase contribution of *m*-ZrO<sub>2</sub>, 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<sub>2</sub> and *m*-ZrO<sub>2</sub> phases, respectively.



**Figure S6.** Refined PDFs of E400, E350 and B400 with both  $t$ -ZrO<sub>2</sub> and  $m$ -ZrO<sub>2</sub> phases. Note that because of very little phase contribution of  $m$ -ZrO<sub>2</sub>, 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.<sup>1,2</sup> From the refinement results, the two methods seem to disagree on the relative crystallite sizes of  $t$ -ZrO<sub>2</sub> and  $m$ -ZrO<sub>2</sub>. From PXRD refinement, the sizes of  $m$ -ZrO<sub>2</sub> are more than two nanometers larger than of  $t$ -ZrO<sub>2</sub>, 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<sub>2</sub> crystal structure and thus unresolved peak overlap and low phase contribution of  $m$ -ZrO<sub>2</sub>, 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 <sup>4+</sup> ]	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 <sub>2</sub>	t-ZrO <sub>2</sub>	t-ZrO <sub>2</sub>	t-ZrO <sub>2</sub>	t-ZrO <sub>2</sub>	t-ZrO <sub>2</sub>
Scale factor (a.u.)	5.60(2)·10 <sup>-6</sup>	2.645(16)·10 <sup>-5</sup>	8.46(7)·10 <sup>-6</sup>	4.29(3)·10 <sup>-6</sup>	2.05(2)·10 <sup>-6</sup>	1.750(7)·10 <sup>-5</sup>
Weight fractions (%)	100	42.8(2)	57.2(2)	69.0(2)	65.2(3)	100
a (Å)	3.6216(4)	3.625(5)	5.1884(6)*	3.638(6)	5.2035(7)*	3.642(4)
b (Å)	3.6216(4)	3.625(5)	5.2229(6)*	3.638(6)	5.2406(7)*	3.642(4)
c (Å)	5.2131(12)	5.2265(14)	5.3646(6)*	5.2491(18)	5.3813(7)*	5.2360(13)
α (°)	90	90	90	90	90	90
β (°)	90	90	99.156(14)*	99.14(11)*	99.27(4)*	90
γ (°)	90	90	90	90	90	90
Z <sub>0,Zr</sub>	0.0569(6)*	0.0524(7) <sup>‡</sup>	-	0.0548(6) <sup>‡</sup>	-	0.0507(10)*
B <sub>iso,Zr</sub> (Å <sup>2</sup> )	1.087(13)*	0.920(14) <sup>‡</sup>	0.458(14)*	1.012(12) <sup>‡</sup>	0.491(16)*	0.696(16)*
B <sub>iso,O</sub> (Å <sup>2</sup> )	0.5 <sup>#</sup>	0.5 <sup>#</sup>	0.5 <sup>#</sup>	0.5 <sup>#</sup>	0.5 <sup>#</sup>	0.5 <sup>#</sup>
Crystallite size (nm)	3.98(3)	4.71(5)	6.82(10) <sup>‡</sup>	4.69(6)	7.67(9) <sup>‡</sup>	5.47(5)

<sup>#</sup> Fixed in all refinements.

\* Refined at final frame and fixed in sequential refinement.

<sup>‡</sup> Refined at frame 600 (most t-ZrO<sub>2</sub> phase) and fixed in sequential refinement.

<sup>†</sup> Refined at frame 1190 to ensure robust sequential refinement. Refined freely above frame 1190.

<sup>‡</sup> Refined at frame 140 (most t-ZrO<sub>2</sub> phase) and fixed in sequential refinement.

<sup>‡</sup> Fixed below frame 280 to ensure robust sequential refinement. Refined freely above frame 280.



**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<sup>-</sup>/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<sup>-</sup>/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. Glaevec, O. Gutowski, M. R. V. Jørgensen and B. B. Iversen, *J. Appl. Crystallogr.*