ONLINE SUPPORTING INFORMATION

for

Synthesis, structure and magnetic properties of nanocrystalline $YMnO_3$

Kristin Bergum,[†] Hiroshi Okamoto,[‡] Helmer Fjellvåg,[‡] Tor Grande,[†] Mari-Ann Einarsrud[†]
and Sverre M. Selbach[†,*]

[†]*Department of Materials Science and Engineering,*
Norwegian University of Science and Technology, N-7491 Trondheim, Norway.
[*]*Corresponding author. E-mail: selbach@material.ntnu.no*

[‡]*Centre for Materials Science and Nanotechnology, Department of Chemistry,*
University of Oslo, P.O. Box 1033N-0315 Oslo, Norway

Additional results from Rietveld refinements.

Oxygen positions in Figure S1 a)-f) refined for average crystallite sizes larger than 50 nm obtained by synthesis route 1 show size-dependent trends below 120 nm, even though deviations in lattice parameters only occurs below 80 nm average crystallite size. The tilting of the MnO_5 bipyramids with respect to the *ab*-plane, φ_{planar}, shows a small decrease with decreasing size, Figure S1 g). φ_{planar} was calculated from $\tan\varphi_{\text{planar}} = a^{-1}c\sqrt{3}\left(1/2 - \mathrm{O3}_z + \mathrm{O4}_z\right)$, where the atomic positions are given in Table S1. The refined oxygen positions all point to more distorted polyhedra with decreasing size. Neither the bipyramid tilting with respect to the polar *c*-axis (Figure S1 g)), φ_{apical}, nor the Mn positions (Figure S1 h)) show any evident size-dependence above 50 nm. φ_{apical} was calculated from from $\tan\varphi_{\text{apical}} = ac^{-1}\left[\left(1 - \mathrm{O1}_x - \mathrm{O2}_x\right)/\left(1/2 + \mathrm{O1}_z - \mathrm{O2}_z\right)\right]$. A typical Rietveld fit of a diffractogram of a two-phase powder from synthesis route 1 (see experimental section of paper) calcined for 12 h at 900 °C, where the hexagonal phase has an estimated crystallite size of 64 ± 2 nm is shown in Figure S2.

Table S1. Atomic positions in $YMnO_3$ with space group $P6_3cm$

Atom	x	y	z
Y1	0	0	0.273
Y2	1/3	2/3	0.233
Mn	0.328	0	0
O1	0.307	0	0.163
O2	0.643	0	0.336
O3	0	0	0.474
O4	1/3	2/3	0.017

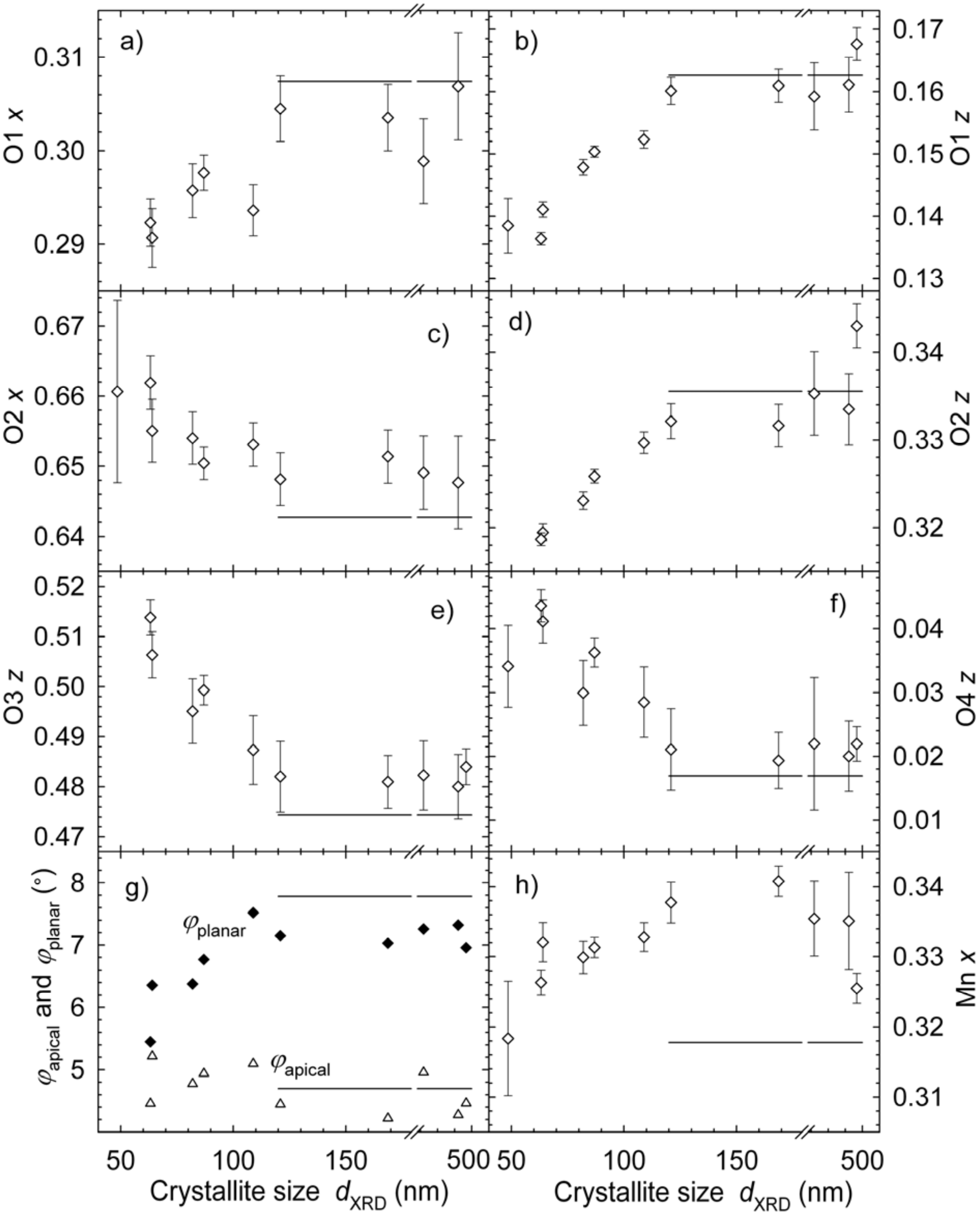

Figure S1 Atomic positions for average crystallite sizes larger than 50 nm, from synthesis route 1. a)-f) Oxygen positions. g) Tilting of the MnO_5 trigonal bipyramids with respect to the *ab*-plane, φ_{planar}, and to the polar *c*-axis, φ_{apical}. h) Mn positions. The horizontal lines are bulk values taken from Gibbs *et al.*, *Phys Rev. B*, 2011, **83**, 094111.

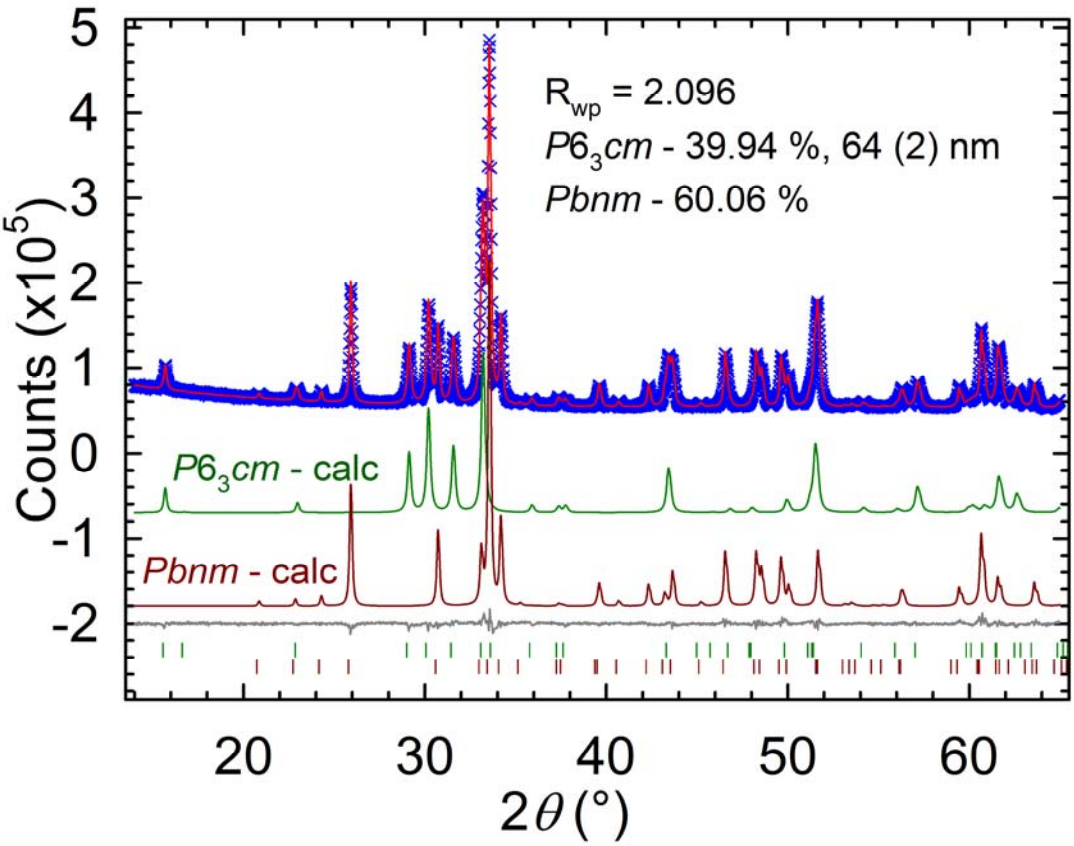

Figure S2 Rietveld fit (red line) to a diffractogram (blue crosses) of powder from synthesis route 1 calcined for 12 h at 900 °C. The ticks marking the positions of Bragg reflections from the hexagonal $P6_3cm$ phase and the calculated diffraction pattern of this phase is shown in dark green. The corresponding ticks and calculated pattern of the orthorhombic *Pbnm* phase is shown in dark red. The refined average crystallite size of the hexagonal phase is 64 ± 2 nm.

XRD of post-annealed 20 nm crystallites for magnetic measurements

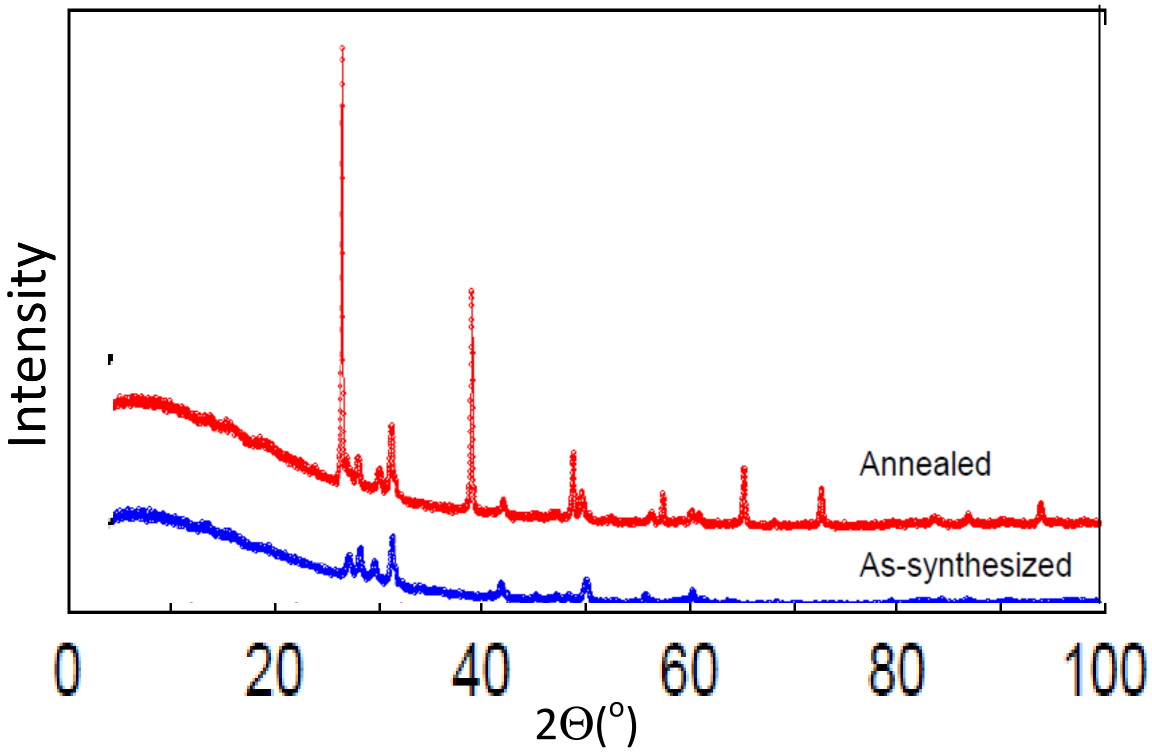

Figure S3 XRD patterns of post-annealed (upper) and as-synthesized (lower) $YMnO_3$ with average crystallite size 20 nm. The new reflections in the pattern of the post-annealed powder sample are from residual $KClO_3$ and KCl. There was no detectable change in the $YMnO_3$ structure.