Electronic Supplementary Material (ESI) for Dalton Transactions.

Hydrothermal synthesis of hexagonal $YMnO_3$ and $YbMnO_3$ below 250 °C. Supporting Information

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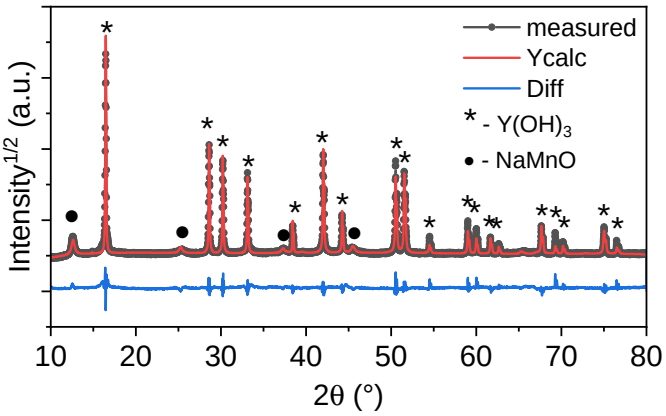

Figure 1: XRD pattern of the product of the reaction between Y_2O_3 and Mn_2O_3 in 12.5 M NaOH at 240 °C (reaction Y17). Only $Y(OH)_3$ and $NaMn_2O_{6-x}$ are present.

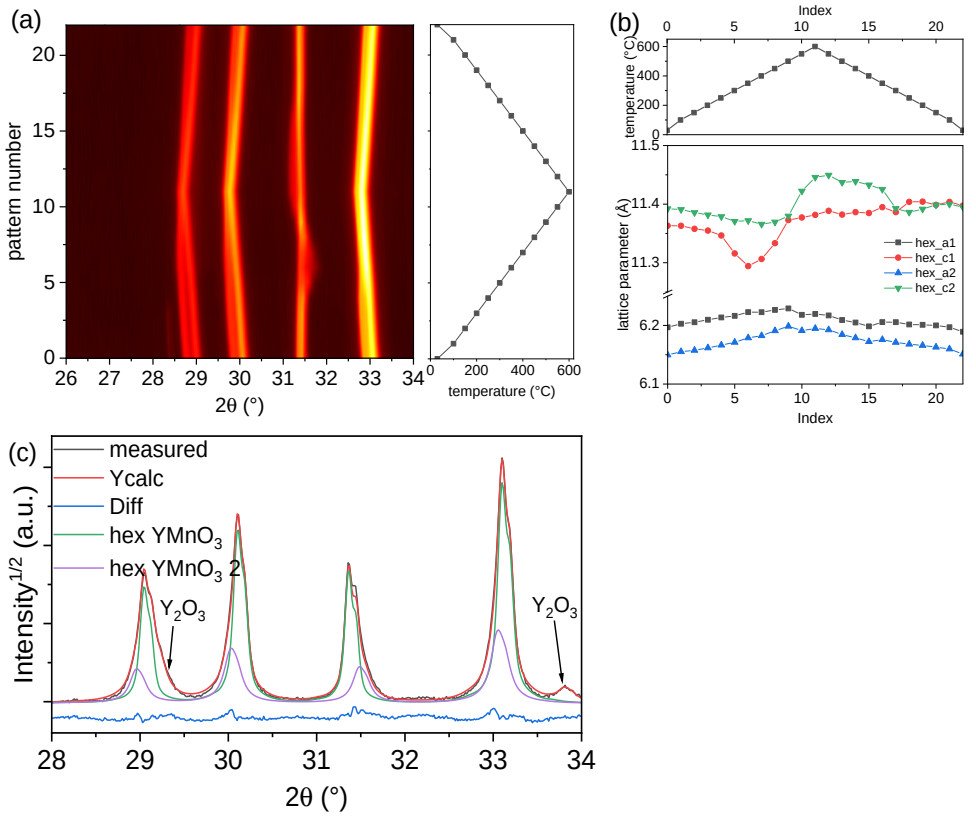

Figure 2: Contour plot of XRD patterns during in situ heating of a 2-phase h-$YMnO_3$ sample, with heating profile adjacent, and **(b)** refined lattice parameters of the two phases during the experiment, with heating profile above. **(c)** Room temperature XRD pattern of a 2-phase sample heat treated at 1150 °C.

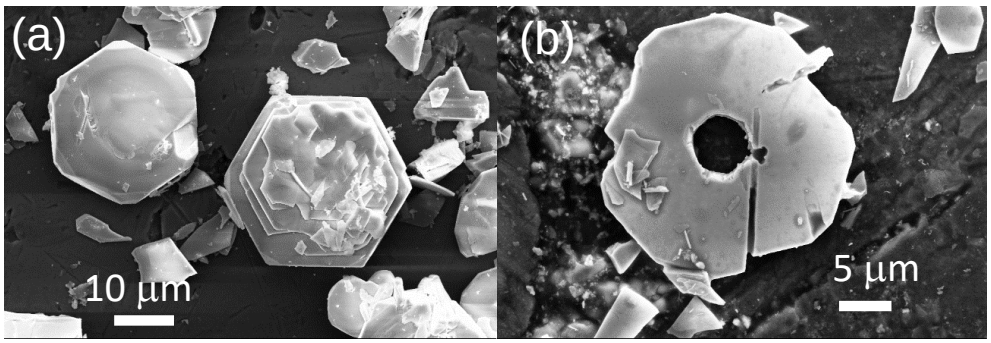

Figure 3: SEM images of h-$YMnO_3$ particles hydrothermally synthesised from $Y(NO_3)_3$, $MnCl_2$, and $KMnO_4$ at 240 °C in 14 M KOH for **(a)** 6 h and **(b)** 72 h.

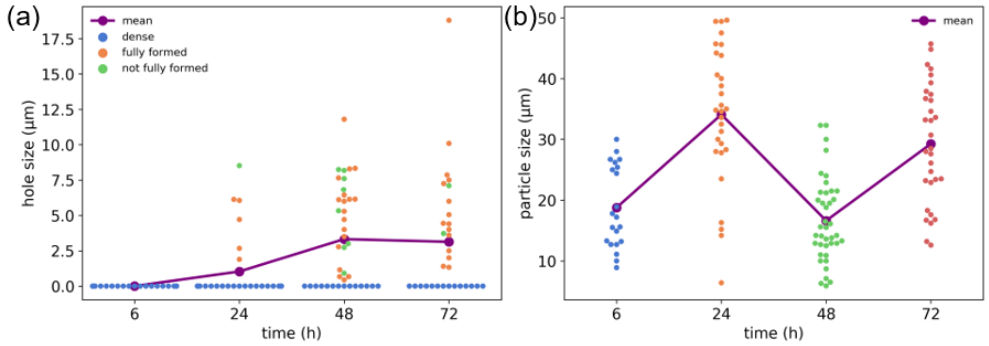

Figure 4: **(a)** Hole sizes and **(b)** particle sizes measured based on SEM images of h-YMnO3 particles synthesised hydrothermally at 240 °C 6 to 72 h in 14 M KOH.

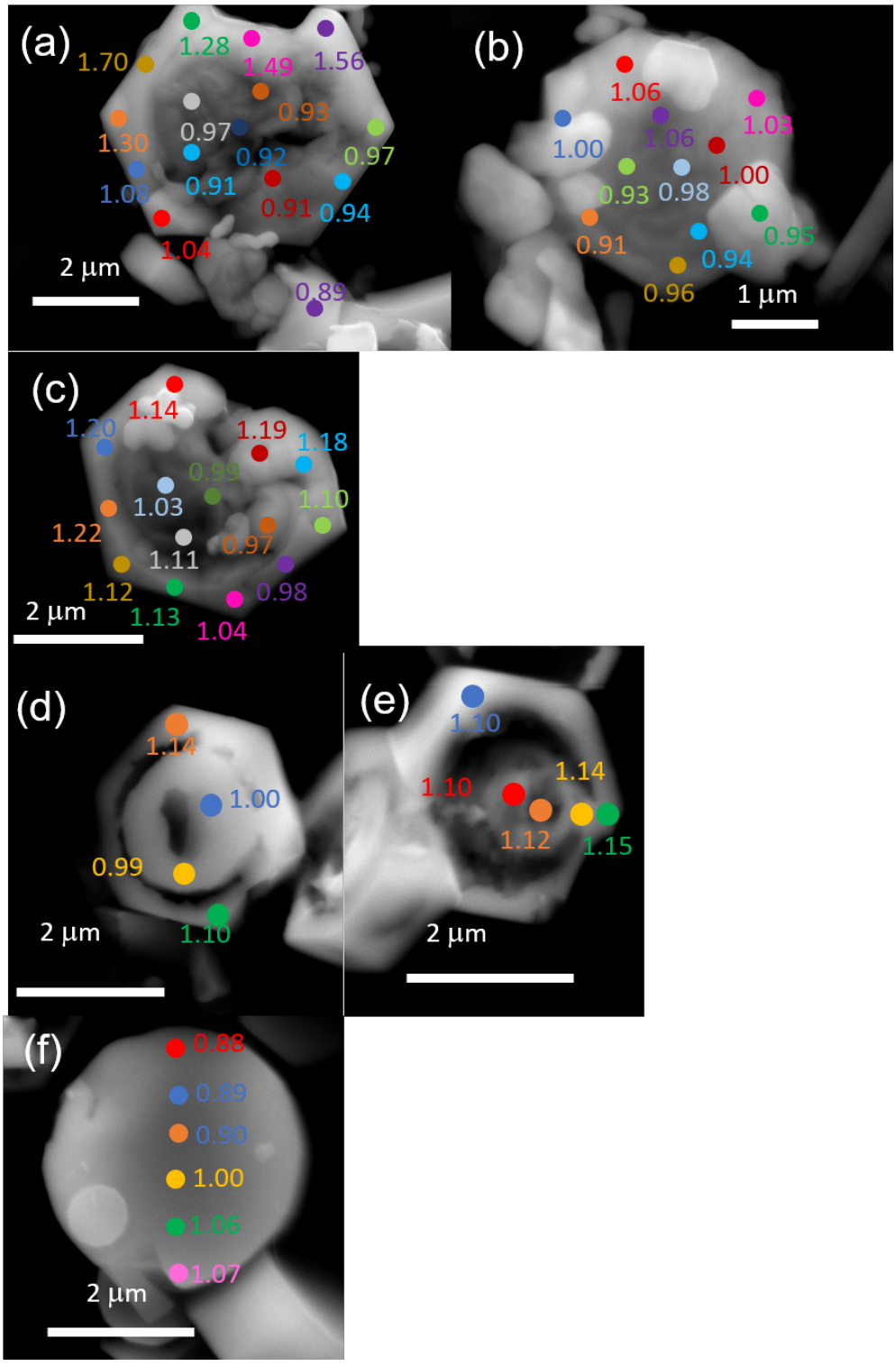

Figure 5: Scanning electron microscopy images of a h-YMnO3 sample made from **(a)**, **(b)** and **(c)** stoichiometric precursors (reaction Y1), and **(d)**, **(e)** and **(f)** with 15 mol% excess Y (reaction Y3), in 12.5 M KOH at 240 °C. Y:Mn atomic ratios measured by EDX shown on the images at the locations EDX spectra were taken.

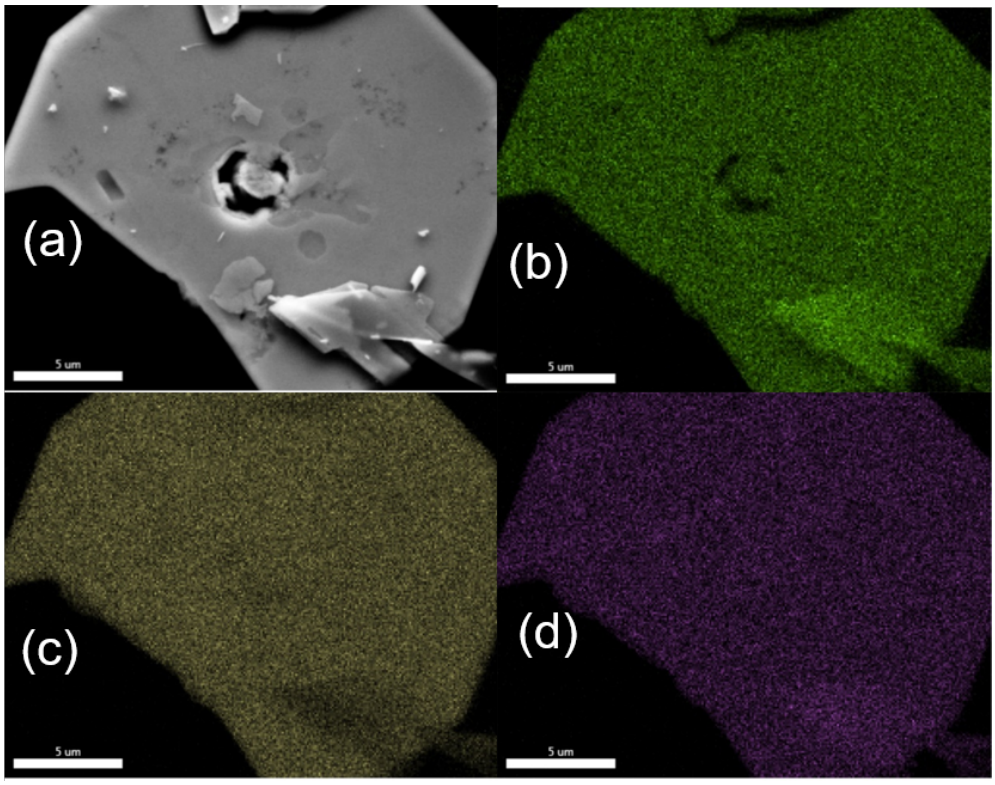

Figure 6: SEM/EDX maps of a h-$YMnO_3$ particle synthesised from $Y(NO_3)_3$, $MnCl_2$ and $KMnO_4$ (reaction Y2). **(a)** SEM image, and **(b)** O, **(c)** Y and **(d)** Mn elemental mappings.

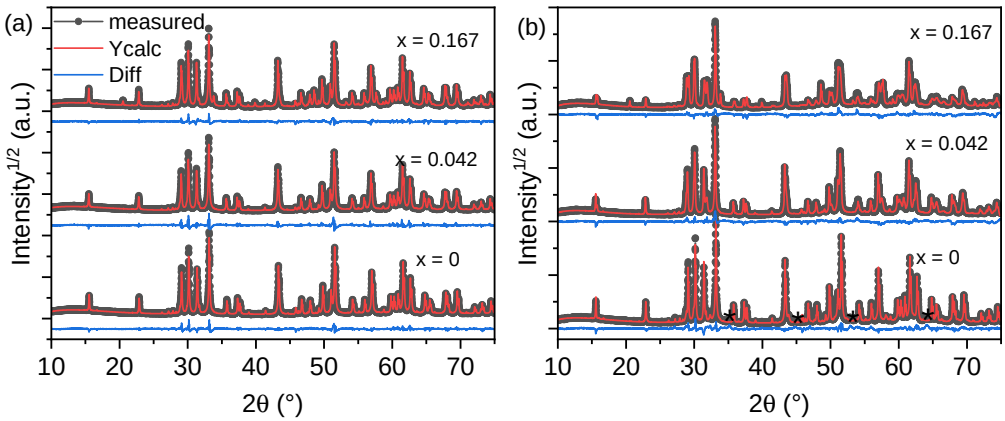

Figure 7: XRD patterns of the bulk $Y_{1+x}MnO_3$ powders prepared by solid state reaction following **(a)** the annealing step under N_2 flow at 1000 °C, and **(b)** the oxidation step under O2 flow at 300 °C. * denotes unidentified peaks.

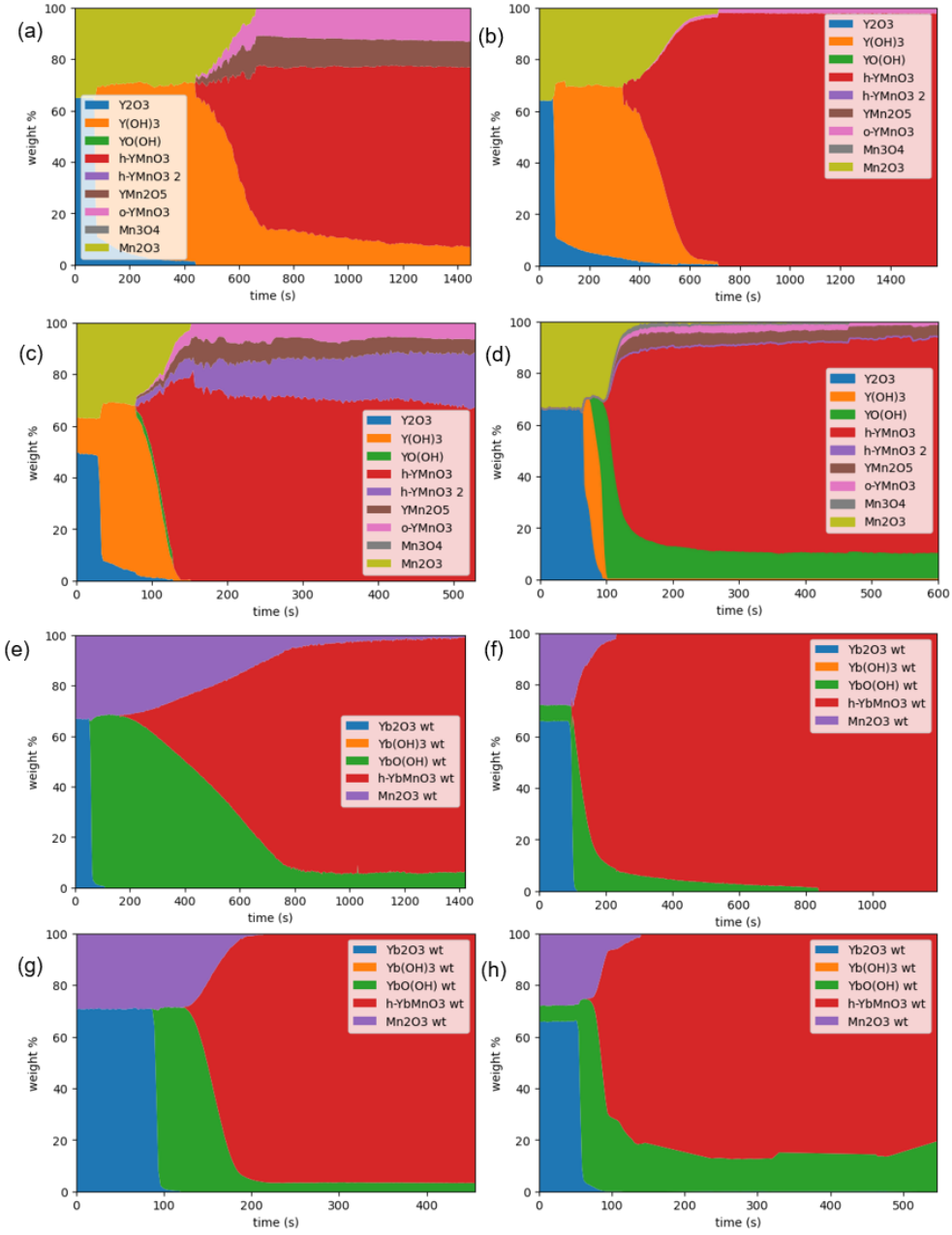

Figure 8: Stacked area plots of the wt % of different phases over the course of reactions, showing the reactions between Y_2O_3 and Mn_2O_3 in 10 M KOH at **(a)** 240 °C (Yi1), (b) 240 °C with $MnCl_2$ added (Yi2), **(c)** 270 °C (Yi3), and **(d)** 300 °C (Yi4), and the reactions between Yb_2O_3 and Mn_2O_3 at **(e)** 240 °C (Yi5), **(f)** 240 °C with $MnCl_2$ added (Yi6), **(g)** 270 °C (Yi7), and **(h)** 300 °C (Yi8).

Table 1: Experimental conditions (Y:Mn or Yb:Mn ratio, temperature, time, mineraliser concentration) of different reactions and weight fractions of products. * Unidentified phase observed.

	Synthesis Parameters				Reaction Products (wt%)						
Reaction	Y:Mn ratio	Temp (°C)	Time (h)	[KOH] (M)	h-$YMnO_3$	h-$YMnO_3$ (2)	YMn_2O_5	$Y(OH)_3$	o-$YMnO_3$	KMn_2O_{6-x}	Mn_3O_4
Y1	1:1	240	20	12.5	97		3	0.01		0.07	
Y2	1:1 (salts)	240	20	12.5	89		7	0.7	1		1
Y3	1.15:1	240	20	12.5	67	30	1	2			
Y4	1.15:1	240	65	12.5	58	41		0.4		0.6	
Y5	1:1	220	20	12.5	95		3	0.3	1	0.7	
Y6	1:1	200	20	12.5	38	47	7		4	1	3
Y7	1:1	180	20	12.5	52	34	11	1		0.4	2
Y8	1:1	160	20	12.5	0.7			66		0.2	
Y9	1:1	240	20	10	39	47	10	0.1	2	2	1
Y10	1:1	220	20	10	42	42	10	1	1	2	2
Y11	1:1	220	44	10	63	14	12	6	4	1	1
Y12	1:1	200	20	10	11		28	48		1	12
Y13	1:1	200	67	10	23		25	39		1	10
Y14	1:1	240	20	7.5	11		28	48		1	12
Y15	1:1	240	20	5	0		30	55		0.5	15
Y16	1.15:0.95: 0.05 (YO1.5: MnO1.5: MnCl2)	240	20	12.5	96			4		0.1	
Y17	1.15:1	240	17	12.5 (NaOH)	0			88		12 (Na)	
Reaction	Yb:Mn ratio	Temp (°C)	Time (h)	[KOH] (M)	h-$YbMnO_3$	h-$YbMnO_3$ (2)	$YbO(OH)$	Mn_2O_3	$Yb_2Mn_2O_7$	KMn_2O_6—x	Mn_3O_4
Yb1	1.15:1	120	165	12.5	8		63	24		4	
Yb2	1.15:1	150	20	12.5	9						
Yb3	1.15:1	150	64	12.5	88		7	5		0.4	
Yb4	1.15:1	180	20	12.5	99					1	
Yb5	1.15:1	240	20	12.5	47	52				1	
Yb6	1:1	240	20	12.5	38	56	2			2	3
Yb7	1:1	180	20	10	54		31	15		0.3	
Yb8	1:1	180	20	7.5	9		66	25		0.2	
Yb9	1:1	240	20	5	95		1	3		0.3	
Yb10	1.1:1	240	88	5	95				4	0.2	
Yb11*	1:1	200	20	5	89		5	5		0.2	
Yb12*	1:1	180	20	5	8		67	25			
Yb13*	1:1	240	20	2.5	93		4	2		1	
Yb14	1:1	220	20	2.5	91		3	5		1	
Yb15*	1:1	200	20	2.5	88		4	8			
Yb16*	1:1	180	20	2.5	4		69	27			
Yb17*	1:1	240	20	1	92		5	3		0.5	
Yb18*	1:1	220	20	1	89		4	4			
Yb19*	1:1	200	20	1	38		45	17			
Yb20*	1:1	180	20	1	0		74	26			
Reaction (in situ)	Ln:Mn ratio	Temp °C	[KOH] (M)	h-$LnMnO_3$	h-$LnMnO_3$ (2)	YMn_2O_5	$Ln(OH)3$	$LnO(OH)$	Mn_2O_3	o-$YMnO_3$	
Yi1	1.15:1	240	10	70		10	7			13	
Yi2	1.15:1:0.05 (MnCl2)	240	10	98						2	
Yi3	1.15:1	270	10	21	68	5				6	
Yi4	1.15:1	300	10	83		5	9			2	
Ybi1	1:1	240	10	93				7			
Ybi2	1.15:1:0.05 (MnCl2)	240	10	100							
Ybi3	1.15:1	270	10	97				3			
Ybi4	1.15:1	300	10	80				20			

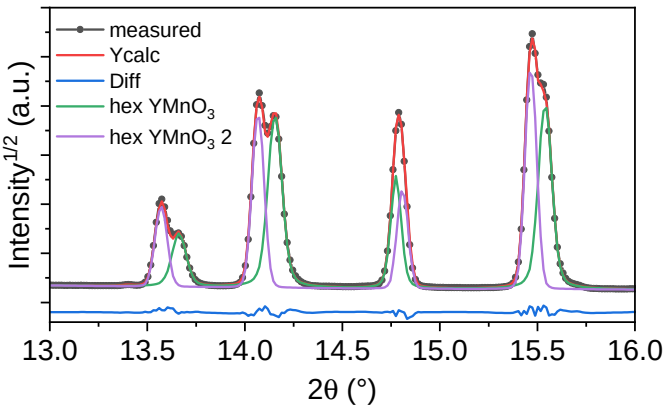

Figure 9: Synchrotron powder XRD pattern of a two-phase h-YMnO3 sample, wavelength = 0.73074 Å. Sample prepared by hydrothermal synthesis from Y2O3 and Mn2O3 (1.15:1 molar ratio) in 12.5 M KOH (repeat of reaction Y3).