Electronic Supplementary Material (ESI) for Materials Advances.

SUPPLEMENTARY INFORMATION FOR

Phase Formation of Manganese Oxide Thin Films by Pulsed Laser Deposition

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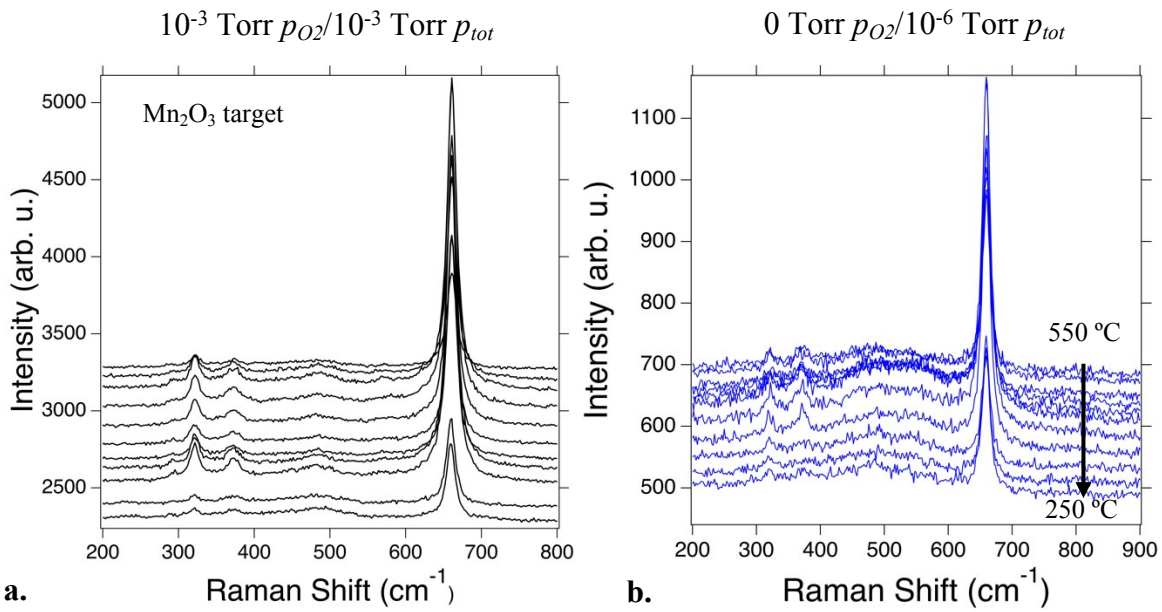
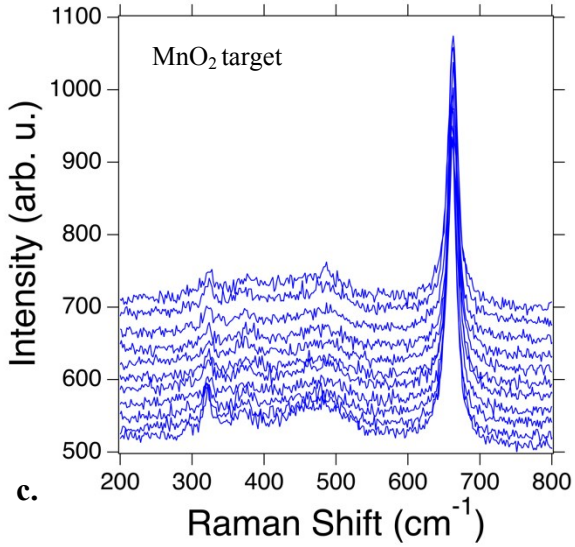
Table S1. The processing parameters, major results and figures for the manganese oxide libraries created in this work. HT stands for high temperature, LT is low temperature, am is amorphous.

Target	p_{O2} (Torr)	p_{tot} (Torr)	Raman Spectroscopy	XRD	Figure
Mn_2O_3	10^{-1}	10^{-1}	Mn_2O_3 (HT: Mn_3O_4)	Mn_2O_3 (LT: am.)	4, S8
Mn_2O_3	10^{-2}	10^{-1}	Mn_2O_3 (HT: Mn_3O_4)	Mn_2O_3	4, S8
Mn_2O_3	10^{-3}	10^{-1}	Mn_2O_3 (HT: Mn_3O_4)	Mn_2O_3	4, S8
Mn_2O_3	10^{-4}	10^{-1}	Mn_3O_4	MnO/Mn_3O_4	4, S8
Mn_2O_3	- (<10^{-6})	10^{-1}	-	MnO	4, S8
Mn_2O_3	10^{-2}	10^{-2}	Mn_2O_3 (HT: Mn_3O_4)	Mn_2O_3	2a, 2b
Mn_2O_3	10^{-3}	10^{-2}	Mn_3O_4	MnO/Mn_3O_4	1a, 1b
Mn_2O_3	10^{-4}	10^{-2}	Mn_3O_4	MnO/Mn_3O_4	4, S8
Mn_2O_3	10^{-5}	10^{-2}	Mn_3O_4	MnO/Mn_3O_4	4, S8
Mn_2O_3	- (<10^{-6})	10^{-2}	-	MnO	4, S8
Mn_2O_3	10^{-3}	10^{-3}	Mn_3O_4	MnO/Mn_3O_4	S1a
Mn_2O_3	10^{-4}	10^{-3}	Mn_3O_4	MnO/Mn_3O_4	4, S8
Mn_2O_3	10^{-5}	10^{-3}	Mn_3O_4	MnO/Mn_3O_4	4, S8
Mn_2O_3	- (<10^{-6})	10^{-3}	-	MnO	S1b
MnO_2	10^{-1}	10^{-1}	Mn_2O_3 (HT: Mn_3O_4)	Mn_2O_3 (LT: am.)	S7b
MnO_2	10^{-2}	10^{-2}	Mn_2O_3 (HT: Mn_3O_4)	Mn_2O_3	S7a
MnO_2	10^{-3}	10^{-3}	Mn_3O_4	MnO/Mn_3O_4	S1c
MnO_2	- (<10^{-6})	10^{-3}	-	MnO	S1d
MnO	10^{-3}	10^{-1}	/	Mn_3O_4 (LT: +Mn_2O_3)	Ref [1]
MnO	2.5 x 10^{-4}	2.5 x 10^{-2}	/	Mn_3O_4 (HT: MnO)	Ref [1]
MnO	5 x 10^{-4}	5 x 10^{-3}	/	Mn_3O_4 (HT: MnO)	Ref [1]
MnO	5 x 10^{-5}	5 x 10^{-3}	/	MnO+Mn_3O_4 (HT:MnO; LT:Mn_3O_4)	Ref [1]
MnO	- (<10^{-6})	5 x 10^{-3}	/	MnO	Ref [1]

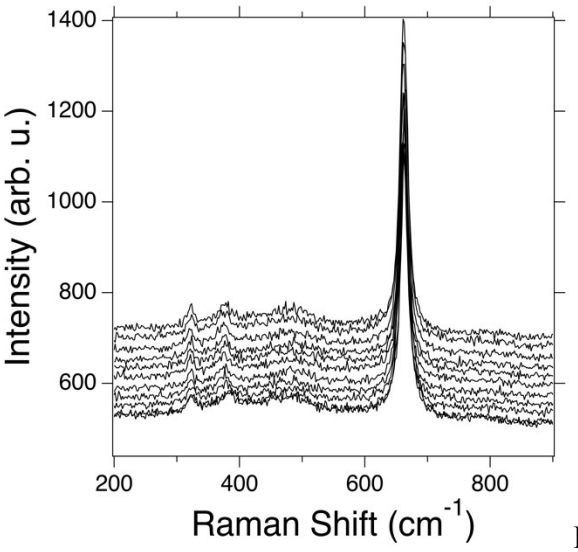
The Raman spectroscopy of libraries deposited from a Mn_2O_3 target at a 10^{-3} Torr p_{O2} (10^{-3} Torr p_{tot}) and total pressure of 0 Torr p_{O2} (10^{-6} Torr p_{tot}) are shown in Figure S1a and Figure S1b, respectively. Figure S1c and Figure S1d show the Raman response over the same temperature and pressure range for films deposited from a MnO_2 targets.



10-3 Torr p_{O2}/10-3 Torr p_{tot}
0 Torr p_{O2}/10-6 Torr p_{tot}



c.



d.

Figures S1. Raman spectroscopy of libraries deposited from a Mn_2O_3 target, grown over a temperature range from 550 ºC to 250 ºC (from highest to lowest) at low p_{O2}: **S1a.** 10^{-3} Torr p_{O2}/10^{-3} Torr p_{tot}, **S1b.** 0 Torr p_{O2}/10^{-6} Torr p_{tot}; and films grown under the same conditions from a MnO_2 target **S1c.** 10^{-3} Torr p_{O2}/10^{-3} Torr p_{tot}, **S1d.** 0 Torr p_{O2}/10^{-6} Torr p_{tot}

Fourier transform infrared spectroscopy (FTIR) and Rutherford backscattering (RBS) were measured on the libraries described in Figure 1 to further corroborate the Raman results. While MnO is not observed by Raman, because it does not have any Raman active modes, the presence of these phases is corroborated by FTIR. The FTIR response for a film deposited at 10^{-3} Torr p_{O2}, at approximately 400 ºC and 500 ºC is shown in Figure S2. There are features that are specific to MnO and Mn_3O_4 in both spectra,[2,3] suggesting that a mixture of phases are present at both

temperatures. These results, while not definitive, are in agreement with the XRD. Furthermore, the average film composition as determined by RBS measured on three spots was $MnO_{1.24}$ (Figure S3) with very little variation between spots, suggesting that there is approximately a 50:50 mixture of MnO and Mn_3O_4 present. A transition from MnO to Mn_3O_4 would be expected with decreasing temperature given the increasing chemical potential of oxygen.[4] Even for the lowest temperatures, films processed at or below 10^{-3} Torr do not favor the compositions of the target, Mn_2O_3 or MnO_2.

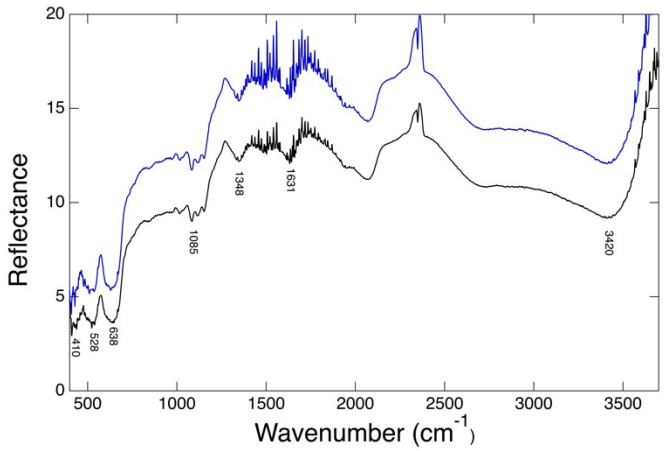


Figure S2: FTIR taken on a library processed at 10^{-3} Torr p_{O2} in regions where the materials were grown at approximately 550 °C (blue) and 400 °C (black).

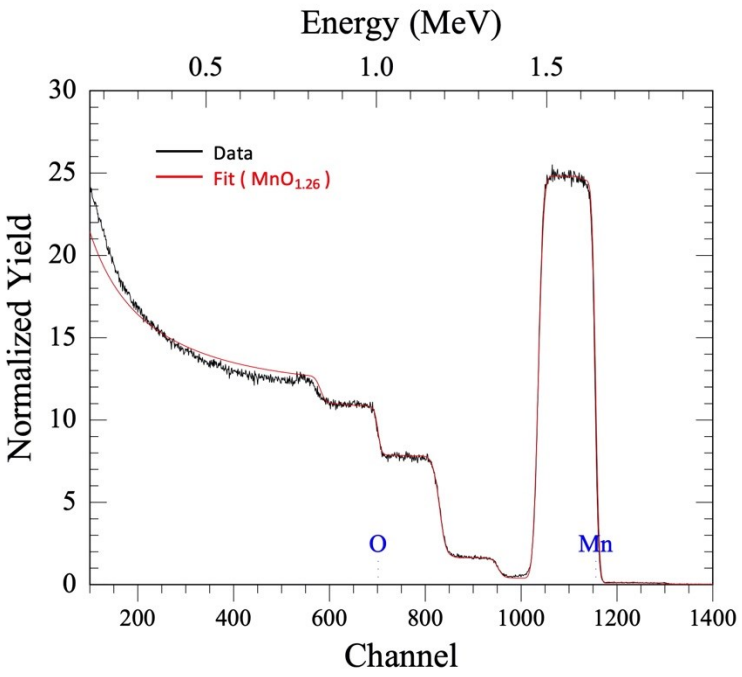


Figure S3. Comparison of measured RBS spectrum (black) and fitted simulation (red) for a thin film grown at a p_{O2} of 10^{-3} Torr and a p_{tot} of 10^{-2} Torr. The high energy edges for film O and film Mn are indicated.

A similar x-ray diffraction pattern to that seen in Figure 2 is observed in libraries deposited from a Mn_2O_3 target without added oxygen (Figure S4a), and for films deposited from MnO_2 targets at or below 10^{-3} Torr partial pressure of oxygen (Figure S4b). The overall intensity is significantly lower for the films processed from an MnO_2 target, but all of the same phases are present.

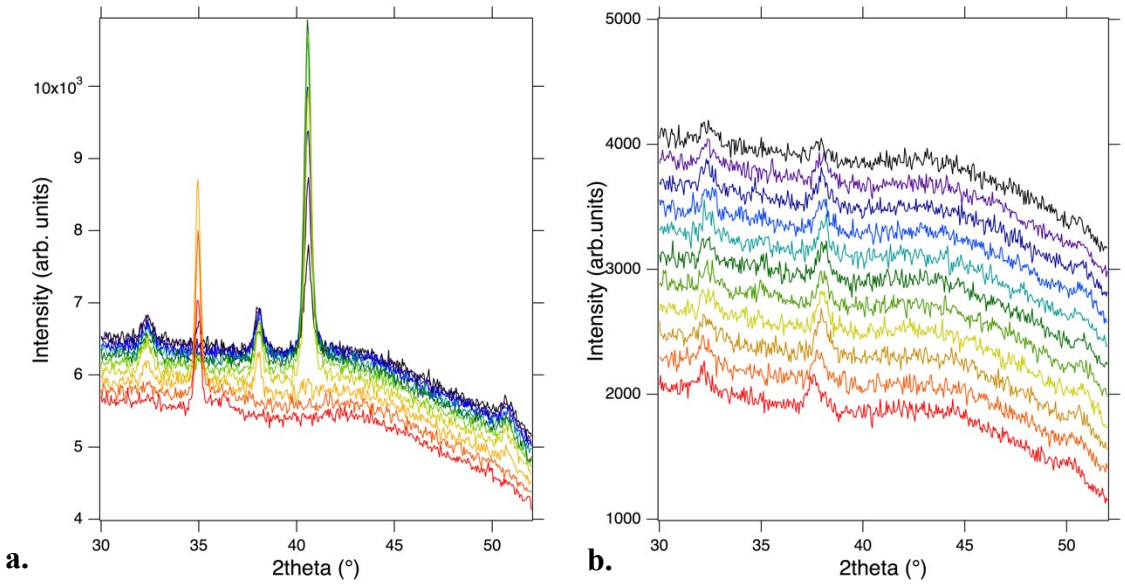
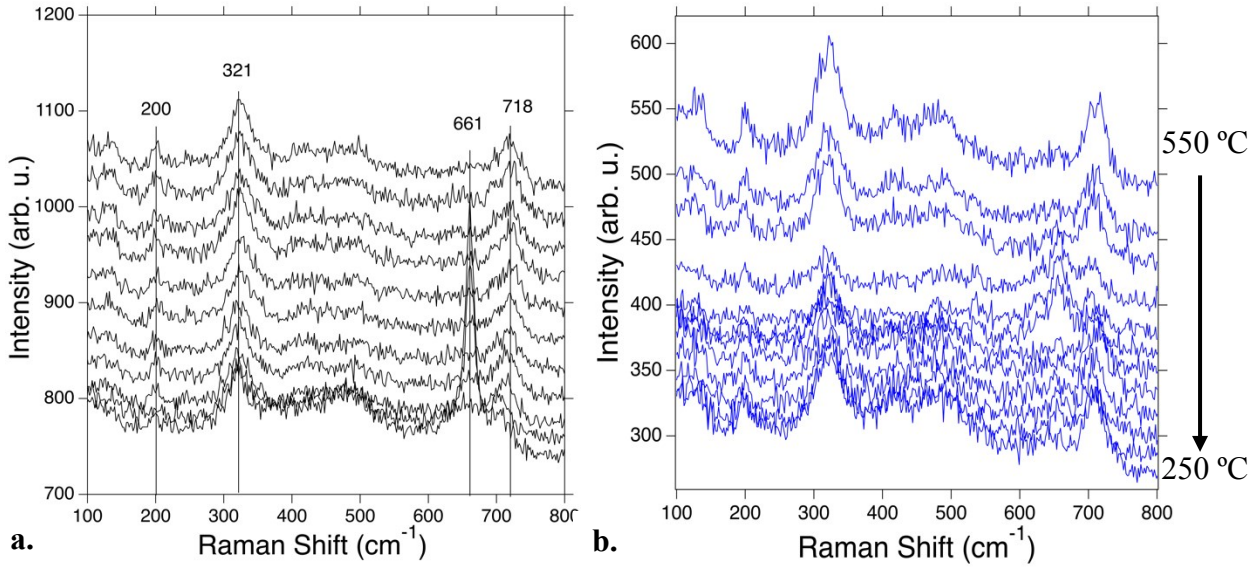


Figure S4a. X-ray diffraction for films deposited in vacuum at 550 ºC to 250 ºC (from red to blue) from a Mn_2O_3 target. The peaks at 35 º and 41º are from MnO, all others are from Mn_3O_4; and **S4b**. Thin films deposited under the same conditions from a MnO_2 target showing similar phase formation but lower crystallinity.

Within each phase regions there were also variations in the crystallinity of a given phase. The crystallinity is often increased towards the center of the phase space. For example, the crystallinity of the MnO phase was the highest with the partial pressure of oxygen was at 1 mTorr. For the Mn_2O_3 phase, the crystallinity decreased as the partial pressure increased. The crystallinity of films deposited from Mn_2O_3 targets is higher than those from MnO_2 targets. Typically, crystallinity increased with increasing temperature, except for in the Mn_3O_4 phase where the highest crystalline quality was between 450 -350 ºC. Further XRD data in Figure S5a shows how increasing total pressure decreases crystallinity for samples grown at a constant p_{O2} and approximately 330 °C. Figure S5b shows decreasing crystallinity with increasing total pressure within the same phase, for thin films processed under low oxygen partial pressures at approximately 330 °C.

The films deposited at the highest and lowest oxygen partial pressures are amorphous, indicated by the open symbols; work is on-going to determine if other oxidation states are present under these conditions that are not observed by XRD or Raman spectroscopy.



Figures S5. Raman spectroscopy of libraries deposited under high p_{O2} from 550 ºC to 250 ºC from a MnO_2 target: **S5a.** 10^{-2} Torr p_{O2}/10^{-2} Torr p_{tot} and **S5b.** 10^{-1} Torr p_{O2}/10^{-1} Torr p_{tot} over a temperature range from 550 ºC to 250 ºC

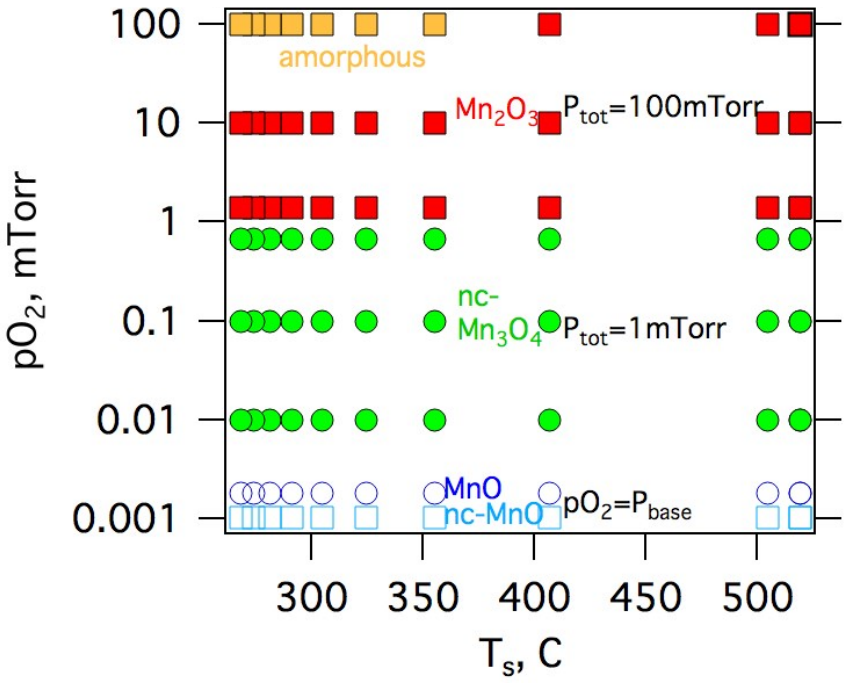


Figure S6. Phase diagram of the phase formation of manganese oxides as a function of temperature and partial pressure of oxygen

References

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