Topotactic oxidative and reductive control of the structures and properties of layered manganese oxychalcogenides.

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Table S1. Refined structural parameters for an as-made Mn-rich oxysulfide derived from SXRD data. U_{eq} measured in $\text{\AA}^2$. See Table 1 in main text for refinement results.

	Compound	$\text{Sr}_4\text{Mn}_{2.94}\text{O}_{7.42}\text{Cu}_2\text{S}_2$
	Sample ID	NB17
Atom	Parameter	
Sr1 ($\frac{1}{2}$ $\frac{1}{2}$ z)	z	0.05980(2)
	$100 \times U_{\text{eq}}$	2.50(2)
Sr2 ($\frac{1}{2}$ $\frac{1}{2}$ z)	z	0.166407(16)
	$100 \times U_{\text{eq}}$	0.99(1)
Mn1 (0 0 z)	z	0.11381(3)
	$100 \times U_{\text{eq}}$	0.97(2)
Mn2 (0, 0, 0)	$100 \times U_{\text{eq}}$	1.22(4)
	<i>Occupancy</i>	0.936(6)
Cu ($\frac{1}{2}$ 0 $\frac{1}{4}$)	$100 \times U_{\text{eq}}$	1.95(2)
S (0 0 z)	z	0.20828(4)
	$100 \times U_{\text{eq}}$	1.12(3)
O1 (0 0 z)	z	0.05432(16)
	$100 \times U_{\text{eq}}$	2.97(14)
O2 ($\frac{1}{2}$ y 0)	y	0.070(8)
	$100 \times U_{\text{eq}}$	4.4(9)
	<i>Occupancy</i>	0.356(12)
O3 ($\frac{1}{2}$ 0 z)	z	0.11957(9)
	$100 \times U_{\text{eq}}$	1.41(5)

^a U_{eq} is defined as one third of the orthogonalized U_{ij} tensor.

Table S2. Selected bond distances and angles for an as-made Mn-rich oxysulfide derived from SXR data.

Compound	$\text{Sr}_4\text{Mn}_{2.94}\text{O}_{7.42}\text{Cu}_2\text{S}_2$
Sample ID	NB17
Bond distance / Å	
Mn1–O1 [1]	2.051(5)
Mn1–O3 [4]	1.9624(3)
Mn2–O1 [2]	1.872(5)
Mn2–O2 [4]	— ^a
Cu–S [4]	2.4248(9)
Bond angle / °	
O1–Mn1–O3 [4]	95.80(9)
O3–Mn1–O3 [4]	89.41(2)
S–Cu–S [2]	107.24(6)
S–Cu–S [4]	110.60(3)

^a omitted due to structural disorder in O2 position

Table S3. Results of PND refinements at 295 K for Mn-rich oxysulfides derived from the $\text{Sr}_4\text{Mn}_{2.91}\text{O}_{7.40}\text{Cu}_2\text{S}_2$ parent from PND data collected on POLARIS.

Compound	$\text{Sr}_4\text{Mn}_{2.91}\text{O}_{6.97}\text{Cu}_2\text{S}_2$	$\text{Sr}_4\text{Mn}_{2.91}\text{O}_{7.05}\text{Cu}_2\text{S}_2$	$\text{Sr}_4\text{Mn}_{2.91}\text{O}_{7.40}\text{Cu}_2\text{S}_2$	$\text{Sr}_4\text{Mn}_{2.91}\text{O}_{7.40}\text{F}_{0.06}\text{Cu}_2\text{S}_2$
Sample ID	GH206	GH195	GH192	GH197
Radiation	Neutron			
Instrument	POLARIS			
Physical form	Black powder	Black powder	Black powder	Black powder
T / K	295	295	295	295
Space group	$I4/mmm$	$I4/mmm$	$I4/mmm$	$I4/mmm$
$a / \text{\AA}$	3.9080(7)	3.89636(4)	3.87248(3)	3.86798(4)
$c / \text{\AA}$	34.697(6)	34.5920(5)	34.5892(4)	34.6537(4)
$V / \text{\AA}^3$	529.9(3)	525.16(2)	518.70(1)	518.46(1)
Z	2	2	2	2
R_{wp}	0.0168	0.0143	0.0196	0.0210
R_{F2}	0.081	0.055	0.044	0.078
χ^2	1.398	2.000	2.290	2.615

Table S4. Refined structural parameters for Mn-rich oxysulfides derived from the $\text{Sr}_4\text{Mn}_{2.91}\text{O}_{7.40}\text{Cu}_2\text{S}_2$ parent from PND data collected on POLARIS. U_{iso} , U_{eq} measured in $\text{\AA}^2$

	Compound	$\text{Sr}_4\text{Mn}_{2.91}\text{O}_{6.97}\text{Cu}_2\text{S}_2$	$\text{Sr}_4\text{Mn}_{2.91}\text{O}_{7.05}\text{Cu}_2\text{S}_2$	$\text{Sr}_4\text{Mn}_{2.91}\text{O}_{7.40}\text{Cu}_2\text{S}_2$	$\text{Sr}_4\text{Mn}_{2.91}\text{O}_{7.40}\text{F}_{0.06}\text{Cu}_2\text{S}_2$
	Sample ID	GH206	GH195	GH192	GH197
Atom	Parameter				
Sr1 ($\frac{1}{2}$ $\frac{1}{2}$ z)	z	0.06293(3)	0.06137(2)	0.05921(2)	0.05823(2)
	$100 \times U_{\text{eq}}$	1.59(4)	1.71(3)	1.32(3)	1.42(3)
Sr2 ($\frac{1}{2}$ $\frac{1}{2}$ z)	z	0.16642(2)	0.16627(2)	0.16677(1)	0.16648(2)
	$100 \times U_{\text{eq}}$	0.57(3)	0.64(2)	0.56(2)	0.63(2)
Mn1 (0 0 z)	z	0.11316(4)	0.11270(3)	0.11279(2)	0.11254(3)
	$100 \times U_{\text{iso}}$	0.24(1)	0.23(1)	0.25(1)	0.36(1)
Mn2 (x , x , 0)	x	0.0710(7)	0.0518(6)	0^b	0^b
	$100 \times U_{\text{iso}}$	1.5(1)	1.13(7)	1.08(4)	0.77(3)
	<i>Occupancy</i>	0.228^b	0.228^b	0.913(6)	0.913^b
Cu ($\frac{1}{2}$ 0 $\frac{1}{4}$)	$100 \times U_{\text{eq}}$	1.67(3)	1.58(2)	1.60(2)	1.60(3)
S (0 0 z)	z	0.20869(5)	0.20828(4)	0.20791(4)	0.20773(5)
	$100 \times U_{\text{iso}}$	0.73(3)	0.79(3)	0.92(3)	1.02(3)

O1 (0 0 z)	z	0.05359(3)	0.05368(3)	0.05443(2)	0.05466(3)
	$100 \times U_{\text{eq}}$	2.37(5)	2.52(4)	1.97(3)	1.99(3)
O2 ($\frac{1}{2}$ 0 0)	$100 \times U_{\text{eq}}$	26(2)	13.5(5)	5.8(1)	4.5(1)
	<i>Occupancy</i>	0.485(6)	0.525(5)	0.698(4)	0.727(4) ^c
O3 ($\frac{1}{2}$ 0 z)	z	0.11961(2)	0.11938(1)	0.11914(1)	0.11920(1)
	$100 \times U_{\text{eq}}$	1.02(3)	1.04(2)	0.79(2)	0.87(2)

^a U_{eq} is defined as one third of the orthogonalized U_{ij} tensor.

^b Not refined

^c Total of occupancy by O and F (given the similarity in O and F scattering lengths)

Table S5. Selected bond distances and angles for Mn-rich oxysulfides from PND data collected on POLARIS.

Compound	$\text{Sr}_4\text{Mn}_{2.91}\text{O}_{6.97}\text{Cu}_2\text{S}_2$	$\text{Sr}_4\text{Mn}_{2.91}\text{O}_{7.05}\text{Cu}_2\text{S}_2$	$\text{Sr}_4\text{Mn}_{2.91}\text{O}_{7.40}\text{Cu}_2\text{S}_2$	$\text{Sr}_4\text{Mn}_{2.91}\text{O}_{7.40}\text{F}_{0.06}\text{Cu}_2\text{S}_2$
Sample ID	GH206	GH195	GH192	GH197
Bond distance / Å				
Mn1–O1 [1]	2.067(2)	2.042(1)	2.019(1)	2.006(1)
Mn1–O3 [4]	1.9667(4)	1.9618(1)	1.9486(1)	1.9477(1)
Mn2–O1 [2]	— ^a	— ^a	1.8825(8)	1.894(1)
Mn2–O2 [4]	— ^a	— ^a	1.93624(2)	1.93399(2)
Cu–S [4]	2.423(1)	2.4245(9)	2.4225(8)	2.426(1)
Bond angle / °				
O1–Mn1–O3 [4]	96.53(4)	96.76(3)	96.47(3)	96.81(3)
O3–Mn1–O3 [4]	89.259(9)	89.205(7)	89.273(6)	89.195(7)
S–Cu–S [2]	107.48(7)	106.94(6)	106.12(5)	105.72(6)
S–Cu–S [4]	110.48(4)	110.75(3)	111.17(3)	111.38(3)

^a omitted due to structural disorder in Mn2 position

Table S6. Results of PND refinements at 295 K for Mn-poor oxysulfides derived from the $\text{Sr}_4\text{Mn}_{2.77}\text{O}_{7.27}\text{Cu}_2\text{S}_2$ parent from PND data collected on POLARIS.

Compound	$\text{Sr}_4\text{Mn}_{2.77}\text{O}_{7.16}\text{Cu}_2\text{S}_2$	$\text{Sr}_4\text{Mn}_{2.77}\text{O}_{7.27}\text{Cu}_2\text{S}_2$	$\text{Sr}_4\text{Mn}_{2.77}\text{O}_{7.27}\text{F}_{0.27}\text{Cu}_2\text{S}_2$
Sample ID	GH340	GH299	GH336
Radiation	Neutron		
Instrument	POLARIS		
Physical form	Black powder	Black powder	Black powder
T / K	295	295	295
Space group	$I4/mmm$	$I4/mmm$	$I4/mmm$
$a / \text{\AA}$	3.9012(3)	3.88635(4)	3.86600(5)
$c / \text{\AA}$	34.775(3)	34.5717(5)	34.6478(6)
$V / \text{\AA}^3$	529.3(1)	522.16(2)	517.84(2)
Z	2	2	2
R_{wp}	0.0210	0.0182	0.0229
R_{F2}	0.047	0.053	0.062
χ^2	4.997	2.942	4.809

Table S7. Refined structural parameters for Mn-poor oxysulfides derived from the $\text{Sr}_4\text{Mn}_{2.77}\text{O}_{7.27}\text{Cu}_2\text{S}_2$ parent from PND data collected on POLARIS. U_{iso} , U_{eq} measured in $\text{\AA}^2$

	Compound	$\text{Sr}_4\text{Mn}_{2.77}\text{O}_{7.16}\text{Cu}_2\text{S}_2$	$\text{Sr}_4\text{Mn}_{2.77}\text{O}_{7.27}\text{Cu}_2\text{S}_2$	$\text{Sr}_4\text{Mn}_{2.77}\text{O}_{7.27}\text{F}_{0.27}\text{Cu}_2\text{S}_2$
	Sample ID	GH340	GH299	GH336
Atom	Parameter			
Sr1 ($\frac{1}{2}$ $\frac{1}{2}$ z)	z	0.06354(3)	0.06003(2)	0.05752(3)
	$100 \times U_{\text{eq}}$	1.40(4)	1.47(3)	1.34(3)
Sr2 ($\frac{1}{2}$ $\frac{1}{2}$ z)	z	0.16649(2)	0.16615(2)	0.16620(2)
	$100 \times U_{\text{eq}}$	0.56(3)	0.71(3)	0.66(3)
Mn1 (0 0 z)	z	0.11238(4)	0.11238(3)	0.11235(3)
	$100 \times U_{\text{iso}}$	0.20(2)	0.31(2)	0.24(2)
Mn2 (x , x , 0)	x	0.081(1)	0^b	0^b
	$100 \times U_{\text{iso}}$	2.8(2)	1.41(7)	0.09(4)
	<i>Occupancy</i>	0.192 ^b	0.769(7)	0.769 ^b
Cu ($\frac{1}{2}$ 0 $\frac{1}{4}$)	$100 \times U_{\text{eq}}$	1.78(4)	1.57(3)	1.44(4)
S (0 0 z)	z	0.20792(7)	0.20769(5)	0.20749(6)
	$100 \times U_{\text{iso}}$	0.74(4)	0.72(3)	0.79(4)

O1 (0 0 z)	z	0.05322(4)	0.05382(3)	0.05472(4)
	$100 \times U_{\text{eq}}$	2.30(5)	2.42(4)	1.83(4)
O2 ($\frac{1}{2}$ y 0)	y	0.212(1)	0^b	0^b
	$100 \times U_{\text{eq}}$	8.6(3)	8.6(2)	4.0(1)
	<i>Occupancy</i>	0.290(4)	0.636(5)	0.77(6)
O3 ($\frac{1}{2}$ 0 z)	z	0.11967(2)	0.11904(2)	0.11899(2)
	$100 \times U_{\text{eq}}$	1.05(3)	0.97(2)	0.87(3)

^a U_{eq} is defined as one third of the orthogonalized U_{ij} tensor.

^b Not refined

^c Total of occupancy by O and F (given the similarity in O and F scattering lengths)

Table S8. Selected bond distances and angles for Mn-poor oxysulfides from PND data collected on POLARIS.

Compound	$\text{Sr}_4\text{Mn}_{2.77}\text{O}_{7.16}\text{Cu}_2\text{S}_2$	$\text{Sr}_4\text{Mn}_{2.77}\text{O}_{7.27}\text{Cu}_2\text{S}_2$	$\text{Sr}_4\text{Mn}_{2.77}\text{O}_{7.27}\text{F}_{0.27}\text{Cu}_2\text{S}_2$
Sample ID	GH340	GH299	GH336
Bond distance / Å			
Mn1–O1 [1]	2.057(2)	2.024(1)	1.997(2)
Mn1–O3 [4]	1.9670(2)	1.9568(1)	1.9467(2)
Mn2–O1 [2]	— ^a	1.861(1)	1.896(1)
Mn2–O2 [4]	— ^a	1.94318(2)	1.93299(3)
Cu–S [4]	2.439(1)	2.4322(9)	2.430(1)
Bond angle / °			
O1–Mn1–O3 [4]	97.41(4)	96.76(3)	96.79(4)
O3–Mn1–O3 [4]	89.05(1)	89.206(7)	89.199(9)
S–Cu–S [2]	106.25(9)	106.06(6)	105.38(8)
S–Cu–S [4]	111.11(4)	111.21(3)	111.55(4)

^a omitted due to structural disorder in O2 and Mn2 positions

Table S9. Results of PND refinements at 295 K for oxyselenides from PND data collected on POLARIS.

Compound	$\text{Sr}_4\text{Mn}_3\text{O}_{7.35}\text{Cu}_2\text{Se}_2$	$\text{Sr}_4\text{Mn}_3\text{O}_{7.56}\text{Cu}_2\text{Se}_2$	$\text{Sr}_4\text{Mn}_3\text{O}_{7.53}\text{Cu}_2\text{Se}_2$	$\text{Sr}_4\text{Mn}_3\text{O}_{7.53}\text{F}_{0.20}\text{Cu}_2\text{Se}_2$
Sample ID	GH198	GH201	GH288	GH319
Radiation	Neutron			
Instrument	POLARIS			
Physical form	Black powder	Black powder	Black powder	Black powder
T / K	295	295	295	295
Space group	$I4/mmm$	$I4/mmm$	$I4/mmm$	$I4/mmm$
$a / \text{\AA}$	3.917(1)	3.900(1)	3.89217(4)	3.8848(8)
$c / \text{\AA}$	35.33(1)	35.44(1)	35.3852(4)	35.414(7)
$V / \text{\AA}^3$	541.9(5)	539.1(5)	536.05(2)	534.5(3)
Z	2	2	2	2
R_{wp}	0.0197	0.0259	0.0185	0.0240
R_{F2}	0.075	0.055	0.044	0.054
χ^2	4.558	4.646	3.296	5.017

Table S10. Refined structural parameters for oxyselenides from PND data collected on POLARIS. U_{iso} , U_{eq} measured in $\text{\AA}^2$.

	Compound	$\text{Sr}_4\text{Mn}_3\text{O}_{7.35}\text{Cu}_2\text{Se}_2$	$\text{Sr}_4\text{Mn}_3\text{O}_{7.56}\text{Cu}_2\text{Se}_2$	$\text{Sr}_4\text{Mn}_3\text{O}_{7.53}\text{Cu}_2\text{Se}_2$	$\text{Sr}_4\text{Mn}_3\text{O}_{7.53}\text{F}_{0.20}\text{Cu}_2\text{Se}_2$
	Sample ID	GH198	GH201	GH288	GH319
Atom	Parameter				
Sr1 ($\frac{1}{2}$ $\frac{1}{2}$ z)	z	0.05804(4)	0.05645(2)	0.05635(2)	0.05496(3)
	$100 \times U_{\text{eq}}$	1.81(6)	1.29(3)	1.16(3)	1.24(3)
Sr2 ($\frac{1}{2}$ $\frac{1}{2}$ z)	z	0.16232(3)	0.16209(2)	0.16204(2)	0.16211(2)
	$100 \times U_{\text{eq}}$	0.51(2)	0.71(2)	0.68(2)	0.62(3)
Mn1 (0 0 z)	z	0.10900(5)	0.10940(3)	0.10924(3)	0.10908(4)
	$100 \times U_{\text{iso}}$	0.45(3)	0.41(2)	0.41(2)	0.42(2)
Mn2 (0, 0, 0)	$100 \times U_{\text{iso}}$	1.72(7)	0.74(3)	0.62(3)	0.60(4)
Cu ($\frac{1}{2}$ 0 $\frac{1}{4}$)	$100 \times U_{\text{eq}}$	1.52(5)	1.41(2)	1.34(2)	1.49(3)
Se (0 0 z)	z	0.20591(3)	0.20555(2)	0.20549(2)	0.20535(2)
	$100 \times U_{\text{eq}}$	0.98(3)	0.85(2)	0.74(2)	0.77(3)
O1 (0 0 z)	z	0.05205(5)	0.05305(3)	0.05301(3)	0.05293(4)
	$100 \times U_{\text{eq}}$	2.44(8)	2.17(4)	2.08(4)	1.47(4)
O2 ($\frac{1}{2}$ 0 0)	$100 \times U_{\text{eq}}$	8.7(3)	4.2(1)	3.7(1)	2.0(1)

	<i>Occupancy</i>	0.67(1)	0.779(5)	0.766(4)	0.864(5) ^c
O3 (½ 0 z)	<i>z</i>	0.11592(3)	0.11613(2)	0.11613(1)	0.11599(2)
	<i>U_{eq}</i>	1.14(5)	1.08(2)	0.97(2)	0.87(3)

^a *U_{eq}* is defined as one third of the orthogonalized *U_{ij}* tensor.

^b Not refined

^c Total of occupancy by O and F (given the similarity in O and F scattering lengths)

Table S11. Selected bond distances and angles for oxyseLENIDES from PND data collected on POLARIS.

Compound	$\text{Sr}_4\text{Mn}_3\text{O}_{7.35}\text{Cu}_2\text{Se}_2$	$\text{Sr}_4\text{Mn}_3\text{O}_{7.56}\text{Cu}_2\text{Se}_2$	$\text{Sr}_4\text{Mn}_3\text{O}_{7.53}\text{Cu}_2\text{Se}_2$	$\text{Sr}_4\text{Mn}_3\text{O}_{7.53}\text{F}_{0.20}\text{Cu}_2\text{Se}_2$
Sample ID	GH198	GH201	GH288	GH319
Bond distance / Å				
Mn1–O1 [1]	2.012(3)	1.997(2)	1.990(1)	1.989(2)
Mn1–O3 [4]	1.9736(7)	1.965(6)	1.9613(1)	1.9577(4)
Mn2–O1 [2]	1.839(2)	1.880(1)	1.876(1)	1.874(1)
Mn2–O2 [4]	1.9584(6)	1.9502(6)	1.94608(2)	1.9424(4)
Cu–Se [4]	2.5023(9)	2.5069(7)	2.5037(4)	2.5046(6)
Bond angle / °				
O1–Mn1–O3 [4]	97.11(6)	96.98(3)	97.14(3)	97.18(4)
O3–Mn1–O3 [4]	89.12(1)	89.155(8)	89.115(7)	89.11(1)
Se–Cu–Se [2]	103.01(5)	102.14(3)	102.03(2)	101.71(1)
Se–Cu–Se [4]	112.80(3)	113.26(2)	113.32(1)	113.49(2)

Figure S1. Electrical resistivity of a sample of $\text{Sr}_4\text{Mn}_{2.9}\text{O}_{7.4}\text{Cu}_2\text{S}_2$ as a function of temperature measured using a 4-probe technique.

Figure S2. The crystal structure of $\text{Sr}_4\text{Mn}_{2.94(2)}\text{O}_{7.42(5)}\text{Cu}_2\text{S}_2$ derived from single crystal X-ray diffraction data.

Figure S3. Electron diffraction patterns for the as-made Mn-rich oxysulfide $\text{Sr}_4\text{Mn}_{2.91}\text{O}_{7.40}\text{Cu}_2\text{S}_2$ showing no signs of vacancy/anion ordering leading to a superstructure on the lengthscale of the electron diffraction experiment. The patterns are indexed on a body centred tetragonal unit cell with the dimensions given in Table 1.

Figure S4. Comparative thermogravimetric analysis results for $\text{Sr}_4\text{Mn}_{2.91}\text{O}_{7.40}\text{Cu}_2\text{S}_2$ and its reduced derivative $\text{Sr}_4\text{Mn}_{2.91}\text{O}_{6.97}\text{Cu}_2\text{S}_2$.

Figure S5. The environments around Mn2 in the central layer obtained by Rietveld refinement against Powder Neutron Diffraction Data collected on the POLARIS diffractometer. As-made, reduced and fluorinated Mn-rich oxysulfides and oxyselenides are shown as a function of the refined fractional occupancy of the O2 site. Displacement ellipsoids are shown at the 80% level

Figure S6. The magnetic susceptibilities of Mn-poor oxysulfides: as-made $\text{Sr}_4\text{Mn}_{2.77}\text{O}_{7.27}\text{Cu}_2\text{S}_2$ (black), reduced $\text{Sr}_4\text{Mn}_{2.77}\text{O}_{7.16}\text{Cu}_2\text{S}_2$ (green) and oxidized $\text{Sr}_4\text{Mn}_{2.77}\text{O}_{7.27}\text{F}_{0.27}\text{Cu}_2\text{S}_2$ (blue). Samples were measured under Zero-Field-Cooled (ZFC) (closed symbols) and Field-Cooled (FC) (open symbols) conditions in a measuring field of 0.01 T. The discernable maximum equated with the Néel temperatures for $\text{Sr}_4\text{Mn}_{2.77}\text{O}_{7.27}\text{F}_{0.27}\text{Cu}_2\text{S}_2$ is indicated by an arrow.

Figure S7. Upper: 5K Magnetization isotherms for Mn-poor oxysulfides: As-made $\text{Sr}_4\text{Mn}_{2.77}\text{O}_{7.27}\text{Cu}_2\text{S}_2$ (black), its reduction product $\text{Sr}_4\text{Mn}_{2.77}\text{O}_{7.16}\text{Cu}_2\text{S}_2$ (green) and its oxidation product $\text{Sr}_4\text{Mn}_{2.77}\text{O}_{7.27}\text{F}_{0.27}\text{Cu}_2\text{S}_2$ (blue). Lower: 5K magnetization isotherms for oxyselenides: as-made $\text{Sr}_4\text{Mn}_3\text{O}_{7.56}\text{Cu}_2\text{Se}_2$ (black, closed circles) and its reduction product $\text{Sr}_4\text{Mn}_3\text{O}_{7.35}\text{Cu}_2\text{Se}_2$ (green closed circles); and as-made $\text{Sr}_4\text{Mn}_3\text{O}_{7.53}\text{Cu}_2\text{Se}_2$ (black open circles) and its oxidation product $\text{Sr}_4\text{Mn}_3\text{O}_{7.53}\text{F}_{0.20}\text{Cu}_2\text{Se}_2$ (blue open circles).