Reversible lithium insertion and copper extrusion in layered oxysulfides

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Supplementary Information

Table S1. Refinement results for $Sr_2MnO_2Li_{1.86(3)}S_2$ (**1Li**) and $Sr_2MnO_2Li_{3.8(1)}S_3$ (**2Li**)

Sample	**1Li**	**2Li**
Refined composition	$Sr_2MnO_2Li_{1.86(3)}S_2$	$Sr_2MnO_2Li_{3.63(3)}S_3$
Radiation	Neutron	
Instrument	POLARIS	
Physical form	Black powder	
T / K	295	
Space group	*I*4/*mmm*	*P*4/*mmm*
Formula weight	338.6	383.5
a / Å	4.07036(8)	4.05416(9)
c / Å	17.8721(4)	11.7964(3)
V / Å^3	296.1(1)	193.885(8)
Z	2	1
R_{wp}	0.0178	0.0170
R_{F2}	0.0314	0.0607
χ^2	3.643	1.832

Table S2. Atomic parameters for **1Li** obtained from PND data collected on POLARIS at 295 K.

Atom	Site	occupancy	*x*	*y*	*z*	$100 \times (U_{iso,eq} / Å^2)$
Sr	4*e*	1[a]	0.5	0.5	0.09218(3)	1.03(2)
Mn	2*a*	1[a]	0	0	0	1.08(4)
O	4*c*	1[a]	0.5	0	0	1.13(3)
S	4*e*	1[a]	0	0	0.17099(7)	1.04(4)
Li	4*d*	0.943(6)	0.5	0	0.25	2.32(8)

[a] not refined

Table S3. Anisotropic displacement parameters[a] for **1Li** obtained from PND data collected on POLARIS at 295 K.

Atom	$100 \times (U_{11} / Å^2)$	$100 \times (U_{22} / Å^2)$	$100 \times (U_{33} / Å^2)$
Sr	1.11(2)	U_{11}	0.88(2)
Mn	0.33(2)	U_{11}	2.59(7)
O	1.15(2)	1.18(2)	1.05(3)
S	1.12(3)	U_{11}	0.88(5)
Li	2.22(6)	U_{11}	2.5(1)

[a]Off-diagonal elements equal zero by symmetry

Table S4. Atomic parameters for **2Li** obtained from PND data collected on POLARIS at 295 K. Li located on the ideal tetrahedral site only.

Atom	Site	occupancy	*x*	*y*	*z*	100 × ($U_{iso,eq}$ / Å^2)
Sr	2*h*	1[a]	0.5	0.5	0.14101(7)	0.94(3)
Mn	1*a*	1[a]	0	0	0	1.3(1)
O	2*f*	1[a]	0	0.5	0	0.96(4)
S1	2*g*	1[a]	0	0	0.2574(2)	1.29(7)
S2	1*d*	1[a]	0.5	0.5	0.5	1.17(8)
Li	4*i*	0.904(7)	0	0.5	0.3830(2)	2.1(2)

[a] not refined

Table S5. Anisotropic displacement parameters[a] for **2Li** obtained from PND data collected on POLARIS at 295 K.

Atom	100 × (U_{11} / Å^2)	100 × (U_{22} / Å^2)	100 × (U_{33} / Å^2)
Sr	0.76(2)	U_{11}	1.31(4)
Mn	0.19(4)	U_{11}	3.4(1)
O	1.12(4)	1.42(4)	0.35(5)
S1	1.22(5)	U_{11}	1.4 (1)
S2	1.13(7)	U_{11}	1.3(1)
Li	1.0(1)	2.0(2)	3.4(2)

[a]Off-diagonal elements equal zero by symmetry

Table S6. Selected metal–anion bond distances in Å and angles in degrees for **1Li**

Mn–O [4][a]	2.03518(4)
Mn–S [2]	3.056(1)
Sr–O [4]	2.6185(3)
Sr–S [4]	3.2043(6)
Li–S [4]	2.4771(7)
O–Sr–O [2]	102.02(2)
O–Sr–O [4]	66.679(9)
O–Sr–S [8]	140.37(1)
O–Sr–S[8]	77.46(2)
S–Sr–S [2]	127.85(4)
S–Sr–S [4]	78.86(2)
S–Li–S [2]	110.49(5)
S–Li–S [4]	108.96(2)

[a] The numbers in square brackets indicate the number of bonds or angles of a particular type.

Table S7. Selected metal–anion bond distances in Å and angles in degrees for **2Li**

Mn–O [4][a]	2.02708(5)
Mn–S1 [2]	3.036(2)
Sr–O [4]	2.6222(6)
Sr–S1 [4]	3.178(1)
Li–S1 [2]	2.511(2)
Li–S2 [2]	2.452(2)
O–Sr–O [2]	101.26(3)
O–Sr–O [4]	66.27(2)
O–Sr–S1 [8]	140.08(2)
O–Sr–S1[8]	77.35(3)
S1–Sr–S1 [2]	128.83(8)
S1–Sr–S1 [4]	79.25(3)
S1–Li–S1 [1]	107.7(1)
S1–Li–S2 [4]	109.4(2)
S2–Li–S2 [1]	111.5(1)

[a] The numbers in square brackets indicate the number of bonds or angles of a particular type.

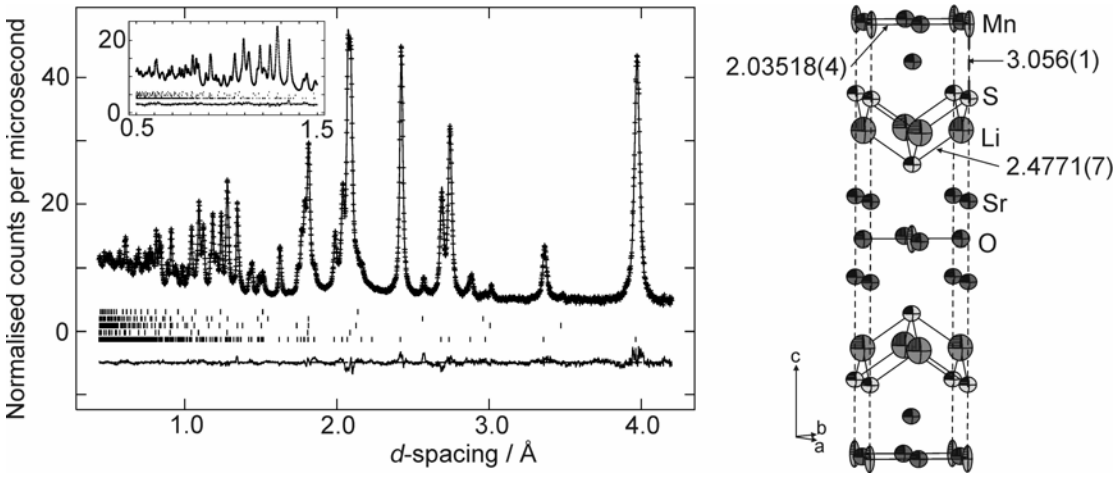

Fig. S1. Rietveld refinement of the structure of $Sr_2MnO_2Li_{1.86(3)}S_2$ (**1Li**) against PND data at 295 K. Peak position markers are for (from bottom) **1Li (**bottom), Cu, small SrS and SrO impurities (~2%) and V (sample container). The structure diagram shows the unit cell with 99 % anisotropic displacement ellipsoids and selected interatomic distances in Å.

Table S8. Kinetic parameters derived[a] from *in situ* measurements

Temperature / °C	m	$10^4 \times k$ / s^{-1}
30	1.20(1)	2.0(3)
45	1.41(3)	7.5(3)
50	1.16(2)	9.9(2)
60	1.7(1)	12(2)

[a]Avrami-Erofe'ev model: $\alpha(t) = 1-\exp(-(kt)^m)$ where $\alpha(t)$ is the extent of reaction at time t, k is the rate constant and the exponent m provides information on the mechanism of the reaction. The fits to the data are shown in Fig. 3 (main text).

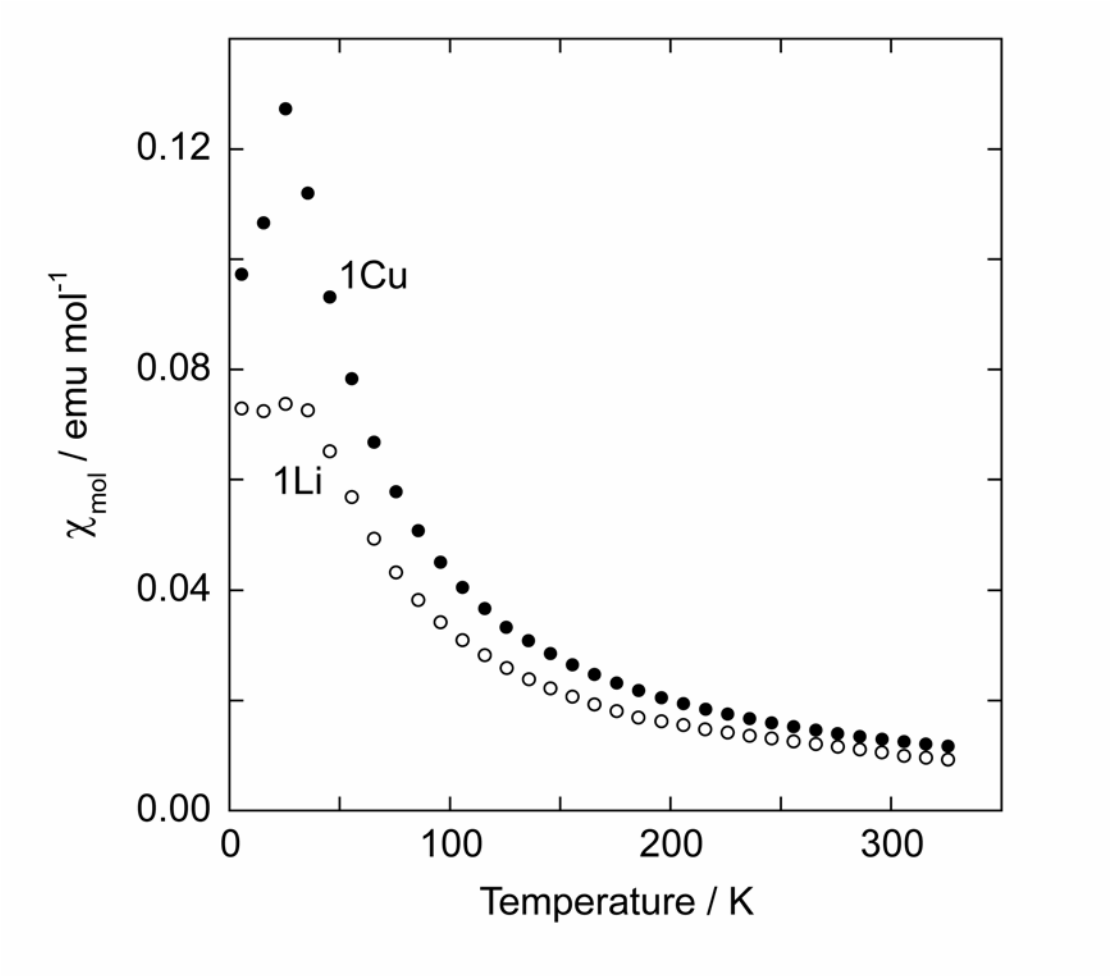

Fig. S2. Magnetic susceptibilities of $Sr_2MnO_2Cu_{1.5}S_2$ (**1Cu**) and $Sr_2MnO_2Li_{1.86(3)}S_2$ (**1Li**) as functions of temperature. Measurements were made by measuring the difference in magnetic moments of each sample in applied magnetic fields of 3 T and 4 T to avoid the effects of small amounts of ferromagnetic impurities. **1Li** does not obey the Curie-Weiss law over the range of temperatures studied and the existence of possible magnetic ordering is under investigation.