

Reversible lithium insertion and copper extrusion in layered oxysulfides†

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Received (in Cambridge, UK) 10th April 2006, Accepted 10th May 2006

First published as an Advance Article on the web 6th June 2006

DOI: 10.1039/b605105g

All of the copper in the layered oxysulfides $\text{Sr}_2\text{MnO}_2\text{Cu}_{1.5}\text{S}_2$ and $\text{Sr}_2\text{MnO}_2\text{Cu}_{3.5}\text{S}_3$ may be extruded as the element and the copper ions replaced quasi-reversibly by lithium ions in reductive topotactic ion exchange reactions; dramatic changes in magnetic properties result.

So-called “soft” chemistry (*chimie douce*) in the solid state is important in the synthesis of novel materials and in the control of electron count, crystal structure and materials properties.^{1,2} Reductive insertion of alkali metals such as lithium into metal oxides is the basis of recent advances in lithium-ion battery technology.^{3,4} Non-redox ion exchange is also useful in the synthesis of novel materials.² These approaches enable the isolation of products which are metastable with respect to the formation of more thermodynamically stable products at elevated temperatures.

As part of an investigation of mixed-anion compounds we are probing a series of layered oxysulfides containing oxide slabs which incorporate the “harder”, more electropositive and oxophilic metals, and sulfide slabs which incorporate the “softer”, more polarising, chalcophilic metals. Layered structures in oxysulfides are common because this is a simple way for two anions with different sizes and chemical requirements to order crystallographically. We have recently characterised an homologous series of oxysulfides of general formula $\text{Sr}_2\text{MnO}_2\text{Cu}_{2m-\delta}\text{S}_{m+1}$ ($m = 1, 2, 3$)⁵ and the intergrowth of the $m = 1$ and $m = 2$ members.⁶ These compounds contain Sr_2MnO_2 slabs separated by copper sulfide layers of varying thickness which resemble fragments of the $\text{Cu}_{2-\delta}\text{S}$ anti-fluorite structure. These semiconducting compounds are all copper deficient ($\delta \sim 0.5$) with manganese oxidised to the $+(2 + \delta)$ (*i.e.* $\sim +2.5$) state to maintain a full valence band.⁵ Below 30 K the compounds are *A*-type antiferromagnets with ferromagnetic alignment of manganese moments in each layer and antiferromagnetic coupling between layers. On application of sufficiently large external magnetic fields the materials become bulk ferromagnets. The correlation of these properties with complex low-temperature structural distortions⁵ are under investigation. Here we demonstrate that all of the Cu^+ ions in the copper sulfide slabs in the $m = 1$ and $m = 2$ members of the series, $\text{Sr}_2\text{MnO}_2\text{Cu}_{1.5}\text{S}_2$ (**1Cu**) and $\text{Sr}_2\text{MnO}_2\text{Cu}_{3.5}\text{S}_3$ (**2Cu**), may be replaced topotactically with Li^+ ions under reductive ion exchange conditions,⁷ to form $\text{Sr}_2\text{MnO}_2\text{Li}_{1.86(3)}\text{S}_2$ (**1Li**) and

$\text{Sr}_2\text{MnO}_2\text{Li}_{3.8(1)}\text{S}_3$ (**2Li**) respectively. The exchange of Cu^+ by Li^+ and concomitant reduction of manganese suppresses long range magnetic ordering.

All manipulations were carried out in an argon-filled dry box or under nitrogen using Schlenk techniques. Black air-stable **1Cu** and **2Cu**⁵ were prepared‡ on the 4 g scale by grinding together stoichiometric amounts of SrS , Mn , MnO_2 , CuO and Cu_2S and heating pellets of the mixtures in alumina-lined evacuated silica tubes at 1000 °C for 19 hours. Ion exchange was carried out by stirring the powders with a 20-fold excess ($\text{Li} : \text{Mn}$ ratio 20 : 1) of 0.25 M *n*-BuLi in a hexane/pentane mixture at 20 °C for 12 hours (**2Cu**) or a 20-fold excess of 2.5 M *n*-BuLi in hexane at 50 °C for 4 days (**1Cu**). The reddish-black air-sensitive products were filtered off, washed with pentane,‡ dried under vacuum and stored in the dry box. No reaction of **2Cu** was observed under non-reductive ion exchange conditions (28-fold excess of LiBr in refluxing hexanol at 160 °C for 8 hours).

The powder X-ray diffraction (PXRD)§ patterns of the lithiated products showed mixtures of copper metal and compounds with powder patterns resembling somewhat those of the starting materials, but with different intensity distributions. The patterns were indexed on similar tetragonal unit cells to those of **1Cu** (body-centred) and **2Cu** (primitive),⁵ suggesting that the reactions are topotactic. Refinement of the lattice parameters showed 1.45% and 0.96% increases in *a* and 4.0% and 3.4% increases in *c* on lithiation of **1Cu** and **2Cu** respectively. The observations are consistent with the replacement of Cu^+ ions by the similarly-sized Li^+ ions with the extrusion of elemental copper and with reduction of manganese resulting in longer Mn–O and Mn–S bonds.

When the Cu ions in the structural models of **1Cu** and **2Cu** were replaced by Li, the intensities in both the X-ray and neutron§ diffractograms of **1Li** and **2Li** were reproduced well. Rietveld refinements of the structures of **1Li** and **2Li** against powder neutron diffraction (PND) data included, as an additional phase, elemental copper which we have been unable to remove chemically⁷ or physically without destroying the lithiated products. Refinement of the structure of **1Li** proceeded without incident yielding satisfactory agreement factors ($\chi^2 = 3.643$, $wR_p = 0.0178$, $R_{F2} = 0.0314$) with lithium ions replacing the copper ions in **1Cu** in tetrahedral coordination by S. Assuming that the natural ${}^6\text{Li} : {}^7\text{Li}$ isotope ratio was maintained in the product, the fractional occupancy of these sites was 0.943(6) yielding a refined composition for **1Li** of $\text{Sr}_2\text{MnO}_2\text{Li}_{1.88(1)}\text{S}_2$ (chemical analysis:‡ $\text{Sr}_2\text{MnO}_2\text{Li}_{1.86(3)}\text{S}_2$). Refinement of the structure of **2Li** with lithium ions located only on the ideal tetrahedral sites in the sulfide layer (Fig. 1) yielded satisfactory agreement factors ($\chi^2 = 1.832$, $wR_p = 0.0170$, $R_{F2} = 0.061$) and a refined composition

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† Electronic supplementary information (ESI) available: Tables of crystallographic data; kinetic parameters and magnetic susceptibility of **1Li**. See DOI: 10.1039/b605105g

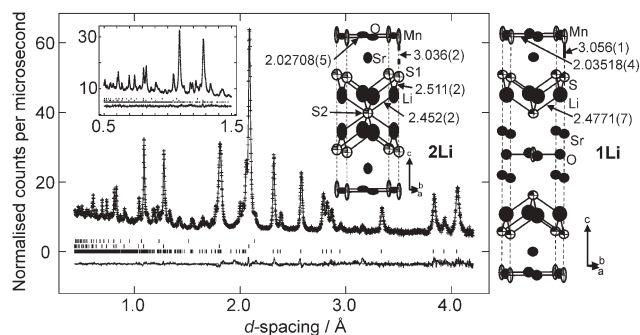


Fig. 1 Rietveld refinement of the structure of **2Li** against PND data. Observed: points; fit: solid line; difference: lower line. Peak positions are marked for **2Li** (bottom), Cu and V (sample container) (top). The structure diagrams show the unit cells with 99% anisotropic displacement ellipsoids and selected interatomic distances in Å.

$\text{Sr}_2\text{MnO}_2\text{Li}_{3.62(3)}\text{S}_3$ (chemical analysis: \ddagger $\text{Sr}_2\text{MnO}_2\text{Li}_{3.79(1)}\text{S}_3$). An improvement in agreement factors ($\chi^2 = 1.779$, $wR_p = 0.0168$, $R_{F2} = 0.059$) was obtained for **2Li** when further lithium ions were located in off-tetrahedral general positions located at short, but not unprecedented,⁸ distances of 2.19(2) Å and 2.11(2) Å from two sulfur atoms. The refined fractional occupancy of these sites (which are not available in **1Li**, and which are not the same off-tetrahedral sites as those occupied by Cu^+ in **2Cu**⁵) was 0.047(2), and this analysis yielded an overall composition of $\text{Sr}_2\text{MnO}_2\text{Li}_{4.44(6)}\text{S}_3$ for **2Li**. The large range of values for the Li content obtained by Rietveld refinement of **2Li** is likely a consequence of the relatively small absolute value of the scattering length of Li compared with those of the other elements and contamination of the diffractogram by more elemental copper than in the case of **1Li**. Further diffraction and solid state NMR measurements are required to determine whether the suggested occupancy of the off-tetrahedral sites in **2Li** is real. Given the excellent contrast between the scattering lengths of Li (−1.90 fm) and Cu (+7.72 fm), the refinements of both **1Li** and **2Li** do indicate full replacement of Cu by Li. The refined molar ratio of **2Li** to Cu metal obtained from the PND refinement was 1 : 3.53(3), also consistent with complete reductive extrusion of all the copper ions from **2Cu**. On lithiation, the four Mn–O distances increase from 2.0061(1) Å in **1Cu** to 2.03518(4) Å in **1Li** (+1.45%) and from 2.0076(1) Å in **2Cu** to 2.02708(5) Å in **2Li** (+0.96%). The two Mn–S distances increase from 2.915(1) Å in **1Cu** to 3.056(1) Å in **1Li** (+4.8%) and from 2.877(1) Å in **2Cu** to 3.036(2) Å in **2Li** (+5.5%). The long Mn–S distances in both **1Li** and **2Li** lead to elongation of the Mn displacement ellipsoids along the Mn–S bonds. Bond valence (BV) calculations using the EUTAX package⁹ produced BV sums for Mn of 2.51 (**1Cu**), 2.55 (**2Cu**), 2.26 (**1Li**) and 2.32 (**2Li**). The structural similarities of the compounds suggest that the changes in BV sum on lithiation are meaningful measures of the degree to which Mn is reduced and imply compositions $\text{Sr}_2\text{MnO}_2\text{Li}_{1.75}\text{S}_2$ (**1Li**) and $\text{Sr}_2\text{MnO}_2\text{Li}_{3.75}\text{S}_3$ (**2Li**). The compositions obtained from chemical analysis, and inferred from BV analysis and supported in the case of **1Li** by the PND refinement results suggest that reasonable compositions are $\text{Sr}_2\text{MnO}_2\text{Li}_{1.86(3)}\text{S}_3$ (**1Li**) and $\text{Sr}_2\text{MnO}_2\text{Li}_{3.8(1)}\text{S}_3$ (**2Li**) with Mn reduced to the +2.14(3) and +2.2(1) oxidation states respectively.

Exposure of the products to moist air resulted in reversal of the ion exchange reaction. PXRD patterns (Fig. 2) of a sample of **2Li** (plus copper metal) taken at intervals after initial air exposure show the intensities of the Cu peaks diminishing and the intensities and positions of the peaks due to the tetragonal phase changing from those characteristic of **2Li** to those characteristic of **2Cu**. After 24 hours the **2Li** and Cu peak intensities were almost zero and **2Cu** was restored as the major phase. However, the presence of small copper peaks even after a week's air exposure suggests incomplete reversibility under these conditions. The mean size of the elemental copper particles in **1Li** and **2Li** estimated by Scherrer analysis was ~50 nm which may explain the reactivity of Cu with **2Li** in air.

The kinetics of lithiation of **2Cu** (**1Cu** reacts more slowly) was investigated using time-resolved *in situ* energy dispersive PXRD measurements.[§] The integrated intensity of the 001 reflection, which accidentally has zero intensity in **2Cu**, was measured as a function of time in four separate runs carried out at 30, 45, 50 and 60 °C. This was converted into the extent of the reaction at time t , $\alpha(t)$ according to $\alpha(t) = I_{001}(t)/I_{001}(\infty)$. This was modelled using the Avrami–Erofe'ev expression^{10,11} which relates $\alpha(t)$ to the rate constant, k , and an exponent, m , characteristic of the rate of nucleation and the mechanism of growth:¹² $\alpha(t) = 1 - \exp(-kt)^m$. Sharp–Hancock¹³ plots: $\ln(-\ln(1 - \alpha))$ vs. $\ln(t)$ (Fig. 3) were used to extract m (the gradient) and k (intercept is $m \ln k$). The plots were linear, confirming the Avrami–Erofe'ev model as a valid description of this system. The values of m between 30 and 60 °C lay in the range $1.16(2) < m < 1.7(1)$. These values are consistent with a 2D diffusion controlled process following deceleratory nucleation.¹² The rate constant k at 50 °C was $9.9(2) \times 10^{-4} \text{ s}^{-1}$, and an Arrhenius plot ($\ln k$ vs. $1/T$) (Fig. 3) produced an estimated activation energy of $58 \pm 8 \text{ kJ mol}^{-1}$.

Magnetic susceptibility[¶] and PND measurements on **2Cu**⁵ show that in zero applied magnetic field the compound is an *A*-type antiferromagnet below 30 K with ferromagnetic MnO_2 sheets coupled antiferromagnetically to each other. The weak antiferromagnetism is overcome by an applied magnetic field of about 1.2 T leading to bulk ferromagnetic behaviour in large applied fields (Fig. 4) (fields exceeding 7 T are required to accomplish this in **1Cu**⁵). On lithiation both the low field antiferromagnetic ordering and the

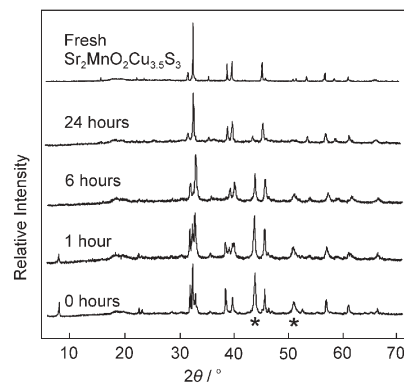


Fig. 2 Evolution of the X-ray powder diffraction pattern following air exposure over a 24 hour period of $\text{Sr}_2\text{MnO}_2\text{Li}_{3.8(1)}\text{S}_3$ (**2Li**). Lines marked (*) are due to elemental copper. The diffractogram of $\text{Sr}_2\text{MnO}_2\text{Cu}_{3.5}\text{S}_3$ (**2Cu**) prior to lithiation is shown for comparison. The 001 reflection at $\sim 8^\circ 2\theta$ was used in the analysis of the *in situ* experiments.

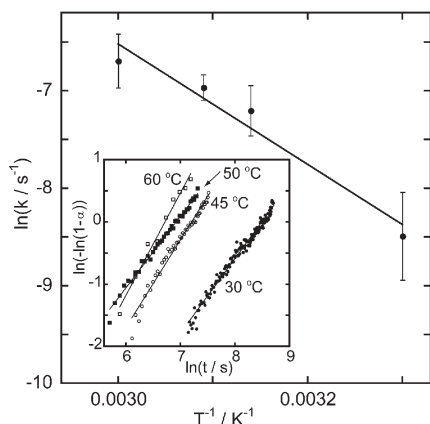


Fig. 3 Arrhenius plot relating the rate of lithiation to reaction temperature. Inset: the Sharp–Hancock¹³ plots from which the rate constants were extracted (see text). In each case the lines are linear fits to the data points.

high field ferromagnetic ordering are apparently lost (Fig. 4). This change is presumably a consequence of reduction of the Mn oxidation state and changes in the between-layer superexchange pathways effected by the substitution of Cu^+ by Li^+ and the large increase in Mn–S bond length. On air exposure the magnetic properties characteristic of **2Cu** were not restored, confirming that the reaction is only quasi-reversible under these conditions.

Preliminary experiments on $\text{Sr}_4\text{Mn}_2\text{O}_4\text{Cu}_5\text{S}_5$ ⁶ and $\text{Sr}_2\text{MnO}_2\text{Cu}_{3.5}\text{S}_4$ ⁵ suggest that full lithiation is possible in these compounds. Investigation of the reversibility of the processes using electrochemical methods, the lithium ion mobility and the relevance of these compounds to novel lithium ion battery materials¹⁴ is in progress,¹⁵ together with further investigation of the reaction kinetics and the magnetic and electronic properties of both the copper- and lithium-containing materials.

We thank the CCLRC for access to ISIS and the SRS, Dr R. I. Smith for assistance on POLARIS, Dr D. Taylor and Mr A. Neild for assistance on Station 16.4, and the EPSRC for providing a studentship for O. J. R.

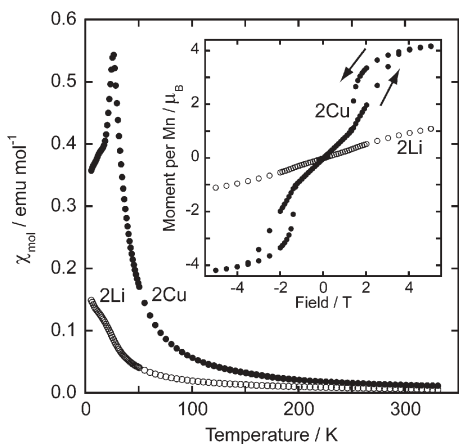


Fig. 4 The zero-field cooled (ZFC) magnetic susceptibilities (measuring field 10 mT) of $\text{Sr}_2\text{MnO}_2\text{Cu}_{3.5}\text{S}_4$ (**2Cu**) (●) and the lithiated product $\text{Sr}_2\text{MnO}_2\text{Li}_{3.8(1)}\text{S}_4$ (**2Li**) (○). The field-cooled susceptibility of **2Li** is coincident with the ZFC susceptibility. The inset shows the magnetisation isotherms at 5 K measured on the same samples.

Notes and references

‡ MnO_2 (ALFA 99.999%), Mn (Aldrich 99.99%), CuO (Aldrich 99.99%); Cu_2S was prepared by reacting Cu powder (ALFA 99.999%) with S (ALFA 99.9995%) in an evacuated silica tube at 400 °C for 1 day then 700 °C for 4 days; SrS was prepared by reaction of SrCO_3 (ALFA 99.99%) with CS_2 vapour (Aldrich 99.9%) in an Ar stream at 800 °C for 4 hours. Pentane for washing lithiated products was dried over 4 Å molecular sieves, refluxed over Na/K alloy under N_2 and collected by distillation. Analysis for Li was carried out using a Thermo Elemental Atomscan 16 ICP analyser; Li ions were leached out by boiling the lithiated solid in 20% nitric acid solution.

§ PXR data were collected using a Philips X'Pert PW3209 diffractometer operating with $\text{CuK}\alpha$ radiation in Bragg–Brentano geometry with samples sealed inside air-tight cells. Time-of-flight PND data (POLARIS diffractometer, ISIS, UK; detector banks at 35°, 90° and 145° 2θ ($0.5 < d < 8$ Å)) were collected on 3 g samples sealed in vanadium cans. Rietveld analysis was performed using the GSAS suite.¹⁶

Crystal data: $\text{Sr}_2\text{MnO}_2\text{Li}_{1.86(3)}\text{S}_2$ (**1Li**): $T = 295$ K, tetragonal, space group $I4/mmm$ (no. 139), $a = 4.07036(8)$, $c = 17.8721(4)$ Å, $Z = 2$; Mn (0 0 0), Sr (0.5 0.5 0.09218(3)), O (0.5 0 0), S (0 0 0.17099(7)), Li (0.5 0 0.25; occupancy 0.943(6)); $\chi^2 = 3.643$; $wR_p = 0.0178$.

$\text{Sr}_2\text{MnO}_2\text{Li}_{3.8(1)}\text{S}_3$ (**2Li**): $T = 295$ K, tetragonal, space group $P4/mmm$ (no. 123), $a = 4.05416(9)$, $c = 11.7962(3)$ Å, $Z = 1$; Mn (0 0 0), Sr (0.5 0.5 0.14101(8)), O (0 0.5 0), S1 (0 0 0.2574(2)), S2 (0.5 0.5 0.5), Li (0 0.5 0.3830(2); occupancy 0.904(7)); $\chi^2 = 1.832$; $wR_p = 0.0170$. Note: this model for **2Li** has Li located only on the “ideal” tetrahedral sites; a second Li site (0.103(5), 0.229(4), 0.415(2)) may be ~5% occupied.

CCDC 604753–604760. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b605105g

In situ energy dispersive PXR data were obtained on Station 16.4 of the SRS, Daresbury Laboratory, UK using apparatus developed by O'Hare and co-workers.¹⁷ 0.3 g of $\text{Sr}_2\text{MnO}_2\text{Cu}_{3.5}\text{S}_3$ powder, 10 cm³ of 2.5 M *n*-BuLi solution (Li : Mn ratio 160 : 1) in hexanes and a glass-coated magnetic follower were sealed inside a Pyrex ampoule. This was placed inside a pre-heated aluminium heating block on Station 16.4 and the reaction was stirred using a magnetic stirrer such that the amount of solid exposed to the beam was constant with time. Slits in the heating block allowed passage of the incident and diffracted beams. Scattered X-rays were measured using three energy discriminating detectors located at 2–6° 2θ and covering a d -spacing range of 1–46 Å.

¶ Magnetic susceptibility (Quantum Design MPMS-XL SQUID magnetometer) measurements were made on warming in an applied field of 10 mT after cooling in zero field (zero-field cooled) and after cooling in the measuring field (field-cooled). Magnetisation isotherms were measured in applied fields of up to ±5 T.

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