

A novel layered oxysulfide intergrowth compound $\text{Sr}_4\text{Mn}_2\text{Cu}_5\text{O}_4\text{S}_5$ containing a fragment of the $\alpha\text{-Cu}_2\text{S}$ antifluorite structure

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$\text{Sr}_4\text{Mn}_2\text{Cu}_5\text{O}_4\text{S}_5$ contains manganese oxide sheets separated by unusual antifluorite-type Cu_3S_3 layers in which copper(I) ions are distributed over three- and four-coordinate sites in a similar fashion to in $\alpha\text{-Cu}_{2-x}\text{S}$ and suggestive of high two-dimensional copper ion mobility.

Ternary manganese oxides are of great importance.¹ Perovskites, pyrochlores and Ruddlesden-Popper (R-P) phases with a range of $\text{Mn}^{\text{III/IV}}$ ratios often exhibit the phenomenon of giant magnetoresistance and have a range of composition-dependent crystallographic, magnetic and electronic properties.

Oxysulfides contain anions with different sizes and chemical requirements which order crystallographically, often resulting in layered structures. Phases reminiscent of the R-P oxides, in which perovskite-type oxide layers are separated by $\text{Cu}_2\text{S}_2^{2-}$ anti-PbO-type puckered layers, have been reported including $\text{Sr}_2\text{MnCu}_2\text{O}_2\text{S}_2^{2-}$ (Mn^{II}) containing MnO_2 sheets alternating with Cu_2S_2 layers, $\text{Sr}_2\text{MnCuO}_3\text{S}^3$ (Mn^{III}) containing double layers of corner-linked MnO_5 pyramids separated by Cu_2S_2 layers and $\text{Sr}_4\text{Mn}_3\text{Cu}_2\text{O}_7.5\text{S}_2^3$ (Mn^{III}) which contains triple oxide layers, similar to those in the $n = 3$ R-P Mn^{IV} manganate $\text{Sr}_4\text{Mn}_3\text{O}_{10}$. Here we demonstrate that more sulfide-rich materials containing thicker sulfide layers are accessible and report the structure, from single crystal X-ray diffraction measurements of $\text{Sr}_4\text{Mn}_2\text{Cu}_5\text{O}_4\text{S}_5$, the first of these complex intergrowth compounds to contain a copper sulfide antifluorite-type layer of approximate stoichiometry Cu_3S_3 which, along with Cu_2S_2 layers, separates MnO_2 layers. This antifluorite layer resembles the Cu_4S_3 layers in the sulfides KCu_4S_3 ,⁴ and the homologous series $\text{TiCu}_{2n}\text{S}_{n+1}$ ⁵ but is highly defective and the Cu^+ ions may be modelled as disordered over two sites with large displacement ellipsoids, suggesting that they are mobile within the copper sulfide slabs. Such an antifluorite layer with copper ion disorder closely resembles a fragment of the high-temperature antifluorite fast copper ion conductor $\alpha\text{-Cu}_{2-x}\text{S}$.⁶

A ground, compacted mixture of MnO_2 , SrO , SrS , Sr and $\text{Cu}_2\text{S}^\ddagger$ in the ratio 2:1:1:1:1 was contained within a 10 mm diameter alumina crucible sealed under vacuum within a silica tube and heated for 18 days at 1050 °C with the intention of synthesising 1.5 g of $\text{Sr}_3\text{Mn}_2\text{Cu}_2\text{O}_5\text{S}_2$, (cf. $\text{Sr}_3\text{Fe}_2\text{Cu}_2\text{O}_5\text{S}_2$.⁷) Energy dispersive analysis of X-rays (EDX)[†] showed that the ratios Sr:Mn:Cu:S in the black, shiny crystals extracted from the pellet were either 2:1.5:1:1.1 or 2:1:2.4:2.6 (estimated standard deviations of 10% on these values.) Reactants were handled in a dry box; the products were air stable.

Single crystal X-ray diffraction measurements[‡] confirmed that the crystals poorer in copper and sulfur were $\text{Sr}_4\text{Mn}_3\text{Cu}_2\text{O}_7.5\text{S}_2$.³ The lattice parameters and body centred tetragonal symmetry of the other crystals identified as $\text{Sr}_4\text{Mn}_2\text{Cu}_5\text{O}_4\text{S}_5$ ($a = 4.0157(1)$, $c = 39.995(1)$) suggested a new layered structure. Structure solution using Direct Methods yielded a structure (Fig. 1) in which MnO_2 sheets are separated alternately by the familiar Cu_2S_2 layers and by unusual antifluorite-type layers of ideal stoichiometry Cu_4S_3 which may be constructed by fusing two of the Cu_2S_2 layers together. Subsequent syntheses using reaction mixtures richer in Cu_2S resulted in a reproducibly higher yield of $\text{Sr}_4\text{Mn}_2\text{Cu}_5\text{O}_4\text{S}_5$,

however reactions carried out using the appropriate stoichiometric mixture of reactants have not enabled preparation of this material as a single phase—the major products being $\text{Sr}_2\text{MnCu}_2\text{O}_2\text{S}_2^{2-}$ occurring with copper sulfide, the title phase and other, as yet unidentified, products.

Refinement against single crystal diffraction data of a model in which a single Cu2 atom was located, as in KCu_4S_3 ,⁴ or TiCu_4S_3 ,⁵ in tetrahedral sites in the antifluorite-type copper sulfide layers produced an isotropic atomic displacement parameter (ADP) for this atom which was four times that of the similarly-coordinated Cu1 atom located in the Cu_2S_2 single sulfide layers. Subsequent refinement of the occupancy of Cu2 to around 0.75 and refinement of anisotropic ADPs for all atoms led to an unacceptably high R -factor ($R(F^2)$) of 0.109 and a residual electron density of 7.87 e \AA^{-3} located 0.79 Å from the Cu2 position. An observed Fourier map (Fig. 1), indicated that the copper ions in the antifluorite-type sulfide layers could be modelled using two sites. Refinement using this model with all ADPs anisotropic and occupancies of all three Cu sites refined produced an R -factor ($R(F^2)$) of 0.038 and a positive residual electron density of 1.74 e \AA^{-3} located 0.72 Å from Mn1. The displacement ellipsoids of Cu2 and Cu2' (Fig. 1) are highly anisotropic and reproduce the electron density distribution

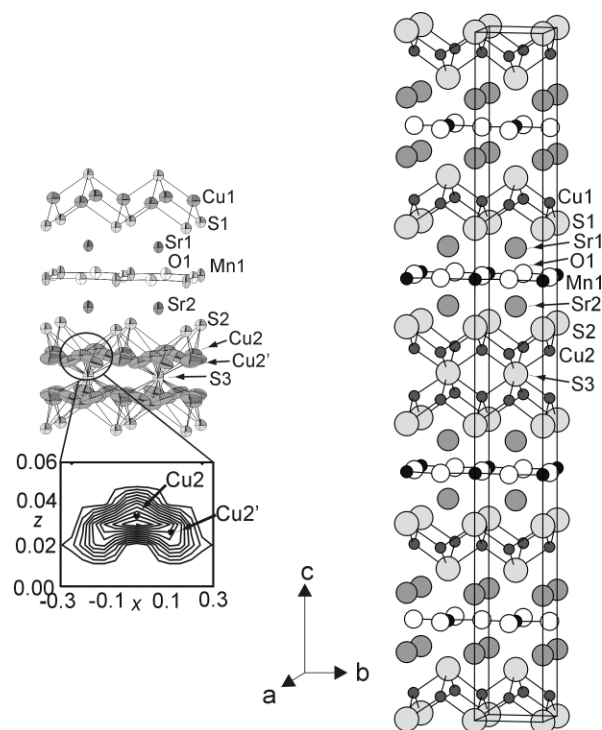


Fig. 1 Right: Idealised crystal structure of $\text{Sr}_4\text{Mn}_2\text{Cu}_5\text{O}_4\text{S}_5$ showing Cu_2S_2 layers and defective Cu_4S_3 antifluorite-type layers separating MnO_2 layers. Left: A portion of the structure derived from single crystal X-ray diffraction (90% displacement ellipsoids). Cu2 is modelled as a split site (Cu2 and Cu2') which accounts for the Fourier map of the observed electron density due to copper ions in the antifluorite-type sulfide layers (blow-up region).

Table 1 Selected structural parameters for Sr₄Mn₂Cu₅O₄S₅^a

Atom	Site	x	y	z	Occ.	$U_{eq}/\text{\AA}^2 \times 100$
Sr1	4e	0.5	0.5	0.31654(2)	1	1.28(2)
Sr2	4e	0.5	0.5	0.59752(2)	1	1.46(2)
Mn1	4e	0	0	0.64055(3)	1	1.29(3)
Cu1	4d	0.5	0	0.25	0.804(6)	2.08(4)
Cu2	8g	0	0.5	0.0342(2)	0.24(2)	3.4(3)
Cu2'	16n	0.157(3)	0.5	0.0259(2)	0.25(1)	4.8(2)
O1	8g	0.5	0	0.64170(9)	1	1.44(8)
S1	4e	0	0	0.28461(5)	1	1.40(4)
S2	4e	0	0	0.42945(5)	1	1.61(4)
S3	2a	0.5	0.5	0.5	0.92(2)	2.4(1)

^a 293 K, Space group *I4/mmm*, *a* = 4.0157(1) Å, *c* = 39.995(1) Å, *Z* = 2. Sr₄Mn₂Cu_{4.6(2)}O_{4.92(1)}, *M* = 974, *D*_c = 5.02 g cm⁻³.

obtained in the observed Fourier map. The composition derived from refinement of the structure against single crystal diffraction data is consistent with that derived from EDX analysis and the stoichiometry of the title compound is Sr₄Mn₂Cu_{4.6(2)}O_{4.92(1)}. In the anti-PbO-type single copper sulfide layer, the Cu1 site is not fully occupied and the formulation is Cu_{1.61(1)}□_{0.39(1)}S₂, where □ represents a cation vacancy. In the antifluorite-type copper sulfide layer the composition departs from the ideal Cu₄S₃ stoichiometry, observed in KCu₄S₃, which would arise from full occupancy of all the available tetrahedral sites and refines to Cu_{3.0(1)}□_{1.0(1)}S_{2.92(1)}□_{0.08(1)} ≈ 'Cu₃S₃' (□ represents cation and anion vacancies). The structure is composed of layers arranged in the sequence (MnO₂)(Cu_{1.6}S₂)(MnO₂)(Cu₃S₃) and separated by Sr²⁺ ions located in eight-coordinate (4 × S and 4 × O) sites.

The crystallographic copper ion disorder in the antifluorite-type sulfide layers is qualitatively similar to that in the fast ion conducting α- and β-forms of Cu₂S.^{6,8} The high-temperature phase α-Cu_{2-x}S (*x* = 0.05(4))⁶ has a modification of the antifluorite structure type in which the mobile copper ions are displaced towards the four trigonal sites located at the faces of the ideal tetrahedral sites and may be modelled, following the results of single crystal neutron diffraction measurements, with anharmonic displacement ellipsoids.⁶ In Sr₄Mn₂Cu₅O₄S₅, the antifluorite-type sulfide layers represent a highly copper-deficient two-dimensional fragment of α-Cu_{2-x}S in which the copper ions are displaced from their ideal tetrahedral positions towards the two trigonal sites on the two faces of a CuS₄ tetrahedron which point towards the central plane of the layers. In Sr₄Mn₂Cu₅O₄S₅ the Cu2 atoms are modelled using split sites (Fig. 1) with anisotropic displacement ellipsoids similar in size to those determined for the mobile copper ions in α- and β-Cu₂S^{6,8} and the mobile silver ions in LaAgOS,⁹ suggesting that the copper ions in Sr₄Mn₂Cu₅O₄S₅ may be similarly mobile in two dimensions. The structure of the antifluorite-type copper sulfide layer in Sr₄Mn₂Cu₅O₄S₅ contrasts with those in KCu₄S₃⁴ and TiCu_{2n}S_{n+1}⁵ in which the copper ions have displacement ellipsoids which are isotropic and very similar in size to those of the Cu1 site in Sr₄Mn₂Cu₅O₄S₅.

The Cu1–S1 distances of 2.439(1) Å are similar to those found in the Cu₂S₂ layers of related phases^{2,3,7} (e.g. Cu–S 2.446(3) Å in Sr₂MnCu₂O₂S₂).² The Cu2–S distances for the analogous tetrahedral sites of the antifluorite-type sulfide layer (Cu2–S2 2.480(5) Å; Cu2–S3 2.429(5) Å) are on average (2.45(3) Å) similar to the Cu–S distances in the idealised α-Cu₂S structure (2.437 Å). The Cu2' sites have a similar triangular coordination by sulfide (Cu2'–S2 2.26(1) Å; Cu2'–S3 2.346(5) Å × 2) to the actual Cu sites in α-Cu_{2-x}S⁶ (2.333 Å × 3).

The Mn1–O1 distances of 2.0084(1) Å (× 4) are similar to those in the Mn²⁺-containing compound Sr₂MnCu₂O₂S₂²

(2.0009 Å × 4) and the mean of the Mn1–S1 (2.993(2) Å) and Mn1–S2 (2.800(2) Å) distances at 2.897 Å is very similar to the two identical Mn–S distances of 2.876 Å in Sr₂MnCu₂O₂S₂² and substantially longer than would be expected for Mn–S bonding distances. Bond valence calculations,¹⁰ applied tentatively to this structure with few free crystallographic parameters,¹¹ and assuming Cu⁺ and S²⁻, suggest a manganese oxidation state of +2.4, consistent with the X-ray derived composition: Sr₄Mn₂Cu_{4.6(2)}O_{4.92(1)} (i.e. Mn +2.6(1)). The similarity of the manganese coordinations in Sr₄Mn₂Cu₅O₄S₅ and Sr₂MnCu₂O₂S₂ suggests that in both, the manganese oxidation state is +2, which would require holes in the copper chalcogenide layers, as in the metals KCu₄S₃,⁴ TiCu_{2n}S_{n+1}⁵ and the layered oxyselenide Bi₂YO₄Cu₂Se₂.¹² Electrical conductivity measurements on Sr₄Mn₂Cu₅O₄S₅ are hampered by the existence only of small single crystals. Preliminary measurements on a non-oriented crystal (dimensions 0.03 × 0.01 × 0.01 cm) using a two-probe arrangement with In/Ga eutectic contacts revealed resistivities of 5(1) Ω cm at 290 K and 7(1) Ω cm at 100 K, suggesting semiconducting behaviour. Further investigation of Sr₄Mn₂Cu₅O₄S₅ and related compounds is in progress.

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Notes and references

† MnO₂ (Aldrich 99.98%), S (Alfa 99.9995%); SrO prepared by decomposing SrCO₃ (Alfa 99.994%) at 900 °C under 2 × 10⁻² mbar, SrS prepared by reacting SrCO₃ with CS₂ (Aldrich 99.9%) carried by flowing argon at 900 °C for 12 h. Cu₂S prepared by reacting Cu (Alfa 99.999%) with S at 700 °C for 7 days in an evacuated silica tube. Elemental analysis on single crystals was performed using a JEOL JSM-840A scanning electron microscope with an Oxford Instruments ISIS300 energy dispersive X-ray analyser.

‡ Single crystal XRD data were collected on a 0.06 × 0.06 × 0.04 mm³ shiny black crystal using a Nonius Kappa CCD diffractometer: Mo-Kα radiation (λ = 0.71073 Å); angular range 2 ≤ 2θ ≤ 70°; 6854 reflections measured (452 independent reflections with *F*² > 2σ(*F*²)). Structure solution (Direct Methods): SIR97;¹³ absorption correction: Gaussian integration method based on the crystal shape,¹⁴ (μ = 26.47 mm⁻¹; max./min. transmission = 0.44/0.26). Refinement: SHELXL97¹⁵ (*R*₁ = 0.038, *wR*₂ = 0.092 for *F*² > 2σ(*F*²)). CCDC 195021. See <http://www.rsc.org/suppdata/cc/b2/b209747h/> for crystallographic data in CIF or other electronic format.

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