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BRIEF COMMUNICATION

Unusual Layered Transition-Metal Oxysulfides: $Sr_2Cu_2MO_2S_2$ (M = Mn, Zn)

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Layered manganese and zinc oxysulfides, $Sr_2Cu_2MnO_2S_2$ and $Sr_2Cu_2ZnO_2S_2$, have been prepared for the first time. They crystallize in an unusual intergrowth structure with alternating square planar MO_2 (M = Mn, Zn) sheets and anti-PbO-type Cu_2S_2 layers. The S atom at the apical sites has a weak bond to atoms Mn or Zn. Both compounds are semiconducting $Sr_2Cu_2MnO_2S_2$ exhibits an antiferromagnetic ordering at about 29 K. © 1997 Academic Press

Extensive research on high-T_c superconductors over the past decade has led to the discovery of a large number of layered cuprates. The limited number of layered phases with other first-row transition metals has retarded parallel studies to reveal possible new novel electronic and magnetic properties. To date, rare examples of oxychalcogenides, which are defined as compounds with metal bonded both to oxygen and chalcogen, have been known for transition metals, possibly owing to their higher chalcophilicity and lower oxophilicity. During our investigation on late transition-metal oxychalcogenidies, new layered cobalt oxysulfides, $A_2Cu_2CoO_2S_2$ (A = Sr, Ba), were discovered (1). These compounds are isostructural with $Sr_2Mn_3As_2O_2$ (2), containing square planar CoO_2 layers alternated with anti-PbO-type Cu_2S_2 layers. As for Mn and Zn, none of their oxychalcogenides in an extended structure have ever been reported. In this communication, we present a first example, layered manganese and zinic oxysulfides: $Sr_2Cu_2MO_2S_2$ (M = Mn, Zn).

Samples with compositions $Sr_2Cu_2MO_2S_2$ (M = Mn, Zn) were synthesized by reacting the stoichiometric amounts of SrS, Mn/Zn, and CuO. The pellets were sealed in evacuated quartz tubes and heated at 920°C for 24 h followed by furnace cooling. A single phase was obtained for both samples. The Mn-containing sample appears dark brown, while the Zn sample is yellow. The X-ray intensity data were collected between $2\theta = 15°$–$105°$ at steps of 0.03° using Cu$K\alpha$ radiation. Preferred orientation along [001] was corrected using the March–Dollase function. The structure (Fig. 1) was refined based on its analogue $Sr_2Cu_2CoO_2S_2$ using a DBWS-9411 version of the Rietveld program (3). The atomic positions and thermal factors are listed in Table 1 with observed and calculated diffraction profiles shown in Fig. 2.

$Sr_2Cu_2MO_2S_2$ (M = Mn, Zn) can be described as a commensurate intergrowth crystal with two alternating different types of layers: square planar MnO_2 or ZnO_2 oxide sheets and anti-PbO-type Cu_2S_2 sulfide layers separated by the Sr cations. Cu in this phase has a formal +1 valence, as in its numerous chalcogenidies. The Mn and Zn atoms have a rather weak bonding to their apical S atoms. The distances Mn–S = 2.8767(45) Å and Zn–S = 3.0205(41) Å are much longer than the regular lengths in their corresponding sulfides (Mn–S = 2.44 Å in Ba_2MnS_3 (4) and Zn–S = 2.334 Å in Wurtzite ZnS (5)). This feature is similar to that of layered cuprates, where the weak bonding of Cu to apical O is due to the Cu^{2+} Jahn–Teller effect. For instance, Cu–O (apical) = 2.79 Å as compared with Cu–O (in-plane) = 1.94 Å in $HgBa_2CuO_4$ (6). In the present case, Sr will be in a higher position above the plane of the larger S atoms, driving the next MnO_2 or ZnO_2 layer far apart from the S plane. The most sterically unfavorable square planar MO_2 is stabilized by the rigid Cu_2S_2 layer that has ever been found in $BaCu_2S_2$, $La_2O_2Cu_2S_2$ and $A_2F_2Cu_2S_2$ (A = Sr, Ba). This metal–oxygen geometrical configuration of Mn and Zn was also observed in their layered oxide pnictide crystals: $A_2M_3X_2O_2$ (A = Sr, Ba; X = P, As, Sb, Bi; M = Mn, Zn) (2, 7) where the M_2X_2 layer was replaced by Cu_2S_2. An unusual copper oxide selenide $Na_{1.9}Cu_2Se_2 \cdot Cu_2O$ (8) has a similar intergrowth structure with alternating anti-square planar CuO_2 oxide layers Cu_2O and selenide layers Cu_2Se_2. Cu in Cu_2O, however, has no bonding to Se. The Cu_2O sheet shifts $(\frac{1}{2}, \frac{1}{2})$ along the ab plane compared with the position of the MO_2 layer relative to the next Cu_2S_2 layer in

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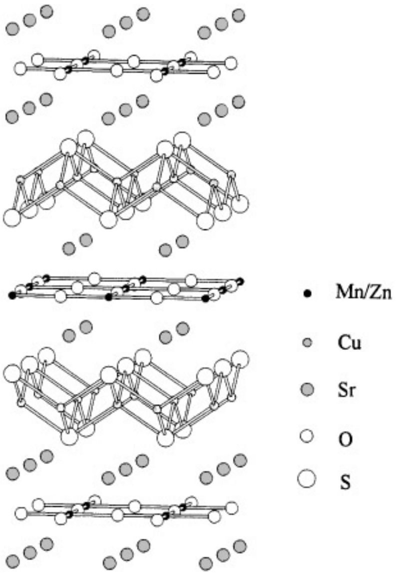

FIG. 1. Structure of $Sr_2Cu_2MO_2S_2$ (M = Mn, Zn) showing alternative stacking of MO_2 (M = Mn, Zn) and Cu_2S_2 layers. Selected atomic distances (Å): Mn–O = 2.0009(8), Mn–S = 2.8767(45); Zn–O = 2.0040(4), Zn–S = 3.0205(41).

$Sr_2Cu_2MO_2S_2$ (M = Mn, Zn). In Cu_2S_2 the Cu–S distances 2.4456(29) and 2.4500(25) Å for $Sr_2Cu_2MnO_2S_2$ and $Sr_2Cu_2ZnO_2S_2$, respectively, are comparable to those found in its related sulfides (2.413 Å in $BaCu_2S_2$ (9)).

Both compounds $Sr_2Cu_2MO_2S_2$ (M = Mn, Zn) have rather low conductivity. All atoms have normal valences.

TABLE 1

Atomic Coordinates and Isotropic Thermal Factors (Å^2) for $Sr_2Cu_2MO_2S_2$ (M = Mn, Zn) with the Values for M = Zn in the Next Line (Space Group: *I4/mmm*; a = 4.0018(15), c = 17.1315(65) Å for M = Mn and a = 4.0079(7), c = 17.7196(34) Å for M = Zn)

	x	*y*	*z*	*B*
M	0	0	0	0.29(9) 0.58(9)
Cu	1/2	0	0.25	1.47(9) 1.23(7)
Sr	1/2	1/2	0.0999(1) 0.0913(1)	0.78(2) 0.87(5)
S	0	0	0.1679(2) 0.1705(2)	0.89(9) 0.76(12)
O	1/2	0	0	1.62(27) 1.22(25)

Note. R_p = 4.65%, R_{wp} = 6.19, R_E = 5.50%, S = 1.12, R_B = 8.51%, R_F = 8.95% for M = Mn and R_p = 4.58%, R_{wp} = 5.92, R_E = 4.87%, S = 1.21, R_B = 8.10%, R_F = 8.87% for M = Zn.

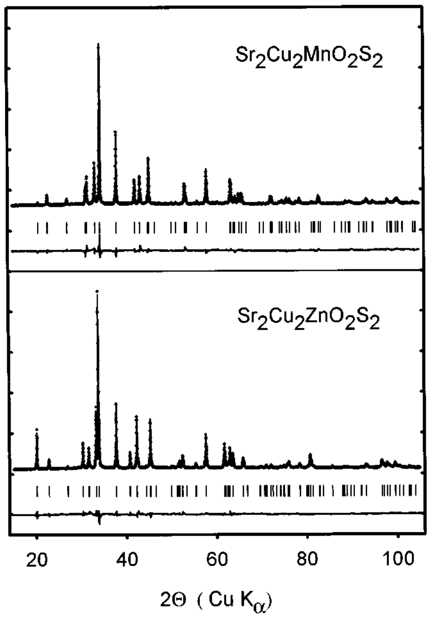

FIG. 2. Observed and calculated X-ray diffraction patterns for $Sr_2Cu_2MO_2S_2$ (M = Mn, Zn) with difference profiles shown below. The vertical bars indicate the reflection positions.

Further element doping study is necessary to induce hole carriers in the S 3*p* band. Figure 3 shows the magnetic susceptibility between 5 and 300 K for $Sr_2Cu_2MnO_2S_2$ measured on a Quantum Design SQUID magnetometer at 0.5 T. A peak shows at $T(\chi_{max})$ = 29.5 K, suggesting antiferromagnetic ordering of the sole magnetic cation Mn^{2+} in this compound. The zero-field-cooled and field-cooled data consistency precludes the possibility of spin-glass freezing in this system. Fitting the data to a Curie–Weiss law from 200 to 300 K gives an effective moment of $n_p = 5.3\ \mu_B$ and a paramagnetic temperature of $\theta = -28$ K. Usually the moment derived from the Curie–Weiss formula is smaller

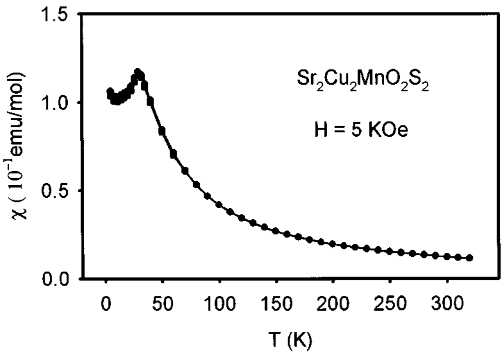

FIG. 3. Zero-field-cooled and field-cooled mangetic susceptibilities for $Sr_2Cu_2MnO_2S_2$ measured at 0.5 T.

than the spin-state of the free ions (for high-spin Mn^{2+}, $S = 5/2$ and $n_p = 5.92\ \mu_B$). Failure to fit the data on a two-dimensional square-planar Heisenberg antiferromagnetic model suggests the significance of interplanar interaction between the MnO_2 sheets. Further neutron diffraction and magnetic property studies on this compound are necessary to solve the magnetic structure and its temperature dependence.

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