Sr_2CuGaO_3S, a Rare Example of Square Pyramidal Gallium

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Layered transition-metal oxides and chalcogenides have been extensively studied for the last several decades because of their novel physical and chemical properties.[1] Only a few studies have been on layered oxychalcogenides that are composed of transition-metal oxide and transition-metal chalcogenide layers. Structure integration of these two types of layers presents a new route to achieving new electronic and magnetic properties via layer interaction. The first related example is copper oxide selenide $Na_{1.9}Cu_2Se_2{\cdot}Cu_2O$,[2] where Cu is bonded to only one kind of anion O or Se. Recently, we prepared and identified several new members $A_2Cu_2MO_2S_2$ (M = Mn, Co, Zn; A = Sr, Ba).[3] They are isostructural with $Sr_2Mn_3As_2O_2$,[4] with square planar MO_2 layers interleaved with Cu_2S_2 layers, where the transition metal M has no significant bonding to S at its apical site. $Sr_2Cu_2CoO_2S_2$ exhibits interesting magnetic properties with two consecutive magnetic and resistive transitions around 100 and 200 K and a spin-glass behavior at low temperature. In this communication, we report the synthesis and characterization of a new gallium oxysulfide, Sr_2CuGaO_3S, with an unusual layered structure, where Ga is in a square pyramidal arrangement of oxygen, a rare coordination geometry for Ga.

The compound Sr_2CuGaO_3S was synthesized by heating a pellet of stoichiometric amounts of SrS, Cu_2O, $Sr_3Ga_2O_6$, and Ga_2O_3 sealed in an evacuated quartz tube at 950 °C for 12 h, which yields a brown single-phase material. EDX analysis on eight crystallites gives the average atomic ratio Sr:Cu:Ga:S = 2.05(12):0.95(8):1.02(8):0.98(6), much close to the stoichiometric composition. X-ray diffraction characterization was performed on a Rigaku-Dmax diffractometer. Intensity data were collected in the range $2\theta = 15-105°$ at steps of 0.02° using Cu Kα radiation. Sr_2CuGaO_3S crystallizes in a tetragonal structure with space group *P*4/*nmm* under the reflection condition $h + k = 2n$ for *hk*0. Lattice parameters were determined to be $a = 3.8606(4)$ Å and $c = 15.730(2)$ Å. The structure model shown in Figure 1 was proposed on the basis of alternating the anti-PbO type Cu_2S_2 layer with a gallium perovskite oxide layer $(GaO_2)(SrO)(SrO)(GaO_2)$ separated by Sr. Initial atomic positional parameters were estimated from the bond valence sum rule.[5] Structure refinement was performed using a DBWS-9411 version of the Rietveld program.[6] Preferred orientation along [001] was corrected using a March−Dollase function. Satisfactory fitting was achieved between observed and calculated patterns. Table 1 lists atomic parameters and thermal factors. The comparatively smaller thermal factor of Sr(1) probably was due to the geometrical constraints of its eight coordination anions, four O(1) and four S, which are arranged highly symmetrically.

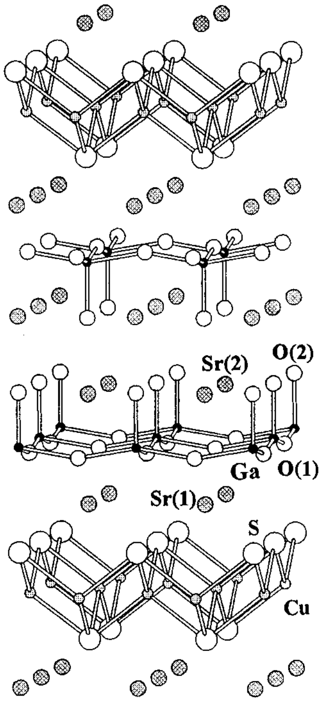

Figure 1. Structure of Sr_2CuGaO_3S, showing alternate stacking of the Cu_2S_2 layers and the square pyramidal GaO_3 layers.

Table 1. Atomic Coordinates and Isotropic Thermal Factors (Å^2) for $Sr_2CuGaO_3S^a$

	x	*y*	*z*	*B*
Ga	$^1/_4$	$^1/_4$	0.3144(2)	0.21(6)
Cu	$^1/_4$	$-^1/_4$	0	0.71(7)
Sr(1)	$-^1/_4$	$-^1/_4$	0.1842(2)	0.06(1)
Sr(2)	$-^1/_4$	$-^1/_4$	0.4140(1)	0.28(6)
S	$^1/_4$	$^1/_4$	0.0940(3)	0.64(13)
O(1)	$^1/_4$	$-^1/_4$	0.2899(4)	0.40(21)
O(2)	$^1/_4$	$^1/_4$	0.4270(6)	0.81(31)

[a] $R_p = 4.41\%$, $R_{wp} = 6.14\%$, $R_E = 5.50\%$, $S = 1.11$, $R_B = 3.48\%$, $R_F = 3.12\%$. See ref 6 for definitions of *B*, *R* factors, and goodness-of-fit *S*.

One important structural feature of Sr_2CuGaO_3S is that Ga and O form a square pyramidal GaO_3 layer. This is the first example of Ga with this coordination configuration in an extended structure. There is no significant bonding between Ga and S at its apical site. Their atomic distance 3.419(6) Å is much longer than the sum (2.46 Å) of their ionic radii. Ga^{3+} usually occurs in either tetrahedral or octahedral geometry. Square pyramidal geometry, which is ordinary for some transition-metal elements such as Fe^{3+}, Cu^{2+}, V^{4+}/V^{5+}, and Mn^{3+}, even is rare in its isolated species, where only $HGa(BH_4)_2$[7a] and two complexes, a Ga(III) amino thiolate complex[7b] and $GaCl(S_2CNMe_2)_2$,[7c] bear such a structural feature. For Sr_2CuGaO_3S, this sterically unfavorable oxygen arrangement

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around Ga forming a layer is stabilized by the good geometrical and charge compatibility of the rigid layer $(Cu_2S_2)^{2-}$ and the gallium perovskite oxide layer $[(GaO_3)(SrO)(SrO)(GaO_3)]^{2-}$. Sr(1) is well above the S plane (1.42 Å), which was defined as perpendicular to the *c* axis, driving the next GaO_3 layer farther away from the S plane. All bond lengths are within their normal ranges. A bond valence calculation gives Ga the atomic valence 2.97, consistent with its ionic valence +3. Although X-ray diffraction analysis cannot determine possible partial antidoping between the Cu and Ga sites, the unreasonably high atomic valence (1.98) estimated for monovalent Cu^+ at the Ga site precludes this possibility. Cu^{2+}, which is usually in a square planar, square pyramidal, or elongated octahedral oxygen environment, is impossible in this system coexisting with the sulfur anion. In numerous sulfides such as CuS,[8] KCu_2S_2,[9] and $NaCu_4S_4$,[10] Cu is always monovalent. S^{2-} was found to be oxidized by Cu^{2+}, resulting in the formation of $SrSO_4$ in the sample with the nominal composition of $Sr_2Cu_3O_2S_2$, which was attempted for the $Sr_2Cu_2CoO_2S_2$-type phase with the CuO_2 sheet. If we assume Cu at the Ga site and Ga at the Cu site, the thermal factor obtained by X-ray structure refinement is negative (−1.3 Å^2) for Cu and much larger (2.2 Å^2) for Ga. Also, the bond of Cu to its apical oxygen (1.820 Å) is too short, never observed in any layered cuprates. This case is quite similar to that of $Sr_2Cu_2CoO_2S_2$, in which no Cu substitution occurs in the square planar CoO_2 sheet. Further neutron diffraction studies are necessary for direct evidence.

One related, but different, layered oxychalcogenide series is $(RO)_n(M_xQ_y)$,[11] where R = rare earth, M = Cu, Ag, Ga, In, Ge, Sn, As, Sb, Bi, and Q = S, Se. These compounds contain rocksalt or antifluorite-type chalcogenide layers of M separated by the fluorite-type oxide layers R_2O_2. There is no bonding between M and oxygen. Sr_2CuGaO_3S presents the first layered oxysulfide with a square lattice of Cu_2S_2 and a perovskite oxide layer, where Ga is in an unusual oxygen coordination geometry. This result prompted us to explore related phases with other elements, revealing several new layered oxysulfides such as $Sr_3Cu_2Fe_2O_5S_2$ and Sr_2CuMO_3S (M = Cr, Fe, In). Details will be reported elsewhere.

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Supporting Information Available: Tables of crystallographic parameters and bond distances and a plot of calculated and observed X-ray diffraction patterns (1 page). Ordering information is given on any current masthead page.

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