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Oxysulfides Formed by a Rare Earth and a Second Metal

II. Shear Structures

D. CARRE, M. GUITTARD, S. JAULMES, A. MAZURIER, M. PALAZZI, M. P. PARDO, P. LARUELLE, AND J. FLAHAUT

Laboratoire de Chimie Minérale Structurale, Associé au CNRS No. 200, Faculté des Sciences Pharmaceutiques et Biologiques, avenue de l'Observatoire 75270 Paris Cedex 06, France

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Many of the oxysulfides containing two metals have layered structures of (RO) sheets and (M_xS_y) sheets (R = rare earth, M = Cu, Ag, Ga, In, Ge, Sn, As, Sb, Bi). In the new compounds $(La_4O_3)(AsS_3)_2$ and $(La_5O_3)In_6S_{17}$, parallel ribbons of stoichiometry (La_4O_3) and (La_5O_3) substitute for the (LaO) sheets. The formation of ribbons is explained by shear mechanisms involving two different orientations of the periodic shear planes in the tetragonal (LaO) sheet. In a third compound La_3GaS_5O or $(La_2O)LaGaS_5$, the formation of (La_2O) ribbons involves similar shear mechanism. All these shear structures preserve the main characters of the layered oxysulfides: oxygen is only bound to lanthanum, and the second metal is only bound to sulfur. © 1984 Academic Press, Inc.

Introduction

New series of layered oxysulfides and oxyselenides with two different metal atoms were recently described by Laruelle (*1*) and Guittard *et al.* (*2*). The general composition is $(RO)M_xX_y$ with R a light rare earth element; M a IB (Cu and Ag), IIIA (Ga and In), IVA (Ge and Sn), or VA metal (As, Sb, Bi); and X sulfur or selenium. In the structures the (RO) sheets alternate with (M_xX_y) sheets. The main structural features are:

—All oxygen atoms are in the center of tetrahedra of rare earth atoms. These tetrahedra share their edges with 4 other tetrahedra, and constitute (RO) sheets of tetragonal or pseudotetragonal symmetry.

—In the M_xX_y sheets, the second metal M is only bound to the sulfur (or selenium) atoms, usually in tetrahedral coordination (Ag, Cu, Ga, Ge, Sn, As) but sometimes in octahedral coordination (Bi).

—The R–O distances are short and indicate a relatively large covalent character. In contrast, the R–X distances are relatively long, so the sheet structure is well defined.

—The M–X distances have the usual values, as in other sulfides or selenides.

In this paper, we describe compounds closely related to the layered oxysulfides. The (RO) sheet is replaced by parallel ribbons of R_4O tetrahedra, and the number of oxygen atoms is no longer equal to the number of R atoms, but the other features of the layered compounds are maintained.

Chains, ribbons, or sheets are made by sharing the apices of the La_4O tetrahedra (Fig. 1). If the tetrahedra share two apices

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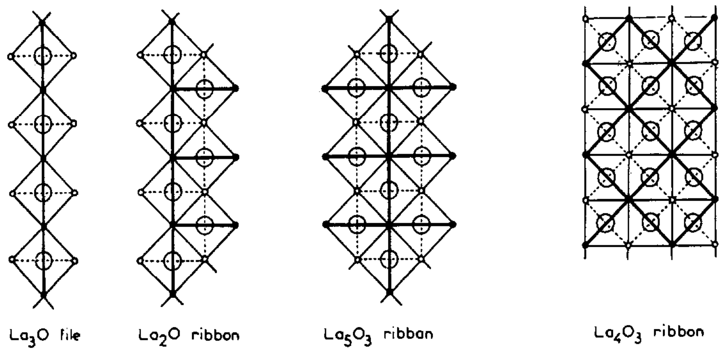

FIG. 1. Formation of various "ribbons" from (La_4O) tetrahedra which share apices or edges.

with two adjoining tetrahedra, a chain with composition (La_3O) is obtained (not yet found in oxysulfides). If the tetrahedra share two edges with two neighboring tetrahedra, a ribbon of composition (La_2O) is formed; the tetrahedra are alternatively disposed on both sides of the median plane of the ribbon (observed in La_3GaS_5O). If a third file of tetrahedra is disposed in a similar way on one side of the ribbon, (La_5O_3) ribbons are formed (observed in (La_5O_3)In_6S_{17}). Another association of 3 tetrahedra chains is observed in the (La_4O_3) ribbons of (La_4O_3)(AsS_3)$_2$.

Finally, by similar repeated juxtaposition of tetrahedra chains to the (La_5O_3) or (La_4O_3) ribbons, the (LaO) sheet of tetragonal symmetry characteristic of the layered oxysulfides (*1, 2*) is obtained.

Preparation of the Oxysulfides

The $GaLa_3S_5O$ compound is easily prepared by reaction of $2La_2S_3$, Ga_2S_3, and La_2O_2S in a sealed ampoule at 1000°C for 1 day. It undergoes a ternary peritectic decomposition at 1106°C.

Single crystals of (La_4O_3)(AsS_3)$_2$ were obtained in the course of crystallization experiments of another sheet oxysulfide: $(LaO)_4As_2S_5$ (*3*). By heating this compound with an excess of As_2S_3, at 800°C for 1 day and at 600°C for 1 week, in a sealed ampoule, some small brown crystals were obtained. Their composition was determined by the crystallographic study.

The (La_5O_3)In_6S_{17} compound was obtained by heating in a sealed ampoule equimolecular proportions of La_2O_2S and In_2S_3, first at 900°C for 1 day, and then at 1200°C for 1 hr, in a graphite crucible. Small needles were present in the heterogeneous mixture. Their composition was established by the crystal structure.

Crystal Structures

La_3GaS_5O. The cell is orthorhombic, space group *Pnam*, with a = 10.78 Å; b = 19.95 Å; c = 4.03 Å; Z = 4.

The structure was solved by Jaulmes *et al.* (*4*). Its main character is the presence of (La_2O) ribbons formed by the La_4O tetrahedra, located on 0, ½, and ½, 0 at the *xy* plane, and parallel to the *z* axis (Fig. 2). The oxygen atoms are only bound to La(1) and La(2) atoms. Between the ribbons, Ga atoms are coordinated by tetrahedra, and La(3) atoms by dicapped trigonal prisms of sulfur atoms. Thus, O is only coordinated to La; Ga and other La atoms are only bound to S. The formula should be written as (La_2O)($LaGaS_5$).

The La(1) and La(2) atoms of the ribbon form relatively short La–O distances, and relatively long (La–S) distances. The latter

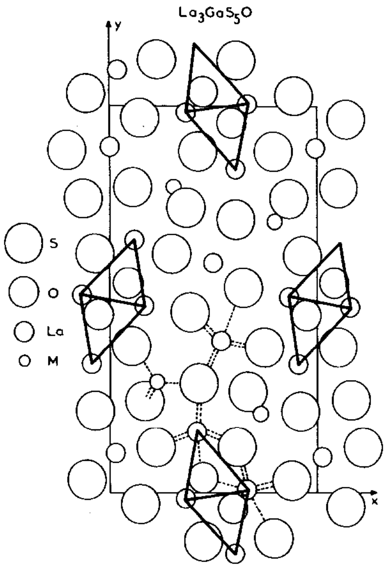

FIG. 2. Projection of the cell content of La_3GaS_5O on the xy plane. Dotted lines: bounds around metal atoms. Full lines: (La_2O) ribbons.

distances are larger than the La(3)–S distance observed in the sulfide region of the cell (Table I). This clearly demonstrates the individuality of the (La_2O) ribbon.

TABLE I

MEAN VALUES OF THE INTERATOMIC DISTANCES IN La_3GaS_5O (OR $La_2O)(LaGaS_5)$, IN ÅNGSTROMS

La atoms of the (La_2O) chain	
La(1)–O: 2.429	La(2)–O: 2.486
La(1)–S: 2.954 (×2)	2.404 (×2)
2.960 (×2)	Mean value: 2.43 (×3)
3.118	La(2)–S: 2.879
3.196 (×2)	3.057 (×2)
3.296	3.078 (×2)
Mean value: 3.08 (×8)	Mean value: 3.07 (×5)
La(3) of the sulfide region ($LaGaS_5$)	
La(3)–S: 2.920 (×2)	
2.968 (×2)	
2.993	
3.034	
3.283 (×2)	
Mean value: 3.02 (×8)	

$(La_4O_3)(AsS_3)_2$ (or $La_4As_2S_6O_3$). The cell is orthorhombic, space group *Ibam*, with a = 19.032 Å; b = 12.051 Å; c = 5.852 Å; Z = 4.

The structure was solved by Palazzi and Jaulmes (*5*), (Fig. 3). It is built up of (La_4O_3) ribbons, parallel to the z axis, made up of La_4O tetrahedra, which share some of their edges. In projection on the xy plane, each ribbon contains 3 La_4O tetrahedra.

The triangular pyramidal AsS_3 groups are between the ribbons. The $4s_2$ electron lone pairs of the As(III) have a stereochemical behavior. All the lone pairs are in a same channel, parallel to the c axis. The As–S distances are similar as observed in thioarsenites, like Na_3AsS_3 (*6*).

$(La_5O_3)_2In_6S_{17}$ (or $La_{10}In_6S_{17}O_6$). The cell is orthorhombic, space group *Immm*, with a = 26.45 Å; b = 15.81 Å; c = 4.06 Å; Z = 2.

The crystal structure was solved by Gastaldi *et al.* (*7*). It consists of alternating sheets of indium sulfide and lanthanum oxysulfide. The latter are formed by (La_5O_3) ribbons, parallel to the z axis and surrounded by sulfur atoms. As in $(La_4O_3)(AsS_3)_2$, the ribbons are made up from La_4O tetrahedra which share edges. In

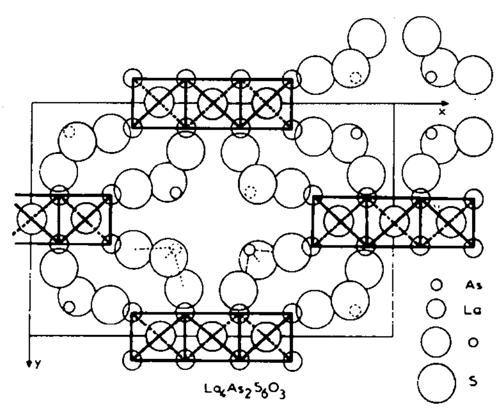

FIG. 3. Projection of the cell content of $(La_4O_3)(AsS_3)_2$ or $La_4As_2S_6O_3$, on the xy plane. Dotted lines: bounds around arsenic atoms. Full lines: $(La_4O)_3$ ribbons.

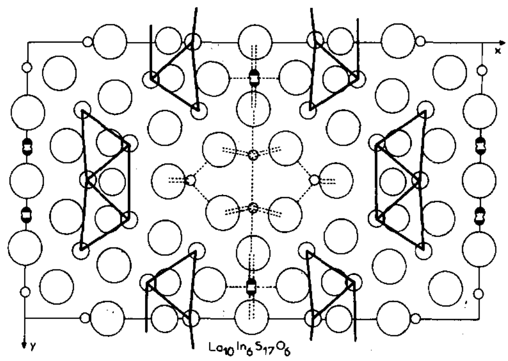

FIG. 4. Projection of the cell content of $(La_5O_3)_2In_6S_{17}$ or $La_{10}In_6S_{17}O_6$ on the xy plane. Dotted lines: bounds around indium atoms. Full lines: (La_5O_3) ribbons.

projection on the xy plane, each ribbon contains 3 La_4O tetrahedra. But, the relative arrangements of the tetrahedra are different in the two structures (Fig. 4).

The indium sulfide sheet contains a relatively complex arrangement, with trivalent indium in tetrahedral and octahedral environments and di-indium pairs. Each indium of an In_2 pair is octahedrally coordinated to 5 sulfur atoms and the second indium atom. These different arrangements are well known from binary indium sulfides (*8, 9*).

Common structural features. In the (La_4O_3) and (La_5O_3) ribbons, the La–O distances are very short, showing partial covalent bonds (Table II). In contrast, the La–S distances are relatively long. Thus, the ribbons are well defined. Moreover, the outer lanthanum atoms (La(1) and La(2) for (La_4O_3) and La(2) for (La_5O_3) ribbons) have shorter La–O distances than the inner lanthanum atoms (Table I). They are not as well surrounded by O atoms as the inner lanthanum atoms, and consequently they seem more strongly attracted by the O atoms than by the S atoms.

In both compounds, oxygen is only bound to lanthanum and the second metal is only bound to sulfur. This is the same structural feature as in the (RO) layer structures.

Formation of Ribbons by Shear Mechanisms

(La_4O_3) and (La_5O_3). Figure 5 shows the formation of both kinds of ribbons from a (LaO) flat sheet of tetragonal symmetry, by periodical shear planes. Two directions are involved for the shear planes (a = length of the edge of the tetrahedra): (1) "side shear planes": parallel to the lateral edges of the tetrahedra, with a period of $1.5a$. They form the (La_5O_3) ribbons and (2) "diagonal shear planes": parallel to the diagonal of the squares formed by the edges of 4 contiguous tetrahedra with a period of $1.5\sqrt{2}\,a$. They form the (La_4O_3) ribbons.

In the two cases, all the oxygen atoms of the (LaO) sheet are maintained and lanthanum atoms must be added to complete

TABLE II

INTERATOMIC DISTANCES RELATED TO THE (La_4O_3) AND (La_5O_3) RIBBONS

	La–O distances in the ribbons (Å)		La–S distances (mean value)
	Side La atoms	Inner La atoms	
$(La_4O_3)In_6S_{17}$	La(1)–O: 2.42 (×1)	—	La(1)–S: 3.035 (×7)
	La(2)–O: 2.38 (×2), 2.34 (×1)	—	La(2)–S: 3.02 (×4)
	—	La(3)–O: 2.50 (×2), 2.46 (×2)	La(3)–S: 3.09 (×4)
$(La_5O_3)As_2S_6$	La(2)–O: 2.33 (×2)	—	La(2)–S: 3.08 (×6)
	—	La(1)–O: 2.38 (×2), 2.46 (×2)	La(1)–S: 3.12 (×4)

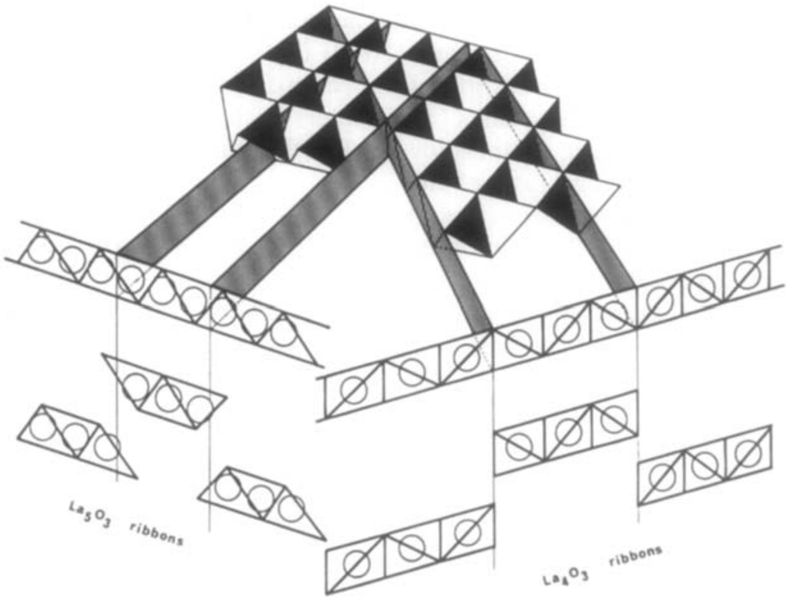

FIG. 5. Formation of the (La_5O_3) and (La_4O_3) ribbons by shear mechanisms from (LaO) sheet.

the La tetrahedra around the lateral oxygen atoms.

In the case of the La–As oxysulfides, we compare the shear structure with the structure of $(LaO)_4As_2S_5$ (Fig. 6) in which parallel sheets of (LaO) composition are separated by sheets of (As_2S_5) sulfide. This compound could thus be regarded as the parent structure of $(La_4O_3)As_2S_6$. But, as a consequence of the change from (LaO) sheets to (La_4O_3) ribbons, the sulfide polyeders are strongly modified: tricoordinated arsenic in isolated AsS_3 anions in $(La_4O_3)As_2S_6$, tetracoordinated arsenic with disordered occupancies of the As sites and some of the S sites in $(LaO)_4As_2S_5$ (*3*). Consequently, the distance between two adjoining (LaO) sheets in $(LaO)_4As_2S_5$ is 6.59 Å and between two parallel ribbons in $(La_4O_3)As_2S_6$ is about 9.5 Å.

There exists another compound, $(LaO)AsS_2$, but its crystal structure is not yet known.

La_3GaS_5O. According to Jaulmes *et al.* (*4*), a (La_2O) ribbon can be derived from the (LaO) sheets of hexagonal symmetry (which exist in La_2O_2S). Actually, it could also be derived from the (LaO) sheets of tetragonal symmetry. In this case,

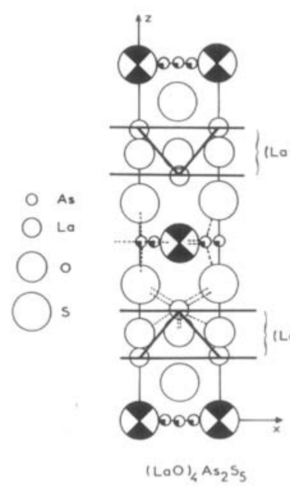

FIG. 6. Projection of the structure of $(LaO)_4As_2S_5$ on the *xz* plane. Dotted lines: bounds around the metal atoms. Black surfaces on the Ga and central S atoms: symbol of the occupancy factors. Full lines: (LaO) sheets.

the periodic shear planes cut the (LaO) sheets with a period a, in order to have two tetrahedra in projection on the section of the ribbon. They are "side shear planes" as for (La_5O_3) ribbons. The basic composition of the ribbon is (La_4O_2). The ratio of the number of oxygen atoms between (La_5O_3) and (La_4O_2) is 1.5, which is the ratio of the correspond shear periods: $1.5a$ and a. The content of lanthanum atoms corresponds in each case to the formation of La_4O tetrahedra around these oxygen atoms.

However, in the structure of La_3GaS_5O, the (La_2O) ribbons have two different orientations relatively to the a and b axis (Fig. 2). These two orientations cannot be explained by the periodic shear, and a more complex mechanism has to be claimed.

Conclusion

Layered oxysulfides with two different metal atoms are formed by alternating tetragonal (LaO) sheets and sulfide sheets; their La/O ratio is always 1. Larger values of this ratio are observed from the same general arrangement, with periodic shears of the (LaO) sheet in parallel ribbons. We have described three different kinds of ribbons, which are presently known in these compounds.

Two different orientations of the shear planes relative to the (LaO) tetragonal sheets are observed: parallel to the lateral edges of the tetrahedra ("side shear planes") and parallel to the diagonal of the squares formed by the edges of 4 contiguous tetrahedra ("diagonal shear planes"). If n is the number of tetrahedra counted in a normal section of the ribbons, the La/O ratios and the compositions of the ribbons are

For the "side shear planes":

$$n = 2 \qquad (La_2O)$$
$$n \geq 3 \qquad (La_{n+2}O_n).$$

The periods of the shear planes are $n \times (a/2)$ if all the oxygen atoms of the (LaO) sheet are maintained in the ribbons at the centers of the tetrahedra.

For the "diagonal shear planes":

$$n = 2 \qquad (La_3O_2)$$
$$n \geq 3 \qquad (La_{n+1}O_n).$$

The periods are $n \times (a\sqrt{2}/2)$, with the same remark as before.

The first representatives of these series are obtained, in compounds with (La_2O), (La_5O_3) and (La_4O_3) ribbons. Probably (La_3O_2) ribbons exist and investigations are in progress. But it is difficult to foresee the sulfide composition which has to be used in preparation of a given ribbon.

Acknowledgment

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