JOURNAL OF SOLID STATE CHEMISTRY **51,** 227–238 (1984)

Oxysulfides and Oxyselenides in Sheets, Formed by a Rare Earth Element and a Second Metal

M. GUITTARD, S. BENAZETH, J. DUGUÉ, S. JAULMES, M. PALAZZI, P. LARUELLE, AND J. FLAHAUT

Laboratoire de Chimie Minérale Structurale, associé au CNRS N°200, Faculté de Pharmacie, 4, avenue de l'Observatoire 75270, Paris Cedex 06, France

Received March 1, 1983; in revised form September 27, 1983

The preparation and structural features of compounds of the general formula $(RO)_n(M_xX_y)$, with R = rare earth, M = IB, IIIA, IVA, or VA elements, and X = S or Se, are described. Four families of oxysulfides can be prepared by the reaction of a rare earth oxysulfide and a post-transition metal sulfide. These include $(RO)_4Ga_2S_5$ for R = Ce (tetragonal *I4/mmm*) and R = Pr to Sm (orthorhombic *Pbca* of the type $(NdO)_4Ga_2S_5$); $(RO)_4Ga_{1.33}S_4$ for R = La and Ce (tetragonal *P4/mmm*); $(RO)_4Ge_{1.5}S_5$ for R = La to Nd (orthorhombic *Pbca* type $(NdO)_4Ga_2S_5$); $(RO)_4Sn_2S_6$ for R = La to Nd (orthorhombic *Pbnm* type $(LaO)_4Sn_2S_6$). The reaction of lanthanum oxyselenide and the metal selenide gives $(LaO)GaSe_2$, $(LaO)InSe_2$, $(LaO)_4Ge_{1.5}Se_5$, $(LaO)_4Sn_2Se_6$, and $(LaO)SbSe_2$. Crystal data are given for these systems. Although these compounds crystallize in several different space groups, they all have sheet structures formed by alternation of an oxide sheet (RO) and a sulfide or selenide sheet (M_xX_y). They belong to 7 new structural types. The (RO) sheets have the same tetragonal or pseudotetragonal array of R_4O tetrahedra, but the (M_xX_y) sheets have various structures, with 2, 3, or 4 layers of X atoms. The structural characters of these compounds are discussed.

Introduction

Two families of rare earth oxysulfides have been described: $(RO)_2S$ and $(RO)_2S_2$. The $(RO)_2S$ compounds (R = La to Yb and Y) have a hexagonal structure, closely related to the La_2O_3 type. Their atomic arrangements involve (RO) sheets and sulfur layers. The $(RO)_2S_2$ compounds (R = La to Nd, Ce excepted) (*1*) have a tetragonal structure (*2*) formed by alternating (RO) sheets and sulfur sheets which contain (S—S) disulfide groups. In the two structures, the (RO) sheets are made by (R_4O) tetrahedra, which share their apices in two different ways, with formation of hexagonal sheets (in $(RO)_2S$) or of tetragonal sheets (in $(RO)_2S_2$).

Rare earth oxysulfides $(RO)_2S$ combine with different metal sulfides to form quaternary combinations, oxysulfides with two metals displaying original structures.

The first example of a quaternary oxysulfide in sheets was described concerning $(CeO)BiS_2$ (*3*). This structural type is observed in the $(RO)BiS_2$ compounds (R = La to Nd) and also for the only derivative of antimony: $(NdO)SbS_2$ (*4*).

Subsequently, the two isostructural compounds (LaO)AgS (*5, 6*) and (LaO)CuS (*7*)

0022-4596/84 $3.00

formed the subject of thorough investigations, as the former is an excellent ionic conductor (5.8).

In contrast, the $RCrS_2O$ (R = La to Sm) quaternary oxysulfides formed by trivalent chromium do not have sheet structures, but three-dimensional arrangements (*28*).

With Ga, Ge, and Sn, two basic structural categories are encountered: three-dimensional structures such as those of $LaGaS_2O$ (*24*), La_3GaS_5O (*25*), and $La_{3.33}Ga_6S_{12}O_2$ (*26*), and sheet structures formed by alternations of a (RO) sheet and a sheet of metal sulfide (M_xS_y). These sheet structures exhibit the same general features as the $(RO)_2S_2$ oxydisulfides structure.

Two families of rare earth oxyselenides are known: $(RO)_2Se$ and $(RO)_4Se_3$. The $(RO)_2Se$ compounds (R = La to Lu and Y) have the same crystal structure as the corresponding oxysulfides. The $(RO)_4Se_3$ compounds (R = La to Yb) have an orthorhombic structure (*16*) which shows a resemblance to the structure of the oxydisulfides $(RO)_2S_2$. This structure is formed by alternation of pseudotetragonal (RO) sheets and selenium sheets, which contain independent Se^{2-} cations and $(Se—Se)^{2-}$ pairs.

Some of the $(RO)_2Se$ oxyselenides—and especially lanthanum oxyselenide—combine with different metal selenides to form quaternary oxyselenides with two metals.

The first example of this new kind of quaternary compounds was obtained with $RCrSe_2O$ (R = La and Ce) (*27*). These compounds have the same crystal structure as the corresponding $CeCrS_2O$ oxysulfides (*28*).

The only quaternary oxyselenides which are known to contain sheets are the lanthanum oxyselenides $(LaO)GaSe_2$, $(LaO)InSe_2$, $(LaO)_4Ge_{1.5}Se_5$, $(LaO)_4Sn_2Se_6$, and $(LaO)SbSe_2$. Other rare earth oxyselenides do not react.

In this paper, we will describe the preparation and the crystal data of the quaternary oxysulfides in sheets formed by Ga, Ge, and Sn, and of all the quaternary oxyselenides in sheets. We will also describe the

TABLE I

CRYSTAL DATA FOR QUATERNARY OXYSULFIDES IN SHEETS

Oxysulfide	Space group	Å *a*	 *b*	 *c*	d_x (g · cm^{-3})	Crystal type
$(LaO)_4Ga_{1.33}S_4$	*P4/mmm*	4.12	—	18.54	4.77	$(LaO)_4Ga_{1.33}S_4$
$(CeO)_4Ga_{1.33}S_4$	*P4/mmm*	4.05	—	18.44	4.99	$(LaO)_4Ga_{1.33}S_4$
$(CeO)_4Ga_2S_5$	*I4/mmm*	3.99	—	18.33	5.25	$(CeO)_4Ga_2S_5$
$(PrO)_4Ga_2S_5$	*Pbca*	18.25	22.69	5.77	5.23	$(NdO)_4Ga_2S_5$
$(NdO)_4Ga_2S_5$	*Pbca*	18.22	22.52	5.73	5.36	$(NdO)_4Ga_2S_5$
$(SmO)_4Ga_2S_5$	*Pbca*	18.06	22.48	5.67	5.66	$(NdO)_4Ga_2S_5$
$(LaO)_4Ge_{1.5}S_5$	*Pbca*	18.20	23.23	5.93	4.71	$(NdO)_4Ga_2S_5$
$(CeO)_4Ge_{1.5}S_5$	*Pbca*	18.11	23.09	5.84	4.86	$(NdO)_4Ga_2S_5$
$(PrO)_4Ge_{1.5}S_5$	*Pbca*	18.07	23.01	5.80	4.94	$(NdO)_4Ga_2S_5$
$(NdO)_4Ge_{1.5}S_5$	*Pbca*	18.03	22.80	5.76	5.09	$(NdO)_4Ga_2S_5$
$(LaO)_4Sn_2S_6$	*Pbnm*	5.876	5.862	19.03	5.33	$(LaO)_4Sn_2S_6$
$(CeO)_4Sn_2S_6$	*Pbnm*	5.767	5.776	19.02	5.52	$(LaO)_4Sn_2S_6$
$(PrO)_4Sn_2S_6$	*Pbnm*	5.731	5.748	19.01	5.64	$(LaO)_4Sn_2S_6$
$(NdO)_4Sn_2S_6$	*Pbnm*	5.710	5.711	19.00	5.74	$(LaO)_4Sn_2S_6$

TABLE II

CRYSTAL DATA FOR QUATERNARY OXYSELENIDES IN SHEETS

Oxyselenide	Space group	Å a	b	c	d_x (g·cm^{-3})	Crystal type
$(LaO)GaSe_2$	$P2_1ab$	5.95	5.96	12.26	5.84	$(LaO)GaSe_2$
$(LaO)InSe_2$	$P2_1ab$	5.89	5.86	13.16	6.25	$(LaO)GaSe_2$
$(LaO)_4Ge_{1.5}Se_5$	$Pbca$	18.92	23.82	5.96	5.56	$(NdO)_4Ga_2S_5$
$(LaO)_4Sn_2Se_6$	$Pbnm$	5.950	5.950	19.81	6.30	$(LaO)_4Sn_2S_6$
$(LaO)SbSe_2$	$P4/nmm$	4.13	—	14.17	5.97	$(CeO)BiS_2$

common structural features of all the structures observed in this new kind of compounds.

Experimental

The oxysulfides listed in Table I were prepared from a mixture of the constituents: $(RO)_2S$, with Ga_2S_3, GeS_2, or SnS_2. The mixture is heated to 1000°C in a vacuum-sealed silica ampule for 2 or 3 days, the interval necessary to obtain homogenous products. Cooling is generally carried out in 6 hr.

The oxyselenides listed in Table II were obtained by direct reaction of the two constituents: the lanthanum oxyselenide and the metal selenide, mixed in suitable ratios. The mixture is heated to 950°C, in vacuum-sealed silica ampule, for 7 days. Cooling is generally carried out in 6 hr.

The crystal parameters were calculated using a least-squares program, based on the X-ray powder diffraction patterns obtained with Cu$K\alpha$ radiation, and calibrated with KBr.

Results

Two oxysulfide combinations are observed in the $(LaO)_2S$–Ga_2S_3 system: $(LaO)_4Ga_{1.33}S_4$ and $LaGaS_2O$. The second compound does not exhibit a sheet structure; both metals are bonded simultaneously to the sulfur and to the oxygen (*24*).

Two compounds appear in the $(CeO)_2S$–Ga_2S_3 system, $(CeO)_4Ga_{1.33}S_4$ and $(CeO)_4Ga_2S_5$. The first is an isotype of that formed with lanthanum.

Starting with praseodymium and up to samarium, only orthorhombic compounds of the $(NdO)_4Ga_2S_5$ type are observed. Another phase appears with europium, which is currently under investigation.

Many tests have been performed to identify a compound of the $(CeO)_4Ga_2S_5$ type in the $(LaO)_2S$–Ga_2S_3 system. While they have failed to show such a phase, the conditions of the formation of $(LaO)_4Ga_{1.33}S_4$ have been further clarified. This compound is unstable at elevated temperature. It undergoes peritectic decomposition at 1085°C, and attempts to prepare it at a higher temperature only give rise, after quenching, to a two-phase mixture formed of La_2O_2S and Ga_2S_3. It is formed rather slowly at 1000°C, and the time of heating must be prolonged for several days.

The formation of $(LaO)_4Ga_{1.33}S_4$ is facilitated by the presence of a liquid in equilibrium with itself, explaining why it is obtained more easily with a higher proportion of Ga_2S_3. A Ga_2S_3-rich mixture has a lower melting point. For these reasons, it is obtained more easily for the compositions $n =$

0.35 to 0.40 $\{n = Ga_2S_3/[Ga_2S_3 + (LaO)_2S]\}$ than for the ideal value $n = 0.25$. Quenching from 1000°C, for $n = 0.35$ or 0.40, yields a glass and crystals of $(LaO)_4Ga_{1.33}S_4$. If the mixture is annealed, two crystallized phases, $(LaO)_4Ga_{1.33}S_4$ and $LaGaS_2O$, appear at temperatures of 600 to 800°C.

These difficulties in preparation explain why this phase was previously described for the composition $n = 0.40$ (*11*). It should be added that no variation in parameter revealed the existence of a range of homogeneity from the formula $(LaO)_4Ga_{1.33}S_4$.

In the R_2O_2S–GeS_2 systems, only one intermediate combination exists with the formula $(RO)_4Ge_{1.5}S_5$, for R = La to Nd. These compounds exhibit the structural pattern of $(NdO)_4Ga_2S_5$; we suppose a disordered distribution of germanium on the two gallium sites. A similar isotypy between the sulfur derivatives formed by gallium and those formed by germanium has already been observed in other ternary sulfur derivatives formed with the rare earths, such as $R_6Ga_{10/3}S_{14}$ and $R_6Ge_{2.5}S_{14}$ (*29*). This is explained by the similarity of the environments of the gallium and germanium in their sulfur combinations.

In the R_2O_2S–SnS_2 systems, only a single series of combinations exists with the formula $(RO)_4Sn_2S_6$ for R = La to Nd.

The $(LaO)GaSe_2$ and $(LaO)InSe_2$ oxyselenides have similar diffraction patterns and have probably the same crystal structure. This structure was solved for $(LaO)GaSe_2$ (*13*). The cell is orthorhombic pseudotetragonal, space group $P2_1ab$. The substitution of Ga by In in this structure causes a large increase of the c parameter, and a small decrease of the a and b parameters. These variations are explained by the parallel decrease of the M—Se bond strength and the related reinforcement of the La—O bond strength. The structure of $(LaO)GaSe_2$ (*13*) can be related to the structure of $(CeO)BiS_2$ (*3*). The main difference between the two structures concerns the M atoms: Bi is inside an octahedron of S and Ga is inside a tetrahedron of Se. This is why the a parameter of $(CeO)BiS_2$ and the a' (and b') parameters of $(LaO)GaSe_2$ have the following relations

$$a\sqrt{2} \approx a' \approx b'$$

The oxyselenides $(LaO)_4Ge_{1.5}Se_5$ and $(LaO)_4Sn_2Se_6$ are isotypic with the corresponding sulfides, and the $(LaO)SbSe_2$ oxyselenide has the same crystal structure as $(NdO)SbS_2$ and the series of the oxysulfides $(RO)BiS_2$ (R = La to Nd) (*4*).

The X-ray powder diffraction of all the crystal types are listed in Tables III to VII.

TABLE III

X-RAY POWDER DIFFRACTION DATA FOR $(LaO)_4Ga_{1.33}S_4$[a]

	Å		
hkl	d_{obs}	d_{cal}	I/I_0
002	9.28	9.270	7
101	4.03	4.028	1
103	3.43	3.432	22
006	3.09	3.090	3
110	2.912	2.918	100
105	2.753	2.758	24
114 016	2.470	2.474 2.470	2
116	2.116	2.122	87
200	2.056	2.064	29
202	2.010	2.014	8
109 211	1.843	1.843 1.837	17
118 122	1.812	1.815 1.810	5
213	1.764	1.768	17
206 124	1.711	1.716 1.715	7
125	1.646	1.652	40
11.10 10.11	1.562	1.565 1.560	12

[a] Tetragonal $a = 4.127$ Å; $c = 18.54$ Å.

TABLE IV

X-RAY POWDER DIFFRACTION DATA FOR $(\mathrm{CeO})_4\mathrm{Ga}_2\mathrm{S}_5$[a]

h k l	*d* (Å)	I/I_0
0 0 2	9.16	22
0 0 4	4.58	1
1 0 1	3.895	<1
1 0 3	3.395	100
0 0 6	3.055	9
1 1 0	2.819	29
1 0 5	2.698	55
1 1 4	2.400	3
0 0 8	2.291	<1
1 0 7	2.189	2
1 1 6	2.072	15
2 0 0	1.993	40
2 0 2	1.947	9
0 0 10	1.833	2
1 0 9	1.814	20
1 1 8	1.778	8
2 1 3	1.711	17
2 0 6	1.669	8

[a] Tetragonal $a = 3.98$ Å, $c = 18.33$ Å.

Discussion

Comparison of the Crystal Structures

The structures of all of the sulfides and selenides in Tables I and II include sheets (RO) and (M_xX_y) which alternate regularly along one axis of the crystal, often a fourfold axis.

(RO) Sheets

These are similar in all cases, exactly planar in the tetragonal and pseudotetragonal structures, wavy in the structure of $(\mathrm{NdO})_4\mathrm{Ga}_2\mathrm{S}_5$. They consist of $R_4\mathrm{O}$ tetrahedra which share four edges with four neighboring tetrahedra, in a tetragonal or quasi-tetragonal arrangement. The oxygen is bonded exclusively to the rare earth, and never to the second metal.

(M_xX_y) Sheets

While the (RO) sheets exhibit a constant arrangement, the (M_xX_y) sheets display widely varying structures. The (M_xX_y) sheets can be divided into three groups, according to the number of their X layers.

TABLE V

X-RAY POWDER DIFFRACTION DATA FOR $(\mathrm{NdO})_4\mathrm{Ga}_2\mathrm{S}_5$[a]

	Å		
hkl	d_{obs}	d_{calc}	I/I_0
200	9.13	9.146	15
400	4.572	4.573	6
221 131	4.445	4.464 4.428	2
231	4.081	4.083	3
141	3.931	3.930	2
331	3.654	3.653	9
341	3.361	3.359	100
450	3.213	3.214	8
351 600	3.062	3.067 3.049	38
521	2.976	2.976	2
002 531	2.866	2.868 2.854	40
080 112 451	2.817	2.823 2.812 2.804	39
122 202	2.744	2.749 2.737	18
541 280	2.704	2.707 2.698	39
551 631 322	2.540	2.547 2.535 2.530	5
402 290	2.427	2.430 2.420	5
810 731	2.274	2.275 2.268	13
512 820	2.244	2.246 2.241	4
670 522	2.215	2.216 2.214	6
490 741 661	2.194	2.200 2.192 2.190	10

[a] Orthorhombic $a = 18.22$ Å; $b = 22.52$ Å; $c = 5.73$ Å.

TABLE VI

X-RAY POWDER DIFFRACTION DATA FOR $(LaO)_4Sn_2S_6$[a]

	(Å)		
hkl	d_{obs}	d_{calc}	I/I_0
002	9.40	9.501	2
101	5.57	5.576	3
004	4.73	4.751	6
103	4.34	4.291	3
110	4.12	4.129	3
112	3.72	3.789	6
113	3.40	3.458	91
105	3.15	3.184	30
006		3.168	
020	2.928	2.923	80
200		2.917	
115	2.803	2.796	88
022		2.793	
202		2.789	
023	2.654	2.654	11
120	2.597	2.613	3
210		2.611	
122	2.518	2.519	16
212		2.517	
116		2.513	
117	2.268	2.268	36
125	2.149	2.153	100
215		2.153	
026		2.148	
206		2.145	
220	2.069	2.065	92
118		2.059	
221		2.053	

[a] Orthorhombic $a = 5.84$ Å; $b = 5.85$ Å; $c = 19.02$ Å.

Number of X layers:	Structural types
2	(LaO)AgS (6) $(NdO)_4Ga_2S_5$ (10)
3	$(LaO)_4Ga_{1.33}S_4$ (11) $(CeO)_4Ga_2S_5$ (12) $(LaO)_4Sn_2S_6$ (13)
4	$(CeO)BiS_2$ (3) $(LaO)GaSe_2$ (14)

1. Sheet structures with two X layers (Fig. 1)

Structure of the (LaO)AgS type (*6*). This structure is also observed in (LaO)CuS (*7*). The sulfur atoms lie on two parallel planes, which are relatively close to one another (3.48 Å in (LaO)AgS, 2.79 Å in (LaO)CuS). The Ag or Cu atoms lie in intermediate positions, inside tetrahedra of S atoms. The Ag—S and Cu—S distances have usual values with respect to the related chalcogenides (Tables VIII and IX).

Structure of the $(NdO)_4Ga_2S_5$ type (*10*). This structure shows remarkable waves of matter. The sulfur atoms lie approximately in two parallel layers, displaying more pronounced waviness than that of the (NdO) sheets. The gallium atoms lie in the median position within sulfur tetrahedra to form a sheet of gallium sulfide. All gallium and sulfur sites are fully occupied.

The reason for the waves is not known. In a first approach, it can be ascribed to the constraint resulting from the superimposi-

TABLE VII

X-RAY POWDER DIFFRACTION DATA FOR $(LaO)GaSe_2$[a]

	Å		
h k l	d_{obs}	d_{calc}	I/I_0
0 0 2	6.12	6.13	1
0 1 2	4.28	4.27	1
1 1 1	4.00	3.98	<1
1 1 2	3.47	3.47	48
0 1 3	3.37	3.370	10
0 0 4	3.063	3.064	2
0 2 0	2.980	2.982	61
1 1 3	2.932	2.933	100
1 2 1	2.604	2.605	7
1 1 4	2.477	2.478	32
0 0 5	2.450	2.451	12
1 2 2		2.444	
0 2 3	2.409	2.408	2
1 2 3	2.231	2.232	6
0 2 4	2.136	2.137	32
2 2 0	2.109	2.106	37
2 2 1	2.078	2.075	10
0 0 6	2.042	2.043	17

[a] Orthorhombic $P2_1ab$: $a = 5.95$ Å, $b = 5.96$ Å, $c = 12.26$ Å.

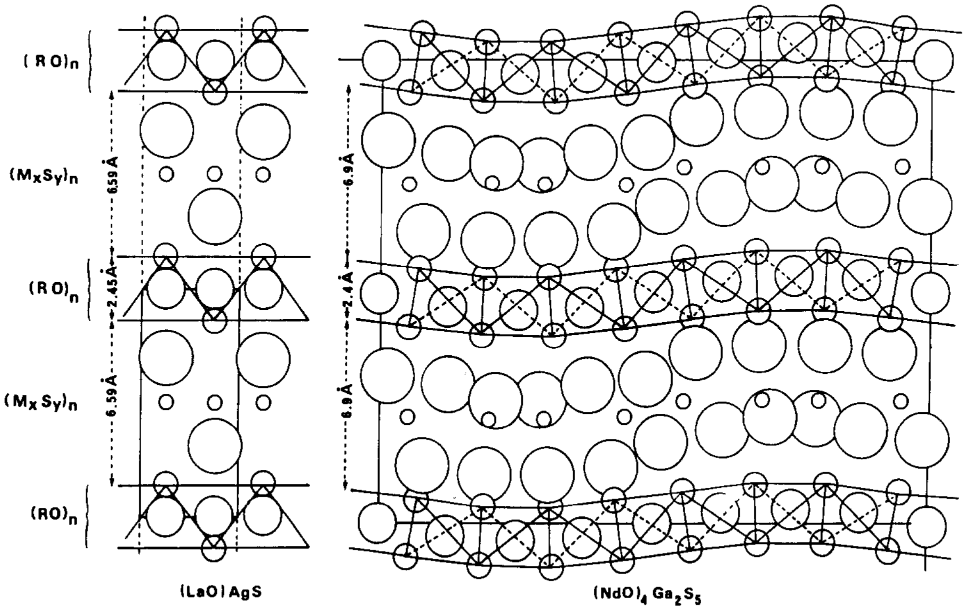

FIG. 1. Comparison of the structures having (M_xX_y) sheets formed by two X layers: (LaO)AgS type and $(NdO)_4Ga_2S_5$ type. The last figure is from Dugué (*10*).

tion of two covalent sheets, which, in a plane arrangement, would not have exactly the same period (*9*).

2. Sheet structures with three X *layers* (*Fig. 2*)

The three structural types—$(LaO)_4Ga_{1.33}S_4$, $(CeO)_4Ga_2S_5$, and $(LaO)_4Sn_2S_6$—have similar tetragonal or quasi-tetragonal structures. In these structures, the sulfur atoms are positioned similarly, in three layers involving two different crystallographic sites: the first site corresponds to the two lateral layers, and the second site to the atom of the central layer. These sulfur atoms thus form octahedra of which one quaternary axis is parallel to 4-axis or pseudo 4-axis. These octahedra may be regarded as formed by juxtaposition of four tetrahedra which have a common edge parallel to axis *c*. Each sulfur atom in the median plane is divided between four contiguous tetrahedra (or four octahedra).

The sites of the gallium atoms are arranged in fourfold positions at the apices of a square situated in the median plane of the sulfur octahedra, so that each metallic site lies within one of the four sulfur tetrahedra (Fig. 3). These sites are indeed too close together (1.04 Å in $(CeO)_4Ga_2S_5$) to be occupied simultaneously by the metallic atoms:

— In $(CeO)_4Ga_2S_5$ and in one of the two sulfide sheets of $(LaO)_4Ga_{1.33}S_4$, one site out of four on the average is occupied in a disordered way by gallium.

— In $(LaO)_4Sn_2S_6$, the arrangement becomes ordered and only one of the four tetrahedral sites is regularly occupied by the tin.

In addition, the sulfur sites display different degrees of occupancy in accordance with the three structures considered, in proportions imposed by the equilibrium of the charges between the anions and cations within the structure.

When the metallic atom is trivalent (Ga), the charge equilibrium imposes the presence of 2.5 sulfur atoms at the apices of the

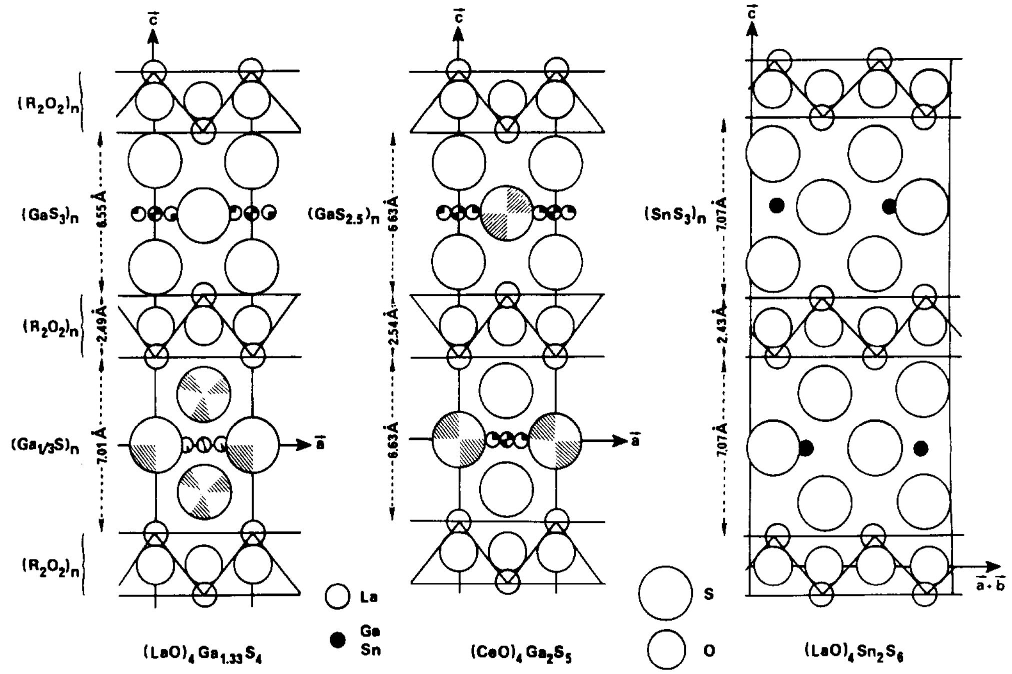

FIG. 2. Comparison of the structures having (M_xX_y) sheets formed by three X layers.

surrounding octahedron. These sulfur atoms only partly occupy the sites offered to them. Among the two series of sulfur positions, only the series in the median plane of the sulfur octahedron displays partial vacancies with an occupancy ratio of 0.5. This is the case of the two sulfide sheets $(GaS_{2.5})$ of $(CeO)_4Ga_2S_5$, which are identical by symmetry.

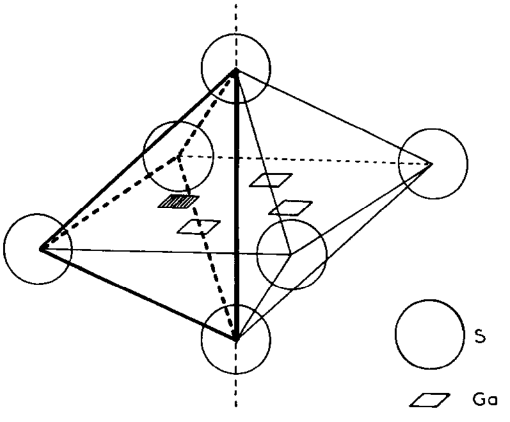

FIG. 3. Tetrahedral coordination of gallium in the sheet structures having (M_xX_y) sheets formed by three X layers.

In $(LaO)_4Ga_{1.33}S_4$, the two gallium sulfide sheets are no longer identical to each other. The atomic positions remain similar to the foregoing, but their occupancy ratios are different. In one of the gallium sulfide sheets, the gallium has exactly the same arrangement as above, but the sulfur sites are totally filled, and the sheet has the composition (GaS_3). In the second sheet, the occupancy ratios of the sites of the two series of atoms are much lower: only one-third of an atom is found on the four gallium sites, and one atom on the three sulfur sites, and the composition of the sheet becomes $(Ga_{0.33}S)$. This region of the crystal space, which exhibits a very low atomic density, displays weak bonds, and the sheet becomes much broader than the previous one, with 7.01 instead of 6.55 Å (*11*).

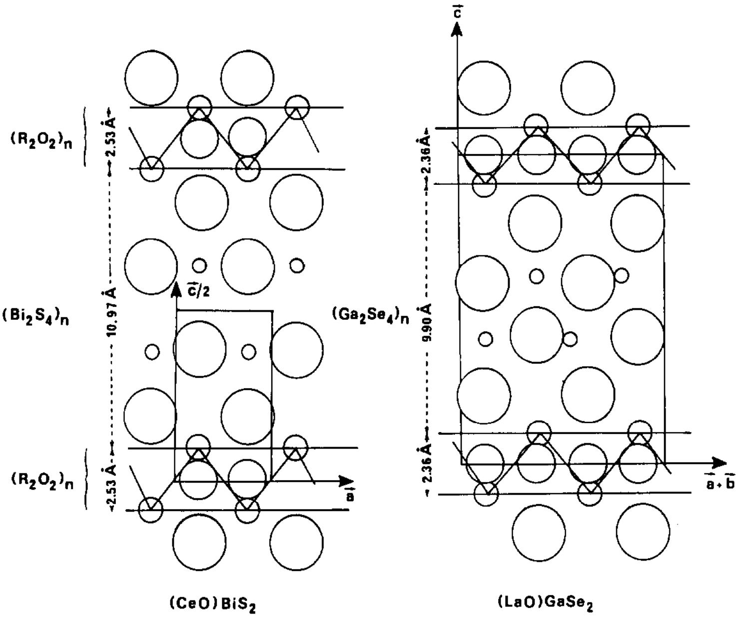

FIG. 4. Comparison of the structures having (M_xX_y) sheets formed by four X layers.

In the case of the tetravalent Sn, the charge equilibrium and the space group allow the filling of the sulfur or selenium sites. This is the case of $(LaO)_4Sn_2X_6$ (X = S or Se). Here also, the two (SnX_3) sheets of the cell are identical.

3. Sheet structures formed with four X *layers (Fig. 4)*

The $(CeO)BiS_2$ (*3*) and the $(LaO)GaSe_2$ structures (*14*) are very similar: four layers of X atoms are disposed in the same way relatively to the (RO) sheets. The main difference between the two structures concerns the M atoms; they have different ordered arrangements with an octahedral coordination of Bi in $(CeO)BiS_2$ and a tetrahedral coordination of Ga in $(LaO)GaSe_2$. Moreover the S octahedron around the Bi atom is strongly distorted, with a very long Bi—S distance (3.34 Å) parallel to the c axis. This is the reason why the distance between two next (RO) sheets is larger in $(CeO)BiS_2$ than in $(LaO)GaSe_2$.

Crystallochemical Characteristics

The many examples available today serve to clarify the crystallochemical characteristics of this new family of sheet compounds.

1. In all cases, the oxygen is only bonded to the rare earth in the (RO) sheet, and the M metal is only bonded to the sulfur or to the selenium in the (M_xX_y) sheet.

2. The (RO) sheets are always constructed with one rare earth element. They only exist with the lightest rare earth elements, and often only with lanthanum. Hence it would appear that the metal element must be sufficiently large to surround satisfactorily the oxygen.

3. The (RO) sheets are formed by R_4O tetrahedra which share 4 of their 6 edges in a tetragonal arrangement. This arrangement is sometimes slightly distorted giving an orthorhombic (pseudotetragonal) symmetry. The (RO) sheets are always planar,

except in the case of the $(NdO)_4Ga_2S_5$ type, which has a very special wave structure. The hexagonal array of R_4O tetrahedra, which is characteristic of the (RO) sheets of the oxysulfides and oxyselenides $(RO)_2X$, is not observed in the quaternary compounds.

4. The thickness of the (LaO) sheet, estimated by the distance between two lanthanum atoms, is given in Table VIII. It varies from 2.43 to 2.53 Å in oxysulfides, but the differences observed cannot be associated with the composition of the sulfide sheet.

5. The (M_xX_y) sheets have only been observed with the following elements of the main groups of the periodic classification:

— For the oxysulfides

IB	Cu and Ag,
IIIA	Ga and (In)
IVA	Ge and Sn in oxidation state +4
VA	As, (Sb) and Bi in oxidation state +3.

— For the oxyselenides

IIIA	Ga and In
IVA	Ge and Sn in the oxidation state +4
VA	Sb in the oxidation state +3.

The crystal structures of the compounds formed by the elements in parentheses are still unknown. However, they can be expected to exhibit sheet arrangements, due to their crystallographic characteristics (tetragonal or pseudotetragonal cells, space lattices with relatively large *c* parameters). It should be noted that all these elements display a medium or strongly covalent character in their binary sulfides or selenides.

6. The (M_xX_y) sheets are formed by 2, 3, or 4 layers of *X* atoms, which have a compact, tetragonal, or pseudotetragonal arrangements.

A single layer of *X* atoms is not possible in these quaternary compounds, because, in this case, the *M* atom could not be surrounded by *X* atoms. Examples of one layer of *X* atoms are known in the oxydisulfides $(RO)_2S_2$ (*2*) and in the oxyselenides $(RO)_4Se_3$ (*16*). In these structures, all the S atoms or two-thirds of the Se atoms are directly bonded to form *X*—*X* pairs. The (RO) sheets have the same arrangement as in the presently studied quaternary compounds.

7. The *M* metals are coordinated to 4 or 6 sulfur or selenium atoms. The $(CeO)BiS_2$ type is the only example of a (M_xX_y) sheet in which the metal displays octahedral coordination. In all other cases, the second metal has tetrahedral environments. The arrangement of the MX_4 tetrahedra in relation to the (RO) sheets is nearly the same in all the structures which have the same number of *X* layers in the (M_xX_y) sheet.

8. The (M_xX_y) sheets are sometimes the location of disordered distributions of the nonmetal *X* and the metal *M*, ranging up to relatively low occupancy ratios (for example, $(LaO)_4Ga_{1.33}S_3$). Simultaneous vacancies for the two constituents of the (M_xX_y) sheet is possible because the existence of rigid (LaO) sheets, which form a very strong framework in the space lattices.

9. In all the known crystal structures, a shortening of the *R*—O bonds is observed, with a lengthening of the *R*—*X* bonds, in comparison with the sums of the conventional ionic radii, and in relation to the bonds in the oxides R_2O_3 and sulfides or selenides R_2X_3. Table VIII illustrates the case of lanthanum. The *R*—O bond displays a clear covalent character, explaining the stability of the (RO) sheet and its permanence among many combinations.

In the (M_xX_y) sheets, the *M*—*X* interatomic distances have their usual values (Tables VIII and IX).

10. In all foregoing compounds, the number of oxygen atoms is equal to that of the rare earth atoms. However, we are aware of two combinations in which this proportion is no longer observed. These are

TABLE VIII

INTERATOMIC DISTANCES AND THICKNESS OF THE $(LaO)_n$ AND $(M_xS_y)_n$ SHEETS (IN Å) IN THE PRESENTLY DESCRIBED CRYSTAL STRUCTURES OF LANTHANUM OXYSULFIDES

	Distance			Sheet thickness		
	(La—O)	(La—S)	(M—S)	$(RO)_n$	$(MxSy)_n$	References
	Structures with hexagonal sheets					
La_2O_2S	2.424	3.037	—	3.06	—	
	Structures with tetragonal or quasi-tetragonal sheets					
$La_2O_2S_2$	2.41 ± 4	3.17 ± 9	—	2.36		(*2*)
(LaO)CuS	2.367	3.253	2.437	2.53	6.00	(*7*)
(LaO)AgS	2.367	3.255	2.673	2.45	6.59	(*6*)
$(LaO)_4Ga_{1.33}S_4$	2.41 ± 1	3.31 ± 19	2.30 ± 11	2.49	6.55	(*11*)
		3.19 ± 8	2.30 ± 5		7.01	
$(LaO)_4As_2S_5$	2.381	3.234	2.226	2.44	6.59	(*12*)
$(LaO)_4Sn_2S_6$	2.39 ± 1	3.28 ± 4	2.38 ± 5	2.43	7.07	(*13*)
	Compared to the sum of the ionic radii (in Å)					
Goldschmidt	2.64	2.96				
Pauling	2.96	2.99				
Shannon and Prewitt	2.48	—				

the compounds $La_4O_3(AsS_3)_2$ (*17*) and $La_{10}O_6(In_6S_{17})$ (*18*). Their crystal structures retain the basic characteristics of the foregoing sheet structures:

Oxygen bonded only to the rare earth.

Associated OLa_4 tetrahedra, with common edges.

Sulfide groups in which the second metal is only bonded to the sulfur.

Here, however, the OLa_4 tetrahedra form parallel ribbons within a three-dimensional lattice formed by the sulfur of the second metal, and no longer form sheets. It may be surmised that, starting with a network of plane parallel sheets, periodic shears occur every three OLa_4 tetrahedra, leading to the formation of the ribbons. In the two above structures, these dislocations intersect the sheets differently, and lead to different porportions of lanthanum in relation to oxygen. We shall return subsequently to these structures.

TABLE IX

COORDINATION AND INTERATOMIC DISTANCES (IN Å) IN SOME TWO-METAL SULFIDES

	La—S	M—S	References
$LaCuS_2$	VII, 2.94 ± 14	Cu—S: IV, 2.43 ± 10	(*19*)
$LaGaS_3$	VIII, 3.04 ± 42	Ga—S: IV, 2.28 ± 4	(*20*)
La_2SnS_5	VIII, 3.00 ± 26	Sn^{IV}—S: VI, 2.57 ± 3	(*15*)
Cu_4SnS_4		Sn^{IV}—S: IV, 2.42 ± 2	(*23*)
Na_3AsS_3		As^{III}—S: III, 2.25	(*22*)

Conclusions

In these sheet compounds, the join between the oxide sheet and the sulfide (or selenide) sheet is made by weak R—X bonds. In contrast, the bonds are strong inside the oxide sheet, because of the short R—O distances, and the bonds have normal values inside the sulfide sheets, because M—S or M—Se distances are similar to those of pure sulfides or pure selenides. In these conditions, the (RO) and (M_xX_y) sheets are well differentiated in the lattices and these quaternary sheet structures are actually a new class of "oxide-sulfide" or "oxide-selenide" compounds.

References

1. P. Khodadad, Tak Tek, J. Flahaut, and L. Domange, *C.R. Acad. Sci. Paris* **260**, 2235–2238 (1965).
2. W. Wichelhaus, *Naturwissenschaften* **65**, 593–594 (1978).
3. R. Céolin and N. Rodier, *Acta Crystallogr. B* **32**, 1476–1479 (1976).
4. M. P. Pardo, R. Céolin, and M. Guittard, *C. R. Acad. Sci. Paris, Sér. C* **283**, 735–738 (1976).
5. M. Palazzi, C. Carcaly, and J. Flahaut, *J. Solid State Chem.* **35**, 150–155 (1980).
6. M. Palazzi and S. Jaulmes. *Acta Crystallogr. B* **37**, 1337–1339 (1981).
7. M. Palazzi, *C. R. Acad. Sci. Sér. II* **292**, 789–791 (1981).
8. G. Schiffmacher and M. Palazzi. *Mater. Res. Bull.* **16**, 1401–1405 (1981).
9. P. Laruelle, *Ann. Chim. Fr.* **7**, 119–130 (1982).
10. J. Dugué and M. Guittard, *Acta Crystallogr. B* **38**, 2368–2371 (1982).
11. S. Jaulmes *et al.*, in press.
12. S. Jaulmes, E. Godlewski, M. Palazzi, and J. Etienne, *Acta Crystallogr. B* **38**, 1707–1710 (1982).
13. S. Benazeth, M. Guittard, and P. Laruelle, *Acta Crystallogr.*, in press.
14. S. Benazeth, P. Laruelle, and M. Guittard, *Acta Crystallogr.*, in press.
15. S. Jaulmes, *Acta Crystallogr. B* **30**, 2283–2285 (1974).
16. J. Dugué, C. Adolphe, and P. Khodadad, *Acta Crystallogr. B* **26**, 1627–1628 (1970).
17. M. Palazzi and S. Jaulmes, *Acta Crystallogr. B* **37**, 1340–1342 (1981).
18. L. Gastaldi, D. Carré, and M. P. Pardo, *Acta Crystallogr. B* **38**, 2365–2367 (1982).
19. M. Julien-Pouzol, S. Jaulmes, A. Mazurier, and M. Guittard, *Acta Crystallogr. B* **37**, 1901–1903 (1981).
20. M. Julien-Pouzol, S. Jaulmes, and C. Dagron, *Acta Crystallogr. B* **38**, 1566–1568 (1982).
21. A. Mazurier, F. Thevet, P. Besançon, and S. Jaulmes, *Acta Crystallogr.*, in press.
22. M. Palazzi, *Acta Crystallogr. B* **32**, 3175–3177 (1976).
23. S. Jaulmes, J. Rivet, and P. Laruelle, *Acta Crystallogr. B* **33**, 540–542 (1977).
24. S. Jaulmes, *Acta Crystallogr. B* **34**, 2610–2612 (1978).
25. S. Jaulmes, A. Mazurier, and M. Guittard, submitted for publication.
26. A. Mazurier, M. Guittard, and S. Jaulmes, *Acta Crystallogr. B* **38**, 379–382 (1982).
27. T. Vovan and Nguyen Huy Dung, *C. R. Acad. Sci. Paris* **293**, 933–936 (1981).
28. J. Dugué, T. Vovan, and J. Villers, *Acta Crystallogr. B* **36**, 1291–1294 and 1294–1297 (1980).
29. A. Michelet, A. Mazurier, G. Collin, P. Laruelle, and J. Flahaut, *J. Solid State Chem.* **13**, 65–76 (1975).