

Synthesis and Structure Determination of the New Compound $\text{La}_{\sim 10.8}\text{Nb}_5\text{O}_{20}\text{S}_{10}$

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$\text{La}_{\sim 10.8}\text{Nb}_5\text{O}_{20}\text{S}_{10}$ was obtained in an attempt to prepare the La homologue of the $\text{Sm}_3\text{NbO}_4\text{X}_3$ derivatives ($X = \text{S}, \text{Se}$). Its structure was solved by X-ray diffraction on a single crystal, in the *Immm* space group with cell parameters $a = 32.535(8)$ Å, $b = 12.115(3)$ Å, and $c = 3.9999(3)$ Å. Refinement of 58 parameters using 836 unique reflections with $I > 2\sigma(I)$ converged to $R_1 = 5.09\%$ and $wR_2 = 10.87\%$. The structure of $\text{La}_{\sim 10.8}\text{Nb}_5\text{O}_{20}\text{S}_{10}$ can be schematically described as the stacking of $[\text{La}_2\text{S}_2]$ slabs of rock salt type (two-atom-thick layers) pillared by an intricate assembly of La and Nb polyhedra along the *a*-direction. Within this complex part, one of the La sites (La5) is partially occupied. © 2000 Academic Press

Key Words: crystal structure, quaternary oxysulfide of Nb and La.

The rock salt (RS)-type layer was observed for sulfide (4, 5) or oxide (6, 7) 2D misfit derivatives as well as for many other oxychalcogenide derivatives (see for instance the $\text{Ln}_2\text{O}_2\text{X}$ series (8)). This RS-type structure can also be present as small isolated fragments within the structure as observed for the $\text{Sm}_3\text{NbO}_4\text{X}_3$ ($X = \text{S}$ (9), Se (10)), or as pieces of intersecting planes that delimit 1D channels of squared section, as illustrated by $\text{Nd}_{16}\text{Ti}_5\text{S}_{18}\text{O}_{17}$ (11).

It then appears that the two types of anions (X^{II} and O^{II}) are always segregated, their preferential combination with this or that metal element being determined by the relative oxo/chalcophilicity of metal atoms. We report the structure determination of a new oxysulfide compound $\text{La}_{\sim 10.8}\text{Nb}_5\text{O}_{20}\text{S}_{10}$ which shows a rock-salt-type layer $[\text{La}_2\text{S}_2]$ pillared by a complex structural entity.

INTRODUCTION

Very few layered oxychalcogenides are known (1) as compared with either layered oxides (see for instance the high- T_c superconductors) or layered chalcogenides (e.g., the binary dichalcogenides of transition metals or the related ternary 2D misfit chalcogenides). Among the known quaternary oxychalcogenides of *Ln* (rare earth metal) and *M* (transition metal), the structure of $\text{Sm}_2\text{Ti}_2\text{O}_5\text{S}_2$ (2, 3) was described, in a simplified manner, as the “intergrowth” of a sulfide layer $[\text{Sm}_2\text{S}_2]$ of rock salt type and an oxide layer $[\text{Ti}_2\text{O}_5]$ of ReO_3 structure type; such a 2D structural description does not fit the reality of the chemical bondings considering the short interlayer Sm–O and Ti–S connections.

A partial or a total filling of the central site within the ReO_3 -type part leads to the parent perovskite type, generally related to oxide compounds for which interesting physical properties such as high- T_c superconductivity, ferroelectric behavior, giant magnetoresistance, ... are often found.

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EXPERIMENTAL

1. Synthesis and Chemical Analysis

In the effort to get the La homologue of the $\text{Sm}_3\text{NbO}_4\text{X}_3$ derivatives ($X = \text{S}, \text{Se}$), a mixture of La_2O_3 with La_2S_3 and Nb_2O_5 was weighted in a 1:2:1 ratio, respectively. The starting materials were loaded into a silica tube sealed under vacuum ($p = 2 \times 10^{-2}$ atm). The temperature of the furnace was progressively increased (10°C/h) to 400°C and maintained for 24 h. The temperature was then again increased (10°C/h) to 1000°C and maintained for 5 days. The cooling down to room temperature was done at 30°C/h. The major product of the reaction is a mixture of black and red powders. The semiquantitative chemical analysis using an EDS-equipped scanning electron microscope revealed that the powders, made of very small platelets, contain La, Nb, S, and O. The approximate ratios, not considering oxygen atoms, are 2La/1Nb/3S for the black phase, and 2La/1Nb/2S for the other one. The small dimensions of the platelets do not permit an X-ray single-crystal study of these phases.

Another phase (?) crystallizing as small yellow needle-shaped (parallelepiped) single crystals, also stable in air, was chemically analyzed. The EDS results averaged on three

different crystals reveal the presence of oxygen and gave for La, Nb, and S the approximate 2 : 1 : 2 ratio, quite comparable to results for the "red powder". This phase, which corresponds to the title compound, was investigated by the X-ray diffraction technique. The calculated values (atomic percentages) for non-oxygen atoms deduced from the structure refinement are 41.79 (40.2), 19.40 (19.4), and 38.80 (40.4), respectively (average experimental values in parentheses).

2. Symmetry and Unit Cell Parameters

Preliminary X-ray crystal investigation with the use of a Weissenberg camera indicated that this compound crystallizes with an orthorhombic symmetry. Systematic absences (hkl , $h + k + l = 2n$) are indicative of an I -centering condition. A needle-shaped crystal with dimensions $0.01 \times 0.03 \times 0.25 \text{ mm}^3$ was mounted on an Enraf-Nonius CAD4 diffractometer using $\text{MoK}\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$). Final unit cell parameters were determined from a least-squares analysis of setting angles of 23 reflections, in the range $11.8^\circ < 2\theta < 53.8^\circ$, that were automatically centered with the CAD4 diffractometer (CELDIM option). From a refinement with the constraints $\alpha = \beta = \gamma = 90^\circ$, one obtains $a = 32.535(8) \text{ \AA}$, $b = 12.115(3) \text{ \AA}$, and $c = 3.9999(3) \text{ \AA}$.

3. Structure Refinement

A total of 10081 reflections were collected in the θ range $1.5\text{--}40^\circ$ ($-55 < h < 55$, $-20 < k < 20$, $0 < l < 7$). The data were corrected for Lorentz-polarization and for absorption (faces indexed). The systematic absences are consistent with the space groups $I222$ (No. 23), $I2_12_12_1$ (No. 24), $Imm2$ ($Im2m$, $I2mm$) (No. 44), and $Immm$ (No. 71) (see Table 1 for data collection and refinement conditions). The good agreement among Friedel pairs allowed us to select the centrosymmetric space group ($Immm$). The positions of the La and Nb atoms were determined by direct methods with the program SHELXTL (12). The positions for the S and O atoms were determined from subsequent difference Fourier calculations. In the first step, the refinement was done without absorption correction and led to the R factors $R_1 = 9.96\%$ for $835F_o > 4\sigma(F_o)$ and $R_1 = 16.61\%$ for 1382 (all data), 41 variables. Correction for absorption effects slightly improved the reliability factor $R_1 = 9.66\%$, but the isotropic displacement parameter for one lanthanum atom (La5), as well as for one oxygen atom (O8), remained rather high. Therefore, the site occupancy factor (s.o.f) of the La5 atom was refined first. A better solution ($R_1 = 6.18\%$) was obtained for a partial occupancy of this La5 site (around 39%).

Going further by refining the s.o.f. of the O8 site ($0, 0, \frac{1}{2}$), and by adding an extra O9 atom ($0, 0, 0$) that issues from a difference Fourier calculation does not improve the refinement. More, the O9 site should also be partially occupied

TABLE 1
Crystal Data and Structure Refinement Details for
 $\text{La}_{\sim 10.8}\text{Nb}_5\text{O}_{20}\text{S}_{10}$

Crystal Data	
Empirical formula	$\text{La}_{\sim 10.8}\text{Nb}_5\text{O}_{20}\text{S}_{10}$
Symmetry	Orthorhombic
Space group	$Immm$
Cell parameters (\AA)	$a = 32.535(8)$, $b = 12.115(3)$, $c = 3.9999(3)$
Cell volume	1576.6(6)
Z	2
Temperature (K)	293(2)
Density (g cm^{-3})	5.49
μ (mm^{-1})	16.74
Crystal size	$\approx 0.01 \times 0.03 \times 0.25$ bounded by faces $\{100\}$, $\{010\}$, $\{001\}$
Absorption correction	Indexed faces
Max. and min. transmission	0.847–0.585
Data Collection	
Radiation	$\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$)
Diffractometer	Enraf-Nonius CAD4
Scan type	ω/θ
Range of h, k, l	$-45 \leq h \leq 45$, $-17 \leq k \leq 17$, $0 \leq l \leq 5$
θ range (deg)	1.79–30
Refinement	
All reflections	1382
No. of observed reflections ($I \geq 2\sigma(I)$)	836
No. of refined parameters	58
Reliability factor $R_{\text{obs}}/R_{\text{all}}$	5.09%/11.09%
Residual electron density [max, min] (e \AA^{-3})	7.10 – 3.66

because of the too close proximity with the O2 site ($\text{O2--O9} \sim 1.34 \text{ \AA}$); this means that occupancies for both O2 and O9 sites have to be constrained ($1 - x$ and x) to exclude the simultaneous presence of O2 and O9 atoms. So, little by little, other site occupancies should also be refined when considering their surroundings, which will complicate the solution, and finally will not make sense. Finally, La and Nb atoms were refined anisotropically. The final cycle of the least-squares refinement gave agreement factors of $R_1 = 5.09\%$ for 836 reflections with $F_o > 4\sigma(F_o)$ and $R_1 = 11.09\%$ for 1382 unique reflections (2θ limit = 60°) using 58 parameters. A final difference Fourier map showed the largest peak ($+7.1 \text{ e}^- \text{ \AA}^{-3}$) for the $(0, 0, 0)$ position (=O9), at 1.36 \AA from O2. Final values of positional parameters and equivalent displacement parameters are given in Table 2; anisotropic displacement parameters for La and Nb atoms are indicated in Table 3.

DESCRIPTION OF THE STRUCTURE

If one decides on a composite layered-type organization, it then becomes clearer that the structure of $\text{La}_{\sim 10.8}\text{Nb}_5$

TABLE 2
Atomic Positional Parameters, Isotropic Displacement Parameters (\AA^2), and Site Occupancy Factor (s.o.f.) for $\text{La}_{\sim 10.8}\text{Nb}_5\text{O}_{20}\text{S}_{10}$

Atom	Site	x	y	z	$U_{\text{iso, eq}}^*$	s.o.f.
La1	8n	0.18822(3)	0.34081(9)	0	0.0049(2)	1
La2	4e	0.19486(4)	0	0	0.0050(3)	1
La3	4e	0.10280(5)	$\frac{1}{2}$	$\frac{1}{2}$	0.0064(3)	1
La4	4h	0	0.21928(15)	$\frac{1}{2}$	0.0135(4)	1
La5	4e	0.05516(11)	0	0	0.0061(12)	0.386
Nb1	8n	0.12674(5)	0.16222(14)	$\frac{1}{2}$	0.0049(3)	1
Nb2	2d	0	$\frac{1}{2}$	0	0.0210(10)	1
S1	8n	0.05295(14)	0.6444(4)	0	0.0083(9)	1
S2	4e	0.2172(2)	$\frac{1}{2}$	$\frac{1}{2}$	0.0069(12)	1
S3	8n	0.21555(13)	0.1705(4)	$\frac{1}{2}$	0.0074(8)	1
O1	8n	0.1390(4)	0.3166(9)	$\frac{1}{2}$	0.007(3)	1
O2	4g	0	0.1126(18)	0	0.027(6)	1
O3	4f	0.1441(5)	0	$\frac{1}{2}$	0.002(3)	1
O4	4f	0.1427(5)	$\frac{1}{2}$	0	0.006(4)	1
O5	8n	0.1390(4)	0.1557(10)	0	0.006(2)	1
O6	2b	0	$\frac{1}{2}$	$\frac{1}{2}$	0.024(8)	1
O7	8n	0.0731(5)	0.1426(12)	$\frac{1}{2}$	0.020(3)	1
O8	2c	0	0	$\frac{1}{2}$	0.073(15)	1

$\text{O}_{20}\text{S}_{10}$ can be schematically described as the stacking of RS layers pillared by an intricate assembly of La and Nb polyhedra, along the a -direction (see Fig. 1).

The RS part of this structure is very similar to that observed for $\text{Sm}_2\text{Ti}_2\text{O}_5\text{S}_2$, i.e., a double [LaS] sheet where La atoms (La1 and La2) are nine coordinate with five S atoms from the [LaS] entity itself, and four oxygen atoms from the apexes of the adjacent entity. This corresponds to La atoms in a monocapped square antiprismatic coordination environment (Figs. 2a and 2b), with average La1-S and La2-S distances of 3.003 and 2.935 \AA , respectively; the corresponding La1-O and La2-O distances are equal to 2.586 and 2.607 \AA , respectively. Detail of the various La-(O/S) distances is given in Table 4. The RS-type layers are separated by a complex structural arrangement constituted by all the Nb polyhedra and the La3, La4, and La5 polyhedra.

TABLE 3
Anisotropic Displacement Parameters (\AA^2) for $\text{La}_{\sim 10.8}\text{Nb}_5\text{O}_{20}\text{S}_{10}$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
La1	0.0066(5)	0.0052(5)	0.0028(5)	0.0010(4)	0	0
La2	0.0058(8)	0.0062(6)	0.0031(8)	0	0	0
La3	0.0085(7)	0.0062(6)	0.0045(7)	0	0	0
La4	0.0068(7)	0.0254(9)	0.0083(9)	0	0	0
La5	0.0020(18)	0.0092(20)	0.0069(22)	0	0	0
Nb1	0.0070(7)	0.0050(7)	0.0027(7)	-0.0014(7)	0	0
Nb2	0.0067(16)	0.0120(17)	0.044(3)	0	0	0

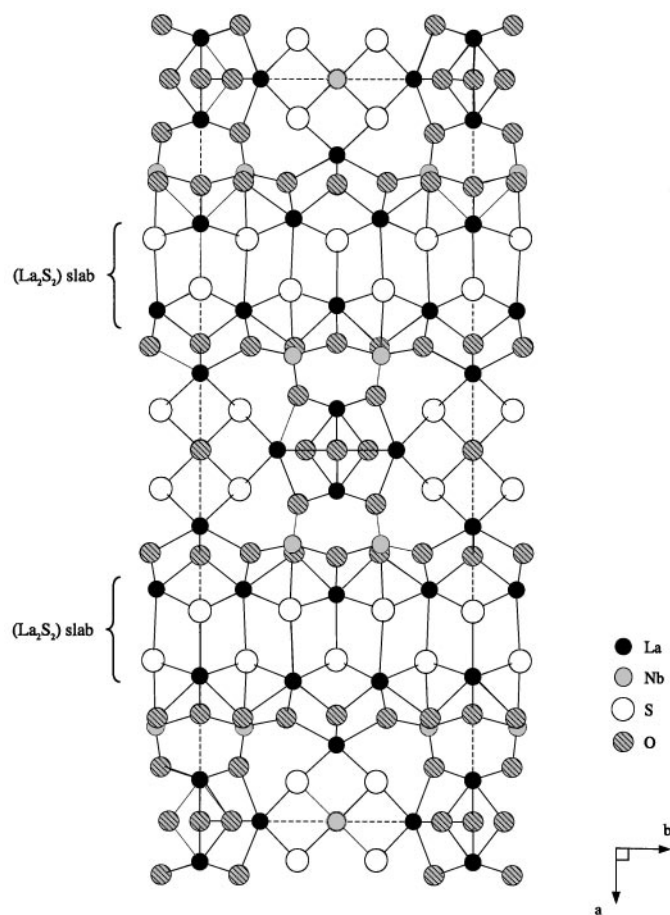


FIG 1. Projection of the structure of $\text{La}_{\sim 10.8}\text{Nb}_5\text{O}_{20}\text{S}_{10}$ onto the (a, b) plane. The $[\text{La}_2\text{S}_2]$ slabs are distinguished.

In contact with the $[\text{La}_2\text{S}_2]$ slab, one observes the Nb1 and La3 polyhedra. Nb1 is in a distorted octahedral coordination (Fig. 3a), with only one S apical atom (S3) at a rather long distance (2.891 \AA), and five O atoms (O1, O3, 2 O5, and O7) with a very short Nb1-O7 distance (1.762 \AA , see Table 4). Such a small Nb-O distance (1.762 \AA) has never been reported to our knowledge; a short one, Nb-O = 1.811 \AA , is mentioned for $\text{La}_3\text{NbSe}_2\text{O}_4\text{F}_2$ (13). La3 is in a square antiprismatic coordination of four O and four S atoms (Fig. 2c), with La3-O distances ranging from 2.385 (with O4) to 2.513 \AA (with O1), and La3-S1 distance equal to 3.111 \AA . Nb2, La4, and La5 polyhedra are located in the central zone of the complex part. The Nb2 atom is coordinated to two O atoms (O6) and four S atoms (S1) in an octahedral arrangement (Fig. 3b). The Nb(2) X_6 octahedron shares a common edge S1-S1 with the La4 polyhedron. Atom La4 sits in a monocapped square antiprismatic site (Fig. 2d) surrounded by four S (4 S1) and five O (2 O2, 2 O7, 1 O8) atoms, with O8 being the capping atom. The La5 atom is coordinated to oxygen atoms only (4 O7, 2 O2, and 2 O8) in

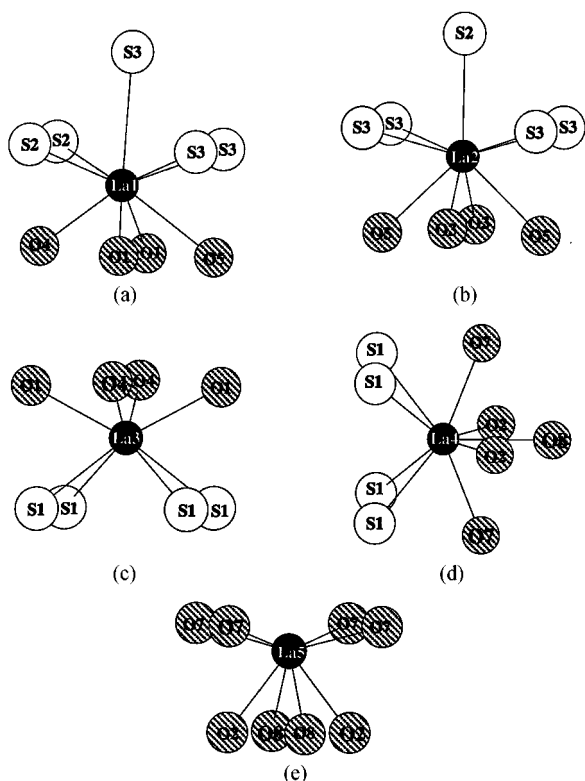


FIG 2. Environments around (a) La1, (b) La2, (c) La3, (d) La4, and (e) La5 atoms.

a square antiprismatic environment (Fig. 2e). The two La5-O2 distances (2.255 Å) are much shorter than the six other ones (2.687 Å with O8, and 2.706 Å with O7). The La5 site is partially occupied ($\sim 39\%$) as revealed by the

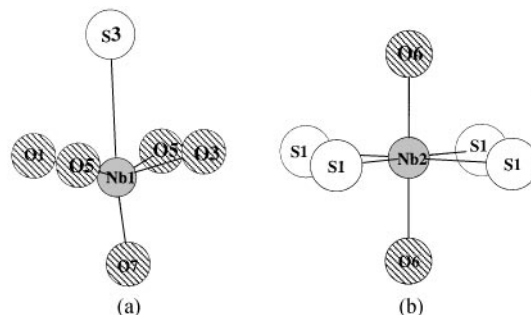


FIG 3. Environments around (a) Nb1, and (b) Nb2 atoms, respectively.

structure refinement. The reason for this is not clear, but in any case, it could be partly related to the short La5-La5 contact (3.589 Å). We have even considered the presence of niobium (Nb3) instead of lanthanum (La5); this led to quite similar R values, with a higher s.o.f. ($\sim 58\%$), but that solution was bad from a charge equilibrium point of view: indeed, a bond valence of +1.5 was calculated for an Nb site.

We have also to recall that a residual peak located at (0, 0, 0) (=O9), close to La5 (1.794 Å), appeared in the difference Fourier map. We have not taken into account this feature because that led us to refine the s.o.f. of the too close O2 atom, and then the other neighborings. The O7 atom which is engaged in a short Nb1-O7 distance is also shared with La4 and La5 atoms. The partial occupancy of the La5 site is probably at the origin of the intricate situation in that localized part.

Given the crystallographic composition $\text{La}_{-10.8}\text{Nb}_5\text{O}_{20}\text{S}_{10}$, charge balance requires La (+III) and Nb (+V) to

TABLE 4
Main Interatomic Distances (Å) for Each La and Nb Polyhedron for $\text{La}_{-10.8}\text{Nb}_5\text{O}_{20}\text{S}_{10}$

Atom 1	Atom 2	Distance	Bond valence	Atom 1	Atom 2	Distance	Bond valence
La1	O4	2.431(11)	0.50	La4	2 × O2	2.381(12)	2 × 0.57
La1	2 × O1	2.580(8)	2 × 0.33	La4	2 × O7	2.553(15)	2 × 0.36
La1	O5	2.756(12)	0.21	La4	O8	2.657(2)	0.27
La1	2 × S2	2.934(2)	2 × 0.45	La4	4 × S1	3.114(4)	4 × 0.28
La1	2 × S3	3.008(4)	2 × 0.37		total		3.25
La1	S3	3.134(5)	0.26	La5	2 × O2	2.255(14)	2 × 0.8
	total		3.27	La5	2 × O8	2.687(3)	2 × 0.25
La2	2 × O3	2.593(10)	2 × 0.32	La5	4 × O7	2.706(10)	4 × 0.23
La2	2 × O5	2.620(12)	2 × 0.30		total		3.02
La2	S2	2.862(7)	0.55	Nb1	O7	1.762(16)	1.49
La2	4 × S3	2.953(4)	4 × 0.43	Nb1	O1	1.912(12)	0.99
	total		3.51	Nb1	2 × O5	2.041(2)	2 × 0.7
La3	2 × O4	2.385(9)	2 × 0.56	Nb1	O3	2.045(5)	0.7
La3	2 × O1	2.514(12)	2 × 0.40	Nb1	S3	2.891(5)	0.24
La3	4 × S1	3.113(4)	4 × 0.28		total		4.82
	total		3.04	Nb2	2 × O6	2.0000(2)	2 × 0.79
				Nb2	4 × S1	2.455(5)	4 × 0.80
					total		4.78

compensate S (–II) and O (–II) as no short S–S bonding is present. Bond valence calculations confirm well these assumptions (see Table 4).

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