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# Synthesis and Structural Characterization of a New Lanthanum Oxychlorosulfide $La_5Ti_6S_3Cl_3O_{15}$

Pierre Palvadeau[1], Marie-Christine Boyer, Alain Meerschaut, and Jean Rouxel

*Institut des Matériaux, Laboratoire de Chimie des Solides, UMR-CNRS 6502, B.P. 32229, 44322 Nantes Cedex 3, France*

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**A new oxychlorosulfide compound $La_5Ti_6S_3Cl_3O_{15}$ has been prepared from the reaction of LaOCl with a mixture of $La_2S_3$ and $TiS_2$. Single crystal X-ray diffraction studies show that this compound crystallizes in the space group *Im*-3 (#204) of the cubic system ($a = 12.4156(6)$ Å, $Z = 4$). Data collection was obtained using a CAD4 Enraf Nonius diffractometer. Structural refinement was made with the program SHELXTL using 783 independent reflections. The final refinement resulted in conventional *R* factors, $R_1 = 0.038$ for 563 reflections, with $F > 4\sigma(F)$, $R = 0.069$, and $Rw\ (F^2) = 0.126$ for all reflections. The structure contains two types of La atoms with coordinations of 10 and 12, and Ti is in a distorted octahedral coordination to five oxygen atoms and one sulfur or chlorine atom.** © 1998 Academic Press

## INTRODUCTION

The MOCl oxychloride compounds show various structural types, all with a lamellar organization (1). The most well-characterized is FeOCl (2), which was intensively studied for its physical properties, particularly for its original magnetic structure (3–5), as well as for numerous possibilities of grafting (6–8), pillaring (9), and intercalation (10–12). LaOCl is another example of a compound that is of great interest. It is not hygroscopic and can be easily obtained by decomposition in air of $LaCl_3,6H_2O$ at 600°C. LaOCl decomposes above 630°C under vacuum to form $La_2O_3$ and a very reactive $LaCl_3$. It can react with many oxides, leading to oxychlorides such as $La_3TiO_4Cl_5$ (13), ternary oxides like $La_3TaO_7$ and $LaTaO_4$ (14), and even silicates such as $La_2Ti_2SiO_9$ (15).

The chemistry of oxychalcogenides is less well-developed than that of oxyhalogenides. Some oxychalogenides are known in nature (Kermesite, $Sb_2S_2O$ (16); Sarabauite, $CaSb_{10}S_6O_{10}$ (17), and Cetineite $Na_{3.6}(Sb_2O_3)_3(SbS_3)(OH)_{0.6},2.4H_2O$ (18)), and some synthetic compounds ($La_5V_3O_7S_6$ (19)) have also been synthesized. In addition one oxychlorosulfide family, $Ln_4OS_4Cl_2$, with $Ln$ = La, Ce, Nd (20–21), is known and one oxyfluoroselenide, $La_3NbSe_2O_4F_2$, has been identified (22).

Many recent studies have mentioned the existence of quaternary oxychalcogenides with rare-earth and transition metal elements that show common structural features. This is the case for $Ln_{20}Ti_{11}S_{44}O_6$ ($Ln$ = La, Ce) (23–24), $La_8Ti_{10}S_{24}O_4$ (25), $Eu_{27}Ti_{20}I_{0.7}Cl_{1.3}S_{54}O_{12}$ (26), $La_{14}Ti_8S_{33}O_4$, and $Sr_{5.8}La_{4.4}Ti_{7.8}S_{24}O_4$ (27). These new phases are potentially of interest for their optical, magnetic, and electrical properties.

In an effort to expand such a series, we have exploited the high reactivity of LaOCl in the presence of binary chalcogenides of transition metal elements. This paper deals with the structure determination of the new oxychlorosulfide, $La_5Ti_6S_3Cl_3O_{15}$, which was obtained under these conditions.

## EXPERIMENTAL

Orange-colored single crystals of $La_5Ti_6S_3Cl_3O_{15}$ were prepared from the reaction of $La_2S_3$, LaOCl, and $TiS_2$. The mixture was ground, sealed in an evacuated silica tube, and heated to 850°C for a week. Semiquantitative analyses of these crystals were carried out using an electron microprobe (PGT IMIX system) mounted on a JEOL 5800 LV scanning electron microscope. Analyses on several crystals revealed the presence of La, Ti, S, Cl, and O with the following mean ratios: Ti/La = 1.2, Ti/S and Ti/Cl = 2.04, S/Cl = 1, and Ti/O = 2.29. This last result must be considered with caution due to the low precision of oxygen analyses.

The stoichiometric chemical reaction can be written

$$15\ LaOCl + 6\ TiS_2 + La_2S_3 \rightarrow La_5Ti_6S_3Cl_3O_{15} + 4\ LaCl_3 + 4\ La_2S_3$$

It also seems possible that a reaction between LaOCl and $TiS_2$ could occur according to the equation

$$15\ LaOCl + 6TiS_2 \rightarrow La_5Ti_6S_3Cl_3O_{15} + 4\ LaCl_3 + 3\ La_2S_3.$$

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[1] To whom correspondence should be addressed. E-mail: palvadeau@cnrs-imn.fr.

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However, it appears that the presence of $La_2S_3$ as a starting material is necessary to stabilize $La_5Ti_6S_3Cl_3O_{15}$. In fact, the reaction yields a mixture of oxides. Elemental sulfur is also produced, but can be condensed at one extremity of the silica tube away from the sample.

## STRUCTURE DETERMINATION

The crystal used was an orange-colored quasicube ($0.02 \times 0.02 \times 0.02$ mm$^3$) mounted on an Enraf-Nonius CAD4 diffractometer for data collection using Mo$K\alpha$ radiation. Unit cell parameters were determined from a least-squares analysis of the setting angles of 25 reflections in the range $5° < \theta < 25°$. Crystal stability was checked by monitoring intensities of three standard reflections each hour. The intensity data were corrected for Lorentz polarization effects. Due to the cubic symmetry and the crystal dimensions, no absorption corrections were applied. Table 1 lists the cell parameters and the data collection parameters. The SHELXTL version 5 package (28) was used for data reduction and calculations.

The systematic absences (hkl with $h + k + l = 2n + 1$) are consistent with the space group $Im$-3 (#204).

The positions of lanthanum were determined by direct methods. The coordinates of the remaining atoms were obtained from subsequent Fourier-difference maps. Chlorine and sulfur were placed at the same sites with occupancies of 50% for each atomic species, consistent with the chemical analyses (see Experimental section); as from the refinement, assignment to either sulfur ($Z = 16$) or chlorine ($Z = 17$) atoms was not possible. This position will be called (S–Cl) in the text.

783 independent reflections, of which 563 correspond to the condition $F > 4\sigma(F)$, were used in the refinement. Atomic scattering factors, which included an anomalous scattering contribution, were taken from Ref. 29. Anisotropic thermal parameters were refined for all atoms. The final refinement gave $R_1(F) = 0.069$ and $R_w(F^2) = 0.126$. For reflections corresponding to $F > \sigma(F)$, the conventional $R$ factor was $R_1 = 0.038$. A final difference map showed no significant residual peaks (1.7 eÅ$^{-3}$ in 0, 0, 0.04). Fractional coordinates and temperature factors ($B_{eq}$) of all atoms are given in Table 2; Table 3 shows the anisotropic thermal parameters.

### TABLE 1
### Details of the Data Collection and Refinement Results

| | |
|---|---|
| $La_5Ti_6S_3Cl_3O_{15}$ | $Z = 4$ |
| Cubic symmetry | Space group $Im$-3 (# 204) |
| $a = 12.4156$ (6) Å | $v = 1923.7$ Å$^3$ |
| Diffractometer | Enraf Nonius CAD 4 |
| Temperature | 293 K |
| Radiation | $\lambda$ (Mo$K\alpha$) = 0.7107 Å |
| Monochromator | Graphite |
| $\rho$calc. | 4.94 g cm$^{-3}$ |
| $\mu$ (cm$^{-1}$) | 140 |
| $\theta$ range | 1.5°–35° |
| Number of independent reflections | 783 |
| Number of reflections ($F > 4\sigma(F)$) | 563 |
| Number of variables | 32 |
| $R_1 = 0.038$ | (563 reflections) |
| $R_1 = 0.069$ and $R_w(F^2) = 0.126$ | (783 reflections) |
| with $R_1 = \sum\|\|Fo\| - \|Fc\|\|/\sum\|Fo\|$ and | |
| $R_w = [\sum [w(Fo^2 - Fc^2)^2]/\sum (Fo^2)^2]]^{1/2}$ | |

### TABLE 2
### Atomic Coordinates and Equivalent Isotropic Thermal Parameters

| Atom | $x$ | $y$ | $z$ | $B_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| La1 | 0 | 0.34044(6) | 0 | 0.0151(2) |
| La2 | 1/4 | 1/4 | 1/4 | 0.0229(3) |
| Ti | 0.19893(12) | 1/2 | 0.14047(13) | 0.0089(3) |
| S–Cl[a] | 0 | 0.1824(2) | 0.2038(2) | 0.0116(4) |
| O1 | 0.1100(3) | 0.3882(4) | 0.1850(3) | 0.0095(7) |
| O2 | 0.1310(7) | 1/2 | 0 | 0.0084(14) |

[a] S and Cl share the same position.

## STRUCTURE DESCRIPTION

The crystal structure viewed down the $c$ axis is shown in Fig. 1. It is built from distorted $TiO_5$(S–Cl) octahedra and two distinct La polyhedra (Fig. 2a–2c). Each titanium octahedron has five oxygen corners shared with adjacent titanium octahedra. The sixth corner, statistically occupied by a sulfur or a chlorine atom, is bonded to lanthanum. Figure 3 gives a schematic representation of the titanium sublattice, showing connections between octahedra. Ti–O (1.858–2.017 Å) and Ti–(S–Cl) (2.509 Å) distances are comparable to those found in other oxysulfides, such as $La_{20}Ti_{11}S_{44}O_6$ (average values Ti–O = 1.952 Å, Ti–S = 2.488 Å) (23) or TiOCl (Ti–O = 2.01 Å and Ti–Cl = 2.30 Å) (30).

Lanthanum has two different coordinations. La1, which is in a ten-fold coordination, is bonded to six oxygen atoms

### TABLE 3
### Anisotropic Thermal Parameters

| Atom | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| La1 | 0.0109(3) | 0.0094(3) | 0.02511(4) | 0 | 0 | 0 |
| La2 | 0.0229(3) | 0.0229(3) | 0.0229(3) | 0.0170(3) | 0.0170(3) | 0.0170(3) |
| Ti | 0.0054(6) | 0.0056(6) | 0.0158(7) | 0 | 0.0020(5) | 0 |
| S–Cl | 0.0136(8) | 0.0095(8) | 0.0118(7) | 0.0010(7) | 0 | 0 |
| O1 | 0.008(2) | 0.012(2) | 0.009(2) | 0.0004(14) | 0.004(1) | 0.000(15) |
| O2 | 0.010(4) | 0.010(4) | 0.005(3) | 0 | 0 | 0 |

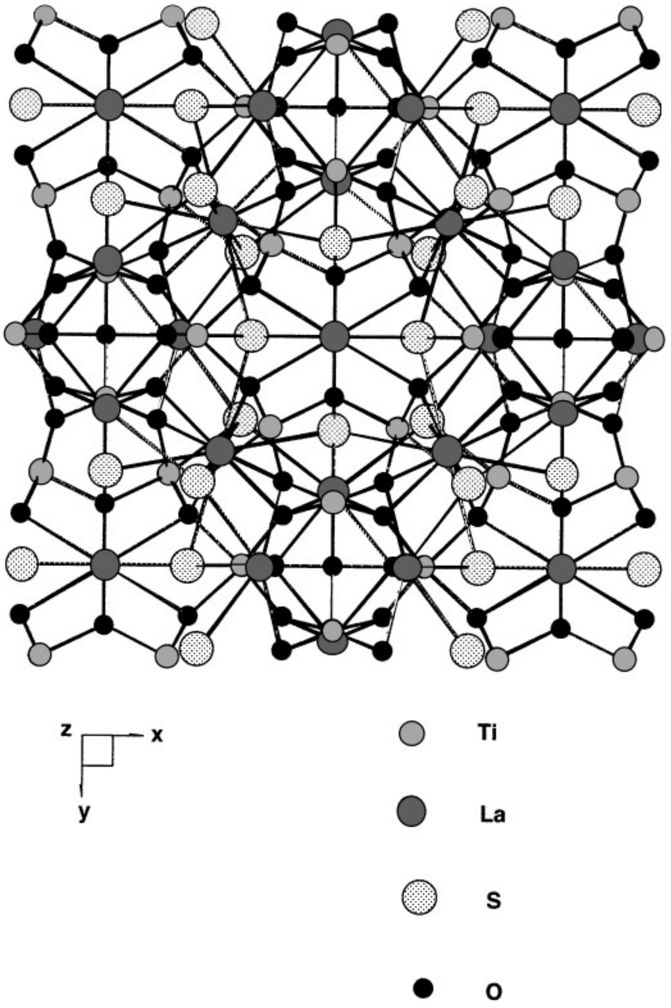

**FIG. 1.** Structure of $La_5Ti_6S_3Cl_3O_{15}$: view down the *c* axis.

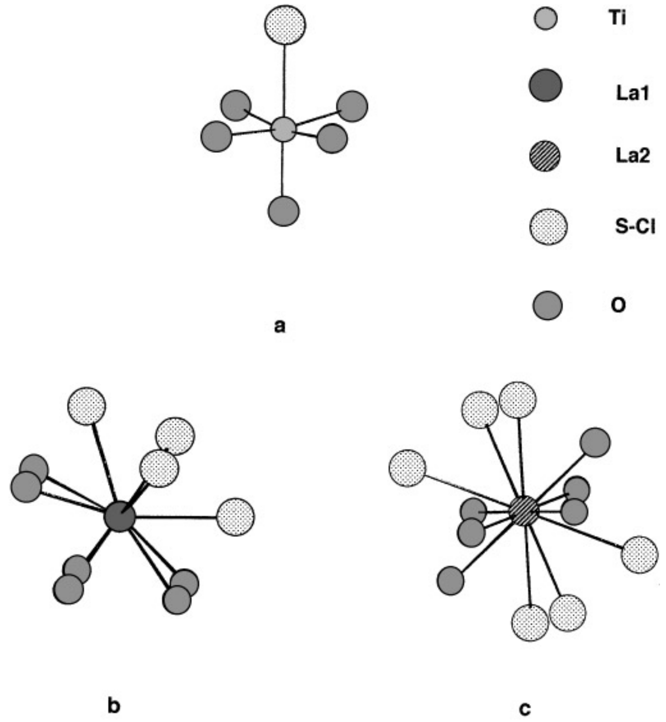

**FIG 2.** The three polyhedra in the structure: (a) titanium octahedron; (b) lanthanum polyhedron (La1); and (c) lanthanum polyhedron (La2).

(four at 2.737 Å and two at 2.563 Å) and four sulfur–chlorine atoms at 2.830 Å and 3.201 Å. La1 polyhedra are bonded together through an edge of oxygen and four corner-sharing (S–Cl) atoms (Fig. 4). La1 and Ti polyhedra are linked by triangular faces built from two O2 and one (S–Cl) atom. La2 is twelve-fold coordinated, with six oxygen atoms at 2.572 Å and six sulfur–chlorine atoms at 3.266 Å. La2 polyhedra share six corner (S–Cl) atoms with the surrounding La2 polyhedra (Fig. 5). They also share triangular faces, constructed from one O2 and two (S–Cl) atoms, with La1 polyhedra. All oxygen atoms in this polyhedron are also bonded to titanium atoms. La2 and Ti polyhedra also share triangular faces built from two O2 and one (S–Cl) atoms. Selected bond distances are gathered in Table 4.

High coordination numbers for La are well known for oxides. In perovskites, for example, La is coordinated to twelve oxygens. In chalcogenides, the La coordination is always lower. In oxychalcogenides, as illustrated by $La_{20}Ti_{11}S_{44}O_6$, La atoms are 7-, 8-, and 9-coordinated in mono-, bi-, or tricapped trigonal prismatic arrangements, respectively. A particular coordination is observed in $Ln_4OS_4Cl_2$, where one lanthanum atom is surrounded by nine (S–Cl) atoms that delimit a tricapped trigonal prism.

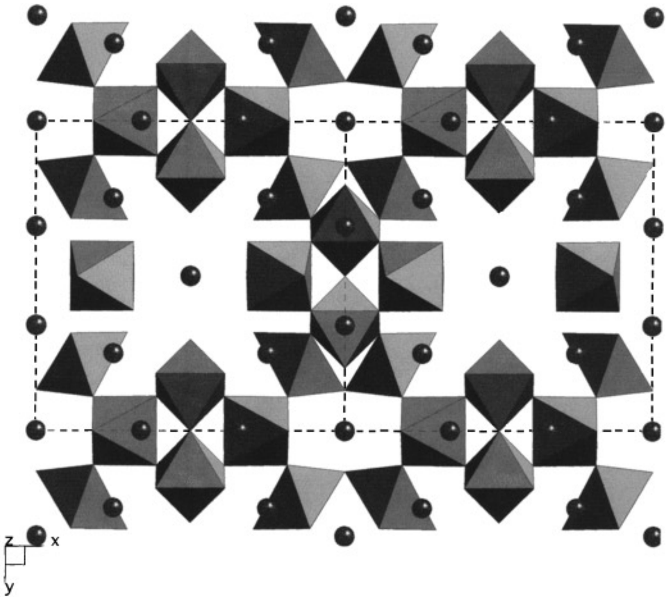

**FIG 3.** Structure of $La_5Ti_6S_3Cl_3O_{15}$: view down the *c* axis (two cells) showing only titanium octahedra.

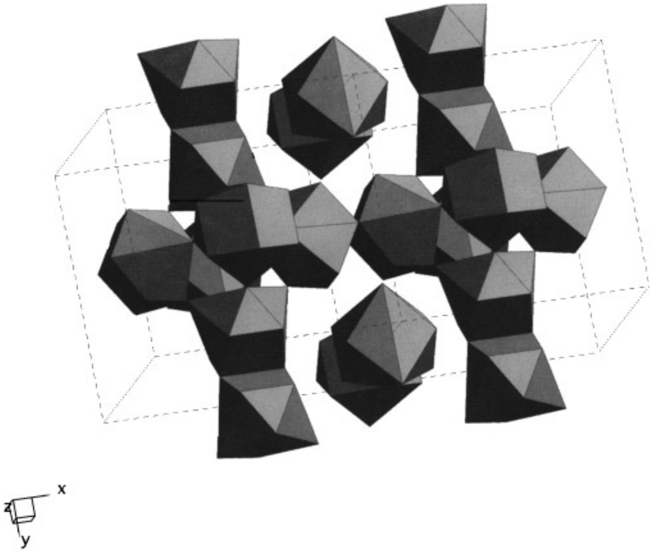

**FIG 4.** Crystalline sublattice of lanthanum La1 polyhedra.

An additional oxygen atom completes the coordination sphere as the tenth ligand.

The shortest metal–metal distances observed between La2–Ti = 3.45 Å and Ti–Ti = 3.495 Å are too long to allow direct metal–metal interactions.

## BOND VALENCE PARAMETER CALCULATIONS

The presence of chlorine substituting 50% of sulfur was assumed on the basis of chemical analyses. It is noteworthy that the presence of chlorine atoms is in agreement with a charge equilibrium, as assuming 5 $La^{3+}$ and 6 $Ti^{4+}$, the 39 positive charges must be balanced by 15 $O^{2-}$, 3 $Cl^{-}$, and 3 $S^{2-}$. Moreover, considering the distances around atoms, it is not possible to substitute oxygen by chlorine atoms. Theoretically, a more precise assignment to sulfur and chlorine atoms could be achieved by neutron diffraction, as the scattering factors are more different ($S = 3.1 \times 10^{-11}$ cm and $Cl = 9.9 \times 10^{-11}$ cm).

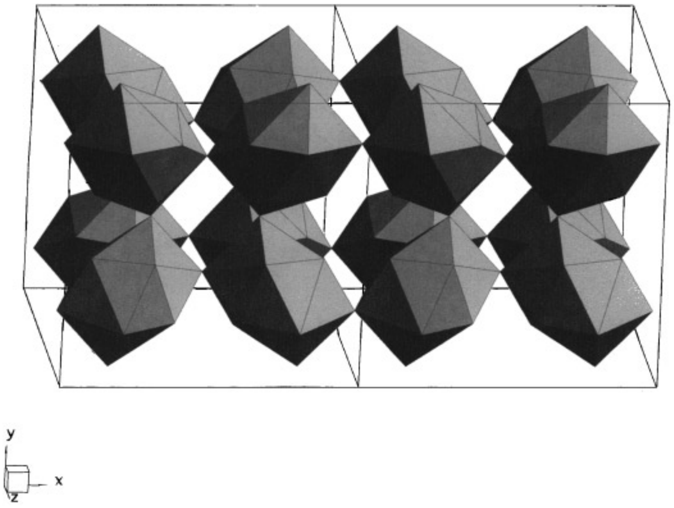

**FIG 5.** Crystalline sublattice of lanthanum La2 polyhedra.

**TABLE 4**
**Bond Distances (Å) in Polyhedra and Shortest Metal–Metal Bonds**

| | | | |
|---|---|---|---|
| La1–O1 | 2 × 2.563(6) | La1–Ti | 3.615(1) |
| –O2 | 4 × 2.737(5) | | |
| –S–Cl | 2 × 2.830(2) | | |
| –S–Cl | 2 × 3.201(2) | | |
| La2–O2 | 6 × 2.572(4) | La2–Ti | 3.447(1) |
| –S–Cl | 6 × 3.266(1) | | |
| Ti–O1 | 1 × 1.937(4) | Ti–Ti | 3.495(5) |
| –O2 | 2 × 1.858(5) | | |
| –O2 | 2 × 2.017(4) | | |
| –S–Cl | 1 × 2.509(3) | | |

Bond valence parameter calculations were performed to check the validity of our model through the computation of the total valence at each site, according to the Brese and O'Keeffe tables (31). A first calculation with the hypothesis of only sulfur atoms leads to a sum valence of 3.22 for La1, 3.12 for La2, 4.14 for Ti, and 1.66 for S. A second calculation with half of the sulfur atoms substituted by chlorine, results in a valence sum of 1.5 for the (S–Cl) site. A final calculation was made using only chlorine atoms. The best agreement with theoretical values for all positions is obtained in the case of a mixed (S–Cl) site (Table 5).

$La_5Ti_6S_3Cl_3O_{15}$ is one of the first oxychlorosulfide compounds reported. This new synthetic method has been extended to other transition metals and rare earths, and physical and spectroscopic characterizations are currently in progress.

**TABLE 5**
**Bond Valence Calculations**

| | Total bond valence | | |
|---|---|---|---|
| Atom | 100% S | 100% Cl | 50% S and 50% Cl |
| La1 | 3.21 | 2.84 | 3.03 |
| La2 | 3.12 | 2.88 | 3.00 |
| Ti | 4.14 | 4.08 | 4.11 |
| O1 | 2.14 | 2.14 | 2.14 |
| O2 | 2.03 | 2.03 | 2.03 |
| S–Cl | 1.65 | 1.34 | 1.53 |

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