Synthesis and Structure Determination of $Nd_{16}Ti_5S_{17}O_{17}$

C. Boyer-Candalen, C. Deudon, and A. Meerschaut[1]

Institut des Matériaux Jean Rouxel, UMR 6502, Laboratoire de Chimie des Solides, 2 rue de la Houssinière, B.P. 32229, 44322 Nantes Cedex 03, France

The structure of the new compound $Nd_{16}Ti_5S_{17}O_{17}$ was determined by single-crystal X-ray diffraction. The following data were obtained: $M_r = 3364.4$ g mol^{-1}, tetragonal symmetry, space group $I4/m$ (No. 87), unit cell parameters $a = 22.153(2)$ Å, $c = 3.9426(3)$ Å, $V = 1935$ Å^3, $Z = 2$. Refinement for 1282 unique reflections and 62 parameters converged to the reliability factor $R = 2.22\%$ (for 1059 reflections with $I \geq 3\sigma(I)$). The structure can be schematically described on the basis of [NdS] plane fragments connected by "(Nd_8S_9)" clusters, which delimit a filled channel of squared section. Within these channels, octahedral Ti-centered chains are developed along the c axis.

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INTRODUCTION

In the recent past, some oxysulfides of rare-earth metals and titanium, having composition $Ln_2Ti_2S_2O_5$ with $Ln = $ Pr, Nd, Sm, have been reported (1, 2). All these representatives which have a 3D structural character can also be schematically viewed as a "2D layered composite-type structure," i.e., with two components built from rare-earth sulfide and titanium oxide slabs. Thus, a rock-salt-type slab corresponding to a double atom-thick-layer ["Ln_2S_2"] is interleaved by a ReO$_3$-type slab built from the 2D network of oxygen corner-sharing Ti-octahedra ["Ti_2O_5S"], two octahedra thick, along the c axis of the lattice. The central site within this ReO$_3$-type slab is empty; in a parent perovskite-type, this site is partially or totally filled. These $Ln_2Ti_2S_2O_5$ compounds have been structurally referenced as defective Ruddlesden–Popper phases (3) of the Sr$_3$Ti$_2$O$_7$ structure-type.

In a continuation of the investigation of this class of materials, aiming this time to study a perovskite-type oxide layer, we tried to synthesize new compounds starting from the mixture of the already known NdTiO$_3$ perovskite and Nd$_2$S$_3$ compounds, in a 1:1 ratio.

This paper deals with the X-ray crystal structure determination of a new phase $Nd_{16}Ti_5S_{17}O_{17}$.

[1]To whom correspondence should be addressed.

SYNTHESIS

A mixture of Nd$_2$O$_3$, Ti$_2$O$_3$, and Nd$_2$S$_3$ with the ratio 1:1:2, respectively, was sealed in a quartz ampoule under vacuum. The tube was progressively heated in a furnace at 1000°C and maintained at this temperature for 5 days. The product was pulverized and reheated at 1050°C for 10 days. In order to promote crystallization, the product of reaction was then ground with a small amount of I$_2$ (<5 mg/cm^3) for 3 weeks. The reaction yielded a mixture of inhomogeneous powder and few orange crystals with a platelet shape characteristic of $Nd_{16}Ti_5S_{17}O_{17}$.

Semiquantitative chemical analyses on two crystals were carried out using a JEOL 5800 SEM equipped with a PGT microanalyzer. The EDS results confirmed the presence of oxygen and corroborated the structure composition of non-oxygen atoms as follows: Nd, 41.2 (42.1); Ti, 12.9 (13.1); S, 45.9 (44.8) (calculated values are in parentheses). The oxygen content was structurally deduced from consideration of interatomic distances where typical Ti–O (≈ 2 Å) and Nd–O (≈ 2.5 Å) distances are occurring.

STRUCTURE DETERMINATION

A small orange ribbon-shaped crystal with dimensions $0.02 \times 0.02 \times 0.84$ mm^3 was mounted on a STOE IPDS single φ axis diffractometer using Mo$K\alpha$ radiation. The time of exposure was 4 mn for each φ position, φ varying from 0° to 150° with an increment of 1°. The crystal-to-detector distance was set to 60 mm. The images were processed with the set of programs of STOE (4). The unit cell parameters for a tetragonal symmetry confirmed preliminary X-ray investigations with Bragg and Weissenberg cameras; the resulting cell parameters from a least-squares refinement on 5000 reflections were $a = 22.153(2)$ Å and $c = 3.9426(3)$ Å. A total of 6838 reflections ($-29 < h < 29$, $-28 < k < 29$, $-4 < l < 5$) were measured over the range $5.2° < 2\theta < 55.8°$. No intensity decay was observed. Systematic absences (hkl with $h + k + l = 2n + 1$) indicated one of the possible space groups: $I4$, $I\bar{4}$, $I4/m$. Intensity statistic favored the centrosymmetric $I4/m$ (No. 87). Data were corrected for

Lorentz and polarization effects. The absorption correction (indexed faces) was applied, although no significant improvement was observed on refinement. Secondary extinction correction was taken into account. The structure was partly solved by direct methods using SHELXTL (5). Sulfur and oxygen atoms were found from subsequent difference-Fourier syntheses and least-squares refinements.

Refinement on 1282 independent reflections was performed using JANA98 (6). It converged well to an R value of 3.17% for 1059 reflections ($I \geq 3\sigma(I)$) and 59 variables. At this stage, a difference-Fourier map showed two large residual peaks that could not be ignored (i.e., 12.35 and 7.33 e$^-$ A^{-3}, far exceeding the value of the "background"). We then took into account these two residuals as additional sulfur atoms, namely S2 and S6, in the structure refinement; because the resulting values of their thermal displacement parameters were too high, we lowered the site occupancy factors (sof) of both S2 and S6; under these conditions, a refinement gave an R value of 2.20% with 63 parameters. Values of the sof for S2 (4d site) and S6 (4c site) were 0.324 and 0.241, respectively, instead of 1 for a full occupancy. Of course, the simultaneous presence of S2 and S6 atoms is excluded when considering these statistical occupancy values, but this implies the existence of S–S pairing (S2–S2 and S6–S6 $\approx$ 1.97 Å). As the lowest S–S distance reported in the literature is around 2.05Å (7), it was difficult to ascertain this S–S hypothesis. To overcome this problem, we imposed a constraint on the site occupancy for both S2 and S6 positions which limits their sum at half the value for a 4c- or 4d-type site; so, we used the equation $a(S2) = 0.125 - a(S6)$, where $a(S2)$ and $a(S6)$ are occupancies of the sites. Now, the statistical distribution of S2 and S6 atoms is such that no S_2^{2-} pairing is present, but rather "isolated" S^{2-} species. A final refinement converged to reliability factors $R = 2.22\%$ for 1059 reflections ($I \geq 3\sigma(I)$), and $R = 2.96\%$ for all 1282 unique reflections with 62 variables. A final difference-Fourier map was featureless. A summary of the crystallographic data is given in Table 1. Atomic coordinates and isotropic displacement parameters are given in Table 2, and anisotropic displacement parameters are listed in Table 3.

DESCRIPTION OF THE STRUCTURE

The Nd$_{16}$Ti$_5$S$_{17}$O$_{17}$ structure can be described on the basis of (NdS) plane fragments that develop perpendicular to the (a, b) plane. These planes that cross themselves perpendicularly to delimit a filled channel of squared-section growing along the c axis (see Fig. 1) are thus interlinked via a "Nd$_8$S$_9$" cluster. Such a cluster type corresponds to a square prismatic arrangement of Nd3 atoms with S2 or S6 atoms in its center (partial filling) and S5 atoms that connect two Nd3 atoms of each face of the square prismatic polyhedron (see Fig. 2). This type of cluster is similar to the

TABLE 1
Crystal Data and Structure Refinement Details for Nd$_{16}$Ti$_5$S$_{17}$O$_{17}$

Chemical empirical formula	Nd$_{16}$Ti$_5$S$_{17}$O$_{17}$
Chemical formula weight (g mol^{-1})	3364.4
Crystal system	Tetragonal
Space group	$I4/m$
Cell parameters (Å)	$a = 22.153(2)$, $c = 3.9426(3)$
Volume (Å^3)	1934.8(2)
Z	2
Crystal dimensions (mm^3)	$0.02 \times 0.02 \times 0.84$ bounded by {100} {010} {001}
Max., min. transmission	0.6586, 0.5027
Isotropic secondary extinction	0.53(6)
Density (g cm^{-3})	5.773
μ (mm^{-1})	22.96
Wavelength (Å)	0.71073 (MoKα)
θ range (deg)	2.60–27.88
Limiting indices	$-29 < h < 29$; $-28 < k < 29$; $-4 < l < 5$
No. of independent reflections	1282
No. of reflections	1059
R and R_w factor (for 1059 reflections with $I > 3\sigma(I)$)	0.0222; 0.0227
No. of parameters	62
Residual peaks (min/max, e$^-$/Å^3)	$-2.83/4.79$

[Ti$_4$S$_2$O$_4$] cluster observed in La$_{20}$Ti$_{11}$S$_{44}$O$_6$ [8], or in Ce$_{20}$Ti$_{11}$S$_{44}$O$_6$ [9], or in some related compounds, such as Sr$_{5.8}$La$_{4.4}$Ti$_{7.8}$S$_{24}$O$_4$ and La$_{14}$Ti$_8$S$_{33}$O$_4$ [10], and in La$_8$Ti$_{10}$S$_{24}$O$_4$ [11, 12].

The plane fragment consists of a {001} slice of a slightly distorted NaCl-structure type, i.e., a double atom-thick-layer [NdS] with Nd atoms protruding outward from the

TABLE 2
Fractional Atomic Coordinates, Isotropic Displacement Parameters (U_{eq}^*, U_{iso}; Å^2), and Site Occupancy Factors (sof)

Atom	Site	x	y	z	U_{eq}^*, U_{iso}	sof
Nd1	8h	0.75857(2)	0.40784(2)	0	0.0040(1)*	1
Nd2	8h	0.65726(2)	0.27256(2)	0	0.0043(1)*	1
Nd3	8h	0.88380(2)	0.54797(2)	0	0.0089(1)*	1
Nd4	8h	0.61272(2)	0.41358(2)	$\frac{1}{2}$	0.0041(1)*	1
Ti1	8h	0.74982(6)	0.53325(5)	$\frac{1}{2}$	0.0031(3)*	1
Ti2	2b	$\frac{1}{2}$	$\frac{1}{2}$	0	0.0180(9)*	1
S1	8h	0.51421(8)	0.39281(8)	0	0.0064(4)	1
S2	4d	0	$\frac{1}{2}$	$\frac{1}{4}$	0.016(3)	0.29
S3	8h	0.75370(8)	0.18653(8)	0	0.0050(3)	1
S4	8h	0.83120(8)	0.62157(8)	$\frac{1}{2}$	0.0079(4)	1
S5	8h	0.85062(8)	0.46172(8)	$\frac{1}{2}$	0.0065(3)	1
S6	4c	0	$\frac{1}{2}$	0	0.015(5)	0.21
O1	8h	0.6978(2)	0.5956(2)	$\frac{1}{2}$	0.007(1)	1
O2	8h	0.7151(2)	0.4587(2)	$\frac{1}{2}$	0.005(1)	1
O3	8h	0.6590(2)	0.3778(2)	0	0.004(1)	1
O4	8h	0.7677(2)	0.5325(2)	0	0.008(1)	1
O5	2a	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.036(4)	1

TABLE 3
Anisotropic Displacement Parameters (Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nd1	0.0048(2)	0.0058(2)	0.0014(2)	−0.0011(1)	0	0
Nd2	0.0060(2)	0.0043(2)	0.0025(2)	0.0006(1)	0	0
Nd3	0.0136(2)	0.0085(2)	0.0045(2)	−0.0056(2)	0	0
Nd4	0.0052(2)	0.0052(2)	0.0017(2)	−0.0007(1)	0	0
Ti1	0.0044(5)	0.0030(5)	0.0017(7)	0.0001(4)	0	0
Ti2	0.0038(7)	0.0038(−)	0.046(3)	0	0	0

plane of sulfur. This type of structure is similar to the (LnS) slabs (Ln = rare earth) encountered in the incommensurate (misfit) layered compounds $[(MX)_{1+x}(TX_2)_m]$ (13), as well as in $Ln_2Ti_2S_2O_5$. Nd1, Nd2, and Nd3 atoms belong to these [NdS] plane fragments: Nd1 and Nd2 atoms are in a tricapped trigonal prismatic environment of five S and four O (sulfur atoms within the plane fragment and oxygen atoms out of this plane) (see Fig. 3a,b). The environment around Nd3 is more complex because of a statistical distribution of S2 and S6 atoms in its coordination sphere (see Fig. 3c). So, Nd3 is seven-coordinated if one considers that only one position for S2 and S6 atoms is statistically occupied, i.e., either $(0, \frac{1}{2}, 0)$ or $(0, \frac{1}{2}, \frac{1}{4})$ or $(0, \frac{1}{2}, \frac{1}{2})$ or $(0, \frac{1}{2}, \frac{3}{4})$; one observes a quadrilateral base with $2 \times$ S4 and $2 \times$ S5 atoms with Nd3 in an excentered position shifted toward $1 \times$ S5 and either S2 or S6. Nd3 is also connected to O4.

Within the square channel, five infinite chains of corner-sharing Ti-centered octahedra (see Fig. 4) run along the c axis (four of Ti1 and one of Ti2). O4 atoms ensure the
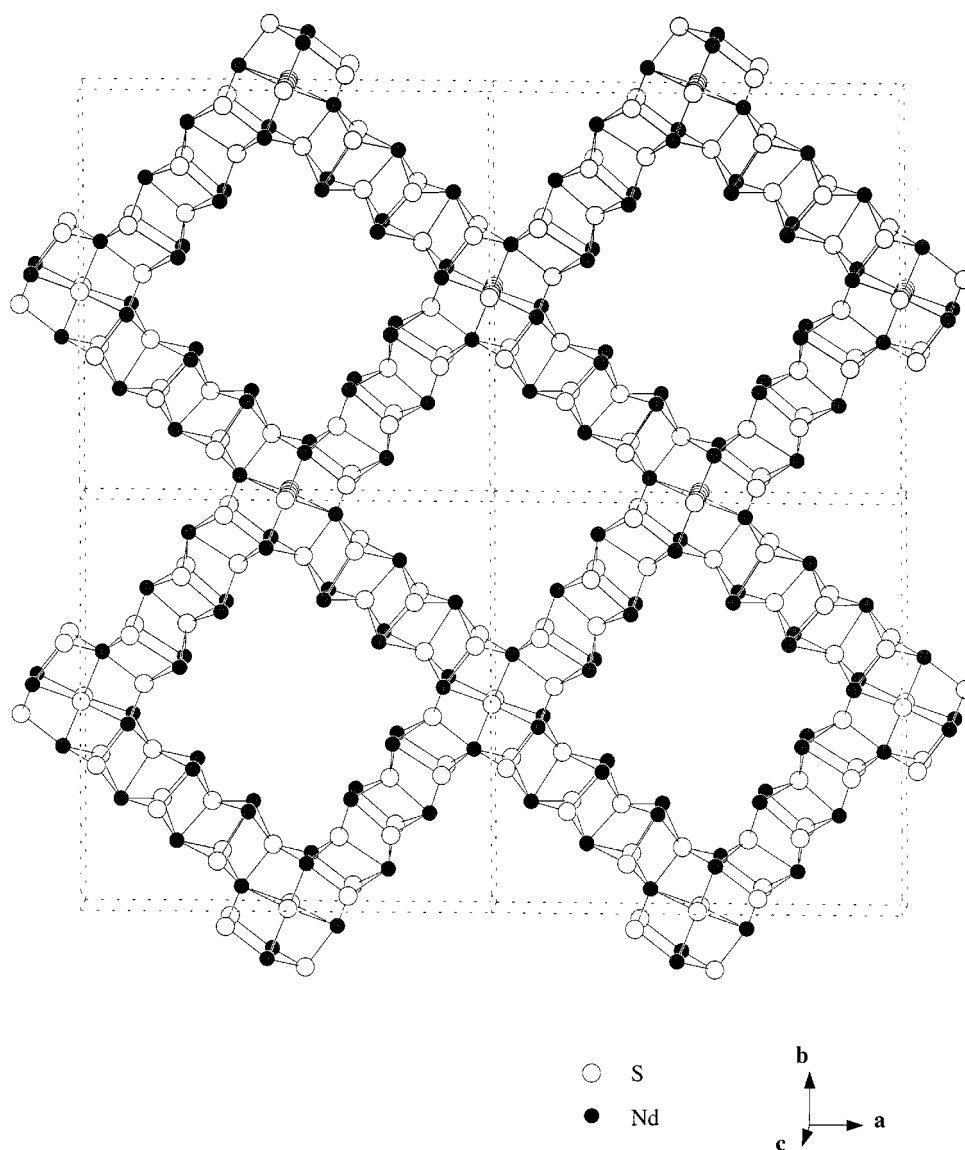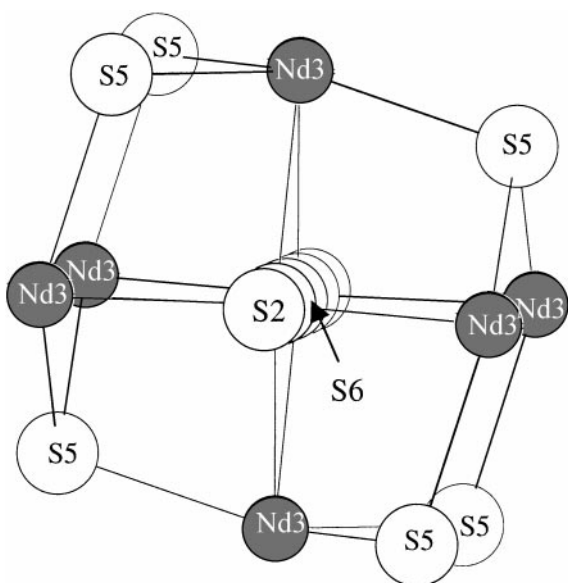

FIG. 1. Projection of the [NdS] plane fragments connected by (Nd$_8$S$_9$) clusters onto the (a,b) plane.

FIG. 2. "Nd_8S_9" cluster.

connected to $4 \times S1$ (2.395(2) Å) describing a square-base with Ti2-centered, and it is also bound to two apical O5 atoms (1.9713(3) Å). The quadrilateral base for Ti1 is built up from S4, S5, O2, and O1; the two apical bounds are established by $2 \times O4$ (2.011(1) Å).

From bond valence calculations (14), it can be argued that the results (see Table 4) roughly agree with a tetravalent oxidation state for both Ti atoms and a trivalent state for Nd atoms.

DISCUSSION AND CONCLUDING REMARKS

The new structure type exhibited by $Nd_{16}Ti_5S_{17}O_{17}$ does not relate to the hypothetical Ruddlesden–Popper type layered perovskite ($n = 1$) that we attempted to synthesize. We only recognize the presence of a rock-salt-type [NdS] plane fragments which enclose 1D rutile chains (oxygen corner-sharing Ti octahedra), such an arrangement being quite different to the expected 2D composite layered one.

The formation of [LnS] slabs with a rock-salt-type structure was encountered in the incommensurate misfit layer chalcogenides compounds $[(MX)_{1+x}(TX_2)]$ (13), as well as in oxychalcogenides derivatives such as $Ln_2Ti_2S_2O_5$ phases, or $La_{\sim 10.8}Nb_5O_{20}S_{10}$ (15). For all these compounds, these 2D [LnS] layers are separated by either a chalcogenide layer or an oxide layer. Of course, this structural characteristic of "segregated layers" (oxides against sulfides) is strongly dependent on the Ln/T (T = Ti, Nb …) and O/X (X = S, Se) ratios. But, whatever the values of these ratios, atomic positions with a mixed occupancies (i.e., Ln and T, or O

connection between successive Ti1 octahedra, and O5 atoms between Ti2 octahedra, along the c direction. The infinite chains of Ti2-centered octahedra are situated at the center of the cavity. The connection between these two types of octahedra is done by the polyhedra around Nd4, which is in a bicapped trigonal prismatic environment (see Fig. 3d). Table 4 summarizes the main interatomic distances for each Nd and Ti polyhedra. A more regular octahedron for Ti2 was observed compared to the Ti1 one. Indeed, Ti2 is

FIG. 3. Atomic environments around (a) Nd1, (b) Nd2, (c) Nd3, and (d) Nd4 atoms.

TABLE 4
Interatomic Distances (Å) and Bond Valences

Atom A	Atom B	Distance	Bond valence	Atom A	Atom B	Distance	Bond valence
Nd1	$2 \times S5$	3.077(1)	2×0.27	Nd4	$2 \times S1$	2.977(1)	2×0.35
Nd1	S4	3.151(2)	0.22	Nd4	$2 \times S1$	2.978(1)	2×0.35
Nd1	$2 \times S3$	2.886(1)	2×0.45	Nd4	$2 \times O3$	2.359(3)	2×0.52
Nd1	O3	2.304(5)	0.60	Nd4	O2	2.479(5)	0.37
Nd1	$2 \times O2$	2.466(3)	2×0.39	Nd4	O1	2.497(5)	0.35
Nd1	O4	2.769(5)	0.17			Total	3.16
		Total	3.21	Ti1	S5	2.738(2)	0.26
Nd2	$2 \times S4$	3.130(1)	2×0.23	Ti1	S4	2.661(2)	0.32
Nd2	S3	2.863(2)	0.48	Ti1	O2	1.822(5)	0.98
Nd2	$2 \times S3$	2.932(1)	2×0.39	Ti1	$2 \times O4$	2.011(1)	2×0.59
Nd2	O3	2.332(5)	0.56	Ti1	O1	1.799(5)	1.04
Nd2	O4	2.905(5)	0.12			Total	3.78
Nd2	$2 \times O1$	2.486(3)	2×0.37	Ti2	$4 \times S1$	2.395(2)	4×0.66
		Total	3.14	Ti2	$2 \times O5$	1.9713(3)	2×0.65
Nd3	$2 \times S5$	2.842(1)	2×0.51			Total	3.94
Nd3	S5	2.833(2)	0.52				
Nd3	$2 \times S4$	2.811(1)	2×0.55				
Nd3	O4	2.594(5)	0.28				
Nd3	$S2^a$	2.9541(4)	0.22				
Nd3	$S6^a$	2.7849(4)	0.12				
		Total	3.26				

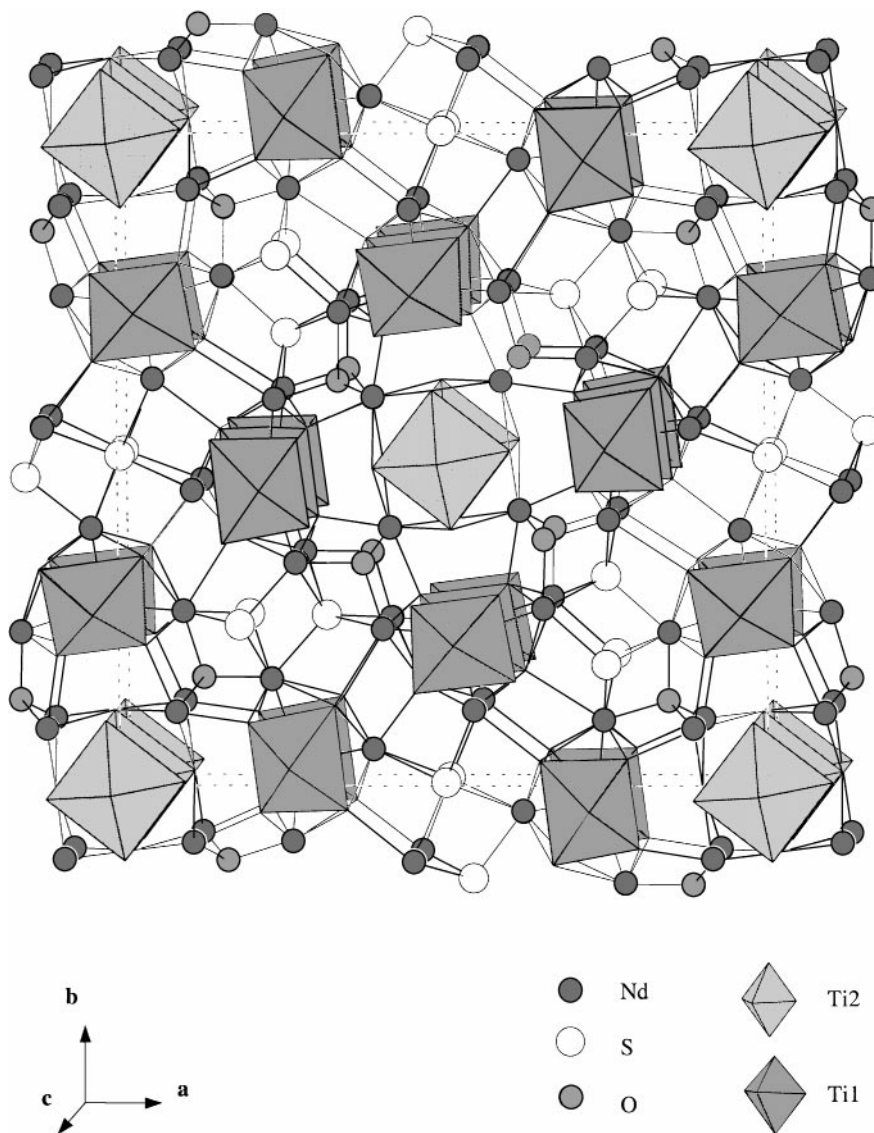^{a} Calculated values when taking into account the statistical occupancy.

FIG. 4.   Chains of Ti octahedra within the square-based channel delimited by [NdS] plane fragments.

and X) have never been reported to our knowledge. Indeed, a separation between these corresponding elements is always occurring. Even for the limit where Ln and T elements have a similar O/X environment (because of a similar oxo-/ chalcophilicity) as exemplified in $Sm_3NbO_4X_3$ compounds ($X = S$ (16) and Se (17), respectively), these respective Sm and Nb atoms are separated on distinct site locations. So, the tendencies for Sm and Nb to prefer chalcogen or oxygen atoms in their coordinating sphere is not as marked as for the Ln/Ti couple where the titanium element is preferably bonded to oxygen. In the opposite direction, for the family of compounds corresponding to the general formulation $(LnO)_n(T_xX_y)$ with $T =$ IB, IIIA, IVA, or VA elements (18), the oxygen is only bonded to the rare-earth metal, and the sulfur to the T element; the structure is thus built from the regular alternation of an oxide slab (LnO) and a chalcogenide one (TX). It has to be mentioned that this (LnO) layer does not exhibit a rock-salt-type structure, as it is the case for the (LnS) layer with the $Ln_2Ti_2S_2O_5$ compounds.

Because of the very small size of crystals, electrical measurements were not performed. However, the orange-transparent color and the fact that all Ti atoms are in the $+$ IV oxidation state militate in favor of a nonmetallic character.

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