

Syntheses and Crystal Structures of the Lanthanum Titanium Oxyselenides $\text{La}_4\text{Ti}_2\text{O}_4\text{Se}_5$ and $\text{La}_6\text{Ti}_3\text{O}_5\text{Se}_9$

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Received September 1, 2000; accepted December 8, 2000

The new compounds $\text{La}_4\text{Ti}_2\text{O}_4\text{Se}_5$ and $\text{La}_6\text{Ti}_3\text{O}_5\text{Se}_9$ have been obtained from stoichiometric reactions of La, Ti, TiO_2 , and Se in fused-silica tubes at 1223 K. Potassium halide fluxes were used to promote the crystallization. The compounds have been characterized by single-crystal X-ray diffraction methods. $\text{La}_4\text{Ti}_2\text{O}_4\text{Se}_5$ crystallizes in the orthorhombic space group $Cmcm$ with eight formula units in a cell at 153 K of dimensions $a = 3.9695(4)$ Å, $b = 33.115(3)$ Å, $c = 18.6380(18)$ Å. The five independent La atoms in the structure are found in four different coordination polyhedra, namely tricapped trigonal prism, bicapped trigonal prism, square antiprism, and 7-octahedron, whereas the three independent Ti atoms have octahedral coordination. The crystal structure comprises infinite layers that stack along the b -axis. Two adjacent layers are linked by La–Se bonds. $\text{La}_4\text{Ti}_2\text{O}_4\text{Se}_5$ represents the first rare-earth titanium oxychalcogenide containing only Ti^{3+} cations. $\text{La}_6\text{Ti}_3\text{O}_5\text{Se}_9$ crystallizes in the monoclinic space group $C2/m$ with four formula units in a cell at 153 K of dimensions $a = 43.999(6)$ Å, $b = 3.9454(6)$ Å, $c = 11.1093(16)$ Å, $\beta = 96.882(2)^\circ$. The six independent La atoms in the structure are found in three different coordination polyhedra, namely tricapped trigonal prism, bicapped trigonal prism, and 7-octahedron. The four independent Ti atoms have octahedral coordination. The crystal structure comprises infinite condensed layers of composition $\frac{2}{3}[\text{La}_2\text{Ti}_1\text{O}_2\text{Se}_3]$ that stack successively with extended slabs of composition $\frac{2}{3}[\text{La}_4\text{Ti}_2\text{O}_3\text{Se}_6]$ along the a -axis. $\text{La}_6\text{Ti}_3\text{O}_5\text{Se}_9$ is a mixed-valence compound in which two-thirds of the Ti cations are Ti^{3+} and one-third are Ti^{4+} . © 2001 Academic Press

Key Words: rare-earth; oxychalcogenide; mixed-valence; oxide.

INTRODUCTION

Recently, several rare-earth titanium oxychalcogenide compounds have been characterized by single-crystal X-ray diffraction methods to reveal interesting structural features (1–7). With the exception of $\text{Ln}_2\text{Ti}_2\text{O}_5\text{S}_2$ ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}$) (7), their crystal structures differ significantly from their

oxide and chalcogenide counterparts, independent of the O/Q ratio ($Q = \text{S}, \text{Se}$). For example, the chalcogen-rich compounds $\text{La}_{20}\text{Ti}_{11}\text{O}_6\text{S}_{44}$ (2) and $\text{La}_{14}\text{Ti}_8\text{O}_4\text{S}_{33}$ (3) and the oxygen-rich compounds $\text{Ln}_3\text{Ti}_3\text{O}_8\text{Se}_2$ ($\text{Ln} = \text{Nd}, \text{Sm}$) (8) exhibit structural features not known for ternary rare-earth titanium oxides or chalcogenides. Besides providing new structure types, oxychalcogenides also provide complex anionic environments that can result in marked changes in the electronic configurations of the $3d$ cations. For most of the rare-earth titanium oxychalcogenides, Ti cations are generally octahedrally coordinated by Q^{2-} anions or by a combination of O^{2-} and Q^{2-} anions. The connectivity between these octahedra occurs by corner sharing, edge sharing, or face sharing. Face sharing results in short Ti–Ti distances, giving rise to metal–metal bonds or at least strong metal–metal interactions. As is typical of oxychalcogenides, there are no Q–Q, Q–O, or O–O bonds in these compounds so the formal oxidation states of O (–II) and Q (–II) can be assigned. Invariably the oxidation state $\text{Ln}(\text{+III})$ can be assigned, leaving only the question of the formal oxidation state of Ti, either $\text{Ti}(\text{+III})$ or $\text{Ti}(\text{+IV})$ or both. Among these compounds, some have been classified as mixed-valence compounds (2, 5, 6) containing Ti^{3+} and Ti^{4+} cations randomly distributed over nonequivalent crystallographic sites.

Here we describe the syntheses and the crystal structures of two new quaternary lanthanum titanium oxyselenides, $\text{La}_4\text{Ti}_2\text{O}_4\text{Se}_5$ and $\text{La}_6\text{Ti}_3\text{O}_5\text{Se}_9$. On the basis of charge balance, $\text{La}_4\text{Ti}_2\text{O}_4\text{Se}_5$ contains only Ti^{3+} cations whereas $\text{La}_6\text{Ti}_3\text{O}_5\text{Se}_9$ contains two Ti^{3+} cations for every Ti^{4+} cation. In this latter mixed-valence compound a reasonable assignment of its Ti cations to specific sites has been made.

EXPERIMENTAL

Syntheses

Single crystals of $\text{La}_4\text{Ti}_2\text{O}_4\text{Se}_5$ and $\text{La}_6\text{Ti}_3\text{O}_5\text{Se}_9$ were prepared from the reaction of La (Alfa, 40 mesh, 99.9%), Ti (Alfa, 100 mesh, 99.9%), TiO_2 (Alfa, 100 mesh, 99.99%), and Se (Alfa, 325 mesh, 99.5%) in stoichiometric ratios. A KCl

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flux for $\text{La}_4\text{Ti}_2\text{O}_4\text{Se}_5$ and a KI flux for $\text{La}_6\text{Ti}_3\text{O}_5\text{Se}_9$ were used to promote crystal growth. For each preparation 3.5 mmol of material was loaded into a fused-silica tube that was then sealed under a vacuum of approximately 10^{-4} Torr. The tube was heated to 1223 K, kept there for 100 h, cooled at 3 K/h to 973 K, and then the furnace was turned off. The final products are black needles. Both phases are stable in moist air. Semiquantitative analyses were performed with a Hitachi 3500N SEM. For several single crystals from each preparation, oxygen was detected, but could not be quantified. EDX results for the heavier elements gave average atomic ratios La ((35(3)), Ti ((17(2)), Se ((48(3)) and La ((35(3)), Ti ((16(2)), Se ((49(2)), which may be compared to the values La (36.4), Ti (18.2), Se (45.4) and La (33.3), Ti (16.7), Se (50) calculated for $\text{La}_4\text{Ti}_2\text{O}_4\text{Se}_5$ and $\text{La}_6\text{Ti}_3\text{O}_5\text{Se}_9$. No trace of K, Cl, or I was detected.

Crystallography

X-ray diffraction data were collected on a Bruker Smart 1000 CCD diffractometer at 153 K with the use of monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The diffracted intensities generated by a scan of 0.3° in ω were recorded on multiple sets of 606 frames covering more than a hemisphere of the Ewald sphere. Between each set, the ϕ setting was rotated by 90° and 120° for the collection of $\text{La}_4\text{Ti}_2\text{O}_4\text{Se}_5$ and $\text{La}_6\text{Ti}_3\text{O}_5\text{Se}_9$, respectively. The exposure times were 20 s/frame for $\text{La}_4\text{Ti}_2\text{O}_4\text{Se}_5$ and 25 s/frame for $\text{La}_6\text{Ti}_3\text{O}_5\text{Se}_9$. For both compounds, cell refinement and data reduction were carried out with the use of the program SAINT + (9) and a face-indexed absorption correction was

TABLE 1
X-Ray Crystallographic Details

	$\text{La}_4\text{Ti}_2\text{O}_4\text{Se}_5$	$\text{La}_6\text{Ti}_3\text{O}_5\text{Se}_9$
Space group	<i>Cmcm</i>	<i>C2/m</i>
<i>a</i> (Å)	3.9695(4)	43.999(6)
<i>b</i> (Å)	33.115(3)	3.9454(6)
<i>c</i> (Å)	18.6380(18)	11.1093(16)
β ($^\circ$)	90	96.882(2)
<i>V</i> (Å ³)	2450.0(4)	1914.6(5)
<i>T</i> (K)	153	153
<i>Z</i>	8	4
ρ_c (g/cm ³)	6.020	6.133
μ (cm ⁻¹)	297.2	313.7
Transmission factors	0.104–0.672	0.068–0.701
Crystal color and habit	Black needle	Black needle
Number of measured reflections	14796	8753
<i>R</i> _{int}	0.0412	0.0345
Number of unique reflections	1811	2635
Number of variables	108	141
<i>R</i> (<i>F</i>) ^a for all reflections	0.0350	0.0361
<i>R</i> _w (<i>F</i> _o) ^b for all reflections	0.0676	0.0646

^a $R(F) = \sum \|F_o\| - |F_c| / \sum \|F_o\|$. ^b $R_w(F_o^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^2]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$ for $F_o^2 > 0$ and $w = 1/\sigma^2(F_o^2)$ for $F_o^2 \leq 0$.

TABLE 2
Atomic Coordinates and Equivalent Isotropic Displacement Parameters for $\text{La}_4\text{Ti}_2\text{O}_4\text{Se}_5$

Atom	Wyckoff position ^a	<i>y</i>	<i>z</i>	<i>U</i> _{eq} (Å ²) ^b
La(1)	8 <i>f</i>	0.103285(14)	0.04615(3)	0.00840(12)
La(2)	8 <i>f</i>	0.258857(14)	0.63642(3)	0.00848(12)
La(3)	8 <i>f</i>	0.434277(14)	0.12108(3)	0.00729(12)
La(4)	4 <i>c</i>	0.31565(2)	0.25	0.00895(15)
La(5)	4 <i>c</i>	0.54316(2)	0.25	0.01120(16)
Se(1)	8 <i>f</i>	0.13610(2)	0.64997(4)	0.00796(17)
Se(2)	8 <i>f</i>	0.19865(3)	0.01711(5)	0.00968(18)
Se(3)	8 <i>f</i>	0.52759(3)	0.08639(4)	0.00897(18)
Se(4)	4 <i>c</i>	0.20825(4)	0.25	0.0115(3)
Se(5)	4 <i>c</i>	0.96729(4)	0.25	0.0086(2)
Se(6) ^c	8 <i>f</i>	0.62849(9)	0.1616(2)	0.0100(6)
Se(7) ^c	8 <i>f</i>	0.64184(9)	0.1511(2)	0.0101(6)
Ti(1)	8 <i>f</i>	0.32911(5)	0.06349(8)	0.0098(3)
Ti(2)	4 <i>c</i>	0.13186(7)	0.25	0.0173(5)
Ti(3)	4 <i>a</i>	0	0	0.0103(4)
O(1)	8 <i>f</i>	0.05118(16)	0.5511(3)	0.0080(11)
O(2)	8 <i>f</i>	0.28398(17)	0.1288(3)	0.0089(12)
O(3)	8 <i>f</i>	0.38313(17)	0.0221(3)	0.0085(11)
O(4)	4 <i>c</i>	0.7791(2)	0.25	0.0078(16)
O(5) ^c	8 <i>f</i>	0.0747(3)	0.2315(6)	0.014(3)

^aAll atoms have *x* = 0. ^b*U*_{eq} is defined as one-third of the trace of the orthogonalized *U*_{ij} tensor. ^cOccupancy = 0.50.

made with the use of the program XPREP (9). The program SADABS (9) was then employed to make incident beam and decay corrections.

The crystal structure of $\text{La}_4\text{Ti}_2\text{O}_4\text{Se}_5$ was solved and refined in the orthorhombic space group *Cmcm*. The positions of the heavy atoms (La, Se, Ti) were determined by direct methods with the program SHELXS of the SHELXTL-PC suite of programs (10) and the positions of the O atoms were located from successive difference electron density syntheses. The structure, including anisotropic displacement for all the atoms, was refined by full-matrix least-squares techniques with the use of the program SHELXL (10). At this stage, despite low agreement indices (*R*(*F*) = 0.0388, *R*_w(*F*_o²) = 0.0753), the displacement ellipsoids for one Se position and one O position were abnormally high. In the difference electron density synthesis two residual peaks approximately 50% of the height of a Se atom were located about 0.5 Å from the initial position of the Se atom in question and a third residual peak about 50% of the height of an O atom was located near the O atom in question. Therefore, the initial Se position was split into two approximately half Se positions and the initial O position, which was on a 4*c* Wyckoff site, was changed to an approximately half oxygen position on an 8*f* Wyckoff site. Subsequent refinements, including unconstrained occupancies for the newly introduced positions, led to improved

TABLE 3
Atomic Coordinates and Equivalent Isotropic Displacement Parameters for La₆Ti₃O₅Se₉

Atom	Wyckoff position	x	y	z	$U_{eq}(\text{Å}^2)$
La(1)	4i	0.041050(12)	0	0.25385(4)	0.00711(12)
La(2)	4i	0.111875(12)	0	0.01300(5)	0.00813(12)
La(3)	4i	0.210751(12)	0	0.45807(4)	0.00707(12)
La(4)	4i	0.211333(12)	0	0.00796(4)	0.00726(12)
La(5)	4i	0.362455(12)	0	0.34766(5)	0.00791(12)
La(6)	4i	0.462572(12)	0	0.25386(4)	0.00721(12)
Se(1)	4i	0.09283(2)	0	0.74608(8)	0.00862(18)
Se(2)	4i	0.11227(2)	0	0.44776(8)	0.00853(18)
Se(3)	4i	0.16300(2)	0	0.22515(8)	0.00771(18)
Se(4)	4i	0.18959(2)	0	0.71727(8)	0.00800(18)
Se(5)	4i	0.34416(2)	0	0.06103(8)	0.00804(18)
Se(6)	4i	0.45914(2)	0	0.52542(8)	0.00784(18)
Se(7)	4i	0.59085(2)	0	0.18561(8)	0.00790(18)
Se(8)	4i	0.72747(2)	0	0.23600(8)	0.00844(18)
Se(9)	4i	0.95977(2)	0	0.02967(8)	0.00750(18)
Ti(1)	4i	0.26948(4)	0	0.25985(14)	0.0091(3)
Ti(2)	4i	0.64132(4)	0	0.34291(15)	0.0100(3)
Ti(3)	2c	0	0	0.5	0.0112(5)
Ti(4)	2b	0	0.5	0	0.0092(5)
O(1)	4i	0.01117(15)	0	0.6700(5)	0.0087(13)
O(2)	4i	0.26608(14)	0	0.4310(5)	0.0096(13)
O(3)	4i	0.26776(15)	0	0.0816(5)	0.0100(13)
O(4)	4i	0.51309(15)	0	0.1725(5)	0.0086(13)
O(5)	4i	0.67119(15)	0	0.4665(6)	0.0104(13)

agreement indices, and to more reasonable displacement ellipsoids and occupancies near 0.5 for these atoms (Se(6), Se(7), and O(5)). In the final refinement occupancies for these atoms were set to 0.5. The Se(6)–Se(7) of 0.484(3) Å indicates

TABLE 4
Selected Interatomic Distances (Å) and Selected Angles (°) about the Ti Cations in La₄Ti₂O₄Se₅

Ti(1)–O(2)	1.927(6)	Ti(2)–O(5)	1.925(11)
Ti(1)–O(3)	1.948(6)	Ti(2)–Se(4)	2.529(3)
Ti(1)–Se(2) × 2	2.653(1)	Ti(2)–Se(6) × 2	2.581(3)
Ti(1)–Se(1) × 2	2.804(1)	Ti(2)–Se(7) × 2	2.729(3)
O(2)–Ti(1)–O(3)	164.2(3)	O(5)–Ti(2)–Se(4)	169.7(3)
O(2)–Ti(1)–Se(2)	95.1(1)	O(5)–Ti(2)–Se(6)	94.1(2)
O(3)–Ti(1)–Se(2)	95.4(1)	Se(4)–Ti(2)–Se(6)	92.48(8)
Se(2)–Ti(1)–Se(2)	96.83(5)	Se(6)–Ti(2)–Se(6)	75.0(2)
O(2)–Ti(1)–Se(1)	87.5(1)	O(5)–Ti(2)–Se(7)	89.9(2)
Se(2)–Ti(1)–Se(1)	175.62(6)	Se(6)–Ti(2)–Se(7)	174.5(1)
Se(2)–Ti(1)–Se(1)	86.46(1)		
O(2)–Ti(1)–Se(1)	87.5(1)		
Se(1)–Ti(1)–Se(1)	90.10(5)		
Ti(3)–O(1) × 2	1.944(5)	O(1)–Ti(3)–O(1)	180
Ti(3)–Se(3) × 4	2.7141(6)	O(1)–Ti(3)–Se(3)	89.8(1)
		O(1)–Ti(3)–Se(3)	90.2(1)
		Se(3)–Ti(3)–Se(3)	180

TABLE 5
Selected Interatomic Distances (Å) and Selected Angles (°) about the Ti Cations in La₆Ti₃O₅Se₉

Ti(1)–O(2)	1.925(6)	Ti(2)–O(5)	1.783(7)
Ti(1)–O(3)	1.972(6)	Ti(2)–Se(3) × 2	2.610(1)
Ti(1)–Se(4) × 2	2.663(1)	Ti(2)–Se(7)	2.656(2)
Ti(1)–Se(8) × 2	2.695(1)	Ti(2)–Se(2) × 2	2.691(1)
O(2)–Ti(1)–O(3)	173.4(3)	O(5)–Ti(2)–Se(3)	96.08(14)
O(2)–Ti(1)–Se(4)	92.14(14)	Se(3)–Ti(2)–Se(3)	98.19(6)
O(3)–Ti(1)–Se(4)	92.29(14)	O(5)–Ti(2)–Se(7)	170.9(2)
Se(4)–Ti(1)–Se(4)	95.61(6)	Se(3)–Ti(2)–Se(7)	89.84(5)
O(2)–Ti(1)–Se(8)	87.91(14)	O(5)–Ti(2)–Se(2)	90.65(15)
O(3)–Ti(1)–Se(8)	87.59(14)	Se(3)–Ti(2)–Se(2)	83.34(2)
Se(4)–Ti(1)–Se(8)	179.25(6)	Se(3)–Ti(2)–Se(2)	172.88(8)
Se(4)–Ti(1)–Se(8)	85.14(2)	Se(7)–Ti(2)–Se(2)	83.20(5)
		O(5)–Ti(2)–Se(2)	90.65(15)
		Se(7)–Ti(2)–Se(2)	83.20(5)
		Se(2)–Ti(2)–Se(2)	94.31(6)
Ti(3)–O(1) × 2	1.893(6)	Ti(4)–O(4) × 2	1.934(6)
Ti(3)–Se(6) × 4	2.7065(7)	Ti(4)–Se(9) × 4	2.6969(7)
O(1)–Ti(3)–O(1)	180	O(4)–Ti(4)–O(4)	180
O(1)–Ti(3)–Se(6)	90.45(13)	O(4)–Ti(4)–Se(9)	90.05(13)
O(1)–Ti(3)–Se(6)	89.55(13)	O(4)–Ti(4)–Se(9)	89.95(13)
Se(6)–Ti(3)–Se(6)	180	Se(9)–Ti(4)–Se(9)	180

that both sites cannot be occupied in the same unit cell; a similar situation exists for O(5), since the O(5)–O(5') contact is 0.69 Å. No evidence of a supercell could be found on the frames. Refinements of the structure in *Cmc2*₁ and *C2cm* were unsuccessful. Crystallographic details are given in Table 1. Fractional coordinates and equivalent atomic displacement parameters are listed in Table 2.

The crystal structure of La₆Ti₃O₅Se₉ was solved and refined in the monoclinic space group *C2/m*. The procedures used parallel those above. Table 1 summarizes crystallographic details. Fractional coordinates and equivalent atomic displacement parameters are listed in Table 3.

DESCRIPTION OF THE CRYSTAL STRUCTURES

The compounds La₄Ti₂O₄Se₅ and La₆Ti₃O₅Se₉ crystallize in new structure types. Selected interatomic distances and angles around the Ti cations for La₄Ti₂O₄Se₅ are given in Table 4 and for La₆Ti₃O₅Se₉ in Table 5.

The Coordination Polyhedra around the La and Ti Cations

In La₄Ti₂O₄Se₅ and La₆Ti₃O₅Se₉ the polyhedra around the La cations are of four different geometries and involve either a pure Se²⁻ or a mixed O²⁻/Se²⁻ environment. Details, including La–O and La–Se distances, are summarized in Table 6 and in Fig. 1. All the Ti cations have a distorted octahedral environment. Each has four Se atoms forming the equatorial plane with one *trans* O and one *trans*

TABLE 6
Coordination Number, Geometrical Motif, and Range of Interatomic Distances (Å) about the La Cations in $\text{La}_4\text{Ti}_2\text{O}_4\text{Se}_5$ and $\text{La}_6\text{Ti}_3\text{O}_5\text{Se}_9$

C.N. ^a	Basic unit	Polyhedron ^b	Range La-O (Å)	Range La-Se (Å)	Figure No.
$\text{La}_4\text{Ti}_2\text{O}_4\text{Se}_5$					
9	$\text{La}(2)\text{O}_3\text{Se}_6$	ttp	2.444(3)–2.462(4)	3.010(1)–3.488(1)	1a
8	$\text{La}(1)\text{O}_3\text{Se}_5$	btp	2.400(3)–2.502(6)	3.044(3)–3.284(1)	1b
8	$\text{La}(3)\text{O}_3\text{Se}_5$	btp	2.423(3)–2.505(6)	3.108(1)–3.303(6)	1b
8	$\text{La}(4)\text{O}_4\text{Se}_4$	Square antiprism	2.325(4)–2.490(6)	3.157(1)	1c
7	$\text{La}(5)\text{O}_2\text{Se}_5$	7-Octahedron	2.269(5)	3.093(1)–3.271(3)	1d
$\text{La}_6\text{Ti}_3\text{O}_5\text{Se}_9$					
9	$\text{La}(3)\text{O}_3\text{Se}_6$	ttp	2.480(4)–2.640(4)	3.131(1)–3.310(1)	1a
9	$\text{La}(4)\text{O}_3\text{Se}_5$	ttp	2.439(4)–2.519(6)	3.161(1)–3.402(1)	1a
8	$\text{La}(1)\text{O}_3\text{Se}_5$	btp	2.423(3)–2.505(6)	3.108(1)–3.303(6)	1b
8	$\text{La}(5)\text{OSe}_7$	btp	2.681(6)	3.043(1)–3.190(1)	1b
8	$\text{La}(6)\text{O}_3\text{Se}_5$	btp	2.389(4)–2.498(6)	3.039(1)–3.168(1)	1b
7	$\text{La}(2)\text{Se}_7$	7-Octahedron		2.948(1)–3.131(1)	1d

^aC.N. = coordination number, ^bttp = tricapped trigonal prism, btp = bicapped trigonal prism.

Se atom around atom Ti(2) in both structures, and two *trans* O atoms around the other five independent Ti cations in the two structures.

3.2. Description of the Structures

Projections along the short axis of the structures of both $\text{La}_4\text{Ti}_2\text{O}_4\text{Se}_5$ and $\text{La}_6\text{Ti}_3\text{O}_5\text{Se}_9$ are displayed in Figs. 2

and 3, respectively. Each crystal structure can be viewed as a succession of layers interconnected along its longest axis.

The crystal structure of $\text{La}_6\text{Ti}_3\text{O}_5\text{Se}_9$ comprises two types of slabs, a compact slab, which we call type 1, and an extended slab (Fig. 4). The type-1 compact slab (Fig. 4a) has parallel sides; it results from the packing of $\text{La}(1)\text{O}_3\text{Se}_5$, $\text{La}(6)\text{O}_3\text{Se}_5$, $\text{Ti}(3)\text{O}_2\text{Se}_4$, and $\text{Ti}(4)\text{O}_2\text{Se}_4$ polyhedra. Each TiO_2Se_4 octahedron shares two triangular faces and two

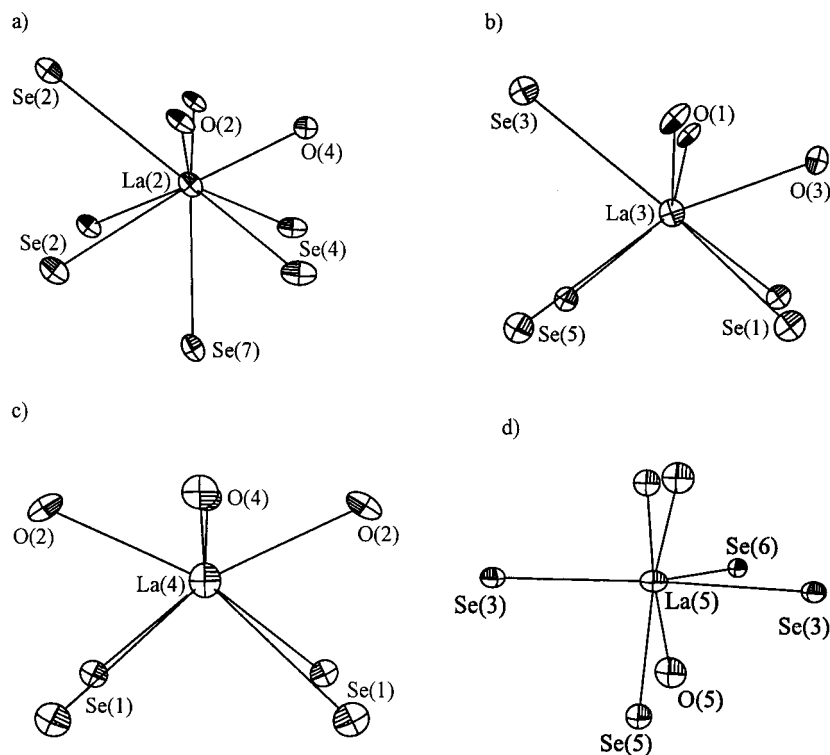


FIG. 1. The four environments about the La^{3+} cations: (a) tricapped trigonal prism, (b) bicapped trigonal prism, (c) square antiprism, and (d) 7-octahedron.

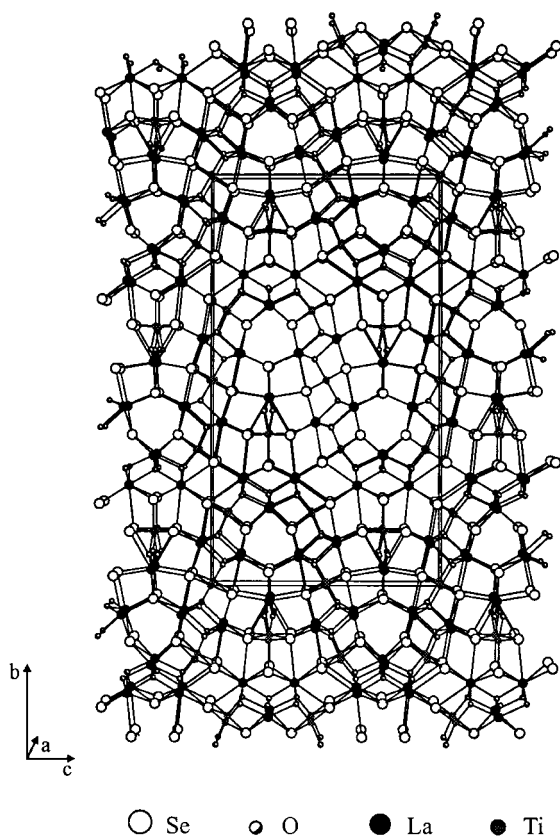


FIG. 2. View of the unit cell of La₄Ti₂O₄Se₅ along the *a*-axis.

edges with four near-neighbor bicapped trigonal prisms. The borders of these slabs are infinite planes perpendicular to [010] of alternating La(1)–Se(6)–La(6)–Se(9) chains. A very similar kind of layer has been found recently in the series of compounds $Ln_{3.67}Ti_2O_3Se_6$ ($Ln = Ce, Nd, Sm$) (11). A fragment of the extended layer is displayed in Fig. 4b. It comprises a compact layer, which we call type 2, sandwiched between slabs formed from the joining of La(2)Se₇, La(5)O₂Se₆, and Ti(2)OSe₅ polyhedra. The type-2 compact layer differs from the type-1 slab because it is slightly rippled; it results from the packing of La(3)O₅Se₄, La(4)O₃Se₆, and Ti(1)O₂Se₄ units. Each Ti(1)O₂Se₄ octahedron shares two triangular faces and two edges with four near-neighbor tricapped trigonal prisms. The resulting infinite La(3)–Se(8)–La(4)–Se(4) chains alternate and have alternating angles Se(3)–La(3)–Se(4) of 121.06(3)° and Se(4)–La(4)–Se(3) of 124.68(3)°. Finally, the three-dimensional connection is made by edge sharing and face sharing between La(1)O₃Se₅ and La(6)O₃Se₅, the bicapped trigonal prisms belonging to the compact type-1 slab, and La(2)Se₇, the 7-octahedron belonging to the extended layer. The junction also defines a vacant trigonal prismatic site of six Se atoms.

The crystal structure of La₄Ti₂O₄Se₅ comprises only one kind of strongly corrugated layer. For clarity, it has been

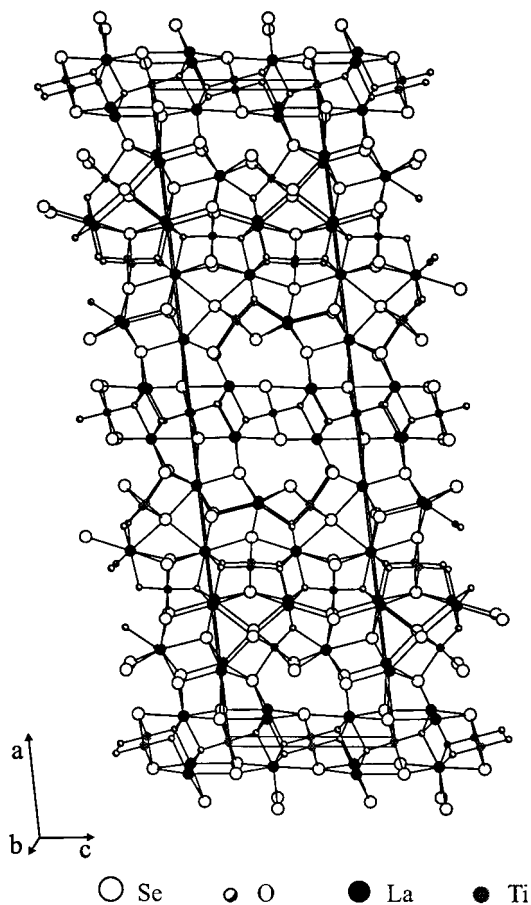


FIG. 3. View of the unit cell of La₆Ti₃O₅Se₉ along the *c*-axis.

decomposed into three parts (Fig. 5), a straight part (a), a folded part (b), and a capped part (c). The straight part is similar to the type-1 slab described above. It is constructed from the close packing of the two bicapped trigonal prisms and the two TiO₂Se₄ octahedra. The folded part results from the packing of La(2)O₃Se₆ and La(4)O₄Se₆ polyhedra. The square antiprism centered by atom La(4) shares a common triangular face with two near trigonal prisms centered by La(2) atoms. Therefore, the folding angle is defined by the Se(1)–La(4)–Se(1) angle of 119.19(4)°. The fold of the layer is capped by a [LaTiO_{2/2}Se_{9/2}] motif resulting from the face sharing of the La(5)O₂Se₅ antiprism and the Ti(2)OSe₅ distorted octahedron. The borders of the layer are infinite corrugated chains of alternating La–Se atoms. The layers thus constituted stack along the *b*-axis and are connected to one another by La–Se bonds.

DISCUSSION

Since there are no anion–anion interactions in La₄Ti₂O₄Se₅ or La₆Ti₃O₅Se₉, the formal charges on Se and O are – II. Given that La invariably has a formal oxidation state

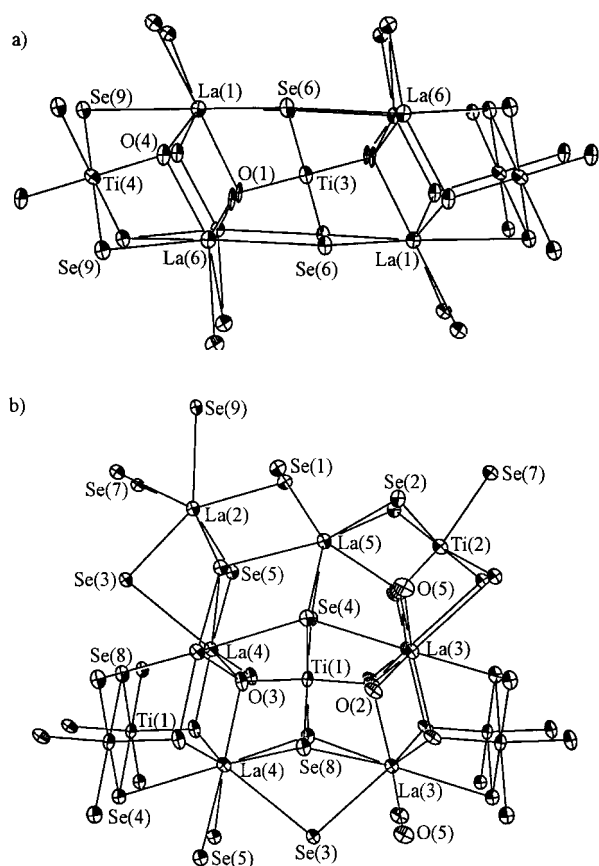


FIG. 4. Fragment of the two types of slabs in $\text{La}_6\text{Ti}_3\text{O}_5\text{Se}_9$: (a) condensed type-1 slab and (b) extended layer, containing the condensed type-2 slab. Displacement ellipsoids are drawn at the 90% probability level.

of + III in oxides and chalcogenides, all Ti cations must be Ti^{3+} in $\text{La}_4\text{Ti}_2\text{O}_4\text{Se}_5$ for charge to be balanced. This is the first example of a rare-earth titanium oxychalcogenide containing only Ti^{3+} cations. To balance charge in $\text{La}_6\text{Ti}_3\text{O}_5\text{Se}_9$, two-thirds of the Ti cations must be Ti^{3+} and one-third must be Ti^{4+} . The question is whether these differently charged cations are ordered on specific sites or disordered over all Ti sites. Recently several mixed-valence rare-earth titanium oxychalcogenides have been reported (2, 5, 6, 11), but in none was a precise assignment of Ti^{3+} and Ti^{4+} sites made. Such assignments are made difficult by the tendency of both Ti^{3+} and Ti^{4+} to be in an octahedral environment and by the small difference in their ionic radii (12). However, Ti^{4+} , being a d^0 ion, often shows distortions from a regular octahedral environment that arise from the second-order Jahn–Teller effect (13). Thus, most Ti^{4+} oxides exhibit distorted TiO_6 octahedra, with two sets of Ti–O bonds, strong ones about 1.75 Å in length and weak ones about 2.20 Å in length. In contrast, most Ti^{3+} oxides exhibit regular TiO_6 octahedra with average Ti–O bonds about 2 Å in length (14, 15).

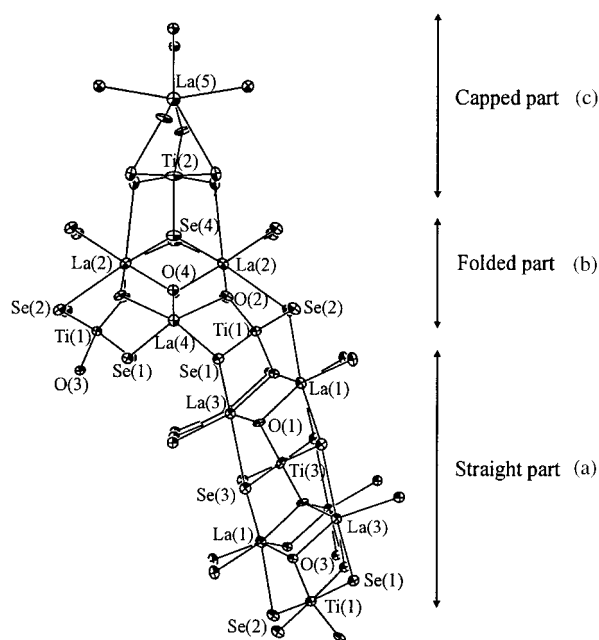


FIG. 5. Fragment of the corrugated layer in $\text{La}_4\text{Ti}_2\text{O}_4\text{Se}_5$: (a) straight part, (b) folded part, and (c) capped part. Displacement ellipsoids are drawn at the 90% probability level.

In titanium oxychalcogenides, the $\text{TiO}_x\text{Q}_{6-x}$ octahedra are inherently distorted and this complicates the use of such distortions to distinguish between Ti^{3+} and Ti^{4+} . Nevertheless, we believe we can make this distinction in $\text{La}_6\text{Ti}_3\text{O}_5\text{Se}_9$. To do this we split the local environment about each Ti cation into a Ti–O and a Ti–Se part. Consider first the two titanium oxychalcogenides $\text{La}_6\text{Ti}_2\text{O}_5\text{S}_8$ (1), which contains only Ti^{4+} cations, and the present $\text{La}_4\text{Ti}_2\text{O}_4\text{Se}_5$, which contains only Ti^{3+} cations. $\text{La}_6\text{Ti}_2\text{O}_5\text{S}_8$ (1) contains two crystallographically independent Ti^{4+} cations, both of which exhibit a distorted octahedral environment, with a short Ti–O distance of about 1.83 Å and a long Ti–S distance close to 2.70 Å. This suggests a 5 + 1 coordination (16) and the drift of Ti^{4+} toward one apex of the octahedron. $\text{La}_4\text{Ti}_2\text{O}_4\text{Se}_5$ contains three crystallographically independent Ti^{3+} cations, all in octahedral environments. The Ti–O distances fall in the narrow range 1.925(11) to 1.948(6) Å. The Ti–Se distances range from 2.529(3) to 2.8044(12) Å. The $\text{Ti}(3)\text{O}_2\text{Se}_4$ octahedron shows angles close to 90° whereas the $\text{Ti}(1)\text{O}_2\text{Se}_4$ and $\text{Ti}(2)\text{OSe}_5$ octahedra are less regular. Nevertheless, both $\text{Ti}(2)$ and $\text{Ti}(3)$ reside in an equatorial plane of four Se atoms, with angles close to 90°. The two *trans* O in the $\text{Ti}(1)\text{O}_2\text{Se}_4$ octahedron are almost equidistant from the equatorial plane. The *trans* Ti–Se bond in the $\text{Ti}(2)\text{OSe}_5$ octahedron is 2.529(3) Å in length, within the range of Ti–Se distances of 2.506(1) to 2.686(7) Å in TiTi_5Se_8 (17), the only Ti^{3+} selenide structure reported in the literature. Consequently, the $\text{Ti}(2)$ cation shows no tendency toward a square-pyramidal environment and each of

the three independent Ti³⁺ cations can be considered to reside in the equatorial plane of its octahedron.

We now turn to the disposition of the two independent Ti³⁺ cations and the one Ti⁴⁺ cation among the Ti sites in the asymmetric unit of the structure of La₆Ti₃O₅Se₉. The Ti(3)O₂Se₄ and Ti(4)O₂Se₄ octahedra are very regular with all angles very close to 90°, whereas the Ti(1)O₂Se₄ octahedron is slightly distorted with angles ranging from 85.14(2) to 95.61(6)° (Table 5). For Ti(1), Ti(3), and Ti(4) the Ti–O and Ti–Se distances are in narrow ranges and are comparable to the distances observed in La₄Ti₂O₄Se₅. On the other hand, the Ti(2)OSe₅ octahedron is markedly distorted. Several angles are around 83° and the Ti–O distance of 1.783(7) Å is similar to numerous short Ti–O distances observed for Ti⁴⁺ oxides. Moreover, the Ti(2) atom is displaced from the equatorial plane toward the O apex, a typical manifestation of the second-order Jahn–Teller distortion around a *d*⁰ cation. The details above lead us to conclude that Ti(1), Ti(3), and Ti(4) are Ti³⁺ sites and Ti(2) is a Ti⁴⁺ site. This assignment results in eight Ti³⁺ cations and four Ti⁴⁺ cations in the asymmetric unit and in charge balance. It is interesting that the Ti³⁺ cations reside in the compact type-1 and type-2 slabs previously described whereas the Ti⁴⁺ cations reside in the extended slabs.

ACKNOWLEDGMENTS

This research was supported by the U.S. National Science Foundation under Grant DMR 97-09351. This work made use of Central Facilities supported by the MRSEC program of the National Science Foundation

(DMR-9632472) at the Materials Research Center of Northwestern University.

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