Synthesis and crystal structure of a new oxychalcogenide La$_5$Ti$_{\sim3.25}$Zr$_{\sim0.25}$S$_5$O$_{9.25}$

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Abstract

A new phase in the quinary system La/Ti/Zr/S/O was obtained from a mixture of La$_2$O$_3$, La$_2$S$_3$, ZrO$_2$, and TiO$_2$ by a solid-state reaction at 1273 K in a sealed fused-silica tube. The structure of this new phase, La$_5$Ti$_{\sim3.25}$Zr$_{\sim0.25}$S$_5$O$_{9.25}$, was solved by single-crystal X-ray diffraction, with $R_{(obs)} = 3.37\%$ for 2764 reflections ($I > 3\sigma(I)$) and 125 variables. This compound crystallizes with four formula units in the monoclinic space group $C2/m$ with lattice constants $a = 18.401(2)$ Å, $b = 3.9032(3)$ Å, $c = 21.944(3)$ Å, and $\beta = 106.100(8)°$. The structure can be viewed as a 2D building constituted from two-atom-thick slabs of rock salt type (= sulfide part) which are interleaved with double-octahedral chains centered on titanium/zirconium atoms (mixed Ti/Zr sites) and drawing a zigzag arrangement (= oxide part). In addition, EDXS analyses show that a solid solution Ti/Zr exists with a general formulation La$_5$Ti$_{3.5-x}$Zr$_x$S$_5$O$_{9.25}$ (where $0.1 \leqslant x \leqslant 0.5$).
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Keywords: Crystal structure; Lanthanum; Titanium; Zirconium; Oxysulfide; Mixed sites

1. Introduction

Compounds of the new family, RE_2Ti$_2$S$_2$O$_5$ (with RE = Pr, Nd, and Sm), have been recently synthesized and characterized [1,2]. They were described as a novel series of defective Ruddlesden–Popper (R–P) phases. Later on, these compounds were successfully prepared with some other RE elements (i.e. Y, Gd, Tb, Dy, Ho, Er) [3], but so far no La- and Ce-derivatives could be synthesized. A possible explanation for these exceptions is a size-adaptation between the [LaS] or [CeS] layer facing the [TiO] layer. One possibility to compensate the larger size of the [LaS] or [CeS] part was then to adjust the [TiO] part by considering another transition metal with a larger size than Ti, for example Zr, at least in a partial substitution with Ti.

Interest for such research was stimulated after Sm$_2$Ti$_2$S$_2$O$_5$ was recognized as a stable photocatalyst for water oxidation and reduction under visible light irradiation [4]; this compound shows a band gap of ~2.1 eV^3. As the chemistry of Zr and of Ti is quite comparable, and also mainly because titanium oxides as well as zirconium oxides are known to be effective photocatalysts, Zr was chosen as a substitute for Ti. Thus, attempts to get the hypothetical La$_2$(Ti/Zr)$_2$S$_2$O$_5$ phase were undertaken. This study led us to discover a new solid solution, La$_5$Ti$_{3.5-x}$Zr$_x$S$_5$O$_{9.25}$ (where $0.1 \leqslant x \leqslant 0.5$) for which the crystal structure has been determined in the case of $x = 0.25$.

2. Experimental section

2.1. Synthesis and chemical analysis

A mixture of La$_2$O$_3$, La$_2$S$_3$, ZrO$_2$, and TiO$_2$, in the molar ratio 1/3:2/3:1:1, respectively, corresponding to

Table 1
EDXS chemical analyses

Crystal	%La	%Ti	%Zr	%(Ti) + %(Zr)	%S
1	36.5 (2)	22.6 (6)	2.9 (5)	25.6	37.9 (2)
2	36.9 (3)	23.7 (4)	2.2 (4)	25.9	37.2 (3)
3	36.4 (6)	21.9 (6)	4.0 (2)	25.9	37.7 (4)
4	36.9 (3)	22.8 (4)	2.5 (1)	25.3	37.8 (5)
5	36.8 (4)	24.5 (7)	0.8 (2)	25.3	37.9 (3)
Average	36.7 (3)	23.1 (1.0)	2.5(1.2)	25.6 (3)	37.7 (3)

Values are atomic percentages. The standard deviations on the average values do not take into account the individual ESD on each averaged values.

the starting stoichiometry $La_2TiZrS_2O_5$, was loaded into a quartz tube and sealed under vacuum ($p \approx 2 \times 10^{-2}$ Torr). The reaction tube was placed in a computer-controlled furnace and progressively heated to 1273 K, maintained at this temperature during 1 week, and then air-quenched. The reaction product was ground and re-heated to 1273 K for another week with a small amount of iodine (~ 3 mg/cm^3) to favor crystallization. Black needle-shaped crystals were obtained together with a powdered product.

Chemical analyses were performed using an EDXS-equipped scanning electron microscope. Five crystals were included in epoxy (araldite type) and then polished. The systematic use of external standards for all the analyzed elements leads to an accurate quantitative analysis especially on polished sections. Table 1 gives the results for all elements except oxygen. The analyses confirm the presence of Zr in all samples with a distribution of the Ti/Zr ratio. It is clear from these results that the dispersion of the Ti and Zr contents overcomes the mean standard deviation of the chemical analysis, which suggests the existence of a solid solution $Ti_{3.5-x}$–Zr_x ($0.1 \leqslant x \leqslant 0.5$). The averaged atomic percentages are: La 36.7(3), Ti + Zr 25.6(3), and S 37.7(3). These values agree well with those calculated from the structural formulation: La 37.04, Ti + Zr 25.92, and S 37.04.

Besides this new phase, a chemical analysis done on other crystals of the crystalline powder revealed, in particular, the presence of a new phase with an experimental composition close to $La_2Zr_2S_2O_5$.

2.2. Single crystal data collection

Numerous crystals were tested for quality (intensity and shape of the spots) with a Nonius Kappa CCD diffractometer using Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å). A needle-shaped crystal delimited by faces {100}, {010}, {001}, and {40-3}, respectively, was used for data collection. The symmetry was monoclinic with unit cell parameters: $a = 18.401(2)$ Å, $b = 3.9032(3)$ Å, $c = 21.944(3)$ Å, and $\beta = 106.100(8)^\circ$. Operating condi-

Table 2
Crystallographic data for $La_5Ti_{\sim3.25}Zr_{\sim0.25}S_5O_{9.25}$

Formula	$La_5Ti_{\sim3.25}Zr_{\sim0.25}S_5O_{9.25}$
Formula weight (g mol^{-1})	4724.51
Color	Black
Dimensions (mm)	$0.016 \times 0.144 \times 0.028 \times 0.016$ bounded by faces {100}, {010}, {001}, {40−3}
Symmetry	Monoclinic
Space group	$C 2/m$ (No. 12)
Z	4
a (Å)	18.401 (2)
b (Å)	3.9032 (3)
c (Å)	21.944 (3)
β (°)	106.100 (8)
V (Å^3)	1514.3 (3)
Density $\rho_{calcc.}$ (g cm^{-3})	5.179 (1)
Absorption coeff. μ (mm^{-1})	16.28
Recording conditions	
Temperature (K)	293
Diffractometer	Kappa CCD-NONIUS
Wavelength λ (Å)	0.71069 (Mo-K_α)
θ range for data collection (°)	5.02–35.00
h,k,l ranges	$-29 \leqslant h \leqslant 29$; $-6 \leqslant k \leqslant 6$; $-35 \leqslant l \leqslant 35$
Reflections collected	21,759
Independent reflections	
($I \geqslant 3\sigma(I)$) obs; all–$R_{[int]}$ obs; all	2764; 3714−0.042; 0.048
Absorption corrections	Gaussian method based on the shape of the crystal
Trans. coeff. Min–Max	0.324–0.812
Refinement	
No. of refined parameters	125
R indices [2764, $I > 3\sigma(I)$]	$R_{obs} = 0.0337$; $Rw_{obs} = 0.0464$
R indices [3714, all data]	$R_{all} = 0.0580$; $Rw_{all} = 0.0480$
Largest peak and hole(e Å^{-3})	+ 4.46; −3.98

tions and X-ray crystallographic details are given in Table 2.

3. Structure determination

The crystal structure was solved by means of direct methods using the SHELXTL software package [5]. Initial analysis of the diffraction data (21,759 reflections) with the use of the program XPREP revealed three possible space groups: *C2*, *Cm*, and *C2/m*. The latter resulted in the lowest figure of merit.

Refinement was conducted with the JANA2000 program [6] starting with the *C2/m* space group. It was not possible to get a satisfying solution by following the normal process, i.e., refinement and subsequent Fourier differences maps; the *R*-value remained above 20%. At this stage, this difficulty could be attributed to the presence of mixed Ti/Zr sites. We then proceeded with the *Cm* space group; an acceptable solution was found but it appeared that most of the atoms could be

associated into pairs through a common "central point". Thus we took this "center" as the origin (0,0,0), which brought back to the centrosymmetric situation, i.e. to the $C2/m$ space group. Thereafter, refinement converged to the R-value of 0.049 for the following stoichiometry $La_5Ti_{3.5}S_5O_9$, but some problems were still unresolved: (i) a negative U_{eq} value for one Ti atom (= Ti2); (ii) a large U_{eq} value for another Ti (= Ti4); (iii) presence of several large residual peaks. Concerning Ti2, we have considered a mixed Ti/Zr site; a full occupancy of the site was fixed through the $1-x/x$ relation and both coordinates and displacement parameters were constrained to be identical for the two atomic species. This led to the percentages of 84% for Ti2 and then 16% for Zr2. For Ti4, the same constraints as above were applied. In addition, the presence of a residual peak close to Ti4 led us to take into account a third atom (Ti5) that was located on a general position ($8j$: x,y,z) even if such a position gives rise to a too short Ti5–Ti5 contact (~1.2 Å). Indeed, as occupancy of this Ti5-site is much less than 50%, a simultaneous presence of two Ti5 atoms on the equivalent (closed) positions can be discarded from a statistical point of view. Of course, the occupancy in all these three sites, namely Ti4, Zr4, and Ti5, is refined so that the sum corresponds to a fully occupied $4i$ site (= four atoms in the cell),

coupled with the fact that occupancy for Ti5 cannot exceed 50%. This gave the resulting values for the three sites: Ti4 = 66.2% ($4i$ site), Zr4 = 8.8% ($4i$ site), and Ti5 = 12.5% ($8j$ site). A final problem arose with the O10 position. The O10 atom is coordinated to Ti5 considering the normal bond length of 1.856 Å, which implies, as for Ti5, an equivalent statistical occupancy, that is to say 25% ($4i$ site). Even if the U_{iso} value is found slightly negative for O10 (= −0.009(2) Å^2), this solution is the most appropriate one (converging on the lowest R value: $R_{obs} = 0.0337$) for many reasons. First, the doubling of the amount of O10 (= 50%) would increase both the U_{eq} value of Ti5 (= 0.050(5) Å^2) and the R factor ($R_{obs} = 0.0346$). Secondly, the charge equilibrium is in agreement with results from the bond valence calculations as reported subsequently in the discussion section (vide infra). Therefore, the chemical composition deduced from the last stage of refinement keeping a quarter-filled O10 position is $La_5Ti_{\sim 3.25}Zr_{\sim 0.25}S_5O_{9.25}$. The final refinement, with all atoms (except oxygen) refined anisotropically, converged to the R-values: $R_{obs} = 0.0337$ for 2764 reflections ($I > 3\sigma(I)$) and $R_{all} = 0.0580$ for all the 3714 reflections ($R_{wobs} = 0.0464$ and $R_{wall} = 0.0480$), with 125 variables. Fractional coordinates and equivalent atomic displacement parameters are given in Table 3.

Table 3
Atomic coordinates and equivalent isotropic displacement parameters for $La_5Ti_{\sim 3.25}Zr_{\sim 0.25}S_5O_{9.25}$

Atom	Site	x	y	z	$U_{(eq, iso^*)}$ (Å^2)	Occupancy (%)
La1	$4i$	0.19514(2)	0	0.05481(2)	0.00686(11)	100
La2	$4i$	0.03741(2)	0.5	0.14692(2)	0.00751(12)	100
La3	$4i$	0.28556(3)	0	0.25294(2)	0.01165(13)	100
La4	$4i$	0.11014(3)	0.5	0.34814(2)	0.01021(12)	100
La5	$4i$	0.34081(3)	0	0.45423(2)	0.01168(13)	100
Zr2	$4i$	0.34096(6)	0.5	0.13663(5)	0.0083(3)	16.0 (−)
Zr4	$4i$	0.51800(10)	0.5	0.43593(8)	0.0139(6)	8.8 (−)
Ti1	$2a$	0	0	0	0.0140(6)	100
Ti2	$4i$	0.34096(6)	0.5	0.13663(5)	0.0083(3)	84.0 (8)
Ti3	$4i$	0.47024(7)	0.5	0.25501(6)	0.0074(3)	100
Ti4	$4i$	0.51800(10)	0.5	0.43593(8)	0.0139(6)	66.2 (8)
Ti5	$8j$	0.4749(4)	0.352(2)	0.4042(3)	0.005(2)	12.5 (−)
S1	$4i$	0.41866(10)	0	0.02398(9)	0.0099(5)	100
S2	$4i$	0.20335(10)	0.5	0.15793(9)	0.0090(5)	100
S3	$4i$	0.11608(11)	0	0.24875(9)	0.0114(5)	100
S4	$4i$	0.27264(12)	0.5	0.35056(9)	0.0155(6)	100
S5	$4i$	0.17784(11)	0	0.44889(8)	0.0114(5)	100
O1	$4i$	0.0616(3)	0	0.0844(2)	0.0102(10)	100
O2	$4i$	0.2807(3)	0.5	0.0524(2)	0.0088(9)	100
O3	$4i$	0.3242(3)	0	0.1441(2)	0.0085(9)	100
O4	$4i$	0.4473(3)	0.5	0.1590(2)	0.0119(10)	100
O5	$4i$	0.3659(3)	0.5	0.2397(2)	0.0121(10)	100
O6	$4i$	0.4881(3)	0	0.2522(3)	0.0181(12)	100
O7	$4i$	0.5197(3)	0.5	0.3439(3)	0.0188(12)	100
O8	$4i$	0.5417(4)	0	0.4403(3)	0.0253(14)	100
O9	$4i$	0.4300(4)	0.5	0.4622(3)	0.0297(15)	100
O10	$4i$	0.4148(8)	0	0.3602(6)	−0.009(2)	25 (−)
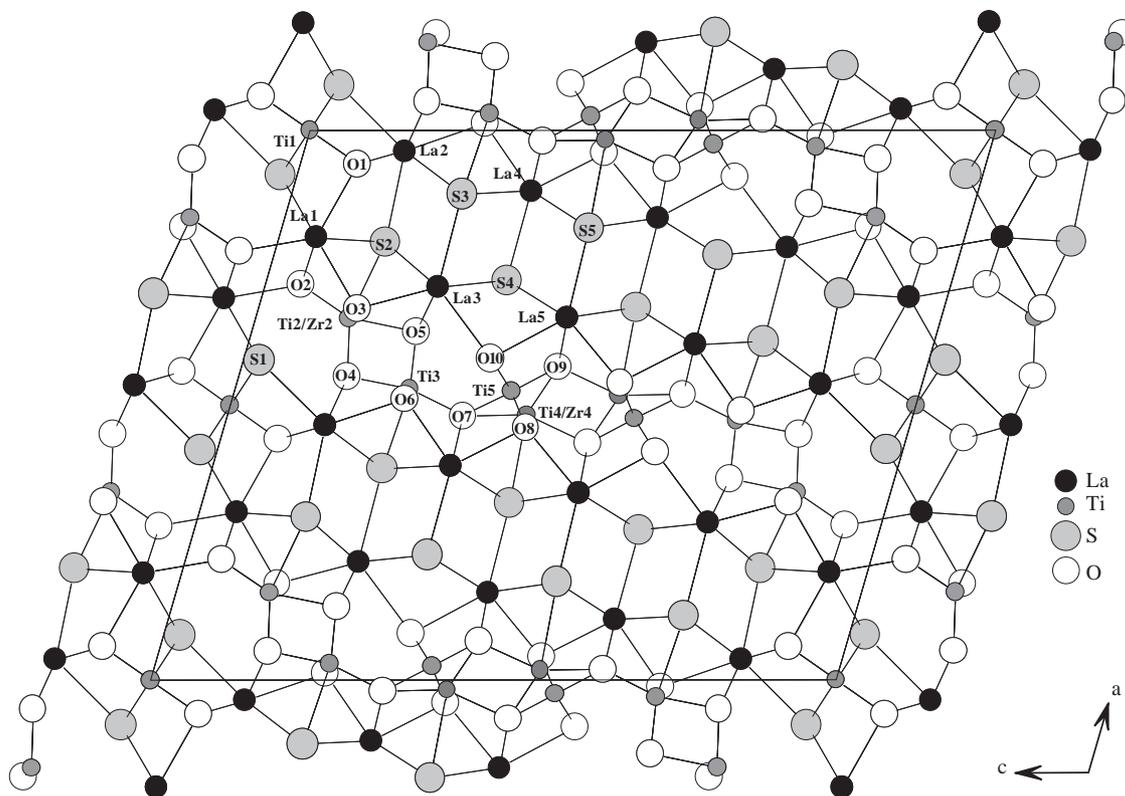
Fig. 1. Projection of the structure of $La_5Ti_{\sim3.25}Zr_{\sim0.25}S_5O_{9.25}$ onto the (a,c) plane.

4. Structure description

Fig. 1 shows a projection of $La_5Ti_{\sim3.25}Zr_{\sim0.25}S_5O_{9.25}$ along [010]. The structure can be viewed as a "two-dimensional solid" built up from a two-atom-thick slabs structurally similar to rock salt (= sulfide part) interleaved with double-octahedral chains centered on titanium/zirconium atoms and drawing a zigzag arrangement (= oxide part). Interconnection between both parts is established through La–O and Ti–S ionocovalent bonds but are not drawn on this figure for clarity. The rock-salt layer, which extends perpendicularly to the a-direction, is interrupted at every tenth La-atom by a single inserted octahedron (= TiS_4O_2) centered on a Ti atom (Ti1).

The La atoms in $La_5Ti_{\sim3.25}Zr_{\sim0.25}S_5O_{9.25}$ are eight- and nine-coordinated, in the form of bicapped- (= LaS_5O_3 for La3 and La5 atoms) and tricapped-trigonal prisms (= LaS_4O_5 for La1 and La2 atoms, and LaS_5O_4 for La4), respectively. A view of the environments of these five La atoms is given in Fig. 2a. Three of the five unique Ti atoms are located in distorted $TiSO_5$ octahedra (Ti2, Ti3, and Ti4), one Ti atom is found in a regular TiS_4O_2 octahedron (Ti1), and the fifth Ti atom (Ti5) is tetrahedrally coordinated by four oxygen atoms. Coordination polyhedra are shown in Fig. 2b. Table 4 contains the interatomic distances for all polyhedra centered around metal atoms (La, Ti, Zr).

The rock salt layer ("sulfide slab") is built up from the association of contiguous $[La_{10}S_8]$ segments, interconnected by a $[TiS_4O_2]$ octahedron. These planes are separated from each other by a layer ("oxide slab") of double edge sharing Ti-octahedra in a zigzag type-linking, as clearly shown in Fig. 3a. This strongly resembles the structure of $La_4Ti_3S_4O_8$ [7]. Indeed, the architecture of $La_4Ti_3S_4O_8$ (see Fig. 3b) can also be described as an alternate stacking of sulfide [LaS] and oxide [TiOS] layers, both layers exhibiting similar structural characteristics with those in $La_5Ti_{\sim3.25}Zr_{\sim0.25}S_5O_{9.25}$. In $La_4Ti_3S_4O_8$, the sulfide layer [LaS] (of rock salt type) is also built from adjacent segments $[La_8S_6]$ (shorter than in the Ti/Zr derivative) that are interconnected by the same $[TiS_4O_2]$ octahedra as observed in the Ti/Zr derivative. Consequently, the oxide counter-layer is shortened, i.e. it contains five Ti-centered polyhedra instead of six as found in the $La_5Ti_{\sim3.25}Zr_{\sim0.25}S_5O_{9.25}$ structure; to get this, two double edge-shared octahedra are interconnected by a single Ti-polyhedron (namely, a tetrahedral $[TiO_4]$ entity). Such modular description highlights the close relationship between structures of $La_5Ti_{\sim3.25}Zr_{\sim0.25}S_5O_{9.25}$ and $La_4Ti_3S_4O_8$ [7].

Special attention to the complex situation of the mixed Ti4/Zr4/Ti5 site in association with the O10 one is needed. Apart from the fact that the O10 atom is at distances of 2.845 and 2.77 Å from La3 and La5, which
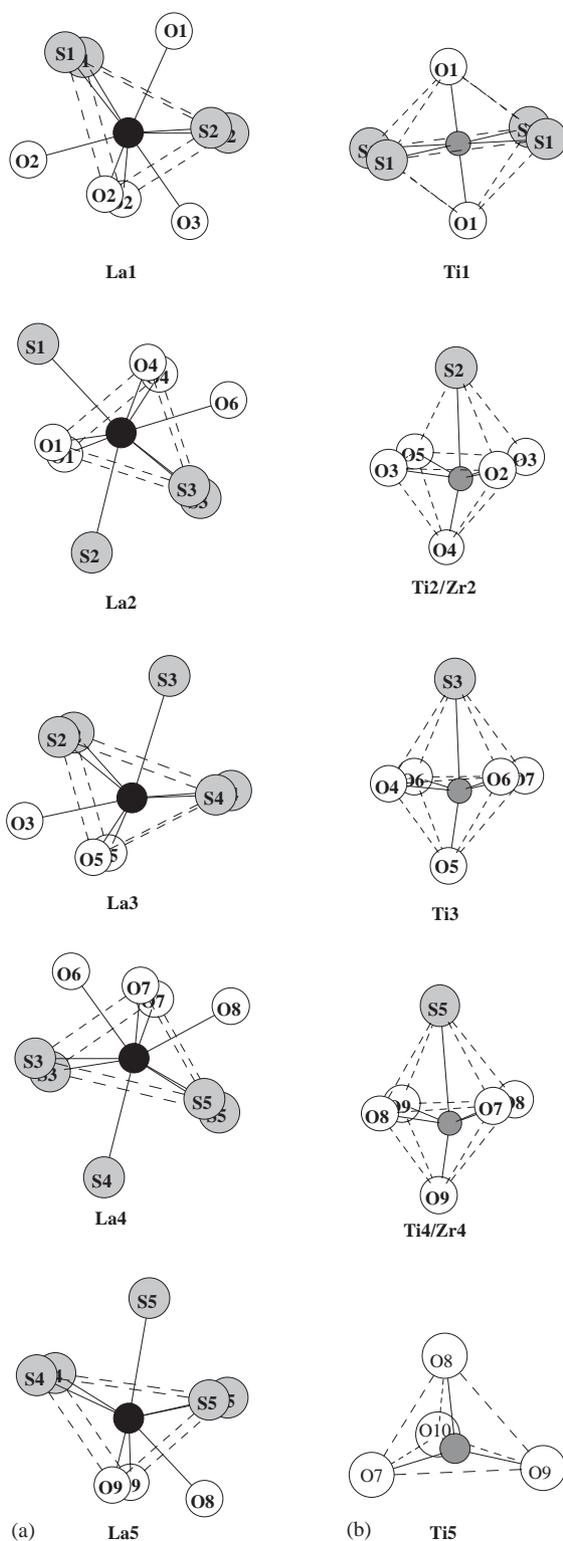
Fig. 2. Detailed environments around La atoms (a) and around Ti atoms (b).

in terms of exchanged valence gives a value of 0.04 and 0.05, respectively (see Table 4), O10 is above all closely bonded to Ti5 (Ti5–O10 = 1.856 Å), which led us to constrain the amount of O10 and Ti5 to be equal. Ti5 is

surrounded by six oxygen atoms, with $2 \times O8$ and $2 \times O10$ atoms in the basal plane and O7 with O9 atoms as apices. If Ti5 was located at the center of this octahedron (site 4i: x,0,z), the resulting Ti5–O7 and Ti5–O9 apical distances would have been too short. In fact, Ti5 is moved from this center, along the b-direction, towards a general position (i.e., site 8j: x,y,z, and x,$-y$,z). This reduces the strain for the two apical Ti5–O bondings, changing the octahedral coordination for a tetrahedral one (see Fig. 4) with four similar Ti5–O distances (see Table 4). This description is consistent with the following observations: in the same unit cell, the [Ti1O$_2$S$_4$] octahedron (centered at 0,0,0) is oriented in the same direction with the basal plane of four S atoms parallel to the b-axis. Thus, when the octahedron surrounding Ti5 contains only O atoms, the repeat distance is too large for normal Ti–O distances thus requiring the displacement of the central Ti5 atom. This is parallel to the geometrical constraints and Ti disorder seen in La$_4$Ti$_3$S$_4$O$_8$.

5. Discussion and concluding remarks

We have solved the structure of the first RE/transition metal oxychalcogenide containing Zr atoms. This study clearly establishes a partial Ti–Zr substitution in La$_5$Ti$_{\sim 3.25}$Zr$_{\sim 0.25}$S$_5$O$_{9.25}$. EDXS analyses on many crystals indicated an inhomogeneous range of Zr composition (from 0.8 to 4 at%). This means that we are far from the 1 Ti/1 Zr ratio as introduced at the beginning. The structure type of La$_5$Ti$_{\sim 3.25}$Zr$_{\sim 0.25}$S$_5$O$_{9.25}$ seems to indicate that the Ti/Zr substitution is only occurring on two Ti-positions (2 sites 4i giving 8 Ti atoms per cell), corresponding to a more general composition La$_5$Ti$_{1.5}$(Ti$_{1-y}$Zr$_y$)$_2$S$_5$O$_{9.25}$ with $0.05 \leqslant y \leqslant 0.25$.

As usual, the following oxidation states $RE(+III)$, $O(-II)$ and $X(-II)$ can be assigned. For the title compound, this implies a mixed valence state for Ti to obtain a charge equilibrium, i.e. Ti($+III$) and Ti($+IV$) in the 1:6 proportion, respectively. To confirm this assumption, and also to identify which Ti atoms are at the $+III$ or $+IV$ oxidation states, the valences of Ti, Zr and La atoms were calculated using the bond valence equation:

$V_i = \Sigma \exp[(R_{ij}^{\circ} - d_{ij})/b]$, where $b = 0.37$ is a universal constant, d_{ij} is the interatomic distance (in Å) between atoms i and j, and R_{ij}° is the bond valence parameter depending on the chemical nature of both elements i and j [8]. Calculated values for the La atoms (from La1 to La5) are consistent with the expected oxidation state $+III$ (see Table 4). Concerning the Ti (/Zr) atoms, only the pure Ti1-site (i.e., Ti-oct. within the sulfide part) can be undoubtedly associated with the oxidation state $+III$, while the two other pure Ti-sites (i.e., Ti3 and Ti5)

Table 4
Selected interatomic distances and bond valence values for $La_5Ti_{\sim3.25}Zr_{\sim0.25}S_5O_{9.25}$

Atom1/Atom2		s.o.*	Distance (Å)	Valence	Atom1/Atom2		s.o.*	Distance (Å)	Valence
La1	2 × S1	#2; #3	3.0291 (12)	0.35	Ti1	4 × S1	#2; #3; #5; #7	2.6005 (13)	0.38
La1	2 × S2	#1; #4	2.960 (2)	0.42	Ti1	2 × O1	#1; #12	1.884 (5)	0.78
La1	O1	#1	2.710 (6)	0.23				Σv = 3.08	
La1	2 × O2	#1; #4	2.517 (3)	0.39					
La1	O2	#3	2.514 (5)	0.40					Ti2/Zr2
La1	O3	#1	2.627 (4)	0.29	Ti2/Zr2	S2	#1	2.700 (2)	0.29/0.46
			Σv = 3.24		Ti2/Zr2	O2	#1	1.873(4)	0.85/1.19
					Ti2/Zr2	2 × O3	#6; #6	1.9896(11)	0.62/0.87
La2	S1	#5	2.964 (2)	0.42	Ti2/Zr2	O4	#1	1.881 (5)	0.84/1.16
La2	S2	#1	2.995 (2)	0.38	Ti2/Zr2	O5	#1	2.179 (5)	0.37/0.52
La2	2 × S3	#1; #6	3.0172 (13)	0.36				Σv = 3.59/5.07	
La2	2 × O1	#1; #6	2.496 (3)	0.42					
La2	2 × O4	#5; #7	2.621 (4)	0.30	Ti3	S3	#3	2.725 (2)	0.27
La2	O6	#5	2.706 (7)	0.24	Ti3	O4	#1	2.030 (5)	0.56
			Σv = 3.20		Ti3	O5	#1	1.855 (6)	0.90
					Ti3	2 × O6	#1; #6	1.9830 (12)	0.64
La3	2 × S2	#1; #4	2.9486 (13)	0.43	Ti3	O7	#1	1.910 (6)	0.77
La3	S3	#1	3.094 (2)	0.29				Σv = 3.78	
La3	2 × S4	#1; #4	2.956 (2)	0.43					
La3	O3	#1	2.674 (5)	0.26					Ti4/Zr4
La3	2 × O5	#1; #4	2.514 (4)	0.40	Ti4/Zr4	S5	#3	2.875 (2)	0.18/0.28
La3	O10	#1	2.845 (12)	0.04	Ti4/Zr4	O7	#1	2.029 (6)	0.56/0.78
			Σv = 3.11		Ti4/Zr4	2 × O8	#1;#6	1.9961 (14)	0.61/0.85
					Ti4/Zr4	O9	#1	1.863 (8)	0.88/1.22
La4	2 × S3	#1; #6	2.951 (2)	0.43	Ti4/Zr4	O9	#11	2.174 (7)	0.38/0.53
La4	S4	#1	2.976 (2)	0.40				Σv = 3.22/4.51	
La4	2 × S5	#1; #6	2.9531 (13)	0.43					
La4	O6	#5	2.617 (5)	0.30	Ti5	O7	#1	1.837 (10)	0.94
La4	2 × O7	#5; #7	2.550 (4)	0.36	Ti5	O8	#1	1.866 (8)	0.87
La4	O8	#5	2.663 (7)	0.27	Ti5	O9	#1	1.794 (11)	1.06
			Σv = 3.41		Ti5	O10	#1	1.856 (10)	0.89
								Σv = 3.76	
La5	2 × S4	#1; #4	2.9958 (13)	0.38					
La5	S5	#1	2.968 (2)	0.41					
La5	2 × S5	#8; #9	2.975 (2)	0.40					
La5	O8	#10	2.694 (6)	0.24					
La5	2 × O9	#1; #4	2.525 (5)	0.39					
La5	O10	#1	2.77 (2)	0.05					
			Σv = 3.04						

*s.o.: symmetry code: #1: x, y, z; #2: $1/2-x, -1/2-y, -z$; #3: $1/2-x, 1/2-y, -z$; #4: $-x, -1-y, -z$; #5: $-1/2-x, 1/2-y, -z$; #6: $-x, 1-y, -z$; #7: $-1/2-x, -1/2-y, -z$; #8: $1/2-x, -1/2-y, 1-z$; #9: $1/2-x, 1/2-y, 1-z$; #10: $1-x, -y, 1-z$; #11: $1-x, 1-y, 1-z$; #12: $-x, -y, -z$.
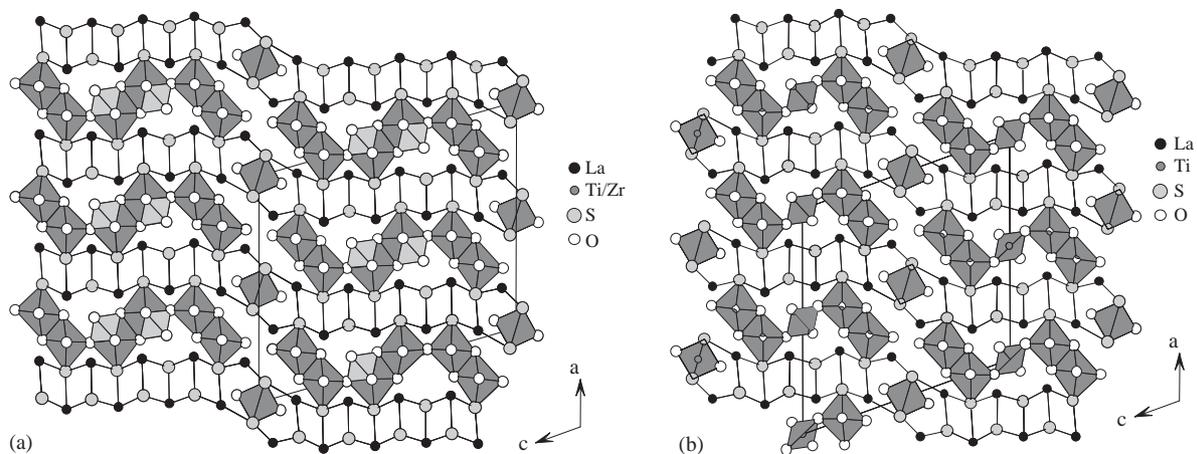

Fig. 3. Network of edge- and corner-sharing TiS_xO_y polyhedrons (hatched) within the $La_5Ti_{\sim3.25}Zr_{\sim0.25}S_5O_{9.25}$ structure (a), and within the $La_4Ti_3S_4O_8$ structure (b); La–O bondings are omitted for clarity.
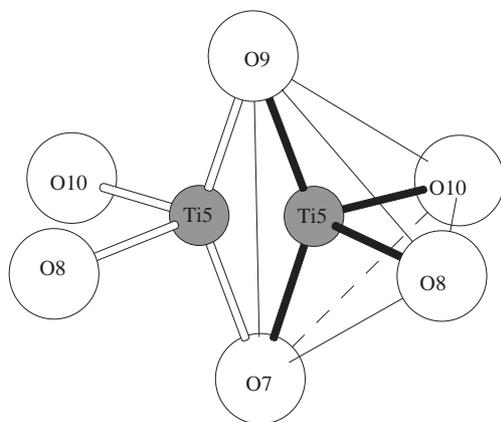
Fig. 4. Octahedra built of oxygen atoms surrounding the split position of Ti5 leading to a tetrahedral coordination for Ti5.

are assigned to be $+IV$ (see Table 4). This agrees well with the fact that the highest oxidation state ($= +IV$) is observed for the Ti atoms that are principally surrounded with oxygen atoms (five oxygen atoms and one sulfur around Ti3, and four oxygen atoms around Ti5). Concerning the two mixed Ti2/Zr2 and Ti4/Zr4 sites, both atoms that have different atomic radii share the same atomic coordinates ($=$ averaged position). This implies that bond valence calculations will give an overestimated value for the atom having the largest radius (Zr), but an underestimated one for the smaller (Ti). Bond valence calculations for Ti2 and Ti4 give values well above 3 which suggests a $+IV$ oxidation state (see Table 4). Consequently, Ti1 seems to be the only Ti atom at the $+III$ oxidation state, all the others being Ti($+IV$). This corresponds exactly to a Ti($+III$)/ Ti($+IV$) proportion of 1/6 as we were expecting from the charge balance.

The presence of a mixed valence for Ti is in good agreement with the black color observed for the crystals of this new phase. Unfortunately, this opacity precludes our compound $La_5Ti_{\sim3.25}Zr_{\sim0.25}S_5O_{9.25}$ from having any interesting photocatalytic properties, and such study was not undertaken.

"Further details of the crystal structure investigation (CIF file) can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), e-mail:crysdata@fiz.karlsruhe.de, on quoting the depository number CSD-391309."

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