Synthesis and Crystal Structure of a New Oxysulfide $Gd_{6+x}Ti_{4-x}S_{10-y}O_{6+y}$ (where $x \sim 0.04$ and $y \sim 0.27$)

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Dedicated to Professor Kurt O. Klepp on the occasion of his 60th birthday

A new phase in the quaternary system Gd/Ti/S/O was obtained from a mixture of Gd_2O_3, Gd_2S_3, TiO_2, TiS_2 and Ti by a solid state reaction at 1323 K in a sealed fused-silica tube. The structure of $Gd_{6+x}Ti_{4-x}S_{10-y}O_{6+y}$ (where $x \sim 0.04$, and $y \sim 0.27$), was solved by single-crystal X-ray diffraction, with $R_{(\mathrm{obs})} = 2.69\%$ for 2391 reflections ($I > 3\sigma(I)$) and 155 variables. This compound crystallizes with four formula units in the orthorhombic space group *Pnma*, and the lattice constants (Å): $a = 13.991(1)$, $b = 3.7124(2)$, $c = 34.029(3)$ Å. The structure is built up from the stacking of ribbons of five Gd-polyhedra alternating with ribbons of five Ti- and Gd/Ti-polyhedra along the ***a***-axis. This is the first example of a rare earth (*RE*) and titanium oxysulfide compound that shows mixed *RE*/Ti sites together with pure *RE*- and Ti-sites. $Gd_{6+x}Ti_{4-x}S_{10-y}O_{6+y}$ is a mixed-valent titanium oxysulfide in which half of the Ti cations are Ti^{3+} and half are Ti^{4+}.

Key words: Oxysulfide, Gadolinium, Mixed-Valent Titanium, Crystal Structure

Introduction

In the last ten years, some oxyselenides and many oxysulfides of rare-earth metals and titanium have been reported. For any of their structures, the two cationic species (*RE* and Ti) were always found on distinct positions. Their different size and electronegativity are certainly responsible for the different coordination types of these cations, with a coordination number ranging from 7 to 9 for *RE*, but of 6 for Ti, and a surrounding preferentially towards one kind of anion (oxygen or heavier chalcogen). In this context, a previous study has shown that there is a tendency to an anionic segregation for the oxysulfide compounds: Ti atoms have more oxygen atoms in their environment (and noticeably for Ti^{+4}) than the *RE* atoms [1].

This paper deals with the crystal structure determination of a new compound, $Gd_{6+x}Ti_{4-x}S_{10-y}O_{6+y}$, which shows for the first time the occurrence of some unusual mixed Gd-Ti positions.

Experimental Section

Synthesis and chemical analysis

A mixture of Gd_2O_3, Gd_2S_3, TiO_2, TiS_2 and Ti, in the molar ratio 1 : 5 : 6 : 3.5 : 1.5 respectively, was loaded into a quartz tube and sealed under vacuum ($p = 2 \times 10^{-2}$ atm). The reaction tube was placed in a computer-controlled furnace and was progressively heated to 1275 K at a rate of 100 K/h, held there for four days, and then quenched to room temperature. The reaction product was ground, mixed with a small amount of iodine (~ 3 mg / cm^3) to favor crystallization, and reheated to 1325 K for ten days. A black powder was obtained with crystals of TiS_2 and $Gd_2Ti_2S_2O_5$, and a large amount of needle-like crystals which turned out to be a new phase. Chemical analysis by means of energy dispersive X-ray spectrometry (EDXS) on crystals of the title compound gave the following atomic percentages: Gd 30.2(5), Ti 19.0(4), S 50.8(8) w.-%, in rather good agreement with the formula $Gd_{6.044}Ti_{3.955}S_{9.732}O_{6.268}$ (in %: Gd 30.6, Ti 20.1, S 49.3).

Single crystal data collection

Numerous crystals of $Gd_{6+x}Ti_{4-x}S_{10-y}O_{6+y}$ were tested for quality (intensity and shape of the spots) with a Nonius Kappa CCD diffractometer using Mo-K_α radiation ($\lambda = 0.71073$ Å), and the best one, a needle-shaped crystal with the dimensions $0.012 \times 0.012 \times 0.20$ mm^3, was selected for the data collection. The crystal-to-detector distance was 47.70 mm. 768 images were collected with a rotation angle of 1° and an exposure time of 150 s per frame. The symmetry was orthorhombic and the resulting cell parameters

Table 1. Crystallographic data for $Gd_{\sim 6}Ti_{\sim 4}S_{\sim 10}O_{\sim 6}$.

Formula	$Gd_{6.044}Ti_{3.955}S_{9.732}O_{6.268}$
Formula weight [g.mol^{-1}]	1552.74
Color	black
Dimensions [mm^3]	$0.07 \times 0.006 \times 0.0045$
Crystal system	orthorhombic
Space group	*Pnma* (No. 62)
Z	4
Unit cell dimensions [Å]:	
a, *b*, *c*	13.991(1), 3.7124(2), 34.029(3)
V [Å^3]	1767.5(2)
Density $\rho_{calc.}$ [(g·cm^{-3}]	5.833(1)
Absorption coeff. μ [mm^{-1}]	25.20
Recording conditions	
Temperature [K]	293
Diffractometer	Kappa CCD-NONIUS
Wavelength λ [Å]	0.71069 (Mo-K$_\alpha$)
θ Range for data collection [°]	5.02 – 35.00
hkl Ranges	$-22 \leq h \leq 22$; $-5 \leq k \leq 5$; $-54 \leq l \leq 54$
Reflections collected	30975
Absorption corrections	Gaussian method based on the shape of the crystal
Trans. Coeff. Min – Max	0.254 – 0.804
Refinement	
Refinement method	Full-matrix least-squares on F^2
Restricted θ range [°]	5.02 – 30
No. of refined parameters	155
R Indices [2391, $I > 3\sigma(I)$]	$R_{obs} = 2.69\%$; $R_{wobs} = 3.37\%$
R Indices [2891, all data]	$R_{all} = 3.82\%$; $R_{wall} = 3.51\%$
Largest peak and hole [e·Å^{-3}]	+1.95 and −3.08

(in Å) were: $a = 13.991(1)$, $b = 3.7124(2)$, $c = 34.029(3)$ Å, $V = 1767.5(2)$ Å^3. Lorentz, polarisation as well as absorption correction using the face indexing option were applied. Crystallographic data are given in Table 1.

Structure Determination

We first used the SHELXTL software package [2] running the XPREP program on the data file (30975 reflections from the data raw file) to select a space group; the two possibilities with the lowest CFOM (Combined Figure Of Merit) were $Pna2_1$ (No 33 – acentric) and *Pnma* (No 62 – centric). The intensity statistics rather indicated a centrosymmetric space group, therefore we proceeded with *Pnma*. The structure was solved with direct methods using the SHELXS program, and then refined with JANA2000 [3]. During the refinement, we considered two mixed Ti/Gd sites, namely Ti3/Gd6 and Ti4/Gd7, and one anionic site S9/O6. Ti and Gd atoms associated to a mixed site had different displacement parameters as well as atomic coordinates; S9 and O6 were refined on distinct positions but with the same displacement parameters. Besides that, the Ti3/Gd6, Ti4/Gd7, and S9/O6 occupancies were constrained so that a full occupancy for the mixed site is fixed through the $1 - x/x$ relation (see Table 2). To overcome the problem of too short interatomic distances for the Ti3/Gd6 pair with the S9/O6 pair, the occupancy factor for S9 was tied to that of Ti3 while that for O6 was correlated with that of Gd6. Thus, statistically speaking, one is only concerned with

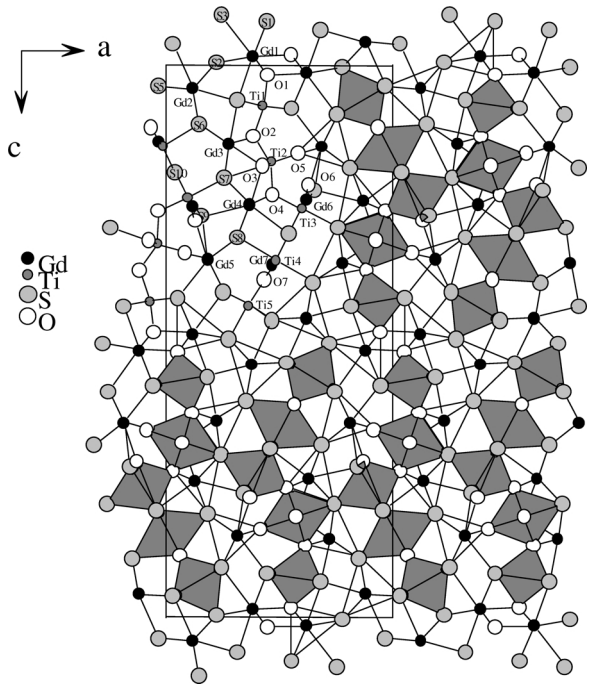

Fig. 1. Projection of the structure of $Gd_{6.044}Ti_{3.956}S_{9.732}O_{6.268}$ onto the (***ac***) plane; Ti-ribbons (dark gray) and Gd-ribbons (light gray), each built from the association of five units, alternate along the *a*-axis.

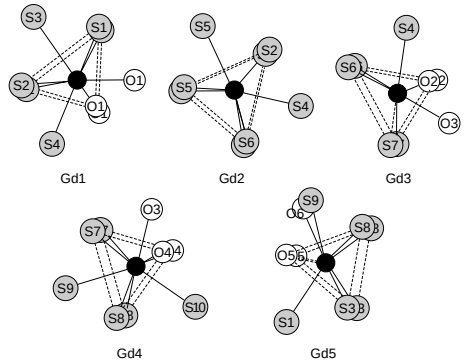

Fig. 2. Detailed environments around the five Gd atoms constituting the Gd-ribbon.

Table 2. Atomic coordinates and equivalent isotropic displacement parameters for $Gd_{6.044}Ti_{3.956}S_{9.732}O_{6.268}$.

Atom	Site	Occ. [%]	x	y	z	$U_{(eq,iso^*)}$ [Å^2]
Gd1	4c	100	0.38210(3)	1/4	−0.015159(11)	0.00823(10)
Gd2	4c	100	0.11955(3)	1/4	0.042289(11)	0.01030(11)
Gd3	4c	100	0.27840(3)	1/4	0.142661(11)	0.00906(10)
Gd4	4c	100	0.37013(3)	1/4	0.252481(11)	0.01376(11)
Gd5	4c	100	0.18430(3)	1/4	0.351596(13)	0.01432(11)
Ti1	4c	100	0.42896(10)	3/4	0.07312(4)	0.0108(4)
Ti2	4c	100	0.46286(10)	3/4	0.17639(4)	0.0087(4)
Ti3	4c	73.2(4)	0.5973(3)	3/4	0.2600(2)	0.0315(11)
Gd6	4c	26.8(4)	0.6180(2)	3/4	0.24506(6)	0.0113(5)
Ti4	4c	22.3(3)	0.4859(13)	3/4	0.3535(5)	0.0233(3)
Gd7	4c	77.7(3)	0.46817(7)	3/4	0.36104(3)	0.0233(3)
Ti5	8d	50	0.36329(13)	0.3040(14)	0.43346(5)	0.0127(12)
S1	4c	100	0.44619(13)	3/4	−0.07938(5)	0.0102(5)
S2	4c	100	0.22240(13)	3/4	−0.00418(5)	0.0088(5)
S3	4c	100	0.2455(2)	1/4	−0.09029(7)	0.0219(6)
S4	4c	100	0.31614(14)	1/4	0.06384(5)	0.0097(5)
S5	4c	100	−0.03275(14)	3/4	0.03855(7)	0.0161(6)
S6	4c	100	0.14693(14)	3/4	0.10706(6)	0.0114(5)
S7	4c	100	0.25829(14)	3/4	0.20531(6)	0.0122(5)
S8	4c	100	0.3157(2)	3/4	0.31253(7)	0.0189(6)
S9	4c	73.2(4)	0.1558(3)	1/4	0.27376(10)	0.0262(11)
S10	4c	100	0.5401(2)	1/4	0.30557(6)	0.0162(6)
O1	4c	100	0.4470(4)	3/4	0.0184(2)	0.0085(10)*
O2	4c	100	0.3851(4)	3/4	0.1297(2)	0.0105(11)*
O3	4c	100	0.4262(4)	1/4	0.1825(2)	0.0113(11)*
O4	4c	100	0.4685(4)	3/4	0.2349(2)	0.0126(11)*
O5	4c	100	0.5834(5)	3/4	0.1601(2)	0.0213(13)*
O6	4c	26.8(4)	0.129(2)	1/4	0.2828(9)	0.0262(11)
O7	4c	100	0.4353(6)	1/4	0.3872(2)	0.036(2)*

Table 3. Anisotropic displacement parameters (Å^2) for $Gd_{6.044}Ti_{3.956}S_{9.732}O_{6.268}$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Gd1	0.0088(2)	0.0069(2)	0.0090(2)	0	0.00095(13)	0
Gd2	0.0100(2)	0.0085(2)	0.0124(2)	0	−0.00101(14)	0
Gd3	0.0125(2)	0.0071(2)	0.0076(2)	0	−0.00071(13)	0
Gd4	0.0253(2)	0.0067(2)	0.0094(2)	0	−0.0036(2)	0
Gd5	0.0128(2)	0.0088(2)	0.0214(2)	0	0.0047(2)	0
Ti1	0.0102(6)	0.0160(7)	0.0062(6)	0	0.0009(5)	0
Ti2	0.0120(6)	0.0071(6)	0.0070(6)	0	−0.0015(5)	0
Ti3	0.018(2)	0.037(2)	0.040(2)	0	−0.018(2)	0
Gd6	0.0107(10)	0.0168(9)	0.0064(10)	0	−0.0024(7)	0
Ti4	0.0219(5)	0.0135(3)	0.0344(6)	0	−0.0147(3)	0
Gd7	0.0219(5)	0.0135(3)	0.0344(6)	0	−0.0147(3)	0
Ti5	0.0103(7)	0.016(3)	0.0114(7)	0.0009(9)	0.0016(6)	0.0016(9)
S1	0.0084(8)	0.0115(9)	0.0107(8)	0	−0.0029(7)	0
S2	0.0079(8)	0.0096(8)	0.0089(8)	0	−0.0009(7)	0
S3	0.0342(13)	0.0112(10)	0.0201(10)	0	0.0125(9)	0
S4	0.0119(8)	0.0084(8)	0.0088(8)	0	0.0008(7)	0
S5	0.0086(9)	0.0113(10)	0.0282(11)	0	−0.0021(8)	0
S6	0.0122(9)	0.0091(9)	0.0128(8)	0	−0.0028(7)	0
S7	0.0156(9)	0.0097(9)	0.0115(8)	0	0.0019(7)	0
S8	0.0206(10)	0.0108(10)	0.0253(10)	0	0.0135(9)	0
S9/O6	0.022(2)	0.043(2)	0.013(2)	0	0.0038(12)	0
S10	0.0148(9)	0.0146(10)	0.0192(10)	0	−0.0012(8)	0

Ti3-S9 and Gd6-O6 distances.Then, because of a large U_{22} value for Ti5, its special position (4c) was split into a general one (8d) with a statistical occupancy of 50%. Under all these conditions, and taking into account an anisotropic refinement for the Gd, Ti, and S atoms, the refinement converged to relatively low R-values, but two difficulties arose with this solution: a negative U_{eq} value for Ti4, and a too short Gd6-O6

Table 4. Selected interatomic distances and bond valence. Values for $Gd_{6.044}Ti_{3.956}S_{9.732}O_{6.268}$.

Symmetry code: #1 x, y, z; #2 $-x, -1-y, -z$; #3 $1-x, 1-y, -z$; #4 $-x, 1-y, -z$; #5 $1/2-x, 1-y, 1/2+z$; #6 $1/2-x, -y, 1/2+z$; #7 $-1/2-x, -1-y, 1/2+z$; #8 $-1/2-x, -y, 1/2+z$; #9 $1-x, 2-y, -z$; #10 $1/2-x, -1-y, 1/2+z$.

Atom1	Atom2	sym	Dist.	B.V.	Atom1	Atom2	sym	Dist.	B.V.
Gd1	S1	#2	3.004(2)	0.278		S4	#4	2.457(2)	0.556
	S1	#1	3.004(2)	0.278		O1	#1	1.879(5)	0.841
	S2	#2	2.929(2)	0.340		O2	#1	2.021(6)	0.573
	S2	#1	2.929(2)	0.340					S = 3.373
	S3	#1	3.192(2)	0.167	Ti2	S7	#1	3.027(2)	0.119
	S4	#1	2.842(2)	0.430		O2	#1	1.926(6)	0.741
	O1	#2	2.361(3)	0.449		O3	#1	1.937(2)	0.719
	O1	#1	2.361(3)	0.449		O3	#4	1.937(2)	0.719
	O1	#3	2.393(5)	0.411		O4	#1	1.994(6)	0.616
				S = 3.143		O5	#1	1.775(7)	1.114
Gd2	S2	#2	2.831(1)	0.443					S = 4.029
	S2	#1	2.831(1)	0.443	Ti3	S7	#6	2.543(5)	0.441
	S4	#1	2.847(2)	0.425		S9	#6	2.331(4)	0.782
	S5	#2	2.829(2)	0.446		S9	#5	2.331(4)	0.782
	S5	#1	2.829(2)	0.446		S10	#1	2.548(4)	0.435
	S5	#4	3.007(2)	0.275		S10	#4	2.548(4)	0.435
	S6	#2	2.907(2)	0.361		O4	#1	1.994(7)	0.616
	S6	#1	2.907(2)	0.361					S = 3.491
				S = 3.200	Gd6	S7	#1	2.589(3)	0.853
Gd3	S4	#1	2.734(2)	0.576		S8	#6	3.389(3)	0.098
	S6	#2	2.880(2)	0.388		S10	#1	2.979(2)	0.297
	S6	#1	2.880(2)	0.388		S10	#4	2.979(2)	0.297
	S7	#2	2.841(2)	0.431		O4	#1	2.120(6)	0.862
	S7	#2	2.841(2)	0.431		O5	#1	2.932(7)	0.096
	O2	#2	2.422(3)	0.380		O6	#6	2.09(2)	0.935
	O2	#1	2.422(3)	0.380		O6	#6	2.09(2)	0.935
	O3	#1	2.473(5)	0.333					S = 4.372
				S = 3.309	Ti4	S6	#6	2.62(2)	0.356
Gd4	S7	#2	2.911(2)	0.358		S8	#1	2.76(2)	0.245
	S7	#1	2.911(2)	0.358		S10	#1	2.585(13)	0.394
	S8	#2	2.864(2)	0.406		S10	#4	2.585(13)	0.394
	S8	#1	2.864(2)	0.406		O7	#1	2.293(12)	0.274
	S9	#1	3.085(4)	0.163		O7	#4	2.293(12)	0.274
	S10	#1	2.987(2)	0.291					S = 1.937
	O3	#1	2.508(5)	0.302	Gd7	S6	#6	2.727(2)	0.589
	O4	#2	2.387(3)	0.419		S8	#1	2.698(3)	0.635
	O4	#1	2.387(3)	0.419		S10	#1	2.832(2)	0.442
				S = 3.121		S10	#4	2.832(2)	0.442
Gd5	S1	#5	2.975(2)	0.300		O7	#1	2.109(4)	0.888
	S3	#6	2.885(2)	0.383		O7	#4	2.109(4)	0.888
	S3	#5	2.885(2)	0.383		S3	#5	3.417(3)	0.091
	S8	#2	2.931(2)	0.338		S5	#6	3.417(3)	0.091
	S3	#6	2.931(2)	0.338					S = 4.066
	S9	#1	2.678(4)	0.669	Ti5	S2	#5	2.446(3)	0.573
	O5	#7	2.366(4)	0.443		S3	#6	2.683(4)	0.302
	O5	#8	2.366(4)	0.443		S3	#5	2.390(4)	0.667
	O6	#1	2.46(3)	0.338		S5	#10	2.693(4)	0.294
				S = 3.210		S5	#6	2.401(4)	0.647
Ti1	S1	#3	2.558(2)	0.423		O7	#1	1.880(8)	0.839
	S1	#9	2.558(2)	0.423					S = 3.322
	S4	#1	2.457(2)	0.556					

distance (= 1.951 Å). In order to skip the problem of the negative U_{eq} value of Ti4, U_{eq} values for both Ti4 and Gd7 atoms (Ti4/Gd7 pair) were constrained to a similar value. This resulted in a positive U_{eq} value and, fortunately, yielded also a much longer Gd6-O6 distance (= 2.091 Å) which is now acceptable; indeed, a comparable Gd-O bond length can be observed in $GaGd_3O_6$ [4]. This final solution led to reliability factors $R_{(obs)} = 2.69\%$ and $R_{w(obs)} = 3.37\%$ for 2391 reflections ($I > 3\sigma(I)$) limited to $\sin\theta/\lambda = 0.7$, and 155 variables; $R_{(all)} = 3.82$ and $R_{w(all)} = 3.51$ for 2891 reflections. The maximum and minimum peaks

on the final Fourier difference corresponded to +1.95 and -3.08 e$^-$/Å^3, respectively. The resulting formula is $Gd_{6.044}Ti_{3.956}S_{9.732}O_{6.268}$. Details on the refinement are given in Table 1. Fractional atomic coordinates and isotropic displacement parameters are given in Table 2, coefficients of the anisotropic displacement parameters are listed in Table 3, and selected interatomic distances are compiled in Table 4.

Structure Description

Figure 1 shows a projection of the $Gd_{6.044}Ti_{3.956}S_{9.732}O_{6.268}$ structure onto the (**ac**) plane. The structure can be viewed as an alternating stacking of ribbons of five polyhedra each, along the ***a***-direction. The first type of ribbon features five edge-sharing polyhedra centered by Gd atoms only, while the second type of ribbon has an association of five octahedra centered by Ti or Ti/Gd atoms (three pure Ti sites and two mixed Ti/Gd sites).

i) Gd-ribbon: Five polyhedra centered by Gd atoms, from Gd1 to Gd5, are sharing a common edges. Gd atoms in this entity are either eightfold coordinated (Gd2, Gd3, and Gd5) or ninefold coordinated (Gd1 and Gd4) in the form of bicapped and tricapped trigonal prisms, respectively. A view of the environment of these five Gd atoms is given in Fig. 2.

ii) Ti- or Ti/Gd-ribbon: Five octahedra centered by Ti atoms or mixed Ti/Gd atoms are associated either by corner- or by edge-sharing to give an entity that is sandwiched by two adjacent Gd-ribbons. The Ti atoms are six-coordinated (distorted octahedra) by four S atoms and two O atoms for Ti1, five O atoms and one S atom for Ti2, and five S atoms with one O atom for Ti5 (see Fig. 3a). The two remaining distorted octahedra this participate in this unit are centered by mixed Ti/Gd positions, namely Ti3/Gd6 and Ti4/Gd7 (see Fig. 3b), as labeled in Table 2. Concerning the Ti4/Gd7 mixed-site, the closeness of both positions can explain why a common displacement parameter was needed for both metal atoms, as discussed above. For the Ti3/Gd6 mixed site, the anionic environment is different for both cations as the presence of S9 is constrained to correspond to that of Ti3 only (Ti3-S9 = 2.331 Å), which means a partial occupancy (73.2%) of this S9 position. This avoids the too short contact with the Gd6 atom (Gd6-2×S9 = 2.033 Å). However, such a statistical vacancy on the S9 position is compensated, for Gd6, by the presence of O6

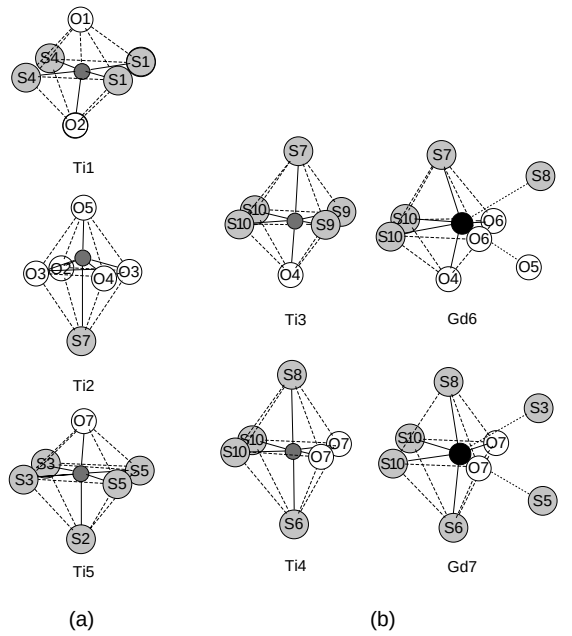

Fig. 3. Detailed environments around the metal atoms constituting the Ti-ribbon; a) for the three Ti-octahedra, and b) for the two mixed Ti/Gd-sites.

in equal amount (26.8%), with Gd6-O6 = 2.091 Å. In addition, Gd6 is very weakly bonded to the O5 and S8 atoms (bond lengths of 2.932 and 3.389 Å, respectively); as a consequence, the coordination around Gd6 is rather an octahedron defined by three O and three S atoms (see Fig. 3b). The coordination around Gd7 is comparable to that of Gd6 (see Fig. 3b), *i.e.* an octahedron of four S and two O atoms, and two additional S atoms (S3 and S5) at a much longer distances (both atoms at 3.417 Å from Gd7). Table 4 summarizes the interatomic distances for all polyhedra centered around metal atoms.

Thus, the structure of $Gd_{6.044}Ti_{3.956}S_{9.732}O_{6.268}$ can be described by corrugated planes stacked along the ***a***-direction, but a 2D-character cannot be envisioned as both types of ribbons are interpenetrating. Indeed, along the ***a***-direction, the successive Ti (with Ti/Gd) ribbons are linked together through a common corner, namely S7. This atom is shared by the Ti3/Gd6 octahedron from one ribbon and the Ti2 octahedron from the adjacent ribbon; in addition, S7 atoms also belong to both the Gd3- and Gd4-polyhedra.

Discussion

The oxidation state for Ti, particularly for the mixed Gd/Ti sites, but also for the pure Ti sites, is question-

able. Indeed, considering the simplest approximate formula $Gd_6Ti_4S_{10}O_6$, a mixed valence state for Ti with equal parts of Ti (+III) and Ti (+IV) is requested to get a valence equilibrium with the *Ln* (+III), S(-II), and O(-II) states. The valence of the Ti and the Gd atoms were calculated using the bond valence equation [5]:

$$V_i = \Sigma \exp[(R^{\circ}_{ij} - d_{ij})/b],$$

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*. Calculated values for the Gd atoms (from Gd1 to Gd5) are consistent with the expected oxidation state +III (see Table 4). Concerning the Ti atoms, and only the pure Ti-sites Ti1, Ti2, and Ti5, the two sites Ti1 and Ti5 are likely associated with the oxidation state +III, while the Ti2 site deals with a +IV state. This result agrees well with the fact that the highest oxidation state is observed for the Ti atom which is surrounded predominantly by oxygen atoms (five oxygen atoms for one sulfur atom). For the mixed-sites Ti/Gd, calculations were made for each atom individually, and the results were weighted by their relative percentage. As an example, for the Ti3/Gd6 pair with the respective proportion $0.732/0.268$, the experimental value is 3.73 as resulting from: $3.491 \times 0.732(= \%Ti3) + 4.372 \times 0.268(= \%Gd6)$; a theoretical value of 3.73 is obtained if one considers a Ti +IV state associated with Gd +III (*i.e.*, $4 \times 0.732 + 3 \times 0.268$), which is in excellent agreement with the experimental value. Similar considerations about the Ti4/Gd7 couple gave the experimental value of 3.59 in rather good agreement with the theoretical value of 3.22 (*i.e.*, $4 \times 0.223 + 3 \times 0.777$). In summary, one gets Ti1 and Ti5 in a +III oxidation state, and Ti2, Ti3 as well as Ti4 in a +IV oxidation state. Taking into account the multiplicity of the sites, it appears that approximately equal amounts of Ti^{+IV} and Ti^{+III} are present (precisely $0.9776/1$) (see Table 4). This is exactly what we were expecting from the approximate formula $Gd_6Ti_4S_{10}O_6$.

Concluding Remarks

To our knowledge, this is the first example of a rare earth titanium oxysulfide where mixed cationic sites are observed. Previously, we found a situation where two metals, Sm and Nb, show roughly identical anionic environment but on different sites (d > 3.8 Å) as illustrated by $Sm_3NbX_3O_4$ [6]. However, nothing comparable was reported when Ti and *Ln* elements were combined in quaternary oxychalcogenides.

The reason why Gd and Ti atoms can share the same type of site in this structure remains an open question. The Ti atoms have not changed their standard type of coordination which is octahedral (slightly distorted) whatever the anionic (O and/or S) surroundings; for the Gd atom, the distorted octahedral coordination presented by Gd6 and Gd7 atoms are more unusual for *R. E.* in oxychalcogenides. However, such a coordination was already observed for Gd in $GaGd_3O_6$ [4].

A crystallographic data file in CIF format has been deposited as Supporting Information; further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD 414125, the name of the authors, and citation of the paper.

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