

A gadolinium and niobium oxide sulfide, $\text{Gd}_3\text{NbS}_3\text{O}_4$

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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{Nb}-\text{O}) = 0.005\text{ \AA}$

R factor = 0.030

wR factor = 0.061

Data-to-parameter ratio = 30.7

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The structure of the title compound, trigadolinium niobium trisulfide tetraoxide, $\text{Gd}_3\text{NbS}_3\text{O}_4$, was determined by single-crystal X-ray diffraction. $\text{Gd}_3\text{NbS}_3\text{O}_4$ crystallizes in the non-centrosymmetric space group $Pn2_1a$ (No.33) of the orthorhombic system. It is isostructural with $\text{Sm}_3\text{NbS}_3\text{O}_4$.

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Comment

Recent explorations in the field of oxychalcogenides have revealed novel interesting layered intergrowth compounds with structures based on the stacking of chalcogenide and oxide layers (Zhu & Hor, 1997; Otschi *et al.*, 1999; Boyer *et al.*, 1999; Goga *et al.*, 1999). As the combination of both types of layer could lead to materials with interesting electronic and magnetic properties, we were looking for new layered intergrowth compounds. We are currently investigating several quaternary systems containing rare earth and transition elements and, during our investigation of the Gd–Nb–S–O system, we obtained $\text{Gd}_3\text{NbS}_3\text{O}_4$ as a side-product. A yellow transparent platelet crystal was mounted on the diffractometer for data collection.

The observed systematic conditions ($k + l = 2n$ for $0kl$; and $h = 2n$ for $hk0$) led to only two possible space groups, $Pn2_1a$ (No. 33) and $Pnma$ (No. 62). As the intensity statistics were rather indicative of a centrosymmetric space group, we first supposed that $\text{Gd}_3\text{NbS}_3\text{O}_4$ was isostructural with $\text{Sm}_3\text{NbSe}_3\text{O}_4$ (Meerschaut *et al.*, 1998) and tried to refine the structure in $Pnma$ (No. 62). However, the refinement led to poor reliability factors ($R = 0.063$ and $wR = 0.144$). Subsequently, we considered that $\text{Gd}_3\text{NbS}_3\text{O}_4$ could be isostructural with $\text{Sm}_3\text{NbS}_3\text{O}_4$ (Boyer-Candalen *et al.*, 2000), *i.e.* we tried to refine the structure in the non-centrosymmetric space group $Pn2_1a$. The refinement led to much better reliability factors ($R = 0.030$ and $wR = 0.061$).

A projection of the structure of $\text{Gd}_3\text{NbS}_3\text{O}_4$ is shown in Fig. 1. All metal atoms are found in mixed environments of oxygen and sulfur. Nb1 and Gd1 are involved in similar coordination polyhedra (very distorted prism with eight surrounding atoms, *viz.* four O and four S atoms). These polyhedra are connected by edge-sharing and alternate regularly along the b axis. In the same way, Gd2 and Gd3 are located in slightly different bicapped trigonal prisms that alternate along the b axis.

The difference between the sulfur and selenium compounds is related to the position of the chalcogen in the structure. In the $\text{Sm}_3\text{NbSe}_3\text{O}_4$ structure, atom Se3 sits on an inversion center (special position $4a$) and is octahedrally coordinated. By contrast, in $\text{Gd}_3\text{NbS}_3\text{O}_4$, atom S3 deviates from this position and no longer occupies the center of the octahedron, but a square pyramid. These structural characteristics lead to the absence of a mirror plane in the structure. Finally, we refined a

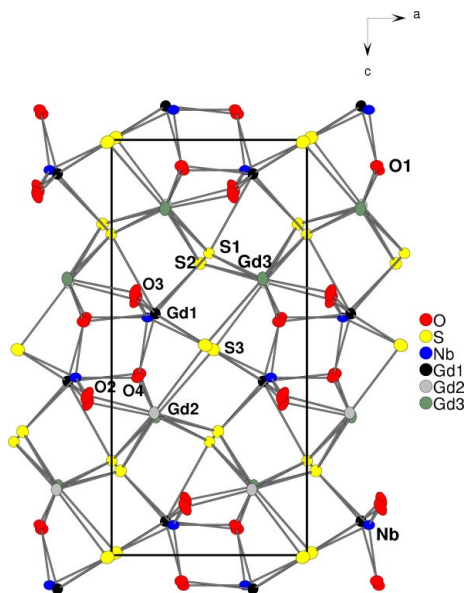


Figure 1
A projection of the structure of $Gd_3NbS_3O_4$ along the b axis, with displacement ellipsoids drawn at the 80% probability level.

Flack (1983) parameter close to 0.5, which indicates that we have a racemic twin.

Experimental

A mixture of Gd_2S_3 , Gd_2O_3 , Nb_2O_5 , and Nb, weighed in the proportion 1.33:1.67:1:0.5, was pressed into a pellet and sealed in a silica tube under vacuum. The tube was progressively heated (100 K h^{-1}) to 1273 K and maintained at that temperature for 12 h. To favor crystallization, a small amount of iodine ($<5\text{ mg cm}^{-3}$) was added to the intermediate reaction product, which was reheated in a temperature gradient furnace at 1273 K for 10 d. Yellow transparent platelet crystals were obtained as a by-product. Chemical analyses performed on these crystals using an EDS-equipped scanning electron microscope revealed the following atomic percentages (except for oxygen): Gd 42.8, Nb 12.7 and S 44.5, in good agreement with the theoretical values Gd 42.8, Nb 14.3 and S 42.8 calculated for $Gd_3NbS_3O_4$.

Crystal data

$Gd_3NbS_3O_4$
 $M_r = 724.84$
Orthorhombic, $Pn2_1a$
 $a = 6.6451$ (1) Å
 $b = 7.5873$ (2) Å
 $c = 14.1809$ (3) Å
 $V = 714.98$ (3) Å³
 $Z = 4$
 $D_x = 6.734\text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
Cell parameters from 21 073 reflections
 $\theta = 2.9\text{--}35.0^\circ$
 $\mu = 29.85\text{ mm}^{-1}$
 $T = 293$ (2) K
Platelet, yellow
 $0.09 \times 0.06 \times 0.02\text{ mm}$

Data collection

Nonius KappaCCD diffractometer
 ω and φ scans
Absorption correction: Gaussian (*SHELXTL*; Bruker, 2001)
 $T_{\min} = 0.192$, $T_{\max} = 0.641$
18 460 measured reflections
3130 independent reflections

2839 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.054$
 $\theta_{\text{max}} = 35.0^\circ$
 $h = -10 \rightarrow 10$
 $k = -12 \rightarrow 12$
 $l = -22 \rightarrow 21$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.061$
 $S = 1.05$
3130 reflections
102 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.0207P)^2 + 6.6189P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 2.23\text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -2.11\text{ e \AA}^{-3}$
Extinction correction: *SHELXL97*
Extinction coefficient: 0.00103 (6)
Absolute structure: Flack (1983)
Flack parameter = 0.554 (14)

Table 1

Selected bondlengths (Å).

Gd1—O2	2.267 (6)	Gd2—S2 ^{viii}	2.913 (2)
Gd1—O4 ⁱ	2.279 (4)	Gd3—O4	2.305 (7)
Gd1—O3	2.299 (6)	Gd3—O3 ^{vi}	2.354 (5)
Gd1—O1 ⁱⁱ	2.459 (4)	Gd3—O1 ⁱ	2.456 (8)
Gd1—S1	2.7536 (14)	Gd3—S1	2.833 (2)
Gd1—S3 ⁱⁱⁱ	2.882 (2)	Gd3—S2	2.904 (2)
Gd1—S3	2.899 (2)	Gd3—S1 ^{vii}	2.910 (2)
Gd1—S1 ^{iv}	3.0952 (14)	Gd3—S2 ^{vii}	2.930 (2)
Gd2—O4 ^v	2.331 (8)	Gd3—S3 ⁱⁱⁱ	2.9996 (19)
Gd2—O2 ^{vi}	2.363 (5)	Nb1—O2 ^{ix}	1.893 (6)
Gd2—O1 ⁱ	2.447 (8)	Nb1—O3	1.903 (6)
Gd2—S1	2.848 (2)	Nb1—O1	1.935 (4)
Gd2—S1 ^{viii}	2.890 (2)	Nb1—O4 ^x	2.104 (4)
Gd2—S2 ^v	2.895 (2)	Nb1—S2	2.5809 (15)
Gd2—S3	2.8957 (19)	Nb1—S3 ⁱⁱⁱ	2.7415 (19)

Symmetry codes: (i) $1-x, y-\frac{1}{2}, 1-z$; (ii) $2-x, y-\frac{1}{2}, 1-z$; (iii) $1-x, \frac{1}{2}+y, 1-z$; (iv) $\frac{1}{2}+x, y, \frac{3}{2}-z$; (v) $x, y-1, z$; (vi) $x-1, y, z$; (vii) $x-\frac{1}{2}, y, \frac{3}{2}-z$; (viii) $x-\frac{1}{2}, y-1, \frac{3}{2}-z$; (ix) $x, 1+y, z$; (x) $1+x, y, z$.

Refinement of the opposite enantiomer leads to identical R values and a complementary Flack parameter [0.446 (14)]. The largest Fourier difference peak was found at 0.83 Å from Gd1 and the deepest Fourier difference hole was found at 0.64 Å from Gd3.

Data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: not used (isotypic); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXTL* (Bruker, 2001).

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