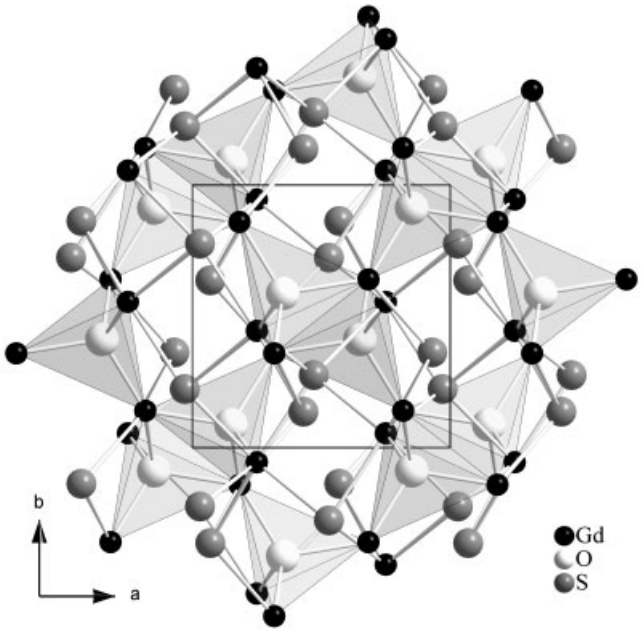
Crystal structure of digadolinium(III) oxide disulfide, Gd_2OS_2

J. Wontcheu and Th. Schleid*

Universität Stuttgart, Institut für Anorganische Chemie, Pfaffenwaldring 55, D-70569 Stuttgart, Germany

Received May 30, 2003, accepted and available on-line July 24, 2003; CSD-No. 409708



Abstract

Gd_2OS_2, monoclinic, $P12_1/c1$ (No. 14), a = 8.3365(6) Å, b = 6.9872(5) Å, c = 6.9231(5) Å, β = 99.463(6)°, V = 397.8 Å^3, Z = 4, $R_{gt}(F)$ = 0.022, $wR_{ref}(F^2)$ = 0.047, T = 293 K.

Source of material

The new oxysulfide Gd_2OS_2 was obtained by reacting a mixture of Gd_2O_3, S and Gd (molar ratio 1:9:6) at 1123 K for seven days in an evacuated sealed silica ampoule when an excess of CsCl is added as flux. Apart from the large, colourless, square brick-shaped single crystals of Gd_2OS_2, which turned out to be air- and water-resistant, traces of Gd_2S_3 were also present as by-product.

Discussion

Since 1990, rare-earth oxysulfides of the general formula M_2OS_2 are already known with M = Sm, Tb, Dy and Y obtained at lower temperature under normal pressure [1–5]. They were also accessible with M = Er, Tm and Yb by using high-pressure/high-temperature techniques [6]. However, the isotypic gadolinium compound was to date unknown.

The title compound Gd_2OS_2 contains two crystallographically different Gd^{3+} cations, each in sevenfold coordination. The anionic coordination polyhedron about Gd1 can be described as a distorted monocapped trigonal prism $[(Gd1)O_3(S1)_{2+1}(S2)]$, while one O^{2-} and six S^{2-} anions build a more perfect monocapped trigonal prism $[(Gd2)O(S1)_2(S2)_4]$ around Gd2 where the cap is formed by the single oxygen above the rectangular (S1,S1,S2,S2) face. The O^{2-} coordination sphere actually consists of four Gd^{3+} cations arranged as $[OGd_4]^{10+}$ tetrahedron with O—Gd distances of 227 pm, 229 pm, 230 pm and 232 pm. Two $[O(Gd1)_3(Gd2)]^{10+}$ tetrahedra are bridged by a common Gd1—Gd1 edge (d(Gd1—Gd1) = 361 pm) to form cationic dimers $[O_2Gd_6]^{14+}$ surrounded by sixteen S^{2-} and six O^{2-} anions. Further connectivity of these dimers occurs via oxygen and terminal Gd1 atoms so that the latter become part of the bridging edge of the next dimers (see figure). When all Gd1 termini are connected, two-dimensional infinite layers stacked along [001] and described as $^2_\infty[O(Gd1)_{3/3}(Gd2)_{1/1}]^{4+}$ appear within the structural framework. Different layers are held together by two crystallographically independent S^{2-} anions occupying free edges and faces of the O^{2-} centred $(Gd^{3+})_4$ tetrahedra. Finally, the crystal structure shows two different S^{2-} anions that exhibit a vicinity of four *plus* one (S1) or five Gd^{3+} cations (S2) in the shape of distorted tetragonal pyramids (d(S—Gd) = 277 pm – 295 pm, 314 pm).

Table 1. Data collection and handling.

Crystal:	colourless, brick-shaped, size 0.06 × 0.08 × 0.09 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	338.85 cm^{-1}
Diffractometer, scan mode:	Nonius Kappa-CCD, φ/ω
$2\theta_{max}$:	55.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7293, 911
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 868
$N(param)_{refined}$:	47
Programs:	SHELXL-97 [7], DIAMOND [8]

* Correspondence author (e-mail: schleid@iac.uni-stuttgart.de)

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Gd(1)	4*e*	0.57804(3)	0.64080(4)	0.81736(4)	0.0073(2)	0.0074(2)	0.0068(2)	–0.0005(1)	0.0014(1)	0.0009(1)
Gd(2)	4*e*	0.13707(3)	0.55507(4)	0.75008(4)	0.0068(2)	0.0075(2)	0.0072(2)	0.0008(1)	0.0005(1)	–0.0002(1)
O	4*e*	0.3832(5)	0.0881(6)	0.3507(6)	0.008(2)	0.004(2)	0.009(2)	0.000(2)	0.003(2)	0.001(2)
S(1)	4*e*	0.6789(2)	0.1371(2)	0.0695(2)	0.0102(7)	0.0091(8)	0.0085(7)	–0.0006(5)	0.0025(5)	–0.0020(5)
S(2)	4*e*	0.0773(2)	0.2762(2)	0.0297(2)	0.0075(7)	0.0079(7)	0.0085(6)	–0.0006(5)	0.0015(5)	–0.0002(6)

Acknowledgments. The authors are indebted to Dr. Helge Müller-Bunz for the single crystal measurement and to the State of Baden-Württemberg (Stuttgart) for financial support.

References

1. Lissner, F.; Schleid, Th.: Über Sulfide und Oxidsulfide des Samariums. Z. Naturforsch. **47 b** (1992) 1614-1620.
2. Schleid, Th.: A New Oxysulfide of Terbium: Tb_2OS_2. Eur. J. Solid State Inorg. Chem. **28** (1991) 557-562.
3. Schleid, Th.: Zwei Formen von Dy_2OS_2. Z. Anorg. Allg. Chem. **602** (1991) 39-47.
4. Schleid, Th.: Crystal Structures of D-Y_2S_3 and Y_2OS_2. Eur. J. Solid State Inorg. Chem. **29** (1992) 1015-1028.
5. Schleid, Th.: Zur Kristallchemie von Selten-Erd-Sesquisulfiden und ihren Derivaten. Habilitationsschrift, Universität Hannover, Germany 1993.
6. Range, K.-J.; Lange, K. G.; Gietl, A.: Rare Earth Sulphide Oxides Ln_2S_2O (Ln = Er, Tm, Yb): High Pressure Synthesis and Crystal Structure. J. Less-Common Met. **158** (1990) 137-145.
7. Sheldrick, G. M.: SHELXL-97. Program System for Crystal Structure Determination and Refinement. Universität Göttingen, Germany 1997.
8. Brandenburg, K.: Diamond (Version 2.1a). Visual Crystal Structure Information System. Crystal Impact GbR, Bonn, Germany 1999.