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Synthesis and crystal structure of Gd_2TeO_6

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Abstract

The new oxotellurate(VI) Gd_2TeO_6 was synthesized by solid-state reaction of equimolar mixtures of Gd_2O_3 and TeO_3 in evacuated silica tubes at 800°C within 10 days. This compound crystallizes in the orthorhombic system with the space group $P2_12_12_1$ (no. 19) and the lattice constants $a = 532.52(4)$, $b = 916.03(8)$, $c = 1004.60(9)$ pm ($Z = 4$). The crystal structure was determined by X-ray single-crystal diffraction techniques and refined with $R_1 = 0.028$, $wR_2 = 0.059$ and a Flack-x parameter of $-0.002(2)$ for 2157 unique reflections. In the La_2TeO_6-type crystal structure of Gd_2TeO_6, the Gd^{3+} cations occupy two of the nine independent atomic positions and are coordinated sevenfold by oxygen. Separately from each other, both coordination polyhedra $[GdO_7]$ build zigzag chains along [100] via common edges (Gd1) and corners (Gd2), respectively. Each of the chains order as hexagonal rod packing. Finally, both of them combine by linkage via edges and corners again to form a complex ${}^3_\infty\{[GdO_3]^{3-}\}$ framework. The isolated $[TeO_6]^{6-}$ octahedra reside in the oval channels of this arrangement.

Keywords: Oxotellurates(VI); Gadolinium; Solid-state synthesis; Crystal structure

1. Introduction

Little is known about ternary oxotellurates(VI) of the lanthanides so far. Only for the formula type M_2TeO_6, two different structures have been described on the basis of single-crystal data. The first rare-earth oxotellurates(VI) of this composition were prepared by reacting equimolar quantities of rare-earth sesquioxide (M_2O_3) and orthotelluric acid (H_6TeO_6) at elevated temperatures. It was possible to index all X-ray powder diffraction patterns on the basis of a hexagonal unit cell, so that the indication of an isostructural series for La, Pr through Tm and Y was supposed [1]. Later, it could be shown that almost all rare-earth(III) oxotellurates(VI) with M = La, Pr through Tm and Y crystallize orthorhombically [2]. Only Yb_2TeO_6 on the other hand proved to be isostructural to trigonal Na_2SiF_6 [3] on the basis of X-ray powder studies, which later was found to be also true for Lu_2TeO_6 [4]. It was possible to obtain single crystals of La_2TeO_6 and Yb_2TeO_6 only after reacting rare-earth sesquioxide (M_2O_3) and tellurium dioxide (TeO_2) in equimolar quantities at 900°C in air, which in turn proved the existence of the structure types mentioned above (La_2TeO_6-type: space group $P2_12_12_1$; Na_2SiF_6-type: space group $P321$) [5] and enabled one to describe the crystal structures of these types in detail. A further rare-earth(III) oxotellurate(VI) composition (M_6TeO_{12}) appeared to be available only as a decomposition product of M_2TeO_6 above 1000°C [6] but structural information is still missing.

2. Experimental

2.1. Synthesis

In a typical solid-state reaction for the titled compound Gd_2TeO_6, Gd_2O_3 (ChemPur, 99.9%) and TeO_3 (Cerac, 99.999%) were mixed in a molar ratio of 1:1 and placed in a silica tube. The vacuum-sealed tube was placed in a furnace and then heated to 800°C. After a reaction time of 10 days, the furnace was cooled down to room temperature with a rate of 5°C/h. On opening the ampoules, colourless pillar-like single crystals could be observed and identified by X-ray structure analysis as Gd_2TeO_6.

2.2. Single crystal X-ray structure determination

A colourless crystal (approximate dimensions: $0.3 \times 0.1 \times 0.05\,mm^3$) was placed in a 0.1 mm diameter

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glass capillary and mounted on a Nonius κ-CCD diffractometer for data collection at 298 K. A preliminary set of cell constants indicating an orthorhombic cell was calculated from reflections harvested from one set of 25 frames. This produced initial orientation matrices determined from 243 reflections. The data collection was carried out using Mo$K\alpha$ radiation (graphite monochromator) with a time frame of 30 s and a detector distance of 4 cm. A randomly oriented region of reciprocal space was surveyed to the extend of 1.5 hemispheres and to a resolution of 62 pm. Four major sections of frames were collected with 0.4° steps in ω at three different φ settings and a detector position of up to 68° in 2θ. The intensity data were corrected for absorption (HABITUS [7]) and decay.

Final cell constants ($a = 532.52(4)$, $b = 916.03(8)$, $c = 1004.60(9)$ pm) were calculated from 9640 reflections of the actual data collection after integration (DENZO-SMN 1.9 [8]). The structure was solved using SHELXS-97 [9] and refined using SHELXL-97 [9]. The space group $P2_12_12_1$ (no. 19) was determined based on the lattice parameters, the intensity statistics and the probable isotypical relationship to La_2TeO_6 [5] finally confirmed by the structure refinement results. A direct-methods solution was calculated which provided all of the atomic positions (Wyckoff sites: 4a) from the E-map. All atoms in the list were refined with anisotropic displacement parameters. The final full-matrix least-squares refinement converged to $R_1 = 0.028$, w$R_2 = 0.050$ and a Flack-x parameter of -0.002 for all data. The crystallographic data are summarized in Table 1. Atomic parameters and important bond distances are given in Tables 2 and 3, respectively.

Table 1
Crystal data and structure refinement for Gd_2TeO_6

Empirical formula	Gd_2O_6Te
Formula weight	538.10 g/mol
Wavelength	71.07 pm (Mo$K\alpha$)
Crystal system	Orthorhombic
Space group	$P2_12_12_1$ (no. 19)
Unit cell dimensions	$a = 532.52(4)$ pm
	$b = 916.03(8)$ pm
	$c = 1004.60(9)$ pm
Molar volume	73.777(8) cm^3/mol
Z	4
Calculated density	7.293 g/cm^3
Absorption coefficient (μ)	32.61 mm^{-1}
Extinction (g)	0.0105(2)
$F(000)$	912
Crystal size	$0.3 \times 0.1 \times 0.05$ mm^3
Theta range	3–35°
Index range	$-8 \leqslant h \leqslant 8$, $-14 \leqslant k \leqslant 14$, $-16 \leqslant l \leqslant 16$
Reflections collected	15,906
Independent reflections	2157
Reflections with $\lvert F_o \rvert > 2\sigma(F_o)$	2078
$R_{int}(R_\sigma)$	0.064 (0.037)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2157/0/83
Goodness-of-fit on F^2	1.078
Final R indices $[\lvert F_o \rvert > 4\sigma(F_o)]$	$R_1 = 0.026$, w$R_2 = 0.050$
R indices (for all data)	$R_1 = 0.028$, w$R_2 = 0.059$
Flack-x parameter	$-0.002(2)$
Largest diff. peak and hole	2.29 and -1.96 $e^- \times 10^6$ pm^{-3}

Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-412447.

Table 2
Atomic coordinates and anisotropic thermal displacement parameters for Gd_2TeO_6

Atom	x/a	y/b	z/c
Gd1	0.03462(5)	0.21732(2)	0.13654(2)
Gd2	0.02304(5)	0.10415(3)	0.53959(2)
Te	0.54009(7)	0.00493(4)	0.35391(3)
O1	0.3347(9)	0.0534(5)	0.2071(4)
O2	0.3168(9)	0.3621(5)	0.2595(4)
O3	0.4199(8)	0.1511(4)	0.4723(4)
O4	0.3137(8)	0.3601(5)	0.6758(4)
O5	0.2268(8)	0.1121(5)	0.9314(4)
O6	0.2561(8)	0.4132(5)	0.0072(4)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Gd1	58(1)	62(1)	51(1)	1(1)	–3(1)	0(1)
Gd2	72(1)	68(1)	49(1)	2(1)	0(1)	4(1)
Te	49(2)	54(1)	40(1)	2(1)	1(1)	1(1)
O1	107(20)	124(20)	48(17)	–1(15)	–47(15)	42(16)
O2	126(20)	96(20)	55(17)	22(15)	–22(15)	–37(16)
O3	118(20)	61(17)	76(16)	–5(14)	7(15)	–24(14)
O4	90(18)	104(18)	36(16)	7(15)	–16(14)	20(14)
O5	72(17)	110(19)	70(17)	–9(16)	2(14)	–22(16)
O6	68(17)	110(20)	49(17)	–24(15)	–15(14)	–8(15)

Table 3
Important internuclear distances for Gd_2TeO_6

Bond	d/pm	Bond	d/pm	Bond	d/pm
Gd1–O1	230.4	Gd2–O3	226.0	Te–O1	188.9
Gd1–O4	233.3	Gd2–O3′	231.1	Te–O2	189.4
Gd1–O2	235.5	Gd2–O2	231.8	Te–O3	190.2
Gd1–O5	236.5	Gd2–O1	234.3	Te–O4	193.4
Gd1–O6	239.0	Gd2–O6	234.3	Te–O5	194.3
Gd1–O5′	249.5	Gd2–O4	245.6	Te–O6	195.7
Gd1–O6′	251.0	Gd2–O5	262.3		

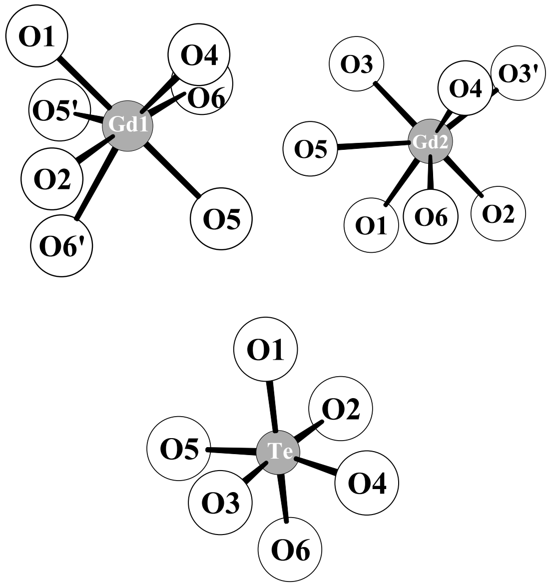

Fig. 1. Oxygen coordination polyhedra about Gd1, Gd2 and Te in Gd_2TeO_6.

3. Results and discussion

In the crystal structure of Gd_2TeO_6, there are nine independent atomic positions as already indicated in the formula for a noncentrosymmetric structure in space group $P2_12_12_1$. The Gd^{3+} cations are coordinated sevenfold by oxygen in form of a square-triangle polyhedron (Gd1) and capped trigonal prism (Gd2), respectively (Fig. 1). The gadolinium–oxygen bond lengths ($d(\mathrm{Gd1-O}) = 230-251\,\mathrm{pm}$, $d(\mathrm{Gd2-O}) = 226-262\,\mathrm{pm}$) are within the normal range as also observed for other gadolinium oxides such as Gd_2O_3 (C-type: 226–239 pm for CN = 6 [10], B-type: 226–274 pm for CN = 7 [11]) or $Gd_2Te_4O_{11}$ (230–255 pm for CN = 8 [12]). Independent of each other, both coordination polyhedra $[GdO_7]$ build chains along [100]: on the one hand Gd1 via edges (two opposite edges of the square: O5–O6) and Gd2 via corners (two corners of an edge of the prism: O3) on the other (Fig. 2). Each of the chains order as hexagonal rod packing. These two kinds of rod packings interpenetrate (Fig. 4) and combine by linkage via edges and corners again (Fig. 3). The result is

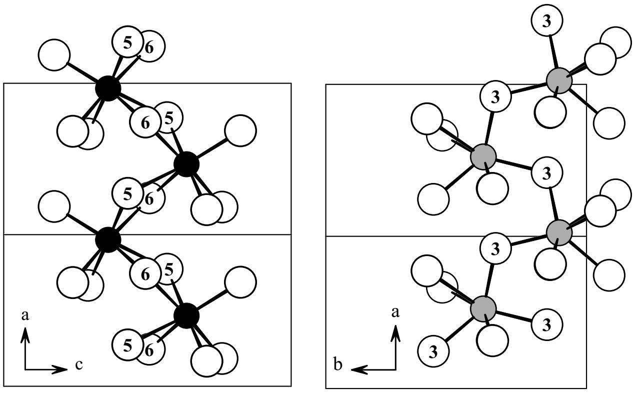

Fig. 2. Linkage of the $[(\mathrm{Gd1})O_7]$ polyhedra via edges and the $[(\mathrm{Gd2})O_7]$ polyhedra via corners to zigzag chains along [100] (view onto (010), left, and (001), right, respectively).

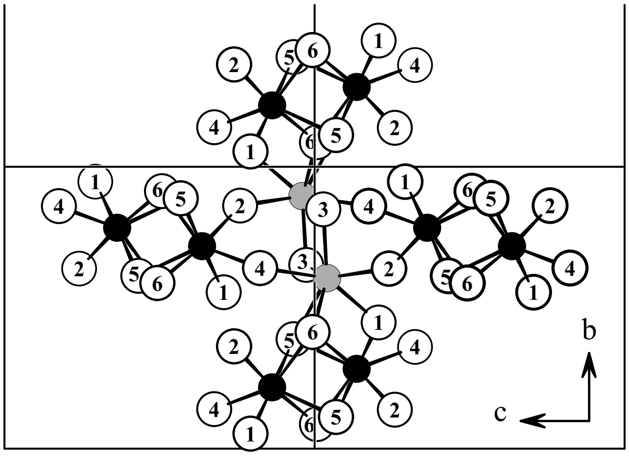

Fig. 3. Linkage of the Gd1 (black) and Gd2 (gray) containing chains leading to a $^{3}_{\infty}\{[GdO_3]^{3-}\}$ framework in Gd_2TeO_6 (O: white spheres, view along [100]).

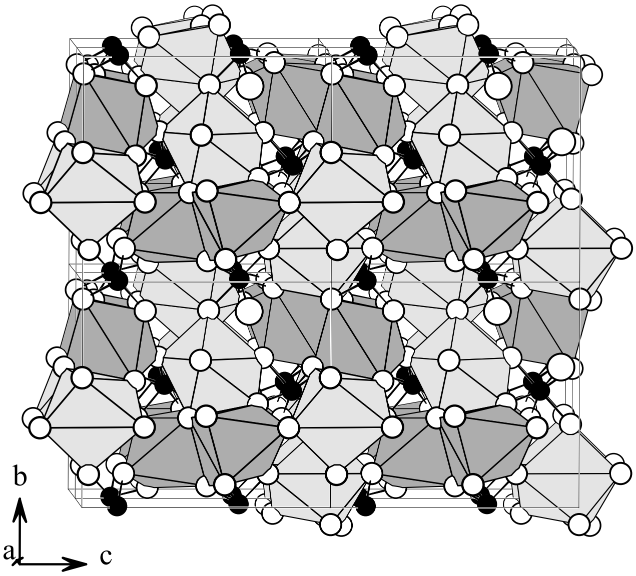

Fig. 4. Crystal structure of Gd_2TeO_6 viewed along [100] (Gd1 polyhedra: medium gray, Gd2 polyhedra: light gray, oxygen atoms are white and tellurium atoms black spheres).

a framework which can be described with the Niggli formula $^3_\infty\{[GdO_3]^{3-}\}$ offering oval channels formed by oxygen atoms. The Te^{6+} cations are surrounded by six oxygen atoms in the shape of a slightly distorted octahedron (Fig. 1, angles $\sphericalangle$(O–Te–O): 84–100°, 165–176°). The tellurium–oxygen distances ($d(Te-O) = 189-196\,pm$) do not differ very much from those in VF_3-type TeO_3 (191 pm, 6×) [13] but also from oxotellurates(IV) (e.g. $Gd_2Te_4O_{11}$ with $d(Te-O) = 186-189\,pm$ for $CN = 3+1$ [12]). In spite of the larger coordination sphere of Te^{6+} ($CN = 6$) versus Te^{4+} ($CN = 3+1+$"lone pair") this fact can be easily understood with the stereochemical "lone-pair" activity in the case of Te^{4+}. Since the Te^{6+} cations do not share any oxygen atoms they are completely isolated from each other, and an extended tellurium–oxygen partial structure can not be described. The isolated $[TeO_6]^{6-}$ octahedra reside in the above-mentioned oval channels of the gadolinium–oxygen framework (Fig. 4). Additional to the good agreement of the internuclear distances (see above) the molar volume of Gd_2TeO_6 ($V_m \approx 73.8\,cm^3/mol$) compares well with the sum of the binaries ($V_m(C\text{-}Gd_2O_3) \approx 47.3$ [10], $V_m(B\text{-}Gd_2O_3) \approx 43.6$ [11] and $V_m(TeO_3) \approx 27.2\,cm^3/mol$ [13]; $\Sigma_1 = 74.5$, $\Sigma_2 = 70.8\,cm^3/mol$). The same holds for the Madelung Parts of the Lattice Energy (MAPLE according to Hoppe [14,15]) where 9722 kcal/mol for Gd_2TeO_6 meet 9748 (Σ_1) or 9729 kcal/mol (Σ_2), respectively, for the sum of the participating binaries ($MAPLE(C\text{-}Gd_2O_3) \approx 3586$ [10], $MAPLE(B\text{-}Gd_2O_3) \approx 3567$ [11] and $MAPLE(TeO_3) \approx 6162\,kcal/mol$ [13]).

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