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Caesium Gadolinium Tetratelluride

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Abstract

The new ternary gadolinium telluride CsGdTe_4 was prepared *via* the molten flux method. It is a layer compound containing Te_2^{2-} tellurium dianions. Layers of Gd centres are sandwiched by Te layers leading to $[\text{GdTe}_4]_n^{n-}$ layers which are separated by Cs cations. Within a $[\text{GdTe}_4]_n^{n-}$ layer, the Gd cations are in a square-antiprismatic coordination of eight Te anions.

Comment

In the alkali metal–lanthanoid–chalcogenide system, beside the two structure types of composition ALnQ_2 crystallizing in the simple NaCl-type structure with statistically distributed A^+ and Ln^{3+} cations or the $\alpha\text{-NaFeO}_2$ structure type, a number of new structure types for ternary and quaternary alkali metal–lanthanoid–chalcogenide compounds have been prepared recently using the polychalcogenide flux method. These include NaLnS_3 ($\text{Ln} = \text{La}, \text{Ce}$; Kanatzidis & Sutorik, 1995), KLn_2CuQ_6 ($\text{Ln} = \text{La}, \text{Ce}$; $Q = \text{S}, \text{Se}$) (Sutorik, Albritton-Thomas, Kannewurf & Kanatzidis, 1994; Sutorik, Albritton-Thomas, Hogan, Kannewurf & Kanatzidis, 1996) and ALnQ_4 ($A = \text{K}, \text{Rb}, \text{Cs}$; $\text{Ln} = \text{Ce}, \text{Tb}, \text{Gd}$; $Q = \text{Se}, \text{Te}$) (Sutorik & Kanatzidis, 1992; Kanatzidis & Sutorik, 1995). Here we report the structure of CsGdTe_4 , a new member in the growing family of compounds with the composition ALnQ_4 .

The structure of CsGdTe_4 is built up from layers of $[\text{GdTe}_4]_n^{n-}$ separated by Cs cations. The $[\text{GdTe}_4]_n^{n-}$ layers comprise a square-planar Gd layer with Te_2^{2-} layers above and below it. The resulting scheme represents a stacking order of Cs—Te—Gd—Te layers along the [001] direction. The Te_2^{2-} layers consist of Te_2^{2-} anions each bridging four Gd centers in a $\mu_4\text{-}\eta^1$ mode. Within the $[\text{GdTe}_4]_n^{n-}$ layers, the Gd cations are in an ideal square-antiprismatic environment of Te with a Gd—Te distance of 3.2132(4) Å. This distance is only slightly longer than the Gd—Te distances in the binary telluride Gd_2Te_3 ($\langle \text{Gd—Te} \rangle = 3.126$ and 3.189 Å for the two crystallographically independent Gd atoms; Swinnea, Steinfink & Danielson, 1987). The Cs

cations are in the same square-antiprismatic environment of Te as the Gd cations. The Cs—Te distance of 3.9112(5) Å is in good agreement with the values reported for CsTe_4 ($\langle \text{Cs—Te} \rangle = 3.954$ Å; Böttcher & Kretschmann, 1982), Cs_2Te_5 ($\langle \text{Cs1—Te} \rangle = 3.929$,

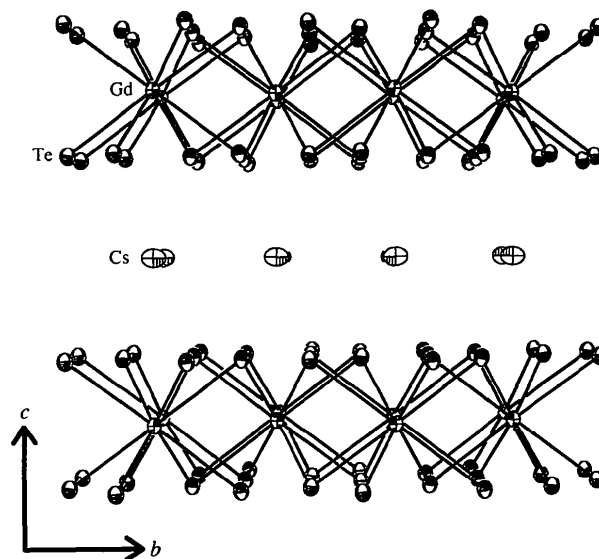


Fig. 1. The structure of CsGdTe_4 . $[\text{GdTe}_4]_n^{n-}$ layers containing channels parallel to [110] are separated by Cs ions. Displacement ellipsoids are plotted at the 70% probability level.

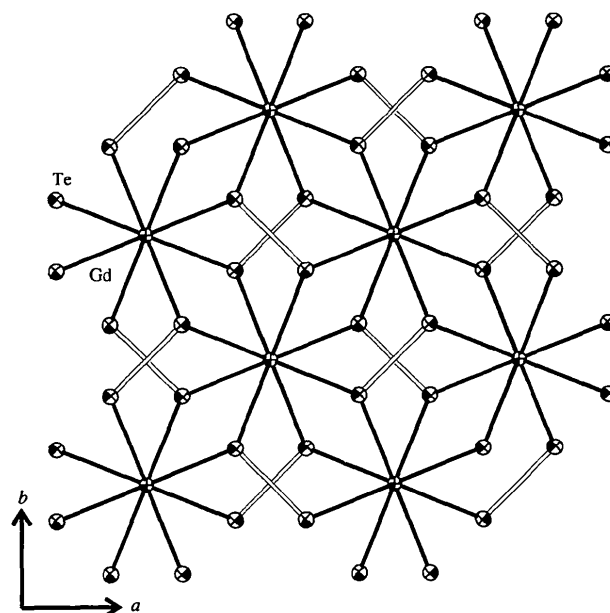


Fig. 2. A view perpendicular to a $[\text{GdTe}_4]_n^{n-}$ layer within the (110) plane (Te—Te bonds are printed open for clarity). Displacement ellipsoids are plotted at the 70% probability level.

$\langle \text{Cs—Te} \rangle = 3.925 \text{ \AA}$; Böttcher & Kretschmann, 1985) or Cs₃Te₂₂ ($\langle \text{Cs—Te} \rangle = 3.892 \text{ \AA}$; Sheldrick & Wachhold, 1995).

Another feature of CsGdTe₄ is the presence of channels bound by Te on two sides and Gd on the others running parallel to the (110) plane within the [GdTe₄]_nⁿ⁻ layers. Their diameters are 4.862 (Gd ··· Gd) and 4.203 Å (Te ··· Te). The structure of CsGdTe₄ is closely related to the structure of NbTe₄ (Selte & Kjekshus, 1964). In NbTe₄, the Nb atoms are in a similar square-antiprismatic Te environment to Cs and Gd in CsGdTe₄. The difference is that in NbTe₄ the layer character is lost and the structure is better described as columns of face-sharing square antiprisms interconnected by Te—Te bonds.

Experimental

The title compound was prepared by the reaction of Cs₂Te₃ (300 mg, 0.46 mmol), Gd (18.9 mg, 0.12 mmol), Cu (14.6 mg, 0.23 mmol) and Te (118.7 mg, 0.93 mmol) in a 4:1:2:8 ratio. Cs₂Te₃ was prepared by the reaction of stoichiometric amounts of Cs and Te in liquid ammonia under an argon atmosphere. In a dry box, the starting materials were thoroughly mixed and then loaded into a Pyrex ampoule which was subsequently evacuated (4×10^{-5} mbar; 1 bar = 10^5 Pa) and sealed. The ampoule was placed in a computer-controlled furnace and was heated to 723 K within 5 h. It was held at this temperature for 6 days and then slowly cooled to room temperature with a cooling rate of 3 K h⁻¹. The resultant melt was washed with degassed DMF to remove unreacted caesium polytelluride. Within the residue small rectangular crystals of CsGdTe₄ with a silver lustre were found.

Crystal data

CsGdTe ₄	Mo K α radiation
$M_r = 800.56$	$\lambda = 0.71073 \text{ \AA}$
Tetragonal	Cell parameters from 62 reflections
<i>P4/nbm</i>	$\theta = 36.2\text{--}48.8^\circ$
$a = 6.8753 (10) \text{ \AA}$	$\mu = 24.221 \text{ mm}^{-1}$
$c = 9.419 (2) \text{ \AA}$	$T = 293 (2) \text{ K}$
$V = 445.23 (13) \text{ \AA}^3$	Plate
$Z = 2$	$0.14 \times 0.14 \times 0.028 \text{ mm}$
$D_x = 5.972 \text{ Mg m}^{-3}$	Black
D_m not measured	

Data collection

Stoe AED-II diffractometer	$R_{\text{int}} = 0.0394$
ω - 2θ scans	$\theta_{\text{max}} = 37.47^\circ$
Absorption correction:	$h = 0 \rightarrow 11$
numerical	$k = 0 \rightarrow 11$
$T_{\text{min}} = 0.1032$, $T_{\text{max}} = 0.5083$	$l = -16 \rightarrow 12$
2196 measured reflections	4 standard reflections
652 independent reflections	frequency: 120 min
	intensity decay: negligible

Refinement

Refinement on F^2	$\Delta\rho_{\text{max}} = 1.26 \text{ e \AA}^{-3}$
$R[F^2 > 2\sigma(F^2)] = 0.021$	$\Delta\rho_{\text{min}} = -2.05 \text{ e \AA}^{-3}$

$wR(F^2) = 0.042$

$S = 1.007$

651 reflections

12 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0183P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.0015 (2)

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
Gd	1/4	1/4	1/2	0.01132 (8)
Te	0.60683 (2)	-1/2 + x	0.30605 (3)	0.01346 (6)
Cs	1/4	1/4	0	0.02749 (12)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Gd—Te ⁱ	3.2132 (4)	Te—Te ⁱⁱⁱ	2.7842 (6)
Gd—Cs ⁱⁱ	4.7095 (10)	Cs—Te ^{iv}	3.9112 (5)
Te ⁱ —Gd—Te ^v	142.281 (9)	Te ^{iv} —Cs—Te ^{ix}	149.199 (8)
Te ⁱ —Gd—Te ^{vi}	80.453 (14)	Te ^{iv} —Cs—Te ^x	57.097 (9)
Te ^v —Gd—Te ^{vi}	71.142 (8)	Te ^{ix} —Cs—Te ^x	150.846 (7)
Te ⁱ —Gd—Te ^{vii}	144.321 (8)	Te ^x —Cs—Te	103.149 (13)
Te ^{vii} —Gd—Te ^{viii}	110.71 (2)	Te ^{ix} —Cs—Te ⁱ	85.04 (2)
Te ^{vii} —Gd—Te ^{viii}	81.687 (13)	Te ^x —Cs—Te ⁱ	102.305 (14)
Te ^{viii} —Te—Gd	108.860 (4)	Te ⁱ —Cs—Te ^{xi}	149.199 (8)
Gd—Te—Gd ⁱⁱ	98.313 (13)		

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

The highest residual peak, $\Delta\rho_{\text{max}}$, is found in the neighbourhood of Gd.

Data collection: *DIF4* (Stoe & Cie, 1991a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1991b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990a). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC XP* (Sheldrick, 1990b). Software used to prepare material for publication: *SHELXL93 CIFTAB*.

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1154). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A New Mixed Oxide with $(\text{Bi}_{12}\text{O}_{14})_n$ Columns: $\text{PbBi}_{12}\text{Mo}_5\text{O}_{34}$

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Abstract

The title compound, lead(II) dodecabis(III) pentamolybdenum(VI) oxide, was prepared by solid-state methods. The structure consists of $(\text{Bi}_{12}\text{O}_{14})_n^{8n+}$ columns surrounded by $(\text{MoO}_4)^{2-}$ tetrahedra. The Pb atoms occupy specific sites between four tetrahedra.

Comment

This work was carried out as part of our studies of $M^*-(\text{V},\text{Mo},\text{W})-\text{O}$ systems with ns^2 lone-pair elements M^* (Galy, Enjalbert, Millan & Castro, 1993; Castro, Millan, Enjalbert, Snoeck & Galy, 1994; Sorokina, Enjalbert, Baules, Castro & Galy, 1996). In the Aurivillius-type series $(\text{Bi}_2\text{O}_2)_2\text{V}_2^{3+}\text{V}_2^{4+}\text{O}_{7-x}$, the $(\text{Bi}_2\text{O}_2)_{2n}$ layers alternate with $(\text{V}_2\text{O}_{7-x})_n$ layers. Oxygen non-stoichiometry, with the simultaneous presence of vanadium(IV) and vanadium(V) in VO_6 octahedra and VO_5 square pyramids, is responsible for their ionic conduction properties. In order to modify these interesting physical properties, we have considered the possible alteration of the two types of layers: on the one hand, the association of lone-pair elements Bi and Pb, and on the other, the association of transition metals V and Mo.

The new compound synthesized, $\text{PbBi}_{12}\text{Mo}_5\text{O}_{34}$, is not a layered structure as expected, but contains columns of $(\text{Bi}_{12}\text{O}_{14})_n$, MoO_4 tetrahedra and specific sites for the Pb atoms. The projection of the structure onto the the (010) plane (Fig. 1) shows the organization of the $(\text{Bi}_{12}\text{O}_{14})_n$ columns in the form of roses formed by Bi and O atoms. One rose is surrounded by ten MoO_4 tetrahedra, two of which are disordered.

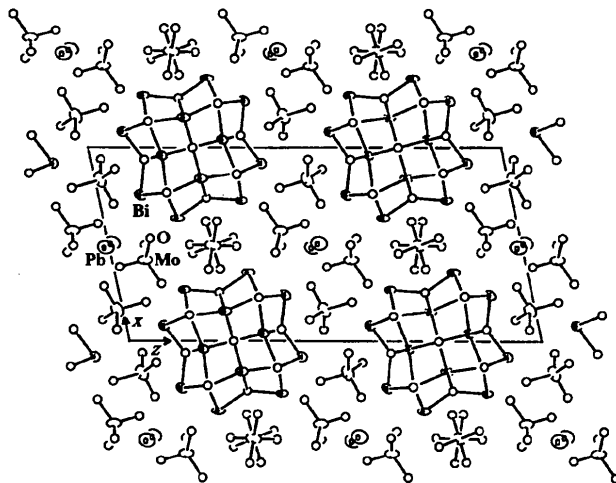


Fig. 1. Projection of the structure onto the (010) plane.

The Pb atoms are disordered around the $2b$ site at $1/2, 1/2, 0$ with 50% site occupancy. The distance between the two potential crystallographic sites is 0.43 \AA . The partial view in Fig. 2, slightly tilted for clarity, specifies the atomic numbering scheme.

The roses are the projections of infinite $(\text{Bi}_{12}\text{O}_{14})_n$ columns along the $[010]$ direction. The Bi1 and Bi2 atoms in the rose are bonded to four O atoms ($\text{Bi}-\text{O} < 2.43 \text{ \AA}$). The external Bi3, Bi4, Bi5 and Bi6 atoms are bonded to three O atoms ($\text{Bi}-\text{O} < 2.20 \text{ \AA}$). Their environment is completed by other O atoms belonging to the tetrahedra. The coordination number of Bi^{3+} increases from 4 to 6 if Bi—O distances of up to 2.72 \AA are included.

The Bi atoms are at the corners of Bi_6 octahedra. Two such octahedra share an edge in the equatorial plane (Fig. 3a). Pairs of such Bi_6 octahedra are then stacked along the $[010]$ direction after a 90° rotation (Fig. 3b). The residual densities lie around Bi atoms at $0.7\text{--}0.8 \text{ \AA}$ from their crystallographic sites indicating possible small displacements. The O atoms of the MoO_4 tetrahedra exhibit relatively large displacement parameters indicative of an important libration. This phenomenon could be reasonably related to the properties of anionic conduction exhibited by these types of compounds. This disorder was evident in the refinement only for the tetrahedron associated with the Mo1 atom