

# Cs<sub>2</sub>Gd<sub>6</sub>N<sub>2</sub>Te<sub>7</sub>: The first quaternary nitride telluride of the lanthanides

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## Abstract

The first quaternary nitride telluride with trivalent gadolinium, Cs<sub>2</sub>Gd<sub>6</sub>N<sub>2</sub>Te<sub>7</sub>, was obtained by the reaction of metallic gadolinium with cesium azide, elemental tellurium, and gadolinium trichloride as well as cesium chloride as flux at 900 °C for 7 days in evacuated silica tubes. Single crystals occur as long black needles and crystallize in the monoclinic space group *C2/m* ( $a = 2403.1(2)$  pm,  $b = 424.03(3)$  pm,  $c = 1142.91(7)$  pm,  $\beta = 103.709(4)^\circ$ ,  $Z = 2$ ). Three crystallographically different Gd<sup>3+</sup> cations constitute the structure, two are coordinated by one N<sup>3-</sup> ( $d(\text{Gd}(1/2)\text{--N}) = 217$  pm) and five Te<sup>2-</sup> anions ( $d(\text{Gd}(1/2)\text{--Te}) = 305\text{--}326$  pm), and the third Gd<sup>3+</sup> by two N<sup>3-</sup> ( $d(\text{Gd}(3)\text{--N}) = 244$  pm) and four Te<sup>2-</sup> anions ( $d(\text{Gd}(3)\text{--Te}) = 316\text{--}317$  pm), all forming distorted octahedra about Gd<sup>3+</sup>. The Cs<sup>+</sup> cation shows a perfect bicapped trigonal prism (C.N. = 8,  $d(\text{Cs}\text{--Te}) = 383\text{--}431$  pm) as coordination sphere. Two of these polyhedra are condensed via a common (non-capped) rectangular face building up double prisms [Cs<sub>2</sub>Te<sub>12</sub>]<sup>22-</sup>. Further linkage via triangular faces (along [0 1 0]) and two of the four caps (along [0 0 1]) results in corrugated layers [Cs<sub>2</sub>Te<sub>7</sub>]<sup>12-</sup> running parallel to (1 0 0). However, the main feature of the crystal structure comprises N<sup>3-</sup>-centered (Gd<sup>3+</sup>)<sub>4</sub> tetrahedra ( $d(\text{N}\text{--Gd}) = 217$  pm (2 ×) and 244 pm (2 ×);  $\angle(\text{Gd}\text{--N}\text{--Gd}) = 107^\circ$  (2 + 2 + 1 ×) and 121° (1 ×)), which are connected via two vertices each to build up one-dimensional infinite chains  $\frac{1}{\infty}\{[\text{N}(\text{Gd}1)_{1/1}^t(\text{Gd}2)_{1/1}^t(\text{Gd}3)_{2/2}^v]^{6+}\}$  (t = terminal, v = vertex-shared) along [0 1 0] like in the structure of the M<sub>3</sub>NCh<sub>3</sub>-type nitride chalcogenides with M = La–Nd, Sm, Gd–Dy, and Ch = S, Se.

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**Keywords:** Lanthanides; Cesium; Gadolinium; Nitrides; Tellurides; Crystal structure

## 1. Introduction

In the last decade, nitride chalcogenides of the lanthanides (and their halide derivatives) have been demonstrated to possess an extremely rich chemistry of formula and structural types [1]. However, N<sup>3-</sup>-centered (M<sup>3+</sup>)<sub>4</sub> tetrahedra, which can occur isolated or condensed, provide the main feature in the crystal structures for all of them. In ternary compounds such as M<sub>3</sub>NCh<sub>3</sub> (M = La–Nd, Sm, Gd–Dy; Ch = S, Se) [2] these [NM<sub>4</sub>]<sup>9+</sup> tetrahedra are connected via two corners forming linear chains  $\frac{1}{\infty}\{[\text{N}(\text{M})_{2/1}^t(\text{M}')_{2/2}^v]\}$  (t = terminal, v = vertex-shared). The ratio N<sup>3-</sup> : M<sup>3+</sup> = 1 : 2, realized for the composition M<sub>4</sub>N<sub>2</sub>Ch<sub>3</sub> (M = La–Nd, Sm, Tb; Ch = S, Se, Te) [3], requires a higher degree of linkage of the N<sup>3-</sup>-centered (M<sup>3+</sup>)<sub>4</sub> tetrahedra. The crystal structures of Sm<sub>4</sub>N<sub>2</sub>S<sub>3</sub> [4] and Tb<sub>4</sub>N<sub>2</sub>Se<sub>3</sub> [5,6] show also infinite chains, but now by sharing *cis*-oriented edges according to  $\frac{1}{\infty}\{[\text{N}(\text{M})_{1/1}^t(\text{M}')_{3/3}^e]^{3+}\}$  (e = edge-connecting) in

this case. The nitride chalcogenides Pr<sub>4</sub>N<sub>2</sub>S<sub>3</sub> [7] and M<sub>4</sub>N<sub>2</sub>Se<sub>3</sub> (M = Pr, Nd) [6,7] present a layered arrangement, dominated by N<sup>3-</sup>-centered (M<sup>3+</sup>)<sub>4</sub> tetrahedra again, which share a common edge first. Continuing linkage of the resulting bitetrahedral [N<sub>2</sub>M<sub>6</sub>]<sup>12+</sup> units (also a discrete feature in the crystal structure of M<sub>5</sub>NSe<sub>6</sub> [8] with M = Pr) via the *non*-connected vertices to layers according to  $\frac{2}{\infty}\{[\text{N}(\text{M})_{2/2}^e(\text{M}')_{2/2}^v]^{3+}\}$  forms different kinds of tetrahedral nets, which can be described as layers consisting of “four- and eight-rings” for Pr<sub>4</sub>N<sub>2</sub>S<sub>3</sub> and as layers of exclusively “six-rings” for Pr<sub>4</sub>N<sub>2</sub>Se<sub>3</sub>. Recently we could prepare and characterize the first nitride tellurides of the lanthanides, M<sub>4</sub>N<sub>2</sub>Te<sub>3</sub> (M = La–Nd) [9], on the basis of single-crystal X-ray diffraction data. The crystal structure is dominated by N<sup>3-</sup>-centered (M<sup>3+</sup>)<sub>4</sub> tetrahedra of course, which build up *non*-linear infinite chains  $\frac{1}{\infty}\{[\text{N}(\text{M})_{4/2}^e]^{3+}\}$  by sharing *trans*-oriented edges.

## 2. Experimental data

Cs<sub>2</sub>Gd<sub>6</sub>N<sub>2</sub>Te<sub>7</sub>, the first quaternary nitride telluride with cesium and gadolinium, was obtained by the reaction of elemental gadolinium (Gd: ChemPur;

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Table 1  
Cs<sub>2</sub>Gd<sub>6</sub>N<sub>2</sub>Te<sub>7</sub>: crystallographic data and their determination

Formula	Cs <sub>2</sub> Gd <sub>6</sub> N <sub>2</sub> Te <sub>7</sub>
Crystal system	Monoclinic
Space group	C2/m (no. 12)
Formula units (Z)	2
Lattice constants <sup>a</sup>	a = 2403.12(15) pm, b = 424.03(3) pm, c = 1142.91(7) pm, β = 103.709(4)°
Molar volume, V <sub>m</sub> (cm <sup>3</sup> mol <sup>-1</sup> )	340.68(4)
Calculated density, D <sub>x</sub> (g cm <sup>-3</sup> )	6.254
F(000)	1744
Diffraction/wavelength	Kappa-CCD (Nonius)/λ = 71.07 pm (Mo-Kα)
Index range	±h <sub>max</sub> = 32, ±k <sub>max</sub> = 5, ±l <sub>max</sub> = 15
Θ <sub>max</sub> (°)	28.3
Absorption coefficient, μ (mm <sup>-1</sup> )	29.33
Data corrections	Background, polarization and Lorentz factors; numerical absorption correction: program X-SHAPE [11]
Collected reflections/unique ones	13978/1590
R <sub>int</sub> /R <sub>σ</sub>	0.092/0.053
Structure solution and refinement	Program package SHELX-93 and -97 [12]
Scattering factors	International Tables, vol. C [13]
R <sub>1</sub> (with 4σ barrier)	0.037 (for 1386 reflections)
R <sub>1</sub> /wR <sub>2</sub> /Goodness of Fit (GooF) (for all reflections)	0.050/0.061/1.122
Extinction (g)	0.00022(3)
Residual electron density, ρ (e <sup>-</sup> × 10 <sup>6</sup> pm <sup>-3</sup> )	1.91 (max.), -1.72 (min.)

<sup>a</sup> Single crystal data, further details of the crystal structure investigation can be obtained from the Fachinformationszentrum (FIZ) Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: +49 7247 808 666; e-mail: [crysdta@fiz-karlsruhe.de](mailto:crysdta@fiz-karlsruhe.de)), on quoting the depository number CSD-391315 for Cs<sub>2</sub>Gd<sub>6</sub>N<sub>2</sub>Te<sub>7</sub>.

Table 2  
Cs<sub>2</sub>Gd<sub>6</sub>N<sub>2</sub>Te<sub>7</sub>: atomic coordinates and anisotropic thermal displacement parameters, U<sub>ij</sub> (pm<sup>2</sup>)<sup>a</sup>

Atom	Wyckoff position	x/a	y/b	z/c
Cs	4i	0.06636(4)	0	0.69714(9)
Gd1	4i	0.16467(2)	0	0.39163(5)
Gd2	4i	0.21612(2)	0	0.13008(5)
Gd3	4i	0.41009(2)	0	0.86393(5)
N	4i	0.1386(4)	0	0.1964(9)
Te1	2a	0	0	0
Te2	4i	0.24075(3)	0	0.66158(8)
Te3	4i	0.33622(3)	0	0.05830(8)
Te4	4i	0.42506(3)	0	0.59543(8)

Atom	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>23</sub>	U <sub>13</sub>	U <sub>12</sub>
Cs	307(5)	300(5)	313(5)	0	28(4)	0
Gd1	144(3)	150(3)	140(3)	0	19(2)	0
Gd2	112(3)	136(3)	170(3)	0	44(2)	0
Gd3	104(3)	141(3)	162(3)	0	23(2)	0
N	81(41)	163(51)	115(50)	0	-3(37)	0
Te1	167(6)	148(6)	374(8)	0	-104(6)	0
Te2	160(4)	153(4)	163(4)	0	13(3)	0
Te3	134(4)	154(4)	171(4)	0	38(3)	0
Te4	163(4)	164(4)	227(5)	0	81(3)	0

<sup>a</sup> Defined as temperature factor according to:  $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$ .

Table 3  
Cs<sub>2</sub>Gd<sub>6</sub>N<sub>2</sub>Te<sub>7</sub>: selected internuclear distances, d (pm), and angles, ∠ (°)

Cs	Gd1	Gd2			
-Te3 (2×)	383.2	-N (1×)	217.0	-N (1×)	217.1
-Te4 (2×)	393.8	-Te4 (2×)	305.3	-Te3 (2×)	307.1
-Te4' (2×)	400.6	-Te2 (1×)	319.2	-Te2 (2×)	317.3
-Te1 (1×)	414.0	-Te2' (2×)	326.9	-Te3' (1×)	318.2
-Te2 (1×)	430.5				
Gd3	N				
-N (2×)	244.1	-Gd1 (1×)	217.0	Gd1-N-Gd3 (2×)	107.0
-Te3 (1×)	315.5	-Gd2 (1×)	217.1	Gd2-N-Gd3 (2×)	107.2
-Te1 (2×)	316.1	-Gd3 (2×)	244.1	Gd1-N-Gd2 (1×)	107.3
-Te4 (1×)	317.3			Gd3-N-Gd3' (2×)	120.6

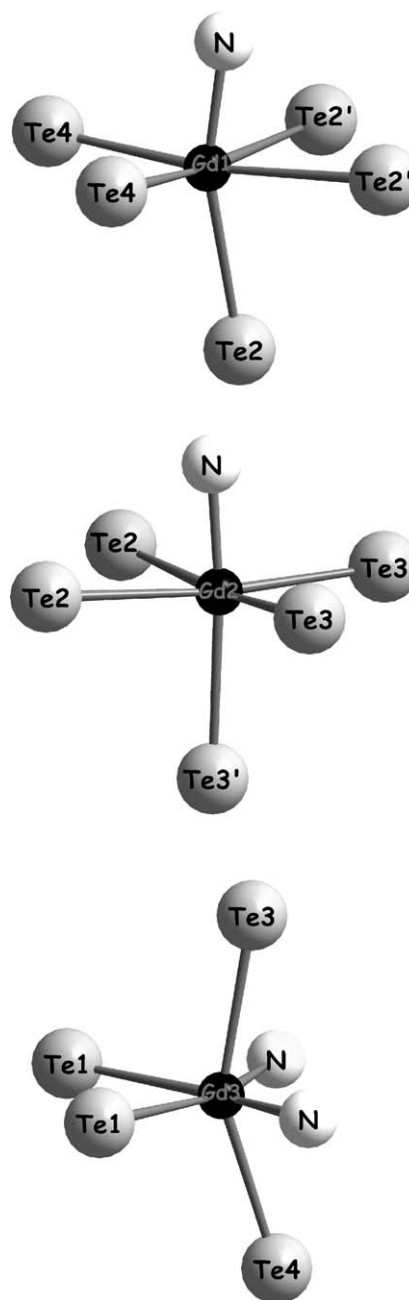
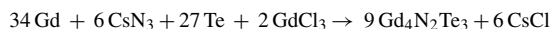


Fig. 1. Coordination polyhedra [(Gd1)NTe<sub>5</sub>], [(Gd2)NTe<sub>5</sub>], and [(Gd3)N<sub>2</sub>Te<sub>4</sub>] (top to bottom) in the crystal structure of Cs<sub>2</sub>Gd<sub>6</sub>N<sub>2</sub>Te<sub>7</sub>.

99.9%) with cesium azide ( $\text{CsN}_3$ ; Ferak; 99.9%), tellurium (Te: ChemPur; 99.9999%) as well as gadolinium trichloride ( $\text{GdCl}_3$ ; prepared from  $\text{Gd}_2\text{O}_3$  (Johnson–Matthey; 99.999%) by the ammonium–chloride route [10]) and cesium chloride ( $\text{CsCl}$ ; ChemPur; 99.9%) as flux. In attempts to obtain  $\text{Gd}_4\text{N}_2\text{Te}_3$  with a crystal structure isotypic to the  $\text{M}_4\text{N}_2\text{Te}_3$ -type homologues with  $\text{M} = \text{La–Nd}$  [9] according to



the reactants ( $\text{Gd}$ ,  $\text{CsN}_3$ ,  $\text{Te}$ ,  $\text{GdCl}_3$ ) were handled under the inert argon atmosphere of a glove box (M. Braun, Garching) and then heated to  $900^\circ\text{C}$  for 7 days in evacuated silica tubes. Single crystals occur as long black needles in amounts of at least 50% and turned out to possess a heretofore unknown basis-centered monoclinic unit cell (space group:  $C2/m$ ) with parameters like  $a = 2403.1(2)$  pm,  $b = 424.03(3)$  pm,  $c = 1142.91(7)$  pm and  $\beta = 103.709(4)^\circ$ . Complete single-crystal X-ray diffraction data refinement (Tables 1 and 2) results in the first quaternary nitride telluride with cesium and gadolinium:  $\text{Cs}_2\text{Gd}_6\text{N}_2\text{Te}_7$ . In order to increase the yield of this new nitride telluride the stoichiometric mixtures of the educts were changed according to



for reactions at  $900^\circ\text{C}$  of 1 week. Under these circumstances  $\text{Cs}_2\text{Gd}_6\text{N}_2\text{Te}_7$  became the single-phase nitride telluride product in almost quantitative yields. It was not possible to isolate a pure sample of this nitride telluride so far, however, because by rinsing off the water-soluble by-products ( $\text{GdCl}_3$  and the fluxing agent  $\text{CsCl}$ )  $\text{Cs}_2\text{Gd}_6\text{N}_2\text{Te}_7$  begins to decompose by hydrolysis after 10–15 min, leaving behind black tellurium and colourless gadolinium hydroxide after ammonia evolution.

### 3. Structure description and discussion

In the crystal structure of  $\text{Cs}_2\text{Gd}_6\text{N}_2\text{Te}_7$  there are three crystallographically different  $\text{Gd}^{3+}$  cations present, two of them coordinated by one  $\text{N}^{3-}$  and five  $\text{Te}^{2-}$  anions, the third by two  $\text{N}^{3-}$  and four  $\text{Te}^{2-}$  anions, forming distorted octahedra about each  $\text{Gd}^{3+}$  (Fig. 1, top to bottom). The distances  $d(\text{Gd}^{3+}–\text{N}^{3-})$  amount to 217–244 pm and  $d(\text{Gd}^{3+}–\text{Te}^{2-})$  to 305–327 pm, respectively, as shown in Table 3. These values are in good agreement with the Gd–N distances in the crystal structures of  $\text{Gd}_3\text{NS}_3$  (220–232 pm) [2] or  $\text{Gd}_2\text{NCl}_3$  (226–228 pm) [14] and  $\text{Gd}_3\text{NCl}_6$  (224–231 pm) [15] as well as with the Gd–Te distances in gadolinium sesquitelluride  $\text{Gd}_2\text{Te}_3$  [16] with  $\text{U}_2\text{S}_3$ -type structure (311–323 pm, C.N. = 7) or  $\text{Cs}_3\text{Gd}_7\text{Te}_{12}$  (304–322 pm, C.N. = 6) [17]. The  $\text{Cs}^+$  cation shows a perfect bicapped trigonal prism (C.N. = 8) as coordination figure due to its site symmetry  $m$  with distances  $d(\text{Cs}^+–\text{Te}^{2-})$  of 383–431 pm (Fig. 2, above). The binary telluride  $\text{Cs}_2\text{Te}$  [18] (in contrast to most of the other alkali-metal chalcogenides,  $\text{A}_2\text{Ch}$ , with *no anti*- $\text{CaF}_2$ -type structure) shows distances that again agree well (371–378 pm, C.N. = 4 and 5) with the title compound and the same is true for the Cs–Te distances in the ternary telluride  $\text{Cs}_3\text{Gd}_7\text{Te}_{12}$  (368–414 pm, C.N. = 6 and 7) [17]. Two of these  $[\text{CsTe}_8]^{15-}$  polyhedra (Fig. 2) are condensed via a common (*non*-capped) rectangular face building up double prisms  $[\text{Cs}_2\text{Te}_{12}]^{22-}$ .

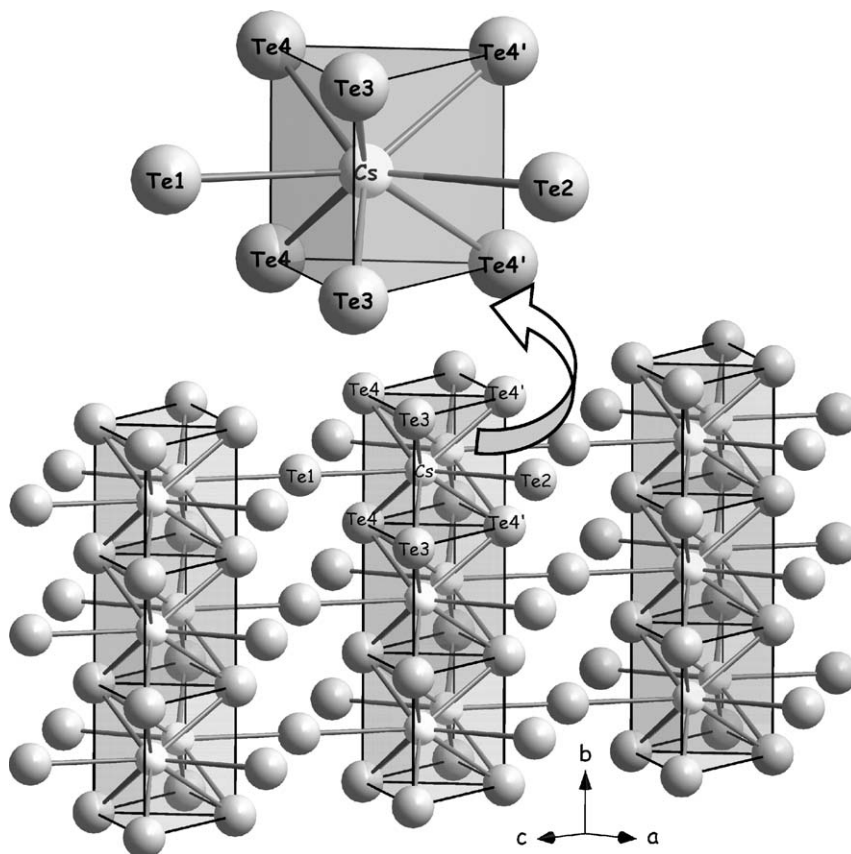


Fig. 2. Coordination polyhedron  $[\text{CsTe}_8]$  (above) and its condensation to corrugated layers  $\frac{2}{\infty} \{([\text{Cs}(\text{Te}_4)_{4/4}^f(\text{Te}_3)_{2/2}^f(\text{Te}_1)_{1/2}^v(\text{Te}_2)_{1/1}^i]_2)^{12-}\}$  (below) in the crystal structure of  $\text{Cs}_2\text{Gd}_6\text{N}_2\text{Te}_7$ .

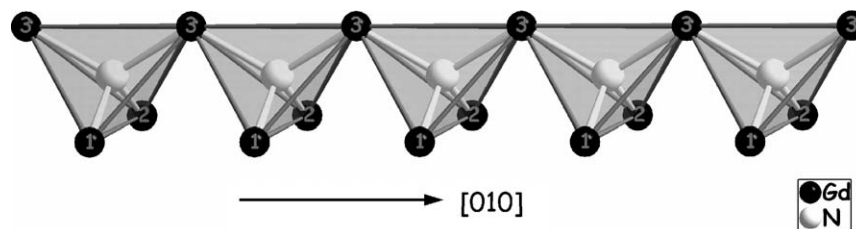


Fig. 3. Infinite chain  ${}^1_{\infty}\{[N(\text{Gd}1)_{1/1}^t(\text{Gd}2)_{1/1}^t(\text{Gd}3)_{2/2}^v]^{6+}\}$  of vertex-connected  $[\text{NGd}_4]^{9+}$  tetrahedra along  $[0\ 1\ 0]$  in the crystal structure of  $\text{Cs}_2\text{Gd}_6\text{N}_2\text{Te}_7$ .

Table 4  
 $\text{Cs}_2\text{Gd}_6\text{N}_2\text{Te}_7$ : motifs of mutual adjunction [21]

	N	Te1	Te2	Te3	Te4	C.N.
Cs	0/0	1/2	1/1	2/2	4/4	8
Gd1	1/1	0/0	3/3	0/0	2/2	6
Gd2	1/1	0/0	2/2	3/3	0/0	6
Gd3	2/2	2/4	0/0	1/1	1/1	6
C.N.	4	6	6	6	7	

Further linkage via triangular faces (along  $[0\ 1\ 0]$ ) and two of the four caps (along  $[0\ 1\ 0]$ ) results in the formation of corrugated layers  ${}^2_{\infty}\{([\text{Cs}(\text{Te}4)_{4/4}^f(\text{Te}3)_{2/2}^f(\text{Te}1)_{1/2}^v(\text{Te}2)_{1/1}^t]^{12-}\}$  ( $t$  = terminal,  $v$  = vertex-connecting,  $f$  = face-connecting; compare also Table 4). However, the main feature of the crystal structure comprises  $\text{N}^{3-}$ -centered  $(\text{Gd}^{3+})_4$  tetrahedra which are fused via two  $(\text{Gd}3)^{3+}$  vertices to build up one-dimensional infinite chains  ${}^1_{\infty}\{[N(\text{Gd}1)_{1/1}^t(\text{Gd}2)_{1/1}^t(\text{Gd}3)_{2/2}^v]^{6+}\}$  ( $t$  = terminal,  $v$  = vertex-sharing) along  $[0\ 1\ 0]$  (Fig. 3). The longest Gd–Gd distance within this chain is 424 pm ( $\equiv a$ ), which corresponds well to the large deviation of the corresponding tetrahedral angle  $\sphericalangle(\text{Gd}–\text{N}–\text{Gd}) = 121^\circ$ . This kind of  $[\text{NM}_4]^{9+}$ -tetrahedral linkage is well-known from the crystal structure of the ternary nitride

chalcogenides  $\text{M}_3\text{NCh}_3$  ( $\text{M} = \text{La}–\text{Nd}$ ,  $\text{Sm}$ ,  $\text{Gd}–\text{Dy}$ ;  $\text{Ch} = \text{S}$ ,  $\text{Se}$ ) [2] already. These strands  ${}^1_{\infty}\{[\text{NGd}_3]^{6+}\}$  reside in the commensurate layer  ${}^2_{\infty}\{[\text{CsTe}_{3.5}]^{6-}\}$  and assure the three-dimensional interconnection to a framework as well as the charge balance for electroneutrality. Fig. 4 shows a view of the complete crystal structure of  $\text{Cs}_2\text{Gd}_6\text{N}_2\text{Te}_7$  along  $[0\ 1\ 0]$ .

With the intention to prepare ternary lanthanide(III) nitride tellurides, we only could successfully obtain the  $\text{M}_4\text{N}_2\text{Te}_3$ -type representatives for  $\text{M} = \text{La}–\text{Nd}$  [9] regardless of the nitrogen source ( $\text{NaN}_3$  or  $\text{CsN}_3$ ) and the flux ( $\text{NaCl}$  or  $\text{CsCl}$ ). Efforts to synthesize isotopic nitride tellurides with  $\text{Sm}^{3+}$  and  $\text{Eu}^{3+}$  failed, but resulted in the formation of  $\text{SmTe}$  and  $\text{EuTe}$  ( $\text{NaCl}$ -type structure) with the divalent cations instead. For the heavier lanthanides starting with gadolinium and using  $\text{NaN}_3$  as nitrogen source (and  $\text{NaCl}$  as flux) only the ternary sodium tellurides  $\text{NaMTe}_2$  ( $\text{M} = \text{Gd}–\text{Lu}$ ) have been detected. These very stable compounds crystallize with the  $\alpha\text{-NaFeO}_2$ -type structure, which has been well-investigated mainly for the sulfides  $\text{NaMS}_2$  ( $\text{M} = \text{Gd}$ ,  $\text{Ho}–\text{Lu}$ ) [19]. Upon replacement of the sodium compounds ( $\text{NaN}_3$  and  $\text{NaCl}$ ) by  $\text{CsN}_3$  and  $\text{CsCl}$ , in the case of gadolinium (and also terbium),  $\text{Cs}^+$  and  $\text{N}^{3-}$  were incorporated into quaternary tellurides such as  $\text{Cs}_2\text{Gd}_6\text{N}_2\text{Te}_7$  (or isotopic  $\text{Cs}_2\text{Tb}_6\text{N}_2\text{Te}_7$  [20],  $a = 2394.8(2)$  pm,  $b = 421.35(3)$  pm,

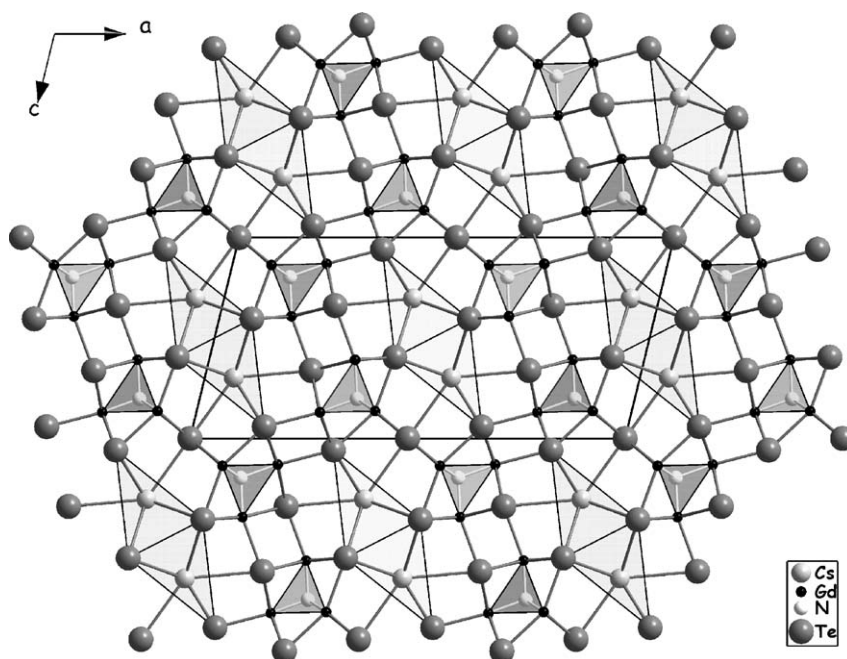


Fig. 4. View of the complete crystal structure of  $\text{Cs}_2\text{Gd}_6\text{N}_2\text{Te}_7$  along the  $b$ -axis.

$c = 1140.49(7)$  pm,  $\beta = 104.031(4)^\circ$ ). The corresponding compounds  $\text{Cs}_2\text{M}_6\text{N}_2\text{Te}_7$  with  $\text{M} = \text{Dy-Lu}$  do obviously not exist, but again the formation of ternary alkali-metal tellurides  $\text{CsMTe}_2$  ( $\text{M} = \text{Dy-Lu}$ ) [19] with the  $\alpha$ - $\text{NaFeO}_2$ -type structure was found to take place.

A comparison of the Madelung Part of the Lattice Energy (MAPLE according to Hoppe [21]) for  $\text{Cs}_2\text{Gd}_6\text{N}_2\text{Te}_7$  with the sum of the formally underlying three binary components  $\text{Cs}_2\text{Te}$  [18],  $\text{Gd}_2\text{Te}_3$  (U type) [16], and  $\text{GdN}$  (NaCl type) [22] also gives a convincing result. By taking  $1 \times 434 + 2 \times 2666 + 2 \times 2092$  kJ/mol a value of 9950 kJ/mol for the sum (MAPLE( $\text{Cs}_2\text{Te}$ ) +  $2 \times$  MAPLE( $\text{Gd}_2\text{Te}_3$ ) +  $2 \times$  MAPLE( $\text{GdN}$ )) emerges, which only deviates by  $-0.7\%$  from MAPLE of  $\text{Cs}_2\text{Gd}_6\text{N}_2\text{Te}_7$  (10016 kJ/mol) itself. This is all the more astonishing, because a structure in which  $\text{N}^{3-}$  anions octahedrally surrounded by  $\text{Gd}^{3+}$  cations as  $\text{GdN}$  ( $d(\text{N}^{3-}-\text{Gd}^{3+}) = 250$  pm,  $6 \times$ ) [22] has to compete with such a one ( $\text{Cs}_2\text{Gd}_6\text{N}_2\text{Te}_7$ ) containing tetrahedrally coordinated  $\text{N}^{3-}$  anions ( $d(\text{N}^{3-}-\text{Gd}^{3+}) = 217-244$  pm, C.N. = 4).

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