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Caesium gadolinium polyphosphate, $CsGd(PO_3)_4$

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Crystals of $CsGd(PO_3)_4$ have been grown by the flux technique from a mixture of CsH_2PO_4, Gd_2O_3 and H_3PO_4. $CsGd(PO_3)_4$ crystallizes in structure type IV of the $M^IM^{III}(PO_3)_4$ (M^I = alkali metal, M^{III} = rare earth or Bi) family of compounds. The structure consists of a three-dimensional framework made up of spiral $(PO_3)_n$ chains linked by GdO_8 polyhedra. Two infinite $(PO_3)_n$ chains with a period of eight tetrahedra run along the [101] direction. Gd and Cs cations are surrounded by eight and eleven O atoms, respectively.

Key indicators

Single-crystal X-ray study
T = 292 K
Mean σ(P–O) = 0.002 Å
R factor = 0.018
wR factor = 0.046
Data-to-parameter ratio = 42.6

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

Comment

$CsGd(PO_3)_4$ belongs to the family of alkali rare earth polyphosphates with the general formula $M^IREP_4O_{12}$ (where M^I = K, Rb, Na, NH_4, Cs and RE = rare earth element). Several members of this family were synthesized and have been characterized by many authors (Hong, 1975*a*,*b*; Koizumi, 1976; Palkina *et al.*, 1977; Mokhtar *et al.*, 1987). Two different types of structural arrangements are known for these compounds that can generally be classified into seven structure types denoted by roman numerals: cyclotetraphosphates $M^IREP_4O_{12}$ with a ring structure formed by four PO_4 tetrahedra that are joined by bridging O atoms, and polyphosphates $M^IRE(PO_3)_4$ consisting of helical ribbons formed by corner-sharing PO_4 tetrahedra (Jouadi *et al.*, 2003; Ettis *et al.*, 2003). Previous structure analyses have shown that rare earth polyphosphates with the general formula $M^IRE(PO_3)_4$ crystallize in two crystal systems: orthorhombic with space group

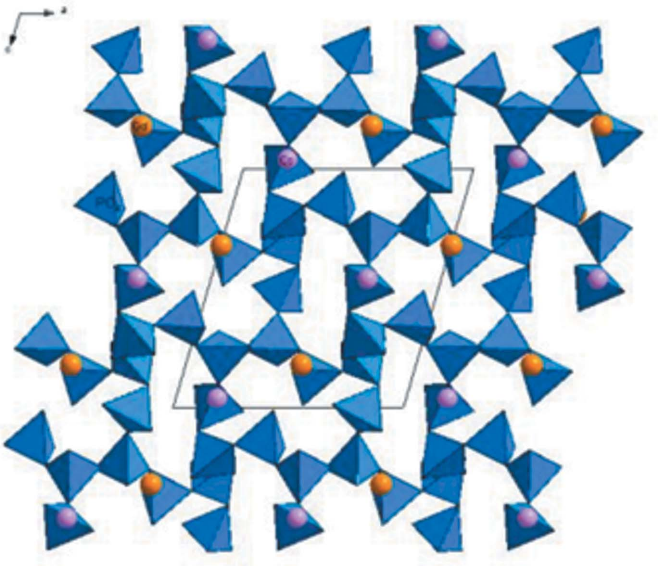

Figure 1
Projection of the $CsGd(PO_3)_4$ crystal structure on to the *ac* plane

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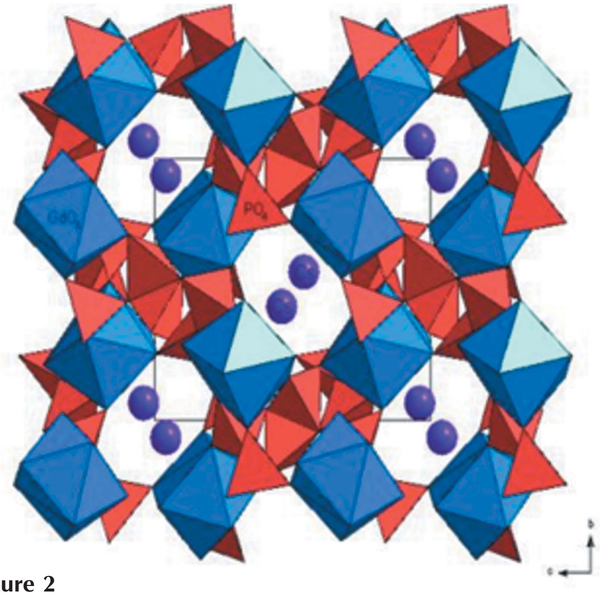


Figure 2
Projection of the $CsGd(PO_3)_4$ crystal structure on to the *bc* plane.

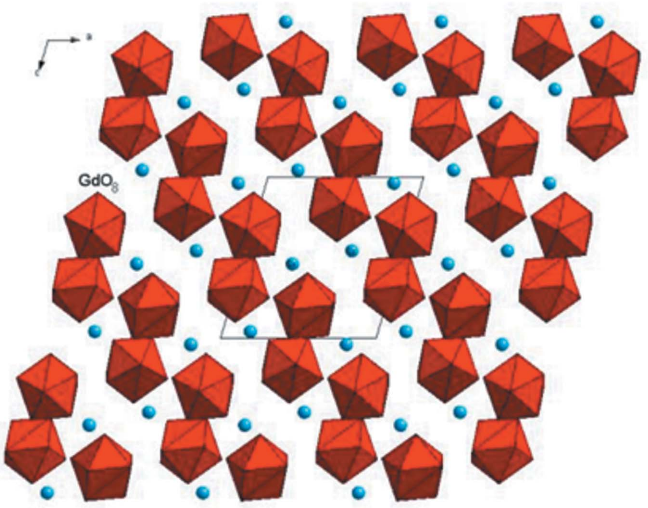
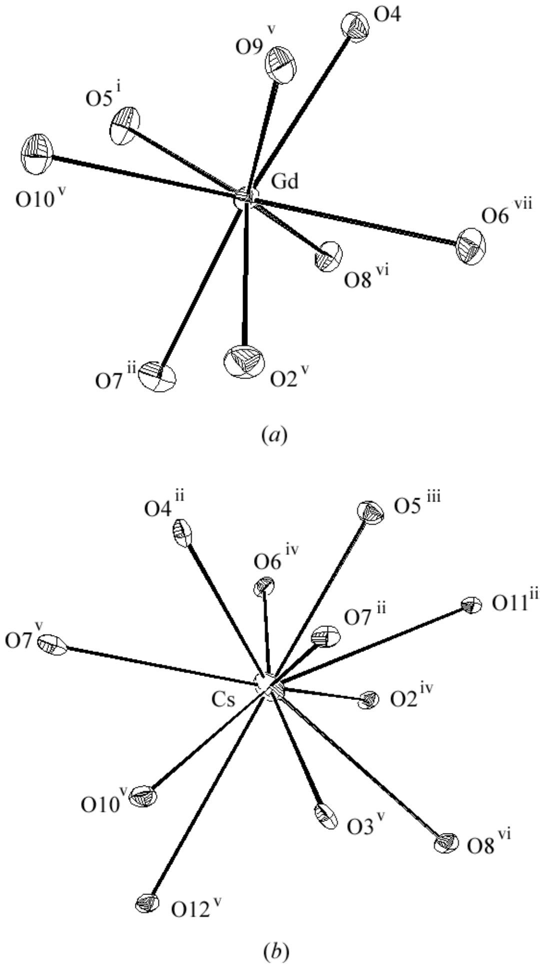


Figure 3
The GdO_8 dodecahedra, viewed along the *b* axis. Intermediate atoms are Cs.

$C222_1$ (type VII) (M^{I} = NH_4, *RE* = Y) (Bagieu-Beucher & Guitel, 1988) or space group *Pbna* (M^{I} = Li, M^{III} = Ga) (Palkina *et al.*, 1981*a*), and monoclinic with space groups *C*2/*c* (Koizumi, 1976; Hamady *et al.*, 1995; Mokhtar *et al.*, 1984) (type I), $P2_1/n$ (Palkina *et al.*, 1981*b*; Maksimova *et al.*, 1978) (types II, IV and V), $P2_1/c$ (Ben Hassen *et al.*, 1982; Dogo *et al.*, 1980) or $P2_1$ (Yong-Hua *et al.*, 1983; Palkina, Maksimova, Kuznetsova & Chibiskova, 1978). All these materials have been intensively studied for their electric and optical properties, and some of them have applications in catalysis. Specifically, condensed phosphates of rare earth elements are applied as laser materials (Danielmeyer & Weber, 1972; Mazurak *et al.*, 1978). $CsGd(PO_3)_4$ was obtained during a systematic investigation of the pseudo-ternary Cs_2O–Gd_2O_3–P_2O_5 system. The present paper reports the synthesis and characterization of $CsGd(PO_3)_4$ by single-crystal X-ray diffraction.



(*a*)

(*b*)

Figure 4
The O-atom coordination around (*a*) the Gd atom and (*b*) the Cs atom, drawn with 50% displacement ellipsoids. [Symmetry codes: (i) $-x+1, -y, -z$; (ii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (iv) $-x+1, -y, -z+1$; (v) $x, y+1, z$; (vi) $x+\frac{1}{2}, -y-\frac{1}{2}, z+\frac{1}{2}$; (vii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.]

The polyphosphate $CsGd(PO_3)_4$ is isotypic with $CsEr(PO_3)_4$ (Palkina Maksimova & Kuzentsova, 1978), and one polymorphic form of the potassium compounds $KBi(PO_3)_4$ (Jouadi *et al.*, 2003) and $KGd(PO_3)_4$ (Rekik *et al.*, 2004). The crystal structures of $CsGd(PO_3)_4$ projected on to the *ac* and *bc* planes are shown in Figs. 1 and 2, respectively. The atomic arrangement is characterized by a three-dimensional framework built of helical ribbons $(PO_3)_n$ that are formed by corner-sharing of PO_4 tetrahedra. Two $(PO_3)_\infty$ chains with a period of eight tetrahedra run along the [101] direction. The Gd atoms are in an eightfold coordination and build dodecahedra arranged two by two along the [101] and [001] directions (Fig. 3). Although the GdO_8 dodecahedron is considerably distorted, no O atom is shared with the adjacent GdO_8 polyhedra. The shortest Gd$\cdots$Gd distance is 5.729 (4) Å. The GdO_8 groups share corners with the neighboring PO_4 tetrahedra. The scatter of the individual Gd—O distances, ranging from 2.327 (2) to 2.456 (2) Å, displays the irregular shape of this polyhedron. Different to the Gd atom, the Cs atom is surrounded by eleven O atoms. The Cs—O distances vary from 3.077 (2) to 3.588 (3) Å. Fig. 4(*a*) and 4(*b*) depict the environments of the independent Gd and Cs atoms, respectively. The P—O distances are in the ranges 1.593 (2)–1.617 (2) and 1.480 (3)–1.497 (2) Å for the bridging P—O_b and terminal P—O_t O atoms, respectively. The existence of bridging and terminal O atoms in PO_4 tetrahedra explains the three types of O—P—O angles observed. The O_b—P—O_b angles vary from 97.8 (1) to 102.4 (1)°, with an average of 99.2°, corresponding to the longest P—O bonds. The O_b—P—O_t angles (mean value = 109.3°) have the values expected for a regular tetrahedron, and the O_t—P—O_t angles range from 117.1 (1) to 121.2 (2)°, corresponding to the shortest P—O distances. The bridging P—O—P angles vary from 124.6 (1) to 134.6 (2)°, which are in good agreement with those usually observed in different types of polyphosphates (Koizumi, 1976; Hong, 1975*b*; Jouadi *et al.*, 2003).

Although $CsGd(PO_3)_4$ and $KGd(PO_3)_4$ (Rekik *et al.*, 2004) present a similar coordination around the Gd atoms, the polyhedra around the alkali atoms are different. In fact, the coordination around Cs is made up from 11 O atoms, whereas the polyhedron around potassium is formed by only nine O atoms. Although $KCe(PO_3)_4$ (type II) (Rzaigui & Ariguib, 1983), $CsGd(PO_3)_4$ (type IV), and $KYb(PO_3)_4$ (type V) (Palkina *et al.*, 1979) crystallize in the same space group ($P2_1/n$), the $(PO_3)_\infty$ chains in these materials differ from one another. In the first compound they are repeated after every four PO_4 tetrahedra along the *a* axis. In the second and last, eight PO_4 tetrahedra are repeated along the [101] direction and the *b* axis, respectively.

Experimental

A mixture of CsH_2PO_4 (5.4 g), Gd_2O_3 (0.4 g) and H_3PO_4 (99%$_{wt}$, 2.8 g) were mixed in a 10 ml platinum crucible which was placed in a tubular furnance and heated progressively to 473 K over a period of 4 h. The temperature was then kept at 823 K for 48 h before cooling to 323 K at a rate of 40 K d^{-1}. The furnance was then switched off. Single crystals of $CsGd(PO_3)_4$ were isolated from the reaction mixture by washing with hot water and with nitric acid (65%$_{wt}$) to eliminate the remaining Gd_2O_3. The compound obtained is stable under normal conditions. Its formula was confirmed by chemical analysis [calculated: P 20.44, Cs 21.93, Gd 25.94%; found: P 19.35 (spectrophotometry), Cs 20.25 (AAS), Gd 25.00% (ICP method)].

Crystal data

$CsGd(PO_3)_4$
M_r = 606.04
Monoclinic, $P2_1/n$
a = 10.3229 (2) Å
b = 8.9307 (2) Å
c = 11.1826 (2) Å
β = 106.371 (1)°
V = 989.13 (3) $Å^3$
Z = 4
D_x = 4.070 Mg m^{-3}
Mo *K*α radiation
Cell parameters from 9641 reflections
θ = 2–40°
μ = 11.04 mm^{-1}
T = 292 (2) K
Block, colourless
0.26 × 0.20 × 0.16 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
T_{min} = 0.177, T_{max} = 0.271
19421 measured reflections
6980 independent reflections
5595 reflections with $I > 2\sigma(I)$
R_{int} = 0.071
θ_{max} = 42.1°
$h = -14 \rightarrow 19$
$k = -16 \rightarrow 15$
$l = -21 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.018
$wR(F^2)$ = 0.046
S = 1.24
6980 reflections
164 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0187P)^2 + 2.8091P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.89 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.58 e $Å^{-3}$

Table 1
Selected geometric parameters (Å, °).

Gd—O9^{i}	2.327 (2)	Cs—O7^{i}	3.588 (3)
Gd—O4	2.349 (2)	P1—O7	1.481 (2)
Gd—O10^{i}	2.363 (2)	P1—O4	1.484 (2)
Gd—O5^{ii}	2.394 (3)	P1—O12	1.593 (2)
Gd—O7^{iii}	2.403 (2)	P1—O3	1.610 (2)
Gd—O6^{iv}	2.406 (2)	P2—O5	1.480 (3)
Gd—O2^{i}	2.426 (2)	P2—O10	1.486 (2)
Gd—O8^{v}	2.456 (2)	P2—O3	1.607 (2)
Cs—O4^{iii}	3.077 (2)	P2—O11	1.617 (2)
Cs—O2^{vi}	3.086 (2)	P3—O6	1.481 (2)
Cs—O5^{vii}	3.087 (2)	P3—O2	1.497 (2)
Cs—O6^{vi}	3.115 (2)	P3—O11	1.603 (2)
Cs—O10^{i}	3.220 (2)	P3—O1	1.609 (2)
Cs—O3^{i}	3.237 (2)	P4—O9	1.487 (2)
Cs—O11^{vii}	3.305 (2)	P4—O8	1.492 (2)
Cs—O7^{iii}	3.341 (3)	P4—O12^{viii}	1.605 (3)
Cs—O8^{v}	3.379 (3)	P4—O1	1.608 (2)
Cs—O12^{i}	3.509 (3)		
O7—P1—O4	118.41 (15)	O2—P3—O11	108.89 (13)
O7—P1—O12	109.23 (13)	O6—P3—O1	107.52 (12)
O4—P1—O12	110.44 (14)	O2—P3—O1	111.11 (13)
O7—P1—O3	108.38 (14)	O11—P3—O1	102.39 (12)
O4—P1—O3	109.87 (13)	O9—P4—O8	117.73 (15)
O12—P1—O3	98.69 (14)	O9—P4—O12^{viii}	110.27 (15)
O5—P2—O10	121.21 (15)	O8—P4—O12^{viii}	110.76 (13)
O5—P2—O3	110.56 (15)	O9—P4—O1	107.87 (12)
O10—P2—O3	107.91 (13)	O8—P4—O1	110.37 (13)
O5—P2—O11	106.33 (12)	O12^{viii}—P4—O1	98.02 (14)
O10—P2—O11	110.51 (13)	P4—O1—P3	124.64 (13)
O3—P2—O11	97.80 (13)	P2—O3—P1	129.22 (17)
O6—P3—O2	117.10 (14)	P3—O11—P2	131.48 (15)
O6—P3—O11	108.81 (14)	P1—O12—P4^{v}	134.56 (18)

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

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

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