Tripraseodymium pentairon(III) dodecaoxide, $Pr_3Fe_5O_{12}$: a synchrotron radiation study

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The title compound, pentairon tripraseodymium dodecaoxide (PrIG), has an iron garnet structure. There are two Fe site symmetries. One of the Fe atoms is coordinated by six O atoms, forming a slightly distorted octahedron, and has $\bar{3}$ site symmetry. The other Fe atom is coordinated by four O atoms, forming a slightly distorted tetrahedron, and has $\bar{4}$ site symmetry. FeO_6 octahedra and FeO_4 tetrahedra are linked together by corners. The Pr atom is coordinated by eight O atoms, forming a distorted dodecahedron, and has 222 site symmetry. The O atoms occupy the general positions.

Related literature

The title compound is isotypic with the $Ia\bar{3}d$ form of $Y_3Fe_5O_{12}$ (YIG). For related structures, see: Bonnet et al. (1975). For details of the crystal growth from low-temperature liquid-phase epitaxy, see: Fratello et al. (1986). For the extinction correction, see: Becker & Coppens (1975). X-ray intensities were measured avoiding multiple diffraction, see: Takenaka et al. (2008).

Experimental

Crystal data

$Pr_3Fe_5O_{12}$
M_r = 893.98
Cubic, $Ia\bar{3}d$
a = 12.6302 (3) Å
V = 2014.79 (8) Å^3
Z = 8

Synchrotron radiation
λ = 0.67171 Å
μ = 17.41 mm^{-1}
T = 298 K
0.035 mm (radius)

Data collection

Rigaku AFC four-circle diffractometer
Absorption correction: for a sphere [transmission coefficients for spheres tabulated in *International Tables C* (1992), Table 6.3.3.3, were interpolated with Lagran-

ge's method (four-point interpolation; Yamauchi et al., 1965)]
T_{min} = 0.413, T_{max} = 0.441
9351 measured reflections
1728 independent reflections
1728 reflections with $F > 3\sigma(F)$
R_{int} = 0.016

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.019
$wR(F^2)$ = 0.021
S = 1.06
9351 reflections

17 parameters
$\Delta\rho_{max}$ = 2.52 e Å^{-3}
$\Delta\rho_{min}$ = −3.16 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pr1—O1	2.42410 (10)	Fe1—O1	2.03220 (10)
Pr1—O1^i	2.54010 (10)	Fe2—O1^{ii}	1.87450 (10)
O1—Fe1—O1^i	85.87 (1)	O1^{ii}—Fe2—O1^{iv}	100.02 (1)
O1^{ii}—Fe2—O1^{iii}	114.39 (1)		

Symmetry codes: (i) z, x, y; (ii) $x+\frac{1}{2}, y, -z+\frac{1}{2}$; (iii) $-x+\frac{1}{4}, z-\frac{1}{4}, y+\frac{1}{4}$; (iv) $x+\frac{1}{2}, -y, z$.

Data collection: *AFC-5*, specially designed for PF-BL14A (Rigaku, 1984) and *IUANGLE* (Tanaka et al., 1994); cell refinement: *RSLC-3 UNICS* system (Sakurai & Kobayashi, 1979); data reduction: *RDEDIT* (Tanaka, 2008); program(s) used to solve structure: *QNTAO* (Tanaka et al., 2008); program(s) used to refine structure: *QNTAO*; molecular graphics: *ATOMS for Windows* (Dowty, 2000); software used to prepare material for publication: *RDEDIT*.

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supporting information

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S1. Comment

The title compound, $Pr_3Fe_5O_{12}$ (PrIG), was difficult to be grown. It was grown by the low-temperature-liquid-phase epitaxy for the first time by Fratello *et al.* (1986). Though the crystal structure was assumed as iron-garnet-type structure by lattice constant and extinction rule, the complete structure was not determined. In this paper, we determine the O atom position and the complete structure by the full matrix least-squares program QNTAO. Since the R-factor is small and the residual density has no significant peaks where no atoms exists, the structure was finally determined to be iron-garnet structure. It is isotypic with the $Ia\bar{3}d$ form of $Y_3Fe_5O_{12}$ (YIG). (Bonnet *et al.*, 1975). The Pr atom is coordinated by eight oxygen atoms. It forms a distorted dodecahedron. There are two Fe site symmetries. One of the Fe atom is coordinated by six oxygen atoms. It forms a slitely distorted octahedron. The other Fe atom is coordinated by four oxygen atoms. It forms a slightly distorted tetrahedron. FeO_6 octahedron and FeO_4 tetrahedron are linked together by corners. The structure of PrIG is drawn in Fig.1. And displacement ellipsoids of PrO_8 is drawn in Fig.2.

S2. Experimental

Single crystals of praseodymium iron garnet were prepared by low temperature liquid phase epitaxy on $Sm_3(ScGa)_5O_{12}$ seeds with lattice parameters near the projected values for PrIG.

S3. Refinement

X-ray intensities were measured avoiding multiple diffraction. (Takenaka *et al.*, 2008).
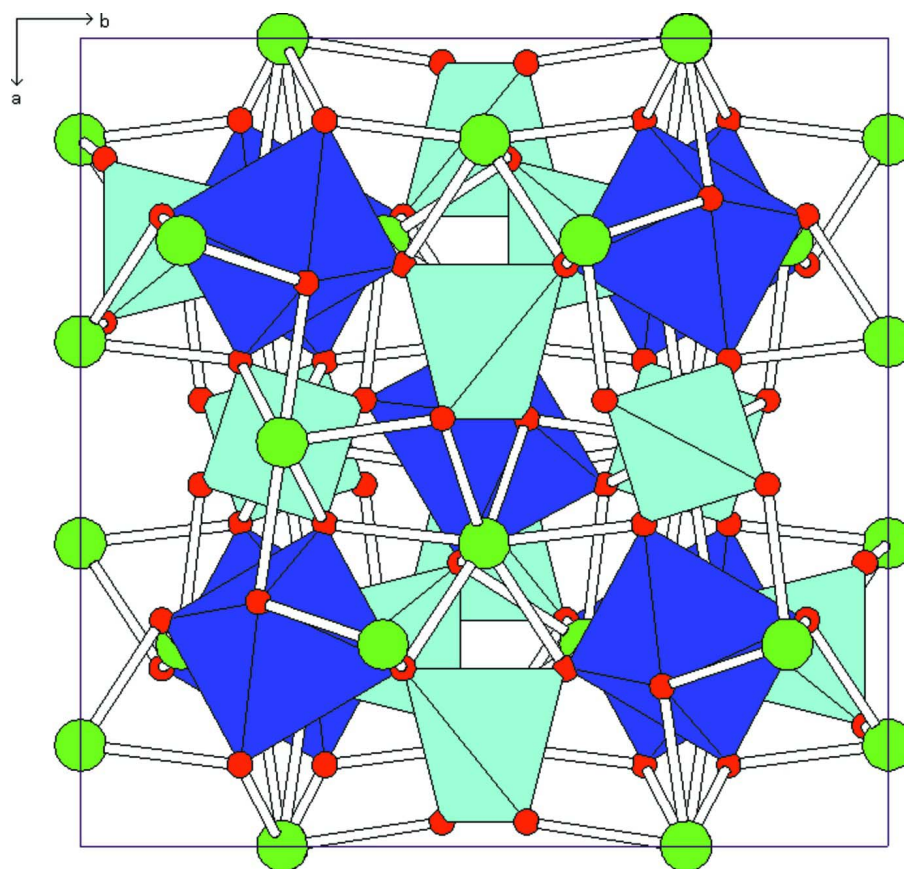
Figure 1

The structure of $Pr_3Fe_5O_{12}$. Small red and large green spheres represent O and Pr atoms, respectively. Purple octahedron and blue tetrahedron represent FeO_6 and FeO_4 units, respectively.
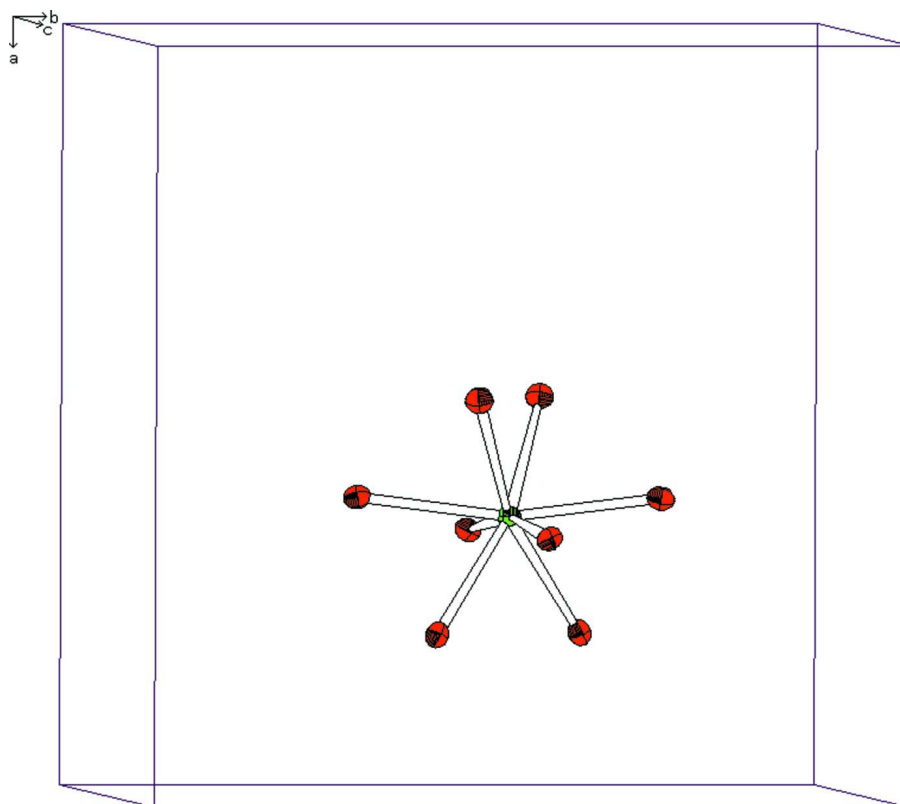
Figure 2

View of PrO_8 with displacement ellipsoids at the 90% probability level. Green and red ellipsoids represent Pr and O atoms, in Fig.1.

Pentairon tripraseodymium dodecaoxide

Crystal data

$Pr_3Fe_5O_{12}$	$D_x = 5.894$ Mg m^{-3}
$M_r = 893.98$	Synchrotron radiation, $\lambda = 0.67171$ Å
Cubic, $Ia\overline{3}d$	Cell parameters from 9 reflections
Hall symbol: -I 4bd 2c 3	$\theta = 17.5$–$52.3°$
$a = 12.6302$ (3) Å	$\mu = 17.41$ mm^{-1}
$V = 2014.79$ (8) Å^3	$T = 298$ K
$Z = 8$	Sphere, black
$F(000) = 3224$	0.04 mm (radius)

Data collection

Rigaku AFC four-circle diffractometer	$T_{min} = 0.413$, $T_{max} = 0.441$
Si 111 monochromator	9351 measured reflections
Detector resolution: $1.25 \times 1.25°$ pixels mm^{-1}	1728 independent reflections
$\omega/2\theta$ scans	1728 reflections with $F > 3\sigma(F)$
Absorption correction: for a sphere [Transmission coefficients for spheres tabulated in International Tables C (1992), Table 6.3.3.3, were interpolated with Lagrange's method (four-point interpolation (Yamauchi *et al.*, 1965)]	$R_{int} = 0.016$
	$\theta_{max} = 68.3°$, $\theta_{min} = 3.7°$
	$h = -9 \rightarrow 34$
	$k = -9 \rightarrow 32$
	$l = -9 \rightarrow 34$

Refinement

Refinement on *F*	Primary atom site location: isomorphous
Least-squares matrix: full	structure methods
$R[F^2 > 2\sigma(F^2)] = 0.019$	Weighting scheme based on measured s.u.'s
$wR(F^2) = 0.021$	$(\Delta/\sigma)_{max} = 0.003$
$S = 1.06$	$\Delta\rho_{max} = 2.52$ e Å^{-3}
9351 reflections	$\Delta\rho_{min} = -3.16$ e Å^{-3}
17 parameters	Extinction correction: B–C type 1 Gaussian
	isotropic (Becker & Coppens, 1975)
	Extinction coefficient: 0.255 (5)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
Pr1	0.125000	0.000000	0.250000	0.00531 (1)
Fe1	0.000000	0.000000	0.000000	0.00512 (1)
Fe2	0.375000	0.000000	0.250000	0.00533 (1)
O1	−0.029622 (2)	0.052553 (2)	0.149166 (2)	0.00711 (5)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pr1	0.00406 (2)	0.00594 (2)	0.00594 (2)	0	0	0.00111 (1)
Fe1	0.00512 (2)	0.00512 (2)	0.00512 (2)	−0.00023 (1)	−0.00023 (1)	−0.00023 (1)
Fe2	0.00411 (3)	0.00594 (2)	0.00594 (2)	0	0	0
O1	0.00718 (8)	0.00829 (8)	0.00587 (7)	−0.00004 (6)	0.00080 (6)	0.00038 (6)

Geometric parameters (Å, º)

Pr1—O1	2.4241 (1)	Fe1—O1^i	2.0322 (1)
Pr1—O1^i	2.5401 (1)	Fe1—O1^{viii}	2.0322 (1)
Pr1—O1^{ii}	2.4241 (1)	Fe1—O1^{ix}	2.0322 (1)
Pr1—O1^{iii}	2.5401 (1)	Fe1—O1^x	2.0322 (1)
Pr1—O1^{iv}	2.4241 (1)	Fe1—O1^{xi}	2.0322 (1)
Pr1—O1^v	2.5401 (1)	Fe2—O1^{xii}	1.8745 (1)
Pr1—O1^{vi}	2.4241 (1)	Fe2—O1^{iv}	1.8745 (1)
Pr1—O1^{vii}	2.5401 (1)	Fe2—O1^{xiii}	1.8745 (1)
Fe1—O1	2.0322 (1)	Fe2—O1^{vi}	1.8745 (1)
O1—Pr1—O1^i	67.75 (1)	O1—Fe1—O1^{viii}	85.87 (1)
O1—Pr1—O1^{ii}	72.66 (1)	O1—Fe1—O1^{ix}	180.00
O1—Pr1—O1^{iii}	124.91 (1)	O1—Fe1—O1^x	94.13 (1)
O1—Pr1—O1^{iv}	111.18 (1)	O1—Fe1—O1^{xi}	94.13 (1)
O1—Pr1—O1^v	73.25 (1)	O1^{xii}—Fe2—O1^{vi}	114.39 (1)
O1—Pr1—O1^{vi}	159.51 (1)	O1^{xii}—Fe2—O1^{iv}	114.39 (1)
O1—Pr1—O1^{vii}	95.43 (1)	O1^{xii}—Fe2—O1^{xiii}	100.02 (1)
O1—Fe1—O1^i	85.87 (1)		

Symmetry codes: (i) z, x, y; (ii) $x, −y, −z+1/2$; (iii) $z, −x, −y+1/2$; (iv) $−x+1/4, −z+1/4, −y+1/4$; (v) $−z+1/4, −y+1/4, −x+1/4$; (vi) $−x+1/4, z−1/4, y+1/4$; (vii) $−z+1/4, y−1/4, x+1/4$; (viii) y, z, x; (ix) $−x, −y, −z$; (x) $−z, −x, −y$; (xi) $−y, −z, −x$; (xii) $x+1/2, y, −z+1/2$; (xiii) $x+1/2, −y, z$.