INORGANIC COMPOUNDS

Acta Cryst. (1999). C**55**, 479–481

Gd_3GaO_6 by X-ray powder diffraction

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(Received 29 September 1998; accepted 30 November 1998)

Abstract

The structure of trigadolinium gallate, Gd_3GaO_6, was solved *ab initio* from conventional X-ray powder diffraction data. Gd_3GaO_6 has a non-centrosymmetric orthorhombic structure ($Cmc2_1$). The structure was refined by the Rietveld method, showing that the Gd atoms are in two different sites of sevenfold coordination and that the Ga atoms are in distorted oxygen tetrahedra. Gd_3GaO_6 was found to be isotypic with Er_3GaS_6.

Comment

Four kinds of compound, RE_3GaO_6, $RE_4Ga_2O_9$, $REGaO_3$ and $RE_3Ga_5O_{12}$, exist in the rare-earth (RE) oxides and gallium oxide binary systems (Schneider *et al.*, 1961; Mizono & Yamada, 1985). The monoclinic phases of $RE_4Ga_2O_9$ (RE = La, Nd, Sm, Eu and Gd) are isostructural with $Eu_4Al_2O_9$ (Brandle & Steinfink, 1969). The structure of $REGaO_3$ (RE = La, Ce, Pr and Nd) is of the perovskite type. Single crystals of rare-earth gallium garnets $RE_3Ga_5O_{12}$ (RE = Nd, Sm, Gd and Dy) have been studied for the substrates of yttrium iron garnets (YIG) film deposition (Brandle & Valentino, 1972). The orthorhombic compounds of RE_3GaO_6 were prepared with RE = Nd, Sm, Eu, Gd, Tb, Dy, Ho and Er. According to the phase diagrams of Sm_2O_3–Ga_2O_3 and Gd_2O_3–Ga_2O_3 (Nicolas *et al.*, 1984; Mizono & Yamada, 1989), Sm_3GaO_6 and Gd_3GaO_6 melt incongruently to Gd_2O_3 and liquid at 2018 and 2033 K, respectively. The reported lattice parameters are a = 11.400, b = 5.515 and c = 9.07 Å for Sm_3GaO_6, and a = 11.278, b = 5.480 and c = 8.99 Å for Gd_3GaO_6 (Nicolas *et al.*, 1984). No non-stoichiometry was observed for these compounds. Nicolas *et al.* (1984) reported that Gd_3GaO_6 and Sm_3GaO_6 are isostructural with Nd_3GaO_6. The X-ray powder diffraction peaks of Nd_3GaO_6 were indexed with an orthorhombic cell; a = 11.53, b = 5.57 and c = 9.17 Å (Coutures *et al.*, 1983). Coutures *et al.* (1983) chose space group *Pnna* from the systematic extinction conditions of hkl: $h + l = 2n$, $0kl$: $k + l = 2n$, $h0l$: $h + l = 2n$, $hk0$: $k = 2n$, $h00$: $h = 2n$, $0k0$: $k = 2n$, $00l$: $l = 2n$. However, these conditions are not in accordance with the systematic extinction conditions of *Pnna* ($0kl$: $k + l = 2n$, $h0l$: $h + l = 2n$, $hk0$: $h = 2n$, $0k0$: $k = 2n$, $00l$: $l = 2n$). The lattice should be a B-centered cell from the first condition of the systematic extinction conditions reported by Coutures *et al.* (1983). They mentioned the presence of three different Nd^{3+} sites, with an average coordination number of seven from the optical absorption spectrum of Nd_3GaO_6, but no structural model was proposed.

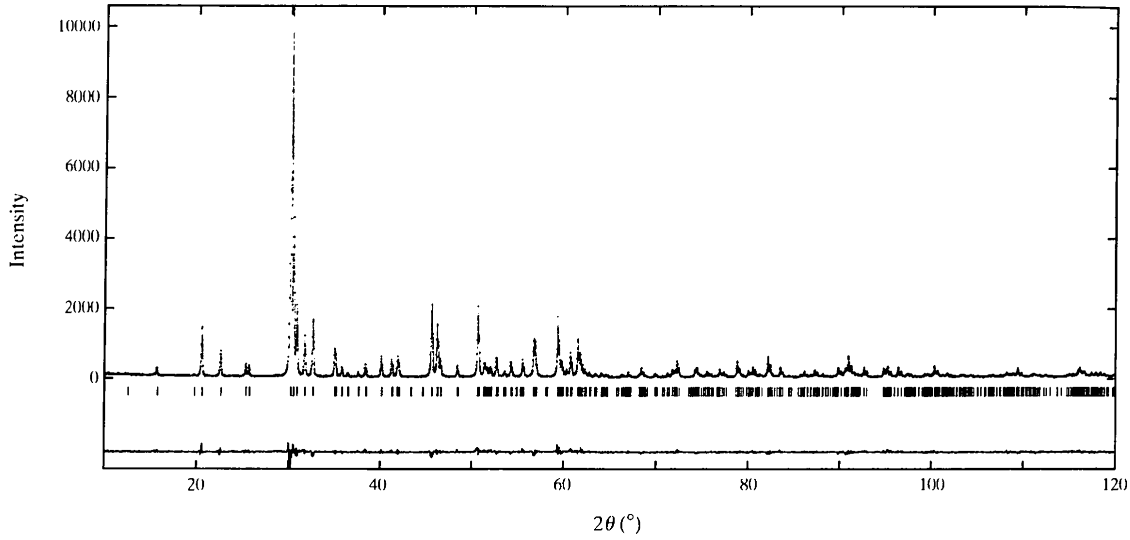

Fig. 1. The observed (dots) and calculated (solid) X-ray diffraction profiles for Gd_3GaO_6. Tick marks below the diffraction pattern represent the allowed Bragg reflections. The difference profile is located at the bottom of the figure.

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ISSN 0108-2701 © 1999

In the present study, we solved the crystal structure of Gd_3GaO_9 by direct methods optimized for powder diffraction data (Altomare *et al.*, 1994) using diffraction intensity data extracted by the Le Bail method (Altomare *et al.*, 1995). The structure was refined by the Rietveld method. Gd_3GaO_9 crystallizes in non-centrosymmetric space group $Cmc2_1$ with the lattice parameters reported by Nicholas *et al.* (1984), although the axis setting was changed to the C-centered cell. A comparison of the experimental X-ray diffraction profile with that obtained by refinement is shown in Fig. 1, along with the calculated residuals. Projections of the structure along the *c* and *b* axes are shown in Fig. 2. Ga_3GaO_6 was found to be isotypic with the previously reported ternary sulfide Er_3GaS_6 (Jaulmes & Laruelle, 1973). Ga atoms are in oxygen tetrahedra which are distorted and elongated along the *c* axis. The Ga—O bond lengths are in the range 1.83–1.89 Å and the average length of 1.85 Å is equal to the Ga—O bond length for the GaO_4 tetrahedron in the structure of $Gd_3Ga_5O_{12}$ (Sasvári & Werner, 1983). The bases of the elongated tetrahedra are in the *a–b* plane and the apical O atoms point in the $-c$ direction. There are two sites for Gd atoms (Wyckoff position 8*b* for Gd1 and 4*a* for Gd2). Gd atoms in both sites are coordinated by seven O atoms. The interatomic distances between the Gd and O atoms are in the range 2.08 (2)–2.74 (2) Å (average 2.38 Å) for Gd1, and 2.21 (2)–2.60 (2) Å (average 2.42 Å) for Gd2. These lengths are close to the Gd—O bond lengths observed in $Gd_3Ga_5O_{12}$ (eightfold coordination, 2.36–2.47 Å, average 2.42 Å; Sasvári & Werner, 1983). O atoms on the O2 site coordinate only to Gd atoms. The shortest Gd—O distances of the sevenfold coordination are seen for the combination of Gd and O2 atoms (Gd1—O2 2.08 and Gd2—O2 2.21 Å).

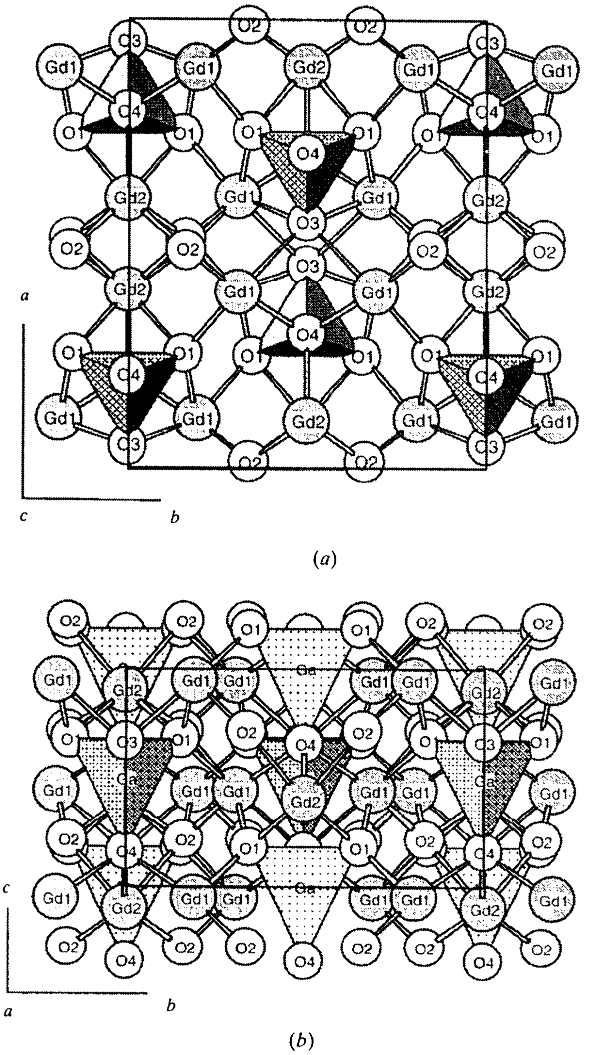

Fig. 2. The structure of Gd_3GaO_6 projected along (*a*) the *c* axis and (*b*) the *b* axis, showing the GaO_4 tetrahedra.

Experimental

Gd_2O_3 powder (99.99% purity, Mitsubishi Kasei Corporation) and Ga_2O_3 powder (99.99% purity, Rare Metallic Co. Ltd) were weighed to give a 3:1 Gd:Ga molar ratio. The powders were mixed in an agate mortar and then pressed into a pellet at 100 MPa. The pellet was heated at 1870 K for 24 h in air on a Pt–Rh (70/30%) plate. After heating, the pellet was cooled in a furnace by shutting off the electric power. The sintered pellet of Ga_3GaO_6 was ground into a fine granular powder for the X-ray diffraction sample.

Crystal data

Gd_3GaO_6
$M_r = 637.47$
Orthorhombic
$Cmc2_1$
$a = 8.9928$ (1) Å
$b = 11.2809$ (2) Å
$c = 5.48116$ (9) Å
$V = 556.05$ (2) $Å^3$
$Z = 4$
$D_x = 7.615$ Mg m^{-3}

Cu $K\alpha_1,\alpha_2$ radiation
$\lambda = 1.540562, 1.544390$ Å
$\mu = 246.9$ mm^{-1}
$T = 293$ (2) K
Specimen shape: flat sheet
Specimen prepared at 101.3 kPa and 1870 K
Particle morphology: fine granular powder
White

Data collection

Rigaku RINT2500V diffractometer
$\theta/2\theta$ step scans
Specimen mounting: 25.0 × 20.0 × 0.5 mm, glass sample holder
Specimen mounted in reflection mode

248 independent reflections
$\theta_{max} = 59.98°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 6$
$2\theta_{min} = 10.00$, $2\theta_{max} = 119.98°$
Increment in $2\theta = 0.030°$

Refinement

$R_p = 0.0792$
$R_{wp} = 0.1031$
$R_{exp} = 0.0801$
$R_B = 0.0361$
$S = 1.3236$

43 parameters
$(\Delta/\sigma)_{max} < 0.001$
Preferred orientation correction: March–Dollase function (Dollase, 1986)

$2\theta_{\min} = 10.00$, $2\theta_{\max} = 119.98°$
Increment in $2\theta = 0.03°$
Profile function: pseudo-Voigt function

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Gd1	0.19320 (14)	0.10615 (14)	0.44679 (9)	0.0008 (4)
Gd2	0	0.3958 (2)	0.4029 (9)	0.0008
Ga	0	0.1947 (4)	0	0.0003 (13)
O1	0.155 (2)	0.2512 (14)	0.183 (3)	0.004 (3)
O2	0.338 (2)	0.013 (2)	0.219 (5)	0.004
O3	0	0.049 (2)	0.167 (5)	0.004
O4	0	0.202 (2)	0.661 (4)	0.004

Table 2. *Selected geometric parameters (Å, °)*

Gd1—O2	2.08 (2)	Gd2—O1	2.46 (2)
Gd1—O1	2.21 (2)	Gd2—O1$^{\rm vi}$	2.46 (2)
Gd1—O4	2.36 (2)	Gd2—O2$^{\rm ii}$	2.49 (2)
Gd1—O2$^{\rm i}$	2.39 (2)	Gd2—O2$^{\rm vii}$	2.49 (2)
Gd1—O3	2.41 (2)	Gd2—O4	2.60 (2)
Gd1—O1$^{\rm ii}$	2.48 (2)	Ga—O1	1.83 (2)
Gd1—O3$^{\rm iii}$	2.74 (2)	Ga—O1$^{\rm vi}$	1.83 (2)
Gd2—O2$^{\rm iv}$	2.21 (2)	Ga—O4$^{\rm viii}$	1.86 (2)
Gd2—O2$^{\rm v}$	2.21 (2)	Ga—O3	1.89 (2)
O1—Ga—O4$^{\rm viii}$	122.1 (7)	O4$^{\rm viii}$—Ga—O3	121.8 (12)
O1—Ga—O3	92.2 (8)	O4$^{\rm viii}$—Ga—O1$^{\rm vi}$	122.1 (7)
O1—Ga—O1$^{\rm vi}$	99.0 (12)	O3—Ga—O1$^{\rm vi}$	92.2 (8)

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

The possible space groups were *Cmc*2_1, *C*2*cm* and *Cmcm* from the systematic extinction conditions. The structure could be solved only in *Cmc*2_1 by direct methods. During the Rietveld refinement, a preferred orientation correction was carried out using the March–Dollase function (Dollase, 1986). The adjustable parameter of the function was refined to be 0.956 (2) for a (100) preferred orientation of plate crystals. The isotropic displacement parameters were constrained to be the same for the Gd atoms and for the O atoms. The atomic parameters were standardized using the program *STRUCTURE TIDY* (Gelato & Parthé, 1987).

Data collection: *RISM* (Rigaku Corporation, 1995). Program(s) used to solve structure: *EXPO* (Altomare *et al.*, 1998). Program(s) used to refine structure: *RIETAN*97 (Izumi, 1997). Molecular graphics: *ATOMS* (Dowty, 1998).

This work was supported in part by a Grant-in-Aid for Scientific Research of the Ministry of Education, Science, Sports and Culture, Japan, and by the Nippon Sheet Glass Foundation for Materials Science and Engineering.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1230). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 481–483

SrFeP$_2$O$_7$, a new homologue in the *AM*P$_2$O$_7$ series

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(Received 13 July 1998; accepted 14 December 1998)

Abstract

Strontium iron diphosphate, SrFeP$_2$O$_7$, was obtained from hydrothermal synthesis and its structure determined by single-crystal X-ray diffraction analysis. The main crystallographic feature is the 4+1 square-pyramidal coordination polyhedron around the Fe atom. The structure is built up from corner-sharing [FeO$_5$] pyramids and [P$_2$O$_7$] bitetrahedral units. Such a connection gives rise to a three-dimensional framework,

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