Sm$_5$Ga$_3$

Guo-Hua Feng, Laurence Lacroix-Orio, Monique Tillard* and Claude Belin

Laboratoire des Agrégats Moléculaires et Matériaux Inorganiques, UMR 5072 CC15, Université de Montpellier II, Sciences et Techniques du Languedoc, 2 Place Eugène Bataillon, 34095 Montpellier Cédex 5, France
Correspondence e-mail: mtillard@univ-montp2.fr

Single crystals of pentasamarium trigallium, Sm$_5$Ga$_3$, display tetragonal symmetry. The crystal structure was solved and refined in space group $P4/ncc$. The present work does not confirm the space group $I4/mcm$ previously deduced from powder data measurements. One Sm atom is in a general position, and the other Sm atom and one of the Ga atoms are at sites with fourfold symmetry. The remaining Ga atom is at a site with twofold symmetry.

Comment

Light rare earth–gallium (R–Ga) systems have been investigated in the past and the structures of some binary Sm$_x$Ga$_y$ compounds have been established, generally from X-ray powder diffraction data. The title compound, Sm$_5$Ga$_3$, has been identified previously (Palenzona & Franceschi, 1968; Dzyana & Krypyakevich, 1969). In those studies, the unit-cell parameters and the space group (tetragonal, $I4/mcm$, a = 7.79 Å and c = 14.28 Å) were obtained from powder diffraction data and were reported without any further structural details.

We have prepared the title compound in the exact 5:3 stoichiometry and obtained a well crystallized and homogeneous product. A small single crystal was selected for collection of diffracted intensities on an Oxford Xcalibur CCD diffractometer. The unit-cell parameters [a = 7.7802 (5) and c = 14.1880 (9) Å] were determined with good accuracy. The statistical tests from *SHELXS97* (Sheldrick, 1997) gave strong evidence for centrosymmetry. The structure was then solved and refined to $R(F)$ = 2.60% in the tetragonal centrosymmetric space group $P4/ncc$. Careful examination of the reflection intensities did not reveal any systematic absences corresponding to Bravais centring. Nevertheless, refinement was tested in the $I4/mcm$ space group, but about 25% of reflections with a mean $I/\sigma(I)$ of 5.8 were rejected (for absence violations) and structural refinement was unsatisfactory.

The structure of Sm$_5$Ga$_3$ is in agreement with those determined (from single-crystal data) for other related R_5Ga$_3$ compounds with R = La, Gd and Y. These structures are also described in the $P4/ncc$ Ba$_5$Si$_3$ structural type (Zhao & Corbett, 1994). Symmetry lowering from $I4/mcm$ (Cr$_5$B$_3$-type) towards the maximal IIa non-isomorphic subgroup $P4/ncc$ (Ba$_5$Si$_3$-type) results from the displacement of atoms Sm1 and Ga1 from the $I4/mcm$ 16l and 4a special positions.

The $P4/ncc$ unit cell of Sm$_5$Ga$_3$ contains four isolated Ga atoms and four Ga$_2$ dumbbells. The isolated Ga1 atom is in a regular square antiprismatic environment of Sm atoms (eight Sm1 and two Sm2). The Ga$_2$ dimers lie inside fused (rectangular face-sharing) distorted trigonal prisms of Sm1 atoms, capped on two rectangular faces by Sm2. Each Ga2 atom of the dimer is located nearly at the centre of one of these prisms. The Ga—Ga distance of 2.653 (3) Å in the dimer compares well with those in the isostructural compounds La$_5$Ga$_3$ [2.665 (3) Å], Gd$_5$Ga$_3$ [2.637 (5) Å] and Y$_5$Ga$_3$ [2.663 (8) Å]. The 6.5% elongation from Pauling's Ga—Ga single bond (2.49 Å; Pauling, 1967) is due to π antibonding repulsions. Formally, Sm$_5$Ga$_3$ can be formulated as $(5\text{Sm})^{13+}\text{Ga}^{5-}(\text{Ga}_2)^{8-}$, with a non-integer charge per Sm atom slightly below its usual (3+) oxidation state.

Experimental

Gallium metal (0.439 g, Rhone Poulenc, 99.9999% pure) and samarium (1.57 g, ingot, AlfaAesar 99.9% pure) were used to prepare the title compound. They were inserted into a tantalum tube which was then weld-sealed under an argon atmosphere. The tantalum tube was then enclosed in a sealed silica jacket filled with argon to protect it from oxidation at high temperatures. The mixture of elements was heated to the appropriate temperature (about 1323 K) and kept at this temperature for 10 h, during which it was shaken several times for good homogenization of the melt. It was then allowed to cool slowly for crystal growth at a rate of 10 K h^{-1} to 1103 K and then at a rate of 20 K h^{-1} to room temperature. Although the product appeared relatively stable in air, crystals were selected under a microscope inside a glove-box filled with purified argon. These crystals were protected from air in sealed thin-walled glass capillaries
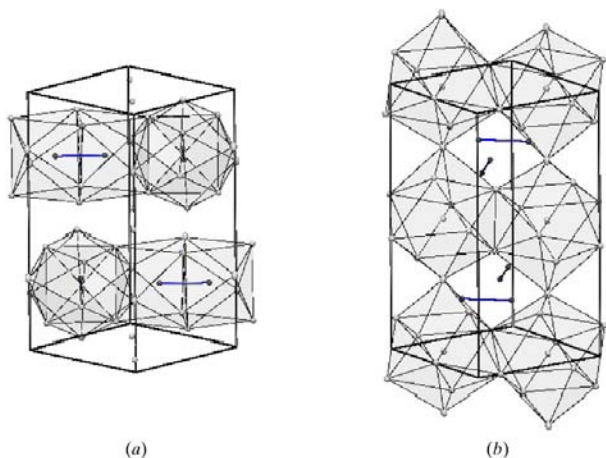
Figure 1
Representations of the tetragonal Sm$_5$Ga$_3$ unit cell, emphasizing the Ga$_2$ dumbbells and isolated Ga atoms in their respective environments, *viz.* (*a*) trigonal prismatic and (*b*) square antiprismatic.

inorganic compounds

to be checked for singularity and diffracting quality. The best diffracting single crystal was chosen for data collection at room temperature and mounted on the four-circle diffractometer.

Crystal data

Sm_5Ga_3
$M_r = 960.91$
Tetragonal, $P4/ncc$
$a = 7.8026$ (5) Å
$c = 14.1880$ (9) Å
$V = 863.77$ (10) Å^3
$Z = 4$
$D_x = 7.389$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 10930 reflections
$\theta = 3.7–26.1°$
$\mu = 42.51$ mm^{-1}
$T = 293$ (2) K
Triangular shape, black
$0.18 \times 0.11 \times 0.09$ mm

Data collection

Oxford Xcalibur CCD area-detector diffractometer
ω scans
Absorption correction: numerical [*CrysAlis RED* (Clark & Reid, 1995; Oxford Diffraction, 2001)]
$T_{min} = 0.048$, $T_{max} = 0.247$
10930 measured reflections

440 independent reflections
440 reflections with $I > 2\sigma(I)$
$R_{int} = 0.073$
$\theta_{max} = 26.1°$
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.055$
$S = 1.52$
440 reflections
22 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0092P)^2 + 14.6963P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 2.51$ e Å^{-3}
$\Delta\rho_{min} = -2.65$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.00135 (9)

The structure was refined in the $P4/ncc$ space group using the final data set corrected from absorption effects ($\mu = 42.5$ cm^{-1}). Absorption corrections were performed using the Oxford Xcalibur

Table 1
Selected geometric parameters (Å).

Sm1—Ga2^i	3.0737 (8)	Sm1—Ga1	3.2968 (9)
Sm1—Ga2^{ii}	3.1432 (12)	Sm2—Ga2	3.1200 (7)
Sm1—Ga2	3.1565 (8)	Sm2—Ga1^{iv}	3.225 (2)
Sm1—Ga1^{iii}	3.1770 (10)	Ga2—Ga2^i	2.653 (3)

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

CrysAlis RED absorption-correction module based on optimization of the crystal shape (Clark & Reid, 1995).

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2001); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2002); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1058). Services for accessing these data are described at the back of the journal.

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