

Gallium tris(iodate), Ga(IO₃)₃Xue-An Chen,* Hai-Ping Xue, Xin-An Chang, He-Gui Zang
and Wei-Qiang XiaoCollege of Materials Science and Engineering, Beijing University of Technology, Ping
Le Yuan 100, Beijing 100022, People's Republic of China
Correspondence e-mail: xueanchen@bjut.edu.cn

Received 7 April 2005

Accepted 19 September 2005

Online 11 October 2005

Ga(IO₃)₃ crystallizes in the space group *P*6₃, with the Ga atom at a site with imposed threefold symmetry. The crystal structure consists of slightly distorted GaO₆ octahedra that are bridged by I atoms of IO₃[−] groups, giving rise to a three-dimensional polar network. The framework contains unoccupied hexagonal channels running parallel to the hexagonal [001] direction. The iodate groups have their stereochemically active non-bonded electron pairs pointing in the same direction along [001], which creates the polarity in the structure. The I–O bond distances and O–I–O angles are normal, being in the ranges 1.783 (3)–1.847 (2) Å and 94.68 (11)–99.61 (12)°, respectively.

Comment

Metal iodates have attracted much attention because some of these compounds exhibit piezoelectric and pyroelectric effects, and they have potential applications in second harmonic generation (SHG) (Morosin *et al.*, 1973). The continued interest in these materials has led to the recent discovery of a series of new iodates, such as AMoO₃(IO₃) (*A* = K, Rb and Cs; Sykora *et al.*, 2002), Hg(IO₃)₂ (Bentria, Benbental, Bagieu-Beucher, Mosset & Zaccaro, 2003) and Bi(IO₃)₃ (Bentria, Benbental, Bagieu-Beucher, Masse & Mosset, 2003), among which Hg(IO₃)₂ and AMoO₃(IO₃) (*A* = Rb and Cs) have been found to show large SHG responses. The title compound, Ga(IO₃)₃, was reported previously by Shklovskaya (1980), who only presented the powder X-ray diffraction patterns; its crystal structure remains as yet undetermined. In the course of our investigation of novel iodate non-linear optical (NLO) materials, we have obtained single crystals of Ga(IO₃)₃. The present X-ray structural analysis establishes that Ga(IO₃)₃ crystallizes in a polar and chiral space group, *viz.*, *P*6₃, being a potential NLO material.

In the structure of Ga(IO₃)₃, the unique Ga³⁺ ion lies on a threefold axis and is coordinated to six O atoms in a slightly distorted octahedral geometry, the unique *trans* angle being 169.98 (10)° and the *cis* octahedral angles in the range 85.24 (10)–98.46 (10)° (Fig. 1 and Table 1). The Ga³⁺ ion shifts from the nominal center of its octahedron towards an octa-

hedral face by about 0.016 Å, resulting in three short Ga–O bonds [3 × 1.960 (2) Å], each of which is *trans* to a long Ga–O bond [1.980 (2) Å]. A similar coordination environment has been found for Ga³⁺ in Na_{1.98}Ga_{10.673}O₁₇, with Ga–O distances of 3 × 1.785 Å and 3 × 1.812 Å (Michiue *et al.*, 1991).

GaO₆ octahedra are arranged around 6₃ screw axes and bridged by I atoms of IO₃[−] groups, leading to an overall three-dimensional framework, as shown in Fig. 2. Each IO₃[−] group acts as a bidentate ligand bonded to two Ga³⁺ centers *via* two μ₂-O atoms, with the third O atom kept 'dangling'. This form of ligation is common for IO₃[−] groups, and was observed in VO₂IO₃·2H₂O (Meschede & Mattes, 1976) and Ce(IO₃)₄·H₂O (Ibers & Cromer, 1958). The I–O bond length for the 'dangling' O atoms [1.783 (3) Å] is slightly shorter than those for the O atoms bound to the Ga³⁺ centers [1.828 (2) and 1.847 (2) Å] and both are very close to those generally found for iodate structures, for example, 1.80 (1)–1.84 (1) Å in Hg(IO₃)₂ and 1.790 (8)–1.828 (8) Å in Bi(IO₃)₃ (Bentria, Benbental, Bagieu-Beucher, Mosset & Zaccaro, 2003; Bentria, Benbental, Bagieu-Beucher, Masse & Mosset, 2003). The O–I–O bond angles are normal, being in the range 94.68 (11)–99.61 (12)°. The pyramidal iodate groups are arranged in such a way that the 'dangling' O atoms form an octahedral hole with a 4.490 (4) Å distance between *trans* O atoms. These holes are connected together to form one-dimensional open channels running parallel to the hexagonal [001] direction, and they are big enough to accommodate interstitial ions, such as Li⁺. However, our difference Fourier analyses did not reveal any significant electron-density peaks within these hexagonal tunnels. The refined structural model was further supported by bond-valence-sum (BVS) calculations (Brown & Altermatt, 1985), which produced reasonable values of 3.13 for Ga and 4.94 for I atoms.

Bi(IO₃)₃ is related to Ga(IO₃)₃ in stoichiometry but differs in the structure. In the former compound, each Bi³⁺ ion is coordinated by nine O atoms, forming a highly distorted monocapped square antiprism. The BiO₉ polyhedra are edge-connected to form zigzag chains extending along the *b* axis; these chains are linked through IO₃[−] groups, forming layers parallel to (101). The layers are held together *via* long I···O contacts, resulting in a three-dimensional framework. It is the variation in the coordination environments around the metal

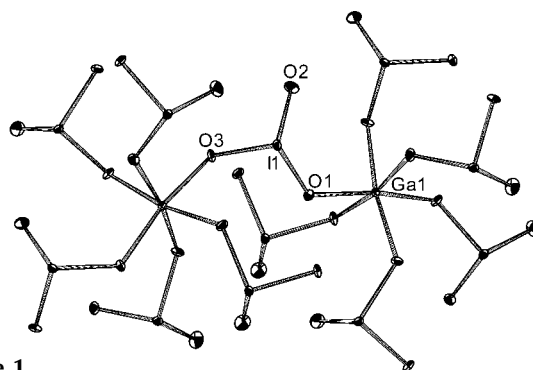
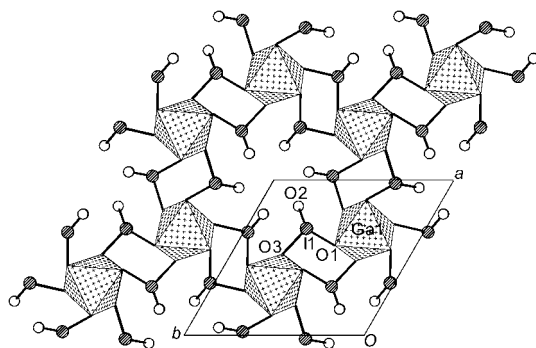


Figure 1
The local coordination geometries of Ga and I in Ga(IO₃)₃, with displacement ellipsoids drawn at the 50% probability level.


Figure 2

The crystal structure of $\text{Ga}(\text{IO}_3)_3$, projected along the hexagonal [001] direction, where single shaded circles and open circles are I and O atoms, respectively, and octahedral GaO_6 units are represented by polyhedra.

cations that is mainly responsible for a structure change from $\text{Ga}(\text{IO}_3)_3$ to $\text{Bi}(\text{IO}_3)_3$.

It is clear from Fig. 2 that the iodate groups in $\text{Ga}(\text{IO}_3)_3$ are all aligned along the polar c axis, which creates the polarity in the structure, and the compound may be a potential NLO material. To confirm this, SHG measurements were performed using a modified Kurtz–NLO system with a 1064 nm light source (Kurtz & Perry, 1968) on powder of the ground crystals. Generation of green light of 532 nm was clearly observed, further supporting the assignment of this structure in a non-centrosymmetric setting.

Experimental

The title compound was synthesized under mild hydrothermal conditions. The starting materials were all of analytical grade purity. Ga_2O_3 (0.046 g, 0.245 mmol), H_5IO_6 (0.334 g, 1.465 mmol), HNO_3 (0.5 ml) and water (2 ml) were sealed in an 15 ml Teflon-lined autoclave, heated at 443 K for one week, and then cooled slowly to room temperature. The product consisted of colorless hexagonal column-like crystals, the largest having dimensions of $0.6 \times 0.6 \times 1.0$ mm, in a colorless mother liquor. The final pH of the reaction system was about 1.0. The crystals, in about 64% yield (based on Ga), were isolated by washing the reaction product with deionized water and anhydrous ethanol, followed by drying with anhydrous acetone. Powder X-ray diffraction analysis revealed that the product is the single phase of $\text{Ga}(\text{IO}_3)_3$, no lines due to impurity phases being observed. The synthesis of $\text{Ga}(\text{IO}_3)_3$ involved a complex redox process in which the I^{7+} ion in IO_4^- was reduced by water to I^{5+} in IO_3^- . This type of reaction has already been noted in the preparation of many other metal iodates (Hector *et al.*, 2002). HNO_3 was found to enhance the solvation processes and crystal growth of the target material. A separate set of experiments was conducted, in which a mixture of Ga_2O_3 , H_5IO_6 and water (1:6:454 ratio) was heated hydrothermally at 443 K for 7 d. The reaction resulted in a fine white powder of unreacted Ga_2O_3 , no crystals of $\text{Ga}(\text{IO}_3)_3$ being obtained.

Crystal data

$\text{Ga}(\text{IO}_3)_3$	Mo $K\alpha$ radiation
$M_r = 594.42$	Cell parameters from 25 reflections
Hexagonal, $P6_3$	$\theta = 20.1\text{--}22.2^\circ$
$a = 9.0924$ (5) Å	$\mu = 15.90$ mm $^{-1}$
$c = 5.2862$ (8) Å	$T = 290$ K
$V = 378.47$ (6) Å 3	Prism, colorless
$Z = 2$	$0.2 \times 0.1 \times 0.1$ mm
$D_x = 5.216$ Mg m $^{-3}$	

Data collection

Rigaku AFC-7R diffractometer	$R_{\text{int}} = 0.033$
2θ - ω scans	$\theta_{\text{max}} = 32.5^\circ$
Absorption correction: ψ scan (Kopfmann & Huber, 1968)	$h = 0 \rightarrow 13$
$T_{\text{min}} = 0.150$, $T_{\text{max}} = 0.210$	$k = -13 \rightarrow 11$
2720 measured reflections	$l = -7 \rightarrow 7$
913 independent reflections	3 standard reflections
902 reflections with $I > 2\sigma(I)$	every 150 reflections
	intensity decay: -0.9%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.016$	$\Delta\rho_{\text{max}} = 0.63$ e Å $^{-3}$
$wR(F^2) = 0.037$	$\Delta\rho_{\text{min}} = -1.02$ e Å $^{-3}$
$S = 1.27$	Extinction correction: <i>SHELXL97</i>
913 reflections	Extinction coefficient: 0.0907 (19)
41 parameters	Absolute structure: Flack (1983),
$w = 1/[\sigma^2(F_o^2) + (0.013P)^2 + 0.3153P]$	412 Friedel pairs
where $P = (F_o^2 + 2F_c^2)/3$	Flack parameter: 0.01 (2)

Table 1

Selected geometric parameters (Å, °).

Ga1–O3 ⁱ	1.960 (2)	I1–O3	1.828 (2)
Ga1–O1	1.980 (2)	I1–O1	1.847 (2)
I1–O2	1.783 (3)		
O3 ⁱ –Ga1–O3 ⁱⁱ	86.28 (10)	O2–I1–O3	96.61 (12)
O3 ⁱ –Ga1–O1 ⁱⁱⁱ	98.46 (10)	O2–I1–O1	99.61 (12)
O3 ^{iv} –Ga1–O1 ⁱⁱⁱ	85.24 (10)	O3–I1–O1	94.68 (11)
O3 ⁱⁱ –Ga1–O1 ⁱⁱⁱ	169.98 (10)	I1–O1–Ga1	130.58 (13)
O1 ⁱⁱⁱ –Ga1–O1 ^v	90.75 (11)	I1–O3–Ga1 ^{vi}	121.80 (12)

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

Data collection: *Rigaku/AFC Diffractometer Control Software* (Rigaku, 1994); cell refinement: *Rigaku/AFC Diffractometer Control Software*; data reduction: *Rigaku/AFC Diffractometer Control Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: EM1002). Services for accessing these data are described at the back of the journal.

References

- Bentria, B., Benbertal, D., Bagieu-Beucher, M., Masse, R. & Mosset, A. (2003). *J. Chem. Crystallogr.* **33**, 867–873.
- Bentria, B., Benbertal, D., Bagieu-Beucher, M., Mosset, A. & Zaccaro, J. (2003). *Solid State Sci.* **5**, 359–363.
- Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* **B41**, 244–247.
- Dowty, E. (1999). *ATOMS*. Version 5.0. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.
- Hector, A. L., Henderson, S. J., Levason, W. & Webster, M. (2002). *Z. Anorg. Allg. Chem.* **628**, 198–202.
- Ibers, J. A. & Cromer, D. T. (1958). *Acta Cryst.* **11**, 794–798.
- Kopfmann, G. & Huber, R. (1968). *Acta Cryst.* **A24**, 348–351.
- Kurtz, S. K. & Perry, T. T. (1968). *J. Appl. Phys.* **39**, 3798–3805.
- Meschede, W. & Mattes, R. (1976). *Z. Anorg. Allg. Chem.* **420**, 25–30.
- Michiue, Y., Watanabe, M. & Fujiki, Y. (1991). *Acta Cryst.* **C47**, 495–498.
- Morosin, B., Bergman, J. G. & Crane, G. R. (1973). *Acta Cryst.* **B29**, 1067–1072.
- Rigaku (1994). *Rigaku/AFC Diffractometer Control Software*. Rigaku Corporation, Tokyo, Japan.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Shklovskaya, R. (1980). *Russ. J. Inorg. Chem. (Engl. Transl.)*, **25**, 618–622.
- Sykora, R. E., Ok, K. M., Halasyamani, P. S. & Albrecht-Schmitt, T. E. (2002). *J. Am. Chem. Soc.* **124**, 1951–1957.