Acta Cryst. (1996). **C52**, 760–761

$Ba_3Ga_2N_4$

HISANORI YAMANE† AND FRANCIS J. DISALVO

Department of Chemistry, Cornell University, Ithaca, New York 14853, USA. E-mail: yamane@imr.tohoku.ac.jp

(*Received 30 August 1995; accepted 24 November 1995*)

Abstract

The crystal structure of tribarium digallium tetranitride is based on a distorted cubic close packing of N atoms with three-quarters of the octahedral holes occupied by Ba atoms and one-quarter of the tetrahedral holes occupied by Ga atoms. The GaN_4 tetrahedra share edges and form $[\mathrm{GaN}_{4/2}^{3-}]$ chains, which are isosteric to the edge-sharing SiS_2 tetrahedra in the SiS_2 structure.

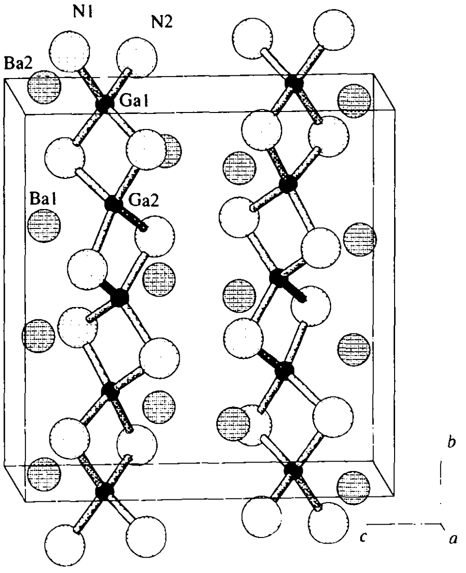

Fig. 1. Crystal structure of $Ba_3Ga_2N_4$.

Comment

Alkaline earth gallium nitrides reported previously are Mg_3GaN_3 (Verdier, Marchand & Lang, 1970) and Ca_6GaN_5 (Cordier, Höhn, Kniep & Rabenau, 1990) for gallium(III), and $Ca_5Ga_2N_4$ (Cordier, 1988) and CaGaN (Verdier, Marchand & Lang, 1973; Verdier, L'Haridon, Maunaye & Marchand, 1974) for gallium(I). The coordination of Ga by N in Ca_6GaN_5 is triangular planar. The triangular-planar $[GaN_3]^{6-}$ anion is isosteric to $[CO_3]^{2-}$. $Ca_5Ga_2N_4$ contains $[(GaN_2)^{5-}]$ infinite chains. The Ga^I atom is tetrahedrally coordinated by two Ga^I atoms along the chain direction and an additional two N atoms in terminal positions. The Ga^I atom in the CaGaN structure has square-pyramidal coordination geometry with four Ga (basal square) and one N (apical) atoms. In the present study, we prepared a new alkaline earth gallium(III) nitride, $Ba_3Ga_2N_4$, using Na as a flux, and analyzed its crystal structure.

$Ba_3Ga_2N_4$ is isostructural with $Sr_3Al_2N_4$ (space group *Pnna*, $a = 5.90$, $b = 10.01$, $c = 9.58$ Å; Blase, Cordier, Ludwig & Kniep, 1994). As shown in Fig. 1, each Ga atom is coordinated by four N atoms in the form of a distorted tetrahedron. The tetrahedra form one-dimensional chains of $[\mathrm{GaN}_{4/2}^{3-}]$ along the *b* axis by sharing edges. Similar edge-sharing tetrahedral nitridometallate chains, $[\mathrm{FeN}_{4/2}^{3-}]$, are also found in the structure of Li_3FeN_2 (Gudat, Kniep & Rabenau, 1990). The average Ga—N bond distance in the $[\mathrm{GaN}_{4/2}^{3-}]$ chains of $Ba_3Ga_2N_4$ is 2.02 Å, which is a little longer than that of Al—N in the $[\mathrm{AlN}_{4/2}^{3-}]$ chains (1.92 Å) in $Sr_3Al_2N_4$ and that of Fe—N in the $[\mathrm{FeN}_{4/2}^{3-}]$ chains in Li_3FeN_2 (1.96 Å). The $[\mathrm{GaN}_{4/2}^{3-}]$ chains, as well as $[\mathrm{AlN}_{4/2}^{3-}]$ and $[\mathrm{FeN}_{4/2}^{3-}]$ chains (Gudat *et al.*, 1991), have an isosteric arrangement similar to that of SiS_2 (Peters & Krebs, 1982).

As pointed out in the study of $Sr_3Al_2N_4$ by Blase *et al.* (1994), the structure of $Ba_3Ga_2N_4$ can be described in terms of a distorted cubic close packing of N anions. Ga cations occupy one-quarter of the tetrahedral holes and Ba cations occupy three-quarters of the octahedral holes. The interatomic distances between N and Ba atoms in the octahedra are in the range 2.623 (6)–3.375 (6) Å. The N1 atoms are coordinated by two Ga and four Ba atoms with distorted octahedral geometry. The N2 atoms are surrounded by two Ga and five Ba atoms (sevenfold coordination).

Experimental

All manipulations were carried out in an Ar-filled glove box. Ba (137 mg, 1.0 mmol), Ga (35 mg, 0.5 mmol), NaN_3 (78 mg, 1.2 mmol) and Na (55.2 mg, 2.4 mmol) were sealed in an Nb tube using an arc furnace under one atmosphere of Ar. The welded Nb tube was then sealed in an evacuated quartz tube to prevent oxidation of Nb at elevated temperatures. The starting materials were heated to 1023 K over 7.5 h, held for 1 h at that temperature and then cooled at a rate of 6.4 K h^{-1}. The sample in the Nb tube was washed with liquid NH_3 to remove the Na flux as detailed previously (Yamane & DiSalvo, 1995). Transparent yellow lamellar crystals and black granular single crystals were obtained from the residual product.

Crystal data

$Ba_3Ga_2N_4$
$M_r = 607.50$
Orthorhombic
Pnna
$a = 6.2010\,(12)$ Å
$b = 10.511\,(2)$ Å
$c = 10.070\,(2)$ Å

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 26 reflections
$\theta = 23.94–24.96°$
$\mu = 25.735$ mm^{-1}
$T = 293\,(2)$ K

---

† Current address: Institute for Materials Research, Tohoku University, Sendai 980-77, Japan.

$V = 656.3\ (2)$ Å^3
$Z = 4$
$D_x = 6.148$ Mg m^{-3}

Prismatic
$0.12 \times 0.09 \times 0.04$ mm
Black

Data collection

Siemens *P*4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (*XEMP*; Siemens, 1989)
$T_{\min} = 0.572$, $T_{\max} = 0.969$
1350 measured reflections
959 independent reflections
811 observed reflections [$I > 2.0\sigma(I)$]

$R_{\rm int} = 0.0306$
$\theta_{\max} = 30°$
$h = -1 \rightarrow 8$
$k = -14 \rightarrow 1$
$l = -1 \rightarrow 14$
3 standard reflections monitored every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0288$
$wR(F^2) = 0.0603$
$S = 1.095$
959 reflections
44 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0228P)^2 + 3.2474P]$ where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 2.16$ e Å^{-3}
$\Delta\rho_{\min} = -1.48$ e Å^{-3}
Extinction correction: $F_c^* = kF_c/[1 + (0.001\chi \times F_c^2\lambda^3/\sin 2\theta)]^{1/4}$
Extinction coefficient: $\chi = 0.0045\ (2)$
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{cq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Ba1	0.11102 (7)	0.34415 (3)	0.91335 (4)	0.00913 (13)
Ba2	1/4	0	0.90519 (6)	0.01121 (15)
Ga1	1/4	0	0.22957 (10)	0.0059 (2)
Ga2	0.1636 (2)	1/4	1/4	0.0060 (2)
N1	0.3612 (10)	0.1467 (5)	0.1281 (6)	0.0095 (11)
N2	0.0176 (10)	0.0955 (5)	0.3294 (6)	0.0100 (11)

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

Ba1—N1$^{\rm i}$	2.623 (6)	Ba2—N2$^{\rm ix}$	3.057 (6)
Ba1—N2$^{\rm ii}$	2.729 (6)	Ba2—N2$^{\rm x}$	3.057 (6)
Ba1—N2$^{\rm iii}$	2.734 (6)	Ga1—N1$^{\rm xi}$	1.974 (6)
Ba1—N2$^{\rm iv}$	2.886 (5)	Ga1—N1	1.974 (6)
Ba1—N1$^{\rm v}$	3.265 (6)	Ga1—N2	2.024 (6)
Ba1—N1$^{\rm vi}$	3.375 (6)	Ga1—N2$^{\rm xi}$	2.024 (6)
Ba2—N1$^{\rm vi}$	2.809 (6)	Ga2—N2	2.024 (5)
Ba2—N1$^{\rm vii}$	2.809 (6)	Ga2—N2$^{\rm xii}$	2.024 (5)
Ba2—N1$^{\rm i}$	2.881 (6)	Ga2—N1$^{\rm xii}$	2.047 (6)
Ba2—N1$^{\rm viii}$	2.881 (6)	Ga2—N1	2.047 (6)
N1$^{\rm xi}$—Ga1—N1	117.7 (3)	N2—Ga2—N2$^{\rm xii}$	126.9 (4)
N1$^{\rm xi}$—Ga1—N2	113.3 (2)	N2—Ga2—N1$^{\rm xii}$	117.2 (2)
N1—Ga1—N2	96.8 (2)	N2$^{\rm xii}$—Ga2—N1$^{\rm xii}$	94.5 (2)
N1$^{\rm xi}$—Ga1—N2$^{\rm xi}$	96.8 (2)	N2—Ga2—N1	94.5 (2)
N1—Ga1—N2$^{\rm xi}$	113.3 (2)	N2$^{\rm xii}$—Ga2—N1	117.2 (2)
N2—Ga1—N2$^{\rm xi}$	120.4 (4)	N1$^{\rm xii}$—Ga2—N1	106.4 (3)

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

Only Ba and Ga were detected in the crystals by energy-dispersive X-ray spectroscopy (EDX). Precession photographs taken with the crystals sealed in a glass capillary showed that both transparent yellow crystals and black crystals had the same orthorhombic symmetry, lattice dimensions and systematic extinction conditions (0*kl*: $k + l = 2n$; *h*0*l*: $h + l = 2n$; *hk*0: $h = 2n$; *h*00: $h = 2n$; 0*k*0: $k = 2n$; 00*l* = 2*n*; space group *Pnna*). We concluded that the transparent yellow crystals and black crystals have an identical structure. The black color was probably caused by defects, a very small amount of impurity or non-stoichiometry. Intensity data were collected from a black granular crystal.

Data collection: *XSCANS* (Siemens, 1991). Cell refinement: *XSCANS*. Data reduction: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ATOMS* (Dowty, 1991). Software used to prepare material for publication: *SHELXTL/PC*.

This work was supported in part by the National Science Foundation through grant DMR-8920583 and by a fellowship for HY from the Ministry of Education, Science and Culture, Japan. We would like to thank Steve Trail and Glen Kowach for their help with sample preparation. We also wish to thank Emil Lobkovsky for aid with X-ray diffraction data collection.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: OH1094). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435–436.

Blase, W., Cordier, G., Ludwig, M. & Kniep, R. (1994). *Z. Naturforsch. Teil B*, **49**, 501–505.

Cordier, G. (1988). *Z. Naturforsch. Teil B*, **43**, 1253–1255.

Cordier, G., Höhn, P., Kniep, R. & Rabenau, A. (1990). *Z. Anorg. Allg. Chem.* **591**, 58–66.

Dowty, E. (1991). *ATOMS. A Computer Program for Displaying Atomic Structures*. Shape Software, USA.

Gudat, A., Haag, S., Höhn, P., Kniep, R., Milius, W. & Rabenau, A. (1991). *J. Alloys Compd.* **177**, L17–L19.

Gudat, A., Kniep, R. & Rabenau, A. (1990). *J. Less-Common Met.* **161**, 31–36.

Peters, J. & Krebs, B. (1982). *Acta Cryst.* B**38**, 1270–1272.

Sheldrick, G. M. (1990). *SHELXTL/PC User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Siemens (1989). *XEMP. Empirical Absorption Correction Program*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1991). *XSCANS User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Verdier, P., L'Haridon, P., Maunaye, M. & Marchand, R. (1974). *Acta Cryst.* B**30**, 226–228.

Verdier, P., Marchand, R. & Lang, J. (1970). *C. R. Acad. Sci. Ser. C*, **271**, 1002–1004.

Verdier, P., Marchand, R. & Lang, J. (1973). *C. R. Acad. Sci. Ser. C*, **276**, 607–609.

Yamane, H. & DiSalvo, F. J. (1995). *Solid State Chem.* **119**, 375–379.