| | | | | |
|---|---|---|---|---|
| O5 | 0,2062 (5) | 0,0638 (3) | 0,9845 (4) | 0,0211 (9) |
| O6 | 0,0577 (5) | 0,3392 (3) | 0,6098 (4) | 0,0137 (8) |
| O7 | 0,2401 (5) | 0,2466 (3) | 0,8826 (4) | 0,0147 (8) |
| O8 | 0,0597 (5) | 0,1371 (3) | 0,6124 (4) | 0,0169 (9) |
| O9 | 0,4374 (5) | 0,1412 (3) | 0,7328 (4) | 0,0179 (9) |

Tableau 2. *Paramètres géométriques (Å, °)*

| | | | |
|---|---|---|---|
| Mo1—O9 | 1,701 (4) | K1—O3 | 2,666 (4) |
| Mo1—O8 | 1,706 (4) | K1—O5$^{iii}$ | 2,704 (4) |
| Mo1—O3 | 1,985 (4) | K1—O1$^{v}$ | 2,713 (4) |
| Mo1—O7 | 2,010 (4) | K1—O9$^{i}$ | 2,765 (4) |
| Mo1—O6 | 2,143 (4) | K1—O4 | 3,042 (4) |
| Mo1—O2 | 2,198 (4) | K1—O2 | 3,254 (4) |
| As1—O1 | 1,637 (4) | K1—O8$^{iii}$ | 3,418 (4) |
| As1—O2$^{i}$ | 1,667 (3) | K2—O6 | 2,761 (4) |
| As1—O3 | 1,698 (4) | K2—O7 | 2,857 (4) |
| As1—O4 | 1,756 (4) | K2—O1$^{iv}$ | 2,876 (4) |
| As2—O5$^{ii}$ | 1,626 (4) | K2—O9$^{iv}$ | 2,888 (4) |
| As2—O6$^{iii}$ | 1,663 (3) | K2—O2 | 2,944 (4) |
| As2—O7$^{ii}$ | 1,703 (4) | K2—O8$^{vi}$ | 3,016 (4) |
| As2—O4 | 1,758 (4) | K2—O1$^{vii}$ | 3,085 (4) |
| K1—O5$^{iv}$ | 2,601 (4) | K2—O8$^{iv}$ | 3,090 (4) |
| O9—Mo1—O8 | 100,9 (2) | O6—Mo1—O2 | 74,5 (1) |
| O9—Mo1—O3 | 96,7 (2) | O1—As1—O2$^{i}$ | 116,2 (2) |
| O8—Mo1—O3 | 95,2 (2) | O1—As1—O3 | 111,5 (2) |
| O9—Mo1—O7 | 95,6 (2) | O2$^{i}$—As1—O3 | 112,0 (2) |
| O8—Mo1—O7 | 97,9 (2) | O1—As1—O4 | 112,9 (2) |
| O3—Mo1—O7 | 160,1 (2) | O2$^{i}$—As1—O4 | 105,2 (2) |
| O9—Mo1—O6 | 166,0 (2) | O3—As1—O4 | 97,3 (2) |
| O8—Mo1—O6 | 93,1 (2) | O5$^{ii}$—As2—O6$^{iii}$ | 116,7 (2) |
| O3—Mo1—O6 | 82,9 (1) | O5$^{ii}$—As2—O7$^{ii}$ | 111,4 (2) |
| O7—Mo1—O6 | 81,4 (1) | O6$^{iii}$—As2—O7$^{ii}$ | 112,6 (2) |
| O9—Mo1—O2 | 91,5 (2) | O5$^{ii}$—As2—O4 | 110,4 (2) |
| O8—Mo1—O2 | 167,5 (2) | O6$^{iii}$—As2—O4 | 103,9 (2) |
| O3—Mo1—O2 | 82,8 (1) | O7$^{ii}$—As2—O4 | 100,3 (2) |
| O7—Mo1—O2 | 81,2 (1) | | |

Codes de symétrie: (i) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $x, y, z - 1$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$; (iv) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (v) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (vi) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (vii) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$.

La largeur de balayage est $(0,83 + 1,50\,\mathrm{tg}\,\theta)^\circ$. Les intensités ont été corrigées des facteurs de Lorentz et de polarisation. La structure a été résolue par la méthode de l'atome lourd (*SHELXS*86; Sheldrick, 1985) puis affinée par la méthode des moindres carrés (*SHELXL*93; Sheldrick, 1993).

Collection des données: *CAD*-4-*Express* (Duisenberg, 1992; Macicek & Yordanov, 1992). Affinement des paramètres de la maille: *CAD*-4-*Express*. Réduction des données: *MolEN* (Fair, 1990).

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Les listes des facteurs de structure, des facteurs d'agitation thermique anisotrope et des paramètres géométriques ont été déposées au dépôt d'archives de l'UICr (Référence: BR1131). On peut en obtenir des copies en s'adressant à: The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.

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# A Reinvestigation of $\beta$-Gallium Oxide

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## Abstract

$\beta$-$Ga_2O_3$ contains two crystallographically different Ga atoms in the asymmetric unit, one with tetrahedral and the other with octahedral coordination geometry. The Ga—O distances are in the range 1.833 (1)–1.863 (2) Å within the tetrahedra, but are longer within the octahedra [1.935 (2)–2.074 (1) Å]. The O atoms have a distorted cubic close packing. The crystal structure of $\beta$-gallium oxide has been determined previously by Geller [*J. Chem. Phys.* (1960), **33**, 676–684].

## Comment

$\beta$-$Ga_2O_3$ belongs to the group of potential optical materials among the aluminium and gallium oxides (Geller, 1960, 1977, and references therein; Aubay & Gourier, 1992; Harwing, Kellendonk & Slappendel, 1978; Matsumoto, Aoki, Kinoshita & Aono, 1974; Büscher & Lehmann, 1987).

The crystal structure of the title compound has been determined previously by Geller (1960) from Weissenberg film data. For a meaningful comparison

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with other structures, more accurate data were needed. When crystals of $\beta$-$Ga_2O_3$ became available during a study of the phase equilibria in the system $Ga_2O_3$–$Li_2O$–PbO–$B_2O_3$, it was decided to redetermine the crystal structure.

In $\alpha$-$Ga_2O_3$, the Ga atoms display only octahedral coordination geometry (Marezio & Remeika, 1967). The $\beta$ phase, however, contains two crystallographically inequivalent Ga positions, one with tetrahedral geometry (Ga1) and one with octahedral geometry (Ga2). The octahedra share edges to form double chains parallel to **b**; these chains are connected by corner-sharing tetrahedra (Fig. 1). The O atoms are in a distorted ccp pattern. The average Ga1—O distance is 1.844 (2) Å and the O—Ga1—O angles are in the range 105.92 (7)–119.59 (9)°, indicating distorted tetrahedral coordination geometry. In $LiGa_5O_8$ (Åhman, Svensson & Albertsson, 1995), Ga is surrounded by a more regular tetrahedron of O atoms with an average O—Ga—O angle of 109.42 (7)° and an average Ga—O distance of 1.879 (2) Å. The average Ga2—O distance for the octahedron is 1.988 (7) Å and the O—Ga2—O angles are in the range 80.91 (6)–103.22 (9)°. The distances are comparable to those in $\alpha$-$Ga_2O_3$, in which the average value is 1.99 (1) Å (Marezio & Remeika, 1967).

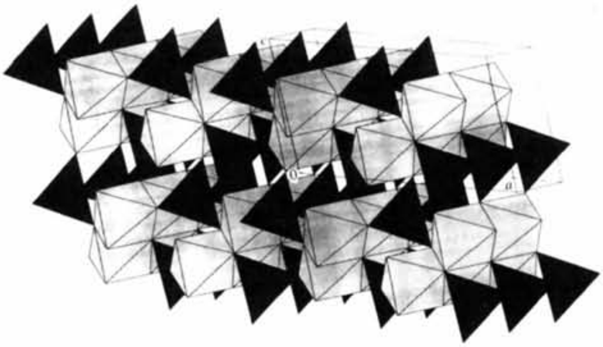

Fig. 1. A polyhedron diagram of $\beta$-$Ga_2O_3$ with the unit-cell orientation indicated. The O atoms form a distorted ccp pattern with Ga1 in tetrahedral and Ga2 in octahedral sites.

Comparison of the present structural model with that determined by Geller (1960) shows rather small differences. However, the precision in the present work is about ten times better than in the previous study.

## Experimental

The crystal used for the single-crystal investigation was grown from a PbO–$B_2O_3$ flux. $Li_2CO_3$ and $Ga_2O_3$ in a molar ratio of 1:5 were mixed in a mortar with twice the amount of PbO and $B_2O_3$. The mixture was placed in a platinum crucible, heated to 473 K and left for 2 h at this temperature to remove possible traces of water. The temperature was then increased at a rate of about 100 K $h^{-1}$ to 1523 K. After soaking for 4 h, the temperature of the mixture was decreased at a rate of 5 K $h^{-1}$ to 773 K, at which point the furnace was turned off. The flux was removed with dilute nitric acid, yielding needle-shaped crystals up to 4 mm long.

*Crystal data*

$Ga_2O_3$
$M_r = 187.44$
Monoclinic
$C2/m$
$a = 12.214\,(3)$ Å
$b = 3.0371\,(9)$ Å
$c = 5.7981\,(9)$ Å
$\beta = 103.83\,(2)°$
$V = 208.85\,(1)$ Å$^3$
$Z = 4$
$D_x = 5.961$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 20 reflections
$\theta = 28.0$–$43.0°$
$\mu = 25.469$ mm$^{-1}$
$T = 273.2$ K
Needle
0.14 × 0.04 × 0.03 mm
Colourless

*Data collection*

CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: numerical by integration from crystal shape
$T_{min} = 0.0983$, $T_{max} = 0.2639$
2787 measured reflections
1481 independent reflections
672 observed reflections $[I > 3\sigma(I)]$

$R_{int} = 0.073$
$\theta_{max} = 39.95°$
$h = 0 \rightarrow 22$
$k = -5 \rightarrow 5$
$l = -10 \rightarrow 10$
3 standard reflections monitored every 200 reflections intensity decay: none

*Refinement*

Refinement on $F$
$R = 0.022$
$wR = 0.032$
$S = 1.08$
672 reflections
32 parameters
$w = 1/3D[\sigma^2(F) + 0.025F^2]$
$(\Delta/\sigma)_{max} = 0.0002$
$\Delta\rho_{max} = 2.89$ e Å$^{-3}$
$\Delta\rho_{min} = -1.61$ e Å$^{-3}$

Extinction correction: isotropic type II Gaussian (Becker & Coppens, 1975)
Extinction coefficient: $1.280 \times 10^3$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Ga1 | 0.09050 (2) | 0 | 0.79460 (5) | 0.0038 (1) |
| Ga2 | 0.15866 (2) | 1/2 | 0.31402 (5) | 0.0040 (1) |
| O1 | 0.1645 (2) | 0 | 0.1098 (3) | 0.0060 (4) |
| O2 | 0.1733 (2) | 0 | 0.5632 (4) | 0.0056 (4) |
| O3 | −0.0041 (2) | 1/2 | 0.2566 (3) | 0.0042 (4) |

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

| | | | |
|---|---|---|---|
| Ga1—O1$^i$ | 1.835 (2) | Ga2—O2 | 2.074 (1) |
| Ga1—O2 | 1.863 (2) | Ga2—O2$^{iii}$ | 2.005 (2) |
| Ga1—O3$^{ii}$ | 1.833 (1) | Ga2—O3 | 1.935 (2) |
| Ga2—O1 | 1.937 (1) | | |

| | | | |
|---|---|---|---|
| $O1^{i}$—Ga1—O2 | 119.59 (9) | O1—Ga2—$O2^{iii}$ | 91.87 (7) |
| $O1^{i}$—Ga1—$O3^{ii}$ | 106.79 (7) | O1—Ga2—O3 | 94.66 (7) |
| O2—Ga1—$O3^{ii}$ | 105.92 (7) | O2—Ga2—$O2^{v}$ | 94.14 (7) |
| $O3^{ii}$—Ga1—$O3^{iv}$ | 111.9 (1) | O2—Ga2—$O2^{iii}$ | 80.91 (6) |
| O1—Ga2—$O1^{v}$ | 103.22 (9) | O2—Ga2—O3 | 91.95 (7) |
| O1—Ga2—O2 | 80.91 (6) | | |

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

The starting parameters for the refinement were taken from Geller (1960). One reflection (234) with $\Delta F/\sigma = 53.6$ was removed since the next largest value (5.2 for $\bar{3}10$) is more than 90% smaller. The large residual electron density (2.89 e Å$^{-3}$) is situated between Ga1 and Ga2. Refinement including this position as possible disorder did not lead to an improved model. Anharmonic tensors were also used in an attempt to describe the residual electron density as thermal displacement. Third and fourth order ($\gamma$, $\delta$) tensor components in the Edgeworth expansion were refined, but neither $\Delta\rho$ nor the $R$ values were significantly improved.

Wolten & Chase (1976) proposed that the space group for $\beta$-$Ga_2O_3$ should be $P1$. No evidence has been found in the present study to support this, since the diffraction symmetry and systematic extinctions clearly indicate a $C$-centered monoclinic cell, as discussed by Geller (1977). Refinement of the structure in space group $P1$ gave no improvement.

Data collection: *CAD*-4 *Software* (Enraf-Nonius, 1989). Cell refinement: *LATCON* (Schwarzenbach & King, 1992). Data reduction: *CRYST* (Lundgren, 1982). Program(s) used to solve structure: *CRYST*. Program(s) used to refine structure: *CRYST*. Software used to prepare material for publication: *TEXSAN* (Molecular Structure Corporation, 1992).

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: FG1144). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# $Ba_3[V_{10}O_{28}].19H_2O$

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## Abstract

The crystal structure of barium decavanadate nonadecahydrate, $Ba_3[V_{10}O_{28}].19H_2O$, has been determined. The polyanion consists of ten distorted $VO_6$ edge-sharing octahedra and has a well established structure. There are two crystallographically independent decavanadate anions in the asymmetric unit, located around the centres of inversion at $\frac{1}{2},0,0$ and $0,\frac{1}{2},\frac{1}{2}$. Each of the three $Ba^{2+}$ cations is surrounded by nine O atoms from water molecules and $[V_{10}O_{28}]^{6-}$ anions in a distorted square antiprism with one additional vertex.

## Comment

Several structures containing the $[V_{10}O_{28}]^{6-}$ anion are known from the literature: $Na_6[V_{10}O_{28}].18H_2O$ (Durif, Averbuch-Pouchot & Guitel, 1980), $Ca_3[V_{10}O_{28}].17H_2O$ (Marvin & Magin, 1959; Swallow, Ahmed & Barnes, 1966), $Sr_3[V_{10}O_{28}].22H_2O$ (Nieto, Salagre, Medina, Sueritas & Solans, 1993), $Er_2[V_{10}O_{28}].25H_2O$ (Rivero, Rigotti, Punte & Navaza, 1984) and double salts such as $K_2Mg_2[V_{10}O_{28}].16H_2O$, $Cs_2Mg_2[V_{10}O_{28}].16H_2O$ and $K_2Zn_2[V_{10}O_{28}].16H_2O$ (Weeks, Cisney & Sherwood, 1951; Evans, 1966). However, although the title compound was prepared 120 years ago (Norblad, 1875), up to now its structure has remained unsolved.

The title compound was prepared and studied as part of our research on molybdates, vanadates and mixed molybdovanadates (Kamenar, Cindrić & Strukan, 1994; Cindrić, Kamenar, Strukan & Veksli, 1995). The decavanadate anion consists of ten distorted $VO_6$ octahedra sharing edges and is basically the same as that found in other inorganic decavanadates. The two crystallographically independent $[V_{10}O_{28}]^{6-}$ anions in the asymmetric

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