

## Monoclinic

 $P2_1/c$  $a = 9.0306(10) \text{ \AA}$  $b = 6.6484(10) \text{ \AA}$  $c = 12.800(2) \text{ \AA}$  $\beta = 96.88(1)^\circ$  $V = 762.97(19) \text{ \AA}^3$  $Z = 4$  $D_x = 4.838 \text{ Mg m}^{-3}$  $D_m = 4.833 \text{ Mg m}^{-3}$  $D_m$  measured by picnometry

Cell parameters from 25 reflections

 $\theta = 5.06\text{--}17.88^\circ$  $\mu = 21.931 \text{ mm}^{-1}$  $T = 293(2) \text{ K}$ 

Parallelepiped

 $0.09 \times 0.08 \times 0.07 \text{ mm}$ 

Dark red

at approximately  $0.85 \text{ \AA}$  from the heavy atom Au1. They are due to the irregular crystal shape and the absorption correction method.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CADAK* and *SORTAV* (Blessing, 1987). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ATOMS* (Dowty, 1985). Software used to prepare material for publication: *SHELXL97*.

We are grateful to Dr Mohamed Souhassou (Laboratoire de Cristallographie et Modélisation des Matériaux Minéraux et Biologiques, Faculté des Sciences de Nancy I) for his help during the data reduction.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1203). Services for accessing these data are described at the back of the journal.

## Data collection

Enraf–Nonius CAD-4 diffractometer

 $\omega 2\theta$  scans

Absorption correction:

 $\psi$  scan (*SORTAV*;

Blessing, 1987)

 $T_{\min} = 0.166$ ,  $T_{\max} = 0.215$ 

2436 measured reflections

1937 independent reflections

1246 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.045$  $\theta_{\text{max}} = 23.92^\circ$  $h = -13 \rightarrow 12$  $k = 0 \rightarrow 9$  $l = 0 \rightarrow 18$ 

2 standard reflections

frequency: 180 min

intensity decay: 0.1%

## Refinement

Refinement on  $F^2$  $R[F^2 > 2\sigma(F^2)] = 0.042$  $wR(F^2) = 0.101$  $S = 1.032$ 

1937 reflections

59 parameters

 $w = 1/[\sigma^2(F_o^2) + (0.0276P)^2 + 0.4389P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\text{max}} < 0.001$  $\Delta\rho_{\text{max}} = 1.298 \text{ e \AA}^{-3}$  $\Delta\rho_{\text{min}} = -2.905 \text{ e \AA}^{-3}$ 

Extinction correction:

*SHELXL97*

Extinction coefficient:

0.0015 (3)

Scattering factors from

*International Tables for Crystallography* (Vol. C)

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Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j$			
	$x$	$y$	$z$	$U_{\text{eq}}$
Au1	0	0	0	0.02609 (18)
Au2	1/2	0	0	0.02917 (19)
K	0.2128 (4)	0.4492 (6)	0.1813 (3)	0.0528 (9)
Br1	−0.13341 (19)	0.2934 (2)	0.04766 (12)	0.0463 (4)
Br2	0.09492 (19)	−0.0538 (3)	0.18234 (11)	0.0442 (4)
Br3	0.5056 (2)	0.1517 (3)	0.17070 (13)	0.0604 (5)
Br4	0.6635 (2)	−0.2664 (3)	0.07207 (13)	0.0516 (4)

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A powder diffraction study of BaCaGa<sub>4</sub>O<sub>8</sub>

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## Abstract

The results of the structural determination of barium calcium tetragallium octaoxide, BaCaGa<sub>4</sub>O<sub>8</sub>, from X-ray (Cu  $K\alpha$ ) powder diffraction data and refinement by the Rietveld technique are presented. In BaCaGa<sub>4</sub>O<sub>8</sub>, GaO<sub>4</sub> tetrahedra are arranged in a tridymite-like framework. The arrangement of GaO<sub>4</sub> tetrahedra has not previously

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Au1—Br1	2.4096 (15)	K··Br1 <sup>ii</sup>	3.395 (4)
Au1—Br2	2.4146 (15)	K··Br2 <sup>iii</sup>	3.454 (4)
Au1—K	4.114 (4)	K··Br2 <sup>iv</sup>	3.472 (4)
Au2—Br3	2.4016 (17)	K··Br2	3.510 (4)
Au2—Br4	2.4172 (15)	K··Br4 <sup>i</sup>	3.525 (4)
K··Br3 <sup>i</sup>	3.274 (4)	K··Br1	3.534 (4)
K··Br3	3.318 (4)	K··Br4 <sup>v</sup>	3.756 (4)
Br1—Au1—Br2	90.31 (5)	Br3—Au2—Br4	90.87 (6)
Br1 <sup>vi</sup> —Au1—Br2	89.69 (5)		

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

In the final electron-density difference map, the minimum [ $-2.91 \text{ e \AA}^{-3}$  at  $(0.0844, -0.0080, -0.0257)$ ] and maximum [ $1.30 \text{ e \AA}^{-3}$  at  $(-0.0208, 0.0685, -0.0537)$ ] peaks both occur

been found among compounds with the stuffed tridymite structure.

### Comment

Many investigations of the crystal structures of compounds which have a derivative structure of tridymite have been performed (Kanamaru & Kiriyama, 1964; Meriani & Slocari, 1970; Hermann-Ronzaud & Bacmann, 1971, 1975; Mitsuda *et al.*, 1971; Deiseroth & Müller-Buschbaum, 1973*a,b*; Hörkner & Müller-Buschbaum, 1973, 1976, 1979; Cadée, 1975; Schulze & Müller-Buschbaum, 1981; Abbas *et al.*, 1983; Leib & Müller-Buschbaum, 1986). In these compounds,  $AO_4$  ( $A = S, Si, Fe, Al, Ga$ ) tetrahedra are arranged in a derivative structure of tridymite, and other larger cations occupy the large cavities of the framework (these latter sites are, of course, unoccupied in tridymite itself). The framework consists of six-membered rings of tetrahedra. In such six-membered rings, there are only eight topologically different arrangements of tetrahedra that point either up or down. One of these, UUDUUD ( $U = \text{up}$  and  $D = \text{down}$ ), has not been observed before and  $BaCaGa_4O_8$  has this arrangement. The Fe of  $BaCaFe_4O_8$  could be substituted partially by Ga; the pure compound  $BaCaGa_2Fe_2O_8$  was prepared by Cadée (1975). An attempt to substitute more Ga was not successful as other phases were formed. The structure is built up from a three-dimensional network of  $GaO_4$  tetrahedra sharing corners where Ba and Ca atoms are inserted.

A set of the first 22 experimental diffraction peaks was used for the automatic indexing with the program *ITO* (Visser, 1969). The results showed cell parameters  $a = 8.246(1)$ ,  $b = 9.202(1)$ ,  $c = 5.195(1)$  Å,  $\alpha = \beta = \gamma = 90^\circ$ . This solution can explain all the observed lines with the minimum cell volume and was selected for the determination of the space group. The systematic absences are consistent with the space groups *I222* (No. 23), *I2\_12\_12\_1* (No. 24), *Imm2* (No. 44) and *Immm* (No. 71) (Vos & Buerger, 1996) only. In order to confirm the unit-cell parameters, electron-diffraction patterns of  $BaCaGa_4O_8$  were registered. Most of the electron-diffraction patterns could be indexed using the above lattice parameters.

The full-profile fitting and peak decomposition were performed in the angular range  $15^\circ < 2\theta < 140^\circ$  with the program *EXTRA* (Altomare, Burla, Cascarano *et al.*, 1994), using the Pearson VII profile function; the  $|F|^2$  set was extracted. The discrepancy factors obtained with *EXTRA* are  $R_{wp} = 22.14$  and  $R_p = 15.8\%$ .

The *SIRPOW.92* (Altomare, Burla, Camalli *et al.*, 1994) program was applied to the  $|F|^2$  data set extracted by *EXTRA*, using the space group *Imm2*. The final  $R$  value was 10.31%. The space groups *I222* (No. 23), *I2\_12\_12\_1* (No. 24) and *Immm* (No. 71) gave final  $R$  values of 22.41, 28.33 and 22.19%, respectively, so these three space groups were rejected.

The structural model obtained in the previous step with space group *Imm2* was used as a starting model for Rietveld profile refinement with *RIETAN94* (Izumi, 1993; Kim & Izumi, 1994). The comparison between the observed and calculated pattern and the difference curve is shown in Fig. 1. Selected bond lengths and angles are given in Table 2.

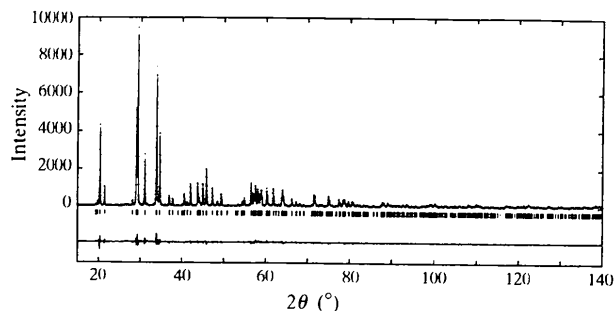


Fig. 1. The comparison between the observed and calculated patterns and the difference curve.

In the structure of  $BaCaGa_4O_8$  (Fig. 2), the Ga atoms are, as expected, tetrahedrally coordinated, with each  $GaO_4$  tetrahedron sharing all of its corners. The tetrahedra form six-membered rings in the directions  $[100]$  and  $[010]$ . It should be noted that the framework is not topologically the same as the tridymite framework. The differences between the structures stem from the fact that in each six-membered ring of the tetrahedra in  $BaCaGa_4O_8$ , four tetrahedra point 'up' the  $a$  axis while the other two point 'down'. Thus, the sequence of 'up' and 'down' tetrahedra in  $BaCaGa_4O_8$  is UUDUUD. As shown in Table 3, in such six-membered rings there are only eight topologically different arrangements of tetrahedra that point either up or down. One of these, UUDUUD, has not been reported so far. Successive layers of tetrahedral rings are almost exactly eclipsed as viewed along the  $b$  and  $c$  axes. Individual layers are joined parallel to the  $a$  axis by connecting tetrahedra that point down in one layer with those that point up in the layer below. The  $GaO_4$  tetrahedra of  $BaCaGa_4O_8$  deviate slightly from the 'ideal tetrahedron'. Ga—O distances vary between 1.821 (8) and 1.869 (6) Å. The angles between the central atoms and the corners of the tetrahedra show pronounced deviations from the ideal value of  $109.47^\circ$ . The Ba and Ca atoms lie approximately at the center of the large cavities in the tetrahedral framework. The Ba atoms are surrounded by ten O atoms. Ba—O distances vary between 2.660 (11) and 3.371 (11) Å; the average distance is 2.992 (11) Å, which is slightly longer than that of 2.89 Å for  $BaGa_2O_4$ . The Ca atoms are surrounded by eight O atoms. Ca—O distances vary between 2.413 (12) and 3.161 (11) Å; the average distance is 2.629 (11) Å, which is slightly longer than that of 2.61 Å for  $CaGa_2O_4$ .

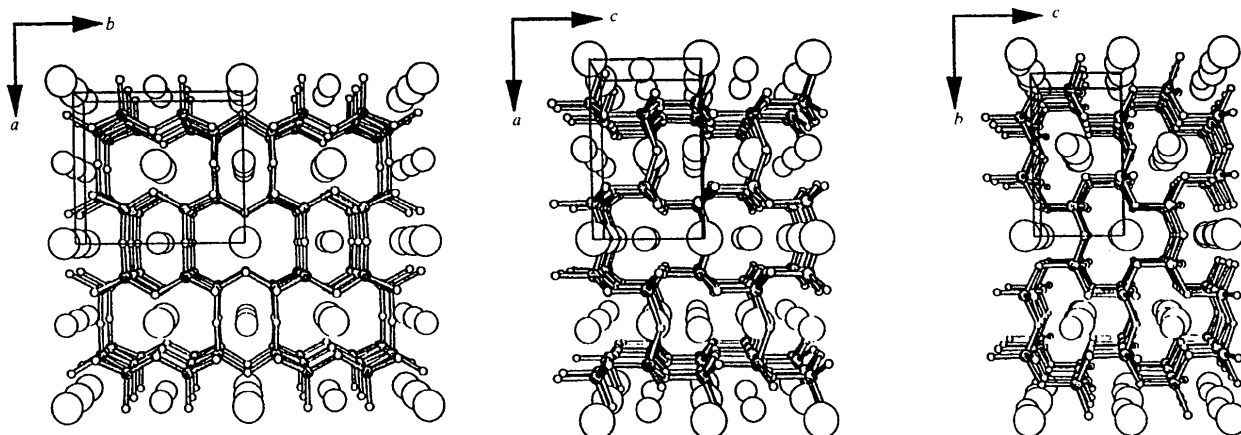


Fig. 2. Projection of the structure showing the arrangement of GaO<sub>4</sub> tetrahedra.

## Experimental

Samples of BaGa<sub>2</sub>O<sub>4</sub> and CaGa<sub>2</sub>O<sub>4</sub> were initially prepared by mixing stoichiometric quantities of BaCO<sub>3</sub>, CaCO<sub>3</sub> and Ga<sub>2</sub>O<sub>3</sub> (Rare Metallic Co. Ltd, purity > 99.99%). The mixtures were fired for 6 h at 1273 K for BaGa<sub>2</sub>O<sub>4</sub> and 1373 K for CaGa<sub>2</sub>O<sub>4</sub> in air. A powder specimen of BaCaGa<sub>4</sub>O<sub>8</sub> was obtained by a solid-state reaction. A pressed pellet mixture of equal amounts of BaGa<sub>2</sub>O<sub>4</sub> and CaGa<sub>2</sub>O<sub>4</sub> was fired for 96 h at 1473 K, which is below the melting point, and quenched. The mixture was then reground, repelleted and refired twice.

### Crystal data

BaCaGa<sub>4</sub>O<sub>8</sub>

*M<sub>r</sub>* = 584.29

Orthorhombic

*Imm*2

*a* = 8.2535 (1) Å

*b* = 9.2084 (1) Å

*c* = 5.1610 (1) Å

*V* = 392.25 (1) Å<sup>3</sup>

*Z* = 2

*D<sub>x</sub>* = 4.9471 (1) Mg m<sup>-3</sup>

Cu Kα radiation

λ = 1.540562, 1.544390 Å

Cell parameters from 494 reflections

θ = 7.5–70.0°

μ = 60.76 mm<sup>-1</sup>

*T* = 293 K

Pale white

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$B_{\text{eq}} = (4/3) \sum_i \sum_j \beta^{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B<sub>eq</sub></i>
Ga	0.2916 (2)	0.1672 (2)	0.4612 (4)	0.46 (4)
Ca	0	1/2	0.4339 (9)	0.11 (4)
Ba	0	0	0	0.75 (4)
O1	0.2939 (8)	0.1694 (8)	0.1052 (14)	1.26 (18)
O2	0	0.3296 (12)	0.079 (2)	1.0 (3)
O3	0.1872 (13)	0	0.581 (2)	1.6 (3)

Table 2. Selected geometric parameters (Å, °)

Ga—O1 <sup>i</sup>	1.821 (8)	Ca—O3 <sup>iii</sup>	3.161 (11)
Ga—O2 <sup>ii</sup>	1.824 (4)	Ba—O3 <sup>iv</sup>	2.660 (11)
Ga—O1	1.837 (7)	Ba—O1	2.935 (7)
Ga—O3	1.869 (6)	Ba—O2	3.062 (11)
Ca—O2	2.413 (12)	Ba—O3	3.371 (11)
Ca—O1 <sup>i</sup>	2.471 (8)		
O1 <sup>i</sup> —Ga—O2 <sup>ii</sup>	102.5 (4)	O2 <sup>ii</sup> —Ga—O1	108.8 (4)
O1 <sup>i</sup> —Ga—O1	113.8 (3)	O2 <sup>ii</sup> —Ga—O3	109.8 (4)
O1 <sup>i</sup> —Ga—O3	111.6 (3)	O1—Ga—O3	110.1 (4)

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

### Data collection

Rigaku RINT2500V diffractometer

θ/2θ scans

Specimen mounting: pellet

Specimen mounted in reflection mode

*T* = 293 K

2θ<sub>min</sub> = 15.01, 2θ<sub>max</sub> = 139.99°

Increment in 2θ = 0.03°

25 × 20 × 0.5 mm sample holder

### Refinement

Refinement on *I<sub>net</sub>*

*R<sub>p</sub>* = 0.082

*R<sub>wp</sub>* = 0.116

*R<sub>exp</sub>* = 0.080

Wavelength of incident radiation: 1.540562, 1.544390 Å

Profile function: pseudo-Voigt function and Pearson VII function

36 parameters

4176 data points

494 reflections

Weighting scheme based on measured s.u.'s

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 3. The arrangement of tetrahedra in compounds which have a derivative structure of tridymite

Arrangement	Compound	Reference
UUUUUU	BaCaFe <sub>4</sub> O <sub>8</sub>	Hermann-Ronzaud & Bacmann (1971)
	BaCaAlFe <sub>3</sub> O <sub>8</sub>	Hermann-Ronzaud & Bacmann (1971)
	BaCaGa <sub>2</sub> Fe <sub>2</sub> O <sub>8</sub>	Hermann-Ronzaud & Bacmann (1971)
	BaSrFe <sub>4</sub> O <sub>8</sub>	Hermann-Ronzaud & Bacmann (1975)
UUUUUD	BaFe <sub>2</sub> O <sub>4</sub>	Mitsuda <i>et al.</i> (1971)
UUUUDD	CaGa <sub>2</sub> O <sub>4</sub>	Deiseroth & Müller-Buschbaum (1973a)
UUUDUD	BaGa <sub>2</sub> O <sub>4</sub>	Deiseroth & Müller-Buschbaum (1973b)
UUUUDD	BaCaGa <sub>4</sub> O <sub>8</sub>	Present work
UUUUDD	BaGa <sub>2</sub> O <sub>4</sub>	Deiseroth & Müller-Buschbaum (1973b)
	NH <sub>4</sub> LiSO <sub>4</sub>	Dollase (1969)
UUDDUD	BaFe <sub>2</sub> O <sub>4</sub>	Leib & Müller-Buschbaum (1986)
	CaAl <sub>2</sub> O <sub>4</sub>	Hörkner & Müller-Buschbaum (1976)
	CaGa <sub>2</sub> O <sub>4</sub>	Hörkner & Müller-Buschbaum (1973)
	SrGa <sub>2</sub> O <sub>4</sub>	Leib & Müller-Buschbaum (1986)
UDUDUD	CaAl <sub>2</sub> O <sub>4</sub>	Hörkner & Müller-Buschbaum (1976)
	SrAl <sub>2</sub> O <sub>4</sub>	Schulze & Müller-Buschbaum (1981)
	BaAl <sub>2</sub> O <sub>4</sub>	Hörkner & Müller-Buschbaum (1979)
	BaGa <sub>2</sub> O <sub>4</sub>	Deiseroth & Müller-Buschbaum (1973b)
	[Tridymite]	Glasser & Glasser (1963)

The Cu  $K\alpha$  radiation was selected by means of a graphite monochromator. A system of diverging, anti-scattering and receiving slits of 0.5, 0.5° and 0.15 mm, respectively, was used; one Soller slit was positioned on the incident beam before the divergent slit, and one was placed on the diffracted beam before the monochromator. The pattern was collected with 35 kV tube voltage and 180 mA tube current in step-scan mode (step width 0.03°, counting time 1 s per step). The electron-diffraction patterns were studied with a JEOL JEM-2000EX microscope (Electron Microscope Laboratory, Tohoku University) operating at 200 kV. Fine powder specimens for electron microscopic observations were prepared by crushing the sintered products in an agate mortar. They were then mounted on colloidal film meshes.

In the *ab initio* structure determination, the following programs were used: *ITO* (Visser, 1969) for the automatic indexing procedure, *EXTRA* (Altomare, Burla, Cascarano *et al.*, 1994) for the full-profile peak decomposition and for extraction of the squared structure-factor moduli ( $|F|^2$ ), the atomic positions were obtained by the direct-methods program *SIRPOW92* (Altomare, Burla, Camalli *et al.*, 1994), and the profile refinement, by the Rietveld method, was performed using *RIETAN94* (Kim & Izumi, 1994). Selected bond lengths and angles were calculated using *ORFFEPPC* (Busing *et al.*, 1964), and the crystal structure information was converted into a standard format by *STRUCTURE TIDY* (Parthé & Gelato, 1984; Gelato & Parthé, 1987).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1030). Services for accessing these data are described at the back of the journal.

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## BaNb<sub>4-x</sub>Ti<sub>x</sub>O<sub>6</sub> (x = 0.53)

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## Abstract

The title compound, barium niobium titanium oxide, is isostructural with BaNb<sub>4</sub>O<sub>6</sub>, *i.e.* it contains alternating NbO and perovskite-type single slabs. The NbO slabs can alternatively be described as layers of Nb<sub>6</sub>O<sub>12</sub> clusters, condensed *via* corner sharing among the central Nb<sub>6</sub> octahedra.

## Comment

A number of compounds with Nb<sub>6</sub>O<sub>12</sub> clusters have been synthesized in the K–, Sr–, Ba– and Eu–Nb–O systems (Köhler *et al.*, 1992). These clusters can be discrete, or condensed *via* corner sharing among the central Nb<sub>6</sub> octahedra. Dimers have been found in K<sub>4</sub>Al<sub>2</sub>Nb<sub>11</sub>O<sub>21</sub> (Köhler *et al.*, 1989), infinite chains in BaNb<sub>5</sub>O<sub>8</sub> (Zubkov, Perelyaev, Berger, Kontsevaya *et al.*, 1990), layers in BaNb<sub>4</sub>O<sub>6</sub> (Zubkov, Perelyaev, Berger, Voronin *et al.*, 1990; Svensson *et al.*, 1991) and three-dimensional condensation in NbO (Brauer, 1941; Schäfer & Schnering, 1964). The compounds with chains or layers of condensed Nb<sub>6</sub>O<sub>12</sub> clusters can be described as intergrowth structures between NbO and BaNbO<sub>3</sub>. Those with alternating layers of NbO and perovskite form a homologous series of the form Ba<sub>n</sub>Nb<sub>3m+n</sub>O<sub>3m+3n</sub> (*n* = width of the perovskite-type slab and *m* = width of the NbO slab); these