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**Cs<sub>2</sub>Ga<sub>2</sub>O(BO<sub>3</sub>)<sub>2</sub>**

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O21	0.667 (2)	0.966 (2)	0.288 (2)	0.041 (5)
O22	0.864 (2)	0.795 (2)	0.831 (3)	0.058 (6)
O23	0.958 (2)	0.839 (2)	0.583 (3)	0.073 (7)

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## Cs<sub>2</sub>Ga<sub>2</sub>O(BO<sub>3</sub>)<sub>2</sub>

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Table 2. Selected bond lengths (Å)

Sm1—O8	2.38 (1)	Mo2—O15	1.885 (2)
Sm1—O2	2.42 (2)	Mo2—O12	2.04 (1)
Sm1—O9	2.44 (1)	Mo2—O19	2.17 (1)
Sm1—O6	2.46 (2)	Mo2—O13	2.23 (1)
Sm1—O4	2.47 (2)	Mo3—O16	1.68 (2)
Sm1—O1	2.52 (2)	Mo3—O9 <sup>i</sup>	1.72 (1)
Sm1—O5	2.56 (2)	Mo3—O19 <sup>ii</sup>	1.89 (1)
Sm1—O7	2.57 (1)	Mo3—O11	1.94 (1)
Sm1—O3	2.66 (2)	Mo3—O17	2.21 (1)
Mo1—O10	1.70 (2)	Mo3—O18	2.34 (1)
Mo1—O7	1.74 (1)	Mo4—O20	1.69 (1)
Mo1—O12	1.89 (1)	Mo4—O18	1.75 (1)
Mo1—O11	1.99 (2)	Mo4—O13	1.92 (1)
Mo1—O17	2.19 (1)	Mo4—O17 <sup>ii</sup>	1.94 (1)
Mo1—O13	2.31 (1)	Mo4—O19	2.13 (1)
Mo2—O14	1.69 (1)	Mo4—O17	2.49 (1)
Mo2—O8	1.78 (1)		

Symmetry codes: (i)  $x, y, 1 + z$ ; (ii)  $1 - x, 1 - y, 1 - z$ .

Data collection: *RCRYSTAN85* (Rigaku Corporation, 1985). Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SAP91* (Fan, 1991). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: AS1146). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Böschchen, I., Buss, B. & Krebs, B. (1974). *Acta Cryst.* **B30**, 48–56.  
 Fan, H.-F. (1991). *SAP91. Structure Analysis Programs with Intelligent Control*. Rigaku Corporation, Tokyo, Japan.  
 Isoobe, M., Marumo, F., Yamase, T. & Ikawa, T. (1978). *Acta Cryst.* **B34**, 2728–2731.  
 Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.  
 Molecular Structure Corporation. (1989). *TEXSAN. Single Crystal Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.  
 Naruke, H., Ozeki, T. & Yamase, T. (1991). *Acta Cryst.* **C47**, 489–492.  
 Naruke, H. & Yamase, T. (1991). *J. Lumin.* **50**, 55–60.  
 North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.  
 Ozeki, T. & Yamase, T. (1994). *Acta Cryst.* **B50**, 128–134.  
 Rigaku Corporation (1985). *RCRYSTAN. X-ray Analysis Program System*. Rigaku Corporation, Tokyo, Japan.  
 Sugeta, M. & Yamase, T. (1993). *Bull. Chem. Soc. Jpn.* **66**, 444–449.  
 Yamase, T. & Naruke, H. (1991). *J. Chem. Soc. Dalton Trans.* pp. 285–292.  
 Yamase, T., Naruke, H. & Sasaki, Y. (1990). *J. Chem. Soc. Dalton Trans.* pp. 1687–1696.

## Abstract

The structure of dicaesium digallium diorthoborate oxide constitutes a new type of oxide borate. It consists of a three-dimensional gallium–oxide–orthoborate lattice with Cs atoms occupying large cavities in the lattice. This lattice is made from pairs of Ga atoms connected through a shared O atom along the [001] direction; these Ga dimers are interconnected through shared O vertices to trigonal BO<sub>3</sub> groups along the [010], [110] and  $\bar{1}10$  directions, completing the tetrahedral coordination environment of each Ga atom.

## Comment

Solid-state borates have been shown to crystallize with a wide variety of structures (Heller, 1986) as a result of the vast number of possible ways of combining the borate anions with the metal-atom polyhedra. The metal-atom polyhedra may be octagonal, tetrahedral or square planar, and the borate anions may be trigonal or tetrahedral orthoborates, pyroborates or combinations thereof, linear chains, or fused rings, thus affording vast numbers of structural types. Partly in order to study such new structural types and partly to search for new non-linear optical materials (of which several examples of borates exist), we recently surveyed the Cs<sub>2</sub>O–Ga<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> phase diagram, the compounds in which have not been reported previously. Among the compounds discovered in this system is an oxide borate of a new structural type, Cs<sub>2</sub>Ga<sub>2</sub>O(BO<sub>3</sub>)<sub>2</sub>.

A unit cell of the title compound is depicted in Fig. 1. The structure consists of a three-dimensional gallium–oxide–orthoborate lattice that affords large vacancies within which Cs atoms are located. The lattice is built from pairs of Ga atoms that are interconnected through an O(7) atom and which lie roughly along the [001] direction. O(7) is an oxide anion since it is not bonded to either of the two crystallographically distinct B atoms. Each Ga atom completes its tetrahedral coordination by bonding to O atoms that constitute the two crystallographically distinct trigonal orthoborate groups. These orthoborate groups connect the Ga–O–Ga dimers roughly along the [010], [110] and  $\bar{1}10$  directions. Because the Ga–O–Ga bond angle is relatively large [140.8(4)°], large cavities are created

between groups of dimers; these also run roughly along the [110] direction. Cs atoms occupy these cavities.

All bond distances and angles are in accordance with expected values. The Cs coordination environments are irregular eight-coordinate polyhedra. The Cs—O bond distances range from 2.885 (7) to 3.456 (8) Å, with an average value of 3.22 (18) Å. These values are reasonable given the expected value of 3.12 Å obtained from the crystal radii of the eight-coordinate Cs<sup>+</sup> ion and the four-coordinate O<sup>2-</sup> ion (Shannon, 1976). Average Ga—O and B—O bond distances are 1.83 (2) and 1.37 (1) Å, respectively, which compare well with the calculated values of 1.85 and 1.39 Å. The shortest Ga—O bonds are to the oxide O(7) [1.794 (7) and 1.822 (7) Å] because this O atom has no electron density removed by the  $\pi$  system of the BO<sub>3</sub> groups.

The O atoms can be three-, four- or five-coordinate. O(3) is three-coordinate, O(1), O(6) and O(7) are four-coordinate, and O(2), O(4) and O(5) are five-coordinate.

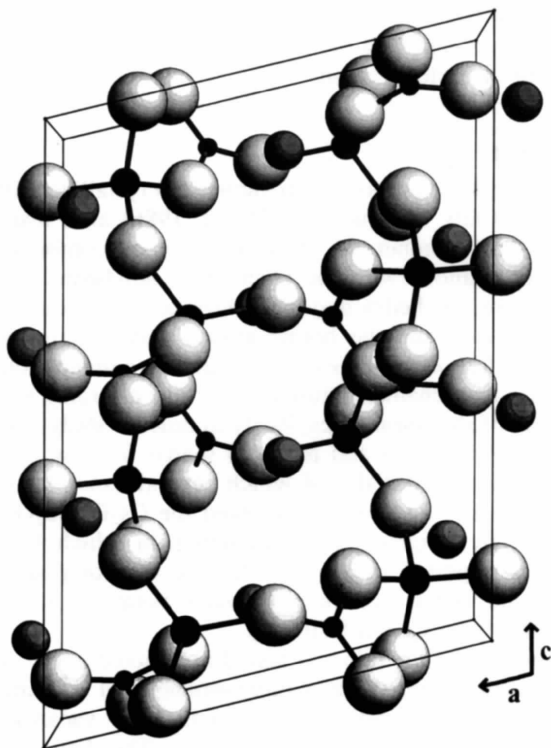


Fig. 1. Sketch of the unit cell of Cs<sub>2</sub>Ga<sub>2</sub>O(BO<sub>3</sub>)<sub>2</sub> viewed down the *b* axis, where the largest circles represent O atoms, the small black circles represent B atoms, and the medium-sized darkly shaded circles represent Ga atoms. Cs atoms are shown as medium-sized lightly shaded circles without bonding interactions.

## Experimental

A crystal of Cs<sub>2</sub>Ga<sub>2</sub>O(BO<sub>3</sub>)<sub>2</sub> was separated from a melt of the compound Cs<sub>3</sub>Ga(BO<sub>3</sub>)<sub>2</sub> in an attempt to grow crystals of the latter material. The latter material was prepared by mixing

CsNO<sub>3</sub> (Johnson Matthey, 99.9%), Ga(NO<sub>3</sub>)<sub>3</sub>·*x*H<sub>2</sub>O (Aldrich, 99.9%) and B<sub>2</sub>O<sub>3</sub> (Johnson Matthey, 99%) in a 3:1:1 molar ratio, grinding the mixture under hexane, heating it to 600 K overnight to decompose the nitrates, and then sintering it at 775 K for 2 d. Crystals of the title material were grown from a melt of this material, which obviated the need to grow them from the pure phase. The material was melted at 1025 K, slowly cooled at 6 K h<sup>-1</sup> to 575 K, and then air-quenched.

## Crystal data

Cs<sub>2</sub>Ga<sub>2</sub>O(BO<sub>3</sub>)<sub>2</sub>  
*M<sub>r</sub>* = 538.87  
 Monoclinic  
*P*2<sub>1</sub>/*c*  
*a* = 8.889 (1) Å  
*b* = 7.998 (1) Å  
*c* = 12.237 (1) Å  
 $\beta$  = 103.82 (1)°  
*V* = 844.8 (2) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 4.236 Mg m<sup>-3</sup>

Mo *K*α radiation  
 $\lambda$  = 0.71069 Å  
 Cell parameters from 20 reflections  
 $\theta$  = 15–18°  
 $\mu$  = 14.795 mm<sup>-1</sup>  
*T* = 295 K  
 Plate  
 0.45 × 0.15 × 0.06 mm  
 Colorless

## Data collection

Rigaku AFC-6R diffractometer  
 $2\theta$ - $\omega$  scans  
 Absorption correction: refined from  $\Delta F$  (DIFABS; Walker & Stuart, 1983)  
 2790 measured reflections  
 2470 independent reflections  
 2002 observed reflections [*F<sub>o</sub>*<sup>2</sup> > 3 $\sigma$ (*F<sub>o</sub>*<sup>2</sup>)]

*R*<sub>int</sub> = 0.051  
 $\theta$ <sub>max</sub> = 30°  
*h* = 0 → 12  
*k* = 0 → 11  
*l* = -17 → 17  
 3 standard reflections monitored every 200 reflections  
 intensity decay: 1.9%

## Refinement

Refinement on *F*  
*R* = 0.054  
*wR* = 0.069  
*S* = 2.53  
 2002 reflections  
 118 parameters  
 $w = 1/\sigma^2(F_o)$   
 $(\Delta/\sigma)_{\max} = 0.015$

$\Delta\rho_{\max} = 2.17 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -4.15 \text{ e \AA}^{-3}$   
 Extinction correction: none  
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j.$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Cs(1)	0.0694 (1)	0.1200 (1)	0.1525 (1)	0.0215 (4)
Cs(2)	0.5345 (1)	0.1227 (1)	0.6309 (1)	0.0210 (4)
Ga(1)	0.8398 (1)	0.1118 (1)	0.3869 (1)	0.0133 (5)
Ga(2)	0.3138 (1)	0.0630 (1)	0.8694 (1)	0.0141 (5)
B(1)	0.649 (1)	0.111 (1)	0.922 (1)	0.013 (4)
B(2)	0.169 (1)	0.143 (1)	0.435 (1)	0.015 (4)
O(1)	0.517 (1)	0.016 (1)	0.877 (1)	0.016 (3)
O(2)	0.741 (1)	0.078 (1)	0.027 (1)	0.019 (4)
O(3)	0.691 (1)	0.227 (1)	0.855 (1)	0.024 (4)
O(4)	0.027 (1)	0.221 (1)	0.406 (1)	0.018 (4)
O(5)	0.296 (1)	0.219 (1)	0.411 (1)	0.018 (4)
O(6)	0.809 (1)	0.010 (1)	0.514 (1)	0.023 (4)
O(7)	0.189 (1)	0.031 (1)	0.732 (1)	0.020 (4)

Table 2. Selected geometric parameters (Å, °)

Cs(1)—O(2 <sup>i</sup> )	2.975 (7)	Ga(1)—O(3 <sup>iv</sup> )	1.824 (7)
Cs(1)—O(2 <sup>h</sup> )	3.456 (8)	Ga(1)—O(4 <sup>ix</sup> )	1.842 (7)
Cs(1)—O(4)	3.316 (8)	Ga(1)—O(6)	1.830 (8)
Cs(1)—O(4 <sup>iii</sup> )	3.337 (8)	Ga(1)—O(7 <sup>viii</sup> )	1.822 (7)
Cs(1)—O(4 <sup>iv</sup> )	3.210 (8)	Ga(2)—O(1)	1.827 (7)
Cs(1)—O(5)	3.410 (7)	Ga(2)—O(2 <sup>viii</sup> )	1.847 (8)
Cs(1)—O(7 <sup>iv</sup> )	3.063 (8)	Ga(2)—O(5 <sup>vii</sup> )	1.836 (8)
Cs(1)—O(7 <sup>v</sup> )	3.204 (8)	Ga(2)—O(7)	1.794 (7)
Cs(2)—O(1)	3.173 (7)	B(1)—O(1)	1.39 (1)
Cs(2)—O(1 <sup>vi</sup> )	3.178 (8)	B(1)—O(2 <sup>s</sup> )	1.37 (1)
Cs(2)—O(2 <sup>vii</sup> )	3.439 (8)	B(1)—O(3)	1.35 (1)
Cs(2)—O(3)	2.885 (7)	B(2)—O(4)	1.38 (1)
Cs(2)—O(5)	3.102 (7)	B(2)—O(5)	1.37 (1)
Cs(2)—O(5 <sup>viii</sup> )	3.221 (8)	B(2)—O(6 <sup>viii</sup> )	1.36 (1)
Cs(2)—O(6)	3.241 (8)		
Cs(2)—O(6 <sup>viii</sup> )	3.321 (8)		
O(3 <sup>iv</sup> )—Ga(1)—O(4 <sup>ix</sup> )	106.2 (4)	O(2 <sup>viii</sup> )—Ga(2)—O(5 <sup>vii</sup> )	109.6 (3)
O(3 <sup>iv</sup> )—Ga(1)—O(6)	104.4 (4)	O(2 <sup>viii</sup> )—Ga(2)—O(7)	110.4 (3)
O(3 <sup>iv</sup> )—Ga(1)—O(7 <sup>viii</sup> )	108.4 (3)	O(5 <sup>vii</sup> )—Ga(2)—O(7)	108.6 (3)
O(4 <sup>ix</sup> )—Ga(1)—O(6)	114.4 (3)	O(1)—B(1)—O(2 <sup>s</sup> )	121 (1)
O(4 <sup>ix</sup> )—Ga(1)—O(7 <sup>viii</sup> )	110.5 (3)	O(2 <sup>s</sup> )—B(1)—O(3)	121 (1)
O(6)—Ga(1)—O(7 <sup>viii</sup> )	112.4 (4)	O(3)—B(1)—O(1)	118 (1)
O(1)—Ga(2)—O(2 <sup>viii</sup> )	104.9 (3)	O(4)—B(2)—O(5)	119 (1)
O(1)—Ga(2)—O(5 <sup>vii</sup> )	109.4 (3)	O(5)—B(2)—O(6 <sup>viii</sup> )	118 (1)
O(1)—Ga(2)—O(7)	113.8 (3)	O(6 <sup>viii</sup> )—B(2)—O(4)	123 (1)

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

A clear, colorless, plate-shaped crystal was mounted on a glass fiber with epoxy for X-ray structure analysis. Data were collected with a scan speed of  $16.0^\circ \text{ min}^{-1}$  in  $\omega$  and a scan width of  $(1.5 + 0.3 \tan \theta)^\circ$ .

The TEXSAN crystallographic software package (Molecular Structure Corporation, 1989) was used to solve the crystal structure. The Laue symmetry  $2/m$  and the systematic absences  $h0l$  ( $l = 2n + 1$ ) and  $0k0$  ( $k = 2n + 1$ ) unambiguously indicated space group  $P2_1/c$ . The positions of the Cs atoms were determined by a Patterson vector map and the remaining atoms were found by examination of the difference electron density maps. After isotropic refinement, the data were averaged and corrected for absorption.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1078). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Heller, G. (1986). *Topics Curr. Chem.* **131**, 39–98.  
 Molecular Structure Corporation (1989). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.  
 Shannon, R. D. (1976). *Acta Cryst.* **A32**, 751–767.  
 Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.

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## Neodymium-Doped $\text{Sr}_5(\text{PO}_4)_3\text{F}$ and $\text{Sr}_5(\text{VO}_4)_3\text{F}$

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## Abstract

Neodymium-doped  $\text{Sr}_5(\text{PO}_4)_3\text{F}$  [neodymium strontium fluoride phosphate,  $(\text{Nd},\text{Sr})_5(\text{PO}_4)_3\text{F}$ ] and neodymium-doped  $\text{Sr}_5(\text{VO}_4)_3\text{F}$  [neodymium strontium fluoride vanadate,  $(\text{Nd},\text{Sr})_5(\text{VO}_4)_3\text{F}$ ] crystallize in space group  $P6_3/m$  and are isostructural with calcium fluorophosphate,  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ . There are two different Sr sites in  $\text{Sr}_5(\text{XO}_4)_3\text{F}$ , denoted Sr(1) and Sr(2). Using single-crystal X-ray diffraction the two structures were refined to  $R$  factors of 2.3 and 2.2%, respectively, showing that Nd is present at both Sr sites in  $(\text{Sr},\text{Nd})_5(\text{VO}_4)_3\text{F}$  but only at the Sr(2) site in  $(\text{Sr},\text{Nd})_5(\text{PO}_4)_3\text{F}$ .

## Comment

Calcium fluorophosphate (FAP) crystals have been investigated previously as laser hosts, and lasing characteristics of rare-earth-doped FAP were reported as early as 1968 (Ohlmann, Steinbruegge & Mazelsky, 1968). Recent developments have reopened investigations into FAP and the whole calcium–strontium fluorophosphate system for use as laser hosts. This paper presents the detailed crystal structure refinements that followed the recent successful crystal growth of neodymium-doped  $\text{Sr}_5(\text{PO}_4)_3\text{F}$  (SFAP) and neodymium-doped  $\text{Sr}_5(\text{VO}_4)_3\text{F}$  (SVAP).

Both crystals were grown by the Czochralski method. SVAP and SFAP are isostructural and belong to the hexagonal space group  $P6_3/m$ . The structure contains layers of  $\text{XO}_4$  tetrahedra ( $X = \text{P}, \text{V}$ ) centred at two levels along [001] and  $\text{F}^-$  ions lying along the  $c$  axis, as can be seen in Fig. 1. V—O and P—O bond lengths are given in Tables 2 and 4, respectively, and show that the  $\text{VO}_4$  tetrahedra are distorted [average/(deviation) for P—O and V—O bond distances are  $1.541 \text{ \AA}/(0.004 \text{ \AA})$  and  $1.711 \text{ \AA}/(0.01 \text{ \AA})$ , respectively].

There are two independent Sr sites in the structures, the first of which, Sr(1), contains 40% of the  $\text{Sr}^{2+}$