Cs$_2$Ga$_2$O(BO$_3$)$_2$

Robert W. Smith

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Table 2. Selected bond lengths (Å)

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<th>Sm1-O2</th>
<th>Sm1-O9</th>
<th>Sm1-O6</th>
<th>Sm1-O4</th>
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<th>Sm1-O5</th>
<th>Sm1-O7</th>
<th>Sm1-O3</th>
<th>Mo1-O10</th>
<th>Mo1-O7</th>
<th>Mo1-O12</th>
<th>Mo1-O11</th>
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Symmetry codes: (i) x, y, 1 + z; (ii) 1 - x, 1 - y, 1 - z.

Data reduction: TExSAN (Molecular Structure Corporation, 1989). Program(s) used to solve structure: SAPIP1 (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

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Abstract
The structure of dicaesium digallium dorthoborate 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 BO3 groups along the [010], [110] and [110] 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 Cs2O–Ga2O3–B2O3 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, Cs2Ga2O(BO3)2.

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 [1$ar{1}$0] directions. Because the Ga–O–Ga bond angle is relatively large [140.8(4)$^\circ$], 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⁺ ion and the four-coordinate O²⁻ ion (Shannon, 1976). 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 π system of the BO₃ 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.

**Experimental**

A crystal of Cs₂Ga₂O(BO₃)₂ was separated from a melt of the compound Cs₃Ga(BO₃)₂ in an attempt to grow crystals of the latter material. The latter material was prepared by mixing CsNO₃ (Johnson Matthey, 99.9%), Ga(NO₃)₃.xH₂O (Aldrich, 99.9%) and B₂O₃ (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⁻¹ to 757 K, and then air-quenched.

**Crystal data**

Cs₂Ga₂O(BO₃)₂  
*Mo Kα radiation*  
λ = 0.71069 Å  
Cell parameters from 20 reflections  
θ = 15–18°  
μ = 14.795 mm⁻¹  
*T = 295 K*  
Plate  
0.45 × 0.15 × 0.06 mm  
Colorless

**Data collection**

Rigaku AFC-6R diffractometer  
R = 0.051  
θmax = 30°  
2θ-ω scans  
*h = 0 → 12*  
Absorption correction: refined from AF  
(DIFABS; Walker & Stuart, 1983)  
2790 measured reflections  
2470 independent reflections  
2002 observed reflections  
I > 2σ(I)  
Refinement on F  
R = 0.054  
wR = 0.069  
S = 2.53  
2002 reflections  
118 parameters  
(Δ/σ)max = 0.015  
Extinction correction: none  

**Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)**

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Ueq</th>
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<tr>
<td>Cs(1)</td>
<td>0.0694 (1)</td>
<td>0.1200 (1)</td>
<td>0.1525 (1)</td>
<td>0.0215 (4)</td>
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<td>Cs(2)</td>
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<td>0.1227 (1)</td>
<td>0.6309 (1)</td>
<td>0.0210 (4)</td>
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<td>Ga(1)</td>
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<td>0.1188 (1)</td>
<td>0.3869 (1)</td>
<td>0.0133 (5)</td>
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<td>Ga(2)</td>
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<td>B(1)</td>
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<td>O(1)</td>
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<td>0.221 (1)</td>
<td>0.406 (1)</td>
<td>0.018 (4)</td>
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<tr>
<td>O(4)</td>
<td>0.027 (1)</td>
<td>0.221 (1)</td>
<td>0.406 (1)</td>
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<td>O(7)</td>
<td>0.189 (1)</td>
<td>0.031 (1)</td>
<td>0.732 (1)</td>
<td>0.020 (4)</td>
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</table>

Fig. 1. Sketch of the unit cell of Cs₂Ga₂O(BO₃)₂ 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.
Table 2. Selected geometric parameters (Å, °)

<table>
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<tr>
<th>Bond/Distance</th>
<th>Value</th>
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<td>O(3)----Ga(1)----O(5)</td>
<td>110.6 (3)</td>
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<tr>
<td>O(3)----Ga(1)----O(6)</td>
<td>104.4 (4)</td>
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<tr>
<td>O(4)----Ga(1)----O(5)</td>
<td>118.6 (3)</td>
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<td>Symmetry codes: (i) x - 1, y, z; (ii) 1 - x, -y, -z; (iii) -x, y - ½, ½ - z; (iv) x, ½ - y, ½ + z; (v) -x, -y, 1 - z; (vi) 1 - x, ½ + y, -z; (vii) x, ½ - y, ½ + z; (viii) 1 - x, -y, 1 - z; (ix) 1 + x, y, z; (x) x, y, 1 + z.</td>
<td></td>
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</table>

A clear, colorless, plate-shaped crystal was mounted on a glass fiber with epoxy for X-ray structure analysis. The crystallographic software package (Molecular Structure Corporation, 1989) was used to solve the crystal structure. The Laue symmetry was determined by examination of the difference electron density maps. After isotropic refinement, the data were averaged and corrected for absorption.

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 00l (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
Molecular Structure Corporation (1989). *TEXSAN, TExRAY Structure Analysis Package.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

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