Crystal structure of caesium gallium(III) *catena*-[monohydrogen-monoborate-bis(monophosphate)], $CsGa[BP_2O_8(OH)]$

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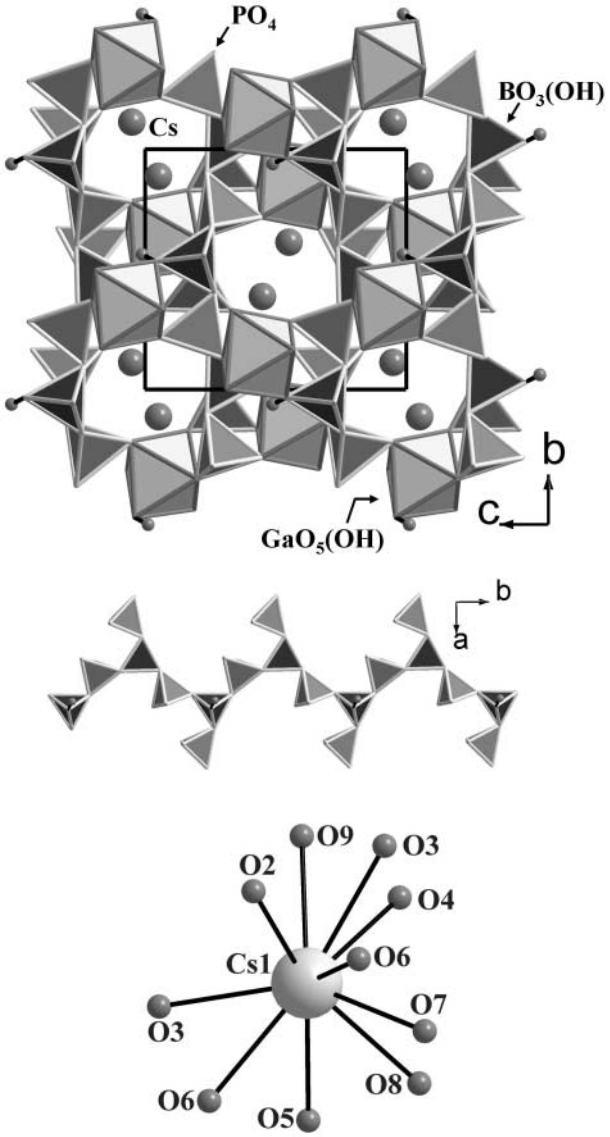

Abstract

$BCsGaHO_9P_2$, monoclinic, $P12_1/c1$ (No. 14), $a = 9.259(1)$ Å, $b = 8.6462(9)$ Å, $c = 9.615(1)$ Å, $\beta = 103.059(6)°$, $V = 749.8$ Å^3, $Z = 4$, $R_{gt}(F) = 0.050$, $wR_{ref}(F^2) = 0.104$, $T = 295$ K.

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Source of material

$CsGa[BP_2O_8(OH)]$ was synthesized under mild hydrothermal conditions. The reactions were carried out with mixtures of $Cs(OH) \cdot H_2O$ (1.679 g), $GaCl_3$ (0.35 g metal gallium dissolved in 2 ml 37% HCl), H_3BO_3 (0.618 g), LiH_2PO_4 (3.118 g) and 2 ml 85% H_3PO_4 with molar ratio of Cs : Ga : B : Li : P = 2 : 1 : 2 : 6 : 12. The mixture was filled in a teflon autoclave with about 20 ml in volume. The degree of filling was about 50%. The autoclave was placed in an oven with subsequent heating at 443 K for 7 days. All starting materials were of analytical grade purity. The composition was confirmed by chemical analysis (ICP) with Cs : Ga : B : P = 0.9(1):1.02(1):0.91(2):2.00(3). The Li content was below the detective limit of the analytical method.

Experimental details

The position of the H atom was determined from a difference Fourier map.

Discussion

In our recent investigations on Ga-containing borophosphates, mild hydrothermal conditions have been proved to be efficient in preparing new compounds with different structures, such as $NaGa[BP_2O_7(OH)_3]$, $KGa[BP_2O_7(OH)_3]$, $(NH_4)Ga[BP_2O_8(OH)]$ and $RbGa[BP_2O_8(OH)]$ [1-4]. The title compound was also synthesized under mild hydrothermal conditions.

The crystal structure of the title compound is isotypic to $CsFe[BP_2O_8(OH)]$ [5] and contains isolated $GaO_5(OH)$ octahedra sharing common O-corners with five phosphate tetrahedra and a common (OH)-corner with a hydrogenborate group to form a three dimensional framework structure. The anionic partial structure consists of open-branched vierer-single chains $[BP_2O_8(OH)]^{4-}$, which are formed by alternating hydrogenborate and phosphate tetrahedra sharing common O-corners. The $[BP_2O_8(OH)]_n$ chains run along the *b* axis and are connected via $GaO_5(OH)$ octahedra sharing common corners. The caesium cations are distributed in a zigzag arrangement within the open channels with an elliptical cross-section and running along the *a* axis. Caesium has ten oxygen neighbours with distances ranging from 3.070 Å to 3.308 Å. The Ga—O and Ga—OH bond distances in the Ga-coordinaton-octahedron range from 1.909 Å to 2.117 Å. The P—O bond distances range from 1.512 Å to 1.572 Å, and those of B—O from 1.458 Å to 1.490 Å. Bond lengths and angles of hydrogenborate and phosphate tetrahedra within the anionic chains are in the same ranges as observed in other borophosphates [1-4].

Table 1. Data collection and handling.

Crystal:	colorless transparente prism, size 0.04 × 0.05 × 0.08 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	89.09 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC7-CCD, 400 images, $\Delta\varphi = 0.6°$, 60-ω scan, $\Delta\omega = 0.6°$, $\chi = 90°$
$2\theta_{max}$:	64.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6603, 2402
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2060
$N(param)_{refined}$:	127
Programs:	SHELXL-97 [6], DIAMOND [7]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	0.1234	0.9385	0.5114	0.05

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs(1)	4*e*	0.30327(6)	0.61291(6)	0.44906(5)	0.0251(2)	0.0197(2)	0.0195(2)	–0.0004(2)	0.0024(2)	0.0035(2)
Ga(1)	4*e*	0.29621(7)	0.15438(8)	0.57305(7)	0.0075(3)	0.0078(3)	0.0052(3)	0.0004(2)	0.0007(2)	0.0000(2)
P(1)	4*e*	0.4294(2)	0.0738(2)	0.3005(2)	0.0062(6)	0.0067(6)	0.0056(6)	0.0009(5)	0.0013(5)	0.0005(5)
P(2)	4*e*	0.0829(2)	0.2689(2)	0.2869(2)	0.0072(7)	0.0075(6)	0.0081(7)	0.0009(5)	0.0011(5)	0.0009(5)
B(1)	4*e*	0.8407(7)	0.4589(7)	0.1955(7)	0.008(3)	0.003(3)	0.008(3)	0.000(2)	0.002(2)	0.002(2)
O(1)	4*e*	0.0792(5)	0.0987(5)	0.2361(5)	0.014(2)	0.007(2)	0.015(2)	–0.001(2)	0.001(2)	–0.002(2)
O(2)	4*e*	0.4187(5)	0.1657(5)	0.4325(5)	0.013(2)	0.015(2)	0.006(2)	–0.005(2)	0.007(2)	–0.005(2)
O(3)	4*e*	0.3077(5)	0.9436(5)	0.2769(5)	0.007(2)	0.014(2)	0.015(2)	–0.002(2)	0.002(2)	–0.003(2)
O(4)	4*e*	0.9171(5)	0.3189(5)	0.2568(5)	0.006(2)	0.011(2)	0.015(2)	0.002(2)	0.002(2)	0.001(2)
O(5)	4*e*	0.1465(5)	0.2822(6)	0.4459(5)	0.016(2)	0.012(2)	0.009(2)	0.006(2)	–0.001(2)	–0.001(2)
O(6)	4*e*	0.4021(5)	0.1709(5)	0.1660(5)	0.015(2)	0.009(2)	0.007(2)	0.004(2)	0.001(2)	0.002(2)
O(7)	4*e*	0.5785(5)	0.9973(5)	0.3123(5)	0.008(2)	0.014(2)	0.010(2)	0.005(2)	0.003(2)	0.006(2)
O(8)	4*e*	0.1622(5)	0.3713(5)	0.1997(5)	0.014(2)	0.012(2)	0.012(2)	–0.003(2)	0.007(2)	–0.001(2)
O(9)	4*e*	0.1767(6)	0.9670(5)	0.4604(5)	0.019(2)	0.012(2)	0.004(2)	–0.004(2)	0.001(2)	0.001(2)

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