Synthesis and Structure of a Novel Microporous Gallophosphate, $Na_3Ga_5(PO_4)_4O_2(OH)_2{\cdot}2H_2O$

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The structure of the title compound, $Na_3Ga_5(PO_4)_4O_2(OH)_2{\cdot}2H_2O$, consists of GaO_6 octahedra, GaO_5 trigonal bipyramids and PO_4 tetrahedra which, by sharing edges and corners, form an open structure containing channels (*ca.* 4 Å diameter) running along the [001] direction; two water molecules per formula unit can be desorbed.

The discovery of a new series of microporous aluminophosphates by Wilson *et al.*[1,2] has led the way to the synthesis of many novel microporous materials with interesting sorption and catalytic properties. The replacement of aluminium by gallium in such syntheses has yielded both novel structure types [3,4] and phases that are analogous to known aluminophosphates and aluminosilicates. [5–7] Most of these phases have a 1 : 1 Ga : P stoichiometry, as in $GaPO_4$. The stereochemical environment of the gallium atoms varies between different structures or within the same structure,[8] and coordinations of four, five and six have been reported. We describe here the synthesis, structure and sorption behaviour of $Na_3Ga_5(PO_4)_4O_2(OH)_2{\cdot}2H_2O$ in which, as in the aluminosilicate zeolites, the framework stoichiometry deviates from 1 : 1 and requires the presence of charge-compensating cations.

The title compound was synthesized hydrothermally in a 23 ml Teflon-lined stainless steel autoclave from a reaction mixture containing $GaCl_3$ (0.86 g), H_3PO_3 (0.6 g) and 1,4-diazabicyclo[2.2.2]octane (DABCO; 0.9 g) in 15 ml deionized water. Solid NaOH was added to the reaction mixture until a pH of *ca.* 10 was reached. The reaction mixture was heated at 10 °C min^{-1} to 190 °C, held at this temperature for 100 h, then cooled in air to room temperature. The crystalline product was separated by suction filtration, washed with water and dried in air. A suitable crystal was selected and its structure determined by four circle X-ray diffractometry.† The material has also been synthesized in the pH range 7–9 using P_2O_5 as the phosphorus source, in the absence of DABCO.

The structure of $Na_3Ga_5(PO_4)_4O_2(OH)_2{\cdot}2H_2O$, viewed along the [001] direction, is shown in Fig. 1. It contains two types of polyhedral chain running along [001]. One chain (Type I) consists of alternately disposed, corner-sharing $Ga(2)O_6$ octahedra [range of Ga–O bond lengths 1.901(3)–2.023(3) Å; O–Ga–O bond angle 90 ± 12.8°] and $P(2)O_4$ tetrahedra [range of P–O bond lengths 1.512(4)–1.547(4) Å; O–P–O bond angle 109.5 ± 2.4°], the other (Type II) contains corner-sharing, distorted $Ga(3)O_5$ trigonal bipyramids [axial Ga–O bond lengths 1.944(3) and 2.130(4) Å; range of equatorial Ga–O bond lengths 1.851(3)–1.873(3) Å]. Two of the former chains and one of the latter combine, by corner and edge sharing, to form a column running along the [001] direction (Fig. 2). In doing so, a $Ga(2)O_6$ octahedron in one of the Type I chains is always connected to a $P(2)O_4$ tetrahedron in the other (Fig. 2). Four such columns are linked together by short chains of three polyhedra to form an open structure containing channels (*ca.* 4 Å diameter) running parallel to the *c* axis (Fig. 1). The short chains of polyhedra occur every 6.39 Å along the *c* axis, and consist of a $Ga(1)O_6$ octahedron [range of Ga–O bond lengths 1.894(3)–2.027(3) Å; O–Ga–O bond angle 90.0 ± 5.3°] between two $P(1)O_4$ tetrahedra [range of P–O bond lengths 1.517(3)–1.548(4) Å; O–P–O bond angle 109.5 ± 3.6°]. Sodium cations Na(1) and Na(2) reside in the spaces between the PO_4 tetrahedra in adjacent short chains and in the centre of the main channel, respectively. The Na(1) cations are coordinated by a distorted octahedral array of oxygen atoms [range of Na–O bond lengths 2.277(4)–2.697(8) Å; O–Na–O bond angle 90 ± 27.5°]. The Na(2) cations are coordinated to eight oxygen atoms, with six short bond distances in the range 2.18(1)–2.775(6) Å and two longer bonds of 2.972(8) and 2.990(8) Å.

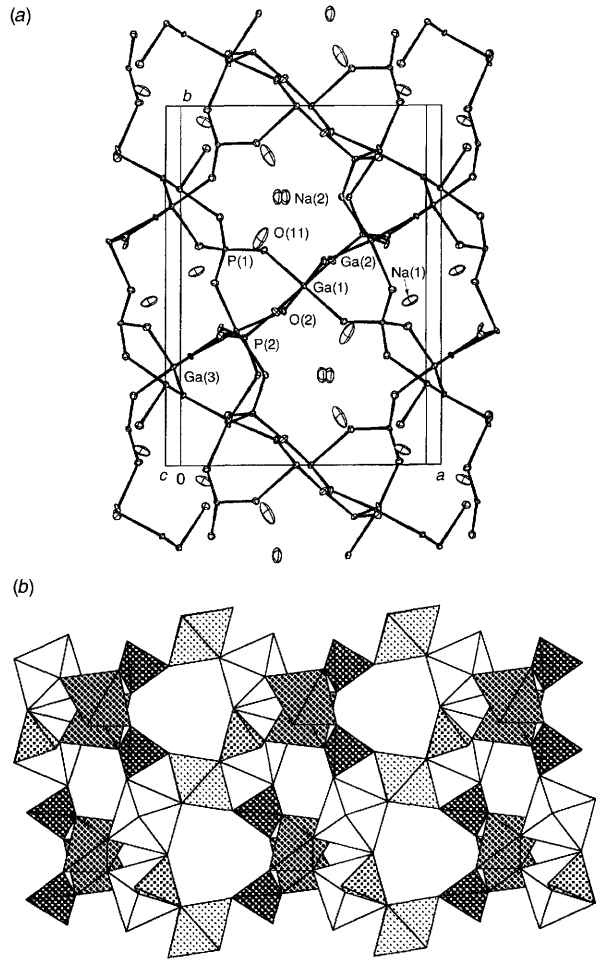

Fig. 1 (*a*) Atomistic and (*b*) polyhedral representations of the structure of $Na_3Ga_5(PO_4)_4O_2(OH)_2{\cdot}2H_2O$ viewed along the [001] direction. Thermal ellipsoids are shown at 50% probability in (*a*). The polyhedra, in order of increased shading, are $Ga(2)O_6$ octahedra, $Ga(1)O_6$ octahedra, $P(2)O_4$ tetrahedra, $Ga(3)O_5$ trigonal bipyramid and $P(1)O_4$ tetrahedra in Fig. 1(*b*).

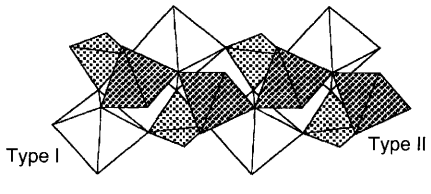

Fig. 2 Chains of types I and II viewed along the [100] direction. Polyhedra are shaded as in Fig. 1(*b*).

Bond valence calculations[9] indicate that O(2) is a hydroxy group and that O(11) is a water molecule. The former is bridging between Ga(1) and Ga(2), and O(11) is coordinated to both sodium cations. Refinement of the occupancy of the Na(2) site indicates that it is only half occupied. The temperature factors of Na(1), Na(2) and O(11) are higher than those of the other atoms in the structure, consistent with them being extra-framework atoms. These conclusions yield a charge-balanced structure with the chemical formula given previously.

TGA–DTA shows a 4% weight loss accompanied by an endothermic energy change between 100 and 300 °C. This corresponds to the loss of the two water molecules per formula unit and is consistent with the desorption of water associated to the sodium atoms (calculated weight loss = 4.0%). Powder X-ray diffraction measurements show that the structure is maintained after heating to 450 °C and adsorption studies on the material indicate that readsorption of approximately 50% of the water lost between 100 and 300 °C occurs. No significant adsorption of larger molecules, for example N_2, is exhibited. An additional 2% mass loss, accompanied by an endothermic energy change, occurs between 400 and 600 °C, and the structure collapses giving $GaPO_4$ and other unidentifiable phases by 750 °C.

M. P. A. would like to thank the Materials Department, UCSB for provision of a research fellowship, the ACA for provision of a scholarship to attend the ACA workshop (Pittsburgh 1993), and Izya Burshtein and Charles Campana for useful discussions concerning the determination of the structure. A. M. and E. G. P. would like to thank the DGICYT (Spain) for financial support. This work made use of the Central Facilities of the UCSB-MRL, which is supported by the MRL Program of the National Science Foundation under Award No. DMR-9123048.

Received, 28th November 1994; Com. 4/07245F

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† *Crystal data* for $Na_{1.5}Ga_{2.5}(PO_4)_2O(OH)\cdot H_2O$: monoclinic, space group P_1/c, a = 9.716(1), b = 13.485(2), c = 6.3907(8) Å, β = 99.82(2)°, V = 825.0(2) Å^3, Z = 4, M_w = 449.7, D_c = 3.62 g cm^{-3}, μ(Cu-Kα) = 149.8 cm^{-1}, λ = 1.5418 Å, nickel filter, crystal dimensions 0.03 × 0.05 × 0.075 mm. The data were collected on an Enraf-Nonius CAD4 diffractometer, using a ω–2θ scan technique, over the range $0 < 2\theta < 70°$. The total number of reflections measured was 1785, of which 1558 were unique and 1282 were considered to be observed, $I > 3.0\sigma(I)$. The structure was solved by direct methods,[10] the Ga and P atoms being found first and all the remaining atoms were located by difference Fourier maps. No hydrogen atoms were found in the difference Fourier maps. Refinement of 161 variables was by full-matrix least-squares analysis,[11] with anisotropic thermal parameters for all atoms. The final residuals were R = 0.035, R_w = 0.038.

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