A Novel Open-Framework Gallium Phosphate Containing Two Different Building Units

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A novel open-framework fluorinated gallium phosphate has been prepared hydrothermally. X-ray diffraction shows each double four-ring (D4R) links four 1D gallium phosphate chains made up of single four-rings (S4R) to form a 3D framework with eight-ring channels where potassium ions reside.

Since the discovery of the family of crystalline aluminophosphates (ALPOs) in 1982,[1] microporous zeolite-like materials have attracted much interest due to their potential applications in, for example, ion-exchangers, catalysts and adsorbents.[2,3] In the past decade, the replacement of Al in ALPOs by Ga has resulted in a large number of gallium phosphates with a wide range of structure types[4,5] because of the ability of gallium to adopt a more variable and expanded coordination environment compared to aluminum. Recently, fluoride ion has been discovered to play a major role in the gallium phosphate system and many fluoride gallium phosphates have been synthesized.[6] Férey and others have prepared a series of fluoride gallium phosphates that show interesting templating effects and structure types. Some of these gallium phosphate materials, such as cloverite,[7] ULM-5,[8] ULM-18[9] and Mu-15,[10] contain a double four-ring unit (D4R), with a fluoride ion occluded at its center. This has resulted in the postulation that the fluoride ion acts as a template for the formation of the D4R species and makes the cuboidal D4R an attractive target because of its rigid 3D shape.[11] In the synthesis of materials containing D4R units, the use of organic amines as structure-directing and charge-compensation agents is very common, but that of alkali metal ions is rare. In this communication, we report a novel gallium phosphate containing fluoride-templating D4R units and potassium ion charge-compensation agents.

In an attempt to prepare new a gallium phosphate material with 1-(2-aminoethyl)piperazine as the structure-directing agent, an open framework fluoride gallium phosphate, $K[(GaPO_4)\{F_{1/4}(GaPO_4)\}_4]$ (**1**), was obtained. This novel material was prepared by a hydrothermal synthesis with KF as a source of fluoride ions. Single-crystal X-ray diffraction indicates that **1** possesses a three-dimensional open framework containing one-dimensional channels along the *c* axis, in which potassium ions reside.

Two crystallographically independent gallium and phosphate centers, Ga(1), P(1) and Ga(2), P(2), which form different second building units (SBUs), are present in the structure. The first SBU is a $Ga_2(PO_4)_2$ single four-ring (S4R; Figure 1, Part I, left) made up of Ga(1) and P(1). The gallium atom is four-coordinate and is linked by corner-sharing PO_4 tetrahedra with an average Ga−O distance of 1.875(4) Å. This distance is slightly longer than that found in complex ULM-16,[5d] in which the $Ga_2(PO_4)_2$ unit links layers to form a 3D open framework. As is well known, the linkage of S4Rs often results in 2D layers containing eight-ring windows, and this phenomenon has been observed for a number of zeolites and zeolite analogues.[12,13] Interestingly, in **1**, a one-dimensional infinite gallium phosphate chain is formed by the linkage of S4Rs, in which the gallium atom and the phosphate tetrahedron alternate (Figure 1, Part I, right).

The second SBU is a double four-ring unit (D4R; Figure 1, Part II) formed by Ga(2) and P(2), similar to that observed in many gallium phosphate molecular sieves.[7−10] A fluoride ion resides in the D4R unit as observed in cloverite[7] and other ULM complexes.[8−10] In this case, the fluoride atoms lie a long distance from the four gallium atoms, with a relatively long contact of 2.459 Å, which is longer than that found in CYCLAM-GaPO (2.286 Å)[14] and illustrates that the fluoride ion less strongly bound in the D4R center. The average Ga−O distance in the D4R unit is 1.865(4) Å, shorter than that in the S4R unit. In previous reports, D4R is usually linked through its corners to other D4R units to give rise to a 2D or 3D ACP topology first reported by Stucky.[15] Surprisingly, in **1**, the D4Rs themselves have no linkage, each D4R links four above mentioned 1D gallium phosphate chains by its four corners with a Ga−O distance of 1.920(4) Å, and a 3D open framework with eight-ring channels (9.657 × 3.763 Å) is formed along the *c* axis, in which the potassium ions reside. As

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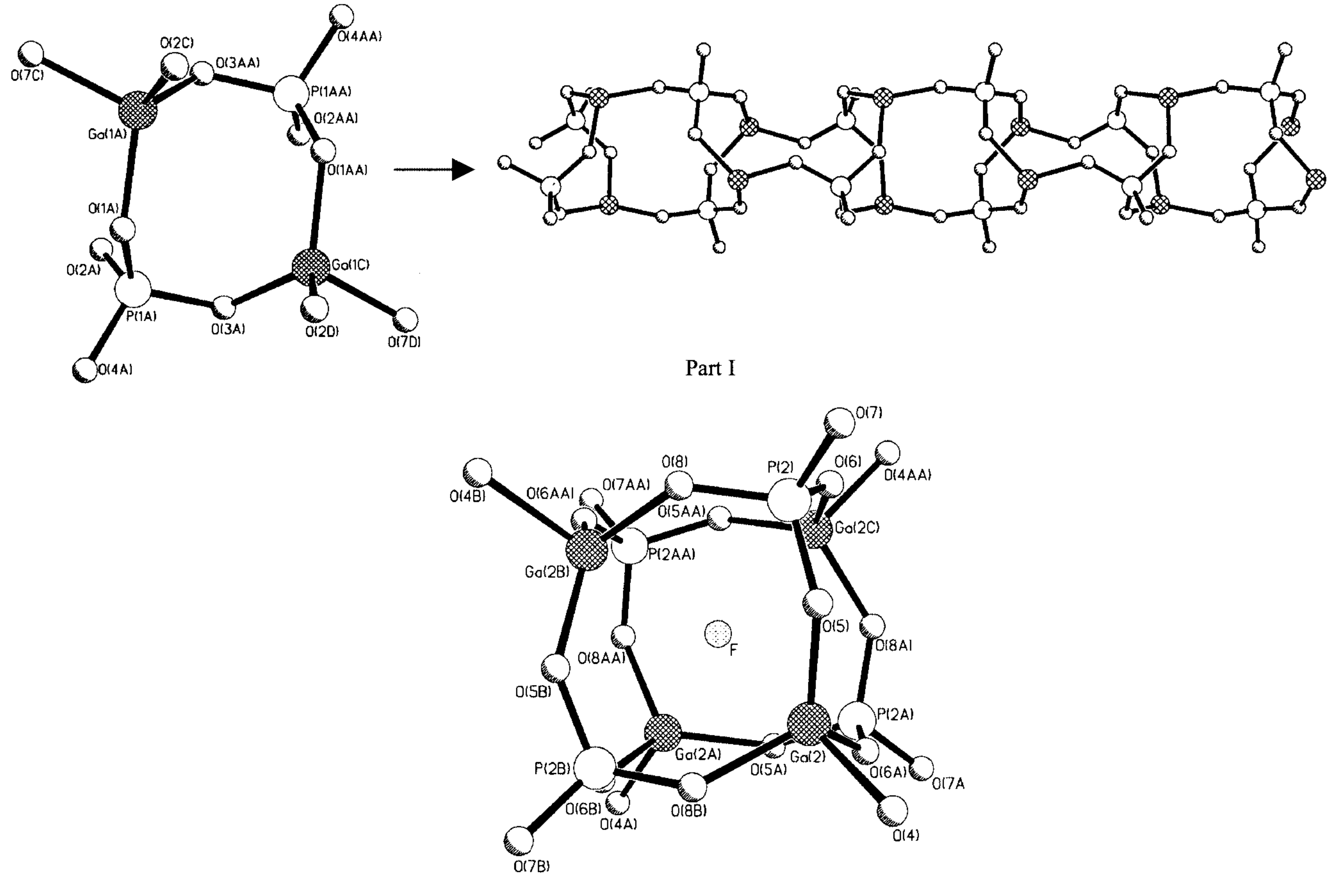
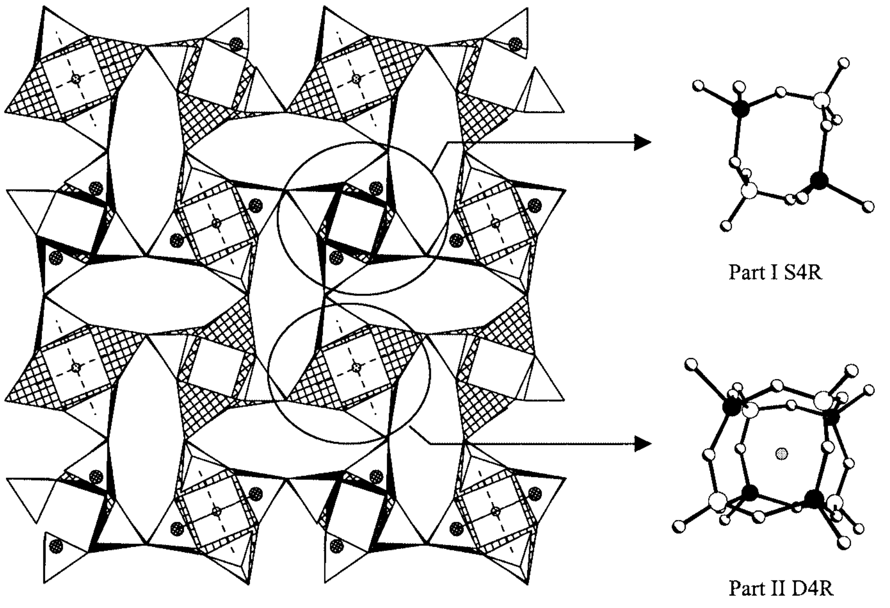


Part I

Part II

Figure 1. The one-dimensional chain and D4R unit in **1**; selected bond lengths (Å) and angles (°): Ga(1)−O(1) 1.880(3), Ga(1)−O(3) 1.884(4), Ga(2)−O(7) 1.834(4), Ga(2)−O(8) 1.850(4), Ga(2)−O(9) 1.856(3), Ga(2)−O(6) 1.920(4), P(1)−O(4) 1.526(4), P(1)−O(6) 1.533(4), P(1)−O(1) 1.534(3), P(1)−O(2) 1.537(3), P(2)−O(7) 1.535(3)



Part I S4R

Part II D4R

Figure 2. The 3D open framework showing the arrangement of single four-ring and double four-ring units to form eight-ring channels along *c* axis; potassium ions are omitted for clarity

shown in Figure 2, every two adjacent eight-membered rings are almost perpendicular to each other.

TGA determination shows that complex **1** possesses a high degree of thermal stability and there is no weight loss even upon heating to more than 800 °C, indicating that **1** is thermally more stable than potassium templating gallium phosphatooxalate.[16] After heating a sample of **1** to 800 °C the XRPD pattern remains essentially the same, although slight changes in the strength of some peaks were observed. This result validates the stability of **1** and is in agreement with the structural data.

Experimental Section

Synthesis of 1: Ga_2O_3 (0.023 g, 0.0625 mmol) was dispersed in 16 mL of distilled water by vigorous stirring, and then phosphoric acid (0.5 g, 85% weight aqueous solution) was added. After stirring for 15 minutes, 1-(2-aminoethyl)piperazine (0.1 mL) and KF (0.03 g, 0.5 mmol) were added and stirred to homogeneity. The mixture was sealed in a Teflon-lined stainless autoclave and heated at 160 °C for three days under autogenous pressure, then cooled to room temperature over 8 hours. The resulting product, consisting of colorless prism-like crystals was collected by filtration. Yield: 35%.

X-ray Crystallography: $F_{0.25}Ga_2KO_8P_2$, (**1**), $M = 373.23$, *tetragonal*, space group $P4_2/n$, $a = 13.2322(19)$, $b = 13.2322(19)$, $c = 8.6535(17)$ Å, $U = 1515.2(4)$ Å^3, $T = 293$ K, $Z = 4$, $D_c = 1.636$ g/cm^3, $\lambda = 0.71073$ Å, 1730 unique reflections were used in the calculations. $R1 = 0.0350$ and $wR2 = 0.1308$. The intensity data were collected on a Smart CCD diffractometer with graphite-monochromated Mo-K_α ($\lambda = 0.71073$ Å) radiation at room temperature in the ω-2θ scan mode. An empirical absorption correction was applied to the data using the SADABS program. The structures were solved by direct methods. All calculations were performed using the SHELXTL program. Crystallographic data for the complex **1** are given in Table 1.

Further details of the crystal-structure investigation(s) may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-412582

Table 1. Crystallographic data for complex **1**

	1
Empirical formula	$F_{0.25}Ga_2KO_8P_2$
F_w	373.23
Crystal system	tetragonal
Space group	$P4_2/n$
a, Å	13.2322(19)
b, Å	13.2322(19)
c, Å	8.6535(17)
α, deg	90
β, deg	90
γ, deg	90
V, Å^3	1515.2(4)
Z	4
D_c, g·cm^{-3}	1.636
μ, mm^{-1}	4.051
R_1 [$I > 2\sigma(I)$][a]	0.0350
wR_2 (all data)[b]	0.1454

[a] $R_1 = \|F_o| - |F_c\|/|F_o|$. [b] $wR_2 = [w(F_o^2 - F_c^2)^2/w(F_o^2)^2]^{1/2}$.

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