

# Self-Assembly of Nanoporous Material Gallophosphate $\text{Ga}_3\text{P}_3\text{O}_{12}\text{F} \cdot 0.5(1,8\text{-C}_8\text{H}_{22}\text{N}_2)$ under Hydrothermal Conditions

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**Abstract**—A three-dimensional nanoporous material gallophosphate  $\text{Ga}_3\text{P}_3\text{O}_{12}\text{F} \cdot 0.5(1,8\text{-C}_8\text{H}_{22}\text{N}_2)$  was synthesized from self-assembly of simple mixture under the mild hydrothermal conditions. The molar ratio of the initial raw mixture was  $1\text{GaOOH}:2\text{H}_3\text{PO}_4:1\text{HF}:1$  1,8-diaminooctane: $555\text{H}_2\text{O}$ . The 3-D anionic framework of the title material is constructed from  $\text{Ga}_3\text{P}_3$  hexamer structural units.  $\text{Ga}_3\text{P}_3$  structural units are linked by vertex-sharing to form a 3-D nanoporous material with 8-ring channels along the [101] direction.

## BACKGROUND

Hydrothermal synthesis refers to the synthesis by chemical reactions of substances in a sealed heated solution above ambient temperature and pressure. It involves the development of novel synthetic methods and techniques, and the preparation of new materials such as nanometer materials [1], nanoporous materials [2], superhard materials [3] and so on. Nanoporous materials have been the subject of intense research owing to their interesting structural chemistry and potential applications in catalysis, adsorption, separation and host-guest assembly [2]. In the past twenty years, the synthesis of new nanoporous metal phosphates has attracted considerable attention. Among metal phosphates, gallophosphates constitute an important family. Since the discovery of the  $\text{GaPO}_4$ -14 molecular sieves in 1985, many novel gallophosphates with 1-D, 2-D and 3-D structures have been synthesized successfully in hydrothermal or solvothermal conditions [4]. The structures of these compounds are built mainly from  $\text{GaO}_4$  tetrahedra,  $\text{GaO}_5$  trigonal bipyramids,  $\text{GaO}_6$  octahedra, or their combination, and  $\text{PO}_4$  tetrahedra, but examples of single polyhedra are also known [5]. The syntheses typically involve the addition of organic amines. It is proposed that in most cases, the amines act as a structure-directing agent (template) when their shapes are related with the frameworks. Among the various organic amines used, the family of diaminoalkanes is more effective than that of monoaminoalkanes in the formation of gallophosphates with open architecture to displays a strong templating effect [6]. Here, we describe the synthesis and structure of a 3-D nanoporous gallophosphate  $\text{Ga}_3\text{P}_3\text{O}_{12}\text{F} \cdot 0.5(\text{C}_8\text{H}_{22}\text{N}_2)$  under hydrothermal conditions.

## CURRENT RESULTS

The title material was hydrothermally prepared from a reaction mixture of 1  $\text{GaOOH}$  : 2  $\text{H}_3\text{PO}_4$  : 1 1,8-diaminooctane : 555  $\text{H}_2\text{O}$  (molar ratio, pH = 3) with vigorous stirring. The mixture was then aged at room temperature for 1h, followed by transferring to the Teflon-lined stainless steel autoclave and heating under autogenous pressure at 160 °C for 7 days. The product was washed with distilled water and dried overnight at

50 °C to give colorless crystals. A suitable single crystal of the title material was selected for single-crystal X-ray diffraction analysis. Structural analysis was performed on a Rigaku R-Axis RAPID IP diffractometer equipped with graphite-monochromated  $\text{Mo K}\alpha$  ( $\lambda = 0.71073$  Å). The data were collected at a temperature of 293 K. Data processing was accomplished with the Process-Auto processing program. The structures were solved by direct methods and refined by full-matrix least squares based on  $F^2$  using the SHELXTL 5.1 software package. The gallium and phosphorus atoms were first located, and oxygen, carbon, nitrogen atoms. All non-hydrogen atoms were refined anisotropically. It crystallizes in the Monoclinic, space group  $\text{P}2_1/\text{n}$ , with  $a = 8.671(1)$ ,  $b = 17.945(1)$ ,  $c = 9.101(1)$  Å,  $\beta = 108.33(1)^\circ$ ,  $V = 1344.3(2)$  Å<sup>3</sup> and  $Z = 4$ . The 3-D anionic framework of the title material is constructed from  $\text{Ga}_3\text{P}_3$  hexamer structural units.  $\text{Ga}_3\text{P}_3$  structural unit is built one  $\text{GaO}_4$  tetrahedron

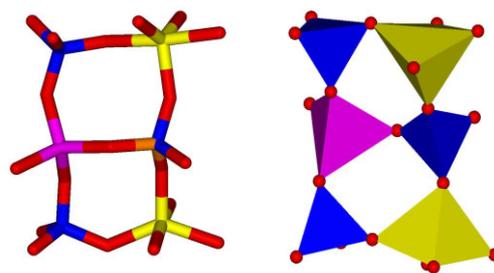


Fig. 1. Stick and polyhedral views of  $\text{Ga}_3\text{P}_3$  hexamer structural units. (blue:  $\text{PO}_4$  tetrahedron, purple:  $\text{GaO}_4$  tetrahedron, yellow:  $\text{GaO}_4\text{F}$  trigonal bipyramid).

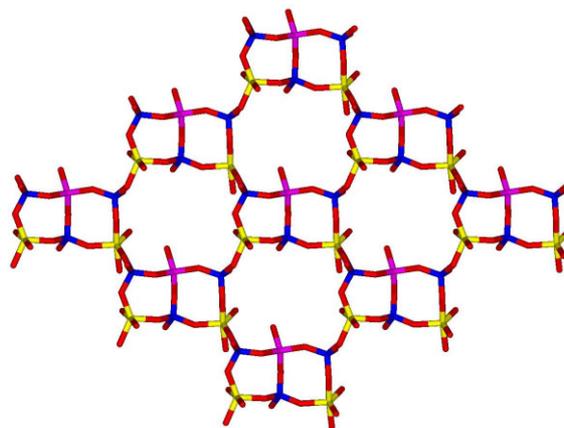


Fig. 2. Stick view of inorganic Layer-S (single layer) containing 10- and 4-rings along [010] direction. (blue:  $\text{PO}_4$  tetrahedron, purple:  $\text{GaO}_4$  tetrahedron, yellow:  $\text{GaO}_4\text{F}$  trigonal bipyramid).

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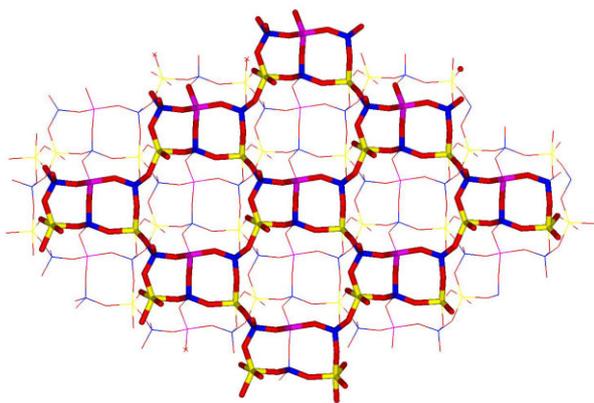


Fig. 3. Stick view of inorganic Layer-D containing 10- and 4-rings along [010] direction. (blue: PO<sub>4</sub> tetrahedron, purple: GaO<sub>4</sub> tetrahedron, yellow: GaO<sub>4</sub>F trigonal bipyramid).

(Ga–O bond distances: 1.802(3)-1.829(3) Å), two GaO<sub>4</sub>F trigonal bipyramids (Ga–O bond distances: 1.847(3)-1.946(3) Å; Ga–F bond distances: 1.889(3) and 1.982(3) Å, respectively), and three PO<sub>4</sub> tetrahedra (P–O bond distances: 1.510(3)-1.545(3) Å) fused together via vertex-sharing Ga–O–P bonds (P–O–Ga bond angles: 126.9(2)-158.2(2)°) (Fig. 1). These hexamer structural units are linked by vertex-sharing to form inorganic Layer-S (single layer) containing 10- and 4-rings along [010] direction (Fig. 2). The novel structural feature of the title material is that two inorganic single layer are linked by bridging oxygen/fluorine atoms to form an inorganic double layer (Layer-D) (Fig. 3). The interesting topology has been observed for JGP-8, which is comprised of 4-rings linked by 8-rings [6]. A series of inorganic double layers are held together in an AAAA stacking sequence, linked by bridging oxygen/fluorine atoms to form a three-dimensional microporous material with 8-ring channels along the [101] direction (Fig. 4). The diprotonated 1,8-diaminooctane cations are located in the 8-ring channels and neutralize the negative charge of the inorganic framework.

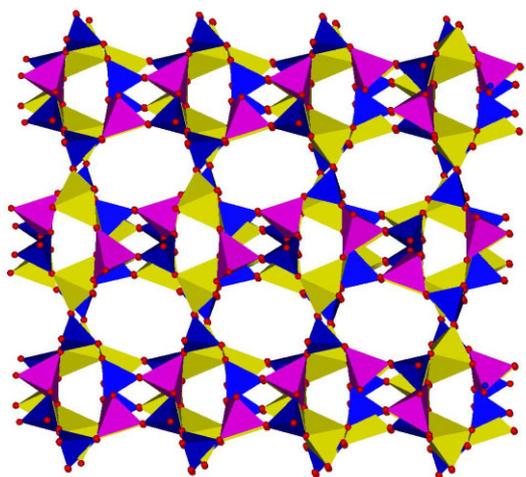
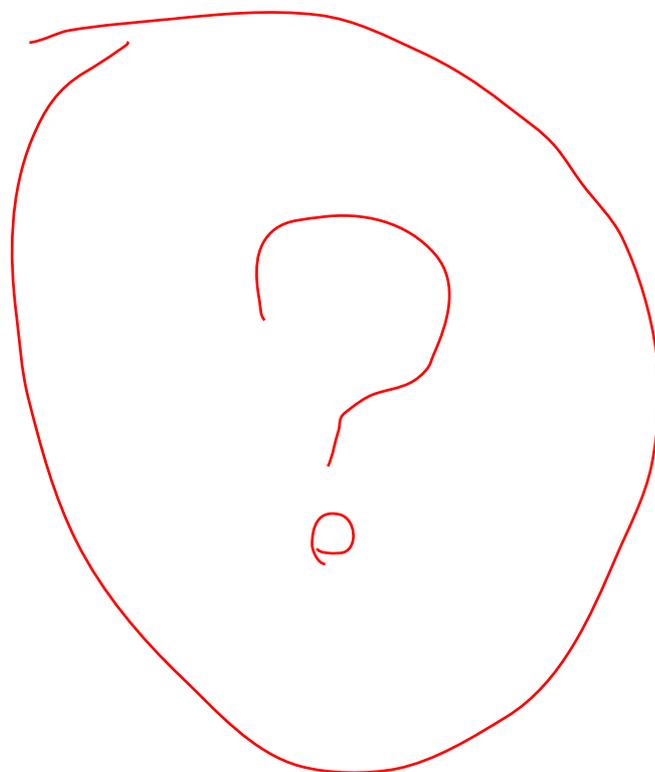


Fig. 4. Polyhedral view of Ga<sub>3</sub>P<sub>3</sub>O<sub>12</sub>F·0.5(C<sub>8</sub>H<sub>22</sub>N<sub>2</sub>) with 8-ring and 4-ring channels along the [101] direction. (blue: PO<sub>4</sub> tetrahedron, purple: GaO<sub>4</sub> tetrahedron, yellow: GaO<sub>4</sub>F trigonal bipyramid).

We will also present the results from these upcoming experiments at the conference.

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