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Hydrothermal synthesis and structure of the new three-dimensional fluorogallophosphate JGP-4 with a Ga/P ratio of 7/8

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Abstract

A new 3-D fluorogallophosphate $Ga_7P_8O_{32}F_4(C_6H_{20}N_4)_2{\cdot}3H_3O^+{\cdot}H_2O$ (denoted JGP-4) with a Ga/P ratio of 7/8 has been synthesized hydrothermally by using triethylenetetramine as the template. It crystallizes in the tetragonal, space group $P\bar{4}2_1c$ (no. 114), with $a = 15.461(2)$, $b = 15.461(2)$, $c = 9.3233(1)$ Å, $V = 2228.67(5)$ Å^3 and $Z = 2$. This is the first metal phosphate with a M/P ratio of 7/8. The 3-D anionic framework of JGP-4 is built up from the vertex linkage of the 1-D chains and Ga_5P_4 building units, forming a 3-D open-framework with 8-membered and four square 4-membered rings along the *c*-axis direction.

Keywords: Synthesis; Structure; Fluorogallophosphate; Ga/P ratio

1. Introduction

Open-framework metal phosphates have been the subject of intense research owing to their interesting structural chemistry and potential applications in catalysis and ion exchange [1–3]. A large number of these materials are synthesized from the utility of various organic templates and substitution of metal ions. Among metal phosphates, gallophosphates constitute an important family. Following the discovery of some microporous gallophosphates by Parise, many novel gallophosphates (GaPOs) with 1-D, 2-D, and 3-D structures have been synthesized successfully under hydrothermal or solvothermal conditions [4,5]. In most gallophosphates, the Ga/P ratio is 1. Recently, a variety of organically templated gallophosphates with the Ga/P ratio of non-unity are beginning to be synthesized that show vast structural and compositional diversities [6]. There are 3-D open-framework GaPOs with the Ga/P ratios of 1/1 [4], 1/2 [7], 4/5 [8], 5/4 [9], a family of 2-D layers with the Ga/P ratios of 1/1 [10], 1/2 [11], 2/3[12], 6/7 [13] and a series of 1-D chains with the Ga/P ratios of 1/2 [14], 1/3 [15], 3/4 [16], 4/7 [17]. Férey and others have synthesized a series of fluorogallophosphates that show interesting templating effects and structure types with various stoichiometries. There are fluorogallophosphates with the Ga/P ratios of 3/2 [18,19], 4/3 [20,21], 5/6 [22], 6/7 [23], 7/6 [24], 9/8 [25].

Yu and Xu predicted that it is possible to be synthesize an aluminophosphate with a Al/P ratio of 7/8 under appropriate conditions [26]. However, no metal phosphate with a M/P ratio of 7/8 has been reported in the literature. Here, we report the synthesis and structure of the first fluorogallophosphate $Ga_7P_8O_{32}F_4(C_6H_{20}N_4)_2{\cdot}3H_3O^+{\cdot}H_2O$ with a Ga/P ratio of 7/8 (JGP-4), using triethylenetetramine as the structure-directing agent.

2. Experimental

2.1. Synthesis and characterization

JGP-4 was hydrothermally prepared from a mixture of amorphous gallium oxide, phosphoric acid (Beijing

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Chemical Plant, 85%), ethylene glycol (EG) (Beijing Chemical Plant, 99%), fluorhydric acid (Beijing Chemical Plant, 40%), triethylenetetramine (Fluka, 70%). Amorphous gallium oxide was obtained by heating a gallium oxide hydroxide at 400°C for 3 h. Gallium oxide hydroxide was prepared by direct reaction of gallium metal with water at 220°C under autogenous pressure for 3 days. The molar ratio of the initial mixture was 1 Ga_2O_3:12 H_3PO_4:7 triethylenetetramine (TETA): 30HF:130EG:2400 H_2O (pH = 4.4–4.8). The mixture was then aged at room temperature for 1 h, followed by transferring to a Teflon-lined stainless-steel autoclave and heating under autogenous pressure at 160°C for 5 days. The final pH was 4.8–5.0. The product was washed with distilled water and dried overnight at 50°C to give the colorless crystals. The yield is 85% based on Gallium.

The powder X-ray diffraction (XRD) patterns were recorded on a Siemens D5005 diffractometer with Cu-$K\alpha$ radiation ($\lambda = 1.5418$ Å). The elemental analysis was performed on a Perkin-Elmer 2400 element analyzer and the inductively coupled plasma (ICP) analysis on a Perkin-Elmer Optima 3300 DV ICP instrument. F^- content was determined using a fluoride ion-selective electrode. Thermogravimetric analysis (TGA) was conducted on a Netzsch STA 449C thermogravimetric analyzer with a heating rate of 10°C min^{-1} in air. IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer using KBr pellets.

2.2. Determination of crystal structure

A suitable single crystal was selected for single-crystal XRD analysis. The data were collected on a Rigaku R-AXIS RAPID IP diffractometer [λ(Mo$K\alpha$) = 0.71073 Å] at 193 ± 2 K. Data processing was accomplished with the Process-Auto processing program. The structure was solved by direct methods and refined by full-matrix, least squares based on F^2 using the SHELXTL 5.1 software package [27]. The gallium and phosphorus atoms were first located, and then the F, O, C, N atoms. All non-hydrogen atoms were refined anisotropically except the C, N and Ow atoms, each of which was disordered. The presence of fluorine has been deduced from chemical analysis. The refined anisotropic thermal parameter diverges when one fluorine atom is placed between two Ga atoms and gives a good value for a full occupancy, whereas when one oxygen atom is placed this position and gives non-positive definite, in agreement with the chemical analysis. The Flack x parameter of JGP-4 was 0.03(3), indicative of correct absolute structure. Final refinement converged to $R_1 = 0.0428$ and $wR_2 = 0.1284 (I > 2\sigma(I))$. CCDC reference number: 209725. Crystal data and details of data collection and refinement are given in Table 1.

Table 1
Crystal data and structure refinement for JGP-4

Identification code	JGP-4
Empirical formula	$Ga_7P_8O_{32}F_4(C_6H_{20}N_4)_2{\cdot}3H_3O^+{\cdot}H_2O$
Formula weight	1694.93
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system	Tetragonal
Space group	$P\bar{4}2_1c$ (No. 114)
Unit cell dimensions (Å)	$a = 15.461(2)$
	$b = 15.461(2)$
	$c = 9.3233(1)$
Volume (Å^3)	2228.67(5)
Z	2
Density (calculated) (Mg m^{-3})	2.526
Absorption coefficient (mm^{-1})	4.593
F(000)	1680
Crystal size (mm)	$0.368 \times 0.294 \times 0.125$
θ Range for data collection	1.86–23.25°
Limiting indices	$-12 <= h <= 17$
	$-17 <= k <= 17$
	$-10 <= l <= 10$
Reflections collected/unique	10421/1602 [R(int) = 0.0995]
Completeness to $\theta = 23.25$	99.6%
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1602/3/164
Absolute structure parameter	0.03(3)
Goodness-of-fit on F^2	1.042
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0428$, $wR_2 = 0.1284$
R indices (all data)	$R_1 = 0.0434$, $wR_2 = 0.1291$
Largest diff. peak and hole	1.047 and −0.761 e A^{-3}

3. Results and discussion

3.1. Characterization

The powder XRD pattern for JGP-4 is entirely consistent with that simulated on the basis of the single-crystal structure. The diffraction peaks in both measured and simulated patterns correspond well to each other in position, indicating the phase purity of the as-synthesized sample. The ICP analysis shows that JGP-4 contains 32.79 wt% Ga and 16.64 wt% P, suggesting that the molar ratio of Ga:P = 7:8. The elemental analysis indicates the contents of F, 4.39 wt%; C, 3.16 wt%; H, 2.25 wt% and N, 6.45 wt%, respectively, in good agreement with the values (F, 4.48 wt%; C, 3.20 wt%; H, 2.13 wt% and N, 6.53 wt%) based on the single-crystal structure formula $Ga_7P_8O_{32}F_4(C_6H_{20}N_4)_2{\cdot}3H_3O^+{\cdot}H_2O$.

TGA shows that the total weight loss of JGP-4 occurs in two steps under air. The first weight loss of ca. 1.02% in the range of 100–200°C corresponds to the removal of the molecular water (calcd. 1.06%). The second weight loss of ca. 20.92% in the range of 300–820°C corresponds to the removal of the TETA and H_3O^+ (calcd. 20.83%). XRD analyses indicate that the

structures of JGP-4 collapse after the removal of the organic templates.

IR spectrum of the JGP-4 compound, as shown in Fig. 1, shows strong and broad bands in the 3500–2800 cm^{-1} range assignable to O–H and N–H bands in agreement with the participation of water molecules and TETA cations in a weak to strong hydrogen bonding [28]. The bands in the 1600–1100 cm^{-1} region are ascribed to vibrations of the TETA template. The bands at 1152 and 1056 cm^{-1} are associated with the stretching vibrations of Ga–O groups and band at 1095 and 565 cm^{-1} are attributed to vibration of PO_4 groups.

3.2. Description of the structure

The XRD analysis of a single crystal of JGP-4 revealed that the 3-D open-framework is constructed from the basic structural unit shown in Fig. 2. It contains three crystallographically distinct Ga atoms. Ga(1) is situated in special positions with site symmetry 4 and is shared by four adjacent units. Ga(1) is octahedrally coordinated and shares four bridging oxygen atoms with adjacent P atoms (dGa(1)–O = 1.952(3)–1.964(3) Å) and two bridging fluorine atoms with adjacent Ga atoms (dGa(1)–F(1) = 1.918(2) Å). Ga(2) is also situated in special positions and is shared by eight adjacent units. Ga(2) is tetrahedrally coordinated and shares four bridging oxygen atoms with adjacent P(1) atoms (dGa(2)–O(2) = 1.825(3) Å). Ga(3) is trigonal bipyramidally coordinated and shares two bridging oxygen atoms with adjacent P(1) and P(2) (dGa(3)–O(6) = 1.843 (3) Å, dGa(3)–O(8) = 1.901(3) Å), one bridging fluorine atom with adjacent Ga atoms (dGa(3)–F(1) = 2.126(2) Å), and two terminal oxygen atoms (dGa(3)–O(5) = 1.830(3) Å, dGa(3)–O(7) = 1.833(3) Å). The distances of the bonds of bridging fluorine have been observed [19,29]. All the gallium-based polyhedra share their vertexes with phosphorus-based tetrahedra or another gallium-based polyhedra. The F–Ga(1)–F bond angle is 177.07(19)°. The O–Ga–O(F) bond angles are in the range of 82.04(12)–178.80(15)°. Of the two crystallographically distinct P atoms, P(1) shares three bridging oxygen atoms with adjacent Ga atoms (dP(1)–O = 1.530(4) – 1.562(4) Å) and one terminal oxygen atom (dP(1)–O(1) = 1.502(4) Å). P(2) shares all its vertexes with adjacent Ga atoms (dP(2)–O = 1.523(3)–1.548(3) Å). The O–P–O bond angles are in the range of 103.4(2)–114.8(2)°. The final atomic coordinates, selected bond lengths and angles are list in Tables 2 and 3, respectively.

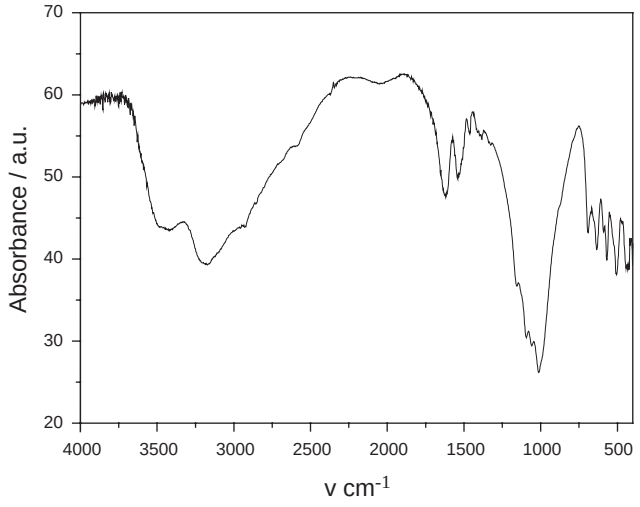

Fig. 1. IR spectrum of JGP-4.

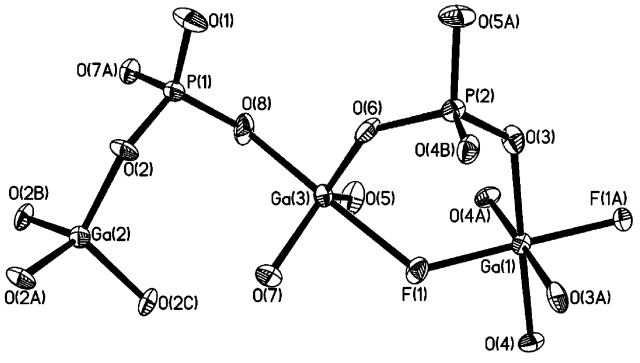

Fig. 2. ORTEP view of the basic structural unit of JGP-4 showing the atom labeling scheme (50% thermal ellipsoids).

The 3-D anionic framework of JGP-4 is built up from the vertex linkage of the 1-D chains and Ga_5P_4 building units. These chains are constructed from alternating 4-membered rings, which are composed of two GaO_4F_2 octahedra and two PO_4 tetrahedra, fused via Ga–O–P vertices. The 4-membered rings connect each other through common GaO_4F_2 octahedra, as shown in Fig. 3(a). To the Ga_5P_4 building units, a central GaO_4 tetrahedra shares all of the vertexes with four PO_4 tetrahedra. Two PO_4 tetrahedra are connected to two other peripheral GaO_4F trigonal bipyramids. The four GaO_4F trigonal bipyramids and one GaO_4 tetrahedron are in one plane, two P tetrahedra are located below the plane, and two are above the plane, forming four square 4-membered rings, as shown in Fig. 3(b). Similar topological structures were previously described [30,31]. It is different from existing fluorogallophosphate fragments such as trimer [32], tetramer (or S4R) [33], pentamer [25], hexamer [34], octamer (or D4R) [35], enneamer [36], and so on. A series of Ga_5P_4 building units are linked to chains. Fig. 3(b) shows a view of the structure, illustrating how the solid is constructed from Ga_5P_4 building units and chains into macroanionic inorganic framework, forming a 3-D open-framework with 1-D 8-membered and 4-membered rings along the *c*-axis direction as shown in Fig. 3(c). The diprotonated TETA, H_3O^+ and H_2O are located in these channels

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for JGP-4

Atom	x	y	z	U(eq)[a]
Ga(1)	0	−5000	−46(1)	13(1)
Ga(2)	0	0	0	17(1)
Ga(3)	−551(1)	−2745(1)	−13(1)	14(1)
P(1)	−1583(1)	−1021(1)	−865(1)	17(1)
P(2)	−961(1)	−4055(1)	−2520(1)	14(1)
F(1)	326(2)	−3804(2)	6(3)	19(1)
O(1)	−2063(2)	−1199(3)	−2234(4)	32(1)
O(2)	−747(2)	−514(2)	−1253(4)	19(1)
O(3)	−921(2)	−4805(2)	−1461(3)	18(1)
O(4)	903(2)	−5216(2)	1373(3)	17(1)
O(5)	−925(3)	−3156(2)	1720(3)	26(1)
O(6)	−912(2)	−3173(2)	−1757(4)	21(1)
O(7)	454(2)	−2126(2)	−190(4)	21(1)
O(8)	−1367(2)	−1825(2)	24(5)	24(1)
N(1)	3497(10)	−4771(11)	1693(13)	197(8)
N(2)	3845(9)	−6378(9)	100(30)	164(5)
N(3)	2374(12)	−4454(7)	−150(20)	162(5)
N(4)	1728(4)	−3705(4)	2455(7)	4(1)
C(1)	3946(10)	−4620(10)	224(17)	181(5)
C(2)	4104(16)	−5480(9)	−550(20)	170(5)
C(3)	2881(9)	−6240(10)	510(20)	178(6)
C(4)	2552(12)	−5432(8)	−250(30)	178(5)
C(5)	2512(17)	−3583(10)	574(15)	134(5)
C(6)	2641(9)	−3368(14)	2148(17)	161(6)
O(1w)	−790(11)	−1944(11)	−5330(20)	115(5)
O(2w)	−2465(12)	−1287(12)	−6754(19)	115(5)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Selected bond lengths (Å) and angles (°) for JGP-4

Ga(1)–*F*(1)#1	1.918(2)	Ga(3)–O(6)	1.843(3)
Ga(1)–*F*(1)	1.918(2)	Ga(3)–O(8)	1.901(3)
Ga(1)–O(4)	1.952(3)	Ga(3)–*F*(1)	2.126(2)
Ga(1)–O(4)#1	1.952(3)	P(1)–O(1)	1.502(4)
Ga(1)–O(3)	1.964(3)	P(1)–O(8)	1.530(4)
Ga(1)–O(3)#1	1.964(3)	P(1)–O(2)	1.555(3)
Ga(2)–O(2)	1.825(3)	P(1)–O(7)#2	1.562(4)
Ga(2)–O(2)#2	1.825(3)	P(2)–O(3)	1.524(3)
Ga(2)–O(2)#3	1.825(3)	P(2)–O(5)#5	1.539(4)
Ga(2)–O(2)#4	1.825(3)	P(2)–O(6)	1.540(4)
Ga(3)–O(5)	1.830(3)	P(2)–O(4)#6	1.548(3)
Ga(3)–O(7)	1.833(3)		

Symmetry transformations used to generate equivalent atoms: $1-x,-y-1,z$; $2y,-x,-z$; $3-x,-y,z$; $4-y,x,-z$; $5-y-1/2,-x-1/2,z-1/2$; $6y+1/2,x-1/2,z-1/2$.

and neutralize the negative charges of the inorganic framework. The TETA molecule shows disorder which only place could be at a general position with a site occupancy factor of 0.5. Similar phenomena have been observed [19,37].

In conclusion, the first 3-D fluorogallophosphate $Ga_7P_8O_{32}F_4(C_6H_{20}N_4)_2{\cdot}3H_3O^+{\cdot}H_2O$ with a Ga/P ratio of 7/8 has been synthesized in the hydrothermal condition. JGP-4 exhibits a 3-D open-framework with

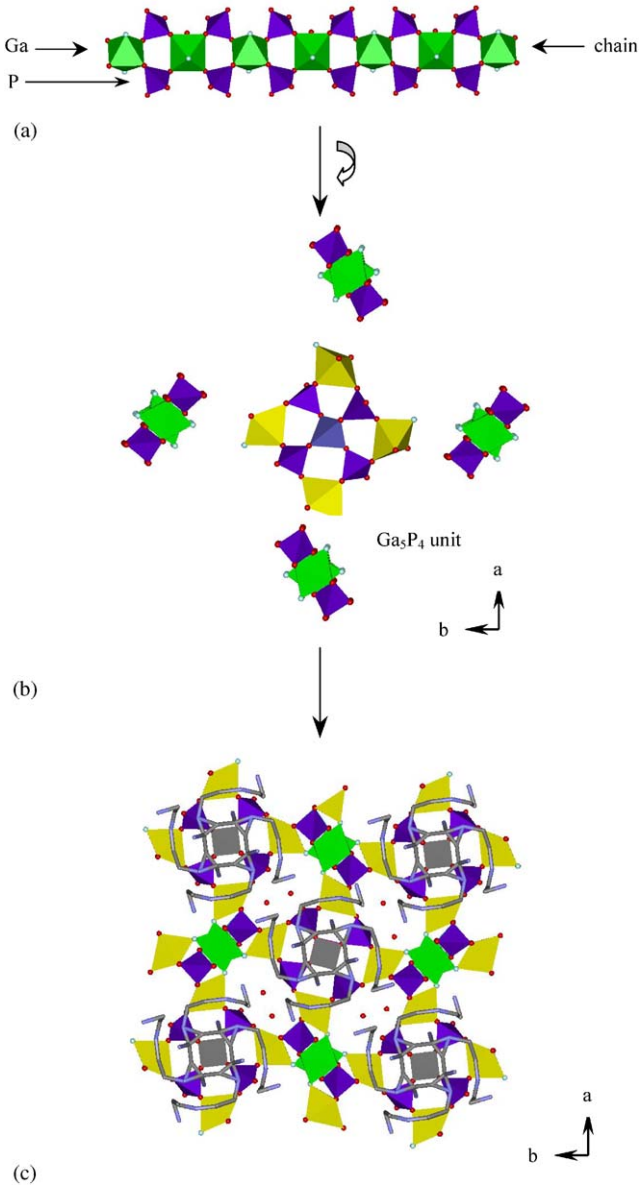

Fig. 3. (a) Polyhedral view of the chain of JGP-4; (b) Polyhedral view of JGP-4 constructed from Ga_5P_4 building units and chains into macroanionic inorganic framework along the c-axis direction; (c) Polyhedral view of JGP-4 with 1-D 8-membered and four square 4-membered rings along the c-axis direction.

8-membered and four square 4-membered rings along the c-axis direction. The organically templated gallophosphates with the Ga/P ratio of non-unity show vast structural and compositional diversities. Many novel open-framework GaPOs with various Ga/P ratios will be synthesized under appropriate conditions.

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