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Journal of Solid State Chemistry 177 (2004) 696–700
JOURNAL OF SOLID STATE CHEMISTRY
http://elsevier.com/locate/jssc

Hydrothermal synthesis and characterization of a new layered gallophosphate JGP-L1 with a Ga/P ratio of non-unity

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Received 2 May 2003; received in revised form 6 August 2003; accepted 20 August 2003

Abstract

A new compound, $Ga_6(OH)_4(HPO_4)_2(PO_4)_5 \cdot C_8H_{28}N_5 \cdot 3H_2O$ (denoted JGP-L1), with a gallophosphate layer and a Ga/P ratio of 6/7 has been synthesized hydrothermally by using tetraethylenepentamine as template. It is characterized by powder X-ray diffraction (XRD), elemental analysis, inductively coupled plasma, and TGA analysis and structurally determined by single-crystal XRD analysis. JGP-L1 crystallizes in the orthorhombic, space group $Pna2_1$ (no. 33), with $a = 16.422(3)$, $b = 11.898(2)$, $c = 18.730(4)$ Å, $V = 3659.6(13)$ Å^3 and $Z = 4$. The structure of JGP-L1 is built up by alternating of $Ga(OH)_2O_4$ octahedra, $Ga(OH)O_4$ trigonal bipyramids and PO_4 (or HPO_4) tetrahedra to form inorganic sheets. It is noteworthy that JGP-L1 was synthesized with extremely low reactant concentration, where the reaction mixture exhibits a H_2O:Ga_2O_3 molar ratio of 2220:1.

Keywords: Synthesis; Characterization; Layered gallophosphate; Tetraethylenepentamine; Extremely low reactional concentration

1. Introduction

Following the discovery of microporous aluminophosphates in 1982 [1], the synthesis of new open-framework metal phosphates has attracted considerable attention because of their potential applications in catalysis, adsorption and separation [2,3]. Among metal phosphates, gallophosphates (GaPOs) constitute an important family. Starting with a structure observation of some microporous GaPO, which are built up by alternation of GaO_4, GaO_5, GaO_6 and PO_4 polyhedra to form open-frameworks with a Ga/P ratio of unity, many novel GaPOs with 1-, 2- and 3-D structures have been synthesized successfully in hydro- or solvothermal conditions [4–6]. In most GaPOs, the Ga/P ratio is 1. Recently, a variety of organically templated GaPOs with Ga/P ratio of non-unity continue to be synthesized, showing vast structural and compositional diversities [7]. There are 3-D open-framework GaPOs with Ga/P ratios of 1/1 [4], 1/2 [8], 4/5 [9], 5/4 [10], a family of 2-D layers with Ga/P ratios of 1/1 [11], 1/2 [12], 2/3 [13], and a series of 1-D chains with Ga/P ratios of 1/2 [14], 1/3 [15], 3/4 [16], 4/7 [17].

Recently, a 3-D fluorogallophosphate with a Ga/P ratio of 6/7 has been reported [18]. To our knowledge, no layered or chain-like structure with a Ga/P molar ratio of 6:7 has been reported in the literature. Herein, we report a new compound with a 2-D $Ga_6(OH)_4(HPO_4)_2(PO_4)_5^{5-}$ anionic layer, which represents the first structural type of GaPO layer with a Ga/P ratio of 6/7. It is noteworthy that JGP-L1 was synthesized with extremely low reactant concentration, where the reaction mixture exhibits a H_2O:Ga_2O_3 molar ratio of 2220:1.

2. Experimental

2.1. Synthesis and characterization

The molar ratio of the initial mixture was $0.25Ga_2O_3$:$4H_3PO_4$:0.8 tetraethylenepentamine (TEPA):$555H_2O$ (pH ≈ 2). The mixture was then aged at room

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doi:10.1016/j.jssc.2003.08.034

temperature for 1 h, followed by transferring to a Teflon-lined stainless steel autoclave and heating under autogenous pressure at 140°C for 7 days. The product was washed with distilled water and dried overnight at 50°C to give colorless crystals.

Powder X-ray diffraction (XRD) data were collected on a Siemens D5005 diffractometer with Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å). The step size was 0.02° and the count time was 4 s. The element analyses were performed on a Perkin–Elmer 2400 element analyzer and the inductively coupled plasma (ICP) analysis was performed on a Perkin–Elmer optima 3300 DV ICP spectrometer. A NETZSCH STA 449C unit was used to carry out the TGA and DTA analyses in air with a heating rate of 10°C/min.

2.2. Determination of crystal structure

A suitable single crystal with dimensions $0.37 \times 0.30 \times 0.10\,mm^3$ 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. 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 [19]. The gallium and phosphorus atoms were first located and carbon, nitrogen, oxygen atoms were found in difference Fourier maps. The hydrogen atoms residing in the amine molecules were located geometrically. All non-hydrogen atoms were refined anisotropically except Ow3, N4 and C7 atoms. Each of them was disordered and occupied two sites, respectively. CCDC reference number 196641. Crystal data and details of data collection and refinement are given in Table 1.

3. Results and discussion

The amount of water used is very important for synthesis of single-crystal JGP-L1. If the molar ratio of H_2O:Ga_2O_3 is less than 275:1, an unidentified gallium phosphate powder phase was obtained. When this molar ratio ranges from 275–555:1, a mixture of an unidentified gallium phosphate phase and a JGP-L1 powder phase was obtained. When this molar ratio ranges from 555–1110:1, JGP-L1 can be formed, but it often contains JGP-L1 polycrystalline phase. When the H_2O:Ga_2O_3 molar ratio is 1110–2220:1, small single-crystal JGP-L1 can be obtained. Only the H_2O:Ga_2O_3 molar ratio is 2220:1, the big single-crystal JGP-L1 is got. The initial gel was well dispersed in large amounts of water for the growth of big single crystal. Therefore, the extremely low reactant concentration is necessary for the synthesis of single crystal of JGP-L1.

Table 1
Crystal data and structure refinement for JGP-L1

Empirical formula	$C_8H_{40}N_5Ga_6P_7O_{35}$
Formula weight	1401.54
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$Pna2_1$
Unit-cell dimensions	$a = 16.422(3)$ Å
	$b = 11.898(2)$ Å
	$c = 18.730(4)$ Å
Volume	3659.6(13) Å^3
Z	4
Density (calculated)	2.538 Mg/m^3
Absorption coefficient	4.790 mm^{-1}
$F(000)$	2764
Crystal size	$0.37 \times 0.30 \times 0.10$ mm
θ range for data collection	2.03–27.40°
Limiting indices	$0 \leqslant h \leqslant 21$, $0 \leqslant k \leqslant 15$, $-24 \leqslant l \leqslant 0$
Reflections collected/ unique	32629/4285 ($R_{(int)} = 0.0348$)
Completeness to $\theta = 23.25$	99.7%
Refinement method	Full-matrix least-squares on F^2
data/restraints/parameters	4285/1/550
Goodness-of-fit on F^2	0.998
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0240$, w$R_2 = 0.0583$
R indices (all data)	$R_1 = 0.0292$, w$R_2 = 0.0595$
Largest diff. peak and hole	0.889 and -0.630 e A^{-3}

3.1. Characterization of JGP-L1

The powder XRD pattern for JGP-L1 is entirely consistent with that simulated on the basis of the single-crystal structure. The diffraction peaks in both patterns correspond well to each other in position, indicating the phase purity of the as-synthesized sample. The ICP analysis shows that the compound contains 30.0 wt% Ga and 15.6 wt% P, suggesting that the molar ratio of Ga:P = 6:7. The elemental analysis indicates that the contents of C, H, and N are 6.82, 2.80 and 4.97 wt%, respectively, in good agreement with the values (6.86, 2.85 and 5.00 wt%, respectively) based on the single-crystal structure formula $Ga_6(OH)_4(HPO_4)_2(PO_4)_5 \cdot C_8H_{28}N_5 \cdot 3H_2O$.

The thermal behavior of JGP-L1 was investigated by TGA thermal analyses. The total weight loss occurs in two steps. The first step, 100–260°C (3.61%) corresponds to the removal of water (calcd. 3.85%). The second step, weight loss of ca. 14.5% in the region 320–600°C corresponding to the removal of the organic component (calcd. 13.8%). XRD analysis indicates that the structure of JGP-L1 collapses after the removal of the organic template.

3.2. Description of the structure

The asymmetric unit, as seen in Fig. 1, contains six crystallographically distinct Ga atoms. Ga(1) and Ga(2) are both octahedrally coordinated and share four oxygen atoms with adjacent P atoms (Ga–O bond

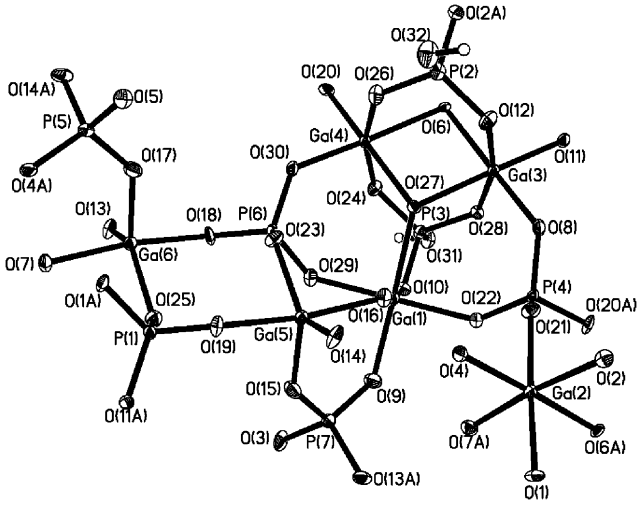

Fig. 1. ORTEP view of the JGP-L1 structure showing the atom labelling scheme (50%thermal ellipsoids).

distances: 1.908(2)–1.958(2) Å), one bridging –OH with adjacent Ga atom (1.990(2) and 1.939(2) Å, respectively), and one tri-bridging –O(27)H with adjacent Ga(3) and Ga(4) atoms (2.152(2) and 2.142(2) Å, respectively). Ga(3) and Ga(4) are also octahedrally coordinated and share four oxygen atoms with adjacent P atoms (Ga–O bond distances: 1.890(2)–2.000(2) Å), and two tri-bridging –O(27)H linking with each other (Ga–O bond distances: 2.038(2)–2.089(2) Å). Ga(5) and Ga(6) are both trigonal bipyramidally coordinated and share four oxygen atoms with adjacent P atoms (Ga–O bond distances: 1.852(2)–1.949(2) Å), and one bridging –OH with adjacent Ga atom (1.947(2) and 1.951(2) Å, respectively). All the GaO_5 and GaO_6 polyhedra share their vertexes with phosphorus-based tetrahedra or GaO_6 polyhedra. The O–Ga–O bond angles are in the range of 83.69(9)–79.92(12)°. Of the seven crystallographically distinct P atoms, P(1), P(4), P(5), P(6) and P(7) each share four oxygens with adjacent Ga atoms (P–O:1.519(2)–1.553(2) Å), whereas P(2) and P(3) each share three oxygens with adjacent Ga atoms (P–O:1.520(2)–1.549(2) Å) and another oxygen from a terminal P–OH (P–OH:1.530(3) and 1.557(3) Å, respectively). The O–P–O bond angles are in the range of 104.45(13)–114.61(14)°. The final atomic coordinates and selected bond lengths are listed in Tables 2 and 3, respectively.

The 2-D anionic framework of JGP-L1 is built up from edge-sharing $Ga(OH)_2O_4$ octahedra and corner-sharing $Ga(OH)_2O_4$ bioctahedra, $Ga(OH)O_4$ trigonal bipyramids and PO_4 (or HPO_4) tetrahedra. Fig. 2 shows a view of the structure perpendicular to a single layer containing three-, four-, non-planar five- and non-planar eight-membered rings along the (001) direction. The inorganic sheets are anionic and the empirical formula of the layer is $[Ga_6(OH)_4(HPO_4)_2(PO_4)_5]^{5-}$, the negative charge is achieved by incorporation of quintu-

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for JGP-L1

Atom	x	y	z	U_{eq} [a]
Ga(1)	−94(1)	5508(1)	3366(1)	10(1)
Ga(2)	−2571(1)	5561(1)	1980(1)	9(1)
Ga(3)	449(1)	8279(1)	2583(1)	9(1)
Ga(4)	1895(1)	6706(1)	2777(1)	9(1)
Ga(5)	−52(1)	3215(1)	2292(1)	9(1)
Ga(6)	2391(1)	1775(1)	2979(1)	10(1)
P(1)	860(1)	839(1)	2358(1)	9(1)
P(2)	1488(1)	7590(1)	1243(1)	12(1)
P(3)	829(1)	7344(1)	4094(1)	10(1)
P(4)	−1339(1)	7305(1)	2693(1)	10(1)
P(5)	3296(1)	1666(1)	1462(1)	10(1)
P(6)	1486(1)	4138(1)	2923(1)	9(1)
P(7)	−941(1)	3221(1)	3779(1)	10(1)
O(1)	−3496(1)	4553(2)	1822(1)	12(1)
O(2)	−2935(1)	6398(2)	1149(1)	12(1)
O(3)	−619(1)	2529(2)	4420(1)	17(1)
O(4)	−1836(1)	4607(2)	1442(1)	15(1)
O(5)	3007(1)	2188(2)	759(1)	15(1)
O(6)	1683(1)	8422(2)	2660(1)	10(1)
O(7)	2688(1)	196(2)	2868(1)	13(1)
O(8)	−671(1)	8075(2)	2389(1)	16(1)
O(9)	−767(2)	4464(2)	3886(1)	16(1)
O(10)	253(1)	6334(2)	4184(1)	12(1)
O(11)	291(1)	9861(2)	2560(1)	15(1)
O(12)	668(1)	7995(2)	1548(1)	16(1)
O(13)	3136(1)	1937(2)	3741(1)	14(1)
O(14)	−786(1)	3060(2)	1526(1)	15(1)
O(15)	−525(2)	2698(2)	3127(1)	17(1)
O(16)	−352(1)	4782(2)	2437(1)	13(1)
O(17)	2846(2)	2234(2)	2092(1)	16(1)
O(18)	2041(1)	3250(2)	3253(1)	14(1)
O(19)	320(1)	1726(2)	2006(1)	13(1)
O(20)	3005(1)	6931(2)	3006(1)	14(1)
O(21)	−1673(1)	6617(2)	2071(1)	14(1)
O(22)	−1015(1)	6521(2)	3279(1)	13(1)
O(23)	1059(1)	3680(2)	2243(1)	13(1)
O(24)	1659(1)	6960(2)	3789(1)	12(1)
O(25)	1289(1)	1305(2)	3028(1)	16(1)
O(26)	1883(2)	6710(2)	1733(1)	15(1)
O(27)	631(1)	6570(2)	2687(1)	10(1)
O(28)	451(1)	8264(2)	3628(1)	13(1)
O(29)	834(1)	4489(2)	3453(1)	13(1)
O(30)	2052(1)	5127(2)	2735(1)	15(1)
O(31)	962(2)	7911(2)	4834(1)	17(1)
O(32)	1385(2)	7034(2)	511(1)	24(1)
N(1)	−3625(2)	2158(4)	827(2)	56(1)
N(2)	−2944(2)	3712(3)	−349(2)	42(1)
N(3)	−2150(2)	6667(3)	−222(2)	39(1)
N(4′)	−780(5)	8512(6)	787(4)	45(2)
N(4)	−1179(8)	9250(11)	382(7)	77(4)
N(5)	−1351(2)	10386(3)	2154(2)	34(1)
C(1)	−4032(3)	3045(5)	415(3)	48(2)
C(2)	−3717(3)	3158(4)	−320(3)	37(1)
C(3)	−2958(3)	4961(4)	−331(3)	42(1)
C(4)	−2116(3)	5435(4)	−211(2)	35(1)
C(5)	−1377(3)	7287(6)	−162(4)	65(2)
C(6)	−1079(5)	7605(10)	492(4)	154(4)
C(7)	−1532(7)	9121(9)	993(6)	37(3)
C(7′)	−911(7)	9834(9)	997(6)	62(3)
C(8)	11454(4)	10201(5)	1381(4)	85(2)
O(1W)	98(3)	370(3)	4383(3)	73(1)
O(2W)	−4621(6)	207(4)	484(3)	164(4)
O(3WA)	−2863(7)	−62(9)	46(6)	135(4)
O(3WB)	−2577(11)	521(16)	−370(11)	122(7)

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

Table 3
Selected bond lengths (Å) for JGP-L1

Ga(1)–O(10)	1.908(2)	Ga(6)–O(13)	1.890(2)
Ga(1)–O(9)	1.926(2)	Ga(6)–O(18)	1.917(2)
Ga(1)–O(22)	1.941(2)	Ga(6)–O(7)	1.951(2)
Ga(1)–O(29)	1.954(2)	P(1)–O(1)#3	1.531(2)
Ga(1)–O(16)	1.990(2)	P(1)–O(19)	1.528(2)
Ga(1)–O(27)	2.152(2)	P(1)–O(11)#4	1.540(2)
Ga(2)–O(2)	1.942(2)	P(1)–O(25)	1.542(3)
Ga(2)–O(4)	1.939(2)	P(2)–O(26)	1.536(2)
Ga(2)–O(21)	1.945(2)	P(2)–O(12)	1.540(2)
Ga(2)–O(1)	1.958(2)	P(2)–O(32)	1.531(3)
Ga(2)–O(7)#1	1.939(2)	P(2)–O(2)#5	1.542(2)
Ga(2)–O(6)#2	2.142(2)	P(3)–O(28)	1.531(2)
Ga(3)–O(8)	1.890(2)	P(3)–O(10)	1.538(2)
Ga(3)–O(11)	1.900(2)	P(3)–O(24)	1.547(2)
Ga(3)–O(12)	2.000(2)	P(3)–O(31)	1.557(3)
Ga(3)–O(28)	1.958(3)	P(4)–O(21)	1.526(2)
Ga(3)–O(6)	2.038(2)	P(4)–O(20)#2	1.527(2)
Ga(3)–O(27)	2.065(2)	P(4)–O(8)	1.539(2)
Ga(4)–O(20)	1.892(2)	P(4)–O(22)	1.535(2)
Ga(4)–O(30)	1.898(2)	P(5)–O(5)	1.531(3)
Ga(4)–O(26)	1.956(2)	P(5)–O(4)#3	1.529(2)
Ga(4)–O(24)	1.957(2)	P(5)–O(14)#3	1.547(3)
Ga(4)–O(6)	2.083(2)	P(5)–O(17)	1.549(3)
Ga(4)–O(27)	2.089(2)	P(6)–O(18)	1.527(2)
Ga(5)–O(14)	1.884(2)	P(6)–O(29)	1.519(2)
Ga(5)–O(15)	1.852(2)	P(6)–O(30)	1.539(2)
Ga(5)–O(23)	1.908(2)	P(6)–O(23)	1.553(2)
Ga(5)–O(19)	1.949(2)	P(7)–O(9)	1.520(2)
Ga(5)–O(16)	1.947(2)	P(7)–O(15)	1.530(3)
Ga(6)–O(17)	1.900(2)	P(7)–O(13)#1	1.528(2)
Ga(6)–O(25)	1.897(2)	P(7)–O(3)	1.549(2)

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

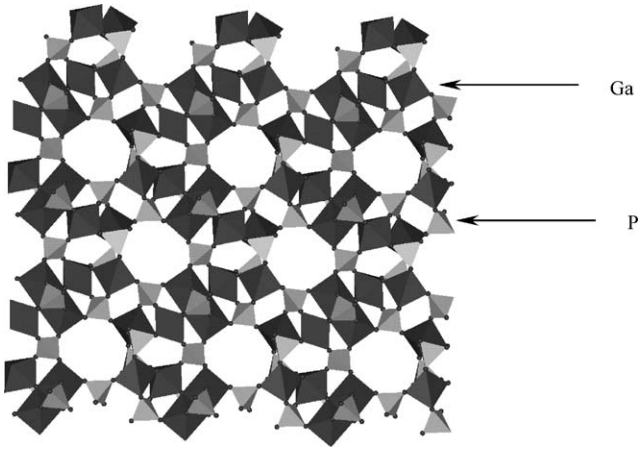

Fig. 2. Polyhedral view of the JGP-L1 structure perpendicular to a single layer, along the (001) direction.

ply protonated TEPA. The TEPA cations occupy the space between the layers, and one $N(1)H_3$ group of the organic cation inserts into the eight-membered ring aperture as seen in Fig. 3. The layered structure is stabilized by the strong hydrogen bonds between the

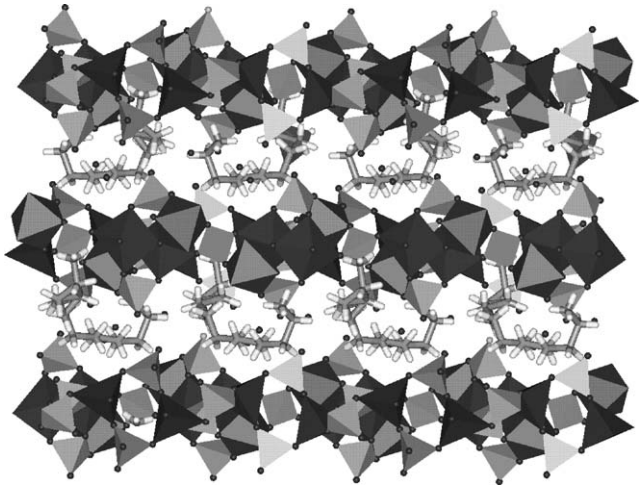

Fig. 3. Polyhedral view of the JGP-L1 structure parallel to the layers, along the (010) direction showing intercalated TEPA cations and waters.

P–OH and the terminal oxygen atoms of the adjacent layer with the distances O(31)–H(31)···O(5) = 2.572(5) Å and O(32)–H(32)···O(3) = 2.456(5) Å. The quintuply protonated molecule TEPA also participates in hydrogen bonding with the framework contributing to the additional structural stability of this compound. The N–H···O distances are in the range of 2.775(5) –3.177(5) Å.

In conclusion, the first layered GaPO with a Ga:P molar ratio of 6:7 has been synthesized with extremely low reactant concentration. We think that open-framework GaPO with various Ga:P ratios is possible to be synthesized under appropriate conditions. Further synthesis of new open-framework GaPO with various Ga:P ratios is in progress.

Acknowledgments

We are grateful to the National Natural Science Foundation of China (20233030) and the State Basic Research Project (G200077507) for financial supports.

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