STRUCTURE REFINEMENT OF ZINC CONTAINING GALLOPHOSPHATE WITH THE ULM-5 STRUCTURE †

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† This paper is dedicated to the late Professor Drago Kolar

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Abstract

A zinc containing microporous gallophosphate with the ULM-5 structure has been hydrothermally synthesised in the presence of fluoride ions and 1,6-diaminohexane as a structure-directing agent. It was characterised using single-crystal X-ray diffraction (R=5.3%) and EDAX elemental analysis. The compound crystallises in the orthorhombic space group $P2_12_12$ with unit cell parameters a = 24.814(13) Å, b = 18.458(5) Å, c = 10.2575(18) Å. EDAX analysis revealed up to 6(2) wt.% of zinc in the structure. The examination of Ga-O bond distances showed that zinc is preferentially located on one of the 5-coordinated gallium sites. No zinc was found on the extra-framework positions. The two 1,6-diaminohexane template molecules are well defined. The nitrogen atoms on both template molecules are ordered and hydrogen bonded to framework oxygen and fluorine atoms. Three of the twelve carbon atoms are disordered, each over two sites.

Introduction

Molecular sieves are crystalline materials with open framework structures, among which zeolites are the most representative group. They are widely used in gas separations, ion exchange and catalysis.[1] Recently, many new zeolite-like structures such as aluminophosphates,[2,3] gallophosphates[4,5] and zincophosphates[6] with new possible applications have been reported. Compared to zeolites, aluminophosphates and gallophosphates possess more complicated framework structures, which result from a variety of coordination possibilities of aluminium and gallium atoms. The introduction of small amounts of transition-metal atoms such as Co, Mn, Ni etc. on the aluminium or gallium framework sites create negative charges in otherwise neutral frameworks, which make this microporous materials potential solid-acid catalysts.[7,8]

The amounts of incorporated metals depend on the structure type and chemical composition of the specific phosphate.

Several papers about the synthesis, characterisation and catalytic properties of gallophasphates have been published until now, with the emphasis on the most well-known open-framework gallophasphate cloverite with supercages of 30 Å diameter and free aperture of 13.2 Å.[9] However, few successful attempts have been reported on the incorporation of foreign atoms into framework or extra-framework sites of cloverite or other microporous gallophasphates. The first two examples were CoGaPO-LAU and CoGaPO-LTA,[10] which were isolated from $GaPO_4$ gels containing small amounts of cobalt. Low contents of heterometals (Zn, Si, Ti, Co, Ni, Fe and Mg) in the cloverite structure type have been reported, but have not yet been quantified.[11]

ULM-5 is a large pore microporous oxofluorinated gallophosphate with chemical composition of $Ga_{16}(PO_4)_{14}(HPO_4)_2(OH)_2F_7$, which was first synthesized and characterized in 1994 by Loiseau Ferey.[12] It crystallises in an orthorhombic space group $P22_12_1$ with unit cell parameters a = 10.252(2) Å, b = 18.409(4) Å, and c = 24.639(7) Å. The three-dimensional network in which gallium atoms are four-, five- and also six-coordinated, contains 16-, 8- and 6-member ring channels. The diprotonated 1,6-diaminohexane molecules are located in the 16-member ring channels, whose free aperture is 12.20 × 8.34 Å. Here we report the synthesis and structure of a zinc containing gallophosphate with the ULM-5 structure type.

Experimental

Synthesis

The synthesis was carried out hydrothermally in Teflon-lined autoclaves under autogeneous pressure. Gallium(III) oxide, orthophosphoric acid, and zinc(II) acetate were used as gallium, phosphorous and zinc sources (Table 1). Higher molar amount of zinc led to the formation of an unidentified zinc gallophosphate.

Table 1. Reaction gel molar composition

Sample	P_2O_5	Ga_2O_3	ZnO	HF	DAH*	H_2O
ZnULM-5	1	0.98	0.02	2	1	100

*DAH=1,6-diaminohexane

The reaction gel was prepared as follows: gallium(III) oxide and a solution of zinc(II) acetate were successively added to stirred diluted orthophosphoric acid solution. Then a dropwise addition of diluted HF and the templating agent, 1,6-diaminohexane was performed. The system was thoroughly stirred at room temperature, each time prior to the addition of the next component. The resulting gel was aged for 2 hours in the air and then the gel was loaded in Teflon-lined stainless steel autoclaves followed by heating at 170 °C under autogenous pressure for 24 hours.

Table 2. Weight amounts of reagents used in synthesis gels for ZnULM-5 (g)

$Zn(CH_3COO)_2{\cdot}2H_2O$	Ga_2O_3	H_3PO_4	$H_2N\text{-}(CH_2)_6\text{-}NH_2$	HF	H_2O
0.09	3.92	4.92	2.48	2.21	36.39

After crystallisation, the autoclaves were cooled down to room temperature and the products were washed and dried at 80-100 °C. The pH of the initial gel raised from 1.5 before reaction to 4 at the end of the reaction. All masses of the reactants used are shown in Table 2.

Characterisation

A transparent crystal of 0.45 x 0.07 x 0.05 mm^3 size was mounted on a glass fibre for room-temperature intensity data collection on a rotating-anode Rigaku AFC5R diffractometer with graphite-monochromated CuKα radiation (1.5418 Å). The orthorhombic cell constants were determined by least-squares refinement on the basis of 25 reflections. Lorentz, polarisation and empirical absorption corrections based on azimuthal scans were applied to the intensity data. Further details of the data

collection and reduction are contained in Table 3. Neutral atomic scattering factors were used for all atoms.[13]

The elemental analysis was carried out on five single crystals using an EDAX (energy dispersion analysis by X-ray) analytical system (TRACOR EDX), attached to a scanning electron microscope (JEOL JXA-840A). The amount of Zn varied from 3(2) to 6(2) wt. %. The variations in the zinc amount reflect an irregular distribution of zinc in the crystals.

Table 3. Crystallographic parameters for ZnULM-5

Empirical formula	$C_{12}H_{36}F_{3.5}Ga_7N_4O_{36}P_8Zn$
Formula weight	1675.1
Crystal colour, habit	transparent, needle
Crystal system	orthorhombic
a(Å)	24.814(13)
b(Å)	18.458(5)
c(Å)	10.2575(18)
V(Å^3)	4698(3)
Z	4
Space group	$P2_12_12$
D_C(Mgm^{-3})	2.380
hkl data limits	$0\leq h\leq 29$, $0\leq k\leq 22$, $0\leq l\leq 12$
$2\theta_{max}$(°)	156.46
3 standard reflections for intensity change	(0 0 6), (4 5 1), (-4, -5, -1)
Intensity decay (%)	2.64
R_{int}	0.0258
μ(CuKα) (mm^{-1})	8.70
Absorption correction	empirical
T_{min}, T_{max}	0.741, 1.000
Total data	8698
Observed data ($I\geq 2\sigma(I)$)	6436
Parameters	586
R (on F^2)	0.053
R_w (on F^2)	0.121
$\Delta\rho_{max}$ (eÅ^{-3})	0.299
$\Delta\rho_{min}$ (eÅ^{-3})	-0.297

Single-crystal structure analysis

The refinement was initiated using the coordinates for the previously solved structure of ULM-5 as a starting point.[12] At the beginning all of the eight gallium sites were refined with full occupancy of gallium. The Ga:Zn ratios on these sites were not refined due to the similar scattering power of both elements. The examination of bond distances led us to refine the Ga(3) site with full occupancy of zinc. The framework non-hydrogen atoms were refined anisotropically. The extra-framework non-hydrogen atoms, O(34) and the nitrogen atoms, were also refined anisotropically. Other non-hydrogen atoms were refined isotropically. H atoms on template molecules were included in calculated positions. There are two 1,6-diaminohexane molecules in the asymmetric unit. The first is reasonalbly well ordered, although some of the thermal parameters of the C atoms are high (Table 5). For the other molecule, there are two sites for C(7) and C(8), whose occupancies were constrained to the sum of 1.0. C(11) was also disordered over 2 sites, each with an occupancy of 0.5. 14 restraints were placed on the bond lengths of both molecules.

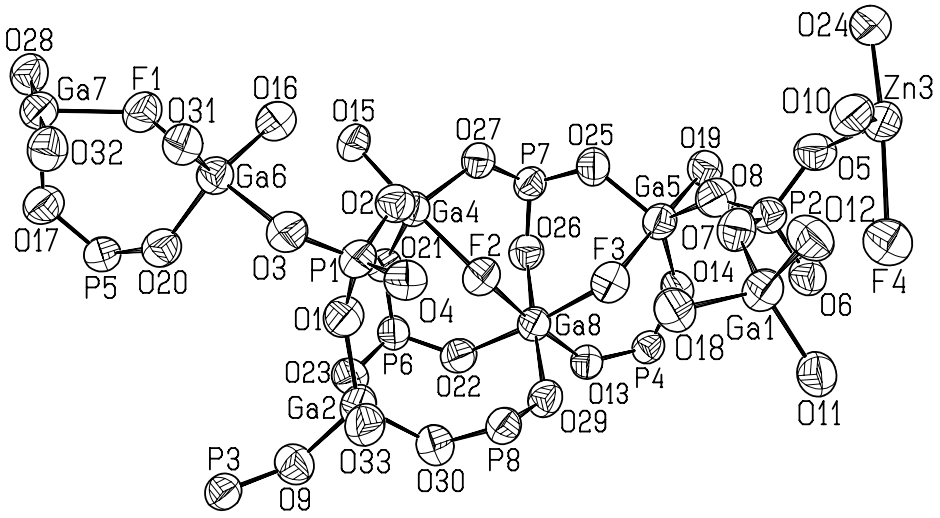
Final atomic parameters of non-hydrogen atoms for the ZnULM-5 structure are listed in Table 4 and Table 5 and selected bond distances and contacts in Table 6 and Table 7. Supplementary material is available from the authors. The TeXan software[14] was used for the correlation and reduction of the data and SHELXL-97[15] for the structure refinement. ATOMS[16] and Ortep3[17] programs were used for the drawings of the structure.

Results and discussion

The title structure is built of alternating PO_4 and 4-, 5-, and 6-coordinated Ga/Zn polyhedra, which form 16-, 8- and 6-member ring channels (Figure 1, 3). The unit cell parameters in ZnULM-5 are longer than those of ULM-5; the differences are 0.175 Å, 0.049Å and 0.005Å for *a*, *b* and *c* dimensions, respectively. This observation is in accordance with zinc incorporation, since zinc usually substitutes gallium in

open-framework structures and the Zn^{2+}-O bond is longer than the Ga^{3+}-O bond.[18] An average tetrahedral Ga-O bond in $Ga_3P_3O_{12}(OH).(CH_3)_2NH_2$ is 1.816(9) Å[19] while the average tetrahedral Zn-O bond in $Na_6[Co_{0.2}Zn_{0.8}PO_4]_6.6H_2O$ is 1.95(2) Å.[20] Mean Ga-O(F) bond lengths of the eight crystallographically different Ga sites are the same or slightly longer in ZnULM-5 than in the zinc-free analogue; the differences are 0.00(2) Å for Ga(1), 0.00(2) Å for Ga(2), 0.030(19) Å for Ga(3), 0.010(16) Å for Ga(4), 0.013(19) Å for Ga(5), 0.010(17) Å for Ga(6), 0.003(19) Å for Ga(7), and 0.007(19) Å for Ga(8). We may conclude that zinc is located on the 5- and also on the 6-coordinated framework gallium sites, although most of the values are within experimental error. Only for the Ga(3) site in trigonal-bipyramidal geometry is the observed increase in bond length significant (Table 7), mostly due to the Ga(3)-F(4) bond length (2.207(7) Å in zinc-free and 2.294(6) Å in our structure). We conclude that zinc is preferentially incorporated on the Ga(3) site in the structure. Full occupation of the Ga(3) site with zinc would correspond to 3.9 wt. % of Zn, which is in accordance with EDAX analysis. There was no evidence for the presence of zinc in extra-framework positions or anywhere else in the structure.

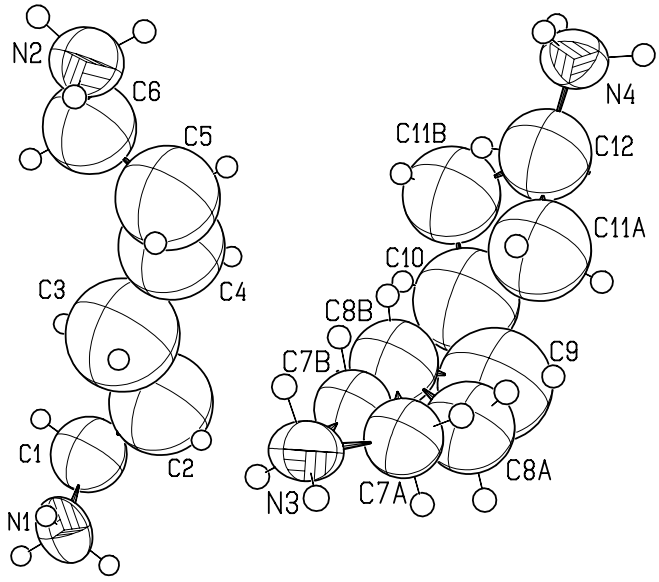
Figure 1. ORTEP drawing and a labelling scheme of framework atoms in the ZnULM-5 asymmetric unit.



For a long time, it was believed that in microporous frameworks transition metal ions are almost exclusively substituting at tetrahedral or octahedral sites. However, in some recent publications it has been shown that transition metal atoms can also be present in other coordinations, especially when fluorine is bonded to the framework metal sites (e.g. CoAPO-CJ2,[21] CoGaPO-LTA[22]).

The negative charge that is induced by the substitution of Ga^{3+} with Zn^{2+} is usually compensated by a protonation of the neighbouring O atoms. However, the examination of electron density around oxygen atoms attached to Zn(3) did not show any peaks, which could be ascribed to hydrogen atoms, so we could not make any conclusions about the proton location. A distorted thermal ellipsoid on Ga(2) site indicates a displacement of Ga over two sites.

Figure 2. ORTEP drawing and a labelling scheme of template molecules in the ZnULM-5 asymmetric unit.



Structure analysis of ZnULM-5 cleared up some uncertainties about the template and water atoms, whose temperature factors were kept fixed in structure determination of ULM-5. There are two 1,6-diaminohexane and three water molecules O(34), O(35) and O(36) in the asymmetric unit of ZnULM-5. The C(7), C(8), and C(11) atoms are disordered, each over two sites (Table 5, Figure 2). The N-O and N-F contacts are short and some of them may represent hydrogen bonds (Table 6).

Figure 3. Tetrahedral presentation of ZnULM-5 structure: 1,6-diaminohexane molecules are located in the 16-member ring channels.

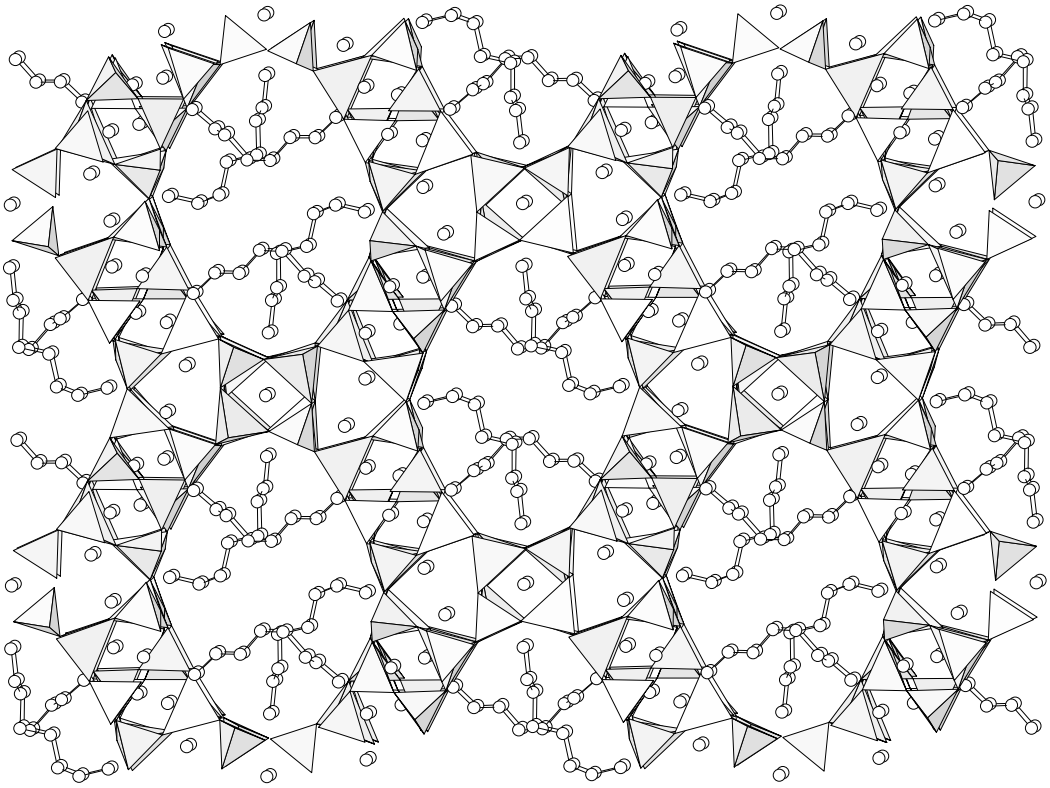


Table 4. Fractional atomic coordinates and equivalent isotropic displacement parameters for framework non-hydrogen atoms ($Å^2$)

	x	y	z	U_{eq}
Ga(1)	0.43750(5)	-0.08422(6)	0.11277(13)	0.0605(5)
Ga(2)	0.16161(6)	-0.34714(8)	0.0723(3)	0.1049(8)
Zn(3)	0.55936(5)	-0.06966(6)	0.37861(14)	0.0572(5)
Ga(4)	0.26464(5)	-0.41705(6)	0.39829(12)	0.0529(5)
Ga(5)	0.34615(5)	-0.17279(6)	0.59097(14)	0.0604(5)
Ga(6)	0.25853(4)	-0.60688(6)	0.10238(12)	0.0531(5)
Ga(7)	0.22369(5)	-0.79764(6)	0.08158(12)	0.0547(5)
Ga(8)	0.23191(5)	-0.22809(6)	0.42260(12)	0.0542(5)
P(1)	0.26747(10)	-0.43510(12)	0.1040(3)	0.0538(6)
P(2)	0.43785(9)	-0.09608(12)	0.4149(3)	0.0532(6)
P(3)	0.06427(10)	-0.41572(12)	-0.0802(3)	0.0550(7)
P(4)	0.23462(10)	-0.08970(12)	0.6054(2)	0.0537(6)
P(5)	0.13934(9)	-0.66826(12)	0.0943(3)	0.0546(6)
P(6)	0.14541(10)	-0.35511(13)	0.4211(3)	0.0579(7)
P(7)	0.30016(11)	-0.32010(13)	0.6223(3)	0.0558(7)
P(8)	0.20858(10)	-0.20549(12)	0.1246(2)	0.0539(7)
F(1)	0.2533(3)	-0.7117(3)	0.1671(6)	0.0631(15)
F(2)	0.2626(3)	-0.3122(3)	0.3331(5)	0.0620(14)
F(3)	0.3071(2)	-0.1877(3)	0.4185(7)	0.0706(15)
F(4)	0.5	0.0	0.2617(10)	0.079(2)
O(1)	0.2083(3)	-0.4140(4)	0.1318(8)	0.0676(19)
O(2)	0.2960(3)	-0.4359(4)	0.2388(7)	0.0611(17)
O(3)	0.2680(3)	-0.5100(4)	0.0417(7)	0.0602(16)
O(4)	0.2975(3)	-0.3823(4)	0.0161(7)	0.0587(16)
O(5)	0.4961(3)	-0.0950(4)	0.4653(7)	0.0641(18)
O(6)	0.4122(3)	-0.0205(3)	0.4192(8)	0.0615(17)
O(7)	0.4363(3)	-0.1269(3)	0.2764(7)	0.0608(17)
O(8)	0.4086(3)	-0.1459(4)	0.5056(8)	0.0666(18)
O(9)	0.0960(3)	-0.3687(4)	0.0134(7)	0.0664(18)
O(10)	0.5715(3)	-0.1144(4)	0.2196(8)	0.0646(18)
O(11)	0.4133(3)	0.0065(4)	0.0726(8)	0.0666(18)
O(12)	0.5056(3)	-0.0899(4)	0.0367(8)	0.069(2)
O(13)	0.2066(3)	-0.1446(3)	0.5195(7)	0.0579(16)
O(14)	0.2949(3)	-0.1048(4)	0.6286(7)	0.0624(17)
O(15)	0.2719(3)	-0.5158(3)	0.4585(7)	0.0571(16)
O(16)	0.2930(3)	-0.5914(3)	0.2585(7)	0.0587(16)
O(17)	0.1550(3)	-0.7461(4)	0.0698(8)	0.0643(18)
O(18)	0.4069(3)	-0.1513(4)	-0.0006(8)	0.070(2)
O(19)	0.3805(3)	-0.1559(4)	0.7662(7)	0.0627(17)
O(20)	0.1854(3)	-0.6141(4)	0.0633(7)	0.0588(16)
O(21)	0.1922(3)	-0.4092(3)	0.4414(7)	0.0607(17)
O(22)	0.1617(3)	-0.2766(4)	0.4265(7)	0.0637(17)
O(23)	0.1195(4)	-0.3700(4)	0.2868(9)	0.079(2)
O(24)	0.6040(3)	-0.1325(4)	0.4724(9)	0.077(2)
O(25)	0.3500(3)	-0.2721(4)	0.6098(7)	0.0638(17)
O(26)	0.2500(3)	-0.2775(3)	0.5833(7)	0.0609(16)
O(27)	0.3082(3)	-0.3866(3)	0.5354(7)	0.0571(16)
O(28)	0.2056(3)	-0.8474(4)	0.2377(7)	0.0667(19)
O(29)	0.2166(3)	-0.1773(3)	0.2623(7)	0.0581(16)
O(30)	0.1578(3)	-0.2527(4)	0.1182(7)	0.0650(18)
O(31)	0.3005(3)	-0.6397(4)	-0.0361(7)	0.0588(16)
O(32)	0.2435(3)	-0.7499(3)	-0.0805(7)	0.0601(16)
O(33)	0.1997(3)	-0.3342(4)	-0.0962(9)	0.0697(19)

Table 5. Fractional atomic coordinates and isotrpic or equivalent isotropic displacement parameters for extra-framework non-hydrogen atoms ($Å^2$)

	x	y	z	U_{is}/U_{eq}
O(34)	0.1949(4)	-0.4513(6)	0.7221(11)	0.103(3)
O(35)	0.3301(6)	-0.0833(8)	0.1965(15)	0.145(5)
O(36)	0.0935(9)	-0.5072(11)	0.242(2)	0.198(8)
N(1)	0.1901(4)	-0.0172(6)	0.2574(12)	0.087(3)
C(1)	0.1360(8)	-0.0023(11)	0.213(2)	0.123(6)
C(2)	0.0925(13)	-0.0305(17)	0.305(3)	0.225(15)
C(3)	0.0799(14)	-0.1088(18)	0.266(4)	0.250(17)
C(4)	0.0219(13)	-0.1358(16)	0.288(4)	0.219(14)
C(5)	0.0210(13)	-0.2177(14)	0.328(3)	0.188(12)
C(6)	0.0092(10)	-0.2602(12)	0.206(2)	0.148(8)
N(2)	0.0014(5)	-0.3367(6)	0.2423(15)	0.102(4)
N(3)	0.1416(4)	-0.2465(6)	0.7130(11)	0.080(3)
C(7A)	0.1043(10)	-0.2012(15)	0.789(3)	0.088(5)
C(7B)	0.0972(14)	-0.1954(19)	0.706(3)	0.088(5)
C(8A)	0.0566(13)	-0.1696(18)	0.710(3)	0.123(8)
C(8B)	0.0783(16)	-0.174(2)	0.844(3)	0.123(8)
C(9)	0.0320(12)	-0.1189(18)	0.821(3)	0.215(14)
C(10)	-0.0147(11)	-0.1130(17)	0.725(3)	0.200(12)
C(11A)	-0.0381(11)	-0.171(3)	0.823(4)	0.167(19)
C(11B)	-0.0628(17)	-0.154(3)	0.659(3)	0.17(2)
C(12)	-0.0945(4)	-0.1818(6)	0.7749(10)	0.142(7)
N(4)	-0.1370(4)	-0.2325(6)	0.7817(10)	0.084(3)

Table 6. Selected contacts (Å)

N(1)..O(3)	3.242	N(2)..O(8)	3.478	N(3)..O(24)	3.078
N(1)..O(34)	3.108	N(2)..O(23)	3.027	N(3)..O(1)	3.176
N(1)..O(29)	3.028	N(3)..O(33)	2.919	N(4)..O(17)	3.015
N(1)..O(15)	3.063	N(3)..F(1)	2.952	N(4)..O(32)	3.014
N(1)..O(27)	3.213	N(3)..O(13)	3.177	N(4)..F(2)	2.877
N(2)..O(12)	3.168	N(3)..O(22)	3.033	N(4)..F(3)	2.883
N(2)..O(19)	3.005	N(3)..O(26)	3.053	N(4)..O(7)	3.225

Table 7. Selected bond distances (Å)

Ga(1)-O(11)	1.826(7)	Ga(4)-O(2)	1.844(7)	Ga(6)-F(1)	2.050(5)
Ga(1)-O(7)	1.855(7)	Ga(4)-O(21)	1.856(7)		
Ga(1)-O(18)	1.861(8)	Ga(4)-O(27)	1.862(7)	Ga(7)-O(28)	1.900(8)
Ga(1)-O(12)	1.863(8)	Ga(4)-O(15)	1.932(6)	Ga(7)-O(4)	1.928(7)
		Ga(4)-F(2)	2.049(6)	Ga(7)-O(32)	1.944(7)
Ga(2)-O(9)	1.781(8)			Ga(7)-F(1)	1.956(6)
Ga(2)-O(1)	1.800(8)	Ga(5)-O(14)	1.827(7)	Ga(7)-O(17)	1.955(7)
Ga(2)-O(30)	1.808(7)	Ga(5)-O(25)	1.8467)	Ga(7)-O(33)	2.023(7)
Ga(2)-O(33)	1.984(9)	Ga(5)-O(8)	1.847(8)		
		Ga(5)-O(19)	2.014(8)	Ga(8)-O(29)	1.930(7)
Zn(3)-O(10)	1.853(8)	Ga(5)-F(3)	2.036(7)	Ga(8)-O(26)	1.937(7)
Zn(3)-O(6)	1.855(7)			Ga(8)-O(13)	1.938(7)
Zn(3)-O(5)	1.863(8)	Ga(6)-O(16)	1.839(7)	Ga(8)-F(2)	1.957(6)
Zn(3)-O(24)	1.871(8)	Ga(6)-O(31)	1.862(7)	Ga(8)-O(22)	1.959(7)
Zn(3)-F(4)	2.294(6)	Ga(6)-O(20)	1.864(7)	Ga(8)-F(3)	2.010(6)
		Ga(6)-O(3)	1.908(7)		

Conclusions

The use of reactive zinc(II) acetate as a metal source has lead to a successful synthesis of zinc gallophosphate molecular sieve with ULM-5 structure type. It was shown that zinc is substituting up to 6(2) wt. % of gallium in the framework. Due to similar ionic radii of zinc and gallium, one would expect more zinc to be incorporated in the structure. Namely, in some open-framework zinc gallophosphates the Zn/Ga ratios are one or even more.[18] The low content of zinc in our structure is partly due to the fact that the ULM-5 structure framework is already negatively charged due to the presence of F^-, and OH^- groups and that the introduction of the additional negative charge by the Zn^{2+} incorporation on Ga^{3+} sites is difficult.

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Povzetek

Mikroporozni cinkov galofosfat strukturnega tipa ULM-5 smo sintetizirali v prisotnosti fluoridnih ionov in strukturnega usmerjevalca 1,6-diaminoheksana. Struktura produkta je bila določena z metodo rentgenske difrakcije na monokristalu in EDAX elementno analizo. Material kristalizira v ortorombski $P2_12_12$ prostorski skupini s parametri osnovne celice a = 24.814(13) Å, b = 18.458(5) Å, c = 10.2575(18) Å. EDAX analiza je pokazala prisotnost 6(2) ut.% cinka v strukturi. Iz pregleda veznih razdalj in kotov smo ugotovili, da se cink preferenčno vgrajuje na 5-koordinirana galijeva mesta. Na izvenogrodnih mestih ni bilo dokazov o prisotnosti cinka. Dve molekuli 1,6-diaminoheksana v asimetrični enoti sta dobro definirani. Dušikovi atomi na obeh molekulah templata so urejeni in vezani na ogrodne kisikove in fluorove atome z vodikovimi vezmi. Trije od dvanajstih atomov ogljika so neurejeni, in sicer na dveh legah.