

Syntheses and Structures of Two Ammonium Zinc Gallophosphates: Analcime and Paracelsian analogs

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Two ammonium zinc gallophosphates (I) $(\text{NH}_4)_{16}[\text{Zn}_{16}\text{Ga}_8\text{P}_{24}\text{O}_{96}]$ and (II) $(\text{NH}_4)_4[\text{Zn}_4\text{Ga}_4\text{P}_8\text{O}_{32}]$ were hydrothermally synthesized and characterized using single crystal X-ray diffraction. The (I) $(\text{NH}_4)_{16}[\text{Zn}_{16}\text{Ga}_8\text{P}_{24}\text{O}_{96}]$ crystallizes in a cubic $I2_13$ space group ($a = 13.456(1) \text{ \AA}$, $V = 2436.5(5) \text{ \AA}^3$, R (on F) = 2.47%, R_w (on F) = 2.48%). It has a zeolite analcime topology with distorted eight-member ring channels. Zn and Ga atoms share the same crystallographic site with a partial occupancy of $\text{Zn}/\text{Ga} = 0.67/0.33$. Ammonium ions lie on the three-fold crystallographic axes and compensate for a negatively charged framework. The second compound (II) $(\text{NH}_4)_4[\text{Zn}_4\text{Ga}_4\text{P}_8\text{O}_{32}]$ has a monoclinic symmetry ($P2_1/a$, $a = 9.406(1) \text{ \AA}$, $b = 9.881(1) \text{ \AA}$, $c = 8.612(1) \text{ \AA}$, $\beta = 90.58(1)^\circ$, R (on F) = 2.7%, R_w (on F) = 3.0%). It is isostructural with a feldspar paracelsian. Zinc and gallium occupy two crystallographic sites with a partial occupancy of $\text{Zn}(1)/\text{Ga}(1) = 0.53(6)/0.47(6)$ and $\text{Zn}(2)/\text{Ga}(2) = 0.47(6)/0.53(6)$. Ammonium ions lie in the elliptical eight-member ring openings of the three-dimensional framework. © 2001 Academic Press

Key Words: gallophosphates; open-frameworks; microporous materials; ZnGaPO; GaPO-ANA; analcime; paracelsian; structure determination.

INTRODUCTION

Open framework aluminophosphates and gallophosphates have been studied intensively in the past years (1). Many have framework topologies analogous to aluminosilicates zeolites, while others have unique structures (2). The introduction of divalent metal cations like Co^{2+} , Mn^{2+} ,

Zn^{2+} , etc., on the Al or Ga framework sites results in negatively charged frameworks, which can be useful for catalytic, absorption or ion-exchange applications. Examples of microporous metal gallophosphates found in the literature are Co-, Zn-, Fe-, or Mn-substituted gallophosphate phases analogous to zeolites gismondine (3, 4), laumontite (5), sodalite (6), thomsonite (6), and new topologies (CGS (7), CGF (8), SBS (9), and SBT (9) structure types (2)). In most of them the Me/Ga ratios ($Me = \text{Co}, \text{Zn}, \text{Mn},$ and Fe) are one or even more. A review of some of the above structures has recently been published by Chippindale and Cowley (10). Here we report on the synthesis and structure determination by single-crystal X-ray diffraction of two synthetic zinc gallophosphates, one with a zeolite analcime topology and an accompanying phase, which is isostructural with a feldspar mineral paracelsian.

Analcime is a well-known natural zeolite, $\text{Na}_{16}[\text{Al}_{16}\text{Si}_{32}\text{O}_{96}] \cdot 16\text{H}_2\text{O}$, with distorted eight-member ring channels ($4.2 \times 1.6 \text{ \AA}$) (2). The minerals leucite and pollucite are isostructural with analcime, but have different chemical compositions (K^+ and Cs^+ instead of Na^+ extraframework cations). Some nonsilica forms of analcime structure type are known as well, namely aluminophosphates $\text{AlPO}_4\text{-}24^2$, $\text{AlPO}_4\text{-pollucite}$ (2), cobalt aluminophosphate $\text{Cs}_{16}[\text{Al}_8\text{Co}_{16}\text{P}_{24}\text{O}_{96}]$ (2, 6), two gallogermanates $(\text{NH}_4)_{16}[\text{Ga}_{16}\text{Ge}_{32}\text{O}_{96}]$ and $\text{Cs}_{16}[\text{Ga}_{16}\text{Ge}_{32}\text{O}_{96}]$ (11), and a family of metal germanate phases $A_2M\text{Ge}_5\text{O}_{12}$: $A = \text{Rb}, \text{Cs}$; $M = \text{Be}, \text{Mg}, \text{Co}, \text{Zn}$ (12). Most of the synthetic forms of analcime analogs were hydrothermally synthesized at temperatures around 200°C . The ideal topological symmetry of analcime structure type is cubic with a space group $Ia\text{-}3d$; however, in many natural and synthetic samples the symmetry is lowered. There are some natural analcime samples with tetragonal and orthorhombic symmetry (13). In the synthetic phosphorous-substituted analcime $\text{Na}_{13}[\text{Al}_{24}\text{Si}_{13}\text{P}_{11}\text{O}_{96}] \cdot$

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16H₂O, with ordered Al and P/Si sites, the structure symmetry was found to be *I*₄32 (14). Recently, Takaishi proposed a trigonal R3 or R-3 symmetry for a stable analcime structures from his Al ordering theory (15). Yokomori and Idaka followed this suggestion and successfully refined a synthetic Na₈[Al₈Si₁₆O₄₈]·8H₂O analcime structure in R-3 space group (16).

On the other hand, almost all the known paracelsian-like structures crystallize in *P*₂₁/*a* space group, with a strong orthorhombic pseudosymmetry ($\beta \sim 90^\circ$, space group *Pnam*). The mineral paracelsian BaAl₂Si₂O₈ (17, 18) belongs to a feldspar group of tectosilicate minerals, which have, compared to zeolites, smaller voids in structures, higher content of Al in the frameworks, and usually low crystallographic symmetry, e.g., triclinic or monoclinic. Paracelsian structure analogs include synthetic SrGa₂Si₂O₈ (19), SrGa₂Ge₂O₈ (20), and BaGa₂Ge₂O₈ (20) structures, and a series of *A*(ZnXO₄)₂ structures, where *A* = Sr, Ba; *X* = P, As (21). Mineral hurlbutite CaBe₂P₂O₈ (22) and its analogs SrZn₂P₂O₈ (23) and α -CaZn₂P₂O₈ (23) are also assumed to be isostructural with paracelsian. Some of the synthetic forms of paracelsian analogs were synthesized by crystallisation from the melt (20) or by high-temperature sintering of stoichiometric amounts of reagents (21). The orthophosphates SrZn₂P₂O₈ and α -CaZn₂P₂O₈ (23) were synthesized during crystal growth of fluorophosphate compounds by chloride flux method (NaCl + ZnCl₂) and by slow cooling from 700°C.

EXPERIMENTAL

Hydrothermal Synthesis and Characterization

The compounds (I) and (II) were obtained by hydrothermal crystallization using gallium (III) oxide (Ga₂O₃, Aldrich, 99.99%), ammonium hydrogenphosphate ((NH₄)₂HPO₄, Laphoma, 99%), zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O, Aldrich, 98%), oxalic acid dihydrate (H₂C₂O₄·2H₂O, Podnart, 99%), tetramethylammoniumbromide ((CH₃)₄NBr, Fluka, 99%), and distilled water. Oxalic acid was used as an organic anion to alternate the reaction mixture and promote structure diversity similar to fluorine in open-framework structures (24). Tetramethylammoniumbromide was used as a structure-directing agent. In the synthesis procedure four solutions were prepared: zinc acetate was dissolved in 52% of distilled water, ammonium hydrogenphosphate in 14%, oxalic acid in 14%, and organic template tetramethylammoniumbromide in 20% of distilled water for the gel composition. Solutions of oxalic acid and ammonium hydrogenphosphate were successively added to the dispersion of gallium oxide, which was added to the solution of zinc acetate. Finally, tetramethylammoniumbromide was added dropwise. The system was thoroughly blended with a magnetic mixer to a homogeneous mixture each time before the

addition of the next component. At the end of the synthesis, when all the components were added, the gel was also mixed for 10 min with an Ultra-Turrax T25 (Jankle-Kunkel) disperser. The resulting gel with a molar composition of 0.5 Ga₂O₃:1.0 Zn(CH₃COO)₂:1.0 (NH₄)₂HPO₄:1.0 H₂C₂O₄·2H₂O:2.0 (CH₃)₄NBr:200.0 H₂O was transferred to a 50-ml stainless-steel, Teflon-lined autoclaves, and heated under static conditions at 150 to 180°C in an oven for 1 to 4 days. The crystallisation products were washed with distilled water and dried at 105°C. In all of the final products there were two zinc gallophosphate phases found in the approximate volume ratio of 1:4, the analcime crystals having the majority. They appeared colorless and cubic in shape and approximately 200 μ m in size, while the paracelsian ones were bigger colorless flat square prisms up to 1 × 1 × 0.3 mm³ in size. Further elemental analysis and structure determination reported in this paper were performed on the crystals, which crystallized for 1 day at 150°C. The oxalate anions present in the reaction mixture were probably washed out, since we could not detect any additional phases in the final product.

The electron microprobe analysis technique was carried out by using EDAX analytical system TRACOR EDX, attached to the scanning electron microscope JEOL JXA-840A. The analysis performed on three polished crystals of two phases yielded similar chemical compositions for each of the two phases. From the analysis the average Ga:Zn ratio in analcime samples was approximately 1:2 (from 1.00(6):1.86(6) to 1.00(6):2.00(6)), and in the paracelsian samples it was found to be approximately 1:1 (from 1.00(3):1.10(3) to 1.00(3):1.14(3)).

Single-crystal X-ray intensity data for both compounds (I) and (II) were collected on an Enraf Nonius CAD4 diffractometer with MoK α radiation and graphite monochromator using ω -2 θ scan mode. Unit cell parameters for the analcime analog were determined by least-square refinement on the basis of 24 reflections and are presented in Table 1. Of the possible cubic derivatives of *Ia*-3*d* space group (topological symmetry of analcime), only *I*₂₁3 proved to be consistent with the observed data according to systematic absences and agreement among equivalent reflections. Unit cell parameters for paracelsian analog were determined by least-square refinement on the basis of 72 reflections and are presented in Table 2. The chosen space group is the same as that of mineral paracelsian *P*₂₁/*a*. Lorentz, polarization, and absorption corrections were applied to the intensity data for both structures. Neutral atomic scattering factors were used for all atoms (25). The Xtal 3.4 system (26) was used for the correlation and reduction of the data, the structure refinement (minimizing the function $\sum [w(|F_o| - |F_c|)^2]$), and the interpretation in both cases. The extinction correction (27) and the calculated weighting function were applied in the refinements. ATOMS (28) program was used for the drawings of the two structures.

TABLE 1
Details for [I]: ZnGaPO-Analcime

Unit cell formula	$[\text{Zn}_{16}\text{Ga}_8\text{P}_{24}\text{O}_{96}] \cdot 16\text{NH}_4$
Formula of asymmetric unit	$(\text{NH}_4)_{2/3}\text{Zn}_{2/3}\text{Ga}_{1/3}\text{PO}_4$
Formula relative weight	173.8
Crystal size (mm)	$0.28 \times 0.28 \times 0.24$
Crystal system	Cubic
a (Å)	13.456(1)
V (Å ³)	2436.5(5)
Z	24
Space group	$I2_13$ (No. 199)
D_c (Mg m ⁻³)	2.843
T (°C)	20(1)
$\lambda(\text{MoK}_\alpha)$ (Å)	0.71069
hkl Data limits	$0 \leq h \leq 17, 0 \leq k \leq 17, 1 \leq l \leq 17$
θ_{max} (°)	28
R_{int}	0.0407
μ (MoK α) (mm ⁻¹)	6.562
Total data	3337
Unique reflections	561
Observed data ($I \geq 3\sigma(I)$)	533
Parameters	62
R (on F) (%)	2.47
R_w (on F) (%)	2.48
$\Delta\rho_{\text{max}}$ (e Å ⁻³)	0.86
$\Delta\rho_{\text{min}}$ (e Å ⁻³)	-0.73

Structure Determination of (I) Analcime Analog

The structure was solved combining the SIR97 program package (29) and Fourier maps calculation using Xtal3.4 program package. After a few cycles of isotropic refinement of framework Ga, P, O atoms and extraframework N atoms, the hydrogen atoms on N were located from the difference Fourier maps and were not refined. Isotropic temperature factors of the two nitrogen atoms were assigned to the attached H atoms. All nonhydrogen atoms were anisotropically refined. The partial occupancy of the Zn and Ga on the same framework T site was fixed according to the elemental analysis and according to the amount of the extraframework NH_4^+ cations to the values of $\frac{2}{3}$ for Zn and $\frac{1}{3}$ for Ga. Two N atoms and two of four H atoms lie on special positions with $\frac{1}{3}$ of the general positions' multiplicity and the total extra-framework species charge in an asymmetric unit is $+\frac{2}{3}$. When Zn isomorphously substitutes $\frac{2}{3}$ of the Ga atoms in the neutral GaPO_4 framework, the charge of the framework atoms in the asymmetric unit is $-\frac{2}{3}$. Final atomic parameters of the $(\text{NH}_4)_{16}[\text{Zn}_{16}\text{Ga}_8\text{P}_{24}\text{O}_{96}]$ analcime-like structure are listed in Table 3 and selected bond and contact distances are given in Table 4. Further details of crystal structure investigation are available from the authors.

Structure determination of (II) Paracelsian Analog

The refinement was initiated by using the known coordinates of the framework atoms of the $\text{SrGa}_2\text{Ge}_2\text{O}_8$ structure

(20) assuming P on the site of Ge. After a few cycles of isotropic refinement, the position of extraframework N atom was determined. Four hydrogen atoms bonded to the N atoms and forming NH_4^+ cation were located from the difference Fourier map. Their positions and isotropic displacement parameters were refined. There were two crystallographic sites where Ga and Zn could be located. Elemental analysis by EDAX showed that the Zn/Ga ratio was approximately 1:1. The examination of bond and contact distances showed no tendency of the NH_4^+ cation to be attracted to one of the two sites only (the framework site of the Zn incorporation should be negative). Additionally, there was no other evidence for the ordering of Zn and Ga on each of the two sites; e.g., bond distances as well as temperature factors were similar on both sites if only Ga was included in the model. Finally, we refined the population of Zn and Ga on both T sites with a constraint that the total population of Zn on both sites is one, and the population of Ga on both sites is one as well. Regardless of the starting populations of Ga(1) before refinement (95%, 50%, 5%) the final population of Ga(1) was 53(6)%. The partial occupancies of Zn(1), Ga(2), and Zn(2) were calculated according to the above-mentioned constraints and were 0.47(6), 0.47(6), and 0.53(6). All nonhydrogen atoms were refined by anisotropic full-matrix least squares. The final atomic parameters and occupancies are collected in Table 5,

TABLE 2
Experimental Details for [II]: ZnGaPO-Paracelsian

Unit cell formula	$[\text{Zn}_4\text{Ga}_4\text{P}_8\text{O}_{32}] \cdot 4\text{NH}_4$
Formula of asymmetric unit	$(\text{NH}_4)\text{ZnGaP}_2\text{O}_8$
Formula weight	343.1
Crystal size (mm)	$0.25 \times 0.39 \times 0.49$
Crystal system	Monoclinic
a (Å)	9.406(1)
b (Å)	9.881(1)
c (Å)	8.612(1)
β (°)	90.58(1)
V (Å ³)	800.4(2)
Z	4
Space group	$P2_1/a$ (No. 14)
D_c (Mg m ⁻³)	2.847
T (°C)	20(1)
$\lambda(\text{MoK}_\alpha)$ (Å)	0.71069
hkl Data limits	$-12 \leq h \leq 12, 0 \leq k \leq 13, -11 \leq l \leq 11$
θ_{max} (°)	28
R_{int}	0.0357
μ (MoK α) (mm ⁻¹)	6.78
Total data	7757
Unique reflections	1922
Observed data ($I \geq 3\sigma(I)$)	1792
Parameters	136
R (on F)	2.7
R_w (on F)	3.0
$\Delta\rho_{\text{max}}$ (e Å ⁻³)	1.24 (0.7832(3) Å from Zn1/Ga1)
$\Delta\rho_{\text{min}}$ (e Å ⁻³)	-1.08 (0.8884(4) Å from Zn1/Ga1)

TABLE 3

Fractional Atomic Coordinates and Isotropic Displacement Parameters for Hydrogen or Equivalent Isotropic Displacement Parameters for Non-hydrogen Atoms (\AA^2) for [I] ZnGaPOAnalcime $U_{\text{eq}} = (\frac{1}{3}) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}/U_{\text{eq}}$
Zn/Ga	0.42149(5)	0.62197(5)	0.84935(5)	0.0140(3) ^a
P	0.3680(1)	0.8301(1)	0.9055(1)	0.0140(7)
O(1)	0.3792(3)	0.7332(3)	0.9419(3)	0.020(2)
O(2)	0.5575(3)	0.6475(3)	0.8215(3)	0.019(2)
O(3)	0.3417(4)	0.6372(4)	0.8215(3)	0.031(2)
O(4)	0.4026(4)	0.4895(4)	0.8905(4)	0.031(3)
N(1)	0.3576(5)	0.3576(5)	0.3576(5)	0.0250(8)
N(2)	0.6234(4)	0.6234(4)	0.6234(4)	0.032(1)
H(11)	0.3410	0.4405	0.3707	0.029
H(12)	0.3167	0.3167	0.3167	0.029
H(21)	0.5886	0.6420	0.7008	0.029
H(22)	0.5779	0.5779	0.5779	0.029

^a Partial occupancy: Zn/Ga = 0.667/0.333.

and selected bond and contact distances in Table 6. Further details of crystal structure investigation are available from the authors.

RESULTS AND DISCUSSION

(I) Analcime Analog

The refinement of the structure revealed a stable and well-defined open framework structure analogous to some known analcime-like structures (Table 3; Figs. 1 and 2). The average Ga(Zn)–O distance, 1.90(2) Å, is within the interval of the distances found in analogous structures (from 1.816(9) Å for an average tetrahedral Ga–O bond in $\text{Ga}_3\text{P}_3\text{O}_{12}(\text{OH}) \cdot (\text{CH}_3)_2\text{NH}_2$ structure (30) to 1.95(2) Å for an average tetrahedral Zn–O bond in $\text{Na}_6[\text{Co}_{0.2}\text{Zn}_{0.8}\text{PO}_4]_6 \cdot 6\text{H}_2\text{O}$ structure (31)). Taking into account that a pure Ga–O bond is 1.816 Å long and a pure Zn–O bond 1.95 Å long, then the average bond, 1.90 Å in our structure, would correspond to 62.7% of Zn on Ga site, which is very close to our value of 66.7% (Table 3).

TABLE 4
Selected Bond and Contact Distances (Å) for [I]
ZnGaPO–Analcime

Zn/Ga–O(1)	1.923(4)	P(1)–O(1)	1.539(4)
Zn/Ga–O(2)	1.900(4)	P(1)–O(2)	1.541(4)
Zn/Ga–O(3)	1.877(5)	P(1)–O(3)	1.520(5)
Zn/Ga–O(4)	1.883(5)	P(1)–O(4)	1.524(5)
N(1) ... O(1)	2.919(8)	N(2) ... O(2)	2.827(7)
N(1) ... H(11) ... O(1)	162.4(3)	N(2) ... H(21) ... O(2)	166.2(3)
N(1) ... O(3)	3.143(8)	N(2) ... O(4)	3.343(8)
N(1) ... H(12) ... O(3)	127.4(4)	N(2) ... H(22) ... O(4)	129.8(3)

TABLE 5

Fractional Atomic Coordinates and Isotropic Displacement Parameters for Hydrogen or Equivalent Isotropic Displacement Parameters for Nonhydrogen Atoms (\AA^2) for [II] ZnGaPO–Paracelsian $U_{\text{eq}} = (\frac{1}{3}) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}/U_{\text{eq}}$
Zn(1)/Ga(1)	0.42888(3)	0.68297(3)	0.42092(4)	0.0118(1) ^a
Zn(2)/Ga(2)	0.29326(3)	0.40952(3)	0.07177(4)	0.0125(1) ^b
P(1)	0.41784(8)	0.69354(7)	0.05396(8)	0.0113(2)
P(2)	0.27541(8)	0.40125(7)	0.44178(8)	0.0119(2)
N	0.4090(4)	1.0751(4)	0.2519(4)	0.0255(9)
O(1)	0.3025(3)	0.5909(2)	0.0070(3)	0.0231(7)
O(2)	0.3105(3)	0.5451(2)	0.4942(3)	0.0243(7)
O(3)	0.3538(3)	0.8360(2)	0.0521(3)	0.0216(6)
O(4)	0.3440(3)	0.8522(2)	0.4530(3)	0.0223(7)
O(5)	0.5377(3)	0.6881(3)	– 0.0647(3)	0.0233(7)
O(6)	0.5941(3)	0.6900(3)	0.5452(3)	0.0228(7)
O(7)	0.4784(3)	0.6589(3)	0.2141(3)	0.0242(7)
O(8)	0.2205(3)	0.3977(3)	0.2745(3)	0.0261(7)
H(1)	0.50(1)	1.075(9)	0.271(9)	0.06(2)
H(2)	0.40(1)	1.01(2)	0.23(2)	0.10(4)
H(3)	0.38(1)	1.13(1)	0.32(2)	0.10(3)
H(4)	0.36(2)	1.11(2)	0.18(2)	0.14(5)

^a Partial occupancy: Zn(1)/Ga(1) = 0.47(6)/0.53(6)

^b Partial occupancy: Zn(2)/Ga(2) = 0.53(6)/0.47(6)

The extraframework NH_4^+ cations are located in a special position (*x*, *x*, *x*) in six-member rings. Similar positions in mineral analcime possess water molecules ($\frac{1}{8}$, $\frac{1}{8}$, $\frac{1}{8}$) and so these sites are labeled as W-sites in the literature. Na^+ cations in analcime occupy special positions in four-member ring channels ($\frac{1}{8}$, 0, $\frac{1}{4}$). These sites are labeled S-sites in the literature and are empty in our structure. Each of the two NH_4^+ cations in our structure forms four hydrogen bonds with framework oxygens, which stabilize the locations of cations in the pores.

The lowering of symmetry from a topological centrosymmetric *Ia-3d* to a noncentrosymmetric *I2₁3* space group in

TABLE 6
Selected Bond and Contact Distances (Å) for [II]
ZnGaPO–Paracelsian

P(1)–O(1)	1.536(3)	Zn(1)/Ga(1)–O(2)	1.873(3)
P(1)–O(3)	1.531(2)	Zn(1)/Ga(1)–O(4)	1.875(2)
P(1)–O(5)	1.530(3)	Zn(1)/Ga(1)–O(6)	1.879(2)
P(1)–O(7)	1.525(3)	Zn(1)/Ga(1)–O(7)	1.861(2)
P(2)–O(2)	1.526(3)	Zn(2)/Ga(2)–O(1)	1.879(2)
P(2)–O(8)	1.526(2)	Zn(2)/Ga(2)–O(8)	1.885(2)
P(2)–O(4)	1.529(3)	Zn(2)/Ga(2)–O(3)	1.884(2)
P(2)–O(6)	1.526(3)	Zn(2)/Ga(2)–O(5)	1.861(2)
N ... O(1)	2.977(4)	N ... O(4)	2.872(4)
N ... O(2)	3.037(5)	N ... O(5)	2.888(5)
N ... O(3)	2.965(4)	N ... O(6)	2.906(5)
		N ... O(8)	2.946(5)

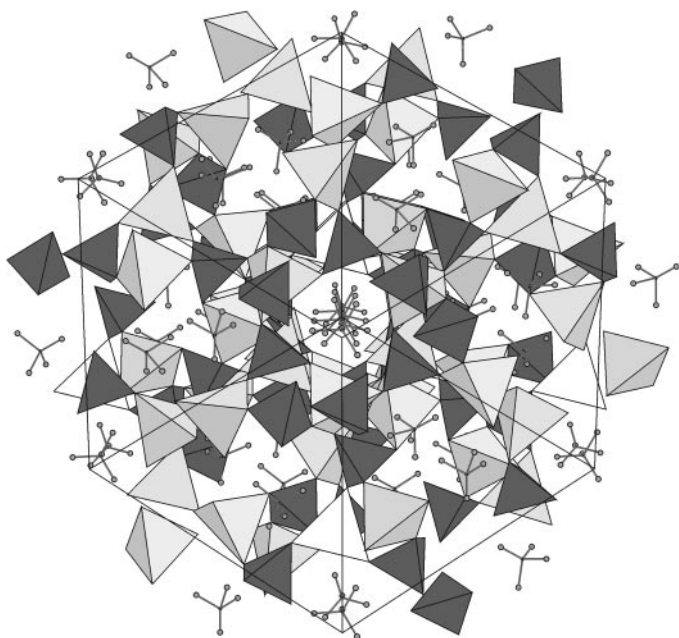


FIG. 1. Tetrahedral presentation of zinc gallophosphate analcime-like structure $(\text{NH}_4)_{16}[\text{Zn}_{16}\text{Ga}_8\text{P}_{24}\text{O}_{96}]$ in $[111]$ direction shows alternating PO_4 (dark gray) and $\text{Ga}(\text{Zn})\text{O}_4$ (bright) tetrahedra in the framework and NH_4^+ cations lying on three-fold axes.

our structure is due to the ordering of $\text{Ga}(\text{Zn})$ and P atoms in the framework over two crystallographically different sites and electrostatic energy of interactions between the framework and NH_4^+ cations.

The splitting of one analcime framework T site ($T = \text{Si}$ or Al) into two or more crystallographically different T sites

was already reported for the aluminosilicophosphate analcime analog (one Al and one $\text{P}(\text{Si})$ site and $I4_132$ structure symmetry) (14) as well as for some other natural analcimes (13). More complex is symmetry lowering due to the framework- NH_4^+ interactions. Hydrogen bonding of NH_4^+ cations with framework oxygens distorts the four-member rings in the framework and displaces the oxygen atoms in the ring from the ideal positions, which are found in analcime (Fig. 2). A similar distortion of four-member rings was reported for at least four analcime analogs. Three of them (gallogermanates $(\text{NH}_4)_{16}[\text{Ga}_{16}\text{Ge}_{32}\text{O}_{96}]$ and $\text{Cs}_{16}[\text{Ga}_{16}\text{Ge}_{32}\text{O}_{96}]$ (11) and rubidium zinc germanate $\text{Rb}_{16}[\text{Zn}_8\text{Ge}_{40}\text{O}_{96}]$ (32)) crystallize in the $I-43d$ space group (one framework T atom) and have all extraframework cations located on structure W -site, while the S -sites in four-member rings are empty. The fourth compound is a mineral hsianghualite $\text{Li}_{16}\text{Ca}_{24}[\text{Be}_{24}\text{Si}_{24}\text{O}_{96}] \cdot 16\text{F}$ (33), which crystallizes in the $I2_13$ space group and where Ca^{2+} cations occupy all the S -sites and F^- all the W -sites. Each Li^+ atom coordinates one F and three framework oxygen atoms. All of the above four compounds have nonstandard distributions and chemical compositions of extraframework cations or molecules, compared to Na^+ and H_2O ordering in analcime. In a recent study of an anhydrous tetragonal NH_4^+ -analcime $(\text{NH}_4)_{15.04}[\text{Al}_{15.04}\text{Si}_{33.6}\text{O}_{96}]$, $I4_1/a$, $a = 13.218(4) \text{ \AA}$, $c = 13.710(6) \text{ \AA}$ (34), it was suggested that the low symmetry is due to the absence of strong and medium $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds between NH_4^+ and framework O sites, which allows orientational disorder of ammonium ions in the structure and displacement of cations from the W -position ($\text{N} \cdots \text{O}$ distances of six neighboring O atoms vary from 3.04 to 3.17 \AA). The energy of

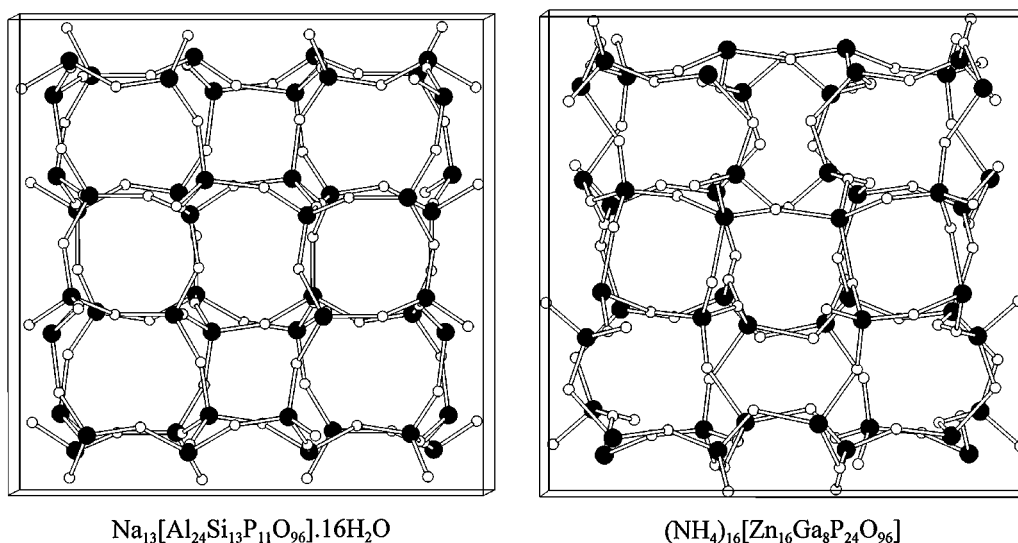


FIG. 2. Schematic presentation of framework distortion of the $(\text{NH}_4)_{16}[\text{Zn}_{16}\text{Ga}_8\text{P}_{24}\text{O}_{96}]$ analcime-like structure compared to analcime (2).

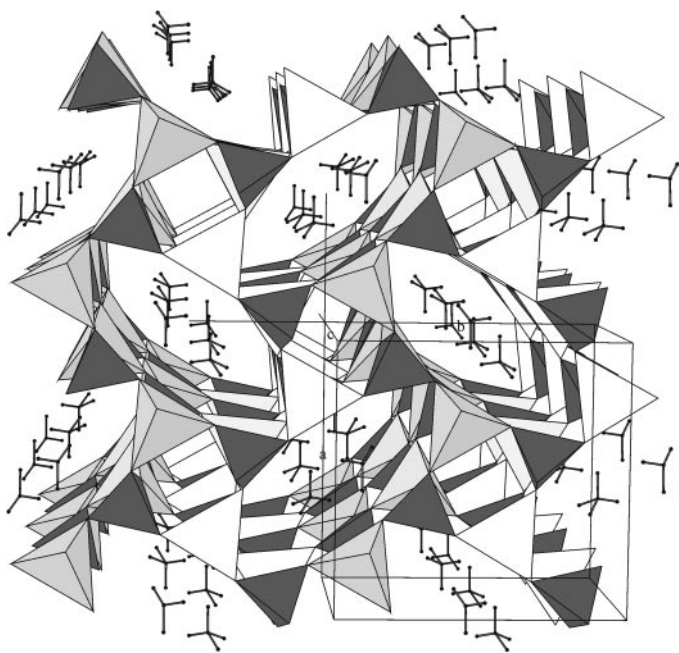


FIG. 3. Tetrahedral presentation of zinc gallophosphate paracelsian analog $(\text{NH}_4)_4[\text{Zn}_4\text{Ga}_4\text{P}_8\text{O}_{32}]$ in $[100]$ direction shows alternating PO_4 (dark gray) and $\text{Ga}(\text{Zn})\text{O}_4$ (bright) tetrahedra in the framework and extraframework NH_4^+ cations, which compensate for the negatively charged framework.

displacement was assumed to be comparable with the energy of the compound phase transition to cubic modification.

(II) Paracelsian Analog

The three-dimensional framework is built from alternating PO_4 and $\text{Ga}(\text{Zn})\text{O}_4$ tetrahedra (Fig. 3). The average $\text{Ga}(\text{Zn})\text{-O}$ bond distances are 1.872(8) Å for $\text{Ga}(1)(\text{Zn}(1))$ site and 1.88(1) Å for $\text{Ga}(2)(\text{Zn}(2))$ site, which shows that Zn replaces Ga in both Ga sites by around 50% (assuming that the lengths of pure Ga-O and Zn-O bonds are 1.816 and 1.95 Å (30, 31)). The refined population values for Ga/Zn are shown in Table 5.

The extraframework NH_4^+ cations are located in the elliptical eight-member ring channels. There are seven different contacts of N atom and framework oxygen atoms found, which could all be assigned as H-bonds. Table 6 shows the $\text{N}\cdots\text{O}$ distances for all different O atoms except for $\text{N}\cdots\text{O}(7)$, which is 4.177(5) Å. A similar seven-fold cation coordination was found for strontium and barium in $\text{SrGa}_2\text{Ge}_2\text{O}_8$ and $\text{BaGa}_2\text{Ge}_2\text{O}_8$ structures (20). Mean Sr-O and mean Ba-O distances were 2.625(2) and 2.765(3) Å, respectively.

The compound crystallises in the $P2_1/a$ space group like the mineral paracelsian and the majority of its known ana-

logs; it enables the ordering of $\text{Ga}(\text{Zn})$ and P tetrahedra in the framework.

CONCLUSIONS

The structure study of analcime-like ammonium zinc gallophosphate and their structure analogs enabled us to conclude that the analcime-like structure symmetry is a complex function of nature and ordering of framework as well as extraframework atoms. The ordering of framework tetrahedra (SiO_4 and AlO_4 or GaO_4 , PO_4 , ZnO_4 , etc.) defines the distribution and nature or energy of extraframework cation sites. At the same time, the size and kind of extraframework cations (Na^+ , Ca^{2+} , NH_4^+ , Cs^+ , etc.) affect the strength of framework–extraframework interactions (e.g., hydrogen bonds). The structure study of the paracelsian-like ammonium zinc gallophosphate showed that the extra framework cations' exchange (NH_4^+ instead of Ba^{2+}) does not affect the structure in such a way, and that the structure is completely isostructural with the mineral paracelsian.

Due to the high amount of incorporated Zn^{2+} on Ga^{3+} sites in both structures the concentration of negative charge in the framework is very high and the compounds have a potential for high ion-exchange capacity. The high concentration of Zn in the gallophosphate framework is probably due to similar Ga^{3+} and Zn^{2+} ionic radii and also to a similar ionic character of Ga-O and Zn-O bonds.

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