

Article

The Crystal Structure of Sergeysmirnovite, $\text{MgZn}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, and Complexity of the Hopeite Group and Related Structures

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Abstract: The crystal structure of sergeysmirnovite, $\text{MgZn}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ (orthorhombic, *Pnma*, $a = 10.6286(4)$, $b = 18.3700(6)$, $c = 5.02060(15)$ Å, $V = 980.26(6)$ Å³, $Z = 4$), a new member of the hopeite group of minerals, was determined and refined to $R_1 = 0.030$ using crystals from the Këster mineral deposit in Sakha-Yakutia, Russia. Similar to other members of the hopeite group, the crystal structure of sergeysmirnovite is based upon $[\text{Zn}(\text{PO}_4)]^-$ layers interlinked via interstitial $[\text{MO}_2(\text{H}_2\text{O})_4]^{2-}$ octahedra, where $M = \text{Mg}^{2+}$. The layers are parallel to the (010) plane. Within the layer, the ZnO_4 tetrahedra share common corners to form chains running along [001]. Sergeysmirnovite is a dimorph of reaphookhillite, a mineral from the Reaphook Hill zinc deposit in South Australia. The relations between sergeysmirnovite and reaphookhillite are the same as those between hopeite and parahopeite. Topological and structural complexity analysis using information theory shows that the hopeite (sergeysmirnovite) structure type is more complex, both structurally and topologically, than the parahopeite (reaphookhillite) structure type. Such complexity relations contradict the general observation that more complex polymorphs possess higher physical density and higher stability, since parahopeite is denser than hopeite. It could be hypothesized that hopeite is metastable under ambient conditions and separated from parahopeite by a structural and topological reconstruction that requires an essential energy barrier that is difficult to overcome.

Keywords: sergeysmirnovite; hopeite group; crystal structure; polymorphism; structural complexity; mineralogical crystallography



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1. Introduction

Hopeite, $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, and related compounds have attracted considerable attention as important constituents of steel coatings [1–8] and dental cements [9,10]. Along with carbonate-hydroxylapatite and parascholzite, hopeite had been found in fibrous capsules surrounding silicone breast implants [11] and is of interest from the viewpoint of biomedical applications [12,13]. Hopeite was first discovered as a mineral by René Just Haüy, who identified it as a variety of stilbite, a zeolite-group mineral. Re-investigation by Brewster [14] indicated that the mineral was in fact zinc phosphate or borate with an “earthly base and little cadmium” [14]. The mineral was named in honor of Thomas Charles Hope (1766–1844), Professor of Chemistry at the University of Edinburgh and the discoverer of the chemical element, strontium. The correct chemical formula, $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, was established by Damour [15], and Friedel and Sarasin [16]. The first crystal-structure study of hopeite was attempted by Mamedov et al. in 1961 [17], but their structural model was incorrect, which was demonstrated several years later by Gamidov et al. [18] and Liebau [19]. Since then, the crystal structure, chemical composition and properties of hopeite have been the subject of numerous studies [20–28]. In 1908, Spenser [29] found out that there are two varieties of hopeite, α - and β -, which were slightly different in their solubilities, but it was

not until 2004 that Herschke et al. [30] demonstrated that the difference between the two forms lies in the different systems of hydrogen bonding in their crystal structures. Spenser also discovered the existence of another polymorph of $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ with completely distinct crystallographic parameters, which he called parahopeite. The determination of the crystal structure of parahopeite [31,32] demonstrated that, in contrast to orthorhombic hopeite, it has a triclinic symmetry and the structure topology is different to that of hopeite. However, an important and interesting feature of both hopeite and parahopeite is that Zn^{2+} ions occur in their structures in both tetrahedral and octahedral coordination. In addition, both crystal structures are based upon two-dimensional layers consisting of ZnO_4 and PO_4 tetrahedra, interlinked into a three-dimensional framework by ZnO_6 octahedra.

In the past twenty years, several new minerals have been described that belong to either hopeite or parahopeite structure types [33–36], but in which either octahedral Zn^{2+} ions are replaced by other di- or trivalent cations (Fe^{2+} , Fe^{3+} , Mg^{2+} , Mn^{2+}), or phosphate ions are replaced by arsenate ions. The relevant crystallographic information on these minerals is provided in Table 1. We note that there also mineral species that do not belong to the hopeite or parahopeite structure types, but nevertheless are based upon tetrahedral layers with the same topology as those that occur in the two $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ polymorphs (see Table 1 for details).

Recently, when studying the mineralogy of the K ster deposit in Yakutia (the location of k sterite, $\text{Cu}_2\text{ZnSnS}_4$ [37], which is known for the application of its synthetic analogues in solar-cell technologies [38]), we found a suite of new natural phosphates, including epifanovite, $\text{NaCaCu}_5(\text{PO}_4)_4[\text{AsO}_2(\text{OH})_2] \cdot 7\text{H}_2\text{O}$ [39,40], and batagayite, $\text{CaZn}_2(\text{Zn,Cu})_6(\text{PO}_4)_4(\text{PO}_3\text{OH})_3 \cdot 12\text{H}_2\text{O}$ [41]. In close association with these minerals, we discovered another new mineral species, sergeysmirnovite [42], which appears to be a Mg analogue of hopeite, with octahedral Zn^{2+} ions replaced by Mg^{2+} ions. In this paper, we report on the crystal structure of sergeysmirnovite and provide an overview of the hopeite-group minerals. We also analyze the structural and topological complexity [43–47] of this interesting and important group, in an attempt to hypothesize on their relative stability and natural and technological occurrence.

Table 1. Crystallographic data for minerals belonging to the hopeite and parahopeite structure types and minerals with related structures.

Mineral Name	Chemical Formula	Space Group	<i>a</i> [�]/ <i>a</i> [�]	<i>b</i> [�]/ <i>b</i> [�]	<i>c</i> [�]/ <i>c</i> [�]	<i>V</i> [� ³]	Ref.
Hopeite structure type							
Hopeite	$\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$	<i>Pnma</i>	10.597/90	18.318/90	5.031/90	976.6	[28]
Nizamoffite	$\text{Mn}^{2+}\text{Zn}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$	<i>Pnma</i>	10.653/90	18.478/90	5.058/90	995.7	[33]
Sergeysmirnovite	$\text{MgZn}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$	<i>Pnma</i>	10.629/90	18.370/90	5.021/90	980.3	this work
Arsenohopeite	$\text{Zn}_3(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$	<i>Pnma</i>	10.804/90	19.003/90	5.112/90	1049.5	[34]
Parahopeite structure type							
Parahopeite	$\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$	<i>P</i> $\bar{1}$	5.768/93.42	7.550/91.18	5.276/91.37	228.3	[32]
Reaphookhillite	$\text{MgZn}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$	<i>P</i> $\bar{1}$	5.759/93.44	7.534/91.27	5.279/91.30	228.5	[35]
Davidlloydite	$\text{Zn}_3(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$	<i>P</i> $\bar{1}$	5.976/84.29	7.600/90.49	5.447/88.00	246.0	[36]
Related structures							
Phosphophyllite	$\text{Fe}^{2+}\text{Zn}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$	<i>P2</i> ₁ / <i>c</i>	10.378/90	5.084/121.14	10.553/90	476.6	[48]
Steinmetzite	$\text{Fe}^{3+}\text{Zn}_2(\text{PO}_4)_2(\text{OH}) \cdot 3\text{H}_2\text{O}$	<i>P</i> $\bar{1}$	10.438/91.37	5.102/115.93	10.546/94.20	502.7	[49]
Stergiouite	$\text{CaZn}_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$	<i>Pc</i>	9.416/90	5.300/91.77	10.893/90	543.4	[50]

2. Materials and Methods

2.1. Sample Description

Sergeysmirnovite was found as colorless tabular crystals flattened on {010} and elongated along [001] with striations. The crystals are up to 2 mm long and possess pinacoidal

faces with the predominant form {001} (Figure 1). The empirical chemical formula was determined by electron microprobe (WDS mode) as $(\text{Zn}_{2.21}\text{Mg}_{0.83})\Sigma_{3.04}\text{P}_{1.96}\text{O}_{7.94}\cdot 4.01\text{H}_2\text{O}$ [42].

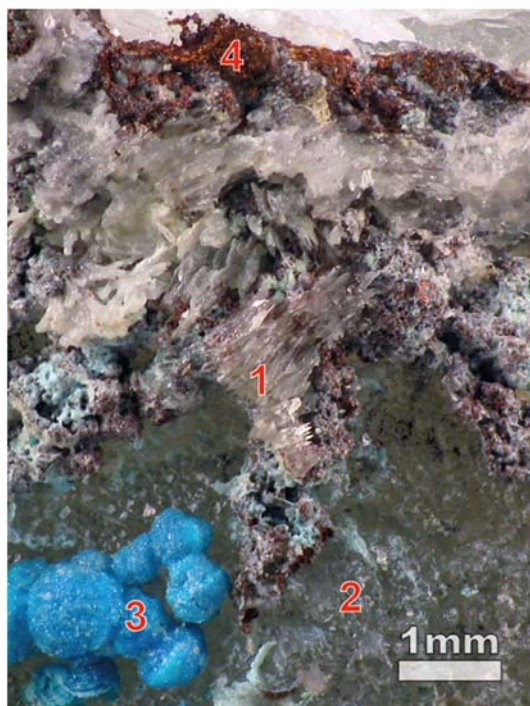


Figure 1. Aggregates of colorless prismatic crystals of sergeysmirnovite (1) growing on fluorapatite (2) together with epifanovite (3) and metallic copper (4).

2.2. Single-Crystal X-ray Diffraction

Single-crystal X-ray diffraction study was performed using an Oxford Diffraction Xcalibur Eos diffractometer equipped with a CCD area detector. The data were integrated and corrected by means of the CrysAlisPro [51] program package, which was also used to apply an empirical absorption correction using spherical harmonics, as implemented in the SCALE3 ABSPACK scaling algorithm. The SHELXL program [52] was used for the crystal-structure refinement. The structure of smirnovite was determined by direct methods and refined to $R_1 = 0.030$ for 1435 ($R_{\text{int}} = 0.025$, $R_{\text{sigma}} = 0.026$) independent reflections with $F_o > 4\sigma(F_o)$. The hydrogen atoms were located using a difference Fourier map. Initially, the H atoms were placed into positions extracted from the difference Fourier syntheses and were included into the refinement in the ‘riding’ model approximation, with $U_{\text{iso}}(\text{H})$ set to $1.5U_{\text{iso}}(\text{O})$ and the restrained O–H distances of 0.96 Å with sigma of 0.02 Å. During the refinement, additional peaks of $\sim 1e^-$ occurred near the O5 and O6 sites, indicating H disorder. The H_2O_5 and H_2O_6 groups have been refined as disordered configurations split over two orientations with the O5–H, O6–H distances restrained as 1.02 Å with sigma of 0.07 Å. Crystal data, data collection information and structure refinement details are shown in Table 2, and atom coordinates and selected interatomic distances are presented in Tables 3 and 4, respectively. Parameters of the hydrogen-bonding system are shown in Table 5.

Table 2. Crystal data and structure refinement for sergeysmirnovite.

Temperature/K	293(2)
Crystal system	orthorhombic
Space group	<i>Pnma</i>
<i>a</i> /Å	10.6286(4)
<i>b</i> /Å	18.3700(6)
<i>c</i> /Å	5.02060(15)
Volume/Å ³	980.26(6)
Z	4
<i>D</i> _{calc} , g/cm ³	2.933
μ /mm ^{−1}	6.130
F(000)	856.0
Crystal size/mm ³	0.23 × 0.14 × 0.12
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	7.668 to 61.952
Index ranges	$-8 \leq h \leq 15, -22 \leq k \leq 24, -7 \leq l \leq 6$
Reflections collected	4164
Independent reflections	1435 [R_{int} = 0.0251, R_{sigma} = 0.0261]
Data/restraints/parameters	1435/3/85
Goodness-of-fit on F^2	1.162
Final <i>R</i> indices [$I \geq 2\sigma(I)$]	$R_1 = 0.0304, wR_2 = 0.0831$
Final <i>R</i> indices [all data]	$R_1 = 0.0359, wR_2 = 0.0861$
Largest diff. peak/hole/ $e \text{ Å}^{-3}$	0.73/−0.80

Table 3. Atomic coordinates, site-occupancy factors (s.o.f.s) and equivalent isotropic displacement parameters (10^{-4} Å^2) for sergeysmirnovite.

Site	s.o.f.	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{iso}
Zn	Zn	0.85696(3)	−0.00084(2)	0.29290(7)	0.00857(13)
Mg	Mg _{0.66} Zn _{0.34}	0.76076(7)	$\frac{1}{4}$	0.92640(16)	0.0089(3)
P	P	0.89752(7)	0.09434(4)	0.77589(14)	0.00931(17)
O1	O	0.8600(2)	0.1727(1)	0.7173(4)	0.0153(5)
O2	O	0.0254(2)	0.0784(1)	0.6446(5)	0.0162(4)
O3	O	0.8999(3)	0.0800(1)	0.0749(4)	0.0256(6)
O4	O	0.69790(19)	−0.0398(1)	0.1428(4)	0.0110(4)
O _w 5	O	0.8906(3)	$\frac{1}{4}$	0.2437(6)	0.0119(6)
O _w 6	O	0.6138(3)	$\frac{1}{4}$	0.6449(6)	0.0141(6)
O _w 7	O	0.6635(2)	0.3307(1)	0.1582(5)	0.0157(4)
H5A	H _{0.50}	0.890421	0.293569	0.371961	0.021 *
H5B	H _{0.50}	0.974113	0.250002	0.110938	0.021 *
H6A	H _{0.50}	0.526323	0.233849	0.713066	0.021 *
H6B	H _{0.50}	0.610751	0.292141	0.539091	0.021 *
H7A	H	0.616338	0.312024	0.308925	0.024 *
H7B	H	0.601176	0.358934	0.065064	0.024 *

* fixed to be equal during refinement.

Table 4. Selected interatomic distances (Å) and bond angles (°) for the crystal structure of sergeysmirnovite.

Zn–O4	1.984(2)	Mg–O _w 7	2.149(2) 2×	P–O4	1.575(2)
Zn–O4	1.995(2)	Mg–O1	2.058(2) 2×	P–O3	1.524(2)
Zn–O3	1.901(2)	Mg–O _w 5	2.108(3)	P–O2	1.539(2)
Zn–O2	1.921(2)	Mg–O _w 6	2.107(3)	P–O1	1.521(2)
<Zn–O>	1.950	<Mg–O>	2.104	<P–O>	1.540
O4–Zn–O4	102.70(6)	O _w 7–Mg–O _w 7	87.2(1) 2×	O3–P–O4	108.5(1)
O4–Zn–O3	105.45(10)	O _w 7–Mg–O1	92.7(1) 2×	O3–P–O2	112.0(1)
O4–Zn–O3	106.59(9)	O _w 7–Mg–O1	177.4(1) 2×	O2–P–O4	105.4(1)
O4–Zn–O2	121.18(11)	O1–Mg–O1	87.3(1)	O1–P–O4	110.6(1)
O4–Zn–O2	110.46(9)	O1–Mg–O _w 6	92.2(1) 2×	O1–P–O3	110.9(1)
O3–Zn–O2	108.87(9)	O1–Mg–O _w 5	92.9(1)	O1–P–O2	109.2(1)
<O–Zn–O>	109.2	O _w 5–Mg–O _w 7	84.5(1) 2×	<O–P–O>	109.4
		O _w 6–Mg–O _w 7	90.4(1) 2×		
		O _w 5–Mg–O _w 6	173.0(1)		

Table 5. Donor(D)–acceptor(A) anion distances (Å) and angles (°) for the hydrogen bonding system in the crystal structure of sergeysmirnovite.

D	H	A	$d(\text{D-H})/\text{\AA}$	$d(\text{H-A})/\text{\AA}$	$d(\text{D-A})/\text{\AA}$	$\text{D-H-A}/^\circ$
O _w 7	H7A	O _w 6	0.97	2.04	2.906(3)	148.3
O _w 7	H7B	O2	0.96	1.76	2.695(3)	163.8
O _w 6	H6A	O1	1.03	2.12	3.126(4)	162.7
O _w 6	H6A	O1	1.03	2.49	3.126(4)	119.1
O _w 6	H6B	O _w 7	0.94	2.11	2.906(3)	141.1
O _w 5	H5A	O1	1.03	1.87	2.789(3)	147.2

2.3. Complexity Calculations

The calculation of structural and topological complexity parameters was done using the methodology formulated previously in [39–43]. Within this approach, which was also developed and implemented in [53–57], complexity is quantitatively estimated as the amounts of Shannon information per atom ($^{\text{str}}I_G$) and per unit cell ($^{\text{str}}I_{G,\text{total}}$) calculated by means of the following equations:

$$^{\text{str}}I_G = \sum_{i=1}^k p_i \log_2 p_i \quad (\text{bit/atom}) \quad (1)$$

$$^{\text{str}}I_{G,\text{total}} = -v \sum_{i=1}^k p_i \log_2 p_i \quad (\text{bit/cell}) \quad (2)$$

where k is the number of different crystallographic orbits (crystallographic Wyckoff sites) in the crystal structure and

$$p_i = m_i/v \quad (3)$$

where m_i is a multiplicity of a crystallographic orbit (i.e., the number of atoms of a specific Wyckoff site in the reduced unit cell), and v is the total number of atoms in the reduced unit cell. The calculation of the structural complexity parameters was done by means of the TOPOSPro software [58].

3. Results

3.1. Structure Description

Similar to other members of the hopeite group, the crystal structure of sergeysmirnovite is based upon $[\text{Zn}(\text{PO}_4)]^-$ layers interlinked via interstitial $[\text{MO}_2(\text{H}_2\text{O})_4]^{2-}$ octahedra, where $M = \text{Mg}^{2+}$ (Figure 2). The layers are parallel to the (010) plane. The projection of the tetrahedral layer along the b axis is shown in Figure 3a. Within the layer, the ZnO_4 tetrahedra share common corners to form chains running along [001]. The PO_4 tetrahedra share all four of their corners with the adjacent ZnO_4 tetrahedra. The O2 and O3 atoms are shared between one ZnO_4 and one PO_4 tetrahedra, whereas the O4 atom is shared between two ZnO_4 and one PO_4 tetrahedra. The O1 atom is pointing out toward the interlayer space and is linked to Mg^{2+} cation. As a consequence, the P–O4 bond is longer (1.575 Å) than other P–O bonds (1.521–1.539 Å) in the structure. The same is also observed for ZnO_4 tetrahedra. The Zn–O4 bonds are longer (1.984–1.995 Å) than other Zn–O bonds (1.901–1.921 Å). The values of the bond angles reported in Table 4 indicate that the ZnO_4 tetrahedra are more strongly distorted than the PO_4 tetrahedra. The deviations of the O–Zn–O angles from the ideal tetrahedral value (ca. 109.4°) go up to 11.8° (for the O4–Zn–O2 angle), whereas the similar value for phosphate groups does not exceed 4.0° (for the O2–P–O4 angle). Therefore, the PO_4 tetrahedra are much more rigid than the ZnO_4 tetrahedra, which could be expected, taking into account differences in the charge and size between Zn^{2+} and P^{5+} cations.

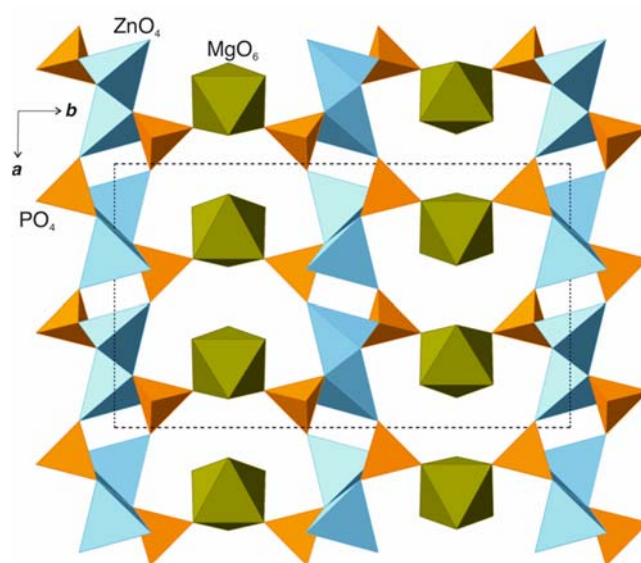


Figure 2. The crystal structure of sergeysmirnovite in projection along the c axis. Legend: ZnO_4 tetrahedra = light-blue, PO_4 tetrahedra = orange, MgO_6 octahedra = dark-green. Hydrogen atoms are omitted for clarity.

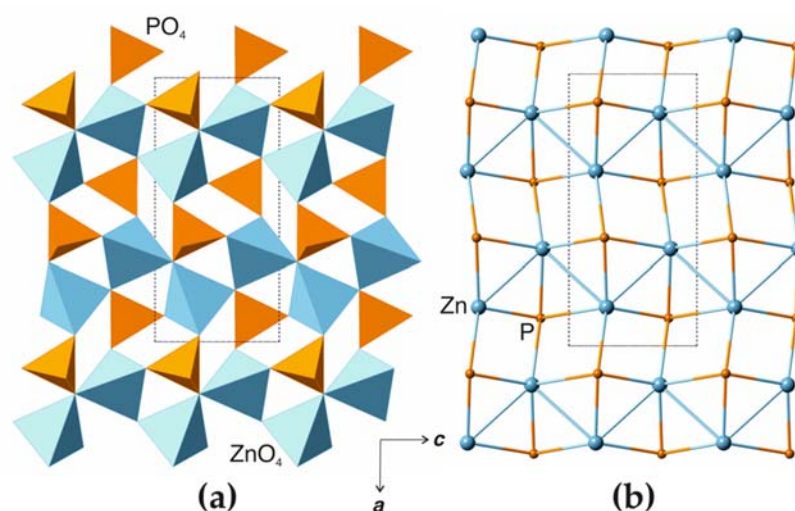


Figure 3. Projection of the $[\text{Zn}(\text{PO}_4)]^-$ layer in the crystal structure of sergeysmirnovite along the b axis (a) and the graph showing the topology of interpolyhedral linkage (b). Legend as in Figure 2.

The topology of the interpolyhedral linkage can be described by using nodal (graph) representation, where each node symbolizes the respective polyhedron, whereas the edge between the two nodes indicates that corresponding polyhedron share common O atoms [59]. Figure 3b shows a bi-colored graph that shows the topology of the tetrahedral layer in sergeysmirnovite. It is obvious that the basis of the topology is a simple square net [41] consisting of four-membered rings formed by Zn and P nodes. However, each second ring contains a diagonal Zn-Zn edge, symbolizing the linkage of two adjacent ZnO_4 tetrahedra through common O atom.

The tetrahedral layers are interlinked by $[\text{MgO}_2(\text{H}_2\text{O})_4]^{2-}$ octahedra. Within each octahedron, two Mg-O bonds that are responsible for the interlayer linkage are oriented in a *cis*-arrangement, in contrast to parahopeite-type structures, where similar M-O bonds are in a *trans*-configuration (see below).

3.2. Hydrogen Bonding

The hydrogen bonding in sergeysmirnovite, as in other hopeite-type structures, occurs in the interlayer space and involves four H₂O groups linked to one Mg²⁺ cation (Figure 4). It is rather complicated, also due to the observed disorder in the positions of H atoms. It should be noted that the disordered hydrogen bonding was also observed in nizamoffite, Mn²⁺Zn₂(PO₄)₂·4H₂O, a Mn²⁺ analogue of sergeysmirnovite. As mentioned in the Introduction, in both natural and synthetic hopeites, two modifications, α - and β -, have been described, which have different hydrogen bonding schemes. It is very likely that the H disorder found in sergeysmirnovite and reported for nizamoffite represents an average configuration corresponding to the α - and β -types of hydrogen bonding schemes similar to those described for hopeite. The scheme shown in Figure 4 corresponds to one of the possible ordered arrangements, where alternative positions are omitted for clarity.

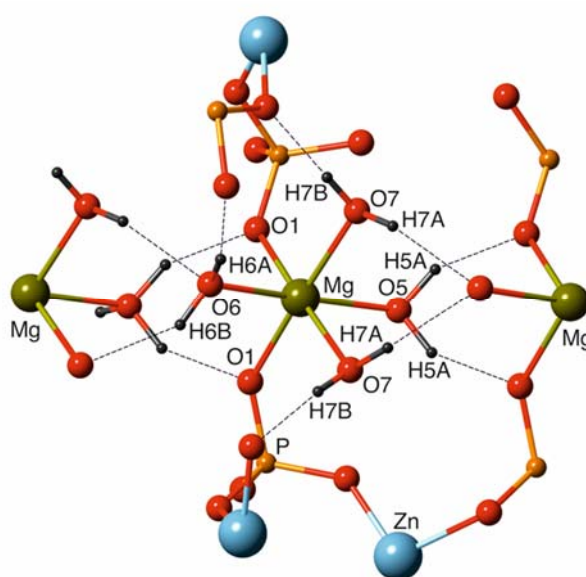


Figure 4. One of the possible ordered arrangements of hydrogen atoms in sergeysmirnovite. Legend: Zn atoms = light-blue; P atoms = orange; O atoms = red; H atoms = black; Mg atoms = dark-green.

4. Discussion

4.1. Comparison to Related Structures

Sergeysmirnovite is isotypic (except for the H positions) to hopeite, nizamoffite, and arsenohopeite. All three minerals are orthorhombic, *Pnma*, and share the same structural architecture. Tetrahedral layers of the same topology (Figure 3) have also been observed in phosphophyllite, Fe²⁺Zn₂(PO₄)₂·4H₂O, steinmetzite, Fe³⁺Zn₂(PO₄)₂(OH)·3H₂O, stergiouite, CaZn₂(AsO₄)₂·4H₂O. However, these three minerals possess lower symmetries (Table 1) compared to hopeite, and in contrast to the latter, have one tetrahedral layer per unit cell. In addition, the interlayer [MO₂(H₂O,OH)₄]^{n−} octahedra (*M* = Fe²⁺, Fe³⁺, Ca²⁺) that links adjacent layers together, possess two *M*-O bonds in a *trans*-configuration.

Sergeysmirnovite is a dimorph of reaphookhillite, which has been described recently in the Reaphook Hill zinc deposit in South Australia [46]. The relationship between sergeysmirnovite and reaphookhillite is the same as that between hopeite and parahopeite. The crystal structure of the latter is shown in Figure 5. Similar to that of hopeite, it is based upon tetrahedral layers interlinked by [MO₂(H₂O,OH)₄]^{n−} octahedra, but with *M*-O bonds in a *trans*-configuration. The layers are parallel to the (010) plane and are built up by the corner-sharing of ZnO₄ and PO₄ tetrahedra (Figure 6a). The layer does not have Zn-Zn interpolyhedral links as in hopeite, and its graph (Figure 6b) is a simple [41] net with no additional edges.

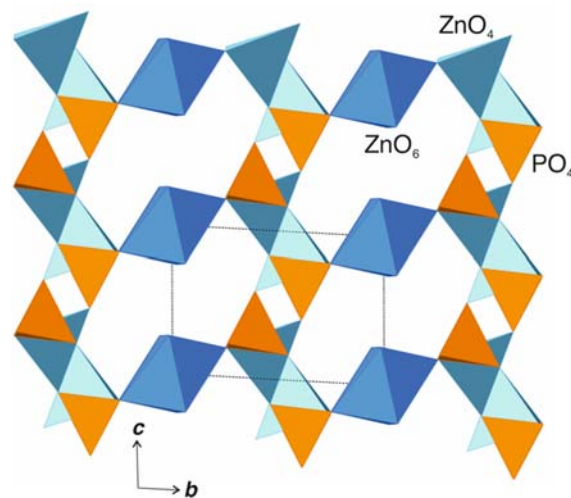


Figure 5. The crystal structure of parahopeite in projection along the a axis. Legend as in Figure 2; ZnO_6 octahedra are dark-blue.

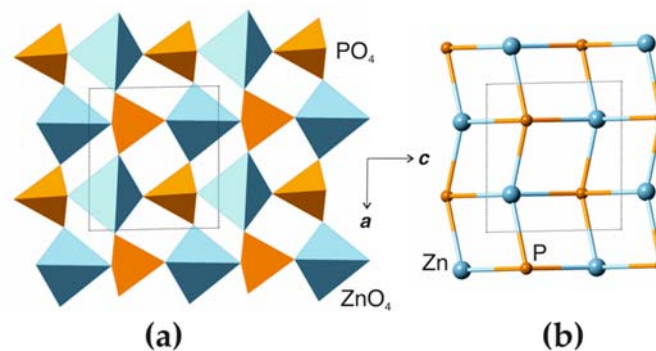


Figure 6. The tetrahedral layer in the crystal structure of parahopeite (a) and a graph showing the topology of interpolyhedral linkage (b). Legend as in Figures 2 and 3.

4.2. Complexity Analysis

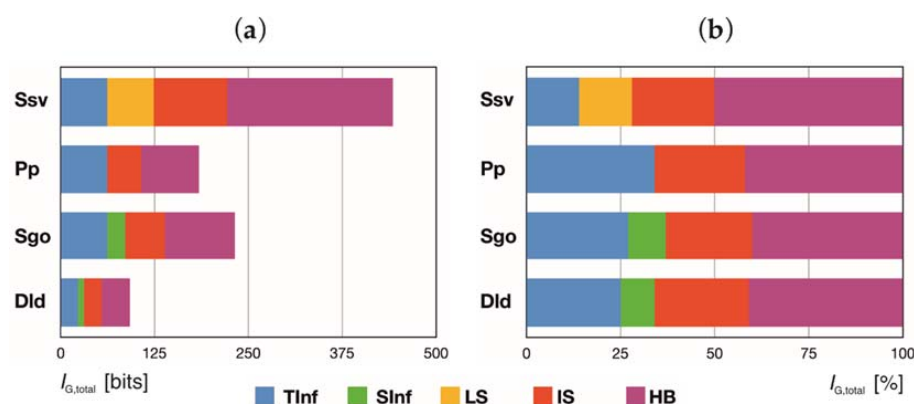
The Shannon information per unit cell for sergeysmirnovite is equal to 442.424 bits. According to the classification proposed in [40], it qualifies the crystal structure of the mineral as that of intermediate complexity (100–500 bits per cell). Selected complexity parameters for sergeysmirnovite and related minerals are presented in Table 6. The data show that the hopeite structure type (orthorhombic, with two layers per unit cell) is more complex than that of parahopeite (triclinic, with one layer per unit cell). Moreover, the topological complexity of the tetrahedral layer in hopeite is higher than that in parahopeite. The ideal layer symmetry group for the layer shown in Figure 3a is $p12_1/a1$ (no. 17) [60], which is realized in the crystal structures of hopeite, sergeysmirnovite and arsenohopeite. Its total topological information is equal to 62.039 bit/cell. The ideal symmetry of the tetrahedral layer in parahopeite and related minerals is much higher and corresponds to the layer group $pmmn$ (no. 46) [60], whereas its real symmetry does not exceed $p\bar{1}$ (no. 2). As a consequence, the real structural information of the tetrahedral layer in parahopeite is higher (31.020 bit/cell) than that the topological information (23.020 bit/cell). This means that the hopeite structure type is both structurally and topologically more complex than the parahopeite structure type.

Table 6. Crystallographic data for minerals belonging to the hopeite and parahopeite structure types and minerals with related structures.

Mineral Name	Chemical Formula	I_G [bit/atom]	$I_{G,total}$ [bit/cell]	r [g/cm ³]	Ref.
Hopeite	$Zn_3(PO_4)_2 \cdot 4H_2O$	3.844	384.386	3.096	[28]
Parahopeite	$Zn_3(PO_4)_2 \cdot 4H_2O$	3.684 *	92.096 *	3.304	[42]
Sergeysmirnovite	$MgZn_2(PO_4)_2 \cdot 4H_2O$	3.950	442.424	2.933	this work
Reaphookhillite	$MgZn_2(PO_4)_2 \cdot 4H_2O$	3.684	92.096	3.090	[43]
Arsenohopeite	$Zn_3(AsO_4)_2 \cdot 4H_2O$	3.844	384.386	3.420	[41]
Davidlloydite	$Zn_3(AsO_4)_2 \cdot 4H_2O$	3.684	92.096	3.661	[44]

* given by analogy with davidlloydite.

In order to estimate the contribution of different factors to the structural complexity of hopeite, parahopeite and related structure types, complexity analysis was performed following the procedure described in detail in [61]. The results of the analysis are presented visually in Figure 7. The following basic factors have been recognized: topological information originating from the maximal-symmetry configuration of the basic structural unit (**TInf**, in the case under consideration, this is the topological complexity of the tetrahedral layers); structural information generated by the distortions of the basic structural unit in crystal structure (**SInf**, which is equal to zero for the hopeite structure type since its real layer symmetry is identical to the ideal one, see above); layer stacking (**LS**, this parameter reflects the number of layers within a single unit cell and is non-zero for hopeite and sergeysmirnovite and zero for other structures); the contribution from non-hydrogen interlayer atoms (**IS**, interlayer structure); and the contribution from hydrogen atoms (**HB**, hydrogen bonding). Figure 7a shows the information generated by different factors in absolute terms (i.e., in bits per cell), whereas Figure 7b depicts the values of respective contributions in percent. It can be clearly seen that among four structure types (hopeite, represented by sergeysmirnovite (**Ssv**); parahopeite, represented by davidlloydite (**Dld**); phosphophyllite (**Pp**); stergiouite (**Sgo**)), the sequence of increasing complexity is **Dld** < **Pp** < **Sgo** < **Ssv** (mineral symbols are given according to [62]). That is, the hopeite structure type is the most complex. From the viewpoint of different structural contributions to complexity, hydrogen atoms contribute essentially in all four structure types (up to 50% for sergeysmirnovite) with about 25% of the information coming from interlayer species. The topological information contribution is the smallest in **Ssv** and the largest in **Pp**. In the crystal structures of **Sgo** and **Dld**, real layers are distorted compared to their ideally symmetrical versions, which makes their **SInf** contributions equal to non-zero values.

**Figure 7.** Complexity diagram for sergeysmirnovite (**Ssv**), phosphophyllite (**Pp**), stergiouite (**Sgo**), and davidlloydite (**Dld**) showing contributions of different factors to the total structural information in bits (a) and as a percentage (b). Legend: **TInf** = topological information; **SInf** = structural information; **LS** = layer stacking; **IS** = interlayer structure; **HB** = hydrogen bonding. See text for details.

4.3. Polymorphism in Hopeite and Related Structures

The complexity parameters and physical density values given in Table 6 unambiguously demonstrate that, in the hopeite group, polymorphs with simpler structures are denser than those with complex structures, which is in contradiction with the general tendency observed for minerals and inorganic compounds [40,63–65]. The anomaly is especially clear for the hopeite-parahopeite modifications. In other cases, a direct comparison of physical densities is less informative, since the chemical composition of minerals does not correspond to the ideal formulas given in Table 6, but may contain admixtures. In contrast, for hopeite and parahopeite, almost chemically pure crystals with the composition $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ have been observed either in nature as minerals or laboratory experiments as artificial crystals. It is, however, worth noting that parahopeite is difficult to synthesize; the only laboratory report that we were able to locate in the literature is the recent paper by Bhakat et al. [66], who reported on the accidental synthesis of parahopeite during the preparation of zinc-oxide quantum dots.

If hopeite and parahopeite can be obtained as pure compounds, their complexity relations contradict the general observation that more complex polymorphs possess higher physical density and higher stability [40,64,65]. Indeed, this tendency has many exceptions, though, in the majority of cases, it holds true. The lower density of hopeite compared to parahopeite may point to its lower stability. If this is the case, it may well be possible that hopeite forms more easily and is metastable under room conditions. The hopeite–parahopeite transition requires sufficient topological reconstruction, which means that the two structures are separated by an essential energetic barrier that is difficult to overcome. This hypothesis can be tested by the measurement of the thermodynamic stability parameters for hopeite and parahopeite, which are absent from the literature for the latter.

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