Na-Alternative to Tinsleyite Obtained under Hydrothermal Conditions: Crystal Structure and Comparative Crystal Chemistry

Olga Yakubovich 1,* 1, Galina Kiriukhina 1,2,*, Polina Verchenko 1, Sergey Simonov 3,*, Anatoly Volkov 1 and Olga Dimitrova 1

1. Department of Crystallography, Geological Faculty, M. V. Lomonosov Moscow State University, Leninskie Gory 1, 119991 Moscow, Russia; g-biralo@yandex.ru (G.K.); yapoletta@mail.ru (P.V.); toljha@yandex.ru (A.V.); dimitrova@list.ru (O.D.)
2. Institute of Experimental Mineralogy RAS, 142432 Chernogolovka, Russia
3. Institute of Solid State Physics RAS, 142432 Chernogolovka, Russia; simonov@issp.ac.ru

Abstract: The synthesis and characterization of a new aluminophosphate, Na2Al2O(PO4)2·0.12H2O obtained as single crystals, is reported. Centrosymmetric tetramers built from AlO5 polyhedra sharing edges and vertices, represent the distinguished feature of the compound. These tetrameric units of AlO5 bipyramids are cross-linked by PO4 tetrahedra to form two-periodic slabs alternating with Na+ ions and a small amount of H2O molecules. The Na2Al2O(PO4)2·0.12H2O with an original crystal architecture is chemically and structurally related to the mineral tinsleyite, KAl2(PO4)(OH)·2H2O. Similar clusters of Al-centered polyhedra are essential building blocks of both monoclinic structures. The main difference between them consists of the type of the Al coordination by O atoms: in tinsleyite, the clusters are designed from AlO4(OH)2 and AlO4(OH)(H2O) octahedra. In both cases, alkali Na or K atoms significantly distinct in size, act as structure regulating agents, determining the character of the developing crystal architecture. The flexibility of aluminophosphate constructions allows them to self-organize around structure-forming Na+ or K+ ions into anionic layers in Na2Al2O(PO4)2·0.12H2O or a framework (tinsleyite). The synthesis of sodium aluminophosphate under mild hydrothermal conditions and the topological resemblance of its structure with that of the mineral tinsleyite suggest a high probability of a mineral equivalent of the Na2Al2O(PO4)2·0.12H2O in nature.

Keywords: aluminophosphate; crystal structure; low-temperature X-ray diffraction; hydrothermal synthesis; tinsleyite; crystal chemical relations

1. Introduction

Most rocks are formed by oxosalts, minerals containing complex anions, including phosphate anions, crystallized under the conditions of a lithophilic geochemical system. The latter is characterized by an excess of oxygen in it, both in the bound forms, and in the free forms of O3, O2−, O2, etc. Rocks, as a rule, contain different types of water—from hydroxyl and crystallization in minerals to capillary, etc. It is with the active participation of water in rocks that various processes of their transformations occur. Statistical data on the chemical composition of natural oxosalts show that most of them are typical metals with amphoteric properties. These are, first of all, iron and aluminum, as well as manganese, copper, beryllium, zirconium, and some others. In high-alkaline medium- and low-temperature natural systems (late pegmatites and hydrothermalites), complexes of these elements often play the role of anion formers, creating, together with acid groups, anionic structures of a mixed crystal chemical nature, for example, aluminophosphate. Under these conditions, zeolite-like macro- and microporous minerals are quite common, which have the properties of sorbents, molecular sieves, ion exchangers, etc. Simulation of such environments in the...
laboratory and subsequent detailed study of synthetic analogs of minerals allows, on the one hand, to trace the regular relationships between the physicochemical parameters of the crystallization system and the specific features of the crystal structures of the forming phases (structural typomorphism), and, on the other hand, to obtain new compounds with promising properties.

The mineral tinsleyite, KAl$_2$(PO$_4$)$_2$(OH)$_2$H$_2$O is a member of the leucophosphate group, with the general formula $AB_2(PO_4)_2$(OH)$_2$H$_2$O ($A = \text{Na, K}$; $B = \text{Al, Fe}$). This mineral group apart from leucophosphate, KFe$_2$[PO$_4$]$_2$(OH)$_2$H$_2$O [1] and tinsleyite, also includes sphenscidite, NH$_4$Fe$_2$(PO$_4$)$_2$(OH)$_2$H$_2$O [2] and ammoniotinsleyite, (NH$_4$)$_2$Al$_2$(PO$_4$)$_2$(OH)$_2$H$_2$O [3]. The above-mentioned species are known to occur in two different paragenetic associations: late products of the hydrothermal alteration of primary phosphates in granitic pegmatites, or biominerals. Tinsleyite was first described from the Tip Top granitic pegmatite, in South Dakota. It is found in pods of highly altered triphylite in the intermediate zone of the pegmatite in association with leucophosphate, on which it commonly occurs as a morphologically continuous overgrowth [4]. Its crystal structure was established and refined by Dick [5], who used a synthetic crystal, obtained by the reaction of gibbsite with a potassium phosphate solution of pH = 7 at 423 K. Two steps in the thermal loss of water, at 341 and 471 K, were observed. A potassium-rich variant of tinsleyite was synthesized under hydrothermal conditions at 553 K from the water solution of KH$_2$PO$_4$ and Al(OH)$_3$ [6]. Compared to the mineral tinsleyite, the new variant with the crystal chemical formula $\text{K}_{1.5}(\text{H}_2\text{O})_{0.5} \times [\text{Al}_2(\text{OH})(\text{OH})_2(\text{H}_2\text{O})_2](\text{PO}_4)_2]$ differs not only in the quantity of K$^+$ cations in the framework channels, but also in the amount of H$_2$O and in the way it is distributed in the structure. It was suggested that the capacity of the minerals of the leucophosphate group to accommodate the K$^+$ (or NH$_4^+$) ions is coupled with the H$_2$O content in the framework interstices, which is, therefore, variable. As it happens, the synthetic NH$_4$Al end member of ammoniotinsleyite called AlPO$_4$-15 has been obtained and investigated [7,8] 25 years before the mineral was discovered. This material was studied by means of a charge-density analysis [9] and first-principal calculations [10]. The same compound was obtained later and described in [11]. The crystal structure of leucophosphate, KFe$_2$[PO$_4$]$_2$(OH)$_2$H$_2$O was refined by Dick and Zeiske [12] using a synthetic crystal. They found hydrogen atom positions by Rietveld refinement based on powder neutron-scattering data. The structure of the NH$_4$Fe end-member sphenscidite, (NH$_4$)$_2$Fe$_2$(PO$_4$)$_2$(OH)$_2$H$_2$O, was refined by Yakubovich and Dadashov [13] with crystals grown at 423 K from a hydrogel with the general formula |K$_2$Fe$_2$(PO$_4$)$_2$(OH)$_2$H$_2$O| (5.6 mL), sealed in a poly(tetrafluoroethylene) (PTFE)-lined stainless steel pressure vessel of 7 mL in volume (fill factor 80%). It was kept in a furnace at a temperature of 553 K and a pressure of 7 MPa for 10 days, followed by slow cooling to room temperature. The reaction products were colorless crystals with an irregular shape up to 0.3 mm long (Figure 1). They were washed with water, dried and subjected to a SEM-EDX analysis and to single-crystal X-ray diffraction. The SEM-EDX analysis was carried out on a Jeol SEM (JSM-6480LV) Oxford X-MaN equipped with an energy-dispersive diffraction spectrometer (Laboratory of Local Methods for Studying Materials, Department of Petrology, Faculty of Geology, M. V. Lomonosov Moscow State University).

2. Materials and Methods

2.1. Hydrothermal Synthesis and Crystallization

Single crystals of the new compound were synthesized under hydrothermal conditions. Chemical compounds of analytical grade were taken in the mass ratio NaCl:Al(OH)$_3$ = 2:3, which corresponds to 1g (17 mmol) NaCl and 1.5 g (19 mmol) Al(OH)$_3$. This starting mixture was melted in a 10% solution of H$_3$PO$_4$ (5.6 mL), sealed in a poly(tetrafluoroethylene) (PTFE)-lined stainless steel pressure vessel of 7 mL in volume (fill factor 80%). It was kept in a furnace at a temperature of 553 K and a pressure of 7 MPa for 10 days, followed by slow cooling to room temperature. The reaction products were colorless crystals with an irregular shape up to 0.3 mm long (Figure 1). They were washed with water, dried and subjected to a SEM-EDX analysis and to single-crystal X-ray diffraction. The SEM-EDX analysis was carried out on a Jeol SEM (JSM-6480LV) Oxford X-MaN equipped with an energy-dispersive diffraction spectrometer (Laboratory of Local Methods for Studying Materials, Department of Petrology, Faculty of Geology, M. V. Lomonosov Moscow State University).
University). The measurements were performed at 20 kV and 0.7 nA using the sample covered by a carbon film with a thickness of about 25 nm. The crystals were stable under these conditions. X-ray spectral semiquantitative analysis of unpolished samples revealed Na, P, Al, and O atoms in their composition with the P:Al:Na ratio close to 1:1:1, which is consistent with the data of our X-ray diffraction structural study.

Figure 1. SEM image (a), showing the sample morphology, and photograph (b) of the crystals.

2.2. X-ray Diffraction and Crystal Structure Determination

X-ray diffraction data were collected from the crystal of 0.05 × 0.15 × 0.26 mm in size at T = 150 K on an Oxford Diffraction Gemini single crystal diffractometer equipped with a CCD detector; Mo Kα radiation (λ = 0.71073 Å). The dataset was corrected for background, Lorentz and polarization effects, and absorption [15]. All calculations were performed within the WinGX program system [16]. The monoclinic crystal structure was solved by direct methods in the space group P2₁/c and refined in anisotropic approximation with the SHELX programs [17,18] using the F² data to residual R = 0.0221 [for 2063 reflections with I > 2σ(I)], S = 1.177. In Table 1, we report the crystallographic characteristics of the new aluminophosphate and the experimental conditions of data collection and refinement. Table S1 presents the final results of the atom positions and equivalent isotropic displacement parameters. Characteristic distances are given in Table 2. A bond-valence calculation (Table 3) was performed using the algorithm and parameters given by Brown and Altermatt [19]. Data from Table 3 clearly confirm the assignment of O and the absence of OH ligands. CDS 2167937 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, accessed on 21 April 2022, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336033.

Table 1. Na₃Al₂O(PO₄)₂·0.12H₂O: crystal data and details of X-ray diffraction and structure refinement.

| Crystal Data                  | Value                      |
|-------------------------------|----------------------------|
| Absorption μ (mm⁻¹)           | 0.933                      |
| Space group, Z                | P2₁/c, 4                   |
| a, b, c (Å)                   | 9.9927(3), 8.8811(2), 9.7005(3) |
| β (°)                         | 116.155(4)                 |
| V (Å³)                        | 772.73(4)                  |
| D_cal (g/cm³)                 | 2.629                      |
| Crystal size (mm)             | 0.046 × 0.147 × 0.262      |
Table 1. Cont.

| Data Collection                                      |
|------------------------------------------------------|
| Diffractometer                                      |
| Radiation Oxford Diffraction Gemini, CCD detector    |
| Temperature (K) 150(2)                               |
| Scanning mode Omega scans                            |
| Measuring range, Θ (°) 2.271–29.996                 |
| Reflections (total)                                 |
| \( R_{\text{int}} \) 0.0365                         |
| \( R_{\sigma} \) 0.0162                             |

| Refinement                                           |
|------------------------------------------------------|
| Reflections unique 2254                              |
| Reflections observed \(| I > 2\sigma(I) \) 2063      |
| Parameters 147                                       |
| Absorption correction Numerical                      |
| \( T_{\text{max}}, T_{\text{min}} \) 0.958,0.792    |
| Residuals \( \bar{R} \) (observed reflections) 0.0221|
| \( R, wR \) (all reflections) 0.0253, 0.0630         |
| \( S \) 1.177                                       |
| \( \Delta \rho \) (max)/(min) (e/Å³) 0.495/−0.373    |

Table 2. \( \text{Na}_2\text{Al}_2\text{O}(\text{PO}_4)_2\cdot 0.12\text{H}_2\text{O} \). Characteristic distances, Å.

| \( \text{P1—Tetrahedron} \) | \( \text{Al1—Bipyramid} \) | \( \text{Na1—Octahedron} \) |
|-------------------------------|-----------------------------|-----------------------------|
| \( \text{P1—O2} \) 1.5289(11)| \( \text{Al1—O1} \) 1.7744(11)| \( \text{Na1—O8} \) 2.190(2) |
| \( \text{O4} \) 1.5291(11)   | \( \text{O9} \) 1.7985(11)  | \( \text{O3} \) 2.316(1)    |
| \( \text{O3} \) 1.5402(11)   | \( \text{O5} \) 1.8313(11)  | \( \text{O4} \) 2.366(1)    |
| \( \text{O5} \) 1.5466(11)   | \( \text{O1'} \) 1.8798(11) | \( \text{O2} \)            |
|                               | \( \text{O4} \) 1.8980(11)  | \( \text{<Na1—O> 2.556} \) |
| \( \langle \text{P1—O> 1.536} \rangle \) | \( \langle \text{Al1—O> 1.836} \rangle \) | \( \langle \text{Na1—octahedron} \rangle \) |
| \( \text{P2—O8} \) 1.5050(11)| \( \text{Al2—O7} \) 1.8158(11)| \( \text{O3} \) 2.30(1)     |
| \( \text{O6} \) 1.5206(11)   | \( \text{O3} \) 1.8248(11)  | \( \text{O4} \) 2.36(2)    |
| \( \text{O7} \) 1.5465(11)   | \( \text{O1} \) 1.8277(11)  | \( \text{O7} \)            |
| \( \text{O9} \) 1.5543(11)   | \( \text{O2} \) 1.8426(11)  | \( \text{<Na1—O> 2.58} \)  |
|                               | \( \text{O6} \) 1.8438(11)  | \( \text{Na2—O9} \) 2.309(1)|
| \( \langle \text{P2—O> 1.532} \rangle \) | \( \langle \text{Al2—O> 1.831} \rangle \) | \( \text{Na2—eight-vertex polyhedron} \) |

\* The oxygen atom of the water molecule with low occupancy.

Table 3. \( \text{Na}_2\text{Al}_2\text{O}(\text{PO}_4)_2\cdot 0.12\text{H}_2\text{O} \). Bond valance data *.

| Atom | \( \text{P1} \) | \( \text{P2} \) | \( \text{Al1} \) | \( \text{Al2} \) | \( \text{Na1} \) | \( \text{Na2} \) | \( \Sigma \) |
|------|----------------|----------------|----------------|----------------|----------------|----------------|---------|
| \( \text{O1} \) | 0.716; 0.539 | 0.620          | 0.036          | 0.218          | 0.090          | 0.175          | 1.88    |
| \( \text{O2} \) | 1.269          | 0.596          | 0.250          | 0.165          | 0.206          | 2.09           |
| \( \text{O3} \) | 1.231          | 0.625          | 0.513          | 0.175          | 2.00           |
| \( \text{O4} \) | 1.268          | 0.513          | 0.090          | 0.218          | 2.09           |
| \( \text{O5} \) | 1.210          | 0.614          | 0.175          | 0.090          | 2.09           |
| \( \text{O6} \) | 1.298          | 0.594          | 0.175          | 0.090          | 2.09           |
| \( \text{O7} \) | 1.210          | 0.640          | 0.165          | 0.218          | 2.09           |
| \( \text{O8} \) | 1.354          | 0.352          | 0.165          | 0.218          | 2.09           |
| \( \text{O9} \) | 1.185          | 0.671          | 0.165          | 0.218          | 2.09           |
| \( \Sigma \) | 4.98           | 5.05           | 3.05           | 3.07           | 1.07           | 2.65           |

\* \( \text{Na1'} \) and \( \text{O10(H}_2\text{O)} \) atoms with low occupancy are not included in the calculation.
3. Results
3.1. Interatomic Distances and Crystal Structure Description

The basic structural elements of the title compound are shown in Figure 2a. The Al$^{3+}$ ions in two symmetrically independent positions are surrounded by O atoms, forming trigonal bipyramids. The Al1-centered polyhedron has three close Al1–O distances that vary from 1.774(1) to 1.831(1) Å, and two longer distances to apical O atoms of 1.880 (1) and 1.898(1) Å. The distortion of the Al2-centered five-vertex polyhedron is different: all Al2–O distances lie in the interval 1.816(1)–1.844(1) Å. The pattern of distortion of the AlO$_5$ polyhedra is consistent with the bond-valence calculation (Table 3). The asymmetric unit of the structure includes two P sites in tetrahedral coordination. In the P1 tetrahedron, there are two pairs of close P1–O bond lengths, one of 1.529(1) Å and another of about 1.54 Å. Similarly, two close P2–O distances are of 1.505(1) and 1.521(1) Å and two longer ones of about 1.55 Å characterize the P2O$_4$ polyhedron. The site of Na1 is split into two positions at 0.46 Å statistically populated by Na atoms for 93 and 7% with six Na1–O distances ranging from 2.190(1) to 3.033(3) Å, and six Na1’–O distances from 2.18(2) to 3.09(3) Å. In Na2-centered eight-vertex polyhedron the Na2–O distances lie between 2.309(1) and 3.086(1) Å.

Centrosymmetric tetramers built from two AlO$_5$ polyhedra sharing an edge and two additional Al$_2$O$_3$ polyhedra attached by corner linkage at each side of this common edge represent the distinguished feature of the title compound (Figure 2b). These tetrameric units of four AlO$_5$ bipyramids are cross-linked by PO$_4$ tetrahedra to form two-periodic slabs parallel to the $yz$ plane. The Na$^+$ ions and a small amount of H$_2$O molecules at the symmetry centers occupy positions between the anionic slabs of the [Al$_2$O(PO$_4$)$_2$]$_2$ composition (Figure 3) with eight-membered windows built from alternating sharing vertices P- and Al-centered polyhedra, and open in the [010] direction (Figure 4).

3.2. Crystal Chemical Regularities in the Family of Aluminum Phosphates/Aluminophosphates

Natural phases, formed within the Al–P–O–(H) compositions, are generally supergene minerals of sedimentary rocks; they also occur in weathering zones and late hydrothermal formations. Although these minerals contain water in a different form, they often have rather dense crystal structures formed by cationic layers (augelite, Al$_2$(OH)$_3$[PO$_4$]) or columns (senegalite, Al$_2$(OH)$_3$[PO$_4$]·H$_2$O) of either edge-sharing AlO$_6$ octahedra and

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**Figure 2.** (a) The main structural units of the Na$_2$Al$_2$O(PO$_4$)$_2$·0.12H$_2$O. Displacement ellipsoids are drawn at the 90% probability level. Symmetry operations: (*) $-x$, $1-y$, $1-z$; (**) $x$, $1/2-y$, $1/2+z$; (+) $-x$, $1/2+y$, $1/2-z$; (’) $1-x$, $-0.5+y$, $1/2-z$. (b) The tetramer of AlO$_5$ bipyramids sharing edges and vertices, and adjacent PO$_4$ tetrahedra.
AlO$_5$ polyhedra, or columns of aluminum octahedra shared faces and vertices (trolleite, Al$_4$(OH)$_3$[PO$_4$]$_3$). Phosphate tetrahedra unite two- or one-periodic cationic fragments designed by Al-centered polyhedra into framework structures. The water-rich representatives in this mineral group are characterized by a microporous architecture with voids and channels containing H$_2$O molecules (wavellite, Al$_3$(OH)$_3$[PO$_4$]$_2$·5H$_2$O, kingite, Al$_3$(OH)$_3$[PO$_4$]$_2$·9H$_2$O, etc.). In the crystal structures of the minerals characterized by the ratio Al:P = 1 (variscite and metavariscite, AlPO$_4$·2H$_2$O), all vertices of AlO$_6$ octahedra are shared with phosphate tetrahedra [20]. In the crystal structure of mineral berlinite, AlPO$_4$ (an indicator of high-temperature conditions of phase formation [21]) with the ratio Al:P = 1, the framework of which represents a superstructure based on quartz, Al atoms are in the tetrahedral coordination.

Figure 3. The Na$_2$Al$_2$O(PO$_4$)$_2$·0.12H$_2$O crystal structure displayed in xz (a) and xy (b) projections.

Figure 4. The Na$_2$Al$_2$O(PO$_4$)$_2$·0.12H$_2$O crystal structure viewed along the [101] direction.

Incorporation of Na into the composition of aluminum phosphates is usually connected with metasomatic reactions. In nature, two minerals are known in the Na-Al-P-O-H system—wwardtite and brazilianite. Both structures are based on mixed anionic frameworks of Al octahedra and P tetrahedra, but the topology of the frameworks differs significantly. Brazilianite, NaAl$_3$(PO$_4$)$_2$(OH)$_4$ is considered to form in granitic pegmatites as a product of Na-metasomatic alteration of primary pegmatite minerals of the montebrasite-amblygonite series. The crystal structure of brazilianite is designed from columns of AlO$_4$(OH)$_2$ and AlO$_3$(OH)$_3$ octahedra sharing edges; these columns are linked by PO$_4$ tetrahedra in a framework with cavities populated by Na atoms [22,23]. The mineral
wardite, NaAl₃(PO₄)₂(OH)₄·2H₂O of hydrothermal origin usually occurs in P-rich zones of granite pegmatites. In its tetragonal crystal structure, Al-centered octahedra sharing OH vertices are aligned in intercrossing chains along the [100] and [010] directions. These chains form cellular layers parallel to the ab plane with Na atoms occupying positions near their centers. The sheets of AlO₃(PO₄)₆(PO₄)₂·18H₂O and NaO₆(H₂O)₂ polyhedra sharing edges and vertices are linked along the c axis via phosphate tetrahedra and hydrogen bonds [24,25].

Natural potassium and aluminum phosphates are mainly weathering products of clay minerals under the action of phosphate-containing solutions of guano or anthropogenic fertilizers. Potassium aluminophosphate tarsanakite, K₃Al₅(HPO₄)₆(PO₄)₂·18H₂O mostly occurs in humid caves where phosphate-rich excrements of birds, penguins, or bats react with clay minerals. It is also known as a reaction product of soil clays with phosphate-containing fertilizers [26]. In the rhombohedral structure of tarsanakite, six [K₃Al₅(HPO₄)₆(PO₄)₂(H₂O)₁₂] layers alternate along [001] with layers of H₂O molecules. Non-exchangeable K atoms are trapped within the layers. Hydrogen bonds in tarsanakite act within the rigid layers, within the water interlayers, and between the layers and interlayers [27]. The product of tarsanakite dehydration, francoanellite, occurs at the contact of “terra rossa” with bat guano in the karst cave. The mineral crystal structure is built of the same “taranakite” [K₃Al₅(HPO₄)₆(PO₄)₂(H₂O)₁₂] layers connected by hydrogen bonds. Hydrogen bonds in francoanellite are formed within the rigid layers and between them. It has been shown that single crystals of synthetic francoanellite could be obtained by topochemical dehydration of tarsanakite crystals with loosing of every second water interlayer, when a first-order staging product of the deintercalation of water from tarsanakite was formed [28].

Known to date, several structural topologies of aluminophosphates are derived from the assemblage of PO₄ tetrahedra and a number of types of Al-centered polyhedra (tetrahedra, octahedra, trigonal bipyramids, and tetragonal pyramids) in the framework. Five-vertex polyhedra formed by O atoms in the Al surrounding are not as common as usual AlO₆ polyhedra having vertex-bridging contacts [29]. Obtained by a high-temperature molten salt method, the Ba₃Al₃P₅O₁₆ phase with an Al/P ratio of 1.2, is characterized by unique [Al₂P₂O₁₆]ₙ chains constructed from PO₄, AlO₄, and AlO₆ groups [30]. Two complex aluminophosphates with an Al/P ratio equal to 5.7, namely, [Al₃(Al₃)(PO₄)₃(Po₃OH)₄][NH₃(CH₂)₄NH₃]₂[2H₂O] and [Al₅(PO₄)₅(PO₄)OH)₄][NH₃(CH₂)₄NH₃]₂[H₂O] are layered materials with aluminum atoms in three different coordination states, AlO₄, AlO₅, and AlO₆, and the interlayer space contains the amines and water molecules [31].

The title compound Na₂Al₂O(PO₄)₁₂·0.12H₂O represents an example of the layered sodium aluminophosphate built from PO₄ and AlO₅ polyhedra. Its monoclinic crystal structure is very similar to that of mineral tinsleyite, KAl₂(PO₄)₂(OH)·2H₂O with K atoms in the framework channels. The main difference between the two structures consists of the type of Al coordination by O atoms. As shown above, clusters of AlO₅ bipyramids sharing edges and vertices are essential building blocks of the Na₂Al₂O(PO₄)₁₂·0.12H₂O. Similar clusters, but designed from AlO₅(OH) and AlO₄(OH)(H₂O) octahedra, form the tinsleyite crystal structure (Figure 5). The topologies of both Al/P substructures within the bc layers are identical; the amount and distribution of alkalali Na⁺ or K⁺ ions and the H₂O molecules are different. Significantly distinct sizes of Na⁺ and K⁺ ionic radii define here not only a type of Al coordination by O atoms in order to arrange the necessary environment around one or another alkalali metal. They also specify a periodicity of the aluminophosphate anionic construction: layers alternating along the [100] direction with Na atoms in the Na₂Al₂O(PO₄)₁₂·0.12H₂O or a framework with channels populated by a two times lower quantity of K atoms in the case of tinsleyite (Table 4). The synthesis of sodium aluminophosphate under mild hydrothermal conditions and the topological resemblance of its structure with that of the mineral tinsleyite and a number of its structural
analogues, suggest a high probability of the existence of a mineral equivalent of the 
$\text{Na}_2\text{Al}_2\text{O}(\text{PO}_4)_2 \cdot 0.12\text{H}_2\text{O}$ in nature.

![Crystal structures of Na$_2$Al$_2$O(PO$_4$)$_2$·0.12H$_2$O (a) and tinsleyite, KAl$_2$(OH)(H$_2$O)(PO$_4$)$_2$·H$_2$O (b) projected along the a axis.](image)

A certain structural resemblance between hydrothermally obtained sodium aluminophosphate hydroxide Na$_2$Al$_3$(OH)$_2$(PO$_4$)$_3$ and the mineral minyulite, KAl$_2$F(H$_2$O)$_4$(PO$_4$)$_2$ has been noticed earlier [32]. Minyulite was first synthesized by Haseman et al. [33], as well as a number of other hydrous phosphates, including tinsleyite, by the treatment of clays with phosphate anions at pH ranges appropriate for soil environments and at a temperature less than 95 °C. A synthetic hydroxide analogue of minyulite, namely, KAl$_2$(OH)(H$_2$O)$_4$(PO$_4$)$_2$ could also be obtained by the reaction of gibbsite with a potassium phosphate solution of pH = 5.5 at 333 K [34].

![Anionic Structural Fragment](image)

**Figure 5.** Crystal structures of Na$_2$Al$_2$O(PO$_4$)$_2$·0.12H$_2$O (a) and tinsleyite, KAl$_2$(OH)(H$_2$O)(PO$_4$)$_2$·H$_2$O (b) projected along the a axis.

![Table 4. Structurally related sodium and potassium microporous aluminophosphates.](image)

| Compound/Mineral | Unit Cell Parameters, $a$, $b$, $c$, $\beta$, $V$, Å$^3$ | Space Group, $Z$, $\rho$, g/cm$^3$ | Clusters of Al-Centered Polyhedra | Anionic Structural Fragment | Reference |
|------------------|------------------------------------------------------------|-------------------------------------|----------------------------------|----------------------------|-----------|
| Tinsleyite, synthetic KAl$_2$(OH)(H$_2$O)(PO$_4$)$_2$·H$_2$O | $a = 9.999(2)$, $b = 9.503(2)$, $c = 9.535(2)$, $\beta = 103.26(3)$, $V = 837.8(2)$ | $P2_1/a$ 4 2.66 | Al$_4$(OH)$_2$(H$_2$O)$_2$O$_{16}$ | Framework | [5] |
| Na$_2$Al$_2$O(PO$_4$)$_2$·0.12H$_2$O * | $a = 9.927(3)$, $b = 8.8811(2)$, $c = 9.7005(3)$, $\beta = 116.155(4)$, $V = 772.73(4)$ | $P2_1/c$ 4 2.63 | Al$_4$O$_{18}$ | Layers | This work |
| Minyulite, KAl$_2$F(H$_2$O)$_4$(PO$_4$)$_2$ | $a = 9.337(5)$, $b = 9.740(5)$, $c = 5.522(3)$, $V = 502.2(5)$ | $P6_3$ 2 2.47 | Al$_2$F(H$_2$O)$_4$O$_{6}$ | Layers | [35] |
| Na$_2$Al$_3$(OH)$_2$(PO$_4$)$_3$ | $a = 8.475(2)$, $b = 8.471(2)$, $c = 14.319(3)$, $V = 1028.0(4)$ | $P2_12_12_1$ 4 2.88 | Al$_3$(OH)$_2$O$_{12}$ | Framework | [32] |

* Geometric characteristics correspond to the temperature of 150 K.
Crystal structures of these Na- and K-bearing pseudo tetragonal compounds look similar in the \( ab \) projection. The elementary blocks of the anionic layers of the mixed type in the minyulite structure are dimers consisting of two Al octahedra sharing F vertices (or OH vertices in the structure of its synthetic variant). These pairs of octahedra are connected in layers via PO\(_4\) tetrahedra. Voids of the octagonal cross-section in layers parallel to the [001] plane contain K\(^+\) ions. In the direction of the \( c \) axis, the aluminophosphate layers are linked by hydrogen bonds [35]. Blocks of sharing vertices Al-centered polyhedra crosslinked by PO\(_4\) tetrahedra can be distinguished in the structure of Na\(_2\)Al\(_3\)(OH)\(_2\)(PO\(_4\))\(_3\); however, in this case, two AlO\(_4\)(OH) polyhedra and one AlO\(_4\)(OH)\(_2\) octahedron form an elementary cluster of a horseshoe appearance (Figure 6). The Al-centered five-vertex polyhedra are moved up and down along [001] from the Al-centered octahedron. As a consequence, the Al\(_3\)(OH)\(_2\)O\(_{12}\) trimers with the AlO\(_4\)(OH)\(_2\) octahedron at their centers occur disposed at two levels along the \( z \) axis (Figure 6b); thus increasing the unit cell \( c \) parameter to 14.319 Å, as compared with \( c = 5.522 \) Å of minyulite having the layered structure (Figure 6c). In the framework structure of sodium aluminophosphate, the clusters are linked via phosphate tetrahedra not only in the \( ab \) plane (as in the minyulite structure), but also in the [001] direction. Each Al-centered polyhedron overlaps along the \( z \) axis with its counterpart at a distance of about 4.9 Å, and the trimeric clusters look like dimers in the \( xy \) projection (Figure 6a).

![Figure 6](image-url)

**Figure 6.** Crystal structures of Na\(_2\)Al\(_3\)(OH)\(_2\)(PO\(_4\))\(_3\) (a) and minyulite (c) projected along the \( c \) axis of their pseudo tetragonal unit cells; (b) fragment of the Na\(_2\)Al\(_3\)(OH)\(_2\)(PO\(_4\))\(_3\) structure showing the horseshoe-like cluster built from the AlO\(_4\)(OH)\(_2\) octahedron and two AlO\(_4\)(OH) five-vertex polyhedra.

The absence, at ambient conditions, of isostructural chemically similar but Na- or K-based compounds is well-known and is mainly due to the difference in ionic radii of Na\(^+\) and K\(^+\). The abovementioned examples demonstrate the crystal chemical variations between Na- and K-representatives of aluminophosphates, the structures of which include clusters of Al-centered polyhedra interconnected in the framework through oxygen-bridging contacts of PO\(_4\) tetrahedra. In both cases, alkali Na or K atoms work as structure regulating agents, determining the character of the developing crystal structure, namely, the types of Al-centered polyhedra and the structure periodicity (layer or framework). The flexibility of aluminophosphate constructions, which include clusters of Al-centered octahedra and/or five-vertex polyhedra connected by phosphate groups, allows them to self-organize around structure-forming Na\(^+\) or K\(^+\) ions into anionic layers or frameworks. The implementation of such structures, also in nature in the form of minerals, is largely determined by the participation of water, in one form or another, which stabilizes the crystallizing phases due to the forming hydrogen bonds.
4. Conclusions

Various structural topologies of aluminophosphates are derived from the grouping of PO₄ tetrahedra and a number of types of Al-centered polyhedra (tetrahedra, octahedra, trigonal bipyramids, and tetragonal pyramids) in the framework. A novel representative Na₂Al₂O(PO₄)₂·0.12H₂O within this family was obtained as single crystals in middle-temperature hydrothermal conditions. Its original layered crystal structure was established by low-temperature X-ray diffraction. A mineralogically probable phase is discussed as a sodium alternative of tinsleyite, KA₁₂(OH)(H₂O)(PO₄)₂·H₂O, a member of the leucophosphate mineral group, which also includes sphenscidite and ammoniotinsleyite. These minerals are known to occur in two different paragenetic associations: as late products of the hydrothermal alteration of primary phosphates in granitic pegmatites, or as biominerals.

The crystal structures Na₂Al₂O(PO₄)₂·0.12H₂O and tinsleyite contain similar fragments: clusters of four Al-centered polyhedra sharing edges and vertices, surrounded by PO₄ tetrahedra. In contrast to tinsleyite, where tetramers are built from AIO₄(OH)₂ and AIO₄(OH)(H₂O) octahedra, analogous clusters of AIO₅ bipyramids are the main structural units of sodium aluminophosphate. We showed that alkali Na or K atoms, which have strongly distinct ionic radii, act as structure regulators, determining the character of the developing crystal structure, namely the types of Al-centered polyhedra and the structure periodicity. The flexibility of aluminophosphate constructions, which include clusters of Al-centered octahedra or five-vertex polyhedra connected by phosphate groups, allows them to self-organize around structure-forming Na⁺ or K⁺ ions into anionic layers or frameworks. We assume that the synthesis of sodium aluminophosphate under mild hydrothermal conditions and the topological resemblance of its structure with that of the mineral tinsleyite and a number of its structural analogues, suggest a high probability of the existence of a mineral equivalent of the Na₂Al₂O(PO₄)₂·0.12H₂O in nature.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/min12050542/s1, Table S1: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²) for Na₂Al₂O(PO₄)₂·0.12H₂O.

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