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Synthesis, crystal structure and properties of $Na_3Zn_4O(AsO_4)_3 \cdot 6H_2O$, a new framework zincoarsenate

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Synthetic $Na_3Zn_4O(AsO_4)_3 \cdot 6H_2O$ is built up from a three-dimensional network of vertex sharing ZnO_4 and AsO_4 tetrahedra with extra-framework sodium cations and water molecules completing the structure. Dehydration of $Na_3Zn_4O(AsO_4)_3 \cdot 6H_2O$ results in a facile, irreversible, framework transformation to hexagonal $NaZnAsO_4$. The title compound is a new member of the $M_3Zn_4O(XO_4)_3 \cdot nH_2O$ (M = univalent cation; X = P or As; n = 3.5–6) family of open-framework phases. It is isostructural with its phosphate congener but the sodium coordination is subtly different for the two phases. Crystal data: $Na_3Zn_4O(AsO_4)_3 \cdot 6H_2O$, M_r = 871.31, trigonal, $R3c$ (No. 161), a = 10.9493 (5), c = 26.7099 (13) Å, V = 2773.2 (2) Å^3, Z = 6, $R(F)$ = 0.021, $wR(F^2)$ = 0.042.

Introduction

The $M_3Zn_4O(XO_4)_3 \cdot nH_2O$ (M = univalent cation; X = P or As; n = 3.5–6) family of open-framework phases,[1–3] some of which display classic zeolitic properties of significant thermal stability, reversible de-/re-hydration and facile cation exchange,[4] are of structural interest for several reasons. These materials contain vertex-sharing ZnO_4 and XO_4 tetrahedral building blocks, which are joined in such a way as to result in spiro-5 secondary building units[5] (SBUs) and novel OZn_4 groupings as a component part of the zinc-rich framework.[1] They display subtle symmetry variations depending on the guest cation involved, which to some extent may be correlated with the size and bonding requirements of the M^+ species in question.[1,2] A notable variant of the $M_3Zn_4O(XO_4)_3 \cdot nH_2O$ structure type occurs for the phases $(H_3CNH_3)_3Zn_4O(XO_4)_3$,[3] where methylammonium cations take the place of alkali metal cations and water molecules to template the same framework topology. Remarkably,[6] the coordination polymer known as MOF-5 $[Zn_4O(BDC)_3 \cdot (DMF)_8(C_6H_5Cl)]$ adopts a very similar structure to that of the $M_3Zn_4O(XO_4)_3 \cdot nH_2O$ types, with rod-like BDC (benzene-1,4-dicarboxylate) ligands replacing the XO_4 groups to fuse the nominal $[OZn_4]^{6+}$ tetrahedra into a neutral, thermally stable, three-dimensional network of exceptional porosity.

MOF-5 is a spectacular example of a continuing effort in materials chemistry, namely the preparation of novel frameworks with extra-large pores.[7] Pore size can be defined in various ways: for example, in terms of the number of polyhedral building blocks making up the framework ring which defines the pore, or some measure of the actual size (in Å) of the pore dimension. One seemingly obvious way to generate larger pore materials, at least in structurally related phases, is to use "larger atoms" for the framework, or more precisely, atoms with longer X–O bonds, for example, arsenate replacing phosphate. In this paper we report the solution-mediated synthesis, single-crystal structure and some properties of sodium zinc arsenate hydrate, $Na_3Zn_4O(AsO_4)_3 \cdot 6H_2O$, which has a similar structure to that of $Na_3Zn_4O(PO_4)_3 \cdot 6H_2O$.[1] Its open-framework structure shows ion-exchange properties but the 8-ring windows in the arsenate are smaller than those in the phosphate.

Experimental

Synthesis

$Na_3Zn_4O(AsO_4)_3 \cdot 6H_2O$ has resisted[1] previous synthesis attempts based on the methodology of adding alkali hydroxide solution to an aqueous zinc–acid mixture. Here, a modified method was used, as follows: 0.42 g ZnO was dissolved in 500 ml of 1 M sodium hydroxide. This sluggish process requires prolonged heating and stirring. Drop-wise addition of about 14.2 ml of 1 M arsenic acid (H_3AsO_4) to a 40 ml portion of the zinc–sodium hydroxide solution resulted in the first traces of the formation of a white precipitate at which point the pH of the mixture was 11.5. This was transferred to a 60 ml Teflon bottle, sealed, and heated to 75 °C for three days. Solid product recovery by vacuum filtration and rinsing with water resulted in about 25 mg (yield based on zinc $\approx$ 75%) of transparent, perfectly faceted, cuboidal crystals (to 0.5 mm linear dimension) of the title compound. The exact amount of arsenic acid added is critical: a few drops more of H_3AsO_4 solution added results in a preponderance of white powder of the sodalite-type $Na_3(ZnAsO_4)_3 \cdot 6H_2O$[8] in the product. However, the synthesis appears to be reproducible based on careful visual observation of precipitate formation.

Characterisation

Powder diffraction data (Siemens D8 powder diffractometer (Cu-Kα_1 radiation, λ = 1.54056 Å, T = 25 °C) were in good accordance with a simulation of the $Na_3Zn_4O(AsO_4)_3 \cdot 6H_2O$ single-crystal structure, indicating phase purity and a high degree of crystallinity. Thermogravimetric analysis (ramp at 5 °C min^{-1} to 300 °C under flowing N_2 gas) was carried out on a Stanton–Redcroft STA-780 instrument.

Ion exchange

Crystals of $Na_3Zn_4O(AsO_4)_3 \cdot 6H_2O$ were shaken with 30 ml of 1 M LiCl solution and placed in an 80 °C oven for 10 minutes. The solid product was recovered by vacuum filtration and air drying. SEM images of the resulting phase were recorded using a JEOL JSM-5200 instrument and Deben image-capture software.

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Table 1 Crystallographic parameters for $Na_3Zn_4O(AsO_4)_3{\cdot}6H_2O$

Empirical formula	$As_3Zn_4Na_3O_{19}H_{12}$
Formula weight	871.31
Crystal system	Trigonal (rhombohedral)
a/Å	10.9493(5)
c/Å	26.7099(13)
V/Å^3	2773.2(2)
Z	6
Space group	$R3c$ (No. 161)
T/°C	25 ± 2
λ/Å (Mo-Kα)	0.71073
ρ_{calc}/g cm^{-3}	3.13
μ/cm^{-1}	110.6
Total data	7427
Merged, observed[a] data	2095, 1954
Parameters	89
$R(F)$[b]	0.021
$wR(F^2)$[c]	0.042

[a] $I > 2\sigma(I)$ after merging. [b] $R = \sum| |F_o|-|F_c||/\Sigma|F_o|$ for observed data. [c] $wR = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]$ with $w_i = 1/[\sigma^2(F_o^2) + (0.0165P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ for all data.

Structure determination†

The structure of $Na_3Zn_4O(AsO_4)_3{\cdot}6H_2O$ was established by single crystal methods. A transparent cube, dimensions ~0.13 × 0.13 × 0.13 mm was mounted on a Bruker SMART 1000 CCD area-detector diffractometer (graphite monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å, $T = 298$ K) and 8076 intensity data were collected in the range $2° < 2\theta < 65°$ by using thin slice (0.3° width) ω scans.[9] The trigonal unit cell parameters were optimised by refinement against 3933 peak positions ($5.27° < 2\theta < 64.39°$) and an empirical absorption correction[10] was applied by comparing the intensities of multiply measured and symmetry equivalent reflections (range of equivalent transmission factors = 0.741–0.928). Data merging ($R_{Int} = 0.036$) resulted in 2095 unique reflections, of which 1954 were considered observed based on the criterion $I > 2\sigma(I)$. The systematic absences indicated space groups $R3c$ or $R\bar{3}c$.

The starting atomic positions were established by direct methods with SHELXS-97[11] in space group $R3c$ (No. 161) and the structure was refined using SHELXL-97.[12] No model could be established in space group $R\bar{3}c$ and the noncentrosymmetric model was assumed thereafter. The H atoms associated with the water molecules (oxygen atoms O6 and O7) were located in difference maps and refined by riding on their parent atoms. Their isotropic thermal factors were constrained such that $U_{iso}(H) = 1.2 \times U_{eq}$(attached O). The occupation factors of the water molecule atoms were varied but did not diverge significantly from unity and were fixed at that value for the final cycles of least-squares. Refinement of the Flack absolute structure parameter[13] to 0.02(2) indicates that we have chosen the correct absolute structure, for the particular crystal studied. Crystallographic parameters are summarised in Table 1.

Results

Characterisation

TGA showed a weight loss of 11.4% over the temperature range 60–150 °C, which corresponds fairly well to the predicted weight loss of 12.4% for the removal of all water from $Na_3Zn_4O(AsO_4)_3{\cdot}6H_2O$ to yield a residue of nominal formula $Na_3Zn_4O(AsO_4)_3$. This process was accompanied by a broad endothermic feature over the temperature range 60–120 °C and weak exotherms at 166 and 186 °C. When the sample was cooled in a damp atmosphere, there was negligible weight gain except for surface adsorption effects at ambient temperature. The same sample was reheated two weeks later and showed no weight change between room temperature and 300 °C, indicating that the dehydration of $Na_3Zn_4O(AsO_4)_3{\cdot}6H_2O$ is irreversible. This was confirmed when the X-ray powder pattern of the heat-treated sample showed a clean, crystalline pattern corresponding to that of the metastable hexagonal polymorph of $NaZnAsO_4$,[14] indicating that the structure of $Na_3Zn_4O(AsO_4)_3{\cdot}6H_2O$ is completely transformed on dehydration (see below).

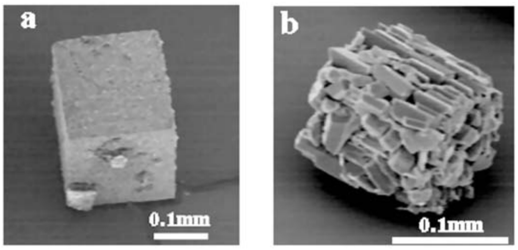

Fig. 1 SEM images of (a) a typical as-synthesised crystal of $Na_3Zn_4O(AsO_4)_3{\cdot}6H_2O$ showing its cubic morphology, and (b) the results of lithium ion-exchange showing the fragmentation of the original crystal whilst maintaining its cubic shape.

Ion exchange

Visual examination of the post-ion exchanged $(Li/Na)_3Zn_4O(AsO_4)_3{\cdot}6H_2O$ crystals indicated that the cube-like morphology was maintained, although the product was more translucent. However, these crystals yielded very smeared diffraction patterns tending towards powder rings indicating a substantial, but not complete, tendency towards a polycrystalline product. This is strikingly confirmed by the SEM images (Fig. 1) which show that the cube-like sodium phase has completely fragmented into a clump of numerous, well formed, rod-like crystallites whilst maintaining the overall shape of the starting cuboids.

Crystal structure

Final atomic positional and thermal parameters for $Na_3Zn_4O(AsO_4)_3{\cdot}6H_2O$, are listed in Table 2, with selected geometrical data in Table 3. An ORTEP-3[15] view of a fragment of $Na_3Zn_4O(AsO_4)_3{\cdot}6H_2O$ is shown in Fig. 2, and the complete crystal structure in Fig. 3.

The two distinct zinc atoms adopt tetrahedral coordination to oxygen atoms with typical[1] geometrical parameters of d_{av}(Zn1–O) = 1.956(2) Å and d_{av}(Zn2–O) = 1.958(2) Å. Zn1 and O1 occupy special positions with 3-fold symmetry. Both

Table 2 Atomic positional/thermal parameters for $Na_3Zn_4O(AsO_4)_3{\cdot}6H_2O$

Atom	x	y	z	U_{eq}[a]
Na1	0.39573(18)	0.50321(19)	0.05957(6)	0.0433(4)
Zn1	0.0	0.0	0.00001(2)	0.01244(11)
Zn2	0.19725(3)	0.10832(3)	0.095521(11)	0.01213(7)
As1	0.32341(3)	0.18134(3)	−0.016944(11)	0.01284(6)
O1	0.0	0.0	0.07307(12)	0.0130(6)
O2	0.2376(2)	0.3004(2)	0.10714(8)	0.0193(4)
O3	0.2392(2)	0.0198(2)	0.15156(8)	0.0214(4)
O4	0.3146(2)	0.1093(3)	0.03986(8)	0.0195(4)
O5	0.1649(2)	0.1593(2)	−0.03174(8)	0.0200(4)
O6	0.5784(3)	0.4418(3)	0.08164(13)	0.0449(8)
H61	0.6293	0.5344	0.0739	0.054
H62	0.6062	0.3927	0.0645	0.054
O7	0.5344(3)	0.7197(3)	0.01635(10)	0.0344(6)
H71	0.5241	0.7251	−0.0181	0.041
H72	0.6173	0.7075	0.0223	0.041

[a] U_{eq} (Å^2) = $1/3[U_1 + U_2 + U_3]$.

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†CCDC reference number 174788. See http://www.rsc.org/suppdata/jm/b1/b110288e/ for crystallographic files in .cif or other electronic format.

Table 3 Selected bond distances (Å) and angles (°) for $Na_3Zn_4O(AsO_4)_3 \cdot 6H_2O$[a]

Na1–O7	2.379(3)	Na1–O2	2.387(3)
Na1–O7a	2.421(3)	Na1–O6	2.479(4)
Na1–O5b	2.581(3)	Na1–O3c	2.815(3)
Zn1–O1	1.952(3)	Zn1–O5	1.968(2)
Zn1–O5d	1.968(2)	Zn1–O5e	1.968(2)
Zn2–O2	1.946(2)	Zn2–O3	1.959(2)
Zn2–O4	1.961(2)	Zn2–O1	1.9670(11)
As1–O5	1.675(2)	As1–O3c	1.682(2)
As1–O2f	1.683(2)	As1–O4	1.690(2)
Zn1–O1–Zn2	107.75(9)	Zn2–O1–Zn2d	111.14(9)
As1g–O2–Zn2	123.49(12)	As1h–O3–Zn2	120.80(12)
As1–O4–Zn2	124.57(13)	As1–O5–Zn1	116.83(11)

O6–H61···O4i	0.90	1.96	2.767(4)	147.5
O7–H71···O6c	0.93	1.86	2.781(4)	168.2
O7–H72···O4i	0.99	2.13	3.119(4)	176.3

[a] For the hydrogen bonds, the four values refer to the O–H, H···O, O···O separations (Å) and the O–H···O bond angle (°), respectively. Symmetry codes: (a) $y - x, 1 - x, z$; (b) $1/3 + x, x - y + 2/3, 1/6 + z$; (c) $2/3 - x + y, 1/3 + y, z - 1/6$; (d) $-y, x - y, z$; (e) $y - x, -x, 2x, -x, z$; (f) $2/3 - y, 1/3 - x, z - 1/6$; (g) $1/3 - y, 2/3 - x, 1/6 + z$; (h) $1/3 - x + y, y - 1/3, z + 1/6$; (i) $1 - x + y, 1 - x, z$.

zinc atoms make three Zn–O–As linkages; in addition a fourth bond is made to a tetrahedrally-coordinated O1 atom, resulting in OZn_4 centres (Fig. 2). The As atom forms the centre of a tetrahedral arsenate group [d_{av}(As1–O) = 1.683(2) Å] with all four O atoms involved in As–O–Zn bridges. The five distinct framework oxygen atoms divide into four Zn–O–As bridges [θ_{av} = 121.4°] and the tetrahedral (to four Zn) O1 species (site symmetry 3). Bond valence sum (BVS) calculations using the Brown formalism[16] for the framework cations yielded BVS(Zn1) = 2.02, BVS(Zn2) = 2.01, and BVS(As1) = 5.03, in good agreement with the expected values of 2.00 for Zn and 5.00 for As.

The framework connectivity in $Na_3Zn_4O(AsO_4)_3 \cdot 6H_2O$ results in a three-dimensional network of polyhedral 3-rings and 8-rings, as described previously.[1] The anionic $[Zn_4O(AsO_4)_3]^{3-}$ framework encloses a three-dimensional network of essentially orthogonal 8-ring windows propagating along $[2\bar{2}1]$, [241], and $[42\bar{1}]$ which interconnect roughly spherical cavities (atom-to-atom dimension ≈ 6.5 Å). An analysis of the volume not occupied by the framework $[Zn_4O(AsO_4)_3]^{3-}$ component of the structure with the CALC SOLV option[17] of PLATON indicated that 1023.4 $Å^3$ (36.9%) of the unit-cell volume is empty space, emphasising the zeolite-like nature of this material.

The extra-framework sodium cation is located in the vicinity of a framework 8-ring window. Its coordination is approximately octahedral [d_{av}(Na–O) = 2.510 (3) Å], assuming a maximum Na–O contact distance of 2.9 Å (Fig. 4). There are three Na–O_f (f = framework) and three Na–O_w (w = water) links. For the Na–O_w links, two are made to water molecules in one adjacent cage, and one to a water molecule in the other adjacent cage. The bond valence sum for Na of 0.95 (expected 1.00) indicates that the sodium bonding requirements are satisfied by this geometry.

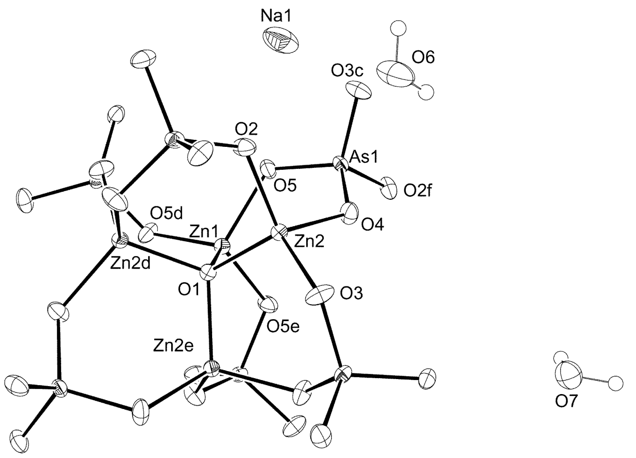

Fig. 2 ORTEP view of the building unit of $Na_3Zn_4O(AsO_4)_3 \cdot 6H_2O$ showing the atom-labelling scheme (50% thermal ellipsoids). Atoms labelled Zn2d *etc*. are symmetry generated with codes as in Table 1.

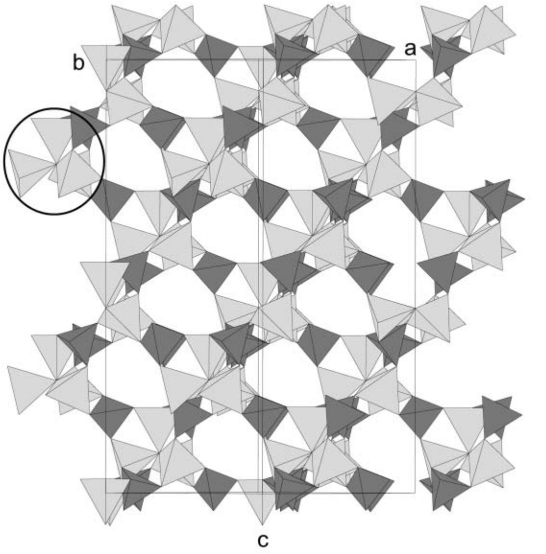

Fig. 3 Polyhedral view (ZnO_4 tetrahedra, light shading; AsO_4 tetrahedra, dark shading) of the framework of $Na_3Zn_4O(AsO_4)_3 \cdot 6H_2O$ with extra-framework species omitted for clarity. One grouping of four ZnO_4 tetrahedra is indicated by a circle.

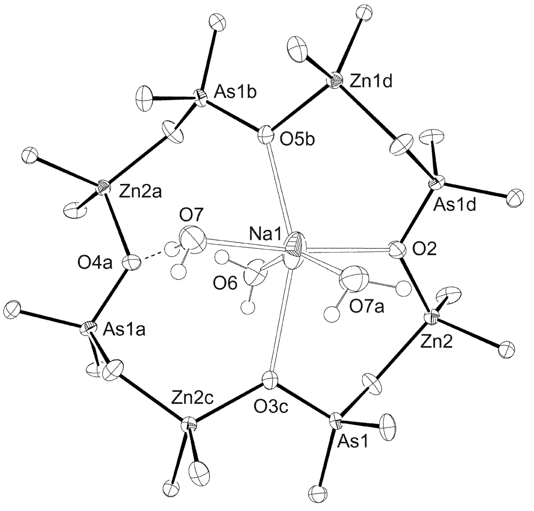

Fig. 4 View of a fragment of $Na_3Zn_4O(AsO_4)_3 \cdot 6H_2O$ showing the 6-fold sodium coordination and its location in the vicinity of a framework 8-ring window. Symmetry codes: (a) $y - x, -x, z$; (b) $1/3 + x, 2/3 + x - y, 1/6 + z$; (c) $2/3 - x + y, 1/3 + y, z - 1/6$; (d) $1/3 - y, 2/3 - x, 1/6 + z$.

The two extra-framework water molecules (oxygen atoms O6 and O7) occupy the spherical cages in this phase. Based on the present refinement of riding H atoms, three of the four hydrogen atoms appear to participate in O–H···O hydrogen bonds (Table 3). Two of these are water···framework interactions and one is a water···water link. Each cage contains four water molecules arranged as a distorted tetrahedron.

Discussion

The new sodium zinc arsenate hydrate, $Na_3Zn_4O(AsO_4)_3 \cdot 6H_2O$, has been prepared as reasonably large single crystals by a mild condition solution method and structurally and physically characterised. It crystallises as a rhombohedral variant of the $M_3Zn_4O(XO_4)_3 \cdot nH_2O$ family which were mostly made in polycrystalline form.[1] Here, the anionic $[Zn_4O(AsO_4)_3]^{3-}$ framework is charge balanced by three sodium cations accompanied by six extra-framework water molecules. As with other members of this family of phases,[1] preliminary ion-exchange experiments on $Na_3Zn_4O(AsO_4)_3 \cdot 6H_2O$ suggest facile replacement of Na^+ by Li^+. However, the ion-exchange process destroys the integrity of the starting single crystals, at least by the simple method tried here.

The most simple structural model for the $[Zn_4O(XO_4)_3]^{3-}$ framework component of this family of phases can be established in the cubic space group $P\bar{4}3m$, with a unit cell parameter $a_0 \approx 7.2$–7.9 Å, depending on chemical composition. In fact, to achieve a reasonable framework geometry, real $M_3Zn_4O(XO_4)_3 \cdot nH_2O$ frameworks show a superstructure with $a \approx 2a_0$ space group $F\bar{4}3c$.[1] For $Na_3Zn_4O(AsO_4)_3 \cdot 6H_2O$, the primitive rhombohedral unit-cell setting of $a = 10.919$ Å and $\alpha = 60.18°$ corresponds to a slight squashing of the body diagonal of the aristotype,[18] cubic, $F\bar{4}3c$ cell. The most important atomic displacement involves the univalent cation shifting towards the side of an 8-ring window, compared to its (sometimes disordered) occupancy of mid-point of an 8-ring window in the cubic cell.[1] $Na_3Zn_4O(AsO_4)_3 \cdot 6H_2O$ shares rhombohedral symmetry with $Na_3Zn_4O(PO_4)_3 \cdot 6H_2O$ and probably with $Li_3Zn_4O(PO_4)_3 \cdot 6H_2O$[19] although the sodium ion coordination is subtly different in the arsenate and the phosphate. Large-cation $M_3Zn_4O(XO_4)_3 \cdot nH_2O$ phases show a different, tetragonal distortion.[2] In $Na_3Zn_4O(PO_4)_3 \cdot 6H_2O$, the sodium ion coordination can be described as capped trigonal prismatic with two long Na–O bonds of 2.886 and 2.929 Å. The next-nearest Na···O contact in the arsenate is 3.147 Å. The degree of empty space[17] in the phosphate, 37.4% of the unit cell volume, is slightly greater than the equivalent value for the title compound.

An interesting effect is observed when comparing the 8-ring window sizes for the arsenate and the phosphate. A simplistic measure of window size can be obtained by adding the areas of the two triangles formed by the framework atoms (O4, O3, and O5), and (O2, O3, and O5) as labelled in Fig. 4. In this case, the area of the window in $Na_3Zn_4O(AsO_4)_3 \cdot 6H_2O$ at 15.1 $Å^2$ is significantly less than the area of 15.7 $Å^2$ for $Na_3Zn_4O(PO_4)_3 \cdot 6H_2O$. At first sight this is surprising because As–O bonds (typically 1.68 Å) are significantly longer than P–O bonds (1.53 Å). However, this window size reduction possibly correlates with the reduction in average Zn–O–X bond angle on going from phosphate to arsenate (126.9° and 121.4°, respectively). Thus, the framework of $Na_3Zn_4O(AsO_4)_3 \cdot 6H_2O$ can be regarded as more folded, or more collapsed, than that of the phosphate and the 8-ring window is consequently smaller. Almost the same bond angles and a similar pore-size-reduction effect (in this case a 6-ring) was seen when comparing the sodalite-type phases $Na_3Zn_3(AsO_4)_3 \cdot 4H_2O$ (Zn–O–As bond angle = 121.1°) and $Na_3Zn_3(PO_4)_3 \cdot 4H_2O$ (Zn–O–P angle = 126.1°).[20]

Dehydration of $Na_3Zn_4O(AsO_4)_3 \cdot 6H_2O$ leads to an irreversible framework transformation in which its 3-/8-ring topology completely reorganises into the hexagonal $NaZnAsO_4$ structure,[9] which consists only of 6-ring loops of tetrahedra and can be regarded as a stuffed tridymite (SiO_2) type structure constructed from sheets of 6^3 nets.[21] The Zn : As ratio has obviously changed from 4 : 3 in the title compound to 1 : 1 in hexagonal $NaZnAsO_4$. indicating that zinc oxide must also be formed in this transformation, presumably in poorly crystalline or amorphous form. A similar *chimie douce* tetrahedral framework rearrangement occurs when sodalite-type $Na_3Zn_3(AsO_4)_3 \cdot 4H_2O$ is dehydrated[14] to also result in hexagonal $NaZnAsO_4$.

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