

Arsenohopeite, a new zinc arsenate mineral from the Tsumeb mine, Namibia

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[Received 20 February 2012; Accepted 14 March 2012; Associate Editor: Stuart Mills]

ABSTRACT

Arsenohopeite, ideally $\text{Zn}_3(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$, is the arsenate analogue of hopeite, $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ (it is isostructural with α -hopeite). It was found as a single colourless to blue crystalline grain from the Tsumeb mine, Namibia. The holotype specimen is $\sim 1 \times 1 \times 1$ mm in size. Arsenohopeite is associated with tiny white fibres of an unidentified Zn- and As-bearing phase. It is orthorhombic, space group *Pnma*, with $a = 10.804(2)$, $b = 19.003(4)$, $c = 5.112(1)$ Å, $V = 1049.5(4)$ Å³ and $Z = 4$. Electron microprobe analysis yielded: ZnO 44.92, Fe₂O₃ 0.92, MnO 0.51, MgO 0.20, CuO 0.02, As₂O₅ 45.84 (wt.%). The empirical formula is $(\text{Zn}_{2.80}\text{Fe}_{0.06}\text{Mn}_{0.04}\text{Mg}_{0.03})_{\Sigma 2.93}(\text{As}_{1.01}\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$, based on 12 oxygen atoms. Optically, the mineral is biaxial negative, with $\alpha = 1.598(2)$, $\beta = 1.606(2)$, $\gamma = 1.613(2)$ (white light) and $2V_{\text{calc}} = 86^\circ$. It is not pleochroic or fluorescent. Arsenohopeite is translucent with a vitreous lustre. It is brittle, has an uneven fracture and (by analogy with hopeite) a cleavage that is perfect on {010}, good on {100} and poor on {001}. The calculated density is 3.420 g cm⁻³. The five strongest calculated powder diffraction lines are [d in Å (hkl): 9.502 (100)(020), 2.926 (95)(241), 4.937 (50)(011), 4.110 (48)(230) and 3.567 (31)(240)]. The crystal structure of arsenohopeite has been solved by direct methods and refined in space group *Pnma* to $R_1 = 0.0353$. Raman spectroscopy confirms the crystal-structure data and indicates the presence of weak hydrogen bonds.

KEYWORDS: arsenohopeite, hopeite, zinc arsenate, crystal structure, Raman spectroscopy, Tsumeb.

Introduction

In 2004 or 2005 one of the authors (FN) acquired a vial containing different grains, crystals and fragments of mineral species from the famous Tsumeb mine, Namibia as a result of an exchange of micromount minerals. The precise origin of the material and the exact locality in the Tsumeb mine is unknown. Among the vial contents was a conspicuous blue grain. This grain was selected for analysis by energy-dispersive X-ray spectrometry (EDS) on a scanning electron microscope (SEM) as its appearance was quite unusual; it

proved to be a new mineral species, $\text{Zn}_3(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$, the arsenate analogue of the zinc phosphate hydrate hopeite [$\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$]. The mineral and its name (arsenohopeite, for the relationship to hopeite) have been approved by the IMA Commission on New Minerals and Mineral Names (IMA 2010-069). Type material has been deposited in the collection of the Natural History Museum, Vienna, Austria (accession number N 8167).

Occurrence and paragenesis

Arsenohopeite is a supergene mineral formed by alteration of tennantite-rich ore in the oxidized zone of the famous Tsumeb mine, a dolostone-hosted polymetallic hydrothermal ore deposit at

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DOI: 10.1180/minmag.2012.076.3.11

Tsumeb, Namibia (Wilson, 1977; Keller, 1984; Gebhard, 1999). The vial containing the arsenohopeite includes other supergene zinc- and arsenic-bearing minerals that are typical of the mine including köttigite, adamite, leiteite and schneiderhöhnite. In addition, grains of quartz, carbonates and minor uninvestigated ore minerals are present. As all of these loose grains and fragments were stored together in the vial, the assumption that all the minerals initially occurred together in a single hand specimen is possible, but speculative. The arsenohopeite grain is only associated with tiny white fibres of an unidentified supergene Zn- and As-bearing phase.

More than thirty zinc or zinc-bearing arsenates and arsenites have been identified from the Tsumeb mine to date. Of these, Tsumeb is the type locality for reinerite, $\text{Zn}_3(\text{AsO}_3)_2$ (Geier and Weber, 1958), leiteite, ZnAs_2O_4 (Cesbron *et al.*, 1977; Ghose *et al.*, 1987), warikahnite, $\text{Zn}_3[(\text{H}_2\text{O})_2](\text{AsO}_4)_2$ (Keller *et al.*, 1979a), koritnigite, $\text{Zn}[\text{H}_2\text{O}]\text{HOAsO}_3$ (Keller *et al.*, 1979b), ianbruceite, $\text{Zn}_2\text{O}[\text{AsO}_3(\text{OH})](\text{H}_2\text{O})_{3.53}$ (Cooper *et al.*, 2011), and davidlloydite, $\text{Zn}_3(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$ (Hawthorne *et al.*, 2012). Furthermore, a new but as yet unnamed Zn-As-O-H species has been reported from Tsumeb (Blaß *et al.*, 2009), and also from the Friedrichsseggen mine, Bad Ems, Germany (Möhn *et al.*, 2009). The majority of the secondary Zn-As-O(-H) minerals from the Tsumeb mine were found in the prolific second oxidation zone and this is likely to be where the arsenohopeite was originally from.

Physical and optical properties

Arsenohopeite occurs as a single colourless to blue polycrystalline grain, with some indistinct crystal faces. The holotype grain is $\sim 1 \times 1 \times 1$ mm in size. The mineral is translucent and colourless in thin fragments. The blue colour has a streaky to cloudy distribution in fragments removed from the grain. Arsenohopeite has a white streak, vitreous lustre and a Mohs hardness of about 3. The tenacity is brittle, the cleavage (by analogy with hopeite) is perfect on {010}, good on {100} and poor on {001}. No twinning is present. A density of 3.42 g cm^{-3} was calculated from the empirical formula, and compares well with the X-ray density of 3.43 g cm^{-3} . A direct density measurement was not feasible because of the paucity of available material. The Gladstone–Dale compatibility index (Mandarino, 1981), based on the empirical formula, is 0.046 (good).

The optical properties were determined in white light. The mineral is colourless in plane-polarized light and it is not pleochroic. The refractive indices, measured with a spindle stage, are $\alpha = 1.598(2)$, $\beta = 1.606(2)$ and $\gamma = 1.613(2)$; birefringence is 0.015. Arsenohopeite is biaxial negative with $2V_{\text{calc}} = 86^\circ$ (a direct measurement of $2V$ was unsuccessful). The dispersion was not determined (fragments show normal interference colours). No fluorescence was observed in either short- or long-wave ultraviolet light.

Chemical Composition

A preliminary qualitative chemical analysis by energy-dispersive X-ray spectrometry (EDS) on a scanning electron microscope (SEM) revealed only zinc and arsenic. Quantitative chemical analyses by wavelength-dispersive spectrometry (WDS) were carried out using a Cameca SX 50 electron microprobe at the Zentrale Elektronen-Mikrosonde, Ruhr-Universität Bochum. Experimental conditions were an acceleration voltage of 15 kV, beam current of 7 nA and a beam diameter of $\sim 8 \mu\text{m}$. The following standards were used: synthetic ZnO (ZnK α), synthetic andradite (Fe), synthetic spessartine (Mn), synthetic pyrope (Mg), synthetic CuO (Cu) and arsenopyrite (AsL α). A wavelength-dispersive scan found no other elements with an atomic number greater than 8. The H_2O content was

TABLE 1. Analytical data for arsenohopeite.

Constituent	Mean composition (wt.%) [*]	Range	Standard deviation
ZnO	44.92	43.61–45.97	0.73
Fe ₂ O ₃	0.92	0.68–1.15	0.15
MnO	0.51	0.48–0.55	0.02
MgO	0.20	0.12–0.28	0.05
CuO	0.02	0.00–0.14	0.05
As ₂ O ₅	45.84	44.61–47.80	1.11
H ₂ O [†]	14.21		
Total	106.62 ^{**}		

^{*} Mean values of eight analyses.

^{**} The high oxide total in the electron-microprobe analysis is attributed to rapid partial dehydration of the sample under the electron beam (see text).

[†] Calculated on the basis of single-crystal X-ray data from stoichiometry.

calculated by stoichiometry from the results of the crystal structure analysis because there was insufficient material for a direct determination. The presence of water was confirmed by Raman spectroscopy (see below). Analytical data are given in Table 1. The high oxide total of the electron microprobe analysis of 106.62 wt.% is attributed to rapid partial dehydration of the sample under the electron beam (defocussing the beam did not improve the results). The empirical formula (based on 12 oxygen atoms) is $(\text{Zn}_{2.80}\text{Fe}_{0.06}\text{Mn}_{0.04}\text{Mg}_{0.03})_{\Sigma 2.93}(\text{As}_{1.01}\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$ (the Fe is assumed to be present as Fe^{3+}). The

possible presence of vacancies at the Zn1 site is discussed below. The ideal formula is $\text{Zn}_3(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$, which requires ZnO 44.72, As_2O_5 42.09, H_2O 13.19, total 100.00 wt.%.

X-ray diffraction and crystal structure

Single-crystal X-ray studies of arsenohopeite were carried out using a Nonius KappaCCD four-circle diffractometer equipped with a charge-coupled device (CCD) detector and a 300 μm diameter capillary-optics collimator to provide increased resolution. Intensity data were collected

TABLE 2. Crystallographic data and refinement parameters for arsenohopeite.

Crystal data	
Empirical formula	$(\text{Zn}_{2.80}\text{Fe}_{0.06}\text{Mn}_{0.04}\text{Mg}_{0.03})_{\Sigma 2.93}(\text{As}_{1.01}\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$
Crystal system	Orthorhombic
Space group	<i>Pnma</i>
Unit-cell parameters <i>a</i> , <i>b</i> , <i>c</i> (Å)	10.804(2), 19.003(4), 5.112(1)
Unit-cell volume (Å ³)	1049.5(4)
<i>Z</i>	4
Calculated density (g cm ⁻³)	3.43
Absorption coefficient (mm ⁻¹)	12.881
Crystal dimensions (mm)	0.07 × 0.07 × 0.08
Data collection	
Diffractometer	Nonius KappaCCD
Temperature (K)	293
Radiation, wavelength (Å)	$\text{MoK}\alpha$, 0.71073
θ range for data collection (°)	3.77–32.57
<i>h</i> , <i>k</i> , <i>l</i> ranges	±16, ±28, ±7
Axis, frame width (°), time per frame (s)	ϕ , ω , 1, 80
Total reflections collected	3550
Unique reflections (<i>R</i> _{int})	1953 (0.0384)
Unique reflections <i>F</i> > 4 σ (<i>F</i>)	1355
Data completeness to θ_{max}	0.996
Absorption correction method	multi-scan (Otwinowski <i>et al.</i> , 2003)
Structure refinement	
Refinement method	full-matrix least-squares on <i>F</i> ²
Weighting coefficients <i>a</i> , <i>b</i> *	0.045, 0.5
Data/restraints/parameters	1953/0/98
Extinction coefficient	0
<i>R</i> ₁ [<i>F</i> > 4 σ (<i>F</i>)], <i>wR</i> ₂ [<i>F</i> > 4 σ (<i>F</i>)]	0.0353, 0.0739
<i>R</i> ₁ all, <i>wR</i> ₂ all	0.0706, 0.0848
Goodness-of-fit on <i>F</i> ²	1.015
Largest diff. peak and hole (e Å ⁻³)	1.24, −0.82

$$R_{\text{int}} = (n/n - 1)^{1/2} [F_o^2 - F_o(\text{mean})^2] / \Sigma F_o^2$$

$$R_1 = \Sigma |F_o| - |F_c| / \Sigma |F_o|; wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2};$$

$$* \text{ weight } = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP], \text{ where } P = (\max(F_o^2, 0) + 2F_c^2) / 3;$$

$$\text{Goof} = \{ \Sigma [w(F_o^2 - F_c^2)^2] / (n - p) \}^{1/2}$$

where *n* is the number of reflections and *p* is the number of refined parameters.

TABLE 3. Fractional atom coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for arsenohopeite.

Atom	x/a	y/b	z/c	$U_{\text{equiv}}/U_{\text{iso}}^\dagger$
As	0.10007(4)	0.095516(19)	0.71834(7)	0.01728(12)
Zn1*	0.23741(6)	0.25	0.57469(13)	0.01912(17)
Zn2*	0.14543(4)	−0.00046(2)	0.20551(8)	0.01842(12)
O4	0.1407(3)	0.17731(15)	0.7895(5)	0.0299(7)
O5	0.0996(3)	0.08142(15)	0.3953(6)	0.0389(8)
O6	0.4619(3)	0.07907(15)	0.6452(6)	0.0290(6)
O7	0.1986(2)	0.03623(14)	0.8592(5)	0.0226(6)
OW1	0.1072(4)	0.25	0.2645(8)	0.0290(10)
OW2	0.3858(4)	0.25	0.8494(10)	0.0366(11)
OW3	0.3354(4)	0.17204(19)	0.3427(8)	0.0375(8)
H11	0.115(6)	0.290(4)	0.169(13)	0.09(2)
H21	0.462(9)	0.25	0.795(15)	0.06(3)
H31	0.380(8)	0.135(6)	0.373(17)	0.13(4)
H32	0.290(9)	0.145(6)	0.286(19)	0.14(4)

* Site occupancies are: $(\text{Zn}_{0.82}\text{Fe}_{0.08}\text{Mn}_{0.05}\text{Mg}_{0.05})$ for Zn1; and $\text{Zn}_{1.00}$ for Zn2 (see text).

† The parameter U_{equiv} is defined according to Fischer and Tillmanns (1988).

from a suitable fragment at room temperature. The crystal structure was solved by direct methods in space group $Pnma$ and refined using standard procedures (*SHELX97*; Sheldrick, 2008). For the final refinement steps, the model and atom labelling scheme of Whitaker (1978a) for hopeite were adopted as starting parameters. The final residual was $R_1(F) = 0.0353$. Crystal data and details of the structure refinement is presented in Table 2. The final positional and displacement parameters are given in Tables 3 and 4. Selected bond lengths are listed in Table 5. A crystallographic information file has been deposited with the Principal Editor of *Mineralogical Magazine*

and is available at www.minersoc.org/pages/e_journals/dep_mat.html.

The asymmetric unit contains two Zn sites, one As site, seven O sites and nominally six H sites. All except one of the hydrogen atoms could be located and freely refined (the O–H distances range between 0.77 and 0.91 Å) but the refined U_{iso} values were fairly large. Fixing either the U_{iso} values of the H atoms or restraining the O–H bond distances slightly worsened the results. The large U_{iso} values are considered a sign of weak hydrogen bonding (which is confirmed by Raman spectroscopy), and also an indirect effect of the metal-for-Zn substitution at the Zn1 site (see

TABLE 4. Anisotropic displacement parameters ($\text{\AA}^2$) for arsenohopeite.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
As	0.0202(2)	0.01588(19)	0.01579(19)	−0.00028(14)	0.00112(14)	0.00072(15)
Zn1	0.0181(3)	0.0218(3)	0.0175(3)	0.0	0.0016(2)	0.0
Zn2	0.0175(2)	0.0217(2)	0.0160(2)	−0.00066(17)	0.00024(17)	−0.00016(16)
O4	0.0461(19)	0.0187(14)	0.0247(15)	−0.0050(12)	0.0138(13)	−0.0117(12)
O5	0.074(3)	0.0271(16)	0.0152(15)	−0.0048(12)	−0.0058(15)	0.0166(15)
O6	0.0194(14)	0.0261(14)	0.0416(17)	0.0077(13)	−0.0045(13)	−0.0025(11)
O7	0.0191(14)	0.0303(15)	0.0184(12)	0.0058(11)	0.0053(11)	0.0041(11)
OW1	0.029(2)	0.034(3)	0.023(2)	0.0	−0.0035(18)	0.0
OW2	0.020(2)	0.055(3)	0.035(3)	0.0	−0.004(2)	0.0
OW3	0.036(2)	0.0329(19)	0.043(2)	0.0027(16)	0.0028(16)	0.0090(15)

TABLE 5. Selected bond distances (Å) for the coordination polyhedra of arsenohopeite.

Zn1—O4 (× 2)	2.051(3)	As—O4	1.655(3)
—Ow1	2.120(4)	—O5	1.673(3)
—Ow2	2.131(5)	—O6	1.677(3)
—Ow3 (× 2)	2.173(4)	—O7	1.709(3)
<Zn1—O>	2.117	<As—O>	1.679
Zn2—O5	1.899(3)		
—O6	1.916(3)		
—O7	1.979(3)		
—O7	1.988(3)		
<Zn2—O>	1.946		
Hydrogen bonds*			
OW1—H11	0.91(10)	OW1...O4	2.817(5)
OW2—H21	0.87(9)	OW2...O4 (× 2)	3.161(5)
OW3—H31	0.86(11)	OW3...O6	2.717(5)
OW3—H32	0.77(10)	OW3...O5	3.087(5)

* The DHA angles are in a close range between 141 and 145°.

below). The Zn1 site is octahedrally coordinated by four H₂O groups and two O atoms, whereas the Zn2 site is tetrahedrally coordinated by four O atoms belonging to AsO₄ groups. The <Zn1—O> distance of 2.117 Å, is significantly smaller than the corresponding 2.171 Å reported by Hill and Jones (1976) in hopeite but slightly larger than the 2.099 Å reported by Whitaker (1978b). The <Zn2—O> distance of 1.946 Å is smaller than the same distance in hopeite (2.106 Å, Hill and Jones, 1976; 1.963 Å, Whitaker, 1978b). These differences are thought to reflect both the minor metal-for-Zn substitution and the indirect influence of the weaker As—O bonds on neighbouring Zn-centred polyhedra.

Corner linkage between the polyhedra results in a framework reinforced by weak hydrogen bonds (>2.7 Å), as shown in Fig. 1. Table 5 lists all the inferred hydrogen-bond distances. The relationship to the hopeite varieties α -hopeite and β -hopeite in the context of the hydrogen-bonding scheme is discussed further below.

The minor non-negligible impurities (Fe, Mn and Mg) were assigned to the octahedrally coordinated Zn1 site because in cation-substituted

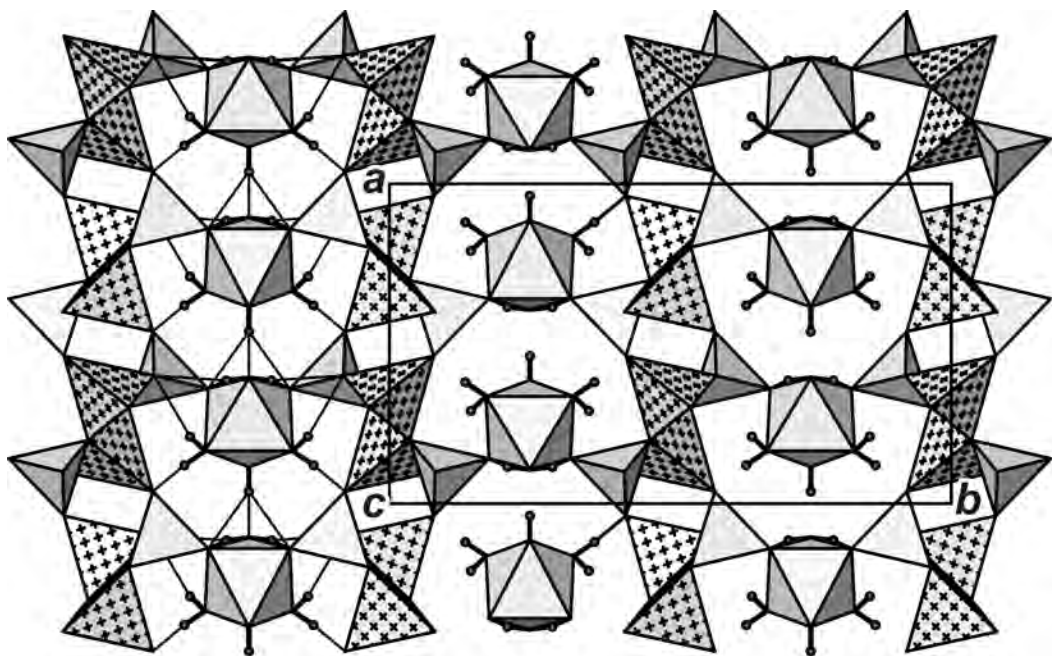


FIG. 1. Polyhedral representation of the crystal structure of arsenohopeite along the *c* axis (pointing down). The Zn1O₆ octahedra share corners with AsO₄ tetrahedra which, in turn, corner-link to Zn2O₄ tetrahedra (marked with crosses); hydrogen atoms are shown as small spheres, hydrogen bonds as thin lines (only shown on the left-hand part of the figure). The unit cell is outlined.

synthetic hopeite, the substituents (Mg, Co and Ni) unequivocally occupy only the Zn1 site (Antraptseva and Shchegrov, 1983, 1984; Haussühl *et al.*, 1991; Wu *et al.*, 2005a,b). This assignment is also supported by the refined occupancies of the two Zn sites: Zn1 = 0.969(3) and Zn2 = 0.989(2).

The impurity content of the Zn1 site was therefore fixed according to the results of the electron-microprobe analysis ($\text{Zn}_{0.82}\text{Fe}_{0.08}\text{Mn}_{0.05}\text{Mg}_{0.05}$) and the apparent presence of minor vacancies was neglected. In the empirical formula, the sum of the cation sites of 2.93 is lower than the ideal value of 3.00. As the minor Fe in arsenohopeite is assumed to be Fe^{3+} (as it formed as a secondary mineral in oxidizing conditions), a small number of vacancies would be required to counterbalance the higher charge of the Fe^{3+} cations. In order to obtain a completely charge-balanced formula, one would have to assume either partial protonation of the AsO_4 group or vacancies at the As site. A similar cation deficiency was also

observed by Hill and Jones (1976) for the Zn1 site in natural hopeite, but these authors did not discuss possible charge-balance schemes.

Due to the exceedingly small amount of material available, the X-ray powder diffraction pattern was not measured. Calculated powder data (with d values in Å for $\text{CuK}\alpha$, $\lambda = 1.5418$ Å, based on the crystal-structure determination) are given in Table 6.

Raman spectroscopy

Single-crystal Raman spectra of arsenohopeite were recorded in the wavenumber range 4000 to 150 cm^{-1} using a Renishaw M1000 MicroRaman imaging system coupled to a Leica DMLM optical microscope at a laser wavelength of 633 nm (using unpolarized laser light in 180° backscatter mode at a resolution of $\pm 2\text{ cm}^{-1}$ and a minimum lateral resolution of $\sim 2\text{ }\mu\text{m}$ in random sample orientation). The crystals were stable under the laser beam and the spectra are of

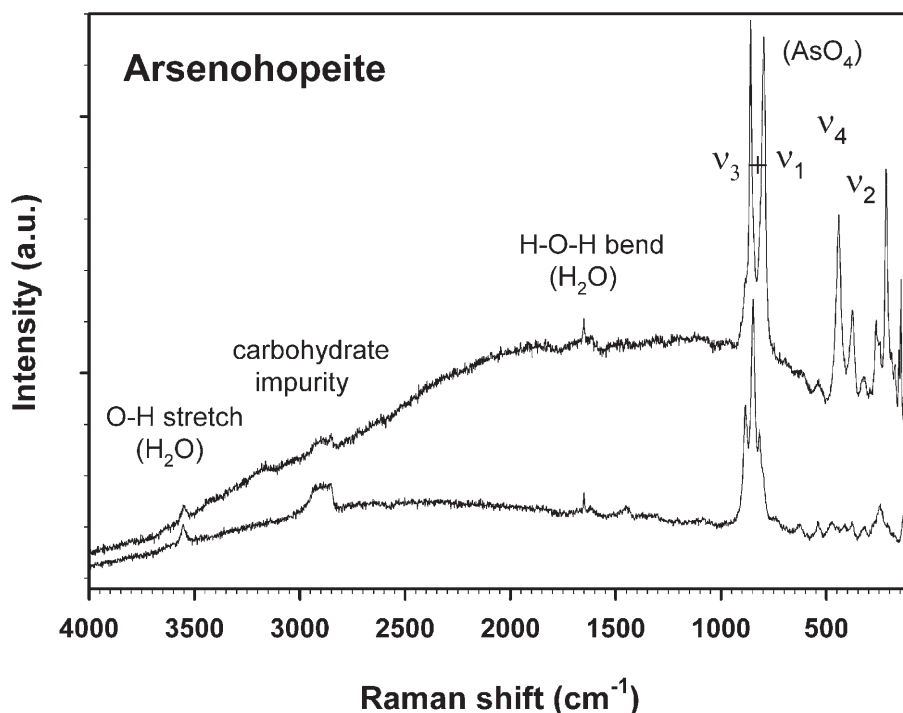


FIG. 2. Two single-crystal Raman spectra of arsenohopeite. The spectra are shown as recorded, i.e. with no background correction or smoothing applied. For wavenumbers of the bands see text. The small broad band at $\sim 2900\text{ cm}^{-1}$ and the very small sharp band at 1651 cm^{-1} are attributed to a contamination resulting from a thin film of Apiezon high-vacuum grease that was used for fixing the arsenohopeite grain. The second band might also be explained by a combination band involving v_1 and/or v_3 .

TABLE 6. Calculated X-ray powder diffraction data for arsenohopeite.

d_{calc} (Å) [†]	I_{calc} *	hkl	d_{calc} (Å) [†]	I_{calc} *	hkl
9.502	100	020	2.036	8	322
5.402	7	200	2.022	1	451
5.196	31	210	2.001	11	281
4.937	50	011	1.990	1	501
4.751	9	040	1.989	1	062
4.696	7	220	1.980	2	511
4.490	28	111	1.967	3	290
4.156	2	121	1.956	1	162
4.110	48	230	1.952	1	091
3.978	28	031	1.948	1	521
3.733	2	131	1.915	1	470
3.713	2	201	1.909	1	342
3.567	31	240	1.900	4	0100
3.458	22	221	1.899	1	<u>531</u>
3.312	2	141	1.867	6	262
3.203	12	231	1.857	14	402
3.167	3	060	1.848	1	412
3.108	2	250	1.836	1	541
3.050	7	051	1.835	3	291
2.944	1	301	1.834	1	172
2.935	2	151	1.822	2	422
2.926	95	241	1.793	1	471
2.909	1	311	1.793	1	2100
2.812	2	321	1.784	1	480
2.732	4	260	1.782	1	432
2.701	19	400	1.769	2	620
2.674	1	410	1.763	1	551
2.670	22	331	1.760	3	272
2.656	2	251	1.741	1	362
2.612	6	161	1.740	1	082
2.598	16	420	1.732	3	630
2.556	21	002	1.729	1	442
2.503	1	341	1.718	5	182
2.487	2	102	1.716	3	391
2.485	3	430	1.692	2	611
2.468	14	022	1.684	2	481
2.426	5	270	1.684	2	640
2.410	21	261	1.672	1	621
2.398	7	071	1.664	1	490
2.388	1	401	1.657	1	123
2.375	4	080	1.653	1	372
2.370	1	411	1.646	5	033
2.341	6	171	1.640	1	631
2.328	1	351	1.627	1	133
2.316	7	421	1.626	4	522
2.315	1	132	1.619	1	213
2.310	1	202	1.618	1	1111
2.294	5	212	1.605	1	<u>571</u>
2.245	2	222	1.599	9	641
2.235	8	431	1.597	1	532
2.204	4	142	1.587	2	143
2.202	1	450	1.584	7	0120
2.192	1	271	1.582	2	491
2.174	3	280	1.565	9	660
2.171	8	232	1.559	2	292
2.156	7	361	1.554	7	<u>4100</u>
2.072	1	312			
2.055	2	460			

[†] The eight strongest reflections are listed in bold face.

* Only reflections with $I_{\text{calc}} \geq 1$ are listed.

reasonable quality, although they have a relatively high background. Two representative spectra are shown in Fig. 2. The strongest Raman bands in the spectra appear in a narrow region at 884, 860, 848, 818 and 797 cm^{-1} (intensities are variable depending on orientation of the measured grain), and can be attributed to the ν_1 and ν_3 vibrational modes of the AsO_4 ion. The next strongest bands are in the region between 540 and 150 cm^{-1} . The strong bands at 443 and 376 cm^{-1} (asymmetric shape) are assigned to the ν_4 and ν_2 vibrational modes of the AsO_4 ion, respectively. The very small and somewhat broad bands at 530 and $\sim 324 \text{ cm}^{-1}$ may also belong to these modes. Distinct bands at 264, 249, 215, 191, 175, 156 and 146 cm^{-1} are probably caused by vibrations of the ZnO_6 and ZnO_4 polyhedra and by lattice modes. A weak band at 3553 cm^{-1} and a very weak, broad band at $\sim 3162 \text{ cm}^{-1}$ are due to O–H stretching vibrations in water molecules. The observed frequencies correspond to approximate

O...O (donor–acceptor) bond lengths of 2.70 and $\sim 2.9 \text{ \AA}$ (Libowitzky, 1999), respectively, which is in good agreement with the results of the single-crystal structure analysis. These bond lengths correspond to weak hydrogen bonds. A very weak sharp band at 1651 cm^{-1} and a very weak broad band at $\sim 1619 \text{ cm}^{-1}$ are attributed to H–O–H bending vibrations of the water molecules. However, the first sharp band might also be a combination band involving ν_1 and/or ν_3 .

Relationship to other species

Arsenohopeite is isostructural with its phosphate analogue, hopeite [$\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$]. A comparison of both species is given in Table 7. The crystal structure of hopeite is well characterized, based on studies of both natural and synthetic material (Liebau, 1962, 1965; Kawahara *et al.*, 1973; Hill and Jones, 1976; Whitaker, 1978*a,b*; Pawlin and Trettin, 1999; Herschke *et al.*, 2004;

TABLE 7. Comparison of hopeite and arsenohopeite.

Mineral	Hopeite	Arsenohopeite
Reference	Hill and Jones (1976); Palache <i>et al.</i> (1951)	This work
Formula	$\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$	$\text{Zn}_3(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$
a ($\text{\AA}$)	10.597(3)	10.804(2)
b ($\text{\AA}$)	18.318(8)	19.003(4)
c ($\text{\AA}$)	5.031(1)	5.112(1)
V ($\text{\AA}^3$)	976.6	1049.5
$a:b:c$	0.5785:1:0.2746	0.5685:1:0.2690
Symmetry	Orthorhombic	Orthorhombic
Space group	<i>Pnma</i>	<i>Pnma</i>
Z	4	4
Six strongest lines in the powder pattern [d (I) hkl]	2.852 (100) 241, 9.153 (50) 020, 4.577 (50) 040, 3.388 (40) 221, 4.411 (38) 111, 3.462 (27) 240	9.502 (100) 020, 2.926 (95) 241, 4.937 (50) 011, 4.110 (48) 230, 5.196 (31) 210, 3.567 (31) 240
D_{calc} (g cm^{-3})	3.116	3.434
Mohs hardness	3–3.5	~ 3
α	1.572–1.574	1.598(2)
β	1.582–1.591	1.606(2)
γ	1.590–1.592	1.613(2)
Birefringence	0.018	0.015
$2V_{\text{calc}}$	26° to 82°	86°
Optical character	biaxial (–)	biaxial (–)
Megascopic colour	yellow, white, colourless, grey or brown	colourless, white, blue to deep blue
Luminescence	not fluorescent	not fluorescent
Lustre	vitreous, pearly	vitreous
Diaphaneity	transparent, translucent	translucent
Streak	white	white

Parhi *et al.*, 2008). The detailed study of hopeite crystals from the Kabwe (Broken Hill) deposit in Zambia by Spencer (1908) showed that two varieties of the mineral, α -hopeite and β -hopeite, exist. These have slightly different optical properties, densities, thermal behaviour (e.g. Nikonenko *et al.*, 1985) and infrared spectra (Herschke *et al.*, 2004), but identical X-ray powder diffraction patterns. Therefore, both varieties are considered to be synonymous with hopeite. The α -variety is the more stable form and can be synthesized from aqueous solutions at temperatures of 90–100°C (e.g. Kawahara *et al.*, 1972, Herschke *et al.*, 2004); β -hopeite is less stable and can be obtained at lower temperatures (20°C). The very small difference between the crystal structures of the two varieties was recently revealed by Herschke *et al.* (2004) who demonstrated that they are distinguished by the position of two hydrogen atoms. Both of these hydrogen atoms belong to a single water molecule which is involved in locally different hydrogen-bonding schemes. This small deviation in the atomic arrangement results in a slightly higher density in the more stable α -hopeite in comparison to β -hopeite (3.130 and 3.122 g cm⁻³, respectively). The question as to whether arsenohopeite is the equivalent of α -hopeite or β -hopeite automatically arises. The hydrogen-bonding scheme in arsenohopeite clearly shows its equivalence with α -hopeite.

Deuterated hopeite and its thermal expansion were characterized by Schofield *et al.* (2007). A synthetic Co-analogue of hopeite and its crystal structure have been reported recently (Lee *et al.*, 2008). Synthetic arsenohopeite has not been described and there is no modern study of the ZnO–As₂O₅–H₂O system. However, a triclinic polymorph of arsenohopeite is known as a synthetic compound (Nabar and Patkar, 1974). Furthermore, a triclinic copper-bearing Zn₃(AsO₄)₂·4H₂O has recently been described as the new mineral species davidlloydite (Hawthorne *et al.*, 2012). Its crystal structure is very closely related to that of parahopeite, triclinic Zn₃(PO₄)₂·4H₂O (Kumbasar and Finney, 1968; Chao, 1969). Two other synthetic zinc arsenates have been reported recently, but are presently unknown as minerals: Zn₉(AsO₄)₆·4H₂O (triclinic; Feng *et al.*, 1997; Jensen *et al.*, 1998) and β -Zn₃(AsO₃)₂ (monoclinic, a polymorph of reinerite; Harrison, 2010).

Arsenohopeite has the same stoichiometry as rollandite, Cu₃(AsO₄)₂·4H₂O (Sarp and Černý,

2000; orthorhombic, *Pnma*, but with an unrelated structure) and sterlinghillite, Mn₃(AsO₄)₂·4H₂O (Dunn, 1981), whose structure is unknown.

Acknowledgements

The authors are grateful to the two referees F. Cámara and D. Atencio, and to Associate Editor Stuart Mills for helpful comments on the manuscript.

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Fe1 0.0181(3) 0.0218(3) 0.0175(3) 0.000 0.0016(2) 0.000
Mn1 0.0181(3) 0.0218(3) 0.0175(3) 0.000 0.0016(2) 0.000
Mg1 0.0181(3) 0.0218(3) 0.0175(3) 0.000 0.0016(2) 0.000
Zn2 0.0175(2) 0.0217(2) 0.0160(2) -0.00066(17) 0.00024(17) -0.00016(16)
O4 0.0461(19) 0.0187(14) 0.0247(15) -0.0050(12) 0.0138(13) -0.0117(12)
O5 0.074(3) 0.0271(16) 0.0152(15) -0.0048(12) -0.0058(15) 0.0166(15)
O6 0.0194(14) 0.0261(14) 0.0416(17) 0.0077(13) -0.0045(13) -0.0025(11)
O7 0.0191(14) 0.0303(15) 0.0184(12) 0.0058(11) 0.0053(11) 0.0041(11)
OW1 0.029(2) 0.034(3) 0.023(2) 0.000 -0.0035(18) 0.000
OW2 0.020(2) 0.055(3) 0.035(3) 0.000 -0.004(2) 0.000
OW3 0.036(2) 0.0329(19) 0.043(2) 0.0027(16) 0.0028(16) 0.0090(15)

_geom_special_details

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All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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loop_

_geom_bond_atom_site_label_1

_geom_bond_atom_site_label_2

_geom_bond_distance

_geom_bond_site_symmetry_2

_geom_bond_publ_flag

As O4 1.655(3) . ?

As O5 1.673(3) . ?

As O6 1.677(3) 6_557 ?

As O7 1.709(3) . ?

Zn1 O4 2.051(3) . ?

Zn1 O4 2.051(3) 7_565 ?

Zn1 OW1 2.120(4) . ?

Zn1 OW2 2.131(5) . ?

Zn1 OW3 2.173(4) . ?

Zn1 OW3 2.173(4) 7_565 ?

Zn2 O5 1.899(3) . ?

Zn2 O6 1.916(3) 2_554 ?

Zn2 O7 1.979(3) 2_554 ?

Zn2 O7 1.988(3) 1_554 ?

O6 As 1.677(3) 6_657 ?

O6 Zn2 1.916(3) 2 ?

O7 Zn2 1.979(3) 2 ?

O7 Zn2 1.988(3) 1_556 ?

OW1 H11 0.91(7) . ?

OW2 H21 0.87(9) . ?

OW3 H31 0.86(11) . ?

OW3 H32 0.77(10) . ?

loop_

_geom_angle_atom_site_label_1

_geom_angle_atom_site_label_2

_geom_angle_atom_site_label_3

_geom_angle

_geom_angle_site_symmetry_1

_geom_angle_site_symmetry_3

_geom_angle_publ_flag

O4 As O5 111.60(15) . . ?

O4 As O6 108.63(14) . 6_557 ?

O5 As O6 112.21(17) . 6_557 ?

O4 As O7 111.18(15) . . ?

O5 As O7 108.19(14) . . ?

O6 As O7 104.86(13) 6_557 . ?

O4 Zn1 O4 84.67(16) . 7_565 ?

O4 Zn1 OW1 93.57(13) . . ?

O4 Zn1 OW1 93.57(13) 7_565 . ?

O4 Zn1 OW2 91.75(14) . . ?

O4 Zn1 OW2 91.75(14) 7_565 . ?

OW1 Zn1 OW2 172.80(19) . . ?

O4 Zn1 OW3 94.67(13) . . ?

O4 Zn1 OW3 178.51(15) 7_565 . ?

OW1 Zn1 OW3 85.14(15) . . ?

OW2 Zn1 OW3 89.60(15) . . ?

O4 Zn1 OW3 178.51(15) . 7_565 ?

O4 Zn1 OW3 94.67(13) 7_565 7_565 ?

OW1 Zn1 OW3 85.14(15) . 7_565 ?

OW2 Zn1 OW3 89.60(15) . 7_565 ?

OW3 Zn1 OW3 85.9(2) . 7_565 ?

O5 Zn2 O6 124.25(14) . 2_554 ?

O5 Zn2 O7 107.49(13) . 2_554 ?

O6 Zn2 O7 108.15(12) 2_554 2_554 ?

O5 Zn2 O7 104.06(13) . 1_554 ?

O6 Zn2 O7 107.78(12) 2_554 1_554 ?

O7 Zn2 O7 103.17(8) 2_554 1_554 ?

As O4 Zn1 130.52(15) . . ?

As O5 Zn2 129.39(17) . . ?

As O6 Zn2 128.12(16) 6_657 2 ?

As O7 Zn2 126.12(14) . 2 ?

As O7 Zn2 115.23(14) . 1_556 ?

Zn2 O7 Zn2 118.63(13) 2 1_556 ?

Zn1 OW1 H11 110(4) . . ?

Zn1 OW2 H21 120(5) . . ?

Zn1 OW3 H31 136(6) . . ?

Zn1 OW3 H32 111(8) . . ?

H31 OW3 H32 83(9) . . ?

loop_

_geom_hbond_atom_site_label_D

_geom_hbond_atom_site_label_H

_geom_hbond_atom_site_label_A

_geom_hbond_distance_DH

_geom_hbond_distance_HA

_geom_hbond_distance_DA

_geom_hbond_angle_DHA

_geom_hbond_site_symmetry_A

OW3 H31 O6 0.86(11) 1.96(10) 2.717(5) 145(9) .

OW3 H32 O5 0.77(10) 2.45(10) 3.087(5) 141(9) .

OW2 H21 O4 0.87(9) 2.41(8) 3.161(5) 144.6(15) 4_556

OW2 H21 O4 0.87(9) 2.41(8) 3.161(5) 144.6(15) 6_657

_diffn_measured_fraction_theta_max 0.996

_diffn_reflns_theta_full 32.57

_diffn_measured_fraction_theta_full 0.996

_refine_diff_density_max 1.244

_refine_diff_density_min -0.824

_refine_diff_density_rms 0.205