

The crystal structure of arsentsumebite, $\text{Pb}_2\text{Cu}[(\text{As}, \text{S})\text{O}_4]_2(\text{OH})$

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With 2 Figures

Received June 24, 2000;

revised version accepted February 8, 2001

Summary

The crystal structure of arsentsumebite, ideally, $\text{Pb}_2\text{Cu}[(\text{As}, \text{S})\text{O}_4]_2(\text{OH})$, monoclinic, space group $P2_1/m$, $a = 7.804(8)$, $b = 5.890(6)$, $c = 8.964(8)$ Å, $\beta = 112.29(6)^\circ$, $V = 381.2$ Å³, $Z = 2$, $d_{\text{calc.}} = 6.481$ has been refined to $R = 0.053$ for 898 unique reflections with $I > 2\sigma(I)$. Arsentsumebite belongs to the brackebuschite group of lead minerals with the general formula $\text{Pb}_2\text{Me}(\text{XO}_4)_2(\text{Z})$ where $\text{Me} = \text{Cu}^{2+}$, Mn^{2+} , Zn^{2+} , Fe^{2+} , Fe^{3+} ; $\text{X} = \text{S}$, Cr , V , As , P ; $\text{Z} = \text{OH}$, H_2O . Members of this group include tsumebite, $\text{Pb}_2\text{Cu}(\text{SO}_4)(\text{PO}_4)(\text{OH})$, vauquelinite, $\text{Pb}_2\text{Cu}(\text{CrO}_4)(\text{PO}_4)(\text{OH})$, brackebuschite, $\text{Pb}_2(\text{Mn}, \text{Fe})(\text{VO}_4)_2(\text{OH})$, arsenbrackebuschite, $\text{Pb}_2(\text{Fe}, \text{Zn})(\text{AsO}_4)_2(\text{OH}, \text{H}_2\text{O})$, fornacite, $\text{Pb}_2\text{Cu}(\text{AsO}_4)(\text{CrO}_4)(\text{OH})$, and feinglosite, $\text{Pb}_2(\text{Zn}, \text{Fe})[(\text{As}, \text{S})\text{O}_4]_2(\text{H}_2\text{O})$. Arsentsumebite and all other group members contain $M = M-T$ chains where $M = M$ means edge-sharing between MO_6 octahedra and $M-T$ represents corner sharing between octahedra and XO_4 tetrahedra. A structural relationship exists to tsumcorite, $\text{Pb}(\text{Zn}, \text{Fe})_2(\text{AsO}_4)_2(\text{OH}, \text{H}_2\text{O})_2$ and tsumcorite-group minerals $\text{Me}(1)\text{Me}(2)_2(\text{XO}_4)_2(\text{OH}, \text{H}_2\text{O})_2$.

Introduction

The rare hypogene sulphato-arsenate of lead and copper, arsentsumebite, $\text{Pb}_2\text{Cu}[(\text{As}, \text{S})\text{O}_4]_2(\text{OH})$, was discovered in Tsumeb, Namibia (Bideaux et al., 1966). The X-ray diffraction study of arsentsumebite revealed that the mineral is monoclinic, with $a = 8.85$, $b = 5.92$, $c = 7.84$ Å, $\beta = 112.6^\circ$; it is a member of the brackebuschite group. The crystal structure of brackebuschite, $\text{Pb}_2\text{Mn}(\text{VO}_4)_2(\text{H}_2\text{O})$, was determined by Donaldson and Barnes (1955) and redefined as $\text{Pb}_2(\text{Mn}^{3+}, \text{Fe}^{3+})(\text{VO}_4)_2(\text{OH})$ by Foley et al. (1997). Nichols (1966) mentioned the most likely

formula of tsumebite to be $\text{Pb}_2\text{Cu}(\text{PO}_4)(\text{SO}_4)(\text{OH})$. However, the atomic coordinates, interatomic distances and some other important structural data were not reported in this abstract. Later on this information was given by *Fanfani and Zanazzi* (1967). Secondary lead minerals that belong to the brackebuschite group, i.e., tsumebite, $\text{Pb}_2\text{Cu}(\text{SO}_4)(\text{PO}_4)(\text{OH})$, vauquelinite, $\text{Pb}_2\text{Cu}(\text{CrO}_4)(\text{PO}_4)(\text{OH})$, brackebuschite, $\text{Pb}_2(\text{Mn, Fe})(\text{VO}_4)_2(\text{H}_2\text{O})$, and fornacite, $\text{Pb}_2\text{Cu}(\text{AsO}_4)(\text{CrO}_4)(\text{OH})$, according to their structural similarity, can be considered as members of a series with general formula $\text{Pb}_2\text{Me}(\text{XO}_4)_2(\text{Z})$ where $\text{Me} = \text{Cu}^{2+}, \text{Mn}^{2+}, \text{Zn}^{2+}, \text{Fe}^{2+}, \text{Fe}^{3+}$; $\text{X} = \text{S, Cr, V, As, P}$; $\text{Z} = \text{OH, H}_2\text{O}$ (*Fanfani and Zanazzi*, 1967). Later on, this group was enlarged by the addition of arsenbrackebuschite, $\text{Pb}_2(\text{Fe, Zn})(\text{AsO}_4)_2(\text{OH, H}_2\text{O})$, the arsenate analogue of brackebuschite (*Abraham et al.*, 1978; *Hofmeister and Tillmanns*, 1978); in 1997 feinglosite, $\text{Pb}_2(\text{Zn, Fe})[(\text{As, S})\text{O}_4]_2(\text{H}_2\text{O})$ was described by *Clark et al.* (1997) and recently *Gurbanova et al.* (2001) reported the structure of new unnamed mineral discovered in the outcrops of the mine Venus (Sierra de Cordoba, Argentina): $\text{Pb}_2\text{Fe}(\text{VO}_4)_2(\text{OH})$. Apart from lead containing members of the brackebuschite group there are also three other structurally related minerals, i.e., gamagarite, $\text{Ba}_2(\text{Fe}^{3+}, \text{Mn})(\text{VO}_4)_2(\text{OH, H}_2\text{O})$ (*Harlow et al.*, 1984), goedkenite, $(\text{Sr, Ca})_2\text{Al}(\text{PO}_4)_2(\text{OH})$ (*Moore et al.*, 1975) and bearthite, $\text{Ca}_2\text{Al}(\text{PO}_4)_2(\text{OH})$ (*Chopin et al.*, 1993). Although all these minerals have similar stoichiometries, they are characterized by different coordination spheres of Pb atoms, sizes of tetrahedral complexes, etc. In this respect, the structure investigation of arsentsumebite, $\text{Pb}_2\text{Cu}[(\text{As, S})\text{O}_4]_2(\text{OH})$, which is the aim of the present study, expands our knowledge of the correlation between the compositions and the structures of these chemically related minerals.

Experimental

The investigated sample of arsentsumebite was found in the oxidation zone of the Berezovskoye gold deposit, Middle Urals, Russia. It was the first discovery of arsentsumebite in Russia (*Kleimenov et al.*, 1998). It occurs in voids of quartz-reefs from near-surface parts of the deposit that contain rich sulphide mineralisation: mainly pyrite, galena and fahlore of intermediate tennantite–tetrahedrite composition. All sulphides are almost completely oxidised. Pyrite and fahlore are replaced by cavernous aggregates of goethite, malachite and bindheimite, the voids of which host several arsenates: mimetite, beudantite, gartrellite, duftite, cornwallite and arsentsumebite. Arsentsumebite shows platy prismatic semitransparent green–blue crystals with maximum dimensions 3×2 mm.

The averaged results of electron microprobe analyses (Table 1) correspond to the chemical formula $\text{Pb}_{2.19}(\text{Cu}_{1.16}\text{Fe}_{0.03})[(\text{As}_{1.14}\text{P}_{0.01})\text{S}_{0.75}\text{O}_8](\text{OH})_{1.01}$. H_2O content was not determined directly but the presence of OH-groups was shown by IR spectroscopic data.

A single crystal with approximate linear dimensions $0.1 \times 0.1 \times 0.06$ mm was selected for the X-ray data collection at room temperature on a Nonius Kappa CCD diffractometer up to $\sin\theta/\lambda < 0.7 \text{ \AA}^{-1}$. An absorption correction ($\mu = 51.4 \text{ mm}^{-1}$) was performed according to the shape of the crystal (transmission factors ranging from 0.07 to 0.03; Rint 0.10 and 0.07 before and after the correction, respectively). The program JANA98 (*Petricek and Dusek*, 1998) was utilised in the structure refinement.

Table 1. *Chemical data for arsentsumebite**

Component	PbO	CuO	ZnO	FeO	P ₂ O ₅	As ₂ O ₅	CrO ₃	SO ₃	Σ
Average content	61.85	11.75	0.03	0.32	0.09	16.54	0.06	7.61	98.25

*Average chemical composition of arsentsumebite calculated using 4 electron microprobe analyses (Camebax SX 50, wavelength dispersion, 15 kv, 2 nA, beam diameter 2–3 microns). No chemical zoning and no destruction of sample was observed. The following standards were used: CuO (synth); mimetite, $\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$; BaSO_4 (synth); ZnS (synth); andradite, $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$; $\text{Ca}_5(\text{PO}_4)_3\text{F}$ (synth) and Cr_2O_3 (synth)

Table 2. *Experimental details of the structure refinement of arsentsumebite*

Chemical formula	$\text{Pb}_2\text{Cu}[(\text{As}, \text{S})\text{O}_4]_2(\text{OH})$
Formula weight	744.22
Radiation and wavelength, Å	MoK_α ; 0.71073
Crystal system	Monoclinic
Space group; Z	$P2_1/m$; 2
Unit cell dimensions, Å	$a = 7.804(8)$, $b = 5.890(6)$, $c = 8.964(8)$; $\beta = 112.29(6)^\circ$
Unit cell volume, Å ³	381.2
$F(000)$	632
Density (calc.), g/cm ³	6.481
Index ranges	$-10 \leq h \leq 9$, $-7 \leq k \leq 7$, $-11 \leq l \leq 11$
Collected reflections	1623
Independent reflections with $I > 2\sigma(I)$	898
Refinement method	full-matrix least-squares on F^2
R for observed reflections (F)	0.0540
wR for observed reflections (F^2)	0.1311
Largest diff. peak and hole	3.52 and $-2.11 \text{ e}/\text{Å}^3$

Table 3. *Atomic coordinates and equivalent isotropic displacement parameters for arsentsumebite (Numbers in parentheses are e.s.d.'s referred to the last digit)*

Atom	x	y	z	B_{eq} (Å ²)
Pb1	0.7163(4)	0.25	0.2412(3)	3.4(1)
Pb2	0.2987(4)	0.25	0.3869(3)	2.8(1)
Cu	0	0	0	1.50(4)
(As, S)1	0.5584(10)	0.25	$-0.1715(7)$	1.0(1)
(As, S)2	$-0.0449(14)$	0.25	$-0.3502(10)$	1.2(2)
O1	0.1707(9)	0.25	0.0811(8)	0.9(2)
O2	$-0.2413(17)$	0.25	$-0.4682(11)$	2.9(3)
O3	1.0928(16)	0.25	0.5563(13)	4.8(2)
O4	0.4336(14)	0.25	0.9346(12)	3.8(2)
O5	0.7754(11)	0.25	$-0.0543(9)$	2.1(3)
O6	$-0.0002(8)$	0.0302(10)	$-0.2410(7)$	2.6(2)
O7	0.5099(8)	0.0252(9)	$-0.2875(7)$	2.5(2)

Content of (As, S)1 site: $\text{As}_{0.63}\text{S}_{0.37}$. Content of (As, S)2 site: $\text{As}_{0.37}\text{S}_{0.63}$

Table 4. Selected interatomic distances (Å) in the structure of arsentsumebite (numbers in parentheses are e.s.d.'s referred to the last digit)

Pb(1) polyhedron			(As _{0.63} S _{0.37}) tetrahedron		
Pb(1)	–O(2)	2.498(8)	As _{0.63} S _{0.37}	–O(4)	1.598(6)
	–O(7)	2.544(7) × 2		–O(5)	1.619(15)
	–O(6)	2.764(8) × 2		–O(7)	1.637(9) × 2
	–O(4)	2.797(5)	(As _{0.37} S _{0.63}) tetrahedron		
	–O(5)	2.856(4)	As _{0.37} S _{0.63}	–O(2)	1.496(8)
	–O(3)	3.212(4)		–O(6)	1.580(8) × 2
	–O(4)	3.336(3) × 2		–O(3)	1.595(15)
Pb(2) polyhedron			Cu octahedron		
Pb(2)	–O(1)	2.537(6)	Cu	–O(1)	1.933(4) × 2
	–O(7)	2.581(5) × 2		–O(6)	2.167(7) × 2
	–O(3)	2.596(4)		–O(5)	2.200(6) × 2
	–O(6)	2.748(6) × 2			
	–O(7)	3.056(5) × 2			
	–O(2)	3.107(4) × 2			
	–O(2)	3.322(5)			

The structure was refined in space group $P2_1/m$ on the basis of the atomic coordinates of tsumebite, $Pb_2Cu(SO_4)(PO_4)(OH)$ (Fanfani and Zanazzi, 1967). The experimental details are given in Table 2. The isotropic refinement by least squares led to $R=0.084$. Conversion to anisotropic displacement factors reduced the residual R to 0.075. A difference Fourier map with residual peaks around Pb and (As, S) atoms showed that their positions should be refined using the anharmonic thermal displacement factors (Gram-Charlier expansion of tensors $F(ijklmn)$). The final residual R is 0.054 and the largest residual electron densities are 3.52 and $-2.11 e/\text{Å}^3$, respectively. Refined atomic parameters are listed in Table 3, selected interatomic distances are given in Table 4.

Discussion

The crystal structure of arsentsumebite is shown in Figs. 1 and 2. Using the classification of Eby et al. (1993) arsentsumebite can be considered as a member of the group of copper oxysalt minerals whose structures are based on infinite chains. Within this group, the chains are further divided on the basis of their internal connectivity. Arsentsumebite and other minerals from the brackebuschite group contain $M=M-T$ chains where $M=M$ means edge-sharing between MO_6 octahedra and $M-T$ represents corner sharing between octahedra and XO_4 tetrahedra (Eby et al., 1993). The basic unit of the mixed chains in arsentsumebite is the chain $[Cu_2\varphi_8]$ formed by edge-sharing CuO_6 octahedra, which is decorated by $(As, S)O_4$ tetrahedra. The heteropolyhedral $[Cu(As, SO_4)_2OH]$ chains are parallel to $[010]$ and thus the length of the b-axis depends on the size of cations located in the centers of octahedra and tetrahedra.

Cu^{2+} cations are located at the inversion centers. Cu has a $[2+4]$ coordination forming distorted tetragonal bipyramids (i.e., an axially compressed octahedron)

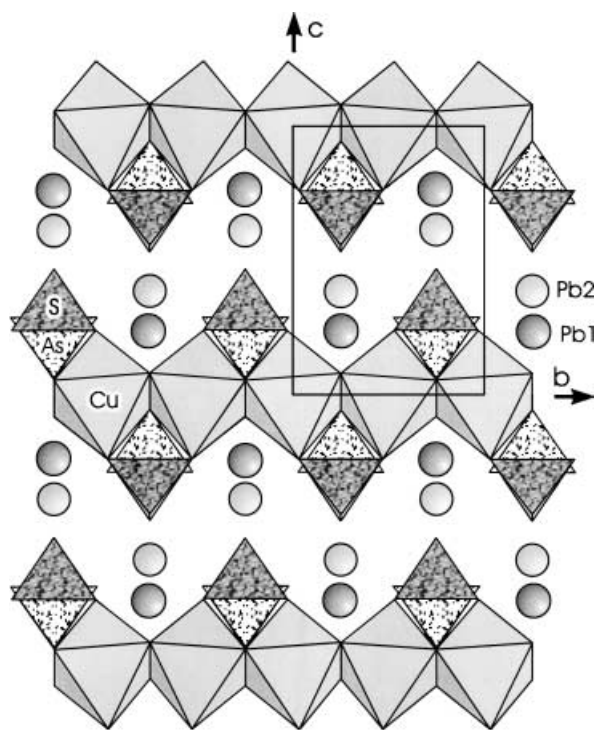


Fig. 1. Crystal structure of arsentsumebite in a projection parallel to [100]. The drawings were done with Atoms (*Dowty, 1999*)

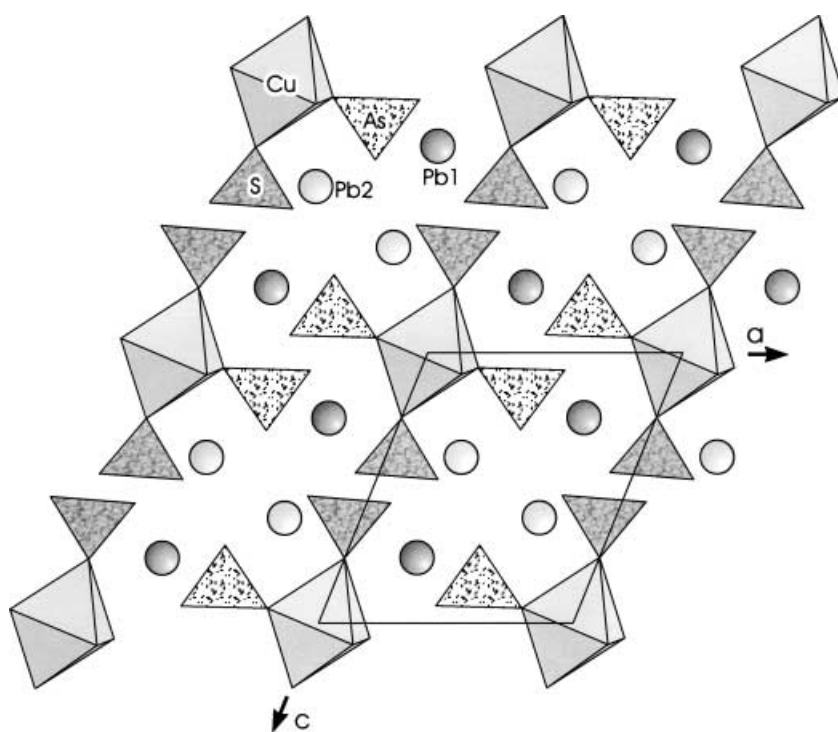


Fig. 2. Crystal structure of arsentsumebite in a projection on (010)

with distances ranging from 1.93 (Cu–OH) to 2.20 Å. This type of coordination is attributed to the single occupancy of dz^2 orbitals of Cu^{2+} (Orgel, 1966). The short distances in this unusual Cu polyhedron are formed with two non-bridging O(1)=OH, shared only with Pb polyhedra, whereas the other four vertices are occupied by O atoms of (As, S)O₄ tetrahedra.

According to Burns and Hawthorne (1996) such a coordination for Cu^{2+} is known only from a few minerals, e.g. in volborthite, $\text{Cu}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ (Basso et al., 1988) and in demesmaekerite, $\text{Pb}_2\text{Cu}_5(\text{SeO}_3)_6(\text{UO}_2)_2(\text{OH})_6(\text{H}_2\text{O})_2$ (Ginderow and Cesbron, 1983). Further, in the synthetic inorganic compounds $\text{KCu}_3(\text{OH})_2[(\text{AsO}_4)\text{H}(\text{AsO}_4)]$ (Effenberger, 1989) and in two metallorganic complexes: diaquobis(methoxyacetato)copper(II) (Prout et al., 1968) and octa- μ -dichloroacetato-(o,o')-bis(dichloroactato)-hexa- μ_3 -(2-dimethylamino-ethanolato)-di- μ_3 -hydroxo-nonacopper(II) (Turpeinen et al., 1985).

In contrast to previous X-ray studies of members of the brackebuschite group with chemically different kinds of tetrahedra, in arsentsumebite As and S atoms are partially disordered in both independent (As, S)O₄ tetrahedra which are characterised by different As/S ratios, $\text{As}_{0.63}\text{S}_{0.37}$ and $\text{As}_{0.37}\text{S}_{0.63}$. These refined ratios of tetrahedral sites correlate with different interatomic distances in these tetrahedra: for the first one they range from 1.60 to 1.63 Å and for the second one from 1.51 to 1.60 Å. The role of [(As, S)O₄](1) and [(As, S)O₄](2) tetrahedra is different in the structure: the latter reinforces the contacts between adjacent CuO₆ octahedra sharing its two vertices whereas the former shares only one vertex with one CuO₆ octahedron. Consequently the heteropolyhedral chain formed by CuO₆ octahedra and by [(As, S)O₄](2) tetrahedra is very similar to that revealed in linarite, $\text{CuPb}[\text{SO}_4](\text{OH})_2$.

Harlow et al. (1984) assigned a partially acide vanadate containing $[\text{HVO}_4]^{2-}$ tetrahedral in gamagarite. However, arsentsumebite does not indicate the presence of protonated tetrahedral units.

The heteropolyhedral $[\text{Cu}((\text{As, S})\text{O}_4)_2\text{OH}]$ chains are linked by irregularly 10- and 11-coordinated Pb atoms with Pb–O bond lengths in a range from 2.498 to 3.336 Å and from 2.537 to 3.322 Å, respectively. The sum of the bond strengths on anions is given in Table 5 (Brown and Shannon, 1973). The number of ligands

Table 5. The sum of the bond strengths on anions in the structure of arsentsumebite*

	Pb1		Pb2		Cu		As, S		S, As		Σ
O1			0.32		0.5×2						1.32
O2	0.35		0.07×2						1.66		2.19
			0.04								
O3	0.05		0.27						1.27		1.59
O4	0.16						1.40				1.64
			0.04×2								
O5	0.13				0.25×2		1.31				1.94
O6	0.17×2	0.17	0.18×2	0.18	0.27×2	0.27			1.32×2	1.32	1.94
O7	0.31×2	0.31	0.28×2	0.28			1.31×2	1.31			1.98
			0.08×2	0.08							
Σ	1.73		1.85		2.04		5.33		5.57		

*Contribution to the balance of cations is marked with italic. The parameters for calculation of the bond strengths for Pb-polyhedra were taken the same as for Hg-polyhedra

Table 6. Chemical formulae, lattice parameters, space groups, and references for brackebuschite – group minerals

Mineral	a (Å)	b (Å)	c (Å)	β (°)	Space group	References
$\text{Pb}_2(\text{Mn}, \text{Fe})(\text{VO}_4)_2\text{H}_2\text{O}$ brackebuschite	7.68	6.15	8.88	111.6	$P2_1/m$	Donaldson and Barnes (1955)
$\text{Pb}_2(\text{Mn}, \text{Fe})(\text{VO}_4)_2\text{OH}$ brackebuschite	7.65	6.14	8.86	111.8	$P2_1/m$	Foley et al. (1997)
$\text{Pb}_2(\text{Fe}, \text{Zn})(\text{AsO}_4)_2(\text{OH}, \text{H}_2\text{O})$ arsenbrackebuschite	7.76	6.05	9.02	112.5	$P2_1/m$	Abraham et al. (1978); Hofmeister and Tillmanns (1978)
$\text{Pb}_2\text{Cu}(\text{CrO}_4)(\text{PO}_4)(\text{OH})$ vauquelinite	8.06×2	5.81	8.68×2	110.5	$P2_1/n$	Fanfani and Zanazzi (1968)
$\text{Pb}_2\text{Cu}(\text{AsO}_4)(\text{CrO}_4)(\text{OH})$ formacite	8.10	5.89	8.77×2	110.0	$P2_1/c$	Cocco et al. (1967)
$\text{Pb}_2(\text{Zn}, \text{Fe})[(\text{As}, \text{S})\text{O}_4]_2\text{H}_2\text{O}$ feinglosite	8.97	5.96	7.78	112.2	$P2_1$ or $P2_1/m$	Clark et al. (1997)
$\text{Pb}_2\text{Cu}(\text{SO}_4)(\text{PO}_4)(\text{OH})$ tsumebite	7.85	5.80	8.70	111.5	$P2_1/m$	Nichols (1966)
$\text{Pb}_2\text{Cu}(\text{SO}_4)(\text{AsO}_4)(\text{OH})$ 'As-tsumebite'	7.84	5.92	8.85	112.6	$P2_1/m$	Bideaux et al. (1966)
$\text{Pb}_2\text{Cu}[(\text{As}, \text{S})\text{O}_4]_2(\text{OH})$ arsenesumbite	7.80	5.89	8.96	112.3	$P2_1/m$	this work
$\text{Pb}_2\text{Fe}(\text{VO}_4)_2(\text{OH})$ unnamed	7.628	6.148	8.782	111.1	$P2_1/m$	Gurbanova et al. (2001)
$\text{Ba}_2(\text{Fe}^{3+}, \text{Mn})(\text{VO}_4)_2(\text{OH}, \text{H}_2\text{O})$ gamagarite	7.88	6.17	9.15	112.7	$P2_1/m$	Harlow et al. (1984)
$\text{Ca}_2\text{Al}(\text{PO}_4)_2(\text{OH})$ bearthite	7.23	5.73	8.26	112.6	$P2_1/m$	Chopin et al. (1993)
$(\text{Sr}, \text{Ca})_2\text{Al}(\text{PO}_4)_2(\text{OH})$ goedkenite	7.26	5.74	8.45	113.7	$P2_1/m$	Moore et al. (1975)

With the name 'As-tsumebite' we indicate the analogue of tsumebite discovered by Nichols (1966)

included in PbO_n polyhedra is within the range 6–11 reported for other minerals of the brackebuschite group. The irregular shape of the PbO_n polyhedra is attributed to the $6s^2$ lone electron pair of the Pb^{2+} cation.

The atomic array, the lattice dimensions and the symmetry of all Pb containing minerals of the brackebuschite group are very similar to those of arsentsumebite (Table 6). Only vauquelinite (Fanfani and Zanazzi, 1967, 1968) and fornacite (Cocco et al., 1966) are described in different settings ($P2_1/n$ and $P2_1/c$, respectively) and exhibit the doubling of a and c (vauquelinite) or c (fornacite) edges.

A structural relationship of brackebuschite-group minerals exists to tsumcorite $\text{Pb}(\text{Zn}, \text{Fe})_2(\text{AsO}_4)_2(\text{OH}, \text{H}_2\text{O})_2$ (Geier et al., 1971; Tillmanns and Gebert, 1973) and tsumcorite-group minerals with general formula $\text{Me}(1)\text{Me}(2)_2(\text{XO}_4)_2(\text{OH}, \text{H}_2\text{O})_2$ where $\text{Me}(1) = \text{Pb}, \text{Ca}, \text{Na}$, and partly Bi ; $\text{Me}(2) = \text{Fe}, \text{Mn}, \text{Cu}, \text{Zn}, \text{Co}, \text{Ni}$, and partly Al ; $\text{X} = \text{P}, \text{As}, \text{V}, \text{S}$ (Krause et al., 1998). Both groups are characterised by different $\text{Me}(1) : \text{Me}(2)$ ratios: in the brackebuschite group it is 2 : 1 and in tsumcorite 1 : 2. The structural peculiarities of both groups are closely connected with their compositions. According to Hofmeister and Tillmanns (1978) in tsumcorite two $(\text{OH}, \text{H}_2\text{O})$ groups substitute two Pb atoms (Pb2 site in arsentsumebite); the thereby formed octahedral void in the centre of the unit cell is occupied by an additional $\text{Me}(2)$ atom.

Acknowledgements

This work was supported in part by the Russian Scientific Foundation (grants 00-05-65999, 00-15-96633) and by The Russian Universities program. A travel grant by the Dean of the Faculty of Natural Sciences of the University of Vienna for a research stay in Vienna is gratefully acknowledged. The authors thank Dr. U. Kolitsch for helpful remarks.

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