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The Crystal Structure of $PbFe[AsO_4]\,[AsO_3(OH)]$

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Summary. Light green to nearly colourless crystals of $PbFe[AsO_4][AsO_3(OH)]$ were synthesized under moderate hydrothermal conditions ($a = 4.846(2)$, $b = 8.482(4)$, $c = 15.560(6)$ Å, $\beta = 92.82(3)°$, space group $P2_1/n$, $Z = 4$). For a single-crystal structure determination, 110 variable parameters were refined to $R = 0.042$, $R_w = 0.031$ (1545 X-ray reflections with $F_o > 3\sigma(F_0)$ and $\sin\theta/\lambda \leqslant 70°$). The crystal structure is characterized by a three-dimensional corner-connection of the FeO_6 octahedra with the arsenate tetrahedra and the protonated arsenate groups. Each two PbO_7 polyhedra are edge-connected to Pb_2O_{12} dimers which are located within interstitial holes.

Keywords. $PbFe[AsO_4][AsO_3(OH)]$; Synthesis, hydrothermal; Crystal structure; Crystal chemistry.

Die Kristallstruktur von $PbFe[AsO_4][AsO_3(OH)]$

Zusammenfassung. Hellgrüne bis nahezu farblose Kristalle von $PbFe[AsO_4][AsO_3(OH)]$ wurden unter niedrig-hydrothermalen Bedingungen synthetisiert ($a = 4.846(2)$, $b = 8.482(4)$, $c = 15.560(6)$ Å, $\beta = 92.82(3)°$, Raumgruppe $P2_1/n$, $Z = 4$). Für die Einkristall-Strukturbestimmung wurden 110 freie Parameter auf $R = 0.042$, $R_w = 0.031$ verfeinert (1545 Röntgenbeugungsreflexe mit $F_o > 3\sigma(F_0)$ und $\sin\theta/\lambda \leqslant 70°$). Die Kristallstruktur wird durch eine dreidimensionale Ecken-Verknüpfung der FeO_6-Oktaeder mit den Arsenattetraedern und den protonierten Arsenatgruppen charakterisiert. Jeweils zwei PbO_7-Polyeder sind über eine Kante zu Pb_2O_{12}-Dimeren verknüpft, die in Zwischenräumen angeordnet sind.

Introduction

A small number of lead(II) arsenates(V) have been investigated so far. Many of these compounds are known to occur as minerals. Structures have been determined for *e.g.* $Pb_3(AsO_4)_2$ [1], $Pb(HAsO_4)$ (schultenite) [2], $Pb[H_2(As,P)O_4]_2$ [3], $PbFe_2(OH)_2(AsO_4)_2$ (carminite) [4], $Pb_2(Fe,Zn)(OH,OH_2)(AsO_4)_2$ (arsenbrackebuschite) [5], $Pb(Fe,Zn)_2(OH,OH_2)_2(AsO_4)_2$ (mawbyite and tsumcorite) [6, 7], $PbCu(AsO_4)$ [8], $Pb_2Cu_7(AsO_4)_6$ [9], $Pb_2Cu_2Cu_6(AsO_4)_6$ [9], $PbCu(As_2O_7)$ [10], $Pb(Cu,Zn)_3(OH)_2(AsO_4)_2$ (bayldonite) [11], $Pb(Fe,Al)_3(OH)_6[(As,S)O_4]_2$ (beudantite) [12], (Pb, Ca, Sr) (Cu, Mn) (OH) [(As, V)O_4] (descloizite group) [13], $Pb_2(Cu,Fe)(OH)[(Cr,Mo)O_4][(As,P)O_4]$ (fornacite and molybdofornacite) [14, 15], $Pb_5Cl(AsO_4)_3$ (mimetite and clinomimetite) [16, 17], and $Pb_3Ca_2Cl(AsO_4)_3$ (hedyphane) [18]. In the course of syntheses in systems with Pb(II)O, $As(V)_2O_5$, H_2O, and different transition metals, the new compound $PbFe[AsO_4][AsO_3(OH)]$ was obtained; the crystal structure is described in the present paper.

Results and Discussion

The crystal structure of $PbFe[AsO_4][AsO_3(OH)]$ is characterized by a three-dimensional corner-connection of isolated FeO_6 octahedra, AsO_4 tetrahedra, and $AsO_3(OH)$ groups. The Pb atoms are located in interstitial holes which are arranged channel-like parallel to (100). Structural parameters are compiled in Table 1, selected interatomic bond lengths and bond strengths in Table 2. Topologically, the structure may be described as a two-dimensional linkage of the FeO_6 octahedra and the PbO_7 polyhedra parallel to (101); these layer-like arrangements are connected by the arsenate tetrahedra and by the hydrogen bonds (Fig. 1). Such a formal layer formed by the lead and iron polyhedra with the arsenate tetrahedra and hydrogen bonds beneath is shown in Fig. 2. It should be mentioned that the topological description as "layers" does not correspond with the order of strengths for the particular interatomic bonds.

The Pb atom is coordinated to seven ligands from 2.41 to 2.89 Å, the average bond length is 2.624 Å; the longest bond (2.89 Å) is formed with the oxygen atom of the hydroxyl group. Further Pb–O distances exceed 3.38 Å and are excluded from discussion of coordination. The ligands are placed at the corners of a compressed tetragonal antiprism whose eighth corner remains unoccupied. The basis and top faces are formed by the atoms O(14)–O(22)–O(23)–O(24) and O(14)–O(13)–O(21) –□. □ is the vacant corner; in its region, the stereochemically active lone-pair electrons are expected. The distortion of the coordination is predominantly caused by the edge-connection with two FeO_6 octahedra (O(21)–O(23) = 2.70 Å, O(21) –Pb–O(23) = 59.3(2)°; O(13)–O(22) = 2.79 Å, O(13)–Pb–O(22) = 67.8(2)°) and with the $AsO_3(OH)$ group (O(23)–O(24) = 2.63 Å, O(23)–Pb–O(24) = 56.6(2)°). The PbO_7 polyhedra are edge-connected to Pb_2O_{12} dimers with symmetry $\bar{1}$: O(14) –O(14) = 2.94 Å, O(14)–Pb–O(14) = 71.3(2)°; Pb–Pb = 4.09 Å.

Coordinations for divalent Pb atoms like that in $PbFe[AsO_4][AsO_3(OH)]$ are rare; due to electrostatic reasons, seven ligands are scarce: energetically, six or even eight ligands are clearly favoured. On the other hand, the Pb(*II*) atoms show a tendency towards a coordination with three to four nearest neighbours; usually a noticeable gap to the next-nearest ligands is observed. Examples for a coordination with more or less equally distributed seven Pb–O bond distances have been found for some inorganic compounds only; *cf. e.g.* $K_2Pb(PO_3)_4$ [22], atom Pb(2) in $Pb_3(P_3O_9)_2 \cdot 3H_2O$ [23], $PbWO_4$ (raspite) [24], $PbGe_3O_7$ [25], atom Pb(2) in $Pb_2(UO_2)(TeO_3)_3$ [26], atom Pb(3) in $Pb_3P_4O_{13}$ [27], atom Pb(2) in $(NH_4)Pb(PO_3)_3$ [28], and $LiPb_2(PO_3)_5$ [29]. For these PbO_7 polyhedra, the average Pb–O bond lengths vary only from 2.61 to 2.65 Å. It should be mentioned that the consideration of examples for PbO_7 coordinations featuring a splitting of the bond-length distribution into two or even three groups causes a rapid change of the average ⟨Pb–O⟩ distance.

The Fe atom exhibits an octahedral coordination with an average ⟨Fe–O⟩ distance of 2.028 Å as characteristic for *tri*valent iron atoms. The O–Fe–O bond angles vary from 82.7(3) to 101.9(3)° for ligands in a *cis*-arrangement and they are $> 169°$ for *trans*-arranged ligands.

As expected, the two *penta*valent As atoms are tetrahedrally 4-coordinated with average ⟨As–O⟩ bond lengths of 1.694 and 1.687 Å. The O–As–O bond angles vary

Table 1. Structural parameters for PbFe[AsO$_4$][AsO$_3$(OH)]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	B_{eq}
Pb	0.81064(8)	0.03628(6)	0.11279(3)	0.0152(2)	0.0197(2)	0.0155(2)	0.0002(1)	0.0006(1)	−0.0007(2)	1.33
As(1)	0.30490(20)	0.31590(14)	0.02346(6)	0.0091(5)	0.0183(6)	0.0102(5)	0.0001(2)	0.0002(3)	−0.0008(4)	0.99
As(2)	0.33310(20)	0.26138(14)	0.25970(6)	0.0082(4)	0.0172(6)	0.0102(5)	0.0001(2)	0.0004(3)	−0.0002(4)	0.94
Fe	0.82922(28)	0.45413(20)	0.14863(9)	0.0106(6)	0.0166(8)	0.0116(6)	0.0000(3)	0.0000(5)	−0.0005(6)	1.02
O(11)	0.1407(14)	0.4604(10)	0.0744(4)	0.013(3)	0.023(4)	0.015(3)	0.002(2)	0.005(2)	0.002(3)	1.32
O(12)	0.3387(14)	0.3629(10)	−0.0817(4)	0.010(3)	0.025(5)	0.011(3)	0.002(2)	0.003(2)	0.003(3)	1.21
O(13)	0.6276(14)	0.2988(10)	0.0709(5)	0.006(3)	0.025(5)	0.020(4)	0.000(2)	−0.004(3)	0.003(3)	1.35
O(14)	0.1779(14)	0.1320(9)	0.0279(5)	0.020(4)	0.017(4)	0.020(4)	−0.004(2)	0.004(3)	−0.006(3)	1.48
O(21)	0.5012(14)	0.0901(10)	0.2572(4)	0.016(4)	0.021(4)	0.017(4)	−0.002(2)	0.001(3)	0.001(3)	1.41
O(22)	0.0383(14)	0.2541(9)	0.1996(4)	0.012(3)	0.015(4)	0.020(4)	0.001(2)	−0.001(3)	−0.001(3)	1.23
O(23)	0.5381(14)	0.4126(9)	0.2370(4)	0.010(3)	0.021(4)	0.014(3)	0.000(2)	0.000(2)	−0.003(3)	1.16
O(24)	0.2563(14)	0.3046(10)	0.3643(5)	0.015(4)	0.024(5)	0.020(4)	−0.001(2)	0.000(3)	−0.004(3)	1.53

Anisotropic displacement parameters: $\exp(-2\pi^2\Sigma_{i=1}^3\Sigma_{j=1}^3 U_{ij}a_i^*a_j^*h_ih_j)$, B_{eq} according to Ref. [19]

Table 2. Interatomic distances (Å) and bond strengths v (v.u.)

Pb–O(14), v	2.413(7)	0.44	As(1)–O(14), v	1.683(8)	1.25
Pb–O(13), v	2.478(8)	0.37	As(1)–O(11), v	1.684(8)	1.25
Pb–O(22), v	2.518(7)	0.33	As(1)–O(12), v	1.703(7)	1.19
Pb–O(14), v	2.622(7)	0.25	As(1)–O(13), v	1.707(7)	1.18
Pb–O(23), v	2.639(7)	0.24	$\sum v$		4.87
Pb–O(21), v	2.804(7)	0.15			
Pb–O(24), v	2.891(7)	0.12			
$\sum v$		1.90			
			O(24)...O(12)	2.648(10)	
Fe–O(11), v	1.949(7)	0.60	As(2)–O(21), v	1.671(8)	1.30
Fe–O(21), v	2.013(7)	0.50	As(2)–O(23), v	1.674(7)	1.29
Fe–O(13), v	2.014(8)	0.50	As(2)–O(22), v	1.674(7)	1.29
Fe–O(12), v	2.023(8)	0.49	As(2)–O(24), v	1.730(7)	1.01
Fe–O(23), v	2.116(8)	0.45	$\sum v$		4.89
Fe–O(22), v	2.116(8)	0.38			
$\sum v$		2.92			

Bond strengths according to Ref. [20]

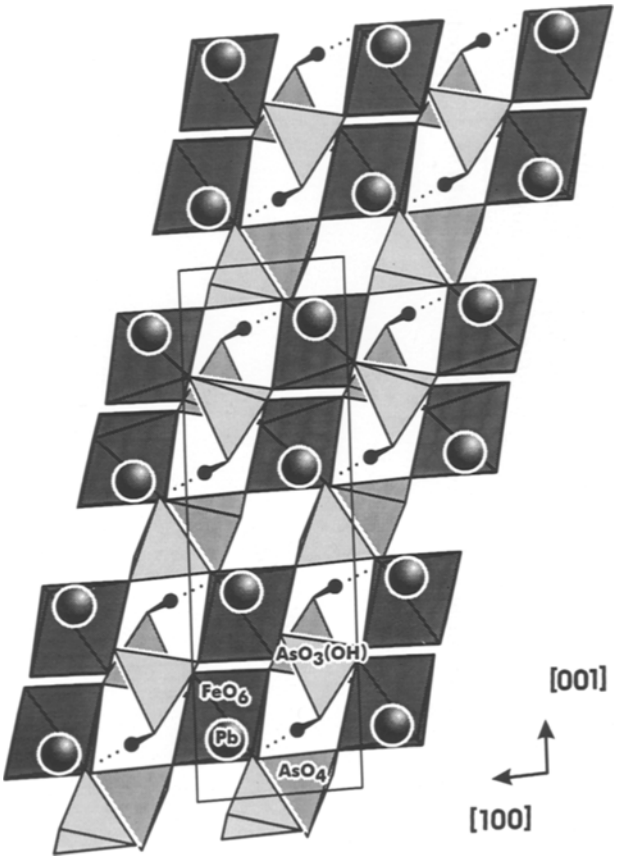

Fig. 1. The crystal structure of PbFe[AsO_4][$AsO_3(OH)$] in a projection parallel to [010]; program ATOMS [21]

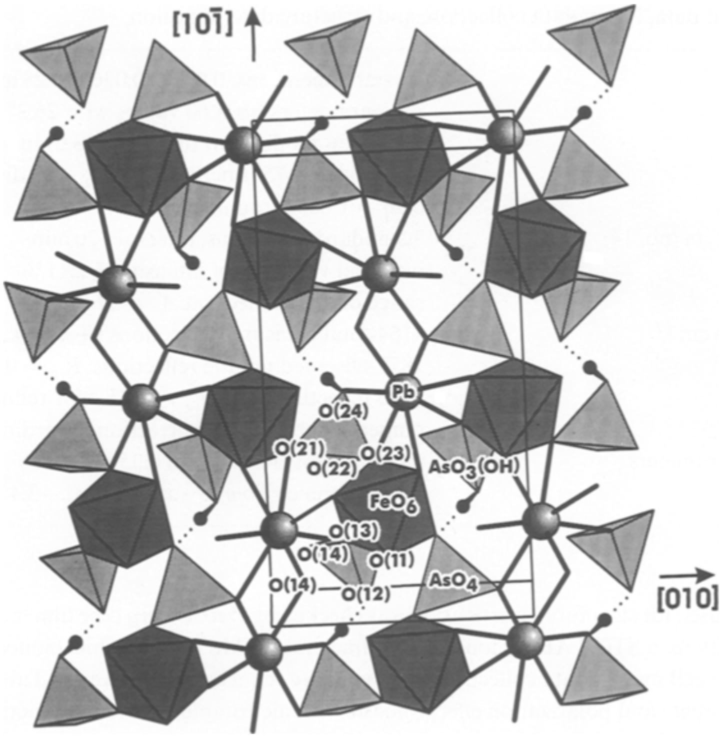

Fig. 2. The crystal structure of PbFe[AsO$_4$][AsO$_3$(OH)] in a projection on [101]; program ATOMS [21]

from 101.1(4) to 118.4(4)°, O–O edges from 2.63(1) to 2.89(1) Å: the smallest values are caused by edge-sharing between the As(2)O$_4$ tetrahedron and the PbO$_7$ polyhedron. Due to the formation of the hydrogen bond, the two crystallographically different arsenate groups show definitely distinct As–O bond lengths. The long As(2)–O(24) distance is a hint that the atom O(24) is the donor of the hydrogen bond. Such long bonds are characteristic for protonated oxoanions; after *Ferraris* and *Ivaldi* [30], the average $\langle$As(V)–O(H)$\rangle$ value in inorganic compounds is 1.731 Å. These geometrical considerations are in accordance with the bond valences [20]: values from 1.75 to 2.05 v.u. were calculated for all atoms but O(24) and O(12), the values for the two latter atoms being 1.13 and 1.68 v.u. Including the contribution of the hydrogen bond to the acceptor atom O(12) and to the donor atom O(24) according to [31] gives in total 2.00 and 1.81 v.u. for these two O atoms. Furthermore, the O(24)–H$\cdots$O(12) distance of 2.65(1) Å represents the shortest O–O contact that forms no edge in any of the coordination polyhedra.

Experimental

Crystals of PbFe[AsO$_4$][AsO$_3$(OH)] suitable for structure investigations were synthesized under hydrothermal conditions as described in Ref. [9]. The compound is soft light green to nearly colourless. The crystals show symmetry 2/*m*. The crystallographic forms {011}, {001}, and {100} have been observed; the obtained crystals are prismatic parallel to (100). Diameters to not exceed some tenths of a millimeter.

Table 3. Crystal data, X-ray data collection, and structure determination

$a = 4.846(2)$ Å
$b = 8.482(4)$ Å
$c = 15.560(6)$ Å
$\beta = 92.82(3)^\circ$
$V = 638.8$ Å^3
space group $P2_1/n$ (no. 14)
$Z = 4$
$\rho_{\text{calc}} = 5.64\,\text{gcm}^{-3}$
$\mu(\text{Mo}K\alpha) = 388\,\text{cm}^{-1}$
$R = 0.042$
$R_w = 0.031$
$w = 0.995\,[\sigma(F_o)]^{-2}$
110 variable parameters
max $\Delta/\sigma \leqslant 0.001$

crystal dimensions: $0.032 \times 0.036 \times 0.28\,\text{mm}^3$
cell parameters from 60 values with $26.2^\circ < 2\theta < 34.9^\circ$
$2\theta/\omega$ scan mode, scan time 0.9 to $3.6^\circ\,\text{min}^{-1}$
scan width: 0.75° (increased for $\alpha_1 - \alpha_2$ dispersion)
0.36° for background correction
3 standard reflections, interval 120 min
maximal variation of intensity $\pm 2.11\%$
range of data collection: $4^\circ < 2\theta < 70^\circ$
4164 total measured reflections ($\pm h$, $+k$, $\pm l$)
1879 observed unique reflections: $R_{\text{int}} = 0.045$
1545 reflections with $F_o > 3\sigma(F_o)$ for refinements
numerical absorption correction according to the shape
transmission factors from 0.354 to 0.276
final difference *Fourier* summation: -3.4 to $2.53\,\text{eÅ}^{-3}$

The crystal used for structure investigation was checked by *Weissenberg* type film methods first. For further investigations, a STOE AED 2 four-circle diffractometer (Mo tube, graphite monochromator) was used. Details on cell metric, data collection, and structure refinement are given in Table 3. Data were corrected for *Lorentz* and polarization effects; neutral atomic complex scattering functions were taken from [32]. The positions of the Pb atoms were derived from a *Patterson* summation; the other atoms were located by subsequent *Fourier* and difference *Fourier* calculations. The structural parameters including the parameter for the correction of the isotropic extinction were refined by full-matrix least-squares techniques [33, 34]. The highest peaks in the final difference *Fourier* summation are located in the surroundings of the Pb atoms.

References

[1] Viswanathan K, Miehe G (1978) Z Krist **148**: 275
[2] Wilson CC (1994) Mineral Mag **58**: 629
[3] Worzala H, Howie RA, Jost KH (1991) Z Anorg Allgem Chem **606**: 213
[4] Finney JJ (1963) Am Mineral **48**: 1
[5] Hofmeister W, Tillmanns E (1978) Tschermaks Mineral Petrogr Mitt **25**: 153
[6] Pring A, McBriar EM, Birch WD (1989) Am Mineral **74**: 1377
[7] Tillmanns E, Gebert W (1973) Acta Cryst **B29**: 2789
[8] Pertlik F (1986) Acta Cryst **C42**: 774
[9] Effenberger H (1995) J Solid State Chem **114**: 413
[10] Pertlik F (1986) Monatsh Chem **117**: 1343
[11] Ghose G, Che'ng Wan (1979) Acta Cryst **B35**: 819
[12] Szymański JT (1988) Can Mineral **26**: 923
[13] Basso R, Palenzona A, Zefiro L (1989) N Jahrb Mineral Monatsh **1989**: 300
[14] Cocco G, Fanfani L, Zanazzi PF (1967) Z Krist **124**: 385
[15] Medenbach O, Abraham K, Gebert W (1983) N Jahrb Mineral Mh **1983**: 289
[16] Calos NJ, Kennard CHL, Davis RL (1990) Z Krist **191**: 125
[17] Dai Y, Hughes JM, Moore PB (1991) Can Mineral **29**: 369
[18] Rouse RC, Dunn PJ, Peacor DR (1984) Am Mineral **69**: 920
[19] Fischer RX, Tillmanns E (1988) Acta Cryst **C44**: 775
[20] Brese NE, O'Keeffe M (1991) Acta Cryst **B47**: 192

[21] Dowty E (1991) Atoms, a computer program for displaying atomic structures, Version 2.0. Kingsport, TN

[22] Brunel-Laügt M, Guitel J-C (1977) Acta Cryst **B33**: 937

[23] Brunel-Laügt M, Tordjman I, Durif A (1976) Acta Cryst **B32**: 3246

[24] Fujita T, Kawada I, Kato K (1977) Acta Cryst **B33**: 162

[25] Otto HH (1979) Z Krist **149**: 197

[26] Brandstätter F (1981) Z Krist **155**: 193

[27] Averbuch-Pouchot MT, Durif A (1987) Acta Cryst **C43**: 631

[28] Gatehouse BM, Guddat LW (1987) Acta Cryst **C43**: 1659

[29] El-Horr N, Bagieu-Beucher M (1986) Acta Cryst **C42**: 647

[30] Ferraris G, Ivaldi G (1984) Acta Cryst **B40**: 1

[31] Brown ID, Altermatt D (1985) Acta Cryst **B41**: 244

[32] Wilson AJC (1992) International tables for crystallography, vol C. Kluwer Academic, Dordrecht Boston London

[33] Sheldrick GM (1976) SHELX-76, programs for crystal structure determination. University of Cambridge

[34] Frenz BA, and Associates (1992) Inc., Personal SDP, College Station, TX

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