

Crystal structure of pushcharovskite

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Abstract: Pushcharovskite, $K_{0.02}Cu_{1.125}As_{0.94}O_{5.515}H_{4.06}$ (ideally $CuAsO_3(OH) \cdot 1.5H_2O$), $M = 235.02$, is triclinic, with space group $P1$, $a = 13.6164(7)$, $b = 15.6672(8)$, $c = 19.1869(9)$ Å, $\alpha = 106.933(2)$, $\beta = 91.531(2)$, $\gamma = 98.401(2)^\circ$, $V = 3863.3(3)$ Å³, $Z = 32$, $\rho_o = 3.35$, $\rho_c = 3.235$ g/cm³, $\mu = 11.40$ mm⁻¹. The crystal structure of pushcharovskite was solved and refined against data collected at the Daresbury Synchrotron Radiation Facility, using a $60 \times 20 \times 5$ µm³ single crystal, $\lambda = 0.6883$ Å, $F(000) = 3590$, R 0.054 for 8343 reflections with $I > 2\sigma(I)$. Pushcharovskite is a mineral characterized by some structural disorder and by the following general formula: $K_{0.6}Cu_{18}[AsO_{2.8}(OH)_{1.2}]_{15}(OH)_{9.6} \cdot 18.6(H_2O)$; the corresponding structural formula is $K_{0.6}Cu_{18}[AsO_2(OH)_2]_4[AsO_3(OH)]_{10}[AsO_4(OH)_{0.6} \cdot 18.6(H_2O)]$. The structure contains heteropolyhedral sheets (110) formed by Cu₂O polyhedra (square bipyramids and square pyramids) and by As₂O₄OH tetrahedra. The sheets are linked by hydrogen bonding involving the water molecules of the Cu square bipyramids and pyramids, the OH groups of the As₂O₄OH tetrahedra and H₂O molecules localized in the interlayers. A small amount of distorted K octahedra with partial occupancy reinforce these contacts. Some vacancies in the positions of Cu atoms were revealed. The mineral is structurally related to geminite, $Cu(AsO_3OH) \cdot H_2O$, yvonite, $Cu(AsO_3OH) \cdot 2H_2O$ and fluckite, $CaMn(AsO_3OH)_2 \cdot 2H_2O$.

Key-words: pushcharovskite, crystal structure, arsenate, geminite, yvonite.

Introduction

The copper arsenate, pushcharovskite, with an initial formula $Cu[AsO_3OH]H_2O$, was recently discovered at Cap Garonne, Var, France (Sarp & Sanz-Gysler, 1997) and approved by the CNMMN of IMA before publication. Its second occurrence was reported in the gold-bearing sulfo-arsenic mine Salsigne in the department of Aude, France.

The preliminary X-ray diffraction study of pushcharovskite (powder diagram) (Sarp & Sanz-Gysler, 1997) revealed that the mineral is triclinic, with $a = 6.435$, $b = 11.257$, $c = 18.662$ Å, $\alpha = 79.40$,

$\beta = 86.48$, $\gamma = 83.59^\circ$. Crystals of pushcharovskite are thin elongated plates, with maximum and minimum dimensions of 0.5 and 0.04 mm respectively. Sarp & Sanz-Gysler (1997) emphasized that pushcharovskite is characterized by the same chemical formula and by the same crystallographic system as geminite (Cooper & Hawthorne, 1995; Prencipe *et al.*, 1996). It was, therefore, anticipated that pushcharovskite can be considered as a polymorphic modification of geminite and its structure can be related to the structures of geminite, $CuAsO_3(OH) \cdot H_2O$, its isotype koritnigite $Zn(AsO_3OH) \cdot H_2O$ (Keller *et al.*, 1980) and

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Table 1. Crystal data, structure solution and refinement for pushcharovskite.

Chemical formula	$K_{0.02}Cu_{1.125}As_{0.94}O_{5.515}H_{4.06}$
Formula weight	235.02
Temperature	293(2) K
Radiation and wavelength	synchrotron, 0.68830 Å
Crystal system, space group	triclinic, $P\bar{1}$
Unit cell dimensions	$a = 13.6164(7)$ Å $\alpha = 106.933(2)^\circ$ $b = 15.6672(8)$ Å $\beta = 91.531(2)^\circ$ $c = 19.1869(9)$ Å $\gamma = 98.401(2)^\circ$
Volume	$3863.3(3)$ Å ³
Z	32
Density (calculated)	3.235 g/cm ³
Absorption coefficient μ	11.40 mm ⁻¹
F(000)	3590
Reflections for cell refinement	8408 (θ range $2.55 - 29.13^\circ$)
Crystal colour	colourless
Crystal size	$0.06 \times 0.02 \times 0.005$ mm
Data collection method	Bruker SMART CCD diffractometer, ω rotation with narrow frames
θ range for data collection	1.33 to 25.00°
Index ranges	$-16 \leq h \leq 16, -19 \leq k \leq 17, -23 \leq l \leq 21$
Intensity decay	10%
Reflections collected	21299
Independent reflections	14598 ($R_{int} = 0.043$)
Reflections with $I > 2\sigma(I)$	8343
Absorption correction	multiscans
Max. and min. transmission	0.94 and 0.55
Structure solution	direct methods
Refinement method	full-matrix least-squares on F^2
Weighting parameters a, b	0.0519, 0.0000
Data / restraints / parameters	14598 / 1 / 720
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.054, wR2 = 0.113$
R indices (all data)	$R1 = 0.112, wR2 = 0.136$
Goodness-of-fit on F^2	0.944
Largest and mean shift/esd	0.002 and 0.000
Largest diff. peak and hole	1.76 and -1.42 e/Å ³

yvonite, $Cu(AsO_3OH) \cdot 2H_2O$ (Sarp & Černý, 1998). However without having structural data for pushcharovskite it is difficult to reliably determine its relationship to these chemically similar minerals. Data collection is not possible by a conventional single crystal XRD technique due to the small size and shape of the crystals. Therefore, it was decided to carry out a structural study of pushcharovskite using the synchrotron radiation source (SRS) at Daresbury Laboratory for data collection. The results of this work are reported below.

Experimental

A single crystal with dimensions $60 \times 20 \times 5$ μm^3 was used for the structure determination at room temperature. It was very difficult to separate a single crystal from its aggregate of thin elongated plates, hence the crystal, which was a part of this from the type material discovered in Cap Garonne, had such small dimensions. The data were collected at $\lambda = 0.6883$ Å using a Bruker AXS SMART CCD area detector diffractometer

on station 9.8 of the SRS Daresbury (Cernik *et al.*, 1997). A nominal hemisphere of diffraction data was collected with ω -rotations and processed (Clegg *et al.*, 1998). This yielded refined triclinic cell constants of $a = 13.6164(7)$, $b = 15.6672(8)$, $c = 19.1869(9)$ Å, $\alpha = 106.933(2)$, $\beta = 91.531(2)$, $\gamma = 98.401(2)^\circ$, $V = 3863.3(3)$ Å³. This unit cell has a volume three times bigger than that determined using a precession camera and reported by Sarp & Sanz-Gysler (1997). However, if we apply a transformation of $(-1 \ -1 \ 0 / -2 \ 1 \ 0 / 1 \ 0 \ -1)$ to the cell reported by Sarp & Sanz-Gysler this gives the values of $a = 13.57$, $b = 16.12$, $c = 19.36$ Å, $\alpha = 108.4$, $\beta = 90.8$, $\gamma = 99.4^\circ$. These unit cell parameters are very close to those derived from single-crystal diffraction data during the present investigation, suggesting that the crystal selected for structural study is pushcharovskite. The details of the crystal data and of the data collection are summarized in Table 1.

SHELXTL (Sheldrick, 1993) yielded solution and refinement of the crystal structure (space group $P\bar{1}$) by using 21299 reflections merged to 14598 independent reflections, of which 8343 reflections have $I > 2\sigma(I)$ with $R(int) = 0.043$. A

Table 2. Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for cations and isotropic displacement parameters for O atoms in pushcharovskite*.

Atom	x	y	z	U(eq)
As(1)	3528.1(9)	6136.0(9)	2654.1(6)	10.6(3)
As(2)	10266.6(9)	12872.5(9)	2833.5(6)	10.4(3)
As(3)	6865.7(9)	9508.6(9)	2740.6(6)	9.1(3)
As(4)	4690.2(9)	4076.1(9)	3378.3(6)	9.7(3)
As(5)	2658.2(9)	2180.7(9)	1741.8(6)	8.8(3)
As(6)	11160.0(9)	10702.3(9)	3165.2(6)	9.1(3)
As(7)	5894.8(9)	5592.5(9)	1715.9(6)	9.4(3)
As(8)	7920.1(9)	7439.4(8)	3319.9(6)	8.0(3)
As(9)	9205.9(9)	8854.9(9)	1553.0(6)	10.3(3)
As(10)	6096.7(9)	7844.0(9)	5075.1(6)	9.4(3)
As(11)	2862.0(9)	4384.0(9)	5036.2(6)	9.6(3)
As(12)	7949.1(9)	6513.1(9)	-11.0(6)	10.1(3)
As(13)	10337.2(9)	8848.4(9)	4744.7(6)	9.3(3)
As(14)	8699.4(9)	10387.6(9)	262.1(7)	11.4(3)
As(15)	5261.8(9)	6894.9(9)	-21.7(6)	10.3(3)
Cu(1)	4818.2(11)	5869.7(10)	4863.6(7)	10.2(3)
Cu(2)	5968.5(11)	6082.4(10)	3497.7(7)	10.0(3)
Cu(3)	5573.0(11)	7521.9(10)	2670.1(8)	10.9(3)
Cu(4)	7186.7(11)	7517.1(11)	1591.9(7)	11.3(3)
Cu(5)	7231.9(11)	8469.9(10)	329.7(8)	11.6(3)
Cu(6)	9187.9(11)	8311.6(11)	-344.3(8)	12.4(3)
Cu(7)	10561.9(11)	10721.4(11)	1570.3(7)	10.9(3)
Cu(8)	8922.3(11)	10905.9(10)	2745.0(8)	11.4(3)
Cu(9)	9153.1(11)	9405.8(11)	3439.7(8)	11.4(3)
Cu(10)	8092.0(11)	9262.8(11)	4865.8(8)	11.3(3)
Cu(11)	8416.1(11)	7551.7(11)	5158.4(8)	11.5(3)
Cu(12)	2706.3(11)	2664.4(11)	3466.3(7)	11.3(3)
Cu(13)	2320.2(11)	4149.9(11)	2671.4(8)	10.7(3)
Cu(14)	3855.5(11)	4115.8(10)	1551.8(7)	10.2(3)
Cu(15)	4003.5(10)	5054.2(10)	289.9(8)	10.7(3)
Cu(16)	9416.6(13)	7158.5(13)	2005.4(9)	11.7(6)
Cu(17)	4548.8(11)	7650.9(11)	6221.9(8)	10.3(5)
Cu(18)	8649.7(12)	5751.8(11)	3772.7(8)	13.2(5)
K	4604(5)	9897(5)	2191(4)	62(2)
O(1)	4742(6)	6488(6)	2828(4)	14(2)
O(2)	3040(6)	6524(6)	2021(5)	22(2)
O(3)	2972(6)	6461(6)	3431(4)	16(2)
O(4)	3278(6)	4975(6)	2361(4)	15(2)
O(5)	9791(6)	13284(6)	3631(4)	19(2)
O(6)	11502(6)	13150(6)	2862(4)	16(2)
O(7)	9953(6)	11755(6)	2511(4)	13(2)
O(8)	9800(6)	13341(6)	2225(5)	23(2)
O(9)	6415(6)	9960(6)	2152(4)	17(2)
O(10)	6280(6)	9824(6)	3513(4)	16(2)
O(11)	8106(6)	9860(6)	2919(4)	12(2)
O(12)	6602(6)	8361(6)	2410(4)	14(2)
O(13)	3468(6)	3771(6)	3350(4)	11(2)
O(14)	4958(6)	5198(6)	3671(4)	15(2)
O(15)	5336(6)	3592(6)	3862(4)	18(2)
O(16)	5064(6)	3770(6)	2489(4)	19(2)
O(17)	1532(6)	1677(6)	1416(4)	11(2)
O(18)	3068(6)	1974(6)	2500(4)	13(2)
O(19)	2769(6)	3283(6)	1801(4)	11(2)
O(20)	3462(6)	1765(6)	1082(4)	14(2)
O(21)	11644(6)	11756(6)	3619(4)	15(2)
O(22)	11381(6)	10391(6)	2283(4)	13(2)
O(23)	9929(6)	10506(6)	3317(4)	12(2)
O(24)	11713(6)	10016(6)	3563(4)	15(2)
O(25)	4744(6)	5120(6)	1391(4)	12(2)

small peak was located in a difference Fourier map during the refinement and was modelled as a partially occupied K, giving a final occupancy of 0.623 with sensible thermal parameter; this value is close to ~0.3 wt % K_2O from one electron microprobe analysis.

Other residual electron density peaks were found in the interlayer region and modelled as disordered water molecules down to a peak height of $1.76 \text{ e/\AA}^3$. As the refinement progressed an electron density peak with $x = 0.721(2)$, $y = 1.042(2)$, $z = 0.1485(15)$ appeared in the difference map.

Table 2 (continued).

Atom	x	y	z	U(eq)
O(26)	6049(6)	6691(6)	1800(4)	10(2)
O(27)	6217(6)	5305(6)	2458(4)	12(2)
O(28)	6693(6)	5171(6)	1060(4)	16(2)
O(29)	8143(6)	8570(6)	3666(4)	10(2)
O(30)	8591(6)	6996(6)	3820(4)	16(2)
O(31)	8164(6)	7097(6)	2436(4)	16(2)
O(32)	6699(6)	7152(6)	3380(4)	11(2)
O(33)	7983(6)	8519(6)	1379(4)	11(2)
O(34)	9560(6)	8506(6)	2252(4)	16(2)
O(35)	9384(6)	9969(6)	1711(4)	13(2)
O(36)	9843(6)	8392(6)	826(4)	16(2)
O(37)	5443(6)	8553(6)	4832(4)	14(2)
O(38)	5702(6)	6776(6)	4548(4)	13(2)
O(39)	5918(6)	7897(6)	5949(4)	13(2)
O(40)	7313(6)	8172(6)	4997(4)	10(2)
O(41)	2213(6)	5109(6)	4809(4)	16(2)
O(42)	2698(6)	4375(6)	5903(4)	15(2)
O(43)	4066(6)	4689(6)	4914(4)	10(2)
O(44)	2462(6)	3307(6)	4492(4)	12(2)
O(45)	8982(6)	6115(6)	-272(4)	18(2)
O(46)	6972(6)	5820(6)	-522(4)	14(2)
O(47)	7817(6)	6599(6)	888(4)	14(2)
O(48)	7998(6)	7535(6)	-170(4)	10(2)
O(49)	10897(6)	7974(6)	4743(4)	18(2)
O(50)	11009(6)	9776(6)	5320(4)	12(2)
O(51)	10259(6)	8940(6)	3883(4)	13(2)
O(52)	9192(6)	8676(6)	5069(4)	10(2)
O(53)	7833(6)	10914(6)	728(4)	21(2)
O(54)	9862(6)	10815(6)	643(4)	11(2)
O(55)	8410(6)	9270(6)	145(4)	12(2)
O(56)	8694(6)	10518(6)	-589(4)	19(2)
O(57)	4185(6)	7273(6)	170(5)	22(2)
O(58)	6208(6)	7605(6)	531(4)	15(2)
O(59)	5489(6)	6832(6)	-909(4)	15(2)
O(60)	5161(5)	5866(5)	130(4)	7(2)
O(61)	3178(6)	6009(6)	607(4)	16(2)
O(62)	3643(6)	6421(6)	4757(4)	16(2)
O(63)	6919(6)	9871(6)	4844(4)	15(2)
O(64)	9500(6)	6837(6)	5097(4)	16(2)
O(65)	4976(6)	8383(6)	3437(4)	16(2)
O(66)	9983(6)	7346(6)	-720(5)	23(2)
O(67)	4115(7)	8587(7)	5832(5)	18(2)
O(68)	8083(7)	5035(6)	2584(5)	18(2)
O(69)	6482(6)	9471(6)	709(4)	16(2)
O(70)	7873(6)	11282(6)	2213(4)	19(2)
O(71)	1750(6)	5042(6)	3416(4)	20(2)
O(72)	9342(7)	5806(7)	1751(5)	13(2)
O(73)	10041(8)	5914(8)	3454(5)	32(3)
O(74)	5088(7)	8431(7)	7374(5)	24(2)
O(75)	3160(8)	7384(8)	6497(6)	32(3)
O(76)	10578(7)	7339(7)	2944(5)	16(2)
O(77)	8689(16)	4552(15)	3936(11)	11(5)
O(78)	10431(8)	7112(8)	1251(6)	23(3)
O(79)	4531(10)	8262(10)	1748(7)	20(3)
O(80)	3807(11)	10087(11)	3308(8)	28(4)
O(81)	4530(2)	10310(2)	990(13)	22(7)
O(82)	2776(15)	9402(14)	1739(10)	21(5)

* Occupancy coefficient for K = 0.632 was fixed during the refinement and checked by the reasonable size of the thermal parameter.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor. Numbers in parentheses are the estimated standard deviations on the last digits.

The square planar geometry around this peak was consistent with a site being occupied by additional copper atom. On refining the peak as a partially occupied Cu site, occupancy was $\sim 0.07(1)$; conventional unweighted $R = 0.054$. The final differ-

ence Fourier map was featureless: $\delta\rho$ maximum and minimum were $1.76 \text{ e}/\text{\AA}^3$ and $-1.42 \text{ e}/\text{\AA}^3$. The atomic coordinates, displacement parameters, selected interatomic distances and bond angles are collected in Tables 2 and 3.

Appendix to Table 2. Atomic coordinates ($\times 10^3$), isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) and site occupancy factors for non-bonded H_2O molecules in pushcharovskite*.

Atom	x	y	z	s.o.f.	U
O(83)	1112(1)	528(1)	157.9(7)	0.6	18(3)
O(84)	409(1)	782(1)	844.4(8)	0.6	21(3)
O(85)	994(1)	552(1)	43.5(8)	0.6	26(4)
O(86)	876(2)	1174(2)	-65(1)	0.4	33(6)
O(87)	219(2)	721(2)	-59(2)	0.25	26(9)
O(88)a	786(2)	1317(2)	205(1)	0.5	37(6)
O(88)b	774(2)	1320(2)	205(1)	0.4	28(6)
O(89)a	258(2)	815(1)	433(1)	0.5	15(4)
O(89)b	258(3)	824(2)	407(2)	0.25	18(9)
O(90)a	240(2)	809(2)	266(1)	0.3	14(6)
O(90)b	210(2)	789(2)	222(2)	0.3	20(7)
O(91)a	867(2)	442(2)	32(1)	0.4	31(6)
O(91)b	885(2)	418(2)	-2(2)	0.3	21(7)
O(92)a	330(3)	831(3)	-16(2)	0.25	39(10)
O(92)b	392(2)	879(2)	-13(1)	0.3	25(7)
O(92)c	454(3)	898(3)	-5(2)	0.25	40(11)

* Occupancy coefficients for O(83-92) were fixed during the refinement and checked by the reasonable sizes of the thermal parameters. The splitted sites marked with letters a, b, c.

Table 3. Ranges of bond lengths (l , $\text{\AA}$) and of bond angles ($^\circ$) in pushcharovskite.

Polyhedron	C.N.	Distances cation-anion			O-As-O	<O-O>
		$l_{\min}$	$l_{\max}$	average		
As(1) ^{##}	4	1.657(8)	1.719(9)	1.680	106.3(4)-112.6(4)	2.742
As(2) ^{##}	4	1.664(9)	1.703(9)	1.676	106.6(4)-113.6(4)	2.736
As(3) ^{##}	4	1.656(8)	1.703(9)	1.683	107.4(4)-110.9(4)	2.744
As(4) [#]	4	1.658(8)	1.743(8)	1.683	105.2(4)-113.8(4)	2.745
As(5) [#]	4	1.643(8)	1.740(8)	1.686	104.0(4)-115.3(4)	2.744
As(6) [#]	4	1.653(9)	1.729(8)	1.690	104.7(4)-114.6(4)	2.756
As(7) [#]	4	1.652(8)	1.732(8)	1.682	104.0(4)-116.7(4)	2.743
As(8) [#]	4	1.662(8)	1.678(8)	1.674	104.8(4)-111.4(4)	2.733
As(9) [#]	4	1.662(9)	1.697(8)	1.675	105.7(4)-111.7(4)	2.735
As(10) [#]	4	1.677(8)	1.685(8)	1.681	108.6(4)-109.3(4)	2.745
As(11) [#]	4	1.680(8)	1.706(8)	1.689	107.8(4)-111.8(4)	2.758
As(12) [#]	4	1.652(8)	1.707(8)	1.685	107.4(4)-109.6(4)	2.751
As(13) ^{##}	4	1.662(9)	1.709(8)	1.687	108.0(4)-110.9(4)	2.753
As(14) ^{##}	4	1.668(9)	1.704(8)	1.685	105.6(4)-113.2(4)	2.750
As(15) [#]	4	1.670(9)	1.709(8)	1.693	109.0(4)-110.5(4)	2.765
Cu(1)	6	1.957(8)	2.369(8)	2.086	5.5	
Cu(2)	6	1.896(8)	2.426(8)	2.121	8.7	
Cu(3)	5	1.940(9)	2.270(7)	2.024		
Cu(4)	5	1.925(8)	2.365(8)	2.054		
Cu(5)	5	1.926(8)	2.209(7)	2.011		
Cu(6)	6	1.963(8)	2.356(8)	2.085	5.4	
Cu(7)	5	1.921(8)	2.310(8)	2.039		
Cu(8)	5	1.943(8)	2.263(8)	2.033		
Cu(9)	6	1.906(8)	2.431(8)	2.127	8.5	
Cu(10)	5	1.921(8)	2.249(8)	2.014		
Cu(11)	5	1.946(8)	2.289(8)	2.028		
Cu(12)	5	1.961(8)	2.321(8)	2.043		
Cu(13)	5	1.917(9)	2.259(8)	2.011		
Cu(14)	5	1.945(8)	2.283(8)	2.042		
Cu(15)	5	1.922(8)	2.285(8)	2.022		
Cu(16)	5	1.917(8)	2.291(10)	2.050		
Cu(17)	5	1.937(9)	2.235(10)	2.023		
Cu(18)	5	1.939(9)	2.284(9)	2.038		
K		2.388(16)	2.570(30)	2.480		

* $\Delta = \sum[(l-l_0)/l_0]^2/6$ -bond-length distortion

$\text{AsO}_3(\text{OH})$ tetrahedron

$\text{AsO}_2(\text{OH})_2$ tetrahedron.

Calculation of the sum of the bond strengths on the anions (Brown & Shannon, 1973) allowed the assignment of O, OH and H_2O to oxygen

positions (Table 4). Due to the partial occupancies of the non-bonded water molecules, pushcharovskite can be considered as a mineral with some

Table 4. Total bond strengths (Σs) for oxygen atoms in the crystal structure of pushcharovskite*.

Atom	Σs	Atom	Σs	Atom	Σs
O(1)	2.00	O(28) (OH)	1.10	O(55)	2.11
O(2) (OH)	1.30	O(29)	2.02	O(56) (OH)	1.19
O(3) (OH)	1.30	O(30)	1.83	O(57) (OH)	1.30
O(4)	2.07	O(31)	1.96	O(58)	1.75
O(5) (OH)	1.31	O(32)	2.05	O(59)	1.60
O(6)	2.01	O(33)	2.06	O(60)	2.10
O(7)	1.99	O(34)	1.84	O(61) [(OH) _{0.5} (H ₂ O) _{0.5}]	0.46
O(8) (OH)	1.19	O(35)	2.05	O(62) [(OH) _{0.5} (H ₂ O) _{0.5}]	0.47
O(9) (OH)	1.35	O(36) (OH)	1.37	O(63) [(OH) _{0.5} (H ₂ O) _{0.5}]	0.44
O(10) (OH)	1.26	O(37) (OH)	1.28	O(64) [(OH) _{0.5} (H ₂ O) _{0.5}]	0.46
O(11)	2.07	O(38)	2.07	O(65) [(OH) _{0.5} (H ₂ O) _{0.5}]	0.46
O(12)	2.09	O(39)	1.73	O(66) [(OH) _{0.5} (H ₂ O) _{0.5}]	0.46
O(13)	2.02	O(40)	2.18	O(67) [(OH) _{0.5} (H ₂ O) _{0.5}]	0.44
O(14)	2.06	O(41) (OH)	1.27	O(68) [(OH) _{1/3} (H ₂ O) _{2/3}]	0.19
O(15)	1.97	O(42)	1.84	O(69) [(OH) _{0.5} (H ₂ O) _{0.5}]	0.46
O(16) (OH)	1.07	O(43)	2.14	O(70) [(OH) _{0.5} (H ₂ O) _{0.5}]	0.43
O(17)	2.10	O(44)	2.10	O(71) [(OH) _{0.5} (H ₂ O) _{0.5}]	0.48
O(18)	1.72	O(45) (OH)	1.36	O(72) [(OH) _{0.5} (H ₂ O) _{0.5}]	0.40
O(19)	2.11	O(46)	2.01	O(73) [(OH) _{0.5} (H ₂ O) _{0.5}]	0.41
O(20) (OH)	1.08	O(47)	1.62	O(74) [(OH) _{1/3} (H ₂ O) _{2/3}]	0.22
O(21)	2.01	O(48)	2.10	O(75) [(OH) _{0.5} (H ₂ O) _{0.5}]	0.42
O(22)	1.76	O(49) (OH)	1.33	O(76) [(OH) _{1/3} (H ₂ O) _{2/3}]	0.19
O(23)	2.05	O(50)	1.97	O(77) [(OH) _{0.5} (H ₂ O) _{0.5}]	0.42
O(24) (OH)	1.11	O(51)	1.57	O(78) [(OH) _{0.5} (H ₂ O) _{0.5}]	0.40
O(25)	2.04	O(52)	2.10	O(79) [(OH) _{1/4} (H ₂ O) _{3/4}]	0.17
O(26)	2.20	O(53) (OH)	1.31	O(80) [(OH) _{1/3} (H ₂ O) _{2/3}]	0.19
O(27)	1.61	O(54)	2.08	O(81) [(OH) _{1/4} (H ₂ O) _{3/4}]	0.15
				O(82) [(OH) _{1/4} (H ₂ O) _{3/4}]	0.16

* The strict definition of the atoms O(61) – O(82) as [(OH)_{0.5}(H₂O)_{0.5}], [(OH)_{1/3}(H₂O)_{2/3}] and [(OH)_{1/4}(H₂O)_{3/4}] can be considered as a model one. Due to the partial occupancies of one Cu atom and of K atom some disorder according to [(OH), (H₂O)] sites should be allowed.

structural disorder and its general formula, mainly in accordance with electron microprobe analysis, is: $K_{0.6}Cu_{18}[AsO_{2.8}(OH)_{1.2}]_{15}(OH)_{9.6} \cdot 18.6H_2O$. The corresponding structural formula is $K_{0.6}Cu_{18}[AsO_2(OH)_2]_4[AsO_3(OH)]_{10}[AsO_4](OH)_{9.6} \cdot 18.6(H_2O)$. Both chemical and structural formulae lead to the elementary composition $K_{0.02}Cu_{1.125}As_{0.94}O_{5.515}H_{4.06}$ with $Z = 32$, which exhibits some deviations with respect to the initial composition $CuAsO_5H_3$ (Sarp & Sanz-Gysler, 1997), mainly due to the low content of H_2O molecules in the latter. The difference between the structural and electron microprobe data can be explained by the partial decomposition of mineral and by loss of some of water molecules in the process of electron microprobe analysis. Consequently, as is often the case with hydrated minerals, the results obtained with the electron microprobe reproduce the higher content of some elements, namely As in pushcharovskite. The revision of chemical data of pushcharovskite after its structure was solved allowed the conclusion that its idealized formula can be presented as $CuAsO_3(OH) \cdot 1.5H_2O$. The value of density calculated on the basis of the structural formula, 3.235 g/cm³, essentially matches the experimental density of 3.35 g/cm³.

The intensity calculations (Yvon *et al.*, 1977)

for pushcharovskite (Table 5) demonstrated an agreement with powder diffraction data despite

Table 5. X-ray powder diffraction data of pushcharovskite*.

h	k	l	d_{calc}	d_{meas}	I_{calc}	I_{obs}
0	0	1	18.306	18.30	1	25
1	-1	0	10.852	11.00	100	100
1	-1	-1	8.742	8.77	2	5
0	0	3	6.102	6.11	1	10
1	-1	3	5.724	5.79	3	15
0	0	4	4.576	4.585	3	10
1	-1	4	4.481	4.518	2	10
3	0	1	4.425	4.330	1	5
0	3	-4	4.002		1	
1	-1	-4	3.994		1	
2	1	-4	3.948	3.965	0.5	15
0	3	2	3.882	3.878	1	20
3	-3	1	3.662	3.668	0.8	5
1	4	-1	3.564		1	
3	0	3	3.490		1	
			}	3.483	}	<5
1	-4	-1	3.564		1	
0	3	3	3.374	3.389	2	15
4	-1	1	3.342		2	
			}	3.333	}	10
1	-1	-5	3.313		2	
2	-2	5	3.288	3.304	1	5
2	-2	-4	3.252		3	
			}	3.251	}	5
1	2	4	3.248		0.6	
3	-3	-2	3.194	3.200	2	5

* XRD pattern performed with a Guinier-Hagg camera (Cu $K\alpha_1$ radiation), d_{calc} and I_{calc} calculated using the program LAZY PULVERIX (Yvon *et al.*, 1977).

some discrepancies between I_{obs} and I_{calc} . This can be explained as preferred orientation of plate-like grains resulting in variations of I_{obs} .

The figures were obtained with the use of the program ATOMS (Dowty, 1995).

Discussion

The most specific features of the pushcharovskite structure are the centrosymmetric sheets (110) (Fig. 1), which comprise 18 symmetrically independent distorted Cu bipyramids ($\text{Cu}\phi_6$) and Cu 5-vertices square pyramids ($\text{Cu}\phi_5$), where ϕ is an unspecified ligand. The strongest reflection (110) in the powder diffraction pattern (Table 5) confirms the orientation of these sheets. The columns with 15 Cu-polyhedra in the period which match the distance between two inversion centers are elongated along [223]. The links between Cu-polyhedra are reinforced by $\text{As}\phi_4$ tetrahedra and thus the compact and thick sheets are formed (Fig. 2). All the Cu polyhedra are involved in the formation of the sheets and share either two edges or one edge and one vertex with their neighbours. Three Cu polyhedra (Cu16,

Cu17 and Cu18) extend into the region between the columns and provide the linkage between them (Fig. 1); their central cations are characterized by partial occupancies and by 5-fold coordination. However, the O-Cu(17)-O angles suggest that the coordination polyhedron around Cu(17) can be better described as intermediate between a tetragonal pyramid and a trigonal bipyramid (180° between the axial ligands, 152° , 105° and 103° within the equatorial plane and 87° to 93° between an axial and an equatorial ligand). Such transitions were described by Effenberger (1988) and later on by Burns & Hawthorne (1995).

A partially occupied K-site is located in the interlayer region and forms a distorted octahedron with oxygen, hydroxyls and water molecules (O-K-O angles 77° - 173°), similar to that occurring in some layer silicates (Fig. 2). Apparently the structural role of K is to connect the polyhedral sheets together. The interlayer region is also filled by disordered, uncoordinated water molecules. Their positions are characterized by relatively small values of occupancy coefficients and are listed in Table 2. Moreover, the sheets are also linked by hydrogen bonding involving the water molecules of the $\text{Cu}\phi_6$ and $\text{Cu}\phi_5$ polyhedra, the

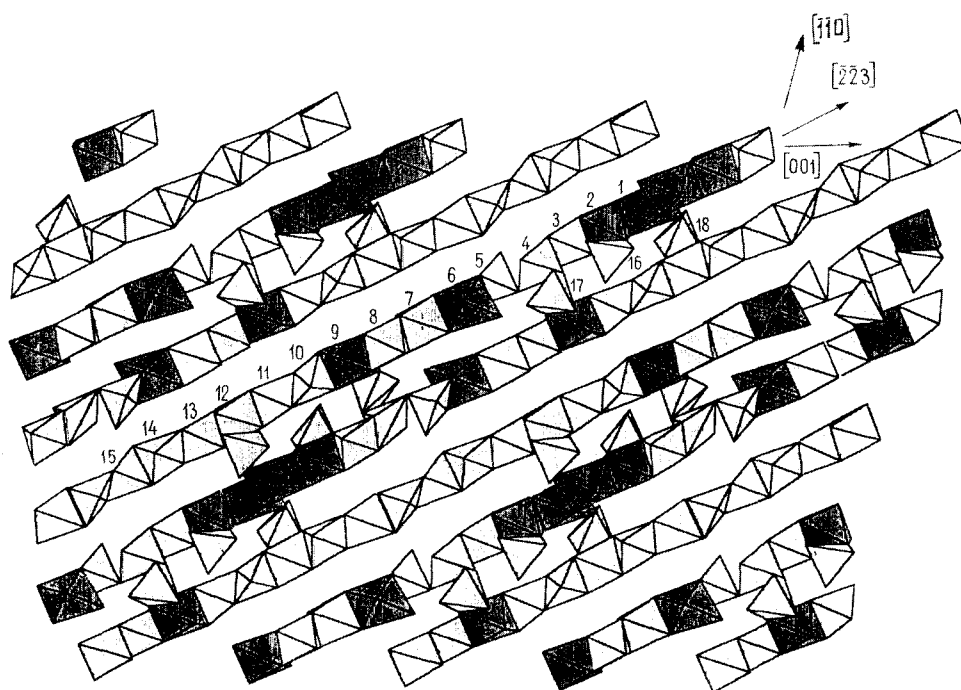


Fig. 1. The sheets (110) formed by Cu,O square bipyramids (black) and by Cu,O square pyramids (grey). The eighteen independent Cu sites are shown.

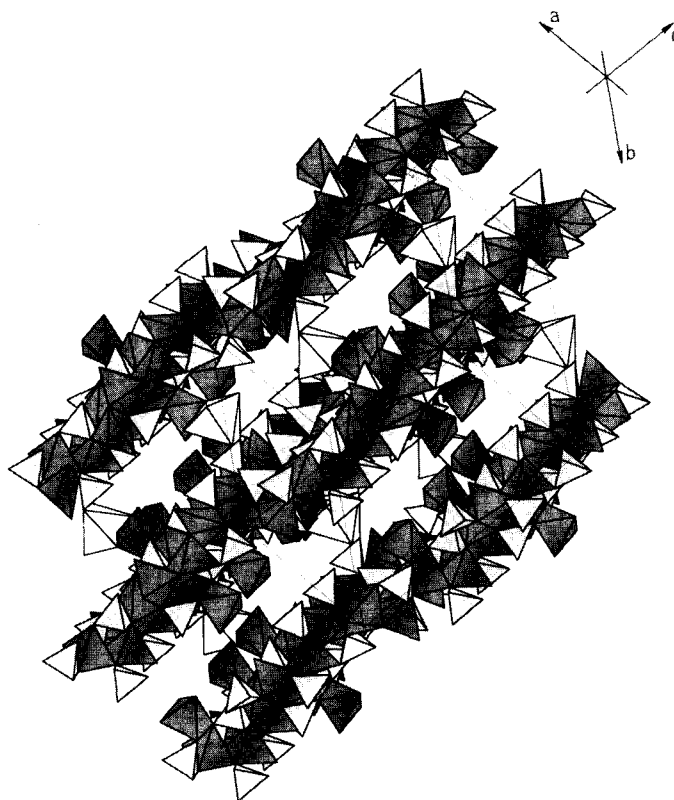


Fig. 2. A general view of the structure of pushcharovskite. Cu₂O polyhedra and AsO₃OH tetrahedra are shown with dark and light grey color, respectively. Big white octahedra between heteropolyhedral layers are filled by K atoms with partial occupancies.

OH groups of the As₂O₃OH tetrahedra and H₂O molecules present in the interlayers. Since the H atoms have not been located, a scheme of hydrogen bonding can only be inferred on the basis of distances and angles involving the O atoms. The formation of the mixed (bipyramidal - square pyramidal - tetrahedral) sheets in pushcharovskite is in accordance with its Cu/As ratio ~ 1.17 (Eby & Hawthorne, 1993).

The mixed sheets formed by Cu-polyhedra and by As-tetrahedra can also be identified in geminite (Cooper & Hawthorne, 1995; Prencipe *et al.*, 1996), yvonite (Sarp & Černý, 1998) and fluckite, CaMn(AsO₃OH)₂·2(H₂O) (Catti *et al.*, 1980). The heteropolyhedral sheets in pushcharovskite are parallel to (110) with d-spacing = 10.90 Å. This peculiarity allows the direct comparison between pushcharovskite, geminite and yvonite. In geminite the Cu,As,O sheets are parallel to (001), the c-axis = 15.764 Å and the separation between

them is 7.822 Å. In yvonite the similar sheets are perpendicular to the a-axis (7.632 Å, approximately half of the c cell dimension in geminite) and in fluckite - to the b-axis = 7.613 Å. The separation of the layers in these structures is 7.624 Å and 7.534 Å, respectively. The longer distance between two sheets in pushcharovskite is due to their greater thickness and to larger interlayer spacing as compared to the other mentioned minerals.

Four symmetrically independent Cuφ₆ square bipyramids (Cu 1,2,6,9) with two axial elongated distances Cu-φ (Table 3) exhibit typical distortion associated with the Jahn-Teller effect. Due to this effect, the bond-length distribution in Cu square bipyramids corresponds to [4+2] coordination. The dependence of mean values of Cu-φ bond length on the bond length distortion (Table 3) follows the linear relationship given by Eby & Hawthorne (1993). Although octahedral coordina-

tion is by far the most common in oxysalt minerals, 14 of 18 independent Cu atoms in pushcharovskite are in square-pyramidal coordination. Square-pyramidal Cu polyhedra can be derived from octahedra by removing an axial ligand. Consequently, there is no orbital degeneracy and these polyhedra exhibit much smaller distortions from regularity than the Cu square bipyramids. However, it is worth stressing that four square pyramids (Cu 4, 7, 11, 12) have a sixth ligand between 2.450 and 2.547 Å. Consequently, their coordination is not clearly defined and a weak interaction to these additional ligands should be considered.

14 of 15 symmetrically independent As-tetrahedra contain OH groups and four of them (As1, 2, 3, 14) are biprotonated $[\text{AsO}_2(\text{OH})_2]$. The biprotonated tetrahedra are considered as an element of the structure of kaatialaite, $\text{Fe}(\text{H}_2\text{AsO}_2)_3 \cdot 5\text{H}_2\text{O}$ (Boudjada & Guitel, 1981; Raade *et al.*, 1984) and are seen in many synthetic arsenates and phosphates (Ferraris & Ivaldi, 1984). All OH groups in As tetrahedra are not shared with Cu polyhedra and occupy the nonbridging sites. A survey of the As-OH distances in As₂O₂(OH)₂ tetrahedra shows that usually these bonds are the longest and they correlate with the coordination numbers of the relevant O atoms; their average lengths in AsO₃(OH) tetrahedra are ~ 1.731 Å and in AsO₂(OH)₂ ~ 1.709 Å (Ferraris & Ivaldi, 1984). In pushcharovskite some of these bonds are longer as compared with usual As-O distances (1.695 Å) but shorter than the values given above (Table 3). These deviations from the correlations reported by Ferraris & Ivaldi, (1984) are due to some peculiarities of data collection and to the specific features of the structure: i) the reflections are weak, even with the synchrotron radiation, due to the small size and the anisotropic shape of the crystal and to its high absorption; ii) the relatively small atomic displacement parameters (Table 2) could be explained by a non-ideal absorption correction applied; iii) the above mentioned structural disorder in the interlayers could lead to the delocalization of the protons in some (OH)-groups and consequently to the shortening of anion-ligand distances.

The atomic arrangement of pushcharovskite corresponds to a lower packing density compared with other chemically related supergene secondary alteration hydrated geminite, lindackerite (Sarp & Dominik, 1995) and yvonite discovered in paragenesis with it. The volume per oxygen atom in pushcharovskite is ~ 22.1 Å³, while in yvonite and in geminite these values are 20.6 and 20.3 Å³

respectively. Thus the structural peculiarities of pushcharovskite are in accordance with mineralogical observations which allow to consider its formation on the latest stage of supergene alteration of sulfo-arsenic minerals in the Cap Garonne and in Salsigne mines. The subsequent replacement of double Cu octahedra in geminite by the octahedral chains in yvonite and by the heteropolyhedral sheets in pushcharovskite correlates with the reinforcement of cationic role of Cu polyhedra during the evolution of the crystallization of the secondary copper arsenates.

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