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Crystal Structure of Synthetic $Cu_3SeO_4(OH)_4$

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Summary. The crystal structure of synthetic $Cu_3SeO_4(OH)_4$ was determined by single crystal X-ray methods: $a = 8.382(2)$ Å, $b = 6.087(1)$ Å, $c = 12.285(2)$ Å, $V = 626.8$ Å^3, $Z = 4$, space group Pnma, $R = 0.026$, $R_w = 0.021$ for 1255 independent reflections ($\sin\theta/\lambda \leqslant 0.8$ Å^{-1}). The crystal structure is isotypic to that of the mineral antlerite, $Cu_3SO_4(OH)_4$. The copper atoms are Jahn-Teller distorted with $Cu^{[4+2]}O_6$ polyhedra forming triple chains along [010]. These chains are linked via SeO_4 tetrahedra and weak hydrogen bonds to a framework structure.

Keywords. $Cu_3SeO_4(OH)_4$; Antlerite type structure; Hydrothermal synthesis; Crystal chemistry.

Die Kristallstruktur von synthetischem $Cu_3SeO_4(OH)_4$

Zusammenfassung. Die Kristallstruktur von synthetischem $Cu_3SeO_4(OH)_4$ wurde mittels Einkristall-Röntgenmethoden ermittelt: $a = 8.382(2)$ Å, $b = 6.087(1)$ Å, $c = 12.285(2)$ Å, $V = 626.8$ Å^3, $Z = 4$, Raumgruppe Pnma, $R = 0.026$, $R_w = 0.021$ für 1255 unabhängige Reflexe ($\sin\theta/\lambda \leqslant 0.8$ Å^{-1}). Die Kristallstruktur ist isotyp mit der des Minerals Antlerit, $Cu_3SO_4(OH)_4$. Die Kupferatome sind Jahn-Teller-verzerrt, die $Cu^{[4+2]}O_6$ Polyeder bilden Dreierketten entlang [010]. Diese Ketten sind über SeO_4-Tetraeder und schwache Wasserstoffbrücken zu einer Gerüststruktur verbunden.

Introduction

Crystals of $Cu_3SeO_4(OH)_4$ were obtained in course of experiments on the synthesis of natrochalcite type compounds [1, 2]. The structure determination revealed isotypy of $Cu_3SeO_4(OH)_4$ with antlerite, $Cu_3SO_4(OH)_4$, a mineral found in the oxidation zone of sulfidic copper ores. The crystal structure of antlerite was solved by Finney and Araki [3], a structure refinement [4] additionally established the arrangement of the hydrogen bond system.

Experimental

Preparation of $Cu_3SeO_4(OH)_4$ was done under hydrothermal conditions: Copper oxide rods (Kupferoxid Drahtform, Art. 2767 Fa. E. Merck, Darmstadt, FRG) were heated in "Teflon"-lined steel vessels of ~ 6 cm^3 capacity together with $Na_2CO_3 \cdot 10\,H_2O$, H_2SeO_4 and little water to ~ 500 K for one week. Upon cooling to room temperature, several phases could be isolated, among them $NaCu_2(SeO_4)_2 \cdot H_3O_2$ and $Cu_3SeO_4(OH)_4$. Crystals of $Cu_3SeO_4(OH)_4$ are of darkgreen color, they are elongated along [010] up to several mm in length.

A preliminary investigation of the title compound was made by Weissenberg techniques. Final lattice parameters were obtained from 44 reflections, their accurate $2\,\theta$-values being measured in the

Table 1. Details on data collection and structure refinement of $Cu_3SeO_4(OH)_4$. AED2 four-circle diffractometer, program system STRUCSY (Stoe and Cie, Darmstadt, FRG); computer ECLIPSE S140 (Data General); graphite monochromatized MoKα-radiation; 3 standard reflections measured each 120 min; range of data collection: $5° < 2\theta < 70°$; time per step: 0.5 to 1.5 s; $2\theta - \Omega$ scan, step width 0.03°; space group Pnma; $Z = 4$

a [Å]	8.382(2)
b [Å]	6.087(1)
c [Å]	12.285(2)
V [A^3]	626.8
ρ_{calc} [g cm^{-3}]	4.256
$\mu_{(MoK\alpha)}$ [cm^{-1}]	154.91
Extinction coefficient $g \cdot 10^6$ (according to Zachariasen, 1967)	5.0(4)
Steps/reflection	44
Steps for background	7
Total measured reflections	3806
Unique data	1478
$F_0 > 3\sigma(F_0)$ (structure refinement)	1255
R	0.026
R_w; $w = 1/[\sigma(F_0)]^2$	0.021
Number of variables	72

Table 2. Structural parameters of $Cu_3SeO_4(OH)_4$, e.s.d.'s in parentheses. $ATF = \exp[-2\pi^2 \sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij} h_i h_j a_i^* a_j^*]$; U_{ij} are given in pm^2

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	0.00453(6)	0.25	0.00115(4)	139(2)	104(2)	131(2)	0	−27(1)	0
Cu(2)	0.28182(3)	0.00046(5)	0.12724(2)	114(1)	117(1)	139(1)	−2(1)	−17(1)	7(1)
Se	0.12942(4)	0.25	0.36489(3)	96(1)	119(1)	109(1)	0	−2(1)	0
O(1)	0.2698(3)	0.25	0.2729(2)	167(11)	190(12)	150(10)	0	52(10)	0
O(2)	0.2124(3)	0.25	0.4858(2)	210(12)	153(12)	121(10)	0	−32(9)	0
O(3)	0.0237(2)	0.0233(3)	0.3504(2)	129(7)	147(8)	244(8)	−22(6)	0(6)	−44(7)
OH(1)	0.2780(3)	0.25	0.0300(2)	138(10)	145(11)	146(10)	0	8(9)	0
OH(2)	0.7152(3)	0.25	0.7783(2)	150(11)	153(11)	135(10)	0	22(9)	0
OH(3)	0.0399(2)	0.5056(3)	0.1011(1)	142(7)	152(8)	110(6)	5(7)	2(6)	2(7)
H(1)	0.325(6)	0.25	0.988(4)						
H(2)	0.223(6)	0.75	0.256(4)						
H(3)	0.482(4)	0.000(6)	0.648(3)						

range $26° < 2\theta < 48°$ with a four-circle diffractometer. A summary of crystal data, X-ray data collection and details of the structure refinement is given in Table 1.

The X-ray intensities were corrected for absorption (spherical correction), Lorentz- and polarisation effects. Complex scattering functions were taken from [5]. Atomic coordinates of antlerite [3] were used as starting set for the structure refinement of $Cu_3SeO_4(OH)_4$ [full-matrix least-squares techniques]. Subsequent difference-Fourier summations revealed the positions of the hydrogen atoms

Table 3. Interatomic distances [Å], bond angles [°] and bond valences [v. u.] [6] in $Cu_3SeO_4(OH)_4$; the atoms are indexed according to [4]

Equivalent positions

a:	x,	$1/2-y$,	z	b:	$-x$,	$1-y$,	$-z$
c:	$-x$,	$y-1/2$,	$-z$	d:	$x-1/2$,	y,	$1/2-z$
e:	$1/2+x$,	y,	$1/2-z$	f:	$1-x$,	$-y$,	$1-z$
g:	$1/2-x$,	$-y$,	$z-1/2$				

	[Å]		[v. u.]		[Å]	[°]	
Cu(1)−OH(3), a	2.004(1)	2×	0.415	OH(1)−OH(3)	2.677(3)	76.1(1)	2×
Cu(1)−OH(3) b, c	1.982(1)	2×	0.441	OH(1)−OH(3) c	3.450(3)	106.4(1)	2×
Cu(1)−OH(1)	2.319(2)	1×	0.177	OH(3)−O(2) d	3.331(3)	96.2(1)	2×
Cu(1)−O(2) d	2.454(2)	1×	0.123	OH(3)−OH(3) b	2.572(3)	80.4(1)	2×
				OH(3)−OH(3) b	3.112(4)	101.9(1)	1×
⟨Cu−O⟩ [4]	1.993			O(2) d−OH(3) c	2.921(3)	81.6(1)	2×
⟨Cu−O⟩ [6]	2.124	Σ	2.013	OH(3) b−OH(3) c	2.975(4)	97.3(1)	1×
					⟨2.999⟩		
Cu(2)−OH(1)	1.933(1)	1×	0.503	O(1)−OH(1)	2.985(4)	87.8(1)	1×
Cu(2)−O(3) e	2.051(1)	1×	0.366	O(1)−O(3) e	2.955(3)	84.1(1)	1×
Cu(2)−OH(2) f	1.916(1)	1×	0.527	O(1)−OH(2) f	3.110(1)	93.1(1)	1×
Cu(2)−OH(3) a	2.054(1)	1×	0.363	O(1)−OH(3) a	3.254(3)	95.1(1)	1×
Cu(2)−O(2) g	2.313(1)	1×	0.180	OH(1)−O(2) g	3.093(1)	93.1(1)	1×
Cu(2)−O(1)	2.349(1)	1×	0.164	OH(1)−O(3) e	2.882(3)	92.6(1)	1×
				OH(1)−OH(3) a	2.677(3)	84.3(1)	1×
⟨Cu−O⟩	1.999			O(2) g−O(3) e	3.276(3)	97.1(1)	1×
⟨Cu−O⟩	2.103	Σ	2.103	O(2) g−OH(2) f	2.899(3)	86.0(1)	1×
				O(2) g−OH(3) a	2.921(3)	83.8(1)	1×
				O(3) e−OH(2) f	2.750(3)	87.7(1)	1×
				OH(2) f−OH(3) a	2.937(3)	95.4(1)	1×
					⟨2.978⟩		
Se−O(1)	1.631(2)	1×	1.529	O(1)−O(2)	2.659(3)	108.8(1)	1×
Se−O(2)	1.640(2)	1×	1.492	O(1)−O(3)	2.658(3)	108.2(1)	2×
Se−O(3), a	1.650(1)	2×	1.452	O(2)−O(3)	2.678(3)	109.0(1)	2×
				O(3)−O(3) a	2.760(4)	113.6(1)	1×
⟨Se−O⟩	1.643	Σ	5.925				
					⟨2.682⟩	⟨109.46⟩	

H(1) and H(3). The position of the atom H(2) could not be located by this method, but when put on the most reasonable position taking stereochemical aspects into consideration, the atomic coordinates of H(2) also refined satisfactorily. During refinement of the hydrogen atoms H(1), H(2), and H(3), their isotropic temperature factors were fixed at $U_{iso} = 200\,pm^2$. The hydrogen bond scheme found for the title compound agrees with that in antlerite [4]; Fig. 1 shows the arrangements of hydroxyl groups and hydrogen bonds in $Cu_3SeO_4(OH)_4$. Table 2 lists finally obtained structural parameters for $Cu_3SeO_4(OH)_4$. Selected interatomic bond distances, bond angles and bond valence calculations [6] are compiled in Tables 3 and 4.

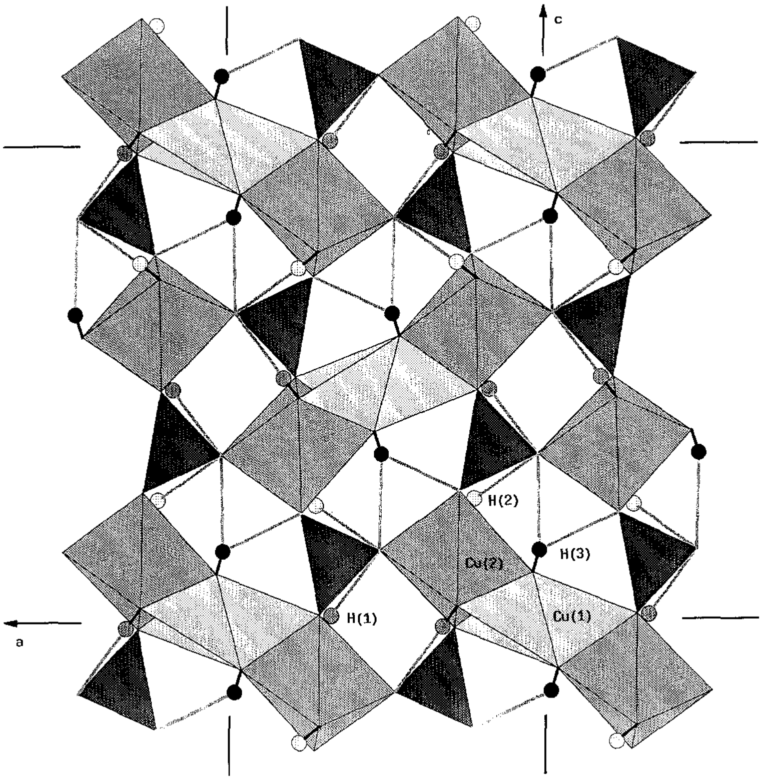

Fig. 1. Crystal structure of $Cu_3SeO_4(OH)_4$ in a projection on (010), showing the hydrogen bond system

Table 4. Hydrogen bond scheme in $Cu_3SeO_4(OH)_4$

OH(1)···O(3)	2×	3.224(3) Å	OH(3)···O(3)	3.071(2) Å
OH(1)−H(1)		0.65(5) Å	OH(3)···O(1)	3.154(3) Å
H(1)···O(3)	2×	2.69(4) Å	OH(3)−H(3)	0.60(3) Å
OH(1)−H(1)···O(3)		142(4)°	H(3)···O(3)	2.50(3) Å
			H(3)···O(1)	2.76(4) Å
			OH(3)−H(3)···O(1)	127(4)°
OH(2)···O(3)	2×	3.171(3) Å	OH(3)−H(3)···O(3)	161(8)°
OH(2)−H(2)		0.67(5) Å		
H(2)···O(3)	2×	2.63(4) Å		
OH(2)−H(2)···O(3)		141(3)°		

Results and Discussion

The copper atoms Cu (1) [point symmetry m] and Cu (2) [point symmetry 1] are each coordinated by six oxygen atoms forming elongated "octahedra" $Cu^{[4+2]}O_6$. These distortions, well known for Cu(II)-atoms, are caused by the Jahn-Teller effect. The CuO_6 polyhedra share edges to form triple chains along [010], which are linked via the [SeO_4]-groups and weak hydrogen bonds to a framework structure

Table 5. Bond valence calculations [6] of the oxygen atoms in $Cu_3SeO_4(OH)_4$

			[v.u.]				[v.u.]
O(1):	O−Cu(2)	2×	0.16	OH(1):	OH−Cu(1)	1×	0.18
	O−Se	1×	1.53		OH−Cu(2)	2×	0.50
		Σ	1.86			Σ	1.18
O(2):	O−Cu(1)	1×	0.12	OH(2):	OH−Cu(2)	2×	0.53
	O−Cu(2)	2×	0.18			Σ	1.05
	O−Se	1×	1.64				
		Σ	1.86				
O(3):	O−Cu(2)	1×	0.37	OH(3):	OH−Cu(1)	1×	0.42
	O−Se	1×	1.45		OH−Cu(1)	1×	0.44
		Σ	1.82		OH−Cu(2)	1×	0.36
						Σ	1.22

Table 6. Bond length distortions Δ and bond angle distortions σ^2 [4] of the copper atoms in antlerite [4] and $Cu_3SeO_4(OH)_4$. $\Delta=\sum[(l-\langle l\rangle)/\langle l\rangle]^2$, $\sigma^2=\sum(90-\theta)^2/12$

		$Cu_3SO_4(OH)_4$	$Cu_3SeO_4(OH)_4$
Cu(1):	Δ	0.064	0.048
	σ^2	133.9	126.8
Cu(2):	Δ	0.053	0.039
	σ^2	21.6	22.0

(Fig. 1). The Se(VI) atom [point symmetry m] is tetrahedrally bound to four oxygen atoms [O(1), O(2), 2×O(3)], bond distances and angles are in accordance to literature. Bond valence calculations (Table 5) of the atoms OH(1), OH(2) and OH(3) established their nature as oxygen atoms of hydroxyl groups. A detailed comparison between the isotypic crystal structures of antlerite as given by Hawthorne et al. [4] and $Cu_3SeO_4(OH)_4$ led to the following results:

The elongation of the "octahedra" $Cu(1)^{[4+2]}O_6$ and $Cu(2)^{[4+2]}O_6$ is more pronounced in antlerite. In both compounds the copper atoms Cu(1) are surrounded by four OH(3) atoms forming a "square" with Cu(1)−O distances of ~ 2 Å and each one OH(1) and O(2) atom completing the polyhedron. While bond distances Cu(1)−OH(1) are nearly the same (about 2.3 Å), the distance Cu(1)−O(2) is significantly shorter in $Cu_3SeO_4(OH)_4$; 2.454 Å as compared with 2.543 Å in antlerite. Within the "squares" of the copper atoms Cu(2) the Cu−O bond lengths are in good agreement (~ 1.92 Å − 2.05 Å). The apical atoms O(2) and O(1) have Cu(2)−O distances of ~ 2.31 Å and 2.35 Å (respective 2.34 Å and 2.41 Å in antlerite). Bondlength distortions Δ and bondangle distortions σ^2 [4] for $Cu_3SeO_4(OH)_4$ are given in Table 6. The geometry of the selenate- and sulfate-tetrahedra (relationships of bondlengths and bondangles) is quite the same.

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