The crystal structure of christelite $Zn_3Cu_2(SO_4)_2(OH)_6 \cdot 4\,H_2O$

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Dedicated to Professor Otto H. Jarchow on the occasion of his 65th birthday

Received November 11, 1995; accepted March 1, 1996

Natural single crystal / Zn-Cu minerals / Christelite

Abstract. The crystal structure of christelite $Zn_3Cu_2 \cdot (SO_4)_2(OH)_6 \cdot 4\,H_2O$ (space group $P\bar{1}$; lattice parameters $a = 5.4143(8)$ Å, $b = 6.336(1)$ Å, $c = 10.470(3)$ Å, $\alpha = 94.32(3)°$, $\beta = 90.06(2)°$, $\gamma = 90.27(2)°$) was solved using direct methods and difference Fourier-syntheses. The structure was refined to a final $R(F)$-value of 0.033.

The structure contains distorted $[(Zn, Cu)O_6]$ octahedra which are connected as to form sheets of composition $^2_\infty[(Cu,Zn)_2(OH)_3O]^-$. These sheets are similar to those observed in the mineral ktenasite. In both structures sulphate groups are attached to the sheets of octahedra through common vertices. In christelite the tetrahedral $[SO_4]$ groups are linked to isolated $[Zn(H_2O)_4O_2]$ octahedra thus forming a three-dimensional structure, whereas in the structure of ktenasite the $[SO_4]$ tetrahedra are bonded to isolated $[Zn(H_2O)_6]$ by a system of hydrogen bonds.

The relationship of christelite with other minerals is pointed out and discussed.

Introduction

Christelite was first found in the San Francisco mine, Sierra Gorda, northeast of Antofagasta, 2nd region in Chile. Associated minerals are paratacamite, anglesite, hemimorphite, quartz and one more unidentified mineral.

Christelite was described by Schlüter, Klaska, Adiwidjaja and Gebhard [12] who reported optical as well as crystallographic data. The unit cell parameters given are $a = 5.415(1)$ Å, $b = 6.338(1)$ Å, $c = 10.475(1)$ Å, $\alpha = 94.38(1)°$, $\beta = 90.08(1)°$, $\gamma = 90.24(1)°$ (space group $P\bar{1}$) and the ideal formula assumed is $Zn_3Cu_2(SO_4)_2(OH)_6 \cdot 4\,H_2O$. The new mineral has been accepted by the IMA Commission on New Minerals and Mineral Names.

So far no other occurrence of christelite has been reported.

Experimental

Weissenberg photographs of a small crystal (20 μm × 60 μm × 60 μm) showed triclinic symmetry. No extinction rules were observed leading to the possible space groups $P1$ or $P\bar{1}$. The lattice parameters were determined by least-squares fitting of the θ values of 25 reflections measured with a CAD4 single crystal diffractometer using AgK_α radiation; their values are $a = 5.4143(8)$ Å, $b = 6.336(1)$ Å, $c = 10.470(3)$ Å, $\alpha = 94.32(3)°$, $\beta = 90.06(2)°$, $\gamma = 90.27(2)°$.

Intensity data were collected on the same diffractometer also using AgK_α radiation with an $\omega - 2\theta$ scan in the θ-range 2°–23°. The individual ω-scan angle for a reflection was given by $0.7 + 0.45 \cdot \tan\theta$. Nearly a full sphere was measured (hkl-range: $\bar{7},\bar{8},\overline{14}$ – 7,8,8) resulting in altogether 3599 reflections. Averaging with Laue symmetry $\bar{1}$ led to 2214 reflections of which 891 were classified as unobserved, having F_o less than three times the corresponding standard deviation σF_o. The internal R-value based on F_o was 2.1% for observed reflections and 7.3% for all reflections.

Due to the small size and irregular shape of the crystal it was not possible to approximate the crystal by faces and thus an experimental absorption correction according to North, Phillips and Mathews [9] using ψ-scans (measured every 10°) was applied. The minimum relative transmission was found to be 72.60%, the maximum was 99.70%.

Structure determination

The structure was solved in space group $P\bar{1}$ using direct methods with the program SIR92 [1]. The atomic positions of the heavy atoms as well as the positions of the sulphur and oxygen atoms were determined this way.

The coordinates of the atoms and the individual isotropic atomic displacement parameters were refined by full-matrix least squares cycles using the program SHELXL-93 [14] to an $R(F)$-value $R_1 = 0.065$.[1] At this stage of refinement the difference Fourier map showed the positions of all the hydrogen atoms. In further refinement cycles anisotropic displacement parameters for the Cu, Zn, S and oxygen atoms were introduced and a weighting scheme according to $w = 1/[\sigma^2(F_o)^2 + (a \cdot P)^2 + b \cdot P]$ with $P = (\max(F_o^2) + 2F_c^2)/3$ was used. The final values for a and b were 0.0528 and 0.47.

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[1] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

Table 1. Positional and isotropic displacement parameters for the atoms with e.s.d.'s in parentheses.

Atom	x	y	z	U_{eq}
Zn1	0	0	0	0.0145(2)
Zn2	0.51228(7)	0.24973(6)	0.49511(4)	0.0127(1)
Cu1	0	0	1/2	0.0110(1)
Cu2	0	1/2	1/2	0.0116(1)
S	0.7771(2)	0.7040	0.22146(8)	0.0126(2)
O1	0.7947(5)	0.7289(4)	0.3637(2)	0.0141(5)
O2	0.5206(5)	0.6551(6)	0.1854(3)	0.0275(7)
O3	0.9370(6)	0.5294(5)	0.1729(3)	0.0246(6)
O4	0.8590(6)	0.9034(5)	0.1722(3)	0.0269(7)
O5	0.6807(4)	0.0026(4)	0.5889(2)	0.0114(4)
O6	0.6829(5)	0.5153(4)	0.5872(2)	0.0125(5)
O7	0.1381(5)	0.7641(4)	0.5888(2)	0.0127(5)
O8	0.7246(5)	0.2267(4)	0.0160(2)	0.0172(5)
O9	0.2469(5)	0.1890(5)	0.1179(3)	0.0242(6)
H1	0.242	0.690	0.944	0.05
H2	0.344	0.731	0.052	0.05
H3	0.217	0.312	0.146	0.05
H4	0.410	0.195	0.098	0.05
H5	0.123	0.772	0.666	0.05
H6	0.687	0.006	0.677	0.05
H7	0.697	0.517	0.680	0.05

The positional and displacement parameters of the hydrogen atoms were not refined.

The final R_1 value was 0.033 for 1436 data $> 4\sigma$ and 0.070 for all 2031 data; wR_2 was 0.089 and $S = 0.969$.[2]

Since in the final result no indication was found that the structure was non-centric, the chosen space group $P\bar{1}$ was assumed to be correct.

Final atomic positional and isotropic displacement parameters are given in Table 1.[3]

Description and discussion of the structure

Fig. 1 shows a projection along [100] of the crystal structure of christelite. The coordination polyhedra of Zn1, Cu1, Cu2 and sulphur are shown. Coordination polyhedra around Zn2 are not drawn for reasons of clearness. Bond lengths within the polyhedra are given in Table 2.

The main feature of the structure are continuous sheets parallel (001) of the octahedrally coordinated Cu1, Cu2 and Zn2 atoms. Ideally the symmetry of the sheet is trigonal yet due to the pronounced tetragonal distortions of the octahedra the sheets are corrugated and the symmetry is reduced.

The distortions of the octahedra can be explained on the basis of the Jahn-Teller effect and give an important hint for the identification of Zn and Cu atoms (see below).

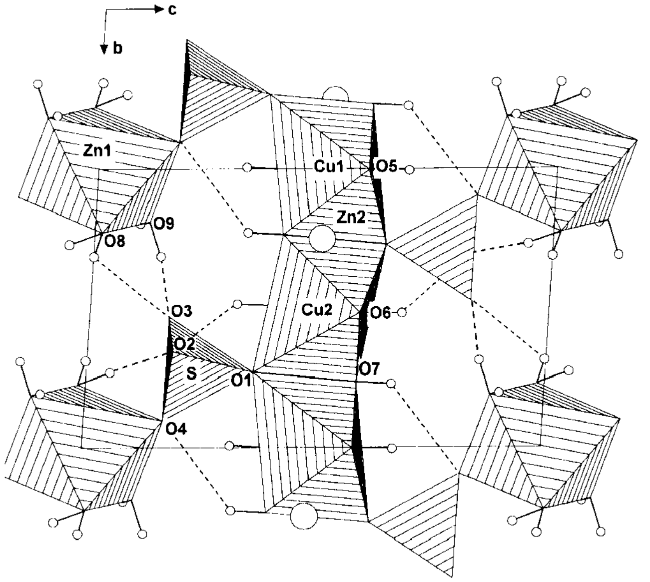

Fig. 1. Projection of the structure of christelite parallel [100]; octahedra around Cu1, Cu2, Zn1 and $[SO_4]$ tetrahedra are shown; Zn2 atoms appear as large open circles; polyhedra around Zn2 are not drawn for reasons of clearness; polyhedra atoms are representated by small circles; the hydrogen bonding system is shown (drawn with STRUPLO [3]).

Sulphate groups link the sheets of octahedra to isolated $[Zn1O_6]$ octahedra thus forming a three dimensional structure, which in addition is held together by a system of hydrogen bonds.

The $[Cu1O_6]$ and $[Cu2O_6]$ octahedra have nearly $2/m$ symmetry, the $[Zn2O_6]$ octahedron has symmetry 1. In the coordination sphere of Cu1 and Cu2 the equatorial plane is formed by oxygen atoms belonging to hydroxyl anions (O5, O6, O7) whereas the oxygen atoms (O1) at the apices belong to the sulphate tetrahedra. For Cu1 the equatorial bond distances range from 1.964 Å–1.970 Å and the axial bond distances are 2.415 Å.

Table 2. Bond distances in Å in the coordination polyhedra with e.s.d.'s in parentheses.[a]

Zn1 –	$O8^{x}$	2.073(3)	Zn2 –	$O5^{v}$	2.047(2)
	$O8^{iv}$	2.073(3)		$O6^{vi}$	2.069(2)
	$O4^{xii}$	2.091(3)		$O7^{vi}$	2.087(2)
	$O4^{ix}$	2.091(3)		O6	2.087(3)
	O9	2.122(3)		O5	2.120(2)
	$O9^{xi}$	2.122(3)		$O1^{vi}$	2.224(3)
Cu1 –	$O5^{v}$	1.964(2)	Cu2 –	$O6^{vi}$	1.945(2)
	$O5^{iv}$	1.964(2)		$O6^{iv}$	1.945(2)
	$O7^{viii}$	1.969(2)		O7	1.994(3)
	$O7^{vii}$	1.969(2)		$O7^{viii}$	1.994(3)
	$O1^{vi}$	2.415(3)		$O1^{iv}$	2.387(2)
	$O1^{ix}$	2.415(3)		$O1^{vi}$	2.387(2)
S –	O2	1.464(3)			
	O4	1.467(3)			
	O3	1.469(3)			
	O1	1.489(3)			

[a] Symmetry operators for generating equivalent atoms.
(i) $x+1, y, z$; (ii) $x, y+1, z$; (iii) $x+1, y+1, z$; (iv) $x-1, y, z$; (v) $-x+1, -y, -z+1$; (vi) $-x+1, -y+1, -z+1$; (vii) $x, y-1, z$; (viii) $-x, -y+1, -z+1$; (ix) $x-1, y-1, z$; (x) $-x+1, -y, -z$; (xi) $-x, -y, -z$; (xii) $-x+1, -y+1, -z$.

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[2] $wR_2 = [\sum [w(F_o^2 - F_c^2)^2]/\sum [w(F_o^2)^2]]^{1/2}$ and $S = [\sum [w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}$ with n = number of reflections and p = total number of parameters.

[3] Additional materials to this paper can be ordered referring to the no. CSD 404835, names of the authors and citations of the paper at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. The list of F_o/F_c-data is available from the author up to one year after the publication has appeared.

For Cu2 the equatorial bonds have values between 1.945 Å and 1.994 Å, the axial bond lengths again being significantly longer with 2.388 Å. The mean Cu1 – O bond length in the octahedra is 2.116 Å, the mean Cu2 – O bond length is 2.109 Å.

Five of the oxygen atoms (O5, O6, O7) in the coordination sphere of Zn2 form parts of hydroxyl anions, the remaining atom O1 is part of the sulphate group. In the Zn2 octahedra the degree of tetragonal distortion is comparatively small with bond lengths between 2.047 Å and 2.087 Å in the equatorial plane and axial bond lengths of 2.120 Å–2.225 Å. The mean Zn2 – O bond length is 2.106 Å.

Each tetrahedral sulphate group is connected to the sheet by the atom O1 which is a common vertex of three octahedra. The bond lengths in the sulphate tetrahedra are in the range 1.465 Å–1.489 Å.

The O4 oxygen atoms of the sulphate groups are also part of isolated $[Zn1O_6]$ octahedra which show slight distortions from the ideal symmetry with bond lengths between 2.073 Å–2.122 Å. The mean Zn1 – O bond length of 2.096 Å is nearly exactly the same as observed in the isolated octahedra of ktenasite [8] and compares well with the value of 2.105 Å calculated from the ionic radii of Shannon [13].

The distribution of copper and zinc

The chemical analysis as given by [12] suggests the presence of three Zn-atoms and two Cu-atoms within one asymmetric unit. Due to the similar scattering power and the fact that copper and zinc have nearly the same size, it is not possible to identify these two cations unambiguously by simply looking at the observed bond lengths or occupation factors.

Yet the copper atoms are likely to show a Jahn-Teller effect and this should lead to higher distortions of octahedra in which a larger amount of copper is incorporated. Taking into account the small distortions of the isolated $[Zn1O_6]$ octahedra one can almost be sure that the centres of these are fully occupied by Zn with no Cu at these sites. As the $[Cu1O_6]$ and $[Cu2O_6]$ octahedra are more distorted than the $[Zn2O_6]$ octahedra it is likely that these two contain most of the copper. The question of the distribution of Zn and Cu arose also in the structural analyses of other minerals like serpierite [10], veszelyite [5] and ktenasite [8], all of them having a structure closely related to that of christelite (see Table 3), and was answered qualitatively on the basis of octahedral distortions. As shown by Mellini and Merlino [8] the values of ΔL, defined as the difference between the average values of axial and equatorial bond distances in the octahedra, can be used as a basis for the calculation of the copper content. The authors assumed a linear correlation between the copper content and the ΔL-value with $\Delta L = 0.0$ for 100% Zn and $\Delta L = 0.57$ for 100% Cu (observed as the maximum value of distortion for the Cu(1)-site in veszelyite). This computation can be done since in all of the cited structures the sheets of octahedra are nearly identical. The calculation for the structure of christelite leads to the following contents of copper and zinc:

site	ΔL	calc. content	site	ΔL	calc. content
Zn1	0.040	7% Cu	Cu1	0.447	78% Cu
Cu2	0.418	73% Cu	Zn2	0.100	17% Cu

Taking into account the different crystallographic sites this corresponds to a chemical formula of $Zn_{3.08}Cu_{1.92} \cdot (SO_4)_2(OH)_6 \cdot 4\,H_2O$ which is in good agreement to the proposed ideal formula of $Zn_3Cu_2(SO_4)_2(OH)_6 \cdot 4\,H_2O$.

However as Mellini and Merlino [8] already pointed out, the approach has its weakness and the results must be considered as a rough approximation of the real conditions.

Hydrogen bond system

In Fig. 1 the hydrogen bonding system is shown. A list of all the hydrogen bonds shorter than 3.20 Å is given in Table 4. The valence balances for the oxygen atoms were calculated according to Brese and O'Keeffe [2]. They are further improved when the valence sums are corrected for the contributions of the hydrogen bonds. Hydrogen bond valence strengths were estimated by the procedure of Lippincott and Schroeder [6].

Table 3. Lattice parameters and chemical composition of related minerals.

Christelite $Zn_2(Cu,Zn)_3(SO_4)_2(OH)_6 \cdot 4\,H_2O$	$a = 5.4143$ Å $\alpha = 94.32°$	$b = 6.336$ Å $\beta = 90.06°$	$c = 10.470$ Å $\gamma = 90.27°$	$P\bar{1}$	this work
Ktenasite $Zn(Cu,Zn)_4(SO_4)_2(OH)_6 \cdot 6\,H_2O$	$a = 5.598$ Å	$b = 6.121$ Å $\beta = 95.55°$	$c = 23.751$ Å	$P2_1/c$	[8]
Serpierite $Ca(Cu,Zn)_4(SO_4)_2(OH)_6 \cdot 3\,H_2O$	$c = 21.853$ Å	$b = 6.250$ Å $\beta = 113.36°$	$a = 22.186$ Å	$C2/c$	[10]
Devillite $CaCu_4(SO_4)_2(OH)_6 \cdot 3\,H_2O$	$c = 22.191$ Å	$b = 6.135$ Å $\beta = 102.73°$	$a = 20.870$ Å	$P2_1/c$	[11]
Lautenthalite $PbCu_4(SO_4)_2(OH)_6 \cdot 3\,H_2O$	$c = 22.544$ Å	$b = 6.040$ Å $\beta = 108.2°$	$a = 21.642$ Å	$P2_1/c$	[7]
Langite $Cu_4(SO_4)(OH)_6 \cdot 2\,H_2O$	$c = 11.217$ Å	$b = 6.031$ Å $\alpha = 90°$	$a = 7.137$ Å	Pc	[4]

Table 4. Hydrogen bond system: O – H ··· O distances in Å and bond-valence contribution calculated after Lippincott and Schroeder [6].

	O – O distance	bond-valence strength
$\mathrm{O8} \overset{0.864}{\text{——}} \mathrm{H2} \overset{1.789}{\cdots\cdots} \mathrm{O2}$	2.648	0.233
$\mathrm{O8} \overset{0.673}{\text{——}} \mathrm{H1} \overset{2.024}{\cdots\cdots} \mathrm{O3}$	2.683	0.218
$\mathrm{O9} \overset{0.829}{\text{——}} \mathrm{H3} \overset{2.058}{\cdots\cdots} \mathrm{O3}$	2.765	0.180
$\mathrm{O9} \overset{0.909}{\text{——}} \mathrm{H4} \overset{1.925}{\cdots\cdots} \mathrm{O8}$	2.815	0.159
$\mathrm{O6} \overset{0.974}{\text{——}} \mathrm{H7} \overset{2.188}{\cdots\cdots} \mathrm{O2}$	2.903	0.129
$\mathrm{O7} \overset{0.810}{\text{——}} \mathrm{H5} \overset{2.566}{\cdots\cdots} \mathrm{O4}$	3.147	0.070

Table 5. Bond-valence balance calculated using parameters by Brese and O'Keeffe [2]; $\sum c_v$: bond valences reaching the anion; $\sum c'_v$: sum of the bond valences reaching the anion after introduction of the hydrogen bond contribution.

	$Zn1^{2+}$	$Zn2^{2-}$	$Cu1^{2+}$	$Cu2^{2-}$	S^{6+}	$\sum c_v$	$\sum c'_v$	
O1		0.245	0.137	0.148	1.440	1.970	1.970	O^{2-}
O2					1.541	1.541	1.903	O^{2-}
O3					1.520	1.520	1.918	O^{2-}
O4	0.351				1.529	1.880	1.950	O^{2-}
O5		0.396 0.325	0.463			1.183	1.183	OH^-
O6		0.373 0.355		0.487		1.215	1.086	OH^-
O7		0.355	0.457	0.427		1.239	1.169	OH^-
O8	0.369					0.369	0.077	H_2O
O9	0.323					0.323	−0.016	H_2O

As can be clearly seen from Table 5 O1 to O4 are oxygen atoms, O5 to O7 form part of hydroxyl anions and the remaining O8 and O9 atoms belong to water molecules.

The two water molecules are donors in the strongest bonds. Three of these bonds (O8 – H2 ··· O2, O8 – H1 ··· O3, O9 – H3 ··· O3) connect the isolated octahedra with the sulphate group, the remaining one (O9 – H4 ··· O8) forms a bond between the oxygen atoms of the isolated octahedra. The sheets of octahedra are connected to the sulphate groups through the two weaker bonds (O6 – H7 ··· O2, O7 – H5 ··· O4). The two free vertices (O2, O3) of the sulphate group are acceptors in two hydrogen bonds whereas O4 as common vertex of the tetrahedra and the isolated octahedra is acceptor in one hydrogen bond only.

O1 as common vertex of three octahedra and the sulphate tetrahedra as well as the hydroxyl anion $(O5–H6)^-$ are not engaged in the bonding system.

Relationships to other minerals

The corrugated sheet of octahedra parallel to (001) with crystallographic formula ${}^2_\infty[(Cu, Zn)_2(OH)_3O]^-$ is a feature which is also found in other minerals as for example in langite [4], serpierite [10], devillite [11], lautenthalite [7] and ktenasite [8] (Table 3). The layered structure accounts well for the crystal habit of these minerals. They form flat plates on {001} and exhibit a good {001} cleavage.

In all these minerals the sulphate tetrahedra are attached to the sheets of octahedra. The close relationship between the different structures is reflected in the lattice parameters and of course in the similar chemical composition (see Table 3).

The main difference between the minerals is the connection between the layers and as a consequence the different water contents in the structures.

In christelite and ktenasite the tetrahedra are bonded to isolated $[ZnO_6]$ octahedra thus connecting subsequent layers. In ktenasite each Zn cation is surrounded by six water molecules which are linked to the sulphate group merely by hydrogen bonding whereas in christelite only four of the oxygen atoms surrounding Zn1 belong to water molecules and the sulphate groups are directly attached to the octahedra.

In serpierite, devillite and lautenthalite the conditions are very similar yet in these structures sevenfold coordinated calcium atoms form the centres of the isolated polyhedra (Pb atoms in the case of lautenthalite) and even less water is incorporated between subsequent layers.

In langite the corrugated sheets of octahedra are linked directly to each other through bridging sulphate groups without the insertion of other cations at all, and the amount of water molecules is further reduced.

Acknowledgment. The authors would like to thank Dr. G. Gebhard for providing us with the crystal.

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