The Canadian Mineralogist
Vol. 38, pp. 809-816 (2000)

JUABITE, $CaCu_{10}(Te^{4+}O_3)_4(AsO_4)_4(OH)_2(H_2O)_4$: CRYSTAL STRUCTURE AND REVISION OF THE CHEMICAL FORMULA

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ABSTRACT

The crystal structure of juabite, $CaCu_{10}(Te^{4+}O_3)_4(AsO_4)_4(OH)_2(H_2O)_4$, triclinic, *a* 8.9903(7), *b* 10.1197(8), *c* 8.9959(7) Å, α 102.654(1), β 92.432(1), γ 70.432(1)°, *V* 752.0(2) $Å^3$, space group $P1$, $Z = 1$, has been solved by direct methods and refined by least-squares techniques on the basis of F^2 for 3358 unique reflections collected for a microcrystal using graphite-monochromated Mo*K*α X-radiation and a CCD area detector. The agreement index (*R*1) was 7.3%, calculated for 2288 unique observed [$F \geq 4\sigma_F$] reflections, and the goodness-of-fit (*S*) was 1.03. The structure determination has shown that the formula originally proposed for juabite is incorrect with regards to the oxidation state of Te, as well as the absence of Ca. The structure contains five unique Cu^{2+} positions that are each in square pyramidal coordination. The two symmetrically distinct Te^{4+} cations are in the usual one-sided coordination owing to the presence of a lone pair of electrons on the cation; there are three short Te^{4+}–O bonds with lengths ~1.9 Å in each polyhedron, as well as two or three longer bonds. The structure contains two unique As^{5+} cations that are tetrahedrally coordinated by O^{2-} anions, and one Ca position that is octahedrally coordinated by O^{2-} anions. Juabite possesses a layered heteropolyhedral framework structure; layers parallel to (010) are weakly bonded in the [010] direction, resulting in a perfect {010} cleavage. Each layer contains all of the cation polyhedra of the structure, and involves two symmetrically identical sheets that contain four of the $Cu\phi_5$ square pyramids [ϕ: O^{2-}, $(OH)^-$, H_2O], both $Te^{4+}\phi_n$ polyhedra, and both AsO_4 tetrahedra. The sheets are parallel to (010), and chains of edge-sharing CaO_6 octahedra and $Cu\phi_5$ square pyramids extending parallel to [001] are sandwiched between adjacent symmetrically identical sheets, such that all anions contained within the chains are also linked to the sheets on either side, resulting in the heteropolyhedral layers.

Keywords: juabite, crystal structure, copper oxysalt, tellurite, arsenate.

SOMMAIRE

Nous avons résolu la structure cristalline de la juabite, $CaCu_{10}(Te^{4+}O_3)_4(AsO_4)_4(OH)_2(H_2O)_4$, triclinique, *a* 8.9903(7), *b* 10.1197(8), *c* 8.9959(7) Å, α 102.654(1), β 92.432(1), γ 70.432(1)°, *V* 752.0(2) $Å^3$, groupe spatial $P1$, $Z = 1$, par méthodes directes, et nous avons l'avons affiné par moindres carrés en utilisant les valeurs F^2 pour 3358 réflexions uniques prélevées sur un microcristal avec rayonnement Mo*K*α, monochromatisation au graphite, et un détecteur à aire de type CCD. Le résidu (*R*1) atteint est de 7.3%, calculé pour 2288 réflexions uniques observées [$F \geq 4\sigma_F$], et le facteur de concordance (*S*) est de 1.03. L'ébauche de la structure montre que la formule proposée antérieurement pour la juabite n'est pas correcte par rapport à la valence du Te et à l'absence de Ca. La structure contient cinq positions distinctes occupées par le Cu^{2+}, dans chaque cas situé dans une pyramide carrée. Les deux cations distincts de Te^{4+} font preuve d'une coordinence asymmétrique à cause de la présence d'une paire d'électrons isolés. Il y a trois liaisons Te^{4+}–O courtes (~1.9 Å) dans chaque polyèdre, de même que deux ou trois liaisons plus longues. La structure contient deux cations As^{5+} distincts en coordinence tétraédrique avec des anions O^{2-}, et une position occupée par le Ca en coordinence octaédrique avec des anions O^{2-}. La juabite possède une trame hétéropolyédrique en couches parallèles à (010). Celles-ci sont faiblement liées dans la direction [010], expliquant ainsi le clivage {010} parfait. Chaque couche contient tous les polyèdres de la structure, et implique deux feuillets symétriquement identiques contenant quatre des pyramides carrées $Cu\phi_5$ [ϕ: O^{2-}, $(OH)^-$, H_2O], les deux polyèdres $Te^{4+}\phi_n$, et les deux tétraèdres AsO_4. Les feuillets sont

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parallèles à (010), et les chaînes d'octaèdres CaO_6 à arêtes partagées et les pyramides carrées $Cu\phi_5$ alignées parallèles à [001] sont interposées entre feuillets adjacents symétriquement identiques; tous les anions faisant partie des chaînes sont également rattachées aux feuillets de chaque côté, et définissent ainsi les couches hétéropolyédriques.

(Traduit par la Rédaction)

Mots-clés: juabite, structure cristalline, oxysel de cuivre, tellurite, arsenate.

INTRODUCTION

Juabite was described by Roberts *et al.* (1997) from the Centennial Eureka mine, Juab County, Utah. Only a few microcrystals have been found on a single specimen taken from the mine dumps. Details about the specimen and associated minerals are given by Roberts *et al.* (1997), who provided the formula $Cu_5(Te^{6+}O_4)_2(As^{5+}O_4)_2 \cdot 3H_2O$ for juabite, on the basis of a chemical analysis done using an electron microprobe. The oxidation state of the Te was assumed to be 6+ because only tellurate minerals had previously been found at the locality.

A structure determination would have provided useful constraints on the composition of juabite, but at the time the mineral was first described, it was impossible to obtain useful X-ray counting statistics because the available crystals are too small (Roberts *et al.* 1997). However, the recent introduction of CCD-based detectors of X-rays has made it possible to successfully determine the structure of crystals that are as much as an order of magnitude smaller in all dimensions than was possible with a conventional scintillation detector mounted on a serial diffractometer (Burns 1998). We have used a CCD-based detector mounted on a three-circle diffractometer to collect data for one of the crystals that was originally studied by Roberts *et al.* (1997), and have determined the details of the structure. The results are presented herein. This study has resulted in revision of the chemical formula for juabite.

EXPERIMENTAL

X-ray diffraction

Roberts *et al.* (1997) obtained precession photographs of two small crystals of juabite, and reported that attempts to collect data for a structure determination using a conventional single-crystal diffractometer were unsuccessful owing to the small size of the crystals. We collected data for each of those crystals using a CCD-based detector system, and report the results for the best refinement (the refinement obtained for the other crystal was similar although slightly inferior). The crystal for which results are reported has dimensions 0.04 × 0.04 × 0.004 mm. The crystal was mounted on a Bruker PLATFORM goniometer equipped with a 1K SMART CCD (charge-coupled device) detector with a crystal-to-detector distance of 5 cm. Burns (1998) discussed the application of CCD detectors to the analysis of mineral structures.

The data were collected using monochromatic Mo*K*α X-radiation and framewidths of 0.3° in ω, with 160 s used to acquire each frame, resulting in a scan-rate of 0.11° per minute. The slow scan-speed and long count-time per frame were essential to obtain appropriate counting statistics, owing to the small size of the crystal. A complete sphere of three-dimensional data was collected, and the data were analyzed to locate peaks for the determination of the unit-cell dimensions (Table 1). These were refined with 3207 reflections using least-squares techniques. Data were collected for $3° \leq 2\theta \leq 56.6°$ in approximately 103 hours; the intensities of equivalent reflections collected at various times throughout the data collection showed no significant decay. The three-dimensional data were reduced using the Bruker program SAINT. A semi-empirical absorption-correction based upon the intensities of equivalent reflections was applied using the program SADABS (G. Sheldrick, unpublished), and the data were corrected for Lorentz, polarization, and background effects. A total of 7615 intensities was measured; there were 3358 unique reflections (R_{INT} = 5.9% after absorption correction) with 2288 classed as observed ($F_o \geq 4\sigma_F$).

Chemical analysis

The determination of the crystal structure reported herein indicated that juabite contains additional cations that were not reported in the original description of Roberts *et al.* (1997) (see below). Therefore, a single crystal of juabite, from the same specimen as the crystal used for the collection of the X-ray-diffraction data, was

TABLE 1. MISCELLANEOUS INFORMATION FOR JUABITE

a (Å)	8.9903(7)	Crystal size (mm)	0.04x0.04 x0.004
b (Å)	10.1197(8)		
c (Å)	8.9959(7)	Total Int.	7615
α (°)	102.654(1)	Unique ref.	3358
β (°)	92.432(1)	R_{int}	5.9%
γ (°)	70.432(1)	Unique $\lvert F_o\rvert \geq 4\sigma_F$	2288
V (Å^3)	752.0(2)	Final *R*	7.3%
Space group	$P\bar{1}$	*S*	1.03
F(000)	932		
μ (mm^{-1})	15.4		
D_{calc}	4.50 g/cm^3		

$R1 = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$

$S = [\Sigma w(|F_o|-|F_c|)^2/(m-n)]^{1/2}$, for *m* observations and *n* parameters

Unit cell contents: $1[CaCu_{10}(Te^{4+}O_3)_4(AsO_4)_4(OH)_2(H_2O)_4]$

mounted, polished, and coated with carbon. Chemical analysis was done in wavelength-dispersion (WD) mode on a JEOL 733 electron microprobe using Tracor Northern 5500 and 5600 automation. Data reduction was done with a conventional PAP routine. The operating voltage was 15 kV, and the beam current was 20 μA. A beam 10 μm in diameter was employed. Data for all elements in the sample were collected for 25 s or 0.50% precision, whichever was attained first. The elements Pb, Se and K were sought in WD scans, but were not detected. Standards used for the electron-microprobe analysis were: synthetic $FeTe_2O_5(OH)$ (Te*L*α), cuprite (Cu*K*α), mimetite (As*L*α), synthetic $CaTa_4O_{11}$ (Ca*K*α), and synthetic mackayite (Fe*K*α). The proportion of H_2O was calculated by stoichiometry from the results of the crystal-structure analysis. The results of the analysis are: TeO_2 29.99, As_2O_5 23.17, CuO 38.51, CaO 2.52, FeO 0.26 and H_2O 4.39, total 98.84 wt.%. The empirical formula based on 34 atoms of oxygen is: $(Ca_{0.92}Fe_{0.07})_{\Sigma 0.99}Cu_{9.94}(Te^{4+}{}_{0.96}O_3)_4(As_{1.04}O_4)_4(OH)_2(H_2O)_4$, or, ideally, $CaCu_{10}(Te^{4+}O_3)_4(AsO_4)_4(OH)_2(H_2O)_4$.

STRUCTURE SOLUTION AND REFINEMENT

Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from *International Tables for X-Ray Crystallography, Vol. IV* (Ibers & Hamilton 1974). The Bruker SHELXTL Version 5.1 system of programs was used for the determination and refinement of the crystal structure.

Assigning phases to a set of normalized structure-factors gave a mean value $|E^2 - 1|$ of 0.93, suggesting the space group $P\bar{1}$, which was verified by the successful solution of the structure by direct methods. Refinement of the structure was done on the basis of F^2 for all 3358 unique reflections. Refinement of the positional parameters of all atoms, and allowing for isotropic atomic-displacement, gave a model with an agreement index ($R1$) of 11.4%. Conversion of the Te, As, Cu and Ca displacement parameters to an anisotropic form, together with the inclusion of a weighting scheme of the structure factors, provided a final model with an $R1$ of 7.3%, calculated for the 2288 observed reflections ($F_o \geq 4\sigma_F$), and a goodness-of-fit (S) of 1.03. A model with anisotropic-displacement parameters for the O atoms was tried, but the parameters were found to be unstable. In the final cycle of refinement, the average parameter shift/esd was 0.000, and the maximum peaks in the final difference-Fourier maps were 4.23 and –3.18 $e/Å^3$, respectively.

TABLE 2. ATOMIC PARAMETERS FOR JUABITE

	x	y	z	$*U_{eq}$
Ca	½	½	0	248(17)
Cu(1)	-0.1919(1)	0.7993(2)	0.0021(2)	117(5)
Cu(2)	0.2967(2)	0.8412(2)	-0.4883(2)	104(4)
Cu(3)	0.3921(2)	0.5072(2)	-0.3755(2)	142(5)
Cu(4)	0.6845(2)	0.8487(2)	-0.3708(2)	129(5)
Cu(5)	-0.0734(2)	0.7991(3)	0.3909(2)	154(5)
Te(1)	0.4568(1)	0.8379(1)	-0.1518(1)	114(3)
Te(2)	0.1303(1)	0.8342(1)	0.1698(1)	196(3)
As(1)	0.0656(2)	0.7706(2)	-0.2751(2)	97(4)
As(2)	0.5743(2)	0.7899(2)	-0.7274(2)	82(4)
O(1)	-0.066(1)	0.798(1)	0.178(1)	167(26)
O(2)	-0.003(1)	0.814(1)	-0.095(1)	175(27)
O(3)	0.185(1)	0.866(1)	-0.290(1)	145(25)
O(4)	0.121(1)	0.840(1)	0.388(1)	176(27)
O(5)	-0.328(1)	0.835(1)	-0.163(1)	103(23)
O(6)	-0.091(1)	0.820(1)	-0.388(1)	122(24)
O(7)	0.469(1)	0.848(1)	-0.364(1)	192(27)
OH(8)	0.390(1)	0.597(1)	-0.548(1)	166(26)
O(9)	0.387(1)	0.888(1)	-0.660(1)	104(23)
O(10)	0.607(1)	0.842(1)	-0.883(1)	95(23)
O(11)	0.601(1)	0.614(1)	-0.773(1)	131(24)
O(12)	0.265(2)	0.654(2)	0.107(2)	381(38)
O(13)	0.163(1)	0.594(1)	-0.336(1)	197(28)
O(14)	0.704(1)	0.818(1)	-0.593(1)	142(25)
$H_2O(15)$	0.039(2)	0.552(2)	0.356(2)	439(42)
$H_2O(16)$	-0.131(2)	0.558(2)	-0.057(2)	527(48)
O(17)	0.490(1)	0.645(1)	-0.177(1)	169(26)

$*U_{eq} = U_{eq}$ $Å^2 \times 10^4$

The structure refinement converged to a final $R1$ that is higher than is typical for oxysalts of similar composition. Also, the anisotropic-displacement parameters for the cations display features that are indicative of imperfections in the data. Only two crystals of juabite were available for study, and each is very small. Improvements over the current structural model are only likely to be realized if additional, superior crystals are located. The study provides the full structural connectivity of juabite, as well as a corrected formula. The structure determination has also demonstrated that juabite is a tellurite, as opposed to a tellurate as indicated by Roberts *et al.* (1997), and revealed an additional atom in the structure that was shown to be Ca by results of our chemical analysis. Thus, although the structure refinement exhibits imperfections owing to the nature of the material available for study, considerable insight into both the structure and chemical composition of juabite has resulted from the structure determination.

The final atomic parameters are given in Table 2, anisotropic-displacement parameters are in Table 3, selected interatomic-distances and angles are given in Table 4, and a bond-valence analysis is presented in Table 5. Calculated and observed structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

TABLE 3. ANISOTROPIC-DISPLACEMENT PARAMETERS FOR JUABITE

	$*U_{11}$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca	468(35)	188(28)	59(22)	-83(23)	-50(19)	18(17)
Cu(1)	85(10)	258(13)	29(9)	-74(9)	-32(7)	55(8)
Cu(2)	71(9)	222(12)	45(9)	-63(8)	-44(7)	65(8)
Cu(3)	124(10)	202(12)	93(10)	-25(9)	-36(8)	72(8)
Cu(4)	66(10)	323(13)	31(9)	-95(9)	-31(7)	66(9)
Cu(5)	95(10)	340(14)	60(9)	-104(10)	-51(8)	73(9)
Te(1)	99(5)	216(6)	56(5)	-81(5)	-27(4)	47(4)
Te(2)	162(6)	358(8)	108(6)	-121(6)	-37(5)	86(5)
As(1)	56(8)	220(10)	31(7)	-60(7)	-40(6)	46(6)
As(2)	61(8)	178(9)	18(7)	-46(7)	-31(6)	41(6)

$*U_{ij} = U_{ij}$ $Å^2 \times 10^4$

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) FOR JUABITE

Te(1)-O(17)	1.83(1)	Te(2)-O(12)	1.80(2)
Te(1)-O(5)a	1.93(1)	Te(2)-O(1)	1.92(1)
Te(1)-O(7)	1.94(1)	Te(2)-O(4)	1.95(1)
Te(1)-O(3)	2.65(1)	Te(2)-O(2)	2.62(1)
Te(1)-O(10)b	2.72(1)	Te(2)-O(9)b	2.86(1)
Te(1)-O(10)c	3.04(1)	<Te(2)-ϕ>	2.23
<Te(1)-ϕ>	1.90	<Te(2)-ϕ_{short}>	1.89
<Te(1)-ϕ_{short}>	2.35		
Cu(1)-O(5)	1.90(1)	Cu(2)-O(7)	1.89(1)
Cu(1)-O(1)	1.90(1)	Cu(2)-O(4)e	1.90(1)
Cu(1)-O(10)d	1.99(1)	Cu(2)-O(9)	1.99(1)
Cu(1)-O(2)	2.00(1)	Cu(2)-O(3)	2.01(1)
Cu(1)-H_2O(16)	2.26(2)	Cu(2)-OH(8)	2.27(1)
<Cu(1)-ϕ>	2.01	<Cu(2)-ϕ>	2.01
Cu(3)-OH(8)	1.96(1)	Cu(4)-O(5)a	1.91(1)
Cu(3)-OH(8)f	1.96(1)	Cu(4)-O(7)	1.94(1)
Cu(3)-O(13)	1.96(1)	Cu(4)-O(6)a	1.95(1)
Cu(3)-O(11)f	1.98(1)	Cu(4)-O(14)	1.96(1)
Cu(3)-O(17)	2.35(1)	Cu(4)-O(9)c	2.47(1)
<Cu(3)-ϕ>	2.04	<Cu(4)-ϕ>	2.05
Cu(5)-O(1)	1.92(1)	Ca-O(12),g	2.27(2) x2
Cu(5)-O(4)	1.93(1)	Ca-O(17),g	2.37(1) x2
Cu(5)-O(14)d	1.96(1)	Ca-O(11)f,b	2.42(1) x2
Cu(5)-O(6)b	1.96(1)	<Ca-ϕ>	2.35
Cu(5)-H_2O(15)	2.31(2)		
<Cu5-ϕ>	2.02		
As(1)-O(2)	1.67(1)	As(2)-O(10)	1.67(1)
As(1)-O(13)	1.68(1)	As(2)-O(11)	1.67(1)
As(1)-O(3)	1.69(1)	As(2)-O(14)	1.68(1)
As(1)-O(6)	1.70(1)	As(2)-O(9)	1.70(1)
<As(1)-O>	1.68	<As(2)-O>	1.68

a = x + 1, y, z; b = x, y, z + 1; c = 1 – x, 2 – y, –1 – z; d = x – 1, y, z + 1; e = x, y, z – 1; f = 1 – x, 1 – y, –1 – z; g = 1 – x, 1 – y, –z.

DESCRIPTION OF THE STRUCTURE

Cation coordination

The structure contains two symmetrically distinct Te positions; both the polyhedron geometries (Fig. 1) and the bond-valence sums (Table 5) are consistent with each site containing Te^{4+}. The Te^{4+} cation contains a lone pair of electrons, resulting in a distinctly one-sided coordination. Both the Te(1) and Te(2) polyhedra are coordinated only by O^{2-} anions, and involve three short Te–O bonds with lengths of ~1.9 Å; in each polyhedron, the three tightly bonded anions occur on one side of the cation. Both Te polyhedra also include weak bonds to anions on the same side of the cation as the electron lone-pair; the Te(1) cation is weakly bonded to three anions, whereas the Te(2) cation is only weakly bonded to two anions. Similar coordination geometries about Te^{4+} have been observed in several structures (*e.g.*, Grice 1989, Fischer *et al.* 1975, Galy *et al.* 1975).

The structure contains five symmetrically distinct Cu positions, and consideration of the polyhedron geometries (Table 4) and bond-valence sums (Table 5) indicates that the Cu is present as Cu^{2+}. Each Cu^{2+} cation is coordinated by five anions arranged at the corners of a square pyramid, such that each polyhedron contains four Cu–ϕ [ϕ: O^{2-}, (OH)$^{-}$, H_2O] bond lengths of ~1.95 Å that form the base of the square pyramid, and one apical ligand at ~2.3 Å. It is well known that Cu^{2+} occurs in a variety of coordination polyhedra in minerals, and that geometries transitional between common coordination polyhedra also are observed (Burns & Hawthorne 1996). However, in the case of juabite, each Cu^{2+} polyhedron may unambiguously be classified as a square pyramid, owing to the absence of a second apical ligand that

TABLE 5. BOND-VALENCE* ANALYSIS (*vu*) FOR JUABITE

	Te(1)	Te(2)	Cu(1)	Cu(2)	Cu(3)	Cu(4)	Cu(5)	As(1)	As(2)	Ca	H(1)	H(2)	H(3)	H(4)	H(5)	Σ
O(1)		1.17	0.55				0.52									2.24
O(2)		0.18	0.42					1.30								1.90
O(3)	0.16			0.41				1.23								1.80
O(4)		1.08		0.55			0.51									2.14
O(5)	1.14		0.55			0.54										2.23
O(6)						0.48	0.47	1.20								2.15
O(7)	1.11			0.57		0.49										2.17
OH(8)				0.21	$0.47^{\times 2}$						1.0					2.15
O(9)		0.09		0.43		0.12			1.20							1.84
O(10)	0.13 0.06		0.43						1.30							1.92
O(11)					0.44				1.30	$0.29^{\times 2\downarrow}$						2.03
O(12)		1.61								$0.44^{\times 2\downarrow}$					0.1	2.15
O(13)					0.47			1.27				0.2				1.94
O(14)						0.47	0.47		1.27							2.21
H_2O(15)							0.18					0.8	0.8	0.2		1.98
H_2O(16)			0.21										0.2	0.8	0.9	2.11
O(17)	1.49				0.16					$0.34^{\times 2\downarrow}$						1.99
Σ	4.09	4.13	2.16	2.17	2.01	2.10	2.15	5.00	5.07	2.14	1.0	1.0	1.0	1.0	1.0	

*Bond-valence parameters from Brese & O'Keeffe (1991)

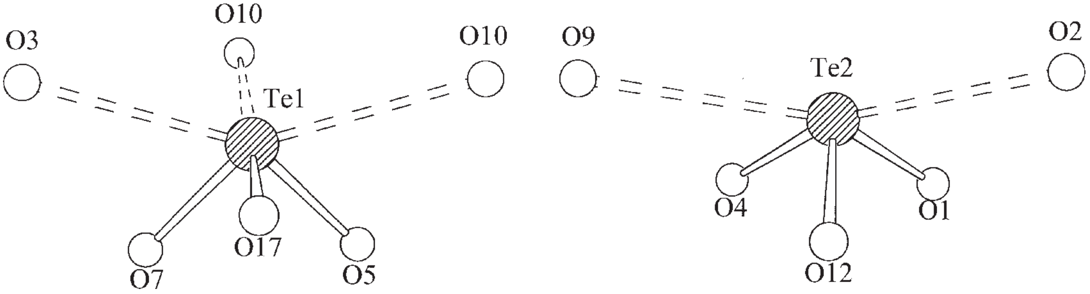

FIG. 1. The coordination polyhedra about Te^{4+} in the structure of juabite. Short (< 2.0 Å) and long (> 2.5 Å) bonds are shown by solid and broken lines, respectively.

would indicate either a (4+2)-distorted or (4+1+1)-distorted octahedral coordination. Eby & Hawthorne (1993) noted that the square bipyramid is the most common five-coordinated Cu^{2+} polyhedron, although triangular bipyramids also occur in several structures.

The $Cu\phi_5$ polyhedra contain a variety of ligands. The Cu(4) cation is coordinated by O^{2-} anions only, the Cu(2) cation is bonded to four O^{2-} anions arranged at the base of the square pyramid as well as a $(OH)^-$ group at the apex, the Cu(3) cation is coordinated by three O^{2-} anions and two $(OH)^-$ groups, with one $(OH)^-$ group at the apex of the square pyramid, and both the Cu(1) and Cu(5) cations are coordinated by four O^{2-} anions and a H_2O group, with the H_2O group located at the apex of the square pyramid in each case.

The two symmetrically distinct As positions are each coordinated by four O atoms in a tetrahedral arrangement. The <As(1)–O> and <As(2)–O> bond-lengths are both 1.68 Å, which is in good agreement with the value of 1.69 Å expected from the sums of effective ion radii for $^{[4]}As^{5+}$ and $^{[3]}O^{2-}$ (Shannon 1976).

The structure contains a single Ca site that is octahedrally coordinated by O^{2-} anions, with a <Ca–O> bond-length of 2.35 Å. The mean bond-length is in good agreement with the expected value of 2.36 Å from the sum of effective ionic radii for $^{[6]}Ca$ and $^{[3]}O^{2-}$ (Shannon 1976). However, site-occupancy refinement for the Ca site provided an occupancy factor of 1.20(2), indicating partial incorporation of a heavier cation at the site. The chemical composition of a crystal from the same specimen indicates that it contains 0.26 wt% FeO; it is possible that minor amounts of Fe^{2+} also occur at the Ca site.

Formula for juabite

The structure determination has shown the formula provided by Roberts *et al.* (1997) to be incorrect in the assumption that juabite contains Te^{6+}, and also in the omission of essential Ca. The formula derived from the structure determination, and confirmed by results of a new chemical analysis of juabite using an electron microprobe, is $CaCu_{10}(Te^{4+}O_3)_4(AsO_4)_4(OH)_2(H_2O)_4$, $Z = 1$.

Structure connectivity

Projection of the structure along [001] demonstrates that juabite possesses a heteropolyhedral framework structure (Fig. 2). However, the structure has a distinct layering parallel to (010), and adjacent layers are weakly bonded in the [010] direction, resulting in a perfect {010} cleavage (Roberts *et al.* 1997). An isolated (010) layer of the structure is shown in Figure 3a; these layers are linked into the framework structure *via* apical anions of the $Cu\phi_5$ square pyramids and by long Te^{4+}–O bonds (Fig. 2).

Each individual layer is composed of all of the cation polyhedra that are contained in the structure (Fig. 3), and involves two symmetrically equivalent heteropolyhedral sheets that are parallel to (010) (Fig. 3b), as well as chains of edge-sharing polyhedra that are parallel to [001] (Fig. 3c). Consider first the sheets of polyhedra (Fig. 3b). Each contains the $Cu(1)\phi_5$, $Cu(2)\phi_5$, $Cu(4)\phi_5$, and $Cu(5)\phi_5$ square pyramids, both TeO_n polyhedra, and both AsO_4 tetrahedra. The $Cu(4)\phi_5$ and $Cu(5)\phi_5$ square pyramids share basal edges to form a dimer with composition $Cu_2\phi_8$, with the apical ligands of adjacent pyramids pointing in opposite directions. The $Cu_2\phi_8$ dimers share four corners with $Cu\phi_5$ square pyramids; two are $Cu(1)\phi_5$, and two are $Cu(2)\phi_5$. Each of the $Cu(1)\phi_5$ and $Cu(2)\phi_5$ square pyramids share *trans* corners with two symmetrically distinct $Cu_2\phi_8$ dimers, resulting in an open sheet of $Cu\phi_5$ square pyramids, with the Cu–ϕ apical bonds of the pyramids directed approximately perpendicular to the sheets. The AsO_4 tetrahedra are located within the sheet of $Cu\phi_5$ square pyramids, and share three corners with $Cu\phi_5$ polyhedra, with the fourth tetrahedrally coordinated ligand directed roughly perpendicular to the sheet. The result is a sheet that contains large openings; these are the locations of the $Te^{4+}O_n$ polyhedra, which are arranged such that the lone pairs of electrons are directed into the openings (Fig. 3b).

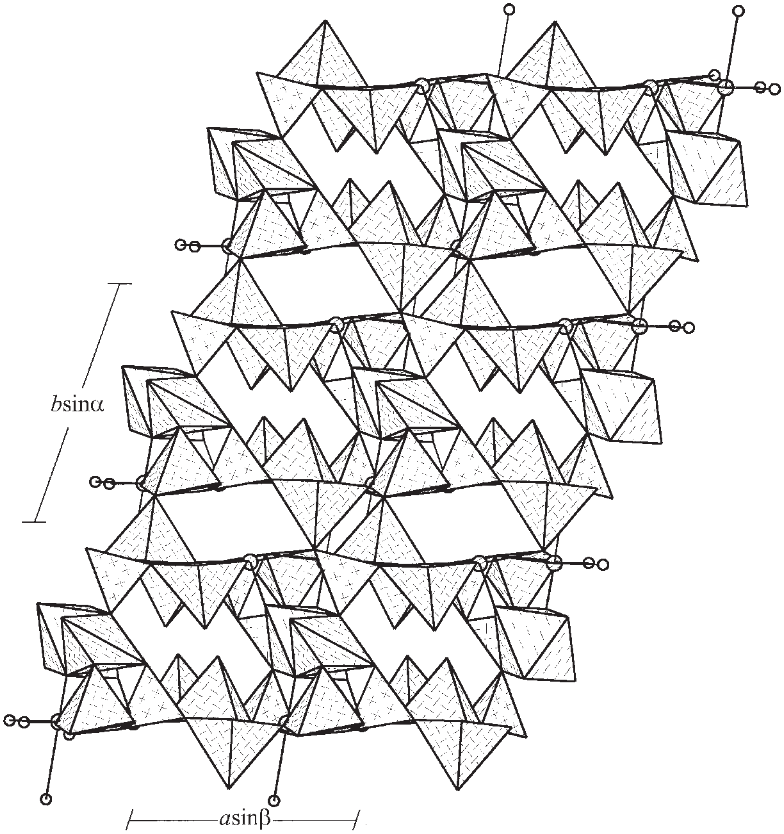

FIG. 2. The structure of juabite projected along [001]. The $Cu\phi_5$ square pyramids are shaded with a herring-bone pattern, the AsO_4 tetrahedra are shaded with crosses, the CaO_6 octahedra are shaded with broken parallel lines, the Te^{4+} cations are shown as circles shaded with parallel lines, and O atoms are shown as open circles.

The chains of polyhedra that are sandwiched between the heteropolyhedral layers are shown in Figure 3c. Each chain contains CaO_6 and $Cu(3)\phi_5$ polyhedra. The $Cu(3)\phi_5$ square pyramids share basal OH(8)–OH(8) edges to form dimers of composition $Cu_2\phi_8$. The CaO_6 octahedra are linked to the dimers of $Cu(3)\phi_5$ square pyramids by edge-sharing, such that the shared edge is a basal-apical edge of the square pyramid.

The linkage between the sheets and chains of polyhedra is assured by apical ligands of $Cu\phi_5$ square pyramids and AsO_4 tetrahedra, as well as Te^{4+}–O bonds (Fig. 3a). Note that every anion contained within the heteropolyhedral chain is shared with the sheets on either side.

Hydrogen bonding

The $H_2O(15)$ and $H_2O(16)$ groups each donate two H bonds, and it is possible to identify the likely acceptors on the basis of anion–anion separations. The H bonds donated by the $H_2O(15)$ group are most likely accepted by O(13) and $H_2O(16)$, located 2.69 and 2.71 Å away, respectively, with a O(13)–$H_2O(15)$–$H_2O(16)$ angle of 92°. The $H_2O(16)$ group donates H bonds that are accepted by O(12) and $H_2O(15)$, with separations of 2.72 and 2.71 Å, respectively, and a O(12)–$H_2O(16)$–$H_2O(15)$ angle of 84°. Thus, each H_2O group is in an approximately tetrahedral coordination, as is common for H_2O groups in mineral structures (Hawthorne 1992), with a bond to a Cu^{2+} cation, the donation of two H bonds, and the acceptance of one H bond.

The OH(8) anion also has the potential to donate a H bond, but inspection of the structure failed to reveal a suitable acceptor anion. All anions that are less than 3 Å from the donor anion are contained within the same polyhedron as the donor, and it is unlikely that a H bond will occur along the edge of a $Cu\phi_5$ square pyramid.

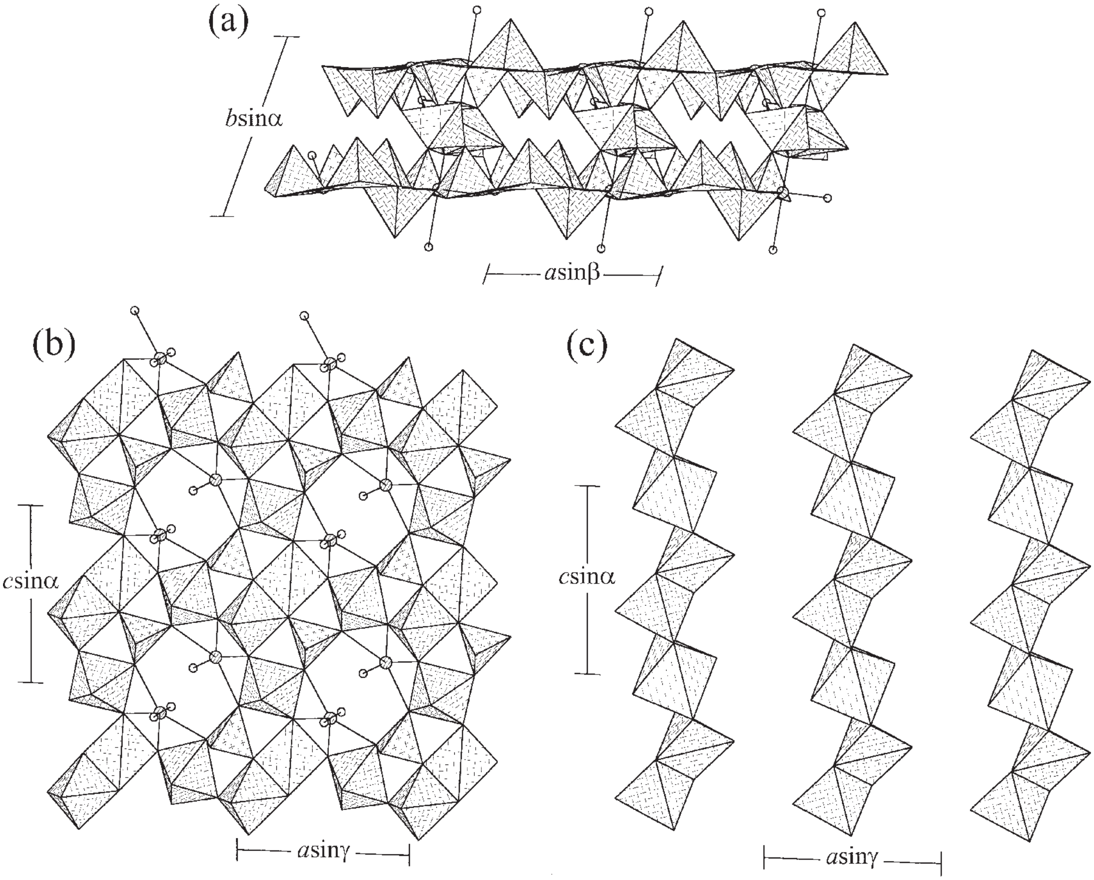

FIG. 3. Portions of the structure of juabite. (a) The heteropolyhedral layer. (b) The heteropolyhedral sheet, two of which combine to form the heteropolyhedral layer. (c) The chain of $Cu\phi_5$ square pyramids and CaO_6 octahedra that is located between the heteropolyhedral sheets within the heteropolyhedral layer. Legend as in Figure 2.

Relation to other species

The $Cu\phi_5$ square pyramid is the second most common coordination geometry about Cu^{2+} in minerals; only (4+2)-distorted octahedra are more common. However, most minerals that contain $Cu\phi_5$ square pyramids also contain $Cu\phi_6$ octahedra; only ziesite, blossite, kinoite, and juabite contain Cu^{2+} that is only present in square pyramidal coordination. The structures of ziesite (Mercurio-Lavaud & Frit 1973) and blossite (Calvo & Faggiani 1975) are similar, with edge-sharing $Cu_2\phi_8$ dimers that share corners to form chains that are cross-linked by divanadate groups. The structure of kinoite (Laughon 1971) contains chains of edge-sharing $Cu\phi_5$ square pyramids that are linked to trimers of SiO_4 tetrahedra and $Ca\phi_6$ octahedra that share edges to form dimers.

ACKNOWLEDGEMENTS

The crystal mount used in this study was provided by Mr. Andy Roberts. Resources used for the acquisition of the single-crystal diffractometer were provided by the University of Notre Dame. We are grateful to Dr. Scott Wilson, University of Illinois in Urbana, for collecting preliminary X-ray data. We thank Dr. Mark Welch, an anonymous referee, and Dr. Robert Martin for their comments concerning the manuscript.

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Received December 17, 1999, revised manuscript accepted May 29, 2000.