



Chemical and structural characterization of henryite, $(\text{Cu,Ag})_{3+x}\text{Te}_2$ ($x \approx 0.40$): A new structure type in the (Ag)–Cu–Te system



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ABSTRACT

The crystal structure of the mineral henryite, a rare copper–silver telluride, was solved using intensity data collected using a crystal from the type locality, the Campbell orebody, Bisbee, Arizona (U.S.A.). The study revealed that the structure is cubic, space group $Fd\bar{3}c$, with cell parameters: $a = 12.1987(5)$ Å, and $V = 1815.3(2)$ Å³. The refinement of an anisotropic model led to an R index of 0.0301 for 168 independent reflections. The structure consists of a face-centered cubic close-packing of Te atoms with a disordered distribution of Cu and Ag atoms in the partially-occupied tetrahedral interstices. It represents a new structure type in the Cu–Te system closely resembling the cubic structure of the well known phase A. Electron microprobe analyses of the crystal used for the structural study led to the formula $(\text{Cu}_{1.91}\text{Ag}_{1.47}\text{Fe}_{0.02})_{\Sigma=3.40}\text{Te}_2$, on the basis of 2 Te atoms per formula unit. On the basis of information gained from the structural and chemical characterization, the crystal-chemical formula was revised yielding $(\text{Cu,Ag})_{3+x}\text{Te}_2$ ($Z = 16$) with $x \approx 0.40$ instead of $[\text{Cu}_{3.77}\text{Ag}_{3.01}\text{Te}_4]$ ($Z = 8$) as previously reported.

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1. Introduction

Henryite was defined as a new mineral species by Criddle et al. [1] during a study of the ores coming from the Campbell orebody, Bisbee, Arizona (U.S.A.). The mineral was found to form fine intergrowths with hessite and petzite. An X-ray single-crystal study was not attempted by Criddle et al. [1] owing to the paucity of the mineral, and their structural study was limited to a low-quality X-ray powder investigation made difficult by the several coexisting phases in the selected material for the experiment. Despite the difficulties encountered in the X-ray study, Criddle et al. [1] were able to assign a cubic cell of $12.20(2)$ Å to henryite and a possible face-centered Bravais lattice. Moreover, these authors reported also some structural speculation based on the analysis of some hkl reflections which should be present/absent with respect to the conditions issued by the hypothetical cubic F -centered space group and on ‘true cell’/subcell relationships.

Henryite was also described some years later by Howell et al. [2] in the mineralization of the Ashanti gold mine, Ghana. However, no additional specific investigations on the mineral were carried out.

In the course of a research project dealing with the description and structural characterization of natural copper and silver tellurides [3–12], a fragment from the type locality (Bisbee, Arizona, U.S.A.) belonging to the mineralogical collections of the Museo di Storia Naturale of the University of Florence (catalogue number 46002/G) has been examined. The sample consists of tiny henryite grains closely associated with hessite, petzite and pyrite.

To help resolve the concerns relating to the structure of henryite, new crystal structure data for the mineral from its type locality together with new chemical data are presented here.

2. Experimental

2.1. Electron microprobe analysis

The chemical composition was determined using wavelength dispersive analysis (WDS) by means of a JEOL JXA-8200 electron microprobe on the same crystal used for the structural study (see below). Concentrations of major and minor elements were determined at an accelerating voltage of 20 kV and a beam current of 40 nA, with 10 s as the counting time. For the WDS analyses the following lines were used: $SK\alpha$, $FeK\alpha$, $CuK\alpha$, $ZnK\alpha$, $AsL\alpha$, $SeL\alpha$, $AgL\alpha$, $SbL\beta$, $TeL\alpha$, $PbM\alpha$, $BiM\beta$. The standards employed were: native elements for Cu and Ag, galena for Pb, pyrite for Fe and S, synthetic Sb_2Te_3 for Sb and Te, synthetic As_2S_3 for As, synthetic Bi_2S_3 for Bi,

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Table 1

Electron microprobe data (averages and ranges in wt. % of elements), atomic ratios (on the basis of 2 Te atoms) with their standard deviations (σ) for the selected henryite crystal.

	wt. %	Range	Atomic ratios	σ
Ag	29.51	28.33–30.13	1.47	0.09
Cu	22.58	22.30–23.11	1.91	0.11
Bi	0.01	0.00–0.04	–	–
Pb	0.01	0.00–0.03	–	–
Zn	0.01	0.00–0.04	–	–
Fe	0.21	0.09–0.26	0.02	0.01
Sb	0.01	0.00–0.02	–	–
As	0.01	0.00–0.03	–	–
S	0.01	0.00–0.02	–	–
Se	0.02	0.00–0.05	–	–
Te	47.49	47.01–48.22	2.00	0.10
Total	99.87	98.99–100.41		

Table 2

Data and experimental details for the selected henryite crystal.

Crystal data	
Formula	(Cu,Ag) _{3+x} Te ₂ with $x \approx 0.40$
Crystal size (mm)	0.055 × 0.075 × 0.080
Form	Block
Colour	Black
Crystal system	Cubic
Space group	$Fd\bar{3}c$ (#228 – origin choice#2)
a (Å)	12.1987(5)
V (Å ³)	1815.3(2)
Z	16
Data collection	
Instrument	Oxford Diffraction Xcalibur 3
Radiation type	MoK α ($\lambda = 0.71073$ Å)
Temperature (K)	293(3)
Detector to sample distance (cm)	6
Number of frames	602
Measuring time (s)	60
Maximum covered 2θ (°)	69.62
Absorption correction	Multi-scan (ABSPACK; Oxford Diffraction 2006)
Collected reflections	7938
Unique reflections	168
Reflections with $F_o > 4\sigma(F_o)$	81
R_{int}	0.0310
R_σ	0.0406
Range of h, k, l	$-19 \leq h \leq 19, -19 \leq k \leq 19, -19 \leq l \leq 19$
Refinement	
Refinement	Full-matrix least squares on F^2
Final R_1 [$F_o > 4\sigma(F_o)$]	0.0254
Final R_1 (all data)	0.0301
wR_2 [$F_o > 4\sigma(F_o)$]	0.0588
wR_2 (all data)	0.0645
Number refined parameters	8
Goodness-of-fit	0.986
$\Delta\rho_{max}$ (e Å ⁻³)	0.42
$\Delta\rho_{min}$ (e Å ⁻³)	-0.74

synthetic ZnS for Zn, and synthetic PtSe₂ for Se. The crystal fragment was found to be homogeneous within analytical uncertainty. The average chemical compositions (5 analyses on different spots), together with ranges of wt. % of elements, are reported in Table 1. On the basis of 2 Te atoms, the chemical formula for henryite can be written as (Cu_{1.91}Ag_{1.47}Fe_{0.02})_{Σ=3.40}Te₂ or, according to the revised

Table 3

Atoms, Wyckoff positions, fractional atomic coordinates and atomic displacement parameters (Å²) for the selected henryite crystal.

Atom	Wyckoff	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}
M1	16a	1/8	1/8	1/8	0.063(3)	U_{11}	U_{11}	0	0	0	0.063(3)
M2	48d	7/8	1/8	1/8	0.065(3)	0.063(3)	U_{22}	0	0	0	0.064(3)
Te	32c	0	0	0	0.068(3)	U_{11}	U_{11}	-0.0010(1)	U_{12}	U_{12}	0.068(3)

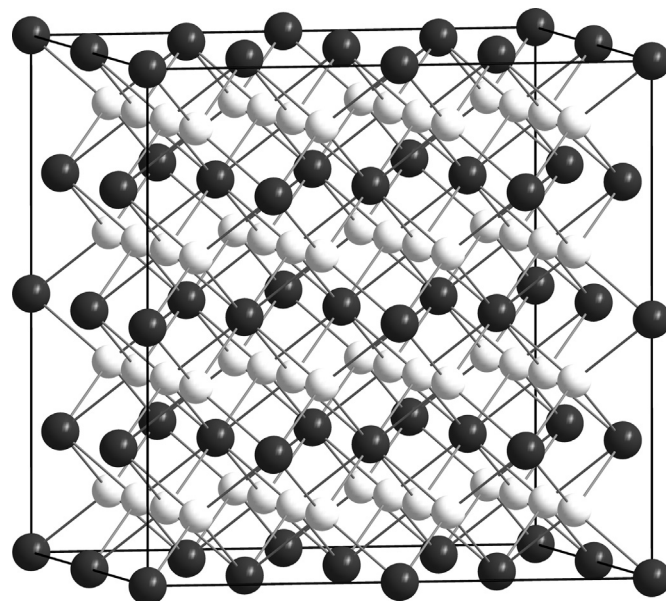


Fig. 1. The crystal structure of henryite down [001] (perspective view). Black and white spheres indicate Te and (Ag,Cu) atoms, respectively. The unit-cell is outlined.

chemical formula obtained on the basis of the structural results (see below), (Cu,Ag)_{3+x}Te₂ with $x \approx 0.40$.

2.2. Single-crystal X-ray diffraction and structure solution and refinement

A small crystal fragment (55 × 75 × 80 μm) was selected for the single-crystal X-ray diffraction study. The intensity data collection (see Table 2 for details) was carried out by means of an Oxford Diffraction Xcalibur 3 single-crystal diffractometer (X-ray radiation MoK α , $\lambda = 0.71073$ Å) fitted with a Sapphire 2 CCD detector. A total of 602 frames of data were collected at room temperature as 8 sets of omega runs with an exposure time of 60 s per frame and a frame width of 1.00°. This afforded an overall data collection of 7938 reflections (168 unique). The refined cubic unit-cell parameters are $a = 12.1987(5)$ Å, and $V = 1815.3(2)$ Å³, which are in good agreement to those found by Criddle et al. [1] [$a = 12.20(2)$ Å, $V = 1815.8(3.9)$ Å³].

Data frames were processed using the *CrysAlis* software package [13] running on the Xcalibur 3 control PC. The program ABSPACK [13] was used for the absorption correction. The merging R for the data set decreased from 0.160 before the absorption correction to 0.031 after this correction. The observed reflection conditions, together with the statistical tests on the distribution of $|E|$ values that strongly indicated the presence of an inversion centre ($|E^2 - 1| = 0.968$), pointed unequivocally to the choice of the space group $Fd\bar{3}c$. The structure solution was then initiated in this space group. The positions of the atoms were determined by means of direct methods [14]. The program SHELXL [14] was used for the refinement of the structure. Neutral scattering curves for Ag and Te were taken from the *International Tables for X-ray Crystallography* [15]. The occupancy of all sites was left free to vary (Ag vs. vacancy

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