The Canadian Mineralogist
Vol. 35, pp. 759-763 (1997)

THE CRYSTAL STRUCTURE OF LEISINGITE, $(Cu^{2+},Mg,Zn)_2(Mg,Fe)Te^{6+}O_6{\cdot}6H_2O$

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ABSTRACT

The crystal structure of leisingite, ideally $(Cu^{2+},Mg,Zn)_2(Mg,Fe)Te^{6+}O_6{\cdot}6H_2O$, a 5.316(1), c 9.719(2) Å, V 237.8(2) Å^3, space group $P\bar{3}1m$, $Z = 1$, has been solved by direct methods, and refined to an R index of 4.2% based on 191 observed reflections measured with Mo$K\alpha$ radiation on an automated four-circle diffractometer. There are three distinct cation positions in the structure; all cations are in octahedral coordination with oxygen. One position is fully occupied by Te^{6+}. The Cu site shows Mg (and probably some Zn) substitution, and the Mg site contains a substantial amount of Fe. Sheets of stoichiometry $(Cu^{2+},Mg,Zn)_2Te^{6+}O_6$ form along the (001) faces of the unit cell. The Mg site is halfway between these sheets, with a stoichiometry of $(Mg,Fe){\cdot}6H_2O$. The sheets are connected to these isolated octahedra by hydrogen bonding, which accounts for the perfect {001} cleavage. Results of electron-microprobe analyses, in combination with those of the structural analysis, give the empirical formula $(Cu^{2+}_{1.56}Mg_{0.25}Zn_{0.03})_{\Sigma 1.84}(Mg_{0.52}Fe_{0.48})_{\Sigma 1.00}Te^{6+}_{1.06}O_6{\cdot}6H_2O$.

Keywords: leisingite, crystal structure, tellurate, cupric, hexagonal closest packing.

SOMMAIRE

Nous avons affiné la structure cristalline de la leisingite, de formule idéale $(Cu^{2+},Mg,Zn)_2(Mg,Fe)Te^{6+}O_6{\cdot}6H_2O$, a 5.316(1), c 9.719(2) Å, V 237.8(2) Å^3, groupe spatial $P\bar{3}1m$, $Z = 1$, par méthodes directes, jusqu'à un résidu R de 4.2%, en utilisant 191 réflexions observées et mesurées avec rayonnement Mo$K\alpha$ et un diffractomètre automatisé à quatre cercles. Ce minéral possède trois positions distinctes occupées par des cations, tous en coordinence octaédrique avec l'oxygène. Le Te^{6+} occupe entièrement une de ces positions. Le site occupé par le Cu contient aussi du Mg, et probablement du Zn, et le site Mg contient une proportion importante de Fe. Des feuillets possédant la stoechiométrie $(Cu^{2+},Mg,Zn)_2Te^{6+}O_6$ sont disposés le long des faces (001) de la maille élémentaire. Le site Mg est situé à mi-chemin entre ces feuillets, et possède une stoechiométrie $(Mg,Fe){\cdot}6H_2O$. Les feuillets sont rattachés à ces octaèdres isolés par liaisons hydrogène, ce qui rend compte du clivage {001} parfait. Les résultats des analyses à la microsonde électronique et de l'ébauche de la structure mènent à la formule empirique $(Cu^{2+}_{1.56}Mg_{0.25}Zn_{0.03})_{\Sigma 1.84}(Mg_{0.52}Fe_{0.48})_{\Sigma 1.00}Te^{6+}_{1.06}O_6{\cdot}6H_2O$.

(Traduit par la Rédaction)

Mots-clés: leisingite, structure cristalline, tellurate, ion cuprique, empilement hexagonal compact.

INTRODUCTION

Leisingite was first described by Roberts *et al.* (1996b) as an extremely rare mineral collected from the dumps of the Centennial Eureka mine, Juab County, Utah [see Marty *et al.* (1993) and Roberts *et al.* (1994) for a description of the deposit]. Only about 2 µg of the mineral has been discovered. It is associated with jensenite (Grice *et al.* 1996a, Roberts *et al.* 1996a), cesbronite, and hematite. Other copper- and tellurium-bearing minerals present in the dumps include mcalpineite (Roberts *et al.* 1994), frankhawthorneite (Roberts *et al.* 1995, Grice &

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Roberts 1995), xocomecatlite, dugganite, quetzalcoatlite, and several identified phases currently under investigation.

Roberts *et al.* (1996b) used single-crystal precession photography to study the symmetry of leisingite. They reported that, on the basis of systematic absences of reflections, possible space-groups are $P\bar{3}1m$, $P31m$, and $P321$. In addition, they reported an average chemical composition (in wt.%) of 36.94% TeO_3, 24.71% CuO, 6.86% FeO, 0.45% ZnO, and 6.19% MgO (average result of three electron-microprobe analyses). The presence of H_2O was confirmed by infrared absorption analysis.

EXPERIMENTAL

The crystal studied was taken from the sample described by Roberts *et al.* (1996b). Because of the small size of the crystal, no attempt was made to grind a sphere, despite the high absorption-coefficient associated with tellurium. The crystal was mounted on a Siemens *P3* automated four-circle diffractometer equipped with a molybdenum-target X-ray tube (operating at 50 kV, 35 mA) and a precisely oriented graphite crystal monochromator mounted with equatorial geometry. Twenty-five reflections were centered using an automated search routine, and the correct unit-cell was selected from an array of real-space vectors corresponding to potential unit-cell axes. Least-squares refinement of these reflections produced the hexagonally constrained unit-cell dimensions given in Table 1, together with the orientation matrix relating the crystal axes to the diffractometer axes.

TABLE 1. MISCELLANEOUS INFORMATION FOR LEISINGITE

a (Å)	5.316(3)	Total reflections	2795
c	9.719(2)	Unique reflections	280
V (Å^3)	237.8(2)	[I ≥ 3σ (I)]	191
Space group	$P\bar{3}1m$	Minimum transmission	0.365
Z	1	Maximum transmission	0.424
μ (mm^{-1})	12.1	*R* (observed) %	4.2
Crystal size (mm)	0.01 × 0.10 × 0.12	R_w (observed) %	3.1

$R = \sum(|F_o|-|F_c|) / \sum|F_o|$

$R_w = [\sum w(|F_o|-|F_c|)^2 / \sum wF_o{}^2]^{0.5}, w = [\sigma^2(F_o)]^{-1}$

Intensity data were collected in the θ–2θ scan mode, using 96 steps with a scan range from [2θ (Mo$K\alpha_1$) – 1.1]° to [2θ (Mo$K\alpha_2$) + 1.1]° and a variable scan-rate between 0.5 and 29.3°/min depending on the intensity of an initial one-second count at the center of the scan range. Backgrounds were measured for half the scan time at the beginning and end of each scan. The stability of the crystal alignment was monitored by collecting two standard reflections every 23 measurements. A complete sphere of reflection (2795 measurements) was measured from 3 to 60° 2θ. Eleven strong reflections uniformly distributed with regard to 2θ were measured at 10° intervals of ψ (the azimuthal angle corresponding to rotation of the crystal about its diffraction vector) from 0 to 350°, after the method of North *et al.* (1968). The merging *R* for the ψ-scan data set (305 reflections) decreased from 3.1% before the absorption correction to 1.9% after the absorption correction. This correction was then applied to the entire data-set; minimum and maximum transmissions were 0.365 and 0.424, respectively. The data were also corrected for Lorentz, polarization and background effects, averaged and reduced to structure factors. Of the 280 unique reflections, 191 were classed as observed [I ≥ 3σ (I)].

STRUCTURE SOLUTION AND REFINEMENT

The Siemens SHELXTL PC system of programs was used throughout this work. Scattering curves for neutral atoms, together with anomalous dispersion coefficients, were taken from Cromer & Mann (1968) and Cromer & Liberman (1970). Miscellaneous information about data collection and refinement is given in Table 1.

Assignment of phases to a set of normalized structure-factors gave a mean value [$E^2 - 1$] of 1.01, suggesting a centrosymmetric space-group. Systematic absences in the complete data-set suggested space group $P\bar{3}$. The structure was solved (by direct methods) and refined in $P\bar{3}$ to an *R* value of 4.6%. However, the resulting formula did not correlate well with results of the electron-

TABLE 2. POSITIONAL AND THERMAL PARAMETERS (× 10^3, Å^2) FOR LEISINGITE

Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Te	0	0	0	11.4(7)	11.4(7)	60(2)	0	0	5.7(3)	27.5(8)
Cu	1/3	2/3	0	11.5(8)	11.5(8)	30(2)	0	0	5.8(4)	17.8(8)
Mg	0	0	1/2	14(2)	14(2)	38(4)	0	0	7.1(9)	22(2)
O(1)	0.307(1)	0	0.1045(6)	31(3)	32(4)	63(4)	0	-17(4)	16(2)	42(3)
O(2)	0.307(2)	0	0.3769(7)	79(5)	243(18)	45(5)	0	0(4)	121(9)	104(10)

microprobe analyses, and inspection of the refined atomic positions in $P\bar{3}$ suggested higher symmetry. The program MISSYM (Le Page 1987) was used to confirm that the correct space-group is $P\bar{3}1m$. The structure was refined in this space group to an R index of 7.8% for an isotropic displacement model. Conversion to anisotropic displacement factors for all of the atoms in the structure resulted in convergence at R and R_w indices of 4.2 and 3.1%, respectively (R = 10.4% for all 280 reflections). The addition of an isotropic extinction correction did not improve the results. Positional coordinates and anisotropic and equivalent isotropic displacement factors are given in Table 2. Selected interatomic distances and angles are given in Table 3, and a bond-valence analysis in Table 4. Structure factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.

TABLE 3. INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR LEISINGITE

Te –O(1)	× 6	1.922(7)	O(1)–Te–O(1)a	× 6	94.7(3)
<Te –O>		1.922	O(1)–Te–O(1)b	× 6	85.3(3)
			<O–Te–O>		90.0
Cu –O(1)	× 6	2.107(5)			
<Cu –O>		2.107	O(1)c–Cu–O(1)a	× 6	98.7(2)
			O(1)c–Cu–O(1)d	× 3	86.5(3)
Mg –O(2)	× 6	2.022(9)	O(1)c–Cu–O(1)e	× 3	76.4(4)
<Mg –O>		2.022	<O–Cu–O>		90.1
O(1)–O(2)		2.648(9)	O(2)–Mg–O(2)a	× 6	88.6(3)
			O(2)–Mg–O(2)f	× 6	91.4(3)
			<O–Mg–O>		90.0

Symmetry operations: a: $0, x, z$; b: $0, \bar{x}, \bar{z}$; c: $x, 1, z$; d: $-x + 1, 1, \bar{z}$; e: $0, -x + 1, \bar{z}$; f: $0, \bar{x}, \bar{z} + 1$.

TABLE 4. BOND-VALENCE* ARRANGEMENT IN LEISINGITE

	Te	Cu	Mg	Total
O(1)	$0.99^{\times 6\downarrow}$	$0.32_{\times 6\downarrow}^{\times 2\rightarrow}$		1.63
O(2)			$0.45^{\times 6\downarrow}$	0.45
Total	5.94	1.90	2.70	

*Calculated using constants from Brese & O'Keeffe (1991). Values for Cu and Mg are weighted for substitutions (11% Mg at the Cu site, 46% Fe^{3+} at the Mg site).

DESCRIPTION OF THE STRUCTURE

There are three distinct positions occupied by cations in the structure of leisingite. The Te site, at special position 1a (0,0,0), is fully occupied by Te^{6+}, and is coordinated by six atoms of oxygen forming a regular octahedron. The Te–O distances are 1.922 Å, and the O–Te–O angles vary from 85.3 to 94.7°. The Cu site, at special position 2c (1/3, 2/3, 0), is also coordinated by six atoms of oxygen forming a regular octahedron. Refinement of the site occupancies and comparison with the electron-microprobe data show that there is a significant amount (approximately 11%) of Mg, and probably some Zn, substituting for Cu at this position. The Cu–O distances are 2.107 Å, and the O–Cu–O angles vary from 76.4 to 98.7°. The consistency of the Cu–O distances is not in agreement with the expected Jahn–Teller distortion usually associated with the Cu^{2+} d^9 configuration. The lack of distortion may be due to the presence of substituents at the Cu position. In paratacamite, the Jahn–Teller effect appears to be obviated by the presence of small amounts of Zn (as little as 2%; Grice *et al.* 1996b), Co, or Ni (Jambor *et al.* 1996) at the Cu site. We suggest that incorporation of Mg or Fe (or both) at the Cu position in leisingite may be sufficient to stabilize a symmetrically bonded cation site.

The Te and Cu octahedra share edges to form hexagonal close-packed (HCP) $M{=}M$ sheets of stoichiometry $(Cu,Mg,Zn)_2Te^{6+}O_6$, based on the classification by Eby & Hawthorne (1993), in which M corresponds to octahedrally coordinated cations, and the equal sign represents edge sharing. The sheets are oriented parallel to (001) at the top and bottom of the unit cell. Part of one of these sheets is shown in Figure 1.

There is one Mg site per unit cell, at special position 1b (0,0,1/2). Refinement of site occupancies with reference to the electron-microprobe results shows that there is a significant amount (approximately 46%) of Fe substituting for Mg at this position. The site is coordinated by six O(2) atoms forming an octahedron. Bond-valence analysis shows that O(2) is occupied by H_2O molecules. The Mg–H_2O distances are 2.022 Å, and the H_2O–Mg–H_2O angles are consistent with regular octahedral coordination, ranging from 88.6 to 91.4°. The octahedra are oriented such that two sets of three H_2O groups lie in planes parallel to (001).

The weighted bond-valence sum for the Mg position is 2.58 (assuming Fe^{2+}) or 2.70 valence units (assuming Fe^{3+}). This suggests that the Fe substituting for Mg is trivalent. In other minerals from the Centennial Eureka mine, cations with variable oxidation states have maximum positive charge (*e.g.*, As^{5+}, Te^{6+}), and hematite is present (Marty *et al.* 1993, Roberts *et al.* 1994).

The $(Cu,Mg,Zn)_2Te^{6+}O_6$ sheets are bound to the isolated Mg octahedra by a double hydrogen bond between the H atoms in the H_2O molecules and the oxygen atoms in the sheets (Fig. 2). The presence of a double hydrogen bond is consistent with the bond-valence analysis for O(1). The hydrogen bonding accounts for the perfect {001} cleavage. The O(1)–O(2) distance is 2.648 Å, and the O(1)–O(2) vector is approximately parallel to [001]. Attempts to refine the positions of the H atoms were unsuccessful.

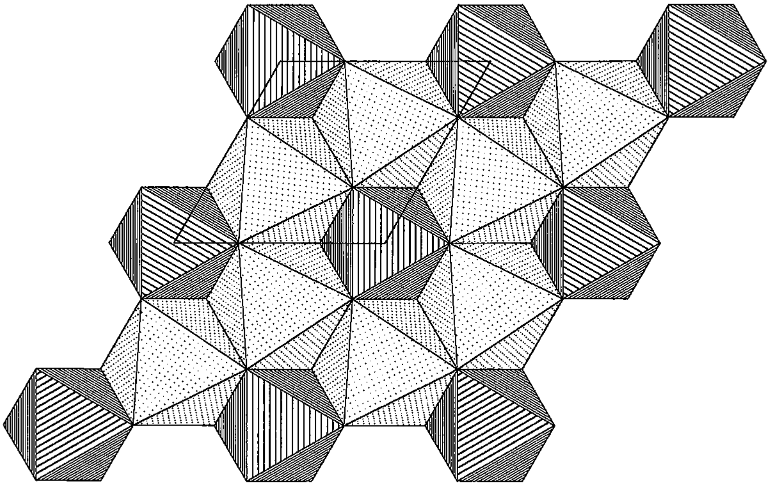

FIG. 1. The $(Cu,Mg,Zn)_2Te^{6+}O_6$ layer in the structure of leisingite, viewed down [001]. The Te and Cu octahedra are shown by parallel line and normal dot patterns, respectively.

Leisingite is structurally similar to jensenite (Grice *et al.* 1996a), which also consists of HCP layers of composition $Cu_2Te^{6+}O_6$. In jensenite, however, the layers are held together through corner-sharing with $Cu_2\varphi_8$ dimers, forming an infinite framework structure classified as *M=M–M=M* (Eby & Hawthorne 1993), in which the hyphen represents corner sharing. The structure of frankhawthorneite (Grice & Roberts 1995) also consists of HCP layers, but only half of the octahedrally coordinated cation sites in the layers are filled. Leisingite is the first known copper tellurate mineral to contain isolated octahedra.

The ideal formula of leisingite is $(Cu^{2+},Mg,Zn)_2(Mg,Fe)TeO_6 \cdot 6H_2O$. The empirical formula, based on the average results of electron-microprobe analyses in Roberts *et al.* (1996b), and calculated on the basis of 12 anions (six H_2O molecules) and a filled Mg site, is $(Cu^{2+}_{1.56}Mg_{0.25}Zn_{0.03})_{\Sigma 1.84}(Mg_{0.52}Fe_{0.48})_{\Sigma 1.00}Te^{6+}_{1.06}O_6 \cdot 6H_2O$. This is similar to the formula based on the structure analysis, which is $(Cu^{2+},Zn_{1.78}Mg_{0.22})_{\Sigma 2.00}(Mg_{0.54}Fe_{0.46})_{\Sigma 1.00}Te^{6+}O_6 \cdot 6H_2O$.

ACKNOWLEDGEMENTS

The authors thank Jim Trotter for helping with the space-group determination. The comments of an anonymous reviewer were especially helpful. Financial support was provided by the Natural Sciences and Engineering Research Council of Canada in the form of an Operating Grant to LAG, and by equipment grants from the B.C. Science and Technology Development Fund and the University of British Columbia.

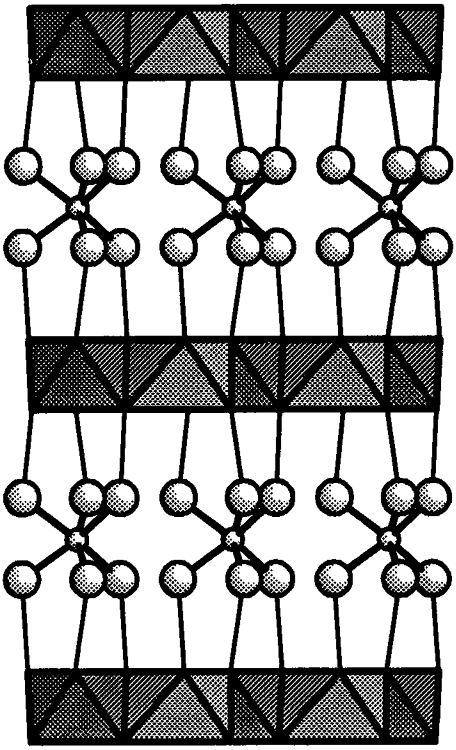

FIG. 2. Perspective view of the leisingite structure projected onto (010).

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Received August 20, 1996, revised manuscript accepted April 30, 1997.