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THE CRYSTAL STRUCTURE OF OWENSITE, $(Ba,Pb)_6(Cu,Fe,Ni)_{25}S_{27}$, A NEW MEMBER OF THE DJERFISHERITE GROUP

JAN T. SZYMAŃSKI

Mineral Sciences Laboratories, CANMET, Natural Resources Canada, 555 Booth Street, Ottawa, Ontario K1A 0G1

ABSTRACT

The crystal structure of the new mineral species owensite, $(Ba,Pb)_6(Cu,Fe,Ni)_{25}S_{27}$, is cubic, a 10.349(1) Å, space group $Pm3m$. Nine S atoms bond to each (Ba,Pb) atom. The unit cell contains a single (Cu,Fe,Ni) atom that is octahedrally coordinated by S; the other twenty-four (Cu,Fe,Ni) atoms are tetrahedrally coordinated. The structure is analogous to that of djerfisherite, $K_6Na(Fe,Ni,Cu)_{24}S_{26}Cl$, but it contains no monovalent ions. The K sites in djerfisherite are here occupied by (Ba,Pb) atoms; the Na site is occupied by one of the (Cu,Fe,Ni) atoms, whereas the Cl site is occupied by a S atom. The structure was solved and refined to an R index of 5.2% for Mo$K\alpha$ data to $2\theta = 100°$. The bond lengths and angles are all within the expected limits: Ba-S between 3.132(2) and 3.300(5) Å, (Cu,Fe)-S between 2.302(3) and 2.356(2) Å [tetrahedral], or 2.501(5) Å [octahedral]. The Pb atom replaces the Ba atom within the S coordination cage, but is disordered and displaced from the Ba atom position as a result of the presence of the $6s^2$ Pb electron pair. Four disordered Pb satellite positions exist, all 0.38 Å from the Ba position, and in a square with a side of 0.31 Å.

Keywords: owensite, barium copper–iron sulfide, structure refinement, atomic ratios, disordered lead, djerfisherite-group mineral.

SOMMAIRE

La structure cristalline de l'owensite, nouvelle espèce minérale de formule $(Ba,Pb)_6(Cu,Fe,Ni)_{25}S_{27}$, est cubique, $a = 10.349(1)$ Å, et de groupe spatial $Pm3m$. Chaque atome de (Ba,Pb) est lié à neuf atomes de S. Un seul atome (Cu,Fe,Ni) par maille est en coordination octaédrique avec des atomes de S, les 24 autres étant en coordination tétraédrique. L'owensite est isostructurale avec la djerfisherite, $K_6Na(Fe,Ni,Cu)_{24}S_{26}Cl$, mais en diffère par l'absence d'ions monovalents. Les atomes de K, Na et Cl de la djerfisherite correspondent respectivement à (Ba,Pb), (Cu,Fe,Ni) et S dans l'owensite. La structure a été résolue et affinée jusqu'à un résidu R de 5.2% sur des données de diffraction mesurées avec rayonnement au molybdène jusqu'à $2\theta = 100°$. Les valeurs des distances et angles de liaisons respectent les limites attendues: Ba–S entre 3.132(2) et 3.300(5) Å; (Cu,Fe,Ni)–S entre 2.302(3) et 2.356(2) Å [tétraèdres] ou 2.501(5) Å [octaèdre]. L'atome Pb remplace le Ba à l'intérieur de la cage de S, mais il est déplacé par rapport à la position du Ba en raison de la présence des orbitales électroniques $6s^2$ du Pb, et est désordonné. On distingue quatre pics satellites dus au Pb, tous à 0.38 Å de la position du Ba, qui forment un carré de 0.31 Å de côté.

Mots-clés: owensite, sulfure de baryum, cuivre et fer, affinement de structure, rapports atomiques, plomb désordonné, minéral de type djerfisherite.

INTRODUCTION

The new mineral species owensite, found in the Wellgreen deposit, Yukon Territory (Cabri *et al.* 1993), has been described in the previous paper (Laflamme *et al.* 1995). Interest in this mineral developed when it was realized that it promised to be a Ba transition-metal sulfide, as no Ba sulfide minerals have hitherto been described. It was expected from the chemistry and the X-ray powder-diffraction data that this mineral would have an argentopentlandite structure (Hall & Stewart 1973). However, electron-microprobe analyses on owensite grains indicated atomic proportions $[(Ba_{5.42}Pb_{0.56})_{\Sigma 5.98}(Cu_{12.87}Fe_{11.70}Ni_{0.14})_{\Sigma 24.71}S_{27.31}$, based on 58 atoms] that are incompatible with the expected 9:8 metal:sulfur ratio. Given the observed proportions of Ba, Pb, Cu, Fe, Ni and S, it was not possible to acccount for the chemistry in terms of atomic sites within the known structural types. To this end, a structural determination was undertaken to elucidate the formula and to explain the determined chemical composition.

EXPERIMENTAL

An irregular fragment of owensite, dug out of a polished section and measuring <50 μm across, was

mounted on a CAD4 single-crystal diffractometer. This grain had been used previously to obtain the powder-diffraction data and to characterize the mineral by a single-crystal precession study. Unit-cell dimensions were refined from 45 unique reflections in the range $22.3 < 2\theta < 45.7°$, using the NRCVAX routine TRUANG. This computer program measures and averages the angular positions for each of the four equivalent reflections (*hkl* and *–h–k–l* at $+2\theta$ and -2θ). Mo$K\alpha$ radiation was used throughout the data-collection procedure. The value of the *a* parameter quoted here [10.349(1) Å] differs slightly from that quoted in the previous paper (Laflamme *et al.* 1995); the latter value (10.373 Å) was obtained from a refinement of X-ray powder-diffraction film data, uncorrected for film shrinkage. Four equivalent segments of diffraction data were collected in diffraction symmetry $3m$ (equivalent to eight segments in symmetry $m3m$, or one quarter of the sphere of reflection), to a limit of $2\theta = 100°$. In view of the very small size of the crystal, slow scans (½° in 2θ min^{-1}.) were used. Nevertheless, some reflections were still observed at the 2θ limit of data collection, though most were unobserved, and the observed reflections were all weak. Empirical absorption-corrections were applied from correction curves obtained from ψ-sweeps for four reflections with widely differing 2θ values. The intensities were measured at intervals of 5° in ψ, and the corrected data were reduced in both diffraction symmetry $3m$ and $m3m$. With no systematic absences in the cubic system, the space group was identified as being one of the following: $Pm3m$, $P432$, $P\bar{4}3m$, $Pm3$, or $P23$.

Structure Determination and Refinement

The structure was solved using direct methods initially in space group $Pm3$. It was being refined in this space group, until it was realized that the very high matrix correlations observed in the least-squares refinement were due to an additional mirror plane in the determined structure. Reassignment of the space group as $Pm3m$ yielded a model that refined to an acceptable residual with little difficulty. Scattering curves for neutral atoms (Cromer & Mann 1968) were used throughout the refinement. Population parameters were allowed to vary for the atoms in the metal sites (refined as Ba and Cu, respectively), with the population parameter of the S sites fixed at unity as a reference. With the proposed Ba site at about full occupancy and both Cu sites showing about 92% occupancy, weighted dual scattering factors were introduced. The scattering curve for the Ba site was adjusted to include the partial incorporation of Pb in that site, Ba:Pb = 0.9064:0.0936. Similarly, the Cu scattering curve was adjusted for the presence of Fe in the Cu:Fe proportion indicated by the microprobe results. Unfortunately, in the currently used software for structure refinement, a maximum of only two atomic types can be assigned to a single site; Ni was therefore omitted. This is not likely to introduce any significant error, as the proportion of Ni is very small [<0.6% of the (Cu,Fe,Ni)], and the composite curve of Cu and Fe, in the proportions found in the microprobe analyses, is very close to the Ni curve. The structure refined using anisotropic thermal parameters to a residual R of 6.2%. Of the 1209 unique reflections measured, 554 were observed with the criterion that $I_{obs} > 3\sigma(I_{obs})$. This residual is higher than one would like to see in a well-refined structure, but it was considered that this was an artifact of collecting the data on such a small crystal to the high 2θ limit of 100°. Truncating the data to the more usual limit of $2\theta = 60°$ improved the residual to 3.9%. Near the end of the refinement, the population parameters of all metal sites were allowed to vary in an attempt to check for incomplete occupancy of these sites in the structure. The resultant parameters did not differ significantly from unity for the (Cu,Fe) site [0.99(2)], and it must be concluded that all (Cu,Fe) sites are fully occupied. However, the Ba population parameter did decrease to less than the expected value. A difference synthesis calculated at this point in the refinement revealed small peaks distributed about the fourfold axis and about 0.5 Å from the Ba position. These were interpreted as being due to a disordered Pb atom, moved *away* from the Ba position by the interaction of the remaining Pb $6s^2$ valence electrons with the anion coordinating sphere (see Moore *et al.* 1993, Szymański 1988). As the proportion of Ba:Pb is 0.9064:0.0936, and as the 0.0936 population parameter for Pb is now equally divided among the four disordered sites, its value is now only 0.0234 at each new site. Refinement of the position, of the occupancy and isotropic thermal parameter of this very small peak (corresponding to 0.0234×82, or ~2 electrons) was strongly correlated, and very severe damping had to be used for the block-diagonal least-squares employed. The structure refined to $R = 5.2\%$ for all data and $R = 3.5\%$ for data below $2\theta = 60°$. A difference synthesis did not reveal any peaks beyond 1 electron, and these were at high-symmetry positions, where cumulative errors in data tend to generate peaks. All crystallographic calculations were carried out using the NRCVAX system of programs (Gabe *et al.* 1989) on a 486–P.C. The crystal data on owensite are summarized in Table 1.

Description of the Structure of Owensite

There are four unique S sites. These are: S1 at the origin [0,0,0], (multiplicity 1); S2 at [*x*,½,0], (multiplicity 12); S3 at [½,½,*z*], (multiplicity 6); S4 at [*x*,*x*,*x*] (multiplicity 8). There are thus 27 S atoms within the unit cell. The (Cu,Fe,Ni) atom is found at the [½,½,½]

TABLE 1. CRYSTAL DATA FOR OWENSITE

Owensite, simplified formula:	$(Ba,Pb)_6(Cu,Fe,Ni)_{25}S_{27}$.
Electron-microprobe formula, based on 58 atoms*:	$(Ba_{3.42}Pb_{0.58})_{\Sigma 3.98}(Cu_{12.67}Fe_{11.70}Ni_{0.14})_{\Sigma 24.71}S_{27.31}$
Symmetry:	cubic, a 10.349(1) Å, $Pm3m$ (#221), Z = 1.
Systematic absences:	none
Space-group choices:	$Pm3m$, $P432$, $P\bar{4}3m$, $Pm3$, or $P23$. $Pm3m$ from structure determination.
Source:	Wellgreen Cu-Ni-Pt-Pd deposit, Yukon Territory (Cabri *et al.* 1993).
Density:	$D_{calc.}$ = 4.83 Mg m^{-3} for stoichiometric formula, 4.78 Mg m^{-3} for empirical formula derived from electron-microprobe data; $D_{obs.}$ not determined.
Absorption:	μ(MoKα) = 180.4 cm^{-1}.
Intensity data:	4 unique segments collected in diffraction symmetry $3m$ (equivalent to 8 segments in $m3m$) to a limit of 2θ = 100° using MoKα radiation. Averaged to yield 1209 unique reflections measured, 554 with $I_{obs.} > 3\sigma(I_{obs.})$.
Refinement:	full-matrix least-squares to R = 5.2%, block-diagonal in final cycles to refine disordered Pb position.

*Laflamme *et al.* (1995).

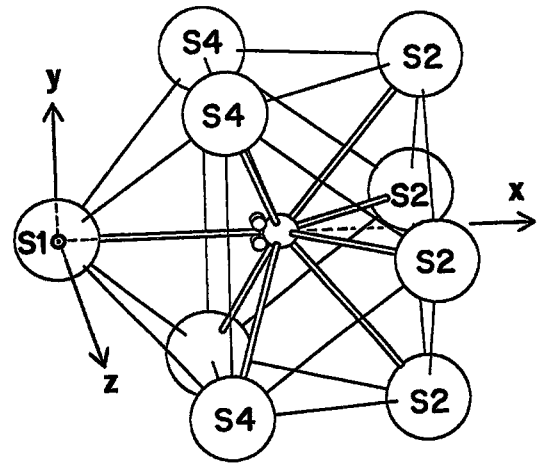

FIG. 1. Coordination of (Ba,Pb). S1 is at the origin, with a fourfold axis through S1 and Ba (larger circle at center). Pb is displaced from the Ba position and disordered over the four sites close to the axis (small circles near Ba). S4 lies along the body-diagonal of the cell, whereas S2 is in the plane of two axes. A square antiprism is thus formed from the four S2 and four S4, whereas S1 occupies an axial position above the antiprism. Each S4–S1–S4 triangular face is face-shared to form a cruciform assembly around the origin.

position (multiplicity 1) and at [x,y,y] (multiplicity 24) for a total of 25 (Cu,Fe,Ni) atoms in the unit cell. The Ba atom is found at a six-fold site at [0,0,z], and the Pb atom is within the same S cage, but is displaced from the Ba position toward the origin and away from the fourfold axis. It is positionally disordered, and statistically distributed in a site at [x,x,z] with 24-fold multiplicity and located 0.380(12) Å from the Ba atom. This results in the formula $(Ba,Pb)_6(Cu,Fe,Ni)_{25}S_{27}$, with Z = 1.

Discussion of the coordination polyhedra around the Ba and Cu atoms follows. For Ba, the coordination is illustrated in Figure 1. With S1 at the origin and Ba along each axis, there is a fourfold axis through these two atoms. There are four S2 atoms [at 3.239(3) Å] and four S4 atoms [at 3.302(3) Å] arranged in a somewhat distorted square antiprism. S1 is the ninth coordinating sulfur atom at 3.148(2) Å. A tridecahedron (13 faces) with nine vertices is thus formed around Ba. This poly-

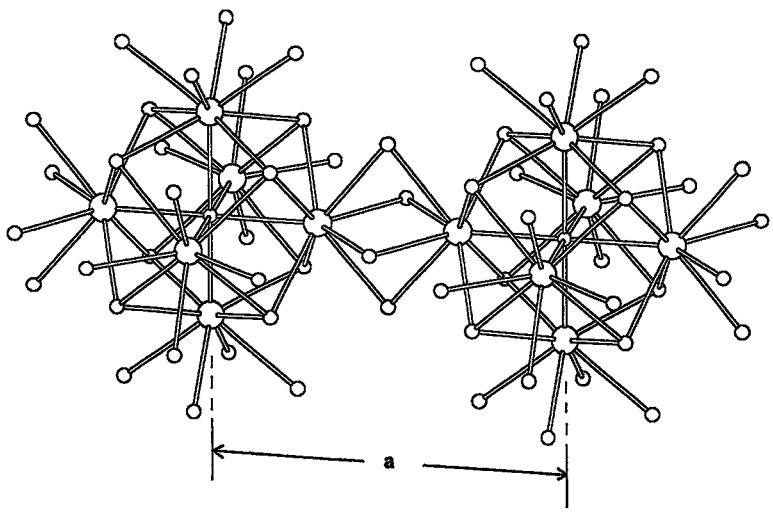

FIG. 2. The (Ba,Pb)–S polyhedra, comprising the units shown in Figure 1 (but without the Pb) face-sharing to form a cruciform assembly at each origin and between adjacent origins. The unit-cell edge is indicated. These polyhedra extend along and fill the space close to each of the three axes.

hedron is repeated in each of the positive and negative axial directions, with the S2 atoms midway along the axes being shared between adjacent polyhedra (Fig. 2). The edges of the cell are thus fully defined, and the space between adjacent origins is filled with these Ba–S polyhedra.

Cu1 is at the center of the unit cell, and is surrounded by six S3 atoms (at ½,½,*z*) at a distance of 2.499(5) Å in perfect octahedral coordination. Cu2 is in a somewhat distorted tetrahedral coordination, with an S2 at 2.357(2) Å, a second S2 at 2.358(3) Å, an S3 at 2.347(4) Å and an S4 at 2.304(3) Å. One angle (S3–Cu–S4) is opened up to 127.1°; the remainder are between 105.1° and 106.3°.

The coordination of the S atoms is as follows: S1, at the origin, is in perfect octahedral coordination by Ba atoms at 3.148(2) Å. S2 is bonded to two Ba atoms and four Cu atoms in a distorted triangular prism (Fig. 3). The distances to Ba are 3.239(3) Å and to Cu are 2.357(2) Å. S3 is bonded to four Cu2 atoms [2.347(3) Å] at the base of a square pyramid, with Cu1 [2.499(5) Å] at the apex (Fig. 4). S4 has three Cu2 atoms [2.302(3) Å] adjacent to each other and three Ba atoms [3.304(3) Å] adjacent to each other. A distorted octahedron is thus formed with Cu and Ba atoms always *trans* to each other across the S4 atoms.

It is clear that the Ba coordination polyhedra account for the space between adjacent origins, that the Cu1 octahedron occupies the center of the cell, and that the rest of the space within the unit cell is filled with tetrahedrally coordinated Cu2 atoms.

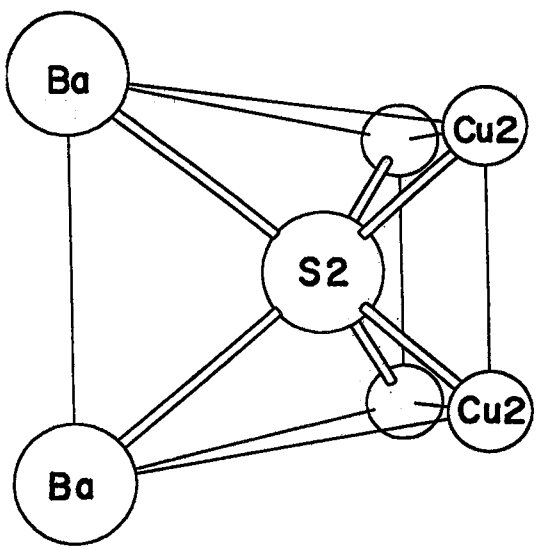

FIG. 3. Distorted triangular prism around S2. The four Cu2 atoms are in a square, with Ba in the plane that is half-way between copper atoms and includes S2. The polyhedron has *mm* symmetry.

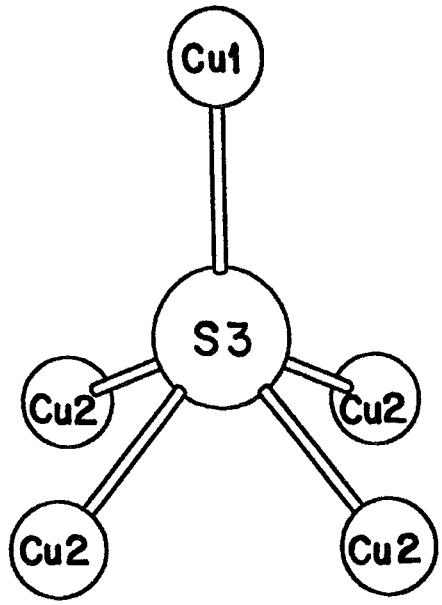

FIG. 4. The square pyramid coordination of S3. A fourfold axis passes through Cu1 (at the apex) and S3.

The refined atomic parameters are listed in Table 2. These parameters can be related to those published for djerfisherite (Dmitrieva *et al.* 1979) by transforming the origin to the center of the cell. Bond lengths and

TABLE 2. ATOMIC PARAMETERS WITH STANDARD DEVIATIONS

Atomic Parameters *x,y,z* and $B_{eq.}$
E.S.D.'s refer to the last digit printed.

Atom	site	occ.	*x*	*y*	*z*	$B_{eq.}$(Å²)
S1	1*a*	1.0	0	0	0	1.10(10)
S2	12*h*	1.0	0.24422(35)	0.5	0	1.10(11)
S3	6*f*	1.0	0.5	0.5	0.25858(50)	1.06(10)
S4	8*g*	1.0	0.21703(30)	0.21703	0.21703	1.26(4)
Ba	6*e*	.9064*	0	0	0.30420(14)	1.13(3)
Pb	24*m*	.0234*	0.0149(15)	0.0149	0.2740(15)	1.22(33)
Cu1	1*b*	.5237‡	0.5	0.5	0.5	1.09(5)
Cu2	24*m*	.5237‡	0.36416(10)	0.36416	0.13806(17)	1.45(4)

* [(Pb+Ba) = 1.00]; ‡ (Fe = .4763)

Table of u(i,j) values x 100.
E.S.Ds. refer to the last digit printed

	u11(U)	u22	u33	u12	u13	u23
S1	1.39(21)	1.39	1.39	.000	.00	.00
S2	1.38(14)	1.47(14)	1.33(13)	.000	.00	.00
S3	1.50(12)	1.50	1.02(19)	.000	.00	.00
S4	1.60(7)	1.60	1.60	.23(09)	.23	.23
Ba	1.54(3)	1.54	1.20(5)	.000	.00	.00
Cu1	1.60(12)	1.60	1.60	.000	.00	.00
Cu2	1.67(3)	1.67	2.17(6)	-.16(5)	.04(4)	.04
Pb	U(iso) = 1.52(42)					

Anisotropic Temperature Factors are of the form:
Temp= $-2\pi^2*(h^2u_{11}*astar^2+\cdots+2*h*k*u_{12}*astar*bstar+\cdots)$

TABLE 3. BOND LENGTHS (Å) AND ANGLES (°) FOR OWENSITE

1. Coordination of S1 - Regular octahedron.
S1 - Ba 3.1483(15) All angles 90 or 180

2. Coordination of S2 - Distorted triangular prism.
S2 - Ba(*b*,*f*) 2 x 3.239(3)
S2 - Cu2(,*g*,*h*,*i*) 4 x 2.357(2)
Ba*b*- S2 - Ba*f* 77.4(1)
Ba - S2 - Cu2 4 x 92.2(1)
Ba - S2 - Cu2 4 x 141.6(1)
Cu2- S2 - Cu2*g* 74.6(1) Cu2*g*- S2 - Cu2*h* 116.5(1)
Cu2- S2 - Cu2*h* 73.2(1) Cu2*g*- S2 - Cu2*i* 73.2(1)
Cu2- S2 - Cu2*i* 116.5(2) Cu2*h*- S2 - Cu2*i* 74.6(1)

3. Coordination of S3 - Square pyramid.
S3 - Cu1 1 x 2.499(5) (apical bond)
S3 - Cu2(,*j*,*h*,*k*) 4 x 2.347(3) (square base)
Cu1 - S3 - Cu2 4 x 122.1(1)
Cu2 - S3 - Cu2 4 x 73.6(1)
Cu2 - S3 - Cu2 2 x 115.8(2)

4. Coordination of S4 - triangular antiprism, or distorted octahedron.
S4 - Cu2(,*b*,*d*) 3 x 2.304(3)
S4 - Ba(,*b*,*d*) 3 x 3.302(4)
Ba - S4 - Ba 3 x 84.8(1) Ba - S4 - Cu 6 x 91.6(1)
Cu - S4 - Cu 3 x 91.8(1) Ba - S4 - Cu 3 x 175.1(2)

5. Coordination of Ba - distorted square antiprism with ninth atom at apex.
Ba - S1 1 x 3.1483(15)
Ba - S2(*d*,*l*,*m*,*n*) 4 x 3.239(3)
Ba - S4(,*o*,*p*,*q*) 4 x 3.302(5)
S1 - Ba - S2 4 x 128.7(1) S2*d*- Ba - S4*o* 134.6(1)
S1 - Ba - S4 4 x 74.1(1) S2*d*- Ba - S4*p* 68.9(1)
S2*d*- Ba - S2*l* 102.6(1) S2*d*- Ba - S4*q* 134.6(1)
S2*d*- Ba - S2*m* 67.0(1) S4 - Ba - S4*o* 148.3(1)
S2*d*- Ba - S2*n* 67.0(1) S4 - Ba - S4*p* 85.7(1)
S2*l*- Ba - S2*m* 67.0(1) S4 - Ba - S4*q* 85.7(1)
S2*l*- Ba - S2*n* 67.0(1) S4*o*- Ba - S4*p* 85.7(1)
S2*m*- Ba - S2*n* 102.6(1) S4*o*- Ba - S4*q* 85.7(1)
S2*d*- Ba - S4 68.9(1) S4*p*- Ba - S4*q* 148.3(1)

6. Coordination of Cu1 - regular octahedron.
Cu1 - S3(,*b*,*d*,*s*,*t*,*u*) - 2.499(5)

7. Coordination of Cu2 - distorted tetrahedron.

		S2 - Cu2 - S2*v*	105.1(1)
Cu2 - S2	2.358(2)	S2 - Cu2 - S3	106.3(1)
Cu2 - S2*v*	2.358(2)	S2 - Cu2 - S4	105.1(1)
Cu2 - S3	2.347(3)	S2*v*- Cu2 - S3	106.3(1)
Cu2 - S4	2.304(3)	S2*v*- Cu2 - S4	105.1(1)
		S3 - Cu2 - S4	127.1(2)

The following Atoms are the Symmetry Equivalents

Name	*x*	*y*	*z*	*x'*	*y'*	*z'*
Ba*a*	0	0	-0.30260	-*x*	-*y*	-*z*
Ba*b*	0	0.30260	0	*y*	*z*	*x*
Ba*c*	0	-0.30260	0	-*y*	-*z*	-*x*
Ba*d*	0.30260	0	0	*z*	*x*	*y*
Ba*e*	-0.30260	0	0	-*z*	-*x*	-*y*
Ba*f*	0	0.69740	0	-*y*	*1.0-z*	-*x*
Cu2*g*	0.36427	0.36425	-0.13810	*x*	*y*	-*z*
Cu2*h*	0.36427	0.63575	0.13810	*x*	*1.0-y*	*z*
Cu2*i*	0.36427	0.63575	-0.13810	*x*	*1.0-y*	-*z*
Cu2*j*	0.63573	0.63575	0.13810	*1.0-x*	*1.0-y*	*z*
Cu2*k*	0.63573	0.36425	0.13810	*1.0-x*	*y*	*z*
Cu2*b*	0.36425	0.13810	0.36427	*y*	*z*	*x*
Cu2*d*	0.13810	0.36427	0.36425	*z*	*x*	*y*
S2*d*	0	0.24458	0.5	*z*	*x*	*z*
S2*l*	0	-0.24458	0.5	-*z*	-*x*	*1.0-y*
S2*m*	0.24458	0	0.5	*x*	*z*	*y*
S2*n*	-0.24458	0	0.5	-*x*	-*z*	*1.0-y*
S4*o*	-0.21722	-0.21722	0.21722	-*x*	-*y*	*z*
S4*p*	-0.21722	0.21722	0.21722	-*y*	*z*	*x*
S4*q*	0.21722	-0.21722	0.21722	*z*	-*x*	*y*
Ba*r*	0	0	0.69740	-*x*	-*y*	*1.0-z*
S3*s*	0.5	0.5	0.74164	*1.0-x*	*1.0-y*	*1.0-z*
S3*b*	0.5	0.25836	0.5	*y*	*z*	*x*
S3*t*	0.5	0.74164	0.5	*1.0-y*	*1.0-z*	*1.0-x*
S3*d*	0.25836	0.5	0.5	*z*	*x*	*y*
S3*u*	0.74164	0.5	0.5	*1.0-z*	*1.0-x*	*1.0-y*
S2*v*	0.5	0.24458	0.5	*y*	*x*	*z*

angles are given in Table 3. The observed structure-factors ($10 \times F_o$) with standard deviations and calculated ($10 \times F_c$) structure-factors are given in Table 4, which is available at a nominal charge from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

Discussion

From its powder-diffraction pattern and from its proportions of heavy-metal, transition-metal and sulfur atoms as obtained from electron-microprobe analyses, owensite was initially considered a derivative of the argentopentlandite structure, $AgFe_8S_8$ (Hall & Stewart 1973). Indeed, stoichiometrically owensite *is* close to argentopentlandite; the metal/sulfur ratio in owensite is 31/27 (1.148), and in argentopentlandite it is 9/8 (1.125). Owensite is the first example of a Ba-containing sulfide mineral. The total absence of monovalent cations and of Cl made the relationship to djerfisherite unclear, until it was kindly pointed out to the author by two (anonymous) members of the Committee on New Minerals and Mineral Names, IMA, during the name approval process. When the structure had been solved, and the relationship of owensite to djerfisherite was understood, specimens of owensite were probed again, to determine the absolute level of possible Cl presence. At the detection limit of the microprobe (Laflamme *et al.* 1995), the possible limit for Cl is less than 0.012 atom/formula unit. Structurally, Cl can play no part in owensite. The difference between the two structural types is that owensite and djerfisherite have space group *Pm3m*, whereas argentopentlandite is *Fm3m*; the cell edges for the three are similar: owensite, 10.373(1) Å (this work); djerfisherite 10.465(1) Å (Dmitrieva *et al.* 1978); argentopentlandite 10.521(3) Å (Hall & Stewart 1973). The development of the owensite structure from that of argentopentlandite can be rationalized as follows: in argentopentlandite, where the Ag atom occupies one of the octahedrally coordinated metal sites of the reference structure of pentlandite, the Ag–S distance is only 2.676 Å. In owensite, the presence of the much larger (Ba,Pb) atom demands a larger hole, and this results in an increased coordination number from six to nine. The S atoms in the structure are required to surround this large Ba atom, and fewer are thus available for octahedral coordination throughout the cell. Only the unique Cu1 atom retains an octahedral coordination at the center of the

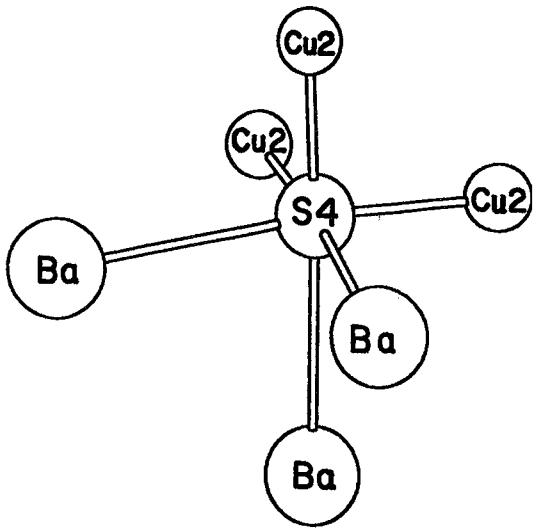

FIG. 5. The distorted octahedral coordination around S4, showing three barium atoms (larger circles) and three Cu2 atoms (smaller circles). Each copper is *trans* to a barium atom.

cell. It appears that the larger coordination-polyhedron needed for Ba in owensite cannot be reproduced at the face-centering position; it is just too large. The structure reduces to a primitive cell, and gives rise to a somewhat different metal:sulfur ratio. Once the primitive cell of diffraction symmetry *m3m* has been achieved, it is found to be isostructural with that of djerfisherite. This appears to be a "chicken-and-egg" argument, but the end result is that what was previously thought of as a simple *structure*, namely the djerfisherite structure, is truly a *structural type*, with djerfisherite, thalfenisite [the Tl derivative, $Tl_6(Fe,Ni,Cu)_{25}S_{27}Cl$, (Rudashevskiy *et al.* 1979)], and now owensite as group members. In thalfenisite, the Na atom is replaced by a divalent ion. Owensite represents the next stage of replacement, where (Ba,Pb) replaces Tl and S replaces Cl.

The disorder that occurs as Pb replaces Ba in the large heavy-metal site has been discussed at some length by Moore *et al.* (1993) and has been observed in many lead salts and minerals, where the coordination sphere of anions around the Pb atom is asymmetrical. The effect is to displace the $6s^2$ electron density (which is about the size of an O^{2-} anion) away from the smaller bond-pair densities. Moore *et al.* (1993) proposed that this effect is electrostatic in origin. A pear-shaped orbital results, and the greater part of the electron density is moved *away* from the position where, in the present case, the Ba atom is located within the same S cage. The refined atomic position of Pb is on the (*x*,*x*,*z*) mirror plane and around the four-fold axis. This results in four possible atomic sites, in a square of 0.307(30) Å, with the Pb site being 0.380(12) Å from the Ba site. Only one of the Pb sites can be occupied in any given sulfur cage at any given time, and only if Pb has replaced Ba within that cage. There is thus no point in discussing at length all Ba–Pb distances and angles, as these cannot exist in reality.

The residual *R*, achieved before invoking disorder (6.2%), was somewhat higher in the present refinement than one would like to see in a well-refined structure. However, it was considered originally that this was an artifact of collecting the data out to $2\theta = 100°$ on such a small crystal. The large number of weak reflections observed at high diffraction-angles from this very small crystal results in an artificial raising of the agreement factor to above what should be expected. When refinement was restricted to data below $2\theta = 60°$, the *R* value converged to about 3.9%. With the structural model involving Pb disorder away from the Ba position, the residual for all data dropped to 5.2%, with the data below $2\theta = 60°$ giving an *R* of 3.5%. The improvement in the refinement using the disordered model is *very* significant The process of averaging the eight segments of intensity data in symmetry *m3m* gives rise to an agreement factor of about 3% between equivalent segments, and this is usually a good barometer of the possible degree of refinement and the ultimate *R* value that can be obtained with a well-refined, nondisordered structure. Thus, in the present case, the refinement achieved for the final disordered model is not significantly greater than the expected 3% for the observed data to a 2θ of 60°.

CONCLUSIONS

Djerfisherite-group minerals have been considered to have a chemical composition in which Cl is essential (1 Cl per formula unit), monovalent ions are present (6 K and 1 Na), and the proportion of the transition metal has been reported as less than stoichiometric (Clarke *et al.* 1994). Owensite obeys none of these conditions. It has large divalent (Ba,Pb) atoms replacing K, a (Cu,Fe,Ni) atom replacing Na, and a S atom replacing Cl, and its (Cu,Fe,Ni) sites are fully occupied. Other than that, it is isostructural with djerfisherite and with the Tl equivalent, thalfenisite. These structures should be considered as a *group*, with the crystal symmetry, rather than the chemistry, being the common factor.

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