

Leiteite, ZnAs_2O_4 : A novel type of tetrahedral layer structure with arsenite chains¹

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ABSTRACT

Leiteite, ZnAs_2O_4 , from Tsumeb, Namibia, is monoclinic, $a = 4.542(1)$, $b = 5.022(1)$, $c = 17.597(5)$ Å, $\beta = 90.81(3)^\circ$, space group $P2_1/c$, $Z = 2$. The crystal structure has been determined by direct methods and refined by the method of least squares to an R factor of 0.048 based on 731 independent reflections measured on an automatic single-crystal X-ray diffractometer. The crystal structure consists of open Zn tetrahedral sheets flanked by single arsenite chains on either side. The composite layers are cross-linked through weak (2.8–3.3 Å) As–O bonds. Leiteite represents a new structure type. The average tetrahedral Zn–O distance is 1.99 Å, and the average As–O distances and O–As–O angles in the two distinct trigonal pyramidal arsenite groups are 1.79 Å, 95.5° for As(1) and 1.78 Å, 95.8° for As(2).

INTRODUCTION

The rare zinc arsenite mineral leiteite, ZnAs_2O_4 , was discovered by Luis Teixeira Leite from the oxidation zone in Tsumeb, Namibia. It occurs in association with tennantite, chalcocite, smithsonite, and schneiderhöhnite. Its association with the arsenite mineral schneiderhöhnite, $\text{Fe}^{2+}\text{Fe}_3^+\text{As}_5\text{O}_{13}$, which is considered to have formed at 40°C (Otteman et al., 1973), would indicate a low-temperature origin for leiteite. Its chemical composition, optical, crystallographic, and physical properties were described by Cesbron et al. (1977). In Tsumeb, it occurs as colorless to brown, transparent, cleavable masses with pearly luster. The lamellar cleavage is extremely good, reminiscent of micas and talc. The cleavage lamellae are soft (Mohs' hardness 1.5–2), somewhat sectile, flexible, and easily bent. No crystal forms have been observed. Leiteite is monoclinic and optically biaxial positive. The unit-cell dimensions, determined from a least-squares refinement of a powder-diffraction pattern, were reported as $a = 17.645(5)$, $b = 5.019(2)$, $c = 4.547(2)$ Å, $\beta = 90^\circ(59)(4)$, space group $P2_1/a$ (Cesbron et al., 1977). We have previously described the crystal structure of another zinc arsenite mineral from Tsumeb: reinerite, $\text{Zn}_3(\text{AsO}_3)_2$ (Ghose et al., 1977), which occurs in the same horizon of the oxidation zone as leiteite. In this paper, we present the details of the crystal structure of leiteite, which contains a novel type of Zn tetrahedral layer flanked by arsenite chains. This structure is distinctly different from that of its chemical analogue, CuAs_2O_4 (trippkeite) and represents a new structure type.

EXPERIMENTAL

The chemical composition of leiteite from Tsumeb is $(\text{Zn}_{0.98}\text{Fe}_{0.02})\text{As}_2\text{O}_4$ (Cesbron et al., 1977). For the purposes of crystal-structure determination, we have assumed the ideal composition ZnAs_2O_4 . The unit-cell dimensions were determined from a small cleavage fragment ($0.11 \times 0.20 \times 0.42$ mm) on an Enraf Nonius X-ray diffractometer from least-squares refinement of 20 reflections measured with $\text{MoK}\alpha$ radiation (Table 1). They are in fairly good agreement with those reported by Cesbron et al. (1977) in $P2_1/a$ orientation. Note that we have used the $P2_1/c$ orientation, which involves an interchange of a and c dimensions. The intensity data were collected with $\text{MoK}\alpha$ radiation and a graphite monochromator using the θ – 2θ scan technique. A total of 1029 reflections were measured within the 2θ range of 60° , out of which 731 reflections had intensities greater than $3\sigma(I_0)$, where $\sigma(I_0)$ is the standard deviation of the mea-

TABLE 1. Crystal data for leiteite, ZnAs_2O_4

Leiteite, ($\text{Zn}_{0.98}\text{Fe}_{0.02}$) As_2O_4 Transparent, colorless cleavage flakes Tsumeb, Namibia Monoclinic, $2/m$ Space group		$P2_1/c$
a (Å)	4.542(1)	
b (Å)	5.022(1)	
c (Å)	17.597(5)	
β ($^\circ$)	90.81(3)	
V (Å ³)	401.346	
Z	4	
μ (cm ⁻¹)	401.35	
d_c (g/cm ³)	4.619	
d_m (g/cm ³)	4.3(1)	
Crystal size (mm)	0.11 × 0.20 × 0.42	
λ (MoK α) (Å)	0.71069	

¹ Structural chemistry of Cu and Zn minerals, part VII.

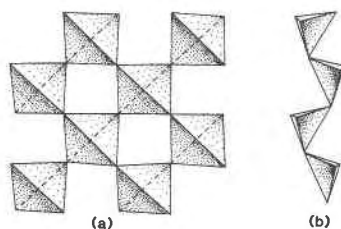


Fig. 1. Building blocks of the leiteite, ZnAs₂O₄ structure: (a) open Zn tetrahedral sheet; (b) arsenite chains.

sured intensity, I_0 . The scan width, $\theta = (A + B \tan \theta)$ with $A = 1.2$, and $B = 0.35$, and the variable horizontal width, $W = A + B \tan \theta$ with $A = 4.0$ and $B = 1.0$, were used for the scans, the maximum scan time being 90 s. The crystal orientation was checked after every 200 reflections. Intensities of three monitor reflections were measured after every 2 h of X-ray exposure time. Because the crystal used was a thin flake, the minimum and maximum transmission factors were 2.99 and 79.43. The intensities were approximately corrected for absorption by the psi-scan method and for Lorentz and polarization factors. However, because of the somewhat bent crystal shape and the high absorption factors, the quality of the intensity data was less than satisfactory.

DETERMINATION AND REFINEMENT OF THE CRYSTAL STRUCTURE

The heavy atom positions (Zn and As) were determined by direct method using the XTAL system of programs (XTAL83). Structure-factor calculations followed by Fourier and difference Fourier syntheses yielded the oxygen atom positions. The positional and isotropic thermal parameters followed by anisotropic ones were refined using a full-matrix least-squares refinement program (ORXFL4). The final R factor for 731 independent reflections is 0.048. The X-ray scattering factors were taken from *International Tables for X-ray Crystallography* and were corrected for anomalous dispersion. The positional and isotropic thermal parameters are listed in Table 2 and anisotropic temperature factors in Table 3. The observed and calculated structure factors are listed in Table 4², and the interatomic bond distances and angles in Table 5.

² To obtain a copy of Table 4, order Document AM-87-337 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit \$5.00 in advance for the microfiche.

TABLE 2. Positional parameters ($\times 10^4$) and equivalent isotropic temperature factors for leiteite, ZnAs₂O₄

Atoms	x	y	z	U_{eq}
As(1)	9920(3)	2136(2)	9056(1)	0.0126(7)
As(2)	4893(3)	7751(2)	9080(1)	0.0120(8)
Zn	2547(3)	4869(3)	7511(1)	0.0139(6)
O(1)	6078(21)	1190(19)	9111(7)	0.0184(50)
O(2)	1065(17)	-1300(17)	9153(6)	0.0132(44)
O(3)	70(23)	2376(17)	8072(8)	0.0224(63)
O(4)	5090(23)	-2616(18)	8108(8)	0.0201(61)

Note: Standard deviations of the last digit are in parentheses.

* $U_{eq} = \frac{1}{3}$ trace of orthogonalized U tensor.

TABLE 3. Anisotropic thermal parameters ($\times 10^4$) of leiteite, ZnAs₂O₄

Atoms	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
As(1)	62(6)	105(5)	209(12)	-8(2)	-2(3)	-7(3)
As(2)	42(6)	86(5)	232(12)	4(2)	2(3)	2(3)
Zn	72(5)	95(6)	251(8)	-3(2)	0(2)	3(3)
O(1)	128(41)	157(40)	266(69)	2(16)	-4(20)	8(20)
O(2)	22(33)	111(36)	264(65)	7(13)	0(17)	14(18)
O(3)	139(46)	62(38)	469(101)	-22(14)	-19(26)	-6(19)
O(4)	84(45)	145(42)	375(95)	-10(15)	11(25)	2(19)

Note: Standard deviations of the last digit are in parentheses.

DESCRIPTION OF THE CRYSTAL STRUCTURE

The building blocks of the leiteite structure are (a) an open Zn tetrahedral layer parallel to (001) and (b) single arsenite chains parallel to [100] (Figs. 1 a, 1b). Each Zn tetrahedral layer is flanked by arsenite chains on either side (Fig. 2). The resulting composite layers are cross-linked through long As-O bonds (Fig. 3). The perfect {001} cleavage breaks through these weak As-O bonds.

The Zn tetrahedral sheet

Each [ZnO₄] tetrahedra shares corners [O(3) and O(4)] with adjacent ones to form a layer with holes, which are distributed in a checkerboard pattern (Fig. 1a). To our knowledge, this is the first report of an open Zn tetrahedral layer of this type. The Zn tetrahedra are fairly regular with an average Zn-O distance of 1.986 Å (avg. Zn-O

TABLE 5. Interatomic distances (Å) and angles* (°) for leiteite, ZnAs₂O₄

The As(1) arsenite group			
As(1)-O(1)	1.812(10)	O(1)-O(2)	2.588(13)
-O(2)	1.810(8)	O(1)-O(3)	2.660(16)
-O(3)	1.738(15)	O(2)-O(3)	2.684(15)
Mean	1.787	Mean	2.644
As(1)-O(1)'	2.837(10)		
-O(2)''	3.218(11)		
-O(2)''	3.341(9)		
The As(2) arsenite group			
As(2)-O(1)	1.810(10)	O(1)-O(2)	2.588(13)
-O(2)	1.809(8)	O(1)-O(4)	2.636(15)
-O(4)	1.725(14)	O(2)-O(4)	2.694(15)
Mean	1.781	Mean	2.639
As(2)-O(1)'	3.339(10)		
-O(1)''	3.264(12)		
-O(2)''	2.845(8)		
The Zn tetrahedron			
Zn-O(3)	1.959(11)	O(3)-O(3)'	3.218(18)
-O(3)'	2.004(10)	O(3)-O(4)	3.045(13)
-O(4)	1.982(11)	O(3)-O(4)'	3.109(13)
-O(4)'	1.999(11)	O(3)''-O(4)	3.378(15)
Mean	1.986	O(3)''-O(4)'	3.384(16)
		O(4)-O(4)'	3.298(18)
		Mean	3.239
As-O-As			
As(1)-O(1)-As(2)	122.3(5)	As-O-Zn and Zn-O-Zn angles	
As(1)-O(2)-As(2)	121.3(5)	As(2)-O(4)-Zn	120.9(5)
As(1)-O(3)-Zn(1)	125.2(6)	As(2)-O(4)-Zn'	123.4(6)
As(1)-O(3)-Zn(1)'	115.8(6)	Zn-O(3)-Zn'	119.0(7)
		Zn-O(4)-Zn'	115.0(7)

Note: Standard deviations are in parentheses.

* For angles, read O(1)-As(1)-O(2), etc.

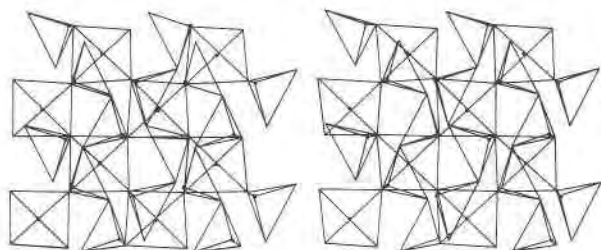


Fig. 2. A composite zinc arsenite layer in leiteite viewed down the *c* axis.

distance in reinerite, 1.961 Å) and the O–Zn–O angles ranging from 102 to 116°.

The arsenite chains

There are two distinct trigonal pyramidal (As^{3+}O_3)³⁻ groups with average As–O distances of 1.79 and 1.78 Å and average O–As–O angles 95.5 and 95.8° for the As(1) and As(2) groups, respectively, which fall within the general range of values surveyed by Hawthorne (1985). These groups alternate and share corners [O(1) and O(2)] to form single trigonal pyramidal chains running parallel to [100] (Figs. 1b and 2). The two distinct As–O–As angles are very close and average 122°. Within each (AsO_3) group, the non-bridging bonds (1.76 and 1.73 Å) are significantly shorter than the average bridging As–O bonds (1.82 and 1.80 Å), as is commonly found in chain silicates. Because of this difference in the As–O bonds, each arsenite group shows an approximate site symmetry $m(C_s)$. The non-bridging oxygen atoms [O(3) and O(4)] show trigonal planar (sp^2) coordination with one As and two Zn.

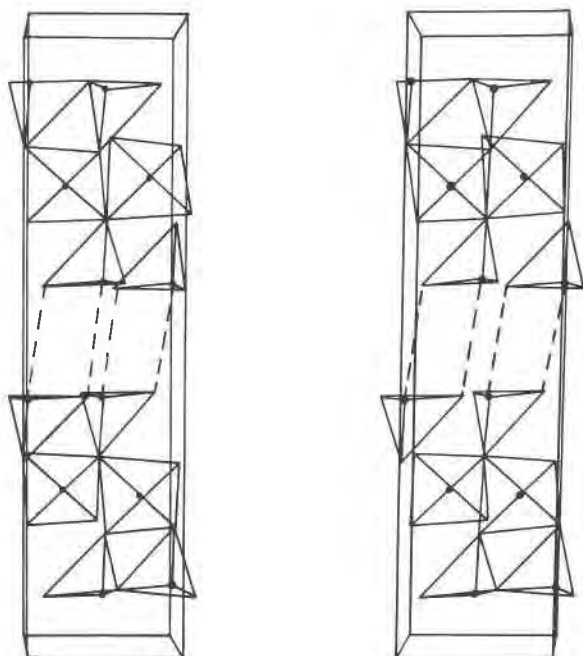


Fig. 3. A view of the leiteite structure down the *b* axis; note the long As–O bonds between layers holding them together.

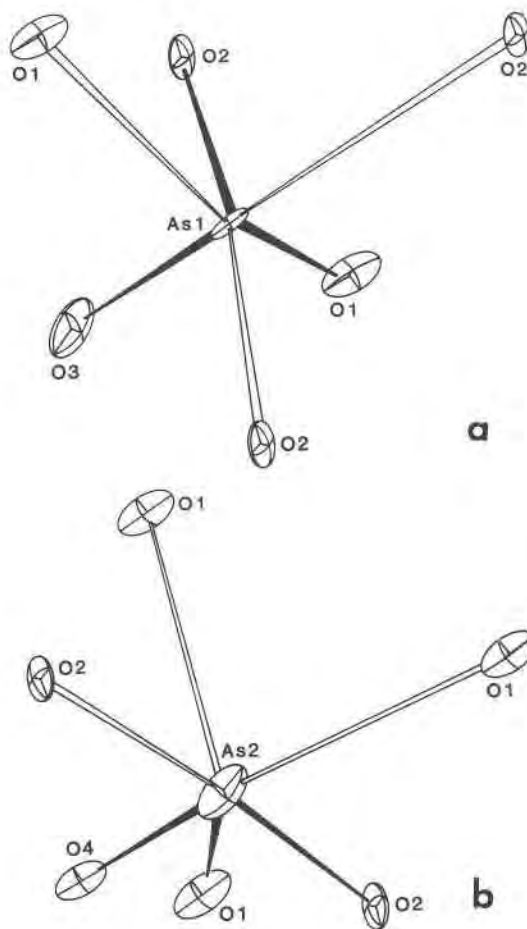


Fig. 4. Configuration of the trigonal pyramidal (AsO_3) groups with long As–O interactions.

All oxygen atoms are formally charge-balanced, if one considers the coordination of As^{3+} to consist of three nearest oxygens at an average distance of 1.79 Å. However, the lone electron pair ($4s^2$) of each As atom is shielded by three further oxygen atoms at distances ranging from 2.84 to 3.34 Å (Figs. 3 and 4, Table 5). These long As–O interactions must be considered as weak bonds, which hold the composite layers together. In this respect, the structures of arsenite compounds are similar to those of iodates, selenates, tellurates, etc., all of which have trigonal pyramidal coordinations and additional weak bonds due to the existence of lone electron pairs. For example, the structure of $\gamma\text{-Cu}(\text{IO}_3)_2$ consists of columns of Cu octahedral chains flanked by iodate groups, which are held together by long I–O bonds (2.6–3.3 Å) (Liminga et al., 1978).

DISCUSSION

Leiteite represents a new structure type with a novel type of open Zn tetrahedral sheet. The only other compound that might have the same structure is BeAs_2O_4 (cf. willemite, ZnSiO_4 , and phenacite, BeSiO_4 , in which both Zn and Be have tetrahedral coordination).

In contrast, trippkeite, CuAs_2O_4 , the chemical analogue of leiteite, is tetragonal and belongs to the structure group of shafarzikite, FeSb_2O_4 , in which the divalent cations (Cu^{2+} , Fe^{2+} , Mn^{2+} , Zn^{2+}) are in regular or distorted octahedral coordination (Zemann, 1951a, 1951b; Chater, 1986). In trippkeite, the Cu^{2+} octahedra share edges to form chains parallel to the fourfold axis, the corners of which are connected to single arsenite chains (Zemann, 1951a; Pertlik, 1975). In trippkeite, the arsenite group has the site symmetry $m(C_s)$; the nonbridging As–O bond length is 1.765(9) Å, and the bridging bond lengths average 1.814(6) Å (Pertlik, 1975). In trippkeite, Pertlik did not consider the long As–O interaction (3.15 Å) as a weak bond, but as a steric effect. In view of the leiteite structure, in which such weak bonds hold the structure together, the long As–O interactions have to be considered as weak but significant chemical bonds.

Finally, as the cation coordination number increases with pressure, a high-pressure phase of ZnAs_2O_4 with the shafarzikite structure is very likely.

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REFERENCES

- Cesbron, F.P., Erd, R.C., Czamanski, G.K., and Vachey, H. (1977) Leiteite: A new mineral from Tsumeb. *Mineralogical Record*, Tsumeb issue, 95–97.
- Chater, R. (1986) Etude des antimonites MeSb_2O_4 à basse température. Thèse, Université Pierre et Marie Curie, Paris VI.
- Ghose, S., Boving, P., LaChapelle, W.A., and Wan, C. (1977) Reinerite, $\text{Zn}_3(\text{AsO}_3)_2$: An arsenite with a novel type of Zn-tetrahedral double chain. *American Mineralogist*, 62, 1129–1134.
- Hawthorne, F.C. (1985) Schneiderhöhnite, $\text{Fe}^{2+}\text{Fe}_3^+\text{As}_3^+\text{O}_{13}$, a densely packed arsenite structure. *Canadian Mineralogist*, 23, 675–679.
- Liminga, R., Booles, S.R., Ghose, S., and Wan, C. (1978) The crystal structure and magnetic behavior of $\gamma\text{-Cu}(\text{IO}_3)_2$. *Acta Crystallographica*, B34, 2398–2402.
- Ottman, J., Nuber, B., and Geier, B.H. (1973) Schneiderhöhnit: Ein natürliches Eisen-Arsen-Oxid aus der tiefen Oxidationszone von Tsumeb. *Neues Jahrbuch für Mineralogie, Monatshefte*, 517–523.
- Pertlik, F. (1975) Verfeinerung der Kristallstruktur von synthetischem Trippkeit, CuAs_2O_4 . *Tschermaks Mineralogische und Petrologische Mitteilungen*, 22, 211–217.
- Zemann, J. (1951a) Formel und Kristallstruktur des Trippkeits. *Tschermaks Mineralogische und Petrologische Mitteilungen*, 2, 417–423.
- (1951b) Formel und Kristallstruktur des Schafarzikits. *Tschermaks Mineralogische und Petrologische Mitteilungen*, 2, 166–175.

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