Asisite, a silicon-bearing lead oxychloride from the Kombat mine, South West Africa (Namibia)*

ROLAND C. ROUSE, DONALD R. PEACOR

Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan 48109, U.S.A.

PETE J. DUNN

Department of Mineral Sciences, Smithsonian Institution, Washington, D.C. 20560, U.S.A.

ALAN J. CRIDDLE, CHRIS J. STANLEY

Department of Mineralogy, British Museum (Natural History), London SW7 5BD, England

JOHN INNES

182 Bielby Road, Kenmore Hills 4069, Brisbane, Queensland, Australia

ABSTRACT

Asisite, ideally $Pb_7SiO_8Cl_2$, is a new species from the Kombat mine in South West Africa (Namibia). Its unit cell is tetragonal, $I4/mmm$, with $a = 3.897(2)$, $c = 22.81(2)$ Å, and $Z = 1$. It occurs as transparent yellow to yellow-green platy crystals having an adamantine luster, a perfect {001} cleavage, and a calculated density of 8.041 g/cm³. Optically, asisite is uniaxial negative with $\omega_{calc} = 2.39$ and $\epsilon'_{calc} = 2.32$ at 590 nm and $r < v$ for the refractive indices and absorption. In reflected light, it possesses characteristic greenish-yellow internal reflections. Luminance values in air (C luminant) are 17.1% (O) and 16.2% (E') and in oil ($N_D = 1.515$) 5.27% (O) and 4.63% (E'). The strongest powder-diffraction lines are $[d_{obs} (Å), I_{obs}, hkl]$ 2.957(100) (015), 2.752(60) (110), 1.627(60) (0.0.14,125), 1.602(50) (208,0.1.13) 3.46(40) (013), and 1.757(40) (1.1.10). The crystal structure, which has been refined to an unweighted residual of 0.075 for all 147 reflections, consists of layers of the tetragonal (red) PbO structure alternating with single sheets of Cl⁻ ions, all arranged in layers normal to c. The Si could not be located experimentally, and its structural role is uncertain. Asisite is a naturally occurring member of a large family of nonstoichiometric Pb–transition element and post–transition element oxyhalides.

INTRODUCTION

During the past 10 years, the Kombat mine in South West Africa (Namibia) has produced a number of rare and interesting minerals. Most of these have been found in manganese silicate lenses associated with, but not in contact with, the sulfide orebody. Some of the assemblages mimic those of the two classic localities Långban, Sweden, and Franklin, New Jersey. Among the new minerals recently described from the lenticular bodies at the Kombat mine are kombatite (Rouse et al., 1986), johninnesite (Dunn et al., 1986), ribbeite (Peacor et al., 1987), and holdawayite (Peacor et al., 1988).

As part of our continuing investigation of the rare minerals found at the Kombat mine, we have studied a specimen composed predominantly of hematophanite, with numerous lead oxychlorides as associated minerals. One of these, a light greenish-yellow to yellow platy mineral, was found to be a new species. We have named this mineral *asisite* for the Asis Farm, where the Kombat mine is located. In the Nama language, *asis* means "drinking

place." The new mineral and the name were approved prior to publication by the Commission on New Minerals and Mineral Names, IMA. Type material is preserved at the Geological Survey of Canada (GSC no. 64565) and the British Museum (Natural History) (BM no. 1986,304).

PHYSICAL AND OPTICAL PROPERTIES

Asisite forms yellow to greenish-yellow, 0.5-mm, platy crystals having a light yellow to white streak, an adamantine luster, and a perfect {001} cleavage. The density could not be measured because of the paucity of material, but the calculated value is 8.041 g/cm³. The hardness (VHN_{50}) is 146–186 for 10 indentations, which are fractured and slightly concave.

In polished sections, asisite is seen to occur as euhedral to subhedral lathlike grains in colorless barite in the interstices of coarsely crystalline hematophanite (Fig. 1A). Less perfect grains are intergrown with other minerals and partially fill fractures and cavities in the hematophanite (Fig. 1B). In this association, asisite is closely associated with another, unnamed, oxychloride phase, which is currently under investigation. Other minerals present in the barite matrix are jacobsite (containing inclusions
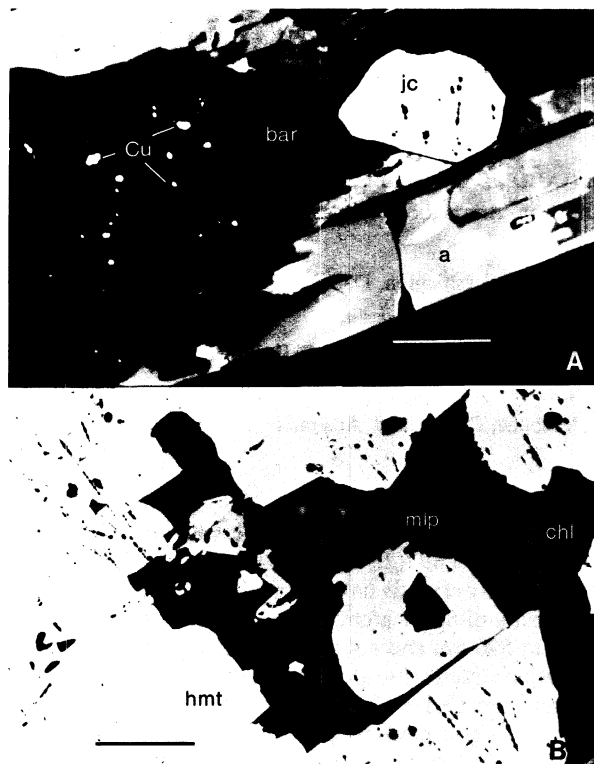
Fig. 1. (A) Reflected-light photomicrograph of a lath of as-isite (a) with abundant internal reflections. In addition to asisite, a subhedral grain of jacobsite (jc) and minute inclusions of native copper occur in the barite (bar) matrix. Plane-polarized light. Oil immersion. Scale bar = 60 μm. (B) Reflected-light photomicrograph of asisite (a) with molybdophyllite (mlp) and chlorite (chl) infilling a cavity in hematophanite (hmt). Plane-polarized light. Scale bar = 90 μm.

of hematite and native copper), blades of molybdo-phyllite, and serrated laths of chlorite. Minute blebs of native copper are also distributed along cleavage traces in the barite and as overgrowths on some of the laths of asisite and molydophyllite.

Because the refractive indices of the mineral are 2.3 or more, its optical properties were determined from pol-ished sections in reflected light. In plane-polarized light, asisite is gray and has a distinctly lower reflectance than the associated white hematophanite. Bireflectance is not perceptible, except at grain boundaries. It is not pleo-chroic. A characteristic feature of the mineral is the abun-dance of internal reflections: uncolored in plane-polar-ized light, these are a brilliant pale greenish yellow between crossed polars. Anisotropy is not noticeable in air and is only weakly so in oil; the rotation tints are gray.

Reflectance measurements were restricted to areas of asisite free from internal reflections, since it is known that reflectances are highly susceptible to such reflections in minerals that are essentially transparent, e.g., ingersonite (Dunn et al., 1988). It was not possible to extract a single crystal of asisite from its matrix for oriented measure-ments. Instead, several randomly oriented grains in the polished section were measured at a few wavelengths, and from these measurements, it was determined that the mineral is uniaxial. Clearly defined extinction positions were not identifiable, so the photometer was used to se-lect orientations of maximum and minimum reflectance at 550 nm that were later used for spectral-scanning mea-surements. For all of the grains, these positions were or-thogonal and consistent with the straight extinction ex-pected from a uniaxial mineral.

Reflectance data for two of the most bireflectant grains (Table 1 and Fig. 2) show that the sign of the bireflectance is negative. The dispersion of R_O and $^{im}R_O$ for both grains is similar, with a monotonic descent from 400 nm to 700 nm. (Here R and ^{im}R are the reflectances in air and im-mersion oil of refractive index N, respectively.) It is also clear from these data that asisite is not pleochroic because there is little difference in the dispersion of R_O and R'_E. This has the consequence that the color values, dominant wavelength, and excitation purity for the two vibration directions (Table 1) are virtually identical. The weak bir-eflectance displayed by asisite is confirmed by the small difference in luminance values for the most bireflectant grain, grain 1, of 0.9% (Table 1).

Refractive indices were calculated from the R and ^{im}R data using the Koenigsberger equations. These showed that the calculated value of the absorption coefficient, k_{calc} was "oscillating" about zero; i.e., the constants derived from the pairs of reflectances were very close to the $k = 0$ boundary of the $R/^{im}R$ "cigar" diagram (Embrey and Criddle, 1978). Inspection of the differences between the measured R and ^{im}R values and those recalculated indi-vidually for R and ^{im}R, assuming $k = 0$, showed that they were significantly within measurement error. Thus, fol-lowing the recommendation of Embrey and Criddle, the refractive indices were recalculated for R and ^{im}R using the simpler reflectance equation for transparent minerals. The largest differences between n for R and ^{im}R of 0.01, or less, were found between 400 nm and 420 nm. For the rest of the spectrum, the differences were smaller than 0.005, i.e., beyond the accuracy attainable from reflec-tance-derived data. The refractive indices in Table 1 are the arithmetic mean values of the indices calculated from R and from ^{im}R (weighting of the mean, as suggested by Embrey and Criddle, is unnecessary in this instance). Al-though the absorption coefficients calculated for this very weakly absorbing mineral are probably erroneous, the trend in the absorption is reliable and $r < v$. The disper-sion of the refractive indices (Fig. 3) show that $r < v$, and that the sign of the birefringence is negative. It is stressed that, even for grain 1, ϵ could not be determined from randomly oriented sections and that the values for ϵ' are the closest approach to the extreme values for the ex-traordinary vibration that could be obtained.

CHEMISTRY AND CRYSTALLOGRAPHY

Asisite was chemically analyzed using electron-micro-probe techniques in the laboratories of both the Smith-

TABLE 1. Reflectance data and color values for two grains of asisite

λ (nm)	1 R_O	1 $^{im}R_O$	1 ω	2 R_O	2 $^{im}R_O$	2 ω	1 R'_E	1 $^{im}R'_E$	1 ϵ'	2 R'_E	2 $^{im}R'_E$	2 ϵ'
400	20.7	7.38	2.68	20.6	7.51	2.68	20.2	7.08	2.64	20.35	7.40	2.66
410	20.2	7.10	2.64	20.2	7.15	2.64	19.6	6.65	2.59	19.9	6.90	2.62
420	19.8	6.85	2.61	19.8	6.82	2.61	19.05	6.27	2.55	19.5	6.52	2.58
430	19.5	6.64	2.59	19.4	6.58	2.58	18.6	5.98	2.52	19.1	6.24	2.55
440	19.15	6.44	2.56	19.0	6.37	2.56	18.2	5.77	2.49	18.7	6.03	2.52
450	18.9	6.28	2.54	18.8	6.19	2.53	17.9	5.60	2.47	18.35	5.85	2.50
460	18.65	6.13	2.53	18.5	6.03	2.52	17.7	5.46	2.45	18.1	5.70	2.48
470	18.4	5.99	2.51	18.3	5.90	2.50	17.45	5.33	2.44	17.8	5.56	2.46
480	18.2	5.86	2.49	18.1	5.78	2.48	17.3	5.21	2.42	17.6	5.43	2.45
490	18.0	5.75	2.48	17.9	5.67	2.47	17.1	5.10	2.41	17.4	5.31	2.43
500	17.9	5.65	2.47	17.7	5.58	2.46	16.9	5.00	2.40	17.2	5.20	2.42
510	17.7	5.57	2.46	17.6	5.48	2.45	16.75	4.92	2.39	17.0	5.10	2.41
520	17.55	5.49	2.44	17.4	5.40	2.44	16.6	4.84	2.38	16.9	5.00	2.39
530	17.4	5.41	2.43	17.3	5.32	2.43	16.5	4.77	2.37	16.7	4.91	2.38
540	17.3	5.34	2.43	17.15	5.25	2.42	16.3	4.70	2.36	16.6	4.83	2.37
550	17.15	5.28	2.42	17.0	5.18	2.41	16.2	4.63	2.35	16.5	4.77	2.37
560	17.0	5.22	2.41	16.9	5.11	2.40	16.1	4.57	2.34	16.35	4.71	2.36
570	16.9	5.16	2.40	16.8	5.06	2.39	16.0	4.51	2.33	16.25	4.65	2.35
580	16.8	5.10	2.40	16.7	5.01	2.39	15.9	4.46	2.33	16.15	4.60	2.34
590	16.75	5.06	2.39	16.7	4.96	2.38	15.8	4.41	2.32	16.1	4.55	2.34
600	16.7	5.02	2.38	16.6	4.92	2.38	15.7	4.37	2.31	16.0	4.51	2.33
610	16.6	4.98	2.38	16.5	4.88	2.37	15.6	4.34	2.31	15.9	4.47	2.33
620	16.5	4.95	2.37	16.5	4.84	2.37	15.55	4.30	2.30	15.8	4.44	2.32
630	16.5	4.91	2.37	16.4	4.81	2.36	15.5	4.26	2.30	15.8	4.41	2.32
640	16.4	4.88	2.37	16.3	4.78	2.36	15.4	4.23	2.29	15.7	4.38	2.31
650	16.3	4.85	2.36	16.3	4.76	2.35	15.35	4.20	2.29	15.7	4.35	2.31
660	16.3	4.81	2.36	16.2	4.73	2.35	15.3	4.17	2.29	15.6	4.33	2.31
670	16.2	4.78	2.35	16.2	4.71	2.35	15.2	4.14	2.28	15.6	4.30	2.30
680	16.2	4.75	2.35	16.1	4.68	2.34	15.2	4.11	2.28	15.5	4.28	2.30
690	16.1	4.73	2.35	16.1	4.66	2.34	15.3	4.08	2.27	15.5	4.26	2.30
700	16.1	4.71	2.34	16.0	4.64	2.34	15.1	4.06	2.27	15.4	4.24	2.29

Color values: Illuminant C (6774 K)

	1	1		2	2		1	1		2	2	
x	0.2997	0.2918		0.2999	0.2912		0.2990	0.2896		0.2986	0.2888	
y	0.3050	0.2955		0.3049	0.2948		0.3042	0.2930		0.3033	0.2916	
Y (%)	17.1	5.27		17.0	5.18		16.2	4.63		16.5	4.78	
λ_d	476	475		476	475		476	475		475	475	
P_e (%)	5.1	9.1		5.0	9.4		5.5	10.2		5.7	10.7	

Note: R and ^{im}R were measured relative to SiC (Zeiss no. 472) with Zeiss oil $N_D = 1.515$ for ^{im}R, using the equipment and procedures described by Criddle et al. (1983). The refractive indices are the arithmetic mean values for n_{calc} from R and ^{im}R, assuming $k = 0$ (Embrey and Criddle, 1978).

sonian Institution and the British Museum (Natural History). The operating conditions, standards, and analytical results are given in Table 2. The empirical formulae, calculated on the basis of 7 Pb per unit cell as indicated by the crystal-structure determination (see below), are $Pb_7Si_{0.77}O_{7.62}Cl_{1.80}$ for sample 4 and $Pb_7Si_{0.55}O_{7.07}Cl_{2.07}$ for the average of samples 1 to 3. These may be idealized as $Pb_7SiO_8Cl_2$.

The unit cell and space group were determined using the Weissenberg, precession, and oscillating-crystal methods. Asisite is tetragonal, space group $I4/mmm$, $I4mm$, $I\bar{4}2m$, or $I422$, with $a = 3.897(2)$, $c = 22.81(2)$ Å, and $Z = 1$. A determination of the crystal structure showed $I4/mmm$ to be the correct choice. The cell volume and axial ratio c/a are 346.3(3) Å³ and 5.853, respectively. The cell parameters were refined by least-squares from the powder X-ray diffraction data (Table 3), which were obtained using a 114.6-mm Gandolfi camera, Cu$K\alpha$ radiation, and NBS Si ($a = 5.43088$ Å) as an internal standard.

STRUCTURE SOLUTION AND REFINEMENT

The intensities of 382 reflections comprising four asymmetric units were obtained from a tabular cleavage fragment of dimensions $0.16 \times 0.12 \times 0.08$ mm using a

TABLE 2. Electron-microprobe analyses of asisite

Sample	PbO	SiO_2	Cl	$-(O \equiv Cl)$	Total
1	93.8	2.0	4.3	1.0	99.1
2	94.2	2.2	4.3	1.0	99.7
	94.1	1.9	4.6	1.0	99.6
3	93.1	2.0	4.5	1.0	98.6
	93.4	2.0	4.3	1.0	98.7
Mean*	93.7	2.0	4.4	1.0	99.1
4	95.4	2.8	3.9	0.9	101.2

Note: Samples 1 to 3: Cambridge Instruments Microscan IX microprobe operated at 20 kV and a beam current of 2.50×10^{-8} A on a Faraday cup. Standards were PbS for Pb, KCl for Cl, and wollastonite for Si. Sample 4: ARL-SEMQ microprobe operated at 15 kV and 0.025 μA. Standards were PbO for Pb, NaCl for Cl, and hornblende for Si. Data were corrected by a modified version of MAGIC-4.
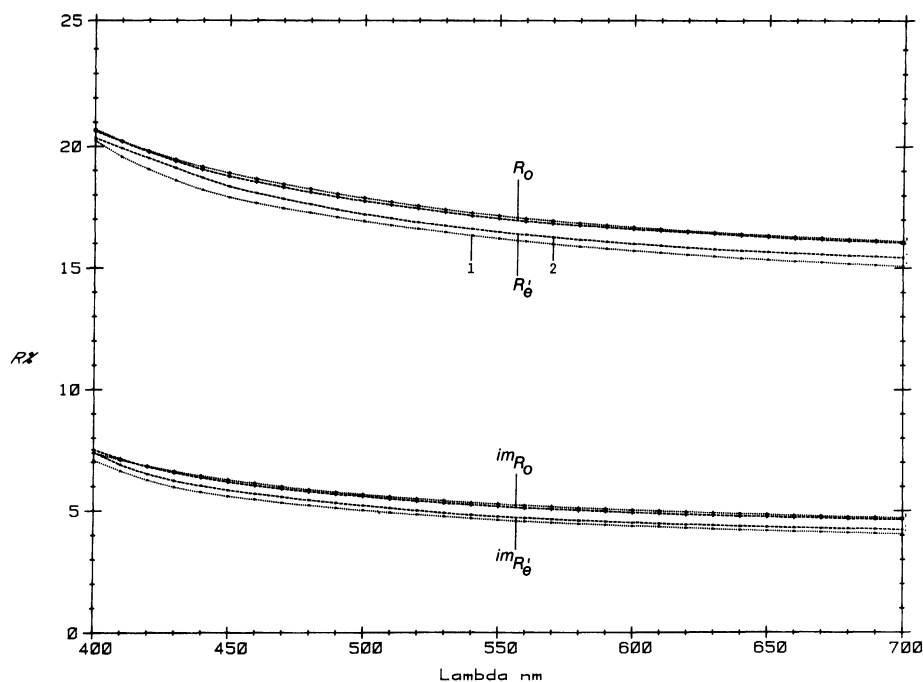* Mean of samples 1 to 3.

Fig. 2. Reflectance R and ^{im}R spectra for two grains of asisite.

computer-controlled Supper-Pace diffractometer system, graphite-monochromatized Mo$K\alpha$ radiation, and Weissenberg equi-inclination geometry. The data were corrected for Lorentz-polarization and absorption effects ($\mu_1 = 858$ cm^{-1}) and symmetry equivalents were averaged by the program SHELX-76 (Sheldrick, 1976) into a final data set of 150 reflections (internal consistency index = 0.12). Of these, nine had $|F|_{obs} < 3\sigma|F|_{obs}$ and were considered to be unobserved.

The locations of the Pb and Cl atoms were determined

TABLE 3. Powder X-ray diffraction data for asisite

I_{obs}	d_{obs}	d_{calc}	hkl	I_{obs}	d_{obs}	d_{calc}	hkl
10	5.67	5.70	004	2	1.567	1.565	1.1.12
30	3.83	3.84	011	30	1.482	1.482	0.2.10
		3.80	006	10	1.419	1.418	0.1.15
40	3.46	3.47	013	20	1.377	1.378	220
100	2.957	2.963	015	1	1.334	1.339	224
10	2.850	2.851	008			1.334	1.2.11
60	2.752	2.756	110	5	1.269	1.269	0.1.17
5	2.495	2.500	017			1.267	0.0.18
20	2.276	2.281	0.0.10	30	1.236	1.241	228
10	2.233	2.231	116			1.236	1.2.13
40	1.984	1.983	118	1	1.179	1.179	2.2.10
30	1.947	1.948	020	5	1.153	1.151	1.1.18
40	1.757	1.757	1.1.10	2	1.148	1.147	0.1.19
10	1.736	1.738	121			1.146	1.2.15
		1.734	026	10	1.132	1.131	138
5	1.700	1.699	123	10	1.084	1.084	1.3.10
60	1.627	1.629	0.0.14	20	1.064	1.063	1.2.17
		1.628	125			1.062	0.2.18
50	1.602	1.609	208	10	1.053	1.052	235
		1.600	0.1.13				

Note: 114.6-mm Gandolfi camera, Cu$K\alpha$ radiation, visually estimated intensities. Indexed with the aid of the structure-factor data.

by direct methods (Main, 1978), and since these positions conformed to the requirements of $I4/mmm$, refinement was continued in this space group. A difference synthesis clearly revealed the oxygen positions, but there was nothing in the difference map that could be attributed with any certainty to the Si atom. Using neutral-atom scattering factors and anomalous dispersion factors (*International Tables for X-Ray Crystallography*, 1974), the reciprocal variances of the $|F|_{obs}$ as weights, and isotropic temperature factors, the refinement converged to a residual of 0.12 for 4 Pb(1) in 4e, 4 Pb(2) in 4e, 2 Cl in 2b, and 8 O in 8g of $I4/mmm$. A refinement of site-occupancy factors indicated full occupancy of all sites except Pb(2), which was 75% occupied; i.e., there are seven rather than eight Pb per unit cell. Including this feature in the refinement and introducing anisotropic temperature factors for Pb and Cl reduced the residual to 0.086. At this point, it was noted that there was poor agreement between $|F|_{obs}$ and $|F|_{calc}$ for the low-angle axial reflections 006, 008, and 0.0.10, all of which suffer from severe absorption effects, having transmission factors of 0.005, 0.008, and 0.010, respectively. Omitting these three reflections from the refinement reduced the residual to 0.075 (unweighted) and 0.058 (weighted) for all 147 reflections including the unobserved ones.

The refinement having evidently converged, a second difference synthesis was calculated in the hope of locating the Si atom, but again this effort failed. It must be assumed that, given the data in hand, this atom is not locatable owing to the inconsiderable scattering power of ca. one Si atom per cell relative to that of the Pb atoms.
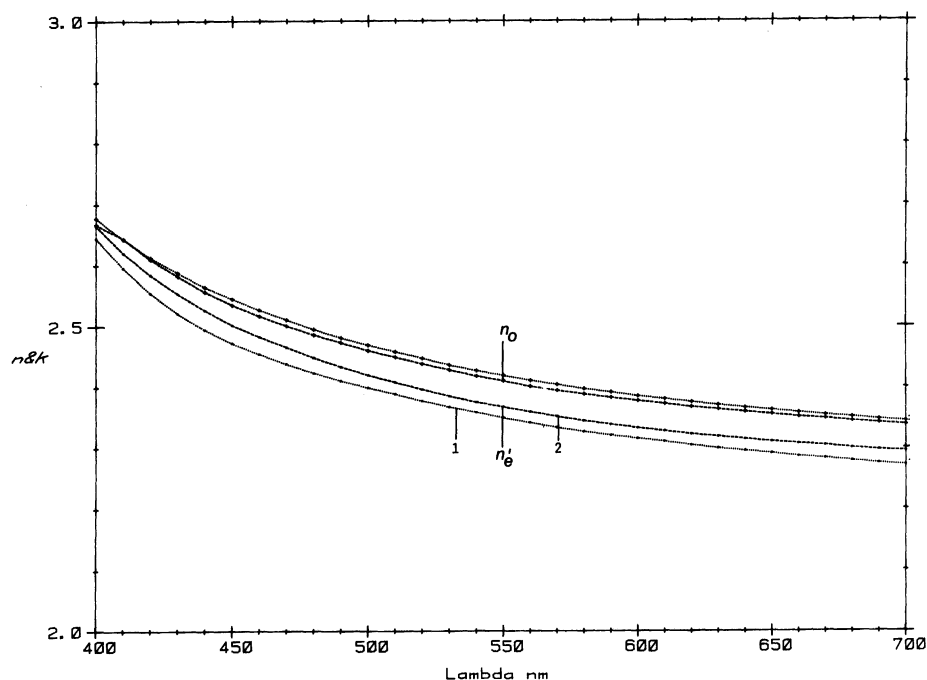
Fig. 3. Refractive indices for two grains of asisite.

An attempt to refine the structure in $I4mm$ symmetry also failed, and since the structure in $I\bar{4}2m$ and $I422$ is identical to that in $I4/mmm$, the latter is confirmed as the space group of asisite.

As a final test of the validity of the model with 7 Pb per cell, the structure was refined with the Pb(2) site fully occupied (8 Pb per cell) and anisotropic temperature factors. The resulting residuals were 0.090 (unweighted) and 0.069 (weighted) for all 147 reflections. Application of Hamilton's R-factor ratio test (Hamilton, 1974) with $\mathfrak{R}_{1,136,0.005} = 1.160$ shows that the improvement in the residual for the 7-Pb model over the 8-Pb model is statistically significant at the 0.005 level. Refined positional and thermal parameters for the 7-Pb model are listed in Table 4, observed and calculated structure factors in Table 5,[1] and selected interatomic distances and angles in Table 6.

The chemical formula produced by the structure refinement is $Pb_7O_8Cl_2$, which has an excess of four negative charges. Although the presence of Si could not be experimentally verified from the diffraction data, its presence is evidently necessary to produce a charge-balanced formula, i.e., $Pb_7SiO_8Cl_2$ with $Z = 1$. The microprobe analyses in Table 1 suggest that the actual amount of Si present is slightly lower than this at 0.6–0.8 Si per unit cell and that the numbers of O and Cl atoms are also

slightly lower than indicated by the formula. The site-occupancy-factor refinements for Cl and O indicated full occupancy, but, in view of the small contributions of these atoms to the intensities, those results are of doubtful reliability. The formula $Pb_7SiO_8Cl_2$ must therefore be regarded as idealized.

STRUCTURE DESCRIPTION

The structure of asisite (Fig. 4) consists of layers of edge-sharing PbO_4 square pyramids like those in tetragonal (red) PbO (Leciejewicz, 1961) alternating along c with sheets of Cl^- ions in the ratio 2:1; i.e., the layer sequence in the unit cell is $Cl-PbO_2Pb-PbO_2Pb-Cl-PbO_2Pb-PbO_2Pb-Cl$, where PbO_2Pb represents a pyramidal layer and Cl a chloride sheet. Alternatively, the structure may be viewed as consisting of layers of the red PbO structure one unit cell thick along c separated by single-thickness chloride sheets at $(x,y,0)$ and $(x,y,\frac{1}{2})$. The "unit cell" of the red PbO–like layer has dimensions $a' = 3.897$

[1] A copy of Table 5 may be ordered as Document AM-88-378 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 4. Positional ($\times 10^4$) and thermal ($\text{Å}^2 \times 10^3$) parameters in asisite

	x	y	z	U_{11}	U_{22}	U_{33}	U_{eq}
Pb(1)	0	0	0838(2)	20(1)	20(1)	7(1)	16
Pb(2)	0	0	3047(2)	20(1)	20(1)	10(2)	17
Cl	0	0	½	60(18)	60(18)	30(22)	50
O	0	½	1440(31)	74(17)			

Note: Esd's are in parentheses. The O atom was refined isotropically and for the remaining atoms $U_{12} = U_{13} = U_{23} = 0$ by symmetry in $I4/mmm$. The Pb(2) site is 75% occupied.
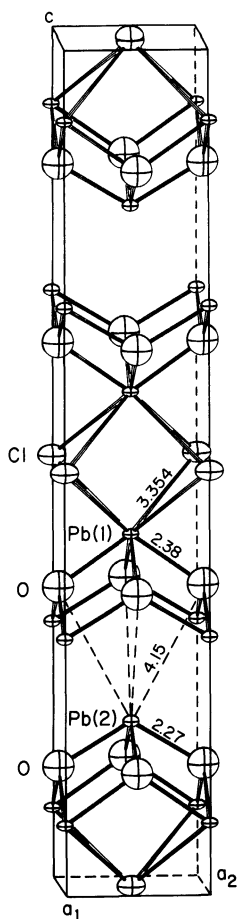
Fig. 4. The unit cell of asisite as drawn by ORTEP-II (Johnson, 1976). The long (nonbonding) Pb(2)-O distances are shown as dashed lines for one of the Pb(2) atoms.

TABLE 6. Selected interatomic distances (Å) and angles (°) in asisite

$Pb(1)O_4Cl_4$ antiprism and $Pb(2)O_4$ pyramid			
Pb(1)-O	2.38(4) × 4	O-Pb(1)-O	71(1) × 4
Pb(1)-Cl	3.354(2) × 4	O-Pb(1)-O	110(3) × 2
		Mean	84
Pb(2)-O	2.27(4) × 4	O-Pb(2)-O	75(1) × 4
Pb(2)-O	4.15(6) × 4	O-Pb(2)-O	118(3) × 2
		Mean	89
OPb_4 tetrahedron			
O-Pb(2)	2.27(4) × 2	Pb(1)-O-Pb(2)	107.2(2) × 4
O-Pb(1)	2.38(4) × 2	Pb(1)-O-Pb(1)	110(3)
Mean	2.32	Pb(2)-O-Pb(2)	118(3)
		Mean	109
Shortest Pb-Pb and anion-anion distances			
Pb(2)-Pb(2)	3.718(7)	O-O	2.755(1)
Pb(1)-Pb(2)	3.749(4)	O-Cl	3.82(6)
Pb(1)-Pb(1)	3.823(8)	Cl-Cl	3.897(1)

Note: Esd's are in parentheses.

and $c' = 5.041$ Å, which are similar to the parameters $a = 3.96$ and $c = 5.01$ Å reported for red PbO by Leciejewicz (1961). The asisite structure is also closely related to the $LiBi_3O_4Cl_2$ or "X_1" structure type (Sillén, 1939, 1942), which differs from asisite in having one rather than two MO_2M layers alternating with single halide layers along c of its tetragonal cell. That is, its layer sequence is $X-MO_2M-X-MO_2X-X$, where M = metal and X = Cl, Br, or I. The structure of another natural lead oxychloride, thorikosite ($(Pb_3Sb_{0.6}As_{0.3})$ $(O_3OH)Cl_2$), has recently been described by Rouse and Dunn (1985) as being of the X_1 type.

Atoms Pb(1) and Pb(2) in asisite are each coordinated to four oxygens to form a PbO_4 pyramid having Pb as its apex and the oxygens as its base. The Pb–O distances are 2.38(4) Å (× 4) and 2.27(4) Å (× 4) for Pb(1) and Pb(2), respectively (Table 6). The former atom has four additional ligands, namely four chlorines at 3.354(2) Å, which together with the four oxygens define a distorted square Archimedean antiprism around Pb(1). In a sense, Pb(2) is also eight-coordinated, as there are four additional oxygens at 4.15(6) Å, completing a tetragonally distorted cube

around Pb(2). However, these are much too distant to be considered chemically bonded. As for the anions, O is surrounded by a moderately distorted tetrahedron of two Pb(1) and two Pb(2), whereas Cl is coordinated by a tetragonal prism of eight Pb(1). The sums of the empirical bond valences (in v.u.) are 2.11 for Pb(1), 2.24 for Pb(2), 0.78 for Cl, and 1.98 for O (Brown and Wu, 1976; Brown, pers. comm.).

A well-known feature of Pb^{2+} is its $6s^2$ electron lone pair, which, when it occupies a hybrid sp_n or sp_nd_m orbital, is an important factor in the stereochemical behavior of this element (Sahl, 1970; Galy et al., 1975; Harrison, 1976). In the case of the PbO_4 group, it is usually assumed that the lone pair is situated on the fourfold axis of the pyramid opposite the oxygens; i.e., the lone pair functions in effect as a fifth ligand coordinated to the central Pb atom (Byström, 1947). In red PbO and its orthorhombic polymorph yellow PbO, the lone pairs are believed to have an additional function, which is to provide the only form of interlayer bonding through van der Waals attractions between lone-pair orbitals in adjacent PbO_2Pb layers (Dickens, 1965; Vigouroux et al., 1982). Within the layers, the Pb–O bonds are essentially covalent, with the O atoms sp^3 hybridized (Dickens, 1965). These interpretations will also apply to the red PbO–like portions of the asisite structure. On the other hand, the Pb-Cl distances of 3.354(2) Å in asisite exceed even the sum of the ionic radii, 3.10 Å for eight-coordinated Pb^{2+} (Shannon, 1976), and must represent only weak electrostatic interactions. Breakage should occur preferentially through these bonds (and the lone pair–lone pair linkages), accounting for the perfect {001} cleavage observed in this mineral.

DISCUSSION

Related compounds

Asisite is chemically and crystallographically related to seven groups of synthetic Pb–transition element and post-transition element oxyhalides described by Aurivillius (1982, 1983). All are composed of tetragonal (red) PbO–

like layers alternating with single sheets of halide ions. They are tetragonal or monoclinic with tetragonal (or pseudotetragonal) subcells of symmetry (or pseudosymmetry) $I4/mmm$ and parameters $a \approx 4$ and $c \approx 23$ Å. The group represented by the general formula $n\text{PbO}\cdot\text{RO}_y\cdot\text{PbX}_2$, where R = Si, Ge, V, As, Mo, W, or Nb and X = Cl, Br, or I, is of particular interest as it includes the compound $6\text{PbO}\cdot\text{SiO}_2\cdot\text{PbCl}_2$ or $\text{Pb}_7\text{SiO}_8\text{Cl}_2$. This may be the synthetic analogue of asisite. The unit cell of asisite corresponds in symmetry and cell dimensions to the subcells of its synthetic relatives. Aurivillius (1982) also reported the existence of a bromine analogue ($6\text{PbO}\cdot\text{SiO}_2\cdot\text{PbBr}_2$), two germanium analogues ($6\text{PbO}\cdot\text{GeO}_2\cdot\text{PbCl}_2$ and $6\text{PbO}\cdot\text{GeO}_2\cdot\text{PbBr}_2$), and the related phases $7\text{PbO}\cdot\text{SiO}_2\cdot\text{PbCl}_2$ and $7\text{PbO}\cdot1.25\text{SiO}_2\cdot0.75\text{SiO}_2$ (which belongs to group $7\text{PbO}\cdot n\text{RO}_y\cdot(2 - n)\text{PbX}_2$). It should be noted, however, that Aurivillius did not chemically analyze his synthesis products and the formulae given in his papers must therefore be viewed with some caution.

Aurivillius determined partial crystal structures for the subcells of four members of group $n\text{PbO}\cdot\text{RO}_y\cdot\text{PbX}_2$ having $n = 7$, R = Nb, Mo, W, or P, and X = Cl or Br and also for two members of group $(7 - n)\text{PbO}\cdot n\text{RO}_y\cdot\text{PbX}_2$ having $n = 0.5$, R = Cr or S, and X = Cl. These structures are the same in all cases and are also identical to the asisite structure reported here, except that in asisite, one of the two four-fold Pb sites [Pb(2)] is only 75% occupied, resulting in seven Pb per cell rather than eight. The same should be true for the $(7 - n)\text{PbO}\cdot n\text{RO}_y\cdot\text{PbX}_2$ compounds, but Aurivillius assumed full occupancy for both Pb sites in his refinements. As with asisite, it was not possible to locate the lighter (R) cation.

Asisite is similar in its chemical composition and X-ray powder pattern to "lorettoite," which has traditionally been considered to be the mineral analogue of synthetic α-$\text{Pb}_7\text{O}_6\text{Cl}_2$. The latter is reported on JCPDS card 6-0393 to be orthorhombic-pseudotetragonal, probably *Fmmm*, with $a = 5.49$, $b = 22.9$, and $c = 5.50$ Å. This cell corresponds metrically to the body-centered tetragonal cell of asisite reoriented so that $a_O = a_T\sqrt{2}$, $c_O = b_T\sqrt{2}$, and $b_O = c_T$ and with the concomitant change from body-centered to face-centered lattice type; i.e., the reported cell of lorettoite is just an orthorhombic supercell of asisite. However, Aurivillius (1983) was unable to synthesize α-$\text{Pb}_7\text{O}_6\text{Cl}_2$ and expressed the opinion that it is, in fact, another lead oxychloride containing minor (but essential) oxides "RO_y" absorbed from the crucible or other container during synthesis. In addition, White (1979) reexamined the type specimen of lorettoite and found it to be of synthetic origin, thereby discrediting it as a mineral species. White also reviewed the evidence concerning the material known as "chubutite" (which has been regarded as being identical to lorettoite) but could arrive at no firm conclusion concerning its nature and relationship to lorettoite, except that its validity as a natural species was highly doubtful.

The original chemical analysis of lorettoite, here recalculated, yielded PbO 96.6, Cl 4.38, less O $\equiv$ Cl 0.98, sum

100 wt% (Wells and Larsen, 1916). We have re-analyzed the type specimen using the electron microprobe, and although its bulk composition agrees with that reported by Wells and Larsen, the microprobe shows it to be an intimate mixture of very fine-grained Si- and Al-bearing Pb oxychlorides.

Structural role of Si

The failure to directly locate Si by structure analysis calls into question its apparently essential role in asisite. Even though electron-microprobe analyses consistently and unambiguously showed its presence, there was still a chance that it was due to contamination by another phase. A sample was therefore carefully examined by energy-dispersive analysis and backscattered-electron imaging using a scanning electron microscope. The ratios of peak heights of Pb, Cl, and Si were constant throughout the specimen. It is possible, but unlikely, that Si exists in homogeneously distributed, submicrometer-sized grains of a Si-rich phase; however, the amount required should give rise to diffraction of X-rays. No such diffraction was detected. The presence of a homogenous Si distribution in the chemical analyses, the analogy to the occurrence of Si in synthetic phases (albeit inadequately characterized), and the results of the structure analysis, which imply a formula requiring an additional cation for charge balance, collectively imply the presence of essential Si.

The presence of a number of vacancies on a Pb site that matches (within error) the number of Si per cell implies a direct relationship between these parameters. The X-ray scattering power of Si is so much smaller than that of Pb that direct substitution of Si for Pb would still give rise to the determined occupancies within error. More important, the coordination of Pb is incompatible with a reasonable coordination (presumably tetrahedral) for substituted Si. Substitution of Si would require a significant local perturbation of the structure with rearrangement of oxygen ligands. No evidence for this was detected in difference–electron density syntheses. Nevertheless, local rearrangements of similar magnitude are apparently required for Si at all other potential sites.

We conclude, therefore, that Si is an essential component of the structure. Even though its presence must be associated with significant local changes in the structure, these changes must be disordered relative to the average structure that has been characterized in this structure analysis, as no superstructure of lower symmetry is observed. The average structure is determined by the Pb atoms, which account for over 80% of the scattering power in the unit cell. The local perturbations due to Si and its coordinating anions are exceedingly small when averaged over several cells and are not detectable with single-crystal X-ray methods.

REFERENCES CITED

Aurivillius, B. (1982) On the crystal structure of a number of non-stoichiometric mixed lead oxide halides composed of PbO-like blocks and single halogen layers. Chemica Scripta, 19, 97–107.

———(1983) On the crystal structure of some non-stoichiometric mixed lead oxide halides and their relation to the minerals "lorettoite" and sunduisite. Chemica Scripta, 22, 5–11.

Brown, I.D., and Wu, K.K. (1976) Empirical parameters for calculating cation-oxygen bond valences. Acta Crystallographica, B32, 1957–1959.

Byström, A. (1947) On the stereochemistry of lead and some metals with similar atomic structure. Archiv för Kemi, Mineralogi och Geologi, 25A, no. 13.

Criddle, A.J., Stanley, C.J., Chisholm, J.E., and Fejer, E.F. (1983) Henryite, a new copper-silver telluride from Bisbee, Arizona. Bulletin de Minéralogie, 106, 511–517.

Dickens, B. (1965) The bonding in red PbO. Journal of Inorganic and Nuclear Chemistry, 27, 1503–1507.

Dunn, P.J., Peacor, D.R., Su, S.-C., Nelen, J.A., and von Knorring, O. (1986) Johninnesite, a new sodium manganese arsenosilicate from the Kombat mine, Namibia. Mineralogical Magazine, 50, 667–670.

Dunn, P.J., Peacor, D.R., Criddle, A.J., and Stanley, C.J. (1988) Ingersonite, a new calcium-manganese antimonate related to pyrochlore, from Långban, Sweden. American Mineralogist, 73, 405–412.

Embrey, P.G., and Criddle, A.J. (1978) Error problems in the two-media method of deriving the optical constants n and k from measured reflectances. American Mineralogist, 63, 853–862.

Galy, J., Meunier, G., Andersson, S., and Åstrom, A. (1975) Stéréochemie des éléments comportant des paires non liées: Ge(II), As(III), Se(IV), Br(V), Sn(II), Sb(III), Te(IV), I(V), Xe(VI), Tl(I), Pb(II), et Bi(III) (oxydes, fluorures et oxyfluorures). Journal of Solid State Chemistry, 13, 142–159.

Hamilton, W.C. (1974) Tests for statistical significance. In J.A. Ibers and W.C. Hamilton, Eds., International tables for X-ray crystallography, vol. IV, p. 285–420. Kynoch Press, Birmingham, England.

Harrison, P.G. (1976) The structural chemistry of bivalent germanium, tin and lead. Coordination Chemistry Reviews, 20, 1–36.

International tables for x-Ray crystallography. (1974) J.A. Ibers and W.C. Hamilton, Eds., vol. IV, p. 99–101, 149–150. Kynoch Press, Birmingham, England.

Johnson, C.K. (1976) ORTEP-II: A Fortran thermal ellipsoid program for crystal structure illustrations. ORNL-5138, Oak Ridge National Laboratory.

Leciejewicz, J. (1961) On the crystal structure of tetragonal (red) PbO. Acta Crystallographica, 14, 1304.

Main, P. (1978) MULTAN 78. A system of computer programmes for the automatic solution of crystal structures. University of York, York, England.

Peacor, D.R., Dunn, P.J., Su, S.-C., and Innes, J. (1987) Ribbeite, a polymorph of alleghanyite and member of the leucophoenicite group from the Kombat mine, Namibia. American Mineralogist, 72, 213–216.

Peacor, D.R., Essene, E.J., Rouse, R.C., Dunn, P.J., Nelen, J.A., Grice, J.D., Innes, J., and von Knorring, O. (1988) Holdawayite, a new manganese hydroxyl-carbonate from the Kombat mine, Namibia. American Mineralogist, 73, 632–636.

Rouse, R.C., and Dunn, P.J. (1985) The structure of thorikosite, a naturally occurring member of the bismuth oxyhalide group. Journal of Solid State Chemistry, 57, 389–395.

Rouse, R.C., Dunn, P.J., and Innes, J. (1986) Kombatite, the vanadium analogue of sahlinite, from the Kombat mine, South West Africa. Neues Jahrbuch für Mineralogie Monatshefte, 519–522.

Sahl, K. (1970) Lead. Crystal chemistry. In K.H. Wedepohl, Ed., Handbook of geochemistry, vol. II/5, p. 82A1–82A6. Springer-Verlag, Berlin.

Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallographica, A32, 751–767.

Sheldrick, G. (1976) SHELX-76. Programme for crystal structure determination. University of Cambridge, England.

Sillén, L.G. (1939) Röntgenuntersuchung von LiBi₃O₄Cl₂ und verwandten Stoffen. Zeitschrift für Anorganische und Allgemeine Chemie, 242, 41–46.

———(1942) Über eine Familie von Oxyhalogeniden. Die Naturwissenschaften, 22, 318–324.

Vigouroux, J.P., Calvarin, G., and Husson, E. (1982) Etude vibrationnelle des oxydes PbO α et PbO β: Interpretation en relation avec la dilatation thermique. Journal of Solid State Chemistry, 45, 343–352.

Wells, R.C., and Larsen, E.S. (1916) Lorettoite, a new mineral. Journal of the Washington Academy of Sciences, 6, 669–672.

White, J.S. (1979) Lorettoite discredited and chubutite reviewed. American Mineralogist, 64, 1303–1305.