AM-85-260

American Mineralogist, Volume 70, pages 165–170, 1985

Crystal structure refinement of an arsenic-bearing argentian tetrahedrite

MARY L. JOHNSON

Department of Chemistry and Biochemistry
University of California, Los Angeles, California 90024

AND CHARLES W. BURNHAM

Department of Geological Sciences
Harvard University, Cambridge, Massachusetts 02138

Abstract

The crystal structure of a synthetic tetrahedrite, composition $Cu_{8.44}Ag_{2.12}Fe_{1.44}Sb_{2.70}As_{1.30}S_{13}$, has been refined using full-matrix least-squares methods to a weighted disagreement index of 4.6% for 169 independent observed diffractions. The effects of the substitutions of Ag for Cu and As for Sb on the distances and bond-angles in the tetrahedrite structure are separable, as has been noted previously for substitutional effects on the tetrahedrite lattice parameter. The presence of arsenic in natural tetrahedrite appears to restrict the amount of silver present. This restriction can be rationalized crystallographically.

Introduction

The tetrahedrite group of minerals consists of tetrahedrite, $(Cu,Fe)_{12}Sb_4S_{13}$; tennantite, $(Cu,Fe)_{12}As_4S_{13}$; freibergite, $(Ag,Cu,Fe)_{12}(Sb,As)_4S_{13}$; goldfieldite, $Cu_{12}(Sb,As)_4(Te,S)_{13}$; and hakite, $(Cu,Hg,Ag)_{12}Sb_4(Se,S)_{13}$ (Fleischer, 1980). These minerals have body-centered cubic structures, space group $I\bar{4}3m$. The currently-accepted structure for minerals in the tetrahedrite group was proposed by Pauling and Neuman (1934) in their examination of tennantite. More recent structural determinations have confirmed this general structure for a number of these minerals—tetrahedrite (Wuensch, 1964), mercurian tetrahedrite (Kalbskopf, 1971; Kaplunnik et al., 1980), argentian tetrahedrite (Kalbskopf, 1972), goldfieldite (Kalbskopf, 1974), and copper-rich and copper-poor synthetic tetrahedrites (Makovicky and Skinner, 1979). The structure of tennantite was reexamined by Wuensch et al. (1966).

Although the effects of single substitutions on the tetrahedrite structure have been reported (arsenic for antimony by Wuensch et al. (1966); silver for copper by Kalbskopf (1972)), there have been no previous crystallographic studies of multiply-substituted tetrahedrites. Charlat and Levy (1975) determined that the effects of substitutions on the unit-cell parameter of tetrahedrite are independent for Ag substitution for Cu, Cu^{2+} substitution for Fe, Hg substitution for Fe, and As substitution for Sb. However, the same authors have noted a negative correlation between silver and arsenic in natural tetrahedrites from world-wide occurrences (Charlat and Levy, 1974, Fig. 6), which suggests possible interaction between Ag/Cu and As/Sb substitutions. More recent electron microprobe analyses (Fig. 1) confirm the trend seen by Charlat and Levy; however, many of the newer analyses are richer in silver for their antimony content than previously noted.

In order to determine whether a crystallographic control could account for the observed silver-arsenic antipathy, we determined the crystal structure of a (Ag, As)-bearing synthetic tetrahedrite.

Crystal structure refinement: experimental

Starting material

Tetrahedrite was synthesized using a flux technique modified from Boorman (1967). Starting material was a homogeneous glass made as described by Maske and Skinner (1971) from reagent Cu, S (Maske and Skinner, 1971), Ag (American Smelting and Refining Co., catalog #65844, Lot 1, 99.99+% pure), Fe sponge (United Mineral and Chemical Corporation, Lot 15890, 99.999% pure, reduced under hydrogen gas as described in Tatsuka and Morimoto (1977)), and 2:1 antimony-arsenic alloy (Laboratory of B. J. Skinner, Yale University, batch labeled "CTB 229 Sb/As 67/33"). The charge contained Ag, Fe, Cu, Sb, As, and S in the ratio 6.70:1.00:6.80:4.44:2.19:6.42 by weight.

The glass was then ground under acetone and mixed with an approximately equal volume of eutectic KCl/LiCl flux at 110°C, baked in silica-glass capsules at 400°C for four periods of one week each, with transfer into new capsules at 110°C between successive bakings. The charge was quenched in cold water,

0003–004X/85/0102–0165$02.00

TABLE 2

TNAG2MLJ

H	J	L	F(OBS)	F(CALC)	A(CALC)	B(CALC)
0	0	2	87.266	72.388	-72.282	-3.911
0	0	4	536.215	507.920	506.946	31.431
0	0	8	489.061	471.937	471.353	23.485
0	0	14	64.569	73.463	73.178	6.469
0	0	16	64.422	57.246	57.015	5.136
0	1	7	114.659	96.036	-95.918	-4.760
0	1	5	149.536	147.086	147.005	4.884
0	1	3	38.301	46.379	46.366	-1.115
0	2	2	149.536	140.102	139.999	5.372
0	2	4	82.130	69.104	-68.965	-4.392
0	2	6	103.310	105.506	105.366	5.430
0	2	8	54.981	63.818	-63.698	-3.908
0	2	12	55.079	7.301	-7.287	-0.451
0	2	20	69.754	32.816	32.554	4.136
0	3	13	62.466	56.444	-56.176	-5.498
0	3	11	51.753	19.408	-19.390	-0.841
0	3	5	56.645	35.106	-35.051	-1.950
0	3	3	97.147	102.134	-102.067	-3.708
0	4	4	748.901	755.571	754.912	31.559
0	4	8	134.616	161.527	160.628	17.019
0	4	10	49.698	55.853	55.736	3.619
0	4	12	168.368	160.939	160.554	11.125
0	5	11	98.027	95.738	-95.453	-7.381
0	5	9	86.043	94.786	94.607	5.829
0	5	7	72.591	53.809	-53.521	-5.558
0	5	5	133.638	142.259	142.071	7.313
0	6	6	73.961	103.946	103.812	5.282
0	6	18	63.884	26.800	-26.637	-2.949
0	7	11	71.711	57.032	56.937	3.283
0	7	9	110.012	103.894	-103.574	-8.144
0	8	8	232.057	231.123	230.666	14.529
0	8	16	71.368	42.041	41.812	4.384
0	9	13	60.069	52.290	52.066	4.841
0	9	11	64.911	79.493	-79.014	-8.714
0	9	9	92.695	84.417	84.176	6.371
0	10	10	57.770	27.823	27.793	1.297
0	10	12	58.895	29.714	29.549	3.124
0	11	13	84.331	79.915	-79.422	-8.863
0	12	12	63.591	61.956	61.670	5.949
0	13	13	67.406	45.811	45.586	4.537
1	8	11	65.594	46.225	-19.930	41.708
1	7	8	109.131	107.570	-78.740	73.289
1	7	12	84.184	83.625	-23.315	80.309
1	6	9	102.283	101.680	49.584	88.771
1	6	7	72.298	74.726	34.833	-66.111
1	5	6	114.365	114.398	57.824	98.708
1	5	8	96.951	102.825	16.597	-101.476

TABLE 2 (cont.)

H	J	L	F(OBS)	F(CALC)	A(CALC)	B(CALC)
1	5	10	139.753	146.162	56.753	134.694
1	5	12	67.797	77.502	-9.651	-76.899
1	4	11	63.297	66.268	-64.461	15.368
1	4	9	48.133	42.698	30.532	-29.843
1	4	7	783.695	84.669	-35.928	76.668
1	4	5	68.629	83.338	54.420	-63.116
1	3	4	127.572	127.660	-83.575	96.501
1	3	6	92.598	97.435	29.705	-92.796
1	3	8	162.596	155.444	-43.071	149.358
1	3	10	143.030	137.686	59.468	-124.182
1	3	12	104.729	106.514	-51.706	93.122
1	3	14	68.238	79.580	19.872	-77.059
1	3	16	74.401	72.486	-15.108	70.894
1	3	18	63.493	47.847	15.705	-45.196
1	2	5	134.861	138.699	87.056	107.975
1	2	3	89.858	93.926	-12.335	-93.113
1	1	2	63.297	45.285	39.790	21.621
1	1	4	151.297	148.092	88.167	-118.987
1	1	6	214.202	205.640	80.589	189.192
1	1	8	132.024	134.040	-30.963	-130.415
1	1	10	110.207	132.846	31.269	129.113
1	1	12	117.643	124.370	-8.707	-124.065
1	1	14	107.517	106.265	25.146	103.247
1	1	16	72.493	64.759	-6.006	-64.480
2	2	2	783.583	821.050	-782.903	24.358
2	2	4	70.781	63.219	62.366	-10.347
2	2	6	466.608	471.059	-438.542	-171.981
2	2	10	192.973	202.824	-184.226	84.843
2	2	14	73.472	70.976	-58.706	-39.890
2	3	11	50.824	34.798	-34.206	6.390
2	3	9	89.125	94.627	85.321	-40.922
2	3	7	101.207	96.545	-90.970	32.334
2	3	5	76.260	72.617	72.578	-2.366
2	3	3	120.577	123.899	-122.680	17.336
2	4	4	74.059	86.556	-86.194	7.917
2	4	6	47.840	70.077	69.863	5.472
2	4	8	53.465	55.852	-55.533	-5.965
2	5	11	55.830	80.089	79.237	11.649
2	5	9	53.172	46.041	-1.033	46.030
2	5	7	81.983	89.813	85.234	-28.309
2	5	5	54.639	43.287	41.434	12.531
2	6	6	321.279	312.310	-283.950	130.039
2	6	14	71.808	64.898	-52.011	38.815
2	7	13	58.308	77.381	77.316	-3.160
2	7	9	78.119	94.741	93.221	16.903
2	7	7	107.957	99.093	-98.112	13.908
2	10	10	103.555	94.741	-76.946	55.274

TABLE 2 (cont.)

H	J	L	F(OBS)	F(CALC)	A(CALC)	B(CALC)
2	11	13	74.401	74.187	72.485	15.802
2	11	11	72.689	56.692	-56.665	1.757
2	13	13	63.297	40.865	-40.082	-7.950
2	14	14	68.482	31.414	-25.747	17.999
3	9	10	71.466	79.580	53.560	-58.859
3	8	9	54.639	52.826	-40.785	33.574
3	7	8	109.571	105.059	-8.592	-104.707
3	7	10	75.233	64.631	-4.807	64.452
3	7	12	57.525	64.153	-28.892	-57.279
3	6	11	53.758	28.090	-18.224	21.375
3	6	7	74.646	69.798	-42.333	55.495
3	5	6	141.562	147.676	95.243	-112.858
3	5	8	93.429	96.240	-65.592	73.135
3	5	10	67.064	89.597	46.344	-76.681
3	5	12	80.613	86.006	-28.726	81.068
3	5	14	81.885	78.427	35.147	-70.111
3	5	16	60.851	44.997	-16.649	41.804
3	4	9	55.617	61.659	-60.573	11.523
3	4	7	90.250	90.280	-62.901	-64.761
3	4	5	62.368	65.305	-10.569	64.444
3	3	4	137.600	135.452	-16.490	-134.445
3	3	6	116.811	119.059	-30.849	114.994
3	3	8	139.655	147.993	-75.024	-127.567
3	3	10	83.548	98.578	-1.341	98.569
3	3	12	108.544	120.561	-11.902	-119.972
3	3	14	77.287	77.061	10.689	76.316
3	3	20	64.369	31.996	-0.809	-31.985
4	4	4	259.107	282.027	281.151	-22.207
4	4	8	312.866	325.158	324.525	-20.267
4	4	14	59.090	58.723	56.470	16.111
4	5	19	66.428	75.869	69.871	-29.616
4	5	7	108.593	104.819	-101.804	24.959
4	5	5	127.572	128.315	115.857	-55.152
4	6	6	46.861	49.348	44.888	-20.502
4	7	13	70.145	75.687	-74.624	-12.643
4	7	9	53.074	75.080	-74.798	6.501
4	7	7	53.416	59.788	32.799	-49.988
4	8	8	51.557	78.691	65.097	-44.211
4	8	12	99.642	100.928	98.200	-23.310
4	9	13	62.123	46.597	46.512	-2.814
4	9	11	81.494	88.754	-88.144	-10.387
4	9	9	55.960	67.929	66.321	-14.691
5	8	11	56.596	61.890	-61.292	8.587
5	8	9	56.791	49.611	31.623	-38.226
5	7	8	71.124	78.855	-49.084	61.716
5	7	10	77.678	79.998	59.645	-53.312
5	5	19	63.786	32.204	26.920	17.675

TABLE 2 (cont.)

H	J	L	F(OSB)	F(CALC)	A(CALC)	B(CALC)
5	6	11	62.466	71.484	71.177	-6.616
5	5	6	135.839	140.820	59.202	127.771
5	5	8	63.591	82.116	35.436	-74.076
5	5	10	75.966	75.182	16.118	73.434
5	5	12	74.303	65.885	6.029	-65.609
6	6	6	189.598	185.096	-180.049	-42.930
6	6	8	49.014	19.342	8.053	-17.587
6	6	10	137.726	141.048	-103.176	96.173
6	6	14	61.683	37.250	-37.121	3.093
6	7	9	78.265	89.129	85.217	-26.117
6	7	7	88.244	74.604	-59.650	44.807
6	9	11	71.319	69.194	68.147	11.990
6	10	10	59.090	51.662	-30.481	10.985
6	10	14	72.347	60.026	-36.213	47.873
6	11	13	60.949	59.319	58.843	7.498
6	11	11	60.411	39.824	-39.709	3.033
6	12	12	61.976	31.249	4.754	30.885
6	13	13	63.444	23.302	-23.172	-2.452
7	8	9	73.765	71.011	-70.576	7.850
7	7	12	57.036	49.469	-0.219	-49.468
8	8	8	138.676	137.274	129.702	-44.962
8	11	11	60.753	12.608	12.045	3.724
8	12	12	71.075	56.367	44.966	-33.989
10	10	10	87.902	82.560	-45.842	68.663
10	10	14	63.737	33.588	-20.768	26.398

TABLE 5:

Ellipsoids and Errors, TNAG2MLJ

	Parameter	Value	Error
Ellipsoid of vibration for Cu(1) (½½0)			
	Equivalent isotropic B	1.20	0.20
Axis 1	RMS amplitude	0.095	0.011Å
	Angle with the A axis	90.00	0.00°
	Angle with the B axis	90.00	0.00°
	Angle with the C axis	0.00	0.00°
Axis 2	RMS amplitude	0.095	0.011Å
	Angle with the A axis	90.00	0.00°
	Angle with the B axis	0.00	0.00°
	Angle with the C axis	90.00	0.00°
Axis 3	RMS amplitude	0.166	0.013Å
	Angle with the A axis	0.00	0.00°
	Angle with the B axis	90.00	0.00°
	Angle with the C axis	90.00	0.00°
Ellipsoid of vibration for Cu(2) (x00)			
	Equivalent isotropic B	5.11	0.80
Axis 1	RMS amplitude	0.174	0.015Å
	Angle with the A axis	90.00	0.00°
	Angle with the B axis	45.00	0.00°
	Angle with the C axis	45.00	0.00°
Axis 2	RMS amplitude	0.238	0.008Å
	Angle with the A axis	180.00	0.00°
	Angle with the B axis	90.00	0.00°
	Angle with the C axis	90.00	0.00°
Axis 3	RMS amplitude	0.327	0.023Å
	Angle with the A axis	90.00	0.00°
	Angle with the B axis	135.00	0.00°
	Angle with the C axis	45.00	0.00°

TABLE 5 (CONT.):

	Parameter	Value	Error
Ellipsoid of vibration for Sb(1) (xxx)			
	Equivalent isotropic B	1.00	0.16
Axis 1	RMS amplitude	0.091	0.011A
	Angle with the A axis	54.74	0.00°
	Angle with the B axis	54.74	0.00°
	Angle with the C axis	54.74	0.00°
Axis 2	RMS amplitude	0.122	0.007A
	Angle with the A axis	66.05	*
	Angle with the B axis	66.05	*
	Angle with the C axis	144.96	*
Axis 3	RMS amplitude	0.122	0.007A
	Angle with the A axis	66.05	*
	Angle with the B axis	144.96	*
	Angle with the C axis	66.05	*
Ellipsoid of vibration for S(1) (xxz)			
	Equivalent isotropic B	2.52	0.40
Axis 1	RMS amplitude	0.141	0.015A
	Angle with the A axis	79.84	*
	Angle with the B axis	79.84	*
	Angle with the C axis	14.44	*
Axis 2	RMS amplitude	0.141	0.015A
	Angle with the A axis	100.18	*
	Angle with the B axis	100.18	*
	Angle with the C axis	165.53	*
Axis 3	RMS amplitude	0.237	0.020A
	Angle with the A axis	133.22	0.04°
	Angle with the B axis	133.22	0.04°
	Angle with the C axis	75.55	4.86°
Ellipsoid of vibration for S(2) (000)			
	Isotropic B	5.20	0.70
	RMS amplitude	0.26	0.09A

* Error meaningless