Crystal chemistry of the system As-Sb-S (I): Synthesis of wakabayashilite and synthetic study on the solid solutions in the As_2S_3 - Sb_2S_3 system

Izumi NAKAI, Hitoshi YOKOI*, and Kozo NAGASHIMA**

Department of Chemistry, The University of Tsukuba, Ibaraki, 305, Japan

Abstract

Stibnite, getchellite, wakabayashilite, and orpiment were synthesized by hydrothermal treatment of $(\text{Sb}_{1-x}, \text{As}_x)_2\text{S}_3$ glass ($0 < x < 1$) with solvent of Na_2S aqueous solution at $250 - 400^\circ\text{C}$, and 1000 kg/cm^2 pressure to determine their formation conditions and solid solution ranges. The As-Sb substitution occurred up to $x=0.24$ in the above formula for stibnite, $0.54 - 0.64$ for getchellite, $0.84 - 0.86$ for wakabayashilite, and up to 0.83 for orpiment, respectively. Substitution of As for Sb in stibnite caused the elongation of the a axis and shortening of the b and c axes of the unit cell, and finally the a and b lengths became equal at about 25 mol% As. Wakabayashilite, synthesized for the first time in the present experiment, does not have the superstructure known for natural materials and its powder diffraction data are presented.

Introduction

Arsenic and antimony have different crystallochemical behavior in their sulfides, though they are chemically analogous elements. So far, four minerals are known near the As_2S_3 - Sb_2S_3 join, i.e. orpiment As_2S_3 , wakabayashilite $(\text{As,Sb})_2\text{S}_3$, getchellite AsSbS_3 , and stibnite Sb_2S_3 , and their crystal structures differ one from the other. In contrast to the common occurrences of the end members, the occurrences of getchellite and wakabayashilite are rare. Therefore, synthetic studies are useful to estimate formation conditions of the latter two phases in nature. This paper reports the synthetic conditions of each phase including the first synthesis of wakabayashilite.

Preliminary synthetic studies by Dickson *et al.* (1975) on the system As-Sb-S demonstrated the existence of incomplete solid solution series between stibnite and orpiment, together with the result of semiquantitative spectrographic analyses of stibnite and orpiment from Nevada and Utah: stibnite max. 70,000 ppm As an orpiment max. 15,000 ppm Sb. Here we present new information about the solid solution ranges of synthetic stibnite, getchellite, wakabayashilite, and orpiment. A series

* Present address: NGK SPARK PLUG Co., Ltd., 2808 Iwasaki, Komaki-shi, Aichi, 485

** Deceased on January 6, 1985.

of our study on the system As-Sb-S is made not only to contribute to the mineralogy of sulfides but also to reveal the crystallochemical behavior of arsenic and antimony in sulfides.

Materials and Technique

Preparation of starting materials

Firstly, As_2S_3 and Sb_2S_3 were synthesized from the elements of 3N or higher purity in evacuated silica tubes at 600°C for 12 days. Starting materials were prepared using powder mixtures of As_2S_3 and Sb_2S_3 having the following composition: $(\text{As}_x\text{Sb}_{1-x})_2\text{S}_3$, $x=0, 0.1, 0.2, \dots, 1.0$. The charges were sealed into evacuated silica tubes, which were kept in a furnace for 3 days at 700°C . The tubes were occasionally shaken in order to mix the charges, and finally quenched in cold water. In case the products were apparently inhomogeneous, the charges were reground and the reaction was repeated.

Synthesis

Crystals were synthesized by the hydrothermal method. Ten milligrams of the starting materials and 0.07 ml of Na_2S aqueous solution (from 0.5 to 1.25 wt%) were sealed in gold tubes (length: 30 mm; internal diameter: 2.7 mm). The tubes were kept under H_2O pressure in a test-tube type bomb of 1/4 inch in internal diameter. The syntheses were carried out at temperatures ranging from 250 to 400°C , for 1 to 3 weeks, under 1000 kg/cm^2 pressure. The pressure vessel was removed from a furnace and air quenched at the end of each experiment.

Characterization of products

The products were carefully separated from each other under a binocular microscope. They were examined by powder diffraction methods using a Gandolfi camera, Guinier-Hägg camera, or diffractometer. X-ray single crystal studies were made using Weissenberg and precession cameras. Synthetic products and some natural specimens were semiquantitatively analyzed by SEM-EDX. Quantitative chemical analyses were carried out by JEOL JEX-50A electron microprobe analyzer under the following conditions: standards – synthetic As_2S_3 (for As) and Sb_2S_3 (for Sb and S); accelerating voltage – 20 kV; probe current – $0.02 \mu\text{A}$; analyzing crystals – LiF (for $\text{AsK}\alpha$) and PET (for $\text{SK}\alpha$ and $\text{SbL}\alpha$). The data were corrected by the conventional ZAF method.

Results and Discussion

Products of synthesis

Crystalline phases appeared under the present synthetic conditions are stibnite, getchellite, wakabayashilite, and orpiment. They were easily identified by their appearance under the binocular microscope. Crystallization usually occurred on the lower

FIG. 1. A typical morphology of synthetic getchellite.

FIG. 2. SEM photograph of synthetic wakabayashilite.

TABLE 1. X-ray powder diffraction data of wakabayashilite.

hkl [†]	Present study*				Scott and Nowacki (1975)**		
	d _{calc}	d _{obs}	2 θ _{obs}	I/I ₀	d _{obs}	I/I ₀	hkl [†]
					12.57	5	100
200	6.31	6.31	14.014	9	6.28	100	200
101	5.78	5.78	15.323	10	5.77	25	101
210	4.773	4.771	18.584	6	4.78	70	210
201	4.531	4.533	19.568	3	4.520	5	201
300	4.209	4.211	21.083	1	4.204	5	300
					4.038	5	(702)
211	3.848	3.847	23.103	5	3.834	30	211
301	3.534	3.534	25.179	4			
310	3.502	3.504	25.402	6	3.488	80	310
002	3.253	3.249	27.427	8	3.239	40	002
102	3.150	3.152	28.291	6	3.150	5b	400, 102
311	3.084	3.083	28.940	6	3.078	40	311, (902)
					2.980	5	(718)
112	2.970	2.971	30.058	4	2.963	10	112
202	2.891	2.893	30.883	8	2.883	20	202
401	2.840	2.841	31.460	3	2.836	10	401
410	2.755	2.757	32.446	2	2.753	30	410
212	2.688	2.690	33.281	2			
321	2.646	2.648	33.828	3	2.638	10	321
302	2.574	2.573	34.840	7	2.565	25	302
411	2.537	2.534	35.395	5	2.535	35	411
222	2.427	2.425	37.045	5	2.423	40	330, 222
420	2.386	2.387	37.649	1			
421	2.240	2.241	40.205	4	2.239	30	421
511	2.141				2.139	25	511
103	2.137	2.139	42.123	6b ^{††}			
430	2.076	2.071	43.663	1	2.071	20	430
520	2.022	2.016	44.922	2	2.020	20	520
332	1.947	1.946	46.629	1	1.939	8b	332
303	1.928						
610	1.926	1.926	47.141	2			
313	1.844	1.843	49.403	5b	1.843	30	611
440	1.823	1.824	49.972	3	1.818	20	440
403	1.787	1.784	51.173	1			
602	1.767	1.765	51.757	1			
441	1.755	1.755	52.086	1			
531	1.738	1.738	52.618	3	1.734	8b	531, 323
522	1.717	1.718	53.276	3	1.712	8b	522, 413
413	1.704	1.702	53.828	3			
621	1.691	1.690	54.237	1			
710	1.672	1.672	54.854	2	1.670	15	710
612	1.657	1.656	55.426	1			
503	1.645	1.642	55.970	1			
004	1.626	1.626	56.547	9b			

104	1.613	1.613	57.045	2	1.616	8b	540, 004
630	1.591				1.590	40	630, 442
442	1.590	1.592	57.860	4b			
532	1.5775	1.5772	58.472	3			
433	1.4995	1.4988	61.856	1			
404	1.4457	1.4463	64.364	1			
613	1.4398	1.4398	64.687	1	1.439	10	811, 613
533	1.3867	1.3862	67.518	1			
713	1.3243	1.3248	71.108	1	1.322	8	650, 713

* Guinier-Hägg camera, monochromator: quartz (10 $\bar{1}$ 1), Johanson type, Cu K α_1 radiation, maximum d value obtainable is 11.8 Å.

** 114.6 mm camera, Ni-filtered Cu K α radiation.

† The data are indexed on the hexagonal cell. Indices in brackets refer to the monoclinic super-cell.

†† b=broad.

temperature side of the gold tubes, and beautiful euhedral crystals were often attached to inside wall of the gold tubes.

Stibnite crystal were needle-like or short prismatic with the maximum size, 0.08×0.08×1.15 mm. Getchellite was formed as transparent dark-red euhedral crystals of 1.3×1.4×1.8 mm in maximum size. A typical morphology of getchellite crystal is illustrated in Fig. 1. The crystals show remarkable internal reflections and are sectile, fragile, and readily cleavable upon slight mechanical manipulation. These properties are similar to those of natural materials. Higher antimony contents in the initial charge provided darker colors. Single crystals of wakabayashilite up to 1.8 mm long have been synthesized. They are brilliant yellow and transparent. The habit is prismatic or fibrous elongated along the *c* axis (hexagonal setting; see below). The appearance and crystal habit closely resemble those of natural materials from the White Caps mine, Manhattan, Nevada. Figure 2 is a SEM photograph of synthetic wakabayashilite, showing its hexagonal morphology. Table 1 lists the X-ray powder diffraction data of wakabayashilite obtained by Guinier-Hägg camera (CuK α_1 , $\lambda=1.540598$ Å). The data were successfully indexed on the hexagonal cell reported by Scott and Nowacki (1975). The cell parameters are $a=14.580(2)$ and $c=6.5052(9)$ Å, calculated from the powder data using the least-squares refinement program of Appleman and Evans (1973). These values are comparable to those given for a specimen from the White Caps mine by Scott and Nowacki: $a=14.564(3)$ and $c=6.480(4)$ Å. They also reported presence of a monoclinic super cell with $a=29.128$, $b=6.480$, $c=29.128$ Å, and $\beta=120^\circ$. The superstructure reflections are observable even in their powder diffraction pattern (Table 1), but they are absent in our Weissenberg and Guinier photographs. Scott and Nowacki (1975) stated the variable intensities of the superstructure reflections for different crystals and that they are enhanced by the grinding of specimen, yielding the conclusion that stress to the crystal is responsible for the formation of the super-

structure. Orpiment crystallized in a form of spherulitic aggregates. The spherulites are made up of tabular crystals with the maximum size, $0.03 \times 0.25 \times 1$ mm, radiating from the centers of the spherulites. The growth process of orpiment crystals observed in this experiment can be well explained by the model reported by Fujiki and Hasegawa (1975).

Condition of formation

It appears that reaction time affected only the sizes of synthesized crystals. Generally, it took two or three weeks for crystal growth of a millimeter order. The effect of the concentrations of the Na_2S solvents on the formations of stibnite and orpiment was examined. No apparent differences were found in crystals obtained from 0.5% and 1.0% solution. Concentrations of Na_2S higher than 1.25% were not favorable for growth of orpiment crystals and crystallization was observed only for stibnite. In this case it is considered that the following reaction proceeded: $\text{As}_2\text{S}_3 + 3\text{S}^{2-} \rightarrow 2\text{AsS}_3^{3-}$, resulting in a decomposition of orpiment and a lowering of the pH of the solvent from 12.5 to 8.0.

The hydrothermal synthesis was carried out at 250, 300, 350 and 400°C. Crystals of stibnite were formed at all temperatures examined, whereas those of getchellite and orpiment were obtained only at 250 and 300°C. Red amorphous arsenic sulfide

FIG. 3. Formation ranges of crystalline phases against the initial glass compositions.

was produced at 350 and 400°C, and was observed on acicular crystals of stibnite as droplet-like particles. Figure 3 shows the formation ranges of each phase against the compositions of initial glass. The solid lines indicate the regions where euhedral crystals were observed. Stibnite and orpiment were predominantly stable until the molar ratio of As/Sb in the initial glass composition reached to 8/2 and 2/8, respectively. Getchellite was observed as a minor phase where As/Sb<1, but it became a dominant phase with increasing the ratio. Wakabayashilite did not appear at As/Sb<6/4.

TABLE 2. Chemical compositions of the synthetic crystals.

sample	T*	As:Sb**	Composition (wt%)				Empirical formula†
			As	Sb	S	Total	
stibnite	b	1:9	1.26	70.16	28.74	100.16	Sb _{1.93} As _{0.06} S _{3.01}
	b	2:8	2.18	68.57	29.22	99.97	Sb _{1.87} As _{0.10} S _{3.03}
	c	2:8	2.48	68.19	28.97	99.64	Sb _{1.87} As _{0.11} S _{3.02}
	c	3:7	0.04	71.80	28.13	99.97	Sb _{2.01} As _{0.00} S _{2.99}
	c	4:6	5.52	64.75	29.49	99.76	Sb _{1.74} As _{0.24} S _{3.02}
	c	5:5	8.68	61.97	29.58	100.23	Sb _{1.64} As _{0.37} S _{2.99}
	c	6:4	5.28	65.33	29.35	99.96	Sb _{1.76} As _{0.23} S _{3.01}
	b	7:3	11.06	58.32	29.27	98.65	Sb _{1.56} As _{0.48} S _{2.96}
	b	8:2	11.11	59.07	29.60	99.78	Sb _{1.56} As _{0.48} S _{2.96}
	a	9:1	9.17	58.22	29.99	97.38	Sb _{1.56} As _{0.40} S _{3.05}
getchellite	b	3:7	31.70	34.35	34.76	100.81	As _{1.18} Sb _{0.79} S _{3.03}
	b	5:5	29.17	37.27	33.77	100.21	As _{1.11} Sb _{0.88} S _{3.01}
	b	6:4	30.71	36.27	34.23	101.21	As _{1.15} Sb _{0.84} S _{3.01}
	b	6:4	28.73	38.14	33.80	100.67	As _{1.09} Sb _{0.90} S _{3.01}
	a	7:3	31.73	35.94	34.31	101.98	As _{1.18} Sb _{0.83} S _{2.99}
	b	7:3	34.43	30.80	35.35	100.58	As _{1.27} Sb _{0.70} S _{3.03}
	b	8:2	33.25	28.42	39.05	100.72	As _{1.09} Sb _{0.92} S _{2.99}
wakabayashilite	b	9:1	49.87	13.95	36.70	100.52	As _{1.73} Sb _{0.30} S _{2.97}
	b	7:3	50.17	13.06	36.68	99.91	As _{1.74} Sb _{0.28} S _{2.98}
	b	7:3	47.79	14.53	36.79	99.11	As _{1.67} Sb _{0.31} S _{3.01}
orpiment	b	3:7	47.32	15.97	38.11	101.40	As _{1.62} Sb _{0.34} S _{3.05}
	a	4:6	47.44	13.67	38.60	99.71	As _{1.62} Sb _{0.29} S _{3.09}
	a	6:4	52.17	13.09	38.89	104.15	As _{1.73} Sb _{0.27} S _{3.00}
	a	7:3	48.40	13.78	38.83	101.01	As _{1.64} Sb _{0.29} S _{3.07}
	b	7:3	53.13	7.99	37.33	98.45	As _{1.83} Sb _{0.17} S _{3.00}
	a	8:2	48.51	13.26	38.35	100.12	As _{1.66} Sb _{0.28} S _{3.06}
	b	8:2	49.84	15.35	39.64	104.83	As _{1.64} Sb _{0.31} S _{3.05}
	b	9:1	50.22	10.80	39.14	100.16	As _{1.69} Sb _{0.22} S _{3.09}

* Synthetic temperature, a: 250°C, b: 300°C, c: 400°C.

** Initial glass composition (mole ratio).

† The mole numbers were calculated based on As+Sb+S=5.0.

Study of solid solutions

The chemical compositions of the products obtained under various synthetic conditions are listed in Table 2. The mole numbers in the chemical formulas were calculated on the basis of $\text{As}+\text{Sb}+\text{S}=5.0$. Figure 4 summarizes the solid solution ranges of produced crystalline phases expressed in terms of the Sb:As ratios.

Stibnite: The concentration of As in synthetic stibnite was roughly proportional to the composition of initial glass at 300°C. The upper limit of the Sb-As substitution was found to be 24 mol%, corresponding to $x=0.24$ in $(\text{Sb}_{1-x}\text{As}_x)_2\text{S}_3$. Stibnite crystals formed at higher temperatures, 350 and 400°C, had a rather narrower Sb-As substitution range. In this case, red amorphous arsenic sulfide was dominantly formed, especially when the As/Sb ratios of the starting materials were high.

The crystal data for the products were obtained using Weissenberg and precession

FIG. 4. Solid solution ranges of the synthetic crystalline phases in the $\text{As}_2\text{S}_3 - \text{Sb}_2\text{S}_3$ system.

TABLE 3. Unit cell parameters of synthetic stibnite containing various amounts of As.

compounds	a/Å	b/Å	c/Å	V/Å ³
Sb_2S_3^*	11.2285(5)	11.3109(9)	3.8364(4)	487.2
Sb_2S_3	11.227(4)	11.312(7)	3.839(2)	487.5(4)
$\text{Sb}_{1.93}\text{As}_{0.06}\text{S}_{3.01}$	11.231(3)	11.317(3)	3.827(1)	486.5(2)
$\text{Sb}_{1.87}\text{As}_{0.10}\text{S}_{3.03}$	11.250(3)	11.303(4)	3.827(1)	486.1(2)
$\text{Sb}_{1.76}\text{As}_{0.23}\text{S}_{3.01}$	11.253(2)	11.293*3)	3.809(1)	484.0(2)
$\text{Sb}_{1.56}\text{As}_{0.48}\text{S}_{2.97}$	11.282(3)	11.279(4)	3.786(1)	481.7(3)

* Natural material, Bayliss and Nowacki (1972)

cameras, and the four-circle diffractometer. Listed in Table 3 are their unit cell parameters, which were determined by least-squares refinement of 25 strong reflections having 2θ values between 25 and 35° measured on the four-circle diffractometer using monochromatized $\text{MoK}\alpha$ radiation ($\lambda=0.71069 \text{ \AA}$). Figure 5 illustrates the relationship between the As concentration and the unit cell parameters of stibnite. The variations of the cell dimensions and volumes are found to be continuous and linear. Although the covalent radius of As is much smaller than that of Sb, the substitution of As for Sb in stibnite causes the elongation of the a axis and shortening of the b and c axes. As a result, the lengths of a and b axes approached each other, and finally at about

FIG. 5. Relationships between the As concentration and the cell parameters of synthetic stibnite.

25 mol% As, the both lengths became equal within the range of experimental error. This crystal was found to be pseudo-tetragonal because its diffraction photographs showed orthorhombic symmetry. A detailed structural study of stibnite containing 25 mol% As will be reported in our subsequent study (Yokoi *et al.*, 1986).

Getchellite: The chemical composition of natural getchellite was first reported to be $\text{As}_{0.98}\text{Sb}_{1.01}\text{S}_3$, which is idealized as AsSbS_3 (Weissberg, 1965). Ever since getchellite has been believed to have an As/Sb ratio fixed at 1. As can be seen from Fig. 4, however, the substitution of As for Sb extensively occurs in the synthetic getchellite. It is noteworthy that the chemical composition deviates from the ideal AsSbS_3 only toward As rich side. The As/Sb ratio in a synthesized phase did not always relate with the As/Sb ratio in the initial glass. Namely, getchellite with $\text{As} > \text{Sb}$ was formed from a starting material with $\text{Sb} > \text{As}$. The mechanism of substitution will be discussed in our report on the structure analysis of synthetic getchellite (Yokoi, *et al.*, 1986).

Wakabayashilite: The chemical formula of wakabayashilite was initially given as $(\text{As,Sb})_{11}\text{S}_{18}$ with $\text{As} > \text{Sb}$ (Kato *et al.*, 1970) and later revised to $(\text{As}_x\text{Sb}_{6-x})\text{As}_{14}\text{S}_{30}$, or ideally $(\text{As,Sb})_{20}\text{S}_{30}$ by Scott and Nowacki (1976) after their structure analysis of the subcell. Our chemical analysis of the synthetic materials has supported the latter formula. The solid solution range of As for Sb in wakabayashilite is narrower than the other three sulfides. As indicated in Fig. 4, the chemical compositions of synthesized wakabayashilite overlap with the solid solution range of orpiment, though real dimorphic relation between the two is not fully substantiated. The electron microprobe analysis is not suitable for detecting the nonstoichiometry of a substance. To solve this problem, further studies including the determination of the monoclinic superstructure will be necessary.

Orpiment: The upper limit of the substitution of Sb for As was found to be 17 mol% (Fig. 4). The substitution range is narrower than those observed in stibnite and getchellite. This trend is similar to that found in natural materials as described below.

Natural materials: Dickson *et al.* (1975) reported solid solution ranges of natural orpiment and stibnite. The maximum substitution rate is 1.5 mol% Sb for orpiment and 15 mol% As for stibnite both from Carlin-type deposit, Nevada. Natural orpiment with the highest antimony content has been discovered by one of the authors (I.N.) in the U.S. National Museum specimen of getchellite from the Getchell mine, Nevada. The mineral contains 11 mol% Sb_2S_3 and has a slightly greenish color. It is closely associated with stibnite and getchellite. Generally speaking, the solid solution ranges observed in the natural phases were narrower than those found in the corresponding synthetic phases.

Conclusion

This study has revealed that the As-Sb substitution occurs extensively in the synthetic phases. Because properties of arsenic and antimony such as covalent radii and coordination geometry are different, the As-Sb substitution causes distortion of local environment around the metal atoms in a structure. This results in deformation of unit cells with variation of the cell parameters as is observed in Fig. 5. The limits of such a deformation may be responsible for the observed limits of the solid solution and structural discontinuity along the $\text{As}_2\text{S}_3 - \text{Sb}_2\text{S}_3$ join. These phenomena will be discussed from a structural point of view in our subsequent study (Yokoi *et al.*, 1986).

Acknowledgements—A part of the synthetic study was carried out at the Smithsonian Institution, Washington, D.C., U.S.A. after the sponsorship of U.S. National Research Council to which our sincere gratitude is subjected. Thanks are to Messrs. K. Nishida and R. Miyawaki of the University of Tsukuba for their help in the electron microprobe analyses. The authors also thank an anonymous referee for his advices pertinent to the improvement of the text.

References

- APPLEMAN, D. E. & EVANS, H. T. Jr. (1973) *Nat. Tech. Inf. Serv.*, U. S. Dep. Commerce, Springfield, VA., Document PB 216 188.
- BAYLISS, P. & NOWACKI, W. (1972) *Z. Kristallogr.*, Bd. **135**, 308-315.
- DICKSON, F. W., RADTKE, A. S., WEISSBERG, B. G. & HEROPOULOS, C. (1975) *Econ. Geol.*, **70**, 591-594.
- FUJIKI, Y. & HASEGAWA, Y. (1975) *Miner. Journ.*, **7**, 542-556.
- KATO, A., SAKURAI, K. & OHSUMI, K. (1970) Introduction to Japanese Minerals. Geol. Surv. Japan, 92-93.
- SCOTT, J. D. & NOWACKI, W. (1975) *Can. Mineral.*, **13**, 418-419.
- SCOTT, J. D. & NOWACKI, W. (1976) *Z. Kristallogr.*, Bd. **144**, 422.
- WEISSBERG, B. G. (1965) *Am. Mineral.*, **50**, 1817-1826.
- YOKOI, H., NAKAI, I., MIYAWAKI, R. & NAGASHIMA, K. (1986) *Miner. Journ.*, in preparation.

Received July 11, 1986.