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BAUMSTARKITE FROM THE KORYU MINE, HOKKAIDO, JAPAN

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ABSTRACT

Baumstarkite, ideally $AgSbS_2$, was found as aggregates of euhedral crystals in the Koryu mine, Hokkaido, Japan. The optical properties, chemical composition, and cell parameters of this mineral are presented. The compositional ranges are from 1.8 to 7.0 at.% As (7.4 to 28.2 mol.% $AgAsS_2$). The unit cell of a sample with 10 mol.% $AgAsS_2$ is triclinic, $P\bar{1}$ with *a* 7.778(1), *b* 8.326(1), *c* 8.814(1) Å, α 100.90(1), β 104.01(1), γ 90.06(1) , and *V* 543.2(1) Å^3; these values are in very good accordance with those of the type mineral as well as those of synthetic material.

INTRODUCTION

Baumstarkite is the triclinic form of $AgSbS_2$, which was defined by Effenberger *et al.* (2002) based on samples from the San Genaro mine (Huancavelica department, Peru). A crystal structure study of baumstarkite and aramayoite from an Argentinian deposit showed that these two sulfosalts are isotypic, with the general structural formula $Ag_3(Sb,As)_2(Sb,Bi)S_6$. At the mixed (Sb,Bi) site, As > Sb in baumstarkite, and Bi > Sb in aramayoite.

Approximately 25 years ago (Sugaki *et al.* 1984a,b) an unknown Ag-Sb-As sulfosalt mineral from the Koryu mine in Hokkaido Japan was described as "arsenian aramayoite" or "koryuite". Unfortunately, this material could not be validated as a new mineral, as crystal structure data were lacking. This paper reports the reexamination of this mineral, which corresponds to a new occurrence of baumstarkite. Optical properties, chemical analyses, and crystallographic data are presented, together with mineral synthesis, and the conditions of formation of baumstarkite according to phase equilibrium studies within the system Ag_2S-Sb_2S_3-As_2S_3 are discussed.

OCCURRENCE

The Koryu mine in Hokkaido, Japan, is an epithermal gold-silver vein deposit. The veins occur in a black mudstone of Miocene age and are composed of quartz in association with minor amounts of adularia, chlorite, vermiculite, johansenite, calcite, pyrite, chalcopyrite, sphalerite, galena, hematite, electrum, and silver minerals such as aguilarite, pearcite-polybasite series minerals, pyrargyrite-proustite solid solution, miargyrite, baumstarkite, and silver-bearing tetrahedrite. The ore veins show crustification banding structure. Many druses and vugs are found in the central portion of the quartz veins. Many sulfide minerals occur as small crystals in the druses, including aguilarite, pearcite-polybasite series minerals, pyrargyrite-proustite solid solution, miargyrite, baumstarkite, and silver-bearing tetrahedrite (Sugaki *et al.* 1984a). The mine is closed at the present time.

From the mineral assemblages and fluid inclusion studies, temperatures of formation and sulfur fugacity of gold-silver mineralization in the Koryu mine are estimated to be 175 to 240°C, and –15.5 to –11.5 in log fs_2 (atm), respectively (Sugaki *et al.* 1984a).

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Adularia from the +20 m sublevel of the 60 m level of the No. 1 vein gave a K-Ar age of 1.0 ± 0.3 Ma. This is the youngest reported age for gold-silver mineralization in Japan (Sugaki & Isobe 1985).

Baumstarkite occurs as aggregates of short, prismatic, euhedral crystals in the druses in a high-grade Ag-Au ore vein from the 60 m level of the No. 3 vein at the Koryu mine. In the druses, baumstarkite occurs in association with a pyrargyrite-proustite solid-solution, as seen in Figures 1A and B. A euhedral, prismatic, polyhedral crystal of miargyrite is found in the same druses. SEM photographs of these samples are presented in Figures 2A & B.

Physical Properties

Baumstarkite is grayish white on fresh surfaces, its streak is grayish red, and the luster is metallic. Viewed with a reflecting microscope, baumstarkite exhibits moderate bireflectance with a light bluish gray to light brownish white color (Fig. 3A). With crossed polars, it has a strong anisotropy from brownish yellow to bluish gray (Fig. 3B). Cleavage is perfect along the (001) plane. Twinning is commonly observed on [001]. It sometimes exhibits deep red internal reflections. The mineral is easily distinguished from other silver-bearing sulfosalts, such as miargyrite, polybasite-pearcite series minerals, and pyrargyrite-proustite solid solution, under crossed polars because its anisotropy is very strong.

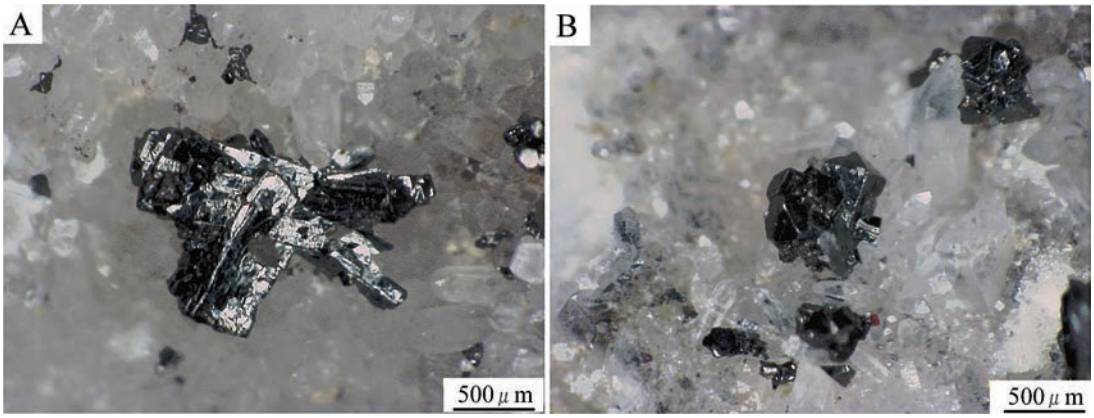

Fig. 1. A & B: Aggregates of black prismatic crystals of baumstarkite from the Koryu mine under the binocular microscope. A minute red crystal of pyrargyrite is visible in B.

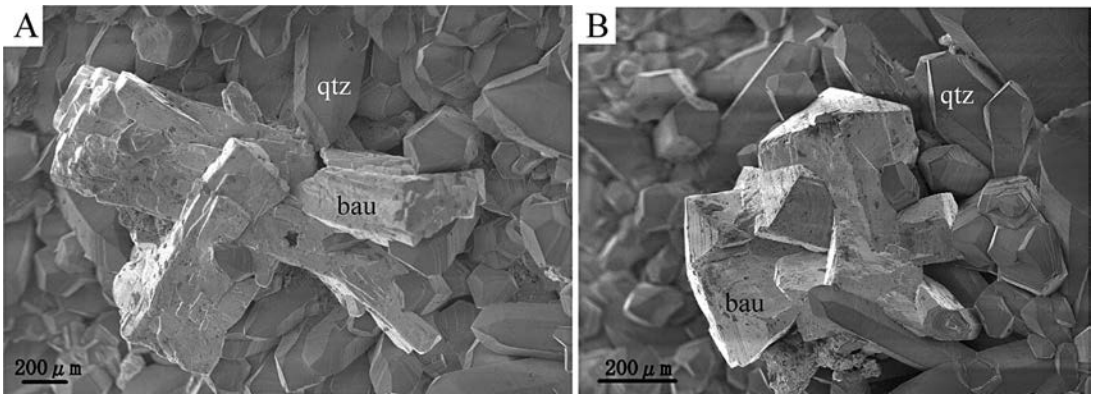

Fig. 2. A & B: SEM images of a baumstarkite crystal (bau) associated with quartz (qtz). The aggregates are the same as in Fig. 1A & B. Crystals of B aggregate are twinned.

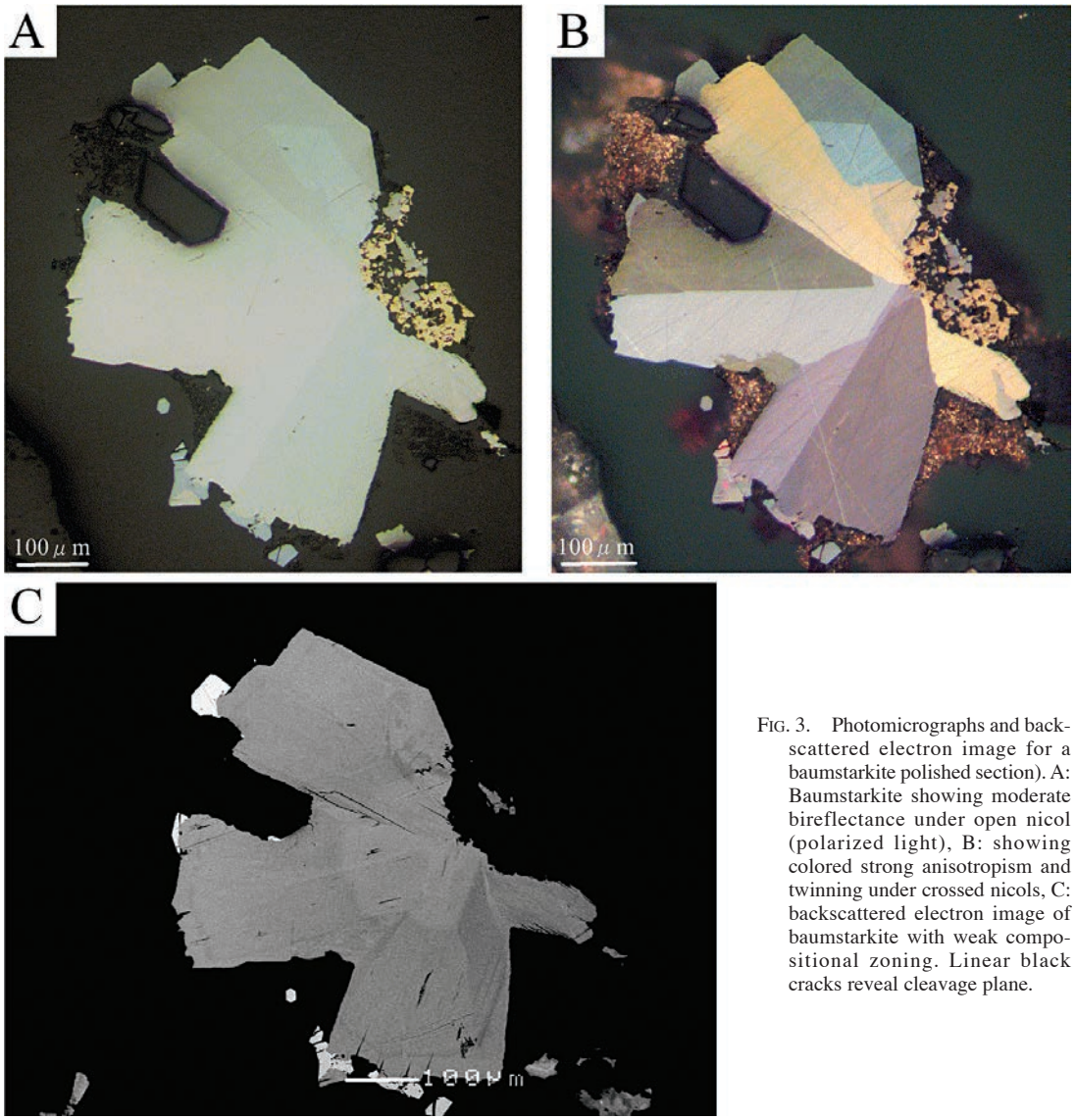

FIG. 3. Photomicrographs and backscattered electron image for a baumstarkite polished section). A: Baumstarkite showing moderate bireflectance under open nicol (polarized light), B: showing colored strong anisotropism and twinning under crossed nicols, C: backscattered electron image of baumstarkite with weak compositional zoning. Linear black cracks reveal cleavage plane.

Etching reactions for standard solutions are as follows: HNO_3 (1:1), slowly stains to brown; KOH (sat.), quickly stains iridescent. No effect was observed for $FeCl_3$ (20%), KCN (20%), $HgCl_2$ (sat.), or HCl (1:1). The Vickers hardness VHN_{25} ranges from 46 to 98 kg/mm^3.

Reflectance was measured with a Leitz MPV II, microscopic spectrophotometer with WTiC as a standard. Reflectance data in air and oil are given in Table 1 and Figure 4 and are compared with those from Effenberger *et al*. (2002). The mineral from the Koryu mine has somewhat lighter reflectance than the type specimen in the high wavelength region under air and oil.

CHEMICAL COMPOSITION

Baumstarkite from the Koryu mine shows a distinct compositional zoning in backscattered electron images (Fig. 3C) due to variation in the As:Sb ratio.

The detailed chemical composition was studied by electron microprobe (JEOL JXA 8800, 20 kV, 10 nA, beam diameter 2 μm). The standards were synthetic $AgSbS_2$ (Ag$L\alpha$, Sb$L\alpha$, and S$K\alpha$) and synthetic $AgAsS_2$ (As$L\alpha$). Cu and Bi were sought but not found; the detection limit is 0.1 wt.%.

The analytical results are given in Table 2. The As content ranges from 1.9 to 7.4 at.% As. Averaged

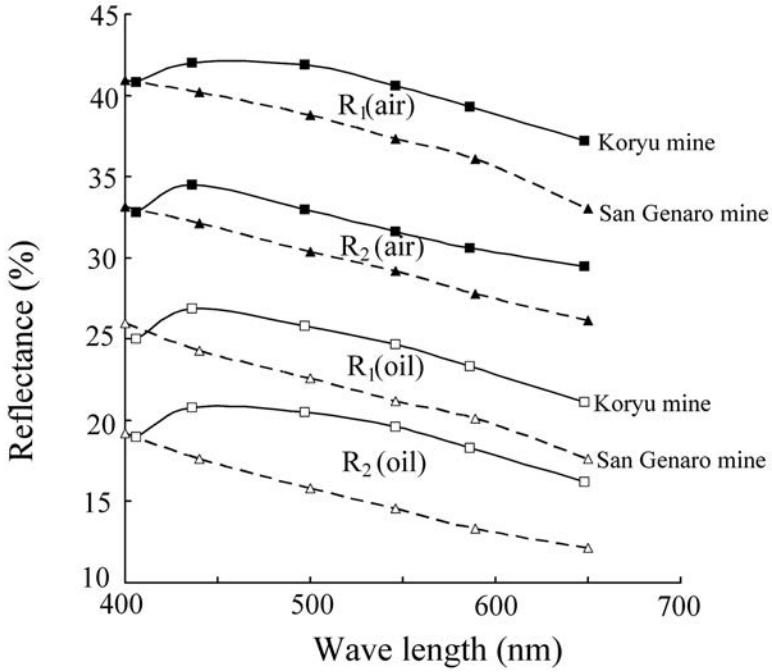

FIG. 4. Reflectance spectra of baumstarkite from the Koryu and San Genaro mines baumstarkite from the Koryu and San Genaro mines.

TABLE 1. REFLECTANCE OF BAUMSTARKITE FROM KORYU MINE IN AIR AND OIL

λ(nm)	Baumstarkite Koryu mine				Baumstarkite* San Genaro mine				
	R_1 (%)	R_2 (%)	R_1 (%) oil	R_2 (%) oil	λ (nm)	R_1 (%)	R_2 (%)	R_1 (%) oil	R_2 (%) oil
406	32.8	40.8	19.0	25.0	400	33.15	40.95	19.20	25.95
436	34.5	42.0	20.8	26.9	440	32.15	40.20	17.60	24.30
497	33.0	41.9	20.5	25.8	500	30.40	38.80	15.80	22.60
546	31.6	40.6	19.6	24.7	546	29.20	37.30	14.60	21.15
586	30.6	39.3	18.3	23 3	589	27.80	26.10	13.35	20.10
648	29.5	37.2	16.2	21.1	650	26.15	33.05	12.15	17.60

*After Effenberger *et. al*. (2002)

compositions for baumstarkite from the San Genaro mine (Effenberger *et al*. 2002) are also given in Table 2. The As content of composition C from Effenberger *et al*. (2002) is lower than the minimum value found for the Koryu mine.

Miargyrite in the same druses contains 1.0 at.% As. Both minerals have compositional gaps between 1.0~1.9 at.% corresponding to As/(Sb + As) = 0.04-0.08.

X-RAY INVESTIGATION

The X-ray single-crystal study of baumstarkite from the Koryu mine was performed using a precession camera, which permitted determination of the unit cell parameters and confirmation of the space group as $P\bar{1}$. X-ray powder diffraction data was obtained with a Guinier camera using the Cu$K\alpha_1$ line. The diffraction

TABLE 2. ELECTRON MICROPROBE ANALYSIS OF BAUMSTARKITE FROM THE KORYU MINE

	Koryu mine															San Genaro mine		
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	A	B	C
wt.%																		
Ag	37.3	37.2	37.0	37.3	37.0	37.1	37.8	37.5	37.6	37.6	37.6	37.9	38.0	38.4	38.4	36.5	38.3	37.4
Sb	38.3	38.4	38.5	38.1	38.5	37.9	36.6	37.0	36.6	35.7	35.2	34.2	33.4	32.8	30.8	40.2	27.9	33.1
As	1.9	2.0	2.2	2.3	2.4	2.7	3.3	3.4	3.6	4.4	4.5	5.2	5.8	6.7	7.4	0.7	10.1	6.2
S	22.1	22.1	22.0	22.0	22.1	22.2	22.4	22.5	22.4	22.4	22.3	22.6	22.5	22.8	22.9	22.0	23.1	22.6
Total	99.6	99.7	99.7	99.7	100.0	99.9	100.1	100.4	100.2	100.1	99.6	99.9	99.7	100.7	99.5	99.4	99.4	99.3
atomic %																		
Ag	25.1	25.1	25.0	25.1	24.8	24.9	25.1	24.9	25.0	24.9	25.0	25.0	25.1	25.0	25.0	24.7	24.7	24.7
Sb	22.9	22.9	23.0	22.7	22.9	22.5	21.6	21.7	21.5	21.0	20.8	20.0	19.5	18.9	17.8	24.2	15.9	19.3
As	1.8	1.9	2.1	2.2	2.3	2.6	3.2	3.2	3.4	4.2	4.3	4.9	5.4	5.2	7.0	0.7	9.4	5.9
S	50.1	50.1	49.9	49.9	49.9	50.0	50.1	50.2	50.0	49.9	49.9	50.1	49.9	49.9	50.2	50.4	50.0	50.1
total atoms=12																		
Ag	3.01	3.01	3.00	3.01	2.98	2.99	3.01	2.99	3.00	2.99	3.00	3.00	3.01	3.00	3.00	2.97	2.96	2.96
Sb	2.75	2.75	2.76	2.72	2.75	2.70	2.59	2.60	2.58	2.52	2.50	2.40	2.34	2.27	2.14	2.91	1.91	2.32
As	0.22	0.23	0.25	0.26	0.28	0.31	0.38	0.38	0.41	0.50	0.52	0.59	0.65	0.62	0.84	0.08	1.12	0.71
S	6.01	6.01	5.99	5.99	5.99	6.00	6.01	6.02	6.00	5.99	5.99	6.01	5.99	5.99	6.02	6.04	6.01	6.02

A, B, C: San Genaro mine, A: matrix (average), B: lamellae 1, C: lamellae 2 (after Effenberger *et al*. 2002)

patterns (Table 3) were measured and indexed according to Kitakaze (1996). X-ray powder data for baumstarkite from the Koryu and San Genoa mines, and synthetic material with composition $Ag_3Sb_{2.7}As_{0.3}S_6$ (obtained by the dry method starting from a mixture of $AgSbS_2$ and $AgAsS_2$; Sugaki *et al*. 1978), are given in Table 3.

Table 4 shows refined unit cell parameters for the natural and synthetic samples. Those for the San Genoa mine sample were calculated from the crystal structure data in Effenberger *et al*. (2002).

Table 4 also shows that the unit cell parameters of baumstarkite from the Koryu mine are about the same as those for synthetic baumstarkite and very close to those determined by Effenberger *et al*. (2002) from the San Genoa mine with a formula of $Ag_3Sb_{2.934}As_{0.040}Bi_{0.026}S_6$ (according to the crystal structure study). The unit cell volume of synthetic baumstarkite is the same as that for the sample from the Koryu mine.

Baumstarkite in Experimental Data

Baumstarkite belongs in the Ag-Sb-As-S system, but phase diagrams for this quaternary system have not been reported. However, many experimental studies have been performed on the ternary systems Ag-Sb-S and Ag-As-S. In the Ag-Sb-S system, Sb-rich billingsleyite, pyrargyrite, miargyrite (low temperature form), and the high temperature form of miargyrite (cuboargyrite, Walenta 1998) were synthesized and their phase relations established by Barstad (1959), Cambi & Elli (1965), Somanchi (1966), Hall (1968), Keighin & Honea (1969), and Wehmeier *et al*. (1968). In the Ag-As-S system, billingsleyite, proustite, smithite, and trechmannite were synthesized and their phase equilibria were determined by Toulmin (1963), Hall (1966, 1968), Roland (1970), and Wehmeier *et al*. (1968). The synthesis method, optical properties, and X-ray powder data for pyrargyrite, high temperature miargyrite (cuboargyrite), and miargyrite in the Ag-Sb-S system and proustite, smithite, and trechmannite in the Ag-As-S system were reported by Sugaki *et al*. (1978).

In the quaternary system, the Ag_2S-Sb_2S_3-As_2S_3 pseudo-ternary sub-system was studied by Chang *et al*. (1977), Ouwa *et al*. (1977), Shima *et al*. (1978), and Sugaki & Kitakaze (1984, 1992). Change *et al*. (1977) found a new synthetic phase which corresponds to baumstarkite on the $AgSbS_2$-$AgAsS_2$ join. The phase relations on the system were reexamined using dry and hydrothermal methods by Sugaki & Kitakaze (1984, 1992). They also obtained more detailed solid-solution ranges and crystallographic data for a new synthetic phase. Their phase diagram at 350ºC is depicted in Figure 5.

The phase diagram of the $AgSbS_2$-$AgAsS_2$ system is shown in Figure 6 (Sugaki & Kitakaze 1984, 1992). The end-members cuboargyrite and smithite have a wide range of solid solutions at high temperature. Baumstarkite is stable below 398ºC and has a significant range of solid solutions from 8 to 33 mol.% $AgAsS_2$ at low temperature.

Discussion

Effenberger *et al*. (2002) assumed that baumstarkite is the third naturally occurring modification of $AgSbS_2$, in addition to miargyrite and cuboargyrite. However, baumstarkite associated with miargyrite (As content less than 1.0 at.%, 4.0 mol.% $AgAsS_2$) from the Koryu

TABLE 3. X-RAY POWDER DIFFRACTION DATA FOR NATURAL AND SYNTHETIC BAUMSTARKITE

	Baumstarkite Koryu mine $Ag_{2.99}Sb_{2.70}As_{0.31}S_6$			Baumstarkite synthetic $Ag_{3.00}Sb_{2.70}As_{0.30}S_6$			Baumstarkite San Genaro mine $Ag_3Sb_{2.934}As_{0.040}Bi_{0.026}S_6$				
hkl	I	d(obs.)	d(calc.)	I	d(obs.)	d(calc.)	I*	d(obs.)*	d(calc.)*	I(calc.)**	d(calc.)**
$\bar{1}10$	4	5.675	5.679	5	5.675	5.677					
$1\bar{1}1$	5	4.592	4.596	7	4.592	4 595				3	4.5907
$10\bar{2}$	5	4.126	4.123	3	4.126	4.122					
$11\bar{2}$	2	3.950	3.952	3	3.952	3 953				4	3.9445
200	3	3.766	3.769	4	3.766	3.768				1	3.7623
$21\bar{1}$	6	3.501	3.503	6	3.503	3 504				8	3.4942
$2\bar{1}0$	20	3.485	3.488	15	3.485	3.487				11	3.4845
$1\bar{2}1$	50	3.428	3.429	40	3.428	3.428	8	3.425	3.429	75	3.4245
021	2	3.417	3.418	2	3.414	3.417				2	3.4017
210	2	3.360	3.360	2	3.359	3 360				3	3.3531
$0\bar{2}2$	30	3.258	3.260	30	3.258	3 261	3	3.258	3.259	61	3.2540
$20\bar{2}$	20	3.228	3.227	25	3.230	3 227	6	3.224	3.230	48	3.2260
201	25	3.157	3.159	15	3.160	3.157	4	3.158	3.159	42	3.1543
$22\bar{1}$	100	2.839	2.840	100	2.839	3 841	8	2.841	(2.844)	81	2.8329
$22\bar{0}$			2.840			3 839			2.837	81	2.8402
003	75	2.795	2.796	80	2.799	2.795	100	2.798	2.802	100	2.7979
$\bar{2}21$	4	2.732	2.732	2	2.730	2.731				6	2.7355
022	1	2.675	2.676	1	2.672	2.675				2	2.6823
$\bar{3}10$	1	2.435	2.435	2	2.439	2.437				2	2.4327
$2\bar{2}2$	2	2.297	2.298	2	2.296	2 297					
$23\bar{2}$	1	2.202	2.201	1	2.202	2 202					
$04\bar{1}$	20	2.0785	2.0789	20	2.0785	2.0787				26	2.0775
$\bar{2}23$	10	2.0445	2.0446	15	2.0440	2.0437				26	2.0493
040	5	2.0410	2.0415	2	2.0410	2.0410				2	2.0422
$2\bar{1}3$			2.0414			2.0407				3	2.0397
222	20	2.0098	2 0094	15	2.0090	2.0088	5	2.013	2 013	25	2.0097
$22\bar{4}$	20	1.9763	1.9757	25	1.9763	1.9764	5	1.971	1.975	24	1.9722
$40\bar{1}$	15	1.9445	1.9442	10	1.9445	1.9441				19	1.9415
$2\bar{2}3$			1.9441	15	1.9430	1.9432				15	1.9409
$\bar{3}30$	4	1.8934	1.8933	8	1.8930	1.8932				2	1.8919
$41\bar{1}$	3	1.8884	1.8889	4	1.8900	1.8892				5	1.8848
114	2	1.7799	1.7800	3	1.7789	1.7791				1	1.7793
$\bar{2}41$	10	1.7708	1.7707	15	1.7700	1.7699				11	1.7734
$11\bar{5}$	7	1.7621	1.7622	5	1.7620	1.7620					
240	2	1.7597	1.7593	4	1.7594	1.7592				9	1.7577
024	1	1.7329	1.7330	1	1.7320	1.7321				9	1.7366
$24\bar{3}$	15	1.7253	1.7256	15	1.7265	1.7262				9	1.7211
$\bar{2}42$	20	1.7148	1.7149	25	1.7145	1.7141				8	1.7131
042	20	1.7091	1.7091	20	1.7085	1.7084				12	1.7122
$\bar{4}22$	5	1.7003	1.7000	4	1.6693	1.6997				5	1.7009
$\bar{2}05$	4	1.6962	1.6959	5	1.6960	1.6658				6	1.6972
420	5	1.6798	1.6800	7	1.6798	1.6804				4	1.6765
$42\bar{3}$			1.6797			1.6800				4	1.6758
$02\bar{5}$	15	1.6703	1.6705	20	1.6700	1.6702				6	1.6688
a (Å)			7.778(1)			7.778(1)				7.768(1)	
b (Å)			8.326(1)			8.325(1)				8.325(1)	
c (Å)			8.814(1)			8.814(1)				8.814(1)	
α (°)			100.89(1)			100.93(1)				100.93(1)	
β (°)			104.03(1)			104.06(1)				104.06(1)	
γ (°)			90.06(1)			90.02(1)				90.02(1)	

*After Effenberger *et al*. (2002), **Am. Min. Database code 0002820; (2.844): index is doutful

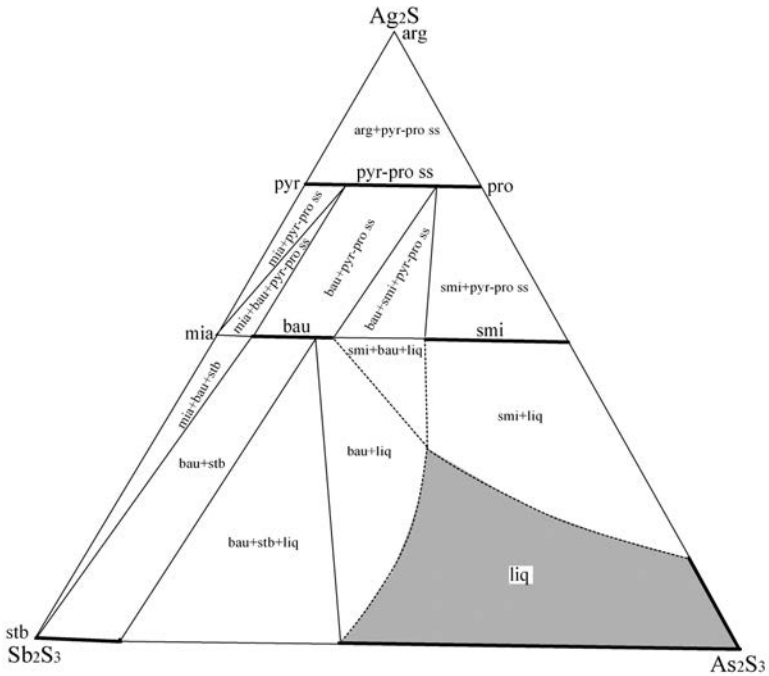

FIG. 5. Phase diagram of Ag_2S-Sb_2S_3-As_2S_3 pseudo-ternary system at 350ºC (Sugaki & Kitakaze 1984, 1992). Abbreviations are bau: baumstarkite, stb: stibnite, mia: miargyrite, smi: smithite, pyr-pro ss: pyrargyrite-proustite solid solution, liq: liquid.

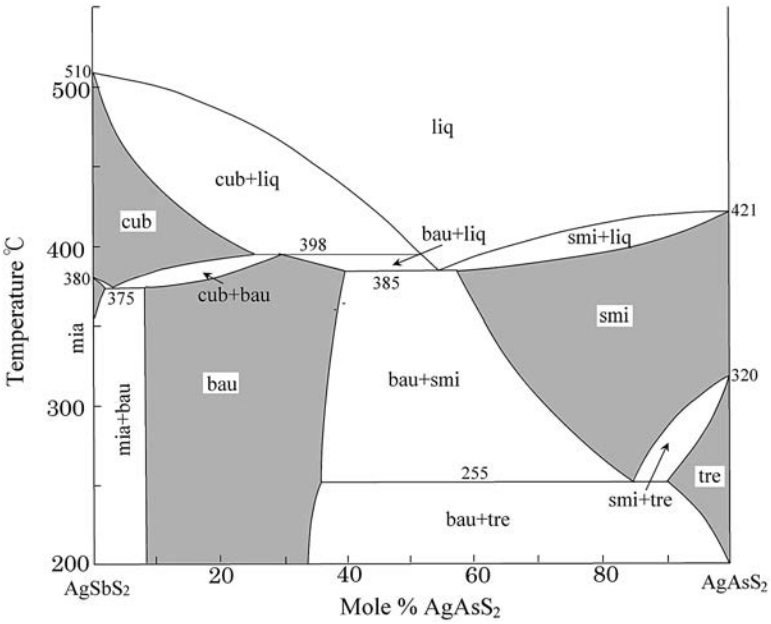

FIG. 6. Phase diagram of the $AgSbS_2$-$AgAsS_2$ pseudo-binary system according to Sugaki & Kitakaze (1984, 1992). Abbreviations are bau:baumstarkite, mia:miargyrite, cub:cuboargyrite, smi:smithite, tre:trechmannite, liq:liquid.

TABLE 4. CRYSTALLOGRAPHIC DATA FOR NATURAL AND SYNTHETIC BAUMSTARKITE

Name Locality Chemical formura	Baumstarkite Koryu mine $Ag_{2.99}Sb_{2.70}As_{0.31}S_6$	Baumstarkite synthetic $Ag_3Sb_{2.7}As_{0.3}S_6$	Baumstarkite* San Genoa mine $Ag_3Sb_{2.934}As_{0.040}Bi_{0.026}S_6$
a (Å)	7.778(1)	7.778(1)	7.766(2)
b (Å)	8.326(1)	8.325(1)	8.322(2)
c (Å)	8.814(1)	8.814(1)	8.814(2)
α	100.90(1)	100.93(1)	100.62(2)
β	104.01(1)	104.06(1)	104.03(2)
γ	90.06(1)	90.02(1)	90.22(2)
V(Å^3)	543.2(1)	542.9(1)	542

*After Effenberger *et al.*(2002)

mine contains the lowest As content at 1.8 at.% As (7.4 mole % $AgAsS_2$). At the San Genaro mine, the texture for baumstarkite crystals associated with or randomly intergrown with miargyrite are found in Fig.1B, C in Effenberger *et al*. (2002), although neither chemical composition is given. Baumstarkite was crystallized at about same P-T conditions as are associated with miargyrite. There is no evidence of transition in the photographs.

Regarding the $AgSbS_2$-$AgAsS_2$ join, the Sb-rich baumstarkite composition at 300ºC is 7.5 mol.% $AgAsS_2$ and there is a compositional gap between baumstarkite and miargyrite. From these results, it is assumed that these minerals have no dimorphic relationship. Naturally occurring cuboargyrite does not contain As, so the mineral has a pure $AgSbS_2$ composition (Walenta 1998). In that case, baumstarkite and cuboargyrite have no dimorphic relationship, either.

Effenberger *et al*. (2002) showed that in baumstarkite Sb occupies the M1, M2, and M3 sites and As substitutes at the M1 and M2 sites. In the most As-rich synthetic sample (33 mol.% $AgAsS_2$) it is assumed that the M1 and M2 sites are 50% occupied by As, corresponding to $Ag_3(Sb_{1.0}As_{1.0})SbS_6$.

In the crystal structure of aramayoite, Sb is distributed among the M1, M2, and M3 sites. However, Bi mainly occupies the M3 site. The substitutions found in naturally occurring baumstarkite and/or aramayoite are As for Sb at the M1 and M2 sites, and/or Bi for Sb at the M3 site. In Fig. 1C (Effenberger *et al*. 2002), a small grain of aramayoite was found as an inclusion in Bi-poor baumstarkite, which suggests that it is a transformation product of baumstarkite.

The phase diagram of the $AgSbS_2$-$AgBiS_2$ system using dry and hydrothermal methods was obtained by Shima *et. al*. (1979), and most Bi-rich aramayoite has 34 mol.% $AgBiS_2$, which corresponds to $Ag_3Sb_2BiS_6$.

According to studies of the phase relations of the $AgSbS_2$-$AgAsS_2$-$AgBiS_2$ system at 350 and 300ºC using dry and hydrothermal synthesis by Miyazaki (1986) and Sugaki & Kitakaze (1992), baumstarkite and aramayoite have two solid solutions: the former is As for Sb and the latter is Sb for Bi, and there is an immiscibility gap between the minerals. They concluded that baumstarkite and aramayoite have very similar crystal structures, but no solid solution. From the results of synthetic experiments and natural occurrences, baumstarkite and aramayoite are different mineral species.

We conclude that naturally occurring baumstarkite is an independent mineral having limited solid-solution substitution for Sb and As. The phase relations in the Ag_2S-Sb_2S_3-As_2S_3-Bi_2S_3 system will be described in the near future.

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