American Mineralogist, Volume 89, pages 696–700, 2004

Structural reinvestigation of getchellite $As_{0.98}Sb_{1.02}S_{3.00}$

ATSUSHI KYONO[1,]* AND MITSUYOSHI KIMATA[2]

[1]Laboratory for Entrepreneurship, University of Tsukuba, Tennodai 1-1-1, Tsukuba, Ibaraki 305-8573, Japan
[2]Institute of Geoscience, University of Tsukuba, Tennodai 1-1-1, Tsukuba, Ibaraki 305-8571, Japan

ABSTRACT

The crystal structure of getchellite, $As_{0.98}Sb_{1.02}S_{3.00}$, from the type-locality (the Getchell mine, Humboldt County, Nevada), monoclinic, $P2_1/a$, $a = 11.949(3)$, $b = 9.028(1)$, $c = 10.130(2)$ Å, $\beta = 116.15(1)°$, $V = 980.9(4)$ Å^3, $Z = 8$, was solved by direct methods and refined with full-matrix least-squares techniques to $R = 0.058$ and $Rw = 0.062$ for 505 observed reflections [$I_o > 5\sigma(I_o)$] collected using Mo$K\alpha$ radiation. The structure is made up of $(As,Sb)S_3$ trigonal pyramids forming an eight-membered $(As,Sb)_8S_8$ ring; the sheets formed by the eight-membered rings are connected to each other by S1 and S6 atoms are parallel to (001). The sheet structure is responsible for the cleavage and twin planes of getchellite. The cations predominantly occupy the M2 site in natural getchellite, because the $M2S_6$ polyhedron has the most distorted (irregular) geometry compared with other metal polyhedra in the structure. The amount of As incorporated at the M1 sites correlates strongly with M2 site composition. An important feature of As^{3+} sulfide minerals is that the crystal structures are composed of a 3-dimensional network consisting not only of AsS_3 pyramids but also containing trigonal pyramids of other constituent cations because the structures are governed strongly by the stereochemical requirement of As^{3+} cations for MS_3 trigonal pyramids.

INTRODUCTION

Structural coordinations surrounding As^{3+} and Sb^{3+} cations are always characterized by a one-sided coordination of trigonal pyramids because of the stereochemical activity of inert $4s^2$ or $5s^2$ lone-pair electrons of the metal atoms (e.g., Ondruš et al. 2002; Berlepsch et al. 2002; Effenberger et al. 1999, 2002). In the group V elements (As, Sb, Bi) stereochemical activity caused by ns^2 inert lone-pair electrons ($n = 4, 5, 6$) is known to decrease with increasing atomic number, which is ascribed to the contraction of inert pair orbitals explained in terms of relative contractions (Pitzer 1979; Pyykko and Desclaux 1979). That is, *s* electrons in the 4*s* shell are the most weakly bound with the metal nucleus, resulting in the greatly stereochemical behavior of the lone-pair electrons. Therefore, although Sb-Bi substitution can take place continuously in a stibnite (Sb_2S_3)-bismuthinite (Bi_2S_3) solid solution (Springer and Laflamme 1971; Nayak et al. 1983), several different structures occur between orpiment (As_2S_3) and stibnite (Sb_2S_3). There are three different phases in As-Sb sulfides: getchellite $AsSbS_3$ (Weissberg 1965; Guillermo and Wuensch 1973), pääkkönenite Sb_2AsS_2 (Borodayev et al. 1982; Bonazzi et al. 1995), and wakabayashilite $(As,Sb)_{11}S_{18}$ (Kato et al. 1972). Guillermo and Wuensch (1973) showed that the crystal structure of getchellite is not derived from that of either stibnite or orpiment. Experimental methods for the structural determination of getchellite described by Guillermo and Wuensch (1973) had to surmount two serious obstacles: (1) the intensities of the reflections were measured unfavorably with monochromatized Cu$K\alpha$ radiation because of the large absorption coefficients for arsenic antimony sulfide and (2) their refined crystal was not investigated for quantitative chemical composition.

We present a redetermined crystal structure of getchellite and elucidate structural behaviors of As and Sb coordination environments in getchellite relative to stibnite and orpiment. For the purpose of this study, a natural getchellite crystal from the type locality was studied with single crystal X-ray diffraction techniques.

EXPERIMENTAL METHOD

The sample used in this study is from the type locality, the Getchell mine, Humboldt County, Nevada, U.S.A. It is extremely difficult to select a single crystal whose diffraction spots display a low degree of splitting because the crystals are commonly twinned and plastically deformed with even slight mechanical manipulation (Weissberg 1965; Guillermo and Wuensch 1973). Dozens of crystal fragments were examined with a Rigaku RAXIS RAPID imaging plate diffractometer. After many trials, a small crystal with platelet shape (0.40 × 0.10 × 0.05 mm) was found to be suitable for structural investigation. The selected crystal was fixed on a 0.1 mm diameter glass capillary, then mounted on the imaging plate diffractometer system mentioned above, which uses graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å). A total of 44 images were collected in continuous omega-rotation mode in 5.0° steps between 130° and 190° ($\chi = 45°$, $\phi = 0°$) and between 0° and 160° ($\chi = 45°$, $\phi = 180°$); each image was irradiated for 4 min. Intensity data were corrected for Lorentz and polarization effects. Empirical absorption correction (Higashi 1995) was employed. The structure was resolved by direct methods with the program package SIR92 (Altomare et al. 1992) and refined by full-matrix least squares method with the program CRYSTALS (Watkin et al. 1996). Systematic absences confirmed the space group $P2_1/a$ previously determined by Guillermo and Wuensch (1973); the *R* index sharply lowered to 7.2% without site occupancy refinement. Site occupancy refinement was performed based on the chemical composition mentioned below. Refinement of the structure with 91 parameters on the basis of 505 unique reflections $I_o > 5\sigma(I_o)$ yielded residuals of $R = 0.058$, $Rw = 0.062$, and $GOF = 1.16$. Although we tried using the TWIN routine in the SHELXL program (Sheldrick 1993), there is no appreciable difference between results with and without it. Therefore, we have excluded completely the possibility of twinning in this study. Table 1 shows crystal data and details concerning intensity data collection and structural refinement. Tables 2 and 3 show atomic coordinates and thermal displacement parameters along with bond lengths and angles.

The chemical composition of getchellite was determined after the intensity data collection using an electron microprobe equipped with fully automated X-ray

---

* E-mail: kyono@arsia.geo.tsukuba.ac.jp

wave dispersive spectrometers (JXA8621 Superprobe; JEOL, Inc.). The operating conditions were 25 kV with a beam current of 10 nA. The raw data were corrected with a conventional ZAF program. Pyrite (S*K*α), GaAs (As*L*α), and stibnite (Sb*L*α) were used as standards. The EMPA yielded the following composition (wt%, average for seven points): As 24.91, Sb 41.81, and S 32.59; the total was 99.31. Other elements (Ag, Fe, Cu, Zn, Sn, Pb, Tl, and Bi) were sought but not detected. These results imply the empirical formula $As_{0.98(2)}Sb_{1.02(1)}S_{3.00(1)}$. The chemical composition of our getchellite crystal is approximately consistent with previously reported data (Weissberg 1965).

RESULTS AND DISCUSSION

The getchellite structure, as previously described by Guillermo and Wuensch (1973), is made up of $(As,Sb)S_3$ trigonal pyramids that join to form eight-membered $(As,Sb)_8S_8$ rings stacked along the **b** axis (Fig. 1); the eight-membered rings are connected by eight M cations and eight sulfur atoms in the following manner: (M1-S5-M3-S4-M2-S3-M4-S2)-(M1-S5-M3-S4-M2-S3-M4-S2), and are interconnected by S1 and S6 atoms. The refined structure of natural getchellite is in fundamental agreement with that of synthetic getchellite (Guillermo and Wuensch 1973). According to Guillermo and Wuensch (1973), the getchellite structure consists of sheets parallel to (001), which are responsible for cleavage and twin planes (Fig. 1). The cleavage is perfectly parallel to $\{001\}$, $\{011\}$, $\{01\bar{1}\}$, $\{11\bar{1}\}$, $\{\bar{1}11\}$, $\{210\}$, $\{\bar{2}10\}$, $\{211\}$, $\{\bar{2}11\}$, $\{20\bar{1}\}$, and $\{\bar{2}01\}$, which often represent cleavage faces (Fig. 2). Indexing is based on recalculation from the refined crystal structure.

Our getchellite crystal shows very different metal distributions over the four metal sites. Although site preferences in synthetic getchellite showed disordering of the As cation (Guillermo and Wuensch 1973), there is a strong preference for ordering of As in natural getchellite (Table 2). This may be attributed to slow crystallization in nature over an extended period of time (Guillermo and Wuensch 1973). In our sample, the M1 and M4 sites are chiefly occupied by Sb with minor substitution of As. However, the M2 site is occupied predominantly by As with extremely small amounts of Sb. Approximately equal amounts of As and Sb occupy the M3 site. A linear relation exists between the As cation content at the M site and M-S distances (Fig. 3). Therefore, the amount of As cation incorporated at M1 sites is associated strongly with the M2 site composition; e.g., less As at the M2 site should promote incorporation of As at the M1 site. On the other hand, incorporation of As at the M3 site appears to be related to the M4 site composition. In the getchellite crystal structure the M1 and M2 sites are located at the outside position in the eight-membered $(As,Sb)_8S_8$ ring (Fig. 1); the lone-pair electrons of the M cations at the vertex of the trigonal pyramid apparently point toward the interlayer separation. In contrast, the M3 and M4 sites are inside the eight-membered $(As,Sb)_8S_8$ ring, with the lone-pair electrons pointing toward the center (Fig. 1). Importantly, the amount of As at the M1 and M2 sites (M1 + M2 = 1.25) and at the M3 and M4 sites (M3 + M4 = 0.70) are approximately equal to those in synthetic getchellite (M1 + M2 = 1.24 and M3 + M4 = 0.76; Guillermo and Wuensch 1973). Therefore, the incorporation of As into getchellite may be responsible for a constant As ratio at (M1 + M2) and (M3 + M4). Furthermore, the As cation, with a stronger tendency to form stereoactive lone-pair electrons than the Sb cation, appears to occupy the (M1 + M2) sites preferentially, where the lone pair of electrons direct toward and contribute to interlayer separation in the structure. Orpiment and stibnite show similar orientations of inert lone-pair electrons (Mullen and Nowacki 1972; Kyono et al. 2002). That contribution is characteristic of elements with stereoactive lone-pair electrons. The strong site-preference of As for the M2 site is suggested by the polyhedral geometry of the $M2S_6$ coordination. In particular, the sphericity parameter (Balić-Žunić and Makovicky 1996) was calculated with the IVTON computer program (Balić-Žunić and Vickovic 1996). This parameter is a measure for the degree of deformation and irregularity of the coordination polyhedra. In this study, we used it as an indicator for site preferences (Table 4). As shown by sphericity (*s*) in Table 4, the $M2S_6$ polyhedron has the most distorted (irregular) geometry compared with other metal polyhedra. The As cations should tend to occupy the *M*2 site preferentially and thereby avoid increasing the polyhedral deformation because stereochemical activity of the As cation is much greater than that of the Sb cation.

TABLE 1. Crystal data and details of the structure refinements for getchellite

Formula	$As_{0.980}Sb_{1.020}S_{3.000}$
Temperature (K)	293
Crystal system	Monoclinic
Space group	$P2_1/a$
a (Å)	11.949(3)
b (Å)	9.028(1)
c (Å)	10.130(2)
β (°)	116.15(1)
V (Å^3)	980.9(4)
Z	8
D_{calc} (g/cm^3)	3.978
Absorption coefficient (cm^{-1})	133.73
F(000)	1058.88
Reflections collected	3836
Independent reflections	1932
R_{int}	0.109
Observed reflections	505
Refined parameters	91
GOF	1.16
R [$I > 5\sigma(I)$]	0.058
Rw [$I > 5\sigma(I)$]	0.062
$\Delta\rho_{max}$ (e/Å^3)	1.90
$\Delta\rho_{min}$ (e/Å^3)	–1.71

Figure 4 shows the relationship between the S-M-S inter-

TABLE 2. Site occupancies, atomic coordinates, and thermal displacement parameters (Å^2) for getchellite

Atom	Site occupancy		*x*	*y*	*z*	B_{eq}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
M1	As: 0.31(3)	Sb: 0.69(3)	0.1230(2)	0.3545(2)	0.1692(2)	2.61(9)	0.025(2)	0.028(2)	0.044(3)	–0.005(1)	0.013(2)	0.004(2)
M2	As: 0.94(3)	Sb: 0.06(3)	0.2333(3)	0.7245(3)	0.1424(3)	2.30(11)	0.026(3)	0.022(2)	0.041(4)	–0.001(2)	0.017(2)	–0.000(2)
M3	As: 0.48(3)	Sb: 0.52(3)	0.4854(2)	0.4401(2)	0.3182(2)	2.40(9)	0.026(2)	0.021(2)	0.048(3)	–0.000(1)	0.019(2)	–0.002(2)
M4	As: 0.22(3)	Sb: 0.78(3)	0.8257(2)	0.5221(2)	0.4610(2)	2.65(8)	0.029(2)	0.026(2)	0.048(3)	–0.002(1)	0.019(2)	–0.001(2)
S1			0.0739(9)	0.6164(9)	0.1780(9)	2.68(22)	0.022(5)	0.017(4)	0.064(8)	–0.005(4)	0.020(5)	–0.003(5)
S2			0.2842(9)	0.3478(10)	0.4235(12)	2.99(26)	0.035(6)	0.028(6)	0.059(9)	–0.003(5)	0.028(6)	–0.014(6)
S3			0.3877(10)	0.7545(11)	0.3751(12)	2.99(26)	0.039(7)	0.031(5)	0.032(8)	0.005(5)	0.005(6)	–0.017(5)
S4			0.3171(9)	0.5197(11)	0.0899(13)	2.55(23)	0.026(6)	0.030(5)	0.041(7)	0.002(4)	0.014(5)	–0.011(5)
S5			0.4486(11)	0.1843(10)	0.2369(14)	2.90(25)	0.039(6)	0.023(5)	0.055(9)	–0.012(5)	0.027(6)	–0.008(5)
S6			0.6392(9)	0.4932(11)	0.2321(12)	2.52(22)	0.031(6)	0.025(5)	0.039(7)	–0.006(4)	0.015(5)	–0.003(5)

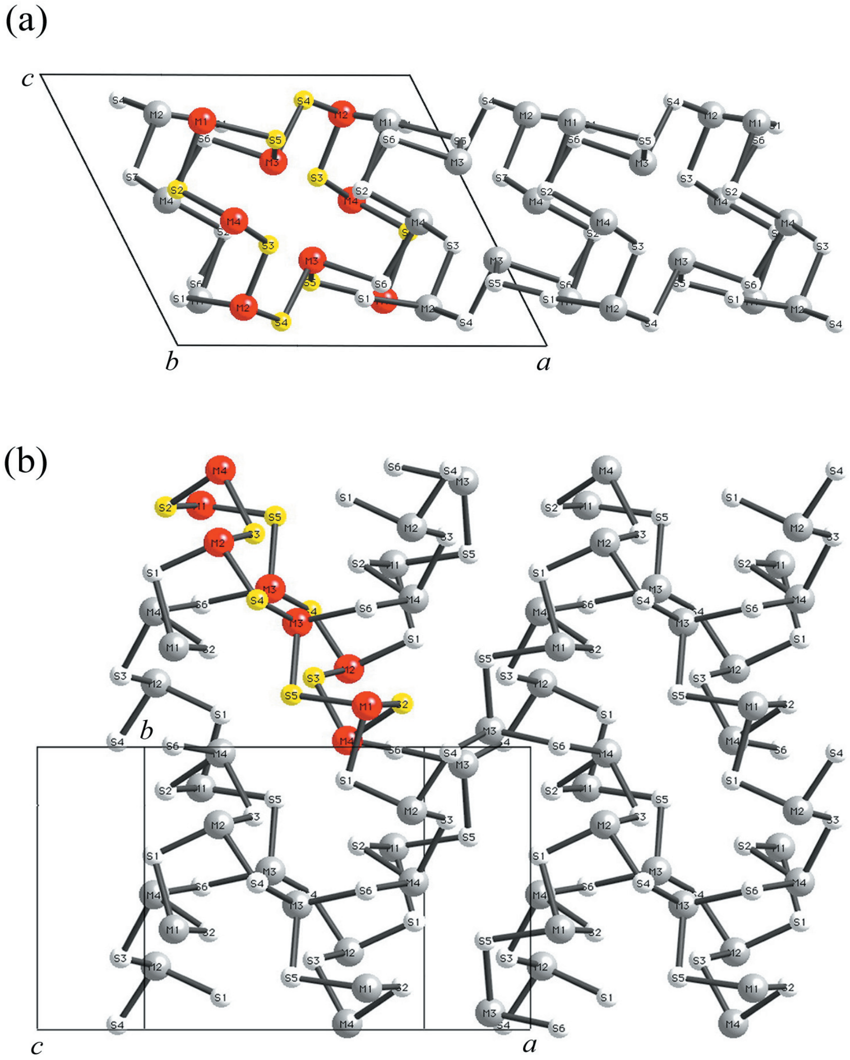

Figure 1. The crystal structure of getchellite composed of eight-membered rings projected parallel to (**a**) [010] and (**b**) [104]. One eight-membered ring represents yellow (S anion) and red (M cation) spheres.

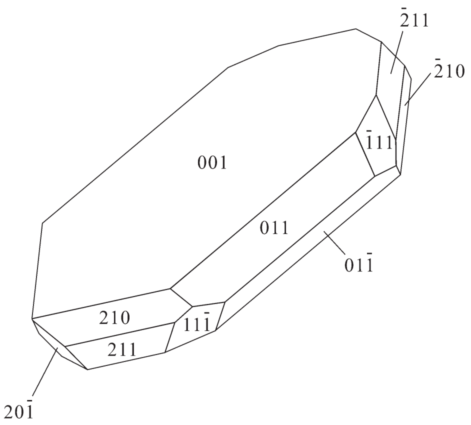

Figure 2. Morphology of getchellite; the twin plane is (001) (program SHAPE, Dowty 1999).

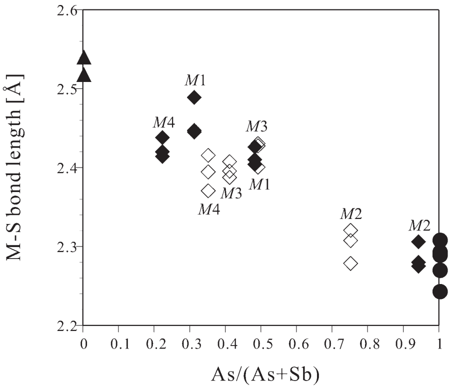

Figure 3. M-S bond lengths in MS_3 trigonal pyramids as a function of As concentration at the M site. The As-S and Sb-S bond lengths are calculated from AsS_3 and SbS_3 units forming trigonal pyramids in orpiment and stibnite, after Mullen and Nowacki (1972) and Kyono et al. (2002), respectively. Natural getchellite used in this study is represented by solid diamond symbols. Synthetic getchellite from Guillermo and Wuensch (1973) is shown by open diamond symbols. Stibnite is shown by solid triangles, and orpiment by solid circles.

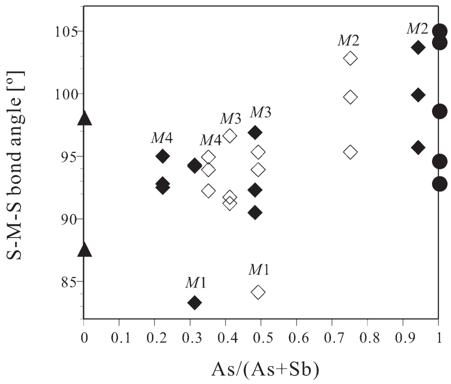

FIGURE 4. S-M-S bond angles in MS_3 trigonal pyramids as a function of As concentration at the M site. As-S and Sb-S bond lengths are calculated from AsS_3 and SbS_3 units forming trigonal pyramids in orpiment and stibnite, after Mullen and Nowacki (1972) and Kyono et al. (2002) respectively. See Figure 3 for legends.

TABLE 3. Selected bond distances and angles

M1 = $As_{0.31}Sb_{0.69}$			
M1-S2	2.445(9) Å	S2-*M*1-S1	94.3(3)°
M1-S1	2.447(9) Å	S2-*M*1-S5^{a}	94.2(4)°
M1-S5	^{a}2.489(16) Å	S1-*M*1-S5^{a}	83.3(4)°
<M1-S>	2.460 Å	S4-*M*1-S6	122.1(3)°
M1-S4	3.145(13) Å	S4-*M*1-S1^{b}	87.1(3)°
M1-S6	^{a}3.192(10) Å	S6^{a}-*M*1-S1^{b}	104.2(3)°
M1-S1	^{b}3.268(8) Å		
M2 = $As_{0.94}Sb_{0.06}$			
M2-S4	2.275(12) Å	S4-*M*2-S3	95.7(4)°
M2-S3	2.280(10) Å	S4-*M*2-S1	99.9(4)°
M2-S1	2.306(12) Å	S3-*M*2-S1	103.7(4)°
<M2-S>	2.287 Å	S6^{c}-*M*2-S4^{d}	65.3(3)°
M2-S6	^{c}3.080(12) Å	S6^{c}-*M*2-S5^{d}	106.2(3)°
M2-S4	^{d}3.428(12) Å	S4^{d}-*M*2-S5^{d}	59.4(3)°
M2-S5	^{d}3.501(12)		
M3 = $As_{0.48}Sb_{0.52}$			
M3-S6	2.404(14) Å	S6-*M*3-S5	96.9(4)°
M3-S4	2.410(10) Å	S6-*M*3-S4	92.3(4)°
M3-S5	2.426(10) Å	S4-*M*3-S5	90.5(4)°
<M3-S>	2.413 Å	S2-*M*3-S3	77.3(3)°
M3-S2	3.142(13) Å	S2-*M*3-S3^{e}	69.0(3)°
M3-S3	3.216(11) Å	S2-*M*3-S2^{e}	111.5(4)°
M3-S3	^{e}3.299(11) Å	S3-*M*3-S3^{e}	110.7(4)°
M3-S2	^{e}3.427(9) Å	S3-*M*3-S2^{e}	66.6(3)°
		S3^{e}-*M*3-S2^{e}	72.4(3)°
M4 = $As_{0.22}Sb_{0.78}$			
M4-S6	2.420(9) Å	S6-*M*4-S2^{f}	92.8(4)°
M4-S2	^{f}2.414(13) Å	S6-*M*4-S3^{g}	92.5(4)°
M4-S3	^{g}2.438(12) Å	S2^{f}-*M*4-S3^{g}	95.0(4)°
<M4-S>	2.424 Å	S2^{h}-*M*4-S5^{i}	123.2(3)°
M4-S2	^{h}3.373(9) Å	S2^{h}-*M*4-S1^{f}	74.5(2)°
M4-S5	^{i}3.392(10) Å	S5^{i}-*M*4-S1^{f}	56.5(3)°
M4-S1	^{f}3.537(9) Å		

Symmetry transformations: (a) $-1/2 + x, 1/2 - y, z$; (b) $-x, 1 - y, -z$; (c) $-1/2 + x, 1/2 + 1 - y, z$; (d) $1/2 - x, 1/2 + y, -z$; (e) $1 - x, 1 - y, 1 - z$; (f) $1 - x, 1 - y, 1 - z$, (g) $1/2 + x, 1/2 + 1 - y, z$; (h) $1/2 + x, 1/2 - y, z$; (i) $1/2 + 1 - x, 1/2 + y, 1 - z$.

TABLE 4. Polyhedral distortion parameters calculated with the program IVTON (Balić-Žunić and Vickovic 1996)

	CN	*r* (Å)	*d* (Å)	*s*
M1	6	2.968	0.764	0.988
M2	6	2.799	0.838	0.951
M3	7	2.908	0.777	0.988
M4	6	3.045	0.943	0.975

Notes: CN = coordination number; *r* = mean distance from centroid to ligands; *d* = centroid-central atom distance; *s* = sphericity of coordination polyhedron.

atomic angles and As cation contents. Interatomic angles for the M1, M3, and M4 sites should be independent of As and Sb contents. In constant conditions, the S-M2-S interatomic angles are clearly distinguishable from other angles. This correlation also appears in orpiment. That is, the M2 site differs completely from the other three M sites by structural similarities to orpiment. Moreover, linkages of MS_3 trigonal pyramids sharing their mutual three corners with each other are not common in stibnite (Kyono et al. 2002), but they are common in getchellite and orpiment (Mullen and Nowacki 1972). An important feature of arsenic (III) sulfide minerals is that crystal structures, e.g., ellisite Tl_3AsS_3 (Gostojić 1980), laffittite $AgHgAsS_3$ (Nakai and Appleman 1983), and xanthoconite Ag_3AsS_3 (Engel and Nowacki 1968) are composed of a three-dimensional network consisting not only of AsS_3 pyramids, but also containing trigonal pyramids of other constituent cations. Therefore, the As cation induces configurations of constituent cations to form threefold coordination because of the great stereochemical activity of the As^{3+} cation. Where an As cation is crystallized with tellurium or selenium, crystal structures of laphamite As_2Te_3 (Stergiou and Rentzeperis 1985a) and As_2Se_3 (Stergiou and Rentzeperis 1985b) are structurally identical to that of orpiment (Mullen and Nowacki 1972). This identity suggests that the crystal structure of orpiment is very suitable for trigonal coordination of As^{3+} cations. Therefore, because crystal structures of arsenic minerals are governed strongly by the stereochemical activity of the As^{3+} cation, formation of getchellite is also influenced strongly by incorporation of As cation.

ACKNOWLEDGMENTS

Single-crystal X-ray data collection and electron microprobe analysis were performed at the Chemical Analysis Center, University of Tsukuba. We thank Associated Editor P. Burns, referee P. Bonazzi, and an anonymous referee for their useful reviews.

REFERENCES CITED

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M.C., Polidori, G., and Camalli, M. (1992) SIR92—a program for automatic solution of structures by direct methods. Journal of Applied Crystallography, 27, 435.

Balić-Žunić, T. and Makovicky, E. (1996) Determination of the centroid or 'the best center' of the coordination polyhedron. Acta Crystallographica, B52, 78–81.

Balić-Žunić, T. and Vickovic, I. (1996) IVTON—program for the calculation of geometrical aspects of crystal structures and some crystal chemical applications. Journal of Applied Crystallography, 29, 305–306.

Berlepsch, P., Armbruster, T., and Topa, D. (2002) Structural and chemical variations in rathite, $Pb_8Pb_{4-x}(Tl_2As_2)_x(Ag_2As_2)As_{16}S_{40}$: modulations of a parent structure. Zeitschrift für Kristallographie, 217, 581–590.

Bonazzi, P., Borrini, D., Mazzi, F., and Olmi, F. (1995) Crystal structure and twinning of Sb_2AsS_2, the synthetic analogue of pääkkönenite. American Mineralogist, 80, 1054–1058.

Borodayev, Ju.S., Mozgova, N.N., Ozerova, N.A., Bortnikov, N.S., Ojvanen, P., and Ileutujnen, V. (1982) Pääkkönenite, Sb_2AsS_2, a new mineral from Seinäjoki ore region in Finland. International Geology Review, 24, 1234–1240.

Dowty, E. (1999) SHAPE 6.0. Professional Edition. A Computer Program for Crystal Morphology. Kingsport, TN 37663, U.S.A.

Effenberger, H., Paar, W.H., Topa, D., Culetto, F.J., and Giester, G. (1999) Toward the crystal structure of nagyagite, $[Pb(Pb,Sb)S_2][(Au,Te)]$. American Mineralogist, 84, 669–676.

Effenberger, H., Paar, W.H., Topa, Criddle, A.J., and Fleck, M. (2002) The new mineral baumstarkite and a structural reinvestigation of aramayoite and miargyrite. American Mineralogist, 87, 753–764.

Engel, V.P. and Nowacki, W. (1968) Die kristallstruktur von xanthokon, Ag_3AsS_3. Acta Crystallographica, B24, 77–81.

Gostojić, M. (1980) Die Kristallstruktur von synthetischem ellisit, Tl_3AsS_3. Zeitschrift für Kristallographie, 151, 249–254.

Guillermo, T.R. and Wuensch, B.J. (1973) The crystal structure of getchellite, $AsSbS_3$. Acta Crystallographica, B29, 2536–2541.

Higashi, T. (1995) Abscor—Empirical absorption correction based on Fourier series approximation. Rigaku Corp., Tokyo, Japan.

Kato, A., Sakurai, K.I., and Ohsumi, K. (1972) Introduction of Japanese minerals (abs.). American Mineralogist, 57, 1311–1312.

Kyono, A., Kimata, M., Matsuhisa, M., Miyashita, Y., and Okamoto, K. (2002) Low-temperature crystal structures of stibnite implying orbital overlap of Sb $5s^2$ inert pair electrons. Physics and Chemistry of Minerals, 29, 254–260.

Mullen, D.J.E. and Nowacki, W. (1972) Refinement of the crystal structure of realgar, AsS and orpiment, As_2S_3. Zeitschrift für Kristallographie, 136, 48–65.

Nakai, I. and Appleman, D.E. (1983) Laffittite, $AgHgAsS_3$: crystal structure and second occurrence from the Getchell mine, Nevada. American Mineralogist, 68, 235–244.

Nayak, B.B., Acharya, H.N., Mitra, G.B., and Mathur, B.K. (1983) Structural characterization of $Bi_{2-x}Sb_xS_3$ films prepared by the dip-dry method. Thin Solid Films, 105, 17–24.

Ondruš, P., Skála, R., Císařová, I., Veselovský, F., Frýda, J., and Čejka, J. (2002) Description and crystal structure of vajdakite, $[(Mo^{6+}O_2)_2(H_2O)_2As^{3+}{}_2O_5]\cdot H_2O$—A new mineral from Jáchymov, Czech Republic. American Mineralogist, 87, 983–990.

Pitzer, K.S. (1979) Relativistic effects on chemical properties. Accounts of Chemical Research, 12, 271–276.

Pyykko, P. and Desclaux, J.P. (1979) Relativity and periodic system of element. Accounts of Chemical Research, 12, 276–281.

Sheldrick, G.M. (1993) SHELXL-93. A program for the refinement of crystal structures. Universität of Göttingen, Germany.

Springer, G. and Laflamme, J.H.G. (1971) The system Bi_2S_3-Sb_2S_3. Canadian Mineralogist, 10, 847–853.

Stergiou, A.C. and Rentzeperis, P.J. (1985a) Hydrothermal growth and the crystal structure of arsenic telluride, As_2Te_3. Zeitschrift für Kristallographie, 172, 139–145.

———(1985b) The crystal structure of arsenic selenide, As_2Se_3. Zeitschrift für Kristallographie, 173, 185–191.

Watkin, D.J., Prout, C.K., Carruthers, J.R., and Betteridge, P.W. (1996) CRYSTALS. Issue 10, Chemical crystallography laboratory, Oxford, U.K.

Weissberg, B.G. (1965) Getchellite, $AsSbS_3$, a new mineral from Humboldt County, Nevada. American Mineralogist, 50, 1817–1826.

MANUSCRIPT RECEIVED MAY 6, 2003
MANUSCRIPT ACCEPTED NOVEMBER 10, 2003
MANUSCRIPT HANDLED BY PETER BURNS