

Wakabayashilite, [(As,Sb)₆S₉][As₄S₅]: Crystal structure, pseudosymmetry, twinning, and revised chemical formula

PAOLA BONAZZI,^{1,*} GIULIO I. LAMPRONTI,¹ LUCA BINDI,^{1,2} AND STEFANO ZANARDI³

¹Dipartimento di Scienze della Terra, Università degli Studi di Firenze, via La Pira 4, I-50121 Firenze, Italy

²Museo di Storia Naturale, sezione di Mineralogia, Università degli Studi di Firenze, via La Pira 4, I-50121 Firenze, Italy

³Dipartimento di Scienze della Terra, Università degli Studi di Ferrara, Corso Ercole I d'Este 32, I-44100 Ferrara, Italy

ABSTRACT

The crystal structure of the rare mineral wakabayashilite was solved by direct methods using intensity data collected from a twinned crystal. This study revealed that, in spite of the strong hexagonal pseudosymmetry, the structure is orthorhombic (space group $Pna2_1$) with $a_0 = 25.262(1)$, $b_0 = 14.563(1)$, $c_0 = 6.492(1)$ Å, and $V_0 = 2388.4(2)$ Å³. The refinement of an anisotropic model led to an R index of 6.08% for 3135 observed reflections [$F_o > 4\sigma(F_o)$] and 8.71% for all 4260 independent reflections. Wakabayashilite is twinned by reticular merohedry [twin plane (110)]. There are two structural units in the structure: (1) $[M_6S_9]$ bundle-like chains running along the [001] axis, consisting of corner-sharing MS_3 trigonal pyramids ($M = As, Sb$), and (2) rods of As_4S_5 cage-like molecules, located in the space between three bundles and held together by van der Waals forces. The crystal chemical formula was therefore revised according to the structural results, yielding $[(As,Sb)_6S_9][As_4S_5]$ ($Z = 4$). Both the intramolecular As-S and As-As bond distances and those within the bundle-like units match closely the values commonly observed in the molecule-formed structures of other arsenic sulfides and those found in orpiment, respectively. To contribute to the understanding of the effects of light exposure on the structure of the arsenic sulfides, the crystal was exposed to filtered polychromatic light. The unit-cell parameters were measured after each exposure. The results showed that the As_4S_5 molecules do not undergo any transformations, as previously found by exposing uzonite to light.

INTRODUCTION

The rare mineral wakabayashilite was first identified by Kato et al. (1970) in druses of quartz associated with realgar, orpiment, stibnite, and pyrite at the Nishinomaki As deposit (Gumma Prefecture, Japan) and at the White Caps Au-As-Sb deposit (Nevada, U.S.A.), where wakabayashilite was found embedded in calcite in association with realgar and orpiment. Wakabayashilite associated with realgar, orpiment, and pyrite has also been found in the Gal-Khaya As-Sb-Hg deposits (Yakutia, Russian Federation; Gruzdev et al. 1975) and Khaidarkan (Kyrgyzstan) (Gruzdev et al. 1975; Spiridonov 1989), in the Shuiluo As deposit in the Zhuang region, Guangxi, China (Zhang 1985), and in the Lukhumi As deposit in the central Caucasus, Georgia (Samsonova et al. 1990). More recently, wakabayashilite was found in the thallium-rich assemblage at Jas Roux, Hautes-Alpes, France (Johan and Mantiene 2000).

Wakabayashilite is one of the three natural ternary phases of the As-Sb-S system, the other two being getchellite, $AsSbS_3$ (Weissberg 1965; Guillermo and Wuensch 1973; Kyono and Kimata 2004), and pääkkönenite, Sb_2AsS_2 (Borodayev et al. 1982; Bonazzi et al. 1995a). Nakai et al. (1986) reported hydrothermal synthesis of wakabayashilite after thermal treatment of a $(Sb_{1-x}, As_x)_2S_3$ glass ($0 < x < 1$) at 250–400 °C in Na_2S aqueous solutions.

According to Kato et al. (1970), the mineral is monoclinic

pseudo-hexagonal, with $a_m = 25.17(4)$, $b_m = 6.48(1)$, and $c_m = 25.24(8)$ Å, $\beta = 120.0^\circ$, $Z = 6$, and space group $P2_1$ or $P2_1/m$. Electron probe analyses yielded the ideal chemical formula $(As,Sb)_{11}S_{18}$. A preliminary structural study was carried out by Scott and Nowacki (1975) using Weissenberg and precession methods; according to these authors the X-ray diffraction pattern of the mineral showed a marked hexagonal subcell [$a_h = 14.564(3)$, $c_h = 6.480(4)$ Å] with $6/mmm$ Laue symmetry and systematic absences for $hhl: l = 2n + 1$ and $00l: l = 2n + 1$. Because the statistical $|E|$ test pointed to a centric structure, $P6_3/mmc$ was assumed as the most probable space group for the average structure. In fact, additional weaker reflections yielding a fourfold pseudo-hexagonal monoclinic supercell [$a_h = b_h = 2a_h = 29.128$ Å, $c_h = 6.480$ Å, $\gamma = 120^\circ$] were also clearly visible in photographs. A year later, the same authors published a condensed abstract reporting a model for the average structure of wakabayashilite refined to $R = 11.3\%$ for isotropic atoms in the acentric $P6_3mc$ space group. Although no atomic coordinates were given in that report, the hexagonal substructure (i.e., the average structure) was described and graphically represented. It appears to consist of two distinct structural components: (1) $(As,Sb)_6S_9$ “complex double-spiral chains” running parallel to the hexagonal [001] axis (translation period 6.480 Å) and located around the 6_3 axes, and (2) As_4S_5 molecular groups on the threefold axes. Due to the evident average character of this structural model, however, the two As sites belonging to the chains are statistically half-occupied, thus giving four different possible kinds of chain per unit cell (Scott and Nowacki 1976). Therefore, the crystal chemical

*E-mail: paola.bonazzi@geo.unifi.it

formula was revised according to the structural model proposed to be $[(As,Sb)_6S_9][As_4S_6]$.

It is noteworthy that the As_4S_6 cage-like molecule has never been found in any other arsenic sulfide. Indeed, As_4S_3 molecules are present in the structure of both α -dimorphite (Whitfield 1970) and β -dimorphite (Whitfield 1973a) and As_4S_4 molecules are present in the structure of realgar (Mullen and Nowacki 1972), β - As_4S_4 (Porter and Sheldrick 1972), pararealgar (Bonazzi et al. 1995b), and in the As_4S_4 compound synthesized by Kutoglu (1976). As_4S_5 groups occur in the structure of uzonite (Bindi et al. 2003), while the structure of alacranite consists of an ordered packing of both As_4S_4 and As_4S_5 molecules (Bonazzi et al. 2003a). On the contrary, orpiment, which fits the atomic ratio As:S = 4:6, exhibits a layered structural arrangement (Mullen and Nowacki 1972). For this reason, we were very intrigued by the possible existence of As_4S_6 molecules in the structure of wakabayashilite.

EXPERIMENTAL METHODS

Several acicular crystals of wakabayashilite were selected from a sample coming from the White Caps mine, belonging to the collection of the Museo di Storia Naturale, sezione di Mineralogia, Università di Firenze (catalogue number 44293/G). These were examined with an Enraf-Nonius CAD4 single-crystal diffractometer using graphite-monochromatized $MoK\alpha$ radiation. The wakabayashilite crystals are very brittle and split upon the slightest mechanical manipulation into radiating aggregates of acicular crystals. In fact, most of them produced diffraction effects typical of multiple fiber-like crystallites. A crystal (approximately $30 \times 90 \times 550 \mu\text{m}$) of relatively high diffraction quality was selected for the structural study. A quick peak-searching routine identified 25 strong reflections which on centering yielded the pseudohexagonal basic unit cell $a_h = 14.543(5)$, $b_h = 14.557(5)$, and $c_h = 6.468(3) \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 119.92(8)^\circ$. Nonetheless, using a lower detection limit and longer counting times, additional reflections leading to a doubling of both a and b parameters were detected, in agreement with the finding of Scott and Nowacki (1975, 1976).

To solve, as a preliminary goal, the average structure of wakabayashilite, a collection of the intensity data matching the basic unit cell was carried out. Data were subsequently reduced for Lorentz-polarization effects and corrected for absorption using the semi-empirical method of North et al. (1968). Afterward, an overall intensity data collection was carried out using an automatic four-circle Nonius KappaCCD diffractometer equipped with a CCD detector. Experimental details relative to data collection are reported in Table 1. The package DENZO-SMN (Otwinosky and Minor 1997) was used for unit-cell refinement and data reduction; the empirical method proposed by Blessing (1995) was applied for the absorption correction. This afforded a redundant data set of 38,020 reflections [average $I/\sigma(I) = 7$] yielding the fourfold pseudohexagonal unit cell $a_h = 29.110(1)$, $b_h = 29.135(2)$, $c_h = 6.4881(4) \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120.003(2)^\circ$, $V_h = 4765.3(5) \text{ \AA}^3$. However, 25,851 reflections [average $I/\sigma(I) = 11$] were consistent with the twofold orthorhombic unit cell $a_o = 25.262(1)$, $b_o = 14.563(1)$, and $c_o = 6.492(1) \text{ \AA}$, $V_o = 2388.4(2) \text{ \AA}^3$. Details of both data collections are reported in Table 1.

STRUCTURE SOLUTION

Average structure

The geometrical relationships among the different unit cells are shown in Figure 1. Taking into account the systematic absences ($hkl: l = 2n + 1$ and $00l: l = 2n + 1$) and the results of the statistical tests on $|E|$ suggesting a non-centric structure, the average structure was solved by direct methods (Sheldrick 1997a) in space group $P6_3mc$ and an anisotropic model was refined (Sheldrick 1997b) up to a conventional crystallographic $R1$ (F_o -based) factor equal to 6.24% for 821 data and 69 refined parameters. On the whole, the resulting structural arrangement is very similar to the basic model proposed by Scott and Nowacki

TABLE 1. Crystal data and experimental details for wakabayashilite

	Hexagonal average structure	Orthorhombic structure
a (Å)	14.553(3)	25.262(1)
b (Å)	14.553(3)	14.563(1)
c (Å)	6.484(5)	6.492(1)
V (Å ³)	1189.3(8)	2388.4(2)
Space group	$P6_3mc$	$Pna2_1$
Diffractometer	CAD4	Kappa/CCD
Radiation	$MoK\alpha$	$MoK\alpha$
	26 mA \times 50 kV	30 mA \times 55 kV
θ range (°)	2.0–30.0	2.9–32.0
Scan speed (°/min)	3.30	
Scan mode	ω	
Scan width (°)	2.60	
Crystal to detector distance (mm)		40
Number of images:		
Cell determination		10
Data collection		91 ϕ ; 131 ω
Exposure time (s/frame):		
Cell determination		80
Data collection		180
Total rotation width (°)		182 ϕ ; 262 ω
Total measured reflections	7346	25851
Total unique reflections	694	4260
Observed unique refl. [$F_o > 4\sigma(F_o)$]	445	3135
R_{int} (%)	18.49	11.86
$R1$ (%) [$F_o > 4\sigma(F_o)$]	6.24	6.08
R_{σ} (%)	11.9	8.71
Refined parameters	69	225
Goof	1.061	1.068
Min ΔF peak ($e^{-}/\text{Å}^3$)	-1.19	-1.53
Max ΔF peak ($e^{-}/\text{Å}^3$)	1.25	2.67

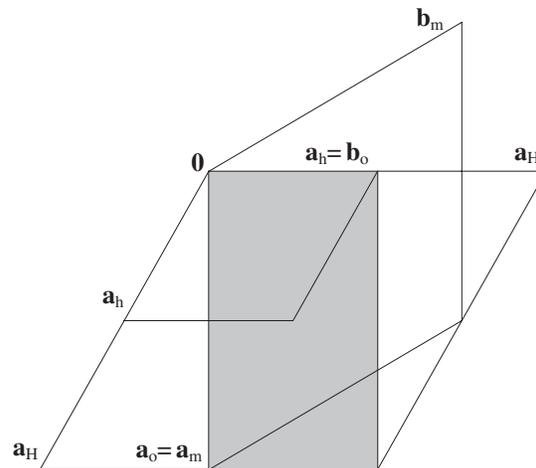


FIGURE 1. Geometrical relationships among the different unit cells used in the literature to describe the wakabayashilite lattice. The subscript indices refer to unit cells as follows: m = monoclinic unit cell (Kato et al. 1970); h = hexagonal basic unit cell (Scott and Nowacki 1975, 1976); H = fourfold hexagonal unit cell (Scott and Nowacki 1975); o = twofold orthorhombic unit cell (Scott and Nowacki 1976; this study). The latter unit cell is shaded in grey.

(1976) and confirms the average character of the hexagonal unit cell. As in the previous model, complex chains $[(As,Sb)_6S_9]$ are located around the 6_3 axis, with (As,Sb) distributed at half-occupied As positions, whereas the S atoms do not exhibit any positional disorder. Furthermore, both the As and S atoms within

the As_4S_6 molecular unit exhibit suspiciously high displacement parameters and unusual mixed As-S or S-□ occupancies.

Twinned structure

Taking into account the effective systematic absences ($00l: l = 2n + 1$), the first attempts to solve by direct methods (Sheldrick 1997a) the fourfold superstructure in $P6_3$ and $P2_1$ space groups were unsuccessful. On the other hand, no convergence was achieved by starting with different models derived from the average structure by progressively decreasing the symmetry constraints. Thus, the possibility of twinning was taken into account. Indeed, the peculiar geometry of the twofold orthorhombic unit cell (with $a_o = 3^{1/2} b_o$) makes $\{110\}$ twinning very likely. In this case all the reflections yielding the fourfold lattice can be sorted into two sets (Fig. 2). The first set yields the orthorhombic unit cell by the transformation matrix $[\frac{1}{2} \ 1 \ 0; -\frac{1}{2} \ 0 \ 0; 0 \ 0 \ 1]$, while the second set yields the same cell by the transformation matrix $[1 \ \frac{1}{2} \ 0; 0 \ -\frac{1}{2} \ 0; 0 \ 0 \ 1]$. However, one half of each set can be indexed by both transformations (overlapped reflections, shaded in grey in Fig. 2). The conditions for reflection overlapping are: $h_o + k_o = 2n$. The Miller indices of the superimposed reflections are $h_{o,I} \ k_{o,I} \ l_{o,I}$ for the first domain, and $h_{o,II} = \frac{1}{2} h_{o,I} - \frac{3}{2} k_{o,I}$, $k_{o,II} = -\frac{1}{2} h_{o,I} - \frac{1}{2} k_{o,I}$, $l_{o,II} = l_{o,I}$ for the second domain. This is consistent with the coexistence of two crystalline domains related by a (110) twin plane (orthorhombic orientation). Before attempting any structure solution, this possibility was carefully verified by measuring the intensity of 20 pairs of non-overlapped reflections for each twin-related component. As expected, the $I(h_1k_1l_1)/I(h_2k_2l_2) + I(h_1k_1l_1)$ ratio was an almost constant value [0.66(5)], thus strengthening the twinning hypothesis. Therefore the intensity data set previously reduced according to the orthorhombic unit cell was reduced using the HKLF5 program for non-merohedral twinned structures (Bolte 2004).

In the orthorhombic orientation, the following systematic absences were observed: $h00: h = 2n + 1$; $0k0: k = 2n + 1$; $00l: l = 2n + 1$; $0kl: k + l = 2n + 1$; $h0l: h = 2n + 1$. Although the $|E|$ statistical test did not give unambiguous indications, the struc-

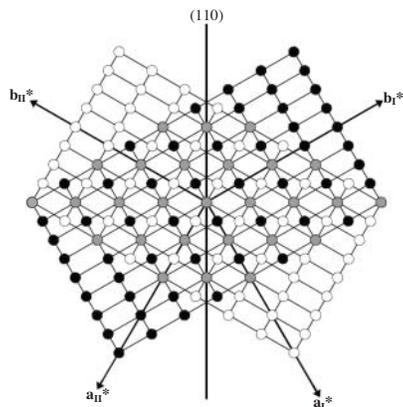


FIGURE 2. The $hk0$ layer of the reciprocal lattice of the twinned wakabayashilite crystal. The black-dotted lattice belongs to the first domain (I) and the open-circled lattice to the second domain (II). Circles shaded in grey belong to both twin components. The twin plane (110) is indicated.

ture was assumed to be acentric, based on the average structure model previously obtained. The structure was solved by direct methods (Sheldrick 1997a) in the polar space group $Pna2_1$ and subsequently refined (Sheldrick 1997b). The As vs. Sb occupancy was refined for all the M sites using scattering factors for neutral atoms (Ibers and Hamilton 1974), while full occupancy of neutral S was assigned to the S sites throughout the refinement. Using a weighting scheme $w = k/\sigma^2(F_o)$, convergence was quickly achieved for an anisotropic model resulting in $R1 = 6.08\%$ for 3135 observed reflections [$F_o > 4\sigma(F_o)$] and 8.71% for all 4260 independent reflections (Table 1). The refined twin fraction was 0.62(1). Inspection of the difference-Fourier map revealed maximum positive and negative peaks of 2.67 and 1.53 $e^-/\text{\AA}^3$, respectively. Final fractional atomic coordinates, site occupancies, and anisotropic displacement parameters are listed in Table 2. Table 3¹ lists the observed and calculated structure factors.

Description of the structure

The twofold orthorhombic superstructure of wakabayashilite is illustrated in Figure 3. There are two structural units: (1) $[\text{M}_6\text{S}_9]$ bundle-like chains running along the $[001]$ axis (Fig. 4), consisting of corner-sharing MS_3 trigonal pyramids ($\text{M} = \text{As}, \text{Sb}$), and (2) rods of As_4S_5 cage-like molecules (Fig. 5), located in the space between bundles and held together by van der Waals forces. Selected bond distance and angles are given in Table 4.

$[\text{M}_6\text{S}_9]$ bundle-like chains

In the six independent M sites belonging to the bundles, variable amounts of Sb substitute for As (Table 4). With the increasing Sb content at the M sites (ranging from 0.00 to 0.21 molar fraction), the mean M-S bond distance increases accord-

¹ For a copy of Table 3, Document item AM-05-019, contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. Deposit items may also be available on the American Mineralogist web site at <http://www.minsocam.org>.

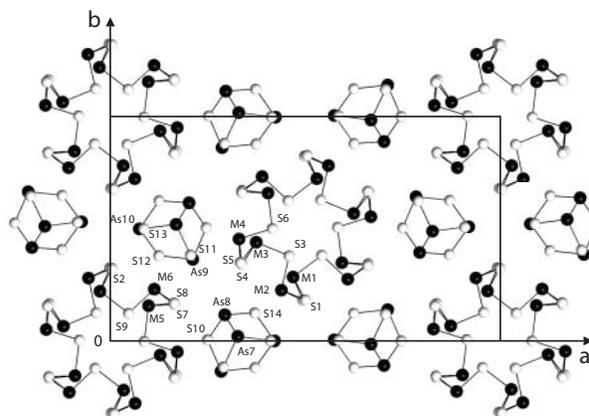


FIGURE 3. The crystal structure of wakabayashilite projected along $[001]$. Sulfur and metal positions are pictured in pale grey and black, respectively. Labels refer to the asymmetric unit ($0 \leq x \leq 0.5$; $0 \leq y \leq 0.5$; $0 \leq z \leq 1.0$).

TABLE 2. Fractional atomic coordinates, anisotropic and equivalent isotropic atomic displacement parameters (\AA^2) for the crystal structure of wakabayashilite

	s.s.*	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}
M1	36.8	0.4694(1)	0.2798(2)	0.2510(8)	0.036(2)	0.049(2)	0.037(2)	-0.005(1)	-0.000(2)	0.004(2)	0.041(1)
M2	33.0	0.4398(1)	0.2207(2)	0.7445(9)	0.034(1)	0.050(2)	0.041(2)	0.005(1)	-0.001(2)	-0.003(2)	0.0416(8)
M3	36.4	0.3752(1)	0.4355(2)	0.7495(7)	0.031(2)	0.053(2)	0.033(2)	0.002(1)	0.004(2)	0.001(2)	0.039(1)
M4	33.4	0.3309(1)	0.4503(2)	0.2427(8)	0.038(2)	0.046(2)	0.032(2)	0.000(1)	0.004(2)	-0.001(2)	0.038(1)
M5	36.4	0.0948(1)	0.1560(2)	0.7508(7)	0.041(2)	0.047(2)	0.034(2)	-0.004(1)	0.002(2)	0.008(2)	0.040(1)
M6	34.6	0.1098(1)	0.2295(2)	0.2438(8)	0.036(2)	0.052(2)	0.037(2)	0.001(1)	0.002(2)	0.002(2)	0.042(1)
As7	33.0	0.3289(3)	0.0167(3)	0.758(1)	0.074(4)	0.076(3)	0.062(2)	-0.024(6)	0.013(4)	-0.018(3)	0.071(2)
As8	33.0	0.2964(2)	0.1114(4)	0.432(1)	0.044(3)	0.071(3)	0.122(6)	-0.010(2)	0.016(3)	-0.023(3)	0.079(2)
As9	33.0	0.2129(2)	0.3614(2)	0.8339(6)	0.039(2)	0.045(2)	0.032(1)	-0.005(1)	-0.001(2)	-0.004(1)	0.0387(7)
As10	33.0	0.0770(3)	0.4973(4)	0.843(1)	0.054(3)	0.061(3)	0.076(3)	0.002(2)	0.021(3)	0.005(3)	0.064(1)
S1	16.0	0.4946(5)	0.1738(9)	0.997(2)	0.041(5)	0.068(7)	0.029(4)	0.005(4)	-0.004(4)	-0.005(4)	0.046(2)
S2	16.0	0.0011(5)	0.3218(8)	0.494(2)	0.036(4)	0.051(5)	0.036(5)	-0.0010(4)	-0.002(4)	0.004(4)	0.041(2)
S3	16.0	0.4589(4)	0.3746(5)	0.745(2)	0.039(5)	0.041(4)	0.060(5)	0.003(3)	-0.0012(6)	0.001(5)	0.047(2)
S4	16.0	0.3393(4)	0.3371(7)	0.995(2)	0.033(4)	0.053(5)	0.032(4)	-0.006(4)	0.006(4)	0.005(4)	0.039(2)
S5	16.0	0.3344(5)	0.3451(7)	0.497(2)	0.050(6)	0.046(5)	0.043(5)	-0.013(4)	-0.004(5)	0.004(4)	0.046(2)
S6	16.0	0.4169(4)	0.4970(6)	0.247(2)	0.038(5)	0.041(4)	0.062(6)	0.002(3)	-0.014(6)	-0.008(6)	0.047(2)
S7	16.0	0.1623(4)	0.1601(6)	0.998(2)	0.032(4)	0.038(4)	0.041(5)	-0.006(3)	0.001(4)	-0.002(4)	0.037(2)
S8	16.0	0.1607(5)	0.1683(9)	0.500(2)	0.032(5)	0.068(6)	0.041(5)	0.008(4)	0.001(5)	-0.012(5)	0.047(2)
S9	16.0	0.0431(4)	0.1225(5)	0.243(2)	0.037(5)	0.039(3)	0.055(4)	0.002(3)	0.005(5)	-0.004(5)	0.044(2)
S10	16.0	0.2528(6)	0.0020(8)	0.260(3)	0.048(7)	0.067(6)	0.060(6)	0.004(5)	0.005(7)	0.015(6)	0.058(3)
S11	16.0	0.2077(5)	0.3802(7)	0.179(2)	0.047(6)	0.048(4)	0.054(5)	0.003(4)	-0.005(5)	0.007(4)	0.050(2)
S12	16.0	0.1267(4)	0.3779(5)	0.723(2)	0.046(5)	0.033(3)	0.058(6)	0.007(3)	-0.008(5)	-0.011(3)	0.046(2)
S13	16.0	0.0876(6)	0.4987(9)	0.189(2)	0.047(6)	0.065(6)	0.063(7)	0.007(5)	-0.004(6)	0.005(5)	0.058(3)
S14	16.0	0.3726(4)	0.1209(6)	0.256(2)	0.056(6)	0.037(3)	0.056(5)	0.008(3)	0.003(6)	0.002(4)	0.050(2)

* The site scattering for the M = (As, Sb) positions was recalculated from the refined site-occupancy factor obtained by constraining the sum As + Sb to 1.0.

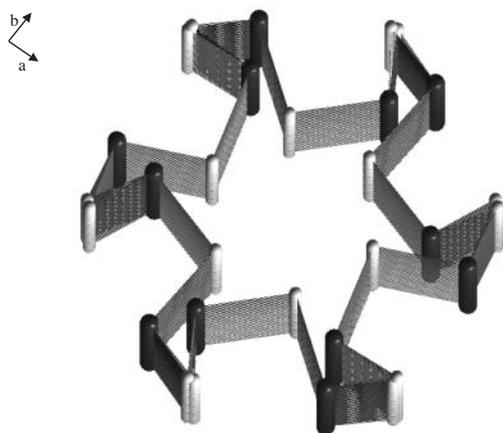


FIGURE 4. A schematic view of the $[M_6S_9]$ bundle-like unit in the structure of wakabayashilite (20 translation periods along $[001]$ are considered). M and S atoms are pictured in dark and pale grey, respectively.

ingly (ranging from 2.28 to 2.34 \AA) (Fig. 6). The linear regression obtained, $\langle M-S \rangle = 2.282(6) + 0.24(4) [Sb/(As + Sb)]$ ($r = 0.94$), also works well for the $\langle M-S \rangle$ observed in natural getchellite (empty squares in Fig. 6; Kyono and Kimata 2004). The extrapolation toward Sb = 1.00 (2.52 \AA) matches closely the $\langle Sb^{III}-S \rangle$ value observed in the structure of stibnite (2.53 \AA ; Bayliss and Nowacki 1972). The $\langle M-S \rangle$ value predicted for As = 1.00 (2.282 \AA) is slightly larger than those usually observed for As-S bonds in minerals containing As_4S_5 molecules (2.21–2.26 \AA ; Mullen and Nowacki 1972; Bonazzi et al. 1995b, 2003a; Burns and Percival 2001; Bindi et al. 2003), whereas it matches perfectly those observed in the layered structure of orpiment (2.284 and 2.281 \AA ; Mullen and Nowacki 1972). Indeed, a layer very similar to that present in the orpiment structure is obtained when the cylindrical surface forming the $[M_6S_9]$ -bundle is ideally developed. Both the “ideal layer” of wakabayashilite and the actual layer in orpiment

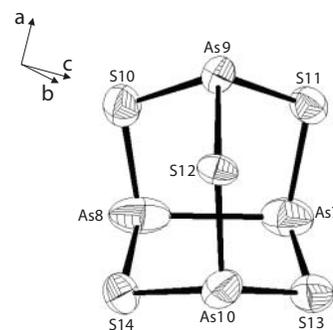


FIGURE 5. The As_4S_5 cage-like molecule in the structure of wakabayashilite. Vibrational ellipsoids are scaled for 50% probability.

consist of corrugated twelve-membered -As-S-As-S- rings (Fig. 7), wherein each As and S atom is shared by three and two rings, respectively. The mean value of the S-As-S angles in the bundle-like unit of wakabayashilite (97.5°) is identical to the homologous value in orpiment (97.5°), while the mean value of the As-S-As angles (95.3°) is slightly lower (99.0° in orpiment); this feature indicates that the rolling of the layer in wakabayashilite involves a greater bending of the As-S-As angle without any deformation of the rigid MS_3 pyramids.

The bundle-like arrangement of the $[M_6S_9]$ layer in wakabayashilite leads to a hexagonal channel (apparent free diameter of 4.19 \AA) wherein S3, S6, and S9 are arranged around the 2_1 axis, forming octahedral cavities; such an arrangement, in principle, allows the possible entry of cations (cation-sulfur distances ≤ 2.65 \AA). No residual electron density, however, was found in the final difference-Fourier map for this position.

As_4S_5 cage-like molecules

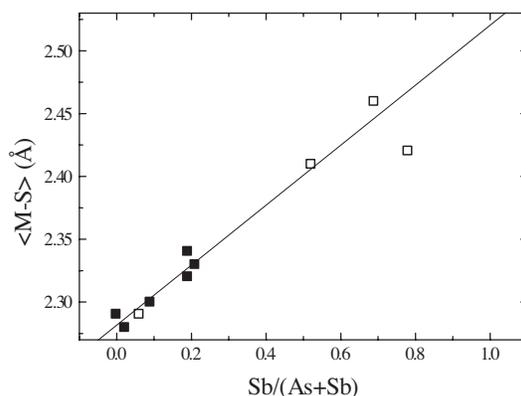
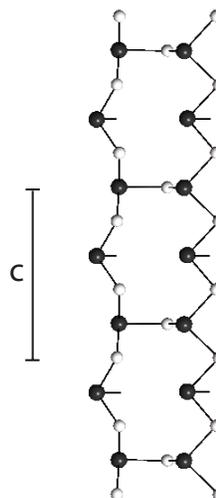
The presence of As_4S_5 molecular groups, rather than As_4S_6 as previously supposed on the basis of the sublattice diffraction data alone, was readily detected during the structure-solution routine

TABLE 4. Selected interatomic distances (Å) and angles with their standard deviations (in parentheses) together with the As/(As + Sb) molar fraction for wakabayashilite

Interatomic bond distances in the bundle			
M1-S2(i)	2.30(1)	M2-S1	2.25(1)
M1-S9(i)	2.344(9)	M2-S3	2.292(8)
M1-S1(ii)	2.34(1)	M2-S2(i)	2.33(1)
mean	2.33	mean	2.29
As/(As + Sb)	0.79(4)	As/(As + Sb)	1.0(4)
M3-S3	2.29(1)	M4-S5	2.26(1)
M3-S4	2.33(1)	M4-S6	2.27(1)
M3-S5	2.34(1)	M4-S4(ii)	2.31(1)
mean	2.32	mean	2.28
As/(As + Sb)	0.81(4)	As/(As + Sb)	0.98(4)
M5-S6(iii)	2.335(9)	M6-S8	2.28(1)
M5-S8	2.34(1)	M6-S9	2.296(8)
M5-S7	2.34(1)	M6-S7(ii)	2.31(1)
mean	2.34	mean	2.30
As/(As + Sb)	0.81(4)	As/(As + Sb)	0.91(4)
Bond angles in the bundle			
S2(i)-M1-S9(i)	97.4(4)	S8-M5-S7	87.6(3)
S2(i)-M1-S1(ii)	87.9(3)	S8-M6-S9	98.7(5)
S9(i)-M1-S1(ii)	99.6(4)	S8-M6-S7(ii)	90.5(4)
S1-M2-S3	99.6(5)	S9-M6-S7(ii)	97.0(4)
S1-M2-S2(i)	91.2(3)	M2-S1-M1(iv)	98.4(5)
S3-M2-S2(i)	97.0(5)	M1(vi)-S2-M2(vi)	94.4(4)
S3-M3-S4	97.5(4)	M2-S3-M3	100.6(3)
S3-M3-S5	100.3(5)	M4(iv)-S4-M3	94.2(4)
S4-M3-S5	87.8(3)	M4(i)-S5-M3	98.5(4)
S5-M4-S6	99.0(5)	M4-S6-M5(viii)	100.2(4)
S5-M4-S4(ii)	91.2(4)	M6(iv)-S7-M5	93.8(4)
S6-M4-S4(ii)	97.7(4)	M6-S8-M5	97.9(4)
S6(iii)-M5-S8	99.1(4)	M6-S9-M1(vi)	99.6(4)
S6(iii)-M5-S7	97.1(4)		
Molecular interatomic bond distances			
As7-S13(iii)	2.17(2)	As8-S10	2.24(2)
As7-S11(iii)	2.25(1)	As8-S14	2.24(1)
As7-As8	2.66(1)	As8-As7	2.66(1)
As/(As + Sb)	1.0	As/(As + Sb)	1.0
As9-S11(iv)	2.26(1)	As10-S13(iv)	2.25(2)
As9-S10(v)	2.27(1)	As10-S14(v)	2.28(1)
As9-S12	2.31(1)	As10-S12	2.28(1)
As/(As + Sb)	1.0	As/(As + Sb)	1.0
Molecular bond angles			
S13(iii)-As7-S11(iii)	104.1(5)	S11(iv)-As9-S10(v)	97.0(5)
S13(iii)-As7-As8	101.3(5)	S11(iv)-As9-S12	104.1(4)
S11(iii)-As7-As8	98.5(4)	S10(v)-As9-S12	101.6(4)
S10-As8-S14	102.3(5)	S13(iv)-As10-S14(v)	100.1(6)
S10-As8-As7	100.4(4)	S13(iv)-As10-S12	106.5(4)
S14-As8-As7	100.0(4)	S14(v)-As10-S12	102.0(4)
Intermolecular contacts			
As7-S14(iv)	3.74(1)	As7-S12(iii)	3.80(1)
As7-S10(iv)	3.79(2)		
Molecule-bundle contacts			
As8-S8	3.56(1)	S11-M4	3.30(1)
As8-S5	3.56(1)	S11-M6	3.33(1)
As9-S7	3.37(1)	S11-S4(ii)	3.59(2)
As9-S4	3.38(1)	S11-S7(ii)	3.60(1)
As9-S5	3.78(1)	S12-M5	3.336(8)
As9-S8	3.79(1)	S12-S8	3.49(2)
As10-S1(vi)	3.40(1)	S12-S2	3.60(1)
As10-S2(vii)	3.43(1)	S13-M2(viii)	3.33(1)
As10-S1(viii)	3.86(1)	S13-S1(x)	3.66(2)
S10-M3(ix)	3.38(1)	S13-S2(xi)	3.67(2)
S10-S5(ix)	3.60(2)	S14-M1	3.37(1)
S10-S7(ii)	3.66(2)	S14-S1(ii)	3.59(2)
S10-S4(ix)	3.67(2)	S14-S4(ii)	3.67(1)
S10-S8	3.70(2)	S14-S2(i)	3.69(2)

Note: Symmetry codes are: (i) $1/2 + x, 1/2 - y, z$; (ii) $x, y, -1 + z$; (iii) $1/2 - x, -1/2 + y, 1/2 + z$; (iv) $x, y, 1 + z$; (v) $1/2 - x, 1/2 + y, 1/2 + z$; (vi) $-1/2 + x, 1/2 - y, z$; (vii) $-x, 1 - y, 1/2 + z$; (viii) $1/2 - x, 1/2 + y, -1/2 + z$; (ix) $1/2 - x, -1/2 + y, -1/2 + z$; (x) $-1/2 + x, 1/2 + y, -1/2 + z$; (xi) $-x, 1 - y, -1/2 + z$.

described above. Such a molecule is quite similar to that found in both the synthetic and natural (uzonite) As_4S_5 compound (Whitfield 1973b; Bindi et al. 2003), and in the structure of alacranites

**FIGURE 6.** Mean M-S bond distance plotted against the molar Sb/(As + Sb) ratio. The linear regression ($r = 0.94$) was obtained with the wakabayashilite data (filled squares). The empty squares refer to natural getchellite (Kyono and Kimata 2004).**FIGURE 7.** Sequence of a corrugated twelve-membered -As-S-As-S- ring along [001]. The M and S atoms are pictured in dark and pale grey, respectively.

(Bonazzi et al. 2003a,b). The molecule in β - P_4S_5 also exhibits the same cage-like structure (Wells 1984). The mean As-S distance (2.25 Å) compares favorably with the values usually observed for As-S bonds, although a wider spread of the individual As-S values [from 2.17(2) to 2.31(1) Å] is observed here. The As-As bond distance [2.66(1) Å] is slightly longer than those observed in the other As_4S_5 molecules (2.546 Å, Whitfield 1973b; 2.566 Å, Bonazzi et al. 2003a; 2.527 Å, Bindi et al. 2003). The shortest intermolecular contacts occur between molecules which succeed each other along the [001] direction; in particular, three contacts suitable for van der Waals interactions exist between the apical As7 atom and three S atoms of the nearest molecule [As7-S12(iii) = 3.74(1), As7-S10(iv) = 3.79(2), As7-S12(iv) = 3.80(1) Å].

For this reason, the arrangement of the cage-like molecules in wakabayashilite can be described as forming rods parallel to [001]. By contrast, distances between molecules belonging to different rods are greater than 4.2 Å. In turn, rods of molecules

and bundle-like units are connected by van der Waals interactions. Contacts shorter than 3.85 Å are reported in Table 4. This limit corresponds to that adopted by Mullen and Nowacki (1972) for the case of realgar on the basis of the sum of the van der Waals radii of As and S given by Pauling (1960).

DISCUSSION

Relationships with the average structure

Looking at the orthorhombic unit cell of wakabayashilite (Fig. 3), the reasons for the doubling of the unit-cell volume become evident. Bundle-like units exhibit two different orientations around the 2_1 axis at $0,0, z$ and $1/2, 1/2, z$, respectively; namely, a $[1/2 \ 1/2 \ 0]$ translation vector works for all the S atoms of the bundle-like unit, but does not work for all the As atoms. Therefore, the edges of the pseudo-hexagonal subcell do not correspond to translation vectors for all the atoms.

It is also evident that the occupational disorder and high displacement parameters for both As and S positions of the molecule found in the average structure are due to the different orientation of the As-As bond in the As_4S_5 molecules related by a $[1/2 \ 1/2 \ 0]$ vector. This leads to an apparent $As_4S_4(S\text{---}\square)_2$ molecule in the average model.

Twinning

As shown in Figure 2, half of the nodes of the reciprocal lattice of one individual are overlapped with nodes of the other individual; thus, the ratio of the nodes in the twin cell and in the individual cell is 2. In other words, the reciprocal cell of the orthorhombic individual is two times larger than that of the twin. Therefore, twinning in wakabayashilite can be classified as *non-merohedric*, with the twin index $n_T = 2$. According to Nespolo and Ferraris (2003), the adjective *merohedric* or *non-merohedric* should be preferred to the more ambiguous *merohedral* or *non-merohedral* to avoid any confusion with the characteristics of the individual, which may exhibit a merohedral or non-merohedral point symmetry.

The twin plane (110), which is not a symmetry element in the orthorhombic holohedry, leads to an increase in the symmetry of the lattice $[D(L)]$ from $mmm [D(L)_I]$ to $6/mmm [D(L)_T]$. Obviously, since in this case the twin fraction (0.62) is rather far from 0.50, the hexagonal symmetry only roughly appears in the measured diffraction pattern.

According to the criteria of the new classification recently proposed by Nespolo and Ferraris (2004), the case of wakabayashilite [$n_T > 1$; $D(L)_T \neq D(L)_I$] corresponds to twinning by *reticular merohedry*.

Due to the accidentally specialized metric of the lattice of wakabayashilite involving a strong hexagonal pseudosymmetry, the value of twin obliquity is very low ($\omega = 0.08^\circ$); accordingly, no splitting of reflections was clearly visible, even at relatively high theta angles. Thus, a distinction between *reticular merohedry* and *reticular pseudomerohedry* remains merely speculative.

Effects of light

Previous studies (Douglass et al. 1992; Muniz-Miranda et al. 1996) showed that visible light induces alteration of some arsenic sulfides; in particular, both realgar (α - As_4S_4) and the high temperature polymorph (β - As_4S_4) gradually transform

to pararealgar when exposed to filtered polychromatic light (550 nm long-wavelength pass filter). The initial steps of the light-induced process occur with a strong increase of the unit-cell volume in both realgar and β - As_4S_4 (Bonazzi et al. 1996). Preliminary investigations on non-stoichiometric As_8S_{9-x} crystals (unpublished data), which consist of a disordered mixture of As_4S_4 and As_4S_5 molecules (Bonazzi et al. 2003b), also point toward a light-induced increase of the unit-cell volume. On the contrary, no variations of the unit-cell parameters of uzonite (As_4S_5) were observed after light exposure (Bindi et al. 2003). Therefore, it was hypothesized that the As_4S_4 molecule is able to incorporate additional sulfur to change to As_4S_5 according to the reaction $5As_4S_4 + 3O_2 \rightarrow 4As_4S_5 + 2As_2O_3$, whereas As_4S_5 is not subjected to any sulfur addition (Bindi et al. 2003). To verify this hypothesis, a crystal of wakabayashilite was exposed to light following the same procedure used previously (Bindi et al. 2003) for a total time of 1800 min, with steps of 360 min. The unit-cell parameters, measured after each exposure to light, did not exhibit any significant change (the shifts were within the standard deviations). The results obtained confirm the previous finding of the high stability of the As_4S_5 molecule: in the structure of wakabayashilite, due to its strong hexagonal pseudosymmetry, no crystallographic constraint would prevent the As_4S_5 molecule from transforming into As_4S_6 . Nevertheless this transformation does not occur.

It should also be noted that the (As,Sb):S ratio in wakabayashilite (0.71) is intermediate between that of uzonite (0.80) and orpiment (0.67). Accordingly, its structure contains both cage-like molecular units as in the case of uzonite and arsenic sulfides having As:S < 0.80, and layers, although rolled, as in orpiment. Again, this indicates the non-stability of a hypothetical As_4S_6 cage-like molecule.

ACKNOWLEDGMENTS

The authors thank H. Effenberger and an anonymous referee for their accurate revisions. This work was funded by M.I.U.R., CoFin 2003, project "Structural complexity in minerals: modulation and modularity".

REFERENCES CITED

- Bayliss, P. and Nowacki, W. (1972) Refinement of the crystal structure of stibnite, Sb_2S_3 . *Zeitschrift für Kristallographie*, 135, 308–315.
- Bindi, L., Popova, V., and Bonazzi, P. (2003) Uzonite, As_4S_5 , from the type locality: single-crystal X-ray study and effects of exposure to light. *Canadian Mineralogist*, 41, 1419–1424.
- Blessing, R.H. (1995) An empirical correction for absorption anisotropy. *Acta Crystallographica*, A51, 33–38.
- Bolte, M. (2004) TWINLAW and HKLF5: two programs for the handling of non-merohedral twins. *Journal of Applied Crystallography*, 37, 162–165.
- Bonazzi, P., Borrini, D., Mazzi, F., and Olmi, F. (1995a) Crystal structure and twinning of $Sb_2As_2S_2$, the synthetic analogue of päikkönenite. *American Mineralogist*, 80, 1054–1058.
- Bonazzi, P., Menchetti, S., and Pratesi, G. (1995b) The crystal structure of pararealgar, As_4S_4 . *American Mineralogist*, 80, 400–403.
- Bonazzi, P., Menchetti, S., Pratesi, G., Muniz-Miranda, M., and Sbrana, G. (1996) Light-induced variations in realgar and β - As_4S_4 : X-ray diffraction and Raman studies. *American Mineralogist*, 81, 874–880.
- Bonazzi, P., Bindi, L., Popova, V., Pratesi, G., and Menchetti, S. (2003a) Alacranite, As_8S_9 : structural study and re-assignment of the original chemical formula. *American Mineralogist*, 88, 1796–1800.
- Bonazzi, P., Bindi, L., Olmi, F., and Menchetti, S. (2003b) How many alacranites do exist? A structural study of non-stoichiometric As_8S_{9-x} crystals. *European Journal of Mineralogy*, 15, 283–288.
- Borodayev, Ju.S., Mozgova, N.N., Ozerova, N.A., Bortnikov, N.S., Ojvanen, P., and lleutujnen, V. (1982) Päikkönenite, $Sb_2As_2S_2$, a new mineral from Seinäjoki ore region in Finland. *International Geology Review*, 24, 1234–1240.
- Burns, P.C. and Percival, J.B. (2001) Alacranite, As_4S_4 : a new occurrence, new

- formula, and determination of the crystal structure. *Canadian Mineralogist*, 39, 809–818.
- Dougllass, D.L., Shing, C., and Wang, G. (1992) The light-induced alteration of realgar to pararealgar. *American Mineralogist*, 77, 1266–1274.
- Gruzdev, V.S., Volgin, V.Y., Shumkova, N.G., Chernitsova, N.M., and Ivanov, V.S. (1975) Wakabayashilite, $(\text{As,Sb})_2\text{S}_3$, from arsenic-antimony-mercury deposits of the U.S.S.R. *Doklady Earth Science Sections*, 224, 418–421.
- Guillermo, T.R. and Wuensch, B.J. (1973) The crystal structure of getchellite, AsSbS_3 . *Acta Crystallographica*, B29, 2536–2541.
- Ibers, J.A. and Hamilton, W.C., Eds. (1974) *International Tables for X-ray Crystallography*, IV, 366. Kynock, Dordrecht, The Netherlands.
- Johan, Z. and Mantiene, J. (2000) Thallium-rich mineralization at Jas Roux, Hautes-Alpes, France: a complex epithermal, sediment-hosted, ore-forming system. *Journal of Czech Geological Society*, 45, 81–98.
- Kato, A., Sakurai, K.I., and Oshumi, K. (1970) Introduction to Japanese minerals. Geological Survey of Japan, 1970, 92–93.
- Kutoglu, A. (1976) Darstellung und Kristallstruktur einer neuen isomeren Form von As_4S_4 . *Zeitschrift für anorganische und allgemeine Chemie*, 419, 176–184.
- Kyono, A. and Kimata, M. (2004) Structural reinvestigation of getchellite $\text{As}_{0.98}\text{Sb}_{1.02}\text{S}_{3.00}$. *American Mineralogist*, 89, 696–700.
- Mullen, D.J.E. and Nowacki, W. (1972) Refinement of the crystal structures of realgar AsS and orpiment As_2S_3 . *Zeitschrift für Kristallographie*, 136, 48–65.
- Muniz-Miranda, M., Sbrana, G., Bonazzi, P., Menchetti, S., and Pratesi G. (1996) Spectroscopic investigation and normal mode analysis of As_4S_4 polymorphs. *Spectrochimica Acta*, A52, 1391–1401.
- Nakai, I., Yokoi, H., and Nagashima, K. (1986) Crystal chemistry of the system As-Sb-S: synthesis of wakabayashilite and synthetic study on the solid solutions in the As_2S_3 - Sb_2S_3 system. *Mineralogical Journal*, 13, 212–222.
- Nespolo, M. and Ferraris, G. (2003) Geminography—The science of twinning applied to the early-stage derivation of non-merohedric twin laws. *Zeitschrift für Kristallographie*, 218, 178–181.
- — — (2004) Applied geminography—symmetry analysis of twinned crystals and definition of twinning by reticular polyhohedry. *Acta Crystallographica*, A60, 89–95.
- North, A.C.T., Phillips, D.C., and Mathews, F.S. (1968) A semiempirical method of absorption correction. *Acta Crystallographica*, A24, 351–359.
- Otwinosky, Z. and Minor, W. (1997) Processing of X-ray diffraction data collected in oscillation mode. In C.W. Carter Jr. and R.M. Sweet, Eds., *Method in Enzymology: Molecular Crystallography*, Part A, p. 30–326. Academic, New York.
- Pauling, L. (1960) The nature of the chemical bond and the structure of molecules and crystals: An introduction to modern structural chemistry (3rd edition), 644 p. Cornell University Press, Ithaca, New York.
- Porter, E.J. and Sheldrick, G.M. (1972) Crystal structure of a new crystalline modification of tetra-arsenic tetrasulphide (2,4,6,8-tetrathia-1,3,5,7-tetra-arsatricyclo [3,3,0,0] octane). *Journal of Chemical Society, Dalton Transactions*, 13, 1347–1349.
- Samsonova, N.S., Zhabin, A.G., Chvileva, T.N., and Georgievskaya, O.M. (1990) New data on the mineralogy of the Lukhumi arsenic deposit (central Caucasus). *Mineralogicheskii Zhurnal*, 12, 84–94.
- Scott, D.J. and Nowacki, W. (1975) New data on wakabayashilite. *Canadian Mineralogist*, 13, 418–419.
- — — (1976) The substructure of wakabayashilite $(\text{As,Sb})_{20}\text{S}_{30}$. *Zeitschrift für Kristallographie*, 144, 422.
- Sheldrick, G.M. (1997a) SHELXS-97. A program for automatic solution of crystal structures. University of Göttingen, Germany.
- — — (1997b) SHELXL-97. A program for crystal structure refinement. University of Göttingen, Germany.
- Spiridonov, E.M. (1989) Wakabayashilite $(\text{As,Sb})_{11}\text{S}_{18}$ of the Khaidarkan deposit. *Novye Dannye Mineralakh*, 36, 166–170.
- Weissberg, B.G. (1965) Getchellite, AsSbS_3 , a new mineral from Humboldt County, Nevada. *American Mineralogist*, 50, 1817–1826.
- Wells, A.F. (1984) *Structural Inorganic Chemistry*. 5th Ed. Oxford University Press, London, UK.
- Whitfield, H.J. (1970) The crystal structure of tetra-arsenic trisulfide. *Journal of Chemical Society, Dalton Transactions*, 1800–1803.
- — — (1973a) Crystal structure of the β -form of tetra-arsenic trisulfide. *Journal of Chemical Society, Dalton Transactions*, 1737–1738.
- — — (1973b) Crystal and molecular structure of tetra-arsenic pentasulphide. *Journal of Chemical Society, Dalton Transactions*, 1740–1742.
- Zhang, B. (1985) The discovery of wakabayashilite in China. *Acta Mineralogica Sinica*, 5, 270–274.

MANUSCRIPT RECEIVED SEPTEMBER 4, 2004

MANUSCRIPT ACCEPTED DECEMBER 18, 2004

MANUSCRIPT HANDLED BY BRYAN C. CHAKOUMAKOS