Alacranite, As$_8$S$_9$: structural study of the holotype and re-assignment of the original chemical formula

Paola Bonazzi,[1,*] Luca Bindi,[1,2] Valentina Popova,[3] Giovanni Pratesi,[1,2] and Silvio Menchetti[1]

[1]Dipartimento di Scienze della Terra, Università degli Studi di Firenze, via La Pira 4, Firenze, Italy
[2]Museo di Storia Naturale, sez. di Mineralogia e Litologia, Università degli Studi di Firenze, via La Pira 4, Firenze, Italy
[3]Institute for Mineralogy, Urals Branch of RAS, Chelyabinsk district, Miass 456317, Russian Federation

Abstract

Alacranite from the type locality (Uzon caldera, Kamchatka, Russian Federation) was submitted for structural analysis. A single crystal was selected and the following lattice parameters were determined: a = 9.942(4), b = 9.601(2), c = 9.178(3) Å, β = 101.94(3)°, V = 857.1 (5) Å^3. The crystal structure was solved in the $P2/c$ space group using direct methods and refined to R = 6.79% for 472 observed reflections. The structure of alacranite consists of an ordered sequence of As$_4$S$_4$ and As$_4$S$_5$ cage-like molecules, with a molecular packing closely resembling that found in the β-As$_4$S$_4$ phase. Both As-As and As-S intramolecular distances are in the range usually observed for covalent bonds. The structural model confirms the chemical formula As$_8$S$_9$ for alacranite, and accounts for differences in the unit-cell parameters of alacranite compared to those of the natural analogue of β-As$_4$S$_4$. This latter mineral, therefore, should receive a new name.

Introduction

Alacranite, As$_8$S$_9$, was first found by Popova et al. (1986) at the Uzon caldera (Kamchatka, Russian Federation). Due to the similarity of its XRD powder pattern, these authors assumed the mineral to be identical to the species occurring in the Ag-As-Sb vein deposit at Alacràn (Chile) and described by Clark (1970) as a natural high-temperature As$_4$S$_4$ phase. For this reason, the mineral was named alacranite. However, the lattice parameters of alacranite resemble barely those of the natural β-phase from Alacràn (Clark 1970) and those of synthetic β-As$_4$S$_4$ (Porter and Sheldrick 1972; Bonazzi et al. 1996). In particular, alacranite exhibits a greater unit-cell volume, in keeping with the different chemical composition. Due to the low diffraction quality of alacranite crystals, the crystal structure remained unsolved; however, single crystal X-ray rotation photographs indicated space group $P2/c$, while synthetic β-As$_4$S$_4$ crystallizes in space group $C2/c$ (Porter and Sheldrick 1972). The mineral and name were approved by the NMMN-IMA Commission (Hawthorne et al. 1988) for a species having chemical formula As$_8$S$_9$ and space group $P2/c$.

During seafloor sampling around Lihir Island (Papua New Guinea), a specimen consisting mainly of pyrite, sphalerite, and galena, together with red and orange arsenic sulfides, was recovered from the top of Conical Seamount (Percival et al. 1999). According to these authors, the XRD analysis of both the deep-red and orange crystals revealed a mixture of realgar and alacranite. Subsequently, Burns and Percival (2001) showed that the mineral from Papua New Guinea was structurally and chemically identical to synthetic β-As$_4$S$_4$, and supposed that the original formula of alacranite (As$_8$S$_9$) had been incorrectly determined. As a consequence, alacranite was reported with chemical formula As$_4$S$_4$ and space group $C2/c$ in the recently published *Mineralogical Tables* (Strunz and Nickel 2001) as well as in *The American Mineralogist crystal structure database* (Downs and Hall-Wallace 2003).

More recently, Bonazzi et al. (2003) studied non-stoichiometric sulfide minerals from the Katerina mine (Czeck Republic) with chemical compositions ranging continuously from As$_8$S$_8$ to As$_8$S$_9$, and observed a gradual change of the translation lattice symmetry from C to P, together with a linear increase of unit-cell volume as a function of the S content.

From the results of their structural study, Bonazzi et al. (2003) also found that the non-stoichiometric As$_8$S$_{9–x}$ compounds crystallize as disordered mixtures of As$_4$S$_4$ and As$_4$S$_5$ molecules packed in the same way as in the β–As$_4$S$_4$ phase. Because the As$_8$S$_9$ stoichiometry (alacranite s.s.) seems to be the upper limit of the compositional range, the non-stoichiometric sulfides from Katerina mine were assumed to consist of both As$_4$S$_4$ ($C2/c$) and As$_8$S$_9$ ($P2/c$) microdomains. This hypothesis explains the observed gradual change of the translation symmetry along the series. On this basis, one can speculate that the alacranite structure consists of an ordered sequence of As$_4$S$_4$ and As$_4$S$_5$ molecules.

In order to check this hypothesis, a crystal of the original sample from the Uzon caldera was examined from the structural point of view.

Experimental and structure solution

Several crystals of the alacranite holotype (preserved at the Institute for Mineralogy, Urals Branch of RAS, Chelyabinsk district, Miass 456317, Russian Federation, catalogue number U-2) were mounted on an Enraf-Nonius CAD4 single-crystal diffractometer and examined with graphite-monochromatized Mo$K\alpha$ radiation. Most were found to be composed of multiple crystallites. A single crystal (approximately 30 × 60 × 120 mm) of relatively high diffraction quality was selected for the structural study.

Unit-cell dimensions (reported in Table 1 together with data from the litera-

* E-mail: pbcry@geo.unifi.it

ture) were determined by least-squares refinement of the setting angles of 25 reflections ($10° < \theta_{MoK\alpha} < 13°$). Although the strongest reflections were those having $h + k = 2n$, several intensities violating the C lattice symmetry were observed. Moreover, $h0l$ reflections with $l = 2n+1$ were systematically absent. Therefore, the space group $P2/c$ previously determined by Popova et al. (1986) was confirmed. Intensity data were collected ($-9 < h < 9$, $-9 < k < 9$, $0 < l < 8$) in the range $2 < \theta_{MoK\alpha} < 20°$, ω-scan mode, with a scan-width of 3.2° and a scan-speed of 1.65 °/min. Intensities were treated for Lorentz-polarization effects and subsequently corrected for absorption following the semi-empirical method of North et al. (1968). Monoclinic-equivalent reflections (1738) were averaged ($R_{sym} = 13.5\%$) and reduced to structure factors.

The crystal structure was solved in the $P2/c$ space group using direct methods in the SHELXS-97 package (Sheldrick 1997) and Fourier syntheses. The positions of all of the atoms were located on an F_o– Fourier map. Structure refinement was performed using SHELXL-93 (Sheldrick 1993). The scattering curves for neutral As and S were taken from the *International Tables for X-ray Crystallography,* volume IV (Ibers and Hamilton 1974). By means of anisotropic full-matrix least-squares cycles (80 parameters refined), the refinement quickly converged to $R = 6.79 \%$ for 472 observed reflections [according to the criterion $F_o > 4\sigma(F_o)$] and $R = 12.58\%$ for all 806 independent reflections. Inspection of the difference Fourier map revealed maximum positive and negative peaks of 1.81 and 0.82 e$^-$/Å^3, respectively. Fractional atomic coordinates and anisotropic-displacement parameters are shown in Table 2. Table 3[1] lists the observed and calculated structure factors.

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[1]For a copy of Table 3, document item AM-03-044, 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.

TABLE 1. Unit-cell parameters for crystals ranging from β-As_4S_4 to alacranite

	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)
CL*	9.97(1)	9.29(1)	8.88(1)	102.6(1)	803(2)
B2	9.958(2)	9.311(2)	8.867(2)	102.57(1)	802.4(3)
B1	9.962(2)	9.313(1)	8.871(2)	102.54(1)	803.4(2)
PS	9.957(3)	9.335(4)	8.889(5)	102.48(4)	806.7(6)
BP	9.943(1)	9.366(1)	8.908(1)	102.007(2)	811.4(1)
ALA15	9.940(2)	9.398(2)	9.033(2)	102.12(2)	825.0(3)
KG	9.89(1)	9.46(1)	9.05(1)	103.0(5)	825(2)
ALA2	9.936(2)	9.458(2)	9.106(2)	101.90(2)	837.3(3)
ZO	9.87(1)	9.73(3)	9.16(2)	101.52(4)	858(4)
PPV	9.89(2)	9.73(2)	9.13(1)	101.84(5)	860(3)
This study	9.942(4)	9.601(2)	9.178(3)	101.94(3)	857.1(5)

Note: CL = natural β-As_4S_4 from Alacràn Mine, Chile (Clark 1970); B2, B1 = synthetic β-As_4S_4 phase (Bonazzi et al. 1996); PS = synthetic β-As_4S_4 (Porter and Sheldrick 1972); BP = natural β-As_4S_4 (Burns and Percival 2001); ALA15 = $As_8S_{8.42}$ crystal from the burning dump at Katerina Mine (Bonazzi et al. 2003); KG = synthetic $As_2S_{2.15}$ (Kothiyal and Ghosh 1976); ALA2 = $As_8S_{8.70}$ crystal from the burning dump at Katerina Mine (Bonazzi et al. 2003); ZO = alacranite from Katerina Mine (Žáček and Ondruš 1997); PPV = alacranite from Uzon caldera, Kamchatka (Popova et al. 1986).
* Indexed by the present authors.

RESULTS AND DISCUSSION

The structure of alacranite consists of an ordered sequence of two different kinds of cage-like molecules, with a molecular packing closely resembling that found in the β-phase (Figs. 1 and 2). The first one (2As1 + 2As2 + S1 + S2 + 2S3) is identical to the As_4S_4 molecule found in the structures of both realgar and the β-phase (Mullen and Nowacki 1972; Porter and Sheldrick 1972), in that each As atom links one As and two S atoms. The other molecule (2As3 + 2As4 + S5 + 2S4 + 2S6) is chemically and structurally identical to that found in the As_4S_5 compound (Whitfield 1973a). In such a molecule, two As atoms link one As and two S atoms, whereas the other two As atoms link three S atoms. As shown in Figures 1 and 2, the ordering of these two different kinds of molecules accounts for the change of the translation symmetry from C (β-phase) to P (alacranite).

Table 4 gives the intramolecular distances in the alacranite structure. The As-S bond distances are within the range (2.21–2.24 Å) usually observed for covalent As-S bonds (2.228–2.247 Å in the structure of realgar, Mullen and Nowacki 1972; 2.238–2.252 Å in the synthetic β-phase, Porter and Sheldrick 1972; 2.216–2.232 Å in the natural β-phase from Papua New Guinea, Burns and Percival 2001; 2.23–2.26 Å in pararealgar, Bonazzi et al. 1995; 2.229–2.268 Å in synthetic As_4S_5, Whitfield 1973a; 2.199–2.220 Å in synthetic α-As_4S_3, Whitfield 1970; 2.218–2.234 Å in synthetic β-As_4S_3, Whitfield 1973b). The As-As bond distances within the As_4S_4 molecule [2.579(5) Å] are similar to those observed in both synthetic and natural β-phase [2.593(6) Å, Porter and Sheldrick 1972; 2.596(2) Å, Burns and Percival 2001] and somewhat longer than those observed in the As_4S_4 molecule in pararealgar [2.484(4) and 2.534(4) Å, Bonazzi et al. 1995]. The As-As bond distance within the As_4S_5 molecule [2.566(6) Å] compares favorably with the value observed in synthetic As_4S_5 (2.546 Å, Whitfield 1973a).

The shortest S-S, As-S, and As-As intermolecular contacts are the following: 3.55(1) (S3-S4), 3.348(8) (As2-S6), and 3.690(4) Å (As2-As3).

The X-ray powder pattern calculated using the structural data obtained in this study matches closely that originally observed for the type material (Table 5).

CRYSTAL CHEMICAL REMARKS

Both the As_4S_4 and As_4S_5 molecules, as well as the As_4S_3 molecule found in the structure of both α-dimorphite (Whitfield 1970) and β-dimorphite (Whitfield 1973b), can be described as $As_4S_n\square_{6-n}$ ($n = 3$, 4, and 5) groups, with As atoms located at the vertices of a disphenoid (more or less regular) and S atoms

TABLE 2 Fractional atomic coordinates and anisotropic displacement parameters for alacranite from the type locality

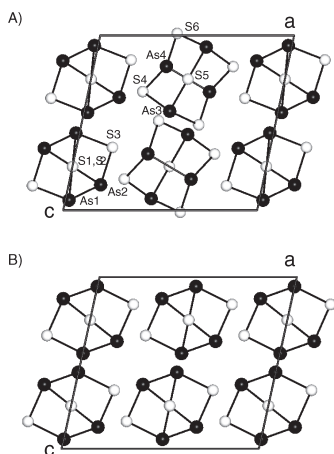|	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}
As1	0.0190(3)	0.2227(4)	0.9418(4)	0.054(2)	0.075(3)	0.043(2)	0.011(2)	0.008(2)	0.018(2)	0.058(1)
As2	0.1653(3)	0.4149(3)	0.8541(4)	0.036(2)	0.043(2)	0.064(2)	−0.003(2)	0.001(2)	−0.009(2)	0.049(1)
As3	0.4408(3)	0.3214(3)	0.4333(3)	0.058(2)	0.035(2)	0.037(2)	−0.010(2)	0.013(2)	−0.005(2)	0.043(1)
As4	0.3750(3)	0.0312(3)	0.1774(3)	0.057(2)	0.045(2)	0.036(2)	−0.017(2)	0.015(2)	−0.015(2)	0.045(1)
S1	0	0.0768(12)	3/4	0.082(9)	0.034(8)	0.098(10)	0	0.012(8)	0	0.072(4)
S2	0	0.5590(13)	3/4	0.076(9)	0.031(8)	0.165(15)	0	−0.020(9)	0	0.097(6)
S3	0.1854(8)	0.3210(12)	0.6404(9)	0.034(5)	0.117(9)	0.053(6)	−0.005(5)	0.021(4)	0.002(6)	0.067(3)
S4	0.2806(7)	0.1733(8)	0.3216(8)	0.029(4)	0.051(5)	0.035(4)	0.008(4)	0.019(4)	−0.006(4)	0.036(2)
S5	1/2	0.4457(11)	1/4	0.071(8)	0.031(6)	0.043(7)	0	0.027(6)	0	0.046(3)
S6	0.3944(8)	0.1671(8)	−0.0114(9)	0.056(5)	0.040(5)	0.037(4)	0.009(4)	0.008(4)	0.007(4)	0.045(2)

FIGURE 1. Crystal structure of alacranite (**A**) viewed along the **b** axis, compared with the homologous projection of the structure of the β-As$_4$S$_4$ phase (**B**).

FIGURE 2. Crystal structure of alacranite (**A**) viewed along the **c** axis, compared with the homologous projection of the structure of the β-As$_4$S$_4$ phase (**B**).

TABLE 4. Selected interatomic distances (Å) and angles (°) for alacranite from the type locality

As$_4$S$_4$ molecule			As$_4$S$_5$ molecule		
Intramolecular bond distances					
As1-S3*	2.226(9)		As3-S6†		2.215(9)
As1-S1	2.227(9)		As3-S4		2.221(8)
As1-As2	2.579(5)		As3-S5		2.238(7)
As2-S3	2.205(9)		As4-S6		2.209(8)
As2-S2	2.209(9)		As4-S4		2.238(8)
As2-As1	2.579(5)		As4-As4†		2.566(6)
Intramolecular bond angles					
S1-	As1-S3*	94.4(3)	S4 -	As3-S5	105.6(3)
	As1-As2	99.5(2)		As3-S6†	97.6(3)
S3*-	As1-As2	97.2(3)	S5-	As3-S6†	107.9(3)
S3-	As2-S2	93.9(3)	S4-	As4-S6	102.7(3)
	As2-As1	98.4(3)		As4-As4†	99.9(2)
S2-	As2-As1	99.6(3)	S6-	As4-As4†	100.1(3)
As-	S1-As1*	102.1(5)	As3-	S4-As4	108.4(3)
As2-	S2-As2*	102.4(5)		S5-As3†	115.6(5)
	S3-As1*	103.3(3)	As4-	S6-As3†	108.7(4)

Notes: symmetry codes: * = −*x*, *y*, 3/2−*z*; † = 1−*x*, *y*, 1/2−*z*.

FIGURE 3. As$_4$ polyhedral volume vs. the [$n/(6 − n)$] ratio (saturation factor). Filled circles refer to As$_4$S$_4$ and As$_4$S$_5$ molecules in the structure of alacranite from Kamchatka (this study). Empty symbols refer to data from literature: α-As$_4$S$_3$ (Whitfield 1970); β-As$_4$S$_3$ (Whitfield 1973b); β-As$_4$S$_4$ (Porter and Sheldrick 1972); As$_4$S$_5$ (Whitfield 1973a).

bridging *n* among the six available (As-As) edges. There are (6–*n*) disphenoid edges corresponding to As-As bonds, while the other *n* correspond to longer non-bonded As-As distances. As a consequence, the number of long edges increases with increasing S content. Accordingly, the polyhedral volume of the As$_4$ disphenoidic group also increases. As shown in Figure 3, a linear relationship between the As$_4$ polyhedral volume and the $n/(6 − n)$ ratio (saturation factor) exists: V(As$_4$) = 2.37(2) + 0.444(7) [$n / (6 − n)$] (Å^3). Data (solid symbols in Fig. 3) relative to both molecular groups in alacranite fit the regression line very well, thus further confirming the ordered location of S atoms around the As$_4$ groups. Due to the generally low diffraction quality of most of the molecular As-sulfides, probably related to non-stoichiometry or/and S disorder around the As$_4$-group, this model can represent an useful tool to evaluate the degree of S-saturation in this kind of molecule. As previously shown by Bonazzi et al. (2003) for compounds with chemical compositions ranging from As$_4$S$_4$ to As$_8$S$_9$, the unit-cell vol-
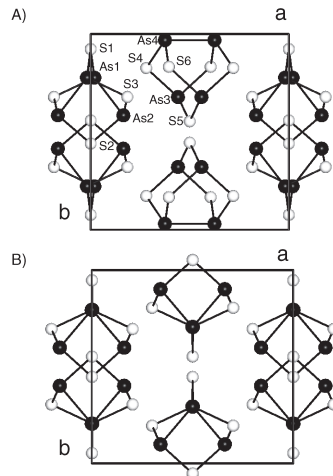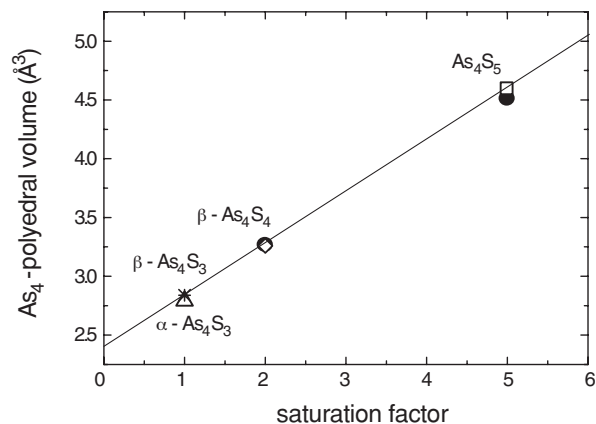
ume increases linearly with increasing S content. In Figure 4, the linear relationship between the unit-cell volume (normalized to 16 As atoms per unit cell) and the S content is shown. Data for duranusite (As$_4$S, unknown crystal structure), α-dimorphite (As$_4$S$_3$, space group *Pnam*), β-dimorphite (As$_4$S$_3$, space group *Pnam*), and uzonite (As$_4$S$_5$, space group *P*2$_1$/*m*), despite the different molecular packings, are also consistent with the model obtained (Bonazzi et al. 2003). These data were therefore included and a new regression line was obtained. Taken together, data shown in Figures 3 and 4 clearly indicate that, as S increases, the unit-cell volume increases accordingly, not only as a consequence of the "external" hindrance of the molecule, but also because of the increase of the As$_4$ group volume.

Structural evidence, together with the previously acquired chemical data (Popova et al. 1986), definitively confirms the chemical formula As$_8$S$_9$ for the mineral found at the Uzon

TABLE 5. Calculated and observed X-ray powder diffraction data for alacranite from the type locality

h k l	d_{calc} (Å)	I/I_{calc}	d_{obs} (Å)*	I/I_o*	h k l /*	h k l	d_{calc} (Å)	I/I_{calc}	d_{obs} (Å)*	I/I_o*	h k l /*
1 1 0	6.8330	33	6.89	40	1 1 0	$\bar{1}$ 4 2	2.1116	18	–	–	
$\bar{1}$ 1 1	5.8638	89	5.91	90	$\bar{1}$ 1 1	$\bar{4}$ 1 3	2.0640	5			
1 1 1	5.0927	71	5.11	80	1 1 1	1 1 4	2.0463	6	–	–	
2 0 0	4.8635	29	4.87	30	0 2 0	4 2 1	2.0250	8 }	2.017	20	4 2 1
$\bar{1}$ 0 2	4.4410	8	–	–		$\bar{2}$ 2 4	2.0153	5 }			
1 2 0	4.3048	7	4.25	10	0 2 1	$\bar{3}$ 1 4	2.0098	6	–	–	
0 2 1	4.2335	12 }				$\bar{4}$ 3 1	1.9604	6 }	1.9584	20	$\bar{3}$ 3 3
$\bar{2}$ 1 1	4.2238	4 }				3 1 3	1.9603	4 }			
$\bar{1}$ 1 2	4.0307	58	4.05	70	$\bar{1}$ 1 2	$\bar{3}$ 3 3	1.9546	8			
2 1 1	3.6514	5	–	–		5 0 0	1.9454	12	–	–	
2 2 0	3.4165	9	3.38	30	$\bar{2}$ 2 1	4 3 0	1.9362	5 }	1.9326	20	
0 2 2	3.2791	69	3.291	50	0 2 2	4 1 2	1.9336	6 }			
3 1 0	3.0719	68	3.064	100	3 1 0	3 4 0	1.9292	8			
2 2 1	3.0493	87 }				$\bar{4}$ 3 2	1.8951	7			
1 3 0	3.0400	19 }				0 4 3	1.8725	12	–	–	
2 0 2	3.0037	19				$\bar{1}$ 5 1	1.8587	6	–	–	
$\bar{1}$ 3 1	2.9377	16 }	2.950	90	$\bar{2}$ 2 2	3 4 1	1.8402	5	–	–	
$\bar{2}$ 2 2	2.9319	100 }				$\bar{1}$ 1 5	1.8025	4	–	–	
$\bar{1}$ 1 3	2.9010	36	2.903	20	$\bar{1}$ 1 3	5 1 1	1.7927	5	1.7954	10	
$\bar{3}$ 2 1	2.7046	29	2.707	30	$\bar{3}$ 2 1	1 3 4	1.7525	5	–	–	
$\bar{2}$ 3 1	2.6459	4	–	–		$\bar{4}$ 4 1	1.7248	18	1.7295	20	
1 1 3	2.6060	13	2.606	20	$\bar{1}$ 3 2	1 5 2	1.7128	7	–	–	
1 3 2	2.4449	10	2.419	20	4 0 0	$\bar{3}$ 1 5	1.7026	19	1.7054	20	
$\bar{2}$ 2 3	2.4335	5 }				3 0 4	1.6893	12 }	1.6821	30	3 0 4
$\bar{4}$ 1 1	2.4014	4 }				0 2 5	1.6820	17 }			
1 2 3	2.3584	16 }	2.346	20	$\bar{4}$ 0 2	2 4 3	1.6762	26			
3 1 2	2.3312	12 }				$\bar{5}$ 3 2	1.6572	7	–	–	
$\bar{3}$ 3 1	2.2884	6 }	2.286	10	3 3 0	$\bar{6}$ 1 1	1.6323	11 }	1.6281	20	$\bar{6}$ 1 1
3 3 0	2.2777	5 }				2 3 4	1.6303	5 }			
1 4 1	2.2289	9 }	2.224	30	$\bar{2}$ 0 4	$\bar{5}$ 1 4	1.6248	7	–	–	
$\bar{2}$ 0 4	2.2205	22 }				2 5 2	1.6179	8	–	–	
$\bar{1}$ 3 3	2.2053	24 }				$\bar{3}$ 5 2	1.6064	4 }	1.5922	10	6 1 0
4 1 1	2.1754	4	–	–		$\bar{2}$ 5 3	1.5877	5 }			
4 2 0	2.1693	10 }	2.166	20	4 2 0	$\bar{4}$ 4 3	1.5862	5	–	–	
$\bar{3}$ 3 2	2.1620	8 }				1 6 0	1.5789	9	–	–	
3 2 2	2.1489	16 }	2.136	20	3 3 1	5 2 2	1.5721	8	–	–	
3 3 1	2.1350	6 }				$\bar{6}$ 1 3	1.5473	5	–	–	

Notes: d values calculated on the basis of a = 9.942(4), b = 9.601(2), c = 9.178(3) Å, β = 101.94(3)°. Intensities calculated using XPOW software, version 2.0 (Downs et al. 1993). Only reflections with I/I_{calc} > 4 are listed.
* = observed powder pattern originally reported by Popova et al. (1986).
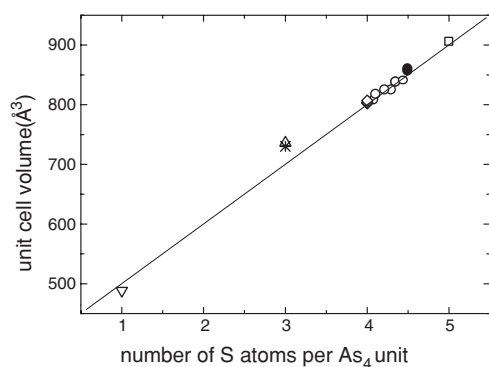

FIGURE 4. Unit-cell volume vs. the S content (atoms per As₄ unit); empty circles refer to As₈S₉₋ₓ compounds (Kothiyal and Ghosh 1976; Bonazzi et al. 2003); filled circles refer to alacranite from Kamchatka (Popova et al. 1986; this study); diamonds: synthetic β-As₄S₄ (Porter and Sheldrick 1972; Bonazzi et al. 1996); square: synthetic As₄S₅ (Whitfield 1973a); empty up-triangle and star refer to α-dimorphite (Whitfield 1970) and β-dimorphite (Whitfield 1973b), respectively; down-triangle refers to duranusite (Márquez-Zavalía et al. 1999). Data fit the regression line: y = 407.6 + 99.6x; r = 0.992.

caldera (Kamchatka, Russian Federation) and named alacranite in 1986. In this context, it also appears that the mineral discovered on the seafloor around Lihir Island (Papua New Guinea) is the natural analogue of β-As₄S₄. Due to its different chemical composition and space group, this mineral should not be called alacranite, but it deserves its own name.

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