Mineralogical Magazine, February 2015, Vol. 79(1), pp. 121–131

From ancient pigments to modern optoelectronic applications of arsenic sulfides: bonazziite, the natural analogue of β-As_4S_4 from Khaidarkan deposit, Kyrgyzstan

Luca Bindi[1,*], Giovanni Pratesi[1,2], Maurizio Muniz-Miranda[3], Matteo Zoppi[2], Laura Chelazzi[4], Giovanni O. Lepore[1] and Silvio Menchetti[1]

[1] Dipartimento di Scienze della Terra, Università degli Studi di Firenze, Via La Pira 4, I-50121, Florence, Italy
[2] Museo di Storia Naturale, Sezione Mineralogia e Litologia, Università degli Studi di Firenze, Via La Pira 4, I-50121, Florence, Italy
[3] Dipartimento di Chimica "Ugo Schiff", Università degli Studi di Firenze, Via della Lastruccia 3, I-50019, Sesto Fiorentino, Florence, Italy
[4] Dipartimento di Chimica "G. Ciamician", Università di Bologna, Via Zamboni 33, I-40126, Bologna, Italy

[*Received 21 May 2014; Accepted 10 July 2014; Associate Editor: A. Christy*]

ABSTRACT

Bonazziite is a new mineral from Khaidarkan deposit, Kyrgyzstan and represents the natural analogue of the β-form of the well known As_4S_4 compound. It occurs as rare crystals up to 100 μm across associated with realgar, sulfur, wakabayashilite, alacránite, non-stoichiometric As_4S_{4+x} sulfides and stibnite in a calcite matrix. In thick section, bonazziite is opaque with a resinous lustre and a dark-orange streak. It is brittle; the Vickers hardness (VHN_{15}) is 70 kg/mm^2 (range: 60−76) (Mohs hardness of ~2½). In plane-polarized incident light, bonazziite is strongly bireflectant and pleochroic from orange to light red. The mineral shows orange to red internal reflections. Between crossed polars, the mineral is strongly anisotropic with greyish to light-blue rotation tints. Reflectance percentages in air for $R_{\min}$ and $R_{\max}$ are 19.9, 22.2 (471.1 nm), 19.1, 21.3 (548.3 nm), 18.8, 19.7 (586.6 nm) and 17.8, 18.9 (652.3 nm), respectively. Bonazziite is monoclinic, space group $C2/c$, with $a = 9.956(1)$, $b = 9.308(1)$, $c = 8.869(1)$ Å, $\beta = 102.55(2)^\circ$ and $V = 802.3(2)$ Å^3, $Z = 4$. The crystal structure [$R_1 = 0.0263$ for 735 reflections with $F_o > 4\sigma(F_o)$] is based on the As_4S_4 cage-like molecule, in which each As atom links one As and two S atoms. The As_4S_4 molecule is identical to that found in the structure of realgar. The six strongest powder diffraction lines [d in Å (I/I_0) (hkl)] are: 5.74 (100) ($\bar{1}11$); 4.10 (60) (021); 3.92 (50) ($\bar{1}12$); 3.12 (60) (022, 310); 2.95 (50) (221, 202); 2.86 (80) ($\bar{2}22$, $\bar{1}31$). A mean of six electron microprobe analyses gave the formula $As_{3.95}S_{4.05}$, on the basis of eight atoms. The new mineral has been approved by the International Mineralogical Association Commission on New Minerals, Nomenclature and Classification (IMA No. 2013-141) and named for Paola Bonazzi, in recognition of her seminal contributions to the study of arsenic sulfides and their alteration induced by exposure to light.

Keywords: arsenic sulfides, chemical composition, Raman spectroscopy, X-ray diffraction, new mineral, molecules, bonazziite.

Introduction

Synthetic analogues of certain arsenic-sulfide minerals, as well as bulk glasses and thin films in the As−S system, are of interest to physicists and material scientists and are widely studied for their potential or actual application in optics and optoelectronics, mainly because of reversible and/or irreversible photo-induced changes of their physico-chemical properties (Holomb *et al.*, 2005; Němec *et al.*, 2005). Due to their

---

[*] E-mail: luca.bindi@unifi.it

DOI: 10.1180/minmag.2015.079.1.10

vivid colours, ranging from yellow to orange or red, arsenic-sulfide minerals have been used largely as pigments. Their presence has been documented on Ancient Egyptian funerary papyri (Daniels and Leach, 2004), medieval illuminated manuscripts (Clark and Gibbs, 1998; Jurado-Lopez *et al*., 2004) and in 15th–18th centuries Greek icons (Burgio *et al*., 2003). Thus, the study of these compounds and their light-induced alteration finds application in the examination and conservation of works of art (e.g. Trentelman *et al*., 1996).

Most arsenic sulfides have a crystal structure consisting of a packing of cage-like, covalently bonded As_4S_n (n = 3, 4 and 5) molecules, held together by van der Waals forces. Four types of As_4S_n molecular units are known: (1) As_4S_3 molecule (molecular symmetry C_{3v}), present in both low- ($T < \sim 70$ºC) and high-temperature ($T > \sim 70$ºC) forms of dimorphite (Whitfield, 1973*a*, 1970); (2) As_4S_4 molecule (molecular symmetry D_{2d}), present in the structure of realgar (Mullen and Nowacki, 1972) and in the high-temperature ($T > 256$ºC) polymorph β-As_4S_4 (Porter and Sheldrick, 1972); (3) As_4S_4 molecule (molecular symmetry C_{2v}), found in pararealgar (Bonazzi *et al*., 1995) and in the As_4S_4(II) compound synthesized by Kutoglu (1976); (4) As_4S_5 (molecular symmetry C_{2v}) molecule found in uzonite (Whitfield 1973*b*; Bindi *et al*., 2003) and wakabayashilite, $[(As,Sb)_6S_9][As_4S_5]$ (Bonazzi *et al*., 2005; Bindi *et al*., 2014*a*). The structure of alacránite, As_8S_9, contains both As_4S_4 (realgar type) and As_4S_5 molecular groups (Bonazzi *et al*., 2003*a*; Pagliai *et al*., 2011). Non-stoichiometric sulfides with chemical composition ranging from As_4S_4 to As_8S_9 have also been reported (Bonazzi *et al*., 2003*b*; Bonazzi and Bindi, 2008).

In the course of a research project dealing with the characterization of natural and synthetic arsenic sulfides (Bonazzi and Bindi, 2008 and references therein; Bonazzi *et al*., 2011; Pagliai *et al*., 2011; Lepore *et al*., 2012; Zoppi and Pratesi, 2012; Zoppi *et al*., 2013), we had the chance to study a rock sample from the Khaidarkan deposit, Kyrgyzstan containing the natural analogue of β-As_4S_4. The present paper reports the results of a structural, chemical and spectroscopic study leading to the definition and description of this new mineral, which was named bonazziite after Paola Bonazzi (b. 1960), Full Professor in Mineralogy at the University of Florence, in recognition of her seminal contributions to the study of arsenic sulfides and their alteration induced by exposure to light. The mineral and its name have been approved by the International Mineralogical Association (IMA) Commission on New Minerals, Nomenclature and Classification (IMA No. 2013-141, Bindi *et al*., 2014*b*). The holotype material is deposited in the mineralogical collections of the Museo di Storia Naturale, Università di Firenze (Italy), under catalogue number 3143/I.

Background information on β-As_4S_4

Three natural crystalline modifications of tetra-arsenic tetrasulfide are known: realgar, α-As_4S_4 (Hall, 1966; Clark, 1970; Roland, 1972; Blachnik *et al*., 1980; Bryndzya and Kleppa, 1988), pararealgar (Roberts *et al*., 1980; Bonazzi *et al*., 1995) and the β-As_4S_4 phase, stable in the As–S system at temperatures higher than 256 ±5ºC (Hall, 1966). Although all the three phases have been found to occur in nature, the natural β-As_4S_4 phase remained unnamed.

The occurrence of a natural phase exhibiting a diffraction pattern quite similar to that of the synthetic β-As_4S_4 was first reported by Clark (1970), who found both low- and high-temperature forms in the Ag-As-Sb vein deposit at Alacràn (Chile). According to Clark (1970), the natural β-As_4S_4 phase forms irregular masses and exhibits optical properties similar to those of realgar, but the colour is slightly paler and more yellowish than realgar. At the Alacràn mine the mineral occurs associated closely with smithite, orpiment and arsenolamprite. Although the main properties of the mineral (X-ray data, chemical composition, optical properties and Vickers hardness) were defined by Clark (1970), the proposal of a new mineral species corresponding to the natural β-As_4S_4 polymorph was not approved by the New Minerals and Mineral Names IMA Commission (Popova *et al*., 1986), and the mineral, according to the system of codification for unnamed minerals (Smith and Nickel, 2007), was listed as UM1970-19-S:As.

Later, a new arsenic sulfide was found at the Uzon caldera (Kamchatka, Russian Federation) by Popova *et al*. (1986). Those authors assumed this mineral to be identical to the species previously described by Clark (1970) due to the similarity of their powder diffraction patterns. For this reason, the mineral was named alacránite (Popova *et al*., 1986). The monoclinic lattice parameters of alacránite resemble reasonably well those of the synthetic β-As_4S_4 (Porter and

Sheldrick, 1972) and those of the natural β-phase from Alacràn (Clark, 1970). In keeping with the greater unit-cell volume, alacránite exhibits a different chemical composition (As_8S_9). According to Popova *et al.* (1986), alacránite is monoclinic, *P*2/*c*, while the synthetic β-As_4S_4 crystallizes in the *C*2/*c* space group.

During a sampling of the seafloor around Lihir Island (Papua New Guinea), a specimen consisting mainly of pyrite, sphalerite and galena, together with red and orange arsenic sulfides, was recovered at the top of a conical seamount (Percival *et al.*, 1999). According to these authors, the X-ray analysis of both the deep-red and orange crystals revealed a mixture of realgar and alacránite. The subsequent detailed investigation (Burns and Percival, 2001) showed the mineral from Papua New Guinea to be structurally and chemically identical to the synthetic β-As_4S_4 and quite similar to that from Alàcran (Clark, 1970). However, given the confusion between alacránite and β-As_4S_4, a proposal for the new mineral species was not submitted to the IMA.

Later, Bonazzi *et al.* (2003*b*) found crystals of arsenic sulfide with an intermediate composition between alacránite (As_8S_9) and β-As_4S_4 from the burning dump of Kateřina colliery, Radvanice, Czech Republic. These crystals were investigated by single-crystal X-ray diffraction (XRD) and chemical microanalysis. Although both analytical data and unit-cell parameters suggested strongly the existence of a continuous series between the high-temperature polymorph (β-As_4S_4) and the mineral alacránite (As_8S_9), Bonazzi *et al.* (2003*b*) did not propose the β-As_4S_4 phase as a new mineral species given the anthropogenic nature of the type deposit. For the same reasons, G. Favreau and J.-F. Carpentier (pers. comm., 2008) did not consider the orange crystals corresponding to β-As_4S_4 found at the burning coal dump of La Ricamarie, Saint-Etienne, Loire, Rhône-Alpes, France to be natural products.

Occurrence

The sample containing bonazziite was not found *in situ*, but originates from the Mineralogical Collection of the Museo di Storia Naturale, Sezione di Mineralogia e Litologia, Università di Firenze, where it was labelled "wakabayashilite – Khaidarkan, Osh Oblast, Kyrgyzstan".

The Khaidarkan Sb-Hg deposit is situated in the Fergana Valley, Alai Range, Osh Oblast, Kyrgyzstan and it is the type locality for seven other minerals: chursinite, galkhaite, khaidarkanite, kuznetsovite, poyarkovite, shakhovite and velikite. Geological data concerning this district have been reported by Chukanov *et al.* (1999).

In the rock sample, ~4 cm × 5 cm × 9 cm in size, bonazziite occurs rarely in the intermediate region between sulfur and realgar in a calcite matrix (Fig. 1). The mineral exhibits a subhedral to anhedral grain morphology and shows no inclusions of, or intergrowths with other minerals. The maximum grain size of bonazziite is ~100 μm. Other spatially associated minerals are wakabayashilite, alacránite, non-stoichiometric As_4S_{4+x} sulfides and stibnite.

Physical and optical properties

Bonazziite is orange in colour and shows a dark-orange streak. In thick section, the mineral is opaque and exhibits a resinous lustre. It is brittle, no cleavage is observed and the fracture is irregular. The calculated density, using the ideal As_4S_4 formula and the unit-cell volume from single-crystal data (see below), is 3.542 g/cm^3.

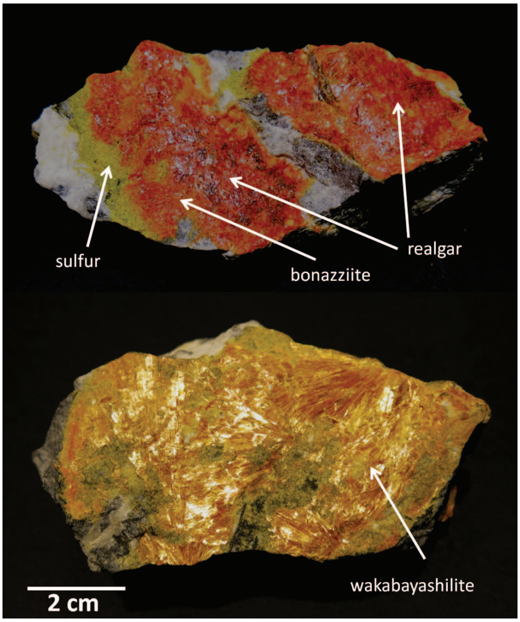

FIG. 1. The rock sample (belonging to the collections of the Museo di Storia Naturale, Università di Firenze, Italy) containing bonazziite. The images show the two sides of the sample, which is ~4 cm × 5 cm × 9 cm in size.

Unfortunately, the density could not be measured in this present study because of the small grain size. Micro-indentation measurements carried out with a VHN load of 15 g give a mean value of 70 kg/mm^2 (range: 60–76) corresponding to a Mohs hardness of ~2½.

In plane-polarized incident light, bonazziite is strongly bireflectant and pleochroic from orange to light red. The mineral shows orange to red internal reflections. Between crossed polars, bonazziite is strongly anisotropic with greyish to light-blue rotation tints.

Reflectance measurements were performed in air by means of a MPM-200 Zeiss microphotometer equipped with a MSP-20 system processor on a Zeiss Axioplan ore microscope. The filament temperature was ~3350 K. An interference filter was adjusted, in turn, to select four wavelengths for measurement (471.1, 548.3, 586.6 and 652.3 nm). Readings were taken for specimen and standard (SiC) maintained under the same focus conditions. The diameter of the circular measuring area was 0.1 mm. Reflectance percentages in air for $R_{\min}$ and $R_{\max}$ are 19.9, 22.2 (471.1 nm), 19.1, 21.3 (548.3 nm), 18.8, 19.7 (586.6 nm) and 17.8, 18.9 (652.3 nm), respectively.

Experimental methods

X-ray diffraction and structure refinement

Three crystals were selected from the rock sample, mounted on a 0.008 mm diameter carbon fibre and checked on a CCD-equipped Oxford Diffraction Xcalibur 3 diffractometer. The crystal (70 μm × 90 μm × 100 μm across) showing the best diffraction quality was chosen for the full data collection. The refined unit-cell dimensions, a = 9.956(1), b = 9.308(1), c = 8.869(1) Å, β = 102.55(2)° and V = 802.3(2) Å^3, are nearly identical to those observed for the synthetic β-As_4S_4 [a = 9.957(3), b = 9.335(4), c = 8.889(5) Å, β = 102.48(4)° and V = 806.7(6) Å^3; Porter and Sheldrick, 1972]. Intensity integration and standard Lorentz-polarization corrections were carried out with the *CrysAlis RED* software package (Oxford Diffraction, 2006). The program *ABSPACK* in *CrysAlis RED* (Oxford Diffraction, 2006) was used for the absorption correction and the structure refinement was carried out in the *C*2/*c* space group starting from the atomic coordinates reported by Porter and Sheldrick (1972) for the synthetic β-As_4S_4 and using the full matrix least-squares program *SHELXL-97* (Sheldrick, 2008). Scattering curves for neutral As and S were taken from the *International Tables for X-ray Crystallography* (Ibers and Hamilton, 1974). The scattering power was allowed initially to vary (As *vs*. structural vacancy and S *vs*. structural vacancy) for all the sites. All the As and S sites were found to be fully occupied by As and S, respectively, and fixed accordingly. Refinement of the anisotropic atomic displacement parameters for all the atoms led to an R_1 index of 0.0263 (for 735 reflections with $F_o > 4\sigma(F_o)$) and 0.0474 (for all 962 independent reflections) with 39 refined parameters. Details of the data collection and refinement are given in Table 1 whereas final atomic coordinates and atomic displacement parameters are listed in Table 2. Structure factors (Table 3) have been deposited with the Principal Editor of *Mineralogical Magazine* and are available from www.minersoc.org/pages/e_journals/dep_mat_mm.html.

The diffraction rings from a few grains of bonazziite were collected with a CCD-equipped diffractometer Xcalibur PX Ultra using Cu*K*α radiation (50 kV and 40 mA) and then converted into a conventional XRD pattern. The crystal-to-detector distance was 7 cm. Data were processed using the *CrysAlis* software package version 1.171.31.2 (Oxford diffraction, 2006) running on the Xcalibur PX control PC. Observed and calculated powder XRD data are listed in Table 4. The unit-cell parameters from powder data are: a = 9.943(2), b = 9.339(1), c = 8.888(1) Å, β = 103.60(2)° and V = 793.2(2) Å^3, in good agreement with the values obtained from single-crystal data (Table 1).

Chemical analyses

The same crystal used for the structural study was embedded in epoxy and then polished for electron microprobe analysis, which was performed with a JEOL 8200 electron microprobe in wavelength dispersion mode at 15 kV, 15 nA beam current, 2 μm as beam size and 20 s as counting time. Synthetic As_2S_3 was used as standard for both As (As*L*α) and S (S*K*α). Six point analyses on different spots were performed. Se, Sb, Pb and Bi were sought but found to be below their respective detection limits. The crystal fragment was found to be homogeneous within the analytical uncertainty. The chemical analyses (means and ranges in wt.% of elements), standard deviations and atomic ratios calculated on eight atoms per formula unit are reported in Table 5.

TABLE 1. Data and experimental details for the bonazziite crystal selected.

Crystal data	
Formula	As_4S_4
Crystal size (mm)	0.070 × 0.090 × 0.100
Form	block
Colour	orange
Crystal system	monoclinic
Space group	*C*2/*c* (#15)
a (Å)	9.956(1)
b (Å)	9.308(1)
c (Å)	8.869(1)
β (°)	102.55(2)
V (Å^3)	802.3(2)
Z	4
Data collection	
Instrument	Oxford Diffraction Xcalibur 3
Radiation type	Mo$K\alpha$ (λ = 0.71073)
Temperature (K)	298(3)
Detector to sample distance (cm)	5
Number of frames	425
Measuring time (s)	25
Maximum covered 2θ (°)	55.93
Absorption correction	multi-scan (ABSPACK; Oxford Diffraction, 2006)
Collected reflections	1972
Unique reflections	962
Reflections with $F_o > 4\sigma(F_o)$	735
R_{int}	0.0481
Range of h, k, l	$-13 \leqslant h \leqslant 12$, $-12 \leqslant k \leqslant 12$, $0 \leqslant l \leqslant 11$
Refinement	
Refinement	Full-matrix least squares on F^2
Final R_1 [$F_o > 4\sigma(F_o)$]	0.0263
Final R_1 (all data)	0.0474
Number of least squares parameters	39
$\Delta\rho_{max}$ (e Å^{-3})	0.94
$\Delta\rho_{min}$ (e Å^{-3})	−0.87

$R_{int} = (n/n - 1)^{1/2}[F_o^2 - F_o\ (\text{mean})^2]/\Sigma F_o^2$
$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$

Raman spectroscopy

The Raman spectrum of bonazziite (Fig. 2) in the region 150–400 cm^{-1} was collected using a RenishawRM2000 micro-Raman apparatus, coupled with a diode laser source emitting at 785 nm, using a crystal exhibiting flat surfaces. Sample irradiation was accomplished using the 50× microscope objective of a Leica Microscope DMLM. The beam power was ~3 mW and the laser spot size was adjusted between 1 and 3 µm. Raman scattering was filtered by a double holographic notch filter system and collected by an air-cooled CCD detector. The acquisition time for the measurement was 100 s. The spectrum was calibrated with respect to a silicon wafer at 520 cm^{-1}.

Results and discussion

Crystal structure

The crystal structure of bonazziite (Fig. 3) is based on the As_4S_4 cage-like molecule, in which each As atom links one As and two S atoms. The As_4S_4 molecule is identical to that found in the structure of realgar (Mullen and Nowacki, 1972). In the As_4S_4 molecule of the two structures, two

TABLE 2. Fractional atomic coordinates and anisotropic displacement parameters U_{ij} (Å^2) for bonazziite.

	x/a	y/b	z/c	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}	U_{eq}
As1	−0.00188(5)	−0.20545(5)	0.05491(5)	0.0349(3)	0.0341(3)	0.0175(2)	0.0067(2)	0.0059(2)	0.0055(2)	0.0288(2)
As2	−0.16022(4)	−0.40158(5)	0.12611(5)	0.0237(2)	0.0319(3)	0.0250(2)	−0.0065(2)	−0.0038(2)	0.0005(2)	0.0283(2)
S1	0	0.0540(2)	¼	0.0446(9)	0.0226(7)	0.0336(8)	0	0.0079(7)	0	0.0337(4)
S2	0	0.5536(2)	¼	0.0362(8)	0.0222(7)	0.0435(9)	0	−0.0046(7)	0	0.0360(4)
S3	−0.2012(1)	−0.3040(1)	0.3403(1)	0.0267(5)	0.0494(6)	0.0309(6)	−0.0064(6)	0.0118(5)	−0.0044(5)	0.0348(3)

TABLE 4. Powder X-ray diffraction data for bonazziite.

	1		2	
hkl	d_{calc} (Å)	I_{calc}	d_{obs} (Å)	I_{rel}
110	6.7221	10		
$\bar{1}11$	5.7441	100	5.74	100
111	4.9605	32		
200	4.8591	24	4.86	30
020	4.6540	13		
021	4.0992	76	4.10	60
$\bar{1}12$	3.9171	42	3.92	50
022	3.1696	28	3.12	60
310	3.0594	51		
221	2.9854	26	2.95	50
202	2.9312	22		
$\bar{2}22$	2.8720	73	2.86	80
$\bar{1}31$	2.8554	17		
$\bar{1}13$	2.8091	34	2.805	25
113	2.5180	22		
$\bar{2}23$	2.3728	40	2.371	30
041	2.2472	10		
330	2.2407	26	2.242	25
420	2.1537	10		
$\bar{1}33$	2.1366	14		
$\bar{2}41$	2.0850	21		
$\bar{2}42$	1.9621	11		
$\bar{3}33$	1.9147	13		
150	1.8284	16		
422	1.7952	16		
$\bar{5}13$	1.7709	16		
152	1.6601	24	1.662	20
$\bar{3}15$	1.6599	17		
600	1.6197	17		
423	1.5858	10		
$\bar{1}35$	1.5390	10		
$\bar{5}52$	1.3423	10		
$\bar{4}45$	1.3082	10		

Notes – 1: Calculated powder pattern and indexing for bonazziite on the basis of a = 9.956(1), b = 9.308(1), c = 8.869(1) Å, β = 102.55(2)° and with the atom coordinates reported in Table 2. Intensities were calculated using *XPOW* software, version 2.0 (Downs *et al*., 1993). Only reflections with $I > 10\sigma(I)$ are listed.
2: Observed powder pattern for bonazziite obtained with a CCD-equipped single-crystal diffractometer (Cu$K\alpha$ radiation).

edges of the disphenoid correspond to As–As bonds, while the other four edges are bridged by S atoms, which form a square parallel to (102). The As_4S_4 molecule possesses a D_{2d} symmetry within the experimental errors.

TABLE 5. Electron microprobe analyses (means, ranges and standard deviations in wt.% of elements) and atomic ratios (on the basis of eight atoms) for bonazziite.

Element	Wt.%	Ranges	σ	Atomic ratios
As	68.94	67.88–69.35	0.50	3.95
S	30.20	28.61–30.83	0.30	4.05
Total	99.14			

In the molecule, the As–S bond distances range from 2.222 to 2.234 Å (Table 6). Such values compare favourably with both those found in the structure of realgar (from 2.228 to 2.247 Å; Mullen and Nowacki, 1972) and in the synthetic β-phase (from 2.238 to 2.252 Å; Porter and Sheldrick, 1972). The As–As bond distances in bonazziite (2.579 ×2 Å) are very similar to those observed in the synthetic β-phase (2.593 Å; Porter and Sheldrick, 1972) and in the β-phase from Papua New Guinea (2.596 Å; Burns and Percival, 2001).

In general, with respect to bond distances, angles and molecular volumes, the molecules in both realgar and bonazziiite are largely identical. However, the shortest B–B distances (distances among the barycentre of the molecules – see Bonazzi and Bindi, 2008) in realgar (5.62 Å) are shorter than those observed in bonazziite (5.75 Å).

The bonazziite structure can be also described as a sequence of layers, with molecules grouped parallel to the ($\bar{1}11$) planes (Bonazzi and Bindi, 2008). Each layer, in turn, can be described as a sequence of rods parallel to [101]. In each rod, the As_4S_4 molecules follow each other in two different orientations, which are related by a rotation of 90º around their $\bar{4}$ axis directed along [102]. Alternating layers are related by inversion centres.

Spectroscopic considerations

The Raman spectrum of bonazziite is nearly identical to that of the synthetic β-As_4S_4 (Muniz-Miranda *et al*., 1996). Most of the bands are due either to the As–As/As–S stretching modes (e.g. 187, 343, 352 and 362 cm^{-1}) or to As–S–As/As–As–S/S–As–S/As–As–As bending modes

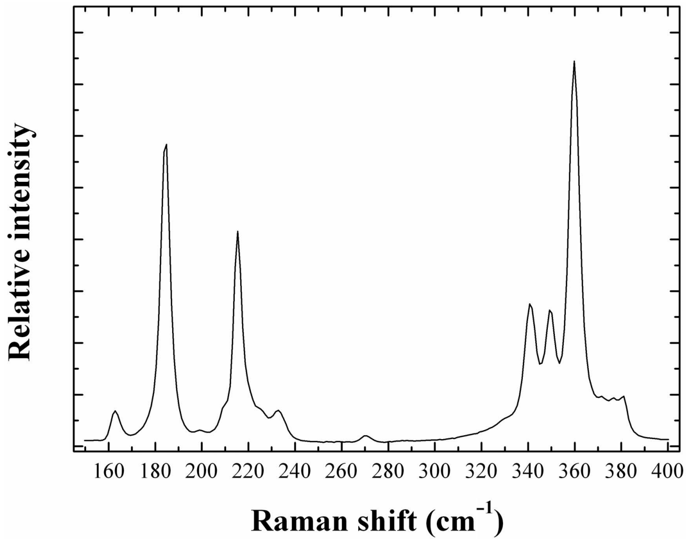

FIG. 2. The Raman spectrum of bonazziite (laser source emitting at 785 nm) in the region 150–400 cm^{-1}.

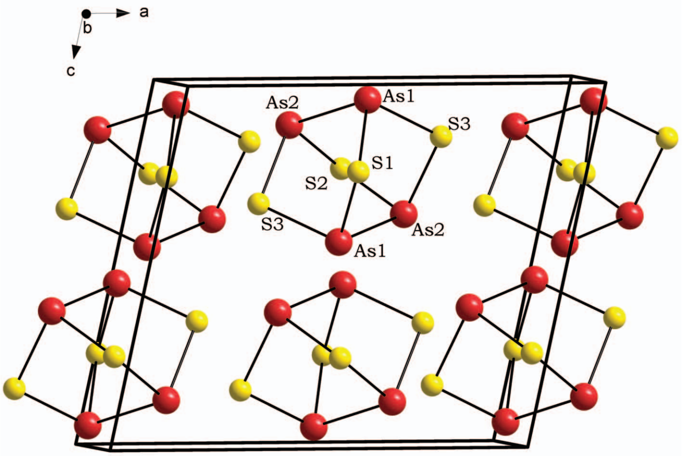

FIG. 3. The crystal structure of bonazziite projected along approximately [010]. Red and yellow circles refer to As and S, respectively. The unit-cell and the orientation of the structure are outlined.

(e.g. 164 and 217 cm^{-1}). Note the presence of the weak peak at 275 cm^{-1}, which is indicative of the presence of minor amounts of pararealgar (Bonazzi *et al*., 1995; Muniz-Miranda *et al*., 1996). The presence of pararealgar indicates that the bonazziite crystal selected for the Raman investigation had begun to undergo the alteration process induced by light. Both polychromatic and monochromatic light are known to alter realgar and the β-phase (now bonazziite) to pararealgar (Douglass *et al*., 1992; Bonazzi *et al*., 1996; Muniz-Miranda *et al*., 1996).

Bonazziite–alacránite series

In the rock sample studied, bonazziite is associated with non-stoichiometric arsenic sulfides with an intermediate composition between bonazziite and alacránite. This represents the first report of such phases from a completely natural occurrence. The first discovery of As_4S_{4+x} compounds, was at the burning dump of Kateřina mine (Bonazzi *et al*., 2003*b*). Three natural As_4S_{4+x} crystals from Kyrgyzstan were analysed in the present study by single-crystal XRD yielding the following range of unit-cell parameters: a = 9.855–9.931, b = 9.355–9.429, c = 8.966–9.045 Å, β = 100.79–102.06º and V = 817.3–828.2 Å^3. Electron microprobe analysis was not carried out on these crystals but, on the basis of qualitative SEM-EDS data, an increase in the amount of S was observed to be related to an increase of the unit-cell volume, thus indicating that the minerals from Kyrgyzstan exhibit a chemical composition ranging from As_8S_8 to As_8S_9. The indication of a continuous series between bonazziite (As_8S_8) and alacránite (As_8S_9) is in agreement with the structural and chemical

TABLE 6. Bond distances (Å) and angles (º) for bonazziite.

As1–S1	2.229(1)	As1–S1–As1	101.51(6)
As1–S3	2.231(1)	As2–S2–As2	101.41(6)
As1–As2	2.579(1)	As2–S3–As1 × 2	101.90(5)
		S1–As1–S3	94.74(4)
As2–S3	2.222(1)	S1–As1–As2	99.22(3)
As2–S2	2.234(1)	S3–As1–As2	98.85(4)
As2–As1	2.579(1)	S3–As2–S2	94.74(4)
		S3–As2–As1	98.94(4)
		S2–As2–As1	99.19(3)

evidence obtained by Bonazzi *et al*. (2003*b*) for non-stoichiometric compounds from Kateřina mine.

Origin

Except for pararealgar, which occurs as an alteration product of realgar and bonazziite, arsenic-sulfide minerals typically occur either as sublimation products in active volcanic areas or as minor constituents in low-temperature hydrothermal sulfide veins. They are also found in lead, silver, or gold ore deposits associated with other As-bearing sulfides such as getchellite and/or wakabayashilite. To date, the non-stoichiometric As_4S_{4+x} sulfides were reported only as sublimation products formed from escaping gasses and vapours of a subsurface colliery fire (Žáček and Ondruš, 1997; Bonazzi *et al*., 2003*b*).

The presence of native S in the mineral association studied suggests a very high sulfidation state of the system: i.e. the mineral association has been formed at very high sulfur fugacity. On the other hand, native Hg (found in abundance in the Khaidarkan deposit) in association with As-Sb-minerals is interpreted to form with the participation of magmatic vapours. Therefore, the As-Sb-Hg-mineral association in the Khaidarkan deposit in general and the As-Sb minerals in the specimen studied attest to a large volatile input (possibly during magmatic degassing) during mineral deposition. In other words, the mineral association studied is believed to form with the contribution of a direct magmatic volatile component.

Acknowledgements

This research was supported by "progetto d'Ateneo 2012, University of Florence" to LB. X-ray intensity data were collected at CRIST, Centro di Cristallografia Strutturale, University of Florence, Italy. The manuscript benefitted from the comments of Peter Leverett and two anonymous reviewers.

References

Bindi, L., Popova, V.I. and Bonazzi, P. (2003) Uzonite, As_4S_5, from the type-locality: X-ray single crystal study and lighting experiments. *The Canadian Mineralogist*, **41**, 1463–1468.

Bindi, L., Bonazzi, P., Zoppi, M. and Spry, P.G. (2014*a*) Chemical variability in wakabayashilite: a real feature or an analytical artefact? *Mineralogical Magazine*, **78**, 693–702.

Bindi, L., Pratesi, G., Muniz-Miranda, M., Zoppi, M., Chelazzi, L., Lepore, G.O. and Menchetti, S. (2014*b*) Bonazziite, IMA 2013-141. CNMNC Newsletter No. 20, June 2014, page 554; *Mineralogical Magazine*, **78**, 549–558.

Blachnik, R., Hoppe, A. and Wickel, U. (1980) Die Systeme Arsen-Schwefel und Arsen-Selen und die thermodynamischen Daten ihrer Verbindungen. *Zeitschrift für anorganische und allgemeine Chemie*, **463**, 78–90.

Bonazzi, P. and Bindi, L. (2008) A crystallographic review of arsenic sulfides: Effects of chemical variations and changes induced by light exposure. *Zeitschrift für Kristallographie*, **223**, 132–147.

Bonazzi, P., Menchetti, S. and Pratesi, G. (1995) 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.I., Pratesi, P. and Menchetti, S. (2003*a*) Alacránite, As_8S_9: structural study of the holotype and re-assignment of the original chemical formula. *American Mineralogist*, **88**, 1796–1800.

Bonazzi, P., Bindi, L., Olmi, F. and Menchetti, S. (2003*b*) How many alacránites do exist? A structural study of non-stoichiometric As_8S_{9-x} crystals. *European Journal of Mineralogy*, **15**, 282–288.

Bonazzi, P., Lampronti, G.I., Bindi, L. and Zanardi, S. (2005) Wakabayashilite, $[(As,Sb)_6S_9][As_4S_5]$: Crystal structure, pseudosymmetry, twinning, and revised chemical formula. *American Mineralogist*, **90**, 1108–1114.

Bonazzi, P., Bindi, L., Muniz Miranda, M., Chelazzi, L., Rödl, T. and Pfitzner, A. (2011) Light-induced molecular change in synthetic $HgI_2{\cdot}As_4S_4$: evidence by single-crystal X-ray diffraction and Raman spectroscopy. *American Mineralogist*, **96**, 646–653.

Bryndzya, L.T. and Kleppa, O.J. (1988) Standard molar enthalpies of formation of realgar (α-AsS) and orpiment (As_2S_3) by high-temperature direct-synthesis calorimetry. *Journal of Chemical Thermodynamics*, **20**, 755–764.

Burgio, L., Clark, R.J.H. and Theodoraki, K. (2003) Raman microscopy of Greek icons: identification of unusual pigments. *Spectrochimica Acta*, **A59**, 2371–2389.

Burns, P.C. and Percival, J.B. (2001) Alacránite, As_4S_4: a new occurrence, new formula, and determination of the crystal structure. *The Canadian Mineralogist*, **39**, 809–818.

Chukanov, N.V., Karpenko, V.Y., Rastsvetaeva, R.K., Zadov, A.E. and Kuz'mina, O.V. (1999) Khaidarkanite $Cu_4Al_3(OH)_{14}F_3{\cdot}2H_2O$, a new mineral from the Khaidarkan deposit, Kyrgyzstan. *Zapiski Vsesoyuznogo Mineralogicheskogo Obshchestva*, **128**, 58–63.

Clark, A.H. (1970) Alpha-arsenic sulfide, from Mina Alacràn, Pampa Larga, Chile. *American Mineralogist*, **55**, 1338–1344.

Clark, R.J.H. and Gibbs, P.J. (1998) Analytical approach: Raman microscopy of a 13th-century illuminated text. *Analytical Chemistry*, **70**, 99–104.

Daniels, V. and Leach, B. (2004) The occurrence and alteration of realgar on Ancient Egyptian papyri. *Studies in Conservation*, **49**, 73–84.

Douglass, D.L., Shing, C. and Wang, G. (1992) The light-induced alteration of realgar to pararealgar. *American Mineralogist*, **77**, 1266–1274.

Downs, R.T., Bartelmehs, K.L., Gibbs, G.V. and Boisen, M.B. Jr (1993) Interactive software for calculating and displaying X-ray or neutron powder diffractometer patterns of crystalline materials. *American Mineralogist*, **78**, 1104–1107.

Hall, H.T. (1966) *The system Ag-Sb-S, Ag-As-S, and Ag-Bi-S: Phase relations and Mineralogical Significance*. PhD Thesis, Brown University, Providence, Rhode Island, USA.

Holomb, R., Mitza, V., Johansson, P., Mateleshko, N., Matic, A. and Veresh, M. (2005) Energy-dependence of light-induced changes in g-$As_{45}S_{55}$ during recording the micro-Raman spectra. *Chalcogenide Letters*, **2**, 63–69.

Kutoglu, A. (1976) Darstellung und Kristallstruktur einer neuen isomeren Form von As_4S_4. *Zeitschrift für anorganische und allgemeine Chemie*, **419**, 176–184.

Jurado-Lopez, A., Demko, O., Clark, R.J.H. and Jacobs, D. (2004) Analysis of the palette of a precious 16th century illuminated Turkish manuscript by Raman microscopy. *Journal of Raman Spectroscopy*, **35**, 119–124.

Ibers, J.A. and Hamilton, W.C. (Editors) (1974) *International Tables for X-ray Crystallography*, vol. IV. Kynock, Dordrecht, The Netherlands, pp. 366.

Lepore, G.O., Boffa Ballaran, T., Nestola, F., Bindi, L., Pasqual, D. and Bonazzi, P. (2012) Compressibility of synthetic β-As_4S_4: *In situ* high-pressure single-crystal X-ray study. *Mineralogical Magazine*, **76**, 963–973.

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.

Němec, P., Jedelský, J., Frumar, M., Černošek, Z. and Vlček, M. (2005) Structure of pulsed-laser deposited arsenic-rich As-S amorphous thin films, and effect of light and temperature. *Journal of Non-Crystalline Solids*, **351**, 3497–3502.

Oxford Diffraction (2006) *CrysAlis* RED (Version 1.171.31.2) and ABSPACK in *CrysAlis* RED. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.

Pagliai, M., Bonazzi, P., Bindi, L., Muniz-Miranda, M. and Cardini, G. (2011) Structural and vibrational properties of arsenic sulfides: alacránite (As_8S_9). *Journal of Physical Chemistry A*, **115**, 4558–4562.

Percival, J.B., Hannington, M.D., Herzig, P.M. and Jonasson, I.R. (1999) Clay mineral associations in sulphide-bearing volcanic rocks and sediments from the Lihir area, Papua New Guinea. Pp. 689–696 in: *Clays for our Future* (H. Kodama, A.R. Mermut and J.K. Torrance, editors). Proceedings of the 11th International Clay Conference, ICC97 Organizing Committee, Ottawa.

Popova, V.I., Popov, V.A., Clark, A., Polyakov, V.O. and Borisovski, S.E. (1986) Alacránite As_8S_9; a new mineral. *Proceedings of the Russian Mineralogical Society (ZVMO)*, **115**, 360–368 [in Russian].

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[3,3,0,03,7]-octane). *Journal of the Chemical Society*, *Dalton Transactions*, **13**, 1347–1349.

Roberts, A.C., Ansell, H.G. and Bonardi, M. (1980) Pararealgar, a new polymorph of AsS, from British Columbia. *The Canadian Mineralogist*, **18**, 525–527.

Roland, G.W. (1972) Concerning the α-AsS realgar inversion. *The Canadian Mineralogist*, **11**, 520–525.

Sheldrick, G.M. (2008) A short history of SHELX. *Acta Crystallographica*, **A64**, 112–122.

Smith, D.G.W. and Nickel, E.H. (2007) A system for codification for unnamed minerals: report of the Subcommittee for Unnamed Minerals of the IMA Commission on New Minerals, Nomenclature and Classification. *The Canadian Mineralogist*, **45**, 983–1055.

Trentelman, K., Stodulski, L. and Pavlosky, M. (1996) Characterization of pararealgar and other light-induced transformation products from realgar by Raman microspectroscopy. *Analytical Chemistry*, **68**, 1755–1761.

Whitfield, H.J. (1970) The crystal structure of tetra-arsenic trisulphide. *Journal of Chemical Society, Dalton Transactions*, 1800–1803.

Whitfield, H.J. (1973*a*) Crystal structure of the β-form of tetra-arsenic trisulphide. *Journal of the Chemical Society, Dalton Transactions*, 1737–1738.

Whitfield, H.J. (1973*b*) Crystal and molecular structure of tetra-arsenic pentasulphide. *Journal of the Chemical Society, Dalton Transactions*, 1740−1742.

Žáček, V. and Ondruš, P. (1997) Mineralogy of recently formed sublimates from Kateřina colliery in Radvanice, Eastern Bohemia, Czech Republic. *Bulletin of the Czech Geological Survey*, **72**, 289−302.

Zoppi, M. and Pratesi, G. (2012) The dual behavior of the β-As_4S_4 altered by light. *American Mineralogist*, **97**, 890−896.

Zoppi, M., Bindi, L., Rödl, T., Pfitzner, A. and Bonazzi, P. (2013) Light-induced structural changes in $(HgBr_2)_3(As_4S_4)_2$: An X-ray single-crystal diffraction, Raman spectroscopy and *ab initio* study. *Solid State Sciences*, **23**, 88−95.