

Light-induced alteration of arsenic sulfides: A new product with an orthorhombic crystal structure

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ABSTRACT

The crystal structure of a new light-induced alteration product obtained from a natural non-stoichiometric arsenic sulfide (original chemical formula $\text{As}_4\text{S}_{4.35}$) was solved in the space group *Pccn*, and refined to a final *R* index of 9.89%. Unit-cell parameters are: $a = 19.352(7)$, $b = 10.166(3)$, $c = 8.697(4)$ Å, $V = 1711(1)$ Å³; $Z = 8$. The structural refinement results yielded a chemical formula close to As_4S_5 . The structure consists of discrete, covalently bonded As_4S_5 molecules, which are held together by van der Waals forces. The molecular packing is similar to that of the original crystal, which, in turn, is the same as to that of $\beta\text{-As}_4\text{S}_4$. The phase originated from a continuous, room-temperature, light-induced alteration process that does not require a complete rearrangement of the molecular packing and therefore does not imply the loss of coherency between crystalline domains.

Keywords: XRD data, arsenic sulfide, crystal structure, light-induced alteration, molecular packing

INTRODUCTION

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-temperature ($T < 70$ °C) and high-temperature ($T > 70$ °C) forms of dimorphite (Whitfield 1973a, 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 ($T > 256$ °C) polymorph $\beta\text{-As}_4\text{S}_4$ (Porter and Sheldrick 1972); (3) As_4S_4 molecule (molecular symmetry C_{2v}), found in pararealgar (Bonazzi et al. 1995) and in the $\text{As}_4\text{S}_4(\text{II})$ compound synthesized by Kutoglu (1976); (4) As_4S_5 (molecular symmetry C_{2v}) molecule found in uzonite (Whitfield 1973b; Bindi et al. 2003) and wakabayashilite, $[(\text{As,Sb})_6\text{S}_9][\text{As}_4\text{S}_5]$ (Bonazzi et al. 2005). The structure of alacranite, As_8S_9 , contains both As_4S_4 (realgar type) and As_4S_5 molecular groups (Bonazzi et al. 2003b).

It has been long known that exposure of realgar to light induces its alteration at the surface into friable, yellow films consisting of pararealgar (Roberts et al. 1980). Moreover, it was also shown that light alters both realgar and the high-temperature polymorph ($\beta\text{-As}_4\text{S}_4$) into pararealgar through an intermediate product first described by Douglass et al. (1992) as χ -phase. The process starting from realgar is discontinuous and it can be monitored on altered single crystals only during the first steps of alteration (Bonazzi et al. 1996; Muniz-Miranda et al. 1996; Kyono et al. 2005). In contrast, the light-induced conversion

of the β -phase to the χ -phase and eventually to pararealgar is a continuous process that can be monitored step by step following the powder diffraction pattern as well as the Raman spectrum (Bonazzi et al. 1996; Muniz-Miranda et al. 1996).

Recently, Bonazzi et al. (2006) carried out structure refinements of crystals belonging to the $\beta\text{-As}_4\text{S}_4\text{--As}_8\text{S}_9$ series at selected steps of the light-induced transformation process. The structural results clearly showed that the percentage of the As_4S_5 molecule in the structure increases when a crystal is exposed to light. Therefore, the increment of the unit-cell volume induced by light exposure appears to be related to the variation of the As/S ratio in the structure according to the reaction $5\text{As}_4\text{S}_4 + 3\text{O}_2 \rightarrow 4\text{As}_4\text{S}_5 + 2\text{As}_2\text{O}_3$. Indeed, the formation of arsenolite in the light-induced process of alteration of realgar to pararealgar has been reported (Ballirano and Maras 2002). According to the model elaborated by Kyono et al. (2005) to explain the realgar $\rightarrow$ pararealgar conversion, the sulfur released in the arsenolite formation and incorporated to produce As_4S_5 molecules could be then released by breaking an equivalent As-S-As linkage to form the As_4S_4 molecules of pararealgar. The process could cyclically continue by re-attachment of the free S to another As_4S_4 (realgar-type) until a complete conversion to pararealgar. In the case of the $\beta\text{-As}_4\text{S}_4\text{--As}_8\text{S}_9$ sulfides, however, a complete conversion to pararealgar was observed only for pure $\beta\text{-As}_4\text{S}_4$, whereas non-stoichiometric $\text{As}_8\text{S}_{9-x}$ crystals exhibited a more complex behavior. In particular, two crystals having the original chemical formula $\text{As}_8\text{S}_{8.26}$ (ALA16) and $\text{As}_8\text{S}_{8.42}$ (ALA15) were found to consist of a mixture of alacranite and pararealgar, whereas the alteration product deriving from a more sulfur-rich crystal (ALA2: $\text{As}_8\text{S}_{8.70}$) remained unknown (Bonazzi et al. 2006). The ALA2 crystal, left in sunlight at room temperature for several months, was re-examined by single-crystal X-ray diffraction.

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Diffraction effects were consistent with a new orthorhombic unit cell. Here we report the structural study of this new light-induced alteration product.

EXPERIMENTAL METHODS

The original, untreated ALA2 crystal was found among the products formed from escaping gasses and vapors at a burning dump of Kateřina colliery, Czech Republic (Bonazzi et al. 2003a). Before light exposure the unit-cell dimensions were: $a = 9.936(2)$, $b = 9.458(2)$, $c = 9.106(2)$ Å, $\beta = 101.90(2)^\circ$, $V = 837.3(3)$ Å³, and the chemical formula derived from the structure refinement was $\text{As}_4\text{S}_{4.35}$. The crystal had experienced an exposure to filtered polychromatic light [550 nm long-wavelength pass filter; apparatus described by Bonazzi et al. (1996)] for a total of 4300 min. The unit-cell parameters determined after increasing light-exposure times are reported by Bonazzi et al. (2006). The crystal was left in sunlight at room temperature for approximately ten months, and was re-examined by a CCD-equipped Oxford Xcalibur 2 diffractometer (exposure time of 100 s per frame; 40 mA $\times$ 40 kV). The intensity of peaks and their broad profiles indicated an extremely low diffraction quality. The unit-cell parameters were $a = 19.352(7)$, $b = 10.166(3)$, $c = 8.697(4)$ Å, $V = 1711(1)$ Å³. No additional spots or diffraction rings were detected.

Intensity data were collected using an Enraf Nonius CAD4 diffractometer, with MoK α radiation monochromatized by a flat graphite crystal. Intensities were corrected for Lorentz and polarization effects and subsequently for absorption following the semi-empirical method of North et al. (1968). Experimental details are reported in Table 1.

STRUCTURE SOLUTION AND REFINEMENT

The analysis of the systematic absences ($0kl$: $l = 2n$; $h0l$: $l = 2n$; $h k 0$: $h + k = 2n$; $h00$: $h = 2n$; $0k0$: $k = 2n$; $00l$: $l = 2n$) led to the unique choice of the space group $Pccn$. Statistical tests on the distribution of $|E|$ values strongly supported the presence of an inversion center ($|E^2 - 1| = 0.942$).

The crystal structure was solved using the direct methods of the SHELXS-97 package (Sheldrick 1997a) and Fourier syntheses. All atoms were located on an F_o -Fourier map. Structure refinement was performed using SHELXL-97 (Sheldrick 1997b). Isotropic full-matrix least-squares cycles were initially run with the atom sites fully occupied, although the unusually high value of the isotropic displacement factor for the S5 atom suggested partial occupancy at this site. Successive least squares cycles were done by fixing, alternately, the site-occupancy factor and the isotropic displacement parameter for all the S atoms. Final occupancy factors were close to 1.00, except for the S5 position [0.93(5)], and the resulting R factor was 14.35%. Subsequently, the S5 occupancy was fixed and an anisotropic model of the whole structure was refined. Convergence was achieved to $R = 9.89\%$ for 308 observed reflections [$F_o > 4\sigma(F_o)$]. Scattering curves for neutral As and S were taken from the *International Tables for X-ray Crystallography* (Ibers and Hamilton 1974).

TABLE 1. Data and experimental details for the selected crystal

Space group	$Pccn$
Cell parameters	$a = 19.352(7)$ (Å) $b = 10.166(3)$ (Å) $c = 8.697(4)$ (Å) $V = 1711(1)$ (Å ³)
Crystal size (μm)	$30 \times 50 \times 60$
Wavelength	MoK α (26 mA $\times$ 50 kV)
θ -range ($^\circ$)	1–20
Ranges of h, k, l	$-18 \leq h \leq 18$; $-8 \leq k \leq 0$; $-8 \leq l \leq 8$
Scan mode	ω
Scan width ($^\circ$)	3.20
Scan speed ($^\circ/\text{min}$)	0.91
Independent refl.	783
Refl. with $F_o > 4\sigma(F_o)$	308
R_{obs} (%)	9.89

Inspection of the difference-Fourier map revealed that maximum positive and negative peaks were 0.84 and 0.93 $e^-/\text{\AA}^3$, respectively. Fractional atomic coordinates and anisotropic displacement parameters are given in Table 2.

RESULTS AND DISCUSSION

The crystal structure of the orthorhombic phase obtained by light-induced alteration of a non-stoichiometric arsenic sulfide (original formula $\text{As}_4\text{S}_{4.35}$) consists of a molecular packing of discrete cage-like As_4S_5 molecules which are held together by van der Waals forces (Fig. 1). Intramolecular bond distances and angles are given in Table 3. Assuming that the occupancy obtained from the structural refinement is reliable, the chemical formula is $\text{As}_4\text{S}_{4.93}$. Whenever the S5 position is vacant [7($\pm$ 5)%], an As_4S_4 molecule would be identical to that observed in pararealgar (Fig. 2). If the S5 position is occupied by sulfur [93($\pm$ 5)%], a molecule identical to that observed in the structure

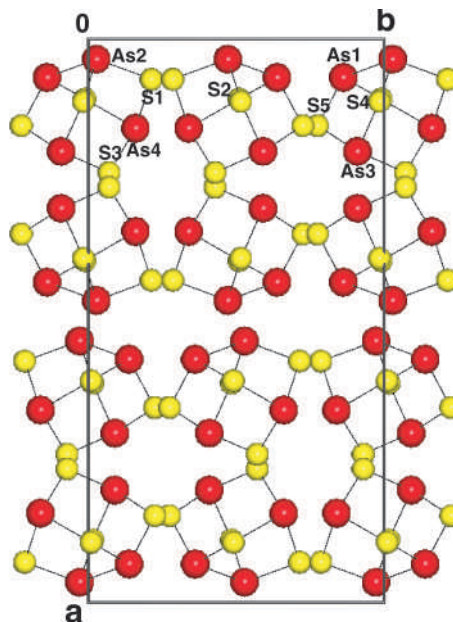


FIGURE 1. Crystal structure of the orthorhombic As_4S_5 phase viewed down [001]. The unit cell is outlined. Dark and light gray circles (red and yellow circles in the online version) refer to the As and S atoms, respectively.

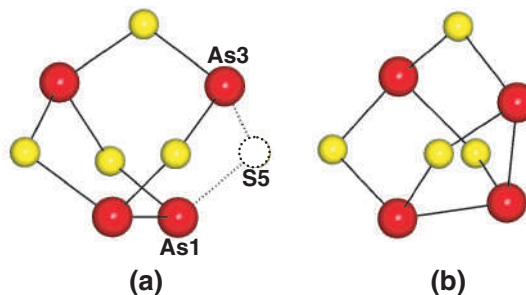


FIGURE 2. (a) As_4S_5 molecule, with the dashed circle representing the partially occupied S5 position; (b) As_4S_4 molecule (pararealgar-type). Dark and light gray circles (red and yellow circles in the online version) refer to the As and S atoms, respectively.

TABLE 2. Fractional atomic coordinates and anisotropic displacement parameters for the selected crystal

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}
As1	0.0684(4)	0.8619(8)	0.103(1)	0.099(5)	0.092(6)	0.151(8)	-0.018(4)	0.026(5)	-0.027(6)	0.114(3)
As2	0.0360(4)	0.0283(8)	0.303(1)	0.107(5)	0.116(7)	0.112(7)	-0.023(5)	0.038(5)	-0.021(6)	0.111(3)
As3	0.1995(4)	0.9092(8)	0.3448(9)	0.104(5)	0.083(5)	0.123(7)	0.030(4)	0.018(5)	0.026(5)	0.103(3)
As4	0.1584(3)	0.1606(6)	0.0434(8)	0.061(3)	0.074(5)	0.086(5)	-0.007(4)	-0.002(4)	0.013(4)	0.074(2)
S1	0.0716(7)	0.214(2)	0.202(2)	0.065(9)	0.09(1)	0.12(1)	0.019(9)	0.01(1)	-0.01(1)	0.092(6)
S2	0.1066(8)	0.510(2)	0.430(2)	0.071(9)	0.11(2)	0.13(2)	-0.01(1)	-0.02(1)	0.03(1)	0.103(7)
S3	0.2370(6)	0.071(2)	0.197(2)	0.035(7)	0.09(1)	0.09(1)	-0.009(7)	0.002(8)	0.01(1)	0.073(5)
S4	0.111(1)	0.984(2)	0.468(3)	0.14(1)	0.10(1)	0.16(2)	-0.02(1)	0.06(2)	-0.02(2)	0.132(8)
S5	0.154(1)	0.775(2)	0.188(3)	0.17(2)	0.11(2)	0.15(3)	0.01(1)	-0.03(2)	-0.02(2)	0.14(1)

TABLE 3. Intramolecular bond distances (Å) and angles (°) for the selected crystal

As1-	S5	2.02(2)	S5-	As1-	S2(ii)	104.0(9)
	S2(i)	2.13(2)			As2(ii)	104.4(8)
	As2(ii)	2.50(1)	S2(i)-	As1-	As2(ii)	99.5(6)
As2(ii)-	S4	2.09(3)	S4-	As2(ii)-	S1(ii)	104.0(8)
	S1(ii)	2.19(2)		As1		99.0(7)
	As1	2.50(1)	S1(ii)-	As2(ii)-	As1	103.0(6)
As3-	S5	2.12(2)	S5-	As3-	S4	102.5(9)
	S4	2.16(2)			S3(ii)	104.0(9)
	S3	2.21(2)	S4-	As3-	S3(ii)	106.7(8)
As4(ii)-	S3(ii)	2.22(2)	S3(ii)-	As4(ii)-	S2(i)	104.8(7)
	S2(i)	2.23(2)			S1(ii)	104.0(7)
	S1(ii)	2.24(2)	S2(i)-	As4(ii)-	S1(ii)	97.1(7)
			As2(ii)-	S1(ii)-	As4(ii)	105.9(7)
			As1-	S2(i)-	As4(ii)	108.6(8)
			As3-	S3(ii)-	As4(ii)	115.5(8)
			As2(ii)-	S4-	As3	106.6(7)
			As1-	S5-	As3	107.1(9)

Notes: Symmetry codes are: (i) = $x, 3/2 - y, -1/2 + z$; (ii) = $x, 1 + y, z$.

of uzonite is obtained (Fig. 2). Nonetheless, the low quality of the diffraction data leading to unusually high displacement parameters (Table 2) and to some As-S distances (Table 3) shorter than those observed in the other molecular arsenic sulfides, does not allow us to consider significant with complete confidence the reduction of the site fraction at S5. Thus, although this phase appears as defective from the refinement results, it is more likely a polymorph of uzonite, As_4S_5 . The molecular packing, however, is quite different from that of the structure of uzonite (space group $P2_1/m$). The structural relationships between the orthorhombic phase and uzonite can be described by considering the structure of the orthorhombic phase as consisting of layers parallel to $\{211\}$. Each of these layers, in turn, can be described as a sequence of two kinds of rods (A and B in Fig. 3a) parallel to $[10\bar{2}]$. The A and B rods appear to be very similar to those found in the structure of uzonite along $[1\bar{1}0]$ (Fig. 3b) and $[101]$ (Fig. 3c), respectively; in the orthorhombic phase A rods alternate with B rods in successive layers along $[011]$.

In both structures the As_4S_5 molecules exhibit a molecular symmetry C_{2v} . Therefore, we can describe the orientation of a molecule by considering the angle ($\mathbf{ma}$) between the direction of the twofold molecular axis projected on the plane of the layer and the crystallographic $\mathbf{a}$ axis of the orthorhombic form (or $\mathbf{a} \sin \beta$ direction in uzonite). In uzonite adjacent molecules in both A and B rods assume two orientations ($\mathbf{ma} = \pm 180^\circ$ in rod A; $\mathbf{ma} = +4^\circ$ and $+176^\circ$ in rod B), whereas in the phase studied here molecules are arranged in succession along $[10\bar{2}]$ with four orientations ($\mathbf{ma} = +166^\circ, +14^\circ, -166^\circ$, and -14° in rod A; $\mathbf{ma} = +168^\circ, +12^\circ, -168^\circ$, and -12° in rod B). The different molecular packing leads to a different value of the unit-cell

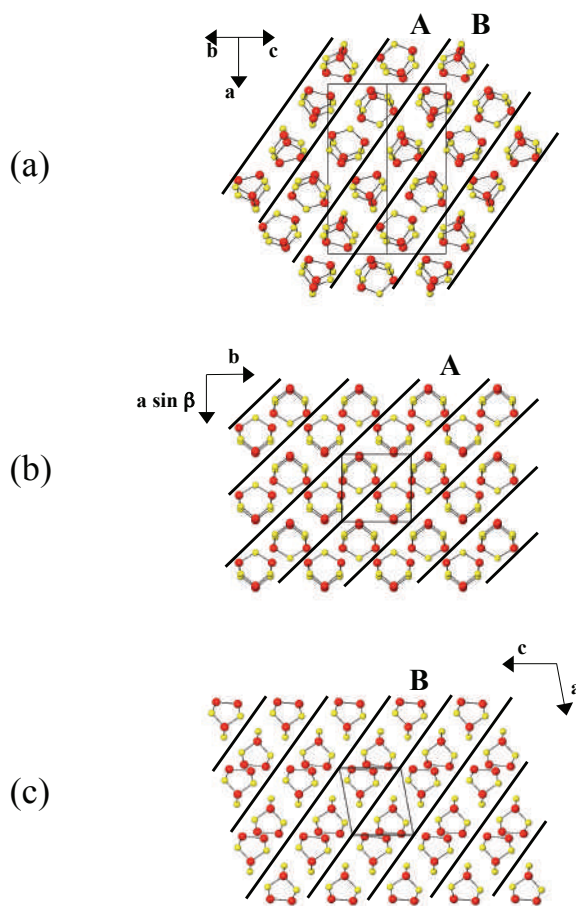


FIGURE 3. (a) A layer in the structure of the orthorhombic As_4S_5 phase projected down $[011]$. Each layer can be described as a sequence of two kinds of rod (A and B) parallel to $[10\bar{2}]$. Similar rods are found in the structure of uzonite along (b) $[1\bar{1}0]$ and (c) $[101]$.

volume per molecular unit ($V/Z = 213.9$ and 226.5 Å^3 for the orthorhombic phase and uzonite, respectively), which indicates a denser packing for the compound studied in the present work. The reason for this feature may relate to the origin of this phase, which formed by a continuous, room-temperature, light-induced alteration process occurring without any dramatic change of the molecular packing of the original, untreated phase, which, in turn, had the same molecular packing of the $\beta\text{-As}_4\text{S}_5$ phase (Bonazzi et al. 2003a). It was recently shown (Bonazzi et al. 2006) that the transformation of $\beta\text{-As}_4\text{S}_5$ into pararealgar occurs through a

continuous process that does not imply the loss of coherency between crystalline domains and does not require a complete rearrangement of the molecular packing. Therefore, one can speculate that the light-induced formation of the orthorhombic As_4S_5 phase rather than uzonite is favored owing to its similarity with the molecular packing of the original, untreated phase. Altogether, our results show that the light-exposure induces a complete conversion to pararealgar starting from stoichiometric As_4S_4 , whereas the orthorhombic As_4S_5 can be produced starting from a phase richer in sulfur, $\text{As}_4\text{S}_{4+x}$. As shown in Figure 4, the molecular packing in the structure of the orthorhombic As_4S_5 phase is very similar to the packing of the As_4S_4 molecules (realgar type) in the structure of $\beta\text{-As}_4\text{S}_4$ and of the As_4S_4 molecules (pararealgar type) in the structure of pararealgar. Indeed, the orthorhombic As_4S_5 phase shows a unit-cell geometry resembling that of pararealgar ($a_{\text{orth}} \approx 2 a_{\text{para}} \sin \beta = 19.66$; $b_{\text{orth}} \approx b_{\text{para}} = 9.66$; $c_{\text{orth}} \approx c_{\text{para}} = 8.50 \text{ \AA}$), although the unit-cell volume per molecular unit ($V/Z = 213.9$ and $201.7 \text{ \AA}^3$ for the orthorhombic phase and pararealgar, respectively) is higher, in keeping with the larger size of the As_4S_5 molecules compared to that of As_4S_4 .

As shown by Bonazzi et al. (2006) for the crystals belonging to the $\beta\text{-As}_4\text{S}_4\text{--As}_8\text{S}_{9-x}$ series, the percentage of the As_4S_5 molecule increases when a crystal is exposed to light. However, in the case of the stoichiometric β -phase, a final complete conversion to para-

realgar was observed, supporting the hypothesis that the additional sulfur is released so that the original As/S ratio is restored. In contrast, in the product studied here the sulfur release, if any, has not yet begun. Whether the orthorhombic As_4S_5 phase is a final, stable phase or a metastable precursor of pararealgar is an unanswered question at present and will require further experiments.

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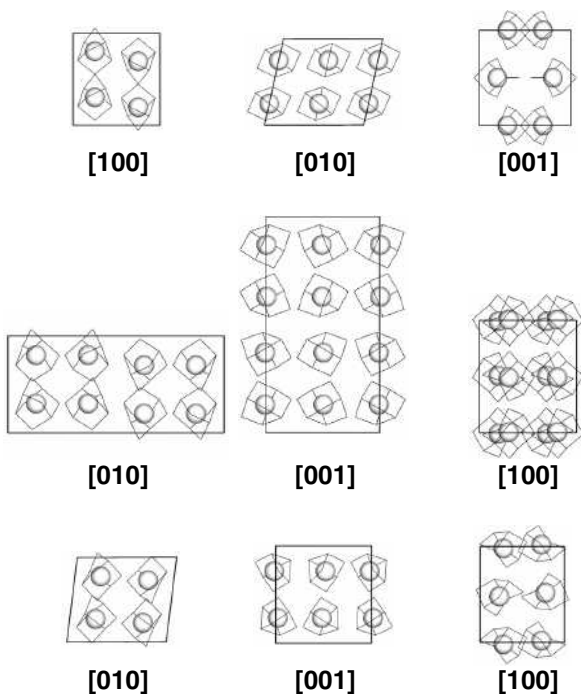


FIGURE 4. Molecular packing in the structure of the orthorhombic $\text{As}_4\text{S}_{5-x}$ phase (middle row) compared with those in the structure of $\beta\text{-As}_4\text{S}_4$ (upper row) and pararealgar (lower row). Gray circles represent the centroid of the As_4 groups; black sticks indicate the As-S and As-As bonds within the cage-like molecules.

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