UZONITE, As$_4$S$_5$, FROM THE TYPE LOCALITY:
SINGLE-CRYSTAL X-RAY STUDY AND EFFECTS OF EXPOSURE TO LIGHT

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ABSTRACT

The crystal structure of uzonite from the Uzon caldera, Kamchatka, Russian Federation, has been refined in space group $P2_1/m$ to a final R index of 2.66%. Unit-cell parameters are: a 7.973(2), b 8.096(2), c 7.148(2) Å, β 101.01(2)°, V 452.9(2) Å^3, $Z = 2$. The structural model previously reported for the synthetic analogue is confirmed, although a higher precision was achieved. The structure consists of discrete covalently bonded As$_4$S$_5$ molecules, which are held together by van der Waals forces. Both the intramolecular As–S (2.237–2.261 Å) and As–As (2.527 Å) bond lengths match closely the values commonly observed in the molecule-based structures of other arsenic sulfides. In order to contribute to the understanding of the effects of light exposure on the structure of the arsenic sulfides, we exposed the crystal to filtered polychromatic light. The unit-cell parameters were measured after each exposure. The results obtained seem to indicate that the As$_4$S$_4$ molecules easily undergo such a transformation, whereas the As$_4$S$_5$ molecules do not.

Keywords: uzonite, crystal-structure refinement, light-exposure effects, arsenic sulfide, Uzon caldera, Russia.

SOMMAIRE

Nous avons affiné la structure cristalline de l'uzonite provenant de la localité type, la caldeira de Uzon, au Kamchatka, en Russie, dans le groupe spatial $P2_1/m$ jusqu'à un résidu R de 2.66%. Les paramètres réticulaires sont: a 7.973(2), b 8.096(2), c 7.148(2) Å, β 101.01(2)°, V 452.9(2) Å^3, $Z = 2$. Le modèle structural proposé antérieurement pour l'analogue synthétique a été confirmé, tout en atteignant une précision plus élevée. La structure contient des molécules distinctes de As$_4$S$_5$ à liaisons covalentes, retenues par liaisons van der Waals. Les liaisons intramoléculaires As–S (2.237–2.261 Å) et As–As (2.527 Å) correspondent étroitement aux valeurs observées dans la structure d'autres sulfures d'arsenic à base de molécules. Afin de contribuer à une explication des effets sur la structure des sulfures d'arsenic d'une exposition à la lumière, nous avons exposé le cristal à une lumière polychromatique filtrée, et nous avons mesuré les paramètres réticulaires après chaque exposition. Les résultats semblent indiquer que seules les molécules de As$_4$S$_4$ sont facilement transformées, tandis que les molécules de As$_4$S$_5$ ne montrent aucune réaction.

(Traduit par la Rédaction)

Mots-clés: uzonite, affinement de la structure cristalline, effets d'une exposition à la lumière, sulfure d'arsenic, caldeira de Uzon, Russie.

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INTRODUCTION

Tetra-arsenic pentasulfide, As_4S_5, was first synthesized by Whitfield (1973a), who solved the crystal structure in space group $P2_1/m$ using X-ray-diffraction data derived from film techniques ($R = 11\%$ for 613 observed reflections). Later, Popova & Polyakov (1985) found the natural analogue of the synthetic As_4S_5 at the Uzon caldera, Kamchatka, in the Russian Federation. The mineral, named uzonite, was recovered in realgar-enriched sand–gravel and gravel–pebble tuff sediments at 10–30 cm depth, where it is associated with realgar, As_4S_4, and alacranite, As_8S_9. The following unit-cell parameters were obtained from the X-ray powder data (Popova & Polyakov 1985); a 7.98(1), b 8.10(1), c 7.09(1) Å, β 100.14(3)°. Owing to the presence of complex twins and intergrowths with realgar and alacranite, a crystal-structure refinement of the natural material was not done at that time. In this paper, we report the refinement of the crystal structure of uzonite from the type locality.

Filtered light induces alteration of both realgar (α-As_4S_4) and the high-temperature polymorph (β-As_4S_4) (Douglass et $al.$ 1992, Muniz-Miranda et $al.$ 1996) to pararealgar. In particular, the initial steps of this process occur with a strong increase of the unit-cell volume in both realgar and β-As_4S_4 (Bonazzi et $al.$ 1996). Thus, an additional goal of this study was to verify possible variations in the unit-cell parameters of the uzonite crystal following exposure to light.

EXPERIMENTAL METHODS AND STRUCTURE REFINEMENT

Several crystals of the original sample (preserved at Institute for Mineralogy, Urals Branch of the Russian Academy of Sciences, Chelyabinsk district, Miass 456317, Russian Federation, catalogue number U–16) were examined by means of an Enraf–Nonius CAD4 diffractometer.

A single crystal of uzonite (90 $\times$ 110 $\times$ 170 μm) giving relatively high-quality diffraction maxima was selected for the structural study. The unit-cell dimensions were determined by least-squares refinement of the setting angles of 25 reflections ($12° < \theta_{MoK\alpha} < 17°$): a 7.973(2) Å, b 8.096(2) Å, c 7.148(2) Å, β 101.01(2)°.

Intensity data were collected ($\overline{11} < h < 11$, $\overline{11} < k < 11$, $0 < l < 10$) in the θ-range 2 – 30° using graphite-monochromatized $MoK\alpha$ radiation, with ω-scan mode, a scan width of 2.2°, and scan speed of 2.75°/min. The intensities of 2771 reflections were corrected for Lorentz and polarization effects and subsequently for absorption following the semi-empirical method of North et $al.$ (1968). The systematic absences of $0k0$ reflections with $k = 2n + 1$ confirm space group $P2_1/m$, as previously determined by Whitfield (1973a). Pairs of equivalent reflections in the monoclinic system were merged ($R_{symm} = 3.25\%$). The structure refinement was performed in space group $P2_1/m$, starting from the atom coordinates of synthetic As_4S_5 (Whitfield 1973a), using the program SHELXL–93 (Sheldrick 1993). Neutral-atom scattering curves for As and S were taken from The $International$ $Tables$ of X-ray $Crystallography$, volume IV (Ibers & Hamilton 1974). Convergence was rapidly obtained for an anisotropic model of the structure. Using a weighting scheme $w = k/\sigma^2(F_o)$, the structure refinement converged to a final $R = 2.66\%$ for 1000 reflections with $F_o > 4\sigma(F_o)$, and $R = 5.19\%$ for all 1393 independent reflections. Inspection of the difference-Fourier map revealed maximum positive and negative peaks of 0.73 $e^-/Å^3$ and –0.55 $e^-/Å^3$, respectively. The fractional coordinates of atoms and their anisotropic-displacement parameters are given in Table 1. A list of the observed and calculated structure-factors is available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

An electronic apparatus equipped with optical fibers and a dichroic halogen lamp was used to irradiate the crystal with filtered polychromatic light (550 nm long-wavelength pass filter). The crystal was exposed to light for 1440 min, with steps of 240 min. The unit-cell parameters were measured after each exposure.

RESULTS

In addition to a much higher precision attained in the refinement, we found that the arrangement of atoms

TABLE 1. FRACTIONAL COORDINATES AND ANISOTROPIC DISPLACEMENT PARAMETERS OF ATOMS IN UZONITE

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}
As1	0.02032(6)	¼	0.80254(8)	0.0216(3)	0.0258(3)	0.0284(3)	0	0.0092(2)	0	0.0247(1)
As2	0.04931(7)	¼	0.45664(8)	0.0284(3)	0.0206(2)	0.0212(3)	0	-0.0020(2)	0	0.0243(1)
As3	0.39269(5)	0.48893(4)	0.74424(6)	0.0232(2)	0.0257(2)	0.0346(2)	-0.0044(2)	0.0060(2)	-0.0048(2)	0.0278(1)
S1	0.1848(1)	0.4664(1)	0.9131(1)	0.0294(5)	0.0315(5)	0.0285(5)	-0.0019(4)	0.0088(4)	-0.0093(4)	0.0293(2)
S2	0.2292(1)	0.4634(1)	0.4520(1)	0.0320(5)	0.0224(4)	0.0259(5)	-0.0009(4)	0.0076(4)	0.0043(4)	0.0265(2)
S3	0.5419(1)	¼	0.7885(2)	0.0183(6)	0.0322(7)	0.0438(9)	0	0.0030(6)	0	0.0318(3)

in the natural uzonite is quite similar to that reported for the synthetic analogue by Whitfield (1973a). The structure consists of discrete covalently bonded As_4S_5 molecules, which are held together by van der Waals forces to form zig-zag strings parallel to [010]. In the As_4S_5 molecule, the As atoms exhibit two different crystal-chemical environments. Atoms As1 and As2 are linked together and to two S atoms, whereas the two As3 atoms are linked to three S atoms (Fig. 1).

In Table 2, we report the intramolecular bond distances and angles in the structure of uzonite. The As–S bond distances (2.237–2.261 Å) match closely the value observed commonly for covalent As–S bonds [2.228–2.247 Å in the structure of realgar (Mullen & Nowacki 1972), 2.238–2.252 Å in the synthetic β-phase (Porter & Sheldrick 1972), 2.216–2.232 Å in the natural β-phase from Papua New Guinea (Burns & Percival 2001), 2.23–2.26 Å in pararealgar (Bonazzi *et al.* 1995), 2.199–2.220 Å in the synthetic α-As_4S_3 (Whitfield 1970), 2.218–2.234 Å in the synthetic β-As_4S_3 (Whitfield 1973b), and 2.205–2.238 Å in alacranite (Bonazzi *et al.* 2003b)]. The As–As bond distance (2.527 Å) is within the range observed in the molecules of the other arsenic sulfides [2.566–2.571 Å in the structure of realgar (Mullen & Nowacki 1972), 2.593 Å in the synthetic β-phase (Porter & Sheldrick 1972), 2.596 Å in the natural β-phase from Papua New Guinea (Burns & Percival 2001), 2.484–2.534 Å in pararealgar (Bonazzi *et al.* 1995), 2.443–2.451 Å in the synthetic α-As_4S_3 (Whitfield 1970), 2.460–2.480 Å in the synthetic β-As_4S_3 (Whitfield 1973b), and 2.566–2.579 Å in alacranite (Bonazzi *et al.* 2003b)].

The shortest S–S, As–S, As–As intermolecular contacts are the following: 3.453(2) Å (S1–S1), 3.357(1) Å (S2–As1), 3.734(1) Å (As3–As3), respectively. Figure 2 shows a projection of the uzonite structure along [001]. The shortest intermolecular contacts in the structure [S2–As1 = 3.357(1) Å and S2–As2 = 3.361(1) Å] are

between molecules that are aligned in zig-zag strings along the **b** axis.

In Table 3, we compare the X-ray powder-diffraction pattern originally observed for the type material (Popova & Polyakov 1985) with that calculated using the structural parameters obtained in this study. The calculated and observed data match closely, although in the observed pattern, a few lines (namely $d = 6.42$, $d = 3.233$ Å) cannot be indexed on the basis of the unit cell of uzonite.

EFFECTS OF LIGHTING

The unit-cell parameters of the uzonite measured after each exposure to light did not exhibit any significant change (the shifts were within the standard deviations). Figure 3 shows the variations of the unit-cell volume *versus* time of exposure for the uzonite crystal, together with the corresponding data previously obtained by Bonazzi *et al.* (1996) for crystals of natural realgar and synthetic β-As_4S_4, respectively. Preliminary investigations on non-stoichiometric As_8S_{9-x} crystals (unpubl. data), which consist of a disordered mixture of As_4S_4 and As_4S_5 molecules (Bonazzi *et al.* 2003a), also point toward a light-induced increase of the unit-cell volume. On the basis of these observations, it seems that only the As_4S_4 molecules easily undergo a transformation, whereas the As_4S_5 molecules do not. One should also consider that the unit-cell volume of the arsenic sulfides (see Bonazzi *et al.* 2003a, Fig. 4) increases linearly with an increase of the percentage of As_4S_5 molecules. Likewise, one can speculate that the increase of the unit-cell volume induced by lighting is due to an increase of sulfur in the structure. Sulfur incorporation, or, in other terms, an increase of the percentage of the As_4S_5 molecules in the structure, could occur if the reaction $5As_4S_4 + 3O_2 \rightarrow 4As_4S_5 + 2 As_2O_3$ takes place. Indeed, the formation of arsenolite in the light-induced process of alteration of realgar to pararealgar has been reported (Ballirano & Maras 2002). Thus, it appears likely that the As_4S_4 molecule is able to incorporate additional sulfur to change to the As_4S_5 molecule, whereas the As_4S_5 is not subjected to any addition. Indeed, no cage-like As_4S_6 molecule is known, the layered structure of orpiment being the As_2S_3 stable phase. Further experimental work will be necessary to verify this hypothesis.

ACKNOWLEDGEMENTS

TABLE 2. INTRAMOLECULAR BOND DISTANCES (Å) AND ANGLES (°) FOR UZONITE

As1	- S1	2.240(1)	S1 -	As1 -	S1(*i*)	102.91(6)
	S1(*i*)	2.240(1)			As2	100.86(3)
	As2	2.527(1)	S1(*i*) -	As1 -	As2	100.86(3)
As2	- S2	2.249(1)	S2 -	As2 -	S2(*i*)	100.34(5)
	S2(*i*)	2.249(1)			As1	101.08(3)
	As1	2.527(1)	S2(*i*) -	As2 -	As1	101.08(3)
As3	- S1	2.237(1)	S1 -	As3 -	S2	97.81(4)
	S2	2.251(1)			S3	106.20(5)
	S3	2.261(1)	S2 -	As3 -	S3	104.32(5)
			As2-	S2-	As3	108.34(4)
			As3-	S1-	As1	108.52(4)
				S3-	As3(*i*)	117.62(6)

Note: Symmetry code is: (*i*): *x*, ½ − *y*, *z*.

TABLE 3. CALCULATED AND OBSERVED X-RAY POWDER-DIFFRACTION DATA FOR UZONITE

	This work		Popova & Polyakov (1985)		
hkl	d_{calc} (Å)	I/I_{calc}	d_{obs} (Å)	I/I_0	hkl
100	7.8262	8			
001	7.0164	17	6.99	20	001
			6.42	30	
$\bar{1}$01	5.8042	74	5.81	100	$\bar{1}$01
110	5.6269	27	5.69	20	110
011	5.3023	64	5.31	60	011
101	4.7894	12	4.82	10	101
111	4.1221	5			
020	4.0480	13			
200	3.9131	11	3.96	20	020
$\bar{2}$01	3.7344	13	3.75	20	$\bar{2}$01
120	3.5955	100	3.602	80	120
210	3.5232	17	3.521	20	021
002	3.5082	9			
$\bar{1}$02	3.4572	5			
$\bar{2}$11	3.3910	7			
			3.233	20	
012	3.2190	28	3.207	40	012
$\bar{1}$12	3.1795	21	3.181	40	$\bar{1}$12
201	3.1697	11			
121	3.0916	55	3.100	60	121
102	2.9949	54	3.000	40	102
211	2.9516	18	2.954	20	211
$\bar{2}$02	2.9021	41	2.905	80	$\bar{2}$02
220	2.8135	66	2.820	60	220
$\bar{2}$21	2.7448	47	2.745	50	$\bar{2}$21
$\bar{2}$12	2.7319	12			
$\bar{3}$01	2.6137	18	2.619	40	301
221	2.4957	10	2.499	20	221
122	2.4076	21	2.412	20	122
003	2.3388	10	2.344	10	$\bar{1}$03
$\bar{1}$13	2.2731	5			

	This work		Popova & Polyakov (1985)		
hkl	d_{calc} (Å)	I/I_{calc}	d_{obs} (Å)	I/I_0	hkl
013	2.2469	11			
$\bar{2}$03	2.2012	13			
$\bar{3}$21	2.1958	14	2.203	?	320
320	2.1928	6			
103	2.1320	13	2.128	40	103
$\bar{2}$13	2.1241	15			
231	2.0548	7			
$\bar{1}$23	2.0442	10			
023	2.0251	6			
040	2.0240	39	2.026	50	040
321	2.0034	10			
$\bar{1}$41	1.9111	7	1.8818	20	203
240	1.7978	6			
232	1.7912	9			
$\bar{1}$04	1.7860	8			
420	1.7616	12			
$\bar{3}$32	1.7575	13	1.7554	20	042
004	1.7541	6			
$\bar{3}$23	1.7456	8			
322	1.7383	11			
$\bar{2}$33	1.7057	6			
$\bar{4}$22	1.6955	31	1.6879	50	$\bar{4}$22
223	1.6882	38			
142	1.6770	11			
$\bar{2}$42	1.6601	8			
421	1.6431	7			
$\bar{1}$24	1.6340	14	1.6331	20	
$\bar{4}$13	1.6312	6			
$\bar{3}$41	1.6003	6			
150	1.5856	5			
430	1.5840	8			
500	1.5652	8			

Note: In this work, the d values were calculated on the basis of a 7.973(2), b 8.096(2), c 7.148(2) Å, β 101.01(2)°. The intensities were calculated using the XPOW software version 2.0 (Downs *et al*. 1993). Only reflections with $I/I_{calc} > 5$ are listed. The new data are contrasted with the observed powder-diffraction pattern and indexing originally reported by Popova & Polyakov (1985).
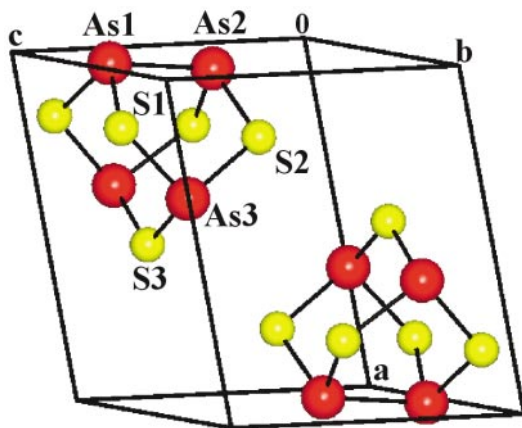

FIG. 1. The crystal structure of uzonite. The unit cell is outlined. The red and yellow circles refer to the As and S atoms, respectively.
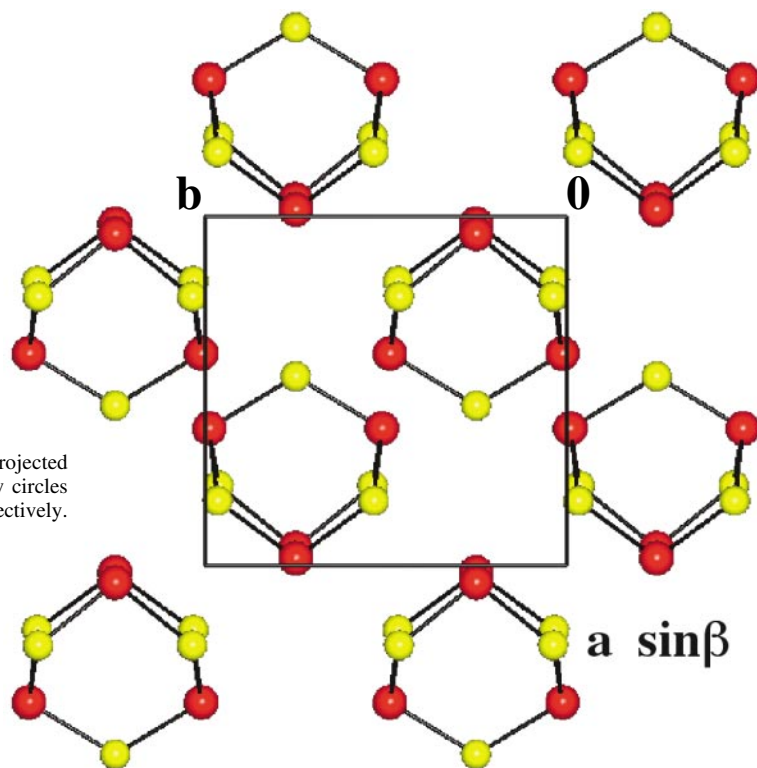
FIG. 2. The structure of uzonite projected down [001]. The red and yellow circles refer to the As and S atoms, respectively.
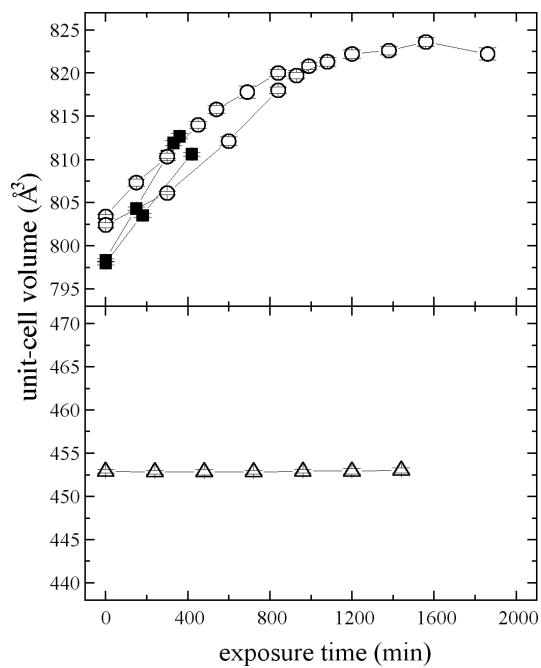
FIG. 3. Unit-cell volume *versus* length of exposure to light. The filled squares refer to A1 and A2 crystals of natural realgar (Bonazzi *et al.* 1996); the open circles refer to B1 and B2 crystals of the synthetic β-As₄S₄ phase (Bonazzi *et al.* 1996); open upward-pointing triangles refer to the uzonite crystal reported on in this study.

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