

## Light-induced variations in realgar and $\beta$ -As<sub>4</sub>S<sub>4</sub>: X-ray diffraction and Raman studies

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### ABSTRACT

Transformations induced by light in realgar and  $\beta$ -As<sub>4</sub>S<sub>4</sub> have been studied by means of X-ray diffraction (powder and single-crystal) and Raman laser spectroscopy. Both polychromatic and monochromatic light alter realgar and the  $\beta$  phase into pararealgar. By lowering the reaction rate (long-wavelength pass filter, low laser power) an intermediate product, corresponding to the so-called " $\chi$  phase," can be observed during the alteration process from  $\beta$ -As<sub>4</sub>S<sub>4</sub> to pararealgar (polychromatic filtered light and laser light) and that from realgar to pararealgar (only with polychromatic filtered light). The powder pattern of the  $\chi$  phase is fairly similar to that of  $\beta$ -As<sub>4</sub>S<sub>4</sub> but differs from realgar, and it can be indexed on the basis of an expanded  $\beta$ -phase unit cell. Lattice parameters are as follows:  $a = 9.758(5)$ ,  $b = 9.522(5)$ ,  $c = 9.074(5)$  Å,  $\beta = 100.84(5)^\circ$ , and  $a = 9.757(4)$ ,  $b = 9.512(7)$ ,  $c = 9.089(4)$  Å,  $\beta = 100.97(3)^\circ$  for the  $\chi$  phase obtained from alteration of realgar and  $\beta$ -As<sub>4</sub>S<sub>4</sub>, respectively. The formation of the  $\chi$  phase is preceded by a strong anisotropic increase of the unit-cell volume of realgar and the  $\beta$  phase. The effects of light exposure on lattice parameters were studied using single-crystal X-ray diffraction: In realgar  $a$  and  $c \sin \beta$  increase linearly with increasing exposure times, whereas  $b$  remains substantially unchanged. In the  $\beta$ -As<sub>4</sub>S<sub>4</sub> crystals,  $b$  and  $c \sin \beta$  increase while  $a$  decreases so that, after 1560 min, the unit-cell dimensions match those of the  $\chi$  phase. Raman spectroscopy, which allows monitoring of the alteration process in real time, indicates the presence of the same As<sub>4</sub>S<sub>4</sub> cage molecule in the  $\chi$  phase as in realgar and  $\beta$ -As<sub>4</sub>S<sub>4</sub> and confirms the similarity between the structure of  $\chi$  and that of  $\beta$ . However, a less-ordered crystal structure and a lower molecular symmetry is suggested from analysis of the spectroscopic results.

### INTRODUCTION

Four crystalline modifications of tetraarsenic tetrasulfide are known: realgar,  $\beta$ -As<sub>4</sub>S<sub>4</sub>, As<sub>4</sub>S<sub>4</sub> (II), and pararealgar.

The mineral realgar is the low-temperature polymorph,  $\alpha$ -As<sub>4</sub>S<sub>4</sub> (Hall 1966; Clark 1970; Roland 1972; Blachnik et al. 1980; Bryndzia and Kleppa 1988). It is commonly found as a minor constituent of lead, silver, and gold ore veins associated with orpiment and other arsenic minerals. It also frequently occurs as a sublimation product in active volcanic areas.

The  $\beta$ -As<sub>4</sub>S<sub>4</sub> phase is the high-temperature form, stable in the system As-S at temperatures higher than  $256 \pm 5$  °C (Hall 1966). However, according to Roland (1972), the temperature of the  $\alpha$ - $\beta$  transition is sensitive to composition: It occurs at  $239 \pm 3$  °C in the presence of elemental As, at  $252 \pm 2$  °C for stoichiometric composition, and at  $263 \pm 3$  °C in the presence of orpiment As<sub>2</sub>S<sub>3</sub>. Clark (1970) reported the coexistence of realgar and the  $\beta$  phase in silver-arsenic-tin veins in the Mina Alacran ore de-

posit, northern Chile. Exposure of this natural  $\beta$  phase to sunlight for two years, surprisingly led to no changes in its X-ray powder pattern. Later, Popova et al. (1986) realized that the mineral from the Mina Alacran deposit (identical to that from the Uzon caldera, Kamchatka, USSR) was a new mineral species and named it "alacranite." In spite of the slightly different chemical composition (As:S = 8:9), the powder pattern of alacranite is quite similar to that of the  $\beta$  phase.

Kutoglu (1976) obtained another As<sub>4</sub>S<sub>4</sub> polymorph from the recrystallization of a product formed by quenching an AsS melt from 500 to 600 °C. This compound, named As<sub>4</sub>S<sub>4</sub> (II), has never been found as a mineral.

The mineral pararealgar, As<sub>4</sub>S<sub>4</sub>, was first described by Roberts et al. (1980). These authors also clarified that the yellow film commonly covering realgar that has been exposed to light consists of pararealgar and not of orpiment as previously proposed.

Besides these four polymorphs with known crystal structure, another phase named " $\chi$  phase" was described by Douglass et al. (1992). They observed that the trans-

**TABLE 1.** Lattice parameters of realgar ( $\alpha$ -As<sub>4</sub>S<sub>4</sub>) and the  $\beta$  phase

Sample	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta$ (°)	<i>V</i> (Å <sup>3</sup> )	
<b><math>\alpha</math>-As<sub>4</sub>S<sub>4</sub></b>						
BMP	pd	9.303(1)	13.517(2)	6.641(2)	106.2 (3)	802.1(4)
SM1	pd-m	9.316(4)	13.541(6)	6.588(2)	106.37(2)	797.4(6)
SM2	pd-m	9.329(2)	13.560(4)	6.581(4)	106.39(2)	798.7(6)
MN	sc	9.325(3)	13.571(5)	6.587(3)	106.38(8)	799.7(6)
JC	pd	9.327(5)	13.56(1)	6.588(1)	106.49	798.4
CLA	pd-i	9.39(2)	13.54(3)	6.627(5)	106.0(2)	810(3)
A1	sc	9.323(2)	13.555(2)	6.588(1)	106.48(2)	798.3(2)
A2	sc	9.326(2)	13.560(2)	6.582(1)	106.53(1)	798.0(2)
<b><math>\beta</math>-As<sub>4</sub>S<sub>4</sub></b>						
CLB	pd-i	9.97(1)	9.29(1)	8.88(1)	102.6(1)	803(2)
SM	pd-m	9.960(4)	9.323(5)	8.882(3)	102.36(4)	805.6(6)
PS	sc	9.957(3)	9.335(4)	8.889(5)	102.48(4)	806.7(6)
RL	sc	9.92(3)	9.48(2)	8.91(4)	101.8(2)	820(5)
YZ	sc-pd	9.58	9.67	9.08	100.83	826.2
B1	sc	9.962(2)	9.313(1)	8.871(2)	102.54(1)	803.4(2)
B2	sc	9.958(2)	9.311(2)	8.867(2)	102.57(1)	802.4(3)

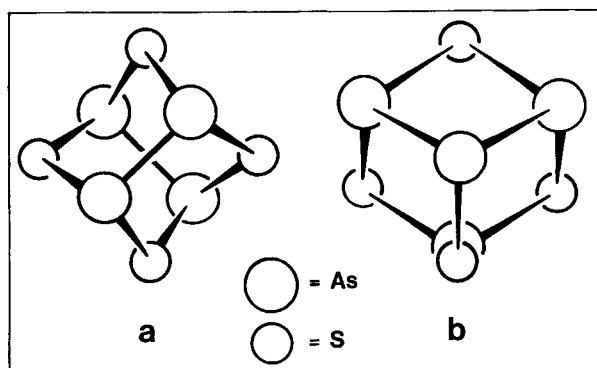
Note: pd = powder data, sc = single-crystal data, m = indexing modified by the present authors, i = indexed by the present authors. BMP = realgar from Monte Sughereto, Latium, Italy (Barrese et al. 1994); SM1 = synthetic  $\alpha$ -As<sub>4</sub>S<sub>4</sub> (Street and Munir 1970); SM2 = realgar from Humboldt County, Nevada (Street and Munir 1970); MN = realgar from Binnental, Switzerland (Mullen and Nowacki 1972); JC = realgar from Humboldt County, Nevada, JCPDS card no. 41-1494; CLA = realgar from Mina Alacrán, Pampa Larga, Chile (Clark 1970); A1 = realgar from Shimen, Hunan Province, China (this study); A2 = realgar from Monte Sughereto, Latium, Italy (this study). CLB = high-temperature phase from Mina Alacrán, Pampa Larga, Chile (Clark 1970); SM = synthetic  $\beta$ -As<sub>4</sub>S<sub>4</sub> (Street and Munir 1970); PS = synthetic  $\beta$ -As<sub>4</sub>S<sub>4</sub> (Porter and Sheldrick 1972); RL = synthetic  $\beta$ -As<sub>4</sub>S<sub>4</sub> (Roland 1972); YZ = synthetic  $\beta$ -As<sub>4</sub>S<sub>4</sub> (Yu and Zoltai 1972); B1 and B2 = synthetic  $\beta$ -As<sub>4</sub>S<sub>4</sub> (this study).

formation rate of realgar to pararealgar, when exposed to sunlight, decreases if filtered light with  $\lambda > 560$  nm is used. According to these authors, by lowering the rate of the light-induced process, a new phase occurs as an intermediate product, which is a precursor to the formation of pararealgar.  $\chi$  phase was also obtained by heating pararealgar at 175 °C as a precursor to the formation of the  $\beta$  phase. Bonazzi et al. (1994), in a preliminary study on the structural adjustments induced by light in realgar, observed that the  $\chi$ -phase formation is preceded by a strong anisotropic increase of the unit-cell volume of realgar.

The present work studies the variations induced by light on the structures of both realgar and the  $\beta$  phase and "sheds some light" on the  $\chi$ -phase problem.

## BACKGROUND

The crystal structures of realgar (Ito et al. 1952; Mullen and Nowacki 1972) and the  $\beta$  phase (Porter and Sheldrick 1972) are based on the same covalently bonded As<sub>4</sub>S<sub>4</sub> cage molecule. Molecules are held together by van der Waals forces resulting in two crystal structures: Realgar crystallizes in the  $P2_1/n$  space group, the  $\beta$  phase in the  $C2/c$  space group. Table 1 reports the lattice parameters of these two phases. As<sub>4</sub>S<sub>4</sub> (II) (Kutoglu 1976) and pararealgar (Bonazzi et al. 1995) also have a crystal structure based on a molecular packing. The covalently bonded As<sub>4</sub>S<sub>4</sub> cage molecule is identical in both structures but differs from that found in the structures of realgar and



**FIGURE 1.** As<sub>4</sub>S<sub>4</sub> cage molecules found in the structure of realgar and the  $\beta$  phase (a) and in the structure of As<sub>4</sub>S<sub>4</sub> (II) and pararealgar (b).

the  $\beta$  phase (Fig. 1). The As<sub>4</sub>S<sub>4</sub> (II) phase crystallizes in the  $P2_1/n$  space group [lattice parameters:  $a = 11.193(6)$ ,  $b = 9.994(6)$ ,  $c = 7.153(4)$  Å,  $\beta = 92.8(5)^\circ$ ,  $V = 799.2(8)$  Å<sup>3</sup>,  $Z = 4$ ], pararealgar in the  $P2_1/c$  space group [lattice parameters:  $a = 9.909(2)$ ,  $b = 9.655(1)$ ,  $c = 8.502(1)$  Å,  $\beta = 97.29(1)^\circ$ ,  $V = 806.8(2)$  Å<sup>3</sup>,  $Z = 4$ ]. No crystallographic data have been published regarding the  $\chi$  phase except for the X-ray powder lines observed by Douglass et al. (1992): According to these authors the lines could not be indexed as  $\alpha$  phase,  $\beta$  phase, or pararealgar.

Spectroscopic studies have also contributed toward understanding the As<sub>4</sub>S<sub>4</sub> phases. Vibrational features of the  $\alpha$  and  $\beta$  phases were investigated by means of IR and Raman spectroscopy (Forneris 1969; Porter and Sheldrick 1972; Bues et al. 1983). Raman spectra of both crystalline forms at 10 K were obtained by Slade and Zallen (1979), and a vibrational assignment of realgar was proposed by Ystenes et al. (1994) on the basis of ab initio quantum mechanical calculations. The spectral behavior of realgar in the visible region was studied by Hunt et al. (1971), who observed a well-defined absorption edge near 550 nm.

## EXPERIMENTAL METHODS

### Samples

The realgar used in the present study is from Shimen, Hunan Province, China (specimen no. 46768 Museo di Mineralogia dell'Università di Firenze), and from Monte Sughereto, Latium, Italy (collected by the authors). To obtain the high-temperature polymorph ( $\beta$ -As<sub>4</sub>S<sub>4</sub>), the sample from Shimen was ground and heated at 295 °C in an evacuated silica tube in a horizontal furnace for 24 h. It was then quenched to room temperature.

### X-ray diffraction

The alteration process that produces pararealgar from realgar and the  $\beta$  phase was monitored closely by recording X-ray data after each successive light treatment. A Schott KL 1500 electronic apparatus equipped with optical fibers and a 150 FFR Sylvania dichroic halogen lamp

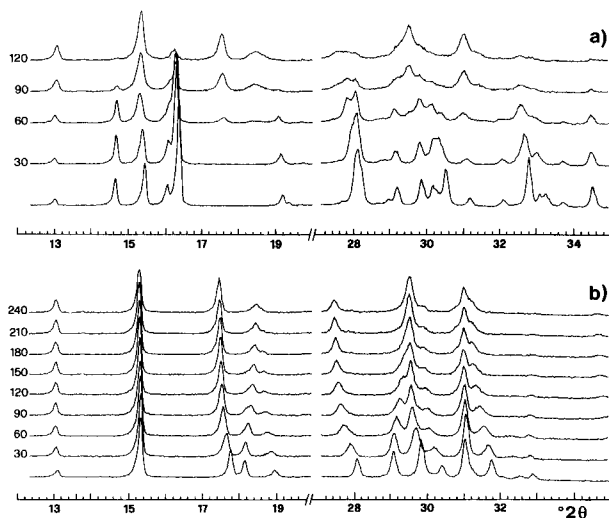


FIGURE 2. Selected portions of the X-ray powder patterns (CuK $\alpha$  radiation) recorded after different light exposures (minutes) for realgar (a) and  $\beta$ -As<sub>4</sub>S<sub>4</sub> (b).

was used to irradiate the sample with polychromatic light at a distance of 3 cm. This apparatus, also equipped with a visible pass filter, prevented infrared radiation from reaching the sample (IR transmittance  $< 1/1000$ ). Following Douglass et al. (1992), the  $\chi$  phase was obtained using a 550 nm long-wavelength pass filter (Schott-Germany) to cut off the region of the visible spectrum where the absorption by  $\alpha$ - and  $\beta$ -As<sub>4</sub>S<sub>4</sub> is maximum. The emission spectrum of the filtered light ranged from 550 to 800 nm, with an emission maximum at  $\sim 600$  nm. The power density on the sample, measured with a power-meter instrument (model 362; Scientech, Boulder, Colorado), was about 70 mW/cm<sup>2</sup>.

X-ray powder data were collected with a Philips PW-3710 automated diffractometer (Bragg-Brentano assembly) equipped with incident- and diffracted-beam Soller slits, 0.2 mm receiving slit, and a diffracted-beam graphite monochromator. Powder patterns were recorded at steps of 0.02° 2 $\theta$  and a counting time of 1 s/step, using CuK $\alpha$  radiation at 50 kV and 25 mA.

Two single crystals of realgar (A1 and A2) and two of the  $\beta$  phase (B1 and B2) were selected. Unit-cell parameters were determined by least-squares refinement of 25 reflections ( $18^\circ < \theta_{\text{MoK}\alpha} < 29^\circ$ ) measured with an Enraf-Nonius CAD4 single-crystal diffractometer. The crystals were exposed to filtered light ( $\lambda > 550$  nm), and the unit-cell parameters were determined after each exposure until loss of crystallinity.

### Raman spectroscopy

Raman measurements were performed on solid samples placed in a rotating device to minimize local heating, using the 568.2 nm exciting line of a Kr ion laser (Coherent, Palo Alto, California) with a power density of 15 mW/cm<sup>2</sup>. The alteration of the various As<sub>4</sub>S<sub>4</sub> polymorphs

TABLE 2. Lattice parameters of realgar and  $\beta$ -As<sub>4</sub>S<sub>4</sub> measured after various light exposures

Sample	t (min)	a (Å)	b (Å)	c (Å)	$\beta$ (°)	V (Å <sup>3</sup> )
<b><math>\alpha</math>-As<sub>4</sub>S<sub>4</sub></b>						
A1	0	9.323(2)	13.555(2)	6.588(1)	106.48(2)	798.3(2)
A1	150	9.351(2)	13.570(2)	6.592(1)	105.95(2)	804.3(2)
A1	300	9.384(2)	13.568(2)	6.602(1)	105.41(2)	810.4(3)
A1	330	9.393(2)	13.565(2)	6.605(2)	105.26(2)	811.9(3)
A1	360	9.401(2)	13.559(2)	6.605(2)	105.14(2)	812.7(3)
A2	0	9.326(2)	13.560(2)	6.582(1)	106.53(1)	798.0(2)
A2	180	9.351(2)	13.574(2)	6.587(1)	106.05(1)	803.5(2)
A2	420	9.392(2)	13.570(2)	6.596(1)	105.38(2)	810.6(2)
<b><math>\beta</math>-As<sub>4</sub>S<sub>4</sub></b>						
B1	0	9.962(2)	9.313(1)	8.871(2)	102.54(1)	803.4(2)
B1	150	9.945(3)	9.337(2)	8.894(3)	102.15(2)	807.3(4)
B1	300	9.926(2)	9.365(3)	8.909(3)	101.91(2)	810.3(4)
B1	450	9.887(2)	9.401(4)	8.940(3)	101.59(2)	814.0(4)
B1	540	9.864(2)	9.414(4)	8.963(3)	101.44(2)	815.8(5)
B1	690	9.842(3)	9.432(6)	8.986(4)	101.34(3)	817.8(7)
B1	840	9.818(2)	9.445(3)	9.017(3)	101.27(2)	820.0(4)
B1	990	9.798(3)	9.452(3)	9.036(3)	101.20(3)	820.8(4)
B2	0	9.958(2)	9.311(2)	8.867(2)	102.57(1)	802.4(3)
B2	300	9.946(2)	9.331(2)	8.889(2)	102.27(2)	806.1(2)
B2	600	9.881(3)	9.397(5)	8.930(2)	101.64(2)	812.1(5)
B2	840	9.831(2)	9.444(2)	8.986(3)	101.36(2)	818.0(4)
B2	930	9.815(3)	9.454(3)	9.010(2)	101.35(2)	819.7(4)
B2	1080	9.793(4)	9.465(3)	9.034(3)	101.23(3)	821.3(5)
B2	1200	9.784(4)	9.470(3)	9.046(2)	101.19(2)	822.2(5)
B2	1380	9.769(4)	9.475(4)	9.058(2)	101.13(2)	822.6(5)
B2	1560	9.763(4)	9.485(3)	9.063(2)	101.09(2)	823.6(5)
B2	1860	9.757(6)	9.478(5)	9.057(3)	100.99(4)	822.2(7)
$\chi_\alpha$		9.758(5)	9.522(5)	9.074(5)	100.84(5)	828.1(8)
$\chi_\beta$		9.757(4)	9.512(7)	9.089(4)	100.97(3)	828.1(8)
$\chi_D$		9.707(6)	9.49(2)	9.04(1)	101.05(8)	817.7(20)

Note: A1 = realgar from Shimen, Hunan Province, China; A2 = realgar from Monte Sughere, Latium, Italy; B1 and B2 = synthetic  $\beta$ -As<sub>4</sub>S<sub>4</sub> (single-crystal data);  $\chi_\alpha$  and  $\chi_\beta$  =  $\chi$  phase obtained by light exposure of  $\alpha$ -As<sub>4</sub>S<sub>4</sub> and  $\beta$ -As<sub>4</sub>S<sub>4</sub>, respectively;  $\chi_D$  =  $\chi$  phase obtained by Douglass et al. (1992) (powder data).

to pararealgar was monitored by recording Raman spectra as a function of time. The rotating sample was continually irradiated with a defocused laser beam. This procedure was particularly suitable to obtain Raman spectra of the sample during the irradiation and provided a continuous monitoring of the crystal modifications. The Raman instrument was equipped with a Jobin-Yvon HG-2S monochromator, a cooled RCA-C31034A photomultiplier, and a data acquisition system.

## RESULTS AND DISCUSSION

From the analysis of the X-ray powder patterns obtained after each successive exposure to filtered light, it became evident that the diffraction peaks of both polymorphs had shifted in angular positions, resulting in an increase of the volume of the unit cell. This feature, previously observed during the first steps of alteration of realgar (Bonazzi et al. 1994), also occurs in the  $\beta$  phase. However, in this case, the light-induced alteration process that forms the  $\chi$  phase follows a different route: With increasing exposure, the unit cell of the  $\beta$  phase gradually changes, and after 300 min the powder pattern becomes very similar to that published by Douglass et al. (1992)

TABLE 3. X-ray powder data for the  $\beta$ -As<sub>4</sub>S<sub>4</sub> phase and the " $\chi$  phases"

hkl	1			2			3			4		
	$d_{\text{calc}}$	$d_{\text{obs}}$	$l/l_0$	$d_{\text{calc}}$	$d_{\text{obs}}$	$l/l_0$	$d_{\text{calc}}$	$d_{\text{obs}}$	$l/l_0$	$d_{\text{calc}}$	$d_{\text{obs}}$	$l/l_0$
110	6.7374	6.75	10	6.7495	6.77	30	6.7548	6.77	35			
011*				6.5079	6.50	5	6.5067	6.50	5			
										(5.81)**		100
11 $\bar{1}$	5.7569	5.76	100	5.7679	5.78	100	5.7636	5.78	100	5.7449	5.74	60
111	4.9708	4.98	50	5.0661	5.07	70	5.0694	5.08	60	5.0395	5.05	45
200	4.8700	4.87	30	4.7892	4.80	20	4.7919	4.80	20	4.7633	4.77	15
020	4.6648	4.67	10									
021	4.1083	4.11	10	4.1972	4.20	10	4.1993	4.20	10	4.1832	4.18	5
11 $\bar{2}$	3.9253	3.93	40	3.9752	3.98	35	3.9693	3.97	25	3.9562	3.96	25
112	3.4200	3.42	5	3.5116	3.51	10	3.5117	3.50	5			
220	3.3687	3.37	5	3.3747	3.38	5	3.3774	3.38	<5			
22 $\bar{1}$	3.3129	3.31	10	3.3066	3.30	10	3.3068	3.30	10	3.2943	3.30	10
022	3.1762	3.18	30	3.2540	3.25	30	3.2534	3.25	20	3.2397	3.24	25
300*				3.1928	3.21	5	3.1946	3.20	5	3.1755	3.19	10
310	3.0663	3.07	50	3.0269			3.0287			3.0113		
221	2.9919	2.990	70	3.0252	3.03	80	3.0280	3.03	70	3.0111	3.01	60
202	2.9370	2.939	25	2.9928	2.996	15	2.9944	3.00	5			
22 $\bar{2}$	2.8785	2.880	70	2.8840	2.886	50	2.8818	2.885	50	2.8724	2.87	55
13 $\bar{1}$	2.8620	2.864	15	2.9053	2.907	15						
113	2.8148	2.816	30	2.8674	2.866	20	2.8627	2.865	5			
131	2.7484	2.749	10									
311	2.7207	2.722	10									
113	2.5229			2.5964	2.596	10	2.5955	2.595	5			
13 $\bar{2}$	2.5253	2.524	15									
222	2.4854	2.487	10	2.5330	2.535	<5	2.5347	2.537	5			
023	2.4575	2.458	5									
400	2.4350	2.435	5	2.3946	2.396	5	2.3959	2.391	5			
223	2.3779			2.3965			2.3935					
132	2.3742	2.378	15	2.4289	2.427	5						
33 $\bar{1}$	2.2581	2.259	10	2.2544	2.252	5	2.2552	2.254	5			
330	2.2458	2.246	15	2.2498			2.2516					
42 $\bar{1}$	2.1963	2.197	10									
204	2.1635	2.161	10									
133	2.1412	2.141	10	2.1820	2.184	5	2.1809	2.180	5			
332	2.1294	2.129	5	2.1268	2.125	<5	2.1263	2.130	<5			
240	2.1036	2.100	5									
133	2.0039	2.004	5									
242	1.9666	1.969	5									
333	1.9190	1.919	5	1.9226	1.923	<5	1.9212	1.921	<5			
313	1.9162	1.916	5									
150	1.8326	1.832	10				1.8679	1.867	<5			
043	1.8153	1.815	10									
422	1.7990	1.798	10	1.8123	1.811	<5						

Note: 1 =  $\beta$ -As<sub>4</sub>S<sub>4</sub> phase [ $a = 9.979(3)$ ,  $b = 9.330(3)$ ,  $c = 8.886(2)$  Å,  $\beta = 102.56(2)^\circ$ ]; 2 =  $\chi$  phase obtained from light-induced alteration of the  $\beta$ -As<sub>4</sub>S<sub>4</sub> phase [ $a = 9.757(4)$ ,  $b = 9.512(7)$ ,  $c = 9.089(4)$  Å,  $\beta = 100.97(3)^\circ$ ]; 3 =  $\chi$  phase obtained from light-induced alteration of realgar [ $a = 9.758(5)$ ,  $b = 9.522(5)$ ,  $c = 9.074(5)$  Å,  $\beta = 100.84(5)^\circ$ ]; 4 =  $\chi$  phase obtained by Douglass et al. (1992) from alteration of realgar [ $a = 9.707(6)$ ,  $b = 9.49(2)$ ,  $c = 9.04(1)$  Å,  $\beta = 101.05(8)^\circ$ ].

\* Reflection forbidden in space group C2/c (not used in the least-squares calculation).

\*\* Not indexed. This line was not observed in the powder pattern of the  $\chi$  phases obtained in this work.

for the  $\chi$  phase. The evolution of the powder diffraction patterns with exposure to filtered light for the  $\alpha$  and  $\beta$  phases is shown in Figure 2. The powder pattern of the  $\chi$  phase differs substantially from that of realgar, but it is fairly similar to that of the  $\beta$  phase. This observation allowed for an indexing of the  $\chi$ -phase powder pattern on the basis of a modified unit cell of the  $\beta$  phase. The same indexing was then applied to the lines observed in the powder patterns of the  $\chi$  phase obtained from alteration of realgar. Lattice parameters of  $\chi_\alpha$  (inversion from realgar),  $\chi_\beta$  (inversion from  $\beta$ -As<sub>4</sub>S<sub>4</sub>), and  $\chi_D$  (recalculation of the powder pattern of Douglass et al. 1992) are given in Table 2.

Table 3 reports powder data for the three  $\chi$  phases. The strict similarity between the powder patterns of the  $\chi$  and  $\beta$  phases suggests that these phases have similar structural

arrangements. However, it is possible that the change in the relative position of molecules, which is required by the change in the shape and volume of the unit cell, involves a different space group. This is suggested by the presence of two diffraction peaks: The first, with  $d = 6.50$  Å, matches the  $d_{\text{calc}, 011}$ ; the second,  $d = 3.20$  Å, is close to the  $d$  value calculated for the reflection 300. The presence of these lines (both forbidden for the C-type lattice) suggests that some changes in the structural arrangement may have occurred.

As already inferred from powder data, exposure to light modifies the structures of both  $\alpha$ - and  $\beta$ -As<sub>4</sub>S<sub>4</sub>, resulting in an increase of the unit-cell volumes. This behavior is confirmed by the variations of the unit-cell dimensions of the single crystals (Table 2). For fresh, unaltered realgar, the unit-cell volume was in the range 798–800 Å<sup>3</sup>

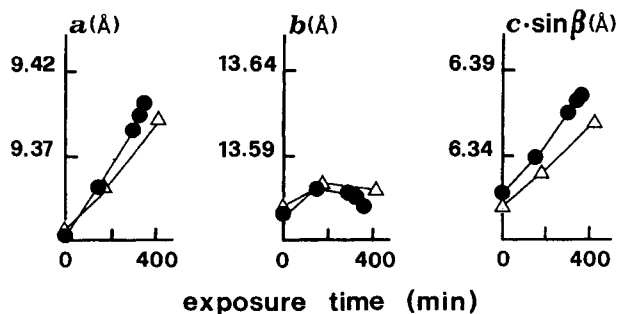


FIGURE 3. The  $a$ ,  $b$ , and  $c \sin \beta$  parameters of realgar vs. light exposure (single-crystal data).

(see Table 1); after exposure to light it reached  $\sim 813 \text{ \AA}^3$  in A1 and A2 crystals. The peaks then became weaker and broader, and the crystals were not suitable for measurement of the unit-cell dimensions.

For the  $\beta$  phase (crystal B2), the unit-cell volume was  $802.4 \text{ \AA}^3$  before the light treatment and reached  $823.6 \text{ \AA}^3$  after 1560 min of exposure, a value close to that of the  $\chi$  phase. After a subsequent exposure (300 min) the unit-cell volume ceased to increase. A further exposure led to the breakdown of the crystal structure. The B1 crystal exhibits the same alteration path; however, the experiment was terminated after 990 min of lighting exposure because the crystal was lost.

Figures 3 and 4 show the variations of the lattice parameters vs. time of exposure for the crystals of realgar and the  $\beta$  phase, respectively. The expansion of the unit cell discussed above appears considerably anisotropic: In realgar (Fig. 3)  $a$  and  $c \sin \beta$  increase linearly, whereas  $b$  remains substantially unchanged. In  $\beta$ -As<sub>4</sub>S<sub>4</sub> (Fig. 4)  $b$  and  $c \sin \beta$  increase while  $a$  decreases.

Figure 5a shows a plot of the values of the  $a$  parameter vs. the corresponding values of  $b$  with the advancement of the light-induced alteration process for crystals B1 and B2 together with those of the  $\chi$  phase. Figure 5b shows an analogous diagram for  $c$  vs. the  $\beta$  angle. It can be seen that not only the unit-cell volumes but also each single parameter of the  $\chi$  phase nicely matches the corresponding value reached by the  $\beta$  phase after the light treatment. Both diagrams also report data from the literature; it is evident from Figure 5b that some of these data, located on the alteration path of the  $\beta$  phase, are relative to samples already altered by exposure to light.

Raman spectra of  $\alpha$ -As<sub>4</sub>S<sub>4</sub> were taken as a function of irradiation time: Realgar is directly transformed into pararealgar as shown by the disappearance of the doublet at  $184\text{--}194 \text{ cm}^{-1}$  and the increase in intensity of the typical pararealgar peaks at  $230\text{--}236 \text{ cm}^{-1}$  (authors' unpublished data). The  $\chi$  phase cannot be identified. On the other hand, by exposing the  $\beta$  phase to the defocused laser beam, the  $\chi$  phase was gradually formed, and the transformation of  $\beta$  to  $\chi$  was monitored through the intensity changes of the most significant bands. After 3 h exposure the intensities of the  $\chi$  peaks remain unaltered, and the most sig-

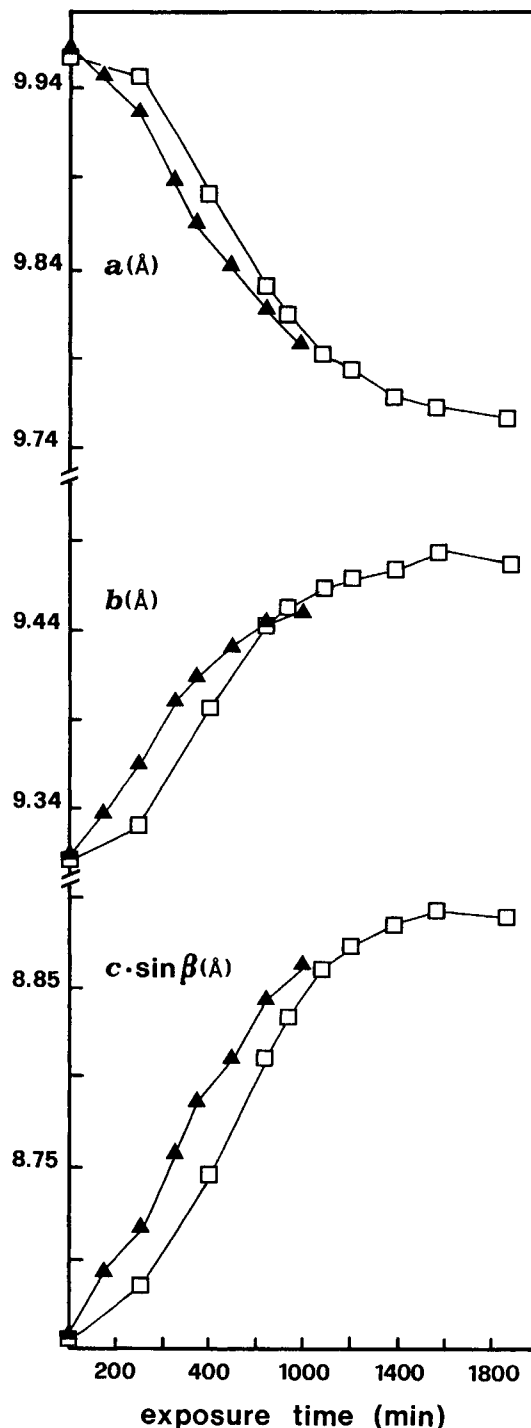


FIGURE 4. The  $a$ ,  $b$ , and  $c \sin \beta$  parameters of  $\beta$ -As<sub>4</sub>S<sub>4</sub> vs. light exposure (single-crystal data).

nificant band of this phase at  $235 \text{ cm}^{-1}$  gains its maximum intensity. The presence of the  $\chi$  phase was confirmed by means of X-ray powder diffraction performed on the samples irradiated during the Raman experiments.

As shown in Figure 6, the  $\chi$  phase and  $\beta$ -As<sub>4</sub>S<sub>4</sub> exhibit

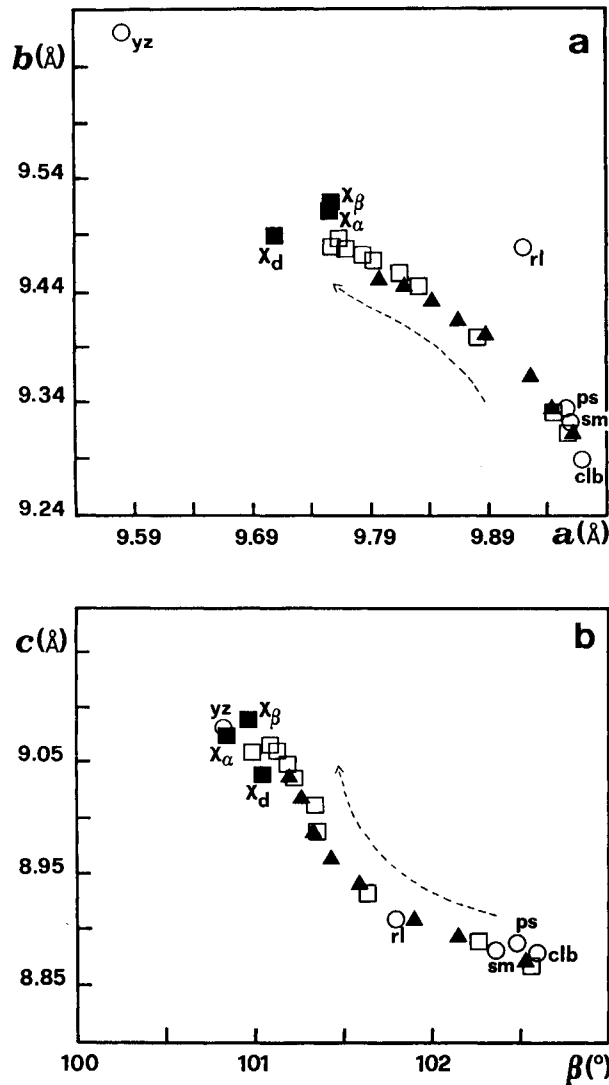


FIGURE 5. Alteration paths of the  $\beta$  phase. (a) Variation of  $b$  parameter plotted against  $a$ , and (b)  $c$  parameter vs.  $\beta$  angle. Solid triangles and open squares represent crystals B1 and B2, respectively; solid squares refer to the  $\chi$  phase (powder data); and circles show data from the literature (labels as in Table 1).

a close similarity in the lattice mode region, where realgar differs substantially. The assignment of the internal modes of the  $\chi$  phase, occurring in the 100–400  $\text{cm}^{-1}$  range, generally matches that of the  $\alpha$  or  $\beta$  phases. This is also evident from Table 4, which shows that the As-S as well as the As-As stretching modes occur essentially at the same frequencies as in realgar and  $\beta$ -As<sub>4</sub>S<sub>4</sub>. The Raman spectrum of the  $\chi$  phase closely resembles that of the  $\beta$  phase, especially for the strong bands at 188, 345, 351, and 363  $\text{cm}^{-1}$ , but it is also characterized by the presence of broader bands, which suggests a less-ordered molecular arrangement than in the  $\alpha$  and  $\beta$  phases.

The greater number of bands observed in the spectrum of the  $\chi$  phase might be attributed to the lowering of the

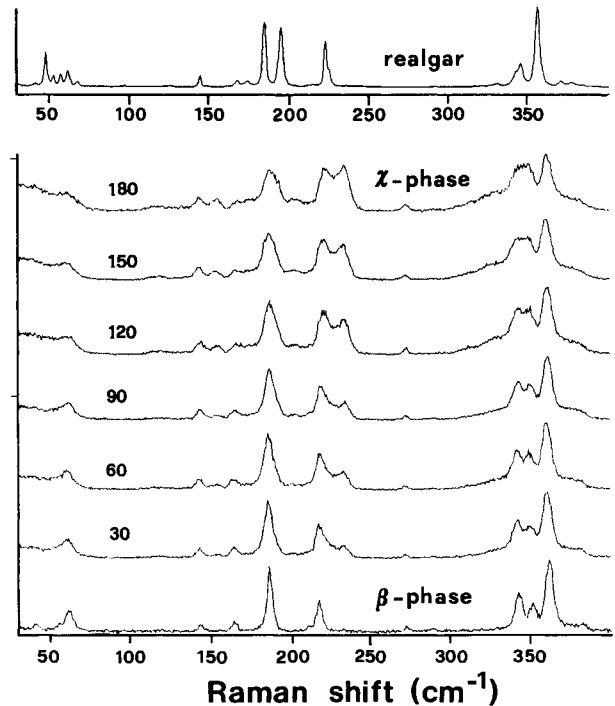


FIGURE 6. Raman spectra of  $\beta$ -As<sub>4</sub>S<sub>4</sub> irradiated with the 568.2 nm laser line at different times (in minutes); the Raman spectrum of realgar is at the top.

TABLE 4. Raman frequencies of As<sub>4</sub>S<sub>4</sub> polymorphs

S	$\alpha$ -As <sub>4</sub> S <sub>4</sub>	$\chi$ phase	$\beta$ -As <sub>4</sub> S <sub>4</sub>	Approximate description*
A <sub>2</sub>	28 s		32 w	Lattice modes
	41 w		42 w	
	48 s		56 sh	
	52 m		63 m	
	57 m			
	61 m			
A <sub>2</sub>	67 w	63 w	63 m	As-As-S bending
	126 vw	118 br	120 vw	
B <sub>1</sub>	144 m	137 vw	144 m	As-As-S bending
		146 m		
E	167 w	167 w	164 m	As-As-S bending
	173 w	176 vw		As-As stretching
A <sub>1</sub>	184 vs	188 s	187 vs	As-As stretching + As-S-As bending
	196 vs			
E	210 vw	202 vw	211 sh	As-As-S bending
	214 vw			
B <sub>2</sub>	222 s	222 s	217 s	As-As-S bending
		235 s		
		274 br		
		315 sh		
A <sub>2</sub>	330 w	326 sh	332 sh	As-S stretching
E	345 m	345 s	343 s	As-S stretching
B <sub>1</sub>	355 vs	351 s	352 m	As-S stretching
A <sub>1</sub>	355 vs	363 vs	362 vs	As-S stretching
E	370 w		376 w	As-S stretching
B <sub>2</sub>	376 w	380 sh	383 w	As-S stretching

Note: S = molecular species, vs = very strong, s = strong, m = medium, w = weak, vw = very weak, br = broad, and sh = shoulder.

\* According to Ystenes et al. (1994).

$D_{2d}$  symmetry of the molecules in the  $\alpha$ - and  $\beta$ -As<sub>4</sub>S<sub>4</sub>. Consequently, modes of the E type can split into two components; namely, the bands at 164 and 211 cm<sup>-1</sup> of the  $\beta$ -As<sub>4</sub>S<sub>4</sub> spectrum can result in the doublets at 155–167 and 202–235 cm<sup>-1</sup>, respectively.

Diffraction and spectroscopic data suggest a close similarity between  $\beta$ -As<sub>4</sub>S<sub>4</sub> and the so-called “ $\chi$  phase.” The latter can be considered as an expanded, less-ordered  $\beta$  phase, probably characterized by a lower molecular symmetry. This proposal also accounts for the unexpected result obtained by Douglass et al. (1992), who observed the “unknown  $\chi$ -phase” as a precursor of the  $\beta$  phase by heating pararealgar to 175 °C.

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