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Experimental study of the effect of light intensity on arsenic sulfide (As_4S_4) alteration

Atsushi Kyono *

Division of Earth Evolution Sciences, Graduate School of Life and Environmental Sciences, University of Tsukuba, Tennodai 1-1-1, Tsukuba, Ibaraki 305-8572, Japan

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Abstract

Correlation between light-induced alteration of arsenic sulfide (mineral name: realgar, As_4S_4) and irradiated light intensity was investigated using *in situ* single-crystal X-ray diffractometry. The exposure time required for the phase transformation increases gradually as the light intensity decreases. The X-ray diffraction intensities of (2 6 1) and (3 6 1) reflections decrease sharply, indicating that the As–As bonds in As_4S_4 molecules are broken by insertion of an additional S atom. The As–As bond cleavage and As_4S_4 molecule deformation are largely produced throughout the crystal structure when the unit cell volume reaches approximately 802 $Å^3$, followed by rearrangement of the As_4S_4 pararealgar molecular packing. It continues until the unit the cell volume expands continuously to approximately 810 $Å^3$. The feature of the continuous increase of the a cell parameter was observed within the light intensity range. The value of the b cell parameter remained constant during light treatment. Nevertheless, the linear increase in the $c \sin \beta$ value was not confirmed as the light intensity decreased. Variation of the unit cell volume correlates with that of the $c \sin \beta$ value. Consequently, no continuous increase of unit cell volume was apparent in realgar exposed to light of 5 W/m^2. Such a discontinuous increase in $c \sin \beta$ value is attributed mainly to the value of the c cell parameter, which varies widely with light exposure. The highest sensitivity for lighting is shown at the a and β angles in unit cell parameters. It increases or decreases linearly up to the loss of crystallinity.

Keywords: Arsenic sulfide; Realgar; Phase transformation; Single-crystal X-ray diffraction; Light intensity

1. Introduction

Arsenic shows diverse chemical behaviors in the natural environment. It can readily change its oxidation state and bonding configuration, thereby creating a rich inorganic chemistry. Exposure of deep-red arsenic sulfide (mineral name realgar; As_4S_4) to sunlight engenders alteration to friable yellow-orange micronodules on the surface and fissures at some critical thickness [1]. The yellow-orange products covering the realgar surface consist of pararealgar (different As_4S_4 polymorph), which transforms not with ultraviolet (UV) or infrared (IR) radiation, but with light at wavelengths of ca. 500–670 nm [1]. Such alteration always proceeds from realgar via the so-called χ phase to pararealgar. Many studies have been performed on the phase transformation of realgar since the pioneering work of Douglass et al. [1]. Very recently, the χ phase has been proven definitively to consist of a β-As_4S_4 structure with As_4S_5 molecules that are randomly substituted for As_4S_4 [2]. Those studies specifically examined the transformation dynamics of arsenic sulfides [3–6]. However, none of those studies investigated light irradiated to realgar. According to the earth's annual global mean energy budget, solar radiation reaching the earth's surface was estimated as 168 W/m^2 [7]. Uncertainty of approximately 20–25 W/m^2 pertains because of cloudy sky absorption: water vapor differs considerably between clear and cloudy conditions [7]. Therefore, the net energy at the earth's surface would always be close to 150 W/m^2. According to Douglass et al. [1] realgar crystal under sunlight is readily transformed into pararealgar at exposure times of 6–12 h. On the other hand, no reaction occurred during exposure for at least 1 month in the laboratory under fluorescent lighting [1] and for 20 years in a mine dump in Pampa Larga, Chile under sunlight [8]. The presence of threshold light intensity for the phase transformation remains unknown. Lighting power data for realgar are necessary for examination of light-induced phase transformation from realgar to pararealgar. This study is intended to elucidate a correlation between light

* Tel.: +81 29 853 7176; fax: +81 29 853 7887.
E-mail address: kyono@arsia.geo.tsukuba.ac.jp.

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Table 1
Lattice parameters of realgar measured after light exposure using 30 W/m^2 power density

Exposure time (h)	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)
0	9.331 (9)	13.567 (3)	6.585 (9)	106.31 (4)	800.0 (1.3)
6	9.344 (6)	13.564 (2)	6.586 (6)	106.27 (3)	800.4 (9)
12	9.340 (5)	13.564 (1)	6.587 (5)	106.17 (2)	801.4 (7)
18	9.347 (6)	13.566 (2)	6.587 (5)	106.08 (3)	802.6 (9)
24	9.354 (5)	13.568 (1)	6.589 (5)	105.97 (2)	804.0 (8)
30	9.360 (4)	13.570 (1)	6.589 (4)	105.87 (2)	804.9 (7)
36	9.360 (7)	13.568 (2)	6.591 (7)	105.74 (3)	805.7 (1.1)
42	9.365 (9)	13.563 (3)	6.600 (9)	105.67 (5)	807.1 (1.3)
48	9.370 (9)	13.562 (3)	6.601 (7)	105.55 (5)	808.5 (1.3)
54	9.379 (9)	13.565 (3)	6.603 (8)	105.46 (6)	810.0 (1.7)

intensity and light-induced alteration of realgar using *in situ* single-crystal X-ray diffractometry (XRD). The results reveal the presence of threshold light intensity for phase transformation.

2. Experimental methods

The realgar crystals investigated in this study were obtained from the Nevada's Getchell mine. The sample composition was verified using an electron microprobe equipped with a fully automated X-ray wave-dispersive spectrometer (JXA8621 Superprobe; JEOL). Analyses revealed that the sample was pure As_4S_4. No other elements were detected in concentrations above trace levels. Preliminary X-ray powder diffractometry revealed only one phase: realgar α-As_4S_4 structure. No impurities or other As_4S_4 polymorphs were detected. The time-dependence of the whole diffraction intensity was investigated using powder X-ray diffractometry (RAD-A; Rigaku Intl. Corp., Japan) with Cu Kα radiation, operated at 40 kV and 20 mA, with a scan speed of 2.0 ° min^{-1} in 2θ. The data were obtained from 10° to 50° in 2θ with a step width of 0.02° (Fig. 1). A "fresh" realgar surfaces for single-crystal XRD were prepared by crushing and grounding a realgar crystal to a grain size of ca. 100 μm, followed by cleaning in acetone. Suitable single crystals (ca. 0.2 mm × 0.1 mm × 0.1 mm) were selected using a binocular microscope, then mounted on a single-crystal diffractometer (CAD4; Enraf-Nonius B.V.) with graphite-monochromatized Mo Kα radiation at room temperature: 20 ± 1 °C. The light source that produces alteration of the realgar crystal was a 15 V and 150 W quartz–tungsten–halogen lamp (Philips Japan Ltd.), which uses optical fibers to prevent overheating. Its fiber position was set at 3–12 cm separated from the single crystal on the diffractometer. The emission spectrum was 350–850 nm. Incident light was measured using a spectroradiometer (MS-720; Eko Instruments Co. Ltd.). The incident light intensity to the sample was set at 5–30 W/m^2, the values of which were estimated approximately as the intensity of light reflected by the earth's surface [7]. The realgar crystal was irradiated with respective lighting power levels on the diffractometer; the unit cell parameters were determined using least-squares refinement of the setting angles of 25 reflections ($10° < \theta_{Mo\ K\alpha} < 14°$) after each successive light treatment. With increasing exposure time, the X-ray diffraction peaks weaken and broaden; crystallinity of the investigated realgar worsened steadily. So long as the 25 reflections were measured, the unit cell parameters were calculated using the same reflections. For long-term exposure to light, however, no diffraction effects were detected. The XRD measurements were terminated when the number of undetected reflections increased to more than 5 reflections among the 25 reflections. Variations of unit cell parameters during light exposure with light power density of 30, 10, and 5 W/m^2 are listed,

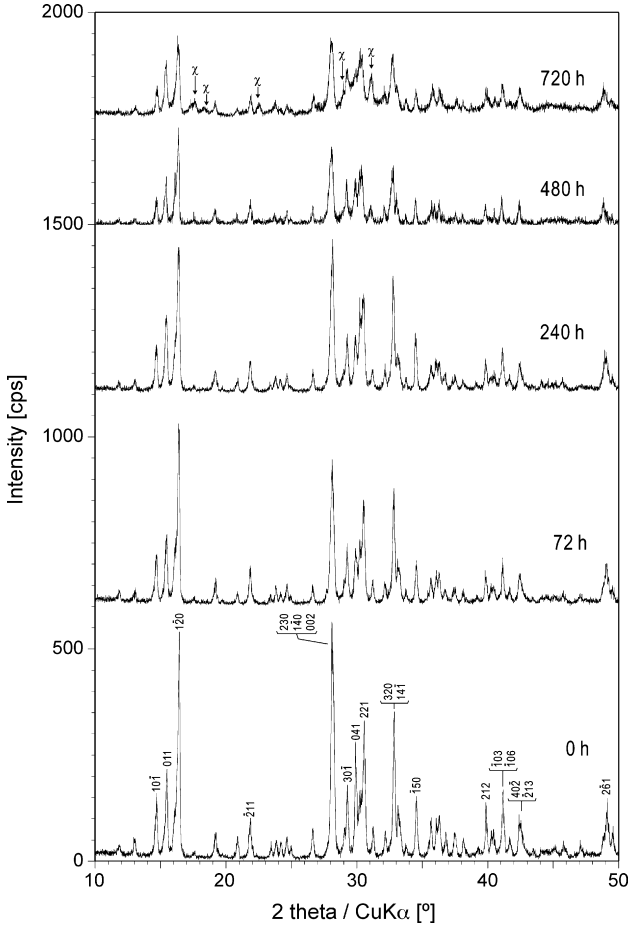

Fig. 1. Powder XRD profiles of realgar irradiated with 5 W/m^2 light intensity. Effects of exposure time showing the phase transformation of realgar into χ phase, composed of a β-As_4S_4 structure with As_4S_5 molecules substituted randomly for As_4S_4. The χ phase was detected after 720 h.

Table 2
Lattice parameters of realgar measured after light exposure using 10 W/m^2 power density

Exposure time (h)	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)
0	9.333 (7)	13.566 (2)	6.592 (7)	106.45 (3)	800.5 (1.0)
12	9.331 (4)	13.564 (1)	6.591 (4)	106.42 (2)	800.2 (6)
24	9.331 (5)	13.562 (1)	6.591 (5)	106.39 (3)	800.2 (8)
36	9.333 (4)	13.562 (1)	6.590 (4)	106.35 (2)	800.4 (6)
48	9.337 (4)	13.563 (1)	6.592 (4)	106.27 (2)	801.3 (6)
60	9.339 (4)	13.566 (1)	6.592 (4)	106.20 (2)	801.9 (6)
72	9.342 (4)	13.567 (1)	6.593 (4)	106.15 (2)	802.5 (7)
84	9.345 (5)	13.570 (1)	6.591 (4)	106.11 (2)	803.0 (7)
96	9.349 (5)	13.570 (1)	6.591 (5)	106.05 (3)	803.6 (8)
108	9.352 (6)	13.570 (1)	6.590 (5)	106.02 (3)	803.8 (8)
120	9.355 (6)	13.572 (2)	6.590 (6)	105.96 (3)	804.5 (1.0)
132	9.360 (6)	13.570 (2)	6.591 (6)	105.87 (3)	805.2 (9)
144	9.362 (6)	13.571 (2)	6.592 (6)	105.81 (3)	805.9 (9)
156	9.368 (7)	13.569 (2)	6.592 (6)	105.75 (3)	806.5 (1.0)
168	9.371 (6)	13.569 (2)	6.595 (6)	105.65 (3)	807.5 (9)
180	9.376 (6)	13.568 (2)	6.594 (6)	105.60 (3)	807.9 (9)
192	9.380 (5)	13.566 (1)	6.599 (4)	105.50 (2)	809.2 (7)
204	9.384 (6)	13.565 (2)	6.600 (6)	105.38 (3)	810.5 (9)
216	9.390 (7)	13.564 (2)	6.600 (6)	105.38 (3)	810.5 (1.0)
228	9.391 (6)	13.562 (2)	6.600 (6)	105.32 (3)	810.8 (1.0)
240	9.390 (6)	13.565 (2)	6.603 (6)	105.27 (3)	811.4 (9)
252	9.393 (7)	13.563 (2)	6.611 (7)	105.23 (3)	812.7 (1.1)
264	9.396 (7)	13.564 (2)	6.607 (7)	105.24 (3)	812.4 (1.1)

respectively, in Tables 1–3. The X-ray apparatus was covered completely with a blackout curtain to exclude the possibility that the realgar crystals were altered by other light sources during measurements.

3. Results and discussion

Fig. 1 shows that the powder X-ray diffraction intensity decreases with increasing exposure time of 5 W/m^2 light intensity. The peaks corresponding to the so-called χ phase appeared at 720 h. Experimental measurements of the unit cell parameters using single-crystal XRD were terminated after 60 h for 30 W/m^2, 276 h for 10 W/m^2, and 648 h for 5 W/m^2 (Tables 1–3). Careful monitoring of the unit cell parameters during each light treatment revealed that the exposure time required for

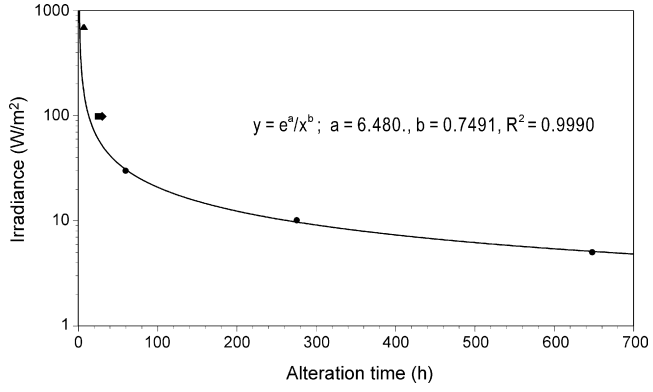

Fig. 2. Effect of light intensity for phase transformation of realgar. Experimental data obtained by Bonazzi et al. [2], Kyono et al. [5], and Bullen et al. [9] are shown along with these data. Symbols: (●) this study; Bonazzi et al. [2]; (♦) Kyono et al. [5]; (■) Bullen et al. [9].

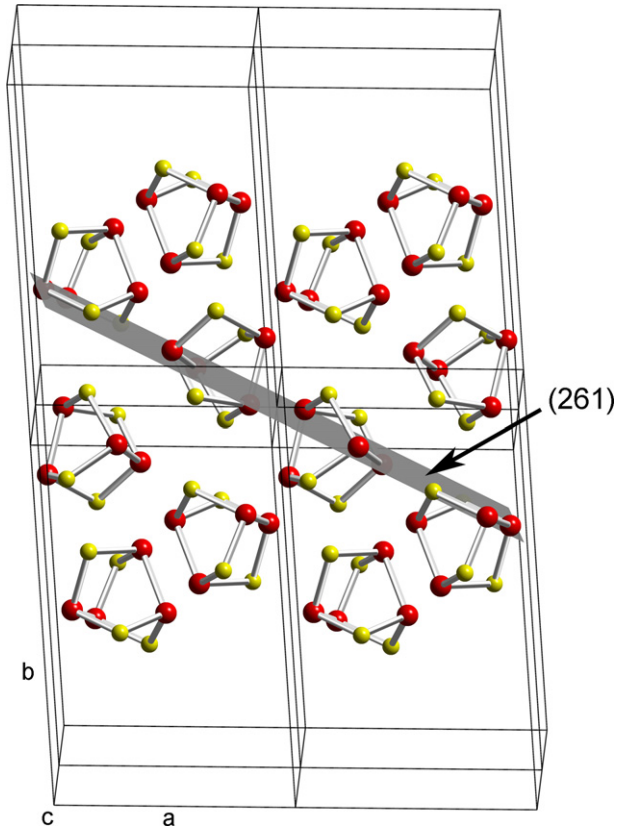

Fig. 3. Ball and stick representation of the As_4S_4 molecule in the realgar structure. As and S atoms are shown, respectively, as red and yellow spheres. The (2 6 1) plane running through the As–As bonds in As_4S_4 molecules is given.

Table 3
Lattice parameters of realgar measured after light exposure using 5 W/m^2 power density

Exposure time (h)	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)
0	9.338 (8)	13.564 (2)	6.579 (8)	106.33 (4)	799.6 (1.2)
12	9.337 (7)	13.557 (2)	6.582 (6)	106.24 (3)	799.8 (1.0)
24	9.336 (7)	13.554 (2)	6.586 (6)	106.20 (3)	800.3 (1.0)
36	9.336 (7)	13.556 (2)	6.581 (7)	106.22 (3)	799.7 (1.1)
48	9.338 (6)	13.557 (2)	6.583 (6)	106.20 (3)	800.3 (1.0)
60	9.339 (3)	13.557 (2)	6.584 (3)	106.16 (3)	800.7 (9)
72	9.339 (6)	13.560 (2)	6.585 (6)	106.15 (3)	801.0 (1.0)
84	9.340 (7)	13.559 (2)	6.585 (6)	106.12 (3)	801.2 (1.0)
96	9.343 (6)	13.561 (2)	6.587 (6)	106.08 (3)	801.9 (9)
108	9.344 (8)	13.561 (2)	6.589 (6)	106.07 (3)	802.2 (1.0)
120	9.345 (7)	13.562 (2)	6.591 (7)	106.00 (3)	803.0 (1.0)
132	9.344 (6)	13.563 (2)	6.585 (6)	106.05 (3)	802.0 (9)
144	9.345 (6)	13.563 (1)	6.587 (5)	106.03 (3)	802.4 (8)
156	9.346 (6)	13.565 (2)	6.588 (6)	106.03 (3)	802.7 (9)
168	9.349 (6)	13.564 (2)	6.587 (6)	105.99 (3)	803.0 (9)
180	9.349 (6)	13.565 (2)	6.591 (6)	105.95 (3)	803.8 (9)
192	9.351 (7)	13.564 (2)	6.594 (7)	105.92 (4)	804.2 (1.1)
204	9.351 (6)	13.565 (2)	6.592 (6)	105.92 (3)	804.2 (9)
216	9.352 (6)	13.566 (2)	6.592 (6)	105.89 (3)	804.3 (1.0)
228	9.353 (6)	13.565 (2)	6.590 (6)	105.89 (3)	804.1 (1.0)
240	9.354 (6)	13.566 (2)	6.591 (6)	105.87 (3)	804.5 (1.0)
252	9.355 (6)	13.567 (2)	6.593 (6)	105.85 (3)	805.0 (1.0)
264	9.356 (6)	13.567 (2)	6.592 (6)	105.83 (3)	805.0 (9)
276	9.355 (6)	13.563 (2)	6.594 (6)	105.81 (3)	805.0 (9)
288	9.354 (5)	13.564 (1)	6.595 (5)	105.78 (3)	805.2 (7)
300	9.354 (6)	13.567 (2)	6.587 (6)	105.81 (3)	804.4 (1.0)
312	9.355 (6)	13.567 (2)	6.586 (6)	105.81 (3)	804.3 (9)
324	9.356 (7)	13.566 (2)	6.585 (7)	105.82 (3)	804.0 (1.1)
336	9.356 (8)	13.564 (2)	6.590 (8)	105.78 (4)	804.9 (1.3)
348	9.357 (8)	13.567 (2)	6.587 (8)	105.79 (4)	804.6 (1.2)
360	9.358 (8)	13.566 (2)	6.592 (7)	105.75 (4)	805.4 (1.2)
372	9.359 (9)	13.567 (2)	6.591 (8)	105.76 (4)	805.4 (1.3)
384	9.359 (8)	13.568 (2)	6.594 (8)	105.72 (4)	806.0 (1.3)
396	9.359 (8)	13.566 (2)	6.594 (8)	105.72 (4)	806.0 (1.2)
408	9.359 (9)	13.565 (3)	6.597 (9)	105.70 (5)	806.3 (1.4)
420	9.358 (10)	13.561 (3)	6.598 (10)	105.69 (5)	806.1 (1.5)
432	9.356 (10)	13.366 (3)	6.597 (10)	105.70 (5)	806.0 (1.5)
444	9.357 (8)	13.566 (2)	6.601 (8)	105.64 (4)	806.9 (1.3)
456	9.361 (8)	13.568 (2)	6.603 (8)	105.60 (4)	807.7 (1.3)
468	9.362 (10)	13.567 (3)	6.603 (10)	105.59 (5)	807.8 (1.6)
480	9.364 (11)	13.566 (3)	6.603 (10)	105.55 (6)	808.1 (1.6)
492	9.364 (9)	13.566 (3)	6.604 (9)	105.55 (5)	808.2 (1.4)
504	9.363 (10)	13.568 (3)	6.605 (10)	105.54 (5)	808.4 (1.5)
516	9.363 (11)	13.569 (3)	6.602 (10)	105.56 (5)	808.0 (1.6)
528	9.364 (10)	13.568 (3)	6.604 (9)	105.52 (5)	808.4 (1.5)
540	9.363 (11)	13.570 (3)	6.601 (10)	105.57 (6)	807.9 (1.7)
552	9.362 (11)	13.572 (3)	6.602 (11)	105.55 (6)	808.2 (1.7)
564	9.363 (13)	13.572 (4)	6.603 (12)	105.51 (6)	808.6 (1.9)
576	9.366 (10)	13.570 (3)	6.605 (10)	105.48 (5)	809.0 (1.5)
588	9.362 (14)	13.573 (4)	6.603 (13)	105.52 (7)	808.3 (2.1)
600	9.362 (14)	13.571 (4)	6.604 (13)	105.52 (7)	808.4 (2.1)
612	9.361 (14)	13.571 (4)	6.609 (13)	105.49 (7)	809.1 (2.1)
624	9.364 (14)	13.569 (4)	6.607 (13)	105.49 (7)	809.1 (2.1)
636	9.365 (14)	13.571 (4)	6.606 (13)	105.49 (7)	809.1 (2.1)

phase transformation increases gradually as the light intensity decreases. Bonazzi et al. [2] reported that the crystallinity of realgar exposed with about 700 W/m^2 light is lost after 7 h of light exposure. Bullen et al. [9] noted that the realgar irradiated with incident light of greater power than 100 W/m^2 is transformed completely into pararealgar for 24 h. Recently, we confirmed that light exposure for 30 h with 100 W/m^2 light breaks down the realgar's crystalline structure [5]. Previous studies showed complete agreement with the tendency between irradiation time and light intensity. Nevertheless, concerning the unaltered realgar problem proposed by Douglass et al. [1], the lowest light intensity at which realgar is transformed with light exposure

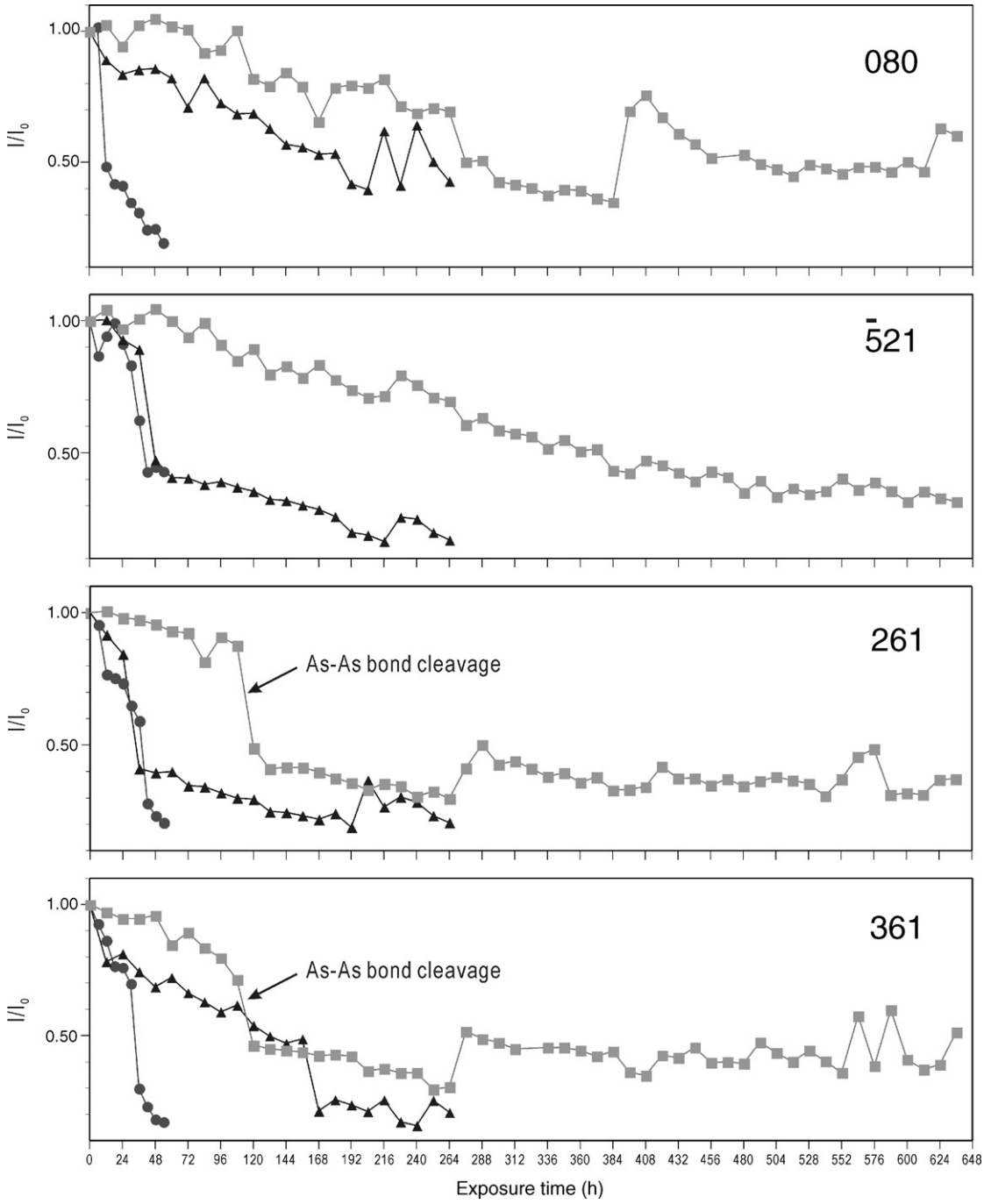

Fig. 4. X-ray intensity of the reflections (0 8 0), ($\bar{5}$ 2 1), (2 6 1), and (3 6 1) as a function of time. Symbols: (●) 30 W/m^2; (▲) 10 W/m^2; (■) 5 W/m^2.

cannot be found within the light intensity range. To reveal the relation between the alteration time and the light intensity for the phase transformation, the alteration time were estimated by fitting a regression curve. Fig. 2 shows the slope of the regression of the light intensity versus the alteration time in the study. The regression equation for the data is: $y = e^a/x^b$; $a = 6.480$, $b = 0.7491$ ($R^2 = 0.9990$) (X-axis by the alteration time; Y-axis by irradiance). Although there is no definite threshold value of light intensity for phase transformation, the result suggests that light exposure of 1.0 W/m^2 requires approximately 5700 h for the phase transformation. For light exposure under fluorescent lighting in the laboratory, realgar might be maintained for approximately 1 month, as Douglass et al. [1] noted.

The phase transformation of realgar into pararealgar occurs through formation of a χ phase comprising As_4S_5 molecules randomly substituted for As_4S_4 [2]. The As_4S_5 molecules are produced by the additional S atom inserted between one As–As bond in the As_4S_4 molecule [2,5]. The X-ray diffraction intensity derived from the refraction planes running through the As–As bonds such as (2 6 1) or (3 6 1) should be changed characteristically if the As–As bond in As_4S_4 molecules is broken by the inserted S atom during transformation (Fig. 3). To verify that

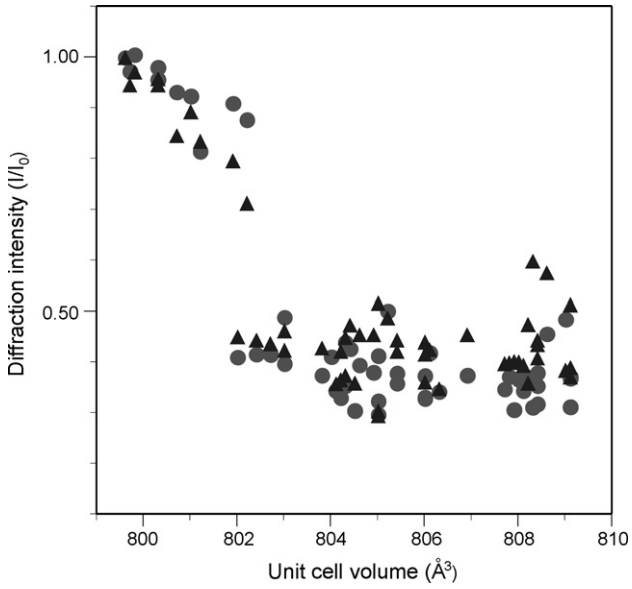

Fig. 5. Plot of unit cell volume vs. X-ray diffraction intensities of (2 6 1) and (3 6 1) reflections. Symbols: (●) (2 6 1); (▲) (3 6 1).

conjecture, variations of X-ray diffraction intensities were investigated, the results of which are shown in Fig. 4. The diffraction intensity of light exposure to 30 W/m^2 was decreased drastically as a function of irradiation time. Crystallinity of the realgar exposed to 30 W/m^2 light was decomposed immediately after the diffraction intensity was reduced, whereas that of the realgar irradiated with 10 W/m^2 light was decomposed gradually. The most important feature of the changes was observed in each 5 W/m^2 light treatment because the phase transformation of realgar occurs very slowly. Variations of diffraction intensity of (2 6 1) and (3 6 1) reflections irradiated with 5 W/m^2 light exhibit characteristic decreases compared to those of (0 8 0) and ($\bar{5}$ 2 1). The diffraction intensity of (2 6 1) and (3 6 1) reflections decreases sharply between 108 and 120 h, followed by a slow decrease of the diffraction intensity. In addition, similar variations include some temporary increases of the diffraction intensity. Fig. 5 shows that the diffraction intensity apparently decreases just as the unit cell volume reaches into approximately 802 Å^3. Bindi et al. [4] expected that the expansion of the unit cell volume induced by lighting is attributable to an increase in the percentage of the As_4S_5 molecules in the crystal structure, which derives from the following reaction: $5As_4S_4 + 3O_2 \rightarrow 4As_4S_5 + 2As_2O_3$. However, no continuous formation of As_2O_3 during light irradiation was observed in the previous study [5]. Therefore, the result indicates that As_4S_5 molecules produced simultaneously by lighting together with As_2O_3 do not occur continuously in the structure. According to the model elaborated by Kyono et al. [5], a partial As_4S_4 molecule in the structure is transformed temporally into the As_4S_5 molecule. It is transformed subsequently into the larger As_4S_4 pararealgar molecule. The S atom released from As_4S_5 molecule is re-attached to another As_4S_4 realgar molecule in the structure, followed by reproduction of the next As_4S_4 pararealgar molecule from the As_4S_5 molecule. Therefore, the sharp decreases of diffraction intensity of (2 6 1) and (3 6 1) reflections suggest that the cleavage of As–As bonds arises

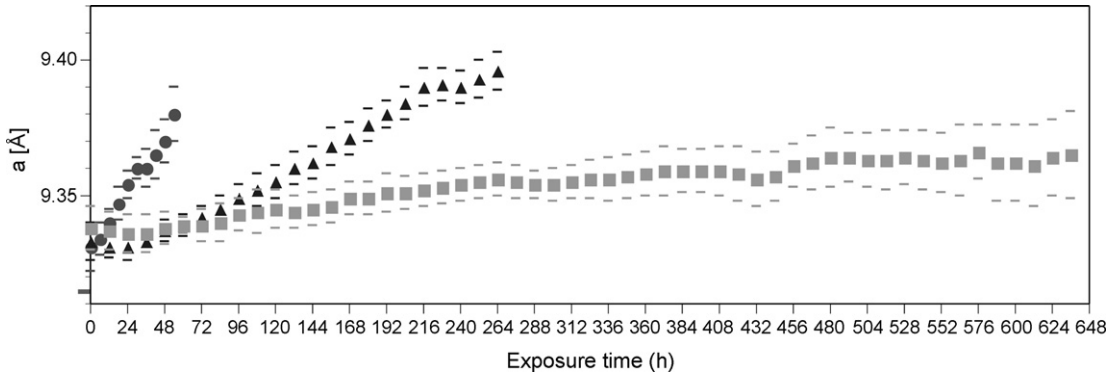

Fig. 6. Variation in the *a* cell parameter for light exposure with each light power density as a function of time. Symbols: (●) 30 W/m^2; (▲) 10 W/m^2; (■) 5 W/m^2.

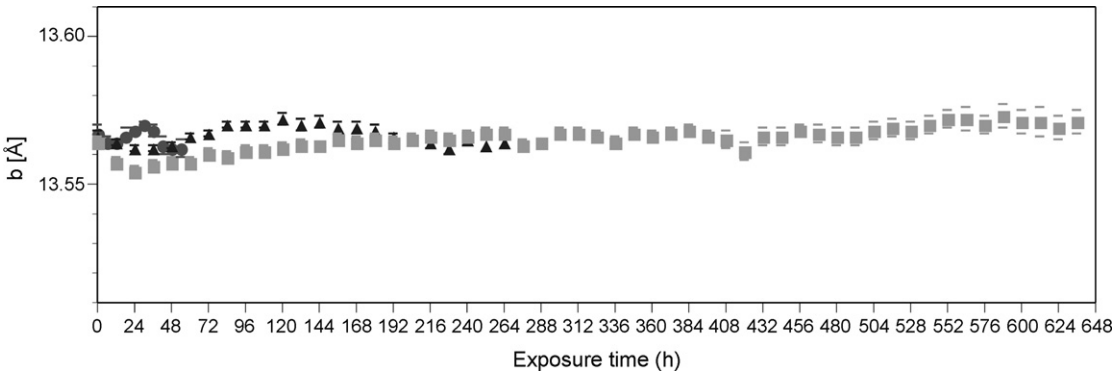

Fig. 7. Variation in the *b* cell parameter for light exposure with each light power density as a function of time. Symbols: (●) 30 W/m^2; (▲) 10 W/m^2; (■) 5 W/m^2.

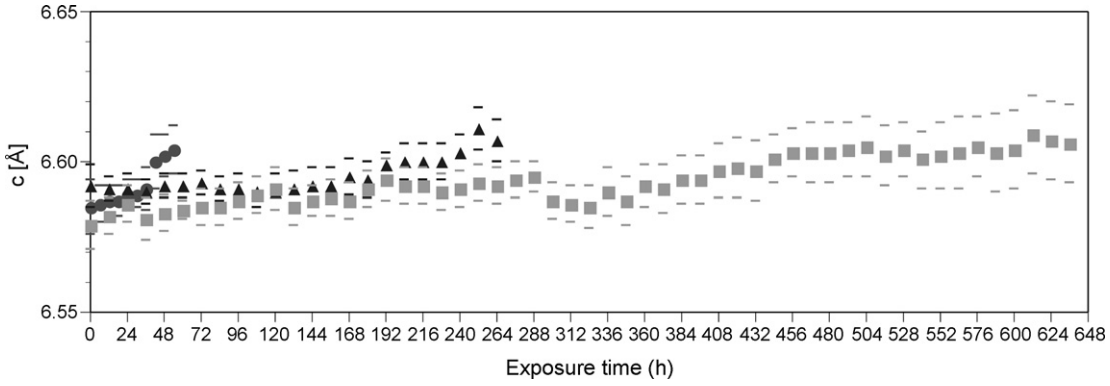

Fig. 8. Variation in the c cell parameter for light exposure with each light power density as a function of time. Symbols: (●) 30 W/m^2; (▲) 10 W/m^2; (■) 5 W/m^2.

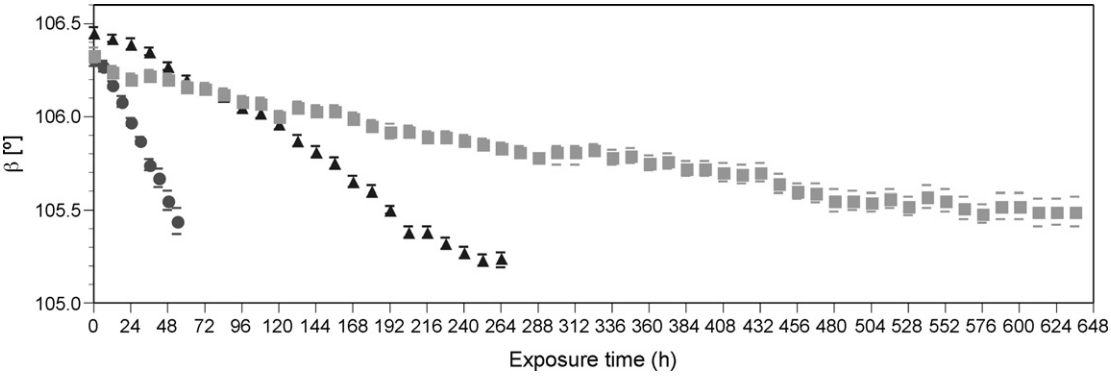

Fig. 9. Variation in the β angle for light exposure with each light power density as a function of time. Symbols: (●) 30 W/m^2; (▲) 10 W/m^2; (■) 5 W/m^2.

throughout the crystal structure. That is, deformations of As_4S_4 molecules into As_4S_5 molecule are largely produced when the unit cell volume reaches approximately 802 Å^3 (Fig. 5), followed by rearrangement of the As_4S_4 pararealgar molecular packing. It continues until the unit the cell volume expands to approximately 810 Å^3.

Figs. 6–9 show evolutions of unit cell parameters with light exposure for the examined crystal. Variations of $c \sin \beta$ value and unit cell volume with lighting are shown in Figs. 10 and 11. It has already been demonstrated experimentally [3,5] that light-induced alteration for realgar is always accompanied by anisotropic unit cell expansion: the a cell parameter and $c \sin \beta$ value increase linearly, whereas the b cell parameter remains substantially unchanged with light exposure. Anisotropic variation in the measured unit cell concurs with data collected in previous studies [3,5]. The a cell parameter shows a continuous increase with light-exposure time (Fig. 6). Furthermore, the feature of a continuous increase of the a cell parameter was observed definitively within the light intensity range investigated in this study. The value of the b cell parameter remained fairly constant during light treatment (Fig. 7), which shows excellent agreement with experimental results documented by Bonazzi et al. [3] and Kyono et al. [5]. But the linear increase in the $c \sin \beta$ value as the light intensity decreases was not confirmed clearly (Fig. 10). In particular, with light exposure of 5 W/m^2, the $c \sin \beta$ value does not change continuously as a function of the irradiation time.

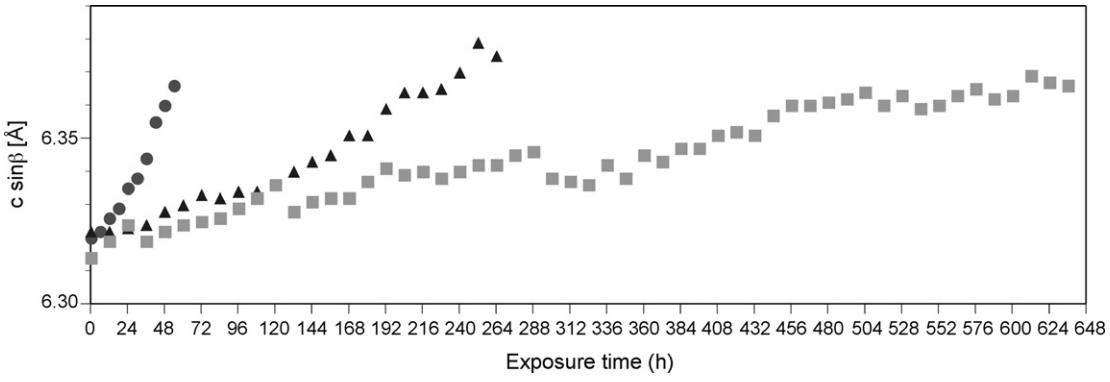

Fig. 10. Variation in the $c \sin \beta$ value for light exposure with each light power density as a function of time. Symbols: (●) 30 W/m^2; (▲) 10 W/m^2; (■) 5 W/m^2.

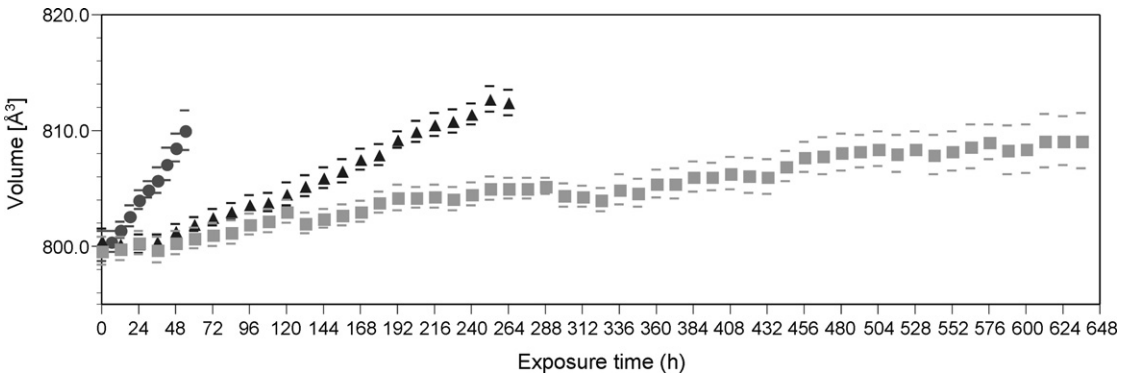

Fig. 11. Evolution of the unit cell volume for light exposure with each light power density as a function of time. Symbols: (●) 30 W/m^2; (▲) 10 W/m^2; (■) 5 W/m^2.

Fig. 11 shows that variation of the unit cell volume correlates with that of the $c \sin \beta$ value shown in Fig. 10. No continuous increase of unit cell volume is observed in the realgar exposed with light exposure of 5 W/m^2. The discontinuous increase in the $c \sin \beta$ value is mainly attributable to the c cell parameter value, which varies widely during light exposure (Fig. 8). In contrast, the most sensitive variation of unit cell parameters is found at the β angle as a function not only of the irradiation time but also of the light intensity (Fig. 9). Therefore, the highest sensitivity for lighting is shown at the a and β angles in unit cell parameters, which increase or decrease linearly up to the loss of crystallinity.

4. Conclusions

This study examined the effect of light intensity on arsenic sulfide (mineral name: realgar, As_4S_4) alteration. Single-crystal XRD results indicate that the exposure time required for the phase transformation increases gradually as the light intensity decreases. However, the experimental results show no definite threshold value of light intensity for the phase transformation. The single-crystal X-ray diffraction intensities of (2 6 1) and (3 6 1) reflections decreases sharply just when the unit cell volume reaches approximately 802 Å^3, with a subsequent slow decrease of the diffraction intensity. This pattern of decrease suggests that the cleavage of As–As bonds in As_4S_4 realgar molecule occurs at that time, followed by rearrangement of the As_4S_4 pararealgar molecular packing, which continues until the unit the cell volume expands continuously to approximately 810 Å^3. The highest sensitivity for lighting is shown at the a and β angles in unit cell parameters. In contrast, the value of the b cell parameter remained fairly constant during light treatment. The variations of unit cell parameters according to light exposure might be considered as a more certain, objective, and reliable indication of light intensity and cumulative exposure time.

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