

Light-induced molecular change in $\text{HgI}_2 \cdot \text{As}_4\text{S}_4$: Evidence by single-crystal X-ray diffraction and Raman spectroscopy

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ABSTRACT

To investigate the behavior of the As_4S_4 molecule within a crystal-chemical environment differing from realgar, $\alpha\text{-As}_4\text{S}_4$, and its high-temperature polymorph, $\beta\text{-As}_4\text{S}_4$, the effects of the light exposure on the structure of the $\text{HgI}_2 \cdot \text{As}_4\text{S}_4$ adduct have been studied. The structure of this compound consists of a packing of nearly linear HgI_2 molecules and As_4S_4 cage-molecules. A crystal [$V = 1295.9(4) \text{ \AA}^3$] was exposed to filtered polychromatic light (550 nm long-wavelength pass filter). A marked increase of the unit-cell volume as a function of the exposure time was observed up to $V = 1338.9 \text{ \AA}^3$ at 3060 min of exposure. Structure refinements indicated that the increase of the unit-cell volume is to ascribe to the formation of an increasing fraction (up to 59%) of pararealgar replacing the realgar-type molecule. After this point, further light-exposure did not cause any further increase of the lattice parameters. On the contrary, a slow, continuous decrease of the unit-cell volume down to 1292.9 \AA^3 occurred by keeping the crystal in the dark (39 days). The “reverse” evolution of the unit-cell parameters in the dark almost overlap that observed during the light-induced process and the structural model obtained after the “dark stage” was found to be identical to that of the unaltered crystal, although the diffraction quality was lower and powder-like diffraction rings were observed together with single-crystal reflections. Apart from few peaks belonging to the original unaltered $\text{HgI}_2 \cdot \text{As}_4\text{S}_4$ adduct, most of the collected peaks can be assigned to $\beta\text{-As}_4\text{S}_4$. This feature could indicate decomposition into micro-crystalline $\beta\text{-As}_4\text{S}_4$ and HgI_2 ; no diffraction effect ascribable to any HgI_2 phase, however, was observed. Micro-Raman spectra were collected on crystals exposed to the above-mentioned wavelength light for increasing times (up to 3000 min). The peak at $274(\pm 1) \text{ cm}^{-1}$ whose intensity increases as a function of the exposure time confirms the transition from a realgar- to a pararealgar-type molecule in the $\text{HgI}_2 \cdot \text{As}_4\text{S}_4$ adduct.

Keywords: Crystal structure, $\text{HgI}_2 \cdot \text{As}_4\text{S}_4$, Raman spectroscopy, arsenic sulfides, light-induced alteration, realgar, pararealgar

INTRODUCTION

Realgar, $\alpha\text{-As}_4\text{S}_4$ (Mullen and Nowacki 1972), and the high-temperature polymorph, $\beta\text{-As}_4\text{S}_4$ (Porter and Sheldrick 1972), although showing a different molecular packing involving two distinct monoclinic lattices, are based on the same cage-like molecule. Both of these polymorphs undergo an alteration when exposed to visible light, the final product of the photo-induced transition being pararealgar, As_4S_4 , in both cases. The structure of pararealgar (Bonazzi et al. 1995) is based on a different As_4S_4 molecule, so that the transition from a realgar-type to a pararealgar-type molecule implies the displacement of one As-As and one As-S covalent bond. Since the first identification of pararealgar as light-induced alteration product of realgar (Roberts et al. 1980), many studies have focused on the effects of the exposure of realgar or other arsenic sulfides to light, starting from the detailed study of Douglass et al. (1992) up to the recent

investigations by single-crystal (Kyono et al. 2005; Bonazzi et al. 2006; Kyono 2007; Naumov et al. 2007) and powder X-ray diffraction (Ballirano and Maras 2006). According to the previous literature, during the initial photoreaction step the realgar-type (r-type) As_4S_4 molecule transforms to the uzonite-type As_4S_5 molecule according to the oxidation reaction: $5\text{As}_4\text{S}_4$ (r-type) + $3\text{O}_2 \rightarrow 4\text{As}_4\text{S}_5 + 2\text{As}_2\text{O}_3$. As a consequence of the increment in the number of the As_4S_5 molecules, an anisotropic expansion of the unit cell is observed in light-exposed $\beta\text{-As}_4\text{S}_{4+x}$ crystals (Bonazzi et al. 2006) and, to lesser extent, in realgar (Kyono et al. 2005). The process proceeds through the release of a sulfur atom by breaking an As-S-As linkage to form a pararealgar-type (p-type) As_4S_4 molecule: $\text{As}_4\text{S}_5 \rightarrow \text{As}_4\text{S}_4$ (p-type) + S, and it could cyclically continue by re-attachment of the free S to another realgar-type As_4S_4 molecule. According to Naumov et al. (2007), the transformation of realgar to pararealgar consists of two dynamic reaction regimes: the first stage producing arsenolite requires photoexcitation (“light stage”), whereas the second one represents a self-accelerated solid-state chain

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reaction, which does not need the exposure to light (“dark stage”). Recently, Naumov et al. (2010) were able to obtain structural evidences of the migration of a sulfur atom between molecules within the realgar structure; moreover, they monitored the dependence of the realgar → pararealgar conversion on the excitation power density through the integrated intensity of a Raman peak of pararealgar.

From the previous literature, it becomes evident that the extent of sulfur incorporation, which is the percentage of As₄S₅ molecules in the crystalline structure, seems to be strictly controlled by the type of molecular packing. In the case of the β-As₄S_{4+x} crystals, the molecular packing allows to sustain the stress induced by the increase of As₄S₅ molecules, so that the overall crystalline order is retained and the structural changes can be followed step by step through single-crystal X-ray diffraction (Bonazzi et al. 2006). On the contrary, only very small changes of unit-cell parameters were observed in realgar before a loss of single-crystal diffraction quality occurred (Bonazzi et al. 1996; Kyono et al. 2005; Kyono 2007) due to the inability of its molecular packing to incorporate a larger amount of As₄S₅ cages. Nonetheless, Naumov et al. (2007) obtained direct evidence of the formation of the intermediate product by single-crystal X-ray diffraction, which indicates that the formation of the pararealgar molecule occurs through the formation of the As₄S₅ molecule, although the fraction of As₄S₅ was not clearly reported in the article. However, the residual electron density peak indicating the presence of As₄S₅ (i.e., the S3' peak) in their Figure 5b (Naumov et al. 2007) does not exceed 1.5 e⁻/Å³, a value much lower than those observed for the light-exposed β-As₄S_{4+x} crystals (Bonazzi et al. 2006). Although the As₄S₄ molecules in both realgar and β-As₄S_{4+x} structures are quite identical, their transformation to pararealgar upon exposure to light follows different mechanisms, which have to be ascribed to the different molecular packing. Nonetheless, the mineral alacranite, As₈S₉, which contains a molecular packing identical to that of β-As₄S₄ apart from the ordered replacement of one half of the As₄S₄ molecules by As₄S₅ molecules (Bonazzi et al. 2003a), did not undergo any modification when exposed to light (Bonazzi et al. 2006). Therefore, it appears interesting to investigate the behavior of the As₄S₄ molecule within different crystal-chemical environments. The recently reported adduct of mercury iodide and molecular arsenic sulfide (Bräu and Pfitzner 2006) offers an interesting new alley to study the light-induced transformations of this molecule. The crystal structure of HgI₂·As₄S₄, indeed, consists of a packing of nearly linear HgI₂ molecules and As₄S₄ cage-molecules, quite similar to those found in realgar, β-As₄S₄, and alacranite.

EXPERIMENTAL METHODS

HgI₂·As₄S₄ was obtained by heating HgI₂, gray arsenic, and sulfur in the molar ratio 1:4:4 in evacuated quartz ampoules. The reactants were molten at 400 °C and then annealed at 200 °C for two weeks. A transparent crystal (160 × 210 × 230 μm approximately), orange in color, was selected and mounted on a Bruker Mach3 diffractometer; before any exposure to light, unit-cell dimensions in the P2₁/n setting were: *a* = 9.421(1), *b* = 14.982(3), *c* = 9.476(1) Å, β = 104.32(2)°. Intensity data were collected using MoKα radiation monochromatized by a flat graphite crystal and corrected for Lorentz-, polarization effects, and subsequently for absorption (see Table 1 for experimental details). Monoclinic-equivalent reflections were averaged.

The crystal was then exposed to filtered polychromatic light (550 nm long-wavelength pass filter) using the apparatus described by Bonazzi et al. (1996). After

each light exposure, unit-cell parameters were determined (Table 2) by centering 25 relatively strong reflections (θ < 13°) as long as it was still possible to center the same set of reflections. With the increase of the light-exposure time the crystal became opaque and the diffraction quality lowered progressively; nonetheless, we decided to carry out the whole intensity data collection after light-exposures of 930 and 3060 min, corresponding to an increase of the unit-cell volume of 1.9 and 3.3%, respectively (see Table 1 for details). After this point, no further changes were observed and after 3360 min of light exposure from the beginning of the experiment, the unit-cell parameters were found essentially unchanged. The crystal was then kept in the dark for several days and the unit-cell parameters were measured at selected times. The unit-cell volume continuously decreased down to a value very

TABLE 1. Experimental details of data collections and structure refinements of the HgI₂·As₄S₄ adduct

| | (a) | (b) | (c) | (d) |
|---|---------------------|---------------------|---------------------|--------------------------|
| Exposure time (min) | 0 | 930 | 3060 | 3060+39 days in the dark |
| Space group | P2 ₁ /n | P2 ₁ /n | P2 ₁ /n | P2 ₁ /n |
| instrument | Bruker Mach3 | Bruker Mach3 | Oxford Xcalibur3 | Oxford Xcalibur3 |
| Wavelength | MoKα | MoKα | MoKα | MoKα |
| | (26 mA x 50 kV) | | (40 mA x 40 kV) | |
| Cell parameters | | | | |
| <i>a</i> (Å) | 9.421(1) | 9.500(6) | 9.532(2) | 9.423(2) |
| <i>b</i> (Å) | 14.982(3) | 15.024(8) | 15.094(2) | 14.960(2) |
| <i>c</i> (Å) | 9.476(1) | 9.518(5) | 9.558(1) | 9.458(2) |
| β (°) | 104.32(2) | 103.61(6) | 103.18(2) | 104.13(2) |
| <i>V</i> (Å ³) | 1295.9(3) | 1320(1) | 1338.9(4) | 1292.9(4) |
| θ-range (°) | 1–30 | 1–25 | 1–32.2 | 1–26.2 |
| Range of <i>hkl</i> | –13 ≤ <i>h</i> ≤ 12 | –11 ≤ <i>h</i> ≤ 10 | –12 ≤ <i>h</i> ≤ 9 | –11 ≤ <i>h</i> ≤ 9 |
| | –20 ≤ <i>k</i> ≤ 20 | –17 ≤ <i>k</i> ≤ 17 | –20 ≤ <i>k</i> ≤ 22 | –17 ≤ <i>k</i> ≤ 17 |
| | 0 ≤ <i>l</i> ≤ 13 | –5 ≤ <i>l</i> ≤ 11 | –9 ≤ <i>l</i> ≤ 14 | –11 ≤ <i>l</i> ≤ 11 |
| Scan mode | ω | ω | φ/ω | φ/ω |
| Scan width (°) | 2.40 | 2.80 | – | – |
| Scan speed (°/min) | 3.10 | 2.60 | – | – |
| Exposure time per frame (s) | – | – | 30 | 30 |
| Frame width (°) | – | – | 0.75 | 0.75 |
| Detector to sample distance (cm) | – | – | 5 | 5 |
| Absorption correction | ψ-scan* | ψ-scan* | multiscan† | multiscan† |
| Number of parameters | 100 | 120 | 129 | 100 |
| Collected reflections | 7550 | 4950 | 7559 | 4369 |
| Independent refl. | 3775 | 2320 | 3711 | 2069 |
| Ref. with <i>F</i> _o > 4σ(<i>F</i> _o) | 1954 | 1270 | 1229 | 658 |
| <i>R</i> _{int} (%) | 5.87 | 10.50 | 8.42 | 14.92 |
| <i>R</i> _{obs} (%) | 2.76 | 8.21 | 8.06 | 9.51 |
| Δρ _{max} (eÅ ⁻³) | 2.08 | 1.92 | 1.72 | 2.22 |
| Δρ _{min} (eÅ ⁻³) | –2.14 | –1.29 | –1.18 | –1.47 |
| Extinction correction | none | none | none | none |

Notes: * Semi-empirical method of North et al. (1968); † ABSPACK in CrysAlis RED software package (Oxford Diffraction 2006).

TABLE 2. Unit-cell parameters of the HgI₂·As₄S₄ adduct measured after different times of light exposure and dark

| Time in the dark (days) | Total light-exposure times (min) | <i>a</i> (Å) | <i>b</i> (Å) | <i>c</i> (Å) | β (°) | <i>V</i> (Å ³) |
|-------------------------|----------------------------------|--------------|--------------|--------------|------------|----------------------------|
| | 0* | 9.421(1) | 14.982(3) | 9.476(1) | 104.32(2) | 1295.9(3) |
| | 30 | 9.422(5) | 14.984(3) | 9.479(6) | 104.30(4) | 1297(1) |
| | 60 | 9.427(5) | 14.985(3) | 9.482(6) | 104.27(4) | 1298(1) |
| | 330 | 9.444(6) | 14.994(4) | 9.489(5) | 104.16(5) | 1303(1) |
| | 630 | 9.481(6) | 15.007(5) | 9.513(7) | 103.86(6) | 1314(1) |
| | 930* | 9.500(6) | 15.024(8) | 9.518(5) | 103.61(6) | 1320(1) |
| | 1200 | 9.512(7) | 15.037(8) | 9.532(5) | 103.45(6) | 1326(1) |
| | 1500 | 9.521(7) | 15.050(8) | 9.546(5) | 103.33(6) | 1331(1) |
| | 1860 | 9.520(7) | 15.064(8) | 9.552(5) | 103.40(7) | 1333(1) |
| | 2160 | 9.524(7) | 15.067(9) | 9.557(5) | 103.32(7) | 1335(1) |
| | 3060* | 9.532(2) | 15.094(2) | 9.558(1) | 103.18(2) | 1338.9(4) |
| 3 | 3060 | 9.527(6) | 15.075(9) | 9.546(5) | 103.13(7) | 1335(1) |
| 12 | 3060 | 9.508(7) | 15.047(9) | 9.543(6) | 103.24(9) | 1329(2) |
| 19 | 3060 | 9.487(9) | 15.009(11) | 9.529(9) | 103.81(11) | 1318(2) |
| 28 | 3060 | 9.411(11) | 14.995(15) | 9.480(10) | 103.85(12) | 1299(3) |
| 39 | 3060* | 9.423(2) | 14.960(2) | 9.458(2) | 104.13(2) | 1292.9(4) |

* Intensity data collection was performed at this stage.

similar to that of the pristine crystal (Table 2). At this stage, an intensity data set was collected again (Table 1). A further check after a long period of time during, which the crystal was kept in the dark (three months approximately) showed few weak single-crystal reflections together with powder diffraction rings revealing the formation of a microcrystalline phase (inset of Fig. 1). The observed diffraction rings were then collected with a CCD-equipped diffractometer Xcalibur PX Ultra using $\text{CuK}\alpha$ radiation (50 kV and 40 mA). 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. The diffraction pattern is shown in Figure 1.

Raman spectra were collected on selected $\text{HgI}_2 \cdot \text{As}_4\text{S}_4$ crystals exposed to light of the above mentioned wavelength at increasing times (0, 600, 2400, 3000 min) using a Renishaw RM2000 microRaman apparatus, coupled with a diode laser source emitting at 785 nm. Sample irradiation was accomplished using the $\times 50$ microscope objective of a Leica Microscope DMLM. The beam power was ~ 3 mW, 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 each measurement was 10 s. All spectra were calibrated with respect to a silicon wafer at 520 cm^{-1} .

STRUCTURE REFINEMENTS

For the untreated crystal, the structural data published by Bräu and Pfitzner (2006) (transformed to the $P2_1/n$ setting) were used as starting model. Structure refinement was performed on F^2 using the SHELXL-97 program (Sheldrick 1997). Convergence was quickly achieved for an anisotropic model ($R1 = 2.76\%$). Structure refinements after exposure to light were not as straightforward. Isotropic full-matrix least-squares cycles were initially run assuming the atom sites as fully occupied, although

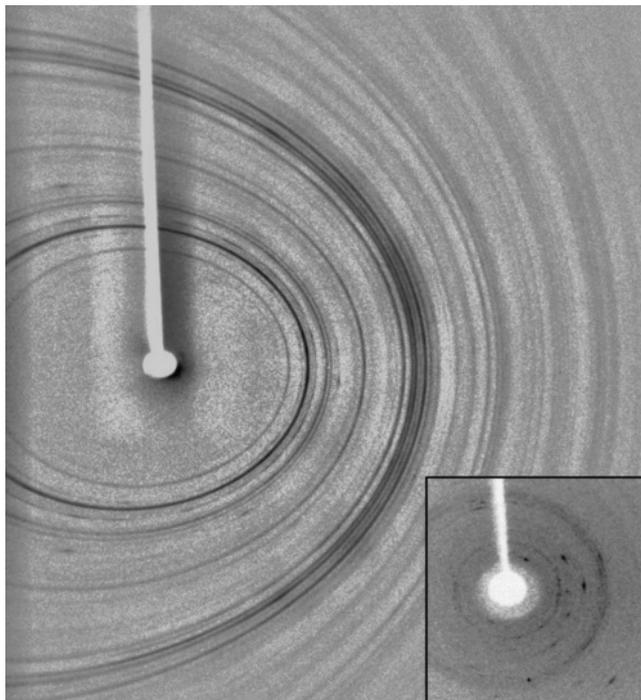


FIGURE 1. Image obtained with a CCD-equipped diffractometer Xcalibur PX Ultra using $\text{CuK}\alpha$ radiation. Only diffraction rings revealing decomposition into microcrystalline phases are visible. The inset shows an overexposed frame obtained with a CCD-equipped diffractometer “Xcalibur 3” single-crystal diffractometer fitted with a Sapphire 2 CCD detector using $\text{MoK}\alpha$ radiation. Both single-crystal reflections and diffraction rings revealing decomposition into microcrystalline phases are recognizable.

the unusually high value of the isotropic displacement factor for one sulfur atom (S2) strongly suggested partial occupancy at this site. Indeed, the refinement of the occupancy factor indicated full occupancy for all sulfur atoms except for S2. Examination of the ΔF -Fourier map revealed the presence of a residual peak (S2b). The convergence was quickly achieved by adding this peak to the atom array without constraints on its site occupancy factor (sof). The sum sof (S2) + sof (S2b) was found to exceed the value of 1.00 by $\sim 2 + 3$ times the standard deviation. This suggests the coexistence of r-type and p-type As_4S_4 molecules with only very minor amounts of As_4S_5 molecules, if any. When a model with anisotropic displacement parameters was adopted, splitting of As atoms (As2 for the 930 data set, As1 and As2 for the 3060 data set) was observed, with the split positions being consistent with the bond requirements of the r-type and the p-type molecule, respectively, and their relative occupancies are equal, within the experimental uncertainty, to those of S2 and S2b, respectively. Therefore, to reduce the number of the free variables and to obtain a reliable model, only one parameter was refined as free variable. Thus, the fraction of r- and p-type molecules was constrained to sum to 1.00, disregarding the minor replacement of As_4S_5 molecules.

The structural model obtained after the “dark stage” was found to be identical to that of the unaltered crystal within the experimental errors (column d in Table 1).

Atomic coordinates, site occupancies, and isotropic displacement parameters are reported in Table 3. CIF is on deposit¹.

RESULTS

X-ray diffraction

As in the case of other arsenic sulfides containing As_4S_4 realgar-type molecules, the most evident change upon exposure to light is a considerable increase of the unit-cell volume as a function of the exposure time. The total increase observed in the case of the $\text{HgI}_2 \cdot \text{As}_4\text{S}_4$ adduct (3.3%) is much larger than that observed for light-exposed single crystals of realgar (α - As_4S_4) [~ 1.6 – 1.8% and $\sim 1.4\%$ as reported by Bonazzi et al. (1996) and Kyono et al. (2005), respectively] and even larger than that observed for β - As_4S_4 (2.6%) (Bonazzi et al. 2006). As it appears by plotting the individual parameters vs. the unit-cell volume, the expansion of the unit cell (filled symbols in Fig. 2), is essentially isotropic and proceeds up to a volume of 1338.9 \AA^3 by a continuous increase of the a , b , and c parameters and a strong decrease of the monoclinic angle β . After this point, further exposure to light did not cause any increase of the lattice parameters. A slow, continuous decrease of the unit-cell volume down to 1292.9 \AA^3 , a value very similar to that of the unaltered crystal, occurred by keeping the crystal in the dark (39 days). The marks indicating the process occurring in the dark (empty symbols in Fig. 2) almost overlap those observed during the light-induced process.

¹ Deposit item AM-11-023. CIF. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at <http://www.minsocam.org>, go to the *American Mineralogist* Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

TABLE 3. Fractional atomic coordinates, site occupancy factors (sof), and equivalent displacement parameters for the $\text{HgI}_2 \cdot \text{As}_4\text{S}_4$ crystal at different steps of alteration

| | x/a | y/b | z/c | sof | U_{eq} |
|------------|------------|------------|------------|---------|-----------------|
| (a) | | | | | |
| Hg | 0.50681(3) | 0.04548(2) | 0.71384(3) | 1.00 | 0.04473(8) |
| I1 | 0.46882(4) | 0.12288(3) | 0.34549(4) | 1.00 | 0.0400(1) |
| I2 | 0.55190(4) | 0.21088(3) | 0.79512(4) | 1.00 | 0.0401(1) |
| As1 | 0.87733(6) | 0.03938(4) | 0.26554(6) | 1.00 | 0.0356(1) |
| As2 | 0.89975(6) | 0.04369(4) | 0.77385(6) | 1.00 | 0.0329(1) |
| As3 | 0.13648(6) | 0.18982(4) | 0.66381(6) | 1.00 | 0.0329(1) |
| As4 | 0.21784(6) | 0.15688(5) | 0.93664(6) | 1.00 | 0.0350(1) |
| S1 | 0.7100(2) | -0.0140(1) | 0.0741(2) | 1.00 | 0.0389(3) |
| S2 | 0.0003(2) | 0.1232(1) | -0.0262(2) | 1.00 | 0.0408(4) |
| S3 | 0.8988(2) | 0.1584(1) | 0.6236(2) | 1.00 | 0.0408(4) |
| S4 | 0.1866(2) | 0.0558(1) | 0.5770(2) | 1.00 | 0.0389(3) |
| (b) | | | | | |
| Hg | 0.5079(2) | 0.05157(9) | 0.7057(2) | 1.00 | 0.0816(6) |
| I1 | 0.4648(3) | 0.1174(1) | 0.3426(3) | 1.00 | 0.0637(7) |
| I2 | 0.5557(3) | 0.2147(2) | 0.7925(3) | 1.00 | 0.0772(8) |
| As1 | 0.8630(5) | 0.0417(2) | 0.2584(4) | 1.00 | 0.078(1) |
| As2 | 0.9040(5) | 0.0450(4) | 0.7730(6) | 0.67(2) | 0.048(2) |
| As2b | 0.930(1) | 0.102(1) | 0.858(2) | 0.33 | 0.072(7) |
| As3 | 0.1411(5) | 0.1885(2) | 0.6639(4) | 1.00 | 0.070(1) |
| As4 | 0.2087(4) | 0.1576(2) | 0.9345(4) | 1.00 | 0.064(1) |
| S1 | 0.7054(9) | -0.0183(5) | 0.0671(9) | 1.00 | 0.056(2) |
| S2 | -0.001(2) | 0.1264(7) | -0.030(1) | 0.67 | 0.052(3) |
| S2b | 0.042(3) | 0.035(2) | 0.201(3) | 0.33 | 0.067(9) |
| S3 | 0.904(1) | 0.1621(6) | 0.627(1) | 1.00 | 0.077(3) |
| S4 | 0.188(1) | 0.0531(6) | 0.5795(9) | 1.00 | 0.065(2) |
| (c) | | | | | |
| Hg | 0.5041(2) | 0.05577(8) | 0.6953(1) | 1.00 | 0.0906(6) |
| I1 | 0.4584(2) | 0.1137(1) | 0.3392(2) | 1.00 | 0.0705(6) |
| I2 | 0.5506(2) | 0.2181(1) | 0.7852(2) | 1.00 | 0.0838(7) |
| As1 | 0.872(1) | 0.0364(7) | 0.266(1) | 0.41(1) | 0.051(3) |
| As1b | 0.816(1) | 0.0576(7) | 0.231(1) | 0.59 | 0.060(2) |
| As2 | 0.9029(8) | 0.0452(5) | 0.7738(8) | 0.41 | 0.068(3) |
| As2b | 0.9272(5) | 0.1024(4) | 0.8580(5) | 0.59 | 0.069(2) |
| As3 | 0.1418(3) | 0.1852(2) | 0.6598(3) | 1.00 | 0.079(1) |
| As4 | 0.1952(3) | 0.1580(2) | 0.9264(3) | 1.00 | 0.0735(9) |
| S1 | 0.7020(7) | -0.0262(5) | 0.0619(6) | 1.00 | 0.068(2) |
| S2 | -0.007(2) | 0.124(1) | -0.032(2) | 0.41 | 0.069(5) |
| S2b | 0.041(1) | 0.0392(9) | 0.196(1) | 0.59 | 0.070(4) |
| S3 | 0.9016(8) | 0.1658(6) | 0.6329(8) | 1.00 | 0.089(2) |
| S4 | 0.1883(8) | 0.0476(5) | 0.5836(6) | 1.00 | 0.072(2) |
| (d) | | | | | |
| Hg | 0.5075(3) | 0.0455(1) | 0.7136(3) | 1.00 | 0.0749(9) |
| I1 | 0.4693(4) | 0.1231(2) | 0.3453(4) | 1.00 | 0.056(1) |
| I2 | 0.5515(4) | 0.2112(2) | 0.7960(4) | 1.00 | 0.067(1) |
| As1 | 0.8769(5) | 0.0394(3) | 0.2659(5) | 1.00 | 0.047(1) |
| As2 | 0.9011(5) | 0.0437(3) | 0.7753(6) | 1.00 | 0.053(2) |
| As3 | 0.1366(6) | 0.1912(3) | 0.6636(6) | 1.00 | 0.057(2) |
| As4 | 0.2179(6) | 0.1565(3) | 0.9376(6) | 1.00 | 0.054(2) |
| S1 | 0.713(1) | -0.0158(8) | 0.074(1) | 1.00 | 0.058(4) |
| S2 | 0.001(1) | 0.1233(9) | -0.028(1) | 1.00 | 0.066(4) |
| S3 | 0.895(1) | 0.1586(8) | 0.620(1) | 1.00 | 0.056(4) |
| S4 | 0.186(1) | 0.0558(8) | 0.578(1) | 1.00 | 0.053(4) |

Notes: (a) = unaltered crystal; (b) and (c) = crystal exposed to light (>550 nm) for 930 and 3060 min, respectively; (d) = crystal kept in the dark (39 days) after light-induced alteration.

Structure refinements performed after different exposure times indicated the coexistence of two kinds of cage-like molecules. The first one is identical to the As_4S_4 molecule found in the structure of both realgar and β -phase (Mullen and Nowacki 1972; Porter and Sheldrick 1972), where each As atom links one As and two S atoms (r-type in Fig. 3). The other molecule (derived from the r-type molecule by removing S2 and adding S2b atom) is chemically and structurally identical to the molecule (p-type in Fig. 3) found in pararealgar (Bonazzi et al. 1995) and in the synthetic As_4S_4 -II phase (Kutoglu 1976). The

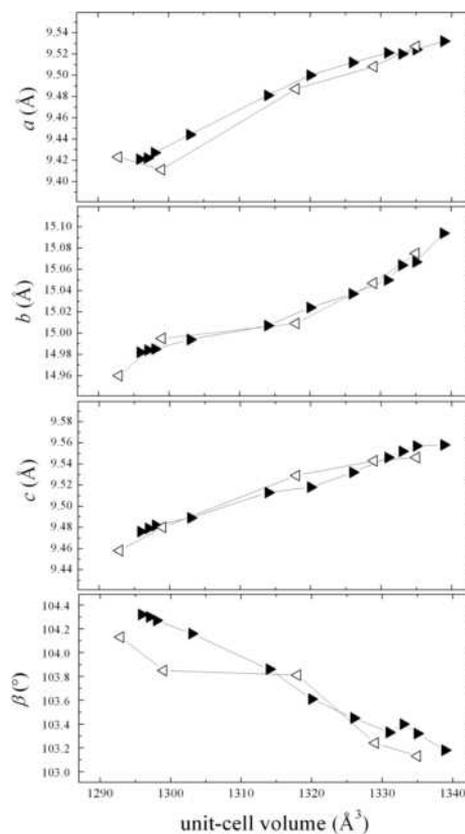


FIGURE 2. Variation of a , b , c (Å), and β (°) parameters vs. the unit-cell volumes (Å³). Full symbols show expansion obtained by exposing crystal to light; empty symbols show the apparent contraction observed after keeping the crystal in the dark. Standard deviations within symbol size (see Table 2).

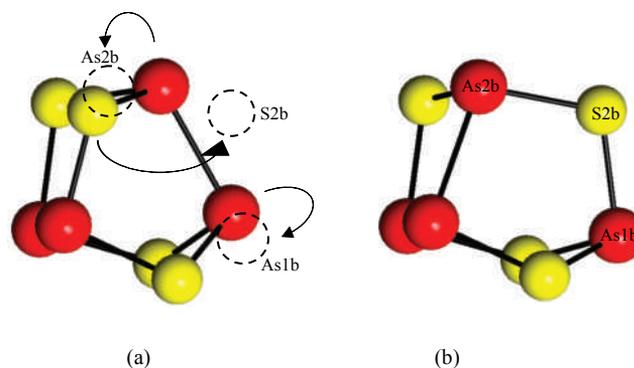


FIGURE 3. Transition from realgar-type (a) to pararealgar-type (b) As_4S_4 molecule.

refined percentage of the fraction of the p-type molecule was 33% after 930 and 59% after 3060 min of exposure to light. In the structural models where only the r-type molecule is present (columns a and d in Table 4), bond distances and angles closely match those already observed for the unaltered $\text{HgI}_2 \cdot \text{As}_4\text{S}_4$ (Bräu and Pfitzner 2006). In the models including both r-type and p-type As_4S_4 molecules, however, some distances deviate slightly from the expected values. This is due to the fact that

TABLE 4. Selected interatomic distances (Å) for the HgI₂·As₄S₄ adduct at different at different steps of alteration

| a | | b | | c | | d | |
|--|-----------|--|----------|--|----------|--|----------|
| Hg-I1 | 2.6068(7) | Hg-I1 | 2.603(3) | Hg-I1 | 2.614(2) | Hg-I1 | 2.603(4) |
| Hg-I2 | 2.5986(7) | Hg-I2 | 2.592(3) | Hg-I2 | 2.600(2) | Hg-I2 | 2.601(4) |
| I1-Hg-I2 | 165.9(2) | I1-Hg-I2 | 163.9(1) | I1-Hg-I2 | 161.0(1) | I1-Hg-I2 | 166.3(1) |
| Hg-S4 | 2.978(2) | Hg-S4 | 2.99(1) | Hg-S4 | 2.958(7) | Hg-S4 | 2.99(1) |
| Hg-S1 | 3.234(2) | Hg-S1 | 3.332(9) | Hg-S1 | 3.394(7) | Hg-S1 | 3.26(1) |
| As ₄ S ₄ (realgar-type mol.) | | As ₄ S ₄ (realgar-type mol.) | | As ₄ S ₄ (realgar-type mol.) | | As ₄ S ₄ (realgar-type mol.) | |
| As1-S1 | 2.237(2) | As1-S1 | 2.26(1) | As1-S1 | 2.43(1) | As1-S1 | 2.23(1) |
| As1-S4 | 2.252(2) | As1-S4 | 2.236(9) | As1-S4 | 2.09(1) | As1-S4 | 2.23(1) |
| As1-As2 | 2.547(1) | As1-As2 | 2.646(7) | As1-As2 | 2.57(1) | As1-As2 | 2.545(6) |
| As2-S3 | 2.230(2) | As2-S3 | 2.24(1) | As2-S3 | 2.26(1) | As2-S3 | 2.26(1) |
| As2-S2 | 2.240(2) | As2-S2 | 2.24(2) | As2-S2 | 2.21(2) | As2-S2 | 2.21(1) |
| As2-As1 | 2.547(1) | As2-As1 | 2.646(7) | As2-As1 | 2.57(1) | As2-As1 | 2.545(6) |
| As3-S3 | 2.227(2) | As3-S3 | 2.23(1) | As3-S3 | 2.264(8) | As3-S3 | 2.26(1) |
| As3-S4 | 2.263(2) | As3-S4 | 2.27(1) | As3-S4 | 2.278(8) | As3-S4 | 2.17(1) |
| As3-As4 | 2.556(1) | As3-As4 | 2.547(5) | As3-As4 | 2.516(4) | As3-As4 | 2.570(7) |
| As4-S2 | 2.222(2) | As4-S2 | 2.15(1) | As4-S2 | 2.11(2) | As4-S2 | 2.21(1) |
| As4-S1 | 2.255(2) | As4-S1 | 2.248(9) | As4-S1 | 2.208(8) | As4-S1 | 2.21(1) |
| As4-As3 | 2.556(1) | As4-As3 | 2.547(5) | As4-As3 | 2.516(4) | As4-As3 | 2.570(7) |
| | | As ₄ S ₄ (pararealgar-type mol.) | | As ₄ S ₄ (pararealgar-type mol.) | | | |
| | | As1-S1 | 2.26(1) | As1b-S1 | 2.15(1) | | |
| | | As1-S4 | 2.236(9) | As1b-S4 | 2.38(1) | | |
| | | As1-S2b | 1.91(3) | As1b-S2b | 2.27(1) | | |
| | | As2b-S3 | 2.34(2) | As2b-S3 | 2.316(9) | | |
| | | As2b-S2b | 2.17(3) | As2b-S2b | 2.24(1) | | |
| | | As2b-As4 | 2.71(1) | As2b-As4 | 2.626(6) | | |
| | | As3-S3 | 2.23(1) | As3-S3 | 2.264(8) | | |
| | | As3-S4 | 2.27(1) | As3-S4 | 2.278(8) | | |
| | | As3-As4 | 2.547(5) | As3-As4 | 2.516(4) | | |
| | | As4-S1 | 2.248(9) | As4-S1 | 2.208(8) | | |
| | | As4-As2b | 2.71(1) | As4-As2b | 2.626(6) | | |
| | | As4-As3 | 2.547(5) | As4-As3 | 2.516(4) | | |

Notes: a = unaltered crystal; b and c = crystal exposed to light (>550 nm) for 930 and 3060 min, respectively; d = crystal kept in the dark (39 days) after light-induced alteration.

S1, S3, and S4 are average positions for both r-type and p-type molecules. On the other hand, the Hg-I bond distances of the HgI₂ moieties appear unaffected by the increase of the p-type replacing the r-type molecules. Nonetheless, the intermolecular distances between HgI₂ and the As₄S₄ cages become longer. The I-Hg-I bending increases from 165.9 to 161.0° as a function of the time of exposure to light indicating that with the increase of sulfur at S2b the As₄S₄ molecule rotates. As a consequence, the Hg-S1 distance becomes longer than the sum of their Van der Waals radii (Bondi 1964) so that the only weak bonding interaction between HgI₂ and the As₄S₄ cages occurs through the Hg-S4 bonds (Table 4).

Because only powder diffraction rings were observed by exposing the altered “single crystal” to CuKα radiation (Fig. 1), whereas single-crystal reflections were still detectable using the more penetrating MoKα radiation (inset of Fig. 1), it can be inferred that the core of the unaltered “single crystal” is covered by a rim of a randomly oriented microcrystalline product and the thickness of this rim is smaller than the penetration path of the MoKα radiation ($\mu = 27.368 \text{ mm}^{-1}$) but larger or equal to that of the CuKα radiation ($\mu = 75.695 \text{ mm}^{-1}$). Table 5 reports the list of the *d* values, obtained by converting the diffraction rings into a conventional XRD pattern, compared with the powder pattern of β-As₄S₄. The most intense peaks closely correspond to those of the β-phase indicating that the original compound was decomposed into microcrystalline β-As₄S₄ [*a* = 9.9477(4), *b* = 9.3603(4), *c* = 8.8935(4) Å, β = 102.302(4)°, *V* = 809.08(4) Å³] and another unidentified phase containing HgI₂ molecules. Almost all the residuals peaks that are not explained by β-As₄S₄

are ascribable to α-As₄S₄ (denoted with asterisks in Table 5). Among the numerous HgI₂ polymorphs (Schwarzenbach et al. 2007 and references therein), the only phase whose presence cannot be excluded on the basis of our diffraction data is the orthorhombic yellow metastable polymorph (yellow_M, ICDD-PDF 27-1287; Jeffrey and Vlasse 1967). In contrast to the red and orange HgI₂ polymorphs, this compound is molecular with linear I-Hg-I molecules (Hostettler and Schwarzenbach 2005). There is a complete overlapping with several lines of the β-As₄S₄ pattern and a comparison between the expected and the observed relative intensities suggests that the residual HgI₂ is present in a poorly crystallized or amorphous state. The only diffraction lines, although very weak, which are not justified by the coexistence of β-As₄S₄ and minor quantities of α-As₄S₄ are that at *d* = 5.57 Å and the shoulder at 5.11 Å. These lines, indeed, might correspond to the most intense peaks (*I*/*I*₀ = 100 and 90, respectively) of pararealgar.

Micro-Raman spectroscopy

Figure 4 reports the Raman spectra collected on crystals exposed to visible light but not to X-ray radiation. The Raman spectrum obtained for the unaltered HgI₂·As₄S₄ (Fig. 4a) is identical to that previously published by Bräu and Pfitzner (2006). In the portion investigated here, however, the vibrational frequencies assigned to the HgI₂ groups are not visible due to the operative conditions (wavenumbers <200 cm⁻¹ are cut by a Notch filter) and the peaks observed correspond to those of the As₄S₄ cage-molecule alone. In particular, the spectrum closely resembles that of realgar (Muniz-Miranda et

TABLE 5. XRD pattern obtained by the altered microcrystalline rim compared with the powder pattern of β-As₄S₄

| hkl | d _{calc} | (1) | | (2) | |
|--------|-------------------|------------------|------------------|------------------|------------------|
| | | d _{obs} | I/I _o | d _{obs} | I/I _o |
| 1 1 0 | 6.7421 | 6.76 | m | 6.75 | 10 |
| 1̄ 1 1 | 5.7545 | 6.01* | w | 5.76 | 100 |
| | | 5.57† | w | | |
| | | 5.40* | m | | |
| | | 5.11† | sh | | |
| 1 1 1 | 4.9820 | 4.99 | m | 4.98 | 50 |
| 2 0 0 | 4.8596 | 4.85 | m | 4.87 | 30 |
| 0 2 0 | 4.6801 | 4.70 | vw | 4.67 | 10 |
| 0 2 1 | 4.1205 | 4.14 | w | 4.11 | 10 |
| | | 4.07* | w | | |
| 1̄ 1 2 | 3.9258 | 3.92 | m | 3.93 | 40 |
| | | 3.75* | w | | |
| 1 1 2 | 3.4286 | 3.43 | vw | 3.42 | 5 |
| 2 2 0 | 3.3710 | 3.38 | vw | 3.37 | 5 |
| 2̄ 2 1 | 3.3122 | 3.30 | vw | 3.31 | 10 |
| 0 2 2 | 3.1841 | 3.18 | m | 3.18 | 30 |
| 3 1 0 | 3.0616 | 3.05 | s | 3.07 | 50 |
| 2 2 1 | 2.9970 | 3.00 | s | 2.990 | 70 |
| 2 0 2 | 2.9424 | 2.94 | m | 2.939 | 25 |
| 2̄ 2 2 | 2.8773 | 2.88 | s | 2.880 | 70 |
| 1̄ 1 3 | 2.8165 | 2.81 | m | 2.816 | 30 |
| 1 3 1 | 2.7566 | 2.73 | m | 2.749 | 10 |
| 3 1 1 | 2.7210 | 2.72 | m | 2.722 | 10 |
| | | 2.65* | vw | | |
| | | 2.59* | vw | | |
| 1 1 3 | 2.5291 | 2.52 | w | 2.524 | 15 |
| 2 2 2 | 2.4910 | 2.47 | vw | 2.487 | 10 |
| 0 2 3 | 2.4629 | – | – | 2.458 | 5 |
| 4 0 0 | 2.4298 | 2.42 | vw | 2.435 | 5 |
| 2̄ 2 3 | 2.3774 | 2.38 | w | 2.378 | 15 |
| 1 3 2 | 2.3811 | – | – | – | – |
| 3̄ 3 1 | 2.2582 | 2.25 | w | 2.259 | 10 |
| 3 3 0 | 2.2474 | – | – | 2.246 | 15 |
| 4 2 1 | 2.1922 | 2.191 | w | 2.197 | 10 |
| 2̄ 0 4 | 2.1622 | 2.164 | w | 2.161 | 10 |
| 4 2 0 | 2.1565 | 2.156 | w | – | – |
| 1̄ 3 3 | 2.1449 | 2.136 | w | 2.141 | 10 |
| 3̄ 3 2 | 2.1286 | 2.129 | vw | 2.129 | 5 |
| 2 4 0 | 2.1084 | 2.109 | sh | 2.100 | 5 |
| 3 3 1 | 2.1018 | – | – | – | – |
| 3 1 4 | 1.9686 | 1.972 | vw | – | – |
| 2 4 2 | 1.9697 | 1.969 | vw | 1.969 | 5 |
| 3 3 3 | 1.9182 | 1.918 | vw | 1.919 | 5 |
| 3 1 3 | 1.9199 | – | – | 1.916 | 5 |
| | | 1.860* | vw | | |
| 1 5 0 | 1.8383 | 1.837 | vw | 1.832 | 10 |
| 0 4 3 | 1.8202 | 1.819 | vw | 1.815 | 10 |
| 4 2 2 | 1.8008 | 1.801 | vw | 1.798 | 10 |
| 5 1 1 | 1.7831 | 1.785 | vw | – | – |
| 5 1 3 | 1.7689 | 1.765 | vw | – | – |
| 1 5 2 | 1.6690 | 1.679 | vw | – | – |
| 3 1 5 | 1.6618 | 1.664 | vw | – | – |
| 2 4 3 | 1.6342 | 1.633 | vw | – | – |
| 0 2 5 | 1.6292 | – | – | – | – |
| 6 0 0 | 1.6199 | 1.625 | vw | – | – |

Notes: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, and sh = shoulder; (1) calculated and observed diffraction pattern (CuKα; 2θ range: 8–65°); data yield the following unit cell: $a = 9.9477(4)$, $b = 9.3603(4)$, $c = 8.8935(4)$ Å, $\beta = 102.302(4)^\circ$, $V = 809.08(4)$ Å³; not indexed reflections denoted with * and † belong to realgar and pararealgar, respectively; (2) observed powder diffraction data from synthetic β-As₄S₄ (Bonazzi et al. 1996).

al. 1996; Banerjee et al. 2003), but slightly differs from that of the β-As₄S₄ phase. In the spectrum collected on the crystal exposed for 600 min (Fig. 4b), some additional peaks occur. Peaks at 233(±2) and 274(±1) cm⁻¹ unequivocally correspond to the presence of the p-type As₄S₄ molecular group (Muniz-Miranda et al. 1996; Trentelman et al. 1996), while the peak at about 312(±2) cm⁻¹, which is also observed in the spectrum of alacranite (Pagliai et al. in review), uzonite, and As₂S_{8-x} sulfides

(Bonazzi et al. unpublished data), indicates the presence of the As₄S₅ molecular group. As the exposure time increases (Fig. 4c), the relative intensity of the peaks corresponding to the p-type As₄S₄ molecule increases. Finally, in the spectrum of the crystal exposed for 3000 min (Fig. 4d), the peak at 359(±1) cm⁻¹ could correspond to r-type As₄S₄ molecules packed in an arrangement similar to the one found in the β-phase (Muniz-Miranda et al. 1996; Bonazzi et al. unpublished data).

The Raman spectrum collected on the X-rayed crystal kept in the dark (used to obtain the structural data given in Table 1) exhibited strong fluorescence, which masked the Raman features. The same phenomenon was observed on light-exposed crystals, which previously have given Raman spectra without fluorescence (Fig. 4), after prolonged X-ray exposure. This feature is probably related to the formation of yellow HgI₂ and/or minor other not identified degradation products.

DISCUSSION

The previous literature (Kyono et al. 2005; Ballirano and Maras 2006; Bonazzi et al. 2006; Bindi and Bonazzi 2007; Kyono 2007; Naumov et al. 2007, 2010) unanimously attributes the

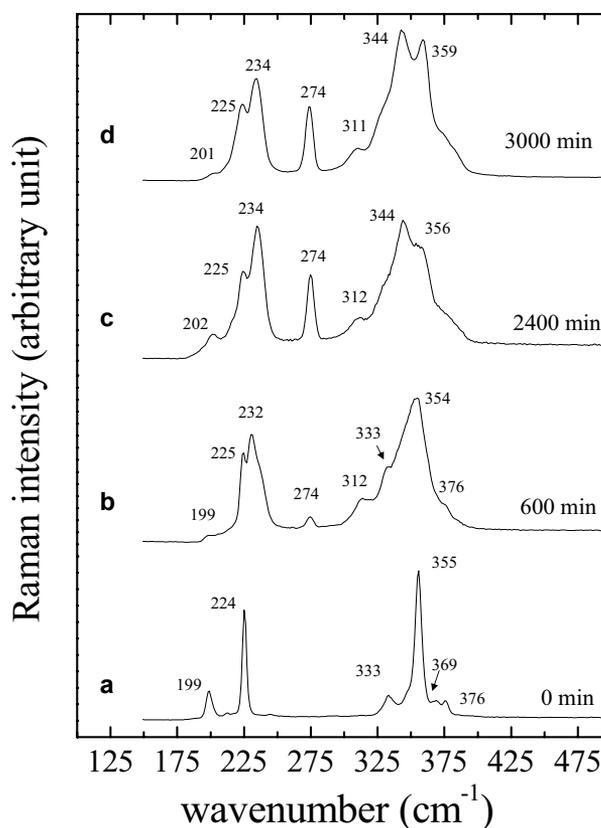


FIGURE 4. Raman spectra collected on crystals exposed to filtered light (>550 nm) with increasing times. In **b**, the additional peaks at 232(±2) and 274(±1) cm⁻¹ unequivocally correspond to the presence of the p-type As₄S₄ molecular group, while the peak at about 312(±2) cm⁻¹ indicates the presence of the As₄S₅ molecular group. As the exposure time increases (**c**), the relative intensity of the peaks corresponding to the p-type As₄S₄ molecule increases. In **d**, the peak at 359(±1) cm⁻¹ could correspond to r-type As₄S₄ molecules packed in an arrangement as in the β-phase.

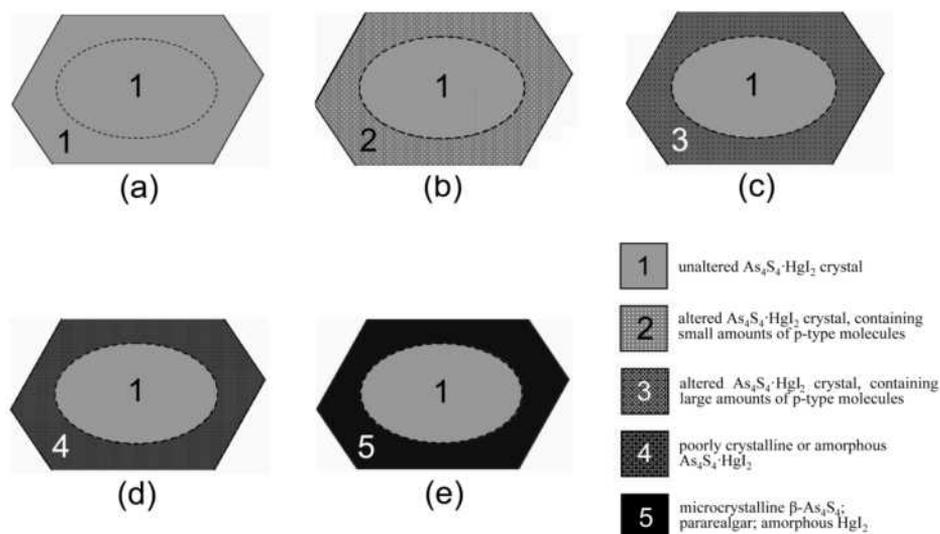


FIGURE 5. Schematic step by step description of the light-induced alteration process: (a) unaltered crystal not exposed to light; (b) and (c) crystal exposed to light for 930 and 3060 min, respectively; (d) crystal kept in the dark (39 days) after light-induced alteration; (e) crystal kept in the dark three months approximately.

cause of the increase of the unit-cell volume observed during the alteration of realgar or $\beta\text{-As}_4\text{S}_4$ phase to a temporary increase of the content of the As_4S_5 molecules within the structure occurring with the development of the following reaction: $5\text{As}_4\text{S}_4(\text{r-type}) + 3\text{O}_2 \rightarrow 4\text{As}_4\text{S}_5 + 2\text{As}_2\text{O}_3$. In contrast, no evidence of significant amounts of As_4S_5 molecules were found in the light-exposed $\text{HgI}_2 \cdot \text{As}_4\text{S}_4$ crystal studied here, although a considerable increase of the unit-cell volume was observed. Accordingly, no diffraction peak belonging to arsenolite was found among the reflections diffracted by the altered rim of the crystal (Table 5). Despite the same stoichiometry, the p-type molecule exhibits a molecular volume ($15.65\text{--}15.82 \text{ \AA}^3$; Bonazzi and Bindi 2008) significantly larger than that of a r-type molecule ($14.65\text{--}14.82 \text{ \AA}^3$; Bonazzi and Bindi 2008). Thus, the increase of the unit-cell volume could be caused by a partial replacement of realgar-type with pararealgar-type molecules together with a general rearrangement of the molecular packing leading to larger intramolecular contacts. Nonetheless, as it can be inferred by micro-Raman investigations, As_4S_5 molecules are formed during the light-induced alteration process. From the linear relationship between unit-cell volume and the percentage of As_4S_5 molecules in crystals of the continuous $\beta\text{-As}_4\text{S}_4\text{--As}_8\text{S}_9$ series (Bonazzi et al. 2003b), we can estimate that the microcrystalline $\beta\text{-As}_4\text{S}_4$, formed during the breakdown of the $\text{HgI}_2 \cdot \text{As}_4\text{S}_4$ adduct, contains about 8% of As_4S_5 . Whether these molecules are present only in a microcrystalline decomposition product or also substitute the r-type and p-type As_4S_4 molecules in the adduct is not easy to establish.

The paths describing the “reverse” variation obtained in the “dark” stage (empty triangles in Fig. 2) might let us hypothesize that in the $\text{HgI}_2 \cdot \text{As}_4\text{S}_4$ adduct the transition from realgar- to pararealgar-type molecule is reversible. Nonetheless, this possibility is quite unlikely since pararealgar is the final product of the light-induced alteration process. A different interpretation, therefore, should be taken into account. In Figure 5, which provides a schematic elucidation of the process, the dashed line qualitatively marks the limit of a rim where the visible light could be transmitted through the crystal. Because the X-ray radiation is more penetrating than visible light, it is possible that the

reflections measured using $\text{MoK}\alpha$ radiation are produced from both the external rim and the core of the crystal. Thus, we can suppose that in the first stage of alteration (“light” stage) the reflections diffracted from the unaltered core coalesce with lower θ -angle reflections produced by the altered rim consisting of adduct, which contains increasing amounts of p-type molecules (Figs. 5a, 5b, and 5c). As the amount of p-type molecules in the rim increases, the unit-cell volume increases accordingly and the barycenter of the measured peak shifts progressively toward lower θ angles. On the other hand, the progressive shift toward higher θ -angles observed along the “reverse” path (“dark” stage) could be reasonably due to a progressive decrease of the intensity diffracted from the altered rim, which gradually becomes microcrystalline and/or amorphous (Fig. 5d) and breaks down into different phases after long times in the dark (Fig. 5e). In this view, the absence of the p-type molecule in the structure determination after the dark stage [(d) in Table 3] cannot be seen as a reversible transformation but as due to amorphization of the layer containing the p-molecule.

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