Molecular conformation and anion configuration variations for As₄S₄ and As₄Se₄ in an anion-substituted solid solution

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ABSTRACT

Molecular crystals of an As₄S₄₋ₓSeₓ (0 ≤ x ≤ 4) solid solution were grown at 400 °C using vacuum-sublimation and were characterized using single-crystal X-ray diffraction and electron microprobe analyses. The solid solution crystallizes in the monoclinic space group P2₁/n with lattice parameters of a = 9.33–9.57 Å, b = 13.57–13.82 Å, c = 6.60–6.74 Å, β = 106.4–106.7°, V = 801–854 Å³, and Z = 4. Substitution of Se for S in the As₄X₄ molecule causes nearly isotropic unit-cell expansion retaining identical molecular packing to the low-temperature form α-As₄S₄ (natural realgar). Crystal structure refinements show that Se is distributed with a strong preference for the X2 site. The As-X3 bond is slightly elongated in the solid-solution series. The bond length difference between As-X3 and the other As-X bonds increases with the Se content, thereby inducing atomic shift of the As₄S₄ bonds to X3 and X4 toward the side of X3. The atomic position of As₄ returns to the place on the bisector between X3 and X4 at the As₄Se₄ end-member composition. Although As-As bonds shorten with Se content, the volume of the As₄X₄ molecule and the intercentroid distance between the nearest As₄X₄ molecules increase continuously, resulting in isotropic expansion of the unit cell in this solid-solution series.

The strong site preference of Se for the X2 site suggests that S may be detached from that site more easily than from the remaining ones. On the contrary, very slight substitution of Se for S in the X3 site indicates that S in the X3 site is strongly bonded to two As atoms. Therefore, S is more stably incorporated into the X3 site than into the X2 site; these molecular features of the Se substitution in the As₄X₄ molecule are consistent with the proposed photoinduced transformation dynamics in realgar. Continuous illumination of the Se-containing realgar engenders alteration to pararealgar under identical transformation mechanisms to those of the realgar.

Keywords: Realgar, As₄S₄, seleno-realgar, As₄Se₄, solid solution, crystal structure

INTRODUCTION

The ratio between sulfur and selenium is regarded as important information for resolving the origin of hydrothermal ore deposits. Selenium, which is several thousand times less abundant than sulfur in the Earth’s crust (Mason and Moore 1982), can substitute for sulfur in various sulfide minerals (Simon et al. 1997) because of the similarity of their respective crystallographical properties such as electronegativity, electronic polarizability, and ionic radius (Pauling 1927; Shannon 1981; Emsley 1998). According to Anderson (1969) and Huston et al. (1995), the Se/S ratio is useful for determining not only the sources of S but also geothermometry and the redox gradients. High Se/S ratios can be considered as typical indicators of deposition in a volcanic environment. Therefore, the high Se contents in realgar As₄S₄ and orpiment As₄S₄ are consistent with a subvolcanic volcanic origin of the sulfur (Ferrini et al. 2003).

To date, extensive studies with various experimental approaches have been conducted to understand and interpret the substitution effects of S for Se on crystal structures of many sulfides, especially on an amorphous arsenic chalcogenide, to investigate the nature and mechanisms of photoinduced changes in local bonding structures and localized electronic gap states (e.g., Salaneck et al. 1975; Bullett 1976; Watanabe et al. 1988; Elliott and Shimakawa 1990; Mikla 1996; Iwadate et al. 1999; Chen et al. 2006). Moreover, several reviews of photoinduced modifications have been published (e.g., Tanaka 1990; Pfeiffer et al. 1991; Shimakawa et al. 1995; Kolobov and Tanaka 1999; Shpotyuk 2004). The photoinduced transformation of crystalline arsenic sulfide As₄S₄, both as the low-temperature polymorph α-As₄S₄, realgar, and the high-temperature β-As₄S₄, is a widely recognized phenomenon that has been investigated thoroughly (Clark 1970; Douglass et al. 1992; Bonazzi et al. 1996, 2006; Kyono et al. 2005; Ballirano and Maras 2006; Kyono 2007; Naumov et al. 2007). Most recently, the substitution effects on crystalline arsenic chalcogenide, laphamite, As₄X₄ (X = S, Se), were examined (Bindi et al. 2008).

This study was undertaken to investigate the effects of Se substitution for S on the crystalline arsenic sulfide realgar (As₄S₄) and to compare its features with the photoinduced transformation dynamics in realgar. This report provides new insight into realgar molecular properties estimated from detailed crystallographic data along the As₄S₄₋ₓSeₓ (0 ≤ x ≤ 4) solid-solution series.
**EXPERIMENTAL METHODS**

Single crystals within the As$_x$S$_y$Se$_z$ solid-solution series were grown using vacuum sublimation. Commercially available As metal (Wako Pure Chemical, purity > 98.0%), S (Wako Pure Chemical, purity > 98.0%), and Se metal (Wako Pure Chemical, purity > 98.0%) were used as starting materials. Compositions of the starting mixtures were as follows: As:S:Se ratios of (1) 1:1:0, (2) 2:1:1, (3) 3:1:2, (4) 4:1:3, (5) 8:1:7, and (6) 1:0:1. Pyrex glass ampoules used in the synthesis were of 8.0 mm inner diameter (10.0 mm outer diameter) and 400 mm length. The very long ampoules were chosen to generate a sufficient temperature gradient between the source materials and the crystal deposition zone. The mixture, with a typical weight of about 300 mg, was placed at the bottom of the ampoule and sealed under a vacuum of about $5 \times 10^{-2}$ Pa. The ampoule was wrapped in aluminum foil and introduced into an electric furnace vertically from the top window. The top end of the ampoule was left outside the furnace to maintain that part close to room temperature. Starting mixtures, put at the bottom of the ampoule, were heated within the furnace from room temperature to 400 °C in 3 h, and the temperature was kept constant for 48 h. Subsequently, the ampoule was cooled by shutting off the power to the furnace. The electric furnace was then allowed to cool down to room temperature and the ampoule was opened using a diamond saw. Finally, single crystals deposited on the glass wall were removed.

Forty suitable crystals were selected using binocular microscopes from batches synthesized under six different As:S:Se molar ratios for single-crystal X-ray diffraction (XRD) and electron microprobe analysis (EMPA). Single crystals were fixed on a 0.1 mm diameter glass capillary, then mounted on a RAXIS-RAPID imaging plate diffractometer (Rigaku Corp.) operating with Mo Kα radiation ($\lambda = 0.71069$ Å) monochromatized using a flat graphite crystal. Diffraction data were collected at room temperature using an $\omega$-oscillation method with an oscillation width of 5.0° between 130 and 190° ($\chi = 45°$, $\phi = 0°$) and between 0 and 160° ($\chi = 45°$, $\phi = 180°$). The exposure rate was of 60 s per degree of oscillation. A total of 44 images were collected. Intensities were corrected for lorentz and polarization effects. An absorption correction was applied from the symmetry-equivalent reflections using the ABSCOR program (Higashi 1995). The structure was solved using direct methods with the SIR97 program package (Altomare et al. 1999). Only reflections with $I > 4\sigma(I)$ were used for structure refinements, in the space group $P2_1/n$, performed using full-matrix least squares on $F^2$ with the CRYSTALS program (Carruthers et al. 1999).

After data collection, each crystal was mounted in epoxy and polished for EMPA that was carried out with a JEOL JXA-8621 equipped with wavelength dispersion spectrometers. Chemical analyses were obtained using a beam diameter of 10 μm, an accelerating voltage of 20 kV, and a beam current of 10 nA with an acquisition time of 10 s on both the peak and background. The chemical composition of each crystal was determined from the averages of several points analyzed. Raw data were corrected using a conventional ZAF program. Synthetic realgar (As$_4$S$_4$ and Se) and synthetic As$_4$Se$_4$ (Se) were used as standards. Empirical formulae were normalized on the basis of eight atoms per formula unit (ppu). Because of the similarity in the atomic scattering factor of As and Se, the distribution of these elements among the atomic positions in the As$_x$S$_y$Se$_z$ crystal was inferred based on crystal-chemical considerations. Site occupancies were refined within the constraint that four As sites are occupied only by As atoms and that four X sites are occupied by the S and Se atoms. Based on the assumption that the S and Se atoms are disordered at four sites, the ratio between S and Se in the molecule, the ratio between S and Se in the formula was refined under the constraint that total S/Se ratio is equal to that determined using the electron microprobe analyses. The final cycle of full-matrix least-squares refinement was based on the observed reflections and 73 variable parameters (atomic coordinates, isotropic displacement parameters, anisotropic displacement parameters, and site occupancy factors). Concomitantly with the increase in the Se content, the maximum and minimum peak heights in the final difference-Fourier map increase and then residual $R$ factors became larger in the structure refinements. As poor convergences result in unreliable crystal-structure information, all refinement results whose final $R$ factors exceeded 10% were eliminated.

**RESULTS**

**Color variations of the solid solutions**

Single crystals obtained using this crystal growth technique were shaped as clear euhedral prisms up to a length of ~2.0 mm (Fig. 1). Crystals are elongated along [001] and show well-developed {120}, {100}, and [001] forms. The length-to-width ratio of the elongated crystals varies from about 3:1 to about 8:1.

![Figure 1](image1.png)

**Figure 1.** Single crystals grown from the starting material contents as follows: As:S:Se ratios of (a) 1:1:0, (b) 2:1:1, (c) 3:1:2, (d) 4:1:3, (e) 8:1:7, and (f) 1:0:1. The scale bars represent 200 μm.

![Figure 2](image2.png)

**Figure 2.** Chemical composition data of S and Se for the single crystal grown using the vacuum-sublimation method, sample S1Se1-9. The scale bar is 50 μm.

No compositional dependence of the crystal morphology or the length to width ratio is apparent. The pure As$_x$S$_y$Se$_z$ crystal grown by this sublimation method has a transparent bright red color. As depicted in Figure 1, the crystal color drastically changes to deep red with slight incorporation of Se. With increasing the Se content, the color turns into nontransparent black, possessing almost resinous luster. A similar color change is observed within the orpiment-laphamite solid solution. In fact, with substitution of Se for S in orpiment, the crystal color changes to a very dark red that is nearly opaque with resinous luster (Dunn et al. 1986; Gaines et al. 1997). Figure 2 shows a representative EMPA composition map of the polished surface of S1Se1-9 single crystal. The composition map displays no chemical zoning of S and Se between the core and rim in the single crystal. Therefore, it can be stated that single crystals obtained via this vacuum-sublimation method are compositionally homogeneous. Table 1 reports a...
summary of the quantitative analysis of each crystal. Although
the S/Se ratios are not always close to the molar ratio used as
starting materials, the variation of Se content is continuous in
the As₄S₄– solid solution.

Crystal-structure investigation

Selenium content was fixed to EMPA values, all structure
refinements were carried out using a structure model having
symmetry of space group P2₁/n. Lattice parameters, details of
X-ray data collection, and agreement parameters are listed in
Table 2. The molecular packing is that of realgar, α-As₄S₄ (Mullen
and Nowacki 1972), throughout the solid solution. Atomic
positional parameters, site occupancy factors, and displacement
parameters are reported in Table 3. Structure refinement results
revealed that considerable differences in the site occupancy
factors exist among the four X sites. Atomic charges of electro-
static potentials in realgar As₄S₄ have been calculated using the
density functional theory (DFT) method by Bullen et al. (2003).
The results indicate that point charges of all S and As atoms are
equivalent in the realgar structure. Based on these results, it can
be inferred that the preferential distribution of Se over the four
X sites is not caused by the delocalized electrostatic potentials of
each X site. Structure refinements indicate that Se is distributed
over the four X sites with a strong preference for X₂, followed
by X₁, whereas it is only slightly incorporated into the X₃ site.
This is the most important characteristic of the As₄S₄– solid-
solution series. The relation between site occupancies and Se
concentration is depicted in Figure 3. Large deviations from the
diagonal indicate a substantially ordered distribution among the
four X sites. Displacement parameters of X₂ are consistently the
smallest even for realgar. The weak preference of Se for the X₃
site is more remarkable below the Se/(S + Se) ratio of 0.5 in the

1 Deposit item AM-09-019, Tables 2 and 3 (lattice parameters, de-
tails of X-ray data collection, and agreement parameters; atomic
positional parameters, site occupancy factors, and displacement
parameters). 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 infor-
mation. For an electronic copy visit the MSA web site at http://
www.minsocam.org, go to the American Mineralogist Contents,
a
table of contents for the specific volume/issue wanted,
and then click on the deposit link there.

**Table 1.** Chemical compositions of the single crystals determined by EMPA

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<td>2.43/1.57</td>
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<td>2.855</td>
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<td>3.05/0.95</td>
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<td>1.01/2.98</td>
<td>1.06/2.88</td>
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<tr>
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<td>2.957</td>
<td>2.855</td>
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<tr>
<td>S/Se</td>
<td>0.85/3.15</td>
<td>1.02/2.98</td>
<td>1.06/2.88</td>
</tr>
</tbody>
</table>
solid-solution range. Site occupancy factors in the X4 site are approximately consistent within the whole ratio in whole Se/(S + Se) concentration values, which results in the clear linear distribution pattern.

Variation of intermolecular and intramolecular configurations

The Se substitution in the As₄X₄ molecule results in a highly ordered distribution among the four X sites. Figure 4 shows functional relations between the variations in the unit-cell parameters and the Se concentration. With increasing Se content, a, b, and c lattice parameters increase monotonically, although the monoclinic β angle remains substantially unchanged. The variation of the a, b, and c lattice parameters range from ca. 9.33 to ca. 9.57 Å, from ca. 13.57 to ca. 13.82 Å, and from ca. 6.60 to ca. 6.74 Å, respectively (Table 2'). The β angle remains constant at ca. 106.5° throughout the whole composition. The lattice parameters of each end-member are in agreement with reference data (e.g., Mullen and Nowacki 1972; Smail and Sheldrick 1973; Kyono et al. 2005). Regarding the effect of Se substitution for S in orpiment (Bindi et al. 2008), both a and b lattice parameters increase linearly as a function of Se content, whereas the c lattice parameter remains unchanged. The β angle exhibits no clear trend in the compositional variation between As₂S₃ and As₂Se₃.
In comparison to the $\text{As}_2\text{X}_3$ ($\text{X} = \text{S}, \text{Se}$) solid-solution series, the replacement of S by Se engenders an almost isotropic expansion of the unit cell in the $\text{As}_4\text{X}_4$ solid-solution series. The isotropic expansion is consistent with the substitution of the larger Se for the smaller S atom (their van der Waals radii are 1.90 and 1.80 Å, respectively). Although Vegard’s law is substantially obeyed over the whole range of the $\text{As}_4\text{X}_4$ solid solution, a slight deviation from linearity is clearly visible in Figure 4. In fact, the variation in unit-cell volume follows Vegard’s law directly (Fig. 4e), but that of $a$ and $b$ lattice parameters depart only marginally from linearity: positive for $a$ and negative for $b$ (Figs. 4a and 4b). The deviations are closely associated with the highly ordered atomic distribution among the four X sites.

The atomic configuration in the molecule and its molecular

![Figure 5](image1.png)

**Figure 5.** Crystal structure of the $\text{As}_8\text{S}_4\text{Se}_4$ solid-solution series projected along [001]. Arsenic and X atoms are depicted in black and pale gray, respectively.

![Figure 6](image2.png)

**Figure 6.** Compositional dependence of the intramolecular bond distances and angles. Changes in As-X bond distances ($a$), As-As bond distances ($b$), As-X-As bond angles ($c$), and X-As-X bond angles ($d$) as a function of Se content. The As-X bond distances shown are averages of two As-X bond distances. The dotted line ($a$) indicates the linear trend.
packing in the unit cell are presented in Figure 5. As might be readily apparent from the figure, X1 and X2, which have a strong preference of Se, are aligned oppositely along the a axis. In contrast, X3, exhibiting very weak preference of Se, is positioned directly across from X1 and X2 along the b axis. These coupled effects explain the positive and negative deviations from Vegard’s law (Figs. 4a and 4b). Composition dependences of As-X bond distances in the As2X3 molecule variations of several torsion angles in the As4X4 molecule are in agreement with reference data (e.g., Mullen and Nowacki 1974). Little variation exists in the As-X-As bond angles, particularly in the As3-X3-As bond angle, which remains constant to 100.5° throughout the series (Fig. 6c). However, all the As-X-As bond angles decrease drastically to about 98° at the AsSe4 end-member composition. Most intramolecular X-As-X bond angles vary between 94 and 96°, but only the X3-As4-X4 bond angle decreases regularly from 95 to 92° as a function of Se content. However, it increases suddenly at the AsSe4 end-member composition (Fig. 6d).

Variations of several torsion angles in the As4X4 molecule are shown in Figure 7. The four X atoms in the As4X4 molecule lie at the vertices of a square conformation parallel to plane (10,53) or (10,53). The angles between the two opposing sides of the square increase as a function of the Se content in the solid solution, which increase constantly from about 0.2° to about 0.7° (Fig. 7a). Interestingly, the variations of the torsion angles As3-As2-As4-As1 and As2-As3-As1-As4 are almost equal to those of X3-X1-X4-X4 and X3-X1-X2-X4 torsion angles. This result proves that the Se substitution causes not only twisting of the square conformation of four X atoms but also that of the As atomic arrangement.

Figure 8 presents the compositional dependence of the As4X4 molecule volumes and the intercentroid distances between the nearest As4X4 molecules. The As4X4 molecule volume and the intercentroid distance increase constantly from 14.9 to 17.4 Å3.
solid solution. Although the As increases are inferred to cause isotropic unit-cell expansion in this (Fig. 8a) and from 5.65 to 5.83 Å (Fig. 8b), respectively. These (S + Se)

<table>
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<th>Sample no.</th>
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<th>As1-X2-As2</th>
<th>As2-X2-As4</th>
<th>As2-X4-As4</th>
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<td>101.32(3)</td>
<td>100.88(3)</td>
<td>100.84(4)</td>
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<td>S1Se1</td>
<td>0.19</td>
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<td>101.29(5)</td>
<td>100.85(5)</td>
<td>100.86(6)</td>
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<tr>
<td>S1Se2</td>
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<td>101.31(6)</td>
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<td>101.25(4)</td>
<td>100.88(4)</td>
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Table 5. Intramolecular bond angles (°) in the As4Se4 solid-solution series

With the increase in the number of electrons per molecule, and therefore with increased molecular weight. The As4Se4 crystal structure consists of discrete As4X4 molecules that are held together by van der Waals forces (Mullen and Nowacki 1972; Goldstein and Paton 1974). Therefore, an increase of van der Waals force is expected to decrease intermolecular distances between the As4X4 molecules. The variations of the intermolecular distances are reported in Figure 9. In general, intermolecular As-As distances decrease with increasing Se content. In particular, the intermolecular As1-As1 distance is shortened considerably from 3.62 to 3.55 Å (Fig. 9a). In contrast, the intermolecular As3-As4 distance remains unchanged throughout the solid-solution range. The respective intermolecular X1-X2 and X3-X4 distances increase monotonically from 3.97 to 4.08 Å and from 3.74 to 3.79 Å, respectively (Fig. 9b). However, they decrease suddenly at the As4Se4 end-member composition. The X3-X4 as well as X2-X3 distances becomes shorter than those in As4S4. The shorter intermolecular distances between the As4Se4 molecules is explained by the increase of van der Waals force, but the increases of intermolecular distances with Se content result from As4X4 molecular conformation change. Although most intermolecular As-As distances shorten with increasing Se content in the molecule, the intercentroid distances between the nearest As4X4 molecules lengthen (Fig. 8b) because of the marked increase of the intramolecular As-X bond distances (Fig. 6a).

**SUMMARY AND DISCUSSION**

Variation of the molecular conformation

Here, the substitution effects of Se for S on crystal structure of realgar can be described in detail. The As4X4 molecular conformation change related to the substitution of S with Se is illustrated schematically in Figure 10. All As-X bond distances increase from As4S4 to As4Se4 end-member and the square conformation of four X atoms is illustrated (Fig. 10b): all As atoms in the As4X4 molecule move outside on the square plane (Fig. 10). In contrast, the As atoms come closer to one another with increasing Se content. The most important conformation change caused by this substitution occurs in the X3-X4 bond angle. The As-X3 bond becomes shorter than any other As-X bond in the molecule (Fig. 6a) because of the strong preference for Se (Fig. 3). Therefore, the difference in the

![Figure 7](image_url)  
**Figure 7.** Compositional dependence of the torsion angles of four X atoms (a) and of four As atoms (b).
bond distance between the As4-X3 and As4-X4 becomes larger with increasing Se content. Consequently, this intramolecular conformation change induces the atomic shift of As4 toward the side of X3 (Fig. 10). The shift appears as a continuous decrease in the X3-As4-X4 bond angle (Fig. 6d). When the As$_4$X$_4$ composition attains the As$_4$Se$_4$ end-member composition, however, the X3-As4-X4 angle returns to approximately the same value of the angle as in As$_4$S$_4$ end-member because all As-Se bond distances become almost identical in the As$_4$Se$_4$ molecule (Fig. 6a) so that As4 is positioned on the bisector between Se3 and Se4. This atomic shift of As4 markedly decreases the As-X4-As bond angle as well (Fig. 6c). Most As-X-As bond angles remain constant during the Se substitution for S, but they decrease drastically at the As$_4$Se$_4$ end-member composition. Therefore, the square of four X atoms expands suddenly in the As$_4$Se$_4$ molecule. The expansion of the square is visible in the sudden decrease of the intermolecular X-X distances at the As$_4$Se$_4$ end-member composition (Fig. 9b). The weak preference of Se for the X3 site in the molecule gives rise to discontinuous changes of the molecular conformation at the As$_4$Se$_4$ end-member composition.

Comparison with photo-induced molecular dynamics

In a recent study, Naumov et al. (2007) examined As$_4$S$_4$ molecular dynamics during the photo-induced transformation of realgar using residual electron density features. The authors showed that the S2 that bridges As1 and As3 is detached from the realgar molecule during transformation and that the half-molecule fragment As2-As3-S4-As4-S3 survives the transformation from the realgar molecule to the pararealgar molecule. Comparison to the photo-induced transformation dynamics reported by Naumov
et al. (2007) reveals that their results are consistent with the Se substitution mechanism acting in the As₄X₄ solid solution series. Results of the present study demonstrate that Se shows a strong preference for the X2 site; it can therefore be substituted easily for S at the X2 site. In contrast, there is little substitution of Se for S in the X3 and X4 sites; especially, Se is only slightly incorporated into the X3 sites throughout the solid solution series. As described previously, Naumov et al. (2007) showed that the S in the S3 site is never dissociated from the two As atoms during photo-induced transformation, although it moves drastically (approximately 1 Å) toward the S4 site from its original position, which suggests that S is more stably incorporated into the X3 site than into the X2 site. Therefore, continuous light exposure of realgar including Se (the so-called “seleno-realgar”) is expected to engender an alteration to pararealgar under the same transformation mechanism as those described by Kyono et al. (2005), Bonazzi et al. (2006), Naumov et al. (2007), and Bonazzi and Bindi (2008). The difference in stability among the four X sites might be related with local bonding structures or localized electronic gap states on S and Se atoms, which are responsible for photo-induced structural changes in amorphous arsenic chalcogenides (e.g., Simyndakin et al. 2005; Golovchak et al. 2007), but further experimental work is necessary to verify this hypothesis.

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