The dual behavior of the $\beta$-As$_4$S$_4$ altered by light

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ABSTRACT

Among the polymorphs of the compound As$_4$S$_4$, realgar ($\alpha$-As$_4$S$_4$) and $\beta$-As$_4$S$_4$ exhibit an interesting phenomenon of light-induced alteration that eventually leads to the transformation to pararealgar and arsenolite through the structural modification of the As$_4$S$_4$ molecule. The mechanism generally invoked to explain the transformation assumes reaction with oxygen, subsequent modification of the molecule through an insertion of a sulfur atom and the eventual production of arsenolite according to the reaction $5\text{As}_4\text{S}_4 + 3\text{O}_2 \rightarrow 4\text{As}_4\text{S}_5 + 2\text{As}_2\text{O}_3$. Early studies showed that the light-induced transition from realgar to pararealgar is reversible through heat and that implies a transition through the $\chi$-phase, even though the presence of arsenolite was not observed. To further assess the action of the oxygen during the process, we carried out experiments of light-induced alteration of $\beta$-As$_4$S$_4$ under ambient air and under isopropyl alcohol. The material was investigated by means of X-ray powder diffraction (XRPD) using quantitative phase analysis (QPA) and the Rietveld method. The further study of the heat-induced transformation of the products showed that $\beta$-As$_4$S$_4$ exhibits a dual behavior: if the light-induced alteration occurs under air, arsenolite plus an amorphous phase is produced and the transformation is not reversible, if the alteration occurs without any contact to air none of such phases is produced and the transformation is reversible. These new experimental evidences suggest that the production of arsenolite is not strictly required for the transformation of the $\beta$-As$_4$S$_4$ into pararealgar and that the current model invoked to explain the mechanism of alteration should be modified to take into account the dual behavior of the $\beta$-As$_4$S$_4$ altered by light.

Keywords: $\beta$-As$_4$S$_4$, light, heat, pararealgar, alacranite, Rietveld

INTRODUCTION

Although interaction of light with minerals forms the foundation of many optical properties, very few mineral species show permanent transformations due to visible radiation. One prominent example is the mineral realgar ($\alpha$-As$_4$S$_4$), and its high-temperature polymorph, $\beta$-As$_4$S$_4$. Both undergo a peculiar process of alteration induced by light. Curiously these materials have also been used as orange pigments by artists through different ages, from ancient Egypt to the Middle Ages and the Renaissance, and this alteration might have implications regarding the study, interpretation, and conservation of antique paintings (Corbeil and Helwig 1995; Trentelman et al. 1996; Clark and Gibbs 1997, 1998; Burgio et al. 2003, 2006). The light-induced alteration causes a change of the beautiful orange color of realgar to the yellow color of pararealgar. This process is highly interesting from a structural point of view. There are four polymorphs of As$_4$S$_4$. Their structure differs in the type of molecules and their packing in the unit cell ($Z = 4$) due to van der Waals forces. Realgar (space group $P_{2_1}/n$) has been described as a regular packing of cage-like molecules (Fig. 1a) where each As atom is covalently bonded to two S and one As atom, and each S atom is bonded to two As atoms (Ito et al. 1952; Street and Munir 1970; Mullen and Nowacki 1972). A different packing of the same molecular unit leads to the $\beta$-phase ($\beta$-As$_4$S$_4$, space group $C2/c$) (Porter and Sheldrick 1972), which is stable up to 252 °C (Roland 1972) and metastable at room temperature. Both polymorphs alter to pararealgar (Bonazzi et al. 1995), as a result of exposure to natural or artificial light (Douglass et al. 1992; Bonazzi et al. 1996). In the molecular unit of As$_4$S$_4$ pararealgar (Fig. 1b), one As atom is covalently bonded to one S and two As atoms, two As atoms are bonded to one As and two S atoms, and each S atom is bonded to two As atoms.

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FIGURE 1. The molecules of realgar and $\beta$-As$_4$S$_4$ (a), and pararealgar and As$_4$S$_4$(II) (b). The arrows point to the bonds to be broken, and the outlined area includes the fragment that is displaced for the molecule of the first two polymorphs to transform to that of pararealgar. The atom labels correspond to those used in the literature.
three S atoms. Each S atom is bonded to two As atoms. This cradle-like molecule can be arranged in two different kinds of packing, that of pararealgar \( (P_2_1/c) \), and the one of a synthetically obtained phase, named \( \text{As}_3\text{S}_4(\text{II}) \), whose space group is \( P2_1/n \) (Kutoglu 1976). The transformation of the molecule of \( \alpha \) and \( \beta \) polymorphs to that of pararealgar implies the breaking of one As-As and one As-S bond. As observed since the study of Douglass et al. (1992), the action of visible light causes an anisotropic increase of the unit-cell volume (up to 2.6% of both the \( \alpha \) and \( \beta \) polymorphs, and during the process of alteration a metastable phase occurs, named \( \chi \)-phase, which is the precursor of pararealgar. Arsenolite \( (\text{As}_2\text{O}_3) \) was reported to form starting from both realgar (Ballirano and Maras 2006) and from \( \beta\text{-As}_3\text{S}_4 \) (Zoppi 1998), and this phenomenon seems to be the result of the breaking of As-As and As-S bonds and the presence of oxygen.

Remarkable work has been done to understand the nature of the transformation and the structural modifications that occur within the different polymorphs (Douglass et al. 1992; Muniz-Miranda et al. 1996; Bonazzi et al. 2006; Bonazzi and Bindi 2008), regarding different species (Bindi et al. 2003; Bonazzi et al. 2003a; Bindi and Bonazzi 2007) and with different conditions of illumination (Kyono 2007; Naumov et al. 2007). Previous experimental work aimed to investigating the role of the oxygen during the process has been carried out by us starting from powdered \( \beta\text{-As}_3\text{S}_4 \) not in contact with air. The alteration proceeded until the complete transformation to pararealgar without any detectable presence of arsenolite. That suggests that the molecule of realgar \( (R\text{-type}) \) can transform to the one of pararealgar \( (P\text{-type}) \) even without the direct contact of the oxygen. An open question on the sudden transformation from \( R \) to \( P \) molecule in the presence of oxygen to form arsenolite is the fate of the released sulfur atoms. This question is still valid in the light of the model proposed by Kyono et al. (2005), based on the hypothesis of Bindi et al. (2003). The authors relate the unit-cell expansion to the substitution of \( \text{As}_3\text{S}_4 \) units by \( \text{As}_2\text{S}_5 \)  

del'I Università degli Studi di Firenze), is an aggregate of large crystals of realgar 

and arsenolite crystallize, while only pararealgar is found as product under anoxic conditions. Is the difference to be only ascribed to the presence of arsenolite?

A different perspective of the problem might arise when considering the reverse transformation from pararealgar to \( \beta\text{-As}_3\text{S}_4 \) and realgar. The modification of the \( \text{As}_3\text{S}_4 \) molecule typical for pararealgar and \( \text{As}_3\text{S}_4(\text{II}) \), to the molecule of the \( \beta\text{-As}_3\text{S}_4 \) and realgar is possible and occurs simply through the action of heat (Douglass et al. 1992). Although only little attention has been given to implications of the reverse transformation, the authors showed that natural pararealgar, sealed in a silica vial, transformed to \( \beta\text{-As}_3\text{S}_4 \) within 5 min at a temperature of 300 °C (in the \( \beta\text{-As}_3\text{S}_4 \) field), while the transformation was slower at a temperature of 220 °C, i.e., in the realgar stability field. At even lower temperatures (195 and 175 °C), the pararealgar transformed first to \( \chi \)-phase, then to \( \beta\text{-As}_3\text{S}_4 \) and eventually to realgar. These results are surprising since \( \beta\text{-As}_3\text{S}_4 \) occurs below the \( \alpha \rightarrow \beta \) transformation temperature. They also show that the \( \chi \)-phase occurs in the reverse transformation from pararealgar to \( \beta\text{-As}_3\text{S}_4 \).

We collected XRPD data from samples of pararealgar obtained by completely altering some \( \beta\text{-As}_3\text{S}_4 \) powder with and without the presence of the air, as well as after the materials have been thermally treated, and the results are noteworthy.

The study of a multistage reverse transformation, from pararealgar to \( \beta\text{-As}_3\text{S}_4 \) and realgar might lead to a better understanding of the light-induced structural modifications of the pararealgar and realgar molecules and of the dynamics of the process. As a result this could bring potential applications in the field of opto-electronics, in the restoration of artwork damaged by the action of the light, as well as in medicine, where the use of realgar is proven to be effective for the treatment of various forms of cancer in vitro and in vivo (Lu et al. 2002; Zhao et al. 2009).

**EXPERIMENTAL METHODS AND RIETVELD REFINEMENTS**

The material used for this study (specimen no. 46768, Museo di Mineralogia dell’Università degli Studi di Firenze), is an aggregate of large crystals of realgar from the locality of Shimen, Hunan Province, China. The mineral is of high purity with minor traces of Sb as confirmed by the formula \( (\text{As}_{0.9997}\text{Sb}_{0.0013})_2\text{-As}_4\text{S}_5 \) based on chemical analyses of samples from this locality (Xiong and Liu 1998). Some fragments of the unaltered crystalline realgar were carefully ground in an agate mortar under acetone; all the operations of manipulation of the sample were carried out in the dark, to avoid alteration. The \( \beta\text{-As}_3\text{S}_4 \) was obtained by placing some powdered realgar in an evacuated silica vial, kept at 290 °C in a horizontal furnace for 4 h, then quenched in water to 0 °C, and ground again. Half of the \( \beta\text{-As}_3\text{S}_4 \) powder was sealed in a transparent glass vial containing pure isopropl alcohol, and the other half was spread on a white porcelain mortar to ensure contact with ambient air. The light-induced alteration of the two samples of \( \beta\text{-As}_3\text{S}_4 \) was obtained by means of an electronic apparatus (Schott KL 1500) equipped with a Philips diffracto halogen lamp and two optical fibers. The complete alteration of the \( \beta\text{-As}_3\text{S}_4 \) to pararealgar was obtained by exposing both the materials for about 300 h to light, while frequently stirring the powder. The altered material was placed in a nitrogen-purged glove box, ground and dried, and finally packed and sealed into 0.5 mm diameter glass capillaries. A total of four samples were prepared: the one labeled A, using the powdered \( \beta\text{-As}_3\text{S}_4 \) altered under air; the one labeled B, using the powdered \( \beta\text{-As}_3\text{S}_4 \) altered in isopropl alcohol; and those labeled C and D were prepared with the same material used for samples A and B, respectively, with the addition of 12 wt% of yttrium-III oxide (analytical grade) used as internal standard to perform quantitative phase analysis (QPA). For all samples, thermal treatment was carried out in a furnace
at a constant temperature of 220 °C for a total of 1, 24, 72, and 264 h, with air quenching the samples after each heating cycle. For samples C and D, XRPD data collections were carried out at each step, and labeled accordingly, adding the suffix 1, 24, 72, and 264. For samples A and B, data collections were carried out only after the last thermal treatment (at 264 h). XRPD data were collected using a Panalytical Xpert-Pro diffractometer (CuKα radiation at 40 KV, 40 mA) equipped with a focusing mirror, a goniometer (PW3050/60) with 2θ geometry, a PIXcel (Medipix2) solid-state detector (de Vries et al. 2007), and a capillary spinner. On the incident beam a Soller slit (0.04 rad) and a divergence slit (1/3°) were mounted, on the diffracted beam an anticascade slit (7.50 mm) and a Soller slit (0.04 rad) were mounted. The setting employed for the data collections used for the structure refinements (samples A and B) was the following: 2θ range of 8–120°, step size of 0.01313°, common counting time (not step time) of 300 s, for a total time of 2:51 h. The setting employed for the data collections used for the QPA (samples C and D) was the following: 2θ range of 10–110°, step size of 0.02626°, common counting time of 118 s, for a total time of 30 min. For assessing the error resulting from QPA, performed with the latter experimental conditions, four samples of pure crystalline realgar were finely grounded, adding 4, 8, 12, and 16 wt% of internal standard, and the powder was sealed in glass capillaries. XRPD data collections were labeled R4, R8, R12, and R16, respectively.

Multiphase Rietveld refinements of the structural parameters were performed with the GSAS software (Larson and Von Dreele 2004), using the graphical user interface EXPGUI (Toby 2001). The following items were modeled by refining the corresponding parameters: background contribution (using a Chebyshev polynomial with a variable number of terms), scale factors, lattice parameters, Lorenzian and Gaussian terms of the pseudo-Voigt peak-shape model, microstrain line broadening parameters (Stephens 1999), atomic positions and isotropic atomic displacement parameters. The starting structural models, for the phases to be refined, have been taken from literature. Damping factors were always applied, especially in the first stages of refinements. QPA was performed applying the Rietveld-RIR method (Guagliieri 2000) and refining the structural parameters of the phases occurring in the samples.

**INTERPRETATION OF XRD PATTERNS AND QPA RESULTS**

The relative error percent as obtained from the QPA refinements performed on samples R4, R8, R12, and R16 are shown in the histogram of Figure 2. It is clear that the lowest error percentage is obtained from the sample R16 but, if compared with the sample R12, the difference is small. An amount of yttrium-III oxide higher or equal to 12% by weight yields diffraction peaks sufficiently resolved to allow an accurate quantification of the phases. We have chosen to add 12 wt% of internal standard for performing the QPA on samples C and D, because this is the smallest amount necessary to minimize the problem of peak overlapping while still yielding an accurate quantification of the As4S4 polymorphs. The use of realgar for this purpose is justified by the fact that all the polymorphs of the As4S4 have, with a good approximation, the same X-ray linear absorption coefficient, and that the realgar used has not been treated, nor obtained synthetically.

**Figure 2.** The relative error percent as obtained from the refinements for the QPA performed on samples R4, R8, R12, and R16.

**Figure 3.** XRPD patterns, shown in the range 10–60 °2θ, as collected from sample C. The main peaks of pararealgar (p), arsenolite (x), alacranite (a) and yttrium-III oxide (y) are labeled.

XRPD patterns collected before and after the various stages of thermal treatment of samples C and D are shown in the Figures 3 and 4, respectively. The data show that, from the alteration of the β-As-S, performed in the presence of air (sample C), pararealgar and arsenolite were obtained, and from the alteration of the same material, carried out under isopropyl alcohol (sample D), only pararealgar was obtained. The treatments performed through the annealing at 220 °C showed very interesting results. From sample C, arsenolite and alacranite crystallized, while from sample D initially an expanded form of β-As-S was identified as the χ-phase, and eventually the β-As-S crystallized. Furthermore, the QPA let us detect a significant amount of amorphous material in sample C after the light-induced alteration, which was not the case in sample D. The weight percent of the phases detected in samples C and D after light-induced alteration and after each stage of the thermal treatment is reported in Table 1, and for the phases of sample C the molar ratio, with respect to two moles of the arsenolite, has been calculated. This is useful for comparing the molar ratios with those of the reaction mentioned in previous work (Bindi et al. 2003; Kyono et al. 2005). The chemical formula of the amorphous phase is expected to be As2S2, as explained further down, and the relative weight of it is 14.82%. For the light-induced alteration stage, the calculated weight percent of the amorphous phase as obtained by the Rietveld-RIR method is very low (0.66%) in sample D and can therefore be considered zero. In fact this value represents the error on the quantification of pararealgar, which in terms of relative error is lower than 2%. The same explanation applies to the partly negative weight percent values reported for the amorphous phase in samples C and D. The results of the experiments are summarized in Figure 5, and it is worth noting that during the light-induced alteration of the β-As-S to pararealgar under isopropyl alcohol, no arsenolite or amorphous phase was detected. Results of Rietveld refinements of patterns from samples A and B with the aim of characterizing alacranite as well as β-As-S formed during the heat-induced transformation of pararealgar are shown in Figures 6 and 7, and Table 2, respectively. For alacranite, which...
was formed during the last stage of the thermal treatment, the fractional atomic coordinates and thermal parameters are reported in Table 3, while the interatomic bond distances and angles are shown in Table 4. The respective values for β-As₄S₄ are reported in Tables 5 and 6. CIFs are available on deposit 1.

**Discussion**

The plan of this work was to study the light-induced alteration of β-As₄S₄ under two different conditions, namely with and without presence of air (i.e., oxygen). The experiment under isopropyl alcohol had the purpose of preventing the contact with oxygen, although this might still occur in a very low concentration in the alcohol, and a catalytic reaction involving the β-As₄S₄ molecules cannot be ruled out. The main result is that the two different conditions of the light-induced alteration led to different results. If exposed to light under air, β-As₄S₄ transformed to pararealgar, arsenolite, and an amorphous phase, while under isopropyl alcohol all of the β-As₄S₄ transformed to pararealgar. The current model proposed for the expansion of the unit-cell of realgar (Bindi et al. 2003; Kyono et al. 2005) and the reaction 5As₄S₄ + 3O₂ → 4As₄S₅ + 2As₂O₃ do not explain the presence of the amorphous phase produced during the transformation of the β-As₄S₄. In the anoxic case (sample D), assuming a catalytic role of sulfur atoms in order to transform the β-As₄S₄ molecules into the ones of pararealgar, arsenolite cannot be formed as a reaction product, and the occurrence of the unit-cell expansion remains unexplained. In the light-induced alteration taking place under air (sample C), it is possible to write a reaction such as the following:

9As₄S₄ + 3O₂ → 7As₄S₄ + 4AsS₂ + 2As₂O₃

where the values of the molar ratios (Table 1) are given by to the formula unit. Thereby, the chemical composition the amorphous phase (AsS₂) is given by the necessity to balance the reaction. Furthermore, the thermal treatment shows that the process of light-induced alteration occurring under air is not reversible by heating the sample, whereas the transformation under exclusion of air seems to be reversible. From the results of the QPA for sample C (Table 1), we find that the amount of arsenolite remains roughly the same from the beginning of the heat-induced alteration through all annealing stages of 1,
24, 72, and 264 h, respectively. Pararealgar and the amorphous phase completely disappear in favor of the crystallization of alacranite during the first heating stage. Its weight percent remains constant throughout the heating process. The following reaction is proposed in accordance with the measured molar ratios of alacranite and arsenolite:

$$7\text{As}_4\text{S}_4 + 4\text{As}_2\text{S}_3 + 2\text{As}_2\text{O}_3 \rightarrow 4\text{As}_8\text{S}_9 + 2\text{As}_2\text{O}_3.$$  

From a structural point of view, alacranite, which was formed from top to bottom: observed, calculated, residual pattern, and reflections positions for alacranite and arsenolite are reported. From top to bottom: observed, calculated, residual pattern, and $\beta$-As$_4$S$_4$ reflections positions are reported.

![Background subtracted diffraction pattern of sample A.](image)

**Figure 6.** Background subtracted diffraction pattern of sample A. From top to bottom: observed, calculated, residual pattern, and reflections positions for alacranite and arsenolite are reported.

![Background subtracted diffraction pattern of sample B.](image)

**Figure 7.** Background subtracted diffraction pattern of sample B. From top to bottom: observed, calculated, residual pattern, and $\beta$-As$_4$S$_4$ reflections positions are reported.

**Table 2.** Residual indices of Rietveld refinements, as defined in GSAS (Larson and Von Dreele 2004) and unit-cell parameters for alacranite (sample A) and $\beta$-As$_4$S$_4$ (sample B)

<table>
<thead>
<tr>
<th></th>
<th>Alacranite</th>
<th>$\beta$-As$_4$S$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_m$ = 2.85%</td>
<td></td>
<td>$\sigma = 9.9342(6)$ Å</td>
</tr>
<tr>
<td>$R_F$ = 2.06%</td>
<td></td>
<td>$b = 9.5566(6)$ Å</td>
</tr>
<tr>
<td>$\chi^2 = 2.76$</td>
<td></td>
<td>$c = 9.1104(5)$ Å</td>
</tr>
<tr>
<td>$R_F(\text{F})$ = 4.89%</td>
<td></td>
<td>$\beta = 102.397(2)^\circ$</td>
</tr>
<tr>
<td>$R_F(\text{R})$ = 2.65%</td>
<td></td>
<td>$V = 844.8(1)$ Å$^3$</td>
</tr>
</tbody>
</table>

**Table 3.** Fractional atomic coordinates and isotropic thermal parameters for alacranite (sample A)

<table>
<thead>
<tr>
<th>Atom</th>
<th>$x/a$</th>
<th>$y/b$</th>
<th>$z/c$</th>
<th>$U_{iso}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As1</td>
<td>0.0186(4)</td>
<td>0.2190(4)</td>
<td>0.9450(4)</td>
<td>0.051(1)</td>
</tr>
<tr>
<td>As2</td>
<td>0.1656(4)</td>
<td>0.4255(5)</td>
<td>0.8627(5)</td>
<td>0.055(2)</td>
</tr>
<tr>
<td>As3</td>
<td>0.4589(4)</td>
<td>0.3154(5)</td>
<td>0.4367(5)</td>
<td>0.086(2)</td>
</tr>
<tr>
<td>As4</td>
<td>0.3712(4)</td>
<td>0.0359(4)</td>
<td>0.1793(6)</td>
<td>0.060(2)</td>
</tr>
<tr>
<td>S1</td>
<td>0</td>
<td>0.0944(14)</td>
<td>3/4</td>
<td>0.018(4)</td>
</tr>
<tr>
<td>S2</td>
<td>0</td>
<td>0.5842(12)</td>
<td>3/4</td>
<td>0.032(4)</td>
</tr>
<tr>
<td>S3</td>
<td>0.1861(6)</td>
<td>0.3162(7)</td>
<td>0.6489(8)</td>
<td>0.015(2)</td>
</tr>
<tr>
<td>S4</td>
<td>0.2837(6)</td>
<td>0.1733(8)</td>
<td>0.3259(9)</td>
<td>0.030(3)</td>
</tr>
<tr>
<td>S5</td>
<td>0/2</td>
<td>0.4385(11)</td>
<td>1/4</td>
<td>0.020(4)</td>
</tr>
<tr>
<td>S6</td>
<td>0.3833(7)</td>
<td>0.1725(8)</td>
<td>0.0023(9)</td>
<td>0.005(3)</td>
</tr>
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</table>

**Table 4.** Intramolecular bond distances (Å) and angles ($^\circ$) for alacranite (sample A)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Angle ($^\circ$)</th>
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<tbody>
<tr>
<td>As1-As1-S1*</td>
<td>2.113(8)</td>
<td>111.5(7)</td>
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<tr>
<td>As1-As2</td>
<td>2.657(6)</td>
<td>111.3(5)</td>
</tr>
<tr>
<td>As2-As2</td>
<td>2.100(8)</td>
<td>112.2(6)</td>
</tr>
<tr>
<td>As2-As3</td>
<td>2.287(8)</td>
<td>114.1(5)</td>
</tr>
<tr>
<td>As2-As4</td>
<td>2.657(6)</td>
<td>115.6(5)</td>
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</table>

**Table 5.** Fractional atomic coordinates and isotropic thermal parameters for $\beta$-As$_4$S$_4$ (sample B)

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<tr>
<th>Atom</th>
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<tr>
<td>As1</td>
<td>0.00032(2)</td>
<td>0.2049(2)</td>
<td>0.0553(2)</td>
<td>0.0049(1)</td>
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<tr>
<td>As2</td>
<td>-0.1579(2)</td>
<td>0.4037(2)</td>
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<tr>
<td>S1</td>
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<td>S2</td>
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<tr>
<td>S3</td>
<td>-0.2026(3)</td>
<td>0.3075(4)</td>
<td>0.3377(5)</td>
<td>0.035(2)</td>
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Intramolecular bond angles

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Angle ($^\circ$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1-As1-S1*</td>
<td>90.5(3)</td>
<td>105.3(3)</td>
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<td>S1-As1-As2</td>
<td>97.8(3)</td>
<td>101.2(3)</td>
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<tr>
<td>S2-As2</td>
<td>96.7(2)</td>
<td>109.0(4)</td>
</tr>
<tr>
<td>S3-As3-As4</td>
<td>94.1(3)</td>
<td>100.1(3)</td>
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<tr>
<td>S4-As4-As5</td>
<td>94.7(3)</td>
<td>100.0(3)</td>
</tr>
<tr>
<td>S5-As5-As6</td>
<td>97.6(3)</td>
<td>100.1(3)</td>
</tr>
<tr>
<td>S6-As6-As7</td>
<td>97.6(3)</td>
<td>100.1(3)</td>
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Intramolecular bond distances

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Angle ($^\circ$)</th>
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<tbody>
<tr>
<td>As1-S1-S3*</td>
<td>90.5(3)</td>
<td>105.3(3)</td>
</tr>
<tr>
<td>As1-As2</td>
<td>97.8(3)</td>
<td>101.2(3)</td>
</tr>
<tr>
<td>S2-As2</td>
<td>96.7(2)</td>
<td>109.0(4)</td>
</tr>
<tr>
<td>S3-As3-As4</td>
<td>94.1(3)</td>
<td>100.1(3)</td>
</tr>
<tr>
<td>S4-As4-As5</td>
<td>94.7(3)</td>
<td>100.0(3)</td>
</tr>
<tr>
<td>S5-As5-As6</td>
<td>97.6(3)</td>
<td>100.1(3)</td>
</tr>
</tbody>
</table>

Note: Symmetry codes: * = x, y, 3/2-z; † = 1-z, y, 3/2-x.

In the As$_4$S$_4$ molecule exhibit a slightly smaller value (S1-As1-S3*) and some slightly higher values (As1-S1-As1*, As2-S2-As2*). Similar variations are also reported for other nonstoichiometric types of alacranites (Bonazzi et al. 2003a, 2006) and can be due to some local disordered distribution of As$_4$S$_4$ and As$_4$S$_5$ molecules. In this case, given the similar topology of the two molecules, the refined atomic coordinates would represent average values of the positions occupied by analogous atoms belonging to the As$_4$S$_4$ and As$_4$S$_5$ molecules, respectively.
This could also explain the slightly higher isotropic thermal parameters shown by some atoms of alacranite. Some remarks should be made about the nature of the amorphous phase formed during the alteration. Its composition is deduced as As$_2$S$_3$ from the need to balance the reaction. Whether it is a single amorphous phase or a mixture of two or more amorphous phases cannot be decided based on the present experiment, however the existence and the nature of a chalcogenide glass of chemical formula As$_{0.33}$S$_{0.67}$ has been well documented (Wagner et al. 2003; Krbal et al. 2007; Hasapis et al. 2010; Kaban et al. 2011). This amorphous phase is the starting material for the Ag$_x$(As$_{0.33}$S$_{0.67}$)$_{100-x}$ bulk glasses (0 ≤ x ≤ 28) studied for the interesting property of persistent photo-generated voltage for which it is used in solid-state photochemical cells. The authors point out that the network of the chalcogenide glass As$_{0.33}$S$_{0.67}$ is based on chains of corner-sharing As$_9$S$_7$ pyramidal units, the same building blocks found in many arsenic sulfides.

The structural refinement of the β-As$_3$S$_4$ crystallized after the thermal treatments (sample B) shows that this phase (Tables 2, 5, and 6) corresponds to the one reported by Porter and Sheldrick (1972). Its unit-cell volume has a slightly larger value (812.0 vs. 806.7 Å$^3$), with all axes a, b, and c, as well as the monoclinic angle β being larger. Small differences in the interatomic bond distances for the As$_3$-S$_2$, As$_3$-S$_3$, and As$_1$-As$_2$ are also noticeable. The results of the QPA for sample D shows that during the thermal treatment pararealgar transforms completely into the β-As$_3$S$_4$ and no amorphous phase occurs during the process. This phenomenon is even more difficult to be explained with the model proposed for realgar by Kyono et al. (2005) and, more generally, for arsenic sulfides by Bonazzi et al. (2006), since it should be presumed that a sulfur atom driven by heat should follow an opposite pattern than the one depicted in Figure 6 of Kyono et al. (2005). These authors explain the expansion of the unit-cell of realgar and β-As$_3$S$_4$, and its alteration to pararealgar by the increasing amount of As$_2$S$_3$ molecules forming in the structure, but that should be proportional to the amount of arsenolite produced, according to the before mentioned reaction. Without the formation of arsenolite, and taking into account the reversibility of the alteration of β-As$_3$S$_4$, as observed for sample D, the model is not suitable to explaining the process.

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