**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 As₄SₓSe₄ (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 As4 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 crystallochemical 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 As₄Sₓ₋ₓSeₓ (0 ≤ x ≤ 4) solid-solution series.