

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

ATSUSHI KYONO*

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

ABSTRACT

Molecular crystals of an As₄S_{4-x}Se_x (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