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Thermal behavior of realgar As_4S_4, and of arsenolite As_2O_3 and non-stoichiometric As_8S_{8+x} crystals produced from As_4S_4 melt recrystallization

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ABSTRACT

An in situ high-temperature X-ray powder diffraction study of the thermal behavior of realgar (α-As_4S_4) has been carried out. Data, measured in transmission geometry on a non-hermetically sealed capillary, indicate that the realgar → β-As_4S_4 phase transition starts at 558 K and is completed at 573 K due to kinetics. Melting starts at 578 K and is completed at 588 K. Thermal expansion of realgar is significant and fairly isotropic. In fact, the *a*- and *b*-parameters expand almost at the same rate, whereas the *c*-parameter is slightly softer against heating. Moreover, the β-angle contracts as temperature is raised. The geometry of the As_4S_4 molecule is largely independent from heating. The lengthening of a few As-S and As-As contacts above or near the sum of the As,S van der Waals radii represents the driving force of the phase transition. In addition, the thermal behavior of arsenolite As_2O_3 and non-stoichiometric As_8S_{8+x} crystals produced from As_4S_4 melt recrystallization has been investigated. Two members located along the β-As_4S_4-alacranite (As_8S_9) series joint were identified at RT: a term close to the β-As_4S_4 end-member (As_8S_{8+x}: x = ca. 0.1) and one term of approximate $As_8S_{8.3}$ composition. The thermal expansion of β-As_4S_4 is significantly anisotropic following the $\alpha_b > \alpha_a > \alpha_c$ relationship. This is clearly the result of the different packing scheme of the As_4S_4 cages in β-As_4S_4 with respect to realgar. The dependence of cell parameters and volume of $As_8S_{8.3}$ is more complicated. In fact, a strong discontinuity on the dependence of cell parameters and volume is observed in the 403–443 K thermal range, i.e., that at which $As_8S_{8.3}$ converts partly to realgar. A significant volume expansion is observed as a result of a change of composition to $As_8S_{8.7}$.

Keywords: Sulfides, realgar, alacranite, β-As_4S_4, arsenolite, high-temperature X-ray powder diffraction, Rietveld method