

Effect of Selenium Incorporation on Crystal Structure and Crystallization Properties of Realgar (As_4S_4)

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Sulfide minerals can readily form a complete solid solution between sulfur and selenium since there is great similarity in the electronic polarizability values between S and Se. Examples are numerous: PbS (galena), ZnS (sphalerite), CdS (greenockite), As_2S_3 (orpiment), Sb_2S_3 (stibnite), Bi_2S_3 (bismuthinite) and so a variety of sulfide minerals have been described. Realgar (As_4S_4) occurs as a minor constituent in hydrothermal sulfides veins with orpiment and other As minerals and as a sublimate in fumaroles. Its crystal structure is composed of separate cage-like As_4S_4 molecules. A large amount of Se is incorporated into orpiment or laphamite which usually occur in association with realgar, but it can hardly be included in realgar as a main component. We cannot explain the reason why realgar can occur as an almost pure mineral in Se-rich environment because very little has been done to study the effects of the substitution of Se for S in realgar. This work investigates the effects of the Se incorporation on the crystal structure and crystallization properties.

Realgar single crystals and those substituted with Se for S have been synthesized under hydrothermal conditions using 25 wt% HCl as a solvent. Orange-red euhedral prismatic crystals having up to 3.0 mm in length could be successfully obtained from the synthesis experiments. These crystal structures and chemical compositions were determined using single-crystal X-ray diffraction method and electron probe microanalysis, respectively. The realgar crystals proved to crystallize in a monoclinic C-centered lattice which corresponds to the high-temperature phase, whereas those slightly containing Se changed to a monoclinic primitive lattice which can be observed as the low-temperature phase. This is because the As_4S_4 molecules partly substituting Se for S will greatly raise the molecular weight and hence this will reduce the average molecular velocity. Since the slowly moving molecules can no longer maintain the crystal structure of the high-temperature phase, Se bearing realgar would be transformed into that of the low-temperature phase. Se is accommodated in the realgar low-temperature structure with a preference for the S(2) site, followed by the S(1) site. With increasing Se concentration in realgar, the As-S intramolecular bondings expand significantly, on the contrary, the van der Waals interaction between the As_4S_4 molecules are forced to keep the intermolecular distances unchanged. Taking into consideration the deformed As_4S_4 molecules and the crystal structure, it is actually impossible to form a complete solid solution between realgar As_4S_4 and seleno-realgar As_4Se_4 .