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The dual behavior of the β-As_4S_4 altered by light

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Abstract

Among the polymorphs of the compound As_4S_4, realgar and β-As_4S_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_4S_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 $5As_4S_4 + 3O_2 \rightarrow 4As_4S_5 + 2As_2O_3$. Early studies showed that the light-induced transition from realgar to pararealgar is reversible through heat and that implies a transition through the χ-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 β-As_4S_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 β-As_4S_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 β-As_4S_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 β-As_4S_4 altered by light.

Keywords: β-As_4S_4, light, heat, pararealgar, alacranite, Rietveld