The dual behavior of the $\beta$-As$_2$S$_3$ altered by light

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ABSTRACT

Among the polymorphs of the compound As$_2$S$_3$, realgar and $\beta$-As$_2$S$_3$ 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$_2$S$_3$ 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 $5\text{As}_2\text{S}_3 + 3\text{O}_2 \rightarrow 4\text{As}_2\text{S}_5 + 2\text{As}_2\text{O}_3$. Early studies showed that the light-induced transition from realgar to pararealgar is reversible through heat and that implies a transition through the $\chi$-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 $\beta$-As$_2$S$_3$ 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 $\beta$-As$_2$S$_3$ 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 $\beta$-As$_2$S$_3$ 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 $\beta$-As$_2$S$_3$ altered by light.

Keywords: $\beta$-As$_2$S$_3$, light, heat, pararealgar, alacranite, Rietveld

INTRODUCTION

Although interaction of light with minerals forms the foundation of many optical properties, very few mineral species show permanent transformations due to visible radiation. One prominent example is the mineral realgar ($\alpha$-As$_2$S$_3$), and its high-temperature polymorph, $\beta$-As$_2$S$_3$. Both undergo a peculiar process of alteration induced by light. Curiously these materials have also been used as orange pigments by artists through different ages, from ancient Egypt to the Middle Ages and the Renaissance, and this alteration might have implications regarding the study, interpretation, and conservation of antique paintings (Corbeil and Helwig 1995; Trentelman et al. 1996; Clark and Gibbs 1997, 1998; Burgio et al. 2003, 2006). The light-induced alteration causes a change of the beautiful orange color of realgar to the yellow color of pararealgar. This process is highly interesting from a structural point of view. There are four polymorphs of As$_2$S$_3$. Their structure differs in the type of molecules and their packing in the unit cell ($Z = 4$) due to van der Waals forces. Realgar (space group $P2_1/n$) has been described as a regular packing of cage-like molecules (Fig. 1a) in which each As atom is covalently bonded to two S and one As atoms, and each S atom is bonded to two As atoms (Ito et al. 1952; Street and Munir 1970; Mullen and Nowacki 1972). A different packing of the same molecular unit leads to the $\beta$-phase ($\beta$-As$_2$S$_3$, space group $C2/c$) (Porter and Sheldrick 1972), which is stable up to 252 °C (Roland 1972) and metastable at room temperature. Both polymorphs alter to pararealgar (Bonazzi et al. 1995), as a result of exposure to natural or artificial light (Douglass et al. 1992; Bonazzi et al. 1996). In the molecular unit of As$_2$S$_3$ pararealgar (Fig. 1b), one As atom is covalently bonded to one S and two As atoms, two As atoms are bonded to one As and two S atoms, while one As atom is bonded to

**Figure 1.** The molecules of realgar and $\beta$-As$_2$S$_3$ (a), and pararealgar and As$_2$S$_3$(II) (b). The arrows point to the bonds to be broken, and the outlined area includes the fragment that is displaced for the molecule of the first two polymorphs to transform to that of pararealgar. The atom labels correspond to those used in the literature.