Thermal behavior of realgar $\text{As}_4\text{S}_4$, and of arsenolite $\text{As}_2\text{O}_3$ and non-stoichiometric $\text{As}_8\text{S}_{8+x}$ crystals produced from $\text{As}_4\text{S}_4$ melt recrystallization

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**ABSTRACT**

An in situ high-temperature X-ray powder diffraction study of the thermal behavior of realgar ($\alpha$-$\text{As}_4\text{S}_4$) has been carried out. Data, measured in transmission geometry on a non-hermetically sealed capillary, indicate that the realgar $\rightarrow$ $\beta$-$\text{As}_4\text{S}_4$ 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 $\beta$-angle contracts as temperature is raised. The geometry of the $\text{As}_4\text{S}_4$ 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 $\text{As}_2\text{O}_3$ and non-stoichiometric $\text{As}_8\text{S}_{8+x}$, crystals produced from $\text{As}_4\text{S}_4$ melt recrystallization has been investigated. Two members located along the $\beta$-$\text{As}_4\text{S}_4$-alacranite ($\text{As}_8\text{S}_9$) series joint were identified at RT: a term close to the $\beta$-$\text{As}_4\text{S}_4$ end-member ($\text{As}_8\text{S}_{9+x}$: $x = ca. 0.1$) and one term of approximate $\text{As}_8\text{S}_{8.3}$ composition. The thermal expansion of $\beta$-$\text{As}_4\text{S}_4$ is significantly anisotropic following the $a_\beta > c_\alpha > b_\alpha$ relationship. This is clearly the result of the different packing scheme of the $\text{As}_8\text{S}_9$ cages in $\beta$-$\text{As}_4\text{S}_4$ with respect to realgar. The dependence of cell parameters and volume of $\text{As}_8\text{S}_{8.3}$ 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 $\text{As}_8\text{S}_{8.3}$ converts partly to realgar. A significant volume expansion is observed as a result of a change of composition to $\text{As}_8\text{S}_{8.7}$.

**Keywords:** Sulfides, realgar, alacranite, $\beta$-$\text{As}_4\text{S}_4$, arsenolite, high-temperature X-ray powder diffraction, Rietveld method

**INTRODUCTION**

Realgar is one of the four naturally occurring $\text{As}_4\text{S}_4$ polymorphs: $\alpha$-$\text{As}_4\text{S}_4$ (realgar), $\beta$-$\text{As}_4\text{S}_4$, $\text{As}_8\text{S}_9$ (II), and pararealgar. A further high-pressure modification has been recently reported (Tuktabiev et al. 2009). The structure of realgar, first described by Ito et al. (1952), is characterized by the presence of covalently bonded $\text{As}_4\text{S}_4$ cages possessing an almost perfect point group $42m$ symmetry. Such cages are arranged in a zigzag way resulting in a layered structure with planes stacked along [010]. A description of the relationships existing among the various $\text{As}_4\text{S}_4$ polymorphs may be found in Ballirano and Maras (2006).

The most relevant and studied property of realgar is its light-induced alteration in ambient air (Clark 1970; Roberts et al. 1980; Douglass et al. 1992; Bonazzi et al. 1996; Kyono et al. 2005; Ballirano and Maras 2006; Bonazzi and Bindi 2008). Recent work agrees in identifying pararealgar and arsenolite ($\text{As}_2\text{O}_3$) as the final products of the process. The transformation proceeds via an intermediate term located along the $\beta$-$\text{As}_4\text{S}_4$-alacranite ($\text{As}_8\text{S}_9$) series joint (Ballirano and Maras 2006) due to the occurrence of the reaction $5\text{As}_4\text{S}_4 + 3\text{O}_2 \rightarrow 4\text{As}_4\text{S}_4 + 2\text{As}_2\text{O}_3$ proposed by Bindi et al. (2003). On the contrary, less effort has been devoted to the analysis of the thermal behavior of realgar. In fact, the only available information is that realgar converts to $\beta$-$\text{As}_4\text{S}_4$ over a composition-dependent temperature range of 512 to 535 K (Hall 1966; Roland 1972; Blachnik et al. 1980) and that melting of $\beta$-$\text{As}_4\text{S}_4$ occurs at 579(3) K (Roland 1966). However, no data about its thermal expansion, or its structure behavior, as a function of temperature are available in literature.

The present work aims to fill such a gap from laboratory parallel-beam X-ray powder diffraction data. Data have been collected in situ, in real-time and analyzed from room temperature (RT) up to melting. Moreover, the thermal behavior of the crystallization products of the corresponding quenched melt has been investigated.

**EXPERIMENTAL METHODS**

A fragment of a large crystal of realgar from Monte Sughereto, Latium, Italy, from the same batch of those previously investigated by Ballirano and Maras (2006), was crushed under ethanol in an agate mortar. The powder was loaded and packed in a 0.5 mm diameter quartz-crucible capillary that was non-hermetically sealed. The capillary/tube assembly was subsequently mounted on a high-purity alumina ceramic (Resbond 989). The capillary/tube assembly was subsequently aligned onto a standard goniometer head and diffraction data were collected on a parallel-beam Bruker AXS D8 Advance, operating in transmission in $\theta-\theta$ geometry, using CuKα radiation. The instrument is fitted with a PSD VANTEC-1 detector set to a $6^\circ$2θ aperture and with a prototype of capillary heating chamber (Ballirano and Melis 2007, 2009). Insertion of the capillary into the chamber prevented the powder from exposure to light.

A preliminary RT X-ray powder diffraction pattern confirmed the absence of alteration products of realgar as $\beta$-$\text{As}_4\text{S}_4$, pararealgar, and arsenolite. Non-ambient data were collected in the 10–140°2θ angular range, step-size of 0.02°2θ, with 3 s...