

## Light-induced molecular change in $\text{HgI}_2 \cdot \text{As}_4\text{S}_4$ : Evidence by single-crystal X-ray diffraction and Raman spectroscopy

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### ABSTRACT

To investigate the behavior of the  $\text{As}_4\text{S}_4$  molecule within a crystal-chemical environment differing from realgar,  $\alpha\text{-As}_4\text{S}_4$ , and its high-temperature polymorph,  $\beta\text{-As}_4\text{S}_4$ , the effects of the light exposure on the structure of the  $\text{HgI}_2 \cdot \text{As}_4\text{S}_4$  adduct have been studied. The structure of this compound consists of a packing of nearly linear  $\text{HgI}_2$  molecules and  $\text{As}_4\text{S}_4$  cage-molecules. A crystal [ $V = 1295.9(4) \text{ \AA}^3$ ] was exposed to filtered polychromatic light (550 nm long-wavelength pass filter). A marked increase of the unit-cell volume as a function of the exposure time was observed up to  $V = 1338.9 \text{ \AA}^3$  at 3060 min of exposure. Structure refinements indicated that the increase of the unit-cell volume is to ascribe to the formation of an increasing fraction (up to 59%) of pararealgar replacing the realgar-type molecule. After this point, further light-exposure did not cause any further increase of the lattice parameters. On the contrary, a slow, continuous decrease of the unit-cell volume down to  $1292.9 \text{ \AA}^3$  occurred by keeping the crystal in the dark (39 days). The “reverse” evolution of the unit-cell parameters in the dark almost overlap that observed during the light-induced process and the structural model obtained after the “dark stage” was found to be identical to that of the unaltered crystal, although the diffraction quality was lower and powder-like diffraction rings were observed together with single-crystal reflections. Apart from few peaks belonging to the original unaltered  $\text{HgI}_2 \cdot \text{As}_4\text{S}_4$  adduct, most of the collected peaks can be assigned to  $\beta\text{-As}_4\text{S}_4$ . This feature could indicate decomposition into micro-crystalline  $\beta\text{-As}_4\text{S}_4$  and  $\text{HgI}_2$ ; no diffraction effect ascribable to any  $\text{HgI}_2$  phase, however, was observed. Micro-Raman spectra were collected on crystals exposed to the above-mentioned wavelength light for increasing times (up to 3000 min). The peak at  $274(\pm 1) \text{ cm}^{-1}$  whose intensity increases as a function of the exposure time confirms the transition from a realgar- to a pararealgar-type molecule in the  $\text{HgI}_2 \cdot \text{As}_4\text{S}_4$  adduct.

**Keywords:** Crystal structure,  $\text{HgI}_2 \cdot \text{As}_4\text{S}_4$ , Raman spectroscopy, arsenic sulfides, light-induced alteration, realgar, pararealgar