

Light-induced changes in molecular arsenic sulfides: State of the art and new evidence by single-crystal X-ray diffraction

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ABSTRACT

Light-induced structural changes in single crystals belonging to the β -As₄S₄-As₈S₉ series and in a crystal of synthetic β -As₄S₃ were monitored step by step by determining the unit-cell dimensions. A marked increase of unit-cell volume as a function of exposure time was observed for all the crystals belonging to the β -As₄S₄-As₈S₉ series except for stoichiometric alacranite (As₈S₉). No significant change upon long exposures to light was observed for the synthetic β -As₄S₃ crystal. Crystal structure refinements were carried out for crystals with different composition at selected steps of the light-induced process. The structural results clearly showed that the percentage of the As₄S₅ molecule in the structure increases when a crystal is exposed to light. Therefore, the increment of the unit-cell volume induced by light exposure appears to be related to a random replacement of As₄S₅ for As₄S₄ in the structure according to the reaction $5\text{As}_4\text{S}_4 + 3\text{O}_2 \rightarrow 4\text{As}_4\text{S}_5 + 2\text{As}_2\text{O}_3$. The results obtained in the present study combined with a critical review of data previously published indicate that the As₄S₄ molecule is able to incorporate sulfur to convert to As₄S₅ upon exposure to light, whereas either As₄S₃ or As₄S₅ molecules do not undergo any modification. It appears that the extent of sulfur incorporation is strictly controlled by the type of molecular packing as well as by the kind of molecule.

A final, complete conversion to pararealgar was observed only for pure β -As₄S₄, whereas non-stoichiometric As₈S_{9-x} crystals initially containing variable amounts of β -As₄S₄ microdomains convert only partially to pararealgar upon light exposure.

Keywords: XRD data, arsenic sulfides, crystal structure, light-induced alteration, alacranite, β -As₄S₄