Light-Induced Degradation Dynamics in Realgar (As_4S_4)

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Light-induced degradation in realgar (As_4S_4) has been studied by means of four-circle XRD and XPS. Because of the alteration of realgar exposed to light, the *a* lattice parameter and *c* sinβ value increase linearly, which leads to a continuous increase of the unit cell volume. Nevertheless, no correlation exists between the continuous increase of the unit cell volume and the bond distance variations in As_4S_4 molecules. The most pronounced change was observed in the distance between centroids in As_4S_4 cage. The spread of As_4S_4 intermolecular distances increases continuously from 5.642 Å to 5.665 Å, which directly affects the unit cell volume expansion of realgar. In addition, the O1s peak increases rapidly after light exposure. The result substantiates the reaction proposed by Bindi et al. [1]. That is, realgar is transformed into pararealgar if oxygen exists and produces As_4S_5 molecule. The additional S atom at As_4S_4 molecule contributes to anisotropic expansion for the **a** and **c** axes because the direction for the additional S atom points toward [4-14] in the unit cell. Furthermore, an S atom in the As_4S_5 molecule is released from one of equivalent As-S-As linkages in As_4S_5; it turns itself into the As_4S_4 molecular of pararealgar. The free S atom is re-attached to another As_4S_4 (realgar type) molecule, and reproduces an As_4S_5 molecule. The reproduced As_4S_5 molecule turns itself into the As_4S_4 molecular of pararealgar again. This cycle that realgar is indirectly transformed into pararealgar via As_4S_5 molecule is repeated during light exposure.

[1] Bindi L., Popova V., Bonazzi P., *Can. Mineral.,* 2003, **41**, 1463.

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