Radiation decay of $(ZnI_2)_3(tpt)_2$ crystal sponge

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Ever since their first description in 2013 [1] crystal sponges have attracted considerable attention, for their ability to provide structural information on hard to crystallize or non-crystalline compounds [2]. However, their analysis proved to be tricky, with infused compounds highly disordered in the structure channels in overlapping disorder with solvent. Since the solution of highly disordered systems requires reliable high-resolution data, and considering large unit cell of crystal sponges, the use of Mo-*Kα* radiation was discouraged in favour of Cu-*Kα* radiation [3]. During our studies of crystal sponge infusion procedure, we have observed gradual darkening of studied crystals combined with gradual disappearance of strong diffractions in measured frames. We have decided to evaluate the possible radiation decay of studied $(ZnI_2)_3(tpt)_2$ crystal sponge, by measuring the series of identical experiments with the same crystal. We have chosen series of five experiments with 12 hours each, resulting in overall irradiation time of 60 hours. The crystal darkening was observed during the measurements, resulting in a black crystal, with apparent loss of strong diffraction spots in measured frames, see Fig. 1a. The data we obtained have shown significant loss of diffraction reliability with $I/\sigma(I)$ decreasing from 3.62 to 1.67 in 0.84-0.81 Å shell and from 6.09 to 3.34 in 0.97-0.92 Å shell. The R_{int} increased in respective shells from 0.166 to 0.335 and from 0.099 to 0.158. The decrease of data quality was also apparent in the structure model, with R_{all} increasing from 8.36 % to 10.56 %. Average U_{eq} increased from 0.071 to 0.099 considering only the framework atoms.

We decided to evaluate the radiation decay using the Mo-*Kα* as well, since the radiation of lower wavelength should be less absorbed by the crystal sponge. As previously stated, the use of Mo-*Kα* is discouraged for possibility of diffraction spot overlaps and presence of low and high angle diffraction spots in one frame, disallowing the longer irradiation times for high angle diffractions. However, both issues are counteracted by increasing the detector distance from the sample. Increasing the detector distance from 53 mm to 140 mm allows an experimental strategy like Cu-*Kα* experiments, with varying irradiation times without detector overflows. During the data collection following the same procedure, no significant crystal darkening or loss of strong diffraction in measured frames was observed, see Fig 1b. Although some loss of diffraction reliability was observed, with $I/\sigma(I)$ decreasing from 4.75 to 4.36 in 0.85-0.82 Å shell and 8.30 to 7.65 in 1.00-0.94 Å shell, it was less pronounced. Only a minor increase of R_{int} in respective shells was observed, with 0.110 increasing to 0.113 and 0.063 to 0.069. The structure model behaves accordingly with R_{all} increasing from 10.48 to 10.97 and average U_{eq} increasing from 0.034 to 0.035.

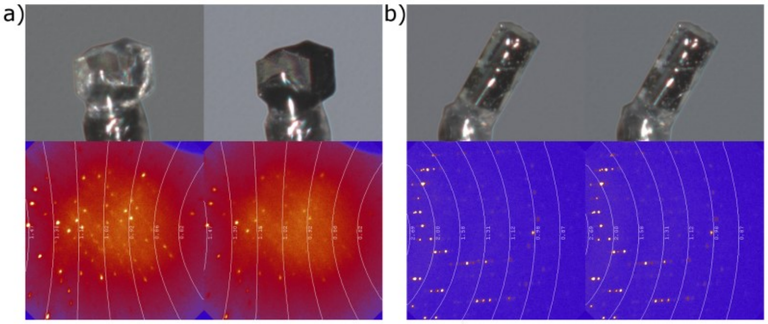

Figure 1. Crystal image and selected frame before and after 60 hours of irradiation using a) Cu-*Kα* radiation, b) Mo-*Kα* radiation.

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