MS15 Mineralogical and inorganic crystallography

MS15-02

Beam-sensitive nano-crystals: why only lowest doses yield the correct structures

H. Klein [1], E. Yörük [1], S. Kodjikian [1]

[1]*Institut Néel, Université Grenoble Alpes and CNRS - Grenoble (France)*

Abstract

There is a wealth of materials that are beam sensitive and only exist in nanometric crystals, because the growth of bigger crystals is either impossible or so complicated that it is not reasonable to spend enough time and resources to grow bigger crystals before knowing their potential for research or applications. In these cases, characterization methods need to be optimized to get the most information out of these particles before the radiation damages them to a point where their structure is altered.

Both, the small size and beam sensitivity, call for electron diffraction as a privileged investigation tool. The strong interaction of electrons (as compared to X-rays) with matter allows single crystal diffraction experiments on nanometre-sized crystals and for the same amount of beam damage, electron diffraction yields more information than X-rays [1]. These inherent advantages of electron diffraction are optimized in the recently developed low-dose electron diffraction tomography (LD-EDT) [2].

Here we present two examples of beam sensitive nanometric crystals: the notoriously beam sensitive metal organic framework Mn-formiate $[Mn(HCOO)_2(H_2O)_2]_\infty$ [3] and the mineral bulachite $[Al_6(AsO_4)_3(OH)_9(H_2O)_4]\cdot 2H_2O$ [4]. In both cases, even small electron doses of a few $e^-/Å^2$ are enough to damage the structure. Comparing the diffraction patterns before and after an irradiation of 3.9 $e^-/Å^2$ of Mn-formiate shows that the high resolution reflections have disappeared (Figure 1).

A much smaller total dose had to be chosen for the structure solution and refinement. We therefore recorded a dataset of 60 frames corresponding to a total dose of 0.15 $e^-/Å^2$. The obtained data quality is high, allowing not only the solution of the structure, but also its refinement taking into account the dynamical diffraction effects (Figure 2).

Likewise, on bulachite the electron dose had to be drastically reduced in order not to destroy the structure and conserve the free water molecules. We acquired a LD-EDT data set containing 105 frames with a total dose of 3 e^- /Å2. The obtained structure solution contained all non-hydrogen atom positions including the free water molecules. The charge valence sums calculated from the model allowed distinguishing the O^{2-}, OH^- and H_2O. A dynamical refinement improved the accuracy of the atom positions with an average distance to the XRD refined positions of 0.1 Å for bonded oxygen (Figure 2).

In this contribution we show that beam sensitive crystals need the extremely low doses that can be obtained by LD-EDT to obtain the correct structures of complex crystals.

References

[1] Henderson, R., Q. Rev. Biophys. 1995, 28, 171–193.

[2] Kodjikian, S.; Klein, H., Ultramicroscopy 2019, 200, 12–19, https://doi.org/10.1016/j.ultramic.2019.02.010.

[3] Poulsen, R.D.; Jørgensen, M.R.V.; Overgaard, J.; Larsen, F.K.; Morgenroth, W.; Graber, T.; Chen, Y.-S.; Iversen, B.B., Chem. Eur. J. 2007, 13, 9775–9790

[4] Grey, I.E.; Yoruk, E.; Kodjikian, S.; Klein, H.; Bougerol, C.; Brand, H.E.A.; Bordet, P.; Mumme, W.G.; Favreau, G.; Mills, S.J., Mineral. Mag. 2020, 84, 608–615, https://doi.org/10.1180/mgm.2020.52.

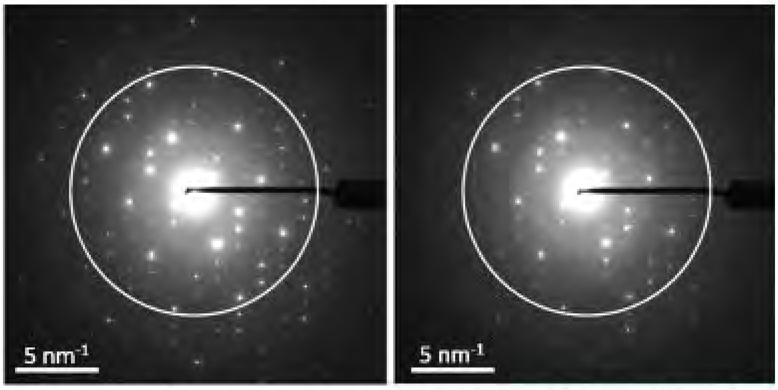

***Figure 1**: diffraction patterns of the pristine Mn-formiate (left) and in the same orientation, but after an irradiation dose of 3.9 e-/Å² (right). The circle represents a resolution of 1 Å.*

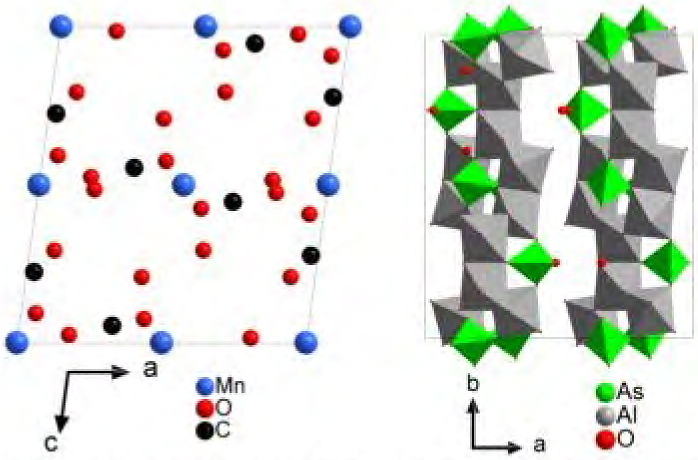

Figure 2 : projections of the dynamically refined structures of Mn-formiate (left) and bulachite (right)