Metal-cyanide frameworks under pressure and radiation

H. L. B. Boström[1,2]

1 Department of Chemistry, Stockholm University, Stockholm, Sweden, 2 Wallenberg Initiative Materials Science for Sustainability, Department of Chemistry, Stockholm University, Stockholm, Sweden

hanna.bostrom@su.se

Studying crystal structures in response to external stimuli is always fascinating, and relatively easily implemented by powder diffraction. A particularly interesting stimulus is pressure, which can be varied to a larger extent than temperature and often causes large changes to the structures of materials [1]. We have studied a number of metal-cyanide frameworks known as Prussian blue analogues under pressure with the aim of exploring their phase space and compressibility behaviour. PBAs are interesting model systems for pressure studies, since the stoichiometry (in addition to the composition) can be varied from dense $A_2MM'(CN)_6$ to porous $M[M'(CN)_6]_{2/3}$. Amongst other things, our combined X-ray and neutron investigation finds that hydration and porosity (unsurprisingly) influence the bulk modulus, Jahn-Teller distortions facilitate pressure-induced amorphisation, and polar phases can be accessed at pressures below 1 GPa [2,3].

A considerably more underexplored stimulus is radiation. During our beamtimes, a range of X-ray-induced responses in metal−cyanide frameworks have become evident, including phase transition suppression [4], X-ray-induced spin transitions [5], and lattice contraction [6]. Motivated by this, we studied the X-ray sensitivity of $M[Co(CN)_6]_{2/3}\cdot n H_2O$ (M = Mn, Fe, Co, Cu, Zn) at I11, Diamond Light Source. This series allows a systematic investigation of both composition and hydration, and is known for its large negative thermal expansion [7] and porosity [8]. We observe large radiation-induced strains—both expansion and contraction—which generally shift to more negative values upon heating. Dehydration appears to give more negative X-ray expansivity. The X-ray-induced contraction contrasts with the cell expansion that is typically taken as a sign of beam damage in macromolecular crystallography [9]. Our investigation highlights the importance of considering radiation damage even in inorganic materials, which is becoming increasingly important as the synchrotrons gets brighter.

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