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Electron Diffraction Tomography as a tool for unraveling pseudosymmetries and intergrown phases at the nanoscale: charoite and Na_2O-Al_2O_3-WO_3

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Many natural and synthetic materials appear only as nanocrystalline polyphasic mixtures or intergrown assembles. Their structure determination is often problematic to access through X-ray powder diffraction (XRPD). Peak overlap is the main problem, especially when materials are characterized by long cell parameters or pseudo-symmetries, and when XRPD peaks are weak and broadened due to the nanometric size of the crystals.
High resolution TEM imaging can directly visualize structural features with atomic resolution, but demands high electron dose and may cause severe beam damage on the material. In contrast electron diffraction needs only a fraction of this electron dose and provides structural data with even higher resolution, but is often biased by dynamical effects and low amount of sampled reflections. Automated electron Diffraction Tomography (ADT) is a recently developed approach for electron diffraction acquisition and analysis [1] able to reduce dynamical effects and increase the number of observed reflections. The idea is to sample the full reciprocal space inside the tilt range of the microscope goniometer in steady steps of 1° avoiding in-zone patterns. Using dedicated software routines [2] the 3D reciprocal space can be reconstructed and investigated. Reflection intensities collected by coupling ADT and Precession Electron Diffraction (PED) [3] proved to be of high quality and can be used for ab-initio structure solution by direct methods without any correction for dynamical effects.
Charoite, ideally $(K,Sr,Ba,Mn)_{15-16}(Ca,Na)_{32}[(Si_{70}(O,OH)_{180})](OH,F)_{4.0}$•$nH_2O$, is a rare mineral from the Murun massif, Russia. Charoite resisted cell determination and structure solution attempts by X-ray for more than fifty years. Indeed we have recently found that charoite forms different polytypes, usually occurring as intimately intergrown inside nanocrystalline fibers. Finally we were able to isolate two ordered charoite polytypes and achieve for both ab-initio structure solution on the basis of ADT data [4,5]. The structural relation between the two polytypes could then be described in terms of order-disorder sequences.
MO_2-$Al2O_3$-WO_3 (M = Li, Na, K) are a class of materials used as media for tunable solid state laser hosts [6]. The M:Al:W ratio can be tuned by using different synthetic routes at different temperatures. $NaAl(WO_4)_2$ is a particularly difficult material to be characterized as it can be produced only in nanocrystalline polyphasic mixtures. ADT data collection from a single nanocrystal of $NaAl(WO_4)_2$ revealed that this phase actually crystallizes with a metrically hexagonal cell, but extinctions and intensity distribution point towards the monoclinic system. Finally the structure was solved ab-initio in spacegroup C2/c, confirming a previous model proposed on the basis of the isotypic $NaFe(MoO_4)_2$ structure [7].

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