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Crystallography at the order-disorder borderline: characterization of nanodomains by electron diffraction and imaging

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Properties of functional nanomaterials strongly depend on their atomic structures and the more or less ordered arrangement of vacancies and defects. Yet, structure characterization by X-ray powder diffraction (XRPD) often suffers from systematic and random peak overlap. Difficulties are drastically enhanced when materials are modulated, with strong discrepancies between sub-cell and satellite reflection intensities, and/or consist of multiple structurally related polytypes. In the last years, electron diffraction tomography (EDT) emerged as an effective method for addressing the atomic structure of natural and synthetic phases available only as sub-micrometric crystals [1]. This method allows collecting 3D diffraction data from coherent regions of few nanometers, also in materials that may just look disordered for standard X-ray diffraction experiments. Anyway, EDT alone may fall short in the characterization of phases where modulations, twinning or stacking faults play a key role and cannot be neglected for a proper understanding of material properties. In this contribution, we present the structure characterization of the highly disordered mineral denisovite and of the modulated plasmonic $Cu_{2-x}Te$ pseudo-cubic nanocrystals, which we eventually achieved combining EDT with high-resolution HAADF-STEM imaging, XRPD and nano-resolved EDX chemical spectroscopies. Denisovite is a nanocrystalline, polytypic, disordered and very complex mineral. Its structure, or, even, the ordered portion of it, ranks among the 1% most complex mineral structures know to date. Additionally, stacking faults and twinning may occur several times within areas consisting of few unit cell repetitions. Coupling EDT data obtained on mostly ordered regions and high-resolution imaging, we could eventually obtain a rather complete description of the denisovite structure and explain it in terms of order-disorder (OD) theory [2]. $Cu_{2-x}Te$ ($x \sim 0.5$) nanocrystals recently attracted a considerable attention for their localized surface plasmon resonance in the near-infrared region. The plasmonic response originates from the presence of Cu vacancies, which lead to the formation of free charges in the valence band of the material. Such vacancies were found to form an ordered arrangement, which results in x3 and x4 modulations in the otherwise pseudo-cubic crystalline structure. A first description of vacancy arrangement was recently proposed [3]. We have pushed forward such investigation coupling nano-beam precession-assisted EDT with nano-resolved STEM imaging and EDX mapping. Low density regions connected with Cu vacancies were localized and correlated with a pseudo-tetragonal twinning, which occurs already for particles of few nanometers

References:

[1] Mugnaioli, E. & Gemmi, M. (2018). Z. Kristallogr. 233, 163-178.
[2] Rozhdestvenskaya, I. V. et al. (2017). IUCrJ 4, 223-242.
[3] Willhammar, T. et al. (2017). Nat. Commun. 8, 14925.

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