Behaviour of magnetite mesocrystals at high temperature

A. Chumakova[1], A. Bosak[1], E. Sturm[2]

[1]European Synchrotron Radiation Facility, 71 Avenue des Martyrs, Grenoble 38000, France, [2]Ludwig-Maximilians-Universität München (LMU), Theresienstr. 41C, 80333 Munich, Germany

aleksandra.chumakova@esrf.fr, bossak@esrf.fr, sturm.elena@lmu.de

Mesocrystals are nanostructured assemblies characterized by a shared crystallographic orientation, exhibit complex architectures spanning multiple length scales. They occur naturally in abiotic and biogenic minerals or can be synthesized artificially [1]. The combination of small- and wide-angle X-ray scattering (SAXS and WAXS) techniques provides a non-destructive means to simultaneously probe mesocrystalline order across different scales, as demonstrated in our previous works [2, 3].

In magnetite mesocrystals, SAXS and WAXS regions are clearly separated, although higher-order SAXS peaks may overlap with low-order WAXS reflections. At sufficiently high momentum transfers, WAXS data can be treated as an incoherent sum of individual nanoparticle diffraction patterns. This feature enables coherent diffraction imaging without isolating single nanoparticles.

We present preliminary results from a high-temperature study conducted on the PILATUS-based ID28 diffractometer at ESRF [2]. Magnetite mesocrystals were annealed in a quartz capillary from room temperature up to 500 °C in 50 °C increments. At ambient conditions, the mesocrystals exhibit a translational symmetry described by the *R-3m* space group, with cell parameters a=131.5 Å, α=64°, and a volume V=1750 nm³. The crystallographic relationship between the mesocrystal lattice and the internal magnetite nanoparticles is defined as $\langle 1\text{–}10\rangle \parallel \langle 1\text{–}10\rangle_S$ and $\langle 111\rangle \parallel \langle 111\rangle_S$, where the subscript S refers to the spinel structure of magnetite.

Upon heating, oxidation of the magnetite nanoparticles initiates, as evidenced by the appearance of superstructural reflections in the diffraction patterns. Above 500 °C, a topotactic transformation into hematite occurs, consistent with expectations.

Notably, between room temperature and 200 °C, the mesocrystal unit cell volume decreases by approximately 20% without structural breakdown. This behavior is attributed to the evaporation of the stabilizing oleic acid layer, promoting direct contact between neighboring nanoparticles.

The small-angle diffraction patterns evolve: the characteristic oscillations weaken as {100} facets of adjacent cubes merge, and contributions from {111}-faceted pores become more prominent. Analysis of SAXS intensities enables the reconstruction of the average nanoparticle shape, accounting for the rotational disorder. The reconstructed particle envelope, derived from the coherent scattering component, is presented in Fig. 1.

These findings highlight the remarkable structural resilience and dynamic rearrangement processes of mesocrystal under thermal treatment.

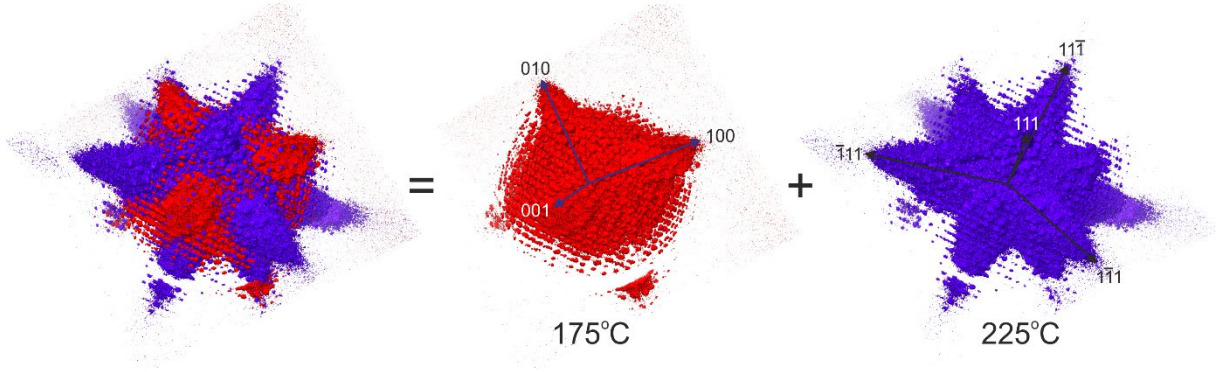

Figure 1. Isosurface representations of small angle diffraction in rhombohedral magnetite mesocrystal below (175°C) and above (225°C) surfactant removal – individual and superposed. Vectors are shown in cubic spinel basis.

.

[1] E.V. Sturm, H. Cölfen, *Chemical Society Reviews* **2016**, 45, 5821-5833

[2] A. Chumakova et al., *Adv. Mater*. **2023**, 35, 2207130

[3] A. Chumakova et al., *Crystals* **2023**, *13*(8), 120