Textures of minerals at nm are intimately linked to their physical & chemical properties

The World of Mineral Polymorphs & Textures

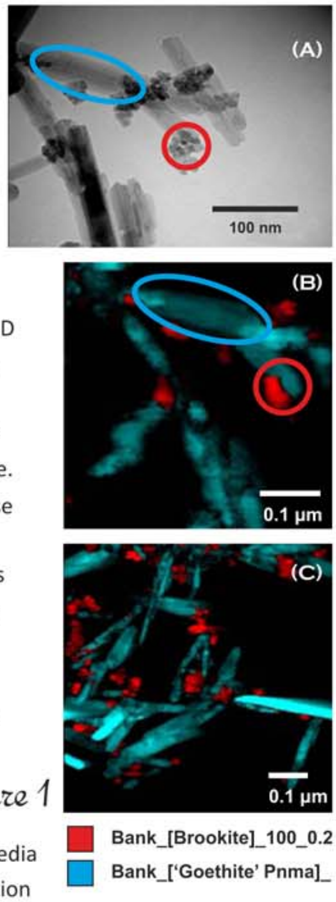


figure 1

(A) Brookite particles & Goethite nanorods TEM bright field image
(B) ASTAR phase map of the same area
(C) ASTAR phase map with <nm resolution taken with aberration corrected Cs-TEM

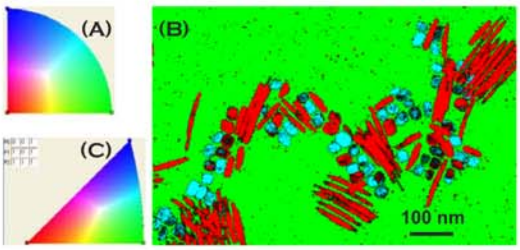
Inorganic nanoparticles are widely used in catalysis. Research has led to control their morphology, crystallographic orientation and assembly. Metal oxide composites can be formed by heteroaggregation using electrostatic forces induced by the surface charges of the nanoparticles. It is important to understand the mechanisms of heteroaggregation and in particular the role of crystallographic facets.

ASTAR and TEM electron tomography has been carried out in order to analyse the heteroaggregates homogeneity and their 3D structure in a case study of rods of goethite (α-FeO(OH)) with particles of brookite (TiO_2) mixture. ASTAR orientation / phase map at nm scale revealed that the rods of goethite are assembled one to each other along their long edges. Particles of brookite are agglomerated and are linked to the tips of the goethite rods (fig.1). It is very important that exactly the same results have been revealed using TEM electron tomography. It is interesting to observe dramatic resolution in ASTAR phase maps generated with Cs corrected TEM in comparison with std Lab6 300 kV TEM (Jeol 3010) Fig.1a-b

The challenge:	Identify orientation / phase of different mineral phases with particle size <50 nm
Solution:	ASTAR technique coupled with precession electron diffraction

Emphasis on the synthesis of nanoparticles is currently directed at designing their crystal structure and morphology and therewith their self-assembling behavior. We employed nonionic water-in-oil microemulsions as reaction medium to explore nanoscopic crystallization pathways for barium carbonate (witherite mineral).

Contrary to what was originally expected is the genesis of stable orthorhombic witherite in these media is not a straightforward process enabling thus the investigation of birth, deterioration and transformation of so far unprecedented metastable amorphous and crystalline nanoparticles. ASTAR gives the opportunity to identify the different polymorph phases in a crystalline nanoparticle ensemble (orientation/phase maps) and to determine major growth directions of individual nanoparticles or the adjacent faces of self-assembled nanoparticles (orientation maps) thus gaining deeper insight into the underlying processes. Fig. 2 shows monoclinic ($P12_1/m1$ (11)) nanocubes together with orthorhombic (Pnma (62)) nanorods that have grown out in a direction.



Crystal Structure

TiO_2 Brookite: Orthorhombic, Pbca
a= 9.17 Å, b= 5.44 Å, c= 5.13 Å
(α-FeO(OH))Goethite: Orthorombic, Pbnm
a= 4.59 Å, b= 9.95 Å, c= 3.02 Å
Whiterite $BaCO_3$: Orthorhombic, Pnma
a=5.31 Å, b= 8.9 Å, c= 6.43 Å
$BaCO_3$: Monoclinic, $P2_1/m$
a = 6,9 Å, b= 5,29 Å , c = 4,51 Å; β= 107,8°

Experimental Data

TEM type: Libra 200 FE Cs(**Fig.1c**)
Map resolution: <1 nm
Scanned area: 2 x 2 µm

TEM type: Tecnai 20 F (**Fig.2**)
Map resolution: 1 nm
Scanned area: 800 x 600 nm

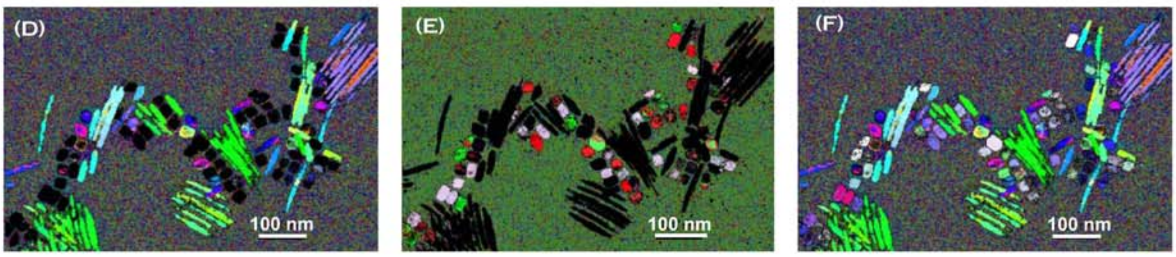


figure 2

ASTAR phase map of different whiterite polymorphs (blue-monoclinic, red ortho $BaCO_3$) (b) colour code for orthorhombic structure (a) and for monoclinic (c) ASTAR orientation map for $BaCO_3$ orthorhombic phase (y axis), (d) same for $BaCO_3$ monoclinic phase (z axis) (e) ASTAR orientation map for both $BaCO_3$ polymorphs (y axis)

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