H2020-MSCA ITN
Grant n. 956099

ESR13 -Electron Crystallography Nanoparticles-

Érica Cordero Oyonarte

BROOKITE TiO2

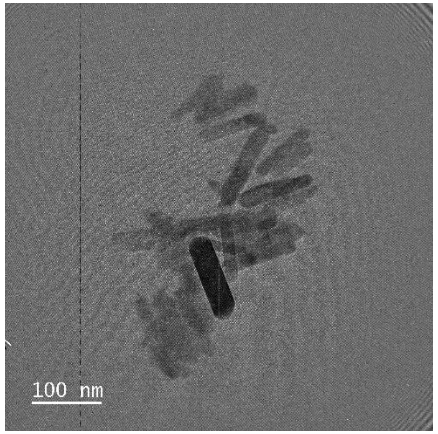
Hydrothermal Synthesis

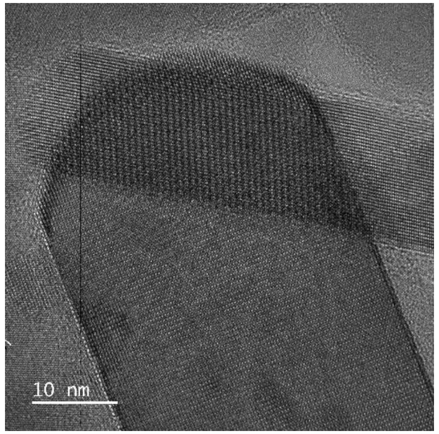
Precursors

Urea + TALH

Conditions

200 °c 24h in the oven

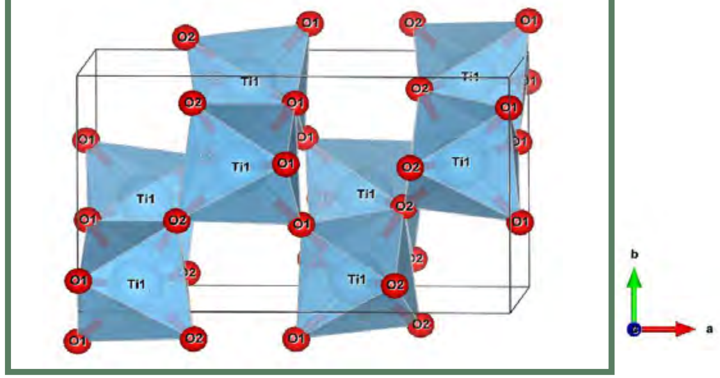


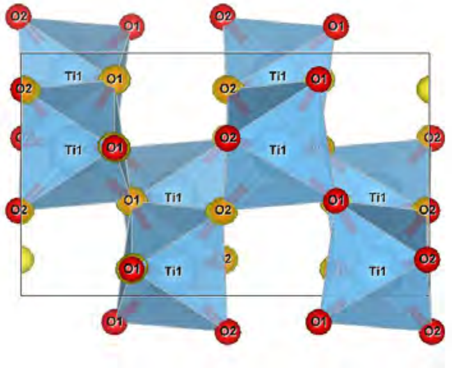


- Adapted beam size (**Ø 70 nm**)
- Particle tracking (Instamatic on JEOL JEM-F200 with hybrid-pixel detector ASI M3 Cheetah)

Precession Electron Diffraction Tomography (PEDT)

REF = TiO2-brookite-ICSD_CollCode36408





Lattice Parameters

a = 9.174 Å b = 5.449 Å c = 5.138 Å
α = β = γ = 90°

Space group Pbca

Lattice Parameters

a = 9.1153 Å b = 5.4154 Å c = 5.1141 Å
α = β = γ = 90°

Space group Pbca

Kinematical Refinement

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-----------------------------------------------------------------------------------------
|R factors : [660=609+51/13],    Damping factor:   1.0000              |
|GOF(obs)= 12.79    GOF(all)= 12.28                               |
|R(obs)=  16.70    wR2(obs)= 39.22    R(all)=   17.09    wR2(all)= 39.24 |
|Last wR2(all): 66.87 48.43 40.74 39.43 39.20 39.24               |
|Maximum change/s.u. :   -0.0295 for x[Ti1]                  |
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Dynamical Refinement

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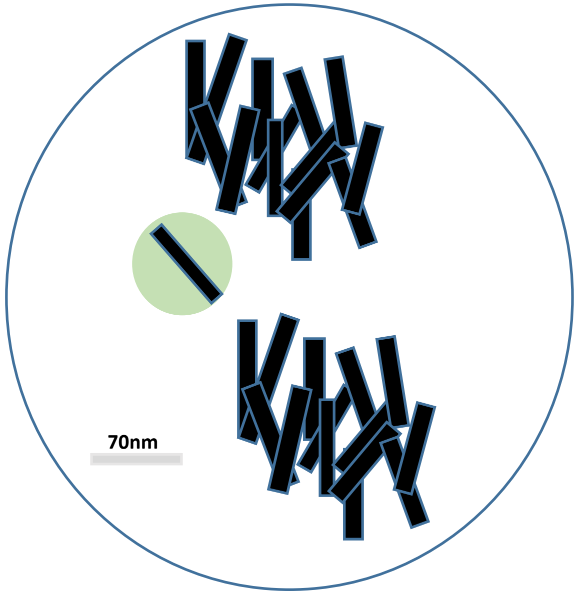
-----------------------------------------------------------------------------------------
|R factors : [2737=1975+762/90],    Damping factor:   1.0000            |
|GOF(obs)=  2.83    GOF(all)=  2.50                               |
|R(obs)=   6.30    wR2(obs)= 14.52    R(all)=    8.26    wR2(all)= 15.06 |
|Last wR2(all): 15.06 15.06                               |
|Maximum change/s.u. :    0.0131 for EDThick[Zone#1]               |
-----------------------------------------------------------------------------------------
```

Using **PETS** and **JANA** for structure solution and Refinement

NanED ESR 13 : EC of Nanoparticles   PhD: Erica Cordero Oyonarte @ CRISMAT (Caen)

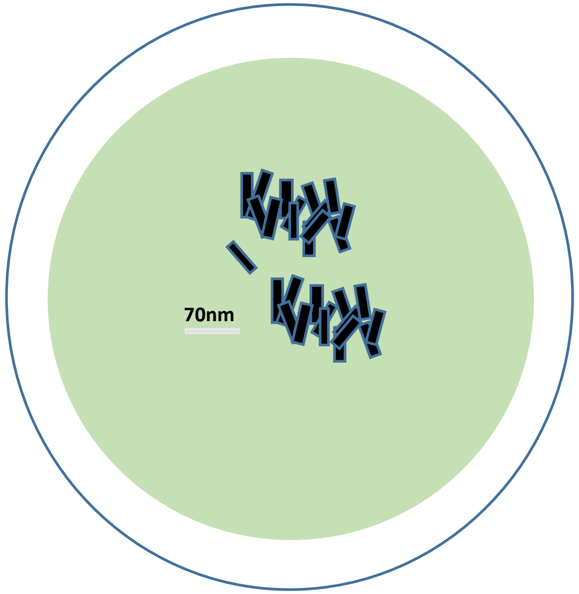
JEOL JEM F200
Precession Electron Diffraction Tomography
CAEN - FRANCE

- Adapted beam size (**Ø 70 nm**)



ELDICO Diffractometer
Continuous Rotation Electron Diffraction
BASSEL – SWITHERLAND

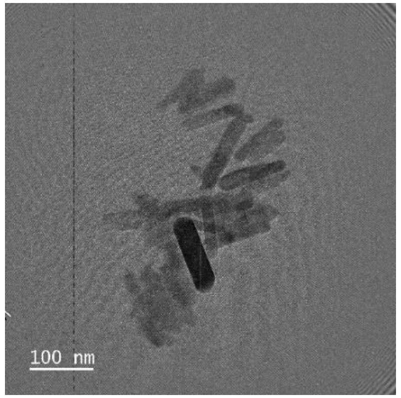
- Adapted beam size (**Ø 700 nm**)

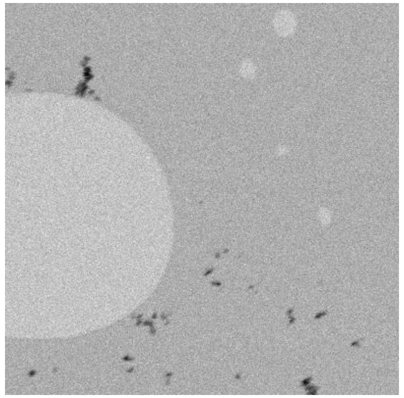


Differences?

- Find an isolated NP
- Low speed for data collection
- Solved crystal structure
- Enough Observed Reflections

- Difficulties to find isolated NP
- Fast data collection
- Solved crystal structure
- Not enough observed reflections





Kinematical Refinement (PED, Caen)

|R factors : [529=**507**+22/**13**], Damping factor: 1.0000 |
|GOF(obs)= 16.69 GOF(all)= 16.42 |
|R(obs)= **17.56** wR2(obs)= 43.19 R(all)= 18.16 wR2(all)= 43.41 |
|Last wR2(all): 69.35 54.42 44.91 43.41 43.24 43.40 43.41 |
|Maximum change/s.u. : 0.0094 for x[O2] |

Dynamical Refinement

|R factors : [1814=**1479**+335/**71**], Damping factor: 1.0000 |
|GOF(obs)= 5.05 GOF(all)= 4.56 |
|R(obs)= **7.35** wR2(obs)= 19.10 R(all)= 7.92 wR2(all)= 19.14 |
|Last wR2(all): 19.45 19.14 19.14 19.14 19.14 |
|Maximum change/s.u. : -0.0385 for EDThick[Zone#2] |

Using PETS and JANA

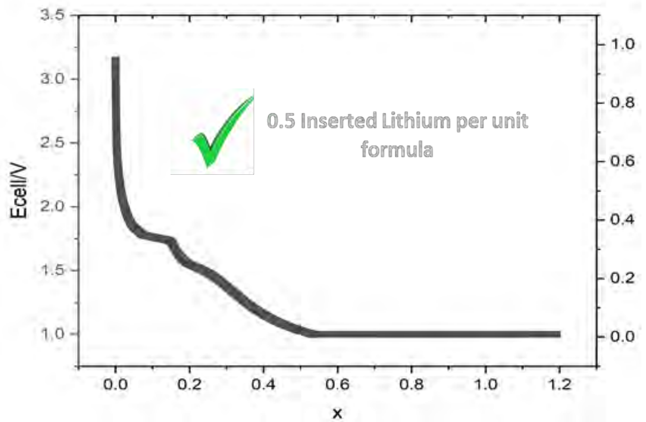
Kinematical Refinement

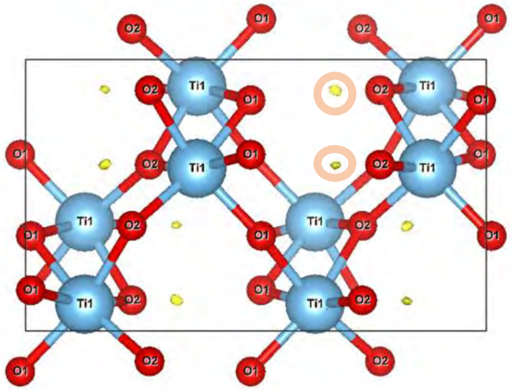
|R factors : [418=**133**+285/**13**], Damping factor: 1.0000 |
|GOF(obs)= 4.44 GOF(all)= 2.71 |
|R(obs)= **20.05** wR2(obs)= 29.55 R(all)= 34.29 wR2(all)= 32.96 |
|Last wR2(all): 32.96 |
|Maximum change/s.u. : 0.0074 for y[O2] |

Dynamical Refinement

|R factors : [1883=**424**+1459/**112**], Damping factor: 1.0000 |
|GOF(obs)= 7.65 GOF(all)= 4.21 |
|R(obs)= **27.46** wR2(obs)= 70.99 R(all)= 41.03 wR2(all)= 81.42 |
|Last wR2(all):955.83245.85 |
|Maximum change/s.u. : -12.1337 for EDScale[Zone#28] |

ELECTROCHEMICAL MEASUREMENTS

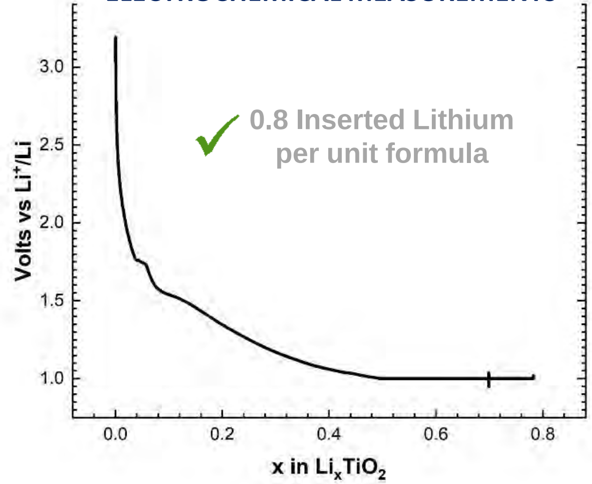


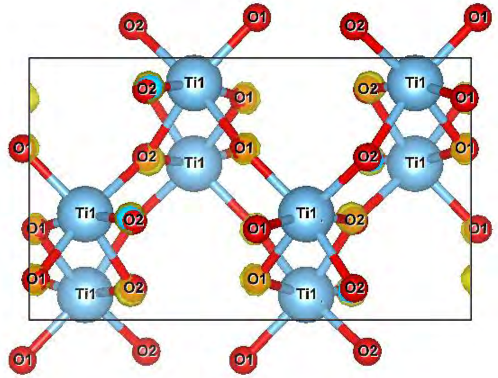


Fourier map after dynamical refinement

Lithium??

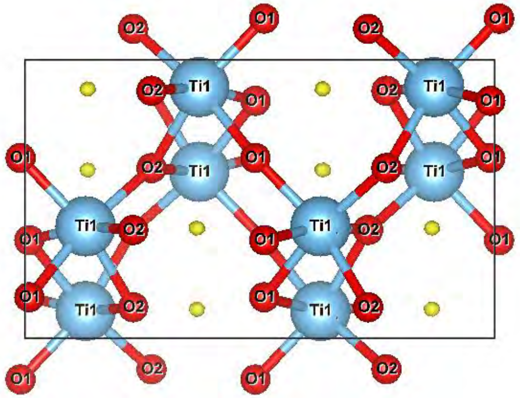
ELECTROCHEMICAL MEASUREMENTS

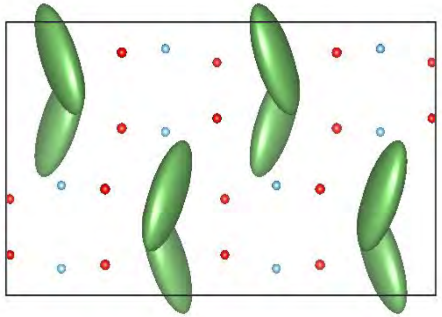


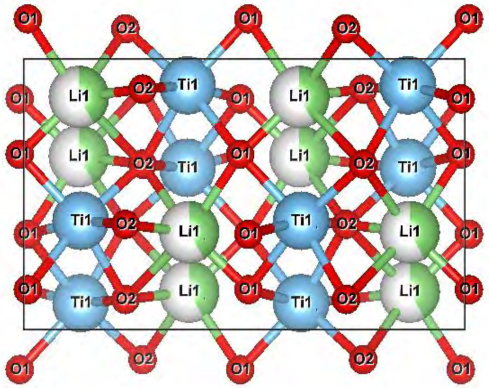


Kinematical Refinement

|R factors : [779=471+308/13], Damping factor: 1.0000 |
|GOF(obs)= 6.55 GOF(all)= 5.24 |
|R(obs)= **26.38** wR2(obs)= 49.42 R(all)= 29.25 wR2(all)= 50.75 |
|Last wR2(all): 60.11 55.66 53.26 51.11 50.82 50.77 50.76 50.75 |
|Maximum change/s.u. : -0.0923 for z[O1] |







Dynamical Refinement

Lithium occupancy 0.4 per unit cell

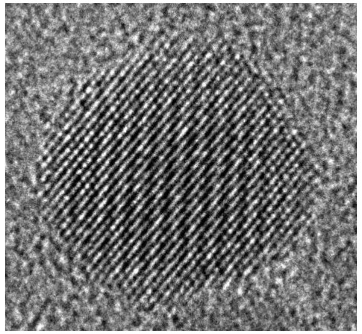
|R factors : [2085=**1747**+338/**59**], Damping factor: 1.0000 |
|GOF(obs)= 4.22 GOF(all)= 3.90 |
|R(obs)= **7.06** wR2(obs)= 16.48 R(all)= 7.71 wR2(all)= 16.61 |
|Last wR2(all): 22.52 16.99 16.61 16.61 |
|Maximum change/s.u. : 0.0500 for EDThick[Zone#2] |

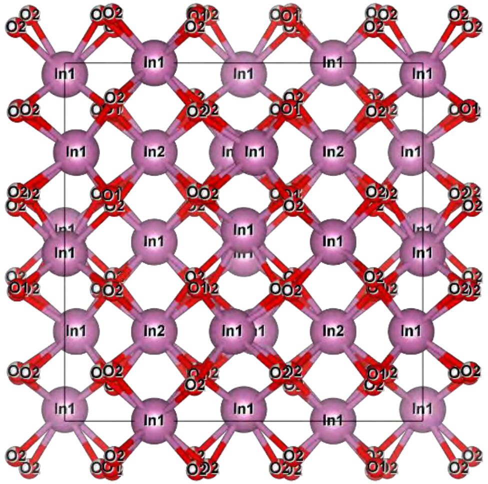
|R factors : [2128=**1778**+350/**69**], Damping factor: 1.0000 |
|GOF(obs)= 4.16 GOF(all)= 3.83 |
|R(obs)= **6.86** wR2(obs)= 16.23 R(all)= 7.55 wR2(all)= 16.36 |
|Last wR2(all): 16.73 16.48 16.39 |
|Maximum change/s.u. : 1.4074 for y[Li1] |

NanED ESR 13 : EC of Nanoparticles — PhD: Erica Cordero Oyonarte @ CRISMAT (Caen)

ITO – from IIT Genova

Diameter = 10.1 +/- 1.2 nm - Sn doping % (mol/mol) = 10.19 %

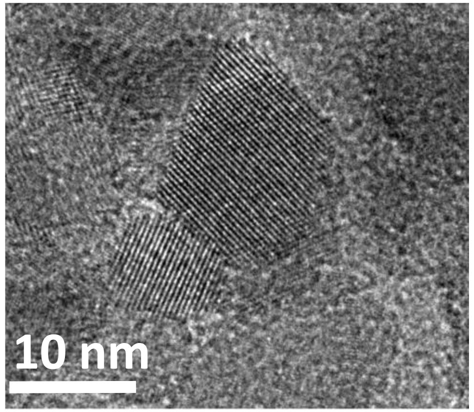


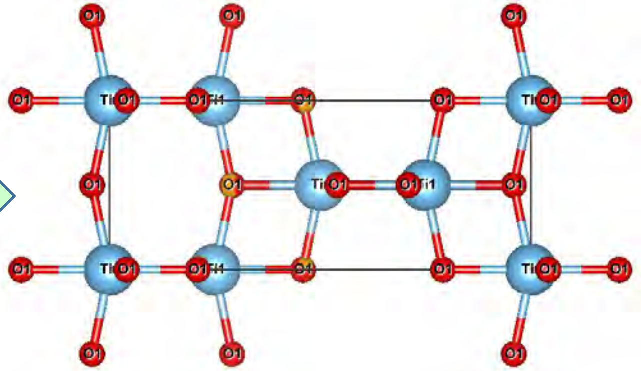


Beam size: 15-20 nm

a = 10.1432 **b** = 10.1432 **c** = 10.1433
alpha = **beta** = **gamma** = 90
Space group – Ia-3

Anatase TiO2 – from CSIC-ICV Madrid





Beam size: 15-20 nm

a = 3.8188 **b** = 3.8188 **c** = 9.4728
alpha = **beta** = **gamma** = 90
Space group – I41|amd

ITO – Kinematical Refinement

```
-------------------------------------------------------------------------
|R factors : [370=89+281/8],    Damping factor:   1.0000               |
|GOF(obs)=  1.85    GOF(all)=  1.01                                    |
|R(obs)=  11.59    wR2(obs)= 22.69    R(all)=   17.42    wR2(all)= 24.95 |
|Last wR2(all): 24.95                                                  |
|Maximum change/s.u. :   -0.0039 for x[O1]                             |
-------------------------------------------------------------------------
```

ITO – Dynamical Refinement

```
-------------------------------------------------------------------------
|R factors : [2274=409+1865/40],    Damping factor:   1.0000           |
|GOF(obs)=  1.48    GOF(all)=  1.12                                    |
|R(obs)=  10.12    wR2(obs)= 16.00    R(all)=   31.40    wR2(all)= 27.61 |
|Last wR2(all): 27.61                                                  |
|Maximum change/s.u. :    0.0009 for EDScale[Zone#10]                  |
-------------------------------------------------------------------------
```

Experiments at low temperature

Anatase TiO2 – Kinematical Refinement

```
-------------------------------------------------------------------------
|R factors : [92=48+44/4],    Damping factor:   1.0000                 |
|GOF(obs)=  5.76    GOF(all)=  4.15                                    |
|R(obs)=  13.14    wR2(obs)= 26.48    R(all)=   19.93    wR2(all)= 27.12 |
|Last wR2(all): 27.12                                                  |
|Maximum change/s.u. :   -0.0005 for scale1                            |
-------------------------------------------------------------------------
```

Anatase TiO2 – Dynamical Refinement

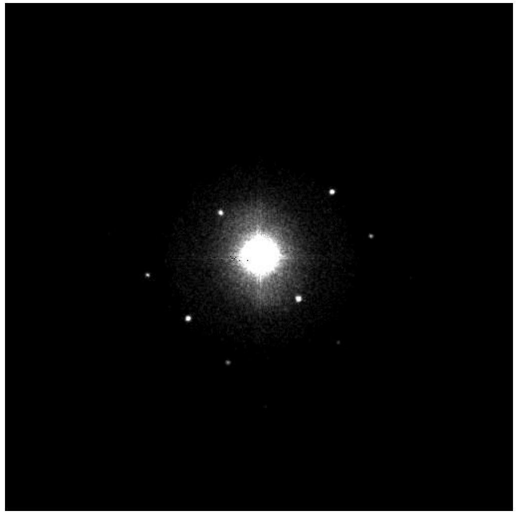
```
-------------------------------------------------------------------------
|R factors : [554=182+372/37],    Damping factor:   1.0000             |
|GOF(obs)=  1.75    GOF(all)=  1.30                                    |
|R(obs)=   7.08    wR2(obs)= 13.83    R(all)=   18.59    wR2(all)= 17.93 |
|Last wR2(all): 17.96 17.94 17.93 17.93 17.93 17.93 17.93 17.93        |
|Maximum change/s.u. :   -0.0690 for EDThick[Zone#1]                   |
-------------------------------------------------------------------------
```

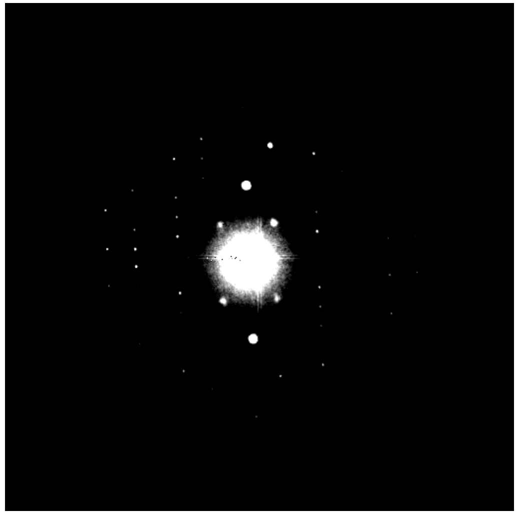
Stream
Console
Stream
fps:
19.96
Interval (ms):
50.1
Increase size
Auto contrast
Exposure (s)
0.20
Brightness
0.05
DisplayRange
11800
Save Image
Input/Ouput
Directory:
C:/instamatic/2022-12-01
Browse...
Sample name:
experiment
1
Flatfield:
Browse...
Open work directory
Open settings directory
Delate last experiment
cRED
TVIPS
cRED_FEI
serialED
autocRED
RED
Learning
Control
advance
about
Rotation Electron Diffraction
Exposure time (s)
4
Tilt range (deg)
2
Step size (deg)
2
Output formats
PETS(.tiff)
REDp(.mrc)
Start collection
Stop Collection

NanED ESR 13 : EC of Nanoparticles PhD: Erica Cordero Oyonarte @ CRISMAT (Caen)

ITO – from IIT Genova

Diameter = 10.1 +/- 1.2 nm - Sn doping % (mol/mol) = 10.19 %





a = 10.1432 **b** = 10.1432 **c** = 10.1433
alpha = **beta** = **gamma** = 90
Space group – Ia-3

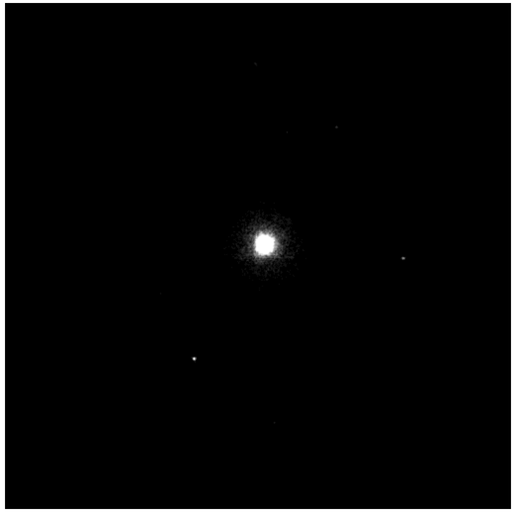
Kinematical Refinement

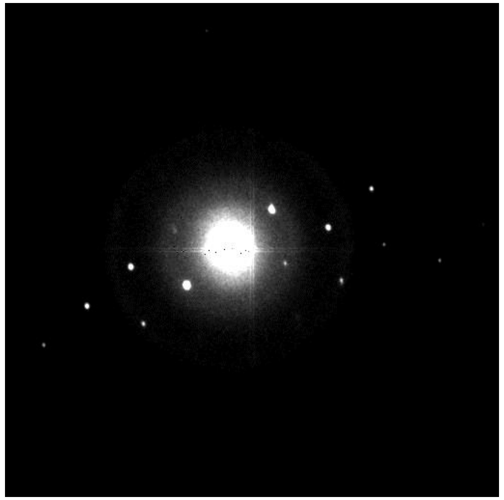
|R factors : [535=**372**+163/**8**], Damping factor: 1.0000 |
|GOF(obs)= 2.05 GOF(all)= 1.77 |
|R(obs)= **7.61** wR2(obs)= 22.67 R(all)= 9.74 wR2(all)= 23.33 |
|Last wR2(all): 28.07 25.35 24.70 24.47 24.41 24.27 23.99 23.62 |
|Maximum change/s.u. : -1.0172 for Uiso[O1] |

Dynamical Refinement

|R factors : [3367=**1470**+1897/**44**], Damping factor: 1.0000 |
|GOF(obs)= 1.41 GOF(all)= 1.02 |
|R(obs)= **4.99** wR2(obs)= 10.59 R(all)= 8.75 wR2(all)= 11.51 |
|Last wR2(all): 11.90 11.51 11.51 |
|Maximum change/s.u. : 0.0131 for EDThick[Zone#1] |

Anatase TiO2 – from CSIC-ICV Madrid





Kinematical Refinement

|R factors : [173=**136**+37/**4**], Damping factor: 1.0000 |
|GOF(obs)= 6.45 GOF(all)= 5.73 |
|R(obs)= **10.38** wR2(obs)= 36.91 R(all)= 12.33 wR2(all)= 37.09 |
|Last wR2(all): 37.09 |
|Maximum change/s.u. : -0.0014 for Uiso[O1] |

Dynamical Refinement

|R factors : [666=**492**+174/**44**], Damping factor: 1.0000 |
|GOF(obs)= 2.39 GOF(all)= 2.09 |
|R(obs)= **3.87** wR2(obs)= 9.77 R(all)= 4.73 wR2(all)= 9.94 |
|Last wR2(all): 9.94 9.94 |
|Maximum change/s.u. : 0.0052 for Uiso[Ti1] |

ITO – from IIT Genova

Kinematical Refinement

Kin Merged from jana refinements

```
---------------------------------------------------------------------------
|R factors : [370=199+171/8],   Damping factor:   1.0000              |
|GOF(obs)=  1.53    GOF(all)=  1.19                                   |
|R(obs)=   6.75   wR2(obs)= 17.03    R(all)=   10.28    wR2(all)= 17.89 |
|Last wR2(all): 17.89                                        |
|Maximum change/s.u. :   -0.0025 for y[In1]                           |
---------------------------------------------------------------------------
```

Kin non Merged from jana refinements

```
---------------------------------------------------------------------------
|R factors : [370=321+49/8],   Damping factor:   1.0000               |
|GOF(obs)=  6.39    GOF(all)=  5.97                                   |
|R(obs)=  10.49   wR2(obs)= 24.76    R(all)=   11.73    wR2(all)= 24.86 |
|Last wR2(all): 50.33 33.16 25.75 24.87 24.86                        |
|Maximum change/s.u. :   -0.0091 for Uiso[O1]                         |
---------------------------------------------------------------------------
```

Dynamical Refinement

dyn Merged from calculation after jana refinement (Paul Klar)

Number of duplicates: 434
All reflections without duplicates: 2068
'P1':   1412 / 2502 observed/all reflections.
Merge: 291 / 369 observed/all reflections.
MRobs   4.43 Robs   6.88
MRall   6.10 Rall   11.20
MwRall   4.52 wRall   7.70

Dyn non-merged from jana refinements

```
---------------------------------------------------------------------------
|R factors : [2502=1412+1090/51],   Damping factor:   1.0000          |
|GOF(obs)=  2.00    GOF(all)=  1.63                                   |
|R(obs)=   6.88   wR2(obs)= 14.13    R(all)=   11.20    wR2(all)= 15.22 |
|Last wR2(all): 19.08 15.26 15.22 15.22 15.22                        |
|Maximum change/s.u. :   0.0110 for EDThick[Zone#2]                   |
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Grant n. 956099

Thank you for your attention