National Institute of Materials Physics

Nanoscale materials characterization in a borderless Central European space: NIMP participation in CERIC-ERIC

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EuroNanoForum 2019

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Introduction

EuroNanoForum
2019

Introduction

- First keyword:

Euro

Introduction

Elementary particles
Deep structure of
matter and Universe

Introduction

- Second Keyword – Nano:

nanomaterials, nanosciences, nanotechnologies

- Size range – below 100 nm, but often below 10 nm
- We need to know the structure of nanometric objects
- Instruments with a high spatial resolution (atomic resolution) are mandatory
- The smaller the structural detail, the larger the scientific instrument. And expensive!

Here comes CERIC-ERIC !

CERIC

Central European Research Infrastructure Consortium

COMMISSION IMPLEMENTING DECISION of 24 June 2014 (2014/392/EU)

Statutory seat: Trieste, Italy

Official website:

http://www.c-eric.eu

Interdisciplinarity & complementarity: starting points and philosophy of CERIC

Modern Materials and Life Sciences require the capability to analyze and characterize the same material with several complementary probes and techniques, and also to manipulate different aspects in its synthesis and preparation.

CERIC offers, in an integrated way at international level, open access to different state-of-the-art complementary characterization and preparation techniques.

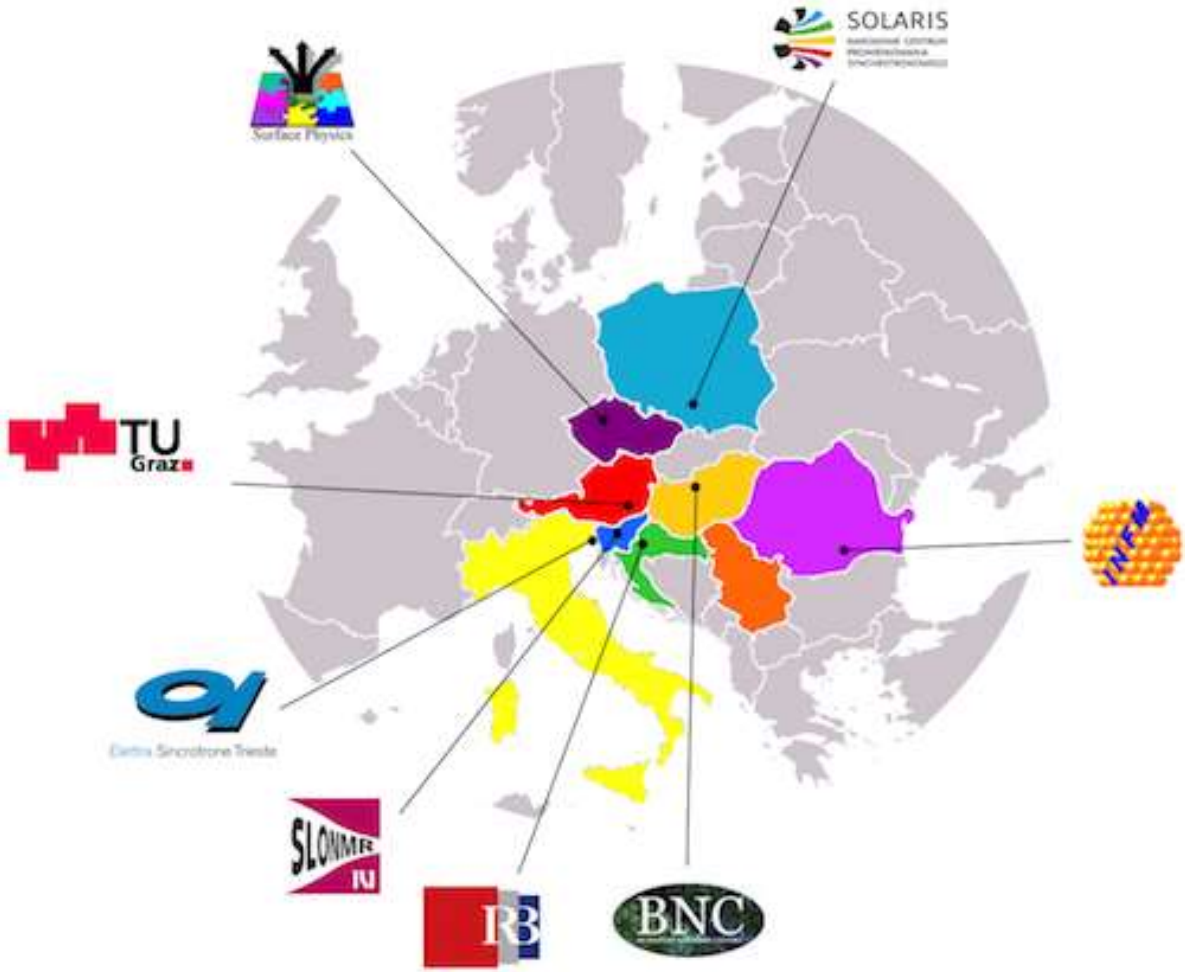
CERIC operates in the wide research area of nanoscale analysis and synthesis of Materials Sciences, including connections to Biomaterials and Structural Biology.

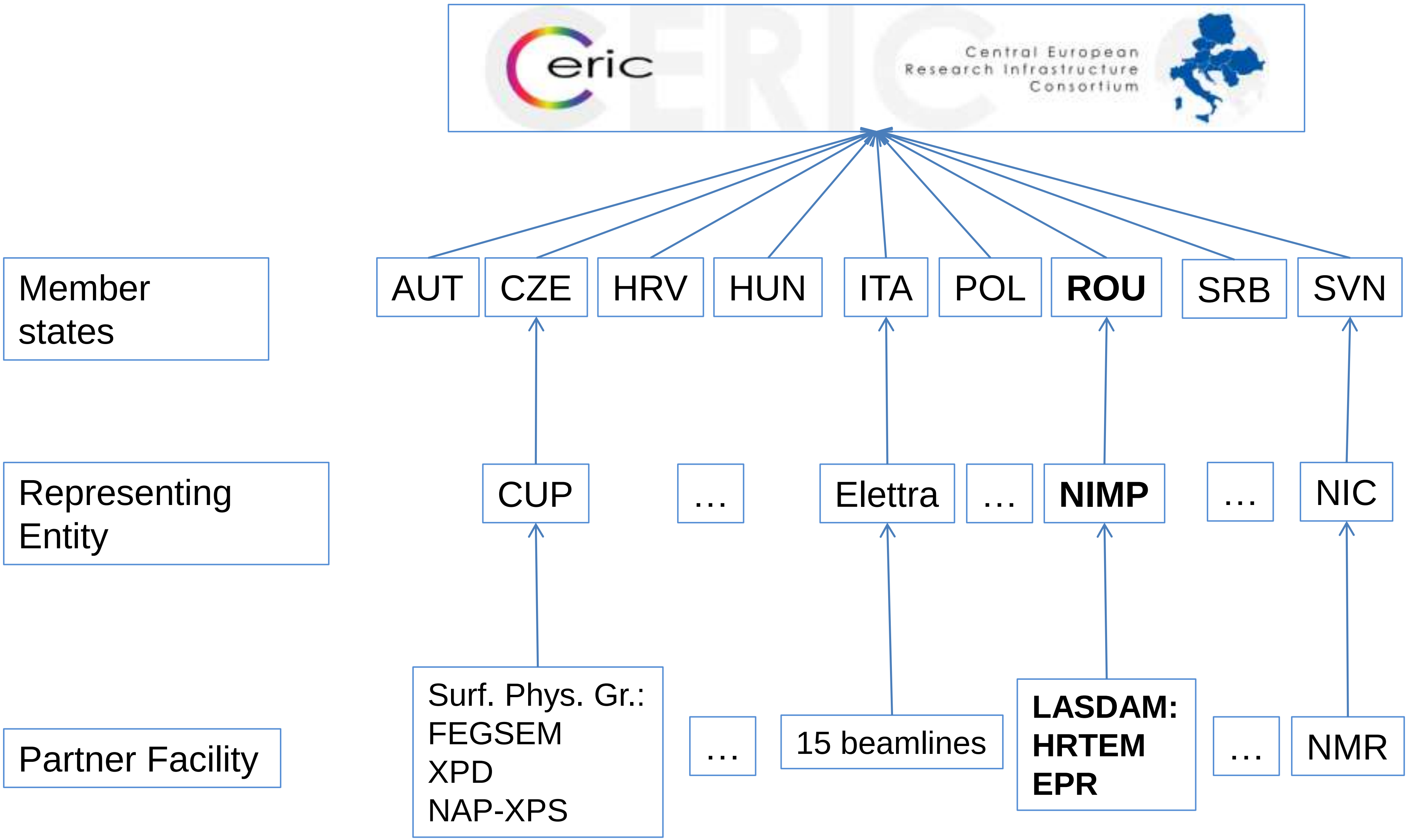
The available equipment and the support staff allow synthesis and analysis of materials and biomaterials down to the nano-scale, using photon, electron, neutron and ion based techniques.

CERIC structure

Founding members:
Austria, Czech Republic, Italy, Romania, Serbia, Slovenia

New members:
Croatia, Hungary, Poland




Central European Research Infrastructure Consortium
Member states
AUT
CZE
HRV
HUN
ITA
POL
ROU
SRB
SVN
Representing Entity
CUP
…
Elettra
…
NIMP
…
NIC
Partner Facility
Surf. Phys. Gr.: FEGSEM XPD NAP-XPS
…
15 beamlines
LASDAM: HRTEM EPR
…
NMR

How it works:

1. Projects calls each 6 months: unique entry point via VUO Elettra
2. Applicants from all over the world
3. Projects of 3 pages max: single technique or multitechnique projects
4. Technical evaluation (2 steps)
5. Scientific evaluation by International Scientific and Technical Advisory Committee (ISTAC)
6. Projects ranking, beamtime granting
7. Experiments scheduling
8. Full support for travel and accommodation
9. Experiments
10. Data processing, publications

Materials characterization by Electron Paramagnetic Resonance (EPR) Spectroscopy

www.cetresav.infim.ro

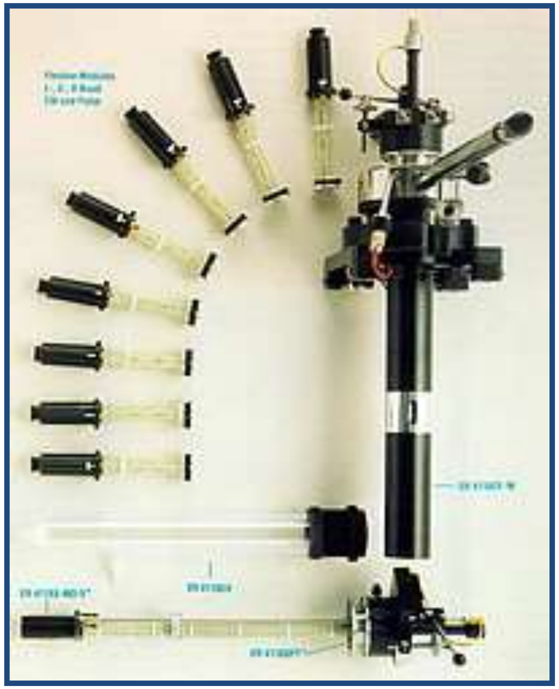
The X-band EMX-plus CW EPR spectrometer with Varian E12 magnet

The Q-band CW EPR spectrometer ELEXSYS 500Q with E560 ENDOR unit

Materials characterization by Electron Paramagnetic Resonance (EPR) Spectroscopy

www.cetresav.infim.ro

The X- band FT/pulse ESR spectrometer ELEXSYS 580 with E560 DICE ENDOR and E540-400 pulse ELDOR



The Flexline resonator and cryostat for pulse X-band ESR

Materials characterization by Electron Paramagnetic Resonance (EPR) Spectroscopy

www.cetresav.infim.ro

The LHeP18 (Cryomec) liquid helium plant. Production: 18 l of liq. He/24 hours. Fully automatic operation. No liquid N_2 required

Parts of the He gas recovery system: the gas bag + helium gas 3-stage compressor.

Materials Characterization by Scanning Electron Microscopy (SEM) & Transmission Electron Microscopy (TEM)

JEM ARM200F

JEM ARM200F

Working modes : CTEM, HRTEM, STEM BF, STEM HAADF, SAED, nano-ED, CBED, EDS, EELS, EFTEM, EELS-SI;

· Schottky FEG
· Accelerating voltages: 120, 200 kV;
· Spherical aberration corrector for STEM mode
· TEM resolution: **0.19 nm**;
· STEM-HAADF resolution: **0.08 nm**;
· EDS : **-** energy resolution EDS: **131,4 eV** (Mn-Ka);
· EELS – energy resolution **0.7 eV**;
· CCD Cameras Gatan: Orius 200D, Ultrascan 1000XP, Ultrascan 1000FT;

JEM 2100

JEM 2100

Working modes : CTEM, HRTEM, STEM BF, STEM ADF, STEM HAADF, SAED, nano-ED, CBED, EDS;

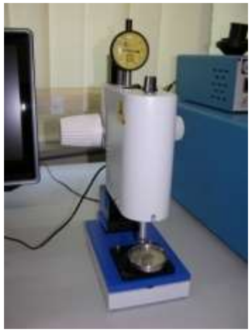
· LaB6 filament
· Accelerating voltages: 80, 200 kV;
· TEM resolution: **0.19 nm**;
· STEM-HAADF resolution: **1 nm**;
· EDS : - energy resolution EDS: 131,4 eV (Mn-Ka);
· CCD Cameras : Olympus Tengra;
- electron tomography;
- Precession Electron Diffraction → structural mapping

Sample preparation

- powders : grinding in a mortar + dripping on TEM grid
- thin films, bulk materials : 2 thinning procedures

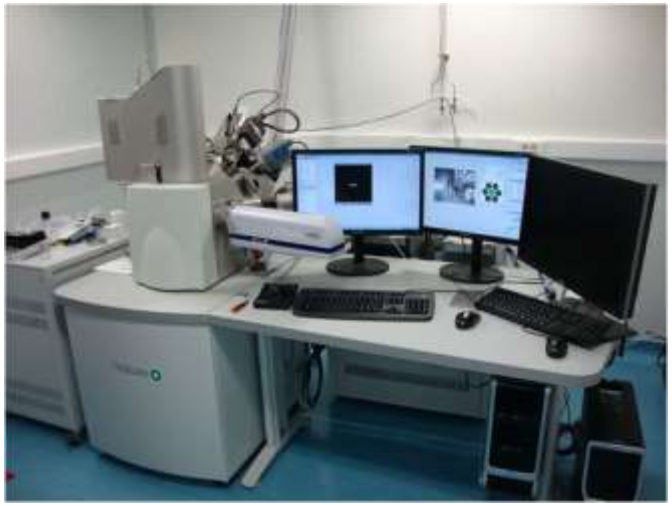
A. Classical method:

Cutting → Mechanical polishing → Ion milling





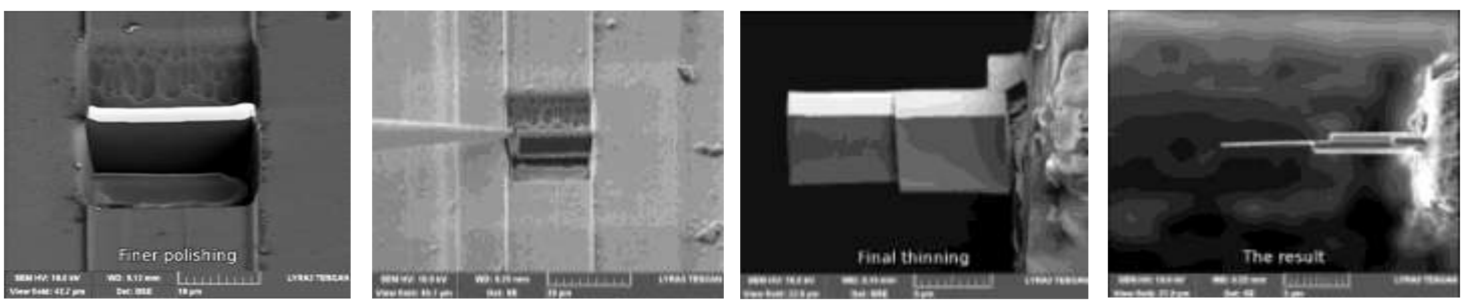
B. Focused Ion Beam:



TESCAN LYRA 3 FMU SEM-FIB

TESCAN LYRA 3 FMU SEM-FIB

- Accelerating voltage: 200 V – 30 kV
- Detectors: secondary electrons (SE),
  backscattered electrons (BSE)
- Resolution SE: **1.2 nm** at 30 kV in High Vacuum Mode
- Resolution BSE: **2.0 nm** at 30 kV
- FIB : - Ga source, 1500 h lifetime
  - Accelerating voltage: 0.5 - 30 kV
  - Detectors: secondary electrons (SE)
  - Resolution: **5 nm** at 30 kV



Main steps in preparing thin lamellae by FIB.

NIMP-HRTEM in CERIC

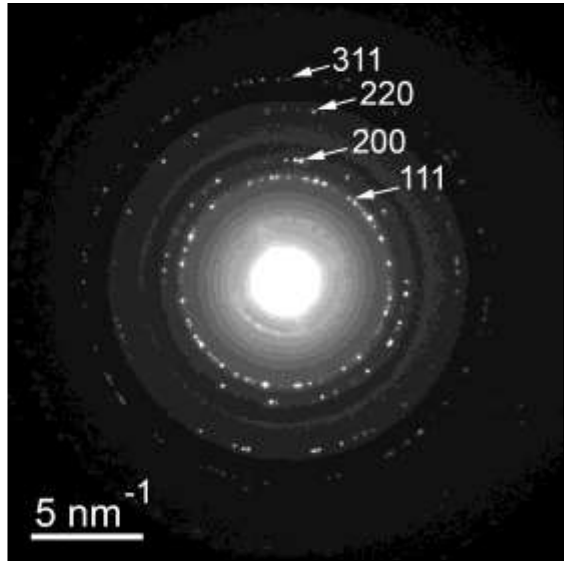
Requests for NIMP-HRTEM facilities June 2014-present (Call 0 – Call 10):

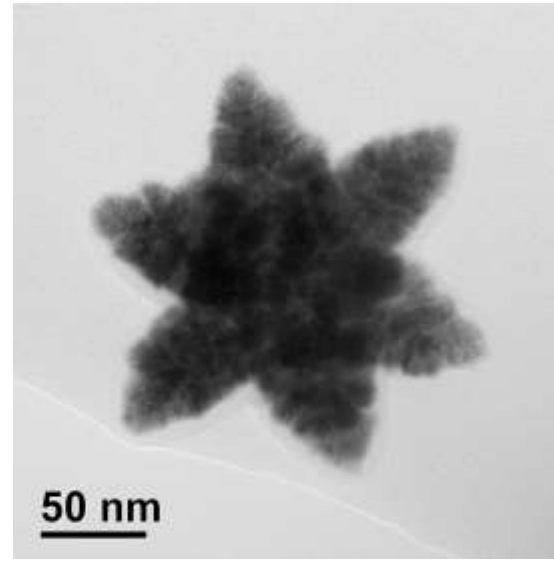
168 requests from users in AUT, BEL, CZE, FRA, GER, HUN, HRV, IND, ITA, PAK, PRT, ROU
48 scheduled proposals
400 h/year HRTEM beamtime

External users from various fields:

Materials science – materials for energy (fuel cells, photovoltaic), gas sensors, catalysis, nuclear applications, microelectronics, special alloys
Cultural heritage
Geology-Biology
Nanomedicine

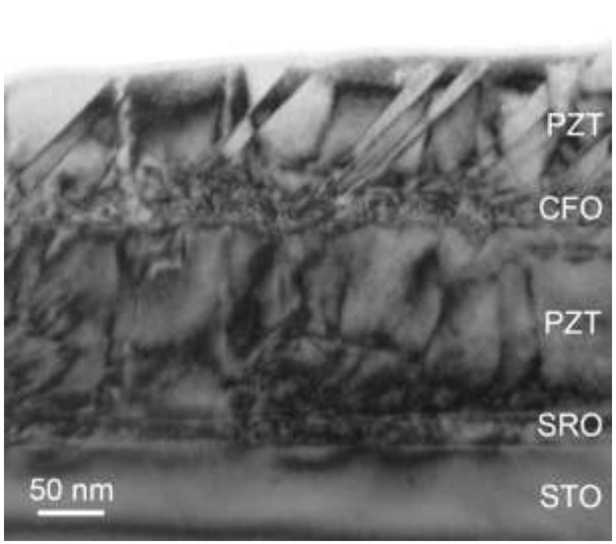
Conventional TEM (CTEM) & Electron Diffraction(ED)

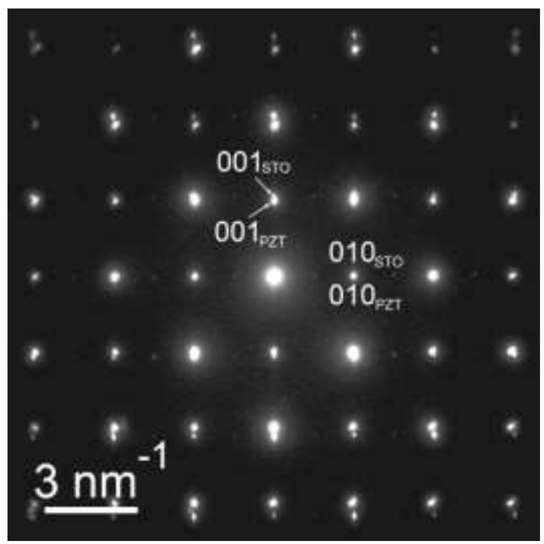




Ni-MgO core-shell structures

Nanostructured W particle





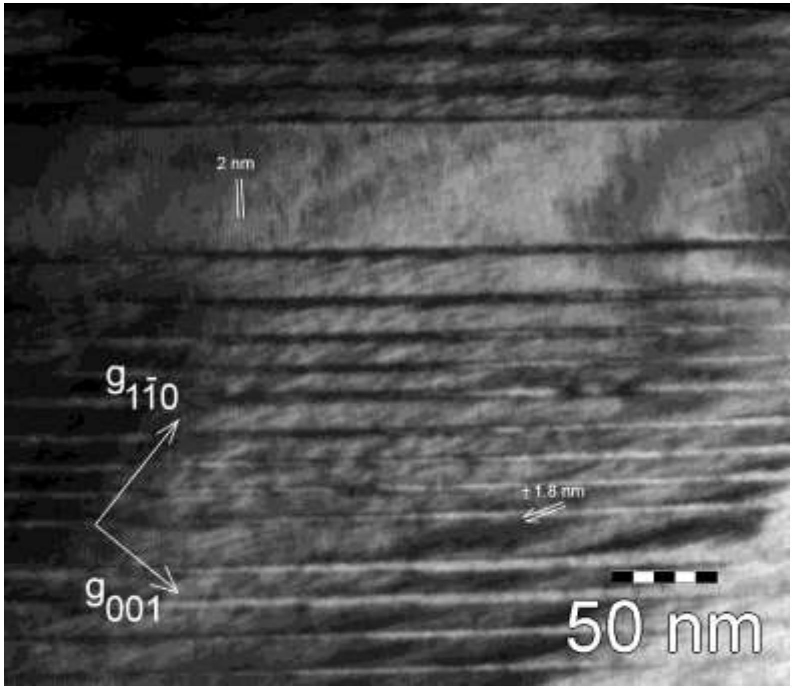
Epitaxial ferroelectric heterostructure

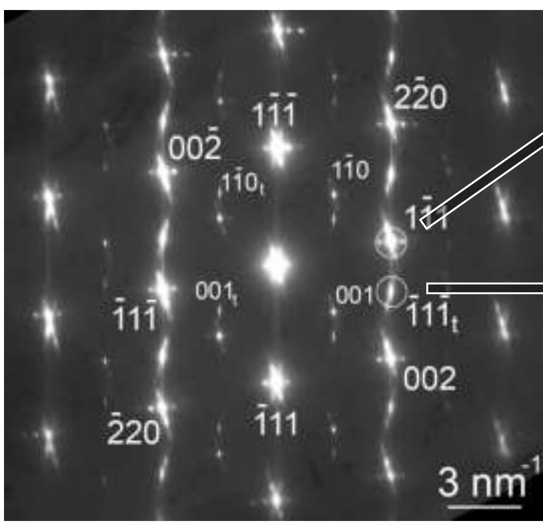
- Size and shape of nanoparticles
- Thickness and growth mode of thin films
- Crystalline structure
- Extended defects (dislocations, planar defects, domains, precipitates)

Conventional TEM – Characterization of structural domains

Hierarchic domain structure in $Ni_{55}Fe_{19}Ga_{25}Co$ shape-memory alloy.

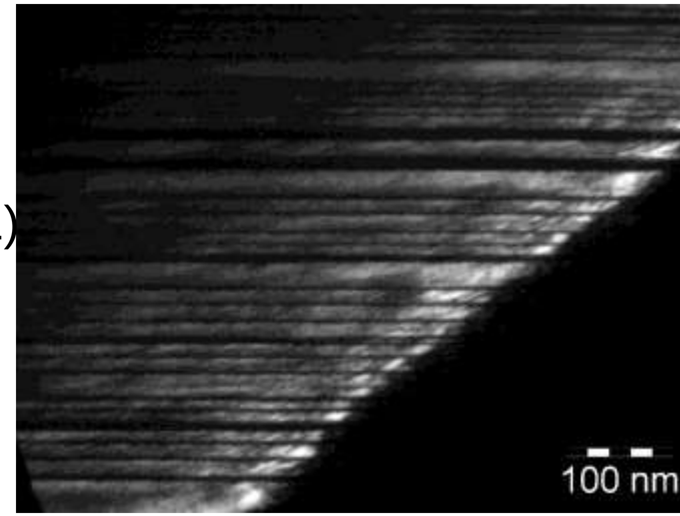
BFI





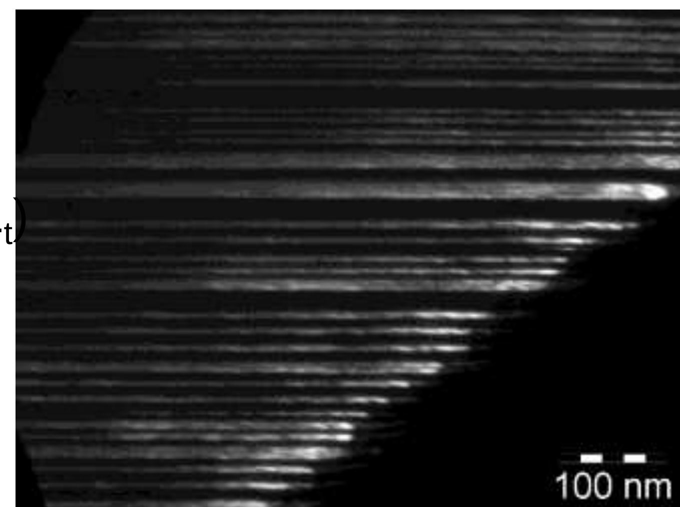
DFI

g=(1-11)



DFI

g=$(-11-1_t)$



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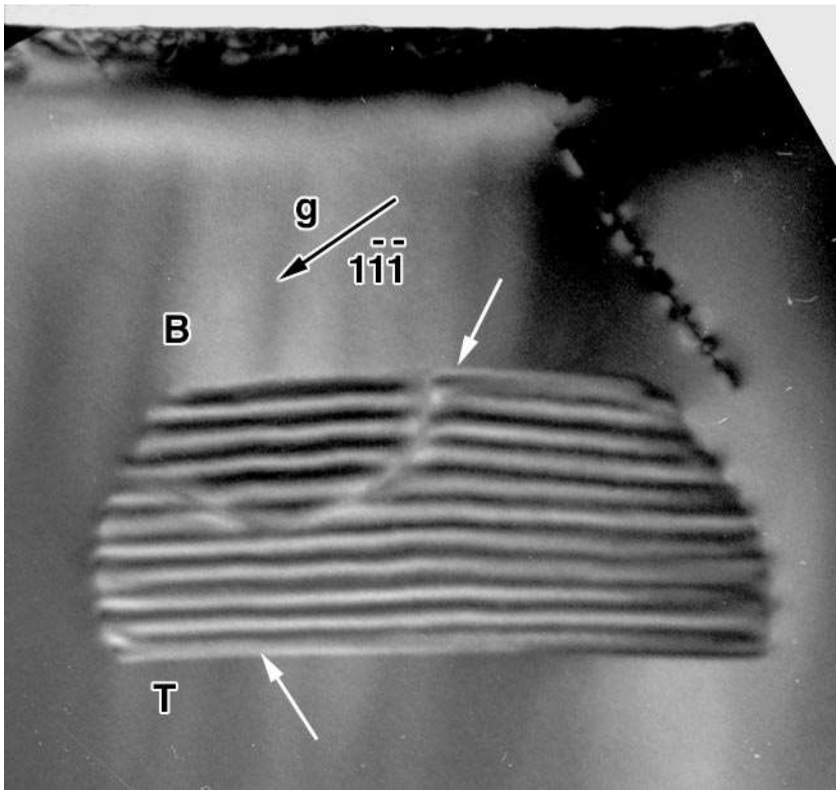
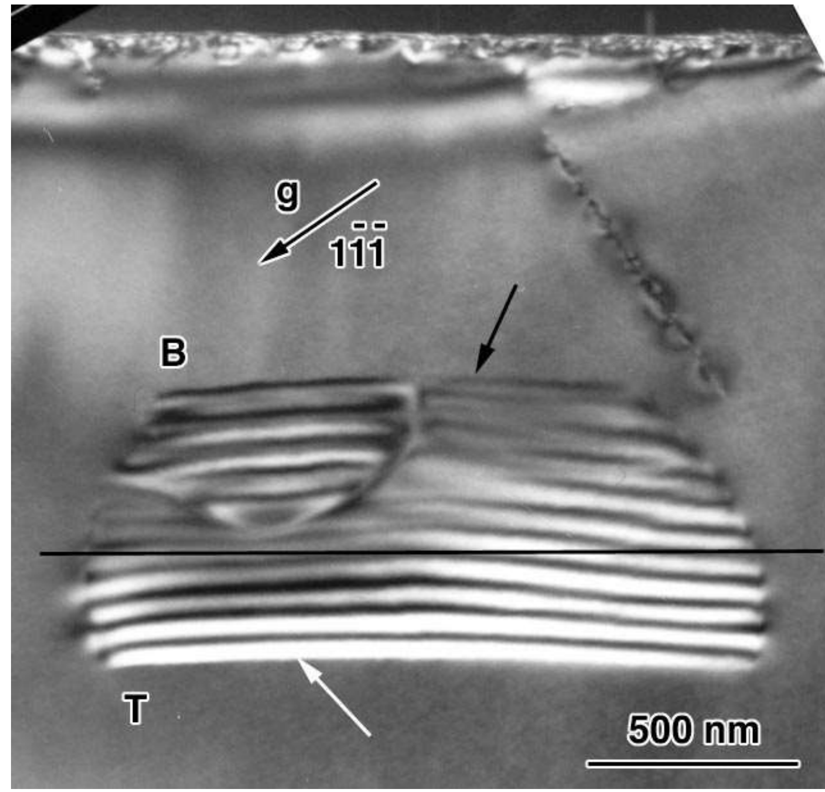
Conventional TEM – Characterization of structural defects

Planar defects

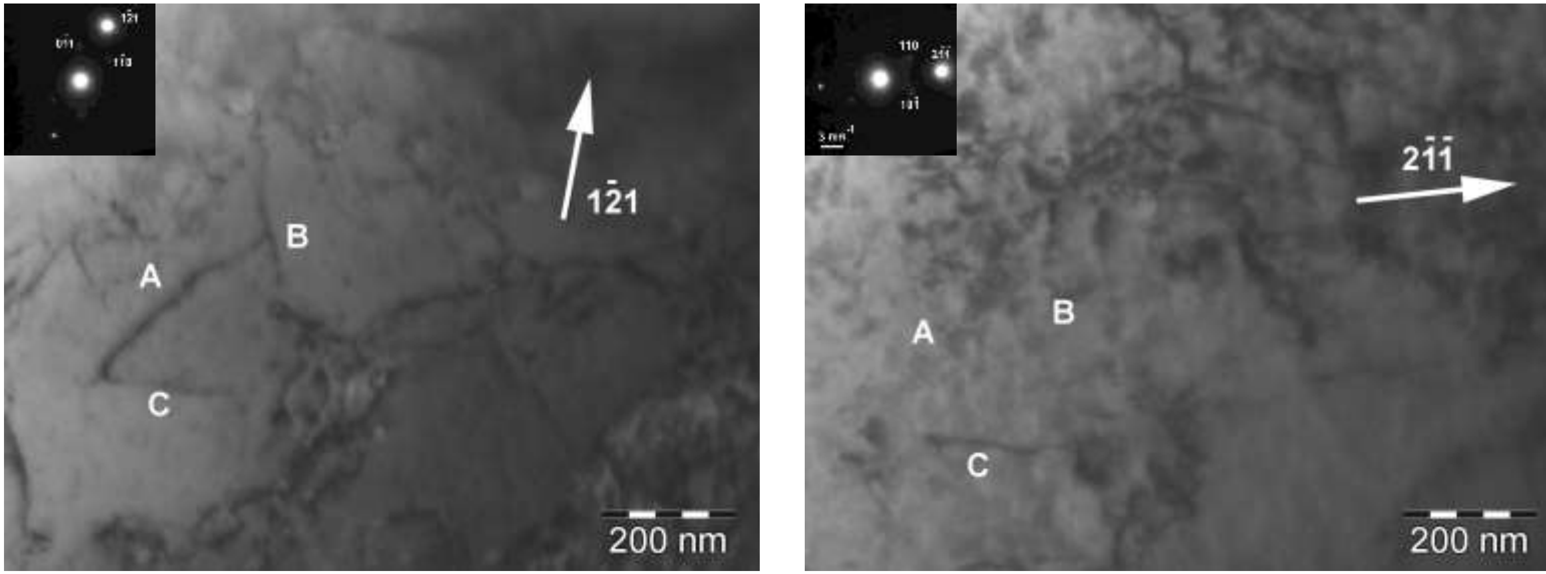




Extrinsic {111} planar defect in hydrogenated Si for SOI technology

Conventional TEM – Characterization of structural defects

Dislocations



Dislocations in FeCr alloy, close to **B**=[111]

Dislocation A: $\mathbf{b} = \frac{1}{8}\left[01\bar{1}\right]$ Dislocation B: $\mathbf{b} = \frac{1}{8}\left[01\bar{1}\right]$ Dislocation C: $\mathbf{b} = \frac{1}{4}\left[21\bar{1}\right]$

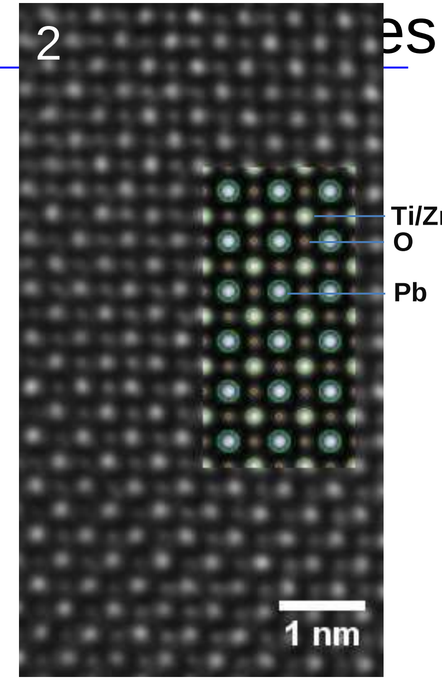
Dissociation of a perfect dislocation into 3 partials on a {110} plane according to the relation:

$$\frac{1}{2}[111] \rightarrow \frac{1}{8}[110] + \frac{1}{4}[112] + \frac{1}{8}[110]$$

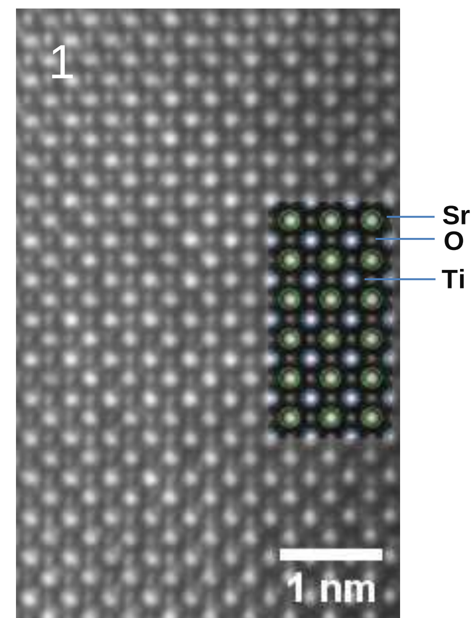
HRTEM - Atomic structure of crystalline materials es

HRTEM image of PZT/SRO/STO epitaxial layers.

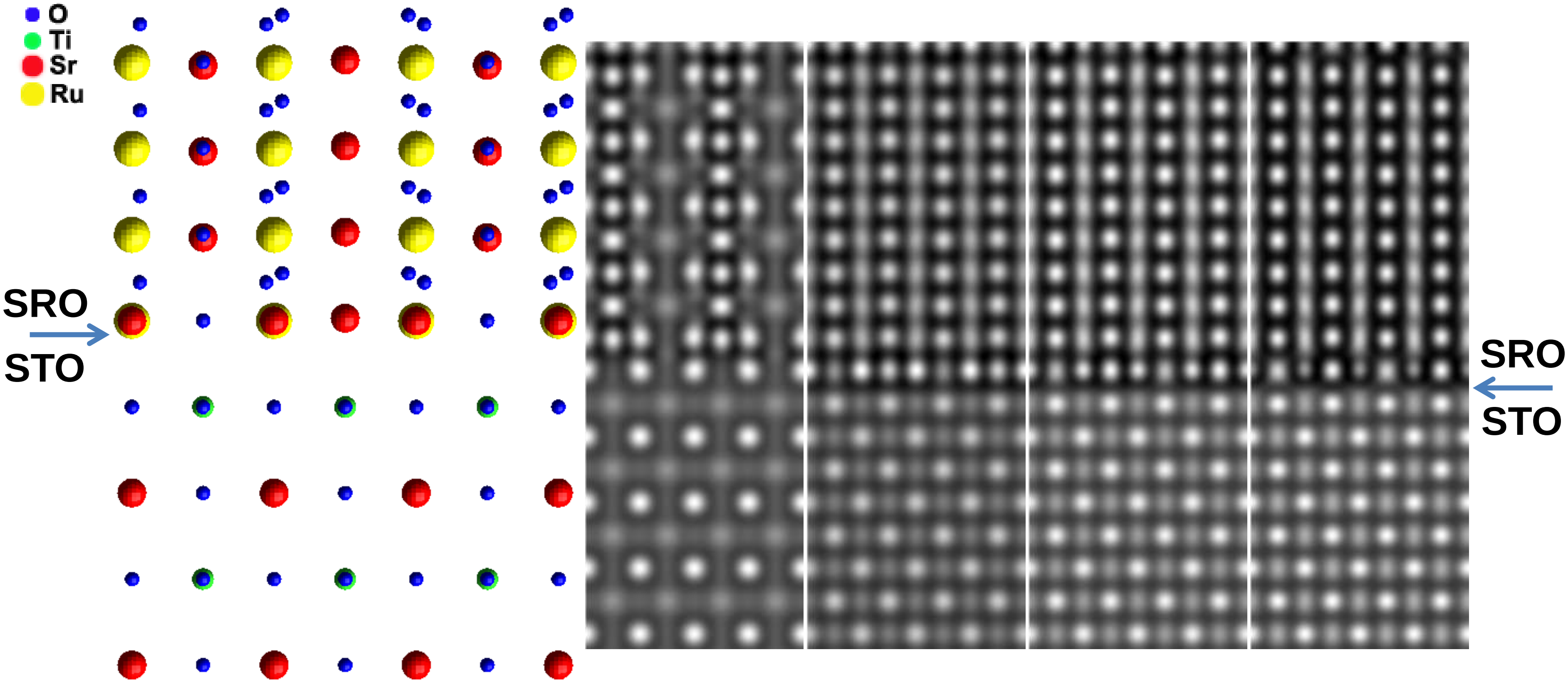
Inserted simulated HRTEM image on PZT (Δf=-40 nm, t=15 nm).



Inserted simulated HRTEM image on SRO (Δf=-40 nm, t=15 nm).



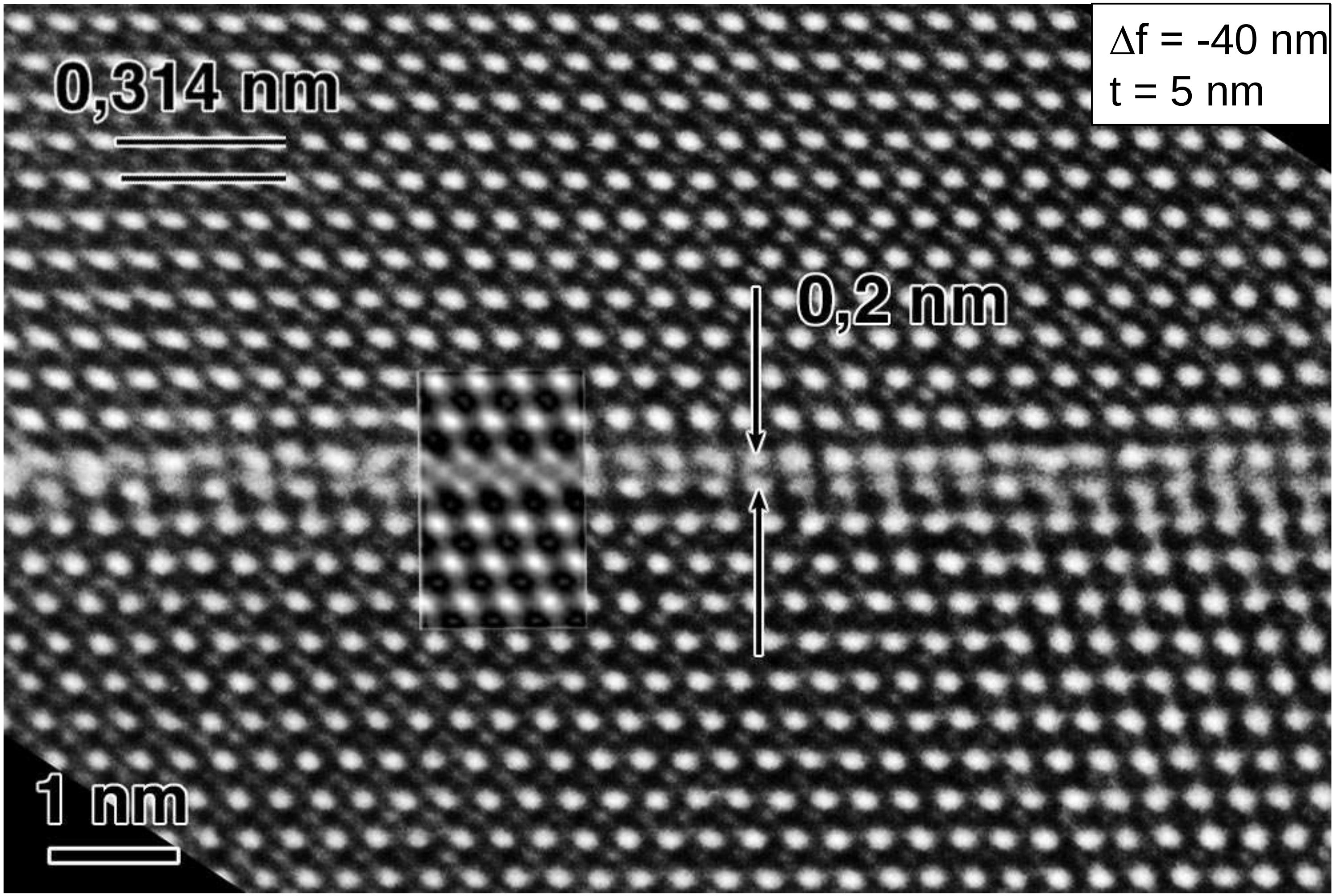
HRTEM - Atomic structure of crystalline materials and interfaces



Thickness 2.4 nm 4.7 nm 9.4 nm 14.1 nm

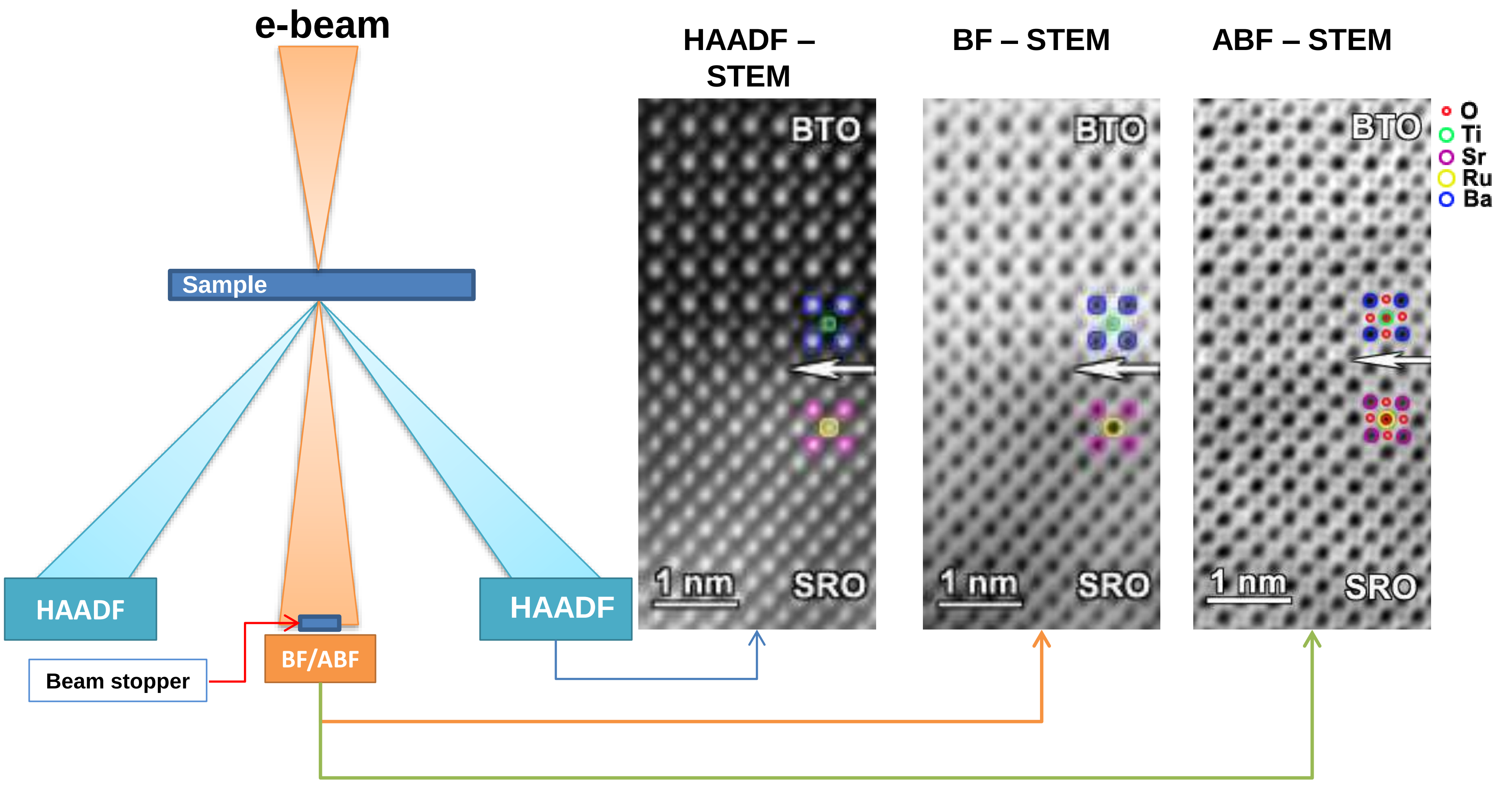
Structural model and simulated HRTEM images of the STO – SRO interface (Δf = -7 nm).

HRTEM - Atomic structure of extended structural defects



Atomic structure of {111} planar defect in hydrogenated Si for SOI technology.

Cs-corrected STEM: ADF/HAADF, BF, ABF



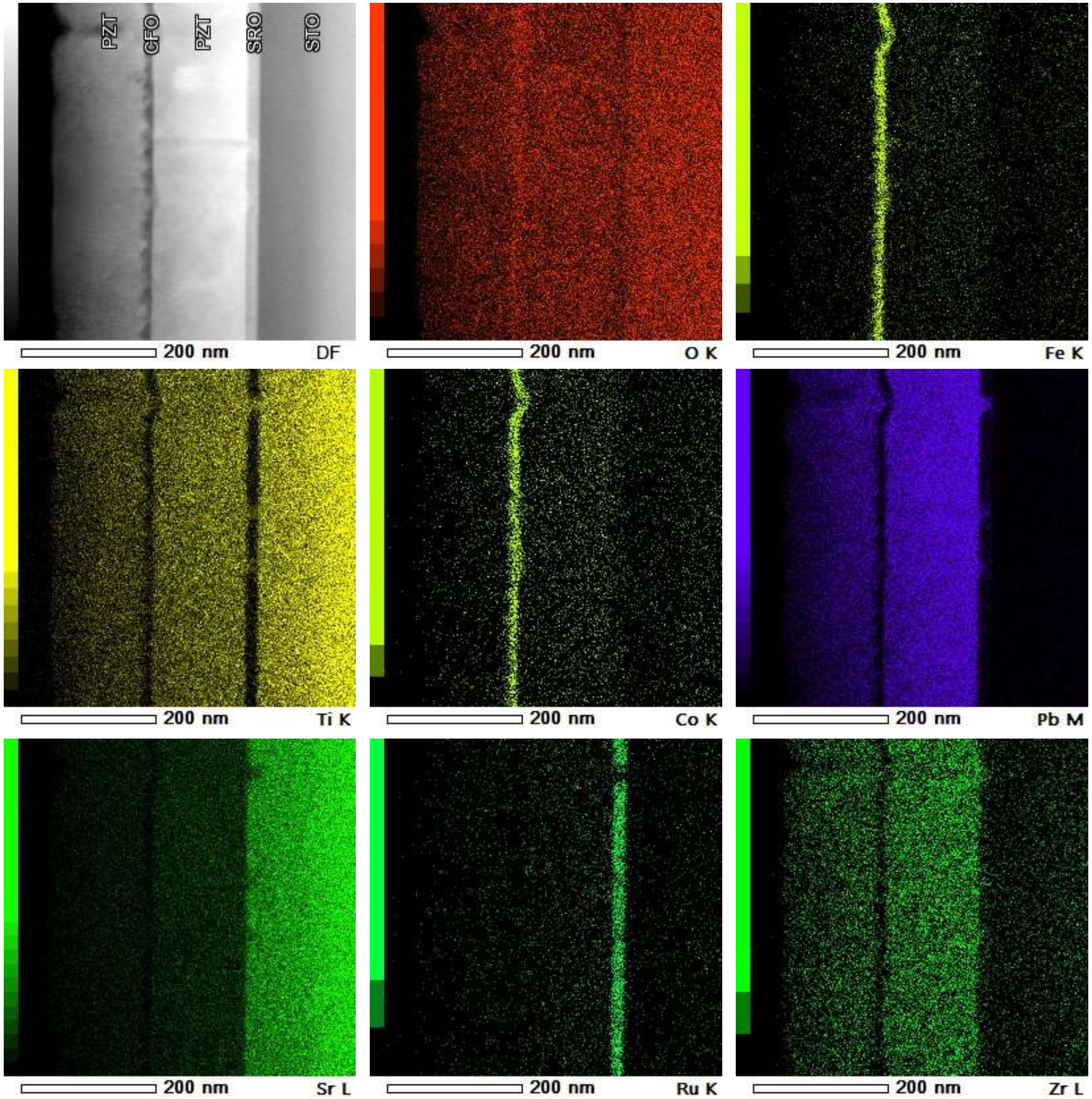
$SrRuO_3$: ^{38}Sr, ^{44}Ru, ^{8}O

$BaTiO_3$: ^{22}Ti, ^{56}Ba

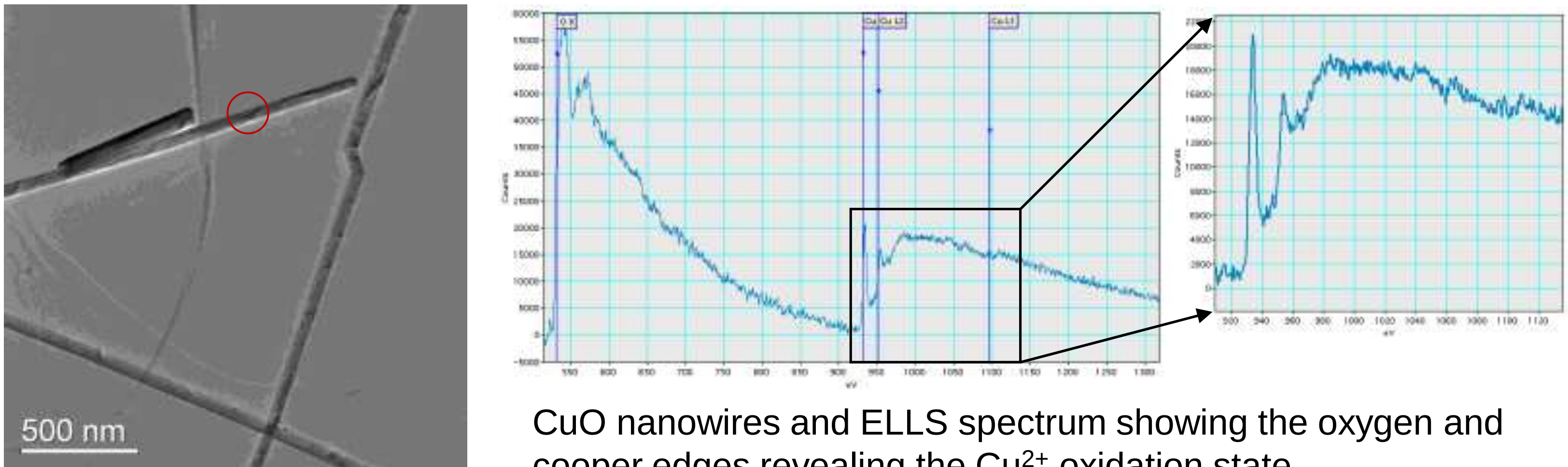
Atomic columns of **low-Z atoms** become visible!

STEM + EDS: elemental mapping

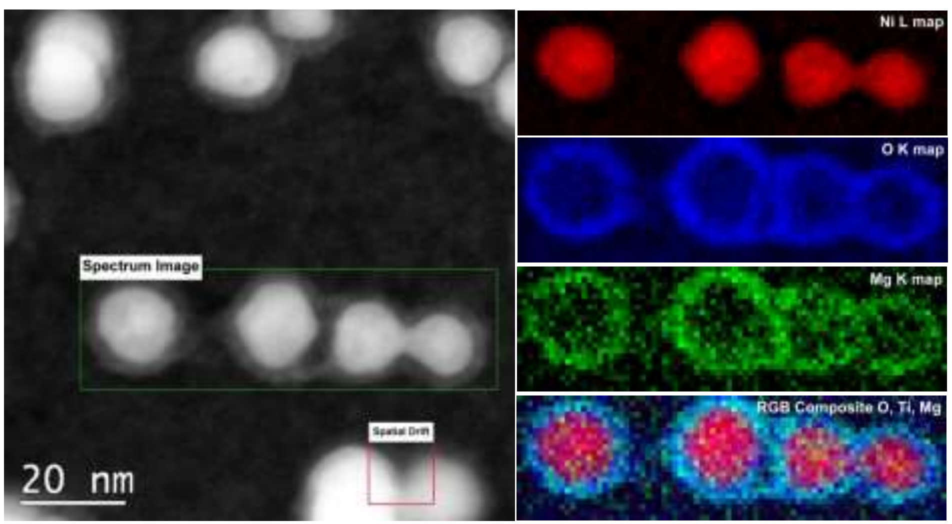
STEM-EDS mapping → data-cube containing chemical information in each image pixel → elemental maps



Electron Energy Loss Spectroscopy (EELS)

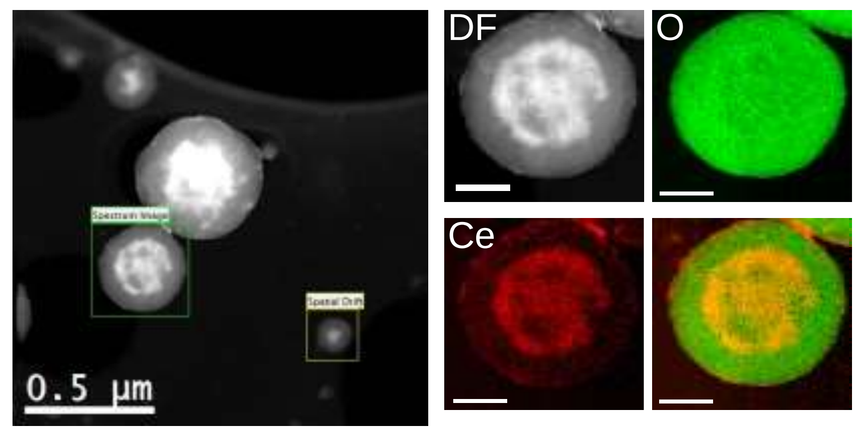


CuO nanowires and ELLS spectrum showing the oxygen and cooper edges revealing the Cu^{2+} oxidation state



Ni-MgO core-shell structures

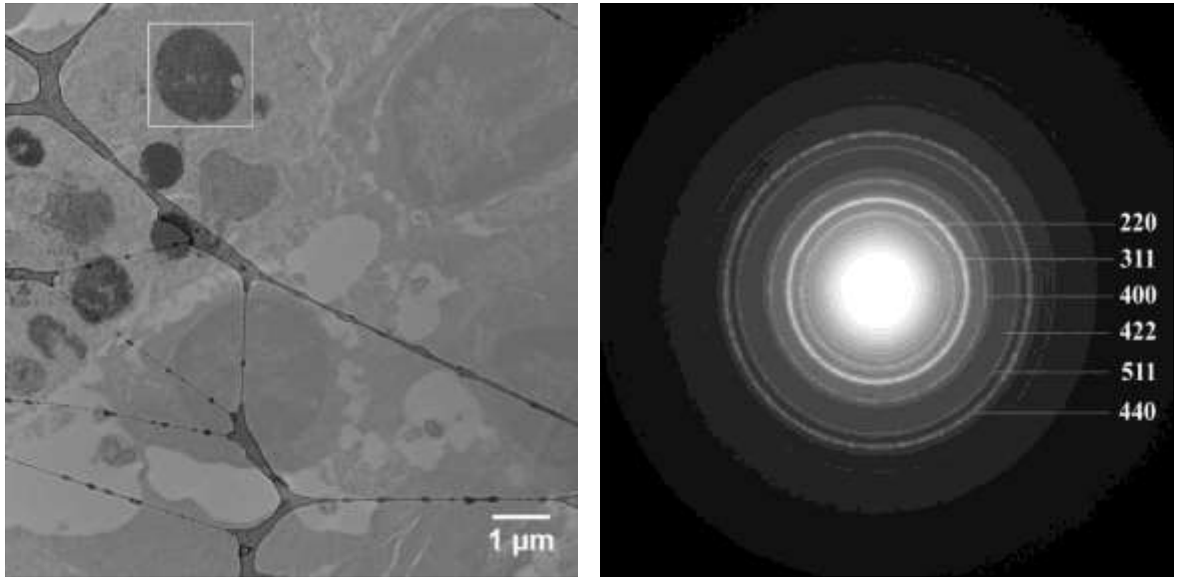
(STEM EELS Spectrum Imaging)



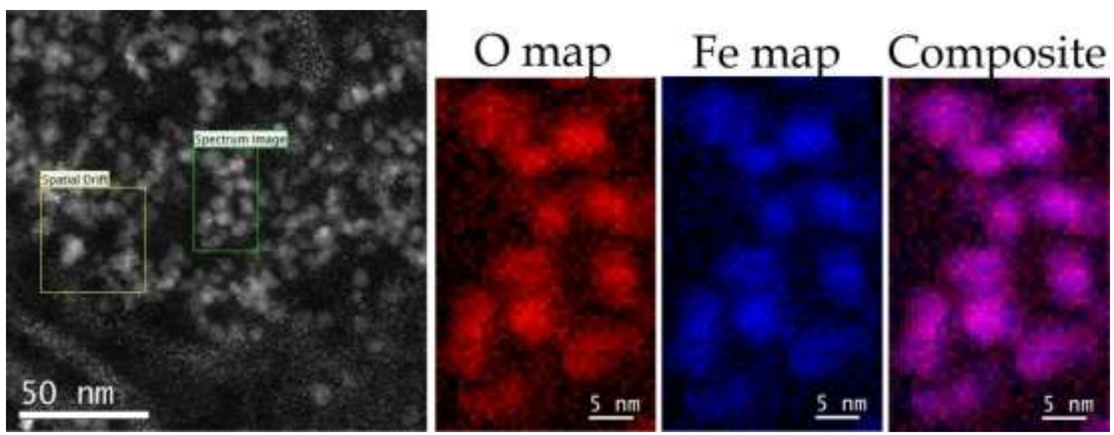
SiO_2 – CeO_2 core-shell structures

(STEM EELS Spectrum Imaging)

Electron Energy Loss Spectroscopy - Spectrum Imaging

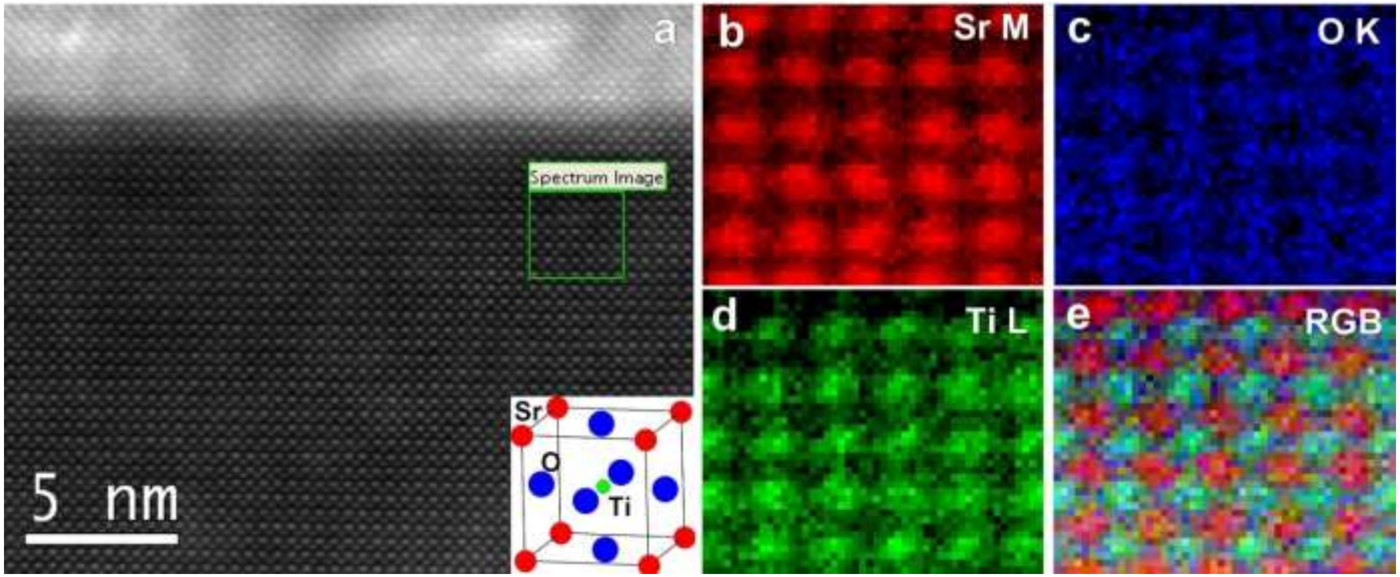


TEM image - Iron oxide nanoparticles in mouse spleen



STEM image and EELS-SI mapping: Iron oxide nanoparticles in mouse spleen

Electron Energy Loss Spectroscopy - Spectrum Imaging



Atomic resolution elemental mapping by STEM-EELS-SI

Conclusions

- EPR and TEM - powerful complementary tools for structural investigations down to atomic level of properties and phenomena in advanced materials

- NIMP-LASDAM - availability for international collaboration in open access conditions

- NIMP – devoted to national and international collaboration with academic, R&D and industrial partners in materials science for applications in materials and life sciences

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Thank you for your attention!