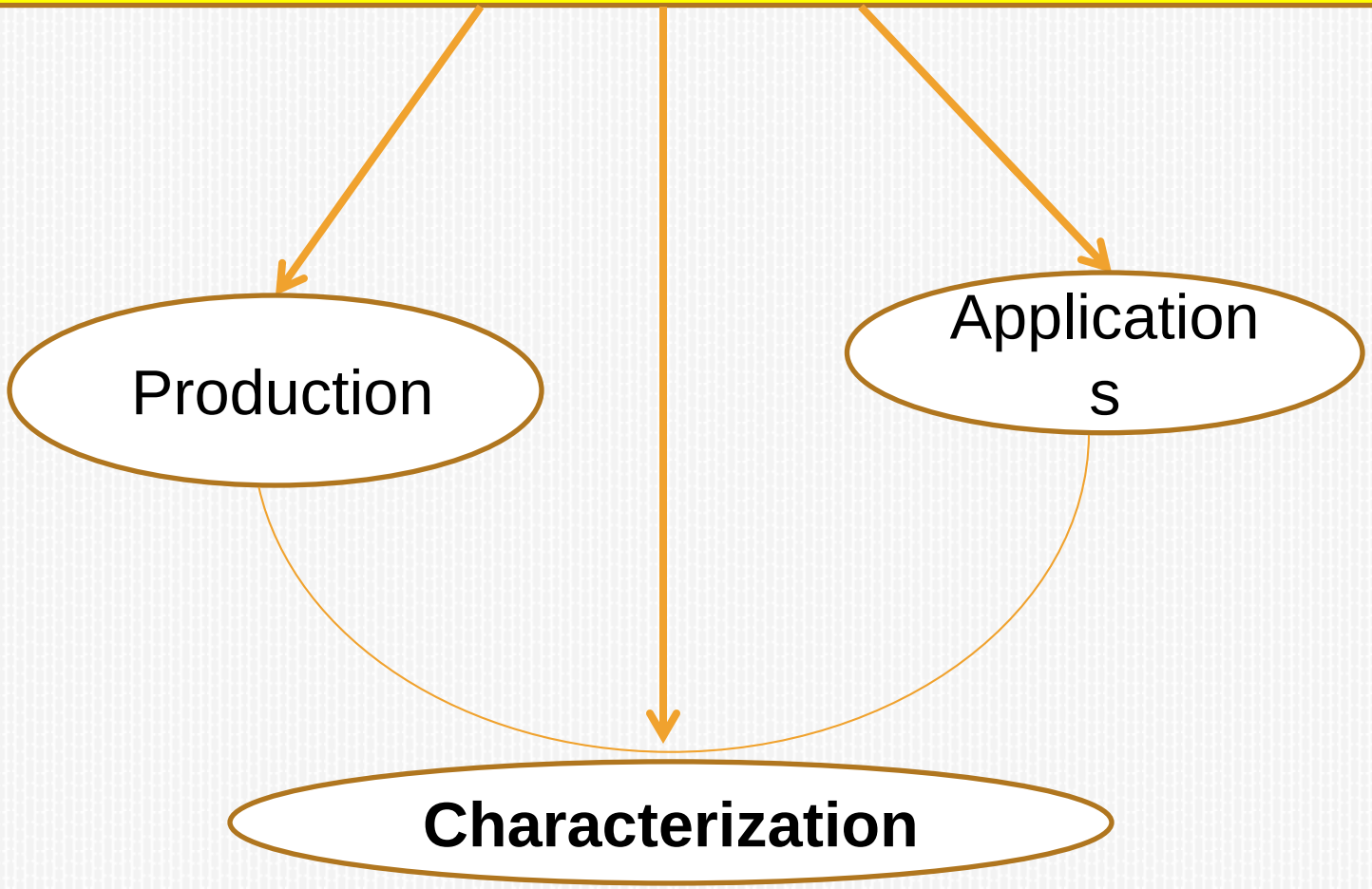
UNIVERSITY OF TRENTO - Italy

elettra

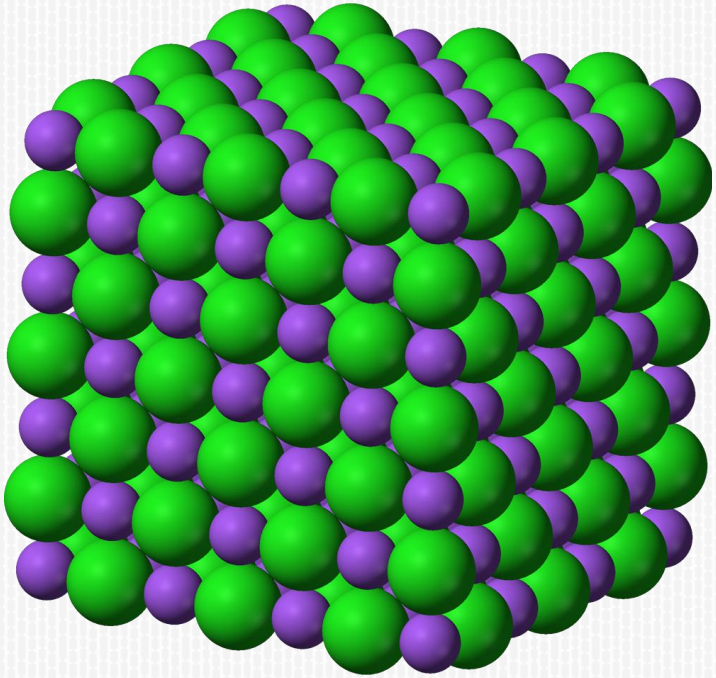
XRD analysis for ground Nanocrystalline-Defected-materials

By:
Mahmoud Abdellatief
Civil-Mechanical and Environmental engineering Department
Trento University
MCX beamline, ELETTRA, Trieste

Structural Defects in Nanotechnology



Structural Defects in Nanotechnology ??



Ideal Crystal Structure

Real crystal structure “Deviation from ideality”

Generally, real crystal structure have defects **?!!**

$$G = E - T S + P V \qquad \text{(Gibbs free energy)}$$

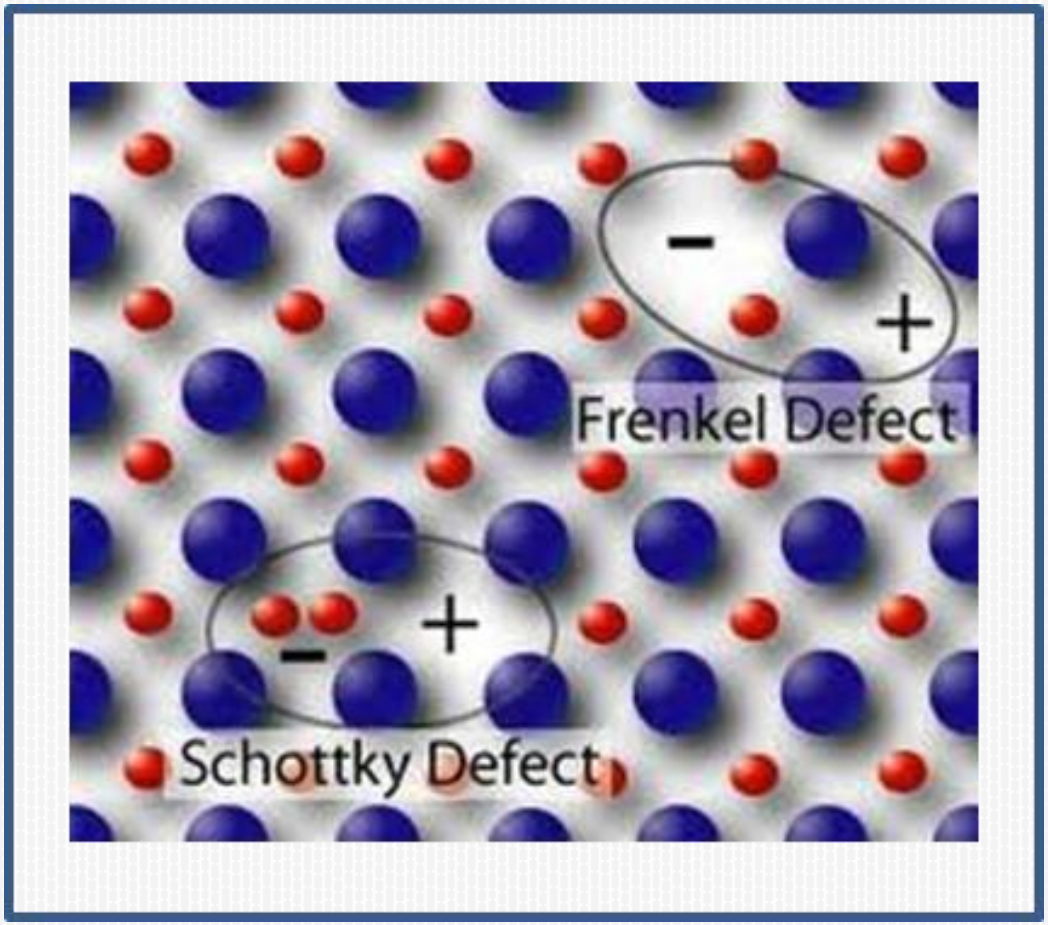
E: Crystal internal energy
T: Temperature
S: Entropy
P: Pressure
V: Volume

Natural system likes to stay with less energy (i.e. within a certain rang increasing S decreases G)

Structural defects classes ?

Point Defects

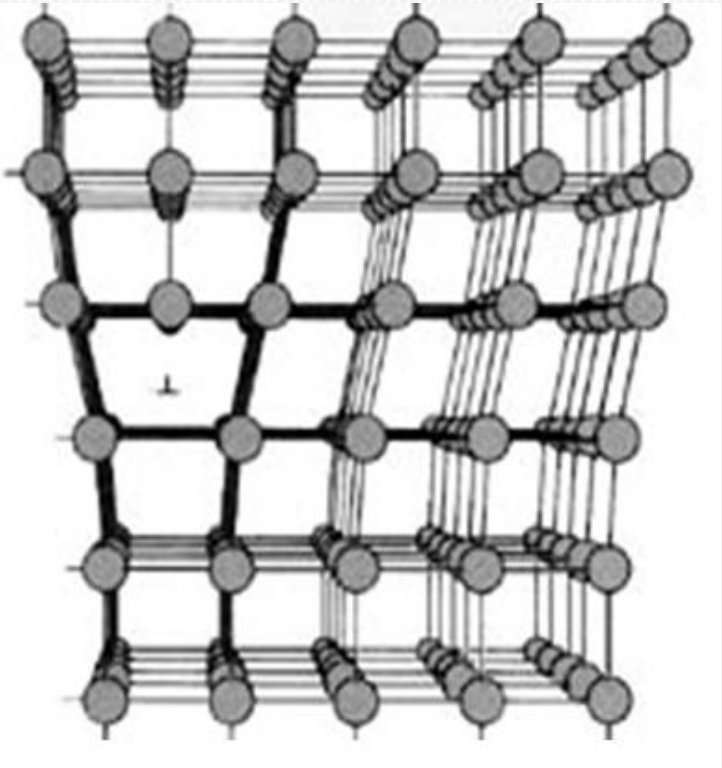
(e.g. Vacancy, Frenkel, Schottky, Interstitial)

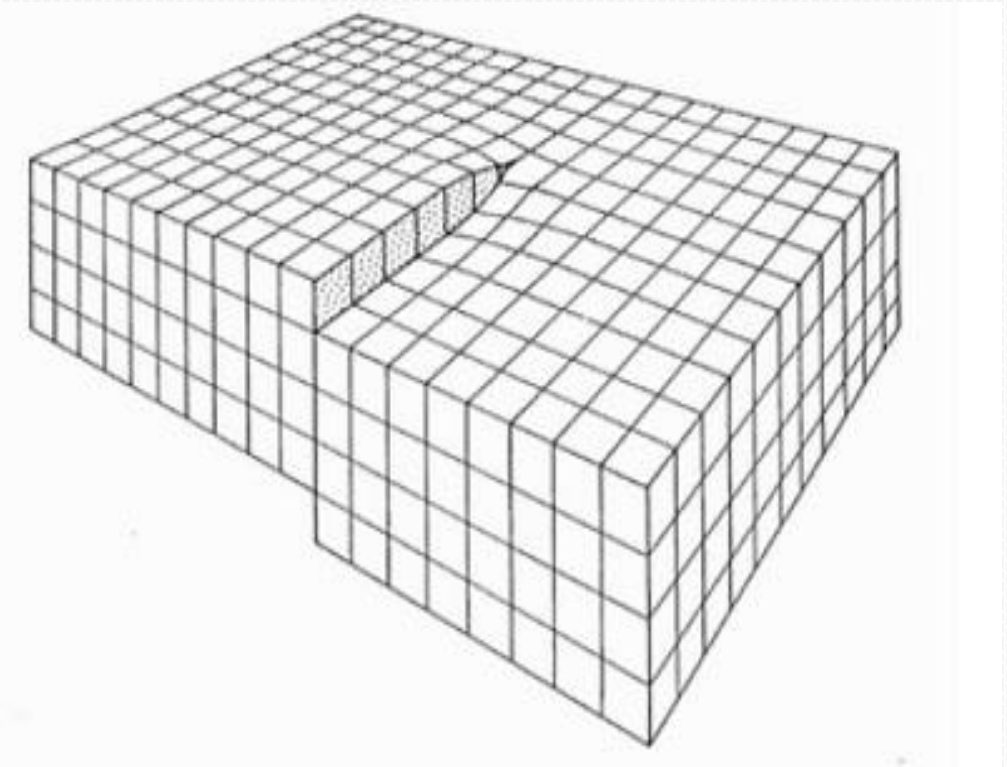


Structural defects classes ?

Line Defects

(e.g. Edge, Screw)

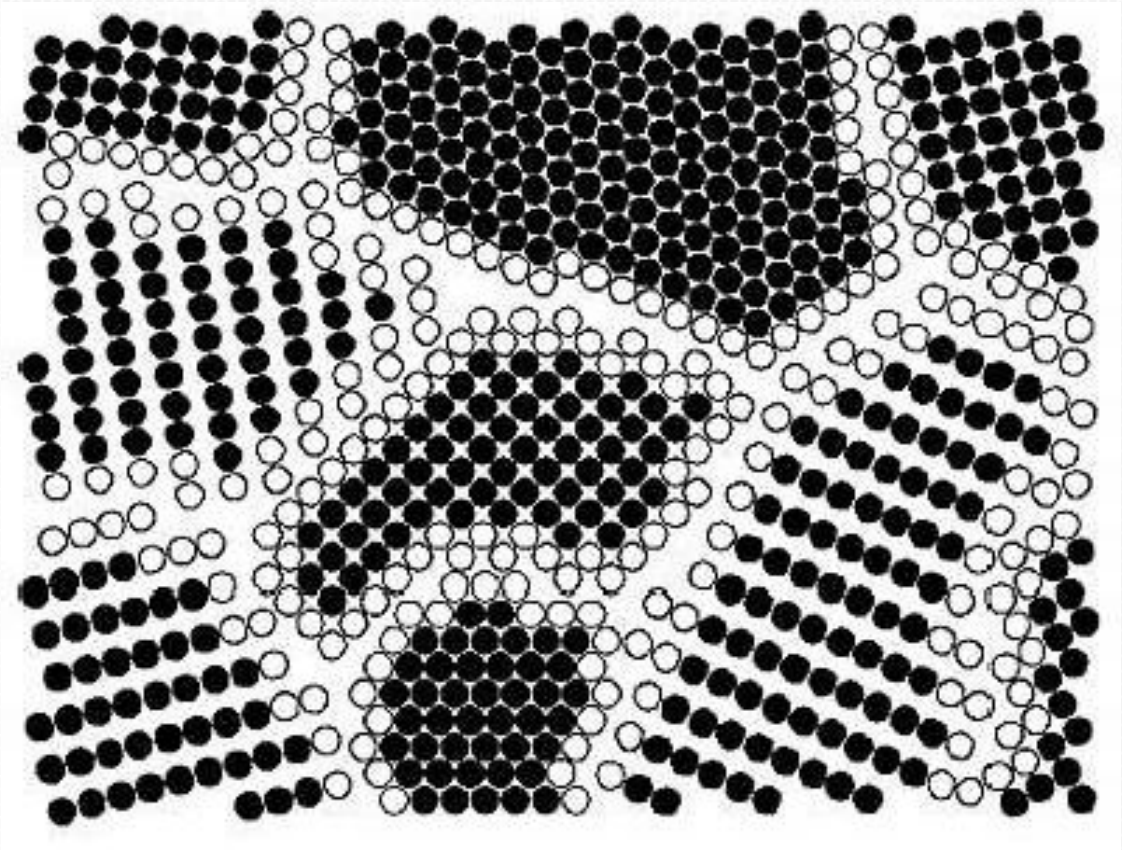


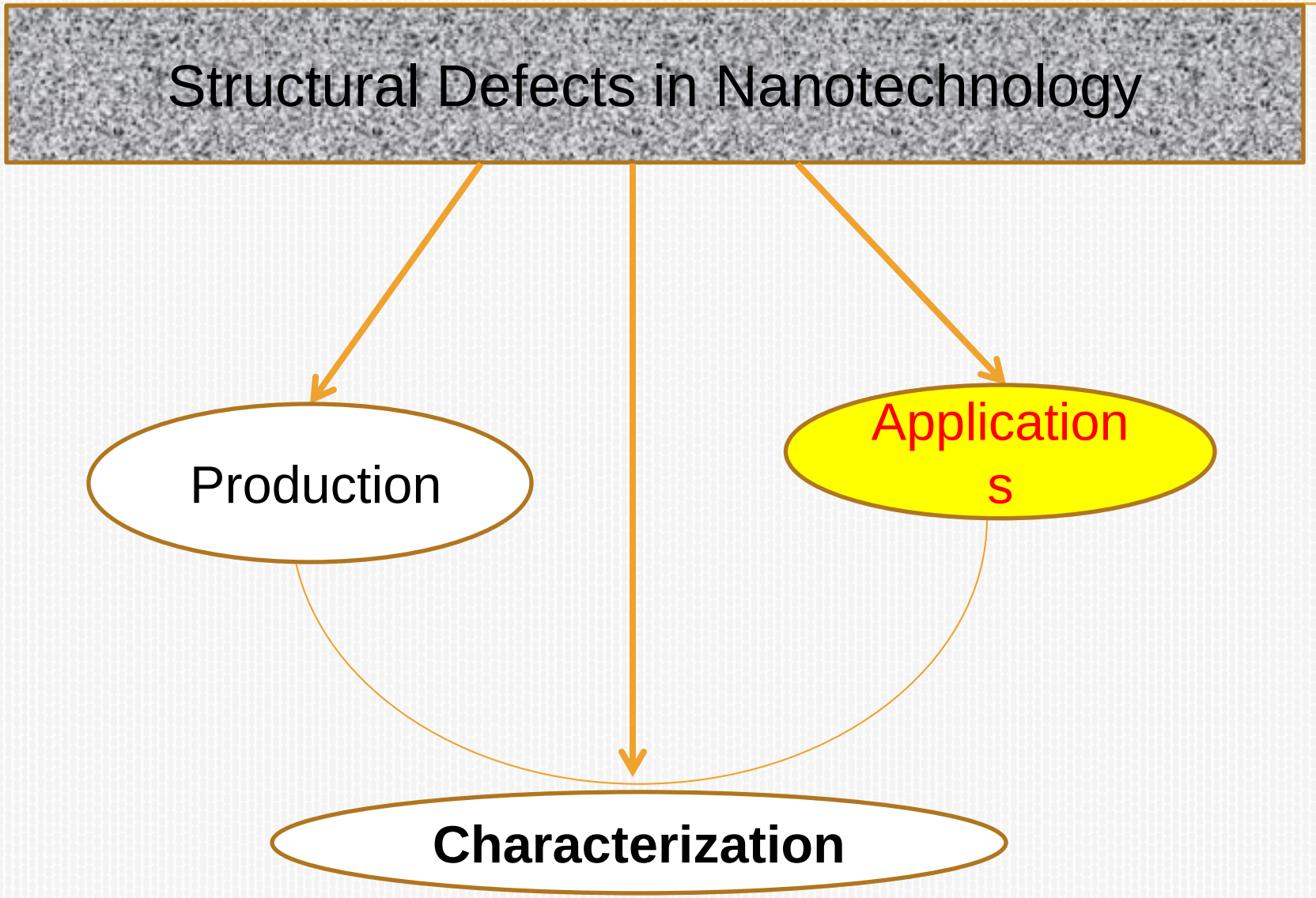


Structural defects classes ?

Two Dimensions Defects

(e.g. Grain boundaries, Twinning)



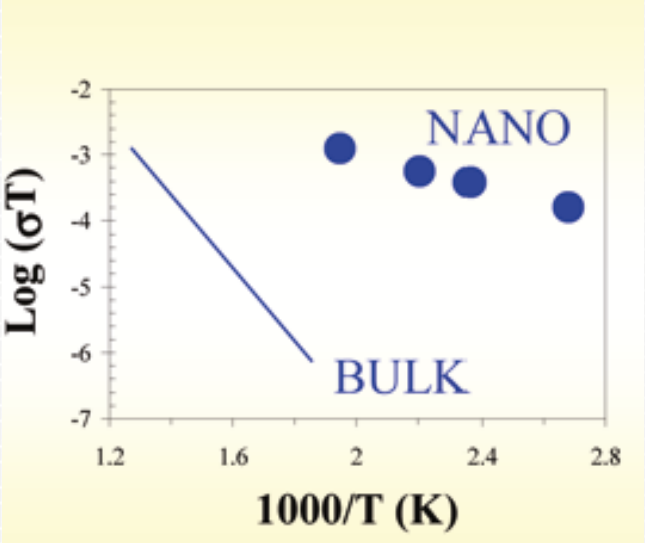

Structural Defects in Nanotechnology
Production
Applications
Characterization

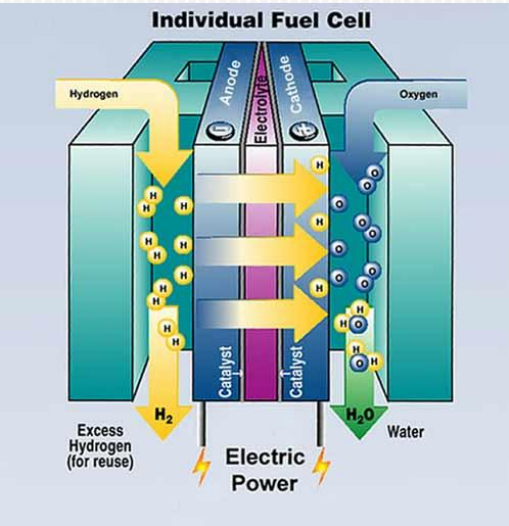
Applications based on structural defects??

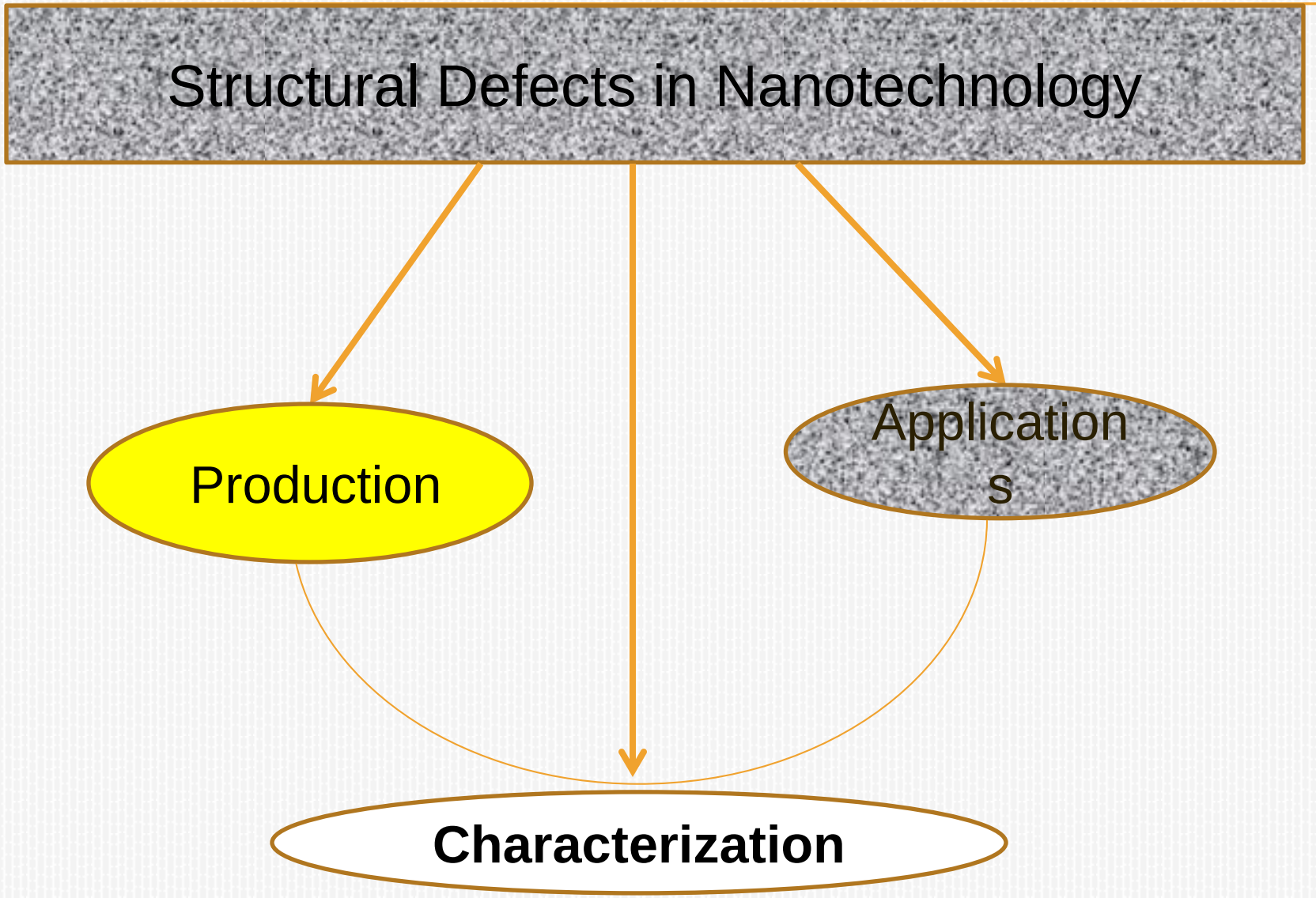
"**Ionic transport** and **diffusion** based applications strongly sensitive to structural defects"

1. Solid electrodes/electrolytes (Batteries)
2. Crystal growth stability
3. Hydrogen diffusion (hydrogen storage applications)
4. Catalysts

etc….






Structural Defects in Nanotechnology
Production
Application
s
Characterization

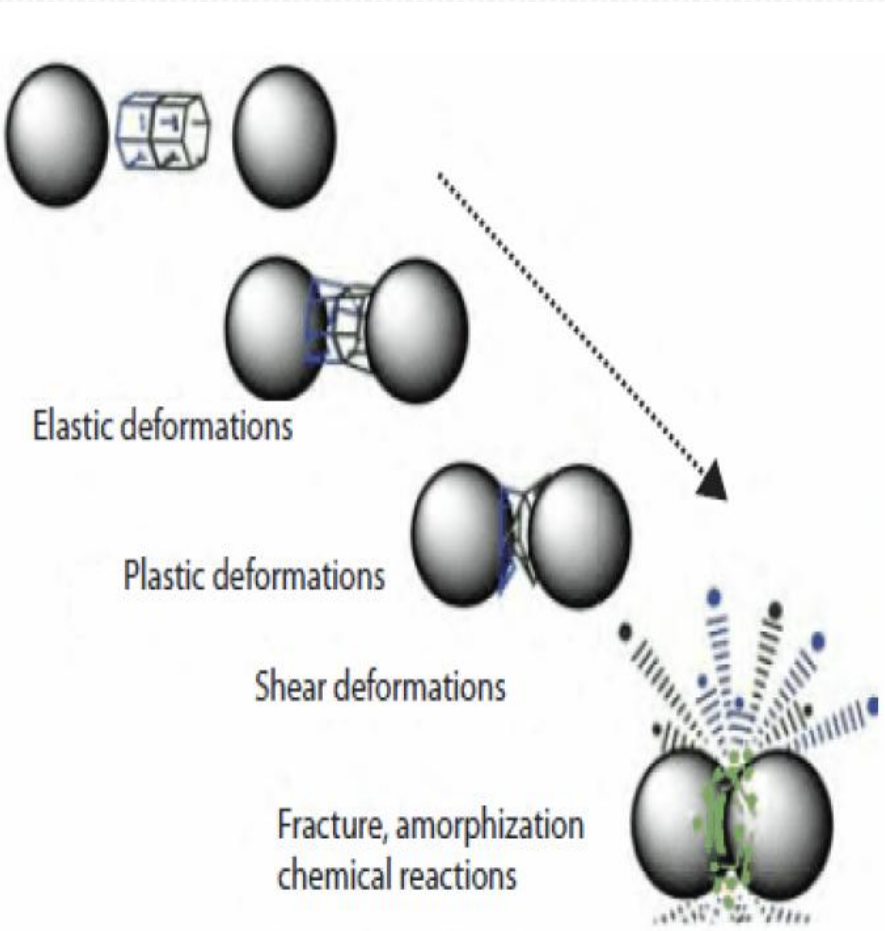
Production of nanocrystalline structurally defected crystals ??

Powder Production by **Ball milling** Technique (*top-down route*)

Optimization fun!!

Milling Parameters

1. Milling machine
2. Speed of rotation
3. Vial and balls materials
4. Vial's shape
5. Milling time
6. Ball to powder weight ratio
7. Powder mechanical and thermal properties
8. Lubricant
9. Pause time Vs. grinding time
10. Milling atmosphere



Main structural parameters characteristics from ball milling

Why Milling Optimization??

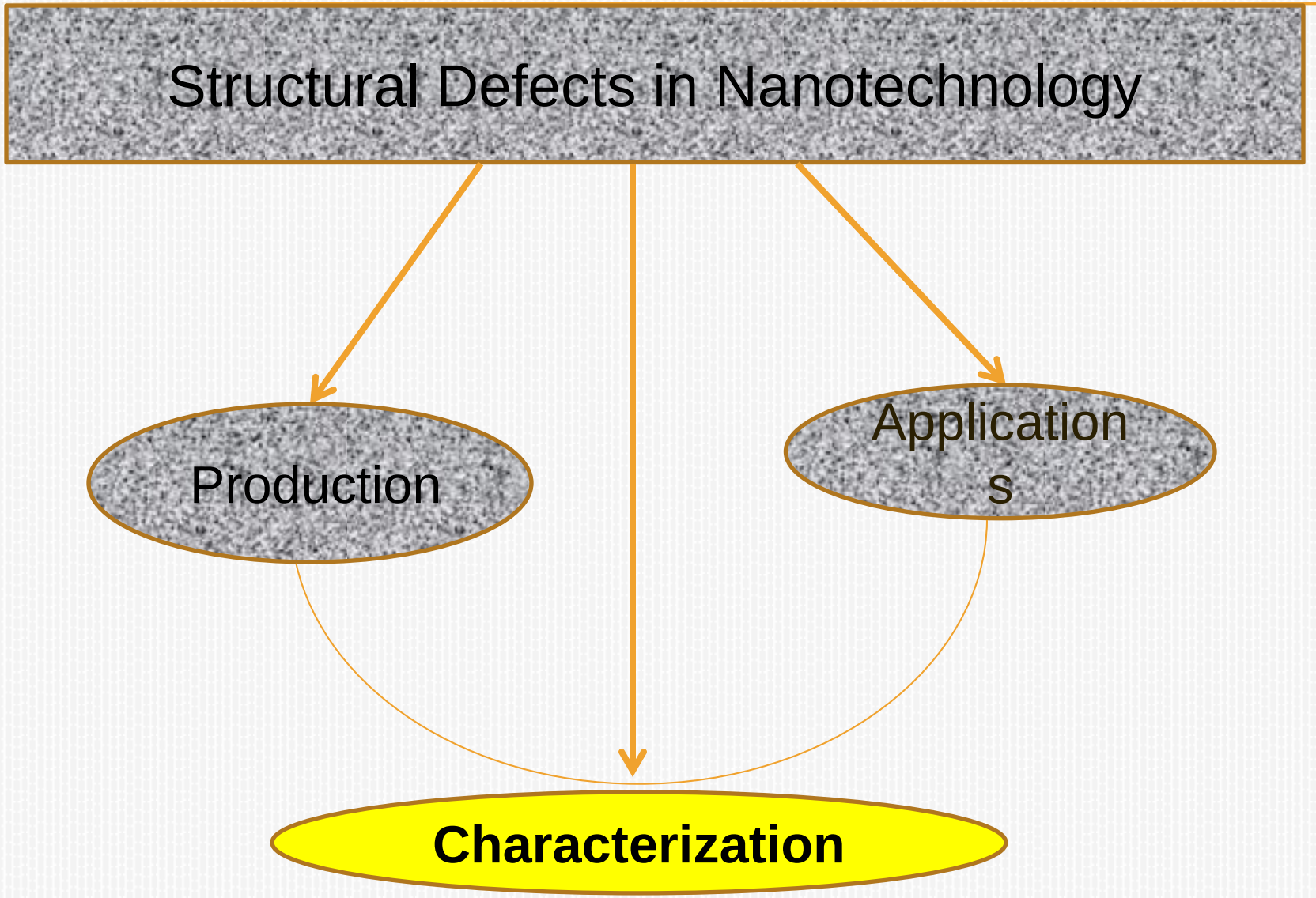
Both have a convergence limit

Crystallite size

Dislocations density

Further milling might not be advised!!

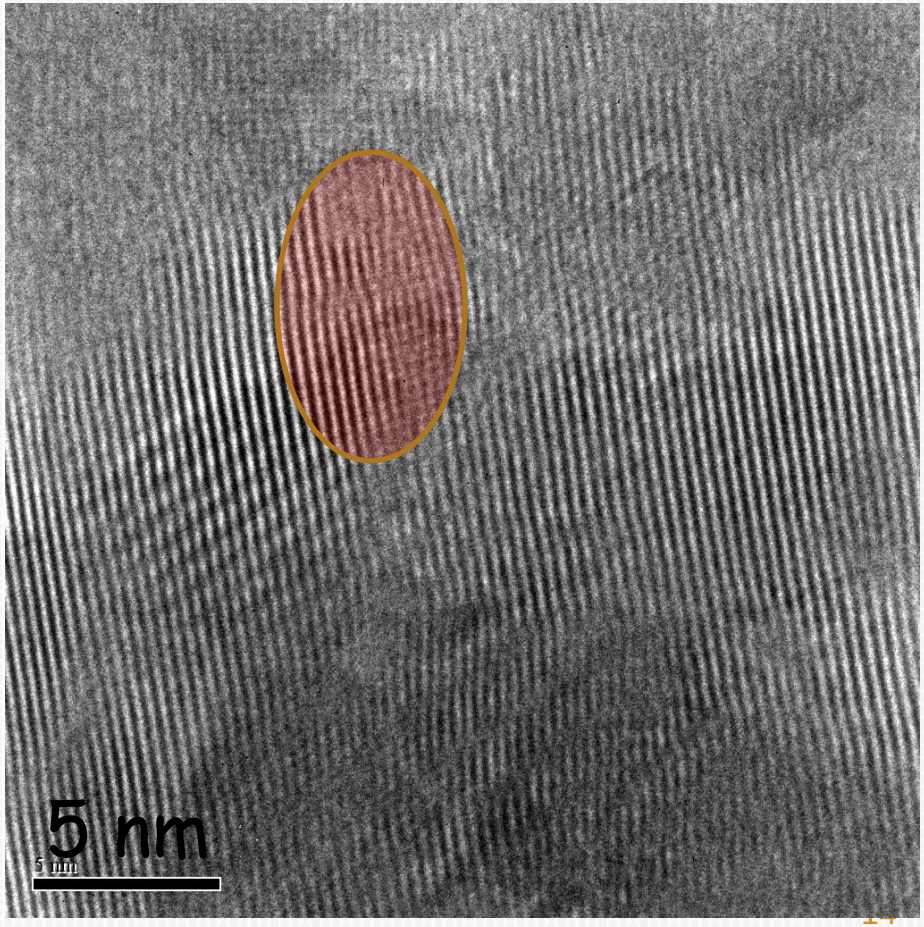
Ground Powder Homogeneity


Structural Defects in Nanotechnology
Production
Applications
Characterization

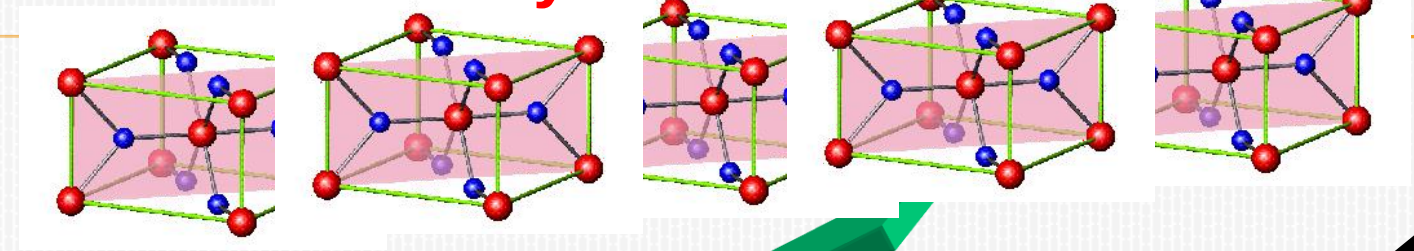
Characterization Techniques

TEM
(Quantitative analysis of dislocation)

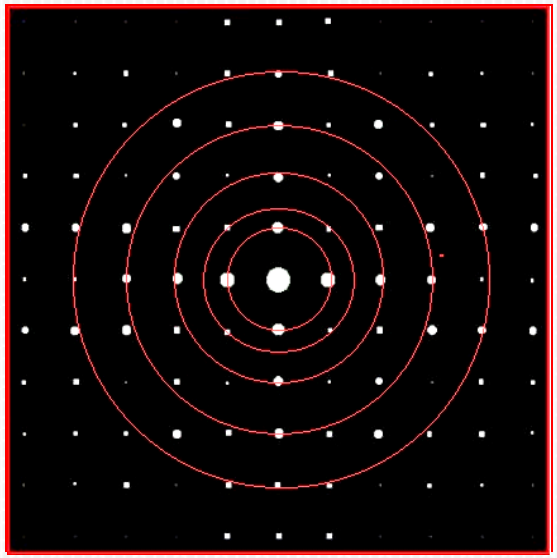
- Resolution
- No. of Images
- high dislocation density ρ is limited

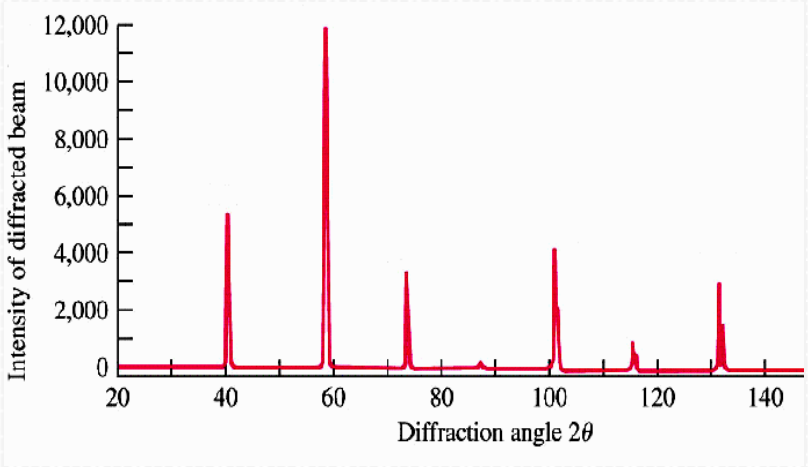


XRD-LPA Approach for structural analysis

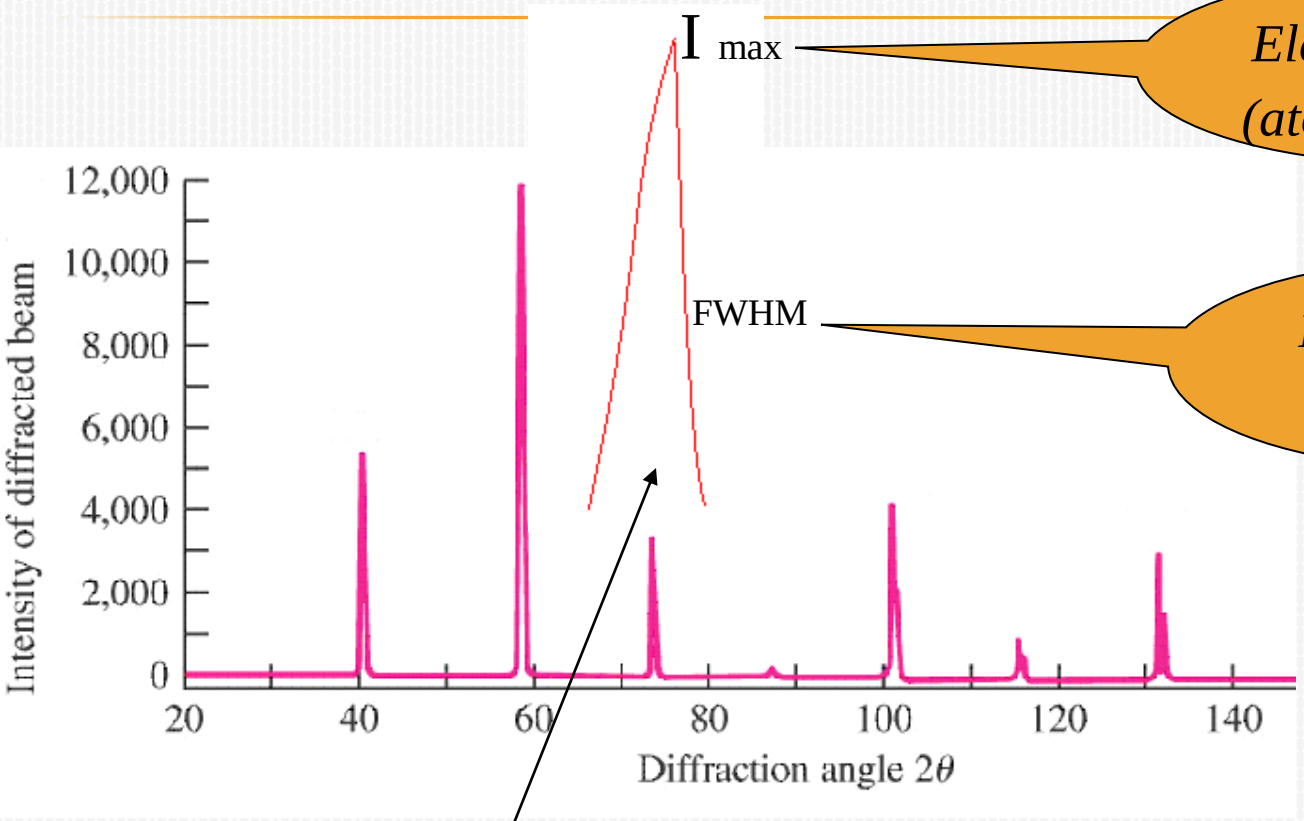


$\lambda = 2\ d \sin\Theta$





INFORMATION FROM DIFFRACTION PATTERN



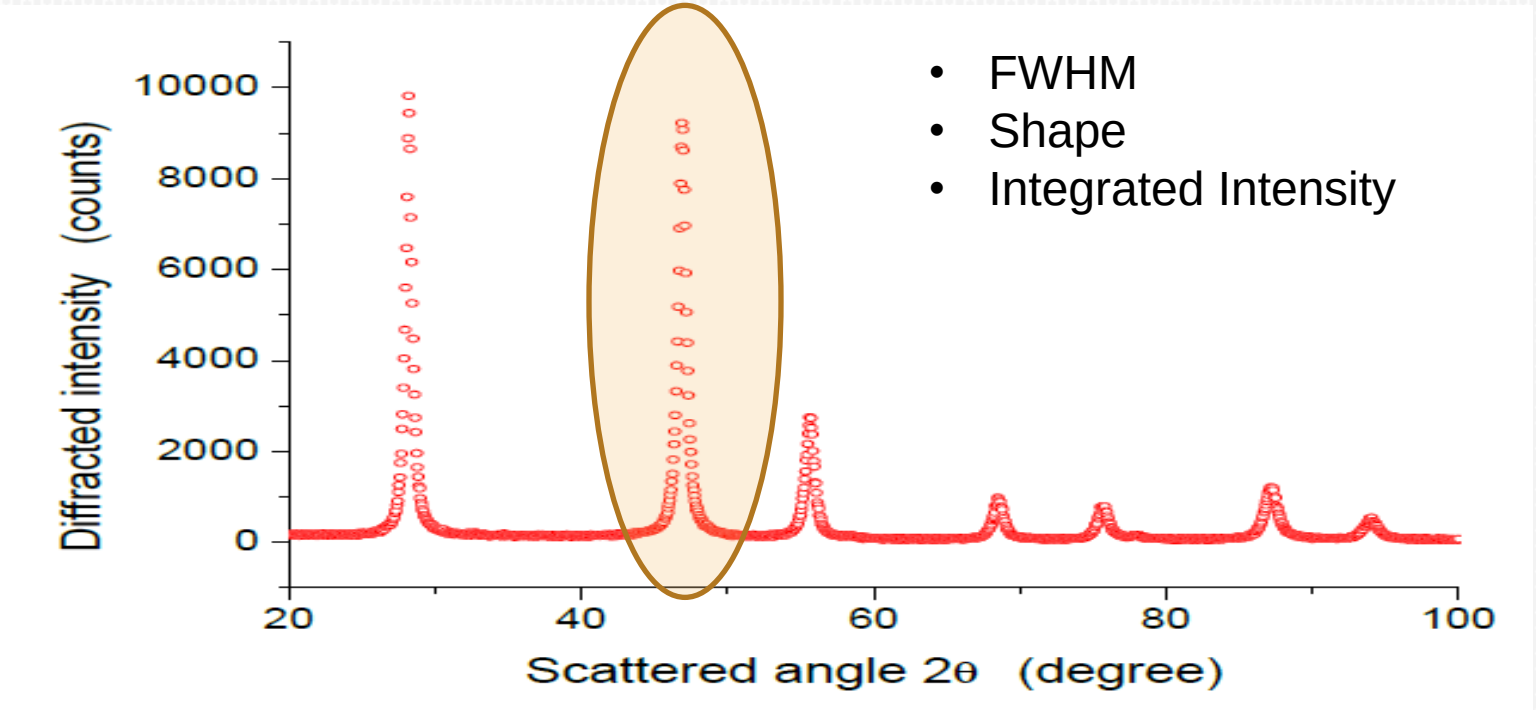
Electron density (atomic position)

Micro structure (size, strain,…

Shape and size of unit cell,…

XRD-LPA Approach for structural analysis

- Effective at high ρ
- Inhomogeneity insensitive (Long rang order technique)



Common methods of XRD-LPA

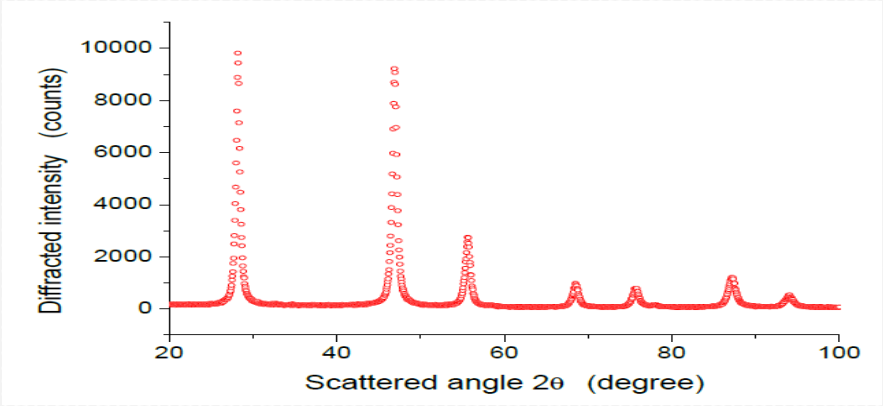
Rietveld/ Whole Powder Pattern Fitting (WPPF)

WPPF Strategy

- Quick
- Effective in many studies

$$I(2\theta) = I_{bg} + S \Sigma m L P |F|^2 \ .....$$

Experimental pattern → Arbitrary function → Profile parameters fitting



Non LLST fit

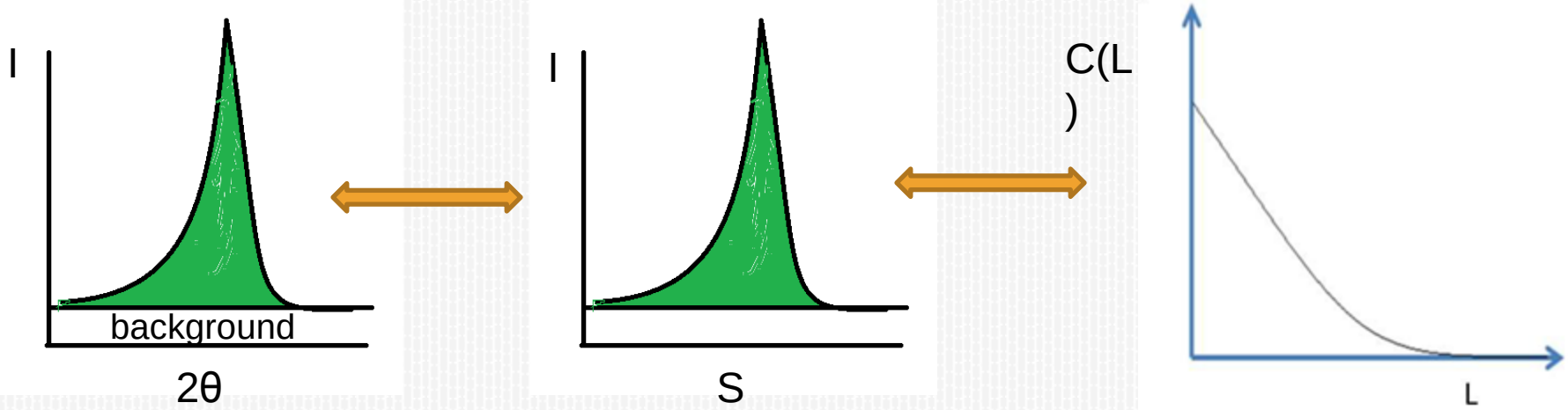
Width, shape, I.I., etc.

Microstructural parameters

BUT Reliability !!

Loosing contact with experimental data

Possible Solution
Whole Powder Pattern Modeling WPPM

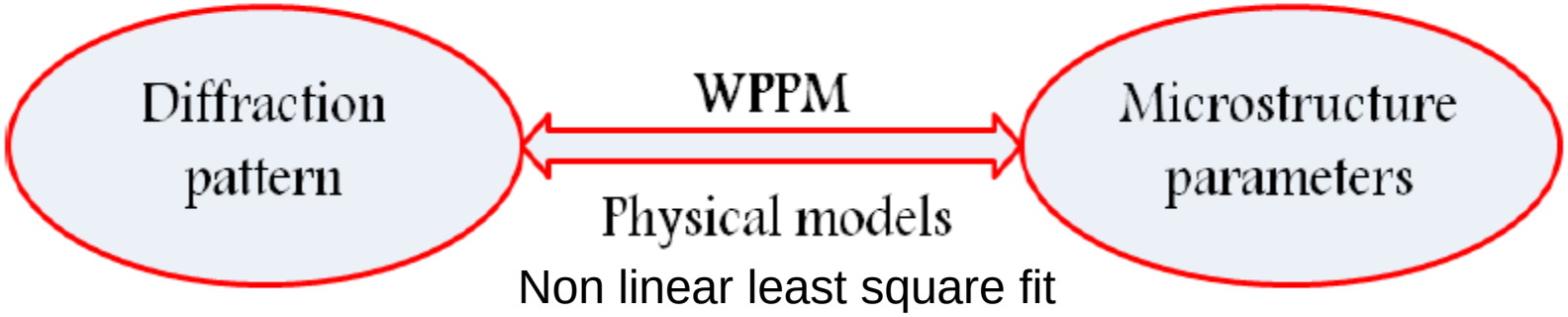


$$I(s) = I^{IP}(s) \otimes I^{S}(s) \otimes I^{D}(s) \otimes I^{F} \otimes I^{APB}(s) \otimes \ldots.$$

$$I(s) = k(s) \int C(L) \exp(2\pi i L s) dL$$

$$C(L) = A^{IP}(L) \,.\, A^{s}(L) .\, A^{D}(L)$$

$$C(L) = A^{IP}(L) \cdot A^{S}(L) \cdot A^{D}(L)$$



Direct contact of experimental pattern via physical structural model without any structural constrains

XRD-LPA-WPPM for ball milled Fluorite CaF_2

Experimental

Milling

- **Steel Vials and balls**
- **Milling time (4, 8, 16, 32, 64) hours**
- **Speed 400 rpm**

Main WPPM Structural contributions

Fixed

- Instrumental

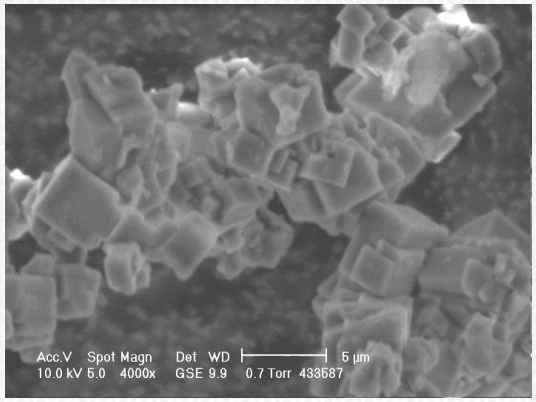
Refined

- Size by lognormal distribution (mu, sigma)
- Dislocations model (Edge/Screw) and ratio

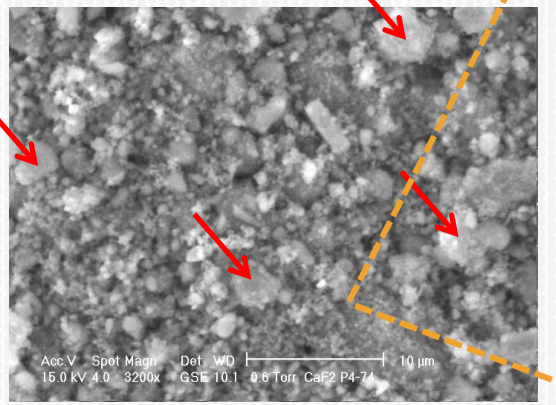
Several ground fractions at short milling times

Milling

unmilled

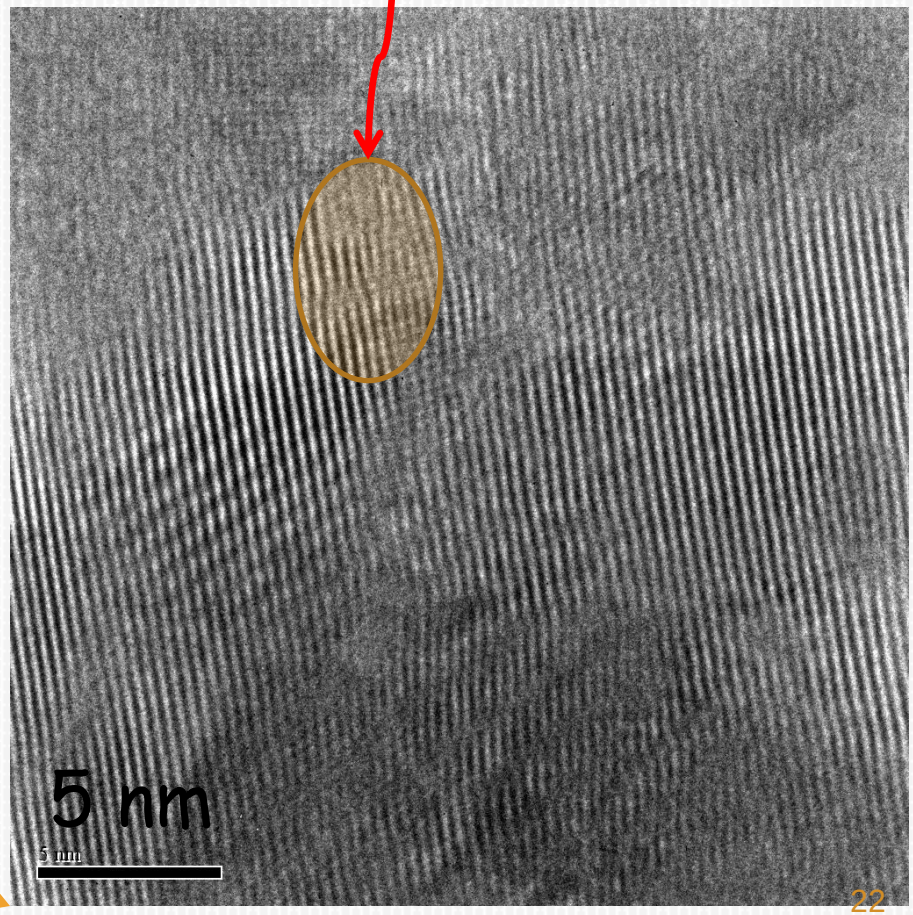


0 h b.m.



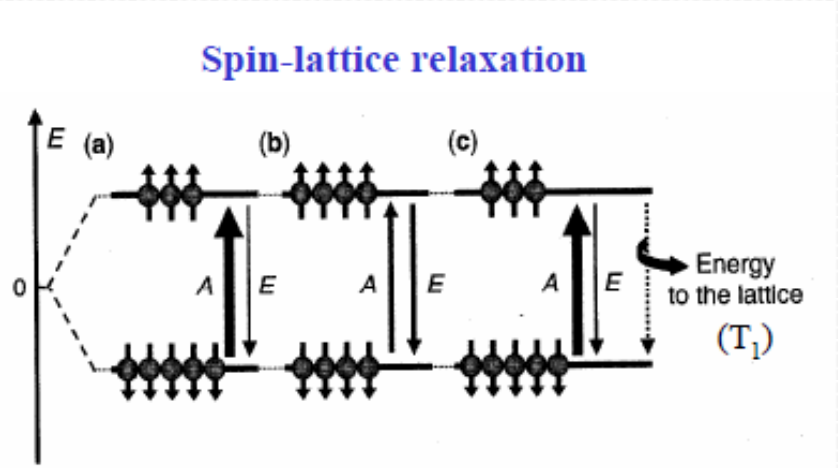
8 h b.m.

dislocations

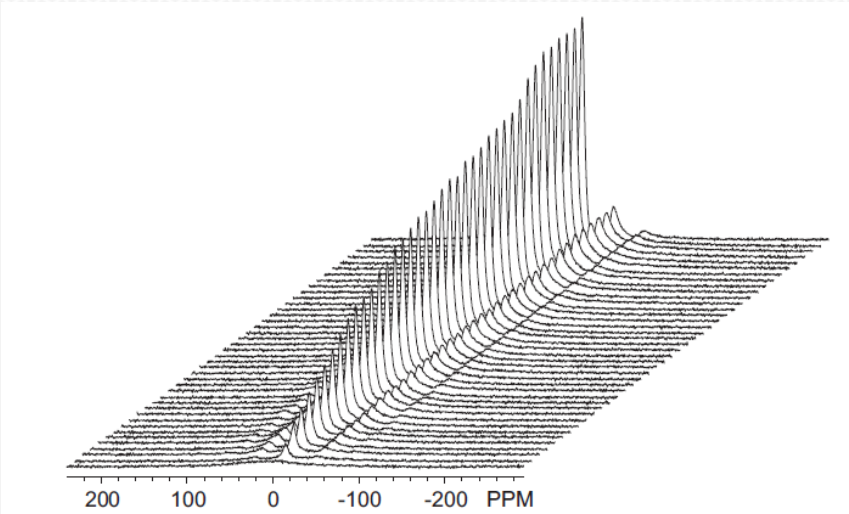


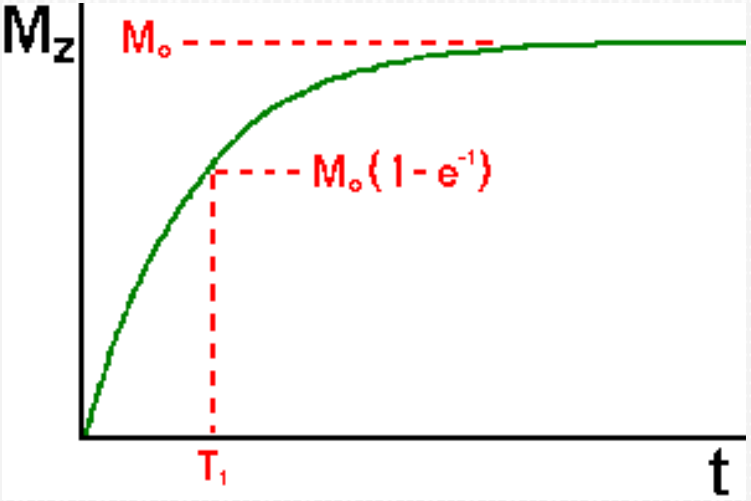
Possible solution to get the full structural picture

- Combining XRD with a short range order technique (e.g. NMR) as a local



Size, dislocations, grain boundaries, ….

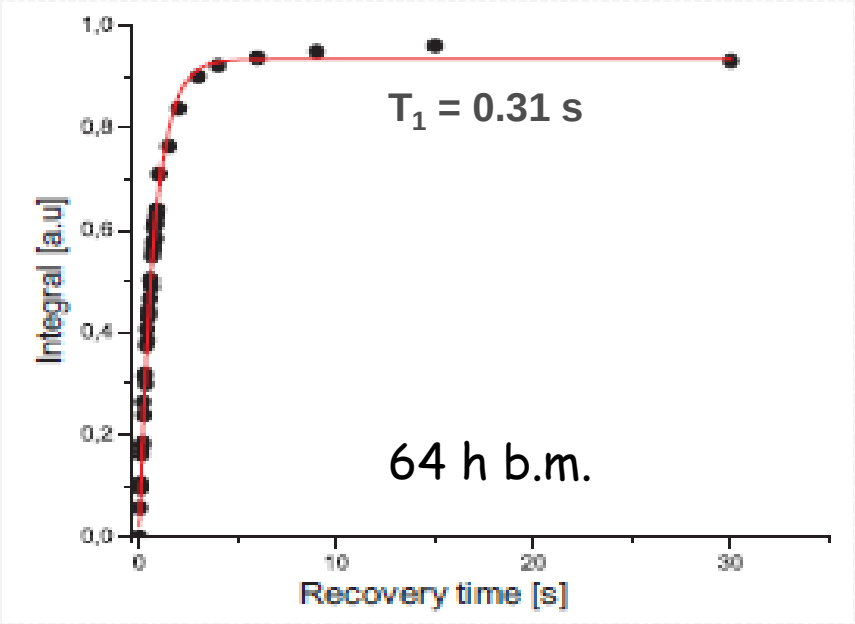


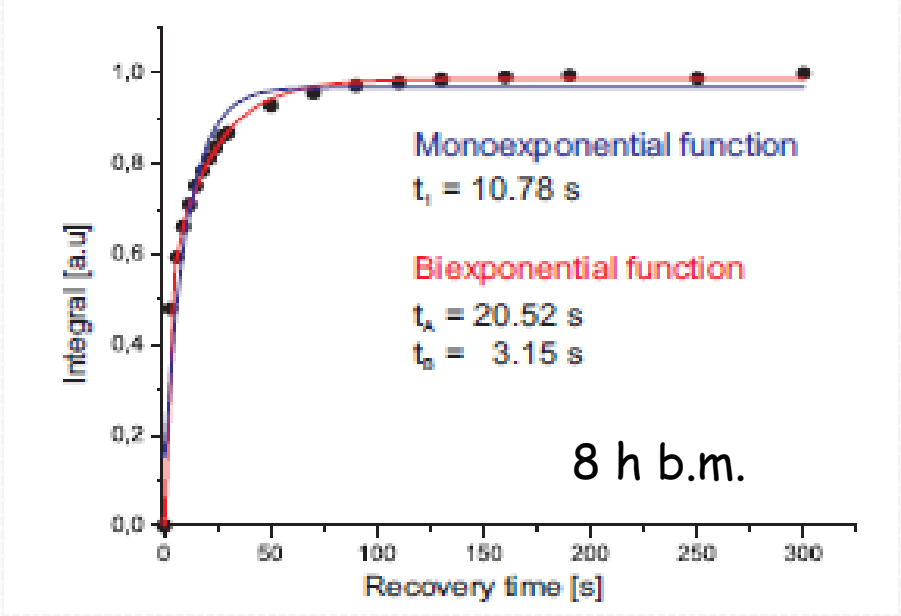


$$M_z(\tau) = C\left[1 - \exp\left(-\tau/T_1\right)\right]$$

Simultaneous XRD/WPPM-NMR/T1 analysis (PM2K program)

Pristine CaF_2: T_1 = 54 s)





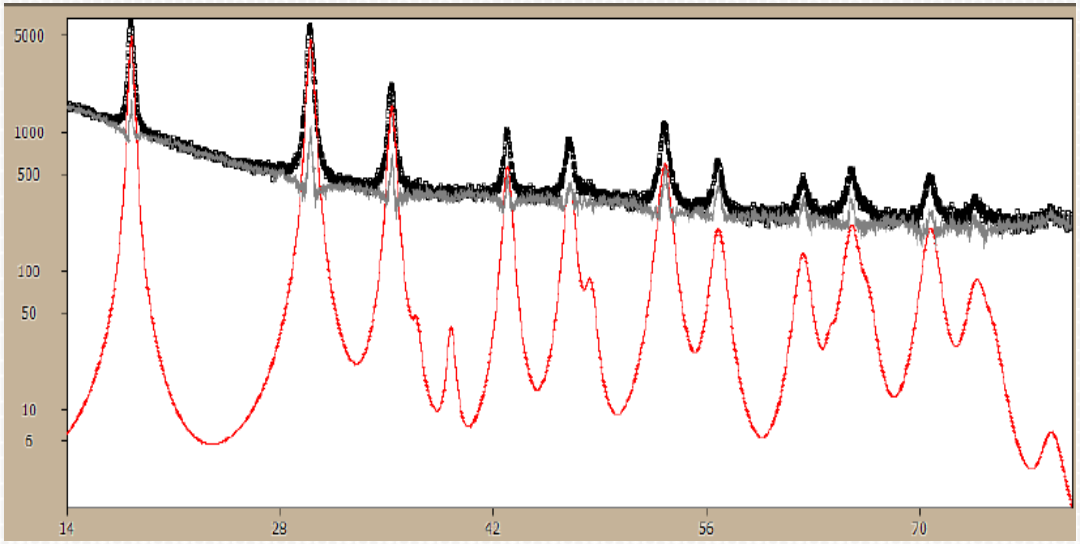
$$M_z(\tau) = C\left[1-\exp\left(-\tau/T_{1A}\right)\right] + (1-C)\left[1-\exp\left(-\tau/T_{1B}\right)\right]$$

$$M_z(\tau) = C\left[1-\exp\left(-\tau/T_{1A}\right)\right] + (1-C)\left[1-\exp\left(-\tau/T_{1B}\right)\right]$$

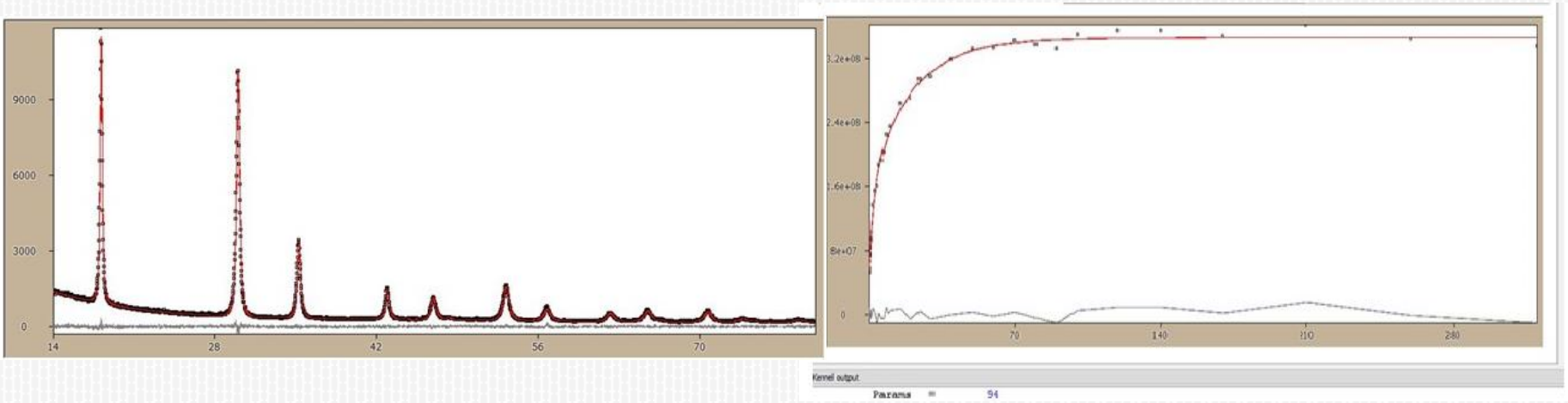
Simultaneous XRD/WPPM-NMR/T1 analysis (PM2K program)

Samples: (**4, 8, 16 h**)Two-phase Model

C ∝ less defected (larger crystallite) fraction (A, long T_1)
(1-C) ∝ highly defected (smaller crystallite) fraction (B, short T_1)

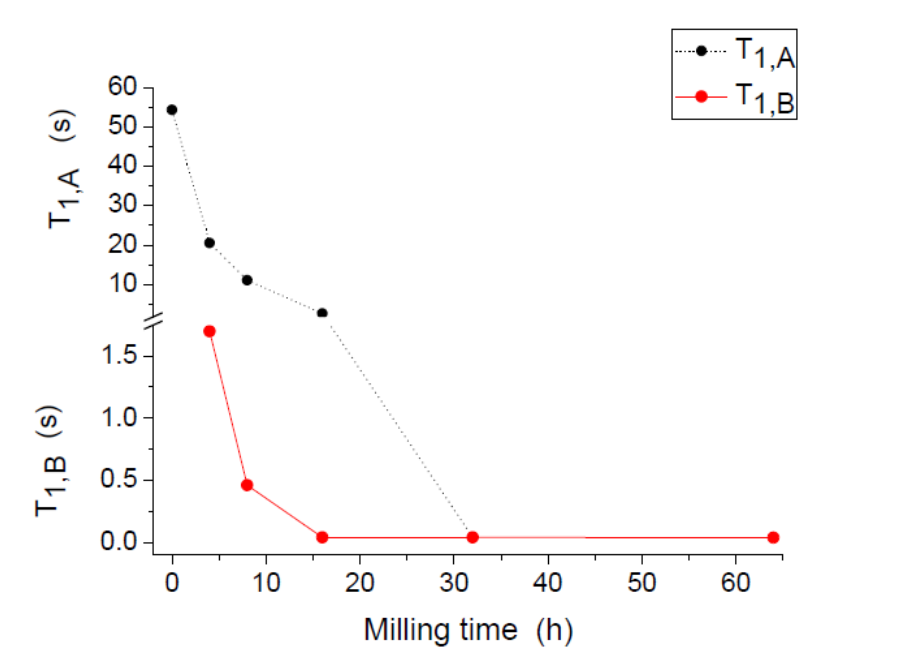


Simultaneous XRD/WPPM-NMR/T1 analysis (PM2K program)

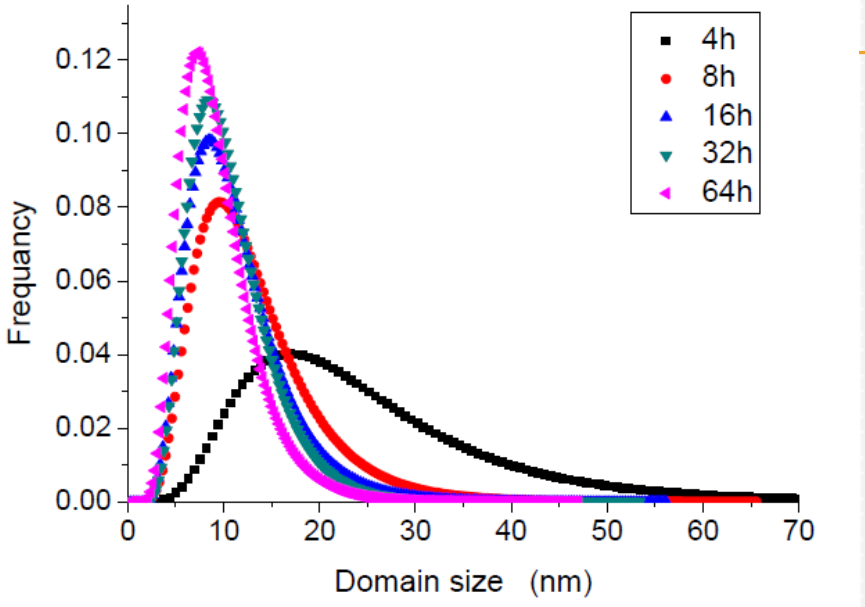


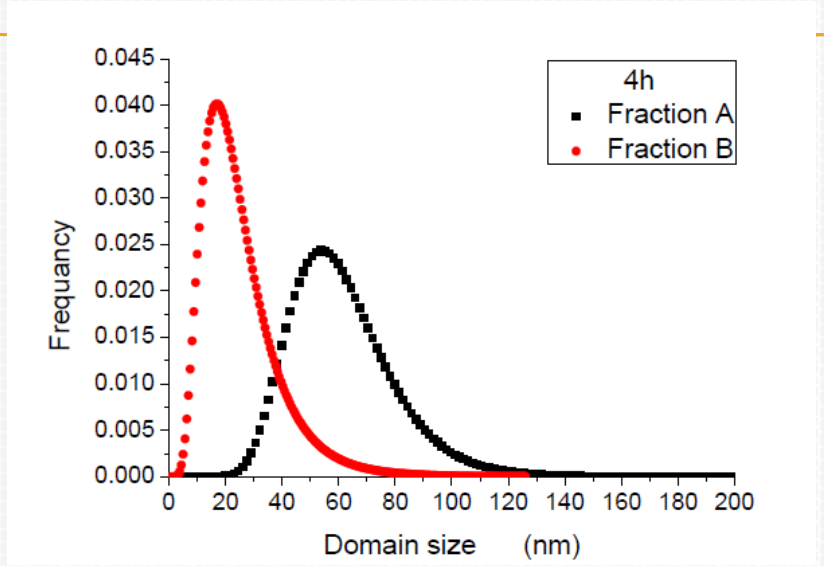
T1 evolution

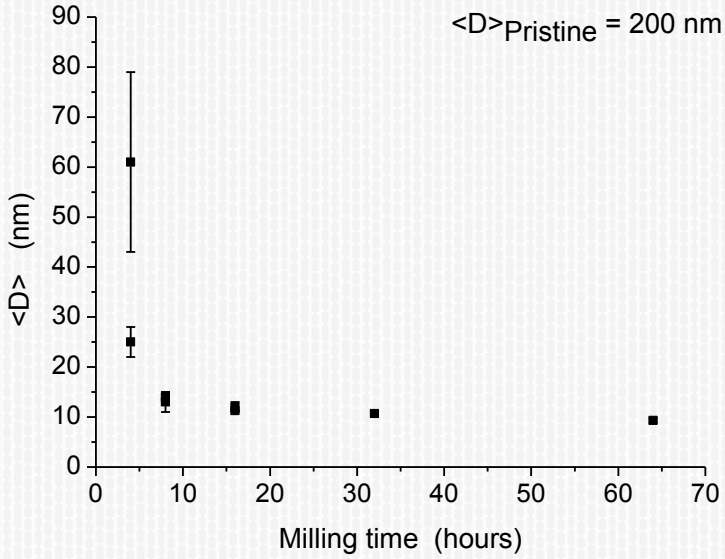
More ground…..Shorter T1 (i.e. faster lattice energy absorption)



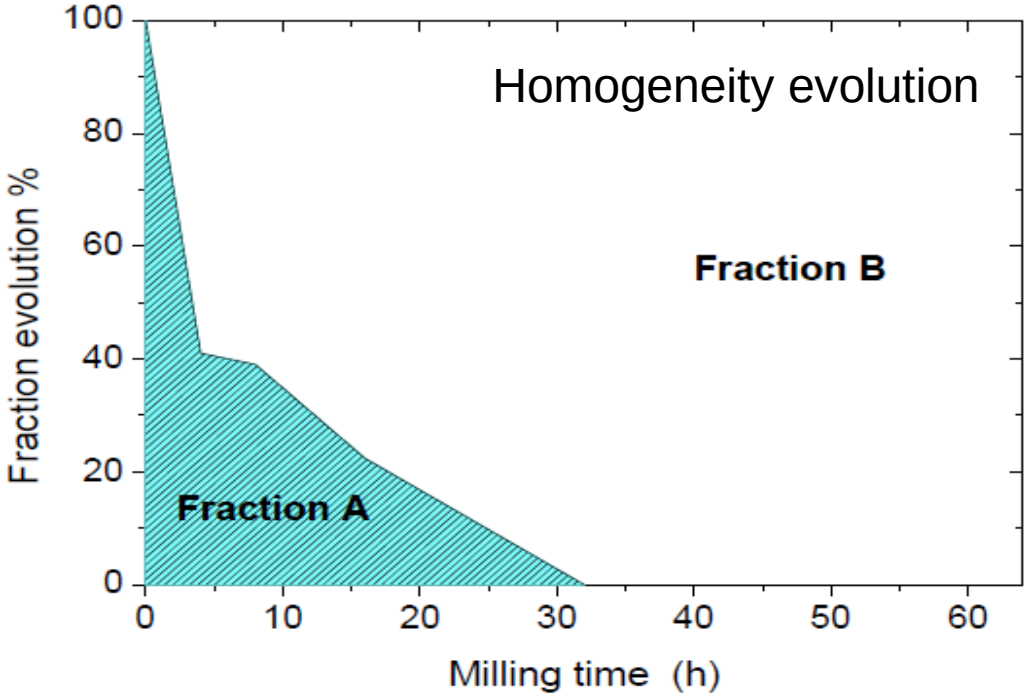
Size evolution

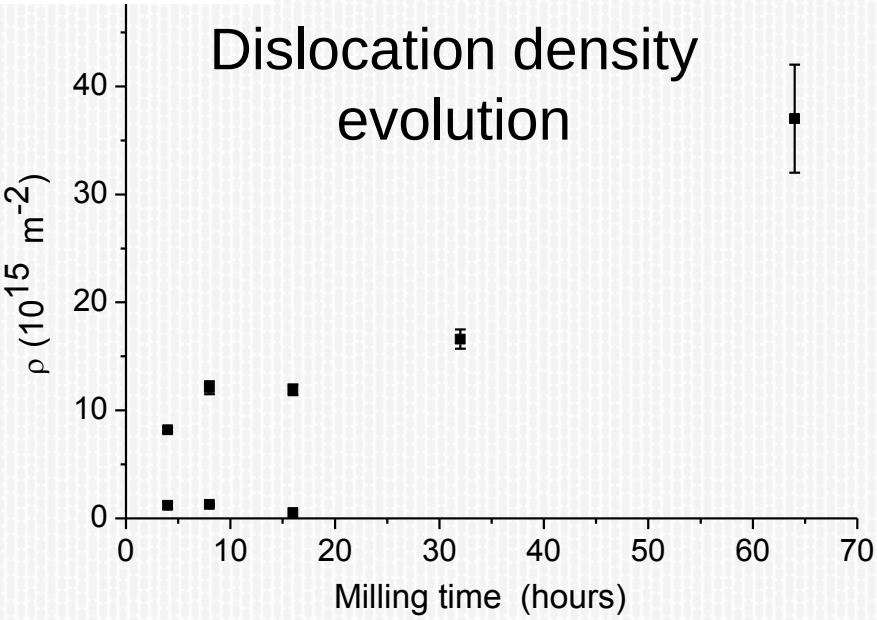




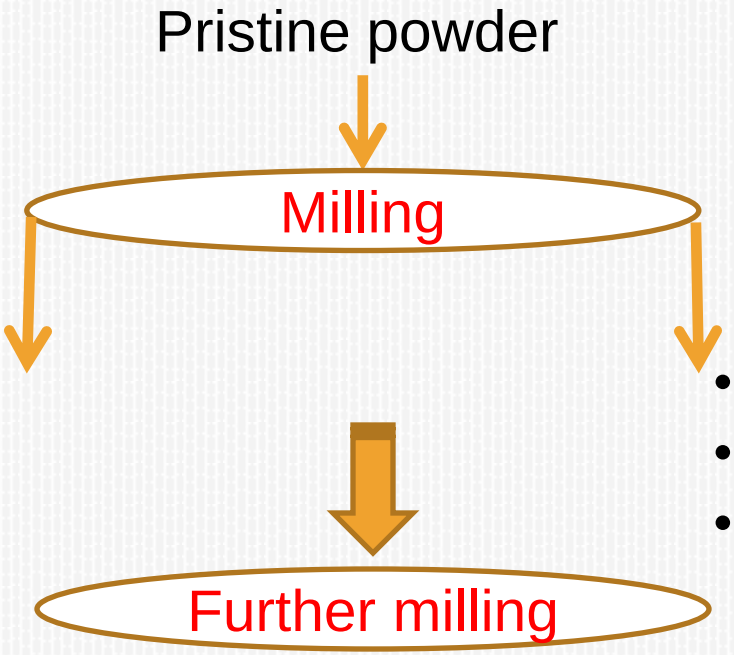


$\langle D \rangle_{Pristine}$ = 200 nm


Homogeneity evolution
Fraction B
Fraction A
Fraction evolution %
Milling time (h)
0
20
40
60
80
100
0
10
20
30
40
50
60


Dislocation density evolution
ρ (10^15 m^-2)
Milling time (hours)
0
10
20
30
40
0
10
20
30
40
50
60
70

Main remarks I



Less defected

- Longer T1
- Lower ρ
- Larger <D>

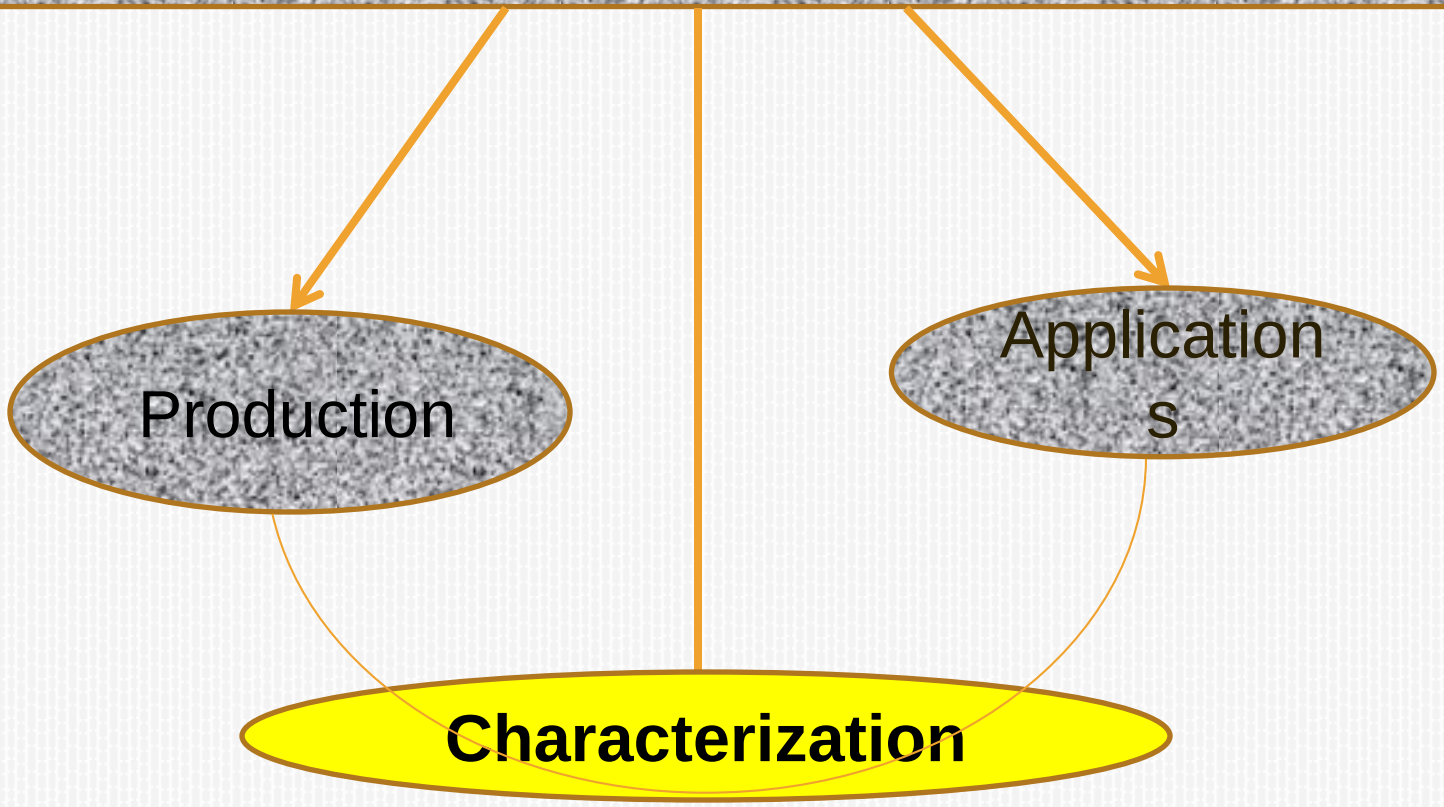
Highly defected

- Shorter T1
- Higher ρ
- Smaller <D>

Homogenous defected powder

- Very small T1 (less than unity)
- Saturated <D>

Structural Defects in Nanotechnology



- **Combined XRD-LPA-WPPM/NMR-T1 approach**

Next question

- **Lattice Strain/Crystallite size with T1 correlation??**

Correlation of lattice strain/domain size with NMR T1 of CaF_2

nanostructured materials

Top Down(e.g. ball milling)

Bottom-up(e.g. chemically)

CaF2 in **WC vial** and balls

Milling time (4,8, 16, 32, 64h)

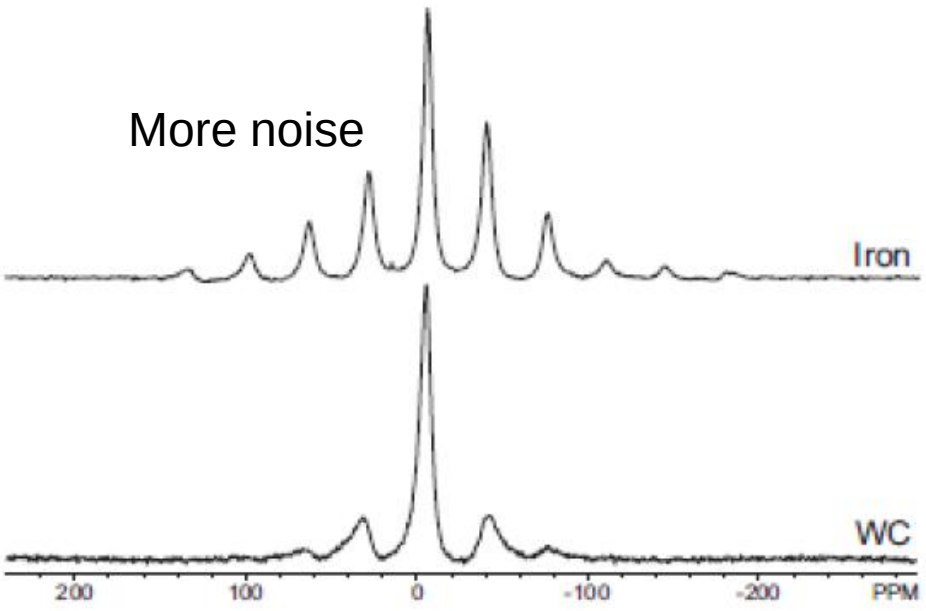
$CaCl_2 + 2NH_4F \rightarrow CaF_2 + 2NH_4Cl$

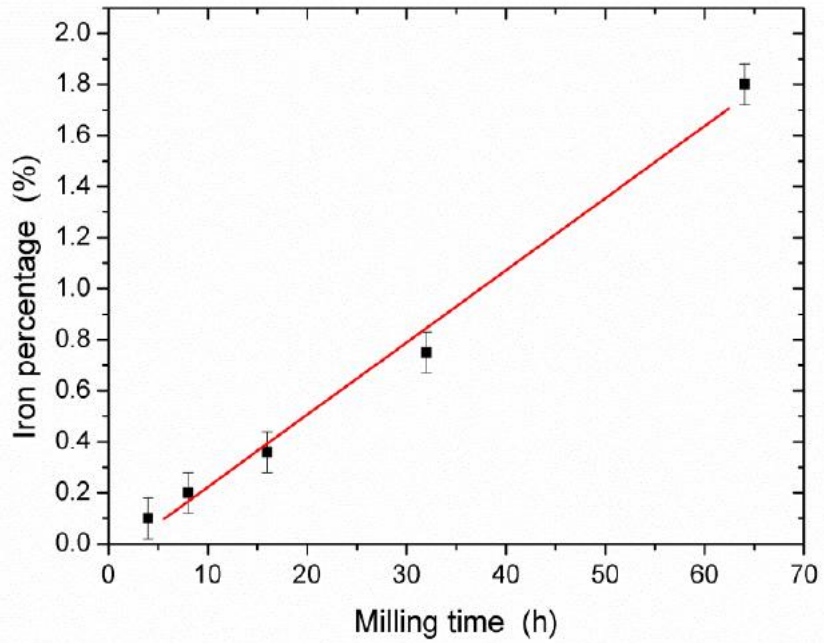
Solvent (ethanol) Conc. (0, 30, 60, 90, 100%)

Main requirements:

- **Extensively defected/un-defected crystals with comparable size**
- **Un-defected crystals with set of different sizes**

Grinding environment contribution



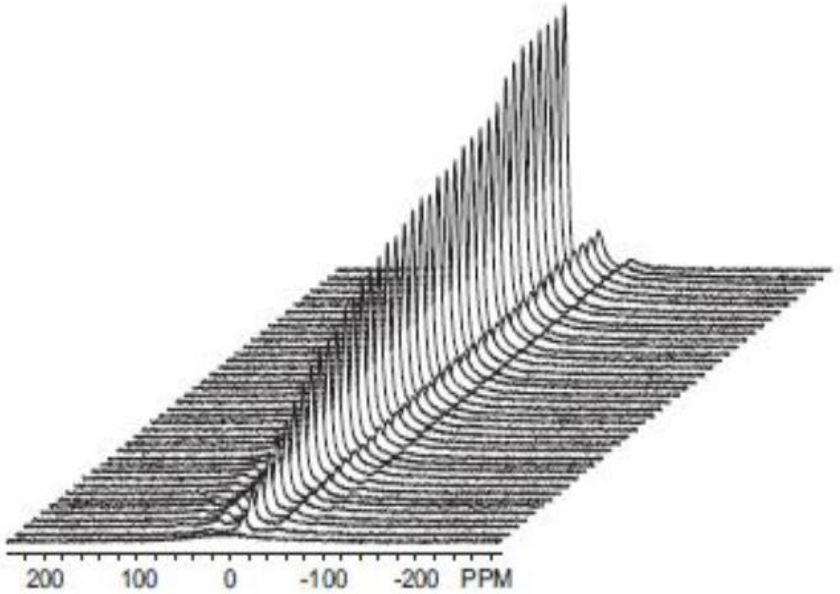


T1 is less in case of Fe grinding environment due to the magnetic contamination

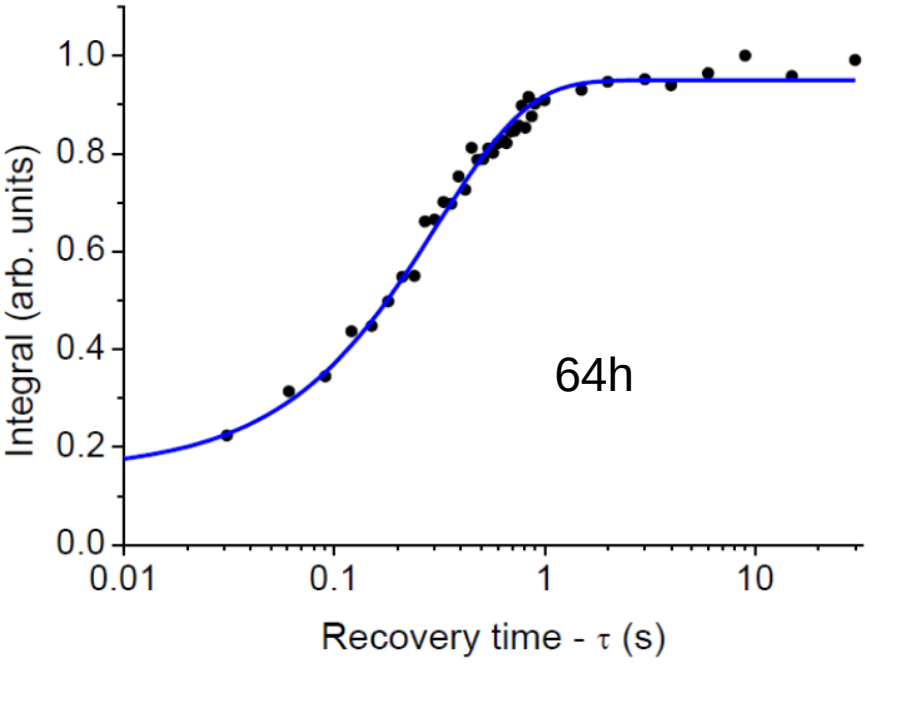
T1@32h ---> 0.79 sec @WC, 0.038 sec @Fe
T1@64h ---> 0.31 sec @WC, 0.036 sec @Fe

Ground series

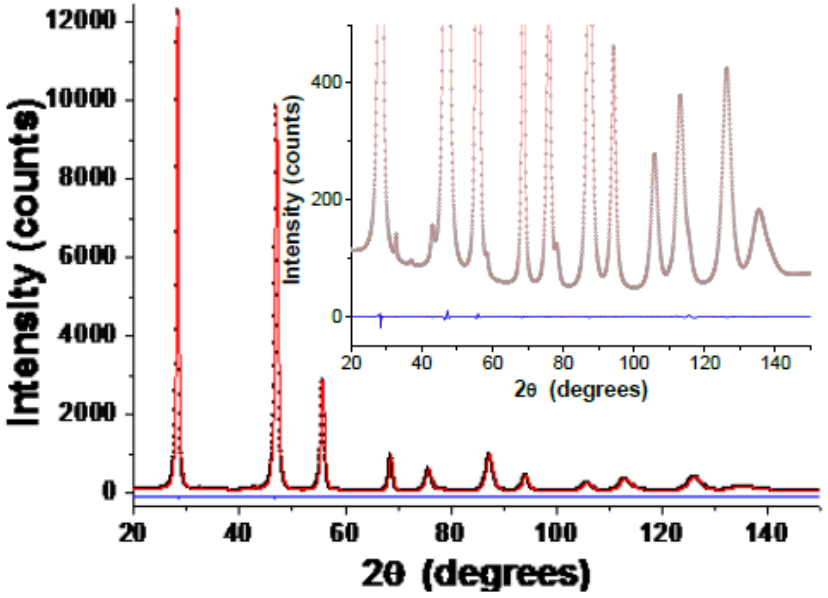
Samples
Pristine, 16h, 32h, 64h

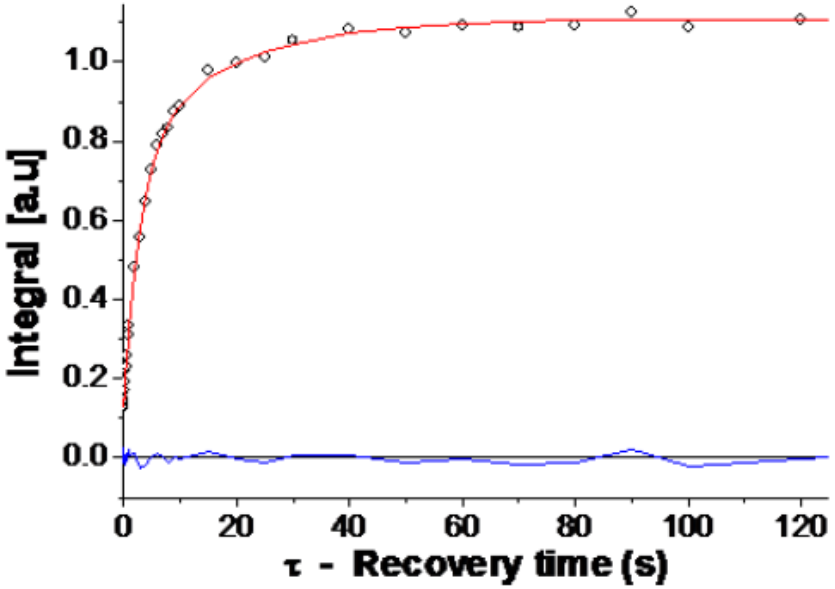


$$M_z(\tau) = K + C\left[1 - \exp\left(-\tau/T_1\right)\right]$$

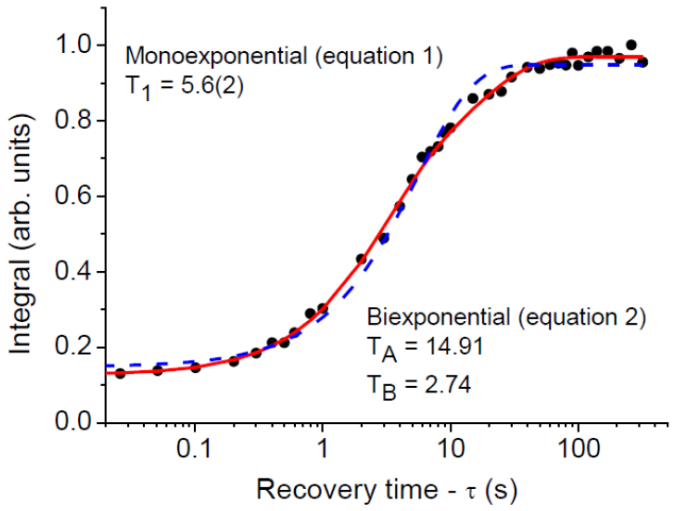


4h, 8h samples with combined XRD/NMR

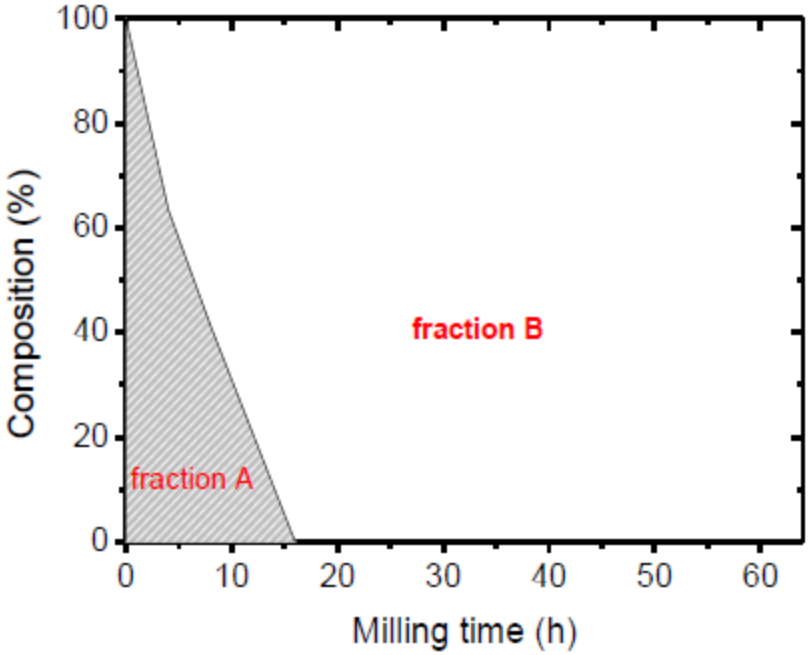


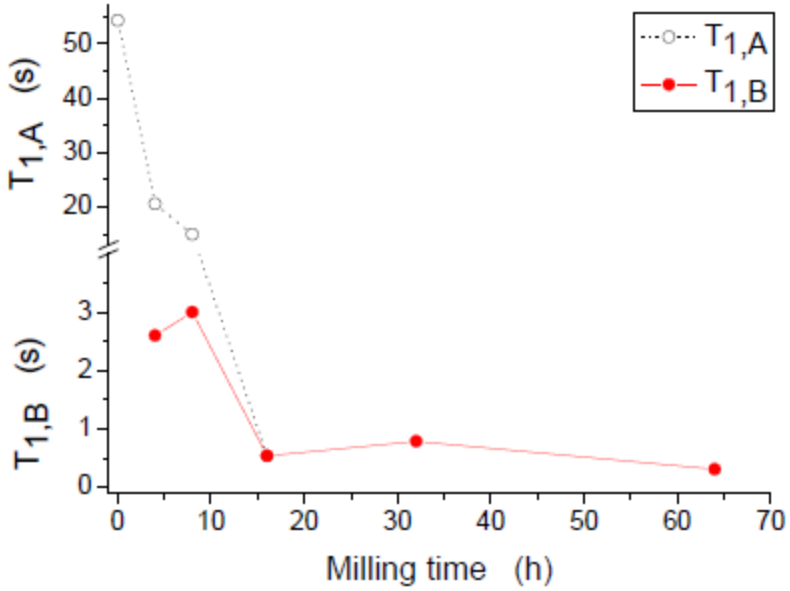


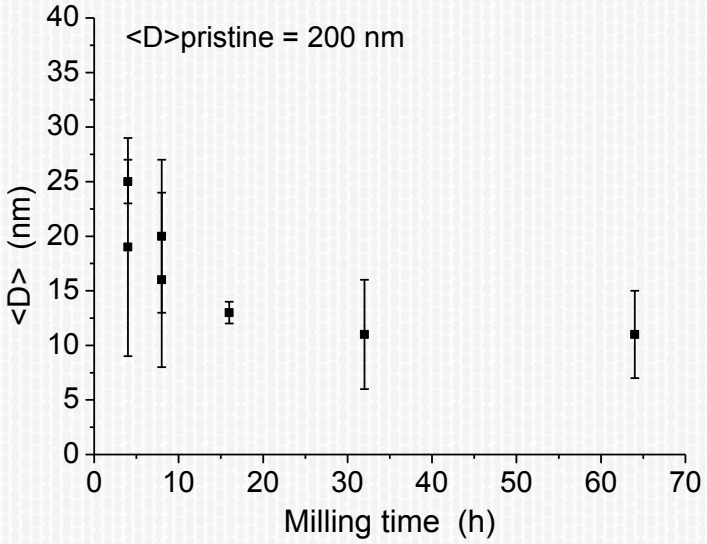
$$M_z(\tau) = K + C\left[1 - \exp\left(-\tau/T_{1,B}\right)\right] + (1-C)\left[1 - \exp\left(-\tau/T_{1,A}\right)\right]$$

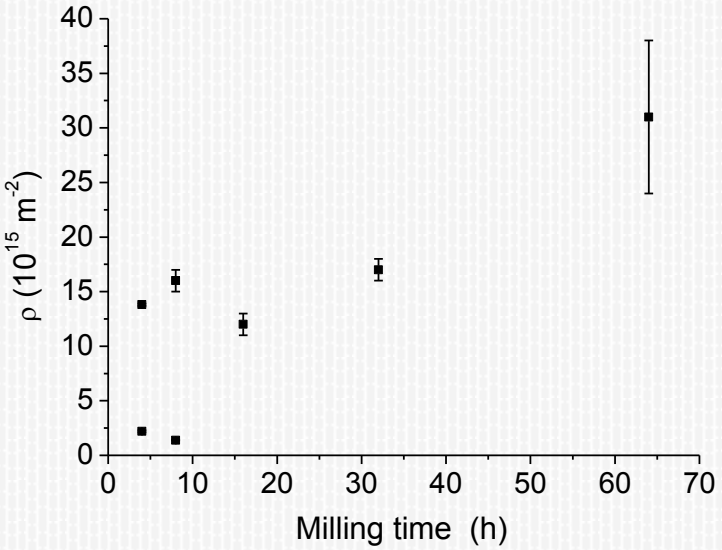


Main ground series results



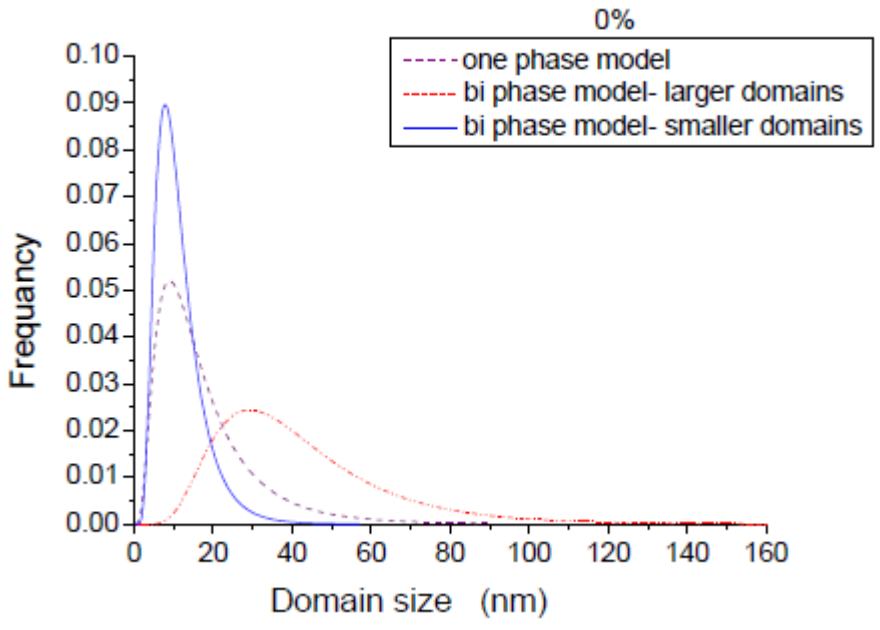


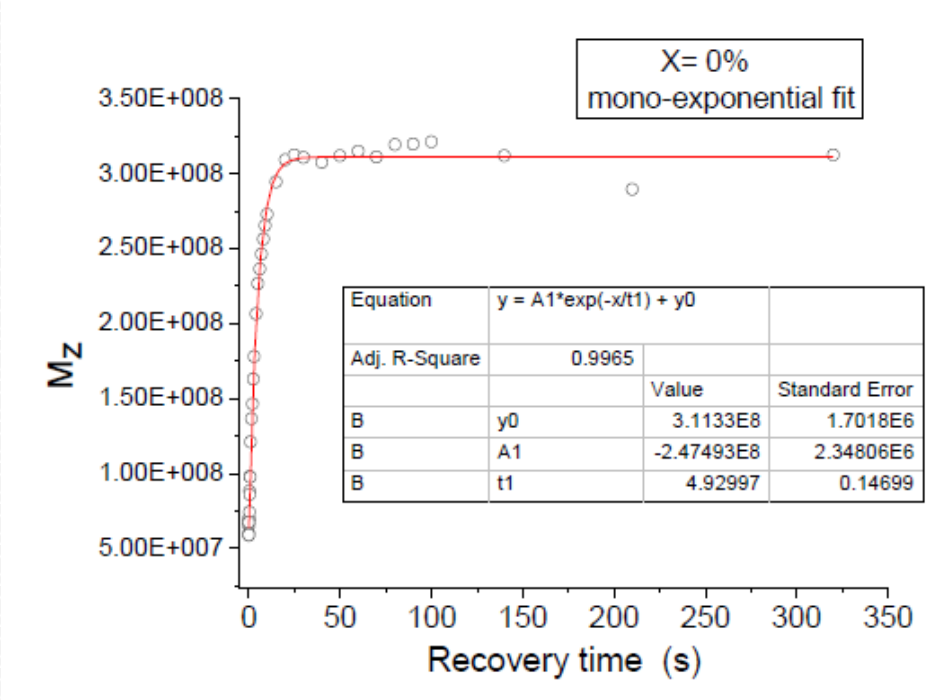




Chemically synthesized series

- Samples 0%, 30% and 60 %



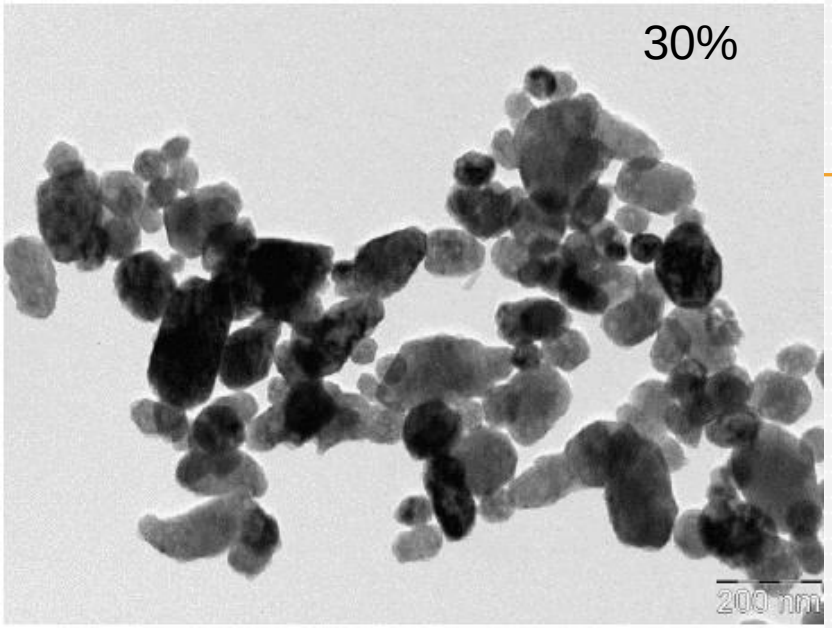


- Mono exponential T1 trend
- Bi XRD models gives less WSS(more agree with TEM images)

Although two size fraction

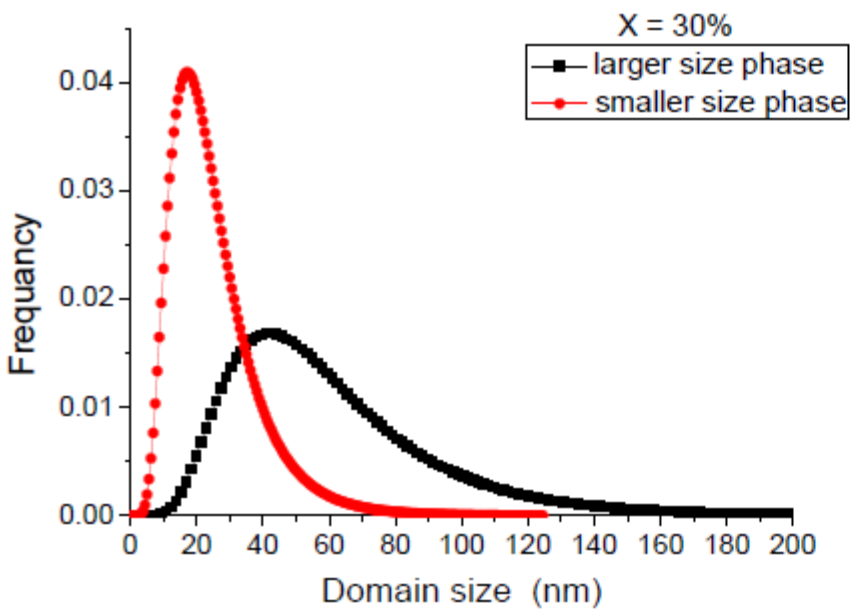
- **T1 does not split**
- **T1 less than pristine (around 7 sec) but does not change**

T1 (Pristine) = 54 sec

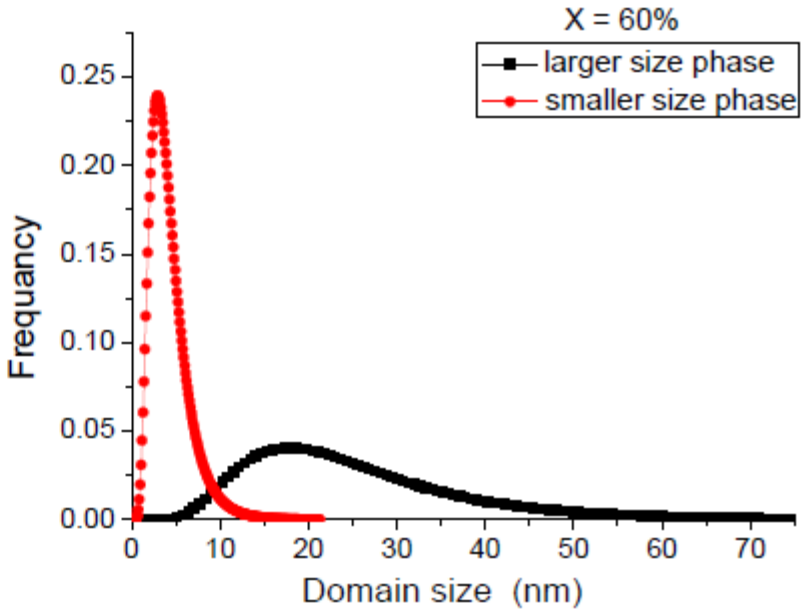


Ethanol content [%]	T_1 [s]
0	5.1(1)
30	8.1(3)
60	4.9(3)

T1 = 8.1



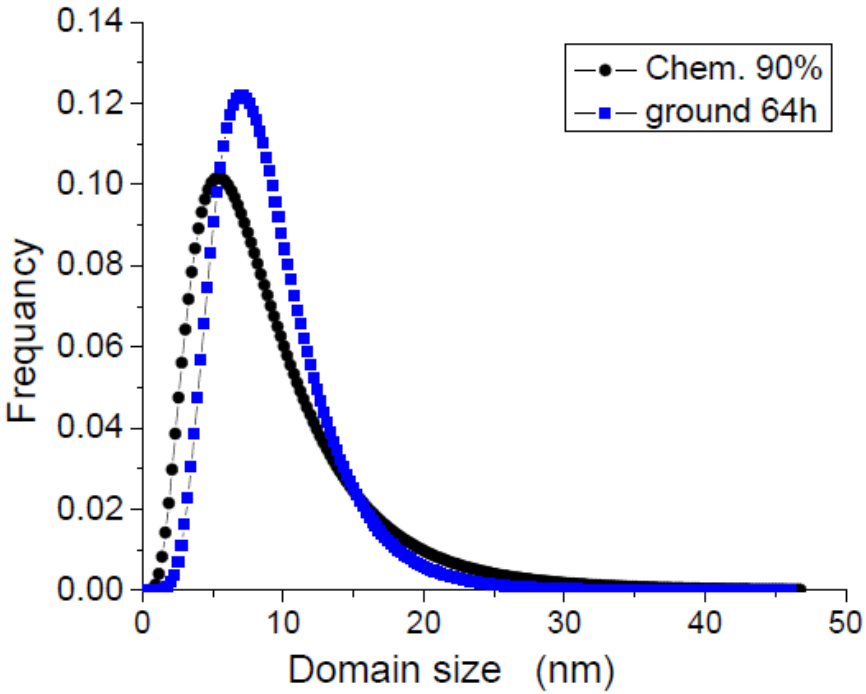
T1 = 4.9



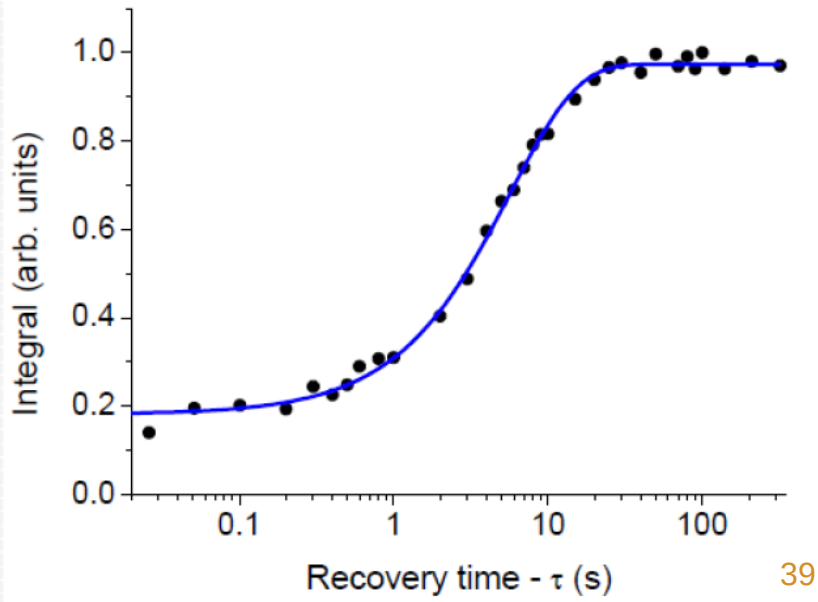
Two size distributions (lognormal) for CaF2@30% and CaF2@60% samples

Sample 90%

Ethanol content [%]	T_1 [s]
0	5.1(1)
30	8.1(3)
60	4.9(3)
90	5.8(3)
100	0.49(2)



T1(64h) = 0.31 sec

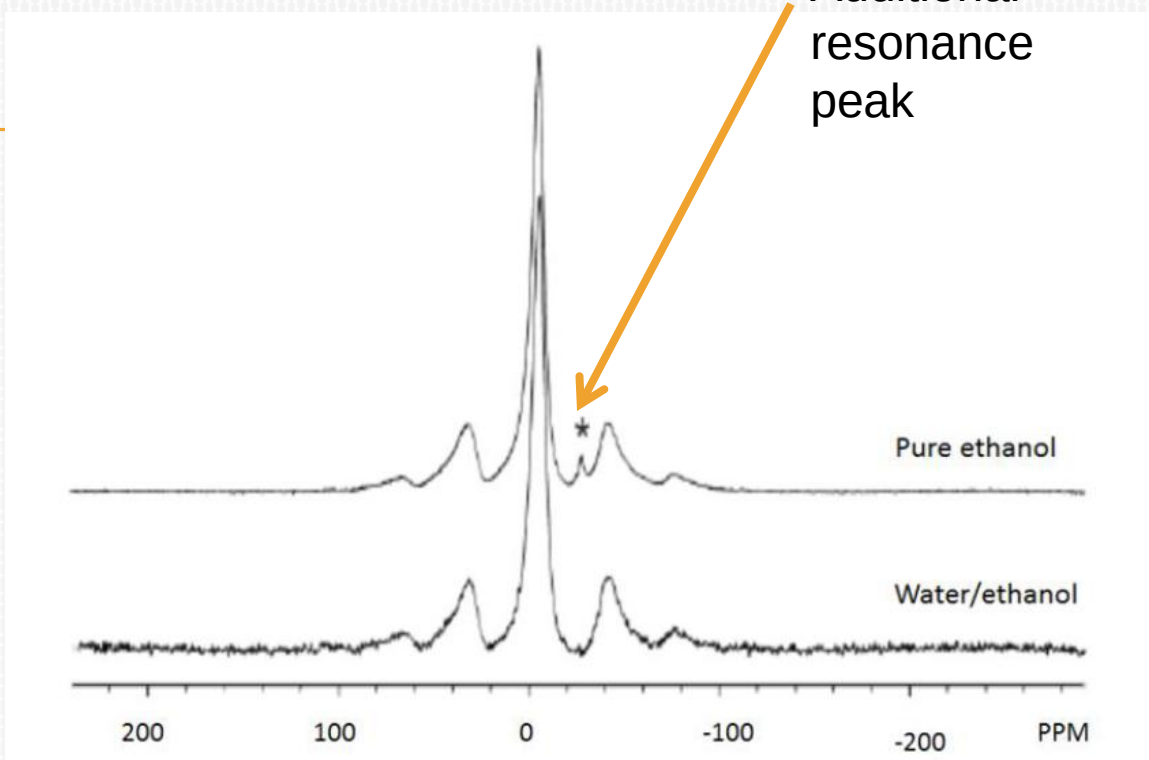


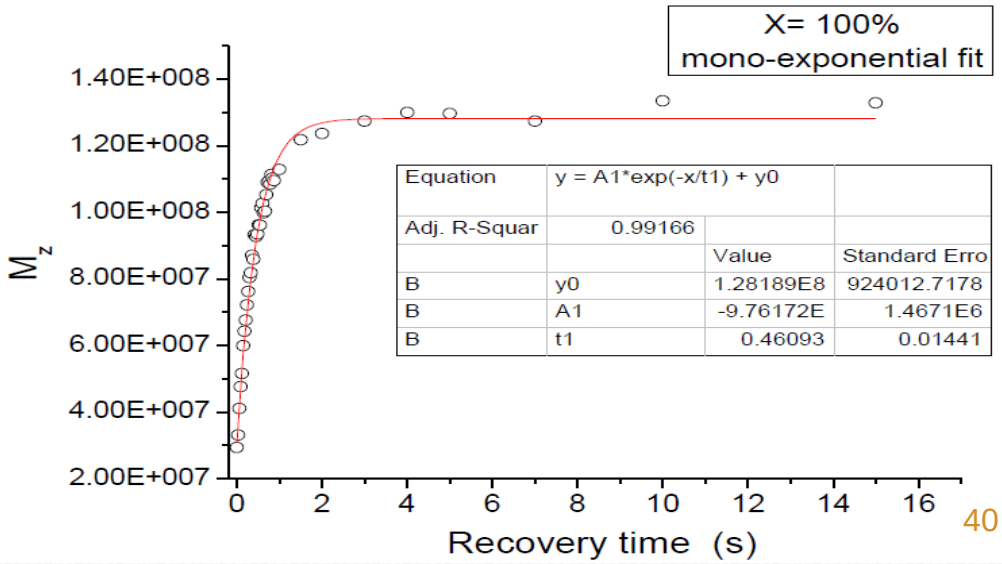
Thus lattice strain (defects) seems to have the main contribution on reducing T1

Sample 100%

Ethanol content [%]	T_1 [s]
0	5.1(1)
30	8.1(3)
60	4.9(3)
90	5.8(3)
100	0.49(2)

<D> = 6nm



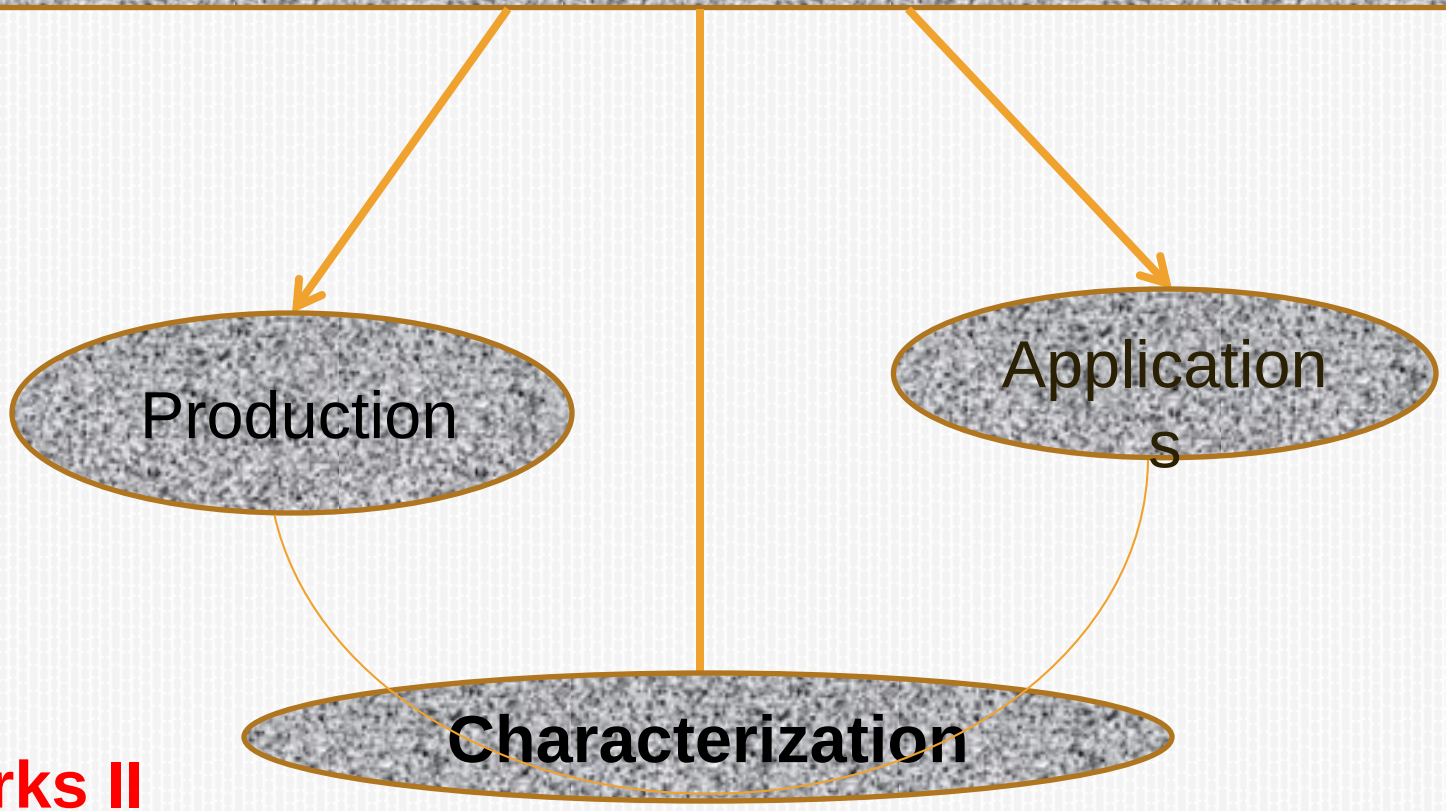


T1 is comparable with highly ground samples

Frenkel defects is clearly seen from the additional resonance peak

T1 is more sensitive to lattice defect

Structural Defects in Nanotechnology

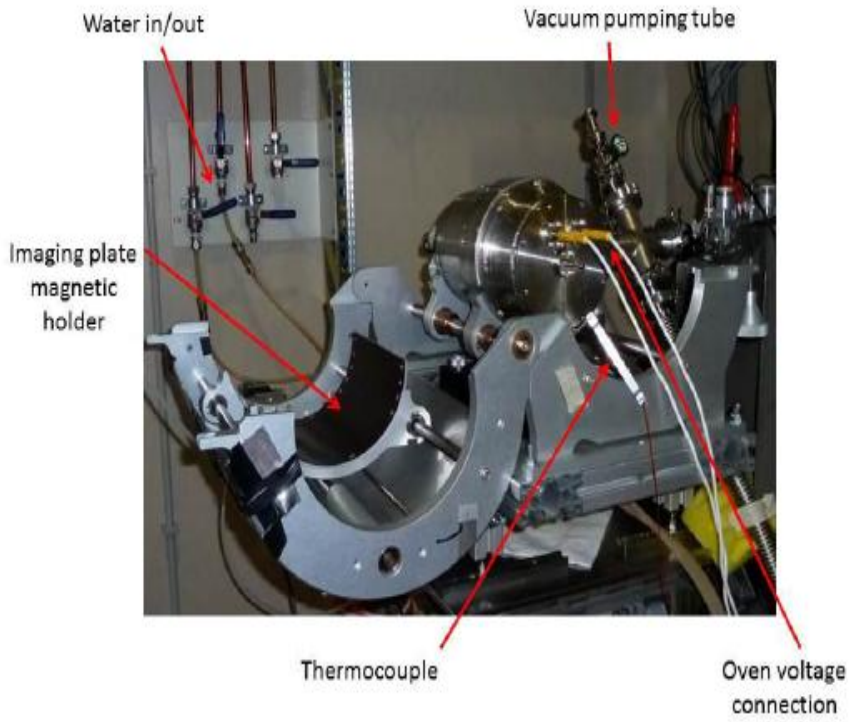


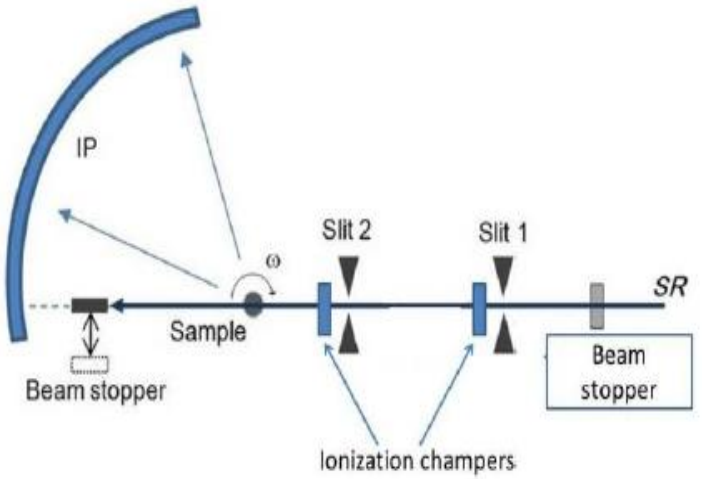
Remarks II

1. *Positive Combination of XRD-NMR to follow structural homogeneity*
2. *Lattice strain leads to a decrease in T1 less than unity and crystallite size influence only when it is less than 10 nm coupled worth a strain lattice*
3. *Further investigation is required to understand the real mechanism of T1/lattice strain correlation*

Furnace for In-Situ XRD experiments at MCX beamline

Applications: High temperature application





Main advantages:
Fast pattern collections coupled with large no. of patterns

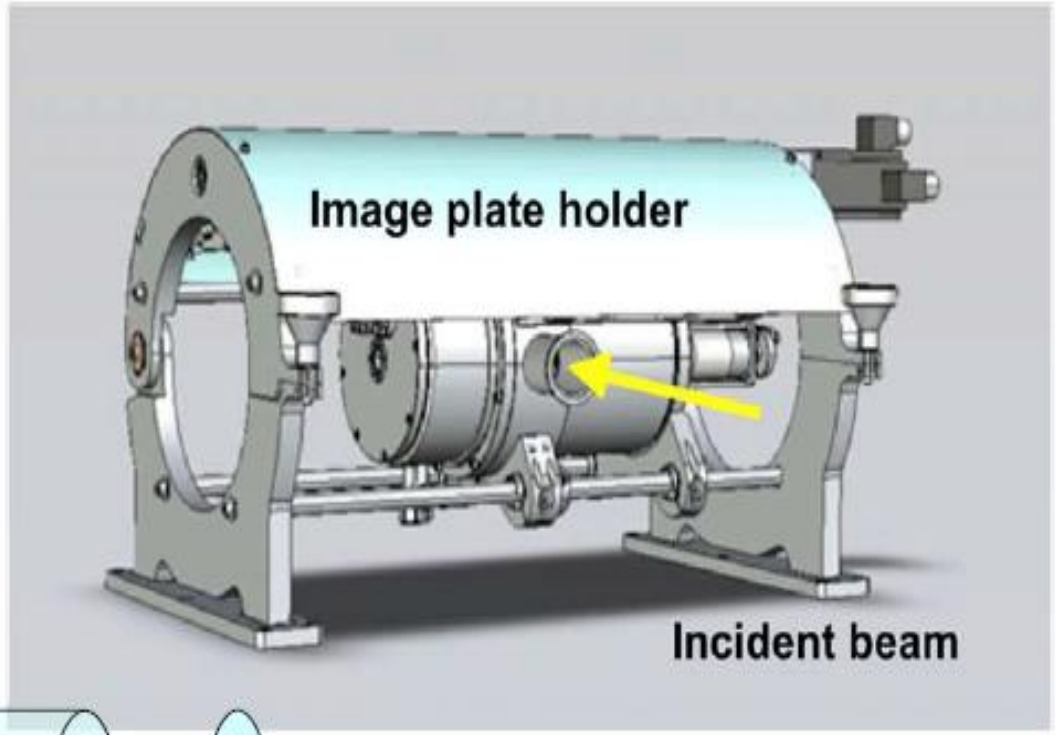
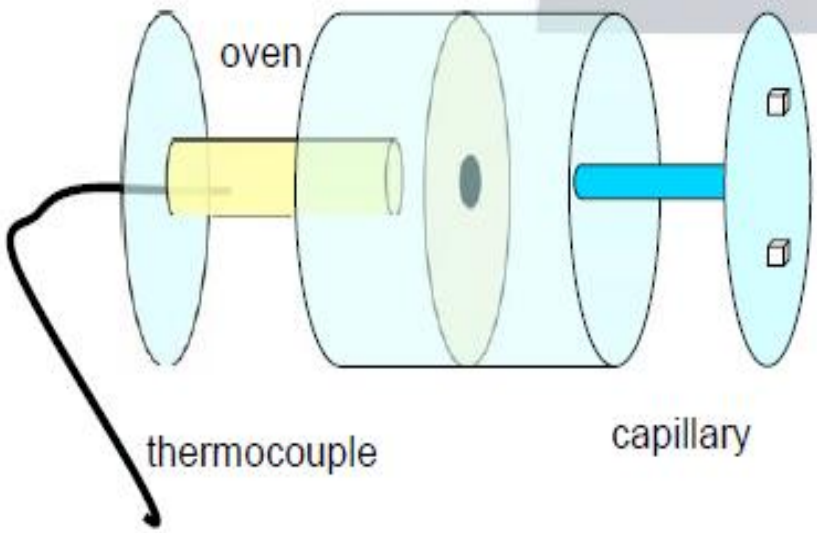
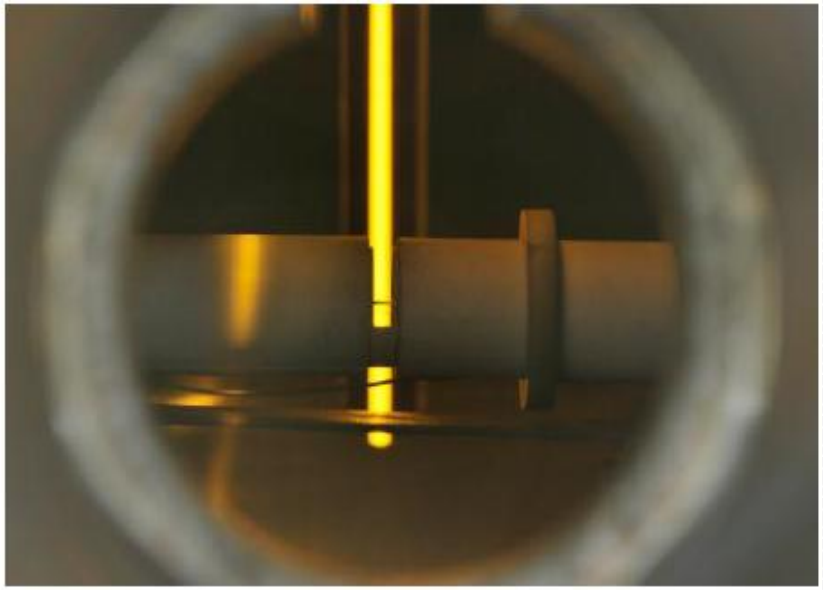
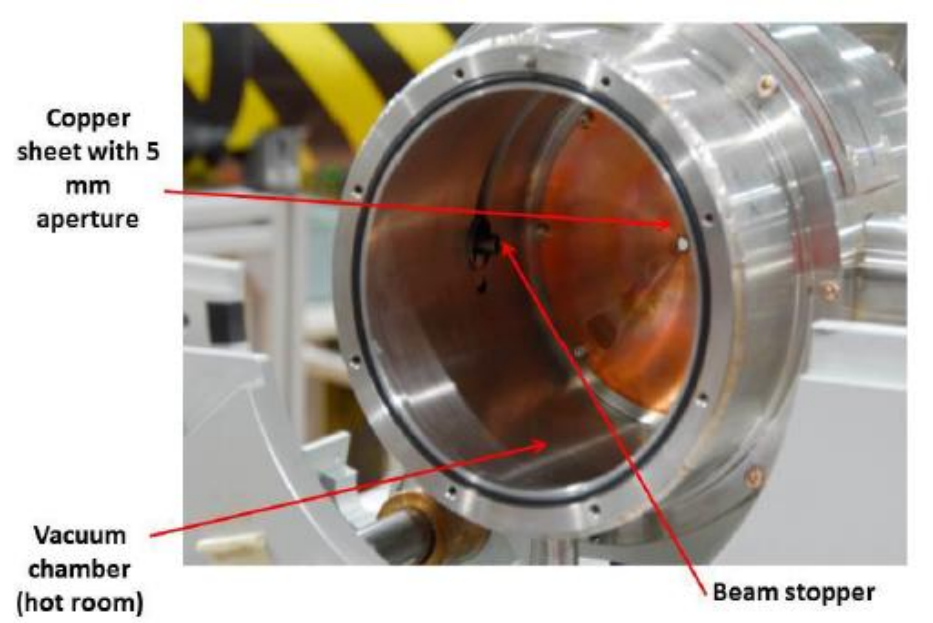


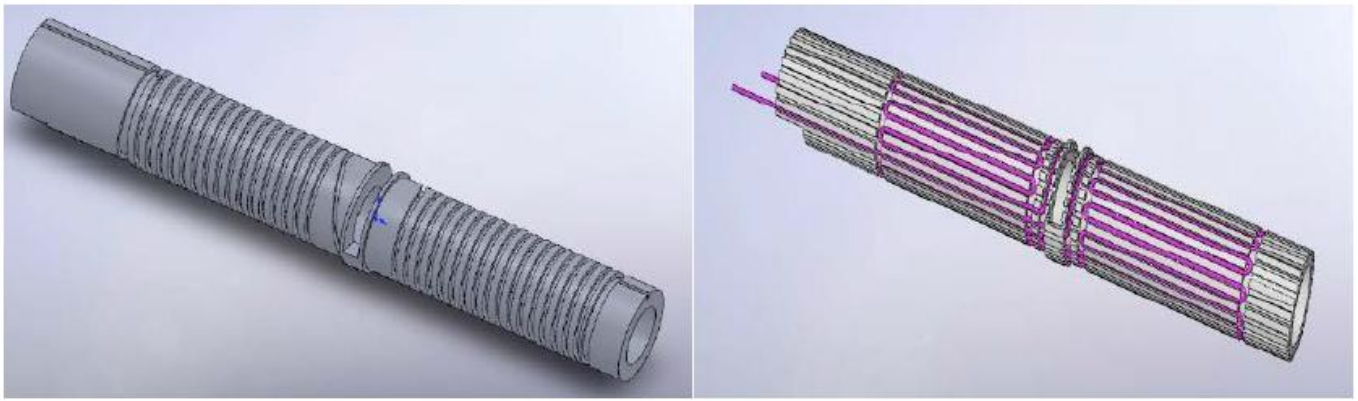
Image plate holder
Incident beam


oven
thermocouple
capillary

Oven main elements and construction

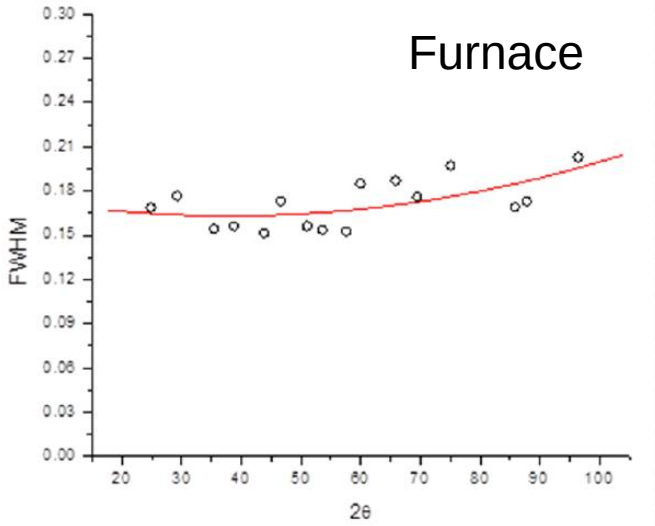


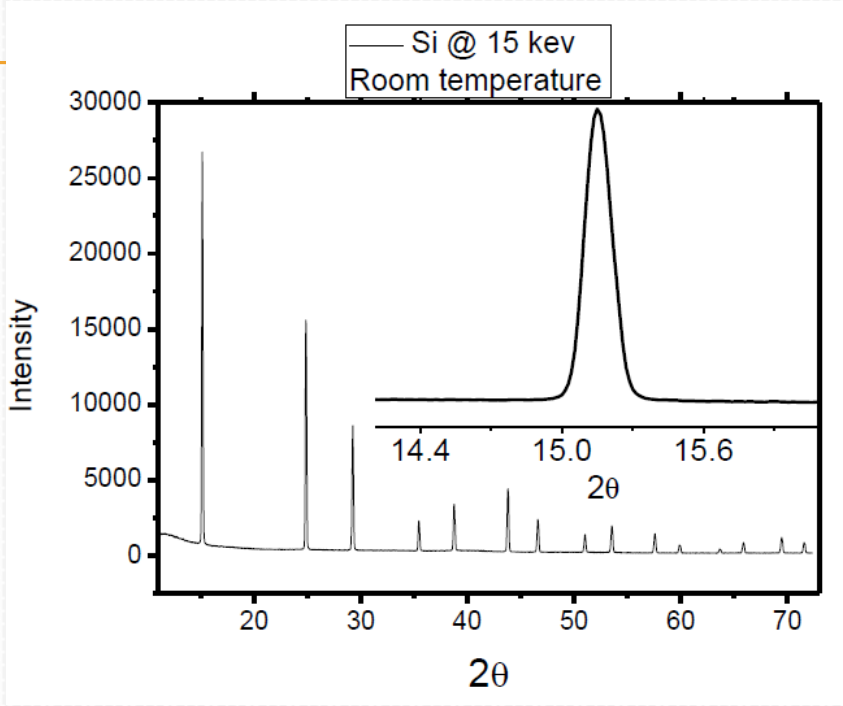




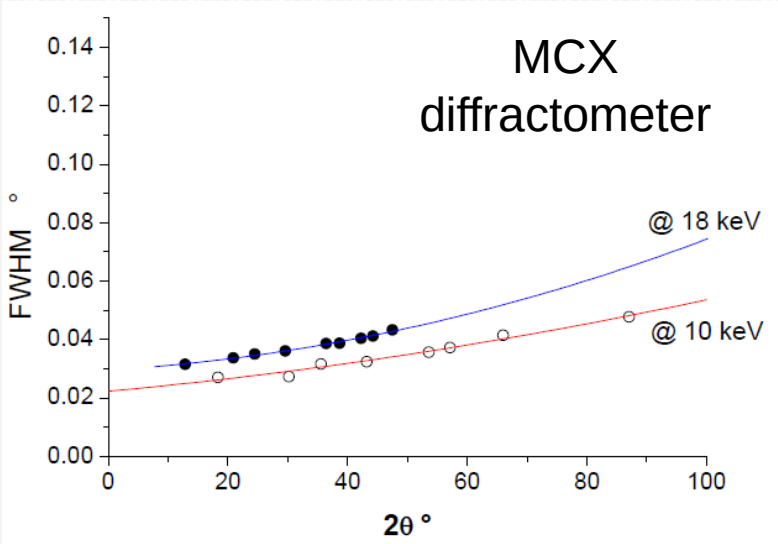
Instrumental contribution of the furnace at MCX beamline

$$FWHM^2 = W + V\tan(\theta) + U\tan^2(\theta)$$



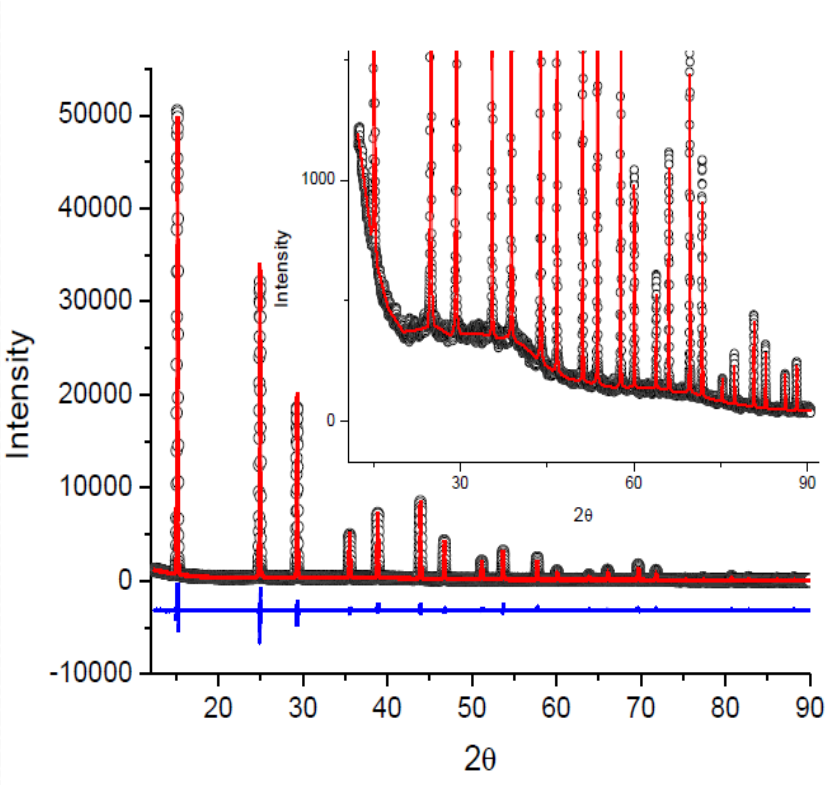


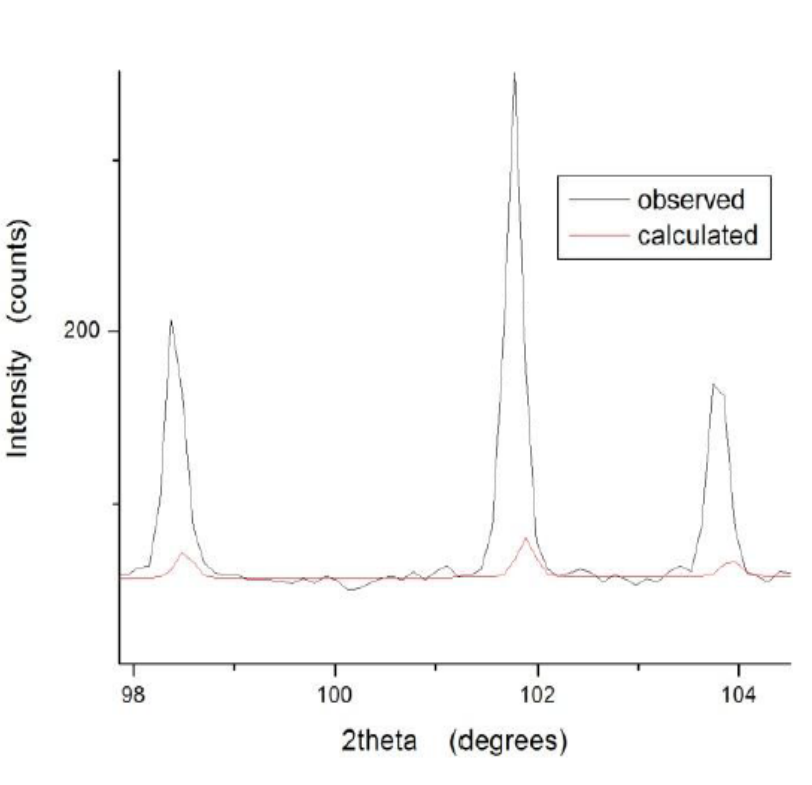
- Furnace Vs MCX diffractometer resolution
- What is required from the XRD experiment??



Oven temperature calibration from lattice parameter

Need very carful care of Pixel-2theta conversion





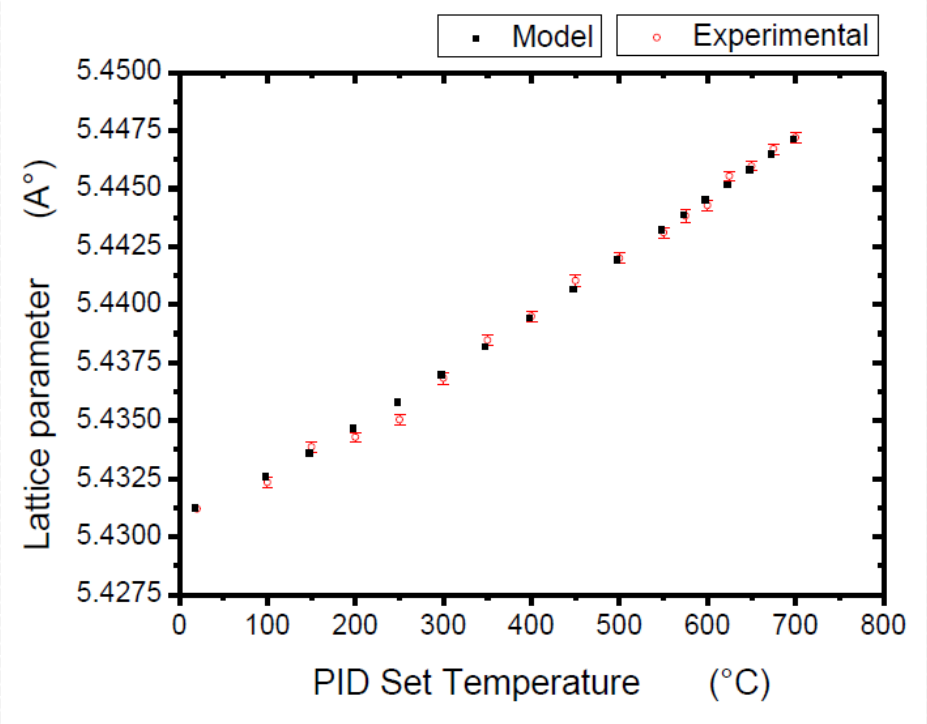
Good conversion

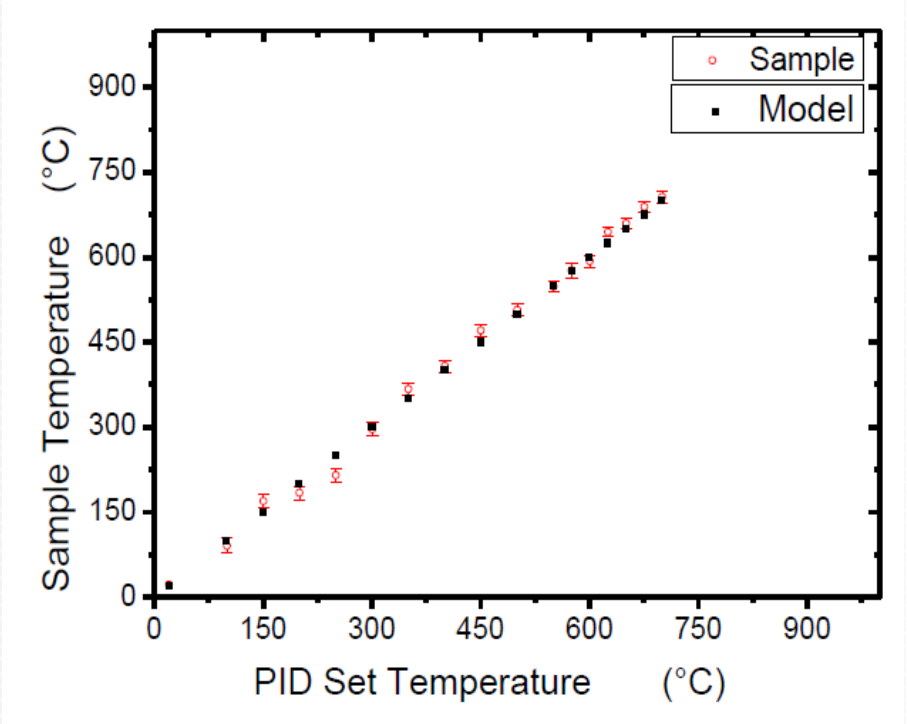
bad conversion

Sample - detector distance

Then from lattice parameter/temperature dependence will known equation for Si standard → Temperature can be obtained

Well matches between PID set temperature and sample temperature

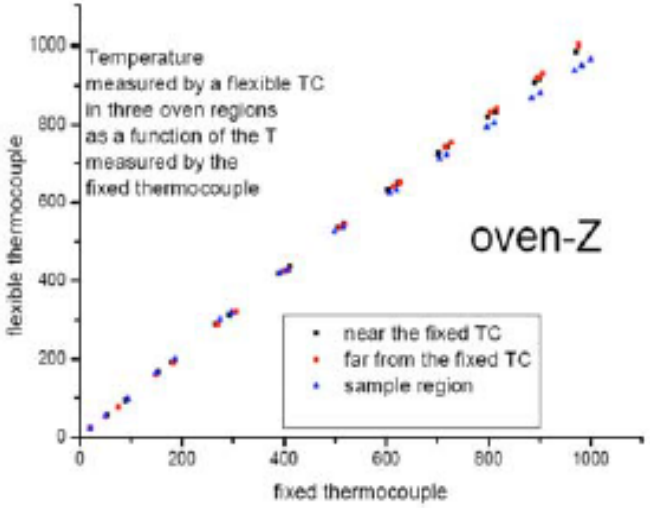




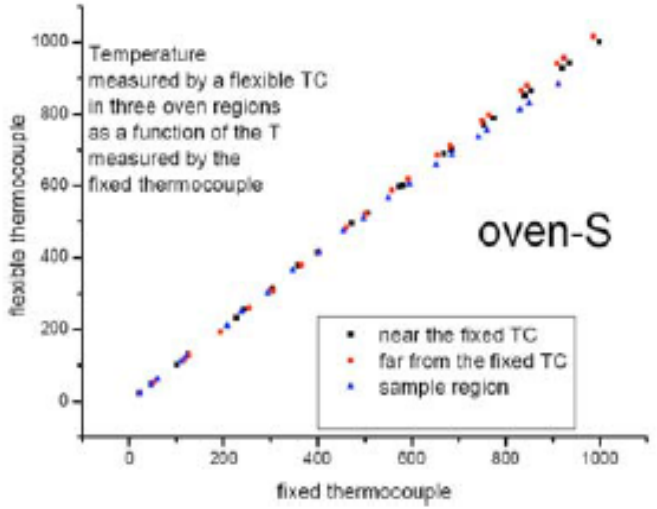
Characterizations of temperature uniformity within the cylindrical ovens

Fixed thermocouple

Flexible Thermocouple 3 positions tested



- linear behaviour of the measurements of the 2 thermocouples.
- We repeatedly measured the difference to be less than 7% of the lower mesasured temperature

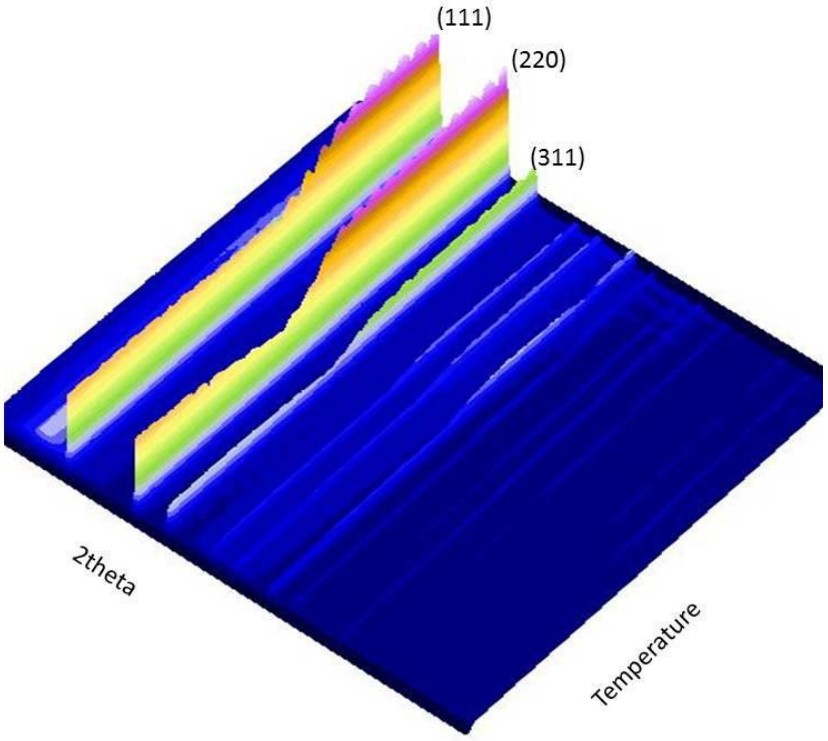


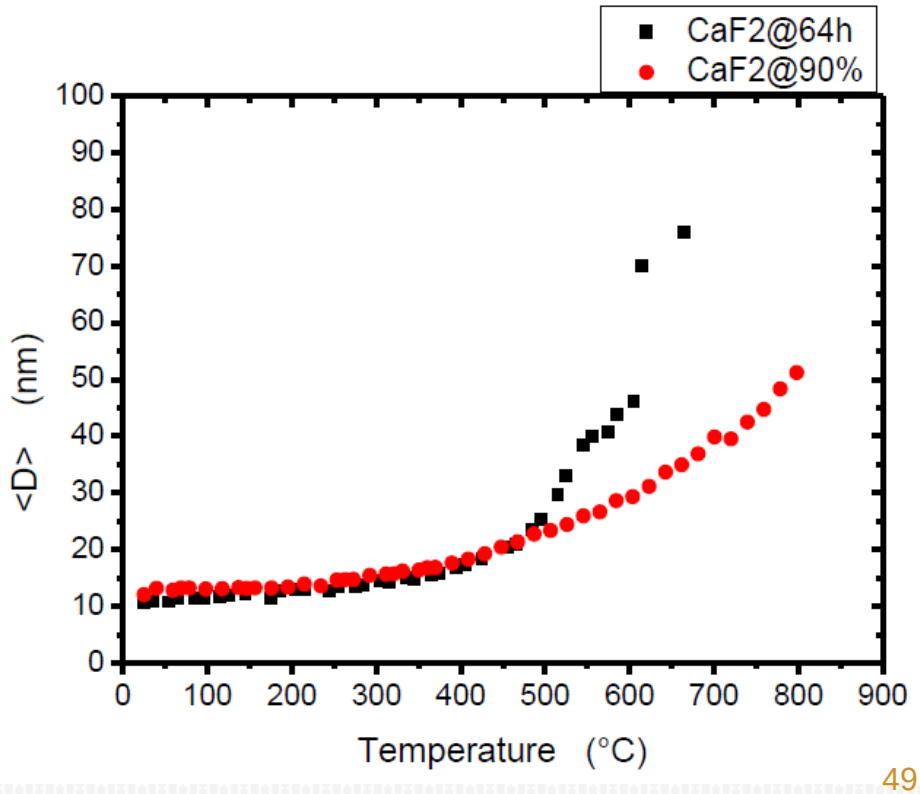
elettra

In-Situ XRD Study of Lattice Defects Influence on Grain Growth Kinetics of Nanocrystalline Fluorite

Ostwald Ripening (OR), Oriented Attachment (OA) growth mechanism

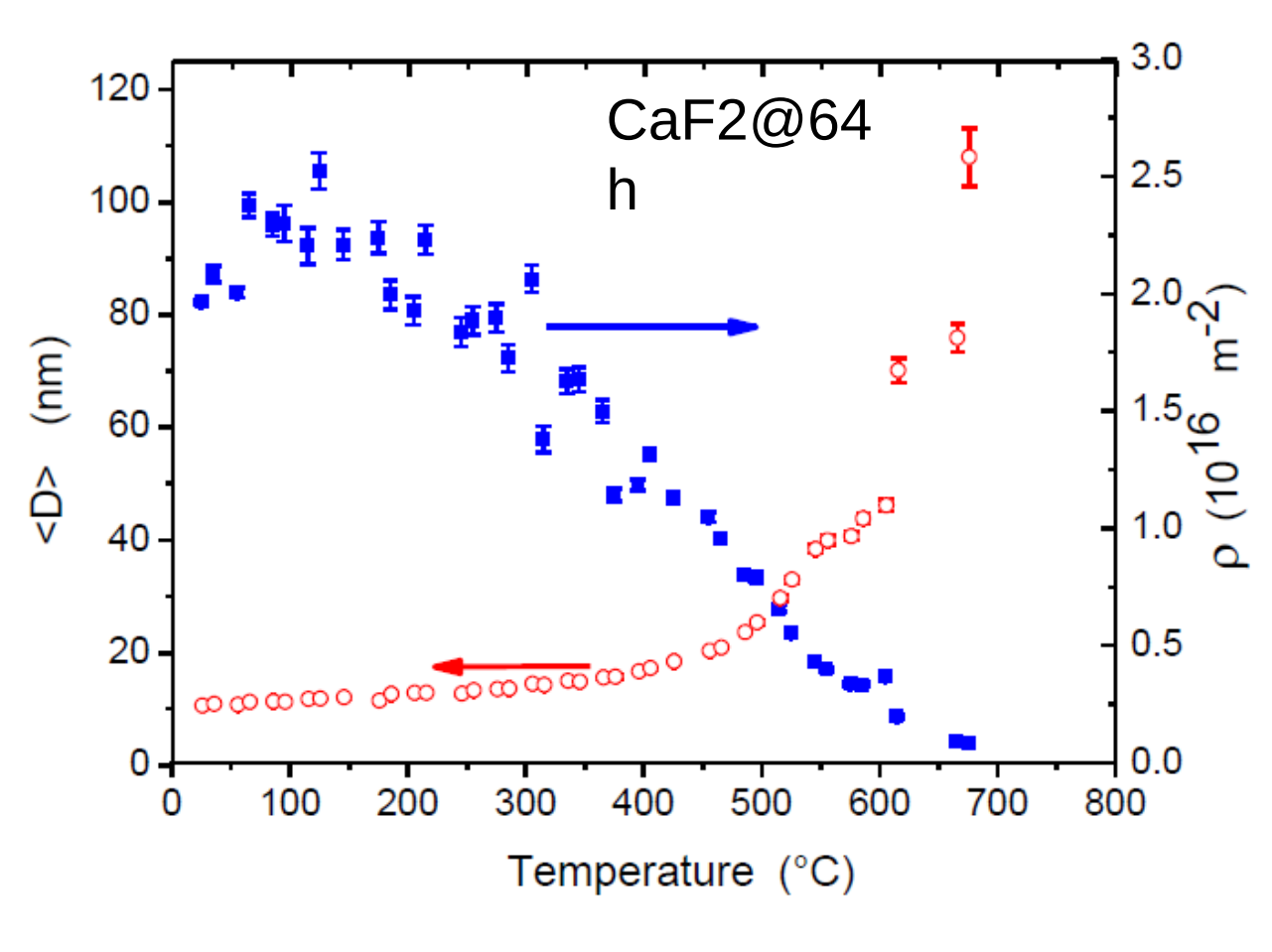
small grains rotate until they adjust to a common crystallographic axis between each two neighbors in order to decrease the (surface) grain boundary free energy





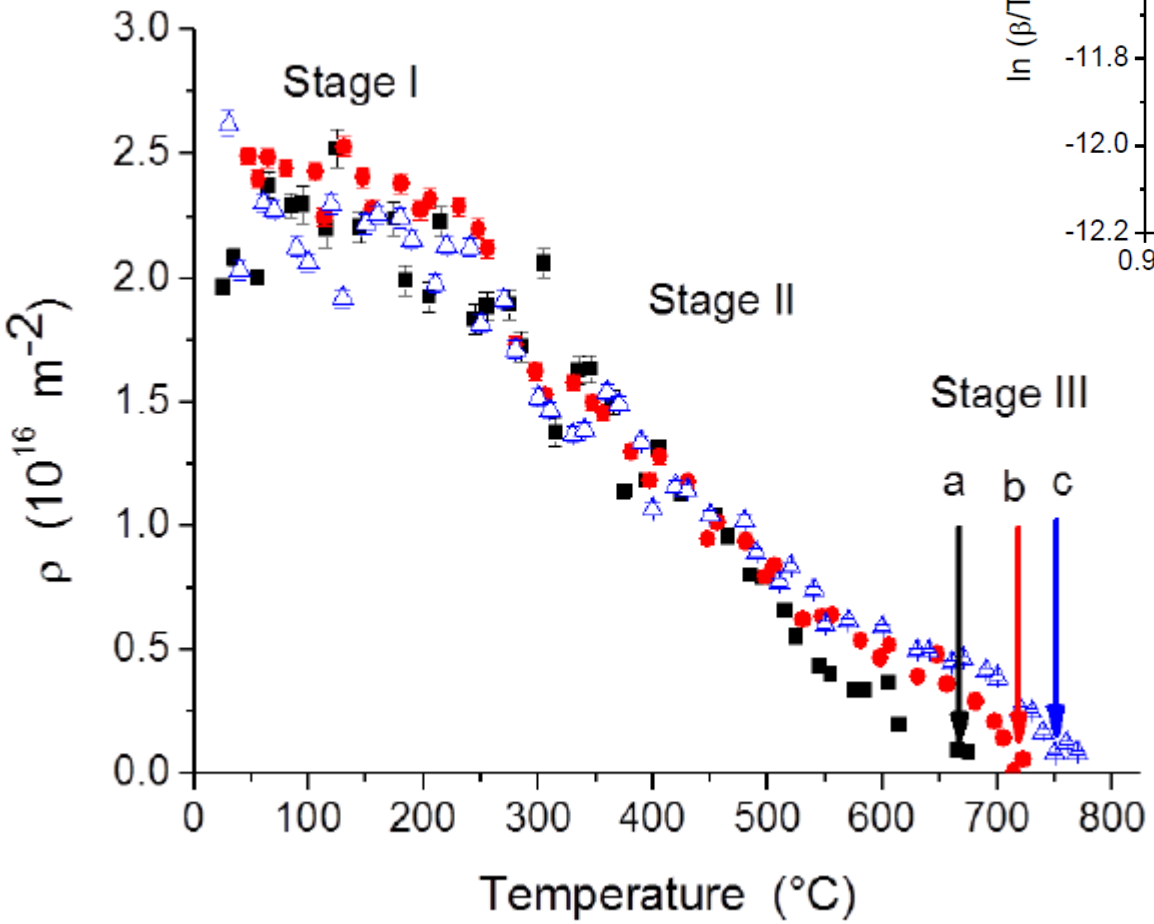
Aim

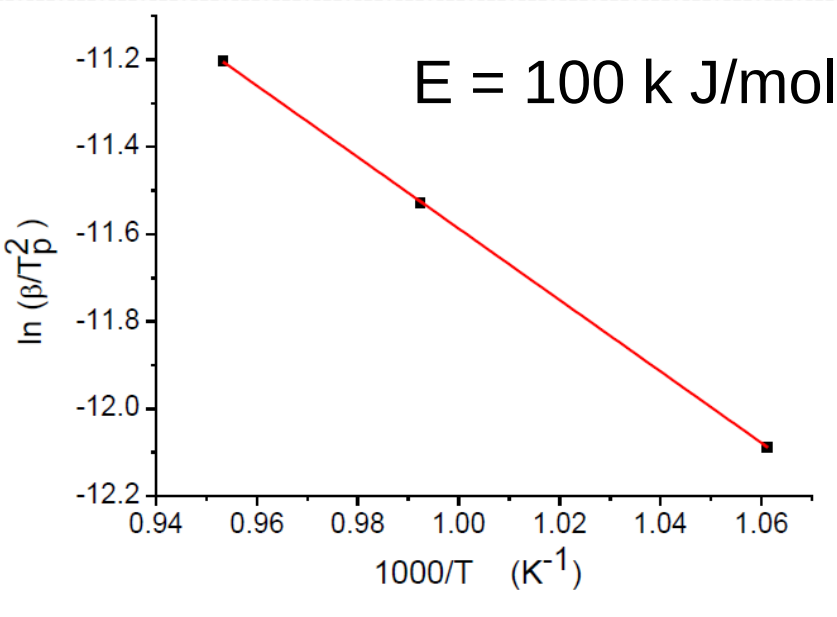
Free surface crystals (chemically synthesized) Vs. aggregated crystals with energy stored in the grain boundaries (ball milled)



Stability, recovery and crystallization

Crystallization Energy



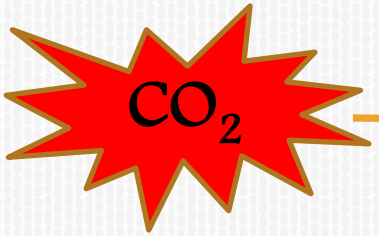


$$ln\left(\frac{\beta}{T_p^2}\right) = A - \frac{E}{RT}$$

Remarks III

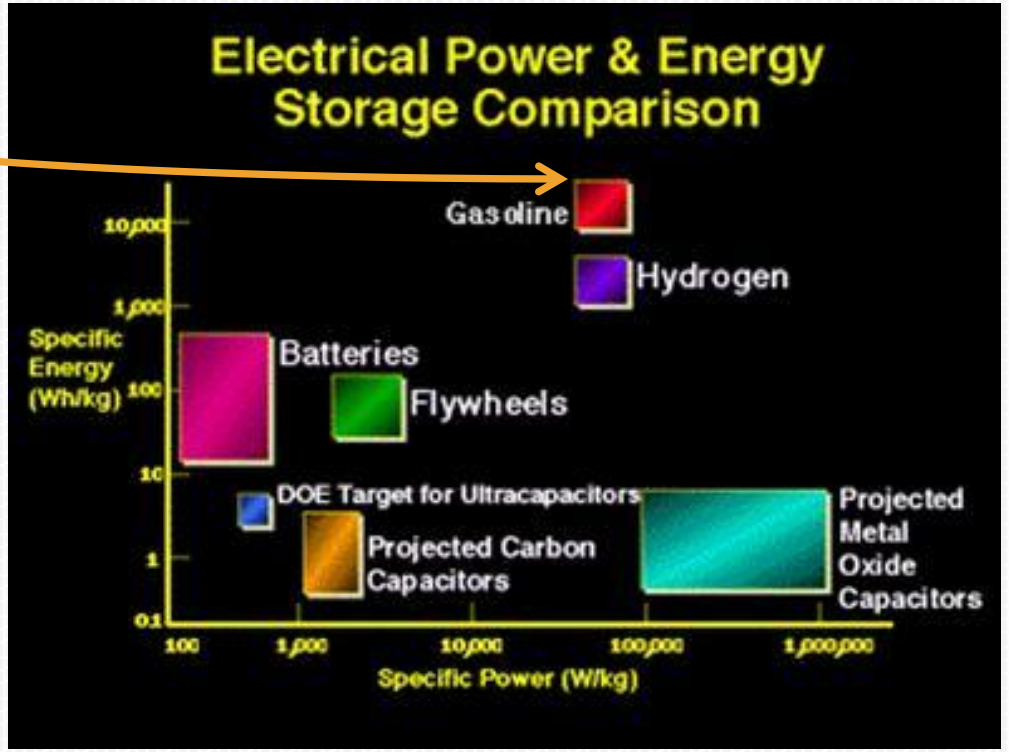
- Stored energy in the grain boundaries responsible for fast growth around 500 C.
- Free surface crystals (chemically synthesized) more thermally stable

In-Situ XRD Study of Hydrogen Storage Materials



Fast climate change

2.7 billion tons in 1990
32.5 billion tons in 2006



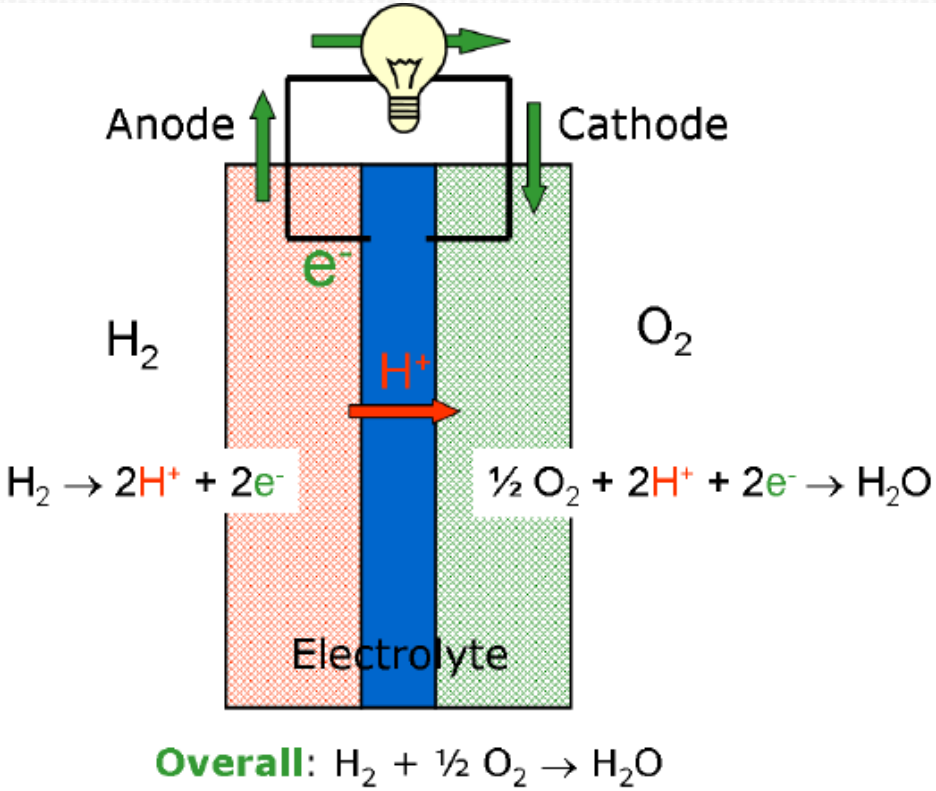
Future energy system

1. Solar
2. Wind
3. Geothermal
4. Hydrogen
5. …..

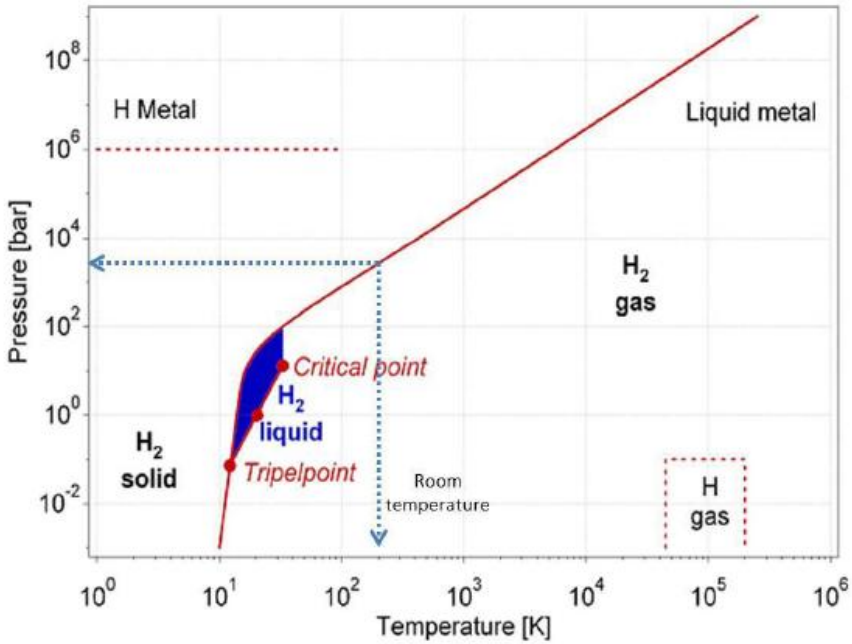
Energy system requirements

Available, Clean, Flexible, Cost efficient,…

Hydrogen fuel cell (promising candidate)



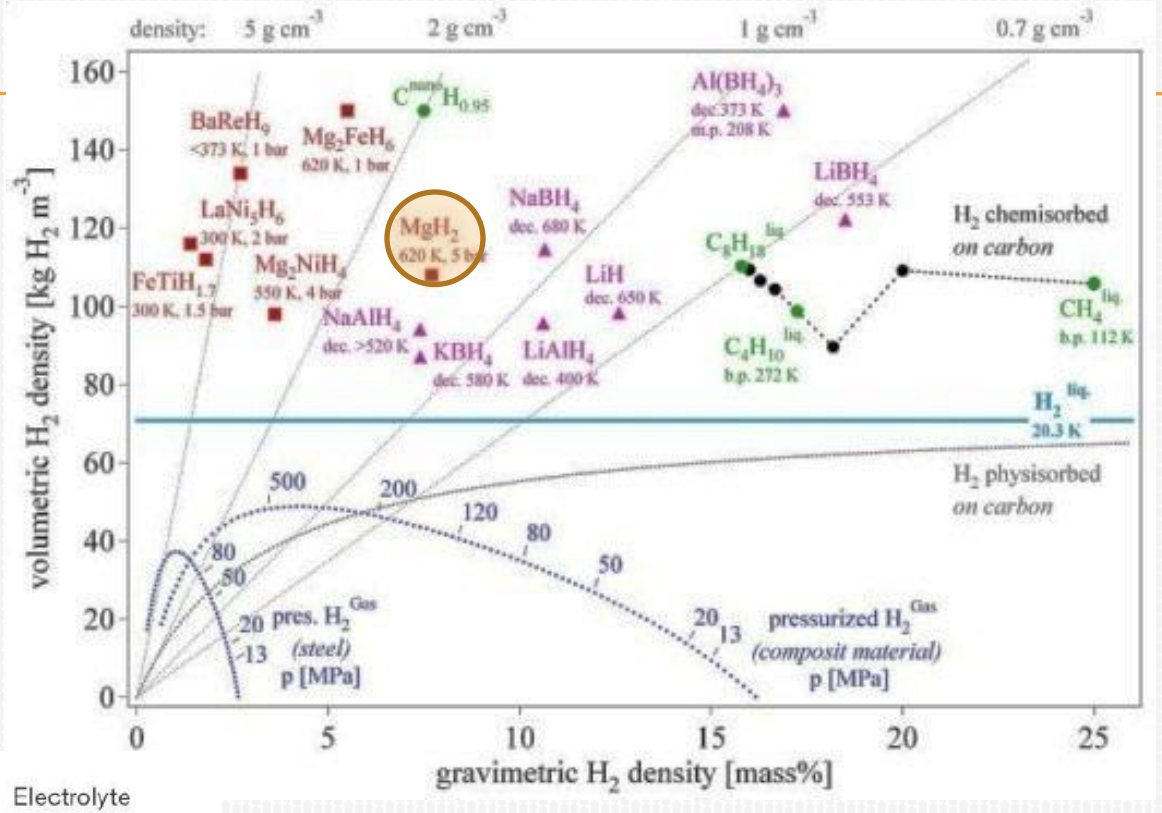
Hydrogen Storage problem

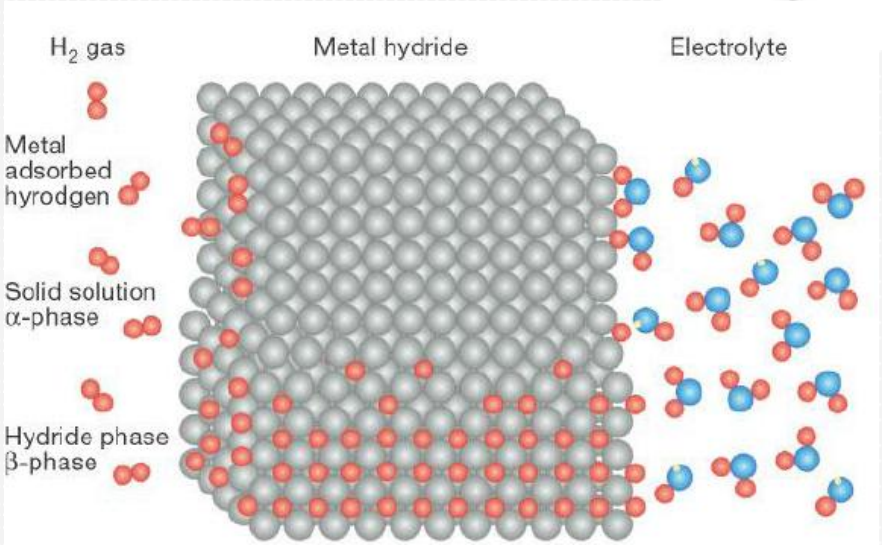


Hydrogen storage materials

Main requirements:

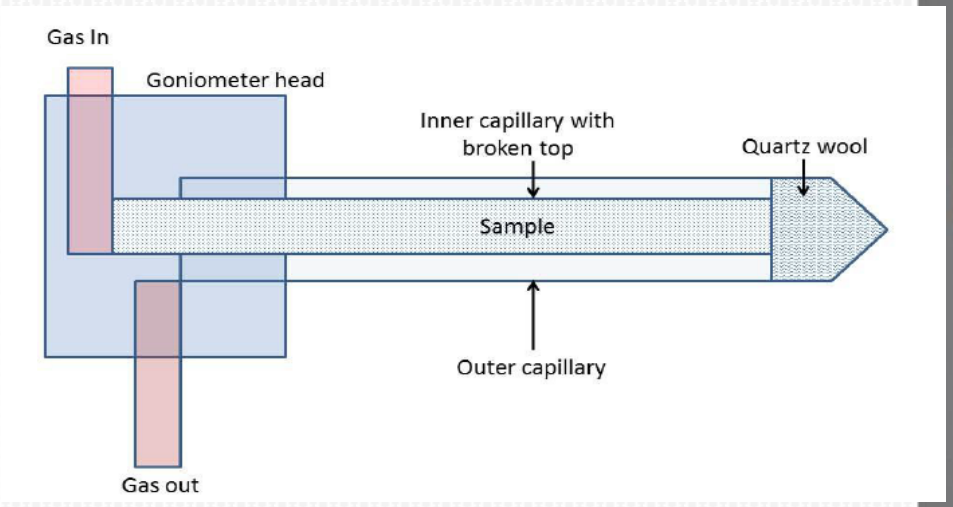
- H2 Capacity (> 6 or 9 %)
- Low thermodynamic stability (Td < 150 C)
- High H kinetics for sorption (around 5 min. refilling time)
- High stability against moisture (>500 cycles)
- Low cost

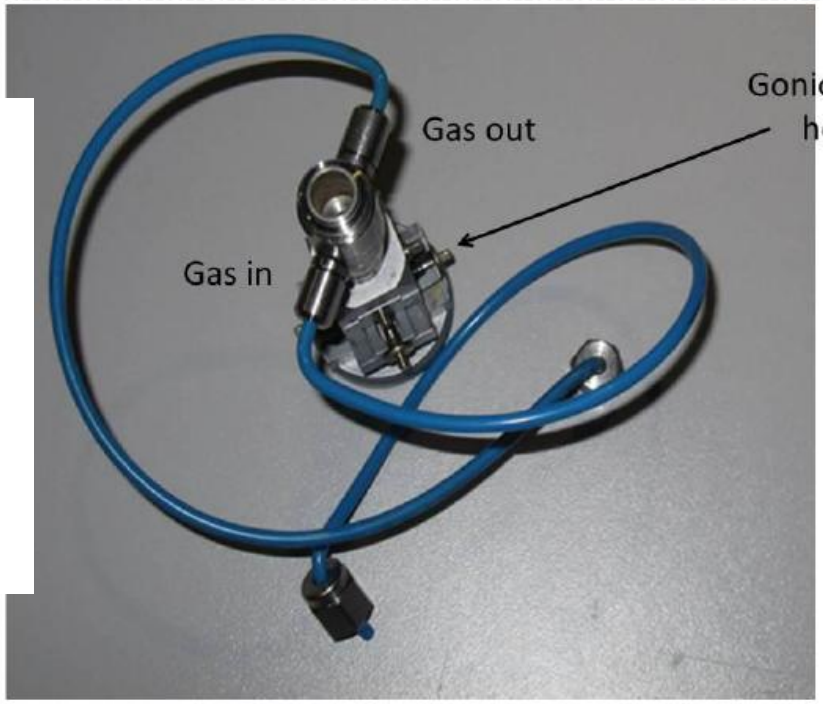




Structural and catalysis keys

Two capillaries system for gas controlled in-situ XRD experiments

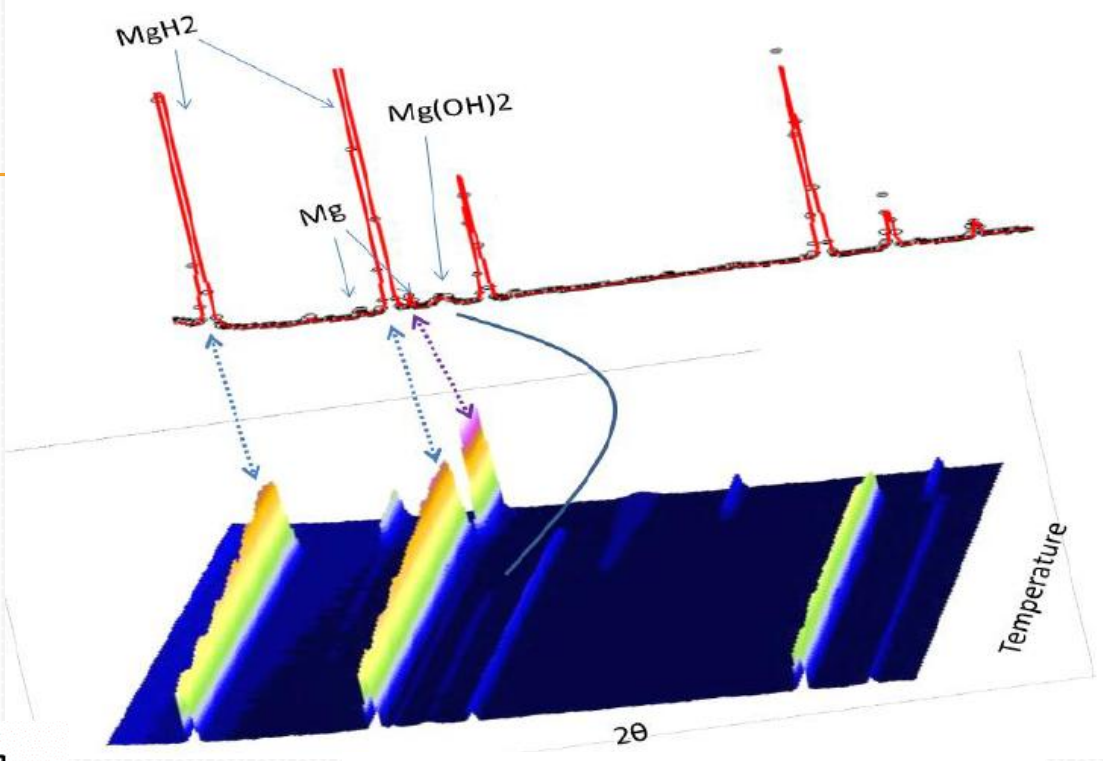


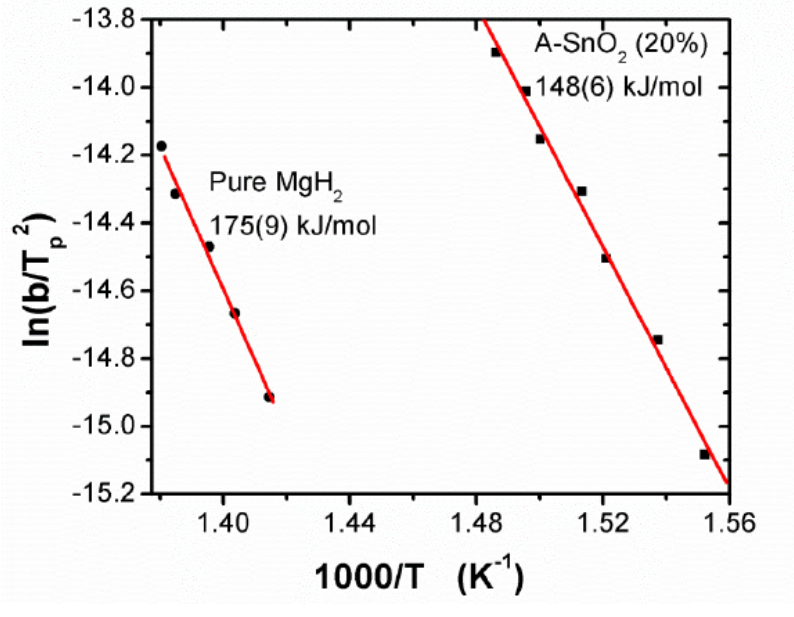


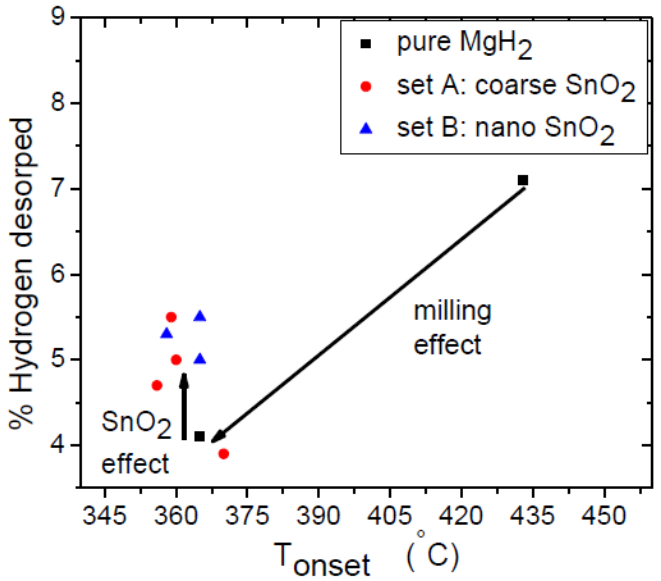
- Some reactions occur only under special environment …
  - Or Oxygen sensitive samples (inert gases needed)

Improvements by:

- Using catalysis
- Increases structural defects by milling







Conclusions

- Simultaneously combining local/long rang order techniques is appreciated
- Lattice absorb energy faster (T1) in the presence structural defects (diffusion improves)
- Defects are much effective on T1 than size unless very small size >7 nm
- Well characterized furnace at MCX beamline for In-situ XRD experiments
- Grain growth is enhanced by dislocations
- Hydrogen desorption of MgH2 by structural defects and catalysis (SnO2)
- In-Situ XRD is powerful tool to investigate structural evolution for Hydrogen storage materials


UNIVERSITY
OF TRENTO - Italy
elettra
Thank You!