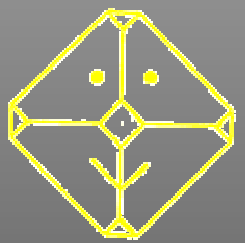
In-situ powder diffraction studies of hydrothermal synthesis and Hydrothermal synthesis of perovskite materials



Poul Norby

Department of Chemistry

and

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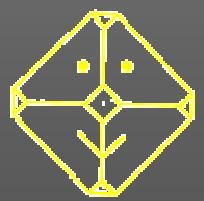
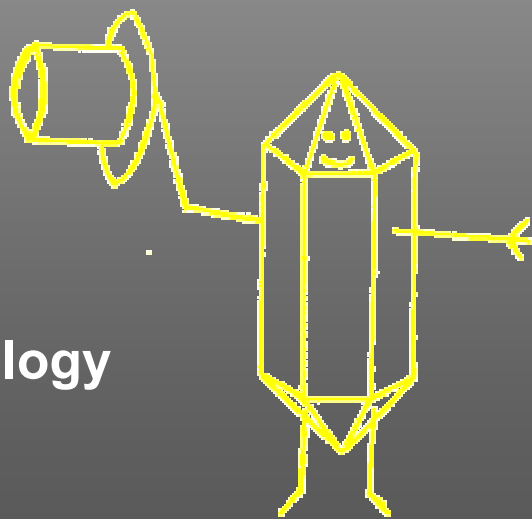
University of Oslo, Norway





Examples of in-situ synchrotron X-ray powder diffraction studies

- Hydrothermal synthesis: **zeolites, aluminophosphates, microporous sulfides, mesoporous materials, layered phosphates**
- Chemical reactions: **Sorel cements, carboxylation of phenolates, solid state synthesis,**
- Solid/gas reactions: **high temp. oxidation/reduction**
- Ion exchange
- Intercalation
- Dehydration and dehydroxylation
- Adsorption/desorption
- Thermal transformations
- Structure determination and Rietveld refinement

In-situ studies using synchrotron and conventional X-ray powder diffraction

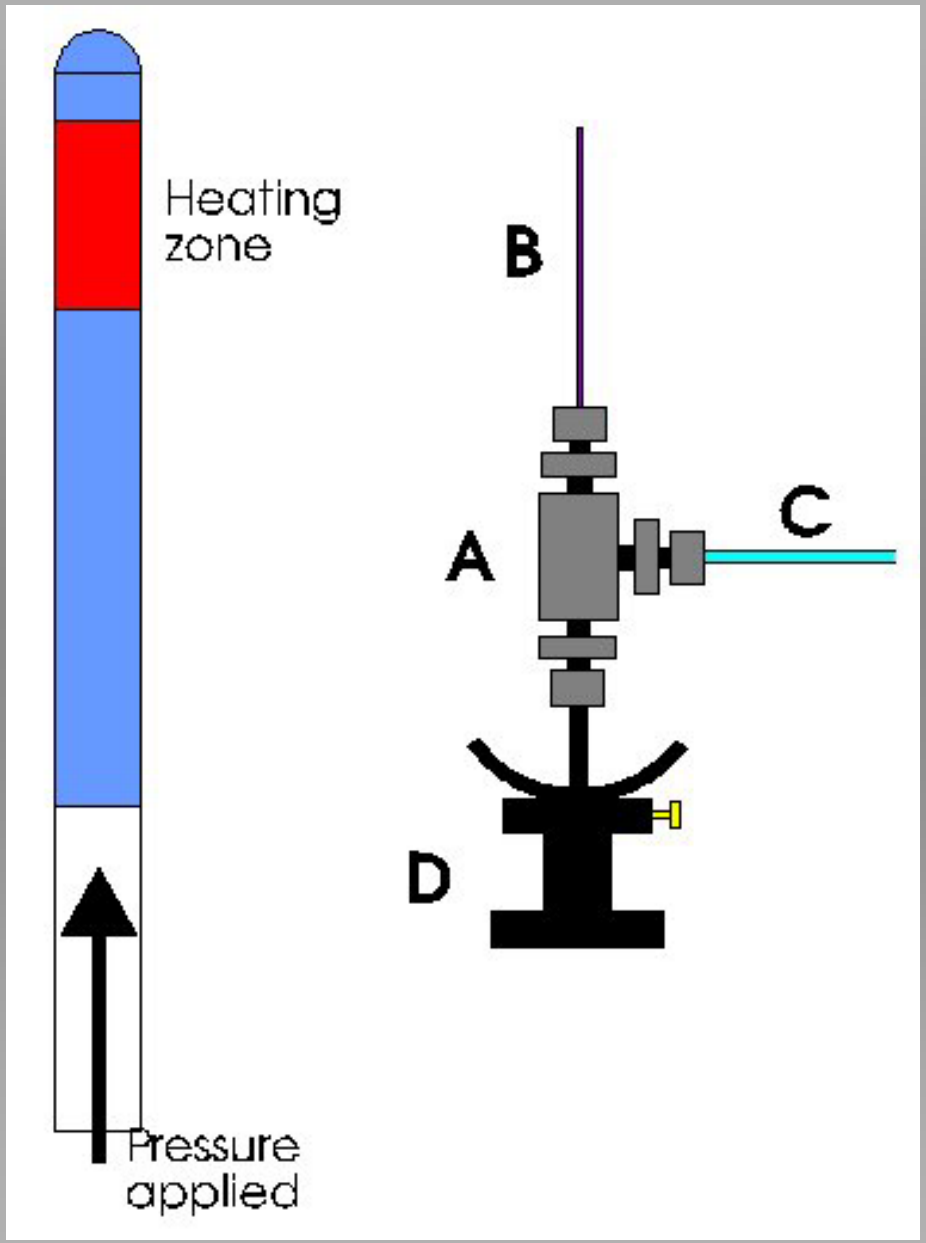
- ➔Time resolved studies of hydrothermal synthesis of catalytic materials
- ➔Hydrothermal synthesis of nanomaterials
- ➔Gas/solid reactions at high temperature

Micro Reaction Cell for In-situ studies of Hydrothermal Synthesis

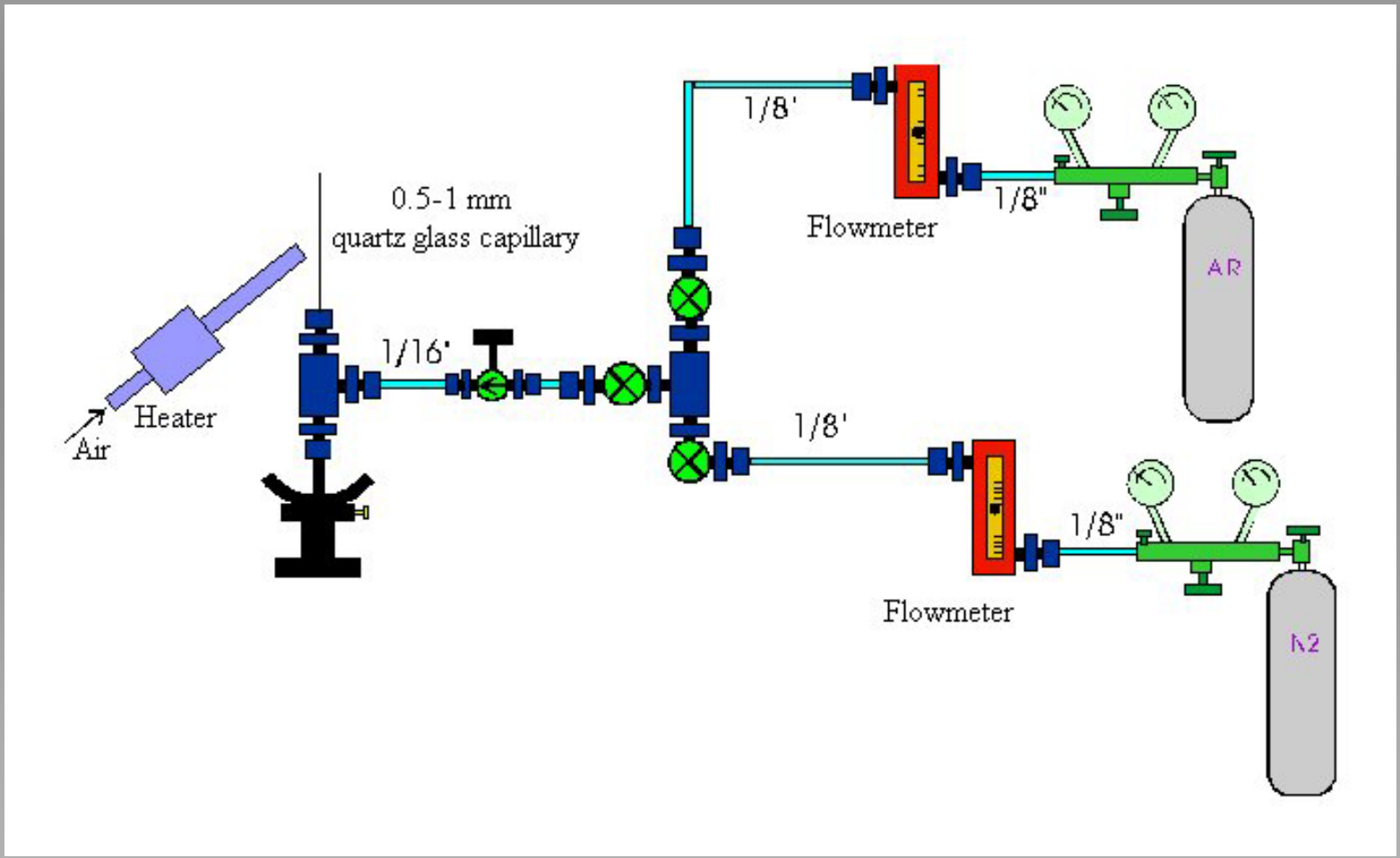
0.5-0.7 mm quartz glass capillaries

Hot Air Heater
Nitrogen pressure applied

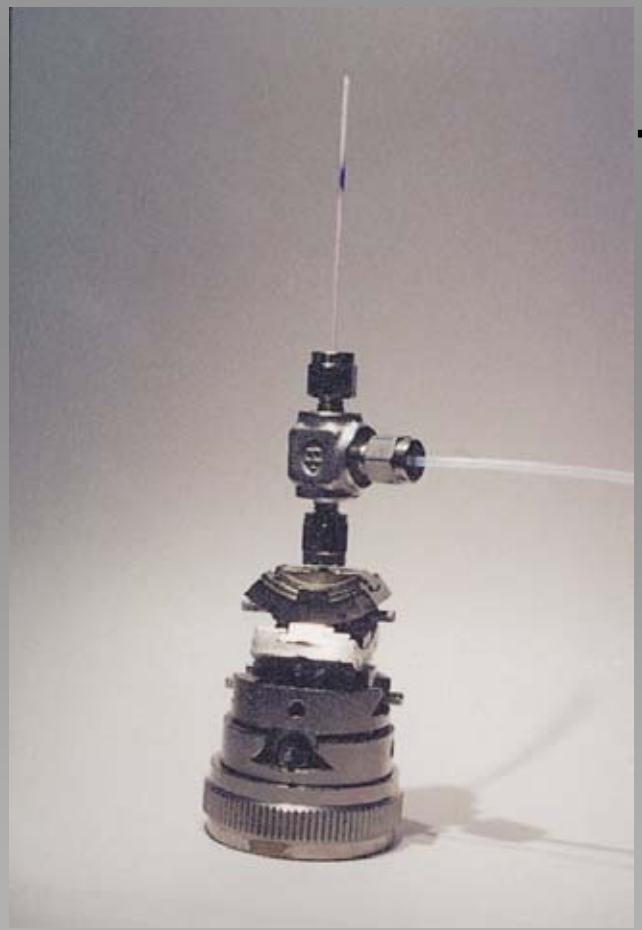
Hydrothermal conditions up to 260°C (45 atm.)



Micro reaction flow cell for studies of solid-gas reactions



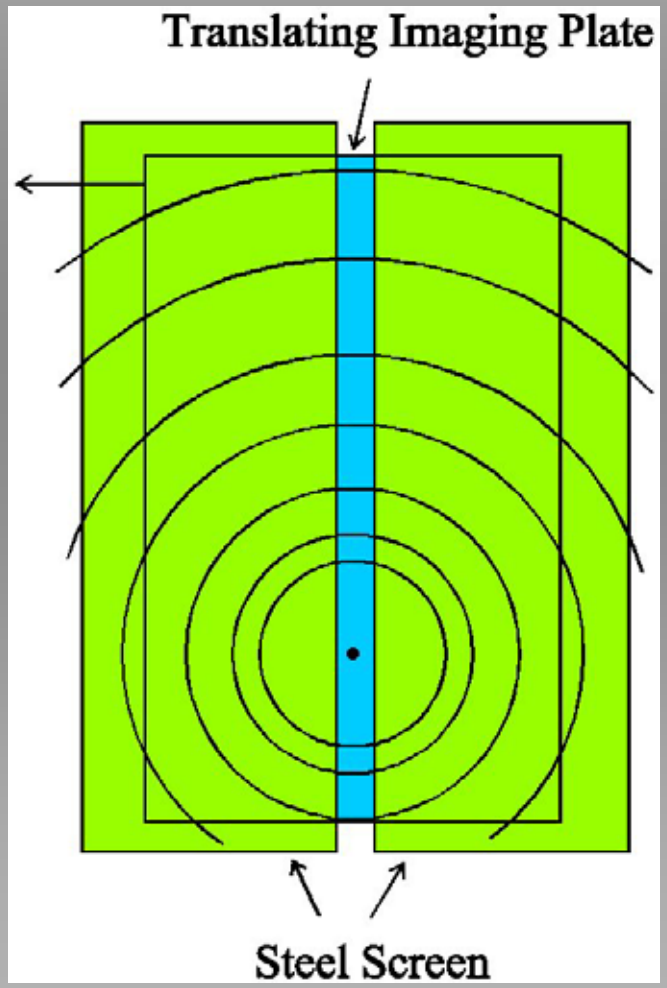
Micro Reaction Cell for In-situ studies of Hydrothermal Synthesis using Synchrotron X-ray Powder Diffraction



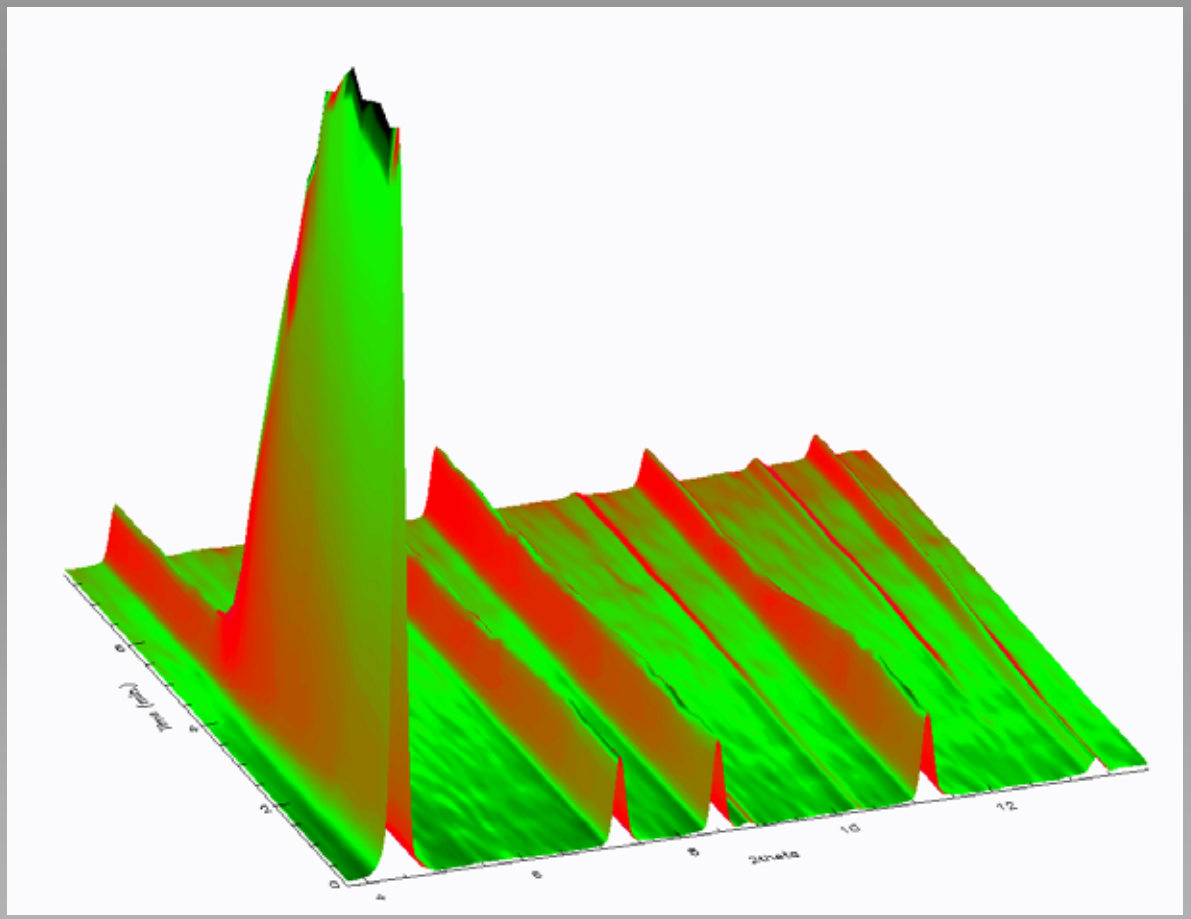
The Micro Reaction Cell

Mounted at beamline
X7B, NSLS, BNL
with hot air heater

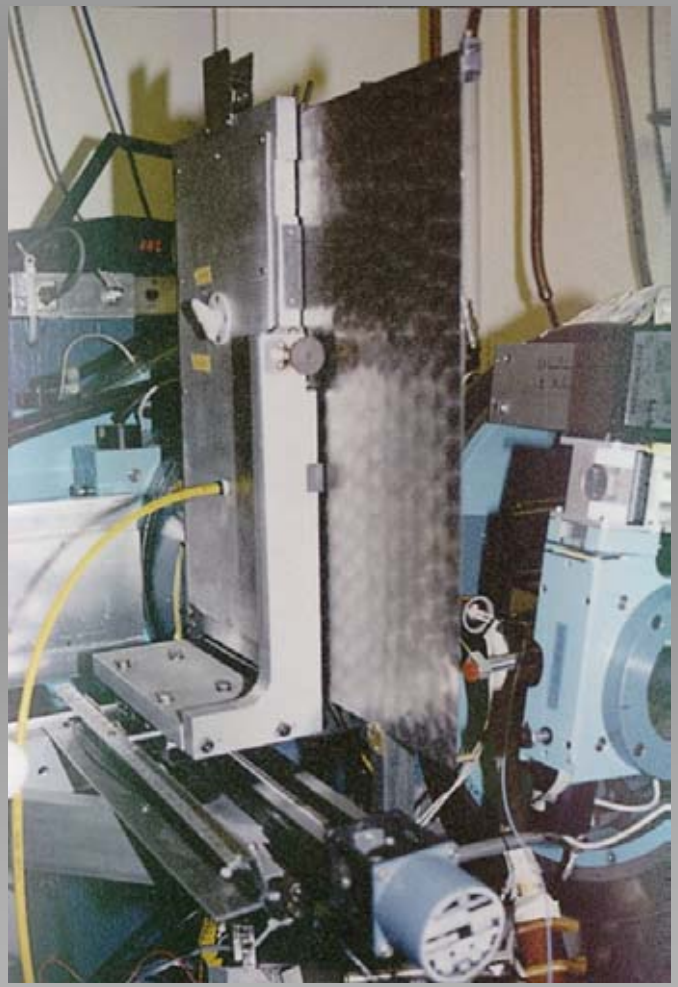
Translating Imaging Plate (TIP) Camera



3-dimensional representation

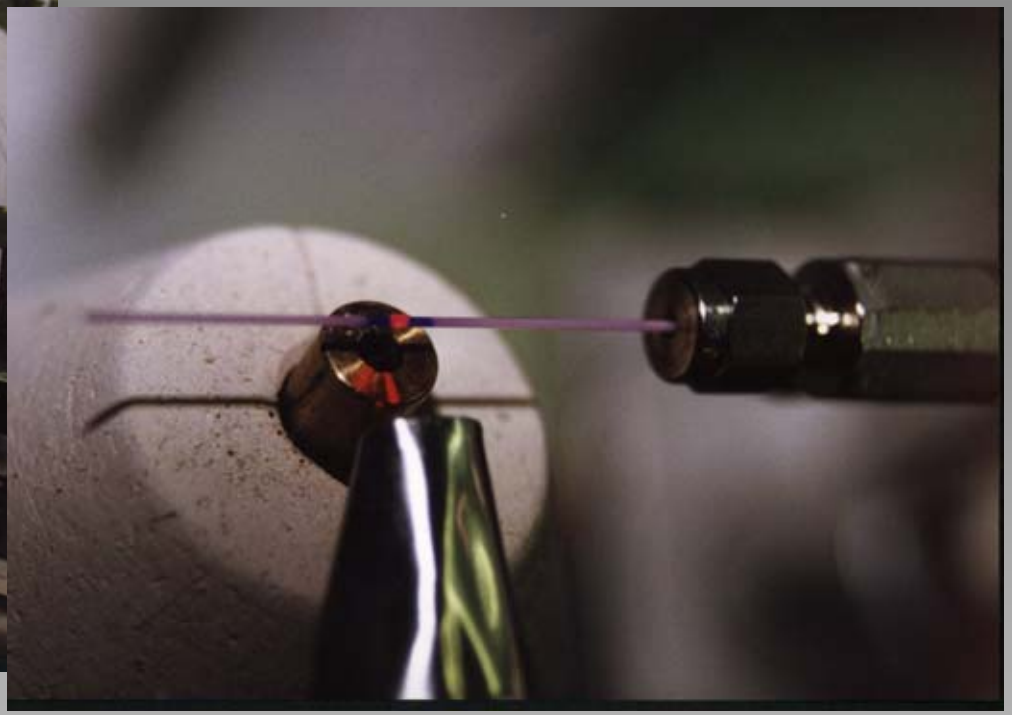


The Translating Imaging Plate (TIP) camera

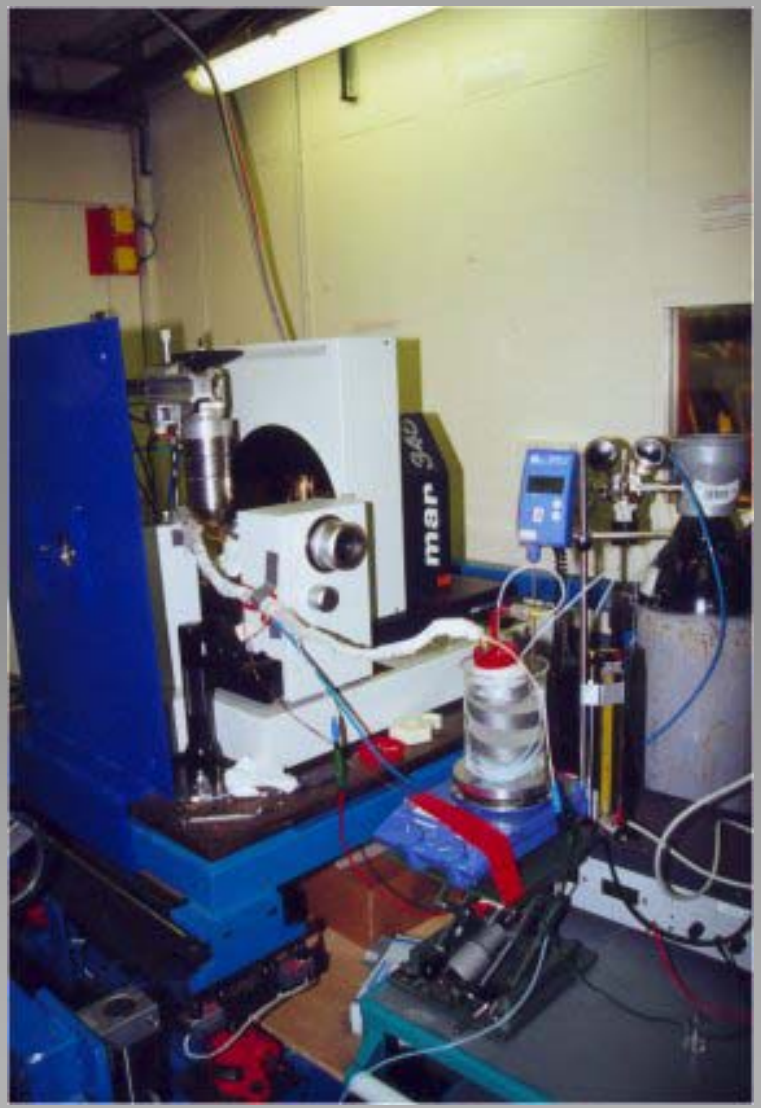


Rear view of TIP camera mounted at X7B, NSLS, BNL

The TIP-II Camera at GILDA, ESRF

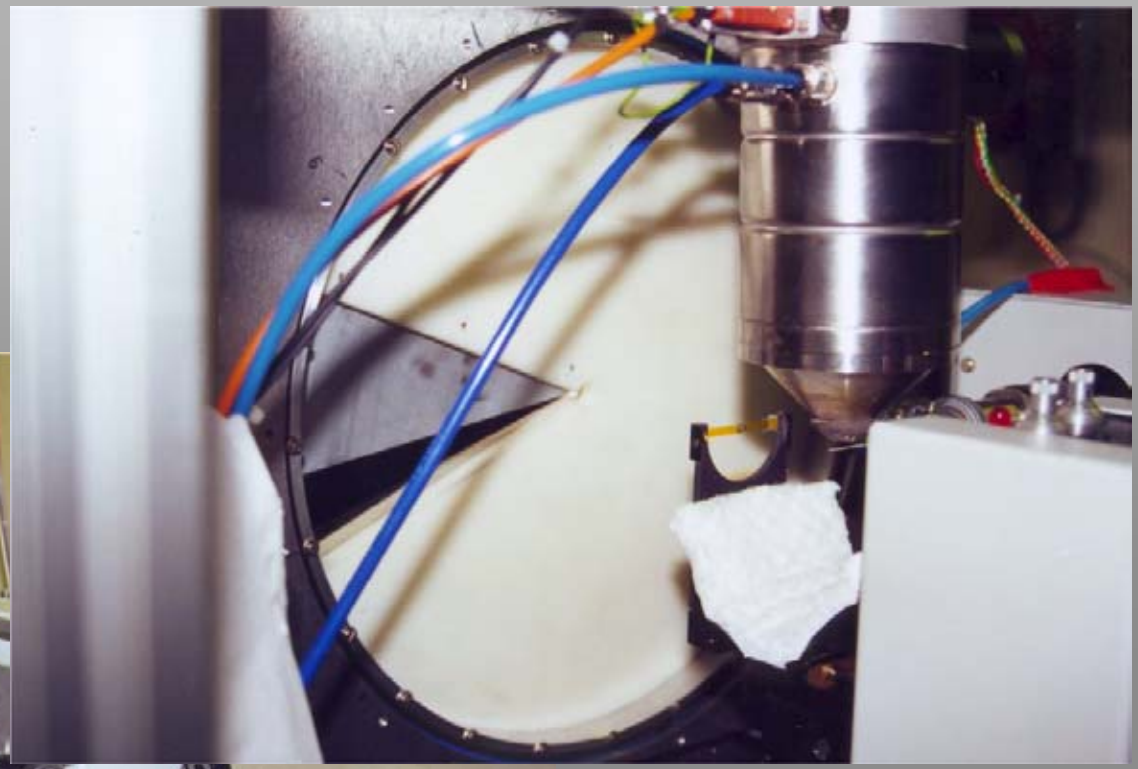


Swiss-Norwegian beamline (SNBL) at ESRF



MAR345 detector
High Temperature heater
Time resolution > 90s

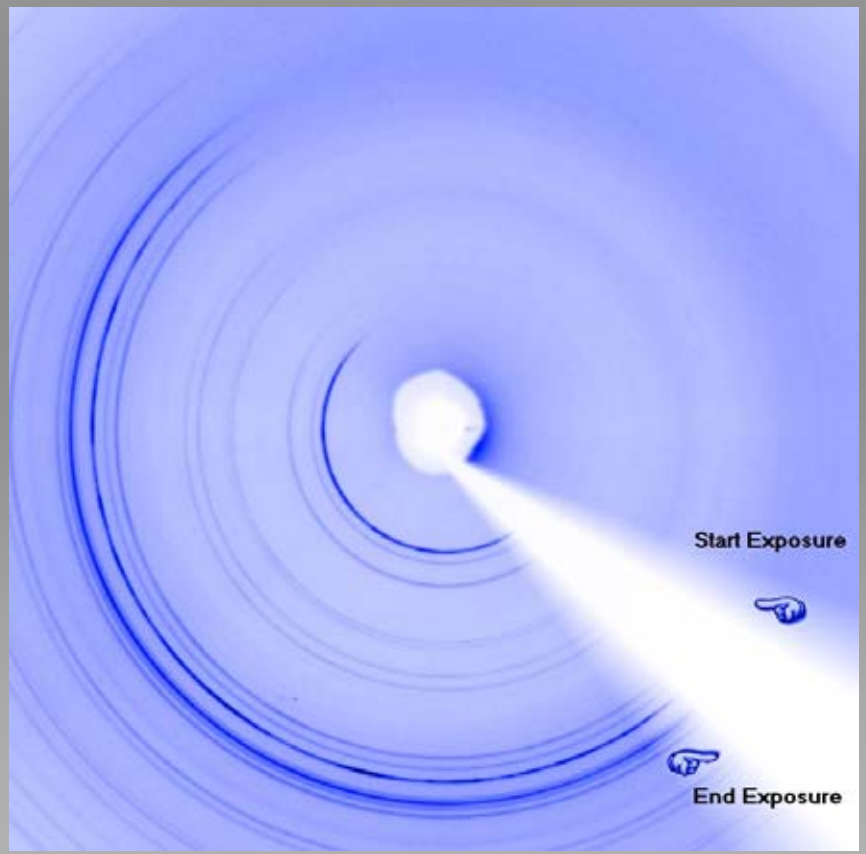
Rotating Slit System MAR345, SNBL

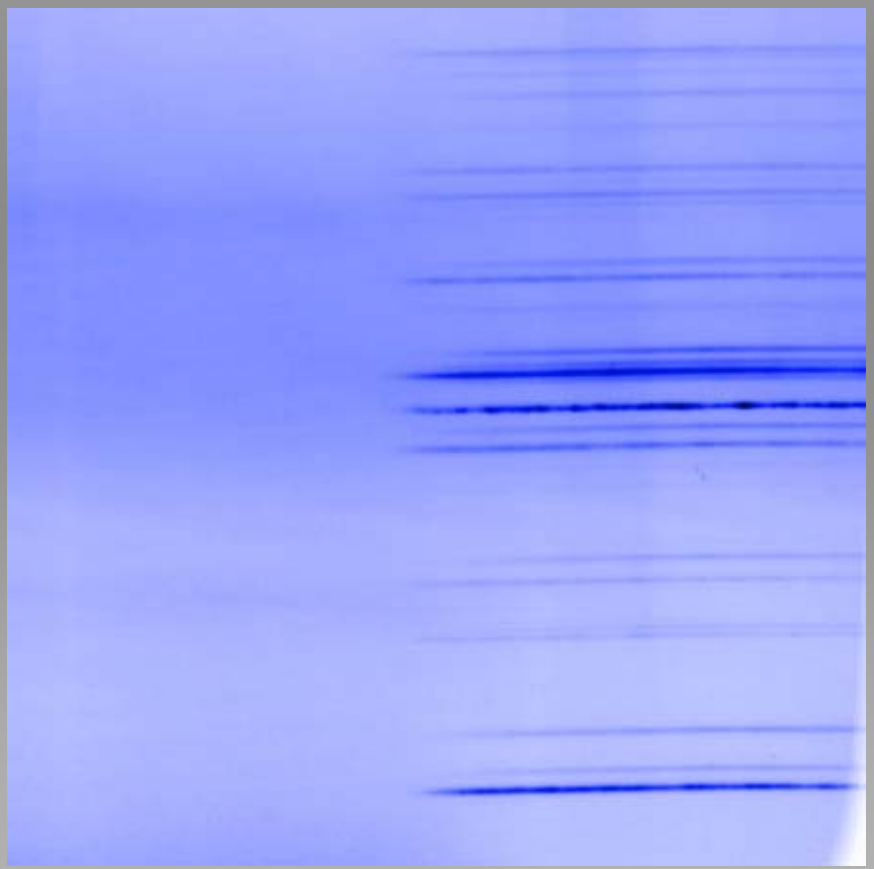


Time resolution 100ms

Rotating Slit System, SNBL, ESRF

Synthesis of cobalt substituted aluminophosphates. Fast ramp, RT-200°C, 15°C/min





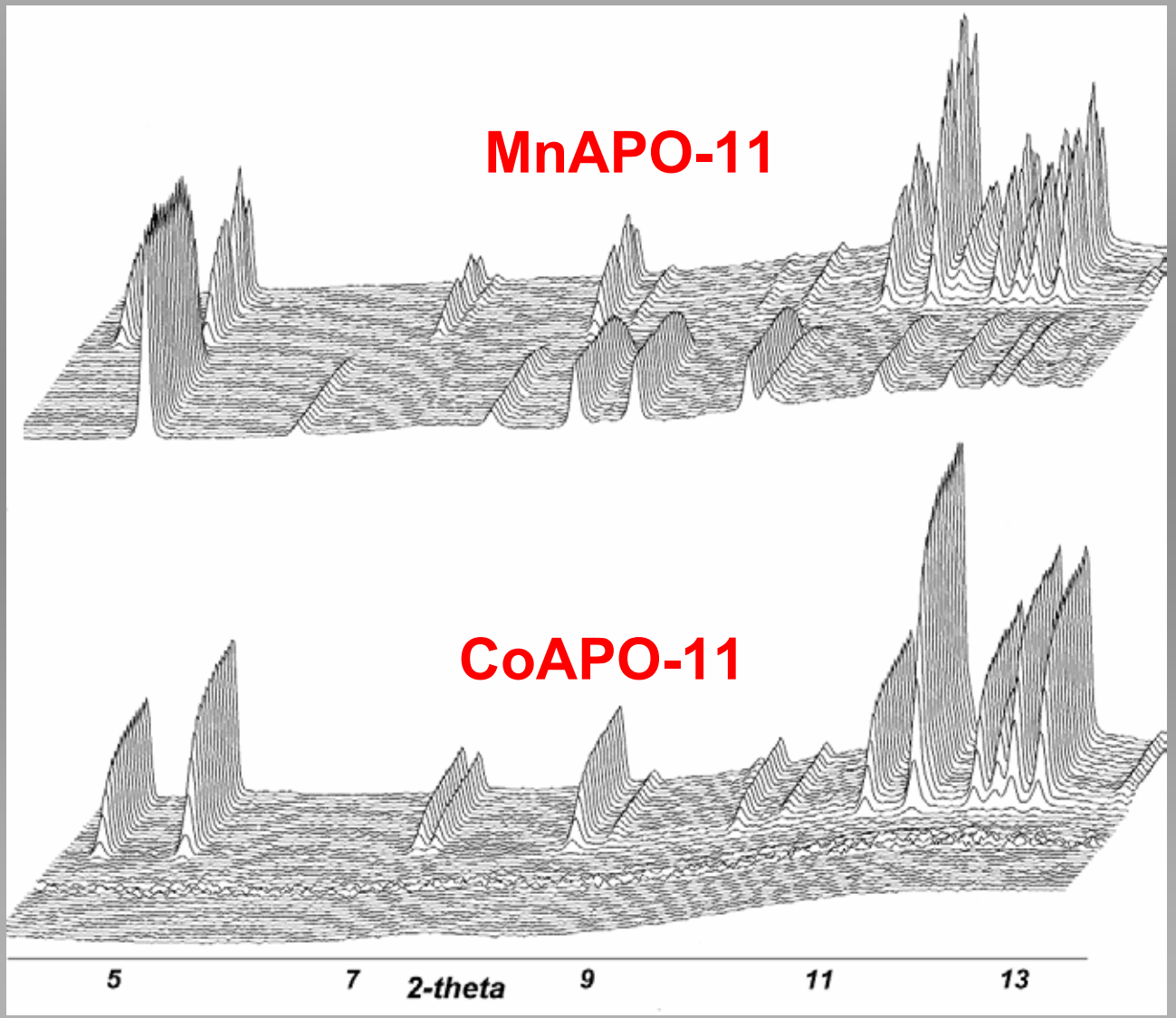
In-situ studies at GILDA

TIP-II camera

GILDA, ESRF

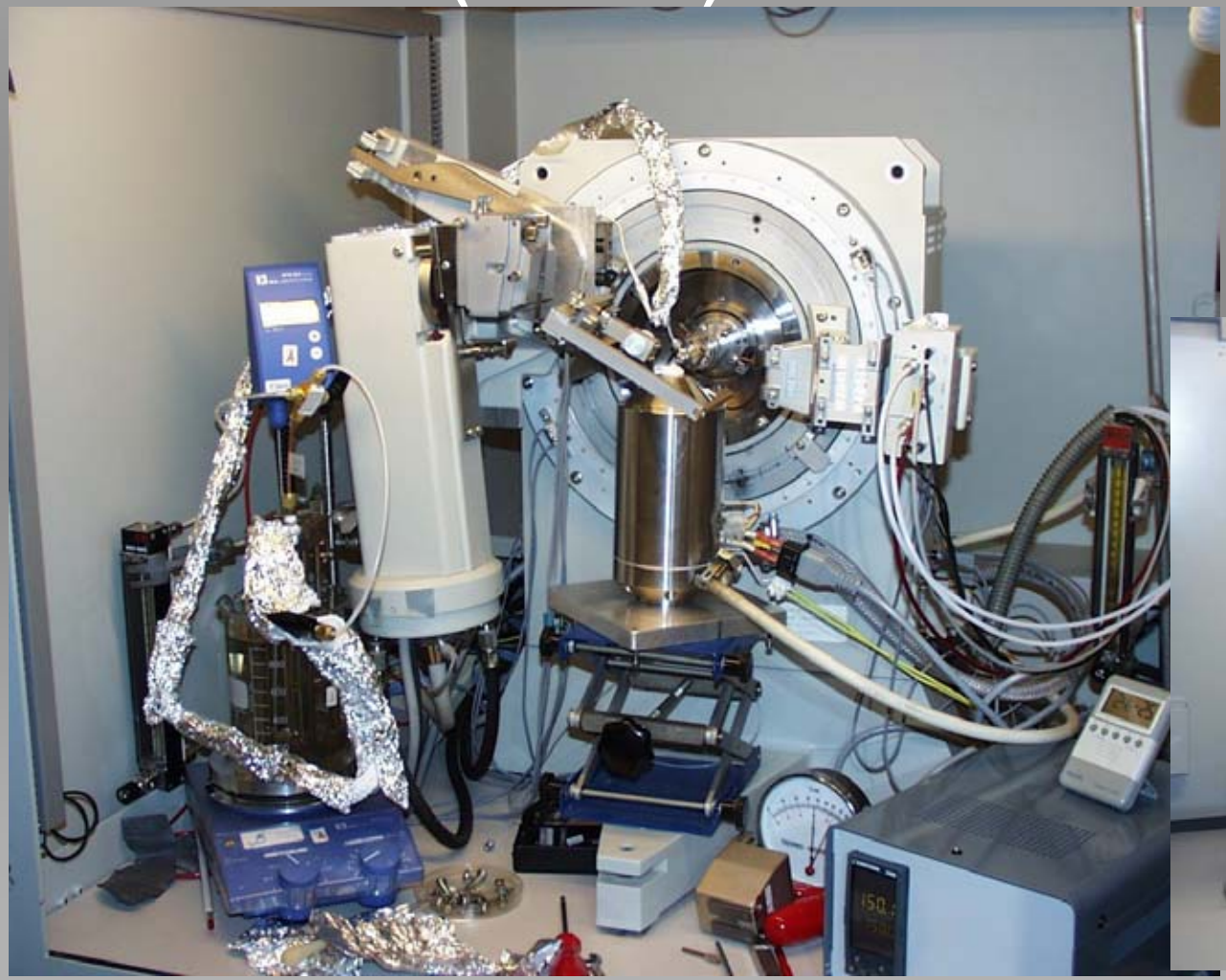
Heating 25-225°C

λ = 0.8251Å



In-situ studies using conventional X-ray sources.

Siemens (Bruker) D5000



Siemens (Bruker) GADDS/APEX II

Hydrothermal synthesis of Microporous Aluminophosphates

Kinetic Analysis

Synthesis of transition metal substituted microporous alumino-phosphates from non-aqueous media.

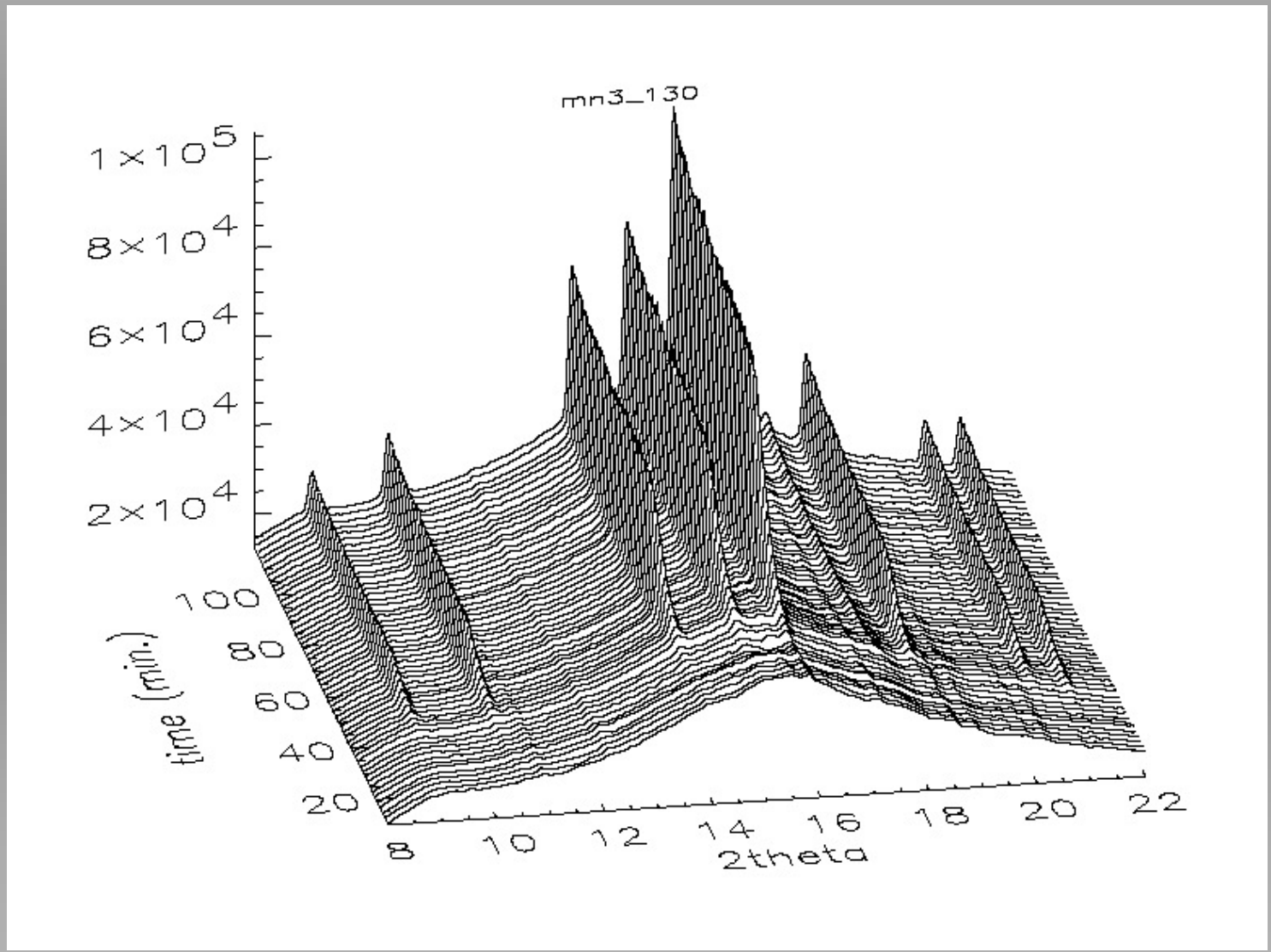
P. Norby et al., *Inorg. Chem*. 38 (1999) 1216-1221

Crystallization of MAPO-5, M = Mn, Co

The effect of mineralizing agents

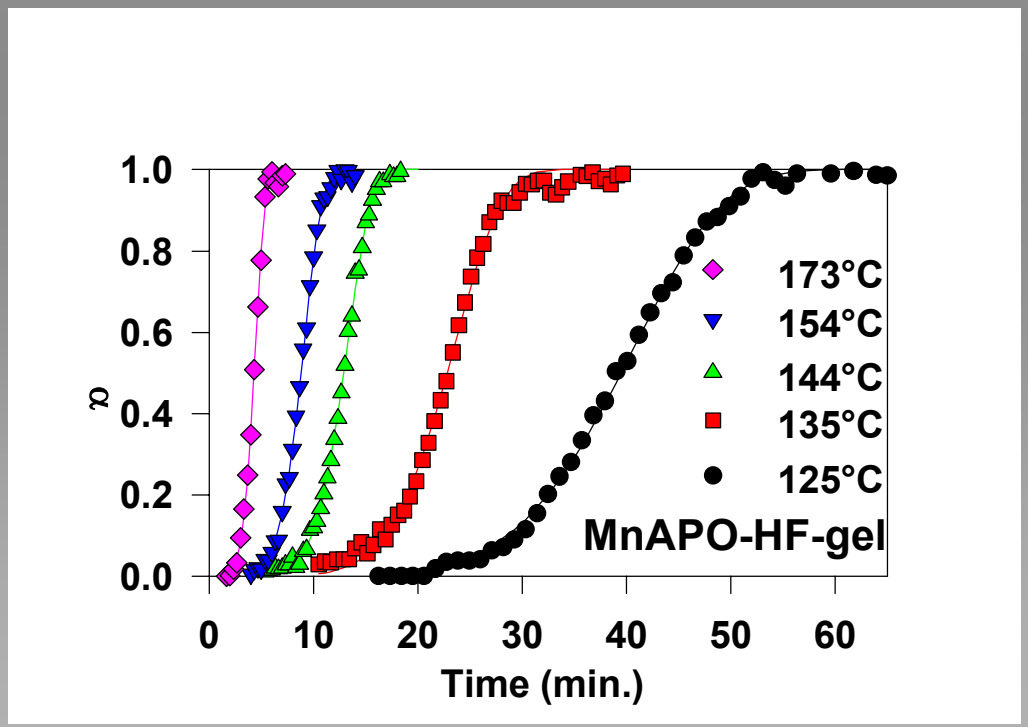
Solvent:	**ethylene glycol**
Template:	**triethylamine, TEA**
Al-source:	**aluminium isopropoxide**
P-source:	**85% H_3PO_4**
Trans. Metal:	**cobalt- and manganese acetates**
Mineralizer:	**HF**
Temperature:	**125-180°C**

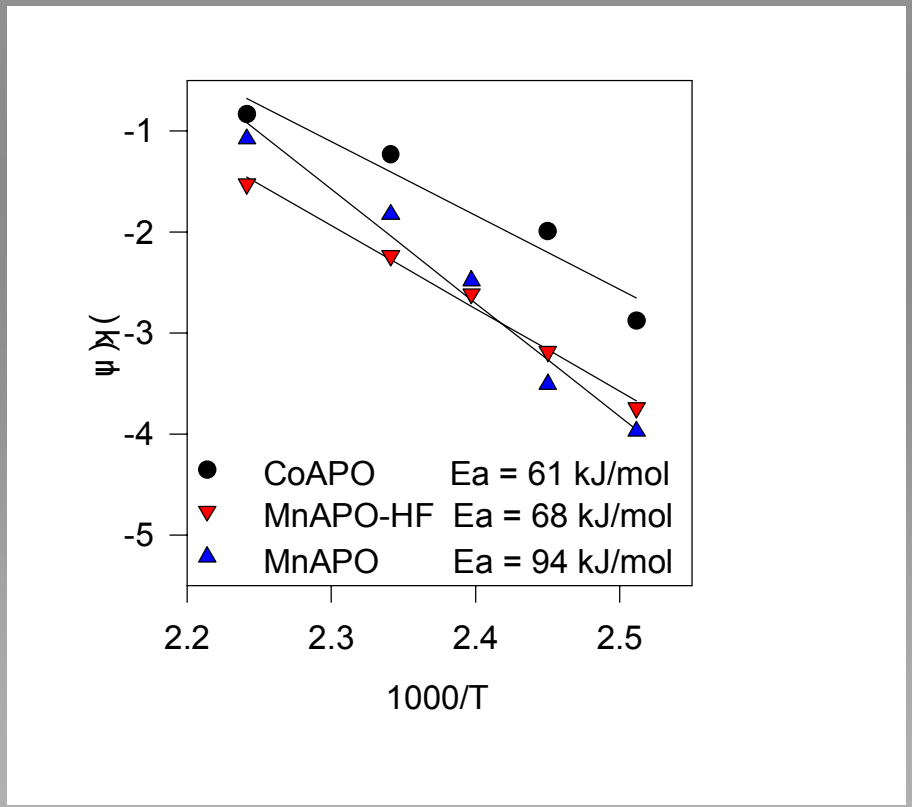
Synthesis of MnAPO-5 at 130°C



Kinetic analysis: MAPO-5 crystallization

Avrami type kinetics expression



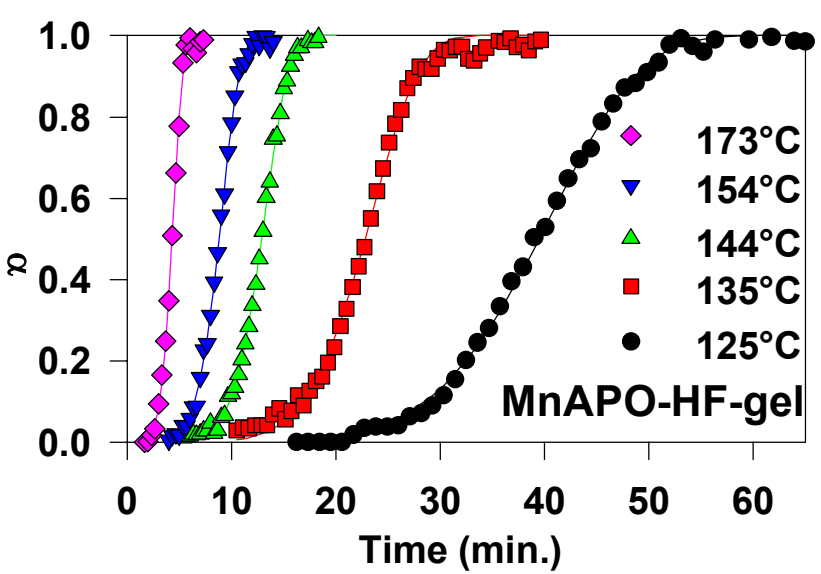


Using the normalized time scale

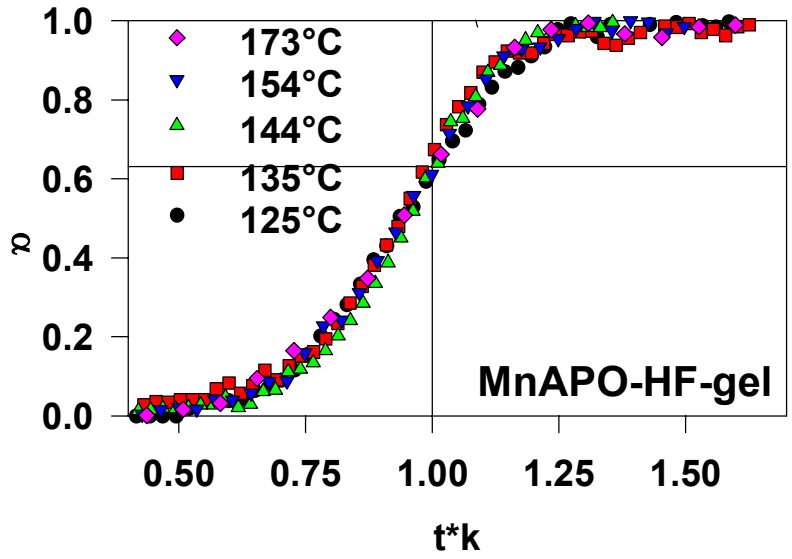
Solvothermal crystallization of MnAPO-5
In-situ synchrotron X-ray powder diffraction

Crystallization curves

Real time



Normalized time



Kinetic analysis using Avrami type expressions.

$$\alpha = 1 - \exp(-(k(t-t_0))^n)$$

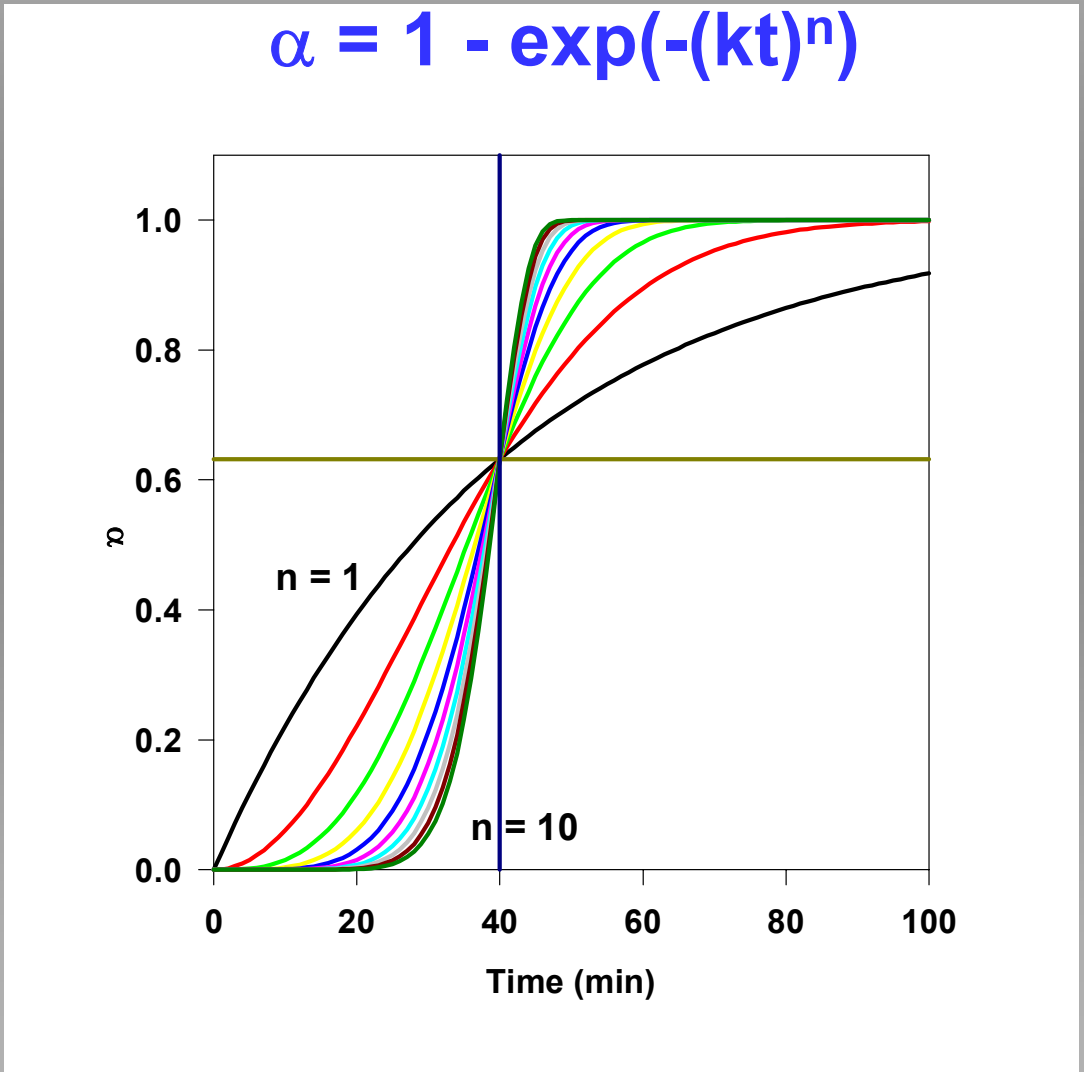
- For most applications, the Avrami expression is empirical
- The equation as used most frequently only describes the initial stage of the conversion
- Care must be taken in comparing results obtained using different n-values.

Using $t_{0.63}$ in kinetics analysis

Calculated crystallization curves using constant k.

All curves intersect at:
t = 1/k,
i.e. kt=1 and
α = 1-exp(-1) = 0.632

Thus k may be determined independently of the value of n by finding the time where α = 0.63, $t_{0.63}$



Synthesis of nanomaterials

➔Preparation of free-standing, non-agglomerated, single nanocrystals with size- and morphology control.

➔Mainly hydrothermal and solvothermal synthesis.

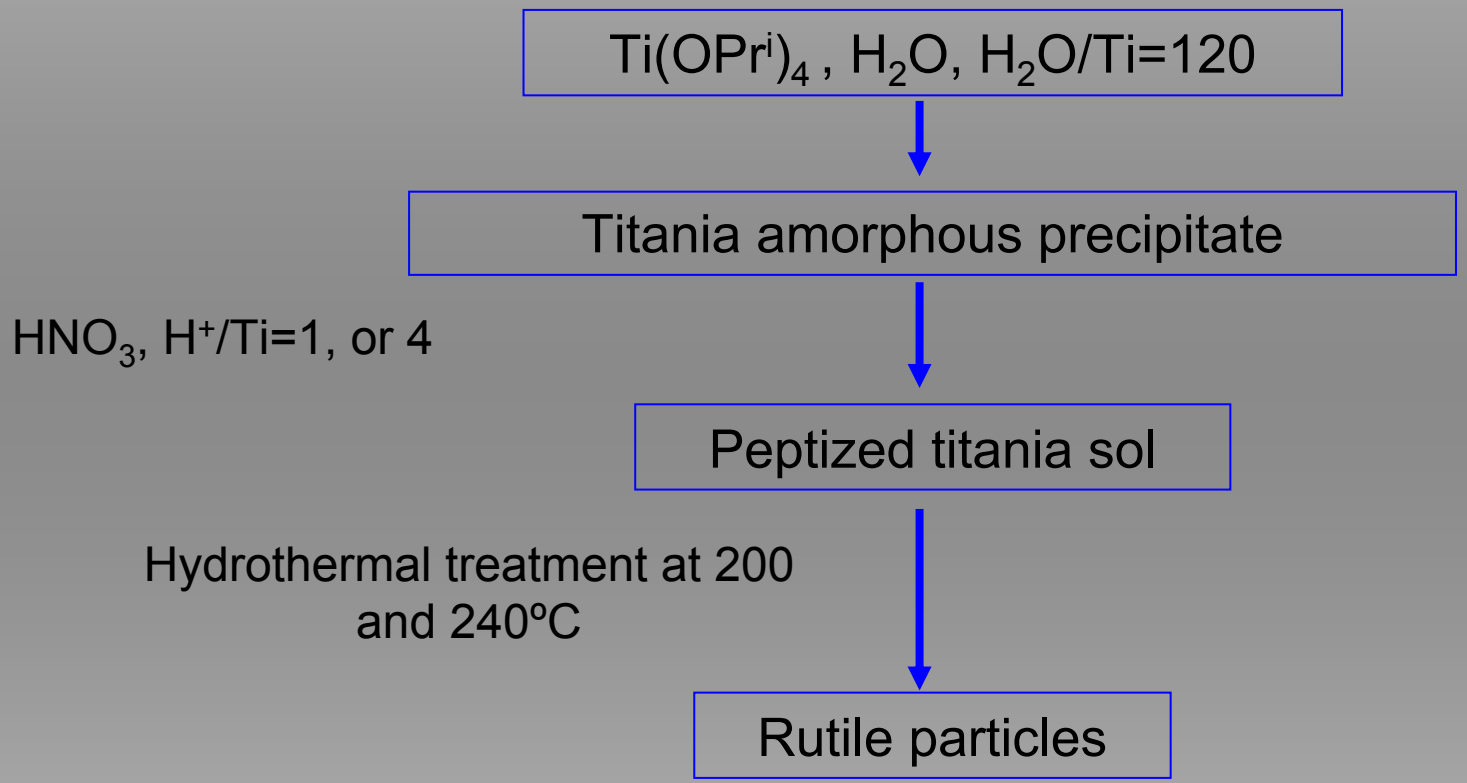
TiO_2 nanocrystals

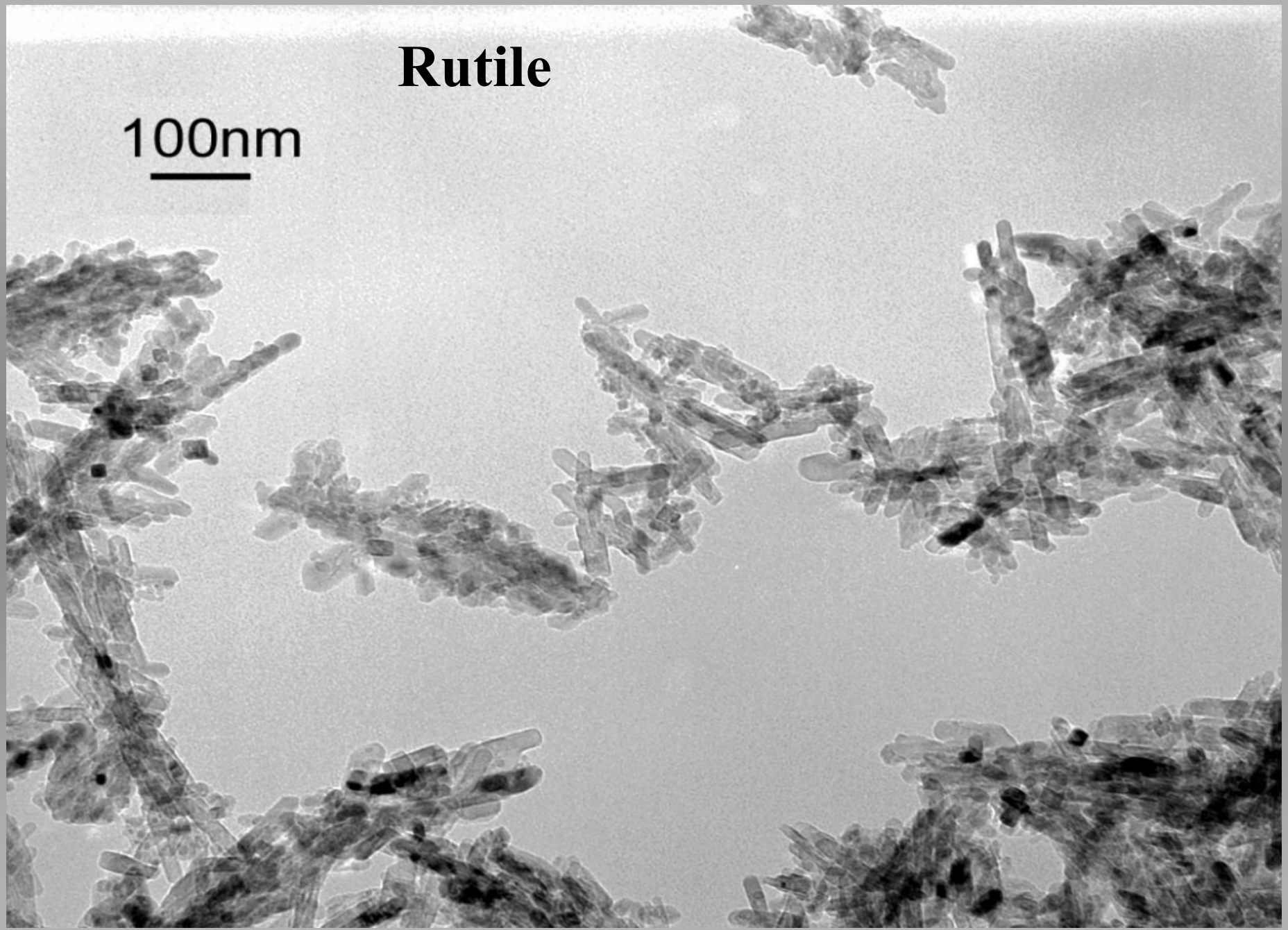
Juan Yang

- ➔Preparation of rutile nanocrystals; the role of HNO_3 as a peptizer
- ➔Preparation of anatase nanocrystals from TMAOH, TEAOH, TBAOH peptized sols.
- ➔Preparation of $Ti(Fe)O_2$ nanorods

Preparation of rutile nanopowders:

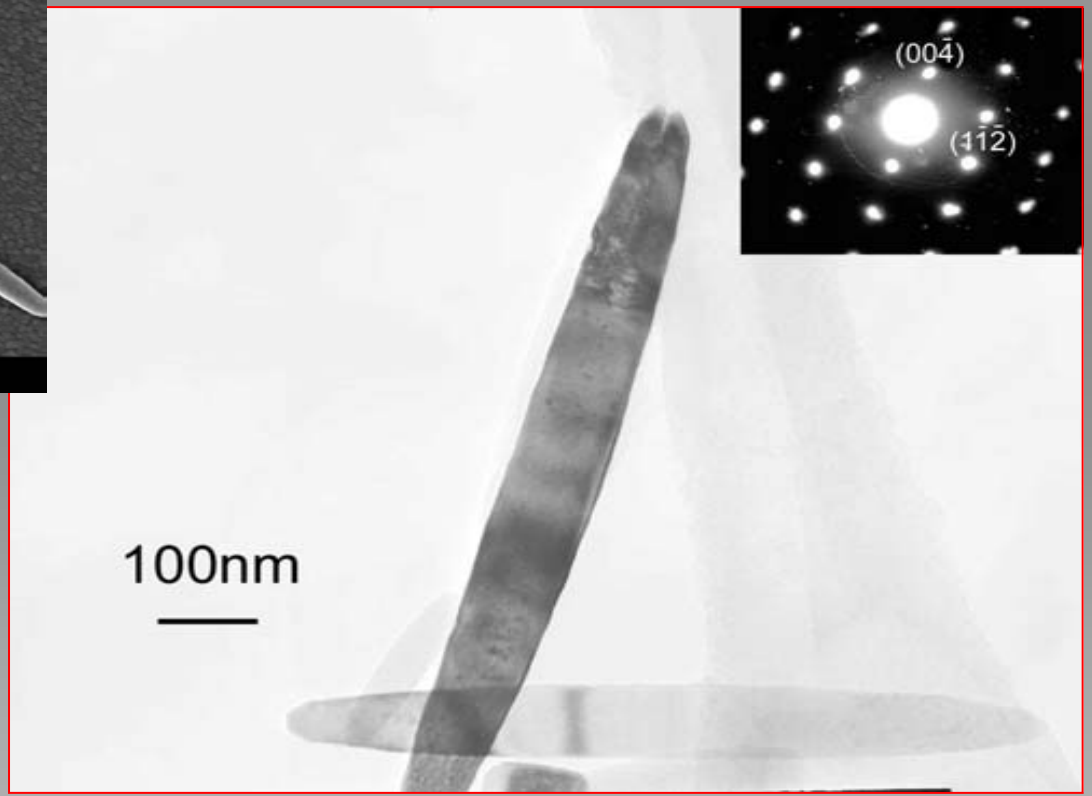
Raw materials: $Ti(OPr^i)_4$, HNO_3, H_2O



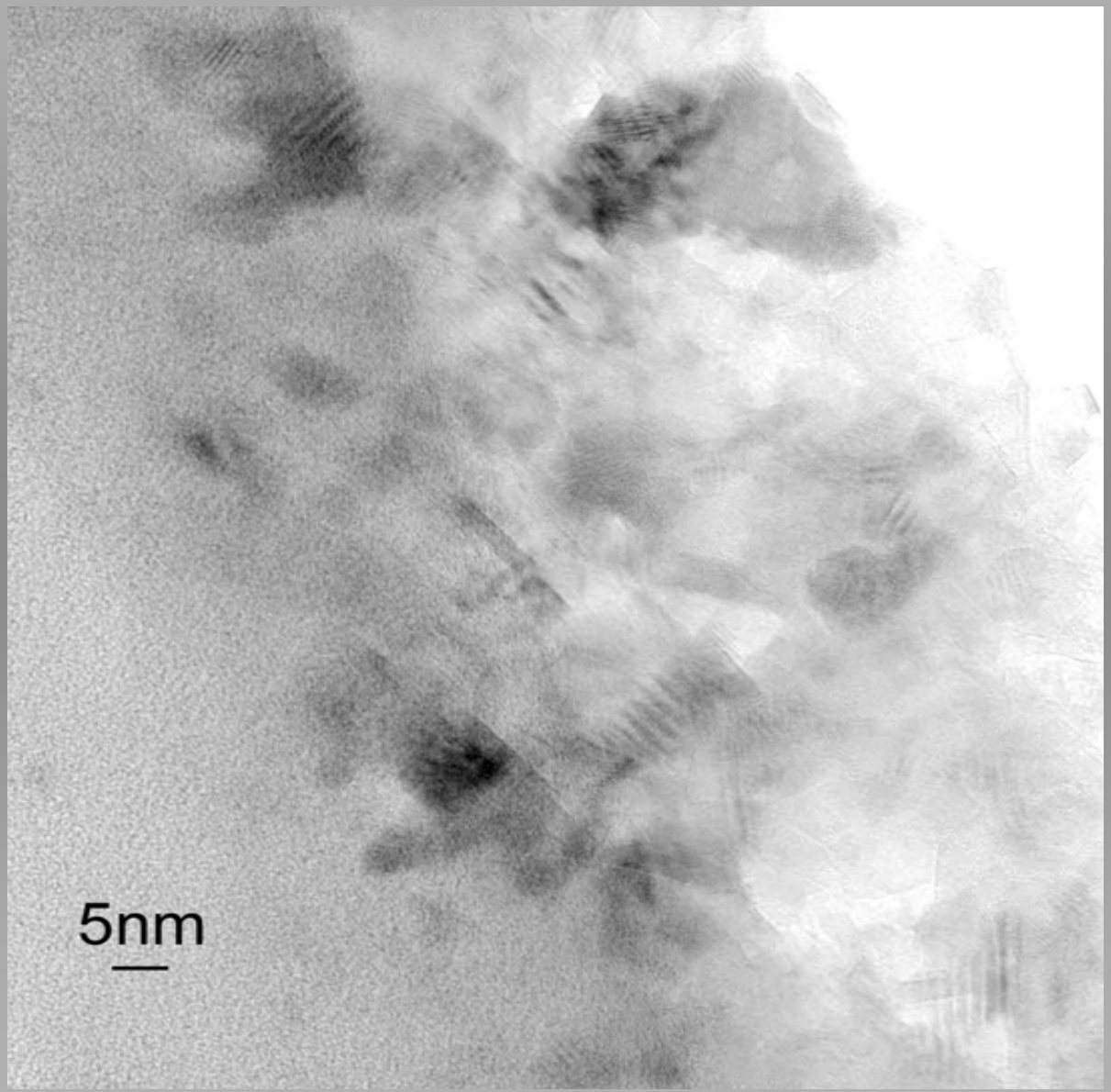

Rutile
100nm

Hydrothermal Synthesis of Fe-doped Anatase (TiO_2) nanorods

TENOH peptized sol
Hydrothermal synthesis



HRTEM morphology of the TENOH-peptized titania sol



Hydrothermal synthesis of Co_3O_4 nanocubes

Starting materials: 0.1M $Co(NO_3)_2$ aqueous solution

tetraethylammonium hydroxide (TENOH), NaOH,

$TENOH/Co^{2+}$ ($NaOH/Co^{2+}$) =2, 6 and 8

$NaNO_3$

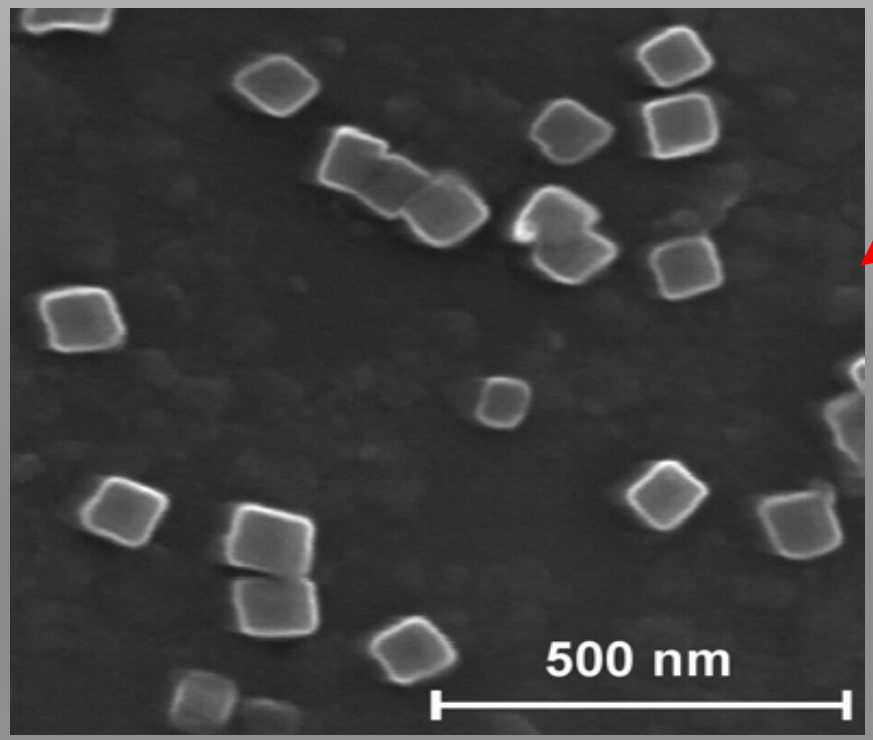
Heated at 80°C for 1.0, 2.5, 4.5 and 6.0 hrs

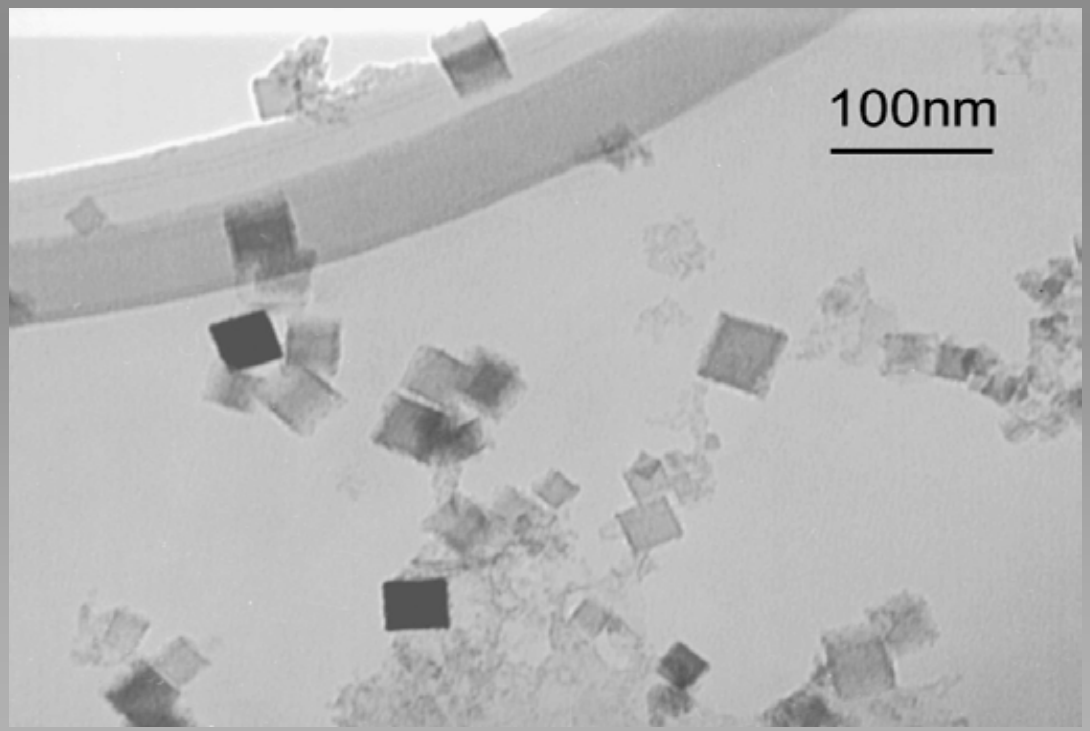
Hydrothermal treatment at 200°C/2hrs

Characterization: XRD, SEM, TEM

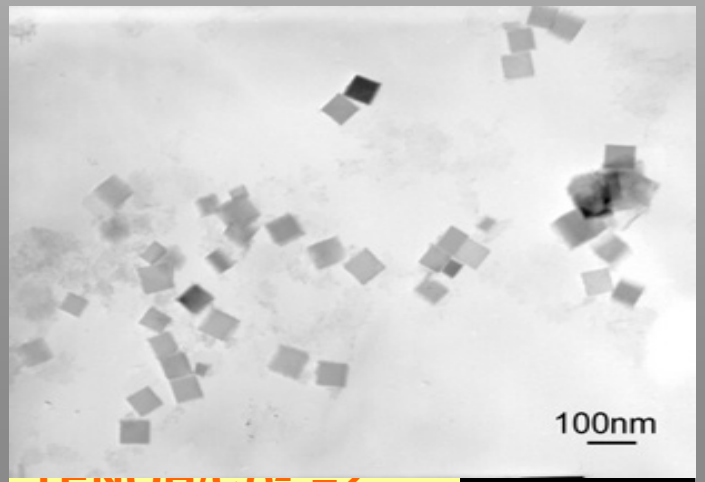
News: Hydrothermnal synthesis using microwave heating

SEM and TEM images of Co_3O_4 nanocubes

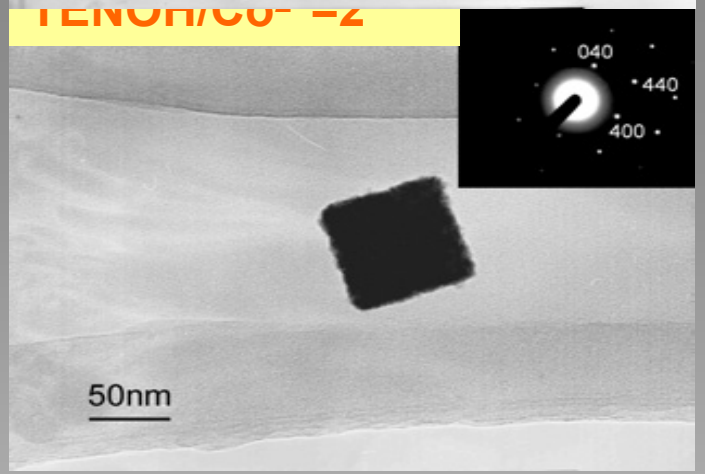


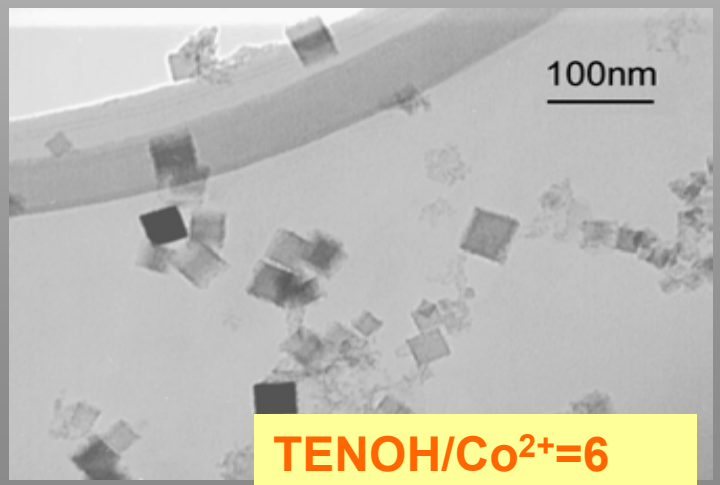


TEM images of the TENOH-peptized powders

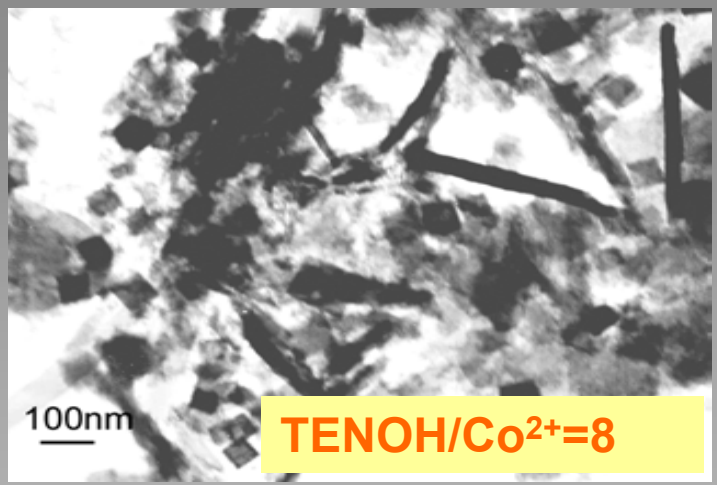


TENOH/Co^{2+}=2





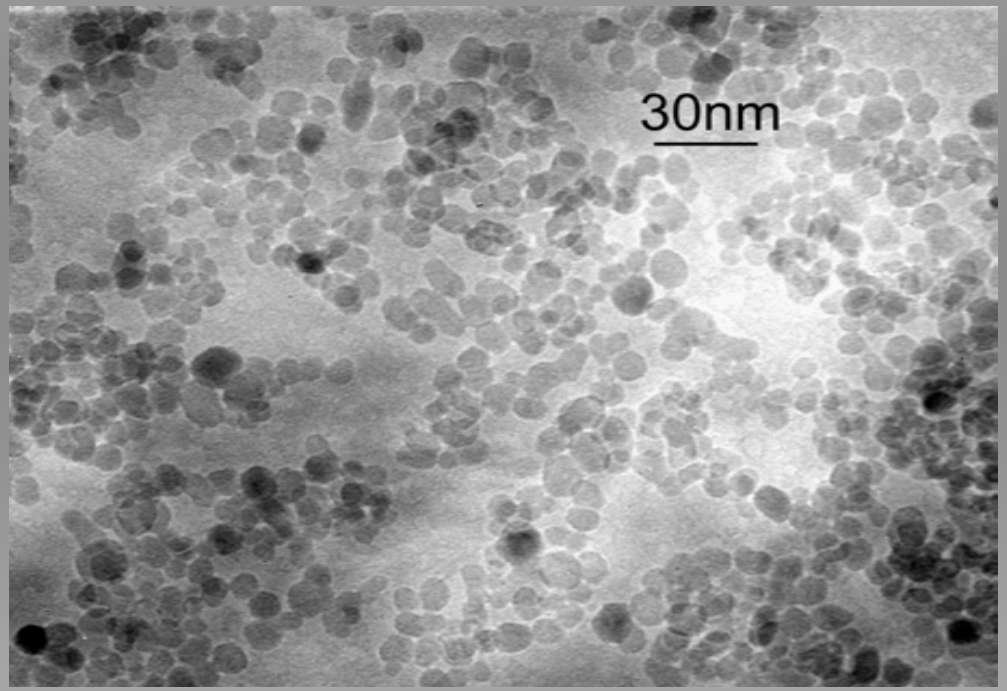
TENOH/Co^{2+}=6



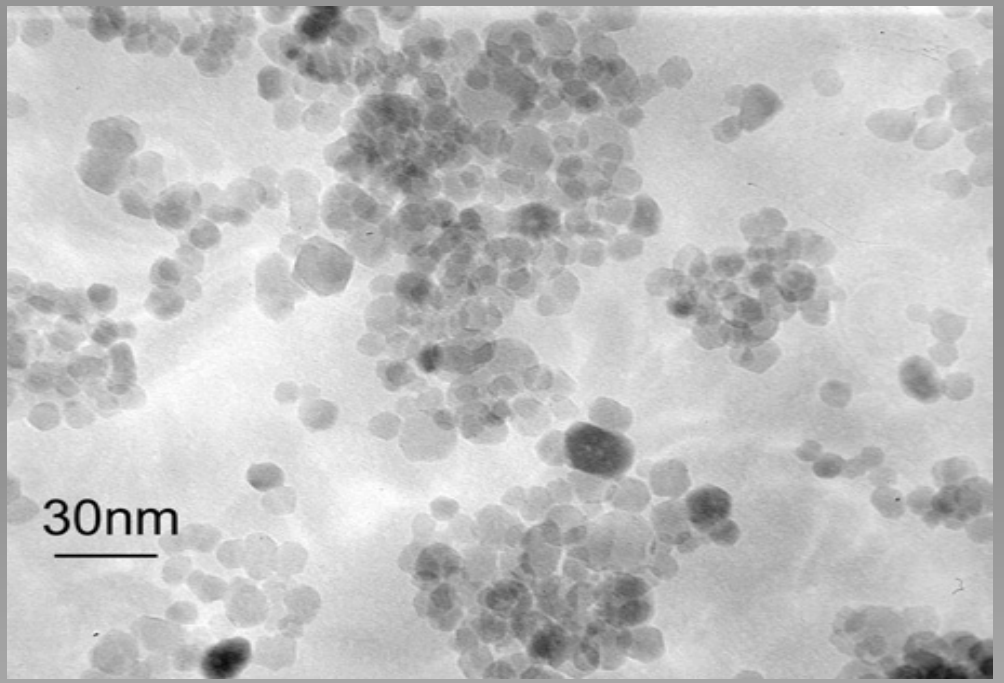
TENOH/Co^{2+}=8

Other spinel type oxides

Magnetic properties



$Co_xZn_{1-x}Fe_2O_4$



$CoFe_2O_4$

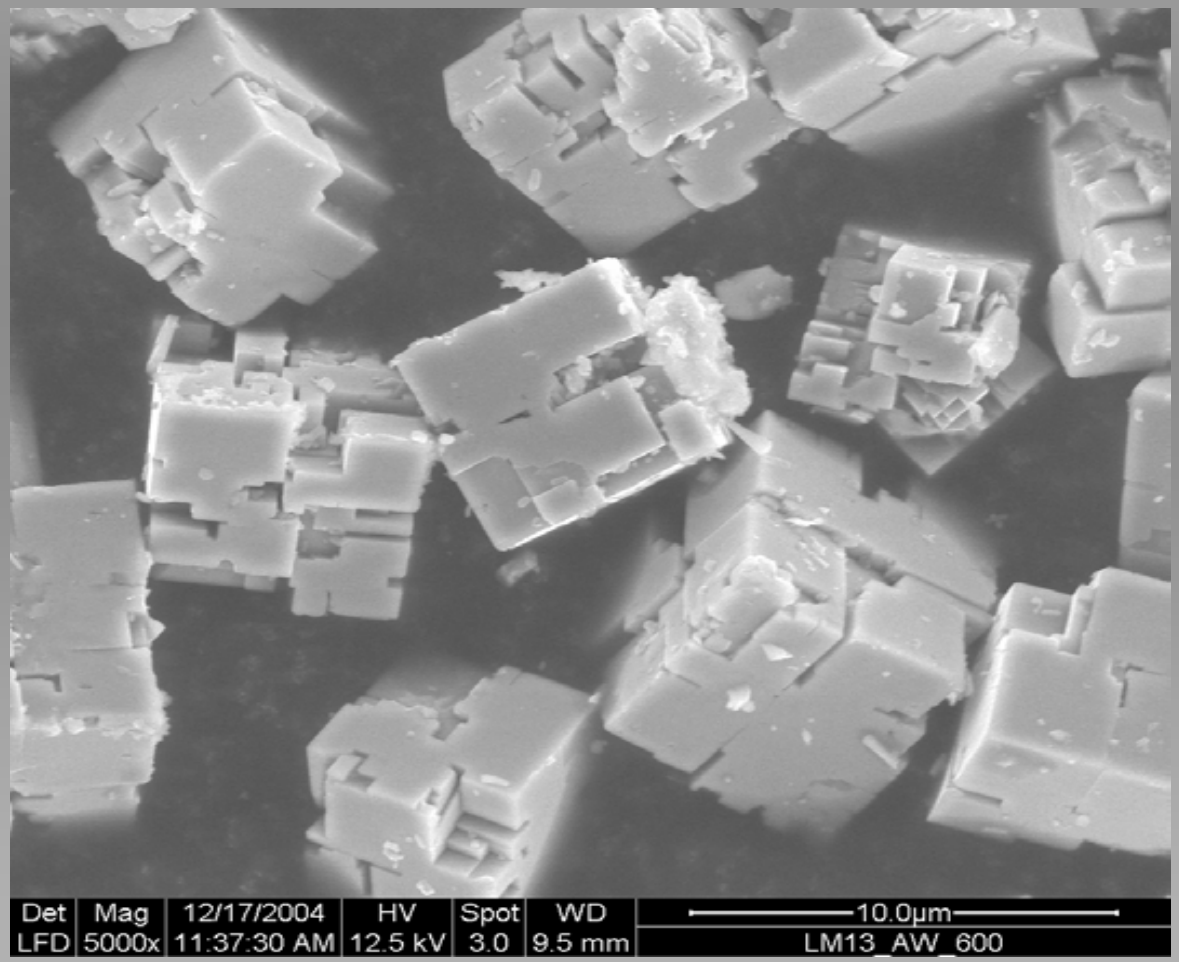
Free-standing perovskite crystals

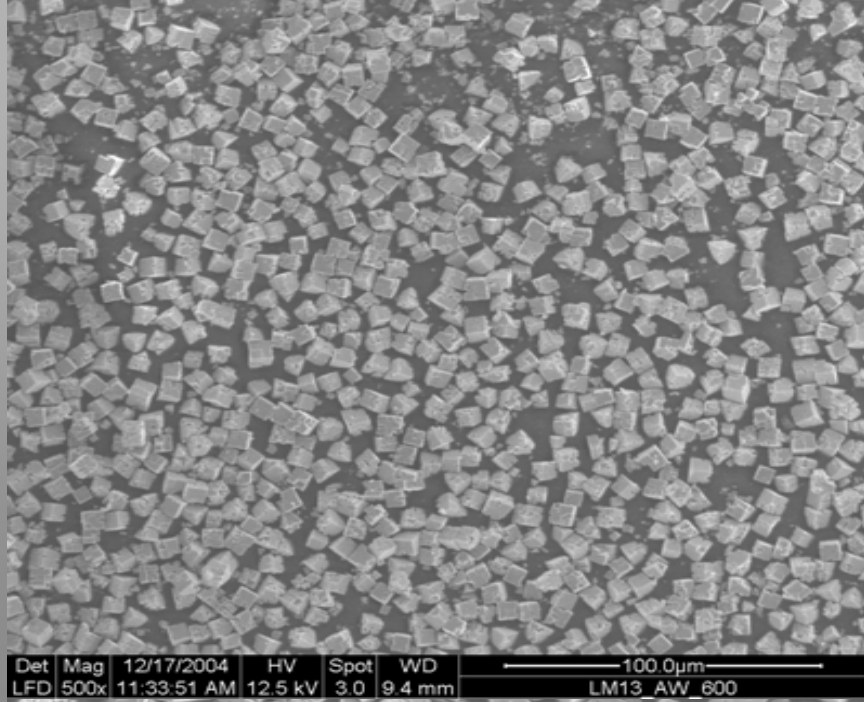
➔Traditional synthesis route; High temperature (Solid state, citrate, combustion, spray pyrolysis…)→ agglomerates

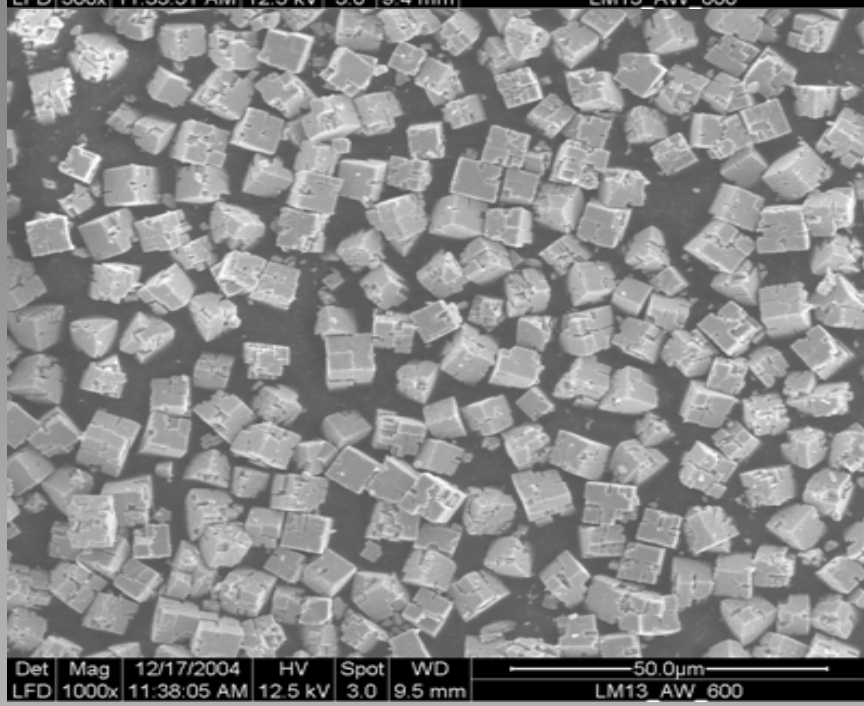
➔Hydrothermal synthesis: Very few examples

(e.g. $BaTiO_3$, hydrothermal)

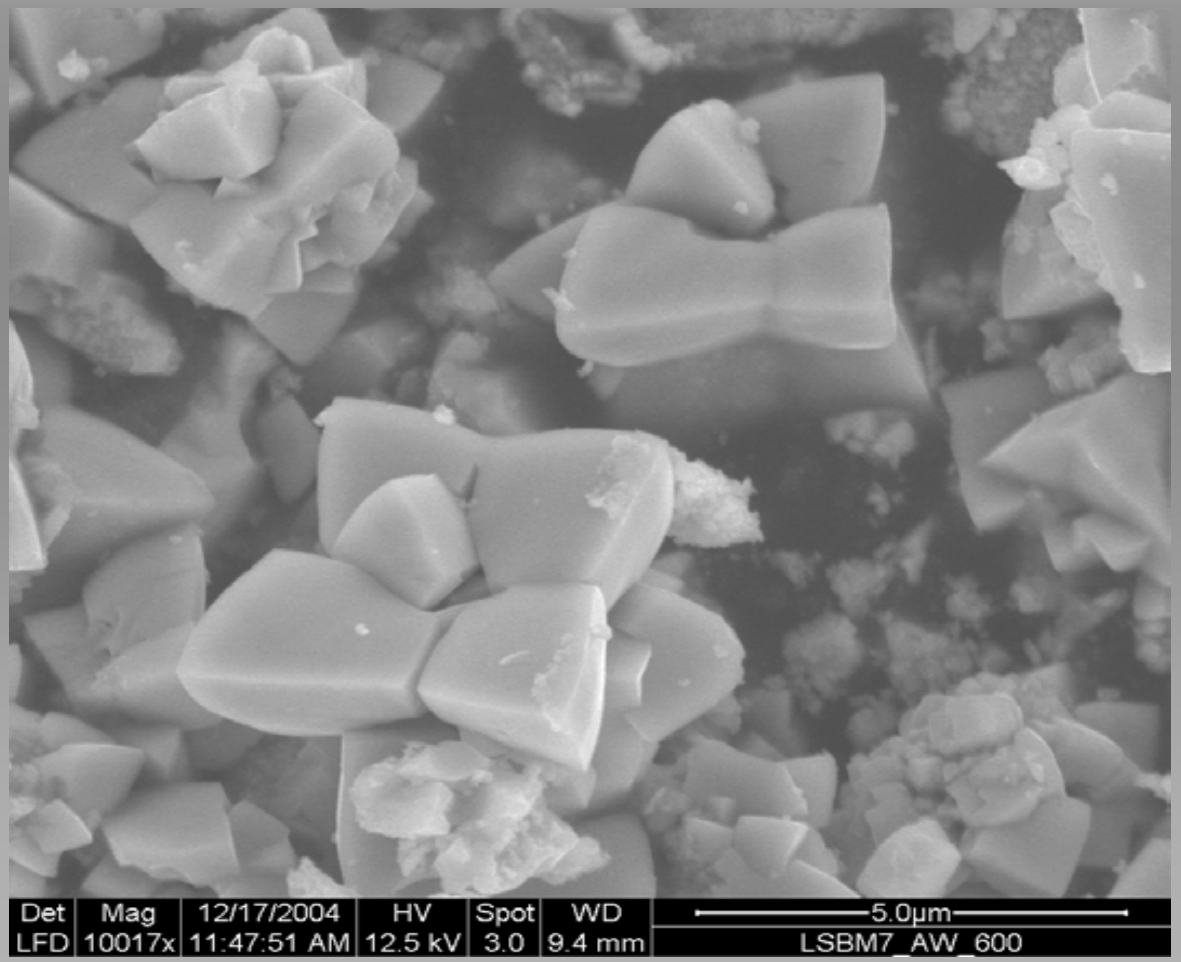
Hydrothermal synthesis: $LaMnO_3$

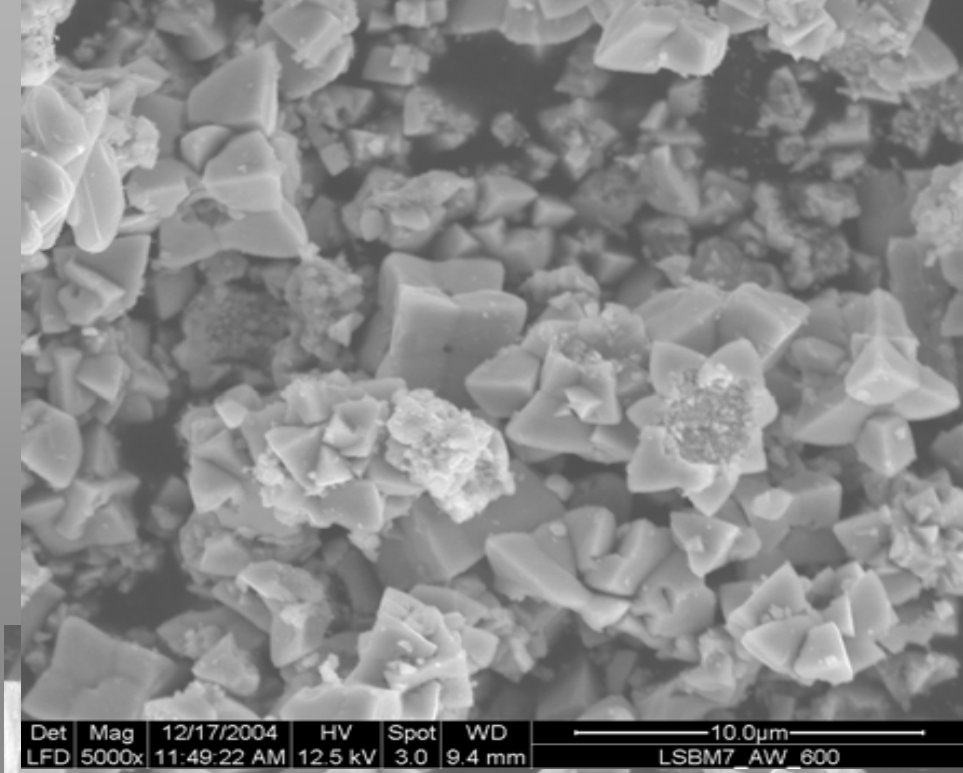


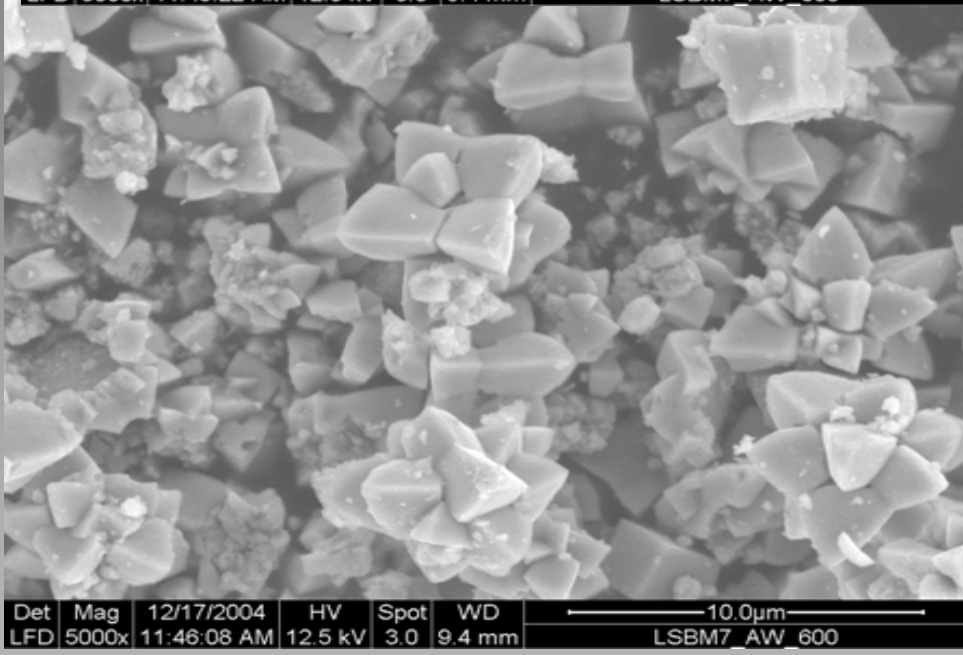




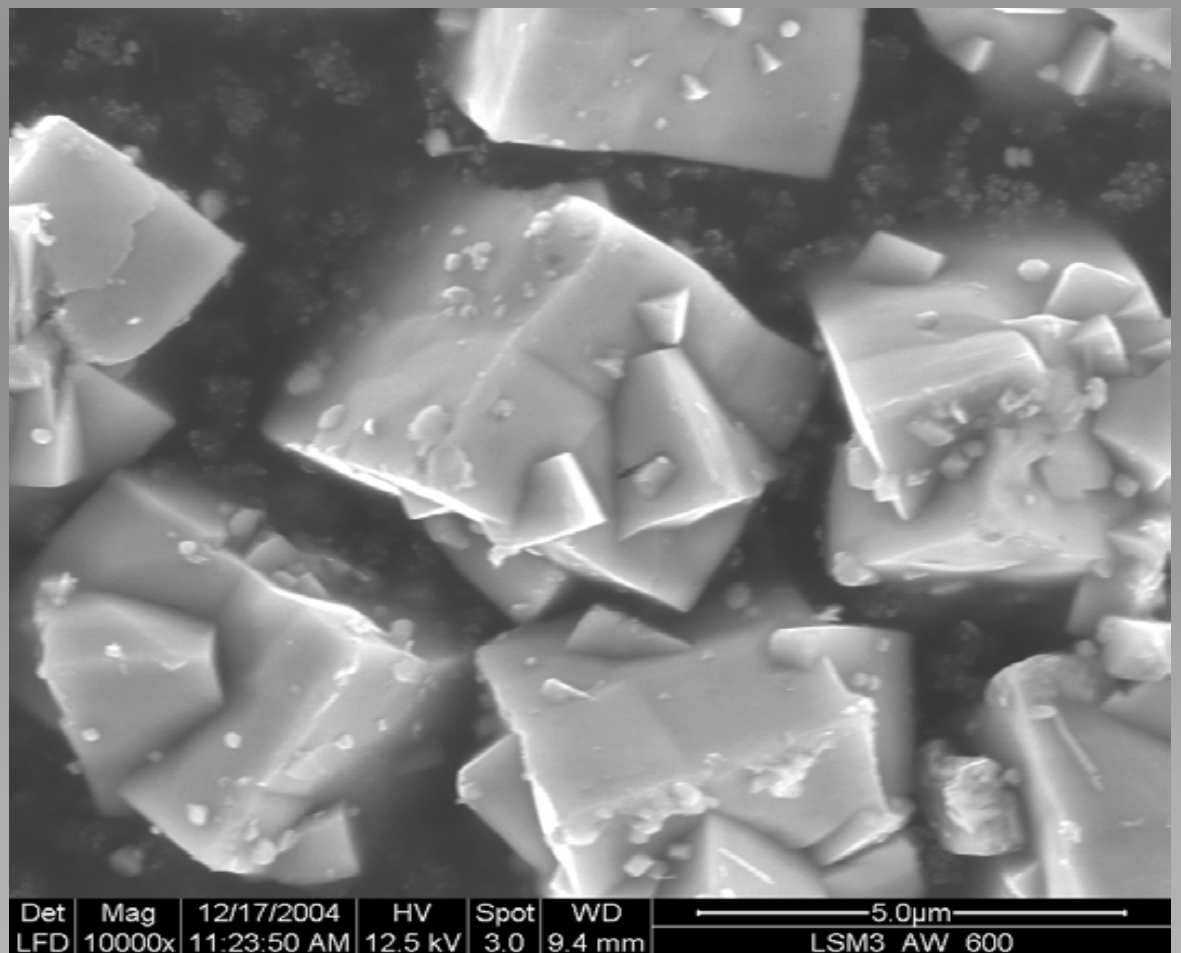
Hydrothermal synthesis: $(La,Sr,Ba)MnO_{3-x}$

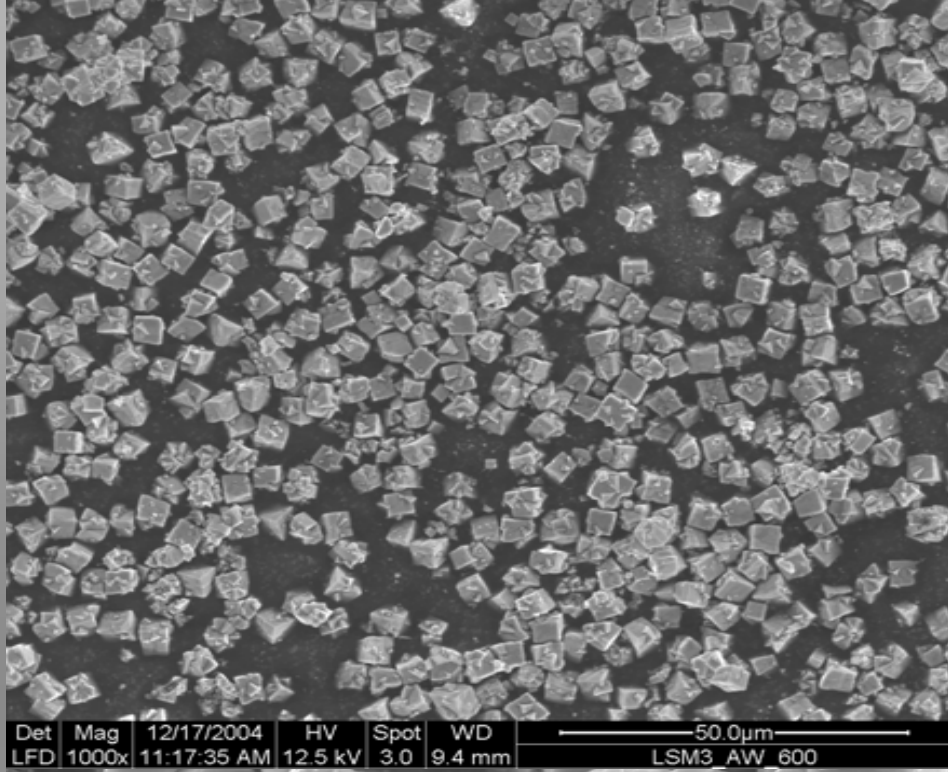


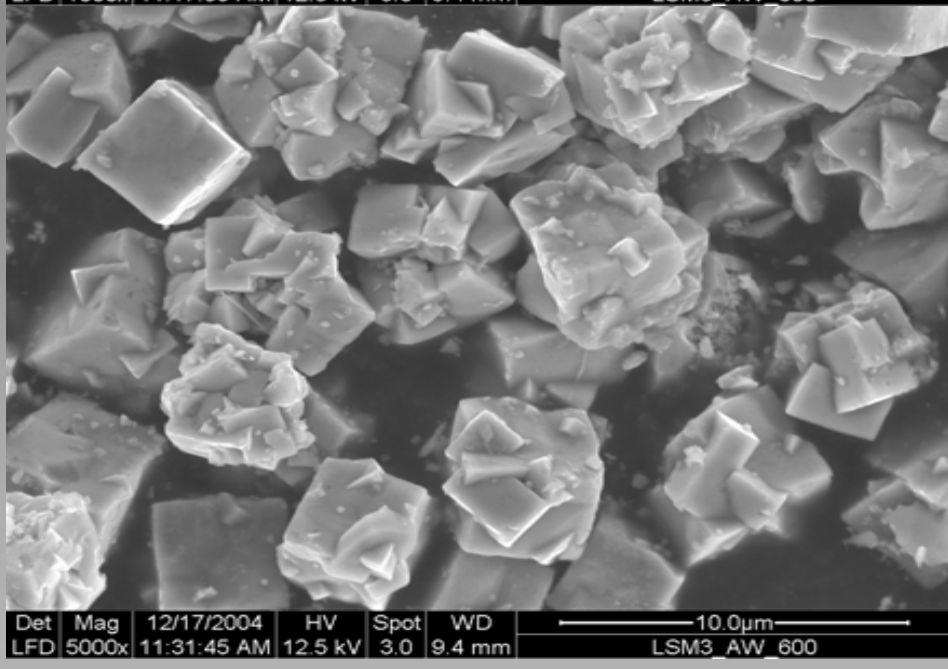




Hydrothermal synthesis: $(La,Sr)MnO_{3-x}$







Perovskite nano-crystals by hydrothermal methods $La_{1-x}Ba_xMnO_3$

Jeffrey J. Urban, Lian Ouyang, Moon-Ho Jo, Dina S. Wang, and Hongkun Park*

NANO LETTERS **4** (2004) 1547-1550

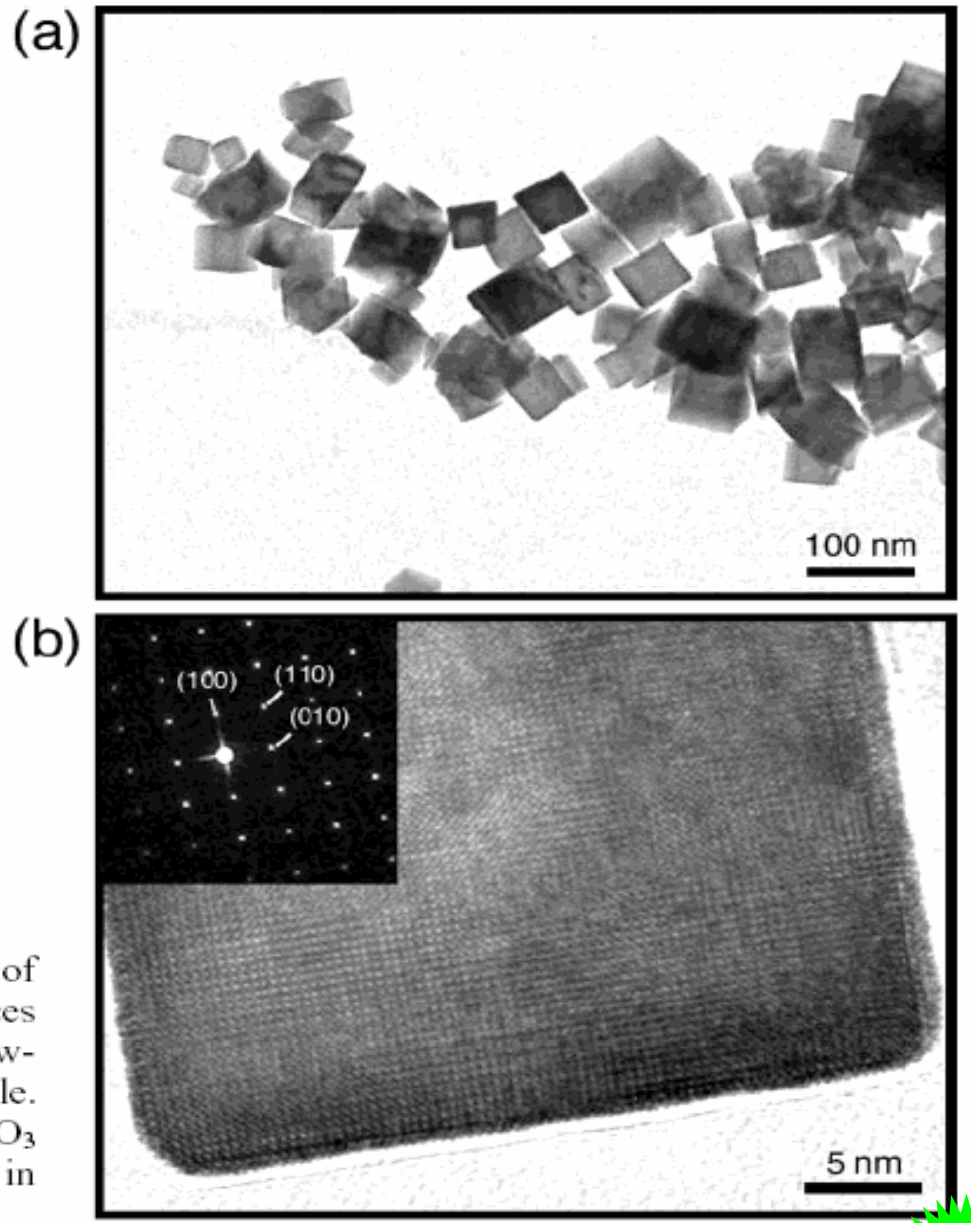


Figure 1. (a) Transmission electron microscopy (TEM) image of $La_{0.5}Ba_{0.5}MnO_3$ nanocubes, illustrating that the reaction produces isolated nanocubes ranging from 20 to 500 nm in size. Low-resolution TEM images for other doping levels are indistinguishable. (b) High-resolution TEM image of a 30-nm $La_{0.7}Ba_{0.3}MnO_3$ nanocube along with a selected area diffraction pattern shown in the inset.

In-situ synchrotron X-ray powder diffraction: Dynamic studies of materials at realistic working conditions.

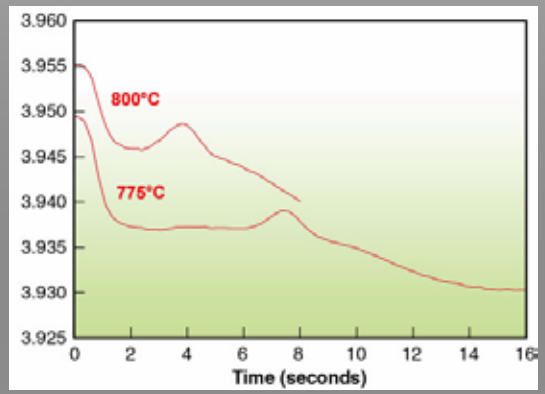
ESRF
European Synchrotron Radiation Facility

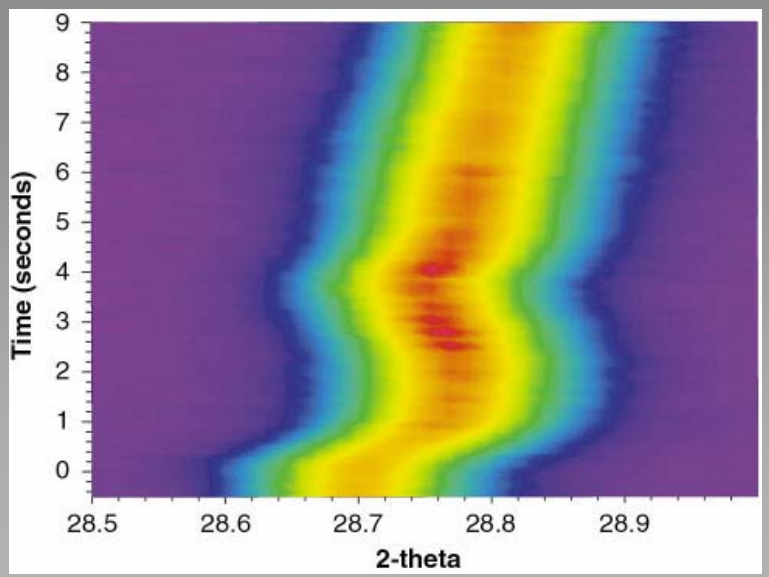
Grenoble

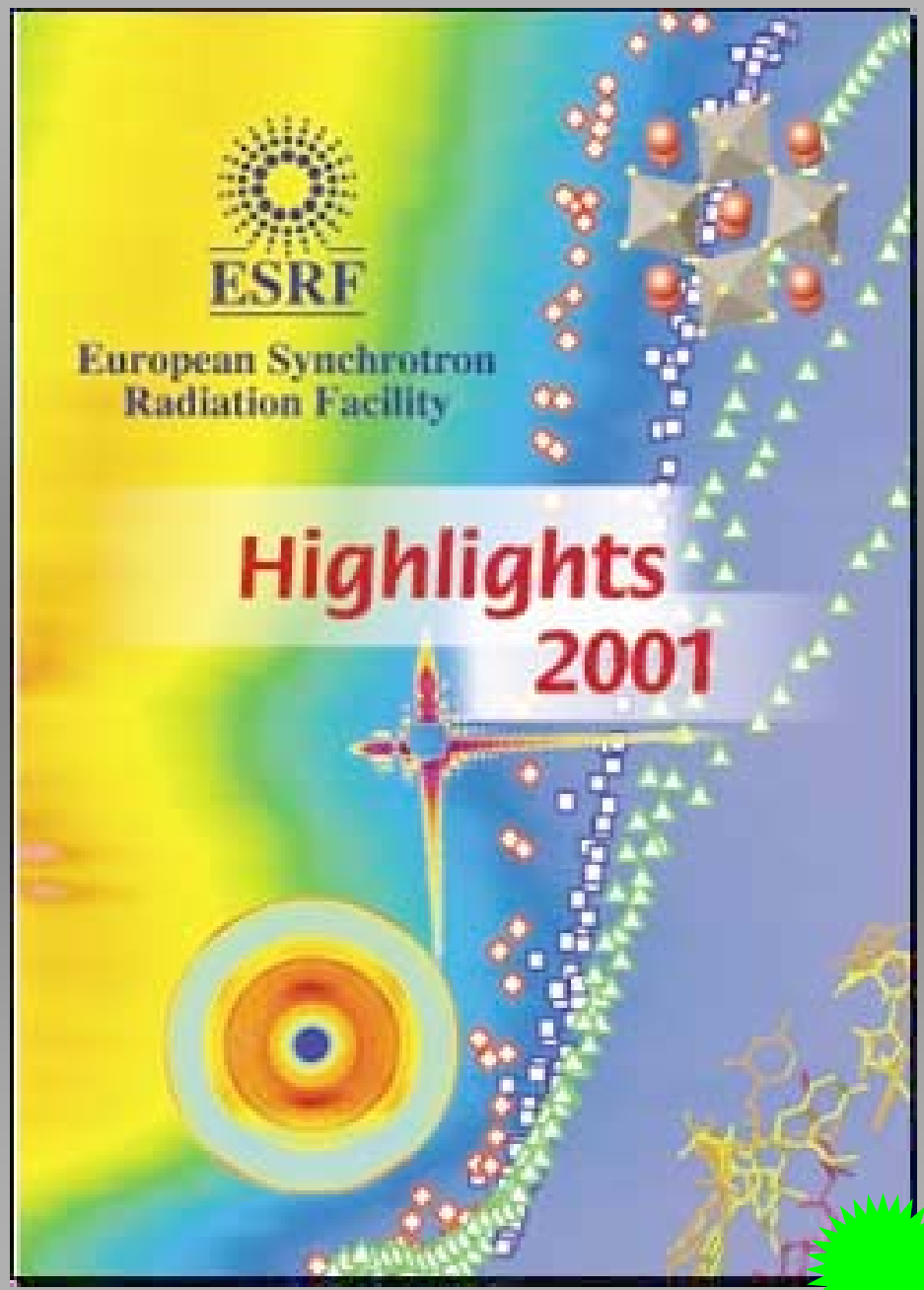
Swiss/Norwegian beam line: SNBL

Materials Science beamline: ID11

Highlights 2001







Oxygen permeable membranes at operating conditions

High Temperature Oxidation/Reduction of materials for oxygen permeable membranes

Material: $SrFe_{0.97}Cr_{0.03}O_{3-\delta}$

$$SrFeO_{2.5} \leftrightarrows SrFeO_{2.75} \leftrightarrows SrFeO_{2.88} \leftrightarrows SrFeO_{3-\delta}$$
$$Sr_2Fe_2O_5 \leftrightarrows Sr_4Fe_4O_{11} \leftrightarrows Sr_8Fe_8O_{23} \leftrightarrows SrFeO_{3-\delta}$$

High Temperature:

$$SrFeO_{2.5} \leftrightarrows SrFeO_{3-\delta}$$

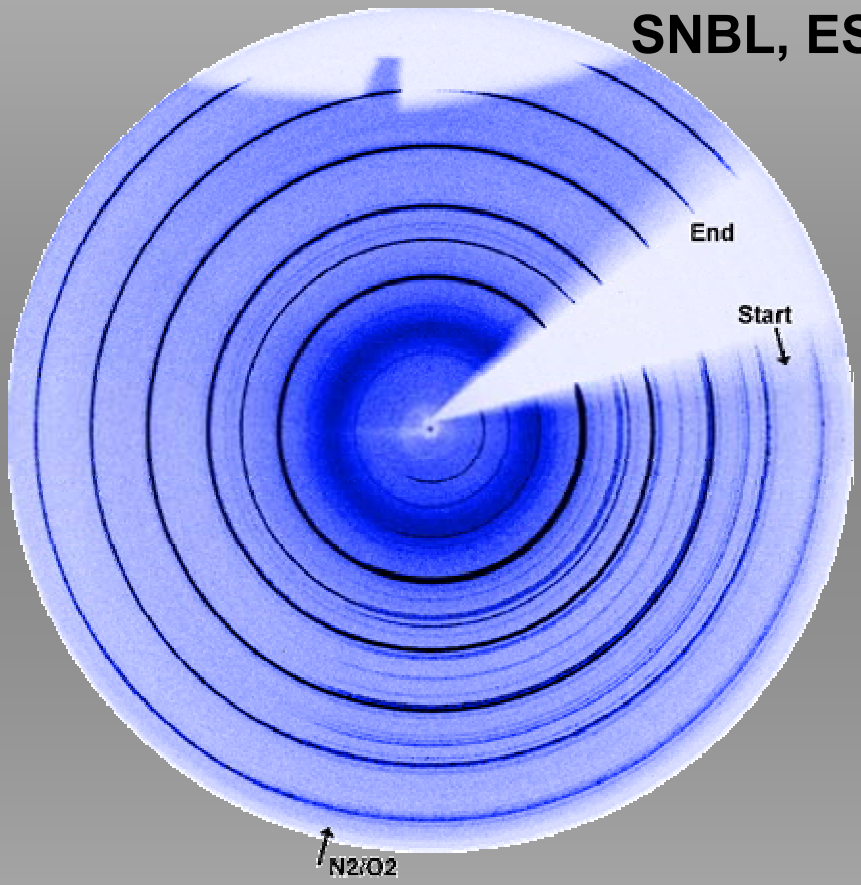
Brownmillerite Perovskite

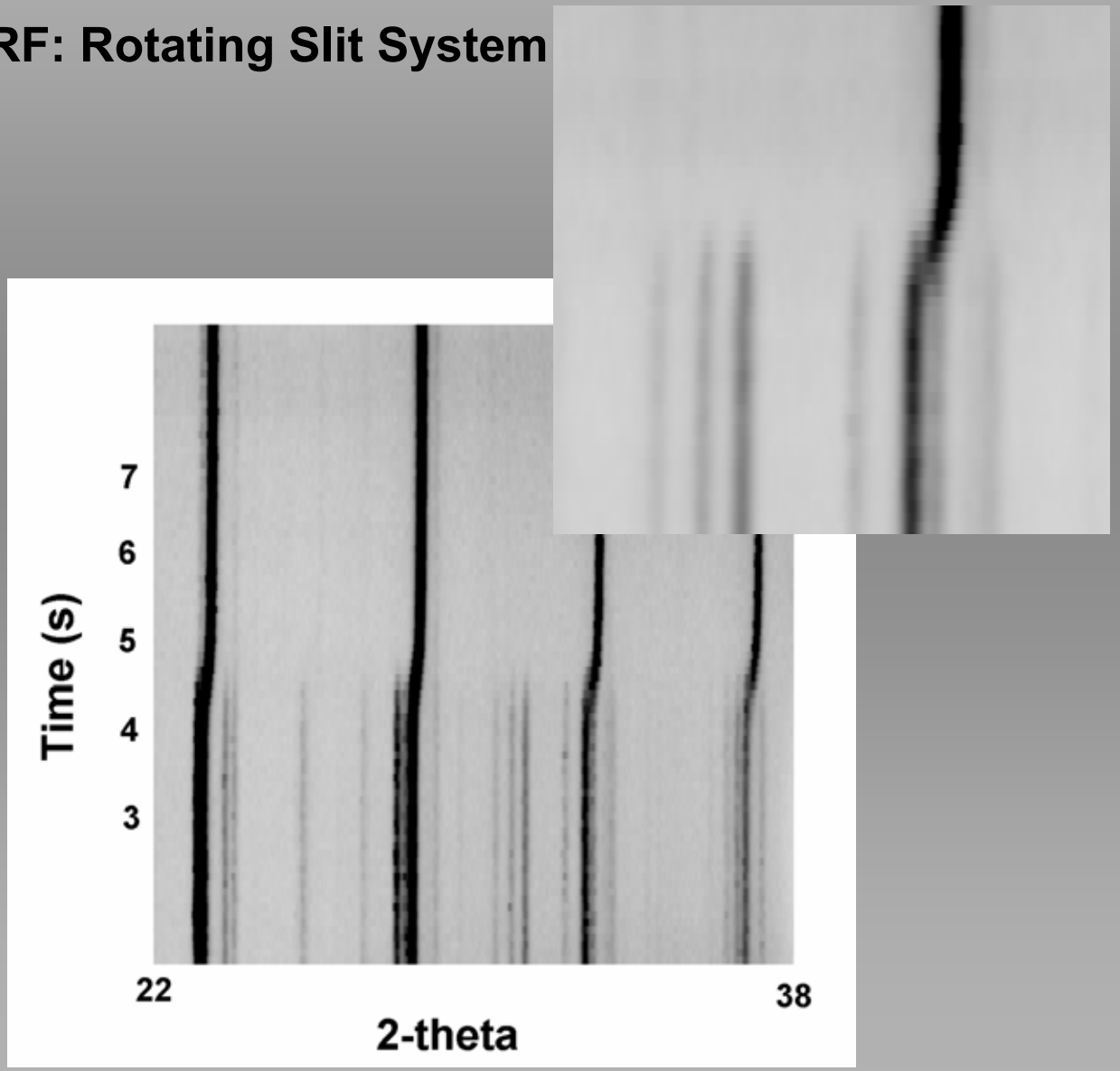
Challenge:
Determine the oxygen stoichiometry through an operating oxygen permeable membrane

- The membrane is 10 mm in diameter and 2-3 mm thick
- Operating temperatures between 600 and 900°C
- Stable oxygen partial pressure gradient over the membrane

Time resolved in-situ studies of oxidation/reduction of $SrFe(Cr)O_{3-d}$

SNBL, ESRF: Rotating Slit System





Oxidation of $SrFe(Cr)O_{3-\delta}$

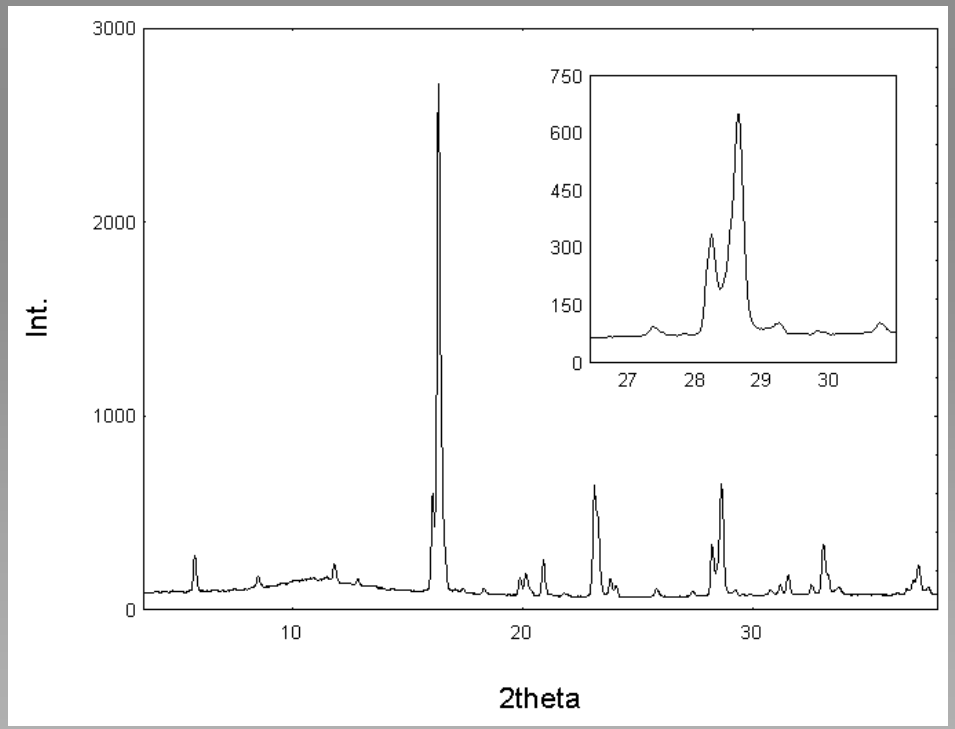
800°C, $N_2 \rightarrow O_2$

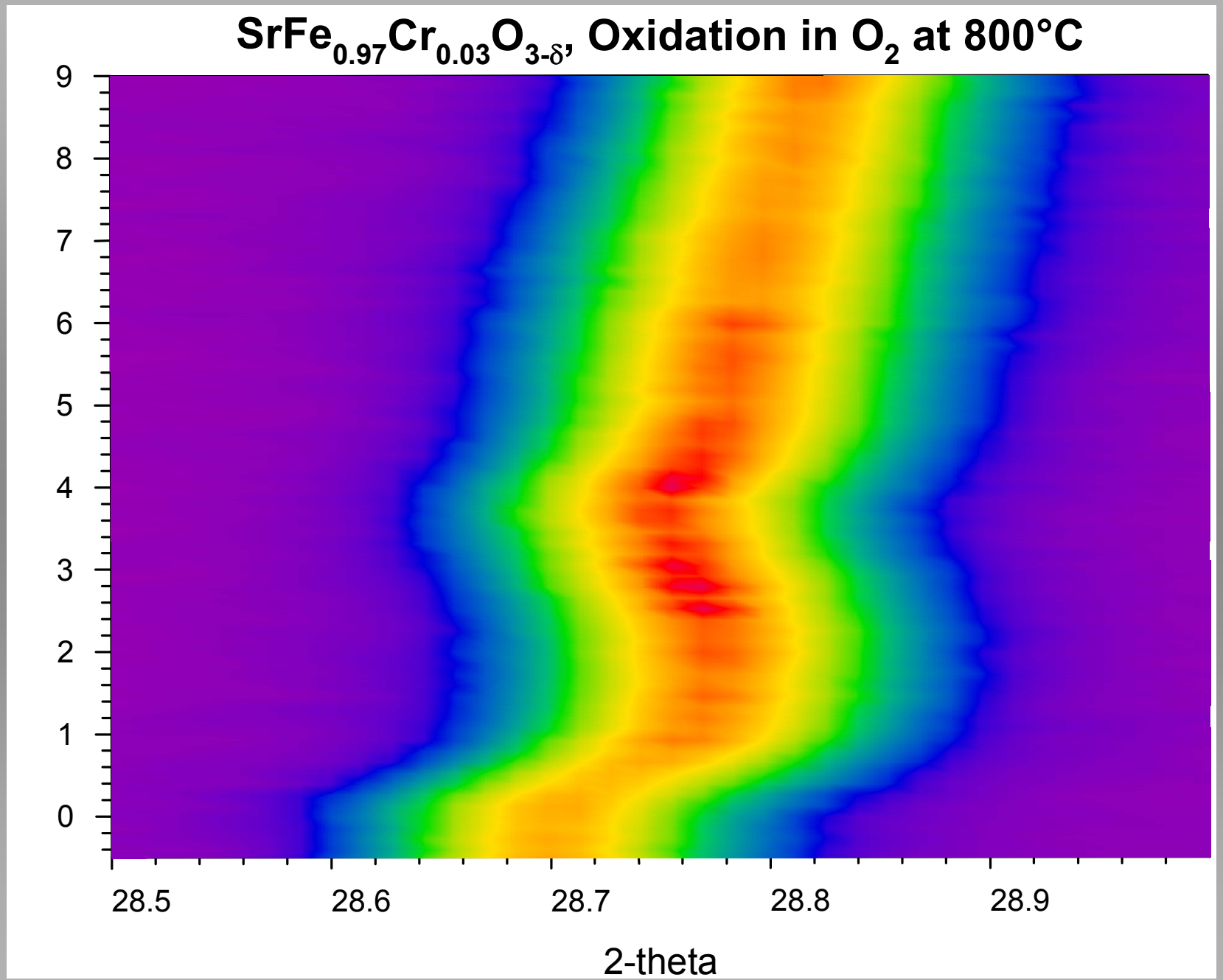
Fast Powder Diffraction using the Rotating Slit System

½ s. exposure time:

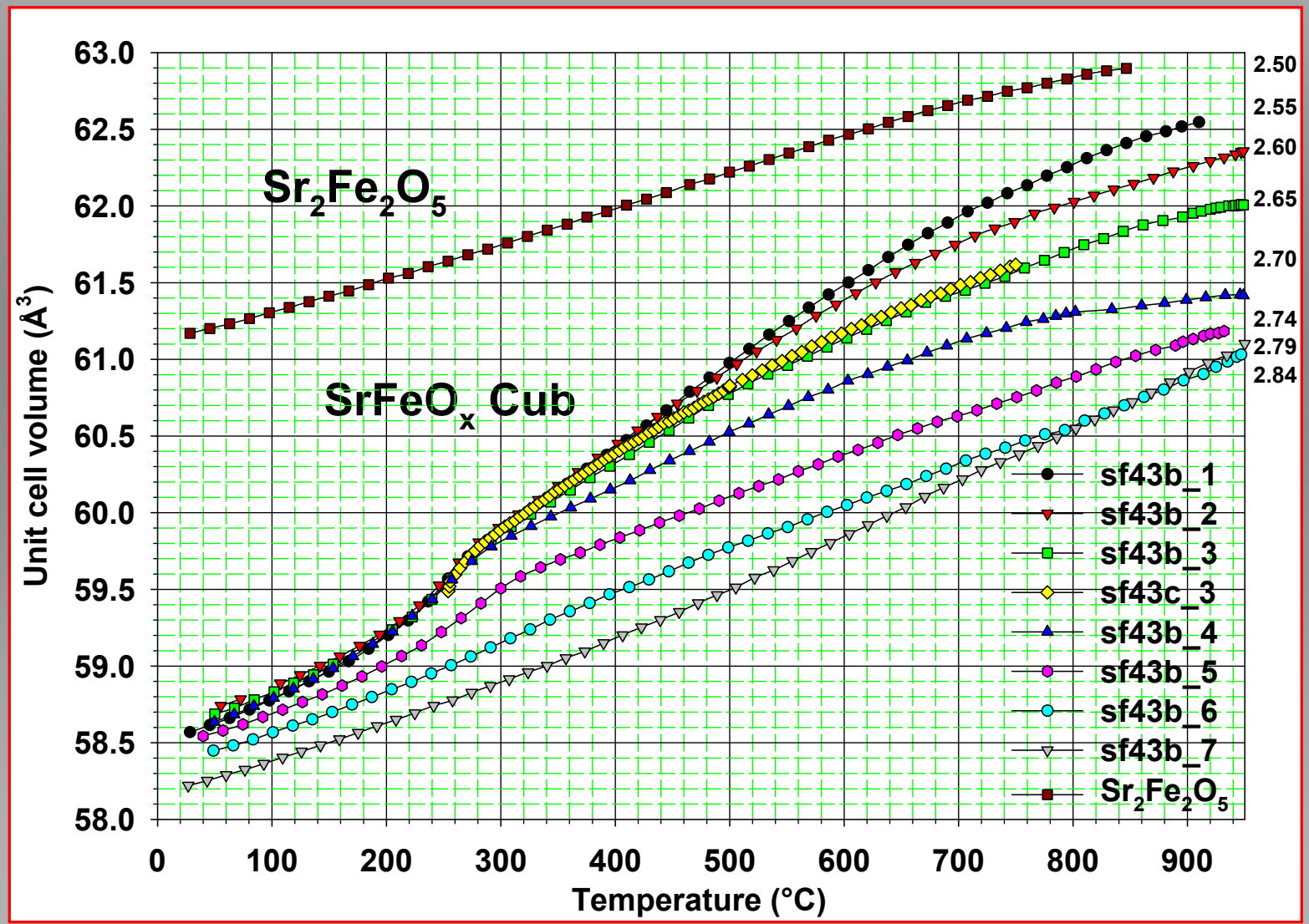
Powder diffraction pattern extracted during oxidation of $SrFe(Cr)O_{3-\delta}$

SNBL, ESRF
MAR345 Imaging Plate System
λ = 0.7991Å

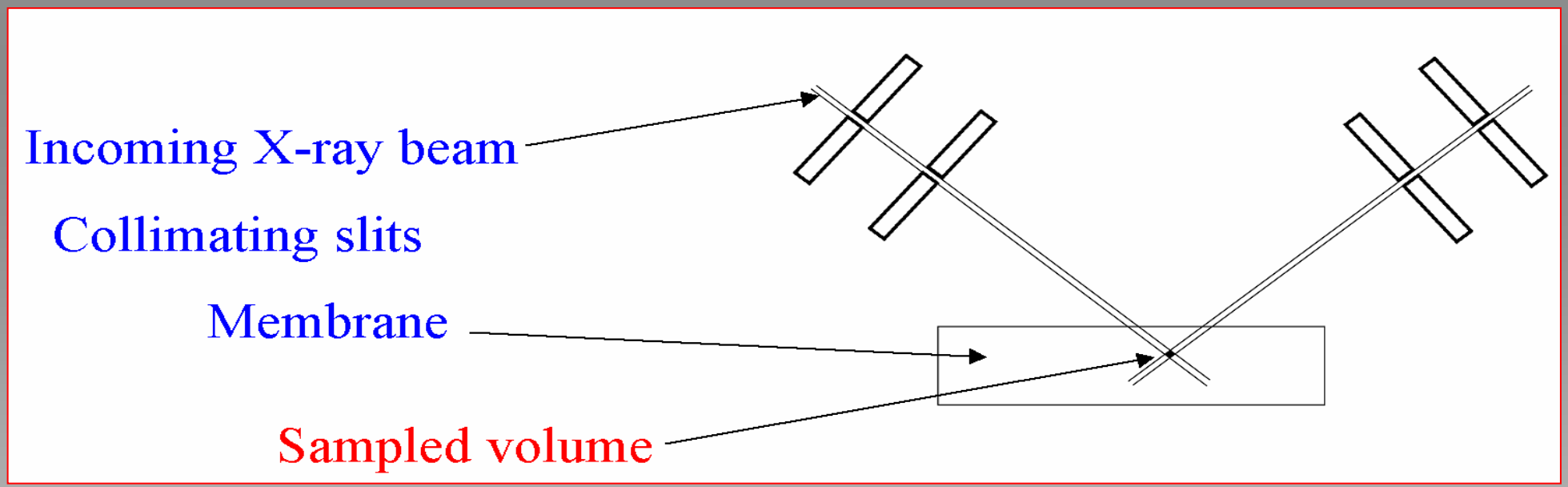



SrFe0.97Cr0.03O3-δ, Oxidation in O2 at 800°C
9
8
7
6
5
4
3
2
1
0
28.5
28.6
28.7
28.8
28.9
2-theta

$SrFe(Cr)O_x$: Unit cell volume as a function of temperature and oxygen stoichiometry



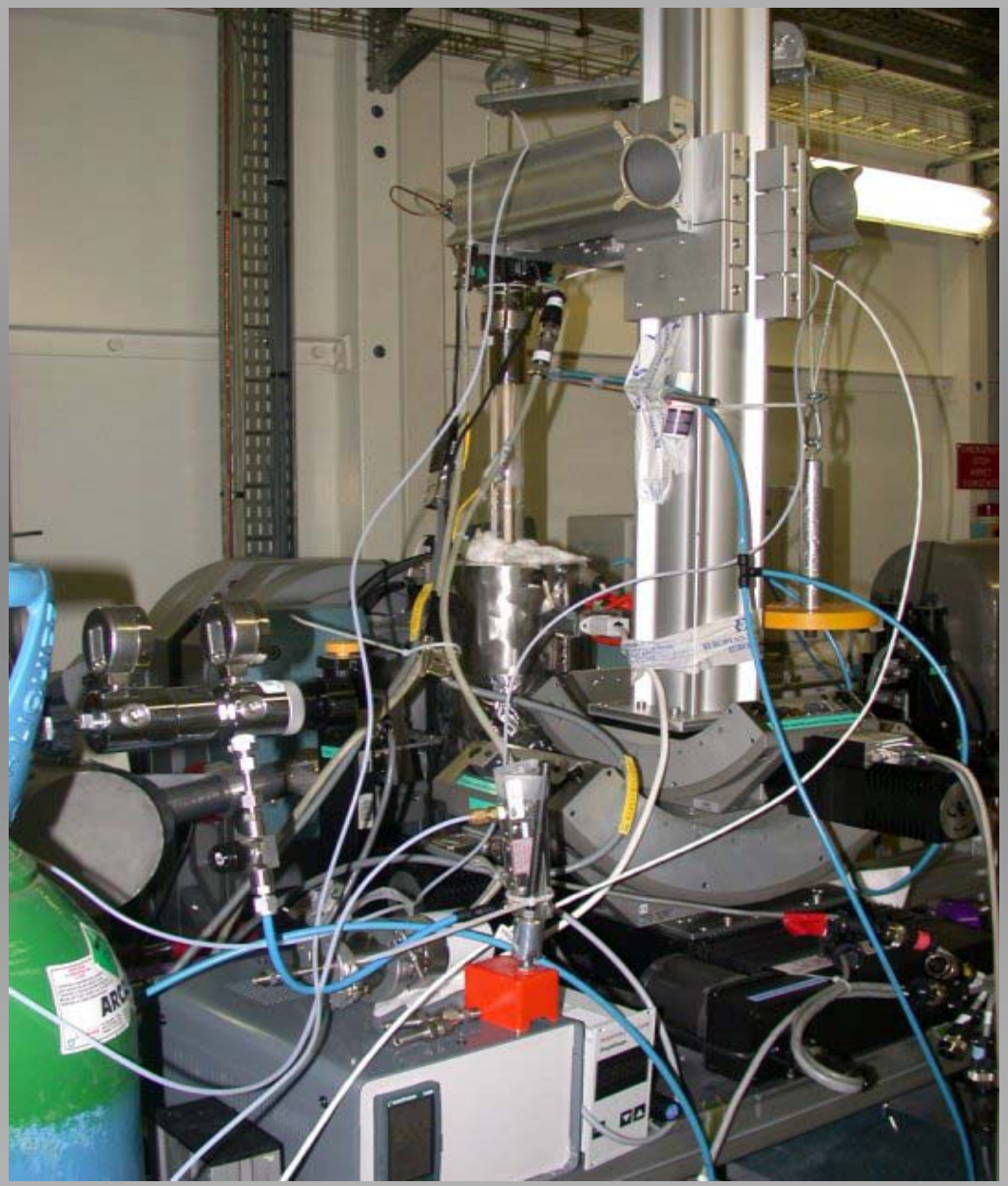
Principle of diffraction from a small volume element within a membrane.



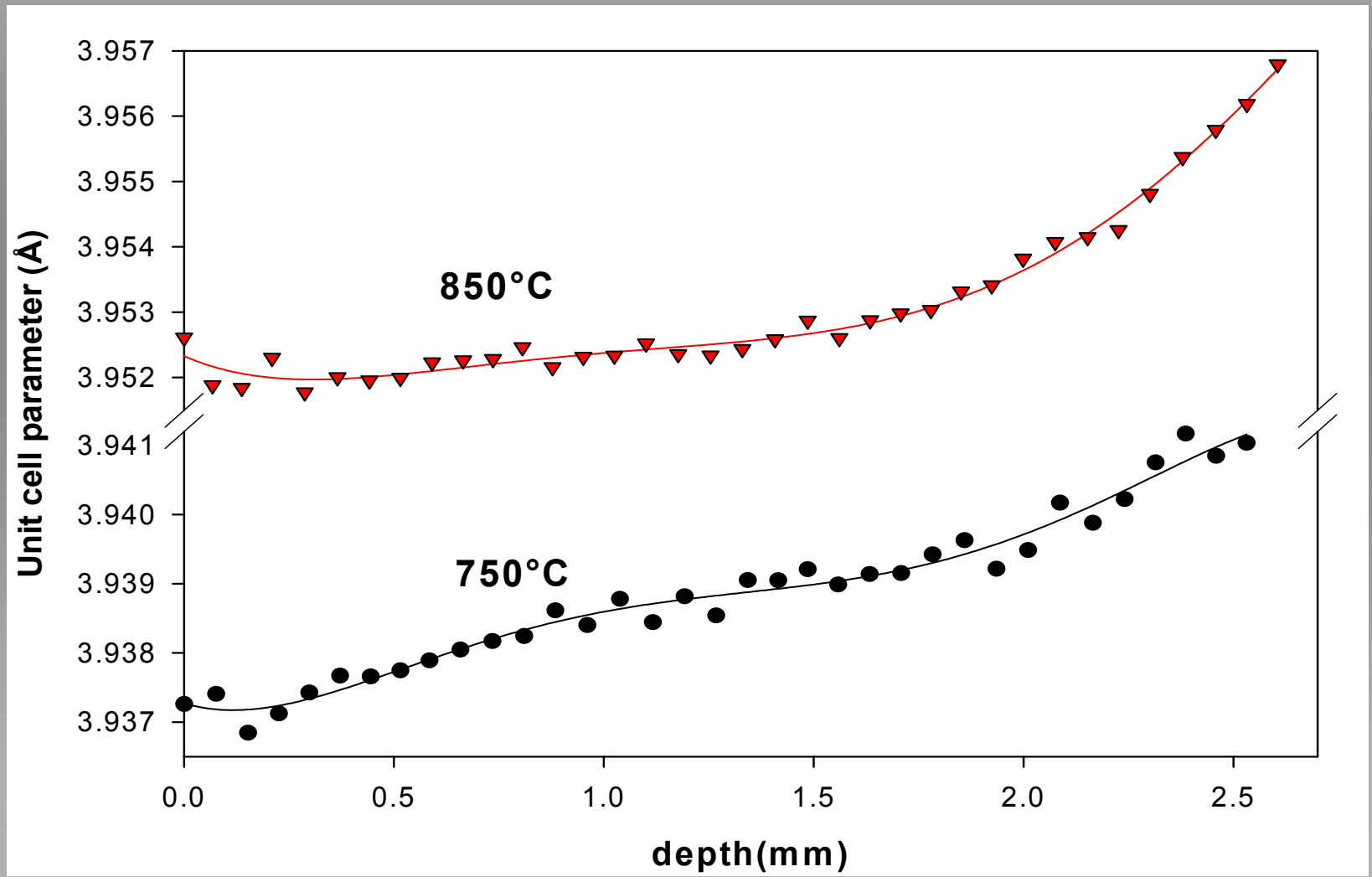
Experimental setup

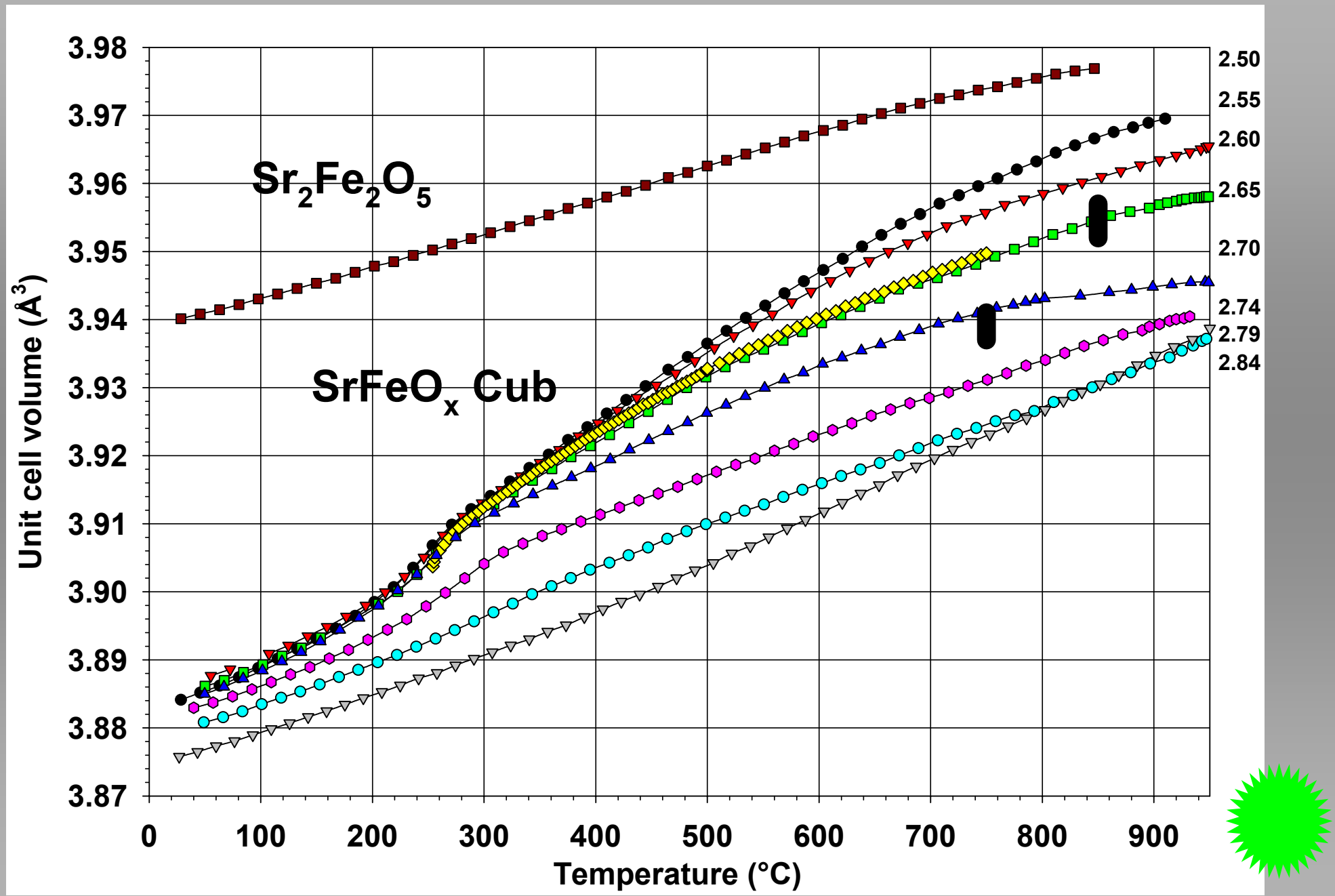
Materials Science beamline

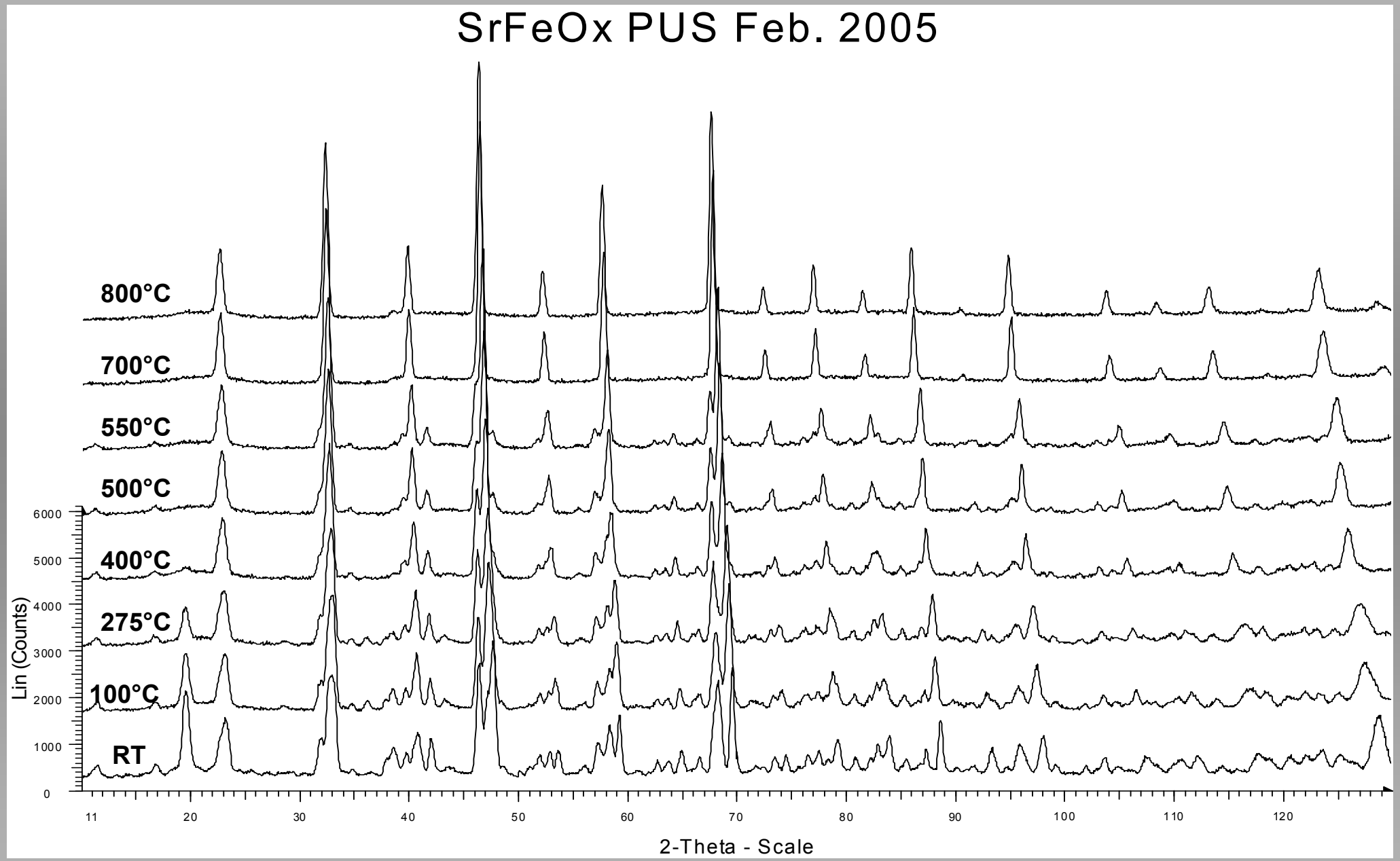
ID11
ESRF

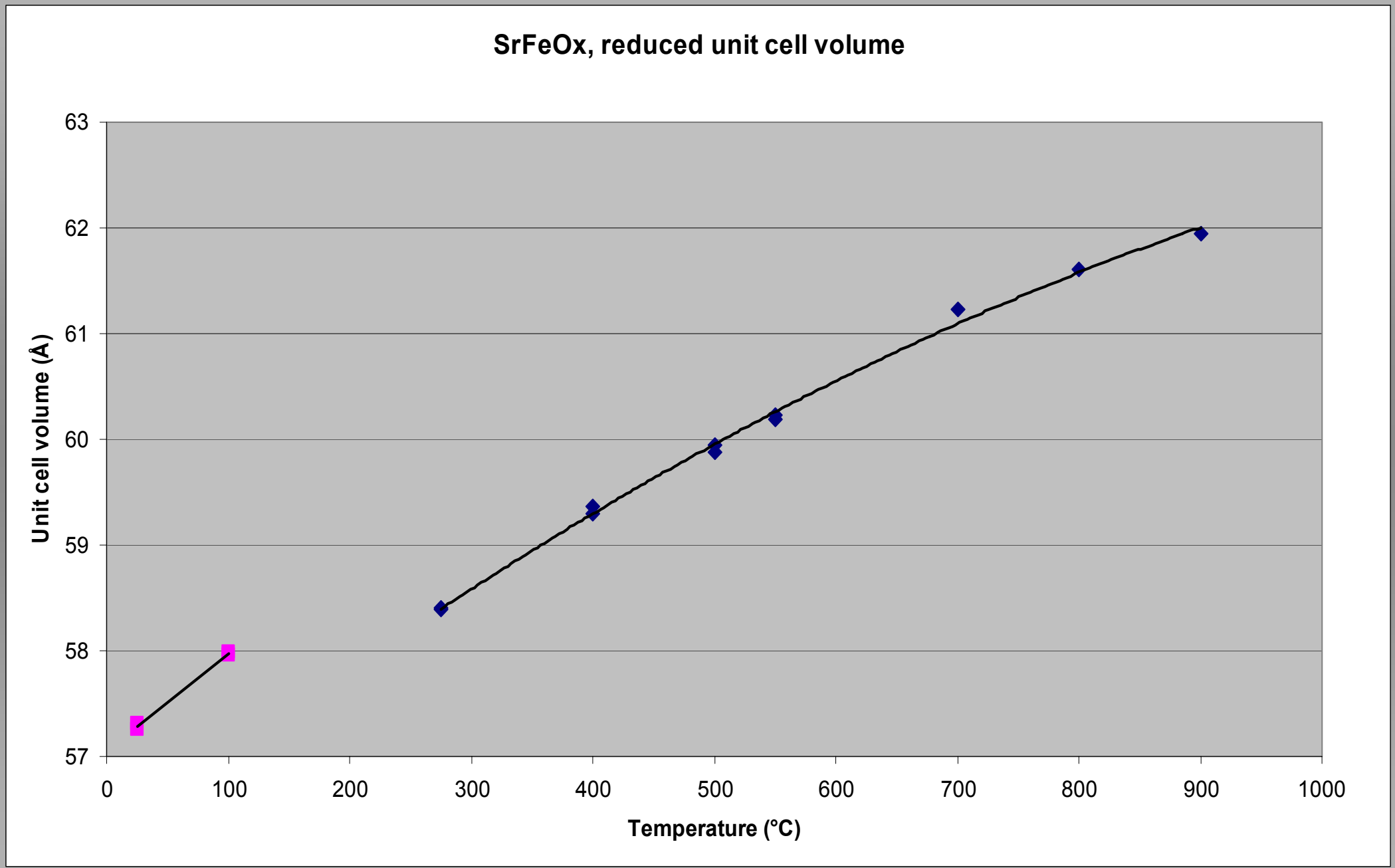


Experimentally determined cubic unit cell parameter through a 2.5 mm thick membrane ($SrFe_{0.97}Cr_{0.03}O_{3-\delta}$) at operating conditions.



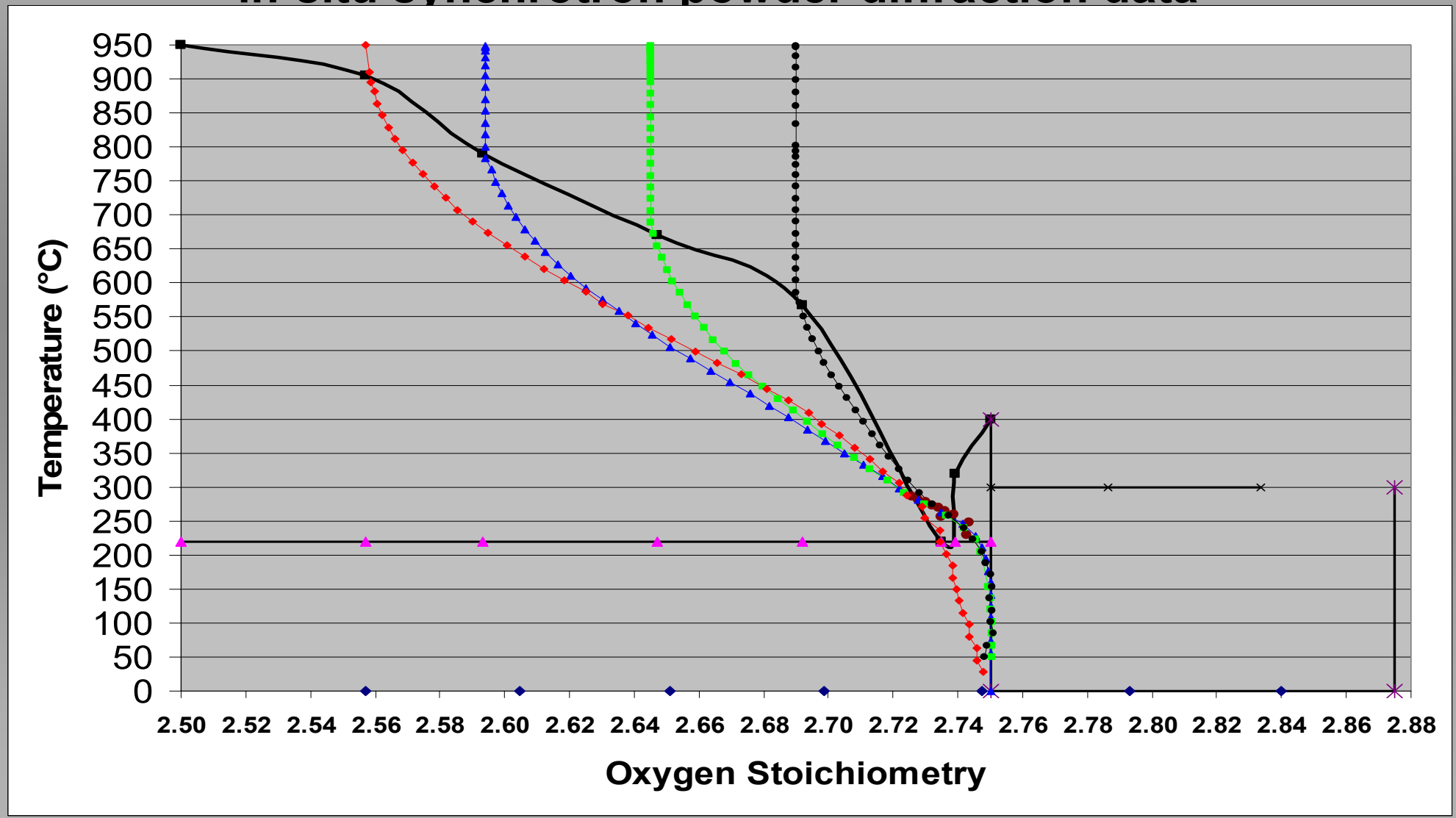

Sr2Fe2O5
SrFeOx Cub
Unit cell volume (Å3)
Temperature (°C)
3.98
3.97
3.96
3.95
3.94
3.93
3.92
3.91
3.90
3.89
3.88
3.87
0
100
200
300
400
500
600
700
800
900
2.50
2.55
2.60
2.65
2.70
2.74
2.79
2.84


SrFeOx PUS Feb. 2005
800°C
700°C
550°C
500°C
400°C
275°C
100°C
RT
Lin (Counts)
0
1000
2000
3000
4000
5000
6000
11
20
30
40
50
60
70
80
90
100
110
120
2-Theta - Scale


SrFeOx, reduced unit cell volume
Unit cell volume (Å)
63
62
61
60
59
58
57
0
100
200
300
400
500
600
700
800
900
1000
Temperature (°C)

$SrFeO_x$

Phase diagram determined by quantitative Rietveld refinement of in-situ synchrotron powder diffraction data



$SrFeO_x$

Phase diagram determined by quantitative Rietveld refinement of in-situ synchrotron powder diffraction data