NATIONAL RESEARCH-DEVELOPMENT INSTITUTE FOR NON-FERROUS AND RARE METALS – I.M.N.R.

High pressure chemical processes for the development of new nanostructured complex systems

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PRESENTATION CONTENT

1. ***Experience of IMNR in the synthesis and development of nanomaterials***
2. ***Introduction***
3. ***TiO2 and ZnO nanopowders***

3.1. *Hydrothermal synthesis of TM-doped TiO2 and ZnO nanopowders*

3.2. *First results on defects formation by EPR spectroscopy*

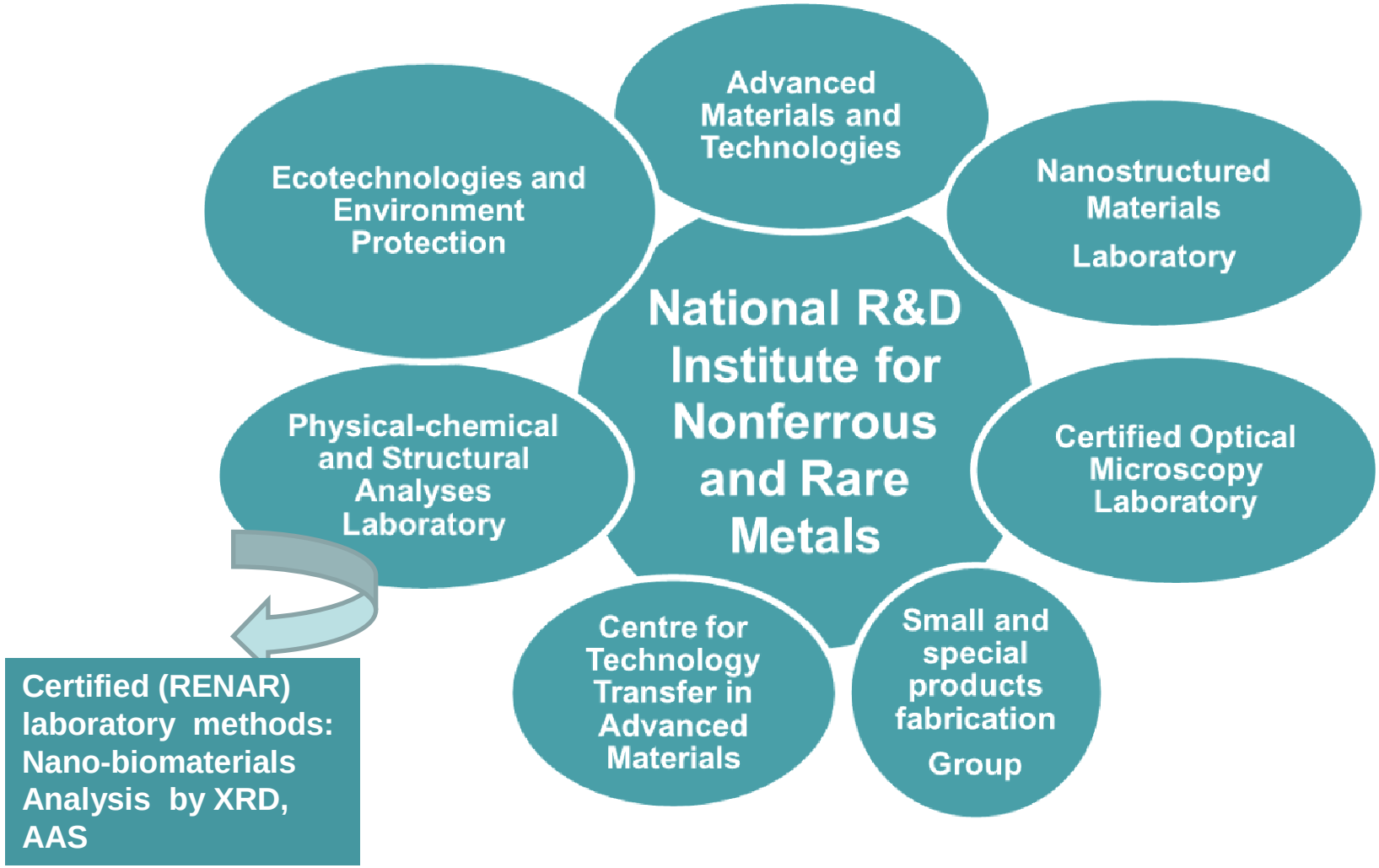
4. ***Complex perovskitic nanostructures***

4.1. *Hydrothermal synthesis of complex perovskitic nanopowders*

5. ***Conclusions and future works***

1. Experience of IMNR in the synthesis and development of nano-materials.

Brief description of the National R/D Institute for Non-ferrous and Rare Metals



Material:

Hybrid inorganic-organic nanomaterials

Doped nanostructured zinc oxide

Nanostructured iron oxide

Doped nanostructured titanium oxide

Doped nanostructured zirconia

Perovskitic materials

Synthesis:

1. Hydrothermal procedure

2. Hydrothermal-electrochemical procedure

Characterisation:

Chemical composition (ICP, AAS, DCS)

Microstructural analysis (XRD)

Microstructure/morphology (SEM, (HR)TEM)

Particle sizes (laser scattering)

Structure (FT-IR)

Thermodynamic/ thermokinetic studies (DSC)

Qualification/ Properties:

Biocompatibility

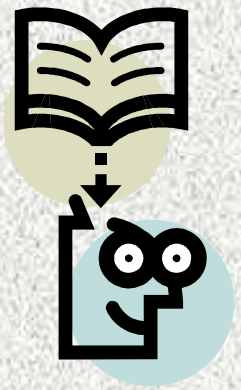
Magnetic properties

Piezoelectric properties

Photocatalytic properties

The chemical technological process at high pressures (developed in IMNR): **high purity materials, increased production yields, low costs and power consumption, quality control during the technological flow.**

Barrier to rational design and controlled synthesis of nanomaterials = lack of fundamental understanding of thermodynamic and kinetic processes at the nanoscale. IMNR offers:



✓Human resources: chemists, physicists, material science engineers

✓ Expertise in materials field (some of them were implemented on the market)

✓Certified analytical methods for compositional and microstructure characterisation of nanobiomaterials (a unique laboratory at national level)

✓Focus the R&D activities to develop cost effective manufacturing methods using chemistry and material science knowledge

Market niches: nanomaterials for regenerative medicine and tissue engineering, nonconventional energy, new sensors and devices

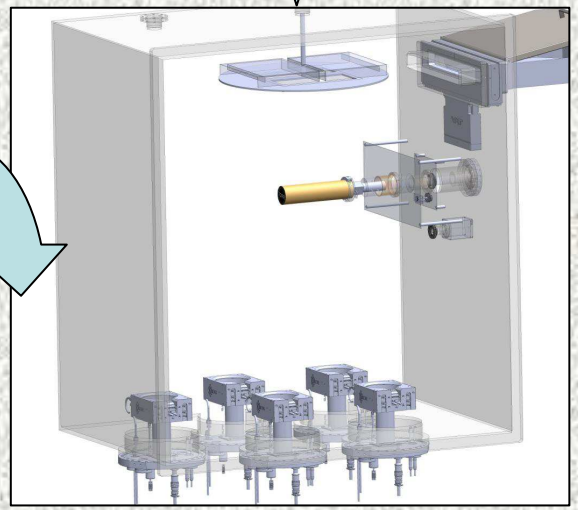
New Centre for Intensification of Metallurgical Processes at High Pressures & Temperatures –High PT Met
Project financed by Structural Funds for Research Infrastructures

High pressure Research Infrastructure

High Temp. Research Infrastructure

Autoclave high capacity

Spray-dry



5-electron guns furnace

2.Introduction

INTRODUCTION

Hydrothermal procedure

There is no unanimity regarding the definition of this procedure.

Definition 1 (*according to O.Schaf, H.Ghobarkar and P.Knauth, book chapter, Nanostructured Materials 2004*):
A non-conventional method to obtain nanocrystalline inorganic materials.

Definition 2 (according to K.Byrappa and Masahiro Yoshimura, Handbook of hydrothermal technology 2001)
Any heterogeneous reaction in the presence of a solvent (aqueous or non-aqueous) which takes place in a closed system at a pressure >1 atm and temperature > room temperature.

INTRODUCTION

Hydrothermal procedure

HISTORICAL

(*according to O.Schaf, H.Ghobarkar and P.Knauth, book chapter, Nanostructured Materials 2004)*

Domain	Period	Examples, materials
Hydrometalurgy	1900	Sulfate ores, oxide ores
Crystals synthesis, growth	1940	Quartz, oxides, sulfides, fluorides, layered compounds
Crystals with controlled composition, shape and sizes	1970	PZT, ZrO2, PSZ, BaTiO3, hydroxyapatite
Whiskers	1980	Hap, Mg sulfate, K titanate
Crystalline films(thin, thick)	1980	BaTiO3, LiNbO3, ferrites, carbon, LiNiO2
Organic materials or biomaterials	1980	Hydrolysis, wet combustion, extraction, polymerization, decomposition, remediation
Solvothermal process	1980	Synthesis, extraction, reaction
Continuous process	1990	Synthesis, extraction, reaction
Modeling	2000	Synthesis and fixing

INTRODUCTION

Hydrothermal procedure

Actual trends in hydrothermal technology

- Materials processing in soft conditions, environmentally friendly
- Solvent behavior should be understand in correlation with pressure and temperature (e.g.: structure in critical, supercritical or sub-critical conditions, dielectric constant, pH modification, viscosity, density)
- Hydrothermal reactions modeling on the basis of thermodynamic principles to enable the control of phases purity, particles sizes, particles sizes distribution, particles morphology

New concepts in hydrothermal technology

- Additional external energy (microwave, ultrasound, mechano-chemical, electrical, magnetic energy)
- Instantaneous hydrothermal reactions to obtain nanoparticles
- Organic synthesis in hydrothermal conditions
- Hybrid inorganic-organic materials in situ synthesized in hydrothermal conditions
- Functionalization inorganic materials with bio-molecules (proteins, organic ligands, DNA, amino-acids)

INTRODUCTION

Hydrothermal procedure

Parameters that influence hydrothermal synthesis

A solvothermal/hydrothermal process concerns chemical reaction(s) involving one or several precursors in presence of a solvent.

→ in a close system,

→ at a temperature higher than the boiling temperature of the solvent.

→**Consequently pressure is involved.**

Two possibilities:

→ autogeneous pressure governs by the temperature,

→ imposed pressure if its starting value is higher than 10^5Pa (1bar).

Two important features:

→ Versus the experimental temperature compared to Tcritical characterizing the solvent→ the system can be in subcritical or supercritical conditions,

→ Versus the solubility of the precursors in the solvent→ the system can be homogeneous or heterogeneous

Source: G. Demazeau, 3rd Workshop Fun Nanos, 29 May 2008, Bucharest

INTRODUCTION

Hydrothermal procedure

Parameters that influence hydrothermal synthesis

Main factors characterizing pressure:

→ **low energy** developed by applying pressure.

For a liquid phase: E_1 to E_2

Temperature scale 5 energy units/step as a consequence **high energy consumption** to achieve the desired energy for the reaction

Pressure scale 4000 energy units/step as a consequence **low energy consumption** to achieve the desired energy for the reaction

→ **negative ΔV value**

$$\Delta V = \Sigma(V/Z)(j) - \Sigma(V/Z)(i)$$

i = precursor
j = product

→ improvement of the chemical reactivity

Source: G. Demazeau, 3rd Workshop Fun Nanos, 29 May 2008, Bucharest

3.1. Hydrothermal synthesis of TM-doped TiO_2 and ZnO nanopowders.

Schematic flow-sheet

Hydrothermal –Electrochemical
CORTEST system

Controlled atmosphere
Oven – MHI

Zetaseizer Malvern

AAS ZEEnit 700
Analytik Jena

DSC Netzsch Maya F200

TiO_2Cl_2
Zn nitrate

Mineralizing agents

Hydrothermal Synthesis

Washing, filtering, drying

Chemical analysis (ICP, DCP, AAS)

Microstructure characterisation:

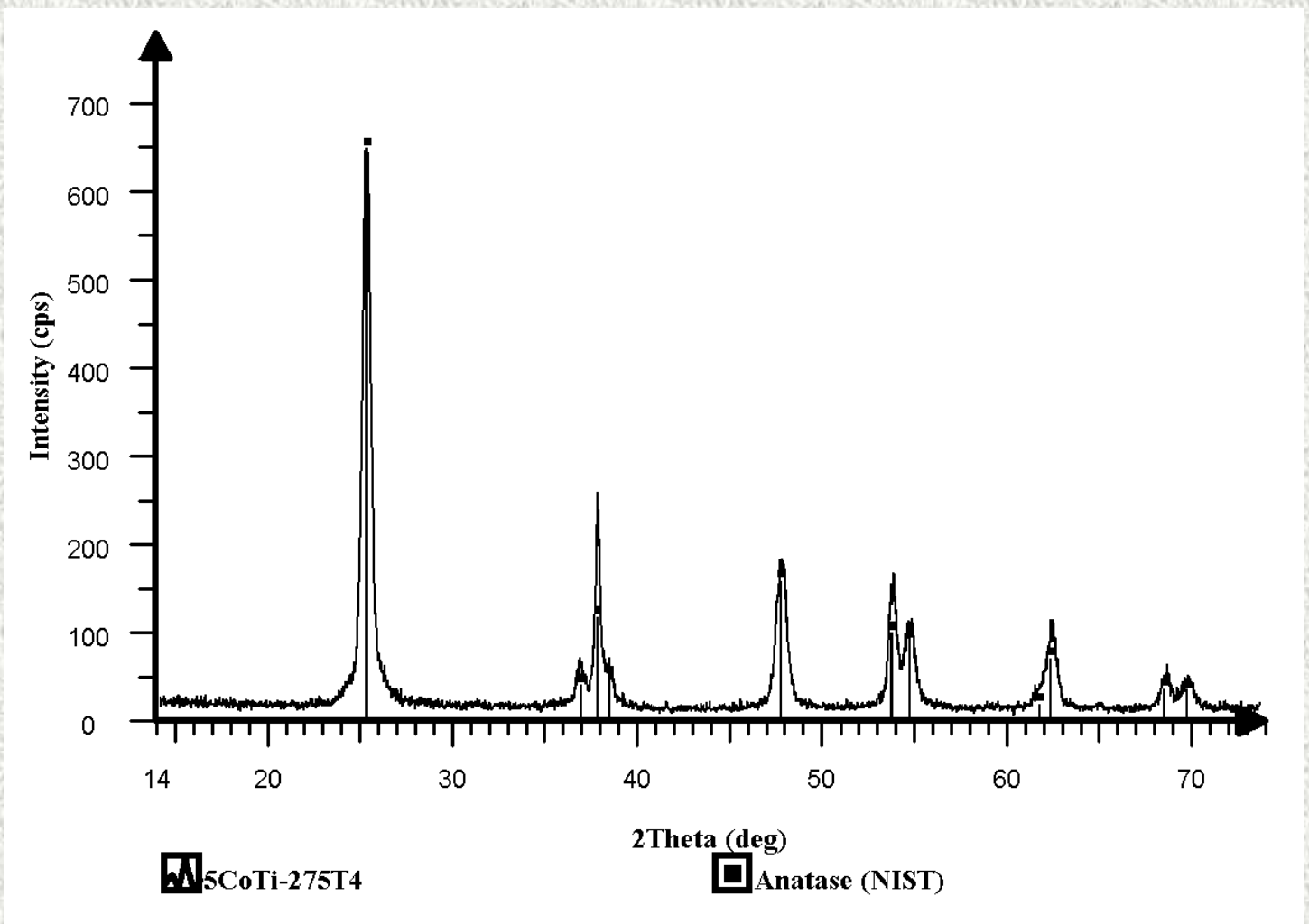
-DRX: Bruker D8 Advance

-SEM, TEM, HREM

- Size distribution & Zeta Potential

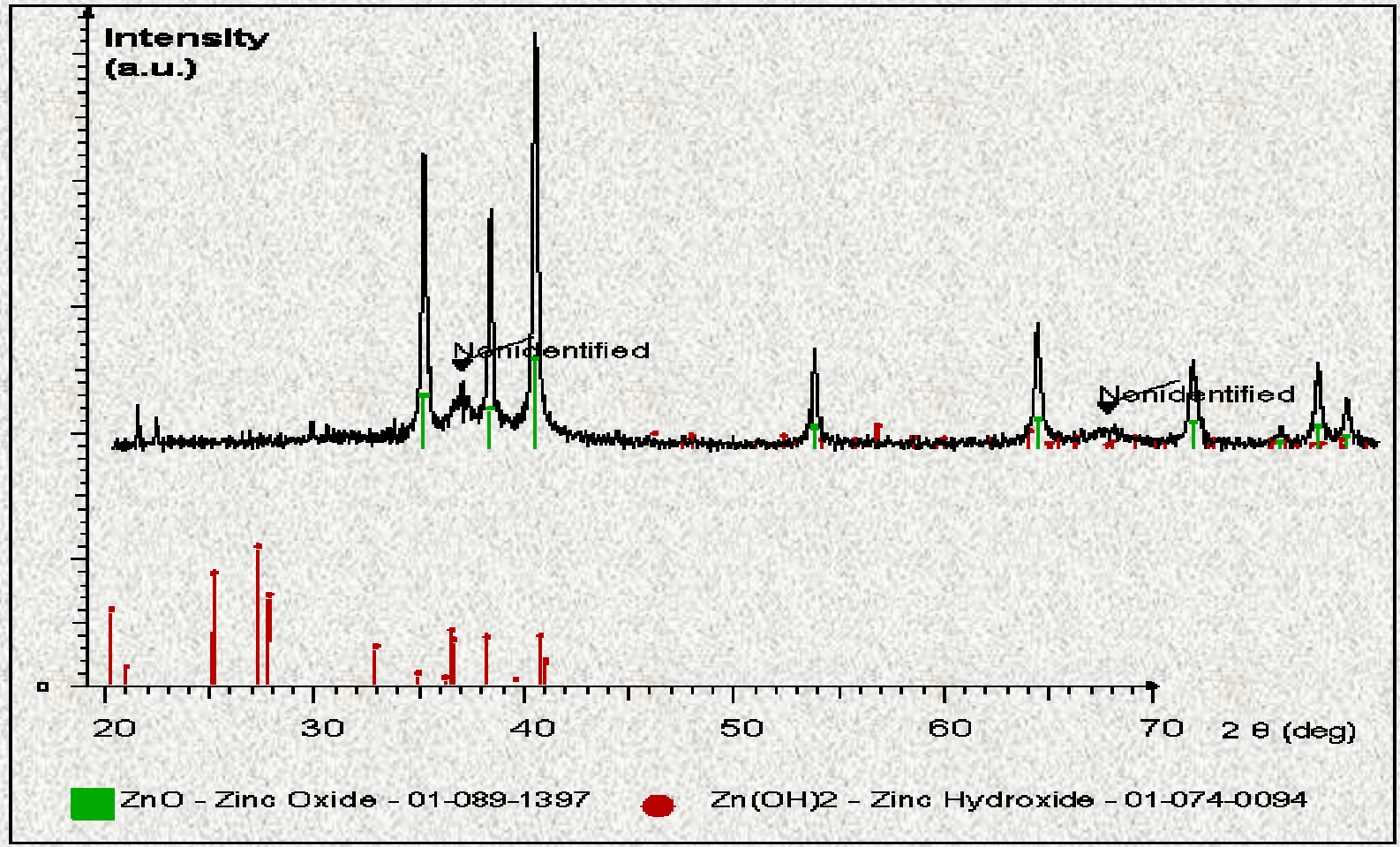
- DSC; DSC-TG

DRX of 5 Co-doped TiO_2 nanopowders



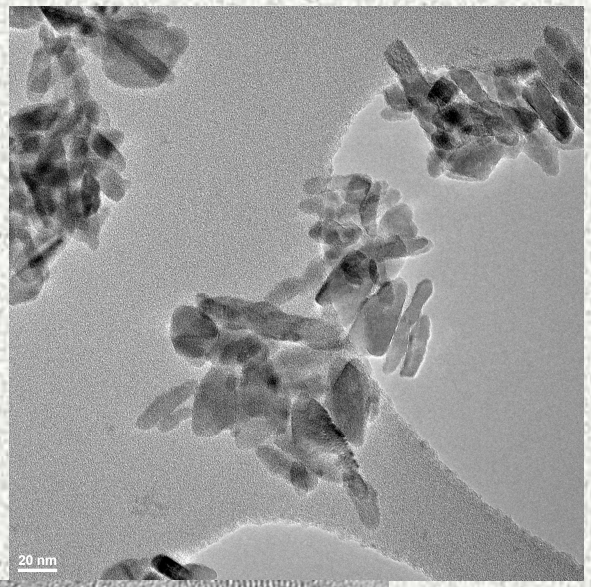
Only TiO_2 anatase was observed.
Crystallite size (Scherrer) = 16 -29 nm

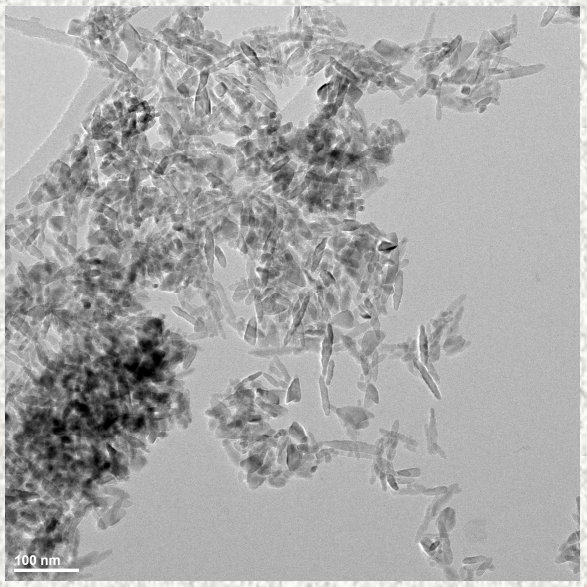
DRX of 5 Co-doped ZnO nanopowders

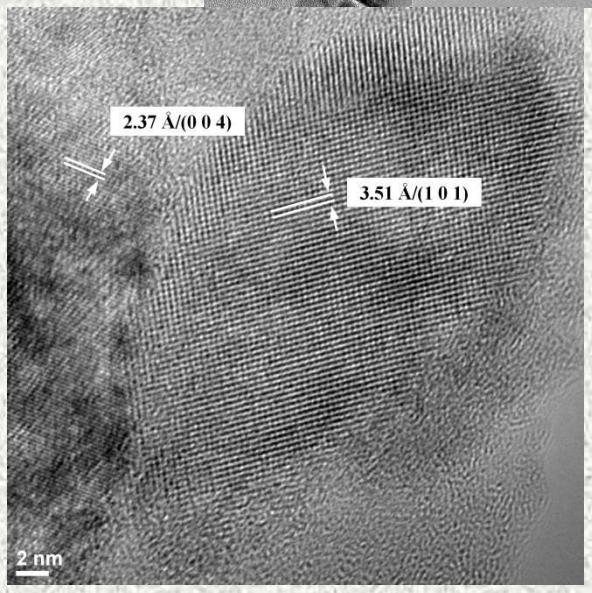


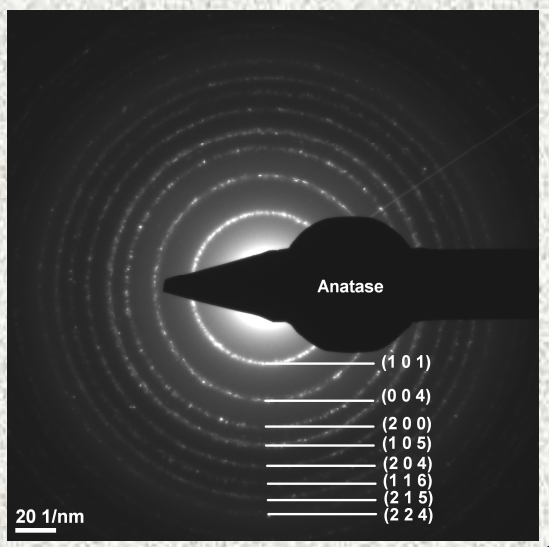
Single phase detected: ZnO zincite.
Crystallite size (Scherrer) =28 - 46.7 nm

Bright field TEM and HREM of 2.5Co-doped TiO_2 nanopowders

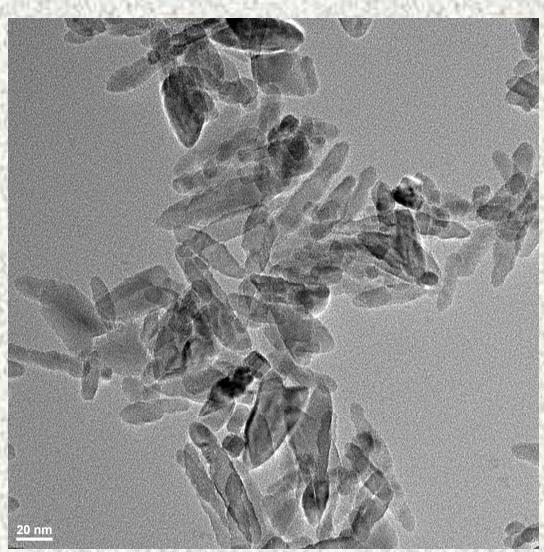


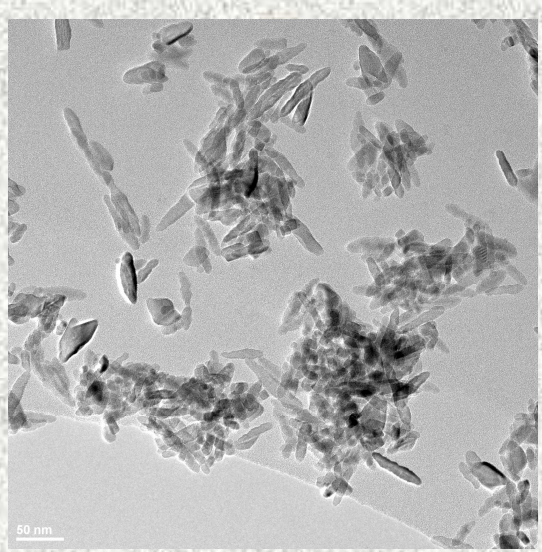


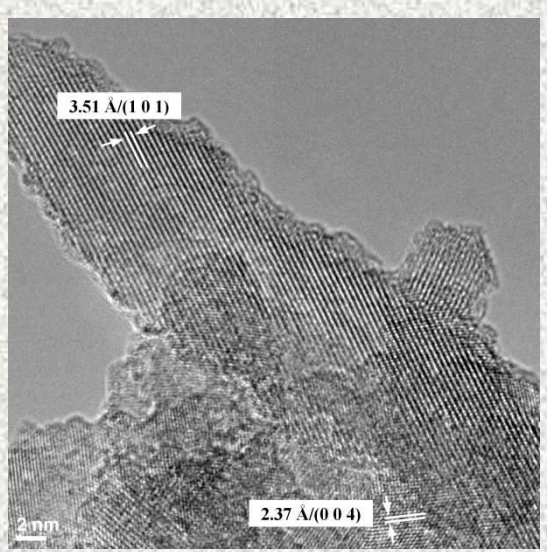




Bright field TEM and HREM of 5Co-doped TiO_2 nanopowders

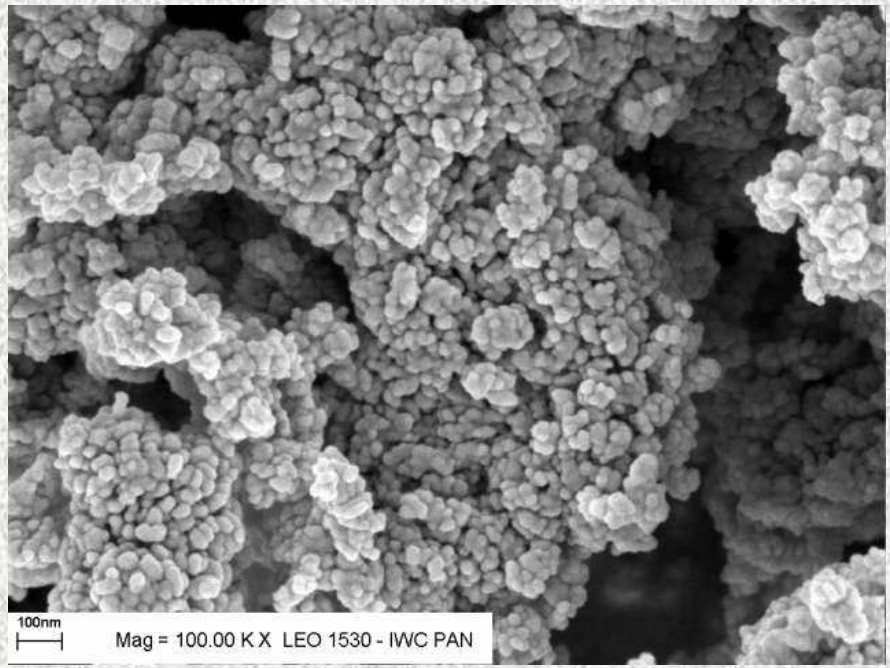


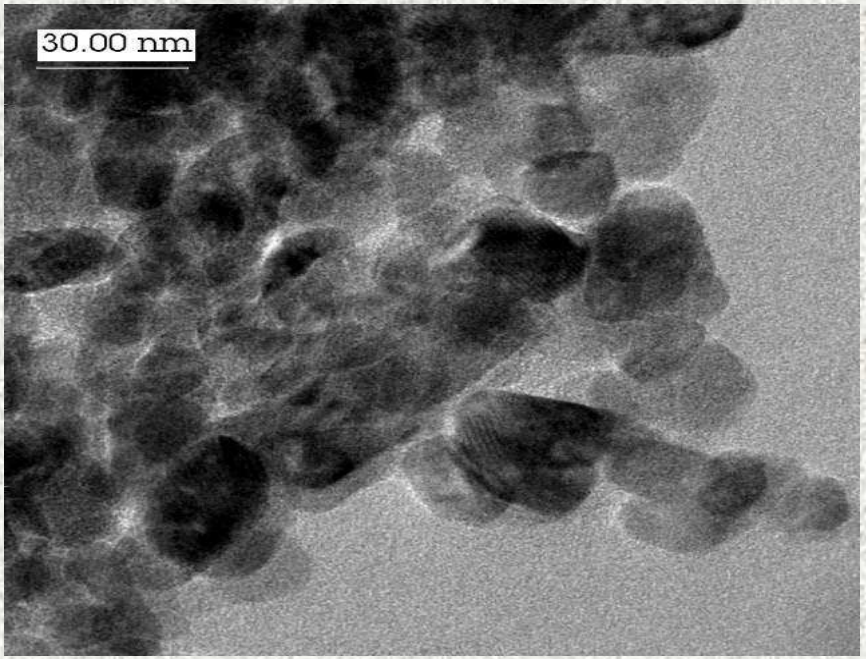




The TEM image reveals that powders are composed from rod like particles. The HREM image shows clear lattice fringes of polycrystalline nanopowder of d = 3.51 and 2.37 Å corresponding to the (1 0 1) and (0 0 4) crystallographic planes of TiO_2 anatase. Also the regular succession of the atomic planes indicates that nanocrystalites are structurally uniform and crystalline.

SEM and TEM of 5Co-doped ZnO nanopowders

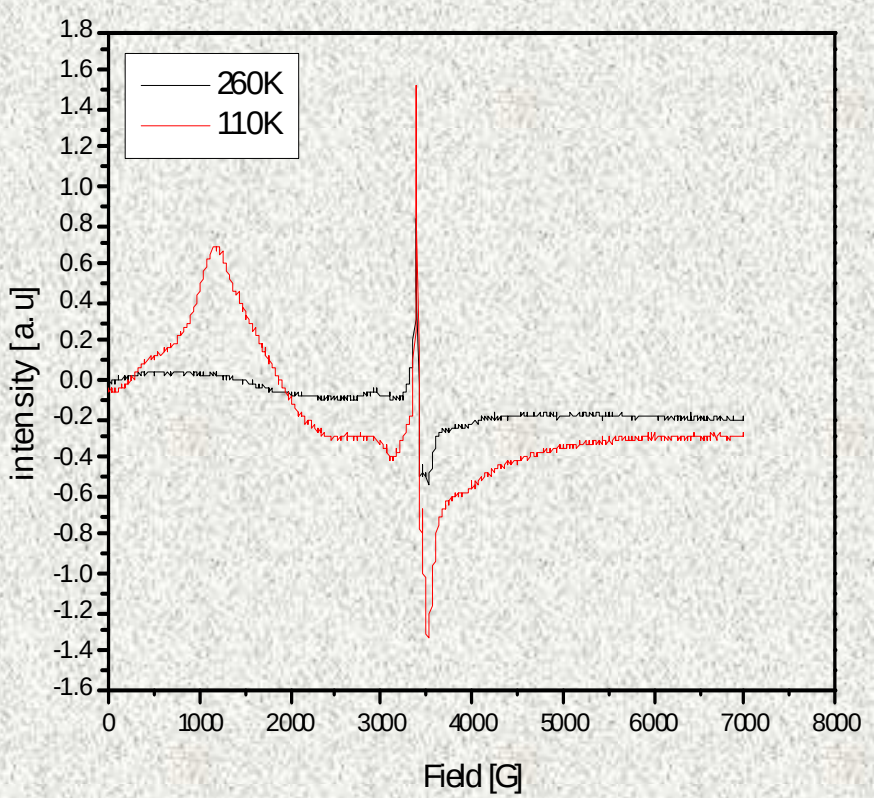


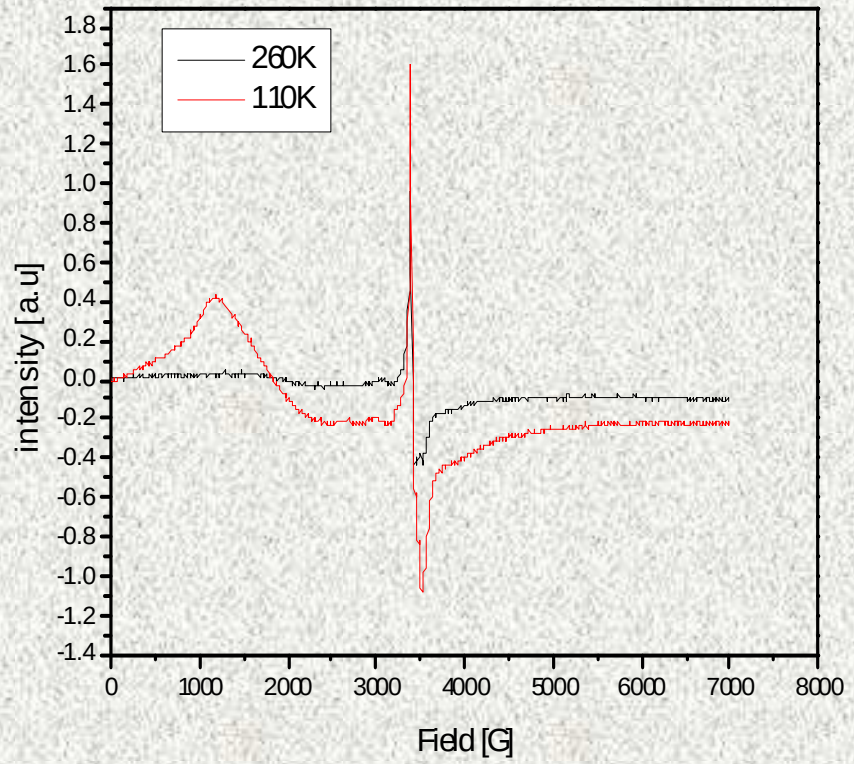


A relatively high degree of agglomeration of initially nucleated nanometer grains is observed.

2.2. First results on defects formation by EPR spectroscopy

EPR results on Co-doped TiO_2 nanopowders





Experimental spectra recorded at two selected temperature for 2.5CoTi275 and 5CoTi275 respectively (temperature range 110-290K)

EPR results on Co-doped TiO_2 nanopowders

The spectra shows two signals, one near 2000G and the other 3100 G.
These signals correspond to the Co^{2+} ions with effective gyro-magnetic factor:

$$g_{\perp} = 3.285 \qquad g_{//} = 2.198$$

The sharp line situated at 3400 G is attributed to the effect centers implying Ti^{3+} ions and implicit formation of O^{2-} vacancies .

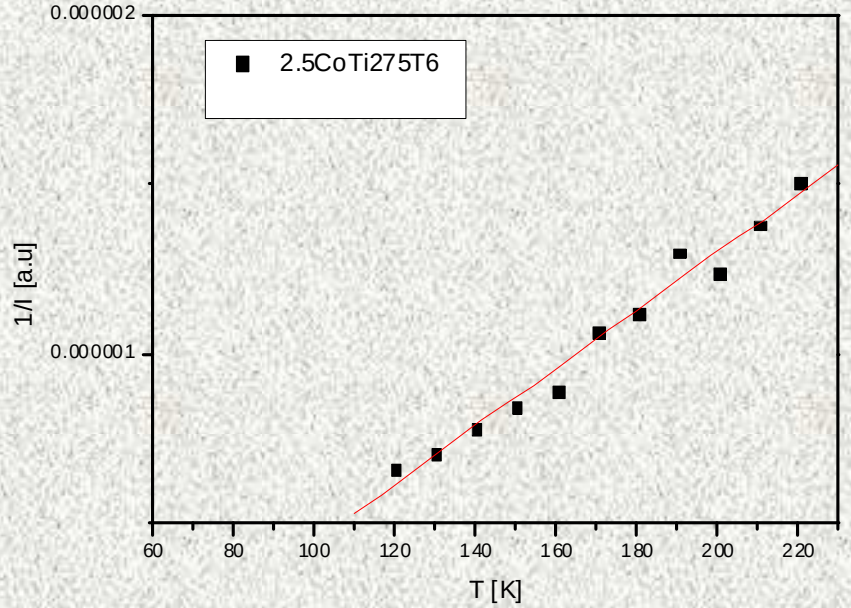
Increasing temperatures the Co ions signal is decreasing due to the very high relaxation time.

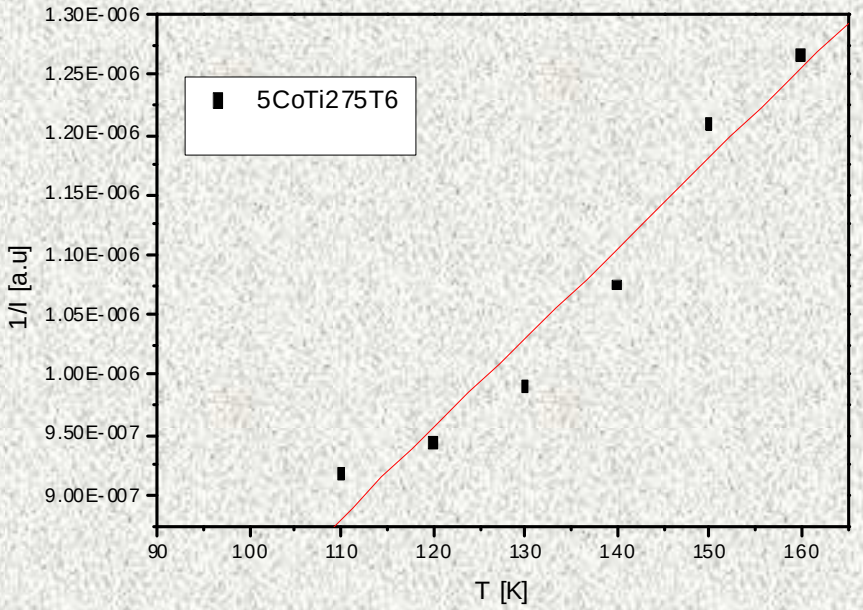
An increase of the line width with the doping concentration appears.

This can be attributed to the spin- spin interactions.

By analyzing the EPR intensity we can estimate magnetic behavior of the samples.

EPR results on Co-doped TiO_2 nanopowders



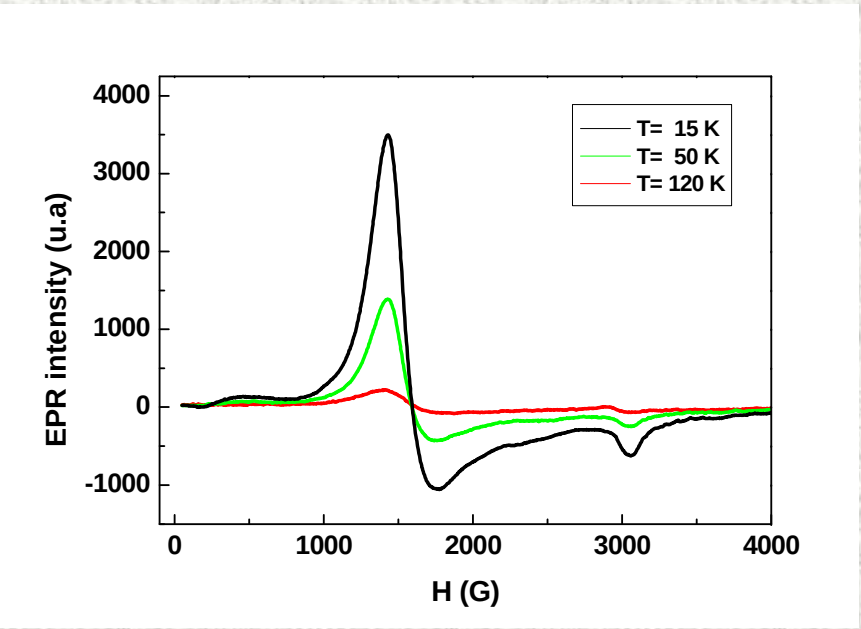


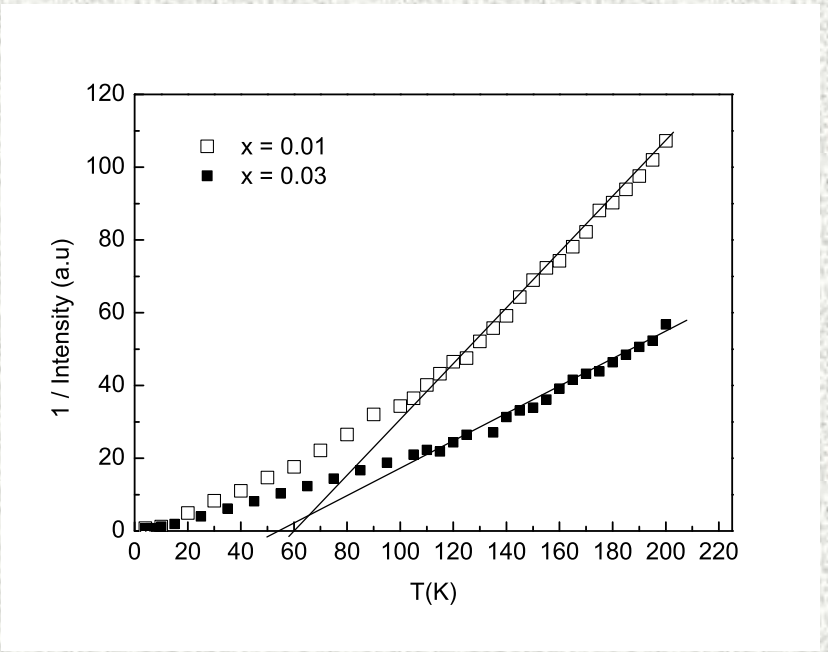
For the 2.5CoTi/275C sample ferromagnetic behaviour was obtained in 110-240K temperature range.

For 5CoTi/275C, in the low temperature range 110-160K, the evaluated θ is 110K while in the high temperature range 170-230K a value of 165K is obtained.

It could means that at higher temperatures the exchange interaction between Co ions increases leading to an increase of the Curie-Weiss temperature.

EPR results on Co-doped ZnO nanopowders





$$I(T) \sim C(x) / (T - \theta(x))$$

The signals near 1500 and 3000 G correspond to the effective $g^{\perp}$ and g||. The origin of the 500 G line is unknown: impurities?

The evaluated θ values are 60 K and 53 K for x = 0.025 and x = 0.05.
The positive sign of the Curie – Weiss temperatures indicate that the Co ions are ferromagnetically coupled.

4.1. Hydrothermal synthesis of complex perovskitic nanopowders

Schematic flow-sheet

Hydrothermal high capacity autoclave

Controlled atmosphere Oven – MHI

Zetaseizer Malvern

AAS ZEEnit 700 Analytik Jena

DSC Netzsch Maya F200

Spray-dryer

Soluble salts of Ba, Sr, Ti

Mineralizing agents

Hydrothermal Synthesis

Filtering, Washing, spray drying

Chemical analysis (ICP, DCP, AAS)

Microstructure characterisation:

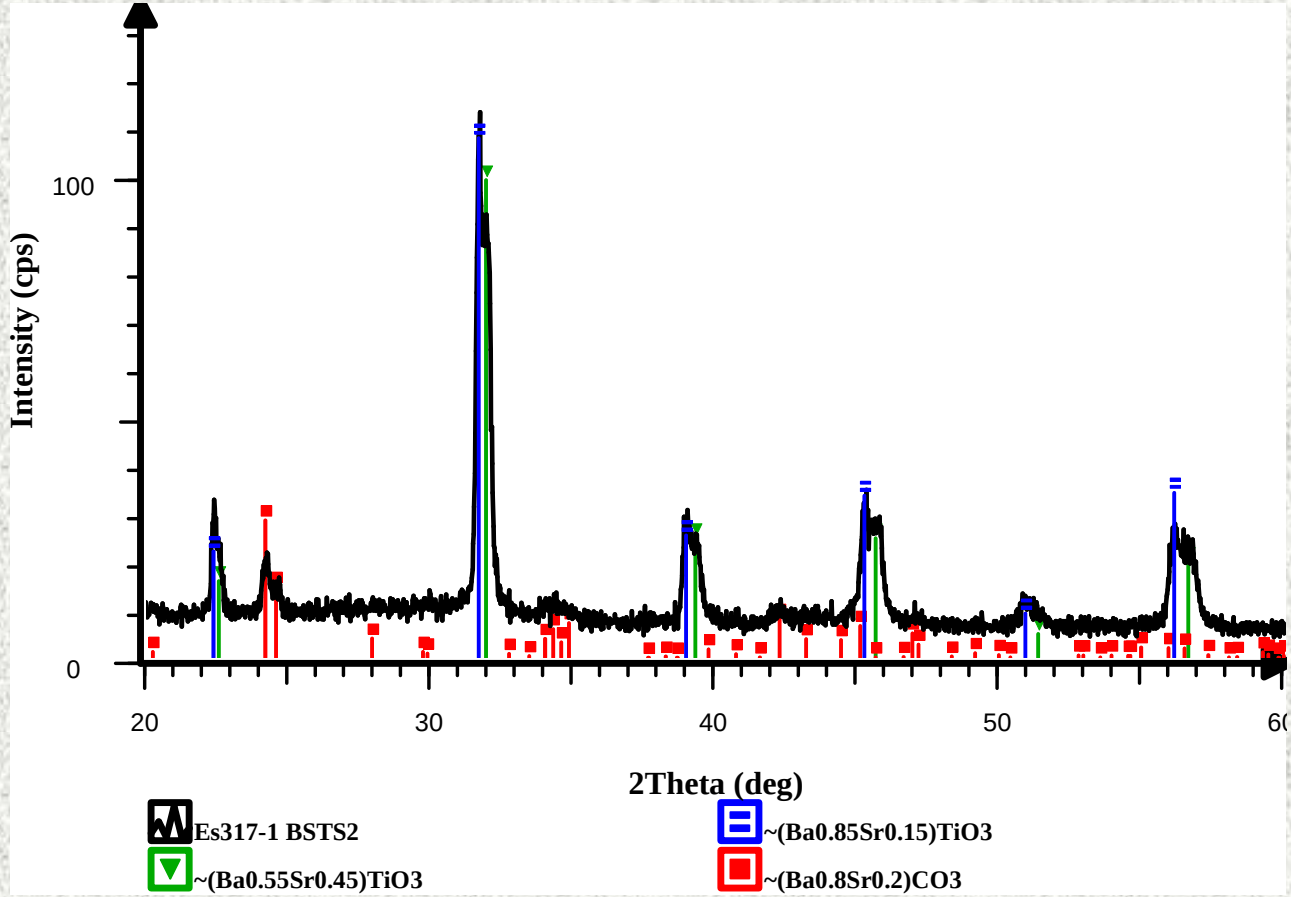
-DRX: Bruker D8 Advance

-SEM, TEM, HREM

- Size distribution & Zeta Potential

- DSC; DSC-TG

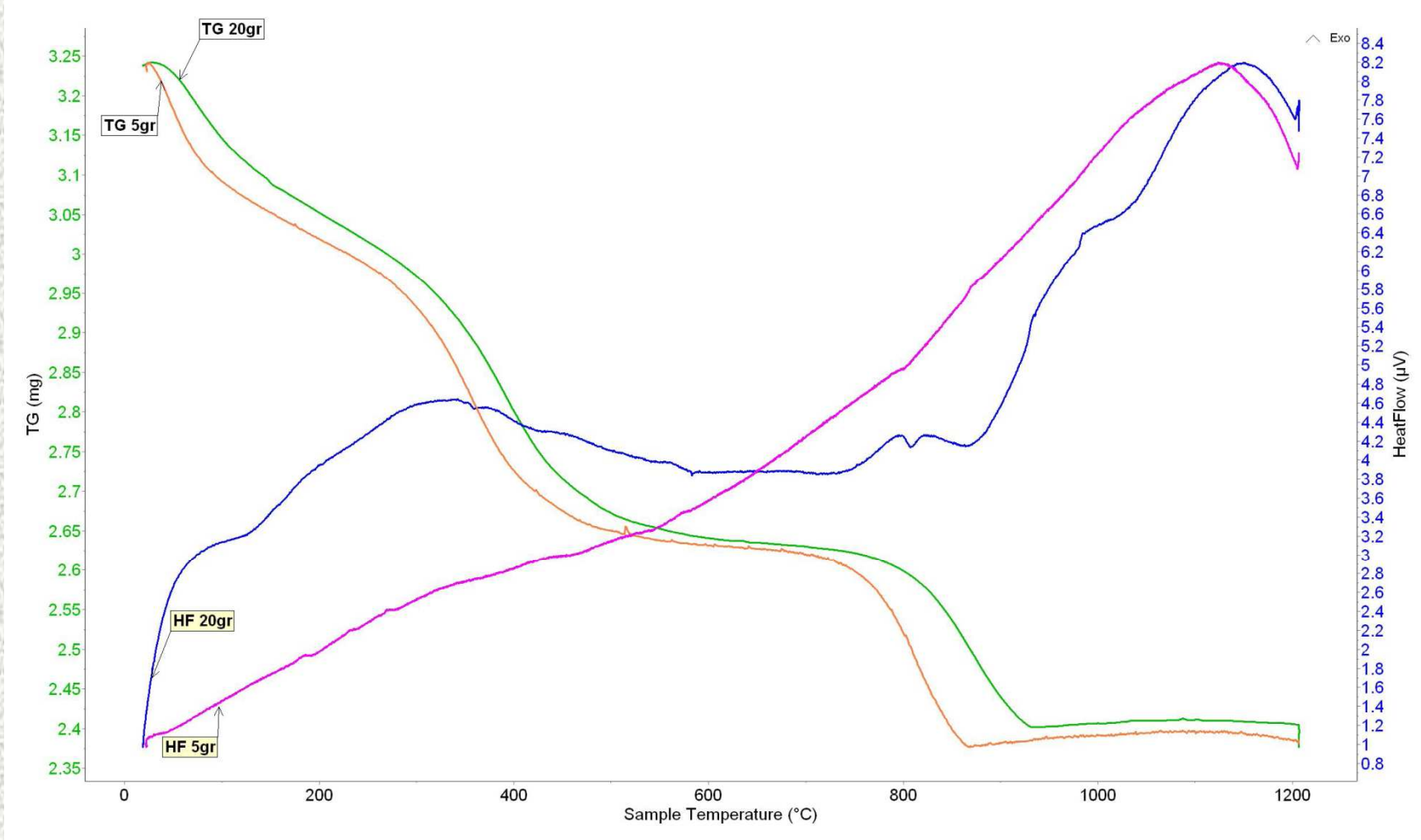
XRD of a BST sample hydrothermal synthesized



$(Ba_{0.85}Sr_{0.15})TiO_3$
Crystallite Size (Scherrer): 42.5 nm; System:Cubic

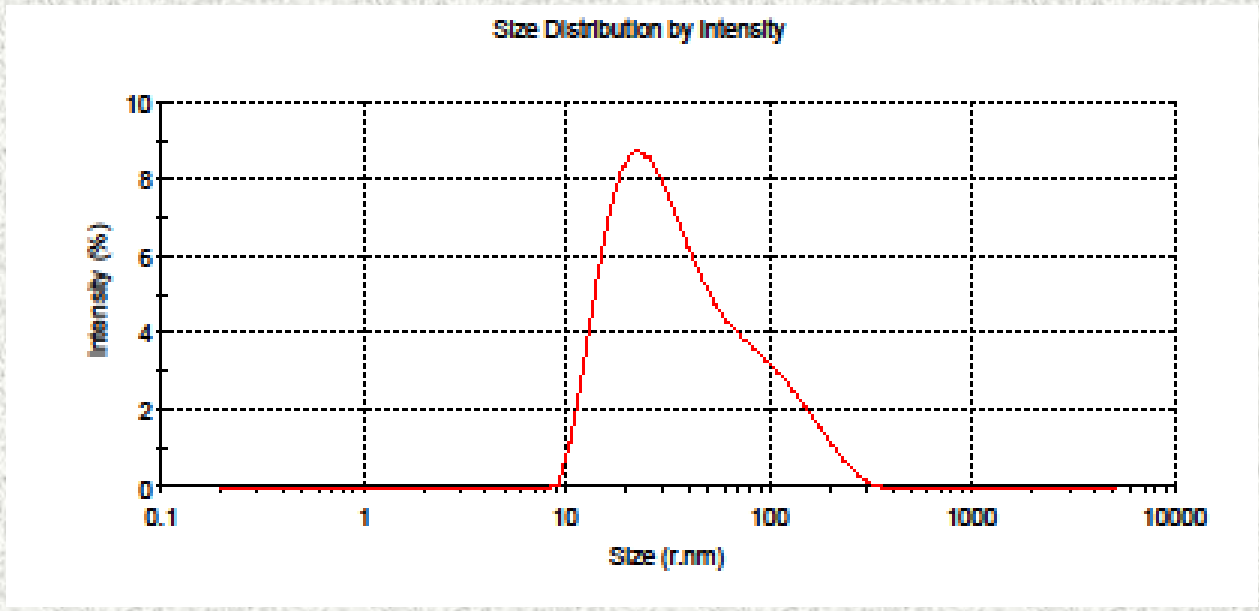
$(Ba_{0.55}Sr_{0.45})TiO_3$
Crystallite Size (Scherrer): 34.6 nm; System:Cubic

DTS-TG of a BST sample hydrothermal synthesized



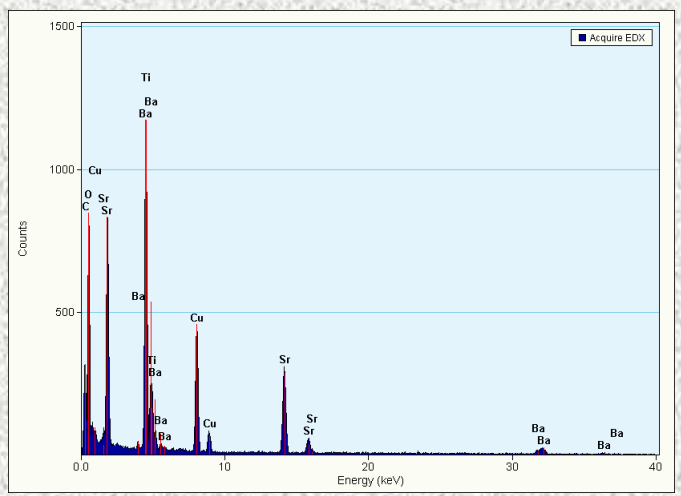
DSC-TG graphs are registered at two different heating rates: 5 and 20 degrees/minute

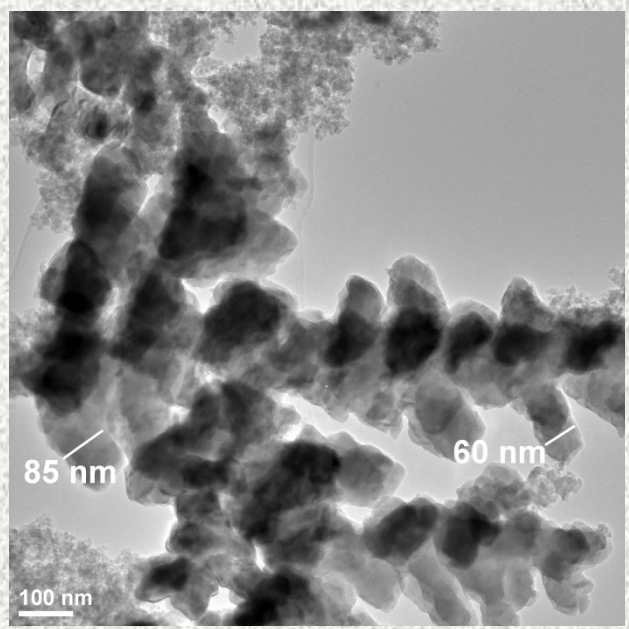
Size distribution by intensity for a BST sample hydrothermal synthesized

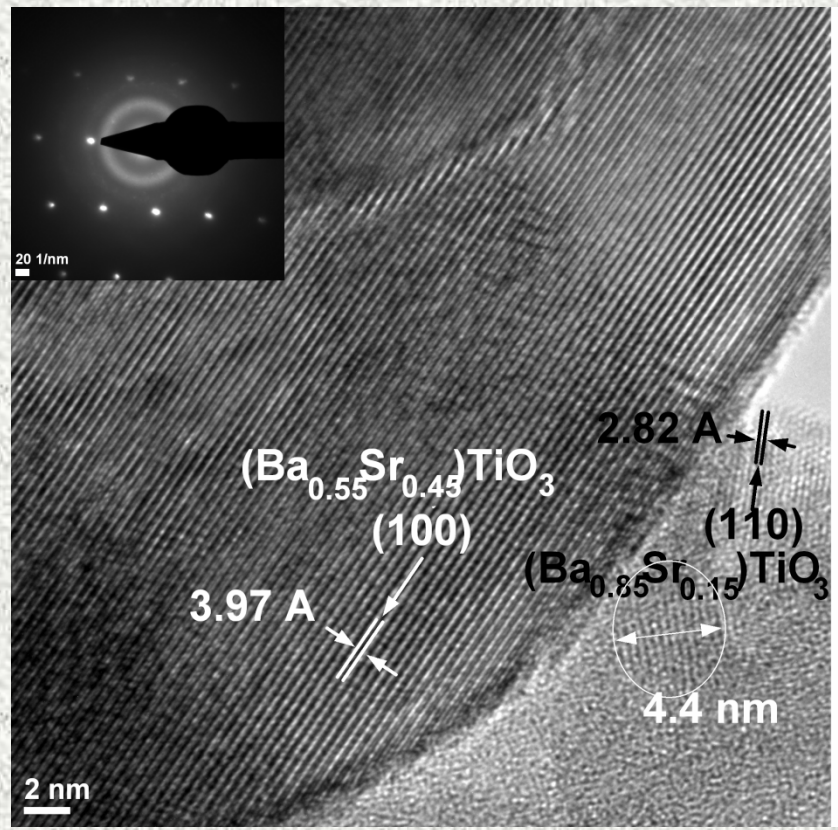


Z-average size (r-nm): 29.1 nm; pdl: 0.263

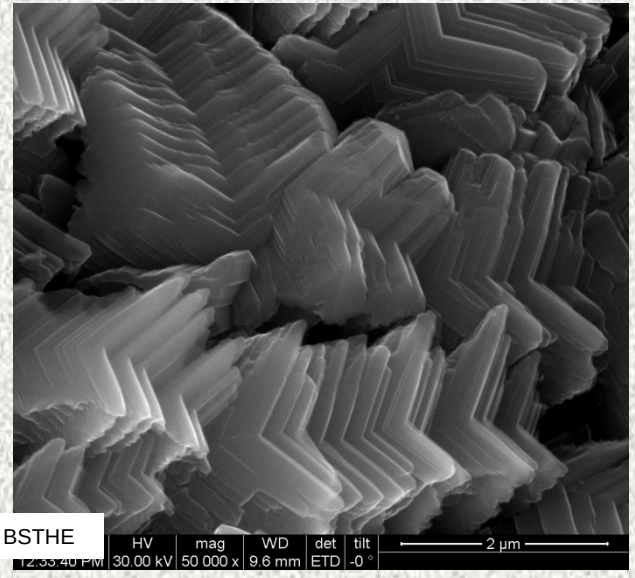
HREM for a BST sample hydrothermal synthesized

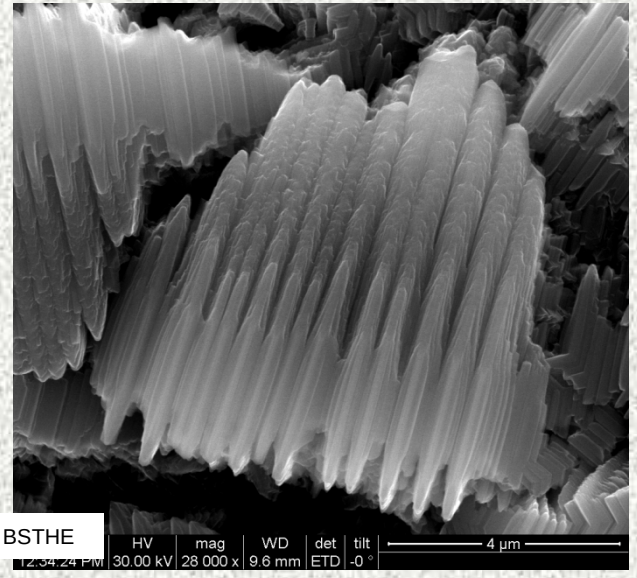


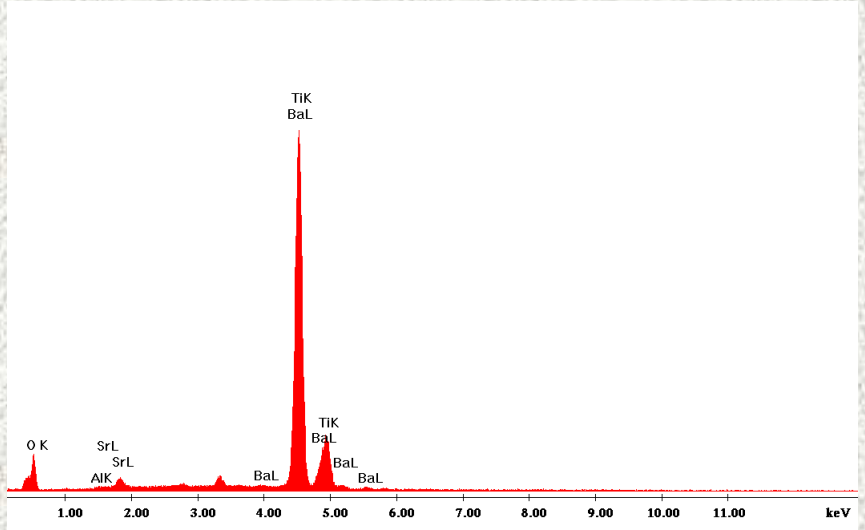




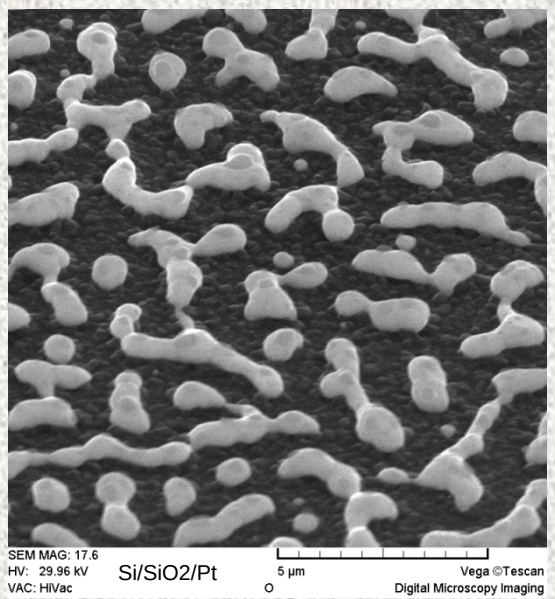
SEM for a BST sample hydrothermal-electrochemical synthesized



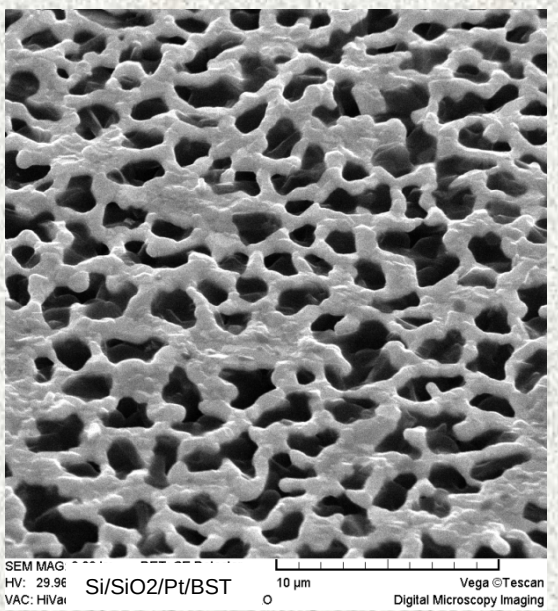




SEM for a BST thin film deposited by hydrothermal-electrochemical procedure



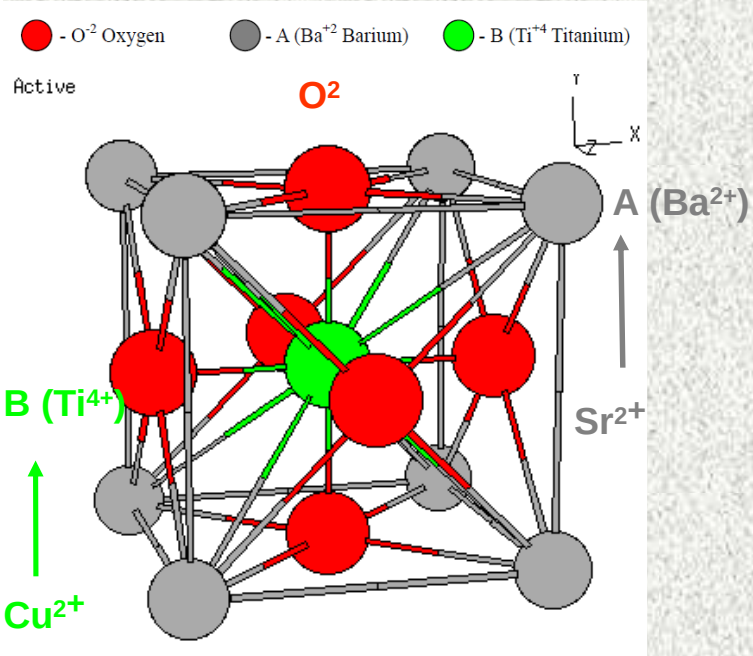
SEM for the substrate Si/SiO2/Pt



SEM for the film deposited on Si/SiO2/Pt substrate

Formation of a porous structure by hydrothermal electrochemical deposition procedure

ABO_3 structure



BST samples hydrothermal synthesised presents compositional heterogeneity : two cubic stable BST phases with similar composition. Hydrothermal synthesis under high pressures (40 -80 atm) lead to the formation of cubic stable BST phases.

A possible explanation could be the main principle of hydrothermal procedure:

negative ΔV value

$\Delta V = \Sigma(V/Z)(j) - \Sigma(V/Z)(i)$

i = precursor

j = product

It is expected that BST samples hydrothermal synthesised with sizes at nano level to have larger specific surface area. Consequently the process activity will be increased.

RBa^{2+}=1.61 A
RSr^{2+}= 1.58 A
RTi^{4+}= 0.605 A
RO^{2-} = 1.40 A
RCu^{2+}=0.73 A

Hydrothermal reaction takes place in situ starting from soluble salts of Ba, Sr, Ti and dopant respectively.

During hydrothermal reaction, based on the previous work, we can assume that the first phase which is formed in situ is

$Ba_{1-x}\ Sr_xTiO_3$ which reacts with copper precursors and leads to

$Ba_{1-x}\ Sr_xTi_{1-y}Cu_yO_3$

Cu^{2+} is an acceptor dopant and determines the formation of oxygen vacancies, being the dominant ionic defects.

At high pressure (hydrothermal conditions) the concentration of oxygen vacancies is dependent on dopant concentration.

[dopant]/2=[oxygen vacancies]

According to PhD thesis Piero Lupetin 'Charge carrier defect chemistry of nanoscopic SrTiO3" University of Sttutgard – Max Plank Institute(2012)

It is expected due to dimensions to have a higher mobility of oxygen vacancies and consequently enhanced reactivity.

$g_{\perp}$

Conclusions and future works

• **Hydrothermal synthesis is suitable to produce Co- doped TiO2 / Co-doped ZnO Nanopowders with controlled chemical and single phase composition.**

• **The ability to produce stable Co-doped anatase is a unique feature of the process.**

•**The EPR investigations show the intrinsic ferromagnetic behavior of both nanopowders.The results support the great potential for further applications. Works are in progress for Fe-doped nanopowders synthesis and their thin film deposition to measure the spin and magnetic properties of the films**.

Hydrothermal synthesis enables the formation of complex perovskite nano structures with controlled stoechiometry and morphology with potential application for hazardous substances detection (e.g. H_2S).

Future Works:

The mechanism at the interface between perovskite sensor and gas should be investigated and assessed.

Acknowledgement:

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THANK YOU FOR YOUR ATTENTION