

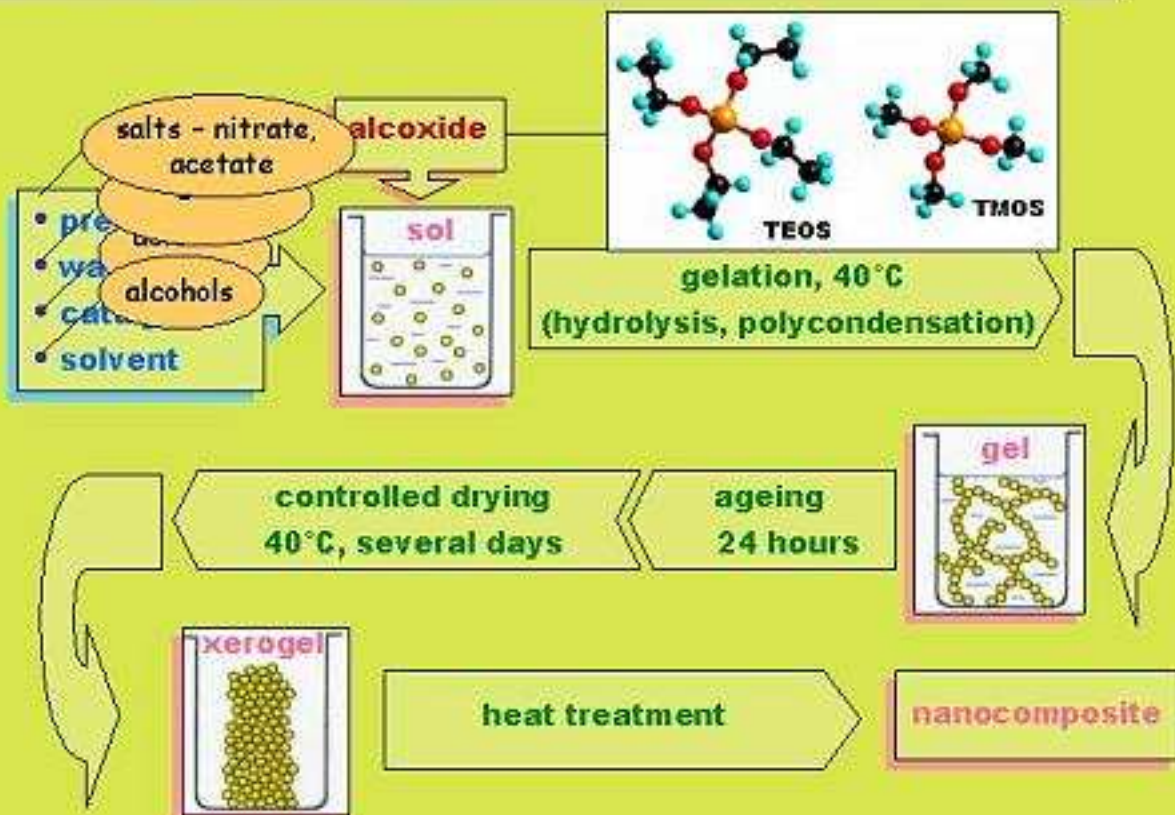
PREPARATION OF SILICA/FERRITE NANOCOMPOSITES

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NANOCOMPOSITE PREPARATION BY SOL - GEL METHOD



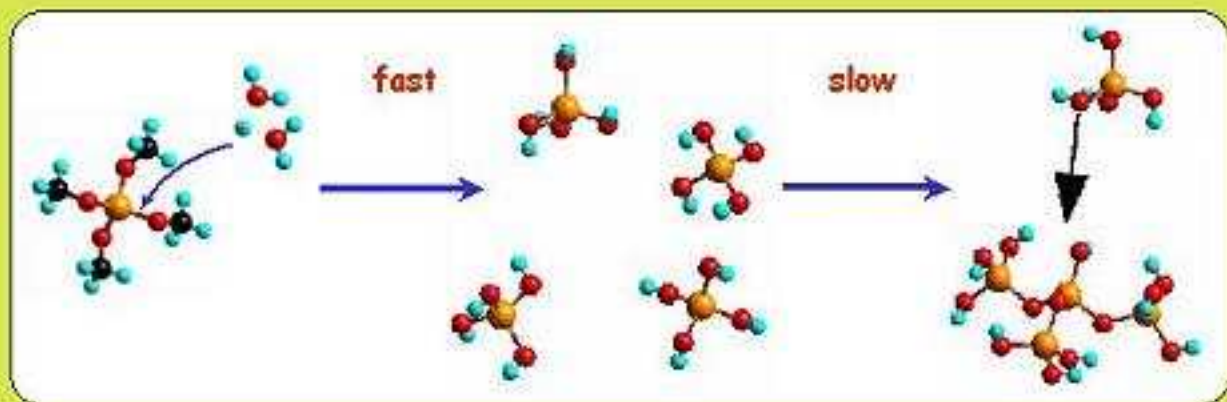
SOL - GEL PROCESS

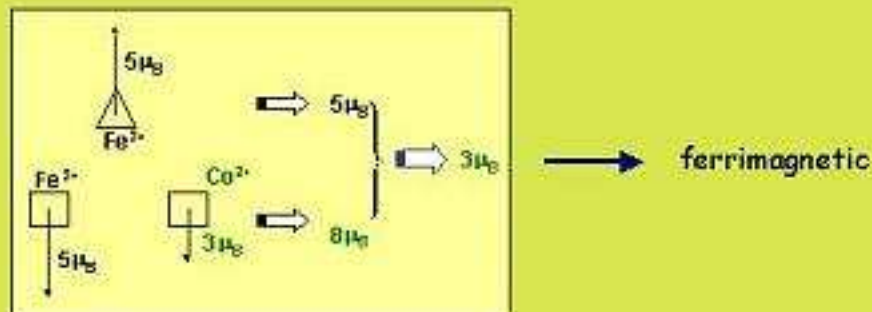
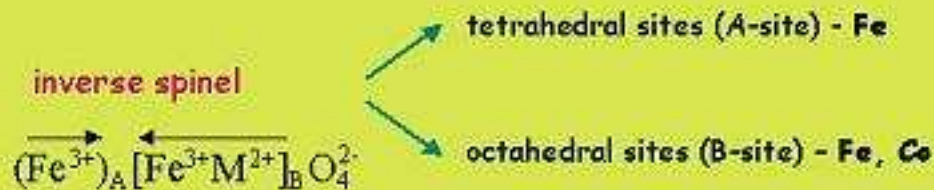
consequent reactions: **hydrolysis** and **polycondensation**



alcoxyde : H_2O
1 : 5

condensation (water elimination):
 $=Si-OH + =Si-OH \leftrightarrow =Si-O-Si= + H_2O$

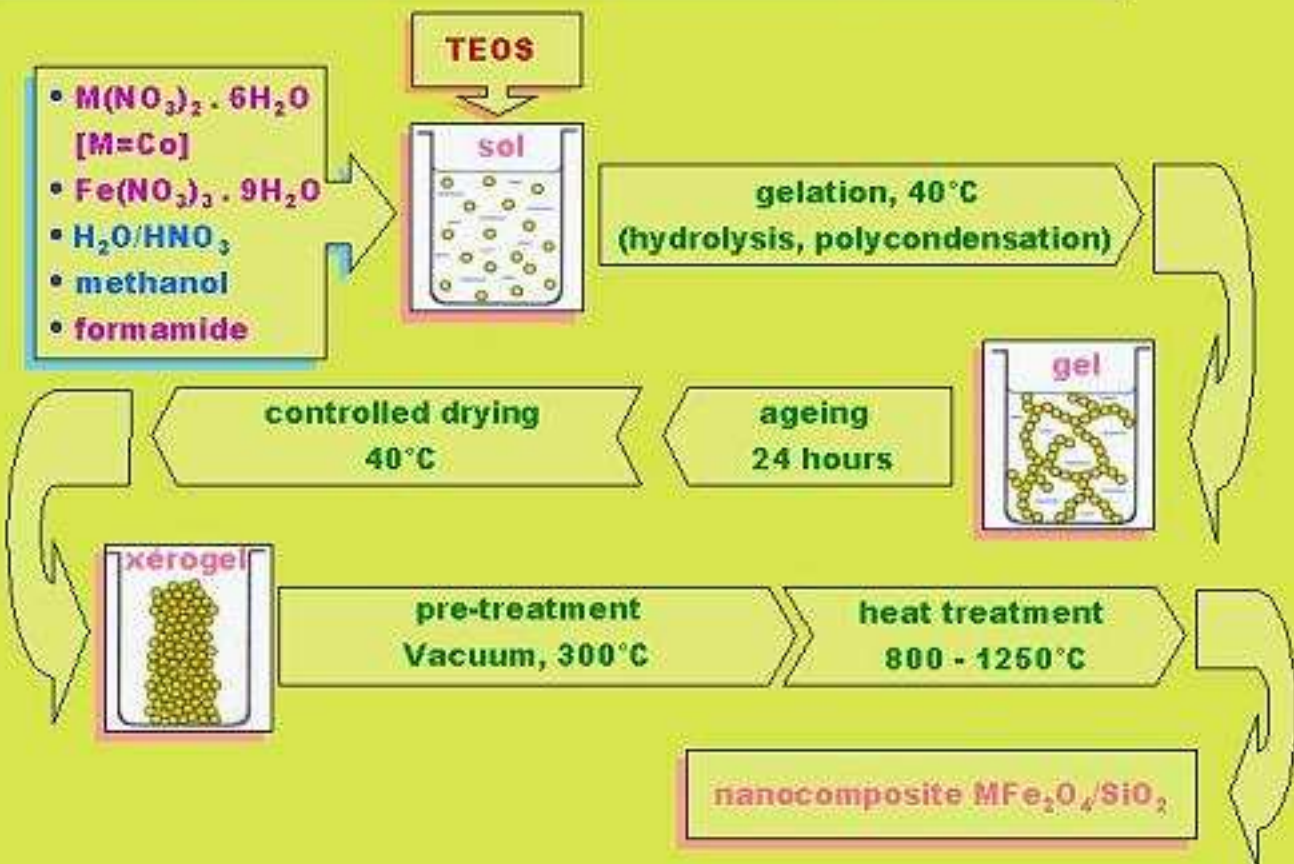




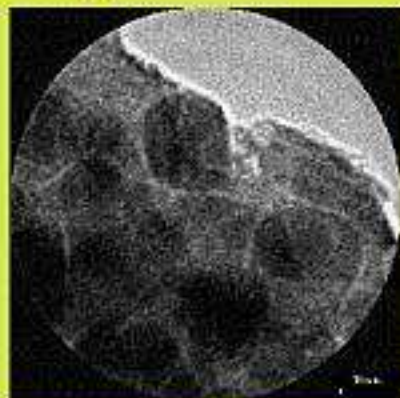
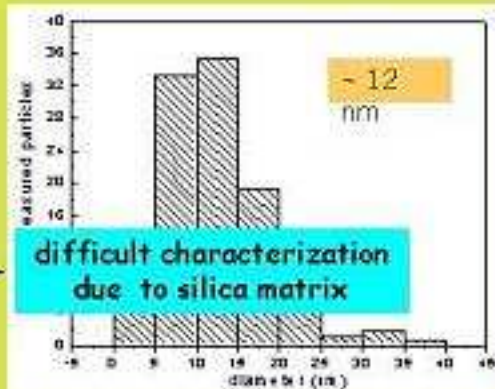
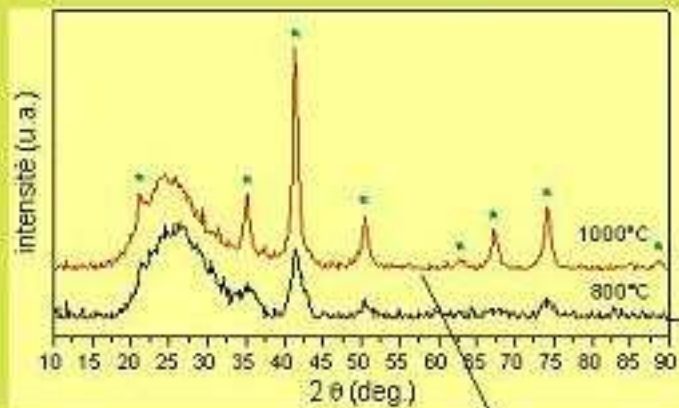
SiO_2 - acid character, react with two-valent metal cations
 \Rightarrow formation of silicates (e.g. Co, Ni)

sol-gel method - preferential formation of spinel ?

PREPARATION OF SPINEL NANOCOMPOSITES

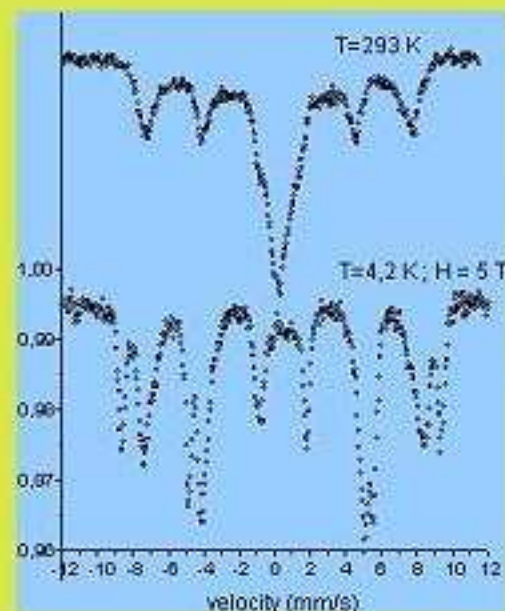


15/100 CoFe₂O₄/SiO₂ - RXD and TEM



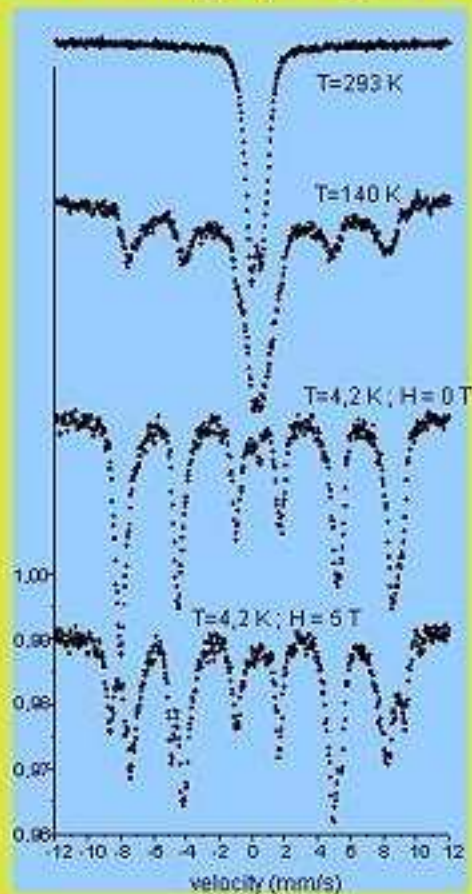
great particles

15/100 CoFe₂O₄/SiO₂ 1000°C - MÖSSBAUER SPECTROSCOPY



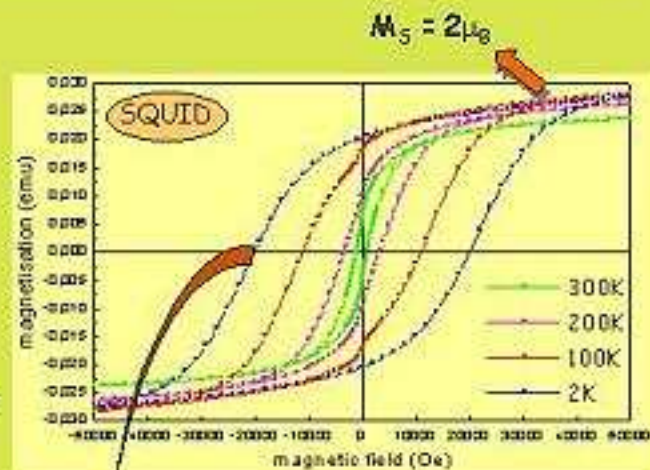
- Room temperature measurement - about 50% in superparamagnetic state
- 4,2 K - magnetically ordered sample
- (Fe \uparrow) [Co \downarrow Fe \downarrow]O₄ - ideal
- (Co_{0,41} Fe_{0,59}) [Co_{0,59} Fe_{1,41}]O₄ - real formula

15/100 CoFe₂O₄/SiO₂ 900°C - MÖSSBAUER SPECTROSCOPY

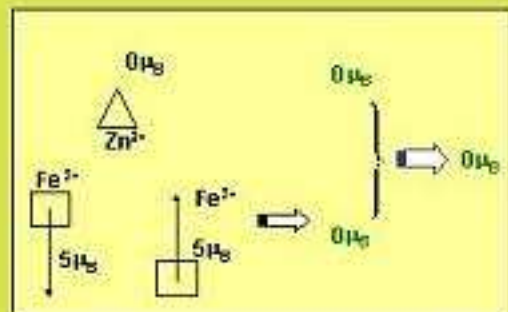


- Smaller particles - 4-5 nm
- Room temperature measurement - superparamagnetic state
- 140 K measurement - about 50% in superparamagnetic state
- 4,2 K - magnetically ordered sample

very high increase of the
coercive field with decreasing
temperature



coercive field >
22 kOe

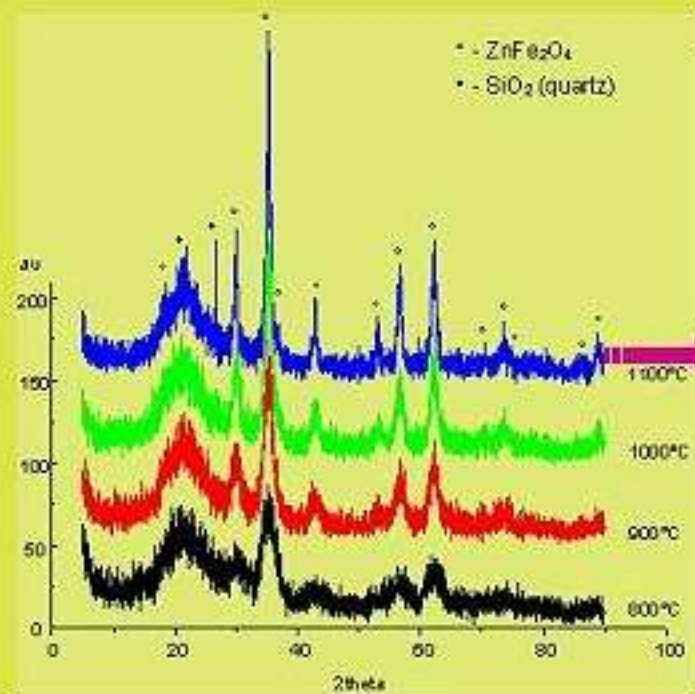


antiferromagnetic
(below 9 K)

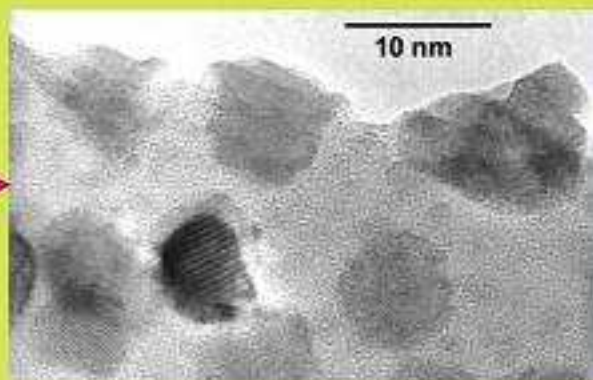
$SiO_2 \Rightarrow$ Zn silicates are not formed

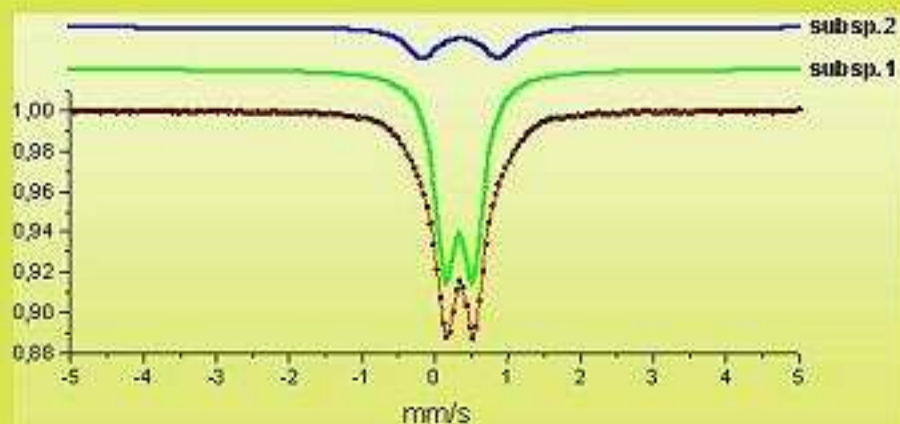
sol-gel method - preferential formation of spinel

ZnFe₂O₄/SiO₂ - RXD and TEM



difficult characterization
due to silica matrix

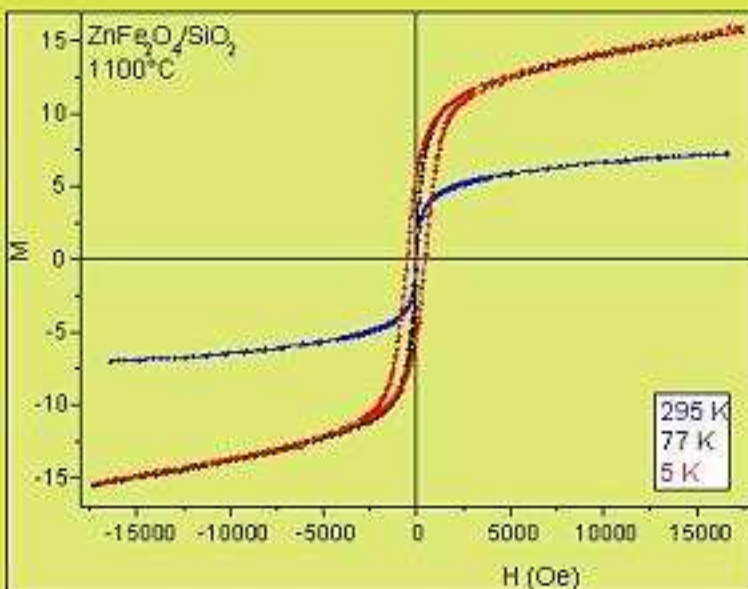




	Subsp. 1	Subsp. 2
Isomer shift δ	0,34 mm/s	0,35 mm/s
Quadrupole splitting ΔE_Q	0,38 mm/s	1,05 mm/s
Relative area (%)	81	19

Room temperature MS – seems to be coherent with theory

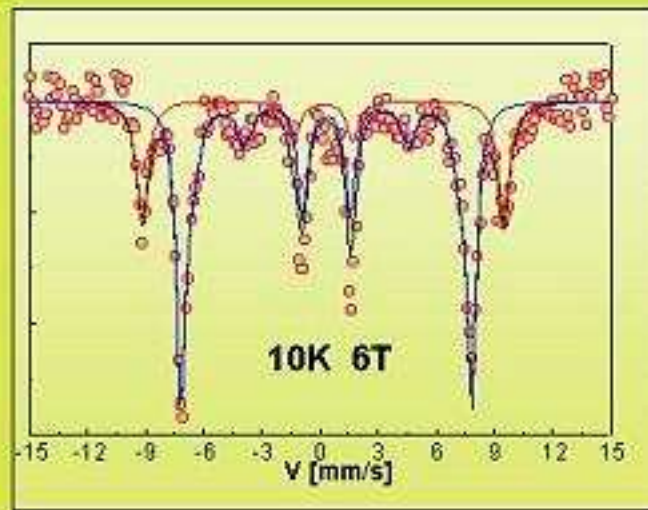
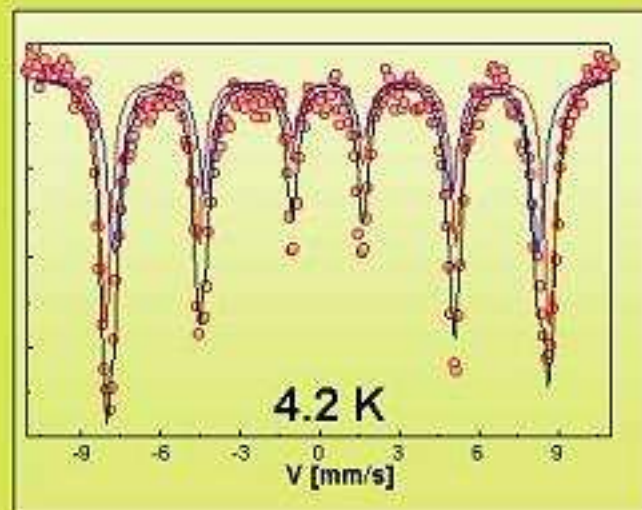
15/100 ZnFe₂O₄/SiO₂ 1100°C - MAGNETIC MEASUREMENT



hysteresis at 5 K -
ferrimagnetic behaviour

77 K and RT measurements
- superparamagnetic state

Fe(III) in tetrahedral
sites ?



4.2K MS – difficult to distinguish tetrahedral and octahedral position

Model core-shell

shell - Fe in octahedral position - canting

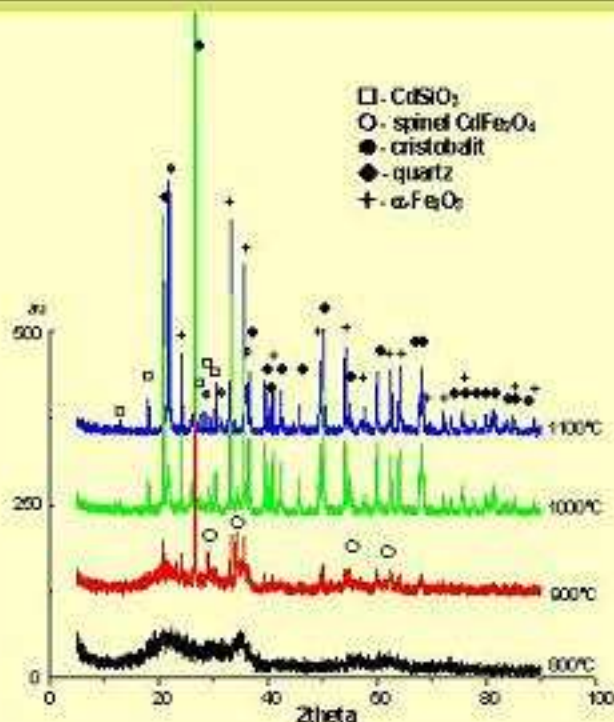
core - Fe in tetrahedral position

800-900°C - amorphous character of SiO_2 matrix

900°C - maximal concentration of spinel phase

1000°C - SiO_2 matrix recrystallization into quartz and cristobalit

1100°C - sample decomposed into hematite

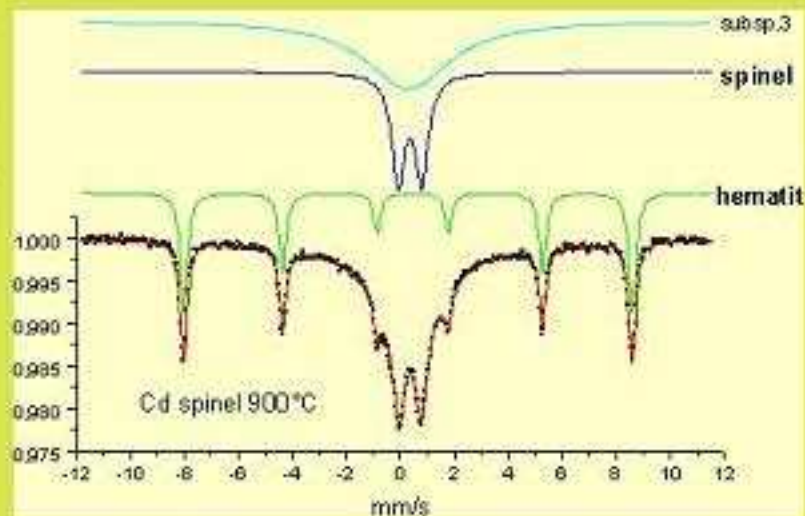


$\text{CdFe}_2\text{O}_4/\text{SiO}_2$ - MÖSSBAUER SPECTROSCOPY

Sample heat treated at 900°C and measured at room temperature

Spinel to hematite ratio
40 / 60

1100°C - sample decomposed into hematite

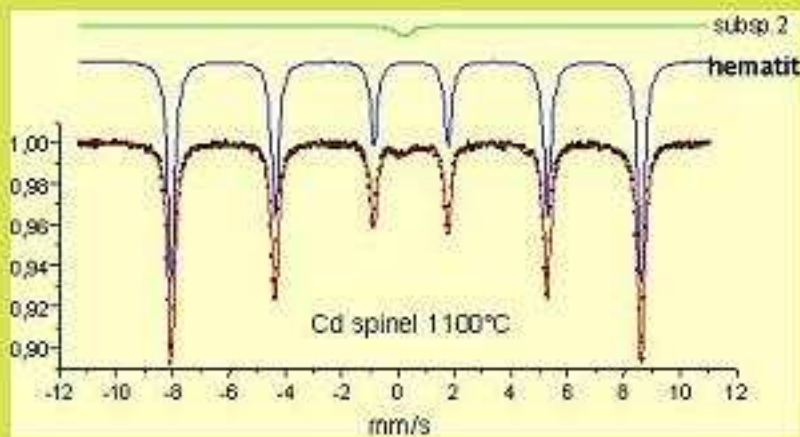


$\text{CdFe}_2\text{O}_4/\text{SiO}_2$ - MÖSSBAUER SPECTROSCOPY

Sample heat treated at 1100°C and measured at room temperature

Spinel to hematite ratio
3 / 97

1100°C - sample decomposed into hematite



- Inverse spinel (mixed state)
- Tetragonal distortion due to Jahn - Teller effect

Fe in tetrahedral position (A-site)

Fe, Cu in octahedral position (B-site)

Ferrimagnetic at room temperature

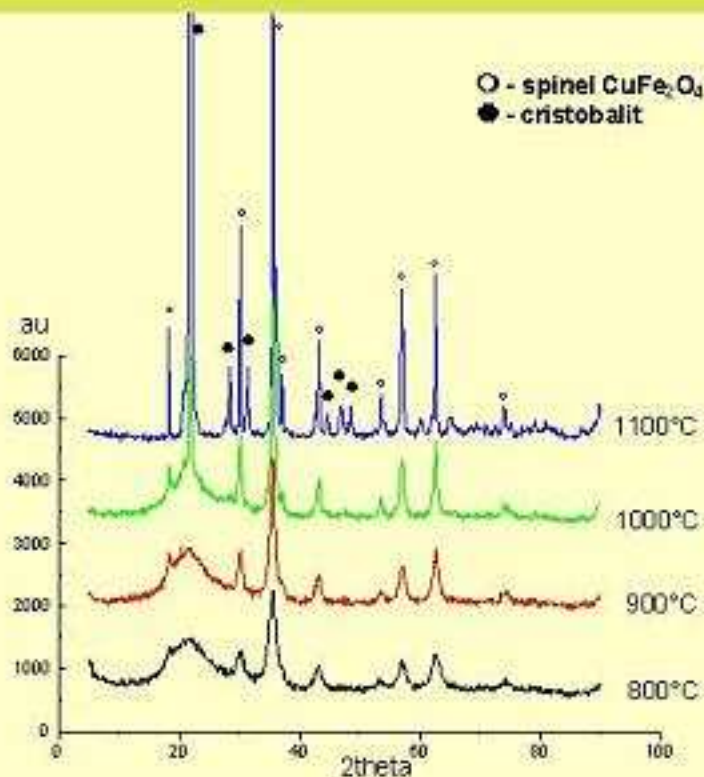
Saturation magnetization and Curie temperature

	σ (emu/g)	T_c (K)
CuFe ₂ O ₄	25	728

$\text{CuFe}_2\text{O}_4/\text{SiO}_2$ - RTG POWDER DIFFRACTION

Iron containing phases
- Only spinel phase is observed

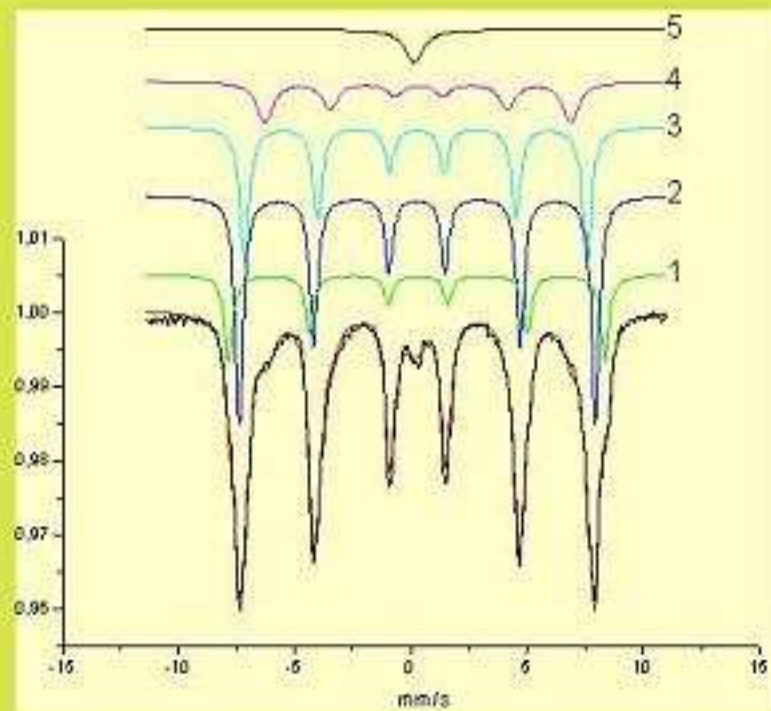
1000°C - SiO_2 matrix
recrystallization into
cristobalite



$\text{CuFe}_2\text{O}_4/\text{SiO}_2$ - MÖSSBAUER SPECTROSCOPY

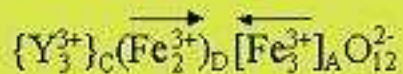
Sample heat treated at 1100°C and measured at room temperature

Due to lower symmetry, 4 non-equivalent iron position can be found

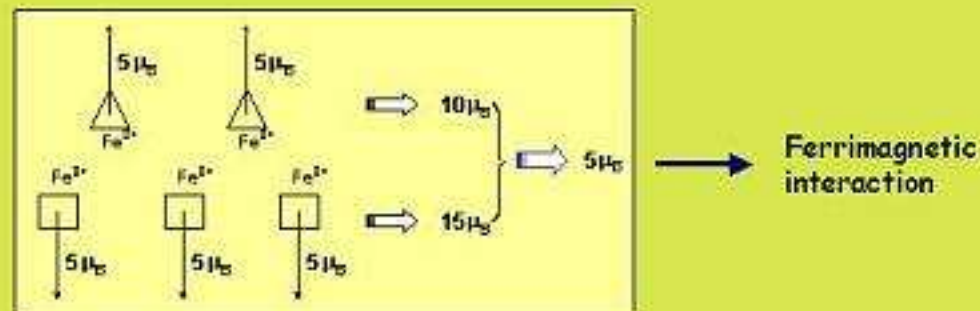


$Y_3Fe_5O_{12}/SiO_2$ NANOCOMPOSITE (YIG)

Yttrium iron garnet



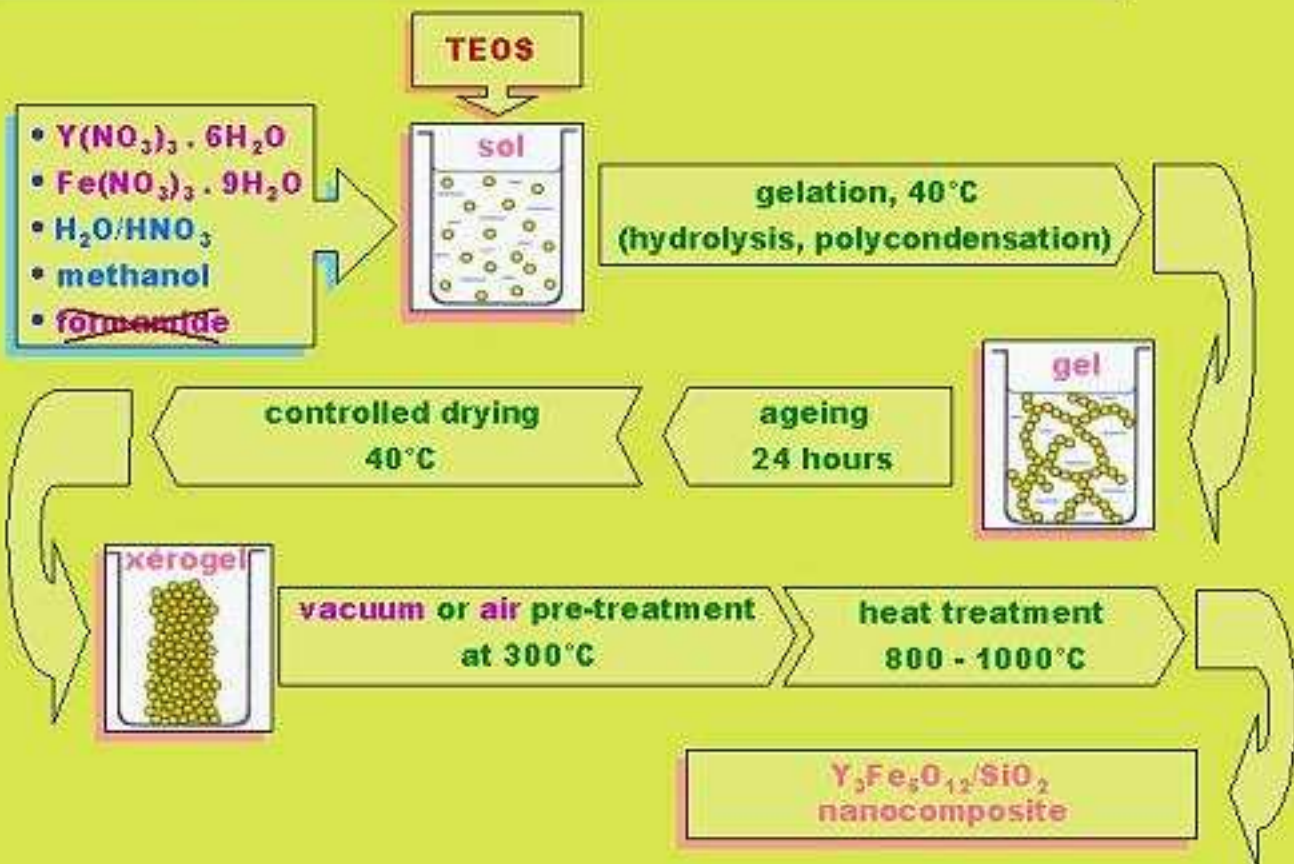
- tetrahedral sites (D-site) - Fe
- octahedral sites (A-site) - Fe
- dodecahedral sites (C-site) - Y



Properties

- ☞ magnetic
- ☞ optic
- ☞ possibility of the cation substitution

PREPARATION OF YIG/SiO_2





Study of influence of the following parameters

- ⌘ effect of formamide
- ⌘ pre-treatment - presence or absence of vacuum
- ⌘ final heat treatment

Prepared samples : molar ratio Fe/Si = 20/100

YIG-VAC,FA
800°C
900°C
1000°C

YIG-VAC
800°C
900°C
1000°C

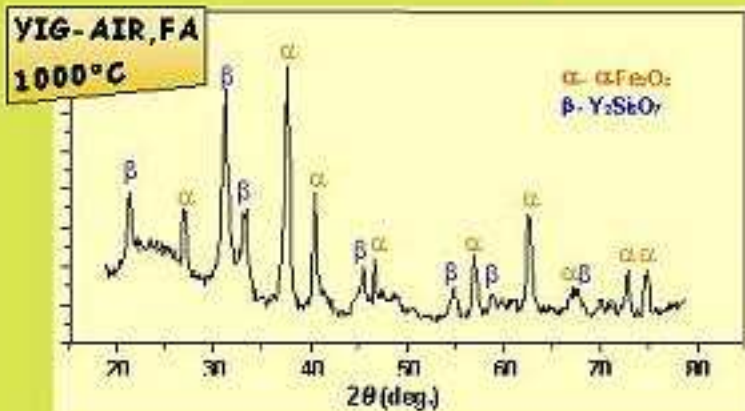
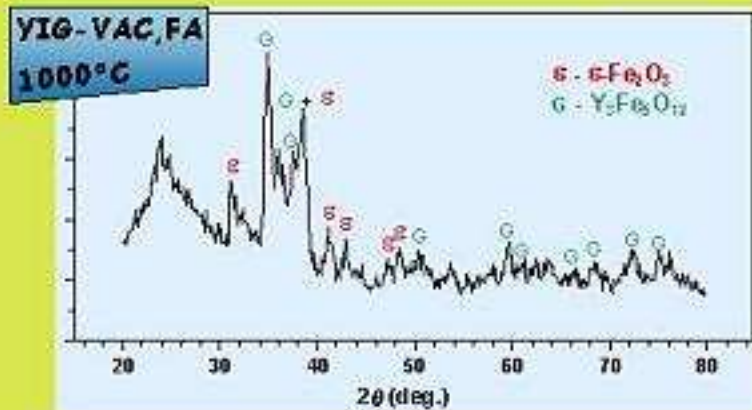
YIG-AIR,FA
800°C
900°C
1000°C

YIG-AIR
800°C
900°C
1000°C

RX-diffraction, transmission electron microscopy,
Mössbauer spectroscopy, magnetic measurement

$Y_3Fe_5O_{12}/SiO_2$ - RXD

800°C et 900°C - poorly
crystallized materials
⇒ no diffraction



➔ different composition
of phases

$Y_3Fe_5O_{12}/SiO_2$ - TEM (x 590.000)

YIG-VAC,FA
1000°C

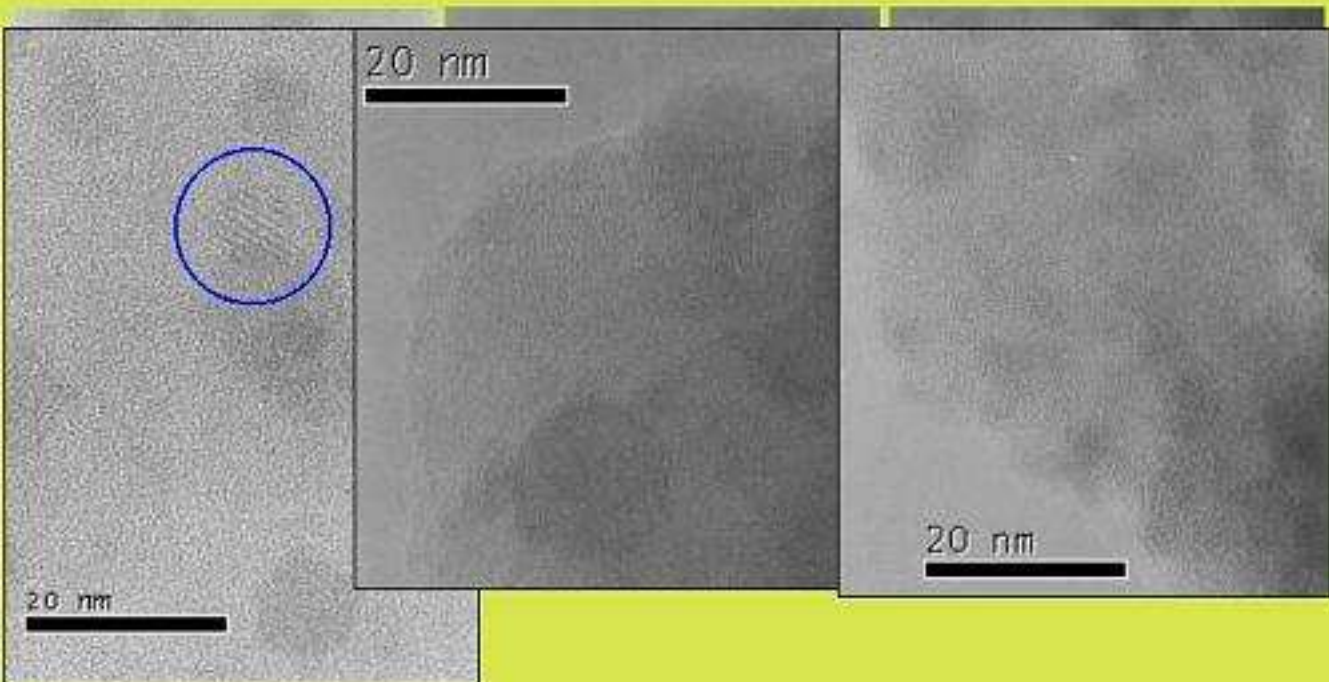
~ 11,0 nm

YIG-VAC
1000°C

~ 10,7 nm

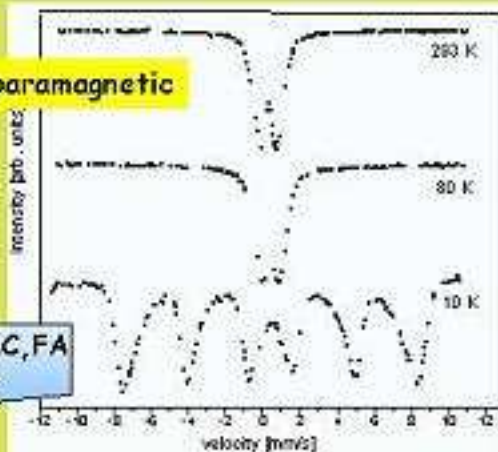
YIG-AIR,FA
1000°C

~ 8,1 nm

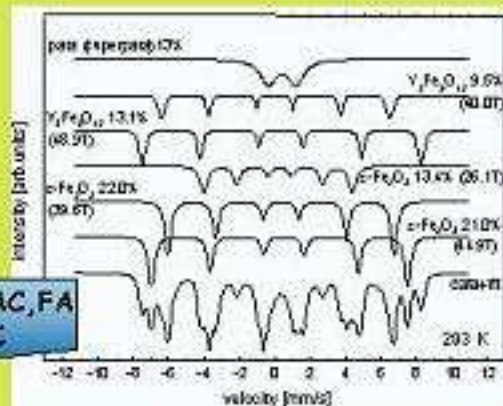


$Y_3Fe_5O_{12}/SiO_2$ - MÖSSBAUER SPECTROSCOPY

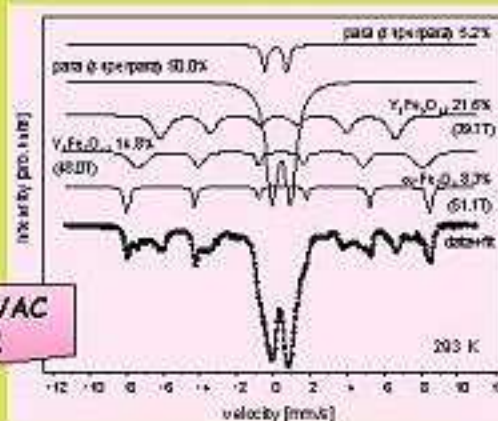
superparamagnetic



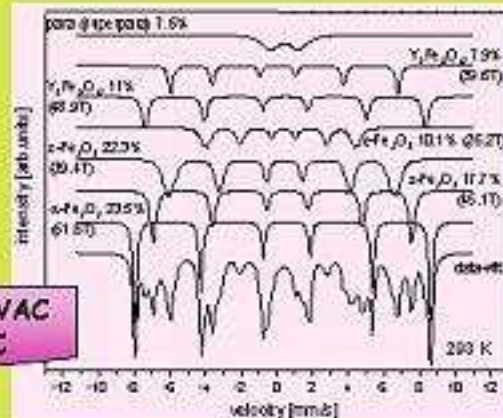
YIG-VAC, FA
800°C



YIG-VAC, FA
1000°C



YIG-VAC
800°C



YIG-VAC
1000°C

New approach of nanocomposite preparation

- Bonding of SiO_2 matrix precursor and nanoparticles building atoms into one molecule via organic bridge
 - ▶ Metal ion complexation
 - ▶ Covalently bonded matrix precursor – $\text{Si}(\text{OR})_3$ (suitable for hydrolysis - condensation reaction)

Aim of the work

- Precursor preparation
- Nanocomposite preparation with the high content of magnetic compound (40 mass % of Fe_2O_3)
- Characterization of prepared nanocomposite

Precursor preparation

➤ $[\text{FeL}^1]^+$



Preparation of nanocomposite

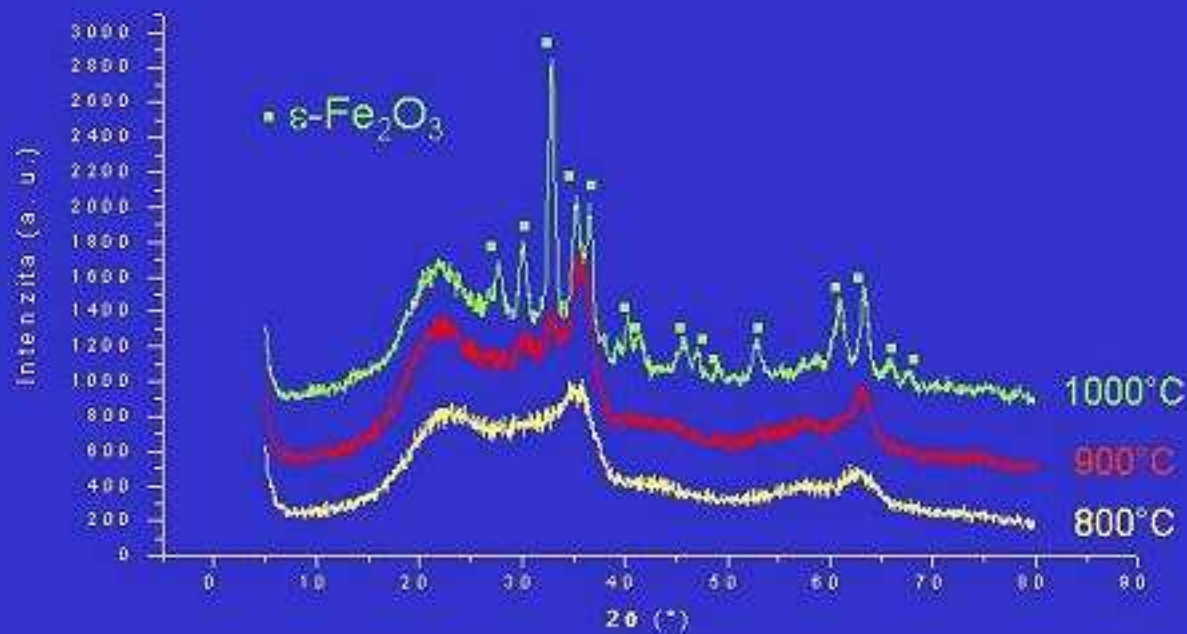
- Condition – Gelation of $[\text{FeL}^1]^+$
- Successful gelation without precipitation assure component distribution at atomic level



Preparation of nanocomposite

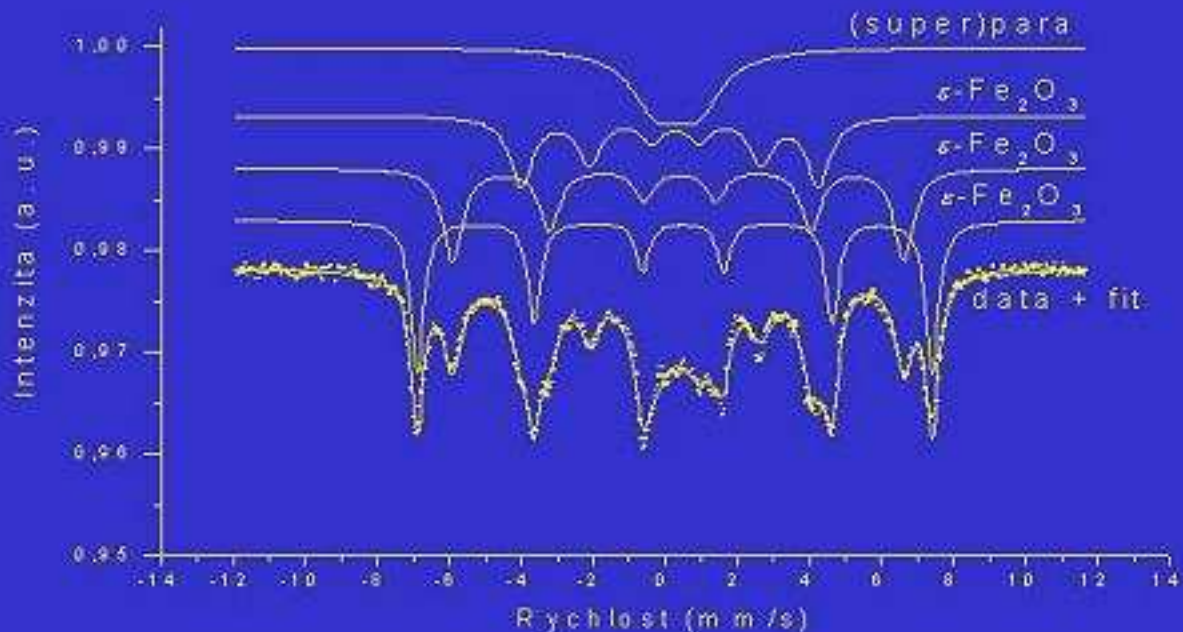
- Gelation
- Drying at controlled condition
- Heat treatment at
 - ▶ 800°C (1°C / min)
 - ▶ 900°C (1°C / min)
 - ▶ 1000°C (1°C / min)

XRD



Mössbauer spectroscopy

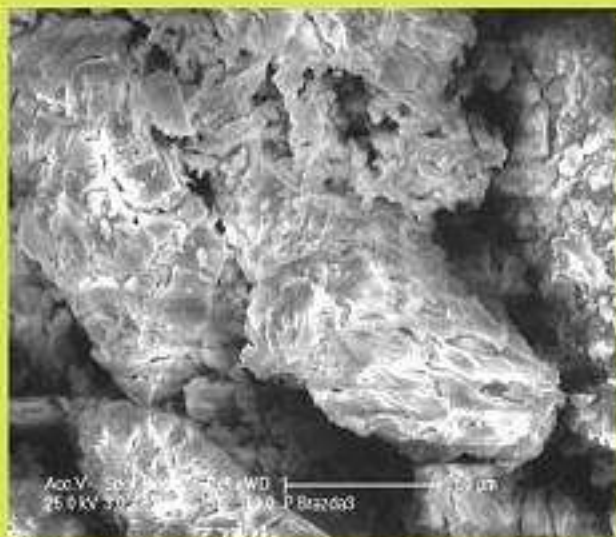
Sample heated at 1000°C



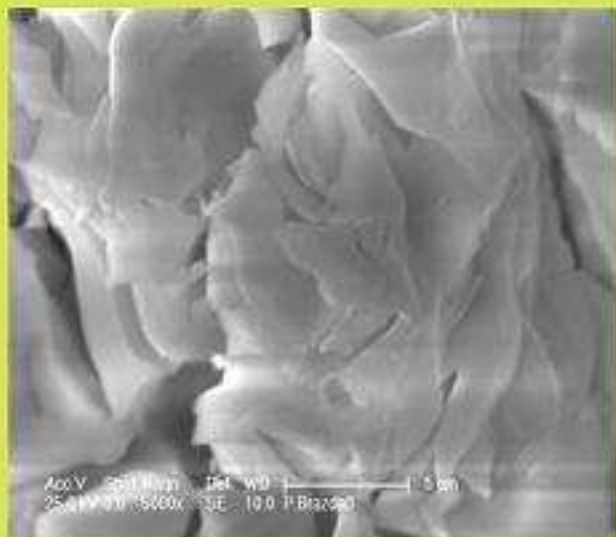
SEM

Sample heated at 1000°C

Magnification - 625x

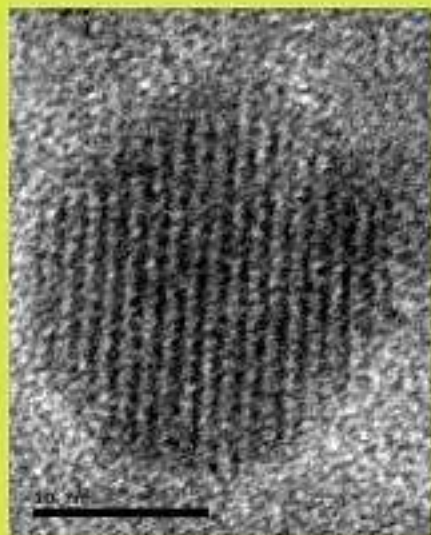
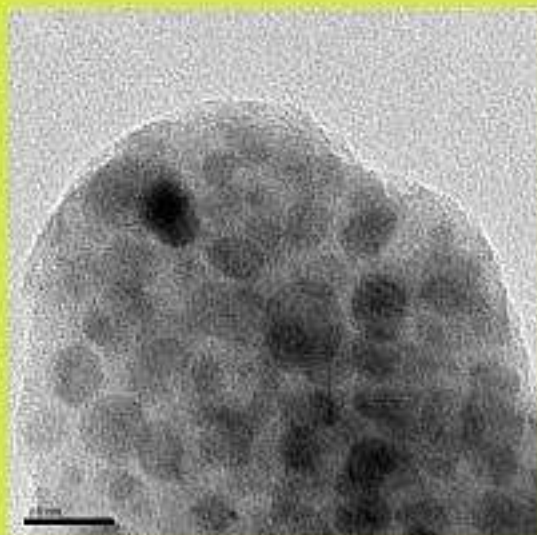


Magnification - 5000x

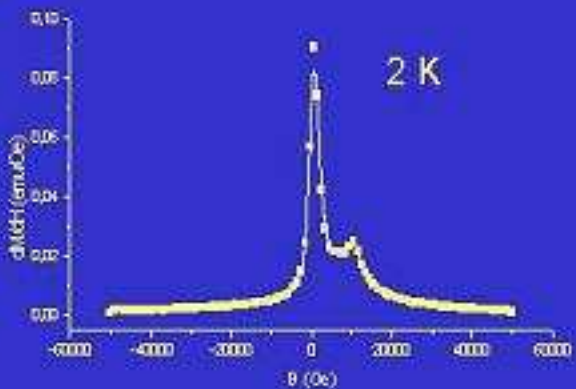
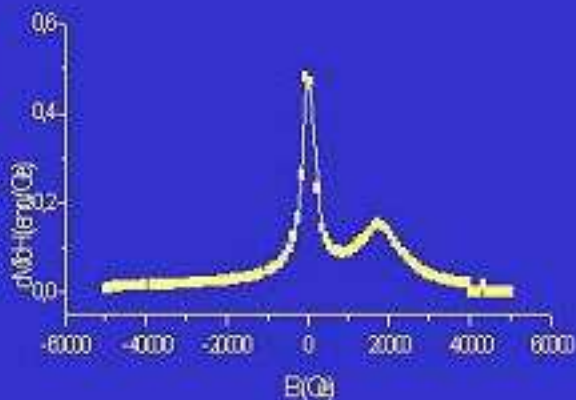
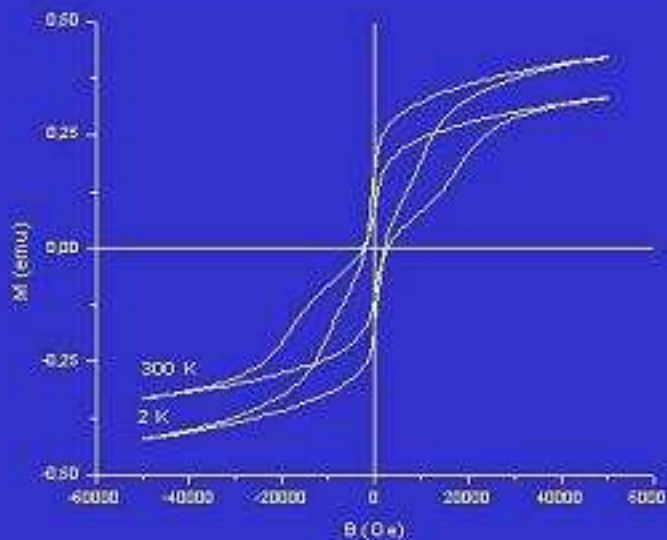


HR-TEM

Sample heated at 1000°C



Magnetic measurement



ACKNOWLEDGEMENT

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