Effect of reaction temperature on properties of iron(III) oxide nanoparticles prepared by solid-state route from iron(II) acetate

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The aim of the work

- Synthesis of magnetic nanoparticles Fe-O-based by thermally induced oxidative decomposition of iron(II) acetate through the possibility to control their magnetic properties and their size and size distribution by temperature of the synthesis

- Testing these magnetic nanoparticles in MRI as contrast agents

Methods of syntheses of maghemite

- many kinds of methods of syntheses which can control particle size and microstructure during their reaction

- But they are <u>expensive</u> ⟶

• gel-sol method
• microwave plasma method
• coprecipitation technique in combination with piezoelectric nozzle method
• laser pyrolysis
• electrochemical method
• aerosol technique

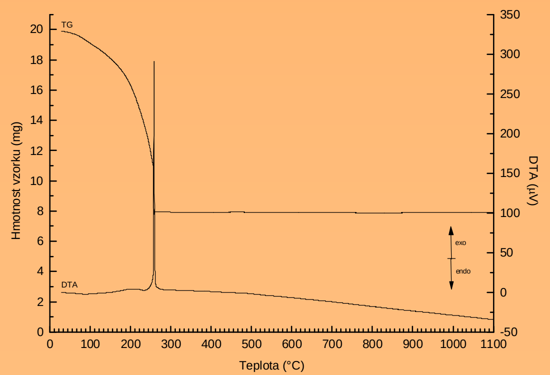
For syntheses of our samples we have used a THERMALLY-INDUCED SOLID-STATE REACTION

Simplicity of synthesis

High quantity and quality of the product

Our chosen organic precursor: Iron(II) acetate:

- firstly used
- simply decomposition process
- cheap organic material



← release and evaporation of organic compounds

DTA and TGcurve on air, increase of the temperature 5°C/min.

Materials and experimental techniques

Our precursor: Iron(II) acetate - $(CH_3COO)_2Fe$ (Sigma Aldrich)

Alwas - the same kind of a ceramic bowl

- **the same embankment of homogenized precursor: 1.2g, thin layer of sample**
- **the oven LM 312.27 (LINN HIGH THERM)**
- **syntheses in air in the temperature range of 245 – 400 °C for 2 or 1hour**

Materials and experimental techniques

- The transmission ^{57}Fe Mössbauer spectra

- Room temperature spectrometer in a constant acceleration mode with $^{57}Co(Rh)$ source
- Low temperature/external field Mössbauer spectrometer (1.5–300 K, 10 T)

- XRD - a Seifert-FPM diffractometer with CuKα radiation and conventional θ-2θ geometry

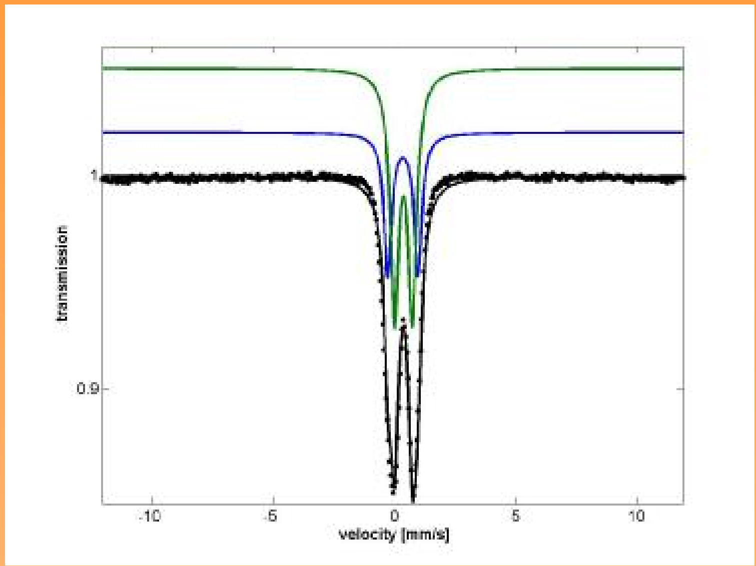
- BET - surface area analyzer, Sorptomatic 1990 (Thermofinnigan).

- TEM - JEM 2010 (JEOL)

- MRI - tomography by General Electric (1.5 T) Hospital Prostějov

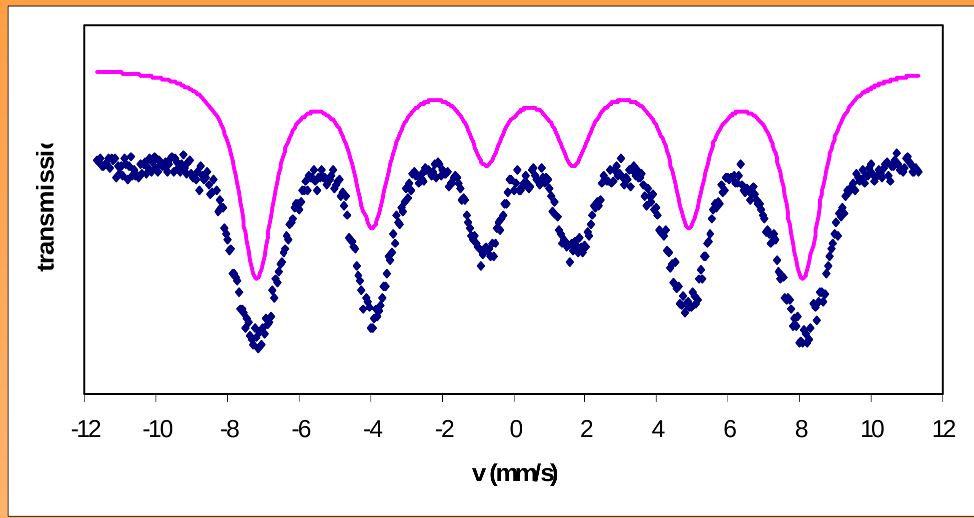
Results – temperature of synthesis 245 °C

- Time of the synthesis: 2 hours



RT MSspectrum of sample synthesized at 245°C for 2 hours

Low temperature (22K) Mössbauer spectrum in external field (5 T) of sample synthesized at 245 °C



doublet 1: – δ = 0.34 mm/s, ΔE_Q = 0.62 mm/s
doublet 2: – δ = 0.36 mm/s, ΔE_Q = 0.36 mm/s

→ presence of Fe^{3+}

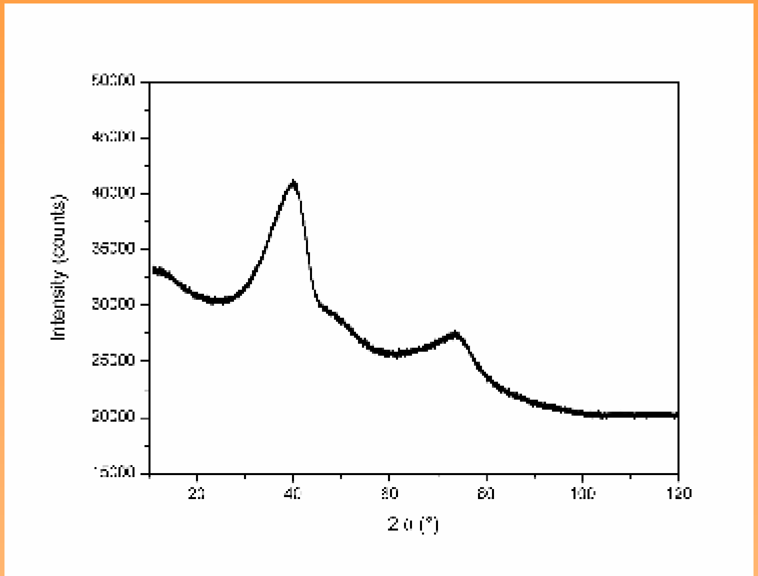
δ = 0.46mm/s
ΔE_Q = 0.01 mm/s
H = 47.5 T
Intensity ratio of lines is 3:2:1

→ **Amorphous iron oxide**

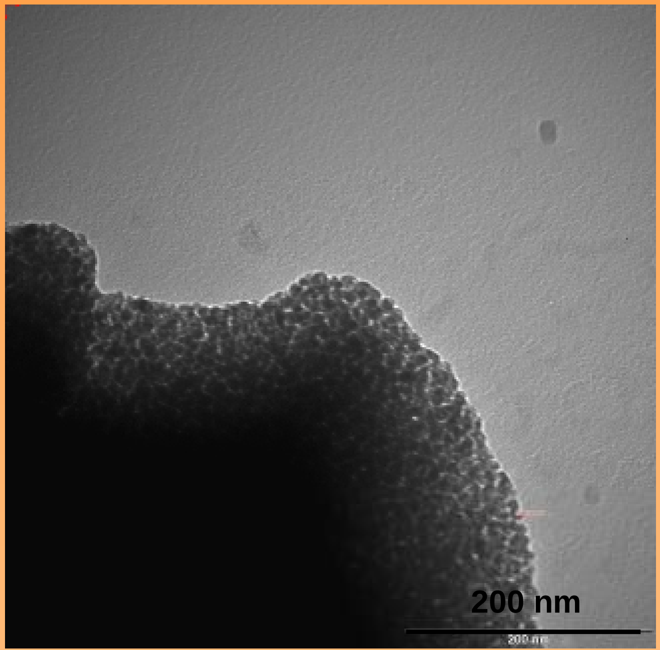
- no separation of subspectra
- high degree of surface magnetic anizotropy and spin canting

BET surface area measurement of amorpous iron oxide : 103 m^2/g

Results – temperature of synthesis 245 °C



XRD of the sample synthesized at 245 °C

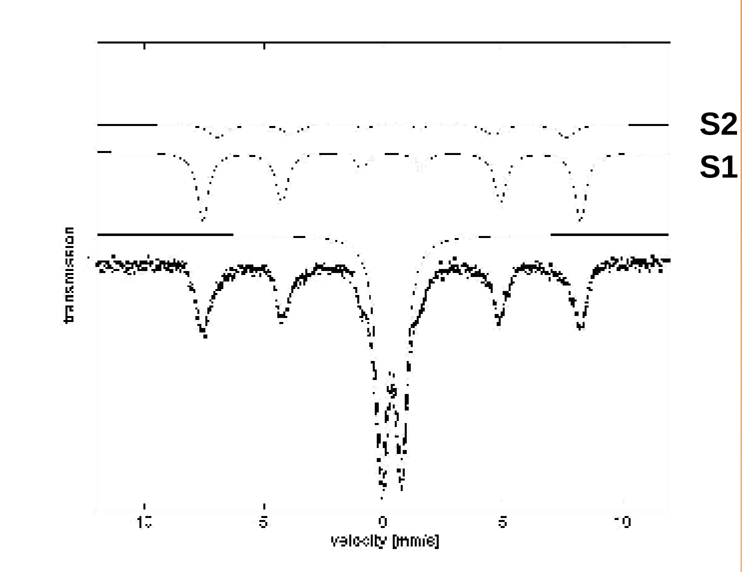


TEM of the sample synthesized at 245 °C

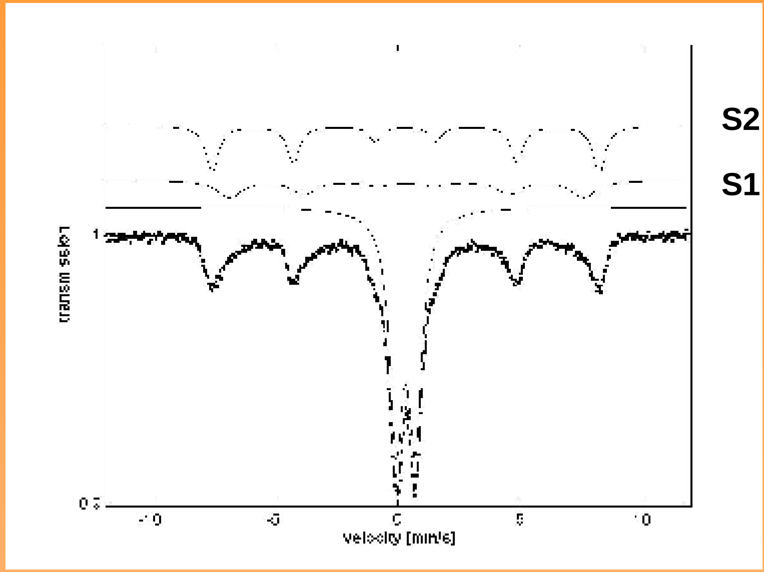
- Confirming of amorphous character

- Monodispesrse magnetic nanoparticles with size of 6 nm

Results – reaction temperatures (270-300) °C



Spectrum of maghemite synthesized at 270°C



Spectrum of maghemite synthesized at 300°C

doublet: – δ = 0.34 mm/s, ΔE_Q= 0.82 mm/s
sextet 1: – δ = 0.32 mm/s, ε_Q = 0.02 mm/s
sextet 2: – δ = 0.35 mm/s, ε_Q = 0 mm/s

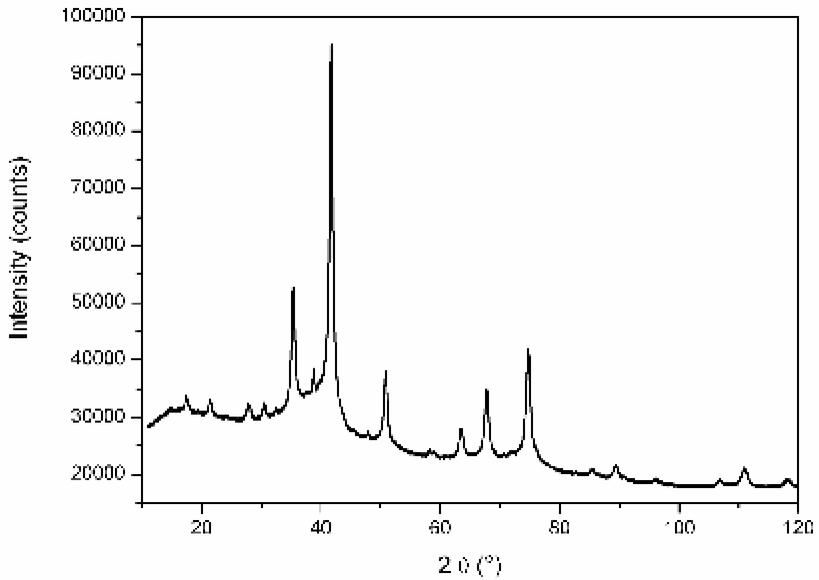
doublet: – δ = 0.32 mm/s, ΔE_Q= 0.78 mm/s
sextet 1: – δ = 0.34 mm/s, ε_Q = 0 mm/s
sextet 2 : – δ = 0.31 mm/s, ε_Q = 0 mm/s

- spectra are consist of maghemite(SP and ferrimagnetic) and amorphous phases of iron oxide

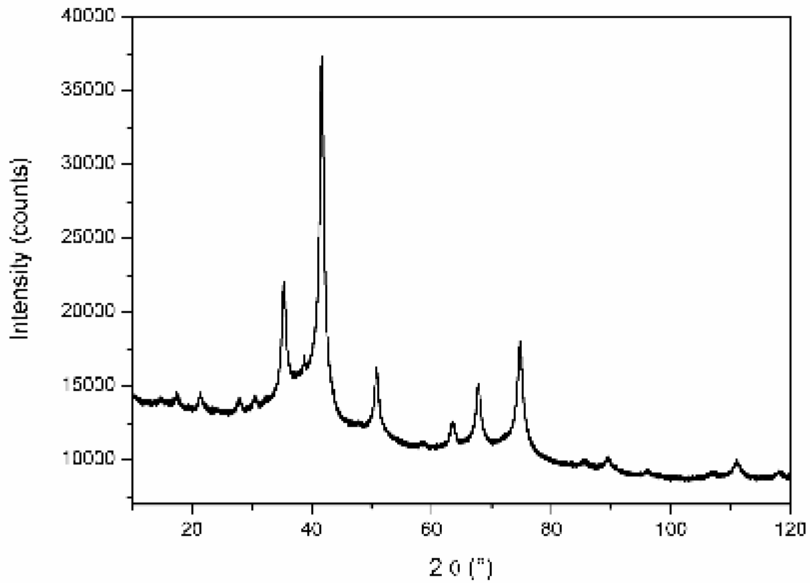
-primarily formed amorphous phase crystalizes to nanomaghemite while the superparamagnetic nanomaghemite stays in doublet

- two processes: crystallization of amorphous phase and formation of SP maghemite

Results – reaction temperature (270-300) °C



XRD of the sample synthesized at 270 °C



XRD of the sample synthesized at 300 °C

XRD patern is typical for maghemite structure

- narrower lines, more crystalline sample

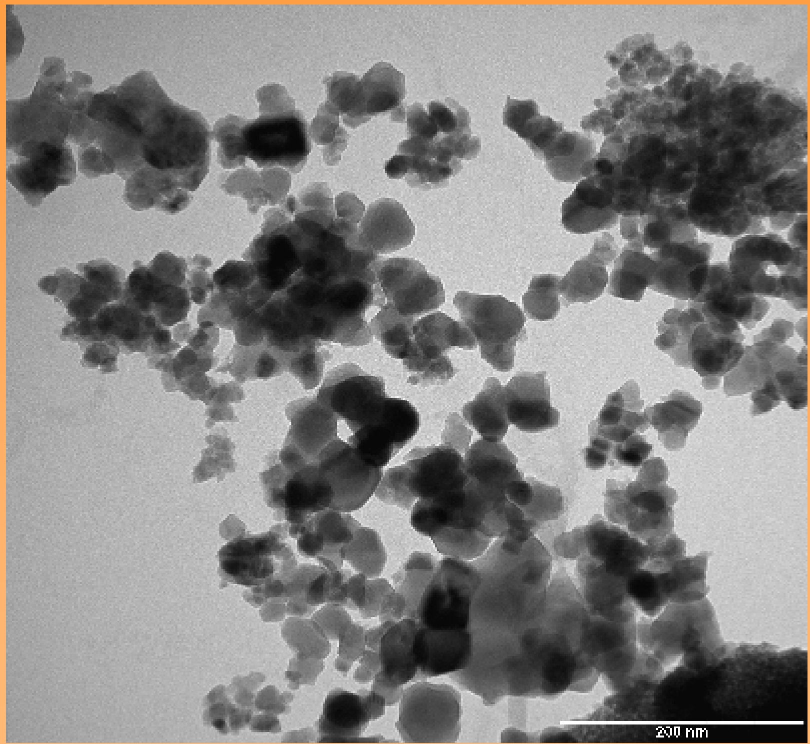
- wider size distribution broader lines

- BET : 110 m^2/g

- BET : 114 m^2/g

good agreement with RT MS

Results – reaction temperature (270-300) °C

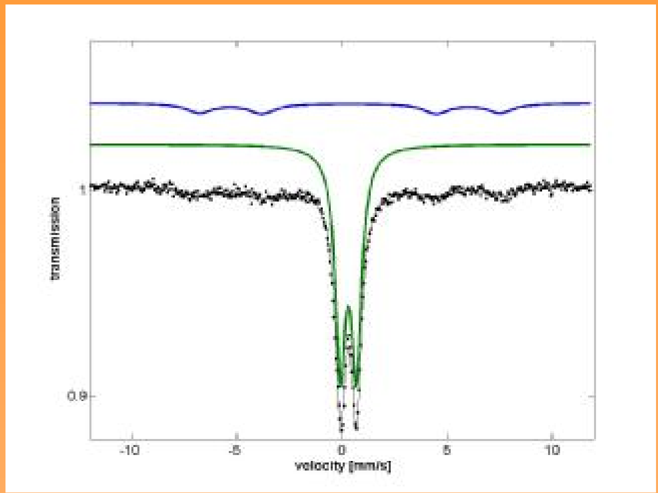


TEM of the sample synthesized at 270 °C

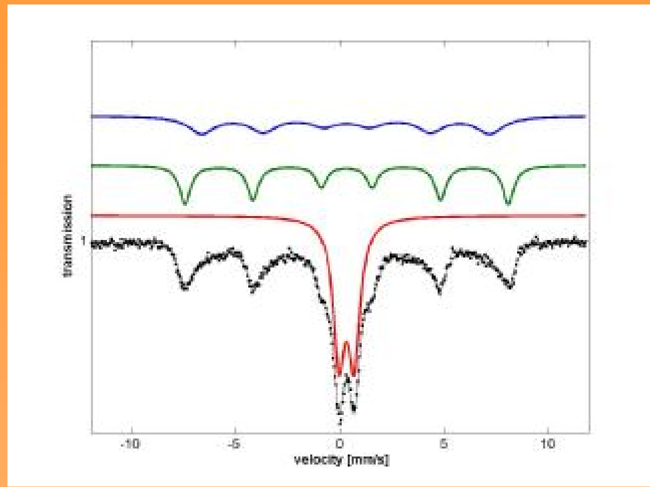
- polydisperse character
- amorphous phase (6nm) and polydispers crystalline particles

Results – reaction temperature (320–400) °C

RT MS spectra



Spectrum of maghemite synthesized at 320°C



Spectrum of maghemite synthesized at 360°C

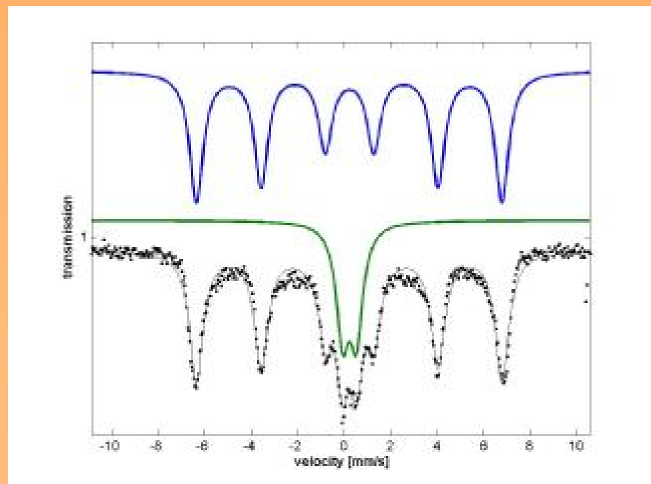
Doublet: δ= 0.32 mm/s
ΔE_Q= 0.73 mm/s

sextet(green):
δ= 0.31 mm/s, ε_Q = 0

sextet(blue):
δ= 0.30 mm/s, ε_Q = 0

-Superparamagnetic maghemite (coexistence of sextet and doublet)

doublet: – δ = 0.30 mm/s,ΔE_Q= 0.76 mm/s
sextet: – δ = 0.35 mm/s,ε_Q = 0 mm/s

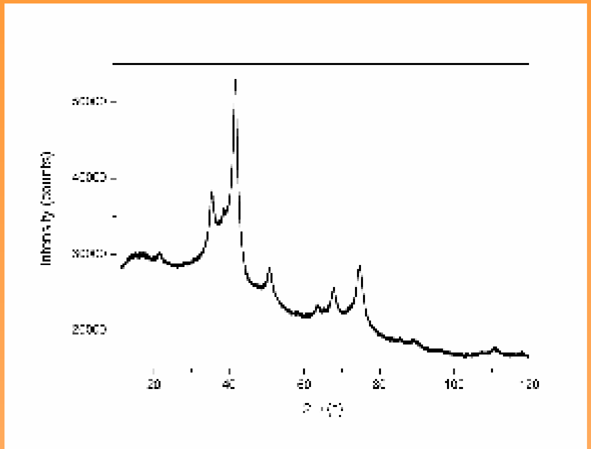


Spectrum of maghemite synthesized at 400°C

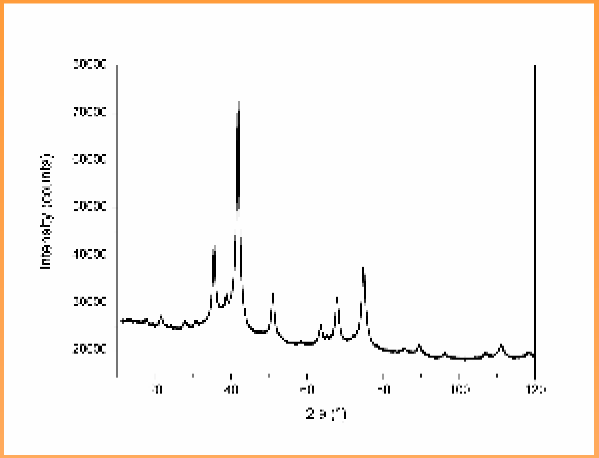
Doublet: δ= 0.35 mm/s
ΔE_Q= 0.64 mm/s

sextet(blue):
δ= 0.27 mm/s, ε_Q = 0

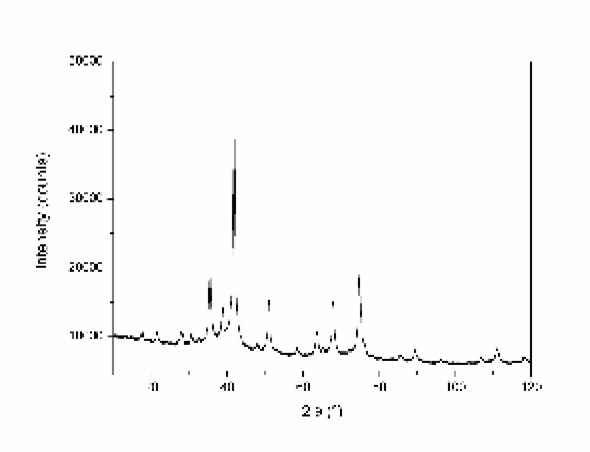
Results – reaction temperature (320-400) °C



XRD of the sample synthesized at 320 °C



XRD of the sample synthesized at 360 °C



XRD of the sample synthesized at 400 °C

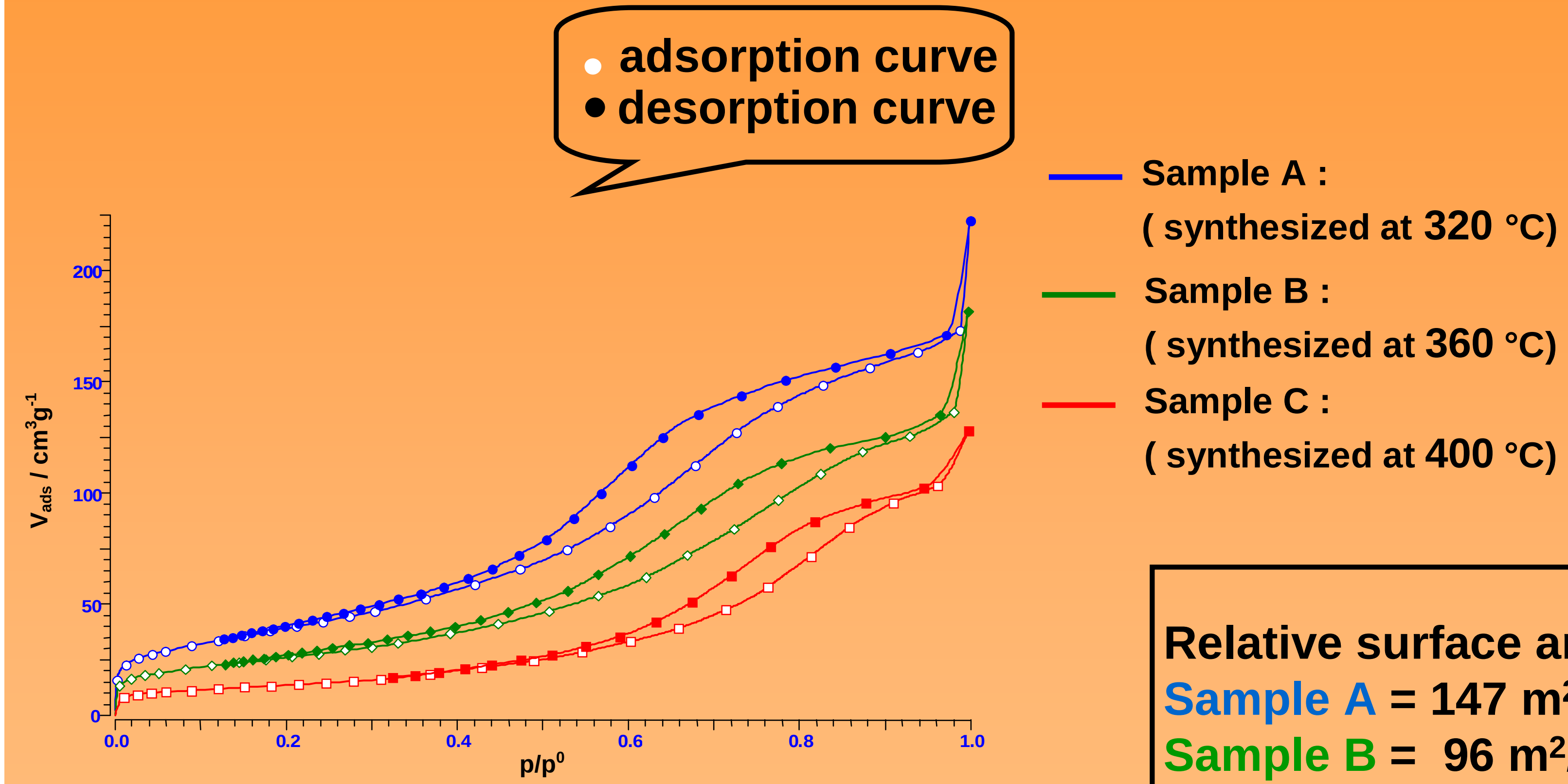
With increasing temperature of synthesis

↓

narrower diffraction lines ⟶ more crystalline maghemite ⟶ larger sizes of maghemite particles

Results – reaction temperature (320–400) °C

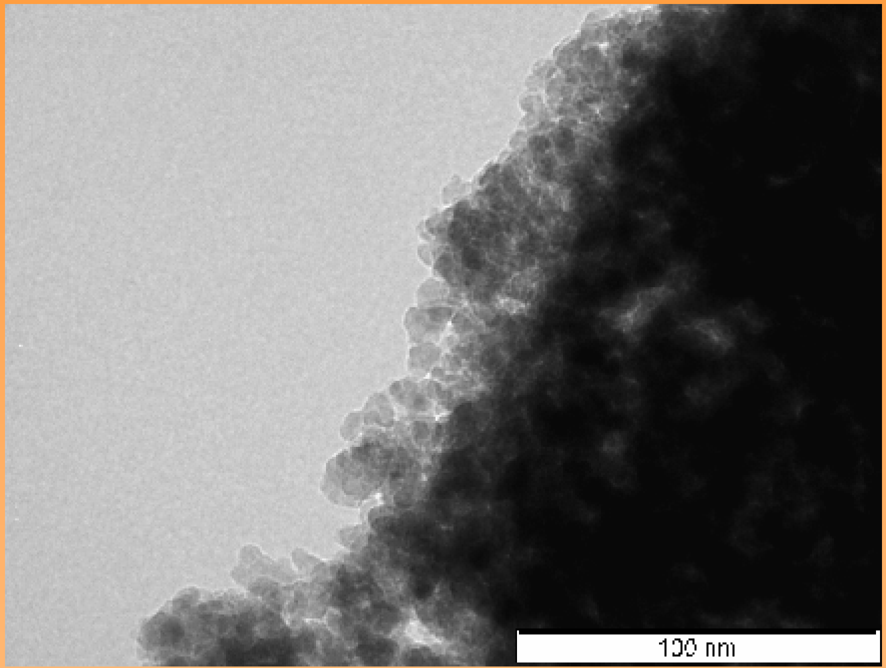
BET: specific surface area measurements



Nanopowders of maghemite with non-porous character

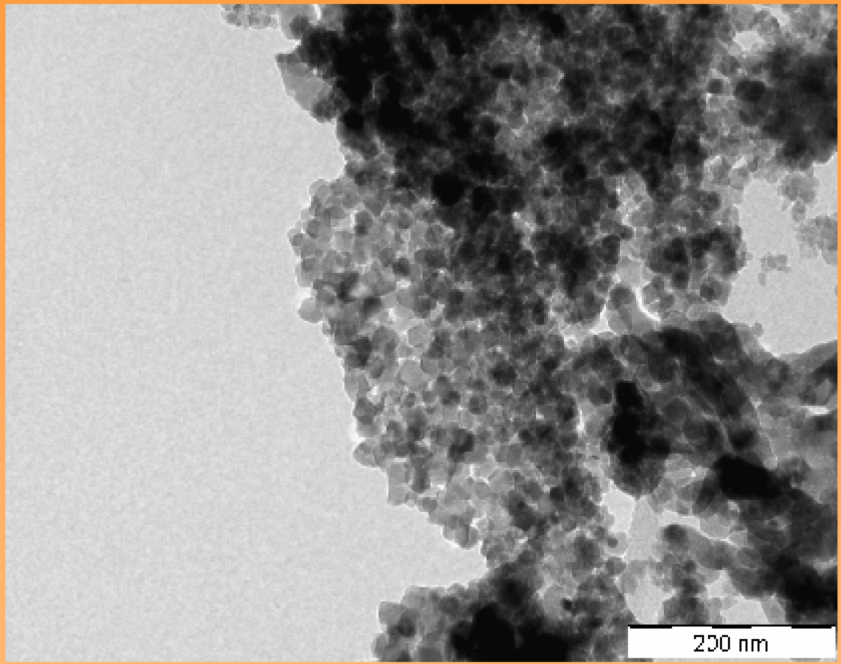
Relative surface areas :
Sample A = 147 m^2/g
Sample B = 96 m^2/g
Sample C = 51 m^2/g

Results – reaction temperature (320–400) °C



TEM of sample synthesized at 320 °C

- narrow size distribution
- size of nanoparticles 3-6 nm



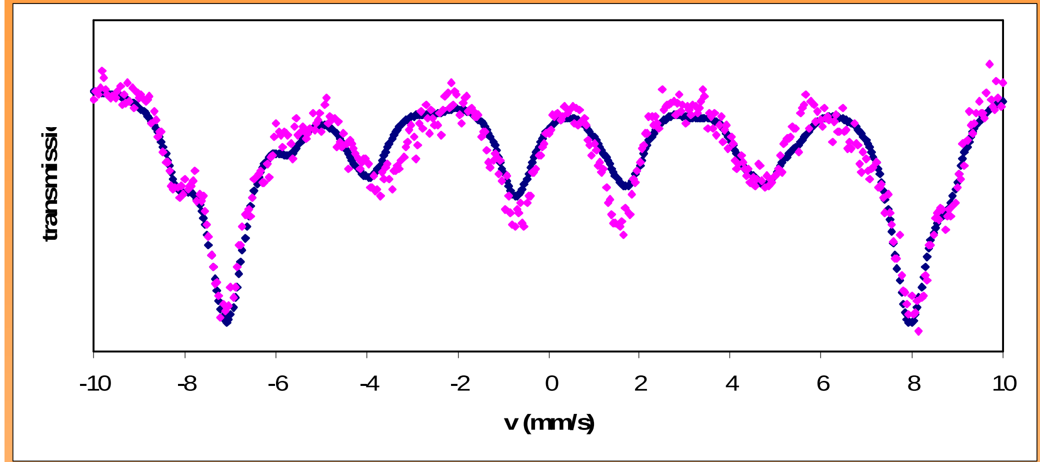
TEM of sample synthesized at 400 °C

- narrow size distribution
- size of nanoparticles 20 nm

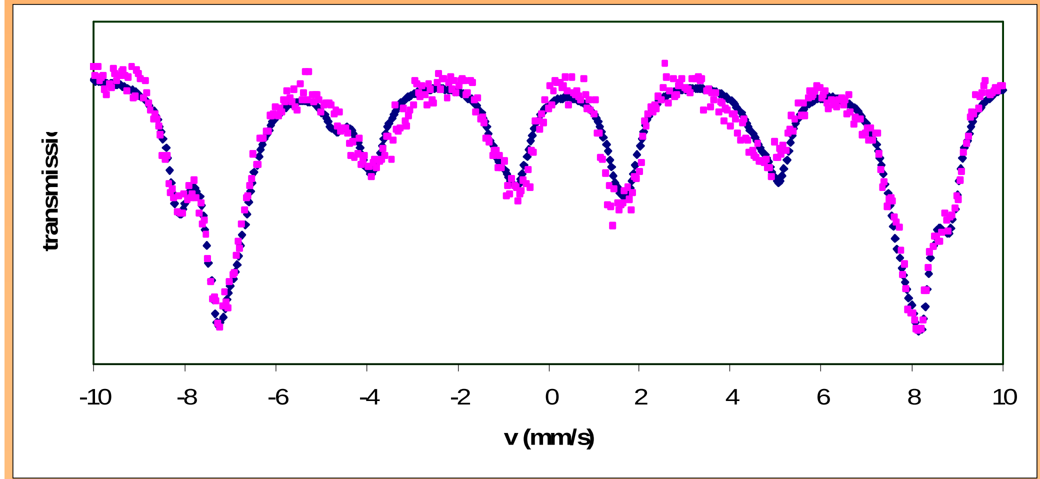
Results – LT MS in external field (50K, 5T)

- External field applied parallel to the direction of gamma-rays

Spectrum of maghemite synthesized at 270°C



Spectrum of maghemite synthesized at 360°C



Both spectra were fitted by 3sextets

Presence of amorphous phase (3:2:1)
Area fraction= 17 % ?

Splitting of octahedral and tetrahedral phase of maghemite, spin canting

Presence of amorphous phase
Area fraction = 6 % ?

Change of the intensity ratio 5:3 → redistribution of vacancies, nonstechiometric maghemite

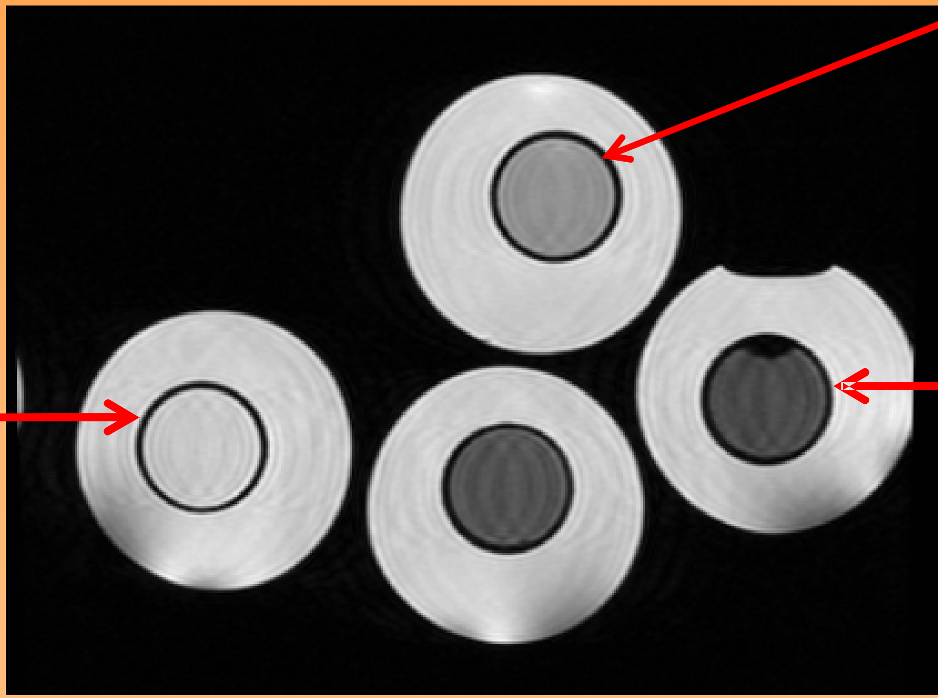
Nanoparticles of maghemite tested as contrast agents in MRI

- **All samples of maghemite were mixed with bentonite in water, then dried under vacuum**

- **The concentration of maghemite/bentonite compound in water was of 0.02 %**

Maghemite Synthesized at 270 °C

Blind sample-water



Maghemite Synthesized at 400 °C

- total relaxation time is given by the sum of Neel and Brown rotation

Conclusion

-First solid-state synthesis allowing the control of size and size distribution by the reaction temperature

- product of syntheses : pure maghemite in wide range of temperature of syntheses (320 – 400) °C

Iron(II) acetate → (245 °C) → Amorphous phase → (270-300 °C) → Crystallization of amorphous,forming of SP maghemite

Iron(II) acetate → (320 °C) → SP maghemite → (360-400 °C) → Crystallization of SP maghemite

- Symmetrical and spherical character of nanoparticles

- Excellent contrast effect in MRI