Synthesis and Phase Composition of Nanosized Particles in Iron-containing Silicate Glasses

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MFe_2O_4 nanosized particles, where M = Fe, Mn

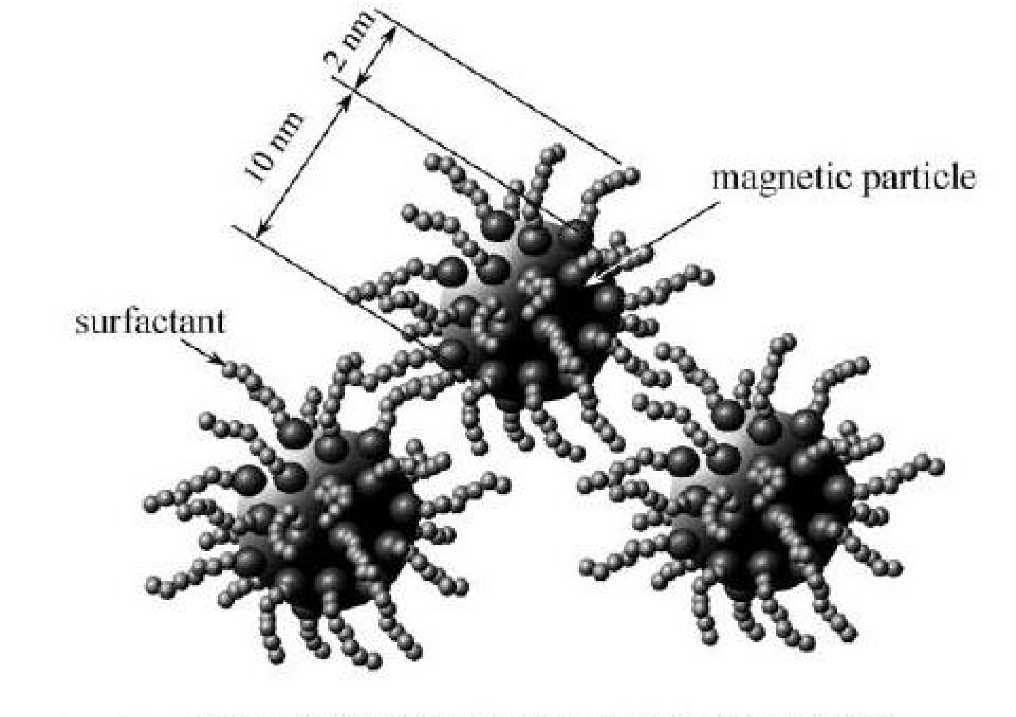
Shielding of electronic components

Biomedical applications

drug delivery systems

hyperthermia

contrast agents for magnetic resonance imaging



A schematic view of the coated magnetic particles in a ferrofluid.

Polymer-coated nanosized superparamagnetic crystals, S. Odenbach, J. Phys.: Cond. Matt. 16 (2004) 1135.

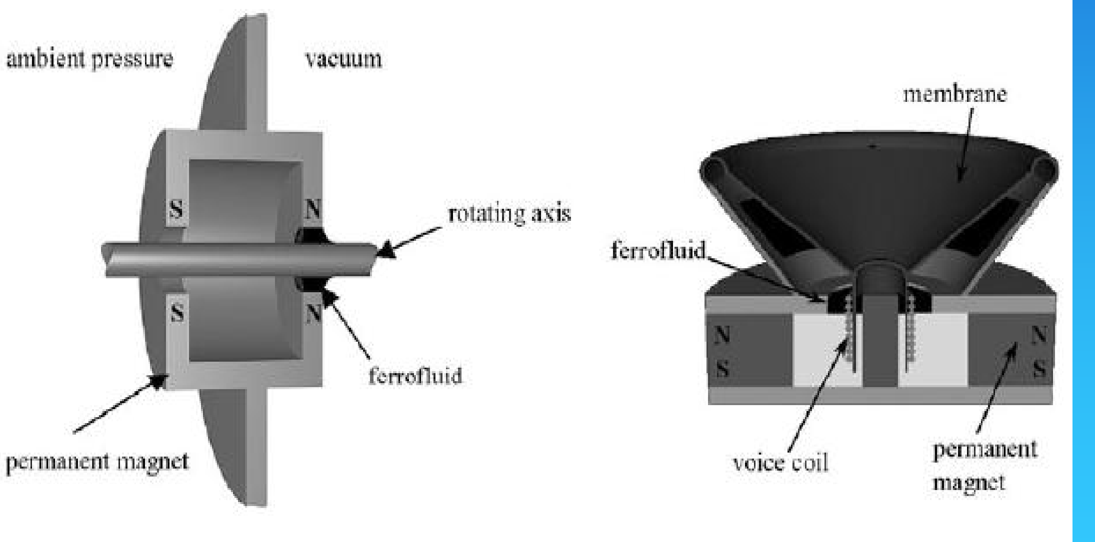
***MFe$_2$O$_4$* nanosized particles, where M = Fe, Mn**

Technique

cooling of different systems

part of inks

sealings and solder materials



A schematic view of two important technical applications of ferrofluids: on the left-hand side the sealing of a rotary shaft and on the right-hand side the cooling of loudspeakers.

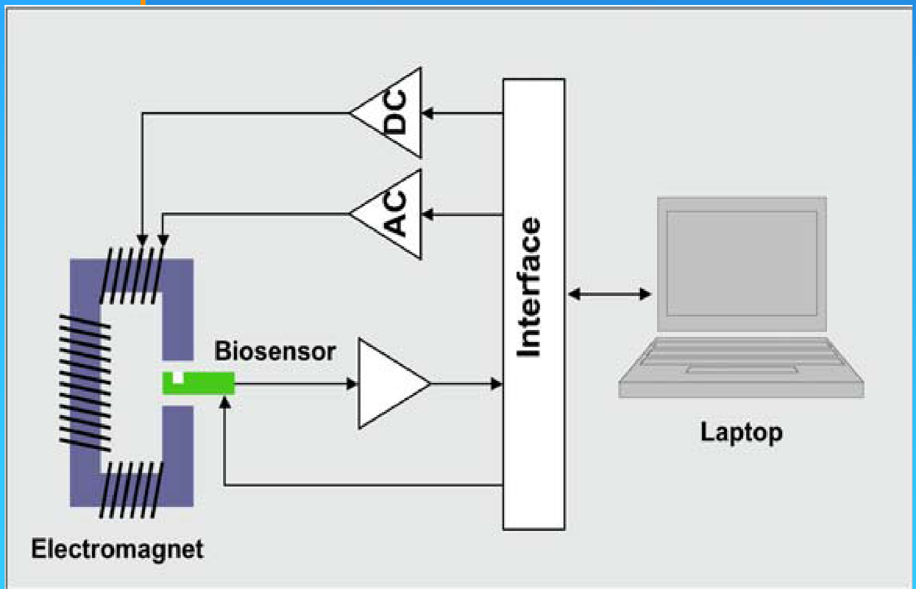
Application of nanosized crystals as parts of ferrofluids in rheology, S. Odenbach, J. Phys.: Cond. Matt. 16 (2004) 1135.

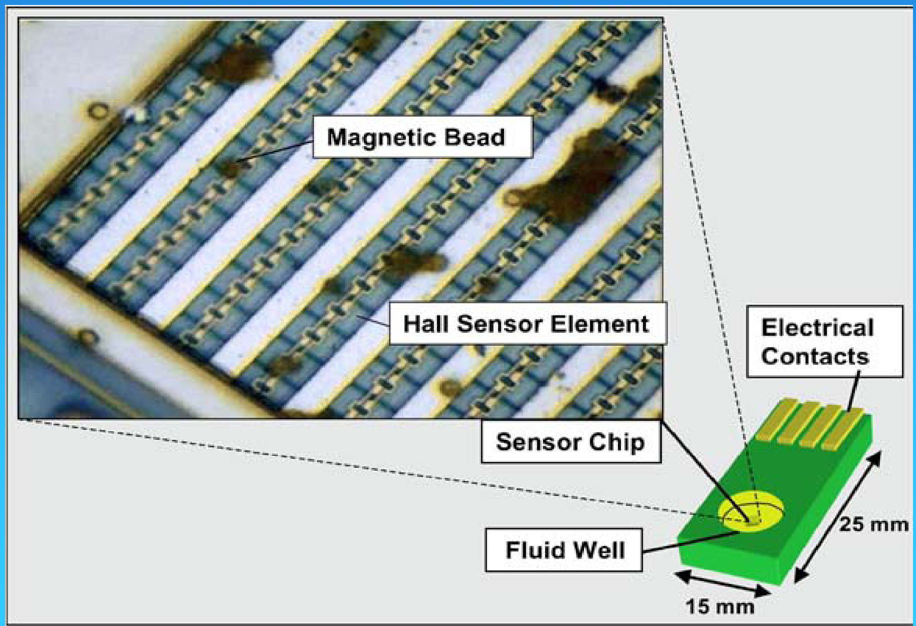
MFe_2O_4 nanosized particles, where M = Fe, Mn

Sensor technology

biochemical sensors for detection of different biological and chemical species

biosensors for diagnosis of infectious diseases.





Scheme of reader with interface between sensor chip and computer, T. Aytur et al. / Journal of Immunological Methods 314 (2006) 21.

Aims of the Work:

- ✓ Investigation of the glass formation in the system $Na_2O/SiO_2/MnO/Fe_2O_3$.
- ✓ Synthesis of glasses and nanosized superparamagnetic glass-ceramics in the studied system.
- ✓ Establishment of the influence of chemical composition on the phase composition and the microstructure of the obtained glass-ceramics.
- ✓ Characterization of the phase composition of the precipitated nanocrystals.
- ✓ Magnetic measurements on precipitated nanocrystals.

Investigated system and synthesis conditions

- **Investigated system**

$$(1\text{-}x)(16Na_2O/10MnO/74SiO_2)/xFe_2O_3$$
$$\text{for } x = 0.05 \div 0.30$$

- **Raw materials:** Na_2CO_3; $MnCO_3$; SiO_2; Fe_2O_3 or FeC_2O_4

- **Synthesis conditions:** SiO_2 crucible, $MoSi_2$ furnace, 1400–1450°C, 0.5–2.5 h, quenching between Cu blocks, annealing at 480°C for 10 min after pouring in a pre-heated C mould.

- **Crystallisation** by applying different temperature/time regimes in order to precipitate nano-sized ferrimagnetic crystals.

Characterization methods

- **Phase composition and microstructure**

- X-ray diffraction analysis;
- SEM/TEM analysis.

- **Additional phase composition investigation**

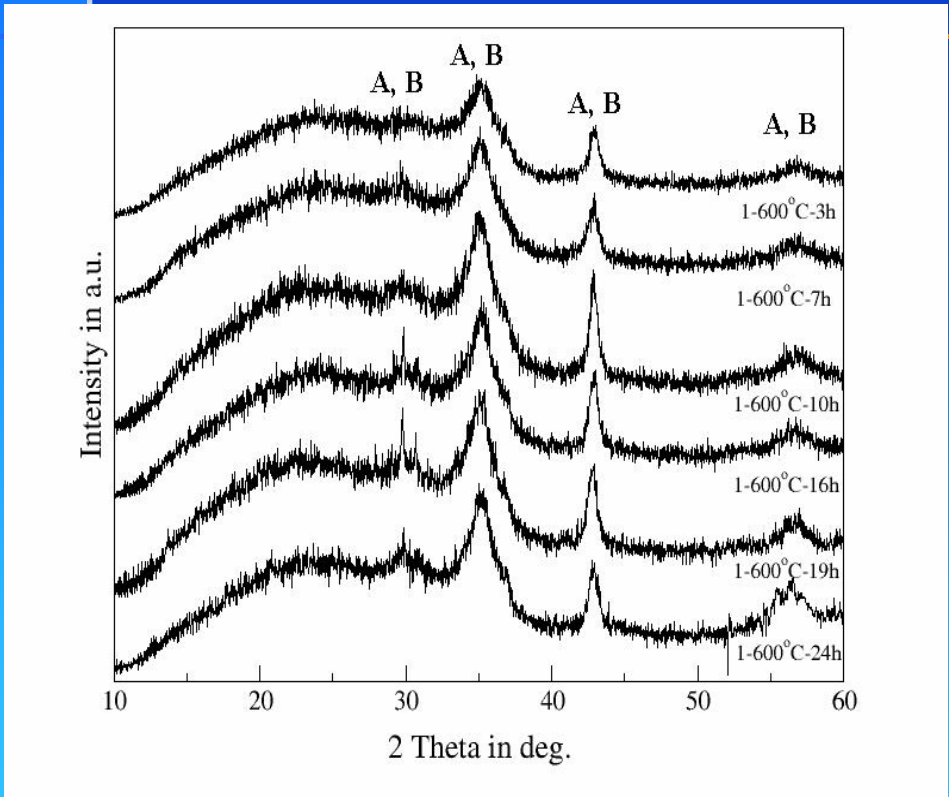
- Anomalous small angle x-ray scattering (ASAXS).

- **Magnetometry**

- Vibration magnetometer

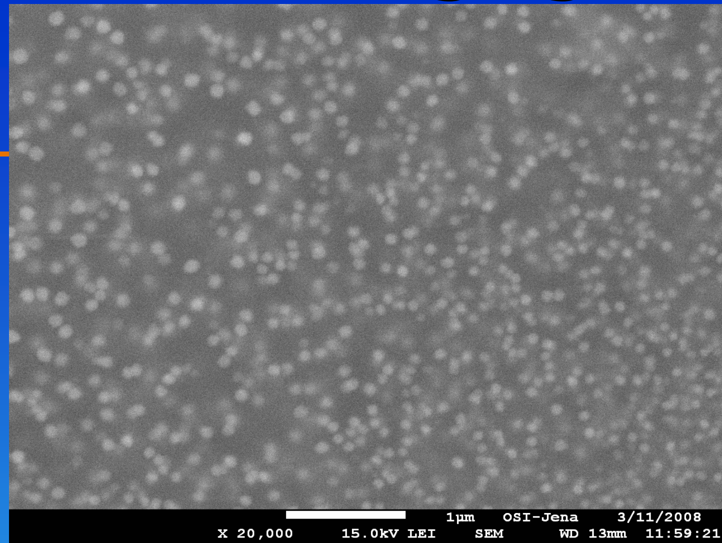
Results: phase composition and microstructure

– X-ray diffraction

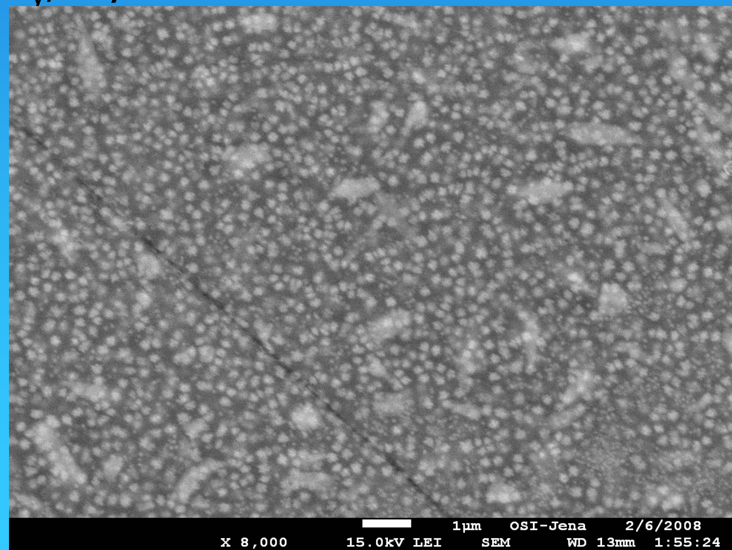


XRD patterns of reduced samples **$13{,}6Na_2O/8{,}5MnO/62{,}9SiO_2/15{,}0Fe_2O_{3-y}$**, heat-treated at 600°C for different time: formation of mixed crystals **$MnFe_2O_4$ (A)** and **Fe_3O_4 (B)**.

– SEM imaging

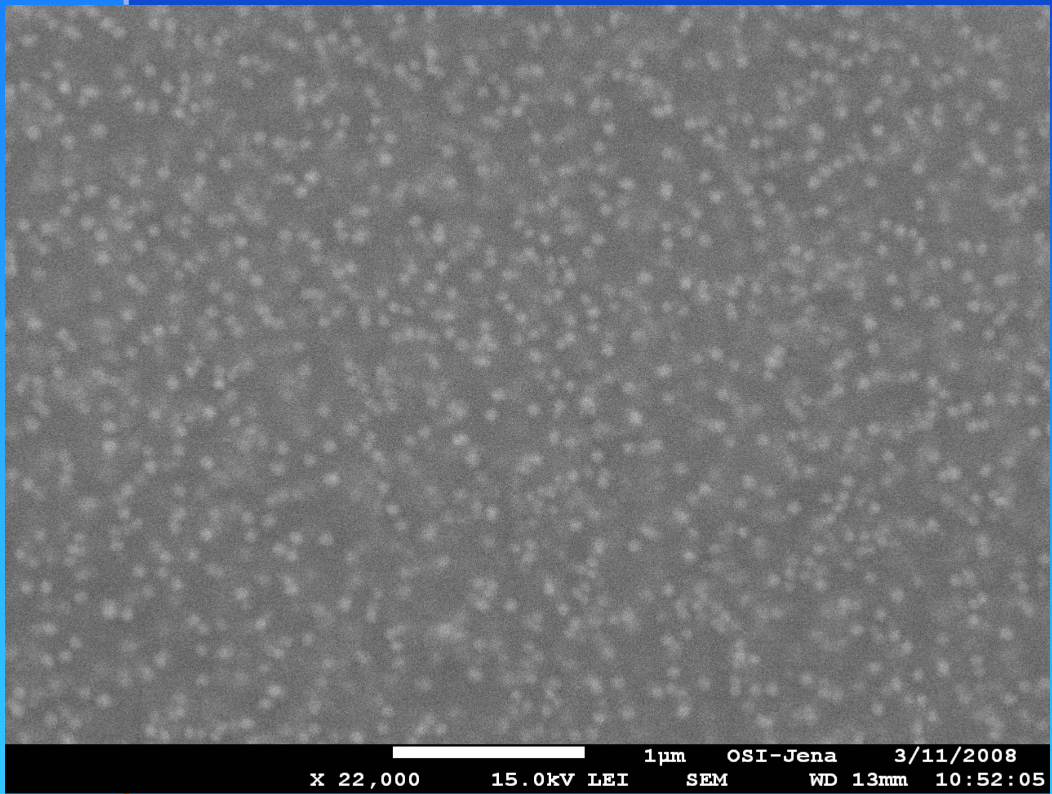


SEM (SE) image of C-covered sample with 15 mol% Fe_2O_{3-y}, crystallized for 10 h at 550°C.

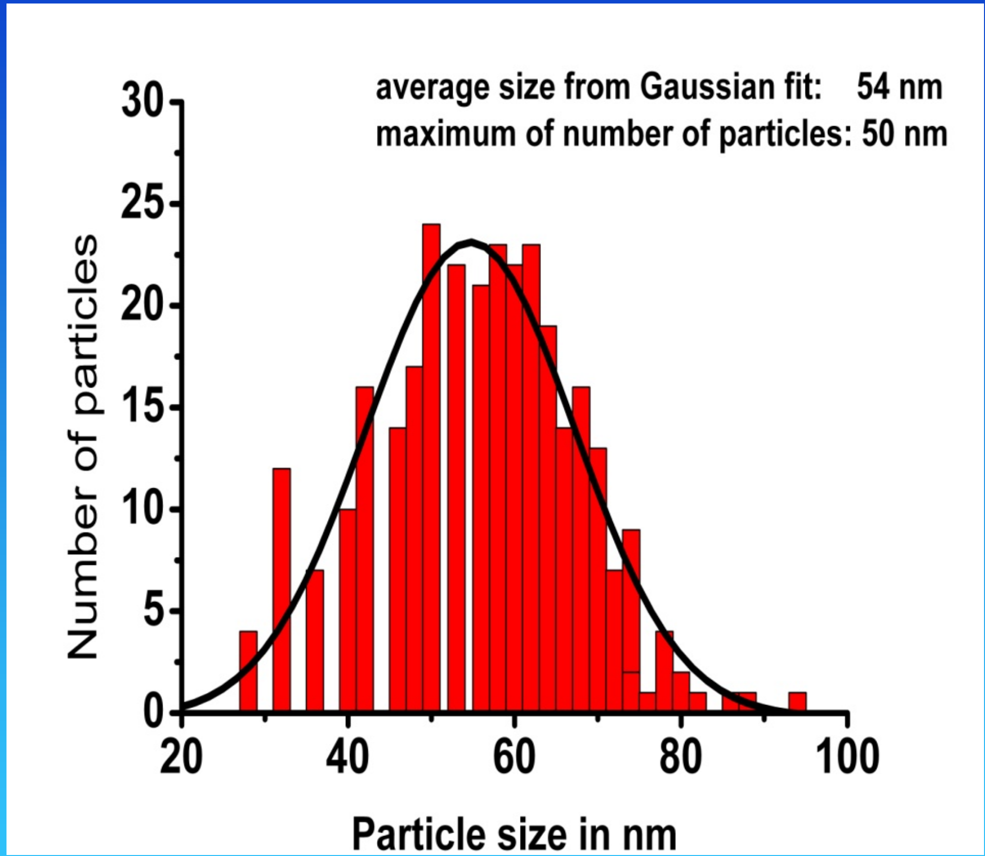


SEM (SE) image of C-covered sample with 15 mol% Fe_2O_{3-y}, annealed for 24 h at 600°C.

Results: microstructure and average particle size



SEM (SE) image of C-covered sample with 15 mol% Fe_2O_{3-y} and 8,5 mol% MnO, annealed for 3h at 550°C.



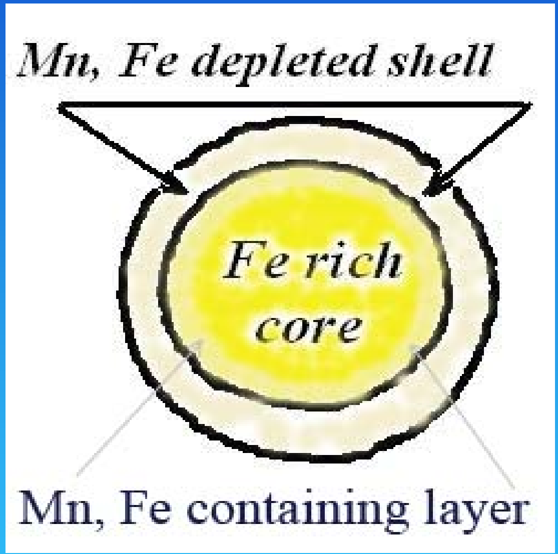
Particle size distribution for a sample annealed at 550° for 3 h.

Results: ASAXS – elemental composition and average particle size

1) SAXS on samples annealed for 40 min for 3 h at 550°C showed formation of nanocrystals with sizes from 14 to 44 nm, respectively.

6) From ASAXS data: the formation of both Fe and Mn enriched nanoparticles leads to formation around them of a Fe, Mn depleted viscous shell.

2) ASAXS effect is observed near the absorption edges of both Fe and Mn.



5) ASAXS data also suggests**:**

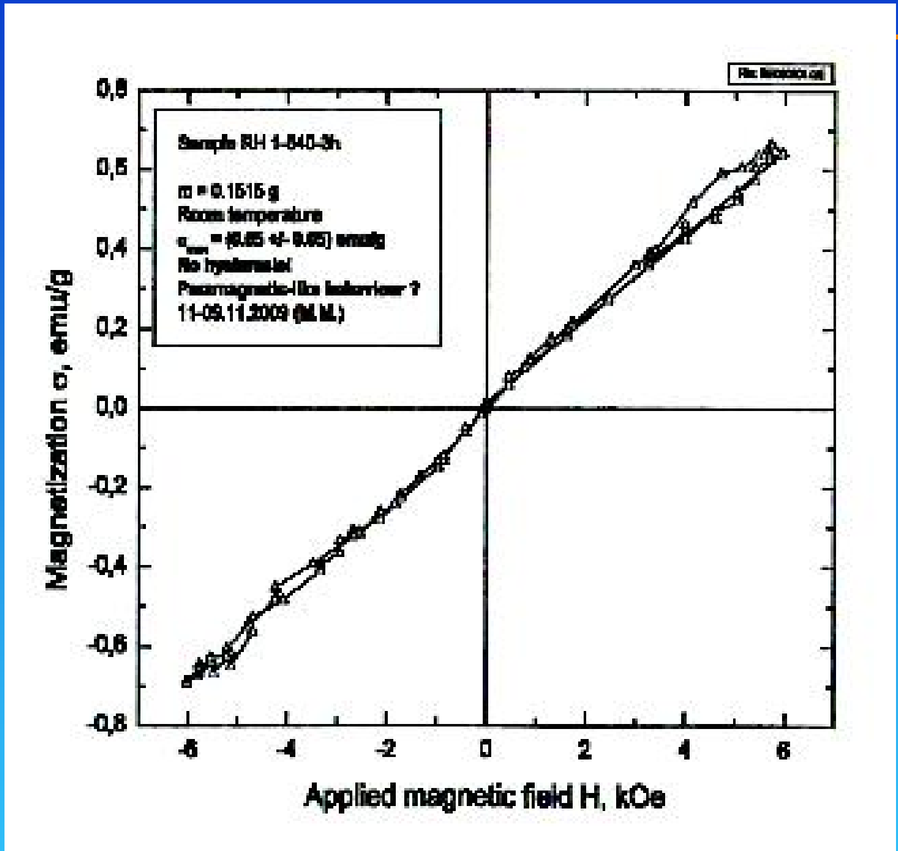
rising concentration of Mn in the vicinity of the growing Fe-rich core causes heterogenous nucleation and growth of Mn,Fe-containg spinel layer.

3) ASAXS data curves interpretaion suggests formation of nearly shperical core-shell particles, containing Fe, Mn and O.

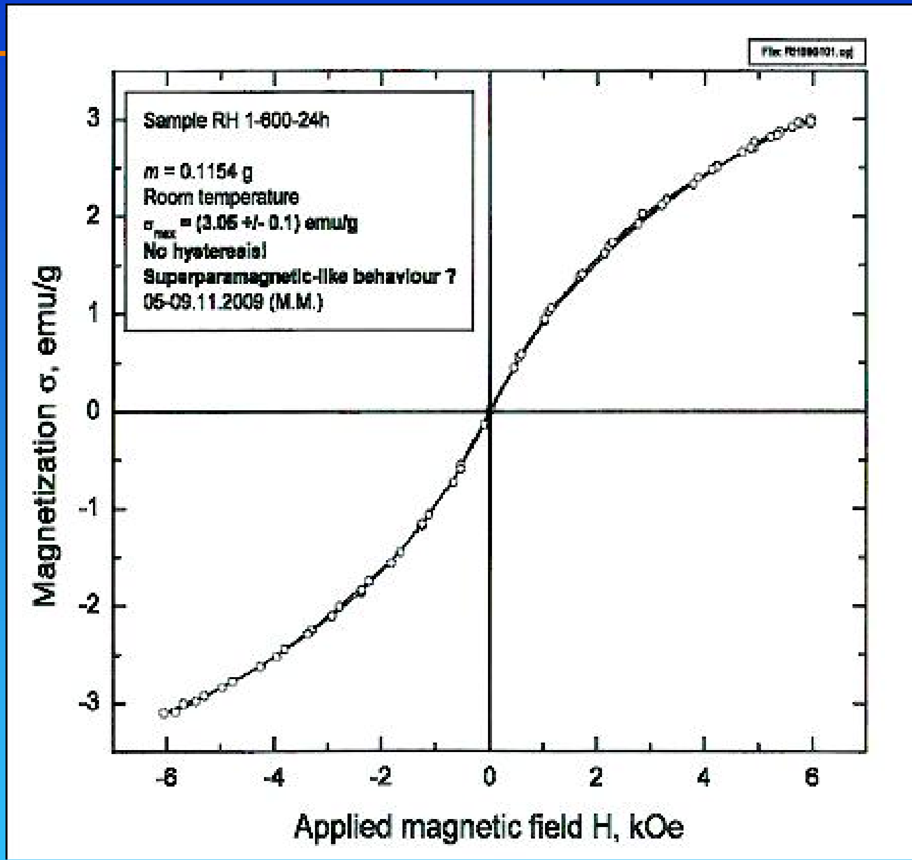
4) ASAXS predicts:

Initially formation of a Fe-rich homogenously nucleating and further growing spinel phase core.

Results: magnetic measurements



Magnetization vs. external magnetic field for a sample with 15 mol% Fe_2O_{3-y}, annealed at 540°C for 3 h.



Magnetization vs. external magnetic field for a sample with 15 mol% Fe_2O_{3-y}, annealed at 600°C for 24 h.

Summary of the results

- Nanosized spinel phase of the type $(Mn, Fe)^{II}(Fe,Mn)^{III}{}_2O_4$ is precipitated in the investigated compositions up to 600°C.

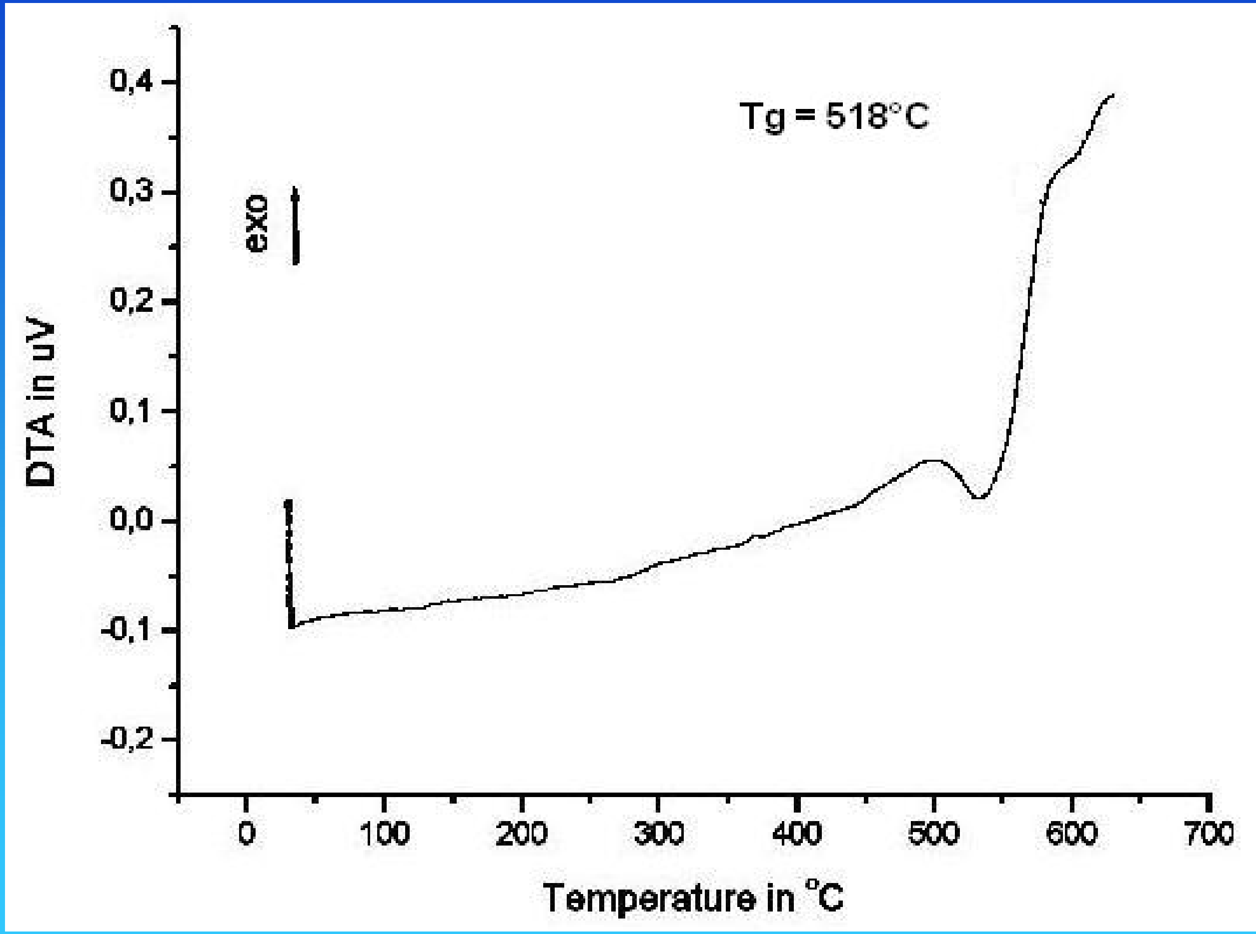
- For crystallization time over 3 h, for all temperatures, the average size of the formed nanocrystals is about 50 nm and hardly changes with time. The precipitation of the spinel nanosized phase is kinetically constrained.

- The chemical composition of the obtained nanoparticles as studied by ASAXS shows formation of Fe-Mn-O-based core-shell structures in which the core is enriched in Fe and the shell is depleted in both Fe and Mn.

- The magnetic properties of the precipitated nanocrystals vary from paramagnetic to superparamagnetic, depending on the applied time-temperature annealing programs.

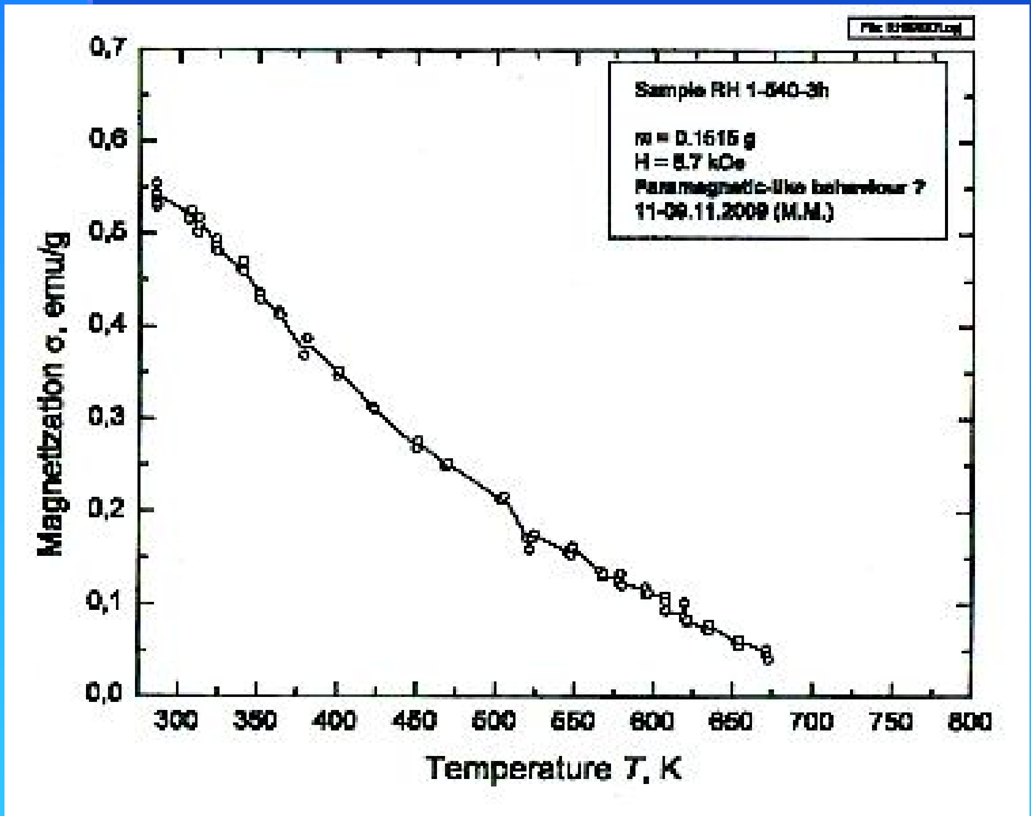
Thank you for your attention!

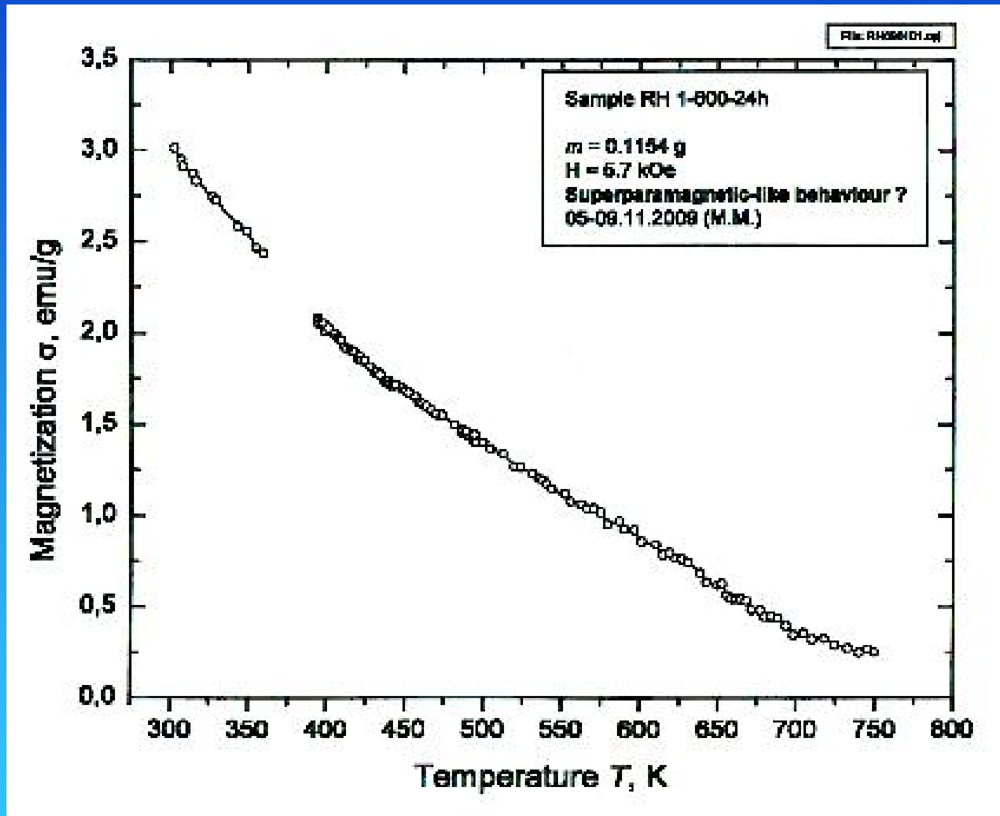
DSC Results



Tg = 518°C
exo
DTA in uV
0,4
0,3
0,2
0,1
0,0
-0,1
-0,2
0
100
200
300
400
500
600
700
Temperature in °C

Magnetization versus Temperature

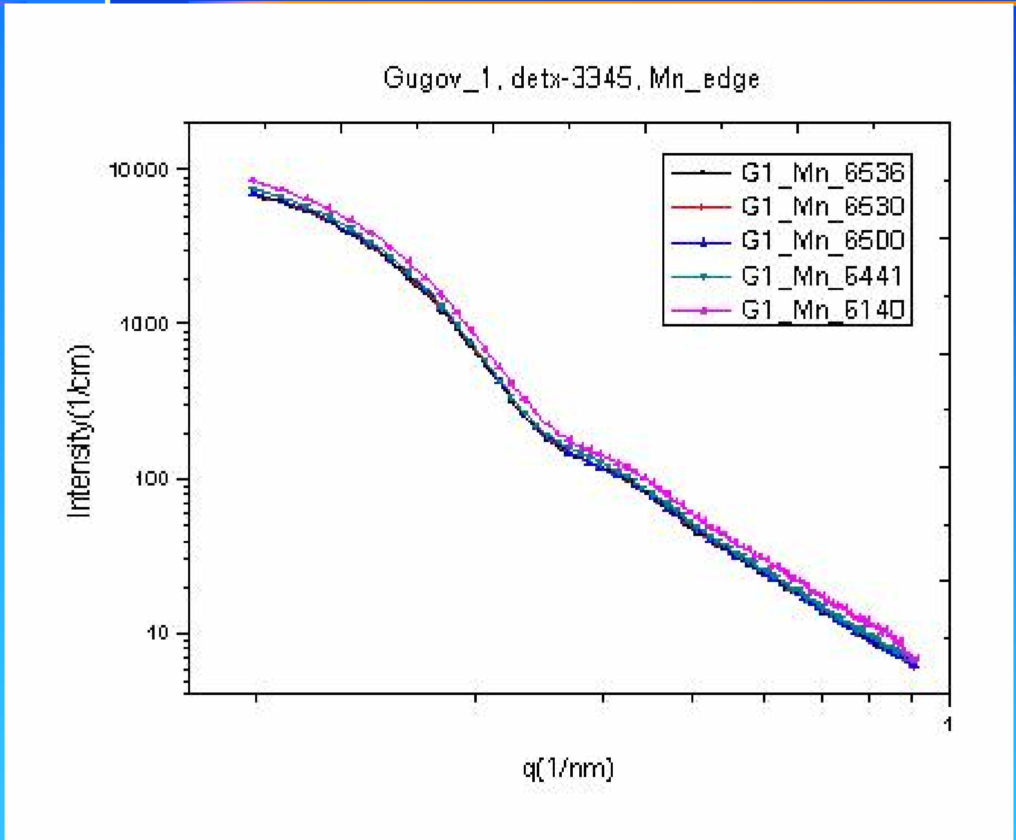


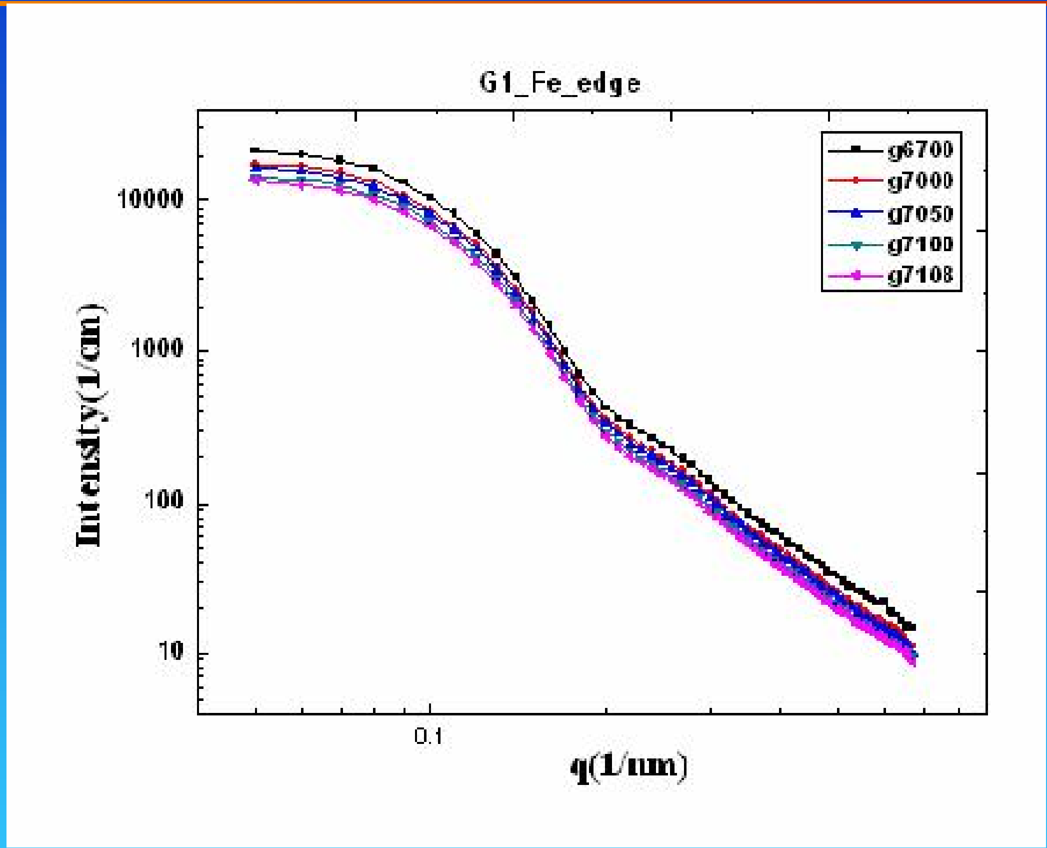


Sample 540C/3h

Sample 600C/24h

ASAXS curves





ASAXS effect at the Mn-absorption edge

ASAXS effect at the Fe-absorption edge