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International Conference on Green Technologies and Environmental Protection
26 - 29 May 2011, Sofia, Bulgaria

Institute of Catalysis, Bulgarian Academy of Sciences

STUDY OF NANOSIZED FERRITE MATERIALS PREPARED BY CO-PRECIPITATION METHOD

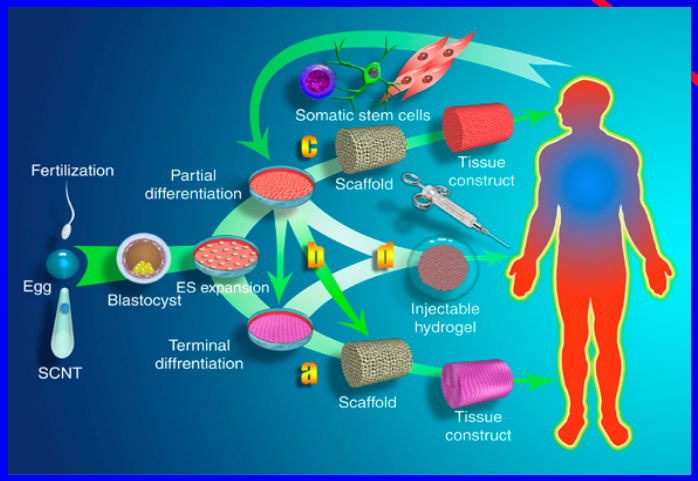
Z. Cherkezova-Zheleva

- ✓ Why it is important to study ferrite nanomaterials
- ✓ Experimental part of the presented study
- ✓ Results and discussion
- ✓ Some conclusions

The study of ferrites is of great importance

Ferrites

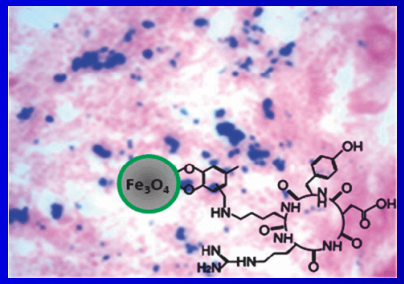
- magnetic materials
- electronics
- catalysts
- ceramic materials
- biomaterials for medical diagnostics and therapy

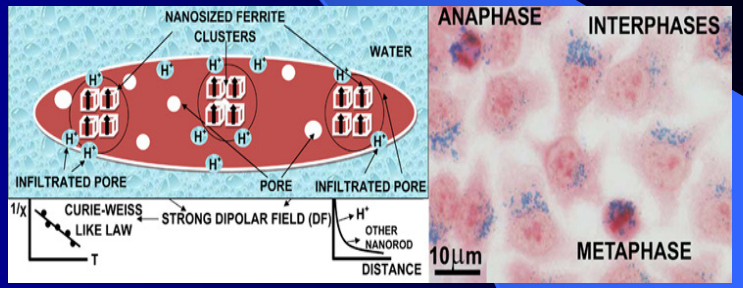


The study of ferrites is of great importance

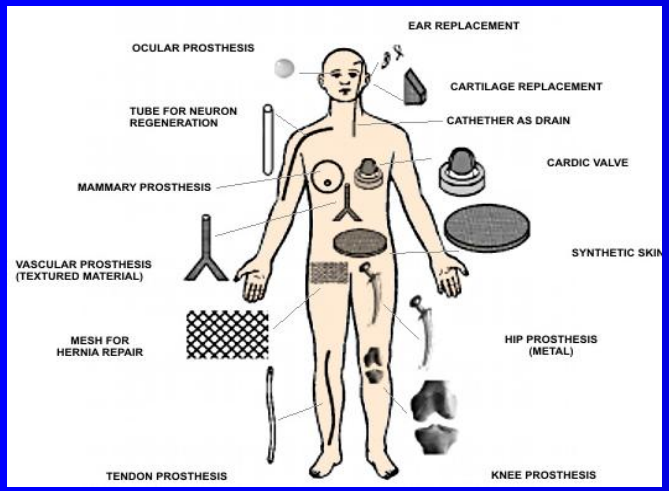
Ferrites - biomaterials

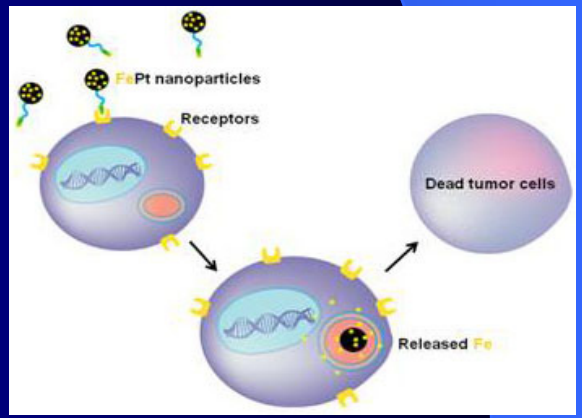
for medical diagnostics as contrast agents



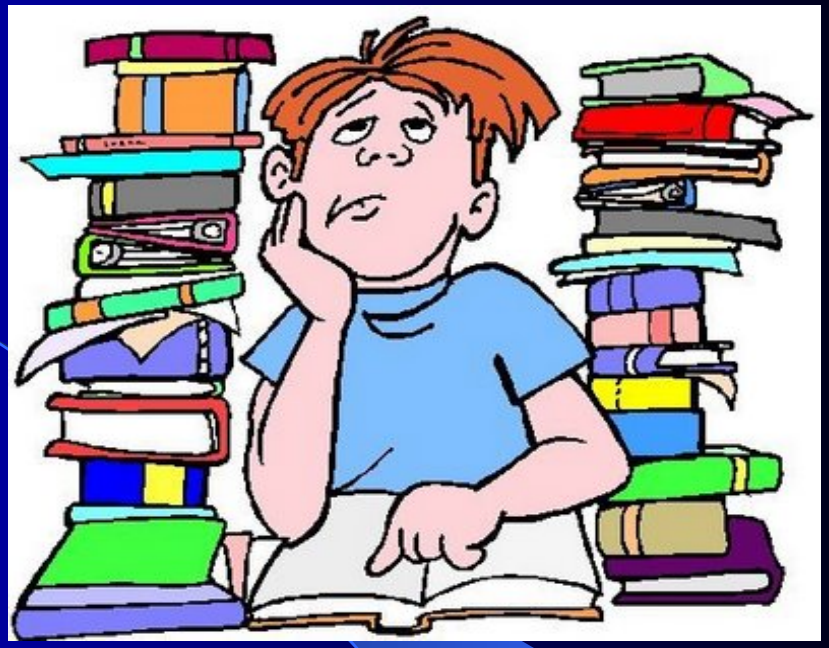


for therapy



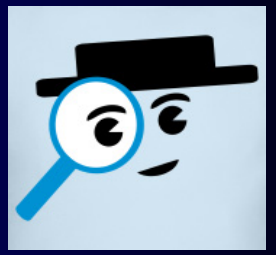


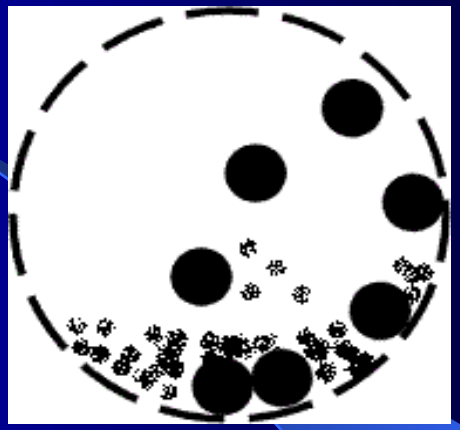
How to obtain better performance of ferrite material ?



- Ferrite preparation – object of huge number of studies, but not well resolved problem ;
- Change of chemical composition ;
- Change of particle size – down to nano-scale.

Methods of nano-ferrites preparation





1、High-energy grinding;

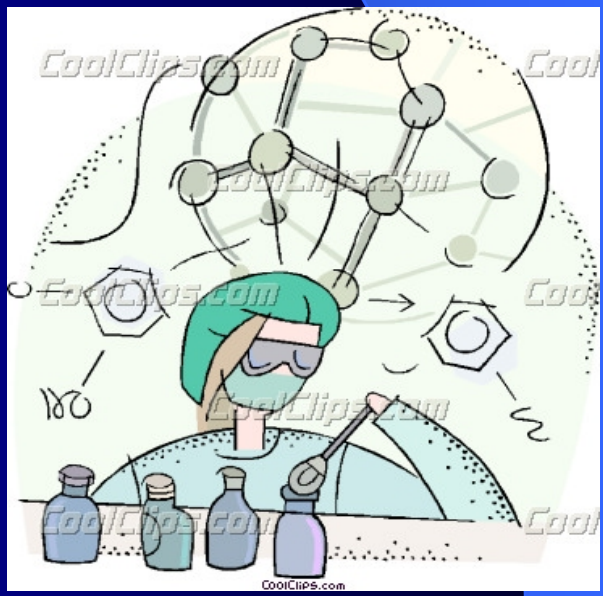
2、Wet chemical processes – co-precipitation, sol-gel, hydrothermal preparation;

3、Plasma flame pyrolysis, electrical exposion, laser ablation, high-temperature evaporation, plasma synthesis techniques

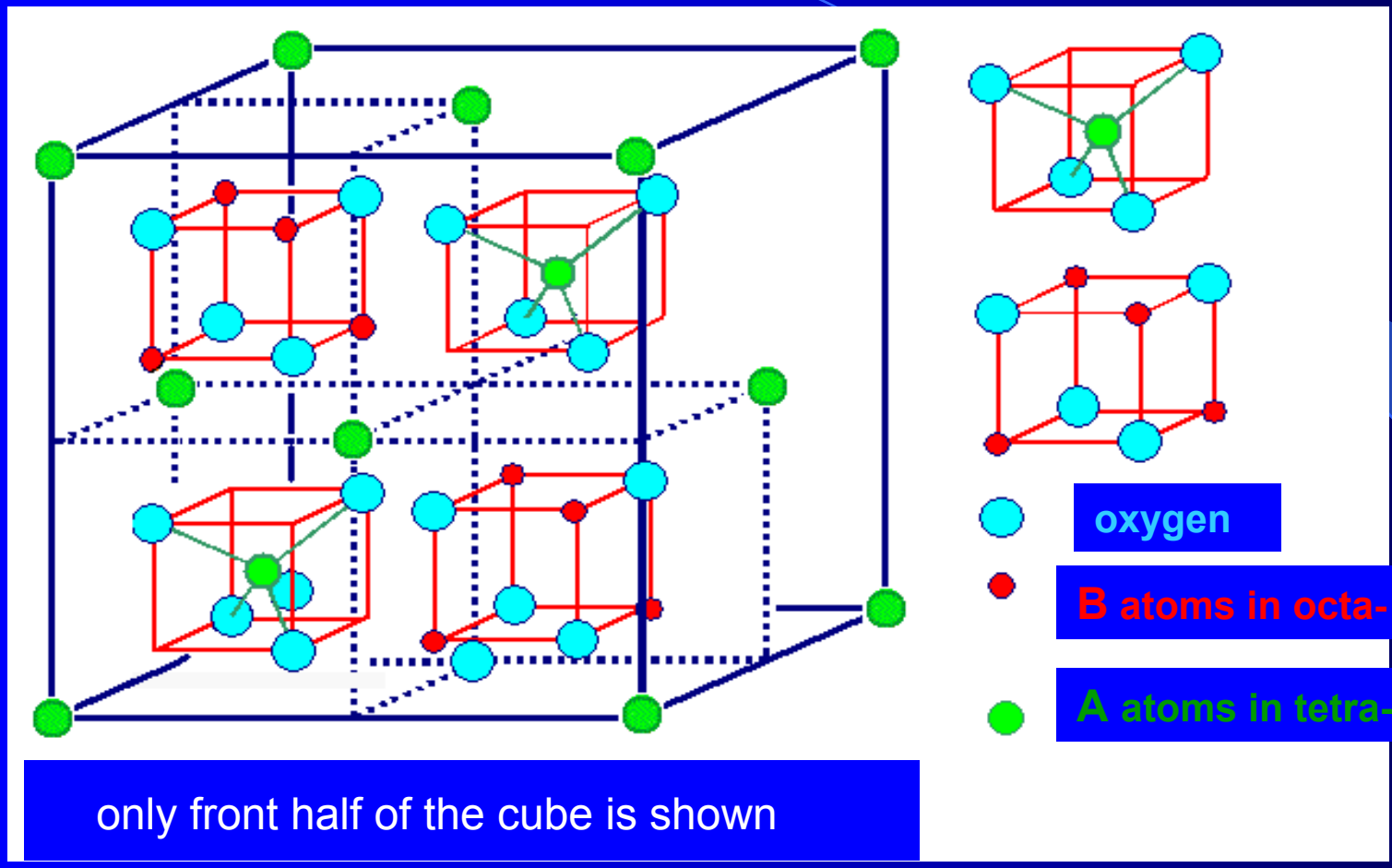
4、And so on……

Synthesis procedures

Much attention has been paid to the preparation of nanocrystalline materials, because of difficult synthesis procedures and special techniques typically used. Co-precipitation has proved to be a successful method, since co-precipitation of Fe^{2+} and Fe^{3+} in alkaline media can be performed to obtain directly the ferrite material.



Spinel structure $A B_2 O_4$



each **B atom** has **6 oxygen** n.n.
each having just **1 A atom** n.n.

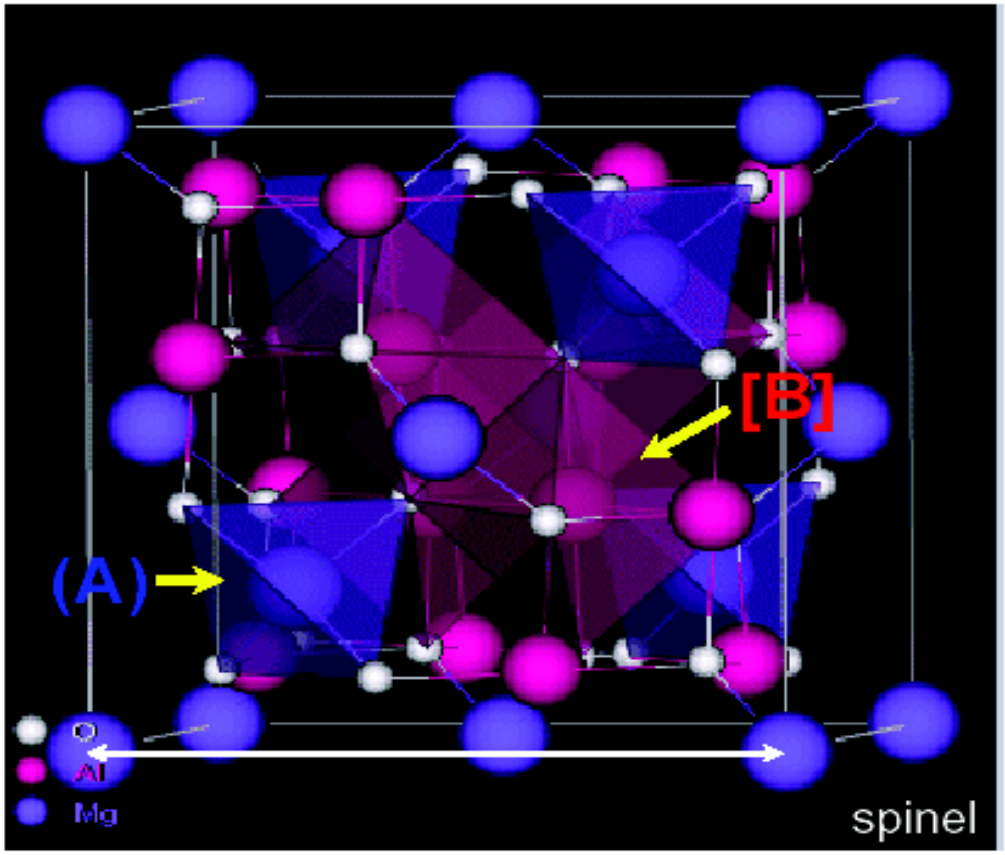
B – O – A paths:
6 starting from B

each **A atom** has **4 oxygen** n.n.
each having **3 B atoms** n.n.

A – O – B paths:
12 starting from A

Spinel structure

2-3 spinels: $M1^{2+}M2_2^{3+}O_4$



space group Fd3m; cubic unit cell consists of **56 atoms**: **32** anions (O^{2-}) and **24** cations ($M(1)^{2+}$ and $M(2)^{3+}$)

96 interstices between the ions:
64 tetrahedral (A) (8a, 8b, 48f)
32 octahedral [B] (16c, 16d)

only **24 interstices are occupied** by cations:
8 (A) sites (8a) and **16** [B] sites (16d)

a	unit cell dimension
u	oxygen parameter
λ	degree of inversion

	(A)	[B]
Spinel ferrites:	$(M_{1-\lambda}Fe_{\lambda})$	$[M_{\lambda}Fe_{2-\lambda}]O_4$
Spinel aluminates:	$(M_{1-\lambda}Al_{\lambda})$	$[M_{\lambda}Al_{2-\lambda}]O_4$

$\lambda = 0$	normal spinel
$0 < \lambda < 1$	partly inverse spinel
$\lambda = 1$	inverse spinel
$\lambda = 2/3$	random distribution

V. Šepelák, F. J. Litterst, K. D. Becker, **A Modified Core-Shell Model of Ferrimagnetic Oxide Nanoparticles**

Co ferrite – distribution of cations over A and B sites

inverse

Fe^{3+} $Co^{2+}Fe^{3+}$ O^{2-}_4

tetra-hedral positions **octa-** **f.c.c. "frame"**

$5\mu_B$ $3\mu_B$ $5\mu_B$

with magnetic moments

normal

Co^{2+} Fe^{3+} Fe^{3+} O^{2-}_4

tetra-hedral positions **octa-** **f.c.c. "frame"**

$3\mu_B$ $5\mu_B$ $5\mu_B$

with magnetic moments

mixed with i = degree of inversion

Co^{2+}_{1-i} Fe^{3+}_{i} Co^{2+}_{i} Fe^{3+}_{2-i}

$$M = M_B - M_A = [3i+5(2-i)]-(5i+3-3i) = [10-2i] - (3+2i) = \{7 - 4i\}\ [\mu_B]$$

A. Lančok, K. Závěta, M. Veverka, E. Pollert,
MÖSSBAUER STUDY OF Co AND Co-Zn FERRITES

VALENCE SEPARATION (Verwey-type)

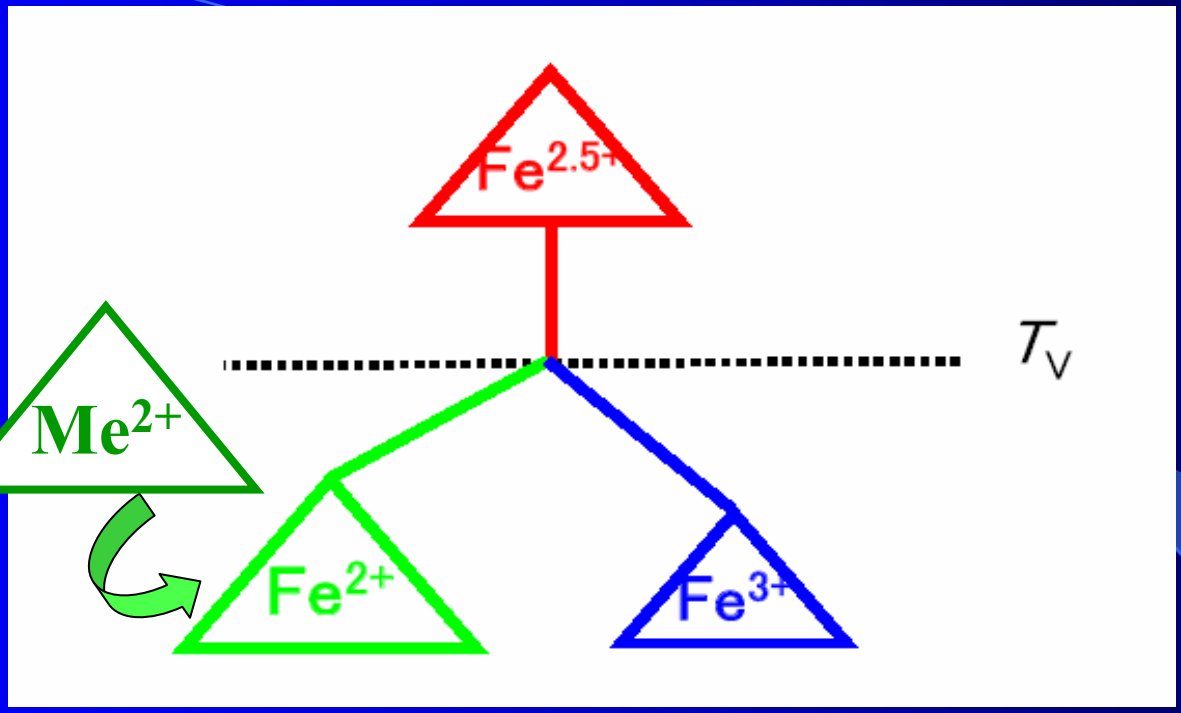
$$2\,M^{m+0.5} \rightarrow M^{m} + M^{m+1}$$

(fluctuating valence state) → (valence-separated state)

Example: Magnetite Fe_3O_4

- Inverse spinel structure: $Fe^{III}_{tet}[Fe^{II}Fe^{III}]_{oct}O_4$
- Verwey transition at 120 K: $2\,Fe^{2.5} \leftrightarrow Fe^{II} + Fe^{III}$
  (Class III) ↔ (Class II)
- Halfmetal

Magnetite (Fe_3O_4), has an inverse spinel structure, the oxygen atom forms a closed packing, and the iron cations take up the interstitial tetrahedral or octahedral positions. Electrons can jump from Fe^{2+} to Fe^{3+} at room temperature.



The presence of different ions like Mg^{2+}, Co^{2+}, Cu^{2+}, etc., blocks this electron hopping.

The compounds magnetite (Fe_3O_4) and $Me_{0.5}Fe_{2.5}O_4$ ferrite (Me = Mg^{2+}, Co^{2+}, Cu^{2+}, etc.) are members of solid solution series, which permits to synthesise samples of different electron delocalization degree.

Aim:

The aim of this investigation is

- to synthesise and

- to characterise different nanosized magnetite and magnetite-type samples

$Me_{0.5}Fe_{2.5}O_4$, Me^{2+}=Fe, Mg, Co, Cu

- to study their physicochemical and catalytic properties with respect to different chemical composition and electronic properties.

Experimental:

- Preparation
- Characterisation
- Catalytic tests

Preparation
Co-precipitation method

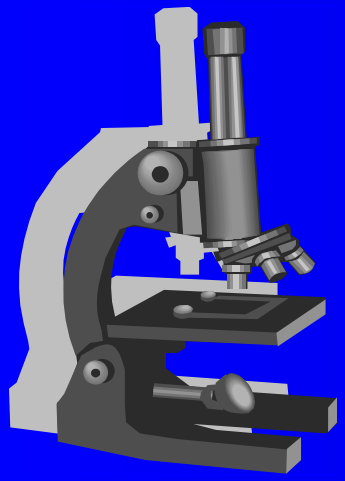
Solutions of $FeCl_2 \cdot 4H_2O$, $FeCl_3 \cdot 6H_2O$ and $MeCl_2 \cdot xH_2O$ – Me=Fe, Mg, Co and Cu, with distilled water were prepared.

The main solutions of Fe^{2+}, Fe^{3+} and Me^{2+} were mixed at a ratio of 1:4:1 and the co-precipitation process was performed by adding the alkaline solution of NaOH to the mixture.

The precipitate obtained was washed to pH=7 and dried. A black precipitate was obtained in all cases.

Sample characterisaton

- Phase composition
- Crystal structure and lattice parameters
- Particle size
- Particle shape
- Magnetic structure
- Temperature behaviour
- Catalytic behaviour



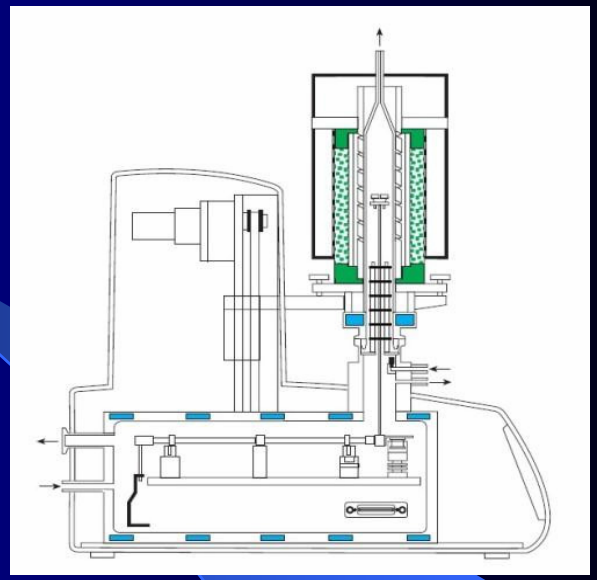
Used methods

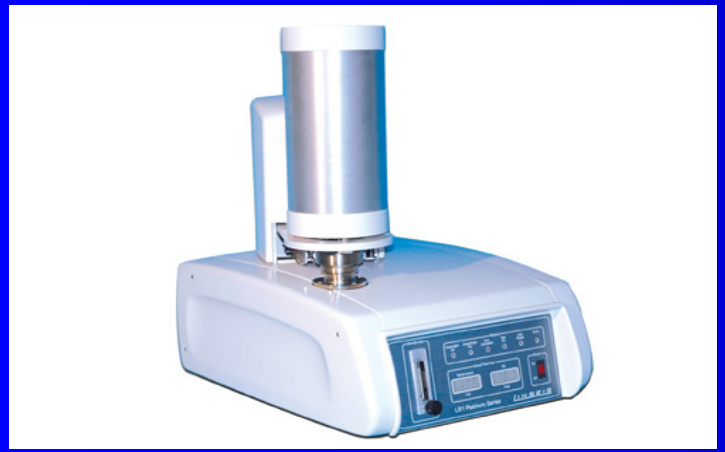
- X-ray powder diffraction
- Mössbauer analysis
- Infrared spectroscopy
- Thermal analysis
- HR-TEM with SAED
- Catalytic measurements

Experimental

Thermal analysis

Ssimultaneous thermogravimetry-differential scanning calorimetry was carried out by Linseis STA-PT1600 thermobalance in static air at a heating rate of 10°C/min .

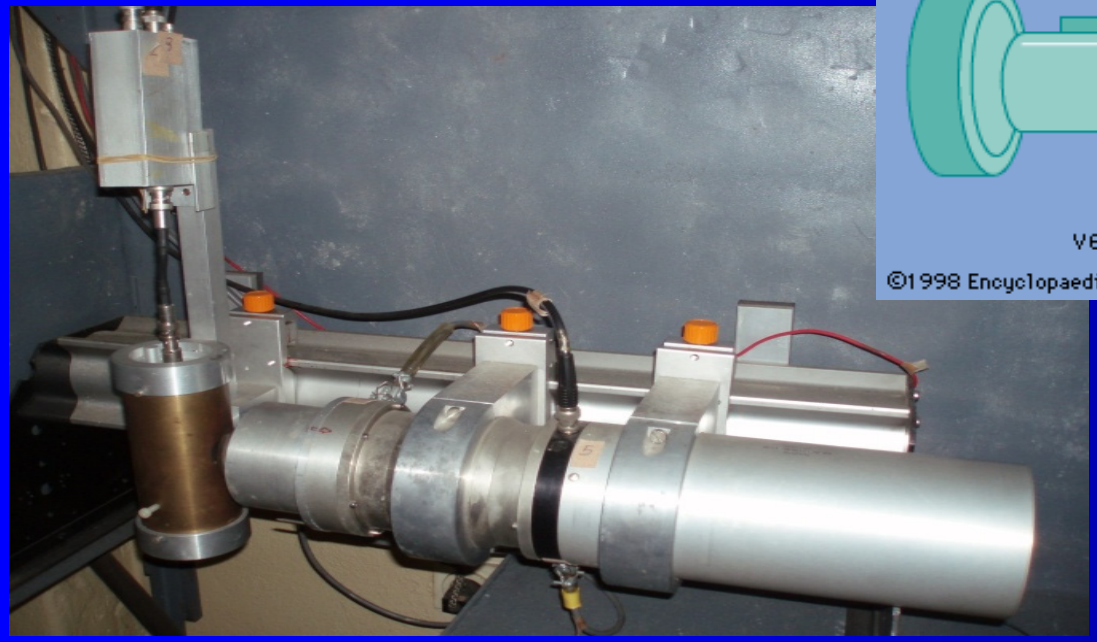


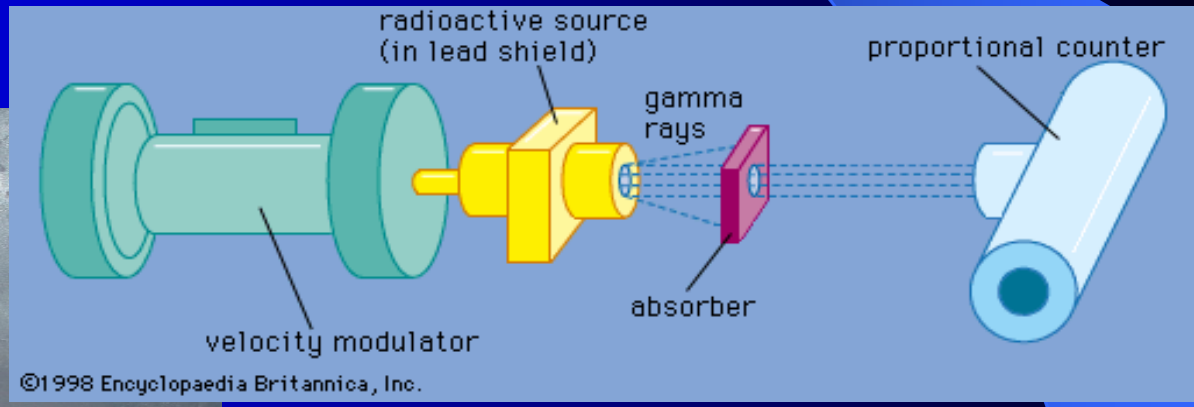


Experimental

Mössbauer analysis

The transmission Mössbauer spectra of 57Fe were taken at RT and LNT by Wissel Wissenshaftliche Electronik GMBH (Germany) spectrometer equipped with a source of 57Co in Rh matrix and working in the constant-acceleration mode. The calibration of the velocity scale was made by a standard α-Fe foil at room temperature and the isomer shift is also given with respect to this standard.





Experimental

X-ray powder diffraction

TUR M62 apparatus, HZG-4 goniometer with Bregg-Brentano geometry, CoKα radiation and Fe filter. Data base (Powder Diffraction Files, Joint Committee on Powder Diffraction Standards, Philadelphia PA, USA, 1997) was used for identification of the phases. Voigt profile was used to resolve instrumental, strain and size contributions to peak broadening.

$$W_{exp} = \alpha W_L + \beta W_G$$

$$D = k\,\lambda / W_L \cos\theta$$

$$e = W_G / (4 \tan\theta)$$

Infrared spectroscopy

IR and far-IR spectra were recorded by a Nicolet 6700 IR spectro-photometer in KBr pellets within the 250–650–4000 cm^{-1} range.

Experimental

HR TEM SAED

A JEOL 2100 microscope has been developed to achieve the highest image quality and the highest analytical performance in the 200-kV class analytical TEM with a probe size below 0.5 nm.

Experimental

Catalytic measurements

- ✓ ***In situ*** diffuse-reflectance measurements (DRIFTS) on Nicolet 6700 FTIR spectrometer by high temperature/vacuum chamber (Thermo Spectra-Tech) in the region of 1111–4000 cm^{-1} were carried out by using CaF_2 windows.
- ✓ The catalytic tests were performed in the reaction of CO oxidation.

Preparation

Fe_3O_4

$FeCl_2.4H_2O$, $FeCl_3.6H_2O$ - main solutions, alkaline solution of NaOH

$FeCl_2 + FeCl_3 + NaOH \rightarrow$

$$Fe[H_2O]_6^{2+} + Fe[H_2O]_6^{3+} + Na^+ + OH^- + Cl^- \rightarrow$$

$$Fe(OH)_2 + Fe(OH)_3 + NaCl + H_2O \rightarrow$$

$$[(Fe^{3+})(Fe^{2+})_2(OH^-)(O^{2-})_2]^{2-} + NaCl + H_2O \rightarrow$$

$Fe_3O_4 \downarrow$ $+ NaCl + H_2O$

Preparation

$Cu_{0.5}Fe_{2.5}O_4$

$FeCl_2.4H_2O$, $FeCl_3.6H_2O$, $CuCl_2.2H_2O$
main solutions, alkaline solution of NaOH

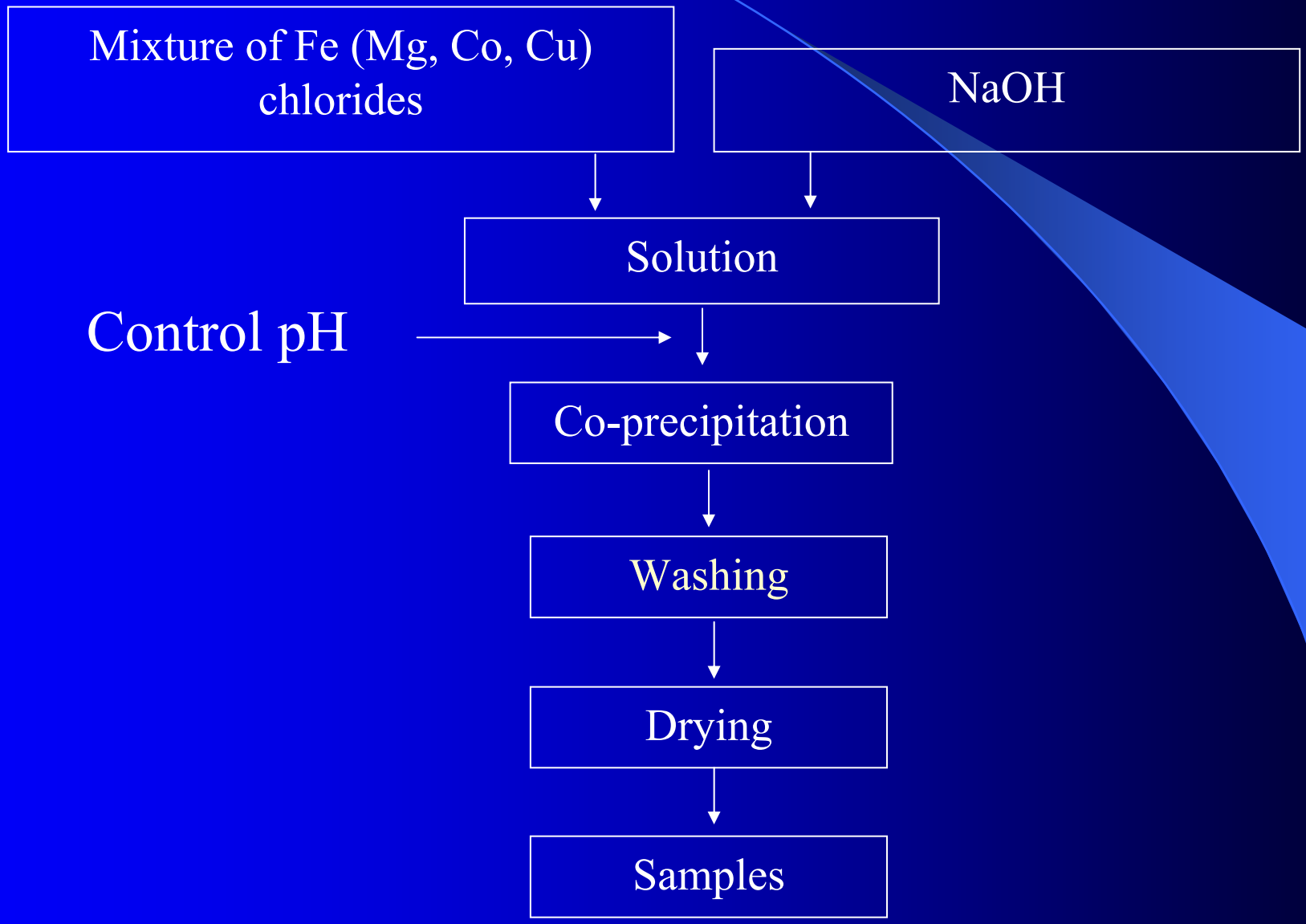
$Mg_{0.5}Fe_3O_4$

$FeCl_2.4H_2O$, $FeCl_3.6H_2O$, $MgCl_2.6H_2O$
main solutions, alkaline solution of NaOH

$Co_{0.5}Fe_2O_4$

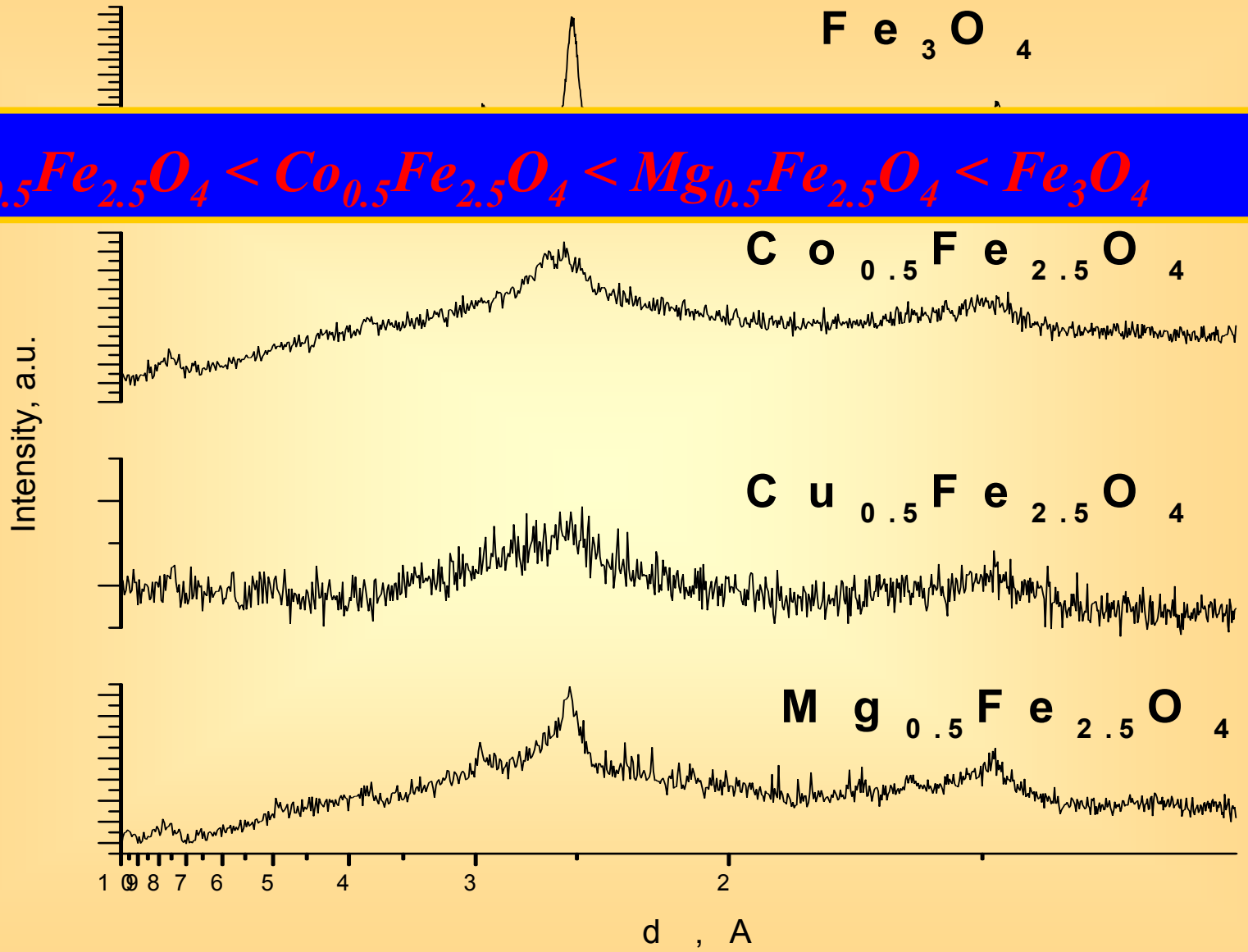
$FeCl_2.4H_2O$, $FeCl_3.6H_2O$, $CoCl_2.6H_2O$
main solutions, alkaline solution of NaOH

Chart of preparation

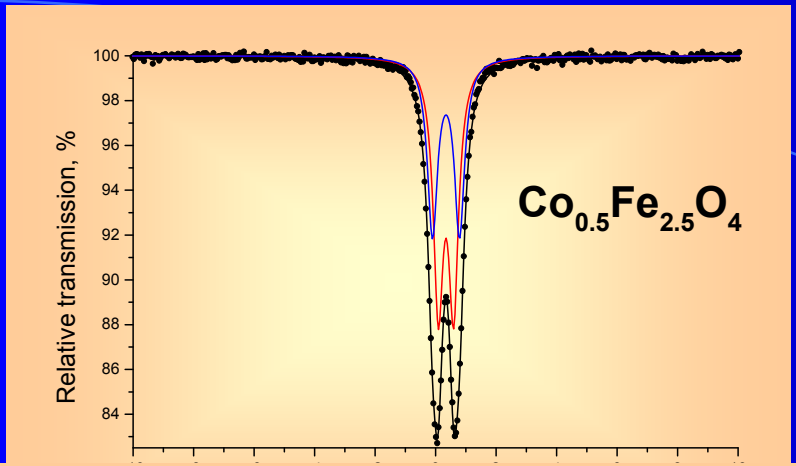


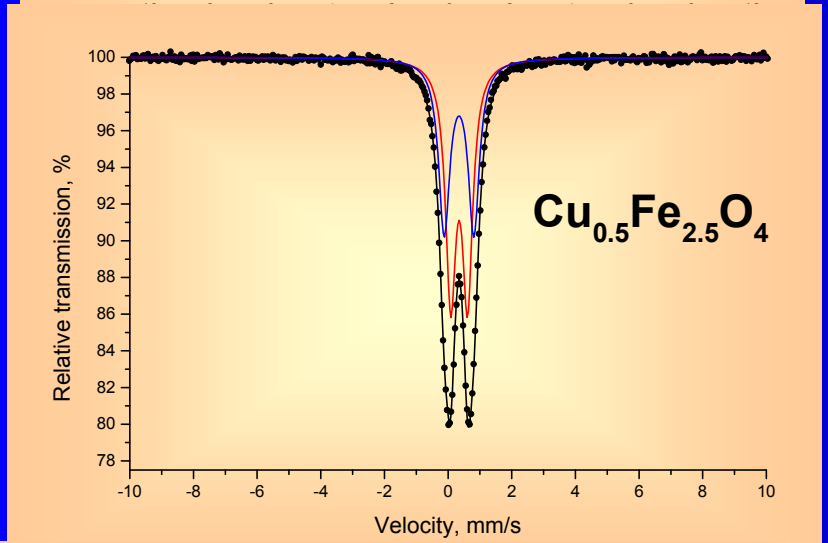
XRD study

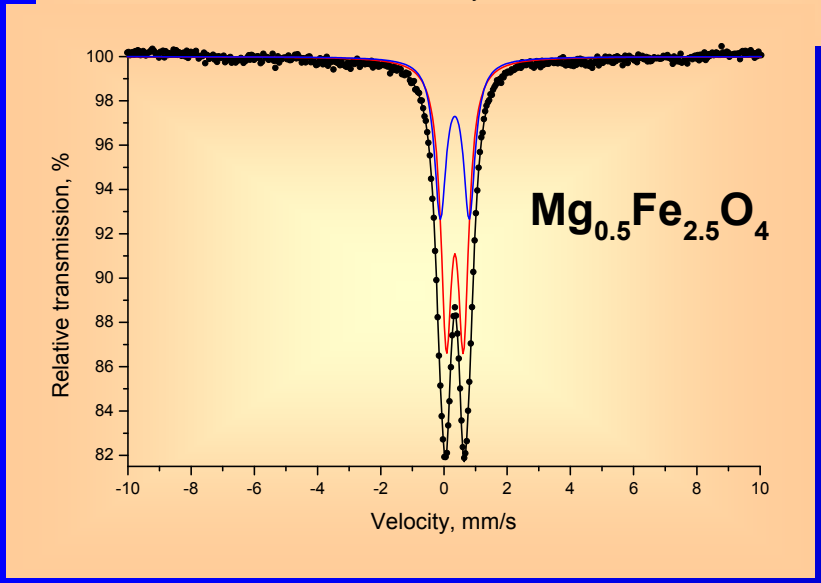
$$Cu_{0.5}Fe_{2.5}O_4 < Co_{0.5}Fe_{2.5}O_4 < Mg_{0.5}Fe_{2.5}O_4 < Fe_3O_4$$

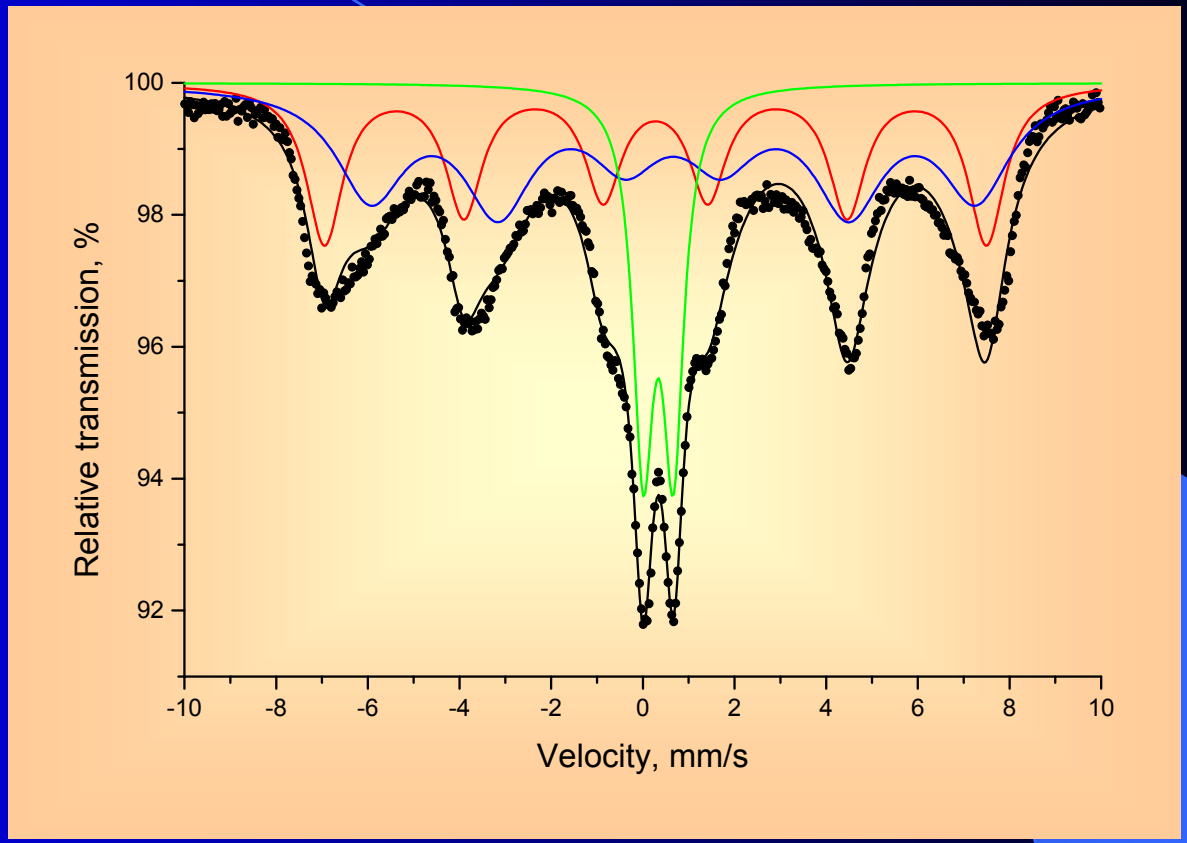


Mössbauer study -RT



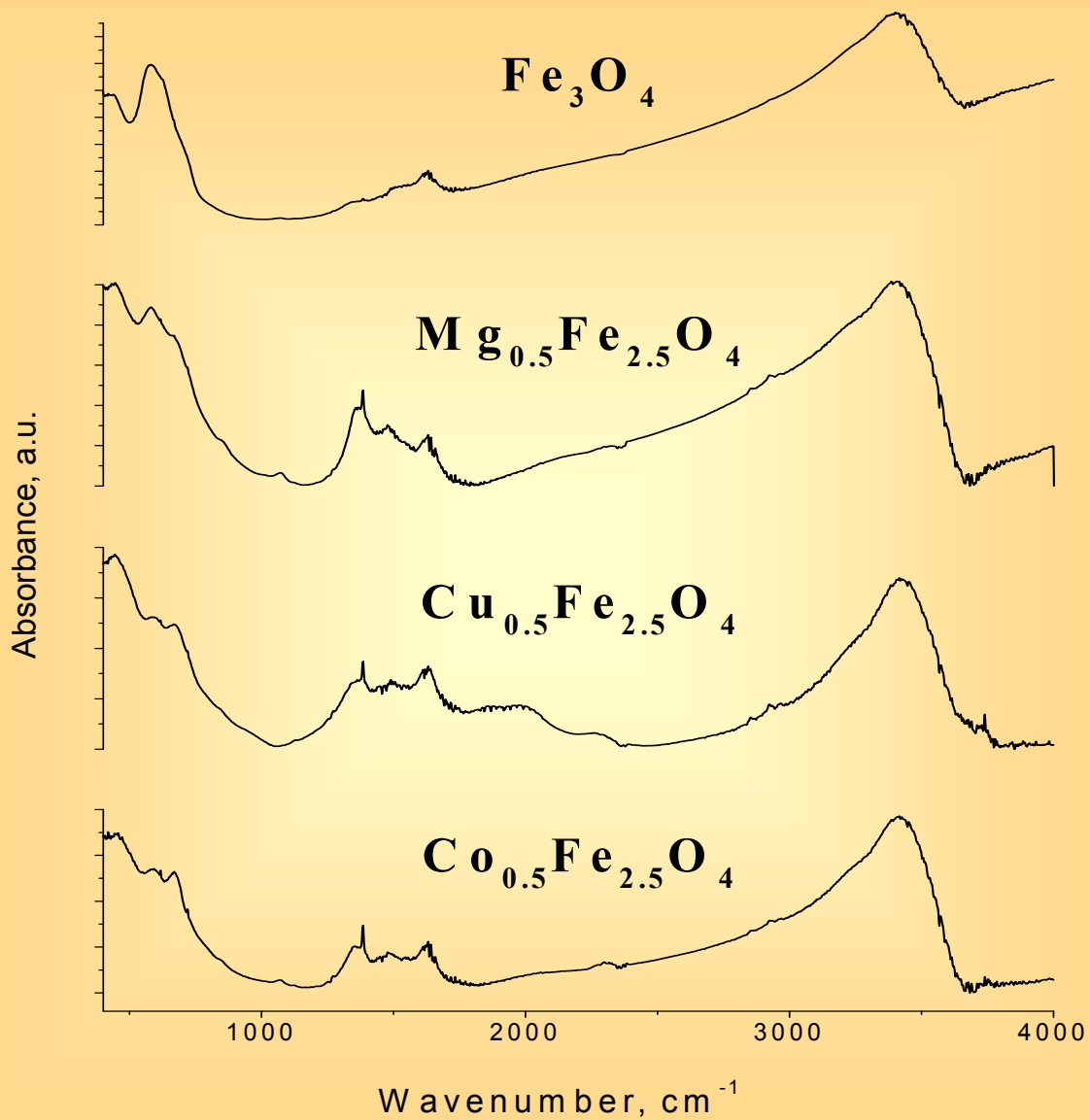


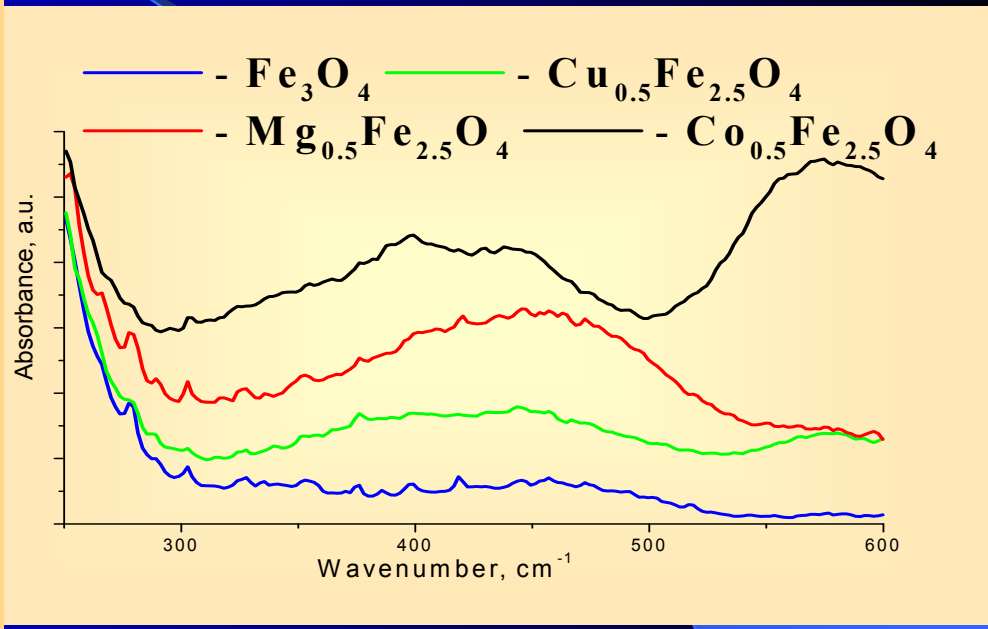




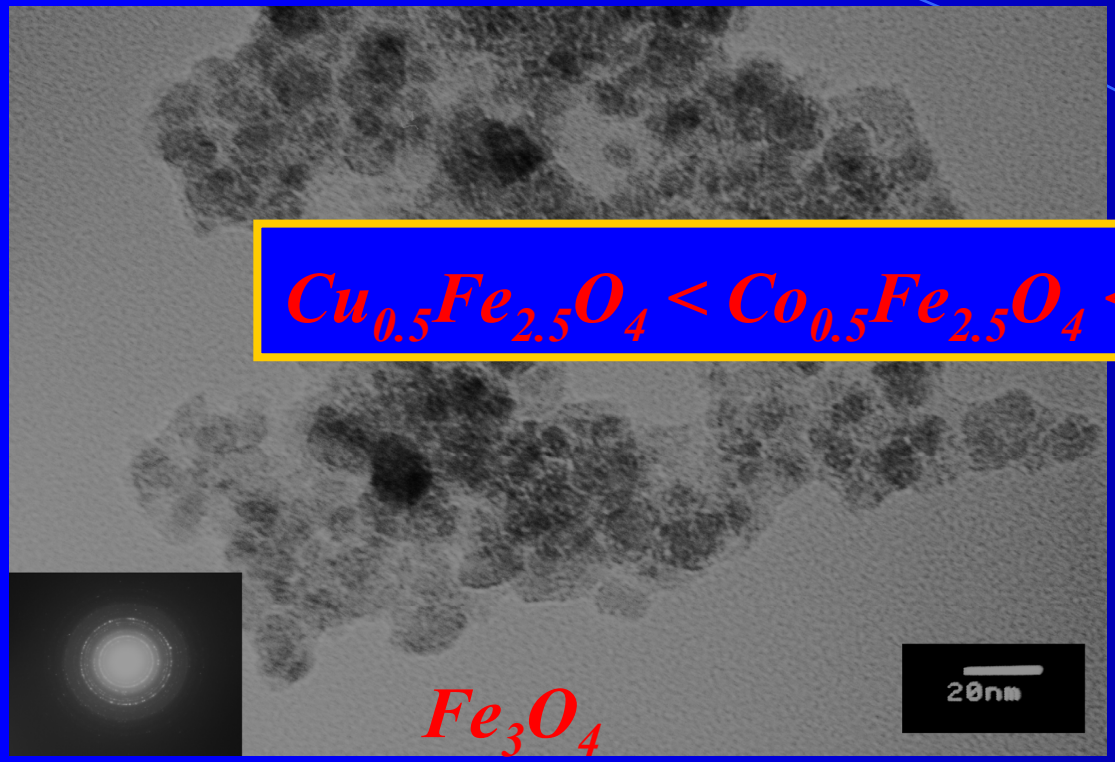
$Fe^{3+}{}_2Fe^{2+}O_4$

IR study


Fe3O4
Mg0.5Fe2.5O4
Cu0.5Fe2.5O4
Co0.5Fe2.5O4
Absorbance, a.u.
1000
2000
3000
4000
Wavenumber, cm-1

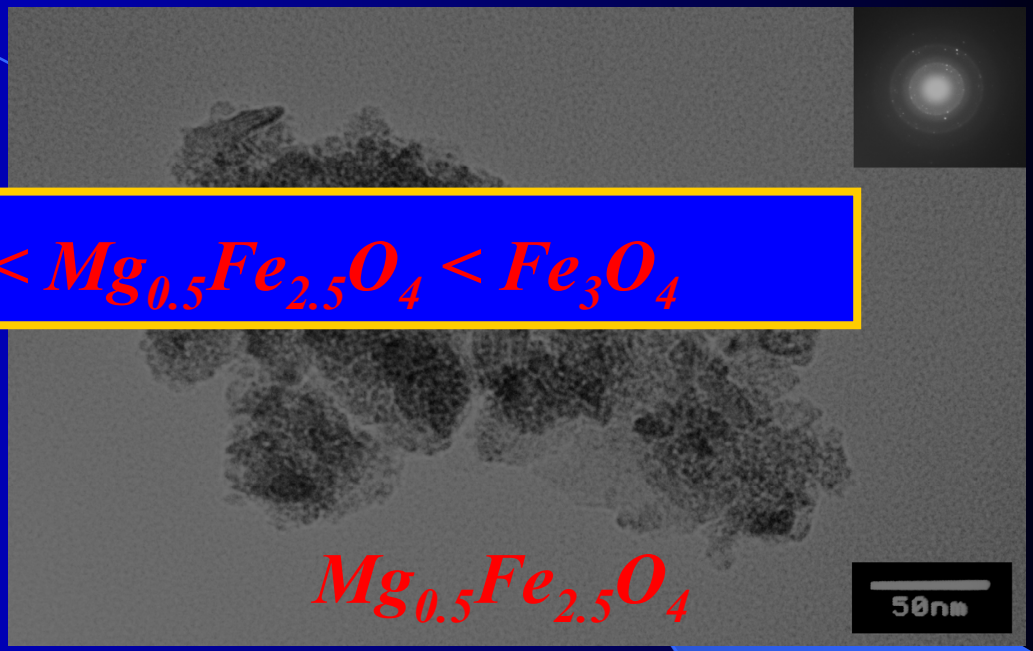

- Fe3O4
- Cu0.5Fe2.5O4
- Mg0.5Fe2.5O4
- Co0.5Fe2.5O4
Absorbance, a.u.
300
400
500
600
Wavenumber, cm-1

HR TEM study - SAED

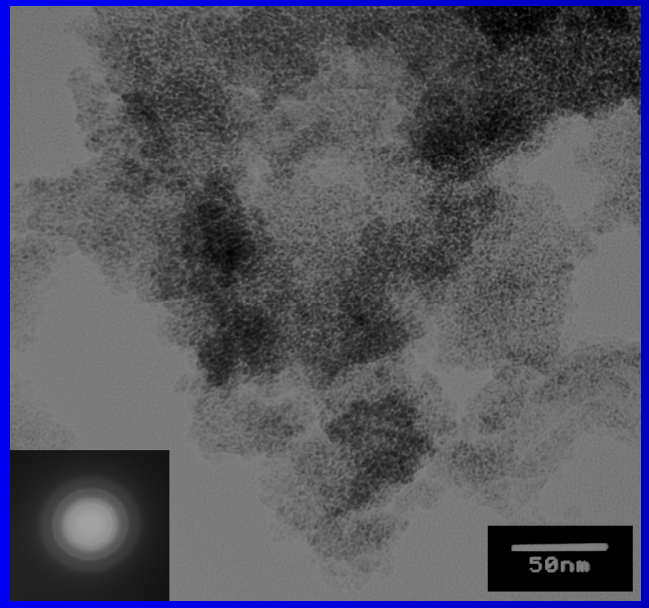


Fe_3O_4

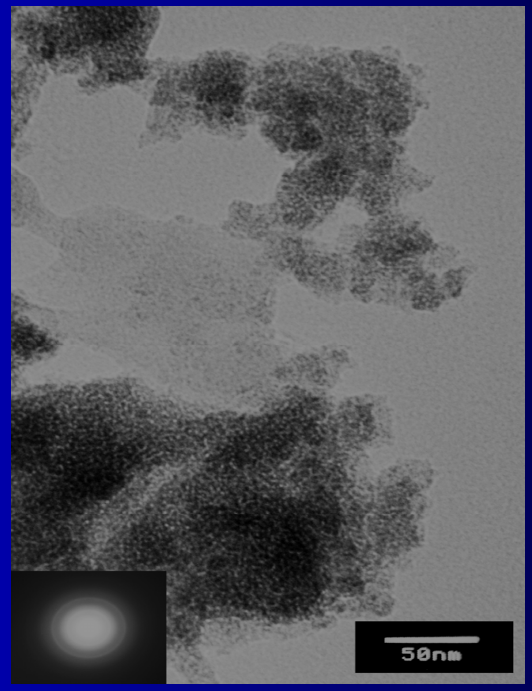
$Cu_{0.5}Fe_{2.5}O_4 < Co_{0.5}Fe_{2.5}O_4 < Mg_{0.5}Fe_{2.5}O_4 < Fe_3O_4$



$Mg_{0.5}Fe_{2.5}O_4$

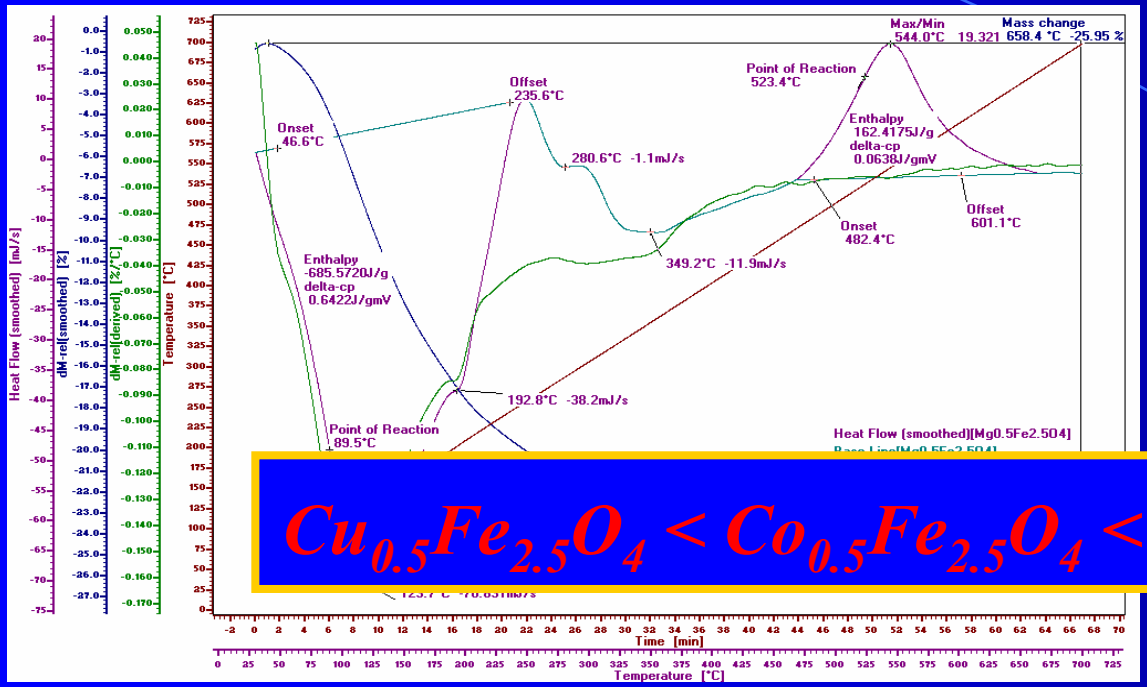


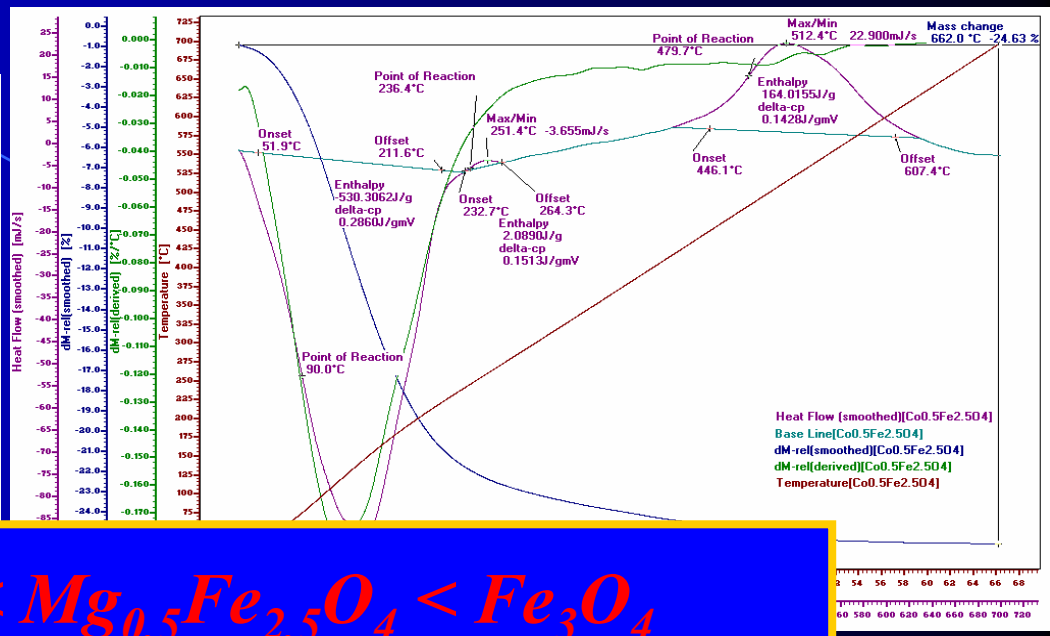
$Co_{0.5}Fe_{2.5}O_4$



$Cu_{0.5}Fe_{2.5}O_4$

DSC study

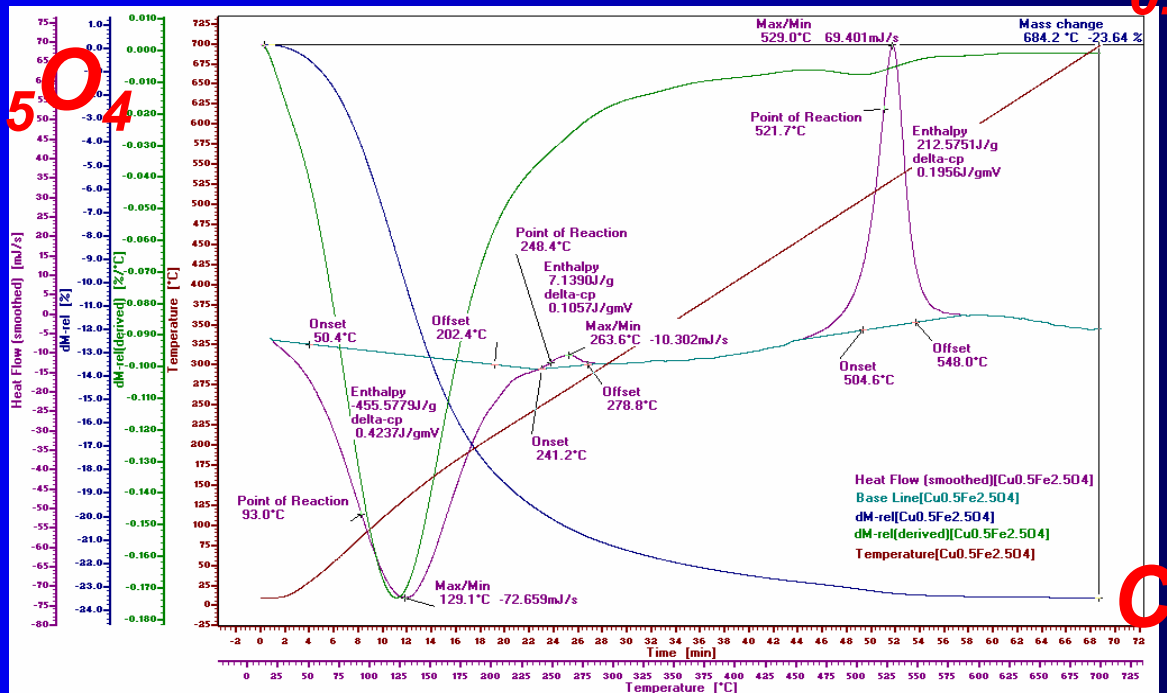




$$Cu_{0.5}Fe_{2.5}O_4 < Co_{0.5}Fe_{2.5}O_4 < Mg_{0.5}Fe_{2.5}O_4 < Fe_3O_4$$

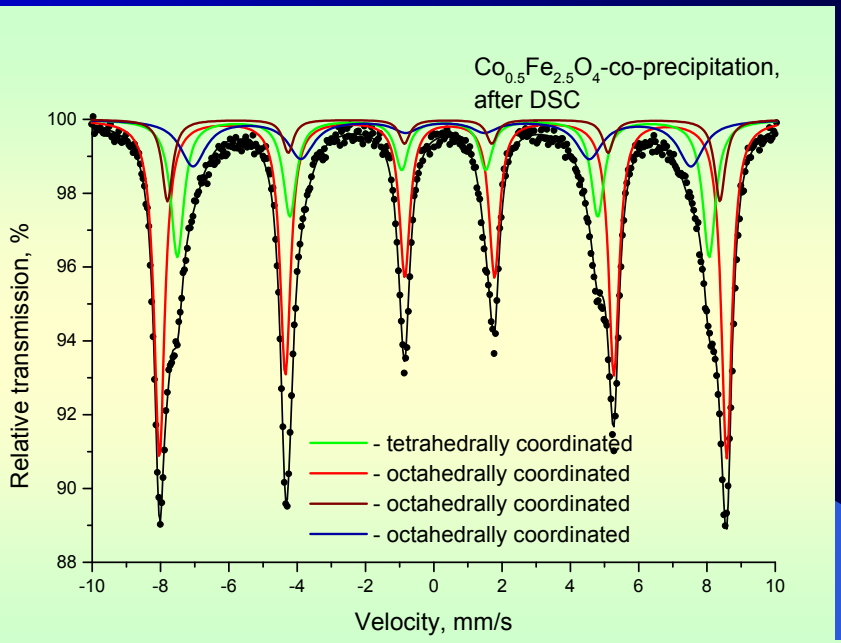
$Co_{0.5}Fe_{2.5}O_4$

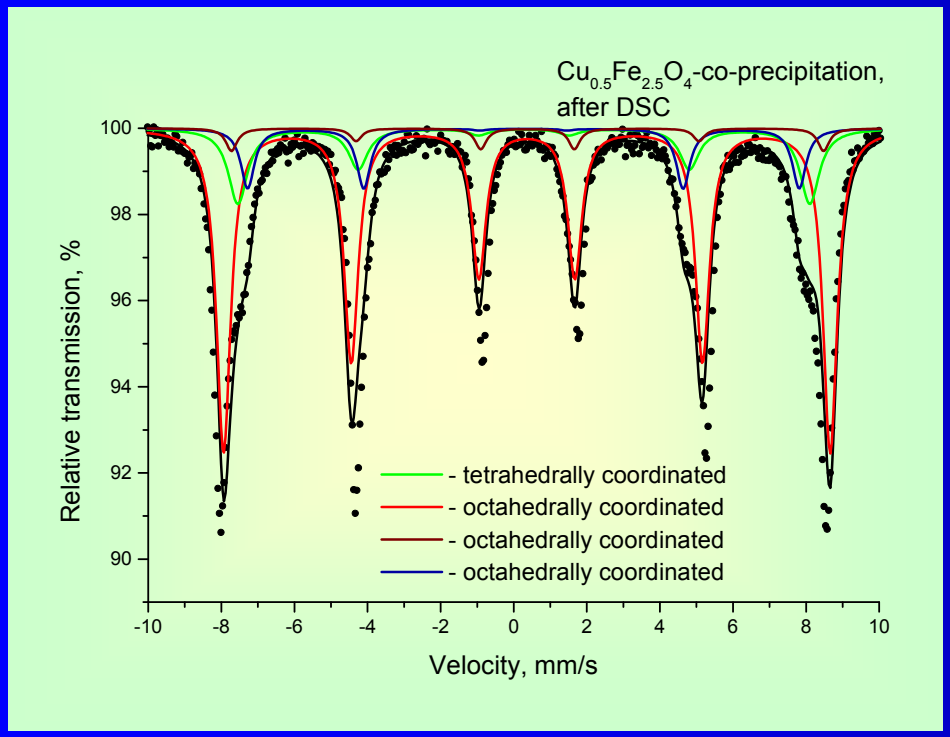
$Mg_{0.5}Fe_{2.5}O_4$

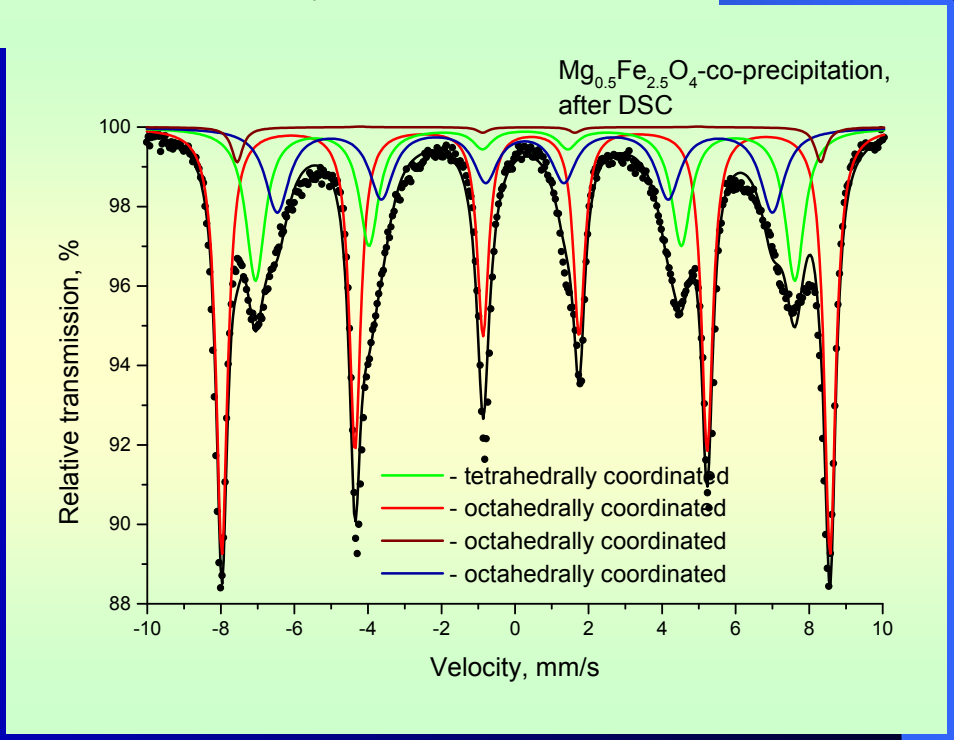


$Cu_{0.5}Fe_{2.5}O_4$

After DSC study – Mössbauer analysis



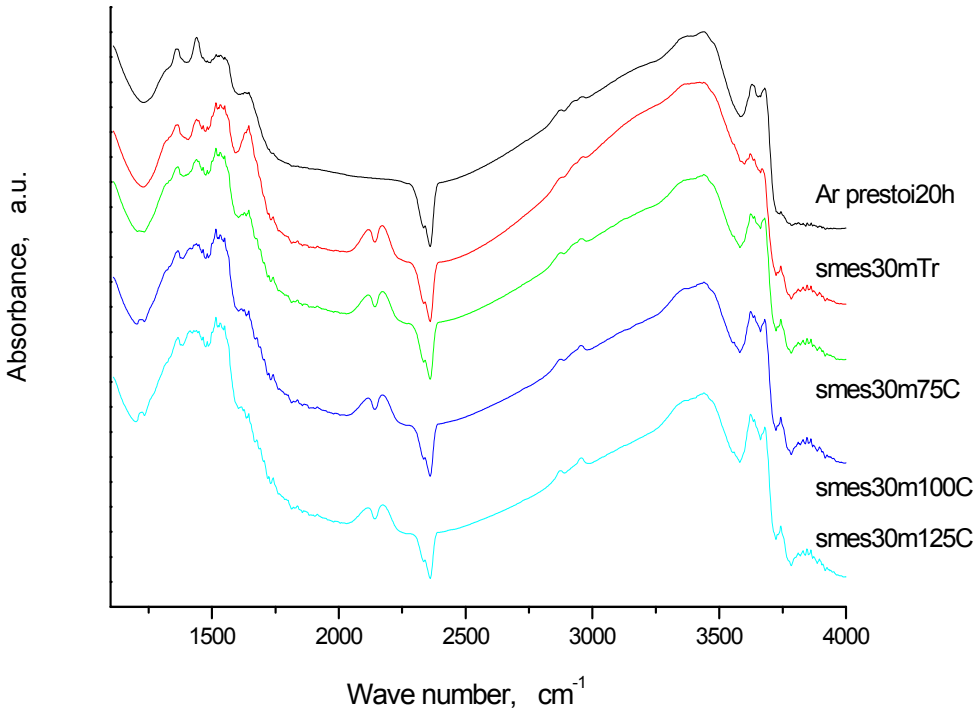


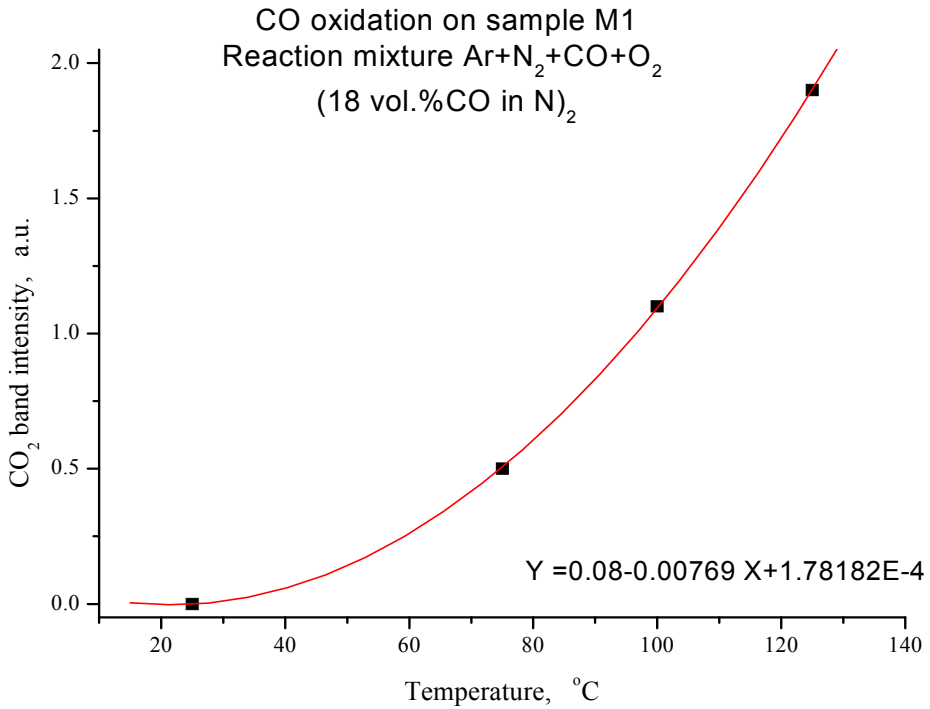


Catalytic measurements

In situ **diffuse-reflectance measurements (DRIFTS): catalytic tests were carried out in the reaction of CO oxidation.**

$$2\,CO + O_2 \rightarrow 2\,CO_2$$

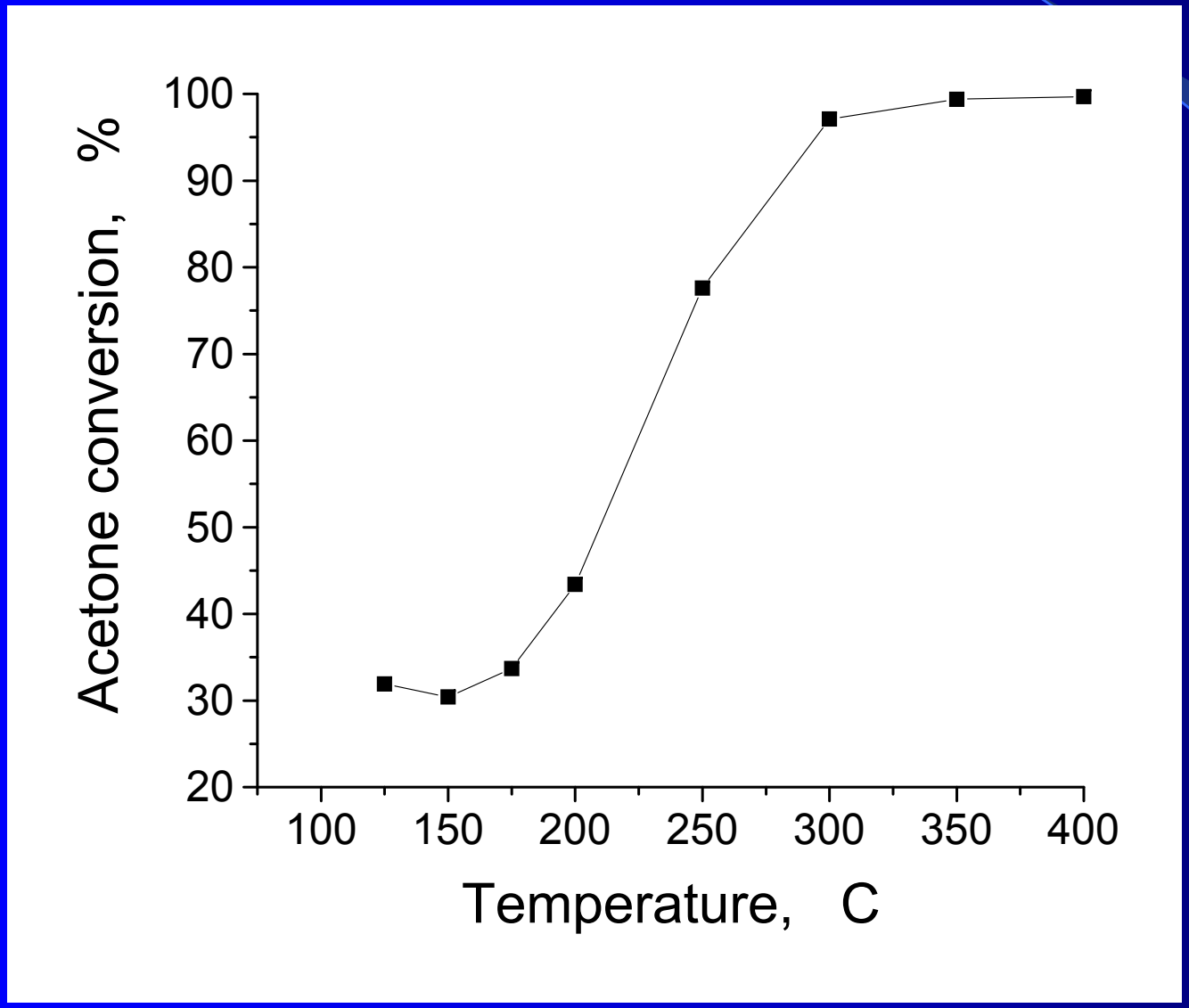




Activity

Catalytic measurements

Study of acetone conversion reaction



Activity

Conclusions

1. **The design of synthesis conditions leads to preparation of single phase spinel ferrite materials - Fe_3O_4, $Cu_{0.5}Fe_{2.5}O_4$, $Co_{0.5}Fe_{2.5}O_4$, $Mg_{0.5}Fe_{2.5}O_4$**
2. **Their particle size is nanodimensional, about 3-12 nm, and changes on varying chemical composition in the following order: $Fe_3O_4 > Mg_{0.5}Fe_{2.5}O_4 > Co_{0.5}Fe_{2.5}O_4 > Cu_{0.5}Fe_{2.5}O_4$.**
3. **Particles have spherical shape and close size distribution.**
4. **Study of the magnetic properties of prepared materials shows**
   - **CME behaviour of magnetite sample at RT;**
   - **SPM behaviour of all magnetite-type materials at RT and LNT.**
4. **Initial catalytic tests reveal their good catalytic activity and the potential to use materials as catalysts.**

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