THE EFFECT OF PRECURSORS CONCENTRATION ON THE STRUCTURE AND MICROMAGNETIC PROPERTIES OF ULTRAFINE IRON OXIDES OBTAINED BY SOL-GEL ROUTE

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Abstract. Nanodispersed composite materials γ-Fe_2O_3/α-Fe_2O_3 were obtained by thermal decomposition of iron citrate xerogel hydrate synthesized by iron nitrate and citrate acid solutions with different colloidal solutions of $Fe(NO_3)_3 \cdot 9H_2O$ and $C_6H_8O_7 \cdot H_2O$ for different molar ratio between precursors. The influence of the precursors molar concentration and calcination temperature on the material phase composition, crystalline and magnetic microstructure, surface condition was studied. Methods of X-ray diffraction, Mössbauer spectroscopy, electron microscopy and IR - spectroscopy were used.

Keywords: iron citrate, sol-gel, molar ratio, nanoscale, magnetic microstructure, superparamagnetic.

1. INTRODUCTION

Ultrafine and nanostructured iron oxides are applicated as materials for spintronic [1], catalysts [2], drug delivery [3], MRI contrasts [4] and Photoanode for Water Splitting [5]. These materials are perspective for photocatalytic treatment of environmental pollutants [6], the components of magnetic fluids [7] and electrode material for lithium power sources [8]. The material efficiency in a particular area is determined by the phase composition, the characteristics of the crystal and magnetic microstructure and surface morphology. For example, ultrafine γ-Fe_2O_3 are efficient, green, heterogeneous and reusable catalyst for many multi-step organic syntheses at ambient temperature for their greater reactivity and high surface area with mesoporous structure cause the significant improvement of reaction efficiency [9]. Therefore development and improvement of methods for the nanostructured iron oxides synthesis can open the possibilities of functional materials obtaining with controlled and predetermined properties adapted for specific sphere of the use. Iron oxides nanoparticles have been synthesized by different methods [10] – from chemical precipitation and sol-gel techniques to electrochemical and mechanochemical methods. The combination of some methods is promising variant. The determination of synthesis conditions effects on the material phase composition and morphology is an important and hot topic.

The aim of this paper is an investigation the influence of precursors molar contents on the phase composition and crystal and magnetic microstructures ultrafine iron oxides obtained by thermal decomposition of sol-gel obtained iron citrate xerogel hydrate process.

2. MATERIALS AND METHODS

Iron oxides were synthesized by sol-gel route: slow drying (60°C) on the air of colloidal solutions of $Fe(NO_3)_3 \cdot 9H_2O$ and $C_6H_8O_7 \cdot H_2O$ for different molar ratio between precursors (samples obtained at 1:0.5, 1:1, 1:4 and 1:12 ratio were marked S1, S2 S3 and S4, respectively). Sedimentated during 12-15 days iron citrate hydrate was dried out in the air at 50-60°C. Obtained gels were annealed at 200, 300 and 400 C during 1 hour.

Systems of samples were investigated by X-ray diffractometry, Mossbauer spectroscopy, infra-red optical spectroscopy and scanning electron microscopy.

Diffraction patterns were obtained with diffractometer DRON-4-07 (Cu K_α radiation). Bragg-Brentano geometry type and a Ni K_β - filter were used. Quantitative analysis was realized using full pattern Rietveld refinement procedure using FullFrof Suite Program. XRD measurements were collected in a 2θ range of 16–65°.

Scanning electron microscopy images were obtained using an microscope JSM- 6490 LV JEOL, at a 30 kV.

The Mössbauer spectra were measured with a MS-1104Em spectrometer using a 57Co γ-ray source and calibrated at room temperature with α-Fe as a standard (linewidth 0.29 mm/s). The isomer shifts (δ) are relative to Fe metal. The model fitting and hyperfine field distributions recovering was performed using Mosswin 3.0 software.

Infrared spectra were recorded at Thermo-Nicolet Nexus 670 FT-IR spectrometer in the region of $4000 – 400 \text{ cm}^{-1}$. The mixture TiO_2/ KBr after vibrating milling was pressed into pellets and measured in the transmission mode.

3. RESULTS AND DISCUSSION

Accordingly to XRD analysis data (Fig. 1), S1, S2 and S4 samples obtained by the annealing of initial xerogels at 200°C are the mixture of γ-Fe_2O_3 and α-Fe_2O_3 phases. Meantime S3 sample (molar ratio $Fe(NO_3)_3 \cdot 9H_2O$: $C_6H_8O_7 \cdot H_2O$ = 1:4) was unexpectedly X-ray amorphous.
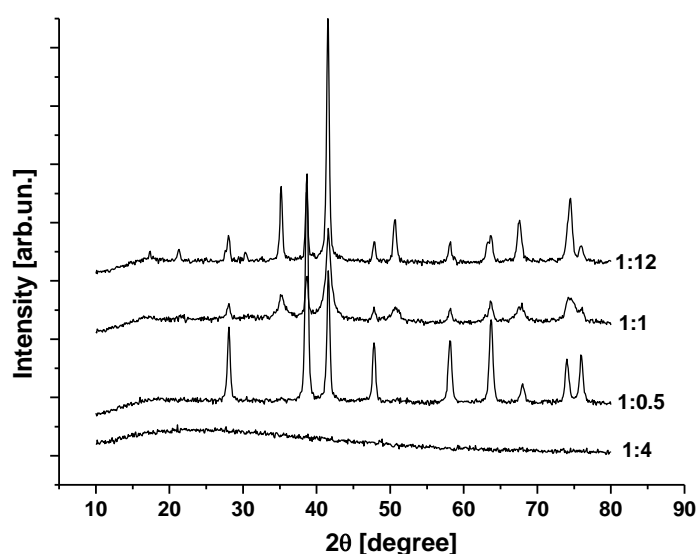

Fig. 1. XRD patterns of materials obtained by the annealing of initial xerogels at 200°C.

The content of γ-Fe_2O_3 phase nonlinear changes with the $C_6H_8O_7 \cdot H_2O$ concentration increasing (9±1, 47±3 and 43±2 mass % for S1, S2 and S4 samples, respectively). This result is correlated with changes of γ-Fe_2O_3 X-ray scattering coherent blocks average sizes 16, 6 and 14 nm for S1, S2 and S4 samples. The enlarging of annealing temperature to 300°C leads to crystallization of S3 sample (α-Fe_2O_3 phase content became 88 mass. %). Phase composition of S2 sample didn't change after calcination at 300°C when for S1 and S4 α-Fe_2O_3 content has been grown to 86 and 93 mass.%. After calcinations at 400°C only S2 sample contains γ-Fe_2O_3 (about 7 mass.%).

Accordingly to Fourier transform infrared spectroscopy (Fig. 2) all sample systems contained molecular non-dissociated water –a broad absorption band between 3200 and 3400 cm^{-1} corresponds to vibrational modes of ν (H – O) [11]. There were also presence bound OH groups (bands at 1618 cm^{-1} [12] but it's content is relatively low.
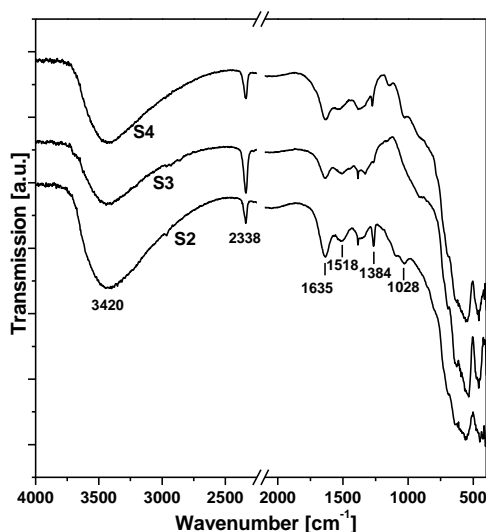

Fig. 2. FTIR spectra of iron oxides
obtained by iniatiial xerogels annealing at 300°C.

The sharp band at 2338 cm^{-1} for all samples is associated with the vibrational modes of ν (C – O) in absorbed CO_2 [13]. A band with a maximum at 1384 cm^{-1} corresponds to deformation vibration COO–Fe^{3+} bonds [14]. Bands around 535–550 cm^{-1} are associated with O–Fe bond [15], absorption maximum at 453 см$^{-1}$ linled to vibrational modes octahedral coordinated Fe^{3+}–OH. The band broadening in Fourier transform infrared spectra is characteristic of structurally disordered materials. As a result the presents of amorphous γ- FeOOH phase in all samples is very possible.

Additional information about synthesized materials of phase composition and magnetic properties was obtained by mossbauer spectroscopy (Fig. 3).
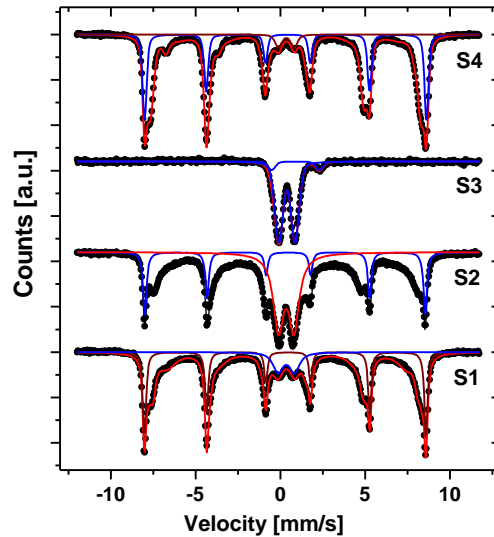
*Fig. 3. Mossbauer spectra (room temperature) of iron oxides
obtained by iniatial xerogels annealing at 200°C.*

Mossbauer spectra for S1, S2 and S4 materials after annealing at 200°C are the superposition of two different parts: six-line pattern components corresponds to a magnetically ordered fraction of the sample and a doublet components caused by sizes effects and superparamagnetism phenomena. Sextet component which respond to the resonance absorption by ^{57}Fe nucleus in the α-Fe$_2$O$_3$ particles are clear separated due specific values of quadrupole splitting ($\Delta = -0.19 – -0.21$mm/s) and hyperfine magnetic field more than 51 T. Comparatively low line width for these components indicates the relatively good crystallinity of this phase. Meantime sextets corresponding to γ-Fe$_2$O$_3$ are broadered so the γ-Fe$_2$O$_3$ phase consist of separate nanoparticles. For this case doublet component is the result of some particles transition to superparamegnetic state. For of γ-Fe$_2$O$_3$ nanoparticles with the diameter <10 nm monodomain state is energy favorable with temperature induced fluctuation of magnetic moments. This fluctuations cause the spectral components broadening and disappearance of magnetic hyperfine structure at a certain value of material magnetic anisotropy which determines the relaxation time τ_r of a particle magnetic moment. Relaxation time is calculated as $\tau_r = \tau_0 \exp\left(\dfrac{KV}{kT}\right)$, where $\tau_0 \approx 10^{-9}$-10^{-10} s, $V–$ particle volume, $K–$ constant of anisotropy, $T–$ temperature. So doublet components correspond to γ-quantum resonance absorption in the γ-Fe$_2$O$_3$ particles. Accordingly to this conclusion we can refine the information about S1 sample phase composition – actually content of γ-Fe$_2$O$_3$ is about 81 %. Mismatch to XRD data is caused by nanoscale sizes of most γ-Fe$_2$O$_3$ particles which formed mesoporous 3D-grid. Paramagnetic parts of the spectra contain two components which have close values of isomeric shift about δ=0,34–0,36 mm/s and different values of quadrupole splitting Δ, which are determined by neighbour encirclement of Fe^{57} nuclei. The constant of magnetic anisotropy for the particles of γ-Fe$_2$O$_3$ is 1.2·10^6 J/m^3 [16] so we can estimate particles size. Accordingly this calculation average particles size S3 sample is less than about 5 nm at room temperature for superparamagnetic state implementation.

Component with Δ=0,88-0.90 mm/c is respond to resonance absorption in nanoparticles γ-Fe$_2$O$_3$ with non-zero values of electric field gradient on Fe^{57} nuclei and is explained by deformation effects in crystal lattice of maghemite. Zero values of Δ for second doublet component are determined by cubic symmetry of particle structure, which are in non-stressed state. We can suppose that the presence two types of Fe^{57} surroundings respond to the resonance absorption by nucleus in the superficial and inner regions of separate particles (grid nodes). That composition is typical for S1, S2 and S4 materials annealed at 200°C –γ-Fe$_2$O$_3$ phase is dominant for all cases. For S3 sample no any magnetically ordered structure hasn't been detected. Moreover, presence Fe^{2+} ions (10%) was observed.

The S2 magnetic microstructure transformation with annealing at 250, 300 and 400°C was studied by function of hyperfime field distributions recovering methods which allows obtain additional information magnetic ordering changes. The calculated distributions are non monotonous (Fig.4) and are characterized by some maxima in low field region (22-33T), region of magnetic hyperfine interaction probability smooth growth (35-45T) and major maxima (48±3 T). Optimal fitting results for samples obtained after sinering at 250°C and 300°C became possible only in case of wide doublet component addition with close to zero quadrupole splitting (Fig. 4, a, b). This component represents an intermediate stage between magnetically ordered and superparamagnetic states of a particle in the case of strong dipole-dipole interaction [17]. This component is a result of resonance absorption by the ^{57}Fe nucleu, for which the hyperfine field has the value between zero and saturation level. Thermal fluctuation of magnetic moment of particles takes place but the "temporary freezing" is possible. At the same time, the transition to superparamagnetic state is not observed although the energy of thermal fluctuations exceeds the anisotropy energy.
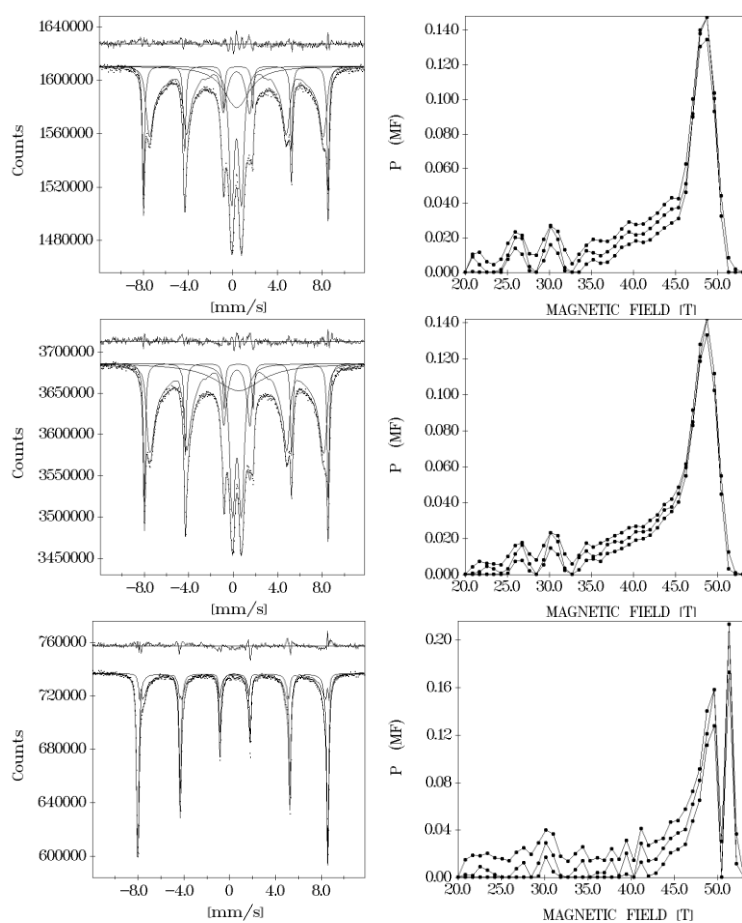

Fig. 4. Mossbauer spectra of S2 sample after annealing at 250 (a), 300 (b) and 400°C; additional plots – recovered functions of hyperfine fields on ^{57}Fe nucleus probabilities distributions (central line) and confidential intervals of computations (zones confine upper and confine lines).

General peculiarities of samples microstructure which were detected by XRD and Mossbauer methods are reflected on the scanning electron microscopy data (Fig. 5). Materials of all series are characterized by porous structure as a result of evaporation of metal-organic precursor decomposition products. For S1 and S4 samples sizes of separate particles which formed the agglomerates are relatively larger comparatively to S2 and S3 samples (especially S3). At the same time the density of S2 and S3 sample is higher.
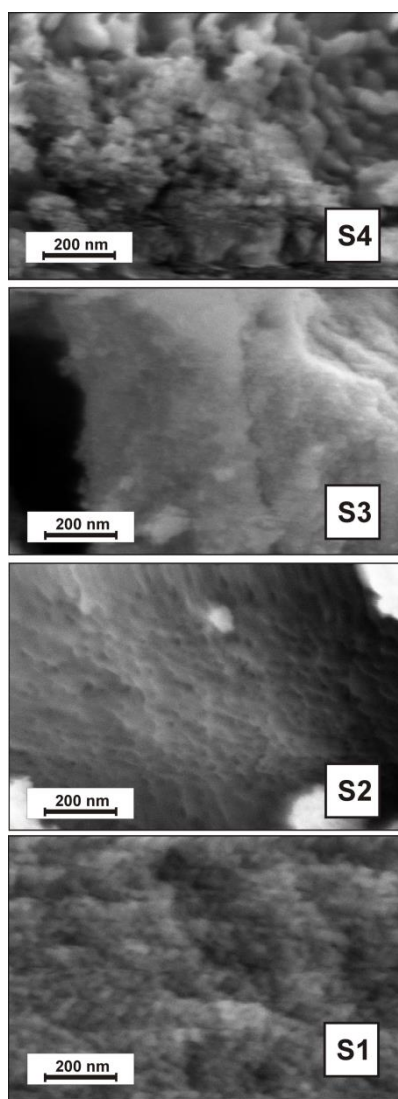
Fig.5. SEM images of γ-Fe₂O samples obtained at different sintering temperatures.

4. CONCLUSIONS

To sum up the experimental data we can allow that the molar ratio between $Fe(NO_3)_3 \cdot 9H_2O$ and $C_6H_8O_7 \cdot H_2O$ precursors is the determination factors of the phase composition, magnetic microstructure and morphological peculiarities of the nanodispersed composite γ-Fe_2O_3 / α-Fe_2O_3 obtained by the thermal decomposition of the synthesized iron citrate hydrate. It was determined that the material syntesized at $Fe(NO_3)_3 \cdot 9H_2O$ and $C_6H_8O_7 \cdot H_2O$ precursors molar ratio equal 1:4 consist of nanoparticles iron oxides in superparamagnetic state with the <5 nm sizes with the maximal content of γ-Fe_2O_3 and minimal macroporous precence. At the same time all composites are characterized by porous structure as a result of organic components evaporation. The investigations of the magnetic microstructure thermal-induced transformation for obtained composites have shown that the phase transition γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$ practically finished after sintering at 400°C. Interparticle dipoledipole magnetic interaction is observed be Mossbauer spectroscopy method. Obtained results are interesting for the approach formulation of magnetic nanomaterials controlled obtaining.

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Нанодисперсні композитні матеріали γ-Fe_2O_3/α-Fe_2O_3 синтезовано термічним розкладанням ксерогелів гідрату цитрату заліза сформованих в результаті висушування золів цитрату заліза, які отримували шляхом змішування розчинів нітрату заліза та лимонної кислоти у різних співвідношеннях. Досліджено вплив молярного співвідношення $Fe(NO_3)_3 \cdot 9H_2O$ та $C_6H_8O_7 \cdot H_2O$, а також температури відпалювання ксерогелю на фазовий склад, кристалічну та магнітну структури та стан поверхні композитних матеріалів. Застосовувалися методи рентгеноструктурного аналізу, месбауерівської спектроскопії, електронної мікроскопії та оптичної спектроскопії у інфрачервоному діапазоні.

Ключові слова: цитрат заліза, золь-гель, молярне співвідношення, нанорозмірні, магнітна мікроструктура, суперпарамагнетизм.