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SYNTHESIS AND PROPERTIES OF SUPERPARAMAGNETIC $\gamma - Fe_2O_3$

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Abstract: Method of nanodispersed γ-Fe2O3 synthesis by thermal decomposition of iron citrate is proposed. The investigations of obtained oxides crystalline and magnetic structures are done. Nanodispersed γ-Fe2O3 with sizes of coherent scattering regions about 4-7 nm was is only one phase after gel sintering at 200, 250 and 300°C; the particles of synthesized materials are in a state of magnetic ordering and in superparamagnetic state. The influence of magnetic dipole interparticles interaction on parameters of Mossbauer spectra is observed. The phenomenological model of the differences between nanodispersed γ-Fe2O3 magnetic microstructures obtained after annealing at different temperatures is presented.

Keywords: γ-Fe2O3, mossbauer, superparamagnetic.

1. INTRODUCTION

The sphere of the practical use of nanodispersed iron oxide includes information store devices, magnetic sensors, controlled drag transference, separation biological objects and environment polluting substances (blue-green algae toxins). The use of iron oxide nanopowder in photocatalytic hydrogen generation devices is of great perspective.

2. EXPERIMENTAL

Nanodispersed γ-Fe2O3 was synthesized by a sol-gel method: slow drying (60°C) in the air of colloidal solute $Fe(NO_3)_3 \cdot 9H_2O$ and $C_6H_8O_7 \cdot H_2O$ for different molar ratio between precursors. The sedimentated iron citrate hydrate during 12-15 days was dried out in the air at 50-60°C.

Obtained xerogel was sintered at temperatures 100, 150, 200, 250, 300 °C during 1 hour. The systems of samples were investigated by X-ray diffractometry (Cu Kα radiation), Mossbauer spectroscopy (calibration relatively α-Fe), scanning electron microscopy

Sintering at the temperature of 100 and 150°C does not change an X-ray amorphous state of the material but after the sintering at the temperatures of 200, 250 and 300°C the only one X-ray crystal phase in the material is γ-Fe2O3 with lattice parameter a =0.83388±0.00015 nm (Fig. 1).

Halos on the XRD patterns are caused by the presence in the samples of X-ray amorphous component.

Average sizes of X-ray coherent scattering areas (CSA) after sintering at temperature of 200°C is 5±1nm and after sintering at 250 and 300°C is about 6±1 nm.

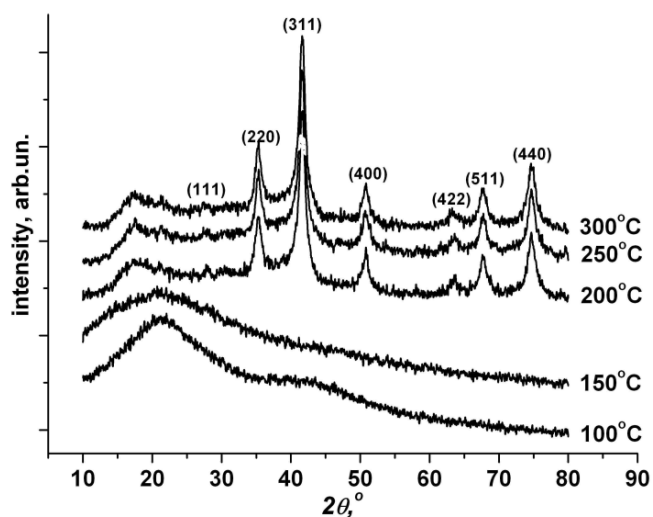*Fig. 1. X-ray diffraction patterns of γ-Fe₂O₃ samples obtained at the different sintering temperatures*

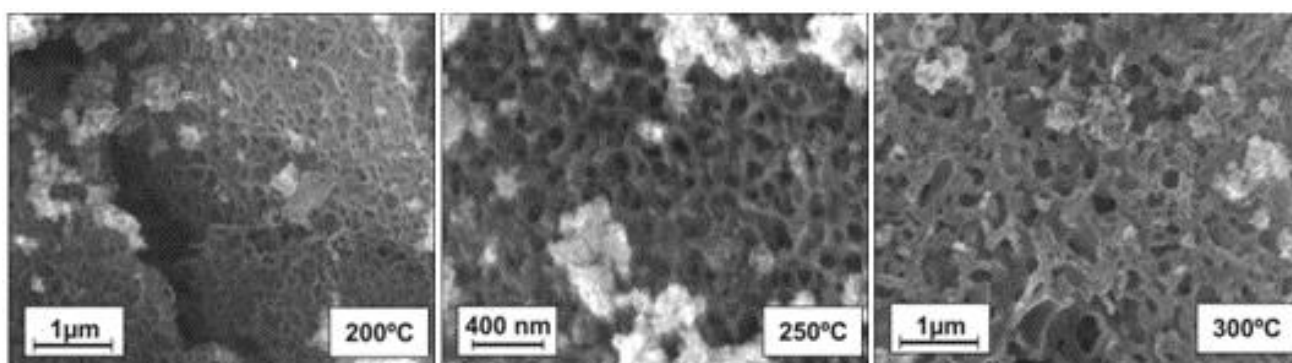*Fig. 2. SEM images of γ-Fe₂O₃ samples obtained at the different sintering temperatures*

Accordingly to scanning electron microscopy data all materials obtained by sintering during 1 hour at 200, 250 and 300°C are characterized by porous structures as a result of evaporation of metal-organic precursor decomposition products (Fig. 2).

Mossbauer spectroscopy gave an independent information about phase composition, magnetic microstructure, iron ions valence. At the conditions of partially disordered magnetic system (samples sintered at 200, 250 and 300°C) it was impossible to establish the responsibility between each partial component of Mossbauer spectra and some type of ^{57}Fe magnetic neighborhood. So, we used the suggestion about the formation in these cases non-interrupted distribution of hyperfine magnetic field on the ^{57}Fe nucleus in the γ-Fe₂O₃ structure.based on the methods [2].

3. RESULTS AND DISCUSSION

Mossbauer spectra synthesized materials with the deconvolution on the partial components are presented in the Fig. 3 and 4, generalization of it parameters – in Tab. 1.

Sintering at the 100°C does not cause any substantial changes in the crystal and magnetic microstructure of the origin sample The values of isomeric shift (δ=0.41 mm/s) and quadrupole splitting (Δ=0.50-0.56 mm/s) for doublet component of the origin and sintered at 100°C samples (Fig. 3) are different form the data for iron citrate [8] and are close to the results in the report [3], where the super-paramagnetic (SP) particles γ-Fe₂O₃ with the diameter <10 nm in polymeric matrix are studied

Sample	H, kOe	δ_s, mm/s	Δ_s, mm/s	ω, mm/s	S, %
Origin xerogel	–	0.41	0.55	0.35	100
100°C	–	0.41	0.57	0.37	100
150 °C	–	0.53	0.81	0.34	49.3
	–	0.52	1.33	0.40	43.8
	–	1.37	2.19	0.30	6.9
200 °C	–	0.48	0.80	0.45	27.7
	–	0.48	1.32	0.45	15.1
	–	0.46	-0.08	3.61	21.6
	429.10*	0.44	-0.03	0.43	35.6
250 °C 1 hour	–	0.47	0.73	0.43	18.0
	–	0.47	1.25	0.49	13.6
	–	0.53	0.01	4.20	24.2
	439.50*	0.45	-0.01	0.37	44.1
250 °C 3 hour	–	0.35	0.75	0.38	19.7
	–	0.33	1.20	0.63	80.2
300 °C	–	0.48	0.74	0.40	36.9
	–	0.47	1.24	0.51	43.0
	412.00*	0.48	-0.09	0.36	20.1

*for materials, obtained sintering at 200, 250 and 300°C average most probably values of hyperfine magnetic field H are presented

Tab. 1. Parameters of Mossbauer Spectra for Synthesized Materials

Annealing at 150°C causes an increase of δ and Δ values and spectra is a superposition of the three partial components (Fig. 4). The two doublet components have the isomeric shift 0.52-0.53 mm/s and Δ 0.80 and 1.32 mm/s, respectively, and correspondence to resonance absorption by the nucleus of tetrahedral coordinated ions Fe^{3+} in the highspin state.
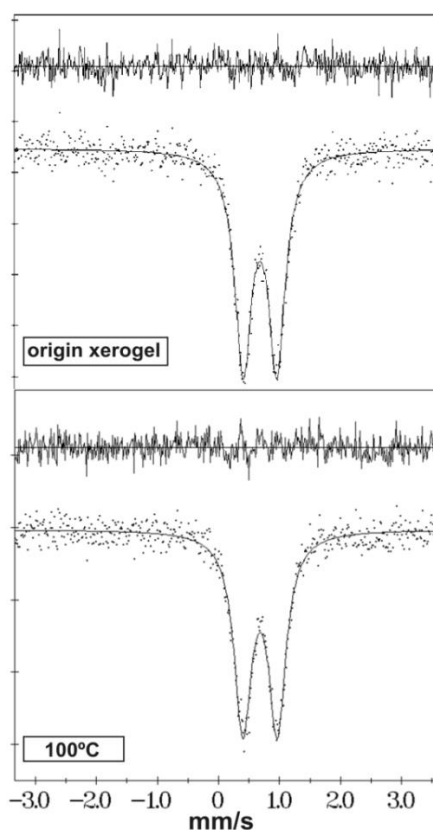

Fig. 3. Mossbauer spectra of synthesized materials: origin xerogel before and after sintering at 100°C during 1 hour

The values of quadrupole splitting depend on the lattice deformation under the Laplace preassure. The third doublet with $\delta=1.37$ mm/s and $\Delta=2.19$ mm/s is formed as a result of resonance absorption by nucleus of Fe^{2+} ions.

Magnetic ordered components of Mossbauer spectra for materials obtained sintering at 200 and 250°C are 35.6 and 44.1% of integral intensity responsively that reflect the particles enlarging with temperature increase. A function of hyperfine field distribution is characterized by one maximum at about 490 kOe. Paramagnetic parts of the spectra contain two components which response to the resonance absorption by ^{57}Fe nucleus in the superficial and inner regions of mesoporous $\gamma\text{-}Fe_2O_3$ 3D-grid. The tendency to decreasing δ and Δ is caused by particle (domain) enlarging and increasing of covalence degree of Fe-O bonds. The presence of wide doublet component with $\Delta\approx0$ is the characteristic peculiarity of these spectra. Similar spectra content was observed for iron oxide nanoclasters obtained by ferric oxalate thermal decomposition in [7].

In the spectra of a sample sintered at the 300°C DC with $\Delta = 0$ is absent, a magnetically ordered part does not exceed 20% of integral intensity with the saving of two component composition of the central doublet .

Values of δ and Δ for the materials obtained by sintering at 200, 250 and 300°C are lower as compared to the data for microcrystal $\gamma\text{-}Fe_2O_3$ [6]. It is caused by attenuation of the superexchange interaction as a result of an increase of the amount of ^{57}Fe nucleus with destroyed bonds (Fig. 2).
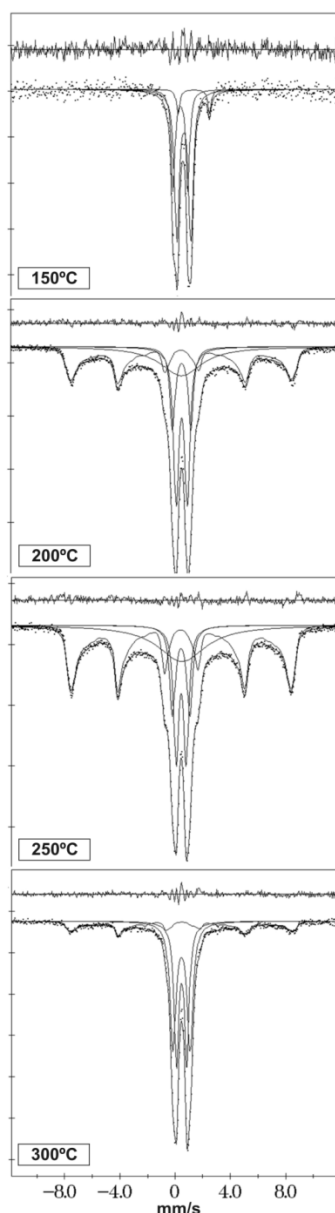

Fig. 4. Mossbauer spectra of materials obtained by sintering at 150, 200, 250 and 300°C during 1 hour

The changes of magnetic microstructures of synthesized material are caused by sizes effects and SP phenomena. The obtained materials are the systems of monodomain clusters with fluctuated magnetic moments This fluctuations cause the broadening of spectra lines and disappearance of magnetic hyperfine structure at a certain value of material magnetic anisotropy which determine the relaxation time τ_r of particle magnetic moment. Relaxation time is calculated as $\tau_r = \tau_0 \exp\left(\frac{KV}{kT}\right)$, where $\tau_r \approx 10^{-9} - 10^{-10} e$, V – particle volume, K – constant of anisotropy, T – temperature. For a particle with the certain values K and V the conversion from superparamagnetic to magnetically ordered state is occurred at the blocking temperature (T_B). For the system of magnetic nanoparticles the variant of magnetic interaction energy (sum of exchange and dipole energies) between two neighbors particles dominance up to anisotropy energy became possible [4]. Influence of exchanged effects on the macroscopic magnetic characteristics of materials is reflected in the appearance of magnetic nanomaterials peculiarities similar to the characteristics of spin glass, the appearance of blocking temperature shift, disagreement of structural and magnetic researches data. Transitions are stimulated by defects, cluster interactions, strains on the interphases boundaries which is typical for nanoclusters system. Oscillation blocking takes place at the effective temperature $T_{ef}=T_B+T^*$ where temperature shift T^* reflects influence of dipole-dipole interaction and determines the value of it energy. Activation of interaction effects will be determined by a module of difference between T_{ef} and temperature of magnetic moment oscillation blocking. Wide doublet component components in the spectra of samples obtained by sintering at 200 and 250 are an intermediate stage between magnetically ordered and SP state of particle in the case of strong dipole-interaction. These systems show SP properties at temperatures higher than TB. At temperatures lower TB these systems are like spin glass and its spectra contains broad doublet. This component is a result of resonance absorption by the ^{57}Fe nucleus for which hyperfine field has the value between a zero and saturation level. Thermal fluctuation of magnetic moment of particles take place however the "temporary hangings up" are possible.

Constant of magnetic anisotropy for the particles of γ-Fe$_2$O$_3$ (d≈6.5 nm) is K=1.2·10^6 J/m^3 [1]. There are another values K =(2.1±0.3)·10^5 J/m^3 for γ-Fe$_2$O$_3$ particle with size 10 nm [8]. For value K =5·10^5 J/m^3 it is obtained that at the T=290 K in SP state there are particles with the sizes less than 4.2-4.8 nm that corresponds to X-ray analysis data.

With sintering at 250°C an increase of treatment time to 3 hours causes the disappearance of magnetic ordered component of Mossbauer spectra. Accordingly to XRD data this sample is amorphous. So, structural and magnetic properties of obtained materials depend on thermal treatment conditions.
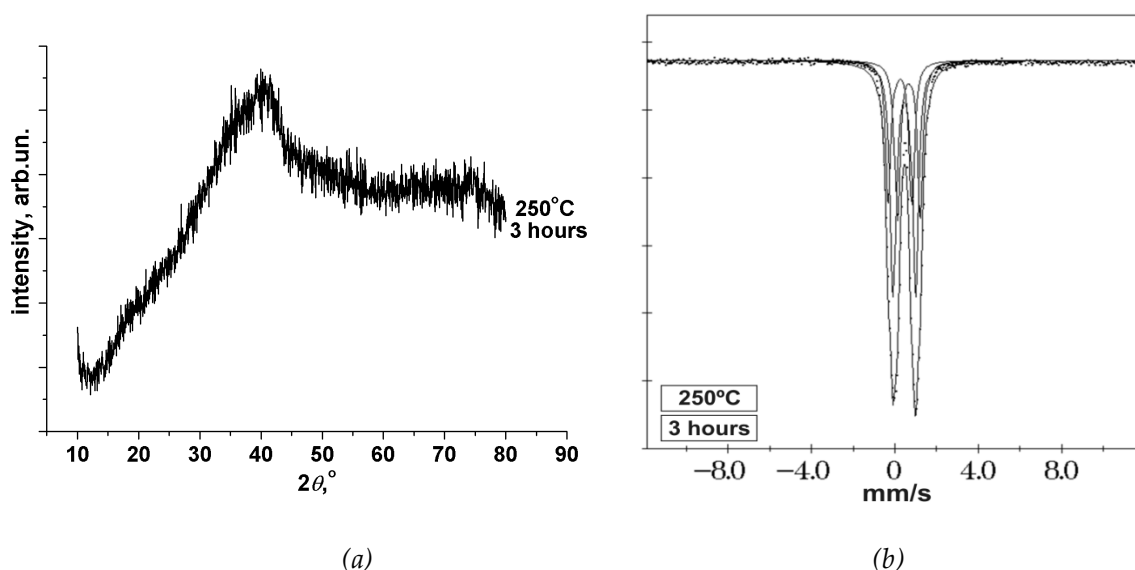

(a)   *(b)*

Fig. 5. XRD pattern (a) and Mossbauer spectra (b) of materials obtained by sintering at 250°C during 3 hour

Doublet component characteristic parameters-based comparative analysis of the systems sintered at $250^{o}C$ during 1 and 3 hours we can take a conclusion about an increase of Fe-O bonding covalence degree without magnetic neighborhood changes.

4. CONCLUSIONS

Generalizing of the experimental data we can build a phenomenological model. As a result of thermal destruction of origin xerogel in the material amorphous regions of γ-Fe_2O_3 phase are nucleated. After sintering at $200^{o}C$ it is partially crystallized with the forming of mesoporous 3D-grid as the result of NO_2, CO_2 and H_2O evaporation. Particle size distribution causes the coexisting of magnetic ordered and superparamagnetic state of a different part of the grid. Sintering temperature increase (up to 250 and $300^{o}C$) leads to the intensification of these processes with an increase of pore sizes and chain thickness. Interparticle dipole-dipole magnetic interaction has been fixed for the materials obtained by xerogel sintering at 200 and $250^{o}C$. Sintering at $250^{o}C$ during 3 hours lead to full dehydration of the material with the bridges destroyed between particles and fragmentation of grid structure with the formation of paramagnetic amorphous product.

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Запропоновано спосіб одержання нанодисперсного γ-Fe₂O₃ шляхом термічного розкладу цитрату заліза. Проведено комплексні дослідження кристалічної та магнітної мікроструктури отриманого оксиду заліза. Виявлено, що після відпалу при температурі 200, 250 та 300 ºC єдиною рентгенокристалічною фазою в матеріалі є нанодисперсний γ-Fe₂O₃ з розміром областей когерентного розсіювання 4-7 нм , частинки якого перебувають в магнітовпорядкованому та в суперпарамагнітному станах. Спостерігався вплив магнітної дипольної міжчастинкової взаємодії на параметри месбауерівських спектрів отриманих матеріалів. Пропонується модель, що пояснює відмінності магнітної мікроструктури нанодисперсного γ-Fe₂O₃, отриманого після відпалу при різних температурах.

Ключові слова: γ-Fe₂O₃ , магнітні наноматеріали, суперпарамагнетизм, месбауерівська спектроскопія.