Nanostructured $\gamma$-Fe$_2$O$_3$: the Correlation between Physical Characteristic and Synthesis Conditions

V. Kotsyubynsky$^1$, A. Hrubiak$^2$, V. Moklyak$^2$, L. Mohnatska$^1$, S. Fedorchenko$^1$

$^1$Vasyl Stefanyk Precarpathian National University, 57 Shevchenko Str., 76018 Ivano-Frankivsk, Ukraine
$^2$Institute of Metal Physics, National Academy of Science, 36 Acad. Vernadsky Boulevard, 03680 Kyiv, Ukraine

Nanostructured iron oxides, in particular $\gamma$-Fe$_2$O$_3$, have numerous applications – both biomedical (magnetic hyperthermia, drug and gene delivery, magnetic resonance imaging) and technological (memristors, cathodes for lithium batteries and pseudocapacitors). The efficiency of material using in each sphere depends on the peculiarities of the crystal and magnetic microstructure, particles sizes and morphology. The investigation of synthesis conditions effect on $\gamma$-Fe$_2$O$_3$ properties is important and topical.

The samples of $\gamma$-Fe$_2$O$_3$ were obtained by slowly mixing of Fe(NO$_3$)$_3$·9H$_2$O and C$_6$H$_8$O$_7$·H$_2$O solutions (molarity 0.025M, 0.1M, 0.3M, 0.5M) with the next iron citrate xerogel annealing at 200°C [1]. The sizes of coherent scattering areas growth in the range 6-12 nm with the increase of initial molarity were determined (XRD data). The correlation between particles sizes and synthesis conditions was observed by Mossbauer spectroscopy as a change of Fe$^{57}$ nuclei relative contents with different local surroundings in the inner and outer layers of particles (Fig.1). It was determined that the obtained oxides are the systems of monodomain particles with fluctuated magnetic moments. All obtained materials are characterized by porous structure (scanning electron microscopy data) as a result of organic products evaporation. The tendency to porosity increasing with the molarity enlarging was found. The frequency dependences of samples complex conductivity (impedance spectroscopy data) are typical for disordered semiconductors and explained by small polaron hopping mechanism between metal sites with the valence interchange process. The dc-conductivity and charge carriers hopping frequency both despite with the particle size enlarging.

Adsorption/desorption isotherms for all samples have H4 hysteresis (typical for mesoporous materials). Specific surface areas (low temperature nitrogen adsorption data) non-linear vary depending on the molarity of precursors in a range of 95-165 m$^2$/g with the maximum for 0.3M sample. Dependences of the pores volume on pores size are characterized by the pore sizes in the range of 3-7 nm. The contribution of small mesopores (diameter about 2-3 nm) is insignificant. For all materials optical band gap energies (optical adsorption spectroscopy data) is close to 2 eV and correspond to direct transitions. The relationship between the effective band gaps and the average particle sizes based on the Brus model was proposed