Synthesis and microstructural investigation of Mn $_x$Zn $_{1-x}$Fe $_2$O$_4$ magnetic fluids

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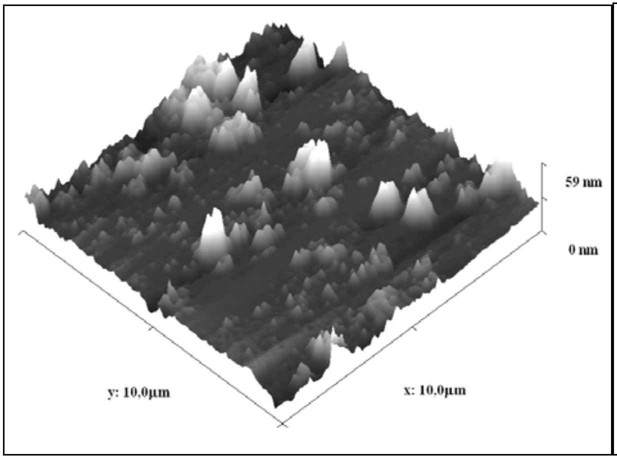
Magnetic materials in the form of colloidal nanoparticles have received many attention because of their unique magnetic proprieties, which are dominated by superparamagnetism. These materials can be used in many applications, including magnetic fluids. For most biological purposes the magnetic nanoparticles should have between 5 and 15 nm in diameter that ensure their stable dispersion in normal environmental conditions [1-2]. There are many methods for the preparation of ferrite powders, such as: co-precipitation method [3], hydrothermal method [4], micro-emulsion method [5], the sol-gel method [6] and others. Co-precipitation from metal salts solutions is a rather simple and available method still widely applied. The purpose of this work was to prepare colloidal aqueous suspensions of $Mn_xZn_{1-x}Fe_2O_4$ (x= 0.9, 0.7, 0.5, 0.3) and to study the structure, morphology as well magnetic proprieties of the obtained materials.
Ferrofluid preparation. Ferrophase particles were prepared by chemical precipitation from $FeCl_3x7H_2O$ on a side and $MnSO_4x6H_2O$ and $ZnSO_4x6H_2O$ solutions on the other side, in the presence of NaOH under continuous magnetic stirring at constant temperature of about 80 ^{0}C for 1h. Sodium oleate in aqueous solution was used to coat the ferrophase particles. Coating of surfactant was carried out at 80^0 C for 1h under continuous stirring.
Microstructural characterization. SEM device was used to characterize the shape and average size of submicron magnetic particles. AFM device, provided with commercial standard silicon nitride cantilevers (NSC21) having a force constant of 17.5 Nm^{-1}, 210 kHz resonance frequency and tips with radii between 10 and 20 nm (intermittent contact, tapping mode cantilevers) was utilized also to investigate nanoparticle and nanoparticle aggregation topology.
X-ray analysis. Shimadzu XRD 6000 device with CuKα radiation and corresponding soft package were utilized.
Magnetization measurements were performed using a vibrating sample magnetometer ***Quantum Design, model 6000*** on native ferrofluid samples.

Results and discussion. The magnetic fluid samples were dark brown materials that exhibited obvious magnetic behavior in the presence of a permanent magnet. The SEM micrographs revealed that the investigated colloidal magnetic particles are mostly spherical ranging between 0.1 μm and 1.7 μm for all three samples. AFM scanning provided additional data regarding the height of the investigated colloidal particles as well as for the rare aggregates or short chains evidenced within the samples - no more than 60 nm height. Typical hysteresis plot obtained from VSM measurement for $Mn_{0.3}Zn_{0.7}Fe_2O_4$ sample (for example) indicated the saturation value of 70 Am^2/kg (Fig. 2). Saturation magnetization is increasing with the Mn concentration due to the arrangement within the spinel structural units. Using magnetization data, the average sizes of magnetic diameter were calculated following Langevin's equation. The most relevant data regarding the influence of the ratio Mn:Zn were provided by the XRD analysis XRD graphs (Fig. 3) that allowed the calculation of the crystalite diameter in each case (applying the Debye- Scherrer equation)- that increased with the content of Mn.
Conclusion. The various ratios of Mn:Zn within the magnetic particles representing the ferrophase of several aqueous magnetic fluids led to the increase of the saturation magnetization as well as of the spinel chrystalyte diameter. Further applications in plant biotechnology are intended based on the magnetic properties and microstructural features (rather uniform granulation) of the discussed magnetic fluids.

References:
[1] T. Neuberger, B. Schoepf, H. Hoffman, et al., J. Magn. Magn. Mater. 293, (2005), 483;
[2] A.K. Gupta, M. Gupta, Biomater. 26 (2005), 3995;

[3] E. Blums, M. Mihail, G. Kronkalns, J., IEEE Trans. Magn., 1993, 29 (6):3267-3269;
[4] S. Verma, P.A. Joy, Y.B. Khollam, Mater. Lett., 2004, 1092- 1095;
[5] A. Kosak, D. Makovec, A. Znidarsic, et al , J. Eur. Cer. Soc., 2004, 959-962;
[6] Z.X. Yue, W.Y. Guo, J. Zhou, et al, J. Magn. Magn. Mater., 2004, 364-374;



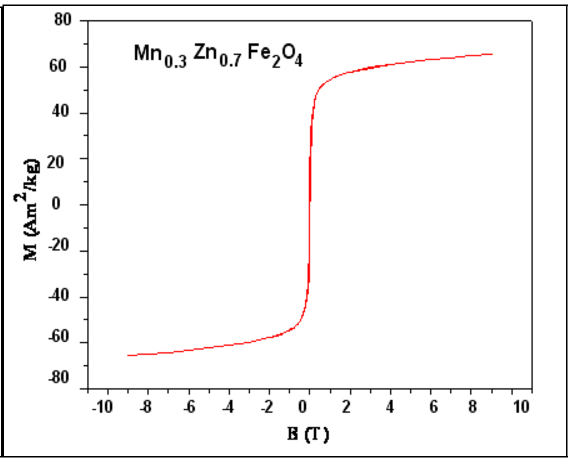


Fig. 1. AFM investigation result – 3D image (left); Fig. 2. Magnetization curve of MnZn ferrite colloidal particles (right)

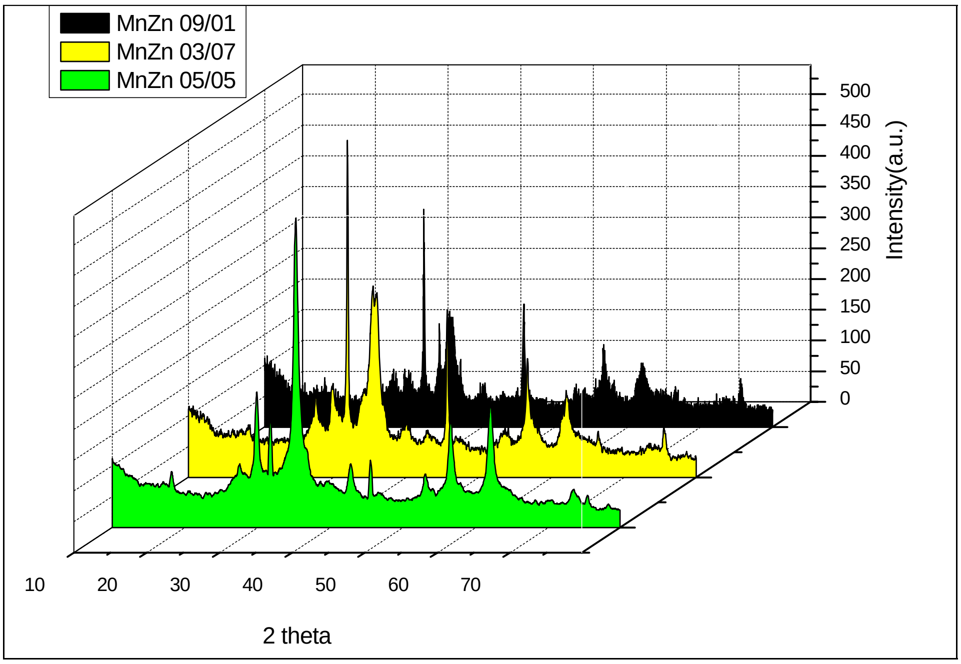


Fig. 3. XRD recordings for $Mn_xZn_{1-x}\,Fe_2O_4$ samples