THE EFFECT OF IRON DOPING ON MAGNETIC AND STRUCTURAL PROPERTIES OF ZnO NANOPARTICLES PREPARED BY WET CHEMICAL METHODS

I. Kuryliszyn-Kudelska[1*], A. Grabias[2], W. Dobrowolski[1], M. Arciszewska[1], D. Sibera[3], U. Narkiewicz[3], J. Rosowska[1], J. Kaszewski[1], B. Witkowski[1], Ł. Wachnicki[1], M. Godlewski[1]

[1] *Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland*

[2] *Łukasiewicz Research Network – Institute of Microelectronics and Photonics, Wólczyńska 133, 01-919 Warsaw, Poland*

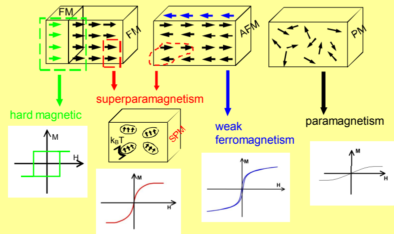
[3] *West Pomeranian University of Technology, Institute of Chemical and Environment Engineering, Pulaskiego 10, 70-322 Szczecin, Poland*

[*]Correspondance to: kuryl@ifpan.edu.pl

Why nanosized Diluted Magnetic Oxides (DMO)?

- **DMO** (e.g. **TM** doped **ZnO**) - one of the most intensively studied materials due to theoretically predicted HT ferromagnetism.
- **magnetic properties of DMO under debate**; there is no understanding of the origin of the observed magnetic properties in the literature; various magnetic properties are observed (HT ferromagnetism, LT ferromagnetism, superparamagnetism, paramagnetism, spin-glass behavior).
- additional effects at the nanoscale e.g. **superparamagnetism** - important due to the applications in biomedicine.
- **inorganic magnetic nanomaterials** - number of practical applications: biotechnology, medical diagnostics, adressed drug delivery, cancer treatment, MRI, high density data storage, magnetic sensors.
- **iron oxide nanoparticles** - biocompatibility, non-toxicity, in clinical use.

Magnetic Nanoparticles



Superparamagnetism

- Relaxation time of the moment of a particle τ (Néel-Brown expression – noninteracting particles), $\tau = \tau_0 \exp(KV/k_BT)$; $\tau_0 = 10^{-9}$ s - 10^{-13} s .
- If the particles moments reverse at times shorter than experimental times scales, the system is in superparamagnetic state, if not, it is in the so-called blocked state. T_B separates these two regimes.
- T_B is not uniquely defined. It depends on the timescale of experimental technique (a shorter experimental time window then a larger value of T_B is obtained).

Real systems of magnetic nanoparticles

agglomeration

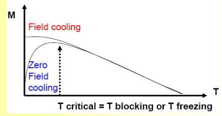
interparticle interactions:
- long range dipole interactions
- exchange interactions

surface effects:
- surface spin glass like behavior
- core-surface anisotropy
- noncllinear ordering of spins

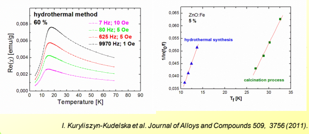
spin glass-like behavior

- J.L. Dorman et al. NanoStructured Materials, Vol 12, 757, 1999
- K. Parekh et al. Appl. Phys A, Vol 106, 223, 2012

- sometimes it becomes hard to distinguish between SPM and SG-like systems
- superparamagnetism and spin glass exhibit similar behavior from DC magnetization



Frequency dependence of AC magnetic susceptibility is important tool to study the assembly of magnetic nanoparticles and distinguish between SPM and SG-like systems.



very sensitive technique

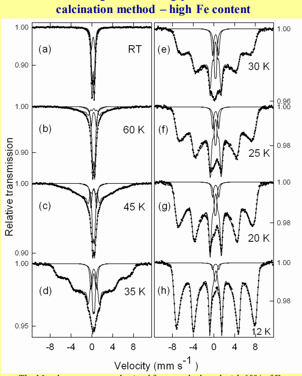
$\chi_{material}(f, T, H)$

$\Phi = \Delta T_B / T_f \Delta \log_{10}(f)$

I. Kuryliszyn-Kudelska et al. Journal of Alloys and Compounds 509, 3756 (2011).

Mössbauer Spectroscopy Measurements

calcination method – high Fe content

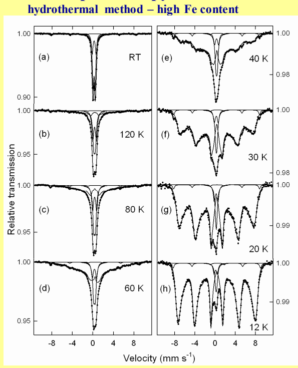


The Mössbauer spectra obtained for sample doped with 60% of Fe.

The Mössbauer spectra obtained at RT as well as at temperatures exceeding 60 K are composed of the nonmagnetic quadrupole doublets with hyperfine parameters (QS_1 = 0.40 mm s^{-1}, QS_2 = 0.70 mm s^{-1}). The isomer shifts related to both quadrupole doublets reveal almost identical value of 0.34 mm s^{-1} for all samples. Such isomer shift is typical for trivalent iron (Fe^{3+}) in octahedral coordination. The core - shell morphology of the nanoparticles was proposed in order to interpret the QS_1 and QS_2 quadrupole doublets, respectively. **These spectra reveal the presence of the nanoparticles of $ZnFe_2O_4$ spinel.**

Mössbauer Spectroscopy Measurements

hydrothermal method – high Fe content

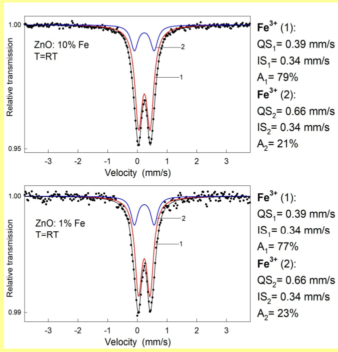


The Mössbauer spectra obtained for sample doped with 70% of Fe.

The Mössbauer spectra are very similar to that obtained for calcination method. The presence of two quadrupole doublets revealed that Fe^{3+} ions are located in two structural positions with a higher (QS_1) and lower (QS_2) local symmetry. At room temperature all Mössbauer spectra consist of two quadrupole doublets characteristic of Fe^{3+} ions with quadrupole splitting values of QS_1 = 0.42 mm s^{-1} and QS_2 = 0.75 mm s^{-1}. **The presence of $ZnFe_2O_4$ spinel was confirmed.** The core - shell morphology of the nanoparticles was proposed in order to interpret the QS_1 and QS_2 quadrupole doublets, respectively.

Mössbauer Spectroscopy Measurements

hydrothermal method – low Fe content (10%, 1%)

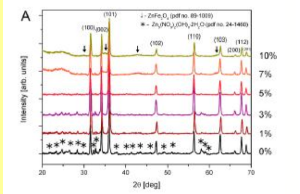


The presence of two quadrupole doublets with hyperfine parameters (QS_1 = 0.39 mm s^{-1}, QS_2 = 0.66 mm s^{-1}) shows that Fe^{3+} ions are located in two structural positions with a higher (QS_1) and lower (QS_2) local symmetry. **Similarly to high concentration regime, the presence of $ZnFe_2O_4$ spinel was confirmed.**

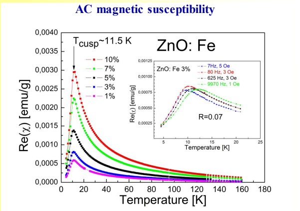
Hydrothermal method – low Fe content

- hydrothermal method (from 1% up to 7% of Fe).
- **XRD revealed the presence of only ZnO for sample with 1% of Fe.**
- supermaganetic behavior is observed in AC magnetic susceptibility for all doped samples.
- **Mössbauer spectroscopy revealed the presence of $ZnFe_2O_4$ nanocrystals with core/shell morphology (QS_1/QS_2) for all the samples.**
- Fe^{2+} ions are not detected.

XRD measurements

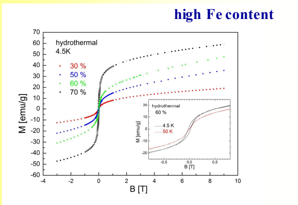


AC magnetic susceptibility

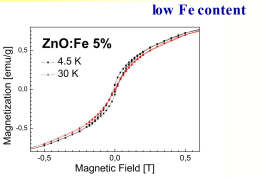


Hydrothermal method – magnetization data

high Fe content



low Fe content



The low values of coercivity field H_C (depending on the Fe concentration).

Summary

- if possible the solubility of Fe in nanoscopic ZnO obtained by chemical methods is below the observation limit.
- very extensive characterization is required to understand the magnetic properties of nanosized ZnO:Fe.
- magnetic properties are associated with the presence of nanoscopic $ZnFe_2O_4$.
- magnetic nanocomposities ZnO/$ZnFe_2O_4$ can be useful from the point of view of future applications (non-toxicity and biocompability of ZnO, low toxicity of $ZnFe_2O_4$).