The Effect of Iron Content on Properties of ZnO:Fe Nanoparticles Prepared by Microwave Hydrothermal Method.

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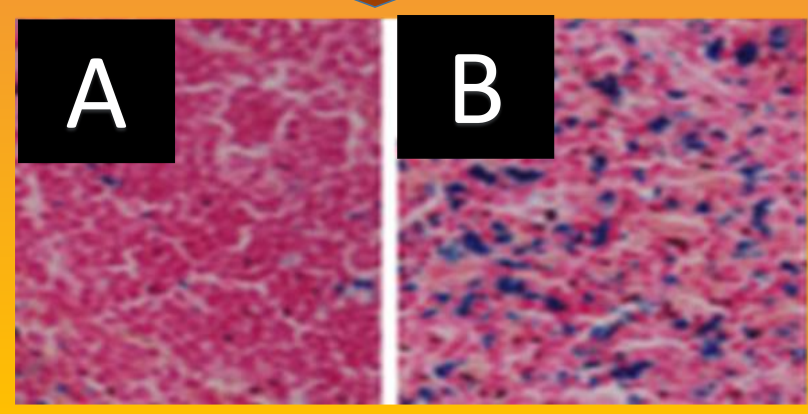
Motivation

Zinc oxide (ZnO) is a II-VI semiconductor, which has been extensively studied since the 1930s. Undying interest in this material results from its unique properties such as a relatively high exciton binding energy (60 meV) at room temperature, direct wide band gap (3.37 eV), piezoelectricity, high transparency at heavy n-type doping. Furthermore, good biocompatibility, low-cost, antibacterial properties of ZnO make it an adequate material for biomedical applications. Nanoparticles based on ZnO are readily biodegradable to the Zn ionic form in target tissues. It is an important property of ZnO nanoparticles leading to simple and rapid elimination from a living organism. To increase the applicability of ZnO nanoparticles in the field of biology and medicine, they are often doped with rare earth or transition metals, e.g. Fe. It is worth mentioning the possibility of using nanoparticles doped with iron as a good carriers of exogenous iron in the living body. ZnO:Fe nanoparticles may be a novel, more effective form of delivery of bioactive substances. Preliminary studies have been carried out and proved to be very promising. On the other hand, the introduction of iron ions into ZnO nanoparticles can have many consequences and may strongly affect the structural and physical properties. Among others, the substitution Zn by Fe ions may introduce some impurity levels, change the energy level structure of materials and modification of magnetic properties. The main goal of the work was to obtain ZnO nanoparticles applicable in biology and medicine and to conduct research to check the effect of Fe content on the morphologies, crystal structures, optical and magnetic properties of Fe-doped ZnO nanopowders.

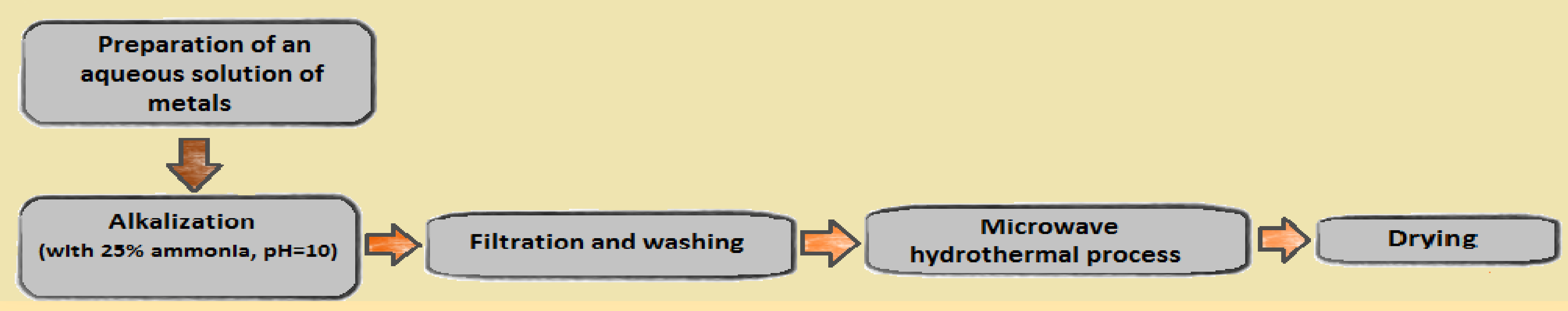
Proof of concept



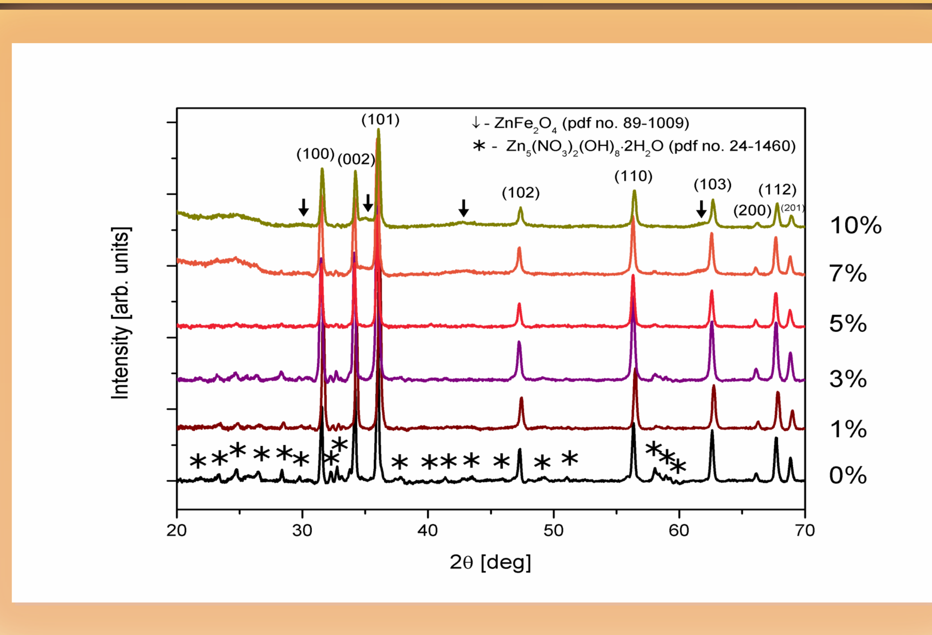
Two representative microphotographs of spleen sections. Comparison of the presence of iron (blue areas) in control and experimental group of mice (with administered 24 h before ZnO:Fe NPs) [Kielbik et al. Nanoscale Research Letters 2019, 14:373].

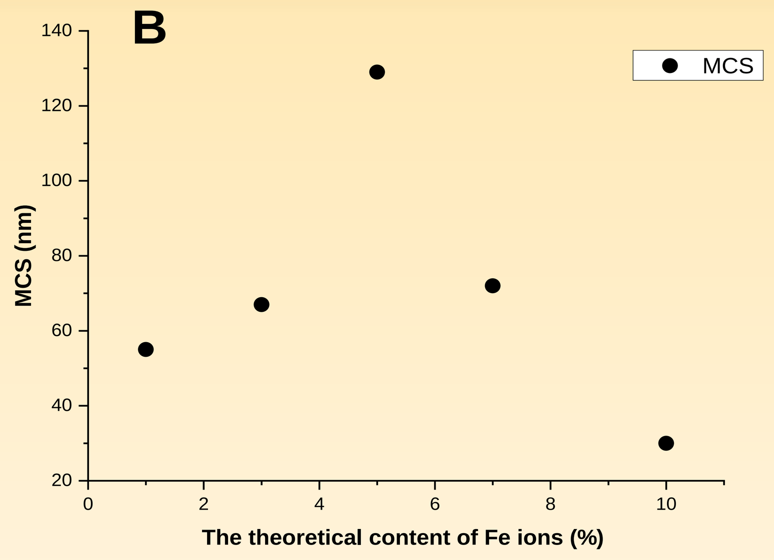
Synthesis

ZnO nanopowders doped with x mol % of Fe (x=0, 1, 3, 5, 7, 10) were prepared by a microwave hydrothermal method using zinc and iron nitrates: $Zn(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$, respectively. The solutions were alkalized with aqueous ammonia solution (25%, Carl Roth) to pH=9.5. Hydrothermal process was conducted at 60 bar by 20 min. The samples were dried overnight. All ZnO: xFe nanopowders were prepared with the same procedure to study the effect of iron content on properties of our nanoparticles.



Phase analysis

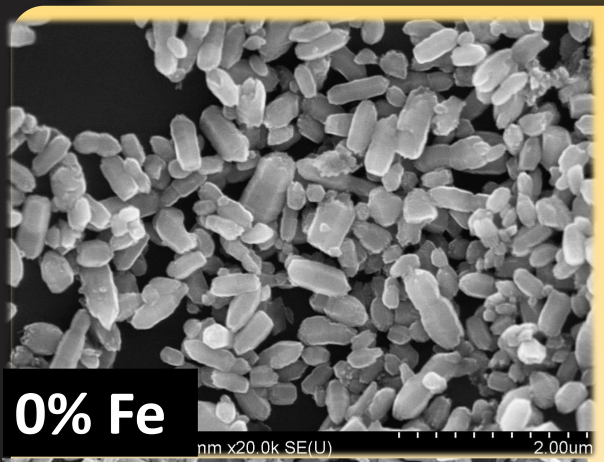




- The XRD diffraction peaks for (100), (002) and (101) Miller planes confirm the hexagonal wurtzite structure with space group $P6_3mc$ in all tested samples;
- In each of the samples, some inclusions were observed (especially in sample c), resulting from the presence of nitrate groups: $Zn_5(NO_3)_2(OH)_8 \cdot 2H_2O$;
- Samples with the highest iron concentration (sample E and F) reveal additional reflexes, which are probably associated with the presence of zinc ferrite $ZnFe_2O_4$ phase (PDF No. 89-1009);
- ZnO: 5%mol. Fe - sample without additional visible foreign phases

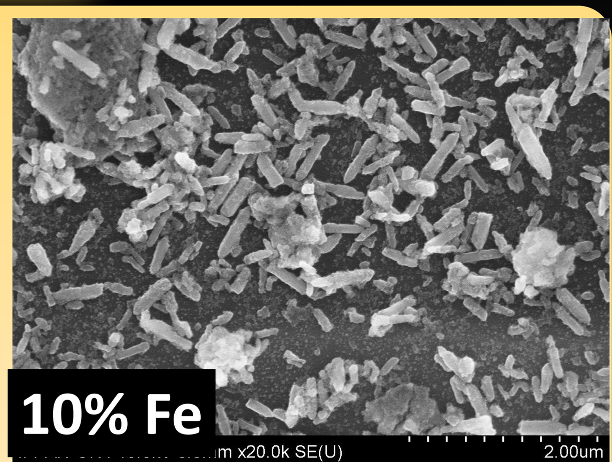
Diffraction patterns (A) and MCS (mean crystallite size) (B) of ZnO nanoparticles doped with different content of Fe ions.

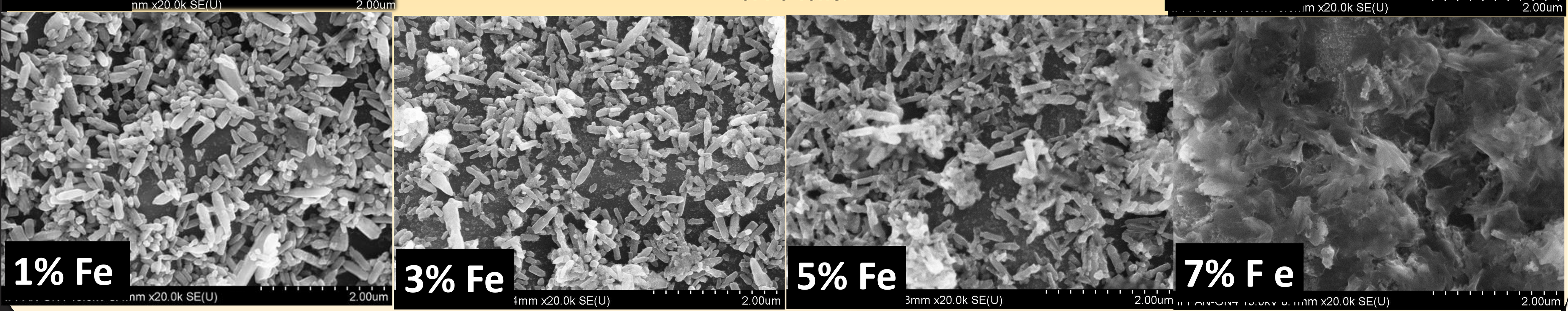
SEM studies



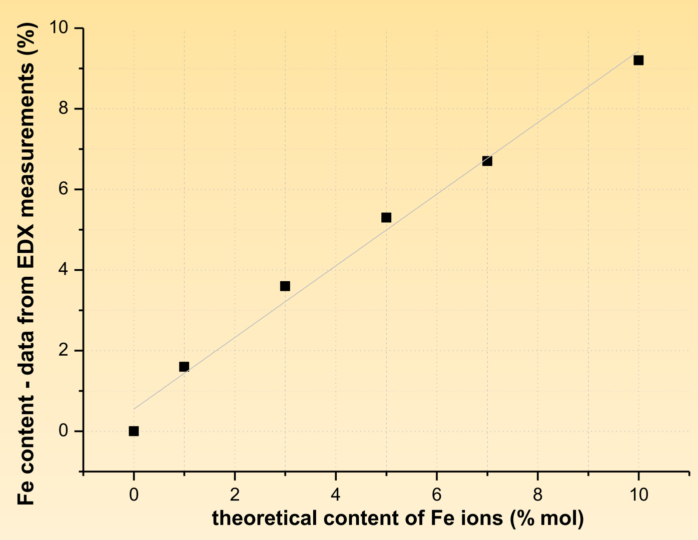
- In the majority (except for sample E with an iron content of 7%), the the SEM images indicate longitudinal shape of grains;
- the size of NPs reduces with Fe doping,
- The largest size of grains is obtained for sample A (pure ZnO) – (392±142)nm.

SEM images of ZnO nanoparticles doped with different concentrations of Fe ions.



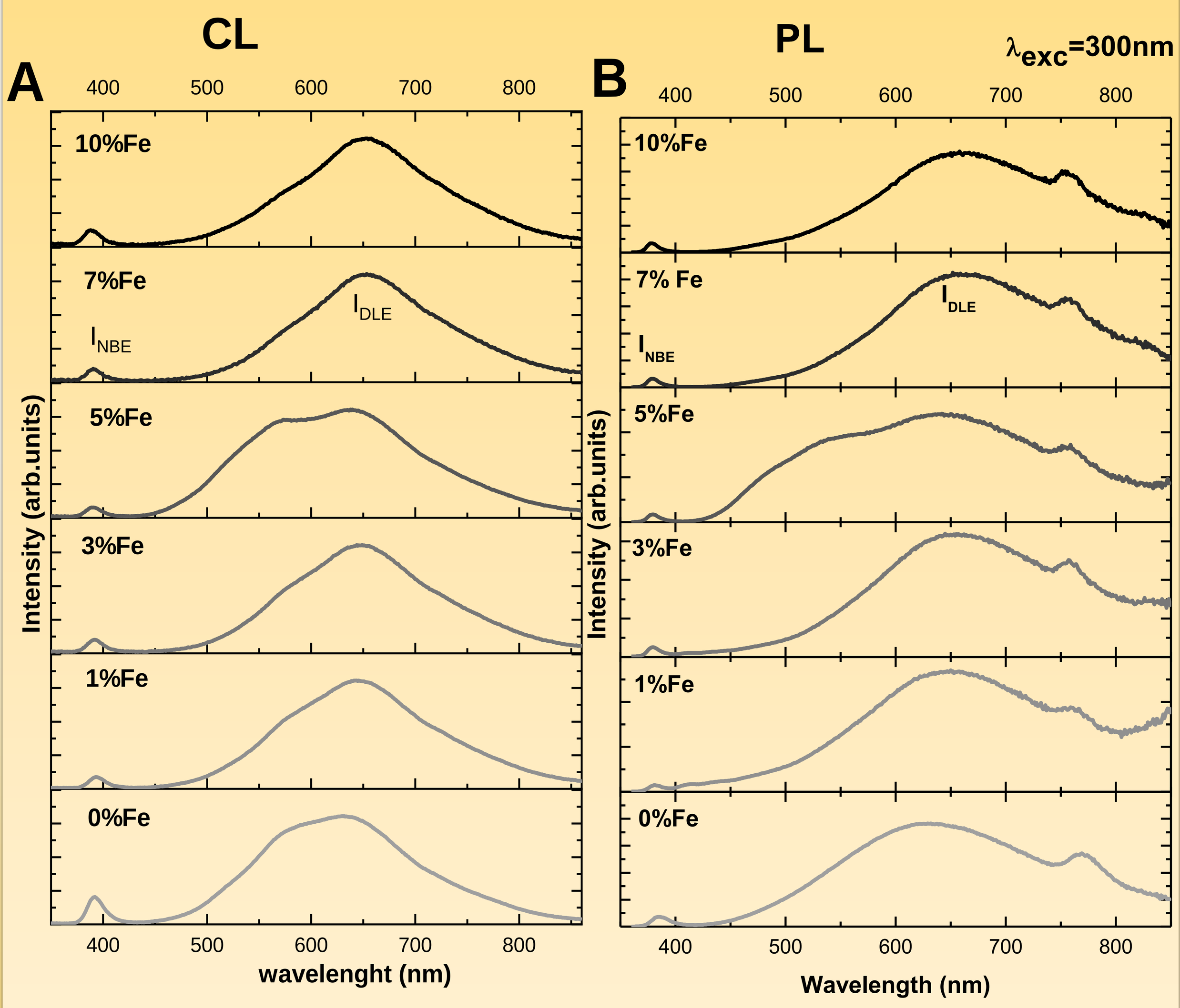


EDX measurements



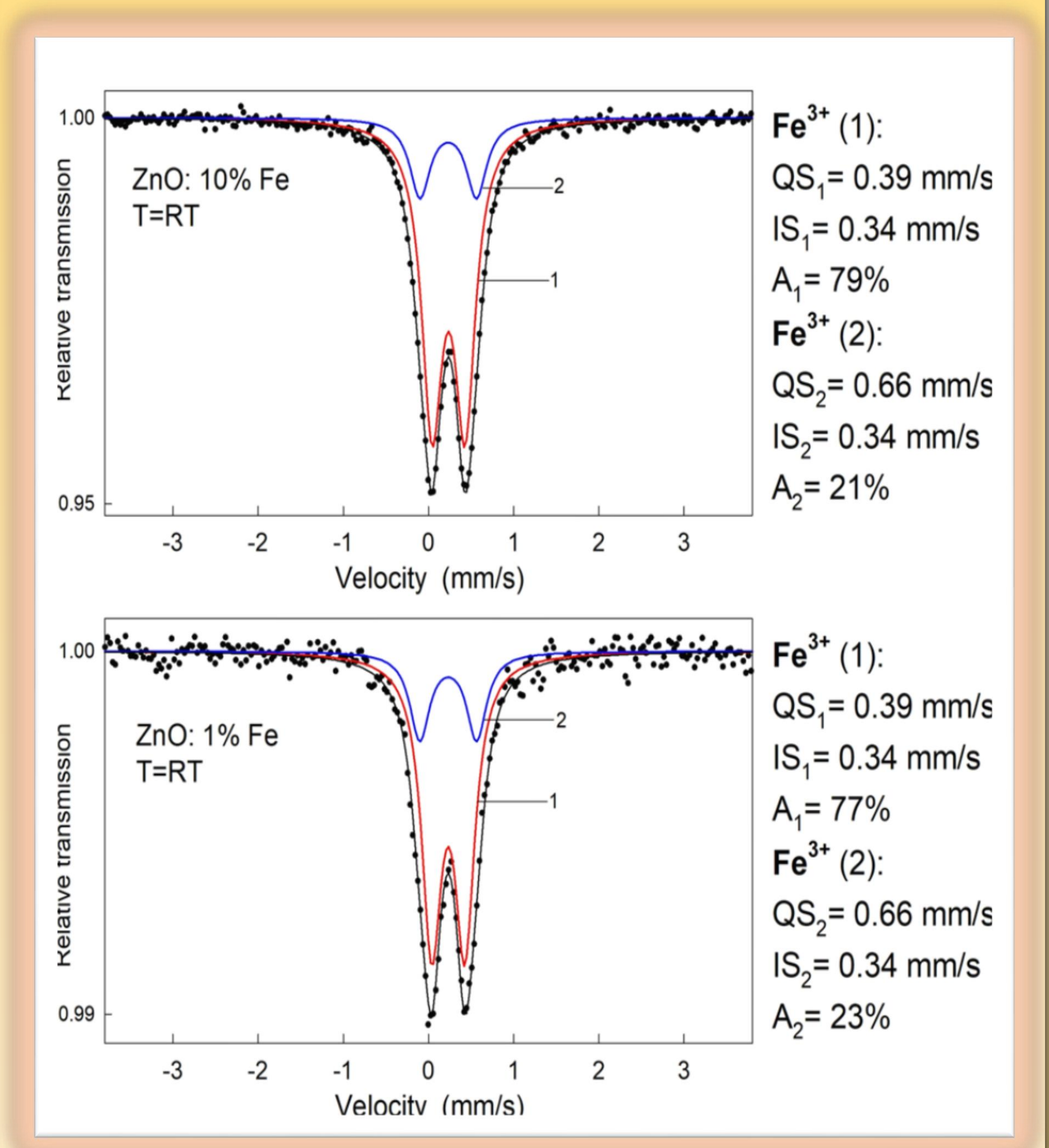
- The percentage of iron in ZnO samples obtained from EDX measurements is close to the theoretical values.
- This may indicate that the Fe atoms were succesfully incorporated into the ZnO nanoparticles.

CL and PL measurements

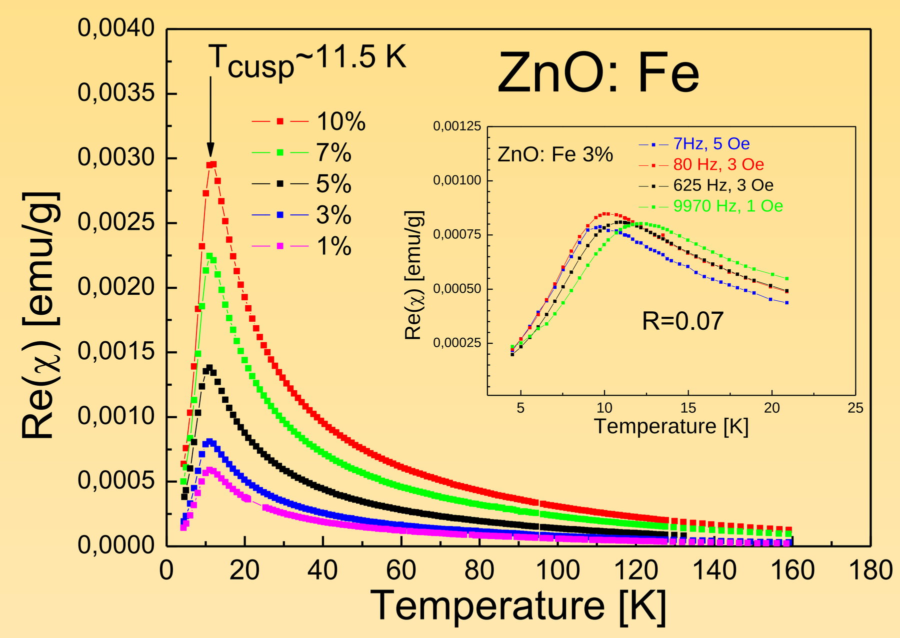


A: CL spectra of ZnO nanoparticles;
B: PL spectra excited at 300 nm;

Mőssbauer spectroscopy



Magnetic properties



The temperature dependence of the real part of the AC susceptibility for nanosized ZnO samples doped with: 1%, 3%, 5%, 7% and 10% of Fe at f=625 Hz .

- the Re(χ) curves show pronounced maxima. The above described experimental feature can be observed in both the superparamagnetic and spin glass like systems;
- For all samples we observed that the positions of the maxima (T_{cusp}) shift towards higher values with increasing driving frequency (the inset in Figure);
- the observed frequency-dependent behavior in Re(χ) data may be attributed to the blocking process of superparamagnetism or freezing process in spin glass systems;
- From the relation: $R = \Delta T_{cusp} / T_{cusp} \Delta \log_{10}(f)$, where:

ΔT_{cusp} - the difference between the peak temperature measured in the $\Delta \log_{10}(f)$
f - the AC magnetic field frequency

we find $R \approx 0.07$ → **superparamagnetic behavior**.

Conclusions

- Optical investigations have shown that the increasing concentration of Fe ions does not quench the ZnO luminescence, which is quite a suprising result; Fe ions do not act as a killer center of CL and PL emission!
- magnetic studies indicate that the nanoparticles exhibit superparamagnetic behaviour; from Mőssbauer spectra – presence of Fe^{2+} ions was not observed;
- the obtained ZnO:Fe nanoparticles, after appropriate optimization may be used as a good carriers of exogenous iron in the living body – verification of our ideas was performed on laboratory animals.