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Heating of Zn-substituted manganese ferrite magnetic nanoparticles in alternating magnetic field

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Abstract. In this work, the heating capability of Zn-substituted manganese ferrite $Zn_xMn_{1-x}Fe_2O_4$ magnetic nanoparticles with Zn content varying from 0% to 90% has been studied. The nanoparticles of diameter 5-25 nm were synthesized by co-precipitation of metal salt solution with NaOH solution. It was shown that specific absorption rate has a peak for the compound with 20% Zn content. Also the magnetic liquids, based on the synthesized ferrite powders, show higher absorption rate what indicates the existence of Brown relaxation mechanism in the system.

Introduction. Nowadays magnetic nanoparticles (MNps) are used in increasing number of applications including biomedical ones due to the possibility of MNps injection and accumulation in the target tissue [1]. Heating of MNps in alternating (AC) magnetic field leads to the therapeutic effect either through direct thermal treatment (magnetic hyperthermia, MH) or due to the release of the drug encapsulated in the MNps. During MH, a magnetic liquid (a suspension of MNps in a biocompatible solution) is heated up inside the tumour under an external ac magnetic field of 1 kHz- 1 MHz frequency. As the result, tumor is also heated up. At the temperature of about 42-43°C irreversible changes start in the tumor, but the healthy tissue remains unaffected [1].

Up to now, only few materials are used in vivo – magnetite and maghemite [1]. Various nontoxic ferrites are now being considered for MH since they have crystal structure similar to mentioned above compounds. Zn-substituted manganese ferrites have high saturation magnetization and low coercivity which makes them promising for MH [2]. High saturation magnetization helps to use less amounts of magnetic materials and decreases the harmful influence on the patient body keeping the same heating rate [3]. Moreover, a MNp with size below the critical one behaves as a superparamagnetic. One more important criterion is uniformity of the particles. It helps to control uniform heating rate of the magnetic liquid and, hence, the heated tissue.

Experimental. *Preparation of ferrite samples.* All samples have been synthesized using co-precipitation method in the Ar atmosphere. For synthesis of the sample with 50% Zn substitution 0.5M $MnCl_2$, $ZnNO_3$ and 1M $FeCl_3$ solutions were mixed in ratio 1:1:2 and heated up to 85 ºC, stirred, then 0.64 M NaOH solution has been added as a catalyst. All the solution was heated up to 95 ºC for 1 hour and then washed and characterized. The rest of samples with Zn substitution equal 10%, 20%,…, 90% have been prepared in a similar way [4]. Following ion formula describes the process (Eq.1).

$$Fe^{3+}+xZn^{2+}+(1-x)Mn^{2+} \xrightarrow{8OH^-} Zn_xMn_{1-x}Fe_2O_4+4H_2O \qquad (1)$$

Obtained nanoparticles have size ca. 10 nm; one should note that for the traditional co-precipitation method the size of produced particles is normally bigger.

Magnetic liquid preparation. Magnetic liquids have been prepared using the samples with 10%, 20% and 60% Zn. The MNps powder was dispersed in Millipore water and sonicated in the ultrasound bath.

Heating measurements. To measure the heating rate of the nanoparticles we developed the setup comprising the magnetic field generator that provides the AC magnetic field of 72 Oe with the frequency 100 kHz. To measure the temperature of the sample the differential thermocouple, voltmeter Agilent 34410A and computer data acquisition system were used. Cooling system was developed to prevent the parasitic heating of the sample through the direct heat exchange with the coil.

Results. *TEM measurements.* MNps have well established spherical shape. Size of grains is varying in a wide range from 5 nm for the sample with 60% of Zn up to 25 nm for 20% Zn sample (Fig. 1).

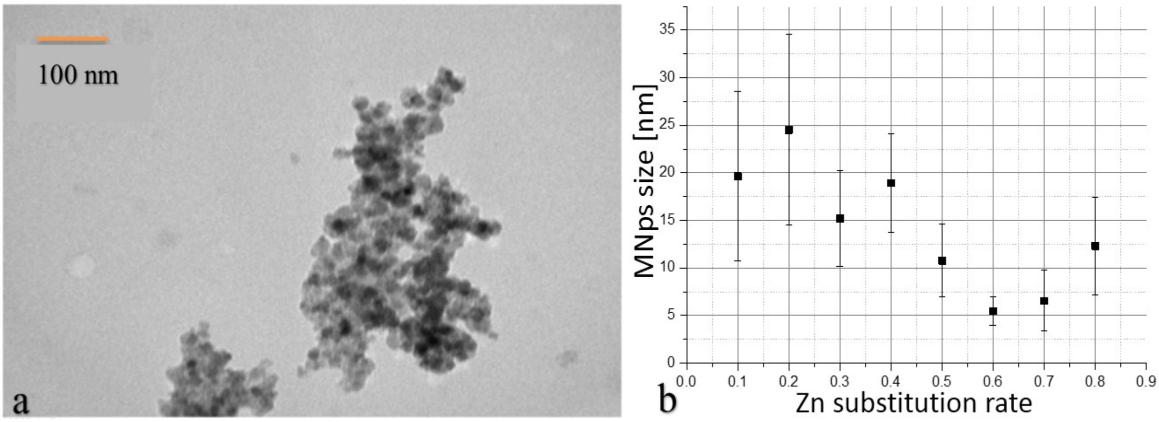

Fig. 1. a – TEM image of the sample with 40% Zn, b – Size distribution obtained using the statistical analysis of TEM images (ImageJ editor).

Dispersion follows the same tendency – it is ±1.5 nm for 60% Zn sample and ±10 nm for 20% Zn sample. TEM image shows that the particles are agglomerated into clusters, which indicates either magnetic nature of the MNps or the inhomogeneity of TEM sample drop drying. To prove it one of the theories dynamic light scattering measurement (DLS) has been performed. Determined radii of MNps suspended in water appeared to be between 195 and 396 nm, which is few times more than for dry nanoparticles, and no tendency in size changes was mentioned. This indicates that dispersed nanoparticles in water agglomerate in huge clusters of diameter about 0.4 µm.

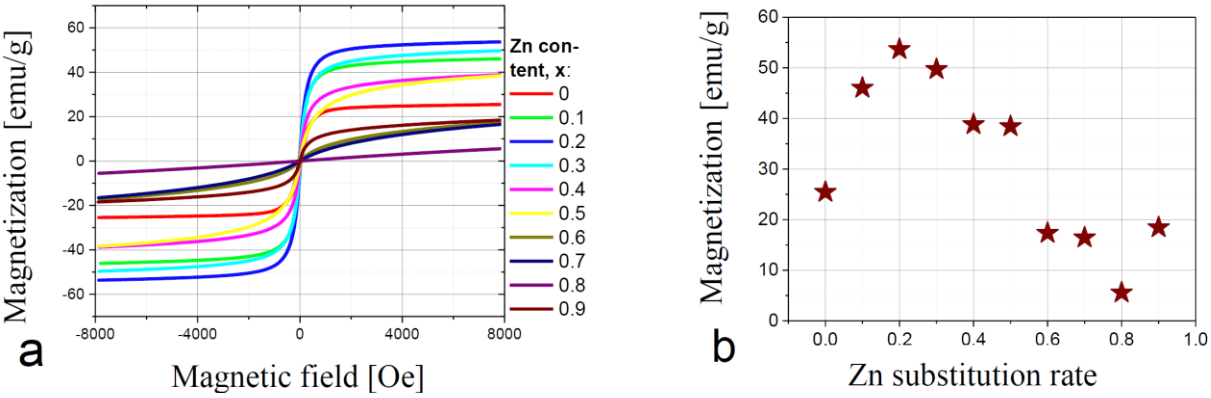

Fig. 2. a – M(H) curves for $Zn_xMn_{1-x}Fe_2O_4$ samples at RT; b – magnetization value taken at maximal magnetic field.

X-ray diffraction. Samples crystal structure was investigated on XRD RIGAKU D/MAX 2500 (Japan), graphite monochromator on a copper wavelength 1.5418 Å, angles 2θ between 10° and 70° with step of 0.02°. As the result, all the samples showed predicted spinel structure with characteristic grain size 6.5 nm that is in the confinement with TEM measurements.

Magnetic properties measurements. Magnetic properties of the samples were investigated using Lake Shore 7407 vibrating sample magnetometer in the magnetic field up to 1.6 T at 80-400 K temperature. The results for room temperature (RT) measurements are presented on Fig. 2.

Magnetization was found to be maximal for the sample with 20% Zn substitution, then magnetization decreases for higher Zn concentration (Fig. 2b) which is similar to earlier reported results [5,6]. The given samples show superparamagnetic non-hysteretic behavior at RT excepting samples with 0% and 10% Zn (see Fig. 3a). We suppose that this is due to the higher size of these particles. Concentration of Zn also causes decreasing of coercivity of the samples that is similar to [5].

FC and ZFC curves. FC and ZFC curves were measured for the samples with 20%, 50% and 70% Zn at 80-400 K. The curves reveal the superparamagnetic behavior of the MNps where maximum moves to higher temperature for bigger MNps (Fig. 3b).

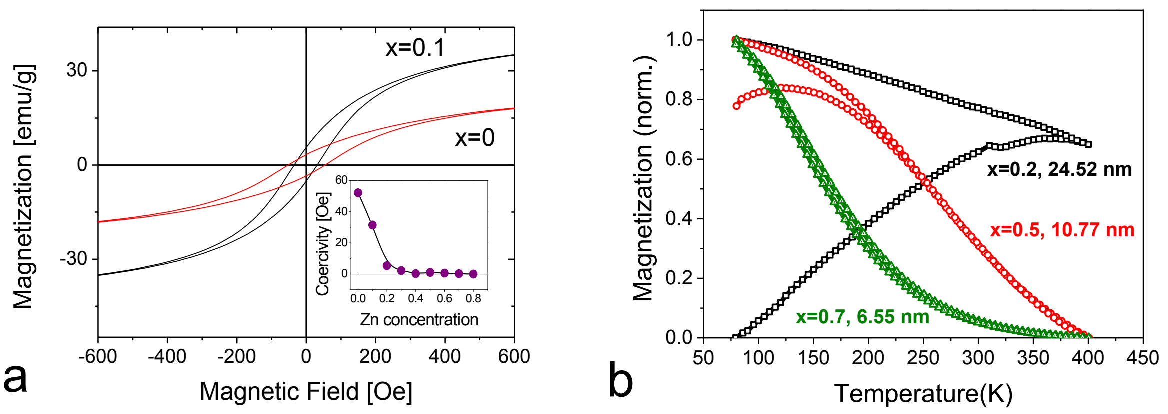

Fig. 3. a - M(H) curves for samples with 0 and 10% Zn at RT. Inset shows the coercivity dependence on Zn concentration at RT; b – ZFC-FC curves for samples with 20%, 50% and 70% Zn (normalized to the maximal value of magnetic moment at 80 K).

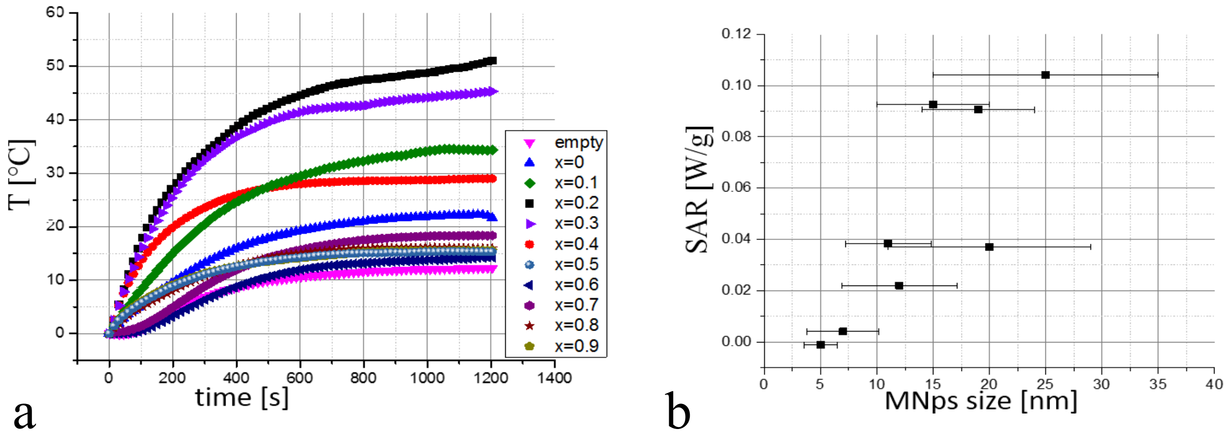

Fig. 4. a - Heating in AC magnetic field measured for samples with different Zn concentration x. Empty test tube is also shown. b - SAR dependence on MNps size.

Heating in AC magnetic field. The results are presented in the Fig. 4. In spite of the special efforts to isolate the test tube thermally, the residual parasitic heating was observed even in the case of the empty test tube (see Fig. 4a line 1 – empty test tube). The test tubes loaded with $Zn_xMn_{1-x}Fe_2O_4$ MNps always demonstrated larger temperature change than in the case of empty test tube while the amount of extra heating varied with the Zn content. The maximum temperature change exceeding 50°C was observed for 20% Zn-substituted MNps while the samples with higher or lower Zn content demonstrated moderate heating (see Fig. 4a). Various factors that might

influence the heating efficiency (size, saturation magnetization, coercivity) were analyzed. The first two factors have been shown to be the crucial for heating efficiency.
On the Fig. 4a you can see the values of the heating curves, brought to 0°C temperature. To calculate the specific absorption rate (SAR) we used the subsequent formula (Eq.2).

$$SAR = \frac{\partial T}{\partial t} C \frac{\partial m_w}{\partial m_p} \tag{2}$$

where C is the water specific heat, m_p is powder mass, m_w is water mass. The time derivative $\partial T/\partial t$ of temperature was taken in the initial linear stage of heating. SAR value has been calculated for dry ferrite powders and for magnetic liquids based on 3 samples of ferrite. The heating process in AC field is shown on the Fig. 5. Obtained SAR values depending on concentration of Zn are summarized in Table 1. Powder specific capacity was taken into account as a constant 0.65 W/g*K. As can be seen from the Fig. 5 the sample with 20% of Zn heats better then the others because of its maximal coercivity and saturation magnetization. To compare the results with published in literature ones the recalculation using formula in (Eq.3) is necessary.

$$SAR \sim f * H^2 \tag{3}$$

It means that the best result from the literature [3] corresponds to 11 W/g in our measurement conditions (the 100 kHz AC magnetic field of amplitude 72 Oe).

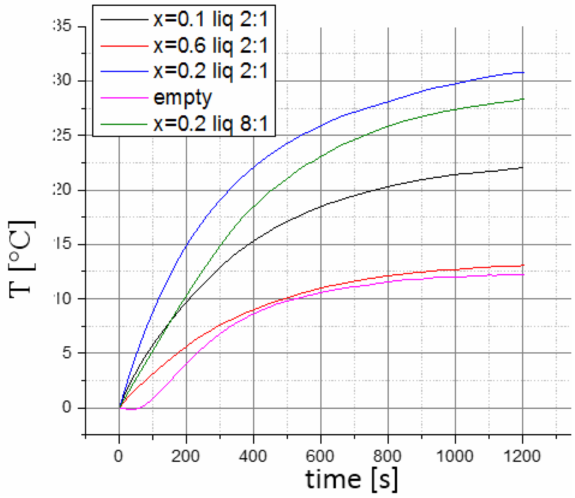

Fig. 5. Heating in AC magnetic field measured for magnetic liquids based on ferrite powder with various mass ratio liquid particles.

Table. 1. Calculated SAR values for powder of ferrite particles and corresponding magnetic liquids.

	SAR_{powder}, W/g	SAR_{liq}, W/g (ratio liq:particles)	
x=0.1	0.06	2:1	0,68
x=0.2	0.13	2:1	1.5
		8:1	1.9
x=0.6	0.02	2:1	0,88

In the end, we would like to compare the magnetic liquids heating. Calculated SAR values appeared to be more than 2 times larger than for the corresponding dry MNps powders (see Table 1). It can be the evidence of the starting of another heating mechanism, for example, Brown relaxation.

Conclusions. For the series of samples $Zn_xMn_{1-x}Fe_2O_4$ (x= 0, 0.1, 0.2, … 0.9) a complex investigation of structure, magnetic properties and magnetic hyperthermia was carried out. The heating curves were measured in the field of 72 Oe amplitude and 100 kHz frequency. The synthesized MNps have cubic lattice and have smaller lattice parameters than bulk materials. Depending on the Zn substitution, size of the MNps varies between 5 and 25 nm. When dispersed in the liquid MNps tend to agglomerate and form cluster of about 400 nm. Magnetic measurements showed down going tendency of saturation magnetization after 20% Zn substitution, which is in agreement with bulk materials behavior. The samples are superparamagnetic that appears in the shape of M(H) curves and the best heating in AC magnetic field. Magnetic liquid samples have much bigger SAR values that indicates the Brown relaxation heating mechanism, blocked for the dry sample.

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