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Dynamic magnetic properties of ZnO nanocrystals incorporating Fe

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ABSTRACT

The aim of the present work is to study the magnetic properties of ZnO(Fe) nanocrystalline samples prepared by two methods of synthesis. We have used the microwave assisted hydrothermal synthesis and traditional wet chemistry method followed by calcination. The detailed structural characterization was performed by means of X-ray diffraction and micro-Raman spectroscopy measurements. The dynamic magnetic properties were studied by means of AC susceptibility χ. The measurements were performed at small AC magnetic field with amplitude not exceeding 5 Oe and different frequency values (from 7 Hz to 9970 Hz). The AC susceptibility maxima have been found for in-phase susceptibility $Re(\chi)$ and for out of phase susceptibility $Im(\chi)$. We analyzed the observed frequency dependence of the peak temperature in the AC susceptibility curve using the empirical parameter Φ that is a quantitative measure of the frequency shift and is given by the relative shift of the peak temperature per decade shift in frequency, as well as Vogel–Fulcher law.

1. Introduction

Studies on nanoscale inorganic materials have attracted recently much attention due to their potential applications in electronic, magnetic or optical devices. Particularly, magnetic nanoparticles offer exciting opportunities for technologies at the interfaces between chemistry, physics, biology and medicine. Below a critical size, magnetic particles become single domain in contrast to the usual multidomain structure of the bulk magnetic materials and exhibit interesting magnetic properties such as superparamagnetism. Superparamagnetic nanoparticles are of great interest for researchers mainly due to the perspectives of their use in e.g. magnetic resonance imaging (MRI), magnetic microsensors, magnetically guided drug delivery, cell-, DNA-, protein-separation (see e.g. [1,2,and references therein]). Recently, it was shown that superparamagnetic nanoparticles based on a core consisting iron oxides are very promising for in vivo applications (e.g. hyperthermia and radiotherapy in vivo) [3]. In an effort to design better materials for specific applications, many problems must be solved that include: narrow particle size distribution and morphology control, precise knowledge of the relationship between the nanostructural features and the resultant macroscopic magnetic properties, lower cost, etc. At present, many groups started to synthesize magnetic nanoparticles by means of chemical methods, which allow one to achieve the size uniformity (see e.g. [1,2]). Due to the simplicity and low cost these techniques are perfectly suited for the production of nanomaterials for future industrial applications.

Currently, nanostructures made of a wide-gap II–VI semiconductor ZnO bear important potential application in electro-optical devices, transparent ultraviolet protection films, and spintronic devices [4,5]. New possible applications of ZnO doped with transition metal (Fe, Mn, Co, etc.) are connected with possible ferromagnetic properties at room temperature (see e.g. [6] and references therein). However, the magnetic properties of these compounds are still under debate.

In the context of commercial applications, doped ZnO nanoparticles are of particular interest. The aim of the present work was to examine the effect of ZnO nanocrystals iron doping on the dynamic magnetic properties of the resultant nanosized material. The structural properties, vibrational modes, low-frequency acoustic modes were studied elsewhere [7,8].

2. Samples and characterization

The nanocrystalline samples of ZnO doped Fe_2O_3 were obtained by use of two methods [7]. In the coprecipitation-calcination method, a mixture of iron and zinc hydroxides was obtained by addition of an ammonia solution or 2 M solution of KOH to a 20% solution of a proper amount of $Zn(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 4H_2O$

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in water. The obtained hydroxides were filtered, dried and calcined at 300 °C for 1 h. In the hydrothermal synthesis the obtained hydroxides were put in the reactor with microwave emission. The microwave assisted synthesis was conducted under a pressure of 3.8 MPa during 15 min. The synthesized product was filtered and dried.

These two methods allowed to obtain the series of nanosized ZnO samples with nominal concentration of Fe_2O_3 from 5 to 70 wt.%. In the present paper we present the results of dynamic magnetic responses, i.e. the frequency and temperature dependence of the linear AC susceptibility for selected samples.

The detailed characterization studies including X-ray diffraction (XRD) measurements, micro-Raman and low-frequency Raman spectroscopy investigations, scanning electron microscopy (SEM) measurements and specific surface area measurements were presented elsewhere [7–9]. The detailed structural investigations revealed the presence of crystalline phases of hexagonal ZnO and cubic $ZnFe_2O_4$ in both methods. The XRD measurements revealed that in a given sample, prepared using hydrothermal synthesis, the amount of spinel phase ($ZnFe_2O_4$) is lower comparing with the same sample synthesized using calcination method. The mean crystallite size of the detected phases was determined using Scherrer formula [7]. In particular, the mean crystallite size of $ZnFe_2O_4$ varied from 8 to 12 nm in both methods [7]. Raman spectroscopy measurements allowed to determine the detailed structural characterization [8,9]. In particular, XRD analysis did not reveal the presence of ZnO phase in samples doped with high content of magnetic dopants. Despite of the fact that XRD does not evident ZnO, sharp peaks at 436 cm^{-1} was clearly E_2 $^{(2)}$ mode of ZnO. This peak is typical for undoped ZnO nanoparticles [10]. The magnetic resonance studies confirmed the presence of iron in the form of $ZnFe_2O_4$ in the investigated samples [11]. The SEM investigations allowed to distinguish two morphologies – spherical and hexagonal nanograins are observed [7] and confirmed the results of structural measurements. It was shown that the degree of agglomeration of nanocrystals depends on the amount of Fe_2O_3 and decreases with increasing nominal Fe_2O_3 content [7].

3. Results and discussion

The dynamic magnetic properties were studied by means of AC susceptibility χ. The real, $Re(\chi)$, as well as imaginary, $Im(\chi)$ parts of magnetic susceptibility were measured using a mutual inductance method in an AC magnetic field of frequency (f) range 7–10,000 Hz and amplitude (H_{AC}) not exceeding 5 Oe. The measurements were performed in the temperature from 4.5 to 160 K.

Fig. 1a and b shows the temperature dependence of the real part of the AC susceptibility for ZnO:Fe_2O_3 samples in the wide range of magnetic dopant, measured at f = 625 Hz. This quantity was measured on warming up the sample after cooling down in zero magnetic field. The $Re(\chi)$ curves show pronounced maxima (the positions of maxima T_f derived at f = 625 Hz are summarized in Table 1). The above described experimental feature can be observed in both the superparamagnetic system and spin glass like systems. The inspection of Table 1 shows the pronounced changes in the positions of the temperature maxima T_f with the nominal Fe_2O_3 concentration. It should be stressed that the mean crystalline size d for magnetic crystalline phase ($ZnFe_2O_4$) varied in the narrow range from 8 nm to 12 nm and should not be responsible for the observed distinct increase in T_f.

The most common method to distinguish between superparamagnetic and spin glass like systems is analysis of $T_f(f)$ behavior. The measurements of AC susceptibility as a function of frequency f were performed for selected samples synthesized by two methods. For all samples we observed that the positions of the maxima (T_f) shift towards higher values with increasing driving frequency. The results are shown in Fig. 2a–d for selected samples with low and high concentration of Fe_2O_3. The observed frequency-dependent behavior in $Re(\chi)$ data may be attributed to the blocking process of superparamagnetism or freezing process in spin glass systems.

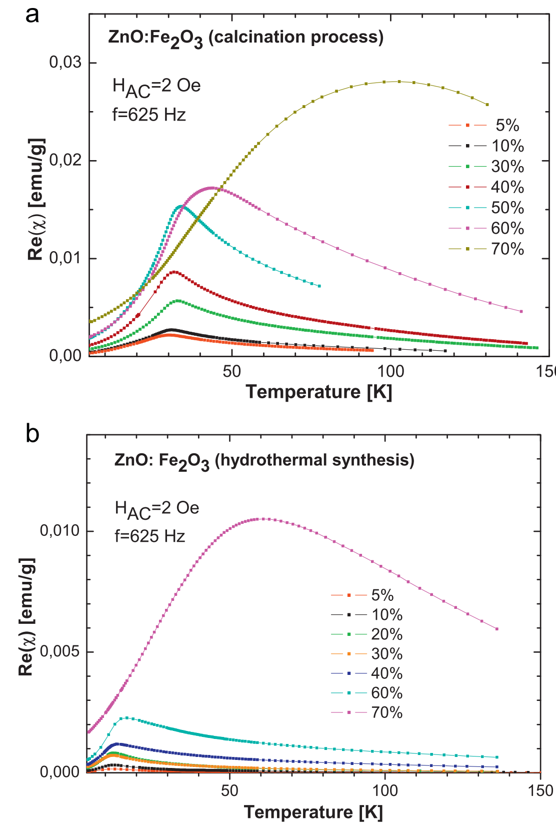

Fig. 1. (a) The temperature dependence of $Re(\chi)$ for selected ZnO:Fe_2O_3 nanocrystalline samples (calcination process). (b) The temperature dependence of $Re(\chi)$ for selected ZnO:Fe_2O_3 nanocrystalline samples (hydrothermal synthesis).

A useful criterion for classifying the observed freezing/blocking process is the empirical parameter Φ [12,13] that is a quantitative measure of the frequency shift and is given by the relative shift of the peak temperature per decade shift in frequency:

$$\phi = \frac{\Delta T_f}{T_f} \Delta \log_{10}(f) \quad (1)$$

Table 1
The positions of maxima T_f derived at f = 625 Hz, the determined values of parameter Φ and ratio $(T_f - T_0)/T_f$ for selected ZnO:Fe_2O_3 synthesized in calcinations and hydrothermal processes ("–"denotes that measurements and/or analysis were not performed).

Nominal concentration	Calcinations process			Hydrothermal process		
	T_f (K)	Φ	$(T_f - T_0)/T_f$	T_f (K)	Φ	$(T_f - T_0)/T_f$
5 wt.%	30.2	0.06	0.5	12.4	0.07	0.7
10 wt.%	30.9	–	–	12.6	0.06	0.6
20 wt.%	–	–	–	12.8	0.07	0.7
30 wt.%	33	0.03	0.4	12.3	0.06	0.7
40 wt.%	31.8	0.04	0.3	14.03	0.06	0.7
50 wt.%	34	0.04	0.3	15.1	0.06	0.6
60 wt.%	43.3	0.04	–	16.4	0.06	0.7
70 wt.%	99	0.04	0.4	57.5	0.06	–

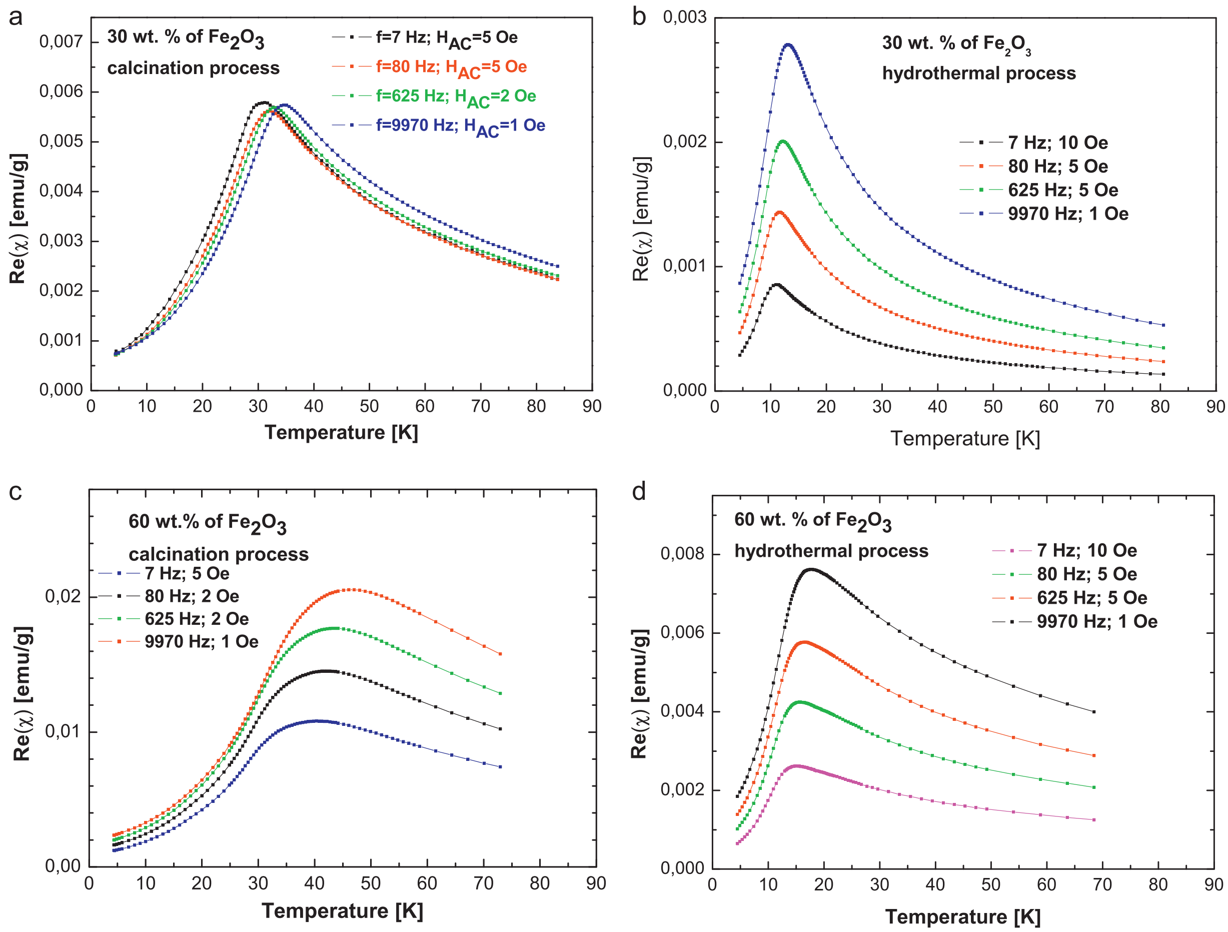

Fig. 2. The frequency dependence of $Re(\chi)$ for nanocrystalline sample with low and high concentration of Fe_2O_3 (a) $x = 30$ wt.% (calcination process); (b) $x = 30$ wt.% (hydrothermal process); (c) $x = 60$ wt.% (calcination process); (d) $x = 60$ wt.% (hydrothermal process).

where ΔT_f is the difference between the peak temperature measured in the $\Delta \log_{10}(f)$, and f is the AC magnetic field frequency.

For interacting nanoparticles, superparamagnetic systems exhibit values of Φ between 0.05 and 0.10, in spin-glass systems $\Phi < 0.05$ [12,14,15]. The determined values of parameter Φ are gathered in Table 1. For calcination process, only for the lowest concentration of Fe_2O_3 (5 wt.%), the value typical for superparamagnetic system of interacting nanoparticles was determined. For higher concentration of Fe_2O_3, the calculated values of Φ are in the regime typical for spin-glass systems (0.03–0.04). For hydrothermal method, the values of parameter Φ are in the range 0.06–0.07 for all measured samples (from 5 wt.% to 70 wt.% of Fe_2O_3). It was shown in our previous studies that hydrothermal method leads to lower agglomeration degree of nanocrystals. The dynamic magnetic properties of the system of nanoparticles strongly depend on the degree of agglomeration and particularly random agglomeration of magnetic nanoparticles can lead to the spin glass like behavior.

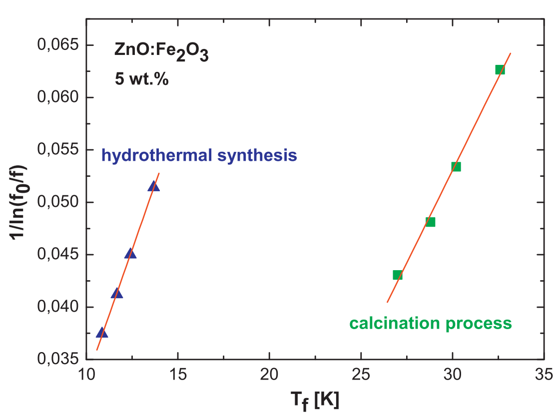

Fig. 3. The variation of T_f with the frequency f at the AC magnetic field for ZnO doped 5 wt.% of Fe_2O_3 in calcination and hydrothermal processes. The solid line represents the VF law fitted to the experimental data.

Additionally we used the phenomenological Vogel–Fucher (VF) law to explain the dynamic magnetic behavior of investigated systems. Various phenomenological laws have been used to explain the dynamic magnetic behavior of such systems [12–14]. The Arrhenius law is applicable for an assembly of noninteracting superparamagnetic particles (see e.g. [12,13]). The interactions between superparamagnetic spin clusters have been taken into account in the Vogel–Fulcher (VF) law [12,14], which is a modification of the Arrhenius law:

$$f = f_0 \exp[-\frac{E_a}{k_B}(T_f - T_0)] \qquad (2)$$

where f is the driving frequency of H_{AC}, f_0 *is* the frequency factor for the relaxation process, E_a the height of the energy barrier due to magnetic anisotropies, and k_B is a Boltzman's constant, T_0 is a physically unclear parameter but has been regarded as a phenomenological parameter which describes the interactions between particles.

The VF law was introduced in the field of spin glasses and disordered magnetism and it has been stated clearly that this law is phenomenological, T_0 can be only an estimate of the interaction strength. The VF law is useful to compare the frequency sensitivity of T_f for different magnetic systems (spin glasses, superparamagnetic-like systems) through the ratio $(T_f - T_0)/T_f$. For small coupled particles (superparamagnetic system) the values of criterium $(T_f - T_0)/T_f$ are in the range 0.25–1.0.

We fitted our experimental data with Eq. (2). The results of the fitting procedure, the values of the ratio $(T_f - T_0)/T_f$ are shown in Table 1. The example results of the fitting procedure for VF law are shown in Fig. 3. It is clearly visible that our data follow the expected linear behavior. The determined values of the ratio $(T_f - T_0)/T_f$ are higher in the case of hydrothermal method. This is in agreement with calculated Φ criterion.

4. Conclusions

We have studied structural and magnetic properties of nanocrystalline ZnO doped with iron oxide in hydrothermal synthesis and calcination process. The structural studies revealed that in the samples obtained using both methods the peaks belonging to ZnO and $ZnFe_2O_4$ can be found. We analyzed the observed frequency dependence of the peak temperature in the AC susceptibility curve using the empirical parameter Φ that is a quantitative measure of the frequency shift and is given by the relative shift of the peak temperature per decade shift in frequency as well as Vogel–Fulcher law with equally good fit. For nanocrystals synthesized by hydrothermal process the results of low-field AC susceptibility are satisfactorily explained by superparamagnetic model including inter-particle interactions. For samples synthesized by calcinations process with the increase of magnetic Fe_2O_3 content, the spin-glasslike behavior is observed.

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