Abstract:

Currently, wide-gap ZnO nanoparticles bear important potential application in electro-optical devices, transparent ultraviolet protection films, and spintronic devices. We have studied the magnetic properties of nanocrystals of ZnO(Fe, Co, Mn) 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 morphology of the samples was studied by means of SEM and TEM microscopy. The results of systematic measurements of AC magnetic susceptibility as a function of temperature and frequency as well as SQUID magnetization are presented. The SQUID magnetization measurements revealed a clear bifurcation of the FC and ZFC plots. Such behavior suggested superparamagnetic behavior above the blocking temperature. The dynamic magnetic measurements were performed at small AC magnetic field with amplitude not exceeding 5 Oe and different frequency values (from 7 Hz to 9970 Hz). For ZnO(Fe) and ZnO(Mn), the AC susceptibility maxima has been found for in-phase susceptibility Re(χ) and for out of phase susceptibility Im(χ). 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. We observed two different types of magnetic behavior, spin-glasslike behavior or superparamagnetic behavior, depending on the synthesis process. For ZnO(Co) nanocrystalline samples high temperature Curie-Weiss behavior in AC magnetic susceptibility was observed. We observed that the determined negative values of the Curie-Weiss temperature θ depend strongly on the nominal content of cobalt oxide. It was shown that for calcination method the values of θ increase with the increase of magnetic ion content indicating enhancement of predominance of antiferromagnetic interactions. For hydrothermal method the opposite effect was observed indicating the breakdown of predominance of antiferromagnetic coupling with the increase of nominal magnetic ion content.

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This paper gives an in-depth discussion of the structural and magnetic properties of ZnO nanocrystals in addition to the technological issues such as different methods of wet chemical synthesis.

**Key words:** Semiconductors, Magnetization, Magnetic measurements, Absorption and light scattering.

1. Introduction

Nanocrystalline materials derive their interesting and technologically useful properties with respect to bulk mainly from quantum confinement effects and the increasing role of surface atoms with the decrease in particle size. Magnetic nanocrystals are currently in the focus of activity of a wide scientific community: physics, chemistry, biology, medicine [1,2].

Superparamagnetic nanoparticles based on a core consisting iron oxides are very promising for in vivo applications (e.g. hypothermia and radiotherapy in vivo). In particular, there is an urgent need to increase the efficacy of cancer therapy by overcoming several limitations of conventional hyperthermia and chemotherapy. Composite nanoparticles based on magnetic oxides can be loaded with cytotoxic drugs, dispersed in a carrier fluid, injected into the bloodstream, and targeted to the tumor using an external magnetic field gradient. These particles release the drug following localization in the tumor, resulting in increased tumor drug concentration with minimal systemic toxicity ([3] and references therein). In addition, superparamagnetic nanoparticles are biocompatible and are in routine clinical use. Nanosized magnetic oxides are of particular interest due to the potential commercial applications [see e.g. 4-7]. There are several reasons why wide-gap oxides were chosen in our studies. The intense interest in dilute magnetic oxides is mainly driven by the search for new device applications in spin-based technologies. Unlike the diluted magnetic semiconductors based on III–V or II–VI group of elements showing ferromagnetism only at very low temperatures, these oxide-based DMS’s exhibit ferromagnetism at higher temperatures and even above RT. They are also optically transparent making them suitable for magneto–optoelectronic applications, particularly for electrodes in solar cells. However, the magnetic properties of these compounds are still under debate.

Transition metal (TM) doped ZnO received recently much attention [8]. However, the literature shows reports claiming for intrinsic ferromagnetism [9], paramagnetism [8], extrinsic ferromagnetism [9] or spin-glass behavior [10] in ZnO:TM . Recently, it was shown that the ferromagnetism in these materials can be induced by inclusions of nanoscale oxides of transitions metals [11] and/or nanoparticles containing a large concentration of magnetic ions [12]. Novel methods enabling a control of nanoassembling of magnetic nanocrystals in nonconducting matrices as well as functionalities specific to such a system were described [12]. Grain boundary defects have been also proposed to play role in facilitating magnetic ordering of oxide diluted magnetic semiconductors (see e.g. [13]). Still the reports to date have been contradictory. Despite of a number of available reports and experimentally observed evidences for ferromagnetism of ZnO:TM, there is still an open question about the origin of ferromagnetism in these compounds. That is due to the poor reproducibility by using different preparation methods or the poor resolutions of the commonly used structural characterization methods. Further intensive studies are necessary, particularly discriminating materials characterization could provide insight on the understanding of the magnetic properties in TM doped ZnO.

At present there are many studies reporting the preparation and experimental studies of TM-doped nanoparticulate ZnO compounds (see eg. [4, 8, 14-22]). The present review gives an in-depth discussion of the structural and magnetic properties of
ZnO nanocrystals in addition to the technological issues such as different methods of wet chemical synthesis. Our aim was to examine the effect of ZnO nanocrystals transition metal (TM) doping on the magnetic properties of the resultant nanosized material. The systematic magnetic studies including AC magnetic susceptibility measurements and DC SQUID magnetometry were carried out. The micro-Raman spectroscopy measurements were performed. The samples were characterized by means of X-ray diffraction, scanning electron microscopy and transmission electron microscopy.

2. Experimental results and discussion

2.1. Structural characterization

The nanocrystalline samples of ZnO doped with Fe$_2$O$_3$, CoO and MnO were synthesized by use of two methods [23-26]. In the coprecipitation-calcination method, a mixture of transition metal hydroxides and zinc hydroxides from an aqueous solution of nitrates were obtained. The obtained hydroxides were filtered, dried at the temperature of 70°C and calcined at 300°C during 1 hour. 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 samples with nominal concentration of Fe$_2$O$_3$ from 5 to 70 wt.%, CoO from 5 to 80 wt.% (for calcination method) and from 5wt.% to 50 wt.% (for hydrothermal method), MnO from 5 to 95 wt.% in calcination method.

The detailed characterization studies including X-ray diffraction (XRD) measurements, micro-Raman and low-frequency Raman spectroscopy investigations, scanning electron microscopy, transmission electron microscopy, specific surface area measurements were performed [23-28].

![Fig.1.](attachment:image.png)  
Fig.1. The selected XRD spectra for several nanocrystalline samples of ZnO doped with Fe$_2$O$_3$ prepared by calcination method (a) and hydrothermal synthesis (b). The characteristic peaks attributed to ZnO (squares) are marked. The not marked peaks are attributed to ZnFe$_2$O$_4$.

For ZnO doped with Fe$_2$O$_3$ the detailed structural investigations revealed the presence of crystalline phases of hexagonal ZnO and cubic ZnFe$_2$O$_4$ in both methods. The results of XRD studies are shown in Fig. 1. The mean crystallite size of the detected phases was determined using Scherrer formula [29]. In particular, the mean crystallite size of ZnFe$_2$O$_4$ varied from 8 to 12 nm in both methods [23]. In the samples prepared using hydrothermal...
synthesis the amount of spinel phase is lower comparing with calcination method. For example in the XRD spectrum of the sample containing 50 wt.% Fe₂O₃ in the hydrothermally prepared sample (Fig. 1b) the clear peaks attributed to ZnO phase are visible and in case of the same sample prepared by calcination (Fig. 1a) the peaks of ZnO phase are much less distinguishable.

![Raman spectrum for ZnO:Fe₂O₃ with 5 wt.% prepared by calcination method.](image)

Raman spectroscopy measurements allowed to determine the detailed structural characterization [28, 30]. The advantage of micro-Raman technique is the very accurate chemical phases determination. Raman spectroscopy has already proven to be a unique tool for probing nanophases dispersed in a matrix (see eg. [31]). The micro-Raman spectra were taken in the backscattering configuration and analyzed using a Jobin Yvon T64000 spectrometer, equipped with nitrogen cooled charge-coupled-device detector. As an excitation source we used the 514.5 nm line of an Ar-ion laser. The exemplary Raman spectrum is shown in Fig. 2. For ZnO:Fe₂O₃ samples, the main characteristics of experimental Raman spectrum in 200 to 1600 cm⁻¹ spectral region are sharp peak at 436 cm⁻¹ and broad two-phonon structure at ~1150 cm⁻¹, typical for ZnO. Raman spectrum in region below 400 cm⁻¹ is superposition of characteristic frequencies of ZnO phase and spectrum of ZnFe₂O₄ nanoparticles. Broad structure below 700 cm⁻¹ corresponds to ZnFe₂O₄ nanoparticles.

XRD analysis did not reveal the presence of ZnO phase in samples doped with high content of magnetic dopants. Despite the fact that XRD does not evident ZnO sharp peak at 436 cm⁻¹ was clearly E₂ (2) mode of ZnO. This peak is typical for undoped ZnO nanoparticles [32].

A magnetic resonance study performed with an electron paramagnetic resonance spectrometer was carried out at room temperature for the calcinated samples [27]. A very intense magnetic resonance line with asymmetry depending on the iron oxide concentration was recorded for all samples. The resonance line is centred at g = 2.005(2) and its integrated intensity increases with the ferrite content, reaching a maximum for a sample with a nominal 70 wt.% content of iron oxide. The presence of iron in the form of ZnFe₂O₄ was confirmed in all the investigated in present paper calcinated samples [27].

The morphology was studied by use of SEM and HRTEM. The investigations allowed to distinguish two morphologies – spherical and hexagonal nanograins are observed. Figs. 3 and 4 show selected SEM and TEM images. We assume the hexagonal crystals correspond to the ZnO, while the small spheroidal crystals — to the ZnFe₂O₄ spinel. It was shown that the degree of agglomeration of nanocrystals depends on the amount of Fe₂O₃ and decreases with increasing nominal Fe₂O₃ content [23]. In addition SEM measurements
showed that for hydrothermal process the tendency to the formation of agglomerates is less in comparison to the calcination process. The formation of agglomerates is minimized because during the hydrothermal process elevated under pressure of 3.8 MPa the synthesis temperature is only 250°C and reaction time is short: 15 min. Due to the agglomeration process the size of nanocrystallites determined from TEM is much smaller in comparison to the SEM studies. The size of nanocrystallites determined from TEM is in agreement with the results of XRD studies.

![SEM images of ZnO nanocrystalline samples doped in calcination process: (a) 10 wt.% Fe₂O₃, (c) 30 wt.%, (e) 70 wt.% and in hydrothermal process: (b) 10 wt.% Fe₂O₃, (d) 30 wt.%, (f) 70 wt.%.](image)

**Fig. 3.** SEM images of ZnO nanocrystalline samples doped in calcination process: (a) 10 wt.% Fe₂O₃, (c) 30 wt.%, (e) 70 wt.% and in hydrothermal process: (b) 10 wt.% Fe₂O₃, (d) 30 wt.%, (f) 70 wt.%

For ZnO doped with CoO, the crystalline phases of hexagonal ZnO and cubic Co₃O₄ for calcinated samples, hexagonal ZnO and cubic ZnCo₂O₄ for hydrothermal method were determined. The detailed results of structural investigations will be presented elsewhere. The selected results of XRD are shown in Fig. 5. The mean crystallite size of Co₃O₄ varied from 55 nm to 21 nm with the increase of CoO content. For calcination process the mean
crystalline size varied from 39 nm to 49 nm with the increase of CoO content.

![HRTEM images](image1)

**Fig. 4.** HRTEM images images of ZnO nanocrystalline samples doped in calcination process: (a) 10 wt.% Fe₂O₃, (c) 70 wt.% and in hydrothermal process: (b) 10 wt.% Fe₂O₃, (d) 70 wt.%.

![XRD patterns](image2)

**Fig. 5.** The selected XRD patterns of ZnO doped CoO in calcination and hydrothermal processes. Peaks attributed to ZnO are marked as squares. The not marked peaks are attributed to Co₃O₄ in calcination process (a) and to ZnCo₂O₄ (b) in hydrothermal method.

Raman spectroscopy measurements confirmed XRD results. The detailed micro-Raman characterization will be shown elsewhere. Fig. 6 a and 6 b show micro-Raman spectra for selected samples. For all samples Raman peak at 436 cm⁻¹ was observed. This peak is
clearly \( E_2^{(2)} \) mode of ZnO nanoparticles. Modes observed at \( \sim 204, 330, 379, 410, 541, 577, 592, 660, 1153 \) are also typical for ZnO. For the samples of ZnO doped with CoO by calcinations method, the Raman spectrum showed a band at \( \sim 691 \text{ cm}^{-1} \). The presence of this band is typical for \( \text{Co}_3\text{O}_4 \). We also observed bands at \( \sim 194, 482, 521 \) and \( 618 \text{ cm}^{-1} \), which are also typical for \( \text{Co}_3\text{O}_4 \). For samples prepared by hydrothermal method bands at \( \sim 185, 475, 520, 610, 690 \text{ cm}^{-1} \) typical for \( \text{ZnCo}_2\text{O}_4 \) were observed.

![Fig. 6a. The Raman spectra of selected nanocrystalline ZnO:CoO samples prepared by (a) calcination method, (b) hydrothermal process.](image)

The morphology of ZnO:CoO nanocrystalline samples were studied using SEM. The selected results are shown in Fig. 7. Two morphologies can be distinguished — spherical and hexagonal nanograins are observed. We assume the hexagonal nanocrystals correspond to the ZnO, while the spheroidal nanocrystals — to the spinel phases (\( \text{Co}_3\text{O}_4 \) for calcinations process and \( \text{ZnCo}_2\text{O}_4 \) for hydrothermal method). The obtained nanocrystalites size dependences from XRD measurements are clearly visible in SEM images.

![Fig. 7. The selected SEM images of ZnO:CoO nanopowders (30 wt.%) prepared in calcination process (a) and hydrothermal process (b).](image)

For ZnO doped with MnO, XRD measurements revealed the presence of the crystalline phases of hexagonal ZnO, and/or cubic \( \text{ZnMnO}_3 \), and/or cubic \( \text{Mn}_3\text{O}_4 \), and/or cubic \( \text{ZnMn}_2\text{O}_4 \).
Fig. 8. The selected spectra for several nanocrystalline samples of ZnO doped with MnO. The characteristic peaks attributed to ZnO (arrows) and ZnMnO₃ (solid lines) are marked. The inset shows the characteristic peaks attributed to Mn₃O₄ (diamonds) and ZnMn₂O₄ (dashed lines) for selected samples.

Fig. 9. The Raman spectra of selected nanocrystalline ZnO:MnO samples prepared by calcination method.

Fig. 8 presents the XRD patterns of ZnO doped with MnO demonstrating the presence of spinel, manganium oxide and zinc oxide phases in the system. In samples with low nominal content of MnO two phases: ZnO and ZnMnO₃ are observed. With increasing MnO concentration the content of ZnO phase decreases and the peak attributed to this phase disappears in sample containing 60 wt.% of MnO. The peak of ZnO disappears, because all zinc is now bonded in the spinel phase. In samples containing 60 wt% of MnO and more, the
phases of $\text{ZnMn}_2\text{O}_4$ and $\text{Mn}_3\text{O}_4$ are found. The detailed results of XRD analysis are presented in [25]. In particular the deconvolution of a single XRD line for sample with high content of MnO content is shown. XRD method was applied to determine a mean crystallite size in prepared samples, using the Scherrer formula. The results of XRD analysis and micro-Raman spectroscopy measurements are compared in Table I. The micro-Raman measurements were performed for selected samples (see Fig. 9). The Raman peak at 660 cm$^{-1}$ is observed. This peak is typical for spinel structure. In these samples, especially in the case of high doping level, bands from $\text{ZnMnO}_3$ and $\text{Mn}_3\text{O}_4$ crystal structures were identified at about 315 and 525 cm$^{-1}$. For samples with high content of magnetic dopant, the Raman measurements revealed the presence of MnO crystalline phase. It should be stressed that XRD analysis did not show the presence of this crystalline phase.

Tab. I. The results of XRD and micro-Raman measurements for ZnO:MnO prepared by calcination method. The determined crystalline phases are denoted by “+”. The mean crystallite size $d$ was determined by use of Scherrer’s formula for selected samples. The micro-Raman measurements were performed for selected samples (denoted as “+”). The XRD did not reveal the presence of ZnO phases for samples with high content of magnetic dopant.

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<th>ZnO: MnO</th>
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<th>ZnMn$_2$O$_4$ phase</th>
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<td>95 wt.%</td>
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The magnetic resonance investigations have been carried out at room temperature [25]. Slightly asymmetric, broad and intense magnetic resonance line is recorded for all studied samples. It was shown that the phases ZnO and ZnMnO$_3$ dominate for samples with low content of nominal dopant, below 60 wt. %. For higher concentrations of the phases Mn$_3$O$_4$ and ZnMn$_2$O$_4$ are recorded. The EPR measurements of samples with nominal MnO content below 60 wt.% have shown that the resonance line is centered above $g_{\text{eff}} = 2$ and is attributed to ZnMnO$_3$ phase. The integrated intensity increases with increasing MnO content. Above 60 wt. % the recorded EPR line is centered below $g_{\text{eff}} = 2$ and it could be attributed to ZnMn$_2$O$_4$ phase. The morphology of the samples was studied by use of TEM. The selected TEM images are show in Fig. 10. For samples with low content of MnO the hexagonal and
spherical nanograins were observed. We assume that hexagonal nanograins correspond to ZnO and spherical nanograins correspond to ZnMnO₃. For samples with higher content of MnO mainly spherical nanograins were observed. These results corroborate with XRD and Raman spectroscopy studies.

![Fig. 10. The selected TEM images of ZnO:MnO prepared by calcination method a) 5 wt.%, b) 40 wt.%.

2.2. Magnetic properties
2.2.1. Magnetic properties of ZnO:Fe₂O₃

The dynamic magnetic properties were studied by means of AC susceptibility $\chi$. The real, Re($\chi$), as well as imaginary, Im($\chi$) parts of magnetic susceptibility were measured by use of 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. 11 shows the temperature dependence of the real part of the AC susceptibility for ZnO:Fe₂O₃ samples prepared by calcination method (a) and hydrothermal process (b) in the wide range of magnetic dopant, measured at $f=625$ Hz.

![Fig. 11. The temperature dependence of Re($\chi$) for selected ZnO: Fe₂O₃ nanocrystalline samples a) (calcination process), b) (hydrothermal method).

The Re($\chi$) curves show pronounced maxima. The above described experimental feature can be observed in both the superparamagnetic system and spin-glasslike systems. It is
clearly visible that the temperature maxima \( T_f \) shift towards higher temperatures with the nominal \( \text{Fe}_2\text{O}_3 \) concentration. It should be stressed that the mean crystalline size \( d \) for magnetic crystalline phase \( (\text{ZnFe}_2\text{O}_4) \) 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-glasslike systems is analysis of \( T_f(f) \) behavior. It was shown that useful criterion for classifying the observed freezing/blocking process is the empirical parameter \( \Phi [33] \).

\[
\Phi = \frac{\Delta T_f}{T_f \Delta \log_{10}(f)} \tag{1}
\]

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

We performed the measurements of AC susceptibility as a function of frequency \( f \) 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 (see Fig. 12). The observed frequency-dependent behavior in \( \text{Re}(\chi) \) data may be attributed to the blocking process of superparamagnetism or freezing process in spin-glass systems. It was shown that for interacting nanoparticles, superparamagnetic systems exhibit values of \( \Phi \) between 0.05 and 0.10, in spin-glass systems \( \Phi < 0.05 \) [34-36].

![Fig. 12. The frequency dependence of Re(\( \chi \)) for nanocrystalline sample with low and high concentration of \( \text{Fe}_2\text{O}_3 \); a) \( x = 30 \text{ wt.\%} \) (calcination process); b) \( x = 30 \text{ wt.\%} \) (hydrothermal process); c) \( x = 60 \text{ wt.\%} \) (calcination process); d) \( x = 60 \text{ wt.\%} \) (hydrothermal process).]
For calcination process, only for the lowest concentration of Fe₂O₃ (5 wt. %), the value typical for superparamagnetic system of interacting nanoparticles was determined. For higher concentration of Fe₂O₃, 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 Fe₂O₃). It was shown in our structural 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-glasslike behavior.

Additionally we used the phenomenological Vogel-Fucher (VF) law to explain the dynamic magnetic behavior of investigated systems [37]. 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:

\[ f = f_0 \exp\left[-\frac{E_a}{k_B(T_f - T_0)}\right] \]  

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 is useful to compare the frequency sensitivity of \( T_f \) for different magnetic systems (spin-glasses, superparamagnetic-like systems) through the ratio \( (T_f - T_0)/T_f \), where \( T_0 \) is the phenomenological parameter and can be only an estimate of the interaction strength [34-35]. For small coupled particles (superparamagnetic system) the values of criterium \( (T_f - T_0)/T_f \) are in the range 0.25-1.0.

![Graph](image_url)

**Fig. 13.** The variation of \( T_f \) with the frequency \( f \) at the AC magnetic field for ZnO doped 30 wt.% of Fe₂O₃ in calcination and hydrothermal processes. The solid line represents the VF law fitted to the experimental data.

We fitted our experimental data with Eq. (2). The example results of the fitting procedure for VF law are shown in Fig. 13. 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.

### 2.1.2. Magnetic properties of ZnO:CoO

The systematic magnetic measurements were performed. The AC magnetic
susceptibility $\chi$ studies in the temperature range $4.2 - 150$ K using a mutual inductance method were carried out. The selected results of susceptibility measurements are shown in Fig. 14. In our experiment we have not observed any evidence of antiferromagnetic or superparamagnetic behavior at low temperatures for all the investigated samples. The high temperature behavior of the inverse low-field susceptibility $\chi^{-1}$ was nearly linear for all samples prepared by calcination and hydrothermal method samples. All samples exhibited Curie-Weiss law behavior at high temperatures. The diamagnetic AC susceptibility of $-0.33 \cdot 10^{-6}$ emu/g for ZnO [38] was substracted from the measured magnetic susceptibility.

![Graph a)](image1.png)

**Fig. 14.** The selected results of AC susceptibility measurements as a function of temperature ($f=625$ Hz, $H_{AC}=5$ Oe) a) 40 wt.% (calcination process) b) 40 wt.% (hydrothermal method). The solid lines represent the Curie-Weiss law fitted to the experimental data.

The selected results of the fitting procedure to the Curie-Weiss law are shown in Fig. 15. For all samples the negative values of the Curie-Weiss temperature $\theta$ were determined. The obtained negative values of $\theta$ indicate that the antiferromagnetic interactions are predominant for all studied samples, calcinated as well as hydrothermal. For calcinated ZnO:CoO samples the Curie-Weiss temperature increases significantly with the content of magnetic dopant, indicating the enhancement of the predominant antiferromagnetic coupling. For the hydrothermal method, the opposite effect is observed. We observe the considerable decrease of Curie-Weiss temperature with the content of CoO indicating the breakdown of the predominant antiferromagnetic interaction. The magnetic parameters like Curie-Weiss temperature depend on the size of the nanoparticles. It is well known effect that the role of the surface atoms increases with the decrease in particle size. The structural measurements revealed that the ZnO phase is much less distinguishable for samples with higher content of magnetic dopant. Thus, the predomiance of Co$_3$O$_4$ phase can be the reason of the increase of Curie-Weiss temperature values with the content of magnetic dopant for calcination method. In the case of hydrothermal method, the considerable amount of ZnCo$_2$O$_4$ phase for samples with higher content of magnetic dopant can cause the breakdown of predominant antiferromagnetic coupling and result in the observed decrease of $\theta$ values.
2.1.3. Magnetic properties of ZnO:MnO

The results of magnetic AC susceptibility for selected samples of ZnO doped with MnO are shown in Fig. 16. For the samples with low content of MnO (up to 50 wt. %) the broad peak in the real part of magnetic susceptibility was observed. We did not observe the shift of the maximum of the peaks with the frequency for all the samples. However one should notice that observed peaks in AC susceptibility are very broad. This can be a result of a large nanocrystallite size distribution in the sample.

For samples with higher content of magnetic dopant we observed peak at around 43 K, characteristic of a Mn$_3$O$_4$ ferrimagnet. This is consistent with the structural measurements (the presence of Mn$_3$O$_4$ crystalline phase for samples above 60 wt.% of MnO).
To better understand the magnetic properties of these systems we performed SQUID magnetization measurements as a function of temperature at small applied magnetic fields. The inset in Fig. 16 shows typical SQUID magnetization for sample with low content of magnetic dopant. A clear bifurcation of the FC and ZFC plots is visible. The furcation of ZFC and FC curves at a certain temperature is one of the characteristic features of superparamagnetic system. However, the coinciding broad maximum observed on the ZFC curve occurs at a slight lower temperature than temperature maximum observed for AC magnetic susceptibility. Such behavior usually signalizes a certain particle size distribution in nanocomposite. For ZnO:MnO samples we observed five different crystalline phases. One should realize that interpretation of magnetic results in such a case is quite a difficult task. However the results of magnetic measurements corroborate very well with the magnetic resonance studies [25].

3. Conclusions

We have studied structural and magnetic properties of nanocrystalline ZnO doped with transition metal oxides.

For ZnO:Fe₂O₃ the structural studies revealed that in the samples obtained using both methods the peaks belonging to ZnO and ZnFe₂O₄ can be found. We analyzed the observed frequency dependence of the peak temperature in the AC susceptibility curve using the empirical parameter \( \Phi \) 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 Fe₂O₃ content, the spin-glasslike behavior is observed.

For ZnO:CoO the structural studies revealed that in the samples obtained using calcination method the peaks belonging to ZnO and Co₃O₄ can be found. For hydrothermal method ZnO and ZnCo₂O₄ phases were recognized. For all samples high temperature Curie-Weiss behavior in AC magnetic susceptibility was observed. We observed that the determined negative values of the Curie-Weiss temperature \( \theta \) depend strongly on the nominal content of cobalt oxide. It was shown that for calcination method the values of \( \theta \) increase with the increase of magnetic dopant indicating enhancement of predominance of antiferromagnetic interactions. For hydrothermal method the opposite effect was observed indicating the breakdown of predominance of aniferromagnetic coupling with the increase of nominal magnetic dopant.

For ZnO doped with MnO (up to 50 wt. %) the peak in low temperature magnetic susceptibility is observed. The DC magnetic measurements suggested superparamagnetic behavior. Futher magnetic studies, including nonlinear magnetic susceptibility could be helpful in studying magnetic properties of ZnO:MnO. For samples with higher magnetic dopant, the presence of ferrimagnetic Mn₃O₄ is clearly visible. The structural measurements revealed the presence of Mn₃O₄ crystal structure for samples with MnO content above 50 wt. %.

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4. References

Садржај: Широко-зонске ZnO наночестице тренутно имају важну потенцијалну примену у електро-оптичким уређајима, транспарентним заштитним филмовима од узрађувања рачења и уређаја за примену у спектроскопији. У раду смо проучавали магнетна својства нанокристала ZnO(Fe, Co, Mn) припремљених помоћу електро-оптичког метода. Користили смо микроталасну потпомогнуту хидротермалну синтезу и традиционални хемијски поступак уз каснију калцинацију. Детаљна структурна карактеризација извршена је помоћу рентгенске дифракције и микроскопије. Морфолошка узорак проучавања је помоћу ЦЕМ и ТЕМ микроскопије. Приказани су резултати систематских меренја AC магнетне сусцептивности у зависности од температуре и фреквенције, као и магнетизације мерене помоћу SQUID магнетометра. Мерење магнетизације је показало јасно развојање између FC и ZFC кријива. Тако понашање сугерише суперпарамагнетно понашање наночестица ZnO(Mn), максимум у AC сусцептивности је нађен у реалном Re(χ) и имагинарном Im(χ) делу AC сусцептивности. Уочену зависност температуре максимума у AC кријива од фреквенције смо анализирали користећи емпиријски параметар Φ који је квантификациона мера фреквенцијског помераја, као и помоћу Вогел-Фулхер закона. Уочили смо два типа магнетног понашања, понашање налик линеарном стаклу и понашање налик суперпарамагнетизму, зависно од начина синтезе. За ZnO(Fe) нанокристалне узорке, уочено је Кирли-Вајсово понашање у високотемпературном делу AC магнетне сусцептивности. Уочили смо да негативне вредности Кирли-Вајсова температуре θ јако зависе од наночастичног садржаја кобалта оксида. Показано је да за поступак калцинације зависимости вредности θ расту са порастом садржаја магнетних јона, указујући на јачање доминације антиферомагнетних интеракција. За хидротермалну методу уочен је супротан ефект указујући на слабљење доминације антиферомагнетног спрелања при порасту наночастичног садржаја магнетних јона.
Овај рад даје детаљну дискусију структурних и магнетних својстава ZnO нанокристала, поред технологијских разматрања као што су различити поступци хемијске синтезе.

Кључне речи: полупроводници, магнетизација, магнетна мерења, апсорпција и расејање светлости