

Dependence of Magnetic Properties of ZnO:Mn Nanocrystals on Synthesis Conditions

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(Received 24 September 2021; revised manuscript received 26 June 2022; published online 30 June 2022)

The results of studies of samples of ZnO:Mn nanocrystals with a Mn concentration of 2 at. % obtained by ultrasonic spray pyrolysis and cryochemical synthesis methods are presented. The precursors were zinc and manganese nitrates and acetates, respectively. Samples were studied by XRD, EPR and vibrational sample magnetometry. It was found by XRD that the crystal lattice parameters of nanocrystals in the samples are much lower than those of single-crystal ZnO. This indicates the presence of defects and deformation stresses in nanocrystals. The EPR method shows that in the samples obtained by ultrasonic spray pyrolysis, defects and Mn²⁺ impurity ions are located not in the bulk, but in the surface layer of nanocrystals. Samples obtained by cryochemical synthesis method have a large number of acceptor-type defects. The magnetization of these samples is significantly higher than that of the samples obtained by ultrasonic aerosol pyrolysis. This may be due to the fact that in the samples obtained by ultrasonic spray pyrolysis ferromagnetism occurs on the surface, and in the samples obtained by cryochemical synthesis – in the bulk of nanocrystals. It is caused by the destructive action of special gaseous medium, which is formed during the thermal decomposition of zinc acetate. Such conditions of cryochemical synthesis methods lead to the appearance of a large number of bulk defects in nanocrystals.

Keywords: Zinc oxide, Nanocrystals, Ultrasonic spray pyrolysis, Cryochemical synthesis, Defects.

DOI: [10.21272/jnep.14\(3\).03030](https://doi.org/10.21272/jnep.14(3).03030)

PACS numbers: 75.75. + a, 81.07. – b, 85.35.p

1. INTRODUCTION

Diluted magnetic semiconductors (DMS), which include ZnO doped with manganese (ZnO:Mn), attract attention due to the possibility of their use in spintronics as well as in many other areas of application of nanoelectronics. Such semiconductors combine electrical and ferromagnetic properties (FP), promising from the point of view of practical use, with optical transparency, thermal and radiation resistance. The main requirements for DMS are the presence of FP at room temperature and high values of the specific magnetization of the samples in the saturation state – the M_s value. Experimental studies have shown that regardless of the method of preparation, samples of ZnO:Mn nanocrystals (NCs) acquire FP during the synthesis at low temperatures ($T_c < 500$ °C) and at low concentrations of the dopant Mn [1]. The decisive role of defects in the formation of ferromagnetism in DMS has also been recently established [2]. On this basis, it is clear that the goal of the synthesis of such NCs is the formation of defects in the samples of the appropriate structure, which are responsible for FP. For this purpose, it is necessary to carry out the synthesis in non-equilibrium conditions, or to perform the heat treatment of the samples in a reducing gas medium, such as hydrogen [3]. At present, DMS have not yet been obtained that would have high values of specific magnetization and fully meet the requirements of practical use. Therefore, the improvement of methods of DMS synthesis, which allow to obtain samples with high level of defects and corresponding FP, is a crucial task. This work presents the results of studies of the structural and magnetic properties of ZnO:Mn NC samples obtained by ultrasonic spray pyrolysis (USP) and low-temperature cryochemical synthesis (CCS).

2. EXPERIMENTAL

USP method is based on thermal decomposition of aerosol droplets of the initial solution when they pass through the high-temperature zone of the furnace [4]. The main feature of the synthesis by the USP method is that the formation of NCs occurs in the volume of microdroplets in non-equilibrium conditions for a limited time while the aerosol drop passes through the heated furnace. Such synthesis conditions cause the appearance of numerous structural defects in NCs.

CCS method is based on the thermal decomposition of salts of the initial components, solutions of which were previously frozen in the form of small drops and dried by the sublimation method [5]. NC formation occurs over a long period of time in equilibrium conditions. The use of this method in the synthesis of DMS allows to achieve high homogeneity in the distribution of the initial components as well as to ensure high purity of the process.

By USP and CCS methods, we synthesized ZnO:Mn NC samples with a Mn concentration of 2 at. % at temperatures $T_c = 550$ °C and 350 °C, respectively. Zinc nitrates ($Zn(NO_3)_2 \cdot 6H_2O$) and manganese $Mn(NO_3)_2 \cdot 6H_2O$ were precursors in the synthesis of samples using the USP method (USP samples). The prepared 10 % aqueous solution of zinc nitrate with the required amount of manganese nitrate was sprayed onto aerosol droplets with $d = 1 \div 2$ μm . These droplets were transported by carrier gas (air) through the reaction zone of the furnace heated up to 550 °C, where for a limited time ($7 \div 10$ s) the droplets were dried, and NCs were synthesized. The product in the form of spherical granules was accumulated on the filter at 250 °C [6].

For synthesis of the samples by the CCS method

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(CCS samples), a 10 % aqueous solution of zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) was used, to which manganese acetate ($\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) was added. Such a solution with Mn concentration of 2 at. % was sprayed on droplets with $d = 20\text{--}100 \mu\text{m}$, which were then frozen in liquid nitrogen. Drying of the obtained cryogranules was carried out in a freeze-drier for 16 h [7]. The synthesis of NCs occurred at thermal decomposition of dry salts of zinc and manganese acetate at 350°C . The duration of thermal decomposition affects the size of the synthesized NCs. Therefore, in order to obtain small sizes of ZnO:Mn NCs, heat treatment was carried out for 20 min in air, and cooling was performed in the cold zone of the furnace in a stream of gaseous nitrogen for 15 min.

The crystal structure and phase composition of the samples were studied by X-ray diffraction (XRD) analysis on the DRON-2M diffractometer using $\text{CoK}\alpha$ radiation ($\lambda = 1.7902 \text{ \AA}$). Samples were studied by EPR method on the RADIOPAN SE/X 2543 radio spectrometer. Magnetic properties of the samples were studied by vibrational sample magnetometry (VSM).

Calculation of the unit cell parameters a and c was carried out with the position of individual reflections after re-scanning of the diffraction peak profiles with a small step (0.01 deg). When measuring the EPR spectra, all samples had equal masses and were studied at the same operating conditions of the spectrometer. This allowed to carry out a comparative analysis of spectra by intensity. When obtaining magnetic characteristics, the samples were weighed and placed in sealed polyethylene ampules. Magnetization of ampules was deducted from sample magnetization.

3. RESULTS AND DISCUSSION

The results of XRD studies of ZnO:Mn-2 at. % samples obtained by USP and CCS are shown in Fig. 1. It was found that the crystal structure of the samples has a hexagonal lattice of the wurtzite type (according to the standard, JCPDS card 36-1451). The XRD pattern of the CCS sample does not show additional reflections of the synthesis products. This indicates that the duration of heat treatment (20 min) is sufficient for complete decomposition of the initial components.

A common feature of reflections in XRD patterns is that they are shifted in the direction of large angles relative to the standard positions for the ZnO sample. The reason for this shift is the decrease in the interplanar distances $d(hkl)$, according to the Wulff-Bragg equation [8]:

$$2d(hkl)\sin\theta = n\lambda, \quad (1)$$

where $d(hkl)$ is the interplanar distance; h , k and l are the Miller indices; θ is the diffraction angle; n is the order of diffraction reflection; λ is the X-ray wavelength.

As a consequence, this shift leads to a decrease in the crystal lattice parameters a and c in comparison with the standard, single-crystalline ZnO. This was confirmed by the results of calculations using formulas (4) and (5) (Table 1). It is believed that doping of ZnO NCs with Mn impurities under equilibrium conditions

leads to an increase in the crystal lattice parameters a and c , so the ionic radius of Mn^{2+} (0.83 \AA) is greater than in Zn^{2+} (0.74 \AA).

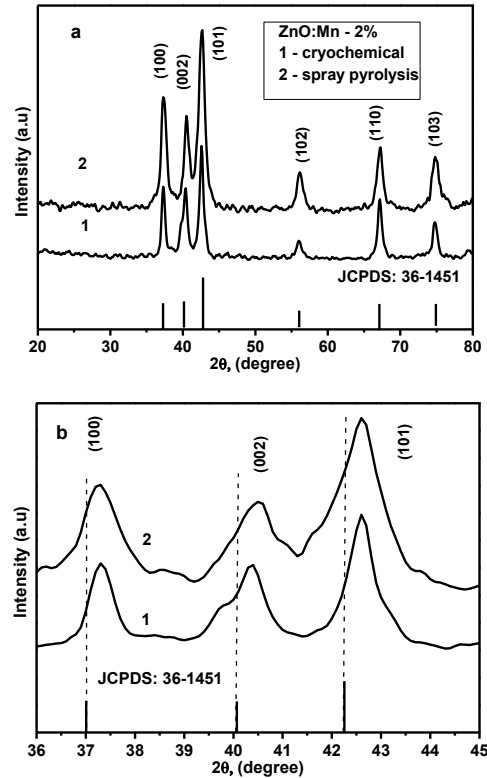


Fig. 1 – XRD patterns of ZnO:Mn-2 at. % NC samples: (a) obtained by CCS (1) and USP (2) methods; (b) shift of reflections (101), (002), (101) of XRD patterns in relation to the standard positions for ZnO

This fact is manifested in the shift of reflections in the XRD pattern towards small angles. Thus, it can be concluded that there is no effective doping of Mn in our samples. A similar decrease in the crystal lattice parameters of ZnO NCs compared to single-crystalline ZnO was obtained in [9, 10]. In [11], it is assumed that the cause of this phenomenon may be the presence of numerous vacancies in the crystal lattices of samples (oxygen V_{O} and zinc V_{Zn}). XRD patterns of the samples were used to determine the average NC size, crystal lattice parameters, and unit cell volume (Table 1). The average size of the ZnO:Mn NC was calculated using the Scherrer formula [15]. For the hexagonal structure of ZnO, the interplanar distance $d(hkl)$ is related to the lattice parameters a and c by such a ratio [8]:

$$\frac{1}{d_{(hkl)}^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right), \quad (2)$$

from which, taking into account (1), in the approximation of the first order of reflection $n = 1$:

$$\sin^2\theta = \frac{\lambda}{4a^2} = \left[\frac{4}{3} (h^2 + hk + k^2) + \left(\frac{a}{c} \right)^2 l^2 \right]. \quad (3)$$

The values of the lattice parameters a and c for the samples were determined by the equation:

$$a = \frac{\lambda}{2 \sin \theta} = \sqrt{\frac{4}{3} (h^2 \alpha + hk + k^2) + \frac{l^2}{(c/a)^2}}, \quad (4)$$

$$c = \frac{\lambda}{2 \sin \theta} = \sqrt{\frac{4l^2}{3(c/a)^2} ((h^2 + hk + k^2) + l^2)}. \quad (5)$$

The unit cell volume for the hexagonal phase was calculated using the equation:

$$V = \frac{\sqrt{3}a^2c}{2} = 0.866a^2c. \quad (6)$$

The analysis of the obtained results shows that under both non-equilibrium (USP method) and equilibrium (CCS method) conditions for the synthesis of ZnO:Mn NCs, the parameters of their crystal lattices a and c are significantly lower than in single-crystalline ZnO. This may be due to the presence of numerous defects and deformation stresses specific to NCs. After annealing at 850 °C for 1 h, these parameters increase and become equal to the standard Mn impurity.

Table 1 – Parameters of the crystal lattice (a and c), unit cell volume (V), and the average size (d) of ZnO:Mn-2 at. % NCs

Type of samples	Parameters of the crystal lattice			NC size
	a , Å	c , Å	V , Å ³	d , nm
USP synthesis at $T_c = 550$ °C	3.2396	5.1873	47.145	34.9
CCS synthesis at $T_c = 350$ °C	3.2364	5.1976	47.129	65.5
Annealing at $T = 850$ °C, (1 h) [13]	3.2541	5.2074	47.753	100.5
ZnO [JCPDS card: 36-1451]	3.2492	5.2053	47.589	–

The EPR spectrum of the CCS sample (Fig. 2a) consists of a wide resonant line of high intensity absorption located in the region of magnetic field values $H = 250$ -375 mT. This result is not typical for pure ZnO. It is known that the EPR spectra of undoped ZnO are of low intensity and are caused by the presence of a small amount of uncontrolled Mn impurity. In our case, the intensive resonance line of EPR can be caused by the presence of numerous intrinsic defects in the samples. These defects are the result of the destructive action of gas environment, which is a product of thermal decomposition of zinc and manganese acetates [14]. A similar EPR spectrum of a ZnO NC sample was obtained in [15]. The synthesis was carried out from zinc acetate by the sol-gel method.

The analysis of the EPR spectrum of the sample obtained by the CCS method shows that in addition to the wide absorption line, it also contains six weak in intensity lines of the hyperfine structure (HFS) of Mn²⁺ ions. In Fig. 2a, they are marked with arrows. This structure is caused by Mn²⁺ ions located in the sites of the ZnO crystal lattice. This confirms the fact of partial doping of ZnO with Mn impurity during the synthesis by the low-temperature CCS method.

The EPR spectrum of the USP sample is shown in Fig. 2b at high resolution. It has an asymmetrical shape. This is a consequence of the fact that at low values of the magnetic field, the spectrum has an additional component. It is caused by acceptor-type defects and magnetic clusters. These clusters lead to the appearance of ferromagnetic resonance (FMR) lines in the spectrum [16]. The EPR spectrum consists of a wide background absorption line caused by the spin-spin interaction of manganese ions, and six lines of low-temperature fusion of Mn²⁺ ions, which are substituted isovalent for Zn²⁺ ions in the ZnO crystal lattice. A feature of the EPR spectra of our samples obtained under nonequilibrium conditions is the bifurcation of HFS lines. In addition to the main group of HFS1 lines, the spectra also show a group of HFS2 lines shifted from the first one by $\Delta H = 3.9$ mT. The appearance of additional HFS lines is associated with Mn²⁺ ions which are located in a different local environment, possibly, on the NC surface in a deformed near-surface layer [17]. Thus, it can be concluded that the arrangement of the Mn dopant and intrinsic defects in the bulk of the ZnO NC is heterogeneous. They are mainly located in the near-surface layer of NCs, and the defect structure of NCs has the form of a "core – shell": a defect-free core and a defective near-surface layer.

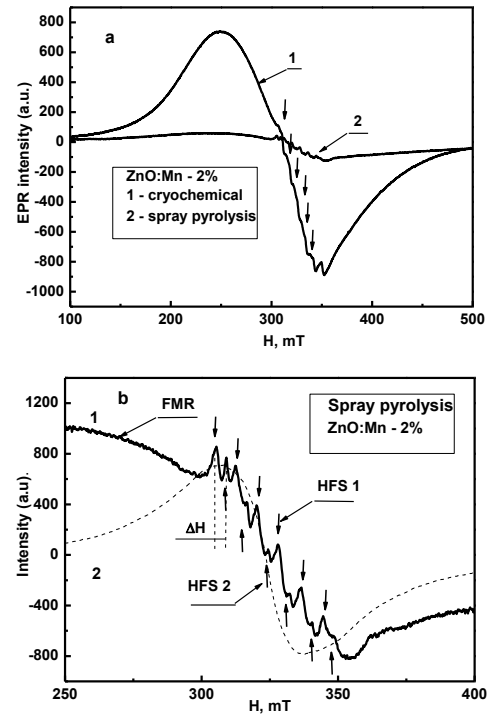


Fig. 2 – EPR spectra of ZnO:Mn-2 at. % NC samples: (a) CCS sample (1) and USP sample (2); (b) detailed structure of the USP sample EPR spectrum, which consists of the ferromagnetic resonance (FMR) line, wide absorption line (2), and two groups of HFS lines of Mn²⁺ ions (HFS1 and HFS2)

Comparison of the intensities of the EPR spectra (Fig. 2a) leads to the conclusion that the number of defects in the CCS samples is much greater than in the USP samples. It is known that the crystal lattice defects are critical in the appearance of FP in DMS. It is shown in [2] that FP in ZnO:Mn NCs are caused by the

presence of intrinsic and impurity defects. According to the theoretical model of bound magnetic polarons [18], the magnetic interaction of these defects is the cause of the appearance of FP in the samples at room temperature. In this case, intrinsic defects, such as oxygen vacancies V_o , act as intermediaries in the exchange interaction between impurity defects – interstitial Mn ions. The study of the magnetic properties of ZnO:Mn-2 at. % NC samples shows that their FP depend on the synthesis method and, as a consequence, on the defective state of the samples (Fig. 3). It was found that the CCS method allows to obtain ZnO:Mn NC samples with high magnetization, which is much higher than that of the samples synthesized by the USP method. The general characteristic of the samples is that their magnetization curves do not have a saturation state at high magnetic field values. This indicates that the magnetization consists of ferromagnetic and paramagnetic components. The number of the paramagnetic phase is determined by the slope of the lines touching these curves. After separation of the paramagnetic component, it was found that the specific magnetization in the saturation state M_s for CCS and USP samples is 0.094 emu/g and 0.028 emu/g, respectively. Thus, the magnetic characteristics of ZnO:Mn NC samples synthesized by the CCS method are more than three times higher than those of NC samples obtained by the USP method. The reason for this may be different conditions

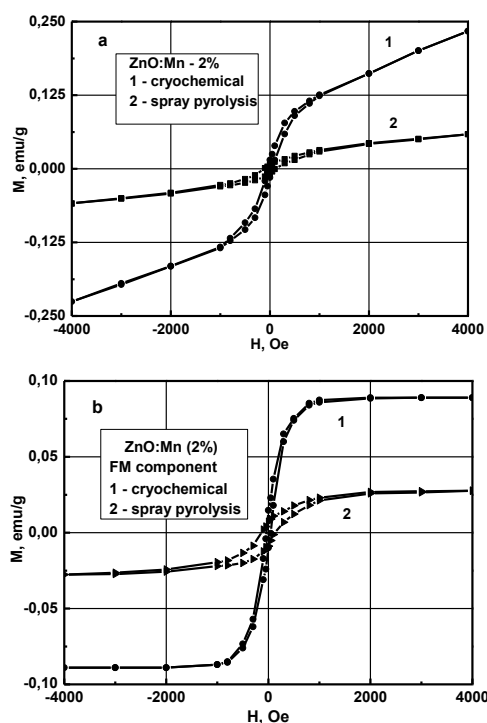


Fig. 3 – Magnetization curves of ZnO:Mn-2 at. % NC samples: (a) experimental curve; (b) their ferromagnetic components after separation of the paramagnetic phase; (1) CCS sample, (2) USP sample

for the formation of ZnO:Mn NCs when synthesized by these methods.

The CCS method is a long-term synthesis method, in which the formation of NCs occurs in equilibrium conditions and in a reducing atmosphere enriched with OH^- hydroxide and CO^- ions. They are formed during thermal decomposition of organic precursors – zinc and manganese acetates [14, 19]. The action of such a gas environment during the formation of ZnO:Mn NCs leads to the appearance of numerous both intrinsic (oxygen vacancies – V_o) and impurity (Mn^{2+} ions) defects throughout the NC volume. Therefore, in the synthesis by the CCS method, the physical processes that determine FP of the samples have a bulk nature. In contrast, USP synthesis is a short-term process. Formation of NCs occurs in nonequilibrium conditions. Under such conditions, NCs with a heterogeneous defect structure are formed: a defect-free core and a defective surface layer where intrinsic and impurity defects are located. Therefore, the nature of ferromagnetism during synthesis by this method has a surface nature. Therefore, the magnetic characteristics of such NCs are less important than those of the CCS samples.

4. CONCLUSIONS

Synthesis of ZnO:Mn-2 at. % NC samples was carried out by USP and CCS methods. The XRD study of the samples showed that the crystal lattice parameters a and c , as well as the unit cell volume V of the samples have much lower values in comparison with single-crystalline ZnO. This is due to the presence of numerous defects and existence of deformation stresses in the crystal lattice.

The study of the EPR spectra showed that the crystal lattice defects and Mn^{2+} ions in the USP samples are located on the surface, while in the CCS samples – in the bulk of the NC. At the same time, the number of defects in CCS samples is much higher than in USP samples.

It is shown that there is a significant influence of the conditions for the synthesis of ZnO:Mn-2 at. % NC cutoffs on their magnetic properties. The magnetization of samples obtained by CCS significantly exceeds the magnetization of samples obtained by USP. This fact is explained by different conditions of NC formation. In the samples obtained by CCS, structural defects and magnetic clusters are formed during synthesis in the NC volume as a result of the action of a reducing gaseous medium. This occurs during thermal decomposition of zinc and manganese acetates. Therefore, the nature of ferromagnetism in these samples has a volume character. In the USP method, structural defects and magnetic clusters are formed on the NC surface; therefore, the nature of ferromagnetism in this case has a surface character.

The results obtained are of practical importance and can be used to create dilute magnetic semiconductors based on ZnO.

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Залежність магнітних властивостей нанокристалів ZnO:Mn від умов синтезу

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Приведено результати досліджень зразків нанокристалів ZnO:Mn з концентрацією Mn 2 ат. %, отриманих методами ультразвукового піролізу аерозолу та крихімічного синтезу. Прекурсорами були нітрати та ацетати цинку та марганцю, відповідно. Зразки досліджувались методами XRD, EPR та методом магнітометрії з вібраційним зразком. Методом XRD встановлено, що параметри кристалічної ґратки нанокристалів мають значно менші значення ніж у монокристалічного ZnO. Це свідчить про наявність у нанокристалах дефектів та деформаційних напружень. Методом EPR показано, що у зразках, отриманих методом ультразвукового піролізу аерозолу, дефекти та домішкові іони Mn²⁺ розташовані не в об'ємі, а у приповерхневому шарі нанокристалів. Зразки, отримані методом крихімічного синтезу, мають велику кількість власних дефектів акцепторного типу. Намагніченість цих зразків значно більша, ніж зразків, отриманих методом ультразвукового піролізу аерозолу. Це може бути наслідком того, що у зразках, отриманих методом ультразвукового піролізу аерозолу, феромагнетизм виникає на поверхні, а у зразках, отриманих крихімічним синтезом, – у об'ємі нанокристалів. Він обумовлений деструктивною дією газового середовища, яке утворюється під час термічного розкладу ацетату цинку. Такі умови крихімічного синтезу приводять до появи у нанокристалах великої кількості об'ємних дефектів.

Ключові слова: Оксид цинку, Нанокристал, Ультразвуковий піроліз аерозолу, Крихімічний синтез, Дефекти.