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Structural and magnetic properties of ZnO:Mn nanocrystals obtained by ultrasonic spray pyrolysis

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ZnO:Mn nanopowders with Mn concentrations of 2, 4, and 8 at.%, obtained by ultrasonic spray pyrolysis at different synthesis temperatures, were studied. The structure of the nanoparticles were studied with methods of X-ray diffraction. Magnetic properties were measured using a vibrating magnetometer. It was found that an increase in the Mn impurity concentration leads to a decrease in the nanocrystal size and crystalline quality of the samples. At low synthesis temperatures of $T = 650^{\circ}\text{C}$, secondary phases are observed in samples with a Mn concentration of > 4 at.%, indicating a low solubility of Mn impurity in ZnO. It is shown that the unit cell volume in these samples is significantly smaller compared to single-crystal ZnO. This is an indication of the presence of a large number of intrinsic defects in the crystal lattice, which cause deformation stresses. When synthesizing samples at $T = 750^{\circ}\text{C}$, the unit cell volume is larger than that of single-crystal ZnO. This is the result of a more efficient Mn doping process during synthesis and a reduction in the number of defects in the samples. At the same time, the solubility limit increases, allowing the production of single-phase samples with a Mn concentration of > 8 at.%. The resulting samples were found to possess ferromagnetic properties at room temperature. Magnetization M_s in the samples decreased with increasing Mn concentration and synthesis temperature. The maximum magnetization ($M_s = 0.035$ emu/g) was observed in samples with a Mn concentration of 2 at.%, obtained at a temperature of $T = 550^{\circ}\text{C}$, which corresponds to the maximum defect state of the samples.

Keywords: nanocrystals, zinc oxide, Mn impurity, ultrasonic spray pyrolysis, crystal lattice defects, X-ray diffraction, oxygen vacancy, ferromagnetic properties.

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Introduction

Dilute magnetic semiconductors (DMSs), produced by doping semiconductors with transition metal atoms, are the focus of scientific attention due to their potential use in spintronic devices [1]. The key requirement for dilute magnetic semiconductors is a high saturation magnetization, M_s , at room temperature. Manganese-doped zinc oxide is a promising material for constructing spintronic devices. The Mn^{2+} ion has five unpaired electrons in the $3d^5$ state. This creates a significant magnetic moment for the Mn^{2+} ion and determines the high ferromagnetic properties (FP) of the samples. Numerous studies have shown that, regardless of the synthesis method, increasing the Mn impurity concentration decreases the magnetization of DMSs [2, 3]. The effect of Mn impurity on the structural properties and

FP of ZnO:Mn nanopowders was studied in [3]. The synthesis of nanocrystals (NCs) was carried out by chemical precipitation from zinc acetate and manganese acetate solutions at $T = 50^{\circ}\text{C}$. It was shown that the doping process leads to an increase in the number of defects in the crystal lattice (CL), including oxygen vacancies (Vo). ZnO:Mn samples had FP, their magnetization in the saturation state M_s decreased with an increase in the Mn concentration. In [2] it was shown that during the synthesis of ZnO:Mn nanopowders (2 at.%) by the solid state reaction technique, an increase in the synthesis temperature from $T = 500^{\circ}\text{C}$ to $T = 700^{\circ}\text{C}$ leads to a decrease in the magnetization M_s . According to the authors, this is due to a decrease in the number of intrinsic defects in the samples, which play a major role in the appearance of FP. This is confirmed by the studies presented in [4], where the possibility of influencing the

FP in ZnO:Mn NCs by their mechanical grinding was established. It was proven that the magnetization of the samples increased with increasing milling time due to the increase in the amount of Vo on the NCs surface. In [5], the possibility of converting ZnO:Mn NCs from the paramagnetic state to the ferromagnetic state by mechanical milling in an inert atmosphere was demonstrated. This became possible due to the appearance of Vo defects on the NCs surface. In other studies, it was established that for FP to appear, it is necessary to achieve an appropriate defect structure in NCs [6,7]. The ultrasonic spray pyrolysis (USP) method makes it possible to control the defect state of NCs and create in them the defect structure necessary for the appearance of FP [8, 9]. However, at present, there are no comprehensive studies of the magnetic properties of ZnO:Mn NCs obtained by this method. Only in [10] were ZnO:Mn films synthesized by the USP method investigated and the presence of FP in them was established. It is known that the synthesis of NCs by the USP method occurs under special conditions - in the volume of one drop of the aerosol solution during its passage through the thermal zone of the furnace [8]. Under these synthesis conditions, the NCs develop a corresponding defect structure that cannot be reproduced by other synthesis methods. Therefore, conducting structural studies and establishing the influence of defects on the FP of ZnO:Mn NCs obtained by the USP method is an urgent task.

I. Synthesis Method

For the study, ZnO and ZnO:Mn NCs samples with Mn concentrations of 2, 4, and 8 at.% were obtained by the USP method at various synthesis temperatures. Synthesis was performed from zinc and manganese nitrate solutions under the conditions specified in [9]. The prepared solution of the components was sprayed into aerosol droplets with a size of $d = 1-2 \mu\text{m}$. These droplets were transported, using a carrier gas (air), through a reaction zone of a furnace heated to temperatures of $T = 550^\circ\text{C}$, $T = 650^\circ\text{C}$, or $T = 750^\circ\text{C}$, where the droplet drying and ZnO:Mn NCs synthesis occurred for a limited

time ($7-10$ s). The final product, in the form of spherical granules, was collected on a filter at $T = 250^\circ\text{C}$. The crystal structure and phase composition of the samples were studied by X-ray diffraction (XRD) analysis on a DRON-2M diffractometer using Cu-K α radiation ($\lambda = 1.5417$). The magnetic properties of the samples were investigated by vibration magnetometry on an experimental setup with a sensitivity of 10^{-4} emu/g. Pure nickel powder was used as a reference sample.

II. Results and Discussion

X-ray diffraction patterns of the samples synthesized at temperatures of $T = 650^\circ\text{C}$ and $T = 750^\circ\text{C}$ are shown in Fig. 1. Analysis of the X-ray diffraction patterns reveals that the crystal structure of the samples is hexagonal, wurtzite-type (in accordance with JCPDS standard: 36-1451). With increasing Mn concentration, the intensity of the reflections decreases, and the lines become more broad, indicating a decrease in the crystalline quality of the samples. In the X-ray diffraction patterns of samples obtained at $T = 650^\circ\text{C}$ with a concentration of more than 2 at.%, there is the presence of secondary phases ZnMn₂O₄ and Mn₂O₃. This indicates a low solubility level of the Mn impurity in ZnO; the solubility limit can be determined to be less than 4 at.%.

After increasing the synthesis temperature to $T = 750^\circ\text{C}$, samples with a homogeneous phase composition were obtained. The X-ray diffraction patterns of these samples show no secondary phase reflections. Under these synthesis conditions, the solubility limit of the Mn impurity increases and can exceed 8 at.%. Improvement in the doping process of ZnO:Mn NCs is a consequence of additional thermal annealing of the dry granule at high synthesis temperatures while moving it within the furnace thermal zone [8].

Based on the X-ray diffraction data, the structural parameters of the CL (a , c), the unit cell volume (V), and the nanocrystal dimensions (d) were obtained at different synthesis temperatures (Table 1).

It was found that with increasing Mn impurity concentration, the nanocrystal size decreases at different

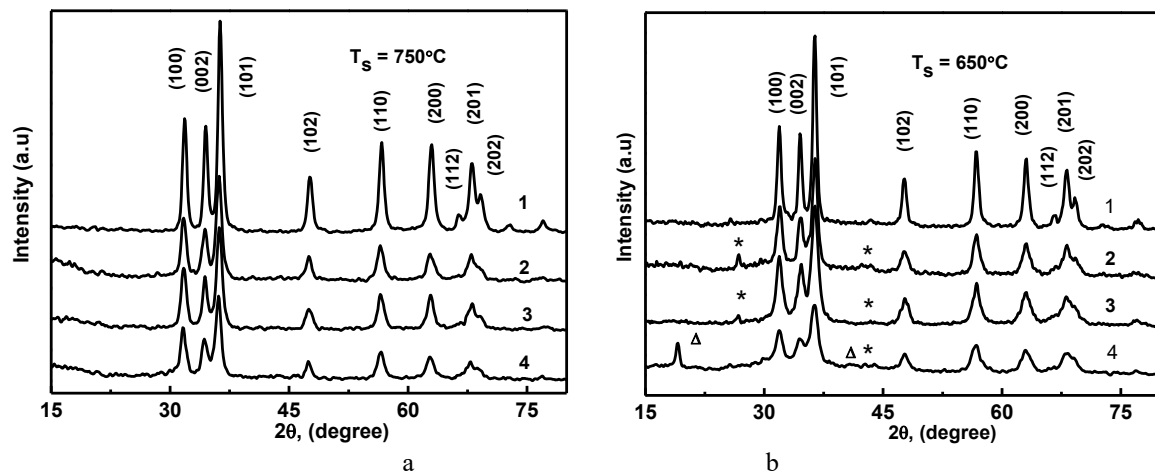


Fig. 1. X-ray diffraction patterns of samples obtained at $T = 650^\circ\text{C}$ - (a) and $T = 750^\circ\text{C}$ - (b): samples ZnO NCs - (1); ZnO:Mn NCs with Mn concentration of 2 at.% - (2); 4 at.% - (3) and 8 at.% - (4). Secondary phases are designated by symbols: * - ZnMn₂O₄, Δ - Mn₂O₃.

synthesis temperatures (Table 1). This result has been observed in many other studies [11, 12]. This pattern can be explained in accordance with the molecular kinetic theory of crystal growth from a supersaturated solution. It is believed that the crystal growth rate in one of the crystallographic directions decreases if impurity atoms appear on an atomic plane. The probability of impurity atoms appearing on atomic planes in all growth directions is equal, therefore, after some time, the increase in the NC size slows down [13].

From the presented results (Table 1), it is evident that in the samples obtained at $T = 650^\circ\text{C}$, the CL parameters, as well as the unit cell volume V , are significantly smaller compared to single-crystal ZnO [14]. This indicates the presence of deformation stresses in the CL caused by the appearance of a large number of CL defects, primarily V_o [15], with an increase in the Mn impurity concentration to the solubility limit of 4 at.%. Beyond the solubility limit, some of the Mn ions are part of secondary phases (ZnMn_2O_4 and Mn_2O_3), and therefore do not increase the deformation stresses of the CL. At the same time, the number of oxygen vacancies V_o does not increase. This result is consistent with the conclusion made in [3], which showed that in ZnO:Mn NCs, the intensity of green emission in the photoluminescence spectra, caused by oxygen vacancies V_o , increases only with an increase in the Mn impurity concentration to 5 at.%. Further doping does not affect the emission in this region of the photoluminescence spectrum. Thus, it can be assumed that synthesis at $T = 650^\circ\text{C}$ does not lead to significant doping of ZnO NCs with Mn impurity. Mn ions that are not incorporated into ZnO CLs are located on the NCs surface

in the form of amorphous clusters [16] or form secondary phases - ZnMn_2O_4 and Mn_2O_3 . Therefore, the defective structure of NC can look like a structurally ordered core and a defective shell in which the Mn impurity is located.

The non-uniform distribution of Mn impurity within the bulk of ZnO:Mn NCs during synthesis at $T = 650^\circ\text{C}$ is explained by the specific features of NC formation using the USP method. NC synthesis occurs under nonequilibrium conditions in a very short time, with the formation of a large number of defects. The structure of defects in NC is due to the fact that, some time after the nucleation of the NC core, subsequent synthesis occurs from a depleted solution. Therefore, vacancies and other structural defects arise on the growth planes [13].

Synthesis of ZnO:Mn NCs samples at $T = 750^\circ\text{C}$ is characterized by a more intense doping process. This is indicated by the unit cell volume V in these samples being larger than that of single-crystal ZnO (Table 1). This difference increases with increasing Mn impurity concentration, which is a consequence of ZnO doping by substituting Zn^{2+} ions (ionic radius $0.67 \text{ \AA}$) with Mn^{2+} ions with a similar ionic radius ($0.74 \text{ \AA}$).

A study of the magnetic properties of the samples revealed that ZnO:Mn NCs exhibit FP at room temperature. Analysis of the magnetization curves, shown in Figure 2, suggests that the magnetization of the $M(H)$ samples does not exhibit a clear hysteresis. This indicates that, in addition to magnetization from the ferromagnetic phase $M_f(H)$, the samples also contain magnetization from the paramagnetic phase $M_p(H)$, therefore: $M(H) = M_f(H) + M_p(H)$. As is known, the magnetization of the paramagnetic phase is determined by the slope of

Table 1.

Type of samples	Structural parameters							
	Synthesis $T = 650^\circ\text{C}$				Synthesis $T = 750^\circ\text{C}$			
	a, $\text{\AA}^\circ$	c, $\text{\AA}^\circ$	V, $\text{\AA}^3$	d, nm	a, $\text{\AA}^\circ$	c, $\text{\AA}^\circ$	V, $\text{\AA}^3$	d, nm
ZnO, synthesized	3,241	5,195	47,29	56,4	3,241	5,212	47,59	58,5
ZnO:Mn(2at.%)	3,243	5,197	47,34	36,2	3,249	5,207	47,76	40,7
ZnO:Mn(4at.%)	3,240	5,196	47,25	31,2	3,257	5,205	47,83	40,2
ZnO:Mn(8at.%)	3,239	5,198	47,23	30,0	3,254	5,219	47,86	36,0
ZnO, [14]	3,249	5,205	47,59	-	3,249	5,205	47,59	-

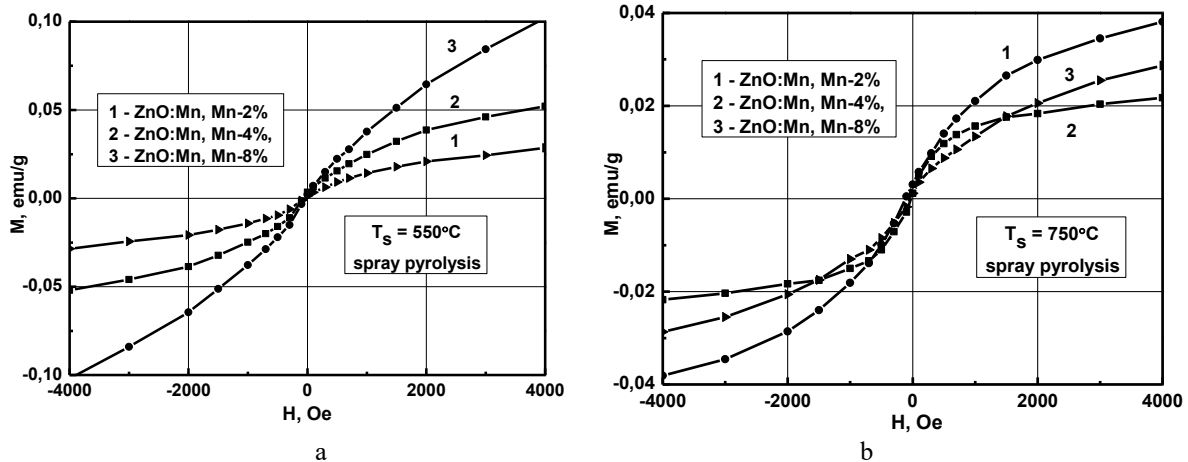


Fig. 2. Magnetization curves of ZnO:Mn samples synthesized at $T = 550^\circ\text{C}$ - (a) and $T = 750^\circ\text{C}$ - (b) with Mn impurity concentrations of: 2 at.% - 1; 4 at.% - 2; 8 at.% - 3.

the lines associated with the magnetization curves. The paramagnetic properties of the samples are linearly dependent on the magnetic field H , and their magnetization is defined as $M_p(H) = \chi H$, where χ is the specific susceptibility. Therefore, it is possible to separate the ferromagnetic component from the paramagnetic component using experimental magnetization curves, thereby determining the specific magnetization of the samples in the saturation state, M_s (Table 2). After separating the paramagnetic component, hysteresis curves of magnetization $M_f(H)$ of the ferromagnetic phase were obtained (Fig. 3).

From these results, it can be concluded that the magnetization M_s of the ZnO:Mn NCs samples decreases with increasing Mn impurity concentration. Thus, for the samples obtained at $T = 550^\circ\text{C}$, the value of M_s changes from 0.035 to 0.018 emu/g with a change in the Mn impurity concentration from 2 to 8 at.%, respectively. Similar results were also obtained in [2, 3]. To explain such results, a theoretical model of ferromagnetism in DMSs [17] was proposed, based on the concept of mediated magnetic interaction of impurity ions - the model of bound magnetic polarons (BMP). According to this model, FP in ZnO:Mn NC are caused by the interaction between Mn^{2+} ions indirectly due to the intrinsic defects of the CL. In this case, intrinsic defects, for example oxygen vacancies V_o , act as intermediaries in the exchange interaction between impurity defects - Mn^{2+} ions. The magnetic polaron in ZnO:Mn NC is an electron captured by an oxygen vacancy V_o , which interacts with the $3d^5$ electrons of Mn^{2+} ions. During this interaction, the magnetic moments of the Mn^{2+} ions are oriented in the same direction, leading to the formation of local ferromagnetic clusters that determine the FP of the

sample. At low impurity concentrations, the probability of such ions being located close to each other in the NCs is very low, which hinders their direct interaction. In this case, only Mn^{2+} ions bound by the magnetic polaron participate in the exchange interaction and determine the FP of the NCs [18]. Free Mn^{2+} ions, for which there are not enough oxygen vacancies V_o to create magnetic polarons, determine the paramagnetic properties of the NCs. The decrease in sample magnetization with increasing Mn^{2+} ion concentration above 2 at.% within the BMP model is explained by the fact that under these conditions the probability of direct interaction of Mn^{2+} ions increases, leading to the emergence of antiferromagnetic properties. In this case, the overall magnetization of the samples can decrease, and then $M(H) = M_f(H) + M_p(H) - M_{af}(H)$, where $M_{af}(H)$ is the antiferromagnetic magnetization. Thus, for the appearance of FP, it is necessary to form an appropriate balance between the concentration of Mn impurity and the concentration of oxygen vacancies V_o .

A decrease in sample magnetization M_s with increasing Mn impurity concentration also occurs at high synthesis temperatures of $T = 750^\circ\text{C}$ (Table 2). According to the BMP model this may be due to a decrease in the number of V_o defects. In the USP method, NCs synthesis occurs rapidly at high temperatures, therefore the dry granule in the thermal zone of the furnace is additionally subjected to thermal annealing, after which the number of defects decreases [19].

At the synthesis temperature $T = 550^\circ\text{C}$, the magnetization of ZnO:Mn NCs increases due to an increase in the paramagnetic component (Fig. 2a), which, in turn, increases due to an increase in the concentration of free Mn^{2+} ions. Thus, in accordance with the well-

Table 2.

Magnetic characteristics of ZnO:Mn NCs samples

Type of samples	Synthesis $T = 550^\circ\text{C}$		Synthesis $T = 750^\circ\text{C}$	
	M_s , emu/g	χ , cm^3/g	M_s , emu/g	χ , cm^3/g
ZnO:Mn(2at.%)	0,035	$3,9 \cdot 10^{-6}$	0,023	$3,8 \cdot 10^{-6}$
ZnO:Mn(4at.%)	0,028	$6,5 \cdot 10^{-6}$	0,015	$1,7 \cdot 10^{-6}$
ZnO:Mn(8at.%)	0,018	$1,7 \cdot 10^{-5}$	0,011	$3,2 \cdot 10^{-6}$

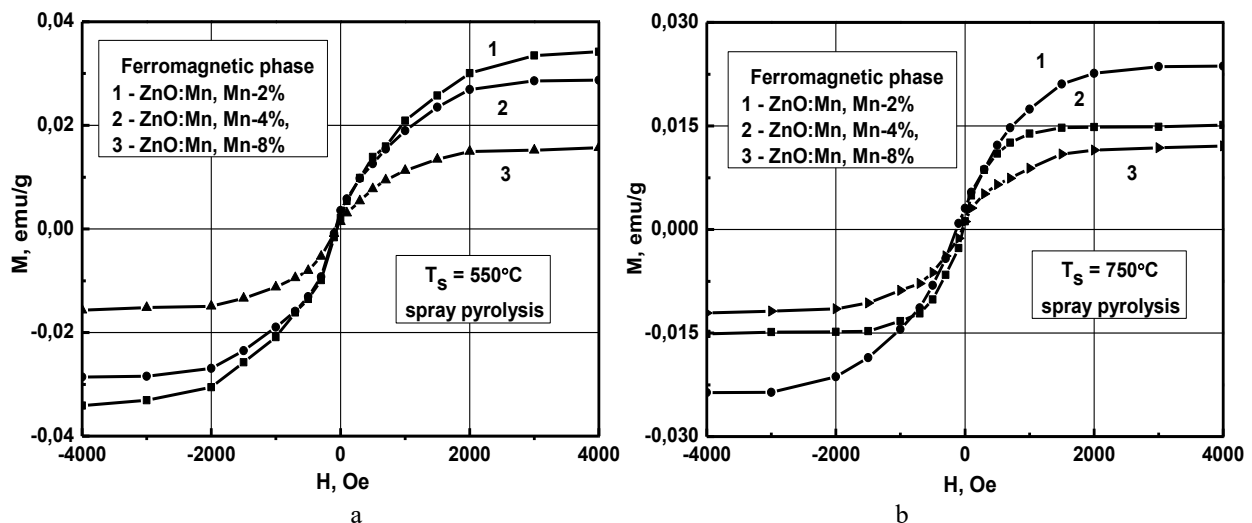


Fig. 3. Magnetization curves $M_f(H)$ of the ferromagnetic phase of ZnO:Mn samples synthesized at $T = 550^\circ\text{C}$ - (a) and $T = 750^\circ\text{C}$ - (b) with Mn impurity concentrations of: 2 at.% - 1; 4 at.% - 2; 8 at.% - 3.

known Curie-Weiss relation, the specific susceptibility $\chi = N\mu^2 / 3kT$, where $N\mu$ is the number of magnetic moments associated with free Mn^{2+} ions; μ is the magnetic moment of free Mn^{2+} ions, in Bohr magnetons; k is the Boltzmann constant; T is the temperature. Due to the increase in $N\mu$ with a change in the concentration of Mn impurity from 2 to 8 at.%, the specific susceptibility χ increases fourfold (Table 2). A similar dependence of the change in the concentration of free Mn^{2+} ions on the Mn impurity concentration was obtained in [20] during the synthesis of ZnO:Mn NCs by the sol-gel method. To explain this nature of the change in the magnetization of the samples within the framework of the BMP model, it is necessary to take into account that the magnetic properties of the samples depend not only on the number of participants in the exchange interaction – oxygen vacancies Vo and Mn^{2+} ions, but also on the ratio of their concentrations. At low Mn concentrations in the synthesized ZnO:Mn NCs samples, the concentration of Mn^{2+} ions always exceeds the concentration of oxygen vacancies Vo [21]. In this case, the magnetization of the samples contains not only a ferromagnetic but also a paramagnetic component.

Conclusions

ZnO:Mn NCs with Mn impurity concentration of 2, 4 and 8 at.% was synthesized using UPA method at different temperatures. Studies of defect state of ZnO:Mn NCs showed that their CL are in a nonequilibrium state and have deformation stresses. It is shown that the doping process is partial: the solubility limit of Mn during synthesis at $T = 650^\circ\text{C}$ does not exceed 4 at.%. At the same time, the increase of Mn concentration to the solubility limit increases the number of intrinsic defects in them – oxygen vacancies Vo . Synthesis at high temperatures ($T = 750^\circ\text{C}$) is accompanied by a decrease in the number

of defects and deformation stresses in NCs, as well as an increase in the solubility limit of Mn impurity, it exceeds 8 at.%. It is shown that the non-uniform arrangement of Mn impurity in the volume of ZnO:Mn NCs determines the defective structure of the NCs. It consists of a structurally ordered core and a defective shell containing a Mn impurity and Vo oxygen vacancies. Changes in the CL parameters and dimensions of ZnO:Mn NCs were analyzed depending on the synthesis temperature and Mn impurity concentration.

Studies of the magnetic properties of ZnO:Mn NCs revealed the presence of FP at room temperature. The dependence of the magnetization of these samples on the Mn impurity concentration and synthesis temperature was established. It was shown that at low synthesis temperatures ($T = 550^\circ\text{C}$), their magnetization increases upon doping due to an increase in the paramagnetic component, but the magnetization M_s of the ferromagnetic component decreases from 0.035 to 0.018 emu/g with varying concentrations. Synthesis at high temperatures ($T = 750^\circ\text{C}$) leads to a decrease in the magnetization of the samples due to a reduction in the number of Vo defects. It is shown that when analyzing the magnetic properties of samples within the framework of the theoretical model of BMP, it is necessary to take into account not only the concentration of oxygen vacancies Vo and Mn^{2+} ions, but also their mutual relationship. The obtained results confirm the existence of a relationship between Vo structural defects and Mn^{2+} impurity ions, which determines the FP of the samples.

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Структурні та магнітні властивості нанокристалів ZnO:Mn, отриманих методом ультразвукового піролізу аерозолі

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Досліджено нанопорошки ZnO:Mn з концентрацією Mn 2, 4 та 8 ат.%, отримані методом ультразвукового піролізу аерозолі при різних температурах синтезу. Структура наночастинок досліджувалась методами рентгенівської дифракції. Магнітні властивості вимірювалися за допомогою вібраційного магнітометра. Встановлено, що збільшення концентрації домішки Mn приводить до зменшення розмірів нанокристалів та кристалічної якості зразків. При низьких температурах синтезу $T = 650^{\circ}\text{C}$ у зразках при концентрації Mn > 4 ат.% фіксуються вторинні фази, що свідчить про низький рівень розчинності домішки Mn в ZnO. Показано, що у цих зразках об'єм елементарної комірки є значно меншим у порівнянні з монокристалічним ZnO. Це є ознакою наявності у кристалічній ґратці великої кількості власних дефектів, які обумовлюють наявність деформаційних напружень. При синтезі зразків при $T = 750^{\circ}\text{C}$ об'єм комірки є більшим ніж у монокристалічного ZnO. Це є наслідком більш ефективного процесу легування домішкою Mn під час синтезу та зменшення кількості дефектів у зразках. При цьому межа розчинності збільшується, що дозволяє отримувати однофазні зразки з концентрацією Mn > 8 ат.%. Встановлено, що отримані зразки мали феромагнітні властивості при кімнатній температурі. Намагніченість M_s у зразках зменшувалась при збільшенні концентрації Mn та температури синтезу. Максимальну намагніченість ($M_s = 0,035 \text{ Гс}\cdot\text{см}^3/\text{г}$) мають зразки отримані при температурі $T = 550^{\circ}\text{C}$ з концентрацією Mn 2 ат.%, що відповідає максимальному стану дефектності зразків.

Ключові слова: нанокристали, оксид цинку, домішка Mn, ультразвуковий піроліз аерозолі, дефекти кристалічної ґратки, рентгенівська дифракція, киснева вакансія, феромагнітні властивості.