CRYSTAL STRUCTURE OF ZnO NANOCRYSTALS SYNTHESIZED BY THE SPRAY PYROLYSIS METHOD

O. V. Kovalenko*, V. V. Slavnyi

Oles Honchar Dnipro National University, Dnipro,Ukraine
**e-mail:kovalenko.dnu@gmail.com*

The paper discusses the issues related to the influence of technological conditions of synthesis by ultrasonic spray pyrolysis on the size and lattice parameters of ZnO:Mn nanocrystals. It is found that, depending on the concentration of zinc nitrate in the base solution from 5% to 10%, the synthesized nanocrystals have sizes ranging from 36÷40 nm for small solution droplets and 51÷55 nm for large droplets, respectively. Based on the X-ray diffraction data, it is found that the nanocrystals of small sizes have a more perfect crystal structure with a small number of intrinsic defects compared to the nanocrystals of larger sizes.

Keywords: method of ultrasonic spray pyrolysis, zinc oxide, zinc nitrate, nanocrystals, X-ray phase analysis, lattice parameter.

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1. Introduction

The method of ultrasonic spray pyrolysis (USP) favorably differs from other methods of nanocrystal (NC) synthesis in that it does not require expensive equipment, is environmentally friendly, and allows to obtain NCs both in the form of powder and epitaxial films [1]. This method is used to obtain ZnO:Mn NCs that have ferromagnetic [2, 3], sensory [4] properties, and are also promising for the construction of spintronics devices [5]. The peculiarity of the USP method is that the formation of NCs occurs within a short period of time (several seconds) under non-equilibrium conditions. This produces samples with a core-shell structure, where the "core" is the crystal embryo of the NC, and the "shell" is the outer defective layer around the "core". It is this layer that determines the physical properties of NC [3,4]. Based on this, it is clear that the influence of technological conditions of synthesis on the size of NCs and the formation of the said "shell" in them is of great practical importance. Among the factors that affect the formation of ZnO NCs, the main ones should be noted, namely: the size of the droplets of aqueous solution from which NCs are synthesized, the concentration of the base material (zinc nitrate or zinc acetate) in the solution, the presence of impurities and their concentration in the solution, the rate of solution consumption during the synthesis, the time and temperature of synthesis, etc.

It is known from the literature that one of the factors that affects the physical properties of NCs during the synthesis by the USP method is the concentration of the base material in the initial solution. Thus, in [6], it was shown that during the synthesis of ZnO NCs by the USP method at $T = 500^{o}$C, a decrease in the concentration of zinc nitrate (ZN) from 10 % to 1 % causes a change in the size of NCs, namely, a decrease in size from 55 nm to 23 nm. The synthesis of ZnO from a solution of zinc acetate with a concentration of 0.3 % (0.01M) allows to obtain NCs with a size of 15 nm [7]. Also, the possibility of reducing the size of ZnONCs by reducing the concentration of ZN was shown in [8]. At the same time, it is important to investigate how a change in the initial solution concentration affects the structural parameters of NCs during the synthesis of ZnO:Mnnanopowder at different concentrations of Mn impurity.

Studies that can provide information on the state of the defective "shell" of NCs require additional attention. Such data can be obtained on the basis of X-ray diffraction (XRD) analysis, which allows to determine the presence of defective states in the crystal lattice by shifting the X-ray peak reflexes relative to the standard values for ZnO crystals (JCPDS: 36-1451). Thus, the shift of the X-ray reflexes towards larger angles indicates an unbalanced

state of the crystal lattice with the presence of its own point defects such as oxygen vacancies or zinc vacancies.

The aim of this work is to determine the technological conditions of synthesis that determine the quality of ZnO:Mn NCs and to assess the presence of defective states in them based on XRD data.

2. Experimental part

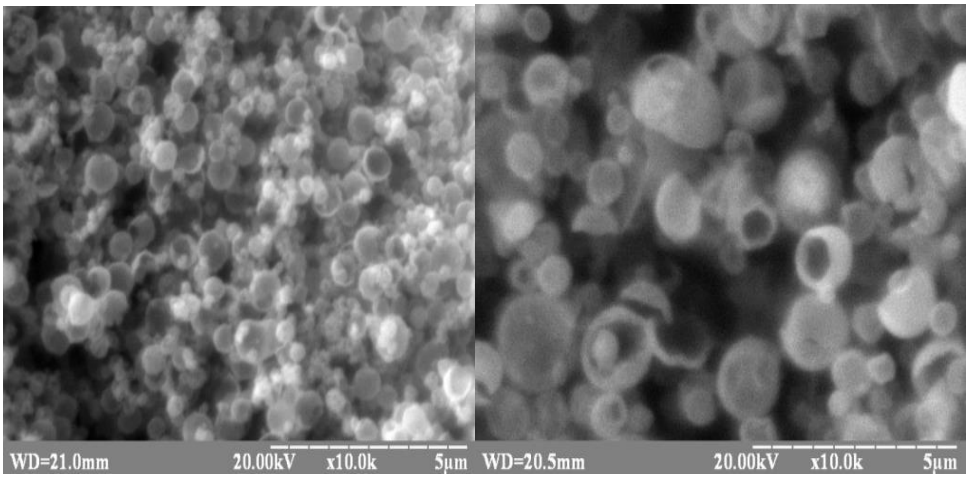
The USP method is based on the thermal decomposition of the spray droplets of the initial solution as they pass through the thermal zone. In this case, thermal decomposition occurs in a carrier gas atmosphere. For the synthesis of NCs ZnO and ZnO:Mn by this method, an aqueous solution of ZN was used: 1%–10% (0,03–0,3M). The doping of the samples with an Mn impurity was carried out by adding a manganese nitrate to the base ZN solution, which corresponded to the atomic concentration of Mn in NCs of 2 at. %, 4 at. %, and 8 at. %, respectively. During the synthesis, air was used as a carrier gas, the solution flow rate was 20 l/h, the synthesis temperature was T = 550°C, and the residence time of the solution droplets in the thermal zone was 6–8 s. The obtained powder was separated from water vapor and other synthesis products on a filter made of stainless mesh and heated to T = 230–250°C. The XRD analysis of the powder was performed with a DRON-2M diffractometer using Co Kα radiation (λ = 1.7902 Å), and the image of the powder particles was obtained using a REMMA-102-02 electron microscope.

It is known that the crystal structure and size of NCs are determined by the size of droplets of the aqueous solution of the ZN base material in it. In ultrasonic spraying, the droplet size is determined by the expression [8]:

$$d = 0{,}34\left(\frac{8\pi w}{\rho f^2}\right)^{\frac{1}{3}}, \qquad (1)$$

where ρ is the solution density, f is the spraying frequency, and w is the surface tension of the solution, which depends on the ZN concentration.

Such dimensions can be easily calculated using the parameter w according to [7]. In turn, such calculations are in good agreement with the size of the powder granules obtained using an electron microscope (Fig. 1).



a **b**

Fig. 1. Appearance of ZnO NC granules obtained using ZN solutions of 1% (a) and 10% (b).

These granules are spherical in shape, and their size decreases with decreasing concentration of ZN in the solution, as well as in accordance with the value of the parameter *w* in (1).

It has been established that in the synthesis of ZnO nanocrystals using a 1% ZN solution, the diameter of the granules is 0.3÷1 μm, and when using a 10% Zn solution, the diameter of the granules *D* is 1÷3 μm. Such microcrystalline granules consist of NCs with a wurtzite lattice crystal structure. The size of NCs calculated using the Scherrer method also decreases with the decrease in the size of the granules *D* in accordance with the ratio:

$$D = \frac{k\lambda}{\beta\cos\theta}, \qquad (2)$$

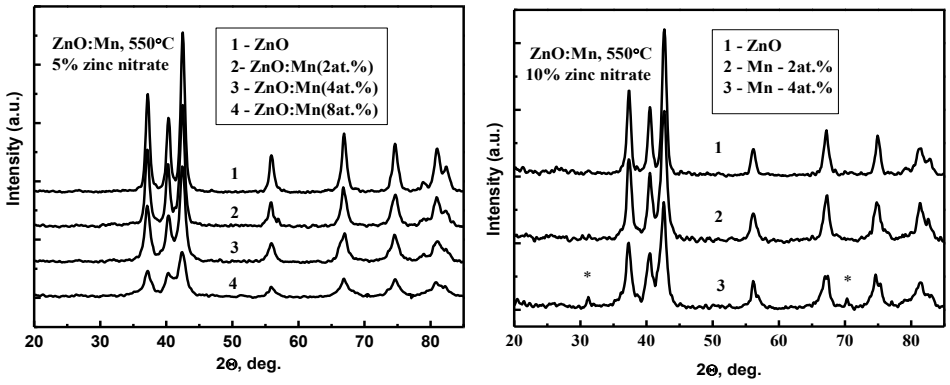
where k = 0.9; λ is the X-ray wavelength (λ= 1.7902Å), β is the angular width of the X-ray reflex at half the peak height, θis the angle between the incident X-ray and the reflection plane.

These sizes were found to be 36÷40 nm for small granules and 51÷55 nm for large granules, respectively.

The synthesis of NCs by the USP method takes place in the volume of a microdroplet of solution as it passes through the thermal zone of the furnace. In this case, the following processes occur sequentially: evaporation of the solvent (water) from the droplet surface to form a solid shell, drying of the substance, synthesis of NC by thermal decomposition of the components, and heat treatment of the dry granule. Increasing the heat treatment time is possible if the time for the previous synthesis steps is reduced.

Reducing the volume of the solution microdroplet and the concentration of ZN (5%) leads to a decrease in the mass of the substance in the droplet. Therefore, the processes of water evaporation, drying, and thermal synthesis of ZnO:Mn NCs occur faster than in a large microdroplet with a higher ZN concentration (10%). This increases the heat treatment time during the passage of the dry pellet through the thermal zone of the furnace. The sign of such a process of ZnO:Mn NC formation, characterized by an extended heat treatment time, is the absence of impurity phases in the X-ray diffraction patterns of samples obtained from a solution of ZN of 5% (Fig. 2).

The parameters of the ZnO crystal lattice are also significantly affected by the concentration of Mn impurity. The analysis of the given X-ray diffraction patterns (Fig. 2) shows that the obtained samples have a wurtzite crystal structure. An important result is that at all concentrations of Mn impurity, X-ray diffraction patterns of samples obtained from ZN concentrations of 5% show no X-ray reflexes from impurity phases. This indicates that homogeneous NCs were obtained under such synthesis conditions. In contrast, in the ZnO:Mn NCs (4 wt.%) obtained from a solution of 10% ZN, there is an impurity phase MnO_2 (Fig. 2b). In turn, this indicates that not all impurity Mn ions at such a concentration of ZN in solution and the concentration of the alloying impurity have time to find their place in the ZnO crystal lattice. Therefore, they begin to form a "shell" of the ZnO NC crystal core.



a **b**

Fig. 2. XRD data of ZnO:Mn NC samples obtained from ZN solution with a concentration of 5% (a) and 10% (b) depending on the concentration of Mn impurity (*- reflexes from the MnO_2).

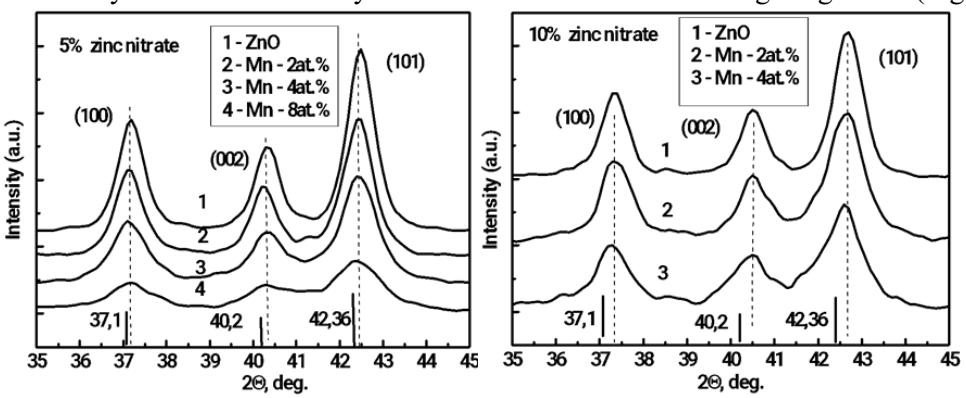
It is also important to note that with an increase in the concentration of Mn impurity, the intensity of the reflexes decreases and their width increases. This is a sign of a decrease in the size of NCs, which is confirmed by the corresponding calculations by the Scherrer method (Table 1).

Table 1

Dependence of the crystal lattice parameters (a, c), its volume (V), and the size of ZnO:Mn NCs (d) on the concentration of Mn impurity in comparison with the corresponding parameters of ZnO single crystals

Impurity Mn, at. %	Structural parameters of ZnO:Mn NCs							
	ZNsolution - 5%				ZN solution - 10%			
	a, Å	c, Å	V, Å^3	d, нм	a, Å	c, Å	V, Å^3	d, нм
0	3,2463	5,2111	47,555	49,4	3,2300	5,1698	46,714	54,4
2,0	3,2480	5,2067	47,570	44,2	3,2352	5,1951	47,088	40,6
4,0	3,2480	5,2125	47,623	30,6	3,2396	5,1873	47,146	34,8
8,0	3,2454	5,1968	47,404	28,5	3,2389	5,1983	47,225	30,0
Structural parameters of ZnO crystals [10]								
			a, Å	c, Å	V, Å^3			
			3,2492	5,2053	47,590			

The study of the position of ZnO:Mn NC X-ray reflexes in X-ray diffraction patterns shows that they are characterized by a shift of all reflexes towards large angles 2Θ (Fig. 3).



a **b**

Fig. 3. Shifts of X-ray reflexes (100), (002) and (101) in ZnO:Mn NCs obtained from ZN solutions with the concentration of 5% (a) and 10% (b) depending on the concentration of Mn impurity in the synthesized samples.

In the synthesis of NCs from a solution of ZN 5%, such shifts were much smaller compared to similar shifts in the synthesis of NCs from a solution of ZN 10%. For a more detailed analysis, a study was conducted on the displacement of the single most intense X-ray reflex (101). It was found that for samples obtained from a solution of ZN 5%, this reflex has a maximum shift of $\Delta(2\Theta) = 0.14°$, and for samples obtained from a solution of NC 10%, this shift is equal to $\Delta(2\Theta) = 0.34°$ (Fig. 4). At the same time, with an increase in the concentration of Mn impurity, the position of the X-ray reflexes also shifts towards small angles 2Θ.

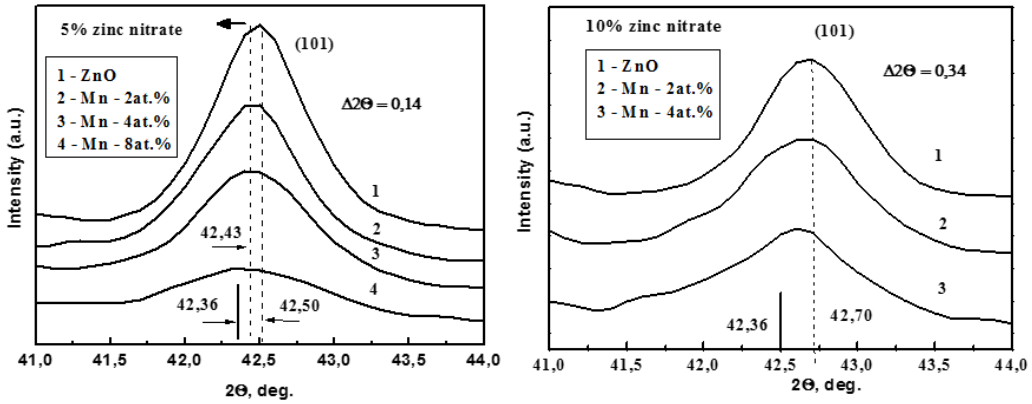


Fig. 4. The X-ray reflex shifts (101) in ZnO:Mn NCs obtained from solutions of ZN with the concentrations of 5% (a) and 10% (b) depending on the concentration of Mn impurity in the synthesized samples.

Such a shift in X-ray reflexes may indicate the fact that the samples are doped with a Mn impurity in accordance with the fact that the ionic radius of Mn^{2+} (0.83 Å) is larger than the ionic radius of Zn^{2+} (0.74 Å) [9]. When a Zn^{2+} ion is replaced by a Mn^{2+} ion in a ZnO lattice unit, its expansion occurs. This leads to an increase in the interplanar distances *d(hkl)* and the volume of the crystal cell. At the same time, the reflection angles of the X-ray reflex will decrease in accordance with the Wulff-Bragg equation:

$$2d(hkl)\sin\theta = n\lambda, \qquad (3)$$

where θ is the angle between the incident X-ray beam and the reflection plane, *n* is an integer (reflection order), λ is the wavelength of X-ray radiation.

According to the results of calculations, it can be noted that the unit cell volume in the synthesized NC samples for all concentrations of Mn impurity is much larger than the unit cell volume for single crystal ZnO. In addition, by analyzing the values of the lattice parameters of ZnO:Mn NCs in comparison with the corresponding parameters of single crystal ZnO, it can be concluded that NCs synthesized from a solution of ZN 5% have a smaller number of defects such as vacancies, and their crystal structure is more ordered than in NC samples synthesized from a solution of ZN 10%. At the same time, the size of NCs decreases with increasing Mn concentration, which is a well-known and natural fact of the impurity's influence on the NC growth process. In addition, the increase in the volume of a unit cell with a decrease in the concentration of ZN in solution from 5% to 10% may be due to a higher intensity of heat treatment of the samples. This heat treatment reduces the number of defects such as vacancies, and the crystal lattice becomes more equilibrium.

3. Conclusions

The studies have shown that during the synthesis of ZnO:Mn NCs by the USP method, a decrease in the concentration of the ZN solution from 10% to 5% leads to an improvement in the process of doping with Mn impurity, as well as to a decrease in the size of NCs. At the same time, the number of defects of the vacancy type decreases in the samples, and their crystal lattice goes into a more equilibrium state. These results are due to the fact that a decrease in the ZN concentration leads to a decrease in the size of spray droplets. Therefore, the formation of NC occurs in a shorter period of time, and the dry granule stays in the thermal annealing state for a longer time. These results make it possible, by changing the technological parameters of the synthesis of ZnO:Mn NCs using the USP method, to influence the crystallographic parameters of the samples and, therefore, their physical properties.

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