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Features of the local environment of ions Mn^{2+} in ZnS crystals and nanocrystal $ZnS_xSe_{1-x}:Mn$ and $Zn_xCd_{1-x}S:Mn$

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$ZnS_xSe_{1-x}:Mn$ and $Zn_xCd_{1-x}S:Mn$ nanocrystals were obtained by the method of self-propagating high-temperature synthesis. The EPR spectra of Mn^{2+} ions in these nanocrystals and in crystals of the same compounds grown from the melt under inert gas pressure were studied. It has been found that the ultrafine structure constant of the EPR spectra of Mn^{2+} ions in both nanocrystals and crystals has a jump-like dependence: in $ZnS_xSe_{1-x}:Mn$ compounds at a parameter value of $x = 0.2$; in $Zn_xCd_{1-x}S:Mn$ compounds at $x = 0.6-0.7$. These changes correlate with changes in other physical properties of nanocrystals, namely, the values of microstrain stresses and dislocation density.

Keywords: $ZnS_xSe_{1-x}:Mn$, $Zn_xCd_{1-x}S:Mn$, crystals, nanocrystals, self-propagating high-temperature synthesis, X-ray diffraction analysis, phases composition, crystal structure, EPR spectra.

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Introduction

It is known that crystals of $A^2B^6 - A^2'B^6'$ compounds based on Zn, Cd, S, and Se, namely ternary materials ZnS_xSe_{1-x} and $Zn_xCd_{1-x}S$, attract special attention of scientists due to the wide possibilities of their practical use in optoelectronics devices. The physical and chemical properties of such materials, as well as the technologies for their production, have been thoroughly investigated [1,2]. Depending on the value of the parameter x in ZnS_xSe_{1-x} crystals, the band gap varies in the range of 2.7-3.7 eV, and in $Zn_xCd_{1-x}S$ crystals, respectively, in the range of 2.6-3.7 eV. In nanocrystals (NCs) of such compounds, depending on the size of the nanograins, these limits are expanded. This, in turn, determines the prospects for the development of a new generation of short-wave photoconverters, LEDs, and lasers in the blue region of the spectrum [3-5]. The above stimulates the development of effective technologies for obtaining such NCs with reproducible and controlled physical properties. Among the various technologies, the method of self-propagating high-temperature synthesis (SHS) has a certain prospect. This method is characterized by a high rate of production of NPs in sufficiently large volumes,

low cost per unit of product, and the use of simple and environmentally friendly equipment. Both ZnS_xSe_{1-x} NCs [6] and $Zn_xCd_{1-x}S$ NCs [7] were obtained by this method.

In the present work, the physical properties of $ZnS_xSe_{1-x}:Mn$ NCs and $Zn_xCd_{1-x}S:Mn$ NCs prepared by the SHS method were investigated. The Mn impurity in the NCs was introduced to form paramagnetic Mn^{2+} centers. The study of the parameters of such centers by the EPR method provides additional information that refines the X-ray diffraction (XRD) data on the structure of the NC lattice, the peculiarities of the formation of ion-covalent bonds and the local environment of the paramagnetic centers.

I. Experimental procedure

NCs $ZnS_xSe_{1-x}:Mn$ and $Zn_xCd_{1-x}S:Mn$ were obtained by the SHS method as a result of a high-temperature chemical reaction of the basic fine powders Zn, S, Se or Zn, Cd, S. The basic powders were mechanically mixed in certain proportions with the addition of ethyl alcohol to the charge to improve the mixing process. The alloying of NC with Mn impurity was carried out by adding $MnCl_2$

salt to the charge in the amount of 10^{-2} at%. After drying, the charge in a quartz ampoule was placed in a sealed steel reactor. The chemical reaction was provoked by a powerful thermal pulse. The heat was generated by a nichrome spiral built into the reactor structure. The studies indicate that the value of the parameters x in the charge prepared for synthesis does not coincide with the value of the parameter x in the NC. Therefore, the values of the parameters x were finally determined from the XRD data and they were subsequently used to characterize the chemical composition of the obtained samples. XRD analysis of NC was performed on a DRON- 2M diffractometer using $\text{CoK}\alpha$ radiation. The EPR spectra were studied on a Radiopan SE/X-2543 radiospectrometer.

II. Experimental results and discussion

Using XRD data (Fig. 1a), it was found that the synthesized $\text{ZnS}_x\text{Se}_{1-x}:\text{Mn}$ powder consisted of polycrystals with sizes of 1-5 μm . They, in turn, were formed by NCs with dimensions of 55 ± 5 nm. The minimum size of NCs was characteristic of the compound with a parameter value of $x = 0.2$, and the maximum size was for the composition where $x = 1$. The NCs had a mixed crystal structure. In NCs with the value of parameter $x = 1$, the proportion of the hexagonal phase

was 65 ± 5 %, and the cubic phase was 35 ± 5 %. With a decrease in the value of the parameter x , the proportion of the cubic phase in the NC increased, and the hexagonal phase decreased accordingly. Thus, in NCs with the value of the parameter $x = 0$, the proportion of the hexagonal phase was $30 \pm 5\%$, and the cubic phase was $70 \pm 5\%$. The parameters of the crystal lattice in NCs were smaller compared to the known parameters of the crystal lattice for bulk crystals. This is an indication that the crystal lattice of NC is deformed. The degree of microstrain ($\Delta a/a$) in NC is in the range of $5 \cdot 10^{-4} - 2 \cdot 10^{-3}$. At the same time, the maximum value of the degree of microstrain is characteristic of the composition of NCs with a parameter value of $x = 0.2$; the minimum value is, respectively, for NCs with $x = 1$. The dislocation density was calculated in the synthesized NCs. It was in the range of $5 \cdot 10^{10} - 10^{12} \text{ cm}^{-2}$. The maximum value of the dislocation density is characteristic of NCs with $x = 0.2$; the minimum value is for $x = 1$ and $x = 0$.

According to the XRD data (Fig. 1b), the following characteristics of the synthesized $\text{Zn}_x\text{Cd}_{1-x}:\text{S}:\text{Mn}$ powder were determined. It also consists of polycrystals of 1-5 μm in size, which were formed from NCs. Their size discrepancy was larger compared to $\text{ZnS}_x\text{Se}_{1-x}:\text{Mn}$ NCs.

Thus, in the compositions with the value of the parameter $x = 0.3$ and with $x = 0.7- 1$, $\text{Zn}_x\text{Cd}_{1-x}:\text{S}:\text{Mn}$ NCs had a size of 60 ± 5 nm. For NCs with the value of the

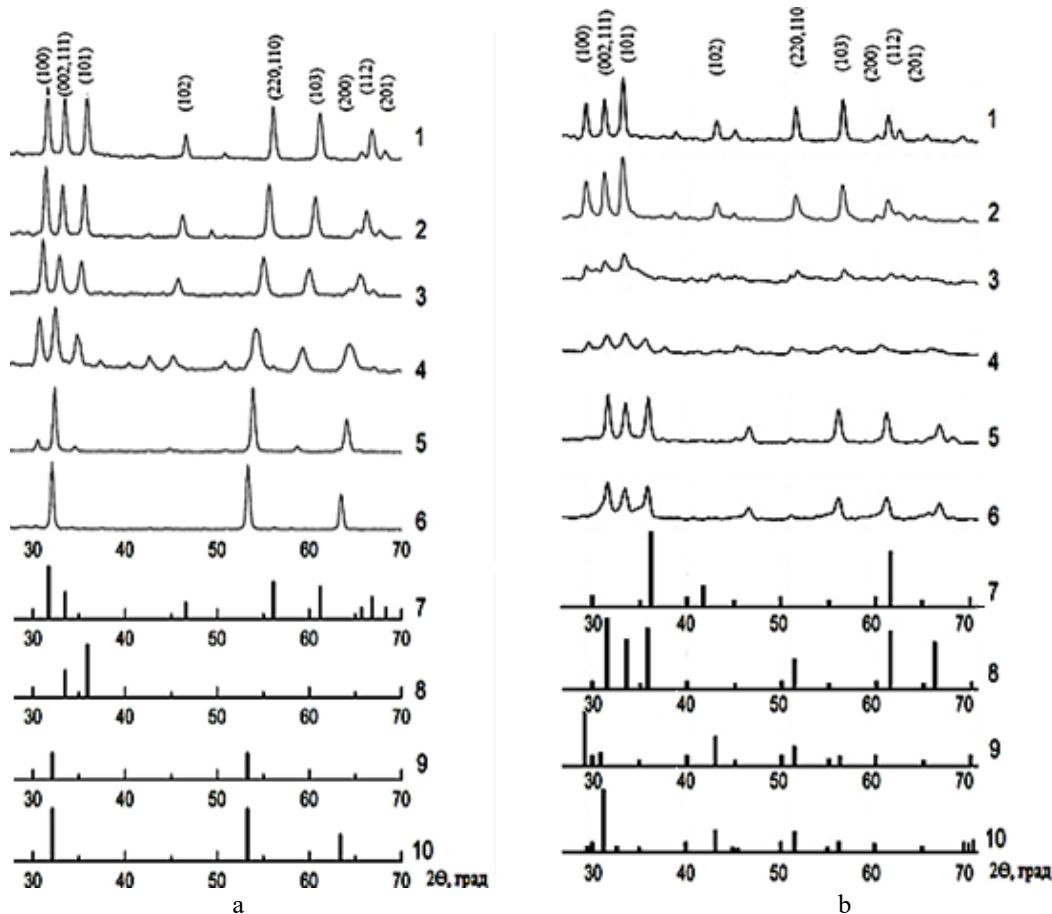


Fig. 1. XRD data of NCs $\text{ZnS}_x\text{Se}_{1-x}:\text{Mn}$ (a): $x = 1$ (1), $x = 0.8$ (2), $x = 0.6$ (3), $x = 0.4$ (4), $x = 0.2$ (5), $x = 0$ (6), XRD patterns of the cubic ZnS structure (7), hexagonal ZnS structure (8), cubic ZnSe structure (9), and hexagonal ZnSe structure (10); XRD data of $\text{Zn}_x\text{Cd}_{1-x}:\text{S}:\text{Mn}$ NCs (b): $x = 0$ (1), $x = 0.2$ (2), $x = 0.4$ (3), $x = 0.6$ (4), $x = 0.8$ (5), $x = 0.9$ (6), XRD patterns of the cubic ZnS structure (7), hexagonal ZnS structure (8), cubic CdS structure (9), and hexagonal CdS structure (10).

parameter $x = 0.4-0.6$, their size was significantly smaller - 40 ± 5 nm. The NCs also had a mixed crystal structure. For compounds with a parameter value of $x = 1$, the proportion of the hexagonal phase was $65 \pm 5\%$, and the cubic phase was $35 \pm 5\%$. With a decrease in the value of the parameter x , the proportion of the hexagonal phase in these NCs increased, and the cubic phase decreased. In NCs with the value of the parameter $x = 0$, the proportion of the hexagonal phase was $85 \pm 5\%$, and the cubic phase was only $15 \pm 5\%$. The microstrain stresses in $Zn_xCd_{1-x}S:Mn$ NCs, in accordance with the value of the parameter x , are in the range of $1.05 \cdot 10^{-4} - 4.95 \cdot 10^{-3}$; and the dislocation density is $7.9 \cdot 10^{10} - 4.1 \cdot 10^{11} \text{ cm}^{-2}$. The studies have established the fact that the indicated changes in physical properties in both $ZnS_xSe_{1-x}:Mn$ NCs and $Zn_xCd_{1-x}S:Mn$ NCs do not correspond to a linear dependence on the value of the parameter x . On the contrary, these dependences are characterized by a certain jump that occurs at $x = 0.2$ for $ZnS_xSe_{1-x}:Mn$ NCs and at $x = 0.6-0.7$ for $Zn_xCd_{1-x}S:Mn$ NCs.

The data obtained by XRD are in good agreement with the analysis of the EPR spectra of Mn^{2+} ions in the obtained samples (Fig. 2). The general appearance of the EPR spectra indicates the presence of a mixed crystal structure in the NC. This is manifested in the fact that the ultrafine structure lines of the EPR spectra of Mn^{2+} ions, consisting of six equidistant lines, are double. The explanation for this fact is that the EPR spectra of Mn^{2+} ions are a superposition of two spectra - one belonging to cubic local symmetry and the other to hexagonal symmetry. In the EPR spectra of $ZnS_xSe_{1-x}:Mn$ NCs and $Zn_xCd_{1-x}S:Mn$ NCs at the value of the parameter $x = 1$, weak lines (dashed lines in Fig. 2) were recorded, which are most likely associated with forbidden transitions. For these transitions, both the electron spin ($\Delta M = \pm 1$) and the

nucleus spin ($\Delta m = \pm 1$) change simultaneously. They can be caused by strain stresses in the crystal lattice of the NC. Such transitions in quantum dots have been reported by other authors [8].

A weak single EPR line with $g = 1.998$ was found in the synthesized NCs with parameter $x = 1$, which is probably associated with an uncontrolled Cr^{+} impurity. This line is recorded in bulk ZnS crystals under UV excitation.

In unexcited crystals, the chromium impurity is in the Cr^{2+} state and replaces Zn^{2+} ions in the ZnS lattice. Under UV excitation, the chromium impurity captures a free electron and transitions to the Cr^{+} state, which causes the EPR signal. The registration of such paramagnetic centers without UV excitation in NCs indicates that they have n-type conductivity. With a decrease in the value of the parameter x , the EPR spectra in NCs are simplified and at $x = 0$ they contain only the lines of the ultrafine structure of the EPR spectra of Mn^{2+} ions.

The dependence of the change in the ultrafine structure constant A of Mn^{2+} ions on the value of the parameter x was investigated both in $ZnS_xSe_{1-x}:Mn$, $Zn_xCd_{1-x}S:Mn$ crystals obtained from a melt under inert gas pressure and in $ZnS_xSe_{1-x}:Mn$, $Zn_xCd_{1-x}S:Mn$ NCs obtained by the SHS method (Fig. 3). These changes are similar in that they record a jump-like dependence of the value of the constant A on the value of the parameter x . For both crystals and NCs, this jump occurs at $x = 0.2$ for $ZnS_xSe_{1-x}:Mn$ samples and at $x = 0.6-0.7$ for $Zn_xCd_{1-x}S:Mn$ samples.

Such data suggest that Mn^{2+} ions in $ZnS_xSe_{1-x}:Mn$ samples at $x < 0.2$ tend to gravitate to the sulfur ion environment, i.e., to the ZnS crystal lattice, where they replace Zn^{2+} ions. At $x > 0.2$, this environment is abruptly replaced by selenium ions. In this case, Mn^{2+} ions replace

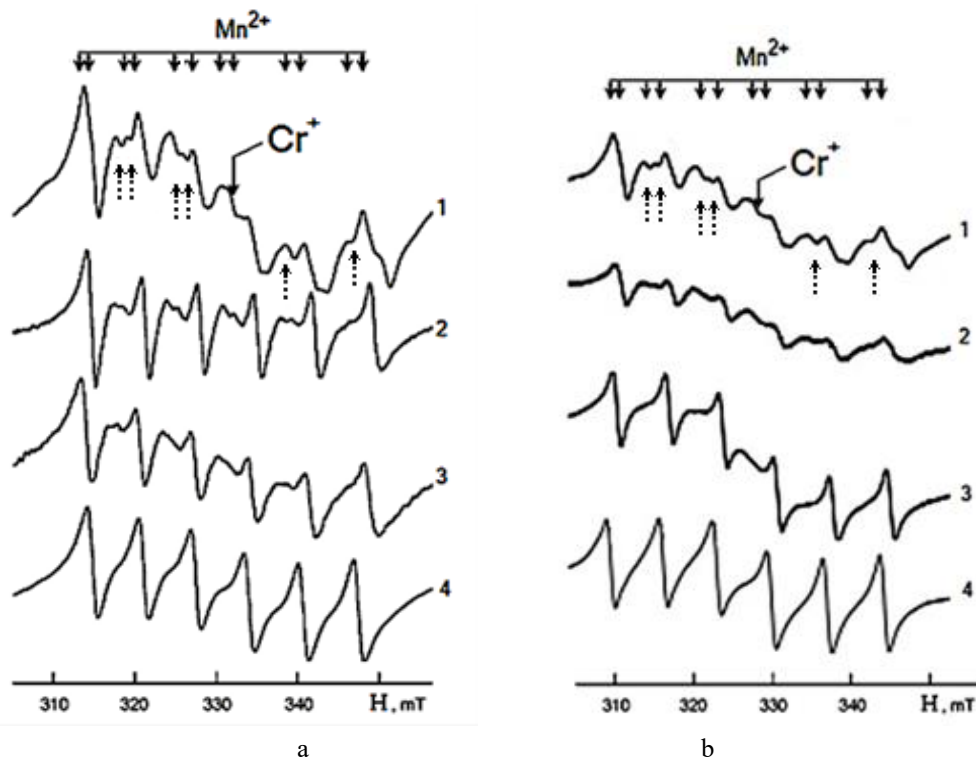


Fig. 2. EPR spectra of $ZnS_xSe_{1-x}:Mn$ NCs (a): $x = 1$ (1), $x = 0.9$ (2), $x = 0.2$ (3), $x = 0$ (4) and $Zn_xCd_{1-x}S:Mn$ (b): $x = 1$ (1), $x = 0.8$ (2), $x = 0.2$ (3), $x = 0$ (4).

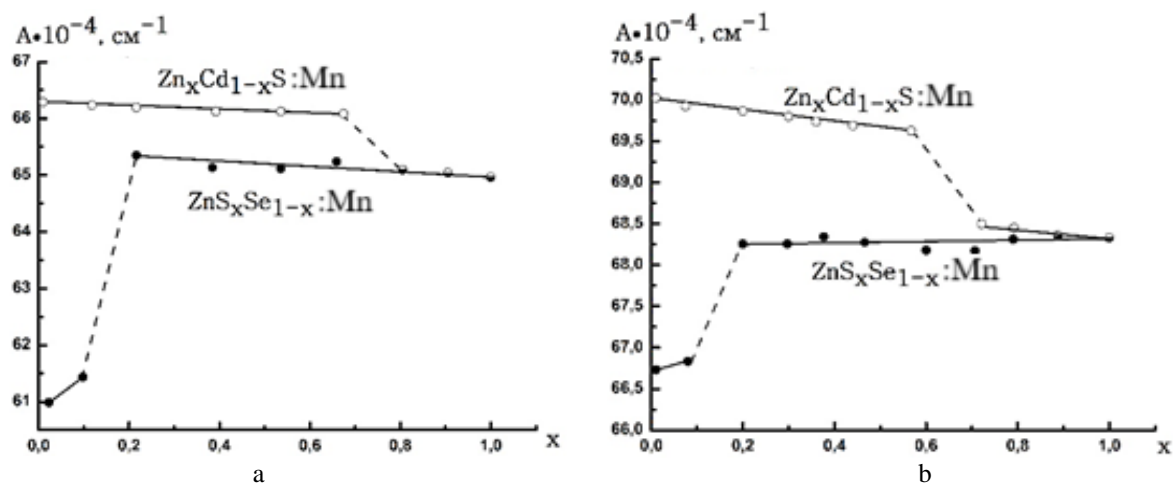


Fig. 3. Dependence of the ultrafine structure constant A of Mn^{2+} ions on the value of the parameter x in crystals (a) and NCs (b) of $ZnS_xSe_{1-x}:Mn$, $Zn_xCd_{1-x}S:Mn$.

Zn^{2+} ions in the $ZnSe$ crystal lattice.

In $Zn_xCd_{1-x}S:Mn$ crystals and NCs at a value of $x < 0.6-0.7$, Mn^{2+} ions tend to be located in place of Cd^{2+} ions in the CdS lattice. At a value of the parameter $x > 0.8$, Mn^{2+} ions abruptly change their environment and, as a result, tend to be located in the ZnS lattice, where they replace Zn^{2+} ions. It is likely that this abrupt change in the environment of Mn^{2+} ions in the NCs of the studied samples causes other changes in physical properties, namely, the values of microstrain stresses and dislocation density

Conclusions

The $ZnS_xSe_{1-x}:Mn$ and $Zn_xCd_{1-x}S:Mn$ nanocrystals were obtained by a self-propagating high-temperature synthesis. X-ray diffraction analysis showed that the samples consist of polycrystals with a size of 1-5 μm , which are composed of nanocrystals with a size of 40-60 nm. The mixed crystal structure of the nanocrystals was found to be the case, where the ratio of cubic and hexagonal phases varies depending on the value of the x parameter. The lattice parameters of the nanocrystals are smaller compared to the corresponding values for bulk crystals, which indicates the presence of strain stresses in

them. EPR spectroscopy has revealed that Mn^{2+} ions in $ZnS_xSe_{1-x}:Mn$ and $Zn_xCd_{1-x}S:Mn$ nanocrystals can be in two different crystal environments: cubic and hexagonal. At certain values of the parameter x , an abrupt change in the ultrafine structure constant of the EPR spectra of Mn^{2+} ions is observed: at $x = 0.2$ for $ZnS_xSe_{1-x}:Mn$ and at $x = 0.6-0.7$ for $Zn_xCd_{1-x}S:Mn$. This change indicates that when these values of the parameter x are reached, a sharp transition of Mn^{2+} ions from one type of crystal environment to another occurs. This phenomenon was also observed in bulk crystals of $ZnS_xSe_{1-x}:Mn$ and $Zn_xCd_{1-x}S:Mn$.

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Особливості локального оточення іонів Mn^{2+} в кристалах і нанокристалах $ZnS_xSe_{1-x}:Mn$ та $Zn_xCd_{1-x}:S:Mn$

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Методом самопоширювального високотемпературного синтезу отримано нанокристали $ZnS_xSe_{1-x}:Mn$ та $Zn_xCd_{1-x}:S:Mn$. Досліджено спектри ЕПР іонів Mn^{2+} як в цих нанокристалах так і в кристалах таких самих сполук, зрощених з розплаву під тиском інертного газу. Було встановлено що константа надтонкої структури спектрів ЕПР іонів Mn^{2+} як в нанокристалах так і в кристалах має стрибкоподібну залежність: в сполуках $ZnS_xSe_{1-x}:Mn$ при значенні параметра $x=0,2$; в сполуках $Zn_xCd_{1-x}:S:Mn$ при $x=0,6-0,7$. Ці зміни корелюють із змінами інших фізичних властивостей нанокристалів, а саме значеннями мікродеформаційних напружень та густини дислокацій.

Ключові слова: $ZnS_xSe_{1-x}:Mn$, $Zn_xCd_{1-x}:S:Mn$, кристали, нанокристали, саморозповсюджувальний високотемпературний синтез, рентгеноструктурний аналіз, фазовий склад, кристалічна структура, спектри ЕПР.