



Optical properties of oxide magnetic ZnO, Zn_{0.95}Mn_{0.05}O and Cu₂O nanopowders

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ABSTRACT

ZnO, Zn_{0.95}Mn_{0.05}O and Cu₂O nanocrystals are synthesized. Excitonic lines in absorption spectra of these materials are detected. In photoluminescence and photoluminescence excitation spectra of Zn_{0.95}Mn_{0.05}O the dangling bond hybrid (DBH) state is found. It has splitted out from the top of the valence band due to the hybridization between d-states of the Mn impurity and the p-states of oxygen.

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Recently, it was found that the ZnO, TiO₂, Cu₂O and SnO₂ oxide semiconductors, doped by 3Delements can be ferromagnetic with the Curie temperature significantly above room temperature when the magnetic ions concentration is significantly lower than the percolation threshold [1–3]. As a rule these compounds are prepared in the form of nanocrystals by means of substantially nonequilibrium technique with large number of defects (for example, the vacancies in anion (oxygen) or cation sublattice as well as surface defects). The analysis of published experimental data shows that oxygen vacancies can play the key role in the formation of magnetic order in oxide semiconductors doped with 3Delements. Therefore, it seems very important to investigate with the optical methods the defects in Cu₂O, ZnO and Zn_{0.95}Mn_{0.05}O nanopowders. In this work the light absorption, photoluminescence (PL) and photoluminescence excitation (PLE) spectra of oxide nanopowders were observed with the aim of indirect control of defectness in nanocrystals. Earlier, we had observed the excitonic states in Cu₂O nanocrystals and part of these results was presented in Ref. [4]. The Cu₂O monocrystals have the developed system of excitonic states, which are very sensitive to the crystal defects. Therefore, we thought it is important to investigate the excitonic states in Cu₂O nanopowders.

Cu₂O, ZnO and Zn_{0.95}Mn_{0.05}O nanopowders were prepared by the gas phase method, when drop of melted metal (Cu, Zn) was blown over by the mixture of the inert gas and oxygen. Nanoparticles of the oxide of metal are formed near the evaporation zone and collected on a filter without contact with the ambient medium. The concentration of oxygen was controlled by the injection of a necessary oxygen quantity into the buffer gas (for example, Ar). The thickness of the settled layer depends on the process time. The size of nanocrystallites depends on the flow rate and the pressure of the buffer gas. The layer of nanoparticles of the desired composition and thickness were deposited on the substrate in the process of melted drop evaporation. The Cu₂O nanopowders with the size of nanocrystals 90 and 15 nm were investigated. ZnO and Zn_{0.95}Mn_{0.05}O nanocrystals had the size of 30 nm. The sizes of nanocrystals were determined directly by the transmission electron microscopy (TEM) and by the width of the X-ray diffraction peaks. The level of defectness was evaluated according to the data of the sample compositions. Deposition of very thin (several hundreds of nanometer thick) layer of nanocrystals onto substrate allows to observe of intense exciton lines.

Figs. 1 and 2 show the absorption spectra of the Cu₂O, ZnO and Zn_{0.95}Mn_{0.05}O films. We can see that the Cu₂O excitonic lines are expressed more clearly at the temperature of 4.2 K. The head line of the blue series (the quantum number $n = 1, I_7^+, \dots, I_8^-$ transitions) exhibits a shoulder at the temperature of 77.3 K [4] and it transforms into absorption peak form at 4.2 K. The head line of the indigo series

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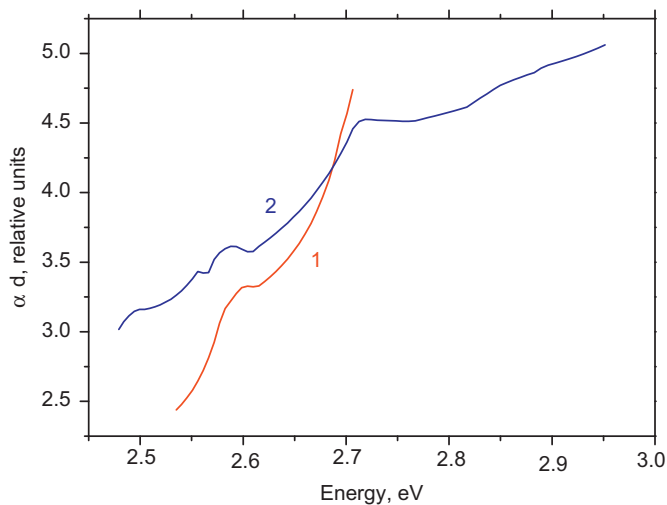


Fig. 1. Absorption spectra of Cu_2O nanocrystals with the average size of 15 nm at the temperatures of 77.3 K (1) [4] and 4.2 K (2).

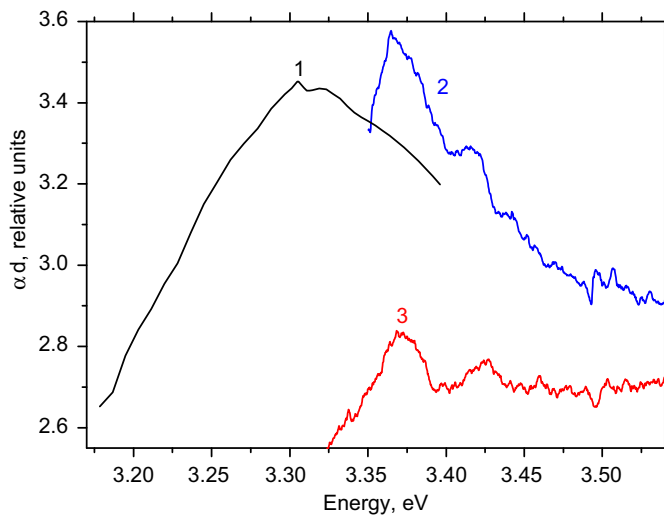


Fig. 2. Absorption spectra of annealed in air ZnO nanocrystals with the average size of 30 nm at 300 K (1) and 77.3 K (2) and annealed in air $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ nanocrystals with the average size of 30 nm at 77.3 K (3).

(the quantum number $n = 1, \Gamma_8^+, \dots, \Gamma_8^-$ transitions) at 77.3 K was not registered [4], and it had a distinct shoulder at 4.2 K. The positions of the peak and the shoulder for nanocrystals having the size of 15 nm present a more convincing evidence of the shift of these positions towards higher energies by approximately 15 meV as compared to the excitonic lines for 90 nm nanocrystals.

For ZnO monocrystals, the excitonic lines differ for the light polarizations perpendicularly and parallel to the C -axis. In our case, nanocrystals on the substrate are randomly oriented and so we used unpolarized light. For the ZnO nanocrystals at room temperature, a broad absorption peak with the maximum at the light quantum energy 3.30 eV was observed. With the decrease of temperature to 77.3 K, the peak became narrower and shifted towards the energy 3.36 eV. The second peak appeared at the energy of 3.42 eV as well. The transformation of the absorption spectra at the temperature decreasing and energy positions of the peaks at 77.3 K are convincing evidences to interpretate the peaks in the absorption spectrum as excitonic lines. In the PL spectrum of ZnO nanocrystals, the broad exciton line was observed at the energy of 3.30 eV at 300 K [5]. For $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ nanocrystals at 77.3 K, two broad lines were distinctly seen at the energies of 3.37 and 3.42 eV. The first line

corresponded well to the zero phonon line of the A exciton series with the quantum number $n = 1$ [6]. This series arose due to the transitions from the top valence subband Γ_7 into the conduction band Γ_7 . At the energy level higher by 8 meV, the B series ($\Gamma_9-\Gamma_7$ transition) has to be observed for the single crystals. The second broad peak corresponded to two closely placed lines, one of them being the line of the C series with the quantum number $n = 1$ ($\Gamma_7-\Gamma_7$ transition) and the second line belongs to the A series with the quantum number $n = 2$. The resolution of our optical device did not allow us to distinguish these two contributions for both broad lines. They can be clearly resolved on single crystals while using the polarized light. Let us mark the fact that both lines for nanocrystals $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ are somewhat shifted (by 10 meV) towards higher energies as compared to the lines of the ZnO nanocrystals.

The PL, cathodeluminescence and PLE spectra for as-grown ZnO and $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ nanocrystals and ZnO:Mn monocrystals are presented in Figs. 3 and 4. At the light quantum energy region of 2.1 eV, the PL peak was observed for the ZnO nanopowder. This peak can be attributed to the yellow–orange luminescence, which is characteristic for the monocrystals of ZnO synthesized by the gas phase method or having undergone the temperature treatment in oxygen and argon atmosphere at high temperatures. Under this treatment the surface defects appear, which is the source of yellow–orange luminescence. This luminescence is especially intensive for the ZnO nanopowders which had the temperature treatment. It is assumed that the yellow–orange luminescence of the ZnO monocrystals is caused by the local excess of oxygen near

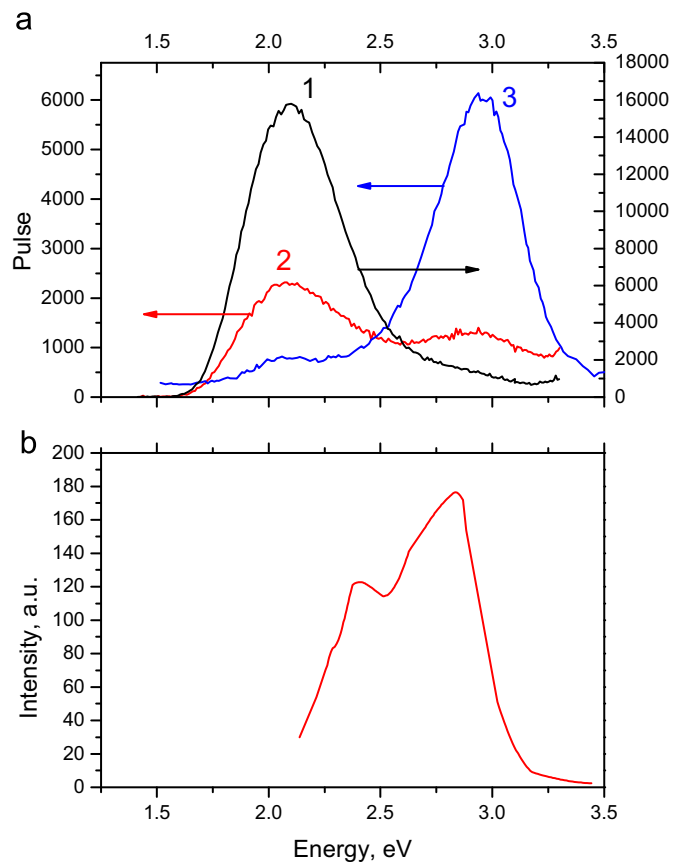


Fig. 3. (a)—PL spectra of the nanocrystals of ZnO (1), $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ (2) and the monocrystals of ZnO:Mn (0.1 wt%) (3). For the cases of (1) and (2): excitation energy $E = 3.64$ eV; temperature $T = 86$ K. For the case (3): excitation energy $E = 3.84$ eV; temperature $T = 80$ K (b)—cathode luminescence spectrum of the nanocrystals of $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$. The conditions of excitation: impulse electronic beam with the duration of $\tau = 0.4$ μs ; accelerating voltage $U = 40$ kV; average current $i = 1$ μA ; and temperature $T = 80$ K.

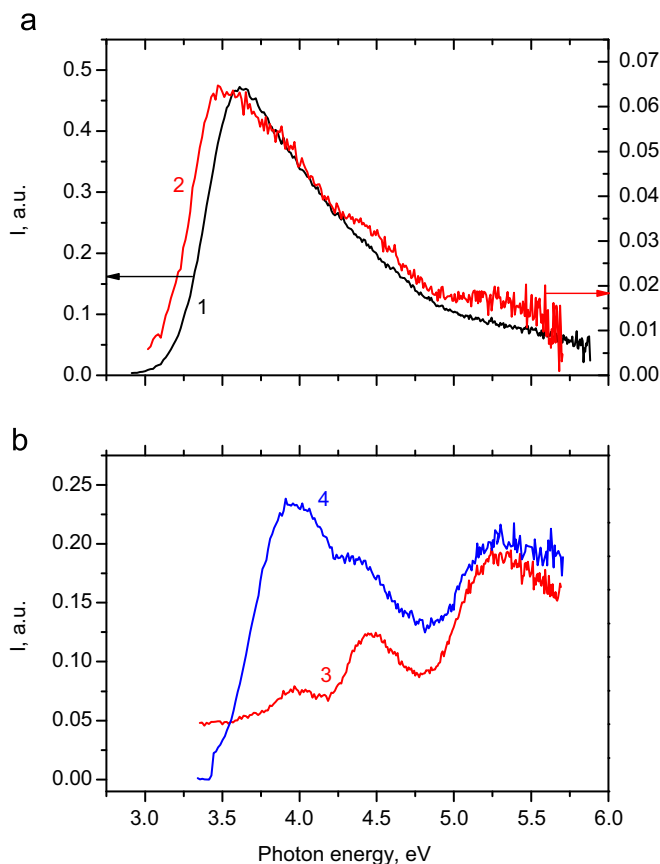


Fig. 4. (a)—PLE spectra for the peak 2.1 eV for ZnO (1) and $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ (2) nanocrystals (b)—PLE spectra for the peak 2.9 eV for $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ nanocrystal; $T = 86\text{ K}$ (3) and for ZnO:Mn monocrystals; $T = 80\text{ K}$ (4).

the structure defects, which are typical for the nanocrystal surface [6]. The emergence of such a luminescence peak is natural for the nanocrystals of ZnO obtained by the gas phase method.

Of a greater interest is the PL spectrum of $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ nanocrystals. It consists of two broad peaks at the energies of 2.1 and 2.9 eV. The first peak arises due to transitions forming the yellow–orange band of the luminescence in ZnO with the possible contribution of the intracentral transitions ${}^4\text{T}_1\text{--}{}^6\text{A}_1$ of Mn^{2+} ion. The energy of the intracentral transition ${}^4\text{T}_1\text{--}{}^6\text{A}_1$ of Mn^{2+} ion in ZnS:Mn and ZnSe:Mn is equal to approximately 2.1 eV [7,8]. The appearance of the second peak at the energy of 2.9 eV is caused by the presence of Mn impurities. In the cathodoluminescence spectrum of $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ nanocrystals, the two peaks were also seen at the energies of 2.4 and 2.85 eV. The first of them is connected with the deep center forming the yellow–orange luminescence, the second is most probably connected with the presence of the Mn impurity. For ZnO:Mn monocrystal, peaks were observed at the same energies but with another ratio of intensities. In principle, a peak at the energy of 2.9 eV can be caused by the more high-energy intracentral transition of the Mn^{2+} ion. But the another reason seems to be more important. To clarify it, we should issue from the difference of the PLE peaks for the ZnO and $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ luminescence 2.1 eV band. These peaks have approximately the same shapes, but the low-energy onset for $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ nanocrystals was shifted by 0.15 eV towards the lower energy as compared to the data for ZnO nanocrystals. The other difference was that the PLE spectrum for $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ nanocrystals had the weak peaks in the regions of 4.5 and 5.5 eV, whereas the fair drop towards the high energies was observed for the ZnO nanocrystals. A significant difference was observed in the PLE peak having the energy of 2.9 eV (Fig. 4). It is obvious that the intensity of the excitation spectrum increased with

the growing of the energy of the light quantum and had some maxima at the energies of 3.9, 4.5 and 5.25 eV. The same phenomenon was observed for the ZnO:Mn monocrystal. As the preliminary explanation of such a difference of the two PLE spectra, we assume that the perturbation of the valence band states takes place due to the hybridization between the d-states of the Mn^{2+} ion and the p-states of the four nearest oxygen ions O^{2-} . One of the manifestations of the perturbation is the splitting out of the dangling bond hybrid (DBH) state from the top of the valence band into the band gap. It can be seen well in Fig. 11 from paper [9]. As a result of the interband excitation of the 2.1 luminescence band must begin with the lower energies which was observed experimentally. Through the split out, the DBH state, the luminescence could take place at the interband excitation. This band has the maximum at the light quantum energy of 2.9 eV, and its high-energy part begins in the region of 3.25 eV. Thus, the distance from the fundamental absorption edge at the temperature of 80 K is approximately 0.2 eV. In fact this is the value of the splitting out of the DBH state from the valence band top (Fig. 5). The peaks in the PLE spectrum of 2.9 eV peak can be interpreted as the result of the perturbation of the host valence subbands by the presence of the Mn atom (Fig. 7 from Ref. [9]). In Fig. 5 they are conditionally denoted as V_1 , V_2 and V_3 . It is conventionally recognized that the donor level ($0/+$) of Mn^{2+} ion and the ground state ${}^6\text{A}_1$ level, coinciding with it are lower the valence band top [10,11]. That is why the hybridization between the d-states of the Mn and the V_1 , V_2 and V_3 deep valence subbands will be stronger manifested and probably influences on the intensity of the photoluminescence through the DBH level (transition 2 in Fig. 5).

The ZnO and $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ nanocrystals were synthesized by the gas phase technique. Direct observation of exciton lines (inherent in single crystals) in the absorption spectra indicate that the crystal structure of ZnO and $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ nanocrystals is quite perfect and close to the structure of ZnO and $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ single crystals, as it was noted earlier for the Cu_2O nanocrystals [4]. So, we demonstrate that the observation of intense free excitons in

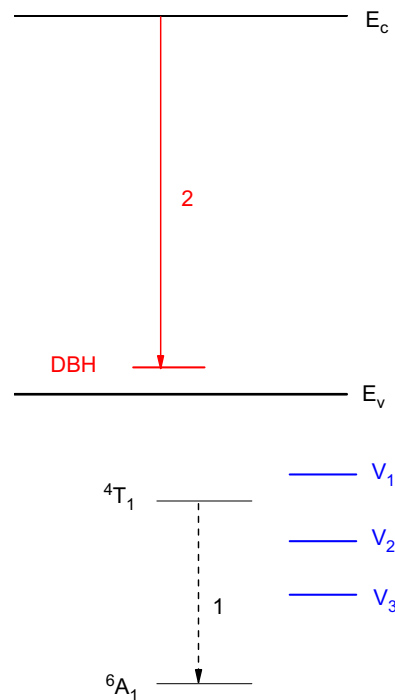


Fig. 5. Schematic presentation of energy levels of Mn^{2+} ion. The transitions “ ${}^4\text{T}_1\text{--}{}^6\text{A}_1$ ”, (which possibly give contribution to the band of 2.1 eV) (1) and “conduction band-DBH-state”, (which forms the peak 2.9 eV) (2) are shown. The valence subbands V_1 , V_2 and V_3 which form 3 peaks in PLE spectrum of 2.9 eV for $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ are conditionally shown.

absorption spectra of Cu_2O , ZnO and $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ is a powerful method for investigation of nanocrystals. It is shown that the Mn^{2+} ions generate the impurity DBH state splitted from the top of the valence band, which is very important for the understanding of the ferromagnetic ordering in the ZnMnO system. It is firstly demonstrated the very strong perturbation of the valence subbands in the ZnMnO crystal, due to the hybridization between the d-states of the Mn and the deep valence subbands.

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