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Deep state in the bandgap and photoluminescence of $Zn_{1-x}Mn_xO$

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The impurity absorption in $Zn_{1-x}Mn_xO$ is formed by dipole allowed *p–s* transitions from deep antibonding *p–d* hybrid (*pdh*) state to the conduction band. In this paper, photoluminescence of $Zn_{1-x}Mn_xO$ single crystals was investigated in the temperature range of 7–340 K at laser excitation with the energy of 3.06 eV. Intensive photoluminescence band was observed in the energy region of 2.40–1.6 eV with the maximum at the energy of 2.17 eV. The energy of the impurity center ionization 2.35 eV was determined in this paper. The analysis of photoluminescence band form, and also close coincidence of its headline and impurity band edge allow us to interprete this band as a result of radiative dipole allowed *s–p* transitions from the conduction band to impurity *pdh* level.

Keywords: photoluminescence, ZnO:Mn, impurity photoionization, intracenter transitions.

Introduction

Semiconductors II–VI doped with 3*d*-metals impurities are actively investigated many years for an understanding of energy spectrum of crystal for modification of luminescent, magnetic, optical, photocatalytic, and other properties of semiconductors. Results of investigations indicate that 3*d*-metal impurities generate in the II–VI semiconductor bandgap two types of energy states: *d–p* hybrid (*dph*) and *p–d* hybrid (*pdh*). The type of a 3*d*-impurity state in the semiconductor bandgap depends on the position of the atomic 3*d* level relative to the energy corresponding to the peak of the density of the *p* states in the valence band. If the energy level lies higher, the antibonding localized *dph* state (d^n+p) with the essentially 3*d* character arises in the bandgap. The bonding state ($p + d^n$) with the essentially *p* character remains deeply in the valence band. If the 3*d* atomic level lies lower, the antibonding localized *pdh* state ($p + d^n$) of the essentially *p* nature is expelled into the bandgap. The bonding state (d^n+p) with the essentially 3*d* character remains deeply in the valence band [1, 2].

The investigations of ZnMnO especially attract the attention of researchers. During the last two decades absorption, photoconductivity, and photoluminescence spectra of thin films and nanocrystals were observed in this compound. In the optical absorption spectrum, a broad intense impurity absorption band was revealed in the energy range of 2.1–3.3 eV. The authors of [3, 4] assumed that this impurity absorption band was due to electron transitions from the d^5/d^4-donor level to the bottom of the conduction band. In the photoluminescence spectra the broad bands with the maxima in the region of 2 eV were observed and interpreted as intracenter $^4T_1 \rightarrow {}^6A_1$ transition of d^5-configuration of Mn^{2+} ions [5–8]. In the photoluminescence spectra of nanostructures [9, 10], the lines in the green-violet part of the spectra were observed. These lines also were interpreted as lines due to intracenter transitions of d^5-configuration of Mn^{2+} ions. But in [9, 10] the weak peaks near the 636 nm were observed too. We can state that photoluminescence of ZnO:Mn compound is far from the classic version when absorption and photoluminescence spectra of ZnS:Mn and CdS:Mn in the region of 2 eV are formed only by intracenter transitions [11, 12].

In the optical absorption spectrum of Zn$_{1-x}$Mn$_x$O ($x = 0.0009$) single crystals the lines of donor excitons (*de*) [$(h_{\text{loc}} + d^5)e$] were discovered at the temperatures of 4.2 and 77.3 K in an energy interval of 1.87–1.95 eV below the impurity absorption band edge [13, 14]. These new experimental results provide the evidence that the impurity absorption of Zn$_{1-x}$Mn$_x$O is caused by allowed dipole *p*–*s* transitions of electrons from antibonding hybridized *pdh* state (p+d^5) to the conduction band. In this paper, photoluminescence spectra were registered for the discovering of radiative transitions from the bottom of the conduction band to *pdh* state in the bandgap of Zn$_{1-x}$Mn$_x$O. The impurity absorption edge was calculated with the formula of direct allowed transitions for the trustworthy definition of energy E_I of impurity center ionization.

Experiment

The samples of solid solutions Zn$_{1-x}$Mn$_x$O ($x = 0.0009$) for measurements of optical absorption and photoluminescence spectra were prepared by the hydrothermal method in the Institute of Solid State Physics (Chernogolovka, Moscow district). These samples had the shape of wafers of size 0.6×0.35×0.07 cm, whose crystallographic symmetry axis *C* was perpendicular to the larger face. During the impurity absorption spectrum measurement unpolarized light was propagated along the *C* axis ($\mathbf{k} \| C$). Formally this geometry gives a result similar to σ-polarization ($\mathbf{E} \perp C$). The absorption spectrum was registered at the temperature of 4.2 K.

For the registration of photoluminescence spectra, the laser with the excitation energy of $E_{\text{exc}} = 3.06$ eV was used. The laser light was incident to the larger face of the sample at a small angle to *C* axis; luminescent irradiation from the sample was registered at a small angle too. We can assume that the conditions of the experiment approximately correspond to σ-polarization. Irradiation of luminescence was detected using the MDR-23U monochromator and photoelectronic amplifier R6358-10 (Hamamatsu). Photoluminescence spectra were registered in a temperature region of 8–340 K. The UXL-500D deuterium lamp and the MCD-1 monochromator were used as an excitation-light source for registration of photoluminescence excitation spectra at the temperature of 8 K.

Results

In Fig. 1 photoluminescence spectra of Zn$_{1-x}$Mn$_x$O ($x = 0.0009$) at the temperatures of 8, 80, 140, 300, and 340 K are presented. It can be seen that these are wide, intensive and asymmetric photoluminescence bands in an energy interval of 1.6–2.4 eV. All these bands begin at the energy of 2.4 eV, reach the maximum at the energy of 2.17 eV and smoothly fall towards lower energies. With the increasing of temperature up to 340 K the wide spectrum with the maximum at the energy of 2.17 eV is conserved at all temperatures, although it is reduced approximately 2.5 times. On the low energy slope at the temperature of 8 K two structures are observed: the first in energy interval of 1.7–1.8 eV, and the second in energy interval of 1.86–1.945 eV. These structures consist of narrow lines. When the temperature rises to 80 K intensities and distinguishability of lines of both these structures reduce significantly; at the temperature of 140 K these structures are significantly blurred and have a low intensity; at the temperature of 300 K they become not visible.

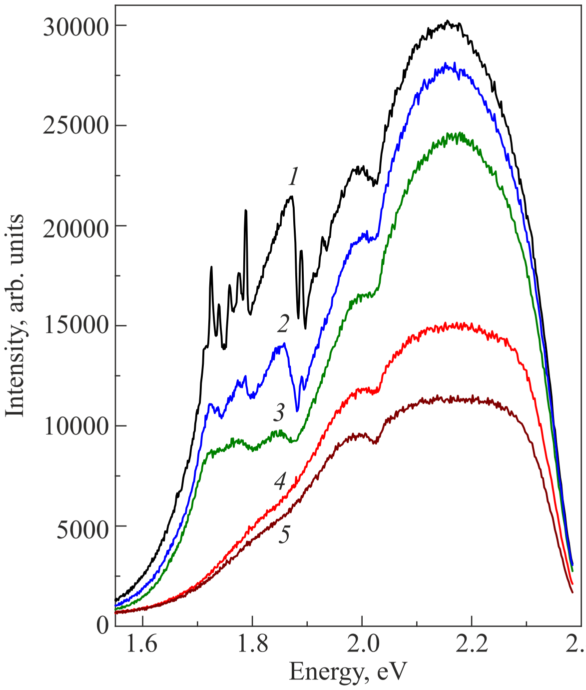

Fig. 1. Photoluminescence spectra of Zn$_{1-x}$Mn$_x$O ($x = 0.0009$) single crystal at the temperatures of 8 (*1*), 80 (*2*), 140 (*3*), 300 (*4*) and 340 (*5*) K, excitation energy $E_{\text{exc}} = 3.06$ eV.

Figure 2(a) shows photoluminescence spectra at the temperature of $T = 8$ K and impurity absorption edge at $T = 4.2$ K in Zn$_{1-x}$Mn$_x$O ($x = 0.0009$) single crystal. In Figure 2(b) one can see transitions, which correspond to processes of optical absorption, photoluminescence and photoluminescence excitation through the *pdh* (p+d^5) state. Photoluminescence excitation spectrum of the sample Zn$_{1-x}$Mn$_x$O ($x = 0.0009$) (luminescence energy $E_{\text{lum}} = 2.1$ eV; temperature $T = 8$ K) is presented in Fig. 3.

Figure 4(a) demonstrates the structure of narrow lines in the region of 1.87–1.95 eV. In Fig. 4(b) intensive lines in optical absorption spectrum of Zn$_{1-x}$Mn$_x$O ($x = 0.0009$) for the case of σ-polarization of the light are shown; earlier these lines have been revealed in [14].

In Fig. 5 the second structure of narrow lines in the region of photoluminescence decreasing in the energy range of 1.7–1.8 eV is shown.

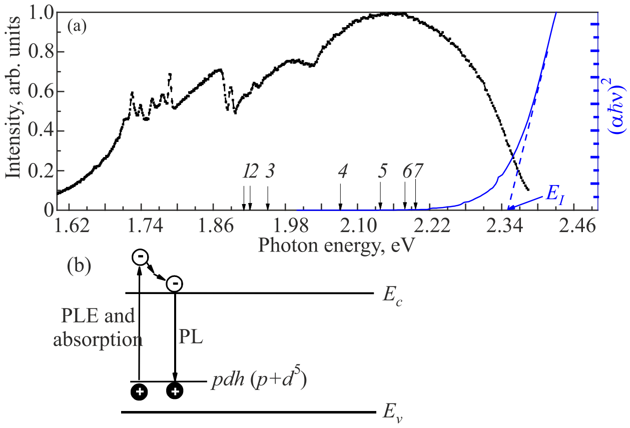

Fig. 2. (a) Spectra of photoluminescence ($E_{\text{exc}} = 3.06$ eV; $T = 8$ K) and $(\alpha\hbar\omega)^2$ value (α is the absorption coefficient) of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($x = 0.0009$) single crystal. Arrows indicate the positions of maxima of photoluminescence spectra of ZnMnO, ZnS:Mn, ZnSe:Mn, CdS:Mn from the papers of other authors: 1.91 eV [8] (*1*); 1.92 eV [7] (*2*); 1.95 eV [9, 10] (*3*); 2.067 eV [6] (*4*); 2.138 eV (ZnS:Mn, ZnSe:Mn) [15] (*5*); 2.178 eV (cathodoluminescence, ZnMnO) [5] (*6*); 2.196 eV (CdS:Mn) [11] (*7*). Extrapolation for the determination of E_I value is shown. (b) Schematic illustration of processes of optical absorption, photoluminescence, and photoluminescence excitation through the deep *pdh* ($p+d^5$) state.

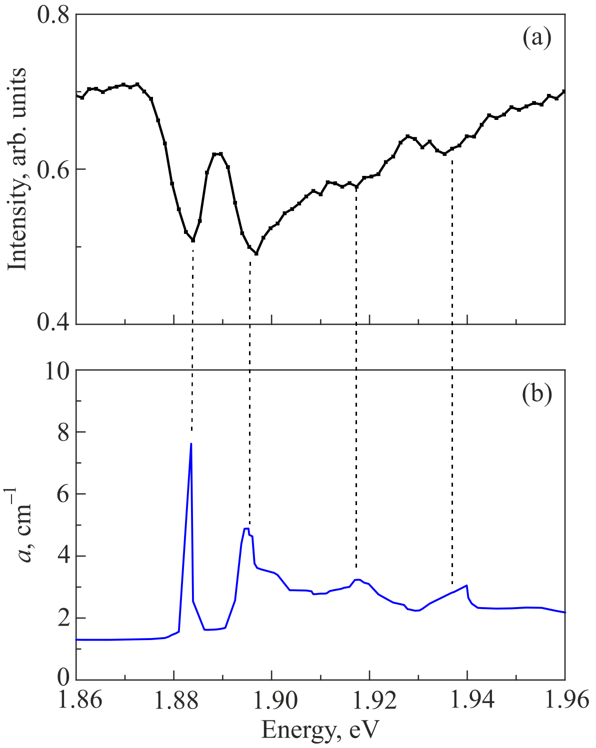

Fig. 4. (a) Part of photoluminescence spectrum ($E_{\text{exc}} = 3.06$ eV; $T = 8$ K) of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($x = 0.0009$) single crystal in the energy interval of 1.86–1.96 eV. (b) Optical absorption spectrum ($T = 4.2$ K) of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($x = 0.0009$) single crystal for σ-polarization of falling light in energy interval of 1.86–1.96 eV.

Discussion of results

In II–VI compounds which have a cubic and hexagonal symmetry and contain the Mn^{2+} ions peaks in the optical absorption and photoluminescence spectra are observed. These peaks are due to intracenter transitions of the d^5-configuration of Mn^{2+} ions. In absorption spectra of ZnS:Mn and ZnSe:Mn compounds some peaks, which are results of transition from the ground state $^6A_1$ to excited states $^4T_1$,

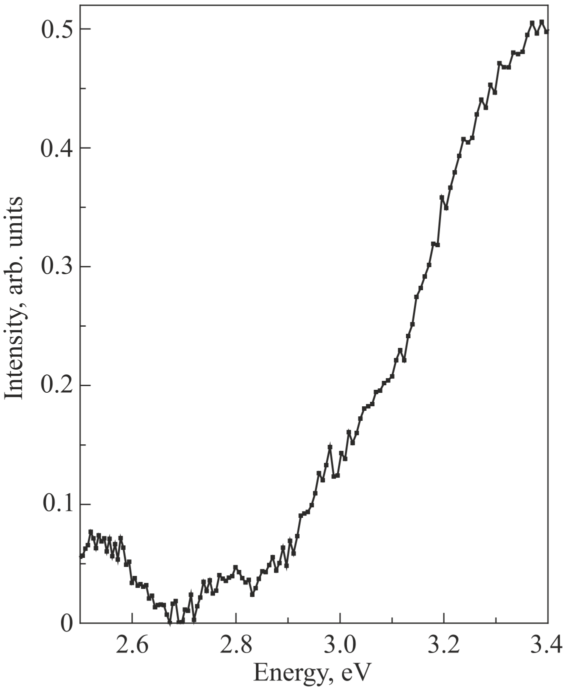

Fig. 3. Photoluminescence excitation spectrum (luminescence energy $E_{\text{lum}} = 2.1$ eV; $T = 8$ K) of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($x = 0.0009$) single crystal.

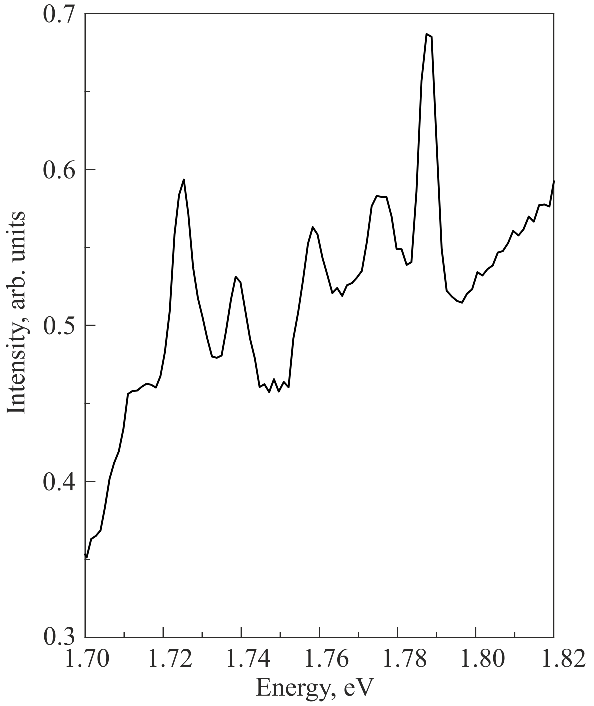

Fig. 5. Structure of narrow lines in the region of photoluminescence decreasing in the energy interval of 1.7–1.8 eV.

$^4T_2$ and ^4E, $^4A_1$ are observed [15]. All these transitions are forbidden because they take place between the states with the same parity (Laport rule) and are accompanied by the changing of spin. Because of this, at a low concentration of Mn^{2+} ions the peaks in the absorption spectrum are weak. In the photoluminescence spectrum at low temperature and low concentration of Mn^{2+} ions can be seen only one band due to the electronic transition $^4T_1 \rightarrow {}^6A_1$ [which is called a head line, or zero phonon line (ZPL)], and vibrational repetitions due to the emission of phonons. The irradiation band, which increases toward energy decreasing and reaches the maximum near ~ 2 eV and decreases after that is called a yellow band. Excited states $^4T_2$ and ^4E, $^4A_1$ do not manifest themselves in the photoluminescence spectrum [15]. The photoluminescence band is described by the energies of ZPL and maximum, and also by the full width on the half of maximum intensity (FWHM) and by the time of decay. Energy parameters of photoluminescence lines in widegap compounds ZnS:Mn and CdS:Mn have the following energy values at low temperature and low concentration of Mn: ZPL 2.219 and 2.310 eV, maximum 2.138 and 2.196 eV, FWHM 0.13 and 0.11 eV, decay constant $\tau = 1.7$ and 0.65 ms, respectively [11]. Since the photoluminescence peak is very weak, the concentration of Mn impurity should be increased to rise its intensity. Peaks in the absorption spectrum increase but the peak in the photoluminescence spectrum changes differently due to the appearance of nonradiative recombination channels in unhomogeneous crystal. These nonradiative recombination channels arise due to the formation of Mn–O–Mn pairs. As a result, infrared photoluminescence band with an energy near 1.3 eV arises; the intensity of this band is significantly weaker than the intensity of the yellow band [11, 12]. The presence of these states in crystals with the high concentration of Mn leads to the dumping of the yellow luminescence with increasing of the temperature. At the increasing of Mn concentration in CdS:Mn the photoluminescence decay profile becomes nonexponential due to the inhomogeneity of crystal [11].

The photoluminescence band of $Zn_{1-x}Mn_xO$ ($x = 0.0009$), which is presented in Fig. 2, has the next energy parameters: ZPL — 2.40 eV, maximum — 2.17 eV, FWHM — approximately 0.40 eV, decay time is unknown. In [6–10] bands or weak peaks of photoluminescence were observed, the maxima of these peaks are marked by arrows in Fig. 2(a) together with the positions of photoluminescence maxima for ZnS:Mn, ZnSe:Mn, and CdS:Mn. It is clear that all these maxima are close to the maximum of photoluminescence spectrum at the energy of 2.17 eV. The positions on maxima of cathodeluminescence peaks of $Zn_{1-x}Mn_xO$ ($x = 0.0011$) single crystals [5] are also presented in Fig. 2(a). This closeness of peaks from [5–8] and peaks for ZnS:Mn, ZnSe:Mn, and CdS:Mn was considered as a sufficiently convincing argument for interpretation of peaks at [5–8] as intracenter transitions $^4T_1 \rightarrow {}^6A_1$ of d^5-configuration of Mn^{2+} ion.

In [6] the wide photoluminescence spectrum of $Zn_{1-x}Mn_xO$ ($x = 0.05$) epitaxial film (thickness 100 nm) grown on a $(000\bar{1})$ ZnO crystal substrate was observed at $T = 10$ K (the source of excitation was a xenon lamp; excitation energy $E_{\text{exc}} = 3.289$ eV). Authors [6] especially emphasize that the luminescence spectrum of $Zn_{0.95}Mn_{0.05}O$ film differs significantly from the photoluminescence spectrum of ZnO:Cu, in which intensive vibration repetitions of ZPL manifest themselves. These vibration repetitions are typical for the luminescence with the participation of Cu^{2+} ions, which have the deep charge transfer state d^9/d^{10} in the bandgap [16]. In Fig. 6(a) the photoluminescence spectrum of $Zn_{1-x}Mn_xO$ ($x = 0.0009$) at 8 K (Fig. 1) and the photoluminescence spectrum of $Zn_{0.95}Mn_{0.05}O$ from [6] at 10 K with the energy of ZPL near 2.5 eV are presented (maximum at the energy of 2.067 eV, FWHM is close to FWHM of our line). On longwave slope of the photoluminescence spectrum additional details are not detected. The photoluminescence decay, which was observed in [6] in the ms region was nonexponential, this fact was explained by authors as related inhomogeneity of $Zn_{1-x}Mn_xO$ ($x = 0.05$) thin film due to high concentration of Mn. Since the decay took place in ms region, authors [6] interpreted the wide luminescence band as a result of intracenter transition of

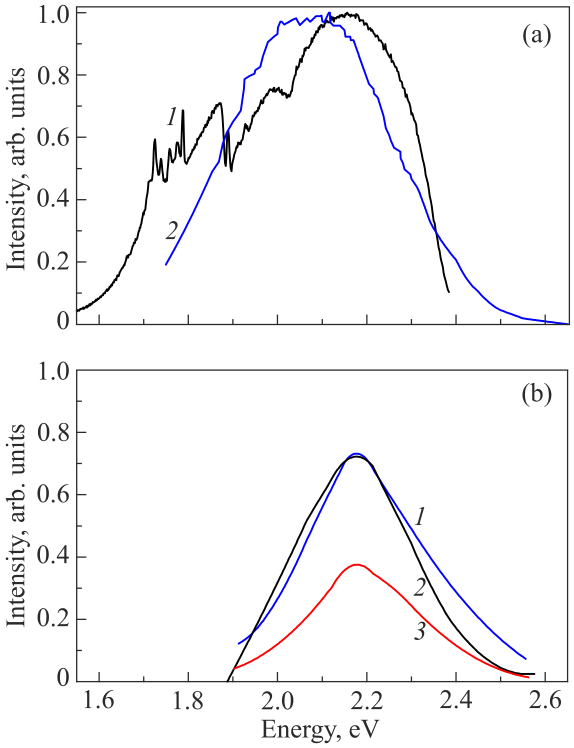

Fig. 6. (a) Photoluminescence spectra of $Zn_{1-x}Mn_xO$ ($x = 0.0009$) single crystal at laser excitation at the temperature of 8 K (*1*) and $Zn_{1-x}Mn_xO$ ($x = 0.05$) thin films from [6] (thickness of films 100 nm) at the excitation by xenon lamp (excitation energy $E_{\text{exc}} = 3.289$ eV; $T = 10$ K) (*2*). (b) Cathodoluminescence spectrum of $Zn_{1-x}Mn_xO$ ($x = 0.0011$) single crystals for $T = 5$ (*1*), 78 (*2*), and 300 K (*3*) from [5].

d^5-configuration of Mn^{2+} ion. Experimental results for II–VI compounds with a high concentration of Mn indicate that decay of photoluminescence bands during the time may cardinally change due to inhomogeneity of crystal [11]. The authors of [17] expressed the opinion that further investigations of these spectra should be undertaken for the verification of the conclusion of authors [6] about the transition $^4T_1 \rightarrow {}^6A_1$.

In [5] the cathodoluminescence spectrum of $Zn_{1-x}Mn_xO$ ($x = 0.0011$) single crystals for the temperatures of 5, 78, and 300 K under the influence of pulse electronic beam (the duration of pulse $\tau = 0.4$ μs, accelerating voltage 40 kV, average value of current in pulse $i = 1$ μA) was observed [Fig. 6(b)]. Cathodoluminescence bands are wide; without the manifestations of vibrational sideband, have the maxima at the same energy, but they are drawn toward high energies. This fact may be, due to excitation by electrons both from impurity and those appearing due to interband transitions. In this case, different variants of luminescent irradiation (which emerges from the sample) with an energy more than E_I manifest themselves. This irradiation is not suppressed completely by impurity absorption.

In [7] the photoluminescence spectra, light absorption and photoconductivity of ZnO:Mn polycrystalline ceramics (concentration of Mn was 10^{19}–10^{21} cm^{-3}) were observed. Authors of [7] notified that optical absorption increases with increasing of Mn concentration. They assume that absorption is caused by transitions from the deep charge transfer level of d^5/d^4 to the conduction band. In our article [14] we established that transitions take place from *pdh* (p+d^5) level to the conduction band (Fig. 2). The photoluminescence spectrum excited by the light of xenon lamp with a wavelength of 365 nm at the increasing of Mn concentration shifts to low energies as a result of impurity absorption rise. The photoluminescence spectra of ZnO:Mn with Mn concentration of 10^{20} cm^{-3} were registered at $T = 300$ and 77 K. For both spectra the energy of ZPL is near 2.40 eV, energy of maximum is 1.92 eV, and FWHM is 0.40 eV.

In [8] the photoluminescence of polycrystalline ceramics of $Zn_{1-x}Mn_xO$ at the different x in the range of 0–0.3 was investigated at room temperature. All spectra have the same energies of ZPL 2.48 eV, energies of maximum 1.9 eV, and FWHM 0.45 eV. The interpretation of photoluminescence bands in [5–7] as a manifestation of intracenter transitions of Mn^{2+} ions only basing on values of their maxima energies can not be proved since the other parameters of photoluminescence lines in ZnMnO differ significantly from those in ZnS:Mn and CdS:Mn. This fact gives a serious grounds to doubt the intracenter nature of peaks.

In [9, 10] the narrow peaks of photoluminescence and photoluminescence excitation spectra of ZnMnO nanocrystals were registered in the green-violet part of the spectrum. The intensity of peaks increased at the growth of Mn concentration in ZnMnO nanocrystals. In the photoluminescence spectrum of the samples of $Zn_{1-x}Mn_xO$ ($x = 0.01$) powder (the size of crystallin was 40 nm) intensive green line (526 nm) and some less intensive red line (636 nm) were discovered at the excitation by the irradiation with the wavelength of 412 nm at $T = 300$ K [10]. The authors of the paper consider that these lines are caused by intracenter transitions $^4T_1 \rightarrow {}^6A_1$ of Mn^{2+} ions in tetrahedral (526 nm) and octahedral (636 nm) surrounding. In the excitation spectrum of the green line four peaks 396, 412, 432, and 446 nm, caused by $^6A_1\rightarrow{}^4T_2$ (D), $^6A_1\rightarrow{}^1A_1$ (G), ^4E (G), $^6A_1\rightarrow{}^4T_2$ (G) and $^6A_1\rightarrow{}^4T_1$ (G) transitions correspondingly are observed.

In [9] the photoluminescence spectra of $Zn_{1-x}Mn_xO$ nanowires (x in interval of 0.001–1 %, thickness 300 nm, $T = 300$ K) were measured using of pulse laser with irradiation wavelength of 355 nm and nanosecond duration of excitation pulse of 2–3 ns. The luminescence irradiation registered with the time delay in 2 ns in the region from 0 to 50 ns. This method is used when it is necessary to distinguish the luminescent transitions, close to each other by the energy, but have different time decays [11]. The time-delayed photoluminescence spectra contained narrow peaks, intensities and wavelength positions of which were the subject of the delay time, laser excitation intensity and Mn concentration. The lines with maxima wavelengths of 471.8 and 480.2 nm were interpreted as $^4T_1\rightarrow{}^6A_1$ radiative transitions taking into account the splitting of $^4T_1$ term into two states in C_{3v} symmetry. By analogy with this fact lines 433 and 437 nm were interpreted as a result of $^4T_2 \rightarrow {}^6A_1$ irradiating transitions taking into account the splitting of $^4T_2$ term into two states. The lines at wavelengths of 416 and 385 nm were interpreted as radiative transitions of $^4A_1\rightarrow{}^6A_1$ and $^4E\rightarrow{}^6A_1$. The weak peak in the region of 636 nm was discovered in the work and was interpreted as a state of Mn–O–Mn cluster. This peak arises at the time delay of 20 ns and was observed for the samples with Mn concentration more than 0.03 %.

Theoretical calculations of the states of Mn^{2+} ion in ZnMnO predict, that the energies of intracenter transitions of $^6A_1 \rightarrow {}^4T_1$; $^6A_1 \rightarrow {}^4T_2$, and $^6A_1 \rightarrow {}^4A_1\ {}^4E$ are equal to 2.55; 2.85 and 2.99, 2.97 eV, correspondingly [18]. It is seen that there is sufficiently good correspondence between experimental and calculated values. Taking into account the results which were obtained for ZnMnO nanocrystals, we can assume that only in the green-violet part of the spectrum the real intracenter transitions of d^5 configuration of Mn^{2+} ion take place. In the conclusion of this part, we can say that the wide intensive photoluminescence spectrum of $Zn_{1-x}Mn_xO$ ($x = 0.0009$) cannot be interpreted as a result of intracenter transition $^4T_1\rightarrow{}^6A_1$ of Mn^{2+} ion. Taking into account the fact that peak in the red region arises after the excitation pulse within 20 ns [10], we received an additional argument that wide intensive photoluminescence band in $Zn_{1-x}Mn_xO$ ($x = 0.0009$) really is formed by dipole allowed s–p transitions.

In our work, we also registered the edge of the impurity absorption spectrum. The basic result of [13, 14] papers is as follows: the impurity absorption band in ZnMnO is formed by *p–s* transitions from the antibonding *pdh* (p+d^5) state to the edge of conduction band. These transitions are allowed in dipole approximation and the impurity absorption spectrum may be presented in form of direct allowed transitions,

$$\alpha \sim \left(\hbar\omega - E_I\right)^{1/2} / \hbar\omega , \quad (1)$$

$$\left(\alpha\hbar\omega\right)^2 \sim \left(\hbar\omega - E_I\right), \quad (2)$$

where E_I is the energy of ionization of the deep impurity center, α is the absorption coefficient.

The extrapolation of $(\alpha\hbar\omega)^2$ spectrum allows us to determine the energy of E_I. This extrapolation is shown in Fig. 2, and the correspondent ionization energy E_I is determined as 2.35 eV. From Fig. 2 it is clearly seen that near the energy of E_I there is the high energy edge of radiational recombination. The close coincidence of beginning energies in absorption and photoluminescence spectra evidences that observed spectra are due to optical transitions of only *s–p* type [Fig. 2(b)].

In Fig. 3 one can see the excitation spectrum of irradiation with the energy of 2.1 eV. It is seen that the excitation spectrum gradually increases approaching the fundamental absorption edge. A photoluminescence excitation spectrum of a similar appearance was observed in [6]. The excitation spectrum of irradiation with the energy of 2.10 eV in ZnMnO is correlated with the impurity absorption spectrum. This irradiation excitation spectrum does not possess the form of separate peaks due to intracenter transitions of $^6A_1\rightarrow{}^4T_1$, $^6A_1\rightarrow{}^4T_2$, and $^6A_1\rightarrow{}^4A_1\,{}^4E$ of d^5 configuration of Mn^{2+} ion which usually can be clearly observed for the widegap II–VI semiconductors doped with Mn [15].

In Fig. 5 the system of narrow lines in the energy interval of 1.8–1.7 eV is presented. In Fig. 1 and especially in Fig. 2 it is seen that these peaks are positioned higher in energy on the background of the wide photoluminescence band slope. Because of that, we can assert that these lines are due to other luminescence type contributions. The line with the maximal energy of 1.787 eV is the ZPL in the spectrum of this luminescence. Detailed analysis of EPR signals in [14] definitively testify that in the $Zn_{1-x}Mn_xO$ sample ($x = 0.009$) the permanent Fe^{3+} ions with d^5 configuration exist. The relation of intensities of EPR signals from Mn^{2+} and Fe^{3+} ions allowed to estimate that the concentration of Fe^{3+} ions is approximately by 10 times lower than the concentration of Mn^{2+} ions. For ZnO:Fe photoluminescence spectra, which are due to the intracenter transitions of d^5 configuration of Fe^{3+} ion were registered [19]. Line with the energy of 1.787 eV arises as a result of $^4T_1\rightarrow{}^6A_1$ transitions. The essential difference from the spectrum of ZnS:Mn consists of the fact that narrow ZPL is observed, but the continuous phonon wing with the maximum is absent. Lower than ZPL in energy separate peaks are observed; these peaks are vibrational sidebands of ZPL. Furthermore, all structure strongly depends on the temperature. A detailed understanding of the nature of these sidebands requires further investigation.

Let us turn to the system of narrow lines in the interval of 1.86–1.95 eV. From Fig. 1 it is seen, that narrow peaks, which are presented in this figure are more similar to suppression of luminescence. At the temperature increase these peaks disappear, unlike the wide photoluminescence spectrum. In [14] the lines *a*, *b*, *c*, and *d* of the *de* [$(h_{\rm loc} + d^5)e$] were registered in the same energy interval. In Fig. 4 the part of the photoluminescence spectrum in the region of narrow lines is presented in enlarged size at the temperature of 8 K together with the lines *a*, *b*, *c*, and *d* of *de* for σ-polarization [14]. It is clearly seen that four lines of *de* exactly coincide in energies with the minima on the luminescence spectrum. In this way, the self-absorption manifests itself in the photoluminescence spectrum. Luminescence irradiation which arises during excitation deep inside the sample far from the surface of the $Zn_{1-x}Mn_xO$ (x = = 0.0009) may weaken while moving out from the sample which is caused by the presence of optical transitions inside it. In $Zn_{1-x}Mn_xO$ ($x = 0.0009$) these transitions are transitions with the arising of *de*. Judging by the view of photoluminescence spectra at the increasing of temperature (Fig. 1) we can assert that the lines of *de* [$(h_{\rm loc} + d^5)e$] appear in the temperature interval of 8–140 K. The exact coincidence of the lines of *de* in the light absorption spectrum with the lines which manifest themselves in the spectrum of luminescent irradiation at $T = 8$ K presents the evidence of the fact that unpolarized light, which propagates along the *C* axis (or at a small angle to this axis) gives the same information about the electronic transitions as the light of σ-polarization. This fact justifies our variant of measurement of optical absorption and luminescence spectra in an uniaxial material using an unpolarized light that propagates at a small angle to the optical *C* axis. In [14] the bonding energy was evaluated as 250 meV. It seems that these excitons must be more stable in respect to the temperature. For example, free excitons in ZnO with the bonding energy of 60 meV are registered at room temperature. The disappeance of *de* excitons in a temperature region of ~ 150 K is an interesting and important experimental fact for further experimental and theory investigation of *de* [$(h_{\rm loc} + d^5)e$].

A little higher by the energy from two systems of narrow lines on the background of the wide band one can see the minimum at 2.03 eV. By the outward appearance, this minimum is like the minima due to the self-absorption of *a*, *b*, *c*, and *d* lines. Thus this minimum is a result of the absorption of luminescent irradiation due to some electronic transition. In [13] the weak absorption peak at the energy of 2.03 eV was observed. It is quite analogous to the influence of the optical absorption to the formation of high-energy part of luminescence and cathodoluminescence spectra in the energy region of 2.4–2.6 eV. We mentioned this influence above. This absorption needs further investigations.

The comparison of experimentally observed photoluminescence spectra evidences that in the ZnMnO compound there are two types of irradiation recombination due to the presence of Mn. The first type of them is due to dipole allowed *s–p* transitions from the conduction band to the *pdh* level. This irradiation begins at a delay time 20 ns after the excitation pulse. Vibrational sidebands, which are typical for charge transfer transitions to the deep level are absent in luminescence spectra. The second type of the irradiation is traditional intracenter *d–d* transitions. The first type transitions are clearly manifested in the samples of $Zn_{1-x}Mn_xO$ single crystals at $x \approx 0.001$ in photoluminescence and cathodoluminescence spectra in wide range of the temperature. In epitaxial films of $Zn_{1-x}Mn_xO$ at $x = 0.05$ and $T = 10$ K this transition appears too, but the interpretation of a result is more difficult due to the high concentration of Mn [5]. In absorption spectra, first type transitions dominate and hence forbidden *d–d* transitions do not appear. In nanocrystals, situation becomes other due to the different reasons which are discussed in detail in [17]. As a result, intracenter transitions become more probable and appear at an excitation energy close to E_G. In [9, 10] this fact is clearly manifested in photoluminescence and photoluminescence excitation spectra. Since all excitation at high energies are mainly captured by *d–d* transitions, *s–p* transitions manifest themselves weakly or not at all.

Concluding the discussion we can definitely say that optical absorption and photoluminescence spectra of $Zn_{1-x}Mn_xO$ ($x = 0.0009$) single crystal in red-orange part of the spectrum are described as a result of allowing in dipole approximation *p–s* transitions “impurity *pdh* level ⟵⟶ bottom of conduction band”. This understanding of the deep center in the bandgap of ZnMnO allows us to think about a good prospect of a further extensive investigation of this state and application of ZnMnO, for example, for photocatalysis or for photoemitting devices in the red-orange region of the visible spectrum.

Conclusions

The maximum of the wide intensive photoluminescence band in $Zn_{1-x}Mn_xO$ ($x = 0.0009$) single crystal (2.17 eV) formally coincides by the energy with peaks of intracenter transitions of Mn^{2+} ions in ZnS:Mn, ZnSe:Mn, and CdS:Mn compounds. But taking into account the significant difference of band parameters, absence of vibrational sidebands of zero phonon line and the coincidence of energy of band edge with the energy of impurity absorption edge, photoluminescence band in $Zn_{1-x}Mn_xO$ ($x = 0.0009$) is exactly interpreted as a result of allowed in dipole approximation *s–p* transitions from the conduction band to the impurity *pdh* (p+d^5) level. A new understanding of the nature of the deep state in the bandgap of ZnMnO makes this compound one of promising materials for photocatalysis and effective source of light in the yellow-orange range.

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Глибокий стан у забороненій щілині та фотолюмінесценція $Zn_{1-x}Mn_xO$

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Домішкове поглинання в $Zn_{1-x}Mn_xO$ формується дозволеними в дипольному наближенні *p*–*s*-переходами з глибокого антизв’язувального *d*–*p* гібридного (*pdh*) стану в зону провідності. Досліджено фотолюмінесценцію монокристалів $Zn_{1-x}Mn_xO$ в діапазоні температур 7–340 K при лазерному збудженні 3,06 еВ. Спостерігалася інтенсивна смуга фотолюмінесценції в області енергій 2,40–1,6 еВ з максимумом 2,17 еВ. Визначено енергію іонізації домішкового центра 2,35 еВ. Аналіз форми смуги фотолюмінесценції, а також близький збіг головної лінії цієї смуги і краю домішкового поглинання дозволяють однозначно інтерпретувати цю смугу як результат випромінювальних дипольно дозволених *s*–*p*-переходів із зони провідності на домішковий *pdh*-рівень.

Ключові слова: фотолюмінесценція, ZnO:Mn, домішкова фотоіонізація, внутрішньоцентральні переходи.