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PECULIARITIES OF PHOTOLUMINESCENCE EXCITATION IN ZnO CERAMICS DOPED WITH GROUP-I ELEMENTS

Extrinsic luminescence, excitation, and absorption spectra of ZnO ceramics doped with acceptors (lithium, copper, or silver), as well as undoped ZnO ceramics sintered in various atmospheres, have been studied. It is shown that the acceptor doping leads to the appearance of luminescence bands in the visible spectral interval, and their intensity significantly exceeds the intensity of the corresponding emission from undoped specimens. A selective maximum at 390–400 nm, which is usually absent in the excitation spectra of self-activated luminescence bands in undoped ZnO specimens, is found to dominate in the excitation spectra of those bands. It is supposed to be caused by the interaction between the emitting centers and defects arising near the impurities, with the Auger process being the most probable mechanism of energy transfer from these defects to the emitting centers. By sintering ZnO ceramics in the presence of carbon, it is shown that the appearance of the selective maximum in the excitation spectra occurs due to the extraction of oxygen from ZnO ceramics. An assumption has been done concerning the nature of the centers responsible for the excitation of extrinsic luminescence.

Keywords: zinc oxide, ceramics, doping, photoluminescence.

1. Introduction

The development of semiconductor materials emitting in the visible spectral range is one of the key problems in creating the solid-state sources of white radiation. Currently, semiconductor structures containing several materials that emit in different spectral ranges are applied, as a rule, as the sources of white light. It is obvious that the structures of this type are quite complicated. A simpler way to produce white radiation may be the application of a photoluminophore based on a single compound characterized by several luminescence bands, which together provide the white radiation.

Another important problem is the creation of UV sensors. The corresponding interest is associated with the emergence of new scientific data on the influence of UV radiation on human life and health, as well as with the awareness of the fact that the availability of cheap and widely accessible UV sensors is a necessary condition for solving a number of problems of industrial, medical, ecological, and environmental character. Nowadays zinc oxide (ZnO) is considered to be one of the promising materials to reach the both purposes [1].

Doping ZnO with group-I acceptors (Li, Cu, or Ag) can lead to an increase in the emission intensity in the visible spectral interval due to the appearance of additional impurity-associated bands. Furthermore, this may result in a decrease of conductivity. In particular, lithium is considered to be a promising impurity for achieving p-type conductivity, despite rather contradictory views on the realization of the latter at doping ZnO with lithium under equilibrium conditions. Indeed, it is theoretically predicted that Li impurities at Zn sites ($\mathrm{Li_{Zn}}$) form a shallow acceptor level [2], but in most experimental reports it is supposed that $\mathrm{Li_{Zn}}$ is a deep acceptor responsible for "yellow" luminescence with a maximum at about 2.0–2.2 eV [3–5].

Note that in a lot of works on ZnO-based materials, attention is paid to ZnO films. As was reported in works [6, 7], doping thin ZnO films with lithium can affect their crystallinity. It was shown that the insertion of lithium can both inhibit and favor the size growth of nanocrystallites in $\mathrm{Zn_{1-x}Li_xO}$ films during thermal annealing, which, in turn, can affect the luminescence characteristics. At the same time, the effect of doping ceramics with various impurities on its properties has been studied much less, although some differences associated with the peculiarities of the incorporation of impurities into ceramic grains can be expected in this case.

Note also that the sintering of ceramics is one of the most attractive methods for manufacturing ZnO because of its simplicity, low cost, and the ability to modify the characteristics of ceramics by introducing impurities into the initial charge. In addition, ceramic specimens (in particular, thin ceramic layers) can be convenient in a number of practical applications. Therefore, in this work, the luminescence and optical characteristics of ceramic ZnO specimens doped with lithium, copper, and silver were studied.

2. Experimental Technique

Ceramic ZnO specimens doped with Li, Ag, and Cu were formed from commercial ZnO powders (99.99% purity) mixed with distilled water as well as aqueous solutions of $\mathrm{LiNO_3}$, $\mathrm{AgNO_3}$, and $\mathrm{CuSO_4}$. The impurity concentration in doped specimens varied from 10^{17} to 10^{21} $\mathrm{cm^{-3}}$. The prepared charge was dried under normal conditions. Then the specimens were formed in the form of rectangular bars, sintered in air for 3 h at temperatures $T_{\mathrm{sin}} = 1000\div1100$ °C, and cooled down to room temperature together with the oven.

Samples of undoped ZnO were also fabricated. They were sintered in zinc vapor in the nitrogen stream, as well as in the presence of carbon in the air or the nitrogen stream. To sinter the specimens in zinc vapor, they were placed in a crucible with Zn metal powder and annealed in the nitrogen stream. In all cases, dense ceramic specimens with an average size of $10 \times 3 \times 2$ $\mathrm{mm^3}$ were obtained.

The optical properties of the specimens were studied using the photoluminescence (PL), photoluminescence excitation (PLE), and diffuse reflectance methods. To measure those parameters, the specimens were cleft and measurements were made at the cleavage surface.

The diffuse reflectance spectra were registered using a SilverNova spectrometer (StellarNet Inc., USA) and transformed into absorption spectra using the Kubelka–Munch relationship.

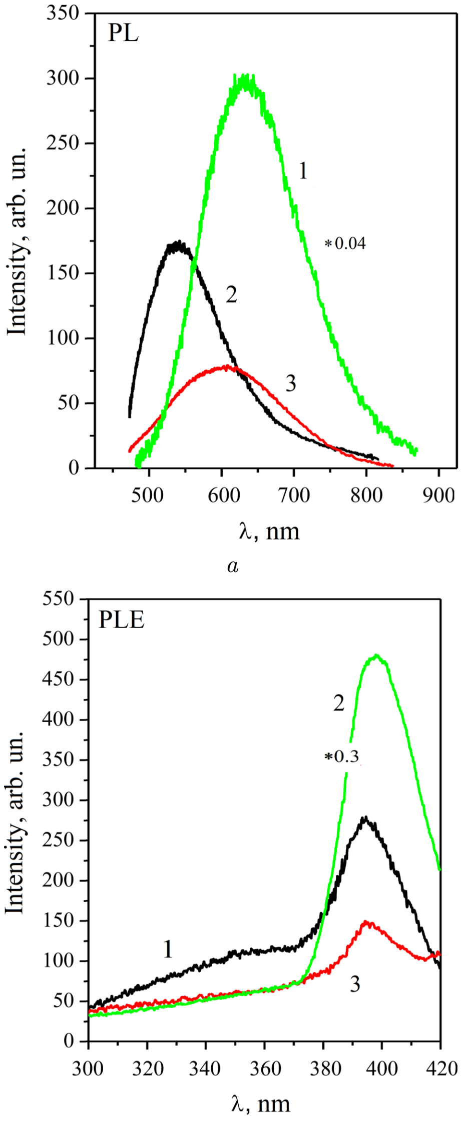
The PL and PLE spectra were measured on an setup with two monochromators: a grating monochromator MDR-23 with an operating interval of 220–900 nm, which was used to change the excitation wavelength, and a modified monochromator IKS-12 with an operating interval of 480–2300 nm for the registration of luminescence signal. The latter was registered using a photoelectric multiplier FEP-79. As an excitation source, radiation of either a halogen lamp whose light was transmitted through a monochromator MDR-23 or a nitrogen laser with a wavelength of 337 nm was used. The PLE spectra were measured at a wavelength corresponding to the maximum of impurity-related and/or self-activated PL. All measurements were performed at room temperature.

3. Results and Their Discussion

It is known that the PL spectra measured at room temperature for undoped ZnO ceramics synthesized in air usually demonstrate the free-exciton radiation and a weak broad defect-related band, which is known to consist of overlapped green (with a maximum at 510–520 nm) and orange (with a maximum at 600–620 nm) bands. The PLE spectra of both bands contain a peak at 380 nm, which corresponds to the free exciton, and a shoulder in the intrinsic light absorption interval.

Doping of the ZnO ceramics with group-I acceptors leads to some changes in the PL and PLE spectra. As one can see from Fig. 1, the specimens doped with Cu, Ag, and Li demonstrate intensive defect-related bands at 540, 580, and 610 nm, respectively, with their intensity substantially exceeding that of the self-activated bands.

A maximum at a longer wavelength of about 395 nm is observed in the PLE spectra, and its position does not depend on the impurity type. It can be a



a

b

Fig. 1. Photoluminescence (PL, *a*) and photoluminescence excitation (PLE, *b*) spectra for ZnO specimens doped with Li (*1*), Cu (*2*), and Ag (*3*)

superposition of a maximum associated with the free exciton and a longer-wavelength maximum probably associated with defects. The intensity of the latter obviously exceeds the intensity of the exciton-induced maximum so that the exciton peak is not observed separately.

To obtain additional information on the maximum in the PLE spectra of impurity bands, they were compared with the absorption spectra.

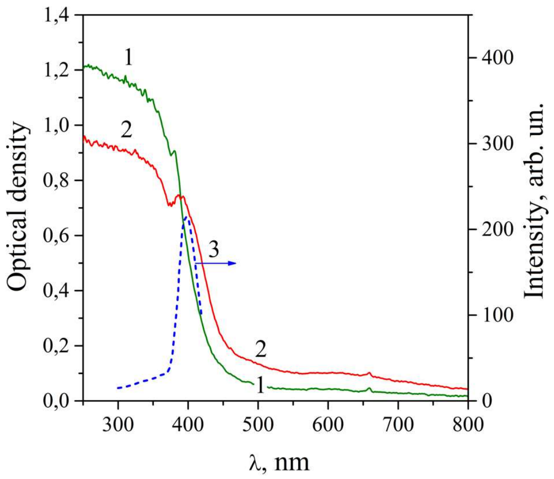
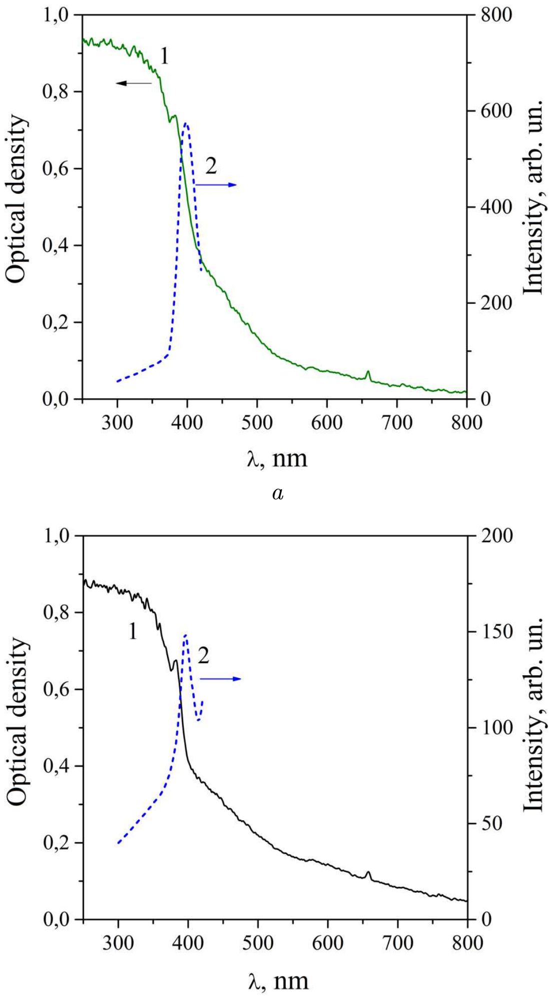


Fig. 2. Optical absorption (*1,2*) and PLE (*3*) spectra of ZnO specimens doped with copper. $N_{\mathrm{Cu}} = 10^{17}$ (*1*) and 5×10^{20} cm^{-3} (*2, 3*). The PLE spectrum was registered at a wavelength of 540 nm

The absorption spectra of copper-doped specimens are shown in Fig. 2. At low Cu concentrations ($N_{\mathrm{Cu}} = 10^{17}\div10^{19}$ cm^{-3}), the absorption spectra demonstrate the free-exciton peak and absorption in the interval of interband transitions (Fig. 2, curve *1*). The growth of the copper concentration to $N_{\mathrm{Cu}} = 5\times10^{20}\div1\times10^{21}$ cm^{-3} leads to the broadening of the absorption peak towards long wavelengths near the free exciton, which can be a result of its overlapping with a longer-wavelength maximum probably associated with defects (curve *2*). As one can see, the maximum of the PLE spectrum (curve *3*) is shifted in the long-wavelength direction with respect to the free-exciton maximum, but it remains within the limits of the peak observed in the absorption spectrum of the strongly doped specimen (Fig. 2, curve *2*).

In the absorption spectra of lithium- and silver-doped specimens with the impurity concentration $N_{\mathrm{Li(Ag)}} \sim 10^{20}$ cm^{-3}, only the free-exciton peak near the absorption edge is observed (see Fig. 3). The maximum of the PLE spectrum is shifted to the long-wavelength direction with respect to the free-exciton one and is not observed in the absorption spectra. Thus, the maximum in the PLE spectra can be a superposition of the maximum associated with the free exciton and the longer-wavelength maximum probably associated with defects. However, at low impurity concentrations, the latter maximum does not reveal itself separately in the absorption spectra.



a

b

Fig. 3. Absorption (*1*) and PLE (*2*) spectra of doped ZnO(Li) (*a*) and ZnO(Ag) (*b*) specimens. $N_{\mathrm{Cu,Ag}} = 10^{20}$ cm^{-3}

The manifestation of this maximum as the impurity concentration increases testifies that it is the incorporation of the impurity into the ZnO lattice that leads to its appearance. Furthermore, the impurity is more effective with respect to PL excitation than the free exciton.

Hence, unlike the undoped specimens where the luminescence of defects is excited, as a rule, owing to light absorption by the free exciton, the impurity luminescence bands in the doped specimens are excited at a specific maximum. At impurity concentrations of $N < 10^{20}$ cm^{-3}, this maximum does not reveal itself in the absorption spectra. This means that the light absorption coefficient at this maximum is lower than that of the exciton and depends on the impurity concentration. Therefore, we may suppose that this peak can be associated with some defects that are formed due to doping and act as excitation centers. Taking into account that the position of the excitation maximum does not depend on the impurity type, we may also suppose that the luminescence of the used acceptor impurities is excited by the same defect, which is the intrinsic defect of the ZnO lattice. Therefore, we may assume that doping gives rise to the formation of a certain complex consisting of an impurity and a lattice defect and governing the energy transfer to the luminescence center.

An important feature of this maximum is its selectivity. There can be several reasons for the appearance of the selective band of luminescence excitation. Some of them are as follows:

1) This band can be associated with the edge of the interband light absorption in the presence of strong non-radiative surface recombination. In this case, the growth of the light absorption coefficient with the decrease of the exciting light wavelength will reduce the recombination flux through the radiative centers. However, such a maximum cannot be more long-wavelength than the exciton one.

2) Selective bands can be induced by light absorption with the formation of free exciton and its subsequent photoactive decay. In this case, the position of the PLE peak must correspond to the exciton absorption bands, which was not observed in our experiment.

3) Another reason can be light absorption with the formation of excitons localized at deep luminescence centers or shallow centers (donors or acceptors) localized close to them. For instance, the excitation transfer as a result of Auger process at exciton annihilation will lead to the appearance of long-wavelength luminescence. However, as was shown in work [9], the position of the exciton localized at a group-I impurity (in particular, Na) is more short-wavelength than the excitation maximum of extrinsic luminescence that was observed in this work. The situation is identical for excitons localized at shallow centers.

4) Selective PLE can be a result of light absorption in a donor-acceptor (DA) pair consisting of shallow donors and acceptors, and the subsequent energy transfer to luminescence centers. In this case, there are several ways for the excited DA pair to relax:

- an ordinary radiative electron transition from the donor level to the acceptor one;
- thermal excitation of an electron from a donor and a hole from an acceptor into permitted bands with their subsequent radiative recombination at a deep center;
- the tunneling transition of a hole from the acceptor level to the deep-center one, followed by radiative recombination of this hole with a free electron excited thermally from the shallow donor in the DA pair;
- ionization of a deep radiative center with the simultaneous appearance of a free electron due to the Auger process.

5) Finally, such a luminescence excitation spectrum can be observed due to light absorption at intracenter transitions in a defect located near a luminescence center and the subsequent energy transfer to it. In this case, the energy transfer of the radiative center can also be a consequence of the Auger process.

Thus, the appearance of the selective maximum at 390–400 nm in the PLE spectra of impurity centers can be explained by the interaction between the radiative centers and certain defects that are formed nearby at doping, with the Auger process being the most probable mechanism of energy transfer to the radiative center. In this case, the energy released in the course of nonradiative recombination of nonequilibrium carriers in defects that are excited by 395-nm light is transferred to electrons at the radiative centers, which leads to their ionization. The electron recapture by an ionized radiative center gives rise to luminescence. This phenomenon was observed in CdS crystals [10].

To elucidate the possible origin of the defects that are responsible for the appearance of the impurity-induced PLE peak (including its possible relation to DA pairs), ceramic specimens were synthesized in various atmospheres. Since the incorporation of impurity atoms into the lattice at zinc sites can lead to the appearance of interstitial zinc Zn_i and/or oxygen vacancies V_O, we may suppose that they participate in the formation of exciting complexes. To verify this assumption, undoped ZnO ceramics was synthesized under the conditions that increased the excess of Zn in ZnO or stimulated the formation of oxygen vacancies, namely:

- in Zn vapor,
- in the N_2 flow, and
- in the presence of carbon in the air or the N_2 flow.

It turned out that sintering ZnO ceramics in zinc vapor brings about a substantial enhancement of the green emission band so that the PLE spectrum demonstrated a maximum at 380 nm and a drastic decrease towards longer wavelengths without any indications of an additional peak.

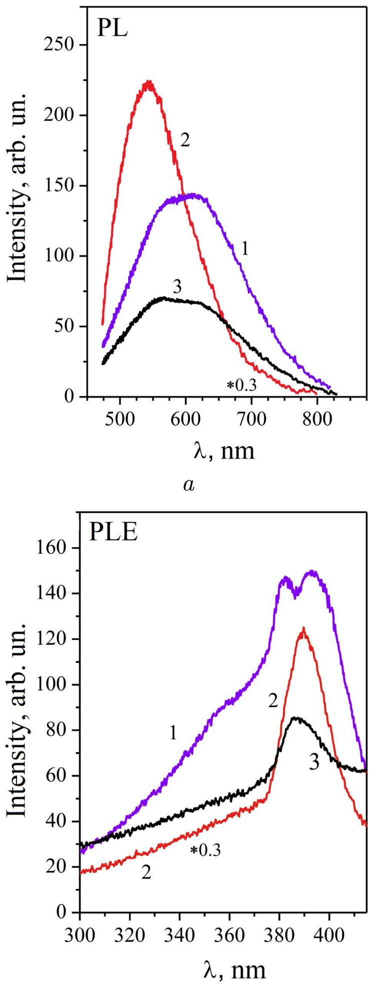
In the PLE spectra of the specimens sintered in the nitrogen stream, a wide peak was observed at about 390 nm with a slow decline towards longer wavelengths, which can be described as the overlapping of the peaks at 380 and 395 nm (Fig. 4). Such PLE maxima were also observed for the specimens sintered in the presence of carbon in the nitrogen stream. The amplitudes of those maxima were close to each other.

One may expect that sintering ZnO in Zn vapor should lead to the appearance of Zn_i atoms. Really, as was shown earlier, the growth in the concentration of those defects results in the enhancement of the green PL band [11]. On the other hand, sintering ZnO in the nitrogen flow in the presence of carbon should lead to the removal of oxygen from the specimen and the formation of oxygen vacancies V_O. Thus, it is quite probable that it is oxygen vacancies that are required to form the PL excitation centers.

Note that additional maxima were observed on the long-wave side of the exciton maximum in the excitation spectra of the blue PL band in ZnO nanoparticles [12]. They were associated with electron transitions from the valence band onto the levels of Zn_i or their complexes. However, in our case, the above experimental results point to the participation of oxygen vacancies rather than interstitial zinc atoms in the formation of PL excitation centers.

Taking this fact into account, the recombination in the DA pair can also be excluded from the above-mentioned possibilities responsible for the appearance of the selective maximum. Really, since the oxygen vacancy is considered to be a deep donor, the PL excitation maximum in an interval of 390–400 nm cannot be associated with the charge carrier recombination in DA pairs that include V_O.

However, one cannot rule out that the formation of oxygen vacancies may lead to the appearance of other defects (including other complexes or extended defects) capable of absorbing light in the indicated spectral interval. In addition, the availability of an excited level in the oxygen vacancy is feasible. In this case, an electron transition from the ground to an



a

b

Fig. 4. PL (*a*) and PLE (*b*) spectra of ZnO specimens sintered in the nitrogen stream (*1*) and in the presence of carbon in the air (*2*) or the nitrogen stream (*3*)

excited state can lead to light absorption in the interval of 390–400 nm, and the relaxation of the excited electron to the ground state can lead to the energy transfer to the impurity luminescence center.

The fact that the oxygen vacancy possesses an excited level that lies in the conduction band was observed, in particular, in ZrO_2 [13]. In this case, despite that the excited level is in the conduction band, the excitation energy transfer to another center is possible if the energy transfer time is short enough.

Thus, doping ZnO ceramics with acceptors (Li, Cu, Ag) gives rise to the appearance of luminescence bands in the visible spectral interval. The intensity of those bands substantially exceeds the intensity of bands in undoped specimens, which testifies that the impurities become incorporated in zinc sites. In parallel, there also appear intrinsic defects in the oxygen sublattice. They form complexes with impurities and participate in the excitation of impurity-related luminescence bands, probably via the Auger process.

4. Conclusions

The spectra of extrinsic luminescence, the spectra of its excitation, and the absorption spectra of ZnO ceramics doped with lithium, copper, and silver, as well as the absorption spectra of undoped ZnO ceramics sintered in various atmospheres, have been studied. It is shown that doping of the ceramics with acceptors gives rise to the appearance of luminescence bands in the visible spectral interval, with the intensity of those bands considerably exceeding the intensity of bands in undoped specimens. It is found that a selective maximum at 390–400 nm associated with defects dominates in the corresponding excitation spectra. It is proposed that its appearance in the PLE spectra of the impurity centers occurs due to the interaction between radiative centers and defects formed near them at the doping, with the Auger process being the most probable mechanism of energy transfer to the radiative center. It is found that the synthesis of ceramic specimens in the presence of carbon in the nitrogen flow leads to the appearance of a PLE maximum at 390–400 nm. Since such synthesis should lead to the removal of oxygen from the specimen and the appearance of oxygen vacancies, it is concluded that just those entities are needed for the formation of PL excitation centers.

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ОСОБЛИВОСТІ ПРОЦЕСІВ ЗБУДЖЕННЯ ФОТОЛЮМІНЕСЦЕНЦІЇ У КЕРАМІЦІ ОКСИДУ ЦИНКУ, ЛЕГОВАНОЇ ЕЛЕМЕНТАМИ І ГРУПИ

Досліджено спектри домішкової фотолюмінесценції, спектри її збудження і спектри поглинання кераміки ZnO, легованої літієм, міддю і сріблом, а також нелегованої кераміки, спеченої в різних атмосферах. Показано, що легування кераміки акцепторами приводить до появи смуг люмінесценції у видимому діапазоні спектра, інтенсивність яких суттєво перевищує інтенсивність видимого випромінювання нелегованих зразків. Виявлено, що в спектрах збудження цих смуг домінує селективний максимум в області 390–400 нм, зазвичай відсутній у спектрах збудження самоактивованих смуг люмінесценції в нелегованих зразках. Запропоновано пояснення, що його поява зумовлена взаємодією між центрами випромінювання і дефектами, які виникають в околі домішок, а оже-процес є найбільш імовірним механізмом передачі енергії від цих дефектів до центрів випромінювання. За допомогою синтезу кераміки у присутності вуглецю показано, що поява такого максимуму в спектрах збудження люмінесценції в нелегованих зразках зумовлена видаленням кисню з кераміки. Зроблено висновок щодо природи центрів збудження домішкової люмінесценції.

Ключові слова: оксид цинку, кераміка, легування, фотолюмінесценція.