Temperature features of ZnO exciton luminescence

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Abstract. The study shows exciton-phonon luminescence (EPL) of free excitons in ZnO crystals within temperatures 77-300 K. It’s been found that low resistivity samples with temperatures above 150 K demonstrate temperature anomalies in the EPL of free excitons, which is supposed to be the result of the exciton – electron interaction. The EPL temperature dynamics is closely related to the nature of a defective crystal structure. This allows that we should propose a method of quality non-destructive operation with zinc oxide crystals. The paper describes conditions for recording the specific luminescence spectrum of ZnO, which can be the result of inelastic scattering of free excitons and which is accompanied by radiation of excited excitons and exciton-phonon complexes.

1. Introduction
Zinc oxide is considered to be a promising material for the construction of a polariton laser capable of operating at room temperature. It also can be used for making different instruments as a source for ultraviolet and visible radiation [1-4]. Earlier [2] we described the results associated with EPL sensitivity increase in zinc oxide. The current report considers anomalies of ultraviolet (UV) exciton luminescence of ZnO within the range of temperatures 77-300 K.

The character of temperature quenching for most EPL bands of free excitons is traditionally similar [1,4] and can be determined by their thermal decomposition. The detected anomalous temperature behaviour of those exciton EPL bands (attributed to a veiled change in the mechanism of emission and the dependence of electron mobility on temperature) is closely related to the electrical conductivity and general defective ZnO crystal structure. This factor should be taken into account when selecting the crystals for obtaining laser radiation on them.

It’s been found that selected high-quality ZnO single crystals in the spectrum of luminescence, except for P-band due to the transition of colliding excitons to the lower photon polariton branch curve, exhibit the radiation of the excited excitons ($n = 2, 3, \ldots, \infty$) and exciton-phonon complexes, which are normally recorded only in the exciton reflection spectra and partly in the photoexcitation of ZnO [4].

2. Experimental results and Discussion
The subject of the research is ZnO single crystals, being obtained by synthesis from the gas phase and ZnO powders of high purity [4]. The experimental methodology has been described [2,3].

In the exciton luminescence spectrum under the normal excitation level ZnO are detected [1-4]: a) at "near helium" temperatures, which represent peaks corresponding to the dominant radiation of excitons connected through shallow donors (Zn, Li, In$_{Zn}$, and others) – radiation occurs under the action of longitudinal optical LO-phonons with two – electron satellites; b) at temperatures close to $T$
of liquid nitrogen, which represent the exciton-phonon strip luminescence (EPL) due to the emission of free \( A^- \) excitons, including \( LO \)-phonons (\( A^-LO, A^-2LO, A^-3LO \), etc.); C) at \( T_c \), close to room temperature, there one can observe a common (almost unresolved) EPL band of free excitons.

As shown in figure 1, the exciton cathodoluminescence spectra (electron energy in a beam of 7 keV, current density \( 3 \times 10^{-6} \) A/cm\(^2\)) were obtained with the temperature range (80 ÷ 300) K. Curves 1 represent one of the input ZnO single crystals, curves 2 represent the powder marked as “of high purity”, curves 3 represent a single crystal, having been heat-treated (\( T = 1150 \) °C) in the saturated vapor of cadmium (in this case as per [2,4], there happens the sensitizing of UV luminescence).

If the input single crystals are comparatively perfect (the degree of perfection can be estimated by data of the exciton emission spectra [4]), then, regardless of the cultivation method, the dominant position in the spectra of their EPL at normal excitation levels, happens to be \( A \) band (the activation energy of temperature quenching is 0.05 − 0.055 eV, which corresponds to the binding energy of free \( A^- \)-excitons [4]).

**Figure 1.** Cathodoluminescence spectra ZnO samples under study. Experiment - solid curves; theory – dashed curves.

It is \( A^-LO \) band that dominates in the EPL spectra of powder samples up to 400K. The intensities of all bands with the increase of \( T \) from 80 K to 105 K go abruptly down, but later the decline gives way to rise: at \( T \approx 200 \) K on the temperature dependence of cathodoluminescence intensity there appears a small maximum (curves 2). Similar is the performance of spectra for relatively defective single crystals with the disrupted, according to the data of exciton reflection spectra, translation symmetry of the crystal lattice [3]; the temperature dependences of the intensity for the yellow - orange and green cathodoluminescence bands as well as the mobility of electrons in single – crystal ZnO samples look similar. We believe, that it is due to the fact that with the temperature increase within the range of 105 K to 200 K, the electron scattering around the crystal lattice defects is getting
less, thus leading to a longer "active" lifespan and mobility of excited electrons, thereby increasing the probability of exciton formation and their subsequent radiative recombination.

No less interesting picture can be observed while the analysis of the temperature dependence of EPL intensity in ZnO samples with low resistivity (1 ÷ 10 Ohm·cm) and higher quantum yield of luminescence (figure 1, curves 3). Band $A\rightarrow LO$ in the photoluminescence spectra to those of the samples with $T$ rising above 80 K quickly disappears (activation energy of 0.075 eV – 0.1 eV) and increase in its intensity no longer occurs (curves 2, 3). However, the initial decline is replaced by a sharp rise in intensity as immediately as around $A\rightarrow 2LO$ band (the maximum is reached at $T$ 180 K). Moreover, within a narrow temperature range (190 - 220 K), the shape of this band changes the asymmetry direction (curves 3). At that, the transformation can hardly be explained just by a temperature change in the shape of the Maxwell distribution [4] (dotted line in figure 1). Besides, at $T \geq 190$ K (compared to that which was to be expected) there occurs a notable increase of temperature coefficient in $A\rightarrow 2LO$ band shift, which is demonstrated by the theoretically [4] predicted behavior of $H$-band in ZnO, figure 1. All this indicates that with low resistivity crystals EPL $A\rightarrow 2LO$ band may have a complex nature: at $T > 150$, it moves to $H$-band, which appearance is determined by the exciton-electronic interaction [4]. A free exciton transfers part of its energy to an electron in the conduction band and moves to the photonic branch of a polariton curve with the subsequent photon emission.

At high excitation levels being accompanied by a sharp concentration increase of free excitons and due to their inelastic propagation [1,4] one can also observe a complex $P$-band in the emission spectra at $T \leq 77$ K.

However, at $T \simeq 85$ K, another type of luminescence accompanying $P$-radiation may emerge in ZnO (see figure 2, where: 1 – $T = 77$ K; 2 – $T = 85$ K; excitation source – nitrogen laser LGI-21, 1 MW/cm2; A, B, C – free excitons, L – exciton-phonon complexes. 3 – exciton reflection spectra of ZnO single crystal at $T = 77$ K). Along with the dominant complex $P$-band, the luminescence of exciton formations is recorded, the fine structure of which can be observed only in the exciton reflection spectra and partly in the photoexcitation spectra [4].

In the radiation spectra (as opposed to reflection or absorption spectra) there is no general background against which the fine structure can be recorded. In particular, we can distinguish the doubletness of the bands associated with the direct annihilation of free $A_1$ ($n = 1$)- and $B_1$ ($n = 1$) - excitons (splitting is about 4 MeV), and the fine structure as a result of radiation of the excited ($n = 2$, $3 \ldots \infty$) excitons and exciton-phonon complexes - L [4]. The effect is confirmed by calculations of the fine structure energy position on both sides of the resonance lines $A_1$- and $B_1$-excitons (figure 2, curve 2, arrows).

To observe the luminescence of exciton-phonon complexes as well as excited exciton states 1) the crystals should have a minimum of defects and possess an intense EPL even at normal level of excitation; 2) the temperature should be high enough so that thermal decomposition of the bound excitons can occur, whereas the excitation level should provide exciton-exciton scattering.
3. Conclusions

Thus, it is believed that the described temperature features of the exciton-phonon luminescence spectra in ZnO crystals should be taken into account both for explaining the mechanism of exciton radiation of samples (notably, when laser effects emerge) and for developing assessment methods of their crystal structure perfection.

It is shown that exciton-exciton scattering at relatively high temperatures (about 85 K) can serve as a unique method of luminescence excitation involving high-energy exciton conditions in crystals.

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References

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