LUMINESCENCE OF ZNSE CRYSTALS GROWN WITH DIFFERENT VAPOR TRANSPORT AGENTS

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ZnSe and related materials have been extensively investigated for their potential application in the blue-near ultraviolet light emitters [1] as well as for the fundamental properties of the dense exciton system [2]. Usually, blue emission from ZnSe and related compounds that are applied to blue optoelectronic devices is associated with donor-acceptor pair (DAP) transitions. One of the main source of blue DAP emission in ZnSe is related to the doping with nitrogen. Photoluminescence is widely used to study the recombination centers in ZnSe crystals and their content depending on the technological processing.

In this paper we compare the luminescence properties of bulk ZnSe crystals grown by vapor transport method with different transport agents in order to establish the influence of the transport agent on the relation between the excitonic, DAP, and deep center emission. ZnSe single crystals were grown using iodine or NH_4Cl transport agents. Photoluminescence (PL) was excited by the 351 nm line of an Ar^+ SpectraPhysics laser and analyzed through a double spectrometer. The resolution was better than 0.5 meV. The samples were mounted on the cold station of a LTS-22-C-330 cryogenic system.

Figures 1 and 2 present the PL spectra of ZnSe crystals grown with NH_4Cl transport agent measured with different excitation power density and different temperatures, respectively. Figure 3 and 4 show the same spectra in the near bangap region in more details. The luminescence related to deep centers consists of two PL bands centered at 1.95 and 2.40 eV. The analysis of the behavior of these bands with increasing excitation power density and temperature suggests that the PL band at 1.95 eV originates from a free to bound electronic transition while the PL band at 2.40 eV is associated with DAP transitions. The 2.40 eV PL band shifts to higher energies when increasing excitation power (Fig. 1), which is consistent with the saturation of distant pairs under increasing excitation, as expected for DAP recombination. At the same time the position of the 1.95 eV PL band is independent on the excitation power density. The temperature dependence of luminescence supports this assignment. The intensity of the 2.40 eV PL band decreases much faster than the intensity of the 1.95 eV PL band. This behavior is attributed to the ionization of the impurity with smaller binding energy involved in DAP transitions.

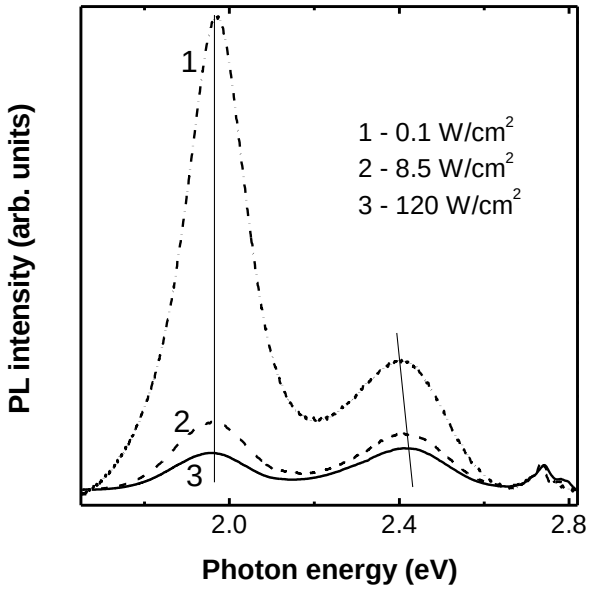

Fig. 1. PL spectra of ZnSe crystals grown with NH_4Cl transport agent measured at 10 K with different excitation power density. The spectra are normalized to the excitonic emission.

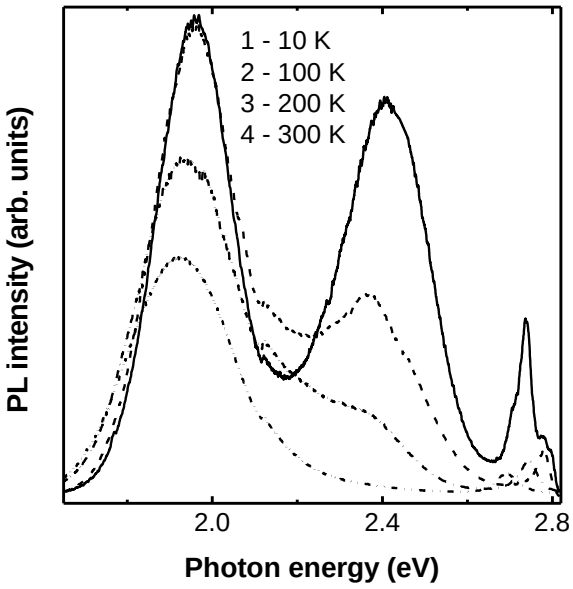

Fig. 2. PL spectra of ZnSe crystals grown with NH_4Cl transport agent measured at different temperatures with excitation power density of 8.5 W/cm^2.

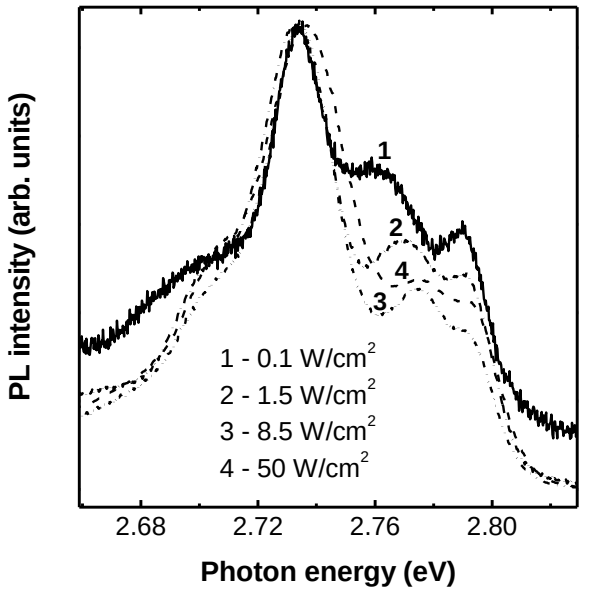

Fig. 3. PL spectra of ZnSe crystals grown with NH_4Cl transport agent measured at 10 K with different excitation power density.

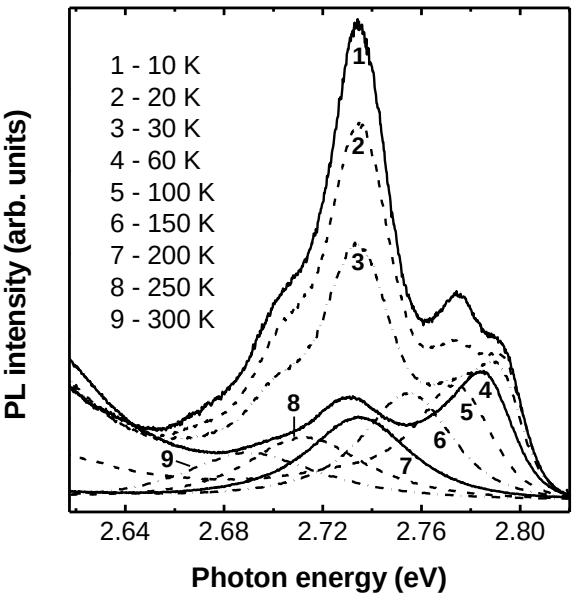

Fig. 4. PL spectra of ZnSe crystals grown with NH_4Cl transport agent measured at different temperatures with excitation power density of 8.5 W/cm^2.

Stringfellow and Bube suggested that the red and green luminescence in ZnSe is related to the recombination of a free electron with a hole localized at a Cu_{Zn}^{+} and a Cu_{Zn}^{++} acceptor, respectively

[3]. On the other hand, Ivanova et al believe that green emission comes from an electron transition from a shallow donor (for instance V_{Se}) to a deep associated (Cu_{Zn}^{++}- Cu_i^{+}) acceptor, while the red luminescence is due to electron transition from a shallow residual donor impurity to a (Cu_{Zn}^{+}- D_{Zn}) complex [4]. Our analysis suggests that the red luminescence is associated with a free to bound electronic transition as supposed by Stringfellow and Bube while the green emission is related to a DAP transition in accordance with Ivanova et al. One should note for completeness that Baltramiejūnas et al suggest that deep level related luminescence in ZnSe may come from structural defects not involving Cu impurity [5,6].

In the near bandgap spectral region the luminescence of ZnSe crystals grown with NH_4Cl transport agent is dominated by a PL band at 2.73 eV and two weaker bands at 2.77 and 2.79 eV. The analysis of the behavior of these bands with increasing excitation power density and temperature (see Figs 3 and 4) according to the methodology described above suggests that the PL bands at 2.73 and 2.77 eV are associated with DAP transitions while the PL band at 2.79 eV originates from a free to bound electronic transition. We suppose that the 2.73 eV blue PL band is related to the nitrogen impurity incorporated in the crystal from the transport agent.

Fig. 5 compares the PL spectra of ZnSe crystals grown with NH_4Cl and iodine transport agents. The emission spectrum of crystals grown with iodine transport agent is dominated by excitonic luminescence which represents an overwhelming of D^0X exciton recombination emission with the maximum at 2.796 eV and FWHM of 4 meV as well as a right and a left side shoulders at 2.785 eV and 2.804 eV related to acceptor bound (AX) and free excitons (FX), respectively. Apart from excitonic luminescence the PL spectrum shows a DAP related band at 2.702 eV with 1LO and 2LO phonon replicas at 2.670 and 2.638 eV, respectively. One can realize a significant difference in photoluminescence properties of ZnSe crystals grown with different transport agents. The samples grown with iodine are of a higher quality in comparison with crystals grown with NH_4Cl transport agent from the point of view of structural defects and impurities. The deep level related luminescence is commonly believed to come from structural defects [5,6], and the relative PL intensity ratio of the near-band edge emission to the deep level related emission is used as a parameter for estimation the quality of the material.

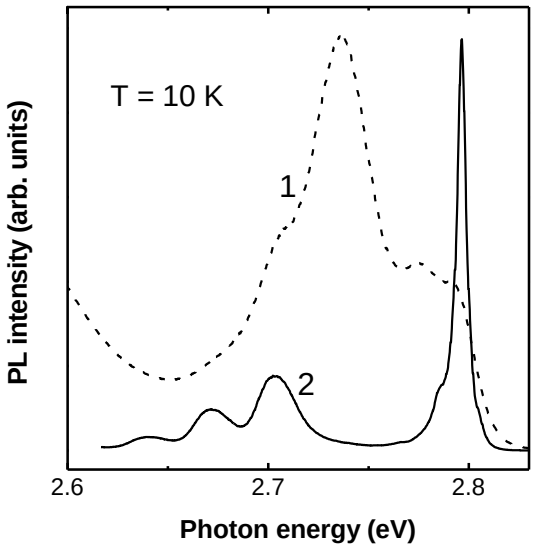

Fig. 5. A comparison of PL spectra of ZnSe crystals grown with NH_4Cl (curve 1) and iodine (curve 2) transport agents.

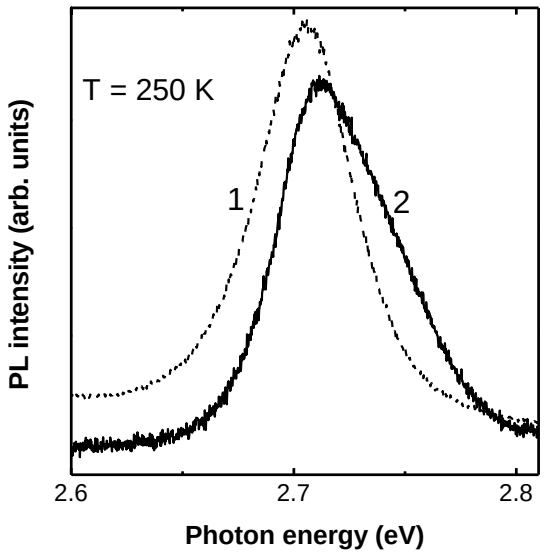

Fig. 6. PL spectra of ZnSe crystals grown with NH_4Cl (curve 1) and iodine (curve 2) transport agents measured at T = 250 K.

One should note that the PL band at 2.79 eV in ZnSe crystals grown with NH_4Cl corresponds to the spectral region characteristic for bound exciton luminescence. However, the analysis of the temperature dependence of this band allows one to attribute it to a free to bound electronic transition rather than to excitonic one. The intensity of this PL band decreases at a much lower rate with the temperature increase in comparison with the intensity of the D^0X luminescence (see Figs 5 and 6), since the ionization energy of the impurity involved in the free to bound transition is significantly bigger that the localization energy of the donor bound exciton. In contrast, the luminescence of ZnSe crystals grown with iodine comes mainly from free excitons at high temperatures.

Therefore, the luminescence of ZnSe crystals grown with iodine is dominated by excitonic emission and this material is suitable for the investigation of fundamental properties of dense exciton systems, while the crystals grown with NH_4Cl exhibit bright blue emission related to nitrogen impurity and are promising for applications in blue light emitters.

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