Low Temperature Luminescence of Ni$_x$Zn$_{1-x}$O Oxide Solid Solutions under VUV/XUV Excitations

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ZnO doped with 3d impurities attract great attention as materials for which ferromagnetic ordering with a Curie temperature above the room one was theoretically predicted. It is very important optical investigation of Ni$_x$Zn$_{1-x}$O solid solutions for obtaining new information on energy states of those very complicated materials.

The present study was carried out by the means of the time-resolved luminescence VUV and XUV spectroscopy. The measurements of PL spectra were made on a SUPERLUMI station using an ARC Spectra Pro-308i monochromator and R6358P Hamamatsu photomultiplier. The PL was recorded in two time windows – fast: delay $\delta t_1 = 0.6$ ns, span of windows $\Delta t_1 = 2.3$ ns; – slow: $\delta t_2 = 58$ ns, $\Delta t_2 = 14$ ns. The time-resolved PL spectra, the PL excitation spectra as well as the PL decay kinetics has been measured on a BW3 beamline. The PL spectra were measured by a VUV monochromator equipped with microchannel plate-photomultiplier (MCP 1645, Hamamatsu). The parameters of time windows – fast: $\delta t_1 = 0.1$ ns, $\Delta t_1 = 5.7$ ns; – slow: $\delta t_2 = 16$ ns, $\Delta t_2 = 21$ ns. The temporal resolution of the whole detection system was 250 ps. The temporary interval between SR excitation pulses is equal 96 ns. ZnO doped with Ni and Co are hydrothermal samples with impurity concentration $x = 0.002$ and 0.007 respectively. The method of rock-salt Ni$_x$Zn$_{1-x}$O solid solutions synthesis is described in Ref. [1].

Photoluminescence (PL) of ZnO:Ni and ZnO:Co oxides due to radiating charge transfer transitions has been observed in this paper. Short wavelength edges of PL bands are defined by donor or acceptor levels of 3d impurities. In fact they are positions of antibonding states, which appear due to hybridization of 3d-states with nearest ions p-states. Observation of bands in PL excitation (PLE) spectra at $\hbar \omega > E_g$ appearing due to transitions through antibonding states allows us to detect the bonding states which have not earlier investigated. Such situation was observed for ZnO:Mn [2-4]. PL spectra for Ni$_x$Zn$_{1-x}$O oxides at excitation energies $\hbar \omega > E_g$ has not been earlier observed as well. From Figure 1 we can see two peaks in the ZnO:Ni PL spectrum and one peak for ZnO:Co. Short wavelength edges of these bands at the energies 2.70 and 3.40 eV which are near to the energies of charge transfer bands in absorption spectra for ZnO:Ni and ZnO:Co.

![Figure 1: PL spectra (left) and PLE spectra (right) of Ni$_x$Zn$_{1-x}$O (x=0.3) (1), Ni$_x$Zn$_{1-x}$O (x=0.5) (2), ZnO:Ni (3) and ZnO:Co (4), T=8 K.](image-url)
Luminescence bands are observed under the VUV excitation at the closely-spaced energies. PL bands have decay time in the microseconds range. PL bands with similar forms are observed for Ni$_x$Zn$_{1-x}$O solid solutions, PL excitation spectra of which have maxima at the energy of 6 eV. NiO luminescence spectra have complicated form depending on registration time (Figure 2). For the fast window we can see three peaks in the PL spectrum, one of them with the energy 2.3 eV has maximum in energy region of 6 eV in PLE spectra. It is significant that the PL peaks decay with the time in ns-region which is substantially faster than the decay-time of the ZnO:Ni PL peaks. The nature of states, through which luminescence takes place in solid solutions with $x=0.3$, 0.5 and 1.0, is yet unclear but peaks observed in PLE spectra may be considered as a results of $d$-$p$ hybridization. Luminescence spectra of Zn$_{0.7}$Ni$_{0.3}$O solid solutions under XUV-excitation are presented at Figure 3. Two narrow lines are revealed with the short decay-time. Similar X-ray luminescence bands were observed for NiO as well. We believe that the very short narrow lines are due to exciton-like states below the charge transfer band edge. The revealing of narrow PL lines having a very fast decay-time for different Zn$_{1-x}$Ni$_x$O solid solution compositions opens new possibilities for further investigations of these very interesting oxides.

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**References**