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Luminescence and optical spectroscopy of charge transfer processes in solid solutions $Ni_CMg_{1-C}O$ and $Ni_xZn_{1-x}O$

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ABSTRACT

In this work photoluminescence spectra for $Ni_cMg_{1-c}O$ and $Ni_xZn_{1-x}O$ solid solutions with the rock-salt crystal structure were obtained under synchrotron radiation excitation. Periodical peaks in the photoluminescence excitation spectrum of $Ni_cMg_{1-c}O$ ($c=0.008$) have been discovered for a wide-gap oxide doped with 3d impurities for the first time. They can be considered as LO phonon repetitions of the narrow zero phonon line resulted from the optical transitions into the p–d charge transfer exciton [d^9h] state. A close coincidence in energy of different peculiarities in the optical absorption and photoluminescence excitation spectra for the $Ni_cMg_{1-c}O$ and $Ni_xZn_{1-x}O$ solid solutions is due to the practically equal interatomic distances Ni–O in the investigated materials. The bulk of new experimental results is the trustworthy evidence that only the p–d charge transfer transitions manifest themselves in the spectral region of 3.5–6.5 eV.

1. Introduction

Research into electronic structure and optical transitions in strongly-correlated oxide systems attracts attention of many scientists. Nickel oxide is a typical material for which many experimental results and theoretical calculations have been obtained [1–6]. When discussing optical properties for NiO in the fundamental absorption range, two types of interband transitions are usually considered. The first one is the transition of electron from oxygen ion O^{2-} to Ni^{2+} ion, which is attributed to the p–d charge transfer transitions. As a result of this transition, a Ni^{1+} ion with the d^9 configuration and the hole in the valence band appear. The second type, which is called a d–d intersite charge transfer transition, is the transition of electron from one Ni^{2+} ion to another Ni^{2+} ion. After this transition, the Ni^{1+} and Ni^{3+} ions with the d^9 and d^7 configurations appear. There are many different methods to observe optical transitions, but it was very difficult to distinguish between the p–d and d–d transitions by these methods. In our work, we used a new approach based on an essential difference between the contributions of the p–d and d–d transitions into optical spectra. We have dealt with the MgO crystal doped with nickel ions at very low concentration. The NiO and MgO compounds have the same cubic rock-salt structure and very similar lattice constants a_0 differing less than by 1%. For MgO doped with nickel, at low concentration, the distance between two nearest sites of nickel should be very long. For example, for $Ni_cMg_{1-c}O$ ($c=0.008$), the average distance is near 13 Å. Therefore, for the $Ni_{0.008}Mg_{0.092}O$ crystal, the d–d transitions in the optical spectra are believed to be hardly observed. On the other hand, the p–d charge transfer transitions for $Ni_{0.008}Mg_{0.092}O$ should take place. In the course of our investigation, we observed optical absorption, photoluminescence (PL) and photoluminescence excitation (PLE) spectra of NiO, $Ni_cMg_{1-c}O$ and $Zn_{1-x}Ni_xO$. In this work we observed, for the first time for oxides, regular peaks in the $Ni_cMg_{1-c}O$ ($c=0.008$) PLE spectra. They are considered as LO repetitions of a p–d charge transfer exciton peak. The close coincidence in energy of the peculiarities in the PLE and optical absorption spectra of these materials allows us to conclude that, for the NiO, $Ni_cMg_{1-c}O$ and $Zn_{1-x}Ni_xO$ materials, only the p–d charge transfer transitions contribute to the fundamental absorption within the energy interval of 3.5–6.5 eV.

2. Experiment

Nanoparticles of $Ni_cMg_{1-c}O$ solid solutions were prepared by evaporation of coarse grained commercially available NiO (99.9%)

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and MgO (99.9%) powder with a particles size in the range of 20–40 µm in the radio-frequency plasma. The elaborated experimental equipment consist of a radio frequency (1.76 MHz) oscillator with the maximum power of 60 kW, quartz discharge tube with the induction coil, raw powder and gas supply systems, water-cooled stainless steel reactor and heat exchangers, and cloth filter for collecting powders. The average particle size of the samples was estimated using the specific surface area (SSA), which was calculated from the nitrogen gas adsorption–desorption isotherm determined at 77 K with the use of a KELVIN 1042 sorptometer. The average particle size can be determined, under assumption that all the particles have the same spherical shape and size, with the use of the Bruntauer–Emmert–Teller equation $d=6/(S\rho)$, where d is the particle diameter, S is the specific surface area per unit mass of the sample, and ρ is the MgO specific density. The average particle diameter is near 50 nm for all compositions. The X-ray diffraction structure for the $Ni_cMg_{1-c}O$ nanopowders was presented in Ref. [7]. The deposition of very thin (several hundreds of nanometer thick) layers of the $Ni_cMg_{1-c}O$ ($c=0.008$) nanopowder by the method of precipitation of nanoparticles in water onto a transparent quartz substrate allowed one to register intense optical absorption. The samples for our measurements of PL and PLE spectra were produced by the tablet pressing of the $Ni_cMg_{1-c}O$ ($c=0.008$) nanopowder at a pressure of 0.5 GPa to provide better conditions for the luminescence registration.

In our work, the PL and PLE spectra of the $Ni_cMg_{1-c}O$ nanopowders and $Ni_xZn_{1-x}O$ oxide ceramics with the rock-salt cubic structure and a grain size of about 10–20 µm have been measured in the region of (2–5.5) eV with the use of two DMR-4 monochromators, a photoelectronic ampliphier R6358-10 (Hamamatsu) and the system of photons counting. For continuous excitation, we used the deuterium lamp DDS-400. The PLE spectra were normalized to the equal number of photons falling on the sample, using for this aim the yellow lumogene which in the given spectral range has energy-independent quantum yield of PL. The PL spectra are presented without any correction for the spectral sensitivity of the optical system. Then, the time-integrated PL and PLE spectra were measured using the synchrotron radiation (SR) with 1-ns pulses running at 96-ns intervals. The time-resolved PL and PLE spectra were measured in two time windows: fast, with a delay time $\delta t_1=0.6$ ns, span of windows $\Delta t_1=2.3$ ns; and slow: $\delta t_2=58$ ns, $\Delta t_2=14$ ns. The PL and PLE spectra were recorded in the 2–3.5 and 3.7–12 eV ranges, respectively. The measurements of the PL spectra under the vacuum ultraviolet (VUV) excitation were made on a SUPERLUMI station [HASYLAB (DESY), Hamburg] using an ARC Spectra Pro-308i monochromator and a R6358P Hamamatsu photomultiplier [6].

3. Results and discussion

The PL and PLE spectra for the $Ni_{0.008}Mg_{0.992}O$ nanocrystals are presented in Fig. 1 for the temperatures 8 K (SR excitation) and 295 K (continuous excitation). We can see that these spectra are very similar in form and the positions of maxima. The decay of PL take places with a time constant of 1.8 ns. Such a quick kinetic cannot be accounted by intracentral crystal field d^8 transitions and has to be attributed to emitting p–d charge transfer transitions. At the maximum of the PLE spectrum, there are weak peculiarities which are more distinctly pronounced in the fast-window mode. They are displayed on a more extended scale in Fig. 2. It is clearly seen that the peaks are approximately equidistant with the energy of MgO LO phonons (90 meV). Such LO repetitions in the optical spectra have not been earlier detected for the wide-gap oxides doped with 3d impurities. However, they have manifold been observed for II–VI semiconductors doped with 3d elements [8–10].

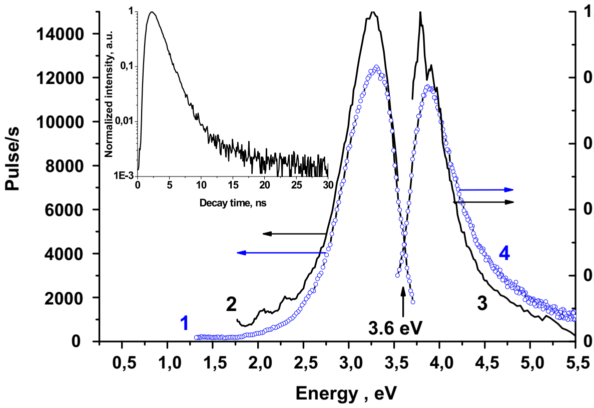

Fig.1. PL and PLE spectra of $Ni_{0.008}Mg_{0.992}O$ ($n_{Ni}\approx 4*10^{20}$ cm^{-3}) nanocrystals. (1) PL (continuous excitation), $T=295$ K, $E_{exc}=4.14$ eV; (2) PL (SR-excitation, time-integrated spectrum), $T=8$ K, $E_{exc}=3.815$ eV; (3) PLE, $T=8$ K, $E_{em}=3.3$ eV; and (4) PLE, $T=295$ K, $E_{em}=3.3$ eV. Inset – PL decay kinetics (SR-excitation) at $T=8$ K, $E_{em}=3.26$ eV, $E_{ex}=3.815$ eV.

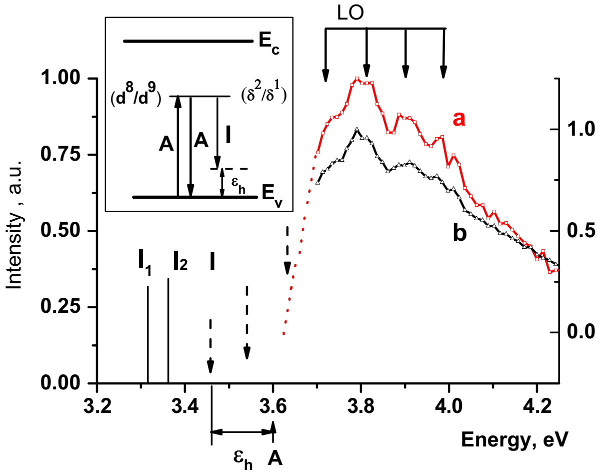

Fig.2. PLE spectra of $Ni_{0.008}Mg_{0.992}O$, $T=8$ K, $E_{em}=3.3$ eV; eV (a – fast mode; b – time-integrated mode). I – conventionally marked position of ZPL; other arrows are LO – phonon repetitions. For comparison with the ZnSe:Ni PLE spectrum see [13]. I_1 and I_2 lines in the XUV excited luminescence spectrum of the solid solution $Ni_{0.6}Zn_{0.4}O$ are shown for comparison [6]. Inset – demonstration of the Ni acceptor level on the energy-band scheme. The impurity ionization transitions (A) and transition into the hydrogen-like state I are presented. ε_h – the hole energy binding for the [d^9h] acceptor exciton [8,11–14].

The impurities of 3d-metals create in these materials deep energy levels. For example, in ZnSe:Ni, there are transitions from the valence band onto the d^8/d^9 Ni acceptor level under illumination with the proper photon energy. Such transition is shown in the inset of Fig. 2 as the A-transition (arrow up). This transition can be presented also as the transition of one of the two d-holes from the acceptor level (δ^2/δ^1) to the valence band (A arrow downward). An impurity negatively charged with respect to the lattice can bind a hole on a hydrogen-like orbit due to a long-range Coulomb field. The arisen formation [d^9h] was denoted as a charge-transfer or acceptor exciton [8] (the square brackets indicate the Coulomb coupling). The energy of system is lowered by the value ε_h, which is the binding energy of the hydrogen-like hole in the Coulomb field of the negatively charged center Ni^{1+} (d^9). The transition into this state is marked as I in the inset of Fig. 2. An extensive discussion of the acceptor and donor excitons of 3d impurities in the II–VI semiconductors was presented in Refs. [8–10]. Usually, the acceptor excitons are observed as a narrow line I at the background of the broad charge-transfer band in the absorption or PLE spectra [8,11–14] with the energy distance

ε_h which is equal, for example, to 20 meV for ZnS, 27 meV for ZnSe [11], and 400 meV for ZnO:Cu [12]. The acceptor exciton line remarkably weakens with rising the temperature from 4.2 K to 50 K [15]. An acceptor exciton should be considered to be rather an extended bound state, and its inherent property is a strong interaction with LO(Γ) lattice vibrations, That is why the absorption and PLE spectra consist of the head (zero phonon) line (ZPL) and a series of intense LO phonon repetitions [8,13]. It is natural to assume that the peculiarities in our PLE spectrum (Fig. 2) are the LO repetitions of the ZPL I. The low energy edge of the PLE band can be considered to be near approximately 3.6 eV (Fig.1) and the energy of the ZPL is smaller than that of the A-transition by the value of hole-binding energy ε_h (inset of Fig. 2). We can suggest that the discovered LO repetitions are a part of the full spectrum, because the PLE spectrum recording begins only at the energy of 3.7 eV. We do not know the real value of ε_h and, therefore, the expected positions of the ZPL I and its first two vibration repetitions are conditionally marked by dash arrows. It should be noted that if the impurity charge state changes from “0” state to “–” state due to the p–d charge transfer transitions, the appearance of local lattice anharmonic vibrations is possible. This problem was discussed in detail for the II–VI compounds doped with Ni in the paper [10]. In our case, anharmonic vibrations are difficult to somehow discuss since the lattice repetitions are not clearly resolved and separated from the background, as it was in the case of the above mentioned paper where the electroabsorption method was used. However, the problem of changes in the lattice vibrations caused by the p–d charge transfer transitions in MgO:Ni is especially interesting for further investigation in view of the effects of strong correlations. For us, it is a matter of principle that the discovery of LO repetitions marked in Fig. 2 is the evidence of the existence of the [d^9h] extended state, and that is why we can believe with certainty that the p–d charge transfer transitions take place. In Fig. 2, the positions of two lines I_1 and I_2 observed earlier in the X-ray excited luminescence spectra of NiO [6] are presented as well. It is important to note that they strongly depend on temperature and are believed to be caused by radiative annihilation of the p–d charge transfer excitons as well [16].

In the optical absorption spectrum of the single crystal $Ni_cMg_{1-c}O$ ($c=0.0006$), quite an intense peak was discovered at the energy of 6.28 eV [17]. This spectrum is presented in Fig.3 together with the more extended absorption spectrum of the NiO nanocrystalls (curve 1). It is clearly seen that the absorption peak for $Ni_xMg_{1-x}O$ ($x=0.0006$) in the region of 6.28 eV (curve 2) correlates well with that in the spectrum for NiO nanocrystals in the region of 6 eV.

In Fig. 4, the PL spectrum of the solid solution $Ni_{0.5}Zn_{0.5}O$ and the PLE spectra of solid solutions $Ni_xZn_{1-x}O$ at $x=0.5$, 0.7, and 1.0 are presented. From the PLE spectra, it is impossible to obtain the E_G value because, unlike the absorption spectra, there is no generally accepted method for the determination of E_G from the PLE spectra. Unfortunately, it is difficult to obtain a reliable value of the energy gap from the absorption spectrum (Fig.3, curve 1) for NiO because of the fact that the p–d charge transfer transitions take place simultaneously with the intraion transitions of Ni^{2+}-ions in the d^8-configuration. A more detailed discussion was presented in Ref. [18]. From the very beginning, the charge transfer transitions cannot be resolved against the background intraion transitions. A rapid increase of the NiO absorption spectrum intensity takes place in the energy range of 3.5–4.0 eV (Fig.3, curve 1). The most significant growth of the PLE spectra intensity for the solid solutions $Ni_xZn_{1-x}O$ is observed in the energy range of 3.4–3.7 eV which is comparable with that for the fast increase of absorption in the NiO spectrum and of the PLE intensity for $Ni_cMg_{1-c}O$ ($c=0.008$). There is no clearly seen tendency to shifting for the PLE spectra under observation. Therefore, we can consider the energy gap to be practically invariant for the solid solutions $Ni_xZn_{1-x}O$ ($0.5 \le x \le 1.0$). The reason for such an invariant behavior may be understood keeping in mind the recent results of EXAFS studies [19]. According to this work, the interatomic distances Ni–O are almost independent of composition of the solid solutions $Ni_xZn_{1-x}O$ ($0.2 \le x \le 1.0$) with the rock-salt crystal structure and, therefore, the electrostatic interaction for a $Ni{-}O_6$ cluster is of the same type. That is why, the energy states both for the d^8 configuration of Ni^{2+} ion and the charge transfer d^9+h should have similar values in solid solutions $Ni_xZn_{1-x}O$. Hence, the optical transitions in the solid solutions $Ni_xZn_{1-x}O$ and $Ni_cMg_{1-c}O$ have to be observed at close energies, owing to the practically identical interatomic distances Ni–O. Taking into account the large Ni^{+2}–Ni^{+2} distances in the crystals $Ni_cMg_{1-c}O$, it is impossible to assume that the d–d charge transfer transitions $d^8+d^8+\hbar\omega \rightarrow d^7+d^9$ would occur. We can reliably state that for the crystals $Ni_cMg_{1-c}O$ and $Ni_xMg_{1-x}O$, only the p–d charge transfer transitions $d^8+\hbar\omega \rightarrow h+d^9$ manifest themselves in the region of 3.5–6.5 eV.

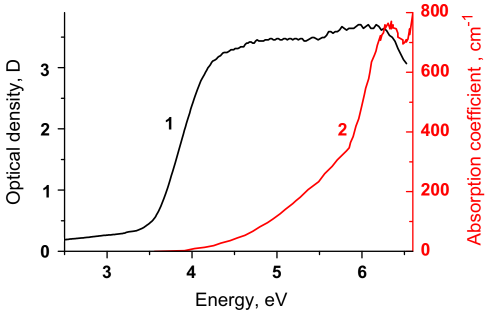

Fig. 3. (1) Extended spectrum of optical density of NiO nanocrystals, 10 nm, $T=300$ K [18]; and (2) optical absorption spectrum of $Ni_cMg_{1-c}O$ ($c=0.0006$, $n_{Ni} \approx 3{*}10^{19}$ cm^{-3}) single crystal [17].

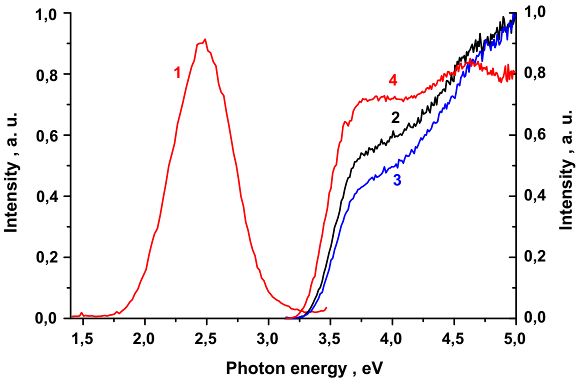

Fig. 4. (1) PL spectrum of solid solution $Ni_{0.5}Zn_{0.5}O$ (continuous excitation), $E_{exc}=4.2$ eV, $T=90$ K. PLE spectra of solid solutions $Ni_xZn_{1-x}O$: (2) $x=1$, $E_{em}=2.5$ eV; (3) $x=0.7$, $E_{em}=2.5$ eV; and (4) $x=0.5$, $E_{em}=$ 2.67 eV.

4. Conclusion

Thus, in this work, the PL and PLE spectra for the solid solutions $Ni_cMg_{1-c}O$ and $Ni_xZn_{1-x}O$ with the rock-salt crystal structure were obtained using synchrotron radiation. In the PLE spectrum of $Ni_cMg_{1-c}O$ ($c=0.008$), periodical peaks have been discovered for the first time. They were interpreted as LO phonon repetitions of the narrow ZPL due to the optical transitions into the [d^9h] exciton state with the charge transfer. Thus, we have obtained a new experimental evidence of the p–d charge transfer transitions in this material. On the one hand, it is gained owing to a small Ni concentration, which conditions the absence of d–d transitions, and, on the other hand, via an indirect observation of the p–d exciton state with the charge transfer. The close coincidence in energy of different peculiarities in the optical absorption and PLE spectra for the solid solutions $Ni_cMg_{1-c}O$ and $Ni_xZn_{1-x}O$ are due to the practically equal interatomic distances Ni–O in the investigated materials. It is a trustworthy evidence that only the p–d charge transfer transitions manifest themselves in the spectral region of 3.5–6.5 eV.

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