Low-temperature photoluminescence in $Ni_xMg_{1-x}O$ nanocrystals

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A study of the photoluminescence and photoluminescence excitation spectra of $Ni_xMg_{1-x}O$ nanocrystals, at low-temperatures. We examine the processes of concentration quenching and supposed mechanisms of energy migration in $Ni_xMg_{1-x}O$. It is shown that the edge energies of the charge-transfer transitions in $Ni_xMg_{1-x}O$ ($x = 0.008$) and NiO are practically identical. *© 2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4915911]

Introduction

Oxide compounds, doped with 3*d*-impurities, exhibit unusual properties that are relevant to the creation of modern high-tech devices and practical applications in optoelectronics, laser technology, spintronics, and photochemistry. Nickel-doped magnesium oxide has been studied for a long time.[1] The nickel impurity, as it replaces magnesium, loses two electrons to the formation of an ionic bond and exists as a Ni^{2+} ion with a d^8 configuration. In a crystal with an octahedral environment, the energy states of the Ni^{2+} ion split and are described in terms of the crystal field theory. In addition to these states, for 3*d*-impurities there exist states with a change in the number of electrons with the formation of $d^{n\pm1}$-states. Spontaneous or light-induced transitions of band electrons to these states are called charge-transfer transitions. For compounds II-VI, doped with Ni (for example, ZnO:Ni, ZnSe:Ni), the light-induced transitions to these states give broader and more intense absorption bands, as opposed to the peaks of the intracenter transitions for d^8-configurations. They ensure the transfer of excitation energy from the matrix to the impurity center.[2,3] The nickel impurity in wide band-gap compounds II-VI is amphoteric. The band-gap of this impurity has both an acceptor level, with an increase in the number of electrons in the *d*-shell d^8/d^9, and a donor level with a decrease in the number of electrons in the *d*-shell d^8/d^7.

For Ni-doped MgO, charge-transfer transitions are virtually unexplored. In Ref. 4, the absorption spectrum of $Ni_xMg_{1-x}O$ ($x = 0.0006$) at a temperature of 25 K, has a weak peak at 3.0 eV, and a broad band of more intense absorption that starts around 3.5 eV and peaks at 6.28 eV. The author of Ref. 4 interpreted this peak as being the edge of the charge-transfer band $d^8 + \hbar\omega \rightarrow h + d^9$, where $\hbar\omega$ is the photon energy; *h* is the hole in the valence band, and d^9 is the configuration of the Ni^{1+} ion. The absorption in the peak region is more than three orders of magnitude higher than the peak intracenter absorption at 3 eV. However, the cause of the light absorption in the 3.0–6.20 eV range was not discussed, which casts doubt on the correctness of how the experimental results were interpreted.[4] Therefore, it is important to experimentally identify the charge-transfer bands $d^8 + \hbar\omega \rightarrow h + d^9$ in the solid solution $Ni_xMg_{1-x}O$.

This study is an examination of the photoluminescence (PL) spectra of $Ni_xMg_{1-x}O$ solid solution nanocrystals. We found both PL and excitation (PLE) bands. We detected concentration quenching of PL in the $Ni_xMg_{1-x}O$ nanocrystals. It is shown that the rapid growth of the PLE band in $Ni_xMg_{1-x}O$ ($x = 0.008$), and the PLE spectrum of NiO nanocrystals, closely coincides in energy. This agreement reinforces our belief that the fundamental absorption edge of NiO is formed by *p-d* charge transfer transitions.

The Experiment

$Ni_xMg_{1-x}O$ solid solution nanoparticles were obtained by decomposing coarse-grained (particle sizes ranging from 20 to 40 μm) powders NiO (99.9%) and MgO (99.9%) in high-frequency plasma. The average particle size was determined according to the Brunauer- Emmett-Teller formula $D = 6/S_{sp}\rho$), where S_{sp} is the specific surface area, and ρ is the density of the material. The specific surface area is calculated from the adsorption-desorption isotherm of nitrogen gas at 77 K. The solid solution $Ni_xMg_{1-x}O$ nanoparticles were measured using a KELVIN 1042 sorptometer. The obtained average grain size *D* was about 50 nm for all compositions of $Ni_xMg_{1-x}O$.

PL spectra in the 1.5–3.5 eV energy range, the PLE spectra in the 3.7–13.0 energy range, and the PL decay kinetics, were measured at a temperature of 8 K using pulsed synchrotron radiation (SR) at the SUPERLUMI station (HASYLAB, German Electron Synchrotron DESY, Hamburg). A monochromator with an aluminum-coated

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grating and a spectral resolution of 3.2Å was used for PL excitation. The PL and PLE spectra were measured using a 0.3-m monochromator, model ARC Spectra Pro-308i, and a R6358P Hamamatsu photomultiplier. The PLE spectra were normalized to an equal number of photons incident on the sample, using sodium salicylate. The duration of the SR pulse was 1 ns. The time interval between SR pulses was 96 ns and the time resolution of the detection system was 0.8 ns.

Results and Discussion

The obtained PL $Ni_xMg_{1-x}O$ spectra (Fig. 1) are represented by a relatively broad band with an intense maximum at 3.28 eV, as well as considerably less intense peaks at 2.05 and 2.3 eV. All observable bands in the PL spectrum have considerable width, explained by deep center luminescence. Such centers are characterized by strong electron-phonon interaction. In addition, the nanopowders have dispersion by particle size, which could make additional contributions to the line width.

PL spectra for $Ni_xMg_{1-x}O$ nanopowders at an excitation greater than 3 eV, are unknown. The PL and PLE spectra for $Ni_xMg_{1-x}O$ nanopowder will be compared to PL and PLE spectra of NiO.[5–7] NiO and MgO have the same lattice symmetry as NaCl and very close lattice constants (4.18 Å for NiO and 4.21 Å for MgO). The cluster composed of one Ni^{2+} ion and six O^{2-} ions, turns out to be the same in both cases. Therefore, we can expect that the energies of both the intraionic and charge-transfer transitions from O^{2-} to Ni^{2+} ions will be close. Previously, a broad PL band was observed for NiO, in the 2–3.5 eV region.[5–7] Luminescence in the visible and near-infrared regions in NiO is interpreted either as an expression of intraionic transitions in Ni^{2+}, or *p-d* transitions. In particular, the green band with a maximum at 2.3 eV observed in NiO, is attributed to $^1T_{2g}\,(D) \rightarrow {}^3A_{2g}\,(F)$ transition with a Stokes shift. In Ref. 7, at $E_{\text{exc}} = 3.81$ eV, an intense violet luminescence with a maximum at 3 eV was observed for NiO. This band was attributed to *p-d* charge transfer transitions. Comparing the known PL spectra for NiO with the measured PL spectra of $Ni_xMg_{1-x}O$, we expect to observe two mechanisms of excitation and relaxation of the electron system in $Ni_xMg_{1-x}O$: the usual band *p-d* transition and intracenter *d-d* transition through the energy levels of the 3*d*-shell of Ni^{2+}. As expected, the bands at 2.05 and 2.3 eV reveal intraionic luminescence, whereas the peak with a maximum at 3.28 eV is a radiative *p-d* charge transfer transition.

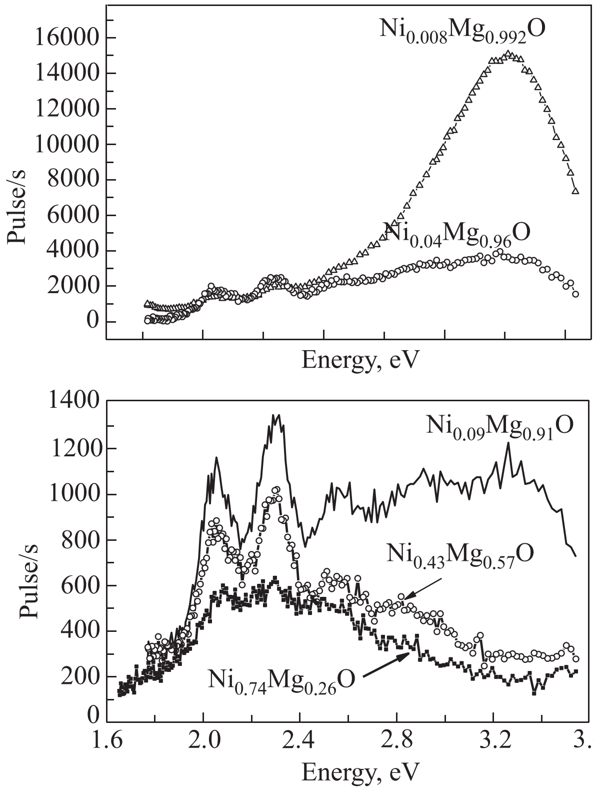

FIG. 1. PL spectra of $Ni_xMg_{1-x}O$ nanocrystals. Excitation energy 3.815 eV, $T = 8\,K$.

We can see that the intensity of the intraionic *d-d* luminescence increases with the concentration of Ni^{2+} ions, whereas the *p-d* charge-transfer luminescence decreases, practically disappearing at a Ni^{2+} concentration of 74%. The decrease in the intensity of *p-d* luminescence with increasing concentration is related to the group of effects known as concentration quenching. As the luminescence centers increase, the electron system excitations start to migrate over the ensemble of the de-excitation centers. The resonance energy transfer from one emission center to another will occur until this energy is intercepted by the quenching center. In the test nanopowders, the quenching centers can be caused by both intrinsic defects and those introduced by Ni impurities. Nickel impurity quenching of the *p-d* excitation occurs as a result of the defect Auger process,[3] wherein the energy released by the destruction of the electron-hole pairs excites the d^8-configuration of the Ni^{2+} ion. We then have a radiative transition to the ground state of the d^8-configuration, which is expressed as an increase in the intracenter luminescence at 2.05 and 2.3 eV.

Fig. 2 shows two possible channels of radiative transition through donor or acceptor levels. The mechanism behind these transitions is as follows. During interband excitation (process 1 in Fig. 2) there is an appearance of free electrons in the conduction band, and a hole in the valence band. The formation of a free carrier due to impurity absorption (process 2) is also possible. After the capture of a hole

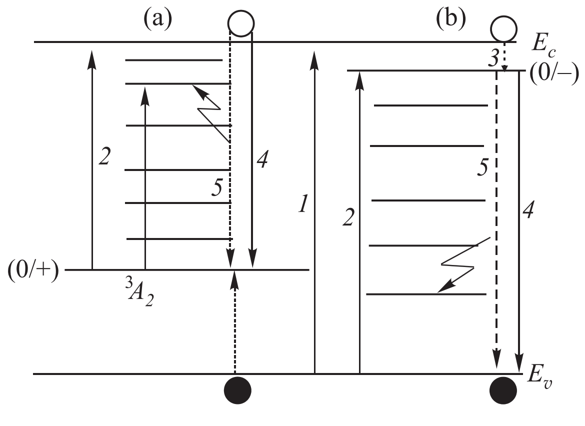

FIG. 2. Radiative recombination options, through the donor (a) and acceptor (b) levels of the Ni^{2+} ions (d^8 configuration). Symbols: (●)—holes; (○)—electrons. *1*—interband excitation; *2*—impurity absorption; *3*—capture of band carrier at the impurity level; *4*—radiative recombination; *5*—nonradiative recombination or Auger process. The zig-zag arrow indicates the transition of the Ni^{2+} ion to one of the excited intracenter states.

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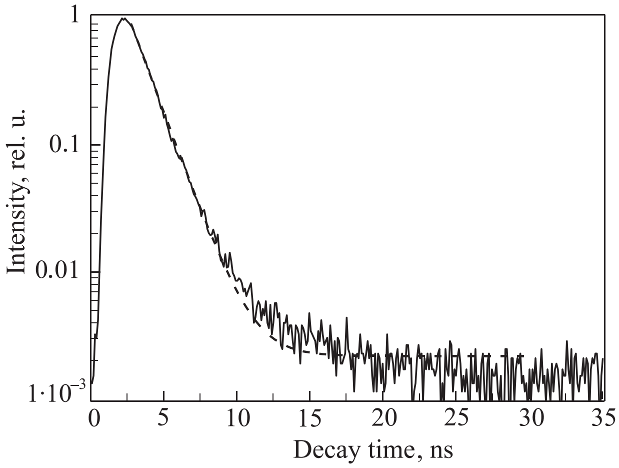

FIG. 3. The luminescence decay kinetics of $\mathrm{Ni_{0.008}Mg_{0.992}O}$ nanocrystals. The excitation energy is 3.815 eV, the emission energy is 3.26 eV, $T = 8$ K. The solid curve represents the experimental spectrum, and the dotted line shows the approximation.

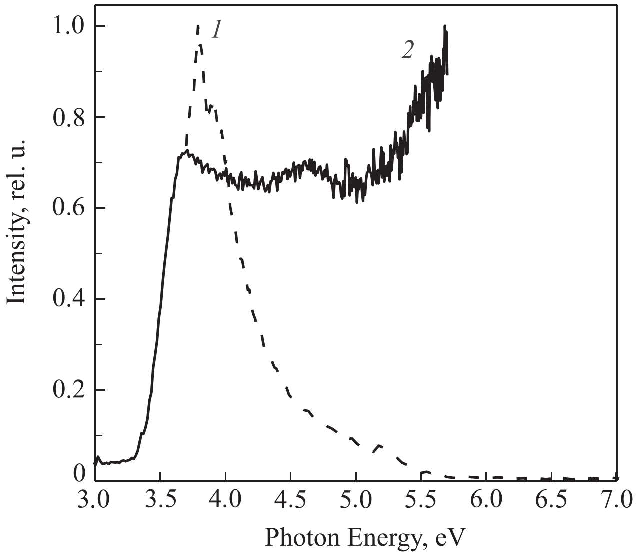

FIG. 4. PLE spectrum of the solid solution $\mathrm{Ni_{0.008}Mg_{0.992}O}$, emission energy $E_{\mathrm{emis}} = 3.28$ eV, $T = 8$ K (1) and NiO PLE spectrum, $E_{\mathrm{emis}} = 2.71$ eV, $T = 90$ K.[7]

at the donor level, or of an electron at the acceptor level (process 3) the system can return to the ground state as a result of electron-hole recombination. There are two options for this recombination. It could be a radiative recombination with photon emission (process 4), or the Auger process, which is a non-radiative transition of the carrier wherein the excitation energy is transferred to the *d*-shell, as a result of which the 3*d*-impurity ion becomes excited. In Fig. 2, this is shown with a zig-zag arrow.

Fig. 3 shows the luminescence decay kinetics in the 3.28 eV band. The resulting curve is well approximated by an exponential decay law with $\tau = 1.39$ ns. The short decay time indicates that the migration of excitation energy toward the luminescence center and further de-excitation is rapid, which points to a radiative charge transfer transition, since intracenter transitions are characterized by longer radiative transition times.

In Fig. 4, the excitation band with a maximum at 3.9 eV is shown together with the edge PLE of the NiO nanocrystal, caused by the charge transfer transitions $d^8 + \hbar\omega \rightarrow h + d^9$.[5–7] The highest growth of the absorption spectrum of the NiO nanocrystals[8] also coincides with the long wavelength edge of the excitation spectrum of the $\mathrm{Ni}_x\mathrm{Mg}_{1-x}\mathrm{O}$ nanopowder ($x = 0.008$). The proximity of curves 1 and 2 in Fig. 4 suggests that the edge of the PLE band in the solid solution $\mathrm{Ni}_x\mathrm{Mg}_{1-x}\mathrm{O}$ ($x = 0.008$) is caused by $d^8 + \hbar\omega \rightarrow h + d^9$ charge transfer transitions. Earlier it was noted that in solid solutions $\mathrm{Ni}_x\mathrm{Mg}_{1-x}\mathrm{O}$,changes in the energies of intracenter transitions and 10*Dq* values do not exceed 1%, and neither do changes in the lattice parameter.[4] Now we can state that the energy of the electron transition from the *p*-shell of the oxygen to the *d*-shell of nickel, which determines the charge-transfer band edge for both compounds, is about the same. Only *p*-*d* charge transfer transitions $d^8 + \hbar\omega \rightarrow h + d^9$ manifest in $\mathrm{Ni}_x\mathrm{Mg}_{1-x}\mathrm{O}$ crystals with a small concentration, and there are no interimpurity *d*-*d* transitions $d^8 + d^8\ \hbar\omega \rightarrow d^7 + d^9$. The coincidence of the PLE band edge for $\mathrm{Ni}_x\mathrm{Mg}_{1-x}\mathrm{O}$ and NiO serves as reliable evidence of the fact that interimpurity *d*-*d* transitions do not contribute to the initial part of the fundamental absorption of NiO.

Thus, this is a study of the PL and PLE spectra of $\mathrm{Ni}_x\mathrm{Mg}_{1-x}\mathrm{O}$ nanocrystals. We have found PL concentration quenching, and examined the proposed mechanisms of energy migration in $\mathrm{Ni}_x\mathrm{Mg}_{1-x}\mathrm{O}$. It is shown that the edge energies of *p*-*d* charge transfer transitions in $\mathrm{Ni}_x\mathrm{Mg}_{1-x}\mathrm{O}$ ($x = 0.008$) and NiO are practically identical. This means that the conceptual approach suggesting the proximity of the transition energies for $\mathrm{Ni}_x\mathrm{Mg}_{1-x}\mathrm{O}$ solid solutions "works," and can be used for further studies of this system.

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