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Origin of visible photoluminescence in NiO and $Ni_cMg_{1-c}O$ single-crystals

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ABSTRACT

A study of the visible photoluminescence in single-crystal NiO and $Ni_cMg_{1-c}O$ (c=0.99, 0.98 and 0.95) solid solutions is presented for the first time. Two wide luminescence bands, peaked at ~12000 cm^{-1} and ~18500 cm^{-1}, were observed. The dependence of their intensity and position on the excitation energy, temperature, and composition were investigated. We attribute the origin of two photoluminescence bands to the impurity- or defect-perturbed Ni^{2+} excitons.

Keywords: NiO, $Ni_cMg_{1-c}O$, photoluminescence

1. INTRODUCTION

Nickel oxide (NiO) is a wide-gap ($E_g \approx 4$ eV) charge-transfer insulator, whose electronic structure attracted continuous attention during years [1]. In the paramagnetic phase, it has a rocksalt-type crystal structure, whereas below the Néel temperature T_N = 523K [2], NiO undergoes a paramagnetic-to-antiferromagnetic transition, accompanied by a week cubic-to-rhombohedral distortion [3]. It is well known that a substitution of nickel ions by magnesium ions, having close size, results in a continuous set of $Ni_cMg_{1-c}O$ solid solutions [4,5], whose physical properties depend strongly on magnesium content.

In the past, a diluted case (c<0.1) attracted most interest in an attempt to create phonon-terminated infrared maser [6]. MgO doped with small amount of Ni^{2+} ions has three luminescence bands [7-14] - green, red and near infrared, which are due to electron transitions between 3d energy levels of Ni^{2+} ions in MgO. In particular, the green luminescence band (19200-21700 cm^{-1}) is attributed to ${}^1T_{2g}(D) \rightarrow {}^3A_{2g}(F)$ transition, the near infrared band (7000-8200 cm^{-1}) is due to ${}^3T_{2g}(F) \rightarrow {}^3A_{2g}(F)$ transition, whereas the red band (11500-14500 cm^{-1}) was attributed in [9] to ${}^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$, but in [10] to ${}^1T_{2g}(D) \rightarrow {}^3T_{2g}(F)$ transition. Note that an increase of the nickel content above 1% leads to an appearance of additional lines in the luminescence spectra [13,14]. These extra lines arise from isolated exchange-coupled Ni^{2+} pairs whose maximum number appears at c=0.05 [13].

After discovering in 1988 of the giant magnetoresistance (GMR) effect [15], an active research continues in the direction toward improving our understanding of the exchange processes that lead to a unidirectional magnetic bias in coupled antiferromagnetic/ferromagnetic bilayers. This topic has great importance for fundamental reasons and due to the use of such layered system as a sensor component in giant magnetoresistive (GMR) devices such as spin valves [16,17]. Nickel oxide based bilayers, as for example NiFe/NiO [16], are among promising candidates, because NiO is well resistant to corrosion and has high value of exchange constant. Since addition of magnesium ions is able to modify in a controlled way the magnetic properties of nickel oxide [4,5], the investigations of $Ni_cMg_{1-c}O$ solid solutions in a limit of high nickel content are desirable.

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Photoluminescence studies of MnO and MnS compounds [18-22], having similar to NiO structure and magnetic properties, showed that the spectra consist of two emission bands at ~10080 cm^{-1} and ~13790 cm^{-1} in MnO and at ~11610 cm^{-1} and ~13225 cm^{-1} in MnS. Only the high-energy band is observed at low temperatures, however its intensity decreases with increasing temperature and disappears completely at the Néel temperature. The low-energy band grows up at the expense of the high-energy band, however its intensity also experience a drop at the Néel temperature and decreases above T_N. This suggest that both emission bands are closely related to the magnetic ordering of Mn^{2+} spins [18-22]. The model proposed in [18-22] to explain the origin of the two bands suggests the radiative decay of self-trapped excitons at unperturbed and/or perturbed by impurities Mn^{2+} sites with simultaneous creation or destruction of spin-wave or other types excitations to conserve the energy and momentum.

The only work on NiO [23] is related to temperature dependent studies of cathodoluminescence (CL). The broad luminescence bands in the visible and near infrared spectral ranges were observed at temperatures well below T_N [23]. They were tentatively attributed, based on the results for MnO and MnS [18-22], to intra-ionic transitions, influenced by magnetic ordering effects.

In this work, we present for the first time temperature dependent (from 10 K to 300 K) studies of visible photoluminescence in NiO and $Ni_cMg_{1-c}O$ (c=0.99, 0.98 and 0.95) solid solutions. The dependence of luminescence intensity and bands position on the temperature, laser excitation energy and chemical composition will be considered.

2. EXPERIMENTAL AND DATA ANALYSIS

Single-crystal NiO and $Ni_cMg_{1-c}O$ (c=0.99, 0.98 and 0.95) solid solutions were grown epitaxially on freshly cutted and polished single-crystal MgO(100) substrates by chemical transport reactions method using HCl gas [24]. Polycrystalline pure NiO or $Ni_cMg_{1-c}O$ solid solutions of the same concentration were used as sources of the material. They were prepared using ceramic technology from the appropriate amounts of aqueous solutions of $Mg(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ salts which were mixed and slowly evaporated. The remaining dry 'flakes' were heated up to 500-600°C to remove NO_2 completely. The obtained polycrystalline solid solutions were pressed, and annealed during 100h at 1200°C temperature in air and then quickly cooled down to room temperature. Thus obtained NiO and $Ni_cMg_{1-c}O$ single-crystals had green colour and the size of about 6×6 mm^2. Their chemical composition was controlled by instrumental neutron-activated analysis [25], and it was confirmed that the content of nickel in the samples was in agreement with the stoichiometric one within ±0.01%.

The photoluminescence spectra were excited by an Ar (514 and 458 nm, 50 mW) and He-Ne (633 nm, 10 mW) ion lasers and analysed through a double-grating monochromator (SPEX spectrometer, model 1401). The optical luminescence was detected with a Hamamatsu R943-02 photomultiplier, connected to a photon-counting system. The measured energy range extended from 10500 cm^{-1} to the laser line energy, with the energy resolution 10 cm^{-1}. The detection system had a nearly constant response above 11700 cm^{-1}, whereas its sensitivity decreased gradually below this energy, thus affecting the low-energy side of the red luminescence band at 12500 cm^{-1}. The specimens for the temperature-dependent measurements in the interval of temperatures from 10 K to 300 K were mounted on the cold finger of a closed-cycle helium cryostat. The temperature was stabilised within ±2 K.

3. RESULTS AND DISCUSSION

The photoluminescence of NiO and $Ni_cMg_{1-c}O$ (c=0.99, 0.98, 0.95) single-crystals in the range 11000-22000 cm^{-1} consists of two broad bands. The red band is centred at 12000 cm^{-1} and the green band at 18500 cm^{-1}. The intensity of both bands decreases with increasing temperature but is still detectable at room temperature.

In Fig. 1 we show temperature variation of the luminescence, excited by green Ar laser line 514 nm, in NiO and $Ni_{0.99}Mg_{0.01}O$. Note a difference in the ratio of amplitudes for two bands at low temperatures: the green band dominates strongly the red one in NiO but their ratio is comparable in $Ni_{0.99}Mg_{0.01}O$. Besides the green band position does not change with temperature, whereas the red band shows progressive shift with increasing temperature to lower energies.

The variation of the integral luminescence intensity over energy range 11000-19000 cm^{-1} for two samples is present in Fig. 2. Though the absolute numbers depend on experimental conditions, we would like to note a character of the temperature dependence: the integral luminescence intensity decreases monotonically in NiO but has some constant region below ~150 K in $Ni_{0.99}Mg_{0.01}O$. The dependence of the luminescence in NiO and $Ni_cMg_{1-c}O$ solid solutions on the excitation wavelength is shown in Fig. 3. The main observed effect is related to the ratio of intensities for the red band versus the green band. Unfortunately, the presence of Cr^{3+} ions in the MgO single-crystal substrate of $Ni_{0.99}Mg_{0.01}O$ and $Ni_{0.98}Mg_{0.02}O$ samples does not allow to perform precise analysis, since the luminescence of chromium ions is very strong and peaks at the high energy side of the red band at about 14500 cm^{-1}. As a result, it strongly increases the background under the red band. However, taking into account the disturbing contribution of Cr^{3+} ions, one can conclude that substitution of nickel by magnesium ions leads to an increase of the red band intensity relative to the green one. Besides this ratio depends also on the excitation wavelength (see two upper panels in Fig. 3).

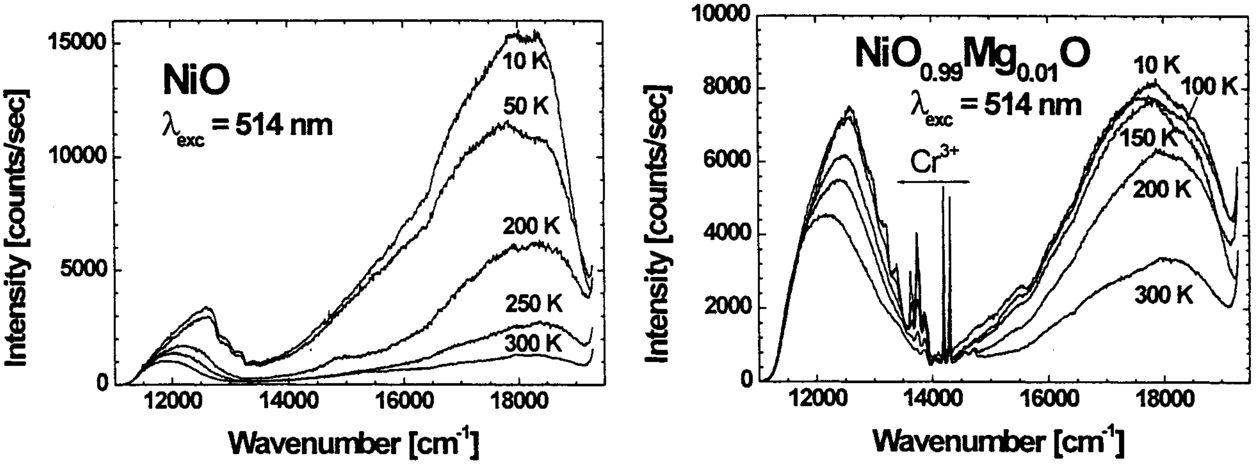

Figure 1: Temperature dependence of the photoluminescence spectra for NiO and $Ni_{0.99}Mg_{0.01}O$ solid solution. The excitation laser wavelength was 514 nm. Note a set of Cr^{3+} lines in $Ni_{0.99}Mg_{0.01}O$ spectrum: they come out from the MgO single-crystal substrate.

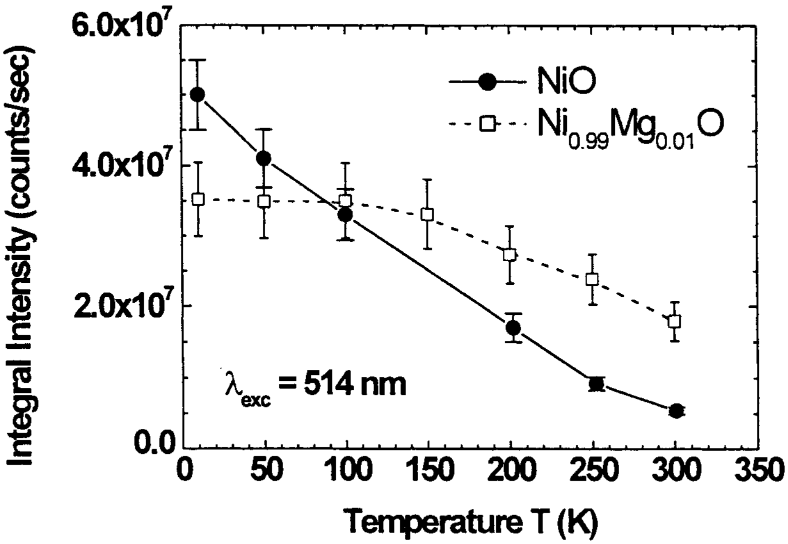

Figure 2: Temperature dependence of the integral luminescence intensity for NiO and $Ni_{0.99}Mg_{0.01}O$ solid solution. The excitation laser wavelength was 514 nm.

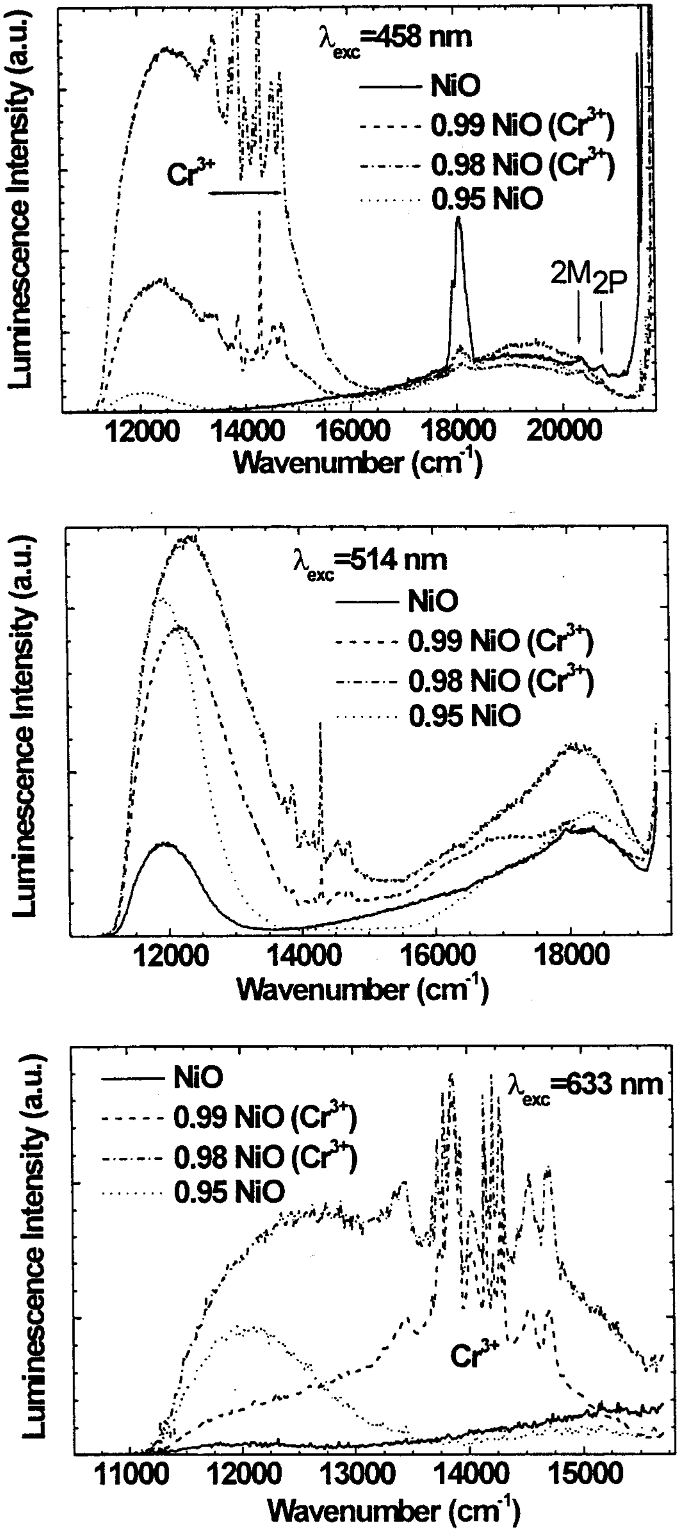

Figure 3: Photoluminescence spectra in NiO and $Ni_cMg_{1-c}O$ solid solutions, excited by different laser wavelengths λ_{exc}= 458, 514 and 633 nm. Note a set of Cr^{3+} lines in $Ni_{0.99}Mg_{0.01}O$ and $Ni_{0.98}Mg_{0.02}O$ compounds: they come out from the MgO single-crystal substrate.

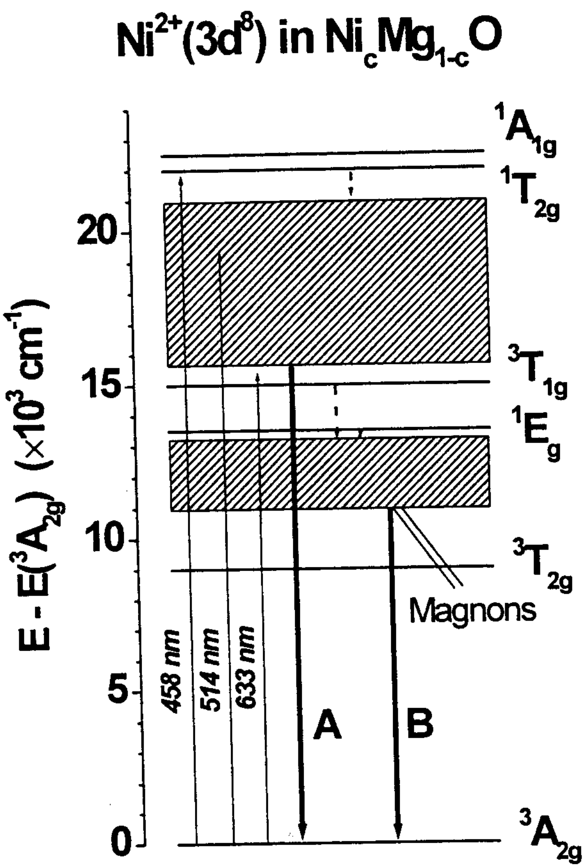

Figure 4: Electron energy scheme for the photoluminescence in NiO and $Ni_cMg_{1-c}O$ single-crystals. The two experimentally observed bands are shown by hatched rectangles. Upward solid arrows indicate excitations by three different laser lines (458, 514 and 613 nm), downward solid arrows show the radiative transitions A and B, downward dashed arrows show non-radiative transitions, and parallel lines indicate interactions.

To understand the observed luminescence bands and their sensitivity to the composition, temperature and excitation wavelength, we will use the energy levels (Tanabe-Sugano) diagram for Ni^{2+} ($3d^8$) ion in NiO (Fig. 4), calculated in [26] and being in agreement with optical absorption spectrum of NiO. The three laser excitations peak in the interval $^3T_{1g}(F)$ -$^1T_{2g}(D)$ between 15000 and 22000 cm^{-1}. Therefore, if the luminescence bands originate from electron transitions between 3d energy levels of unperturbed Ni^{2+} ions as in [7-14], the excitation by 514 and 633 nm lines should result in similar spectra, due to $^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$ transition [9] and, thus, the green band at 18500 cm^{-1} must not be present in the spectrum for 514 nm excitation. On the opposite, experimental results (Fig. 3) indicate that the spectrum for 514 nm excitation is rather similar to that, excited by 458 nm laser line. Therefore, one should thing of some defect levels, located in the gap between $^3T_{1g}(F)$ and $^1T_{2g}(D)$ levels. Similarly, the position of the red band is attributed to the defect levels, located in the gap between $^3T_{2g}(F)$ and $^1E_g(D)$ levels. These defects are associated with Ni^{2+} ions, located close to Ni^{3+} ions or vacancies/impurities in pure NiO and additionally close to Mg^{2+} ions in $Ni_cMg_{1-c}O$ solid solutions. The observed luminescence bands experience inhomogeneous and homogeneous broadening [27] due to compositional disorder, exciton-phonon and exciton-magnon (all samples are in antiferromagnetic phase at all reported temperatures [4,5]) interactions.

The role of inhomogeneous broadening is well evidenced in comparison of temperature dependent spectra of NiO and $Ni_{0.99}Mg_{0.01}O$ (Fig. 1 and 2): the integral intensity for NiO, affected mainly by homogeneous broadening, decreases monotonically with temperature rise, whereas in $Ni_{0.99}Mg_{0.01}O$ the luminescence output remains nearly constant in the range below 150 K, where inhomogeneous broadening due to the presence of magnesium ions is supposed to dominate the exciton-phonon interaction. Note also a shift of the maxima of the red band to lower energies for increasing temperature (Fig. 1). It can be associated with a change of the exciton–two-magnon interaction, similar to that observed in $KNiF_3$ [28] and $Ni_cMg_{1-c}O$ in optical absorption [29].

One can see also in Fig. 3 that the red band is affected by the presence of magnesium ions stronger than the green band. To explain this fact, one should take into account a symmetry of wave functions in the excited state and a change of the local structure around Ni^{2+} ions upon substitution. Our previous structural studies by x-ray absorption spectroscopy [30,31] and x-ray diffraction [32] suggest that nickel ions displace out of centre in $Ni_cMg_{1-c}O$, and a value of the displacement is larger at higher magnesium content. Such shift should affect σ-type bonding via $3d(e_g)$ orbitals stronger than π-type bonding via $3d(t_{2g})$ orbitals. As a result, the $^1E_g(D)$ excited state will be more localised that the $^3T_{2g}(F)$ state and thus its transition matrix element will have higher value, resulting in stronger relative luminescence intensity.

4. CONCLUSIONS

The photoluminescence spectra of NiO and $Ni_cMg_{1-c}O$ (c=0.99, 0.98 and 0.95) solid solutions, excited by the Ar laser (458 and 514 nm), consist of two broad bands, centred at 12500 cm^{-1} and 18500 cm^{-1}, whereas only the first band at 12500 cm^{-1} can be observed under the excitation by the He-Ne laser (633 nm). The intensity of the two bands decreases with increasing temperature. Besides, the intensities ratio for the two bands depends strongly on the sample composition and the excitation laser wavelength. We attribute the two bands to the impurity- or defect-perturbed Ni^{2+} states, similar to that observed in MnO and MnS [18-22]. The band at 12500 cm^{-1} is related to the $^1E_g(D) \rightarrow {}^3A_{2g}(F)$ transition, whereas the band at 18500 cm^{-1} to the $^1T_{2g}(D) \rightarrow {}^3A_{2g}(F)$ transition. The observed luminescence bands experience inhomogeneous and homogeneous broadening [27] due to compositional disorder, exciton-phonon and exciton-magnon. The intensity of the bands is also determined by an off-centre displacement of nickel ions due to substitution by magnesium.

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