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ELECTRON-PHONON COUPLING IN Ni^{2+}-DOPED $MgGa_2O_4$ SPINEL*

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Abstract. Ni^{2+}-doped $MgGa_2O_4$ crystals, with spinel structure, have been reported as promising candidates as active media for broadband optical amplifiers and tunable laser systems in the visible and near infrared regions. In this paper we present and discuss the interaction between electronic transitions of divalent nickel ions and vibration modes of the host lattice $MgGa_2O_4$ (electron-phonon interaction), which is responsible for the wide absorption and emission broad-bands. The Huang-Rhys parameter S=3.18, the breathing phonon-energy $\hbar\omega$=387 and the Zero Phonon Line (ZPL) position at 8 850 cm^{-1} (all estimated in the framework of the single configurational coordinate model and harmonic approximation) are reported. To check the reliability of the obtained values for S and $\hbar\omega$ the emission band modeling has been performed. Good agreement between theoretical and experimental emission spectra and the closeness between theoretical and experimental values of the ZPL energy confirms validity of the estimated parameters of electron-phonon interaction for $MgGa_2O_4$: Ni^{2+}system.

Key words: $MgGa_2O_4$ spinel, Ni^{2+}-ions, electron-phonon coupling.

1. INTRODUCTION

It is well known that transitional ions, corresponding to the iron group, can be used as optically active ions [1, 2], because electronic transitions between energetic states from their external unfilled 3d shell give rise to intensive luminescence. Optical transitions manifest themselves either as sharp or broad emission bands depending on the strength of crystal field produced by impurity ion's environment; other factors as the symmetry properties of the electronic states involved into these transitions, as well as dynamic of the environment surrounding the active ions in the crystal are also very important.

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The Ni^{2+}-doped $MgGa_2O_4$ crystals, with spinel structure, have been reported as promising candidates as active media for broadband optical amplifiers and tunable near-infrared laser systems in the visible and near infrared regions, with a long room temperature lifetime and a high quantum efficiency compared to other Ni-doped material [3–8]. This is because the initial and final states of the Ni^{2+} electronic transitions are strongly coupled in this host to the crystal lattice phonon modes and, thus, the associated emission bandwidth becomes much broader in comparison with other 3d ions. From the experimental point of view the optical spectra of Ni^{2+} ions in four $MgGa_2O_4$ systems, namely i) $MgGa_2O_4$ bulk single crystal [7], ii) powder nano-single crystal [4], iii) ceramics [6, 8] and iv) glass-ceramic [5], have been investigated. In a previous paper [9], we modeled the parameters of the crystal field of $MgGa_2O_4$ bulk single crystal acting on the Ni^{2+} and simulated the energy level scheme for the $MgGa_2O_4$: Ni^{2+}system.

In this work we extend previous studies and discuss the interaction between the Ni^{2+} electronic transitions and vibrational modes of the host lattice $MgGa_2O_4$ (electron-phonon interaction), which is responsible for the wide absorption and emission broad-bands.

2. SAMPLE AND METHOD

$MgGa_2O_4$ is a crystal with the spinel structure which crystallizes (Fig.1) in the cubic space group Fd3m (O_h^7), with lattice constant 8.2721Å, and 56 atoms per unit cell (Z=8)[10].

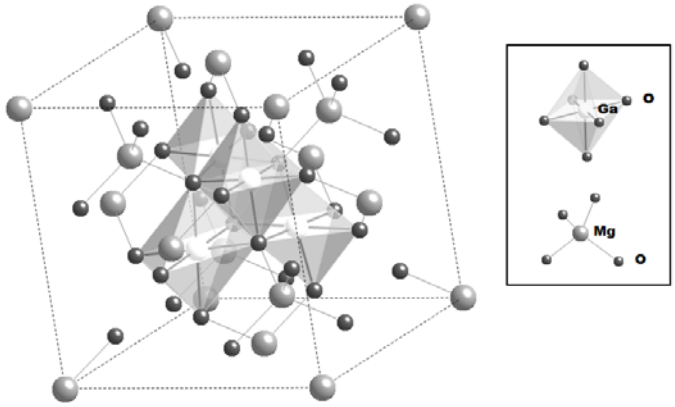

Fig. 1 – Crystal structure of $MgGa_2O_4$.

Ga^{3+} ions have octahedral coordination with O^{2-} ligands and Mg^{2+} ions are inside the tetrahedra made up out of oxygen ions. After doping, Ni^{2+} ions substitute for Ga^{3+} ions, entering octahedral positions. Since electrical charges of both

substituted and substituting ions are not equal, the charge compensating as Mg^+ ion vacancies are needed. The ionic radius of Ni^{2+} (0.69 Å) is different from that of Ga^{3+} (0.62Å) [11], so the actual site symmetry of the Ni^{2+} positions is lower than the O_h symmetry.

For the investigation of the electron-phonon interaction in $MgGa_2O_4:Ni^{2+}$ system, we have used the single coordinate configurationally model [12], which assumes that the distance Q from the active ion to its nearest neighbors (ligands) oscillates harmonically about its equilibrium value Q_0. As a further approximation, the same breathing frequency is considered to model effectively interaction with crystal lattice; it is supposed to not vary from one electronic state of an impurity to another. The equilibrium values for Q are specific for each electronic potential and the difference between the minima of the ground state potential energy surface and that one for an excited state is proportional to the number of coupling phonons in the electronic transitions.

The main parameters which provide quantitative characterizations of the electron-phonon interaction are the Stokes shift ΔE_S (the difference in energy between the lowest in energy absorption and emission peaks), the Huang-Rhys factor S (which is proportional to ΔE_S) and effective phonon energy $\hbar\omega$. All these parameters arise from the shift of the equilibrium positions in the ground and excited states. The values of S and $\hbar\omega$ can be estimated using the following equations [12]:

$$\Delta E_S = (2S-1)\hbar\omega, \tag{1.1}$$

$$\Gamma(T) = \sqrt{8\ln 2}\hbar\omega\left[S\coth\left(\frac{\hbar\omega}{2kT}\right)\right]^{1/2}, \tag{1.2}$$

where $\Gamma(T)$ is the full width at half maximum (FWHM) of the emission band at temperature T and k is Boltzmann constant. These two equations provide a reliable tool for estimations of the electron-phonon interaction parameters, after the Stokes shift and FWHM are extracted from the experimental spectra.

To check out whether the obtained in this way values of S and $\hbar\omega$ are reasonable, the emission band shape can be modeled and compared with experimental spectrum. The intensity of the emission band at energy E can be approximated by the following expression [13]

$$I = \frac{e^{-S}S^p}{p!}\left(1+S^2\frac{e^{-\hbar\omega/kT}}{p+1}\right),\ p=\frac{E_0-E}{\hbar\omega}, \tag{1.3}$$

Here E_0 is the zero-phonon line (ZPL) energy (not estimated yet and thus allowed to vary freely), and p is the number of the effective phonons involved into the emission transition. All other quantities entering Eq. (1.3) have been described above.

3. RESULTS OF CALCULATIONS

The application of above equations allows for estimation of the electron-phonon interaction parameters. Solving the system of equations (1.1)–(1.2), with experimental values of ΔE_S =1 870 cm^{-1} and $\Gamma(T)$ =2 024 cm^{-1} [5], we obtained the values of the Huang-Rhys parameter S = 3.18 and effective phonon energy $\hbar\omega$ = 387 cm^{-1}.

With the zero-phonon line energy of 8 650 cm^{-1} the calculated emission band is shown by the dashed line in Fig. 2. The FWHM, position of the maximum and overall appearance of the calculated emission band reasonably agree with the experimental emission band. The value of ZPL energy used for the emission band modeling is very close to the value of 8 340 cm^{-1} which can be estimated from the position of the point of intersection of the emission and excitation spectra [5].

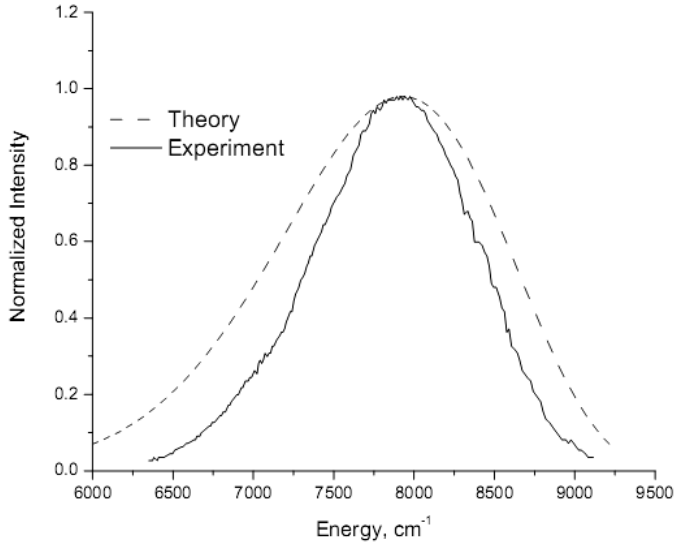

Fig. 1 – Comparison between the calculated (dashed line) and experimental (solid line) emission spectra for $MgGa_2O_4$: Ni^{2+}system.

4. CONCLUSIONS

The electron-phonon coupling for $MgGa_2O_4$: Ni^{2+}system has been investigated, using the single coordinate configurational model, by calculating the Huang-Rhys parameter S = 3.18 and effective phonon energy, $\hbar\omega$ = 387 cm^{-1}, using as an experimental support the data from Ref. [5]. The check of reliability of the obtained values for S and $\hbar\omega$ is the emission band modeling. The ZPL energy

(8 850 cm^{-1}) obtained during this modeling is very close to the value 8 340 cm^{-1}, which has been estimated from the position of the point of intersection of the emission and absorption spectra [5]. Good agreement between theoretical and experimental emission spectra and the closeness between theoretical and experimental values of the ZPL energy confirm validity of the estimated parameters of electron-phonon interaction for $MgGa_2O_4$: Ni^{2+}system.

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