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L. I. Ivleva, A. A. Kaminskii, Yu. S. Kuz' minov, V. N. Shpakov

ABSORPTION, LUMINESCENCE, AND INDUCED EMISSION OF $LiNbO_3$—Nd^{3+} CRYSTALS

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In recent years the $LiNbO_3$ crystal, which has found broad practical application (generation of optical harmonics, modulation and deflection of optical quantum-generator radiation, mixing of light waves, parametric amplification and generation) (^{1}), has begun to attract the attention of researchers also as a matrix for activation by rare-earth ions (TR^{3+}) and elements of the iron group, for the purpose of using it in optical quantum generators. The first report on obtaining induced emission of an optical quantum generator based on $LiNbO_3$—Nd^{3+} crystals was made by the authors of work (^{4}). Possessing the capacity to emit induced radiation when activated by TR^{3+}, and at the same time having high optical nonlinearity, good piezoelectric properties, and linear electro-optic coefficients, this crystal should find still wider application in experiments on nonlinear optics and quantum electronics. Unfortunately, the spectroscopic properties of the $LiNbO_3$ crystal with TR^{3+} ions, so necessary for determining its lasing capabilities, have not been studied at all. This circumstance makes all steps aimed at studying its spectroscopic characteristics highly timely.

In the present work we report some results of a study of the absorption, luminescence, and induced emission (i.e.) spectra of $LiNbO_3$—Nd^{3+} crystals. At 300° K we registered a new induced transition with $\lambda_r = 10932$ Å and a low excitation threshold E_p, and also constructed a scheme of the crystal-field splitting of the terms of Nd^{3+} ions directly associated with stimulated emission.

The methods and experimental technique for studying the spectroscopic properties of $LiNbO_3$—Nd^{3+} crystals did not differ from those used in previous works (^{5}, ^{6}). The analysis was carried out at 77 and 300° K. $LiNbO_3$ crystals were synthesized by the Czochralski method under conditions close to those in work (^{7}). The maximum concentration of activator in our samples was ~ 2 wt.% (in the charge). In the experiments we used polydomain crystals grown with different orientations of the c axis, up to 40 mm long.

We studied all transitions of Nd^{3+} ions, both in absorption and in luminescence, lying in the transparency band of the crystal (0.36-5.5 μ). Here we present only

Fig. 1. Absorption spectra (transition ${}^4I_{9/2} \to {}^2P_{1/2}$) and resonant luminescence (transition ${}^4F_{3/2} \to {}^4I_{9/2}$) of a multidomain $LiNbO_3 - Nd^{3+}$ crystal (2 wt.% in the charge) at 77 and 300°K. The splitting of the Stark levels ${}^4F_{3/2}$ (160 and 168) is indicated in cm^{-1}.

Figure 1: Fig. 1. Absorption spectra (transition ${}^4I_{9/2} \to {}^2P_{1/2}$) and resonant luminescence (transition ${}^4F_{3/2} \to {}^4I_{9/2}$) of a multidomain $LiNbO_3 - Nd^{3+}$ crystal (2 wt.% in the charge) at 77 and 300°K. The splitting of the Stark levels ${}^4F_{3/2}$ (160 and 168) is indicated in cm^{-1}.

Fig. 2. Luminescence spectra (transition ${}^4F_{3/2} \to {}^4I_{11/2}$) of a multidomain $LiNbO_3 - Nd^{3+}$ crystal (2 wt.% in the charge) at 77 and 300°K. *a*—recording along the *c* axis, and *b*—perpendicular to the *c* axis. The arrows indicate induced transitions *A* (according to the data of [6]) and *B*.

Figure 2: Fig. 2. Luminescence spectra (transition ${}^4F_{3/2} \to {}^4I_{11/2}$) of a multidomain $LiNbO_3 - Nd^{3+}$ crystal (2 wt.% in the charge) at 77 and 300°K. *a* —recording along the *c* axis, and *b*—perpendicular to the *c* axis. The arrows indicate induced transitions *A* (according to the data of [6]) and *B*.

certain characteristic spectra. Figure 1 shows the absorption spectra (transition ${}^4I_{9/2} \to {}^2P_{1/2}$) and resonant luminescence (transition ${}^4F_{3/2} \leftrightarrow {}^4I_{9/2}$), and Fig. 2 the luminescence spectra at 77 and 300° K corresponding to the transition ${}^4F_{3/2} \to {}^4I_{11/2}$, which is directly associated with induced emission. Since all spectra of the Nd^{3+} ion in $LiNbO_3$ are characterized by fairly high polarization, Fig. 2 gives spectra for two cases—when the luminescence was recorded along the *c* axis (Fig. 2a) and perpendicular to it (Fig. 2b). The studies also showed that the spectra of Nd^{3+} ions in $LiNbO_3$ are characterized by inhomogeneously broadened lines. This may be connected, on the one hand, with the fact that activator ions may enter the crystal lattice, replacing Li^+ or Nb^{5+} ions ([3], [4]), and, on the other hand, with the polydomain structure samples. Indeed, in many cases at 77°K individual lines in the optical spectra (this is clearly seen in Figs. 1 and 2—the transitions ${}^4I_{9/2} \to {}^2P_{1/2}$, ${}^4F_{3/2} \leftrightarrow {}^4I_{9/2}$ and ${}^4F_{3/2} \to {}^4I_{11/2}$) split into two components of equal intensity with $\Delta E =$ 10-

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Fig. 3. Schemes of the crystal splitting of the terms of Nd^{3+} ions in $LiNbO_3$ at 77 and 300°K.

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20 cm^{-1}, which apparently indicates the existence of two groups of optical

Fig. 3. Schemes of the crystal splitting of the terms $^2P_{1/2}$, $^4F_{3/2}$, $^4I_{11/2}$, and $^4I_{9/2}$ of Nd^{3+} ions in a $LiNbO_3$ crystal at 77 and 300°K. The positions of the levels are given in cm^{-1}, and the transitions between them in Å. The induced transitions are indicated by bold arrows.

centers that are close in structure. Some confirmation of this may be provided by the data of work (2) on the study of the EPR of Nd^{3+} ions in $LiNbO_3$.

Analysis of the results obtained enabled us to construct schemes of the crystal splitting of the levels of Nd^{3+} ions in $LiNbO_3$ for two temperatures.* Fig. 3 shows fragments of them, explaining the transitions between the terms $^4F_{3/2}$ and $^4I_{9/2-11/2}$. It is seen that the splitting of the $^4F_{3/2}$ term in them at 77°K is equal to 168 cm^{-1}, and at 300°K, $\sim$ 160 cm^{-1}. Such a considerable splitting of the $^4F_{3/2}$ term is clearly manifested in the luminescence spectra. At 77°K, the lines connecting the upper level 11417 cm^{-1} with the Stark components of the $^4I_{9/2}$ and $^4I_{11/2}$ terms almost completely disappear from them. All this indicates that the local crystal fields surrounding Nd^{3+} ions in $LiNbO_3$ are of low symmetry. According to the data of works (3,4) on EPR studies, Nd^{3+} ions are in a field of axial symmetry. For ease of comparison of the transitions in the scheme and of the individual lines in the spectra, a connecting numbering has been assigned to them.

In the experiments on stimulated emission, illumination systems with xenon lamps of the IFP type were used, analogous to those described in works (5). A confocal optical resonator was used, consisting of external spherical mirrors with dielectric coatings ($\tau \approx 0.7\%$). At 300°K, an optical quantum generator based on $LiNbO_3$–Nd^{3+} crystals (2 wt.% in the charge, length $\sim$ 12 mm and diameter $\sim$ 3-5 mm) with zero orientation of the c axis generated at the wavelength 10932 Å (9147 cm^{-1}) with $E_p \cong 3$ J (line).** The generation spectrum—

* Mean values of the positions of the lines of two close optical centers were used.

** In work (4), generation was recorded on line A with wavelength 10846 Å, which corresponds to a crystal with perpendicular orientation of the c axis.

tion (see Fig. 4) was photographed on I-1070 film using a DFS-8 diffraction spectrograph (5.9 Å/mm). If one turns to the energy-level scheme, it is seen that the induced transitions A and B recorded by us and by the authors of Ref. (4) (they are indicated in the scheme by heavy arrows) connect the lower level 11250 cm^{-1} of the term $^4F_{3/2}$

Fig. 4. Spectra of induced emission at 300°K of an OQG based on crystals: *a*—$LiNbO_3$—Nd^{3+} and *b*—CaF_2—Nd^{3+} (type II). The arrow indicates the reference line with $\lambda_r = 10561.5$ Å

and the components 2030 and 2103 cm^{-1} of the term $^4I_{11/2}$. With a fivefold excess of E_p, the width of the generation line B at 300°K was about 2 cm^{-1}. The total losses at the wavelength of generation of line B were determined from the formula

$$\alpha = \ln R_{out}^{-1}/2l(\gamma - 1),$$

where R_{out} is the reflection coefficient of the output mirror; l is the crystal length, and γ is the ratio of E_p at a certain value of R_{out} to its value at $R_{out} = 1$. We carried out these measurements with three mirrors with $R = 77$, 88, and 99.3%. The data led to the value $\alpha = (3 \pm 1) \cdot 10^{-2}$ cm^{-1}.

The lifetime of the excited state $^4F_{3/2}$ of Nd^{3+} ions in a $LiNbO_3$ crystal (concentration about 2 wt.% in the charge) at 70 and 300°K was approximately the same and equal to 80 ± 5 μs; for samples with an activator concentration of 1 wt.% it is 85 ± 5 μs. The widths of the luminescence lines corresponding to the induced transitions A and B for a polydomain $LiNbO_3$ crystal with a content of Nd^{3+} ions of about 2 wt.% (in the charge) are: when the radiation is recorded along the c axis, $\Delta\nu_A = 22$ cm^{-1} (10846 Å) and $\Delta\nu_B = 30$ cm^{-1} (10932 Å) at 300°K, and $\Delta\nu_A = 9$ cm^{-1} (10850 Å) and $\Delta\nu_B = 15$ cm^{-1} (10937 Å) at 77°K. When the luminescence is recorded in the direction perpendicular to the c axis, these quantities are respectively equal, at 300°K, to 18 and 28 cm^{-1}, and at 77°K, to 8 and 13 cm^{-1}.

The set of investigations carried out has shown that the $LiNbO_3$—Nd^{3+} crystal is a very interesting object both for studying spectroscopic problems connected with the behavior of TR^{3+} ions in various crystal fields and for generation studies. Here we note that the induced transition B observed by us has extended the operating range of "neodymium" OQGs to 10932 Å. In Fig. 4, for comparison, the i.e. spectrum of an OQG based on a CaF_2 crystal (type II)–Nd^{3+} with $\lambda_g = 10885$ Å is given. The results obtained show that $LiNbO_3$—Nd^{3+} crystals may also be promising for continuous-action OQGs.

Institute of Crystallography
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.