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Spectra and luminescence kinetics of congruent $LiNbO_3$:Er crystals in the temperature range 80−420 K

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In the temperature range 80−420 K the spectra and kinetics of photoluminescence (PL) of congruent $LiNbO_3$: Er crystals were investigated under excitation by a laser at $\lambda = 405$ nm. The PL spectrum of the $LiNbO_3$: Er crystal in the visible wavelength range includes four multiplets with maxima at 413, 526, 551, and 660 nm. It was found that at $T = 300$ K the luminescence decay time (τ_{PL} at wavelengths 526 and 551 nm is $\sim 27\,\mu$s, while the band with a maximum at 413 nm decays faster at $1\,\mu$s, which correlates with numerous literature data. At the same time, τ_{PL} in the 660 nm region was $33\,\mu$s, which is almost 30 times longer than previously published values. Possible reasons for the observed difference are discussed.

Keywords: spectroscopy, luminescence, lithium niobate, erbium.

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1. Introduction

Lithium metaniobate ($LiNbO_3$) combines unique electro-optic, acousto-optic, and nonlinear-optic properties of the crystalline matrix with the possibility of doping it with rare-earth and transition metal ions. The introduction of these impurities substantially alters the physical properties of $LiNbO_3$, such as the refractive index, domain structure, electro-optic coefficients, and optical absorption [1]. Lithium metaniobate can be used both as single crystals and as the main element of low-loss waveguides in solid-state structures. Both pure and doped $LiNbO_3$ crystals are considered as promising materials for modern nanophotonics [2,3], including the creation of nanoscale high-sensitivity luminescent thermometers, whose operating principle is based on the use of temperature-dependent optical parameters such as lifetime, intensity, spectral position, etc. [4,5]. The numerous practical applications of lithium niobate crystals necessitate comprehensive studies of their properties. This work investigates the spectra and kinetics of photoluminescence (PL) of congruent (lithium-deficient) $LiNbO_3$ crystals doped with Er under continuous-wave and pulsed laser excitation. Note that a stoichiometric composition is naturally more desirable for forming optimal optical properties. However, technological difficulties in growing defect-free lithium niobate single crystals result in most studies of this material using congruent crystals [6,7].

2. Experiment details

2.1. Samples

This work examines the PL spectra and kinetics of congruent $LiNbO_3$ crystals (Li/Nb ratio ~ 0.94), doped with Er under continuous-wave and pulsed excitation by semiconductor lasers at wavelengths of $\lambda_{exc} = 405$ or 457 nm. The samples were grown from the melt by the Czochralski method, with doping components added to the melt as oxides Er_2O_3. Monodomainization was performed in a furnace after growth until cooling with a current of 5 mA. The Er^{3+} ion concentration was about 0.25 wt%. Oriented ($\sim 1 \times 5 \times 10$) mm plates were cut from bulk crystals such that the crystallographic c axis was perpendicular to the main surface (z-orientation). It should be noted that although congruent crystals have a less ordered structure compared to stoichiometric ones, this disorder does not lead to the disappearance of erbium spectral structure [8]. At the same time, congruent lithium niobate crystals, as already mentioned, are the most technologically feasible for growth [9].

2.2. Experimental methods

Absorption spectra were measured in the 330−875 nm range (with 0.8 nm step) using a Varian Cary 5000 spectrophotometer. Photoluminescence of $LiNbO_3:Er^{3+}$ crystals in continuous-wave and pulsed modes was excited by semiconductor lasers at wavelengths of 405 and 457 nm. The rise and decay kinetics of PL were detected under excitation by rectangular laser pulses with a duration of $250\,\mu$s and repetition rate of 500 Hz with $0.5\,\mu$s resolution and recorded using a digital oscilloscope interfaced to a computer. The results obtained under PL excitation at different wavelengths were identical (where comparable), so the following presents experimental data obtained under sample excitation at $\lambda_{exc} = 405$ nm unless otherwise specified. For temperature-dependent PL studies, lithium niobate samples were placed in an optical cryostat maintaining the specified

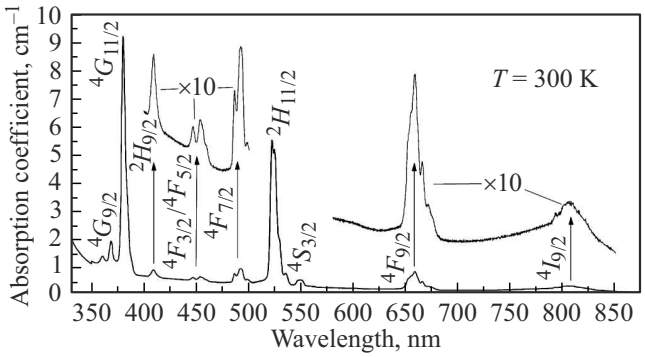

Figure 1. Absorption spectrum of the $LiNbO_3$: Er sample in the 330−875 nm range at T = 300 K.

temperature in the 300−420 K range with accuracy to 1 K. Temperature variation was achieved using an electric heater with a thermostat. PL spectra were recorded using diffraction spectrometers. A photomultiplier tube FEU-79 and a CCD matrix served as photodetectors.

3. Experimental results and discussion

The optical absorption spectrum of the $LiNbO_3$:Er^{3+} single crystal at room temperature in the wavelength range (330−875 nm) is shown in Fig. 1. It consists of numerous lines of varying intensity associated with transitions from the ground state $^4I_{15/2}$ to the excited states of the $4f^{11}$ configuration of the Er^{3+}ion marked in the figure.

As seen from Fig. 1, the 405 nm wavelength used for PL excitation corresponds to the short-wavelength wing of the$^4I_{15/2} \rightarrow {}^2H_{9/2}$ absorption band. In this spectral region (Fig. 1), a rise in the absorption spectrum is observed, associated with the „tail" of the density of states in the intrinsic absorption spectrum of the $LiNbO_3$ crystal. This means that absorption at 405 nm involves not only resonant excitation of $^4f_{11}$ states of Er^{3+} ions but also energy transfer processes from the matrix to Er^{3+}ions [10].

Fig. 2 *a* shows the PL spectrum under 405 nm excitation at temperatures from 300 to 420 K. Notably, in this spectrum, emission from $^4F_{3/2}$, $^4F_{5/2}$ and $^4F_{7/2}$ states is absent in the 420−520 nm region, directly indicating that the decay of these states is predominantly nonradiative. It is also important to note that the emission intensity in the 415−425 nm and 660−670 nm regions is almost temperature-independent, unlike the 520−580 nm spectral region (Fig. 2, *b*), where thermodynamic equilibrium is established between $^2H_{11/2}$ and $^4S_{3/2}$ components. Indeed, Fig. 2, *c* shows the semilogarithmic dependence of the ratio of integrated intensities of PL components corresponding to $^2H_{11/2} \rightarrow {}^4I_{15/2}$ (spectral range 515−540 nm) and $^4S_{3/2}-{}^4I_{15/2}$ (spectral range 540−575 nm) transitions on inverse temperature, confirming this conclusion. This dependence aligns with conclusions from several works about the thermal coupling of such levels and the potential use of these transitions as temperature sensors [11].

To further characterize the transitions in the $LiNbO_3$:Er^{3+} spectrum more deeply, the temporal kinetics of PL pulse rise and decay were studied under pulsed excitation at 405 nm at several temperatures from 100 to 420 K. Components of the $^2H_{9/2}$ multiplet (410−420 nm) decay faster than 1 μs, while the PL lifetime in the green region 525−550 nm is on the order of 20−30 μs. Both results agree with numerous literature data [12–18]. The most surprising result is that the PL decay time in the red region (660 nm) was 33 μs, which, to our knowledge, is almost 30 times longer than previously published values [12,14,15,17]. These results for transitions in the green and red spectral regions are systematized in the table and discussed below. The data in the table highlight the following characteristics of transitions in the „green" (525−550 nm) and „red" (660−675 nm) spectral regions.

1) AtT = 300 K the PL pulse rise times can be satisfactorily described by a monoexponential dependence $I(t) = I_0[1 - \exp(-t/a)]$ with parameter a of (49 ± 1) and (34 ± 1) μs respectively.

2) PL pulse decay times generally include two components — fast and slow—with noticeably different a parameters. The first spans about one natural order of magnitude change in PL intensity, while the second spans more than two decimal orders.

3) The a parameters decrease noticeably with increasing temperature, reflecting, evidently, the increased probability of nonradiative recombination with temperature rise.

Note that all characteristics listed in points 1)−3) for PL kinetics in the „green" spectral region match well under excitation at both 405 nm and 457 nm and, as noted above, agree with all published results. At the same time, in all known works to us, the lifetime of the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition emitting in the „red" (660 nm) spectral region is characterized by a value on the order of 1 μs, which differs by more than 30 times from our values given in the table. The reasons for the anomalously long decay time τ_{PL} (table) observed in the 660 nm region of the investigated sample's PL spectrum are currently unknown and require further investigation. As a possible explanation for the observed τ_{PL} value, the following considerations can be proposed.

(i) Several works [19] have shown that the Er^{3+} ion in the $LiNbO_3$ lattice occupies at least 11 nonequivalent positions. Both the spatial implementation of these positions in stoichiometric and congruent $LiNbO_3$samples and the influence of the crystalline environment on the lifetimes of transitions in the electronic spectrum of the Er^{3+} ion may differ.

(ii) The lifetime of the transition we studied, $^4F_{9/2} \rightarrow {}^4I_{15/2}$ is determined by the relaxation rate from the $4F_{9/2}$ state to the nearest lower-lying state ($4I_{9/2}$ in this case), which in turn depends on the spectrum of phonons involved in energy relaxation and can be substantially accelerated if an integer number of relevant phonons fits into the energy interval ΔE, separating the $^4F_{9/2}$ and $^4I_{9/2}$levels,

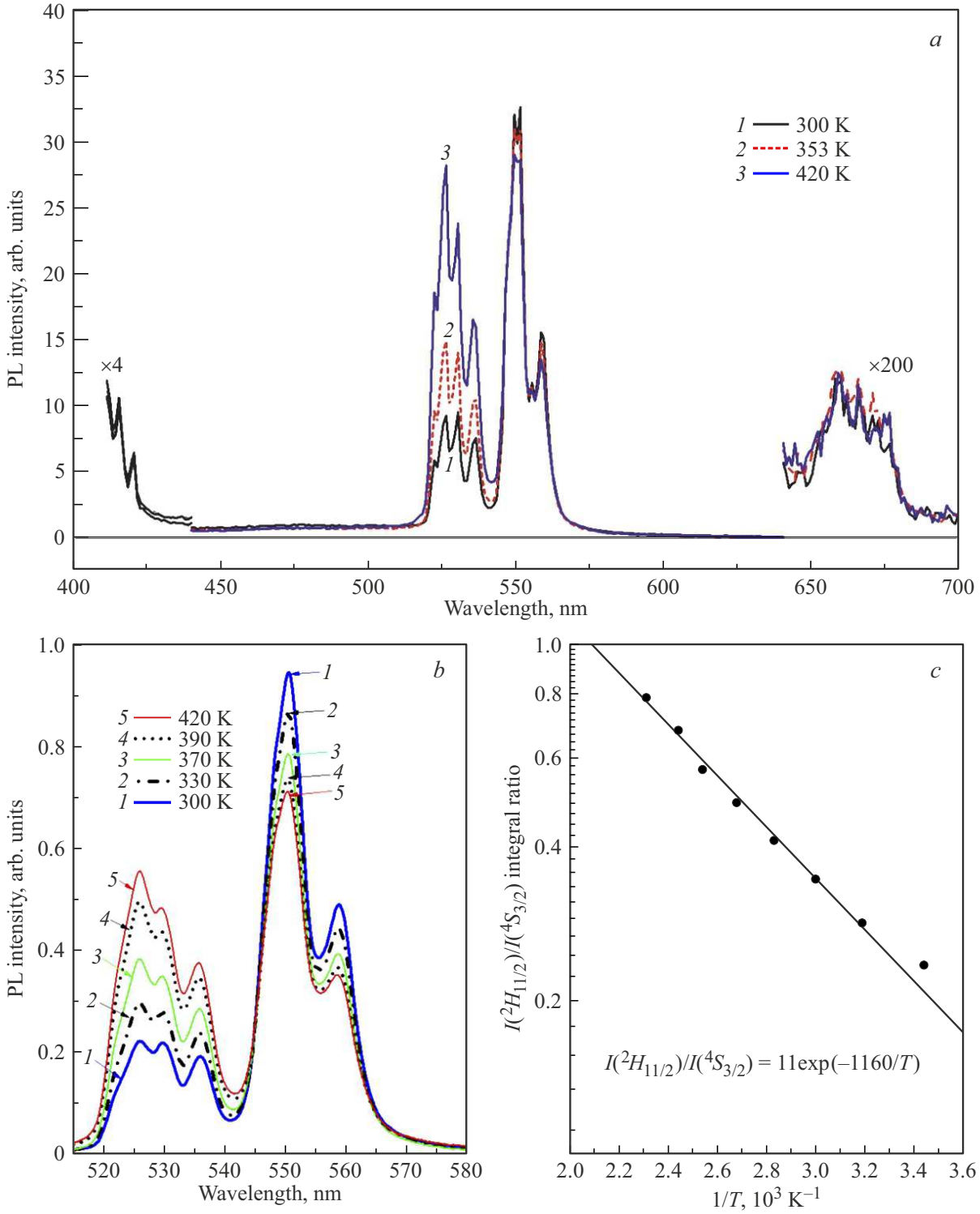

Figure 2. (*a*) PL spectra under 405 nm excitation measured at three temperatures: 300 (*1*), 353 (*2*), 420 K (*3*). (*b*) Sections of PL spectra in the transition region between $^2H_{11/2}$ and $^4S_{3/2}$ components in more detail at $T = 300$ K (*1*), 330 K (*2*), 370 K (*3*), 390 K (*4*), 420 K (*5*). (*c*) Semilogarithmic dependence of the ratio of integrated intensities of the „green" PL band $I(^2H_{11/2})/I(^4S_{3/2})$ on inverse temperature.

depending on the crystalline environment of the erbium ion, or substantially slowed otherwise (so-called „phonon bottleneck").

Thus, the excitation lifetimes at energy levels of the Er^{3+} ion in the $LiNbO_3$ matrix can vary substantially depending on both growth conditions and subsequent

Kinetics of rise and decay of green and red PL bands in the $LiNbO_3$:Er^{3+} crystal at different temperatures

T, K	$^4S_{3/2} \rightarrow {}^4I_{1.5/2}$			$^4F_{9/2} \rightarrow {}^4I_{1.5/2}$		
	λ, nm nm	Rise time rise, μs	Decay time decay (fast/slow), μs	λ, nm	Time rise, μs	Time decay (fast/slow), μs
100	551	72	24/36	666 675	48 48.0	–/37 30/39
300	549	49	24/28	660	34	16/33
353	526 551	43 45	23/26 21/25	660 674	31 32	–/20 –/23
420	526 551	43 43	18/21 17/21	660	31	–/16

thermal processing, necessitating linking the properties of individual transitions in the spectra of rare-earth ions to specific crystal synthesis conditions. This conclusion is supported by numerous data in a recent review [6], which convincingly demonstrates that the defectiveness of $LiNbO_3$ crystals of any composition and their optical properties fundamentally depend on growth conditions and thermal history.

Conflict of interest

The authors declare that they have no conflict of interest.

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