RESEARCH OF ENERGY TRANSFER PROCESSES IN LiNbO₃ CRYSTALS CODOPED WITH Er³⁺ AND Yb³⁺ IONS

V.G. Babajanyan, G.G. Demirkhanyan, R.B. Kostanyan, P.H. Muzhikyan, and R.V. Sargsyan

Institute for Physical Research, NAS RA, 0203 Ashtarak, Armenia, bvahan@ipr.sci.am

Received 5 September, 2009

1. Introduction

In recent years solid state lasers, operating at the 1.5 µm wavelength region, have received much attention for fiber-optic communication systems of metropolitan and local area networks since the highest data rates are achieved using silica glass fibers with minimal transmission losses near this wavelength. In this spectral region the most suitable active ion among the trivalent rareearth (RE³⁺) ions is Er³⁺ with the 4f¹¹ electronic configuration of the ground state. In various crystalline fields it reveals a rich set of energy levels with multiple possible lasing transitions and channels of excitation energy nonradiative transfer. Its transition between excited ${}^{4}I_{13/2}$ and ground ${}^{4}I_{15/2}$ energy levels in diverse crystals corresponds to this wavelength of interest near 1.5 μ m. However, absorption bands of the Er^{3+} ion in the visible and near IR spectral regions, suitable for optical pump by commercial laser diodes, are weak due to their correspondence to parity forbidden transitions between energy levels of the incompletely filled 4f-shell [1, 2]. This drawback can be reduced by co-doping with appropriate sensitizers. As good sensitizers for the Er³⁺ ions in different crystals are the Cr^{3+} , Ce^{3+} and Yb^{3+} ions [3-5], but the most suitable ion for pumping with laser diodes is Yb^{3+} , which has an intensive absorption band in the 0.85–1 µm spectral region and thus provides efficient nonradiative transfer of the absorbed energy to the active ion. Moreover, the ground state electronic configuration of the Yb^{3+} ion is $4f^{13}$, which allows the presence of only two multiplets (${}^{2}F_{5/2}$ and ${}^{2}F_{7/2}$), eliminating all kinds of cross-relaxation and re-absorption processes.

Active media with an advantageous combination of efficient generation characteristics of impurity ions with nonlinear, electro-optical and other properties of a matrix are of great interest in view of their use for compact multifunctional bulk and waveguide lasers. Among the most interesting nonlinear optical materials the LiNbO₃ (LN) crystal compares favorably due to its excellent nonlinear and electro-optical properties, mechanical hardness, high optical quality and large sizes of growing crystals, mechanical hardness, nonhygroscopicity, etc. [6]

In this paper results of investigations of cooperative processes taking place at room temperature in the impurity subsystem of the $LN:Yb^{3+}-Er^{3+}$ crystal under optical excitation at the 1064 nm are presented. Despite the fact that this wavelength differs sufficiently from the absorption peak of the Yb³⁺ ions in LN matrix (near 980 nm), however, its use is suitable because it doesn't

excite Er³⁺ ions in the same matrix and, thereby, allows significantly to simplify the physical picture and carry out separate investigations of involved cooperative processes.

Possible models of optical centers are suggested and cooperative processes responsible for observed phenomena are studied.

2. Theory

Fig.1 represents the energy level diagram of the Yb³⁺ and Er³⁺ ions in LN crystal under optical pumping at 1064 nm relating to the research processes carrying out in the present work Transitions, marked by the arrows, correspond to the processes of absorption (double line), luminescence (continuous straight line), nonradiative relaxation (wavy line) and excitation transfer from Yb³⁺ donor ${}^{2}F_{5/2}$ level to Er³⁺ acceptor ${}^{4}I_{11/2}$ level in the dopant subsystem of the crystal under study (dashed line).



Fig.1. Diagram of energy levels of the Yb^{3+} and Er^{3+} ions in LN crystal relating to the processes under study.

From magnitudes of widths of the ${}^{2}F_{5/2}$ (Yb³⁺) and ${}^{4}I_{11/2}$ (Er³⁺) energy levels, presented in Fig.1, it is clear that in excitation transfer between specified states of the dopant ions in the LN crystalline field at room temperature both the resonance and non-resonance transfer mechanisms can have a significant contribution.

It is known that the probability of elementary act of the resonance nonradiative energy transfer processes (NRETP) in an impurity subsystem of doped crystals can be expressed as

$$W_{res} = \frac{3\pi\hbar e^4 f_1 f_2}{n^4 m^2 \omega^2 R^k} \int g_1(E) g_2(E) dE,$$
(1)

where R is a distance between interacting ions; e and m are the charge and mass of an electron,

correspondingly; *n* is the refractive index of the matrix; $\int g_1(E)g_2(E)dE$ is the overlapping integral between the luminescence spectrum $g_1(E)$ of a donor and the absorption spectrum $g_2(E)$ of an acceptor; ω is the overlapping mean frequency; $f_1(f_2)$ is the oscillator strength of the corresponding transition of donor (acceptor), *k* is an integer equal to 6, 8 or 10 in case of dipole-dipole, dipolequadrupole and quadrupole-quadrupole types of interaction. For non-resonance NRETP processes with ω_p phonon (in Debye model) the emission (absorption) probability of elementary act is determined by

$$W_{nonres} = \frac{2\pi}{\hbar^2} \left| \left\langle \psi_1^* \psi_2^0 | H_{12} | \psi_1^0 \psi_2^* \right\rangle \right|^2 \times \left\{ \frac{3\omega_p}{4\pi^2 \upsilon^5 \hbar \rho} \left| \left\langle \psi_2^* | V_2 | \psi_2^* \right\rangle - \left\langle \psi_2^0 | V_2 | \psi_2^0 \right\rangle + \left\langle \psi_1^0 | V_1 | \psi_1^0 \right\rangle - \left\langle \psi_1^* | V_1 | \psi_1^* \right\rangle \right|^2 \right\} \left(\frac{\overline{n}_p + 1}{\overline{n}_p} \right).$$
(2)

Here $\psi_{1,2}^0$ and $\psi_{1,2}^*$ are fundamental and excited states of the ions; H_{12} is the Hamiltonian of multpole interaction of two ions; $V_{1,2}$ is the dynamic part of orbit-lattice interaction, which acts only on electron wave functions of ions; v is the sound velocity in a crystal; ρ is its density; \overline{n}_D is the phonon occupation number [7,8].

From these expressions it is clear that an effective NRETP via resonance mechanism occurs for the impurity ions with substantial overlapping of the mentioned spectra. In case of nonresonance mechanism effective NRETP can take place when they are shifted from each other by amount of lattice phonon energy. Besides, it is necessary a sufficiently close disposition of interacting ions which generally is achieved by their concentration growth.



Fig.2. The absorption band of Er^{3+} acceptor ions (upper curve) and luminescence spectrum of Yb³⁺ donor ions (lower curve) in the LN matrix. Corresponding transitions between energy levels of the impurities are shown on the curves.

Fig.2 testifies that an overlap exists in a wide spectral range (960–1000 nm). The second condition is also satisfied for our crystals, since recently it was shown that a certain part of trivalent rare-earth impurity ions incorporated into LN matrix, can form pairing centers (PCs) with simultaneous substitution of neighboring lithium and niobium positions [9-14]. Distances between interacting ions in such PCs will be about several angstroms. Under such inhomogeneous distribution of Yb³⁺ and Er³⁺ ions in LN lattice it is possible to split impurity ions into two subsystems: the subsystem of PCs, consisting of close located (~3–4 Å) ions, and the subsystem of single centers (SCs) separated sufficiently from each other. In the crystal under study the (Yb³⁺-Yb³⁺), (Er³⁺-Er³⁺) and (Yb³⁺-Er³⁺) types of PCs are possible with their proper contributions to the kinetics of excitation [15, 16].

As a first approximation let us assume that the concentration of impurity ions in a crystal is so low that PCs and SCs are separated sufficiently far from each other and all transfer processes between them can be neglected. Since the absorption coefficient at 1064 nm for the Yb³⁺ exceeds the same one for Er^{3+} by more than one order of magnitude, then one can accept that initially only the Yb³⁺ ions both in a single and in (Yb³⁺+Er³⁺) pair centers will be excited, and for lack of any energy transfer between them, the (Er³⁺+ Er³⁺) and (Er³⁺) centers can be excluded completely from further discussion. In the framework of such assumptions and by using the rate equations formalism, for the excitation lifetime of the LN:Yb³⁺-Er³⁺ crystal under the optical pump at 1064 nm, the following expression is obtained:

$$\tau = \frac{n_{10}\tau_1^2 + n_{20}\tau_2^2 + n_{30}\tau_{30}^2}{n_{10}\tau_1 + n_{20}\tau_2 + n_{30}\tau_{30}}.$$
(3)

Here n_{10} , n_{20} , and n_{30} are the excited in the initial moment numbers of (Yb³⁺-Er³⁺), (Yb³⁺-Yb³⁺) pairing centers and (Yb³⁺) SCs, accordingly. They can be written as

$$n_{10} = N_1 \exp(-\sigma_2 F \tau_p) [1 - \exp(-\sigma_1 F \tau_p)],$$
(4)

$$n_{20} = 2N_2 \exp(-\sigma_1 F \tau_p) \cdot [1 - \exp(-\sigma_1 F \tau_p)], \qquad (5)$$

$$n_{30} = N_3 [1 - \exp(-\sigma_1 F \tau_p)], \tag{6}$$

where τ_1 , τ_2 and τ_{30} (N_1 , N_2 and N_3) are lifetimes of excitations (concentrations) in the (Yb³⁺- Er³⁺), (Yb³⁺-Yb³⁺) and (Yb³⁺) centers, correspondingly, τ_p is the pump duration; F is the density of photons in the pump pulse. Obviously, $N_1 + N_2 + N_3 = N_{Yb}$ (N_{Yb} is the total concentration of Yb³⁺ ions in the crystal).

4. Experimental results and discussion

Investigations were carried out with samples prepared from the LN crystals, singly doped with Yb^{3+} (1 mol.% in initial melt), Er^{3+} (0.5 mol.%) and doubly co-doped with Yb^{3+} - Er^{3+} (1 mol.%)

+ 0.5 mol%) impurity ions. In kinetic research radiations from a Q-switched pulsed YAG:Nd³⁺ laser (pulse duration ~ 20 ns) at the 1064 nm and 532 nm (fundamental wavelength and its second harmonic) were used as pump sources for the crystals under study. The luminescence decay time of the LN:Yb³⁺ crystal registered at 940 nm (corresponding to the transition ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$) was 540 µs and for the LN:Er³⁺ crystal at 900 nm (${}^{4}I_{11/2} \rightarrow {}^{4}I_{15/2}$) under 532 nm excitation was 220 µs. The luminescence decay dependence for the LN:Yb³⁺+Er³⁺ crystal on the pump energy (at the 1064 nm) is plotted in Fig.3. It is seen that it changes appreciably from ~ 525 µs at low pump energies (smaller than 30 mJ) to ~ 460 µs at pump energies higher than 80 mJ. By using the Wolfram Mathematica-7 programming package the obtained experimental values are fitted with the calculations by equation (3) (Fig.3, solid curve). In these calculations the following expressions for excitation lifetimes of the (Yb³⁺-Er³⁺) and (Yb³⁺-Yb³⁺) pair centers were used [15]:

$$\tau_1 = \frac{2(\tau_{10}^2 + \tau_{30}^2)}{(\tau_{10} + \tau_{30})}; \qquad \tau_2 = 1.8 \times \tau_{30}; \tag{7}$$

where τ_{10} is the lifetime of the ${}^{4}I_{11/2}$ energy level of the single Er^{3+} center.



Fig.3. The LN:Yb³⁺-Er³⁺ crystal excitation lifetime dependence on the pump energy.

Here ARS is the fitting coefficient of the determination and represents the root–mean-square fit of calculated points with experimental ones (the closer the one, the better the fitting).

It is seen that the excitation lifetime of the $LN:Yb^{3+}-Er^{3+}$ crystal depends on the pump energy and differs distinctly from such values for both $LN:Yb^{3+}$ and $LN:Er^{3+}$ crystals. The last fact is the obvious demonstration of the effect of "excitation trapping" [17].

5. Conclusions

Thus, the presence of above mentioned pair centers in doped crystals results in essential changes of the excitation lifetime in the impurity subsystem, predetermining also its dependence on the pump intensity. It is clear that such behavior will result in corresponding changes in the population dynamics of the Er^{3+} ions energy levels responsible for laser generation. In addition, clearly defined visualization of the "excitation trapping" effect is observed.

References

- 1. A.M. Prokhorov (ed.). Handbook of lasers, v.1, M., Sov.Radio, 1978.
- 2. A.A. Kaminskii (ed.). Physics and spectroscopy of laser crystals, M., Nauka, 1986.
- 3. Chr. Wyss, I.W. Liithy, H.P. Weber, et al. Opt. Comm., v.144, 31 (1997).
- 4. J.X. Meng, K.W. Cheah, Zh.P. Shi, et al. Appl. Phys. Lett., v.91, 151107 (2007).
- 5. T.T. Basiev, Yu.V. Orlovskii, V.G. Ostroumov, et al. Kvant. Elektr., v.22, 759 (1995).
- T.F. Fan, A. Cordova Plaza, M.J. Digonnet, R.L. Byer, and H.J. Shaw. JOSA., v.B3, 140 (1986).
- 7. D.L. Dexter. J. Chem. Phys., v.21, 836 (1953).
- G.M. Zverev, I.I. Kuratev, and A.M. Onischenko. Spectroscopy of crystals. M., Nauka, p.184 (1975).
- 9. M. Rico, C. Zaldo, J. Massons, and F. Diaz. J. Phys: Condens. Matt., v.10, 10101 (1998).
- V. Babajanyan, G. Demirkhanyan, E. Kokanyan, and R. Kostanyan. Laser Phys., v.7, 1238 (1997).
- 11. E. Maurice, G. Monnom, B. Dussardier and D.B. Ostrowsky. JOSA, v.B13, 693 (1996).
- 12. O. Witte, H. Stolz, and W. von der Osten. J. Phys. D: Appl. Phys., v.29, 561 (1996).
- 13. V.G. Babajanyan, G.G. Demirkhanyan, J.B.Gruber, et al. Laser Phys., v.15, 1550 (2005).
- V. Babajanyan, G. Demirkhanyan, E. Kokanyan, R. Kostanyan, P. Muzhikyan, and R.Sargsyan. Proc. of Conf. on Laser Physics-2008, Yerevan, Gitutiun, 83 (2009).
- 15. G.G. Demirkhanyan. Doct. thesis. Ashatrak, 2007
- 16. G.G. Demirkhanyan, and R.B. Kostanyan. Phys. Rev., v.B77, 094305 (2008).
- 17. T.T. Basiev, Yu.K. Voronko, V.V. Osiko, et al. JETF, v.70, 1225 (1976).