OPTO-ELECTRONICS REVIEW **7**(2), 145–147 (1999)

Optical absorption and luminescence of $LiTaO_3$:Cr and $LiTaO_3$:Cr,Nd crystals*

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The interest in $LiNbO_3$ and $LiTaO_3$ crystals doped with transition metal or rare earth ions is related to their potential application as self-switching and self-frequency doubling laser materials. In the past considerable attention has been paid to $LiNbO_3$ crystals doped by variety of luminescent ions. In particular $LiNbO_3$:Cr was investigated recently by Macfarlane et al. [1]. Energy transfer between Cr^{3+} and Nd^{3+} in $LiNbO_3$ has been studied and discussed by Vergara et al. [2].

In this work we investigate spectroscopic properties of Cr^{3+} and Cr^{3+}–Nd^{3+} interaction in $LiTaO_3$ using optical absorption, luminescence and luminescence decay times at temperatures between 5 K and 300 K. Some preliminary data obtained with singly doped $LiTaO_3$:Cr at low activator concentration are given in our previous work [3]. Recorded spectra indicate that both the Cr^{3+} and Nd^{3+} are located in several non-equivalent sites that differ in the strength of the crystal field. Luminescence spectrum of Cr^{3+} consists of a broad band whose maximum and intensity depend on temperature. Below about 50 K an additional sharp band with four distinct components appears in the spectrum. The broad band attributed to the spin allowed $^4T_2$–$^4A_2$ transition of Cr^{3+} ions overlaps two absorption bands of Nd^{3+} ions at about 810 nm and 890 nm making the Cr^{3+}–Nd^{3+} energy transfer process feasible. Results of measurements are discussed and compared to those obtained with $LiNbO_3$:Cr.

Keywords: energy transfer, luminescence, non-equivalent sites

1. Introduction

In recent years, number of studies has been directed to improve the efficiency of Nd^{3+} lasers by codoping with donor ions having broad optical bands. Particularly, the interest in $LiNbO_3$ and $LiTaO_3$ crystals doped with rare earth and transition metal ions is related to their potential application as self-frequency doubling and self-Q switching laser materials. Transition ions have been added to rare earth laser materials to sensitise the luminescence and thereby to improve the pumping efficiency. The earlier investigations of crystals: $LiNbO_3$:Cr [1], $LiTaO_3$:Cr [3] and $LiNbO_3$:Nd, $LiTaO_3$:Nd [4,5] show, that both dopant ions are replacing Li^+ and Nb^{5+}/Ta^{5+} or vacancy sites for the reasons of local charge compensation. It is expected that dopant ions in these sites have to be located in near positions and the energy transfer between Cr^{3+} and Nd^{3+} ions is expected to occur in the double doped system. $LiNbO_3$ doped with Cr^{3+} and Nd^{3+} ions has been studied by Vergara et al. [2] to check the possibility of a Cr^{3+} to Nd^{3+} energy transfer process.

In this work the optical properties (absorption, luminescence and lifetimes) of $LiTaO_3$:Cr^{3+} and $LiTaO_3$:Cr,Nd crystals have been studied to check the possibility of Cr^{3+} to Nd^{3+} energy transfer.

2. Experiment

$LiTaO_3$:Cr crystal containing 0.005 wt % of Cr, $LiTaO_3$:Cr,Nd crystal containing 0.1 wt % of Cr (1.7×10^{19} ions/cm^3) and 0.2 wt % of Nd (7.1×10^{19}

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* The paper presented there appears in SPIE Proceedings Vol. 3724, pp. 234–238.

ions/cm^3) and $LiTaO_3$:Cr,Nd crystal containing 0.1 wt % of Cr (1.7×10^{19} ions/cm^3) and 0.4 wt % of Nd (3.51×10^{19} ions/cm^3) were grown by the Czochralski method from a congruent melt. Absorption spectra were measured with the Varian model 2300 absorption spectrophotometer. Luminescence spectra and decay kinetics were obtained after excitation by second harmonic YAG:Nd pumped dye laser (λ_{max} = 621 nm, 10 Hz, 8 ns pulse). Emitted light was dispersed by double grating monochromator (Zeiss GDM1000), detected with a cooled photomultiplier with S-1 spectral response. Resulting signal was averaged with the Stanford Model SRS250 boxcar averager. For 5 K measurements a continuous-flow helium cryostat (Oxford CF1204) with a temperature controller was used.

3. Results and discussion

The room temperature unpolarized absorption spectra of $LiTaO_3$:Cr crystal (lower curve) and $LiTaO_3$:Cr,Nd crystal (upper curve) are shown in Fig. 1. They consist of two broad bands associated with well know spin allowed vibronic transitions: $^4A_2$–$^4T_1$ centered at 21807 cm^{-1} and $^4A_2$–$^4T_2$ located at 15291 cm^{-1}. The line centered at 13918 cm^{-1} is associated with the spin forbidden, non-phonon $^4A_2$–^2E transition. In 800–400 nm spectral region all observed absorption transitions of Nd^{3+} ions take place from the $^4I_{9/2}$ ground state to the excited states and are superposed absorption spectrum of chromium. In Fig. 1 the arrows show the transitions associated with Nd^{3+} ions.

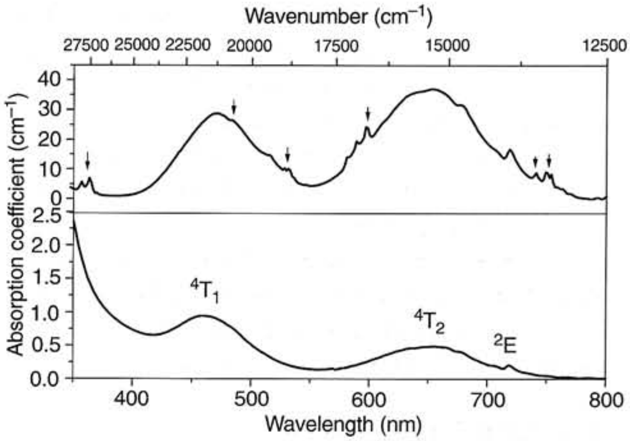

Fig. 1. Unpolarized absorption of $LiTaO_3$:Cr (lower curve) and $LiTaO_3$Cr,Nd (upper curve) recorded at room temperature. The arrows indicate the transitions associated with Nd^{3+} ions.

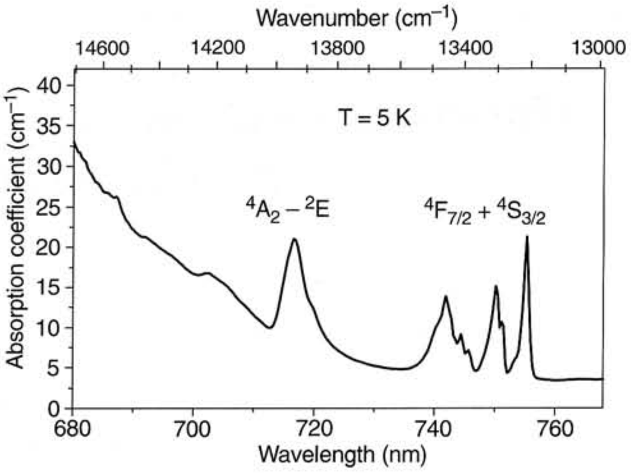

Fig. 2. The absorption spectrum for $LiTaO_3$:Cr,Nd recorded at 5 K.

Figure 2 shows the absorption spectrum of $LiTaO_3$:Cr,Nd crystal recorded at 5 K in 680–760 nm spectral region. The line associated with $^4A_2$–^2E transition is broad and asymmetric what suggests that Cr^{3+} ions occupy several different crystal sites. The absorption transitions from the $^4I_{9/2}$ ground state to the $^4F_{7/2}$ and $^4S_{3/2}$ excited states of Nd^{3+} ions are shown.

Luminescence spectrum for $LiTaO_3$:Cr crystal (lower curve) and for $LiTaO_3$:Cr,Nd crystal (upper curve) recorded under excitation into $^4A_2$–$^2T_2$ band of Cr^{3+} at 5 K is shown in Fig. 3. A broad emission band centered at 11250 cm^{-1} is associated with $^4T_2$–$^4A_2$ vibronic transition of Cr^{3+} ions. The details of the ^2E–$^4A_2$ chromium transition are shown in the inset.

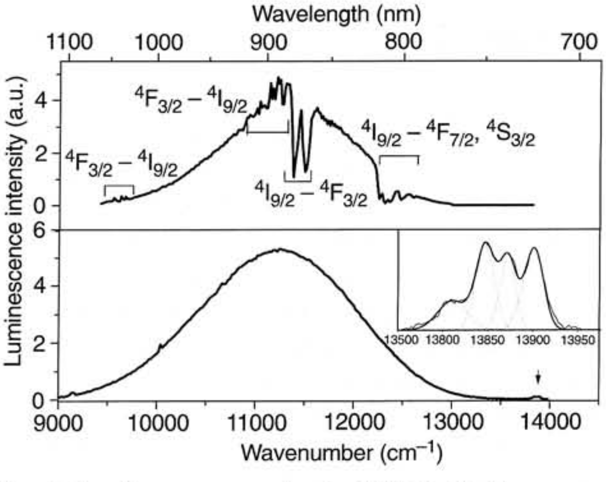

Fig. 3. Luminescence spectra for $LiTaO_3$:Cr (lower curve) and for $LiTaO_3$:Cr,Nd (upper curve) under excitation into $^4A_2$–$^2T_2$ band of Cr^{3+} ions recorded at 5 K. The inset shows the details of ^2E–$^4A_2$ transition of Cr^{3+} inticated by arrow on the lower curve.

We assume that four components of this line are R lines of Cr^{3+} in Ta^{5+} and Li^{+} sites. For $LiTaO_3$:Cr,Nd crystal the observed emission of Cr^{3+} and Nd^{3+} ions is associated with simultaneous absorption of neodymium from the $^4I_9$ ground state to the $^4F_{3/2}$ and ($^4F_{7/2}$, $^4S_{3/2}$) excited states. The emission band associated with ^2E–$^4A_2$ transition of Cr^{3+} is not observed. This is presented in Fig. 3 (upper curve).

The values of Cr^{3+} lifetime for crystals with different concentration of Nd^{3+} ions measured at 5 K are gathered in Table 1.

Table 1. The values of Cr^{3+} lifetime for crystals with different concentration of Nd^{3+} ions, measured at 5 K.

Nd concentration (wt %)	τ_m at 5 K (μs)	
	$^4T_2$	^2E
0.00	8	370
0.20	7.2	100
0.40	5.8	—

The lifetime of Cr^{3+} both at the $^4T_2$ level and at the ^2E level decreases with increasing of Nd^{3+} ions concentration in the crystals. It is an evidence that the Cr^{3+} to Nd^{3+} non-radiative energy transfer occurs. In order to estimate the energy transfer rate we used a simple formula:

$$k_{tr} = \frac{1}{\tau} - \frac{1}{t_0} \tag{1}$$

where τ and τ_0 is the donor (Cr^{3+}) low temperature lifetime of the $^4T_2$ level measured in the presence and the absence of acceptors (Nd^{3+}), respectively.

The efficiency of energy transfer calculated as:

$$\eta = \frac{k_{tr}}{k_{tr} + 1/\tau_0} \tag{2}$$

is equal to 0.1 and 0.27 for the crystals containing 0.2 wt % and 0.4 wt % Nd ions, respectively. The lifetime decrease of the ^2E level is observed, too. It changes from 370 μs for $LiTaO_3$:Cr crystal to 100 μs for $LiTaO_3$:Cr,Nd crystal containing 0.2 wt % of Nd^{3+} ions, and the luminescence from ^2E level is not observed for $LiTaO_3$:Cr,Nd crystal containing 0.4 wt % of Nd. This fact clearly indicates that the non-radiative energy transfer process occurs from this level too. However, the efficiency of this process is relatively low for heavily doped crystals. Probably, this is the reason that non-radiative energy transfer was not observed in the lowest doped $LiNbO_3$:Cr,Nd crystals [2].

4. Conclusion

In $LiTaO_3$:Cr,Nd crystals the lifetimes of the $^4T_2$ and the ^2E levels decreases with increasing of Nd^{3+} ions concentration. The non-radiative energy transfer from Cr^{3+} ions to Nd^{3+} ions occurs, however calculated efficiency of this process is relatively low.

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