

# Spectral properties of Yb<sup>3+</sup> ions in LiNbO<sub>3</sub> single crystals: influences of other rare-earth ions, OH<sup>-</sup> ions, and $\gamma$ -irradiation

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## Abstract

Absorption spectra have been studied in 190–3100 nm region at various temperatures from 16 to 292 K for Yb<sup>3+</sup>-doped and Yb<sup>3+</sup>/Nd<sup>3+</sup>-, Yb<sup>3+</sup>/Er<sup>3+</sup>- and Yb<sup>3+</sup>/Pr<sup>3+</sup>-co-doped LiNbO<sub>3</sub> single crystals before and after  $\gamma$ -irradiation with a dose of 10<sup>5</sup>–10<sup>7</sup> Gy. Intense 400 and 500 nm absorption bands were observed after  $\gamma$ -irradiation, which are due to the creation of oxygen vacancy (F-type color center) and Nb<sup>4+</sup> polaron, respectively. Different change was observed in the 2870 nm OH<sup>-</sup> absorption band intensity among the various rare-earth doped crystals. These are interpreted by discrepancy of ionic radii between substituting rare earth dopant ion and Li<sup>+</sup> or Nb<sup>5+</sup> host ion. The observed temperature dependence of the hot bands is understood by electronic transition from the thermally populated <sup>2</sup>F<sub>7/2</sub> Stark levels to the excited <sup>2</sup>F<sub>5/2</sub> level. The position of the Yb<sup>3+</sup> + <sup>2</sup>F<sub>7/2</sub> → <sup>2</sup>F<sub>5/2</sub> first resonant line was observed to be a slightly different among the co-doped crystals. This is due to the perturbation of Yb<sup>3+</sup> by co-doped rare earth ion which is located at the neighborhood of the Yb<sup>3+</sup>.

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## 1. Introduction

Among many kinds of oxide crystals doped with Yb<sup>3+</sup> ions, Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F and Sr<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F are selected as the favorable hosts for laser action, while LiNbO<sub>3</sub> (LN) is suggested as the most unfavorable one [1]. The LN crystal, however, is one of the useful optical materials because of its nonlinearity. Montoya et al. [2] obtained not only the 1060 nm Yb<sup>3+</sup> laser action with high efficiency of about 47% but also self-frequency doubled laser action using Yb<sup>3+</sup>/Mg<sup>2+</sup>-co-doped LN crystal. Jones et al. [3] achieved lasing with a slope efficiency of about 16% using Yb<sup>3+</sup>/Ti-co-doped LN waveguide. Co-doping is one of the methods to improve the laser efficiency of Yb<sup>3+</sup>-doped LN since the presence of additional impurity ions changes the ligand field of Yb<sup>3+</sup> in LN lattice and changes the electronic states of Yb<sup>3+</sup>. Therefore we are interesting in the spectral properties of Yb<sup>3+</sup>: LN crystals co-doped with rare-earth ions.

No systematic study has been undertaken on the influence of rare-earth ions to Yb<sup>3+</sup> ions in LN crystal. In this paper we investigate the absorption spectra of Yb<sup>3+</sup>:LN crystals co-doped with Pr<sup>3+</sup>, Nd<sup>3+</sup> and Er<sup>3+</sup> ions. It is interesting to investigate: (1) what kind of influence do the co-doped rare earth ions gives to Yb<sup>3+</sup> and (2) whether its influence depends on ionic radius of the co-doped rare earth ions. For this purpose, we check whether the positions of Yb<sup>3+</sup> absorption bands are different among various co-doped crystals. The ionic crystals usually contain OH<sup>-</sup> ions when they are doped with impurity ions such as transition-metal ion and rare-earth ions. It is interesting to study whether the presence of OH<sup>-</sup> ions changes among various co-doped rare earth ions.

We have also an interest on the effect of  $\gamma$ -ray irradiation on Yb<sup>3+</sup> ions. It was reported that Yb<sup>2+</sup> ions are created in Yb<sup>3+</sup>-doped CaF<sub>2</sub> crystal by  $\gamma$ -ray irradiation, giving rise to absorption bands in 200–380 nm range [4]. No report, however, has been made on a question whether such an Yb<sup>3+</sup> → Yb<sup>2+</sup> conversion occurs in LN crystal. Here attention is paid to clarify whether the effect of  $\gamma$ -ray irradiation on Yb<sup>3+</sup> depends on ionic radius and concentration of the co-doped rare earth ions.

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## 2. Experimental procedure

Single crystals were grown by the Czochralski method from a congruent melt at the Institute of Electronic Materials Technology, Warsaw. The conditions of growth were described elsewhere [5]. We studied the following seven LN crystals. Of these crystals, two crystals are not irradiated with  $\gamma$ -rays. The first non- $\gamma$ -rayed LN crystal contains about: 1 wt.%  $\text{Yb}^{3+}$  (called #4 crystal), and the second crystal contains 0.8 wt.%  $\text{Yb}^{3+}$  and 0.1 wt.%  $\text{Pr}^{3+}$  (#8 crystal). The #3 and #7 crystals which were  $\gamma$ -rayed are called #4 and #8 crystals, respectively. The other  $\gamma$ -rayed and co-doped LN crystals contain 0.5 wt.%  $\text{Yb}^{3+}$  ( $1.29 \times 10^{20}$  ions/cm<sup>3</sup>) and 0.3 wt.%  $\text{Nd}^{3+}$  ( $9.3 \times 10^{19}$  ions/cm<sup>3</sup>) (#9), 0.8 wt.%  $\text{Yb}^{3+}$  and 0.5 wt.%  $\text{Pr}^{3+}$  (#10), and 0.5 wt.%  $\text{Yb}^{3+}$  and 1 wt.%  $\text{Er}^{3+}$  (#11). The  $\gamma$ -ray irradiation was undertaken at room temperature from <sup>60</sup>Co source (with dose of  $10^5$ – $10^7$  Gy).

Unpolarized absorption spectra were measured with a Cary-5E spectrophotometer in a spectral range of 190–3100 nm at 16–300 K and with a Lambda-900 of Perkin-Elmer at room temperature. Photoluminescence measurements were carried out using a SS-900 Edinburgh Inc. spectrophotometer at the Institute of Optoelectronics, MUT, Poland.

## 3. Experimental results

### 3.1. Low temperature absorption spectra

Fig. 1 shows the absorption spectra of the #3, 4, 7, 8, 9, 10 and 11 crystals at 17 K in spectral range of 860–1020 nm where  $\text{Yb}^{3+}$  absorption bands appear. The spectra consist of intense and sharp absorption bands due to the  $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$  electronic transition and weak bands due to vibronic transitions. Such vibronic bands are observed in various  $\text{Yb}^{3+}$ -doped oxides [6–8]. The intense bands are observed at 918.5, 955 and about 980.3 nm. In the #9 crystal, ad-

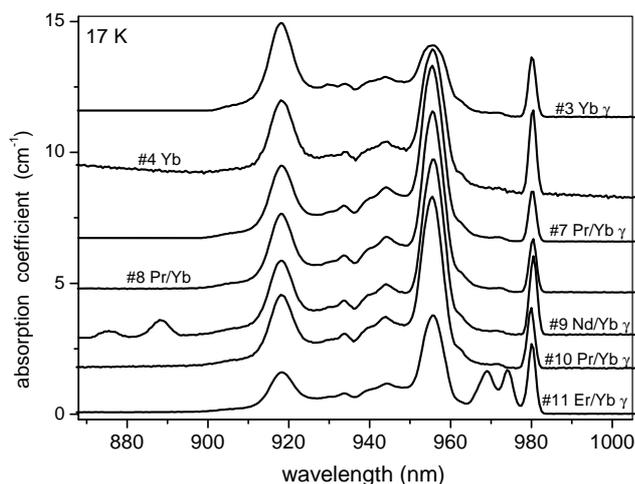


Fig. 1. Near infrared absorption spectra of  $\text{LiNbO}_3$  crystals #3, #4, #7, #8, #9, #10 and #11 at 17 K.

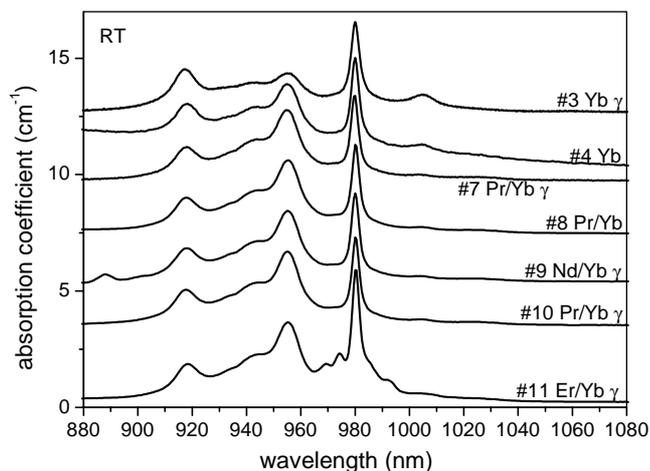


Fig. 2. Near infrared absorption spectra of  $\text{LiNbO}_3$  crystals #3, #4, #7, #8, #9, #10 and #11 crystals at room temperature (288 K).

ditional bands are observed at 875.6 and 888.5 nm. These are attributed to the  $^4\text{I}_{9/2} \rightarrow ^4\text{F}_{3/2}$  electronic transition of  $\text{Nd}^{3+}$ . Similarly additional bands are observed at 969.0 and 974.3 nm in the #11 crystal, which are due to the  $^4\text{I}_{5/2} \rightarrow ^4\text{F}_{11/2}$  transition of  $\text{Er}^{3+}$ , while in the #7, #8 and #10 crystals very weak bands are observed at 987.8, 1019, 1030 and 1057 nm, which are due to the  $^4\text{H}_4 \rightarrow ^4\text{G}_4$  transition of  $\text{Pr}^{3+}$ .

It is observed that the peak position of the sharp line at the lowest energy is different among the crystals. The single-doped crystals #3 and #4 have a peak at 979.7 nm, the  $\text{Pr}^{3+}$ -co-doped crystals #7, #8 and #10 have a peak at 979.8 nm, while the  $\text{Nd}^{3+}$ - and  $\text{Er}^{3+}$ -co-doped crystals #9 and #11 have peaks at 980.0 and 979.7 nm, respectively. The  $\text{Er}^{3+}$ -co-doped crystal seems to have the same peak position as the single-doped crystals. These positions are slightly different from each other—979.71 nm for the former crystal and 979.68 nm for the latter ones.

Fig. 2 shows the absorption spectra of the #3, 4, 7, 8, 9, 10 and 11 crystals at 288 K in spectral range of 870–1090 nm. Weak additional bands are observed at 1004, 1024 and 1060 nm in the absorption spectrum of all crystals. It is noted that the single-doped crystal #3 shows much higher absorption intensity for the 1004 nm band than the other crystals. The 1024 nm band consists of two bands with peak at 1024 and 1031 nm. The 1004, 1024 and 1060 nm bands appear above about 50, 80 and 170 K and their intensities increase with increasing temperature. Thus they are called hot bands. These hot bands have been observed by other scientists (see e.g. [9–11]). In Fig. 3, the absorption intensities of these bands observed in crystal #10 are plotted against temperature.

Fig. 4 shows the  $\text{OH}^-$  absorption band observed in various single and co-doped LN crystals. The measurement was undertaken at the same condition for these crystals. Much intense  $\text{OH}^-$  band is observed in not only  $\text{Pr}^{3+}$ -single doped crystal but also  $\text{Pr}^{3+}/\text{Yb}^{3+}$ -co-doped crystals. Of the

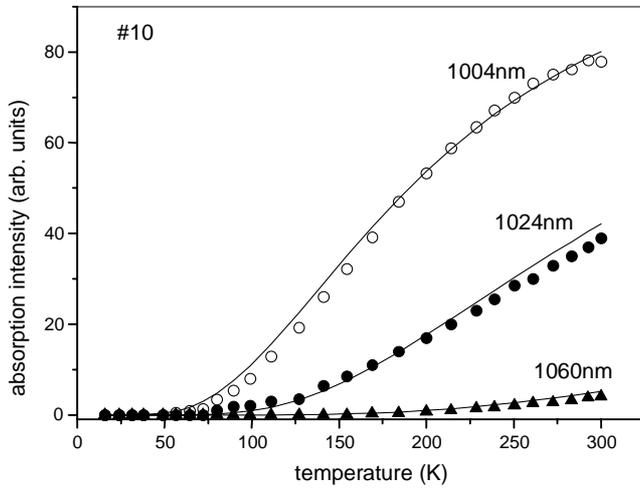


Fig. 3. Temperature dependence of the intensities of the 1004 nm (open circle), 1024 (closed circle) and 1060 nm (triangle) hot bands observed in the #10 crystal. Solid lines are the best fit to the experimental points (see text).

$\text{Pr}^{3+}/\text{Yb}^{3+}$ -co-doped crystals, crystal with higher  $\text{Pr}^{3+}$  concentration shows more intense band than crystal with lower  $\text{Pr}^{3+}$  concentration. When compared with the non-doped LN crystal, only the  $\text{Er}^{3+}$  single doped crystal shows a red shift in the  $\text{OH}^-$  band, while the other crystals show a blue shift.

### 3.2. Effect of $\gamma$ -ray irradiation

Oxygen vacancies are present in the LN lattice for charge compensation, because trivalent rare earth ion is substituted

for  $\text{Li}^+$  ion and  $\text{Nb}^{5+}$  ion. The  $\gamma$ -irradiation introduces electrons to the oxygen sites and F-type color centers are formed. At the same time  $\text{Nb}^{4+}$  polarons are created as an effect of Compton secondary electron capture. Fig. 5 shows the change of the absorption spectra between before and after  $\gamma$ -ray irradiation for non-doped,  $\text{Yb}^{3+}$ -doped, and  $\text{Yb}^{3+}/\text{Nd}^{3+}$ -co-doped LN crystals. A broad band is observed for all the crystals in a 200–700 nm region. The band has a peak at about 400 nm and a shoulder at about 500 nm. Such a double structure band was previously observed and the 400 and 500 nm bands have been attributed to F-type color center and  $\text{Nb}^{4+}$  polaron, respectively [12]. We could not observe any absorption band due to  $\text{Yb}^{2+}$ . This indicates that electrons created in LN host crystal by  $\gamma$ -ray irradiation are not trapped by  $\text{Yb}^{3+}$  ions. Same is true for co-doped rare earth ions such as  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$ .

The intensity of the 400 and 500 nm bands strongly depends on the  $\gamma$ -ray dose. The intensity increases with increasing the dose, but the increase stops above about  $10^6$  Gy. Of the various co-doped crystals,  $\text{Er}^{3+}$  co-doped crystal shows a much smaller increase in the 400 and 500 nm bands than the other co-doped crystals.

In  $\text{Yb}^{3+}/\text{Nd}^{3+}$ -co-doped crystal, a decrease of the  $\text{OH}^-$  absorption band at about 2870 nm is observed after  $\gamma$ -ray irradiation when compared with non-irradiated and non-doped LN crystal. We also measured the absorption spectra of  $\gamma$ -rayed  $\text{Yb}^{3+}/\text{Er}^{3+}$ - and  $\text{Yb}^{3+}/\text{Pr}^{3+}$ -co-doped LN crystals, and observed a decrease of the  $\text{OH}^-$  absorption band in  $\text{Yb}^{3+}/\text{Pr}^{3+}$ -co-doped crystal as observed in  $\text{Yb}^{3+}/\text{Nd}^{3+}$ -co-doped crystal.

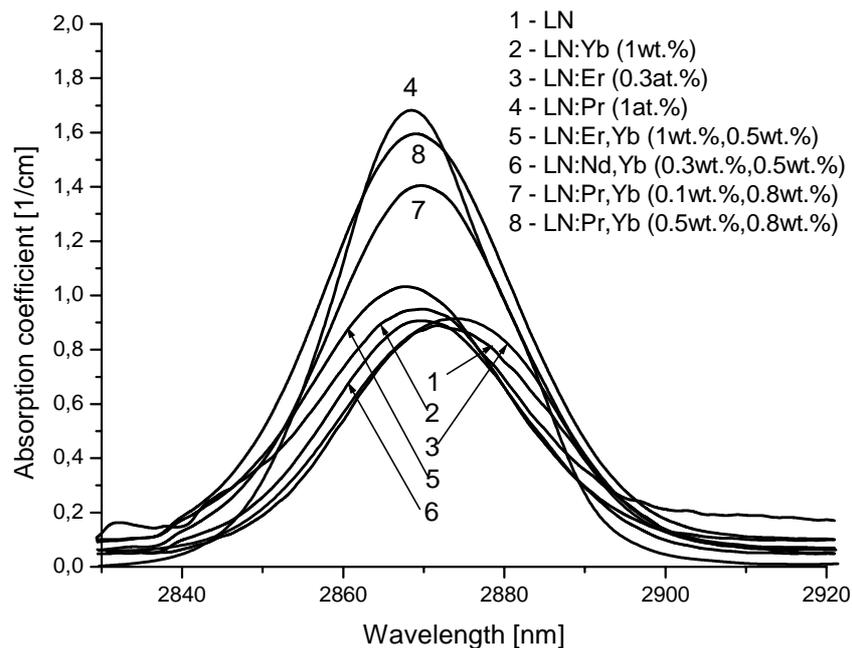


Fig. 4. The  $\text{OH}^-$  absorption band of various  $\text{LiNbO}_3$  (LN) crystals at room temperature. Non-doped LN (curve 1), LN: $\text{Yb}^{3+}$  (1 wt.%) (2), LN: $\text{Er}^{3+}$  (0.3 wt.%) (3), LN: $\text{Pr}^{3+}$  (1 wt.%) (4), LN: $\text{Er}^{3+}$ ,  $\text{Yb}^{3+}$  (1 and 0.5 wt.%) (5), LN: $\text{Nd}^{3+}$ ,  $\text{Yb}^{3+}$  (0.3 and 0.5 wt.%) (6), LN: $\text{Pr}^{3+}$ ,  $\text{Yb}^{3+}$  (0.1 and 0.8 wt.%) (7), and LN: $\text{Pr}^{3+}$ ,  $\text{Yb}^{3+}$  (0.5 and 0.8 wt.%) (8).

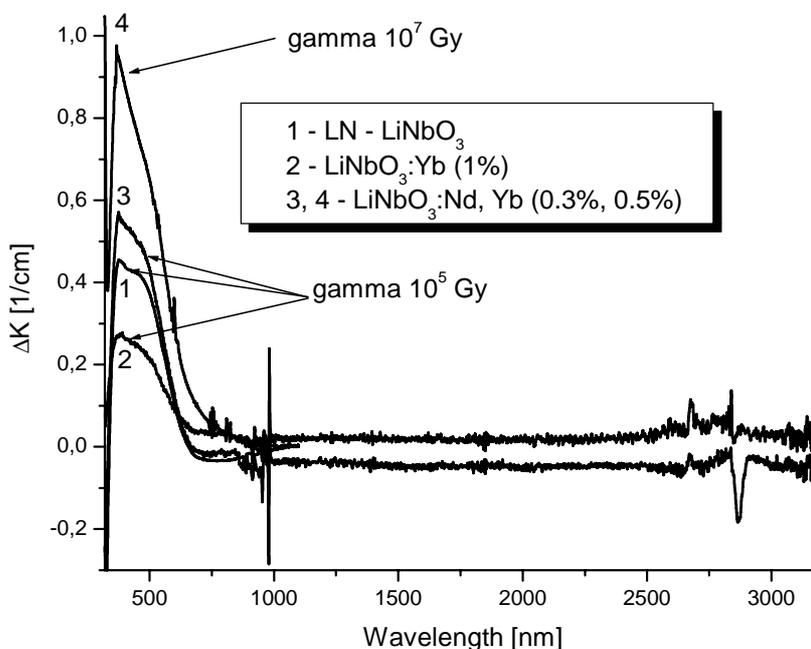


Fig. 5. Change of the absorption spectra ( $\Delta k$ ,  $k$ : absorption coefficient) between before and after  $10^5$  Gy  $\gamma$ -ray irradiation for  $\text{LiNbO}_3$  crystal without any rare-earth ions (curve 1), the #4 crystal (curve 2), and the #9 crystal (curve 3). Curve 4 shows for the #9 crystal after  $10^7$  Gy  $\gamma$ -ray irradiation.

#### 4. Discussion

As seen in Fig. 4, we observed the much higher  $\text{OH}^-$  absorption band intensity in  $\text{Pr}^{3+}$ -doped crystals and the increase of the intensity with increasing  $\text{Pr}^{3+}$  concentration. Why are the  $\text{Pr}^{3+}$ -doped crystals different from the other crystals? Electron spin resonance study shows that rare-earth ions enter both  $\text{Li}^+$  and/or  $\text{Nb}^{5+}$  lattice sites in  $\text{LiNbO}_3$  and the local symmetry is the same  $\text{C}_{3v}$  in the both cases [13]. The Rutherford back-scattering (RBS) study has suggested that they usually enter  $\text{Li}^+$  sites [14–16]. As an example, the  $\text{Nd}^{3+}$  ions are in  $\text{Li}^+$  octahedrons and located at off-center position along the  $c$ -axis. The ionic radii of  $\text{Yb}^{3+}$  and  $\text{Er}^{3+}$  ions are 0.858 and 0.881 nm in octahedral coordination, respectively. They are smaller than the ionic radius of the other rare earth ions. Therefore it is suggested that  $\text{Yb}^{3+}$  and  $\text{Er}^{3+}$  ions are substituted for  $\text{Li}^+$  ion with small ionic radius of 0.74 nm, while  $\text{Pr}^{3+}$  ion with large ionic radius of 1.013 nm is substituted for  $\text{Nb}^{5+}$  ion with much smaller ionic radius of 0.64 nm [5,6]. Such a substitution by much large ion leads to the deformed octahedrons and creation of positively charged defects of  $(\text{Pr}_{\text{Nb}^{5+}}^{3+})^{2+}$  type (where  $\text{Pr}_{\text{Nb}^{5+}}^{3+}$  means vacancy created by substitution of  $\text{Pr}^{3+}$  ion for  $\text{Nb}^{5+}$  ion) for charge compensation, giving rise to easy introduction of negatively charged  $\text{OH}^-$  ions during the crystal growth. Therefore we understand the increase of  $\text{OH}^-$  band in  $\text{Pr}^{3+}$ -doped crystals.

It was observed that the 400 and 500 nm band intensity is weaker in  $\text{Yb}^{3+}$ - and  $\text{Er}^{3+}$ -doped crystals than the other crystals. This is understood by the difference of ionic radius of rare earth ion. It is expected that, as the difference of ionic radius between rare earth ion and

substituted  $\text{Li}^+$  (or  $\text{Nb}^{5+}$ ) ion becomes large, the oxygen vacancies and color centers, which are responsible for the 400 and 500 nm bands, are more easily created by  $\gamma$ -irradiation. The ionic radii of  $\text{Yb}^{3+}$  and  $\text{Er}^{3+}$  are more close to those of  $\text{Li}^+$  and  $\text{Nb}^{5+}$  than those of  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$ , resulting in weaker 400 and 500 nm bands in  $\text{Yb}^{3+}$ - and  $\text{Er}^{3+}$ -doped crystals. Like this we confirm the influence of difference of ionic radius in the rare earth doped LN crystals.

Next we shall consider the  $\text{Yb}^{3+}$  absorption bands observed in 900–1080 nm region.  $\text{Yb}^{3+}$  ion has the ground state  $^2F_{7/2}$  and excited state  $^2F_{5/2}$ , which split into four and three levels in the  $\text{C}_{3v}$  symmetry crystal field, respectively. Fig. 6 shows the energy level diagram deduced from the absorption measurements. From the hot bands at 1004, 1024 and 1060 nm, it is determined that the first, second and third excited levels are at 241, 436 and 767  $\text{cm}^{-1}$  above the ground level, respectively, which are called levels 2, 3 and 4, while the three levels of the  $^2F_{5/2}$  state are called levels 5, 6 and 7 in order of increasing energy. We observed three emission bands at 1004, 1024 and 1060 nm in all the crystals by excitation with 980 nm light. The peak positions of these emission bands are the same as those of the hot absorption bands. These emission bands are attributed to the transition from the relaxed excited level of the  $^2F_{5/2}$  state (i.e. the level 5). In this way we confirmed the presence of the levels 2, 3 and 4 at 241, 436 and 767  $\text{cm}^{-1}$  above the ground level 1 in the  $^2F_{7/2}$  state, respectively.

It is suggested that the intensities  $I_i$  of the hot bands  $i$  are described by the following equation. It consists of two parts. One is the probability  $P_i$  of transition from the levels ( $i = 2, 3$  and 4) in the  $^2F_{7/2}$  state to the level 5 in the  $^2F_{5/2}$  state.

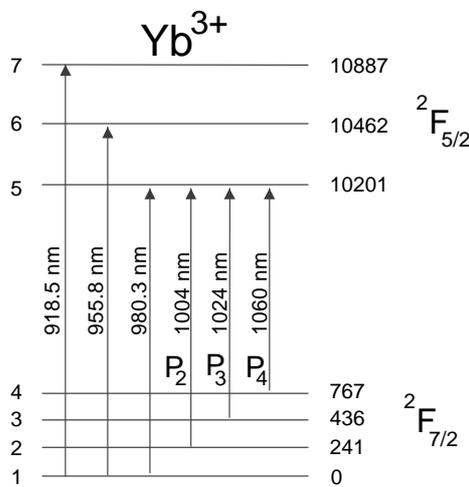


Fig. 6. The  $\text{Yb}^{3+}$  energy level diagram of the  ${}^2F_{7/2}$  and  ${}^2F_{5/2}$  states in the  $C_{3v}$  crystal field and the assignment for the observed absorption bands.  $P_2$ ,  $P_3$  and  $P_4$  are the transition probabilities from the levels 2, 3 and 4 to the level 5, respectively.

The other is the population of  $\text{Yb}^{3+}$  ions in the  $i$  level.

$$I_i \propto P_i \frac{\exp(-E_i/kT)}{\sum \exp(-E_i/kT)}, \quad i = 1, 4$$

where  $E_i$  is the energy measured from the level 1. The denominator is given as a normalization factor. The best fit to the experiment was obtained using  $P_2:P_3:P_4 = 0.745:1.0:0.6$  as shown by solid lines in Fig. 3. This indicates that the transition probability is different among the hot bands, i.e. the  $3 \rightarrow 5$  transition has higher transition probability than the other transitions. So far no work has been done on such a fitting for the hot bands in rare-earth doped crystals.

The absorption band peak due to the transition from the level 1 of  ${}^2F_{7/2}$  state to the level 5 of  ${}^2F_{5/2}$  state is observed at same 979.7 nm in crystals #3, 4, and 11, while at 980.0 nm in crystal #9 and 979.8 nm in crystals #7,8 and 10. No effect was observed on the peak position by  $\gamma$ -irradiation. Such a different position of the  $1 \rightarrow 5$  transition band is explained as follows. In the co-doped crystals, two kinds of  $\text{Yb}^{3+}$  ions are present, one is  $\text{Yb}^{3+}$  accompanied by nearby rare-earth ion such as  $\text{Nd}^{3+}$ , which is called perturbed  $\text{Yb}^{3+}$ , the other is  $\text{Yb}^{3+}$  which is located far from the rare-earth ion, which is called isolated  $\text{Yb}^{3+}$ . The energy levels of the perturbed  $\text{Yb}^{3+}$  are shifted from those of the isolated  $\text{Yb}^{3+}$ . Such a shift is observed in crystals #9 and #10. However, no shift is observed in crystals #7 and #8. The crystals #7 and #8 are co-doped with  $\text{Pr}^{3+}$  ions of much lower concentration than the crystal #10, i.e. presence of the perturbed  $\text{Yb}^{3+}$  ions is negligible. Therefore the  $1 \rightarrow 5$  absorption band in crystals

#7 and #8 is observed at the same position as in the crystals #3 and #4 containing only isolated  $\text{Yb}^{3+}$  ions.

## 5. Summary

Absorption spectra have been studied on  $\text{Yb}^{3+}$ -doped and  $\text{Yb}^{3+}/\text{Nd}^{3+}$ -,  $\text{Yb}^{3+}/\text{Er}^{3+}$ - and  $\text{Yb}^{3+}/\text{Pr}^{3+}$ -co-doped  $\text{LiNbO}_3$  single crystals to investigate the effect of co-doping and  $\gamma$ -irradiation.  $\text{Yb}^{2+}$  and  $\text{Yb}^{4+}$  ions which are converted from  $\text{Yb}^{3+}$  were not observed by the  $\gamma$ -irradiation. However, the intense 400 and 500 nm absorption bands were observed after  $\gamma$ -irradiation, which are due to the creation of oxygen vacancy (F-type color center) and  $\text{Nb}^{4+}$  polaron, respectively. Different change was observed in the 2870 nm  $\text{OH}^-$  absorption band intensity among the various rare-earth doped crystals. These are interpreted by discrepancy of ionic radii between substituting rare earth dopant ion and  $\text{Li}^+$  or  $\text{Nb}^{5+}$  host ion. The observed temperature dependence of the hot bands is understood by electronic transition from the thermally populated  ${}^2F_{7/2}$  Stark levels to the excited  ${}^2F_{5/2}$  level. The position of the  $\text{Yb}^{3+} {}^2F_{7/2} \rightarrow {}^2F_{5/2}$  first resonant line was a slightly different among the co-doped crystals. This is due to the perturbation of  $\text{Yb}^{3+}$  by co-doped rare earth ion which is located at the neighborhood of the  $\text{Yb}^{3+}$ .

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