

Spectral properties of Yb^{3+} ions in LiNbO_3 single crystals: influences of other rare-earth ions, OH^- ions, and γ -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^{3+} -doped and $\text{Yb}^{3+}/\text{Nd}^{3+}$ -, $\text{Yb}^{3+}/\text{Er}^{3+}$ - and $\text{Yb}^{3+}/\text{Pr}^{3+}$ -co-doped LiNbO_3 single crystals before and after γ -irradiation with a dose of 10^5 – 10^7 Gy. Intense 400 and 500 nm absorption bands were observed after γ -irradiation, which are due to the creation of oxygen vacancy (F-type color center) and Nb^{4+} polaron, respectively. Different change was observed in the 2870 nm 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 Li^+ or Nb^{5+} host ion. The observed temperature dependence of the hot bands is understood by electronic transition from the thermally populated $^2\text{F}_{7/2}$ Stark levels to the excited $^2\text{F}_{5/2}$ level. The position of the $\text{Yb}^{3+} + ^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ first resonant line was observed to be a slightly different among the co-doped crystals. This is due to the perturbation of Yb^{3+} by co-doped rare earth ion which is located at the neighborhood of the Yb^{3+} .

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Keywords: Spectral properties; Rare-earth ions; LiNbO_3 single crystals

1. Introduction

Among many kinds of oxide crystals doped with Yb^{3+} ions, $\text{Ca}_5(\text{PO}_4)_3\text{F}$ and $\text{Sr}_5(\text{PO}_4)_3\text{F}$ are selected as the favorable hosts for laser action, while LiNbO_3 (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^{3+} laser action with high efficiency of about 47% but also self-frequency doubled laser action using $\text{Yb}^{3+}/\text{Mg}^{2+}$ -co-doped LN crystal. Jones et al. [3] achieved lasing with a slope efficiency of about 16% using Yb^{3+}/Ti -co-doped LN waveguide. Co-doping is one of the methods to improve the laser efficiency of Yb^{3+} -doped LN since the presence of additional impurity ions changes the ligand field of Yb^{3+} in LN lattice and changes the electronic states of Yb^{3+} . Therefore we are interesting in the spectral properties of Yb^{3+} : LN crystals co-doped with rare-earth ions.

No systematic study has been undertaken on the influence of rare-earth ions to Yb^{3+} ions in LN crystal. In this paper we investigate the absorption spectra of Yb^{3+} :LN crystals co-doped with Pr^{3+} , Nd^{3+} and Er^{3+} ions. It is interesting to investigate: (1) what kind of influence do the co-doped rare earth ions gives to Yb^{3+} 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^{3+} absorption bands are different among various co-doped crystals. The ionic crystals usually contain OH^- 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^- ions changes among various co-doped rare earth ions.

We have also an interest on the effect of γ -ray irradiation on Yb^{3+} ions. It was reported that Yb^{2+} ions are created in Yb^{3+} -doped CaF_2 crystal by γ -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 $\text{Yb}^{3+} \rightarrow \text{Yb}^{2+}$ conversion occurs in LN crystal. Here attention is paid to clarify whether the effect of γ -ray irradiation on Yb^{3+} 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 γ -rays. The first non- γ -rayed LN crystal contains about: 1 wt.% Yb^{3+} (called #4 crystal), and the second crystal contains 0.8 wt.% Yb^{3+} and 0.1 wt.% Pr^{3+} (#8 crystal). The #3 and #7 crystals which were γ -rayed are called #4 and #8 crystals, respectively. The other γ -rayed and co-doped LN crystals contain 0.5 wt.% Yb^{3+} (1.29×10^{20} ions/cm³) and 0.3 wt.% Nd^{3+} (9.3×10^{19} ions/cm³) (#9), 0.8 wt.% Yb^{3+} and 0.5 wt.% Pr^{3+} (#10), and 0.5 wt.% Yb^{3+} and 1 wt.% Er^{3+} (#11). The γ -ray irradiation was undertaken at room temperature from ⁶⁰Co 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 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 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-

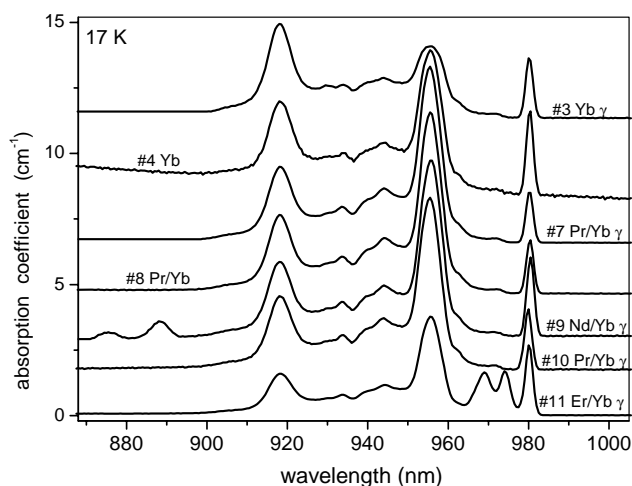


Fig. 1. Near infrared absorption spectra of LiNbO_3 crystals #3, #4, #7, #8, #9, #10 and #11 at 17 K.

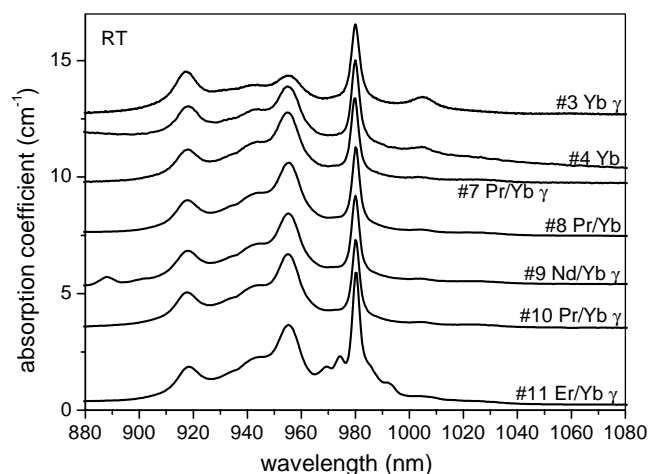


Fig. 2. Near infrared absorption spectra of LiNbO_3 crystals #3, #4, #7, #8, #9, #10 and #11 crystals at room temperature (288 K).

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 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 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 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 Pr^{3+} -co-doped crystals #7, #8 and #10 have a peak at 979.8 nm, while the Nd^{3+} - and Er^{3+} -co-doped crystals #9 and #11 have peaks at 980.0 and 979.7 nm, respectively. The 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 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 OH^- band is observed in not only Pr^{3+} -single doped crystal but also $\text{Pr}^{3+}/\text{Yb}^{3+}$ -co-doped crystals. Of the

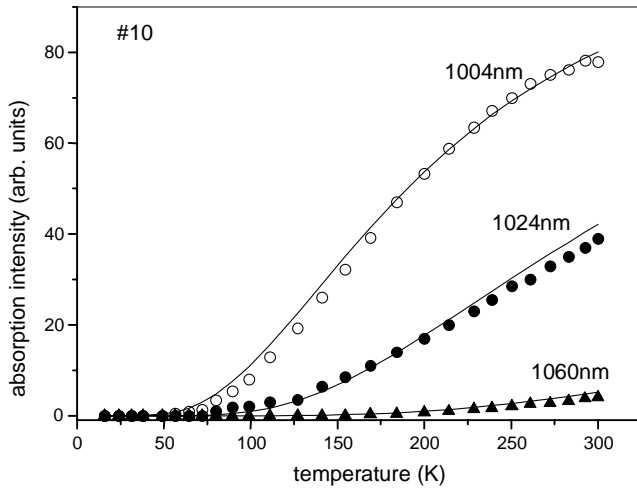


Fig. 3. Temperature dependence of the intensities of the 1004 nm (open circle), 1024 (closed circle) and 1060 nm (triangle) hot bands observed in the #10 crystal. Solid lines are the best fit to the experimental points (see text).

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

3.2. Effect of γ -ray irradiation

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

for Li^+ ion and Nb^{5+} ion. The γ -irradiation introduces electrons to the oxygen sites and F-type color centers are formed. At the same time 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 γ -ray irradiation for non-doped, 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 Nb^{4+} polaron, respectively [12]. We could not observe any absorption band due to Yb^{2+} . This indicates that electrons created in LN host crystal by γ -ray irradiation are not trapped by Yb^{3+} ions. Same is true for co-doped rare earth ions such as Pr^{3+} and Nd^{3+} .

The intensity of the 400 and 500 nm bands strongly depends on the γ -ray dose. The intensity increases with increasing the dose, but the increase stops above about 10^6 Gy. Of the various co-doped crystals, 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 OH^- absorption band at about 2870 nm is observed after γ -ray irradiation when compared with non-irradiated and non-doped LN crystal. We also measured the absorption spectra of γ -rayed $\text{Yb}^{3+}/\text{Er}^{3+}$ - and $\text{Yb}^{3+}/\text{Pr}^{3+}$ -co-doped LN crystals, and observed a decrease of the 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.

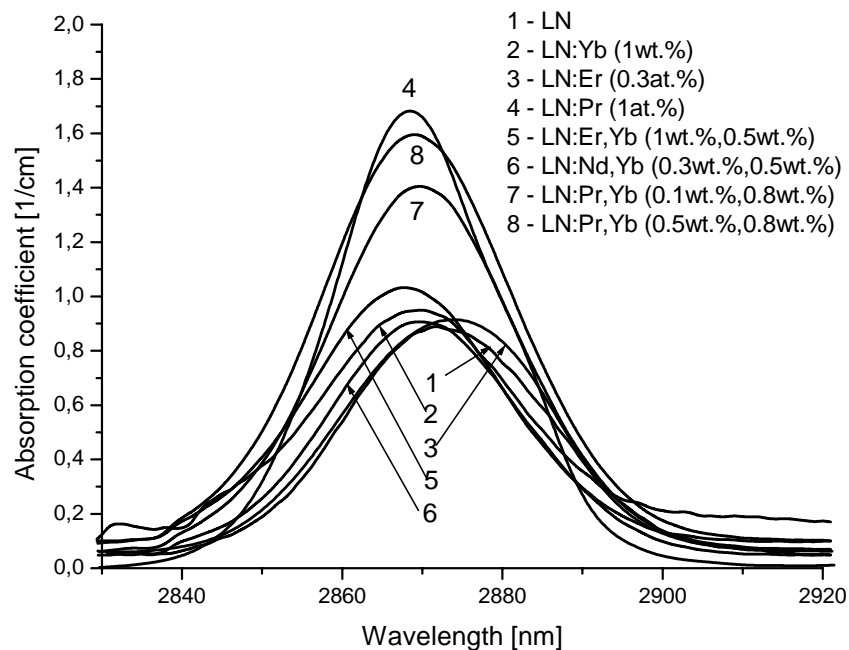


Fig. 4. The OH^- absorption band of various LiNbO_3 (LN) crystals at room temperature. Non-doped LN (curve 1), $\text{LN}:\text{Yb}^{3+}$ (1 wt.%) (2), $\text{LN}:\text{Er}^{3+}$ (0.3 wt.%) (3), $\text{LN}:\text{Pr}^{3+}$ (1 wt.%) (4), $\text{LN}:\text{Er}^{3+}$, Yb^{3+} (1 and 0.5 wt.%) (5), $\text{LN}:\text{Nd}^{3+}$, Yb^{3+} (0.3 and 0.5 wt.%) (6), $\text{LN}:\text{Pr}^{3+}$, Yb^{3+} (0.1 and 0.8 wt.%) (7), and $\text{LN}:\text{Pr}^{3+}$, Yb^{3+} (0.5 and 0.8 wt.%) (8).

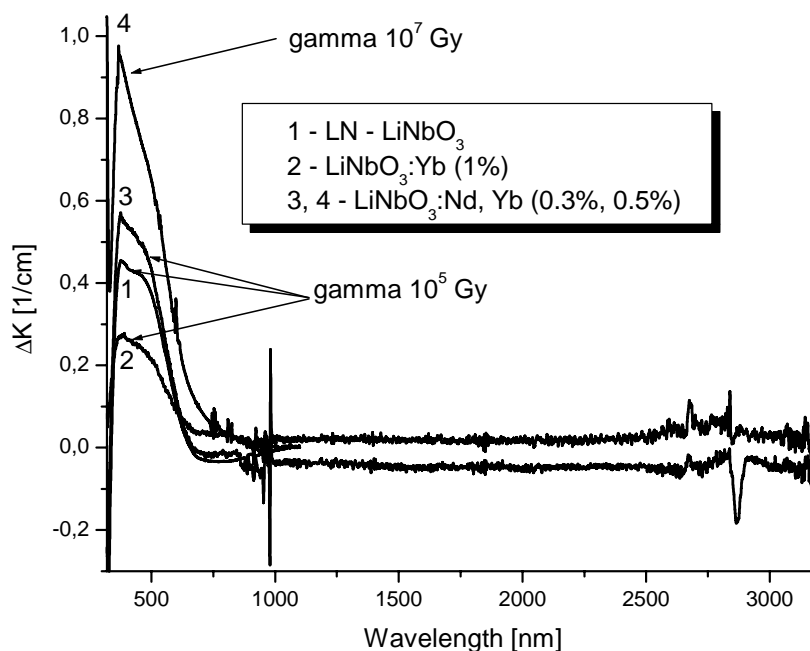


Fig. 5. Change of the absorption spectra (Δk , k : absorption coefficient) between before and after 10^5 Gy γ -ray irradiation for LiNbO₃ crystal without any rare-earth ions (curve 1), the #4 crystal (curve 2), and the #9 crystal (curve 3). Curve 4 shows for the #9 crystal after 10^7 Gy γ -ray irradiation.

4. Discussion

As seen in Fig. 4, we observed the much higher OH⁻ absorption band intensity in Pr³⁺-doped crystals and the increase of the intensity with increasing Pr³⁺ concentration. Why are the Pr³⁺-doped crystals different from the other crystals? Electron spin resonance study shows that rare-earth ions enter both Li⁺ and/or Nb⁵⁺ lattice sites in LiNbO₃ and the local symmetry is the same C_{3v} in the both cases [13]. The Rutherford back-scattering (RBS) study has suggested that they usually enter Li⁺ sites [14–16]. As an example, the Nd³⁺ ions are in Li⁺ octahedrons and located at off-center position along the *c*-axis. The ionic radii of Yb³⁺ and Er³⁺ 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 Yb³⁺ and Er³⁺ ions are substituted for Li⁺ ion with small ionic radius of 0.74 nm, while Pr³⁺ ion with large ionic radius of 1.013 nm is substituted for Nb⁵⁺ 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 (Pr_{Nb5+³⁺})²⁺ type (where Pr_{Nb5+³⁺} means vacancy created by substitution of Pr³⁺ ion for Nb⁵⁺ ion) for charge compensation, giving rise to easy introduction of negatively charged OH⁻ ions during the crystal growth. Therefore we understand the increase of OH⁻ band in Pr³⁺-doped crystals.

It was observed that the 400 and 500 nm band intensity is weaker in Yb³⁺- and Er³⁺-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 Li⁺ (or Nb⁵⁺) ion becomes large, the oxygen vacancies and color centers, which are responsible for the 400 and 500 nm bands, are more easily created by γ -irradiation. The ionic radii of Yb³⁺ and Er³⁺ are more close to those of Li⁺ and Nb⁵⁺ than those of Pr³⁺ and Nd³⁺, resulting in weaker 400 and 500 nm bands in Yb³⁺- and Er³⁺-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 Yb³⁺ absorption bands observed in 900–1080 nm region. Yb³⁺ ion has the ground state ²F_{7/2} and excited state ²F_{5/2}, which split into four and three levels in the 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 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 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.

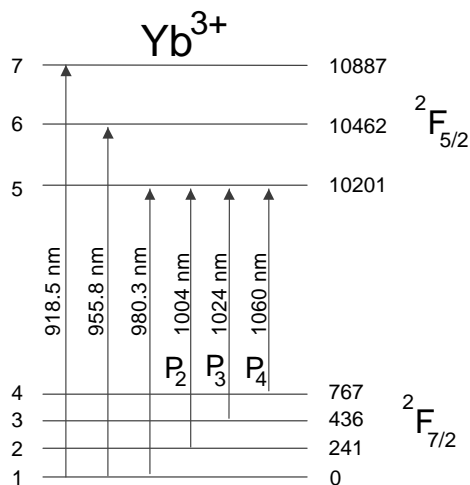


Fig. 6. The Yb³⁺ energy level diagram of the ²F_{7/2} and ²F_{5/2} states in the C_{3v} crystal field and the assignment for the observed absorption bands. P₂, P₃ and P₄ are the transition probabilities from the levels 2, 3 and 4 to the level 5, respectively.

The other is the population of Yb³⁺ 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 γ -irradiation. Such a different position of the $1 \rightarrow 5$ transition band is explained as follows. In the co-doped crystals, two kinds of Yb³⁺ ions are present, one is Yb³⁺ accompanied by nearby rare-earth ion such as Nd³⁺, which is called perturbed Yb³⁺, the other is Yb³⁺ which is located far from the rare-earth ion, which is called isolated Yb³⁺. The energy levels of the perturbed Yb³⁺ are shifted from those of the isolated Yb³⁺. 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 Pr³⁺ ions of much lower concentration than the crystal #10, i.e. presence of the perturbed Yb³⁺ 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 Yb³⁺ ions.

5. Summary

Absorption spectra have been studied on Yb³⁺-doped and Yb³⁺/Nd³⁺-, Yb³⁺/Er³⁺- and Yb³⁺/Pr³⁺-co-doped LiNbO₃ single crystals to investigate the effect of co-doping and γ -irradiation. Yb²⁺ and Yb⁴⁺ ions which are converted from Yb³⁺ were not observed by the γ -irradiation. However, the intense 400 and 500 nm absorption bands were observed after γ -irradiation, which are due to the creation of oxygen vacancy (F-type color center) and Nb⁴⁺ polaron, respectively. Different change was observed in the 2870 nm 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 Li⁺ or Nb⁵⁺ 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 Yb³⁺ 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 Yb³⁺ by co-doped rare earth ion which is located at the neighborhood of the Yb³⁺.

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