Multifrequency spectroscopy of laser active centers Nd\(^{3+}\)
and Yb\(^{3+}\) in nearly stoichiometric LiNbO\(_3\)

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1 Introduction

For many years Lithium Niobate (LN) has been of great interest for both fundamental science and applications because of the unusual richness of its ferro-, pyro- and piezoelectric properties. Conventional LN crystals, grown from a congruent melt with lithium deficiency (X\(_\text{melt}\) = X\(_\text{Crystal}\) \(\approx\) 48.4\%, where X = [Li]/([Li]+[Nb]), contain some percent of intrinsic (non-stoichiometric) defects and, consequently, have strong structural disorder. Crystals grown under special conditions from melts, to which potassium has been added, have extremely low intrinsic defect concentrations. These samples, called stoichiometric, have significantly decreased widths of spectral lines. This leads to the increased resolution of the optical and EPR/ENDOR spectra.

The laser systems LiNbO\(_3\):Nd\(^{3+}\) (LN:Nd) and LiNbO\(_3\):Yb\(^{3+}\) (LN:Yb) are extensively studied by different methods beginning 1967. Since spectroscopic and gain properties of a solid state laser strongly depend on the location of the active ions in the host material, numerous publications were devoted to the study of neodymium and ytterbium location and surrounding. First investigations of LN:Nd have revealed one [1] and two [2] different Nd\(^{3+}\) centers. Later on, a resolution enhancement allowed to distinguish three [3] and even more [4, 5] NEC. It is remarkable that according to independent experiments - Rutherford backscattering spectrometry (RBS) in combination with channeling [6, 7] and extended X-ray absorption fine structure (EXAFS) [8, 9] – the Nd\(^{3+}\) ions substitute for Li\(^{+}\) in all NEC with slightly different displacement from the Li lattice site. The presence of NEC has been related to the defects associated with non-stoichiometry of LN. Similar results were also obtained for LN:Yb system [1, 4, 5, 10–12].

In order to obtain additional information about neodymium and ytterbium centers we carried out the multifrequency EPR/ENDOR study of LN:Nd and LN:Yb crystals of different composition.

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2 Crystals, equipment  Two sets of the samples, grown by the Czochralski method and doped with Nd$_2$O$_3$ or Yb$_2$O$_3$ in the melt, were used. One set of the crystals was grown from a congruent melt; another set was grown under special conditions from the melt with the addition of potassium, leading to Li-rich or nearly stoichiometric samples [13, 14]. Strong blue shift of the absorption edge (about 15-16 nm for the absorption level equal to 20 cm$^{-1}$) was observed in samples grown from melts with potassium. It indicates that these samples have significantly reduced concentration of intrinsic defects (nearly stoichiometric composition).

The EPR/ENDOR measurements were carried out in the temperature range $T=4.2-50$ K by means of Bruker ELEXSYS 560 operating in X- and Q-bands (9.8 and 34.4-35 GHz).

3 The EPR spectra of congruent and stoichiometric samples  Multiband structures of optical absorption were observed in both congruent and nearly stoichiometric crystals. The overlapped bands had nearly the same widths in all samples. In contrast to optical spectra, line widths of observed EPR spectra for congruent and nearly stoichiometric samples (Fig. 1) are completely different. Depending on magnetic field orientation the line widths of Nd$^{3+}$ and Yb$^{3+}$ signals were about 10-15 mT in congruent samples and 1.5-2.5 mT in stoichiometric ones. The EPR lines in congruent samples are so broad that it is too difficult to separate lines of different centers and isotopes (this is the main reason why hyperfine structures were not studied earlier [1, 2]).

![Fig. 1 The assignment of the EPR lines of different Yb$^{3+}$ NEC (nonmagnetic isotopes with nuclear spin $I$ = 0) and hyperfine structures for the isotopes $^{171}$Yb (two vertical bars indicate the estimated line positions) and $^{173}$Yb (six bars) in congruent and nearly stoichiometric LN. $T$ = 8 K.](image-url)

The tremendous narrowing of the EPR lines in Li-rich and nearly stoichiometric samples leads to significant enhancement of spectral resolution. This allowed to distinguish several NEC and to study hyperfine interaction of impurity electrons with nuclear magnetic moments of magnetic isotopes $^{171}$Yb and $^{173}$Yb (Fig. 2) and $^{143}$Nd, $^{145}$Nd [15–17]. Ytterbium has two stable isotopes with non-zero magnetic moment: $^{171}$Yb ($I$ = 1/2, natural abundance 14.4%) and $^{173}$Yb ($I$ = 5/2, 16.2%). Therefore, each magnetically non-equivalent center Yb$^{3+}$ (electron spin $S$ = 1/2) creates 9 EPR lines: one strong line caused by all non-magnetic isotopes, one hyperfine doublet and one sextet. Expected relative intensities of the lines of all non-magnetic isotopes, $^{171}$Yb and $^{173}$Yb are 1:0.1:0.04. At an arbitrary orientation of external magnetic field, every electrically non-equivalent Yb$^{3+}$ center can produce 9 (axial $C_3$-center) or 54 (low-symmetry $C_1$ center) EPR lines. The lines of the $C_3$ centers merge partly at special magnetic field orientation. Using this information facilitates deciphering and interpretation of the EPR spectra.
4 Multifrequency EPR investigations

The multifrequency EPR investigations have many advantages, especially, for the paramagnetic centers with electron spin $S = 1/2$ (like Nd$^{3+}$ and Yb$^{3+}$ ions). Using higher magnetic fields for Q- or W-band measurements leads to larger splitting between lines of different centers and to better accuracy of the g-factor determination. It helps also to clarify mechanisms of the EPR line broadening.

For Nd$^{3+}$ and Yb$^{3+}$ ions there are several basic mechanisms of line broadening: spin-lattice relaxation (this mechanism is very important at high temperatures and negligible at liquid helium temperatures), hyperfine interactions (they do not depend on crystal composition), and a distribution of local fields due to crystal imperfections (this mechanism leads to a distribution of g-factors for Nd$^{3+}$ and Yb$^{3+}$). Since line widths for the Q-band EPR spectra were significantly larger than for the X-band EPR spectra (Fig. 2), we can conclude that some crystal imperfections are still present even in nearly stoichiometric samples.

The line broadening caused by g-factor distribution has lead to remarkable simplification of the Q-band EPR spectra – hyperfine satellite lines have practically disappeared. The simplification allowed easily recognizing of NEC lines for non-magnetic isotopes. However, it was very difficult to obtain information about hyperfine structure from the Q-band spectra. Therefore, using the X-band spectra with narrow EPR lines is preferable for the study of hyperfine interactions.

Fig. 2 The assignment of the lines of different Nd$^{3+}$ NEC in nearly stoichiometric LN. Positions of outermost lines for nonmagnetic isotopes of the NEC in X- and Q-bands are marked by dots. Lines of hyperfine structure of magnetic isotopes $^{145}$Nd and $^{143}$Nd, which are clearly resolved in X-band spectrum (they are indicated by two sets of eight vertical bars), are practically disappeared in Q-band spectrum. The spectra were measured at $B||x$, $T = 19$ K.

5 Multifrequency ENDOR study

Using higher magnetic fields in the Q-band measurements also leads to significant simplification of the ENDOR spectra. Due to increased distance between Larmor frequencies of $^7$Li and $^{89}$Nb nuclei there is no overlapping of their lines (Fig. 3). This facilitates line recognizing and angular dependence tracing. However, due to different observation conditions and different ratios of electron and nuclear spin-relaxation times the ENDOR signal for definite nuclei is sometimes stronger in one of these bands. For instance, very pronounced lines of $^{89}$Nb nuclei were found in the X-band ENDOR spectra for Yb$^{3+}$, but they were not observed in the Q-band spectra. The multifrequency investigations can give complementary data for deciphering and interpretation of the ENDOR spectra.
Non-equivalent centers and angular dependencies of the EPR spectra

The ideal LN lattice (see Fig. 1 in Ref. [14]) has two LiNbO$_3$ molecules in its rhombohedral elementary unit cell, and the space group symmetry is R3c [18, 19]. Two types of centers are admissible in this lattice [20]: the center with C$_3$ point group symmetry (in the following also labeled an “axial” center) and low-symmetry C$_1$ center. Positions of the axial center lines do not change when magnetic field rotates in the plane perpendicular to the crystal C$_3$ axis (xy plane), whereas the EPR lines of the C$_1$ centers have specific angular dependencies with 60° repetition (every C$_1$ center has six magnetically non-equivalent partners). Figure 4 clearly shows the difference of angular dependencies for the C$_3$ and C$_1$ centers. The EPR lines of low-symmetry centers are also split at the deviation of magnetic field direction from z-axis. Any proposed model for an impurity center must be compatible with the center symmetry determined from the angular dependencies. The simplest models the C$_3$ and C$_1$ centers are indicated on Fig. 4.

No splitting of the most intense line (center Nd$_1$) was found at any arbitrary orientation of external magnetic field relative to crystal axes. The center has axial C$_3$ symmetry, since a position of the Nd$_1$ line does not change when magnetic field rotates in the plane perpendicular to the crystal axis. The lines of Nd$_2$, Nd$_3$ and Nd$_4$ split at the deviation of magnetic field direction from z-axis. Therefore, they are low-symmetry C$_1$ centers. Among five observed Yb$^{3+}$ centers the most intense Yb$_1$ and the least intense Yb$_5$ centers have axial symmetry, the Yb$_2$-Yb$_4$ centers have C$_1$ symmetry.

The ENDOR spectra and center models

The narrow EPR lines in stoichiometric samples allowed investigating ENDOR on one selected line only (instead of the mixture of overlapping lines). This makes the identification of the ENDOR lines more reliable.

In the ENDOR spectrum of axial Yb$_1$ center we found a strong nearly equidistant multiplet, which does not split at any relative orientation of external magnetic field and studied crystal. It means that this multiplet is related to the nearest $^{93}$Nb nucleus on the C$_3$ axis. From this observation and the axial center symmetry we can conclude that Yb$^{3+}$ substitutes for Li$^+$, and has no intrinsic defects in the nearest neighborhood. In the low symmetry Yb$_2$ - Yb$_4$ centers the ytterbium also substitutes for Li. However, the centers have some defect in the surrounding (probably, lithium vacancy).

The observed ENDOR lines of the first and second shells of Li nuclei and their angular dependencies were described with the help of similar model for Nd$_1$: Nd$^{3+}$ substitutes for Li$^+$ (Fig. 5).
Fig. 4  Angular dependencies of the EPR spectra in nearly stoichiometric LN:Nd$^{3+}$ (Q-band) and LN:Yb$^{3+}$ X-band.

Fig. 5  Typical ENDOR spectrum of nearly stoichiometric LN:Nd$^{3+}$, a high-frequency fragment of angular dependence of the ENDOR spectra, a proposed model of axial Nd$^{3+}$ center and correspondence of observed ENDOR lines and shells of lithium nuclei (indicated by arrows). $T = 19$ K, Q-band, $B = 821$ mT.
Conclusion

The presence of nonequivalent centers manifests itself in both optical and EPR spectra. In studied samples grown from melts with potassium the observed EPR lines are ten times narrower than for congruent samples, and the concentration of intrinsic defects in the bulk is significantly reduced. Therefore, stoichiometric LN: Nd\textsuperscript{3+} and LN: Yb\textsuperscript{3+} can be considered as promising materials for the construction of high efficiency lasers with frequency doubling [21].

Using multifrequency EPR/ENDOR investigations facilitates deciphering and interpretation of observed spectra. The lattice positions of the Nd\textsuperscript{3+} and Yb\textsuperscript{3+} ions derived from the EPR and ENDOR data are in agreement with results of the cited above RBS, EXAFS and optical studies. The EPR/ENDOR data have led to noteworthy progress in the determination of the surrounding of Nd\textsuperscript{3+} and Yb\textsuperscript{3+} in LN.

Carried out study of the laser active impurity defects on the atomic level is important and helpful for fundamental and applied science, as well as for theoretical calculations [22].

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References