Abstract. The strong dependence of the properties of ferroelectric lithium niobate crystals on the concentration of intrinsic (non-stoichiometric) and extrinsic (impurity) defects is analyzed. Spectra of optical absorption and magnetic resonance spectroscopy are compared for crystals with different compositions. The results show clearly that the possibility to vary the concentration of intrinsic defects offers extraordinary informative opportunities for the investigation of the fundamental physics of the material.

INTRODUCTION

The fast development of opto- and acoustoelectronics as well as photonics requires new ferroelectric materials with improved characteristics. Sometimes the requested quality or parameters can be successfully achieved with a well-known, commonly used material, if its defect system is changed in a prescribed way.

In 1960-1980, the conventional, congruent lithium niobate (LiNbO$_3$, LN) was considered to be a well-known and well-characterized crystal. Conventional LN crystals, grown from a congruent melt with lithium deficiency ($X_{melt} = X_{Crystal} \approx 48.4\%$, where $X = [Li]/([Li]+[Nb])$), contain a rather large percentage of intrinsic (non-stoichiometric) defects.

About 10 years ago, our group found a method to obtain LN crystals with a strongly reduced concentration of intrinsic defects [1, 2]. These samples are often called Li-rich, nearly stoichiometric or stoichiometric crystals. The most perfect among them represent regularly ordered crystals (ROC) [3] or are very close to them. We predicted that such crystals should have properties, which are quite different from those of congruent crystals [4, 5]. This suggestion had considerable impact leading to some kind of revolution in understanding the new and very rich possibilities of stoichiometric materials. Strong changes of crystal properties with the decrease of the concentration of intrinsic defects were found: a tremendous narrowing of spectral lines and corresponding increase of spectral resolution, 5-100 times lower electric field for domain switching, two order slower rate of carrier recombination, two order higher sensitivity to holographic recording, non-linear dependence of the ultraviolet absorption edge on crystal composition, different dynamical mechanical properties etc. [6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16].

Several ways to obtain crystals with low concentrations of intrinsic defects have been developed up to now: growth from melts with Li excess (up to $X_{melt}=60\%$) [17, 18],...
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post-growth vapor transport equilibration (VTE) treatment \(^{[19,20]}\), growth from melts, to which potassium has been added \(^{[1,21]}\) (later on labeled LN\(_{(K)}\)), pulse laser deposition, micropulling down, laser heated pedestal growth etc.

Here we report results of our study of LN crystals by Electron Paramagnetic Resonance (EPR), Electron Nuclear Double Resonance (ENDOR) and optical absorption; these are the most sensitive and informative tools for the study of defect structures. Our goals are to demonstrate the strong dependence of the properties of LN on intrinsic and extrinsic defects and to present spectroscopic data, which could be used as cornerstones for theoretical calculations.

**COMPARISON OF SPECTRA OF CONGRUENT AND STOICHIOMETRIC CRYSTALS**

LN crystals with a very wide range of compositions (from \(x_C \approx 46\%\) to \(x_C \approx 50\%\), doped with different divalent and trivalent impurities, were studied. Below we shall present typical data mainly for congruent \(x_C = 48.4\%\) and stoichiometric LN\(_{(K)}\) with \(x_C \approx 50\%\) doped with Cr\(^{3+}\) or Fe\(^{3+}\) as paramagnetic probes.

Optical absorption spectra of congruent and LN\(_{(K)}\) samples doped with 1 wt.% of Cr are presented in Fig. 1. We observed also a strong blue shift of the fundamental absorption edge for LN\(_{(K)}\) doped with 0.01 and 0.1 wt.% of Cr. This reflects a decrease of the intrinsic defect content in LN\(_{(K)}\) crystals at low levels of chromium doping.

**FIGURE 1.** Optical absorption spectra of Cr doped crystals at room temperature. Light propagation along \(y\) axis, light polarization \(E||z\).

Three broad bands centered approximately at 340, 490 and 660 nm definitely increase with the rise of the Cr concentration. We supposed that the band at 660 nm
could serve as the reference band for the characterization of the concentration of the well-known Cr$_1^{3+}$ centers, which are always observed in congruent crystals. The appearance of a new band near 500-550 nm in the LN$_{(K)}$ sample has to be attributed to other Cr$_3^{3+}$ centers. The concentration of the centers responsible for the absorption at 530 nm in stoichiometric LN$_{(K)}$ sample is several times higher than in congruent sample. To determine definitely the origin of the new optical band and the structure of centers responsible for it, we carried out EPR (Fig. 2) and ENDOR studies of these samples.

![EPR spectra of Cr$_3^{3+}$ and Fe$_3^{3+}$ in stoichiometric and congruent LN.](image)

**FIGURE 2.** The EPR spectra of Cr$_3^{3+}$ and Fe$_3^{3+}$ in stoichiometric and congruent LN.

In congruent LN crystals doped with chromium only the centers with zero-field splitting $\Delta = |2b_2^0| \approx 0.8$ cm$^{-1}$ were observed. In stoichiometric crystals a new group of three EPR lines with a twenty times smaller splitting was registered. The new lines belong to another Cr$_3^{3+}$ center, we labeled it Cr$_{10}^{3+}$. Since a similar appearance of two new Fe$_3^{3+}$ centers was also registered for iron doped stoichiometric crystals (Fig. 2), we can conclude that the structure of impurity centers depends on the concentration of intrinsic defects.

The temperature dependence of the axial crystal field parameters $b_2^0$ for Cr$_1^{3+}$ and Cr$_{10}^{3+}$ centers has an opposite behavior (Fig. 3). In ferroelectric crystals the temperature dependence of the spin-Hamiltonian parameters can often be caused by the lattice transformation due to the phase transition. LN has such a transition from the ferroelectric R3c to the paraelectric R$\bar{3}$c one at $T_C \approx 1200$ C. The observed smooth dependence $b_2^0(T)$ for Cr$_{1}^{3+}$ can originate from this transition [22]. However, in the temperature range between 4.2 and 400 K there are practically no changes of the
positions of lattice ions, therefore, the disappearance of the axial crystal field for \( \text{Cr}_{10}^{3+} \) is related to the ion movements in the nearest surrounding of the Cr impurity.

**FIGURE 3.** Temperature dependence of the axial crystal field parameter \( b_2^0 \) for \( \text{Cr}_1^{3+} \) and \( \text{Cr}_{10}^{3+} \).

The ENDOR data gave us information about the hyperfine interactions of the chromium electrons with the surrounding nuclei and helped to determine the structures of these two centers \([23, 24]\) in a final way. The models of the \( \text{Cr}_1^{3+} \) and \( \text{Cr}_{10}^{3+} \) centers are completely different (Fig. 4). In the first case \( \text{Cr}^{3+} \) substitutes \( \text{Li}^+ (\text{Cr}_1 \text{Li}^{3+}) \) and has an excess of positive charge, which can be compensated by intrinsic defects, like Nb and Li vacancies. These vacancies can be located very far from \( \text{Cr}^{3+} \) (distant compensation, the case of axial center \( \text{Cr}_1^{3+} \)) or in the nearest neighborhood (local compensation, low-symmetry centers \([25]\)). In the second case the \( \text{Cr}^{3+} \) ion replaces \( \text{Nb}^{5+} \) and is negatively charged relative to the regular lattice. The used procedure for the growth of LN(K) crystals reduces the concentration of non-stoichiometric defects up to a very low level, and the \( \text{Cr}_1^{3+} \) centers bind the rest of conventional intrinsic defects. This creates the conditions, under which a chromium ion, looking for the charge compensator, enters the crystals together with some of the other available extrinsic defects. In our case \( \text{Cr}_{\text{Nb}}^{3+} \) associates with a \( \text{H}^+ \) ion, since three groups of lines around the Larmor frequency of hydrogen were found in the ENDOR spectra for \( \text{Cr}_{10}^{3+} \) \([\text{]}\).
Different groups of the ENDOR lines correspond to different locations of $\text{H}^+$ in the surrounding of $\text{Cr}_{\text{Nb}}^{3+}$. It means that both $\text{Cr}_{\text{Li}}^{3+}$ and $\text{Cr}_{\text{Nb}}^{3+}$ create families of similar centers; members of the families have different locations of their charge compensators.

\[ a^i = \frac{8\pi}{3} g_e g_n \beta \beta_n \Phi^i, \]

\[ \Phi^i = |\psi(\vec{R}^i)|_\downarrow^2 - |\psi(\vec{R}^i)|_\uparrow^2. \]
cation neighborhood. It was found that the spin densities on the surrounding nuclei are unexpectedly high. They are positive and decrease with rising a distance from the chromium ion (Fig. 5). The densities at the Nb nuclei are several times larger than on the Li ones; this is obviously related to the stronger binding of the chromium electrons to the larger positive charge of Nb$^{5+}$.

**FIGURE 5.** Distribution of electron spin density for the Cr$^{10+}$ center derived from the ENDOR data. Numbers on circles denote shells of niobium nuclei.

In the case of Nb substitution (Cr$^{3+}$) the nearest cation surroundings are Li nuclei, and measured hyperfine interactions with these nuclei are the strongest ones. Rather high values of isotropic hyperfine interactions give us the evidence for a transfer of the electron density from chromium to neighboring nuclei.
DISCUSSION AND CONCLUSIONS

All microscopic and macroscopic properties of ferroelectric crystals depend to some extent on the concentration of intrinsic defects. For instance, the melting point of congruent LN is about 1240°C, however it decreases to about 100°C, if the crystal composition approaches the stoichiometric one. The temperature of the ferroelectric phase transition varies in the range from 1020°C (for Li-pure crystals) to 1190°C (Li-rich crystals). As a result of these opposite tendencies for stoichiometric composition the melting temperature is lower than the Curie temperature, and a stoichiometric crystal grows initially in the ferroelectric phase. The disappearance of intrinsic defects in stoichiometric crystals also leads to a measured decrease of lattice constants [26], a blue shift of the absorption band edge and a change of the electro-optical coefficients [26].

The refinement of the crystal lattice from non-stoichiometric defects leads also to a tremendous narrowing of the spectral lines of not only EPR (up to 10-40 times) and NMR, but also of Raman scattering (2 times) and luminescence (6-10 times) [27, 28], X-ray structural analyses and other techniques. This increases the resolution of spectroscopic methods considerably and, as a result, the quantity and quality of the obtained information.

The most successful way to study crystal properties proceeds from congruent crystals through nearly stoichiometric, stoichiometric and regularly ordered materials. In the regularly ordered materials the properties are not covered by the presence of intrinsic defects. The use of crystals with different x_C offers many advantages for the crystal investigation, especially, for the study of impurity centers. We found that positions occupied by impurity ions depend on the crystal nonstoichiometry. This interrelation of impurity locations and crystal composition is not very obvious and has to be studied further theoretically and experimentally. The found features give the opportunity to tailor the crystal properties by variation of x_C. In particular, it helped us to find crystals with optimal conditions for the observation of ENDOR signals.

We have shown that the EPR and ENDOR data give us very detailed and reliable information about the fundamental properties of LN crystals. The derived models of the impurity centers, the positions of the optical bands, the parameters of crystal fields and their temperature dependencies, the values of electron spin density, together with the changes of lattice constants and Curie temperature, can be efficiently used as corner stones for theoretical calculations.

The ideas developed in this work have a general character; therefore they should also be valid for other non-stoichiometric oxide ferroelectrics.
REFERENCES