

**OPTIMIZATION OF LITHIUM NIOBATE FOR ADVANCED
APPLICATIONS BY VARIATION OF EXTRINSIC AND
INTRINSIC DEFECT SUBSYSTEMS**

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Abstract A detailed study of magnetic resonance (EPR, ENDOR) spectra of lithium niobate (LN) crystals with different compositions, diverse modifiers and various probe impurities was carried out. Several new chromium and iron centers have been found. Possible impurity locations and charge compensation mechanisms for crystals of different compositions are proposed. The obtained results clearly show a quantitative and qualitative difference of impurity related material properties for congruent LN, crystals with extremely low concentration of intrinsic defects and magnesium doped LN. It is suggested that the strong interrelation found between subsystems of intrinsic and extrinsic defects can be used to optimize LN crystal properties for advanced applications.

Keywords: EPR; ENDOR; defects; lithium niobate.

Fast development of opto-, acoustoelectronics and photonics requires new materials with improved characteristics. Sometimes the requested quality or parameter can be successfully achieved with a well-known, commonly used material with respective changes to its defect system. Results supporting this approach have been recently obtained for ferroelectric Lithium Niobate (LiNbO₃, LN). Conventional LN crystals,

grown from congruent melt with lithium deficiency ($X_{\text{melt}} = X_{\text{Crystal}} \approx 48.4\%$, where $X = [\text{Li}]/([\text{Li}]+[\text{Nb}])$), contain some percent of intrinsic (non-stoichiometric) defects. Several ways to obtain crystals with low concentrations of intrinsic defects have been developed: growth from melts with Li excess (up to $X_{\text{melt}}=60\%$) [1, 2], post-growth vapour transport equilibration (VTE) treatment [3, 4], growth from melts, to which potassium has been added [5, 6] (later on labelled $\text{LN}_{(\text{K})}$). These samples are often called Li-rich, nearly stoichiometric or stoichiometric crystals. The most perfect of them belong or are very close to regularly ordered crystals (ROC) [7]. Predictions [5, 7, 8, 9, 10] that stoichiometric crystals should have unusual physical properties, rather different from properties of congruent materials, are confirmed now by many laboratories in the world. In particular, it was found that nearly stoichiometric crystals are characterized by a two-order higher sensitivity to holographic recording [11, 12], five times lower electric field for domain switching [13], non-linear dependence of the ultraviolet absorption edge on crystal composition [14], different dynamical mechanical properties [15], non-monotonic dependence of electro-optical coefficients on x_{C} [16] etc.

Here we report results of our study of LN crystals with different compositions, diverse modifiers and various probe impurities (chromium and iron) with the help of Electron Paramagnetic Resonance (EPR) and Electron Nuclear Double Resonance (ENDOR), since they are very sensitive and informative tools for the study of defect structure.

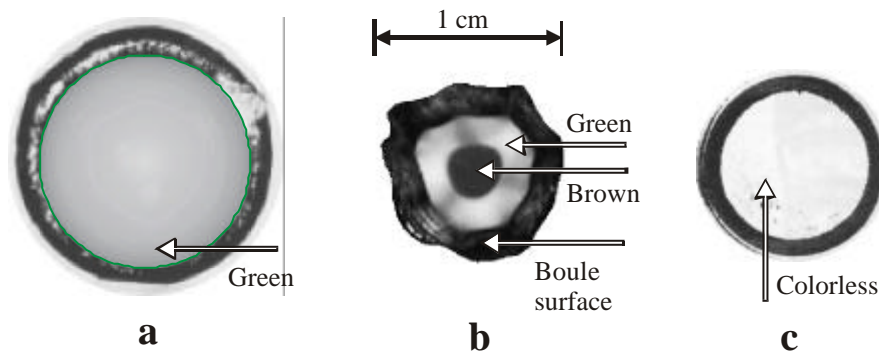


FIGURE 1. Congruent (a) and stoichiometric (b) crystals doped with 1 wt.% Cr; c – $\text{LN}_{(\text{K})}$ doped with 0.45 wt.% Mg. The view is along z -axis (optical c axis).

Chromium centers

Most of the macro- and microscopic properties of LN strongly depend on the nature, concentration and structure of both extrinsic and intrinsic defects [17, 18]. Figure 1 clearly demonstrates a great difference of the coloration of several studied “as-grown” crystals. To clarify the reason of this difference, samples from the brown and green parts (labelled below LN_(K)-brown and LN_(K)-green), as well as crystals with different compositions, undoped and doped with various impurities were studied by electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR).

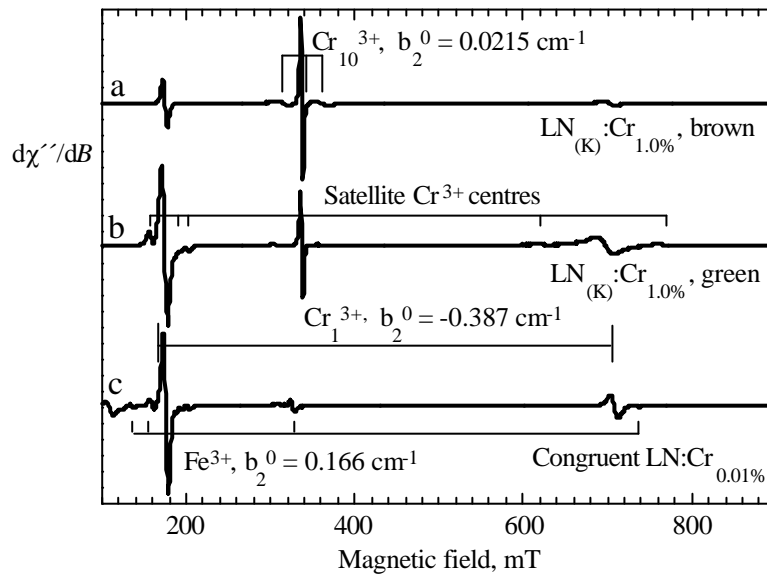


FIGURE 2. EPR spectra of Cr³⁺ for magnetic field $\mathbf{B}||\mathbf{x}$. T=5 K, microwave frequency 9.4 GHz.

Axial and low-symmetry satellite centers (Cr₁₋₉³⁺) with crystal field splitting $2b_2^0$ about 0.7-0.8 cm⁻¹ dominate in chromium doped congruent LN and in LN_(K)-green samples (Figure 2). Cr³⁺ in the centers of this family substitutes for Li⁺ and has an intrinsic defect (Nb vacancy) as local (in the nearest neighbourhood) or distant charge compensator [19]. Distant intrinsic defects cause low-symmetry distortions of crystal fields. This leads to the broadening and asymmetry of EPR lines in non-stoichiometric crystals, especially in congruent LN.

The triplet of the EPR lines of new Cr_{10}^{3+} centers, which appear in $\text{LN}_{(\text{K})}$ crystals doped with 1 wt.% Cr, has twenty times smaller splitting than Cr_{1-9}^{3+} centers. These Cr_{10}^{3+} centers have a higher concentration in $\text{LN}_{(\text{K})}$ -brown, than in $\text{LN}_{(\text{K})}$ -green. A simulation of EPR spectra was made in order to find the origin of the line broadening and the reason for the apparent deviation of the observed ratio of peak-to-peak intensities from the expected ratio 3:4:3 for Cr^{3+} with the electron spin $S=3/2$. A good agreement of experimental and simulated spectra was obtained by assuming that a random distribution of axial crystal fields gives the dominant contribution and that the width of this distribution Δb_2^0 is about 0.006 cm^{-1} (Figure 3). Since complexes consisting of chromium and intrinsic defect (satellite centers) are absent in $\text{LN}_{(\text{K})}$ -brown, it has an extremely small concentration of intrinsic defects. Therefore, some extrinsic defects should be the source of the random distortions of crystal fields. Our ENDOR study has shown that in Cr_{10} centers the Cr^{3+} ion substitutes for Nb^{5+} and has interstitial H^+ or/and additional Li^+ in the nearest neighbourhood as charge compensator. The observed EPR triplets belong to a family of nearly similar centers: members of the family have different locations of protons (or Li^+) relative to Cr_{Nb} .

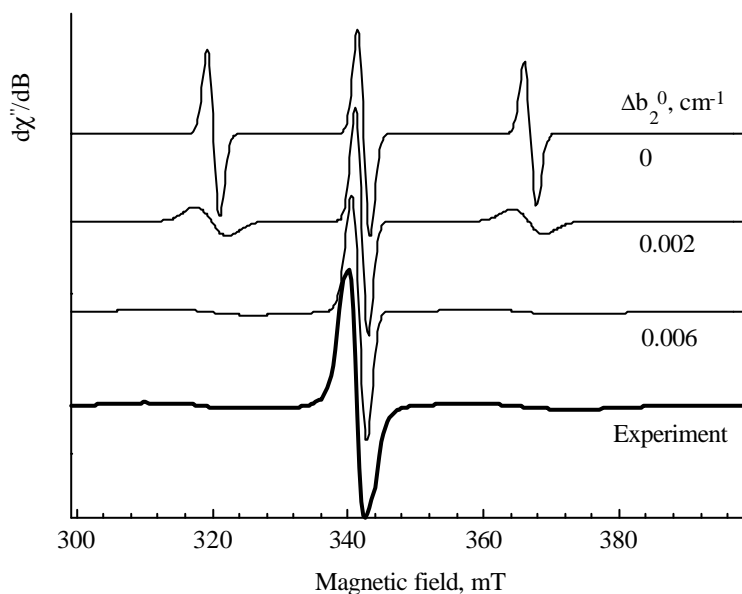


FIGURE 3. Comparison of experimental EPR spectra of Cr_{10}^{3+} and spectra simulated for different width Δb_2^0 of random distribution of axial crystal field. $\mathbf{B} \parallel \mathbf{x}$.

Dependencies of EPR signals on microwave power and their practically constant linewidths (Figure 4) reflect a difference of the spin-lattice relaxation times for the centers of the Cr_{Li} and Cr_{Nb} families, and confirm their different coupling with the LN lattice. The variation of the concentrations of Cr_{1-9}^{3+} (the main band of optical absorption spectrum at about 660 nm) and Cr_{10}^{3+} (the band at about 530 nm) together with a small variation of crystal composition are responsible for the picturesque inhomogeneous coloration of the $\text{LN}_{(\text{K})}:\text{Cr}_{1.0\%}$ boule.

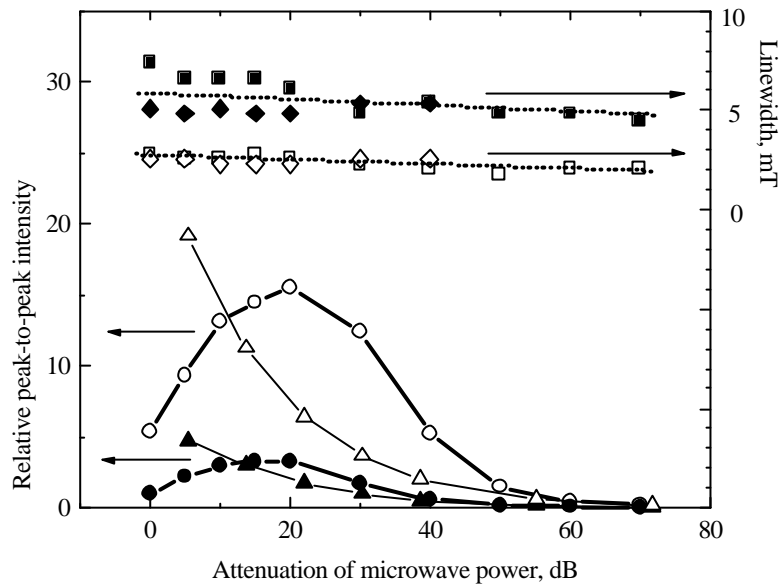


FIGURE 4. Dependencies of peak-to-peak intensities and linewidths (upper part) on the microwave power at 5 K (circles, squares) and 300 K (triangles, diamonds). Solid symbols – the EPR line of Cr_1^{3+} at 174 mT, open symbols – central transition of Cr_{10}^{3+} . $\mathbf{B} \perp \mathbf{z}$, $\nu=9.4$ GHz

Single central lines of chromium centers have been observed in crystals heavily doped with divalent modifiers (LN:Mg:Cr [^{20, 21, 22, 23, 24, 25, 26}], LN:Zn:Cr [²³], LN:Ca:Cr [²⁷]). Although the sidelines were not visible, it was assumed that they belong to Cr^{3+} and that the crystal field parameter b_2^0 is less than 0.01 cm^{-1} for LN:Mg:Cr [²⁰]. These centers were also interpreted as Cr on a Nb site. The difference in the center structure of $\text{Cr}_{\text{Li}}^{3+}$ and $\text{Cr}_{\text{Nb}}^{3+}$ families leads unavoidably to the difference in many other crystal features, closely related to variations of

chromium characteristics: luminescence [28, 29, 30, 31], photorefraction, electro-optical properties [32] etc.

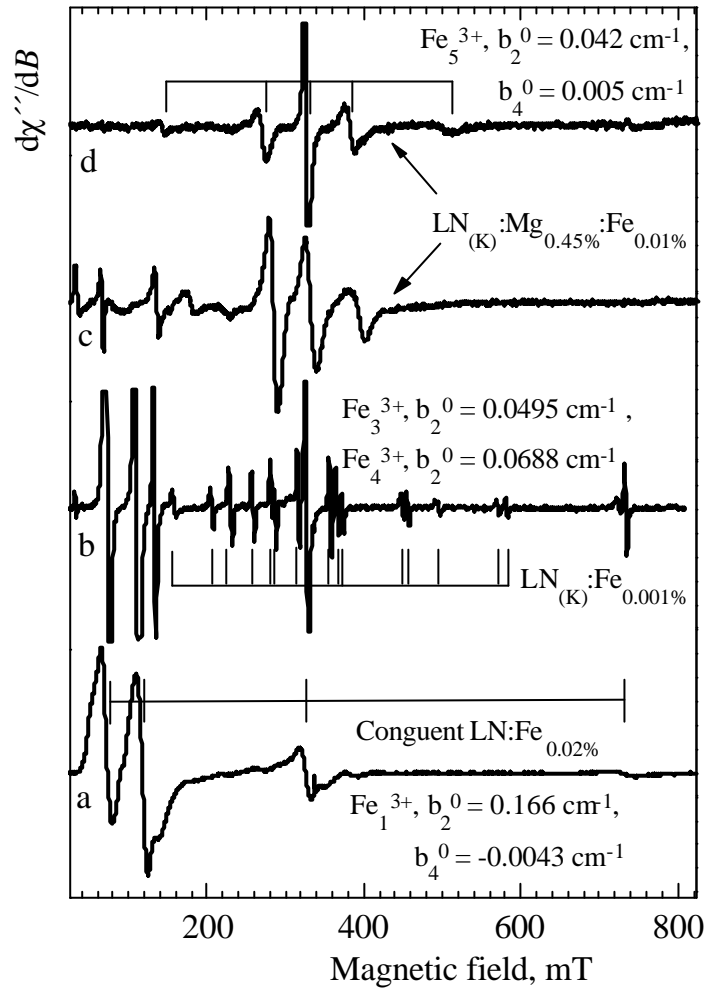


FIGURE 5. EPR spectra of Fe^{3+} of congruent (a), undoped $\text{LN}_{(\text{K})}$ (b) and Mg-doped $\text{LN}_{(\text{K})}$ crystals (c and d). $\mathbf{B} \perp \mathbf{z}$ (a-c) and $\mathbf{B} \parallel \mathbf{z}$ (d). $T=5$ K, X-band.

Iron centers

The transformation of Fe^{3+} centers caused by change of crystal composition is more complex compared to Cr^{3+} centers. Besides the axial center with $2b_2^0$ about 0.33 cm^{-1} , which dominates in congruent crystals and is attributed to Fe_1^{3+} on Li site [33], two other axial iron centers (Fe_3^{3+} and Fe_4^{3+}) were found in $\text{LN}_{(\text{K})}$ (Figure 5). Since crystal field splittings of these centers are several times smaller than for Fe_{Li} , it is reasonable to relate them to Fe^{3+} on Nb site [34]. However, the question is still open, why two centers are observed, but not one. One of possible explanations could be that they have different charge compensators on the center axis.

A different EPR spectrum (Fe_2^{3+}) has been registered in congruent crystals doped with magnesium, when the Mg concentration exceeds a threshold value 4.5% [35, 36, 37]. The random distribution of Mg^{2+} , substituting for Li^+ and requiring charge compensators, causes an even greater disorder in $\text{LN:Mg}_{6.0\%}$ than in the undoped congruent LN, which reveals itself in additional broadening of the EPR lines. This complicates the treatment of the spectra and the reliable determination of spin-Hamiltonian parameters; therefore the interpretation of these centers is still under discussion. The observed non-coincidence of the spectra at $\mathbf{B}||\mathbf{x}$ and $\mathbf{B}||\mathbf{y}$, and non-coincidence of the extrema of angular dependences with the crystal axes [37] is an evidence of the low symmetry of these centers. Probably, Fe^{3+} in these crystals substitutes for Nb^{5+} and has one or two Mg^{2+} ions in the nearest neighborhood for the charge compensation.

One more new center, Fe_5^{3+} was found in crystals grown from the melt with an addition of potassium and relatively low amount of Mg (Fig. 5c, d). Since its crystal field splitting is again smaller than for Fe_{Li} , we relate it to Fe^{3+} at the Nb site, however, the structure of Fe_5^{3+} differs from the structures of Fe_{1-4}^{3+} centers in congruent LN, $\text{LN}_{(\text{K})}$ and $\text{LN:Mg}_{6.0\%}$.

Several remarkable features should be underlined.

1. The appearance of Fe_{Nb} centers means that the threshold Mg concentration for $\text{LN}_{(\text{K})}$ is at least four times smaller than for Li-rich crystals [38] and ten times smaller than for congruent crystals. This gives us a possibility to tailor the LN properties by rather small dopant concentrations.
2. Since the observed EPR lines are rather narrow, the $\text{LN}_{(\text{K})}:\text{Mg}_{0.45\%}$ crystal has an essentially lower disorder than $\text{LN:Mg}_{6.0\%}$, which is also very important for many applications.

- Parameters of $\text{Fe}_{5^{3+}}$ centers differ from those of $\text{Fe}_{2-4^{3+}}$. Moreover, the observed ratio of peak-to-peak intensities deviates from the expected ratio 5:8:9:8:5 for spin $S=5/2$. Therefore, one has to expect that $\text{Fe}_{5^{3+}}$ centers have mechanism of charge compensation other than iron centers in undoped $\text{LN}_{(\text{K})}$ or $\text{LN:Mg}_{6.0\%}$.

Conclusions

The wealth of methods of the crystal preparation - Czochralski, VTE treatment of congruent LN, growth from melts with potassium (Czochralski or top-seeded solution growth), pulse laser deposition, micro-pulling down, laser heated pedestal growth, sol-gel, double crucible growth - necessitate development of precise methods of crystal characterization. The best crystal is the crystal, which is, first, most suitable for your specific research or applications and, second, well characterized in the sense of both intrinsic and extrinsic defects. The materials produced by various ways have a lot of similarities, however, also some essential principal differences.

Our results show the strong interrelation between subsystems of intrinsic and extrinsic defects. If we come nearer to the material having vanishingly small numbers of intrinsic defects, then not only quantitative, but also qualitative changes of crystal characteristics are observed. Li-replacing modifiers (like Mg, Zn, In etc. [³⁹]) have a threshold concentration, at which they start to “push” active impurity ions to Nb positions. Conditions of the appearance of Me_{Nb} , however, can vary from impurity to impurity and correspond to a special concentration balance between the considered kind of impurities and intrinsic defects. In the case of chromium, a part of Cr ions, substituting for Li, plays the role of a modifier for the rest of chromium ions.

The resemblance of some properties of Li-rich and Mg doped LN crystals (blue shift of fundamental absorption edge, appearance of Me_{Nb} centers) co-exists at the same time with the opposite behaviour of many other properties (line widths of EPR, NMR and Raman scattering; lattice constants etc.). Crystals heavily doped with the above-mentioned modifiers obviously have a much higher defect concentration (but not lower), than conventional undoped materials. Since Mg^{2+} ions are not isovalent to Li^+ or Nb^{5+} ions, these extrinsic defects can serve as charge compensators for trivalent ions. For instance, a complex of $\text{Me}_{\text{Nb}}^{3+5+} - 2\text{Mg}_{\text{Li}}^{2+}$ is completely compensated and there is no necessity to involve other extrinsic defects for charge compensation. Another charge compensation mechanism – by protons and additional Li^+ ions – occurs in Li-rich and $\text{LN}_{(\text{K})}$ crystals [⁴⁰]. Congruent LN is tolerant to both

desirable and non-desirable (non-controlled) impurities, which can easily find charge compensators among intrinsic defects. VTE treatment of congruent LN eliminates intrinsic defects. However, non-controlled impurities will be still present in the crystals. Conditions of the growth of Li-rich or $LN_{(K)}$ crystals lead to the decrease of incorporation of all impurities (both intentionally added and non-controlled impurities) due to the lack of proper compensators. This has positive and negative consequences. The very positive moment is that the amount of the trace (non-controlled) impurities can be much lower, than in congruent crystals. The negative consequence is that you have to be very tricky to introduce intentionally some dopants in $LN_{(K)}$ materials (especially in a high concentration). ROC has a lot of advantages (especially, for researchers) as a standard reference point and as a new material with partly different characteristics.

We have shown that both microscopic and macroscopic properties of LN crystals (impurity charges and positions, impurity incorporation and distribution, crystal homogeneity, colour etc.) can be changed by special doping and/or variation of the composition. In our opinion, non-stoichiometric materials offer especially rich opportunities for crystal engineering since subsystems of both intrinsic and impurity defects can be used for a deliberate tailoring of crystal properties.

Acknowledgements. Authors are very grateful to Prof. O. Schirmer for his permanent qualified help and interest to this topic.

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