

STRUCTURES OF POINT DEFECTS IN LITHIUM NIOBATE

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A detailed analysis and a classification of possible complexes of impurities and intrinsic defects in lithium niobate crystals are presented together with experimental data on lattice locations of most studied dopants. The necessity of a charge compensation for non-isovalent substitution leads to the creation of families of electrically non-equivalent impurity centers. Such satellite centers have different relative locations of the impurity ion and its charge compensator. Advantages and disadvantages of non-stoichiometric and stoichiometric crystals for the investigation of impurity centers are discussed.

Point intrinsic and extrinsic defects, especially defects created by radiation or chemical treatment and ions of transition metals and rare-earth elements, belong to the most important defects in lithium niobate (LiNbO_3) LN because of their essential influence on properties of this material [1] (such as domain structure, electro-optical coefficients, light absorption, refractive indices, birth and evolution of wave-front dislocations [2, 3], etc.) and their consequences for present and potential applications. The investigation of defects in LN has a long history and the number of related publications surpasses already some hundreds. A lot of effort was also spent to establish a correlation between the observable data and the crystal composition and to develop experimentally supported models of the defects. Nevertheless, the detailed structure (charges, identities and position of the ions in the lattice, their nearest surroundings, and ways of charge compensation) has been determined definitely for a few defects only.

In the course of the investigation of such defect structures in LN, one meets the following difficulties:

- high quality conventional crystals are usually grown from the congruent melt with $x_m = x_C \approx 48.4\%$ ($x = [\text{Li}]/([\text{Li}]+[\text{Nb}])$); this means that the congruent crystals contain many intrinsic (non-stoichiometric) defects, causing a broadening of the observable spectral lines and ambiguities in their interpretation;

- the crystal composition x_C of the undoped LN depends on the melt composition x_m and the growth conditions; x_C is equal to x_m for the congruent composition only;

- the most probable positions for impurity incorporation, the Li and Nb sites as well as the octahedral structural vacancy, have the same local symmetry C_3 ; this means that they are not distinguishable by many spectroscopic techniques;

- defects at other sites or complexes of two defects, if they are not extending along the crystal axis, have the lowest, C_1 , point group symmetry.

Methods of defect study can be conditionally divided into two groups: direct (Mössbauer spectroscopy [4], Rutherford Backscattering Spectrometry, RBS [5], Extended X-ray Absorption Fine Structure Analysis, EXAFS, Particle Induced X-ray Emission, PIXE combined with channeling [6], Electron Paramagnetic Resonance, EPR and Electron Nuclear Double Resonance, ENDOR [7]) and indirect (optical absorption and luminescence, measurements of electro-optical coefficients, etc.).

Attempts to determine impurity positions by indirect methods often gave contradicting information. Many of the direct methods are often not applicable to the defect structure analysis:

- Mössbauer spectroscopy demands the presence of special nuclei,

- channeling investigations are more successful in the case of heavy, many-electron ions,

- channeling methods are not sensitive to the charge state of the impurity and do not distinguish C_3 and C_1 centers,

- due to the relatively low sensitivity, the EXAFS needs high levels of crystal dopants (about 3–5 mol.%), for which clustering and occupation of both Li and Nb positions become very probable,

- EPR/ENDOR can be observed for paramagnetic defects only, etc.

Therefore, a combined study with the help of different available methods has to be used for a solution of this very difficult task.

Intrinsic Defects

Because of nonstoichiometry the real lattice of conventional congruent LN contains many intrinsic defects, the relative concentrations of which have not yet been determined reliably. The following entities have been considered (their charges with respect to the lattice being given by Kröger–Vink notation in brackets): $\text{Nb}_{\text{Li}}^{5+}$ (Nb_{Li}^4) antisite defect, V_{Li^+} ($V_{\text{Li}^{\prime}}$) lithium vacancy, V_{Nb}^{5+} (V_{Nb}^{\prime}) niobium vacancy, $\text{Nb}_{\text{V}}^{5+}$ (Nb_{V}^5) niobium on structural vacancy, Li_{V}^+ ($\text{Li}_{\text{V}}^{\prime}$) lithium on structural vacancy. During recent years, the existence of the following charge compensated complexes has been postulated most often: $\text{Nb}_{\text{Li}} + 4V_{\text{Li}}$ [8–10], $5\text{Nb}_{\text{Li}} + 4V_{\text{Nb}}$ [11, 12], $2\text{Nb}_{\text{Li}} + 2\text{Nb}_{\text{V}} + 3V_{\text{Li}} + 3V_{\text{Nb}}$ [13] (Fig. 1). Some features accompanying the crystal growth (Li_2O evaporation, variation of oxygen deficiency in $\text{Nb}_2\text{O}_{5-x}$ [14]) and specific changes of some crystal properties after thermal oxidation and/or reduction definitely indicate that the oxygen sublattice is not always perfect and stable as well; therefore the oxygen non-stoichiometry has been discussed for a long time [15–17].

The intrinsic defects by themselves or complexes of them which are not charge compensated can furthermore serve as local or distant charge compensators for non-isocharged extrinsic or radiation defects. Due to the high concentration of these defects, the congruent crystals are very tolerant to di- or trivalent impurities, including non-controlled ones, because the necessary charge compensators (local or distant) can be easily found among the non-stoichiometric defects.

A decrease of the concentration of intrinsic defects by using melts with Li excess [19, 20] or by post-growth vapor transport equilibration (VTE) treatment [21] leads to the essential changes of the conditions for impurity incorporation into LN and, as a consequence, to the changes of crystal properties and characteristics (see, for examples [22, 23]). Even stronger changes were observed [24–26] for crystals grown under special conditions from melts, to which potassium has been added (later on labeled $\text{LN}_{(K)}$). It was found that they have even lower intrinsic defect concentrations and that potassium does not enter the crystal. The samples with high Li content (with the ratio x_{Crystal} close to 50%) are often conventionally named stoichiometric [27–30].

At present, LN crystals with varied compositions are produced by different techniques: by the Czochralski

method [31, 32] and the top seeded solution growth (TSSG) [33] with an addition of K_2O , double crucible growth (DCG) [34, 35], vapour transport equilibration (VTE) treatment of congruent material, pulse laser deposition (PLD), micropulling down (μPD), laser heated pedestal growth (LHPG), etc. Investigations of these crystals gave a lot of interesting and, sometimes, really striking results [36–39], initiating the booming interest in these materials.

Phenomenological description of LN properties often ignores microscopic lattice irregularities. However, the crystal composition (i.e. the presence of intrinsic defects) has an enormously large influence on many characteristics: it changes the sensitivity of the crystals to the light illumination (up to two orders of magnitude [40–42]), the kind of defects participating in photorefractive processes, the rate of carrier recombination (up to two orders of magnitude [43]), electric field for photorefractive gratings and for domain switching (5–200 times [44, 45]), etc.

It should be mentioned that even stoichiometric crystals with $x_C = 50\%$ are not completely free of intrinsic defects. There is a class of intrinsic defects which break the regular order of the LN lattice without a change of x_C : the permutations Nb_{Li} and Li_{Nb} , cyclical permutation of Nb_{Li} Li_{V} , v_{Nb} (Fig. 1, *d*).

Possible Structures of Extrinsic Defects

The ideal LN lattice (Fig. 2) has two LiNbO_3 molecules in its rhombohedral elementary unit cell and the space group symmetry is $R3c$ at room temperature [46–48]. There are several electrically non-equivalent positions in the lattice. Some of them — the sites on the z (or optical c) axis of the crystal, including the sites of Li, Nb and the structural vacancy, V - have the symmetry of the point group C_3 . An isolated defect in any of these positions creates a C_3 (in the following also labeled “axial”) center. All other positions have the lowest possible symmetry, C_1 . A complex of two defects has C_3 symmetry, if both are located on the crystal z axis, and C_1 symmetry in all other cases. If the difference in positions of the nearest oxygen ions is ignored, then each unit cell has the following site sequence along the z -axis: Li, Nb, V_{Oct} , Li, Nb, V_{Oct} . However, oxygen octahedra and next neighbors for two positions of one type cation are not identical, therefore the correct assignment of the sequence should be Li_L , Nb_L , $V_{\text{Oct},L}$, Li_R , Nb_R , $V_{\text{Oct},R}$. The surroundings of the “Right” (R) positions can be transformed to the “Left” (L) ones by a reflection $\mathbf{x} \leftrightarrow -\mathbf{x}$ and a shift by $c/2$, because \mathbf{zy} is a glide mirror plane in the $R3c$ lattice. The

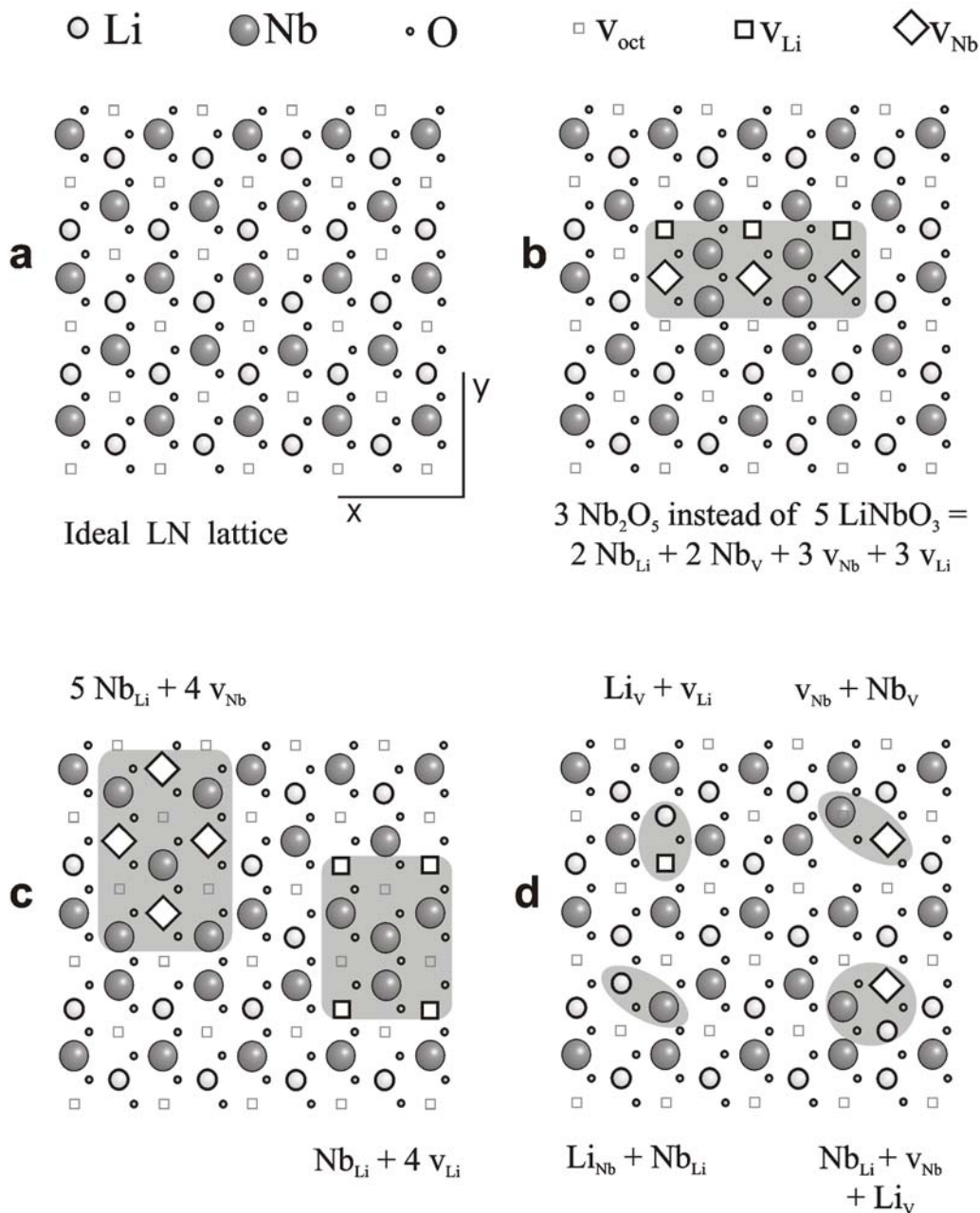


Fig. 1. The projection of ideal LN lattice to xy -plane (a), possible non-stoichiometric defects (b, c) and defects which do not break the stoichiometry (d)

same consideration is applicable to C_1 positions also. This means that each axial (C_3) or low-symmetry (C_1) L center has a corresponding R partner. The L and R partners are electrically identical and are not distinguishable by optical methods, but they are magnetically non-equivalent and can be resolved from

each other in favorable cases (high spin value, small line width) by magnetic resonance techniques.

In the $R3c$ lattice, each C_1 center has two additional magnetically nonequivalent partners, which can be transformed into each other by a rotation around the z -axis of the crystal by 120° and 240° . They can be

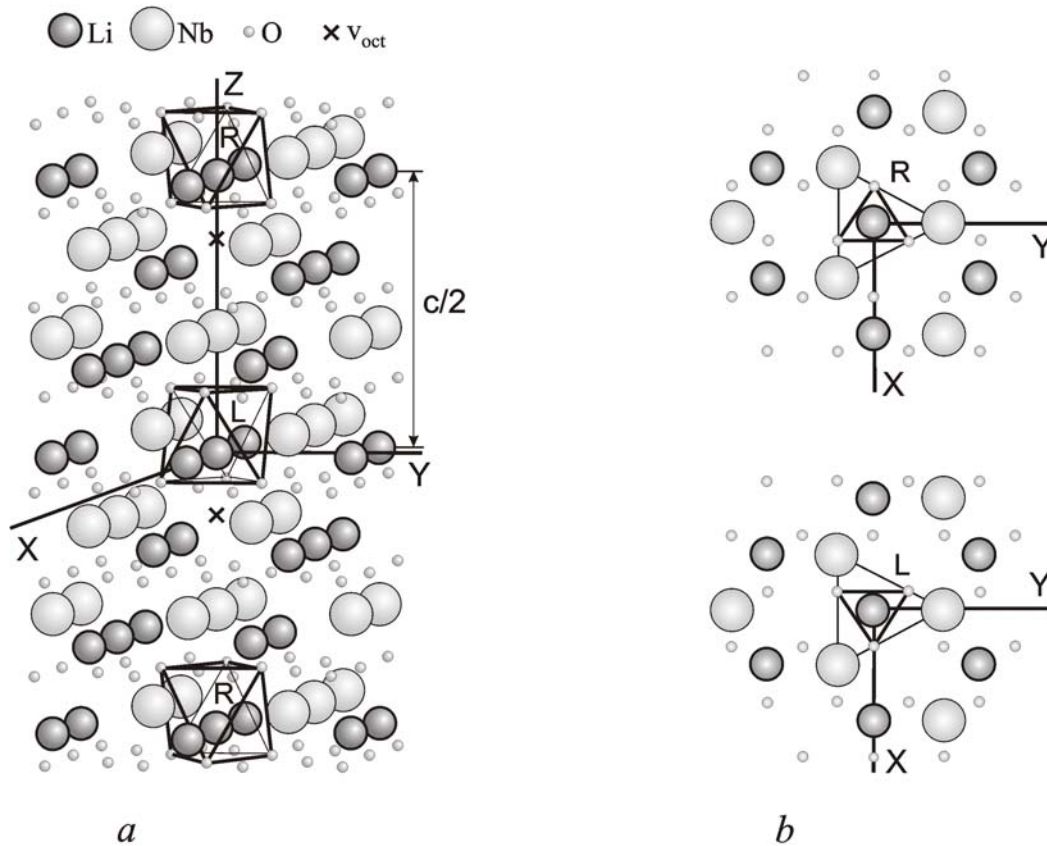


Fig. 2. *a* — ideal lattice of lithium niobate. To simplify the representation of the lattice and defect structures in it, the sizes of “balls” imitating ions were made intentionally different. If real ionic radii are taken into account ($\text{Li}^+ - 0.68\text{\AA}$, $\text{Nb}^{5+} - 0.69\text{\AA}$, $\text{O}^{2-} - 1.32\text{\AA}$), the LN lattice looks like consisting mainly of planar layers of closely packed oxygen ions with small voids between them, filled by Li and Nb. “Left” and “Right” positions are distinguished by their different oxygen surroundings. *b* — illustration of local C_3 symmetry for the nearest surroundings of cation sites. A projection of three Li, Nb and O layers on the xy plane is shown

distinguished by the EPR at arbitrary orientations of the magnetic field.

Angular dependences of the EPR for a center without any other defect in its nearest neighborhood (distant charge compensation) correspond to the symmetry of the occupied site, i.e. C_3 for the sites on the z -axis and C_1 for all other cases. However, the presence of distant defects can reveal itself by a specific broadening of the EPR lines and an asymmetry of their shapes.

The structure of a defect, in which a lattice site is occupied by an extrinsic impurity ion having a charge different from that of the respective lattice site (in the following labeled “non-isocharged replacement”), depends on the charge of the impurity and the mechanism of charge compensation. The real lattice of

conventional LN contains many intrinsic defects, which can serve as local or distant charge compensators for non-isocharged substitutional or interstitial impurities.

The tetrahedral vacancy and oxygen sites have C_1 point group symmetry; therefore all centers based on their occupation have this lowest symmetry. The symmetry of other centers reflects the symmetry of lattice sites occupied by impurity and charge compensator and their relative location.

1. Monovalent Cations

The most probable incorporations of Me^+ are:

— Replacement of Li^+ . No charge compensation is necessary in this case. The Me_{Li}^+ center should have

axial CC_3 symmetry. For some impurities a lowering of symmetry is possible due to the Jahn–Teller effect. For instance, Ni^{2+} center has C_1 symmetry at low temperatures [49] (static Jahn–Teller effect). However, the EPR spectra of the Ni^{2+} at room temperature have axial symmetry (motionally averaged static Jahn–Teller effect).

— Interstitial position in octahedral or tetrahedral structural vacancies. The lithium vacancy can easily compensate the charge excess of the Me_V^+ . Another possibility is that one interstitial O^{2-} ion compensates two Me_V^+ . It is less probably that five Me_V^+ can be clustered around a niobium vacancy. In the case of the octahedral vacancy, the symmetry of the center depends on the relative positions of the interstitial and cation vacancies.

— Off-site position. Protons H^+ occupy positions between two oxygen ions in an oxygen plane.

2. Divalent Cations

For divalent Me^{2+} impurities, a substitution for Li^+ ions and incorporation in structural vacancies have essentially less charge misfit than a substitution for Nb^{5+} . Since the Li–Li distance is much greater larger than Li–Nb or V–Li, V–Nb, the $Me_{Li}^{2+} + V_{Li}$ centers should be less distorted by the presence of a local charge compensator. The lithium vacancies can serve as pins for a Jahn–Teller distortion; this was found for Cu^{2+} [49].

The charge excess of one interstitial Me^{2+} or two Me_{Li}^{2+} can be exactly compensated by an additional O^{2-} ion. However, the ionic radius of O^{2-} (about 1.4 Å) is larger than the sizes of octahedral or tetrahedral vacancies. Therefore, increasing the concentration of lithium vacancies in crystals doped by divalent impurities (in comparison with undoped crystals grown under the same conditions) looks more preferable than increasing the concentration of oxygen interstitials.

3. Trivalent Cations

Below the trivalent state Me^{3+} is considered in detail, because many transition metals (including iron and chromium) and rare-earth elements enter LN in this valence.

If Me^{3+} substitutes Li^+ or is incorporated in a structural vacancy, the positive charge excess can be compensated by both V_{Li}^+ and V_{Nb}^{5+} (because Li and Nb vacancies have negative charges with respect to the ideal lattice). For instance, every impurity ion at a Li site can

be compensated by two lithium vacancies or every five Me_{Li}^{3+} ions by two niobium vacancies.

The positive antisite defect Nb_{Li} can serve as a charge compensator for Me^{3+} replacing Nb^{5+} (but not Me_{Li}^{3+} or Me_V^{3+}). It is remarkable that one Nb_{Li}^{5+} exactly compensates the excess charge of two $Me_{Nb^{5+}}^{3+}$ ions.

The association of Me_{Li}^{3+} with $V_{Nb^{5+}}$ in the nearest Nb shell (partial local charge compensation) leads to an axial center, in the second and third Nb shells — to two different C_1 centers, in the fourth Nb shell — to a second axial center, in the fifth to ninth Nb shells — to further five VC_1 centers ($X_{Li}–Y_{Nb}$ configurations, distances between the replaced ion and these shells and the symmetries of the corresponding complexes are given in [50]). A niobium vacancy in the nearest neighborhood disturbs the Me^{3+} surroundings much stronger than distant V_{Nb} . The distance between Me^{3+} and a defect in the fifth to ninth shells is about 6 Å; however a defect as strongly charged as V_{Nb} is still expected to influence the crystal field parameters even for such a large distance.

The point group symmetries and distances for the $Me_{Nb^{5+}}^{3+} – Nb_{Li}^{5+}$ centers have to be similar to those described above, because these defects are located again at the same Nb and Li positions ($X_{Nb} – Y_{Li}$ configurations).

In the case of Me_{Li}^{5+} compensated by two V_{Li}^+ , three lattice defects are combined and all partners occupy Li sites only ($X_{Li}–Y_{Li}$ and $Y_{Li}^1–X_{Li}–Y_{Li}^2$ configurations). Taking into account that differences in the relative locations of the impurity and vacancies can give electrically non-equivalent centers, 4 distinguishable C_1 configurations can be constructed with two V_{Li}^+ in the first Li shell of Me_{Li}^{3+} (6 possible sites). One V_{Li}^+ in the first shell and one V_{Li}^+ in the second shell (also 6 sites) give 12 electrically non-identical low-symmetry centers. If one of the lithium vacancies is very distant, the presence of only one vacancy in the first shell of Me_{Li}^{3+} gives two electrically different configurations, in the second shell — two further ones. Two nearest Li positions on the C_3 axis are located at 6.93 Å and the following, the third one at 13.86 Å. The presence of lithium vacancies on these sites near Me_{Li}^{3+} does not break the C_3 symmetry and should generate axial centers only. However, since V_{Li}^+ has only one negative charge relative to the ideal lattice, it produces a 4–5 times weaker perturbation of the crystal field than Nb_{Li}^{5+} or V_{Nb}^{5+} . Therefore the centers with V_{Li}^+ at distances of about 6 Å should probably not be distinguishable from axial centers with non-local charge compensation.

Conceivable complexes of $\text{Me}_{\text{Nb}^{5+}}^{3+}$ and a divalent oxygen vacancy, V_{O}^{2-} , (or other defects in the oxygen sublattice, i.e. $X_{\text{Nb}}-Y_{\text{O}}$ configurations) have C_1 symmetry only, but never C_3 symmetry. Oxygen interstitial ions, if present, can compensate only $\text{Me}_{\text{Li}^+}^{3+}$ and, depending on their relative mutual locations ($X_{\text{Li}}-Y_i$ configurations), could give C_3 and C_1 centers.

To complete the enumeration of potential defect clusters, possible interstitial positions of the trivalent impurities in octahedral or tetrahedral structural vacancies, Me_v^{3+} , should also be considered. In both cases an excess charge can be compensated by V_{Li} ($\text{Me}_{V}^{3+} - 3V_{\text{Li}}$), V_{Nb} ($5\text{Me}^{3+} - 3V_{\text{Nb}}$), or by interstitial oxygen ions ($2\text{Me}^{3+} - 3\text{O}_i^{2-}$), but not by oxygen vacancies or Nb_{Li} antisites.

4. Tetra-, Penta-, and Heptavalent Cations

The tetravalent impurities (C and Si) are always present in LN in rather high concentrations (about 50–500 ppm). Since determined concentrations of Cl (50–500) and Mg (1–100) have the same order of magnitudes, no other charge compensators are necessary if C or Si substitutes for Nb creating $C_{\text{Nb}}^{4+} - \text{Cl}_{\text{O}}^-$ or $C_{\text{Nb}}^{4+} - \text{Mg}_{\text{Li}}^{2+}$. The additional possibilities for the charge compensation are supplied by H^+ and Li_V^+ ions. It is supposed that Ti^{4+} substitutes for Nb^{5+} , however, at present a mechanism of charge compensation is not well established.

The Ta^{5+} substitution for Nb^{5+} causes minor lattice distortions only. The heptavalent ions (Mo, W) probably substitute for Nb^{5+} having lithium vacancies as charge compensators.

5. Defects of Anion Sublattice

The halide ions (F^- , Cl^- , ...) can substitute for O^{2-} decreasing the concentration of lithium vacancies in non-stoichiometric crystals. The OH^- ions can also be considered as anion defects, since H^+ ions are located in an xy -plane at a distance about 1 Å from an oxygen site (which is less than the radius of the oxygen ion!).

Radiation Defects

A radiation produces usually interstitial ions and/or recharges of regular lattice or impurity ions. Two kinds of these defects were observed in LN: Nb^{4+} and O^- ions [51–55]. It is remarkable that they have C_1 symmetry, although main possible positions for Nb (regular Nb and Li site, octahedral vacancy) have C_3 symmetry. It

means that these Nb^{4+} ions have charge compensating defects, probably v_{Li} , in the nearest neighborhood (an incorporation of Nb^{4+} into tetrahedral vacancy with C_1 symmetry demands the charge compensator also).

Experimental Study of Structures of Impurity Centers

The positions of many impurity ions were determined by the Extended X-ray Absorption Fine Structure Analysis (EXAFS), Particle Induced X-ray Emission (PIXE)[56] and channeling methods. Lithium substitution was found for most elements including Sc, Ti, Mn, Fe, Co, Ni, In, Pr, Nd, Gd, Ho, Er, Tm, Yb, Lu,[57, 58]. A few ions substitute for Nb in undoped LN (Hf [59], Er [60]) and in LN heavily doped by Mg or Zn (Sc, In, Nd, Lu [61]). Some of the ions can occupy both positions (Cr, Gd, Nd). It should be mentioned that the application of these methods requires relatively high concentrations of impurities at which impurity clusters can appear.

Very detailed information about structures of impurity defects (charge state, point symmetry, hyperfine interactions with neighbour nuclei etc) was obtained with the help of EPR and ENDOR. The charge compensation by lithium vacancies is widely accepted for most of the non-isovalent ions. However, the EPR data for low-symmetry centers and exchange pairs of Cr^{3+} in non-stoichiometric LN can be explained in a natural way by the presence of niobium vacancies in the neighborhood of Cr^{3+} substituted for Li^+ : one V_{Nb} can couple and compensate the excess charge of two $\text{Cr}_{\text{Li}}^{3+}$ ions [50]. For $\text{Cr}_{\text{Nb}}^{3+}$ in stoichiometric LN, the charge compensation by interstitial H^+ and/or Li^+ ions was found [62].

The main results of EPR/ENDOR studies of paramagnetic defects in lithium niobate are collected in the Table 1.

Discussion and Conclusions

The reported detailed analysis and classification of possible complexes of impurity and intrinsic defects allow us to understand the main features of the experimental data.

The presence of non-stoichiometric defects is one of the reasons why LN tolerates a strong incorporation of dopants non-isovalent to Li^+ and Nb^{5+} . As long as the impurity concentration $[\text{Me}]$ is smaller than $\delta x_C = |50\% - x_C|$, the number of intrinsic defects is large enough to compensate the corresponding charge excess. However, for stoichiometric or nearly stoichiometric

samples with high impurity concentrations (when $[Me] > \delta\delta x_C$) and with the lack of charge compensators, a decrease of the distribution coefficient of impurities is observed in comparison with congruent material. A further increase of the $[Me]/\delta x_C$ ratio up to $[Me] \gg \delta x_C$ can result in a change of the charge compensation mechanism; this can reveal itself in the appearance of new impurity centers.

The use of stoichiometric or nearly stoichiometric crystals with $\delta x_C \approx 0$ presents many advantages for the investigation of impurity centers. The decreased concentration of intrinsic defects causes a tremendous narrowing of the spectral lines. This leads to the increase of spectral resolution and sensitivity, facilitates the analysis of the spectra, and simplifies the interpretation of the data. However, together with the disappearance of intrinsic defects, the satellite centers, disappear also. For a detailed investigation of such additional centers, the crystals with high $x_C \approx 49.5$ – 49.85% are more suitable than others: they have more narrow spectral lines than congruent samples, but the satellite centers are still present.

Point defects in lithium niobate studied by the EPR

Defect	Site and defect symmetry	References, specific features
O ⁻	C ₁	[63, 53]; LN:Mg [64–66]
Mg ⁺	Li	[64]; there is an alternative interpretation of this spectrum [55]
Ti ³⁺	Li	[67–70]
	Nb	LN:Mg [71, 72]
Cr ³⁺	Li, C ₃	[73–79]
	Li, C ₁	[80, 81]
	Nb, C ₃	[82]
	Nb, nearly isotropic	LN:Mg [83], ENDOR [84–86]
	Nb, C ₃	ENDOR [62]
	2Cr ↔ Li + Nb, C ₃	[87, 88]
	2Cr ↔ Li + Li, C ₁	[89]
Mn ²⁺	Li	[90, 91, 76]; ENDOR [92]
Fe ³⁺	Li	[91, 93–99]; ENDOR [100]
	Li, Nb	LN:Mg [101–103]
	Nb	LN:Zn [104]
Co ²⁺	C ₃	[105–108]
Ni ⁺	Li	[109, 49]
Ni ²⁺	Li	[110]
Cu ²⁺	Li, C ₃	[111, 105]
	Li, C ₁	[112, 113, 49]
Nb ⁴⁺	Li	[114, 115, 53]; LN:Mg, LN:Zn [116]
	Nb	LN:Mg [65]
Nd ³⁺	Li	[73, 117, 118]
Gd ³⁺	C ₁	[119, 120]
Tb ⁴⁺	C ₃	[121]
Dy ³⁺	C ₃	[73]
Er ³⁺	C ₃	[73, 122, 123]
Yb ³⁺	C ₃	[74, 118, 124]
	C ₃ , C ₁	[125]

The necessity of a charge compensation for non-isovalent substitution usually leads to the creation of families of electrically non-equivalent impurity centers. The families of satellite centers exist due to the different relative locations of the impurity ion and its charge compensator. For instance, besides the main axial Cr_{Li}³⁺ center, eight satellite chromium centers were definitely resolved in the EPR spectra. Two or more different centers were also observed for Cr_{Nb}³⁺, Gd³⁺, Nd³⁺, Er³⁺, Yb³⁺, Cu²⁺, Mn²⁺ and other ions. Since the relative concentrations of satellite centers are comparable with the concentration of the main center, both kinds of centers generally are equally responsible for many of the properties of non-stoichiometric LN crystals, and they should both be taken into consideration, especially in non-stoichiometric crystals.

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СТРУКТУРА ТОЧКОВИХ ДЕФЕКТІВ В НІОБАТІ ЛІТІЮ

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Резюме

Представлено детальний аналіз та класифікацію можливих комплексів домішок та внутрішніх дефектів у криста-

лах ніобату літію разом з експериментальними даними про розміщення в ґратках найбільш вивчених домішок. Необхідність компенсації заряду для неізовалентного заміщення приводить до утворення груп електрично-нееквівалентних домішкових центрів. Такі центри-супутники мають різні відносні положення домішкового іона та компенсатора його заряду. Розглянуто переваги та недоліки стехіометричних і нестехіометричних кристалів для дослідження домішкових центрів.