



'Horror Vacui' in the Oxygen Sublattice of Lithium Niobate Made Affordable by Cationic Flexibility

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Abstract: The present review is intended for a broader audience interested in the resolution of the several decades-long controversy on the possible role of oxygen-vacancy defects in LiNbO₃. Confronting ideas of a selected series of papers from classical experiments to brand new large-scale calculations, a unified interpretation of the defect generation and annealing mechanisms governing processes during thermo- and mechanochemical treatments and irradiations of various types is presented. The dominant role of as-grown and freshly generated Nb antisite defects as traps for small polarons and bipolarons is demonstrated, while mobile lithium vacancies, also acting as hole traps, are shown to provide flexible charge compensation needed for stability. The close relationship between LiNbO₃ and the Li battery materials LiNb₃O₈ and Li₃NbO₄ is pointed out. The oxygen sublattice of the bulk plays a much more passive role, whereas oxygen loss and Li₂O segregation take place in external or internal surface layers of a few nanometers.

Keywords: LiNbO₃; polarons; bipolarons; defect structure and generation; Li diffusion



Citation: Corradi, G.; Kovács, L. 'Horror Vacui' in the Oxygen Sublattice of Lithium Niobate Made Affordable by Cationic Flexibility. *Crystals* **2021**, *11*, 764. https:// doi.org/10.3390/cryst11070764

Academic Editor: Benoit Heinrich

Received: 4 June 2021 Accepted: 27 June 2021 Published: 29 June 2021

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1. Introduction

In most simple oxides, defect generation processes by thermal reduction or irradiation are dominated by defects of the oxygen sublattice. Originally, the same was also assumed for LiNbO₃ (LN), and most authors did not (and many still do not) have any doubts about simply postulating vacant oxygen sites (V_O) capable of trapping one or two electrons (F^+ and F-centers, respectively) in discussions of their experiments and proposed applications (see, e.g., [1,2]). The controversy about the availability of oxygen vacancies manifests in the reviews of Sánchez-Dena et al. [3,4], is touched upon by some topical reviews [5,6], and is also closely related to the topics of other papers [7–11] of the present Special Issue, and deserves a clarifying discussion.

In this short review, aiming to integrate views on this paradigmatic material, we start by summarizing the charge compensation mechanism for Li deficiency followed by a discussion of the various defect generation procedures in congruent LiNbO₃ (cLN), such as thermal reduction, irradiation by ionizing or ion-displacing radiation or mechanochemical treatment. The effect of crystal stoichiometry on the defects produced is revisited before presenting a comparison with recent calculations of basic defect configurations.

2. Structure and Charge Compensation Mechanism

In contrast to ordinary perovskites with less compact anion sublattices, LiNbO₃ has a structure corresponding to a strongly distorted perovskite where the oxygens essentially form a hexagonally close-packed lattice offering a priori identical octahedral sites to the cations, one-third of which remain empty. In domain walls and in some defect clusters, the stacking order of the cations along the C₃-axis (Li, Nb, empty site) changes due to these liberties. The cations Li⁺ and Nb⁵⁺ have very similar ionic radii but otherwise diametrically differing properties. Large polarizability results in ferroelectricity nearly up to the melting point and transforms all surplus charges in the lattice to small polarons by confining

them via local lattice relaxation, as a rule, to a single lattice site. Small polarons still may propagate by thermally activated hopping unless sufficiently stabilized by some defect. Li readily strips an electron, whereas Nb has an intricately covalent character, as shown by the many poliforms of its oxides ranging from pentoxide Nb₂O₅ to monoxide NbO [12,13]. This explains the Li-deficient character of LiNbO₃ accommodated by lithium vacancies (V_{Li}) and Nb_{Li} antisites (Nb on Li site) requiring small formation energies. Compared to compensation involving anion vacancies at larger costs [13,14], compensation only by cationic disorder requires no additional volume and leads to the observed larger density of cLN compared to sLN (stoichiometric LN) [15–19]. Another characteristic property of LN is the high mobility of Li⁺ ions observable already at temperatures near 350 °C (see [9,20–22] and references therein). It should be noted that LN is just an intermediary phase between Li₃NbO₄ and LiNb₃O₈, considered as cathode and anode materials for lithium-ion batteries, respectively [23,24]. Nb has an octahedral coordination in all these systems, the only difference being the varying Li₂O content; however, LN has a closer relationship with LiNb₃O₈ due to its full epitaxial compatibility with LN [25].

On the basis of extensive experimental and theoretical work, this compensation mechanism is by now fully accepted. The Nb_{Li} antisite was proven to be an efficient electron trap, forming the Nb⁴⁺_{Li} small polaron state characterized by an asymmetric absorption band at ~1.6 eV (~760 nm, with a protracted high energy side) attributed to charge transfer to the conduction band, and a broad ten-line EPR spectrum reflecting hyperfine splitting due to the Nb_{Li} nucleus. The EPR spectrum has a non-axial angular dependence due to a quasi-Jahn–Teller effect or a perturbation by charge-compensating defects situated in glide-mirror (zy-type) planes containing the cation neighbors [26–28]. However, no EPR spectrum corresponding to an F⁺-center or its hypothetical relaxed variant [29], a non-axial Nb⁴⁺_{Nb} center next to an anion vacancy situated in zx-type planes, could be identified [27,30].

3. Defect Generation in LiNbO₃

3.1. Defect Generation in cLN by Thermal Reduction

Attempts to explain thermal annealing effects in LN by anionic defects [29–32] were never conclusive. Thermal reduction at high temperatures in vacuum or other reducing atmospheres in cLN results in a broad absorption band with a poorly defined maximum at \sim 2.5 eV (\sim 500 nm) but having no counterpart in EPR [29–33] (see Figure 1). This band is also highly asymmetric, with its protracted high energy side merging with the UV edge and was attributed, similarly to the 1.6 eV band, to charge transfer to the conduction band [34]: asymmetry seems to be a general property of small-polaronic charge-transfer bands in LN mainly due to the structure of target states in the conduction band [35]. By illumination with photon energies above 2 eV, the ~2.5 eV band can be transferred into the ~1.6 eV band of Nb_{Li}^{4+} small polarons [29–32,34]. The same transformation can also be realized by heating the crystal; in fact, the defects responsible for these bands are in thermal equilibrium [36]. The transformation is fully reversible at least in the 122–575 K temperature range, whereby an isosbestic point near 600 nm is conserved, indicating the participation of only two kinds of centers in the transformation [36]. Some authors have also reported the participation of an additional reduction-induced absorption band near 3.2 eV (~390 nm) in these transformations [32,33]; however, due to their assumption about symmetric Gaussian bandshapes, the amplitude of this band was grossly overestimated. The interpretation of the 2.5 and 3.2 eV bands in terms of F and F⁺ centers, respectively, is in immediate conflict with the fact that the 2.5 eV band is the stable one in the reduced crystal corresponding to its ground state [35]; moreover, no EPR spectrum corresponding to the F^+ center could be identified, as pointed out in the previous section.



Figure 1. Reduction-induced absorption in a near-sLN sample covered by Pt foil (full line), a similar uncovered sample (dash-dotted), and a cLN sample (dashed line), measured at RT. The vacuum-reduction temperature was 880 °C (Reprinted with permission from [33]. Copyright 2021 IOP Publishing).

Possible oxygen diffusion was also checked by studies of redox kinetics and defect chemistry, including oxygen-18 tracer diffusion with the conclusion that the oxygen transport is nearly negligible compared to lithium transport and may occur via oxygen interstitials rather than via oxygen vacancies in the whole stoichiometric range [20,21]. It should be noted that the only 'free space' in LN, the octahedral structural vacancy, is an unfavorable site for anions. These results showed that the role of oxygen vacancies in the redox processes of LN is negligible, while oxygen loss/recovery is possible by the decomposition/recovery of the surface layer. For strong reduction treatments above ~650 °C, segregation and evaporation of the volatile compound Li₂O becomes important and leads to a gradual stoichiometry change in the crystal proceeding from the surface towards the bulk. This can be reversed and even overcompensated by embedding the crystal in powder mixtures serving as buffers for Li₂O. The vapor transport equilibration (VTE) method, the first technique used for the production of stoichiometric LN, is based on this procedure [37,38] and does not require the diffusion of anion vacancies either.

It took some time until the cationic interpretation of thermal reduction could be clarified. The starting point was again increased density, signaled for reduced crystals by Smyth [16] and his remark about the "inconsistency to propose one set of defects for Li₂O deficiency, and a different set for oxygen loss". The Nb_{Li} antisite was demonstrated to be a 'negative-U' defect capable of lowering its energy by binding a second electron, whereby a Nb⁴⁺_{Li}-Nb⁴⁺_{Nb} molecular ion involving a regular niobium neighbor is formed along the trigonal axis of the crystal; covalent bonding turns the interaction energy U between the two small polarons negative, despite Coulomb repulsion [35,36]. The oxygen loss was attributed to the depletion of elementary cells on the surface, while the cations left over were assumed to diffuse into the bulk, filling existing Li vacancies, according to the reaction

$$LiNbO_3 + 2V_{Li} \rightarrow Li^+_{Li} + Nb^{4+}_{Li} + \frac{3}{2}O_2\uparrow + 5e^-$$
 (1)

In this scenario, the remaining electrons, transformed into small polarons, follow the cations and are trapped on the antisites. Above ~650 °C, a similar reaction with Li₂O loss (compare Equation (3)) becomes effective. The presence of Nb_{Li} point defects on the surface of reduced LN was supported by RHEED investigations [25]. Accordingly, starting from the surface, polarons and bipolarons gradually turn the crystal non-transparent. The absorption band near 2.5 eV indeed corresponds to that calculated for bipolarons [39–42], whereby further absorption of the same defect or its similar variant in the region near 3 eV is also indicated by recent calculations [10]. The transformations upon photoexcitation in

the 2.5 eV band or upon heating the crystal can be explained by the reversible dissociation of the bipolaron leading to the appearance of only one defect type, the Nb⁴⁺_{Li} center. Due to the absence of trapped-hole centers in reduced crystals, a thermodynamical equilibrium is established between antisite-trapped polarons and bipolarons, as observed in the range 122–575 K [36]. For higher temperatures, both kinds are liberated step by step from their bondage, leading to the appearance of free Nb⁴⁺_{Nb} polarons absorbing near 1 eV [20,43,44]. The underlying kinetics have been observed and modeled in great detail in the whole temperature range, yielding activation energies in full agreement with photoexcitation, DC conductivity, and thermopower experiments [35]. Attempts to interpret the same transformation processes in the oxygen-vacancy scenario encountered difficulties due to the need to accommodate a further unfitting partner in the model: the F⁺ center.

An independent, decisive argument in favor of the cationic interpretation of thermal reduction processes in LN is the lack of ~2.5 and ~3.2 eV bands in crystals where antisites are absent. Such a case, a 5% Mg-doped LN crystal grown from a melt with [Li]/[Nb] = 1:1 molar ratio and reduced at 1000 °C, was investigated by Sweeney et al. [45]. In this study, only an asymmetric band near 1 eV due to a Mg_{Li} -assisted Nb_{Nb}^{4+} polaron was found as a result of reduction (see spectrum (b) of Figure 9 in [45]; it should be noted that the decomposition of this band given in the bottom part of the same figure is incorrect, because trace (d) is already an unphysical difference-band obtained earlier by the comparison of Nb_{Nb}^{4+} and Nb_{Li}^{4+} bands in crystals above and below the photorefractive threshold, respectively. Apart from this controversy and the unconfirmed assignations to vacancy centers, the results in [45] proved to be highly reliable (see also [46])). The crystal used was beyond the photorefractive threshold where no $Nb_{I,i}$ antisites are present; part of the Mg²⁺ ions already form self-compensating complexes on both Li and Nb sites, whereas other Mg_{Li}^{2+} ions may still be charge-compensated by Li vacancies [47]. There is no reason why oxygen loss should have a different mechanism in this case, still the bands tentatively attributed by Ref. [45] to oxygen-vacancy centers in undoped LN are missing. However, a cationic mechanism, also offering a straightforward explanation for this crystal, can be readily suggested: reduction involving O_2 loss may occur by a reaction consuming elementary cells on the surface together with a transfer of nearby Mg ions from Nb to Li sites

$$LiNbO_{3} + Mg_{Nb}^{2+} + 2V_{Li} \rightarrow Li_{Li}^{+} + Nb_{Nb}^{4+} + Mg_{Li}^{2+} + \frac{3}{2}O_{2}\uparrow + 5e^{-}$$
(2)

resulting only in Nb_{Nb}^{4+} polarons. In fact, all electrons on the right-hand side also form such small polarons overtaking the role of lithium vacancies as charge-compensators of further Mg_{Li}^{2+} defects not shown in Equation (2). Based on the above results and model calculations discussed later, the model of thermal reduction based on the formation of oxygen vacancies in cLN could be discarded.

3.2. Defect Generation in cLN by Ionizing Irradiation at Low Temperatures ($T \le 77$ K)

Irradiation at low temperatures (T \leq 77 K) results in polaron formation in the bulk. Various kinds of radiation, including two-photon absorption [26], X-rays [26,32], Co⁶⁰ γ -rays [48], and higher energy electrons up to 1.7 MeV [30] have been used; along with Nb⁴⁺_{Li} polarons having an EPR fingerprint and an absorption band at ~1.7 eV, O⁻ hole polarons (also small) preferably trapped at lithium vacancies were also formed, having another EPR fingerprint and an absorption band near 2.5 eV (see Figure 2), fortuitously coinciding with that of bipolarons. In undoped LiNbO₃, Nb⁴⁺_{Li} polarons become mobile at temperatures between 100 and 150 K and recombine with the trapped holes [26,32] in a non-radiative process [46]; therefore, the original state of the crystal is restored. Arizmendi et al. [32] also reported on the presence of a further smaller band at ~3.2 eV, ascribed to the same trapped-hole polarons in the X-irradiated crystals (again coinciding with similar structures in trapped-electron spectra). Upon heating, the three bands showed a marked parallel decrease in the 100–150 K region up to their complete disappearance below 240 K. An important achievement of this paper was an early derivation of the temperature ~312 K

where $O^-(V_{Li})$ trapped holes became mobile. At the temperature ~312 K, measured in Cudoped LN X-irradiated at low temperature, small polarons trapped as stable Cu⁺ centers became spontaneously converted to Cu²⁺ centers by mobile holes.



Figure 2. Optical absorption induced by 2 h 40 keV X-irradiation in LN samples with different bulk [Li]/[Nb] ratios derived a posteriori from measurements of the UV absorption edge (see Section 3.3). Sample A: 0.98 nearly stoichiometric, sample B: 0.96 nearly congruent, sample D: 0.92 sub-congruent, all irradiated and measured at 77 K. (Reprinted with the permission from Ref [49]. Copyright 2021 American Physical Society).

A peculiarity of high-energy irradiation by electrons was the small intensity of the Nb⁴⁺_{Li} EPR signal compared to that of the O⁻ EPR signal [30], in contrast to the X-ray results where they were comparable [26]. This can be understood by assuming that the relative number of paired polaron trappings increased compared to single trapping due to the large polaron density created in the electron tracks. Therefore, the 2.5 eV band, in addition to the absorption of O⁻ centers, may have also contained an indistinguishable (and larger than usual) contribution of paired electron centers, i.e., bipolarons. However, the stability of the defects was found to be practically unchanged compared to experiments using lower irradiation energies, with recovery occurring for all radiation defects near 200 K. The question about missing fingerprints of F⁺ centers providing deep polaron trapping sites expected by some authors [30,32] remained unanswered. Before proceeding to defect generation by high-energy irradiation at higher temperatures, we discuss similar processes caused by strong mechanical impact.

3.3. Mechanochemical Defect Generation in cLN Nanocrystals

As discussed in the review of Sánchez-Dena and coworkers [4], investigating nanocrystals is another possibility for the study of the defect structure of LiNbO₃. Similar defect generation phenomena as for thermal reduction have been observed upon high-energy ball-milling of polycrystalline cLN [50]. Milling resulted in sample darkening due to mechanochemical reduction via polaron and bipolaron formation detected by optical reflection spectroscopy. The obtained particles of the size of a few hundred nanometers contained monocrystalline grains sized in the range of 30–80 nm. The process was accompanied by oxygen release and Li₂O segregation:

$$2\text{LiNbO}_3 + 2\text{V}_{\text{Li}} \to 2\text{Nb}_{\text{Li}}^{4+} + 8\text{e}^- + \frac{5}{2}\text{O}_2\uparrow + (\text{Li}_2\text{O})_{\text{segr}}$$
(3)

while subsequent oxidizing heat-treatments recovered the white color with the evaporation of Li₂O and crystallization of a LiNb₃O₈ phase on the grain surface requiring minimal adjustment, given its epitaxial compatibility with LN [25]:

$$LiNbO_3 + 2Nb_{Li}^{4+} + 8e^- + \frac{5}{2}O_2 \rightarrow 2V_{Li} + LiNb_3O_8$$
 (4)

The phase transformations occurring during both the grinding and the post-grinding heat treatments were also studied by Raman spectroscopy and X-ray diffraction measurements, whereas the Li₂O content of the as-ground samples was quantitatively measured by coulometric titration. The thickness of the surface layers with modified composition could be estimated to be of the order of 2 nm and 10 nm for the as-milled and oxidized samples, respectively. The latter value is in good agreement with the results of TEM–EDS sampling measurements on similarly prepared nanoparticles of LN:Fe reduced at 650 °C [51], where the Nb and O concentrations in the grains remained unchanged during grinding with the exception of a surface layer of ~14 nm thickness: in this layer, a gradual increase in the Nb and a decrease in the O content towards the surface could be detected, in agreement with Equations (1) or (3), taking into account the evaporation of any Li₂O segregate upon thermal reduction.

These findings show the basic similarity of defect generation processes in the discussed cases: while thermal reduction promotes O_2 and Li_2O loss by lowering the respective chemical potentials, high-energy ball milling squeezes these components out of the crystal, facilitated also by the somewhat increased temperature during grinding. This indicates that the colored cores of the obtained grains have an increased density, as expected for the bipolaron model of reduction.

3.4. Defect Generation in cLN by High-Energy Irradiation at Higher Temperatures (220 °C)

Using high-energy irradiation by electrons or heavier particles at 220 °C in vacuum, absorption bands persisting well above room temperature may be detected. This was demonstrated by Hodgson et al. [52] and revisited in the present Special Issue [1]. Apart from a superficial comparison between LN and $SrTiO_3$ disregarding the deep constitutional differences between these matrices, Ref. [1] only repeats the tentative interpretation of Hodgson et al. [52] based on anion vacancies, referring to some of their figures but partly transforming them in an unexplained manner. Therefore, we confine the discussion to the original paper [52]. For gamma or electron irradiations below an energy threshold, only less structured absorption with very limited amplitude could be achieved. This changed above the threshold where the intensity of the observed spectra showed a nearly linear increase with radiation dose. Their structure and behavior upon heating/cooling strongly resembled those obtained by thermal reduction, showing broad features at ~1.6 eV, ~2.6 eV and ~3.2 eV; however, the main band showed trapped-electron character in contrast to the case of low-temperature irradiation where it was rather of trapped-hole type; upon heating there was again a reversible transformation of the main band at ~2.6 eV to the band at ~1.6 eV, whereby the same isosbestic point near 600 nm was observed as for reduced crystals [36,52]. The particle energy threshold found for increased defect formation was 0.3 MeV, corresponding to an oxygen displacement energy of 53 eV, in reasonable agreement with oxygen displacement thresholds in other oxides (see references in [6,52]). No saturation after five over-threshold doses of 2×10^{18} e/cm² could be observed. The authors proposed that the defects generated were oxygen vacancies trapping one or two electrons (F⁺ and F-centers, respectively), and thermal excitation resulted in the reversible transformation of F-centers into Nb⁴⁺_{Li} trapped polarons. Accordingly, they attributed the observed dominating absorption band near 2.6 eV to F-centers, despite its coincidence with the bipolaron band in reduced crystals, while a weak band at ~3.2 eV was again tentatively attributed to F⁺-centers.

However, due to the perfect similarity with the case of thermal reduction, even in this case an interpretation in terms of bipolaron formation seems to be more appropriate.

The most important difference between the high-energy experiments in Refs. [30,51] is the irradiation temperature. Irradiation at 77 K formed both trapped-electron and trappedhole centers, all disappearing near 200 K, whereas similar irradiation at 220 °C resulted exclusively in trapped-electron defects, this time highly stable at least up to 800 $^{\circ}$ C. As discussed earlier, above room temperature, $O^{-}(V_{Li})$ trapped-holes become mobile. Stable hole-trapping on oxygen interstitials may also be discarded (see Section 4 and [13]); therefore, coloration for T > 220 °C can only be stabilized by oxygen loss similarly to the case of thermal reduction and ball milling. This means that oxygen must have also left the crystal lattice during high-temperature irradiations. Note that the irradiation in [52] was carried out under vacuum. Apparently, high-energy irradiation locally stimulates processes similar to those active during thermal treatments; therefore, they can set in already at 220 °C, whereas normal 'unassisted' thermal reduction only starts at higher temperatures. Oxygen interstitials proved to be mobile at high temperatures [21]; the same may be assumed in local thermal spikes. For this reason, recombination of the oxygen sublattice during and immediately after irradiation is expected to be important. On the other hand, together with oxygen atoms, a large number of lithium atoms must also have been mobilized and partly left the crystal lattice. Thus, with increasing bombardment energy, local phase separation with Li_2O loss and the formation of $LiNb_3O_8$ inclusions may become possible. It can also be assumed that instead of stable oxygen vacancy generation, the formation of neutral Li₂O voids takes place, especially near the surface, and for highest doses their accumulation may turn the samples brittle. Accordingly, these internal segregation processes are expected to be similar to those observed on the surfaces of reduced crystals and nanocrystals. In this way, above a particle energy threshold, the number of Nb_{Li}^{4+} antisites will also increase, similarly to their almost unsaturable multiplication during thermal reduction. Even if present, oxygen vacancies can only offer higher-energy trapping states to polarons than antisites (see the comparison with model calculations in Section 4). Taking into account the sample thickness of ~1 mm roughly corresponding to the penetration depth of the radiation used [52], and a single defect generation event per particle, but neglecting anionic recombination, the 2×10^{18} e/cm² dose corresponds to an average center concentration of 2×10^{19} /cm³ equal to that of Nb_{Li} antisites in cLN. Therefore, even without newly formed antisites, their numbers should be sufficient to trap a great part if not all of the surviving polarons. In summary, again there is no reason to deny the dominating role of cationic defects in defect production in cLN.

3.5. Defect Generation in Nearly Stoichiometric LiNbO₃

After the advent and spreading of techniques capable of producing stoichiometric crystals [38] (for a review see [47]), to the best of our knowledge, no studies on the coloration of sLN crystals have been published. Crystals grown with the Czochralski method from melts with Li surplus but still containing NbLi antisites (although in substantially reduced numbers) were erroneously called stoichiometric up to 1992. For such crystals, we use the term 'nearly stoichiometric LN' (near-sLN). Compared to cLN, the experimental situation in these crystals is different and can be characterized by low saturation levels, slightly shifted absorption bands (see Figures 1 and 2, [33,49]), and the absence of interpretable EPR spectra looked for in γ -irradiated crystals [48] (note that the sensitivity of EPR is reduced due to hyperfine-broadened lines). High-energy electron irradiation of near-sLN at temperatures up to 20 $^{\circ}$ C was reported by [53]. The crystals used in these papers were grown from a melt with a [Li]/[Nb] ratio of 1.2:1 by colleagues in Budapest, with an absorption edge near 311.8 nm in their records (corresponding to an absorption coefficient $\alpha = 20 \text{ cm}^{-1}$) a posteriori used to derive a [Li]/[Nb] = 0.98 ratio in the bulk [54]. In [53], the same particle energy threshold (0.30 MeV) was found for increased defect production as for cLN. For a one-hour irradiation with 1.6 MeV electrons at -50 °C, a structureless absorption with a very broad maximum at ~540 nm (~2.3 eV) could be achieved. Apart from the slight redshift compared to the case of cLN (~500 nm), the spectrum showed a radically reduced stability, with two major, slightly overlapping annealing stages near -25 °C and 40 °C, and a third one near to 350 °C, where the small residual coloration consisting of a broad spectral feature near 760 nm and an even weaker one near 400 nm also disappeared (Figure 3). If, after a given annealing step, the annealing was stopped, the crystal re-cooled below the step temperature and then re-irradiated, fast (minute-timescale) reconstruction of the absorption monitored at 540 nm could be achieved. Such a fast reconstruction was not possible after annealing above 350 °C, but the whole process could be repeated. During some stages of irradiation or annealing, unspecified in [53], the spectrum showed a redistribution of bands from the short ($\lambda < 580$ nm) to the long wavelength ($\lambda > 580$ nm) part, very similar to that observed for congruent samples during heating or selective bleaching.



Figure 3. Irradiation and temperature annealing behavior of the 540 nm band for high-energy electron irradiation at -50 °C (Reprinted with permission from [53]. Copyright 2021 IOP Publishing).

Similarly to the case of cLN, bands at 500-540 nm and 400 nm were attributed to Fand F^+ -centers generated during knock-out processes, respectively [53], disregarding the less defined position of the F band compared to cLN and the parallel behavior of both bands in the reported transformations. Although the important contribution of O⁻ centers to the main absorption band near 540 nm was not mentioned, the two-step annealing of this band was explained by the liberation of holes from two kinds of hole centers. Fast recovery upon re-irradiation was attributed to simple electron re-trapping at the unchanged trap, while full recovery of the lattice was assumed to occur only near 350 °C. The assumption about two kinds of hole centers is indeed supported by the reported existence of two kinds of O⁻ trapped holes having either unresolved or resolved hyperfine structure in their EPR spectra [48,55]. These referenced studies used cLN and photons of similarly high energy above 1 MeV. Trapped holes without distinction were shown to be stable up to ~312 K by [32] in Cu-doped cLN irradiated by 40 keV X-rays, where the lower photon energy or some other difference in preparation might have been the reason for only one annealing stage found. The decay temperature of 312 K perfectly fits the second annealing stage observed by [53].

The authors attributed the final recombination step near 350 °C in near-sLN to the release of oxygen interstitials annihilating the oxygen vacancies. However, this temperature corresponds to the well-known starting temperature of first-stage thermal reduction governed by Li mobility, also identified in ionic conductivity studies (for references see [9]), while the onset of oxygen mobility of any kind is expected at substantially higher temperatures [20–22]. In fact, in the framework of the bipolaron scenario, there is also a straightforward explanation for the observed difference between slow and fast coloration processes near room-temperature: for the stability of the doubly recharged defect, a change in its charge-compensation is required, which can be provided by the time- and energy-consuming diffusion of cation vacancies away and back to the antisite. The observed gradual blueshift of the main absorption band from 540 to 500 nm and further (see Figure 2) upon decreasing the Li/Nb ratio can also be explained by the increasing flexibility of the cation sublattices. Better charge-compensation by further neighboring defects also lowers

the formation energy of the antisite complexes and possibly also that of trapped-hole defects, meaning larger distances of the trapping level from the conduction and valence bands, respectively. This fine-adjustment energy is comparable to the energy of the order of 0.5 eV calculated by [40] for the association of defects. Similar possible stoichiometry-dependent minor shifts of the ~1.6 eV small-polaron band are of the order of the experimental error.

It may be assumed that diffusion is hampered in near-sLN due to the smaller concentration of both Li vacancies and Nb_{Li} antisites. Slower diffusion in near-sLN upon thermal reduction may be the cause of the increased presence of surface coloration which could be eliminated either by polishing or by covering the samples by Pt foil [33] (see Figure 1). Absorption near to the UV edge is also caused by charge-transfer transitions involving the generation of localized excitons; these can be described as Nb⁴⁺–O⁻ excitons having dipolar character, pinned on intrinsic and extrinsic defects of similarly strong dipolar character mainly due to their charge compensators [46].

Accordingly, the discussed experimental results in near-sLN do not support the oxygen vacancy model, whereas those involving high-energy irradiation near room temperature even provide further ingredients for the development of the bipolaron scenario. Moreover, the absence of increased defect formation at higher temperatures in near-sLN, suggested by implication by Hodgson et al. [53], might be a general argument against the oxygen vacancy scenario.

4. Comparison with Model Calculations

Earlier atomistic or cluster models did not consider the role of the ambient; however, more recent calculations also include the effect of the environment via temperature- and pressure-dependent chemical potentials, and also account for the Fermi level changing upon reduction. The formation energies of basic defect types, also including isolated oxygen vacancies and Nb_{Li} antisites, have been calculated and compared by Xu et al. [13] in the framework of density-functional theory as a function of the Fermi energy ε_F , using the perfect state of the chosen 240-atom supercell as a common reference. For values of ε_F between the valence band maximum (VBM) and the conduction band minimum (CBM), the data are shown in Figure 4 for the defect's optimal net charge state in the Li-deficient limit. In the as-grown state at low temperature, $\varepsilon_F \approx E_{gap}/2$, where $E_{gap} = CBM - VBM$ is the gap energy and the energy zero corresponds to the VBM. A direct comparison between the formation energies of uncompensated but relaxed Nb_{Li} and V_O defects shows that the antisite underscores the oxygen vacancy for all relevant values of ε_F . In the as-grown state, the margin is large for a number of reasons:

i. The local density approximation used by [13] calculates an unphysical self-interaction for large electron densities prevailing inside the bipolaron's covalent bond between its $Nb_{I,i}^{4+}$ and its Nb_{Nb}^{4+} constituents, unduly raising its energy. Corrections within the same framework but including the use of hybrid exchange-correlation functionals [40,41] or GIPAW pseudopotentials, self-consistently calculated U values, and the Bethe-Salpeter equation [42] lower the bipolaron level (+2 net-charge state) by more than 0.5 eV, partly underscoring even the single-polaron state (+3 net charge) and thereby verifying the negative-U property of the antisite not displayed for the +3/+2 transition in the results of [13]. It should be noted that the +1 and 0 net-charge transfer levels of the antisite have been shown to correspond to a bipolaron and one or two additional free Nb_{Nb}^{4+} polarons fully separated from each other inside the supercell [42]. This means that the 'states' with more than two electrons trapped on the antisite are spurious levels inside the conduction band or closely below the CBM, but their corrected positions can be used for an independent estimate of the position of the CBM. The corrections and estimates lead to agreement with independently calculated values of E_{gap} considered realistic between 3.8 eV and 5.4 eV [56,57], while the values derived from the position of the UV absorption edge are close to 4.0 eV [54]. The charge densities of bipolaronic states have recently been calculated to extend ~1.5 eV below the CBM [10], also supporting the above estimates;

- ii. The corrections described in (i) do not concern the position of calculated oxygenvacancy levels. In the as-grown crystal, the preferred empty state of the oxygen vacancy is expected to have a formation energy corresponding to the CBM with an error margin of ± 0.5 eV;
- iii. The Nb_{Li} antisite requires more charge compensation than the oxygen vacancy (two more lithium vacancies, if comparing defect complexes with the same net charge), which further increases the energy difference between their realized levels by several tenths of an eV. Associations with charge compensators have been shown to amount to an energy gain of up to 0.52 eV for the Nb_{Li}¹ 4V_{Li} defect [40].



Figure 4. Defect formation energies of various point defects as a function of Fermi energy; the lowest-energy net charge state is given in each case. The Fermi energy ranges from $\varepsilon_F = 0$ (left) at the VBM to $\varepsilon_F = 3.5$ eV (right) at the CBM (without self-interaction correction and charge compensation, Reprinted with the permission from Ref [13]. Copyright 2021 American Physical Society).

Therefore, in as-grown cLN, the formation energy of the F-center exceeds that of bipolarons by 1.4 ± 0.8 eV, making its population highly improbable. However, upon thermal reduction, the outside oxygen chemical potential μ_{O} may be substantially decreased: raising the temperature by 1000 °C and decreasing the oxygen partial pressure from 0.2 to 10^{-8} atm imposes changes of -2 eV and -0.8 eV on μ_{O} , respectively [13], adding up to $\Delta \mu_{\rm O} = -2.8$ eV. This lowers the formation energy of oxygen vacancies inside the crystal which promotes their appearance, but only on the timescale of diffusion processes. Bipolarons do not involve oxygen loss; therefore, their levels remain unaffected. Therefore, a great part of the $\Delta \mu_{\rm O} = 2.8$ eV difference has to be realized before the oxygen vacancy level inside the crystal may approximate that of the bipolaron. Equality between the levels may be assumed to correspond qualitatively to the end of the first annealing stage: for T_{red} < 650 °C, only oxygen loss from the surface together with in-diffusion of the cations and electrons occurs, raising the Fermi energy as well. For T_{red} > 650 °C, a second annealing stage can also be reached, where Li₂O starts to leave the crystal, meaning that the bulk chemical potential of Li₂O begins to be underscored by its outside value. This triggers surface decomposition processes described by Equation (3) and may promote also the formation of Li₂O Schottky defects. In this annealing stage, the crystal is driven towards the Li₂O–Nb₂O₅ decomposition limit corresponding to minimal possible Li₂O content in the stability quadrangle within the triangular chemical potential chart of LN (point C in [13] or point E in [40]). In fact, the Li_2O Schottky defect, the empty oxygen vacancy compensated by two empty lithium vacancies, has a near-zero formation energy already in the as-grown crystal, making it the defect of second choice after the antisite complex

 $Nb_{Li}-4V_{Li}$ [13]. Accordingly, for second-stage reduction followed by cool-down, instead of high-energy F-type centers, neutral Li₂O Schottky defects having much lower energy may form, while antisite-trapped bipolarons will remain the dominating trapped-electron defect. Due to their high mobilities, the movements of small polarons and charge-compensating Li vacancies are always correlated, and upon cool-down defects with zero net charge will dominate. This means that while the formation of oxygen vacancies and new lithium vacancies cannot be excluded for strong reduction treatments, this is not expected to lead to the formation of stable F or F⁺-centers.

On the other hand, the cited calculations on electron polarons and bipolarons trapped at antisite Nb_{Li} defects reproduced the observed spectroscopic features and the values of various other properties in Li-deficient LN, including the spin-Hamiltonian parameters of Nb⁴⁺_{Li} [10,42,58]. All these results give strong additional support to the established small-polaronic models and the cationic mechanism of thermal reduction.

For a refinement of the presented interpretations but also for finding minority effects related to oxygen defects in LN, further experimental and theoretical studies are required, explicitly taking into account the presence of charge-compensating defects together with diffusion and clustering as well as surface effects. In particular, modeling the structure of the modified surface layer on the nanometer scale for various treatments remains a major challenge. The rich potential of the active surfaces of LN has been presented in [59]. Oxygen vacancies as possible charge compensators of aliovalent extrinsic cation dopants, e.g., in $Mo^{4+}-V_O$ defects found stable by cluster calculations of [60] are a separate problem requiring confirmation by experiment and comparative calculations.

5. Conclusions

More than half a century after its first Czochralski preparation, we still have to emphasize that LN is not a 'normal' oxide, such as Al_2O_3 or $SrTiO_3$, but a compound with great freedom of redistribution, although only for its cations, which can also be regarded as an intermediary system between the anode and cathode materials Li_3NbO_4 and $LiNb_3O_8$ considered for lithium-ion batteries. Defect generation in non-stoichiometric LN by thermochemical, mechanochemical or irradiation methods was shown to be subject to a single principle, cationic rearrangement, in fulfillment of the remarks of Smyth [16]. We demonstrated that the repeatedly proposed oxygen-vacancy-type models cannot be sustained in Li-deficient LN. Similarly to the futile attempt to use the reversible transformation between small-polaronic bands to prove these models, the argument about non-saturating defect generation by high-energy irradiation cannot be used as a decisive proof for the generation of F-centers either. On the other hand, there are four basic arguments in favor of cationic motion and small-polaron/bipolaron formation as the main cause of coloration in cLN:

- i. the practically unchanged positions of the absorption bands at ~1.6 and ~2.5 eV obtained in cLN (attributed to small polarons and bipolarons/hole polarons, respectively) under all employed reduction, irradiation and grinding procedures up to 1050 °C; there were only small shifts of the ~2.5 eV band for changing stoichiometry which could be attributed to defect association effects both for bipolarons and hole polarons;
- ii. the lack of the bands at 1.6 and 2.5 eV attributed to small polarons and bipolarons in the absence of antisites in over-threshold LN:Mg [45] and the limited growth and instability of coloration observed in irradiated or reduced near-sLN;
- iii. missing of verifiable fingerprints of F⁺ centers and the lack of a consequent interpretation of their role;
- iv. calculations: bipolarons at Nb_{Li} antisites are predicted to provide deeper trapping sites for small polarons than oxygen vacancies; the latter have larger calculated association energies with lithium vacancies than with electrons.

Coloration in LN doped by an over-threshold amount of Mg was also suggested to occur by cationic rearrangement, i.e., a partial change of Mg incorporation from Nb to the Li site. A key element in stable defect formation is apparently the mobility of Li⁺ ions com-

plementing small-polaronic migration and trapping processes thereby providing charge compensation for changing defects. Characteristic temperature regions below 200 K, near -25 °C/40 °C and near 350 °C, derived earlier from defect annealing experiments, have been interpreted as ranges where electron-polarons, two types of trapped hole polarons, and lithium vacancies become mobile, respectively. Another major aspect are surfaces playing a prominent role as areas for evaporation and phase segregation in thermal reduction and mechanochemical processes, and also during high-energy irradiation at elevated temperatures. Further measurements on variously treated LN crystals of bulk, thin layer, or nanocrystal forms, using optical, (para)magnetic and dielectric spectroscopies and their combinations as well as atomic resolution analytical and imaging methods (see [61] in the present Special Issue), complemented by calculations, may provide additional detail to this picture.

Author Contributions: Conceptualization, G.C.; writing—original draft preparation, G.C.; writing—review and editing, L.K. Both authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Quantum Information National Laboratory of Hungary, supported by the Ministry of Innovation and Technology and the National Research, Development and Innovation Office (No. of Grant Agreement: NKFIH-873-3/2020).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: No new data were created or analyzed in this study.

Acknowledgments: This review and the Special Issue 'New Trends in Lithium Niobate: From Bulk to Nanocrystals' as a whole is dedicated to the memory of Ortwin F. Schirmer, who was one of the initiators of the bipolaron concept in oxides, and whose kind personality and dedicated guidance played a stimulating role in the author's careers.

Conflicts of Interest: The authors declare no conflict of interest.

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