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Nonstoichiometry as a powerful tool for photorefractive material optimization. Lithium Niobate Crystals.

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Abstract: An analysis of our radiospectroscopic and optical data obtained on a great variety of $LiNbO_3$ crystals of different compositions stimulated us to develop a new approach to the intrinsic and extrinsic defect subsystems, considering them as one integrated functional system. Their strong interrelation becomes especially apparent when concentrations of both defect classes are comparable. Typical examples of mutual influence and correlation of subsystems are demonstrated. Crystals with extremely low intrinsic defect contents offer extraordinary informative opportunities. Since both defect subsystems can be used for a deliberate tailoring of properties, nonstoichiometric materials are especially promising for crystal engineering. The developed ideas are also valid for other photorefractive materials.

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Introduction

There are many photorefractive materials, known for their rather attractive natural features, which can be used, for instance, in the field of dynamic holography or for the high-density optical data storage. However, to realize their efficient and wide application the further improvement of different photorefractive characteristics (including faster response time, higher efficiency, better reproducibility etc.) is absolutely necessary. Such an improvement can be successfully reached as a result of the optimization of material characteristics based on the detailed knowledge of defects, responsible for the light-induced charge transport phenomena, and their influence on the bulk material properties.

Among such crystals the Lithium Niobate (LN) is one of the most known, interesting and promising for both fundamental science and applications [1, 2, 3]. Conventional LN crystals, grown from a congruent melt with lithium deficiency ($X_{melt} = X_{Crystal} \approx 48.4\%$, where $X = [Li]/([Li]+[Nb])$, contain some percent of intrinsic (nonstoichiometric) defects. Attempts to obtain crystals with low concentrations of intrinsic defects by using melts with Li excess (up to $X_{melt} = 60\%$) or by post-growth vapor transport equilibration treatment were rather successful. Investigations of these crystals gave a lot of useful information. However, it was found [4] that crystals grown under special conditions from melts to which potassium has been added (later on labeled LN-K) have even lower intrinsic defect concentrations. It should be remarked here that potassium itself practically does not enter the crystals grown in this way. The results of the first studies of these samples [5, 6], often conventionally named stoichiometric, pushed many laboratories in the world to produce such crystals by different growth techniques [7, 8, 9, 10] and to study their properties. Many new interesting features have been discovered (see, for example, [11, 12, 13, 14]), initiating the booming interest in these materials.

The analysis of the present conception of defects in LN from the point of view of a strong mutual dependence of the subsystems of intrinsic and extrinsic defects forms the topic of this review.

It is mainly based on the results of our experimental and theoretical studies (see [15, 16, 17, 18, 19, 20, 21, 22, 23]) combined with available literature data for a more complete characterization.

LN crystals of a wide range of stoichiometric compositions, undoped and doped with various impurities, which are introduced into the crystals in diverse concentrations, have been used in our investigation carried out by means of different techniques. Radiospectroscopic methods - Electron Paramagnetic Resonance (EPR), Nuclear Magnetic Resonance (NMR) and Electron Nuclear Double Resonance (ENDOR) - have been applied as our main techniques, since they are very sensitive and informative tools for the study of defect structure. For complementary characterizations the data of different optical methods and X-ray structural analyses were also employed.

A realization of such comparative investigation and reliable interpretation of the obtained results would not be possible without discovery and then development [4, 5] of the way of crystal growth, making available the crystals with extremely low concentration of intrinsic defects. By this way the LN crystals can be obtain with the nearly perfect lattice (regularly ordered crystal, ROC).

Line narrowing and resolution enhancement

In order to optimize and improve the properties of LN various efficient and skillful procedures were invented: doping with modifiers (such as Mg, Zn, Sc, In); an addition of optically or acoustically active impurities (Fe, Ti, Cr, Er, Nd, Pr, ...)**;** modification of the standard crystal growth technique by Czochralski (double crucible technique, an addition of potassium to the starting materials**,** a top seeded solution growth with the potassium addition); post-growth treatment (reduction, oxidation, VTE etc.). The experimental data show that any manipulations with dopants induce changes in the subsystem of intrinsic defects and, by their common influence, cause variations of the properties of LN. All possible initial changes in the subsystem of intrinsic defects will lead to the quantitative and/or qualitative modifications of the impurity subsystem and as a result they again both together influence the LN characteristics.

Figs. 1, 2 demonstrate the typical EPR spectra in congruent and stoichiometric LN crystals. The concentration of both impurities was 0.01 wt. % in the melt. A similar narrowing of the spectral lines was observed for many other investigated impurities (Cr, Fe, Cu, Nd, Er, Yb, …).

Randomly distributed intrinsic point imperfections, dominating in congruent and nonstoichiometric crystals, lead to strong perturbation of the surroundings of optically or acoustically active impurities, to the broadening of their spectral lines, appearance of forbidden transition and broad asymmetrical wings of EPR, ENDOR, Raman, luminescence and other spectral lines. The significant narrowing of resonance lines in the samples with crystal composition close to the stoichiometric one (another words, with very low intrinsic defect content) enormously increases the spectral resolution. This gives an opportunity to study even non-controlled trace impurities and satellite centers, consisting of dopant itself and intrinsic defects. Such tremendous enhancement of resolution and sensitivity allows investigating many rather delicate effects, which were previously covered by the presence of intrinsic defects. For instance, it is easy to study forbidden transitions of Mn^{2+} (Fig. 2b), which give us a useful information about quadrupole interaction of manganese nucleus with the gradient of crystal electric fields.

Impurity centers in nonstoichiometric and stoichiometric crystals

Due to the high concentration of intrinsic defects the conventional congruent crystals are very tolerant to di- or trivalent impurities, substituting for Li^+ or Nb^{5+}, because the necessary charge compensators (local or distant) can be easily found among the nonstoichiometric defects.

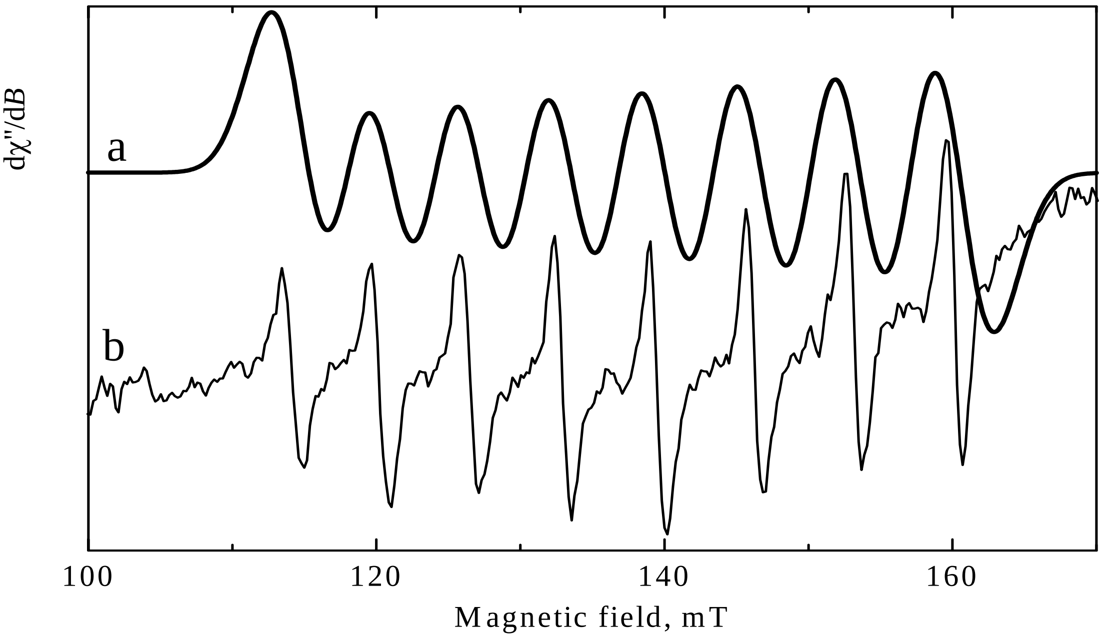

Fig.1. EPR spectra of Co^{2+} in congruent (a) and regularly ordered (b) LN crystals. Magnetic field **B**⊥**c**, *T* = 5 K, X-band.

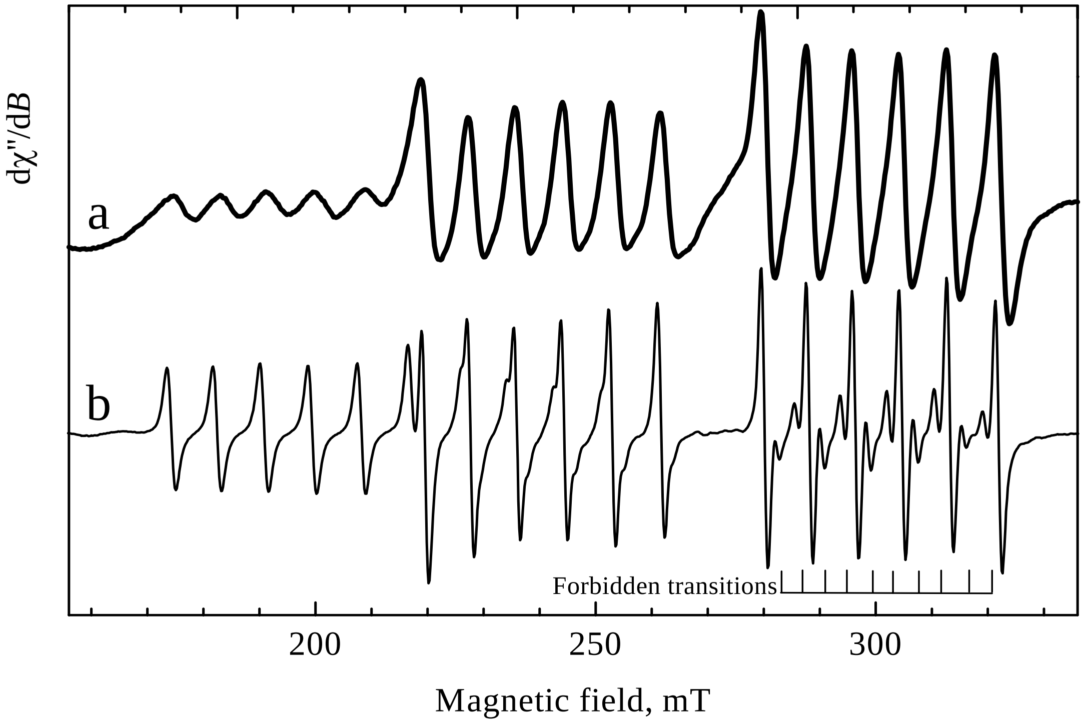

Fig. 2. The part of EPR spectra of Mn^{2+} in congruent (a) and regularly ordered (b) LN crystals. **B**⊥**c**, *T* = 5 K, X-band.

Therefore, in congruent crystals the formation of small complexes, consisting of “impurity ion - intrinsic defect” or two dopants locally compensated by an intrinsic defect can be easily realized (in addition to the single impurity centers). Such complexes are usually revealed in EPR spectra as specific “shoulders” of the main lines (Fig. 3a) or even as separate satellite lines [24]. The “impurity-impurity” exchange-coupled pairs were observed by EPR in congruent crystals at comparatively low (about 0.1-0.25wt. % in the melt) concentrations of impurities [18]. Due to low symmetry of these clusters it is very probable that they additionally include an intrinsic defect, i.e. they are “impurity-intrinsic defect-impurity” complexes.

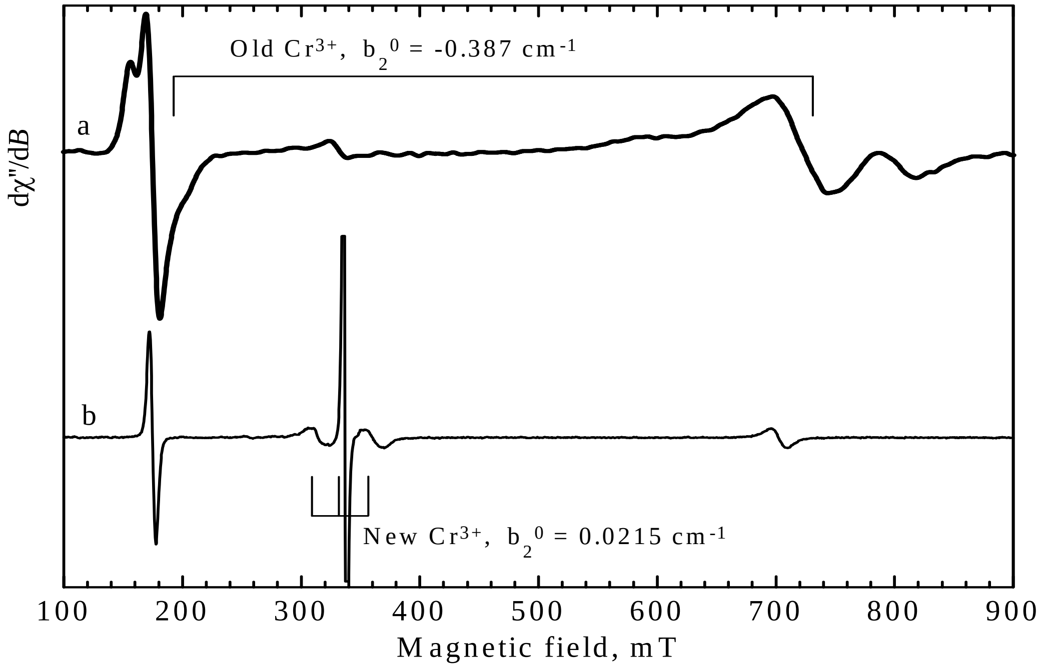

Fig. 3. EPR of Cr^{3+} in congruent (a) and regularly ordered (b) LN crystals. **B**⊥**c**, T = 5 K, X band.

In ROC the situation turns out to be completely different: together with the disappearance of intrinsic defects the complexes of “impurity-intrinsic defect” and “impurity-intrinsic defect- impurity” disappear also. They are absent even at the concentration of about 1wt. % in the melt. Since in ROC and nearly stoichiometric crystals a content of nonstoichiometric (intrinsic) defects is already not sufficient to compensate the excess charge of the “old” centers, the new ones appear; they are randomly distributed over the crystal and do not form the common structural complexes with the old centers. For instance, besides the old Cr^{3+} center (with the parameter of axial crystal field b_2^0 equal to -0.387 cm^{-1}) and Fe^{3+} (b_2^0=0.1768 cm^{-1}), one new axial chromium center and two additional iron axial centers [15] have been discovered (Fig. 3, 4). The distinction of their characteristics reflects the different surroundings and structure of these centers. Apparently the main role of the new centers is to fulfil a self-compensation of the charges of the same dopants. The conditions of their appearance, however, vary from impurity to impurity and correspond to the special concentration balance between the considered kind of impurity and intrinsic defects.

By summing the results of our investigations we can propose a graph with the schematically represented areas of the existence of isolated and complex centers in LN crystals of different compositions (Fig. 5).

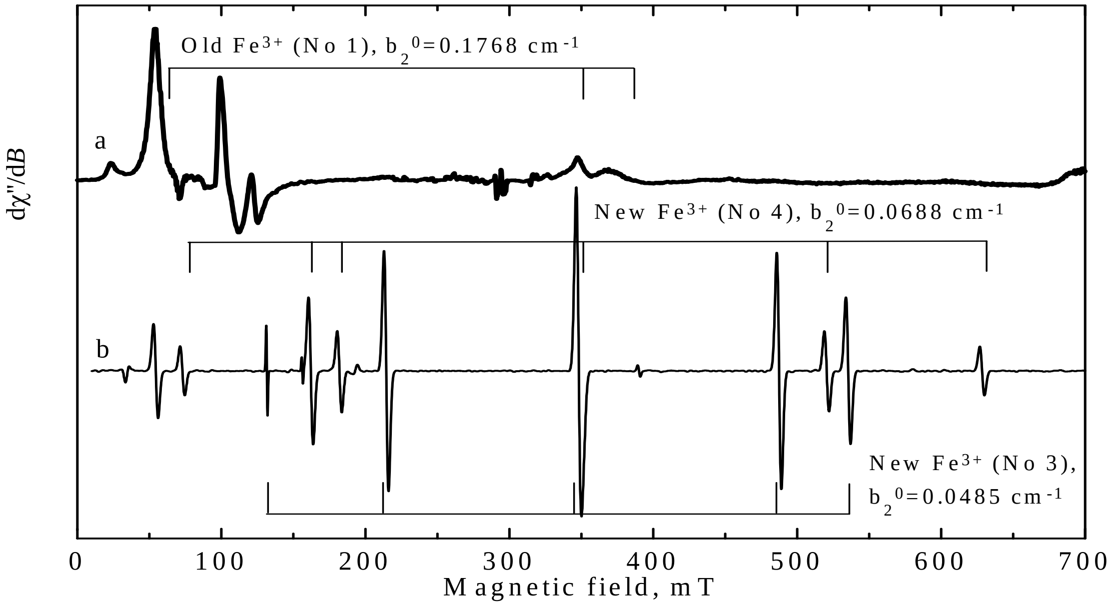

Fig. 4. EPR of Fe^{3+} in congruent (a) and regularly ordered (b) LN crystals. **B**||**c**, $T = 5$ K, X band.

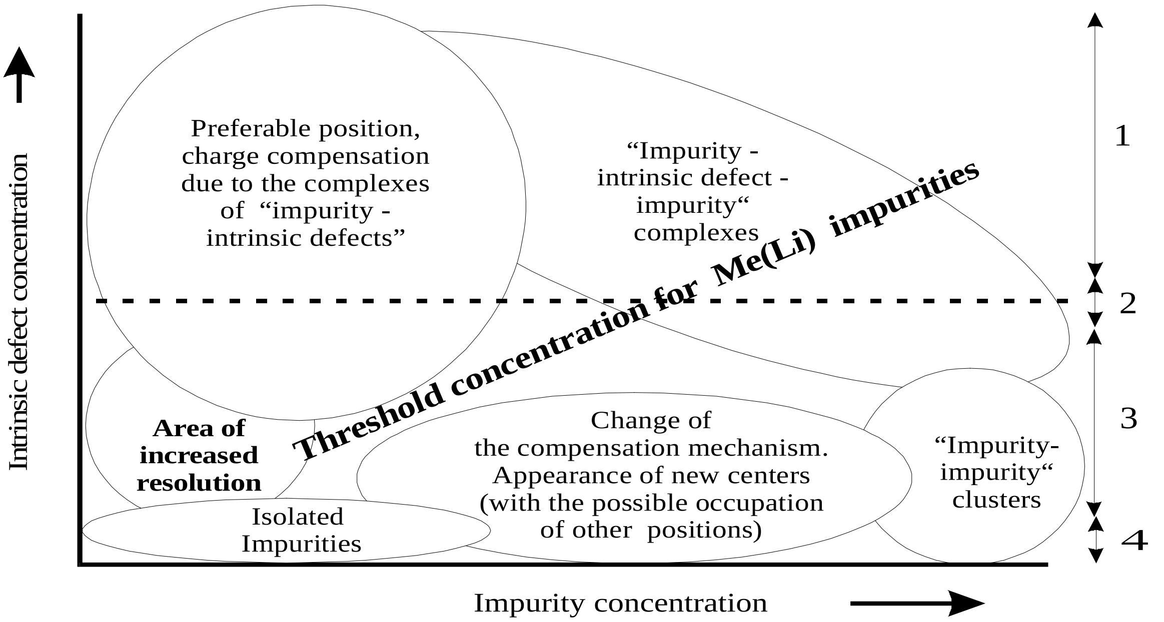

Fig. 5. Areas of the existence of isolated and complex centers. Li-deficient (1), congruent (2), Li-rich (3) and regularly ordered (4) crystal compositions are indicated.

Modification of crystal properties

An improvement of LN microstructure at the increase of Li content in crystals leads to the really amazing transformations of the properties in both quantitative and qualitative senses in comparison with the conventional material. Besides the above discussed new features in EPR spectra, the following essential changes of crystal characteristics were found in Li-rich LN and ROC: a remarkable increase in resolution of different spectroscopic techniques because of considerable narrowing of the spectral lines (EPR - Δ*B*; NMR, ENDOR, Raman scattering - Δν; luminescence, optical absorption etc.), a reduction of lattice constants, blue shift of fundamental optical absorption edge, a decrease of an intensity ratio of OH^- absorption bands at 3466 and 3478 cm^{-1}, a change of electro-optical coefficients and so on. The reduction of distribution coefficient of various impurities in ROC was also observed. Some of LN characteristics have really very strong relative changes at the going over from congruent crystal to ROC (Fig. 6).

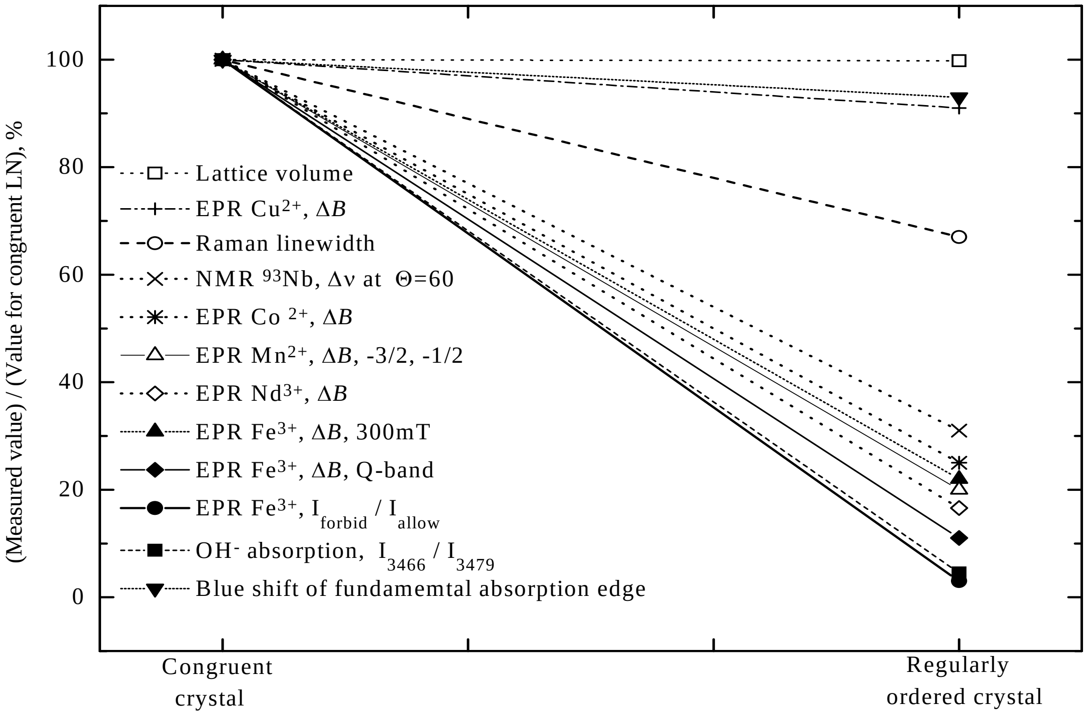

Fig. 6. Comparison of relative changes of some LN characteristics for congruent crystal and ROC.

The disappearance of intrinsic defects and betterment of the crystal lattice may significantly modify a scenario of the performance and redistribute the roles of the main defects-participants, involved in the light-induced charge transport phenomena. This is especially important for the processes of recording, fixation and readout of the holograms, because they are strongly depended on the type, charge state and concentration of the optically active centers, including both extrinsic and intrinsic defects. The coexistence of the centers, which occupy different lattice sites (like two Cr or three Fe centers), can also drastically change the rechargement mechanisms in Li-rich crystals and ROC, leading to the completely new photorefractive and photovoltaic characteristics in comparison with the congruent material. Recently, a rise to an at least two order of magnitude improvement in sensitivity over the best materials reported previously was obtained for nearly stoichiometric LN using the two-photon gated recording method [25].

Discussion and conclusions

Working with different dopants introduced in various concentrations into the crystals of diverse stoichiometry, we came to the conclusion that discrepancies between literature data for some parameters (and, consequently, the interpretation of such data) can be explained by the fact that crystals have generally been used, which were not well characterized with respect to their defect content. Sometimes such discrepancies are caused by the objective reason: the observed feature and/or its changes originated from the complicated combined influence of impurity and intrinsic defects at the same time. After understanding their mutual interrelation we had to develop a basically new approach to the intrinsic and extrinsic defect subsystems of LN material by considering both as partners of one integrated functional system.

The most efficient and reasonable way to get really scientific information about defects would be to base it on the following simplification of the investigation conditions: to study independently, where it is possible, the structure and undisturbed influence of extrinsic defects and, separately, the structure and pure effect of intrinsic defects. The use of regularly ordered (ROC) for such a purpose is very helpful and desirable at this stage. And only during the next step it is reasonable and should be intended to study the combined influence of both defect subsystems on the crystal properties.

For many and varied current applications congruent LN has quite satisfactory quality and characteristics. However, there are known essential drawbacks in the characteristics of congruent crystals, which should first be overcome in order to fit material as much as possible to the specific requirements of the applications, including the photorefractive ones. There is no doubt that on this way the opportunity to vary the nonstoichiometry in addition to the modification by dopants will serve as a very powerful tool for the optimization of crystal parameters. The remarkable features of ROC strikingly illustrate that this relatively new material is far-reaching, interesting and very attractive for both fundamental research and possible applications.

LN is not a unique example of photorefractive crystals having the tendency to grow with deviations from the stoichiometric composition, since the nonstoichiometry is a rather widespread phenomenon in the group of ferroelectric complex oxides (for instance, $Sr_{1-x}Ba_xNb_2O_6$, $Ba_{1-x}Ca_xTiO_3$, $LiTaO_3$, and others). The ideas developed in our work for LN have a general character; therefore they should also be valid and be taken into account at the study of other nonstoichiometric oxide materials.

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