NMR Analysis of Mg Ion Localization in LiNbO$_3$ Crystal

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The analysis of cation sublattices population in magnesium doped LiNbO$_3$ crystals is carried out. It is shown that volume concentration of lithium vacancies ($V_{Li}$) monotonously increases with increasing of MgO content in the crystal up to the threshold value. A series of LiNbO$_3$ crystals with various concentration of Mg$^{2+}$ were investigated by $^{6}$Li and $^{93}$Nb Nuclear Magnetic Resonance (NMR). It is concluded that the peculiarities of NMR spectra in Mg-doped LiNbO$_3$ crystals can be explained by the formation of defect complexes including Mg$^{3+}$ ions and $V_{Li}$ on the shortest distances between them.

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1. Introduction

Lithium niobate (LN) is the material which has found very wide application in modern nonlinear optics and electroacoustics [1]. Along with the investigations of the crystal features for its usage as media for the optical information storing, a special attention is given to the possibility of LN optical properties stabilization during its formation storing, a special attention is given to the possibility of LN optical properties stabilization during its treatment by powerful optical streams. LiNbO$_3$ crystals doped with Mg or Zn are objects of particular interest and extensive investigations because it was found that these dopants are responsible for increase of the LN resistance to optical damage [2]. It is known that LN crystals with MgO content above 4.5-5.0% (so-called threshold content) are non-photorefractive ones. Incorporation of Mg$^{2+}$ ions into the LN structure considerably influences not only the crystals’ optical properties [2, 3] but also the parameters of its unit cell, its density, its electric conductivity etc. [4].

The analysis of Mg$^{2+}$ ions localization in LN structure was made by many researchers and it has been shown that at MgO concentration less than threshold, Mg$^{2+}$ ions usually occupy positions of Li$^{+}$-ions, preventing the appearance of antisite Nb$_{Li}$ ions [5–9]. However, when MgO concentration is above the threshold there are different models of Mg$^{2+}$ ions localization in LN crystal:

1. Mg$^{2+}$ ions substitute Li$^{+}$-ions [6, 7];
2. Mg$^{2+}$ ions substitute Nb$_{Nb}$, ions [8];
3. Mg$^{2+}$ ions occupy both Li$^{+}$-ions and Nb$_{Nb}$ ions [9].

Hence, there are still big divergences about localization of Mg$^{2+}$ ions and mechanisms of charge compensation in LN crystals grown up from congruent melt with addition of MgO. Therefore the analysis of known data about chemical composition of LN crystals with various Mg concentrations as well as their investigation by NMR method were the purposes of given work.

2. The analysis of Mg-doped LN structure

The discussion about congruent LN intrinsic defects goes on during long time and detailed review of possible defect structure models can be found for example in [10]. Decisive arguments in favor of one of the proposed models — so-called lithium vacancy model, when the chemical formula of congruent LN can be written as: Li$_{1-\delta}$Nb$_{1+\delta}$O$_3$ (where $\delta \approx 0.0118$) were obtained by Iyi et al. [11]. These results were confirmed by authors in [12]. That is why the analysis of Mg incorporation in the crystal was carried out by us basing on this particular model.

All considered above models of Mg$^{2+}$ ions localization in LN structure, on the assumption of 100% Nb sublattice filling, can be presented by the following structural formulae:

$$[Li_xMg_yNb_{2-x-y}O_3]^{(1)}$$

for $z > 1$,

$$[Li_xMg_{y+z-x-y}O_3]^{(2)}$$

where $\square$ denotes a vacancy in Li sublattice ($V_{Li}$); $x$, $y$, $z$ — quantity of Li, Mg and Nb atoms that falls on average formulae unit.

In the number of articles devoted to study of magnesium localization in LN crystals [13–15], experimentally obtained dependences of Li/Nb ratio ($R$) in the crystal ($R = x/z$) on MgO molar content ($k$) are presented. It is obvious that $k$ value can be written as $k = \frac{y}{x+y}$.

Taking into account a condition of electroneutrality of the crystal it is possible to define the population of structural positions in cation sublattices...
quadrupolar nuclei are very sensitive to the local distortion in the crystal essentially increases, too.

For the calculation of relative populations of [Li] and [Nb] structural positions in LN:Mg crystals according to expressions (1), (2) we used the data presented in [13–15]. The results of these calculations are shown in Fig. 1. The results of these calculations are shown in Fig. 1. Predicted population of [Li] and [Nb] positions as a function of MgO content in the sample. 1 — calculation according to the data in Ref. [13]; 2 — calculation according to the data in Ref. [12]; 3 — calculation according to the data in Ref. [14].

Typical root-mean-square errors of experimentally defined R and k values are equal accordingly to \( \delta R = 0.005 \) and \( \delta k = 0.004 \) [5, 13], that corresponds to an error of \( V_{Li} \) quantity definition at the level of 0.5%. Therefore, the results presented in Fig. 1 show that during increase of Mg\(^{2+}\) ions concentration up to threshold, the quantity of \( V_{Li} \) within an error monotonously increases as well contrary to the widespread point of view [8, 16]. It should be noticed that similar conclusions were also received at early stages of Mg doped LN crystals study [5].

3. Deficiency evaluation of Mg-doped LN crystals

The general relative defects quantity (n) of Mg doped LN crystal relatively to the stoichiometric one can be defined as [17]:

\[
n = \frac{3(N_1 + N_2 + N_3 + N_4)}{5N_O},
\]

where \( N_O \) is the quantity of O\(^{2-}\) ions in the sample; \( N_1 \ldots N_4 \) are the quantities of \( V_{Li} \), \( Mg_{Li} \), \( Nb_{Li}^{5+} \) and \( Mg_{Nb} \) defects, respectively. Using the data presented in Fig. 1, it is simple to calculate the dependence of n from MgO molar content in the crystal. These results are shown in Fig. 2 and testify that with the increase of Mg\(^{2+}\) ions volume concentration the general relative defects quantity in the crystal essentially increases, too.

It is well known that NMR spectrum lineshapes of quadrupolar nuclei are very sensitive to the local distortions of the crystal lattice caused by different types of defects, such as vacancies, antisite ions, non-isovalent impurities etc. In first approach, broadening of the quadrupolar satellites and the central line of a NMR spectrum is proportional to n at small volume concentration of defects [18]. It has been shown earlier that extrinsic and intrinsic defects strongly affect the parameters of the \(^7\)Li and, especially, \(^{93}\)Nb NMR spectrum in LN crystals [19], therefore this method has been used by us for investigation of LN single crystals with various Mg content.

Additional broadening of NMR lines in crystals without paramagnetic impurities is defined first of all by quadrupolar effects. Since electric field gradient (EFG) on a certain nucleus is determined by the charge distribution in the nearest surrounding of this nucleus, besides the general relative defects quantity (n), it makes sense to consider the crystal charge deficiency (n’). Similarly to (3) it is possible to define n’ as:

\[
n’ = 3 \times \frac{|q_1|N_1 + |q_4 - q_2|N_2 + |q_3 - q_1|N_3 + |q_3 - q_4|N_4}{(|q_1| + |q_4| + 3|q_2|)N_O}
\]

where \( q_1 \ldots q_3 \) are so-called “effective” charges of Li, O and Nb ions in regular positions; \( q_4 \) is the effective charge of Mg. According to [20], it was accepted that \( q_1 = 0.98|e|; q_2 = -1.55|e|; q_3 = 3.67|e| \) and \( q_4 = 2|e|, \) where \( e \) is the charge of electron. Dependence of n’ on the Mg concentration in the crystal is similar to the one for n and is also represented in Fig. 2. According to the data, shown in Fig. 2, the strong dependence of \(^7\)Li and \(^{93}\)Nb NMR spectrum parameters on the Mg concentration in the sample is needed to be checked.

4. NMR analysis of LiNbO\(_3\):Mg crystals

Nominally pure LN single crystals as well as the crystals doped with 5.0 and 7.0 mol.% MgO were grown by the Czochalski technique at SRC “Carat” (Lviv, Ukraine) and the crystal containing 2.0 mol.% MgO was...
grown at Research Laboratory for Crystal Physics (Budapest, Hungary).

The measurements were performed on a continuous-wave NMR spectrometer with specialized autodyne probe [21] in magnetic field $B_0 = 1.0$ T ($^7$Li NMR) and $B_0 = 1.4$ T ($^{93}$Nb NMR). To increase the signal-to-noise ratio we used the digital accumulation and Fourier filtration of the spectra, which allowed increasing it by a factor of 1.5 without introducing the additional error into the line shape [22].

First of all we investigated the influence of Mg doping on the parameters of $^7$Li NMR spectrum in LN. It is estimated that spin–lattice relaxation time ($\tau_1$) for all lines of $^7$Li NMR spectrum exceeds 30 s in all investigated samples, which indicates practically full absence of paramagnetic impurities in the samples. It has been established too, that the value of a quadrupole coupling constant $C_z$ of $^7$Li nuclei, for all investigated crystals, within an error coincides with well-known value $C_z = (55.0 \pm 0.5)$ kc [19] at the keeping of axial symmetry of EFG tensor at site of $^7$Li nuclei. Dependences of the spectrum central line width ($\delta\nu_0$) and quadrupole satellites width ($\delta\nu_1$) on the general relative defects quantity of the crystal at $\theta = 0^\circ$ are the most informative results, obtained during $^7$Li NMR experiments ($\theta$ is the angle between the direction of magnetic field $B_0$ and axis $c$ of the crystal). Respondent results are illustrated in Fig. 3.

**Fig. 3.** Width of the central line $\delta\nu_0$ 1 and satellites $\delta\nu_1$ 2 of $^7$Li NMR spectrum for the series of investigated samples (at $\theta = 0^\circ$) as a function of the general relative defects quantity.

These data completely correlate with the results obtained by $^{93}$Nb NMR in powder LN samples with various MgO content [23]. According to [23], when MgO content in the sample is equal to 2.5%, the width of the central transition ($-1/2 \leftrightarrow +1/2$) line of $^{93}$Nb NMR spectra increases approximately twice in comparison with the linewidth in nominally undoped congruent sample. At the further increase of MgO content in the sample, the linewidth remains practically invariable. The absence of pronounced linewidth dependence on the defect concentration in the $^7$Li and $^{93}$Nb NMR spectra for samples with more than 2% of Mg can testify that defects a crystal lattice at $k \geq 2.0\%$ are not spatially independent but defect complexes are formed.

It should be noted that the results obtained by $^{93}$Nb NMR investigation on a single LN crystals doped with 4.5% MgO [24] are in contradiction to cited above [23]. It has been shown [23] that the linewidth of $-1/2 \leftrightarrow +1/2$ transition of $^{93}$Nb NMR spectrum in the sample doped with 4.5% MgO is essentially higher (up to 5 times) than in nominally pure congruent LN crystal for all the range of crystal orientations in magnetic field.

Earlier it has been shown that the $-1/2 \leftrightarrow +1/2$ transition of $^{93}$Nb NMR spectra in congruent LN single crystal contains the well-resolved additional NMR line, which can be observed at some crystal orientations in magnetic field [25]. This additional line arises from the $^{93}$Nb nuclei of Nb ions, which occupy Li-sites or octahedral vacancy positions.

According to [25] the integral intensity of this line makes up 6% from the intensity of the main line of $^{93}$Nb NMR spectra central transition and these results are considered as the most serious arguments in favor of so-called “niobium vacancy” model [26]. However, later investigations of near-congruent LN crystals showed that relative integral intensity of this line makes up $(0.9 \pm 0.4)\%$ [27]. This value correlates only with lithium vacancy model. The best condition for the observation of this line is when $\theta = (10-35)^\circ$. Since the observation of this line gives direct information about the Nb$_{Li}$ percentage in the crystal, our $^{93}$Nb NMR investigation was concentrated at this problem including repeated investigations of 3 nominally undoped LN samples with near-congruent composition.

**Fig. 4.** Experimental $^{93}$Nb NMR spectra registered at $\theta = 10^\circ$ for a series of investigated samples: 1 — nominally pure congruent LN; 2 — doped with 2.0% MgO; 3 — doped with 5.0% MgO; 4 — doped with 7.0% MgO.

Experimentally obtained lineshapes of the $-1/2 \leftrightarrow +1/2$ transition for some LN samples are presented in Fig. 4. Additional $^{93}$Nb NMR line was fixed only for nominally undoped LN samples and for the sample doped with 2.0% MgO. The calculations of relative integral intensity of additional line for the nominally undoped LN samples is equal to $(1.2 \pm 0.2)\%$ from total.
quantity of $^{93}$Nb nuclei in the sample, and for the sample doped with 2.0% MgO this value is equal to (0.6 ± 0.2)%.

These results are in good agreement with the assumption that at the MgO concentration in the melt up to threshold, Mg$^{2+}$ ions firstly occupy positions of Li$^{+}$ ions preventing the appearance of antisite Nb$\text{ Li}_1$ ions. Nevertheless, it should be noted that the angular dependence of the NMR linewidth of the $^{93}$Nb central transition for the samples doped with 5% MgO and 7% MgO, obtained by us for the angular band $|\theta| \leq 15^\circ$, strongly differs from the known data [24].

5. Conclusions

Basing on the given analysis of cation sites population and on the experimental investigation of LiNbO$_3$ crystals with MgO content up to threshold by $^{93}$Nb NMR it has been shown that the Mg$^{2+}$ ions are localized in Li$^{+}$ positions, gradually decreasing the quantity of antisite Nb$\text{ Li}_1$ ions in spite of increase of the V$_{\text{Li}}$ quantity. When MgO content in the melt is above the threshold, Mg$^{2+}$ ions may occupy both Li and Nb$\text{ Nl}_1$ positions.

According to Ref. [24] the additional broadening of the $^{93}$Nb NMR lines in LiNbO$_3$:Mg crystals can be explained by increasing the deviations of EFG tensor parameters (especially — $C_z$ and EFG asymmetry parameter values, as well as increasing the EFG tensor principal axis off-orientation on $^{93}$Nb nuclei). However, our results show that the additional broadening of $^{93}$Nb NMR line is connected primarily with the increase of dispersion of $C_z$ value distribution on $^{93}$Nb nuclei sites, which is the indirect evidence of the existence of (Mg$\text{Li}_1$—V$_{\text{Li}}$) defect complexes formed in the crystal structure. However, the most correct conclusions about the real structure of Mg-doped LiNbO$_3$ crystals can be made only after carrying out of the careful experimental investigation of the angular dependence of $^{93}$Nb NMR spectra and its computer simulations [28].

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References