Induced Li-site vacancies and non-linear optical behavior of doped lithium niobate crystals

D. Xue, K. Betzler *, H. Hesse

Fachbereich Physik, Universität Osnabrück, D-49069 Osnabrück, Germany

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Abstract

Second-order non-linear optical (NLO) properties of doped lithium niobate (LN) crystals (abbreviated as M:LN, where M = Mg\(^{2+}\), Zn\(^{2+}\), and In\(^{3+}\), respectively) have been quantitatively studied from the chemical bond viewpoint. Our results show that the second-order NLO response of doped LN crystals decreases remarkably with increasing dopant concentration in the crystal. The approximately linear composition-property correlation in these doped LN crystals is quantitatively expressed in the current work. A comparison of the different influences of Mg, Zn and In dopants, respectively, shows that these dopants affect the NLO properties of LN crystals mainly via the number of Li-site vacancies induced. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Due to its large electrooptical and non-linear optical (NLO) coefficients [1,2], lithium niobate, LiNbO\(_3\) (LN), is one of the most interesting inorganic NLO materials suitable for numerous applications in optics (holographic storage, electrooptic devices, waveguide structures, solid-state lasers, frequency doublers and mixers, parametric oscillators, etc.). In spite of the massive research on this material in the past decades there are still many open questions concerning e.g., the formation of efficient self-frequency doubled lasers or the suppression of the so-called photorefractive damage.

Usually grown from a congruently melting composition, LN is a typical non-stoichiometric crystal exhibiting a Li deficit of about 1.5%. Thus it contains specific intrinsic defects in its crystal structure – mainly lattice vacancies at Li sites and Nb\(_{Li}\) antisite defects [3–6].

A rich variety of rare earth [7,8] and metal ions can be introduced as dopant into the LN lattice, either during the growth process or by post-growth techniques like ion implantation, using He\(^{+}\) or H\(^{+}\) [9], or indiffusion, using e.g., Cu [10]. Important photonic applications are thus possible as e.g., holographic memories [11,12], optical demultiplexers [13], or self-frequency doubled lasers [14].

Optical devices fabricated from nominally pure LN usually suffer from so-called optical damage...
due to the photorefractive effect when exposed to intense illumination. This effect can be greatly reduced by co-doping LN crystals with MgO [15,16], ZnO [17], or In$_2$O$_3$ [18], etc., due to the influence of Mg$^{2+}$, Zn$^{2+}$, or In$^{3+}$ on the intrinsic defect structure of LN [18–21]. Yet these defects affect not only the photorefractive but also nearly all other optical properties of LN; their influences on the absorption edge [22] and the refractive indices and the phase matching conditions for different configurations of second harmonic generation (SHG) [23–27] have already been studied in some detail.

The purpose of the present work is a comparison of these impurity influences on the NLO response, i.e., the SHG susceptibility tensor, of LN. As shown previously [28], also the non-linear properties of crystals depend sensitively on the impurity content. Applying the chemical bond viewpoint [29–31], the influence of the dopants on the dielectric response is quantitatively analyzed.

2. Structural analysis of doped lithium niobate

In pure LN of stoichiometric composition, the ideal cation stacking sequence along the polar $c$-axis of the crystal can be described by

$$\cdots \text{Li}^{+} \text{- Nb}^{5+} \text{- Li}^{+} \text{- Nb}^{5+} \cdots,$$

where $\Box$ represents a structural vacancy (an empty oxygen octahedron) [3]. This crystal structure is illustrated by Fig. 1. The structural situation changes when dopants are introduced into the crystal. Nearly all two- or three-valented dopants are found to occupy Li sites [32,33] – at least at low doping levels (up to some percent). Charge compensation is accomplished by the formation of an appropriate number of Li vacancies. This modifies the local chemical bonding state in the crystal in a random way, especially for the oxygen atoms around the dopants and the vacancies. As an exact numerical treatment of such a disturbed crystal is not possible to date, one has to introduce some practical simplifications.

The chemical bond method [29–31] treats a compound as an infinite network of constituent atoms linked by chemical bonds. For pure crystals, this can be reduced to a finite network comprising a single formula unit such as the network of LiNbO$_3$, in which Li$^+$ and Nb$^{5+}$ are six-coordinated (with O$^{2-}$ anions) and O$^{2-}$ is four-coordinated (with two Li$^+$ cations and two Nb$^{5+}$ cations). The detailed chemical bonding description for pure LiNbO$_3$ is shown in Fig. 2(a). In the graphs of Fig. 2, each line represents a different bond, and each atom A in the corresponding lattice is assigned a formal charge equal to its atomic valence or oxidation state ($V_A$) and each bond between atoms A and B is assigned a bond valence ($s_{AB}$). The sum of the bond valences (each with appropriate algebraic sign according to the bond direction) at each node atom in the network equals its formal charge, the sum around any loop is zero [30,31]

$$\sum_B s_{AB} = V_A \quad \text{and} \quad \sum_{\text{loop}} s_{AB} = 0. \quad (1)$$

Calculations of the crystal susceptibility are based on such a suitable decomposition of the crystal into single bonds.

The exact treatment of doped LN would require a large number of such bond graphs, each de-
scribing one of the possible environments around a dopant ion. To avoid such complications with randomly distributed modified bonding situations, we treat doped LN instead as an appropriate mixture of pure LN with pure ‘metal’ niobate (metal = Mg, Zn, In, . . . ). Of course this approximate approach can not be used in general, albeit it can be successfully applied for the calculation of optical properties. This is due to the fact that optical wavelengths are rather large compared to typical interatomic distances, a summation over a fixed distribution of small regions will yield the same optical susceptibility as a summation over a random distribution. Consequently, for the description and decomposition of doped LN, we use the bond graphs of the metal niobates MNb$_2$O$_6$ (M = Mg, Zn) and InNb$_3$O$_9$, as shown in Fig. 2(b) and (c), in addition to that of pure LN (Fig. 2(a)). Thus crystals of doped LN Li$_{1-x}$M$_x$NbO$_3$ and Li$_{1-x}$In$_{x/3}$NbO$_3$ are formally treated as (1 – x) · LiNbO$_3$ + x/2 · MNb$_2$O$_6$ and (1 – x) · LiNbO$_3$ + x/3 · InNb$_3$O$_9$, respectively. As a further approximation in the calculations, the geometrical structure data for the metal niobates are adopted from pure LN. Generally it must be assumed that the crystal lattice would relax its geometry slightly around dopants and vacancies due to the altered ionic charges. Yet, to date no experimental structural data are available which describe the relaxed lattice around impurities in LN correctly.

3. Theoretical method

As shown in previous works [29] – developed from the dielectric theory of solids [34–36] – the chemical bond method regards certain macroscopic physical properties of a crystal as a combination of the contributions of all constituent chemical bonds. Accordingly, the linear and second-order NLO properties of a crystal can be calculated using the appropriate geometric sum of the respective properties of its corresponding constituent chemical bonds. On the basis of the crystallographic structure of an assigned crystal, its linear and second-order NLO susceptibilities $\chi$ and $d_{ij}$ thus can be written as

$$\chi = \sum_{\mu} F^\mu \kappa^\mu = \sum_{\mu} N^\mu_b \kappa^\mu$$

and

$$d_{ij} = \sum_{\mu} \left\{ \frac{G^\mu_N N^\mu_b (0.5) \{(Z^\mu_k)^+ + n(Z^\mu_k)^- \}/\{(Z^\mu_k)^+ - n(Z^\mu_k)^- \}}{d^\mu q^\mu} \right\} \left\{ \frac{G^\mu_d N^\mu_b (2s - 1) \left[ q^\mu / (q^\mu + q^\mu) \right] / d^\mu q^\mu \right\}$$

respectively. Parameters used in Eqs. (2) and (3) include:

- $F^\mu$ Fraction of bonds of type $\mu$ composing the crystal.
- $\kappa^\mu$ Linear susceptibility contribution from $\mu$ type bonds.
- $N^\mu_b$ Number of bonds of type $\mu$ per cm$^3$.
- $\kappa^\mu_b$ Susceptibility of a single bond of type $\mu$.
$G_{ij}^\mu$ Geometrical contribution of chemical bonds of type $\mu$

$(Z^\mu_A)^n, (Z^\mu_B)^n$ Effective number of valence electrons of A and B ions, respectively.

$n$ Ratio of numbers of two elements B and A in the bond valence equation [37].

$f_i^\mu, f_c^\mu$ Fractions of ionic and covalent characteristics of the individual bonds, $f_i^\mu = (E^\mu) - [(E^\mu)^2 + (C^\mu)^2]$ and $f_c^\mu = 1 - f_i^\mu$, where $E^\mu, C^\mu$ are the average energy gaps due to ionic and covalent effects.

$d^\mu$ Bond length of the $\mu$ type bonds in A.

$q^\mu$ Bond charge of the $\mu$th bond.

$s$ Exponent in the bond force constant.

$r_c^\mu = 0.35r_0^\mu$ Core radius, where $r_0^\mu = d^\mu/2$ and $d^\mu$ is the bond length.

$\rho^\mu = (r_A^\mu - r_B^\mu)/(r_A^\mu + r_B^\mu)$ Difference in the atomic sizes, where $r_A^\mu$ and $r_B^\mu$ are the covalent radii of atoms A and B, taken from the periodic table of elements.

According to Levine’s model [36] the susceptibility $\chi^\mu$ of any bond of type $\mu$ is expressed as

$$\chi^\mu = (4\pi)^{-1}\left(\hbar\Omega_{p}^\mu\right)^{2}/\left[(E_{n}^\mu)^{2} + (C_{n}^\mu)^{2}\right],$$  \hspace{1cm} (4)

where $\Omega_{p}^\mu$ is the plasma frequency. The average covalent energy gap $E_{n}^\mu$ of a bond is given by [34,38]

$$E_{n}^\mu = 39.74/(d^\mu)^s, \; \; s = 2.48$$ \hspace{1cm} (5)

and the average ionic gap $C_{n}^\mu$ by

$$C_{n}^\mu = b^\mu\exp(-k_{n}^\mu r_{0}^\mu)[(Z_{A}^\mu)^n - n(Z_{B}^\mu)^n]/r_{0}^\mu,$$ \hspace{1cm} (6)

where $\exp(-k_{n}^\mu r_{0}^\mu)$ is the Thomas–Fermi screening factor and $b^\mu$ is a correction factor of order unity.

The bond charge $q^\mu$ can be expressed as [29,37]

$$q^\mu = (n_{e}^\mu)^{+}[1/(\chi^\mu + 1) + f_c^\mu(2F_c - 1.1)/N_{\text{cation}}]e,$$ \hspace{1cm} (7)

where $(n_{e}^\mu)^{+}$ is the number of valence electrons per bond $\mu$, $F_c = \sum_{\mu} N_{\mu}^a/f_c^\mu$ the crystal covalency, and $N_{\text{cation}}$ the cation coordination number.

The geometrical factors $G_{ij}^\mu$ for the contributions of the respective bond types $\mu$ to the tensor coefficients $d_{ij}$ are deduced from the crystal geometry

$$G_{ij}^\mu = G_{\delta ij}^\mu = 1/n_{\alpha}^\mu \sum_{\lambda} x_{i,j}^\alpha x_{\delta k}^\alpha x_{\lambda}^\mu.$$ \hspace{1cm} (8)

The sum on $\lambda$ is to be taken over all $n_{\alpha}^\mu$ symmetry-equivalent bonds of type $\mu$ in the unit cell. $x_{i,j}^\alpha$ denotes the direction cosine of the $\alpha$th bond of type $\mu$ in the unit cell with respect to the $i$th axis of the optical indicatrix, $ij$ is the contracted form of the full set of indices $ikl$ used in the third rank nonlinear susceptibility tensor.

4. Results and discussion

On the basis of the detailed crystallographic data of pure LN [39] and the modifications for doped LN discussed above, the linear and NLO susceptibilities of all different constituent bonds Li–O, Nb–O, and M–O contained in doped LN are calculated. To increase accuracy, the calculated values of the linear optical susceptibilities were referenced against experimental values. The experimental values of the (ordinary) refractive indices $n_o$ at 1079 nm were taken from previous studies [23,24,26,27] which yield an approximately linear dependence on the dopant concentration at low doping levels:

Mg : LN, $n_o = 2.2311 - 0.00085 c_{\text{Mg}},$ \hspace{1cm} (9)

$\varepsilon_{\text{Mg}} < 9\%,$

Zn : LN, $n_o = 2.2311 + 0.00079 c_{\text{Zn}},$ \hspace{1cm} (10)

$\varepsilon_{\text{Zn}} < 9\%,$
In : LN,  \( n_o = 2.2311 - 0.00280 c_{\text{In}} \),
\[ c_{\text{In}} < 3\% . \] (11)

c denotes the molar percentage of the respective oxide in LN.

These experimental references were used to obtain the exact correction factors \( b \) in Eq. (6).

The calculations of the non-linear susceptibilities also yield approximately linear dependencies on the dopant concentration, which can be summarized by Eqs. (12)–(14):

\[
d_{22} = 2.71 \cdot (1 - 0.026 c_{\text{Mg}} - 0.023 c_{\text{Zn}} - 0.064 c_{\text{In}}),
\] (12)

\[
d_{31} = -4.12 \cdot (1 - 0.028 c_{\text{Mg}} - 0.026 c_{\text{Zn}} - 0.097 c_{\text{In}}),
\] (13)

\[
d_{33} = -22.9 \cdot (1 - 0.027 c_{\text{Mg}} - 0.024 c_{\text{Zn}} - 0.082 c_{\text{In}}),
\] (14)

where \( d_s \) are in pm/V and \( c_s \) are the molar percentages of the respective oxides (MgO, ZnO, In\(_2\)O\(_3\)).

For pure LN (i.e., \( c_{\text{Mg}} = c_{\text{Zn}} = c_{\text{In}} = 0 \)) the calculated results agree well with experimental data at 1064 nm [40]: \( d_{22} = 2.1 \) pm/V, \( d_{31} = -4.3 \) pm/V, and \( d_{33} = -27 \) pm/V, as well as with our previously calculated results at 1064 nm [37].

The dependencies of the three tensor coefficients on the doping concentrations show that all coefficients decrease approximately linearly with increasing doping concentrations. This indicates that the dopants directly or indirectly reduce the acentricity of the material. The decrease is most expressed in In-doped LN, considerably less in the case of Zn or Mg doping, the ratio of the slopes is approximately 4. One explanation for the large difference between three- and two-valent dopants is the scaling used. The \( d \) values in Eqs. (12)–(14) are calculated as a function of the ‘molar’ impurity concentration which usually is referred to the basic oxides composing the material. These basic oxides are Li\(_2\)O, Nb\(_2\)O\(_5\), MgO, ZnO, and In\(_2\)O\(_3\), respectively. Taking this and the respective valence state into account, In\(_2\)O\(_3\) introduces four times as much Li vacancies as MgO or ZnO into the crystallographic frame of LN. The correspondence between this factor four and the slope ratio discussed above suggests that the reduction in the acentricity of LN, introduced by dopants, is mainly due to the number of Li vacancies, fairly independent of the specific impurity used. A similar factor of 4 is also found when regarding the so-called ‘threshold’ values [41] for different dopants in LN which were found to be about 6% in the case of Mg and Zn and about 1.5% in the case of In [21]. The fact that the number of Li vacancies strongly affects the NLO properties of LN assures our previous result that the Li places in the crystallographic frame of LN are the sensitive lattice sites, on which dopants (or vacancies) can modify the dielectric properties most effectively [29,37]. Yet this seems to be mainly true for the non-linear properties (i.e., the acentricity) as the linear dielectric properties behave in a slightly different way: \( n_o \) decreases with Mg doping [23], increases with Zn doping [24], and decreases with In doping [26].

Fig. 3. Non-linear optical tensor coefficients \( d_{ij} \) in doped lithium niobate as a function of the lithium vacancy concentration induced by different dopants. Filled markers: In-doped, small open markers: Zn-doped, large open markers: Mg-doped lithium niobate.
A plot of the SHG tensor coefficients as a function of the lithium vacancy concentration (Fig. 3) shows the approximately coinciding behavior for all three sorts of dopants discussed here. The behavior of the $d$ values can be described by the global formula

$$d_{ij} = d_{ij}^{\text{pure}} \cdot (1 - 0.023 \cdot c_{VLi})$$

with an accuracy of about $\pm 5\%$ for lithium vacancy concentrations $c_{VLi}$ less than $10\%$. For $d_{ij}^{\text{pure}}$ the values given in Eqs. (12)–(14) or the respective experimental values have to be inserted.

5. Conclusion

Dielectric properties of doped LN single crystals at 1079 nm have been quantitatively studied from the chemical bond viewpoint of crystal materials. It is found that different dopants on Li sites in LN affect the second-order NLO response of LN crystals in a different way. Yet all doping dependencies for the dopants regarded here can be described by a global unitary factor when referred to the concentration of lithium vacancies induced by the impurities.

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References


