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The effect of stoichiometry on nonlinear optical properties of LiNbO₃

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Abstract. From the chemical bond viewpoint, second-order nonlinear optical (NLO) tensor coefficients of LiNbO₃ have been investigated. The single-bond contributions to the second-order NLO susceptibility and the linear susceptibility were determined. The tensor values thus calculated are in good agreement with experimental data. Based on theoretical results of LiNbO₃ with Li/Nb = 1, we also have calculated linear and nonlinear optical properties of nonstoichiometric samples with Li/Nb < 1. In the calculation, we find that the Li–O bond is an important type of chemical bond in these LiNbO₃ samples, which have large NLO contributions to the total nonlinearities. The refractive indices and second-order NLO tensor coefficients have been determined as a function of the stoichiometry.

1. Introduction

Lithium niobate is well known as a technologically important single-crystal oxide material, because of its interesting electro-optical, nonlinear optical (NLO) and piezoelectrical properties. Although commonly referred to as LiNbO₃, the phase exists over a wide solid solution range, from compositions near the stoichiometric value to lithium-poor compositions as low as approximately 45 mol% LiO₂ at 1200 °C [1]. Almost all lithium niobate produced commercially is grown by the Czochralski technique and has a composition near the congruently melting value of roughly 48.4 mol% LiO₂ [2, 3]. It is possible to prepare LiNbO₃ samples with stoichiometries different from the congruent one (but always with an Li/Nb ratio smaller than one); however the major difficulty is to determine their actual Li/Nb atom ratio because the methods employed should be very precise. Vapour transport equilibration was well used to prepare LiNbO₃ samples of a variety of controlled off-congruent compositions [4]. Later, the workers found that the Li/Nb ratio in the crystal may be estimated by using the width of some Raman peaks [5]. This makes investigations of composition-dependent lithium niobate physical properties become much easier. LiNbO₃, as generally used in applications, is grown from a congruent melt, with Li/Nb = 0.942, i.e., at this composition the crystal has the same Li/Nb ratio as the melt. Li/Nb then also is homogeneous throughout the crystal. Deviations from this ratio can be obtained by changing the composition of the melt. The elastic constants have been determined by Brillouin scattering as a function of the stoichiometry [6]. Several Raman peaks, which appear when the Li/Nb ratio decreases, are related to the presence of Nb in antisites [6]. A review of the experimental and theoretical aspects of defects in LiNbO₃ [7], as well as

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point defects in its isomorphous LiTaO₃ [8] has been published. Both compounds show that lithium ions play important roles in their optical and transport properties.

The earlier work on crystals pulled from melts with Li/Nb atom ratios, (Li/Nb)_m, of 0.852, 0.946, and 1.083 found the coefficient d_{31} was especially sensitive to the melt composition and increased by about 50% as (Li/Nb)_m increased from 0.852 to 1.083 [9]. This difference was explained by ascribing the nonlinearities of LiNbO₃ to the Nb–O bonds. We believe the macroscopic physical property of a crystal corresponds to its intrinsic structural character, in other words, corresponds to the property of all constituent chemical bonds. Nonstoichiometric samples present structural differences (also different chemical bonding situations) so that, in principle, the physical properties of the material can be modified.

In the present work, refractive indices and NLO coefficients are theoretically predicted and the influence of different stoichiometries on the linear and nonlinear optical properties of LiNbO₃ is discussed.

2. Theory

According to the chemical bond theory of complex crystals [10] and the modified bond charge model [11], the linear and nonlinear optical properties of a complex crystal are a linear combination of contributions of each type of constituent chemical bond. This combination can be directly deduced based on the crystal structure. For example, in a complex crystal A_aB_bD_dG_g (crystal molecular formula) any kind of chemical bond A–B can be written as

$$[N(\text{B-A})a/N_{CA}]A[N(\text{A-B})b/N_{CB}]B \quad (1)$$

where A, B, D, and G are different constituent elements in the crystal formula and a , b , d , and g are numerical numbers of the corresponding elements. $N(\text{B-A})$ is the number of B ions in the coordination group of an A ion and N_{CA} is the nearest coordination number of the atom A in the crystal.

The linear susceptibility of any chemical bond labelled μ is described as [12, 13]

$$\chi^\mu = \frac{(4\pi)^{-1}(\hbar\Omega_p^\mu)^2}{(E_h^\mu)^2 + (C^\mu)^2} \quad (2)$$

The total linear susceptibility χ has a relation with contributions χ^μ of the various types of bond [14]

$$\chi = (n_r^2 - 1)/4\pi = \sum_{\mu} F^\mu \chi^\mu = \sum_{\mu} N_b^\mu \chi_b^\mu \quad (3)$$

where n_r is the refractive index. F^μ is the fraction of bonds of type μ composing the crystal. N_b^μ is the number of chemical bonds of type μ per square centimetre. χ_b^μ is the susceptibility of a single bond of type μ .

In (2), E_h^μ and C^μ are the homopolar and heteropolar parts of the total average energy gap. Figuratively speaking, E_h^μ and C^μ measure the average energy gaps due to covalent and ionic effects. Quantitatively, both parameters can be calculated from [12, 13]

$$E_h^\mu = 39.74/(d^\mu)^{2.48} \quad (4)$$

$$C^\mu = 14.4b^\mu \exp(k_s^\mu r_0^\mu) [(Z_A^\mu)^*/r_0^\mu - n(Z_B^\mu)^*/r_0^\mu] \quad (5)$$

where d^μ is the bond length in ångströms obtained from the observed crystal structure data. n is the ratio of numbers of two elements B and A in the subformula [10]. $r_0^\mu = d^\mu/2$ and $\exp(k_s^\mu r_0^\mu)$ is the Thomas–Fermi screening factor. $(Z_A^\mu)^*$ is the effective valence electron

number of A ions [10]. b^μ is a correction factor depending on the crystal structure; if the refractive index of a crystal is known, its value can be obtained from the following equations:

$$\sum_{\mu} \frac{F^\mu (\hbar\Omega_p^\mu)^2}{(E_h^\mu)^2 + \{14.4b^\mu \exp(k_s^\mu r_0^\mu) [(Z_A^\mu)^*/r_0^\mu - n(Z_B^\mu)^*/r_0^\mu]\}^2} = n_r^2 - 1. \quad (6)$$

In the case of LiNbO₃, we further have

$$b^\mu = \left[\left(\sum_{\mu} F^\mu (\hbar\Omega_p^\mu)^2 / (n_r^2 - 1) - \sum_{\mu} (E_h^\mu)^2 \right) \left(\sum_{\mu} \{14.4 \exp(k_s^\mu r_0^\mu) [(Z_A^\mu)^*/r_0^\mu - n(Z_B^\mu)^*/r_0^\mu]\}^2 \right)^{-1} \right]^{1/2}. \quad (7)$$

According to Phillips' suggestion [12], one can define the fraction of ionic and covalent character of the individual bonds, f_i^μ and f_c^μ , by

$$f_i^\mu = \frac{(C^\mu)^2}{(E_h^\mu)^2 + (C^\mu)^2} \quad f_c^\mu = \frac{(E_h^\mu)^2}{(E_h^\mu)^2 + (C^\mu)^2}. \quad (8)$$

For the total NLO tensor coefficient d_{ij} , we have [14]

$$d_{ij} = \sum_{\mu} d_{ij}^\mu = \sum_{\mu} F^\mu [d_{ij}^\mu(C) + d_{ij}^\mu(E_h)] \quad (9)$$

where d_{ij}^μ is the total macroscopic nonlinear contribution that constituent chemical bonds of type μ would have. $d_{ij}^\mu(C)$ is the ionic fraction of the NLO coefficient, and $d_{ij}^\mu(E_h)$ the covalent fraction,

$$F^\mu d_{ij}^\mu(C) = \frac{G_{ij}^\mu N_b^\mu (0.5) \{[(Z_A^\mu)^* + n(Z_B^\mu)^*] / [(Z_A^\mu)^* - n(Z_B^\mu)^*]\} f_i^\mu (\chi_b^\mu)^2}{d^\mu q^\mu} \quad (10)$$

$$F^\mu d_{ij}^\mu(E_h) = \frac{G_{ij}^\mu N_b^\mu s(2s-1) [r_0^\mu / (r_0^\mu - r_c^\mu)]^2 f_c^\mu (\chi_b^\mu)^2 \rho^\mu}{d^\mu q^\mu} \quad (11)$$

where $\rho^\mu = (r_A^\mu - r_B^\mu) / (r_A^\mu + r_B^\mu)$, is the difference in the atomic sizes and r_A^μ is the covalent radius of the atom A. $r_c^\mu = 0.35r_0^\mu$ is the core radius. q^μ is the bond charge of the μ th bond [11]; its detailed expression is

$$q^\mu = (n_e^\mu)^* [1/(\chi^\mu + 1) + K f_c^\mu] e. \quad (12)$$

In multibond crystals, we have introduced K in (12), in order to take the coordination environment and the influence from other constituent chemical bonds on the assigned chemical bond μ into account. K is a function of the coordination number N_{cat} of the central cation of the μ th bond and the average crystal covalency F_c , which is expressed as

$$K = (2^{F_c} - 1.1) / N_{cat} \quad (13)$$

$$F_c = \sum_{\mu} N_b^\mu f_c^\mu. \quad (14)$$

G_{ij}^μ is the geometrical contribution of chemical bonds of type μ ,

$$G_{ij}^\mu = 1/n_b^\mu \sum_{\lambda} \alpha_i^\mu(\lambda) \alpha_j^\mu(\lambda) \alpha_k^\mu(\lambda) \quad (15)$$

where the sum on λ is over all n_b^μ bonds of type μ in the unit cell, and $\alpha_i^\mu(\lambda)$ is the direction cosine with respect to the i th coordinate axis of the λ th bond of type μ in this cell.

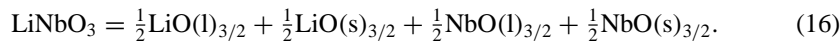
3. Results and discussion

At room temperature the structure of LiNbO_3 [15] is rhombohedral with space group $R3c$. It consists of distorted oxygen octahedra sharing faces and forming a planar hexagonal configuration. The ideal cation stacking sequence along the c axis is $\dots\text{-Li-Nb-}\square\text{-Li-Nb-}\square\text{-}\dots$, where \square represents for a structural vacancy (an empty octahedron). In this crystal the environments of Li^+ and Nb^{5+} are similar, essentially because Li and Nb have nearly identical covalent radii. Both ions are surrounded by distorted octahedra of six O^{2-} ions. Because of this similarity and since the Nb–O bond has more valence electrons than the Li–O one, LiNbO_3 has a tendency to nonstoichiometry with $\text{Li/Nb} < 1$. An investigation of crystals with both congruent and near-stoichiometric composition was performed by Abrahams and Marsh [15]. No atomic disorder was detected in stoichiometric LiNbO_3 but 6% Li is missing from all Li sites in the congruent composition. Each missing Li^+ ion is replaced by an Nb^{5+} ion, with compensating vacancies at the Nb site maintaining charge neutrality, as given by the formula $[\text{Li}_{1-5x}\text{Nb}_{5x}]\text{Nb}_{1-4x}\text{O}_3$ with $x = 0.0118$ in the congruent composition. The stability range of the nonstoichiometric composition corresponds to $0 \leq x \leq 0.02$. Five nonstoichiometric samples, which were grown by the Czochralski method from melts with different Li/Nb ratios, $\text{Li/Nb} = 0.833, 0.942$ (congruent), 1.0, 1.1 and 1.2 [6], were selected as an object of study in this work. The samples and their corresponding crystal formulae are summarized in table 1. We refer to LiNbO_3 with the $\text{Li/Nb} = 1$ composition inside the crystal [15] as the stoichiometric sample.

Table 1. A summary of Li/Nb ratios in the melt and inside the crystals. n_0 refractive index values were theoretical predications at $1.064 \mu\text{m}$.

Li/Nb (in the melt)	0.83	0.942	1.0	1.1	1.2
Li/Nb (inside the crystal from [5])	0.908	0.942	0.948	0.968	0.988
Deviation from stoichiometry ($1 - \text{Li/Nb}$)	0.092	0.058	0.052	0.032	0.012
Crystal formula	$\text{Li}_{0.908}\text{Nb}_{1.0184}\text{O}_3$	$\text{Li}_{0.942}\text{Nb}_{1.0116}\text{O}_3$	$\text{Li}_{0.948}\text{Nb}_{1.0104}\text{O}_3$	$\text{Li}_{0.968}\text{Nb}_{1.0064}\text{O}_3$	$\text{Li}_{0.988}\text{Nb}_{1.0024}\text{O}_3$
n_0 (at $1.064 \mu\text{m}$)	2.210	2.217	2.219	2.223	2.227

By using the structural data of the stoichiometric LiNbO_3 sample [15], we can find the connection between chemical bond properties and physical properties of this crystal. The decomposition of the crystal can be written as

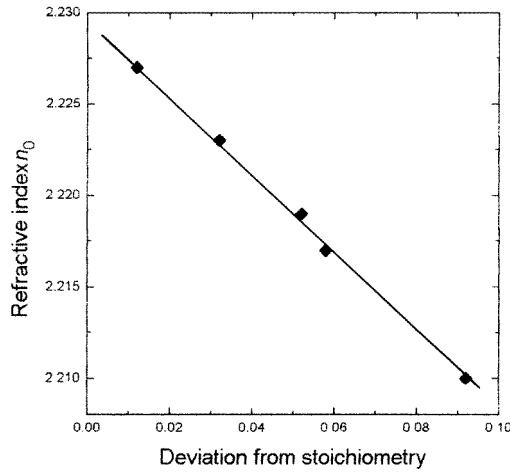


The first term in this equation, $\frac{1}{2}\text{LiO}(\text{l})_{3/2}$, means there is a structural unit only bonded with the long Li–O bonds (2.2711 \AA) in LiNbO_3 , which occupies half of the number of Li–O bonds in the constituent LiO_6 group (including three short Li–O bonds and three long Li–O ones). Since the refractive index of the stoichiometric LiNbO_3 , $n_r = 2.23$ at $1.064 \mu\text{m}$ [16] is known, we can obtain the detailed chemical bond parameters and linearities χ^μ of individual bonds listed in table 2.

Taking the deviation from stoichiometry ($1 - \text{Li/Nb}$) into account, linear dielectric behaviours of these samples can be predicted based on the calculated chemical bond parameters of the stoichiometric LiNbO_3 . Since the different Li/Nb ratio in the crystal finally leads to different numbers of Li–O and Nb–O bonds inside the crystal, the combination of contributions of each type of these chemical bonds in different nonstoichiometric samples

Table 2. Chemical bond parameters and linear and nonlinear optical properties of each type of bond in LiNbO_3 .

	LiNbO_3			
	Li–O(s)	Li–O(l)	Nb–O(l)	Nb–O(s)
d^μ (Å)	2.0498	2.2711	2.1296	1.8763
E_h^μ (eV)	6.7017	5.1971	6.0961	8.3452
C^μ (eV)	4.7809	3.8717	11.5863	15.5645
f_c^μ	0.6627	0.6431	0.2168	0.2233
χ^μ	2.6784	3.1993	5.5660	4.4479
χ_b^μ	0.9412	1.1242	1.9559	1.5630
q/e	0.1999	0.1769	0.5392	0.6433
G_{22}^μ	−0.0144	−0.0263	−0.0319	0.0648
d_{22}^μ ($\times 10^{-9}$ esu)	1.8931	4.8067	4.4289	−0.6363
G_{31}^μ	−0.1467	0.1734	−0.1842	0.1827
d_{31}^μ ($\times 10^{-9}$ esu)	19.2268	−31.7125	2.4780	−1.7954
G_{33}^μ	−0.0357	0.3729	−0.3037	0.1024
d_{33}^μ ($\times 10^{-9}$ esu)	4.6726	−68.1722	4.0847	−1.0066

**Figure 1.** The dependence of the refractive index at $1.064 \mu\text{m}$ on the deviation from the stoichiometric composition inside the crystal.

would naturally modify their physical properties. Consequently, refractive indices at $1.064 \mu\text{m}$ of these five nonstoichiometric samples are obtained and are listed in table 1.

Figure 1 shows the variation of the refractive indices for the five different samples at $1.064 \mu\text{m}$. The refractive indices have been plotted versus the estimated deviation of the stoichiometry inside the crystal ($1 - \text{Li}/\text{Nb}$). This deviation is always larger than zero because the LiNbO_3 crystals are always Li deficient. Theoretically, we obtain a monotonic dependence of the refractive index (n_0^2 is the optical frequency dielectric constant) on the concentration of point defects, which is directly related to deviation from the stoichiometric composition $\text{Li}/\text{Nb} = 1$ in the crystal. This can be explained by considering contributions of Li–O bonds to the total linearity χ . From table 2, we can see not very important linear contributions of Li–O bonds compared with those of Nb–O bonds; therefore, as the Li/Nb

ratio in the crystal decreases, the linear optical property (i.e., the refractive index value) does not change dramatically.

For the stoichiometric LiNbO_3 , chemical bond parameters and linear optical properties of each type of constituent chemical bond have been obtained; NLO properties of each bond in this crystal can further be evaluated using (7). Geometric characters G_{ij}^μ and NLO tensor coefficients d_{ij}^μ of Li–O and Nb–O bonds in the stoichiometric LiNbO_3 are also tabulated in table 2.

Table 3. A comparison between the calculated and experimental d_{ij} values of LiNbO_3 , at $1.064 \mu\text{m}$.

	$d_{22} (\times 10^{-9} \text{ esu})$	$d_{31} (\times 10^{-9} \text{ esu})$	$d_{33} (\times 10^{-9} \text{ esu})$
Calculated	6.4924	−11.8031	−60.4214
Exp. (from [9] and [18])	5.0	−10.3	−64.5

The restrictions imposed by the crystal symmetry [15] and the Kleinman symmetry conditions [17] on the NLO coefficients make the three allowed independent NLO tensor coefficients d_{33} , d_{31} , and d_{22} , exist in the stoichiometric LiNbO_3 . Theoretical results and experimental data of nonlinearities of the stoichiometric LiNbO_3 at $1.064 \mu\text{m}$ are listed in table 3: the agreement is good. Based on contributions of each constituent chemical bond to the total nonlinear tensor coefficient d_{ij} of LiNbO_3 with $\text{Li/Nb} = 1$, NLO tensor coefficients of five other nonstoichiometric samples can be quantitatively predicted: their values at $1.064 \mu\text{m}$ are listed in table 4. In table 5 some measured tensor coefficients d_{ij} of LiNbO_3 crystals with $(\text{Li/Nb})_m = 0.852, 0.946, \text{ and } 1.083$ are given. Both tables show us that in five nonstoichiometric crystals d_{ij} values have the same increasing tendency when the Li/Nb ratio increases in the melt. Therefore, theoretical and experimental results verify that Li–O bonds play a very important role in contributions to the total nonlinear tensor coefficients d_{ij} . In figure 2, we can see that the d_{33} value increases monotonically with the concentration of Li atom in these samples.

Table 4. Theoretical predications of NLO tensor coefficients of LiNbO_3 samples with different Li/Nb ratios, at $1.064 \mu\text{m}$.

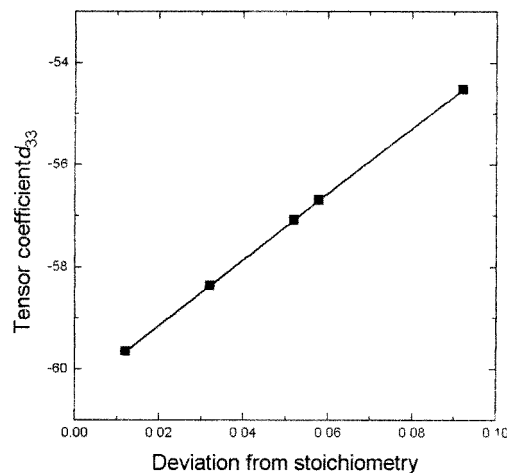
	$d_{22} (\times 10^{-9} \text{ esu})$	$d_{31} (\times 10^{-9} \text{ esu})$	$d_{33} (\times 10^{-9} \text{ esu})$
$\text{Li}_{0.908}\text{Nb}_{1.0184}\text{O}_3$	5.872	−10.642	−54.523
$\text{Li}_{0.942}\text{Nb}_{1.0116}\text{O}_3$	6.101	−11.071	−56.703
$\text{Li}_{0.948}\text{Nb}_{1.0104}\text{O}_3$	6.142	−11.147	−57.087
$\text{Li}_{0.968}\text{Nb}_{1.0064}\text{O}_3$	6.277	−11.399	−58.370
$\text{Li}_{0.988}\text{Nb}_{1.0024}\text{O}_3$	6.412	−11.652	−59.652

From the calculated values listed in table 2, we can find that the NLO behaviour in LiNbO_3 is dominated by the distorted LiO_6 octahedra, not the distorted NbO_6 octahedra. We also found that the values of G_{22}^μ for all bonds are quite small, which finally lead to the smaller d_{22} value compared with the d_{31} and d_{33} values. The signs of G_{31}^μ (or G_{33}^μ) values are opposite to each other in LiO_6 octahedra and in NbO_6 octahedra, which would lead to cancellations among d_{31}^μ (or d_{33}^μ) values, e.g., the strong cancellation between $d_{31}^{\text{Li-O(l)}}$ and $d_{31}^{\text{Li-O(s)}}$, due to the opposite signs of $G_{31}^{\text{Li-O(l)}}$ and $G_{31}^{\text{Li-O(s)}}$, and the near cancellation between $d_{31}^{\text{Nb-O(l)}}$ and $d_{31}^{\text{Nb-O(s)}}$. These calculated results also show that among all constituent

Table 5. Experimentally determined values of NLO tensor coefficients d_{ij} for LiNbO_3 samples pulled from melts with different Li/Nb atom ratios.

$(\text{Li/Nb})_m$	d_{ij}^a		
	d_{22}	d_{31}	d_{33}
0.852	4.8	-7.8	-62.4
0.946	5.2	-10.8	-67.3
1.083	4.4	-13.5	-67.6

^a Taken from [9], the values were estimated to be accurate to $\pm 10\%$. The following conversion unit is used: $d_{36}(\text{KDP}) = 0.93 \times 10^{-9}$ esu (i.e., 0.39 pm V^{-1}), which is recommended by Roberts [18] as a primary standard for second-order nonlinear coefficients.

**Figure 2.** The dependence of the NLO tensor coefficient d_{33} at $1.064 \mu\text{m}$ on the deviation from the stoichiometric composition inside the crystal.

chemical bonds, the long Li–O bonds in the deformed LiO_6 octahedra make the dominant contribution to the total NLO tensor coefficient.

The present results are based on the assumption that there is no obvious difference between stoichiometric and nonstoichiometric lithium borate in atomic coordinates and lattice constants. The assumption has been experimentally verified to be true in [15]; therefore, all calculations are meaningful and reasonable. At the same time, the present work also gives us an important enlightenment that analysis of nonlinearities of LiNbO_3 compounds is not complete if only Nb–O bonds are taken as an object of study.

4. Conclusion

The refractive indices and NLO tensor coefficients of LiNbO_3 compounds have been theoretically predicted as a function of the stoichiometry, by using the chemical bond theory of complex crystals. In both experimental and theoretical aspects, Li–O bonds have been proved to be an important constituent part possessing the dominant nonlinear contributions in the LiNbO_3 samples. In the linear optical contribution, Nb–O bonds surely play a more important role; in contrast, in respect of nonlinearity, Nb–O bonds become less important.

This is the main reason that there is no large difference among the theoretical predictions of refractive indices of LiNbO_3 with different Li/Nb atom ratios inside the crystal. Compared with linearities, the nonlinear tensor coefficient d_{ij} , especially d_{33} , values are very sensitive to the composition of crystals, and are found to be directly proportional to the concentration of Li atom. This shows us the importance of Li–O bonds in these samples: therefore, in dealing with NLO properties of a crystal, all of its constituent chemical bonds should be taken into account. The theoretical samples would be of great interest in the elucidation of the actual influence of the Li–O bond, i.e., the Li site on the optical properties of LiNbO_3 . This would be a useful tool to evaluate the effect of doping ions in modifying physical properties of LiNbO_3 samples.

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