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Chemical bond analysis of the second order nonlinear optical behavior of Zn-doped lithium niobate

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Abstract

Second order nonlinear optical properties of the Zn-doped lithium niobate single crystals have been quantitatively studied from the chemical bond viewpoint. The results show that the second order nonlinear optical response of Zn-doped LiNbO₃ single crystals at 1079 nm decreases linearly with increasing Zn concentration in the crystal. This linear correlation is quantitatively expressed in the current work. Furthermore, in the present work the different influences of Mg and Zn dopants on the dielectric response of lithium niobate single crystals are compared. © 2000 Published by Elsevier Science B.V.

Keywords: Insulators; Crystal structure and symmetry; Optical properties

1. Introduction

Due to its large electrooptic and nonlinear optical (NLO) coefficients [1,2], lithium niobate LiNbO₃ (LN) is of great interest for numerous applications in optics (e.g. holographic memories, photorefractive devices, waveguide structures, electrooptic modulators, frequency doublers and mixers, parametric oscillators, etc.). Since LN is a typical nonstoichiometric crystal, it contains specific structural vacancies (i.e., empty oxygen octahedra) [3] and other intrinsic defects in its crystal structure [4,5]. Therefore, various dopants such as rare earth and transition metal ions can be easily introduced into the crystallo-

graphic frame occupying Li sites [6]. This wide range of dopants accounts for the attractive versatility for many important applications [7]. Nominally pure LN devices suffer under a serious optical damage problem due to the photorefractive effect when exposed to high intensity illumination. This problem can be greatly reduced by doping LN single crystals with MgO at a concentration of about 5 mol% [8–10]. Moreover, it has been shown that the photorefractive damage in LN single crystals can be prevented by doping with ZnO even more efficiently than with MgO [11].

Dopants in such a relatively high concentration will also affect the linear and nonlinear optical properties of lithium niobate in a characteristic way. For a calculation of these properties it is essential to know the location and structural characteristics of these dopants. By now, it seems clear that the Li vacancy model is more reasonable in describing the

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defect structure of nonstoichiometric LN single crystals [5], and that most dopants (except Ta and W) prefer to occupy Li sites [6,12]. Based on this structure model, we can do some predictions of the physical properties of doped LN single crystals, applying the chemical bond method.

Our previous work has shown the important influence of the crystal composition on its dielectric response (the refractive indices, and second order NLO tensor coefficients) [13]. Doping with ZnO in various LN single crystals (pure or doped with other dopants) leads to a satisfactory decrease of the optical damage, due to the influence of Zn^{2+} on the intrinsic defect structure [10]. At the same time, some optical properties such as refractive indices [14], electrooptic coefficients [15] and phase-matching conditions for various configurations of second-harmonic generation (SHG) [16] are influenced by the Zn impurity. Yet up to now, the influence of the Zn doping in the crystal on the second order NLO behavior of lithium niobate has not been quantitatively investigated. On the basis of our studies on Mg-doped LN single crystals [17], we, in the current work, can do some analysis on the dielectric response of Zn-doped LN single crystals. Due to similar cation sizes and ionic charges, Mg^{2+} and Zn^{2+} both are suitable in occupying Li sites.

The chemical bond method allows us to derive dielectric responses of crystal materials from their corresponding crystallographic structures using the constructed structure–property relationship [18]. In a former work [19], we have quantitatively studied linear and second order nonlinear optical responses of LN at 1064 nm from the detailed crystallographic structures at room temperature [3]. In the present work, the second order NLO behavior of Zn-doped LN at 1079 nm will be quantitatively studied on the basis of the chemical bond viewpoint [18,20] and the constitution-property relationship in crystal materials [13].

2. Theoretical method

As shown in the previous works [18], the chemical bond method regards certain macroscopic physical properties of a crystal as the combination of the

contributions of all constituent chemical bonds. According to the relationship between the crystal structure and dielectric response of crystal materials, the linear and second order nonlinear optical properties of any 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 nonlinear optical susceptibilities χ and d_{ij} thus can be written as

$$\chi = \sum_{\mu} F^{\mu} \chi^{\mu} = \sum_{\mu} N_b^{\mu} \chi_b^{\mu} \quad (1)$$

and

$$d_{ij} = \sum_{\mu} \left\{ \frac{G_{ij}^{\mu} N_b^{\mu} (0.5) \{ [(Z_A^{\mu})^* + n(Z_B^{\mu})^*] / [(Z_A^{\mu})^* - n(Z_B^{\mu})^*] \} f_i^{\mu} (\chi_b^{\mu})^2}{d^{\mu} q^{\mu}} + \frac{G_{ij}^{\mu} N_b^{\mu} s(2s-1) [r_0^{\mu} / (r_A^{\mu} - r_B^{\mu})]^2 f_c^{\mu} (\chi_b^{\mu})^2 \rho^{\mu}}{d^{\mu} q^{\mu}} \right\}, \quad (2)$$

respectively. Parameters used in Eqs. (1) and (2), and in Table 1 include:

F^{μ} : Fraction of bonds of type μ composing the crystal.

χ^{μ} : Linear susceptibility contribution from μ type bonds.

N_b^{μ} : Number of bonds of type μ per cm^3 .

χ_b^{μ} : Susceptibility of a single bond of type μ .

G_{ij}^{μ} : Geometrical contribution of chemical bonds of type μ .

$(Z_A^{\mu})^*$, $(Z_B^{\mu})^*$: 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 [19].

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

d^{μ} : Bond length of the μ type bonds in \AA .

q^{μ} : Bond charge of the μ th bond.

s : Exponent in the bond force constant (2.48).

$r_0^{\mu} = 0.35 r_0^{\mu}$: Core radius, where $r_0^{\mu} = d^{\mu} / 2$.

$\rho = (r_A^{\mu} - r_B^{\mu}) / (r_A^{\mu} + r_B^{\mu})$: Difference in the atomic sizes, where r_A^{μ} and r_B^{μ} are the covalent radii of atoms A and B.

Table 1

Calculated chemical bond parameters, linear and second order nonlinear optical properties of all constituent chemical bonds in doped LiNbO_3 single crystals at 1079 nm.

	Constituent chemical bonds in $(\text{LiNbO}_3)(1-x)$				Constituent chemical bonds in $(\text{ZnNb}_2\text{O}_6)(x/2)$			
	Li–O(l)	Li–O(s)	Nb–O(l)	Nb–O(s)	Zn–O(l)	Zn–O(s)	Nb–O(l)	Nb–O(s)
d^μ (Å)	2.245	2.063	2.130	1.876	2.245	2.063	2.130	1.876
f_c^μ	0.649	0.666	0.220	0.226	0.479	0.494	0.241	0.252
χ^μ	3.132	2.705	5.603	4.475	3.802	3.308	4.740	3.833
q^μ/e	0.180	0.199	0.536	0.641	0.294	0.326	0.601	0.711
G_{22}^μ	–0.027	–0.014	–0.032	0.065	–0.027	–0.014	–0.032	0.065
d_{22}^μ (pm/V)	2.029	0.775	0.201	–0.292	0.922	0.363	0.372	–0.556
G_{31}^μ	0.176	–0.152	–0.184	0.183	0.176	–0.152	–0.184	0.183
d_{31}^μ (pm/V)	–13.015	8.559	1.152	–0.826	–5.915	4.008	2.133	–1.575
G_{33}^μ	0.360	–0.041	–0.303	0.103	0.360	–0.041	–0.303	0.103
d_{33}^μ (pm/V)	–26.682	2.322	1.892	–0.466	–12.125	1.087	3.505	–0.889

All of the above parameters can be deduced from the detailed chemical bonding structures of all constituent atoms which are obtained from the corresponding crystallographic structure of the assigned crystal material [18].

3. Results and discussion

In order to determine the linear and second order nonlinear optical properties of each kind of constituent chemical bond quantitatively, one has to know the detailed bonding environments of all constituent atoms, which are related to the structural characteristics of the assigned crystal. The chemical bond method [18,20], applied here, treats a compound as an infinite network of constituent atoms linked by chemical bonds. For crystals, this can be reduced to a finite network consisting of a single formula unit such as the network of LiNbO_3 , the

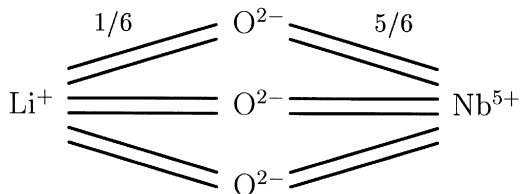


Fig. 1. The bond graph of LiNbO_3 . The valences of atoms and theoretical valences of the bonds are shown. Double lines denote two non-equivalent bonds.

graph of which is shown in Fig. 1. Each line in the graph represents a different bond, such that Li^+ and Nb^{5+} are six-coordinated and O^{2-} is four-coordinated.

In the crystallographic structure of pure LN single crystals, the ideal cation stacking sequence along the

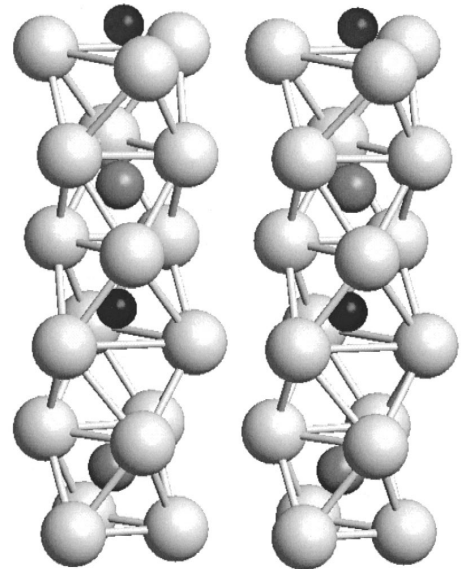


Fig. 2. Stereoscopic view (to be viewed with crossed eyes) of the ideal crystal stacking sequence of lithium niobate along the crystallographic c -axis (light gray: oxygen, dark gray: niobium, black: lithium).

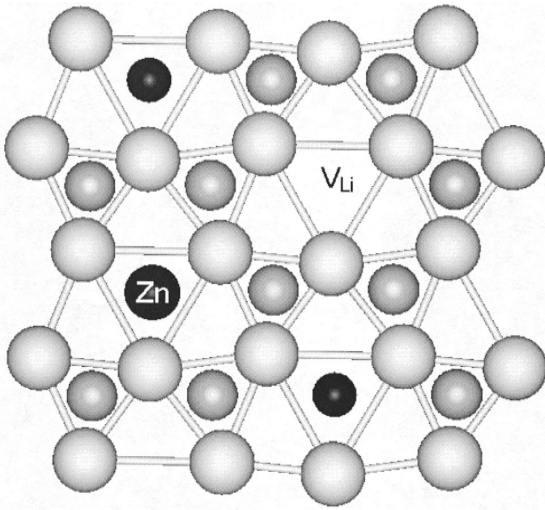


Fig. 3. Crystallographic a - b plane of Zn-doped lithium niobate. One Zn ion replaces two Li ions occupying a Li site and additionally forming a Li vacancy (V_{Li}). Light gray: oxygen lattice, dark gray: niobium, black: lithium or zinc.

c axis is $\dots -\text{Li}-\text{Nb}-\square-\text{Li}-\text{Nb}-\square-\dots$, where \square represents for a structural vacancy (an empty octahedron) [3]. This ideal stacking sequence (constituent octahedra in pure LN) is sketched in Fig. 2. However, when Zn^{2+} cations are introduced as dopants into such a stacking sequence, the situation changes into a different case. Just as analyzed for the case of Mg-doped LiNbO_3 [17], Zn dopants also will occupy Li sites, not Nb sites. A Zn ion will substitute for two Li ions occupying a Li site and forming a corresponding Li vacancy (see the planar view of the a - b plane in Fig. 3). The crystal structure will relax by strengthening some bonds and weakening others until an equilibrium is reached in which the valency sums at the oxygen atoms all are close to 2.0. Formally the environment of the Zn ions can be treated with reasonable accuracy like a new compound, ZnNb_2O_6 , where the structural parameters of LiNbO_3 are adopted. This is justified by the very similar ionic radii [21] of the Li^+ and Zn^{2+} cations. For our calculations of the optical properties we will consequently handle Zn-doped lithium niobate, i.e. $\text{Li}_{(1-x)}\text{Zn}_{x/2}\text{NbO}_3$ as a binary mixture of $(1-x)\text{LiNbO}_3$ and $(x/2)\text{ZnNb}_2\text{O}_6$.

According to the detailed chemical bonding situations of constituent Li, Nb and O atoms in the pure LN, as well as Li, Zn, Nb and O atoms in the doped LN, which are obtained from the crystallographic data of LN [22], and the above analysis for Zn-doped LN, we calculated the chemical bond parameters, linear and second order nonlinear optical properties of all constituent chemical bonds in the Zn-doped LN single crystals (i.e., Li-O, Zn-O and Nb-O bonds). The contributions of the individual bonds (and further of the LiO_6 , ZnO_6 and NbO_6 groups) to the total linear and second order nonlinear optical response of the whole Zn-doped LN crystal were quantitatively determined. The results for a (fundamental) wavelength of 1079 nm are summarized in Table 1. As mentioned above, for the basic calculations two different compounds were assumed, LiNbO_3 and ZnNb_2O_6 , which were separately treated. For the properties of Zn-doped lithium niobate crystals, the results were appropriately combined, yielding the linear and nonlinear optical response of doped crystals. In the basic treatment no structural relaxation was allowed for. Yet to account

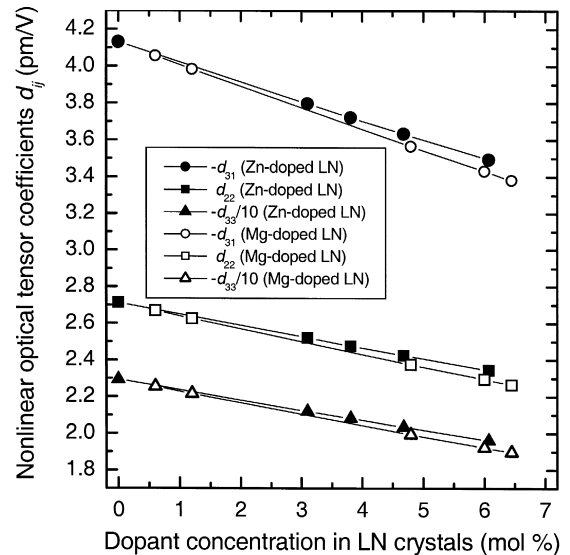


Fig. 4. Dependence of the second order nonlinear optical tensor coefficients d_{ij} of Zn-doped LiNbO_3 crystals at 1079 nm on the Zn concentration in the crystal. For comparison the dependence on Mg doping is also plotted.

for such a relaxation, the results for the linear optical response, i.e. the ordinary refractive index n_o were referenced to experimental values taken from a generalized Sellmeier fit [14].

The final results for all independent second order NLO tensor coefficients d_{22} , d_{31} , and d_{33} at 1079 nm of pure and differently Zn-doped LN crystals are plotted in Fig. 4. The calculated results for pure LN are $d_{22} = 2.713$ pm/V, $d_{31} = -4.130$ pm/V, and $d_{33} = -22.934$ pm/V, respectively, which agree well with the reported experimental data for 1064 nm [23]: $d_{22} = 2.1$ pm/V, $d_{31} = -4.3$ pm/V, and $d_{33} = -27$ pm/V, as well as with our previously calculated results for 1064 nm [19].

For comparison, the corresponding results for Mg-doped lithium niobate are also plotted in Fig. 4. It is obvious that the influence of both valence-2 dopants on the nonlinear optical properties of lithium niobate is quite similar, all tensor coefficients decrease considerably with increasing doping level. The effect of Mg doping is slightly stronger than that of Zn doping. The nearly identical decrease contrasts a little bit to the behavior of the linear optical properties, i.e. the ordinary refractive index. For this refractive index, Zn doping causes an increase [14] whereas Mg doping decreases it [24], due to the very different dielectric polarizabilities of the ions involved (Li^+ : 1.20 \AA^3 , Mg^{2+} : 1.32 \AA^3 , Zn^{2+} : 2.04 \AA^3 [25,26]). For the *nonlinear* optical properties, the acentricity of the crystal is effective, this seems to be reduced by both sorts of dopants. According to our calculations, the dependence is governed by the number of Li vacancies which increases with the doping level and does not depend from the respective dopant. The effect is strong, as the Li places in the crystallographic frame of lithium niobate are the sensitive lattice sites, on which dopants (or vacancies) can modify the dielectric properties most effectively [18,19].

4. Conclusion

Second order NLO properties of the Zn-doped LN single crystals at 1079 nm have been quantitatively studied from the chemical bond viewpoint of crystal materials. From the current work, we find that Zn doping in lithium niobate decreases the nonlinear

optical response linearly with increasing dopant concentration. Yet the effect is slightly less than for Mg doping. Considering the fact that Zn is more effective in suppressing the so-called optical damage, Zn doping should be preferred for the fabrication of damage-resistant nonlinear optical devices versus Mg doping. Both Mg and Zn occupy identical lattice sites (Li) in lithium niobate, their different influence on dielectric properties of LN crystals must be ascribed to their individual ionic characteristics.

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