

Temperature dependence of the dielectric response of lithium niobate

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Abstract

The dielectric response of lithium niobate is quantitatively calculated for different temperatures. Using the chemical bond method, both linear (refractive index) and second order nonlinear optical properties are derived from the corresponding crystallographic structure. Our results show that the dielectric response of lithium niobate at 1.064 μm increases remarkably with increasing temperature. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Lithium niobate (LiNbO_3) presently is one of the most important materials for both fundamental and applied research in optics due to its interesting electrooptical and nonlinear optical (NLO) properties [1,2]. Crystal structure [3–5] and defect features [6,7] have attracted considerable interest in the last few decades. At low temperatures, the crystallographic structure of lithium niobate has been determined to be space group $R3c$ [3,5]. Above the Curie point ($T_c \approx 1430 \text{ K}$), it changes into space group $R\bar{3}c$. A phase transition from the low-temperature ferroelectric phase to the high-temperature paraelectric phase occurs at T_c [5]. With increasing temperature, the crystallographic data show remarkable variations of the atomic coordinates [5]; these variations in turn should affect the corresponding physical properties of lithium niobate, such as the dielectric response.

Previous experimental and theoretical work has shown the important effect of different compositions of lithium niobate on its corresponding dielectric response [8,9]. The influence of temperature usually was only introduced as an appropriate fit parameter [10].

In contrast, experimentally observed data, especially on the nonlinear optical properties of lithium niobate, vary considerably. For example, a range from -29.1 to -43.9 ± 8.2 ($\times 10^{12} \text{ m/V}$) [11] is published in respect of

the second order nonlinear optical tensor coefficient d_{33} . This obviously should be due to different experimental conditions under which the measurements are carried out, particularly the local temperature in the beam area during the measurement.

A thorough study of the influence of temperature on the dielectric response of lithium niobate should therefore be of interest for both the linear and nonlinear optical properties of lithium niobate.

The calculations of the temperature dependence of the optical properties are carried out in the present work using the chemical bond method. This method allows deduction of dielectric properties of crystals from their respective crystallographic structures [12]. The calculations are based on temperature dependent structure data measured by neutron powder diffraction [5].

2. Theoretical method

As shown previously [12], 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}

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Table 1
Calculated chemical bond parameters, linear and nonlinear optical properties of constituent bonds of LiNbO₃, at different temperatures

	300 K			1200 K			1350 K		
	Li–O(l)	Nb–O(l)	Nb–O(s)	Li–O(l)	Nb–O(l)	Nb–O(s)	Li–O(l)	Nb–O(l)	Nb–O(s)
	d^μ / Å	2.2397	2.0696	2.1246	2.4090	2.1099	2.0905	2.5458	2.0986
E_h^μ / (eV)	5.3797	6.5438	6.1317	4.4903	6.2382	6.3827	3.9155	6.3218	6.4391
C^μ / (eV)	3.9987	4.7032	11.7000	3.3784	4.4553	11.9236	2.9444	4.4261	14.4314
f_c^μ	0.6441	0.6594	0.2155	0.6385	0.6622	0.2272	0.6388	0.6711	0.2309
χ^μ	3.0824	2.6886	5.4494	3.7198	2.9493	5.7185	4.8669	3.1318	6.2238
χ_b^μ	1.0855	0.9468	1.9191	1.3639	1.0814	2.0967	1.6250	1.1547	1.9607
q^μ/e	0.1813	0.1992	0.5470	0.1593	0.1875	0.5276	0.1418	0.1808	0.5616
G_{ij}^μ	–0.0280	–0.0134	–0.0328	–0.0331	–0.0054	–0.0507	–0.0325	0.0057	0.0701
d_{32}^μ	4.7235	1.7537	0.4005	8.8490	0.9292	0.9257	13.0543	–1.1862	–1.6836
G_{31}^μ	0.1762	–0.1533	–0.1848	0.1661	–0.1158	–0.1891	0.1588	–0.0839	–0.1911
d_{31}^μ	–29.7116	20.0115	2.2549	–44.3844	19.8578	3.4558	–63.7203	17.3358	5.4197
G_{33}^μ	0.3568	–0.0425	–0.2996	0.4119	–0.0150	–0.2598	0.4473	–0.0052	–0.2341
d_{33}^μ	–60.1485	5.5529	3.6565	–110.0658	2.5721	4.7470	–179.5205	1.0702	6.6404

thus can be written as

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

and

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

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 cm³;
- 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 [9];
- 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 Å;
- q^{μ} Bond charge of the μ -th bond;
- s Exponent in the bond force constant (2.48);
- $r_c^{\mu} = 0.35 r_0^{\mu}$ Core radius, where $r_0^{\mu} = d^{\mu} / 2$; and
- $\rho = (r_A^{\mu} - r_B^{\mu}) / (r_A^{\mu} + r_B^{\mu})$ Difference in the atomic sizes, where r_A^{μ} and r_B^{μ} are the covalent radii of atoms A and B.

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 [12].

3. Results and discussion

The present calculations are carried out on the basis of previous work on lithium niobate [9]. From the detailed crystallographic data of lithium niobate at various temperatures [5], the corresponding chemical bonding structures of all constituent atoms are derived. According to the detailed chemical bonding situations of Li, Nb and O atoms, the chemical bond parameters, linear and second order nonlinear optical properties of constituent Li–O and Nb–O bonds, respectively, are calculated. Contributions of these chemical bonds (and further LiO₆ and NiO₆ clusters) to the total linear and second order nonlinear optical response of

Table 2

Calculated chemical bond parameters of constituent bonds of LiNbO₃, at higher temperatures (above the Curie point T_c)

	1450 K			1480 K			1505 K		
	Li–O(<i>l</i>)	Li–O(<i>s</i>)	Nb–O	Li–O(<i>l</i>)	Li–O(<i>s</i>)	Nb–O	Li–O(<i>l</i>)	Li–O(<i>s</i>)	Nb–O
d^μ (Å)	2.4824	2.1209	1.9950	2.4830	2.1287	1.9944	2.3887	2.1543	1.9964
E_h^μ (eV)	4.1682	6.1583	7.1675	4.1657	6.1024	7.1729	4.5855	5.9242	7.1551
C^μ (eV)	3.1433	4.3739	13.1836	3.1408	4.3408	13.1886	3.4531	4.2843	13.3506
f_c^μ	0.6375	0.6646	0.2281	0.6376	0.6640	0.2283	0.6381	0.6566	0.2231
χ^μ	4.0444	3.0659	5.4625	4.0504	3.0887	5.4668	3.6104	3.0135	5.1630

lithium niobate are then quantitatively determined. The calculated results are shown in Table 1 (temperatures below T_c) and Table 2 (above T_c). In our calculations, Li–O(*l*) and Li–O(*s*) denote Li–O bonds with the long and short bond length, respectively.

To achieve the macroscopic properties from a geometric summation of the bond contributions leads to some ambiguity. Although commonly referred to as LiNbO₃, lithium niobate usually exhibits a more or less expressed lithium deficit. The range of stable compositions extends from 46 to 50 mol% Li₂O at 1300 K and from 48 to 50 mol% at room temperature [13,14]. Furthermore, for the structure of lithium-deficient crystals at least two contrary models have been discussed [3,4].

The crystal structure of lithium niobate consists of distorted oxygen octahedral sharing faces, thus forming a trigonal lattice. The ideal cation stacking sequence along the trigonal axis is $\cdots\text{Li-Nb}-\square\text{-Li-Nb}-\square\cdots$, where \square represents a structural vacancy (an empty octahedron). The different structure models describe how niobium atoms are redistributed in lithium-deficient crystals. As most results—especially recent ones [15]—confirm that the niobium sublattice stays intact, i.e. no

niobium vacancies arise, even in crystals with high lithium deficit, we restrict our calculations to two different structural scenarios:

1. stoichiometric lithium niobate (50 mol% Li₂O) with ideal occupation of the cation sites; and
2. lithium deficient lithium niobate (49 mol% Li₂O) with the experimentally determined occupancies of cation sites [5].

The resulting linear and nonlinear optical properties are summarized in Table 3 and sketched in Figs. 1 and 2.

The calculated parameters collected in Tables 1 and 2 show that—up to the Curie temperature T_c —linear and second order nonlinear optical contributions of the constituent Li–O and Nb–O bonds to the total linear and second order nonlinear optical properties of lithium niobate increase with increasing temperature. Above T_c , the linear contributions vary only slightly whereas the nonlinear contributions vanish due to the changed crystal symmetry. This behavior is reflected by the corresponding items in Table 3, the macroscopic linear and second order nonlinear optical response at 1.064 μm increases with increasing

Table 3

Calculated refractive indices and independent nonlinear optical tensor coefficients d_{ij} of LiNbO₃ at different temperatures for the ideal crystal structure, i.e. ideal site occupancies (A), and the occupancies (B) as reported by Boysen and Altorfer [5], respectively. (All d_{ij} tensors are in units: 10^{-9} esu)

	$R3c$			$R\bar{3}c$		
	300 K	1200 K	1350 K	1450 K	1480 K	1505 K
(A)						
n_0 (1064 nm)	2.214	2.305	2.402	2.347	2.349	2.289
d_{22}	6.3	9.7	12.0	–	–	–
d_{31}	– 9.1	– 23.8	– 45.1	–	–	–
d_{33}	– 51.9	– 104.7	– 175.2	–	–	–
(B)						
n_0 (1064 nm)	2.232	2.250	2.356	2.296	2.315	2.283
d_{22}	6.4	8.2	10.8	–	–	–
d_{31}	– 9.3	– 20.1	– 40.5	–	–	–
d_{33}	– 52.9	– 88.5	– 157.4	–	–	–

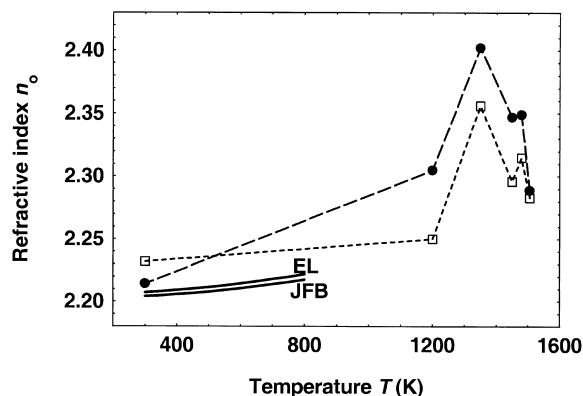


Fig. 1. Calculated temperature dependence of the principal refractive index n_0 of lithium niobate at $1.064 \mu\text{m}$. ●, ideal crystal structure; □, nonstoichiometric (49 mol% Li_2O) with reported site occupancies (dashed lines are drawn as guide for the eye). Solid lines represent experimental data, EL: Ref. [16], JFB: Ref. [17]. The curves are a calculated average over all polarizations using the Sellmeier approximations given by the respective authors.

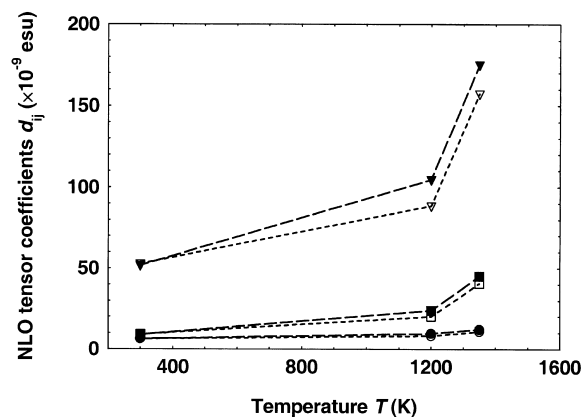


Fig. 2. Calculated temperature dependence of the nonlinear optical tensor coefficients d_{ij} of lithium niobate at $1.064 \mu\text{m}$. Filled markers: ideal crystal structure, open markers: nonstoichiometric (49 mol% Li_2O) with reported site occupancies; circles: d_{22} , squares: d_{31} , triangles: d_{33} . Dashed lines are drawn as guide for the eye.

temperature, above T_c the refractive index is approximately constant.

The increase of the refractive index at low temperatures resulting from our calculations is consistent with experimental data, albeit these are only available in a limited temperature range [16,17].

4. Conclusion

The temperature dependence of the linear and nonlinear optical properties of lithium niobate was calculated from the crystallographic structure parameters using the chemical bond method. The results show that both the linear and nonlinear optical responses of the material increase with rising temperature. In addition to accounting for certain discrepancies in the experimental values for second order nonlinear optical coefficients, this could also be of technical interest for several applications of lithium niobate.

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