Study of Thermo–Polarizability of Ions in Lithium Rich LiNbO₃ by the Point Dipole Approximation

Manoher Pasunooti†* Sathyanarayan Reddy Bavikadi‡ and Ravindharan Ethiraj†

1Department of Physics, Nizam College, Osmania University Hyderabad, India
2Ayabheada Institute of Technology & Science, R.R, Dist; India
3Stanley College of Engineering and Technology for Women, Hyderabad, India

Accepted 25 Nov 2015, Available online 05 Dec 2015, Vol.5, No.4 (Dec 2015)

Abstract

We have used the Point Dipole Approximation and Sellmeier equations to evaluate the variations of ordinary refractive index (nₒ), extraordinary refractive index (nₑ) and the birefringence (dn) in Lithium rich LiNbO₃ with temperature. These values are used to find the possible set of electronic polarizabilities (EP) of Li⁺, Nb⁵⁺ and O²⁻ ions at different temperatures from 298K to 772K for the wave lengths λ = 0.4545 µm, 0.6328 µm and 1.0642 µm. The EP of Li⁺ ion was assumed to be isotropic and temperature independent, the value of which is α_Li ≈ 0.932 × 10⁻²⁴ cm³. It is observed that as the temperature increases, for a given wavelength, the polarizability of Nb⁵⁺ ion decreases and that of O²⁻ ion increases. For a given temperature, with increase of wavelength the polarizabilities of both Nb⁵⁺ and O²⁻ decrease.

Keywords: Thermo–Polarizability, Birefringence, Point Dipole Approximation.

Introduction

It is well known that the optical properties of ferroelectric materials find wide range of applications in laser devices. Particularly in the recent years, there has been tremendous interest in the investigation of the nonlinear optical properties of ferroelectric thin films (Hewing, G.H. et al, 1983; Lee, S.H. et al, 1996) for planar waveguide and integrated-optic devices. Lithium Niobate (LiNbO₃) is a ferroelectric material, having the unique character of exhibiting easily switchable elastic, electrical and optical properties and have attracted the attention of device oriented physics and integrated optics. LiNbO₃ is known to have excellent nonlinear properties, including piezo-electric, acousto-optic, and electro-optic properties. These properties make LiNbO₃ a promising candidate for many opto-electronic applications such as modulators, frequency converters or storage media, if the production of high quality films on substrates with lower refractive index can be achieved. This crystal has long been the dominant material for electro-optic modulation in both data transmission and microwave photonic applications.

Optimization of light sources in terms of efficiency and low noise over broad range temperature dependence require not only an accurate knowledge of refractive indices but also temperature dependence (W. Weichmann, et al, 1993). For material to be useful as a nonlinear optical material it must be possible for fundamental frequency of radiation to stay in phase with the generated second harmonic. Many important applications of non-linear substances involve thermal stability with respect to refractive indices and is important in optical design when system is required to operate at constant temperature. These considerations have prompted many researchers to undertake experimental investigations of these properties in LiNbO₃ which are influenced by temperature variations (H.J. Dieter et al, 1997; D. Xue et al, 2002; H. Chaib et al, 2003; I.R. Tessman et al, 1953).


The electrical and optical properties of LiNbO₃ at room temperature are theoretically calculated by using a microscopic model based on the orbital...
approximation in correlation with the dipole-dipole interaction. Literature survey show that although this material is subject of several scientific investigations, the peculiarities of its thermo polarizable properties at wide range of temperatures are not yet studied. Most of above the mentioned research are involved with the accurate determination of either refractive index or birefringence variation with temperature. The survey also reveals that there is no attempt in modeling the Thermo Birefringence. The Point Dipole Approximation successfully explained the birefringence exhibited by LiNbO$_3$ (N. Ramesh, et al, 1993; S. Ramaseshan, et al, 1969) and in this paper we have extended the same model to explain the variations of birefringence in Lithium rich LiNbO$_3$ with temperature. We have evaluated the Electronic polarizabilities (EP) of Li$^+$, Nb$^{5+}$ and O$^-$ ions at different temperatures and at different wavelengths using the experimental data of birefringence, thermal expansion along with Sellmeier equations.

**Theoretical background**

Pockels first observed that the Thermal variation of refractive indices in solids is due to the following factors:

**I. The physical deformation caused by temperature:** As temperature increases, the inter atomic distance change resulting in the lattice constant being a function of temperature and, these cause change in density and consequently the number of ions per unit volume of the crystal which in turn alter the refractive indices of the crystal.

**II. Change in the electronic polarizability due to temperature:** The ions in the crystal vibrate with the greater amplitude with increase in temperature, resulting in the increase of the overlap of optical electron cloud which in turn modify the electronic polarizability (W.W. Wong, 2002).

In 1909 Lorentz showed that the dielectric properties of a substance could be directly related to the polarizabilities of the individual atoms in the substance. The Clausius-Mossotti, an extension of Lorentz work successfully explained the origin of Refractive Indices in cubic lattices and later used to explain the birefringence in both cubic and non cubic crystals (N. Ramesh, et al, 1993).

In the Point Dipole Approximation Method the continuum representation of a solid is an array of ions or polarizable points that can be accurately approximate the response of a continuum target on large length scales. In this method we can assume that each ion can be treated as a point dipole oscillating under the electric field of the electromagnetic radiation. The total field acting at the site of each ion is the sum of external field and the field due to all the oscillating dipoles at the ion. The relation between the average local field and the average polarization vector is used to define the dielectric constant. The Clausius-Mossotti relation of the following form was used to evaluate the electronic polarizabilities of ions at different temperatures and wavelengths with the refractive indices being obtained from the appropriate Sellmeier equations.

The susceptibility $\chi$ and the dielectric constant $\varepsilon$ are related by the expression

$$\chi = \frac{P}{E} = \frac{\varepsilon - 1}{4\pi}$$

(1)

Since we are concerned with electronic polarizabilities, dielectric constant along X-axis, $\varepsilon_x$, can be replaced by square of refractive index along x-axis $n_x^2$.

$$\chi_x = \frac{P_x}{E_x} = \frac{n_x^2 - 1}{4\pi} = \frac{\sum n_i^2 \alpha_i [1 + \sum D_{ij} \alpha_i]}{1 - \sum N_i \alpha_i [1 + \sum D_{ij} \alpha_i] K_i}$$

(2)

where

$$\sum D_{ij} = \sum \frac{3\chi_j^2 - r_i^2}{r_j^2}$$

is a measure of the geometric anisotropy in the x-direction for all the $j$th ions with $i$th ion at the center. $K_i = 4\pi/3$ is the Depolarization Factor for Spherical Cavity (C. Kittel, 1976).

**Calculations**

The electronic polarizability contribution is being significant in the visible and in the ultra violet region. Consequently electronic polarization alone is considered in the present analysis. The evaluation of EP of ions was carried out in Lithium rich LiNbO$_3$ (mole ratio Li/Nb = 0.996) grown by vapor transport equilibration ($0.325\mu m < \lambda < 1.064\mu m$) (D.N. Nilkogosyan, 2003). The lattice constants are given by $a = 5.1483\pm 0.0005\AA$, $c = 13.8573\pm 0.001\AA$. The appropriate Temperature and Wave length dependent Sellmeier equations used in our calculations are given in equations (3) and (4) (D.N. Nilkogosyan, 2003).

We evaluated $n_x$ and $n_e$ for three different wavelengths $\lambda=0.4545\mu m$, $\lambda=0.6328\mu m$ and $\lambda=1.0642\mu m$ at different temperatures from 298K to 772K using (3) & (4). These values and lattice anisotropy factors ($O$s), calculated using thermal expansion lattice parameters are substituted in equation (2) to find the possible set of EP values of Li$^+$, Nb$^{5+}$ and O$^-$ ions at different temperatures from 298K to 772K for the wave lengths $\lambda=0.4545\mu m$, $\lambda=0.6328\mu m$ and $\lambda=1.0642\mu m$. The EP of Li$^+$ ion is assumed to be isotropic and temperature independent, the value of which is $\alpha_{Li} = 0.032\times 10^{-24} cm^3$ (R.I., Shostak et al, 2004; A.V. Yatsenko, 2001). Through iteration process, we evaluated the possible values of EP for Nb$^{5+}$ and O$^-$ ions and are given in the Table-1, Table-2 and Table-3 respectively. The variation of refractive indices ($n_x$, $n_e$), birefringence ($dn$) and polarizabilities ($\alpha$s) with increase in temperature at various wavelengths are shown in Fig. 1, Fig. 2 and Fig. 3 respectively.
\[
n_2^2 = 4.913 + 1.6 \times 10^{-8} (T^2 - 88506.25) + \frac{0.1163 + 0.94 \times 10^{-7} (T^2 - 88506.25)}{\lambda^2} - 0.0273 \lambda^2
\]

(3)

\[
n_3^2 = 4.546 + 2.72 \times 10^{-7} (T^2 - 88506.25) + \frac{0.0917 + 1.93 \times 10^{-7} (T^2 - 88506.25)}{\lambda^2} - 0.0303 \lambda^2
\]

(4)

Table 1: Polarizabilities, Refractive Indices and Birefringence variation with Temperature in Lithium rich LiNbO\(_3\) at \(\lambda = 0.4545\mu m\).

<table>
<thead>
<tr>
<th>Temperature (in K)</th>
<th>Polarizabilities ((a \times 10^{-24} \text{cm}^3))</th>
<th>Refractive Indices</th>
<th>Birefringence ((dn = n_e - n_o))</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>(\alpha_L = 0.032), (\alpha_B = 1.5800), (\alpha_O = 1.9840)</td>
<td>(n_o = 2.37551), (n_e = 2.26034)</td>
<td>-0.11518</td>
</tr>
<tr>
<td>398</td>
<td>(\alpha_L = 0.032), (\alpha_B = 1.4910), (\alpha_O = 2.0280)</td>
<td>(n_o = 2.37795), (n_e = 2.26806)</td>
<td>-0.10999</td>
</tr>
<tr>
<td>498</td>
<td>(\alpha_L = 0.032), (\alpha_B = 1.3970), (\alpha_O = 2.0749)</td>
<td>(n_o = 2.38097), (n_e = 2.27762)</td>
<td>-0.10335</td>
</tr>
<tr>
<td>598</td>
<td>(\alpha_L = 0.032), (\alpha_B = 1.2877), (\alpha_O = 2.1285)</td>
<td>(n_o = 2.38477), (n_e = 2.28942)</td>
<td>-0.09535</td>
</tr>
<tr>
<td>698</td>
<td>(\alpha_L = 0.032), (\alpha_B = 1.1730), (\alpha_O = 2.1855)</td>
<td>(n_o = 2.38940), (n_e = 2.30352)</td>
<td>-0.08588</td>
</tr>
<tr>
<td>772</td>
<td>(\alpha_L = 0.032), (\alpha_B = 1.0861), (\alpha_O = 2.2296)</td>
<td>(n_o = 2.39353), (n_e = 2.31578)</td>
<td>-0.07775</td>
</tr>
</tbody>
</table>

Table 2: Polarizabilities, Refractive Indices and Birefringence variation with Temperature in Lithium rich LiNbO\(_3\) at \(\lambda = 0.6328\mu m\).

<table>
<thead>
<tr>
<th>Temperature (in K)</th>
<th>Polarizabilities ((a \times 10^{-24} \text{cm}^3))</th>
<th>Refractive Indices</th>
<th>Birefringence ((dn = n_e - n_o))</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>(\alpha_L = 0.032), (\alpha_B = 1.477), (\alpha_O = 1.928)</td>
<td>(n_o = 2.28724), (n_e = 2.18957)</td>
<td>-0.09760</td>
</tr>
<tr>
<td>398</td>
<td>(\alpha_L = 0.032), (\alpha_B = 1.412), (\alpha_O = 1.9622)</td>
<td>(n_o = 2.28871), (n_e = 2.1947)</td>
<td>-0.09401</td>
</tr>
<tr>
<td>498</td>
<td>(\alpha_L = 0.032), (\alpha_B = 1.331), (\alpha_O = 2.0020)</td>
<td>(n_o = 2.28967), (n_e = 2.20107)</td>
<td>-0.0886</td>
</tr>
<tr>
<td>598</td>
<td>(\alpha_L = 0.032), (\alpha_B = 1.205), (\alpha_O = 2.0580)</td>
<td>(n_o = 2.29032), (n_e = 2.21051)</td>
<td>-0.07981</td>
</tr>
<tr>
<td>698</td>
<td>(\alpha_L = 0.032), (\alpha_B = 1.095), (\alpha_O = 2.1100)</td>
<td>(n_o = 2.29205), (n_e = 2.22085)</td>
<td>-0.0712</td>
</tr>
<tr>
<td>772</td>
<td>(\alpha_L = 0.032), (\alpha_B = 1.027), (\alpha_O = 2.1450)</td>
<td>(n_o = 2.29423), (n_e = 2.22905)</td>
<td>-0.06518</td>
</tr>
</tbody>
</table>

Table 3: Polarizabilities, Refractive Indices and Birefringence variation with Temperature in Lithium rich LiNbO\(_3\) at \(\lambda = 1.0642\mu m\).

<table>
<thead>
<tr>
<th>Temperature (in K)</th>
<th>Polarizabilities ((a \times 10^{-24} \text{cm}^3))</th>
<th>Refractive Indices</th>
<th>Birefringence ((dn = n_e - n_o))</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>(\alpha_L = 0.032), (\alpha_B = 1.4500), (\alpha_O = 1.8779)</td>
<td>(n_o = 2.23366), (n_e = 2.14383)</td>
<td>-0.08983</td>
</tr>
<tr>
<td>398</td>
<td>(\alpha_L = 0.032), (\alpha_B = 1.3711), (\alpha_O = 1.9157)</td>
<td>(n_o = 2.23411), (n_e = 2.14860)</td>
<td>-0.08551</td>
</tr>
<tr>
<td>498</td>
<td>(\alpha_L = 0.032), (\alpha_B = 1.2840), (\alpha_O = 1.9570)</td>
<td>(n_o = 2.23468), (n_e = 2.15467)</td>
<td>-0.08001</td>
</tr>
<tr>
<td>598</td>
<td>(\alpha_L = 0.032), (\alpha_B = 1.1789), (\alpha_O = 2.0050)</td>
<td>(n_o = 2.23516), (n_e = 2.16209)</td>
<td>-0.07307</td>
</tr>
<tr>
<td>698</td>
<td>(\alpha_L = 0.032), (\alpha_B = 1.0727), (\alpha_O = 2.0544)</td>
<td>(n_o = 2.23606), (n_e = 2.17081)</td>
<td>-0.06525</td>
</tr>
<tr>
<td>772</td>
<td>(\alpha_L = 0.032), (\alpha_B = 0.9923), (\alpha_O = 2.0920)</td>
<td>(n_o = 2.23671), (n_e = 2.17012)</td>
<td>-0.05859</td>
</tr>
</tbody>
</table>

Fig. 1: Temperature dependence of Refractive Indices of Lithium rich LiNbO\(_3\) at different wavelengths.
Study of Thermo–Polarizability of Ions in Lithium Rich LiNbO₃ by the Point Dipole Approximation

Results and Discussion

The variation of $n_e$ compared with $n_o$ is more with temperature for different wavelengths [Fig. 1].

The variations of $n_o$ and $n_e$ decrease with wavelength at a given temperature [Fig. 1].

The optical birefringence of LiNbO₃ was calculated at $\lambda = 0.4545 \mu m$, $\lambda = 0.6328 \mu m$ and $\lambda = 1.0642 \mu m$ in the temperature range of 298K to 772K [Fig. 2].

It is observed that as the temperature increases polarizability of Nb⁵⁺ ion decreases and O²⁻ ion increases [Fig. 3].

As wavelength increases polarizability values decrease for Nb⁵⁺ and O²⁻ for a given temperature and polarizability value of Li⁺ ion remain almost constant [Fig. 3].

References


Manoher Pasunooti et al  
Study of Thermo-Polarizability of Ions in Lithium Rich LiNbO₃ by the Point Dipole Approximation