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Research Article

Thermo Optic and Thermo Polarizability Coefficients of Lithium Rich $LiNbO_3$ by the Point Dipole Approximation

Sathyanarayan Reddy Bavikadi†, Manoher Pasunooti‡*, Ravindharan Ethiraj† and Ch. Gopal Reddy#

†Aryabhata Institute of Technology & Science, R.R. Dist, India
‡Department of Physics, Nizam College, Osmania University, Hyderabad, India
Stanley College of Engineering and Technology for Women, Hyderabad, India
#Department of Physics, College of Engineering, Osmania University, Hyderabad, India

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Abstract

The Thermo-Optic Coefficients, dn/dT and the Thermo-Polarizability Coefficients, dα/dT of Lithium rich $LiNbO_3$, (mole ratio Li/Nb=0.996) grown by vapour transport equilibration are evaluated in the temperature range of 298K to 772K at λ=0.4545μm, λ=0.6328μm and λ=1.0642μm by using the Point Dipole Approximation and the appropriate Sellmeier equations. This work led to the estimation of possible set of polarizabilties of constituent ions of the crystal and their temperature dependence.

Keywords: *Thermo-Optic Coefficient, Thermo-Polarizability Coefficient, Point Dipole Approximation, Sellmeier equations and Polarizability.*

Introduction

The Thermo-Optic Coefficients (TOC) defined as the Refractive-Index variation with Temperature, dn/dT and the Thermo-Polarizability Coefficients (TPC) defined as the variation of Polarizability with Temperature, dα/dT, are of fundamental importance for the correct design and operation of modern Optoelectronic integrated devices and circuits. Thermal expansion of a crystal is a direct consequence of anharmonicity of lattice vibrations. Many important applications of non linear substances involve thermal stability of physical parameters and hence knowledge of temperature dependence of Refractive Index and Polarizabilities of constituent ions are important in the optical design, when systems are required to operate at variable temperatures. TOC is of fundamental importance for the correct design and operation of modern optoelectronic integrated devices and circuits, (G. Ghosh, 1998). This is especially true for devices where the wavelength dependence scales with the refractive index, such as in distributed feedback filters, interferometric modulators and switches, wavelength demultiplexers, and of course, in all thermo-optic-effect-based devices. The TOC and analysis of their dispersion is essential in characterization of the temperature dependent optical devices. The accuracy of TOC values depend on the accuracy of determining refractive index, n, and the temperature measurements in the experiment. The TOC stems from the temperature dependence of Electronic polarizability (EP) values of the constituent ions of the material used. Temperature variation can change the polarization directly as it changes the material density and the positions of ions in the lattice leading to change in refractive indices. The Thermo-Optic and Thermo-Polarizability variation have their influence in almost all waveguide materials particularly in the operation of high speed signal or data transfer in the optical fiber waveguides. Both effects play a key role in the design of wave guides and switches and these devices have the advantages of relying on guided light waves with no free space optics or any moving parts and thus contributing to their robust behavior .These considerations have prompted us to undertake investigations of these properties in Lithium rich $LiNbO_3$ (LRLN).

LRLN has interesting combination of properties and characteristics that makes possible the realization of different classes of devices and exploited in Optoelectronics and Photonics., Their optical, acoustical, piezo electrical, and photorefractive properties have been widely studied . LRLN has been employed in many optical devices, such as waveguides, high-speed modulators, beam deflectors, optical frequency converters, and tunable sources of coherent light for spectroscopic applications, (V.G. Dmitriev, *et al*, 1991). (G. Ghosh, 1998) gives a theoretical analysis

*Corresponding author: **Manoher Pasunooti** is working as Assistant Professor (c); **Sathyanarayan Reddy Bavikadi** as Associate Professor ; **Ravindharan Ethiraj** as Professor & Director, R & D **and Ch. Gopal Reddy** as Professor & Head

of the TOC in Lithium Niobate and its dependence on the wavelength and temperature. Basic experimental and theoretical works on the optical properties of this crystal have been done by Schlarband Betzler (U. Schlarb *et al*, 1993). However, evaluation of Thermo-Optic coefficient and its dependence on the temperature in LRLN has not been carried out so far. Therefore the study of TOC becomes very relevant. All though this material is very popular and was subjects of lot many scientific investigations, its thermo polarizable properties at wide range of temperatures was not studied. Most of the research is involved with the accurate determination of either refractive index or birefringence and their variation with temperature. It is well known that the optical anisotropy of any substance mainly arises from the polarizability anisotropy of the constituent ions and (S. Hirotsu *et al*, 1968), have shown this to be true in $LiNbO_3$. However, survey of literature reveal that not much work is done in the analysis of Thermo birefringence in terms of polarizabilities of constituent ions of the crystal.

The Point Dipole Approximation successfully explained the birefringence exhibited by $LiNbO_3$ (N. Ramesh, et al, 1993; S. Ramaseshan, et al, 1969).Hence in this paper, using this approximation, we report the study on the TOC and TPC of Lithium rich $LiNbO_3$ (LRLN) (mole ratio Li/Nb = 0.996) grown by vapour transport equilibration. The study led to evaluation of i) The possible set of Electronic polarizabilities (EP) of Li^+, Nb^{5+} and O^{2-} ions ii) thermo birefringence iii)TOCs iv)TPCs at different temperatures and at different wavelengths.

Theoretical background

Polarizability is an atomic property and it allows the understanding of the interactions between non-polar atoms and molecules and other electrically charged species, such as ions or polar molecules via the dipole moments. The dielectric constant depends on the manner in which the atoms are assembled to form a crystal. The dielectric constant is related to polarizabilities which in turn depend on the relation that holds between the macroscopic electric field and local electric field.

The Factors that Influence the Polarizability in a material are

1. The greater the number of electrons, the less control the nuclear charge has on charge distribution, and thus the increased polarizability of the atom.
2. The greater the distance of electrons from nuclear charge, the less control the nuclear charge has on the charge distribution, and thus the increased polarizability of the atom.

Pockels first observed the thermal variation of refractive indices in solids as due to the following factors:

1) **The physical deformation caused by temperature:** As temperature increases, the inter atomic distance change resulting in the lattice constant being a function of temperature which in turn cause a change in density and consequently the number of ions per unit volume of the crystal leading to alteration of the refractive indices of the crystal.
2) **Change in the Electronic Polarizability due to temperature variations:** The ions in the crystal vibrate with the greater amplitude resulting in the increase of the overlap of optical electron cloud which in turn modify the electronic polarizability (S. Ramaseshan, *et.al,* 1969) and (W.W. Wong, 2002).

In the Point Dipole Approximation, 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.

$$\chi_x = \frac{P_x}{E_x} = \frac{\varepsilon_x - 1}{4\pi} = \frac{n_x^2 - 1}{4\pi} = \frac{\sum_j N_j \alpha_j [1 + \sum_i D_{ij}\alpha_i]}{1 - \sum_j N_j \alpha_j [1 + \sum_i D_{ij}\alpha_i] K_x} \quad (1)$$

$$n_x = \left[\left(\frac{4\pi \sum_j N_j \alpha_j \left[1 + \sum_i D_{ij}\alpha_i\right]}{1 - \sum_j N_j \alpha_j \left[1 + \sum_i D_{ij}\alpha_i\right] K_x} \right) + 1 \right]^{1/2} \quad (2)$$

$$n_z = \left[\left(\frac{4\pi \sum_j N_j \alpha_j \left[1 + \sum_i D_{ij}\alpha_i\right]}{1 - \sum_j N_j \alpha_j \left[1 + \sum_i D_{ij}\alpha_i\right] K_z} \right) + 1 \right]^{1/2} \quad (3)$$

where $K_x = K_z = 4\pi/3$, are the depolarization factors for a spherical cavity (Kittel C., 1976) and

$$\sum_i D_{ij} = \sum_i \frac{3x_i^2 - r_i^2}{r_i^5} \quad (4)$$

is a measure of the geometric anisotropy in the *X*-direction for all the j^{th} ions with i^{th} ion at the centre.

For the consideration thermal expansion of lattice parameters we used the following thermal expansions equations (D.N. Nilkogosyan, 2003).

The equation for thermal expansion perpendicular to *c*-axis for temperature range $298K < T < 773K$ is given by

$$L_a(T) = L_a(T_o)\left\{1 + \alpha_o(T - 298) + \beta_o(T - 298)^2\right\} \quad (5)$$

where T in *K*, T_o = 298*K*, α_o = 15.5 x 10^{-6} K^{-1}, β_o = 5.3 x 10^{-9} K^{-2}.

The equation for thermal expansion parallel to *c*-axis for temperature range 298*K* < *T* < 773*K* is given by

$$L_c(T) = L_c(T_o)\left\{1 + \alpha_e(T-298) + \beta_e(T-298)^2\right\} \quad (6)$$

where *T* in *K*, T_o = 298K, α_e = 7.5 x 10^{-6} K^{-1}, β_e = -7.7 x 10^{-9} K^{-2}.

With equations (5) and (6) we calculated lattice parameters at different temperature from 298*K* to 772*K*. Using these Lattice Parameters, we calculated lattice anisotropy factors (*D*'s) at different temperature from 298K to 772*K*. Substituting them in Clasius-Mossotti equations given by (2) and (3), we calculated Refractive Indices at different temperatures.

Calculations

The Sellmeier equations used in this work are given below which takes into account all the effects and the parameters influencing the Refractive Index, (D.N. Nilkogosyan, 2003).

$$n_o^2 = 4.913 + 1.6\times10^{-8}\left(T^2 - 88506.25\right) + \frac{0.1163 + 0.94\times10^{-8}\left(T^2 - 88506.25\right)}{\lambda^2 - \left[0.2201 + 3.98\times10^{-8}\left(T^2 - 88506.25\right)\right]^2} - 0.0273\lambda^2 \quad (7)$$

$$n_e^2 = 4.546 + 2.72\times10^{-7}\left(T^2 - 88506.25\right) + \frac{0.0917 + 1.93\times10^{-8}\left(T^2 - 88506.25\right)}{\lambda^2 - \left[0.2148 + 5.3\times10^{-8}\left(T^2 - 88506.25\right)\right]^2} - 0.0303\lambda^2 \quad (8)$$

We evaluated n_o and n_e for three different wavelengths λ=0.4545μm, λ=0.6328μm and λ=1.0642μm at different temperatures from 298*K* to772*K* using (7) & (8). These values and lattice anisotropy factors (*D*'s) were calculated using thermal expansion lattice parameters and substituted in equation (2)and(3) to get the possible set of EP values of Nb^{5+} and O^{2-} ions at different temperatures from 298*K* to772*K* for the wave lengths λ=0.4545μm, λ=0.6328μm and λ=1.0642μm. The EP of Li^+ ion is assumed to be isotropic and temperature independent, the value of which is $\alpha_{Li} = 0.032\times10^{-24} cm^3$ (R.I., Shostak *et al*, 2004; A.V. Yatsenko, 2001). The lattice constants at room temperature are given by *a*=5.1483± 0.0005Å and *c*=13.8573 ± 0.0001Å. (Nilkogosyan, D. N. 2003). The EP contribution is significant in the visible and in the ultra violet region. Consequently electronic polarization alone is considered in the present analysis. Iteration process was used to evaluate the possible values of EP for Nb^{5+} and O^{2-} ions from which we evaluated the TOC and TPC of LRLN.

Results and Discussions

The possible values of EP for Nb^{5+} and O^{2-} ions, the Refractive Indices and the Birefringence of LRLN at λ=0.4545μm, λ=0.6328μm and λ=1.0642μm in the temperature range of 298*K* to 772*K* are given in the Table-1, Table-2 and Table-3 respectively. With this data we evaluated TOC of LRLN at the same wavelength and temperature range and are given in Table-4 and compared with the results of (D.N., Nilkogosyan, 2003) and (INRAD Data). The variation of TOC with temperature at various wavelengths is given Fig. 1.

The calculated Thermo-Polarizability Coefficients of constituent ions of Lithium rich $LiNbO_3$ are given in Table-5. The variation of TPC with temperature is shown in Fig. 2.

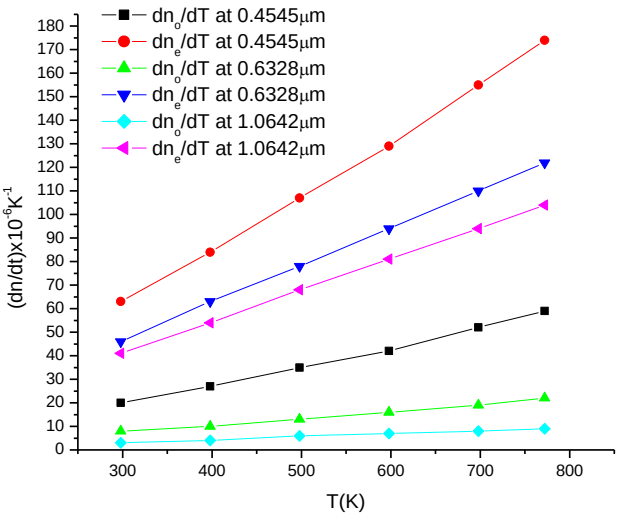

Fig. 1: Thermo-Optic Coefficients vs Temperature for various wavelengths

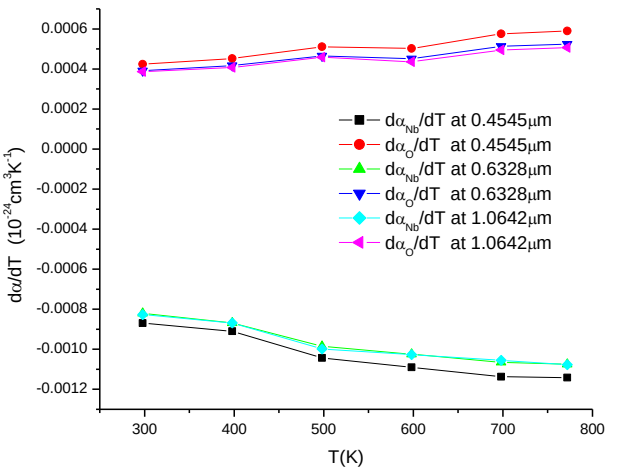

Fig.2: Thermo-Polarizable Coefficients vs Temperature for various wavelengths

Table-1: Variations of Polarizabilities, Refractive Indices and Birefringence with Temperature in Lithium rich $LiNbO_3$ at λ=0.4545μm

Temperature (in *K*)	Polarizabilities ($\alpha\times10^{-24}cm^3$)			Refractive Indices		Birefringence ($\Delta n = n_e - n_o$)
	α_{Li}	α_{Nb}	α_O	n_o	n_e	
298	0.032	1.570950	1.987189	2.375478	2.260855	-0.114623
398	0.032	1.487329	2.029165	2.377800	2.268173	-0.109627
498	0.032	1.392509	2.076388	2.380857	2.277686	-0.103170
598	0.032	1.284370	2.129629	2.384707	2.289477	-0.095230
698	0.032	1.170124	2.186562	2.389423	2.303657	-0.085765
772	0.032	1.084735	2.230103	2.393528	2.315780	-0.077748

Table-2: Variations of Polarizabilities, Refractive Indices and Birefringence with Temperature in Lithium rich $LiNbO_3$ at λ=0.6328μm

Temperature (in K)	Polarizabilities ($\alpha\times10^{-24}cm^3$)			Refractive Indices		Birefringence ($\Delta n = n_e - n_o$)
	α_{Li}	α_{Nb}	α_O	n_o	n_e	
298	0.032	1.486145	1.924984	2.287464	2.189245	-0.098218
398	0.032	1.406990	1.963618	2.288368	2.194699	-0.093668
498	0.032	1.317080	2.006840	2.289542	2.201724	-0.087817
598	0.032	1.214508	2.055294	2.290996	2.210321	-0.080674
698	0.032	1.106213	2.106671	2.292741	2.220496	-0.072244
772	0.032	1.025432	2.145563	2.294227	2.229047	-0.065181

Table-3: Variations of Polarizabilities, Refractive Indices and Birefringence with Temperature in Lithium rich $LiNbO_3$ at λ=1.0642μm

Temperature (in K)	Polarizabilities ($\alpha\times10^{-24}cm^3$)			Refractive Indices		Birefringence ($\Delta n = n_e - n_o$)
	α_{Li}	α_{Nb}	α_O	n_o	n_e	
298	0.032	1.449840	1.877995	2.233690	2.143870	-0.089821
398	0.032	1.370940	1.915748	2.234103	2.148598	-0.085505
498	0.032	1.281300	1.957900	2.234632	2.154670	-0.079962
598	0.032	1.179065	2.005070	2.235283	2.162080	-0.073202
698	0.032	1.071159	2.054940	2.236055	2.170813	-0.065242
772	0.032	0.990632	2.092586	2.236705	2.178121	-0.058585

Table-4: Variations of Thermo Optic Coefficients of Lithium rich $LiNbO_3$ with temperatures and wavelengths using Point Dipole Approximation

T (K)	$\frac{dn_o}{dT}\times10^{-6}K^{-1}$ λ=0.4545μm	$\frac{dn_e}{dT}\times10^{-6}K^{-1}$ λ=0.4545μm	$\frac{dn_o}{dT}\times10^{-6}K^{-1}$ λ=0.6328μm	$\frac{dn_e}{dT}\times10^{-6}K^{-1}$ λ=0.6328μm	$\frac{dn_o}{dT}\times10^{-6}K^{-1}$ λ=1.0642μm	$\frac{dn_e}{dT}\times10^{-6}K^{-1}$ λ=1.0642μm
298	20 19*	63 62*	8 5.2*	46 43*	3 1.4*, 3.3#	41 39*, 37#
398	27	84	10	63	4	54
498	35	107	13	78	6	68
598	42	129	16	94	7	81
698	52	155	19	110	8	94
772	59	174	22	122	9	104

(***Reported** values from (D.N., Nilkogosyan, 2003); **#Reported** values from (INRAD Data))

Table-5: Variations of Thermo Polarizability Coefficients of constituent ions of Lithium rich $LiNbO_3$ with temperatures and wavelengths

T (K)	$\frac{d\alpha_{Nb^{+5}}}{dT}$ λ=0.4545μm	$\frac{d\alpha_{O^{-2}}}{dT}$ λ=0.4545μm	$\frac{d\alpha_{Nb^{+5}}}{dT}$ λ=0.6328μm	$\frac{d\alpha_{O^{-2}}}{dT}$ λ=0.6328μm	$\frac{d\alpha_{Nb^{+5}}}{dT}$ λ=1.0642μm	$\frac{d\alpha_{O^{-2}}}{dT}$ λ=1.0642μm
298	-0.000870	0.000424	-0.000821	0.000391	-0.000827	0.000386
398	-0.000910	0.000452	-0.000869	0.000417	-0.000869	0.000407
498	-0.001043	0.000511	-0.000985	0.000465	-0.000998	0.000459
598	-0.001090	0.000502	-0.001025	0.000451	-0.001027	0.000436
698	-0.001137	0.000576	-0.001065	0.000513	-0.001055	0.000495
772	-0.001142	0.000590	-0.001075	0.000524	-0.001077	0.000507

($d\alpha/dT$ values are in units of $10^{-24} cm^3 K^{-1}$)

It is observed that:

- As wavelength increases the Polarizabilities of Nb^{5+} and O^{2-} decrease for a given temperature with the assumption that polarizability of Li^{+} is invariant to temperature and wavelength.
- As temperature increases TOC for Ordinary and Extraordinary increase.
- As wavelength increases TOC for Ordinary and Extraordinary decrease.
- For the wavelengths λ=0.4545μm, λ=0.6328μm and λ=1.0642μm, the TOC for extraordinary index shows a value which is about two times the ordinary index TOC. (L. Moretti *et al*, 2005) have also arrived at the same conclusion for wave lengths 0.632μm and 1.523μm in the temperature ranges 300K to 500K.
- The ratio of TOC's of Extra ordinary to Ordinary rays for wave lengths λ=0.4545μm, λ=0.6328μm and λ=1.0642μm are 3, 5 and 13 respectively [Table 4]. Our results compare well the findings of (G. Ghosh, 1994) and (L. Moretti *et al*, 2005) who have shown that TOC of Extraordinary Refractive Index is greater than the TOC of Ordinary Refractive Index.
- Thermo-Polarizability Coefficients of O^{2-} ions increase and Nb^{5+} ions decrease with temperature [Fig. 2].
- At a given temperature Thermo- Polarizability Coefficients of O^{2-} ions decrease and Nb^{5+} ions increase with wavelength [Fig. 2].

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