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Evaluation of Some Nonlinear Optical Parameters for Terahertz (THz) Radiating Uniaxial Crystals.

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Abstract

In this work, nonlinear optics is used to study the nonlinear optical parameters such as the electric susceptibility χ and nonlinear index coefficient n of some uniaxial crystals. Theoretical values of these parameters were computed for three uniaxial crystals for second and fourth order harmonics, namely Lithium Niobate ($LiNO_3$), Calcite ($CaCO_3$) and Rutile (TiO_2). This is because they are promising nonlinear optical crystals for THz waveguides. The values of $\chi^{(2)}$ obtained agree with the values obtained by some authors using different methods (~ 10^{-12} m/V), while the values of $\chi^{(4)}$ (~ 10^{-45} m^3/V^3) is a meaningful contribution of this work in nonlinear optics. $LiNO_3$ has the highest nonlinearity to THz radiation of 32 pm/V, while TiO_2 has the least value of 17.3 pm/V in the second order harmonics. The results also hold true for fourth order harmonics and nonlinear index coefficients. These assertions agree with most of the literatures on $LiNO_3$ as a uniaxial crystal that possesses high nonlinear – optical coefficients.

Keywords: Terahertz, Nonlinear index coefficient, Electric susceptibility and Uniaxial crystals.

1.0 Introduction

THz radiation is been generated by the use of laser beam that has very high intensity. According to [1], the laser beams induce a nonlinear polarization and produce second harmonic waves in the interior or at the surface of the medium. THz is broadly applied to sub – millimetre wave energy that fills the wavelength range between 1000 μm - 100 μm (0.001 m – 0.0001 m) corresponding to frequency range between 0.3 THz to 10 THz [2, 3, 4,]. Planken *et al* [5] described the THz region of the electromagnetic spectrum as the region between 0.1 THz and 10 THz, which has vast applications in imaging and spectroscopy. The ability of THz to penetrate packaging, similar to X – rays but without ionizing the content makes THz potentially useful for law enforcement applications such as detecting explosives and illegal drugs [6].

The field of nonlinear optics as described in [7] came into light in 1961 when it was observed that there was frequency doubling of a ruby laser upon passing through a quartz crystal. Nonlinear optics is concerned with the response of matter to intense electromagnetic field such as the one obtained from laser light, in which the matter responds in a nonlinear manner to the incident radiation fields. It is a phenomenon that occurs at high optical intensities [8]. The nonlinear response can result in intensity dependent variation of the propagation characteristics of the radiation fields that propagate at new frequencies or in new directions. Most applications of nonlinear effects and non – centrosymmetric crystals can be seen in frequency conversion processes that can be obtained in suitably designed nonlinear structures [9, 10]. Practical applications of nonlinear optical effects have risen as a direct consequence of the invention of lasers [11]. Nonlinear optics has played an increasing role in laser science, making it possible to generate coherent light more efficiently, and in spectral regions that cannot be directly accessed by laser [12].

Photonic crystals are usually considered as optical analogues of semiconductors that modify the properties of light similar to a microscopic atomic lattice that creates a semiconductor band gap for electrons. It is therefore believed that by replacing relatively slow electrons with photons as carriers of information, the speed and the bandwidth of advanced communication systems can be increased [13]. According to Baldwin [14] optics recognizes three classes of crystals;

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- The cubic crystals, which are optically isotropic, and have their refractive indices the same in all the three axes. i.e $n_x = n_y = n_z = n$.
- The uniaxial crystals, which are optically anisotropic, and have two of the refractive indices to be the same, and are different from the other one. i.e $n_x = n_y = n_o$ and $n_z = n_e$. Example of such crystals are the; trigonal, tetragonal and hexagonal lattice types.
- The biaxial crystals, which are also optically anisotropic, and have all the three refractive indices different from each one. i.e $n_x \neq n_y \neq n_z$. Example of such crystals are the; orthorhombic, monoclinic and triclinic lattice types.

In this work, the theoretical values of the nonlinear optical parameters such as the electric susceptibility and the nonlinear index coefficient were studied. Lithium Niobate ($LiNbO_3$), $CaCO_3$, and Rutile (TiO_2) were considered, since they are typically used in high power and other optical applications [15, 16]. In fact, there have been continuous requirements of NLO materials for potential applications in integrated circuits [17]. For example $LiNbO_3$ is a widely used material both in bulk and planar waveguide [18].

THEORY

The induced polarization **P** in a medium and the electric field **E** of the electromagnetic wave propagating in the medium are related by [19]

$$P = \varepsilon_0 \chi E \tag{1}$$

where χ is the dielectric susceptibility of the medium. It depends on the frequency, but independent of the field **E**. Equation (1) is valid for the field strengths of conventional source. With sufficiently intense laser radiation that THz is generated, equation (1) does not hold good, and hence needs to be generalized [20]. The polarization P induced in a medium by optical fields can be represented by a power series in the optical fields **E** [20,21,23]. The power series of equation (1) is therefore

$$P = \varepsilon_0 (\chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \chi^{(4)} E^4 + \chi^{(5)} E^5 + \chi^{(6)} E^6 \ldots) \tag{2}$$

where $\chi^{(1)}$ is the linear susceptibility, and $\chi^{(2)}$, $\chi^{(3)}$, $\chi^{(4)}$ and so on are the nonlinear susceptibilities. The fourth order susceptibility $\chi^{(4)}$ is responsible for fourth harmonic generation. A medium, which lacks inversion symmetry at the molecular level has non zero second (all even) order susceptibility [24]. Fischer *et al* [25] put it as thus "for a material to exhibit a coherent second order nonlinear optical responses, it needs to be noncentrosymmetric on macroscopic scale." However, this work is mainly concerned with the fourth order, and therefore the power series expansion of equation (2) stops at the fourth order.

The linear electric susceptibility $\chi^{(1)}$ plays a very vital role in the generation of other higher orders. The response of an electron to the optical electric field is that of anharmonic potential well. In mechanical analogy, one can consider an electron of mass *m* and charge *e* attached to the mother ion by a spring. For simplicity, electric dipoles all oriented in the same way in the direction of the field could be considered. The position of the electron varies in response to the electric field *E*(*t*) in a manner governed by the equation of motion for an oscillator [26].

$$m\left[\frac{d^2x}{dt^2} + 2\Gamma\frac{dx}{dt} + \omega_o{}^2 x - \left(ax^2 + bx^3 + \ldots.\right)\right] = eE \tag{3}$$

where *x* is the displacement from the mean position, ax^2, bx^2 and so forth are the anharmonic terms, ω_o is the resonance frequency, and Γ is the damping constant. To obtain the distance from the mean position, the anharmonic terms in equation (3) can be neglected for a while, such that equation (3) is written as

$$m\left[\frac{d^2x}{dt^2} + 2\Gamma\frac{dx}{dt} + \omega_o{}^2 x\right] = eE \tag{4}$$

If the electric field takes the form

$$E = E_o e^{i\omega t} \tag{5}$$

then, equation (4) becomes

$$\frac{d^2x}{dt^2} + 2\Gamma\frac{dx}{dt} + \omega_o{}^2 x = \frac{eE_o e^{i\omega t}}{m} \tag{6}$$

where E_o is the amplitude of the electric field in V/m. Equation (6) has a trial solution of the form [27].

$$x = x_1 e^{i\omega t} \tag{7}$$

so that from equations (6) and (7), one could get

$$x_1 = \frac{eE_o}{m\left(\omega_o^2 - \omega^2 + 2i\Gamma\omega\right)} \tag{8}$$

where x_1 in equation (8) is a complex quantity, but only its real part is physically meaningful, because according to [28], waveforms take only real values. Therefore, equation (8) should be rationalized, so that the real part takes the form

$$x_1 = \frac{eE_o\left(\omega_o^2 - \omega^2\right)}{m\left\{\left(\omega_o^2 - \omega^2\right)^2 - 4\omega^2\Gamma^2\right\}} \tag{9}$$

For $\left(\omega_o^2 - \omega^2\right) >> 4\omega^2\Gamma^2$ and $\omega_o^2 - \omega^2 \equiv \omega^2$, equation (9) becomes

$$x_1 = \frac{eE_o}{m\omega^2} \tag{10}$$

The dipole moment of a dipole is the product of either of the charges (in magnitude) making up the dipole and the charge separation *x*. That is, the dipole moment is

$$p = ex_1 \tag{11}$$

while the polarization P is defined as

$$P = Nex_1 \tag{12}$$

where N (≡ Avogadro's number × the molecular weight of a crystal). From equations (10) and (12), the polarization can be written as

$$P = \frac{Ne^2 E_o}{m\omega^2} \tag{13}$$

One can express the linear dependence of the polarization *P* on the field *E* in terms of the linear susceptibility $\chi^{(1)}$ as [19]

$$P = = \varepsilon_o \chi^{(1)} E_o \tag{14}$$

where ε_o is the permittivity of free space in F/m, such that from equations (13) and (14), $\chi^{(1)}$ is given as

$$\chi^{(1)} = \frac{Ne^2}{\varepsilon_o m\omega^2} \tag{15}$$

Equation (15) defines the linear electric susceptibility in terms of the molecular weight and the frequency of the incident radiation, and is a dimensionless quantity.

METHODOLOGY

To obtain the desired result, the nonlinear electric susceptibilities were generated using an electron of mass *m* and charge *e* attached to the mother ion by a spring. For simplicity, we considered electric dipoles all oriented in the same way in the direction of the field. The nonlinear index coefficients were generated using the Dirac delta form for linear and nonlinear polarizations, and the relationships between the nonlinear index coefficient with dielectric constant and nonlinear electric susceptibilities.

(a) Generation of nonlinear electric susceptibilities

The electric susceptibility χ of a material describes the measure of the materials sensitivity or response to external interference [20]. To generate the second order nonlinear electric susceptibility, the anharmonic terms in equation (3) should be considered. This entails knowing the coefficients, *a*, *b*, e.t.c. For $\chi^{(2)}$, it is the first anharmonic term that is considered, so that the equation of motion becomes [30].

$$\frac{d^2x}{dt^2} + 2\Gamma\frac{dx}{dt} + \omega_o{}^2 x - ax^2 = \frac{eE_o}{m} \tag{16}$$

According to [31], the response of an oscillator can be analyzed by expanding the displacement *x* in components as in [31]

$$x = x_1 + x_2 + x_3 + \ldots \tag{17}$$

If, one considers only $x = x_1 + x_2$, from equations (16) and (17), one obtains three equations after rearranging,

$$\frac{d^2x_1}{dt^2} + 2\Gamma\frac{dx_1}{dt} + \omega_o{}^2 x_1 = \frac{eE_o}{m} \tag{18a}$$

$$\frac{d^2x_2}{dt^2} + 2\Gamma\frac{dx_2}{dt} + \omega_o^2 x_2 - a(x_1)^2 = 0 \tag{18b}$$

$$2x_1x_2 + x_2^2 = 0 \tag{18c}$$

Equation (18b) is the relevant expression for second order harmonics, since it gives the second order equation of motion [30]. Substituting equation (18b) and the expression for $a = \omega^2$ from equation (A.9), yields

$$\frac{d^2x}{dt^2} + 2\Gamma\frac{dx}{dt} + \omega_o^2 x_2 = \frac{e^2E_o^2}{m^2\omega^2} \tag{19}$$

A solution of the homogeneous version of equation (19) can be added to it and the total will still be a solution of equation (19). If the trial solution of equation (19) is

$$x_2 = x_{20}e^{i\omega t} \tag{20}$$

then, from equations (19) and (20), we obtained

$$x_{20} = \frac{e^2E_o^2}{m^2\omega^2\left(\omega_o^2 - \omega^2 + 2i\Gamma\omega\right)} \tag{21}$$

Using the same conditions as is equations (8) and (9), equation (21) becomes

$$x_{20} = \frac{e^2E_o^2}{m^2\omega^4} \tag{22}$$

Recall that the corresponding power series expansion of the second order polarization $P^{(2)}(t)$ is written in terms of the electric field as

$$P^{(2)}(t) = = \varepsilon_o\chi^{(2)}E_o^2 \tag{23}$$

Similarly, $P^{(2)}(t)$ can be written in terms of x_{20} as

$$P = Nex_{20} = \frac{Ne^3E_o^2}{m^2\omega^4} \tag{24}$$

Comparing equations (23) and (24), one obtains the second order nonlinear electric susceptibility as

$$\chi^{(2)} = \frac{Ne^3}{\varepsilon_o m^2\omega^4} \text{ (in m/V)} \tag{25}$$

The fourth order nonlinear electric susceptibility is the susceptibility that is associated with fourth order harmonic generation. To generate it, one has to start solving the equation of motion associated with the third order equation of motion given as [31]

$$\frac{d^2x_3}{dt^2} + 2\Gamma\frac{dx_3}{dt} + \omega_o^2 x_3 - ax_1x_2 - b(x_1)^3 = 0 \tag{26}$$

where from equation (A.9), $a = b = \omega^2$;

$$x_1 = \frac{eE_o}{m\omega^2} \text{ and } x_2 = \frac{e^2E_o^2}{m^2\omega^4} \tag{27}$$

Substituting equations (27) in (26) and rearranging, yields

$$\frac{d^2x_3}{dt^2} + 2\Gamma\frac{dx_3}{dt} + \omega_o^2 x_3 = \frac{e^3E_o^3}{m^3\omega^4} + \frac{e^3E_o^3}{m^3\omega^6} = \frac{e^3E_o^3}{m^3\omega^4}\left(\frac{\omega^2+1}{\omega^2}\right) \tag{28}$$

In equation (28), for $\omega^2 >> 1$,

$$\frac{d^2x_3}{dt^2} + 2\Gamma\frac{dx_3}{dt} + \omega_o^2 x_3 = \frac{e^3E_o^3}{m^3\omega^4} \tag{29}$$

A solution of the homogeneous version of equation (29) can be added to it and the total will still be a solution of (29), such that

$$x_{30} = \frac{e^3E_o^3}{m^3\omega^4\left(\omega_o^2 - \omega^2 + 2i\Gamma\omega\right)} = \frac{e^3E_o^3\left(\omega_o^2 - \omega^2\right)}{m^3\omega^4\left(\omega_o^2 - \omega^2\right)^2} \tag{30}$$

for $\omega_o^2 - \omega^2 \approx \omega^2$, equation (30) becomes

$$x_{30} = \frac{e^3E_o^3}{m^3\omega^6} \tag{31}$$

Equation (26) can be written for the fourth order as

$$\frac{d^2x_4}{dt^2} + 2\Gamma\frac{dx_4}{dt} + \omega_o^2 x_4 - ax_1x_3 - c\left(x_1\right)^4 = 0 \tag{32}$$

where a = c = ω^2. Thus,

$$x_1 = \frac{eE_o}{m\omega^2} \text{ and } x_3 = \frac{e^3E_o^3}{m^3\omega^6} \tag{33}$$

Substituting equations (33) in (32) and rearranging, yields

$$\frac{d^2x_4}{dt^2} + 2\Gamma\frac{dx_4}{dt} + \omega_o^2 x_4 = \frac{e^4E_o^4}{m^4\omega^6} + \frac{e^4E_o^4}{m^4\omega^{14}} = \frac{e^4E_o^4}{m^4\omega^6}\left(\frac{\omega^8+1}{\omega^8}\right) \tag{34}$$

In equation (34), for $\omega^8 >> 1$

$$\frac{d^2x_4}{dt^2} + 2\Gamma\frac{dx_4}{dt} + \omega_o^2 x_4 = \frac{e^4E_o^4}{m^4\omega^6} \tag{35}$$

A solution of the homogeneous version of equation (35) can be added to it and the total will still be a solution of (35), such that

$$x_{40} = \frac{e^4E_o^4}{m^4\omega^6\left(\omega_o^2 - \omega^2 + 2i\Gamma\omega\right)} = \frac{e^4E_o^4\left(\omega_o^2 - \omega^2\right)}{m^4\omega^6\left(\omega_o^2 - \omega^2\right)^2} \tag{36}$$

for $\omega_o^2 - \omega^2 \approx \omega^2$, equation (36) becomes

$$x_{40} = \frac{e^4E_o^4}{m^4\omega^8} \tag{37}$$

Recall that the corresponding power series expansion for the fourth order polarization $P^{(4)}(t)$ is written in terms of the electric field as

$$P^{(4)}(t) = = \varepsilon_o\chi^{(4)}E_o^4 \tag{38}$$

Similarly, $P^{(4)}(t)$ can be written in terms of x_{40} as

$$P = Nex_{40} = \frac{Ne^5E_o^4}{m^4\omega^8} \tag{39}$$

Comparing equations (38) and (39), one obtains

$$\chi^{(4)} = \frac{Ne^5}{\varepsilon_o m^4\omega^8} \text{ (in } \mathrm{m^3/V^3}) \tag{40}$$

Equation (40) is the fourth order nonlinear electric susceptibility.

(b) Generation of nonlinear index Coefficients

For uniaxial crystals, two refractive indices are possible, probably for each transparent wave length. They are the refractive indices associated with the ordinary axis given as $n_o = n_x = n_y$, and the refractive index associated with the extraordinary axis, $n_e = n_z$. These set of refractive indices are dimensionless. The nonlinear index coefficients, on the other hand are the indices that accompany the corresponding nonlinear susceptibilities, and hence they carry the same units as their respective susceptibilities. The relationship between the induced polarization **P** and the electric field **E** is given as

$$P = \varepsilon_o(\chi^{(1)}\, E + \chi^{(2)}.EE + \chi^{(3)}EEE + \chi^{(4)}EEEE + \ldots) \tag{41}$$

where $\chi^{(j)}$ (j = 1,2,3,4,. . .) is the jth order susceptibility. To account for light polarization effects, $\chi^{(j)}$ should be a tensor of rank j +1. The effects are induced through the refractive index n, and the attenuation coefficient α [32]. Media such as anisotropic crystals posses even j, and are said to lack symmetry, while those with odd j are applicable in optical fibres [31, 32, 33]. However, the class of crystals that lack symmetry are of interest in this work.

The physical meaning of equation (41) is that at lower intensity of electromagnetic fields, P is linear, but becomes nonlinear when the fields are of higher intensity. The induced polarization vector can hence be written as

$$P = P_L(r,t) + P_{NL}(r,t) \tag{42}$$

where P_L denotes the linear part, while P_{NL} is the nonlinear part (that corresponds to only even orders). P_L and P_{NL} are expressed as [32]

$$P_L(r,t) = \varepsilon_o \int_{-\infty}^{\infty} \chi^{(1)}(t-t').E(r,t')dt \tag{43}$$

$$\begin{aligned} P_{NL}(r,t) &= \varepsilon_o \int \int_{-\infty}^{\infty} \chi^{(2)}(t-t_1, t-t_2)E(r,t_1)E(r,t_2)dt_1dt_2 \\ &+ \varepsilon_o \int\int\int \int_{-\infty}^{\infty} \chi^{(4)}(t-t_1, t-t_2, t-t_3, t-t_4)E(r,t_1)E(t,t_2)E(r.t_3)E(r,t_4) \\ &\times dt_1dt_2dt_3dt_3 \end{aligned} \tag{44}$$

Equation (44) is the nonlinear polarization associated with second and fourth order nonlinear susceptibilities. According to Usman [33], equation (34) can be written in terms of Dirac delta function as

$$\begin{aligned} P_{NL}(r,t) &= \varepsilon_o \int \int_{-\infty}^{\infty} \chi^{(2)}(t-t_1, t-t_2)E(r,t_1)E(r,t_2)\delta(t-t_1)\delta(t-t_2)dt_1dt_2 \\ &+ \varepsilon_o \int\int\int \int_{-\infty}^{\infty} \chi^{(4)}(t-t_1, t-t_2, t-t_3, t-t_4)E(r,t_1)E(r,t_2)E(r,t_3)E(r,t_4) \\ &\times \delta(t-t_1)\delta(t-t_2)\delta(t-t_3)\delta(t-t_4)dt_1dt_2dt_3dt_4 \\ &= \varepsilon_o\chi^{(2)}E(r,t)E(r,t) + \varepsilon_o\chi^{(4)}E(r,t)E(r,t)E(r,t)E(r,t) \end{aligned} \tag{45}$$

The total dielectric constant is also given as

$$\varepsilon_T = \varepsilon_L + \varepsilon_{NL} \tag{46}$$

where ε_{NL} is the nonlinear dielectric constant. Syms and Cozens [34] defined the linear dielectric constant ε_L as

$$\varepsilon_L = 1 + \chi^{(1)} \tag{47}$$

Timtere *et al* [35] obtained the series of even order nonlinear susceptibility in terms of increasing order as

$$\bar{\chi}(\omega, E) = \chi^{(1)} + \ldots + \frac{(n-1)!2^{-n}}{\left(\frac{n-2}{2}\right)!\left(\frac{n}{2}\right)!}\chi^{(n)}|E|^{n-1} \tag{48}$$

From equation (48), one obtains the coefficient involving the second and the fourth order nonlinear susceptibilities (n = 2 and 4) as thus [35]

$$\bar{\chi}(\omega, E) = \chi^{(1)} + \frac{1}{4}\chi^{(2)}|E| + \frac{3}{16}\chi^{(4)}|E|^3 \tag{49}$$

From equations (46), (47) and (49), one obtains

$$\varepsilon_T = 1 + \chi^{(1)} + \frac{1}{4}\chi^{(2)}|E| + \frac{3}{16}\chi^{(4)}|E|^3 \qquad (50)$$

But from [31] and [36], the expression for the intensity dependent refractive index resulting from the contribution of $\chi^{(3)}$ is given as

$$\bar{n}(\omega, E) = n_0(\omega) + n_2|E|^2 \qquad (51)$$

where $n_0(\omega)$ is the linear refractive index, n_2 is the nonlinear index coefficient related to $\chi^{(3)}$. This intensity dependent refractive index can be extended to $\chi^{(2)}$ and $\chi^{(4)}$, as thus

$$\bar{n}(\omega, E) = n_0(\omega) + n_1|E| + n_3|E|^3 \qquad (52)$$

where n_1 is the second order nonlinear index coefficient and n_3 is the fourth order nonlinear index coefficient associated with $\chi^{(2)}$ and $\chi^{(4)}$ respectively. The total dielectric constant can equally be written in terms of the nonlinear index coefficient as

$$\begin{aligned}\varepsilon_T &= \left[\bar{n}(\omega)\right]^2 \\ &= n_0^2 + 2n_0n_1|E| + 2n_on_3|E|^3 + 2n_1n_3|E|^4 + n_1^2|E|^2 + n_3^2|E|^6 \\ &\cong n_0^2 + 2n_0n_1|E| + 2n_on_3|E|^3 \qquad (53)\end{aligned}$$

In equation (53), what are of interest are n_0, n_1, and n_3. Using equations (53) and (50), for comparison, gives

$$2n_0n_1 = \frac{1}{4}\chi^{(2)} \quad \text{and} \quad 2n_on_3 = \frac{3}{16}\chi^{(4)} \qquad (54\text{a})$$

or

$$n_1 = \frac{1}{8n_0}\chi^{(2)} \quad \text{and} \quad n_3 = \frac{3}{32n_o}\chi^{(4)} \qquad (54\text{b})$$

where n_o is the linear refractive index in the ordinary axis. Using equation (25), n_1 can be written in terms of frequency as

$$n_1 = \frac{1}{8n_o}\left\{\frac{Ne^3}{\varepsilon_o m^2\omega^4}\right\} \qquad (55)$$

while using equation (40), n_3 can be written in terms of the frequency as

$$n_3 = \frac{3}{32n_o}\left\{\frac{Ne^5}{\varepsilon_o m^4\omega^8}\right\} \qquad (56)$$

Equation (55) gives the second order nonlinear index coefficient, while equation (56) gives the fourth order nonlinear index coefficient.

Results and Discussion

The theoretical values of $\chi^{(2)}$, $\chi^{(4)}$, n_1 and n_3 for some uniaxial crystals notability $LiNbO_3$, $CaCO_3$ and TiO_2 were evaluated using equations (25) , (40), (55) and (56).

Table 1. Values of second and fourth order nonlinear susceptibilities and index coefficients for $LiNbO_3$ (Lithium Niobate; molecular weight = 147.85g (Here, $\omega = 2\pi\upsilon$ has been used)

Frequency (THz)	$\chi^{(2)} \times 10^{-12}$ **(m/V)**	$\chi^{(4)} \times 10^{-44}$ **(m^3/V^3)**	$n_1 \times 10^{-13}$ **(m/V)**	$n_3 \times 10^{-45}$ **(m^3/V^3)**
1.0	32.0	63700	17.5	8730
1.5	6.33	2490	3.46	341
2.0	2.00	249	1.10	34.1
2.5	0.82	41.8	0.449	5.72
3.0	0.396	9.71	0.216	1.33
3.5	0.214	2.83	0.117	0.388
4.0	0.125	0.972	0.0685	0.133
4.5	0.0782	0.379	0.0425	0.0519
5.0	0.0513	0.163	0.0280	0.0223
5.5	0.0350	0.0761	0.0192	0.0104
6.0	0.0247	0.0379	0.0135	0.00520
6.5	0.0180	0.0200	0.00982	0.00274
7.0	0.0133	0.0111	0.00730	0.00151
7.5	0.0101	0.00636	0.00554	0.000872
8.0	0.00782	0.00380	0.00428	0.000520
8.5	0.00614	0.00234	0.00336	0.000320
9.0	0.00488	0.00148	0.00267	0.000203
9.5	0.00393	0.000960	0.00215	0.000132
10.0	0.00320	0.000637	0.00175	0.0000873

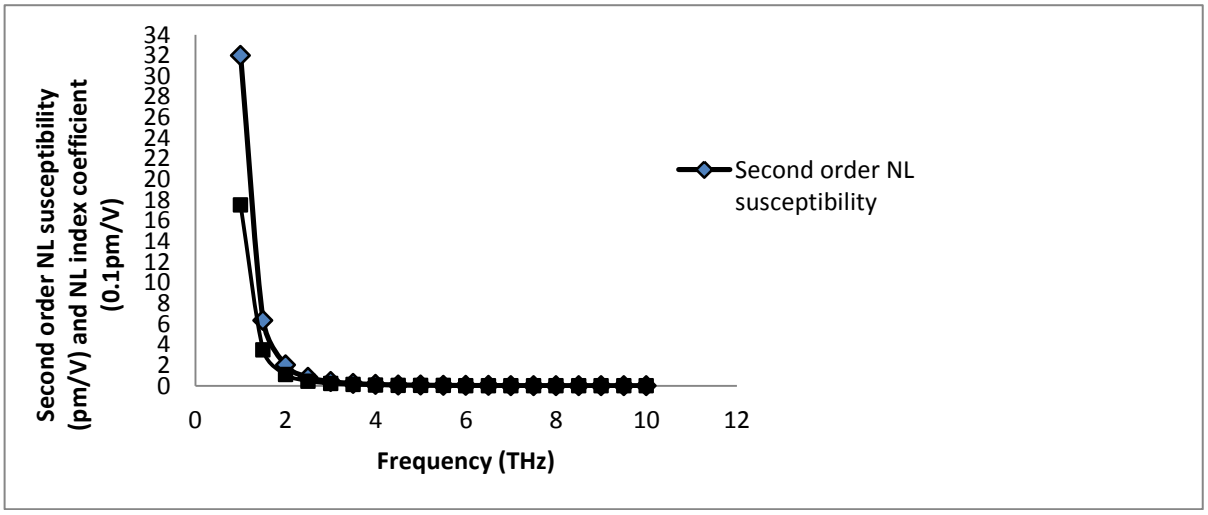

Fig.1 Graph of $\chi^{(2)}(\mathrm{pm/V})$ and n_1 (0.1pm/V) vs Frequency (THz) for $LiNbO_3$.

Table 2. Values of second and fourth order nonlinear susceptibilities and index coefficients for $CaCO_3$ (Calcite; Molecular weight = 100.09g)

Frequency (THz)	$\chi^{(2)} \times 10^{-12}$ **(m/V)**	$\chi^{(4)} \times 10^{-44}$ **(m^3/V^3)**	$n_1 \times 10^{-13}$ **(m/V)**	$n_3 \times 10^{-45}$ **(m^3/V^3)**
1.0	21.7	43100	16.4	8110
1.5	4.29	1680	3.23	316
2.0	1.36	168	1.02	31.7
2.5	0.555	28.3	0.419	5.31
3.0	0.268	6.57	0.202	1.24
3.5	0.145	1.92	0.109	0.36
4.0	0.0847	0.658	0.0639	0.124
4.5	0.0529	0.257	0.0399	0.0482
5.0	0.0347	0.110	0.0262	0.0208
5.5	0.0237	0.0515	0.0179	0.00968
6.0	0.0167	0.0257	0.0126	0.00483
6.5	0.0122	0.0135	0.00916	0.00254
7.0	0.00904	0.00748	0.00681	0.00141
7.5	0.00686	0.00431	0.00517	0.000810
8.0	0.00530	0.00257	0.00399	0.000483
8.5	0.00416	0.00158	0.00313	0.000298
9.0	0.00331	0.00100	0.00249	0.000188
9.5	0.00266	0.00065	0.00201	0.000122
10.0	0.00217	0.000431	0.00164	0.0000811

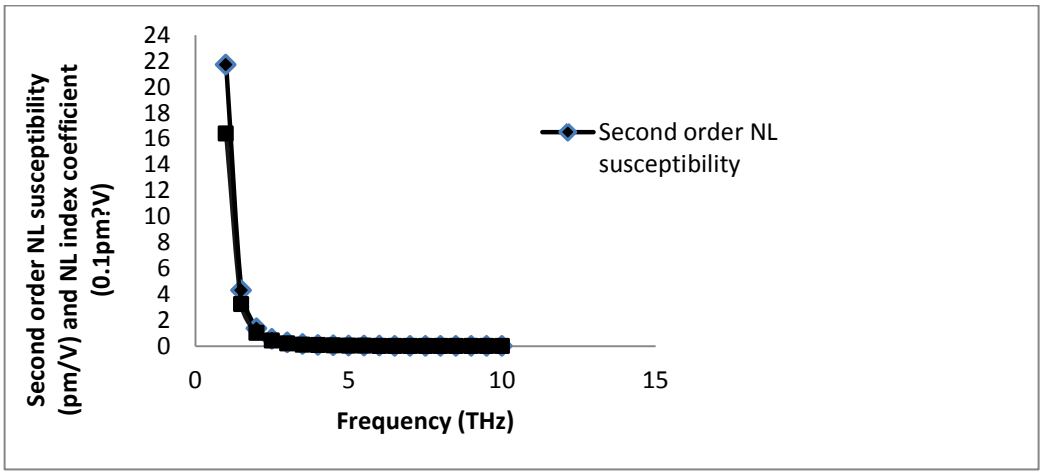

Fig. 2 Graph of $\chi^{(2)}(\mathrm{pm/V})$ and n_1 (0.1pm/V) vs Frequency (THz) for $CaCO_3$

Table 3. Values of second and fourth order nonlinear susceptibilities and index coefficients for TiO_2 (Rutile; Molecular weight = 79.90g)

Frequency (THz)	$\chi^{(2)} \times 10^{-12}$ **(m/V)**	$\chi^{(4)} \times 10^{-44}$ **(m^3/V^3)**	$n_1 \times 10^{-13}$ **(m/V)**	$n_3 \times 10^{-45}$ **(m^3/V^3)**
1.0	17.3	34400	8.28	4100
1.5	3.42	1340	1.64	160
2.0	1.08	135	0.517	16.0
2.5	0.443	22.6	0.212	2.69
3.0	0.214	5.25	0.102	0.625
3.5	0.115	1.53	0.0552	0.182
4.0	0.0677	0.525	0.0323	0.0625
4.5	0.0422	0.205	0.0202	0.0244
5.0	0.0277	0.0881	0.0132	0.0105
5.5	0.0189	0.0411	0.00905	0.00489
6.0	0.0134	0.0205	0.00639	0.00244
6.5	0.0097	0.0108	0.00464	0.00129
7.0	0.00721	0.00597	0.00345	0.000711
7.5	0.00547	0.00344	0.00262	0.000409
8.0	0.00423	0.00205	0.00202	0.000244
8.5	0.00332	0.00126	0.00159	0.000150
9.0	0.00264	0.00080	0.00126	0.0000952
9.5	0.00213	0.000519	0.00102	0.0000618
10.0	0.00173	0.000344	0.000828	0.0000410

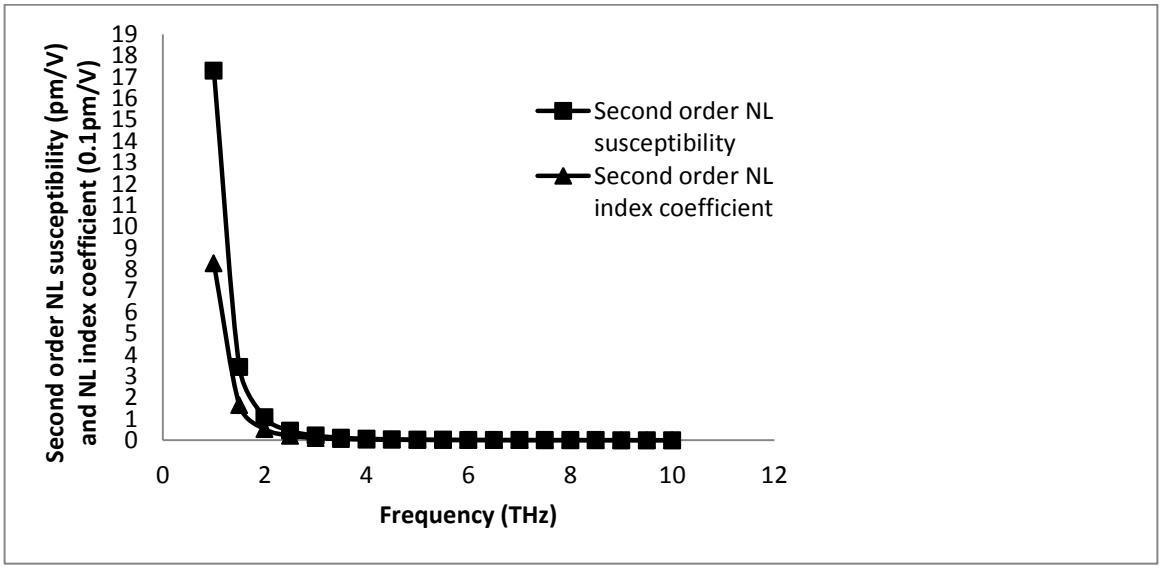

Fig. 3 Graph of $\chi^{(2)}(\text{pm/V})$ and n_1 (0.1pm/V) vs Frequency (THz) for TiO_2

From Tables 1 – 3, the values of $\chi^{(2)}$ and $\chi^{(4)}$ for the three crystals decrease with increase in THz frequency, so also are the values of n_1 and n_3. From Tables 1 – 3, $LiNbO_3$ shows higher nonlinearity to THz radiation of 32 pm/V, followed by $CaCO_3$ of 21.7 pm/V and then TiO_2 of 17.3 pm/V, in the second order harmonics, and 63700 x 10^{-44} m^3/V^3, 43100 x 10^{-44} m^3/V^3 and 34400 x 10^{-44} m^3/V^3 respectively in the fourth order harmonics. Similarly, $LiNbO_3$ has the highest nonlinearity index coefficient in both the second and the fourth order harmonics of n_1 = 1.75 pm/V and n_3 = 8730 x 10^{-45} m^3/V^3

respectively, $CaCO_3$ is next with n_1 = 1.65 pm/V and n_3 = 8110 x 10^{-45} m^3/V^3, then TiO_2 with n_1 = 0.828 pm/V and n_3 = 4100 x 10^{-45} m^3/V^3. These values are higher in $LiNbO_3$ with the highest atomic weight (147.85), then $CaCO_3$ (100.09) and then TiO_2 (79.90). The theoretical values of $\chi^{(2)}$ calculated in this work compare favourably with the ones obtained for Potassium Dihydrogen Phosphate (KDP) ~ 8.8 x 10^{-12} m/V by [37] using stabilized Michelson interferometer. This invariably means that the values of nonlinear electric susceptibilities and nonlinear index coefficients are functions of molecular weight or the composition of the crystal. Any addition of impurity to such crystals might definitely affect these values and can easily be detected. This agrees with the assertion of [38] that introduction of impurity substantially changes the absolute value of the refractive index and the birefringence of a crystal.

Similarly, from Tables 1 – 3, the values of these nonlinear optical parameters decrease drastically as the order of the nonlinearity increases. This could be the reason that most researchers easily ignored higher order effects. This should not be so, since any significant change in these values is an indication of tempering with the composition of the crystal under study. Similarly, at very high field intensity, $\chi^{(4)}$ gives correct description of the physics when the material guides the THz pulse. At this point, the pulse duration is small.

Conclusion

From Figures 1 – 3, $LiNbO_3$ is a better nonlinear optical crystal than $CaCO_3$ and TiO_2, and could therefore be a good material as a waveguide for THz propagation. This is in agreement with [39] that described $LiNbO_2$ as a nonlinear optical crystal with higher second order susceptibility. Similarly, the variation of these nonlinear optical parameters approach zero at higher THz frequencies. This shows that the response of these uniaxial crystals to THz radiation is much more pronounced at lower frequencies than higher frequencies. There is also a good agreement between the plots of nonlinear susceptibilities with THz frequency. For example, in [37], it was observed that nonlinear susceptibility responsible for quadratic electro – optic effect in uniaxial crystals is due mainly to nonlinear interactions of the low frequency electric field with the crystal lattice.

Appendix A

To obtain the anharmonic terms in equation (3), one can consider the Lorentz oscillator model in which the restoring force is associated with the potential energy. The elastic restoring force is thus [39];

$$F = -\frac{dV}{dx} = -m\omega_0^2 x \tag{A.1}$$

The potential energy as defined by [31] is given as

$$V(x) = \frac{1}{2} m\omega_0^2 x^2 \tag{A.2}$$

The effective potential energy for the systems can be written more realistically in many cases as a power series in which equation A.1 is the first term

$$V(x) = \frac{1}{2} m\omega_0^2 x_0^2 + amx^3 + bmx^4 + \ldots \tag{A.3}$$

Using Taylor's series

$$V(x) = V(0) + x\left(\frac{dV}{dx}\right)_{x=0} + \frac{1}{2!}x^2\left(\frac{d^2V}{dx^2}\right)_{x=0} + \frac{1}{3!}x^3\left(\frac{d^3V}{dx^3}\right)_{x=0} + \ldots \tag{A.4}$$

about the equilibrium position, where x = 0, V(0) is the additive constant in the total energy. Since it does not give rise to any force and hence can be neglected. Similarly, at a point of stable equilibrium, there is no force, and therefore

$$\frac{dV}{dx} = 0 \tag{A.5}$$

Thus:

$$V(x) = \frac{1}{2!}x^2\left(\frac{d^2V}{dx^2}\right)_{x=0} + \frac{1}{3!}x^3\left(\frac{d^3V}{dx^3}\right)_{x=0} + \ldots \tag{A.6}$$

The first two terms in (A.6) correspond to those in (A.3), and one can identify all the terms in (A.3) by considering more and more terms in the Taylor's series for V*(x)*. Therefore,

$$F = -\frac{dV}{dx} = -m\omega_0^2 x - 3amx^2 - 4bmx^3 - \ldots \tag{A.8}$$

If this equation is substituted in the equation of motion of an oscillator, the equation becomes a nonlinear differential equation for *x*, because *x* enters in powers other than the first. Such nonlinear equations produced the anharmonic terms in equation (3), and are generally impossible to be treated. The nonlinearities represented by the terms in equation (3) are determined from A.3 and A.6, where

$$a = b = c = \omega^2 \tag{A.9}$$

Equation (A.9) has been used in equations (26) and (33).

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