CHAPTER 2

THEORETICAL ANALYSIS OF NONLINEAR OPTICAL PROPERTIES OF \( \text{La}_2\text{CaB}_{10}\text{O}_{19} \) CRYSTAL

2.1 INTRODUCTION TO NONLINEAR OPTICS

The interaction of light with matter is usually characterized by several phenomena, such as light absorption, refraction, scattering and luminescence etc. All of these were regarded as properties of the material with wavelength dependence, but independent of the light intensity. However, the high intensity lasers can alter the optical properties of matter. Thus the characteristic optical properties of a material become a function of intensity. The study of such interaction of a material system in the presence of high intense electromagnetic field is the field of nonlinear optics (NLO). Typically, only laser light is sufficiently intense to modify the optical properties of a material system (Robert Boyd 1992). The discovery of second-harmonic generation (SHG) (Franken et al 1961) led to the development of many nonlinear optical concepts.

Development in nonlinear optics took place dramatically, especially during the last decade due to the advancement of both experimental techniques and evolution of molecular modelling and quantum chemical theoretical procedures. Molecules with large optical nonlinearities have extensively been studied due to their potential applications in the area of material science and various photonic technologies like, optical switching, data processing and optical communication. NLO also takes a primary part in modern technology involving lasers, sensors, interferometers, memory chips,
detectors, electrical devices and optical components. Frequency conversion is one of the important and popular techniques to extend the useful wavelength range of laboratory laser.

2.2 THEORETICAL EXPLANATION OF NONLINEAR OPTICS

When a beam of electromagnetic radiation propagates through a solid, the nuclei and associated electrons of the atoms form electric dipoles. The electromagnetic radiation interacts with these dipoles causing them to oscillate, which by the classical laws of electromagnetism, results in the dipoles themselves acting as sources of electromagnetic radiation. If the amplitude of vibration is small, the dipoles emit radiation of the same frequency as the incident radiation. As the intensity of the incident radiation increases, the relationship between irradiance and amplitude of vibration becomes nonlinear resulting in the generation of harmonics in the frequency of radiation emitted by the oscillating dipoles. Thus frequency doubling or second harmonic generation and indeed higher order frequency effects occur as the incident intensity is increased.

In a nonlinear medium the induced polarization is a nonlinear function of the applied field. A medium exhibiting SHG is a crystal composed of molecules with asymmetric charge distributions arranged in the crystal in such a way that a polar orientation is maintained throughout the crystal. At very low fields, the induced polarization is directly proportional to the electric field (Nalwa and Miyata 1996).

\[ P = \varepsilon_o \chi E \]  

(2.1)

where \( \chi \) is the linear susceptibility of the material, \( E \) is the electric field vector, \( \varepsilon_o \) is the permittivity of free space. At high fields, polarization
becomes independent of the field and the susceptibility becomes field dependent. Therefore, this nonlinear response is expressed by writing the induced polarization as a power series in the field.

\[
P = \varepsilon_0 \left( \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \ldots \right)
\]

(2.2)

where \( \chi^{(2)}, \chi^{(3)} \ldots \) are the nonlinear susceptibility of the medium. \( \chi^{(1)} \) is the linear term responsible for material’s linear optical properties like, refractive index, dispersion, birefringence and absorption. \( \chi^{(2)} \) is the quadratic term which describes second harmonic generation in non-centrosymmetric materials. \( \chi^{(3)} \) is the cubic term responsible for third harmonic generation, stimulated Raman scattering, phase conjugation and optical bistability. Hence the induced polarization is capable of multiplying the fundamental frequency to second, third and even higher harmonics. The coefficients of \( \chi^{(1)}, \chi^{(2)} \) and \( \chi^{(3)} \) give rise to certain optical effects, which are listed in Table 2.1.

If the molecule or crystal is centro-symmetric then \( \chi^{(2)} = 0 \). If a field \( +E \) is applied to the molecule (or medium), Equation (2.2) predicts that the polarization induced by the first nonlinear term is predicted to be \( +E^2 \), yet if the medium is centro-symmetric the polarization should be \( -E^2 \). This contradiction can only be resolved if \( \chi^{(2)} = 0 \) in centro-symmetric media. If the same argument is used for the next higher order term, \( + E \) produces polarization \( +E^3 \) and \( -E \) produces \( -E^3 \), so that \( \chi^{(3)} \) is the first non-zero nonlinear term in centro-symmetric media. In second harmonic generation, the two input wavelengths have the same frequency i.e. \( 2\omega_1 = \omega_2 \) or \( (\lambda_1 = 2\lambda_2) \). During this process, a polarization wave at the second harmonic frequency \( 2\omega_1 \) is produced. The refractive index, \( n_1 \) is defined by the phase velocity and wavelength of the medium. The energy of the polarization wave is transferred to the electromagnetic wave at a frequency \( \omega_2 \).
Table 2.1 Optical effects of nonlinear optical materials

<table>
<thead>
<tr>
<th>Order</th>
<th>Coefficient</th>
<th>Effects</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>$\chi^{(1)}$</td>
<td>Refraction</td>
<td>Optical fibers</td>
</tr>
<tr>
<td>2.</td>
<td>$\chi^{(2)}$</td>
<td>SHG ($\omega+\omega = 2\omega$) Frequency mixing ($\omega_1 \pm \omega_2 = \omega_3$) Pockel’s effect ($\omega + 0 = \omega$)</td>
<td>Frequency doubling Optical parametric oscillations Electro-optical modulators</td>
</tr>
<tr>
<td>3.</td>
<td>$\chi^{(3)}$</td>
<td>4 wave mixing Gratings Kerr effect Optical amplitude</td>
<td>Raman coherent spectroscopy Real time holography Ultra high speed optical gates Amplifiers, choppers etc.</td>
</tr>
</tbody>
</table>

The phase velocity and wavelength of this electromagnetic wave are determined by $n_2$, the refractive index of the doubled frequency. To obtain high conversion efficiency, the phase vectors of input beams and generated beams are to be matched.

$$\Delta k = 4\pi \frac{(n_1 - n_2)}{\lambda} = 0$$  \hspace{1cm} (2.3)

where $\Delta K$ represents the phase-mismatch (Myoungsik 2004). The phase matching can be obtained by angle tilting, temperature tuning and so on. In general, longer crystal, large nonlinear coefficients and zero phase mismatching will result in higher conversion efficiency. Also, the input power density has to be lower than the damage threshold of the crystal.

2.3 NONLINEAR OPTICAL PROCESSES AND ITS APPLICATIONS

Nonlinear optics gives rise to a host of optical phenomena and following are some of the important nonlinear optical processes those exclusively involved with frequency mixing.
A. Second harmonic generation (SHG)
B. Third harmonic generation (THG)
C. High harmonic generation (HHG)
D. Sum frequency generation (SFG)
E. Difference frequency generation (DFG)
F. Optical parametric amplification (OPA)
G. Optical parametric oscillation (OPO)
H. Optical parametric generation (OPG)
I. Spontaneous parametric down conversion (SPDC)
J. Optical rectification (OR)

Not all wavelength regions of interest are directly accessible with lasers. Therefore, it is common e.g. to generate visible light by nonlinear conversion of infrared light from one or several lasers.

2.4 BIREFERENCENT CRYSTALS

Birefringence, or double refraction, is the decomposition of a ray of light (or electromagnetic radiation) into two rays (the ordinary ray and the extraordinary ray) when it passes through certain types of material, such as calcite crystals or boron nitride, depending on the polarization of the light. This effect can occur only if the structure of the material is anisotropic (directionally dependent). If the material has a single axis of anisotropy or optical axis (i.e. it is uniaxial) birefringence can be formalized by assigning two different refractive indices to the material for different polarizations. The birefringence magnitude is then defined by,

\[ \Delta n = n_e - n_o \] (2.4)
where $n_e$ and $n_o$ are the refractive indices for polarizations parallel (extraordinary) and perpendicular (ordinary) to the axis of anisotropy respectively. The reason for birefringence is the fact that in anisotropic media the electric field vector $\vec{E}$ and the dielectric displacement $\vec{D}$ can be nonparallel (namely for the extraordinary polarisation), although being linearly related. Generally there are two types of birefringent crystals and they are: 1. uniaxial crystals and 2. biaxial crystals.

### 2.4.1 Uniaxial Crystals

In uniaxial crystals a special direction exists called the optic axis (Z axis). The plane containing the Z axis and the wave vector $k$ of the light wave is termed the principal plane. The light beam whose polarization (i.e., the direction of the vector $E$ oscillations) is normal to the principal plane is called an ordinary beam or an o-beam. The beam polarized in the principal plane is known as an extraordinary beam or e-beam. The refractive index of the o-beam does not depend on the propagation direction, whereas for the e-beam it does. Thus, the refractive index in anisotropic crystals generally depends both on light polarization and propagating direction.

The value of $\Delta n$ is equal to zero along the optic axis $Z$ and reaches a maximum in the direction normal to this axis. The refractive indices of the ordinary and extraordinary beams in the plane normal to the Z axis are termed the principal values of the refractive index and are denoted by $n_o$ and $n_e$, respectively.

The dependence of the refractive index on light propagation direction inside the uniaxial crystal (index surface) is a combination of a sphere with radius $n_o$ (for an ordinary beam) and an ellipsoid of rotation with semiaxes $n_o$ and $n_e$ (for an extraordinary beam, the axis of the ellipsoid of
rotation is the Z axis). In the Z axis direction the sphere and ellipsoid are in contact with each other. In a negative crystal the ellipsoid is inscribed in the sphere (Figure 2.1(a)), whereas in a positive crystal the sphere is inscribed in the ellipsoid (Figure 2.1(b)).

Uniaxial birefringent materials are classified as positively (or negatively) birefringent when, for light directed perpendicularly to the optic axis, the refractive index of light polarized parallel to the optic axis is greater (or smaller, respectively,) than light polarized perpendicularly to the optic axis [Brad Amos 2005]. In other words, the polarization of the slow (or fast) wave is parallel to the optical axis when the birefringence of the crystal is positive (or negative, respectively).

Negative uniaxial crystals (eg. Calcite CaCO$_3$, Ruby Al$_2$O$_3$) have $n_e < n_o$ so for these crystals, the extraordinary axis (optic axis) is the fast axis whereas for positive uniaxial crystals (eg. Quartz SiO$_2$, Magnesium fluoride MgF$_2$, utile TiO$_2$), $n_e > n_o$ and thus the extraordinary axis (optic axis) is the slow axis.

Figure 2.1 Dependence of refractive index on light propagation direction and Polarization in negative (a) and positive (b) uniaxial crystals
2.4.2 Biaxial Crystals

In biaxial crystals, the dependence of the refractive index on light propagation direction and its polarization (index surface) corresponds to a much more complex function than for the uniaxial crystals. The resulting surface has a bilayer structure with four points of interlayer contact through which two optic axes pass. Similar to the case of a uniaxial crystal, the propagation direction of plane light wave is defined by two angles: polar $\theta$ and azimuthal $\varphi$.

For simplicity we confine ourselves to the case of light propagation in the principal planes XY, YZ and XZ. In these planes the dependences of the refractive index on the propagation direction of two waves with orthogonal polarizations represent a combination of an ellipse and a circle (Fig. 2.2 a, b). We shall relate dielectric (X, Y, Z) and crystallographic (a,b,c) axes in a biaxial crystal in such a way that the optic axes, whose directions are given by the intersection points of the ellipse and circle, will always lie in the principal plane XZ.

![Diagram of biaxial crystals]

Figure 2.2 Dependence of refractive index on light propagation direction and polarisation in biaxial crystals in relations between principal values of refractive indices are, a) $n_x < n_y < n_z$ and b) $n_x > n_y > n_z$. 
Considering one of two possible cases: \( n_x < n_y < n_z \) (Figure 2.2 (a)), where \( n_x, n_y, \) and \( n_z \) are the principal values of the refractive indices. The angle \( \theta \) formed by one of the optic axes with the axis \( Z \) can be found (Dimitriev 1991) from the expression

\[
\sin \theta = \frac{n_x (n_y^2 - n_x^2)^{1/2}}{n_y (n_z^2 - n_x^2)^{1/2}} \quad (2.5)
\]

The angle between optical axes in the plane \( XZ \) is equal to \( 2\theta \). In the plane \( XY \) the refractive index of the wave polarized normally to this plane is constant and equals \( n_z \), and that of the wave polarized in this plane changes from \( n_y \) to \( n_z \) with \( \varphi \) varying from 0° to 90°. Hence, a biaxial crystal with \( n_x < n_y < n_z \) in the plane \( XY \) is similar to a negative uniaxial crystal with \( n_o = n_z \) and

\[
n_e (\varphi) = n_y \frac{(1 + \tan^2 \varphi)^{1/2}}{[1 + (n_y/n_x)^2 \tan^2 \varphi]^{1/2}} \quad (2.6)
\]

In the plane \( YZ \) the refractive index of the wave polarized normally to this plane is constant and equals \( n_x \), whereas for the wave polarized in this plane the refractive index changes from \( n_y \) to \( n_z \) with \( \theta \) varying from 0° to 90°. Hence, a biaxial crystal with \( n_x < n_y < n_z \) in the plane \( YZ \) is similar to a positive uniaxial crystal with \( n_o = n_x \) and

\[
n_e (\theta) = n_y \frac{(1 + \tan^2 \theta)^{1/2}}{[1 + (n_y/n_z)^2 \tan^2 \theta]^{1/2}} \quad (2.7)
\]

We can also see that in the plane \( XZ \) at \( \theta < \theta \) a biaxial crystal with \( n_x < n_y < n_z \) is similar to a negative uniaxial crystal and, at \( \theta > \theta \), to a positive uniaxial crystal. A biaxial crystal with \( n_x > n_y > n_z \) can be considered in a
similar way (Figure 2.2(b)). Here the angle $V_z$ between the optic axis and the axis $Z$ is expressed as,

$$\cos V_z = \frac{n_x (n^2_X - n^2_Z)^{1/2}}{n_y (n^2_Y - n^2_Z)^{1/2}}$$  (2.8)

The biaxial crystal is said to be optically positive if the bisectrix of the acute angle between optic axes coincides with $n_{\text{max}}$, and optically negative if the bisectrix coincides with $n_{\text{min}}$.

2.5 NONLINEAR OPTICAL BORATE CRYSTALS

The continuing demand for new laser systems with unique wavelength and high power, the search for new specific frequency converting materials continues. In terms of materials that are reasonably well developed today, the materials for NLO applications in the IR (2-20 µm) are chalcopyrites (e.g., AgGaSe$_2$, ZnGeP$_2$), for the visible and near UV materials such as KNbO$_3$, KTiOPO$_4$ are used. For VUV (vacuum ultraviolet) and visible regions mainly borates such as BBO and LBO are suitable. The borate crystals BBO and LBO are two such materials have gained widespread use during the past few years. Their utility derives from exceptional optical damage thresholds, wide transparency ranges, mechanical durability, and favourable linear and non-linear optical properties. The collective existence of these properties in individual compounds has resulted in several unique performance characteristics that include generation of coherent light to wavelengths >200 nm and the production of continuously tunable, high power coherent radiation of wavelength 350-2400nm. Since, both BBO and LBO are commercially success for device applications, many efforts toward the development of new inorganic NLO borates are concentrated by materials scientists and researchers having complementary properties to those of LBO and BBO or improved properties. Some of the main aims of the development
of new borates have been the production of materials with relatively large SHG coefficients, moderate birefringence, short UV cutoff and congruent melting.

Borate NLO crystals for high-power UV light generation and for other NLO processes were developed. CBO, CLBO, GdYCOB, KAB, YCOB, SBBO, KBBF are some of those important crystals which are being used for present technological applications. There are number of borates, the most important ones being lithium triborate (LiB$_3$O$_5$ = LBO), cesium lithium borate (CLBO, CsLiB$_6$O$_{10}$), β-barium borate (β-BaB$_2$O$_4$ = BBO, often used in Pockels cells), bismuth triborate (BiB$_3$O$_6$ = BIBO), and cesium borate (CsB$_3$O$_5$ = CBO). Yttrium calcium oxyborate (YCOB) is also available in rare-earth-doped form and can be used as a laser gain medium. Further it is simultaneously used for generation and frequency-conversion of laser light. Less frequently used are strontium beryllium borate (Sr$_2$Be$_2$B$_2$O$_7$ = SBBO) and K$_2$Al$_2$B$_2$O$_7$ (KAB). LBO, BBO, CLBO, CBO and other borate crystals are suitable for the generation of relatively short wavelengths, e.g. in green and blue laser sources, and for UV generation, because their bandgap energy is relatively high, the crystals are relatively resistant to UV light, and there are suitable phase-matching options. Borates such as LBO and BBO also work well in broadly tunable optical parametric oscillators and optical parametric chirped-pulse amplification.

Lanthanum Calcium Borate (LCB) is a biaxial borate crystal. The birefringence (Δn) of the crystal is 0.053 at 1064 nm (Yicheng Wu et al 2003). Using the LCB single crystals, the phase matching is possible down to 315nm (SHG). The effective nonlinear co-efficient of LCB in XZ plane is about 1.05 pm/V and is 2.7 times greater as that of KDP (KH$_2$PO$_4$ which is 0.384 pm/V). The LCB crystal shows two photon absorption (TPA) induced by a UV laser field and its efficiency is nearly three times that in the case of BiBO crystals. Also it is reported that the crystals can be used as optically
operated limiters over a wide spectral range (Kityk et al. 2006). Further it is reported that, based on the band energy dispersion and density of states calculation shows that LCB is a semiconductor with a small indirect energy gap of 1.5 eV (Reshak et al. 2006). Table 2.2 shows the characteristics of LCB crystal which is compared with other well known borate materials.

Table 2.2 Characteristics of LCB compared with other borate crystal materials

<table>
<thead>
<tr>
<th>Crystal</th>
<th>UV absorption edge nm</th>
<th>Shortest SHG wavelength nm</th>
<th>$\Delta n$ @1064nm</th>
<th>$d_{eff}$ (pm/V)</th>
<th>Hygroscopicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCB</td>
<td>280</td>
<td>288</td>
<td>0.053</td>
<td>1.05</td>
<td>Non-Hygroscopic</td>
</tr>
<tr>
<td>BBO</td>
<td>189</td>
<td>205</td>
<td>0.112</td>
<td>2.01</td>
<td>Hygroscopic</td>
</tr>
<tr>
<td>BiBO</td>
<td>270</td>
<td>286</td>
<td>0.031</td>
<td>3.3</td>
<td>Non-Hygroscopic</td>
</tr>
<tr>
<td>YCOB</td>
<td>220</td>
<td>360</td>
<td>0.041</td>
<td>1.1</td>
<td>Non-Hygroscopic</td>
</tr>
<tr>
<td>GdCOB</td>
<td>320</td>
<td>420</td>
<td>0.033</td>
<td>1.3</td>
<td>Non-Hygroscopic</td>
</tr>
</tbody>
</table>

2.6 SELLMIEIER EQUATION

Sellmeier equation gives the relation between refractive index and wavelength for a particular transparent medium. The equation is used to determine the dispersion of light in the medium. The sellmeier plot gives us the information about the change in the value of the refractive index $n_x$, $n_y$ and $n_z$ of the material in the three different directions along X, Y, Z for a range of wavelength. A Sellmeier equation is a basic tool for calculating phase-matching configurations for nonlinear frequency conversion.

The general form of the sellmeier equation is written as,

$$n^2 = A + \frac{B}{\lambda^2 - C} - D\lambda^2$$  (2.9)
where, $\lambda$ is wavelength expressed in $\mu$m and $A$, $B$, $C$, $D$ are constant parameters and is called sellmeier co-efficients.

Table 2.3  The Sellmeier co-efficient of LCB crystal

<table>
<thead>
<tr>
<th>Refractive index</th>
<th>Sellmeier coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A$</td>
</tr>
<tr>
<td>$n_x$</td>
<td>2.78122</td>
</tr>
<tr>
<td>$n_y$</td>
<td>2.78533</td>
</tr>
<tr>
<td>$n_z$</td>
<td>2.96167</td>
</tr>
</tbody>
</table>

The sellmeier co-efficients of LCB crystal for the three different axes $n_x$, $n_y$, $n_z$ is given as in Table 2.3 (Guiling Wang et al 2002). Sellmeier plot is drawn for the refractive indices along X,Y and Z directions for the entire transparency region of wavelength 0.3 to 3.2 $\mu$m as shown in Figure 2.3. From the Sellmeier plot, variation of refractive index with respect to the wavelength along the three directions is observed. The indices are $n_x < n_y < n_z$, at the same time $n_x$ and $n_y$ are very close to each other, due to this behavior phase matchable region is limited in the XY plane. Hence, for our theoretical study XZ and YZ planes have been taken.

![Figure 2.3: Sellmeier plot of LCB crystal in the X, Y and Z directions](image-url)
2.7 PHASE MATCHING

Phase matching is a technique for achieving efficient nonlinear interactions in a medium. Many phase-sensitive nonlinear processes require phase matching to be efficient. Essentially, this means ensuring that a proper phase relationship between the interacting waves (for optimum nonlinear frequency conversion) is maintained along the propagation direction, so that the amplitude contributions from different locations to the product wave are all in phase. This leads to the condition that some phase mismatch has to be close to zero. For example, for type I phase matching of frequency doubling with collinear beams the phase mismatch is given by,

$$\Delta k = k_2 - 2k_1$$

(2.10)

where $k_1$ and $k_2$ are the wavevectors of the fundamental and second-harmonic beam respectively. Without chromatic dispersion, $k_2 = 2k_1$ would hold, so that the phase mismatch vanishes. However, dispersion generally causes a non-zero phase mismatch (Figure 2.4) if no special measures (as discussed below) are taken to avoid this. Due to chromatic dispersion, the wavenumber of the second harmonic is more than twice as large as that for the fundamental wave. This can be avoided, e.g., by choosing a different polarization in a birefringent crystal.

**Figure 2.4** Phase mismatch for second-harmonic generation. Addition of amplitude contributions from different parts of the crystal
Figure 2.4 illustrates how a phase mismatch keeps the efficiency low. Here, the arrows illustrate the phasors corresponding to the complex amplitude contributions from different parts of the nonlinear crystal to the harmonic wave. Only when phase matching is achieved, these contributions add up constructively, and a high power conversion efficiency is achieved. Otherwise, the direction of energy transfer changes periodically (possibly thousands of times during the passage through the crystal) according to the change in the phase relation between the interacting waves. The energy then oscillates between the waves rather than being transferred in a constant direction. The effect on the power conversion is illustrated in Figure 2.5. Solid curve shows a phase matched case, with the power growing in proportion to the square of the propagation distance. Dashed curve represents non phase-matched case, with the second harmonic power oscillating between zero and a small value.

Figure 2.5 Growth of second harmonic power in a crystal along the propagation direction, assuming constant pump intensity

For devices such as frequency doublers or optical parametric amplifiers, phase matching needs to be actively arranged. On the other hand,
an optical parametric oscillator may automatically choose its signal wavelength so that phase matching is achieved. Wavelength tuning can thus be achieved by influencing the phase-matching conditions e.g. via temperature changes or angular adjustments. In many cases, the nonlinear mixing products can be efficiently accumulated over a greater length of crystal only if phase matching is achieved. Otherwise, the field amplitudes at the exit face, generated at different locations in the crystal, essentially cancel each other, and the apparent nonlinearity is weak.

2.7.1 Phase Matching in Birefringent Crystal

In anisotropic media the ordinary and extraordinary waves can be mixed and phase matching can be obtained because it is possible to tune the index of refraction of the transmitted extraordinary wave by varying the angle between the k-vector and the optical axis of the medium, i.e. the wavelength dependence of the index of refraction. As a result the indices \( n_0 \) and \( n_e \) and therewith \( n_e(\theta) \) are a function of the incoming light.

![Figure 2.6 Sellmeier plot of the XZ plane aiming for phase matching at 1.064 \( \mu \)m](image)

Figure 2.6 Sellmeier plot of the XZ plane aiming for phase matching at 1.064 \( \mu \)m
The two curves for \( n_o \) and \( n_e(\theta) \) in Figure 2.6 represent the maximum and the minimum attainable index of refraction in the XZ plane, and the whole range in between the two curves covers the possible indices of refraction. In particular, the curves \( n_o \) and \( n_e(\theta) \) in Figure 2.6 are drawn to show the phase matching at 1.064 \( \mu \)m fundamental input. Similar curve can be drawn for the YZ plane of phase matching angle \( \theta = 37.54^\circ \).

Considering this wide range of possible indices, and particularly the tunability of the index by the setting the optic axis, the phase matching relation \( \Delta k = 0 \) for second harmonic generation may be fulfilled in the XZ plane. This condition is met when:

\[
n^\omega = n^{2\omega} \quad (2.11)
\]

Because of dispersion it will still not be possible to meet the conditions, but in the case of a negatively birefringent crystal (\( n_e < n_o \)) there exist an angle \( \theta_m \) for which the following condition can be met:

\[
n_{e}^{2\omega}(\theta_m) = n_{o}^{\omega} \quad (2.12)
\]

Before solving in an algebraic way the equations in order to find the particular angle for which the phase matching condition is fulfilled, the so-called phase matching angle, a geometrical procedure to clarify is adopted to clarify the problem. The problem is that of a crystal that is birefringent and dispersive at the same time. The index surfaces for ordinary and extra-ordinary rays can be drawn at both the frequencies \( \omega \) and 2\( \omega \). So we have four different index surfaces as shown in the Figure 2.7.
Figure 2.7 Phase matching of type I ($\omega+\omega\rightarrow\epsilon$) in a negative birefringent crystal of the XZ (YZ) plane

The index surfaces for $n_o$ at frequency $2\omega$ (outward circle) and for $n_e$ at frequency $\omega$ (inner ellipse) are shown as dotted curves, because they are not important for the phase matching problem in negatively birefringent media. The curves for $n_o$ at frequency $\omega$ and for $n_e$ at frequency $2\omega$ determine the phase matching angle. At the point where the circle of $n_o^\omega$ crosses the ellipse of $n_e^{2\omega}$ the phase matching condition is met. The relation then holds for the particular angle $\theta_m$ between the optical axis and the $k$-vector as shown in the figure.

Algebraically the problem of finding the phase matching angle can also be solved. At frequency $2\omega$ the equation for the index ellipsoid is (Ubachs 2001):

\[
n_e^{2\omega} (\theta_m) = \frac{n_e^{2\omega} n_0^{2\omega}}{\sqrt{(n_0^{2\omega})^2 \sin^2 \theta_m + (n_e^{2\omega})^2 \cos^2 \theta_m}} \quad (2.13)
\]
In order to obtain phase matching this needs to equal $n_0^{\omega}$. Thus we obtain an equation with an unknown variable $\theta_m$ and involving a $\sin^2 \theta_m$ and a $\cos^2 \theta_m$ function which may be solved for $\sin^2 \theta_m$:

$$\sin^2 \theta_m = \frac{(n_0^{\omega})^{-2} - (n_0^{2\omega})^{-2}}{(n_e^{2\omega})^{-2} - (n_0^{2\omega})^{-2}}$$ (2.14)

Phase matching, efficient frequency doubling, is achieved when a beam travels through a crystal under a particular angle $\theta_m$ between the $k$-vector and the optical axis. It should be noted that the angle $\theta_m$ is defined for propagation within the crystal; for all calculations (or experiments on finding the phase matching angle) starting from a ray impinging under a certain angle on a crystal surface refraction at the boundary has to be taken into account. Because of the dispersive effect on all three parameters in the above equation ($n_0^{\omega}, n_0^{2\omega}, n_e^{2\omega}$) the phase matching angle will be different for frequency doubling of different frequencies $\omega$. It was assumed that the ray at frequency $\omega$ was an ordinary ray (polarized perpendicular to the optical axis) while the second harmonic is an extra-ordinary ray (polarized in the plane of the optical axis). Thus it is found that in this process the polarization of the second harmonic is perpendicular to the polarization of the fundamental. In this example, it is assumed that the crystal was negatively birefringent; the phase matching condition was found for an ordinary fundamental and an extraordinary second harmonic. Considering index surfaces of positively birefringent media will show that the phase matching condition is fulfilled for an extraordinary fundamental and an ordinary second harmonic.

It is obvious that, the thus found phase matching angle $\theta_m$ in the two different cases are different, although in both the processes the
frequency is doubled. Commonly a distinction is made between these different types of phase matching:

Type I phase matching  \( E_0^\omega + E_0^\omega \rightarrow E_e^{2\omega} \)  negative birefringence
And  \( E_e^\omega + E_e^\omega \rightarrow E_0^{2\omega} \)  positive birefringence

Type II phase matching  \( E_0^\omega + E_e^\omega \rightarrow E_e^{2\omega} \)  negative birefringence
And  \( E_0^\omega + E_e^\omega \rightarrow E_0^{2\omega} \)  positive birefringence

2.7.2 Type I and Type II Phase Matching

Type I phase matching means that (e.g., in sum frequency generation) the two fundamental beams have the same polarization, perpendicular to that of the sum frequency wave.

Figure 2.8 Schematic of type I and type II phase matching

In type II phase matching, the two fundamental beams have different polarization directions; this can be appropriate when the birefringence is relatively strong and/or the phase velocity mismatch is small. The distinction between type I and type II similarly applies to frequency doubling, and to processes such as degenerate or non-degenerate parametric amplification. The different polarization arrangements can have various
practical implications, for example for the combination of several nonlinear conversion stages, or for intracavity frequency doubling. In the present theoretical work, only type I phase matching ($o+o\rightarrow e$) is considered.

### 2.7.3 Phase Matching By Angle Tuning

It is shown that under certain conditions, polarization of incoming waves and the birefringence of the material are matched to produce second harmonic generation at specific wavelengths. With the method described in the preceding paragraphs the phase matching angle for second harmonic generation is as a function of the fundamental wavelength. Figure 2.9 shows the theoretical type I phase matching curve of LCB crystal in the XZ and YZ planes. The curve depicts that the phase matching angle in these planes are close to each other. Hence, the phase matching angle $\theta_m$ difference between the XZ and YZ planes are small. From the curve it is obvious that the LCB crystal can be phase matched from 576 nm to 3200 nm, i.e., 576 nm ($\lambda_1$) → 288 nm ($\lambda_2$). This has been verified by Guiling Wang et al (2002), they observed 25 % of SHG conversion efficiency using a 3.0 mm long LCB crystal.

![Figure 2.9 Type I phase matching curve for SHG in the XZ and YZ plane](image-url)
When using this crystal for frequency doubling of a scanning tunable laser, the angle $\theta_m$ has to be tuned, while scanning the fundamental.

### 2.8 SECOND HARMONIC GENERATION

The phenomena that, an input wave in a nonlinear material can generate a wave with twice the optical frequency (i.e. half the wavelength). This process is also called second harmonic generation. In most cases, the pump wave is delivered in the form of a laser beam, and the frequency doubled (second harmonic) wave is generated in the form of a beam propagating in a similar direction.

![Image](image)

**Figure 2.10** A typical configuration for frequency doubling: an infrared input beam at 1.064 $\mu$m generates a green 0.532 $\mu$m wave during its path through a nonlinear crystal

The intensity of the second harmonic generated wave can be expressed by a simple relation,

\[
I_{2\omega} \propto \sin^2 \left( \frac{\Delta k L}{2} \right)
\]

(2.15)

where L is the length of the crystal. From figure 2.9 it is obvious that LCB crystal can be phase matched in a wide region. However, the ordinary
Nd:YAG lasers can produce the fundamental wavelength of 1.064 µm. We have verified the SHG spectrum by tuning the angle of XZ and YZ planes. Figure 2.11(a) and (b) shows the SHG angle tuning curve for the planes XZ and YZ respectively. The angular acceptance or the full width at half maximum (Δθ) of these planes was measured to be about 0.5° for 1.0 cm long crystal. This means that the phase matching is sensitive to the rotation angle.

![SHG angle tuning curve of XZ (a) and YZ (b) planes at a fixed fundamental wavelength λ = 1.064 µm](image)

Figure 2.11  SHG angle tunig curve of XZ (a) and YZ (b) planes at a fixed fundamental wavelength \( \lambda = 1.064 \) µm
2.9 WALK-OFF ANGLE

The phenomenon that the intensity distribution of a beam in an anisotropic crystal drifts away from the direction of the wave vector is called walk-off angle.

Figure 2.12 Schematic representation of walk-off

For a laser beam propagating in an isotropic medium, the transverse intensity distribution propagates along the beam axis as defined by the medium k vector. In anisotropic (and thus birefringent) crystals, this is not necessarily the case: it can occur that the intensity distribution drifts away from the direction defined by the k vector, as illustrated in Figure 2.12, where the gray lines indicate wavefronts and the blue color the region with significant optical intensity. This phenomenon, called spatial walk-off, birefringent walk-off or Poynting vector walk-off and is associated with some finite angle $\varphi$ (called walk-off angle) between the Poynting vector and the k vector. The Poynting vector defines the direction of energy transport, whereas the k vector is normal to the wavefronts.

Spatial walk-off occurs only for a beam with extraordinary polarization, propagating at some angle $\theta$ against the optical axes, so that the
refractive index $n_e$ and the phase velocity become dependent on that angle. The walk-off angle (Dimitriev 1991) can then be calculated from the equation,

$$\rho(\theta) = \pm \arctan \left[ \left( \frac{n_0}{n_e} \right)^2 \tan \theta \right] \pm \theta$$

(2.16)

where the upper sign refer to a negative crystal and the lower sign to a positive one. The magnitude of the walk-off angle is presented in Figure 2.13 for the LCB crystal. In typical cases, it is in the range between a few milliradians and some tens of milliradians. For propagation directions close to one of the axes of the index ellipsoid, the walk-off can even become much smaller.

![Figure 2.13](image)

Figure 2.13  Spatial walk-off versus fundamental wavelength for SHG in the principal planes of LCB

The result of the walk-off angle of LCB is also compared with BIBO and BBO crystal. Figure 2.14 shows the walk-off of BIBO and BBO crystal. From the comparison it is obvious that the walk-off of LCB is
relatively small with the commercially available and well established BIBO and BBO crystals. For verification, at the phase matching wavelength $\lambda = 1.064 \, \mu\text{m}$, the walk-off of LCB is measured to be 11 mrad, whereas BBO and BIBO are 56 mrad and 23 mrad respectively (Valentin Petrov et al 2010). Hence, the smaller walk-off of LCB crystal makes this as a promising candidate for NLO application.

![Figure 2.14](image)

**Figure 2.14** Spatial walk-off versus fundamental wavelength for SHG in the principal planes of BIBO and BBO

### 2.10 OPTICAL PARAMETRIC OSCILLATION

An optical parametric oscillator (OPO) is a light source similar to a laser, also using a kind of laser resonator, but based on optical gain from parametric amplification in a nonlinear crystal rather than from stimulated emission. Like a laser, such a device exhibits a threshold for the pump power, below which there is negligible output power (only some parametric fluorescence). The schematic of an OPO is shown in Figure 2.15.
Figure 2.15 Schematic of an optical parametric oscillator

A main attraction of OPO is that the signal and idler wavelengths, which are determined by a phase matching condition, can be varied in wide ranges. Thus it is possible to access wavelengths (e.g. in the mid-infrared, far-infrared or terahertz spectral region) which are difficult or impossible to obtain from any laser, and wide wavelength tunability is also often possible. A limitation is that any OPO requires a pump source with high optical intensity and relatively high spatial coherence. Therefore, a laser is essentially always required for pumping an OPO, and as the direct use of a laser diode is in most cases not possible, the system becomes relatively complex, consisting a diode-pumped solid-state laser, and the actual OPO.

Parametric amplification and oscillation may be viewed upon as an inverse sum-frequency process, for which the same phase-matching conditions will hold; it is these phase-matching conditions that determine which frequencies \( \omega_1 \) and \( \omega_2 \) will be generated at a certain setting of the angle of the crystal with respect to the wave vector \( k_3 \) of the pump beam.

\[
\Delta k = 0 \rightarrow k_3 = k_1 + k_2
\]  

(2.17)

for co-linear beams the following relation must hold in order to achieve phase-matching:

\[
n_3 \omega_3 = n_1 \omega_1 + n_2 \omega_2
\]  

(2.18)
Of course the conservation of energy is a strict condition for frequency conversion in an OPO (Ubachs 2001):

\[ \omega_3 = \omega_1 + \omega_2 \quad (2.19) \]

Again, because of dispersion in any medium these relations can only be met under the special conditions of anisotropic crystals with a tunable index; and again we distinguish between Type I and II phase-matching conditions. For example:

\[ \omega_1 \text{ and } \omega_2 \text{ are ordinary waves with index, respectively } n_1^o \text{ and } n_2^o \]
\[ \omega_3 \text{ is an extraordinary wave with index } n^e_3 (\theta) \]

So Type I phase-matched oscillation is obtained at \( \omega_1 \) and \( \omega_2 \) at a specific angle \( \theta = \theta_m \), with the condition:

\[ n^e_3 (\theta_m) = \frac{n_1 \omega_1 + n_2 \omega_2}{\omega_3} \quad (2.20) \]

At each specific phase matching angle \( \theta_m \) the OPO will produce a particular combination of two frequencies that obey the phase-matching condition.

If we rotate the angle \( \theta \) of the crystal for an amount \( \Delta \theta \); so, \( \theta_m \rightarrow \theta_m + \Delta \theta \). As the pump frequency \( \omega_3 \) is fixed at the phase-matched frequencies will change:

\[ \omega_1 \rightarrow \omega_1 + \Delta \omega_1 \quad (2.21) \]
\[ \omega_2 \rightarrow \omega_2 + \Delta \omega_2 \quad (2.22) \]
because of energy conservation: $\Delta \omega_1 = -\Delta \omega_2$. All the indices of refraction will change:

\[ n_1 \rightarrow n_1 + \Delta n_1 \quad (2.23) \]
\[ n_2 \rightarrow n_2 + \Delta n_2 \quad (2.24) \]
\[ n_3 \rightarrow n_3 + \Delta n_3 \quad (2.25) \]

Note that the index at the pump frequency changes, because it is an extraordinary wave and the angle has been rotated; the index of the signal and idler wave change because of dispersion; so the changes in the indices are:

\[ \Delta n_1 = \left[ \frac{\partial n_1}{\partial \omega_1} \right]_{\omega_1} \Delta \omega_1 \quad \text{frequency dependant} \quad (2.26) \]
\[ \Delta n_2 = \left[ \frac{\partial n_2}{\partial \omega_2} \right]_{\omega_2} \Delta \omega_2 \quad \text{frequency dependant} \quad (2.27) \]
\[ \Delta n_3 = \left[ \frac{\partial n_3}{\partial \theta} \right]_{\theta_m} \Delta \theta \quad \text{angle dependance} \quad (2.28) \]

With these relations a new phase-matching condition has to be satisfied, although at a different angle $\theta_m + \Delta \theta$:

\[ (n_3 + \Delta n_3)\omega_3 = (n_1 + \Delta n_1)(\omega_1 + \Delta \omega_1) + (n_2 + \Delta n_2)(\omega_2 + \Delta \omega_2) \quad (2.29) \]

so:

\[ n_3 \omega_3 + \Delta n_3 \omega_3 = n_1 \omega_1 + \Delta n_1 \omega_1 + n_1 \Delta \omega_1 + \Delta n_1 \Delta \omega_1 + n_2 \omega_2 + \omega_2 \Delta n_2 - n_2 \Delta \omega_1 - \Delta n_2 \Delta \omega_1 \quad (2.30) \]

Here $\Delta \omega_2 = -\Delta \omega_1$ was used. With use of the original phase-matching relation at $\theta = \theta_m$ and neglect of second order derivatives, such as $\Delta n_1 \Delta \omega_1$, we solve for:

\[ \Delta \omega_1 = \frac{\omega_3 \Delta n_3 - \omega_1 \Delta n_1 - \omega_2 \Delta n_2}{n_1 - n_2} \quad (2.31) \]
Substituting the above relations in the equation for $\Delta \omega_1$ gives:

$$
\Delta \omega_1 = \frac{\omega_3 \left[ \frac{\partial n_3}{\partial \theta} \right] \Delta \theta - \omega_1 \left[ \frac{\partial n_1}{\partial \omega_1} \right] \Delta \omega_1 + \omega_2 \left[ \frac{\partial n_2}{\partial \omega_2} \right] \Delta \omega_1}{n_1 - n_2}
$$

(2.32)

Solving $\Delta \omega_1$:

$$
\frac{\Delta \omega_1}{\Delta \theta} = \frac{\partial \omega_1}{\partial \theta} = \frac{\omega_3 \left[ \frac{\partial n_3}{\partial \theta} \right]}{n_1 - n_2 + \left[ \omega_1 \frac{\partial n_1}{\partial \omega_1} - \omega_2 \frac{\partial n_2}{\partial \omega_2} \right]}
$$

(2.33)

And $k$ is written in terms of the index of refraction of an extraordinary wave $n_e(\theta)$. Now we use this result for the derivative $\partial n_3/\partial \theta$:

$$
\left[ \frac{\partial n_3}{\partial \theta} \right]_{\theta_m} = -\frac{1}{2} n_0^3 \left[ n_0^{-2}(\omega_3) - n_e^{-2}(\omega_3) \right] \sin 2\theta_m
$$

(2.34)

Finally, we have obtained an equation for the angle dependence of the generated frequency of the signal wave as a function of the indices of refraction and their dispersion relations.

$$
\frac{\partial \omega_1}{\partial \theta} = \frac{-\frac{1}{2} n_0^3(\omega_3) \omega_3 \left[ n_0^{-2}(\omega_3) - n_e^{-2}(\omega_3) \right] \sin 2\theta_m}{n_1 - n_2 + \left[ \omega_1 \frac{\partial n_1}{\partial \omega_1} - \omega_2 \frac{\partial n_2}{\partial \omega_2} \right]}
$$

(2.35)

In an experiment with an OPO, the parameters $\omega_3$ and therewith $n_0(\omega_3)$, $n_e(\omega_3)$, are constants. If the indices of the medium are known, and their frequency dependence then the dependence of the frequency of the signal wave $\omega_1$ as a function of the angle $\theta$ may be calculated numerically, using the above equation. Such an angle tuning curve for an OPO based LCB crystal shown in the Figure 2.16. The wavelength of both the signal and the
corresponding idler (energy conservation) at the particular easily accessible pump wavelength of 0.355 µm is shown.

![Figure 2.16](image)

**Figure 2.16** The calculated phase matching for type I OPO processes in LCB for propagation in the principal refractive-index planes XZ (a) and YZ (b). Pump wavelength $\lambda = 0.355$ µm.
Thus it is observed that a device, an OPO based on the material LCB, and pumped by the UV-output of a Nd-YAG laser, is a source for coherent radiation in the wavelength range 0.4 - 3.2 µm, this means the whole visible and near infrared part of the spectrum (wavelengths longer than 3.2 µm are absorbed in the LCB crystal). And the tuning of such a device may be simply arranged by rotating the crystal over an angle from 37 to 55 degrees in both the planes.

2.11 CONCLUSION

We theoretically analysed the nonlinear optical properties of LCB crystal. The change in refractive indices with respect to the wavelength for the entire transparency region was plotted using a Sellmeier equation to check the phase matching property of the crystal. The indices were $n_x < n_y < n_z$, at the same time $n_x$ and $n_y$ were close to each other, due to this behavior phase matchable region was limited in the XY plane. Hence, for our theoretical study XZ and YZ planes have been taken. SHG, spatial walk-off and OPO for these planes were studied. The phase matching angle for Type - I frequency doubling of fundamental wavelength $\lambda = 1.064 \, \mu m$ was calculated to be 37.38° and 37.54° respectively. The angular acceptance ($\Delta \theta$) of these planes was measured to be about 0.5° for 1.0 cm long crystal. The spatial walk-off was compared with the well established crystals like BBO and BiBO. It was about 11 mrad for LCB crystal of fundamental wavelength $\lambda = 1.064 \, \mu m$, whereas BBO and BiBO were 56 mrad and 23 mrad respectively. Hence, the smaller walk-off makes LCB as a promising candidate for NLO application. In addition to this, the investigation on OPO characteristics of the LCB crystal of input pump 0.355 µm for the wavelength range 0.4 – 3.2 µm was calculated, and the tuning of such a device was calculated to be rotating the crystal over an angle from 37 to 55 degrees in both the planes.