CHAPTER 1

INTRODUCTION

Nonlinear Optics is a revolutionary extension of conventional (linear) optics prompted by laser technology. The main subject of nonlinear optics is the study of various effects and phenomenon related to interaction of intense coherent light with matter. In conventional optics when a beam of light propagates through any dielectric medium, its frequency remains unchanged. The nonlinearity of the medium becomes effective only when intensity of light is considerably high so that it becomes comparable to that of the interatomic field of the medium. The invention of the laser ushered a new field of study — Nonlinear Optics. Because laser light can be so intense, it can actually change the index of refraction of a material through which it passes and thus forces the medium to behave nonlinearly. This means in addition to the incident wavelength, there will be other wavelengths generated by second harmonic, third harmonic and other processes. This generation can be extended to lower as well as higher frequencies and there are ample scopes to enhance the power (or energy) of the generated radiation appreciably through judicious means.

There are two broad categories of tunable laser sources: (i) primary tunable lasers such as dye lasers, solid state lasers, semiconductor and high pressure molecular gas lasers, which are tunable over some portions of the spectral region and (ii) secondary tunable lasers which are realized employing nonlinear optical (NLO) processes i.e. Second harmonic generation (SHG), Sum frequency generation (SFG), Difference frequency generation (DFG), Optical parametric oscillation (OPO) etc. There are limitations of primary laser sources. Dye lasers mainly offer tunability from 308 nm to 1100 nm with different dyes. Semiconductor diode lasers provide very low output levels and their frequency stability is usually not too good. Molecular gas lasers have the limitations in tunability. Again in such gas lasers there are problems while handling toxic and noxious gases. This non-availability of tunable Primary Lasers from UV to IR can be overcome by secondary tunable lasers obtained by frequency conversion of these primary sources by using nonlinear response of a material.

When a dielectric medium is subjected to an applied electric field $E$, it tends to become polarized due to the distortion of its internal charge distribution. The resultant electric dipole moment per unit volume is given by

$$P = \varepsilon_0 \chi^{(1)} E + \varepsilon_0 \chi^{(2)} E^2 + \varepsilon_0 \chi^{(3)} E^3 + \cdots$$
\[ p^{(L)} + p^{(NL)} \]  

where, \( \chi^{(1)} \gg \chi^{(2)} \gg \chi^{(3)} \gg \)

(1.1)

\( p^{(L)} \) and \( p^{(NL)} \) are induced linear and nonlinear polarization respectively. \( \chi^{(1)} \), \( \chi^{(2)} \) and \( \chi^{(3)} \) are first order, second order and third order susceptibilities respectively. While \( \chi^{(1)} \) accounts for the linear optical effects, the higher order terms are responsible for the origin of nonlinear optical effects. Different NLO effects are summarized in Table-1.1 below. Higher is the order of nonlinearity lower becomes the value of susceptibilities. Thus higher and higher value of intensity of the incident radiation is required to get higher order NLO effects.

**Table-1.1**

**Second order and third order nonlinear phenomenon**

<table>
<thead>
<tr>
<th>Second order phenomenon ( \chi^{(2)} )</th>
<th>Third order phenomenon ( \chi^{(3)} )</th>
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<tbody>
<tr>
<td>• Sum frequency generation</td>
<td>• Stimulated Raman scattering</td>
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<tr>
<td>• Difference frequency generation</td>
<td>• Two photon absorption</td>
</tr>
<tr>
<td>• Second harmonic generation</td>
<td>• Optical field induced birefringence</td>
</tr>
<tr>
<td>• Parametric amplification</td>
<td>• Self focusing</td>
</tr>
<tr>
<td>• Optical parametric oscillation</td>
<td>• Phase conjugation</td>
</tr>
<tr>
<td>• Linear electro optic effect</td>
<td>• Third harmonic generation</td>
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<tr>
<td>• Magneto optic effect</td>
<td>• Degenerate four wave mixing</td>
</tr>
<tr>
<td>• Optical rectification</td>
<td>• Coherent spectroscopy</td>
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</table>

The second order NLO effects are possible only in those nonlinear media, which lacks a center of inversion symmetry. In nonlinear frequency conversion process both energy as well as momentum conservation must be satisfied to generate new frequency from input fundamental(s). Generation of tunable UV laser is done utilizing either SHG or SFG.

For SHG:

\[ \omega_{GEN} = 2\omega_{INPUT} \]  

(1.2a)

\( \omega_{INPUT} \) is the frequency of input fundamental laser radiation and \( \omega_{GEN} \) is that of the generated coherent laser radiation having frequency twice that of the fundamental.

For SFG:

\[ \omega_{GEN} = \omega_{INPUT}^1 + \omega_{INPUT}^2 \]  

(1.2b)
Here we require two input fundamental beams ($\omega_{\text{INPUT}}^i, i=1,2$) and $\omega^1 < \omega^2 < \omega_{\text{GEN}}$.

For generation of IR radiation either DFG or OPO process is considered:

For DFG:

$$\omega_{\text{GEN}} = \omega_{\text{INPUT}}^1 - \omega_{\text{INPUT}}^2$$

Here also we require two input fundamentals beams ($\omega_{\text{INPUT}}^i, i=1,2$) and $\omega^1 > \omega^2 > \omega_{\text{GEN}}$.

For OPO:

$$\omega_{\text{PUMP}} = \omega_{\text{SIGNAL}} + \omega_{\text{IDLER}}$$

Here if the pump intensity is high enough (greater than a threshold value) then pump frequency breaks up into two frequencies called signal and idler, where $\omega_{\text{PUMP}} > \omega_{\text{SIGNAL}} > \omega_{\text{IDLER}}$.

All the above Equations (1.2a-1.2d) are obtained from energy conservation. From momentum conservation we obtain the phase-matching angle with respect to optic axis and at this particular orientation of the crystal, we get the generated beam.

Conversion efficiency ($\eta$) of nonlinear frequency converter is the ultimate parameter by which its usefulness is assessed. Conversion efficiency is defined as $\eta = \frac{P_3}{P_1 P_2}$ where $P_3$ is power of the generated radiation and $P_1, P_2$ are those for the input parent fundamental radiations. The generated power ($P_3$) has the following relationship with different parameters like effective nonlinear coefficient ($d_{\text{eff}}$), crystal length ($l$), input power density ($P_1, P_2$) and phase-mismatching ($\Delta k$) as,

$$P_3 \propto P_1 P_2 \varepsilon^2 d_{\text{eff}}^2 \left[ \sin \left( \frac{\Delta k l}{2} \right) \right] \left( \frac{1}{A} \right)$$

Where

$$x = \frac{\Delta k l}{2}$$

and $A$ is the beam area.

Equation (1.3) dictates some important criteria for selection of a nonlinear crystal for a frequency conversion process. It is clearly seen that in general, higher power density, longer crystal length, larger nonlinear coefficients and smaller phase-mismatching will result in higher $P_3$ and hence larger conversion efficiency. However, there are always some limitations coming from nonlinear crystals and lasers. For example, the $d_{\text{eff}}$ is determined by the nonlinear crystal itself and the input power densities have to be lower than the damage threshold of the crystal. Threshold is defined as the least fluency sufficient to induce damage at any site of the crystal. The maximum safe intensity should be lower than this value. The
damage threshold is highly dependent on local defects in the crystal as well as on the surface quality. Thus damage of nonlinear crystals limits the maximum attainable conversion efficiency. In the following Table 1.2 both the laser and crystal parameters are listed for selecting right crystals:

**Table-1.2**

<table>
<thead>
<tr>
<th><strong>Parameter for NLO Crystal Selection</strong></th>
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<tr>
<td><strong>Laser Parameters</strong></td>
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<tr>
<td>NLO Process</td>
</tr>
<tr>
<td>Power or Energy, Repetition Rate</td>
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<tr>
<td>Divergence</td>
</tr>
<tr>
<td>Bandwidth</td>
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<tr>
<td>Beam Size</td>
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<tr>
<td>Pulse Width</td>
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<tr>
<td>Environment</td>
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</table>

Conversion efficiency is also directly proportional to the square of the crystal length. So, apparently longer crystal will provide larger conversion when properly phase-matched. But actually, due to walk-off effect too large crystals give lower conversion. The separation of energy propagation direction of extraordinary wave (e-wave) from the beam propagation direction is called walk-off. Owing to such separation the overlapping of the interacting waves will not occur throughout the entire crystal length and this results in substantial decrease in conversion in longer crystal.

Focusing of the input beams, keeping the pump power same, will give rise to high conversion, as then the parameter 'A' in Equation (1.3) becomes less. The longitudinal dimension of the focal region is defined by $b = \omega_0^2 k$ where $\omega_0$ is the beam radius at the waist and $k$ is the wave propagation vector with magnitude of $2\pi n/\lambda$. Here $n$ and $\lambda$ are being the refractive index and wavelength of the laser radiation respectively. Again due to focusing effect, the walk-off effect becomes large and hence may result in decrease of conversion.
One of the most important mechanisms that can limit the efficiency is imperfect phase-matching i.e. $\Delta k \neq 0$. For efficient operation, the phase-mismatch must be zero. Phase-mismatch is usually adjusted by changing pumping wavelength or angular orientation of the crystal. Imperfect phase-matching can also occur because of large spectral bandwidth or small crystal acceptance.

Another limitation to nonlinear conversion efficiency is the thermally induced birefringence, which increases the phase-mismatch. This problem is serious at high laser power since due to residual absorption the crystal gets heated enough resulting in change of its refractive indices. Crystal absorption also increases due to presence of impurities and inclusions, unavoidably incorporated in the crystal during its growth.

Thus there is no ideal nonlinear crystal that fulfills all the discussed requirements as necessary for successful device applications. It is the judicious choice of the nonlinear crystal with available technology as supported by the material properties that can make a desirable device. The fundamental aims of this work are:

(a) Development and study of tunable coherent radiations from UV to IR by nonlinear interactions.

(b) Enhancement of conversion efficiency of the generated tunable radiations using some novel techniques so that much higher conversion can be obtained from that presently available, without any increase of power of the primary input.

(c) Characterizations of some nonlinear crystals for laser device applications.

In Chapter-2, a new method based on optical feedback mechanism has been predicted and successfully demonstrated for the first time to get considerable enhancement both in SFG and SHG without any change of input energy from the parent laser. By employing our new mechanism, we can achieve same value for $\eta$ as that obtained in a conventional setup but with very less input fundamental energy. In other words for same input energy now there will be a large enhancement in the value of $\eta$. Working on the principle of optical feedback, the fundamental advantages of the scheme are that neither does it require any focusing nor it demands any change in the energy of the primary laser source. Thus deployment of the new configuration will enable one to achieve a very high energy conversion with substantially lower input energy that is easily accessible and very much cost-effective than is presently required in a conventional setup. It can be a very effective mechanism for enhancement of conversion efficiency by SHG in IR region for IR nonlinear crystals having quite low laser damage threshold.
In Chapter-3, the problem of enhancement of conversion efficiency (\( \eta \)) has been approached by walk-off compensation using twin crystal arrangement. In Section-3.1, the enhanced UV generation in a walk-off compensated scheme (WOCS) using twin LB_{4} crystals has been demonstrated. Here without focusing as high as 14% conversion can be achieved while it is only 4% for conventional single crystal arrangement with same input energy. In Section-3.2, the employment of noncollinear configuration to achieve noncritical phase-matching (NCPM) in development of tunable UV source has been discussed. As is well known, NCPM not only totally eliminates walk-off but also provides one with several other advantages like greater acceptance angle for the input beam, maximum effective nonlinear coefficient for LB_{4} that increases the conversion efficiency to a considerable extent.

In Chapter-4, another novel technique called 'Multipass Configuration' in twin crystal arrangement has been discussed for the first time that has enormous capability for enhancing the conversion efficiency of SHG. We have successfully demonstrated the scheme and achieved as high as 4.5 times conversion in comparison to conventional single crystal arrangement. Our scheme combines following advantages:

(i) The effect of multipass: Due to multipass of the fundamental laser radiation through the nonlinear crystal the effective crystal length increases. Actually it increases by \( n/l \) where \( l \) is the length of the crystal and \( n \) is the number of passes. Thus a large enhancement can be obtained even in a crystal having low nonlinearity since the conversion efficiency increases by \( n^{2}l^{2} \).

(ii) In our MPC scheme, the residual fundamental beam gets considerably shifted from its initial path after SHG, so that no costly Faraday rotator is required to prevent its return path into the laser cavity to cause damage of the cavity elements of the laser itself.

(iii) The effect of compensating double refraction: The deleterious walk-off adversely affects the frequency conversion length of the crystal, which subsequently reduces the generated energy. But our new scheme gets rid of the double refraction effect totally as even number of passes are used. This results in higher conversion. Again since the MPC fully compensates the deteriorating effect of walk-off, crystal of any suitable length can be employed to realize higher conversion.

(iv) Focusing: In this MPC one can focus the input radiation for further enhancement of conversion efficiency depending on the laser damage threshold of the nonlinear crystal.
This technique can be successfully implemented at low input intensity level to obtain high output power for the crystals having low laser damage threshold.

There are limited numbers of nonlinear crystals for generation of tunable infrared radiation beyond 12 μm. Tunable coherent radiation in this range are highly desirable because of several applications like molecular spectroscopy, medical diagnostics, remote sensing of atmospheric trace constituents and also in military application like target tracking etc. **Chapter-5** includes the characterization of two such important nonlinear IR crystals, namely Zinc Germanium di Phospide [ZnGeP₂ (ZGP)] and mixed crystal AgGaₙGe(1-ₙ)Se₄ [AgGaGeS₄ or AGGS having x=0.5]. While ZGP is a well known member of chalcopyrite group, the other mixed IR crystal is a result of recent development. The main advantage of this new material is that there is no appreciable absorption in the band edge region. This is in sharp contrast to that obtained in well known IR crystals, namely, ZGP, AgGa₅₂, AgGaSe₂ etc. The existence of significant absorption in the band edge region in these crystals prevented one from using 1.064 μm radiation (from well developed laser source like Nd: YAG laser) as pump. Obviously radiations below 1 μm obtained from other sources like dye laser or harmonics of Nd: YAG laser can also not be used as pump. However, such pump sources can be used in this newly developed crystal AGGS. We have characterized ZnGeP₂ both by measuring its refractive indices and phase matching angles for SHG of CO₂ laser radiations. From the measured refractive indices, new sets of Sellmeier equations have been derived for ZGP. The phase-matching angles for different interactions reported by others as well as those measured during our SHG experiment agree much better with the theoretical predictions using our new Sellmeier equations as compared to those predicted by using the existing ones. We have characterized this biaxial crystal by computing a new set of Sellmeier equations for it. The experimental values of phase-matching angles agree to a much better extent to the predicted phase-matching angles using this new Sellmeier. We have also realized SHG of tunable CO₂ laser radiation in it and compared its nonlinearity with others. The absorption as well as transmission characteristics of both ZGP and AgGaGeS₄ crystals are also measured during their characterization.

In **Chapter-6**, generation of widely tunable infrared source from 5-16 μm has been discussed in Indium (In) doped GaSe crystal. GaSe is a layered structure crystal that has considerably high nonlinear coefficient, a wide visible to infrared transmission. Its nonlinear figure of merit, defined as d²/n³ is very large compared to other IR crystals. Again due to its large birefringence, GaSe can satisfy phase-matching conditions for a variety of optical
interactions. The only deficiency of GaSe is that due to its layered structure, it cannot be cut and polished. Moreover due to its high refractive indices a large rotation of the crystal is required to achieve phase-matching for any interaction (as it can not be cut per requirement). This causes a lot of Fresnel's reflection losses of the incident radiation from the crystal surface. Doping with 'In' shows strengthening of the structural properties of the crystal and this enable one to cut and polish the optical faces in required directions. It is also reported that the value of nonlinearity of the 'In' doped GaSe crystal exceeds that of the pure GaSe crystal. It is also seen that long wavelength transmission cut-off is shortened by 1 \( \mu \text{m} \) by doping with Aluminium (Al). Here we discuss the generation of tunable infrared radiation from 5-16 \( \mu \text{m} \) in 'In' doped (0.5\%) GaSe crystal following DFG technique involving commonly available sources like Nd: YAG laser and harmonic pumped dye laser.

The application of the developed tunable coherent source has also been discussed in Chapter 6. We have used this coherent source to measure the absorption as well as transmission spectra of different substances.

In Chapter 7, conclusions and suggestions for the future work have been detailed.