CHAPTER I

INTRODUCTION TO NONLINEAR OPTICAL INTERACTIONS

ABSTRACT

The invention of the pulsed ruby laser provided a revolutionary new light source, of exceedingly high intensity. This amazing high power, high brightness, good coherence, highly directional, narrow bandwidth and short pulses of laser light beams enable new technologies which profoundly changing our way of life. Thus it opened new frontiers in science and optics. One of the new horizons opened by laser is the field of nonlinear optics. Now it has become a vast and mystifying complex field of research. This chapter tries to have a quick look at their properties and effects.
CHAPTER I

INTRODUCTION TO NONLINEAR OPTICAL INTERACTIONS

1.1 INTRODUCTION

The field of research and the development of nonlinear optical materials has progressed impressively since the invention of laser. Laser as a light source is the fundamental tool for all kinds of photonic applications. As laser technology progressed, nonlinear optics has become increasingly more mature and several comprehensive textbooks have been written on this subject [1-6]. The word photonics encompasses nonlinear interaction of light with matter. Nowadays there is a lot of excitement for photonic technologies in which photons are used for information transmission and manipulation without resorting to conventional electronics. Studies on these new effects and the related novel techniques and the investigation of suitable materials are the major issues of nonlinear optics.

1.2 EXPLANATION OF NONLINEAR OPTICS

Nonlinear optics is a study, which deals mainly with novel phenomena arising from the interactions of intense coherent optical radiation with matter. The nonlinear behaviour will begin once the perturbation to the interatomic field becomes significant. At fields very much below that of the atomic field, the perturbation is not sufficient to generate a measurable nonlinear effect. It is interesting to note that even a vacuum may serve as a nonlinear medium but the photon interaction is very weak.
The nonlinear process is well illustrated by considering the example of a weighed spring, exhibiting nonlinear optical processes in solids. It is a common observation that the force exerted on a string is proportional to its extension, which obeys Hooke's law. But it can be overdriven into nonlinear response by the application of greater force and thus violating the Hooke's law. Likewise, an extremely intense beam of light could generate appreciable nonlinear effects. The electric field associated with the light beams from ordinary or traditional sources are too small to observe such behaviour. It was for this reason, the field had to await the advent of laser in order that sufficient brute force could be brought to bear in the optical region of the spectrum.

**Linear versus nonlinear optics**

The fundamental equations in the area of conventional optics manifested a linear feature. The usual classical treatment of light propagation, superposition, reflection, refraction, dispersion, scattering as well as birefringence assumes a linear relation between the electromagnetic field and the responding atomic system constituting the medium. To show this linear feature, following examples are considered. In linear regime, the electric polarization is simply assumed to be linearly proportional to the electric field strength \( E \) of an applied optical wave i.e.

\[
P = \varepsilon_0 \chi E \quad \ldots \quad (1.1)
\]

\( \varepsilon_0 \)-free space permittivity, \( \chi \)-susceptibility of the medium.
Maxwell's relation led to a set of linear differential equations in which only the terms proportional to the first power of $E$ are involved. Hence, there is no coupling between the light beams. In short, no coherent radiation at new frequency will be generated. After the demonstration of laser, in 1960, simple linear assumptions were no longer adequate when intense beam was incident on certain types of optical materials. Hence, the induced polarization becomes

$$P = \varepsilon_0 \left[ \chi^{(1)} E + \chi^{(2)} EE + \chi^{(3)} EEE + \ldots \right] \quad \ldots \ (1.2)$$

$\chi^{(1)}, \chi^{(2)}, \chi^{(3)}$ – first, second, and third order nonlinear susceptibilities and so on. Here occurs, the coherent optical frequency mixing effects.

**Theoretical aspects**

In 1962, theoretical investigations dealing with the behavior of light waves by solving Maxwell's equation in a nonlinear dielectric and at the boundary of nonlinear media were performed by Bloembergen et al [7,8] respectively.

The explanation of nonlinear optics lies in the way in which a beam of light propagates through a solid. The nuclei and the associated electrons of the atoms in the solid form electric dipoles. The electromagnetic radiation interacts with these dipoles causing them to oscillate, by classical laws of electromagnetism, results in the dipoles themselves acting as sources of electromagnetic radiation. As the intensity of the incident radiation increases, the relation between the radiation and the amplitude of the vibration becomes nonlinear, which results in generation of frequencies that
are different from those of incident fields. Thus second and higher harmonic generation occurs.

**Mathematical aspects**

Light propagating through a medium or through vacuum may be described by a transverse wave, where the oscillating electric and magnetic field components are solutions to the Maxwell equations. The NLO material is a compound, in which nonlinear polarization (P) is invoked on the application of electric field, which results from the application of intense laser source. The nonlinear polarization induced in the medium have to obey these equations.

\[
\nabla \times E = -\frac{\partial}{\partial t} (B) \tag{1.3}
\]

\[
\nabla \times H = J + \left(\frac{\partial}{\partial t}\right) D \tag{1.4}
\]

\[
\nabla \cdot D = \rho \tag{1.5}
\]

\[
\nabla \cdot B = 0 \tag{1.6}
\]

with relations connecting to the polarization of the medium to displacement vector (D).

\[
D = \varepsilon_0 E + P \tag{1.7}
\]

\[
J = \sigma E \tag{1.8}
\]

\[\sigma\] - conductivity
The induced polarization $P$ may be taken to include both linear and nonlinear part ($P^{NL}$).

$$P = \varepsilon_0 \chi E + P^{NL} \quad \ldots \quad (1.9)$$

Substituting this in Maxwell's equation (1.4) for the curl of the magnetic field yields with $[\varepsilon = \varepsilon_0 (1 + \chi)]$

$$\nabla \times \mathbf{H} = \sigma \mathbf{E} + \varepsilon \left( \frac{\partial}{\partial t} \right) \mathbf{E} + \left( \frac{\partial}{\partial t} \right) P^{NL} \quad \ldots \quad (1.10)$$

Taking the curl of the curl of the electric field component the starting form of first equation (1.3) can be written as

$$\nabla \times \nabla \times \mathbf{E} = -\left( \frac{\partial}{\partial t} \right) \nabla \times \mathbf{B}$$

$$= -\mu \left( \frac{\partial}{\partial t} \right) \nabla \times \mathbf{H}$$

$$= -\mu \frac{\partial}{\partial t} \left[ \sigma \mathbf{E} + \varepsilon \left( \frac{\partial}{\partial t} \right) \mathbf{E} + \frac{\partial}{\partial t} P^{NL} \right] \quad \ldots \quad (1.11)$$

Also the general vector relation holds

$$\nabla \times \nabla \times \mathbf{E} = \nabla (\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E} \quad \ldots \quad (1.12)$$

By taking $\nabla \cdot \mathbf{E} = 0$ (for a charge free medium)

$$\nabla^2 \mathbf{E} = \mu \sigma \left( \frac{\partial}{\partial t} \right) \mathbf{E} + \mu \varepsilon \left( \frac{\partial^2}{\partial t^2} \right) \mathbf{E} + \mu \left( \frac{\partial^2}{\partial t^2} \right) P^{NL} \quad \ldots \quad (1.13)$$

This is the wave equation that describes the light propagation in a medium, provided the medium is dispersion free.
1.3 HARMONIC GENERATION

Second Harmonic Generation (SHG)

The first breakthrough of SHG was achieved in 1961, when pulsed laser beam was sent into a piezoelectric crystal sample. Peter A. Franken and several coworkers at the University of Michigan were the first to observe SHG experimentally [9]. They focused a 3-KW pulse of red ruby laser light onto a quartz crystal. Just about one part of $10^8$ of the incident wave converted to the 347.15 nm UV second harmonic. Thus the frequency of the incident light gets doubled which enables one to extend the range of laser wavelength into the blue and UV parts of the spectrum. This is called frequency doubling. Two waves each of frequency $\omega$ simultaneously superimposed constructively. The resulting wave excites an electron from the ground state to a virtual excited state. On relaxation, one wave of frequency $2\omega$ is emitted. To optimize SHG effect, one must optimize $\chi^{(2)}$. $\chi^{(2)}$ is influenced by various structural features. Crystallographically, the compound must be noncentrosymmetric by nature.

**Coupled equations (Sum and difference frequency generation)**

Consider an input wave with electric field components at frequencies $\omega_1$ and $\omega_2$[10]. Recalling the equation (1.13)

$$\nabla^2 E = \mu \sigma \left( \frac{\partial}{\partial t} \right) E + \mu \epsilon \left( \frac{\partial^2}{\partial t^2} \right) E + \mu \left( \frac{\partial^2}{\partial t^2} \right) p_{NL}$$
This is a vectorial expression that may be used in three fold for the three vector components. In the simple case of frequency mixing with two incoming plane waves propagating along z-axis, the assumption of a linear polarization in a single transverse direction is

\[
E_1 (z,t) = E_1(z) \exp (i\omega_1 t - ik_1 z)
\]

\[
E_2 (z,t) = E_2(z) \exp (i\omega_2 t - ik_2 z)
\] (1.14)

The incoming fields induce a nonlinear polarization at frequency \(\omega = \omega_1 + \omega_2\) that may be written as

\[
P_{NL}(z,t) = dE_1(z)E_2(z)\exp[i(\omega_1+\omega_2)t - i(k_1+k_2)z]
\] (1.15)

And we assume that the new field is created at frequency \(\omega_3 = \omega_1 + \omega_2\) with a field.

\[
E_3 (z,t) = E_3(z) \exp (i\omega_3 t - ik_3 z)
\] (1.16)

Substituting these fields into the wave equation. For plane waves traveling in the z-direction the field gradient may be written as

\[
\nabla^2 E_3(z,t) = \frac{\partial^2}{\partial z^2} E_3(z,t)
\] (1.17)

Left side of the above equation becomes
\[
\frac{\partial^2}{\partial z^2} E_3(z,t) + \mu \sigma \frac{\partial}{\partial t} E_3(z,t) - \mu \varepsilon \frac{\partial^2}{\partial t^2} E_3(z,t) = \]

\[
\frac{d^2}{dz^2} E_3(z,t) + 2ik_3 \frac{d}{dz} E_3(z,t) - \kappa_3^2 E_3(z,t) + i\omega_3 \mu \sigma E_3(z,t) + \mu \varepsilon \omega_3^2 E_3(z,t)
\]

...(1.18)

Applying the assumption the variation of amplitude over the distance of one wavelength will be small.

\[
\left| \frac{d^2}{dz^2} E_3(z,t) \right| \ll \left| 2ik_3 \frac{d}{dz} E_3(z,t) \right|
\]

...(1.19)

The relation between the dielectric constant \(\varepsilon\) and magnetic susceptibility \(\mu\) is

\[
\mu \varepsilon \omega_3^2 - k_3^2 = 0
\]

...(1.20)

\[
2ik_3 \frac{d}{dz} E_3(z) \exp(\omega_3 t - ik_3 z) + i\omega_3 \mu \sigma E_3(z) \exp(\omega_3 t - ik_3 z)
\]

...(1.21)

The right side is evaluated as

\[
\mu \left\{ \frac{\partial^2}{\partial t^2} E_{NL}(z,t) = \mu \frac{\partial^2}{\partial t^2} dE_1(z)E_2(z) \exp\{i(\omega_1 + \omega_2)t - i(k_1 + k_2)z\} \right\}
\]

\[
= -\mu(\omega_1 + \omega_2)^2 dE_1(z)E_2(z) \exp[i(\omega_1 + \omega_2)t - i(k_1 + k_2)z]
\]

...(1.22)
Equating two results

\( \frac{d}{dz} E_3(z) = -\sigma \frac{\mu}{\varepsilon_3} E_3(z) - \frac{i\omega_3}{2} \frac{\mu}{\varepsilon_3} dE_1(z)E_2(z)\exp[-i(k_1+k_2-k_3)z] \) \hspace{1cm} (1.23)

This basic equation found implies that the amplitude of the newly produced wave is coupled through the nonlinear constant \( d \) to the incoming wave. At the same time inverse processes will also take place where the newly generated frequency \( \omega_3 \) mixes with one of the two incoming waves in a difference frequency mixing process like \((\omega_3 - \omega_2 = \omega_1)\). By inserting the fields in the Maxwell’s wave equation in a similar fashion one can derive two more coupled amplitude equations:

\( \frac{d}{dZ} E_1(z) = -\sigma \frac{\mu}{\varepsilon_1} E_1(z) - i \frac{\omega_1}{2} \frac{\mu}{\varepsilon_1} dE_3(z)E_2(z)\exp[-i(k_3-k_2-k_1)z] \)

\( \frac{d}{dZ} E_2(z)^* = -\sigma \frac{\mu}{\varepsilon_2} E_2(z)^* + i \frac{\omega_2}{2} \frac{\mu}{\varepsilon_2} dE_1(z)E_3(z)\exp[-i(k_1+k_2-k_3)z] \) \hspace{1cm} (1.24)

One application of sum frequency generation is to produce tunable radiation in the ultraviolet spectral region by choosing one of the input waves to be the output of a fixed frequency visible laser and the other to be the output of a frequency tunable visible laser. Difference frequency generation (DFG) will convert one high-energy photon and one low energy photon into another low energy photon. DFG has several forms like optical parametric generation and optical parametric oscillation.
Third Harmonic Generation (THG)

In the case of centrosymmetric materials, the expression (1.2) will lack terms in even powers of $E$ and it will reduce to

$$P = \varepsilon_0 \chi^{(1)} E + \varepsilon_0 \chi^{(3)} E E E + \ldots \ldots \ldots \ldots (1.25)$$

Or in vector notation

$$P = \varepsilon_0 \chi^{(1)} E + \varepsilon_0 \chi^{(3)} E^2 E + \ldots \ldots \ldots \ldots (1.26)$$

Thus we find the important relation for (inversion) symmetric media. All even powers in the susceptibility expansion are zero $\chi^{(2n)} = 0$.

As a consequence all even orders of the nonlinear polarization cancel:

$$P^{(2n)} = 0 \ldots (1.27)$$

$$P_{NL} = \varepsilon_0 \chi^{(3)} E E E \ldots (1.28)$$

$\chi^{(3)}$ is a material property that governs the nonlinear response of a medium and all nonlinear processes occurring in that medium. But the third order nonlinear processes are generally weak.

1.4 PHASE MATCHING

The generation of new frequencies by nonlinear polarization in matter is more efficient, when the incident light and the newly generated waves are in suitable phase over the interaction length. For improving the efficiency of the double frequencies, the crystal has to be phase matched [11,12]. This can be achieved in crystals by choosing suitable orientation of the crystal.
with respect to the light beam. It is called phase matching. For efficient frequency doubling, the following relation must be satisfied.

\[ k_2 = 2k_1 \Rightarrow \Delta k = k_2 - 2k_1 \quad \text{...(1.29)} \]

where \( k_1 \) and \( k_2 \) represents the propagation wave number of the fundamental and second harmonic radiation.

Since,

\[ k_2 = \frac{2\omega n_{2\omega}}{C} \quad \text{and} \quad k_1 = \frac{\omega n_\omega}{C} \]

\[ \Delta k = \frac{2\omega}{C} (n_{2\omega} - n_\omega) \quad \text{...(1.30)} \]

The relation reduces to \( n_{2\omega} = n_\omega \quad \text{...(1.31)} \)

Thus phase matching becomes a refractive index criterion. In isotropic media phase matching condition cannot be obtained because of dispersion. A birefringent material has different refractive indices for different polarization of light. A light wave entering an anisotropic crystal splits into two waves traveling at different velocities. In uniaxial crystals having single optic axis the ray corresponding to the wave whose refractive index is independent of the direction of propagation is called ordinary ray. The ray corresponding to the other light wave whose refractive index depends upon the direction of propagation is called extraordinary ray. The behaviour of the refractive index is usually described in terms of refractive index surface, i.e., the indicatrix or index ellipsoid. We therefore have to choose a material in which the refractive index for the extraordinary ray at \( 2\omega \) is equal to the
ordinary ray at \( \omega \). This point to the fact that the effective frequency conversion in the second harmonic is possible only in limited number of crystals [13].

Consider a negative uniaxial crystal. i.e., a crystal for which the refractive index for the ordinary ray is greater than that for the extraordinary ray. Fig.1.1 shows a section through the refractive index surfaces (indicatrix) for one such crystal. The dotted curve represents the surface corresponding to the frequency \( 2\omega \) and the solid curve for frequency \( \omega \). OX is the optic axis of the crystal. The refractive index surface of the ordinary wave and that for the extraordinary wave intersects at A. This means, that for the waves propagating in the direction OA.

![Fig. 1.1 Indicatrix for a negative uniaxial crystal](image-url)
\[ \eta(\omega) = \eta_e(2\omega) \] ...

That is, the incident and the second harmonic waves propagating in this direction are phase matched. In anisotropic media, the ordinary and extraordinary waves can be mixed up and it is possible to tune the refractive index of extraordinary beam by varying angle \( \theta \), which is called as phase matching angle.

\[ \eta_e^{2\omega}(\theta_m) = \eta_0^{0\omega} \] ...

In all nonlinear materials, dispersion in the phase velocity (a refractive index which depends on wavelength) ensures the requirements for energy conservation

\[ \omega_3 = \omega_1 + \omega_2 \] ...

and momentum conservation

\[ \Delta k = k_3 - k_2 - k_1 = c(n_3\omega_3 - n_2\omega_2 - n_1\omega_1) = 0 \] ...

cannot be satisfied simultaneously.

### 1.5 ELECTROOPTIC EFFECT OR POCKELS EFFECT

The Pockels effect is a linear change in the refractive index of a medium in the presence of an external electric field. Here a dc field is applied to a medium through which an optical wave propagates. The change in the polarization due to the presence of these two interacting field components effectively alters the refractive index of the medium [14].
1.6 MATERIALS PERSPECTIVE

Applications of the nonlinear effects demand sufficient knowledge of the nonlinear properties of possible materials. The development of nonlinear optics is also intimately connected with the progress in NLO materials. The fast developments in photonics and optoelectronics necessitate the search for novel materials for NLO applications. Hence the progress in this area would be greatly enhanced by the availability of processed materials with sufficiently large NLO responses. With progress in crystal growth technology, materials having attractive nonlinear properties are being discovered at rapid pace [15-17]. This has enabled the commercial development of single crystals with promising NLO properties.

Conversion efficiency ($\eta$)

To select a suitable nonlinear optical crystal, for a frequency conversion process, it is necessary to obtain high efficiency.

The conversion efficiency for SHG is

$$\eta_{SHG} = \frac{p(2\omega)}{p(\omega)} \alpha \omega^2 d^2 L^2 \frac{sin^2\left(\frac{\Delta k L}{2}\right)}{\left(\frac{\Delta k L}{2}\right)^2} \frac{P(\omega)}{A} \quad \text{...(1.36)}$$

From the derivation, it may be concluded that the conversion efficiency is proportional to the power density, so the total amount of generated light at the second harmonic is proportional to $[P(\omega)]^2$. 
Thus second harmonic generation is a process that is nonlinear in the power dependence.

The efficiency is equal to the square of the nonlinear coefficient $d$, or in other terms proportional to $|\chi^{(2)}|^2$.

The efficiency is proportional with $L^2$ and a "sin"-function involving $L$; it seems that longer crystals will produce more second harmonic.

The efficiency is optimal if $\Delta k = 0$ and this is a condition that generally cannot be met in ordinary media. In birefringent media this condition can be written as $k^{(2)} = 2k^{(0)}$ and also the breakdown of inversion symmetry can be met at the same time.

The condition of $\Delta k = 0$ is referred to as the phase-matching condition. With the use of $k = n\omega/c$ the phase matching relation is given by $\Delta k = k^{(2)} - 2k^{(0)}$.

**General considerations**

Nalwa and Miyata et al [18] have formulated a set of characteristics for a nonlinear optical material to be introduced into optical applications. The nonlinear optical material must be highly transmitting at the fundamental and harmonic wavelengths and must have a laser induced damage threshold high enough to allow optical intensities that will provide adequate conversion efficiency. Phase matching must be possible in the material. The harmonic generation process requires that the phase velocities of the fundamental and harmonic radiation be matched. The
material also needs to be of good optical quality to provide optical transmission without distortion. Above all, the crystal must be acentric for SHG and have large refractive indices. Further, the materials must be non-hygroscopic to introduce it into demonstrable applications and have mechanical and thermal stability. The magnitude and speed of the nonlinearities are essential characteristics in any assessment of the materials for NLO applications. i.e. Fast optical response time.

**Types of NLO materials**

There exist three generic classes of NLO materials. Each class possesses its own complement of favourable and unfavorable attributes.

i. Organic

ii. Inorganic

iii. Semiorganic

**Organic crystals**

Studies show that conjugated organic molecules with large delocalized \( \pi \) electron systems exhibit measurable nonlinear optical and electro optical effects. Such materials are used for frequency doubling and tripling of laser light and are of sizeable interest for high speed data processing, essential for optical computing, optical telecommunication system, electrooptic switching and all optic switching. The varied properties of organic compounds are largely due to the unparalleled ability of the carbon atom to form a variety of stable hybridized bonds. The bonding with carbon atom and other elements are of two types. \( \sigma \) and \( \pi \) bonds. \( \sigma \) bond is confined to inter nuclear axis of
carbon-carbon double bond. They show very short absorption wavelength in UV. The \( \pi \) bonds are the regions of delocalized electronic charge distribution above and below inter nuclear axis that shifts the absorption to longer wavelengths. Nonlinear optical effects of molecular crystals depend on polarizability of the electrons in \( \pi \) bonding orbital because of weak intermolecular, bonding (vanderwaals, dipole-dipole interactions and hydrogen bonds). The attachment of functional groups with electron accepting and donating character at opposite ends of conjugation bridge leads to an essentially charge transfer and thereby enhancing second order nonlinearity. Hence certain class of organic molecules possess large second order nonlinear optical co-efficient [19].

![Donor Bridge Acceptor](image)

As telecommunication systems will use ultrafast electrical and optical signals, faster than 50 GHz, they need optical diagnosing systems. This system uses an optical sampling and electro optical sampling through sum frequency generation and electrooptic effect. However in spite of having large NLO and electro optic characteristics, only a few of organic materials could be so far crystallized in reasonable size for possible applications. This is essentially due to the trade off between transparency and efficiency. Hence it is a long and slow process to replace inorganics. The first observation of SHG in organic material (benzopyrene) was made in 1965 by Rentzepis and Pao [20].
Inorganic crystals

Inorganic materials are much more matured in their application to second order NLO than organics. Since they are ionic bonded and possesses high degree of chemical inertness. In the beginning, studies were concentrated on inorganic materials such as quartz, potassium dihydrogen phosphate (KDP), Lithium Niobate (LiNbO₃) for the fabrication of commercial lasers. In recent years, short wavelength coherent radiation in UV range cover the whole field of photonics applications. The solid state lasers using borate crystals have many advantages compared to traditional gas lasers, which involves compactness, high efficiency, long life and stability. Amongst of all the crystals, crystals based on B-O bonds are large band gap materials and are relatively a new entry in the list of NLO materials, which fulfills the need for laser based industry. They are also phase matchable for third harmonic generation of Nd: YAG laser. High storage capacity optical devices require laser sources at short wavelengths typically around blue regions. Borate crystals have relatively high resistance against laser induced damage and high transparency in the range of UV and visible wavelength. Frequency doubling (SHG), tripling (THG) and double doubling (FHG) is very common with lasers producing blue green light. Different lasers allow the generation of light with almost all imaginable properties but usually not in all desired combinations. Thus there is still a need for new lasers with new combinations of light properties such as large spectral tuning ranges or bandwidths with high average output power and good beam quality [5].
Oxide crystals find lot of applications in piezoelectricity, ferroelectricity and electrooptics.

**Semiorganic crystals**

A combination of inorganic and organic materials provides a potentially useful approach to more efficient and stable NLO crystals. Metal complexes satisfy very different demands of second order NLO materials such as switchable, tunable and multi dimensional properties depending on the subtle interplay of structure property relationships. It offers a wide range of metals with different oxidation states and ligands, which can give rise to tunable electronic properties. Metal coordination complexes provide the following advantages.


2. Breaking of centrosymmetry of the ligand in the crystal.

3. Increase in NLO intensity via metal-ligand bridging interactions.

4. The central ion not only offers a certain anisotropic field to keep NLO active chromophores but also involved in NLO process.

5. Hyperpolarizability ($\beta$) value can also be drastically varied with electronic configuration of metal ions [21].
Semiorganics are classified in 2 categories.

**Type I**: Inorganic salts of large conjugated organic molecules.

**Type II**: Coordination complexes of polarizable organics bonded to metal atoms.

Thus the organic – inorganic hybrid complexes present a new promising type of materials for various applications. The benefits are due to the materials such as wide range of electronic characteristics, mechanical hardness and thermal stability and on the other hand structural variety, large polarizability and easy processing of organics. The refractive indices of the crystal could also be tuned due to exchange ability of metal and halogen species within anions. Thus they attract lot of interest because of their application for electroluminescent and optoelectronic materials.