# Chapter-3

# Non-Linear Optics

## 3.1 Introduction

Before the advent of lasers, it was believed that the optical properties of the medium do not depend upon the intensity of the radiation and depends on the frequency of radiation. In the pre-laser era, the field strengths of the conventional light sources ~$10^3$ V/cm were much less than the field strengths of atomic and inter-atomic fields ~$10^7$ to $10^{10}$ V/cm. It is quite natural to believe that the light wave with such a low intensity is not able to affect the atomic fields to the extent of producing a change in the optical parameters. According to linear optics the polarization **P** is proportional to the electric field **E**. That is,

$$\mathbf{P} \propto \mathbf{E} \quad ; \text{Or, } \mathbf{P} = \varepsilon_0 \chi \mathbf{E} \qquad (1)$$

where, $\chi$ is called the dielectric susceptibility of the medium.

The high degree of coherence of the laser radiation has made it possible to have extremely high spatial concentration of light power. It is now possible to generate 1MW pulses, lasting for a few tenths of nanoseconds, using moderately powerful lasers. It can be shown that the field strengths produced by such high-power lasers is in the range of atomic fields. At such high fields one must consider the nonlinear effects of the field strength on dielectric polarization.

Lasers can be used for the generation of light with very high optical intensities. These can give rise to a number of nonlinear optical effects (→ ***nonlinear optics***), the most important of which are:

- Parametric nonlinearities occur in certain crystal materials with $\chi(2)$ nonlinearity, giving rise to effects such as **frequency doubling**, **sum and difference frequency generation**, and **parametric amplification** (→ ***nonlinear frequency conversion***).
- There are also parametric nonlinearities arising from $\chi^{(3)}$. The **Kerr effect** raises the **refractive index** by an amount which is proportional to the intensity. This is related to effects like **self-focusing**, **self-phase modulation**, **cross-phase modulation**, and **four-wave mixing**.
- Spontaneous and stimulated **Raman scattering** is the interaction of light with "optical phonons".
- Spontaneous and stimulated **Brillouin scattering** is the interaction of light with "acoustic phonons" and typically involves counterpropagating waves. Brillouin and Raman scattering are related to the non-instantaneous part of the third-order nonlinear response.
- **Two-photon absorption** is a process where two **photons** are simultaneously absorbed, leading to an excitation for which a single **photon energy** would not be sufficient. Its strength is related to the imaginary part of the $\chi^{(3)}$ tensor, and is generally large for semiconductor media with small **band gap energy**.

There are also various other effects which are not directly based on optical nonlinearities, but are nevertheless affecting optical phenomena:

- Saturation of **gain** occurs particularly in **lasers** and **amplifiers**. Similarly, there are nonlinear losses in **saturable absorbers**, e.g. in **SESAMs** used for passive **mode locking** or **Q switching**.

- Photorefractive effects are observed in certain ferroelectric crystals such as $LiNbO_3$. They are used for, e.g., **holographic** data storage, and can be detrimental in **nonlinear frequency conversion**.
- There are various kinds of effects involving heating, e.g. **thermal lensing** in laser **gain media** or thermal detuning of optical resonators (e.g. **enhancement cavities**).

In optical **fiber technology**, optical nonlinearities are of high interest. In **fibers** there is a particularly long interaction length combined with the high intensity resulting from a small mode area. Therefore, nonlinearities can have strong effects in fibers. Particularly the effects related to the $\chi^{(3)}$ nonlinearity – Kerr effect, Raman scattering, Brillouin scattering – are often important, despite the relatively weak intrinsic **nonlinear coefficient** of silica: either they act as essential nonlinearities for achieving certain functions (e.g. **pulse compression**), or they constitute limiting effects in **high-power fiber lasers and amplifiers**.

Usually, the strength of nonlinear effects is determined by the **peak power**. However, there are cases where stronger effects occur for lower peak powers, as explained in a **Spotlight article**.

Strong nonlinearities also occur at intensities which are high enough to cause ionization in the medium. This can lead to optical **breakdown**, possibly even associated with **laser-induced damage** of the material. In gases, extremely high optical intensities can be applied, which can lead e.g. to **high harmonic generation**.

## 3.2 Non-Linear Polarisation and Harmonic Generation

The phenomenon of harmonic generation can be explained as follows. The polarisation given by eqn.1 is valid for the field strengths of conventional sources. With highly intense laser radiation the relationship between **P** and **E** is nonlinear and one has to consider the higher order terms of the electric field. Thus, the general equation for **P** can be written as,

$$P = \varepsilon_0 \left\{ \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + .......... \right\} \qquad (2)$$

where, $\chi^{(1)}$ is same as $\chi$ in eqn.1. The coefficients $\chi^{(2)}$, $\chi^{(3)}$, ........ define the degree of nonlinearity and are known as nonlinear susceptibilities. If the field intensity is low, we retain only the first term in eqn.2 and neglect all the higher order terms. This is the case of pre-laser optics known as *linear optics*. If the intensity of the field becomes large the higher order terms in eqn.2 are significant. Thus, the susceptibility and hence the optical properties of the medium are nonlinear and the corresponding optics is known as *non-linear optics*.

Let the radiation field be represented by,

$$E = E_0 \cos\omega t \qquad (3)$$

Then eqn.2 becomes,

$$P = \varepsilon_0 \left\{ \chi^{(1)} E_0 \cos\omega t + \chi^{(2)} E_0^2 \cos^2\omega t + \chi^{(3)} E_0^3 \cos^3\omega t + .......... \right\} \qquad (4)$$

Using the trigonometric relations, $\cos^2\theta = \frac{1+\cos 2\theta}{2}$; and $\cos^3\theta = \frac{\cos 3\theta + 3\cos\theta}{4}$

$$P = \varepsilon_0 \left\{ \chi^{(1)} E_0 \cos\omega t + \chi^{(2)} E_0^2 \left( \frac{1+\cos 2\omega t}{2} \right) + \chi^{(3)} E_0^3 \left( \frac{\cos 3\omega t + 3\cos\omega t}{4} \right) + .......... \right\}$$

$$= \varepsilon_0 \left\{ \frac{1}{2}\chi^{(2)} E_0^2 + \left( \chi^{(1)} E_0 + \frac{3}{4}\chi^{(3)} E_0^3 \right)\cos\omega t + \frac{1}{2}\chi^{(2)} E_0^2 \cos 2\omega t + \frac{1}{4}\chi^{(3)} E_0^3 \cos 3\omega t + ..... \right\} \qquad (5a)$$

i.e. $$P = P_0 + P_1 \cos\omega t + P_2 \cos 2\omega t + P_3 \cos 3\omega t + .......... \qquad (5b)$$

The first term is a constant term, which gives rise to a d.c. polarisation. The effect of which has no practical importance. The second term, which oscillates at frequency ω, is called the *first* or *fundamental harmonic of polarisation*. The third term, which oscillates at frequency 2ω, is called the *second harmonic of polarisation* and the fourth, which oscillates at frequency 3ω, is called the *third harmonic of polarisation* and so on.

## 3.3 Wave propagation in anisotropic crystals*

The optical properties of most materials are isotropic. The refractive index and hence the velocity of light are same in all directions in isotropic materials. However, there are a number of crystalline solids that are anisotropic. The two types of anisotropic crystals are uniaxial crystals (examples, calcite, quartz, etc.) and biaxial crystals (examples, aragonite, topaz, etc.). Each category of crystals is a function of symmetry. Crystals of cubic symmetry are isotropic. Crystals that have trigonal, tetragonal and hexagonal symmetries are all uniaxial, whereas crystals with orthorhombic, monoclinic and triclinic symmetries are always biaxial.

In anisotropic crystals the refractive index and hence the velocity of light are different in different directions, or, they depend on the polarization of the light beam. They exhibit the property of double refraction, producing the ordinary and extraordinary rays with orthogonal polarizations. In a uniaxial crystal, there exists one orientation of the crystal for which the index of refraction and wave velocity are independent of the polarization of the beam. This direction is known as the *optic axis*. In biaxial crystals there is no orientation for which the refractive index is same for two orthogonal polarizations.

## 3.4 Second harmonic generation

By eqn.5a or 5b of sec.3.2 we have seen that there are polarisations with different frequencies in a medium with non-linear dependence of polarisation on the electric field. The availability of high-power laser beams has made a considerable progress in the work on nonlinear optics. Non-linear properties of materials in optical region have been demonstrated by the harmonic generation of light. One of the most striking nonlinear effects that occur when high intensity radiation interacts with matter is the phenomenon of *second harmonic generation*, in which an optical frequency 2ω is generated from the interaction of high-power laser beam of frequency ω with a suitable crystal.

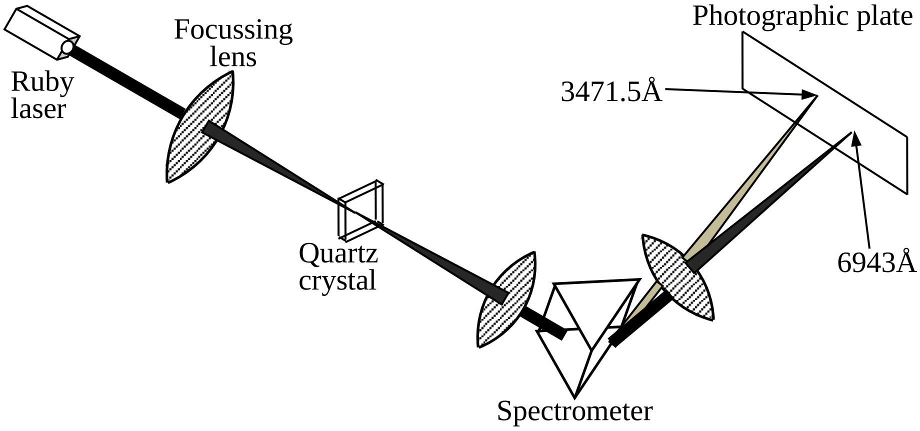


**Fig.a**: Schematic diagram of experimental set up used by Franken and coworkers

The first demonstration of second harmonic generation was made by Franken and co-workers in 1961. Fig.a gives the schematic diagram of the experimental set up. In this experiment light of wavelength 3471.5Å was generated from the interaction of ruby laser of wavelength 3471.5Å with a quartz crystal.

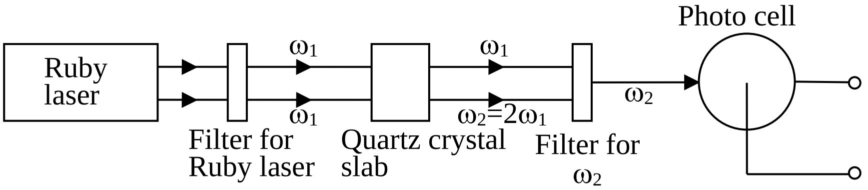


**Fig.b**: Schematic diagram of modern experimental set up for second harmonic generation

A highly intense radiation oscillating at frequency ω can produce a polarisation in the medium that oscillating at frequency 2ω. This polarisation can radiate an electromagnetic wave of frequency 2ω, which propagates with the same velocity as that of the incident radiation. The wave thus produced has the same characteristics of directionality and mono-chromaticity as the incident wave and is emitted in the same direction. This phenomenon is known as the *Second Harmonic Generation* (SHG). It can be shown that the second harmonic generation cannot occur in an isotropic medium.

## 3.5 Symmetry requirement for second Harmonic generation

In second harmonic generation an intense laser beam of angular frequency ω is passed through a crystal having a non-zero value of $\chi^{(2)}$ the emerging beam from the crystal contains the input frequency ω and another frequency twice that of the input frequency (2ω). In most crystalline materials the second order non-linear electric susceptibility $\chi^{(2)}$ depends on the direction of propagation of the beam, polarization of the electric field and the orientation of the optic axis of the crystal. In such crystalline materials, since the vectors **p** and **E** are not necessarily parallel, the coefficients χ must be treated as tensors. The second order polarisation, therefore, may be represented by the relation of the type,

$$p_i^{(2)} = \varepsilon_0 \sum_{j,k} \chi_{ijk}^{(2)} E_j E_k \qquad (6)$$

where, i, j and k represent the coordinates x, y and z. Most of the coefficients $\chi_{ijk}$, however, are usually zero and we have to deal only with one or two components. It must be mentioned here that the SHG represented by eqn.6 occurs only in certain type of crystals.

If the crystal is isotropic, $\chi_{ijk}$ is independent of the direction and hence is a constant. If we now reverse the direction of the axes (i.e. space inversion, $x \to -x$, $y \to -y$ and $z \to -z$) leaving the electric field and the dipole moment unchanged in direction. Then the sign of the electric field and the dipole moment must change. Then by eqn.6,

$$-p_i^{(2)} = \varepsilon_0 \sum_{j,k} \chi_{ijk}^{(2)} \left(-E_j\right)\left(-E_k\right)$$

$$= \varepsilon_0 \sum_{j,k} \chi_{ijk}^{(2)} E_j E_k = p_i^{(2)} \qquad (7)$$

i.e. $-2p_i^{(2)} = 0$ or, $2p_i^{(2)} = 0$

That is, $-p_i^{(2)} = p_i^{(2)} = 0$

Then by eqn.6 or 7, we get,

$$\chi_{ijk}^{(2)} = 0 \qquad (8)$$

Eqn.8 shows that second harmonic generation cannot occur in an isotropic medium such as liquids or gases and in centrosymmetric crystals (crystals symmetrical about a point). That is, only crystals that lack inversion symmetry exhibit SHG.

In the case of non-centrosymmetric materials (anisotropic crystals, such as uniaxial crystals) both quadratic $p^{(2)}$ and cubic $p^{(3)}$ are present. However, generally, the cubic term is substantially smaller than the second order term and may be ignored. Thus, neglecting the higher order terms in eqn.4 we get,

$$P = \varepsilon_0\chi^{(1)}E + \varepsilon_0\chi^{(2)}E^2 \tag{9}$$

and the medium is said to have second order linearity. (Graph between P and $E^2$ is a straight line).

## 3.6 Third Harmonic Generation

In the case of centrosymmetric materials eqn.2 does not contain even powers of E (or, contains only odd powers of E). Thus,

$$\begin{aligned} P &= \varepsilon_0\chi^{(1)}E + \varepsilon_0\chi^{(3)}E^3 + \dots\dots\dots\dots \\ &= \varepsilon_0\chi^{(1)}E + \varepsilon_0\chi^{(3)}E^2E + \varepsilon_0\chi^{(5)}E^4E + \dots\dots\dots\dots \end{aligned} \tag{10}$$

Therefore, Third Harmonic Generation (THG) is possible in crystals that exhibit inversion symmetry. The development of Q-switched lasers had made it possible to generate third harmonics in crystals. However, the energy conversion efficiency in such cases is very low. For example, in calcite the maximum energy conversion efficiency in the third harmonic was 0.01%.

THG can, in principle, occur in all matter, as it does not lead to the condition of non-centrosymmetry. The effect has been investigated in solids and liquids. It has also been investigated in gases, especially in alkali metal vapours. Because of the relatively low density of gases, the third harmonic generation can become quite high up to 10%. Also, the limiting laser intensity in gases is orders of magnitude higher than that in condensed matter.

For wavelengths in infrared, visible and ultraviolet the use of crystals to generate non-linear response is far more effective than using gases. SHG is not possible in gases since they are isotropic materials. However, it is possible to generate higher order harmonics in gases. Third and higher order harmonics up to more than 100 have been generated in gases and vapours. An example is the generation of 109th harmonic in neutral neon atoms by focussing 35 mJ (millijoule), 125 fs (femtosecond) duration Ti:$Al_2O_3$ ultrashort laser pulses at 806.5 nm into a thin layer of neon gas.

## 3.7 Nonlinear refractive index

When an intense laser beam passes through a material, the electric field of the beam can induce a change in the refractive index of the material, that is proportional to the intensity of the beam. This is a non-linear effect and is known as Optical Kerr Effect. The total refractive index of the material is the sum of the refractive index $n_0$ in the absence of the beam and an intensity dependent term $n_{2I}I$, where $n_{2I}$ is the second order non-linear refractive index and I is the intensity of the beam.

i.e. $$n(\omega) = n_0(\omega) + n_{2I}(\omega)I(\omega) \tag{11}$$

$n_0(\omega)$ is known as the fundamental refractive index of the material at any specific frequency ω. The change in the refractive index can be positive or negative. Values of $n_{2I}$ is generally small ($\simeq 3\times10^{-20}\,m^2W^{-1}$ for silica), so that high beam intensities are required to have a significant effect.

It can be shown that the coefficient $n_{2I}(\omega)$ of the non-linear refractive index term in eqn.11 as,

$$n_{2I}(\omega) \cong \frac{9\pi}{n_0^2(\omega)}\chi^{(3)} \tag{12}$$

**Self-focussing or defocussing**: In the time domain Kerr effect leads to phase shift and frequency shift. However, if the refractive index change is positive, the Kerr effect combined with diffraction can lead to self-focussing (or, defocussing). This is because the centre of the beam will have higher intensity and hence a higher refractive index than the edges of the beam. Or, there exists a refractive index gradient from the axis to the edges of the beam. This variation in refractive index acts as a positive lens and focusses the beam inside a dielectric with a strength dependent on the peak power.

For non-magnetic materials we have,

$$n = \sqrt{K} \tag{13}$$

where, K is the dielectric constant (relative permittivity $\varepsilon_r$) of the material, which is related to the electric susceptibility of the material by the relation,

$$K = 1+\chi \tag{14}$$

Thus,

$$n = \sqrt{1+\chi} \tag{15}$$

Since $\chi$ is a function of electric field, the refractive index depends on the electric field. The dependence of refractive index on field is non-linear and it leads to the non-linear effect known as self-focussing of intense beam of light. Since in defocussing there is no change in the frequency of the incident beam, we need to consider only the second term in equation for P (eqn.5a), which describes the fundamental harmonic.

i.e.

$$p^{(1)} = \varepsilon_0\left(\chi^{(1)}E_0 + \frac{3}{4}\chi^{(3)}E_0^3\right)\cos\omega t$$

$$= \varepsilon_0\left(\chi^{(1)} + \frac{3}{4}\chi^{(3)}E_0^2\right)E = \varepsilon_0\chi E$$

$\therefore$

$$\chi = \chi^{(1)} + \frac{3}{4}\chi^{(3)}E_0^2 \tag{16}$$

Thus,

$$n = \sqrt{1+\chi^{(1)} + \frac{3}{4}\chi^{(3)}E_0^2} = \sqrt{\varepsilon_l + \varepsilon_{nl}} \tag{17}$$

where,

$$\varepsilon_l = 1+\chi^{(1)} \tag{18}$$

is the dielectric constant of the linear medium and,

$$\varepsilon_{nl} = \frac{3}{4}\chi^{(3)}E_0^2 \tag{19}$$

is the non-linear increment of the dielectric constant. Eqn.17 gives the relation between non-linear refractive index and the third order susceptibility. Eqn.17 can be written as,

$$n = \sqrt{\varepsilon_l}\sqrt{1+\frac{\varepsilon_{nl}}{\varepsilon_l}} = \sqrt{\varepsilon_l}\left(1+\frac{\varepsilon_{nl}}{\varepsilon_l}\right)^{1/2}$$

Since $\varepsilon_{nl} \ll \varepsilon_l$,

$$n \approx \sqrt{\varepsilon_l}\left(1+\frac{\varepsilon_{nl}}{2\varepsilon_l}\right) = n_l\left(1+\frac{\varepsilon_{nl}}{2n_l^2}\right) = n_l\left(1+\frac{3}{8}\frac{\chi^{(3)}E_0^2}{n_l^2}\right)$$

$$\approx n_l\left(1+n_{nl}E_0^2\right) = n_l + n_l n_{nl}E_0^2 \tag{20}$$

where, $$n_{nl} = \frac{3}{8}\frac{\chi^{(3)}}{n_l^2} \tag{21}$$

Using eqn.19, we get,

$$n_{nl} = \frac{3}{8n_l^2}\times\frac{4}{3}\left(\frac{\varepsilon_{nl}}{E_0^2}\right) = \frac{\varepsilon_{nl}}{2n_l^2E_0^2}$$

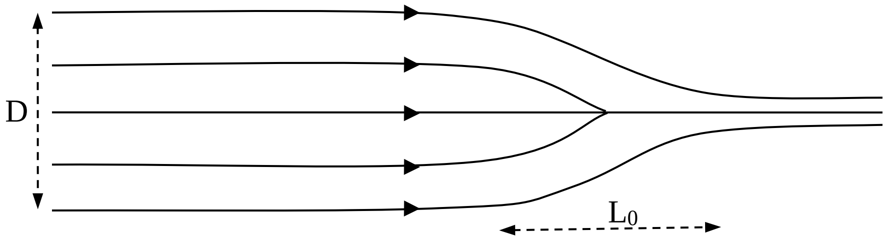
Or, $$n_l n_{nl} E_0^2 = \frac{\varepsilon_{nl}}{2n_l} = \frac{\varepsilon_{nl}}{2\sqrt{\varepsilon_l}} \tag{22}$$

Using eqns.18 and19,

$$n_l n_{nl} E_0^2 = \frac{3}{8}\left(\frac{\chi^{(3)}E_0^2}{\sqrt{1+\chi^{(1)}}}\right) \tag{23}$$

The second term on the RHS of eqn.20 is the non-linear increment in the expression for the refractive index, which is given by eqn.23. We, thus, see that the refractive index is proportional to the square of the amplitude of the field, that is to the intensity of the beam.

The intensity of the laser beam is not constant over its cross section. It is maximum at the axis of the beam and falls off gradually away from the axis. Since the refractive index depends on intensity it also decreases away from the axis of the beam and hence velocity of the beam $\left(v = \frac{c}{n}\right)$ increase with the distance away from the axis of the beam. Consequently, the plane wavefront incident on the material becomes concave (converging beam) as it propagates through the medium and contracts towards the axis of the beam. Or, in other words, the beam in the medium self-focusses and then propagates as a narrow light fibre.



The distance $L_0$ over which the beam self-focusses can be approximately estimated using the formula,

$$L_0 = \frac{D}{\sqrt{n_{nl}E_0^2}} \tag{24}$$

where, D is the diameter of the beam. Self-focussing occurs when the intensity of the reaches a certain limiting value. The threshold intensity is given by,

$$I_{threshold} = \frac{\lambda^2}{n_l^2 n_{nl} D^2} \tag{25}$$

Eqn.25 shows that threshold intensity will be lower for higher frequencies and greater non-linear susceptibilities. ($n_{nl}$ is related to non-linear susceptibility).

## 3.8 Multiphoton absorption

Prior to the appearance of lasers only the two photon processes (one photon absorbed and another emitted: Fluorescence, Hyper Rayleigh scattering, Raman scattering) were observed experimentally. Multiphoton processes have assumed importance only after the advent of lasers. Multiphoton absorption is another mechanism of non-linear absorption in which multiple photons are absorbed simultaneously by the absorbing medium.

At high optical intensity it is possible to bridge the bandgap between valance band and conduction band by simultaneous absorption of two or more lower-energy photons, where the sum of the photon energies must exceed the bandgap energy. Such processes are called *multiphoton absorption*. Substantial multiphoton absorption can occur only at high optical intensities, that can be generated with lasers.

**Multiphoton (multi-quantum) photoelectric effect**: It is a multiphoton process in which an electron needs to absorb a given number of photons to escape from the surface of a metal. According to Einstein's photoelectric equation the energy of the liberated electron is given by,

$$\frac{1}{2}mv^2 = h\nu - W \tag{26}$$

where, W is the photoelectric work function and $h\nu$ is the photon energy. Eqn.26 shows that the photoelectric effect will be observed only if $h\nu > W$. The threshold frequency is given by,

$$\nu_0 = \frac{W}{h} \tag{27}$$

This effect has nothing to do with the intensity of radiation.

In the pre-laser optics, it was assumed that an electron can absorb only one photon at a time and the photoelectric effect could not be observed at frequencies lower than the threshold frequency.

But it is possible to absorb two or more photons simultaneously in an interaction of extremely high intensity laser pulses with the metal surfaces. This is a non-linear effect. In this process Einstein's law of photoelectric effect can be modified as,

$$\frac{1}{2}mv^2 = Nh\nu - W \qquad (26)$$

where, N is the number of photons absorbed in this process. Therefore, the condition for the photoelectric effect now becomes,

$$\nu \geq \frac{W}{Nh} \qquad (27)$$

Then the threshold frequency is given by,

$$\nu_{\text{threshold}} = \frac{W}{Nh} \tag{28}$$

Thus, higher the intensity (higher number of photons), lower the threshold frequency. The photoelectric effect, therefore, depends both on the frequency of radiation as well as on its intensity. The effect may be called as multi-quantum (multiphoton) photoelectric effect.

## 3.9 Nonlinear optical materials

A Nonlinear Optical material is a compound in which a nonlinear polarization is invoked on by the application of an intense electric field. This electric field results from the external application of an intense laser source. Optical nonlinearity is primarly molecular in nature.

Because of the effectiveness in generating new frequencies from the existing lasers, via harmonic generation and sum and difference frequency generation, there has been an extensive effort in recent years to identify effective materials for such processes. These materials should have the following properties.

1. They should have large nonlinearity.
2. These materials must be transparent not only at the laser frequency but also at the newly generated frequencies.
3. They must be resistant to optical damage.
4. They must have high mechanical hardness.
5. They must exhibit good thermal and chemical stability.
6. They must be capable of being grown in useful sizes.
7. They must have appropriate phase-matching properties.

We recall that second harmonic crystals must have no inversion symmetry, which suggests that only crystalline materials can be used for SHG. The third harmonic crystals can have inversion symmetry (can be centrosymmetric).

Bulk second order nonlinear materials are generally inorganic crystals. A number of semiconductor compounds are useful for SHG when used in waveguides and some organic materials have also been under investigation in recent years. Table below lists a number of second order nonlinear optical materials that have high nonlinear conversion coefficients as well as the necessary transparency.

**Second order nonlinear optical materials**

| Crystal | Transparency region in µm |
|---|---|
| $LiB_3O_5$ | 0.16–2.6 |
| β-$BaB_2O_4$ | 0.19–2.5 |
| $KNbO_3$ | 0.40–5.5 |
| $LiNbO_3$ | 0.40–5.0 |
| $Ba_2NaNbO_{15}$ | 0.37–5.0 |
| KDP | 0.20–1.4 |
| KTP | 0.35–4.4 |
| $AgGaS_2$ | 0.50–13.2 |
| AgGaSe | 0.78–18.0 |

## Third-order nonlinear optical organic materials for photonic switching

A long-standing prediction is that the refractive index of organic materials possessing extended electron conjugation can be changed instantaneously by exposure to light, making them attractive for all-optical signal processing. At present only a few of the polydiacetylenes and poly(p-phenylenevinylene)s seem to have properties adequate for this application.

Table 2. Third-order nonlinear optical susceptibilities of selected conjugated polymers with chemical structures shown in Figure 3. $\chi'^{(3)}$ is real and $\chi''^{(3)}$ imaginary part of cubic susceptibility

| **Material** | **Form** | **Fundamental wavelength (µm)** | **$\chi'^{(3)}$ ($10^{-14}$ esu)** | **$\chi''^{(3)}$ ($10^{-14}$ esu)** | **$\lvert\chi^{(3)}\rvert$ ($10^{-14}$ esu)** | **Remark** |
|---|---|---|---|---|---|---|
| PDA–PTS | single crystal | 1.89 | | | 85<br>(50)×$10^3$&lt;1000 | ‖chain,<br>3 ph<br>⊥chain |

| **Material** | **Form** | **Fundamental wavelength (µm)** | **$\chi'^{(3)}$ ($10^{-14}$ esu)** | **$\chi''^{(3)}$ ($10^{-14}$ esu)** | **$\lvert\chi^{(3)}\rvert$ ($10^{-14}$ esu)** | **Remark** |
|---|---|---|---|---|---|---|
| PDA–TCDU | single crystal | 2.62 | | | 16 (10)×$10^3$&lt;200 | ‖chain<br>⊥chain |
| | | 1.89 | | | 7 (5)×$10^3$&lt;70 | ‖ chain<br>⊥chain |
| | | 2.62 | | | 37 (14)×$10^2$&lt;40 | |
| PDA–DCHD | Thin single crystal | 2.1 | | | 1.7×$10^4$ | 3 ph, sp |
| PDA–BTFP | Thin single crystal | 2.1 | | | 1.8×$10^4$ | 3 ph, sp |
| PDA–DFMP | Thin single crystal | 2.1 | | | 0.45×$10^4$ | sp |
| PDA–PTS | Thin single crystal | 2.1 | | | 0.4×$10^4$ | 3 ph, sp |
| PDA–AFA | LB film (blue) | 1.35 | | | 5.6 (1)×$10^3$ | 2 ph, sp |
| PDA–AFA | LB film (blue) | 1.907 | | | 8.3 (8)×$10^3$ | 3 ph, sp |
| PDA–AFA | Thin film (red) | 1.22 | | | 3.8 (4)×$10^3$ | 2 ph, sp |
| pDCH | Isotropic film | 1.35 | | | 7.0 (7)×$10^3$ | 2 ph, sp |
| pDCH | Oriented film | 1.907 | | | 6.0 (6)×$10^4$ | 3 ph, sp |
| PA | Isotropic film | 1.907 | | | 56 (16)×$10^4$ | 3 ph, sp |
| PA | Oriented film | 1.907 | | | 1.7 (7)×$10^6$ | 3 ph |
| PA | Oriented film | 1.907 | | | 2.7×$10^6$ | 3 ph |

| Material | Form | Fundamental wavelength (μm) | $\chi'^{(3)}$ ($10^{-14}$ esu) | $\chi''^{(3)}$ ($10^{-14}$ esu) | $\lvert\chi^{(3)}\rvert$ ($10^{-14}$ esu) | Remark |
|---|---|---|---|---|---|---|
| PPV | Oriented film | 1.45 | | | $1.4\times10^{4}$ | 3 ph, sp |
| β-Carotene | spun film | 1.418 | | | 160 (25) | 3 ph, sp |
| Polysilane | spun film | 1.064 | $10.3\times10^{2}$ | $4\times10^{2}$ | $11\times10^{2}$ | 3 ph c |
| PDHS | | 1.907 | $1.3\times10^{2}$ | | $1.3\times10^{2}$ | |

*Note*: Chemical structures of different polymers are shown in Figure 3.

## 3.10 Nonlinear optical processes*

Nonlinear optics explains nonlinear response of properties such as frequency, polarization, phase or path of incident light. These nonlinear interactions give rise to a host of optical phenomena:

**Frequency-mixing processes**

- Second-harmonic generation (SHG), or *frequency doubling*, generation of light with a doubled frequency (half the wavelength), two photons are destroyed, creating a single photon at two times the frequency.
- Third-harmonic generation (THG), generation of light with a tripled frequency (one-third the wavelength), three photons are destroyed, creating a single photon at three times the frequency.
- High-harmonic generation (HHG), generation of light with frequencies much greater than the original (typically 100 to 1000 times greater).
- Sum-frequency generation (SFG), generation of light with a frequency that is the sum of two other frequencies (SHG is a special case of this).
- Difference-frequency generation (DFG), generation of light with a frequency that is the difference between two other frequencies.
- Optical parametric amplification (OPA), amplification of a signal input in the presence of a higher-frequency pump wave, at the same time generating an *idler* wave (can be considered as DFG).
- Optical parametric oscillation (OPO), generation of a signal and idler wave using a parametric amplifier in a resonator (with no signal input).
- Optical parametric generation (OPG), like parametric oscillation but without a resonator, using a very high gain instead.
- Half-harmonic generation, the special case of OPO or OPG when the signal and idler degenerate in one single frequency,
- Spontaneous parametric down-conversion (SPDC), the amplification of the vacuum fluctuations in the low-gain regime.
- Optical rectification (OR), generation of quasi-static electric fields.
- Nonlinear light-matter interaction with free electrons and plasmas.

**Other nonlinear processes**

- Optical Kerr effect, intensity-dependent refractive index.

  - Self-focusing, an effect due to the optical Kerr effect (and possibly higher-order nonlinearities) caused by the spatial variation in the intensity creating a spatial variation in the refractive index.
  - Kerr-lens modelocking (KLM), the use of self-focusing as a mechanism to mode-lock laser.
  - Self-phase modulation (SPM), an effect due to the optical Kerr effect (and possibly higher-order nonlinearities) caused by the temporal variation in the intensity creating a temporal variation in the refractive index.
  - Optical solitons, an equilibrium solution for either an optical pulse (temporal soliton) or spatial mode (spatial soliton) that does not change during propagation due to a balance between dispersion and the Kerr effect (e.g. self-phase modulation for temporal and self-focusing for spatial solitons).
- Cross-phase modulation (XPM), where one wavelength of light can affect the phase of another wavelength of light through the optical Kerr effect.
- Four-wave mixing (FWM), can also arise from other nonlinearities.
- Cross-polarized wave generation (XPW), a effect in which a wave with polarization vector perpendicular to the input one is generated.
- Modulational instability.
- Raman amplification
- Optical phase conjugation.
- Stimulated Brillouin scattering, interaction of photons with acoustic phonons
- Multi-photon absorption, simultaneous absorption of two or more photons, transferring the energy to a single electron.
- Multiple photoionisation, near-simultaneous removal of many bound electrons by one photon.
- Chaos in optical systems.

**Related processes**

In these processes, the medium has a linear response to the light, but the properties of the medium are affected by other causes:

- Pockels effect, the refractive index is affected by a static electric field; used in electro-optic modulators.
- Acousto-optics, the refractive index is affected by acoustic waves (ultrasound); used in acousto-optic modulators.
- Raman scattering, interaction of photons with optical phonons.

## 3.11 Four wave mixing

Four wave mixing is a nonlinear effect arising from a third order optical nonlinearity as is described with a $\chi^{(3)}$ coefficient. We have already seen that in third harmonic generation the material-photon system destroys three photons of frequency $\omega_1$ and creates one photon of frequency $3\omega_1$. The fig.a indicates three virtual energy levels of the combined material-photon system.

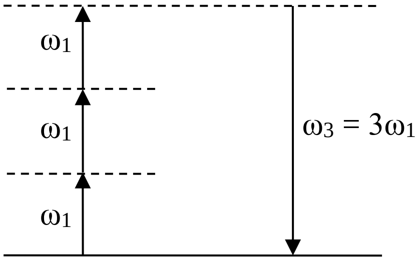


**Fig.a**

When the input beam consists of photons of three different frequencies $\omega_1$, $\omega_2$ and $\omega_3$ the process becomes much more complex because there are many more terms to consider in writing the expression for the third order nonlinear polarisation. Two of these processes are shown in the energy level diagrams given in figures b and c.

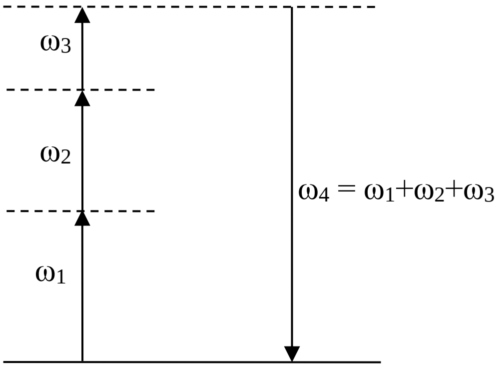


**Fig.b**

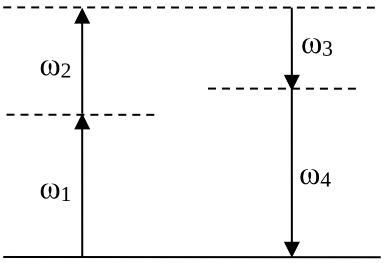


**Fig.c**

The first process (fig.b) is simply the equivalent of the third harmonic generation. In this case three photons of different frequencies combine to form a photon of fourth frequency. The second process (fig.c) involves the creation of two photons of different frequencies at the expense of two other photons of different frequencies. These processes which involves four photons, along with its many ramifications (subdivisions of a complex structure) is known as *four wave mixing*. Or, in other words, FWM or sometimes FPM (four photon mixing) describes a nonlinear optical effect at which four photons interact with each other due to the third order nonlinearity $\chi^{(3)}$ of the material. As a result, new waves of sum and difference frequencies of two waves of different frequencies are generated during the propagation in waveguide. This may cause cross-talks in fibre optics communication systems.

**Nondegenerate and degenerate four wave mixing**: In the above mentioned process, if all the four frequencies are different it is called nondegenerate four wave mixing. If two frequencies out of the four frequencies coincide the process is known as degenerate four wave mixing.

**Phase matching**: Four wave mixing is a phase sensitive process, i.e. the interaction depends on the relative phases of all the beams. Therefore, the effect is produced only if a phase matching condition is satisfied. Four wave mixing in fibres is related to self-phase modulation and cross-phase modulation.

Four wave mixing is relevant in a variety of different situations.

1. It can be involved in strong spectral broadening in fibre amplifiers.
2. The parametric amplification by four wave mixing can be utilized in fibre-based optical parametric amplifiers and oscillators.
3. FWM can have important effects in optical fibre communication, particularly in the context of wavelength division multiplexing, where it can cause cross-talk between different wavelength channels, and/or an imbalance of channel powers.
4. FWM is applied for laser spectroscopy most commonly in the form of coherent anti-stokes Raman spectroscopy, where two input waves generate a detected signal with slightly higher optical frequency.
5. FWM can also be applied for phase conjugation, holographic imaging and optical image processing.

## 3.12 Z-scan Technique

There are several methods for measuring optical nonlinearity of materials. They are,

1. Degenerate four wave mixing.
2. Nearly degenerate three wave mixing.
3. Z-scan based on self-focussing.
4. Optical Kerr effect.
5. Interferometric method
6. Beam self-bending.
7. Third order harmonic generation.

Among these methods the Z-scan method has gained rapid acceptance by the nonlinear community as a standard technique for separately determining the nonlinear changes in refractive index Δn and changes in absorption Δα. This acceptance is primarily due to the simplicity of the technique as well as the simplicity of the interpretation.

In most experiments Δn and Δα can be determined directly from the data.

In 1989 Sheik-Bahae *et al* (et al is a short form of Latin phrase et alia means ‘and others’) developed a sensitive self-focussing measurement technique that involves focussing a laser beam through a thin sample and detected transmitted by a small aperture in the far field.

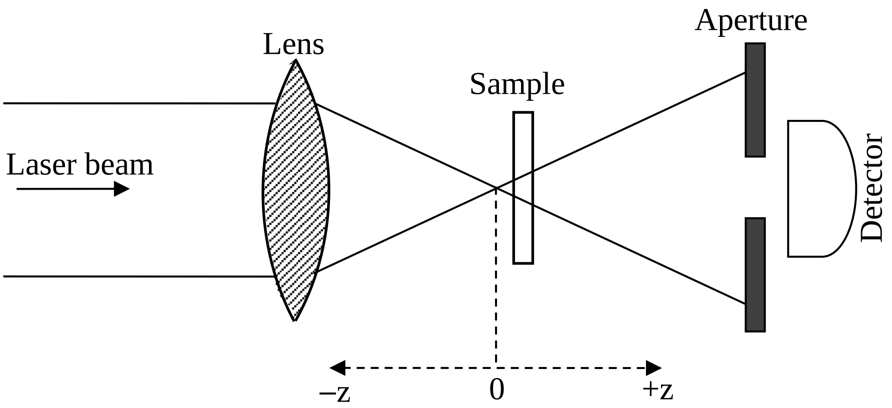


**Fig.a: Schematic diagram for Z-Scan Technique**

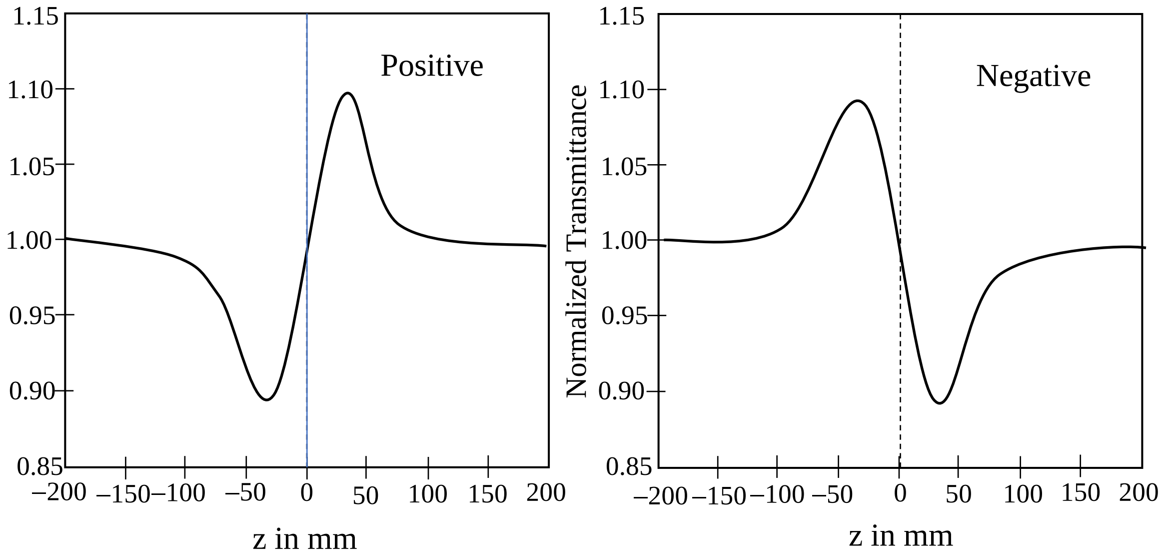


**Fig.b** **Fig.c**

**Characteristic curves depict both positive and negative nonlinear refraction as measured by Z-scan**

The method is as illustrated in fig.a. The far field aperture transmittance is measured for a constant laser input as the sample is moved along the z-direction through the focus of the lens. Hence the measurement method has come to be known as Z-scan. The sample acts as an intensity dependent lens. As it is moved along the beam path, its effective focal length changes because the incident intensity of the beam on the sample changes. This change is reflected in the intensity distribution at the aperture in the far field. The amount of energy transmitted through the aperture depends on the sample location on the z-axis and the sign of the refractive index $n_2$ of the sample.

Consider, for example, a material with positive $n_2$. When the sample is far from the focus of the lens ($z << 0$) the intensity of the beam on the sample is small, and since the sample is thin, the energy transmitted through the aperture remains approximately constant. As the sample is nearer to the focus ($z = 0$), the intensity is high enough to produce a positive lensing effect. For small negative values of z, this lensing of the sample causes the beam to come to focus earlier than $z = 0$, so that it diverges more rapidly in the far field. The result is that the aperture transmittance decreases. On the other hand, for small positive values of z the positive lensing of the sample causes a decrease in the beam divergence. This results an increase in the aperture transmittance. At $z >> 0$, again the sample is far from the focus and the intensity in the sample is small. Then the aperture transmittance returns to its starting value. The net z-scan yields a dispersion-shaped transmittance curve as shown in fig.b. Obviously, a negative $n_2$ material will produce a similar curve (fig.c), but with peak and valley reversed about $z = 0$.

The aperture transmittance as a function of sample position depends on the magnitude and sign of $n_2$. This is the basis of the z-scan technique. The nonlinear medium imposes a phase distortion on the electric field of the transmitted light. The objective of the z-scan technique is to measure this transmittance and extract $n_2$ by the inversion of the formula for the aperture transmittance.

It can be shown that the nonlinear refractive index of the sample,

$$n_2 = \frac{\lambda}{2\pi}\left(\frac{\Delta\phi_0}{L_{eff} I_0}\right) \ cm^2/W \tag{29}$$

where, $\lambda$ is the laser wavelength, $\Delta\phi_0$ is the on-axis phase shift at the focus ($z = 0$), $I_0$ is the on-axis irradiance at the focus and

$$L_{eff} = \frac{1-e^{-\alpha L}}{\alpha} \tag{30}$$

where, L is the length of the sample and $\alpha$ is its linear absorption coefficient.

**Advantages**: The z-scan has several advantages. Among these is its simplicity. As a single-beam technique, it has no difficulty in alignment other than keeping the beam centred on the aperture. He z-scan experiment can be used to determine both the magnitude and sign of $n_2$. The sign is obvious from the shape of the transmittance curve. The data analysis is quick and simple. This makes it a good method for screening new nonlinear materials. Under certain conditions, it is possible to isolate the nonlinear refractive index and nonlinear absorptive contributions to the far field transmittance. The z-scan can determine both the real and imaginary parts of $\chi^{(3)}$. The technique is also highly sensitive, capable of resolving a phase distortion of $\frac{\lambda}{300}$ in samples of high optical quality. The z-scan can also be modified to study nonlinearities on different time scales as well as higher order contributions.

**Disadvantage** of z-scan technique include the fact that it requires a high-quality Gaussian beam ($TEM_{00}$) for absolute measurements. The analysis must be different if the beam is non-Gaussian.