CHAPTER I
INTRODUCTION TO NON LINEAR OPTICS AND FERROELECTRIC PHENOMENON

1.1 Non linear optics

The field of nonlinear optics and nonlinear optical applications has become one of the fastest growing areas of research for the last four decades, impacting upon many other disciplines, such as medicine, signal processing, communications, computing, etc. Although the first nonlinear optical effects were observed in crystalline structures, they were soon extended to organic materials and later to solid state heterostructures. In particular, the area of organic nonlinear optics has been extremely active in the past two decades.

In the absence of external fields, the electromagnetic forces between the positive and the negative charges inside of the material are usually in equilibrium, and the material is electrically neutral. However, when a beam of light is applied to the material, the electromagnetic forces inside the material are perturbed.

Nonlinear optics (NLO) is the study of interaction of intense electromagnetic fields with materials to produce modified fields that are different from the input field in phase, frequency or amplitude. Nonlinear optics is attracting increasing attention due to its wide application in the area of laser technology, optical communication and data storage technology. More over the NLO materials are expected to play a major role in photonics including optical information processing, sensor, data storage etc. Non Linear Optics (NLO) deals with the interactions of applied electromagnetic fields in various materials to generate new electromagnetic field altered in phase, frequency, amplitude or other physical properties [1].

Before the advent of the lasers, optics assumed that optical parameters of the medium are independent of the intensity of the light propagating in the selective mediums. NLO processes can be viewed as dielectric phenomena. Electric fields such as an applied dc field or a propagating electromagnetic wave when, passes through any medium induces
electron displacement. Electrons that are bound to the nearby nuclei in the medium gets slightly perturbed by the external applied electromagnetic field and begin oscillating at the applied frequency. The magnitude of such an induced polarization at modest field strengths will be proportional to the applied field. NLO materials can be broadly classified in two different categories as inorganic and organic materials. Each category i.e. inorganic and organic possesses its own set of advantages and disadvantages.

1.1.1 Inorganic materials

These are covalent and ionic bulk materials where the optical nonlinearity is a bulk effect. The examples of this type of materials are inorganic systems, semi conductors and inorganic photorefractive crystals. Potassium dihydrogen phosphate (KDP) has been used widely for phase matched SHG of high-powered near-IR lasers. Multilayer semiconductor materials, which are synthesized by using new crystal growth techniques [2], which exhibits special optical properties not apparent in the bulk materials [3-6]. Both inorganic and semiconductor are used in commercial applications such as modulators, optical switches etc. but they also have some drawbacks such as, the crystals face a ‘trade-off’ problem between response time and magnitude of optical nonlinearity [7-9]. The semiconductors are costly and difficult to produce, further more they absorb strongly in the visible region and are of poor optical quality, there by discounts many possible applications. To date the inorganic solids, such as LiNbO₃ and KH₂PO₄, have traditionally been the NLO materials of choice.

1.1.2 Organic materials

Organic materials might be preferred for many reasons. First, the origin of the nonlinear optical response in organic system lies in the electronic polarizability of the electrons at the molecular level. The intrinsically electronic nature of the response implies a very fast response for non resonant optical excitations, a great advantage for organic photonic devices over some of the inorganic analogues. Organic materials are also easier to produce, more versatile and potentially cheaper. Yet, the biggest advantage of organic materials is the virtually infinite number of organic molecules that can be synthesized. The
great versatility of organic synthesis means that a wealth of potential strategies for the optimization of the nonlinear response is available. The number of medium size organic molecular structures is enormous.

Organic materials are molecular materials that consist of chemically bonded molecular units interacting in the bulk media through weak Vander Waal interactions. Organic materials are emerging as an alternative to inorganic materials because of their low cost, ease of fabrication and integration into devices, and intrinsic tolerability [10 -17] which allows one to fine tune the chemical structure and properties for a given NLO process. The organic materials possess low dielectric constants, inherent synthetic flexibility, high optical damage thresholds, and large NLO response over a broad frequency range comparable to those of inorganic materials [18]. The NLO property of these molecule-based materials is governed by the NLO characteristics of the constituent individual molecular chromophores. It is observed that chromophores containing D and A substituents linked through an intervening π-backbone such as 1 or 2 shows larger NLO response.

1.1.3 Semi organic materials

Semi organic materials like Potassium Hydrogen Phthalate (KHP also called as KAP), L-Alanine acetate and a few other materials also show the NLO behaviours due to its Vander Waals interactions. Some literature reveals that the NLO behaviours occur due to charge transfer interactions, conjugations, polarisation and crystallisation of materials into non-centrosymmetric lattice. The NLO property of materials is primarily controlled by various orders of non-linear susceptibilities [7].

The Kurtz powder technique is a convenient method for screening large number of powdered materials for the second order NLO activity without needing to grow large single crystals. A laser is directed onto a powdered sample and the emitted light is collected, filtered and detected with a photo multiplier tube. The light propagated through a crystalline solid, which lacks a centre of symmetry, generates light at second and third harmonics of the applied frequency. This important nonlinear property of non-
centrosymmetric crystals is called second harmonic generation (SHG) and this phenomenon and the materials in which it occurs is the subject of intense study [8].

The pioneering experiment in this field is thought to be that of Franken [9] and his co-workers (1961) who first observed SHG by focusing the 694.3 nm output from a ruby laser onto a quartz crystal and obtained a very low intensity output at a wavelength of 347.15 nm (Fig. 1.1).

![Fig. 1.1 Frequency doubling of a Ruby laser: $\lambda = 694.3$ nm $\rightarrow \lambda = 347.1$ nm as shown by Franken et al. [9].](image)

1.4 Theoretical phenomenon of nonlinear optics

In 1962, theoretical investigations dealing with the behaviour of light wave by solving Maxwell’s equation in a nonlinear dielectric and at the boundary of nonlinear media were first performed by Bloembergen et al. [10, 11]. Although the Kerr-effect was discovered in 1875, the birth of modern nonlinear optics should be associated to the first observation of second harmonic generation by Franken et al. in 1961, soon after the invention of the laser in 1960.

The explanation of nonlinear effects lies in the way in which a beam of light propagates through a solid. The nuclei and associated electrons of the atoms in the solid form the 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 (SHG) 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 it 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

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

where \( \varepsilon_0 \) is the permittivity of the free space, \( \chi \) is the linear susceptibility of the material, \( E \) is the electric field vector [12].

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.

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

In nonlinear terms, product of two or more oscillating fields gives oscillation at combination of frequencies and therefore the above equation can be expressed in terms of frequency as:

\[ P (\omega_0) = \varepsilon_0 \chi^{(1)} (-\omega_0, \omega_1), E (\omega_0) + \chi^{(2)} (-\omega_0, \omega_1, \omega_2), E\omega_1, E\omega_2 + \chi^{(3)} (-\omega_0, \omega_1, \omega_2, \omega_3), E\omega_1, E\omega_2, E\omega_3 + \ldots \] (1.3)

where \( \chi^{(2)}, \chi^{(3)} \ldots \) are the nonlinear susceptibilities 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-centrosymmetry materials. \( \chi^{(3)} \) is the cubic term responsible for third harmonic generation, stimulated Raman scattering, phase conjugation and optical instability. The coefficient of \( \chi^{(1)} \), \( \chi^{(2)} \), \( \chi^{(3)} \) give rise to certain optical effects. These optical effects and their applications are given in Table 1.1. If the molecule or crystal is centrosymmetric then \( \chi^{(2)} = 0 \). If a field +E is applied to the molecule (or medium), equation 1.3 predicts that the polarization induced by the first nonlinear term is predicted to be +E\(^2\); yet if the medium is centrosymmetric the polarization should be -E\(^2\). This contradiction can only be resolved if \( \chi^{(2)} = 0 \) in centrosymmetric media. If the same argument is used for the next higher order term, +E produces +E\(^3\) and –E produces –E\(^3\) so that \( \chi^{(3)} \) is the first non-zero nonlinear term in centrosymmetric media.

**Table 1.1 Optical effects of nonlinear materials**

<table>
<thead>
<tr>
<th>Order</th>
<th>Crystal</th>
<th>Effects</th>
<th>Applications</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))</td>
<td>Frequency doubling</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Frequency mixing ((\omega_1\pm \omega_2= \omega_3))</td>
<td>Optical parametric oscillators</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pockels effect ((\omega + 0= \omega))</td>
<td>Electro-optical modulators</td>
</tr>
<tr>
<td>3</td>
<td>( \chi^{(3)} )</td>
<td>4 wave mixing phase gratings</td>
<td>Raman coherent spectroscopy</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Kerr effect</td>
<td>Real time holography</td>
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<tr>
<td></td>
<td></td>
<td>Optical amplitude</td>
<td>Ultra high speed optical gates</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Amplifiers, choppers etc.</td>
</tr>
</tbody>
</table>
In second harmonic generation, the two input wavelengths are the same \( 2\omega_1 = \omega_2 \)
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 \( \omega_2 \).

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 are to be matched.

\[
\Delta K = \frac{2\pi}{\lambda} (n_2 - n_1) = 0
\]

where \( \Delta K \) represents the phase – mismatch. The phase matching can be obtained by angle
tilting, temperature tuning or other methods. Hence, to select a nonlinear optical crystal,
for a frequency conversion process, the necessary criterion is to obtain high conversion
efficiency. The conversion efficiency \( \eta \) is given by

\[
\eta = PL^2 (d_{\text{eff}} \sin(\Delta KL)/\Delta K L)^2
\]

where \( d_{\text{eff}} \) is the effective nonlinear coefficient, \( L \) is the crystal length, \( P \) is the
input power density and \( \Delta K \) is the phase – mismatching. In general, higher power density,
longer crystal, large nonlinear coefficients and smaller phase mismatching will result in
higher conversion efficiency. Also, the input power density has to be lower than the
damage threshold of the crystal. Table 1.2 lists the laser and crystal parameters for
selecting a NLO crystal for a particular application.

Significant advances in the development of NLO materials can be divided into
three different areas.

(i) sighting of new model NLO materials

(ii) growth of capable NLO crystals

(iii) getting better the characteristics of a NLO crystal
Table 1.2 Parameters for selecting a NLO crystal

<table>
<thead>
<tr>
<th>Laser parameters</th>
<th>Crystal parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>NLO process</td>
<td>Type of phase matching</td>
</tr>
<tr>
<td>Power, Repetition rate</td>
<td>Damage threshold</td>
</tr>
<tr>
<td>Divergence</td>
<td>Acceptance angle</td>
</tr>
<tr>
<td>Band width</td>
<td>Spectral acceptance</td>
</tr>
<tr>
<td>Beam size</td>
<td>Crystal size, Walk-off angle</td>
</tr>
<tr>
<td>Pulse width</td>
<td>Group velocity mismatching</td>
</tr>
<tr>
<td>Environment</td>
<td>Moisture, temperature acceptance</td>
</tr>
</tbody>
</table>

Many organic and inorganic materials are highly polarisable and thus are good candidates for study. However, the net polarization of a material depends on its symmetry properties, with respect to the orientation of the impinging fields. It can be shown that the odd order terms in equation are orientationally independent, but the even terms vanish in a centrosymmetric environment. Thus materials for second order NLO must be orientationally noncentric to be functional. No such restriction applies to third order materials.

Moreover nonlinear optical materials will be the key elements for future photonic technologies based on the fact that photons are capable of processing information with the speed of light. The search for new and efficient materials in which to carry out nonlinear optical processes has been an active one since SHG was first observed in single crystal quartz.

In the beginning, studies were concentrated on inorganic materials such as quartz, potassium dihydrogen phosphate (KDP), lithium niobate (LiNbO₃) and semiconductors such as cadmium sulfide, selenium and tellurium [13].

At the end of 1960s, the Kurtz and Perry powder SHG method was introduced (Fig.1.2). In this method, a powdered sample is irradiated with a laser and scattered light is collected and analyzed for its harmonic content with the use of suitable filters. For the first
time, rapid, qualitative screening for second order NLO effect was possible. The stage was set for a rapid introduction of new materials, both inorganic and organic. Early NLO history is chronicled more extensively by Zyss and Chemla [8].

Second order NLO materials are used in optical switching (modulation), frequency conversion (SHG, wave mixing), and electro–optic applications especially in EO modulators. All of these applications rely on the manifestation of the molecular hyperpolarizability of the materials.

Inorganic materials are much more matured in their application to second-order NLO than organic. Most commercial materials are inorganic, especially for high power use. However, organic materials are perceived as being structurally more diverse and therefore are believed to have more long-term promise than inorganic. For optical applications a nonlinear material should have the following characteristics [12]

(i) a wide optical transparency domain
(ii) large nonlinear figure of merit for frequency conversion
(iii) high laser damage threshold
(iv) be readily available as large single crystals
(v) wide phase matchable angle
(vi) ability to process into crystals, thin films
(vii) ease of fabrication
(viii) nontoxicity and good environment stability
(ix) high mechanical strength and thermal stability and
(x) fast optical response time.
In general, the following two key factors determine the existence or absence of SHG in NLO materials. Firstly and fundamentally, the material should crystallize with a non-centrosymmetric crystal structure. Secondly, for maximum SHG efficiency, crystals should possess phase matching properties (i.e., the propagation speeds of the fundamental and harmonic waves should be identical in the crystal).

The advantages of organic nonlinear optical materials are:

(i) high second-order nonlinear optical efficiency
(ii) much greater resistance to damage in the laser beam
(iii) birefringent in nature
(iv) possible to chemically “engineer” molecular properties

Ideally, the perfect organic material would be the one which has a high efficiency, a very low absorption edge cut-off (to allow access into the UV), a high damage threshold and finally, have a favourable crystal growth property. The enhancement in nonlinearity in comparison to inorganic materials arises due to the existence of \( \pi \) electrons in the organic materials. That is in a usual saturated organic material the sequence of carbon is of the type \(-C-C-C-C-C-C-\), where "-" indicates an electron pair that holds the carbon atoms together. All electrons are then strongly bound to the atoms and the material is an insulator, so rather uninteresting from an optical or electronic point of view.
However, in an unsaturated organic material it have a sequence like \(-\text{C}=	ext{C}-\text{C}=-\text{C}=-\text{C}=-\text{C}_{-}\). The extra electrons in the carbon bonds ("=" now indicates two pairs of electrons) are only loosely bound to the carbon atoms. These loosely bound electrons are called pi-electrons. As a result, the material is now a semiconductor, like silicon. Since organic semiconductors can be chemically synthesized with a practically endless variety. Large second order optical nonlinearity originates from organic conjugated molecules having an electron acceptor group at one end and a donor group at the opposite end [14].

1.2 Ferroelectricity

Ferroelectricity is a physical property of a material whereby it exhibits a spontaneous electric polarization, the direction of which can be switched between equivalent states by the application of an external electric field [15-20]. The experimental evidence for this domain switching is a hysteresis loop. The term is used in analogy to ferromagnetism, in which a material exhibits a permanent magnetic moment. Ferromagnetism was already known when ferroelectricity was discovered in 1920 in Rochelle salt by Valasek [17]. Thus, the prefix “ferro”, meaning iron, was used to describe the property despite the fact that most ferroelectric materials do not have iron in their lattice.

Below a certain temperature it is found that some materials spontaneously acquire an electrical dipole moment, which is known as ferroelectrics. This property helps the materials to be used as non-volatile element.

Ferroelectric materials possess usually pyroelectric (the ability of certain material to generate temporary voltage when they are heated or cooled) and piezoelectric (A piezoelectric substance is one that produces an electric charge when a mechanical stress is applied (the substance is squeezed or stretched). Conversely, a mechanical deformation (the substance shrinks or expands) is produced when an electric field is applied. This effect is formed in crystals that have no centre of symmetry) properties, which are applied in sensors, and actuators. Ferroelectricity usually disappears above a certain temperature to form structure of higher symmetry called the transition temperature (Tc), at which the crystal switches over from the polar state to the non-polar state.
1.3 Dielectric materials

Dielectric materials are the electrical insulators that can be polarised by apply electric field. When a dielectric is placed in an electric field electric charge do not flow throw the dielectric but the charge slightly shift from their average equilibrium position causing dielectric polarisation. Because of dielectric polarisation positive charges are move towards the field and negative charges move opposite the field. This creates an internal electric field which reduces the overall field in the dielectric itself. If the dielectric is composed of weakly bonded molecules, those molecules not only polarise but also reorient so that the symmetry axis aligns with the field. Insulator implies low electrical conduction. But dielectric is typically used to describe materials to have polarisabilty. Polarizability is expressed by a number called dielectric constant. Moreover dielectric is used indicate the energy storing capacity of the material (i.e. by means of polarization).

1.3.1 Frequency dependence of the dielectric constant

All polarization mechanisms respond to an electrical field by shifting masses around. This means that masses must be accelerated and de-accelerated, and this will always take some time. So it must expect that the (mechanical) response to a field will depend on the frequency ($\omega$) of the electrical field; on how often per second it changes its sign. If the frequency is very large, no mechanical system will be able to follow. So that at very large frequencies all polarization mechanisms will "die out", i.e. there is no response to an extremely high frequency field. This means that the dielectric constant $\varepsilon_r$ will approach 1 for $\omega$.

It is best to consider our dielectric now as a "black box". A signal in the form of an alternating electrical field $E$ goes in at the input, and something comes out at the output, as shown below. Besides the Black Box scheme, two possible real expressions of such an abstract system are shown: A parallel-plate capacitor containing a dielectric, and an optical lens with an index of refraction $n = \varepsilon_r$. The input would be a simple alternating
voltage in the capacitor case, and a light wave in the lens case (Fig.1.3).

![Fig.1.3](image)

**Fig.1.3** Frequency Dependence of the Dielectric Constant

As long as our system is linear (twice the input = twice the output), a sine wave going in will produce a sine wave coming out, i.e. the frequency does not change.

1) If a sine wave goes in, the output then can only be a sine wave with amplitude and a phase different from the input, as schematically shown above.

2) If a complicated signal goes in, decompose it into its Fourier components, consider the output for all frequencies separately, and then do a Fourier synthesis.

With complex notation, the input will be something like $E_{in} = E_{in} \cdot \exp(i\omega t)$; the output then will be $E_{out} = E_{out} \cdot \exp(i(\omega t + \Phi))$.

1) One could write $E_{out} = f(\omega) \cdot E_{in}$ with $f(\omega)$ = complex number for a given $\omega$ or complex function of $\omega$.

2) $f(\omega)$ is the function that relates the output of a dielectric material to its input the dielectric function of the material. One will see, the dielectric function is a well-defined and very powerful entity for any material - even if one cannot calculate it from scratch. One can however, calculate dielectric functions for some model materials, and that will give us a very good idea of what it is all about.

Since the index of refraction $n$ is directly given by $\varepsilon_r^{1/2}$ (assuming that the material has no magnetic properties), we have a first very general statement:

There exist no microscopes with "optical" lenses for very high frequencies of
electrical fields, which means electromagnetic radiation in the deep ultraviolet or soft X-rays. And indeed, there are no X-ray microscopes with lenses (however, we still have mirrors!) because there are no materials with $\varepsilon_r > 1$ for the frequencies of X-rays.

Looking at the polarization mechanisms discussed, it shows that there is a fundamental difference in the dynamics of the mechanisms with regard to the response to changing forces:

1) In two cases (electron and ionic polarization), the electrical field will try to change the distance between the charges involved. In response, there is a restoring force that is (in our approximation) directly proportional to the separation distance of the dipole charges. We have, in mechanical terms, an oscillator.

2) The characteristic property of any such oscillating system is the phenomena of resonance at a specific frequency.

3) In the case of the orientation polarization, there is no direct mechanical force that "pulls" the dipoles back to random orientation. Instead we have many statistical events that respond in their average results to the driving forces of electrical fields.

4) In other words, if a driving force is present, there is an equilibrium state with an (average) net dipole moment. If the driving force were to disappear suddenly, the ensemble of dipoles will assume a new equilibrium state (random distribution of the dipoles) within some characteristic time called relaxation time. The process knows no resonance phenomena; it is characterized by its relaxation time instead of a resonance frequency.

One thus has to consider just the two basic situations: Dipole relaxation and dipole resonance. Every specific mechanism in real materials will fit one of the two cases.

The study of dielectric property is concerned with the storage and dissipation of electric and magnetic energies in materials. Hence dielectric plays an important role in various phenomena in electronics, optics, and solid state and material science.
1.3.2 Relation between ferroelectric material and dielectricity

The materials which possess spontaneous electric polarisation, that can be reversed by the application of external electric field and have permanent magnetic moment, called ferroelectric materials.

Moreover ferroelectric materials are a special class of dielectric materials. These materials have two stable polarization direction fields. Dielectrics are the materials that electrical field influences the electrical and optical properties. These materials have the following special features,

(i) They possess high dielectric constant along the polar axis which is a function of temperature and reaches a peak value of the Curie temperature.

(ii) The phase transition at transition temperature can be either the first order or of the higher (usually second) order. In the first kind of transition, spontaneous polarization (Ps) abruptly goes to zero at the Curie point.

In the diffused phase transition, Ps gradually decreases in the temperature region, known as the Curie region. In the second order transition, spontaneous polarization smoothly goes to zero at Curie temperature ($T_c$), i.e., there is no release of latent heat but the thermal expansion coefficient shows anomalous behaviour over a finite range of temperature. Again materials that exhibit electric polarization even in the absence of the applied electric field are known as ferroelectric materials. The dielectric constants of these materials are some three orders of magnitude larger than these in ordinary dielectrics [19]. Ferroelectricity is result of dielectric hysteresis. Since these materials exhibit hysteresis effects, similar to those observed in ferromagnetic materials, they are called ferroelectric materials.

Examples: Barium titanate (BaTiO$_3$), Potassium dihydrogen phosphate (KDP), Triglycine sulphate (TGS) and Triglycine sulphophosphate (TGSP).

The existence of a dielectric hysteresis loop in a material implies that the substance possesses a spontaneous polarization i.e. a polarization that persists when the applied field is zero. The existence of permanent electric dipoles and an internal electric field suggest the possibility of spontaneous polarization.
\[ P = N\alpha_e E / (1-(Na_e3\varepsilon_0)) \]

The above equation is for condition for spontaneous polarization. If the denominator becomes zero we get a polarization catastrophe. This can be interpreted as that there is polarization even when there is no external field or other words there is a spontaneous polarization just as there is spontaneous magnetization in ferromagnetics. This is the condition for spontaneous polarization and the dielectric constant will become infinite, but we can conclude that the substance becomes polarized.

1.3.3 Importance of ferroelectric materials

I. Every ferroelectric substance has a characteristic Curie point \((T_c)\) which can be influenced by impurities. The transition from ferroelectric to Para electric state may be accompanied by change in crystal or change in space group of the crystal structure.

II. They possess very high dielectric constants. The dielectric constant is large even in paraelectric phase.

III. Ferroelectric crystals exhibit birefringences i.e., double refraction when a plane polarized light is passed through them. All ferroelectric are pyroelectric and piezoelectric but the reverse may not be true. For example tourmaline is pyroelectric and ferroelectric. Quartz is piezoelectric but not ferroelectric.

IV. Ferroelectric crystals contain an array of domains with different direction of polarization. When an external field is applied, the domain wall may move to permit an enlargement of domains, in which, the direction of polarization \((P)\) nearly becomes parallel to the applied field. At the saturation, all domains have the polarization vectors in the direction of least energy. i.e., in the direction of the applied field.

V. Both the specific heat and thermal expansion co-efficient exhibit a discontinuity at the transition temperature.
1.3.4 Applications of ferroelectrics

The study of ferroelectricity has been closely linked with device applications. The pyroelectric properties of ferroelectrics make them very suitable for thermal detection, while results in a temperature change of crystal. Pyroelectric detectors can be used to record infrared images. The high permittivity values near the transition temperature lead to the use of ferroelectric materials in miniature capacitors, which can be charged electrically. Ferroelectric crystals can be used as dielectric amplifiers and low frequency power amplifiers in remote control. In addition, ferroelectric crystals find wide applications in medical vidicons, FTIR instrumentation, infrared detectors, laser beam characterization, earth observation cameras and astronomical telescopes.

1.4 General scope of the thesis

Literature survey has indicated that the semiorganic crystal, potassium hydrogen phthalate (KAP) crystals find a variety of applications in modern technology. Crystal growth and characterization of KAP has been chosen as the main topic for present investigations. Attempts have been made to improve the quality of crystals and their physical properties in order to enhance the device performances and crystal stability.

The thesis has been divided into two parts; the first part involves the growth of pure and amino acid doped KAP crystal and the second part deals with the studies on the effect of metal ions on the growth of KAP crystals. All the crystals have been subjected to extensive physico-chemical characterizations and the results are compared.

Growth of large sized good quality single crystals requires knowledge on various crystal growth methods. The next chapter deals with the importance of crystal growth and a review of different crystal growth methods.