2. AN OVERVIEW OF NONLINEAR OPTICAL MATERIALS AND KDP SINGLE CRYSTALS

This chapter enumerates the aspects of nonlinear optical effect exhibited by NLO materials and presents a review of the various studies made by investigators on KDP crystal in the recent past.

2.1 NONLINEAR OPTICAL PHENOMENA

Nonlinear optics (NLO) is the study of the interaction of intense electromagnetic field with materials to produce modified fields that are different from the input field in phase, frequency or amplitude. It is a vast area, and undoubtedly one of the most important areas of physics with a diverse range of applications. The field of nonlinear optics is understood to encompass those phenomena in which the electric polarization strongly depends on the higher-order terms in a power expansion of the electric field intensity, and the nonlinear optical phenomenon occurs within a nonlinear medium, usually a crystal.

The origin of nonlinear optical effects lies in the nonlinear response of a material to an electric field. In a dielectric medium, the charged particles are bound together. When an electric field is applied, they are slightly displaced from their usual position. This small movement of positive charges in one direction, and the negative charges in the other results in a collection of induced electric dipole moments. The effect of the field is to induce a polarization. The dipole moment of the molecule induced by an electric field can be described by

\[ \mu_i = \alpha_{ij} E_j + \beta_{ijk} E_j E_k + \gamma_{ijkl} E_j E_k E_l + \ldots \]
Where $\mu_i$ is the component of the induced dipole moment in the coordinate direction $i$, $\alpha_{ij}$ is the polarizability tensor, $\beta_{ijk}$ is the second-order polarizability or first order hyperpolarizability tensor, $\gamma_{ijkl}$ is the second order hyperpolarizability tensor and $E$ is the electric field strength at the location of the molecule. At the macroscopic level, the polarization is given by

$$P_i = \varepsilon_0 \left[ \chi^{(1)}_{ij} E_j + \chi^{(2)}_{ijk} E_j E_k + \chi^{(3)}_{ijkl} E_j E_k E_l + \ldots \right]$$

In both the equations the tensors are frequency dependent and should be written as functions of the frequency of the fields and the polarization produced. The linear term involving $\chi^{(1)}$ gives rise to the index of refraction, absorption, dispersion and birefringence of a medium. Most of the interesting nonlinear optical effects however arise from the terms of electric polarization which are quadratic or cubic in the electric field. The coefficients of the nonlinear terms are extremely small, but under proper circumstances they lead to striking effects. The quadratic polarization $\chi^{(2)}$ gives rise to the phenomenon of second harmonic generation, sum and difference frequency mixing, linear electro-optic modulation, parametric generation, etc. The cubic term $\chi^{(3)}$ is responsible for third harmonic generation, stimulated Raman scattering, optical bistability and phase conjugation. Odd order terms such as $\chi^{(1)}$ and $\chi^{(3)}$ and even order terms such as $\chi^{(2)}$ and $\chi^{(4)}$ are non-zero in noncentrosymmetric media, whereas even order terms are zero in centrosymmetric media. Therefore centrosymmetric media do not exhibit second-order nonlinear effects, although third-order processes are possible in such media.
The high intensity available in the laser beam has made possible the observation of nonlinear effects at optical frequencies. The discovery of second harmonic generation (SHG) of light by a ruby laser pulse in a quartz crystal, propelled the modern field of nonlinear optics and initiated intensive research in material science and crystal technology. Now devices based on nonlinear optical interactions promise to be efficient, compact, easy to operate, and capable of operating in a wide spectral range.

2.2 NONLINEAR OPTICAL MATERIALS

In recent years, major advances have been made in the development of nonlinear materials with improved optical, mechanical characteristics and damage thresholds far higher than the classical crystals. The NLO crystals play an important role in the establishment of nonlinear optics as a major area of laser science and in techniques such as harmonic generation, frequency mixing, and parametric generation which are viable methods for generating coherent radiations in new regions of the optical spectrum.

To date, several thousand nonlinear crystals and their closely related isomorphs have been developed. The properties that are important for an ideal NLO crystal for device applications are high NLO coefficient, wide phase matching angle, high laser damage threshold, wide transparency range, high thermal, mechanical and chemical stability, moderate birefringence, ability to process into crystals, availability in bulk form and easy device fabrication. Further, for exhibiting second order nonlinear effects, the material should crystallize in a noncentrosymmetric crystal class.
These requirements of a NLO crystal, has restricted the number of potential useful materials to a few out of this entire selection.

Traditionally the inorganic crystals have been explored for NLO applications. They are mostly ionic bonded, and easier to synthesize. Often these have high melting point, and high degree of chemical inertness. High-temperature oxide materials are well studied for diverse applications. Some of the most useful crystals discovered are Lithium niobate, Potassium niobate, Potassium dihydrogen phosphate (KDP) and its analogues, Potassium Titanyl Phosphate (KTP) and its analogues, β-Barium Borate, etc. These materials have been successfully used for second harmonic generation, frequency doubling of Nd:YAG laser and also in electro-optical applications. The supersonic crystals like silicates, phosphates and tungstates form a major group of fast 3-dimensional ionic conductors.

Organic materials are also of interest in the recent years. A main advantage of the organic materials is the possibility of altering the molecular structure for optimizing the electro-optic or nonlinear optical properties. Conjugated Donor-Acceptor substituted organic molecules exhibit measurable NLO, electro optic and photo refractive properties. Such materials can be used to double the frequency of laser light and are of considerable interest for the high speed processing of data, which is essential for numerous modern technologies like optical computing and optical telecommunication systems. Some major applications are optical data storage, optical information processing, electro-optic switching etc. The most widely encountered crystals for this type of applications are urea, thiourea, MNA (2-methyl-4-nitroaniline), POM(3-methyl-4-Nitopyridine-1-oxide) etc. Due to the
technological importance of these nonlinear crystals, the need for high quality organic crystals has grown dramatically in the last decade.

The inherent limitation on the maximum attainable nonlinearity in inorganic materials and the moderate success in growing device-grade organic single crystals, have made scientists adopt newer strategies. The obvious one was to develop hybrid inorganic-organic materials with a little trade-off in their respective advantages. A typical case is the formation of complexes of organic material with inorganic acids and salts. The choice of the ligands is unlimited and in fact, the organic part need not be noncentrosymmetric. This is typified by the example of thiourea, which forms excellent complexes with Zn, Cd and Hg. Thiourea is more polarizable than urea because of large sulphur atoms, while hydrogen bonds in the NH$_2$ ensure the lack of center of inversion in many thiourea complexes. The other known choices of ligands are allylthiourea, guanidine and dithiocarbamate.

An alternate approach is to form metal coordination complexes of organic materials. Complexes of amino acids with inorganic acids and salts are promising materials for optical second harmonic generation (SHG), as they tend to combine the advantages of the organic amino acid with that of the inorganic acids and salts. These materials which combine high optical nonlinearity of a purely organic ion with favorable mechanical and thermal properties of an inorganic counter ion are termed as semiorganic materials. They may be considered as superior quality NLO materials as they combine the advantages of organic and inorganic materials.

Comparison of the various properties of organic, inorganic and semiorganic NLO crystals are listed in Table 2.1.
### Table 2.1: Comparison of various classes of NLO crystals

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Inorganic Crystals</th>
<th>Organic Crystals</th>
<th>Semiorganic Crystals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical nature</td>
<td>Ionic bonded salts.</td>
<td>Van der Waals and hydrogen bonded.</td>
<td>It is formed by salts of organic and inorganic compounds.</td>
</tr>
<tr>
<td>Solvent</td>
<td>Water is the best solvent.</td>
<td>Numerous organic solvents available.</td>
<td>Water is used as solvent.</td>
</tr>
<tr>
<td>Effect of pH</td>
<td>Sensitive to pH</td>
<td>Insensitive</td>
<td>Sensitive</td>
</tr>
<tr>
<td>Growth rate</td>
<td>Slow and stable</td>
<td>Fast</td>
<td>Fast</td>
</tr>
<tr>
<td>Growth morphology</td>
<td>Crystal will grow in all three dimensions.</td>
<td>Mostly it will grow as needles and plates.</td>
<td>Crystal will grow in all three dimensions.</td>
</tr>
<tr>
<td>Size of the crystal</td>
<td>No size limit</td>
<td>0.1 to 100 mm$^3$</td>
<td>It will grow to big size.</td>
</tr>
<tr>
<td>X-ray diffraction quality</td>
<td>Good</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
<tr>
<td>UV transmission lower cutoff</td>
<td>150 nm</td>
<td>320 nm</td>
<td>230 nm</td>
</tr>
<tr>
<td>Laser damage threshold</td>
<td>Excellent</td>
<td>Moderate</td>
<td>Excellent</td>
</tr>
<tr>
<td>NLO efficiency</td>
<td>High</td>
<td>Very high</td>
<td>High</td>
</tr>
<tr>
<td>Mechanical strength</td>
<td>Extremely good</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Stability</td>
<td>Most stable</td>
<td>Volatile</td>
<td>Stable</td>
</tr>
</tbody>
</table>

#### 2.3 IMPORTANCE AND GENERAL PROPERTIES OF KDP SINGLE CRYSTALS

Potassium dihydrogen orthophosphate (KDP) is an excellent inorganic NLO material with different device applications. Single crystals of KDP and its isomorphs are representatives of hydrogen bonded materials which possess important piezoelectric, ferroelectric, electro-optic, mechanical and nonlinear optical properties [86].
The easy growth of large single crystals, a broad transparency range, a high optical damage threshold and a relatively low production cost are the qualities that make this phosphate crystal attractive and well suited for a variety of optical applications [90]. KDP crystals possess high optical and structural perfection that make it possible to produce elements for doubling and tripling of laser radiation frequency.

KDP is a model system for nonlinear device application therefore it is used as a standard to characterize the nonlinear optical response of other crystal samples [60]. Since the crystal exhibits excellent electro-optical and nonlinear optical properties it is commonly used in frequency conversion applications such as second, third, and fourth harmonic generation, in electro-optical modulation, optical image storage and optical communication. Due to its high electro-optic coefficient large single crystal plates of KDP are widely applied as Q-switches and laser radiation converters for very high energy Nd-glass lasers used for laser inertial fusion experiments [93]. The electro-optic effect in KDP leads to the applications such as polarization filter, electronic light shutter, optical rectifier, electronic light modulator, piezo-optic resonator, transducer etc. They are also used to control the parameters of laser light such as pulse length, polarization and frequency through the first and second order electro-optic effect [15, 94].

A tunable ruby laser uses a KDP electro optical filter of improved design and construction as the tuning element. The electro-optic deflection property of KDP crystals is used in frequency reformation in neodymium laser. The piezoelectric
property of KDP crystal makes it useful for the construction of crystal filters and frequency stabilization electronic circuits.

KDP crystal is an efficient angle tuned dielectric medium for the optical harmonic generation in and near the visible region. This material offers high transmission throughout the visible spectrum and meets the requirement for optical birefringence, large enough to bracket the refractive index for even the extreme wavelength over which it is transparent [91]. An additional advantage of KDP is its ability to withstand repeated exposure to high power density laser radiation without inducing strains and subsequent inhomogeneities in the refractive index [95]. These characteristics make KDP a desirable material for frequency doubling and mixing experiments with many solid state and dye lasers with fundamental wavelengths between 1060 and 525 nm.

KDP crystals have attracted the interests of many theoretical and experimental researchers, probably because of their comparatively simple structure and very fascinating properties associated with hydrogen bonded system involving large isotope effect. At room temperature, this classical material has a noncentrosymmetric tetragonal lattice (space group $I\overline{4}2d$) with lattice constants $a = b = 7.448 \, \text{Å}$ and $c = 6.977 \, \text{Å}$ [96]. Reported values of lattice parameters evaluated from single crystal and powder XRD studies are shown in Table 2.2.
Table 2.2: Reported values of unit cell parameters from X-ray diffraction studies

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Lattice parameters (Å)</th>
<th>Volume Å³</th>
<th>Interfacial Angles (°)</th>
<th>Reference No.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>c</td>
<td>α</td>
</tr>
<tr>
<td>1</td>
<td>7.434</td>
<td>7.434</td>
<td>6.945</td>
<td>383.810</td>
</tr>
<tr>
<td>2</td>
<td>7.449</td>
<td>7.449</td>
<td>6.977</td>
<td>387.220</td>
</tr>
<tr>
<td>3</td>
<td>7.449</td>
<td>6.966</td>
<td>7.448</td>
<td>386.536</td>
</tr>
<tr>
<td>4</td>
<td>7.434</td>
<td>7.434</td>
<td>6.945</td>
<td>383.810</td>
</tr>
<tr>
<td>5</td>
<td>7.448</td>
<td>7.448</td>
<td>6.977</td>
<td>387.033</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>7.455</td>
<td>7.455</td>
<td>6.975</td>
<td>387.649</td>
</tr>
<tr>
<td>7</td>
<td>7.457</td>
<td>7.457</td>
<td>6.976</td>
<td>387.913</td>
</tr>
<tr>
<td>8</td>
<td>7.452</td>
<td>7.452</td>
<td>6.974</td>
<td>387.282</td>
</tr>
<tr>
<td>9</td>
<td>7.393</td>
<td>7.393</td>
<td>7.048</td>
<td>385.240</td>
</tr>
<tr>
<td>10</td>
<td>7.4545</td>
<td>7.4545</td>
<td>6.8192</td>
<td>378.940</td>
</tr>
</tbody>
</table>

Considering the structure of KDP crystal. There are 32 atoms in the primitive unit cell of KDP, and each unit cell is formed by four formula units. The KDP lattice is composed of two sets of PO₄ groups linked to each other by hydrogen bonds. These PO₄ groups are rotated 16° about the "c" axis, off the "a" axis. There are also two distinct potassium ion positions. In particular, each phosphorus ion is surrounded by four oxygen ions located at the vertices of a nearly regular tetrahedron (contracted along the c axis by approximately 2%). Each PO₄ group is linked to four other PO₄ groups, spaced c/4 apart along the c axis, by hydrogen bonds. Figure 2.1 represents a projection of the tetragonal KDP lattice onto the c plane. The PO₄ groups and the
potassium ions are arranged in such a manner that potassium and phosphorus ions are spaced at a distance of $c/2$ along the $c$ axis. The PO$_4$ tetrahedra are also connected by potassium ions. Each potassium ion is surrounded by eight oxygen ions with four of these oxygens belonging to tetrahedra of neighboring columns.

![Figure 2.1: Room temperature tetragonal structure of KDP crystal](image)

One set of four oxygen ions lies closer to the potassium ion than the other set of four oxygen ions. The K-O bond lengths are 2.89 Å and 2.82 Å, respectively. A hydrogen bond involves one upper and one lower oxygen atom of the neighboring PO$_4$ units. As a result, all hydrogen bonds lie in a plane nearly perpendicular to the $c$ axis of the crystal.

The heavy solid lines in figure 2.1 indicate the unit cell. There are 16 oxygen ions and eight hydrogen ions contained within these solid lines. And there is one phosphorus ion contained within the solid lines and three additional phosphorus ions on the solid lines, which are part of the unit cell. The four potassium ions in the
unit cell are not shown. These potassium ions lie above and below the phosphorus ions. The upper oxygens of one tetrahedron lie at the same level as the lower oxygens of two neighbouring tetrahedra, and the O-O distances are short, about 2.49 Å. These are obvious positions for the hydrogen bond. The hydrogen ions link the tetrahedra into a three-dimensional framework.

KDP is ferroelectric well below room temperature and the Curie temperature $T_c$ is 123 K [102]. Later this temperature was found as 122 K [103]. The low temperature ferroelectric phase has an orthorhombic unit cell having the dimension (at 115 K) given as $a = 10.467$ Å, $b = 10.533$ Å and $c = 6.926$ Å [103]. The high permittivity values near the ferroelectric-paraelectric transition temperature ($T_c$) lead to the use of ferroelectric materials in miniature capacitors. Ferroelectric condensers have values which can be changed electrically. Thus ferroelectric condensers have been used for tuning in superhets and frequency modulators applied as dielectric amplifier and low frequency power amplifier in remote controls.

The molecular weight and density of KDP at room temperature are 136.09 and 2.338 g cm$^{-3}$ respectively. The true melting point of KDP is difficult to determine owing to the evolution of water vapour and condensation of phosphate species. The reported values of melting point differs from author to author. One reported value is 400 °C. KDP is highly soluble in water and sparingly soluble in alcohol [104]. The habit of solution grown KDP single crystals is formed by a combination of prismatic (100) and pyramidal (101) faces as shown in figure 2.2 [105].
2.4 GROWTH TECHNIQUES AND IMPURITY EFFECT

2.4.1 Aspects of conventional growth

In the recent years appreciable attention is given to grow crystals from solution with faster growth rates and by adopting faster cooling rates. The growth kinetics of the crystal are affected by parameters including supersaturation, pH of the solution and impurities. The stability of the grown solution depends on the metastable zone width of the solution in the supersaturation region. Pure and impurity added KDP single crystals were grown from aqueous solutions employing conventional techniques such as slow solvent evaporation method [15, 23, 40, 41, 65, 86, 90, 91, 106-108], slow cooling method [23, 24, 34, 90], temperature lowering method [19, 33, 37, 59, 62, 63, 68], temperature reduction method [35, 56, 60, 61, 75, 79, 93, 109, 110], the three-vessel method [111, 112], and also in gel media [97, 101, 113-121]. Nucleation studies and induction period measurement on aqueous KDP solution with and without impurities have also been studied [58, 60-62, 83, 90, 110].
It is reported that due to the strong chemical bonding interactions between the K\(^+\) and H\(_2\)PO\(_4^-\) ions, the growth rate along the c-axis in KDP is faster than that of ADP [122]. The bond valence model employed to calculate the bond strength of constituent chemical bonds formed between growth units in KDP and ADP crystals show that the (100) and (101) planes of KDP and ADP crystals have the larger areas and the emergence possibilities to be crystal surfaces in aqueous solution [123].

Studies show that the asymmetry of hydro mechanical conditions, fluctuations of supersaturation and processing of seed crystal would lead the edges of KDP type crystal to deviate from the crystallographic shape resulting in incomplete crystal faces with severe defect in the crystal [124]. The anomalous wedge like shape of KDP single crystals called tapering is due to the narrowing of both pyramidal and prismatic sectors. The overall retardation of prismatic growth layers is caused by impurity adsorption, where the narrowing up of pyramidal sector is due to the inability of pyramidal growth layers to reach the prismatic crystal edge [111]. Impurities with large molecular dimensions such as quaternary cations, metaphosphate and boric acid cause tapering of KDP crystal, but the crystal can be recovered by the accumulation of supersaturation which is different from tapering caused by metal ions [125]. The structural defects and crystalline perfection of the thin surface layers of the Z-cut KDP crystal evaluated by white beam synchrotron radiation and High Resolution X-ray Diffraction (HRXRD) analysis show that the crystalline quality is very poor and there are a large number of defects in this surface layers [126].

Changes in the solution acidity does not influence the growth rate of the bipyramidal faces. Also the pH of the growth solution does not affect the free surface
energy of the end faces of steps and their kinetic coefficient [127]. Solubility curves for KDP crystal growth with solutions of different pH values show that the solubility increases with reduction in pH values of solution. With a pH of 1.5, chemical etching experiments reveal that the pyramidal sector of the crystal displays more growth defects [128].

2.4.2 Growth of large scale single crystals and techniques of rapid growth

Zaitseva and his group [129] grew large-scale (40-55 cm) KDP crystals at rates of 10-20 mm/day, by the rapid growth method based on the use of “point seed”. Nakatsuka et al [130] used external energy to grow KDP crystals of 60 mm in size at high rates of excess of 50 mm/day. Sasaki and Yokotani [112] have described the growth of huge KDP crystal which have $40 \times 40$ cm cross section for a frequency converter for high power laser system by using conventional temperature reduction method using the three vessel system. Yang Shangfeng et al [131] added additives such as borates and EDTA to KDP solution in order to increase the stability of solution and obtained KDP single crystals of size up to 50 mm with the growth rate of 10-15 mm/day. The KDP crystal grown from sulfosalicylic acid (SSA) added solution by Guohui et al [110] in a 5000 ml vessel had a size of $52 \times 48 \times 70$ mm$^3$. The addition of SSA does not affect the crystalline quality and laser damage threshold of KDP. The KDP crystal grown by Guohui et al [132] from KCl and NH$_4$Cl added KDP solution had a size of $54 \times 54 \times 42$ mm$^3$ and the growth rate is more than 20 mm/day. Here the X-ray curves recorded for the crystals grown from 5 mol% KCl added solutions proved that KCl incorporation does not affect the crystalline perfection and its quality.
During the rapid growth of large KDP crystals with good optical quality, it has been found that the trivalent impurity in the solution influences the geometric behavior of the crystals and improves the production yield [133]. The rapid growth of large size KDP and DKDP crystals [134] in the defined crystallographic direction (101) shows that the sectorial and zonary unhomogeneities of the crystal together with changing temperature are the main causes of structure defectiveness and property unhomogeneities in the volume of the crystal grown.

Zhuang et al [135] have grown a large 300 kg single crystal of KDP by rapid growth method using a Holden type crystallizer by temperature reduction method in the presence of 0.5 ppm Fe, Cr and Al ion impurities. This is a significant growth process with assurance of solute transportation at the prism face. Guohui Li [136] used the regeneration process of a 330×330×20 mm³ Z-plate seed carried out in a 1.5 metric tonnage volume crystallizer placed in a water bath of temperature fluctuation less than ±0.02°C within 10 days. The surface of the whole crystal was restored by the formation of a box-like structure filled with growth solution, and then the transparent layer of perfect tetragonal KDP crystal without inclusions, crack and milky regions just like those produced by traditional slow cooling technique can be grown from solution. It was observed that the optical transmission and laser damage threshold of the grown KDP crystal is same as that grown by traditional method. By adopting the brief procedure growth Fujioka and his co-workers [137] were able to grow a 64×63×43 mm³ KDP single crystal in one day from a 8 mm cubic seed. The prismatic sector of the crystal included more impurities resulting in UV absorption and the laser damage was observed to be low, but was improved by thermal conditioning.
Growth of KDP from its aqueous solution has been considered under forced convection conditions by Sunil Verma and Muralidhar [138]. The crystal was grown in a conventional top hanging geometry, and the rotation was accelerated so that a uniform concentration field is set up around the growing crystal, resulting in the growth of good quality crystal. Zaitseva et al [139] showed that large KDP and DKDP crystals with linear sizes up to 55 cm can be grown using continuous filtration technique. The design of this system can operate without spontaneous nucleation at supersaturation as high as 20%. This technique yields crystals of high optical quality with extremely low dislocation densities with a high level of optical homogeneity and high damage threshold. The Schlieren method developed by Bredikhin et al [140] was used to investigate the crystal morphology of the growing (100) and (101) faces of KDP crystal under real rapid profiling growth condition.

According to Leroudier and his coworkers [141], large KDP crystals of high purity can be reproducibly obtained by the rapid crystal growth method operating in stationary thermodynamic conditions at constant temperature and supersaturation. Crystals grown under these conditions show high crystal quality.

Effect of addition of KCl in bulk growth unidirectional (001) KDP by Balamurugan et al [142] using SR method resulted in the growth of crystal of 15 mm diameter and 95 mm height, this is because the addition of KCl blocks the metal ions from entering into the crystal lattice thus avoiding the chain structure which enhances the crystalline quality. Balamurugan and Ramasamy [143] have shown that the SR method is suitable to effectively control the orientation of molecules during bulk crystal growth from solution by growing the unidirectional (101) directed KDP
crystal. KDP crystal grown using growth ampoules by SR method with 30 mm diameter and 55 mm height has higher transmittance and hardness compared to crystal grown by conventional method. Dislocation density and dielectric loss is less in crystals grown by SR method. Balamurugan et al [144] have also shown that for diameter 10 mm and 110 mm height the (001) directed KDP crystal grown by SR method have excellent crystalline perfection, proven by HRXRD analysis, with very low angle internal structural grain boundaries. The properties like laser damage threshold, dielectric constant, transmittance and hardness value are also found to be more for the crystals grown by SR method than by conventional method.

Rajesh and his coworkers [145] have shown that the (001) directed KDP crystal of size 30×20×60 mm$^3$ grown by the same SR method has improved crystalline perfection with minimum defects, higher NLO efficiency, high mechanical strength and transparency of 93%. Robert et al [99] used the modified SR method for unidirectional growth to grow KDP crystals of 65 mm length with a period of 13 days. The crystals have cylindrical morphology with a band gap of 3.20 eV and the physical studies on the grown crystal confirm them to be potential material for fabrication of optoelectronic devices.

Bing Teng et al [146] have used the coniform bottom device which is simple and effective for rapid crystal growth at a rate of 25 mm/day. Here the elimination of secondary nucleation is achieved to obtain perfect KDP crystals. KDP and DKDP crystals were grown at the rate of 10-20 mm/day to various linear sizes nearly 90 cm without the introduction of chemical impurities using two techniques by (i) management of the dislocation structure and (ii) orientation of the point seed. This
controls the crystal habit and dislocation structure during growth [147]. Also large size KDP crystals with improved structure perfection were grown from nominally pure raw material by recirculation and temperature lowering method [148]. KDP crystals grown by the temperature reduction method is controlled by good selection of gradience and range of temperature reduction rate during the growth period. The smallness of seed and also its good quality is effective in the growth procedure [149].

Kim and his coworkers [150] have shown that the zonal structure is more pronounced in the peripheral path of the crystal in the final stages of rapid growth but in spite of sectional and zonal inhomogenities the single KDP crystal grown on point seed by rapid growth method are superior in quality to those prepared by other rapid growth methods.

Zhong et al [151] have shown that difference in growth rates of lattice faces is determined by the combination of growth units which is mainly dominated by the angular orientation of the K-O and O-H bonds and it is found that the solution structure at the boundary layer is similar to that of the crystal. Joshi and Antony [152] studied the growth kinetics of KDP crystal examined at various supersaturations and temperature they have found that in an unagitated system the growth rate of KDP follows a parabolic equation at very low supersaturation and a first order equation at higher degrees of supersaturation.

2.4.3 Role of impurities in KDP crystal growth

Impurities are present in all crystallization processes. Usually impurities are adventitious and undesirable but sometimes they are intentionally added and are called additives. The effect of impurities on the growth rate and habit of crystals
growing in solution has been the subject of many experimental and theoretical studies over many years. Most of the impurities suppress growth, some impurities enhance it, while some others can stop growth completely even at a very low level of impurity concentration. Therefore, impurities can be used to change the growth form of crystals as habit modifiers. The impurity effect depends on impurity concentration, supersaturation and temperature. It also depends on the impurity itself and the system concerned. Different impurities have different effects on the crystal growth.

- Some may exert a highly selective effect, acting only on certain crystallographic faces.
- Some are adsorbed onto growing crystal surfaces.
- Adsorption of impurities onto the crystal changes the relative surface free energies of the faces.
- Low concentration of impurities is effective and exhibits a marked specificity in their action \(10^{-9} < X < 10^{-3}\) mole concentration).
- Some impurities may change the growth kinetics.
- Some impurities may modify the habit of the crystalline phase

### 2.4.3.1 Effect of organic impurities

Organic compounds urea, 11-propanol and ethanol were added as organic impurities to KDP by Enqvist et al [16]. In the studied range of organic concentration, the influence of urea on the growth rate of KDP is less important while that of alcohol is significant, this is due to the chemical nature of urea, and it is found that alcohol molecules are adsorbed on the growth surface. Related to this Kuznetsov and his co-workers [17] have shown that increase in the additive concentration of a variety of organic impurities differing in their chemical behaviour leads first to an increase in
the growth of the KDP crystal and then a decrease passing through a maximum, and
the growth promoting effect of additives is due to the chemical nature of materials.

Dongli Xu and Dongfeng Xue [18] have shown that ethanol molecules in the
mother solution of KDP can intensively affect the crystal size and aspect ratio of
KDP. The ideal crystal morphology is greatly determined by intrinsic characteristics
such as bond number, direction and strength in the crystallographic frame. When
EDTA is added in increasing concentration in the growth solution of KDP it inhibits
the growth of both the prismatic and pyramidal sector. Light scatter in pyramidal-
prism sector is heavier than those in pyramidal sector and prism sector but no light
scatter is found in the sector boundary [19].

EDTA addition enhances the metastable zone width in KDP crystal growth
significantly compared to the pure solution. This may be due to the suppression of
chemical activity of the metal ions in the KDP solution and the optical property of the
crystal is enhanced because EDTA cannot enter into KDP molecular structure [20]
Gui-Wu Lu et al [21] studied the macroscopic growth habit of KDP crystal with
EDTA in the growth solution. This additive enhances the growth rate but does not
affect the crystalline quality. The same effect was observed due to the addition of
EDTA and ATA in KDP by Guo-Zong Zheng et al [22]. They showed that both the
additives have the same increased effect of growth rate initially, which then decreases
with increase of organic addition, however the optical transmission increases in the
UV range for the doped KDP crystal.

When organic dyes Amarnath, Rhodamine B and methyl orange were doped
in KDP crystal, it was found that Amarnath in the solution at low supersaturation and
high dye concentration, colored the pyramidal section (101) of the crystal, and KDP with Amaranth indicated a strong interaction between the OH groups. The dye doped crystals have good SHG efficiency and increased microhardness due to doping [23]. Dye doping (amaranth, rhodamine and methyl orange) in KDP crystal improves the NLO properties of the grown crystals and Li$^+$ ion irradiation modifies the optical properties and leads to the depletion of hydrogen from the KDP sample which is attributed to the possible bond breaking mechanism [24].

KDP crystals doped with Xylenol orange (XO) and methylthymol blue (MTB) and grown by method of slow evaporation and temperature lowering revealed that the crystal habit changes in the presence of organic dyes. The laser damage threshold in the prismatic rich colored sectors of KDP:XO is same as that in the prismatic sectors of pure KDP crystals [25]. Results of doping of KDP with Chicago sky blue (CSB) indicate that CSB tends to be incorporated into the pyramidal sector of the KDP crystal and as CSB concentration increases structural perfection of the pyramidal sector is deteriorated and the transmittance of the grown KDP crystal decreases [26].

When dye molecules Amaranth, Chicago sky blue, Xylenol orange, Pentachloro-Ruthenate (PCR) are added to KDP solution, it was found that Amaranth and CSB stain the pyramidal face, whereas XO and PCR stain the prismatic sector. The dielectric constant shows a remarkable increase for the prismatic face while the value remains unchanged for the pyramidal sector [27]. Miki et al [28] grew coloured KDP crystals from a sky blue dye solution produced in a mixed suspension mixed product removal (MSMPR) crystallizer. The growth rate was found to increase with crystal size but decreased as the residence time decreased. Low dye concentration generated
regular shaped crystals while high dye concentration formed a special shaped KDP crystal having no (100) sector.

Due to the addition of sodium metaphosphates, the density of scatters increases with increase of additive concentration. Macro inclusions also occur when dopant concentration is high enough in the sector boundaries and pyramidal sectors [29]. When the complexing agent (1,10-phenanthroline) was added into KDP and ADP solutions it leads to an increase in metastable zone width and decrease in growth rate with increase in impurity concentration. Higher optical transmittance with change in surface morphology and decrease in NLO efficiency is also observed [30]. KDP crystals doped with N,N′ dimethyl urea shows decrease in growth along (100) direction due to attachment of larger size cations on the (100) prismatic face, whereas there is enhanced SHG efficiency due to doping [31].

Alcoholic additives affect the nucleation of KDP and DKDP from aqueous solutions, and since alcohols contain hydroxyl radicals the interaction between molecules is weaker due to the presence of hydrogen bonds in comparison with ionic bonds in organic system [32].

Urea doped KDP crystals were found to have more inclusion when the concentration is increased, whereas KCl doped crystals have less inclusions and higher transparency. XRD studies show that the crystal lattice is distorted and the variations of lattice constant satisfy Vegard’s law [33]. Podder [34] analyzed the effect of the same dopants and found that urea promoted a faster growth rate in KDP than KCl in KDP crystals. Urea doped KDP crystals had higher mechanical strength.
than KCl doped KDP crystals, but KCl doped crystals have better transparency and NLO response than urea doped KDP.

Pritula et al [35] have shown that urea doping enhances the laser damage threshold, SHG efficiency and hardness property in KDP crystals. It is also observed that addition of 0.6 mol% of urea to KDP leads to low permittivity value [15].

Studies on the effect of doping/adding amino acids like L-arginine [36-38], L-alanine [38-40], glycine [37,41], L-glutamic acid [42], L-histidine [37,42,43], L-valine [42], L-lycine [44], L-threonine [45] and L-proline [46] in KDP crystal show that due to the incorporation of these amino acids in KDP crystal lattice there is enhancement in NLO properties, improvement in transparency, with changes in thermal stability and mechanical strength. Low values of dielectric loss and dielectric constant is observed for amino acid doped KDP crystals compared to pure KDP crystals. Effect of doping metal ions and amino acids in KDP crystal show increase in hardness and NLO property due to doping [47]. Doping of thiourea in KDP increases the noncentrosymmetric structure of KDP and enhances its nonlinearity. Thiourea doped KDP crystals have higher optical transmission and are more applicable for optoelectronic application than pure KDP crystals [48]. Doping of organic additives like urea, thiourea and EDTA improves the mechanical strength and optical transparency of the doped KDP crystal [49].

Impurities prevent step propagation of a crystal surface. This effect has been analyzed quantum theoretically. The impurity effect has been investigated using Gaussian software, and their tendencies can be quantitatively considered through
quantum chemistry involving atomic charge and electrostatic potential of impurity [50].

2.4.3.2 Effect of inorganic impurities

It has been reported that the addition of 2 wt % Borax changes the morphology and enhances the transparency, thermal stability and NLO efficiency of KDP, where SHG of the doped KDP crystal is 1.098 times greater than pure KDP [51]. Dendrite single crystals of KDP doped with cadmium iodide have been grown from vapour phase in vacuum. This CdI$_2$ doping results in marked changes in surface features compared with doping with PbI$_2$ and CdBr$_2$ [52].

Begum and Podder [53] in their work on the influence of co-doped bimetallic Mg(II) - Ni(II); Mg(II) - Co(II), Mg(II) - Li(I) impurities of KDP crystal growth found that these impurities enhance the metastable zone width for all temperatures and makes the KDP solution more stable, the metal ion suppresses the activities of heterogeneous nucleation and there is an increase in interfacial energy with decrease in nucleation rate. This technique is useful in the growth of good quality bulk KDP crystal with faster growth rate.

Doping of thallium impurity causes habitat changes in the growing KDP crystals. Optical spectra show that thallium concentration changes the position of the photoluminescence peak. The emission band maximum remains unchanged but the emission intensity increases [54]. Voronov et al [55] have shown that doping of KDP crystal with cerium ions and organo-cerium complexes resulted in an effect that the organometallic cerium complex blocks the growth of the prismatic sector and the
cerium doped KDP crystals exhibits a photoluminescence band peaking at the wavelength $\lambda = 350$ nm [55].

KDP single crystals grown with phosphoric acid added solution by temperature reduction method show that the addition of the acid causes stability of growth and remarkable difference in optical quality between pyramidal and prismatic sectors [56]. The precision X-ray structural characterization of KDP crystal samples doped with chromium impurities were studied by Malakhova et al [57]. It was found that the prismatic growth sector is more perfect than the pyramidal growth sector. The analysis of the IR spectra indicates the presence of the nitrate ions in the sample of both the growth sectors, and the structurally bound water molecules and OH groups are present in the prismatic sector.

Guohui et al [58] have found that when 5 mol%, KCl and 0.01 mol% EDTA additive was added to KDP to grow crystals by rapid growth and solution cooling method, the grown crystals had better optical transmission and laser damage threshold compared to crystals grown by traditional method with enhancement in metastable zone width and good crystalline perfection and quality. When pyrophosphate was added into the KDP growth solution, light scatter in KDP crystal was aggravated which was nonuniformly distributed in the prismatic and pyramidal section of KDP crystal. Also the wavelength of transmission of crystal decreases evidently due to the presence of pyrophosphate [59].

When potassium acetate and potassium citrate were added as additive the results show that the doped KDP crystals do not contain any structural grain boundaries and have good crystalline perfection. The metastable zone width and
induction period increases for the grown crystals, with good transmittance and low $\varepsilon_r$ value which is a suitable parameter for enhancement of SHG coefficient [60].

Dhanaraj and his co-workers [61, 62] studied the effect of addition of 5 mol% of potassium carbonate and 5 mol% potassium thiocyanate in KDP crystal. Nucleation studies show enhancement of zone width and growth rate. HRXRD analysis shows that crystalline perfection of the grown KDP crystals were extremely good with low dielectric constant. SHG, laser damage and optical transparency show a positive effect due to doping.

The addition of cerium in KDP studied by bi-direction seed rotation technique reveals that the trivalent Ce addition prevents other bivalent metals (Co, Ni, Mn) from entering the crystal lattice resulting in reduced defects and dislocations, with more crystalline perfection [63]. When growth rate and effect of doping sodium ions were studied, the thickness and width of the doped crystals were found independent of sodium incorporation and the ratio of concentration of sodium in the crystal to sodium in KDP solution is found to be constant [64].

With increase in concentration of Cr(III) in the KDP growth solution, the mean growth rate increases along the (001) direction but remains constant along the (100) direction. The increase along (001) direction is due to the decrease in free energy of the face, which decreases with an increase in impurity concentration [65].

### 2.4.3.3 Effect of anions and cations

The existence of high valence metal ions in the dopant inhibit the growth of the prismatic face of the KDP crystal. The anions that can form H bonds with $\text{H}_2\text{PO}_4^-$
inhibit the growth of the pyramidal face. The metallic ions are adsorbed at the growth site of the prismatic face for their strong interaction with the \( \text{PO}_4 \) tetrahedron through a coordination bond, because they are difficult to replace by other low value cations such as \( \text{K}^+ \) or \( \text{H}^+ \), so they are easy to incorporate into the bulk crystal when the prismatic growth face forms [66]. Some anionic impurities (Sodium metaphosphate, potassium pyrophosphate, formic acid, acetic acid, oxalic acid and tyrosine) have inhibiting effect on the growth of KDP crystals. Inhibition is caused by the absorption of the anions at the growing crystal surface through the formation of H-bonds between the anions and the \( \text{H}_2\text{PO}_4^- \) groups. The incorporation of these anions have a harmful effect on laser damage threshold [67].

With the increase of \( \text{SO}_4^- \) dopant concentration in KDP growth solution many defects occur, such as mother liquid inclusions, parasite crystals and cracks. When the dopant concentration reaches a certain value the ultraviolet transmittance of the grown KDP crystal decreases a lot compared to KDP crystals with low dopant concentration [68]. Among the anions contributing to the absorption in the UV spectral region are transition metal complex anions (\( \text{Wo}_{2^-}, \text{MoO}_{2^-}, \text{Cr}_2\text{O}_3^{3^-} \) and \( \text{Vo}^{1^-} \)) and \( \text{SiO}_3^{2^-}, \text{CO}_3^{2^-} \) and \( \text{F}^- \). The \( \text{PO}_2^+, \text{ClO}_4^-, \text{SO}_4^{2-} \) and \( \text{Cl}^- \) anions have no effect on the solution transmittance [69].

KDP doped with \( \text{CrO}_4^{2-} \) ions of various concentration grown for electro-optic device applications show that the doped crystals have low half wave voltage as compared to that of pure KDP with no significant change in ferroelectric properties.
Ding et al. [71] showed that KDP crystals doped with $\text{WO}_4^{2-}$ additive inhibited the growth with tapered (100) faces for high additive concentration.

The effective distribution coefficient $K$ in an impurity doped KDP crystal depends on the mechanism of the incorporation of cations and their ionic radius. Increasing the concentration of several divalent cations in solution may reduce their distribution coefficient because of the competition between the cations for interstitial sites in KDP [72]. Also when the structure of KDP crystals doped with trivalent and divalent cation were simulated by minimising the energy of atomic interaction, three types of defects were revealed (i) isolated defects (ii) cluster chain centers and (iii) complex centers and there is change in morphology of the crystal due to the incorporation of these cations into the KDP crystal structure[73].

Eremina and his coworkers [74] studied the influence of bivalent ($\text{Ni}^{2+}, \text{Co}^{2+}, \text{Fe}^{2+}, \text{Mn}^{2+}, \text{Ba}^{2+}, \text{Ca}^{2+}, \text{Sr}^{2+}$) and trivalent ($\text{Fe}^{3+}, \text{Mn}^{3+}, \text{Y}^{3+}, \text{La}^{3+}$) impurity ions on the growth rates, and surface morphology of KDP crystal faces. It was found that the effect of trivalent ions is due adsorption on the crystal faces, while in bivalent impurities the ions are incorporated into the surface crystal layer leading to changes in growth kinetics and surface morphology. It has been also found that $\text{Sn}^{4+}$ ion can greatly improve the stability of KDP growth solution and reduce the crystal growth rate but higher concentration of the dopant affects the transparency of the KDP crystal [75].

Owczarck and Sangwal [76] have shown that adsorption of both $\text{Fe}^{3+}$ and $\text{Cr}^{3+}$ impurities in KDP crystal takes place at kink sites on (100) faces. It was also found that the growth rate at different supersaturation due to these impurities takes place at
(100) and (101) faces [77]. It has been discussed by Javidi et al [78] that incorporation of Ca$^{2+}$ impurity ions in KDP crystal depend on the distribution coefficient of the impurity which affects the habit and surface morphology of the crystal. The presence of Ca$^{2+}$ impurity ion decreases the optical transmission percentage of the KDP crystal. It has also been shown that the presence of La$^{3+}$ retarded the growth rate and induced crystalline lattice defects. Irradiation effect on La$^{3+}$ doped KDP crystals show increase in conductivity and hardness after irradiation [79].

When Ba$^{2+}$ were doped in different concentrations in KDP, it is observed that during the growth process the defect region expands gradually with increasing Ba$^{2+}$ concentration, however non-uniform distribution of Ba$^{2+}$ ions cause remarkable difference in optical quality between prismatic and pyramidal sectors of the grown KDP crystals [80]. It is found that the doping of Fe$^{3+}$ ion can improve the stability of the KDP growth solution when its concentration is less than 30 ppm whereas the growth rate becomes slower with increase in Fe$^{3+}$ concentration and light scatter becomes more and transmittance of KDP becomes lower[81].

The influence of Fe$^{3+}$ and Al$^{3+}$ impurities on the dependence of the layer growth rate versus the solution supersaturation was studied in KDP crystals using the method of in situ interference microscopy investigated by Rashkovich and Kronsky [82]. Analysis of the decelerating action of these impurity stoppers show that they are firmly adsorbed by the KDP crystal growth surface. Alexandru et al [83] measured the growth kinetics of the prismatic faces of KDP crystal in impurified Fe$^{3+}$ solution. He observed that the surface 2-D nucleation mechanism was found to apply at higher supersaturations and increase of the pH of the solution changes the shape of the
growth kinetic curves and the segregation coefficient of impurities. When KDP crystal was grown in a supersaturated solution containing a metallic ion ($\text{Al}^{3+}$, $\text{Fe}^{3+}$ or $\text{Cr}^{3+}$), the growth rate, morphology, and distribution of the metallic ions into the KDP crystal were measured as the ionic concentration and supersaturation in the solution changed. It was found that in the KDP crystal, $\text{Al}^{3+}$ and $\text{Fe}^{3+}$ were greatly concentrated, but $\text{Cr}^{3+}$ was diluted [84].

$\text{Ni}^{2+}$ and $\text{Mg}^{2+}$ when incorporated into the KDP crystal lattice form defects that generate stresses on the crystal surface. These dimetallic dopants have higher transparency, SHG and crystalline quality than undoped KDP crystals [85]. Shirsat et al [86] have shown that $\text{Li}^+$ doped KDP crystals have enhancement of SHG, increase in thermal stability and the dielectric studies show lower value of dielectric constant at higher frequencies. $\text{Cu}^{2+}$ doped single crystals investigated by EPR technique show that $\text{Cu}^{2+}$ ions substitute the $\text{K}^+$ ions. The spectra of the complex contains five sites, of which four are compatible with the tetragonal symmetry and the fifth one belongs to an interstitial site [87].

2.4.3.4 Effect of nanoparticles and complex impurity

Temperature lowering techniques were used to grow KDP crystals containing $\text{TiO}_2$ (anatase) nanocrystals from aqueous solution. Six fold rise of crystal lattice parameters in the doped crystal was noticed relative to the pure one and a giant nonlinear optical response of anatase nanoparticles manifested in KDP crystalline matrix [153]. The optical response in the KDP : $\text{TiO}_2$ composite is explained due to the resonance excitation of the defective states of $\text{TiO}_2$ [154]. The optical characteristics of KDP crystal doped with $\text{TiO}_2$ nanoparticles showed that the optical
quality of the investigated samples decreases insufficiently for the used concentration of nanoparticles and this is due to the scattering property of the novel hybrid material [155].

KDP crystals doped with TiO$_2$ nanoparticles grown by temperature reduction method show that the nanoparticles with adsorbed H$_2$PO$_4^-$ and [H$_2$PO$_4^-_2$] anions were incorporated predominantly into the positively charged (101) face of the pyramidal sector of KDP [156].

Nanorods of KAP and KDP doped with rhodamine were grown using template approach. SEM images of micro and nanorod indicate a crystalline growth tendency. A shift of the emission bands towards red was observed when the luminescent properties of the nanorods were compared to that of the bulk crystal [157].

Bensouici et al [158] have shown that when ZnSe nanocrystals were incorporated in KDP dielectric crystalline matrix the optical absorption spectra, X-ray diffraction and Raman measurements show the presence of these ZnSe nanoparticles in KDP crystal. Halimi and his coworkers [159] used KDP as the host matrix of ZnS semiconductor nanocrystals grown by temperature lowering method at 50 °C. The obtained optical gap for the system was 4.01 eV deduced from UV-Vis absorption spectra and the gap shift $E_g = 3.91$ eV which reveals the intrinsic quantum confinement effect of these nanoparticles.

Structural characterization and UV-Vis absorption spectral reveal incorporation of CdTe nanoparticles in KDP crystalline matrix and a large blue shift is
observed in KDP crystal due to the quantum confinement effect of these nanocrystals [160].

The growth retardation due to polyol admixture is significantly stronger in KDP crystal, reducing overall growth rate and broadening the dead zone of crystal growth compared to other low molecular admixtures with similar functional groups [161].

KDP doped with rare earth (Ce, Sm, Gd, Yb) complexes with alizarin complexone show that these complexes are selectively incorporated into the growth sectors of the crystal, with shift in the absorption bands. The stokes shift of the complexes in the crystal is three to four times greater than that in solutions [162].

2.5 PHYSICAL PROPERTIES

2.5.1 Electrical conductivity and dielectric response

Electrical conductivity of the KDP-group crystals is determined by the proton transport within the framework of hydrogen bonds. Two mechanisms can be considered, the first one is identical to the conductivity mechanism in ice which contains hydrogen bonds. The conductivity of ice is determined by the simultaneous presence of positive and negative ions and orientational defects i.e. vacant hydrogen bonds (L-defects) and doubly occupied hydrogen bonds (D-defects). According to the second mechanism, conductivity is associated with the incorporation of impurities having different valencies into the crystal lattice and the formation of corresponding defects in ionic crystals [163-164]. Experimental data and character of the temperature dependence of conductivity allow us to state that the conductivity of KDP and DKDP crystals is determined by both thermally generated L-defects and the
foreign impurities incorporated into the lattice and generating L-defects there. Lokshin [165] found that HPO$_4^{2-}$ ions are responsible for the formation of vacant hydrogen bonds (L-defects), and the electrical conduction in KDP crystal, is protonic and the K$^+$ ion does not contribute much to conduction which is mainly due to the anions namely (H$_2$PO$_4$)$^{1-}$ ions.

Heating KDP at about 500 K significantly modifies its electrical properties. Two relaxation processes are observed after the treatment. One is associated with a fairly strong dielectric polarizability, and a small conductivity jump is observed close to 440 K [166]. The dielectric constant ($\varepsilon_r$) and dielectric loss of KDP crystal measured in the ferroelectric phase verses the sample thickness ‘t’ show that the $\varepsilon_r$ values change with ‘t’ and become maximum for t approximately equal to one half of the other sample dimensions (in a-axis direction). Also the domain freezing temperature which corresponds to the low temperature decreases with the sample thickness in a logarithmic law [167]. The dielectric properties of samples cut from the pyramidal growth faces (100) and (010) of pure KDP and chromium impurity doped crystals, show that ‘soft’ and ‘hard’ samples occur. Samples from the peripheral regions contain more impurity and have properties belonging to hard crystals [168]. Measurements of the low frequency dielectric response of multi domain KDP in low applied field indicate the existence of two regimes of domain dynamics [169].

Meena and Mahadevan [108] have shown that the electrical parameters, AC and DC conductivity of KDP and ADP crystals added with L-arginine measured along a and c direction increases with increase in temperature, this effect is due to the L-defects in pure KDP crystal. When impurity concentration increases there is
decrease in electrical parameters due to reduction of L-defects created by additional hydrogen bonds of the impurity.

Undoped and KI/NaI doped KDP crystals with/without gold doping were irradiated using Co$^{60}$ source and when electrical conductivity measurements were carried out on the irradiated sample, an increase in electrical conductivity with increase of KI/NaI and with gold doping was observed which increased with increase of temperature [106]. Conductivity is also found to increase due to radiation indicated defects on KDP crystal containing KCl / NaCl with and without gold doping [107]. Priya et al [119] showed that in urea and thiourea impurity added KDP single crystals conductivity increases with increase in temperature and gives evidence that conductivity in KDP is protonic and mainly due to anions and not the cations. Studies on KDP crystals doped with L-lycine monohydrochloride show low value of dielectric constant and dielectric loss [170].

When ammonium compounds were added as impurity the dielectric parameters and conductivity increases with temperature and impurity concentration [97]. Dielectric properties of rapidly grown KDP crystals studied over a wide temperature range show that contribution of domains to permittivity in rapidly grown crystals is considerably less than in conventionally grown crystals [171]. Single crystals of glycine [172] and L-arginine [173] doped KDP grown by SR method show low values of dielectric loss due to fewer defects and enhancement of crystalline perfection.

Electrical DC conductivity and laser damage threshold for urea doped KDP crystals show low electrical conductivity, high resistivity and high laser damage
threshold [174]. When complex organic and inorganic molecules are doped in KDP, the dielectric parameters analyzed in the frequency range 10 mHz to 10 MHz reveals a noticeable dispersion in the paraelectric phase at 30-80 °C. In some crystals the deviation of cole-cole diagram from Debye-type relaxation is observed [175].

Goma et al [15] have shown that with the addition of urea dielectric parameters increase with increase in temperature but do not vary systematically with respect to impurity concentration and 0.6 mole % urea addition leads to low value of dielectric loss.

2.5.2 Phase transition and thermal studies

KDP exhibits an electric dipole even in the absence of external electric field. It undergoes a phase transition from polarized phase to unpolarized phase. The temperature at which the transition takes place is known as the Curie temperature $T_c$ (123 K). When cooled below 123 K, KDP changes to a crystal hybrid in which there is a break up of single crystals into sub-crystalline regions. When the hybrid crystal is warmed above the Curie temperature, the sub-crystalline units merge. The spontaneous polarization for KDP is $4.75 \times 10^{-4}$ coulomb/cm$^2$ at 96 K [102,176].

The room temperature paraelectric phase (tetragonal $I4_2d$) and the low temperature ferroelectric phase are the two phases exhibited by KDP [177]. On the basis of temperature dependence of dielectric constant and infrared spectra, Grinberg et al [178] observed a KDP phase at 180 °C and Rapoport [177] found another at 233°C by differential thermal analysis.
KDP doped with organic Xylenol orange dye has been studied and the annealing temperature effect on the degree of dye protonation in the crystal matrix is established [179-180]. Subramony et al [181] reviewed the high temperature behaviour of pure KDP, and obtained structural identity of the high temperature phases. The phase transition in KDP crystal, the effect of temperature, pressure and external electric field on the crystal structure of KDP have been studied by several groups [182-185]. Raman spectral and pyroelectric measurements in KDP below the transition from the paraelectric phase to ferroelectric phase indicate the occurrence of another phase transition. This transition is explained due to the lowering of the local symmetry of the phosphate ions in the cell [186].

Low temperature polarized Raman scattering measurement of KDP: Mn were performed at temperature ranging from 14 to 300 K over the spectral range 50-1250 cm\(^{-1}\). The results show that the Mn doped KDP crystal undergoes a phase transition between 115 K and 97 K where the crystal changes from paraelectric to ferroelectric phase [187]. The Fe\(^{3+}\) doping in KDP results show that some of the Raman active peaks shift in the frequency and become much more intense at low temperature down to 10 K and investigated at a spectral region up to 1500 cm\(^{-1}\) [188].

Electronic spin-lattice and spin-spin relaxation times \(T_1\) and \(T_2\) were measured for radiation induced free radical ions in selenium doped KDP crystals over a temperature range from 4.2 to 190 K. The Debye temperature was estimated to be 119 K [189]. Thermal depolarization current in KDP doped with Cr\(_2\)O\(_7^{2-}\) has been studied in the temperature range 80-300 K [190] where a single peak is observed at 200 K in KDP due to the proton conduction in (H\(_3\)PO\(_4\))\(^-\) sublattice.
EPR spectra of X-irradiated KDP:CrO$_4^{2-}$ single crystals show that at 77 K uncharged H$_2$PO$_4$ radicals are created parallel with HPO$_4^{-}$ ions and part of the chromium ions enter the lattice in the trivalent state resulting in paramagnetic centers whose thermal stabilities are different [191]. The ESR absorption spectra of Cu$^{2+}$ ion doped KDP were studied both in paraelectric and ferroelectric phases. There are two kinds of Cu$^{2+}$ sites in the crystal and the intensity of the ESR absorption changes abruptly when passing through Curie temperature [192].

KDP crystals doped with Chicago sky blue show a difference in heat capacity of 1 K than pure KDP in the vicinity of $T_c = 122$ K and also reduces the permittivity in the polar phase. These effects are due to the influence of nonisomorphic defects on the ferroelectric phase transition in a piezoelectric crystal [193]. When dye molecules are added to KDP these molecules affect only the domain contribution and do not shift the transition point whereas complex inorganic impurity suppresses the domain contribution and slightly decrease the transition temperature [27].

### 2.5.3 Optical and electro-optical properties

Optical absorption in KDP crystals correlates with the transmittance of the growth solution, which in turn depends on the impurity composition. It is noted that the largest contribution to absorption in the range 200-400 nm are made by Fe$^{3+}$ and Cr$^{3+}$ ions, while Hg$^{2+}$, Sb$^{3+}$, Cu$^{2+}$, and Bi$^{3+}$ cations give raise to new absorption and reduce the transmittance of the solution. Mg$^{2+}$, Ca$^{2+}$, Ni$^{2+}$, Co$^{2+}$, and Sn$^{4+}$, have little or no effect on the solution transmittance [69].

The effect of Pb, Ca, Si impurities on the laser damage threshold and UV absorption of KDP crystals show that the laser damage threshold of $5 \times 10^{-5}$ wt%
impurity was $6 \times 10^{11}$ W/cm$^2$ and decreases nonlinearly with higher concentrations of impurity [194]. The effect of s-p-d- and f- block elements (Mg, Sb, Pd and La) on KDP crystals show that the crystalline perfection of the grown crystals depends on the ability of accommodating the dopants by the crystalline matrix, and the SHG is enhanced considerably for low concentration of dopants [195].

Pritula et al [196] have reported that Xylenol orange (XO) preferentially dyes the (100) and (010) faces of KDP crystal and the crystal habit changes in the presence of organic dyes. In the XO doped KDP crystal, the luminescence is highly polarised and the damage threshold of the doped crystal is same as the pure one. It was also revealed by IR absorption spectral analysis that there is a strong interaction between the incorporated dye molecules and the hydrogen subsystem of the matrix.

In KDP doped with L-arginine, the IR absorption and Raman results show chemical fluctuations between the amino groups of the organic molecule and the phosphate unit of the KDP crystals. Incorporation of amino group into the structure of KDP is revealed by shifting of diffraction lines and appearance of new lines in the XRD results [197].

KDP crystals grown by SR method have higher laser damage threshold since the growth sector boundaries are reduced resulting in better quality crystals [144]. KDP crystals grown to size 40 cm $\times$ 40 cm and used for high power laser have two to three times higher laser damage threshold than conventionally grown crystals [112]. Urea doped KDP crystals have a laser damage threshold 20-25 % higher than that of pure KDP [35]. Also 5 mol% potassium carbonate added KDP have higher laser
damage threshold than pure KDP, which is attributed to the better crystallinity of the bulk crystal [61].

Salo [198] has shown that KDP crystals grown of the rate of 10 mm/day in the direction of a prespecified angle of synchronism ($\theta = 59^\circ$) had high structural quality and the bulk laser damage threshold at the level of $5 \times 10^{10}$ cm$^2$. However Liwang et al [109] have shown that when the growth rate is 5 to 19 mm/day the laser damage threshold of the crystal decreases with increase of absorption coefficient and large scale impurity is an important factor that can cause absorption in the UV range and also reduces the damage threshold. Zhu Sheng-Jun and his coworkers [199] adopted the ‘point seed’ rapid growth method to grow KDP crystals in the presence of diethylene triamine pentaacetic acid (DTPA). It was observed that when the concentration of DTPA, increase growth rate of the KDP crystal increases initially and then decreases passing through a maximum. However the optical transmittance in the UV region was enhanced significantly. Nonuniformity in laser damage threshold is observed for samples cut in the (100) and (101) growth sectors of KDP crystals grown from point seed at the rate of 15 mm/day [200].

When sulfosalicylic acid was added to KDP crystals optical transmission and laser damage threshold were found to be the same as that of crystals grown by traditional method [110]. The same effect in laser damage threshold was observed when KDP crystals were grown by regeneration process of a $330 \times 330 \times 20$ mm$^3$ Z-plate seed [136]. KDP crystals grown in the presence of a series of silicate ($\text{SiO}_3^{2-}$) impurity concentrations revealed that the presence of the impurity could lead to the decrease of transmittance at the region of ultraviolet band for pyramidal sectors and
slightly increased the transmittance for prismatic sectors. The decrease of laser damage threshold was attributed to the lattice defects and the redundant electrons brought by the replacement of SiO$_2^-$ at the PO$_4^{3-}$ position [201].

KDP crystals grown with different concentration of quaternary ammonium salt in solution show that the transmittance ratio is less than unity at some locations. This indicates that the plane wave effect and optical effect are highly displaced in KDP crystals [202]. The first principle calculation of linear and nonlinear optical properties of KDP and urea show, that in the case of KDP crystals the contribution of PO$_4^{4-}$ groups to second harmonic generation is dominant and hydrogen bonds contribute much to birefringence [203].

Measurement of magnitude and sign of quadrupole optic coefficient for KDP and ADP show that the nonlinear susceptibility responsible for the quadratic electrooptic effect is mainly due to the interaction of the low frequency electric field with the crystal lattice [204]. Analysis of quadratic electro-optic response in KDP crystal shows that the calculated values of quadratic coefficient $g_{xyxy}$ are two orders of magnitude greater than measured values for a static field than with the dynamic field. This finding explains the observed spread in some KDP type crystals [205]. Barium impurity in KDP was studied with the first-principle simulation method. The relaxed configurations and density of the states of KDP crystal with impurity were calculated. It is found that the band gap of KDP crystal narrowed down to about 3.9 eV, which is consistent with the experimental data from previously reported studies and indicates that barium may be a source of low-damage threshold [206].
KDP single crystals grown by adding different quantities of MnCl$_2$ in the solution has been investigated. These studies revealed that the grown crystals could accommodate Mn(II) in the interstitial positions of the crystalline matrix of KDP only up to some critical concentration. Enhancement in SHG efficiency and transparency was enhanced at 1 mol% doping concentration [207]. The effect of Co$^{60}$ gamma irradiation on L-alanine cadmium chloride, L-alanine and L-arginine doped KDP crystals show morphological changes in the doped crystals. DC conductivity of L-alanine cadmium chloride and L-alanine doped KDP crystals were found to increase with increase in radiation dose whereas the DC conductivity decrease in the case of L-arginine doped KDP crystals. However no significant change in melting point in these crystals is observed as a result of irradiation [208].