CHAPTER 2

REVIEW OF KDP SINGLE CRYSTALS AND GROWTH AND CHARACTERIZATION OF UNIDIRECTIONAL <100>
KDP SINGLE CRYSTAL BY SANKARANARAYANAN-RAMASAMY (SR) METHOD

2.1 INTRODUCTION

There has been more than 80 years research on the potassium dihydrogen phosphate (KDP) (Kunpeng Wang et al 2006). The National Ignition Facility (NIF), being built at Lawrence Livermore National Laboratory (LLNL), requires large single crystal plates of KDP (KH$_2$PO$_4$) and DKDP (KD$_2$PO$_4$) for pockels cells and frequency converters as a part of its design (Zaitseva et al 1997). These crystals must have high optical quality and, because of the operation at high fluences, be highly resistant to laser radiation damage. The KDP is a transparent dielectric material best known for its nonlinear optical and electro-optical properties. Because of its nonlinear optical properties, it has been incorporated into various laser systems for harmonic generation and optoelectrical switching (Nelson et al 2001). The very high-energy Nd-glass lasers used for inertial confinement fusion (ICF) research need large plates of nonlinear crystals for electro-optic switches and frequency converters (Zaitseva et al 2001). Potassium dihydrogen phosphate (KDP) crystal draws persistent attention of scientists due to its excellent quality and possibility of growing large-size single crystals (Dongli Xu and Dongfeng Xue 2008a, Xiue Ren et al 2008, Dongli Xu and Dongfeng Xue 2008b).
Microscopically, crystal growth includes crystal morphology, crystal defects, and growth rate, which are all related to the constituent growth units and their chemical bonding process (Dongli Xu and Dongfeng Xue 2005, Dongli Xu and Dongfeng Xue 2006, Dongli Xu and Dongfeng Xue 2008c). KDP crystal is at present the only nonlinear crystal, which can be grown to the large sizes needed for laser radiation conversion in laser fusion systems.

At room temperature, KH$_2$PO$_4$ has a noncentrosymmetric tetragonal (ferroelectric) lattice (point group $I\bar{4}2d$) with lattice constants $a = b = 7.448$ Å and $c = 6.977$ Å. 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 PO$_4$ groups linked to each other by hydrogen bonds. These PO$_4$ 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 PO$_4$ group is linked to four other PO$_4$ groups, spaced $c/4$ apart along the $c$ axis, by hydrogen bonds.

In all the methods of growth, planar habit faces contain separate regions common to each facet having their own sharply defined growth direction known as growth sectors. The boundaries between these growth sectors are more strained than the extended growth sectors due to mismatch of lattices on either side of the boundary as a result of preferential incorporation of impurities into the lateral section (Gallagher et al 2003). In the case of KDP it has been reported that the prism sector contains less defects compared to the boundaries (Xun Sun et al 2000). <001> KDP crystals have been already grown by SR method (Balamurugan and Ramasamy 2006, Justin Raj et al 2007). Optimized growth rate of <001> direction KDP crystals is 5 mm/day. However <001> growth contains four growth sector boundaries.
Hence it was decided to evaluate the crystal quality by growing along (100) which will contain a single plane face (Prism plane) and there will not be any growth sector boundary.

In this chapter, the unidirectional growth and characterization details of KDP crystal along the <100> direction are discussed for the first time by Sankaranarayanan-Ramasamy (SR) method. Using the same ingredients KDP crystal was also grown by conventional solution growth method. Identical samples prepared with similar orientation were subjected to all the studies. Several samples were analysed. The results of SR method grown KDP and conventional method grown KDP are compared.

2.2 REVIEW ON THE GROWTH OF KDP CRYSTALS

KH₂PO₄ and its deuterated analogue are technologically important crystals and are grown by the low-temperature solution growth technique from aqueous solution. Busch and Scherrer discovered ferroelectricity (Wadhawan 1999) in KDP in 1935, after the first discovery of Rochelle salt as a ferroelectric crystal. Detailed investigations on KDP and related crystals started only after 1935 (Rashkovich 1991). Investigations on KDP and DKDP crystals got a new impetus after the advent of lasers, when a second harmonic of the fundamental was produced using phase matching in KDP crystal. Presently, KDP-family crystals are the primary materials used in devices like second harmonic generators, third harmonic generators, and electro-optic modulators.

The technological importance of KDP-family crystals is reflected by the fact that hundreds of large sized SHG, THG, and Pockels elements are needed for the ICF programme. Thus the challenge is to grow good-quality large-size single crystals, in order to have SHG and THG elements with cross-sectional areas as large as 40 cm × 40 cm. The challenge is not only to grow
large crystals, but also to do so in the minimum possible time, without any compromise on the quality of the crystals, especially their damage threshold. Zaitseva and co-workers have been successful in growing the crystals with linear dimensions up to 55 cm at rates of 12 – 15 mm per day along z-axis, using a continuous-filtration scheme (Zaitseva et al 1999). Kurnakov and co-workers (Rashkovich 1991) were the first to investigate the K$_2$O-P$_2$O$_5$-H$_2$O system, to which KDP belongs. It was found that KDP crystallizes to only one phase, i.e. the tetragonal phase.

Initially KDP crystals were grown by suspending a seed in the saturated solution, and either lowering the temperature slowly, or allowing slow evaporation to take place. This method, usually called the conventional method, faced the drawback of low growth rates because of low supersaturation. The growth rate achievable by this technique is typically of the order of 1 mm/day. Also, the growth rates along <100> are much lower. Therefore, to have large-cross-section c-plates, one has to start with large area c-cut plates. Moreover, a lot of unusable volume grows because of the large capping region in the crystals grown by this technique.

A better method, wherein a platform is used and the growth is started from an unhurt point seed and carried out at much higher supersaturations, came into practice. This method is called the platform technique.

Most of the large crystals grown from aqueous solution are now grown by the platform technique, at high supersaturations. Further, it is possible to grow isometric crystals from a point seed by using this technique. Since growth rates required are high, the so-called three-vessel method (TVM) has been developed as a solution replenishment method, in which the growth takes place at constant temperature. The advantage of this method over the temperature-reduction method is the use of a small sized crystal-
growth tank. But the method is complicated, and chocking of the interconnecting pipes between the vessels can take place. Using the TVM, Sasaki et al. could grow 40 cm x 40 cm crystals of KDP (Sasaki and Yokotani 1990)

### 2.3 EFFECT OF ETHYLENEDIAMINETETRA ACETIC ACID (EDTA) ON THE LIGHT SCATTER IN KDP CRYSTAL

The scattering of light by KDP single crystal with EDTA added was studied (using argon laser) (Xun Sun et al 2000). Different contents of EDTA (AR) were added into the KDP growth solution. The contents of EDTA in KDP solution were 300, 1000, 5000 ppm of KDP, respectively. In order to study the effect of EDTA on light scatter in different sectors of KDP crystal, 1000 ppm EDTA-doped KDP crystal was chosen as a sample to study the light scatter in pyramidal sector, prism sector and pyramidal-prism sector.

Comparing Figure 2.1 with Figure 2.2, it can be seen that the light scatter increases a little. Those scatter points in the prism not only have larger sizes but also have an extending distribution compared to those found in the pyramidal sector, which concentrate on a line along the [001] direction. Light scatter in pyramidal-prism sector is heavier than those in pyramidal sector and prism sector (Figure 2.3). The light scatter in pyramidal-prism sector is the heaviest one among the three for its density, different size and different shape, which varies from spherical to plates or cylindrical at different observation angles. Although these scatters are different in orientation and size, they mainly concentrate in a band along the [001] direction. The reason for this is that the growth rates of the pyramidal sector and prism are different here, and the crystal lattice does not match very well, which adsorbs impurities in the growth solution easily. The boundary between these growth sectors are more strained than the extended growth sectors due to mismatch of lattices on either
side of the boundary as a result of preferential incorporation of impurities into the lateral section.

![Figure 2.1 Light scatter in different sectors of KDP crystal, pyramidal sector (Xun Sun et al 2000)](image1)

**Figure 2.1** Light scatter in different sectors of KDP crystal, pyramidal sector (Xun Sun et al 2000)

![Figure 2.2 Light scatter in different sectors of KDP crystal, prism sector (Xun Sun et al 2000)](image2)

**Figure 2.2** Light scatter in different sectors of KDP crystal, prism sector (Xun Sun et al 2000)
The above mentioned problems are overcome in the recently employed Sankaranarayanan-Ramasamy method. The novel uniaxial Sankaranarayanan-Ramasamy (SR) solution growth technology attracted the researchers owing to the growth of defect free transparent bulk single crystals along a particular axis. Simple experimental techniques, unidirectional growth with 100% solute-solid conversion, minimum thermal stress and prevention of the microbial growth are some of the interesting features of this technique. It is of great interest at present to grow the KDP single crystals by Sankaranarayanan-Ramasamy (SR) method along <100>, <001>, <101> orientations and the effect of additive was also studied.

2.4 SR METHOD EXPERIMENTAL SETUP

The experimental setup consists of two ring heaters, transparent glass tubes made by borosilicate glass and seed mounting pad (Sethuraman et al 2006) shown in Figure 2.4. The ring heaters are positioned in the top and bottom of the ampoule. The heaters are connected to a dual channel
temperature controller which maintains constant temperature. The entire setup is kept in a water bath. The experimental setup was placed in a dust free hood. The crystal with specific orientation can be grown from solution by Sankaranarayanan–Ramasamy (SR) method (Sankaranarayanan and Ramasamy 2006). The SR-method is suitable method to effectively control the orientation of molecules during the bulk crystal growth from solution at room temperature with 100% solute-crystal conversion efficiency. <100> directional KDP crystals have been grown using this method.


Figure 2.4 Schematic diagram of experimental setup of SR method
2.5 GROWTH ALONG PRISMATIC FACE OF KDP CRYSTAL

The seed crystals collected from the conventional slow solvent evaporation technique were used for the unidirectional growth. A suitable seed crystal having $5 \times 5 \times 5$ mm$^3$ size was selected for single crystal growth. Ampoules of diameter 15 mm and 20 mm were used. Their height was 300 mm. The growth ampoules were carefully mounted with individual seed having the plane (100) facing towards the saturated solution of KDP. The ampoule was carefully designed for the seed crystals to avoid growth of other faces.

The seed crystal was mounted in the ampoules. Three-time recrystallized KDP materials were used in this growth. The ampoule was filled with saturated solution of KDP and porously sealed. The temperature of the top and bottom portion was set as 38°C and 33.5°C respectively. The temperature around the growth region is maintained at ±0.05°C accuracy. The solvent is evaporating with respect to the temperature of the top portion and controlled degree of supersaturation was maintained throughout the process by keeping the top portion temperature as a constant. The initial ring heater temperature of 38°C had resulted in a reduction of 5 ml in the volume of the growth solution after 24 hr. To achieve a constant growth rate, the reduction in the volume of growth solution was compensated with a freshly prepared solution. In the freshly prepared solution, the solute concentration was deliberately kept slightly under-saturated in order to avoid any possible chemical and physical instability at the growth interface. Since the density of the slightly undersaturated solution is lower than the supersaturated and saturated solution, no conspicuous change was observed during the pouring of solution at the top of the ampoule. After a few days, the seed crystal mounted at the bottom starts to grow.
When C-cut plate is used as seed initial growth is having lot of inclusion. After the completion of the pyramid only transparent growth is occurring. However when the (100) face is used as seed very transparent growth is occurring from the beginning. Due to the transparent nature of the solution and experimental set-up real time close-up observation is possible. The growth was allowed to continue for the next few days while keeping a vigil over the volume and the temperature of the growth solution. An average growth rate of upto 3 mm/day was observed in the conical region of the ampoule and the crystal was optically good. Once the growing crystal interface reached the uniform diameter of the growth ampoule, the temperature at the top surface of the solution was increased to 40°C. The effect of change in temperature was felt after 12 hr monitoring as an increase in the growth rate i.e., 7 mm/day and the crystal quality deteriorated.

Growth rate of a unidirectional crystal of particular size along a particular growth axis largely depends on the packing density of that plane, purity of the raw materials, degree of supersaturation and the rate of diffusion of the solute in the solvent medium. The growth rate 3 mm/day was found to be optimum. The sizes of the harvested <100> directional KDP crystals are 20 mm diameter and 30 mm height and 15 mm diameter and 65 mm height. Morphology of (100) plane KDP crystal is shown in Figure 2.5(a) and the cut and polished ingot is shown in Figure 2.5(b).
Figure 2.5(a) Morphology of (100) plane KDP crystal

Figure 2.5(b) Cut and Polished ingot of <100> KDP crystal grown by SR method
2.6. RESULTS AND DISCUSSION

2.6.1 High Resolution X-Ray Diffractometry Analysis

To reveal the crystalline perfection of the grown crystals, a multicrystal X-ray diffractometer (MCD) developed at NPL (Krishan Lal and Bhagavannarayana 1989) has been used to record high-resolution diffraction curves (DCs). In this system a fine focus (0.4 x 8 mm; 2 kW Mo) X-ray source energized by a well-stabilized Philips X-ray generator (PW 1743) was employed. The well-collimated and monochromated MoKα1 beam obtained from the three monochromator Si crystals set in dispersive (+,-,-) configuration has been used as the exploring X-ray beam. This arrangement improves the spectral purity (Δλ/λ << 10⁻⁵) of the MoKα1 beam. The divergence of the exploring beam in the horizontal plane (plane of diffraction) was estimated to be <<3 arc sec. The specimen crystal is aligned in the (+,-,-,+) configuration. The specimen can be rotated about a vertical axis, which is perpendicular to the plane of diffraction, with minimum angular interval of 0.2 arc sec. The diffracted intensity is measured by using a scintillation counter which is mounted on the radial arm of the turn table. The rocking or diffraction curves were recorded by changing the glancing angle (angle between the incident X-ray beam and the surface of the specimen) around the Bragg diffraction peak position θB starting from a suitable arbitrary glancing angle (denoted as zero). The detector was kept at the same angular position 2θB with wide opening for its slit, the so-called ϕ scan. Before recording the diffraction curve, to remove the non-crystallized solute atoms on the surface of the crystal and also to ensure the surface planarity, the specimen was first lapped and chemically etched in a non preferential etchant of water and acetone mixture in 1:2 volume ratio. Figure 2.6 shows the high-resolution diffraction curve (DC) recorded for KDP specimen using (200) diffracting planes in symmetrical Bragg geometry by employing the
multicrystal X-ray diffractometer described above with MoKα₁ radiation. The curve is very sharp having full width at half maximum (FWHM) of 8 arc s as expected for a nearly perfect crystal from the plane wave dynamical theory of X-ray diffraction (Betterman and Cole 1964), while it is 22 arc second for <100> conventional grown KDP crystal in the same (100) plane (Kannan et al. 2006). Absence of additional peaks and the very sharp DC shows that the crystalline perfection of the specimen crystal is very good without having any internal structural grain boundaries and mosaic nature. The high reflectivity (~ 85%) and the low value of FWHM indicate that even the concentration of unavoidable point defects like self interstitials and vacancy defects is very low.

![Graph](image)

**Figure 2.6** High-resolution diffraction curve recorded for (200) diffracting planes using Mo Kα₁ radiation in symmetric Bragg geometry
2.6.2 Etching Studies

The chemical etching studies were carried out on the as grown single crystals of KDP to study the symmetry of the crystal face from the shape of etch pits, and the distribution of structural defects in the grown crystals. Figure 2.7(a) shows the surface of the conventional as grown <100> KDP single crystal. The etching experiment was carried out using water as an etchant at room temperature for 5s. First, the crystal sample was completely immersed in the etchant and then etched sample was cleaned using a tissue paper and the etch patterns were observed using an optical microscope (Magnus MLX). When the crystal was etched for 5s, the elongated rectangular type etch pits were observed. The regular shape of etch pits was damaged while increasing the etching time from 10s to 30s. In conventional grown <100> KDP the EPD is $10.5 \times 10^2$ cm$^{-2}$.

Figure 2.7(b) represents the identical elongated rectangular shaped etch pits for SR <100> KDP observed and the number of etch pits is less. In SR method grown KDP single crystal the EPD is $3 \times 10^2$ cm$^{-2}$. Certain dislocations have a tendency to nucleate at growth sector boundaries. In SR method the growth is on one facet only. There are no growth sector boundaries. Hence the dislocations which are associated with growth sector boundaries are absent in SR method grown crystal. This is the reason for low dislocation density in SR method grown crystal. Decrease in etch pits is associated with more systematic packing of atoms/molecules. The strains formed during growth could be less in SR method. Less number of dislocations in SR method KDP shows that the quality of the crystal grown by SR method is better than conventional method grown crystal.
Figure 2.7(a)  Surface of conventional grown KDP crystal etched by water for 5s

Figure 2.7(b)  Surface of SR grown KDP crystal etched by water for 5s
2.6.3 Transmittance Spectral Studies

The transmittance of the SR grown <100> directional KDP crystal and conventional method grown crystal was measured by PerkinElmer UV-Visible spectrophotometer for the wavelength range 200 nm to 1100 nm covering entire near-ultraviolet, visible, and higher energy part of near infrared region to find the transmission range to know the suitability for optical application. For this study, the cut and polished 3 mm thickness wafers were used. The <100> directional KDP single crystal has transmittance up to 85% in the higher wavelength region. The SR method grown Unidirectional KDP has 12% higher transmittance as against conventional method grown crystals (Figure 2.8).

![Figure 2.8 UV-Vis NIR spectrum of KDP crystals](image-url)
2.6.4 Fourier Transform Infrared spectral Analysis

FTIR spectrum of grown KDP crystal was carried out in the middle IR region between the wave number 400 cm\(^{-1}\) to 4000 cm\(^{-1}\) at a resolution of ±5 cm\(^{-1}\) by using PerkinElmer Fourier transform infrared spectrometer (equipped with a TGS detector, a KBr beam splitter, a He–Ne laser source) to confirm the functional groups and the spectrum is shown in Figure 2.9. A strong band occurring at 1303 cm\(^{-1}\) is due to the P=O stretching vibrations of KDP crystals. A strong band present at 905 cm\(^{-1}\) is assigned to P-O-H stretching vibrations. Very weak bands appearing around 2850 and 2369 cm\(^{-1}\) are due to P-O-H symmetric stretching and bending respectively. Very strong band occurring with 538 cm\(^{-1}\) is contribution of HO-P-OH bending vibrations.

![Figure 2.9 FT-IR spectrum of KDP crystal](image-url)
2.6.5  **Dielectric Studies**

The values of dielectric constants are required for interpretations and applications of various theories of lattice dynamics. When the dielectric material is under the influence of an external driving alternating electric field, the motion of the particles present in the materials need characteristic time to build up an equilibrium polarization. The dielectric parameters depend on the frequency of the a.c voltage applied across the material.

The sample was cut and polished using wet cloth polishing sheet. The sample dimensions were 3 mm x 3 mm surface area and 2 mm thickness. Silver paste electrodes on opposite sides ensure good electrical contacts. The sample was electroded on either side with silver paste to make it behave like parallel plate capacitor. Dielectric measurement was carried out using a precision (Model4284A) LCR meter in the frequency range 20 Hz – 1 MHz. The measurements were carried out in the temperature range 35ºC to 150ºC.

The dielectric constant decreases with increase of frequency. The dielectric constant and dielectric loss increase with the increase in temperature. The variation of dielectric constant as well as dielectric loss with frequency is similar to the results obtained earlier (Chen et al 2006, Udupa et al 1997, Varma et al 1983). The dielectric constant of a material is generally composed of four types of contributions, viz. ionic, electronic, orientational and space charge polarization. All of these may be active at low frequency. The nature of variations of dielectric constant with frequency and temperature indicates the type of contributions that are present in them. The large value of dielectric constant at low frequency is due to the presence of space charge polarization (Suryanarayana et al 1984), which depends on the purity and perfection of the sample. The dielectric constant in SR method grown crystal is higher than conventional method grown crystal and is shown in Figure 2.10(a). Generally the low value of dielectric loss indicates that
sample possesses good crystalline quality with fewer defects (Vijayan et al 2008, Rajarajan et al 2006, Sweta Moitra 2008). The dielectric loss was less in SR method grown crystal as against conventional method grown crystal (Figure 2.10(b)) and this is in agreement with the result of optical transmission studies.

Figure 2.10(a) Dielectric constant Vs Temperature of KDP crystals
2.6.6 Vickers Microhardness Measurement

The smooth surface of KDP crystal was subjected to Vickers static indentation test at room temperature (303 K) using a Shimadzu (Model HMV 2) hardness tester. Load of different magnitudes (25, 50, 100, 200, 300 g) were applied. The indentation time was kept as 5 s for all the loads. The hardness was calculated using the relation $H_v = \frac{1.8544}{d^2} \frac{P}{Kg/mm^2}$, where $P$ is applied load in kilogram, $d$ is the diagonal length of the indentation impression in micrometer, and 1.8544 is a constant of a geometrical factor for the diamond pyramid.
The plot of Vickers hardness (Hv) versus load (P) for the SR method grown and conventional method grown KDP crystals is shown in Figure 2.11. From the graph, it is seen that the hardness value for SR grown crystal is very much higher (≥ twice) than the hardness of the conventional method grown crystal.

![Graph showing Vickers hardness (Hv) versus load (P) for SR method grown and conventional method grown KDP crystals.]

**Figure 2.11 Microhardness number (Hv) Vs Load (p) of KDP crystals**

Due to the application of mechanical stress by the indenter, dislocations are generated locally at the region of indentation. Thus the major contribution to hardness is attributed to the high stress required for homogeneous nucleation of dislocation in the small dislocation-free region indented (Kunjomana 2005). Hence much larger hardness value for SR method grown KDP crystal indicates greater stress required to form dislocation thus confirming greater crystalline perfection.
2.7 CONCLUSION

<100> directional KDP crystals were grown by SR-Method. The 20 mm diameter 30 mm height and 15 mm diameter and 65 mm height crystals were grown with growth rate of 3 mm/day. From the high resolution X-ray diffraction (HRXRD) studies, the structural perfection of the grown crystal was identified. The HRXRD study indicates that the grown crystal does not have very low angle boundary, which is due to excellent quality of the crystal grown in the present investigation. In SR method grown crystal EPD is less compared to conventional method grown KDP crystal. This shows that the quality of the crystal grown by SR method is better than conventional method grown crystal. The SR method grown <100> KDP has 12% higher transmittance as against conventional method grown crystals. The dielectric constant was higher and dielectric loss was less in SR method grown crystal as against conventional method grown crystal. The crystal grown by SR method has much higher hardness value than conventional method grown crystals. This shows that the quality of the crystal grown by SR method is better than conventional method grown crystal for optical device.