CHAPTER 3

CHARACTERIZATION OF KTiOP\textsubscript{4} SINGLE CRYSTALS

3.1 INTRODUCTION

Characterization of a material can be defined as a complete description of its physical and chemical properties. A thorough and extensive characterization of a single crystal is very difficult because it requires a variety of tests using a number of sophisticated instruments. It is obvious that there are no ideal crystals in reality and all crystals grown by any technique contain some defects, impurities and inhomogeneities. Most of the physical properties are sensitive to the deviation from ideality therefore, generally the characterization of the grown crystals is a necessity. No one technique will serve for all purposes.

The assessment of crystalline perfection is essential to interpret the structure dependent properties. Post growth analysis of a crystal provides information on the processes that occurred during growth. Feedback from the analysis can be used to modify the growth process in order to improve the quality of the crystal. Moreover characterization of the grown crystals forms an integral part of the growth studies to be performed by the crystal grower. The demand for crystals of the highest quality is increasing, and only systematic characterization enables the crystal grower to optimize the growth parameters in order to obtain better results.

A single crystal may be characterized by a description of its chemical composition, of its structure, of its defects and of the spatial distribution of these three features. It is very vital to know the degree of purity and perfection of crystals to
interpret structure dependent properties and in order to determine whether the material can be successfully employed in the experiments or device fabrication.

KTP being a technologically important material has elicited a large degree of characterization studies (Belt et al 1985; Bierlein and Vanherzeele 1989a; 1989b; Rejmankova et al 1997). A majority of the characterization of KTP has been directed towards evaluating the dependence of various NLO parameters on the growth technique employed (Angert et al 1994).

In the present work, the grown crystals were subjected to the following characterization studies:

(i) Crystal structure analysis by X-ray powder diffraction technique and rocking curve analysis.
(ii) Rutherford Backscattering Spectrometry
(iii) Etching studies to assess the quality of the crystal
(iv) Hardness measurement to study the mechanical behaviour
(v) UV-Visible-IR transmission spectra to determine the transparency range
(vi) SHG measurement on the fabricated element
(vii) Conductivity and dielectric measurements

3.2 X-RAY DIFFRACTION STUDIES

X-ray diffraction is by far the most popular method for the identification of substances for the investigation of crystal structure and degree of crystal perfection. For accurate determination of lattice constants, powder samples (optimum crystallite size of the order of 5μm) are normally preferred. X-ray powder patterns of KTP were recorded using Reich Siefert X-ray diffractometer. Monochromatic intense X-ray of wavelength 1.5418Å (CuKα) was used. The scan speed employed was 2°/min. The
The powder diffraction data were used to calculate the lattice parameters by the least square fit method and the values are $a=12.83\,\text{Å}$; $b=6.38\,\text{Å}$ and $c=10.56\,\text{Å}$. These values are in good agreement with the values reported in the literature (Thomas et al 1990a; Joseph Kumar et al 1997).

### 3.2.1 X-ray rocking curve

A single crystal contains large number of dislocations, which lead to deflection and distortion of the crystal lattice. In this study the dislocation structure of KTP single crystals was investigated by means of the rocking crystal method. The dislocations generated generally contribute differently to each reflection. Therefore, by studying the rocking curves of different reflections it is possible to determine the dislocation structure of the crystal. Rocking curve of $\{001\}$ surface cut from the interior of TSSG grown KTP crystal is presented in Figure 3.1b. The width of the beam was about 5mm which enables to register the whole $\{001\}$ surface of the sample during the diffraction. A diffraction rocking curve with FWHM of 45 arcsec was obtained. This value is almost close to the one for good-quality crystals which in turn indicates the quality of the grown KTP crystal and the absence of intrinsic stresses in its volume.

### 3.3 RUTHERFORD BACKSCATTERING SPECTROMETRY

Rutherford backscattering spectrometry (RBS) is based on back scattering of ions or projectiles incident on a sample. It allows determination of the masses of the elements in a sample, their depth distribution over distances from 100Å to a few microns from the surface and the crystalline structure in a non-destructive manner. It is useful for measuring thickness, stoichiometry and impurities. RBS can provide...
Figure 3.1a  Powder X-ray diffractogram of KTiOPO$_4$
Figure 3.1b Rocking curve of (001) plate
both atomic composition and depth scales to an accuracy of 5% or better. The
detection limit lies in the range $5 \times 10^{20}$ cm$^{-3}$ but depends on the element and on energy.

The composition of the flux grown KTP single crystals was analysed by
means of RBS with 2 MeV He$^+$ ions and a backscattering angle of 170°. Figure 3.2
shows the RBS spectrum of KTP sample, dotted points are the experimental data and
the line is the simulated data. There is no change in the composition of KTP crystal
and the corresponding yield is in agreement with the reported values (Opfermann et al
1997). A very mild incorporation of platinum is found in the crystal.

3.4 SURFACE ANALYSIS BY OPTICAL MICROSCOPY, SEM AND AFM

The growth mechanism of the crystal forms on KTP is of importance in order
to understand the mechanism of inclusion formation during flux growth (Bolt and van
Enckevort 1992). Since the KTP crystals were grown under very stable conditions,
they do not show any defects or growth patterns on the surface. All the faces are
atomically flat. However most of the faces have a circularly raised region towards the
bottom end of the face (Figures 3.3a and 3.3b). These circular steps are considered to
be formed due to the solution droplets which remained on the crystal faces when it
was pulled upon completion of growth. Because of surface tension forces the solution
has taken a circular form and only one circular step was formed on each face. During
fast cooling (20°C/h) to room temperature, crystal growth continued on these solution
droplets at a faster rate (Elwell and Scheel 1975). These circular steps, grown under
non equilibrium conditions are expected to have more defects than the remaining of
the crystal. Accordingly, growth layers were observed on the rim of the circular steps.
The optical micrograph of the (201) surface shows circular hillock like pattern. On
these circular hillocks there were large number of steps observed (Figure 3.3c). Step
heights and step distances were determined on the (011) and (201) faces by AFM.
AFM pictures of the steps on (201) and (011) faces are shown in Figure 3.3d and
Figure 3.2 RBS spectrum of KT\textsubscript{i}OPO\textsubscript{4}
Figure 3.3a Concentric circle on {201} face
Figure 3.3b Concentric circle on {011} face
Figure 3.3c Layers observed on the {201} face by optical microscope
Figure 3.3d Growth steps on {201} face
Figure 3.3e Growth steps on {011} face
Interestingly, these steps show a certain degree of uniformity in terms of step height on each face.

### 3.5 ETCH PIT DENSITY

Every crystalline solid in contact with its undersaturated environment or in some other corrosive liquid medium, as a rule, undergoes decrystallization (dissolution and etching). Decrystallization always proceeds on the surfaces of the solid and leads to the formation of etch figures (depressions and elevations) and dissolution layers. Etching is the selective dissolution of the crystal - a reverse phenomenon of growth used to reveal the lattice defects and crystal symmetry. This can be effected by specific chemical attacks on the crystal: the rate of reaction of a solution with a crystal surface depends on the crystallographic orientation of the reacting surfaces. When a crystal phase is exposed to a solvent, dissolution begins by the nucleation of unit pits of one molecular depth which then grows in size by the retreating steps across the crystal surface (Burton et al 1951).

Strain in the crystal will cause displacement of atoms from their equilibrium positions. Dislocations occur at regions in the crystal where adjacent planes of atoms fail to meet perfectly. Measurement of the dislocation density (the number of dislocations per unit area of crystal) gives a valuable indication of the perfection of the crystal. In the high temperature solution growth the normal value is between 10 and $10^4$ cm$^{-2}$. Dislocations are normally generated either on nucleation or seeding, or by solvent inclusions. Etch pits are often formed at the emergence points of dislocations.

Since the geometry of an etch pit depends on the arrangement of ions, atoms or molecules composing a crystal surface, the shape of etch pit formed on crystallographically different faces of a crystal is different. This difference forms a basis for the distinction of various faces and in many cases, serves as a quick method
for the identification of the faces or directions on the face of a crystal. Etch pits are exceptionally microscopic in size. Also the shape of the etch pit may be changed by altering the concentration of the solvent (Sangwal 1991).

3.5.1 Scanning electron microscope

There are six crystal forms observed on KTP: \{100\}, \{201\}, \{011\}, \{0\bar{1}1\} and \{110\}. Because of the great similarity between \{201\} and \{\bar{2}01\}, \{011\} and \{0\bar{1}1\} these crystal forms will further be taken together as \{201\} and \{011\}. Since KTP is not soluble in water, another etching medium has to be found. There were many etchants reported in the literature (Dhanaraj 1990; Bolt et al 1991a; Joseph Kumar et al 1997). In the present work as grown crystal faces, which occur on flux grown KTP crystals were etched with 36% HCl for a period of 60 min. A Leica Cambridge Stereoscan 440 scanning electron microscope in the secondary electron emission mode was employed for visualizing the etch pits. The great advantage of the scanning electron microscope is its very large depth of focus, which permits convenient observation of relatively large features on a crystal surface.

After the etching, on all the crystal forms of the KTP crystal etch pits were present. Different etch pit morphologies were seen on the natural crystal faces. Etch pits with and without hollow cores have been observed on all the faces. Etch pits with clearly visible hollow cores are called spike etch pits. Figures 3.4a and 3.4b show the etch pits on \{100\} face. The pits show a line parallel to [010]. The highest dislocation density is estimated on the \{100\} faces. Figures 3.4c and 3.4d show the etch pits on \{201\} face with hollow core. Many spike etch pits are seen on \{201\} face. The hollow cores or spike etch pits are formed because of a dissolution catastrophe occurring around a dislocation with a screw component. Figures 3.4e and 3.4f show the etch pits with five faces and five edges on \{011\} face. In some areas, there is a relatively high pit concentration while in other places they are absent. Figures 3.4g and 3.4h show the etch pits on \{110\} face where the non-hollow core etch pits in
Figure 3.4a  Non-hollow core etchpits on {100}

Figure 3.4b  Hollow core etchpits on {100}

Figure 3.4c  Non-hollow core etch pits on {201}

Figure 3.4d  Hollow core etchpits on {201}
Figure 3.4e  Non-hollow core etchpits on {011}

Figure 3.4f  Hollow core etchpits on {011}

Figure 3.4g  Non-hollow core etchpits on {110}

Figure 3.4h  Hollow core etchpits on {110}
Figure 3.4g have four equal sides. The dislocation densities of the order of $8000\text{cm}^2$ was observed on {100}, $3500\text{ cm}^2$ on {201}, $750\text{ cm}^2$ on {110} and $14000\text{ cm}^2$ on {011} faces.

3.6 HARDNESS MEASUREMENT

Hardness is an important mechanical property which determines the strength of materials and the resistance to local deformation. It is also useful to study the nature of plastic flow, crack propagation, fracture toughness, state of dispersion of impurity and dislocation mobility of crystals (Decker and Rieck 1974). Like etching, hardness properties also are indicative of the dislocation content and plasticity of the crystals.

The hardness test is a technique for subjecting a crystal to relatively high pressures within a localized area. This technique has been employed industrially using different shapes of indentors such as spherical, conical and pyramidal. In its simplest and most popular form, the static indentation test, an indentor of specific geometry is pressed into the surface of a test specimen under a known load. The indentation pressure is directly proportional to the uniaxial flow stress of the material. Upon removal of the indentor, a permanent impression is retained in the specimen. The magnitude of the diagonal length of the indentation gives an indication of the hardness number, which has units of stress. The main pressure or hardness is defined as the load divided by the area of the impression.

3.6.1 Vicker's Test

In this test, microindentation is made on the surface of the crystals with the help of diamond pyramid indentor. The Vicker's indentor consists of two pairs of opposite faces with included angle of $136^\circ$ each and all the four faces meet at a point. The base of the Vicker's pyramid is a square and the depth of indentation diagonal
corresponds to 1/7th of the indentation diagonal. Pyramid indentors are said to be the best suited for hardness test due to the following reasons, (i) the contact pressure for a pyramid indenter is independent of indenter size and (ii) pyramid indenters are less affected by elastic release than other indenters.

The microhardness values are calculated using the relationship

\[ H_v = 1.8544 \left( \frac{P}{d^2} \right) \]  

(3.1)

where \( H_v \) is the Vicker's microhardness number in Kg/mm\(^2\), \( P \) is the applied load in g and \( d \) is the diagonal length of impression in \( \mu m \). Diagonal lengths (d) of the indentations were measured using a micrometer eyepiece.

### 3.6.2 Experimental

As grown crystal faces which were highly smooth and reflecting were subjected to static indentation test using a Leitz Wetzler hardness tester (type P 1191) fitted with a Vicker's diamond pyramid indenter, which is attached to a Metallurgical microscope (Mettalux-II). The diagonals of the impression were measured for various loads (P). Indentations were made at different sites of the crystal surface for a constant indentation time (10s). The distance between two indentation points was kept more than four times the diagonal length of the diamond impression to avoid mutual influence of the indentations for each crystal. Several indentations at each load were made and the average value of the diagonal length (d) of the indentation marks was calculated. These average values of the diagonal length of the indentation mark corresponding to each load were used for estimating the microhardness.

Generally the hardness decreases as shown in Figure 3.5 with increase of load and attains saturation for further increase in load on all crystal faces. The indentation process in the microhardness measurements is generally believed to be involved with
Figure 3.5  Hardness anisotropy on different faces of KTP crystal
any of the following processes: (i) permanent densification and (ii) breaking of bonds. The energy associated with the indenter is low at lower load (5g) and hence dislocations at the point of indentation will not allow the indentor to penetrate further whereas at, higher load (10g) the indentor can easily penetrate owing to the movement of dislocations away from the indentor. Hardness on all the faces is found to decrease as the load is increased and it attains a constant value at the load of 50g. When the indentation load was 50g, cracks were initiated on the crystal surface around the indentor and the crack area increases on increase of the load. Vicker’s hardness index values were 617 kg/mm², 548 kg/mm², 593 kg/mm² and 490 kg/mm² for the natural (100), (110), (011) and (201) faces respectively. It may be noted that the hardness of the (100) face is higher than that of the other faces. It was also observed that the (201) face is more prone to cracking. This may be the result of loosely packed lattice with reduced bond energy.

### 3.7 TRANSMISSION SPECTRA

The transmission range of a good quality KTP crystal is between 340 to 4500nm (Damasyan et al 1986). Metal impurities tend to lower the transmission in this range (Ahmed et al 1986). The UV-Visible spectrum of the grown KTP crystal is shown in Figure 3.6a. A c-cut and polished plate of KTP of thickness 1mm was used for the study. A Shimadzu UV-Visible-IR spectrophotometer was used for recording the spectrum. The spectrum reveals the lower transmission cut-off to be 350nm and shows no absorption peak.

#### 3.7.1 IR spectra

The spectroscopic data related to the structure of KTP in solid state have been presented in detail by many authors (Jacco 1986; Dovgii and Kityk 1989). The structure of KTP is visualized as a three-dimensional chain of PO₄ tetrahedra and TiO₆ octahedra joined at their vertices. The geometry of the TiO₆ group is distorted
Figure 3.6a  UV/VIS transmission of KTP
whereas that of the PO₄ groups is stated as being undistorted. Therefore, a significant amount of vibrational perturbation could be possible in the infrared spectrum of KTP. Also to detect any OH⁻ incorporation can be best detected by IR. The OH⁻ impurities occur in large amounts in hydrothermally grown KTP crystals (Ahmed et al 1986). Traces of OH⁻ in flux grown crystals have also been reported (Bolt et al 1991b). The OH⁻ peaks lie at 3566, 3571 and 3602 cm⁻¹.

The infrared spectrum of KTP shown in Figure 3.6b was obtained by KBr pellet technique. Spectra were recorded on a Perkin Elmer model infrared spectrometer. The samples were scanned between 400 to 4000 cm⁻¹. The broad band between 1250 and 850 cm⁻¹ is resolved into absorption peaks associated with the ν₃ fundamental of the PO₄ groups. Jacco (1986) showed that the ν₃ fundamental has a fine structure consisting of peaks at 1124, 1100, 1048, 1023 and 964 cm⁻¹. This fine structure of the ν₃ symmetry has been attributed to the deformation of the PO₄ tetrahedra that occupy two crystallographic sites of C1 symmetry.

The three peaks at 820, 785 and 712 cm⁻¹ are attributed to Ti-O vibrations of the distorted TiO₆ octahedra. The remainder of the peaks in the region between 660 and 350 cm⁻¹ is ascribed to the splitting of the degenerate ν₄ and ν₂ PO₄ modes. The spectrum showed significant symmetry lowering effects on the intra-molecular vibrations of the PO₄ groups. This was found to be consistent with the distorted tetrahedral structure for the phosphate ions (Jacco 1986).

### 3.8 SECOND HARMONIC GENERATION

KTP is a widely used material for frequency doubling Nd:YAG lasers and other Nd-doped laser systems emitting radiation near 1.06 μm. Its large nonlinear coefficients are phase matchable, resulting in a high figure of merit. This property, combined with low absorption and a wide acceptance angle, makes it the preferred...
Figure 3.6b  Infrared transmission of KTP
frequency doubling crystal when the available peak power is limited (Fan et al 1987; Bierlein and Vanherzeele 1989a). Phase matching in KTP is mainly through angle tuning since the temperature dependence of birefringence is very small.

For Nd:YAG laser the phase matching angle under type II conditions is $\theta=90^\circ$ and $\varphi=21^\circ$. It can also be called as quasi non-critical phase matching, since the birefringence is very small in the xy plane which is associated with a low beam walk off and allows the use of tightly focused laser beams for higher efficiency.

### 3.8.1 Preparation of SHG element

KTP crystals free from visual imperfection is oriented and cut for the observation of frequency doubling. The approximate angle was fixed for cutting using hand type goniometer. The thickness was 5mm. The surfaces of the samples were first lapped using fine alumina powder and later polished with diamond (1/4$\mu$) paste. Figure 3.7a shows the orientation of the KTP parallelopiped in relation to the crystallographic axes. The element fabricated is shown in Figure 3.7b. Both entrance and exit faces of a KTP cube are polished and examined for surface defects by optical microscope. The crystal is aligned so that its entrance face is perpendicular to a 1.06$\mu$m laser beam. The second harmonic and the fundamental pulse energies were both measured with a power meter. A maximum conversion efficiency of 10% without antireflection coating was observed for an incident intensity of about 400mJ. The second harmonic beam is shown in Figure 3.7c. The low conversion efficiency achieved may be attributed to the following reasons. Since the acceptance angle of the SHG in KTP is approximately 1°cm$^{-1}$ in full width at half maximum (FWHM), these variations in the phase matching angle give rise to a reduction in the conversion efficiency of the SHG. Also since the oriented element was prepared using hand type goniometer, there may be an error in the cutting angle itself which largely reduces the
Figure 3.7a  Orientation of KTP paralleopiped

Figure 3.7b  KTP SHG element

Figure 3.7c  Second Harmonic Generation of 1.06μm line of Nd:YAG at 532nm
conversion efficiency. Also the thickness of the crystal plays a major role in the conversion efficiency.

3.9 DIELECTRIC MEASUREMENTS

KTP exhibits not only high optical nonlinearity, but also high ionic conductivity. Due to high ionic conductivity along the c-axis, KTP does not exhibit dielectric hysteresis at room temperature. The electronic properties of KTP make it a typical insulator with a conductivity of $10^{-8}$ to $10^{-11}$ S.cm$^{-1}$ along the c-axis (Bierlein and Arweiler 1986; Furusawa et al 1993; Satyanarayan and Bhat 1998). The ionic conductivity along the c-axis is by four orders of magnitude larger than that perpendicular to the c-axis and thus the K$^+$ ions are considered to move mainly along the channels parallel to the c-axis. The ferroelectric properties of KTP have been studied extensively. Furthermore, KTP is known as a quasi-one-dimensional superionic conductor of K$^+$ ions (Bierlein and Arweiler 1986) and having a phase transition to a paraelectric phase at 934°C (Yanovskii and Voronkova 1985). As for the phase transition, a second order phase transition has been reported on the basis of dielectric and SHG measurements (Furusawa et al 1993). It should be noted that the system does not show ferroelectricity in the conventional sense, since the reversing of polarization is strongly hindered by the high conductivity.

3.9.1 Experimental

Crystal obtained by TSSG was cut into rectangular plate having (001) face. The typical sample size of c-cut plate used in this study was about 8x6x1mm$^3$. The frequency dependent a.c. conductivity of the KTP single crystals was measured in the frequency range from 100Hz to 1Mhz using Solartron SI 1260 impedance/gain-phase analyzer. The temperature range studied was 100-750°C. The broad anomalies of dielectric constants associated with the ion hopping in KTP are shown in this region. Both faces of the sample plate were coated with platinum paste. Samples were heated
in an electric furnace whose temperature was controlled within ±2°C and the temperature was constantly maintained during the measurements. The heating rate was 3°C/min. The recorded data were processed by a microcomputer.

Figure 3.8a shows the frequency dependence of the value of $\sigma_{33}$ at room temperature. It has been reported that the electrical conductivity of KTP crystals depended strongly on the frequency of the measuring electric field. At room temperature the conductivity along the polar axis is in the range $3\times 10^{-6} - 3\times 10^{-8}$ S/cm depending upon the frequency. The frequency dependence of the a.c. conductivity $\sigma_{33}$ at various temperatures is shown in Figure 3.8b. From the graph it can be seen that above 500°C the real part of the conductivity $\sigma_{33}$ shows frequency independent behaviour. This low frequency dynamics is given by the mobility of the K$^+$ ion along the crystallographic c-axis. The crystal lattice of KTP possesses an open skeleton which is formed by chains of distorted TiO$_6$ octahedra along the z axis. The octahedra are interconnected by slightly distorted PO$_4$ tetrahedra in the a- and b-directions respectively (Thomas et al 1990a). The K$^+$ ions are located in the empty spaces of the structure occupying two positions. They are surrounded by eight and nine oxygen ions respectively, in such a way to provide channels for ions to move parallel to the c-axis.

The temperature dependence of the permittivity of (001) sample is plotted in Figure 3.8c. It exhibits a strong anomaly at 200-700°C. The permittivity reached a maximum of 900 with a strong dependence on the frequency of the measuring electric field. A similar observation on the dielectric behaviour of KTP crystal was reported earlier (Yanovskii and Voronkova 1985; Pimenov et al 1996). They suggested that the possible reason for this is K$^+$ hopping relaxation. The results obtained were in good agreement with earlier reports (Pimenov et al 1996) and they confirm that the physical properties of KTiOPo$_4$ crystals are close to those of superionic conductors.
Figure 3.8a Frequency dependence of the room-temperature value of $\sigma_{33}$
Figure 3.8b The a.c. conductivity as a function of frequency for KTP single crystal at various temperatures
Figure 3.8c  Real part of $\varepsilon'$ of KTP as a function of temperature
3.10 CONCLUSION

In the present chapter, the essential characterizations of the KTP crystals grown by TSSG are discussed. Cell dimensions calculated from X-ray powder diffraction technique are in concurrence with the reported values. Composition analysis was made by RBS which detected a minor incorporation of platinum in the crystal. Circular patterns observed on the (201) and (011) faces were analyzed for their growth heights by AFM.

Dislocation density was studied in KTP crystals after etching with concentrated HCl. They appear with well defined morphologies and many areas of the crystal contain only a few dislocations. Etch pits with an interesting feature, of hollow core is observed in all the growth faces of the crystal.

Hardness properties of various faces of the KTP crystals were also studied. The transparency range of the crystal was studied by UV/VIS and FTIR spectroscopy. FTIR did not show the presence of OH\(^-\) incorporation in the grown crystal. Second harmonic conversion efficiency was checked for one of the elements fabricated. At room temperature the a.c. conductivity of \(\sigma_{33}\) depends on the frequency and at high temperatures it becomes frequency independent due to the K\(^+\) ion hopping.