GROWTH AND CHARACTERIZATION OF SINGLE CRYSTALS OF KDP DOPED WITH KCl FROM AQUEOUS SOLUTION

BY

MD. KHAIRUL HASSAN BHUIYAN

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DECLARATION

This thesis work has been done by the candidate himself and does not contain any material extracted from elsewhere or from a work published by anybody else. The work of this thesis has not been presented elsewhere by the author for any degree or diploma. No other person's work has been used without due acknowledgement.

MHassan
06.01.98
(Md. Khairul Hassan Bhuiyan)
Candidate

CERTIFICATE

This is to certify that the research work embodying in this thesis has been carried out under my supervision. The work presented herein is original. This thesis has not been submitted elsewhere for the award of any other degree or diploma in any other University.

Jiban Podder 6.1.98

(Dr. Jiban Podder)
Supervisor
Assistant Professor
Department of Physics
Bangladesh University of
Engineering & Technology
Dhaka, Bangladesh

BANGLADESH UNIVERSITY OF ENGINEERING & TECHNOLOGY
Department of Physics

Certification of thesis work

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By
Md. Khairul Hassan Bhuiyan

has been accepted as satisfactory in partial fulfilment of the requirements for the degree of ***Master of Philosophy*** in ***Physics*** and certify that the student demonstrated a satisfactory knowledge of the field covered by the thesis in an oral examination held on **January 11, 1998.**

Board of Examiners

1) **Dr. Jiban Podder**
Assistant Professor
Department of Physics
BUET, Dhaka

Jiban Podder
Supervisor & Chairman

2) **Prof. Dr. Mominul Huq**
Head, Department of Physics
BUET, Dhaka

Member

3) **Prof. Dr. Tafazzal Hossain**
Department of Physics
BUET, Dhaka

Member

4) **Prof. Dr. Asadur Rahman**
Department of Physics
University of Dhaka
Dhaka - 1000

Member (External)

DEDICATIONS

This volume of work is dedicated to my 'Parents'.

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ABSTRACT

Single crystals of pure potassium dihydrogen orthophosphate KH_2PO_4 (KDP) and KDP doped with KCl crystals in the ratios (viz 95: 05, 90:10, 85:15 and 80:20) have been grown from acqueous solutions by slow evaporation process at room temperature using the seeding technique. The growth rates were measured for all of the five crystals along both the x and z direction. The growth rates along x axis for pure KDP and KDP doped with KCl are found to be 1.28×10^{-5} mm/sec, 1.67×10^{-5} mm/sec, 1.51×10^{-5} mm/sec, 1.32×10^{-5} mm/sec, 1.68×10^{-5} mm/sec and along the z axis the respective values are found to be 3.06×10^{-5} mm/sec, 4.09×10^{-5} mm/sec, 5.32×10^{-5} mm/sec, 5.00×10^{-5} mm/sec, 4.98×10^{-5} mm/sec. The growth rate constants of pure KDP and KDP doped with KCl in different ratios are found to be 31.1×10^{-26} mm^4/sec, 69.4×10^{-26} mm^4/sec, 108.5×10^{-26} mm^4/sec, 70.4×10^{-26} mm^4/sec, 118.7×10^{-26} mm^4/sec respectively.

The grown crystals exhibit the normal habit, a tetragonal prism in combination with a bipyramid. The grown crystals are found to be elongated along the z-axis.

Infrared spectroscopic study and X-ray diffraction analysis are carried out on the grown crystals at room temperature to find the crystal parameters. It has been noted that the PO_4 spectrum seems displaced to higher frequencies. This might indicate weakening of the hydrogen bond and a possible transition to a hydroxyl bond. The tetragonal unit cell of

lattice for pure KDP measures 7.42Å along the base edge 'a' and 7.30Å in height and c/a ratio is found to be 0.98. D.C. electrical conductivity measurements have been carried out for all of the grown crystals at room temperature and with temperature variation upto 200°C and with voltage variation upto 150 V by two probe method. The results reveal that the d.c. electrical conductivity increases with the increase of doping concentration. Conductivity is found in the order of 10^{-7} *mho/m. The increase of conductivity values of KDP crystal doped with chloride impurity may be attributed by the replacement of* $(H_2PO_4)^-$ *ions by* Cl^- *ion. The electrical conduction in KDP crystals is found to be protonic. A.C. breakdown voltage is found to be around 4.68 kV/cm for pure KDP and for KDP doped with KCl in the ratios (viz 95:05, 90:10, 85:15 and 80:20) are 4.42 kV/cm, 4.03 kV/cm, 4.66 kV/cm, 3.90 kV/cm respectively.*

The activation energy for conduction in KDP is found to be 0.78 ± 0.04 eV. For pure KDP the activation energy is 0.374 eV in the temperature range 27°C to 175°C and for the doped crystals energy values are found to be 0.351 eV, 0.236 eV, 0.277 eV and 0.314 eV respectively.

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Chapter 1 Introduction

1.1 Introduction

1.2 Structure of KDP Crystals

1.3 Review of earlier work

1.4 Objectives of the research

1.5 References

1.1 Introduction

Modern technology is mainly based on material science research. The enormous advantages in the modern industry during the first few decades, succeeded rapidly due to the increasing availability of high quality single crystals, such as Semiconductor, Ferrites, Magnetic Garnets, Solid State lasers, Piezoelectric, Ultra-violet and Infrared sensitive crystals, crystalline films for microelectronic and computer industries. Now a days crystals are widely used in watches, transisterized radios, computers, lasers etc and hence the modern technology mainly depends upon crystals. So there is an increasing demand for crystals.

Naturally occuring crystals are inadequate to meet the growing needs of the present day technology. In this connection, the preparation of synthetic crystals ranging in size from very small to large is needed for practical purposes. Single crystals have advantages over the poly-crystals in the way that they have fewer point defects, line defects and dislocations. Therefore, the growth of single crystals of ferro-electric materials such as KDP with high purity, perfection has created considerable interest in the field of present day industry and also in the academic research institutions. KDP crystals have electro optical properties owing to which it is widely used in infrared detection, infrared imaging, and polarization filters.

1.2 Structure of KDP Crystals

Potassium dihydrogen phosphate (KDP) is the best known of the nonlinear material. It can be grown easily from a water solution with dimensions as large as several centimeters. The crystal is usually of good optical quality and can be cut or polished without difficulty. At room temperature KDP is piezo-electric, and belong to the point group $\bar{4}2m$. KDP has one curie temperature $T_c = 123^{\circ}K$. Above the transition temperature it has a tetragonal structure (3 mutually perpendicular axes a, a, c); below T_c it is orthorhombic (3 mutually perpendicular axes a, b, c). The c axis is the direction along which the spontaneous polarization occurs and there is only one polar axis [1].

From an analysis of the structure of KDP it appears that the PO_4 groups form tetrahedrons with the four oxygens at the corners and the phosphorus at the center [2]. These phosphate groups are bound together by what is known as a hydrozen bond [3]. In these bonds, the proton may occupy a number of possible positions, each of which corresponds to a certain polarization of the unit cell.

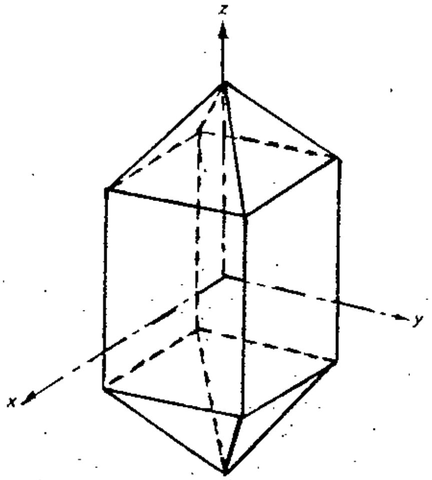

Fig.1: Normal habit of potassium dihydrogen phosphate crystals.

In KDP, both K and P are in tetragonal coordination with oxygen atoms. The hydrogen atom is situated about 0.21Å from the midpoint of the line joining the oxygens. There exists three different bonds: K-O, H-O, and P-O. The contribution of the K-O bond to the linear and nonlinear susceptibility can be neglected due to its high ionicity. The H-O bond is covalent and contributes to the linear susceptibility. However, the almost isotropic distribution of H-O bonds make the contribution to nonlinear susceptibility cancel each other so the only contribution to the electro-optic coefficient comes from P-O bonds. In KDP, the participation of H-O bonds in susceptibility make very difficult (chung-ching shih and Amnon y ariv) for calculating the polarisability of P-O. Since all members in the KDP family have the same structure, the properties and direction cosines of P-O bonds should not deviate much from crystal to crystal.

1.3 Review of early work

Pure KDP crystals have been grown from aqueous solution previously by several workers [4-7]. Joshi and Antony [8] have studied the kinetics of growth and dislocation of KDP crystals in solution. A considerable amount of information has already been reported on the habit modifications of KDP and ADP crystals [9-10]. The most common factor to all these applications is the need for crystals with large electro-optic co-efficients. Though KDP has all the essential qualities, it suffers from a relatively low electro-optic coefficient [11]. The electro-oppical properties of these crystals can be improved by the replacement of K^+ by the larger Rb^+ and Cs^+ and also (PO_4) by (AsO_4) etc. The electro-optic coefficient of KDP mainly orginates from their P-O bonds [12]. Shanmugham et al., [13, 14] have reported the nucleation kinetics of supersaturated aqueous KDP solutions doped with different soluble impurities. The growth and the optical absorption studies have been carried out on coloured crystals of KDP doped with $K_2 CrO_4$ and $HgCl_2$ by Dalal et al., [15]. To the best of the knowledge of the author no systematic studies have been made to visualize the effect of cl^- ions on the electro-optic and ferroelectric properties of KDP crystals.

Highly transparent, good quality large size single crystal of KDP is expected to be grown in aquous solution doped with impurities such as KCl. Measurements of electrical and optical properties such as conductivity and reflectivity of the doped crystals compared to the pure KDP crystal will yield their suitability for practical purposes. Besides these, the result obtained will help in understanding the role of Cl for the electro-optical behaviour of the samples.

1.4 Objectives of the research

With an aim of developing new useful materials for industry and academic uses, ferroelectric materials such as KDP will be grown by means of doping it with KCl in different ratios from aqueous solutions. Present study will help in understanding the role of doping for the electro-optical behaviour of the crystals. No such attempt has been made in Bangladesh to produce such single crystals using doping tecnique in aqueous solution. In the present study an attempt will be made to see the effect of Cl-ions on the replacement of (H_2PO_4) from the KDP crystals to induce changes in the electro-optic and ferroelectric properties of KDP crystals.

The resistivity (and in turn conductivity) for all of the grown crystals are to be measured along the growth axis and perpendicular direction by the conventional two-prove method.

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Chapter 2 Crystal growth

2.1 Introduction

2.2 Solution growth technique

2.3 Advantages of growth from solution

2.4 Low temperature solution growth

2.5 Growth by changing temperature

2.6 Evaporation of solvent

2.7 References

2.1 Intruduction

Crystal growth is a heterogeneous chemical reaction of the type (a) Solid → crystal (b) liquid → crystal and (c) gas → crystal. Crystal growth by liquid-solid equilibrium is probably the most widely practiced method. The growth of crystal by this method is achieved by different techniques; e.g. melt growth, hydrothermal growth, flux growth, solution growth, gel growth etc. The solution growth technique is the most simple, less expensive and convenient method among the above mentioned methods. Growth from saturated solution has many advantages. It is often the only alternative if the substance decomposes below its melting point. If a suitable solvent is found, crystal growing can be performed at ambient temperature well below the melting point. This low temperature overcomes the use of high temperature furnace and power supplies. Furthermore, the reactivity of the solute may be greatly moderated not only by the low temperature but also by the dilution with the solvent. Crystals grown from solution usually have well defined faces as compared to those grown from melts. The chief disadvantage of the solution growth is that the growth rates are appreciably smaller than the process of growth from melt. Linear rates of growth from solution are commonly millimeters per day compared to rates of millimeters per minute from the melt.

Methods of Crystal Growth in generally classified into three categories based on the nature of the starting material,

They are :
(1) Solution Growth
(2) Vapour Growth
(3) Melt Growth.

Crystals are grown to different size and quality by different techniques [1-4]. The following are the important techniques mentioned below.

Solution Growth	**Melt Growth**	**Vapour Growth**
Low temp solution growth	Bridgman	PVT (Physical vapour transportation)
High temp solution growth	Czochralski Pulling	CVT (Chemical vapour transportation)
Gel growth	Zone melting	CVD (Chemical vapour diposition)
Hydrothermal	Travelling solvent zone	
	Flame Fusion verneuil technique	

2.2 Solution growth technique

In solution growth technique, it is extremely difficult to produce spontaneous nucleation in a solution in such a manner that only a single or even a very few nuclei are formed. It is not possible to produce a highly restricted thermal singularity and causes nucleation in only a small volume, since the thermal conductivity will generally spread the thermal perturbation before solute diffusion can assemble enough of the solution to form the nucleus. For this reason the growth of large crystals usually requires seeding. Small crystals suitable for seed can be produced by very slowly approaching the condition in which nuclei form spontaneously. Under these conditions it is usually possible to form sufficiently few nuclei so that crystals of large enough to handle are produced.

The crystal growing processes differ primarily in the manner in which supersaturation is produced in the solution. The three techniques usually employed are

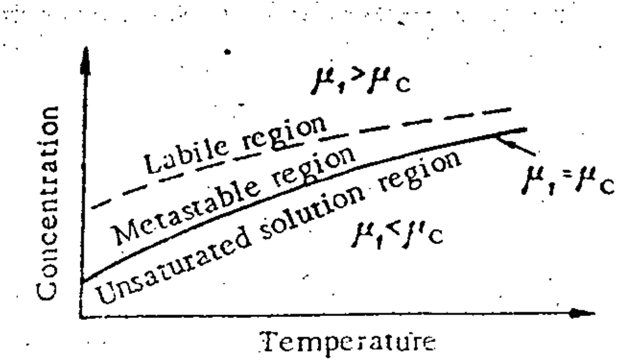
a. A change in temperature.
b. Evaporation of solvent.
c. The addition of solute.

Solutions are usually described in terms of the concentration of substances present in them.

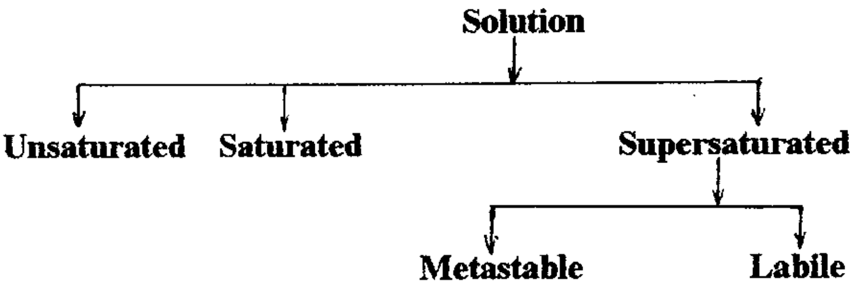
Let us consider a typical solubility diagram (Fig.2.1). The whole concentration-temperature field is separated by the saturated-solution line (solubility curve) into two regions: unsaturated and supersaturated solutions. Saturated solutions are those mixtures which can retain their equilibrium indefinitely in contact with the solid phase with respect to which they are saturated. The solubility of most substances increases when the temperature is increased (the temperature coefficient of the solubility is positive). Crystals can be dissolved only in unsaturated solutions. They crystallize only from supersaturated solutions which contain an excess of the solute above the equilibrium value.

The region of supersaturated solutions can be divided into two subregions: metastable (stable) and labile (unstable) solutions.

The width of the metastable subregion depends on the concentration of chemical, colloidal, and mechanical impurities. The formation of nuclei is usually observed when the supercooling amounts to several degrees. Single crystals grow only in the metastable subregion near the solubility curve.



2.1 Typical solubility diagram; μ_c is the chemical potential of a crystal; μ_l is the chemical potential of the same crystal in solution.



Its a level of super-saturation where sponteneous nucleation can not occur

If sponteneous nucleation is observed in the supersaturated solution the system is said to labile region

2.3 Advantages of growth from solution

The method can be very simple and inexpensive. It can lead to fair quality crystals. It leads itself to continuous operation. In addition, growth from aqueous solution can be visually inspected; in fact it has been extensively used for studying growth parameters (including convection and transport).

Probably the most important advantage of crystal from solution is the control that it provides over the temperature of growth [5]. This makes it possible to grow crystals that are unstable at their melting points or that exist in several crystal forms depending on the temperature. The second advantage is the control of viscosity, thus permitting crystals that tend to form glasses when cooled from their melt to be grown. Low viscosity solvents such as water greatly accelerate the devitrification of silica glass as shown by Walker [6]. Presumably this occurs by a combination of solvent and hydrogen bonding actions, thus providing the increased molecular mobility required. In general, linear rates of growth from melts are the higher order of magnitude than those from solution. The crystals grown from solutions usually have well defined faces as compared to those grown from melt of other techniques and usually contain physical defects.

2.4 Low temperature solution growth

This is the simplest and oldest method for growing crystals and it is based on the principle that the cyrstals can be obtained from supersaturated solution by slow cooling or by removing some of the solvent from the solution by evaporation.

Enormous quanttities of materials such as sugar, salt and of inorganic and organic chemicals are crystallized from solution in water, and excellent quality crystals of such ferroelectric and piezoelectric materials which as ammonium dihydorgen phosphate (ADP), potassium dihydrogen phosphate (KDP), and triglycerine sulphate (TGS) are commercially grown for use in electronic devices.

A supersaturated solution of a substance in a suitable solvent is prepared and cooled slowly in a thermostat whose temperature is lowered at a constant rate. A small seed crystal is suspended in the solution and the seed crystal begins to grow slowly. Seed crystal should be prepared carefully so that well defined crystal is obtained as the seed crystal and care should be taken to avoid any damage to the surface of the crystal.

The main disadvantage of this method is the need to use a range of temperature. The use of range of temperature may vary the properties of grown crystal. This method also requires a programmed temperature controlling device but still the method is used widely with great success for growing crystals. The factors that control the growth process are:

1. character of the solution
2. effect of additives and purity
3. operating variables such as the degree of supersaturation, efficiency of agitation and temperature range and
4. seed crystal.

A linear growth rate of 0.5 to 1mm per day is preferred and the temperature is decreased at the rate of 0.1° to 0.2°C per day.

2.5 Growth by changing temperature

The solubility of most solute in most solvents is a function of temperature. The temperature co-efficient may either be positive or negative and may itself be the function of temperature. Thus, if the temperature of a saturated solution is changed in the appropriate direction, the solution will become supersaturated and the growth of a seed crystal can occur. This property has been used to grow a great variety of crystals. It is the most commonly used technique when the controlled evaporation of solvent of addition of solute is difficult.

A suitable system should be chosen in which both the solubility and its temperature coefficient are large. If the former requirement is not met, an extermely large volume of saturated solution is necessary to grow a large crystal. The latter property permits appreciable growth without too large a swing in temperature. An oven or thermostat is requied which allows a controlled variation of temperature. In growing from aqueous solution near room temperature, a cooling of a few tenths of a degree centigrade per day are commonly employed and the exact rate being determined by the particular system under study.

2.6 Evaporation of solvent

For producing crystals, one of the earliest techniques was evaporation of solvent from a saturated solution. The technique can be usually employed if the temperature co-efficient of solubility is very small, although again the total solubility should be large. The rate of evaporation can be enhanced by the use of vacuum. This is a constant temperature technique with removal of solvent rather than addition of solute.

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Chapter 3 Theory of nucleation

3.1 Introduction

Nucleation is an important phenomena in growing material. It plays a vital role wherever condensation, crystallization and catalytic processes etc take place. The process of nucleation describes the initial formation of one phase in another, where there is a free energy barrier to the formation of new phase. A nucleation barrier does not exist in all instances of the initiation of a phase transformation, but nucleation is a sufficiently wide spsead phenomenon that it deserves detailed discussion in a survey course on crystal growth. So nucleation is important in the first formation of a crystal from a gas, liquid or solution. It is important in the initial stages of point defect or second component precipitation in crystals. It is also important, under conditions which will become apparent, to the crystal growth process itself.

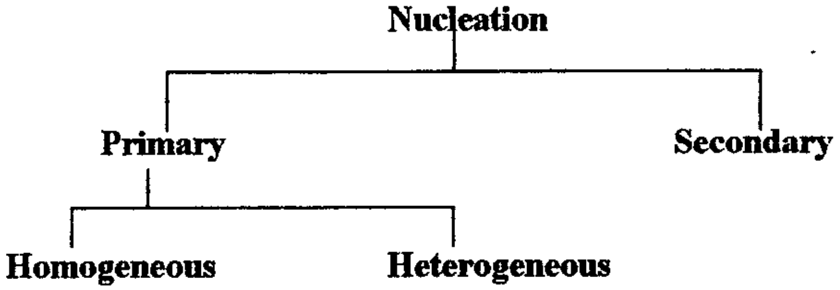
3.2 Types of nucleation

Nucleation is defined as the process of generating, within a metastable mother phase the initial fragments of a new and more stable phase, capable of developing spontaneously into gross fragments of the stable phase.

Nucleation may occur spontaneously or it may be induced artificially and are referred to as homogeneous and heterogeneous nucleation respectively.

The term 'primary' indicates nucleation in systems that do not contain crystalline matter viz, homogeneous and heterogeneous. Nuclei that are often generated in the vicinity of crystals present in supersaturated system is referred to as secondary nucleation.

In general nucleation can be classfield as:



External influences such as agitation, mechanical shock, friction, high pressure, electrical field, magnetic field and spark discharge would often induce nucleation. Moreover nucleation would also be initiated by ultraviolet rays, X-rays, sonic and ultrasonic irradiation and so on.

3.3 Classical theory of nucleation

The formation of crystal nuclei is a difficult and a complex process because the constituent atoms or molecules have to be oriented into a fixed lattice. In practice a number of atoms or molecules may come together as a result of statistical incidents to form an ordinary cluster of molecules known as embryo. The energetic considerations show that this embryo is likely to redissolve unless it reaches a certain critical minimum size. If it does not dissolve, it means that the assembly is stable under the prevailing conditions[1].

3.4 Kinetic theory of nucleation

The main aim of the nucleation theory falls in the calculation of the rate of nucleation. Rate of nucleation is nothing but the number of critical nuclei formed per unit time per unit volume. In the molecular kinetic theory nucleation is treated as the chain reaction of mono-molecular addition to the cluster and ultimately reaching a macroscopic dimensions [2].

The reaction is represented as follows:

$$\begin{array}{l}
A_1 + A_1 \overset{\rightarrow}{\leftarrow} A_2 \\
A_2 + A_1 \overset{\rightarrow}{\leftarrow} A_3 \\
\text{--------------------} \\
\text{--------------------} \\
A_{i-1} + A_1 \overset{\rightarrow}{\leftarrow} A_i \\
A_i + A_1 \overset{\rightarrow}{\leftarrow} A_{i+1} \\
\text{--------------------} \\
\text{--------------------} \\
A_{j-i} + A_1 \overset{\rightarrow}{\leftarrow} A_i
\end{array}$$

Two monomer collide with one another to form a dimer. A monomer joins with a dimer to form a trimer. This reaction builds up to create a cluster having i-molecules known as imer. As the time increases the size distribution of the embryos changes and increase in size. As the size attains a critical size say A_J^*, then further growth into macroscopic size is guaranted, until then, there is a possibility for the reverse reaction i.e. the decay of a cluster into monomers.

3.5 Stability of a nucleus

An isolated droplet of a fluid is most stable when its surface free energy and therefore its area is a minimum. According to Gibbs [3, 4], the total free energy of a crystal in equillibrium would be minimum for a given volume if its surrounding is at constant temperature and pressure. If the volume free energy per unit volume is considered to be constant,

Then

$$\sum^{n} a_i \sigma_i = \text{minimum} \qquad (1)$$

where a_i is the area of the ith face and σ_I is the corresponding surface energy per unit area.

3.6 Energy formation of spherical nucleus

The main aim of the theory of the nucleation is to find the dependence of the rate of nucleation on various factors such as temperature, inter-facial tension, supersaturation etc. Nucleus otherwise called as seed of a crystal is the fundamental unit of crystal. The nucleus, born, proceeds to grow into a large crystal depending on factors like concentration, environmental conditions etc. The minimum size that a nucleus must have to grow into a crystal is called the critical size. Nuclei with this size are called critical nuclei. The number of critical nuclei formed per unit time per unit volume is defined as nucleation rate.

So energy is quite essential for the creation of a new phase.For example the formation of a liquid droplet from vapour or a solid particle from liquid demands an expenditure of certain quantity of energy for the creation of the liquid or solid surface. Therefore the Gibbs free energy (G) required to form a stable crystal nucleus is equal to the sum of the energy required to form the surface G_s' and the energy required to form the bulk of the particle G_v

i.e. $G = G_s + G_v$

or $\Delta G = \Delta G_S + \Delta G_v$ (3.2)

Where ΔG is the change of Gibbs free energy, ΔG_s is the surface excess free energy and ΔG_v is the volume excess free energy.

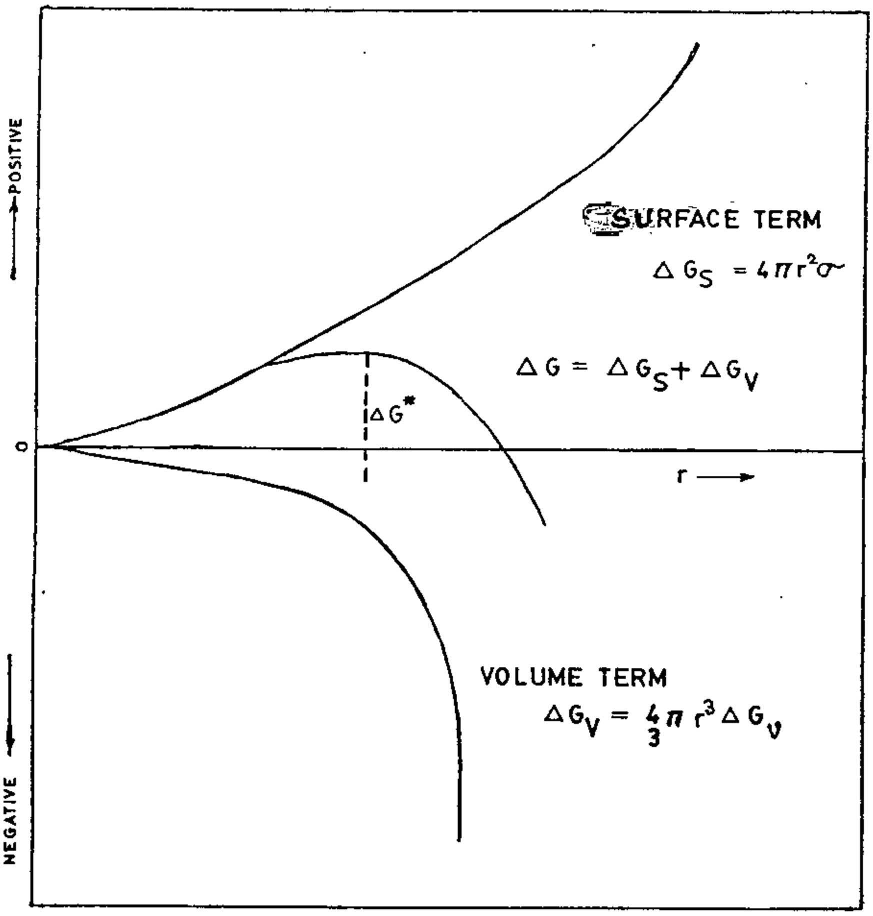


Fig. 3.1 Free energy diagram

For the formation of a spherical nucleus of radius r in a supersaturated vapour, for instance eq'n (3.2) can be written as

$$\Delta G = 4\pi r^2 \sigma + 4/3\pi r^3 \Delta G_v \tag{3.3}$$

where σ is a surface energy of the droplet per unit area, and ΔG_v is the free energy change per unit volume which is a negative quantity.

The quantities ΔG, ΔG_s and ΔG_v are represented in fig. 3.1.The excess surface free energy increases with r^2 and the excess volume free energy decreases with r^3, So, the total free energy change initially increases with increase in size, attains the maximum and then decreases for further increase in the size of nucleus. The size corresponding to the nucleus in which the free energy change in maximum is known as the critical size and can be obtained mathematically by maximizing the equation (2) and setting to zero. This is at maximum ΔG, $r = r^*$ (radius of critical nucleus)

$$\frac{d\Delta G}{dr} = 0$$

$$r = r^*$$

or $$8\,\pi\, r^*\sigma + 4\pi\,(r^*)^2.\Delta g_V = 0$$

or $$r^* = \frac{-2\sigma}{\Delta G_v} \tag{3.4}$$

The free energy change associated with the formation of critical nucleus can be estimated by substituting eqn (3.4) in eqn (3.2).

$$\Delta G^* = 4\pi\sigma\left(-\frac{2\sigma}{\Delta G_v}\right)^2 + \frac{4}{3}\pi\Delta G_v\left(-\frac{2\sigma}{\Delta G_v}\right)^3$$

$$= \frac{16\pi\sigma 3}{\Delta G_v^{\ 2}} - \frac{32\pi\sigma 3}{3\Delta G_v^{\ 2}}$$

$$= \frac{16\pi\sigma 3}{3\Delta G_v^{\,2}} \qquad (3.5)$$

$$\Delta G^{*} = \frac{4\pi\sigma}{3} \times \frac{4\sigma^2}{\Delta G_v^{\,2}} \qquad \text{Since } r^{*} = \frac{2\sigma}{\Delta G_v}$$

$$= \frac{4\pi\sigma\, r^{*2}}{3}$$

$$= \frac{1S\sigma}{3} \qquad (3.6)$$

where S is the surface area of the critical nucleus. Though the present phase is at constant temperature and pressure, there will be variation in the energies of the molecules. The molecules having higher energies temporarily favour the formation of the nucleus. The rate of nucleation, can be given by Arrhenius reaction velocity equation since the nucleation process is basically a thermally activated process.

The nuleation rate J can be expressed as

$$\left(-\frac{\Delta G\, {}^{*}hom}{KT}\right) \qquad (3.7)$$

$$J = A\mathrm{exp}$$

where A is the pre-exponential constant, K the Boltzmann constant and T is the absolute temperature. From Gibbs-Thomson equation for the vapour growth, we have

$$S = \frac{P}{P^{*}}$$

$$\text{or} \qquad \mathrm{In}\frac{P}{P^{*}} = \mathrm{In}\, S \qquad (3.8)$$

where S is the supersaturation ratio of actual pressure and equilibrium pressure.

The volume free energy of nucleus (ΔG_v) is

$$\Delta G_v = -\frac{KT}{V} Ln\left(\frac{P}{P*}\right) \tag{3.9}$$

where V is the molar volume of the compound

$$\text{or} \qquad In\, S = -\frac{\Delta G_v V}{KT}$$

$$\text{or} \qquad In\, S = -\left(\frac{-2\sigma}{r*}\right)\frac{V}{KT}$$

$$In\, S = 2\sigma V / KTr* \tag{3.10}$$

From eqn (3.4) and (3.10) we get

$$-\Delta G_v = \frac{2\sigma}{r*}$$

$$-\Delta G_v = \frac{KT\, In\, S}{V} \tag{3.11}$$

Equation (3.7) can be rewritten using the eqns. (3.5) and (3.11) as

$$J = Ae\left(\frac{-16\pi\sigma^3}{3} \times \frac{v^2}{K^3T^3(InS)^2}\right) \tag{3.12}$$

Eq'n(3.12) shows that the rate of nucleation depends on the absolute temperature T, interfacial tension σ and supersaturation ratio S.

3.7 Structure of real crystal

An ideal crystal can be defined as an infinitely large system consisting of a regular space lattice at each point of which there are identical particles or identical groups of particles. These particles in a crystal may be atoms, ions or molecules [5].

When a real crystal is formed many factors prevent the formation of a perfectly regular lattice of particles, and the crystal may capture foreign particles. Thus, departures from the ideal structure, known as defects, appear in a real crystal.

A real crystal is formed as a result of two opposing tendencies: (1) a tendency to achieve an ordered distribution of particles so as to obtain a maximum compensation of chemical bonds; ordering is realized most easily when the particles are spherical and the number of types of particle in a crystal is strictly limited; (2) a tendency to mixing and disorder due to the thermal motion of particles.

These tendencies depend on the actual conditions (the chemical nature of the medium, temperature, etc) under which crystals are grown. It follows that crystals of different degrees of perfection can be obtained. These two tendencies obey a general law of a decrease in the free energy in a system in any process .

3.8 Crystal defects

Defects can be classified conveniently according to their shape and size. If we assume that the structure units in a crystal (atoms, ions and molecules) have zero dimensions, we can distinguish the following types of defects; (1) Zero-dimensional (2) One dimensional (3) Two-dimensional and (4) Three-dimensional.

The defects influence the properties of the solid in the following different ways:

(1) The defects may scatter conduction electron in a metal increasing its electrical resistance by several percent in many pure metals and much more in alloys.

(2) Some defects, even if present sparingly, decrease the strength of the crystal.

(3) Pure salts having impurities and imperfections are often coloured.

(4) Hysteresis loss of ferromagnets. Those properties which are strongly sensitive to the state of perfection of the crystal are called structure sensitive properties.

Dimension	**Type**	**Nomenclature**
0	Point	Vacancy Interstitial Vacancy-interstitial pair Impurity-substitutional Impurity-interstitial
1	Line	Edge dislocation Screw dislocation Mixed dislocation
2	Surface	Grain boundary Twin boundary Stacking fault
3	Volume	Void or porsity inclusion

3.8a Zero-dimensional defects

Point defects in a crystals are in general, distributed non uniformly. If the deviation from regularity is confined to very small region of only about a few lattice constants, it is called a point defect. The main types of such defects are vacancies (unfilled sites in a crystal), interstitial atoms, and any other impurity particles [6,7].

Vacancies and interstitial atoms are generated primarily by the thermal motion of atoms. The higher the temperature, the larger is the number of vacancies and interstitials in a crystal. Moreover, Vacancies are formed when the valence of impurities introduced into a crystal differs from the valence of the particles in a host matrix.

(a) If a solid is heated to a high temperature and then cooled, the excess vacancies generated migrate away to sinks such a free surface and come down to the equilibrium value at the lower temperature. Instead, if the solid are rapidly cooled to the low temperature from the high temperature there will not be sufficient time for the vacancies to migrate to sinks and excess amount will be retained in the solid. This process is called a generation of vacancies.

(b) If the crystal is bombarded or irradiated with high energy particles such as neutrons, a good concentration of vacancies as well as interestitials are generated. Vacancies play an important role in atomic migration in crystals (This is called diffusion).

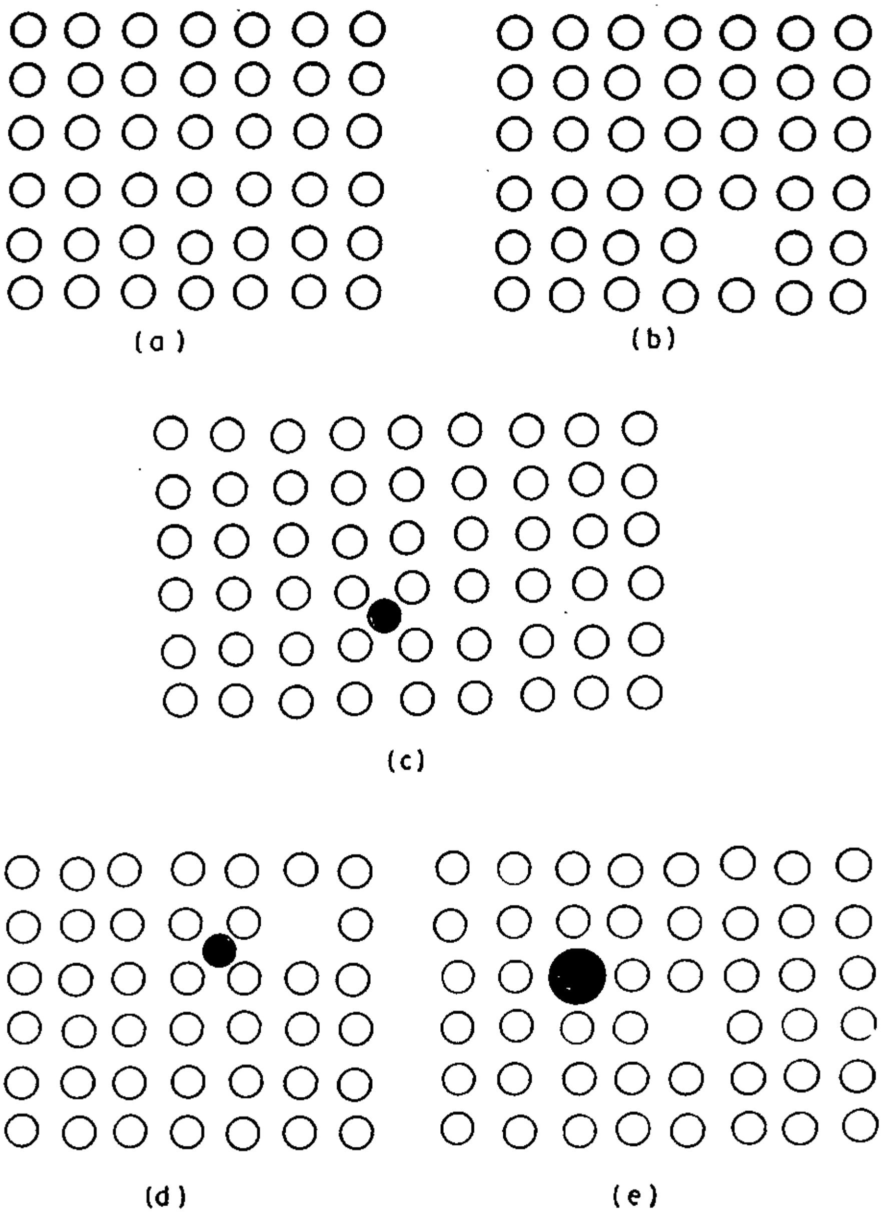


Figure 3.2: Point defectes (a) A perfect atomic place (b) A vacancy (c) An Interstitial (d) A vacancy – Interstitial pair and (e) A substitutional impurity.

3.8b One-dimensional defects

The concept of a line defects in a solid was first postulated in 1934 in an attempt to explain the case with which metals deform plastically. By specifying certain rules, we can draw a closed contour through identical points in an ideal crystal structure (for example, we can draw this contour through the lattice sites). This contour is known as Burgers circuit. The number of steps in such Burger circuit is drawn in one plane in a crystal.

A real crystal does not have an ideal structure but various parts of its are distributed to some extent. We shall define as a good material a substance in which particles suffer only elastic deformations. In a good material, the Burgers circuit around zero-dimensional defect is closed.

However, if a contour drawn, around a defect is open Figure (3.3), such a defect is one-dimensional and is called a dislocation. It is evident from figure (3.3) that in this case a crystal has an extra half-plane in the vertical direction. The edge of this half-plane is known as the dislocation axis.

The gap seperating the ends of the contour around the dislocation is known as the modulus of the Burgers vector b. Thus, a closed contour around a dislocation is equal to the sum of the Burgers circuit and Burgers vector. Two extreme cases of the position of b with respect to the dislocation axis can be distinguished: correspondingly, there are two main types of dislocation. When b is perpendicular to the dislocation axis we have an edge dislocation figure (3.3).

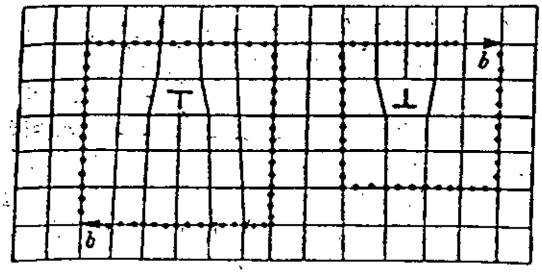


Figure- 3.3. Burgers circuits (represented by dots), closed by Burgers vectors b< around two edge dislocations of opposite signs. The symbol ⊥ represents the edge of half-plane.

Naturally, more than one half-plane may be introduced.The Burgers vector is then correspondingly larger. If b is parallel to the dislocation axis we have a screw dislocation. The nature of screw dislocation can be seen from Figure 3.4. Edge and screw dislocations are the extreme forms of dislocations. There are also dislocation with b having an intermediate orientation with respect to the dislocation axis. They are known as mixed dislocations

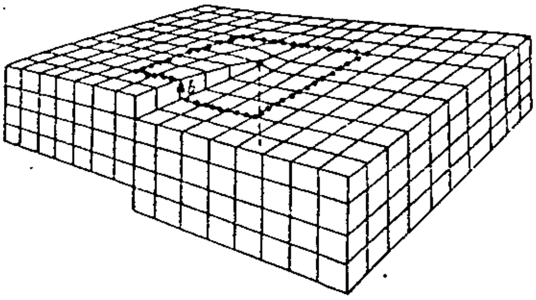


Fig. 3.4. Screw dislocation with its axis (pointing into the interior of a crystal) shown dashed.

3.8c Two-dimensional defects

These defects include first of all the actual surfaces of a crystal. The surface has an excess energy of the particles in the interior of the crystal. This is known as the surface energy. This energy is due to an irregular distribution of particles near the surface compared with the regular distribution in the interior.

(i) Surface defects

Surface defects are of two dimensional crystalline imperfections. Free surface of crystals, which is simply a terminus of the crystal are actually regions where the atoms have neighbours only in 3 directions. Unlike other atoms well inside the crystal the surface atoms have a higher energy and because of this, the surfaces display some special properties such as adsorption. There are three types of surface defects:

(1) Grain boundary, (2) Twin boundary (3) Stacking fault.

(1) Grain boundary

Most common materils consist of many small interlocking crystals or grains having random orientations. Burger suggested that the boundaries of two crystallites or crystal grains at low angle inclination with each other can be considered to be a regular array of dislocations [8]. The boundary between two adjacent grains, therefore, must have a structure that somehow confirms to the structures and orientations of both grains. It is obvious from this that the grain boundary forms a discontinuity in the periodicity of the lattice of either crystalline or grain and is, therefore, a type of lattice imperfaction.

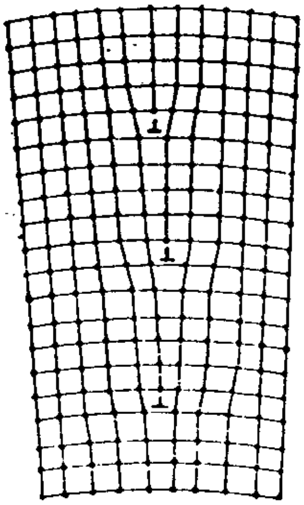


Fig. 3.5. Dislocation boundary between two blocks in a crystal.

(2) Twin boundary

The second type of surface defect is the twin boundary. Figure (3.6) Shows a typical twin. The cyrstal to the left of the boundary is the base crystal.

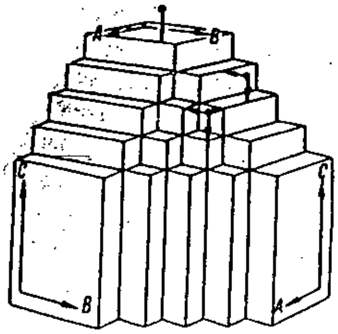


Fig. 3.6 Types of crystal face classified in accordance with surface bonds (A, B, C represent the vectors of strong bonds). Points with arrows represent atoms adsorbed, respectively, on an F face (single arrow), on an S face (two arrows), and on a K face (three arrows)

During growth, deformation or annealing process, twins sometimes form and the normal lattice is not continued. Instead a mirror image of the regular lattice is formed, with the twin boundary acting as a mirror. This is the twin to the right of the boundary. Any point on the left (in the normal lattice) is mirrored across the boundary to form a corresponding point in the twinned lattice that is, point A is mirrored to form point A' and point B to from B'. Because the normal lattice is stopped at the boundary and the twinned lattice begins, a twin boundary forms at the surface between the two orientations [9].

(3) Stacking fault

Stacking faults are surface defects created by a fault in the stacking sequence of atomic planes in crystals. Figure (3.6) shows a stacking fault. The stacking fault can be produced by at least two distinct mechanisms. When a closed-packed plane of atoms forms in a crystal, it is possible for a new layer to start incorrectly; that is a C-layer can start to grow instead of the B-layer required by the preceding stacking sequence. If the crystal grows sufficiently rapidly, this so called growth fault is incorporated in the final crystal.

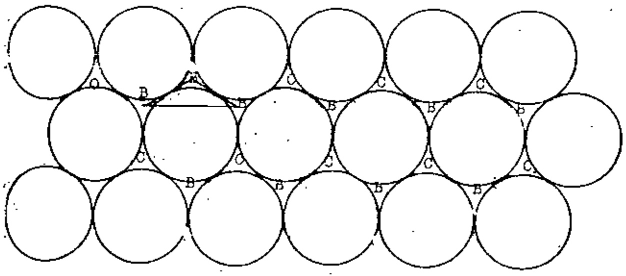


Fig. 3.6 : Production ofdeformation faults in terms of dislocations. When a partial dislocation is formed in a close packed plane a stacking fault is produced.

Similarly, it is possible to displace the atoms in, say B-layer to the sites of a C-layer during the plastic deformation of the crystal. After the force producing the displacement are removed, the so-called deformation fault can persist in the crystal because the immediate co-ordination of each atom is not changed [6].

(ii) Volume defects

Three-dimensional defects include primarily closed cavities (inclusions in a crystal). Depending on the phase state of the ambient medium during crystallization, they may be filled with a vapour, a liquid, or with solid foreign particles, or they may consists of several phases. When a crystal containing liquid or gaseous inclusions is kept for a long time at a temperature ensuring that the concentration of the host crystal particles within the cavities increases appreciably, the usually shapeless inclusions are replaced by facted ones, which are known as *negative crystals*. Small solution containing inclusions in crystals exhibiting a high solubility at room temperature become facted in several days. Three dimensional defects also include open cracks in crystals [10].

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Chapter 4 Experimental details

4.1 Introduction

Any field of technology has its own origin-the 'seed' and developments: after slow evolutionary processes and many refinement it attains a regular shape. Growth of crystals from aqueous solution is no exception to the above. Crystallization of salt from binary solution has been known to mankind for centuries. After undergoing so many modifications and refinements, the process of solution growth now yields good quality crystals for a variety of applications. Materials which decompose on heating or which exhibit any structural transformation while cooling from the melting point can be grown by solution growth provided they dissolve in some solvents. In this chapter the procedure of growing KDP and mixed KDP with KCl crystals and their characterisation by IR spectroscopy. X-ray diffractometry, d.c. electrical conductivity measurement, voltage breakdown strength etc. are discussed in details.

4.2 Preparation of the solution

The important process in the growth of crystals from solution is the preparation of the solution. As it is known that the impurities affect the growth to a large extent, so it is essential to prepare the solution from pure solute and solvent. Anular grade KDP and KCl substances alongwith double distilled water were used for the growth of single crystals. To prepare a solution, it is necessary to know the solubility of a substance in grams per 100g of the selected solvent.

The amount of KDP salt was calculated using the given formula for preparing 2M (molar) concentration of saturated solution at room temperature.

$$Amount = \frac{Strength\ of\ concentration \times molecular\ weight \times volume}{1000} \qquad (4.1)$$

2 molar concentration of KDP and KCl solution were prepared separately. The procedures are discussed below:

1. First, the necessary amount (i.e. about 150ml) of the solvent was measured. Its volume was measured with an accuracy of the order of 0.5-1%. In the absence of an accurate measuring cylinder, the solvent must be weighed. Pipettes was used to add or remove small amounts of the liquid.

   Then, the solvent was heated in a round bottom flask to a temperature 10-15 deg celsius higher than the saturation temperature in order to accelerate the process of dissolution. Excessive overheating was avoided because it results in an appreciable loss of the solvent.

2. Pure KDP salt was ground to a powder of grain size less than 1 mm; the necessary amount (about 40.82 gm) was weighed and added to the hot solvent.

3. The solution must not be allowed to cool before filtration. After filtration, the solution was ready for the next operation. While waiting for the next stage the neck of the flask was covered with filter

paper to prevent dust and other particles present in the atmosphere from contaminating the solution.

Mixing is a very simple process. Solute and solvent of pure KDP or KDP doped with KCl was placed in a beaker. The beaker was then placed on a magnetometer. A magnetic stirrer was droped into the beaker before the electric supply applied to the system for melting the substances.

A reciprocating motion of the magnetic stirrer mixes the solution and accelerates the saturation stage. Usually 2 hours is found sufficient to produce a stage of equilibrium between the solution and the salt.

Solubility of KDP in water

Solubility of KDP in water is shown below

Temperature, °C	Solubility, kg/kg of water
20	0.226
25	0.247
30	0.273
35	0.303
40	0.335

4.3 Test for saturation

The saturation of the solution was tested by observing the path of light beam passed through the seed suspended in the solution; the seed will not deflect the light beam if the solution is saturated. In other words, the seed crystal, when immersed in saturated solution, is not distinguishable from the solution. If some concentration currents are seen moving towards the seed, the solution is supersaturated. In the case of undersaturated solution, the crystal starts dissolving which results in concentration currents moving away from the seed. In the case of stirred system, a test seed with sharp edges was suspended in the solution. After a few hours, if the edges of the seed become blunt, the solution will be undersaturated. The sharpness of the edges remain unaffected if the solution is saturated or supersaturated.

4.4 Preparation and mounting of seed crystals

Initially seed crystals were prepared by making a solution of the required salt saturated at a temperature about 10-15°C above room temperature. The solution was allowed to cool in a covered beaker and to stand for several days during which a large number of interlayered crystals developed on the bottom, some with long clear ends perfectly capped with pyramidal tips. The solution was then poured out and the clear ends were removed carefully with tweezers and dried on filter paper. These crystals (about 3 mm thick and 5 mm long) were used as seeds for growth in the cell.

A seed is any fragment of a crystal or a whole crystal which was used to start the growth of a larger crystal in a solution. The maximum size of a seed cannot be specified *a priori* and, in principle, a crystal of any shape or size can be regarded as a seed if it is used to grow a larger crystal. A seed used to prepare large uniform crystal must satisfy the following requirements:

1. It should be a single crystal free of cracks and block boundaries.
2. It should be free of inclusions.
3. Its surface should be free of sharp cleaved edges.
4. It should be of the minimum size compatible with other requirements.

The first requirement is dictated by the observation that defects in a seed are transferred to a growing crystal. Moreover, the presence of block and other boundaries in a seed gives rise to strong stresses because of the crystallization pressure on the seed and such stresses may give rise to cracks and inclusions.

Now the seed was introduced into the solution, care was taken to avoid any rapid deposition of the solute on the seed. Most of the growth processes were carried out at slightly above the room temperature.

Growth from solution is mainly seeded growth because it is carried out in the metastable state of the solution. The quality of the crystal grown very much depends on the quality of the seed crystal used. Small crystals with no obvious defects such as inclusions and twinning were used as seed to the solution.

4.5 Growth rate investigation

The seeds of pure KDP and mixed KDP-KCl were suspended in a solutions in a petry-dish and the petry-dish was placed in a dust-free glassy-frame chamber. The growth rate was observed by a travelling microscope for every 24 hours. Initially the growth rate was found rapid but within a week growth started slowing down. After 18 days the crystals were collected from the solution and measured by slide callipers.

4.6 Infrared (IR) spectroscopy

Infrared (IR) spectroscopic study provides a valuable information about the nature of the atomic systems of the crystals.

Infrared radiation refers broadly to that part of the electromagnetic spectrum between the visible and microwave regions. Infrared (IR) spectroscopy is applicable to characterize both the organic and inorganic materials. In a molecule total energy (Emole) comes from various sources, like translational, rotational, vibrational and electronic etc. Thus;

$$E_{mole} = E_{trans} + E_{rot} + E_{electronic} \tag{4.2}$$

Rotational spectra result from the absorption of photons by molecules with the complete conversion of the energy of molecular rotation. Whereas vibrational spectra results due to the absorption of radiant energy by the molecules thereby changing the energy of molecular vibration. Vibrational spectra appears as bands rather than lines because of single vibrational energy change is accompanied by a number of rotational energy changes. The frequency or wavelength of absorption depends on the relative masses of the atoms, the force constants of the bonds, and the geometry of the atoms.

Band positions in infrared spectra are presented either as wave number or wave lengths. The wave number unit (cm^{-1}) is used most often since it is directly proportional to the energy of the vibration.

Band intensities are expressed either as transmittance (T) or absorbance (A). Transmittance is the ratio of the radiant power transmitted by a sample to the radiant power incident on the sample. Absorbance is the logarithm to the base 10, of the reciprocal of the transmittance.

$$A=\log_{10} (I/T) \tag{4.3}$$

There are two types of molecular vibrations. Stretching and bending. A stretching vibration is a rhythmical movement along the bond axis such that the interatomic distance is increasing or decreasing. A bending vibration may consist of a change in bond between bonds within a common atom. For example, twisting, rocking, and torsional vibrations involve a change in bond angle with reference to a set of coordinate arbitrarily set up within the molecule.

Two important techniques have been developed for the infrared examination of different materials. One of these is the thin section technique and the second method is the potassium bromide (KBr) pellet technique developed by Schiedt which has become the most popular method of obtaining spectra (2).

4.6a IR Spectrometer

The crystals of pure KDP and KDP doped with KCl in different ratios were studied using infrared spectrometer. The samples were prepared by pressed disc technique. Infrared spectra of all the samples at room temperature were recorded in the wave number region 400-4000 cm^{-1}.

The instrument was calibrated for its accuracy with spectra of a standard KDP film. Here the IR transmittance were taken with KBr pellet technique. Infrared spectrometer of model FTIR-8101 of Shimadzu corporation, Japan, was used in the present work. KBr pellets were prepared by mixing ~1 mg of dry finely powdered KDP with 300 mg of KBr. Pellets of 13 mm in diameter were pressed in an evacuated die under 20000 Psi pressure for one minute.

4.7 X-ray diffraction (XRD)

X-ray diffraction method is very important for the determination of the periodic arrangements atoms in a crystals. Now a days X-ray diffraction is used not only for the determination of crystal structure but also for several complex biological analysis, chemical analysis and measurement of particle size, for the determination of the structure of the crystal and the assemble of orientations in a polycrystalline material.

The energy of diffraction beams can be measured by a counting device which records individual X-ray photons. The samples of pure KDP and KDP doped with KCl were crushed into fine powder by using a pestle and mortar. Sample pested on a glasslide (area of 1.5cm × 2cm) was then placed on the sample mount in the diffractometer (Model No JDX-8P of JEOL Ltd. Tokyo, Japan) for structural studies.

Operating conditions of X-ray diffractometer were

Radiation	:	CuKα
Voltage	:	30 KV
Current	:	20 mA
Scanning Speed	:	2°/min
Chart speed	:	10 mm/min
Full scale	:	1×10^3C.P.S
Range	:	10°- 90°

'd' value was calculated using Bragg's equation (i.e. $2d_{hkl}\sin\theta = n\lambda$)

lattice parameters for the tetragonal system of the crystals were calculated using the given formula

$$d^2_{hkl} = \frac{1}{\frac{h^2+k^2}{a^2}+\frac{l^2}{c^2}} \tag{4.4}$$

and $$d^2_{hko} = \frac{a^2}{h^2+k^2} \quad \text{when } l=0 \tag{4.5}$$

4.8 Crystals cutting and polishing

For various measurement, specially for conductivity, the large shaped crystals were cut into a rectangular form.

The crystals were cut in a very simple way. There are various methods of cutting a crystal. The best method is the wet string technique (2). Defect-free portions of the harvested crystals were cut by silk thread along the desired direction into small plates of parallellopiped shape.

During cutting the crystals, the silk thread was wet with distilled water as the KDP is water soluble crystals. The thread was moved back and forth for several time for its smooth cutting. After cutting the crystal in a desired direction roughly, the slices of crystals were polished in a cotton jacket apparatus and glass plate.

Specimen was thoroughly cleaned in distilled water to remove external foreign impurities on the surface of the specimen. The samples were dried and preserved in precise way for conductivity measurement.

4.9 Theory of electrical conductivity

The transfer of charge carriers through a medium under the influence of a electric field or temperature gradient is the electrical conduction.

If an element of charge dQ is transferred over an area A, in a time dt, then the rate at which the charge dQ is transferred can be given by the current

$$I = dQ/dt = nq\,V_DA \qquad (4.6)$$

where n is the density number of charge carriers, V_D is the Drift velocity under an applied field E. and V_D is proportional to E(Vcm^{-1})

$$\text{So } V_D = \mu E \qquad (4.7)$$

Now applying equation (4.7), (4.6) becomes

$I = nq\mu E\,A$ where $\mu(cm^2\,V^{-1}\,sec^{-1})$ is the drift mobility and E(Vcm^{-1}) is the applied field. The Conductivity σ ($ohm^{-1}cm^{-1}$) is defined by

$$\sigma = id/VA$$

where d is the sample thickness and V is the applied voltage

Let the field E is uniform thus

$$E = \frac{V}{d} \qquad (4.8)$$

$$\text{Now } (4.8) \Rightarrow \sigma = qn\mu \qquad (4.9)$$

If there is more than one type of charge carriers the conductivity is

$$\sigma = \Sigma q_i\, n_i\, \mu_I \qquad (4.10)$$

In any particular system the number of mobility of the charge carriers will depend upon the material and the experimental parameters of voltage, temperature, and ambient atmosphere.

If the material is crystalline or oriented, the conductivity will depend on the direction with respect to some molecular axis in which the measurement is made.

$$\begin{aligned} n &= n(T, V) \\ \mu &= \mu(T, V, Z) \qquad (4.11) \\ \sigma &= \sigma(T, V, Z) \end{aligned}$$

where T is the present temperature, V is the applied potential, and Z is the direction in which the measurement is being made.

From eqn. (4.10) the conductivity is the product on n and μ which are independent variables.

There are two extreme assumptions which can be taken with respect to equation (4.10).

(i) to assume that the number of carriers is independent of temperature and

(ii) to assume that mobility is independent of temperature.

In each case the variation of the assumed temperature dependent parameter has been used to prove some fundamental relationship between the conduction process and molecular structure.

The high resistivity of many sample requires the measurement of small currents. The form of the sample (powder, molded sal etc.), its purity, the presence of solvent, moisture, the ambient atmosphere, and temperature are all important. The electrode should be obmic, that is there should be no potential barrier at the electrode-sample interface. Frequently it is found that the conductivity of most metals particularly ionic crystals varies exponentially [4-5] with temperature T, according to the equation.

$$\sigma = \sigma_o e^{-E/KT} \tag{4.12}$$

where K is the Boltzmann constant, and E is the activation energy, T is the absolute temperature. E is the sum of two terms, $E = \frac{1}{2} E_D + E_A$, where E_D is the energy for dissociation into ion pairs and E_A is the activation energy for mobility. E is determined from a plot of In σ vs T^{-1}. If the experimental curve is not a straight line, then the conductivity is written as a sum of terms similar to

$$\sigma = \sigma_1 \exp(-E_1/KT) + \sigma_2 \exp(-E_2/KT)$$

In the present work, subscripts 1 and 2 are used for the high and low-temperature regions respectively.

4.10 Instrument used in D.C. Electrical Measurements

(a) Electroding

Silver paint was pasted at opposite flat faces of the dry-polished specimen for a good electrical contact. During pasting, a care was taken to avoid the short circuit condition. Then the specimen were kept in precise order for a several hours for complete drying of the paint before taking conductivity measurement.

(b) Keithley 614 Electrometer

Digital electrometer (model 614, Keithley Instrument Inc. C level and Ohio. USA) was used for D.C. current measurement. For high sensitivity it has versatile uses. It has an analog output of V with input impedence of greater than 5 × 10^{13} ohms. This versatile instrument can measure a wide range of D.C. voltage, current, resistance and electric charge. This Keithley 614 electrometer can measures current as low as 10^{-14} A and the voltage from 10μv to 20V.

(c) D.C. Power Supply

Model: 140a - 160 of Metronix corp., Tokyo, Japan of high voltage d.c. power supply was used for measuring the conductivity of all the specimen. The unit was capable of supplying d.c. voltage from 0 to 160 volts with current range of 0~3.5A maximum.

(d) Specimen Chamber

The specimen chamber unit has two main parts, one is the stainless steel tube and other is the sample chamber. A stainless steel tube of 0.24 m length with a inner diameter of 0.045 m was taken. The lower end of the tube was closed by welding a circular piece of stainless steel sheet and at the top end of the tube a square shaped flat stainless steel sheet of 0.09 × 0.09m^2 with a circular hole of diameter 0.045m at its center is welded. Another stainless steel sheet (same as above) with a hole of the same dimension is welded to a stainless steel tube of diameter 0.045m and a length 0.24m. A O-ring is placed in between the two stainless steel sheet. This prevents the air leakage when it is evacuated. The upper portion can be fixed to the lower portion by screws. The top opening is closed tightly with a teflon stopper spring system. Two copper leads (electrodes) is used as a specimen holder. A cromel-Alumel (Cr-Al) thermocouples is inserted through this teflon stopper. A thick layer of mica sheet is attached to the inside wall along with the bottom of the stainless steel tube for electrical insulation. The diameter of each lead is about 0.014 meter. The side tube is welded to the main stainless steel tube of the outlet chamber.

(e) Heating Coil

Four meter long having the resistance of 15 ohm/m a porclain bit insulated nichrome-wire is wound up over the specimen chamber covered by several mica sheet for required heating. Required temperature is controlled by a variable transformer.

4.11 Analysis of chlorine by Volhard's method [6]

Procedure:

A known amount (0.1405g) of sample was taken in approximately 100ml 10% NaOH solution to dissolve the sample and heated until the volume was half. This reduced volume was taken in a 100ml volumetric flask and added water upto its mask.

10ml of the dissolved solution was taken in a conical flask and just neutralized with 6M HNO_3. 10ml of the standard $AgNO_3$ solution was added with it. (If Cl^- present a precipitate of AgCl occurs). A few drops of nitrobenzene was added followed by continuous shaking for 4-5 minutes. 3-

4 drops of Ferric-alum indicator was introduced and then left for titration with standard NH_4SCN solution.

Standardization of NH_4SCN solution is done with standard $AgNO_3$ solution with the help of Ferric-alum indicator.

10ml $AgNO_3$ + 3-4 dorps of indicator + NH_4SCN

Calculation

Standardization of NH_4SCN with standard $AgNO_3$

Strength of $AgNO_3$ = 0.0994N

Volume of $AgNO_3$ in ml	Initial burette reading	Final burette reading	NH_4 Volume of thiocyanate (NH_4SCN)	Mean volume in ml
10	5.2	15.4	10.2	
				10.225
10	15.4	25.65	10.25	

By, $V_1S_1 = V_2S_2$ formula

$$\text{Strength of } \overset{NH_4}{\wedge}\underset{(NH_4SCN)}{\text{thio}} = \frac{10 \times 0.0994}{10.225} = 0.0972(N)$$

Cl$^-$ analysis

Volume of the $AgNO_3$	Volume of solution sample	Initial burette reading	Final burette reading	NH_4 Volume of thiocyanate (NH_4SCN)	Mean volume
10	10	25.8	36.0	10.2	
					10.225
10	10	36.0	46.25	10.25	

$$\text{Excess AgNO}_3 = \frac{10.225 \times 0.0972}{0.0994} = 9.9986\text{ml}$$

$$\text{Consumed AgNO}_3 = 10 - 9.9986$$

$$= 0.0013 \text{ ml}$$

Now

$$1\text{ml } 1\text{N AgNO}_3 \equiv 0.03546 \text{ g Cl}^-$$

$$\therefore 0.0013 \text{ ml } 0.0994\text{N AgNO}_3 = 0.0000004582 \text{ g}$$

$$\therefore 10\text{ml of the sample solution contain} = 0.000004582\text{g Cl}^-$$

$$\therefore 100\text{ml of the sample solution contain} = 0.00004582 \text{ g Cl}^-$$

$$0.1405 \text{ g sample contain} = 0.00004582 \text{ g Cl}^-$$

$$\therefore 100 \text{ g sample contain} = \frac{0.00004582 \times 100}{0.1405}$$

$$= 0.033\%$$

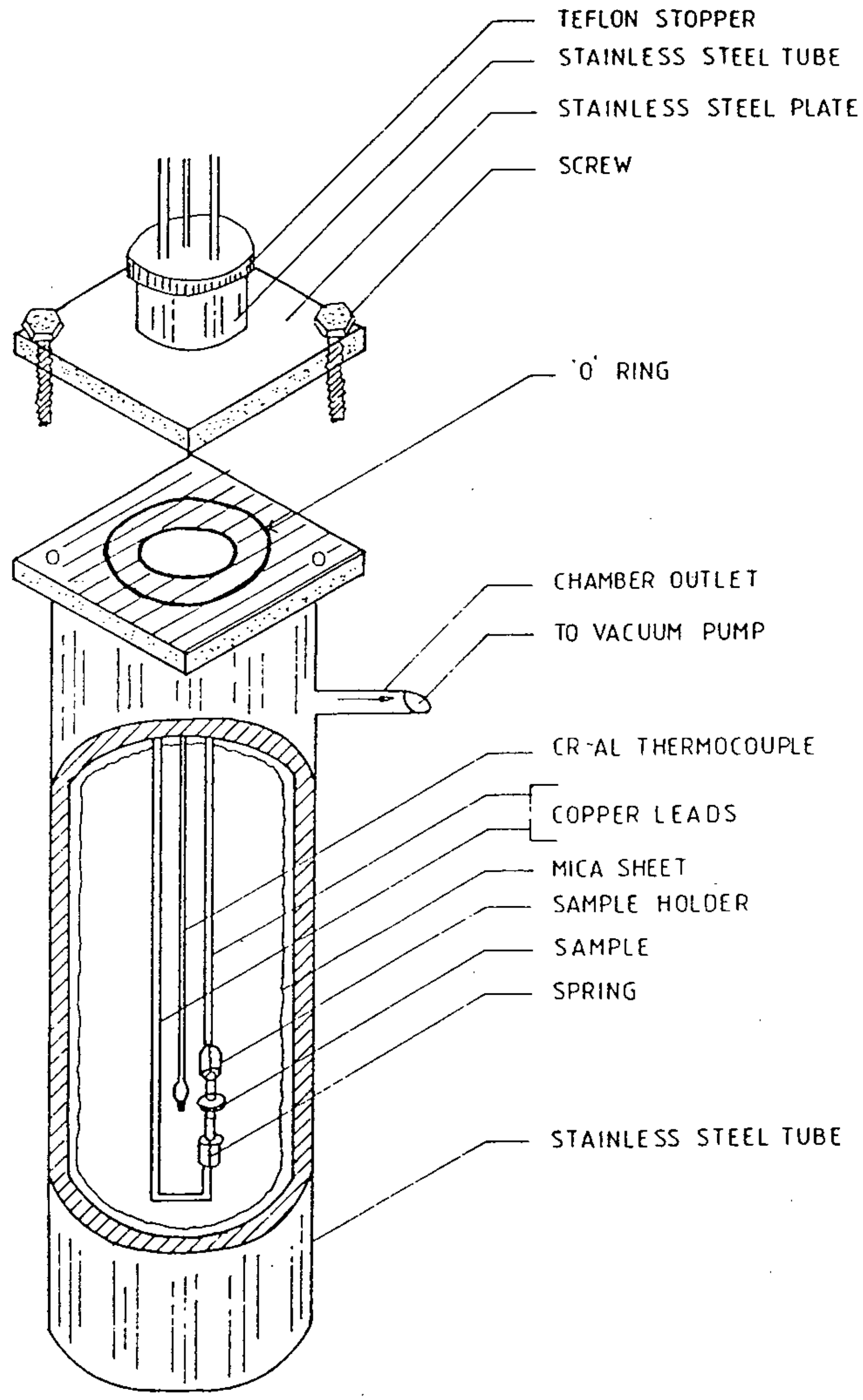

Fig. 4.1 The schematic diagram of the specimen chamber

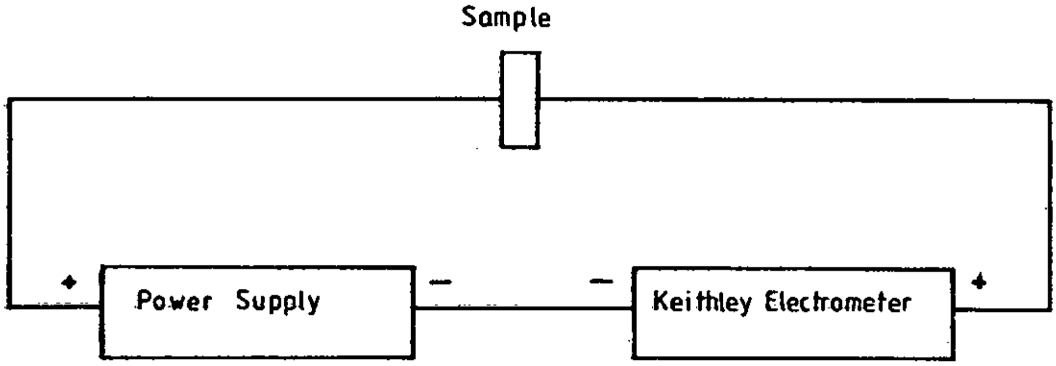

Figure 4.1: Block diagram for I-V measurement

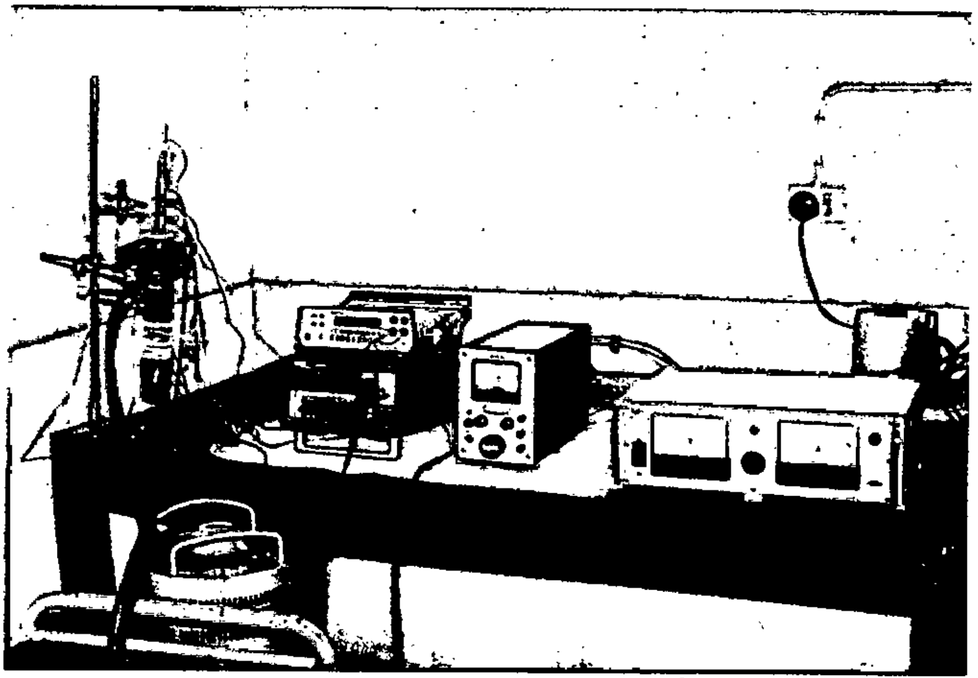

Plate 4.1 : Experimental setup of d.c. electrical measurement.

4.11 References

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4.2. Schiedt, U. Appl. Spectroscopy, 7, 75 (1953).

4.3. Cady, N. W., Piezoelectrics (MC Graw Hill, N. Y., 1966).

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Chapter 5 Results and discussions

5.1 Introduction

In this chapter the results of the grown crystals of pure KDP and KDP doped with KCl in different proportions are presented and discussed. The crystals are grown from 2 molar concentration of supersaturated solution by the slow evaporation process at room temperature. For proper characterization of these grown crystals extensive study viz growth rate, infra-red spectroscopic studies, X-ray diffraction analysis, d.c. electrical conductivity with temperature variation and a.c. breakdown voltage, melting points etc have been carried out and results are presented and discussed.

5.2 Crystal growth

Single crystals of pure KDP and crystals of KDP doped with KCl in different proportions are grown at room temperature by slow evaporation process from their saturated aqueous solutions as mentioned in the previous chapter.

Single crystals of pure KDP and KDP doped with KCl are found to be highly transparent, colourless and having good morphology. The crystal formation took about 12 days after the suspension of the seed crystals in the mother solution. The grown crystals are shown in plates 5.1 to 5.5. The crystals had well defined shape and increased size with dimensions about 26.44mm × 11.1mm × 4.80mm for pure KDP, 35.38mm × 14.48mm × 5.20mm for KDP:KCl = 95.:05, 46.00mm × 13.04mm × 6.20mm for KDP:KCl = 90:10, 43.26mm × 11.42mm × 4.72mm for KDP:KCl = 85:15, 43.08mm × 14.44mm × 6.08mm for KDP:KCl = 80:20 respectively.

5.3 Growth rate measurement

The seeds of KDP, and mixed KDP-KCl are suspended in solutions in a petry disc and then the growth was measured by a travelling microscope. Figure 5.1 shows the surface area (mm^4) versus time (day) for pure KDP and KDP doped with KCl crystals respectively. The growth rates of these crystals were found out from the slope of the curve which followed a parabolic relation, $A^2 = kt$, between the square of the area A and the time of growth t. Hence, K is called the growth rate constants. The growth rate constants of pure KDP and KDP doped with KCl in different ratios are found to be $31.1 \times 10^{-26} mm^4/sec$, $69.4 \times 10^{-26} mm^4/sec$, $108.5 \times 10^{-26} mm^4/sec$, $70.4 \times 10^{-26} mm^4/sec$, $118.7 \times 10^{-26} mm^4/sec$ respectively.

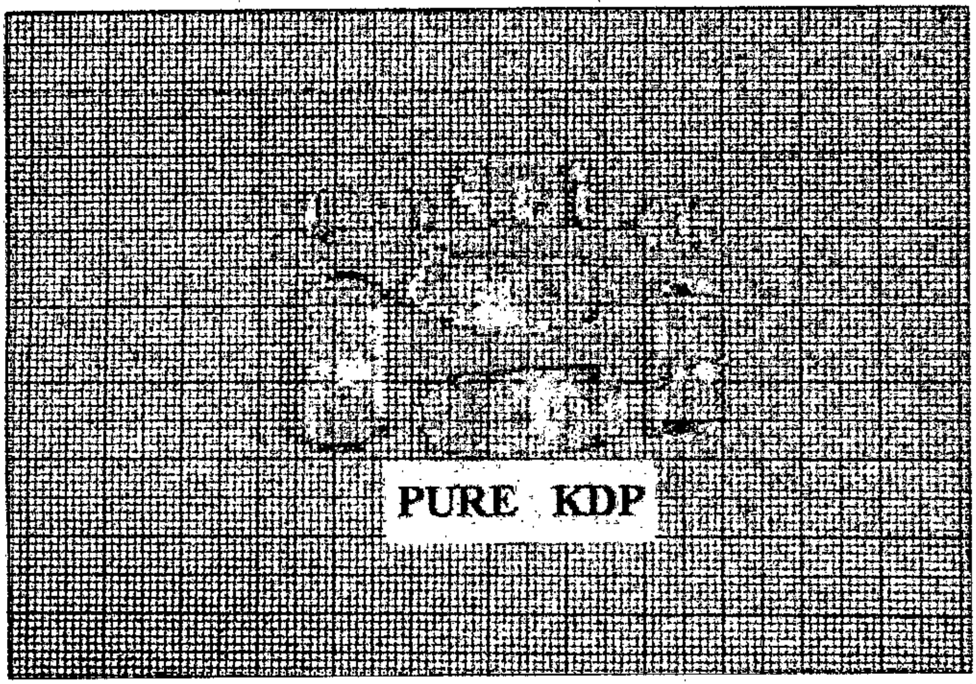


Plate 5.1: Photograph of pure KDP single crystals.

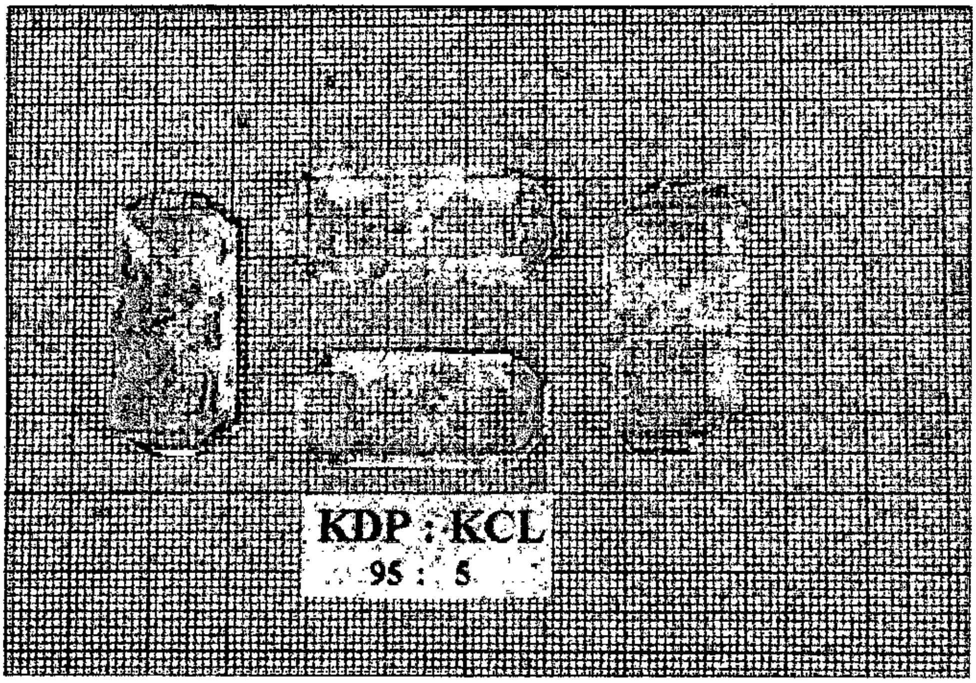


Plate 5.2: Photograph of KDP crystal doped with KCl in the ratio 95:5.

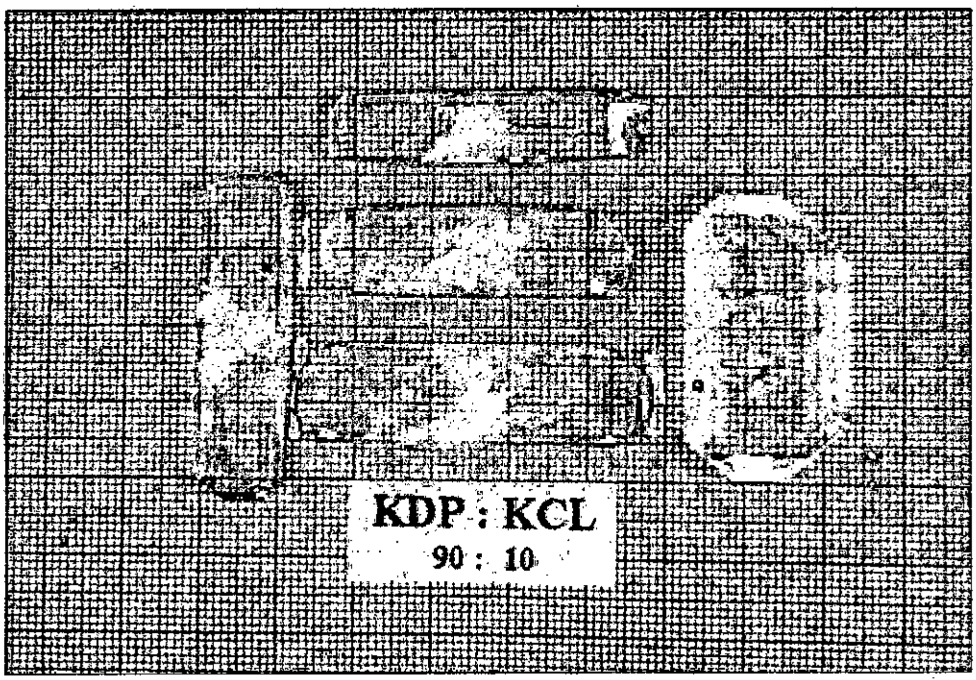


Plate 5.3: Photograph of KDP crystal doped with KCl in ratio 90:10

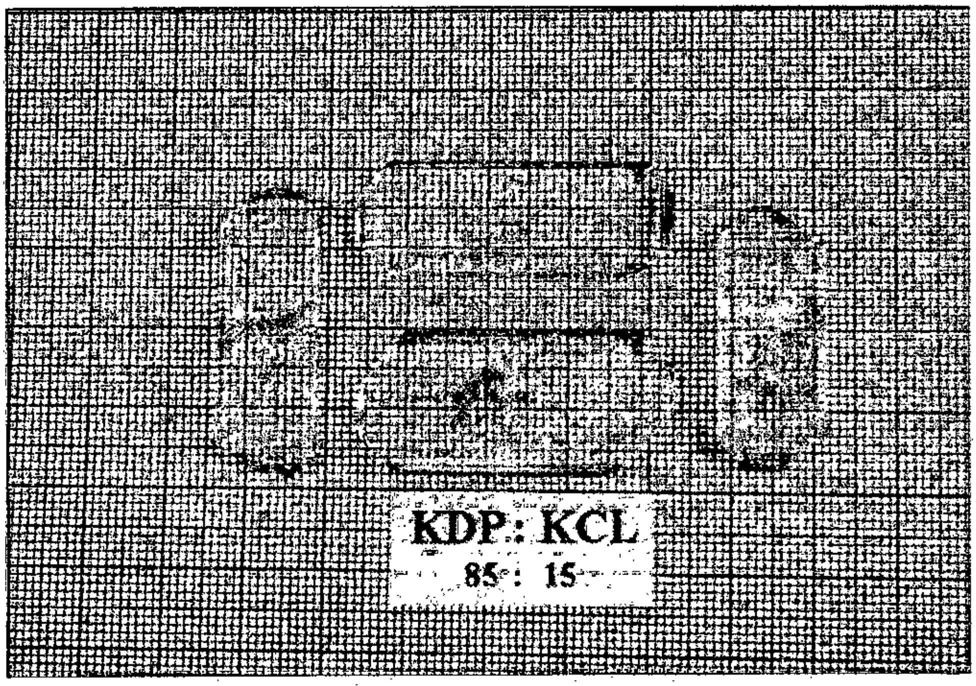


Plate 5.4: Photograph of KDP crystal doped with KCl in ratio 85:15.

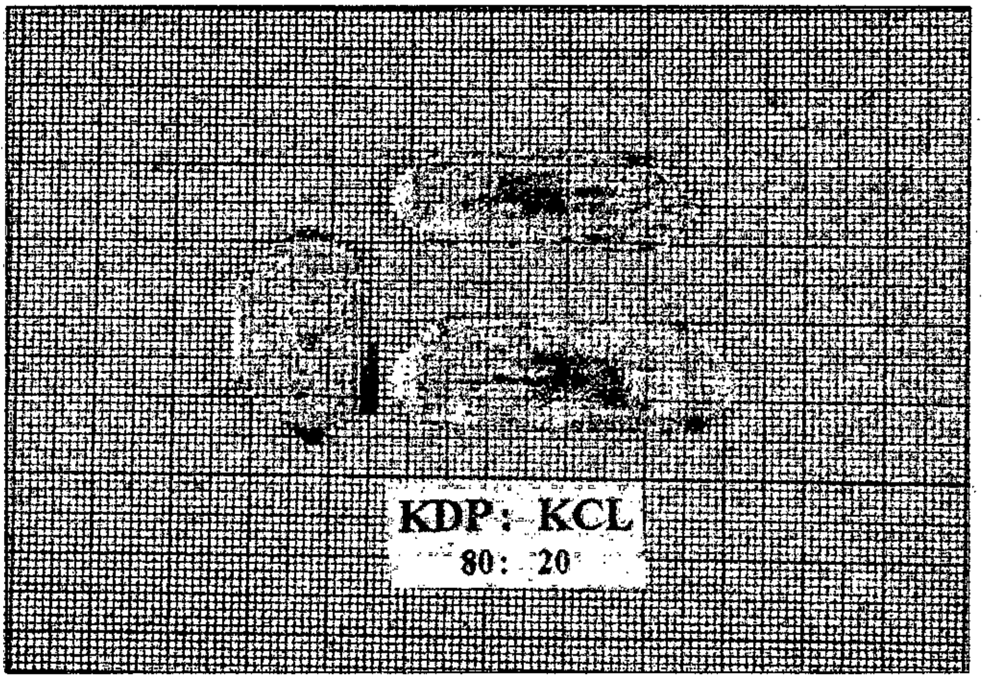


Plate 5.5: Photograph of KDP crystal doped with KCl in ratio 80:20.

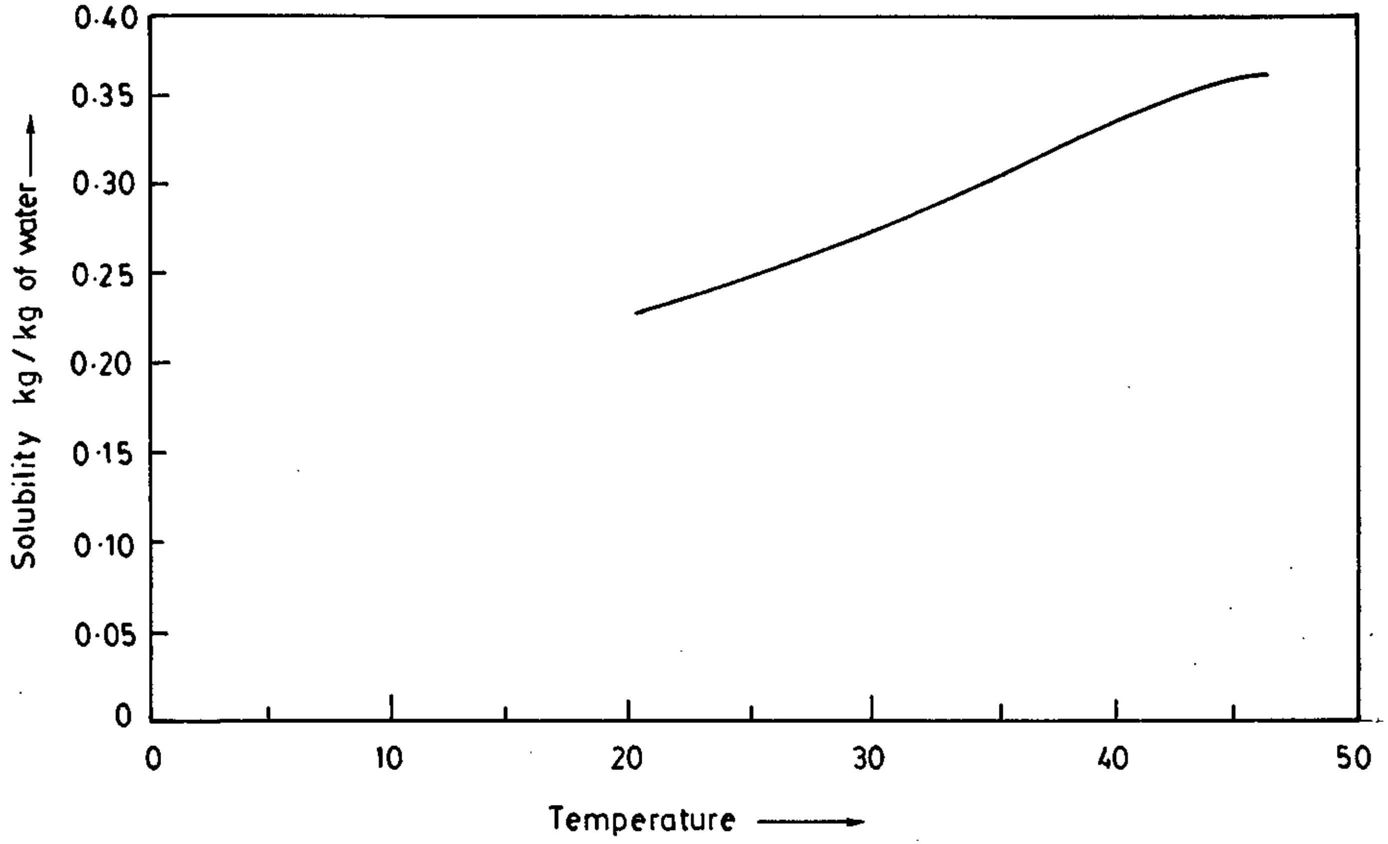


Figure 5.1: Solubility vs Temperature curve for KDP salts.

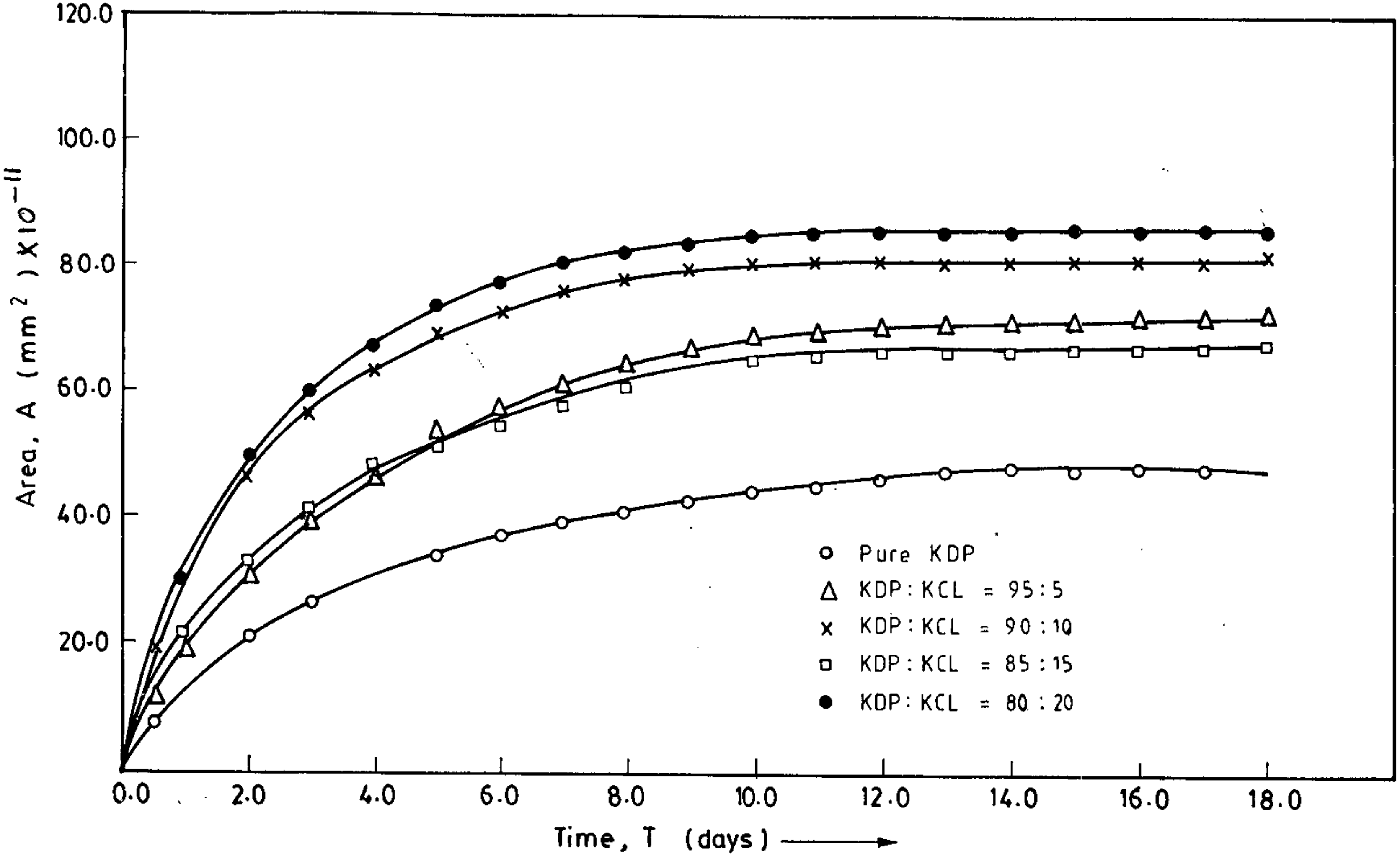


Figure 5.2 : Growth area versus time for pure KDP doped with KCl of various ratios.

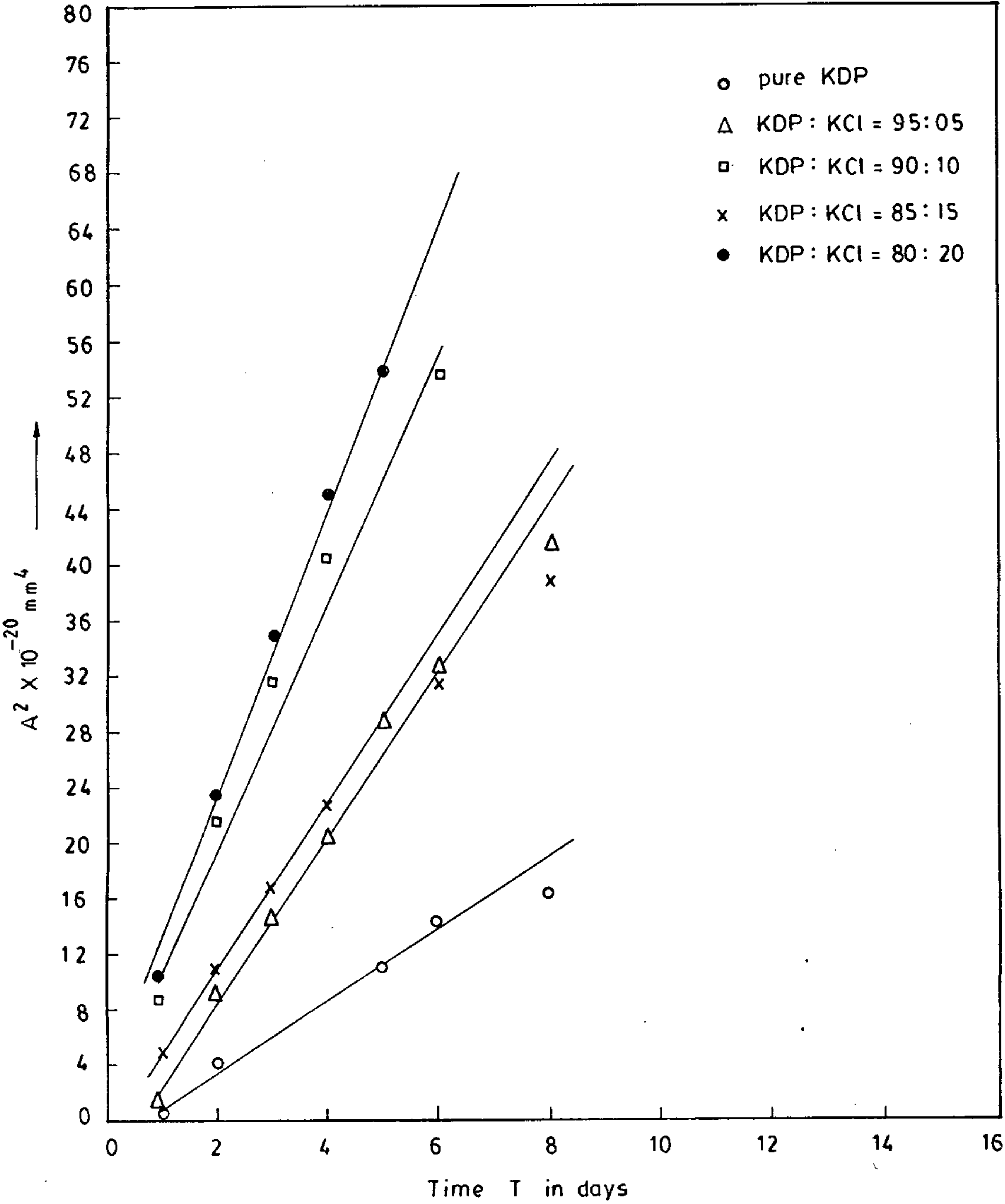


Figure 5.3: Square of growth area versus time for pure KDP and KDP doped with KCl.

Initially, the growth was fast upto one week and then became slower day by day and there after about two weeks it became extremely slow. The figure 5.2 clearly demonstrate that after the formation of seeds, the growth is quite fast for few days and then get slowed-down. The growth becomes insignificantly slow after 2 weeks which has been demonstrated in the figures by the flattened portion of area versus time curve.

5.5 Result of infrared spectroscopy

In our present work Infrared spectra is studied by means of transmittance measurement. The infrared spectra of all of the samples are recorded at room temperature in the wave number region 400 to 4000 cm^{-1}. The infrared spectrums for pure KDP and KDP doped with KCl crystal are presented in figures (5.4 to 5.8). The probable assignment for the respective wave numbers are listed in table(5.1) The wave number about 540 cm^{-1} and 410cm^{-1} corresponds closely to that recorded for a KDP solution. The fact is that it occurs considerably below the ν_1 vibration of the PO_4 ion is probably due to the loosening of the PO_4 structure by hydrogen bonds which, however, do not destroy the tetrahedral symmetry. The PO_4 ion thus seems to behave dynamically in most respects as an idividual having tetrahedral symmetry perturbed by an environment having perhaps the symmetry S_4 or probably C_{2v} or C_2. The two intense bands on the short-wave side of the ν_3 vibration (1280cm^{-1} - 1480cm^{-1} for KDP) appear to be combination bands of the ν_3 frequency with lattice vibrations. The band at 1587 cm^{-1} might be a P-O-H bending vibration suggested [1] by La Lau. La Lau reports a broad O-H. O absorption band at (2793 cm^{-1}) for KDP. This we did not observe in our reflection spectrum, but we recorded about similar band at 2460cm^{-1}

and 1825 cm^{-1} for this crystal and similar bands for the other KCl doped KDP crystal. Bands in this neighborhood were recorded by Rundle and Parasol [2] and Lard Merrifield [3]. These bands are weak in intensity and apparently they are less resolved at the low temperature in constrast with the behaviour of the other bands. In KDP : KCl = 95:05 first transmittance is observed at 435 cm^{-1} and 420 cm^{-1}. This may happened due to presence of chlorine concentration. The major transmittance occurres in the transmittance band at 2000 cm^{-1} - 1500 cm^{-1}. In KDP : KCl = 90:10, a good transmittance is found to occur in the band 540 cm^{-1} - 405 cm^{-1}.

Another clear transmittance occures at 1290 cm^{-1} band. There is also a weak transmittance observed at 1176 cm^{-1}, 1678 cm^{-1}, 1997 cm^{-1}, 2425 cm^{-1} and 3425 cm^{-1} respectively.

In the crystal KDP:KCl = 85:15 a noisable transmittance is observed at 350 cm^{-1}. Hence two large shape transmittance are also found between the bands 1266 cm^{-1} - 700 cm^{-1} and 4000 cm^{-1} - 1260 cm^{-1}.

In the crystal of KDP:KCl = 80:20 a transmittance band is found at 404cm^{-1} - 550cm^{-1} band. A noisable large band is found in the region 980cm^{-1} - 1200cm^{-1}. A smoth transmittance band is also found at 1575 cm^{-1}, 1655 cm^{-1}, 2355 cm^{-1} and 2495 cm^{-1} respectively.

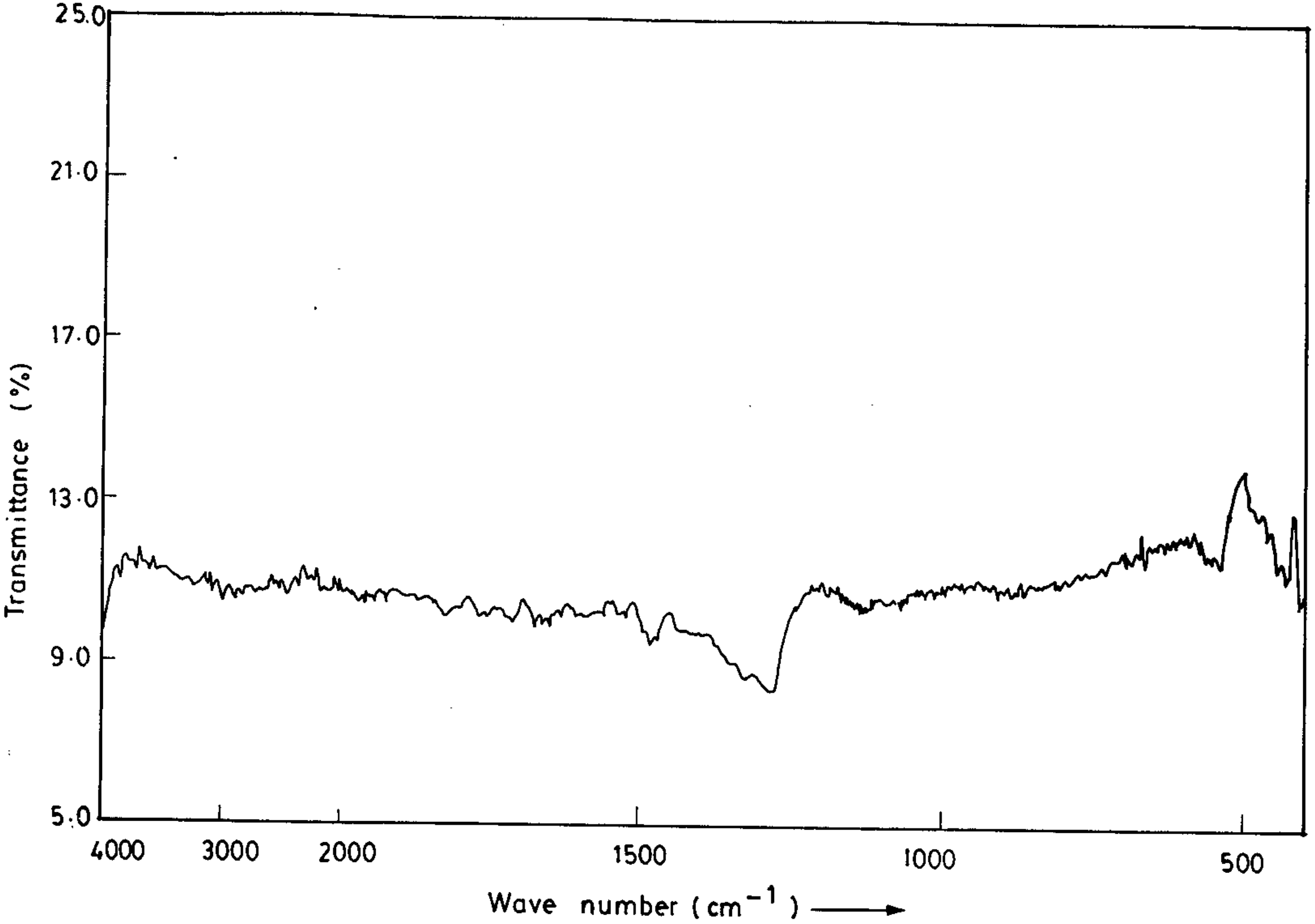


Figure 5.4: Infra red spectrum for pure KDP crystal.

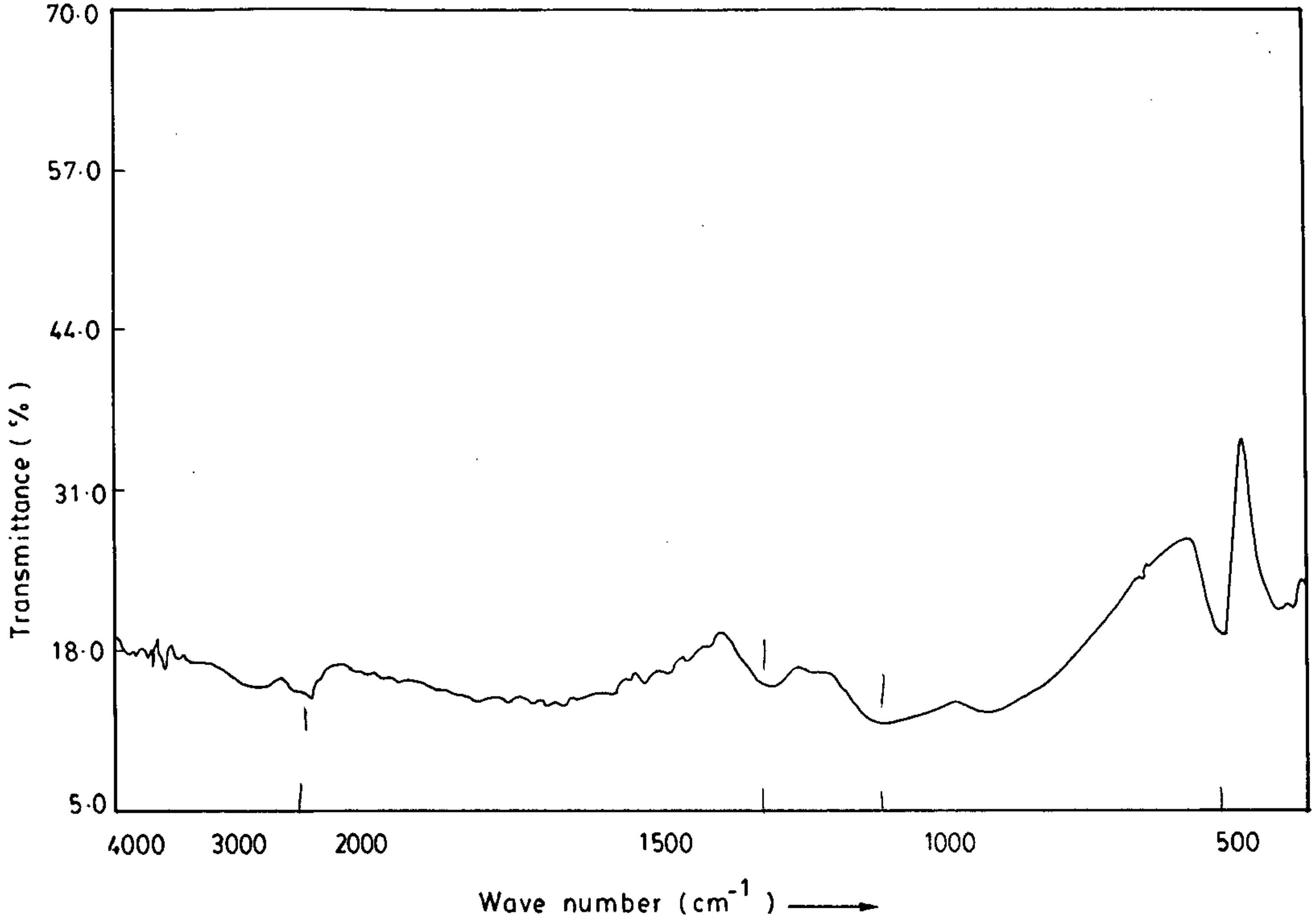


Figure 5·5: Infra red spectrum for mixed KDP and KCl crystal in ratio 95:05 .

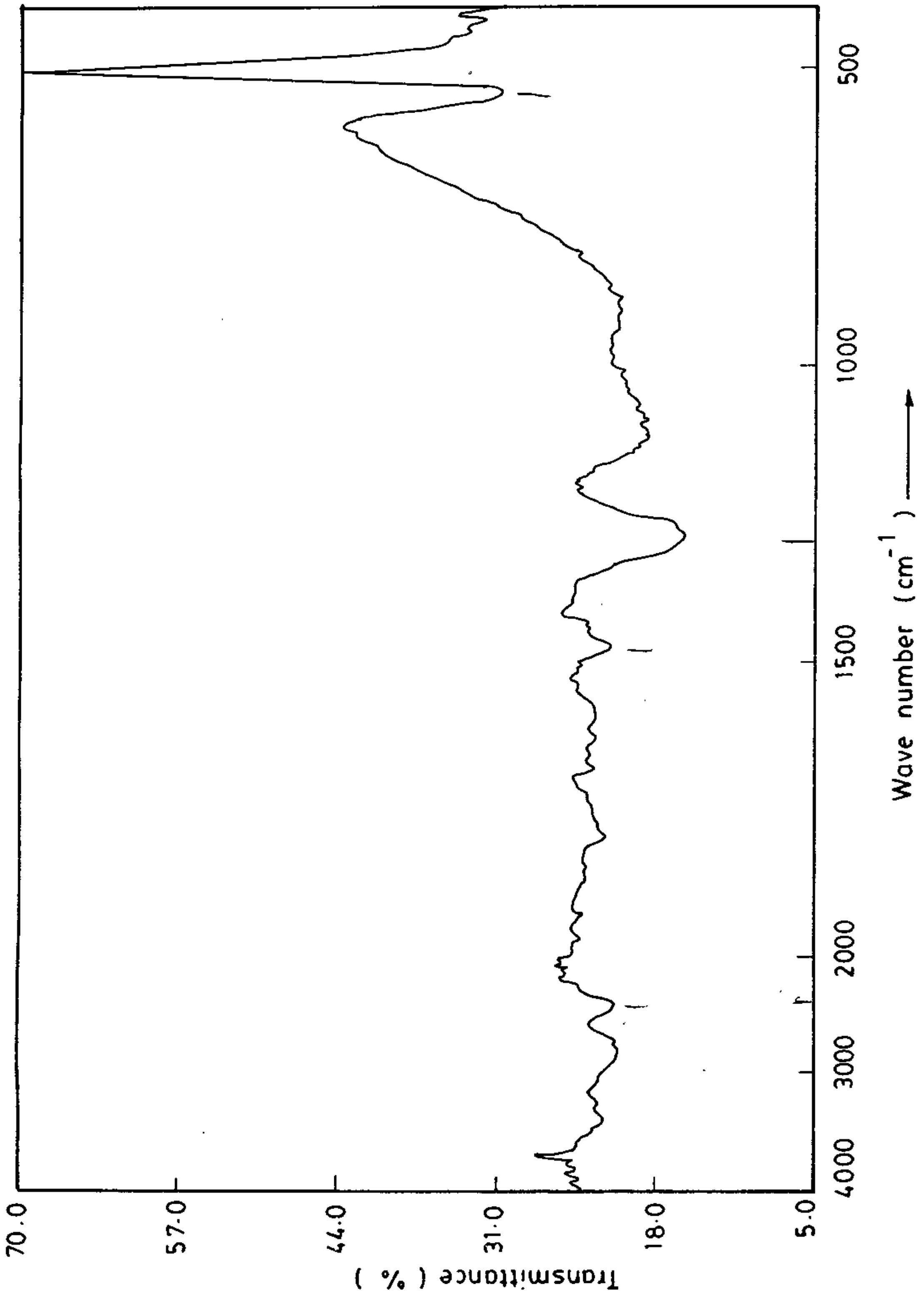


Figure 5.6: Infra red spectrum for mixed KDP and KCl crystal in ratio 90:10

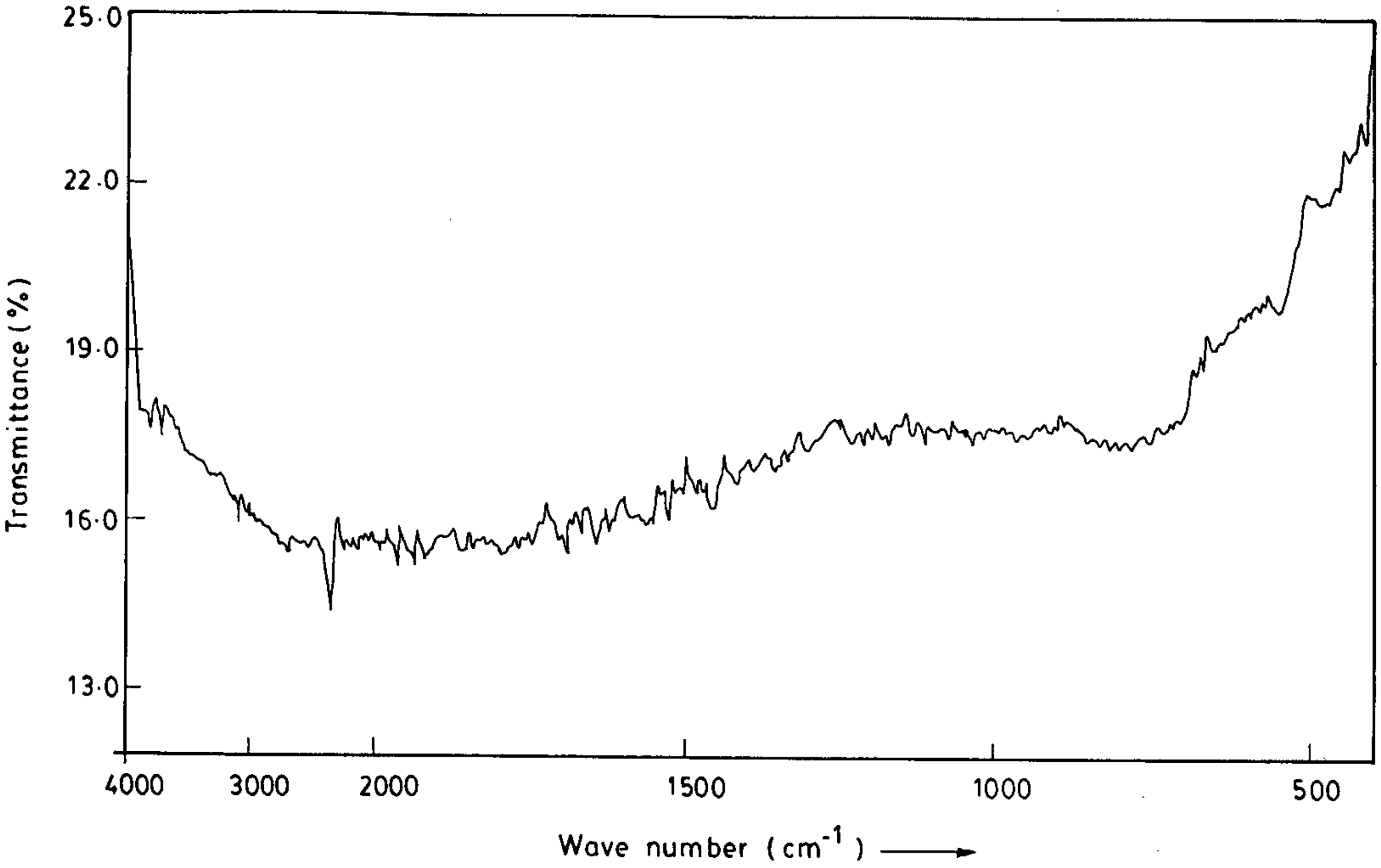


Figure 5·7: Infra red spectrum for mixed KDP and KCl crystal in ratio 85:15

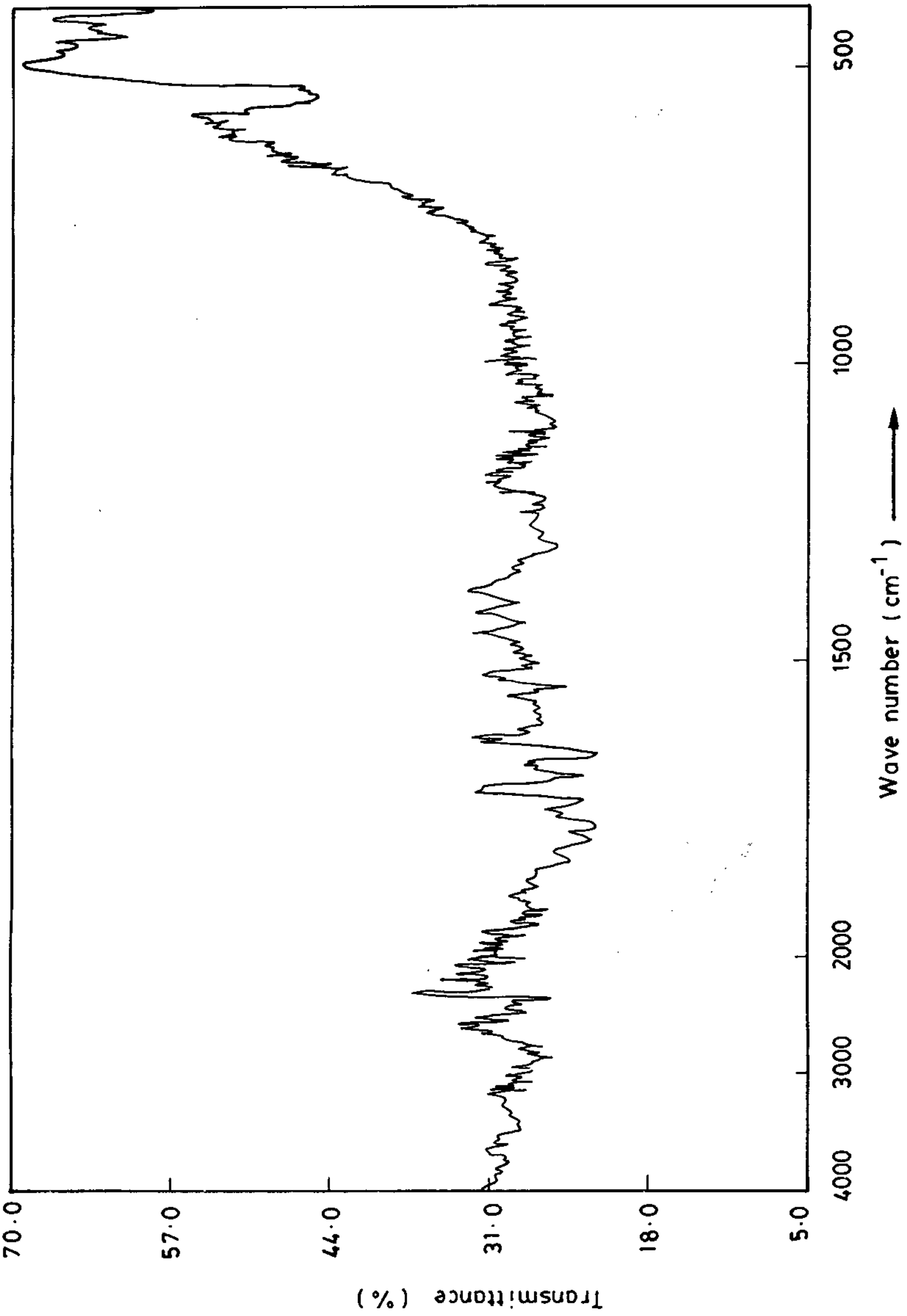


Figure 5.8 : Infra red spectrum for mixed KDP and KCl crystal in ratio 80 : 20

5.5 X-ray diffraction analysis

X-ray diffraction pattern for the powdered samples of grown pure KDP crystals and KDP doped with KCl in different proportions are presented in figures.5.9 to 5.13. The results of the X-ray powder diffraction analysis are presented in Table 7.2-7.6. The lattice parameters are determined and the values are given as a = b = 7.42Å and c = 7.30Å for pure KDP. The values of c/a for pure KDP and KDP doped with KCl in different portions (viz 95:05, 90:10, 85:15 and 80:20 etc) are 0.983, 0.978, 0.981, 0.987, 0.983. respectively. These values are more or less same and are in good agreement with the ASTM standard values.

5.6 I-V characteristics

There is much influence of contacts on the results of electrical measurements on any material. For this reason it is important to perform current voltage (I-V) measurements to explore the behaviour of the contact before any further study.

Figures 5.14 to 1.18 show that I-V characteristic curve for pure KDP and KDP doped with KCl in different proportions measured at room temperature. It is observed that current increases non-linearly with the voltage used in this measurements.

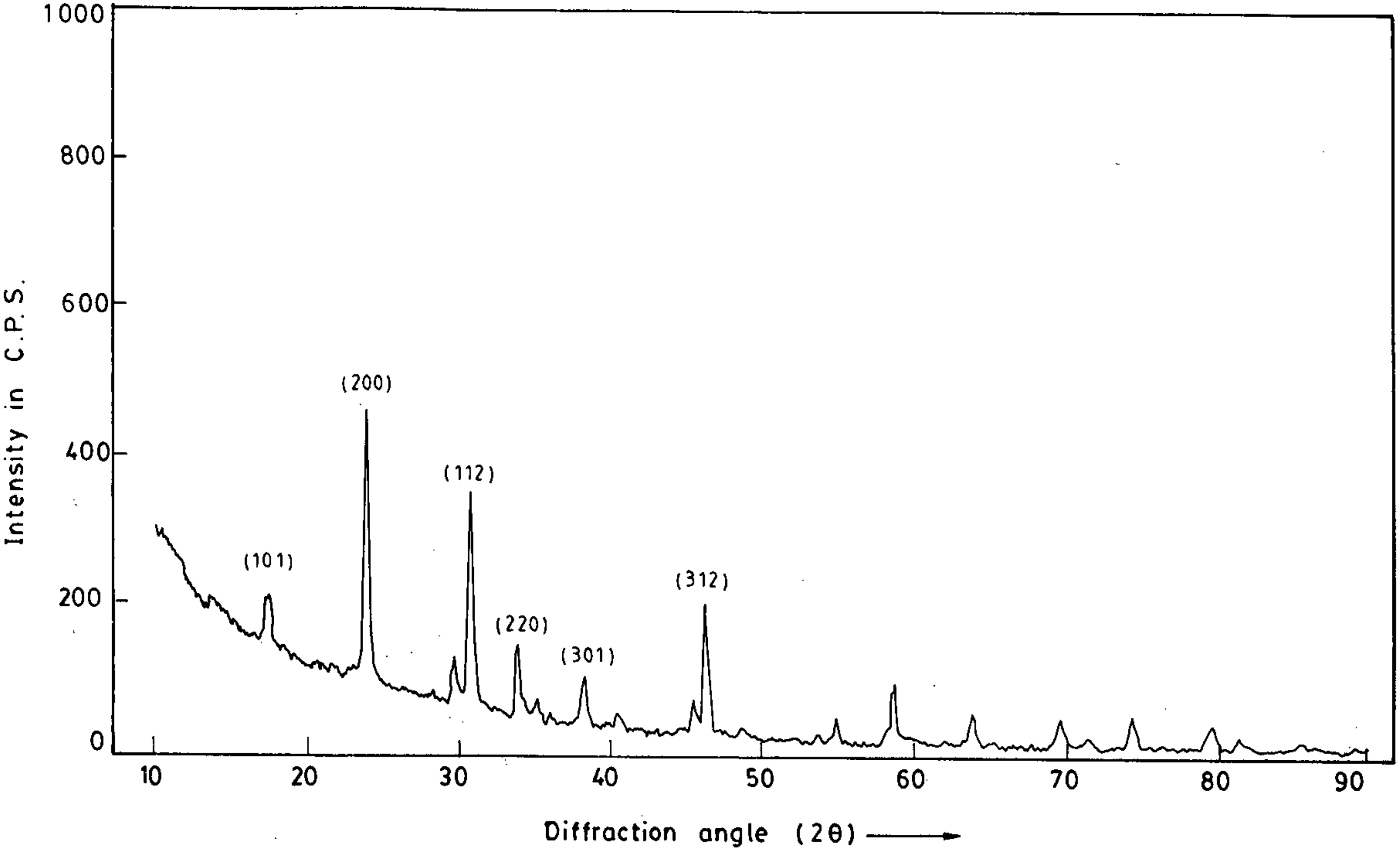


Figure 5.9 : X-ray diffractogram for pure KDP crystal

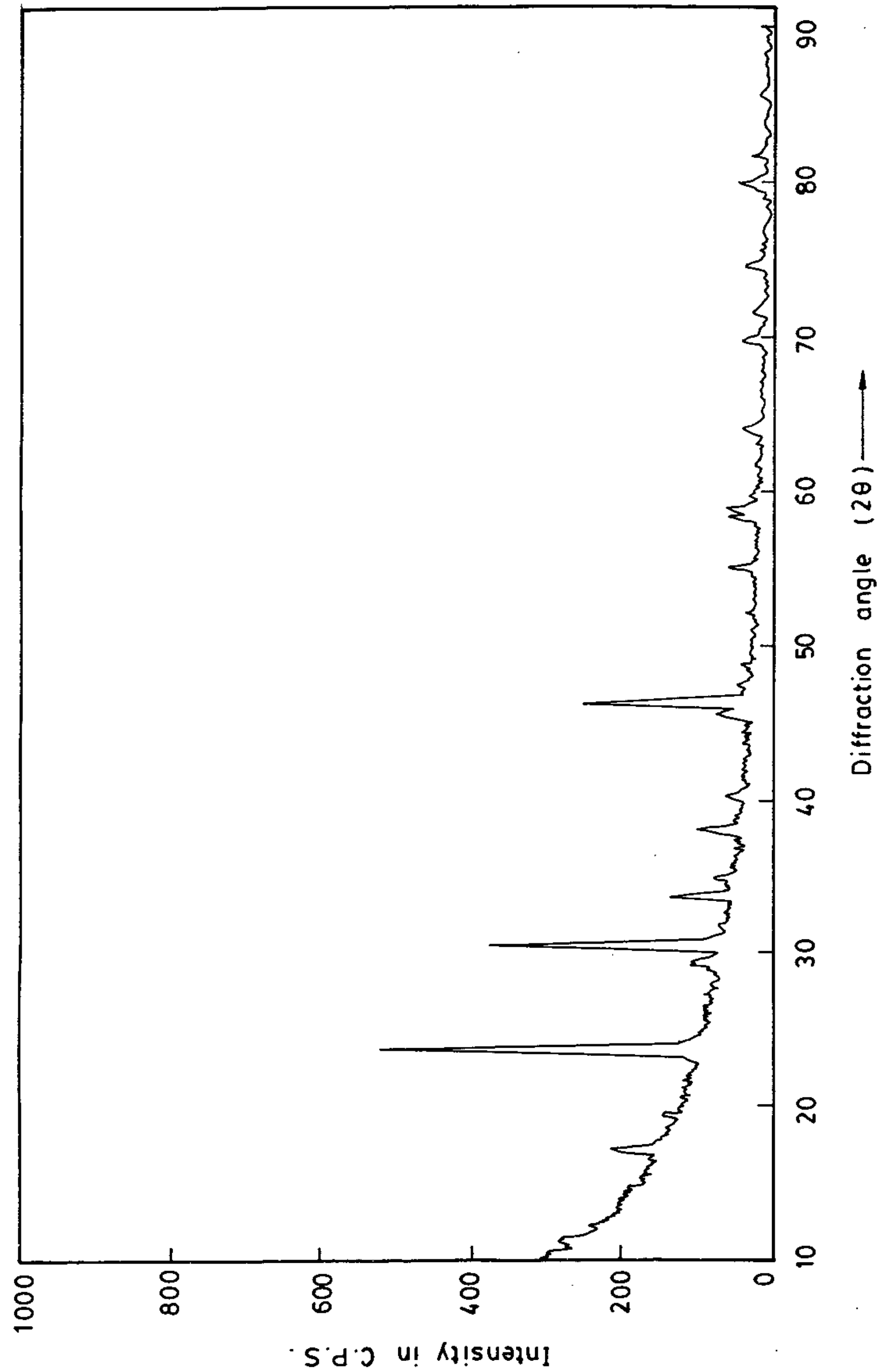


Figure 5.10 X-ray diffractogram for mixed 95% KDP + 5% KCl crystal.

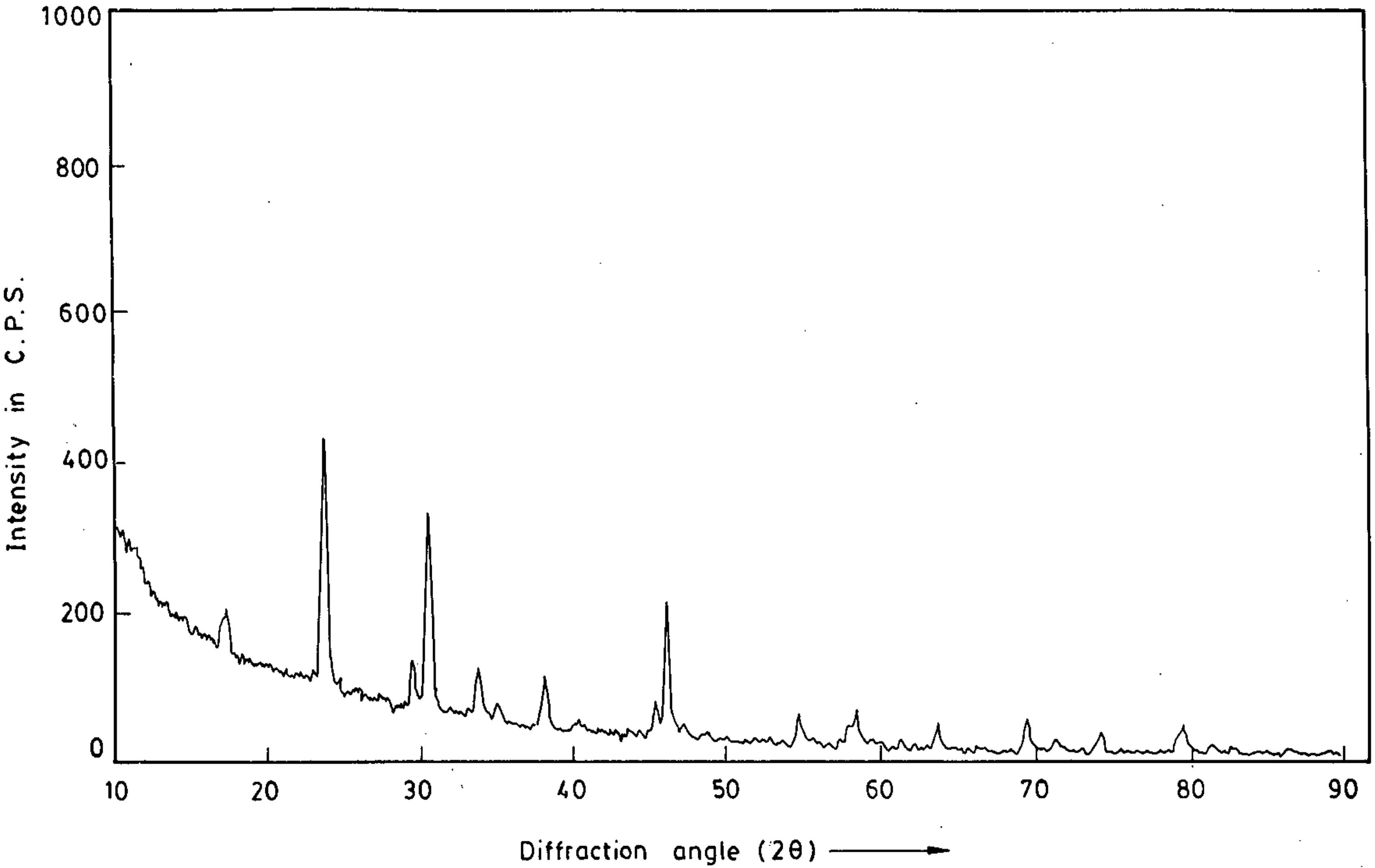


Figure 5.11: X-ray diffractogram for mixed 90% KDP + 10% KCl crystal

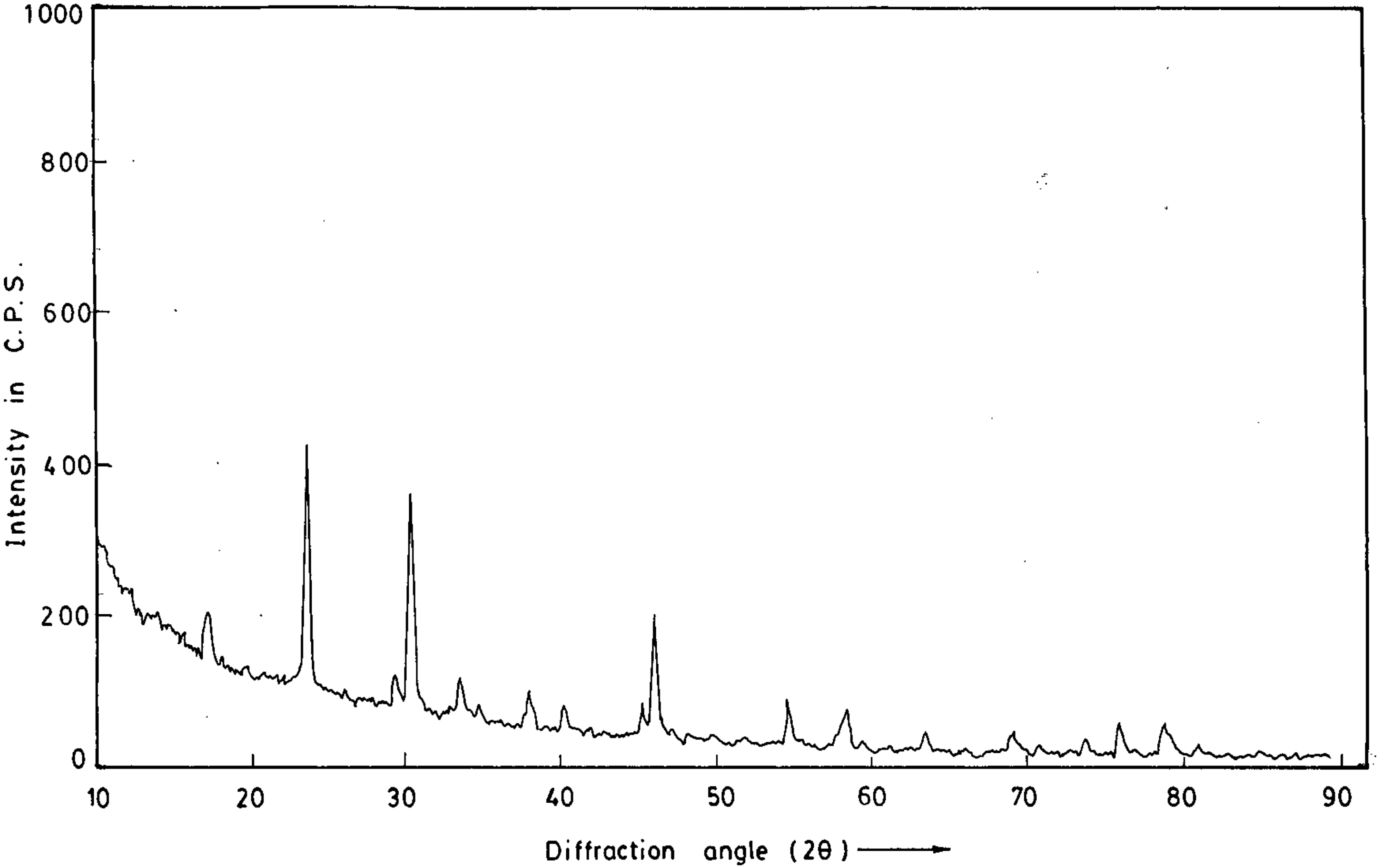


Figure 5.12: X-ray diffractogram for mixed 85 % KDP + 15 % KCl crystal.

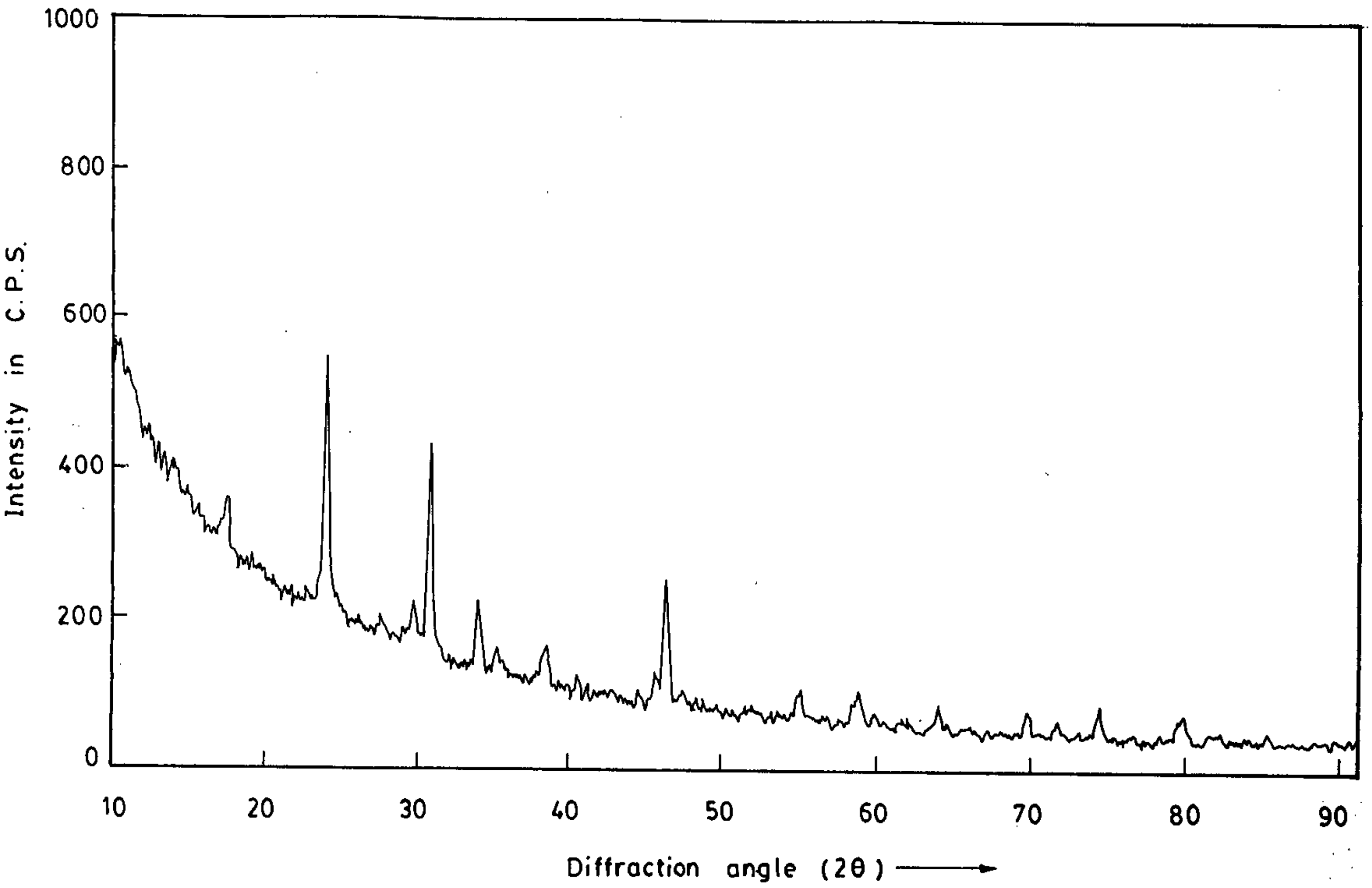


Figure 5.13: X-ray diffractogram for mixed 80% KDP + 20% KCl crystal

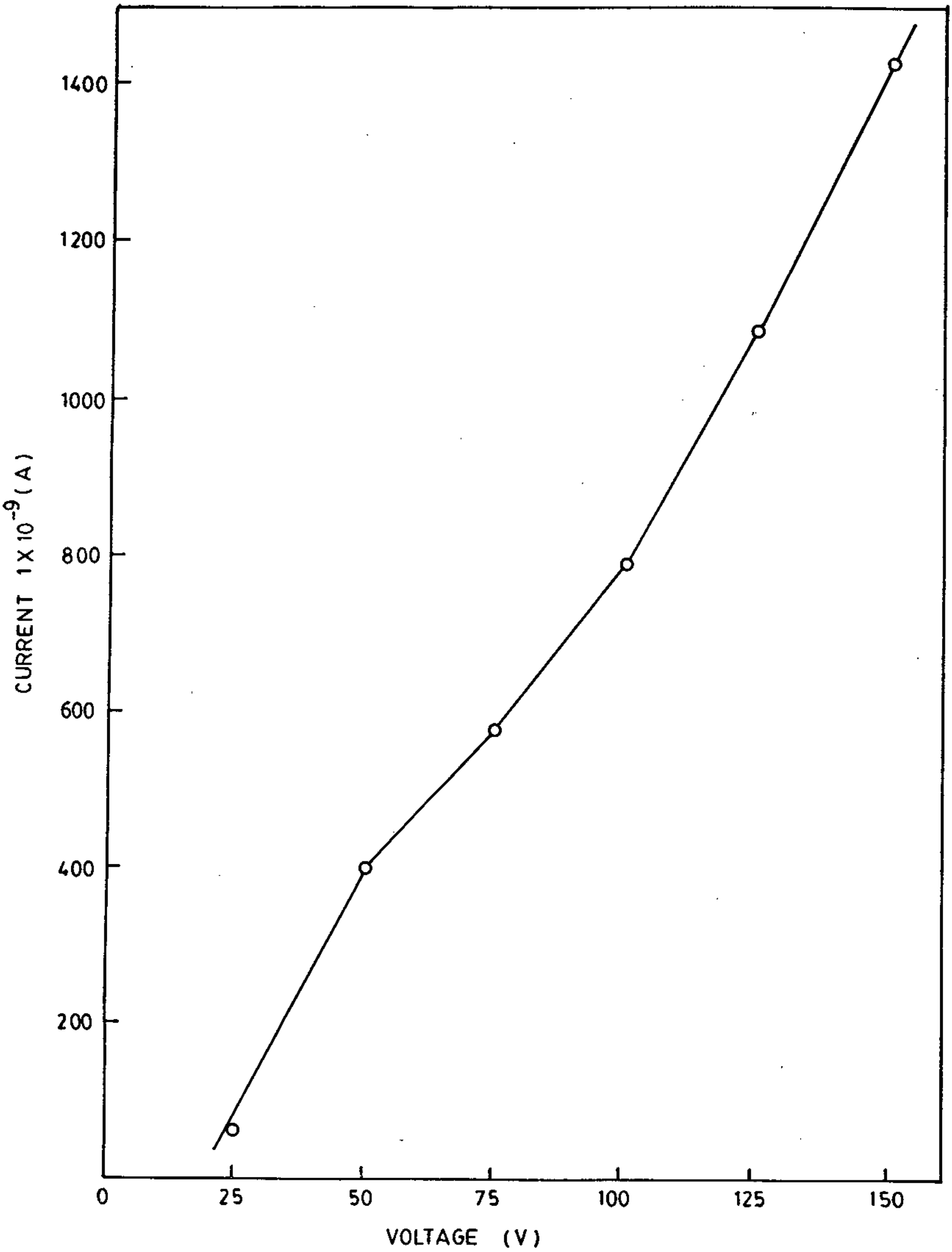


Figure 5.14 : I - V characteristics curve for pure KDP single crystals

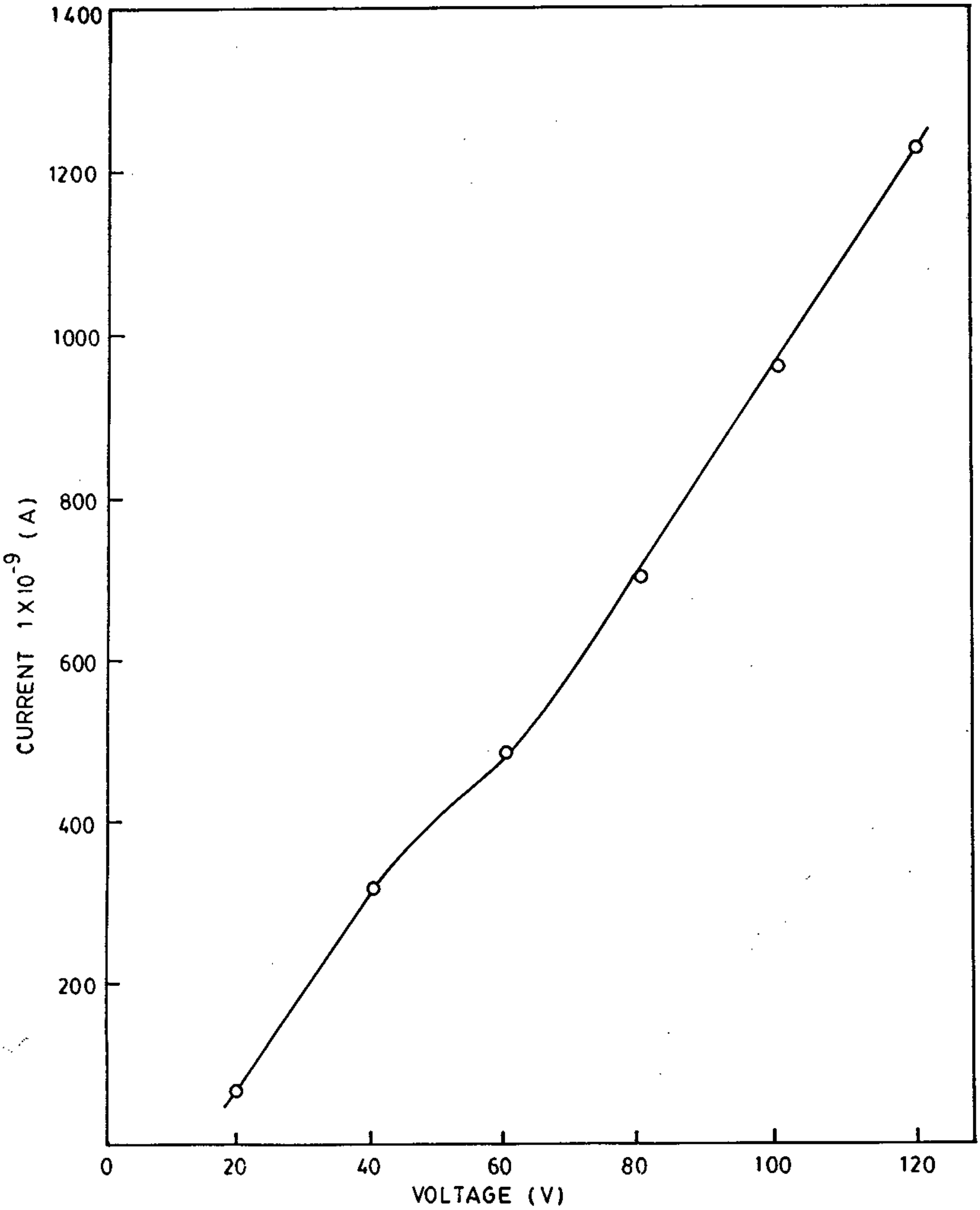


Figure 5.15: I-V characteristic curve for KDP : KCl = 95 : 05

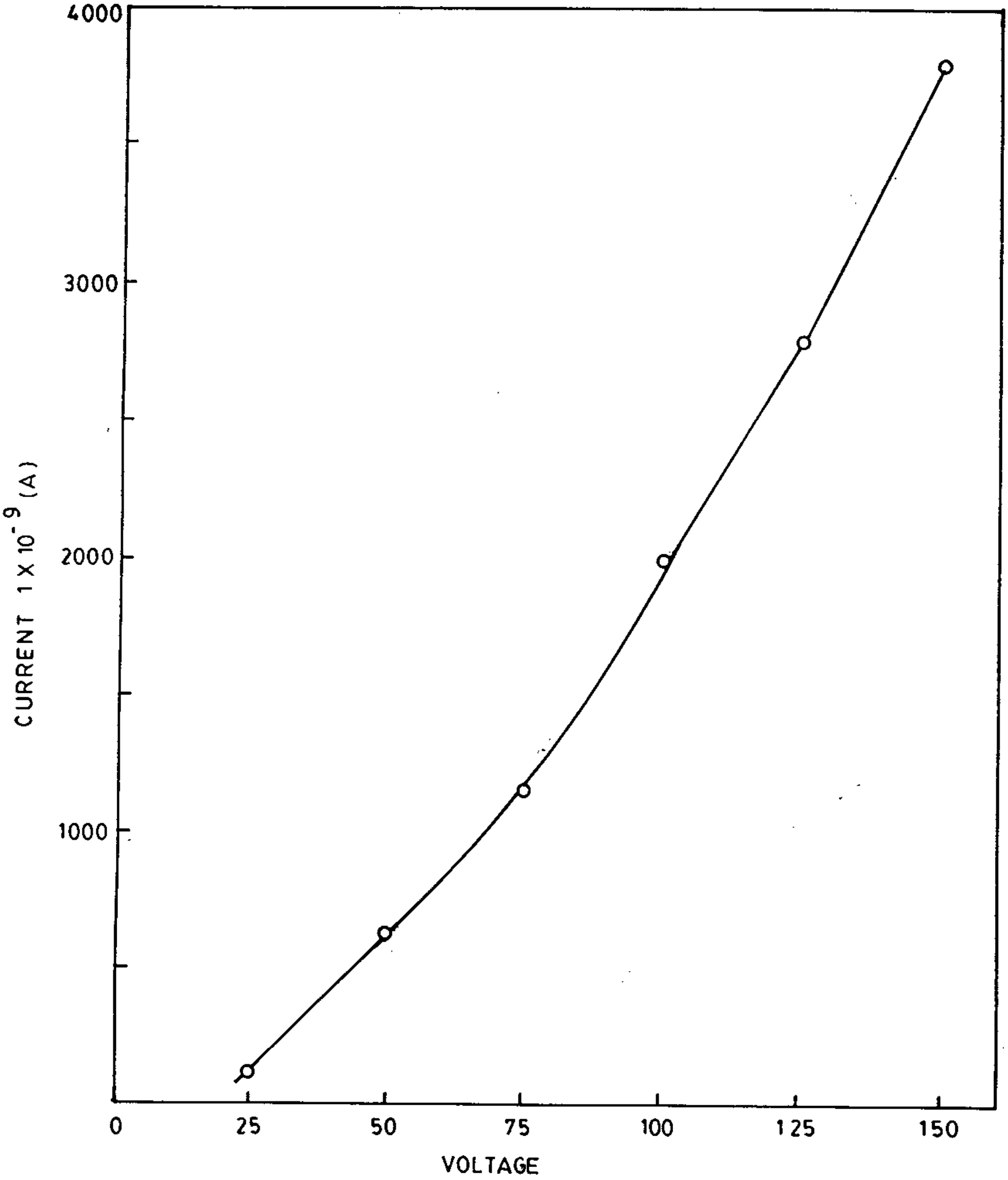


Figure 5.16: I-V characteristic curve for KDP : KCl = 90:10

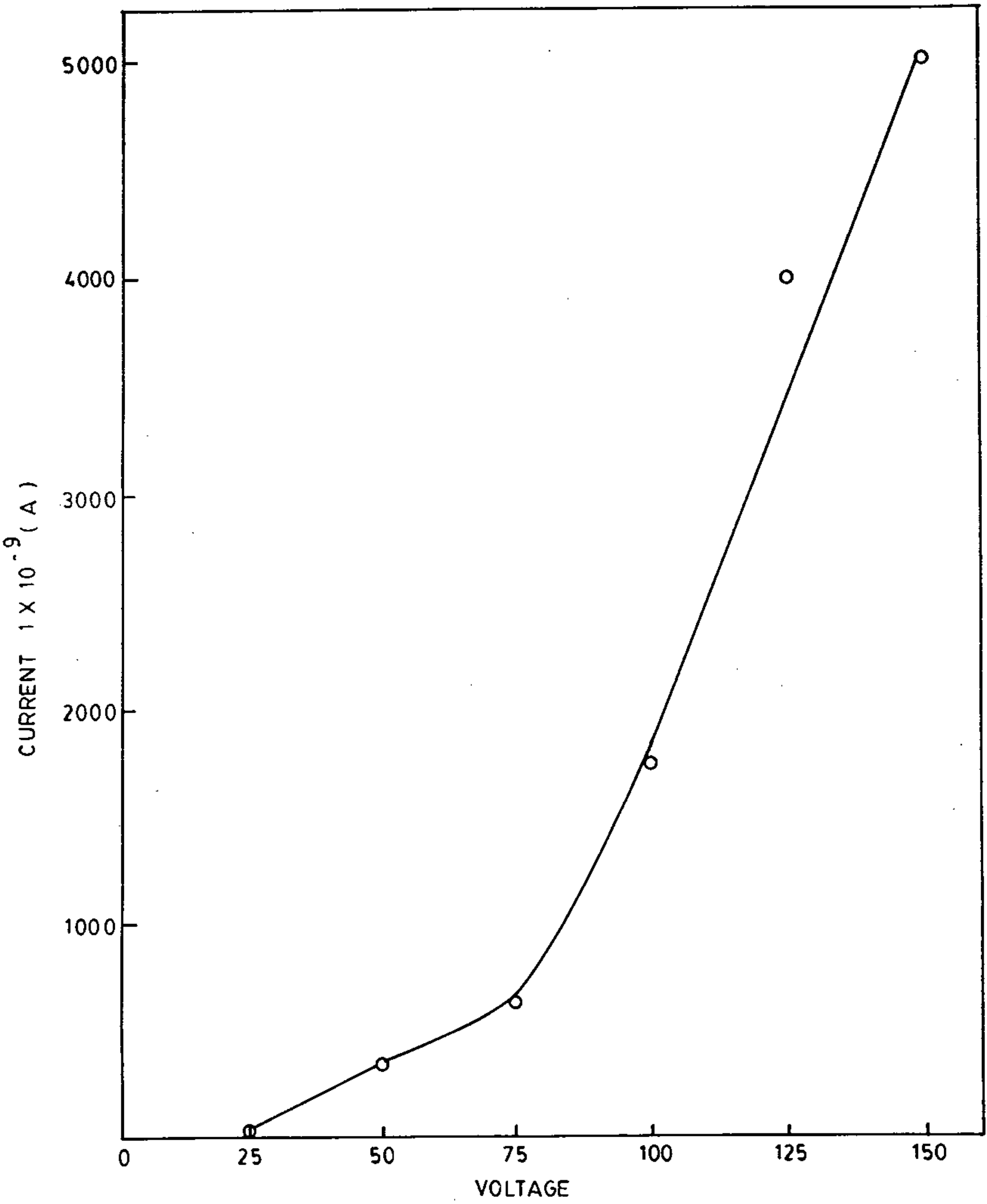


Figure 5.17: I- V characteristic curve for KDP : KCl = 85 :15

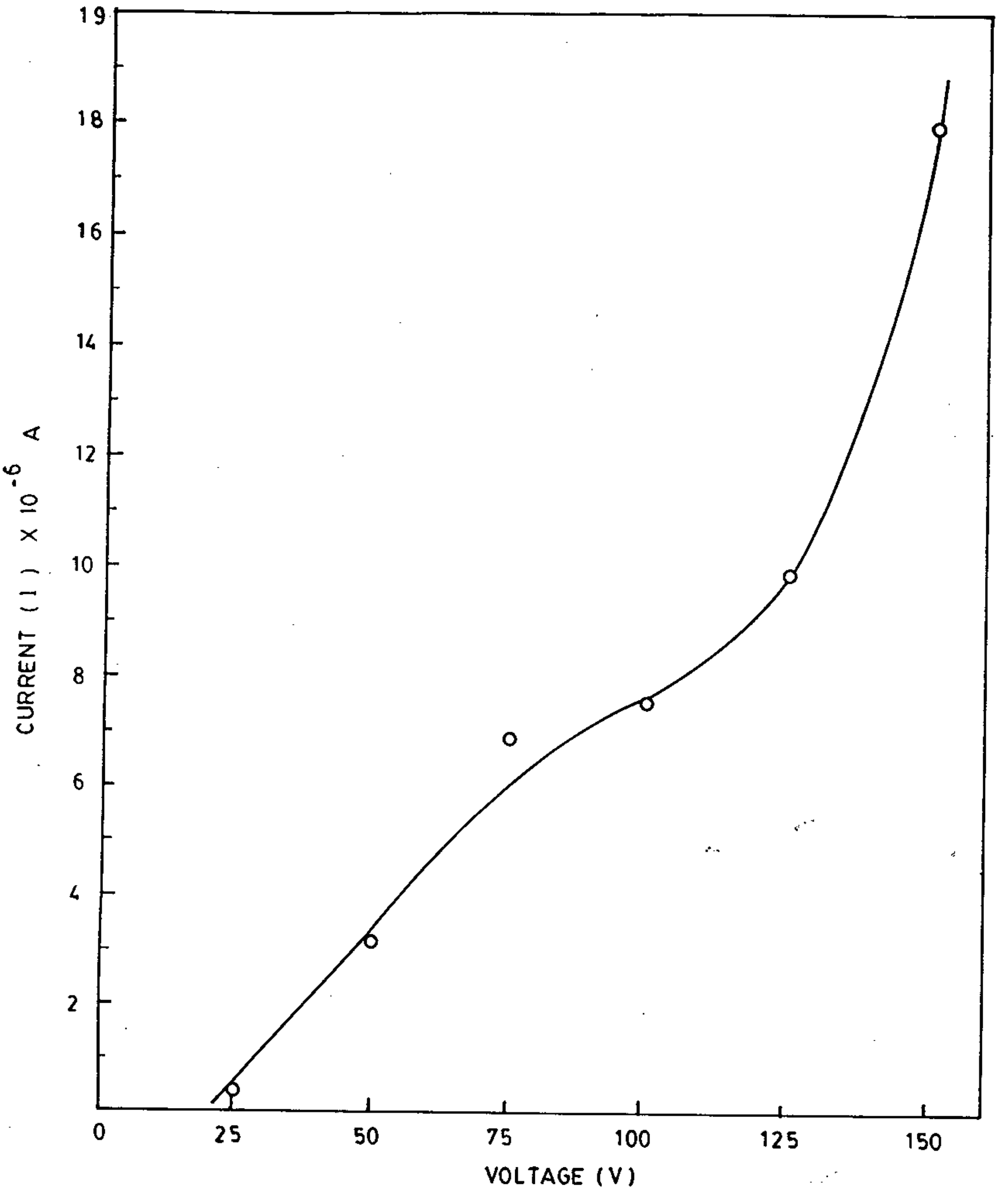


Figure 5.18: I-V characteristic curve for KDP : KCl = 80:20

5.7 Results of D. C. conductivity

The D.C. conductivity studies are made in the temperature range 300-500K on the samples cut from the crystals grown. The crystals are ground and polished to the suitable size. The crystal surfaces are coated with silver point to give good electrical contact between the electrodes and the crystal surfaces. The current in the samples are measured using Keithley electrometer by keeping the samples between two flat electrodes which in turn are kept in a furnace. The sample and the electrodes, the lead wires etc. are all insulated well to avoid stray current that may pickup. The field is applied perpendicular to c-axis.

The Figure 5.19 to 5.23 show the plot of log σ against temperature for KDP, crystals and KDP doped with KCl in different proportions. The results obtained are as follows (i) There are two knees in the conductivity plots one at about 70°C and the second one at about 165°C.

Within a broad range of temperatures the graph showing the dependence of logarithm of conductivity σ on the value of the reciprocal absolute temperature T consisting of two rectilinear portions in the Figure (5.19, 5.21- 5.23) with different angles of inclination to the x-axis.

In the low temperature region i.e.upto 150°Cconductivity increases due to the presence of weakly attached impurities and vacancies in a crystal lattice. At the higher temperature, fracture is observed (5.21, 5.23). At the temperature above the point of fracture (A) conductivity is caused mainly for the intrinsic defects.

The results reveal that the electrical conductivity increases with the increase of doping concentration. This may be attributed to the increase of natural impurities in the supersaturated solution. The conductivity in KDP is due to the migration of protons through L and D defects in the H_2PO_4 sub-lattice. The electrical conduction in KDP crystals is found to be protonic [4.5]. The increase of conductivity values of KDP crystal when doped with chloride impurity can be explained by considering the replacement of $(H_2PO_4)^-$ ions by Cl^- ions. This is in conformity with the result obtained by the previous workers in the case of doped KDP crystal [6.8].

Values of conductivity were unchanged when the current flow through the sample was reversed, provided at least 20 min were allowed for the polarization effect decay.

5.8 Breakdown strength of dielectric

The KDP crystals have high resistivity. These crystals are required to be subjected to high voltages for its electro-optical studies.It is therefore of importance to measure the dielectric breakdown strength. Defect free portions of the harvested crystals are placed in between the two electrode and A.C. voltage was applied with the increased voltage. The corresponding current is noted to get increased. In general if the voltage applied to an insulation is progressively increased a breakdown of the insulation will finally take place. A strongly conductive breakdown channel formed during a breakdown practically produces a short circuit between the electrodes. The maximum voltage V_{br} applied to an insulation at the moment of breakdown is known as the breakdown voltage of insulation. Voltage-ampere characteristic of insulation is illustrated by the graph in Figure 5.24a to 5.24b. Point B on the graph for which $dI/dV \rightarrow \propto$ corresponds to the moment of breakdown. Experiment shows that the breakdown voltage of insulation depends on its thickness (i.e., on the distance between the electrodes) the thicker the layer of a given electrical insulating material, the higher is its breakdown voltage. Breakdown voltages are found 4.68 kV/cm, 4.42 kV/cm, 4.03kV/cm, 4.66kV/cm and 3.90kV/cm for pure KDP and KDP doped with KCl in different proportions (viz 95:5, 90:5, 85:15, 80:20) respectively. It reveals that insulation property of the grown crystals decreases with increasing the percentage of KCl.

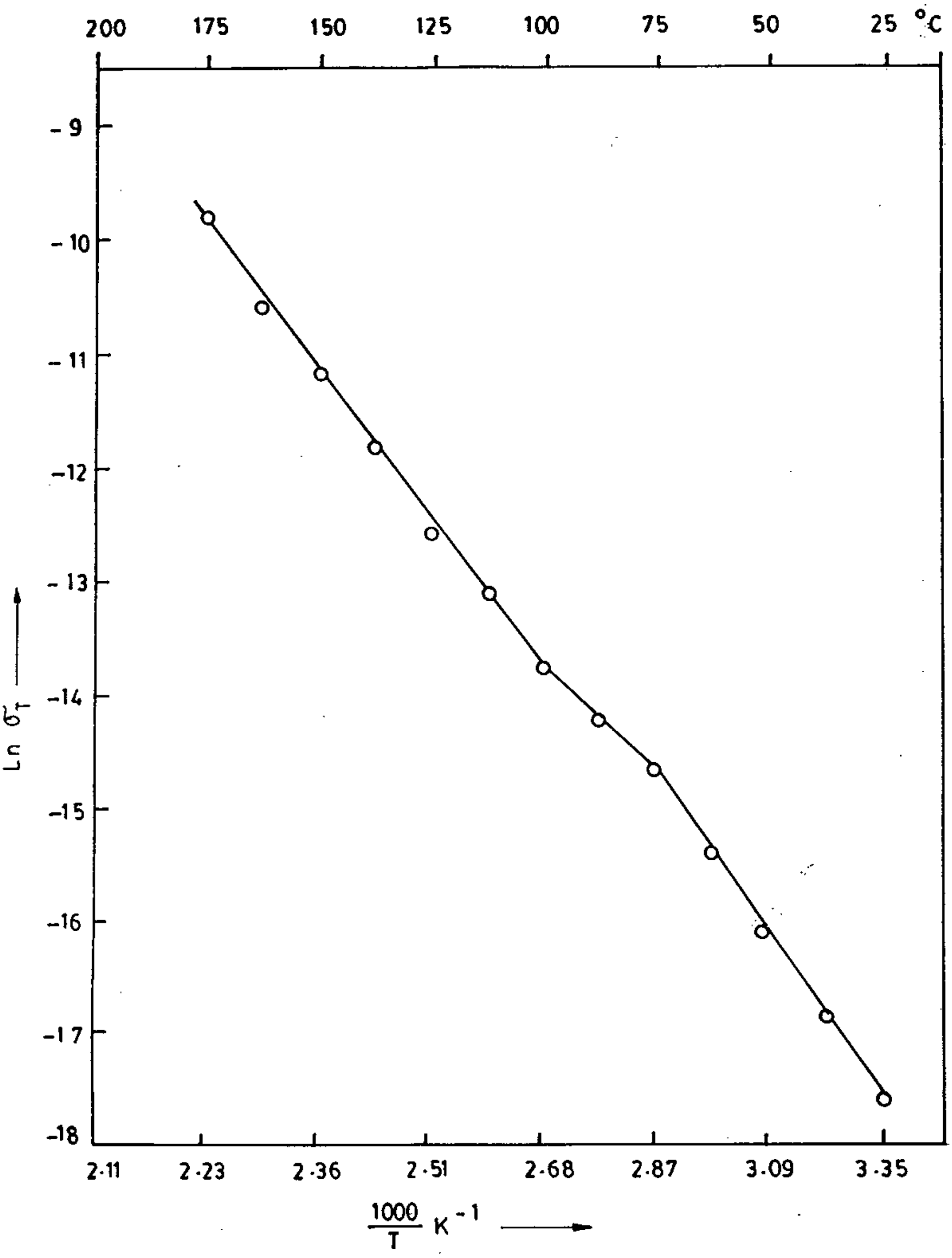


Figure 5.19: Conductivity as function of temperature for pure KDP.

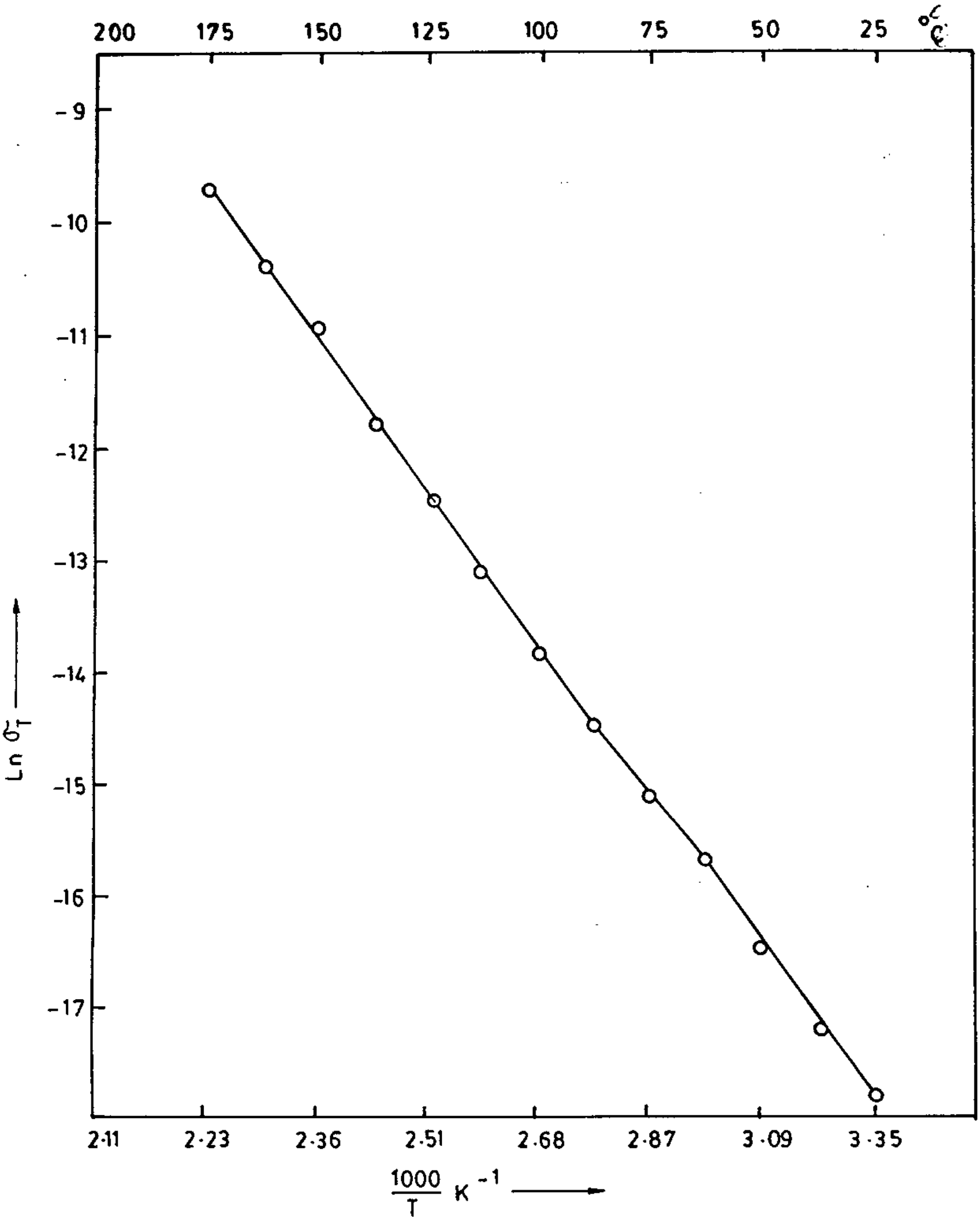


Figure 5.20: Conductivity as function of temperature for KDP doped with KCl in ratio 95:5.

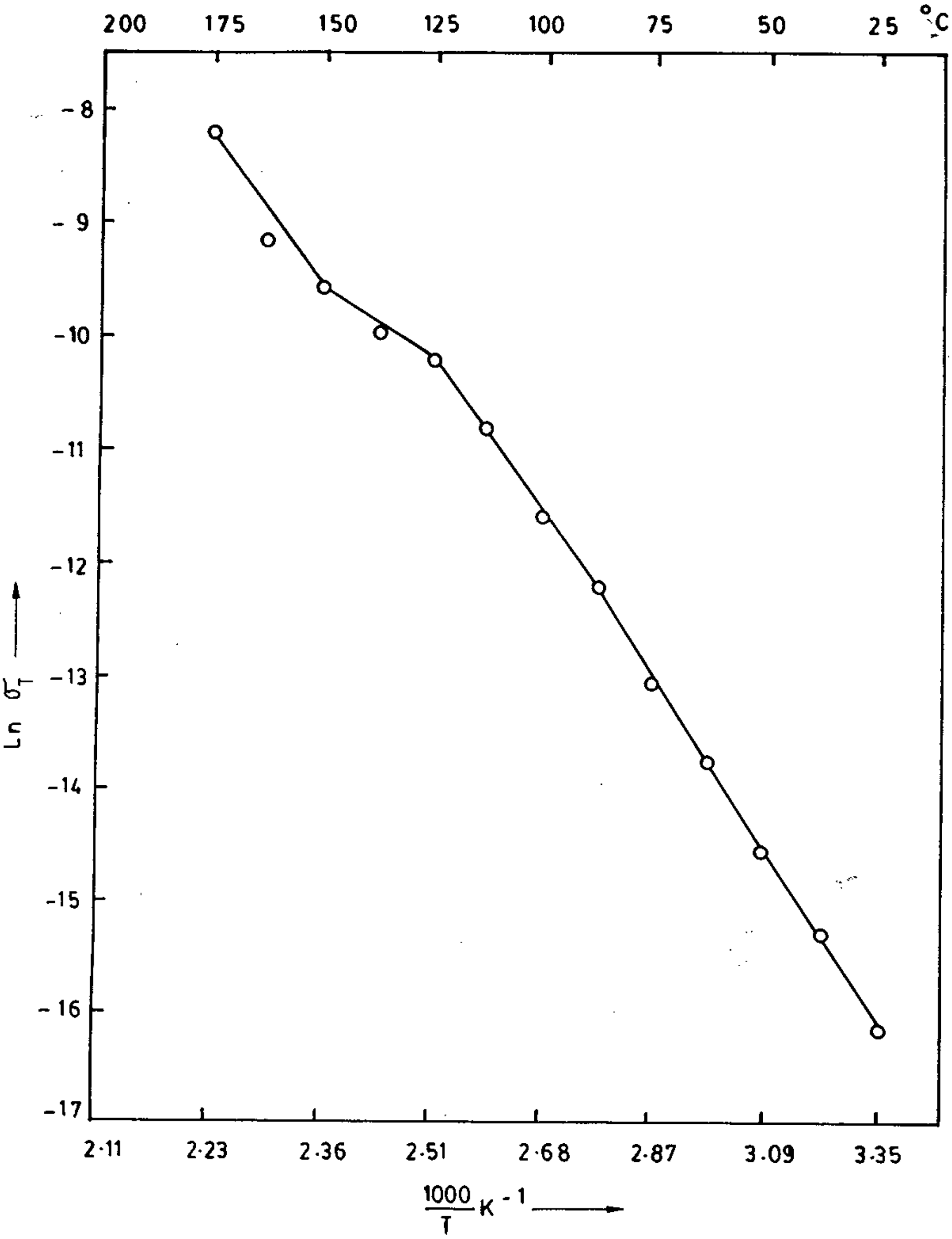


Figure 5·21: Conductivity as function of temperature for KDP doped with KCl in ratio 90 : 10

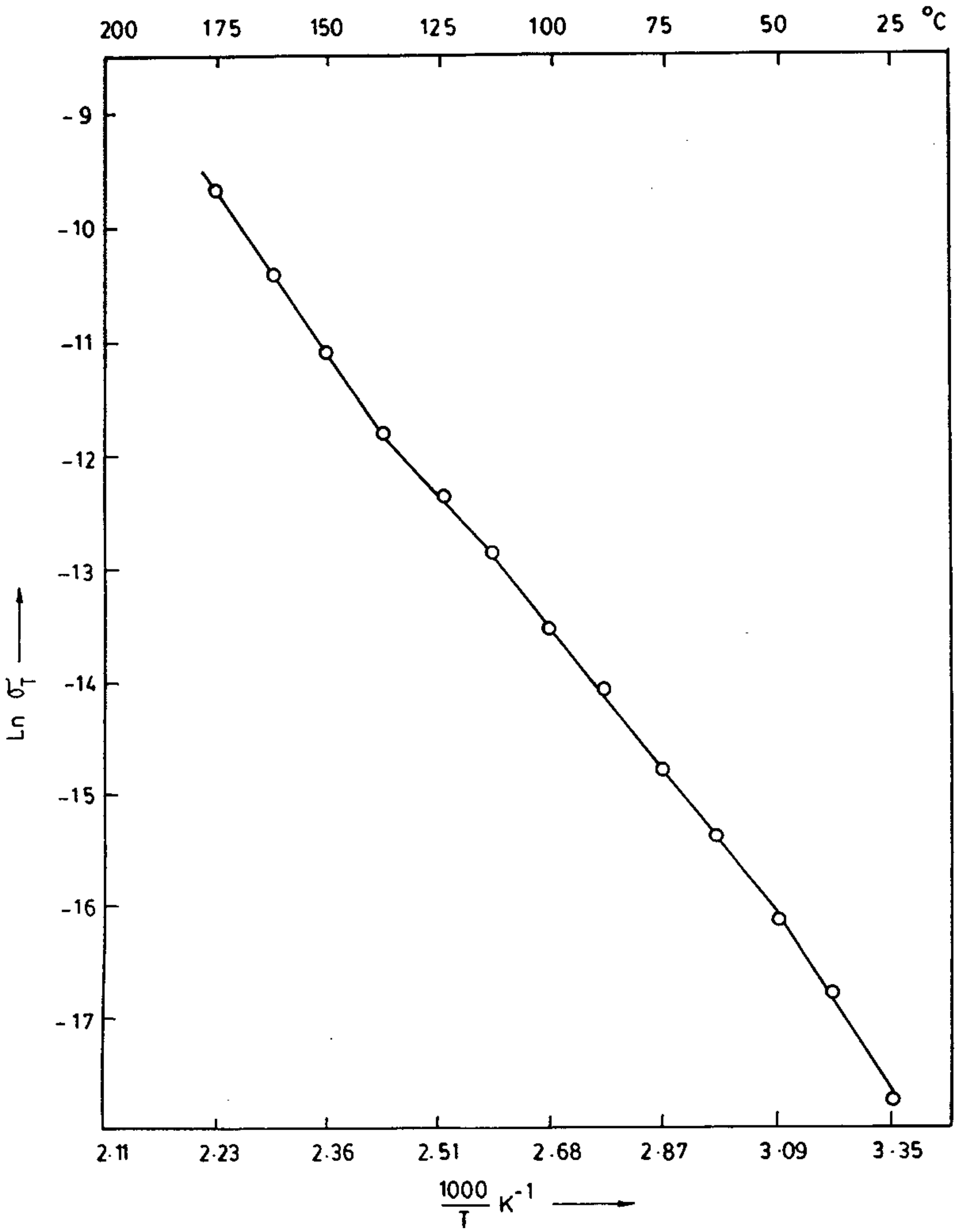


Figure 5.22: Conductivity as function of temperature for KDP doped with KCl in ratio 85 : 15.

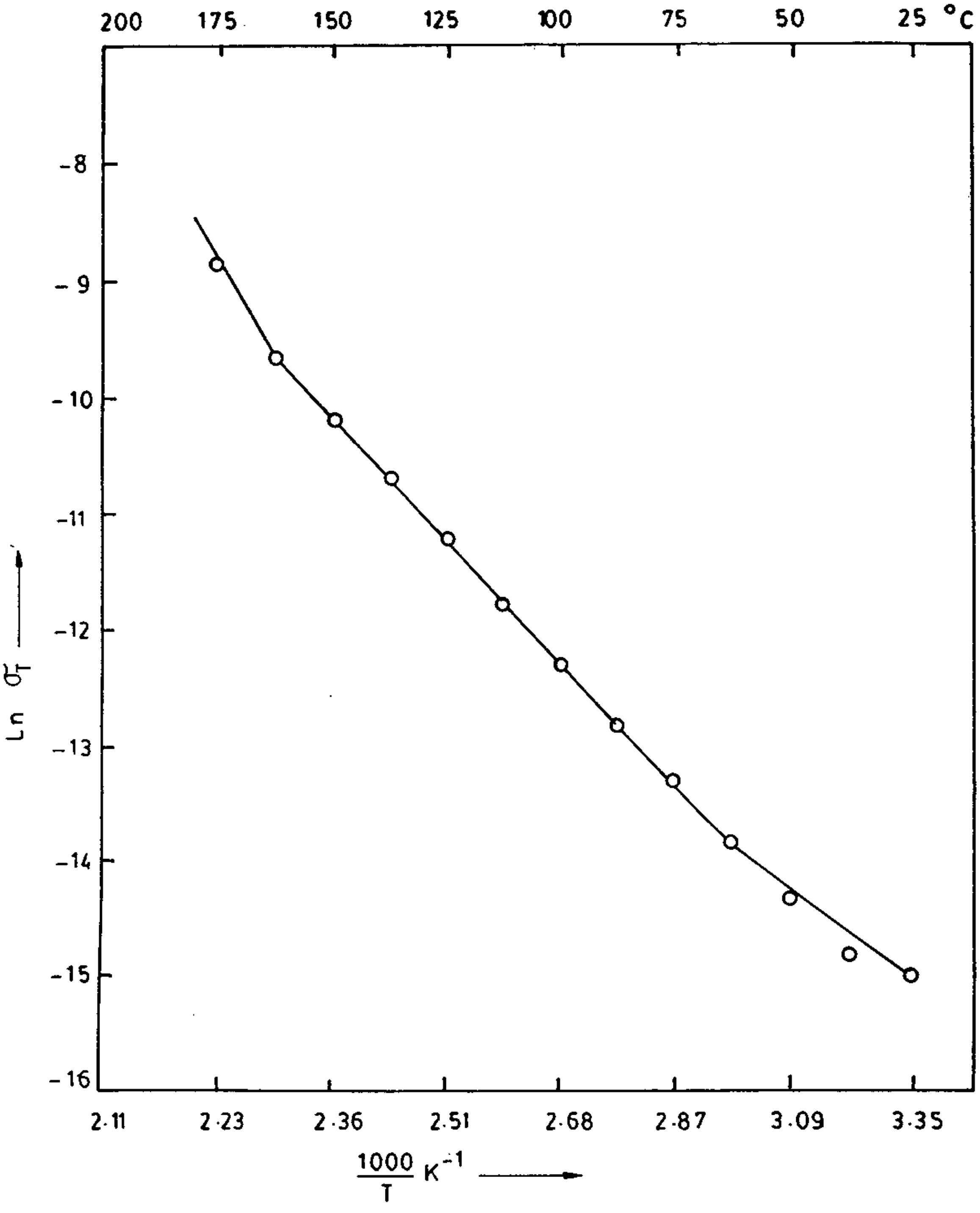
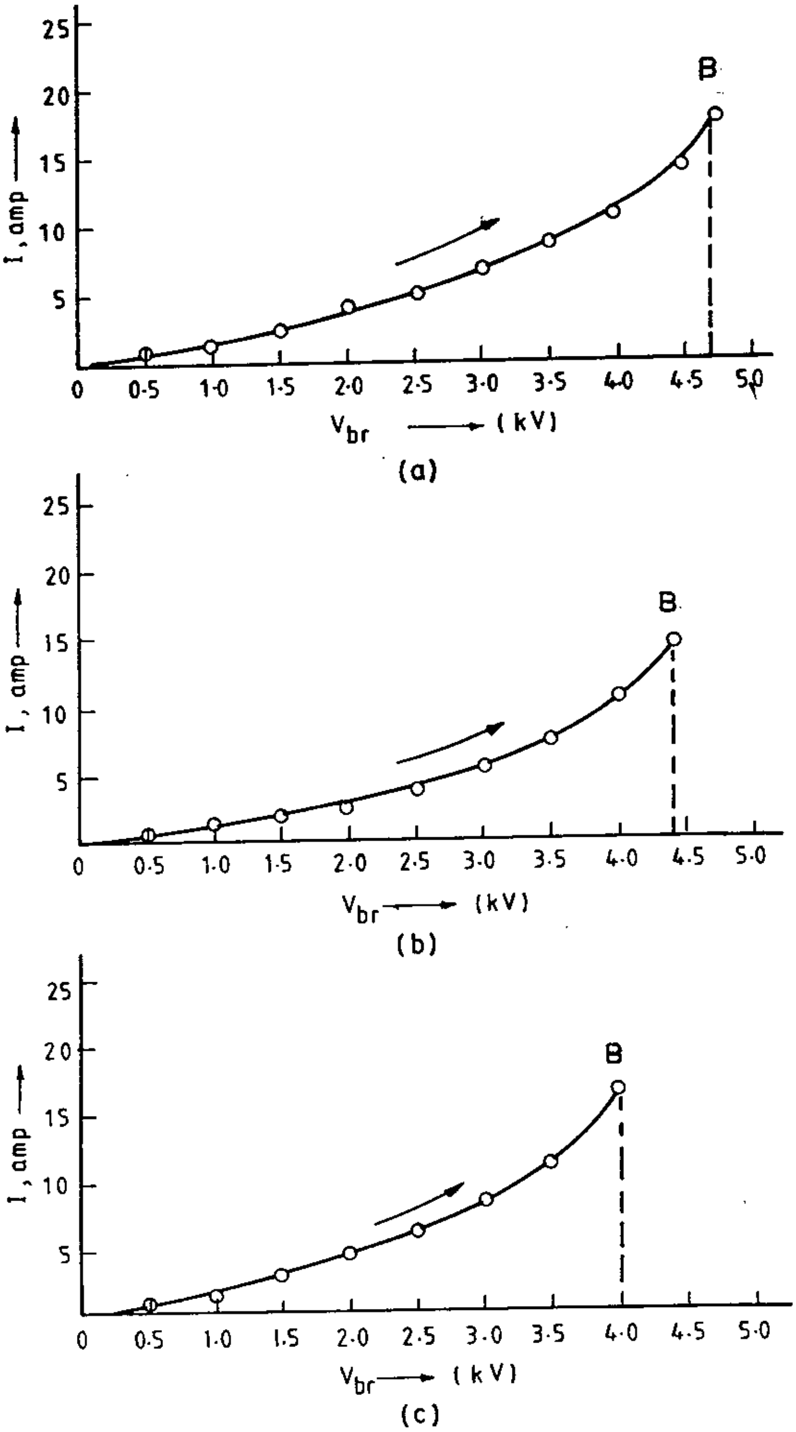


Figure 5.23: Conductivity as function of temperature for KDP doped with KCl in ratio 80 : 20



a

Figure 5.24:Current versus voltage for KDP crystals (a) pure KDP (b) KDP: KCl (95:05) (c) KDP: KCl (95:10).

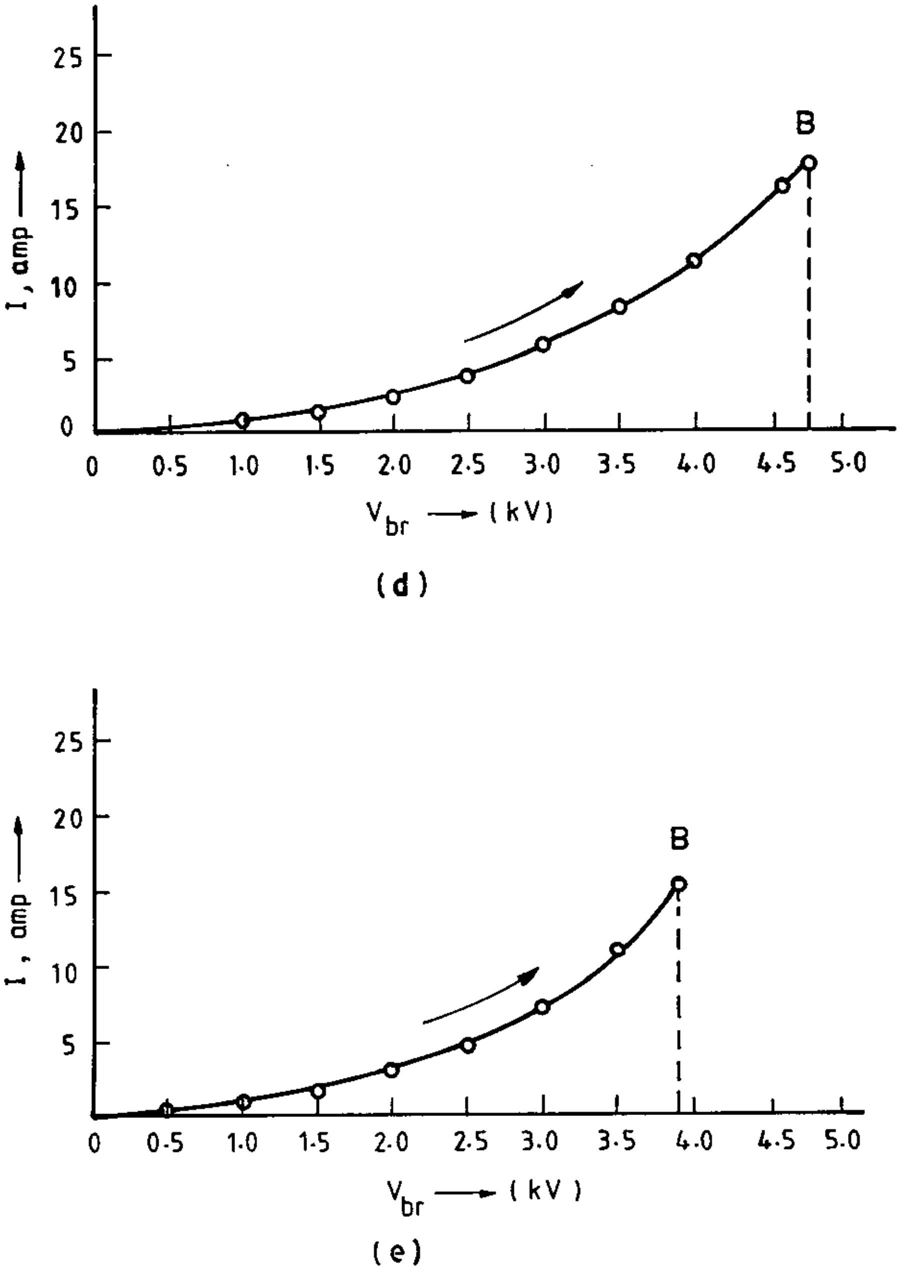


Figure 5:24b: Current versus voltage for KDP crystals (d) KDP: KCl (85:15) (e) KDP: KCl (80: 20)

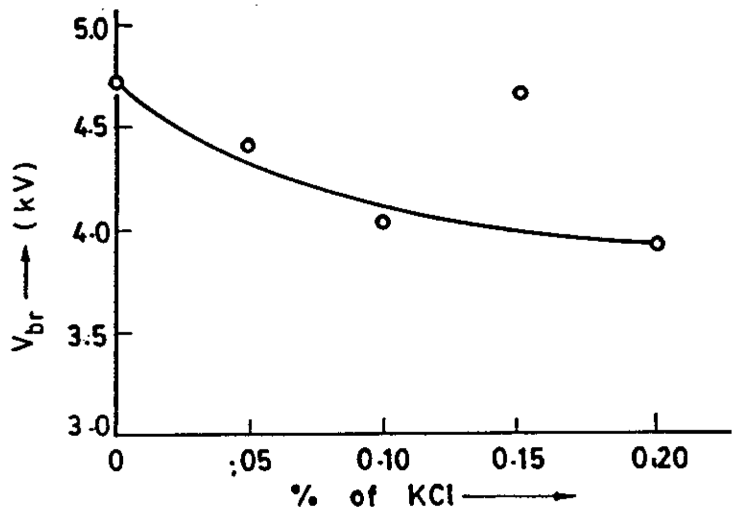


Figure 5.25: Variation of breakdown voltage for the addition of KCl.

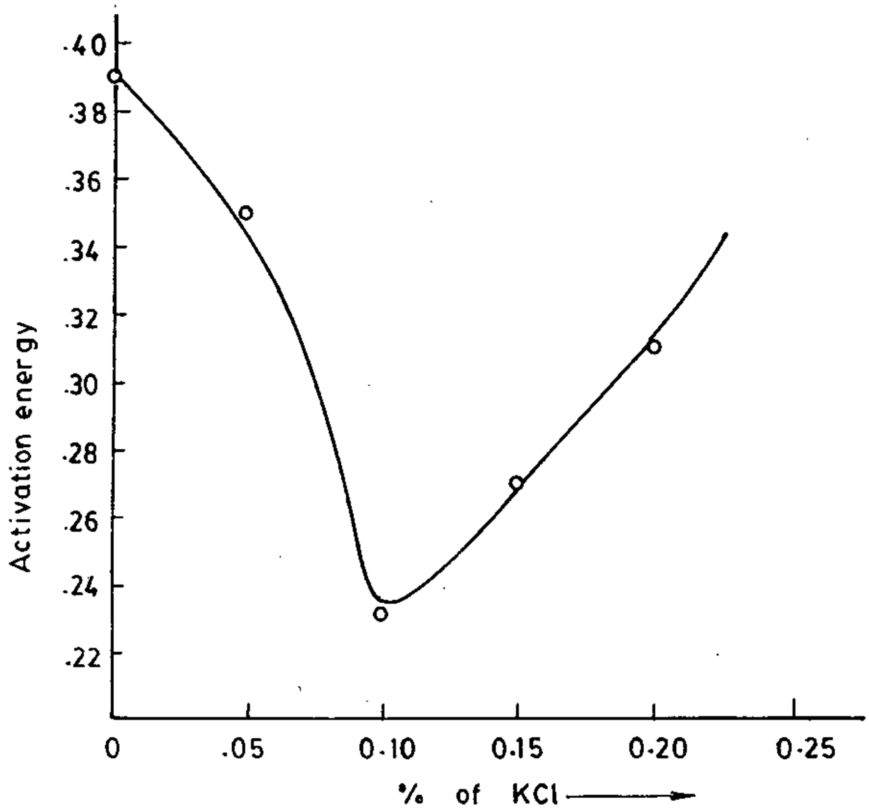


Figure 5.26: Activation energy changes with the addition of KCl.

5.8 References

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Chapter 6 Conclusion

6.1 Conclusion

6.2 Scope for the future work

6.1 Conclusion

The following conclusions are summarized as follows.

1. Very sharp transparent and well defined shape of pure KDP and KDP doped with KCl crystals in different proportions are grown at room temperature by slow evaporation and natural cooling process.

2. Rapid growth rates are observed along the z-direction than that in x-direction.

3. In infrared spectroscopic study (PO_4) ions are enhanced and replaced by Cl^{-1}ions and with the addition of KCl as impurities in KDP, a little change in structural morphology is observed.

4. d.c. electrical conductivity is measured with voltage and temperature variation by two probe method. d.c. conductivity is found to be increased with the increase of temperature and addition of KCl concentration.

5. a.c. voltage breakdown is measured on the grown crystals. Breakdown voltage is found to decrease with the increase of KCl proportion in KDP crystal.

6. By X-ray diffractometry study lattice parameters viz a and c are measured and are found with a little variation from standard values.

6.2 Scope for the future work

The following ideas can be carried out for further extention of this research work.

1. KDP and KDP doped with KCl crystals can be grown with different molar concentration of saturated solution.

2. a.c. conductivity measurement can be done on the grown crystals to see the dielectric behaviour.

3. Microhardness study in other ward bond strength of the doped crystal can be performed.

4. Atomic absorbtion spectrometric study can be carried out to see the presence of KCl in the doped KDP crystals because Volhards method is not suitable to calculate the correct amount of Cl atom as it gives much error.

Chapter 7

Appendix

Activation energy, $\sigma = \sigma_o e^{-E/KT}$

$$\ln\sigma = \ln\sigma_o^{-E/KT}$$

$$\ln\frac{\sigma}{\sigma_o} = -E/KT$$

$$\frac{E}{KT} = \frac{\sigma_o}{\sigma}$$

$$E = KT \quad \ln\frac{\sigma_o}{\sigma}$$

$$\Delta E = K\Delta T \quad \ln\frac{\sigma_o}{\sigma}$$

(1) Pure KDP

$K = 1.38 \times 10^{-23}$ J/mole/k $\qquad$ 1 eV = 1.6×10^{-19} J

$\Delta T = 183.75°C = 456.75$

$\Delta E = 1.38 \times 10^{-23} \times 456.75 \times 9.5$

$= 5987.99 \times 10^{-23}$ J

$$\Delta E = \frac{5.987 \times 10^{-20}}{1.6 \times 10^{-19}}$$

$$= \frac{5.987}{1.6}$$

$= 0.374$ eV.

(2) For 95:05

$\Delta E = 1.38 \times 10^{-23} \times 469.05 \times 8.67$

$= 5611.9956 \times 10^{-23}$ J

$= 5.612 \times 10^{-20}$ J

$$\Delta E = \frac{5.612 \times 10^{-20}}{1.6 \times 10^{-19}} \text{ J}$$

$= 0.351$ eV

(3) For 90:10

$$\Delta E = 1.38 \times 10^{-23} \times 391.75 \times 6.8 \text{ Joule}$$

$$= \frac{3776.18 \times 10^{-23}}{1.6 \times 10^{-19}} \text{ eV}$$

$$= \frac{3.776}{1.6} \text{ eV}$$

$$= 0.236 \text{ eV}$$

(4) For 85:15

$$\Delta E = 1.38 \times 10^{-23} \times 423 \times 6.9 \text{ Joule}$$

$$= \frac{4436.42 \times 10^{-23}}{1.6 \times 10^{-19}} \text{ eV}$$

$$= 0.277 \text{ eV.}$$

(5) For 80:20

$$\Delta E = 1.38 \times 10^{-23} \times 461.75 \times 79 \text{ Joule}$$

$$= \frac{5033.99 \times 10^{-23}}{1.6 \times 10^{-19}}$$

$$= 0.314 \text{ eV}$$

Preparation of the solution

1. 2 Mole concentration of pure KDP solution

$$Amount = \frac{Strength\ of\ concentration \times Mol\ wt\ of\ solute \times Vol\ of\ solution}{1000}$$

Molecular wt of KDP = 136.09 gm

value of the solvent with solute = 150 ml

$$Amount = \frac{2 \times 136.09 \times 150}{1000} = 40.82gm$$

2. 2 mole concentration of KDP:KCl = 95:05

For 95%KDP amount = 40.82 × 0.95

= 38.78gm

For KCl amount for 150ml solution

$$= \frac{2 \times 74 \times 150}{1000} = 22.37\text{gm}$$

For 5% KCl amount = 22.37 × 0.05 = 1.12gm

3. 2 mole concentration of KDP:KCl = 90:10

For 90% KDP amount = 40.82 × 0.90

= 36.74gm

For 10% KCl amount = 22.37 × 0.10 = 2.24gm

4. 2 mole concentration of KDP: KCl = 85:15

For 85% KDP amount = 40.82 × 0.85

= 34.70gm

For 15% KCl amount = 22.37 × 0.15 = 3.36gm

5. 2 mole concentration of KDP:KCl = 80:20

For 80% KDP amount = 40.82 × 0.80

= 32.65gm

For 20% KCl amount = 22.37 × 0.20 = 4.47gm

Table-7.1: Growth rates R_x and R_z respectively along the x and z direction for pure KDP and KDP doped with KCl single crystals

Molar Concentration	KDP:KCl ratio	$R_x \times 10^{-5}$ mm/sec	$R_z \times 10^{-5}$ mm/sec	$R_x \times R_z$ $mm^4 \times 10^{-10}$/sec
2.0 mole	Pure KDP	1.289	3.060	3.943
concentration	95:5	1.675	4.094	6.863
for all	90:10	1.509	5.324	8.035
	85:15	1.321	5.006	6.6164
	80:20	1.671	4.986	8.3326

Table-7.2: X-ray diffraction data for pure KDP crystals

No. of Observation	2θ in degree	θ in degree	$d = \frac{\lambda}{2 Sin\theta} in \overset{o}{A}$	hkl
1	17.40	8.7000	5.0964	101
2	23.80	11.900	3.7385	200
3	29.16	14.580	3.0623	
4	30.66	15.330	2.9159	112
5	33.79	16.895	2.6526	
6	38.24	19.120	2.3536	301
7	40.40	20.200	2.2326	103
8	45.54	22.770	1.9918	321
9	46.32	23.160	1.9601	312
10	54.890	27.445	1.6726	420
11	58.65	29.325	1.5740	332
12	63.46	31.730	1.4658	
13	69.50	34.750	1.3525	
14	74.10	37.050	1.2798	
15	79.57	39.785	1.2047	
16	81.208	40.604	1.1850	

Table-7.3: X-ray diffraction data for KDP : KCl 95:5

No. of Observation	2θ in degree	θ in degree	$d = \frac{\lambda}{2 Sin\theta} in \overset{o}{A}$	hkl
1	17.100	8.5500	5.1852	101
2	23.530	11.7650	3.7808	200
3	30.400	15.2000	2.9402	112
4	33.695	16.8475	2.6599	
5	38.105	19.0525	2.3616	301
6	40.700	20.3500	2.2168	103
7	46.760	23.3800	1.9427	312
8	55.000	27.0000	1.6695	420
9	64.000	32.0000	1.4547	332
10	68.080	34.0400	1.3772	
11	71.605	35.8025	1.3178	
12	74.490	37.2450	1.2737	
13	79.820	39.9100	1.2016	
14	81.720	40.8600	1.1784	

Table-7.4: X-ray diffraction data for KDP : KCl 90:10

No. of Observation	2θ in degree	θ in degree	$d = \frac{\lambda}{2 Sin\theta} in \overset{o}{A}$	hkl
1	17.25	8.6250	5.1405	101
2	23.69	11.8450	3.7556	200
3	29.50	14.7500	3.0279	
4	30.45	15.2250	2.9355	112
5	33.65	16.8250	2.6633	
6	38.08	19.0400	2.3631	301
7	40.25	20.1250	2.2405	103
8	64.15	23.0750	1.9669	312
9	54.50	27.2500	1.6837	420
10	58.40	29.2000	1.5802	332
11	63.52	31.7600	1.4646	
12	69.35	34.6750	1.3550	
13	71.20	35.6000	1.3243	
14	74.05	37.0250	1.2802	
15	79.35	39.6750	1.2075	
16	81.23	40.6150	1.1842	

Table-7.5: X-ray diffraction data for KDP : KC[illegible]85:15

No. of Observation	2θ in degree	θ in degree	$d = \frac{\lambda}{2 Sin\theta} in \overset{o}{A}$	hkl
1	17.050	8.5250	5.2003	101
2	23.550	11.7750	3.7776	200
3	29.205	14.6025	3.0578	
4	30.390	15.1950	2.9412	112
5	33.500	16.7500	2.6749	
6	34.800	17.4000	2.5779	
7	37.950	18.9750	2.3719	301
8	40.155	20.0775	2.2456	103
9	45.255	22.6275	2.0037	
10	46.000	23.0000	1.9730	321
11	54.500	27.2500	1.6837	420
12	58.695	29.3475	1.5729	332
13	63.350	31.6750	1.4681	
14	69.055	34.5275	1.3609	
15	70.800	35.4000	1.3308	
16	73.300	36.6500	1.2915	
17	75.780	37.8900	1.2552	
18	78.700	39.3500	1.2158	
19	80.800	40.4000	1.1894	
20	84.800	42.400	1.1433	

Table-7.6: X-ray diffraction data for KDP : KCl 80:20

No. of Observation	2θ in degree	θ in degree	$d = \frac{\lambda}{2 Sin\theta} in \mathring{A}$	hkl
1	17.500	8.7500	5.0675	101
2	23.800	11.9000	3.7385	200
3	29.600	14.8000	3.0179	
4	30.700	15.3500	2.9121	112
5	33.900	16.9500	2.6442	
6	35.200	17.6000	2.5495	
7	38.400	19.2000	2.3411	301
8	40.500	20.2500	2.2273	321
9	46.400	23.2000	1.9569	420
10	55.050	27.5250	1.6681	332
11	58.800	29.4000	1.5737	
12	64.000	32.0000	1.4547	
13	69.605	34.8025	1.3507	
14	72.390	36.1950	1.3054	
15	74.395	37.1975	1.2752	
16	79.800	39.9000	1.2018	
17	85.205	42.6025	1.1389	
18	95.195	47.5975	1.0440	

Table-7.7: Electrical resistivities & conductivities of pure KDP single crystals

Molar Concentration	Current I in nA	Voltage in volts	Resistance $\times 10^6$ ohm	Resistivity $\times 10^6$ ohm-meter	Conductivity $\times 10^{-7}$ mho/meter
2 mole concentration of pure KDP	64.5	25	387.596	8.809	1.1352
	400.0	50	125.000	2.840	3.5200
	640.0	75	117.187	2.663	3.7540
	924.0	100	108.225	2.459	4.0650
	1220.0	125	102.459	2.328	4.2940
	1560.00	150	96.1538	2.185	4.5760

Table-7.8: Electrical resistivities & conductivities for pure KDP& KDP doped with KCl single crystals (KDP:KCl = 95:5)

Molar Concentration	Current I in nA	Voltage in volts	Resistance $\times 10^6$ ohm	Resistivity $\times 10^7$ ohm-meter	Conductivity $\times 10^{-7}$ mho/meter
2 mole concentration of KDP:KCL = 95:5	67.00	25.00	373.143	0.6029	1.658
	319.00	50.00	156.739	0.2532	3.948
	491.00	75.00	152.742	0.2468	4.050
	703.00	100.00	142.247	0.2298	4.350
	960.00	125.00	130.208	0.2104	4.752
	1233.00	150.00	121.654	0.1965	5.0870

Table-7.9: Electrical resistivities & conductivities for pure KDP & KDP doped with KCl single crystals (KDP:KCl = 90:10)

Molar Concentration	Current I in nA	Voltage in volts	Resistance $\times 10^6$ ohm	Resistivity $\times 10^7$ ohm-meter	Conductivity $\times 10^{-8}$ mho/meter
2 mole concentration of KDP:KCl = 90:10	125.00	25.00	200.00	0.5704	1.753
	652.00	50.00	76.68	0.2147	4.570
	1150.00	75.00	65.21	0.1860	5.376
	2000.00	100.00	50.00	0.1426	7.030
	2800.00	125.00	44.64	0.1273	7.850
	3800.00	150.00	39.47	0.1125	8.880

Table-7.10: Electrical resistivities & conductivities for pure KDP & KDP doped with KCl single crystals (KDP:KCl = 85:15)

Molar Concentration	Current I in nA	Voltage in volts	Resistance $\times 10^6$ ohm	Resistivity $\times 10^7$ ohm-meter	Conductivity $\times 10^{-7}$ mho/meter
2 mole concentration of KDP:KCL = 85:15	36.00	25.00	694.4440	2.190	0.4564
	350.00	50.00	142.8570	0.450	2.2188
	600.00	75.00	125.0000	0.394	2.5358
	1750.00	100.00	57.1420	0.180	5.5472
	4000.00	125.00	31.2500	0.985	10.1430
	5000.00	150.00	30.0000	0.946	10.0560

Table-7.11: Electrical resistivities & conductivities for pure KDP & KDP doped with KCl single crystals (KDP:KCl = 80:20)

Molar Concentration	Current I in μA	Voltage in volts	Resistance × 10^6 ohm	Resistivity × 10^6 ohm-meter	Conductivity × 10^{-6} mho/meter
2 mole concentration of KDP:KCL = 80:20	0.40	25.00	62.5000	1.084	0.9225
	3.19	50.00	15.6730	0.271	3.6781
	6.98	75.00	10.7440	0.186	5.3655
	7.50	100.00	13.3330	0.231	4.3255
	9.92	125.00	12.6000	0.218	4.5750
	17.96	150.00	8.3510	0.144	6.9030

Table-7.12 Electrical resistivities & conductivities for pure KDP (Temperature variation at constant voltage=100V)

Molar Concentration	Volte in mV	Temperature	Current I in μA	Resistivity × 10^6 ohm-meter	Conductivity × 10^{-7} mho/meter
2 molar concentration of pure KDP	1.0	25.0	0.05	45.46	0.219
	1.5	37.5	0.10	22.73	0.439
	2.0	50.0	0.23	9.882	1.012
	2.5	62.5	0.45	50.51	1.979
	3.0	75.0	0.96	2.367	4.223
	3.5	87.5	1.54	1.475	6.775
	4.0	100.0	2.29	0.9925	10.074
	4.5	112.5	4.64	0.1489	20.413
	5.0	125.0	8.13	0.279	35.767
	5.5	137.5	16.38	0.1387	72.063
	6.0	150.0	32.20	0.0705	141.663
	6.5	162.5	57.20	0.0397	251.609
	7.0	175.0	127.60	0.0781	561.372

Table-7.13 Electrical resistivities & conductivities for pure KDP & KDP doped with KCl(Temperature variation at constant voltage=100V, KDP :KCl= 95:5)

Molar Concentration	Volts in mV	Temperature	Current I in μA	Resistivity $\times 10^6$ ohm-meter	Conductivity $\times 10^{-7}$ mho/meter
2 molar concentration of pure KDP: KCl = 95:5	1.0	25.0	0.03	5.386	0.185
	1.5	37.5	0.05	3.232	0.309
	2.0	50.0	0.11	1.469	0.680
	2.5	62.5	0.25	0.646	1.547
	3.0	75.0	0.45	0.359	2.784
	3.5	87.5	0.83	0.194	5.136
	4.0	100.0	1.60	0.101	9.900
	4.5	112.5	3.10	0.521	19.183
	5.0	125.0	6.12	0.264	37.871
	5.5	137.5	12.70	0.127	78.589
	6.0	150.0	29.20	0.0553	180.693
	6.5	162.5	50.80	0.0318	314.356
	7.0	175.0	96.5	0.01674	597.153

Table-7.14 Electrical resistivities & conductivities for pure KDP & KDP doped with KCl(Temperature variation at constant voltage=100V, KDP :KCl= 90:10)

Molar Concentration	Volte in mV	Temperature	Current I in μA	Resistivity × 10^6 ohm-meter	Conductivity × 10^{-7} mho/meter
2 molar concentration of pure KDP: KCl = 90:10	1.0	25.0	0.28	10.185	0.981
	1.5	37.5	0.62	4.600	2.173
	2.0	50.0	1.40	2.037	4.908
	2.5	62.5	3.00	0.950	10.518
	3.0	75.0	6.11	0.466	21.423
	3.5	87.5	14.08	0.202	49.368
	4.0	100.0	26.40	0.108	92.566
	4.5	112.5	55.00	0.051	192.847
	5.0	125.0	103.00	0.027	361.150
	5.5	137.5	133.00	0.021	464.339
	6.0	150.0	203.00	0.014	711.781
	6.5	162.5	300.00	0.0095	1051.893
	7.0	175.0	785.00	0.0036	2752.454

Table-7.15 Electrical resistivities & conductivities for pure KDP & KDP doped with KCl(Temperature variation at constant voltage=100V, KDP :KCl= 85:15)

Molar Concentration	Volte in mV	Temperature	Current I in μA	Resistivity $\times 10^6$ ohm-meter	Conductivity $\times 10^{-7}$ mho/meter
2 molar concentration of pure KDP: KCl = 85:15	1.0	25.0	0.06	52.583	0.190
	1.5	37.5	0.16	19.718	0.507
	2.0	50.0	0.30	10.516	0.950
	2.5	62.5	0.64	4.926	2.028
	3.0	75.0	1.14	2.767	3.613
	3.5	87.5	2.34	1.348	7.416
	4.0	100.0	4.22	0.747	13.375
	4.5	112.5	8.04	0.392	25.483
	5.0	125.0	13.5	0.233	42.789
	5.5	137.5	23.9	0.132	75.752
	6.0	150.0	47.7	0.066	151.188
	6.5	162.5	95.2	0.033	301.743
	7.0	175.0	193.00	0.016	611.727

Table-7.16 Electrical registivities & conductivities for pure KDP & KDP doped with KCl(Temperature Variation at constant voltage=100V, KDP :KCl= 85:15)

Molar Concentration	Volte in mV	Temperature	Current I in μA	Resistivity × 10^6 ohm-meter	Conductivity × 10^{-7} mho/meter
2 molar concentration of pure KDP: KCl= 85:15	1.0	25.0	0.25	3.336	2.997
	1.5	37.5	0.64	2.710	3.688
	2.0	50.0	1.01	1.717	5.821
	2.5	62.5	1.70	1.020	9.798
	3.0	75.0	2.92	0.594	16.829
	3.5	87.5	4.77	0.363	27.492
	4.0	100.0	7.83	0.221	45.129
	4.5	112.5	13.18	0.1316	75.965
	5.0	125.0	23.00	0.0754	132.564
	5.5	137.5	39.01	0.0444	224.841
	6.0	150.0	63.00	0.0275	363.112
	6.5	162.5	108.10	0.0160	622.478
	7.0	175.0	240.00	0.0072	1383.285

Table 7.17: Infrared spectras of pure KDP and KDP doped with KCl in different proportions.

Pure KDP	KDP:KCl 90:05	KDP:KCl 90:10	KDP:KCl 85:15	KDP:KCl 80:20	Band assignments
410	420	405	408	404	$V_4(T_2)$ of XO_4 ion
540	535	540	550	550	Combination band of $V_4(T_2)$ of PO_4 ion and lattice band
1280	1295	1290	1230	1100	Combination band of $V_4(T_2)$ of XO_4 ion with lattice band
1480	1205	1476	1460	1310	Combination band of V_4 with lattice vibration
1680	-	1678	1696	1545	Combination band of V_3 with vibration or X-O-H bending vibration
1725	1735	1797	1795	1655	-
2460	2350	2425	2350	2355	Hydrogen band vibration
3995	3590	3425	-	2495	