# ‘’STUDIES ON POTASSUM DIHYDROGEN ORTHOPHOPHATE (KDP) CRYSTAL’’

A PROJECT REPORT SUBMITTED TO

**SAVITRIBAI PHULE PUNE UNIVERSITY, P**

Savitribai Phule Pune University
सावित्रीबाई फुले पुणे विद्यापीठ

FOR THE DEGREE OF

**MASTER OF SCIENCE**

IN

**PHYSICS**

UNDER THE FACULTY OF SCIENCE

**BY**

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# BONAFIDE CERTIFICATE

This is certifying that the work incorporated in the project report **entitled '' STUDIES ON POTASIUM DIHYDROGEN ORTHOPHOSPHATE (KDP) CRYSTAL''** submitted to Savitribai Phule Pune University, Pune, is benefited work of **Miss. Jorwekar Aarti Chandrabhan** of M.Sc. (Physics) during the academic year 2020-21 who carried out the project work under my supervison

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Date / /2021

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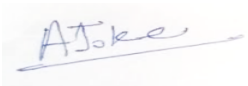
My classmates have been of great help to me the project work. My ideas were shaped and refined progressively through my discussions with them form time to time. I cannot miss to thank them all. There were some persons like **Prof. Virkar A.A. Prof. Bhakare C.H. Prof. Shelke A.P.** who were directly but indirectly involed in my preparator/practical work. I appreciate their contribution and thank them too.



**Place :-** Sonai **Signature of Research Student**

**Date :-** / /2021 (Jorwekar Arati Chandrabhan)

(M.Sc. Physics)

# STUDIES ON POTASSIUM DIHYDROGEN ORTHOPHOSPHATE

# ABSTRACT

The Potassium dihydrogen phosphate (KDP) crystal is an interesting nonlinear optical inorganic material. In this present work, KDP crystal growth the without additive and using additive EDTA solution and added a NaOH solution add the doped KDP crystal has been grown by slow evaporation aqueous solution growth technique. The grown crystals have been investigated through various techniques viz. Fourier. The grown crystal has been subjected to X-ray diffraction for structural analysis. Increase in KDP crystal thermal stability by an organic additive of KCL solution. The conductivity and capacitance of KDP crystal and KCL solution doped KDP has been analyzed .the optically characterization pure KDP and KCL doped KDP crystal has been analyzed.

# INDEX

# CHAPTER:1

## INTRODUCTION AND CRYSTAL SYMMETRY:-

Let us start with the word crystal. The word crystal originates from Greek Kapok (coldness) kpluoc (ice). The father of crystal fabrication technology is A. Vermeil. With his flame-fusion growth method is described in 1902.

Crystallography means the study of the solids which are in the form of Crystal. Discovery of X-rays is a important event in a crystallography but before the discovery of X-ray diffraction (1910), this study was done especially by geologist and mineralogical investigations or by the cleavage method. But discovery of X-rays gives the powerful and precise tool for the exploration of the internal arrangement of atoms in the crystals. And once the internal arrangement of atoms in the crystal is known their physical properties can be studied in detail.

## 1.2) Crystals:-

We know that matter generally exists in three states solid, liquid and gases. Liquid and solid together called as fluid. Solids are generally divided into two categories namely crystalline and amorphous. The distinction between crystalline and amorphous solids is given below:

| Sr. No | **Crystalline** | **Amorphous** |
|---|---|---|

| | | |
|---|---|---|
| 1 | Regular arrangement of particles and atoms | Random arrangement of particles and atoms |
| 2 | They are anisotropic (having different physical properties like thermal conductivity, electrical conductivity, refractive index, etc). | They are isotropic (in all possible directions they have same physical properties.) |
| 3 | Because of purity melting point is very sharp. | The melting point is not sharp. |
| 4 | The cooling curve for them has breaks because of crystallization. | The cooling curve for them is smooth. |
| 5 | The growth process of crystal is slow, so that the atoms or the constituent particles take definite position, where the potential energy of the configuration is minimum during the growth. | The growth process or the phase change is quick so that the atoms do not have sufficient time to obtain the configuration of minimum energy consequently; |

The regular surface geometry shiny and often colorful appearance have made crystal mineral kingdom feasting objects for everybody. Natural crystals have often been formed by temperature by crystallization from solution.

Now a day crystals are produced artificially to satisfy the need of science, technology and to grow high quality crystals has became an essential criterion for the competitiveness of growth specialists have been moved from the periphery to the centre of the material.

New materials are the base of solid state research. Device engineers, researchers or solid state theorists can only be studies and understood the structure

of single crystals, bounding and other chemo-physics properties. Solid is a building block of atoms or molecules. Basically at normal conditions atoms are arranged regularly with specific geometrical symmetry element. Atomic lattice is always with lattice defects and structural atomic arrangements are essential for the usefulness and value of crystals. We know that crystals are ordered arrangement of atoms or molecules in crystalline form are in pure form and with special optical and electrical properties over randomly arranged material.

## 1.3) about crystal arrangement:-

The crystals are with faces which are geometrically plane to a high degree of precision and have sharp and straight edges. In all crystals symmetry is well developed periodic arrangement is characteristic property of the every crystal. In the crystals there are representative unit which is repeated at a regular intervals along any or all directions. In the crystal fact is that material is made up of aggregates of unit cells (single crystals) and the properties of that materials will be same as the unit or single crystal. Sublimation is the process of phase transformation in case of the crystal it is called as crystallization. It means that crystals are formed when substances changes from one state to another. And once crystal is formed its constituents(atoms or molecules) are bounded by chemical bonds like covalent bond ,ionic bond, hydrogen bond, Vander wall's bond. Symmetry of the crystal depend on what type of bonding take place during formation of the crystal depends on what type of bonding take place during formation of the crystal. There is a wide range of sizes, and size of the crystal depends on the rate at which it is formed. Now a day internal study of crystal is done by using x-ray diffraction, electron diffraction or neutron diffraction methods called the science of cryptography.

## 1.4) Features of crystals:-

**1) Faces:**

The crystals are bounded by a number of perfectly flat surfaces. These flat surfaces are called as faces of that crystal. The faces of the crystals may be like or unlike. For different crystals faces are of different shapes i.e. galena which is well known for us. Different crystal contains different shapes of faces.

**2) Forms:**

All the faces corresponding to a crystal are said to constitute a form. The crystals that consist of all like faces is termed to have a simple form, while crystals having two or more like and unlike faces is called combination firm.

**3) Edges and interfacial angles:**

The intersection on two adjacent faces of the crystals forms the edges of the crystals. The angle between any two faces of crystal is termed as an interfacial angle as shown in fig. The relation between planes faces straight edges and interfacial angle is given by:

F+C=E+2

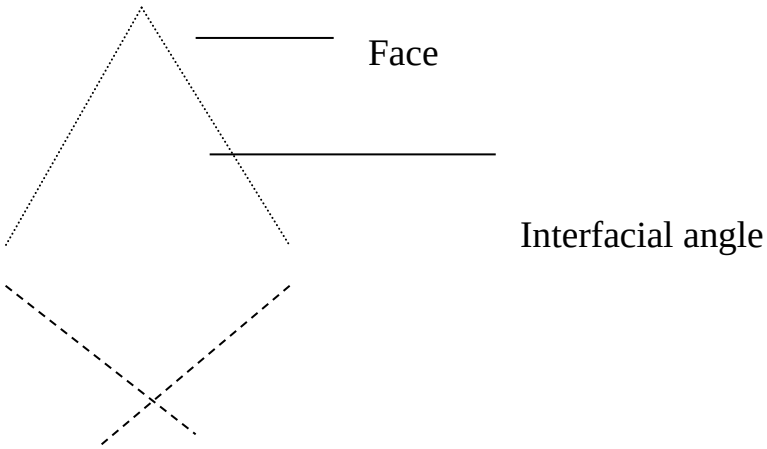
Where,

F=Number of faces

C==Number of angle.

E=number of edges.

Face



And it is observed that "under the same physical condition the angle between the corresponding faces of various crystal of the sane sub stance is constant, also all crystals of one and the same substances have the same symmetry".

## 1.5) Periodicity of the crystals:

**Symmetry elements of crystalline solids:**

We know that crystals are due to different chemical bonds, which hold the atoms, molecules or unit cells together in a uniform or periodic array. No matter what type of bond or faces is responsible to form a crystal, it always exhibits certain symmetry. In crystals there are mainly three types of symmetry:

1) Rotational symmetry
2) Plane of symmetry
3) Center of symmetry

**1) Rotational axis of symmetry:**

When we rotate the cube about a vertical axis passing through the centre of two apposite parallel faces, it is observe that in one complete rotation of $360^0$ we get four position of cube [no. of position may change when we change the position of axis of rotation] coincident with its original position. In simple word we say that in each rotation of $90^0$ brings the cube into its self- coincident position. This axis of rotation is called as an axis of symmetry, and since there are four congruent positions in one complete rotation, this is called as fourfold axis of symmetry or tetrad axis.

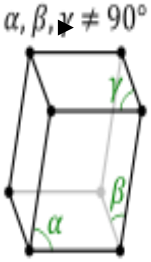
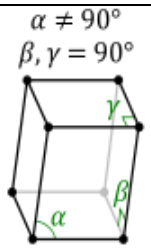
**2) Plane of symmetry:**

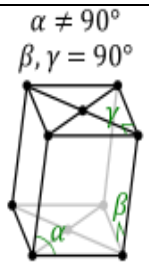
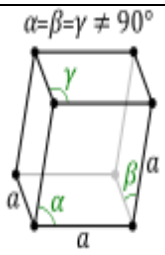
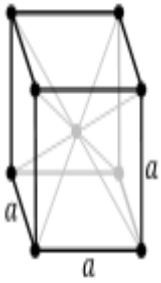
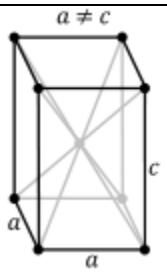
As we know that cube is also bilaterally symmetrical. Consider an imaginary plane which bisects the crystal into two halves which are exactly mirror images in other words one halve is reflection of other halve along plane is called plane of symmetry.

**3. Center of symmetry:**

Center of symmetry is such a point in a crystal in or bodies that if a line is drown from any point on the crystal through this center point and extended an equal distance on either side of this centre point, it will meet at an identical point.

## 1.6) Classification of crystal:-

| Sr no | Crystal system | Axial length | Inter axial length | Example | Structure |
|---|---|---|---|---|---|
| 1. | Triclinic or asymmetric crystal system [primitive] | a≠b≠c | $\alpha\neq\beta\neq\gamma\neq90^0$ | Potassium dichromate($K_2Cr_2O_7$), Sassolite($H_3BO_3$),Albeit( $NaAlSi_3O_8$),Blue Vitriol($CuSO_4$,$5H2_O$) |   |
| 2. | Monoclinic or monosymmetric crystal system [primitive ,Base centered](2-fold) | a≠b≠c | $\alpha=\gamma=90^0$ $\beta\neq90^0$ | Borax($Na_2B_4O_7$-$1OH_2O$), Orthoclase(KAlSi3O8), crinoline($Na_3AlF_6$),etc |   |

| | | | | | |
|---|---|---|---|---|---|
| 3. | Orthorhombic crysta system[primitive, Base centered, body centered, *face* centered](2-fold) | a≠b≠c | α=β=γ=$90^0$ | Celestine(SnSO4),Olivine (Mg2SiO4),Carnality (KClMgCl2,5H2O) |   |
| 4. | Trigonal or Rhombohedral Crystal system | a=b=c | α=β=γ≠$90^0$ | Quartz and Calcite crysta |   |
| 5. | Cubic or regular crystal(primitive, body centered, face centered) (3-fold) | a=b=c | α=β=γ=$90^0$ | Cesium chloride(CsCl),Iron crystal(bcc),Sodium Chloride(NaCl), Germanium(Ge),Silicon( Si),And diamond |   |
| 6. | Tetragonal crystal system(Premitive,bo dy centered) (4-fold) | a=b≠c | α=β=γ=$90^0$ | Ordinary white tin ,Indium(I), Cassiterite($SnO_4$), Anatase($TiO_2$),etc |   |
| 7. | Hexagonal | a=b≠c | α=β=$90^0$, γ=$120^0$ | Mg,Zn,Cd,SiO2 etc. | |

## 1.7) Orientation of project work:-

In this project, I have decided to prepare crystals of KDP (Potassium Dehydrogenate Orthophosphate) by solution growth method by using additives like

KCL (Potassium Chloride) & EDTA (Ethylene Diamine Tetra acetic Acid).And to study the following properties.

1) Growth size of KDP crystal.
2) Effect of KCL & EDTA on KDP crystal.
3) Dielectric constant of KDP crystal.
4) Refractive index of KDP crystal.
    I. At constant temperature.
    II. At varying temperature.

## 1.8) Literature Survey:-

**1. B.M.Lawarw,S D Aghav, V K Dhas [10]:**has reported the all type of crystal structure, crystal angle, classification of crystal structure symmetry explain in details in details solid state physics text book T Y B Sc.

2. **J.R. Hook, H.E. Hall, John Wiley & Sons** [12] has reported the lengths of the edges of a unit cell &the angles between them are called the *lattice parameters*. The symmetry properties of the crystal are embodied in its space group.

3 **I.M. Pritula** [13] has reported Single crystals of potassium dihydrogen phosphate group (KDP, DKDP, ADP) have found wide use in nonlinear optics, optoelectronics and laser engineering.

**4. Y. ENQVIST [11]** has reported the during the past few years, different organic and inorganic compounds have intentionally been used as additives in industrial crystallization, and the positive effects on crystal growth and quality have been reported by several authors .

## 1.9) Reference:-

1.Solid State Physics-S.O.Pillai, 3rd.Edition, New Age International (P) Ltd, Publisher, (1999).

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3. Solid State Physics BySaxena, Gupta and Saxena, PragatiPrakation.

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7 .Problems in Solid State Physics-S.O. Pillai, New Age International (P) Ltd.

8 .Solid State Physics- Palanyswamy.

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11. Y. ENQVIST, J. PARTANEN, M. LOUHI-KULTANEN and J. KALLAS *Department of* Chemical *Technology*, *Lappeenranta University of Technology, Lappeenranta*, *Finland*

12.J.R. Hook, H.E. Hall, John Wiley & Sons. 1996, Effects of impurities on crystal growth processes, *Prog Crystal Growth and Charact*, 32: 3–43.

**13.**I.M. Pritula a,n, A.V Kosinova D.A.Vorontsov , M.IKolybaeva , O.N.Bezkrovnay Single CrystalsNASU,Kharkov61001,Ukraine ,Russia

# CHAPTER : 2

# CRYSTAL GROWTH METHOD

## 2.1) Introduction:-

Let us start with crystal; crystal is of the purest state of the matter. Regular arrangement of atoms and molecules, definite geometry ,advanced and interesting crystallographic properties this all differentiate crystalline substances from amorphous or glassy forms .Crystal shows some optical properties which is frequently used in instrumentation and research application . Natural crystals are formed by temperature, by crystallization from solution.

The father of crystal fabrication technology is A. Vermeil with his Flame fusion growth method is described in 1902.This was start of artificial formation of crystal. Then crystal are produced artificially to satisfy the need of science and technology .Crystal growth specialist tries to grow large size crystals and high quality crystal for that they always search new and advanced growth techniques. New materials are always lifeblood of solid state research and device technology.

Mostly that newly discovered materials are crystal. Single crystals are grown for the studies and understanding of different properties of those crystals. Hence there is need of growth of single crystal and also there is a need to develop such system or techniques of crystal we should get large good quality crystal in very few time.

## 2.2) Goal of crystal growth:-

The internal structure of the crystal can be studied by using X-rays diffraction. X-rays are electromagnetic radiation or waves. The wavelength of the wave is comparable to inter atomic distance in crystals, this is the reason that crystal diffracts X-rays and this diffraction is governed by Bragg's law which is familiar to us. We get spots or line pattern as a result of X-ray diffraction which is the characteristics of internal structure of that crystal .Hence basic requirement of this whole experiment is single crystal and growing of such a single crystal is a first goal. Next goal is to grow crystal of suitable size. The optimum size of crystal is one which has dimensions of 0.2-0.4 mm in at least two or three dimension.

## 2.3) Causes of crystal growth:-

The driving force for crystallization comes from the lowering of the potential energy of the atoms or molecules when they form bonds to each other.

The crystal growth process starts with the nucleation stage several atoms or molecules in a saturated vapor or liquid start forming cluster; the bulk free energy of the cluster is less than that of liquid or vapor. The total free energy of the cluster I increased by the surface energy (surface tension) however this is significant only when the cluster is small. The cluster of radius greater than $r^*$ i.e. critical radius will become stable, will increase its size by addition of the other atoms and thus "growing" eventually becomes a large crystal.

## 2.4) Crystal growth techniques:-

1) Slow evaporation (solution method).
2) Slow cooling.
3) Vapor diffusion.
4) Reactant diffusion.
5) Sublimation.
6) Convection.
7) Counter ions.
8) Ionization of neutral component.

## 2.5) slow evaporation method:-

Crystal growing is an art of many variations to the basic crystal growing recipes as there is crystallography. The recipes given below are ones which we have either tried or I have read about sound reasonable .The technologies chosen will largely depend on the chemical properties of the compound of interest.

Slow evaporation process is a simplest way to grow crystals and works best for compound which are not sensitive to ambient conditions of the laboratory. Prepare a solution of compound in a suitable solvent. The solution should be saturated or nearly saturated. Transfer a solution in a clean crystal growing dish and cover. The covering for the container should not be air tight. Aluminum foil with some holes poked in it works well or flat piece of glass with microscope slides used as a spacer also will do the trick. Place the container in a quit out of the way place and let it evaporate. This method works best where there is enough material to saturate at least a few milliliters solvent.

## 2.6) Literature Survey:-

1. **Zhuan Xinxinn: - [06]** have reported the growth of KDP crystals is significantly affected by the factors of growth environment Super-saturation is the most sensitive parameter.

2. **J.J.De Yoreo**: - **[08]** have been reported the rapid growth technique supplied us with the big crystals of low cost and equivalent optical quality as well.

**3. C.Maunier:- [09]** have reported **t**he quality of crystals depends on the intrinsic impurities contained in solutions and the integrity of the crystallization procedure.

## 1.9) Reference:-


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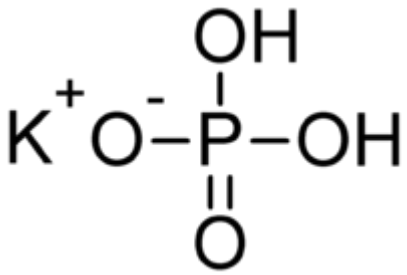
# CHAPTER : 3

## SOME PROPERTIES OF KDP CRYSTAL

| | |
|---|---|
| IUPAC name | Potassium dihydrogen phosphate |
| Other names |  <br>Potassium phosphate monobasic,<br>Phosphoric acid,<br>Monopotassium salt |
| Molecular formula | $KH_2PO_4$ |
| Molar mass | 136.1 g/mol |
| Appearance | White powder |
| Odor | Odorless |
| Density | 2.338 $g/cm^3$ |
| Melting point | 252.6 $^0C$ |
| Boiling point | 400 $^0C$ |
| Solubility in water | 22 g/100 mL (25 $^0C$) |
| Solubility | Slightly soluble in ethanol |

| | |
|---|---|
| Acidity ($pK_a$) | 7.2 |
| Basicity ($pK_b$) | 11.9 |
| Refractive index ($n_D$) | 1.4864 |
| Crystal structure | Tetragonal |

## 3.2) Reference:-


1. Text book of Physics Narendra Prakashan
2. Solid state Physics C. Kittle
3. Physical chemistry S. Y .B. Sc.
4. Solid State Physics Babbar & Puri
5. Crystal nucleation, solution growth and surface morphology.

# CHAPTER:4

# SEED CRYSTAL GROWTH BY SLOW EVAPORATION

## 4.1) Preparation of seed crystal:-

- **Aim**: Preparation of seed crystal by using KDP powder.
- **Requirements**: KDP powder, double distilled water, acetone, beaker, stirrer, stand, measuring cylinder, spoon, forceps etc.
- **Procedure:**

1) Wash all apparatus with water.
2) Clean the apparatus with cotton.
3) Then clean the apparatus with acetone.
4) Take 100ml distilled water with measuring cylinder in the beaker.
5) Stirrer the solution by stirrer in a beaker for uniform stirring of solution and add KDP powder spoon by spoon till the solution becomes super saturated.
6) Keep it for evaporation.
7) After 2 days evaporation the water gets dried up and remaining are the blocks of seed crystals.
8) Pick out the good seed crystals with the help of forceps and keep it for further the seed crystals growing doped in it's the saturated solution all the process done at the room temperature seed crystal images shown in the below figure.
9) After the 2-3 days seed is growing now speedily.

## 4.2) SEED CRYSTAL IMAGES:-

**Fig: seed crystal Images**

## 4.2) Literature Survey:-

**1**. **R. Krishnamurthy- [14]** has reported The KDP salt was dissolved in Millipore water (18.2 MX cm) in under saturation condition. The solution was stirred well for 6 hours continuously by using magnetic stirrer. 100 ml of this solution was taken in a beaker and the L-aspartic acid in molar percent (0.7 mol %) was added. The mixed solution was stirred for 2 hours.

**2. R. Rajasekaran - [14]** has reported the Potassium Dihydrogen Phosphate (KDP) doped with L-aspartic acid has been grown by solvent slow evaporation technique from a mixture of aqueous solution of KDP and 0.7% of L-aspartic acid at room temperature. The grown crystals were characterized by powder X-

ray diffraction, UV–visible, FTIR analysis. The doping of aspartic acid was confirmed by FTIR spectrum.

**3. M.A. Rhode - [15]** has reported the rapid growth technique has been developed to obtain single crystals from a supersaturated solution with high growth rates. This technique has been improved during the 90s to produce large KDP crystals for National Ignition Facility.

**4. Joaquin Zhang-[13]** has reported the KDP crystals were grown from the aqueous solution with different concentration of sulphate by both the traditional temperature-lowering method and the rapid growth method. Sulphate showed a great effect on the growth and the properties of KDP crystals. With the rise of the doping concentration, many defects occur such as mother liquid inclusions, parasite crystals and cracks. When the doping concentration of sulphate reaches a certain value, the ultraviolet transmittance of crystals decreases a lot compared with crystals at low doping concentration.

**5. I.M. Pritula-[16]** Single crystals of potassium dihydrogen phosphate group (KDP, DKDP, and ADP) have found wide use in nonlinear optics, optoelectronics and laser engineering. Due to high laser damage threshold and the possibility to grow large-size crystals, this material is the only one suitable for the making of wide-aperture multipliers of laser radiation frequency.

## 4.3) Reference:-

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[13]. Jianqin Zhang ∗ , Shenglai Wang, ChangShui Fang, Xun Sun, Qingtian Gu, Yiping Li, Bo Wang, State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, China.

[14] R. Krishnamurthy, R. Rajasekaran, Binky Susan Samuel, Physics Department, SKP Engineering College, Tiruvannamalai 606 611, India PG and Research Department of Physics, Govt. Arts College, Tiruvannamalai 606 601, India Bharathiyar University, Coimbatore, India

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# CHAPTER:5

# EFFECT OF ADDITIVES ON CRYSTAL GROWTH

## 5.1) Introduction:-

Impurities and quantification badly affects quality of the reaction product. Many times we follow systematic procedure for avoiding such as impurities like wearing a hand glozes, cleaning apparatus by acetone, sterilizing beakers. This is sufficient if there is no inherent impurity.

If there is impurity with reaction component then we should not remove impurity by above mentioned procedures. Hence for removing such impurities from solution concept of leg and are introduced. Legends are basically chemical compound in liquid and solid forms which are having very important property that the trap metal ion which are unwanted in the solution .After trapping they forms totally soluble complexes these are commonly known as cheats are not participating in to the reactions. Hence our reaction taking place into the purest medium, hence we get good results. In the crystal growth additives plays important role. Additives are the chemical substances which improves the quality and size of the crystal.

## 5.2) Effect of KCL & NAOH on crystal growth:-

Additives are used to grow crystal of good quality. There are different quality factors of the crystal like transparency, strangeness, elasticity, shape,

smooth faces, etc. Strength of the crystal is improved by using KCL as an additive. Growth rate of the crystal is also increases means crystal grows rapidly and we get large size of crystal.

When the added KCL in the saturated solution the fix amount. It increase saturation of the solution and increase the rate of cluster formation in the solution. When more is the cluster formation in the solution there will be rapid growth of seed crystal.

When we add NAOH in the saturated solution in definite amount it increases the PH of given saturated solution.

## 5.3) Growth of KDP by slow evaporation method:-

The principle of this theory is based on the concept of solubility and super saturation. How much amount of solute dissolved in the solvent at a specific temperature, that amount defines the solubility at that particular temperature. Hence we say that solubility is a function of temperature solubility and temperature is directly proportional to each other. By adding solute to solvent until there is no further dissolution of solute in the solvent is commonly called as saturated state. If saturated solution is prepared at a certain temperature and cooled to lower temperature, it contains more salts then permitted by solubility at the lower temperature. The same fact is observed when we allow solution to evaporate .Then the solution is in supersaturated state or meta-stable state. If “seed” crystal is introduced in to the solution, the cluster form the solution will grow around the seed crystal forming a larger single crystal. Even dust particles also provides nucleus for nucleation, hence we observed multiple nucleation. Slow growth rate, prevention of multiple nucleation we must control temperature. Hence, if we want good result we must maintain temperature.

- **Objectives:**

The objectives of this method are to grow large size, good quality and transparency of crystal.

- **Equipments:**

Glassware's like beakers, conical flask Filtration set up, measuring cylinder, stirrer, string, etc.

- **Experimental set up:**

**Fig. Experimental set up for crystal growing**

- **Experiment procedure:-**

1) Prepare a saturated solution with the magnetic stirrer at room temperature.
2) With the help of string tie the seed crystal and suspend it in the solution
3) Cover it with aluminum foil paper cap.
4) Leave it to evaporate for few days.

5) After three days solution should be changed as per growth is needed.

**KDP crystal (After growth):**

- **Note:**

  For preparing good quality crystals the addition of additive is introduced. We added NAOH additive separately and we observed effect of additives on quality and growth rate of KDP crystal. We added KCL additive separately and we observed effect of additives on transparency of KDP crystal. And we added both together and observe the effect.

- **Conclusion:**

1. We obtained crystal without any additives is not a good quality crystal.

2. We observed that when we add KCL as an additive growth rate increases, but we also observed that solution gets turbid in two or more days which lower the quality of the crystal.

3. We also observed that the transparency of KDP crystal is increased by adding KCL solution,

## 5.4) Measurement: -

- ***Observation Table***

| Sr.No | Crystal Name | Pure KDP Solution | KDP + +EDTA Solution/KCL | Days of Reading | Length of Crystal(cm) | Size Of Crystal (cm) |
|---|---|---|---|---|---|---|
| 1 | **A** | **0.6** | **0.65** | **1** | **1.3** | **0.27** |
| 2 | **B** | **2.33** | **3** | **5** | **1.5** | **0.2** |

# CHAPTER : 6

## CHARACTERIZATION TECHNIQUES

## 6.1 Introduction:-

This chapter describes various experimental techniques used in the present investigations for the characterization thin films. Thin films are widely used in electronic, optical and magnetic devices; its structure, surface morphology and nature of crystallites/grains have a prime importance in deciding the suitability of the materials for above mentioned applications. In order to study the different properties of these semi conducting materials in the form of crystal, various characterization techniques are used. These techniques include thickness measurement, structural morphology by X-ray diffraction (XRD), Surface morphology by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM), Optical absorption and transmission by UV-VIS spectrophotometer, Electrical resistivity measurement, I-V characteristics, TEP etc. Following sections describe these methods.

## 6.2 Characterization techniques:-

### 6.2.1 X-Ray Diffraction (XRD):-

X-ray diffraction (XRD) is well known technique to obtain the information of composition, phase and crystallite orientations of the material. Structure

identification, determination of lattice parameters and grain size are based on the X-ray diffraction pattern. Improved detection methods for X-ray, the availability of commercial mono-chromates and intense micro focus X-ray sources have made X-ray diffraction method applicable to film as thin as 100Å. The several workers have described X-ray diffraction arrangement, suited to study of thin films. This technique employs a chromate to provide a diffracted beam, which is further diffracted from the crystal surface oscillating about the mean diffraction position. The X-ray diffraction technique based on monochromatic radiation is more important because the spacing of the planes can be deduced from the observed diffraction angles. The phenomenon of X-ray diffraction can be considered as reflection of X-rays from the crystallographic planes of the material and is governed by the Bragg's equation;

$$2d \sin\theta = n \lambda \qquad (01)$$

Where, d is lattice spacing, λ is the wavelength of the monochromatic X-ray, n is the order is diffraction and θ is diffraction angle. The'd' values are calculated using above relation for known values of θ, λ and n. the X-ray diffraction data thus obtained is compared with American Standards for Testing of material(ASTM) powder diffraction data to identify the unknown material. The sample used may be powder, single crystal or thin film.

The crystallite size (D) of the deposits is estimated from the full width at half maximum (FWHM) of the most intense diffraction line by Scherer's equation as follows.

$$D = \frac{k\lambda}{\beta \cos\theta} \qquad (02)$$

Where, D is crystallite size, λ is wavelength of X-rays used (Cu Kα 1.0542 A$^o$), β is full width of half maxima of the peak (FWHM) in radians, θ is Bragg's angle and K is constant. Value of K varies from 0.89 to 1.39, but for most cases

it is closer to 1. Though this technique is applicable for determination of crystal structure, lattice parameters, particle size etc, it is not useful for identification of individuals of multilayer or percentage of doping material.

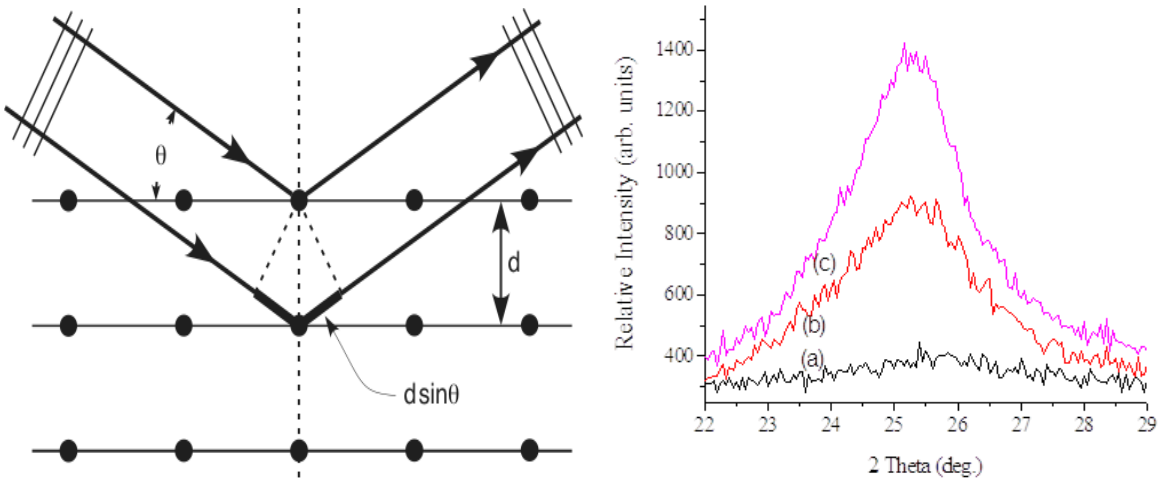


Figure. 3.1 Bragg's diffraction by using X-ray and XRD graph with intensity variation

### 6.2.2 UV-Vis spectroscopy:-

It involves the spectroscopy of photons & spectrophotometer. It uses light in the visible & adjacent near ultraviolet & near infrared ranges. In this region of energy molecules of space undergo electrons transitions. UV/Visible spectroscopy is routinely used in the quantitative determination of solution in the transition metal ions & highly conjugated organic compounds.

1) Solution of transition metal ions can be colored (i.e. absorb visible light) with 'd'-electrons within the metal atoms can be excited from one electronic state to another. The colors of metal ions solution in strongly affected by the other species such certain anions or legends.

2) Organic compounds also absorb light in the UV or visible regions of the electromagnetic spectrum solvents for these determinations are often water for water soluble compounds or ethanol for organic soluble compounds.

3) It is well known that one of the subatomic particles of an atom is the electron. The electrons carry a negative electrostatic charge and under certain conditions can move from atom to atom. The direction of movement between atoms is random unless a force causes the electrons to move in one direction. This directional movement of electrons due to an electromotive force is known as electricity.

1. Ions solution in strongly affected by the other species such certain anions or legends.

2 the value of wave vector K for elements remains unchanged in E-K space and momentum also does not change, while in indirect inter band transition the wave vector K for electros changes in the E-K. It is possible to differentiate the nature of optical transition as direct allowed or direct forbidden by classical relation

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \qquad (03)$$

### 6.2.3 Electrical study:-

I-V characteristic curves are generally used as a tool to determine and understand the basic parameters of a component or device and which can also be used to mathematically model its behavior within an Electronic Circuit. But as with most electronic devices, there are an infinite number of i-v characteristic curves representing the various inputs or parameters and as such we can display a family or group of curves on the same graph to represent the various values.

It is well known that one of the subatomic particles of an atom is the electron. The electrons carry a negative electrostatic charge and under certain conditions can move from atom to atom. The direction of movement between atoms is random unless a force causes the electrons to move in one direction.

This directional movement of electrons due to an electromotive force is known as electricity.

## 6.3 References:-

[1] JCDF cards No. 03-065-3414.

[2] H.K. Sadekar et. al, Composites: part B 44 (2013) 553-557.

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# CHAPTER:7

## RESULTS AND DISCUSSIONS

### 7.1 X- Ray diffraction:-

Structural characterization of the crystal was analyzed from the XRD patterns. Fig. 7(a) shows the diffraction patterns for the pure KDP crystal. From the figure, all the peaks present were identified as diffractions the highest point from (2 0 0), (1 1 3) and (1 2 4) all of show the Fig. 7(a).

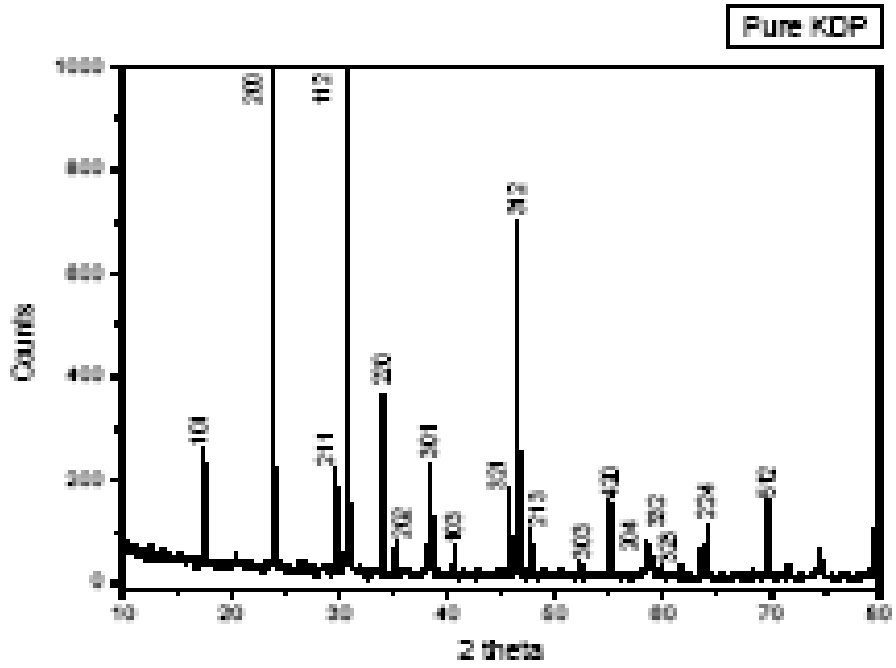


*Fig 7(a). XRD pattern of pure crystal KDP*

The lower graph shown the 1 molar KCL solution doped KDP crystal was analyzed from Fig 7(a) shows the diffraction pattern for the doped KDP crystal. From the figure, all the peaks present were identified as diffractions the highest point from (2 0 0), (1 1 2) and (3 1 2) all of show the Fig. 7(a)

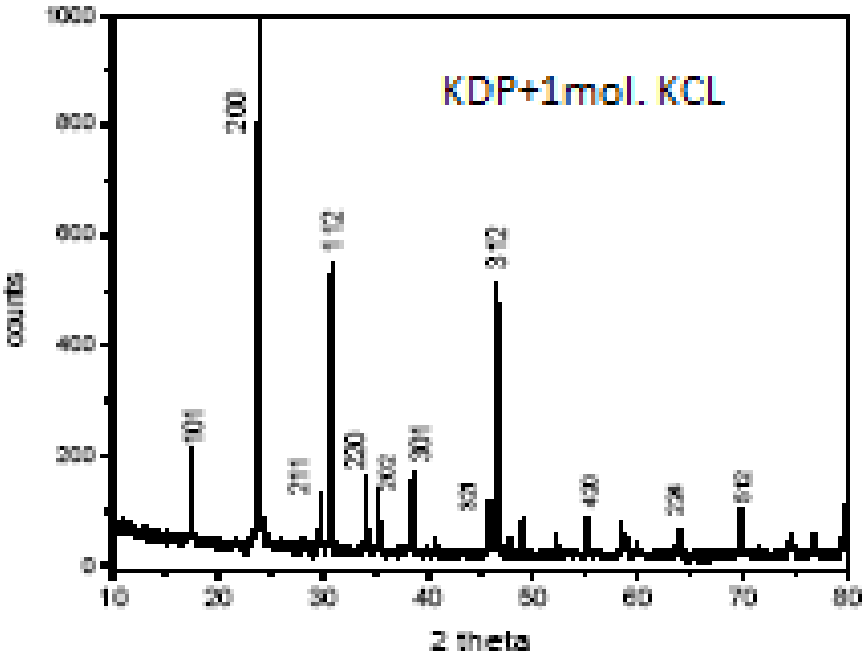


*Fig 7(b). XRD pattern of crystal and 1moler KCL doped KDP.*

The average crystallite size was evaluated from the peak broadening analysis using the Scherer equation [02],

$$t = \frac{0.9\lambda}{\beta \cos\theta}$$

Where, t = Crystallite size (Å).

λ = wavelength of incident X-ray.

B = full width half maxima (FWHM) ,

$\theta$ = angle of diffraction,

0.9 = constant

The average crystallites size was estimated around the approaches the nm.

## 7.2 Optical Analysis:-

Optical characterization was carried out with the help of UV-VIS absorption spectrophotometer (JASCO-UV-VIS-NIR Spectrophotometer; model V-670). Optical absorption measurements are essential for the understanding of the band gap of any semiconducting material. The optical absorption spectra of the film were recorded in the wavelength range 200-1200 nm. Figure7. (c) Shows optical absorption and transmission spectra of as-deposited KDP crystal. The result shows an optical transmittance over 50% in the visible region. Absorption spectra shows that for 1 molar KCL doped KDP the edge green condition shifted as compare to pure KDP crystal as shown below fig.

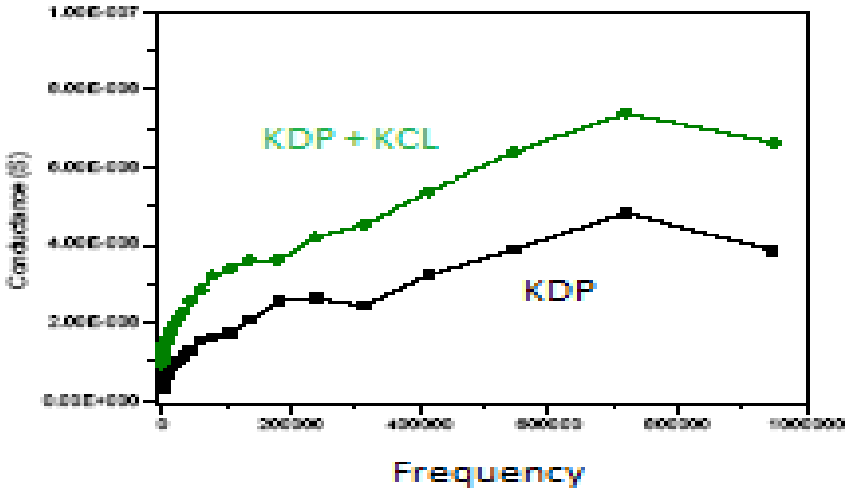


**Fig.7. (c).** Plot of conditions (%) versus Frequency

The relation between the absorption coefficient α and the incident photon energy (hν) can be written as [03],

$$\alpha h\nu = A(h\nu - E_g)^n$$

Where 'A' is constant, n= ½ for direct allowed transition, '$E_g$' is optical band gap of the material. Fig. 7.(b) shows the plot of $(\alpha h\nu)^2$ against (hν) for CdS thin film derived from the absorbance spectra. Extrapolating the straight-line portion of the plot of $(\alpha h\nu)^2$ vs (hν) for zero absorption coefficient value gives the band gap, which is found to be 2.44 eV at room temperature.

## *7.3* References:-


[4] JCDF cards No. 03-065-3414.

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# CHAPTER : 8

APPLICATIONS

1. Crystal growth finds application ranging from jeweler industries to commercialized electronic markets where silicon crystals if purest form are of great importance.
2. With the help of crystal growth technique we can go for characterization of substance. As crystals is the most pure form of the substance occurring in nature. Based on the properties crystals can be used for various applications.
3. In particular KDP crystals are used as Electro Acoustic Transducers. It is used for electro optical application as Q switches for Nd -YAG lasers.

4. Crystal growth finds application ranging from industries to commercialize electronic markets where silicon crystal if purest form are of great importance.

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