

**SYNTHESIS AND CHARACTERIZATION OF SOME HALIDES AND
CHALCOGENIDE CRYSTALS USING SOL-GEL METHOD.**

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**A Thesis submitted in partial fulfillment of the requirement for the
award of the degree of Doctor of Philosophy (Ph.D) in the
department of Physics and Astronomy, University of Nigeria,
Nsukka.**

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Certification

Mr. U.V. Okpala, a postgraduate student in the Department of Physics and Astronomy with registration number PG/Ph.D/05/39463 has satisfactorily completed the requirement for research work for the degree of Doctor of Philosophy (Ph.D) in Physics and Astronomy with emphasis on Solar Energy Physics.

The work embodied in this thesis is original and has not been submitted in full or part thereof for any other diploma or degree or professional qualification of this or any other university.

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Dedication

This work is dedicated to my wife, children, brothers and sisters for their immense contributions, support, patience and understanding in various aspects and to my beloved father and mother who longed to see me graduate but are no more.

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I thank and praise Almighty God who made it possible for me to see the end of this work in spite of all odds from high and low places. I wish to sincerely thank my able supervisor, Prof. Mrs. R.U. Osuji for her understanding, support and encouragements. My resounding gratitude goes to Dr. F.I. Ezema and Prof. J.O.Urama for their wonderful supports.

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Abstract

In this research work, sol-gel technique was used to grow some crystals of halide and chalcogenide compounds. These grown crystals were doped with locally produced dopants from bamboo, raffia and potash to see how they can affect the optical and structural properties of the crystals. Dopants were produced from local materials using top down approach where bulk materials (bamboo, potash and raffia) were whittled down through burning into carbon dioxide, water and residual ashes containing a lot of elemental carbon in the form of soot. The residual ashes were dissolved in water, placed in a centrifuge to remove solid particles. Appropriate quantity of the supernatant liquid was added to the gel as dopant. In some growths, the gel was allowed to age at room temperature for periods of 5, 15 or 25 days before they were dried in an oven at a temperature of 104°C for 30 minutes. CaCl₂ was used as desiccant. Subsequently, they were characterized to determine their optical and structural properties using a JENWAY 6405 UV-VIS spectrophotometer operating at a wavelength range of 200nm to 1200nm at intervals of 5nm and MD-10 Diffractometer, X-ray diffraction machine respectively. The X Ray Diffraction (XRD) and Fourier Transform Infra Red (FTIR) spectroscopy showed that the locally made dopants are crystalline, nano polymers. The presence of locally produced dopants have enabled us to grow and discover hybrid compounds of binary, ternary and quaternary constitutions; Halloysite [Al₂Si₂O₅(OH)₄·2H₂O], Sekaninaite (Fe₂Al₄Si₅O₁₈), Illite [K_{0.7}Al₂(Si,Al)₄O₁₀(OH)₂], Moganite (SiO₂), Ungarettite (Na₃Mn₅Si₈O₂₄), Clinoferrosilite (FeSiO₃), Wollastonite (CaSiO₃), coesite (SiO₂), Vanthoffite [Na₆Mg(SO₄)₄] that can be employed in solar energy, solid state and materials industries. Therefore, we suggest that African materials be used in the growing of crystals for further discoveries and enhanced output.

CHAPTER ONE

1.1INTRODUCTION

Today, solid state physicists and materials scientists have found pure crystals veritable asset; in the investigation of radiation damage, super conductivity, nuclear and electron resonance and for research into molecular structure. Due to advancement in electronic technology, transistors and chips have replaced the valves in every sphere of electronic/solid state industry because they have the great advantage of reduction in size by not requiring heated cathodes, hence they are portable. In the manufacturing of the aforementioned materials, kilograms of semiconductors are extracted, purified and grown into crystals. These crystals are used in the manufacture of diodes, rectifiers, scintillators, particle counters, thermo electric generators, coolers and solar cells etc.

A greater percentage of photovoltaic cells in the market today are made of wafers of high grade silicon. The high cost of silicon solar cells and their complex production process have generated interest in developing alternative photovoltaic technologies. Compared to silicon based devices, polymer solar cells are light weight, potentially disposable, inexpensive to fabricate, flexible, customizable on molecular level and have lower potential for negative environmental impact [1]. These grown crystalline materials are employed in the manufacture of phosphorescent and fluorescent screens, solar energy converters, detectors for visible and infra-red radiation [2]. Nigerians have engaged in growing and characterizing thin films that can be used in solar energy applications [3, 4, 5, 6].

This research work is concentrated to the use of the sol-gel technique to grow some crystals of halide and chalcogenide compounds. Halides are binary compounds of which one part is a halogen and the other part is an element or radical that are less electronegative than halogen. A chalcogen is a chemical compound consisting of at least one chalcogen ion and one or more electropositive element. Chalcogen is reserved for sulphides, selenides and telluride.

1.2. HALIDES AND CHALCOGENIDE CRYSTALS.

The halide and chalcogenide crystals grown in this work are lead chloride (PbCl_2), potassium perchlorate (KClO_4), stannous iodide (SnI_2), stannic iodide (SnI_4) and cadmium chloride (CdS)

a. Lead Chloride Crystal (PbCl_2).

Lead chloride occurs naturally in the form of mineral cotunnite. It is used in the production of infra red transmitting glass and basic chloride of lead known as pateson's white lead [7], ornamental glass called aurene glass and stained glass. It is also used as an intermediate in refining bismuth (Bi) ore, it is used in the synthesis of organometallic (metallocene or plumbocenes), lead titanate and barium titanate [8,9]. The structure of PbCl_2 is orthorhombic dipyramidal.

b. Potassium Perchlorate Crystal (KClO_4).

Potassium Per chlorate (KClO_4) is a colourless rhombus which is slightly soluble in water. The solubility at 0°C is 0.75gm per 100gm of water and is less soluble in aqueous ethyl alcohol. It is used in the separation of the former and acts as a reagent, oxidizing agent, pyrotechnic (manufacture of fireworks), antipyretic (drug relieving fever), sedative (B.P), propellants and source of oxygen [10,11].

c. Stannous Iodide (SnI_2).

Stannous Iodide also known as tin (II) iodide is an ionic compound of tin and iodine. It is a red- orange solid [12].

d. Stannic Iodide (SnI_4).

Stannic iodide also known as tin iv iodide is a tetrahedral molecule that crystallizes as a bright orange solid that dissolves readily in solvent such as benzene [13].

e. Cadmium Sulphide (CdS).

Cadmium sulphide is a semi conductor material of yellow colour. It exists in nature as two different minerals, hexagonal greenockite and hawleyite [14]. It is a direct band gap semiconductor (2.42eV) and has many applications, example in light detectors [15].

1.3. IMPURITIES OF LOCALLY PRODUCED MATERIALS (Bamboo, Raffia, Potash).

The advancement in nanotechnology has called for the manipulation of the chemistry of materials. Nano technology is the engineering and fabrication of materials with structures smaller than 100nm or one tenth of a micron. A nano metre is one over one million or one thousandth of a micron. It is about the size of six carbon atoms aligned or 10 hydrogen atoms. It is also about 60,000 times smaller than the diameter of a human hair. In nano technology manufacturing we use either top-down or bottom-up [16]. Top-down manufacturing starts with bulk materials which are whittled down, until the feature are left in nanoscale. Bottom up involves creating materials from individual atoms or molecules and then joining them together in a specific fashion. In this

research work locally made materials were produced using top-down approach [16].

Wood is largely made up of cellulose, which is in turn composed of repeating units of glucose, a simple sugar. Cellulose is composed of carbon, hydrogen and oxygen. When wood is burnt, the cellulose is oxidized to carbon dioxide and water. The remaining ashes contain a lot of elemental carbon in the form of soot. Soot is a colloidal carbon. It is in nano dimensions and has been used for centuries as pigments in inks, paints and as a reinforcing agent in rubber (tires). It is an approximate perfect black body and as such can be widely employed in solar energy technology. This has prompted us in this research work to consider locally produced materials of about nanostructure to see how they will permeate into the fabrics of known crystals [16].

(a) **Bamboo**

Bamboo is the most marvelous plant in nature. Bamboo is stronger than wood or timber in tension and compression. Chemical analysis reveals that bamboo has about 1.3% ash, 4.6% ethanol-toluene, 26.1% lignin, 49.7% cellulose, 27.7% pentosan [17]. In Hiroshima, Japan the only plant which survived the radiation of the atomic bomb in 1945 was a bamboo plant. In Costa Rica, a building made with bamboo withstood earthquake. It is used in many applications viz; in building it can be used as roof, floor, walls, scaffolds and supports in road construction as bridges. In power generation bamboo is used as check dams in rivers and in agriculture as organic fertilizer and preservative medium. Its charcoal absorbs radiation like nuclear reactor etc [18].

(b) Raffia

The epidemis of the leaflet is the fiber and has been used to fabricate many ethnographical items [19]. Scanning electron microscopy revealed a layered structure: a top layer with a tile-like structure and a bottom layer with a honey comb-like structure. X-ray diffraction shows the presence of cellulose I_B with crystallinity index of 64%. The fiber density is 0.75±0.07, conferring to it the highest known specific mechanical properties among all vegetable fibers [20].

(c) Potash

Potash is a term coined by early American settlers who produced potassium carbonate by evaporating water filtered through wood ashes. The ash like crystalline residue remaining in the large iron pots was called potash and was used in making soap. Potash (or carbonate of potash) is an impure form of potassium carbonate (K₂CO₃) mixed with other potassium salt. Potash has been used since antiquity in the manufacture of soap, glass and fertilizer [21]. Local potash is got by burning woods like tree fiber (ngu).

1.4. PURPOSE OF STUDY

In this research work, crystals of some halides and chalcogenide compounds (PbCl₂, KClO₄, CdS, SnI₂, SnI₄) were grown. Impurities of locally produced materials (bamboo, raffia and potash) of about nanometer dimensions were added to see how they permeate into the fabrics of the crystals and whether applications of thin films would be optimized. After the growth, the films were characterized to determine:

- The film structure,

- The optical properties of the film such as the spectral absorbance, transmittance and reflectance,
- The morphology and structural properties of the grown crystals.

1.5. SCOPE OF THE STUDY

This study was limited to the use of sol gel method of thin film growth because it required:

- No sophisticated equipment for the deposition.
- No heating or externally applied field.
- Cheap and available chemicals and reagents.
- Ambient pressure and temperature.
- Reproducibility and relative uniformity of thin film composition and thickness.
- Densification at a much lower temperature
- Easy control over the film composition
- Easy fabrication of large area thin film with low cost.

CHAPTER TWO

LITERATURE REVIEW

THIN FILM DEPOSITION METHODS

2.1. INTRODUCTION

Thin films are material layers ranging from fractions of a nanometer to several micro metres in thickness [22]. Several deposition techniques have been adopted in the growth of thin films. Thin film deposition is the technique for depositing a thin film of a material unto a substrate or unto previously deposited layers or by liquid based growths. [23]. The deposition processes consist of three major steps: (i) generation of growing species- atom by atom or molecule by molecule or ions by ions (ii) transport of species from source to substrate and (iii) film growth on the substrate.

The process of growing thin films can generally be grouped into two, thus; Vapour Phased Deposition which includes, Evaporation, Molecular Beam Epitaxy (MBE), Sputtering, Chemical Vapour Deposition(CVD) and Atomic Layer Deposition (ALD) and Liquid Based Growth which includes Chemical Solution Deposition, Electrochemical Deposition, Chemical Bath Deposition(CBD), Successive Ionic Layer Adsorption and Reaction (SILAR), Langmuir- blodgett films and Self Assembled Monolayers (SAM) and Sol gel method [24,25].

2.2. VAPOUR PHASED DEPOSITION.

There are several vapour phased deposition techniques which we shall briefly outline.

(a) Evaporation.

This is a common method of thin film deposition. The source is evaporated in a vacuum. The vacuum allows vapour particles to travel directly to the substrate where they condense back to solid state. Evaporation is used in micro fabrication and to make micro-scale products such as metalized plastic films. In evaporation, a hot source material evaporates and condenses onto the substrate. Evaporation takes place in a vacuum. In high vacuum, evaporated particles can travel directly to the deposition target without colliding with the background gas [26].

(b) Molecular Beam Epitaxy (MBE)

Molecular beam epitaxy is widely used in making commercial electronic devices. In molecular beam epitaxy, slow streams of an element can be directed at the substrate so that material deposits one atomic layer at a time. It is essentially a refined Ultra-High Vacuum (UHV) evaporation method of preparing high quality thin film materials and structures for fundamental studies as well as device application [27,28].

(c) SPUTTERING TECHNIQUE

Sputtering technique is used to deposit thin films of material onto a surface (substrate) by creating gaseous plasma and then accelerating the ions from this plasma into some material. The material sputtered from the target reacts with the gas via energy transfer and is ejected in the form of neutral particles-either by individual atoms, cluster of atoms or molecules. As these neutral particles are ejected, they will travel in a

straight line unless they come in contact with something say silicon wafer (Si) they will coat it [29]. This technique has been used for the deposition of oxides of metals and semiconductors [30, 31].

(d) CHEMICAL VAPOUR DEPOSITION (CVD)

This is a chemical process used to produce high purity, high performance solid materials. Chemical Vapour Deposition (CVD) generally uses a gas phase precursor of halide or hydride of the element to be deposited with other gases to produce a volatile solid that deposits atomistically on a suitably placed substrate [32]. The type of precursor used, the deposition conditions applied and the form of energy introduced to the system to activate the chemical reactions desired for the deposition of solid films on substrates determine the various methods of CVD developed. For instance, Metal Organic CVD (MOCVD) is a process in which metal-organic compounds are used as precursor and Plasma Enhanced CVD (PECVD) is one in which plasma is used to promote chemical reaction. We also have Low Pressure CVD (LPCVD), Laser Enhanced or Assisted CVD and Aerosol Assisted CVD (AACVD) [33]

(e) ATOMIC LAYER DEPOSITION

Atomic layer deposition is a thin film deposition technique that is based on the sequential use of a gas phase chemical process. The majority of ALD reactions use two chemicals, typically called precursors. These precursors react with the surface one at a time in a sequential manner, by exposing the precursors to the growth surface repeatedly; a thin film is deposited [34]. ALD is a self limiting (the amount of film

materials deposited in each reaction cycle is constant), sequential surface chemistry that deposit conformal thin films of materials onto a substrate of varying compositions [35,36].

2.3. LIQUID BASED DEPOSITION TECHNIQUES.

There are several liquid based thin film deposition techniques. We shall briefly outline them.

(a) CHEMICAL SOLUTION DEPOSITION.

Chemical Solution Deposition (CSD) uses a liquid precursor usually a solution of organometallic powders dissolved in an organic solvent. This is a relatively inexpensive, simple thin film deposition process that is able to produce stoichiometrically accurate crystalline phases [37].

(b) ELECTROCHEMICAL DEPOSITION TECHNIQUE.

Electrochemical deposition is regarded as a special electrolysis resulting in the deposition of solid material on electrode. Often, a solution of water with a salt of the metal to be deposited is used [38]. This process involves (i) oriented diffusion of charged growth species through a solution when an external field is applied and (ii) reduction of the charged growth species at the growth or deposition surface which also serve as an electrode. Electrochemical deposition only applies to electrical conductive materials such as metals, alloys, semiconductors and electrical conductive polymers. Electrochemical deposition is widely used in metallic coatings through the process known as electroplating [39].

(c) CHEMICAL BATH TECHNIQUE (CBD)

This technique which is often times referred to as electro less deposition, autocatalytic deposition or solution growth technique has been well known as a prevalent low temperature aqueous technique for depositing large area thin films of semiconductor. The principles of direct deposition of films through CBD technique is based on a gradual release of metal ions from supersaturated solution. A chelating agent is usually used to limit the hydrolysis and precipitation. It is used for the deposition of both conducting and non conducting layers from solution by electrochemical processes, without application of external fields [40]. The optical properties of CuS and NiO thin films have been studied using this method [41,42].

(d) SUCCESSIVE IONIC LAYER ADSORPTION AND REACTIONS (SILAR).

This is relatively new and can be used to deposit thin films on substrates at room temperature. It involves immersing a substrate into separate cations and anions precursor solutions and rinsing with purified water after each immersion [43]. This method has been used by researchers in depositing thin films [44].

(e) SELF ASSEMBLED MONOLAYER (SAM).

A Self assembled monolayer (SAM) is an organized layer of amphiphilic molecules in which one end of the molecule the head group shows a special affinity for a substrate. SAMs also consist of a tail with a functional group at the terminal end. SAMs created by chemisorptions of hydrophilic head groups onto a substrate from either the vapour or liquid phase [45] followed by a slow two dimensional organization of

hydrophilic head group [45]. Initially, adsorbate molecules from either a disordered mass of molecules or form a lying down phase [46] and over a period of hours, begin to form crystalline or semi crystalline structure on the substrate surface [47,48]. The hydrophilic head group assemble together on the substrate, while the hydrophilic tail groups assemble far from the substrate. Areas of close-packed molecules nucleate and grow until the surface of the substrate is covered in a single monolayer.

Adsorbate molecules adsorb readily because they lower the surface energy of the substrate and are stable due to strong chemisorptions of the head groups. These bonds create monolayers that are more stable than the physisorbed bonds of Langmuir- Blodgett films [49,40].

(f) SOL-GELL

The interest in sol-gel processing can be traced back in the mid 1880s with the observation that the hydrolysis of tetraethyl orthosilicate (TEOS) under acidic conditions led to the formation of SiO_2 in the form of fibres monoliths [51,52]. Sol- gel process is a wet chemical technique widely used in the fields of materials science and ceramic engineering primarily for the fabrication of materials starting from a chemical solution which acts as the precursor for an integrate network (or gel) of either discrete particle or network of polymers [53]. In sol- gel typical precursors are metal alkoxides and metal chlorides which undergo various forms of hydrolysis and polycondensation reactions. The formation of a metal oxide involves connecting the metal centre with oxo (M-O-M) or hydroxo (M-OH-M) bridges, therefore, generating metal-oxo or metal hydroxo polymer in solution. The sol evolves towards the

formation of a gel like diphasic system containing both a liquid phase and solid phase whose morphology range from discrete particles to continuous polymer networks. A gel is, ña colloidal system in which the dispersed substance forms a continuous, ramifying, space-enclosing cohesive framework [54]. The gel medium prevents turbulence, and remaining chemically inert, provides a three-dimensional structure which permits the reagents to diffuse at a desirable controlled rate.

A disperse system is defined as a system in which one substance (the disperse phase) is dispersed as particles throughout another (the dispersion medium or continuous phase). Often times, mixtures of substances which are obtained are so fine-grained that the constituents cannot be distinguished by the eye, even with a microscope. Such mixtures are known as colloidal systems. A colloidal system is that consisting of two phases; a disperse phase and a dispersion medium. A disperse phase is that forming the particles and the dispersion medium is that in which dispersion of particles take place. Colloidal solutions are known as sols. If the dispersion medium is water they are called hydrosols or aqua sols. If in a liquid as dispersion medium, the disperse phase is the liquid, the colloidal solution is known as emulsion. There are two types of colloidal systems; lyophobic (solvent hating) and lyophilic (solvent loving). In lyophobic sols there is little or no affinity between the disperse phase and the dispersion medium but in lyophilic sols there exist definite affinity between the disperse phase and the dispersion medium. Colloids have optical properties, Brownian movement and electrical properties. In exhibiting optical properties colloids tend to scatter light very well. The motion of colloids under the action of an electric field is called electrophoresis.

The particles of the colloids on further reactions coagulate or flocculate into globules of aggregate loose mass to form gel. That is gels are formed by interlocking of the disperse particles in the form of a loose framework inside which liquid dispersion medium is contained. A gel is a colloidal system in which the disperse phase forms a continuous ramifying space enclosing cohesive framework. There are four methods for the production of gels-

- (a) Flocculation of lyophilic- colloids by salts or precipitating liquids.
- (b) Evaporation of certain colloidal solutions
- (c) Chemical reactions that lead to change in shape of lyophilic molecules (e.g. the denaturation of albumen on heating involves some uncoiling of the protein molecules and a gel structure results).
- (d) Swelling of a dry colloid (xerogel) when placed in contact with a suitable liquid (e.g. starch granules added to water).

The presence of a network formed by the interlocking of particles of the gelling agent gives rise to the rigidity of a gel. The nature of the particles and the type of form that is responsible for the linkages determine the structure of the network and the property of the gel.

The following are the properties of gel; (i) swelling (ii) syneresis (iii) Ageing (iv) rheological properties.

- (i) Swelling occurs if a xerogel is placed in contact with a liquid that solvates it, then an appreciable amount of the liquid is often taken up and the volume of the xerogel increases.
- (ii) Syneresis occur when gels contract spontaneously and exude some of the fluid medium and the degree to which it occurs

usually decreases as the concentration of the gelling agent increases.

- (iii) Ageing occurs when colloidal system exhibit slow spontaneous aggregation. Ageing results in the gradual formation of a denser network of gelling agent.
- (iv) Rheological properties occur when the gel exhibits mechanical properties of rigidity, tensile strength and elasticity that are characteristic of solids.

Aerogels are sol-gel derived solid materials with porosities from about 80-98%. The high porosity is achieved through supercritical drying of wet gel in an autoclave [55,56]. Sol gel is used in the manufacture of multi component glasses, coatings, fibres monoliths, thermal insulation materials, controlled particle size powders, as well as special types of ceramics such as electronic ceramics, superionic conductors and high temperature superconductors [57,58].

Sol gel technique also favours the study of physical, chemical, electrical and magnetic properties of some materials. Bandgopadhyay et al. 59, studied the optical transmittance and reflectance spectra of undoped and aluminum doped zinc oxide films prepared by sol-gel technique and analyzed it from different aspects. The band gap increased with aluminum doping from 3.19 to 3.24eV. Gracium et al. 60, studied the pore walls of columnar type porous silicon (PS) samples of different porosity coated by SnO₂ using sol-gel technique. The Sn signal in RBS spectra revealed that the poles are completely filled with good depth homogeneity. Yoshihara et al. 61, prepared photo catalytic film

using electrophoretic sol-gel deposition. Sol-gel deposition was introduced to immobilize the TiO_2 photocatalytic activity without successive heat treatment. It then showed that non-heated coated films showed high photocatalytic activity because they respond effectively for light, which attributed to the nano-structure of the deposited film. Li-Pin et al. 62, studied the wood surface modification by in-situ sol-gel deposition of hybrid inorganic-organic thin films on wood using a mixture of metal-organic precursors and its effect on weathering properties of the wood surface using sol gel and it was found that wood surfaces coated with sol-gel deposits have enhanced durability when exposed to sunlight and moisture. Mandla et al. 63, studied the sol-gel deposition of inorganic alkoxides on wood surfaces to enhance their durability under exposure to sunlight and moisture. Wood specimens were coated with sol-gel deposits of aluminum isopropoxide, titanium isopropoxide, or zirconium propoxide in the presence of methyltrimethoxysilane. Both zirconium propoxide and titanium isopropoxide sol-gel deposits reduced water sorption compared with uncoated wood specimens. Their differences are ascribed to differences in the distribution of the sol-gel deposits within the surface wood cell walls. Dosch et al. 64, studied single-step sol-gel deposition process that took over from the existing gas-based coating techniques such as chemical vapour and flame-hydrolysis deposition. A sol is synthesized by the hydrolysis and polycondensation of the silicon precursor tetraethoxysilane. A controlled chemistry ensured that the well dispersed silica units have a tailored size distribution. Additives determine the surface properties of the silica units. Ge, Ti and Pb control the refractive index of the glass layers; P and B modify the thermal expansion and

flow properties of the layers. The doping of the silica layers allows the refractive index to be tuned from 1.45 to 1.50 a commercial spinner coats silicon substrate with the sol is then dried. Sintering at 105⁰-1200⁰C depending on the composition, produced optical quality glass layers up to 10µm thick. The absence of impurities in the deposited silica is as deposited on 304 stainless steel by sol-gel method using Zirconium propoxide as precursor and densified in air and in oxygen free (argon or nitrogen) atmosphere. XRD and IR data of the films were practically independent of the atmosphere used in the densification step showing that ceramic oxide is properly formed from the precursor. The corrosion behaviour of the stainless steel substrate was studied by potentio- dynamic polarization curves in the absence and the presence of ZrO²⁻ coatings prepared in air, argon or nitrogen. The coatings extended the lifetime of the material by a factor of almost eight in a very aggressive environment, independently of the preparation procedure.

Funakoshi et al. 65, studied the formation of anatase titanium dioxide (TiO₂) photocatalytic thin films on glass slide and commercial dental mirror substrate surfaces by a hydrolysis of titanium alkoxide and the hydrophilicity, the degree of oxidizing powder and transparency of anatase (TiO₂) coated substrate surfaces. The contact angle of water and decomposition rates of methylene blue on the anatase (TiO₂) photocatalytic thin films improved with the increasing duration of a tetraethyl orthotitanate (TEOT) hydrolysis but they hardly changed for the longer duration. The reflectance of anatase (TiO₂) photo catalytic thin films coated on glass slide substrate surfaces was higher as the duration of a TEOT hydrolysis increased. Similar tendencies concerning hydrophilicity and transparency were organized in cases of commercial

dental mirror substrate surfaces. A hydrolysis of titanium alkoxide obtained super hydrophilic and antibacterial treatments with excellent transparency on commercial dental mirror substrate surfaces. Jung et al. 66, epitaxially grew anatase TiO_2 thin films on LaAlO_3 (LAO) substrates at a temperature as low as 350°C using a simple sol-gel process. X-ray diffraction and high resolution transmission electron microscopy showed that anatase films have the epitaxial relationship of $(001) \text{TiO}_2 // (001) \text{LaAlO}_3$. While the low temperature growth of the anatase film yielded a residual strain, subsequent annealing at higher temperatures can remove the strain and recover the lattice parameters of a perfect anatase crystal. Measurements of the oxygen content in the anatase films by incorporation of oxygen and annihilation of oxygen vacancies. Jung et al. 67, grew epitaxial anatase thin films on single-crystal LaAlO_3 substrates by sol-gel process. The epitaxial relationship between TiO_2 and LaAlO_3 was found to be $[100] \text{TiO}_2 // [1000] \text{LaAlO}_3$ and $[001] \text{TiO}_2 // (001) \text{LaAlO}_3$ based on x-ray diffraction and a high-resolution transmission electron microscopy. The epitaxial anatase films show significantly improved photocatalytic properties, compared with polycrystalline anatase film on fused silica substrate. The increase in the photocatalytic activity of epitaxial anatase films is explained by enhanced charge carrier mobility which is traced to the decreased grain boundary density in the epitaxial anatase film. Rladimir 68, synthesized new bismuth calcium silicon oxide $\text{Ca}_4\text{Bi}_4 \cdot 3(\text{SiO}_4) (\text{HSiO}_4)$ 500.95 with apatite structure. The structure was refined from powder x-ray diffraction data. The refinement revealed that the phase has $P63/m$ (176) space group with unit cell parameters $a=b=9.6090(7)\text{\AA}$, $c=7.0521\text{\AA}$, $V=563.9\text{\AA}^3$, $C/a=0.734$. The Rwp factor at Rietveld refinement was

equal to 0.082. The synthesis phase has an unusual quantity of cation vacancies in a crystal lattice mechanisms of compensation of the excess charge of a lattice are considered and checked experimentally with using FT-IR spectroscopy, thermal analysis and XPS analysis. Vorotilov 69, studied the effect of two factors having the most important influence on spin coating process of sol-gel films: the spin speed and the temperature (of the substrate and the applied solution) during film deposition is studied and it was discovered that film thickness and thickness uniformity are determined by centrifugal driving force dynamic, viscous polymer rheology, solvent evaporation dynamics and films porous microstructure. Andrew et al. 70, investigated the full $\text{LaCo}_{1-x}\text{Rh}_x\text{O}_3$ solid solution utilizing structural, electrical transport, magnetic and thermal conductivity characterization. Strong evidence for at least some conversion of $\text{Rh}^{3+}/\text{Co}^{3+}$ to $\text{Rh}^{4+}/\text{Co}^{2+}$ is found in both structural and electrical transport data. The crystal structure is that of a rhombohedrally distorted perovskite over the range $0.0=x=0.1$. The common orthorhombic distortion of the perovskite structure is found over the range $0.2=x=1.0$. A crossover of all three orthorhombic cell edges occurs at $x=0.5$ giving the appearance of a cubic structure which actually remains orthorhombic.

Maity et al. 71, studied the Electrical characterization and Poole-Frenkel effect in sol-gel derived ZnO:Al thin film, it was found that for different aluminum concentration in the film, current-voltage characteristics of the film at constant temperature showed non-linearity. Zhang et al. 72, synthesized MnO_2 with a sea urchin-like ball chain shape in a high magnetic field via a simple chemical process (sol-gel). The synthesized samples were characterized by XRD, SEM, TEM and

vector network analysis. The dielectric constant and the loss tangent clearly decreased under a magnetic field. The magnetic loss tangent and the imaginary part of the magnetic permeability increased substantially. The theoretically calculated values of reflection loss showed that the absorption peaks shifted to a higher frequency with increases in the magnetic field strength

Satoshi, et al [73] successfully synthesized a missing link of Wadley phases by using sulfur as reducing agent at a low temperature and its structure has been determined by combining electron, x-ray and neutron diffractions. V_4O_9 has an orthorhombic $cmcm$ structure and the lattice parameters are $a = 10.356(2)\text{\AA}$, $b = 8.174(1)\text{\AA}$ and $c = 16.559(3)\text{\AA}$ at room temperature. The structure is composed of shared edges and corners of three types of polyhedral, VO_6 distorted octahedron, a VO_5 pyramid and a VO_4 tetrahedron. The structure of V_4O_9 is very similar to that of vanadyle pyrophosphate $(VO)_2P_2O_7$.

In this review, emphasis is devoted to sol-gel deposition technique because it is the technique we employed in this study. When these crystals are grown they are characterized to determine their properties and possible applications in solar, solid state and electronic properties.

2.4. CHARACTERIZATION OF SEMICONDUCTORS.

The aforegrown crystals were adequately described by considering the following principles:

- The electronic band structure
- The chemical composition
- The crystallographic structure
- Optical properties.

Through the following characterization techniques viz:

- Optical Characterization Techniques
- Microscopy Techniques
- Structural Analysis Methods
- Surface Analysis Methods
- Electrical Methods.

2.4.1. Optical Characterization.

The Optical properties of semiconductors are determined by the interaction of electromagnetic radiation with the material that leads to the formation of various signals as a result of processes such as absorption, reflection, emission and scattering. In this work, the optical and solid state properties of interest are; absorbance (A), Transmittance (T), reflectance (R), absorption coefficient (α), the band gap (E_g), optical constants: refractive index (n), extinction coefficient (K), dielectric constant (ϵ_0) and optical conductivity (σ_{op}).

2.4.2. Optical Absorption.

Optical absorption spectroscopy is performed from the infra red to the ultraviolet ranges. In the near-ultraviolet, visible and near infrared ranges, semiconductors absorb electromagnetic radiation strongly through a mechanism of the generation of electron hole-pairs at photon energies greater than the fundamental energy gap [74]. Optical absorption may occur at various stages due to various impurities, defects and vibrational bonds.

2.4.2a. Absorbance (A).

Absorbance is the common logarithm of the reciprocal transmittance i.e.

$$A = \log_{10}(1/T) = \log_{10}(I_0/I) \quad [2.1]$$

This implies that

$$T = 1/\log^{-1}A \quad [2.2]$$

From the foregoing, it implies that knowing one, the other can be calculated. Thus, for an ideal sample, the sum of absorbance (A), transmittance (T) and reflectance (R) is equal to one i.e.

$$A+T+R = 1 \quad [2.3]$$

Therefore,

$$R = [1 - (T+A)] \quad [2.4]$$

And

$$T = [1 - (A+R)] \quad [2.5] \text{ [75]}$$

2.4.2b. Transmittance (T)

For a given sample, the transmittance is the ratio of the radiant power transmitted by the body to the total radiant power entering the body, i.e.

$$T = I/I_0 \quad [2.6]$$

The incident flux, I_0 , does not have universally fixed value but varies according to the parameters of the instrument producing it [75]

2.4.2c. Absorption Coefficient (α)

Assuming I_0 is the incident flux, I the flux passing through a thickness x (in μm) of a material whose absorption coefficient is (α),

$$I = I_0 \exp(-\alpha x) \quad [2.7]$$

Where α is the absorption coefficient for a true absorption. The absorption coefficient α is a measure of the rate of decrease in intensity of a beam of photons or particles in passing through a particular substance, when applied to electromagnetic radiation, atomic and

subatomic particles. The photon energy E in Joule for a given wavelength λ is given by

$$E \text{ (J)} = h\nu = hc/\lambda \quad [2.8]$$

Where

h = Plank constant = 6.62×10^{-34} JS,

c = Velocity of light = 3.0×10^8 ms⁻¹

λ = Wavelength in meters (m)

and

ν = Frequency

Also,

$$T = \exp(-\alpha x)$$

And

$$\alpha = [\ln T^{-1}] / x \quad \mu\text{m}^{-1}$$

And for unit distance traversed, we have

$$\alpha = \ln(T^{-1}) \mu\text{m}^{-1}$$

Or

$$\alpha = (T^{-1}) \times 10^6 \text{m}^{-1} \quad [2.9]$$

Eqn. (2.9) is used in this work in calculating the absorption coefficient (α).

2.4.2d. Optical Constants n and k , Dielectric Constant ϵ and Optical Conductivity σ_{op} .

The optical constants are the index of refraction (n), and the extinction coefficient (k). The reflectance normal to a surface can be expressed in terms of the optical parameters n and k by

$$R = [(n-1)^2 + k^2] / [(n+1)^2 + K^2] \quad [2.10]$$

When the absorption coefficient is weak within the frequency range, then measurement of reflectance is given by

$$R = (n-1)^2 / (n+1)^2$$

Therefore, we have

$$n = 1 + R^{1/2} / 1 - R^{1/2} \quad [2.11]$$

Where n is the refractive index.

The extinction coefficient is given as

$$K = c\alpha / 4\pi = \alpha\lambda / 4\pi \quad [2.12]$$

The dielectric constant is given by

$$\epsilon_r = \epsilon_R + \epsilon_i = (n+ik)^2 \quad [2.13]$$

Where,

ϵ_r , ϵ_i are the real and imaginary parts of the dielectric and $n + ik$ are the complex refractive index. From equation [2.13] it can be seen that

$$\epsilon_r = n^2 - k^2$$

$$\epsilon_i = 2nk \quad [2.14]$$

The optical conductivity is given by

$$\sigma_{op} = \alpha nc / 4\pi \quad [2.15]$$

Where c is the velocity of light, σ_{op} is the conductivity at the optical frequency concerned and is not generally equal to the d.c. or low frequency conductivity [75].

2.4.2e Band gap.

The transfer of electron from the valence band to the lower part of the conduction band are responsible for the shape of the absorption spectrum and for the dispersion near the fundamental absorption edge. The transfer of electron can be direct, without phonon participation and

without a change in the crystal momentum of an electron or they can be indirect, in which the interaction with phonon produces a considerable change in the crystal momentum if the wavelength of the phonon is short. The various types of transitions give rise to different frequency dependencies of the absorption edge i.e.

$$\alpha \propto (h\nu - E_g)^n \quad (2.16)$$

Where $n=1/2$ is for direct allowed transition, $1/3$ for forbidden indirect allowed, $3/2$ is for a forbidden direct allowed transition and 2 for the indirect allowed transition. When the linear portion of $(\alpha h\nu)^n$ as a function of $h\nu$ is extrapolated to $\alpha=0$, the intercept gives the transition band gaps [76].

The major optical techniques for characterization of semiconductors include optical microscopy, optical absorption, photoluminescence, Raman scattering, ellipsometry and modulation techniques.

2.4.3. Photoluminescence (PL) Spectroscopy.

This is a very sensitive, contactless nondestructive technique for the characterization of various properties of semiconductors, especially, for the analysis of various dopant and impurity levels present in the energy gap of a semiconductor. In photoluminescence, a substance absorbs photons and then re-radiates photons [81].

2.4.4. Raman Spectroscopy.

This is a spectroscopic technique used to study the vibrational, rotational and other low-frequency in a system. It relies on inelastic scattering of monochromatic light, usually from a laser in the visible,

near infrared or near ultraviolet range. Ordinarily, the energy of the scattered light corresponds to the same value as the incident light but in some cases the energy of scattered light is at a different energy due to the inelastic scattering of light, resulting from the molecules changing its motions, then we have Raman scattering. This change in energy is associated with a change in vibrational, rotational or electronic energy of a molecule. The difference in energy between the incident photon and the scattered photon is called Raman shift and it is equal to the energy of a vibration of the scattering molecule [81].

2.4.5. Ellipsometry.

In ellipsometry, the change in the state of polarization of the electromagnetic wave upon reflection or transmission at an interface between two dielectric media is measured. Such a measurement of change in the polarization involves evaluating the amplitude ratio and phase variation between polarization components [81].

2.4.6. Optical Modulation Technique.

The basic principle of modulation spectroscopy is measuring the optical spectral response that is optical reflectance or transmittance of a semiconductor. The optical response is modified by applying a repetitive perturbation, which results in sharp spectral features that are analogous to taking the derivative of the spectrum.

2.4.7. MICROSCOPIC TECHNIQUE.

The main reasons for this method are:

- (i) to detect defect and measure their densities

- (ii) identify them and
- (iii) establish their origin.

The microscopy techniques often used in semiconductor characterization are optical microscopy, electron microscopy and scanning probe microscopy.

2.4.7a. Optical Microscopy.

The main advantages of the optical microscopic methods in comparison with electron beam techniques are thus: the versatility of optical examination, relative simplicity of sample preparation, no vacuum requirement and the absence of specimen charging.

2.4.7b. ELECTRON BEAM TECHNIQUES.

This involves Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

2.4.7bi. Scanning Electron Microscopy (SEM).

The presence of several different modes, providing complementary information on physical, compositional and structural properties of solid state materials and devices constitutes one of the main advantages of this technique. SEM is capable of examining microscopic specimens, example, semiconductor wafers and devices with no special sample preparation steps [77].

2.4.7bii. TRANSMISSION ELECTRON MICROSCOPY (TEM).

This technique uses electrons that can be detected and analyzed in thin samples of the order of 1000Å and less; provides information

related to crystal structure and defects in solid state materials. It involves using a high energy electron beam between 100 and 1000KeV and electrons transmitted through the thin sample are focused by electromagnetic lenses [78,81]. TEMs are capable of imaging at a significantly higher resolution than light microscopes owing to the small de Broglie wavelength [78].

2.4.7c. Scanning Probe Microscopy (SPM).

This is capable of imaging surfaces on the atomic scale. The basic components of SPM are; a fine probe (or tip) which is mechanically scanned in very close proximity to the specimen and a feedback circuit which controls the distance between the tip and the sample surface. A specific signal which is generated as a result of an interaction between a fine probe and a specimen is used to produce an image [79].

2.4.8. Structural Analysis.

The objective of structural characterization is the description of the three dimensional arrangement of the atoms in a solid, measuring the lengths and angles in the unit cell. In structural analysis, we use X-ray diffraction, neutron diffraction, electron microscopy and electron diffraction, Raman spectroscopy [80].

2.4.8a. X-RAY DIFFRACTION (XRD)

X-ray diffraction is a versatile, non destructive analytical technique for identification and quantitative determination of various crystalline forms known as phases of compounds present in powdered and solid samples. In XRD technique, a sample is irradiated with a collimated

beam of X-rays (of wave lengths between about 0.5 and 2Å) and the scattered X-rays are detected with an appropriate detector. Depending on the factors such as orientations of the sample and detector and on the specific crystal structure of the sample material, XRD pattern can be recorded. Such patterns consist of peaks in the scattered X-ray intensity plotted as a function of scattered angle [77]. The peaks are due to constructive interference of the scattered x-rays. In XRD, the rays are diffracted by the crystalline material according to Bragg's law, $n\lambda = 2d\sin\theta$. From this, one can obtain information on phases present, crystal structure, defects, crystallite sizes, crystal orientation and strain. Phase identification is one of the routine applications of XRD and it involves comparing the derived d_{hkl} spacing and peak intensities from diffraction spectra with those for unknown standards given in the literature. Preferred grain orientation can be derived from the relative peak intensities of the crystallographic directions, whereas the strain can be characterized by the position and width of the diffraction peaks and crystallite size can be determined from the width of the diffraction peaks.

2.4.9. STRUCTURAL ANALYSIS OF SURFACES.

This involves the use of low energy electron diffraction (LEED) and reflection high-energy electron diffraction (RHEED). In LEED, a collimated monoenergetic electron beam is diffracted by the sample surface. The electron beam energies used are in the range between 10 and 1000eV. In RHEED, a high energy electron beam, striking the sample at a grazing angle of about $1-5^\circ$ is scattered by the sample surface. The electron-beam energies used in RHEED are in the range of 5 and 50KeV [77]. The pattern produced on a phosphor screen,

positioned opposite the electron gun can be monitored or recorded by various methods; from the features of such RHEED patterns that is the spacing and symmetry of the features, one can derive information on the lattice constant, surface structure and surface symmetry. This technique is extensively employed as an in situ monitoring tool in molecular beam epitaxy.

2.5.1. Surface Analysis Methods.

The most commonly used surface characterization techniques are Auger electron spectroscopy (AES), scanning Auger electron microscopy (SAEM), X-ray Photo Electron Spectroscopy (XPS), Secondary Ion Mass Spectrometry (SIMS) and Rutherford Back Scattering Spectrometry (RBS). The major applications of surface analysis methods involve (i) investigations of surface composition in correlation with other material and device properties. (ii) depth profiling of thin films and thin-film multi layer structures and devices and (iii) obtaining the microscopic description of surface such as surface topography and various types of inhomogenities [79,80].

2.5.1a. Auger Electron Spectroscopy (AES).

This is based on the direction of the electron that has been ejected due to re-arrangement of core electrons in the atom as a result of primary electron beam bombarded with typical energies of about 5keV. In this process, after the ionization of an atomic core level by an electron bombardment, the filling of unoccupied level (e.g. K level) by an electron from a higher energy level is accompanied by the emission of a photon. This energy transferred to another electron that carries off the energy

gained by the first electron; such an escaping electron is called an Auger electron [81].

2.5.1b. X-ray Photoelectron Spectroscopy (XPS).

X-ray Photoelectron Spectroscopy also referred to as Electron Spectroscopy for Chemical Analysis (ESCA) employs X-rays for the excitation of the solid and the detection of emitted photoelectrons with characteristic energies that can provide chemical information about the material [81].

2.5.1c. Ion Beam Techniques.

Ion Beam Technique is distinguished between those that use the excitation ion beam energies in the KeV range and those that employ the ion beams in the MeV range. In the Secondary Ion Mass Spectrometry (SIMS), secondary ions emitted as a result of the incident ion-beam bombardment (with energies up to 20 KeV) are identified using a mass spectrometer and the ion beam sputtering of the sample allows obtaining depth profiling [81].

2.5.1d. Rutherford Backscattering Spectrometry (RBS).

This is a depth profiling technique, which allows obtaining quantitative information about elemental composition or impurity concentration without the need for standards. RBS employs high-energy ion bombardment of the materials surface and the measurement of energy of the backscattered ions [81].

2.6.1. Fourier Transform Infrared Spectroscopy (FTIR).

The term Fourier Transform Infrared Spectroscopy refers to a fairly recent development in the manner in which data is collected and converted from an interference pattern to a spectrum [81]. It is a powerful tool for indentifying types of chemical bonds in a molecule by producing an infrared absorption spectrum that is like a molecular finger print. The energy of most molecular vibrations corresponds to that of the infrared region of the electromagnetic spectrum. The most useful vibrations occur in the narrower range of 2.5μ to 16μ ($1\mu = 10^{-4}\text{cm}$) which most infrared spectrometers cover. The position of an absorption band in the spectrum may be expressed in micron (μ) or in terms of reciprocal of the wavelength (cm^{-1}).

A complex molecule has a large number of vibrational modes which involve the whole molecule. Some of these vibrations are associated with the vibrations of individual bonds or functional groups while others must be considered as vibrations of the whole molecule. The localized vibrations are stretching, bending, rocking, twisting or wagging. The soggy vibrations of the molecules as a whole give rise to a series of absorption bands at low energy, below 1500cm^{-1} , the positions of which are characteristic of that molecule.

Frequently, bands are observed which do not correspond to any of the fundamental vibrations of the molecule and are due to overtone bands and combination bands. It is most useful in identifying chemicals that are either organic or inorganic. When a spectrum has been taken, the region above 1500cm^{-1} showing absorption bands assignable to a number of functional groups and a region, characteristic of the compound in question and no other compound, containing many bands

below 1500cm^{-1} . This region is called the finger print region. The use of finger print region to confirm the identity of a compound with an authentic sample is more reliable. It can be utilized to quantify some components of an unknown mixture. It can be applied in the analysis of solids, liquids and gases.

2.6.2. Electrical Characterization

This involves electrical measurement performed on semiconductors for the analysis of a wide range of semiconductor properties. Important semiconductor materials and devices properties that can be derived using various electrical measurements are (i) the electrical resistivity or conductivity, (ii) the energy band gap and the separation of an impurity level from the band edge, (iii) the majority carrier concentration (iv) the mobility electrons and holes, (v) life time and diffusion length of minority carriers (vi) surface recombination velocity of carriers and (vii) deep impurity levels as well as device parameters such as barrier height, contact resistance, interface state densities, junction depth, channel length and width [81].

2.6.2a. Resistivity and the Hall Effect

One of the most important characteristics of a semi conductor is its electrical resistivity which can be measure using the four point-probe, spreading resistance and Van der Pauw methods. The four point probe technique is essentially a collinear four point probe array, in which the two outer point carry constant current I through the layer, where as across the two inner points a voltage V is monitored. For the probe with equidistance spacing s between the points and a semi-infinite sample,

the resistivity is expressed as $\rho = 2' s (V/I)$. For finite geometry, we have correction factor F , which is related to the sample thickness, the probe spacing and edge effects, Thus, the resistivity can be expressed as $\rho = 2' sF(V/I)$. For wafer (or semiconductor layer) thickness d much lower than s , the resistivity is expressed as $\rho = (\pi / \ln 2)d(V/I)$ [81].

2.6.2b. Capacitance-Voltage Measurements

The capacitance measurement is employed on various diode structures, example, p-n junction, Schottky barrier and metal-insulator-semiconductor diodes. The capacitance measurement depends on the charge distribution within the depletion region. Since the depletion layer width depends on the applied voltage bias, capacitance voltage as function of the voltage bias can be used for determining doping concentration profile in a semiconductor [81].

2.6.2c. Photoconductivity

In photoconductivity measurements, irradiation with photons, whose energies are greater than the semiconductor energy gap, produces photogenerated electron hole pairs that can contribute to the conductivity. At photon energies lower than the energy gap of the semiconductor, photoconductivity can still be produced by excitation of carriers from impurity levels in the energy gap [81].

CHAPTER THREE

RESEARCH METHODOLOGY AND DESIGN

3.1. INTRODUCTION

This chapter focuses on the research methodology and design adopted in carrying out this study. It consists of the method of growth and data collection. It also points out on the various instruments, apparatus and methods used in growing and drying the crystals. In this work, methodology involves:

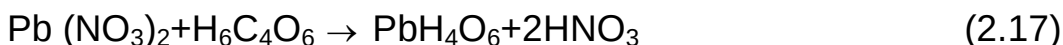
- ❖ Growing thin films of binary and ternary metal halides and chalcogenides using sol-gel technologies.
- ❖ Adding impurities to the set gel to see how they permeate into the fabrics of the crystals.
- ❖ Studying the spectral absorbance, transmittance and reflectance of the films and the influence of various deposition parameters, using UV-VIS-IR spectrophotometers.
- ❖ Studying the structural properties of the films using x-ray diffraction.
- ❖ Studying the types of chemical bond in the grown crystals using Fourier Transform Infrared Spectroscopy (FTIR)
- ❖ Analyzing, interpreting, comparing and correlating the various film characteristics

3.2. EXPERIMENTAL DETAILS

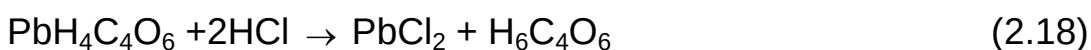
Crystals grown are lead chloride (PbCl_2), stannous and stannic iodides (SnI_2 and SnI_4), potassium per chlorate (KClO_4) and cadmium sulphide (CdS).

3.2.1. Growth of Lead Chloride (PbCl₂)

In growing (PbCl₂), 100ml beaker was added with 25ml of sodium silicate solution of pH greater than eleven. It was titrated with some quantity of 1M of tartaric acid [HOOC (CHOH)₂COOH]. The mixture forms gel at about pH 8. The set gel was added with 20ml of 1M of lead nitrate Pb(NO₃)₂ solution to give lead tartanate as in equation (2.17),



The lead tartanate is generated in the gel as a white column, ring system of gradually increasing thickness. The precipitation of lead tartanate completed within a fortnight. 20ml of 1N of hydrochloric acid (HCl) and a pipette drop of locally produced impurities were placed over the set gel to give,



The HCl reacted with the colloidal precipitate of lead tartanate producing lead chloride (PbCl₂) which grew down into the gel as luminescent needles[82]. The details of the concentrations of the precursors and pH are as shown on table 3.1.

Table 3.1: The concentration, pH and amount of the precursors for the growth of PbCl₂ crystal.

Sample	Mass of Na ₂ SiO ₃ (g)	Quant. of Pb(NO ₃) ₂ (ml)	Quant. of tartaric	Conc. of K ₂ CO ₃ (N)	Quant. Of bamboo	Quant. Of raffia
A	25.0	20	Some quantity	Un-doped	A pipette drop	A pipette drop
B	25.0	20	ñ	0.5	ñ	ñ
C	25.0	20	ñ	0.5	ñ	ñ
D	25.0	20	ñ	0.5	ñ	ñ

3.2.2 Growth of Potassium Per chlorate Crystal (KClO_4) in Silica Gel.

The experiment was performed in 100ml beaker; 25ml of sodium silicate of specific gravity 1.04 was titrated with some quantity of 1N of perchloric acid to form a gel. The gel was formed at about pH 5 or 6. The gel was allowed to age at room temperature for a period of 5, 15 or 25 days after which a feed solution of potassium chloride (KCl) of normalities 0.8, 1.2 and 1.8 was added to the set gels for crystallization. One pipette drop of the impurity was added. The equation for the reaction is



The details of the concentrations of the precursors and pH are as shown on table 3.2.

Table 3.2: The concentration, pH and amount of precursors used for the growth of KClO_4 crystal.

Sample	Mass of Na_2SiO_3 (g)	Quant. of HClO_3 (ml)	Conc. of KCl (N)	Conc. of K_2CO_3 (N)	Quant. of bamboo	Quant. of raffia
E	25.0	Some quantity	0.8	Un-doped	A pipette drop	A pipette drop
F	25.0	ñ	1.2	0.5	ñ	ñ
G	25.0	ñ	1.4	0.5	ñ	ñ
H	25.0	ñ	1.8	0.5	ñ	ñ

3.2.3 Growth of Stannous and Stannic Iodides in Silica Gel (SnI_2 , SnI_4).

Here, 25ml of sodium silicate solution of specific gravity 1.04 was titrated with some quantity of freshly prepared stannous chloride. The stannous chloride was prepared by dissolving it with few drops of concentrated hydrochloric acid to avoid hydrolysis and was diluted to the required strength. The essence of using freshly prepared stannous chloride was to avoid their oxidation. The gel formed after the titration was allowed to set, after which feed solutions of potassium iodide of varying concentration from 0.5 to 2.0N were added. After few hours, yellow whiskers of stannous iodide (SnI_2) were formed and a pipette drop of the impurity was added. The equation for the reaction is as written below,



Or



The details of the concentrations of the precursors and pH are as shown on tables 3.3 and 3.4.

Table 3.3: The concentration, pH and amount of precursors for the growth of SnI_2 crystal.

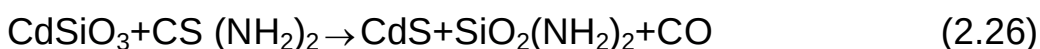
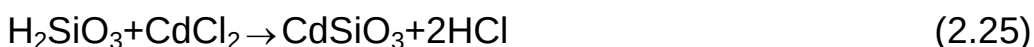
Sample	Mass of Na_2SiO_3 (g)	Quant. of SnCl_2 (ml)	Quant. of KI (ml)	Conc. of K_2CO_3 (N)	Quant. of bamboo	Quant. of raffia
I	25.0	20	0.5	Un-doped	A pipette drop	A pipette drop
J	25.0	20	0.8	0.5	ñ	ñ
K	25.0	20	1.0	0.5	ñ	ñ
L	25.0	20	2.0	0.5	ñ	ñ

Table 3.4: The concentration, pH and amount of the precursors used for the growth of SnI_4 crystal.

Sample	Mass of Na_2SiO_3 (g)	Quant. of SnCl_2 (ml)	Conc. of KI (N)	Conc. of K_2CO_3 (N)	Quant. of bamboo	Quant. of raffia
M	25.0	20	0.5	Un-doped	A pipette drop	A pipette drop
N	25.0	20	0.8	0.5	ñ	ñ
O	25.0	20	1.0	0.5	ñ	ñ
P	25.0	20	2.0	0.5	ñ	ñ

3.2.4. Growth of Cadmium Sulphide (CdS) Crystals in Silica Gel.

In growing cadmium sulphide (CdS) crystal, 25ml of sodium silicate solution was titrated with some quantity of 1N of HCl to form a gel. Aqueous solution of 1M of cadmium chloride (CdCl_2) was mixed with the gel solution and the pH was set at 5.0. The gel was allowed to set at room temperature for a period of 5 days. The gel was then covered with 1M of freshly prepared thiourea and a drop of the impurity material. After about 24hrs, the reaction between cadmium ions from the gel and the sulphide ion from thiourea nucleated some cadmium sulphide nuclei [49]. Thus,



i.e.



The details of the concentrations of the precursors and pH are as shown on table 3.5.

Table 3.5: Concentration, pH and amount of the precursors used for the growth of CdS crystal.

Sample	Mass of Na_2SiO_3 (g)	Quant. of HCl (ml)	Quant. of CdCl_2	Quant. of $\text{CS}(\text{NH}_2)_2$ (ml)	Conc. of K_2CO_3 (N)	Quant. of bamboo	Quant. of raffia
Q	25.0	20	Some quantity	10	Un-doped	A pipette drop	A pipette drop
R	25.0	20	ñ	10	0.5	ñ	ñ
S	25.0	20	ñ	10	0.5	ñ	ñ
T	25.0	20	ñ	10	0.5	ñ	ñ

The aforegrown crystals were dried and adequately described through the following characterization techniques viz:

- Optical Characterization Techniques (UV-VIS-IR analysis)
- Structural Analysis Methods (XRD and FTIR)

3.3 DRYING.

The samples were first treated with all glass distilled water to avoid impurities and made slurry before it was introduced into a Buckner funnel covered with filter paper then attached to a suction flask connected to the vacuum pump through its nozzle. When the pump was put on it created a vacuum that allowed for the absorption of H_2O from the sample. The filter in the Buckner funnel prevented the solid from being sucked.

The sample was then taken to the oven at an appropriate temperature of 104°C for 30 minutes. After which it was placed inside the desiccators to maintain dryness. CaCl_2 was used as a desiccant.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSIONS

4.1 OPTICAL ANALYSIS RESULT.

The optical studies for the sol gel grown crystals were done using a JENWAY 6405 UV- VIS spectrophotometer operating at a wavelength range of 200nm to 1200nm at intervals of 5nm. In the optical absorption study, deionised water was used as reference. The crystal samples were dissolved in deionised water forming a colloidal solution which was then subjected to UV-VIS analysis. The optical result for the grown crystals: PbCl_2 , KClO_4 , SnI_2 , SnI_4 , CdS and impurity materials are as shown on figures 4.1-4.59.

4.1a. Optical Results for Lead Chloride (PbCl_2)

(a) Optical analysis

The graphs of the optical analyses for the grown crystals of un-doped and impurity doped PbCl_2 are shown in figures 4.1-4.10 below.

Figures 4.1-4.10: Optical Analysis for Un-doped and Impurity doped Lead Chloride.

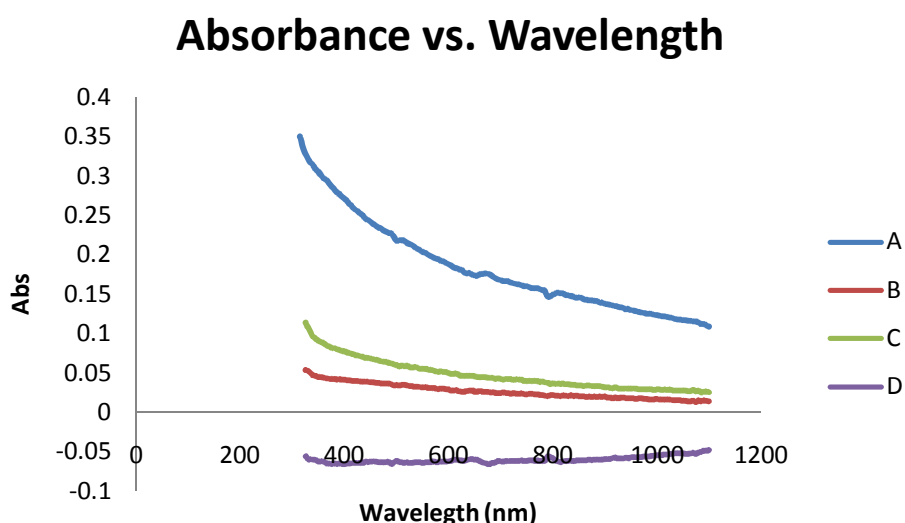


Fig. 4.1: Absorbance against wavelength (nm) for PbCl_2

In figure 4.1, sample A absorbed highly in the visible region and absorbed moderately towards the infrared. Samples B and C have almost the same level of absorbance through 300nm and 350nm and decreased gradually towards the IR but D absorbed little from 300nm and decreased in the negative direction towards the IR. Samples A, B and C can be used in solar cell applications and in poultry house [83].

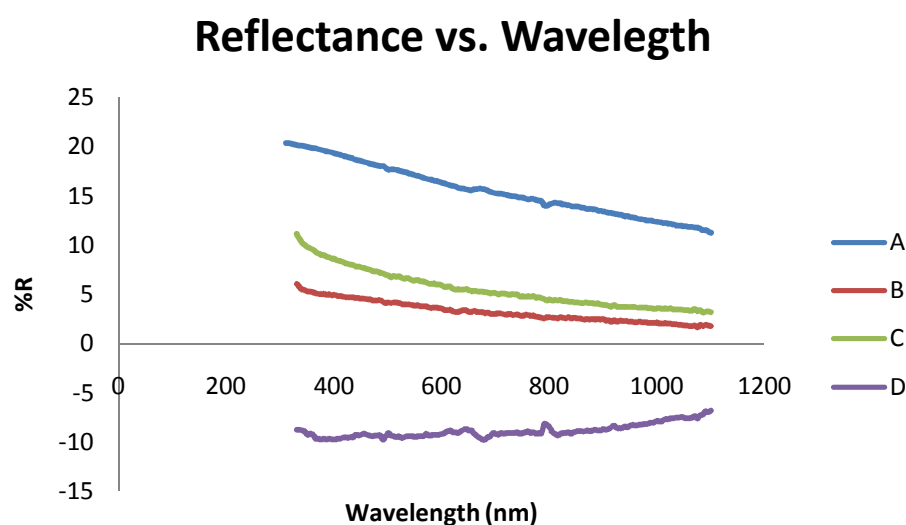


Fig. 4.2: Reflectance against wavelength (nm) for PbCl_2

In figure 4.2, sample A has high reflectance in the VIS region and decreased towards the IR. Samples B and C have moderate reflectance in the VIS region and decreased towards the IR but D has negative reflectance all through.

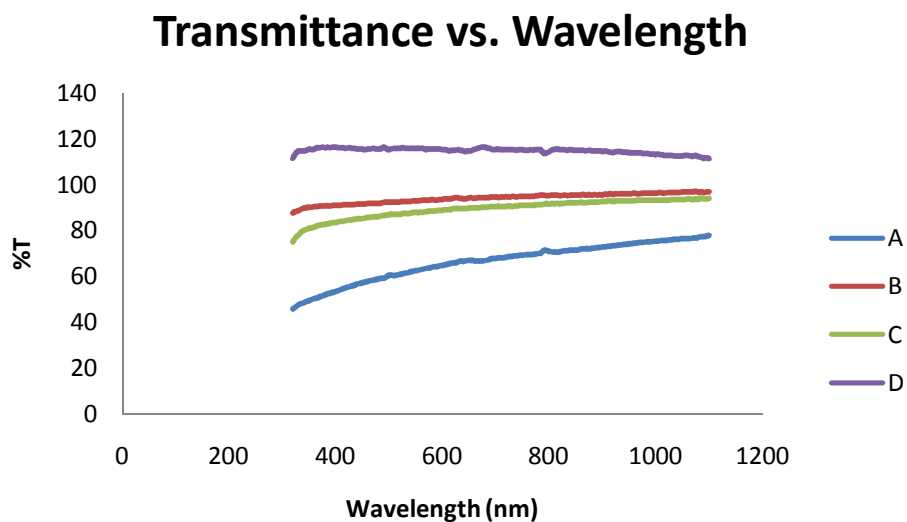


Fig. 4.3: Transmittance against wavelength for PbCl_2

In figure 4.3, all the samples are highly transmitting from the VIS region to the IR. The transmittance ranged from 32% to 120%. Sample D has the highest transmittance. This makes the materials good for poultry roofs and walls [83-87]. These materials do not transmit in the UV region and as such can be used for coating of eye glasses [86].

Absorption coefficient vs. Photon energy

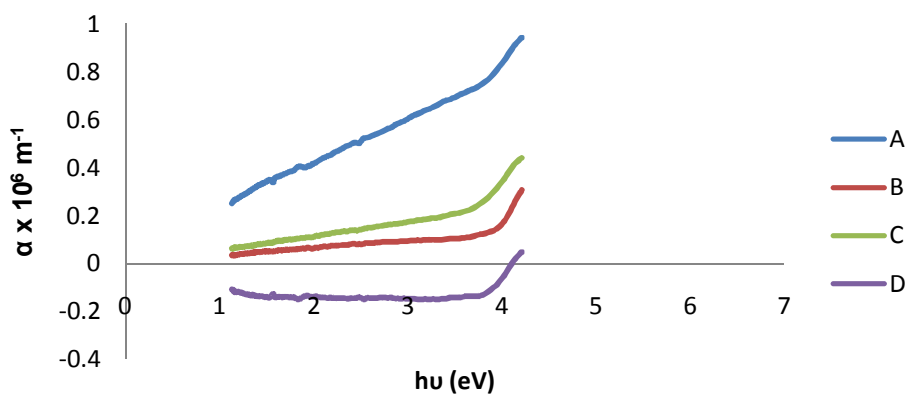


Fig. 4.4: Absorption coefficient against Photon Energy (hν) for PbCl₂

Sample A has very high absorption coefficient between 0.2 and 1.0 while B and C have absorption coefficient from 0.04 to 0.4. D has negative absorption coefficient from -0.18 to 0 and partly positive from 0 to 0.05.

Band gap vs. Photon energy

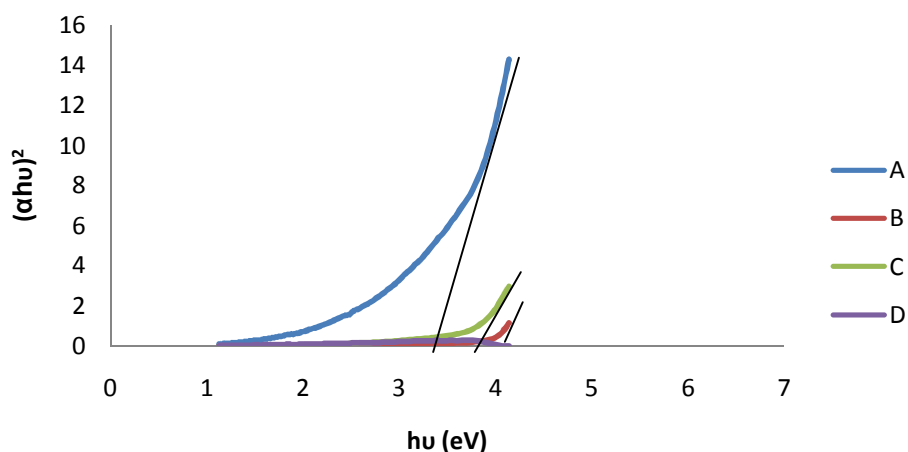


Fig. 4.5: A plot of (αhν)² against photon energy (hν) for PbCl₂.

Figure 4.5 is the plot of $(\alpha h\nu)^2$ against photon energy (eV) for PbCl_2 . The band gaps ranged from 3.4 to 4.1. Sample D has no band gap. Samples A, B and C are wide band gap materials and can be applied in high temperature, high power, high frequency and opto electronic materials [86, 88].

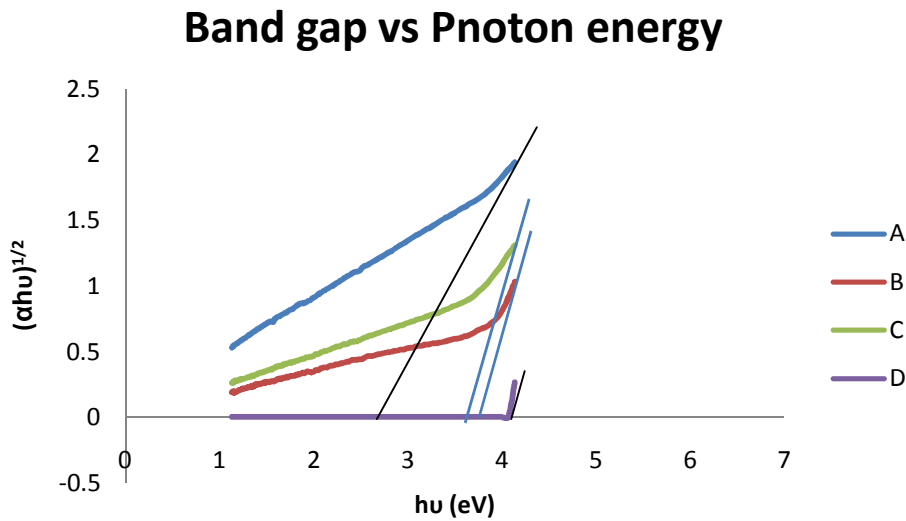


Fig. 4.6: A plot of $(\alpha h\nu)^{1/2}$ against photon energy ($h\nu$) for PbCl_2 .

Figure 4.6 is the plot of $(\alpha h\nu)^{1/2}$ against photon energy (eV) for PbCl_2 . The band gaps for the samples ranged from 2.6 to 4.0 eV. They are wide band gap materials and can be applied in high temperature, high power and high frequency materials [88] in addition to their opto electronic properties [86].

Refractive Index vs. Photon Energy

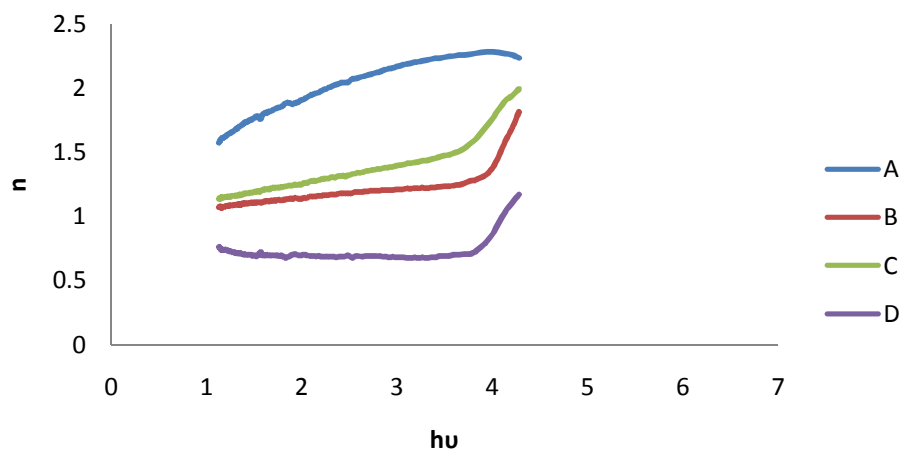


Fig. 4.7: Refractive Index (n) vs. Photon Energy (hν) for PbCl₂

In figure 4.7, samples A, B, C and D have refractive indices from 0.75 to 2.4.

Extinction coefficient vs. Photon energy

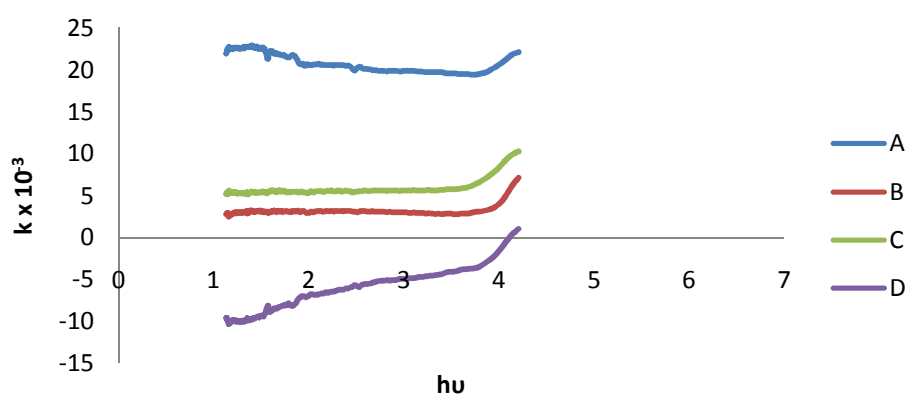


Fig. 4.8: Variation of extinction coefficient (k) with photon energy (hν) for PbCl₂

In figure 4.8, sample A has the highest extinction coefficient from 21 to 25, B and C have close extinction coefficient but D has negative extinction co-efficient.

Real dielectric vs. Photon energy

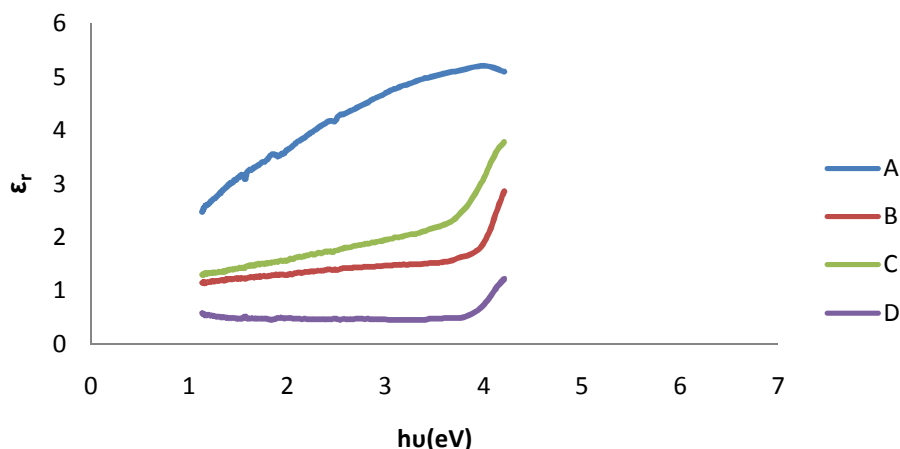


Fig. 4.9: Real dielectric (ϵ_r) with photon energy ($h\nu$) for $PbCl_2$

In figure 4.9, sample A has very high real dielectric of 5.6 while that of B, C and D fall between 0.5 and 3.8 with D as the least.

Imaginary dielectric vs. Photon energy

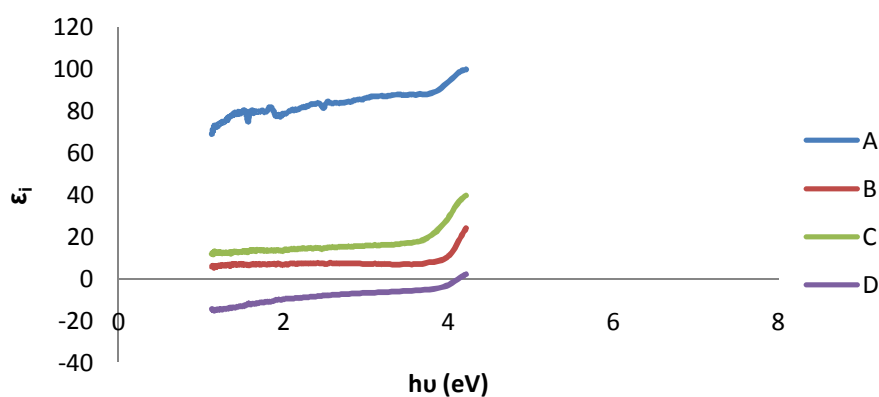


Fig. 4.10: Imaginary dielectric (ϵ_i) with photon energy ($h\nu$) for $PbCl_2$

In figure 4.10, sample A has very high imaginary dielectric from 70 to 110. Samples B and C fall between 4 and 41 but D is negative.

4.1b. Optical Results for Potassium Perchlorate (KClO_4)

The graphs of the optical analyses for the grown crystals of undoped and impurity doped KClO_4 are shown in figures 4.11- 4.20.

Figures 4.11-4.20: GRAPHS OF THE OPTICAL PROPERTIES FOR UN-DOPED AND IMPURITY DOPED POTASSIUM PERCHLORATE CRYSTALS (KClO_4)

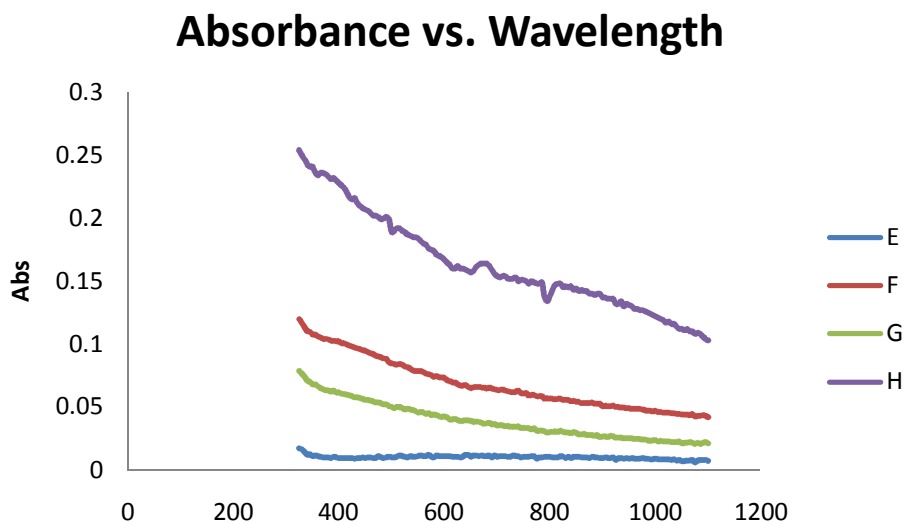


Fig. 4.11: A plot of Absorbance (A) against wavelength (nm) for KClO_4

In figure 4.11, sample E has the least absorbance from the UV-VIS to the IR. Sample H has the highest absorbance in the UV-VIS regions and decreased towards the IR region. Samples F and G have high absorbance in the UV-VIS regions and absorbed moderately towards the IR.

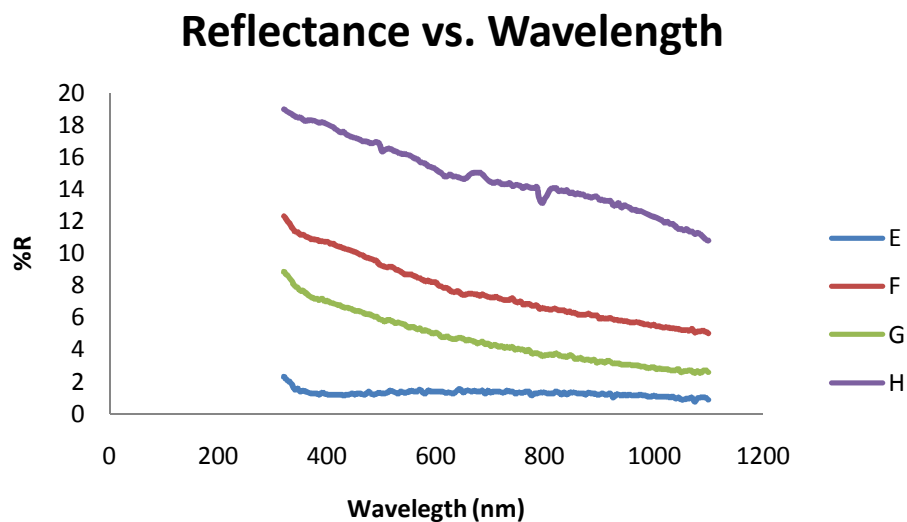


Fig. 4.12: A plot of Reflectance (%) against wavelength (nm) for KClO_4

In figure 4.12, samples E, F and G are reflecting from the VIS-region and decreased towards the IR region. Sample H reflected highly in the UV region and decreased towards the VIS- region then moderately to the IR region.

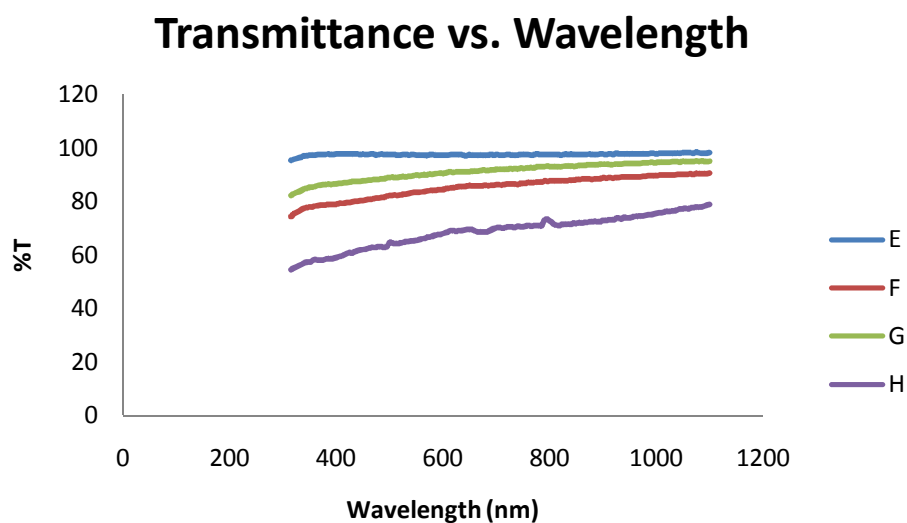


Fig. 4.13: A plot of Transmittance (%T) against wavelength (nm) for KClO_4

In figure 4.13, all the samples are highly transmitting from the visible region to the infra red with transmittance ranging from 50-100%. This makes the materials useful for solar cells applications and poultry house [84, 85].

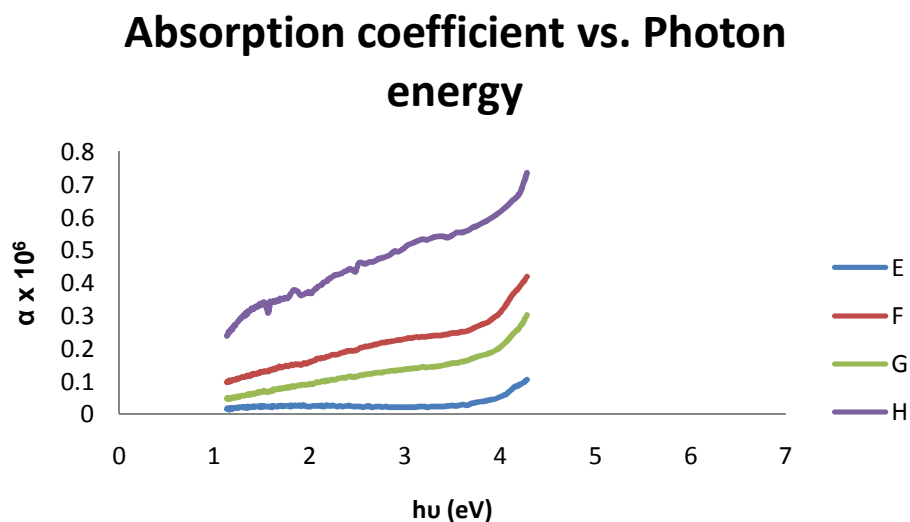


Fig. 4.14: A plot of absorption coefficient (α) against ($h\nu$) for KClO_4

In figure 4.14, samples F and H have the highest absorption coefficient ranging from 0.1 to 0.4. Sample G has absorption coefficient from 0.05 to 0.3 while sample E has the least absorption coefficient from 0.01 to 0.1.

Band gap vs. Photon energy

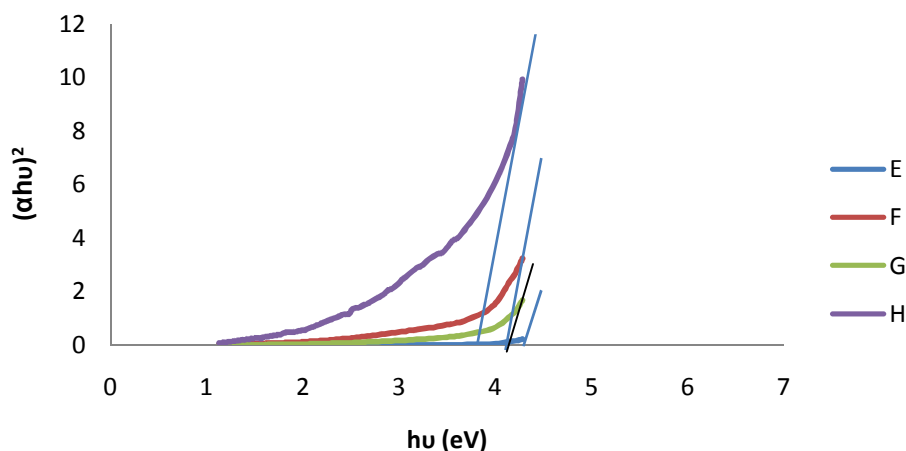


Fig. 4.15: A plot of $(\alpha h\nu)^2$ against photon energy ($h\nu$) for KClO_4

Figure 4.15 is the plot of $(\alpha h\nu)^2$ against photon energy (eV) for the KClO_4 . The band gaps for the samples ranged from 3.8 to 4.2 eV. Samples F and G have the same band gaps. They are all wide band gap materials and can be applied in high temperature, high power and high frequency materials [88] in addition to their pyrotechnic and anti pyretic functions [10].

Band gap vs. Photon energy

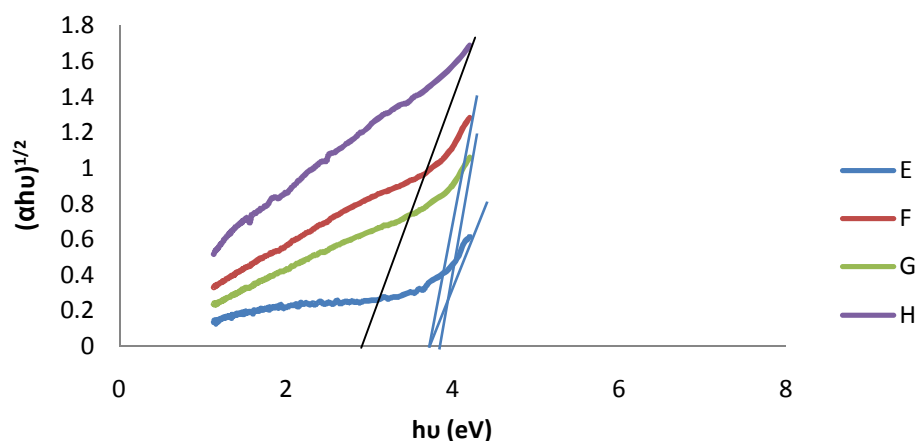


Fig. 4.16: A plot of $(\alpha h\nu)^{1/2}$ against photon energy ($h\nu$) for KClO_4

Figure 4.16 is the plot of $(\alpha h\nu)^{1/2}$ against photon energy (eV) for KClO_4 . The band gaps for the samples ranged from 2.9 to 3.9 eV. They are wide band gap materials and can be applied in high temperature, high power and high frequency materials [88] in addition to their pyretic and anti pyretic functions [10].

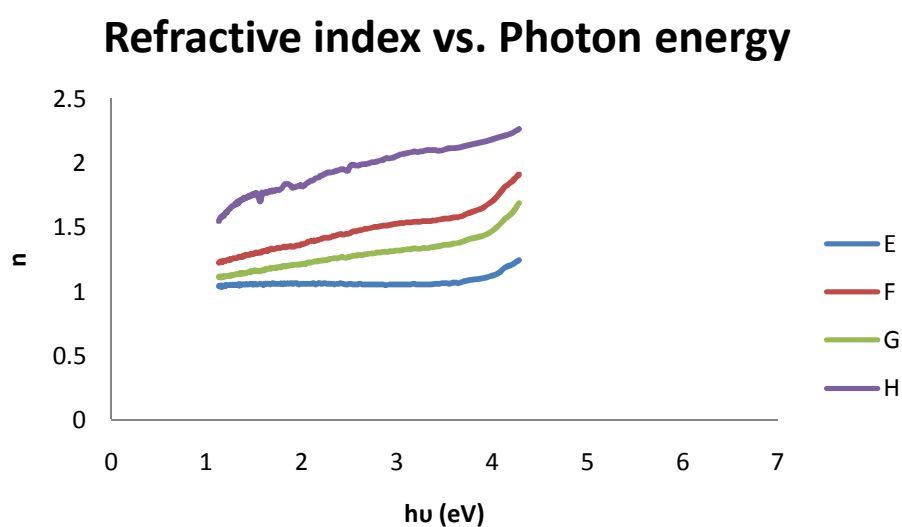


Fig. 4.17: A plot of refractive index (n) against photon energy (hν) for KClO_4

In figure 4.17, all the samples have very high refractive indices from 1.1 to 2.3. Sample H has the highest refractive index.

Extinction coefficient vs. Photon energy

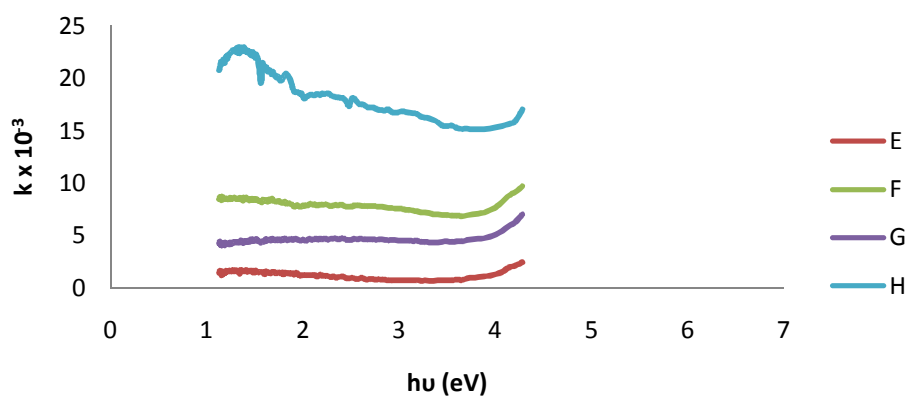


Fig. 4.18: A plot of extinction coefficient (k) against photon energy (eV) for KClO_4

In figure 4.18, sample H has the highest extinction coefficient from 17×10^{-3} to 23×10^{-3} . Samples F and G have extinction coefficient from 4×10^{-3} to 10×10^{-3} but sample E has the least extinction coefficient.

Real dielectric vs. Photon energy

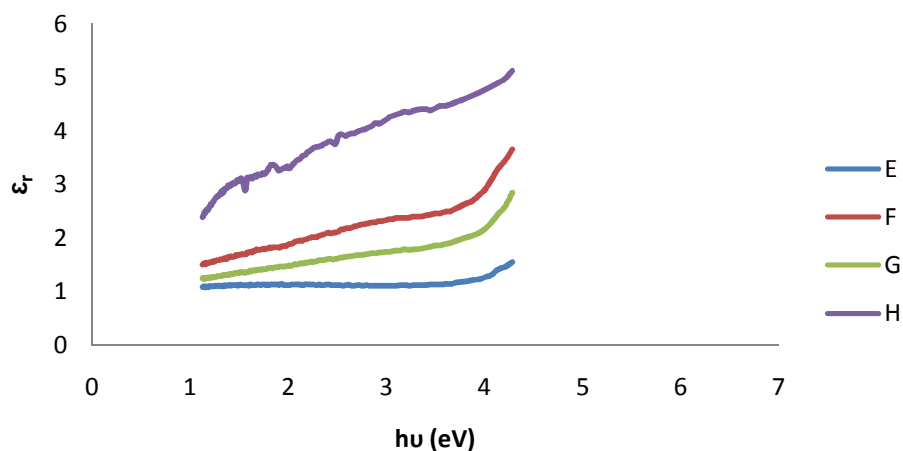


Fig. 4.19: A plot of real dielectric (ϵ_r) against photon energy (eV) for KClO_4

In figure 4.19, samples E, F and G have high real dielectric from 1.0 to 3.4. Sample H have the highest real dielectric from 2.2 increased to 5.0.

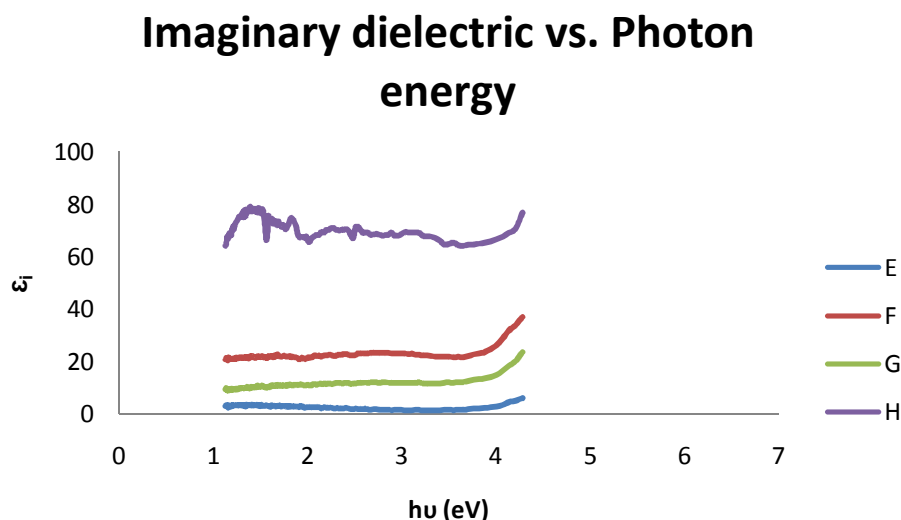


Fig. 4.20: A plot of Imaginary dielectric ϵ_i against photon energy ($h\nu$) for KClO_4

In figure 4.20, samples E, F and G have the imaginary dielectric from 0 to 40. Sample H has the highest imaginary dielectric 60 to 80.

4.1c Optical results for Stannous Iodide (SnI_2).

The graphs of the optical analyses for the grown crystals of un-doped and impurity doped SnI_2 are shown in figures 4.21-4.29.

FIGURES 4.21-4.29: GRAPHS OF THE OPTICAL PROPERTIES OF UN-DOPED AND IMPURITY DOPED TIN II IODIDE.

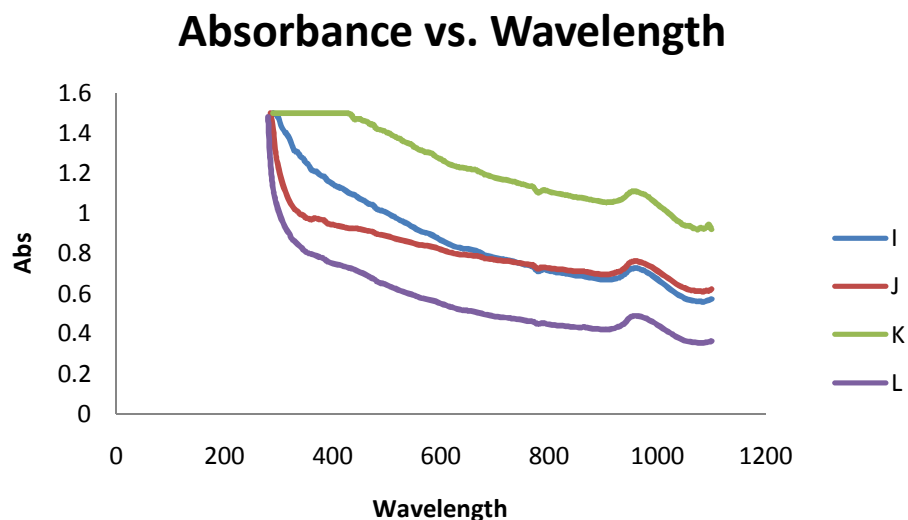


Fig. 4.21: Absorbance (A) against Wavelength (nm) for SnI_2

In figure 4.21, sample K has the highest absorbance. It absorbs highly from the VIS and decreased towards the infra red. Samples I,J,K are all highly absorbing from the near visible region and decreased towards the infra red region. They can be used as oxidizing agent and in solar energy application.

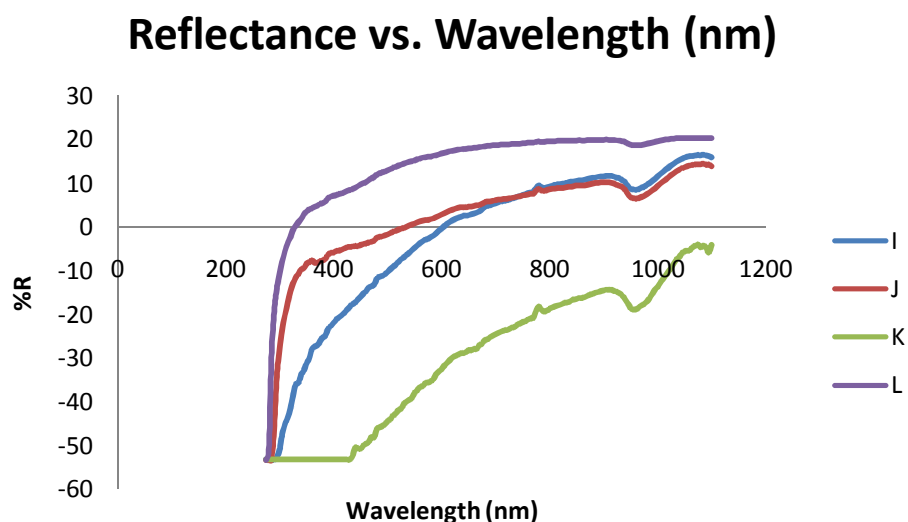


Fig. 4.22: Plot of Reflectance against Wavelength (nm) for SnI_2

In figure 4.22, samples I, J, K have negative reflection up to the VIS region and increased towards the IR. Sample K has negative reflectance although.

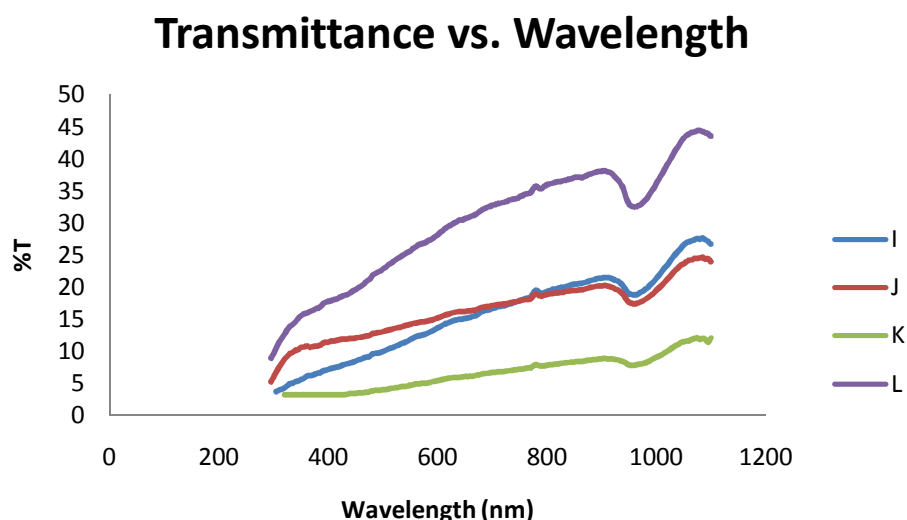


Fig. 4.23: Transmittance (%) against Wavelength (nm) for SnI_2

In figure 4.23, sample K has the least transmittance from the VIS to IR region. I and J are transmitting moderately from the VIS and increased towards the IR. Samples I and J have the same transmittance from 600nm to the NIR. L has the highest transmittance from the near VIS regions and increased towards the infra red region.

Absorption coefficient vs. Photon energy

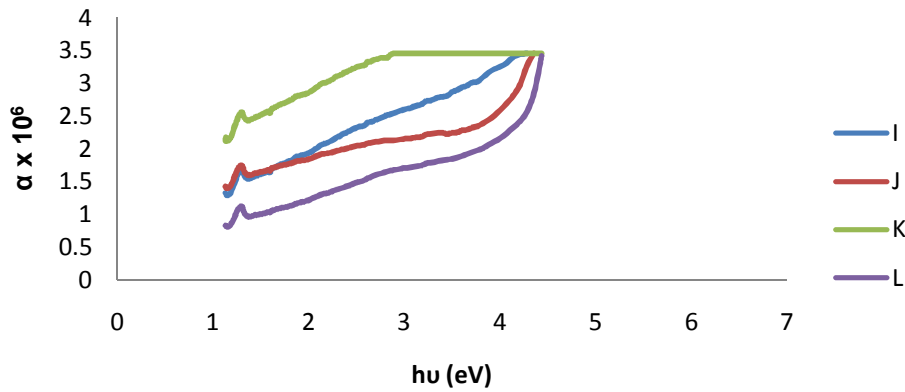


Fig. 4.24: A plot of absorption coefficient against ($h\nu$) for SnI_2

In figure 4.24, samples I, J, K and L have absorption coefficient between 0.6 and 3.4.

Band gap vs. Photon energy

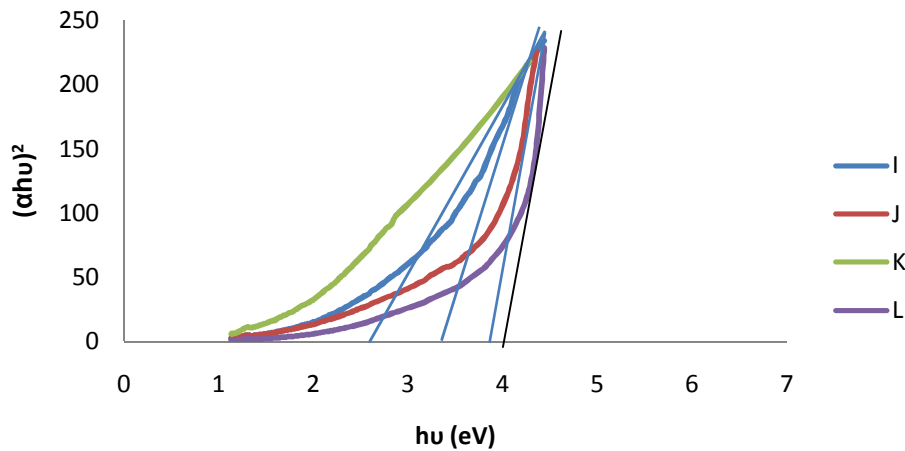


Fig. 4.25: A plot of $(\alpha h\nu)^2$ against photon energy ($h\nu$) for SnI_2

Figure 4.25 is the plot of $(\alpha h\nu)^2$ against photon energy (eV) for the impurities. The band gaps of samples I, J, K and L ranged from 2.6 to 4.0 eV. They are wide band gap materials and can be applied in high temperature, high power and high frequency materials [88].

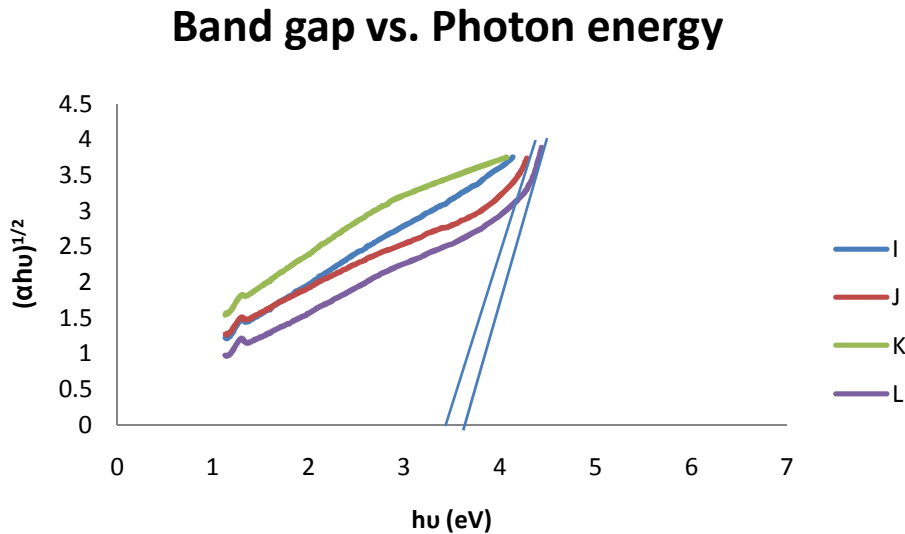


Fig. 4.26: A plot of $(\alpha h\nu)^{1/2}$ against photon energy ($h\nu$) for SnI_2 .

Figure 4.26 is the plot of $(\alpha h\nu)^{1/2}$ against photon energy (eV) for the impurities. Samples J and L have band gaps ranging from 3.4 to 3.6 eV. Samples I and K have no band gaps. Samples J and L are wide band gap materials and can be applied in high temperature, high power and high frequency materials [88].

Refractive index vs. Photon energy

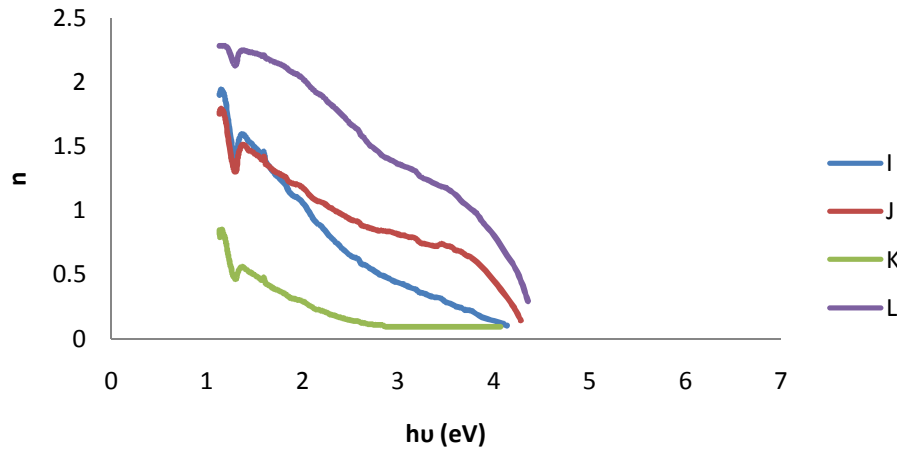


Fig. 4.27: A plot of refractive index (n) against photon energy ($h\nu$) for SnI_2

In figure 4.27, samples I, J, K and L have refractive indices 0.1 and 2.4.

Extinction coefficient vs. Photon energy

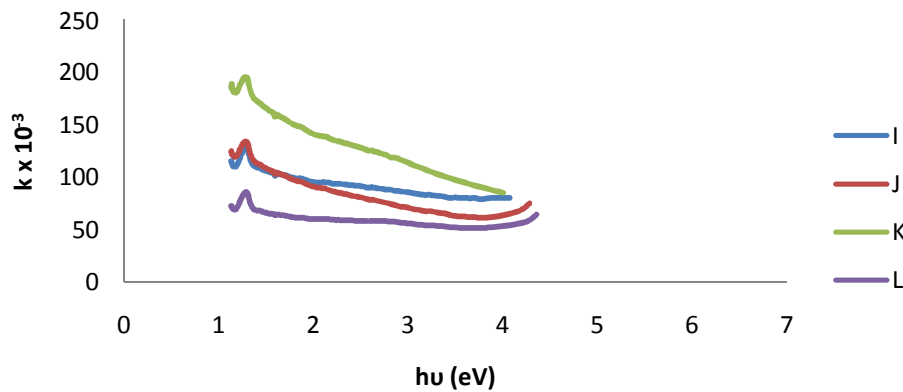


Fig. 4.27: A plot of extinction coefficient (k) against photon energy ($h\nu$) for SnI_2

In figure 4.27, samples I, J, K and L have extinction coefficients from 50×10^{-6} to 200×10^{-6} . Sample K has the highest extinction coefficient.

Real dielectric vs. Photon energy

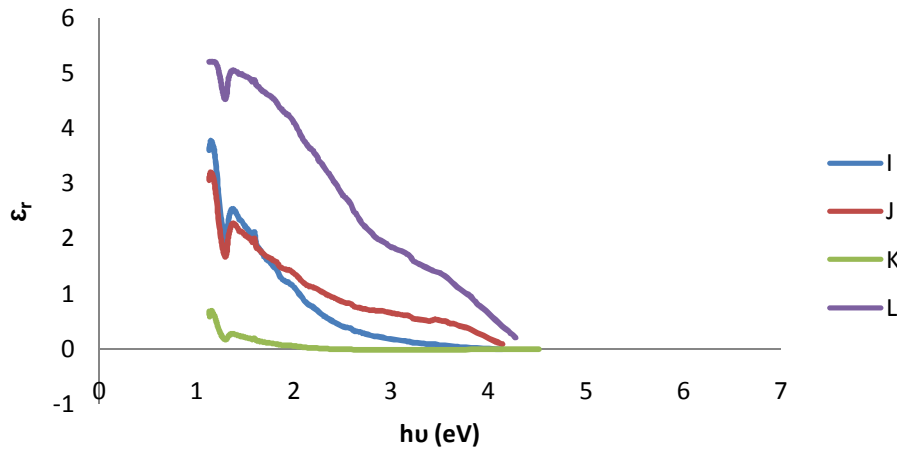


Fig. 4.28: A plot of real dielectric (ϵ_r) against photon energy (eV) for SnI_2

In figure 4.28, samples I, J and K has real dielectric from 0 to 3.9 but L has the highest real dielectric from 1.1 to 5.2.

Imaginary dielectric vs. Photon energy

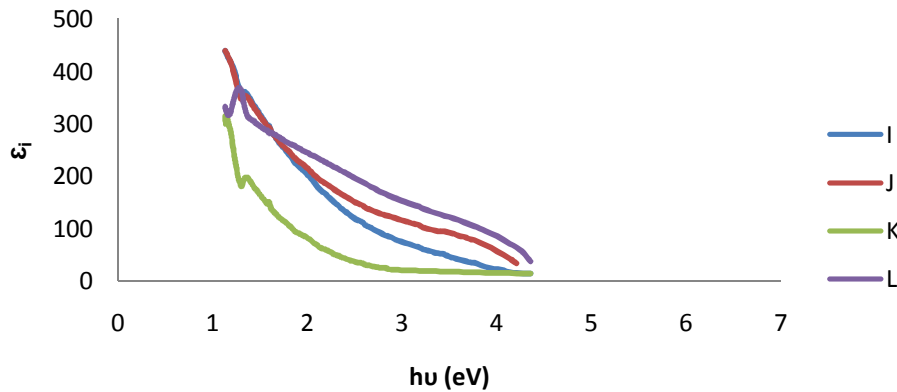


Fig. 4.29: A plot of imaginary dielectric (ϵ_i) against photon energy (hν) for SnI_2

In figure 4.29, samples I, J, K and L have imaginary dielectric from 10 to 450. All the samples have the same dielectric 350 to 450.

4.1d. Optical Results for Stannic Iodide (SnI_4).

The graphs of the optical analyses for the grown crystals of undoped and impurity doped SnI_4 are shown in figures 4.30 - 4.39.

FIGURES 4.30-4.39: Optical Properties of Stannic Iodide (SnI_4)

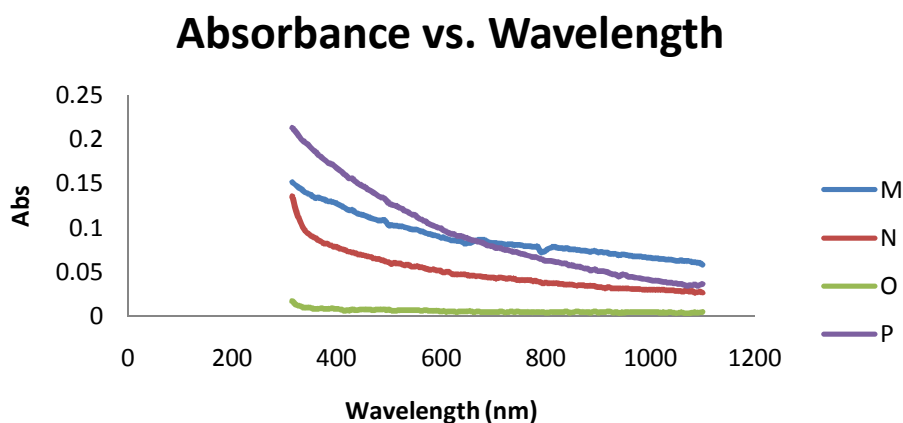


Fig. 4.30: A plot of absorbance (A) against wavelength (nm) for SnI_4

In figure 4.30, sample O absorbs little in the VIS region and has no absorbance up to the IR. Samples M and N have good absorbance from the VIS regions and decreased towards the IR region. Sample P has the highest absorbance in the UV-VIS regions decreased towards the infra red.

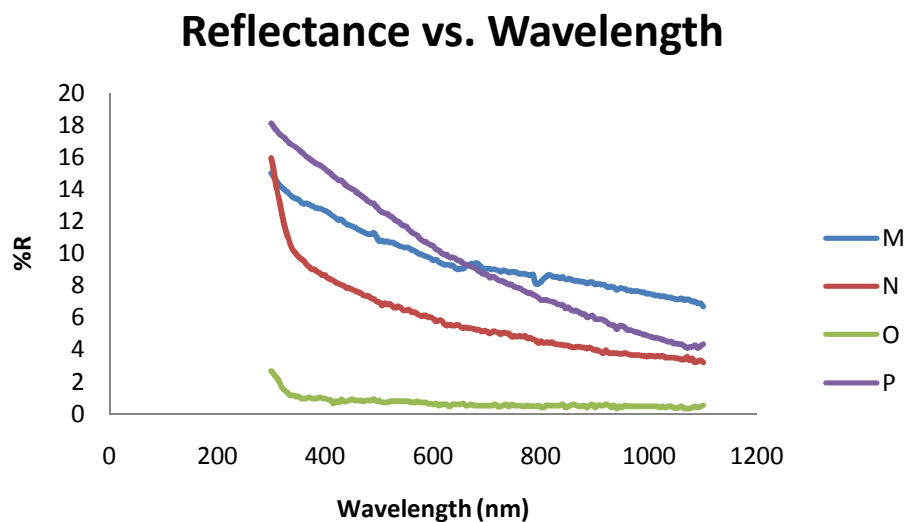


Fig. 4.31: A plot of reflectance (%) against Wavelength (nm) for SnI_4

In figure 4.31, samples M, N and P are reflecting highly in the UV to VIS regions and decreased towards the IR. Samples M and P have the same reflectance at 650nm. Sample O has the least reflectance at 1% from the VIS to the infra red.

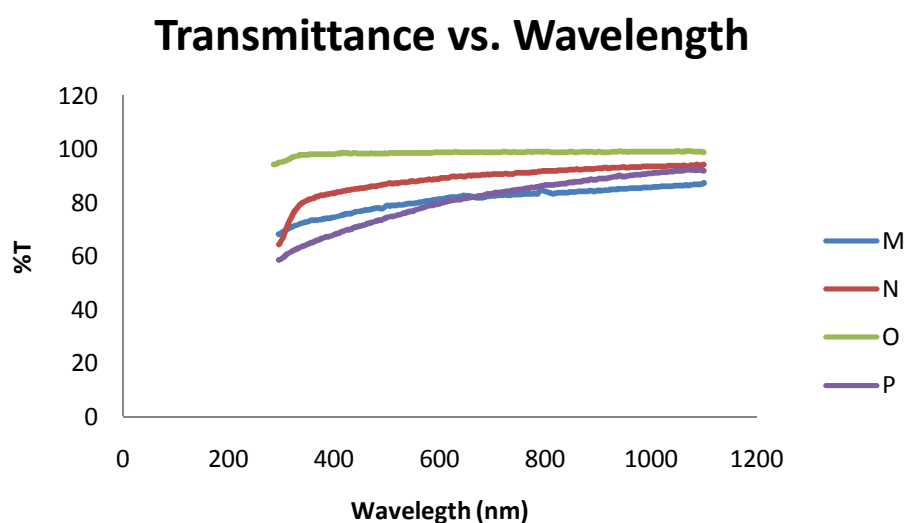


Figure 4.32: A plot of Transmittance (%) against wavelength (nm) for SnI_4

In figure 4.32, sample O has the highest transmittance from the near VIS region to the infra red region. Samples M, N and P have almost the same transmittance from the UV-VIS region to the infra red region. They can be used in solar cell applications [84] in addition to their oxidizing actions.

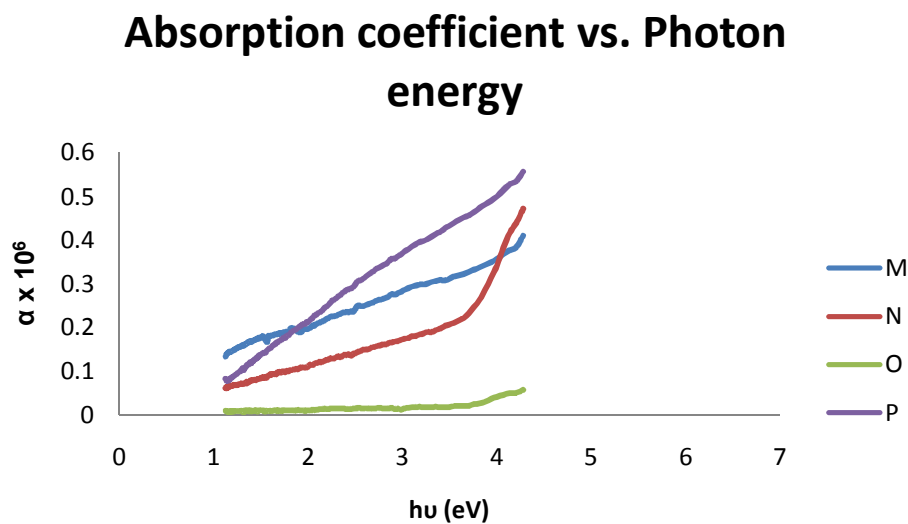


Fig. 4.33: A plot of absorption coefficient (α) against photon energy ($h\nu$) for SnI_4

In figure 4.33, samples M, N and P have absorption coefficient from 0.09×10^6 to 0.59×10^6 . Sample O has absorption coefficient from 0 to 0.1.

Band gap vs. Photon energy

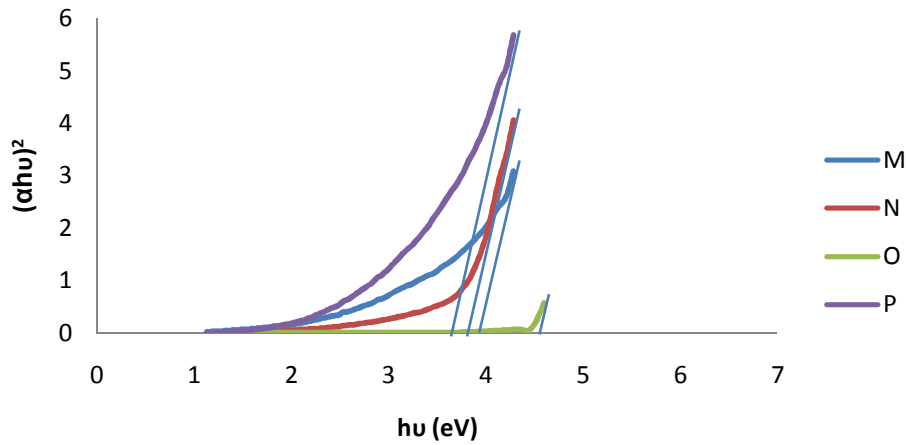


Fig. 4.34: A plot of $(\alpha h\nu)^2$ against photon energy $(h\nu)$ for SnI_4

Figure 4.34 is the plot of $(\alpha h\nu)^2$ against photon energy (eV) for SnI_4 . Samples M, N, O and P have band gaps ranging from 3.6 to 4.5 eV. They are wide band gap materials and can be applied in high temperature, high power and high frequency materials [88].

Band gap vs. Photon energy

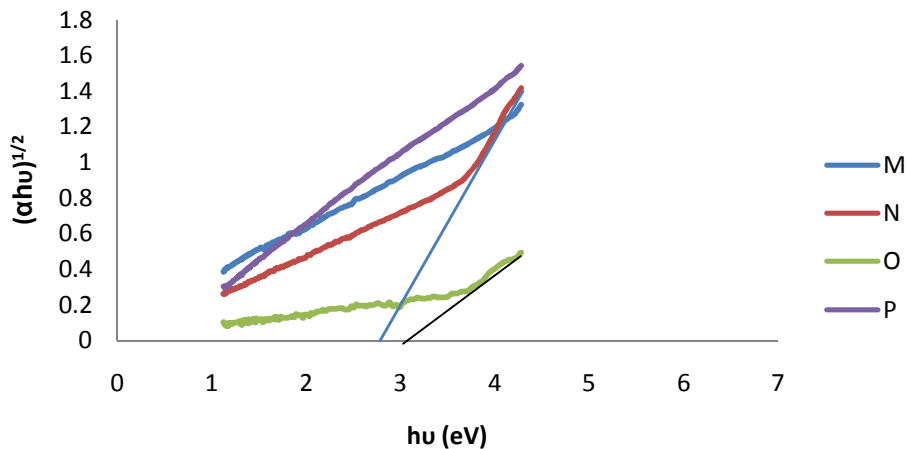


Fig. 4.35: A plot of $(\alpha h\nu)^{1/2}$ against photon energy $(h\nu)$ for SnI_4 .

Figure 4.35 is the plot of $(\tilde{U}h\nu)^{1/2}$ against photon energy (eV) for SnI_4 . Samples N and O have band gaps between 2.7 to 3.0 eV. Samples M and P have no band gaps. Samples N and O are wide band gap materials and can be applied in high temperature, high power and high frequency materials [88].

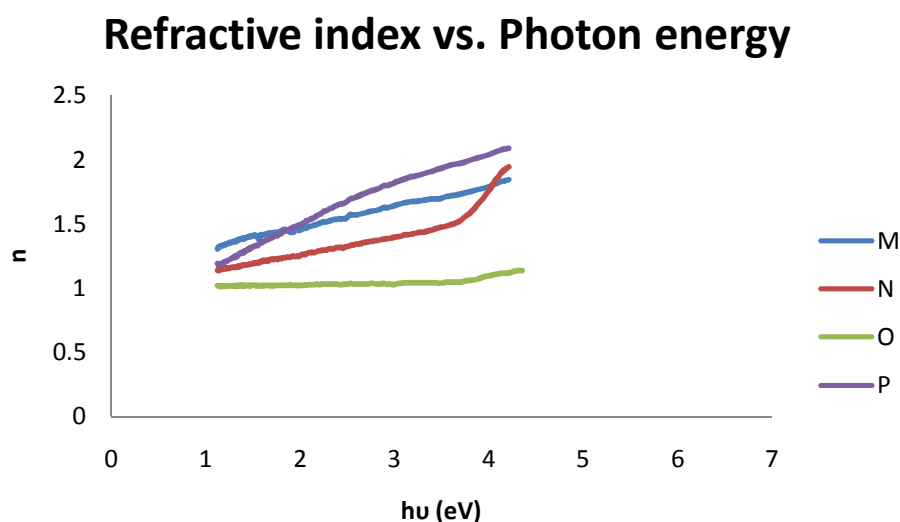


Fig. 4.36: A plot of refractive index against photon energy (eV) for SnI_4 .

Samples M, N and P have refractive indices from 1.2 to 2.0. Sample O has the least and constant refractive index at 1.

Extinction coefficient vs. Photon energy

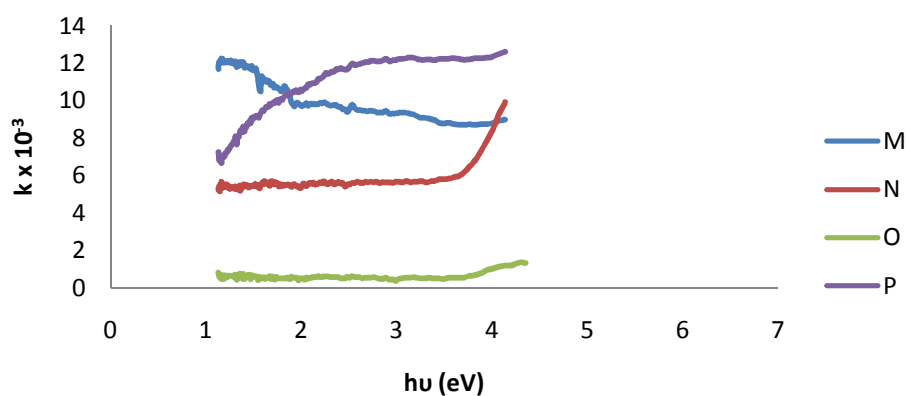


Fig. 4.37: A plot of extinction coefficient (k) against photon energy (eV) for SnI_4 .

In figure 4.37, samples M and P have extinction coefficients from 7×10^{-3} to 13×10^{-3} . Sample M has extinction coefficient from 5 to 10×10^{-3} . Sample O has the least extinction coefficient from 0.9 to 1.9×10^{-3} .

Real dielectric vs. Photon energy

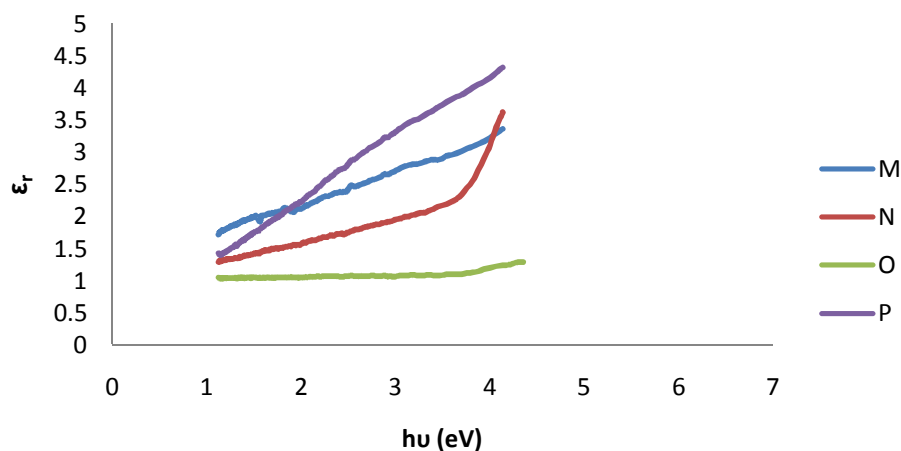


Fig. 4.38: A plot of real dielectric (ϵ_r) against photon energy (eV) for SnI_4 .

In figure 4.38, samples M, N and P have real dielectrics from 1.4 to 3.5. Sample M has the same real dielectric with P at 2. Sample O has the least real dielectric from 1 to 1.4.

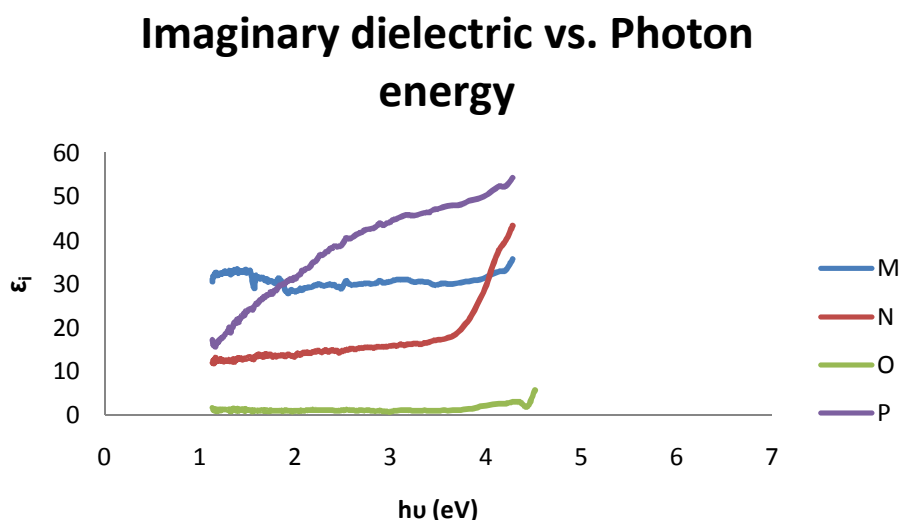


Fig. 4.39: A plot of imaginary dielectric (ϵ_i) against photon energy (eV) for SnI_4 .

In figure 4.39, samples M, N and P have imaginary dielectric from 10 to 55. Sample O has zero imaginary dielectric up to 3.85eV and increased 6 on the imaginary scale.

4.1e. Optical results for Cadmium Sulfide (CdS).

The graphs of the optical analyses for the grown crystals of undoped and impurity doped CdS are shown in figures 4.40 - 4.49.

FIGURES 4.40 - 4.49: Optical Properties of Cadmium Sulfide (CDS).

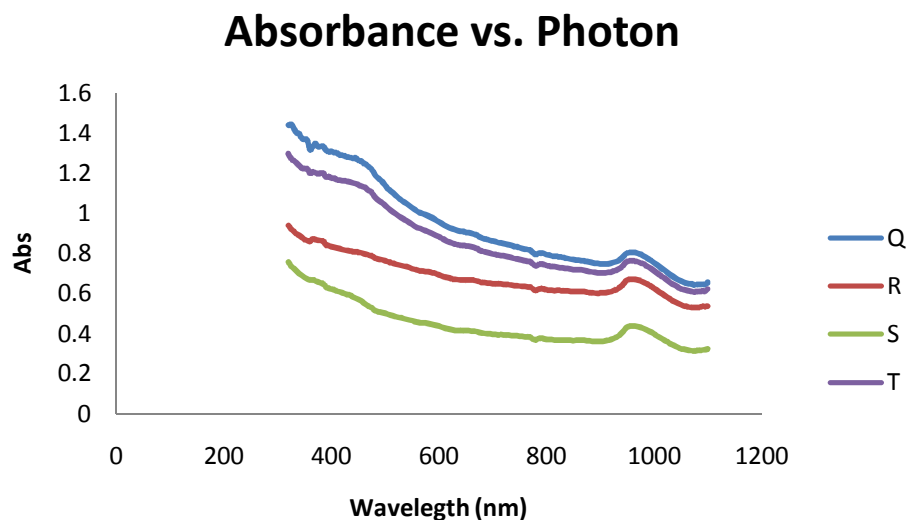


Fig. 4.40: A plot of absorbance against wavelength (nm) for CdS.

In figure 4.40, samples Q, R, S and T have very high absorbance in the visible region and decreased towards the infra red. This suggest that they can be employed in solar cell technology and poultry house applications [84].

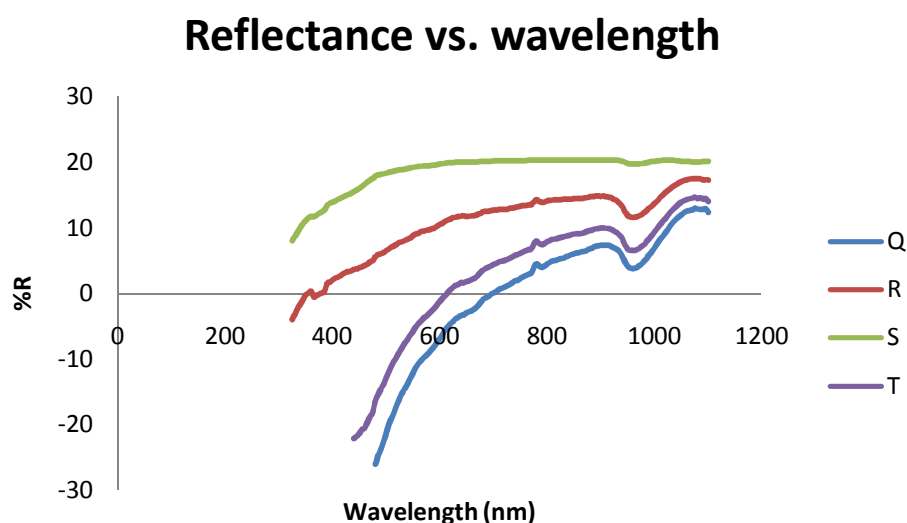


Fig. 4.41: A plot of reflectance (%) against wavelength (nm) for CdS.

In figure 4.41, all the samples have negative reflectance and increased towards the infra red.

Transmittance vs. Wavelength

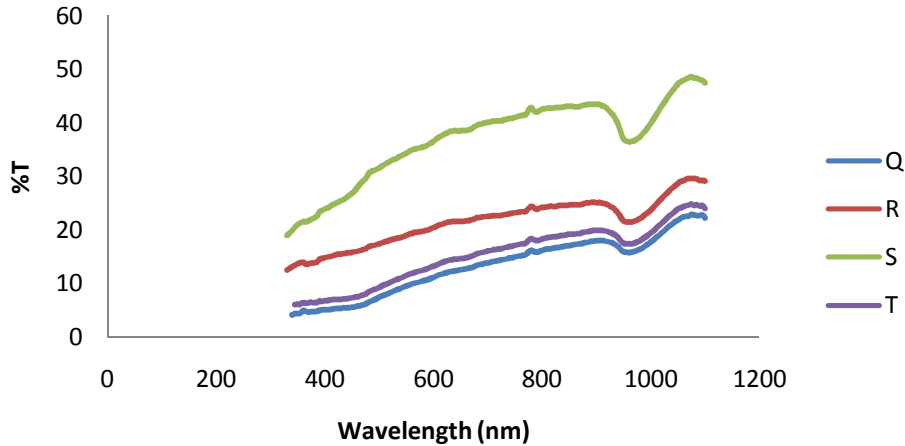


Fig. 4.42: Transmittance (%) against wavelength (nm) for CdS.

In figure 4.42, all the samples are moderately transmitting in the visible region and increased towards the infra red region with S having the highest transmittance. The materials are good for solar cells and poultry applications [83-87].

Absorption coefficient vs. Wavelegth

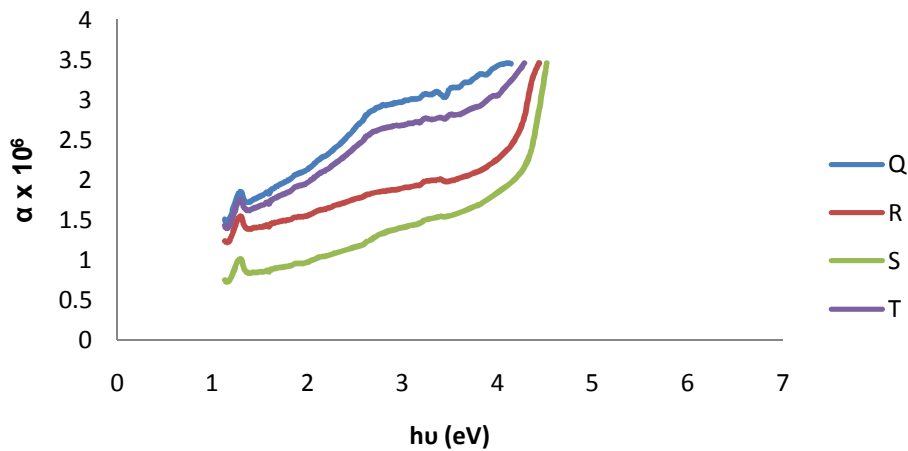


Fig. 4.43: A plot of absorption coefficient (α) against photon energy ($h\nu$) for CdS.

In figure 4.43, samples Q, R, S and T have absorption coefficient from 0.6×10^6 to 3.5×10^6 .

Direct allowed vs. Photon

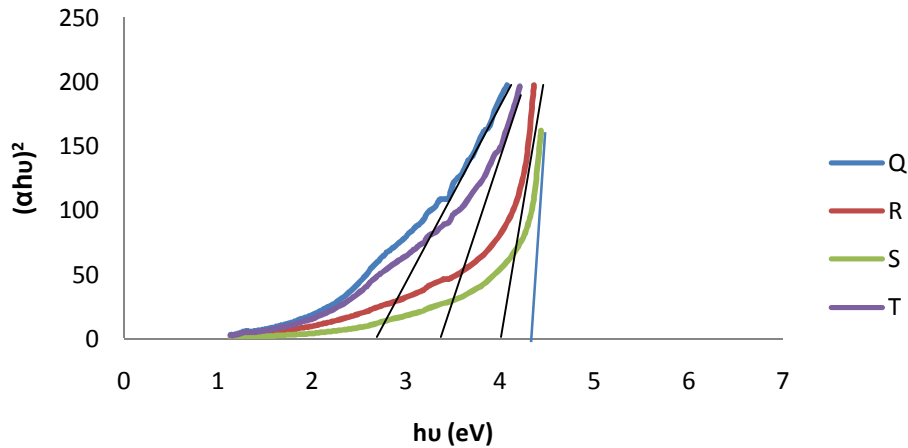


Fig. 4.44: A plot of $(\alpha h\nu)^2$ against photon energy (eV) for CdS.

Figure 4.44 is the plot of $(\alpha h\nu)^2$ against photon energy (eV) for CdS. Samples Q, R, S and T have band gaps ranging from 2.6 to 4.3 eV. They are wide band gap materials and can be applied in high temperature, high power and high frequency materials [88] solar cell applications.

Indirect allowed vs. Photon energy

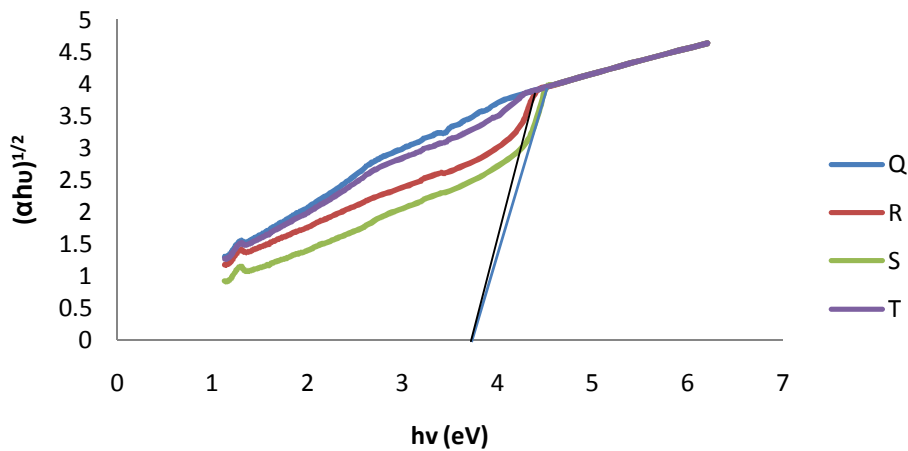


Fig. 4.45: A plot of $(\alpha h\nu)^{1/2}$ against photon energy (eV) for CdS.

Figure 4.45 is the plot of $(\tilde{U}hg)^{1/2}$ against photon energy (eV) for CdS. Samples R and S have the same band gaps at 3.7eV. Samples Q and T have no band gaps. They are wide band gap materials and can be applied in high temperature, high power and high frequency materials [88].

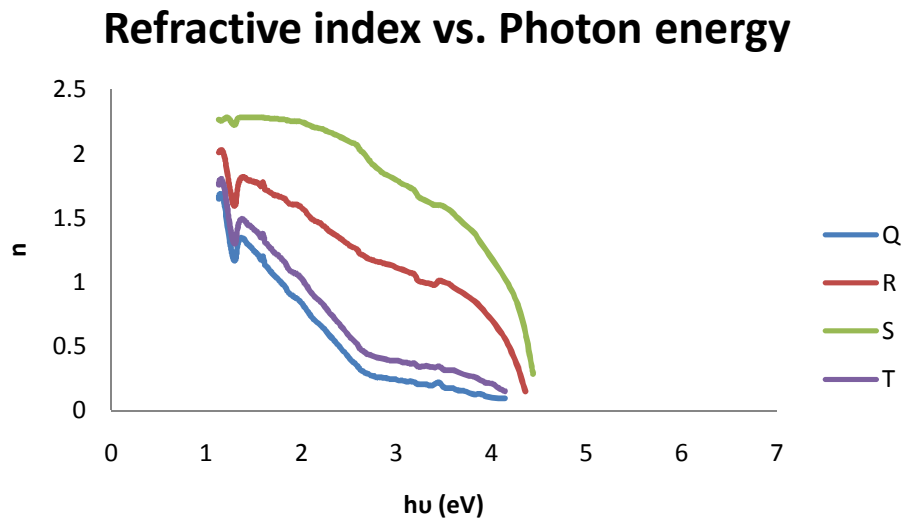


Fig. 4.46: A plot of refractive index against photon energy (eV) for CdS.

In figure 4.46, samples Q, R, S and T have refractive indices from 0.2 to 2.3. Sample S has the highest refractive index.

Extinction coefficient vs. Photon energy

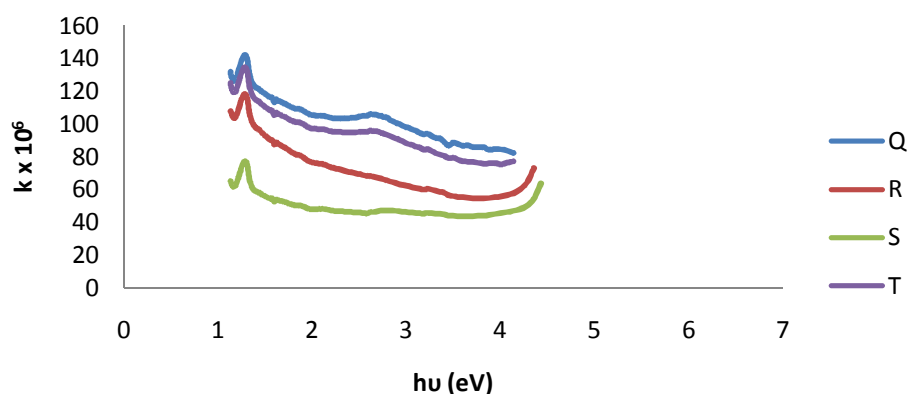


Fig. 4.47: A plot of extinction coefficient against photon energy (eV) for CdS.

In figure 4.47, samples Q, R, S and T have extinction coefficient ranging from 42×10^6 to 140×10^6 .

Real dielectric vs. Photon energy

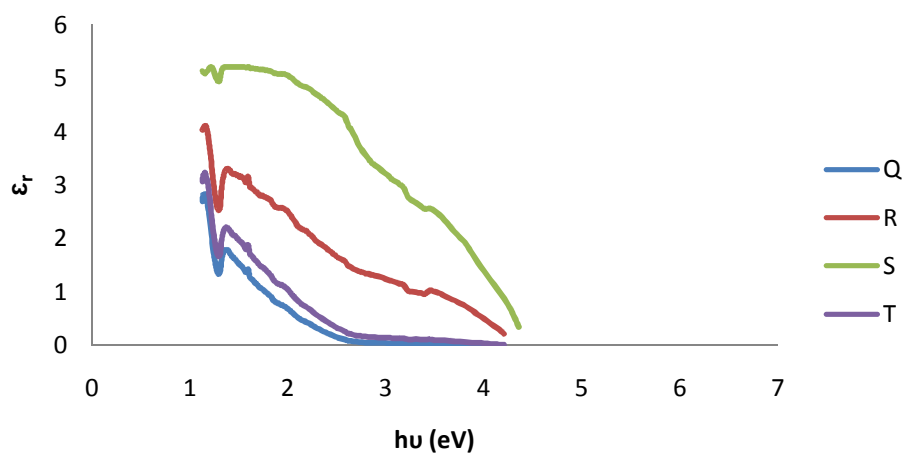


Fig. 4.48: A plot of real dielectric against photon energy (eV) for CdS.

Figure 4.48 is the real dielectric for the sol-gel grown cadmium sulphide. Sample S has the highest real dielectric from 0.4 to 5. Samples Q and T have zero real dielectric from 2.6 to 4.1 eV.

Imaginary dielectric vs. Photon

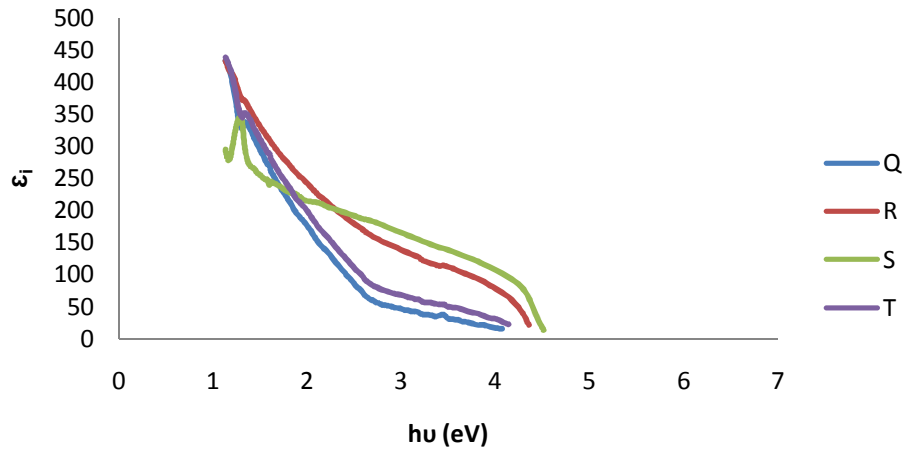


Fig. 4.49: A plot of imaginary dielectric ϵ_i against photon energy (eV) for CdS.

In figure 4.49, samples Q, R, S and T have imaginary dielectric from 10 to 450. All the samples have equal dielectric at 350.

4.1f. Optical Results for Local Impurity.

The graphs of the optical analyses for the locally made impurities are shown in figures 4.50-4.59.

Figures 4.50-4.59: Optical Properties of Local Impurities.

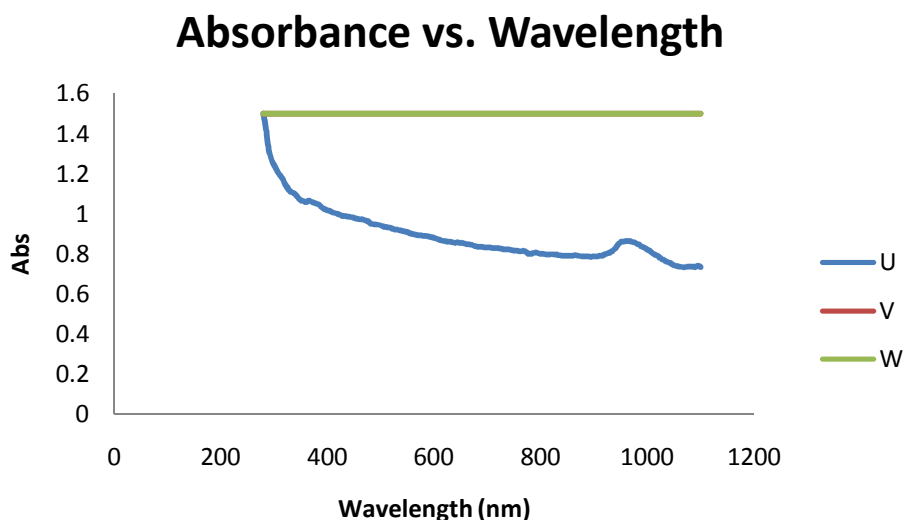


Fig. 4.50: A plot of absorbance (A) against wavelength (nm) for impurities.

In figure 4.50, samples V and W have very high absorbance and of equal strengths at 1.5. They are absorbing from the near VIS to the IR region. Sample U has the least absorbance. It absorbs highly in the visible region and decreased towards the infrared region.

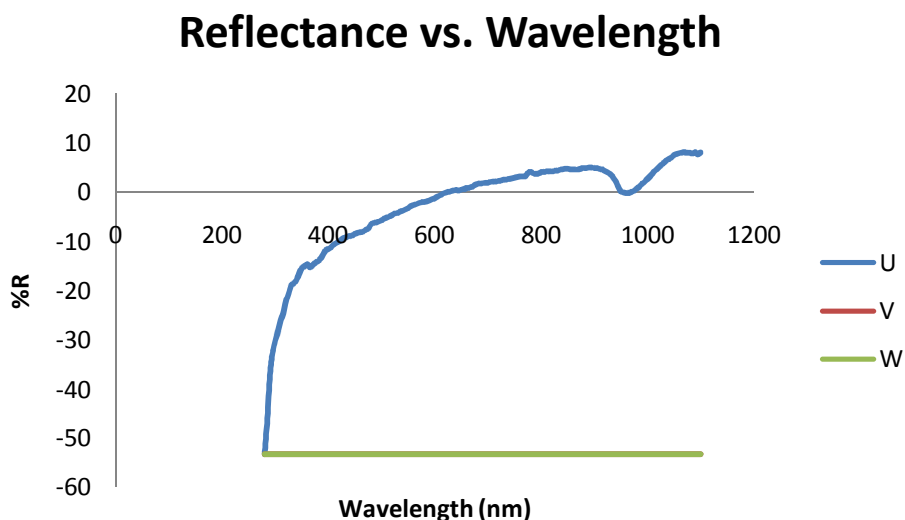


Fig. 4.51: A plot of reflectance (%) against wavelength (nm) for impurities.

In figure 4.51, samples V and W have negative reflectance and are of equal strength at -55%. Sample U has negative reflectance up to visible region and increased towards the infra red region.

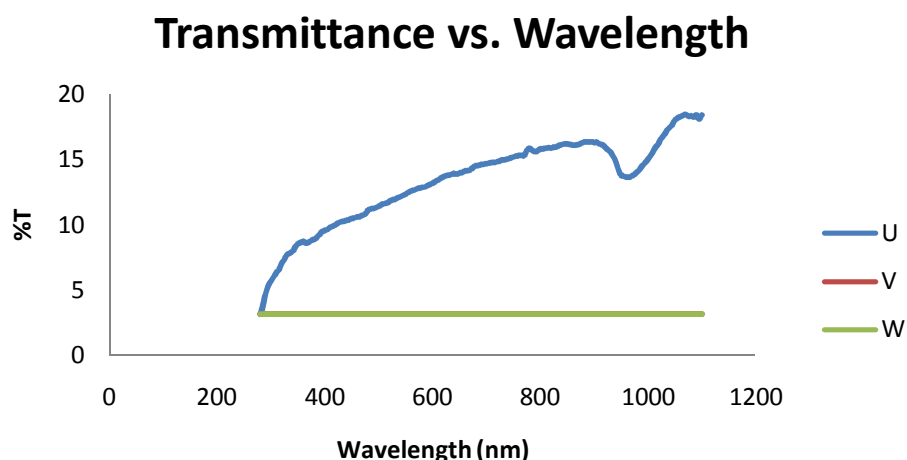


Fig. 4.52: A plot of transmittance (%T) against wavelength (nm) for impurities.

In figure 4.52, samples V and W have very low transmittance and of equal strengths at 2.29%. Samples V and W are moderately transmitting at constant rates and of equal strengths. Sample U is transmitting moderately in the UV-VIS region and increased towards the infra red. It has an inflexion at 1000nm.

Absorption coefficient vs. Photon energy

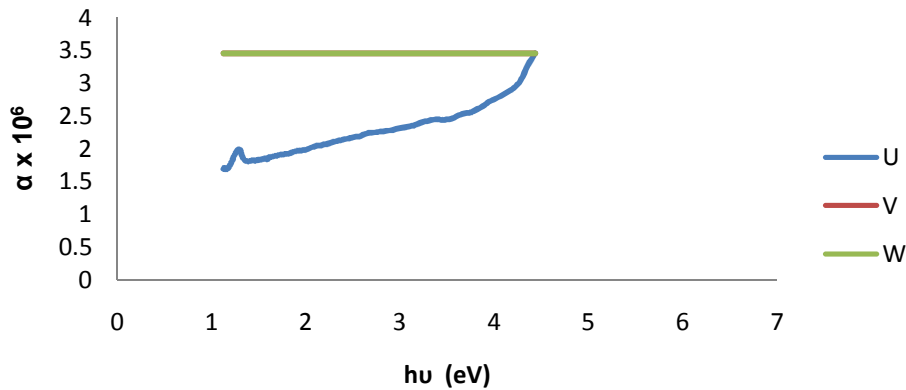


Fig. 4.53: A plot of absorption coefficient (α) against wavelength (nm) for impurities.

In figure 4.53, samples V and W have equal absorption coefficient at 3.5×10^6 . Sample U has the least absorption coefficient ranging from 1.6×10^6 to 3.3×10^6 .

Band gap vs. Photon energy

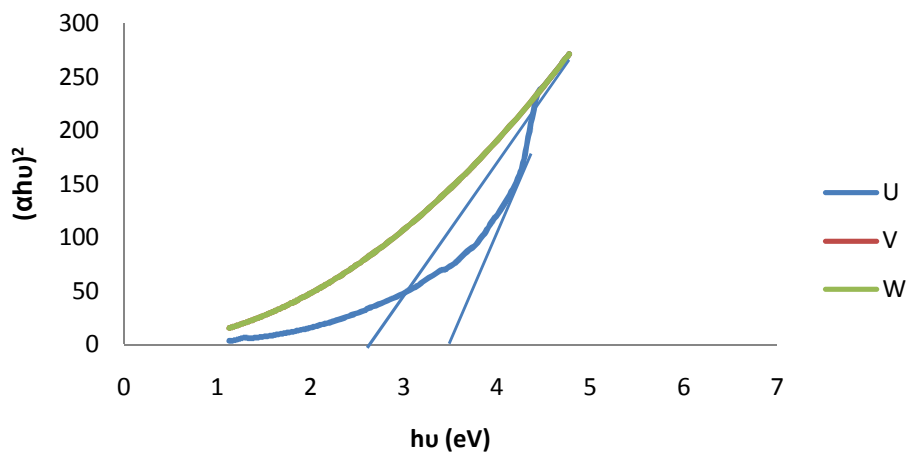


Fig. 4.54: A plot of $(\alpha h\nu)^2$ against wavelength (nm) for impurities.

Figure 4.54 is the plot of $(\alpha h\nu)^2$ against photon energy (eV) for the impurities. Sample U has band gap of 3.5eV. Samples V and W have

the same band gap of 2.6eV. The band gaps ranged from 2.6 to 3.5eV. They are wide band gap materials and can be applied in high temperature, high power and high frequency materials [88].

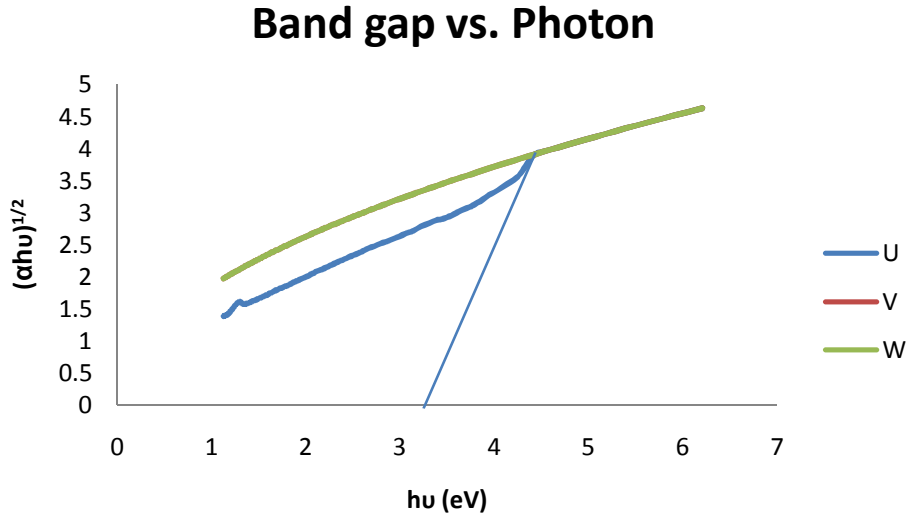


Fig. 4.55: A plot of $(\alpha h\nu)^{1/2}$ against photon energy (eV) for the impurities.

Figure 4.55 is the plot of $(\alpha h\nu)^{1/2}$ against photon energy (eV) for the impurities. Sample U has a band gap of 3.2eV. Samples V and W have no band gaps. Sample U is a wide band gap material and can be applied in high temperature, high power and high frequency materials [88].

Refractive index vs. Photon energy

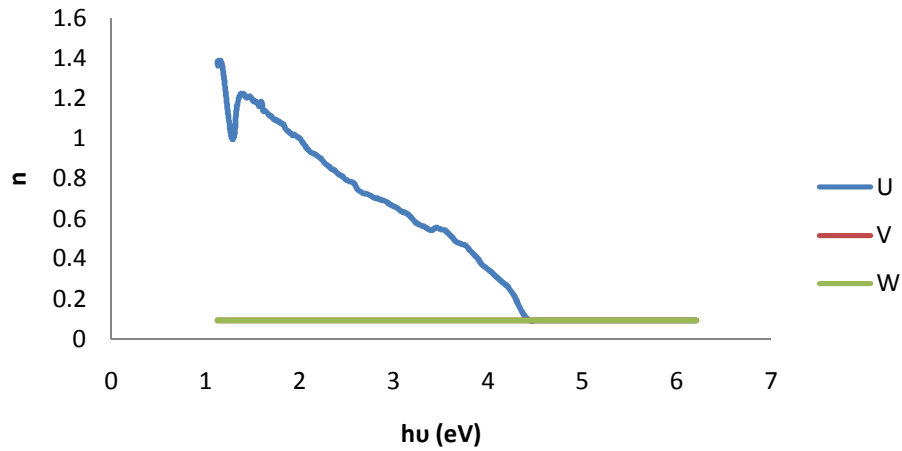


Fig. 4.56: A plot of refractive index against photon energy (eV) for impurities.

In figure 4.56, samples V and W have the same refractive indices at 0.1. Sample U has refractive index from 0.1 to 1.4.

Extinction coefficient vs. Photon energy

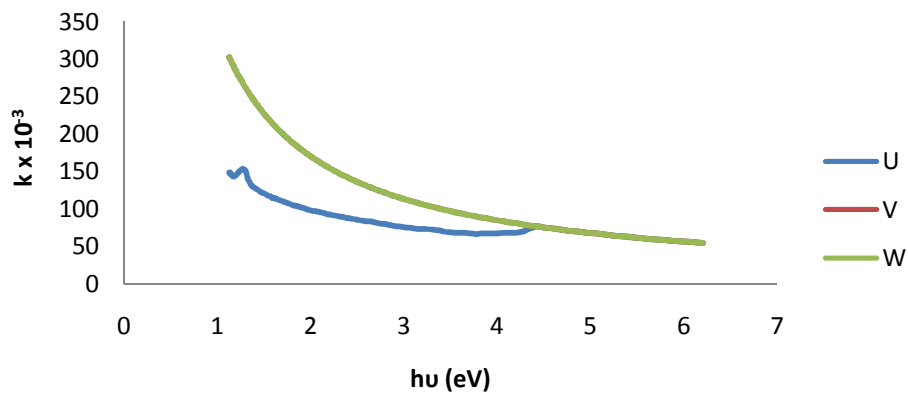


Fig. 4.57: A plot of extinction coefficient against photon energy (eV) for impurities.

In figure 4.57, samples V and W have equal extinction coefficients from 50×10^{-3} to 300×10^{-3} . Sample U has the least extinction coefficient from 70×10^6 to 150×10^6 .

Real dielectric vs. Photon energy

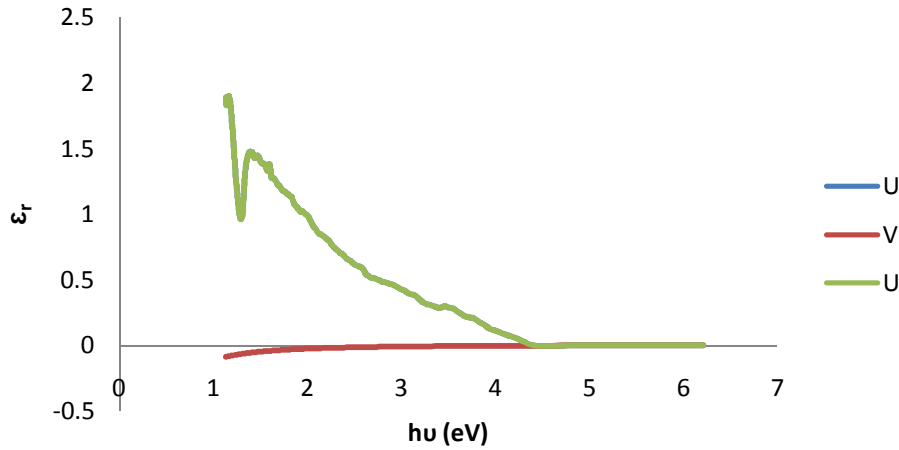


Fig. 4.58: A plot of real dielectric (ϵ_r) against photon energy for impurities.

In figure 4.58, samples V and W have no real dielectric but sample U has dielectric ranging from 0 to 2.0.

Imaginary dielectric vs. Photon energy

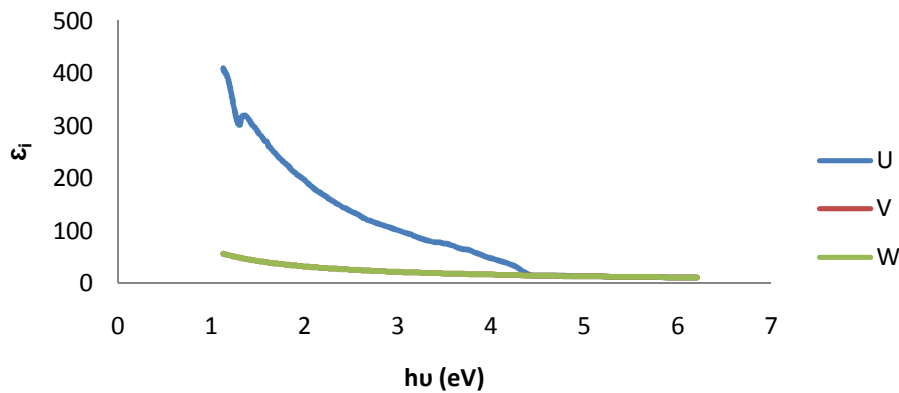


Fig. 4.59: A plot of imaginary dielectric (ϵ_i) against photon energy (eV) for impurities

In figure 4.59, samples V and W have equal imaginary dielectric from 10 to 60 while sample U has imaginary dielectric from 20 to 400. Sample U has the same dielectric with V and W from 4.5 to 6.3eV.

4.2. Structural Properties Results

X-ray diffraction analysis (XRD) was used to identify the crystalline phases present in the crystals and to study the structural properties. The XRD characterization was done using CuK α radiation. Diffraction patterns of the samples were recorded in the 2θ range from 10° to 72° . XRD spectra in figures 4.60-4.96 revealed that the compounds grown are crystalline, nano materials. For each spectrum, the crystallite size was determined using the Debye Scherer formula as given below:

$$D = K\lambda / b \cos\theta$$

Where $K=0.9$ is the shape factor, $\lambda=1.5409\text{\AA}$, θ is the diffraction angle (Bragg's angle) in degrees and b is the full width at half maximum (FWHM).

Figures 4.60-4.63: Diffractogram for un-doped and impurity doped PbCl_2

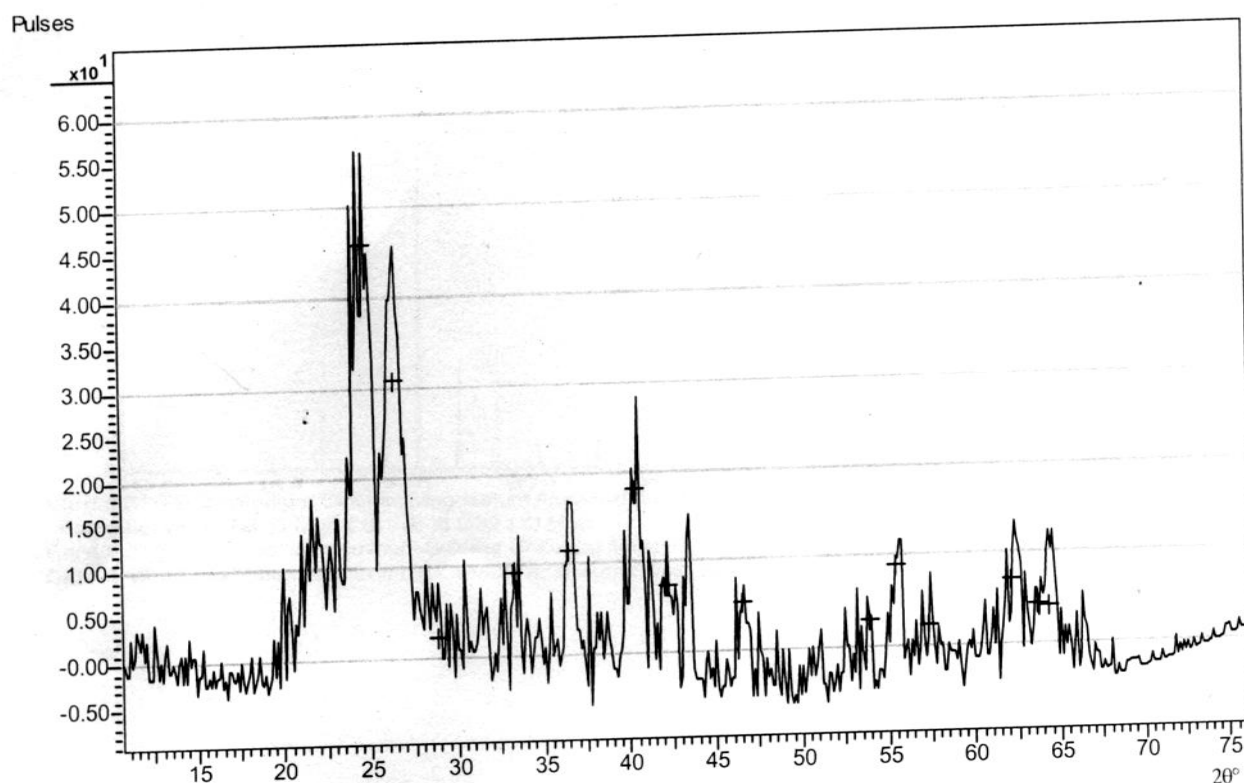


Fig. 4.60: XRD spectra for un-doped PbCl_2 .

In figure 4.60, the un-doped lead chloride has sharp peaks at 23° , 24° , 25° , 26° , 35° , 37.5° , 40.5° , 47.5° , 57° and 67° . The presence of sharp peaks indicates that they are crystalline [86]. The diffractogram has broad base and crystallite size ranging from 0.07108 to 1.36249 showing that they are of nano nature [87, 89-94]

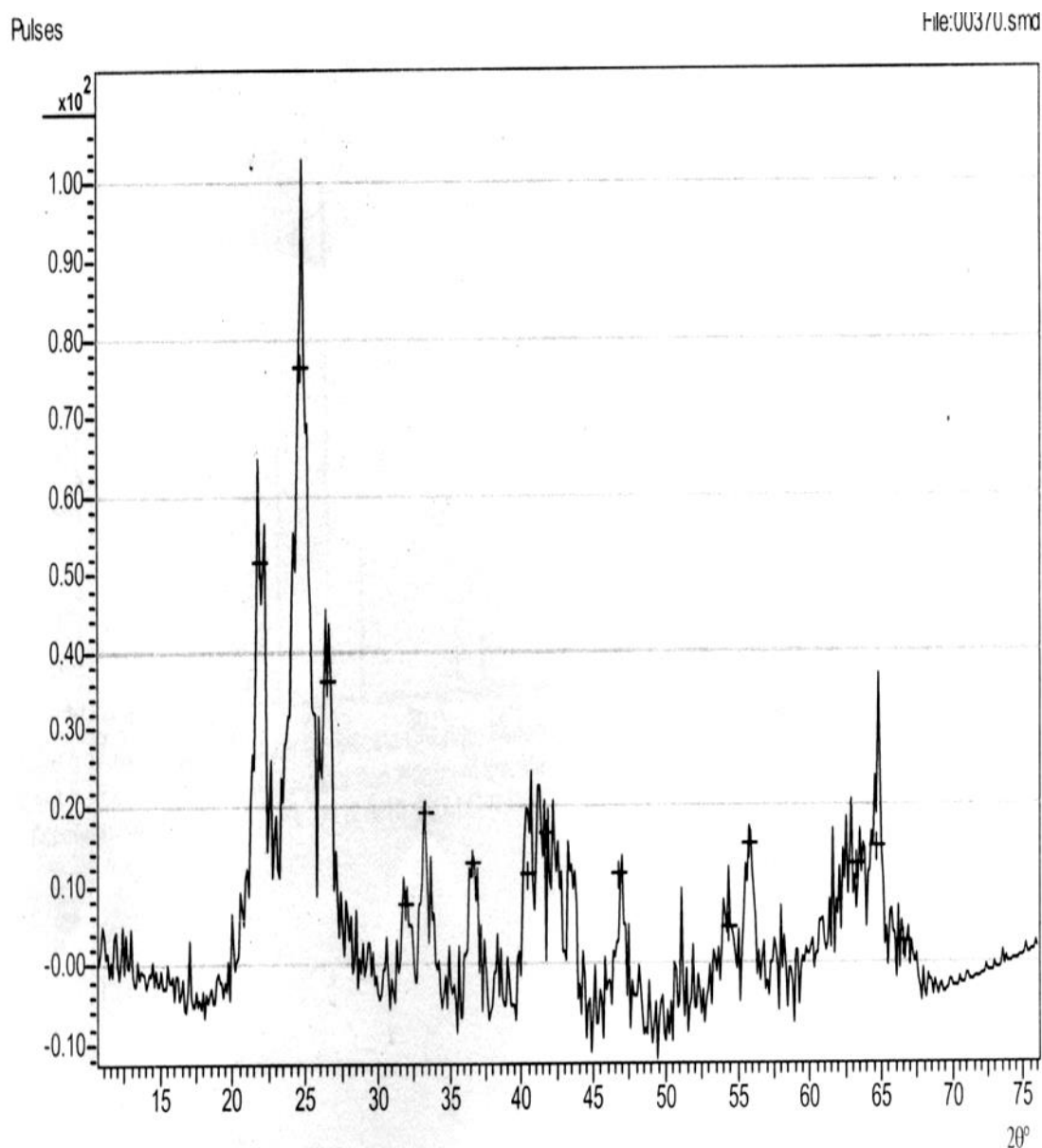


Fig. 4.61: XRD spectra for potash doped PbCl_2 .

Figure 4.61 is potash doped lead chloride crystal. It has sharp peaks at 16° , 23° , 25° , 27.5° , 30° , 36° and 65° . These indicate that they are crystalline. They have broad base and crystallite size ranging from 0.24667 to 1.73365nm, indicating that they are nano crystalline materials [86].

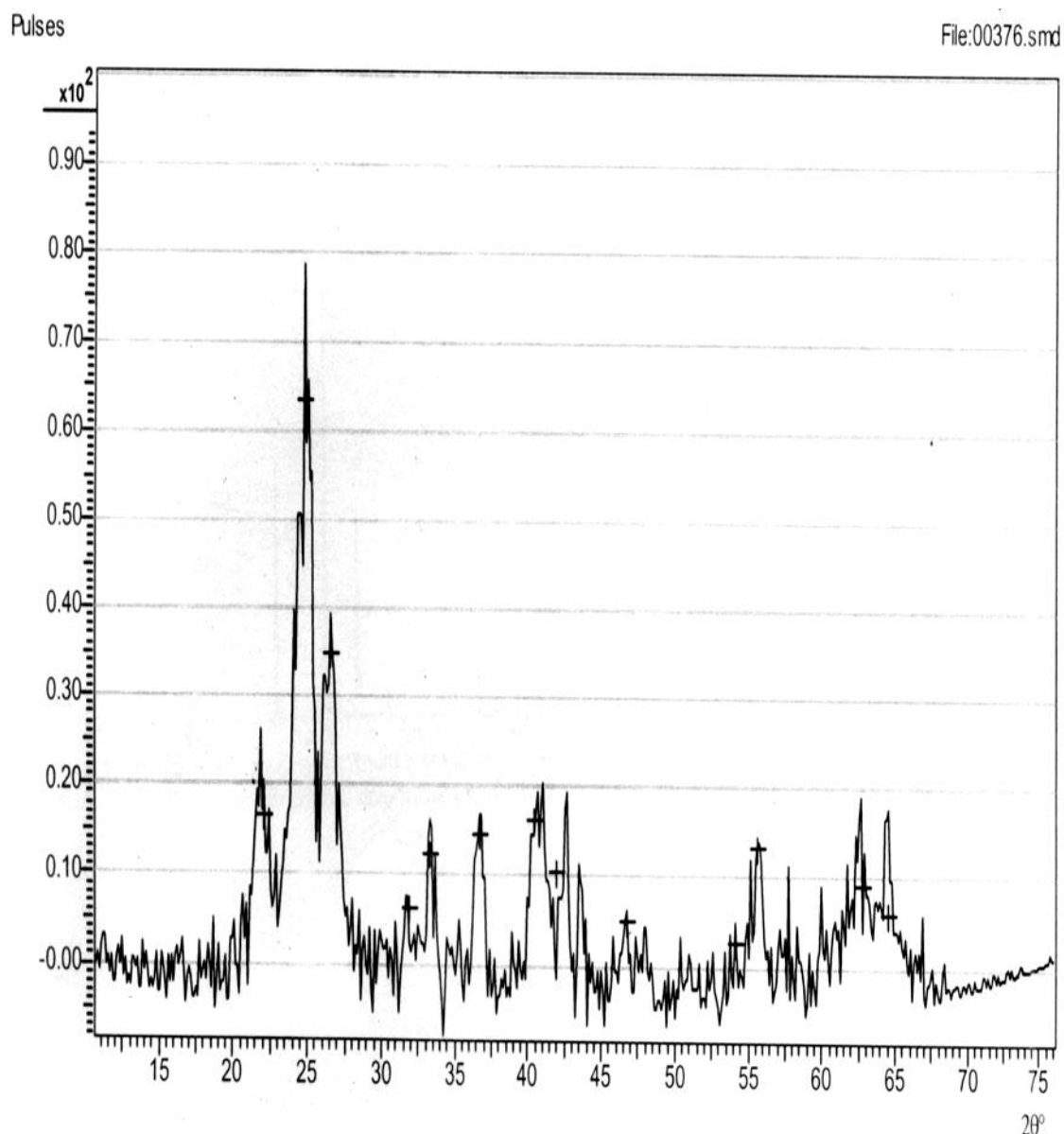


Fig. 4.62: XRD spectra for bamboo doped PbCl_2 .

Figure 4.62 is bamboo doped lead chloride. It has sharp peaks at 25° , 28° , 37.5° , 40° , 47.5° , 52° and 68° . These indicate that they are crystalline [86]. They have broad base and crystallite sizes ranging from 0.09896 to 2.1675 nm, indicating that they are nano materials [87].

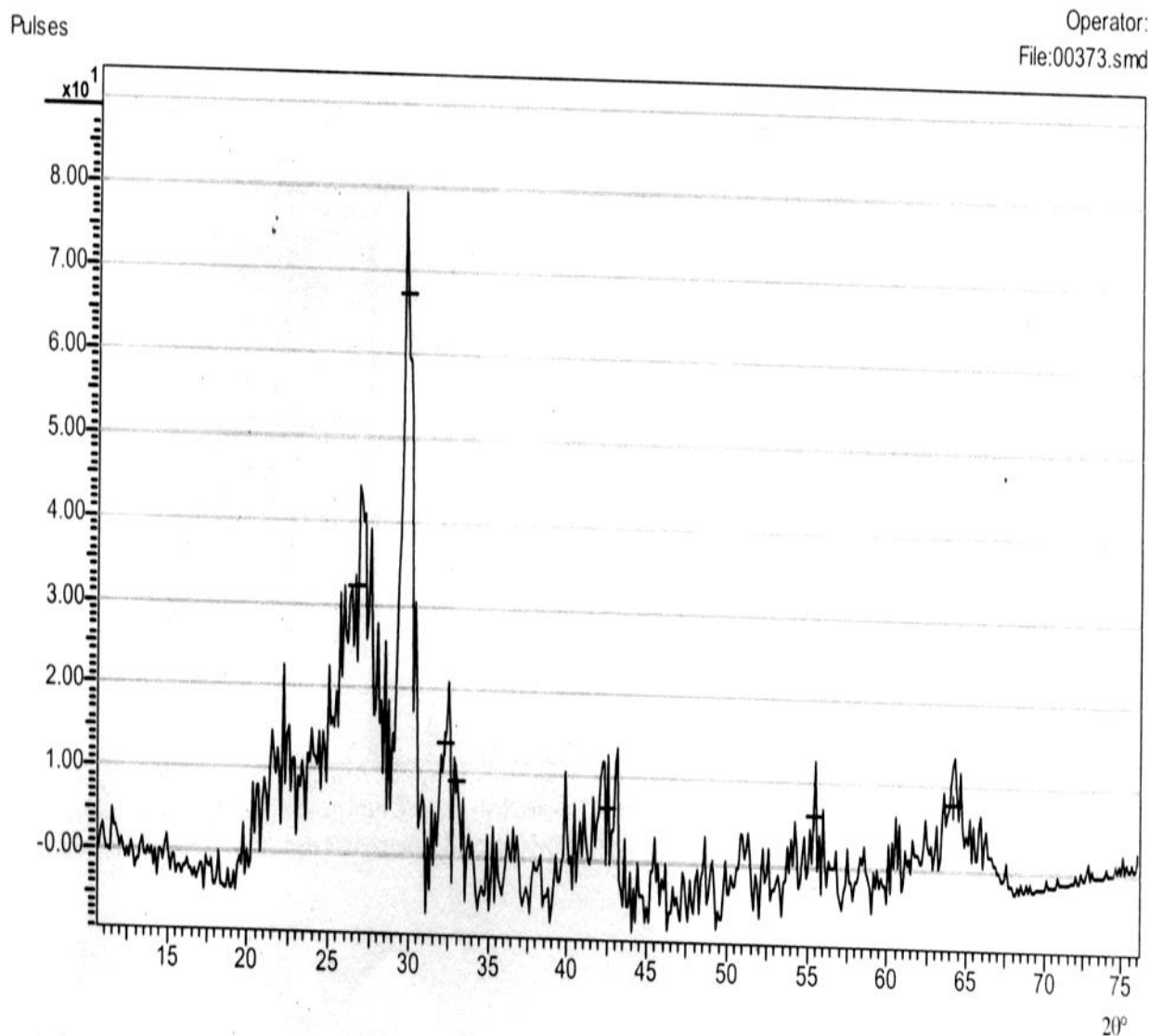


Fig. 4.63: XRD spectra for raffia doped PbCl_2 .

Figure 4.63 is XRD spectra for raffia doped lead chloride. It has sharp peaks at 24° , 26° , 30° , 32.5° , 37.5° , 47.5° , 55° and 65° . These indicate that they crystalline [86]. They have broad base and crystallite sizes ranging from 0.01598 to 1.5396nm, indicating that they are nano materials [89].

Figures 4.64-4.67: Diffractogram for potassium Perchlorate Crystal (KClO_4).

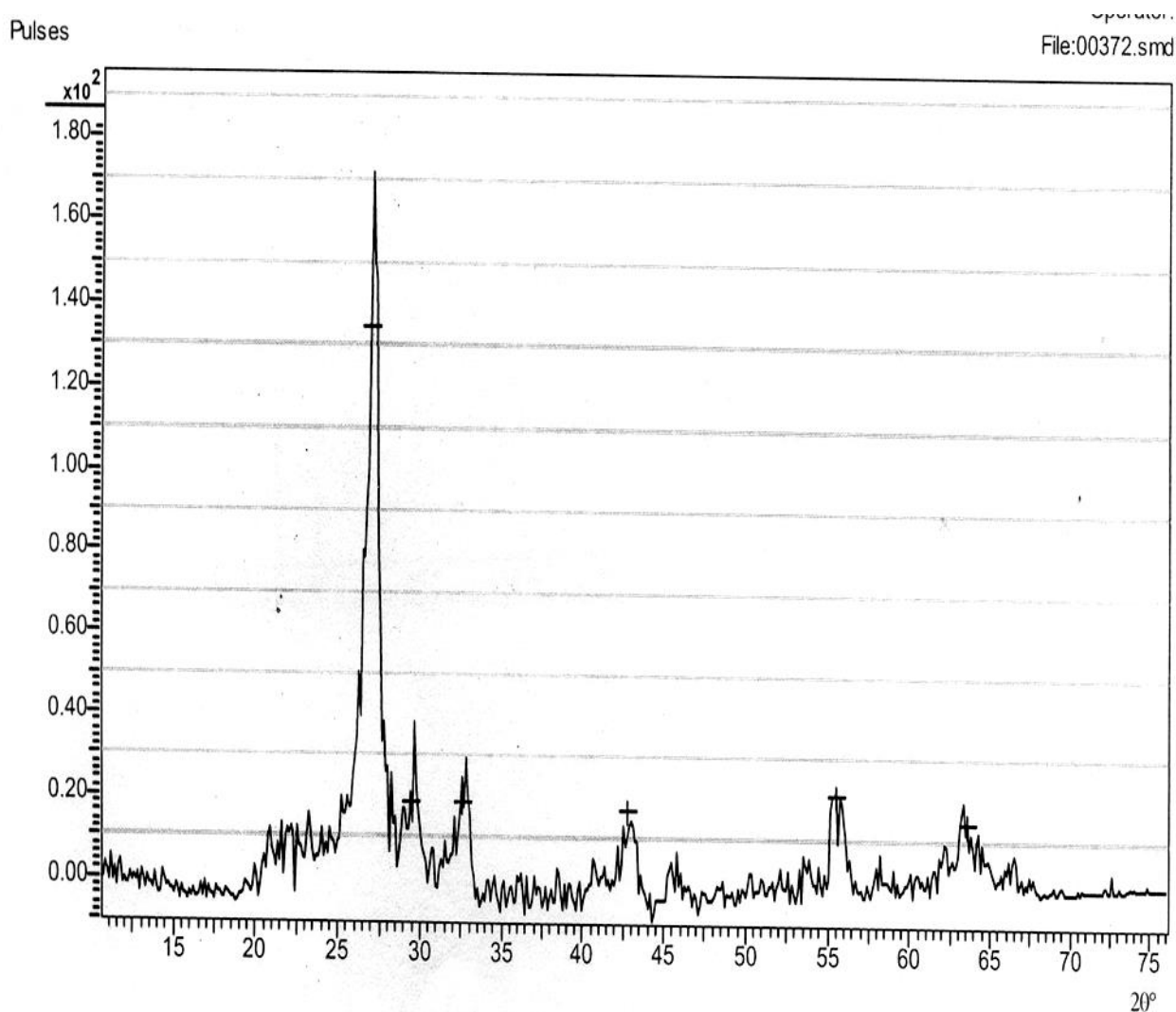


Figure 4.64: XRD spectra for un-doped KClO_4 .

Figure 4.64 is un- potassium perchlorate. It has sharp peaks at 26.98° , 29.43° , 33° , 43° , 46° , 47.5° , 55.5° and 64° . These indicate that they are crystalline [86]. They have broad base and crystallite sizes ranging from 0.68979 to 1.55562nm, indicating that they are nano materials [93].

Pulses

File:00374.smd

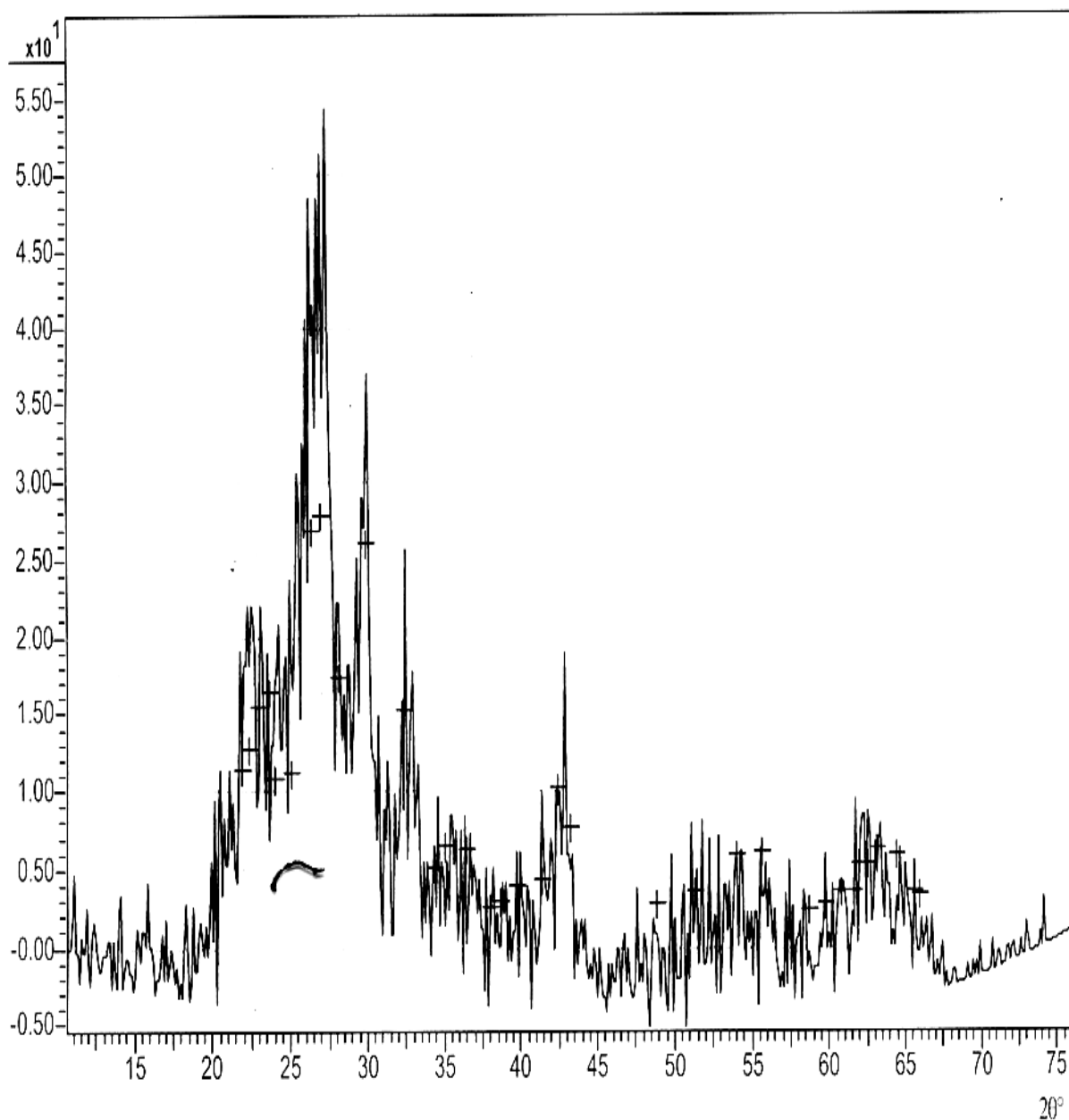


Figure 4.65: XRD spectra for potash doped KClO_4 .

Figure 4.65 is potash doped lead chloride. It has sharp peaks at 2° , 14° , 20.5° , 22° , 25° , 30° , 43° and 65° . These indicate that they crystalline [86]. They have broad base and crystallite sizes ranging from 0.84985 to 1.05131nm, indicating that they are nano materials [92].

Pulses

File:00371.smd

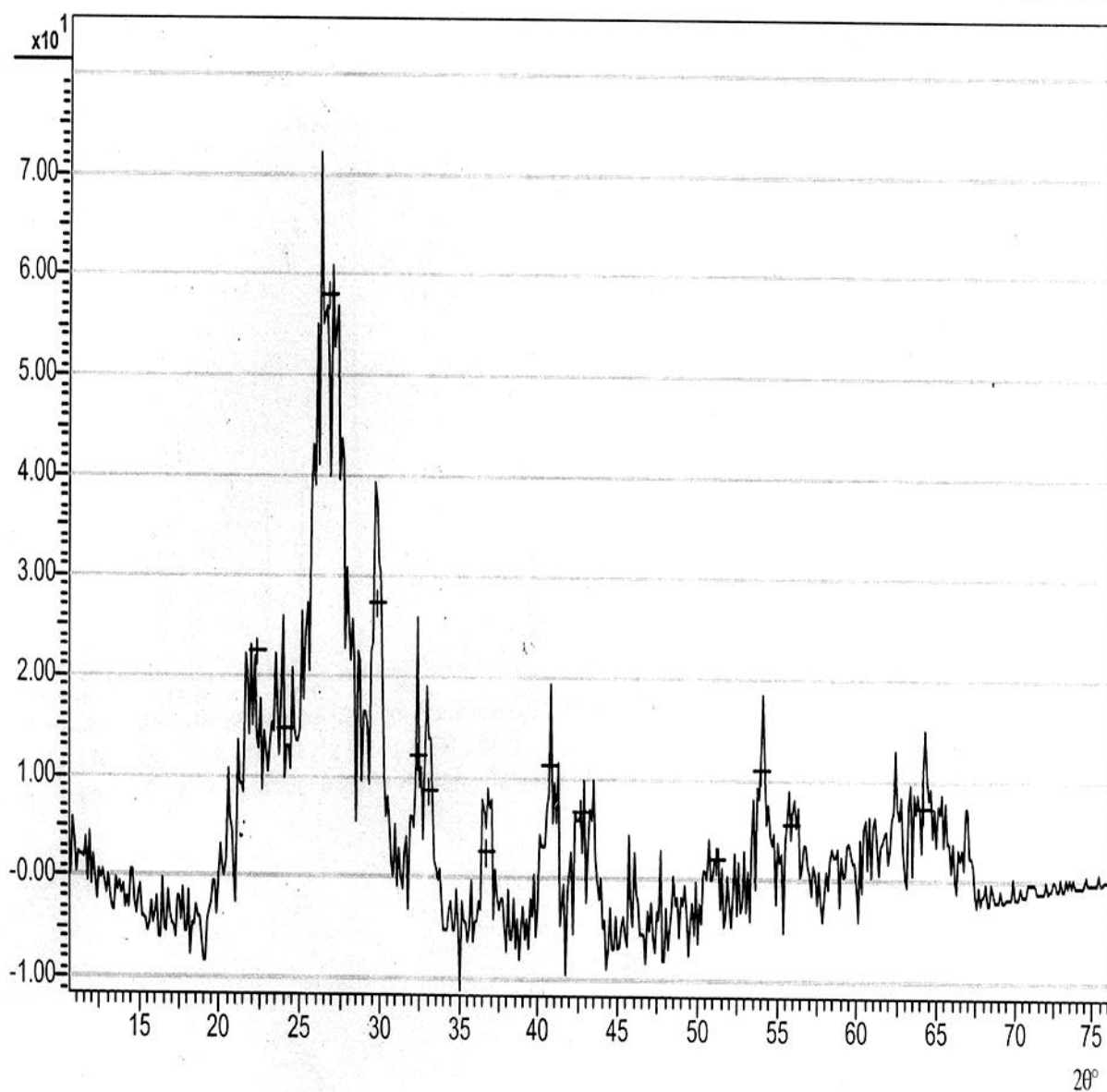


Figure 4.66: XRD spectra for bamboo doped KClO_4

Figure 4.66 is bamboo doped lead chloride. It has sharp peaks at 19.5° , 26° , 29° , 33° , 34° , 44° , 54° and 64° . These indicate that they are crystalline [86]. They have broad base and crystallite sizes ranging from 0.24962 to 5.55826 nm, indicating that they are nano materials [89].

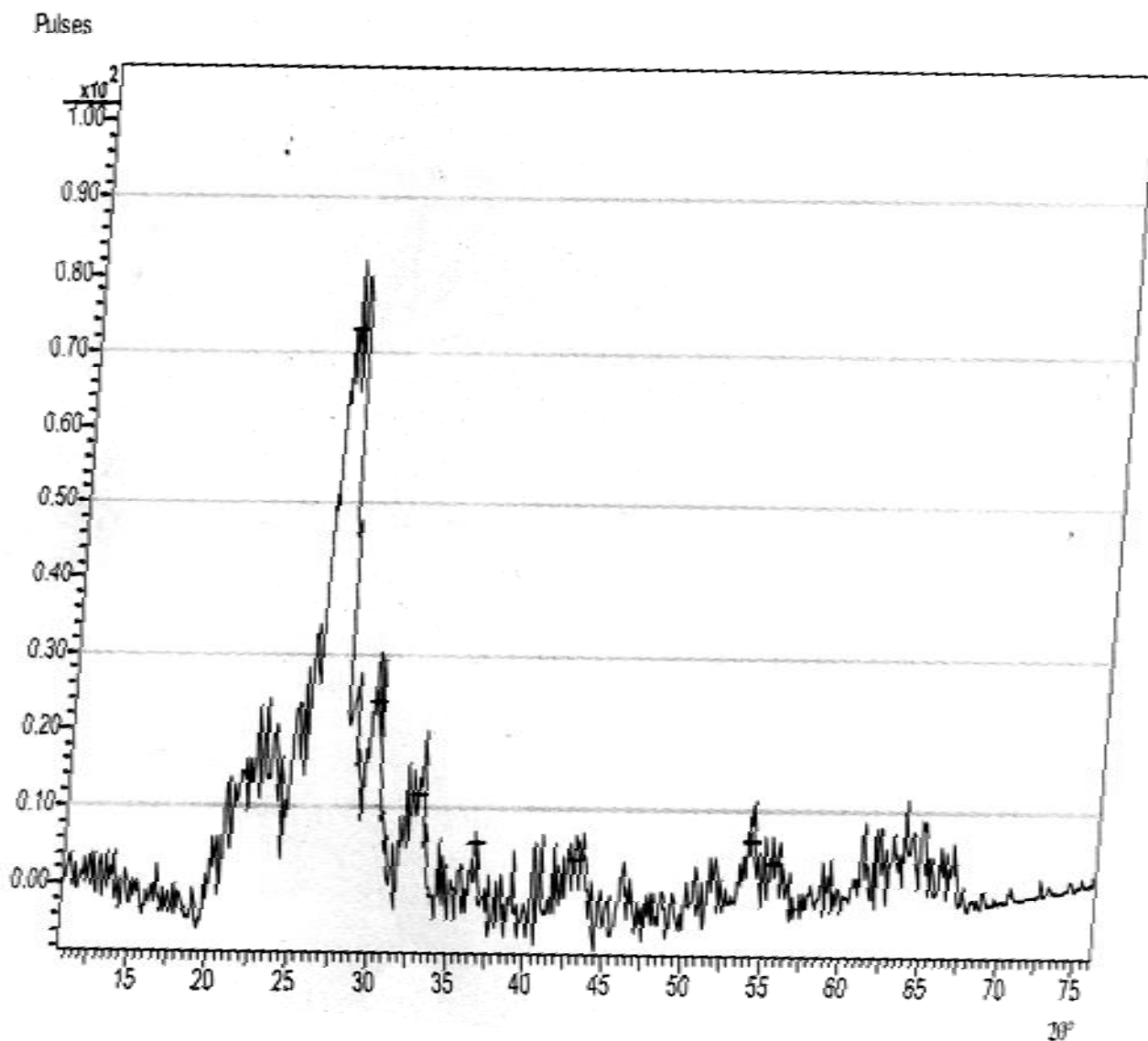


Fig. 4.67: XRD spectra for raffia doped KClO_4 .

Figure 4.67 is raffia doped lead chloride. It has sharp peaks at 23° , 32° , 34° , 41.5° , 44° , 54° , 62° and 64° . These indicate that they crystalline [86]. They have broad base and crystallite sizes ranging from 0.43733 to 4.97363nm, indicating that they are nano materials [91].

Figures 4.68-4.71: Diffractogram for Stannous Iodide (SnI_2).

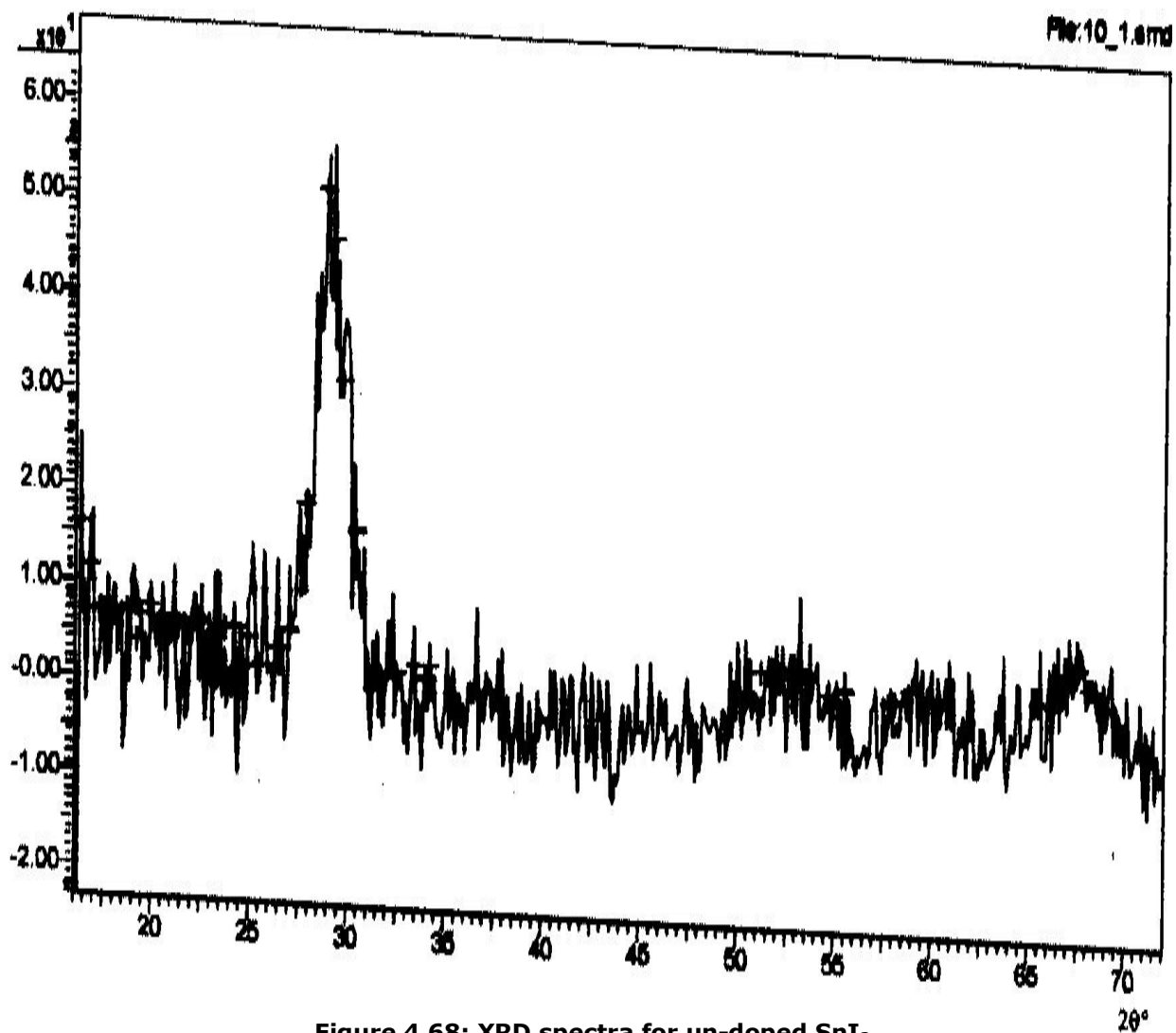


Figure 4.68: XRD spectra for un-doped SnI_2 .

Figure 4.68 is sample I, un-doped thin SnI_2 iodide. It has sharp peaks at 24° , 26° , 30° , 32.5° , 37.5° , 47.5° , 55° and 65° . These indicate that they are crystalline [86]. They have broad bases and crystallite sizes ranging from 0.04084 to 1.99236 nm, indicating that they are nano materials [90].

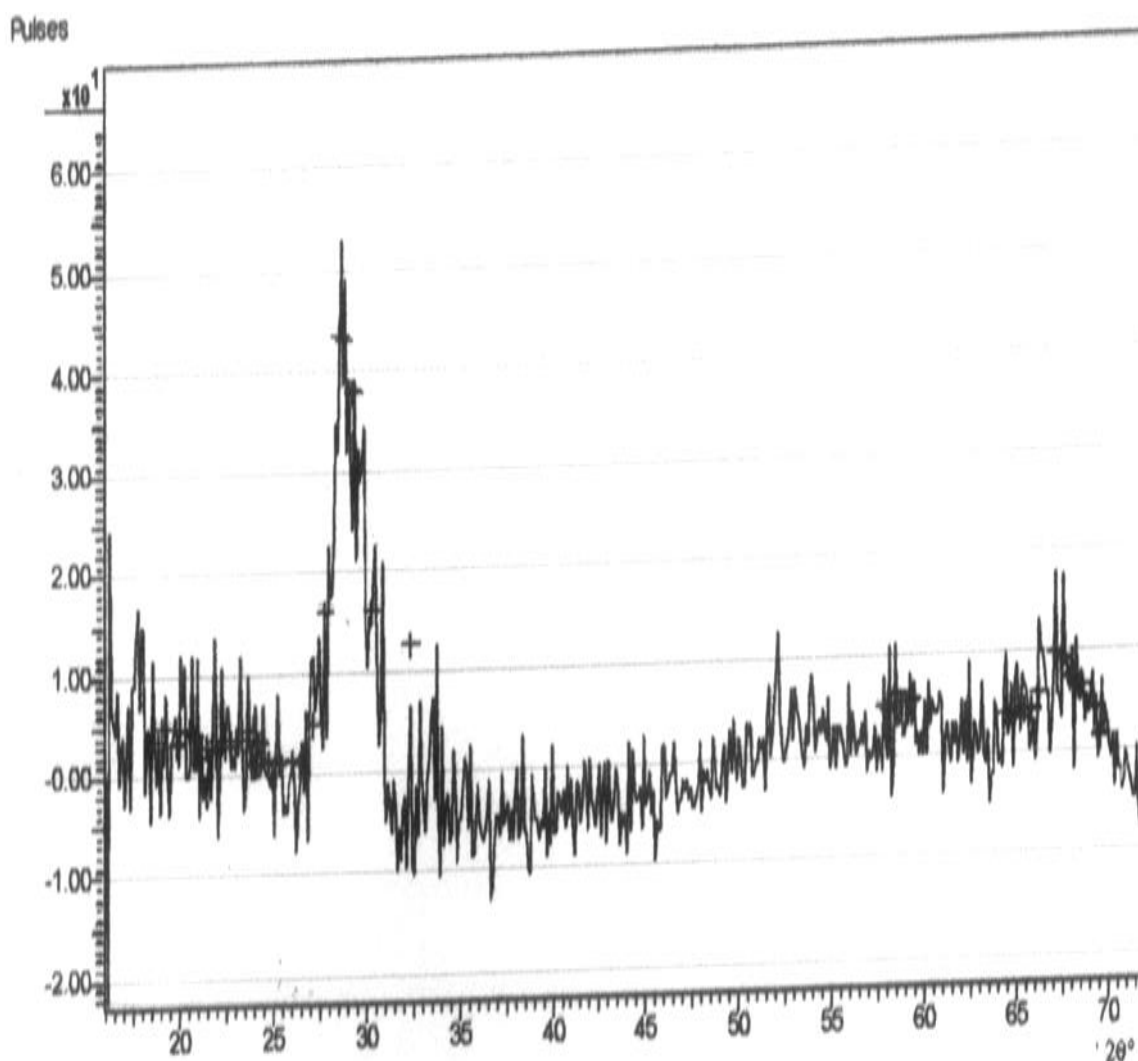


Figure 4.69: XRD spectra for potash doped SnI_2 .

Figure 4.69 is sample J, potash doped tin II iodide. It has sharp peaks at 14° , 23° , 28.20° , 32° , 34° , 36° , 45° and 65° . These indicate that they crystalline [86]. They have broad base and crystallite sizes ranging from 0.01598 to 1.5396nm, indicating that they are nano materials [89]. 19.87° at peak 002 shows sodium 6 silicate ($\text{Na}_6\text{Si}_8\text{O}_{19}$), the sharpest and broadest peak is found at 28.20° as 216 showing the presence of trydynite-20 (silicon oxide), at 28.59° is 100 showing KCl.

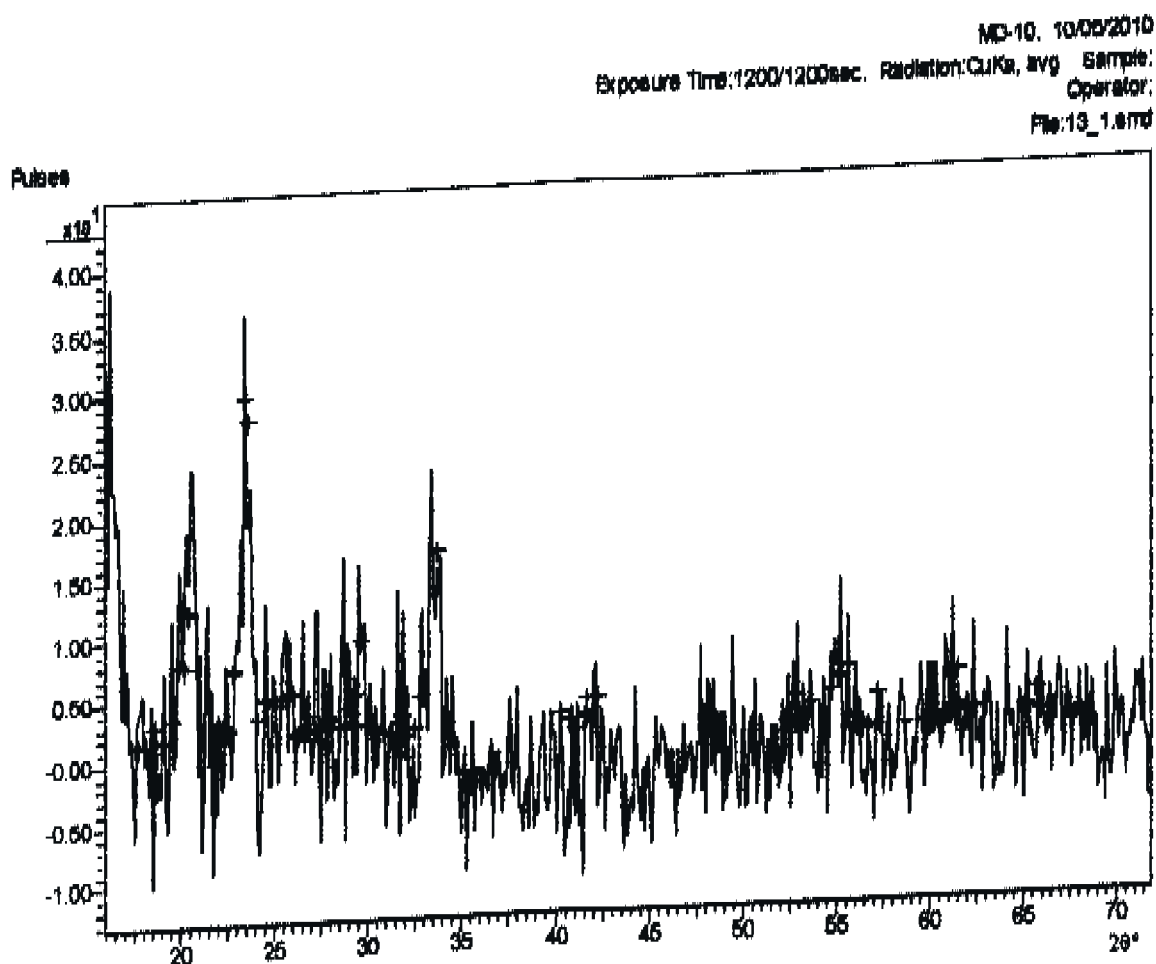


Figure 4.70: XRD spectra for bamboo doped SnI₂.

Figure 4.70 is sample K, bamboo doped tin II iodide. It has sharp peaks at 17.30° , 20.74° , 21.14° , 25.85° , 29° , 34.5° , 37.5° , 47° , 55° , 65° and 70° . These indicate that they crystalline [86]. They have broad base and crystallite sizes ranging from 1.27222 to 2.79841nm, indicating that they are nano materials [87]. 2θ at 17.30 and 25.85 show the presence of sodium strontium phosphate (NaSrPO_4), 2θ at 21.14 and 20.74 is Nitro silicate ($\text{Na}_2\text{Sr}_2\text{O}_5$).

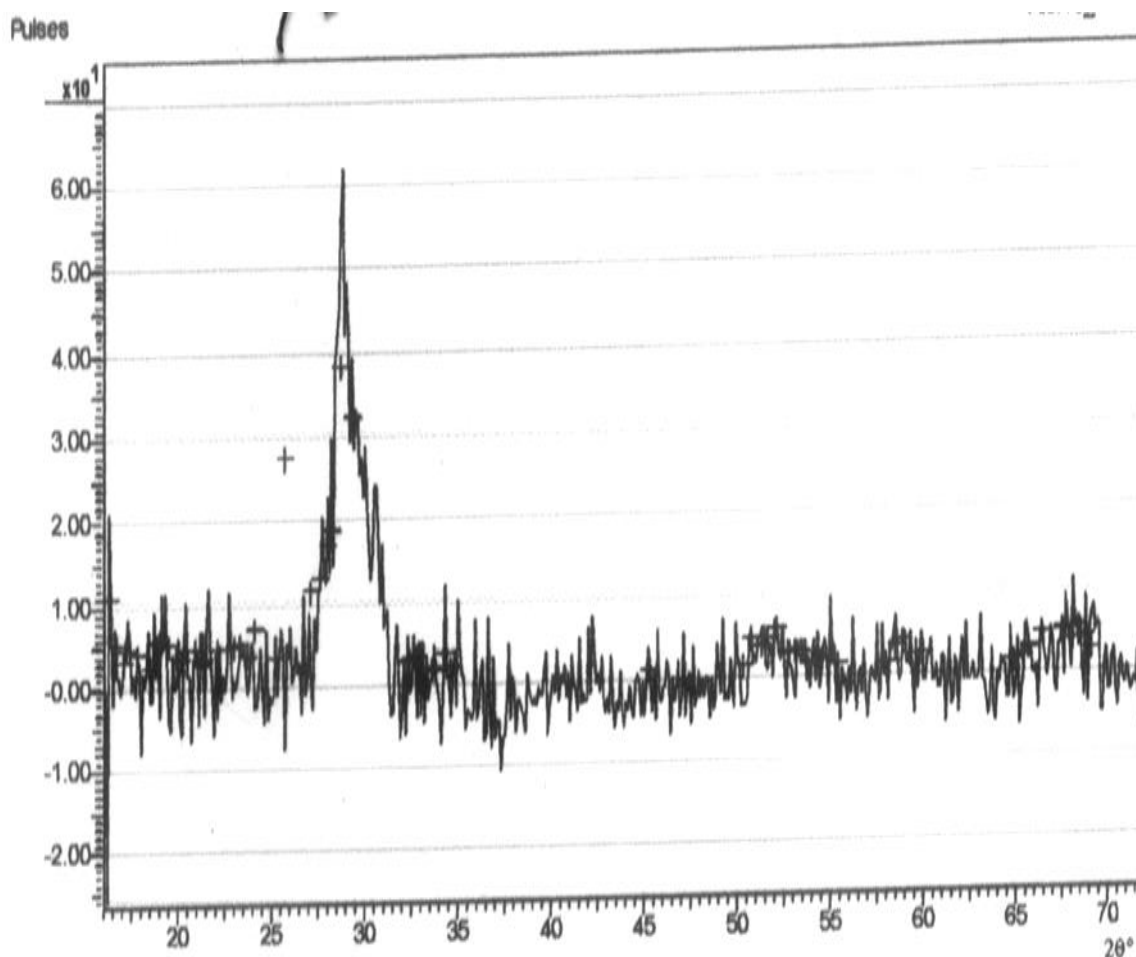


Figure 4.71: XRD spectra for raffia doped SnI_2 .

In figure 4.71 we have sample L, raffia doped tin II iodide. It has sharp peaks at 17.38° , 18.54° , 20.26° , 21.45° , 25.85° , 29° , 34.5° , 38° , 47.5° , 56° , 64.5° and 72° . These indicate that they are crystalline [86]. They have broad base and crystallite sizes ranging from 1.9165 to 2.71854 nm, indicating that they are nano materials [89]. 2θ at 20.26° is coesite (SiO_2) and 2θ at 18.54° shows the presence of sodium silicate (Na_2SiO_5), 2θ at 20.45° is potassium chlorate (KClO_4) and 2θ at 17.39° is potassium iron oxide (K_2FeO_4).

Figures 4.72-4.75: Diffractogram for un-doped and doped Stannic Iodide (SnI_4)

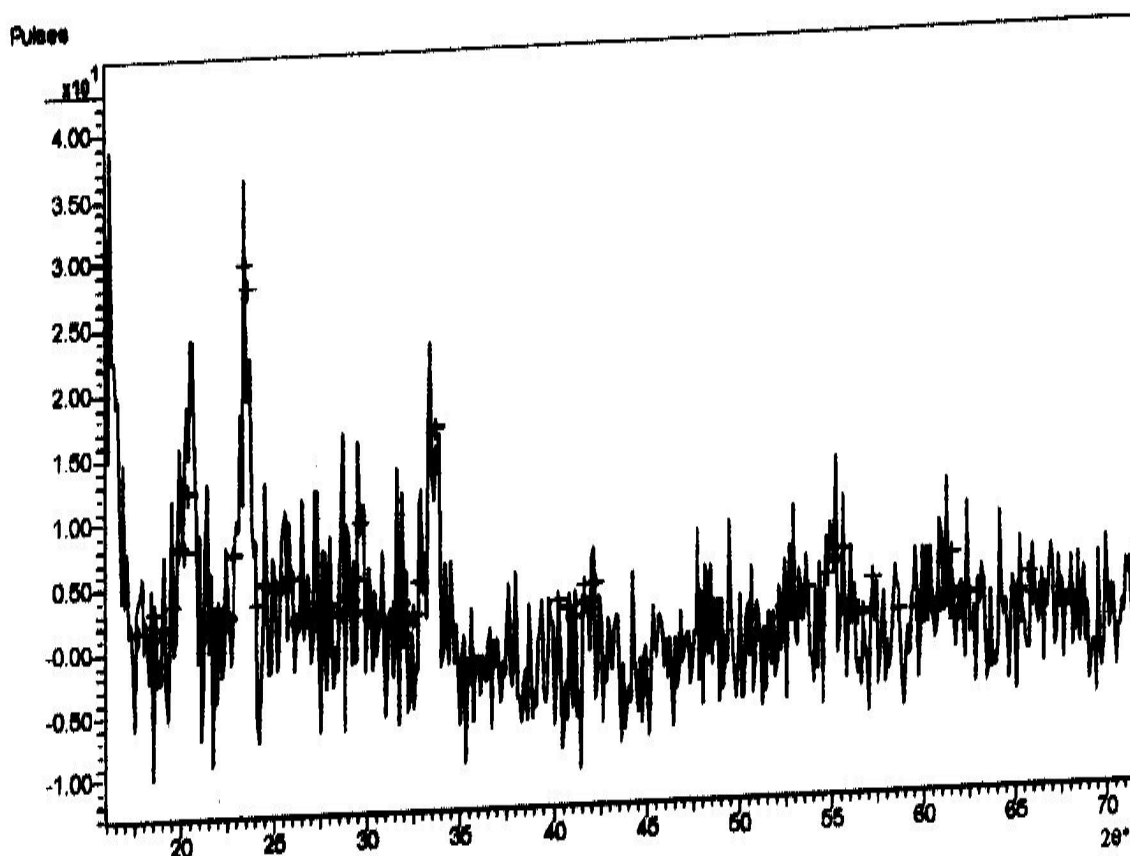


Figure 4.72: XRD spectra of un-doped SnI_4 .

Figure 4.72 is sample M, un-doped tin IV iodide. It has sharp peaks at 21° , 24° , 28° , 30.5° , 34° , 42.5° , 48° , 50° , 52.5° , 56° , 56.5° and 72° . These indicate that they crystalline [86]. They have broad base and crystallite sizes ranging from 0.71037 to 2.42703nm, indicating that they are nano materials [93]. 2θ at 30.5° is stannic iodide (SnI_4) and 2θ at 42.5° shows the presence of Nitrosilicate ($\text{Na}_2\text{SiO}_2\text{O}_5$).

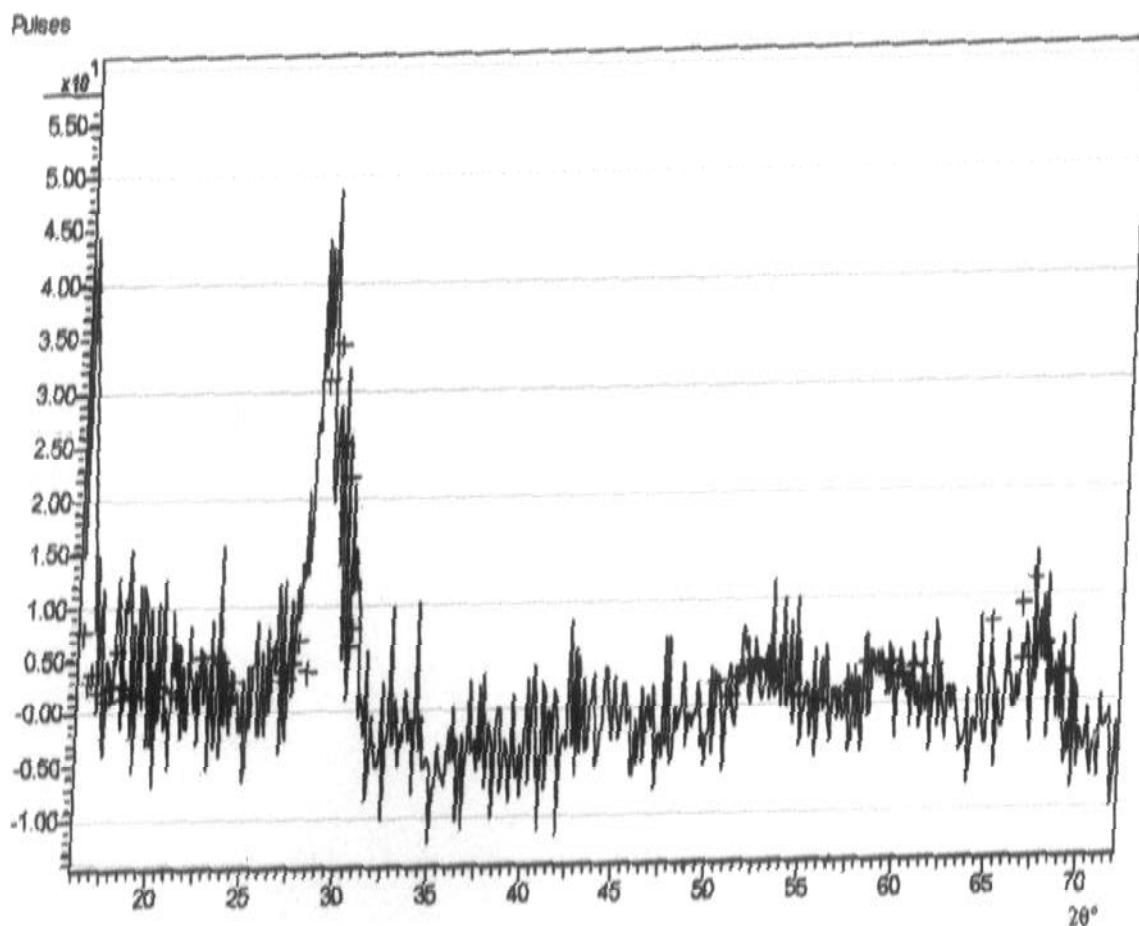


Figure 4.73: XRD spectra of potash doped SnI_4 .

Figure 4.73 is sample N, potash doped tin IV iodide. It has sharp peaks at 18.58° , 20.5° , 23.55° , 28.99° , 32.5° , 37.5° , 47° , 51° , 52.5° , 57° , 63.5° and 72° . These indicate that they crystalline [86]. They have broad base and crystallite sizes ranging from 0.96177 to 2.81011nm, indicating that they are nano materials [92]. 2θ at 23.55° is sodium silicate ($\text{Na}_2\text{Si}_2\text{O}_5$), 2θ at 18.58° shows the presence of potassium silicate ($\text{K}_2\text{Si}_2\text{O}_5$), 2θ at 28.99° is iodine and 2θ at 20.5° is Halloysite [$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_{412}\text{H}_2\text{O}$].

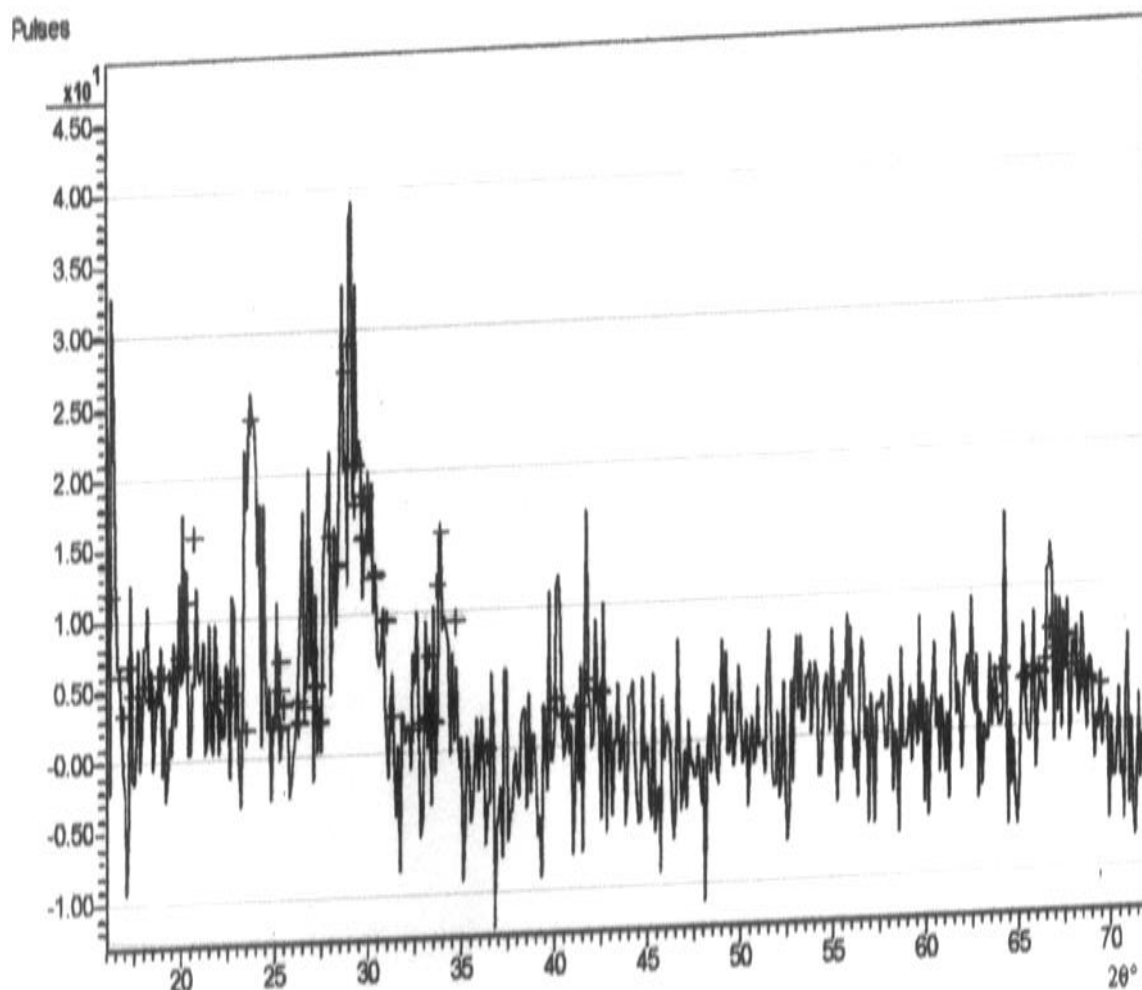


Figure 4.74: XRD spectra for bamboo doped SnI₄.

Figure 4.74 is sample O, bamboo doped tin IV iodide. It has sharp peaks at 11° , 20.5° , 22.5° , 29° , 32.5° , 37.5° , 42° , 51° , 52.5° , 57° , 63.5° and 71° . These indicate that they crystalline [87]. They have broad base and crystallite sizes ranging from 0.47047 to 2.48596nm, indicating that they are nano materials [91]. 2θ at 20.5° is Aluminum silicate hydroxide $[\text{Al}_2\text{SiO}_4(\text{OH})_2]$, 2θ at 29° shows the presence of Aluminum chloride hydroxide hydrate $[\text{Al}_5\text{Cl}(\text{OH})_{12} \cdot 7.5\text{H}_2\text{O}; \text{AlCl}_{3/4}\text{Al}(\text{OH})_{3/7.5}\text{H}_2\text{O}]$.

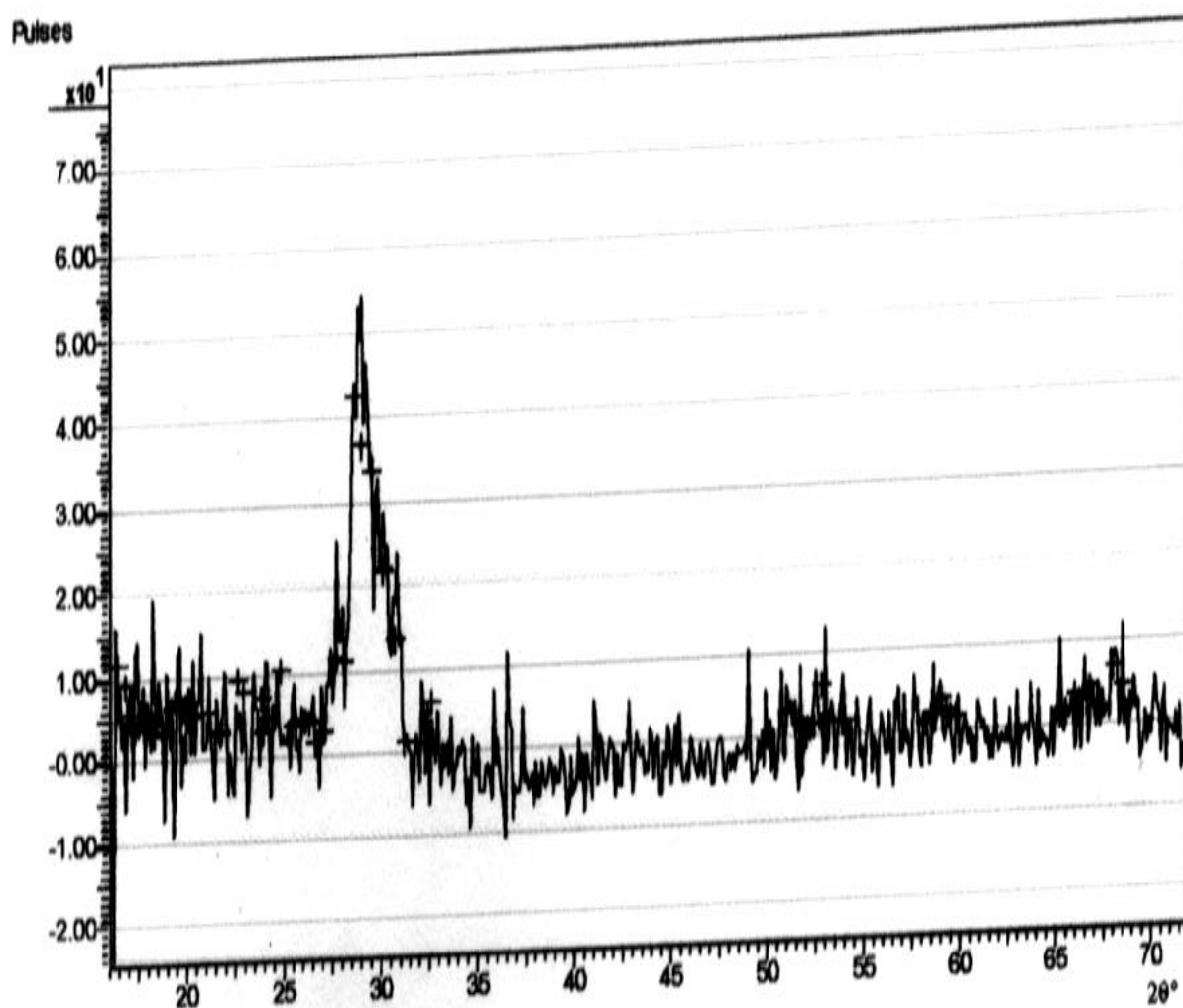


Figure 4.75: XRD spectra of raffia doped SnI_4 .

Figure 4.75 is sample P, raffia doped tin IV iodide. It has sharp peaks at 18.17° , 18.56° , 20.54° , 23.86° , 47° , 51° , 52.5° , 57° , 63.5° and 71° . These indicate that they crystalline [85]. They have broad base and crystallite sizes ranging from 1.94953 to 2.93496nm, indicating that they are nano materials [93]. 2θ at 18.56° is silicon oxide (SiO_2), 2θ at 18.17° shows the presence of potassium silicate ($\text{K}_2\text{Si}_2\text{O}_9$).

Figures 4.76-4.79: XRD for Cadmium Sulphide (CdS).

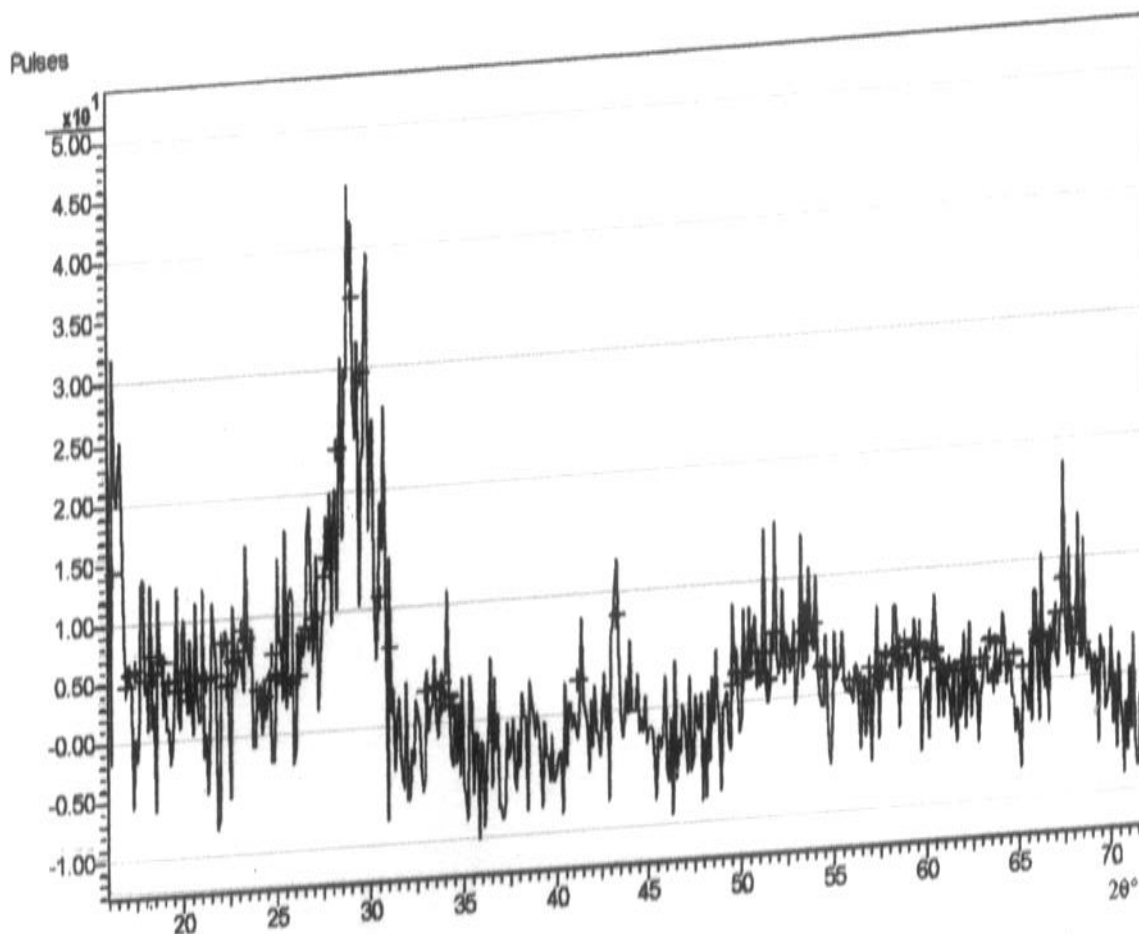


Figure 4.76: XRD spectra for un-doped CdS.

Figure 4.76 is sample Q, un-doped cadmium sulphide. It has sharp peaks at 18.86° , 20.54° , 29° , 30.55° , 36.19° , 47° , 51° , 52.5° , 57° , 63.5° and 70° . These indicate that they crystalline [84]. They have broad base and crystallite sizes ranging from 0.92227 to 2.83579nm, indicating that they are nano materials [92]. 2θ at 18.86° is cadmium sulphide (CdS), 2θ at 36.19° shows the presence of sodium silicate (NaHSi_2O_4).

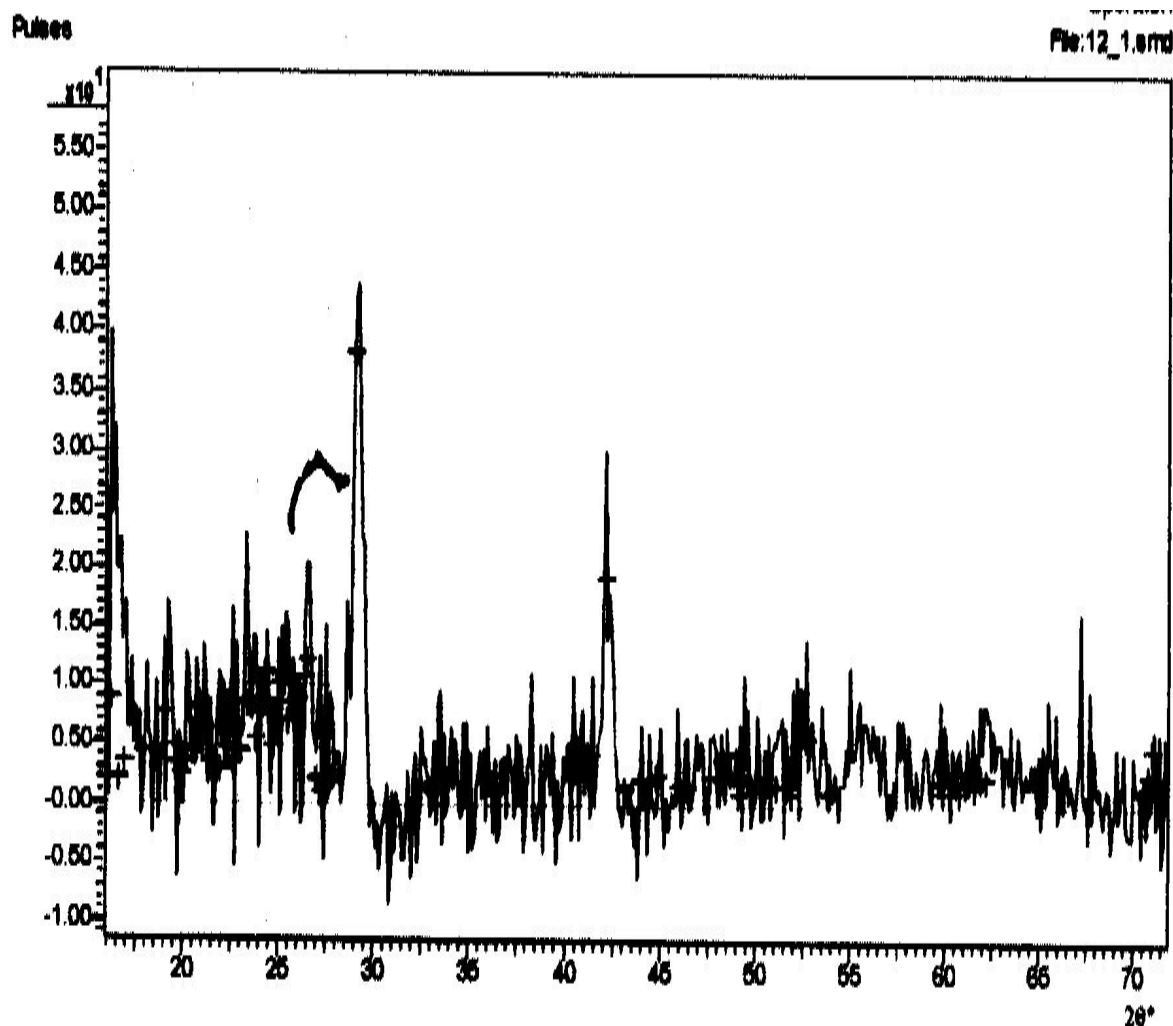


Figure 4.77 is sample R, potash doped cadmium sulphide. It has sharp peaks at 18.66° , 20.63° , 21.76° , 21.81° , 29° , 38° , 48° , 51° , 52.5° , 58° , 63.5° and 69° . These indicate that they crystalline [84]. They have broad base and crystallite sizes ranging from 0.2565 to 2.8231nm, indicating that they are nano materials [92]. 2θ at 18.66° is sodium silicate ($\text{Na}_6\text{Si}_2\text{O}_7$), 2θ at 21.76° shows the presence of sekaninaite ($\text{Fe}_2\text{Al}_4\text{Si}_5\text{O}_{18}$).

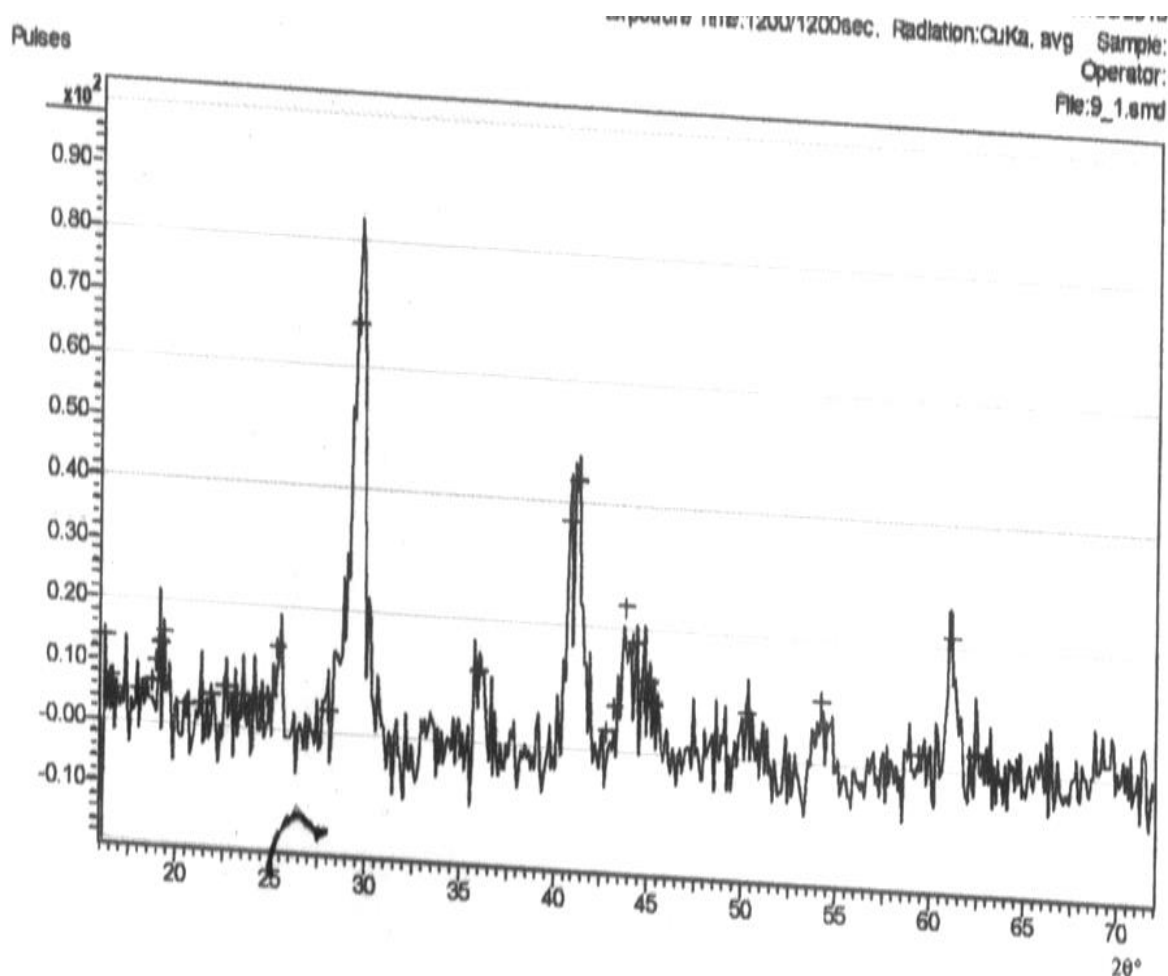


Figure 4.78: XRD spectra for bamboo doped CdS

Figure 4.78 is sample S, bamboo doped cadmium sulphide. It has sharp peaks at 12.05° , 17.76° , 19.46° , 30° , 32° , 42° , 52° , 49° , 62.5° and 72° . These indicate that they crystalline [83]. They have broad base and crystallite sizes ranging from 0.32702 to 2.55827nm, indicating that they are nano materials [91]. 2θ at 19.46° is potassium aluminum silicate (KAlSiO_4), 2θ at 42° shows the presence of illitre [$\text{K}_{0.7}\text{Al}_2(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_2$], 2θ at 52 is cadmium silicate.

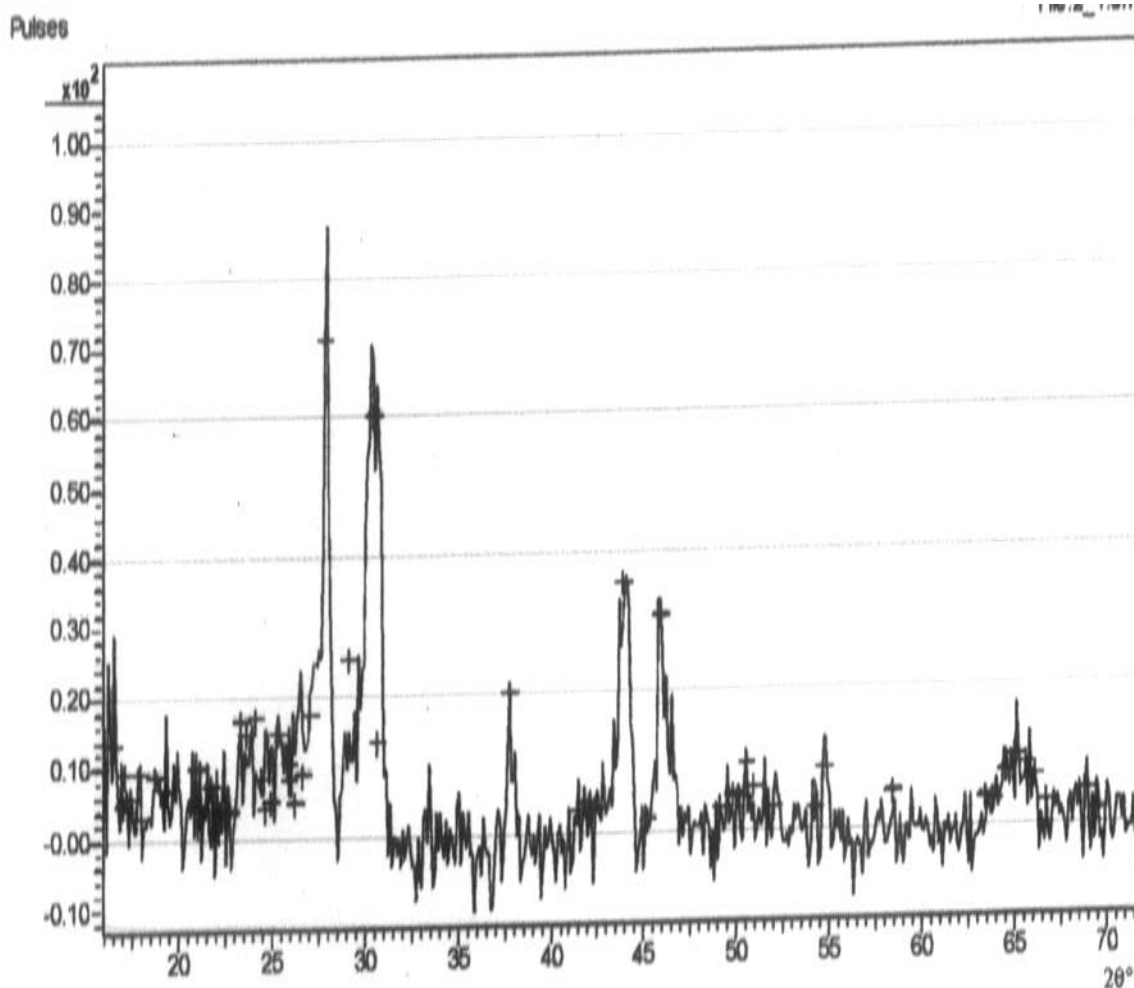


Figure 4.79: XRD spectra of raffia doped CdS.

Figure 4.79 is sample T, raffia doped cadmium sulphide. It has sharp peaks at 19.93° , 20.30° , 28° , 31° , 33° , 37.5° , 44° , 47.5° , 52° , 55° , 66° and 70° . These indicate that they crystalline [82]. They have broad base and crystallite sizes ranging from 1.74353 to 2.67096nm, indicating that they are nano materials [93]. 2θ at 19.93° is monganite (SiO_2), 2θ at 20.30° shows the presence of sodium cadmium oxide (Na_2CdO_2), 2θ at 28° cadmium hydroxide [$\text{Cd}(\text{OH})_2$].

Figures 4.80-4.82: Diffractogram for the impurities.

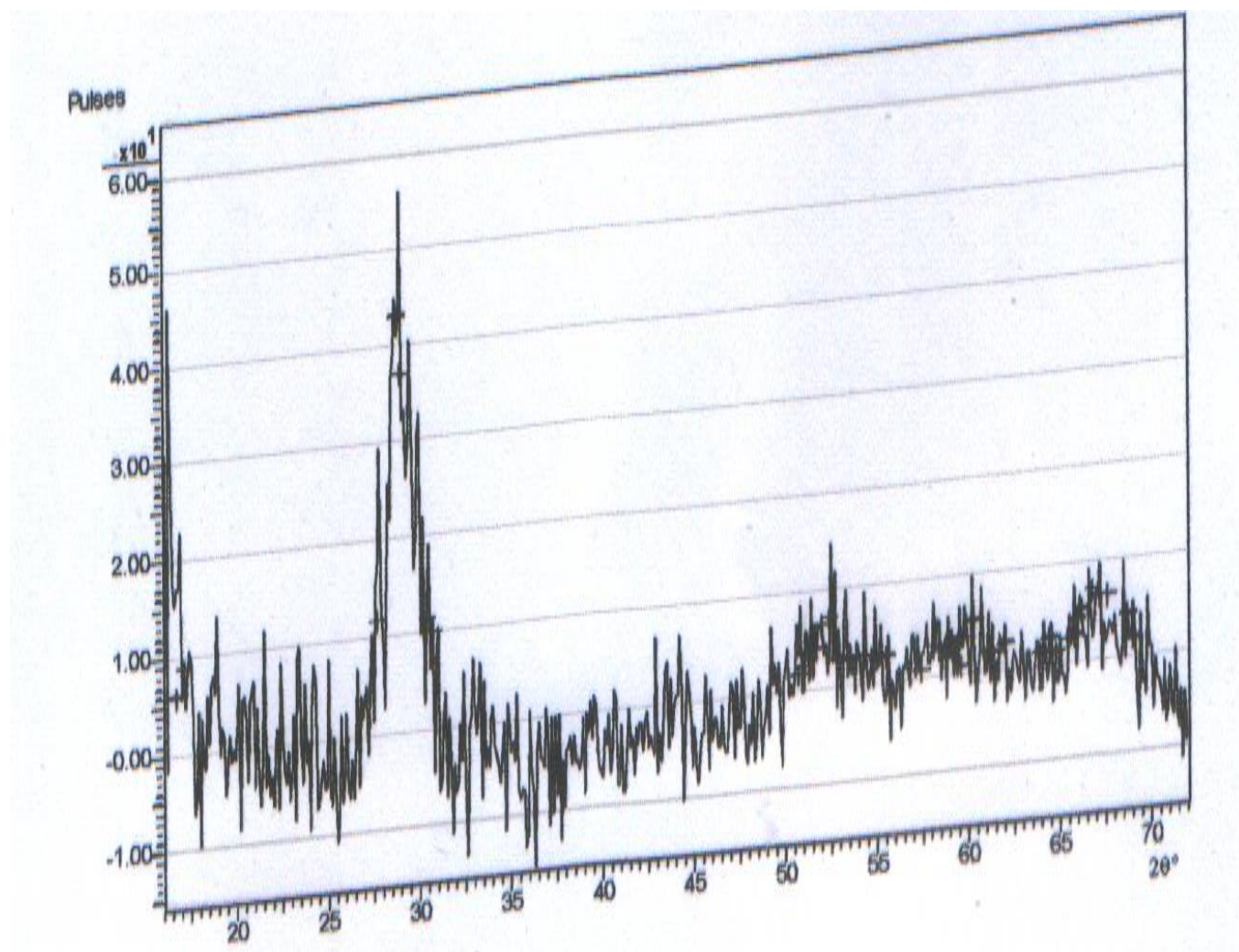


Figure 4.80: XRD spectra for potash.

Figure 4.80 is XRD for potash. It has sharp peaks at 17.13° , 18° , 27° , 30.5° , 32.55° , 36.5° , 43° , 50.5° , 51.5° , 61.5° and 70.5° . These indicate that they are crystalline [83]. They have broad base and crystallite sizes ranging from 1.98027 to 2.68221nm, indicating that they are nano materials [92]. 2θ at 18.86° is potassium iron oxide; 2θ at 18° shows the presence of potassium aluminum silicate (KAlSiO_4).

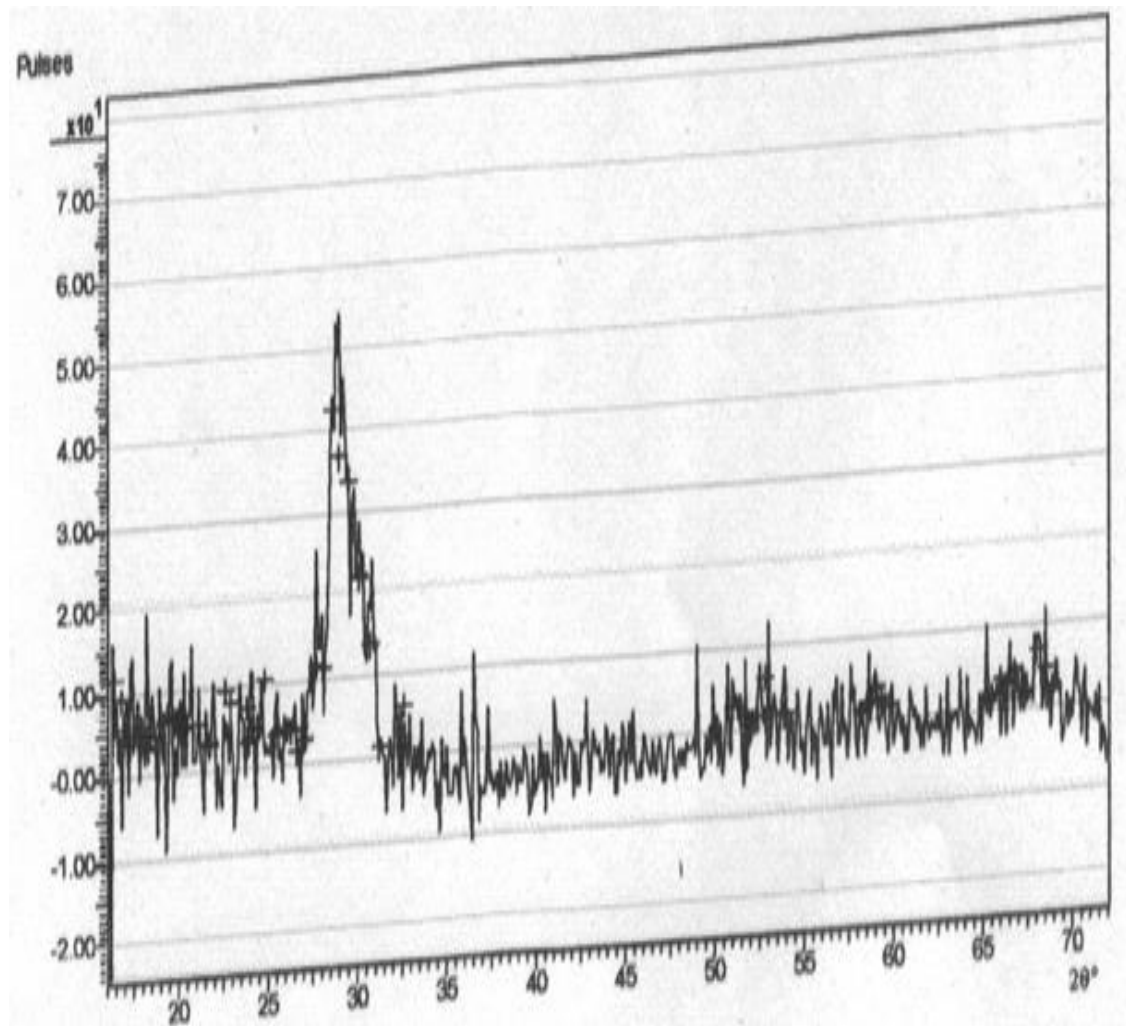


Figure 4.81: XRD spectra for bamboo.

Figure 4.81 is XRD for bamboo. It has sharp peaks at 11.26° , 22° , 30.5° , 38° , 43° , 49.5° , 52.5° , 59.5° , 63.5° and 70° . These indicate that they crystalline [85]. They have broad base and crystallite sizes ranging from 1.66469 to 2.89415nm, indicating that they are nano materials [93]. 2θ at 11.26° is natrosilite ($\text{Na}_2\text{Si}_2\text{O}_5$), 2θ at 22° shows the presence of ungarettite ($\text{Na}_3\text{Mn}_5\text{Si}_8\text{O}_{24}$), 2θ at 30.5° is clinoferrosilite (FeSiO_3), and 2θ at 38° wollastonite (CaSiO_3).

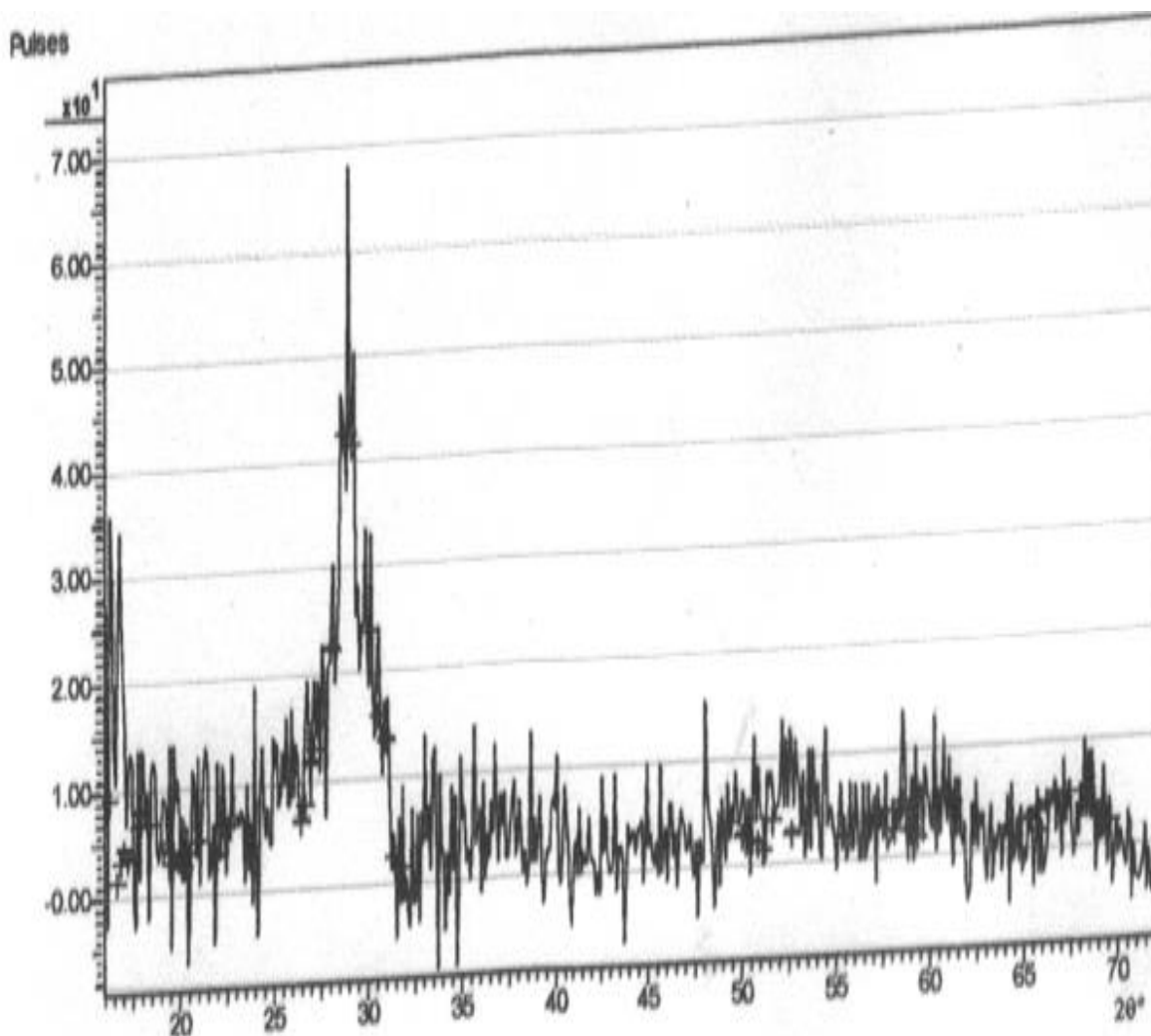


Figure 4.82: XRD spectra for raffia.

Figure 4.82 is XRD for raffia. It has sharp peaks at 4.55° , 19.5° , 29° , 33° , 37° , 47° , 41° , 52.5° , 57° , 63.5° and 71° . These indicate that they crystalline [85]. They have broad base and crystallite sizes ranging from 0.63343 to 2.72001nm, indicating that they are nano materials [94]. 2θ at 4.55° is vanthoffite, 2θ at 19.5° shows the presence of iron silicate (FeSi_2).

4.3. Fourier Transform Infrared Spectroscopy (FTIR).

In this study, FTIR analysis was performed using SHIMADZU FTIR. About 1mg. of each sample was grounded with 10 to 100 times its bulk of pure potassium bromide (KBr) and the mixture pressed into a disc using a special mould and a hydraulic press. The use of KBr was to eliminate the problem of bands due to the mulling agent and tends on the whole to give rather better spectra. The infra red beam was allowed to make a pass through the sample before reaching the detector. The double pass mode was used because it offers the highest level of sensitivity. The results of FTIR are as contained on tables 3.6-4.1. and appendix 2. The FTIR graphs were not scanned because it never appeared clearly on the scan.

TABLE 3.6: FOURIER TRANSFORM INFRA RED BOND STRUCTURE COMPARISON FOR UN-DOPED AND LOCAL IMPURITY DOPED LEAD CHLORIDE (PbCl_2) (cm^{-1}).

S/N	BAND POSITION FOR SAMPLE A WITHOUT	BAND POSITION FOR SAMPLE B WITH POTASH	BAND POSITION FOR SAMPLE C WITH BAMBOO	BAND POSITION FOR SAMPLE D WITH RAFIA	DESCRIPTION/BAND TYPE
1.	470.65	470.65	464.86	466.79	-----
2.	603.74	628.81	806.27	808.20	- CH_2 rocking
3.	704.04	802.41	960.58	956.72	C ÿ H out of plane deformation [95]
4.	800.49	1085.96	1057.75	1066.67	C ÿ O stretching
5.	966.37	1166.97	1145.75	1116.82	C ÿ O deformation bonds
6.	1101.39	1635.69	1383.01	1176.62	C ÿ H deformation
7.	1384.94	2019.54	1647.26	1384.94	C ÿ C stretching
8.	1735.99	3439.19	3452.7	1681.98	N ÿ H stretching
9	3450.77	-	-	3338.89	Free O ÿ H stretching N ÿ H stretching
	-	-	-	3410.26	Free O ÿ H stretching [96]

From table 3.6, sample A which is un-doped lead chloride has FTIR band positions from 470.5 to 3450.77 with the following band types; C-H stretching, C-H deformation, C-C stretching and free O-H stretching. Sample B which is potash doped has band positions from 470.5 to 3439.19 with the following band types C-O stretching, C-H deformation, N-H stretching and free O-H stretching. Sample C which is bamboo doped has band structures from 464.86 to 3452.7 with the following band types; CH_2 rocking, C-H out of plane, C-C stretching and free O-H.

Sample D is potash doped lead chloride. It has band positions from 466.79 to 3410.26 with the following band types C-H out of plane, C-O stratching, N-H stretching, C-H deformation and C-C stretching [96].

TABLE 3.7: FOURIER TRANSFORM INFRA RED BOND STRUCTURE COMPARISON FOR UN-DOPED AND IMPURITY DOPED POTASSIUM PERCHLORATE (KCLO₄) (cm⁻¹).

S/N	SAMPLE E (UN-DOPED)	SAMPLE F (DOPED WITH POTASH)	SAMPLE G (DOPED WITH BAMBOO)	SAMPLE H (DOPED WITH RAFIA)	DESCRIPTION
1.	476.43	468.72	482.22	489.94	-----
2.	628.81	628.81	626.89	628.89	CH ₂ rocking
3.	802.41	802.41	804.34	802.41	C-H deformation for methyl group
4.	1031.95	1043.52	1031.95	1028.09	C-H deformation
5.	1163.11	1203.63	1166.97	1093.67	C ï C deformation bonds
6.	1238.34	1629.90	1637.62	1136.11	C-O deformation and N-H bending.
7.	1633.76	2019.54	2023.4	1203.62	C ï O deformation
8.	3423.76	-	-	2021.47	N ï H stretching
9.	-	-	-	3441.12	Free O ï H stretch[96]

From table 3.7, sample E is the un-doped potassium perchlorate crystal. The sample has band positions from 476.43 to 3423.76 with the following band types; CH₂- rocking, C-H deformation, C-O deformation, N-H stretching and free O-H stretching [96]. F is doped with potash. It has band positions from 468.72 to 2019.54 with the following band types C-H deformation, C-C deformation, N-H bending and N-H stretching. Sample G is doped with bamboo with band position ranging from 482.22 to 2023.4. The band positions are CH₂-rocking, C-C deformation, C-O deformation, N-H deformation and Free O-H stretching. Sample H is doped with raffia with band structure ranging from 489.94 to 3441.12. The band positions are C-H deformation, C-O deformation, N-H stretching, C-C deformation and N-H bending.

TABLE 3.8: FOURIER TRANSFORM INFRA RED BOND STRUCTURE COMPARISON FOR UN-DOPED AND LOCAL IMPURITY DOPED STANNOUS IODIDE (SnI₂) (cm⁻¹).

S/N	SAMPLE I (UN-DOPED)	SAMPLE J (POTASH DOPED)	SAMPLE K (BAMBOO DOPED)	SAMPLE L (RAFFIA DOPED)	DESCRIPTION
1.	461.00	462.93	441.71	426.28	-----
2.	526.58	532.37	538.16	474.50	C ÿ H deformation for alkyl group suspected [95]
3.	781.20	779.27	1008.8	534.30	C ÿ H deformation [96]
4.	1016.52	1037.74	1635.69	1003.02	NO ₂ stretching
5.	1641.48	1369.50	3452.70	1365.65	N ÿ H band
6.	3477.77	1639.55	-	1639.55	N ÿ H bending
7.	-	3464.27	-	3458.48	H- bonded

From table 3.8, sample I is the un-doped stannous iodide crystal. The sample has band positions from 461.00 to 3477.77 with the following band types; C-H deformation, NO₂ stretching, N-H bending, and free H bonded [96]. Sample J is the potash doped stannous iodide with band positions ranging from 462.39 to 3464.27. The band types are NO₂ stretching, N-H bending and H bonded. Sample K is for bamboo doped stannous iodide with band positions from 441.71 to 3452.70. The band types are C-H deformation, NO₂ stretching, N-H bending, and free H bonded [96]. Sample L is raffia doped stannous iodide with band positions ranging from 426.28 to 3458.48. The band types are NO₂ stretching, N-H bending and H bonded.

TABLE 3.9: FOURIER TRANSFORM INFRA RED BOND STRUCTURE COMPARISON FOR UN-DOPED AND IMPURITY DOPED STANNIC IODIDE (SnI₄) (cm⁻¹).

S/N	SAMPLE M (UN-DOPED)	SAMPLE N (WITH POTASH)	SAMPLE O (WITH BAMBOO)	SAMPLE P (WITH RAFIA)	DESCRIPTION
1.	555.52	470.65	555.52	453.29	C Ì H deformation for suspected alkyl group [96]
2.	779.27	526.58	779.27	538.16	C Ì H deformation for methyl groups [95].
3.	968.30	786.98	1039.67	788.91	SO ₂ Stretching [96]

4.	1122.61	1035.81	1363.72	1004.95	P=O deformation [95,96]
5.	1367.58	1361.79	1464.02	1369.50	C ÿ H deformation [96]
6.	1641.48	1469.81	1637.62	1464.02	C ÿ H deformations [95]
7.	3435.34	1637.62	2380.24	1645.33	C = C Double bond
8.	3549.14	3470.06	3464.27	3464.27	Free O ÿ H stretch

From table 3.9, sample M is the un-doped stannic iodide crystal. The sample has band positions from 555.52 to 3549.14 with the following band types; C-H deformation for suspected alkyl group, SO₂ stretching, P=O deformation [95, 96], C = C Double bond and free O-H stretch [96]. Sample N is potash doped stannic iodide with band position from 470.65 to 3470.06. The sample has the following band types; C-H deformation for methyl group, SO₂ stretching, P=O deformation [95, 96], free O-H stretch and C = C Double bond. Sample O is bamboo doped with band positions from 555.52 to 3464.27. The band types are C-H deformation for suspected alkyl group, SO₂ stretching, P=O deformation [95, 96], C = C Double bond and free O-H stretch [96]. Sample P is raffia doped with band positions ranging from 453.29 to 3464.27. The sample has the following band types; C-H deformation for methyl group, SO₂ stretching, P=O deformation [95, 96], free O-H stretch and C = C Double bond.

TABLE 4.0: FOURIER TRANSFORM INFRA RED BOND STRUCTURE COMPARISON FOR UNDOPED AND LOCAL IMPURITY DOPED CADMIUM SULPHIDE (CdS) (cm⁻¹)

S/N	SAMPLE Q (UN-DOPED)	SAMPLE R (POTASH DOPED)	SAMPLES BAMBOO DOPED	SAMPLE T RAFIA DOPED	DESCRIPTION
1.	495.72	466.79	486.08	468.72	-----
2.	630.74	800.49	578.66	798.56	C-H deformation for methyl group
3.	729.12	1089.82	713.69	1087.89	C Ĩ H deformation
4.	1085.96	1411.94	804.34	1415.80	C Ĩ O stretching
5.	1413.87	1629.90	1068.60	1629.90	N Ĩ H bending often too weak to be noticed
6.	1469.81	2179.63	1157.33	2160.35	C Ĩ H deformation
7.	1616.40	3178.79	1394.58	3182.65	S Ĩ H stretching
8.	2366.74	3385.18	1494.88	3383.26	S Ĩ H stretching N Ĩ H stretching [95]

From table 4.0, sample Q is un-doped cadmium sulphide with band positions from 495.72 to 2366.74. The band types are C-H deformation, C-O stretching, N-H bending, C-H deformation and S-H stretching [95]. Sample R is potash doped cadmium chloride with the following band types; C-H deformation for methyl group, C-O stretching, N-H bending, C-H deformation, S-H stretching and N-H stretching [95].

TABLE 4.1: FOURIER TRANSFORM INFRA RED BOND STRUCTURE COMPARISON FOR LOCAL IMPURITIES (POTASH, BAMBOO, RAFIA).

S/N	POTASH	BAMBOO	RAFIA	DESCRIPTION
1.	480.29	464.86	464.86	-----
2.	808.20	615.31	713.69	C $\equiv$ C stretching [96]
3.	958.65	709.83	875.71	C $\ddot{\text{H}}$ out of plane deformation [1]
4.	1039.67	875.71	1114.89	C-O stretching and SO ₂ stretching.
5.	1145.75	1030.02	1437.02	C $\ddot{\text{O}}$ stretching [96]
6.	1383.01	1438.94	1593.25	O $\ddot{\text{H}}$ bending [95]
7.	1631.83	3435.34	2924.18	C = O stretching [96]
8.	1737.92	-	3437.26	N $\ddot{\text{H}}$ Stretching [95]

From table 4.1, potash has band positions ranging from 480.29 to 1737.92. It has the following band types; C $\equiv$ C stretching [96], C-H out of plane deformation, C-O stretching, O-H bending, C = O stretching [96] and N-stretching. Bamboo has band positions ranging from 464.86 to 3435.34. It has the following band types C-H out of plane deformation,

C-O stretching, O-H bending, C = O stretching [96] and N-stretching. Raffia has band positions ranging from 464.86 to 3437.26. It has the following band types C $\equiv$ C stretching [96], C-H out of plane deformation, C-O stretching, O-H bending, C = O stretching [96] and N-stretching. Bamboo has band.

CHAPTER FIVE

5.1. SUMMARY, CONCLUSION AND RECOMMENDATION.

This chapter is made up of the summary of the work, the conclusion and recommendation of possible remedies to the problems we encountered in this work.

5.2. SUMMARY OF WORK

In this work crystals of chalcogenides and halide crystals were grown using sol-gel method. The crystals could be deposited by other techniques; Successive Ionic Layer Adsorption Reaction (SILAR), Solution Growth Technique (SGT) and Physical Vapour Deposition (PVD). The grown samples were doped with dopants made from African environment and dried to enable us characterize the crystals. The characterization was done through optical studies using a JENWAY 6405 UV-VIS Spectrophotometer operating at a wavelength range of 200nm to 1200nm at intervals of 5nm and the XRD was carried out using MD-10 Diffractometer, which recorded diffractograms using CuK α radiation. The main contribution of this work is the successful deposition of crystals of Lead Chloride (PbCl $_2$), Potassium Perchlorate (KClO $_4$), Stannous Iodide (SnI $_2$), Stannic Iodide (SnI $_4$) and Cadmium Chloride (CdS) and doping them using locally made dopant from polymer African materials.

5.2a. Lead Chloride (PbCl $_2$)

The growth rate of lead chloride was fairly uniform, the growth rate increased with increase in the concentration of hydrochloric acid (HCl)

used and decreased with the increase in the density of the gel. Lead tartanate ($\text{PbH}_4\text{C}_4\text{O}_6$) which is an intermediate product in the growth of lead chloride (PbCl_2) can only grow under alkaline condition which is consistent with literature. We also investigated the use of ammonium chloride and potassium chloride of higher concentrations up to 6M as source of chlorine ions but they do not start the chemical reaction in the gel that will lead to the generation and growth of lead chloride needles. When lead acetate was used instead of lead nitrate for the precipitation of lead tartanate, neither good needles nor single crystals was produced. The reason for not obtaining the needles and crystals with ammonium chloride and potassium chloride as chlorine ion donors was not clear. Perhaps, the pH of these reagents and the gel has some part to play.

The grown lead chloride samples are wide band gap materials with band gaps ranging from 2.6 to 4.1 eV. The crystallite size ranges from 0.01598 to 2.1675, refractive indices range from 0.75 to 2.4. All the samples are highly transmitting from 32-120% from the VIS to the IR region thereby making them good for poultry roofs and walls and for coating of eye glasses [83-87]. Sample A has the highest extinction coefficient from 21 to 25, B and C have close extinction coefficient but D has negative extinction coefficient. Sample A has very high real dielectric of 5.6 while that of B, C and D fall between 0.5 to 3.8 with D as the least. Sample A has very high imaginary dielectric from 70 to 110. B and C fall between 8 to 40 and D is negative.

5.2b. Potassium Perchlorate (KClO_4).

Transparent/translucent crystals of potassium perchlorate (KClO_4) have successfully been grown in silica gel, acidified with perchloric acid. As the pH increased, the crystals lost transparency and the physical structure lost definition. Change in concentration of feed solutions had effect on crystal morphology. The size of the crystals increased with increase in the concentration of the feed solution. The crystals grown are wide band gap materials with band gap ranging from 2.9 - 4.2eV. The crystallite size ranged from 0.12848 to 5.55826 and refractive indices ranging from 1.1 to 2.3. All the samples were highly transmitting from 55 to 100% in the VIS to IR regions.

This is an indication that the materials are good for poultry roofs and solar energy applications [83, 84]. They can also be used high temperature, high power and high frequency applications.

5.2c. Stannous and Stannic Iodides (SnI_2)

In this work, single crystals of two different phases, stannous iodide (SnI_2) and stannic iodide (SnI_4) have been grown in the same experimental set up in silica gels. Transparent, bright reddish needles (often times yellow whiskers) of stannous iodide crystals and orange to reddish octahedral stannic iodide crystals were obtained. Stannous iodide (SnI_2) grew faster than the stannic iodide (SnI_4). These crystals can only form and grow under acidic conditions. Change in the concentration of feed solution favored the growth of different crystals. The (0.5N) of potassium iodide (KI) favoured the growth of only stannous iodide (SnI_2) crystals; 0.8N of potassium iodide (KI) favoured the growth of stannic iodide (SnI_4). When the concentration of the feed

solution was 1.0N both stannous and stannic iodides (SnI_2 and SnI_4) growths were favoured.

The crystals are wide band gap materials with band gaps ranging from 2.6 to 4.0eV. The crystallite sizes ranged from 0.04084 to 2.71854. Their refractive indices ranged from 0.1 to 2.4. Samples I, J and K are highly absorbing from the near VIS and decreased towards the IR. Sample K has the least transmittance from VIS to IR but samples I and J are moderately transmitting. All the samples can serve as oxidizing agents. The characteristics of samples qualify them to be used in poultry applications. The wide band gap nature of the materials qualifies them to be used in high temperature applications [88].

5.2d. Stannic iodide (SnI_4)

All the samples are highly transmitting from the UV-VIS regions to the IR. Sample O absorbs little in the VIS region has no absorbance up to IR. Samples M and N have good absorbance in the VIS region and decreased towards the IR. Sample P has the highest absorbance in the UV-VIS regions and decreased towards the IR. They are wide band gap materials and as such can be applied in high temperature applications [88] in addition to their oxidizing actions.

5.2e. Cadmium Sulphide (CdS)

We successfully grew Cadmium sulphide of fair quality. The growth of the crystals were found to be dependent on the concentrations of the reactants involved, selection of the proper ion donors, the specific gravity of the gel at ambient conditions and pH of the mixture. We succeed in growing fair quality crystal under slightly acidic condition (pH between 5.0 and 6.0). The grown crystals are wide band gap materials

with band gaps ranging from 2.6 to 4.3eV. Sample Q is CdS. It has band gap of 2.6eV which is very close to that in literature 2.42eV. The presence of local impurities widened the band gaps. This made the materials suitable for high temperature and high power circuits like power transistors [88] and in light detectors [15]. Samples Q, R, S and T have high absorbance in the VIS region and decreased towards the IR. Sample Q has the highest absorbance. All the samples are moderately transmitting in the UV-VIS regions and increased towards the IR. Sample S which is doped with bamboo has the highest transmittance. The aforementioned qualities made the materials good for solar cell applications and poultry houses [83-87].

5.2f. Local Impurities (Bamboo, Potash and Raffia)

The impurities were made from bamboo, potash and raffia. They were whittled down using top down approach and were used as dopants. Optical characterization proved that the local materials are wide band gap materials with band gaps ranging from 2.6 to 3.eV. Sample U has band gap of 3.5eV but samples V and W have the same band gap of 2.6eV. Samples V and W are moderately transmitting at constant rates and of equal strengths but sample U transmits moderately from UV and decreased towards the IR. They can be used in high temperature and high power materials [88].

5.3. CONCLUSION

In conclusion, local materials from African environment can affect the optical and structural properties of semi conductor materials/ crystals. The presence of locally produced materials and their polymer

nature have enabled us to grow and discover hybrid compounds of binary, ternary and quaternary constitutions such as Halloysite $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}]$, Sekaninaite $(\text{Fe}_2\text{Al}_4\text{Si}_5\text{O}_{18})$, Illite $[\text{K}_{0.7}\text{Al}_2(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_2]$, Moganite (SiO_2) , Ungarettite $(\text{Na}_3\text{Mn}_5\text{Si}_8\text{O}_{24})$, Clinoferrosilite (FeSiO_3) , Wollastonite (CaSiO_3) , Vanthoffite $[\text{Na}_6\text{Mg}(\text{SO}_4)_4]$ that can be employed in solar, solid state and materials industries. The dopants in KClO_4 affected the transparency of the material and as such offer it an opportunity to be used as a semiconductor material and improved pyrotechnic and antipyretic material. In the XRD, it is clear that the presence of local dopants have broadened and sharpened the peaks in such a manner as to make them good nano materials. XRD and FTIR analyses have shown that the aforementioned dopants from local materials are crystalline, nano polymer materials.

5.4. SUGGESTIONS AND RECOMMENDATIONS.

The difficulties experienced in the course of this research have made it necessary for the following suggestions:

- There is need for more research into the optimization of the deposition parameters of the crystals grown in this work since the literature on the films is scanty.
- There is need for further study into the solid state chemistry and solid state physics of the grown materials.
- The electrical, dielectric and thermal parameters used in this study were obtained by calculations from the spectral characteristics. It would be better if these values were obtained

using direct instrumentation and the measured values compared with calculated values.

- There is need in further research to calculate the voltage current characteristics and photocurrent responses of these crystals to enhance the understanding of their main electrical characteristics.
- There is need to measure the thickness of these materials using machine tool equipment or x-ray techniques and compared with calculated values.
- There is need to consider ways of producing these cost effective films on a large scale for commercial use.
- Government should provide functional avenues for funding projects and monitor the distribution of such funds for enhanced output.
- There is need to have a well equipped solid state and materials laboratory at the university of Nigeria to reduce the risk of students travelling to far places like NARICT in Zaria, CERD in Ife, EMDI in Akure and SHETSCO , Abuja in pursuit of characterization.
- Projects like this should be done by more than one person.
- It should be multidisciplinary.
- Further research should look at characterizing these local polymer materials with advanced and sophisticated machines in order to get their real molecular masses.

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Appendix 1: LIST OF GROWN SAMPLES.

SAMPLE	COMPD
A	Un-doped PbCl_2
B	Potash doped PbCl_2
C	Bamboo doped PbCl_2
D	Raffia doped PbCl_2
E	Un-doped KClO_4
F	Potash doped KClO_4
G	Bamboo doped KClO_4
H	Raffia doped KClO_4
I	Un-doped SnI_2
J	Potash doped SnI_2
K	Bamboo doped SnI_2
L	Raffia doped SnI_2
M	Un-doped SnI_4
N	Potash doped SnI_4
O	Bamboo doped SnI_4
P	Raffia doped SnI_4
Q	Un-doped CdS
R	Potash doped CdS
S	Bamboo doped CdS
T	Raffia doped CdS
U	Potash
V	Bamboo
W	Raffia

Appendix 2: List of Abbreviations

S/n	Serial number
Comp.	Compound
Quant	Quantity
Diff.	Diffraction
FWHM	Full Width at Half Maximum
FTIR	Fourier Transform Infra red
Fig.	Figure
LEED	Low Energy Electron Diffraction
RHEED	Reflection High Energy Electron Diffraction
UV	Ultra Violet
VIS	Visible
NIR	Near Infrared
Samp.	Sample
ϵ_r	Real dielectric
ϵ_i	Imaginary dielectric
$\tilde{\sigma}_{op}$	Optical conductivity
n	Refractive index
k	Extinction coefficient
$\tilde{U}$	Absorption coefficient
g	Frequency
t	Thickness
E_g	Band gap
A	Absorbance
R	Reflectance
T	Transmittance
λ	Wavelength
h	Planck's constant
hg	Photon energy

Appendix 3: Graphs of FTIR.

Plates 1-8: Pictures of Experimental Set up and Research Stages.



Plate 1: Picture of the experimental set up



Plate 2: The researcher weighing the samples



Plate 3: Grown samples



Plate 4: Dried samples of SnI_2 , SnI_4 and CdS



Plate 5: Dried samples of PbCl_2 and KClO_4



Plate 6: Picture of all the dried samples



Picture 7: The Researcher with the Analyst during XRD characterization @ CERD Ife.