INVESTIGATING THE PHOTODEGRADATION PROPERTY OF $Cs_2AgIn_{(1-x)}Bi_xCl_6$

Dissertation for
PHY-651
Credits: 16
Submitted in partial fulfillment of Masters Degree

M.Sc in Physics
Goa University
In the subject of Physics

by

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DECLARATION

I hereby declare that the data presented in this Dissertation / Internship report entitled, "**INVESTIGATING THE PHOTODEGRADATION PROPERTY OF** $Cs_2AgIn_{(1-x)}Bi_xCl_6$ " is based on the results of investigations carried out by me in the **Physics Discipline at the School of Physical and Applied Sciences, Goa University** under the **Supervision of Dr.Venkatesha Hathwar** and the same has not been submitted elsewhere for the award of a degree or diploma by me. Further, I understand that Goa University or its authorities will be not be responsible for the correctness of observations / experimental or other findings given the dissertation. I hereby authorize the University authorities to upload this dissertation on the dissertation repository or anywhere else as the UGC regulations demand and make it available to any one as needed.

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This is to certify that the dissertation / internship report "**INVESTIGATING THE PHOTODEGRADATION PROPERTY OF** $Cs_2AgIn_{(1-x)}Bi_xCl_6$" is a bonafide work carried out by **MR. Varun Prashant Chowgule** under my supervision in partial fulfilment of the requirements for the award of the degree of **M.Sc in Physics** at the **School of Physical and Applied Sciences, Goa University**.

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ACKNOWLEDGEMENT

It gives me a great sense of pleasure to present the report of the project work undertaken during MSc final year. Although I have worked hard for the success of this project, it wouldn't have been possible without some people who have helped and guided me throughout the course of my work. So, I would like to express a deep sense of gratitude to those people.

First, I would like to thank our project guide Dr. Venkatesha R. Hathwar sir for his excellent guideship and intelligence. Thank you sir for always motivating and inspiring me. Secondly, I would like to thank Mr. Irshad Shaikh and Mr.Mahendra Choudhary sir for their constant help and support throughout the project work. Thank you so much for being a great guide and friend.

Thirdly, I want to thank all the PhD students of physics who have helped me by explaining how to use different instruments and software.

Next, I want to thank the School of Physical and Applied Sciences for providing me with all the required instruments for my project work.

Next, I want to thank other faculties of physics for providing me with the conceptual knowledge needed. I would like to express my gratitude towards my family for their kind encouragement and appreciation throughout.

Lastly, I want to thank my MSc friends who made work time joyful but always efficient.

Abstract

As we know that Halide perovskites have emerged as a class of promising and cost-effective semiconductor materials for next-generation photoluminescent, electroluminescent, and photovoltaic devices and for photodegradation purpose.From the literature review it is seen that $Cs_2AgBiBr_6$ and $Cs_2AglnCl_6$ shows good photodegradation properties ..

$Cs_2AgIn_{(1-x)}Bi_xCl_6$ synthesized by acid precipitation method and tested it for phototodegradation and all the results were studied and was compared to literature review..

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Chapter 1

Introduction

1.1 Perovskites

”Perovskite” is the name of the $CaTiO_3$ mineral discovered in the Ural Mountains in 1839 by the German scientist Gustav Roth. It takes its name from the Russian statesman and mineralogist Count Lev Alexevich von Perovsky. Today, perovskites are widely used materials , whose structure is based on the ABX_3 crystal structure of the original rock. The unstoppable nature of perovskites is attributed to their excellent physical and chemical properties as well as their excellent chemical properties and simple structure. [4] Perovskite materials attract the attention of users all over the world due to their high photoluminescence quantum yield (PLQY), high color purity, tunable bandgap, wide color gamut, high transmission, and long-term energy. This leads to long-term subdiffusion. These excellent optoelectronic properties make them widely used in many optoelectronic devices. In just ten years, the power conversion efficiency (PCE) of perovskite solar cells has increased from 4% to 25.5%; this is comparable to crystalline silicon solar cells. In addition, perovskites are widely used as the light-emitting layer of light-emitting diodes (LEDs), and the external quantum efficiency (EQE) of perovskite LEDs has rapidly increased from 0.1% to over 20% in 2014. Recently perovskites have also proven competitive in other optoelectronic applications, including photodetectors, X-ray detectors and lasers.

1.1.1 Structure of Perovskite

Perovskites with general formula ABX_3 (where A is monovalent organic or inorganic cation, B is divalent cation, and X is halide anion), consist of continuous corner-sharing metal halide $[BX_6]$4octahedra.Size of A and B ions greatly influences the structure of perovskite crystal lattice, and their radii correlation is expressed through tolerance factor $\boldsymbol{\tau}$

$$\tau = \frac{rA + rC}{\sqrt{2}(rB + rC)} \tag{1.1}$$

where rA, rB and rC are radii of A, B and C ions, respectively. A tolerance factor of 1 indicates a perfect fit; in the range $0.8 \leq t \leq 1$ perovskites generally do form, although in the lower part of this range they may be distorted due to tilting of the $BX6$ octahedra and lowering of the symmetry. If $t > 1$, this indicates the A site cation is too large and generally precludes formation of a perovskite, and if $t < 0.8$, the A cation is too small, again often leading to alternative structures. indicates that A is too small and means A is too large to fit in the cavity between BX_6 octahedrons.[21] A atoms form the corners of cubic cells. B atoms are in centre in 6-fold coordination , surrounded by an octahedron of cations

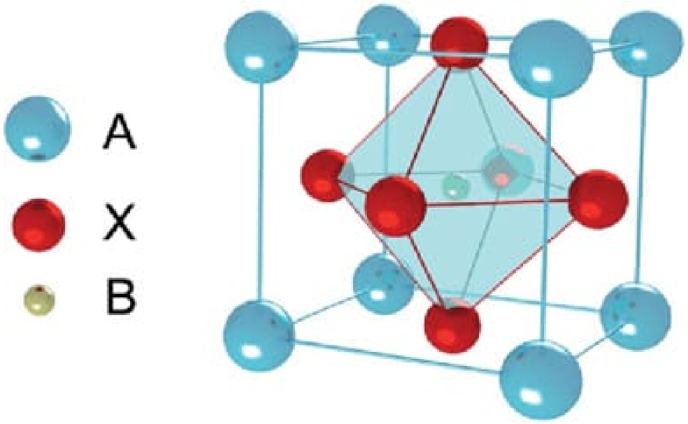

Figure 1.1: Structure of perovskite
pic credit:www.edinst.com/blog/perovskite-applications-improving-todays-technology

1.1.2 Double Perovskites

Double perovskite is the combination of two perovskite structures and its structure is $A_2BB'X_6$. It is formed by replacing half of the cation in the B position with another B' cation. Double perovskites have gained an important role in the field of optoelectronic devices due to their similar properties to halide perovskites.[5]

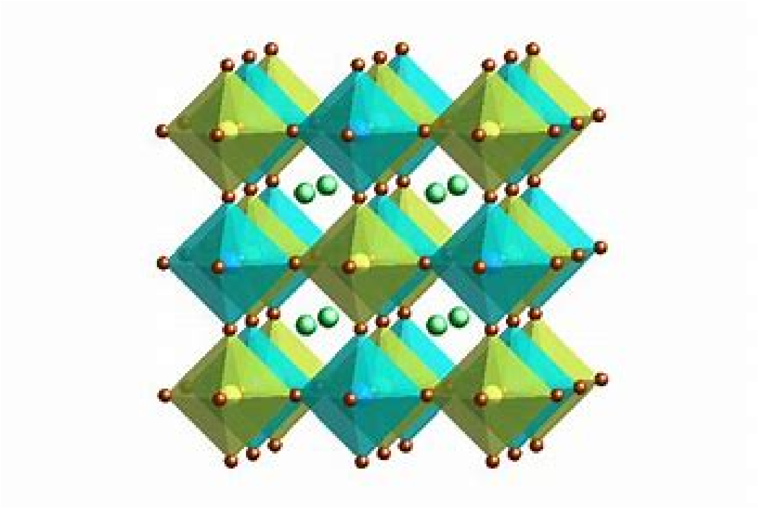

Figure 1.2: Double halide perovskite
Photo credit: Linköping University

1.2 Dyes

Dye, substance used to impart colour to textiles, paper, leather, and other materials such that the colouring is not readily altered by washing, heat, light, or other factors to which the material is likely to be exposed. Dyes differ from pigments, which are finely ground solids dispersed in a liquid, such as paint or ink, or blended with other materials. Most dyes are organic compounds (i.e., they contain carbon), whereas pigments may be inorganic compounds (i.e., they do not contain carbon) or organic compounds. Pigments generally give brighter colours and may be dyes that are insoluble in the medium employed.

Colour has always fascinated humankind, for both aesthetic and social reasons. Until the 1850s virtually all dyes were obtained from natural sources, most commonly from vegetables, such as plants, trees, and lichens, with a few from insects. Solid evidence that dyeing methods are more than 4,000 years old has been provided by dyed fabrics found in Egyptian tombs. [1]

1.2.1 Different Types of Dyes

Natural Dyes: Derived from plant sources, such as vegetables, trees, and lichens. Examples include indigo, obtained from the Indigofera plant, and cochineal, extracted from insects. Historically, natural dyes were widely used, with evidence dating back over 4,000 years in Egyptian tombs.

Synthetic Dyes: Created through chemical processes. Acid dyes, basic (cationic) dyes, and disperse dyes fall into this category. Each type has specific properties and applications.

Anionic and Cationic Dyes: These are subcategories of synthetic dyes. Anionic dyes are negatively charged and are commonly used for dyeing wool and silk. Cationic dyes are positively charged and are suitable for acrylic fibers and certain synthetic materials.

Other Types of Dyes: Azo dyes: Contain azo groups and are widely used in textiles. Vat dyes: Known for their excellent colorfastness. Reactive dyes: Form strong covalent bonds with fibers. Pigment dyes: Insoluble particles that adhere to surfaces. Sulfur dyes, naphthol dyes, and premetallized dyes: Used for specific applications. Metallized dyes: Contain metal ions. Anthraquinone dyes: Used in printing and dyeing.

1.3 Hazards of Dyes

With increasing global air and water pollutions, photocatalysis has attracted considerable attention because this method provides a promising pathway to eliminate environmental pollution problems, mainly due to the capacity of photocatalyst to degrade organic contaminants. Polluted waste water plays significant role in environmental pollution. Industrial effluents contain different chemicals especially synthetic dyes which are carcinogenic in nature. Some dyes decompose aerobically and anaerobically resulting in the formation of carcinogenic compounds. In addition, the coloured pollutants decrease light penetration and prevent photosynthesis. Many conventional methods for the removal of dying effluents from aqueous solutions can be divided into three classes; physical biological and chemical treatments. To find an appropriate and cost effective adsorbent is an important consideration for designing a suitable adsorption method to minimize water pollution. Water pollution is one of the worldwide problems nowadays and this can directly affect the health of living organisms. Because of the industrialization, effluents from most of the industries are discharged directly or indirectly into water sources without treating the harmful or dangerous compounds present in it and this may lead to water pollution. There are wide varieties of water pollutants available, which include waste chemicals, waste organic matter, presence of harmful pathogens, etc. Water pollution is a burning global problem; hence development of suitable eco friendly treatment procedures is a mandatory requirement at present. One of the most harmful pollutants present in industrial waste water is organic dyes. Organic dyes are used for various industrial applications such as paper, leather, cosmetics, drugs, electronics, plastics, textiles, etc. From among these, it was reported that the textile industry alone utilizes 80 percent of the synthetic dyes for printing purpose. Most of the dyes have non-biodegradable compounds. Recently, researchers have developed methods for the treatment of waste water especially for the removal of dyes using techniques based on chemical, physical and biological means. However, these treatment methods are not suitable for large scale due to their high cost. Therefore, alternative treatment methods, which are financially viable and green-chemical in nature, are required by the industrial sectors. Photocatalysis technology is one of the best water treatment technologies, since it is an economically viable and environment friendly technique for the purification of waste water; it removes all kinds of organic and inorganic pollutants and contaminants present in waste water.

1.4 Techniques for dye detection

1.UV-Vis Spectroscopy:UV visible spectroscopy is an inexpensive, simple, flexible, non-invasive analytical method suitable for a wide range of organic compounds and some inorganic chemicals. UV-visible spectrophotometers measure the absorbance or transmittance of light passing through a medium as a function of wavelength.Organic dyes tend to absorb light in the visible range, which can be used to identify and quantify the dye. [15]

2.Fluorescence Spectroscopy:Organic dyes can often emit fluorescent light when excited by a specific wavelength of light. Fluorescence spectroscopy measures this emission, which can be used to identify and quantify the dye
ref:wikipedia

3:High-performance liquid chromatography: (HPLC) is a technique used in analytical chemistry to separate components in a mixture and identify and quantify each component. It was first discovered by analytical methods in the twentieth century and was first used to separate color mixtures. The word chromatography means color collection.[14]

4.Infrared Spectroscopy: Infrared spectroscopy involves measuring the absorption of infrared light by a molecule. Organic dyes have unique infrared spectra that can be used to identify and quantify them.

1.4.1 Catalysis of dyes

Perovskites have emerged as candidates for photocatalytic applications, including the photodegradation of organic dyes, due to their versatile structure and novel optoelectronic properties. The science and technology of catalysis is of great significance as it affects Your daily life. Four major sectors of the world economy; petroleum and energy production, chemicals and polymer production, food industry and pollution control, involve catalytic processes. Semiconductor-based photocatalysis or heterogeneous photocatalysis has received tremendous attention due to its potential application in wastewater treatment and production of hydrogen fuel with the help of sunlight, which is a green and abundant energy source . It is defined as a “reaction assisted by photons in the presence of semiconductor photocatalyst.

1.5 Lead halide perovskites

Lead halide perovskites have been established as efficient materials for photovoltaic (PV) and opto-electronic applications with certified power conversion efficiencies (PCEs) exceeding 23%. [19] Lead halide perovskite nanocrystals (NCs) show great potential in optoelectronic applications due to their excellent optical properties. [23] Lead halide perovskites (LHP) continue to bring new importance to optoelectronic applications. Add a new chapter to the history of optoelectronic devices with chemistry, information science and physics. LHP has become one of the research hotspots due to its high absorption coefficient, carrier mobility, tunablband gap and easy solubility. [10] Lead halide perovskites (LHP) have attracted interest in many applications, including solar cells, light-emitting diodes, lasers, X-ray detectors, and scintillators. They exhibit unique properties such as ”seamless” peak carriers from electronic structure.The composition of LHP colloidal nanocrystals (NCs) has also been extensively studied not only to replace precursors but also to solve production problems. The technique can also be applied to a new class of nanofluorophores. [7] Although this product is very good and offers a high PCE, the mass distribution of this material is limited due to the chemical content of lead and its thermal and moisture instability.Significant efforts have been made to reduce the toxicity issues and improve the stability of lead halide perovskites. Various strategies have been designed and developed for the replacement of Pb. One such approach is replacing the Pb with the substitution of group IV metals with less toxicity, such as Ge^2+ and Sn^2+[19]

1.6 Lead Free Halide Perovskites

Lead-free halide perovskites have drawn wide attention as alternatives to their toxic and poorly stable lead-based counterparts. The toxicity and low stability of lead halide perovskites are still a big problem for practical use. Therefore, it is very important to investigate lead-free metal halide perovskite NCs that are stable and environmentally friendly with excellent optical properties[23].The toxicity of lead (Pb) and the poor stability of materials to electricity, moisture and heat are a serious problem for businesses . Therefore, lead-free perovskites with lower toxicity and higher stability have attracted more attention than other materials for LHP. Initially, most efforts were devoted to investigating the cations $Sn^2+$and Ge^2+ as alternatives to Pb^2+.However, the corresponding halide perovskites are less stable because these elements are not stable and it oxidizes easily in Environmental conditions.[10].Due to their improved stability and non-toxicity, lead-free halide double perovskites have been proposed as competitive materials to replace lead halide perovskites in photovoltaic and optoelectronic applications. However, the limited understanding of the fundamental properties of halide double perovskites has become an obstacle to further improving their functional properties.[24]

1.7 $Cs_2AgBiCl_6$

In the past decades, great efforts have been made to develop novel visible-light photocatalysts to achieve high photocatalytic efficiency by utilizing visible light, the largest proportion of solar energy. As a new type of photocatalyst materials, all-inorganic lead-free halide double perovskites have begun to attract widespread interest. Herein, double perovskite $Cs_2AgBiCl_6$was developed into a visible-light photocatalyst for degrading organic dyes.$Cs_2AgBiCl_6$ was prepared by the hydrochloric acid precipitation and anti-solvent recrystallization methods, respectively, and was used to degrade organic dyes under visible light. Samples prepared by the anti-solvent recrystallization method are smaller than those prepared by the hydrochloric acid precipitation method, which can degrade 95.7 % of Sudan III in 10 min and show excellent photocatalytic activity. The cyclic experiments demonstrate that $Cs_2AgBiCl_6$has a good cycle stability. Moreover, $Cs_2AgBiCl_6$ also exhibits good photocatalytic degradation ability for Methyl red and Malachite green. These distinctive results indicate that $Cs_2AgBiCl_6$ may be a promising material for developing novel, high-efficient and stable visible-light photocatalysts.[6]

1.8 $Cs_2AgInCl_6$

Photocatalytic applications of halide perovskites have attracted increasing attention. However, lack of stability and lead toxicity of lead halide perovskites have hindered their applications. Metal halide double perovskite (DP) $Cs_2AgInCl_6$is a stable, environment-friendly semiconductor with direct band gap, and then the best promising alternative to lead halide perovskites. Here, the applications of $Cs_2AgInCl_6$DP to photocatalytic degradation of organic pollutants have been developed, in which the octahedral $Cs_2AgInCl_6$ DP particles (3.33 eV) were prepared by precipitation from acid solutions. The as-prepared samples exhibit high photocatalytic activity, which can degrade about 98.5% of water-insoluble carcinogen Sudan Red III in only 16 min, and have a good stability for 5 cycle operations. Furthermore, the $Cs_2AgInCl_6$ DP also can degrade Rhodamine B, Methyl orange and Methyl red efficiently, demonstrating a highly-efficient and stable ethanol solvent-based photocatalytic system for organic pollutants degradation. The high photocatalytic activity could be attributed to direct band gap and long carrier lifetime of $Cs_2AgInCl_6$ DP. These unique features of $Cs_2AgInCl_6$ DP indicate that it could have a good application prospect for photocatalytic degradation of organic pollutants.[9]

1.9 Photocatalysis

Industrialization, technologies, and consumption of non-renewable resources have been growing at a rapid rate over the past few decades, as regular increases have continued. Demand for materials related to textiles, dyes, fertilizers, household, plastics etc. As a result, environmental pollution and energy crisis have already reached alarming levels. Industrial wastes are more toxic and nonbiodegradable than municipal wastes as they contain fats, oils, greases, heavy metals, phenols and ammonia. etc. Agricultural and pharmaceutical fluids release pesticides and other chemicals that are responsible for certain chronic diseases, which are harmful to human endocrine.

The term photocatalyst combines two words: photo, which refers to photons, and catalyst, which is a substance that changes the rate of a reaction in its presence. Therefore, a photocatalyst is a substance that changes the rate of a chemical reaction when exposed to light. this This phenomenon is known as photocatalysis. Photocatalysis involves the reactions that occur Use of light and semiconductors A substrate that absorbs light and acts as a catalyst for chemical reactions is called a photocatalyst. Basically all are photocatalysts Semiconductor. Photocatalysis is a phenomenon in which electron-hole pairs are created when a semiconductor material is exposed to light.

Photocatalysis is a branch of chemistry that deals with chemical reactions taking place in the presence of light and a photocatalyst. A photocatalyst is a semiconductor whose presence increases the rate of a reaction. Photocatalysis has a wide range of applications, such as antibacterial, deodorizing, air purification, fogging, self-cleaning, water purification, etc. Superhydrophilicity plays an important role in some of these applications. Photocatalysis is a green chemical pathway and hence the need of the day. Water is a basic necessity for humans, animals and plants. With the ever increasing population, the demand for water is increasing day by day. There is an urgent need to purify the water. Many processes have been used for this, but photocatalysis is widely used in wastewater treatment and plays an important role in water remediation.[2]

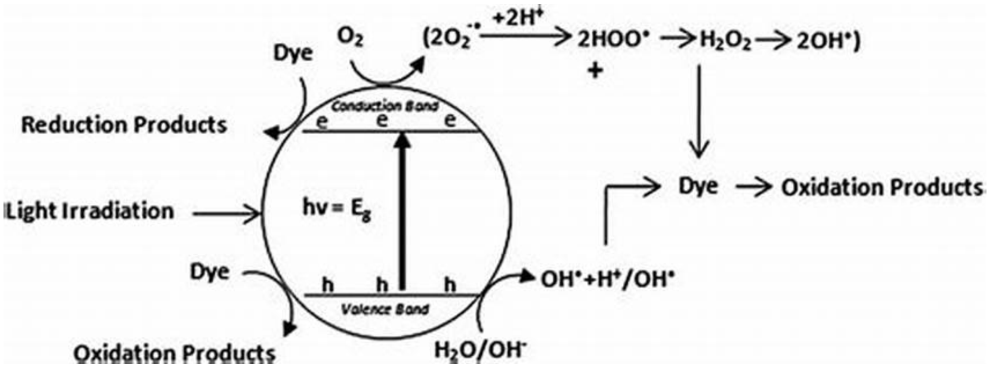

Figure 1.3: Mechanism of photocatalysis
Pic Credit:Journal of Environmental Chemical Engineering

The mechanism of photocatalytic degradation of dyes has been classified into three types:

I.Dye sensitization through charge injection

II.Indirect dye degradation through oxidation/reduction

III.Direct photolysis of dye

There have been many studies on the photocatalytic degradation mechanism of dyes . First, the photocatalyst is irradiated by sunlight with energy greater than the threshold. As a result, the electrons and holes inside the catalyst are separated, leaving the positively charged holes staying in the valence band (VB). Under the induction of the internal electric field, the photogenerated electrons on the surface of the photocatalyst will be transferred to the conductionband (CB), as shown in Eq. (2). The photogenerated electrons in the conduction band are captured by O_2 on the surface of the photocatalyst to generate superoxide anions (O_2^-), which then react with water to generate (HO_2) radicals and OH, as shown in Eqs. (3) and (4). The photoinduced holes in VB react with the OH on the surface of the catalyst to generate hydroxyl radicals (OH.), as shown in Eq. (5), and a small number of the holes directly participate in the photocatalytic reaction, as shown in Eq. (6) . At the same time, the oxidizing substance HO_2 . on the surface of the photocatalyst is reacted with the dye molecules with the help of water molecules, as shown in Eqs. (7), (8), and (9). Afterwards, the fast recombination of the photogenerated electron-hole pairs inside the photocatalyst can increase the lifetime of transient electrons and holes and ultimately lead to an increase in the photocatalytic activity.[18]

$$Cs_2AgIn_{(1-x)}Bi_xCl_6 + h\nu \rightarrow Cs_2AgIn_{(1-x)}Bi_xCl_6 + e^-_{CB} + h^+_{VB} \tag{1.2}$$

$$e^-_{CB} + O_2 \rightarrow O_2^- \tag{1.3}$$

$$O_2^- + H_2O \rightarrow HO_2 + OH \tag{1.4}$$

$$h^+_{CB} + OH \rightarrow OH \tag{1.5}$$

$$h^+_{CB} + \text{dye} \rightarrow CO_2 + H_2O \tag{1.6}$$

$$HO_2 + H_2O \rightarrow H_2O_2 + OH \tag{1.7}$$

$$H_2O_2 + 2OH \rightarrow H_2O + O_2 \tag{1.8}$$

$$OH + \text{dye} \rightarrow CO_2 + H_2O \tag{1.9}$$

1.10 Factors affecting the degradation of dyes

Several factors like concentration of dyes, pH of the solution, catalyst dosage, intensity of light, and intermediate species affect the performance of photocatalytic degradation of dyes. The effects of these factors on the dye degradation performance.[16]

1.10.1 Effect of dye concentration

The concentration of the dye greatly affects the photocatalytic degradation performance of the dye. Dye molecules have many functional groups. The abundance and nature of functional groups present in dyes have an impact on the interaction between dyes and the photocatalyst substrate. Since different colors have different functions, the most suitable color depends on the color of the color. Generally speaking, with the increase of reactant concentration, the reaction increases, but with the increase of the primary color, the photocatalytic degradation efficiency of the dye decreases for the following reasons.[16]

1.As the dye concentration increases, the ratio of photocatalyst active sites to dye molecules decreases.

2. As the dye concentration increases, the ratio of OH radicals to dye molecules decreases.

3. The increase in dye concentration causes more light to be absorbed than normal. get into Catalyst surface

1.10.2 Effect of pH

The pH value of the dye is also an important factor affecting photodegradation performance. The pH value of the dye affects the electrostatic interaction between catalysts, dye molecules, and ROSs during the degradation process.[16]

1.10.3 Effect of Catalyst Dose

The quality of the photocatalyst also affects the photocatalytic degradation performance of pollutants. Generally speaking, the photocatalytic degradation efficiency of pollutants increases with the increase of the catalyst. As the amount of catalyst increases, more electron pairs are produced, causing the reaction rate to increase. However, an increase in catalyst dosage will increase the turbidity of the reaction mixture and thus reduce the penetration of light into the catalyst space. Using more catalyst causes reaction rates to decrease.[16]

1.10.4 Adsorption of dyes

Adsorption of dyes onto the surface of photocatalysts affects the photocatalytic degradation performance of dyes. The adsorption of dyes onto the catalyst surface is due to the combination of binding and electrostatic interaction between the catalyst surface and dye molecules. Adsorption of dyes onto the catalyst surface is the first step in the photodegradation of the dye. Both strong adsorption and weak adsorption of dyes will reduce the photocatalytic performance of the catalyst. Strong adsorption can cause catalyst poisoning, while weak adsorption can cause the dye to bind to the catalyst surface for photodegradation reactions. The high adsorption of dye on the catalyst surface causes the surface to be covered with dye, preventing photons from entering the catalyst surface. Therefore, strong adsorption reduces photocatalytic activity. According to the Sabatier principle, to obtain good photocatalytic activity, the binding of dye molecules to the catalyst surface must be weak or weak. It is good for achieving the efficiency of photodegradation due to the combination of softness, photocatalysis and adsorption.[16]

1.10.5 Intensity of light

The photocatalytic degradation performance of dyes depends on the energy provided by light radiation. Due to the energy provided by electricity, holes and electrons are formed in the valence band and conduction band of the photocatalyst. Only when the electrical energy is equal to or greater than the energy difference of the photocatalyst can the formation of holes and electrons occur.[16]

Chapter 2

Identification of problem

The direct disposal of untreated dye-containing effluent into natural water bodies has an adverse effect on the photosynthetic activity in aquatic ecosystems.
By this compound the reaction time of breaking the bonds will increase and the degradation will take faster..

Figure 2.1: Untreated dye disposed in water body
pic credit:www.huffpost.com

2.1 Main objectives

1. To synthesise $Cs_2AgIn_{(1-x)}Bi_xCl_6$ using acid precipitation method.
2. To characterize the compound by XRD,SEM.
3. To test it for photodegradation for methyl orange dye.

2.2 Literature Survey

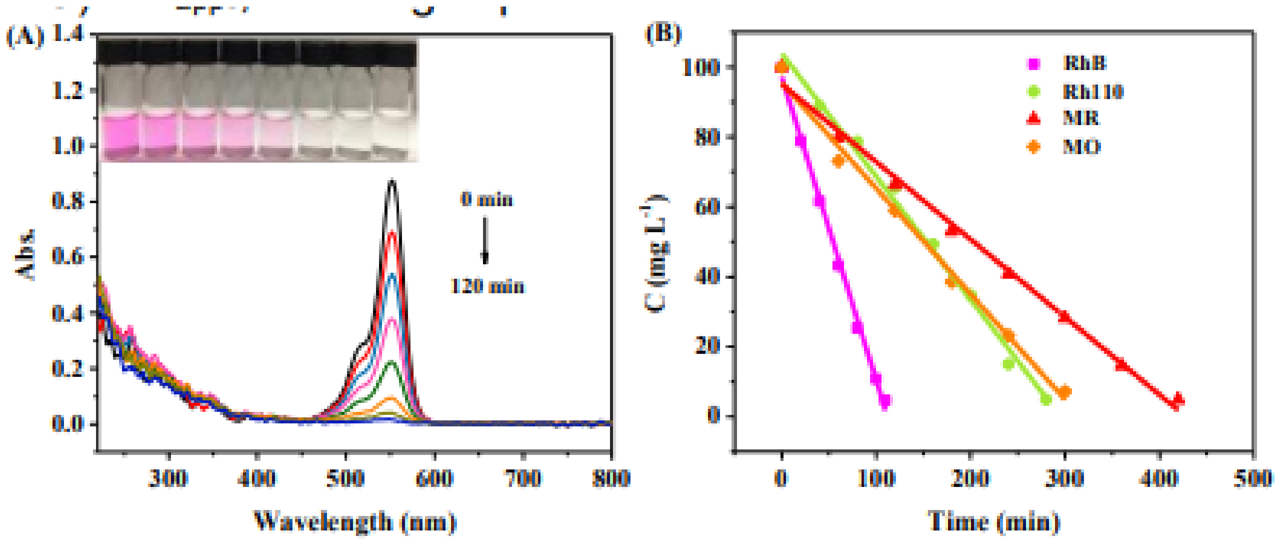

Figure 2.2: (A) UV-vis spectra of RhB at different irradiation time (20, 40, 60, 80, 100, 120 min) in the presence of $Cs_2AgBiBr_6$
(B) Kinetic curves of the RhB (pink curve), Rh110 (green curve), MR (red curve) and MO (orange curve) degradation
pic credit:Angew. Chem. Int. Ed. 2019, 58, 7263.

The as-prepared $Cs_2AgBiBr_6$ was studied as photocatalyst for the degradation of organic dyes including Rhodamine B (RhB), Rhodamine 110 (Rh110), Methyl red (MR) and Methyl orange (MO) under visible light irradiation (λ >420 nm).The RhB degradation rate under monochromatic light with different wavelength was also investigated. Different degradation rates are detected for different wavelengths and are plotted together with the UV-Vis absorption spectrum of the $Cs_2AgBiBr_6$ particles [25]

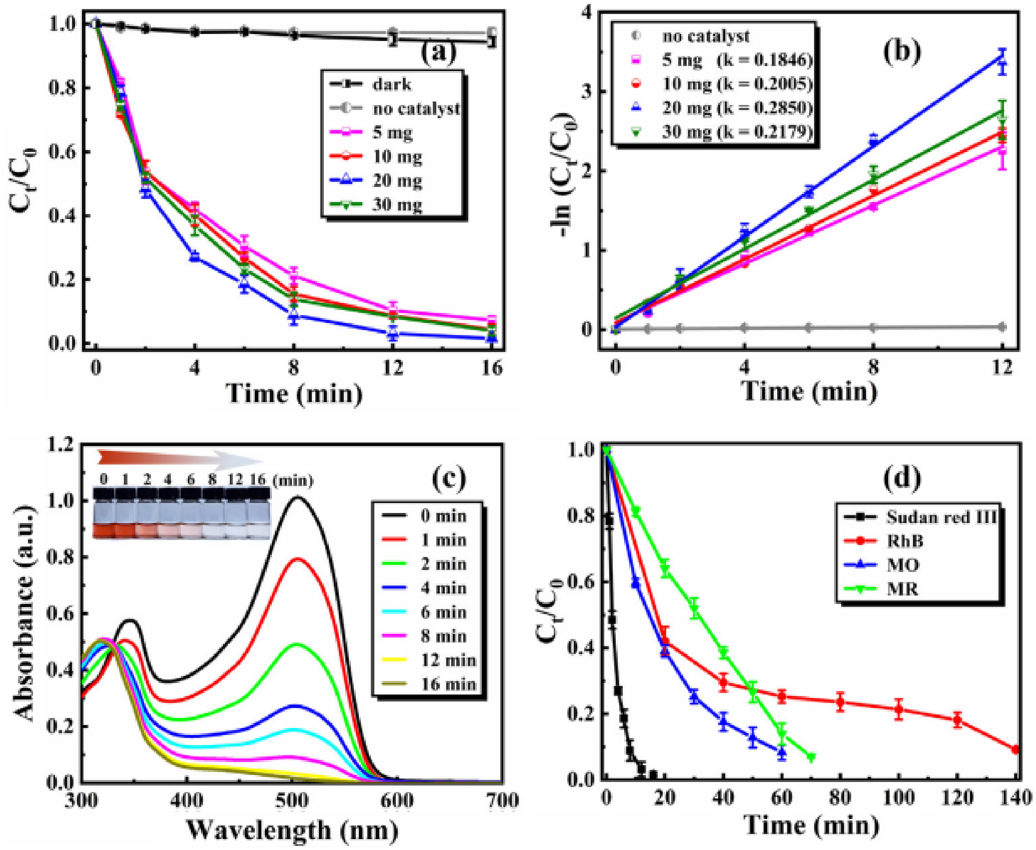

Figure 2.3: (a) Plots of Ct/Co versus the irradiation time for the degradation of Sudan Red III with various mass of $Cs_2AglnCl_6$ and (b) corresponding reaction kinetic curves. (c) UV–visible absorption spectra for Sudan Red III degradation in the presence of $Cs_2AglnCl_6$ DP under various UV-light irradiation times (d) Plots of Ct/Co versus the irradiation time for photocatalytic degradation of Sudan Red III, cationic (RhB), neutral (MR) and anionic (MO) dye pollutants.

pic credit:0021-9797/2021 Elsevier Inc

The photocatalytic activity of $Cs_2AglnCl_6$ DP was evaluated by removing Sudan Red III in ethanol solution under irradiation of a 300 W Mercury lamp. As shown in Fig. 4a, the concentration of Sudan Red III decrease slightly in dark with the presence of $Cs_2AglnCl_6$, indicating that $Cs_2AglnCl_6$ almost does not degrade Sudan Red III in dark (Fig. 4a), similar to that of the reported results. Under UV-light irradiation, the Sudan Red III is hardly degraded within 16 min without catalysts. However, after the addition of $Cs_2AglnCl_6$, Sudan Red III can be degraded quickly under UV-light irradiation. By comparison, the photocatalytic degradation rate is the highest with 20 mg $Cs_2AglnCl_6$ DP.The UV–vis absorption spectra of Sudan Red III are presented in Fig. 4c with 20 mg $Cs_2AglnCl_6$ DP in various UV-light irradiation times, the absorption peak intensity of Sudan Red III decreases significantly with the increase of irradiation time. After 16 min, the characteristic peak of Sudan Red III cannot be observed, which indicates that the degradation is almost complete. [8]

Chapter 3

Experimental Section

3.1 Chemicals Used

Figure 3.1: Chemicals used for synthesis process

Hydrochloric Acid (HCl, 37 wt %), Cesium Chloride (CsCl, 99.9 %),Indium (III) Chloride ($InCl_3$, 99.9 %) and Silver Chloride (AgCl, 99.9 %) and Bismuth (III) Chloride ($BiCl_3$) and ethanol is also used for rinsing purpose.

3.2 Synthesis

The series of $Cs_2AgIn_{(1-x)}Bi_xCl_6$ was synthesised using precipitation method using the following reactants, CsCl (99.9%pure Alfa-Aesar), AgCl (99.9 %pure Alfa-Aesar), $InCl_3$ (99.9 % pure Aldrich)and $BiCl_3$ (99.9 % pure Aldrich) in stoichiometric ratios. The reactants undergo the following reaction in 37 percent HCl which was used as the solvent to facilitate the reaction.

The following reaction takes place.

$$BiCl_3/InCl_3 + AgCl + 2CsCl \rightarrow Cs_2AgIn_{(1-x)}Bi_xCl_6 \tag{3.1}$$

Stoichiometric ratios of AgCl, $InCl_3$,$BiCl_3$ were taken in about 10 ml HCl and stirred continuously while heating. The mixture was heated at 75^oC for thirty minutes before adding calculated amount of CsCl.

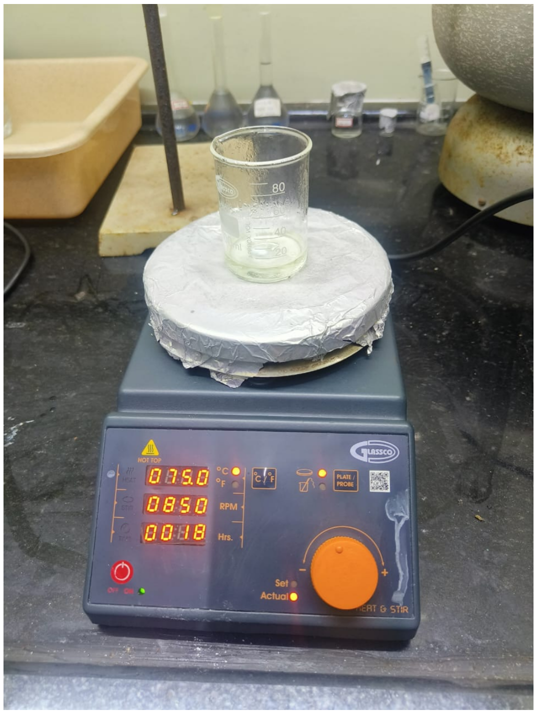

Figure 3.2: Stirring the compound

After adding CsCl the mixture was stirred for 30 minutes. After stirring it was collected in beaker and the HCl was drained off and it was transferred to centrifuge tube by adding ethanol to remove HCl and was centrifuged for around 2-3 minutes to remove HCl. This process was done four times. After that we dry our compound at 90 degree celcius for 60 minutes. After drying the compound is ready for grinding.

After this we synthesised other series (x=0,0.1,0.15,0.20,0.25). In this method we stir the compound for 30 minutes at 75^oC. After that we dry our compound at 90^oC for 60 minutes. After drying the compound is ready for grinding.

After grinding it for 45 minutes, the sample is filled in the respective tube and is marked with the number of concentration and with the date on which is synthesiszed.

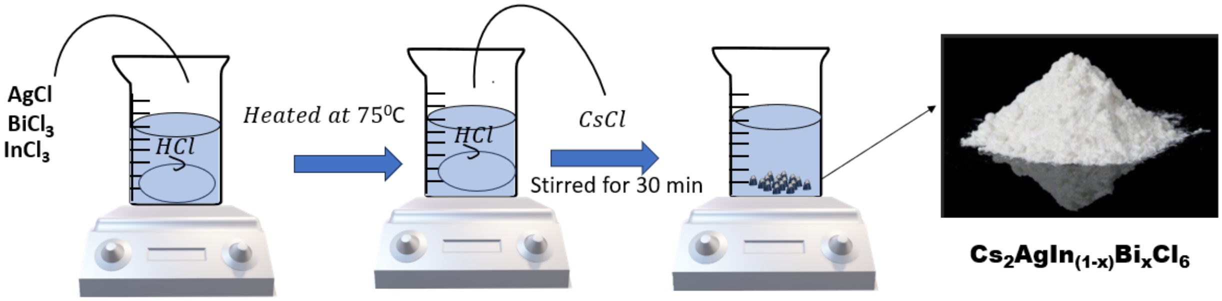

Figure 3.3: Schematic diagrams of the synthesis process of $Cs_2AgIn_{(1-x)}Bi_xCl_6$

Figure 3.4: Tubes with filled sample

Chapter 4

Characterization

Characterization, refers to the broad and general process by which a material's structure and properties are probed and measured. It is a fundamental process in the field of materials science, without which no scientific understanding of engineering materials could be ascertained.
Characterization of any material consists of phase analysis, structural and compositional characterization, microstructural analysis and spectroscopic analysis. One single technique is not capable of providing complete characterization of a solid. In this chapter different analytical instrumental techniques are discussed which were used to characterize the samples prepared.

4.1 XRD

Since the discovery of X-rays at the end of the 19th century and the first works on diffraction of X-rays by crystals, huge developments were achieved in the application of these methods for material characterization. In particular, in the field of materials science and engineering, several applications were developed to become state of the art techniques. This chapter first presents a condensed overview of the production of X-rays as well as of the theory of diffraction of X-rays by crystals. A short survey of the hardware for X-ray diffraction (XRD) measurements is given. The methods of phase analysis, residual stress measurements, and texture investigations of polycrystalline materials are then described with examples, and finally, special methods and future trends are presented.[13]

X-ray diffraction (XRD) is one of several scientific techniques that are applied to the materials analysis and cultural interpretation of inorganic mineralized artifacts such as ceramics, lithics, ores, plaster, faience, pigments, slag, and metal. It can also be used to study crystalline phases in some colored and opaque glasses, as well as being applied to crystalline organic materials such as bone and teeth. The technique is used to characterize and in some cases quantify the mineral constituents of these types of artifacts, which in turn can provide information about their raw material sources. In the case of synthetic materials such as ceramics, plaster, pigments, metals, and slag, XRD data can also be used to investigate their manufacturing technology, use, and alteration.[13]

(XRD) is a highly versatile technique that provides chemical information for elemental analysis as well as for phase analysis. Besides chemical characterization, XRD is extremely useful for stress measurements as well as for texture analysis. Samples to be analyzed using XRD must be crystalline however the technique can provide the degree of crystallinity in polymers. XRD has traditionally been used for bulk sample's analysis but with the advent of new optical systems thin film analysis can also be carried out using XRD.

4.1.1 Generation of X rays

The resulting X-ray spectra usually have two components: a broad spectrum of wavelengths known as white radiation and a number of fixed or monochromatic wavelengths. X-rays which are used in X Ray diffractometers are monochromatic X-rays. A beam of electrons when accelerated through high potential differences are allowed to strike a metal target such as Cu. The incident electron beam has sufficient energy to ionize some of the Cu K shell electrons. An electron in the outer orbit (such as L, M) can fill the vacancy created in the K shell and the energy released in the transition appears as X-radiation. For Cu, transition from L-shell to Kshell appears as K radiation X-rays are electromagnetic radiation having wavelength 1Å. X-rays are produced when high energy particles such as electrons are accelerated through high potential to collide with target material.and transition from M-shell to K-shell appears as K radiation.

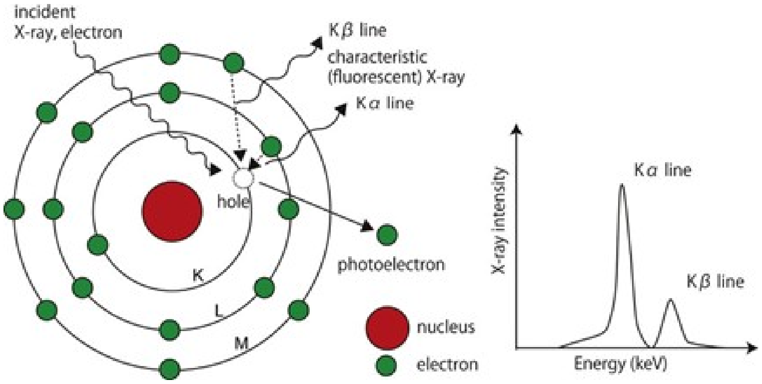

Figure 4.1: Generation of Cu K X-rays
Pic Credit:www.radiologystar.com

4.1.2 Interaction of X-rays

Bragg's diffraction method treats the crystal as formed in layers or planes, with each plane being a translucent glass. When X-rays with wavelengths similar to the atomic spacing fall on a crystalline material, some of the X-rays are reflected out of the plane at an angle equal to the angle of reflection, the rest is emitted and reflected. by plane. next plane. Bragg's Law

$$2dSin\theta = n\lambda \tag{4.1}$$

Where; d is interplanar spacing, θ is Bragg's angle of diffraction angle, λ is Wavelength of X-rays used and n is order of diffraction.

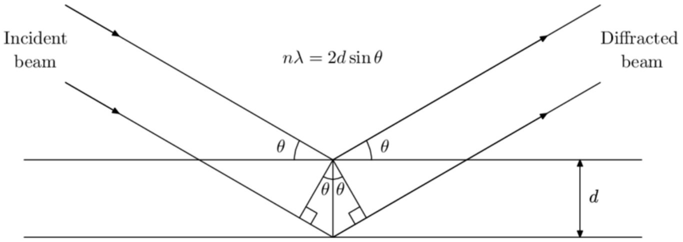

Figure 4.2: Braggs-Law
Pic credit: High Throughput Software for Powder Diffraction and its Application to Heterogeneous Catalysis

When Bragg's law is satisfied, light affects phase and structure. Angles other than the Bragg angle are out of phase and reflect damage. Bragg's law tightly governs the angles at which reflection occurs.

4.2 PXRD

Powder X-ray diffraction (PXRD) is a technique used to analyze the structure of crystalline materials.It operates the assumption that the sample is randomly arranged. In PXRD, the 3D information is converted to 1D.In powder X-ray diffraction, the diffraction pattern is obtained from a powder of the material, rather than an individual crystal. Powder diffraction is often easier and more convenient than single crystal diffraction since it does not require individual crystals be made. Powder X-ray diffraction (XRD) also obtains a diffraction pattern for the bulk material of a crystalline solid, rather than of a single crystal, which doesn't necessarily represent the overall material. A diffraction pattern plots intensity against the angle of the detector, 2θ.

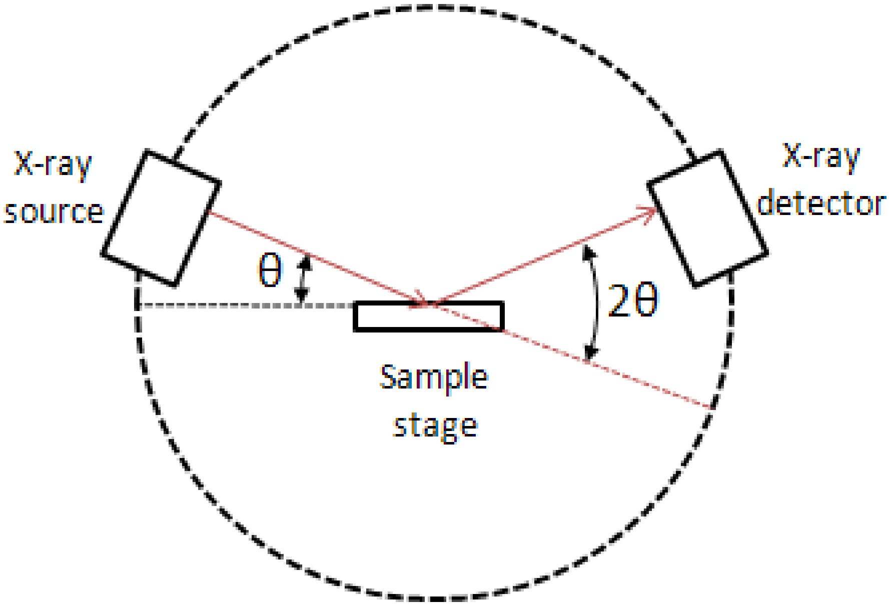

Figure 4.3: Representation of Pxrd setup
Pic credit: Analytical Chemistry/Supplemental Modules Analytical Chemistry Instrumentation and Analysis/Diffraction Scattering Techniques Powder X-ray Diffraction

4.3 PXRD Diffractrometer

Pxrd has following components

1] Source: The source is X-Ray source. High energy electrons are produced from heated tungsten filament and this is allowed to impinge on small metal target example Copper in a sealed diffraction tube.

2] Collimator: X-rays are generated by target material and then it passes through the collimator. It consists of two metal plates close together and separated by a small distance. The collimator absorbs all X-rays except the narrow beam passing through it.

3]Monochromators: Monochromators separate polychromatic light into a range of individual wavelengths. Graphite Monochromator is used in Rigaku SmartLab X-ray diffractometer. The graphite monochromator optimizes sensitivity by lowering the background level. It improves signal-to-noise by eliminating fluorescence from Co, Ni, Fe, Mn containing materials.

4]Filters: Filters absorb undesirable radiations but allow the radiation of desired wavelength to pass. Example nickel filter is used to remove K radiations of copper. These filters are used as an alternative to monochromators.

5]Detector:A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor.

4.4 Advantages of Using PXRD

1] Used in lattice parameter and structure determination.
2] Polymorphisim study.
3] Thin film thickness,orientation, material density.
4] Phase quantification(to find the relative percent of amounts in given sample).
5] Phase identification (to find chemical composition in given sample).
6] PXRD allows analysis without damaging the sample.
7] PXRD experiments can be performed relatively quickly, allowing efficient characterization.
8] XRD experiments can be performed relatively quickly, allowing efficient characterization.

4.5 Limitations of Using PXRD

1] Not applicable for gases and liquid due to lack of periodicity.
2] Locating the position of hydrogen is very difficult.
3] Not applicable for locating light atoms in presence of heavy atom.
4] Bond lengths determined by X- Ray method is not always correct for lighter elements.
5] High sample purity is required.
6] PXRD data contains overlapping reflections from broad peaks.
7] The instruments used for PXRD is expensive, which might limit its use in some cases.

4.5.1 Criteria for good X-Ray data

1] Peak to noise ratio should be high .
2] Number of peaks.
3] Using well aligned diffractometers.

4.5.2 Example of PXRD graph

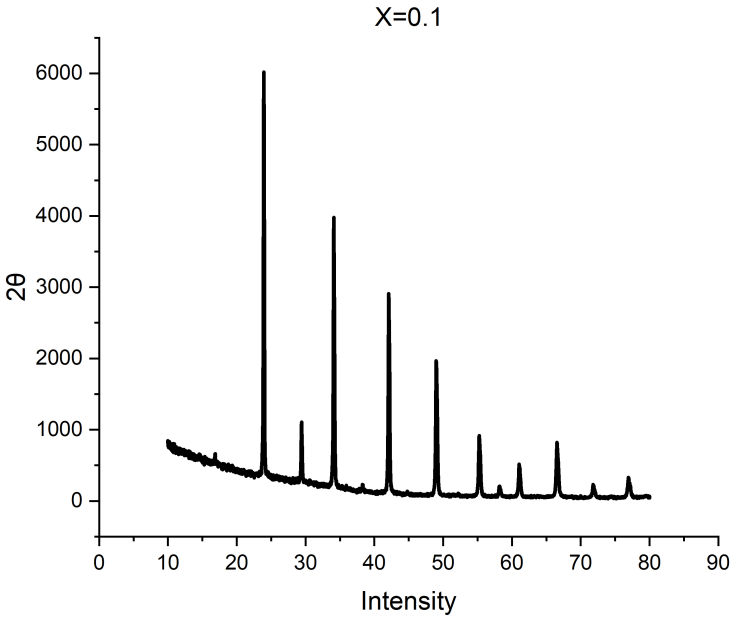

Figure 4.4: Graph of $Cs_2AgIn_{(1-x)}Bi_xCl_6$

Figure 4.5: PXRD setup of Goa University

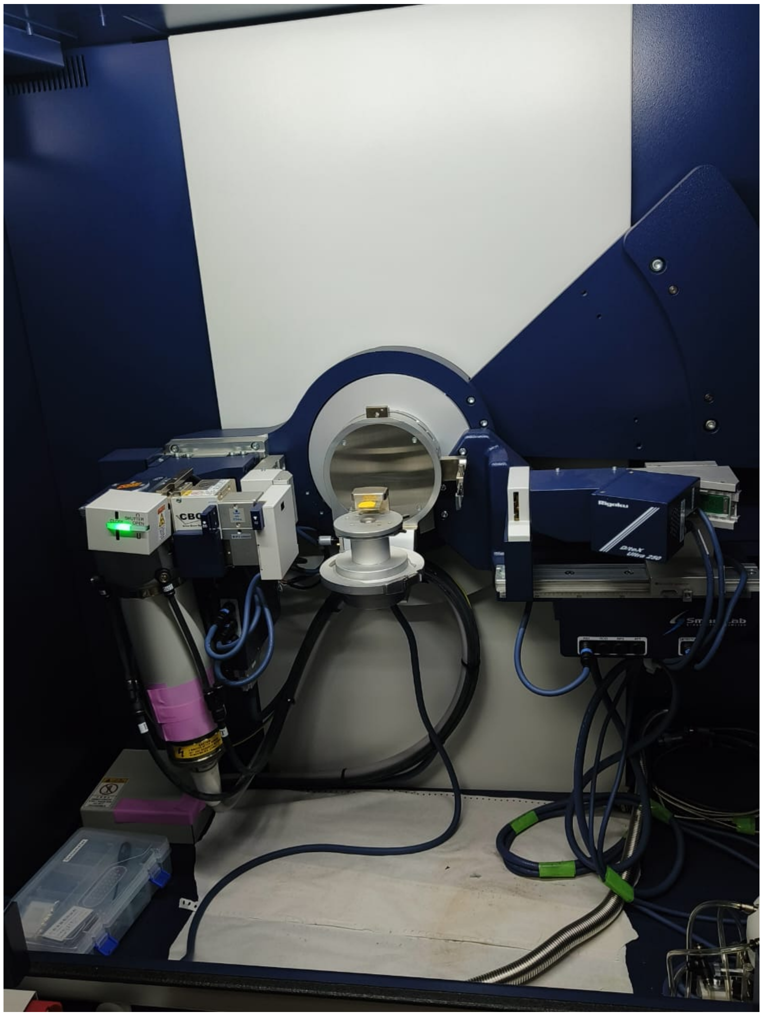

Figure 4.6: Rigaku Smart Lab Powder X-ray diffractometer

4.6 UV Spectroscopy

UV-visible spectroscopy involves measuring the absorption or transmission of energy in the ultraviolet region and visible region of the electromagnetic spectrum. UV-visible spectroscopy is an analytical technique used to measure the amount of ultraviolet or visible light of different wavelengths absorbed or transmitted by a sample compared to a reference or white sample contamination. This device is affected by the composition of the sample and can provide information about the composition and concentration in the sample. The principle behind UV spectroscopy is the absorption of visible and UV radiation (200-400 nm); This involves the activation of electrons in atoms and molecules from lower to higher levels. Since the energy level of matter is quantized, only light that has clean energy that causes a transition from one energy level to another will be absorbed . UV spectrophotometric based on the principles of additivity and absorbance, data and mathematics to realize the absorption process of the sample solution and the same or different sample solution.[3]

Light has a certain energy that is inversely proportional to its wavelength. Therefore, short wavelength light has more energy, while long wavelength light has less energy. A certain amount of energy is needed to bring the electrons in the material to a higher energy state that we can detect as absorption. Electrons in different bonding environments in an object require different specific energies to induce the electrons to reach higher energies. Therefore, different materials absorb different wavelengths of light. Humans can see visible light from approximately 380 nm (the color we see red) to 780 nm (the color we see red). Thus, light can be described by wavelength, which can be used in UV visibility spectroscopy to analyze or identify different substances by finding specific wavelengths corresponding to maximum absorbance.[20]

4.7 How does a UV-Vis spectrophotometer work?

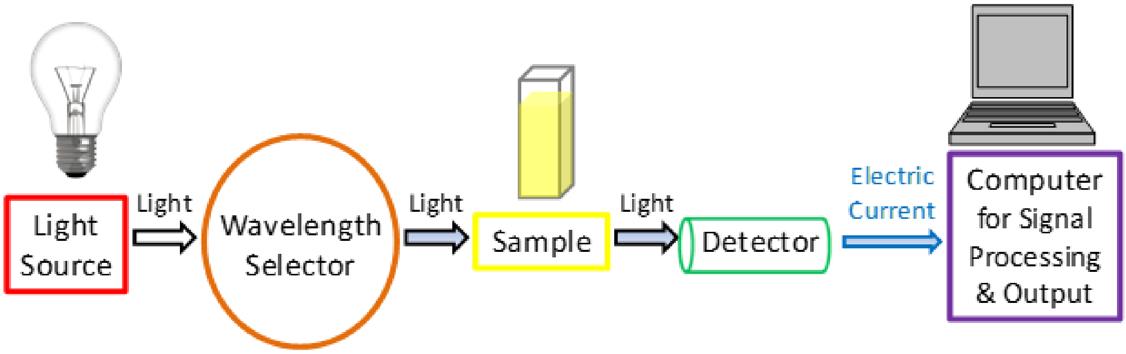

Figure 4.7: schematic of the main components in a UV-Vis spectrophotometer.
Credit: Dr. Justin Tom.

1]**Light Source**: As a light-based technology, a fixed light source that can emit light of different wavelengths is important. The same xenon lamp is often used as a high energy source in the ultraviolet and visible range. However, xenon lamps are more expensive and less stable than tungsten and halogen lamps. 2 Deuterium light is a form of UV light. In practice, this change usually occurs in tests between 300 and 350 nm, where the light emission from the two sources is similar and allows easy conversion.

2]**Wavelength selection**: In the next step, light of specific wavelengths suitable for the sample type and the presence of the analyte should be selected for sample analysis from the wide wavelength emitted by the light source.

3]**Monochromator**: A monochromator separates light into narrow wavelength bands. It is usually based on a diffraction grating that can be rotated to select the angle of incidence and reflection and hence the desired light. The higher frequency groove provides better resolution but a narrower range of usable wavelengths. Lower frequency provides a greater usable length but poorer resolution. For UV visibility spectroscopy purposes, 300 to 2000 grooves per millimeter can be used, but generally at least 1200 grooves per millimeter are required. The advantage of spectral measurement is that it is sensitive to physical defects in the diffraction grating and optical light. Therefore, notched diffraction gratings will have more defects than flame holographic diffraction gratings.

4]**Absorption filters** : Absorption filters are commonly made of colored glass or plastic designed to absorb particular wavelengths of light.

5]**Cutoff filters**: Cutoff filters allow light either below (shortpass) or above (longpass) a certain wavelength to pass through. These are commonly implemented using interference filters.

6]**Bandpass filters** :Bandpass filters allow a range of wavelengths to pass through that can be implemented by combining shortpass and longpass filters together.

Sample Analysis: Regardless of where the wavelength selector is used in the spectrophotometer, light passes through the sample. For each test, a reference sample (often called a ”blank”) must be measured; that is, a cuvette containing the same solvent used to prepare the sample. If the measurement is performed using a buffered aqueous solution containing the sample, use a buffered aqueous solution that does not contain the substance of interest as a reference. Sterile medium will be used as a reference when testing for bacterial infections. The device then automatically uses the reference signal to help obtain the correct absorbance value of the device. For example, most plastic cuvettes are not suitable for studying UV absorption because most plastics absorb UV light. Glass generally acts as a filter, absorbing most of UVC (100–280 nm)2 and UVB (280–315 nm)2 but allowing some UVA (315–400 nm)2 to pass through. Therefore UV analysis requires a quartz standard because quartz is transparent to most UV light. Air can also be considered a filter because light wavelengths shorter than 200 nm are absorbed by molecular oxygen in the air. Measurements at wavelengths shorter than 200 nm often require specialized and more expensive setups, including optical systems equipped with pure argon gas.

Detection: After the light has passed through the sample, a detector is used to convert the light into a readable electronic signal. Generally, detectors are based on photoelectric coatings or semiconductors. Photoelectric coatings emit negatively charged electrons when exposed to light. When electrons are ejected, an electric current is produced that is proportional to the intensity of the light. Photomultiplier tube (PMT) is one of the most widely used equipment in UV-visible spectroscopy. When a semiconductor is exposed to light, it will pass an electric current proportional to the intensity of the light. In particular, photodiodes and charge-coupled devices (CCD) are the two most widely used devices based on semiconductor technology and when the signal is detected the output is connected to computer screen.[20]

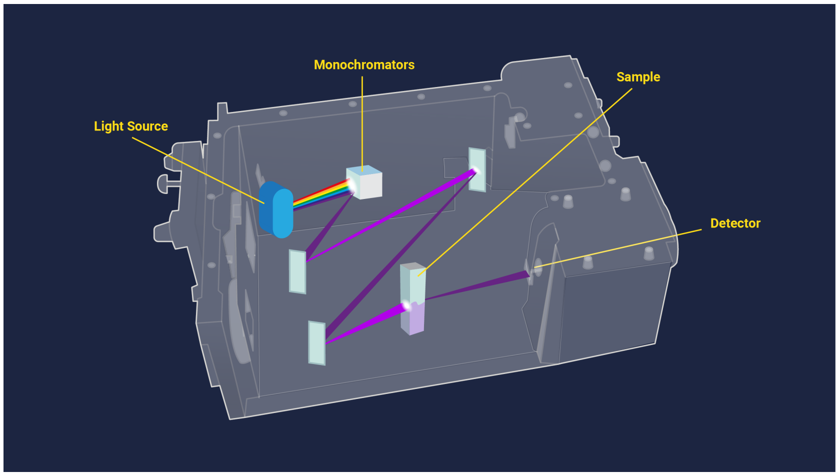

Figure 4.8: Schematic diagram of a cuvette-based UV-Vis spectroscopy system.
Credit: Technology Networks

Figure 4.9: UV Spectroscopy setup at Goa University

4.8 Principle

A compound appears coloured if it selectively absorbs light from the visible region. The absorbed energy raises the molecule from ground energy state (E0) to higher excited energy state (E1).

$$E = E1 - E0 = h\nu = hc/\lambda \tag{4.2}$$

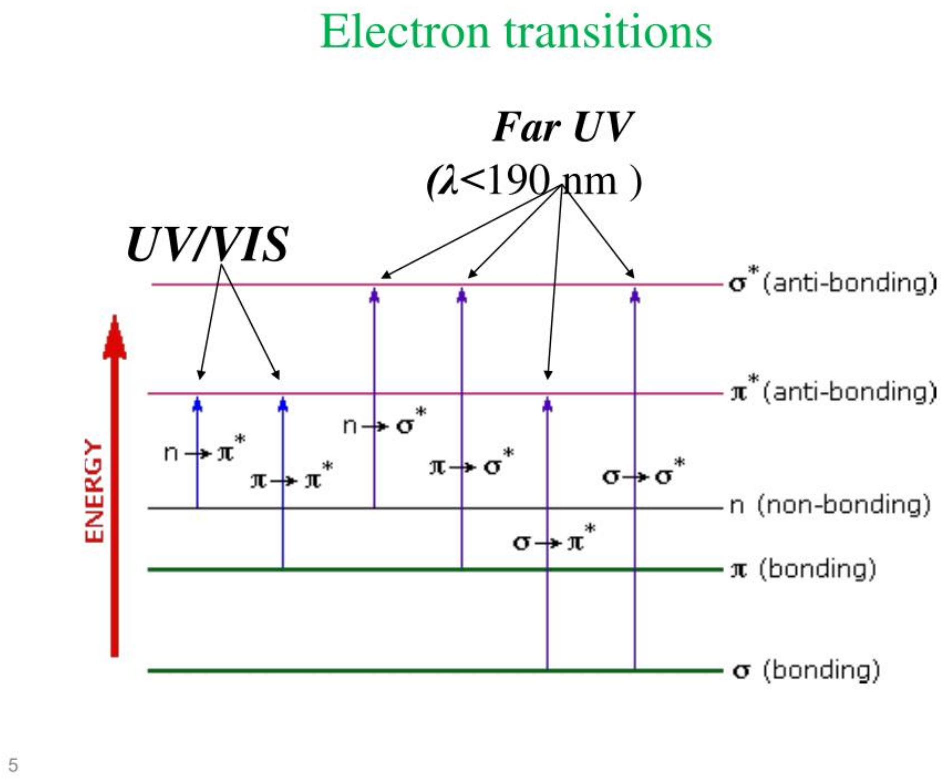

Figure 4.10: Electronic transitions in UV-Visible spectroscopy
Pic Credit:Slideshare

There are four types of ground state orbitals in molecules:

- Sigma to Sigma Star Transition ($\sigma \rightarrow \sigma *$)

A transition of an electron from a bonding sigma orbital to a higher energy antibonding sigma orbital.Alkenes are showing this type of transition.

- n to sigma star transition (n $\rightarrow \sigma *$)

n to sigma star transition involves saturated compounds with one hetero atom like oxygen, nitrogen, fluorine, chlorine, etc. Normally, saturated halides, alcohols, ethers, aldehydes, ketones, and amines participate in this type of transition..These transitions require comparatively less energy than the $\sigma \rightarrow \sigma * transition.$

- Pi to Pi Star Transition ($\pi \rightarrow \pi *$)

Pi to pi star transition in uv vis spectroscopy is available in compounds with unsaturated centers like unsaturated hydrocarbons and carbonyl compounds. It requires lesser energy than n to sigma star transition . In simple alkenes several transitions are available but the n $\rightarrow \pi * transitionrequiresthelowestenergy.$

- n to pi Star Transition (n $\rightarrow \pi*$)

In n to pi star transition , an electron in an unshared pair on a hetero atom is excited to $\pi*$ antibonding orbital. It involves the least amount of energy than all types of transition in ultraviolet visible spectroscopy. Therefore, the n $\rightarrow$ transition gives the absorption with a longer wavelength.

4.9 Beer-Lambert Law

The Beer-Lambert law is the most important law in spectroscopy and is necessary for accurate and quantitative interpretation of spectral data.The greatest and most understandable hope is that this is true; that is, it provides an accurate description of the effects of the interaction of light with matter. Therefore, change is often defined as a change in chemical interactions within the structure of the cell unit or a change in molecular structure. All these effects often lead to changes in the energy difference between electronic/vibrational states[11] Beer–Lambert's law is especially useful for obtaining the concentration of a substance if a linear relationship exists using a measured set of standard solutions containing the same substance. Equation 1 shows the mathematical relationships between absorbance, Beer–Lambert's law, the light intensities measured in the instrument, and transmittance Beer–Lambert's law is often applied to obtain the concentration of the sample (c) after measuring the absorbance (A) when the molar absorptivity (ϵ) and the path length (l) are known. Typically, is expressed with units of L mol-1cm-1, L has units of cm, and c is expressed with units of mol-1. As a consequence, A has no units.[20]

$$A = \epsilon \cdot l \cdot c \tag{4.3}$$

Transmittance (T) is given by :

$$T = \frac{I}{Io} \tag{4.4}$$

Where I is intensity of incident light and Io is the intensity of light detected and absorbance is the inverse of transmittance given by

$$A = \log(1T) = \log(\frac{I}{Io}) = \epsilon \cdot c \cdot l \tag{4.5}$$

4.10 Strengths and limitations of UV-Vis spectroscopy

The Strenghts of the UV-spectroscopy are

- The technique is non-destructive, allowing the sample to be reused or proceed to further processing or analyses.
- Measurements can be made quickly, allowing easy integration into experimental protocols.
- Instruments are easy to use, requiring little user training prior to use.
- Data analysis generally requires minimal processing, again meaning little user training is required.
- The instrument is generally inexpensive to acquire and operate, making it accessible for many laboratories.

Although the advantages of this process seems promising, it has some disadvantages:

- **Stray light** - In a real instrument, wavelength selectors are not perfect and a small amount of light from a wide wavelength range may still be transmitted from the light source, possibly causing serious measurement errors. Stray light may also come from the environment or a loosely fitted compartment in the instrument.
- **Light scattering** - Light scattering is often caused by suspended solids in liquid samples, which may cause serious measurement errors. The presence of bubbles in the cuvette or sample will scatter light, resulting in irreproducible results.
- **Interference from multiple absorbing species** - A sample may, for example, have multiple types of the green pigment chlorophyll. The different chlorophylls will have overlapping spectra when examined together in the same sample. For a proper quantitative analysis, each chemical species should be separated from the sample and examined individually.
- **Geometrical considerations** - Misaligned positioning of any one of the instrument's components, especially the cuvette holding the sample, may yield irreproducible and inaccurate results. Therefore, it is important that every component in the instrument is aligned in the same orientation and is placed in the same position for every measurement. [20]

4.11 Applications of UV-Vis spectroscopy

- **DNA and RNA analysis**: Quickly verifying the purity and concentration of RNA and DNA
- **Pharmaceutical analysis**: One of the most common uses of UV-Vis spectroscopy is in the pharmaceuticals industry.In particular, processing UV-Vis spectra using mathematical derivatives allows overlapping absorbance peaks in the original spectra to be resolved to identify individual pharmaceutical compounds.
- B**acterial culture**: UV-Vis spectroscopy is often used in bacterial culturing. OD measurements are routinely and quickly taken using a wavelength of 600 nm to estimate the cell concentration and to track growth.
- **Beverage analysis**: The identification of particular compounds in drinks is another common application of UV-Vis spectroscopy. Caffeine content must be within certain legal limits, for which UV light can facilitate quantification. Certain classes of colored substances, such as anthocyanin found in blueberries, raspberries, blackberries, and cherries, are easily identified by matching their known peak absorbance wavelengths in wine for quality control using UV-Vis absorbance.
- **Other applications**: This technique may also be used in many other industries. For example, measuring a color index is useful for monitoring transformer oil as a preventative measure to ensure electric power is being delivered safely. Measuring the absorbance of hemoglobin to determine hemoglobin concentrations may be used in cancer research.In wastewater treatments, UV-Vis spectroscopy can be used in kinetic and monitoring studies to ensure certain dyes or dye by-products have been removed properly by comparing their spectra over time. It also finds great utility in food authenticity analysis and air quality monitoring.[20]

4.12 Scanning Electron Microscope

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. Unlike optical microscopes, which use visible light, SEM utilizes electrons to interact with atoms in the sample.(Ref: wikipedia.org) The scanning electron microscopes developed by McMullan have now been used for many years and have gained enough experience to allow the field to evaluate the potential of using this tool. [17] In the electron microscope, electrons are accelerated to high energies, between 2 and 1000 keV. There are many possible interactions between the high-energy electron beam and the atoms in specimen.If the specimen is very thin, then electrons may be transmitted through it unabsorbed and used to form the image in TEM. If the specimen is thicker, then electrons are no longer transmitted so only particles (e.g. electrons, x-rays and pho tons) emerging from the surface can give us information.These are the signals used in a conventional SEM.[22]

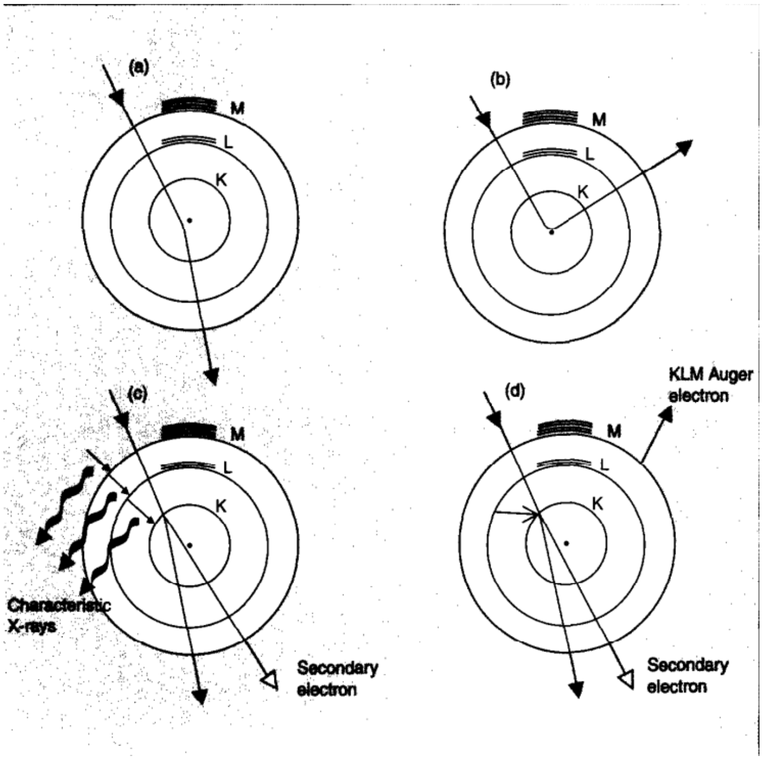

Figure 4.11: (a) Low-angle scattering - electrons scattered in this way pass to the next layer of atoms with very little loss of energy (b) Back (or high-angle) scattering; (c) Emission of a secondary electron and characteristic x-rays; (d) Emission of a secondary electron and an Auger electron.
pic credit:0961-1290/00/ 2000 Elsevier Science Ltd.

SEM can provide information on surface topography, crystalline structure, chemical composition and electrical behaviour of the top 1 urn or so of specimen. Various specialised stages (e.g. hot, cold or designed to permit in situ mechanical testing) can be attached to enable behaviour under various conditions to be examined. For example, cathodoluminescence (emission of light) at temperatures near absolute zero is much stronger than at room temperature, so images formed from the light emitted by a cold specimen are much less noisy.[22]

4.13 Working Principle

The Scanning electron microscope works on the principle of applying kinetic energy to produce signals on the interaction of the electrons. These electrons are secondary electrons, backscattered electrons, and diffracted backscattered electrons which are used to view crystallized elements and photons. Secondary and backscattered electrons are used to produce an image. The secondary electrons are emitted from the specimen play the primary role of detecting the morphology and topography of the specimen while the backscattered electrons show contrast in the composition of the elements of the specimen.

4.13.1 How SEM works?

The source of the electrons and the electromagnetic lenses are from tungsten filament lamps that are placed at the top of the column and it is similar to those of the transmission electron Microscope. The electrons are emitted after thermal energy is applied to the electron source and allowed to move in a fast motion to the anode, which has a positive charge.

The beam of electrons activates the emission of primary scattered (Primary) electrons at high energy levels and secondary electrons at low-energy levels from the specimen surface. The beam of electrons interacts with the specimen to produce signals that give information about the surface topography and composition of the specimen.

The specimen does not need special treatment for visualization under the SEM, even air-dried samples can be examined directly. However, microbial specimens need fixation, dehydration, and drying in order to maintain the structural features of the cells and to prevent collapsing of the cells when exposed to the high vacuum of the microscope.

The samples are mounted and coated with thin layer of heavy metal elements to allow spatial scattering of electric charges on the surface of the specimen allowing better image production, with high clarity. Scanning by this microscope is attained by tapering a beam of electrons back and forth over a thin section of the microscope. When the electrons reach the specimen, the surface releases a tiny staw of electrons known as secondary electrons which are then trapped by a special detector apparatus.

When the secondary electrons reach and enter the detector, they strike a scintillator (a luminescence material that fluoresces when struck by a charged particle or high-energy photon). This emits flashes of light which get converted into an electric current by a photomultiplier, sending a signal to the cathode ray tube. This produces an image that looks like a television picture that can be viewed and photographed. The quantity of secondary electrons that enter the detector is highly defined by the nature of the specimen i.e raised surfaces to receive high quantities of electrons, entering the detector while depressed surfaces have fewer electrons reaching the surface and hence fewer electrons enter the detector. Therefore raised surfaces will appear brighter on the screen while depressed surfaces appear darker. [12]

4.13.2 Parts of a Scanning Electron Microscope (SEM)

1]Electron Source – This is where electrons are produced under thermal heat at a voltage of 1-40kV. the electrons condense into a beam that is used for the creation of an image and analysis. There are three types of electron sources that can be used i. e Tungsten filament, Lanthanum hexaboride, and Field emission gun (FEG)

2]Lenses – it has several condenser lenses that focus the beam of electrons from the source through the column forming a narrow beam of electrons that form a spot called a spot size.

3]Scanning Coil – they are used to deflect the beam over the specimen surface.

4]Detector – It's made up of several detectors that are able to differentiate the secondary electrons, backscattered electrons, and diffracted backscattered electrons. The functioning of the detectors highly depends on the voltage speed, the density of the specimen.

5]The display device (data output devices).

6]Power supply.

7]Vacuum system.

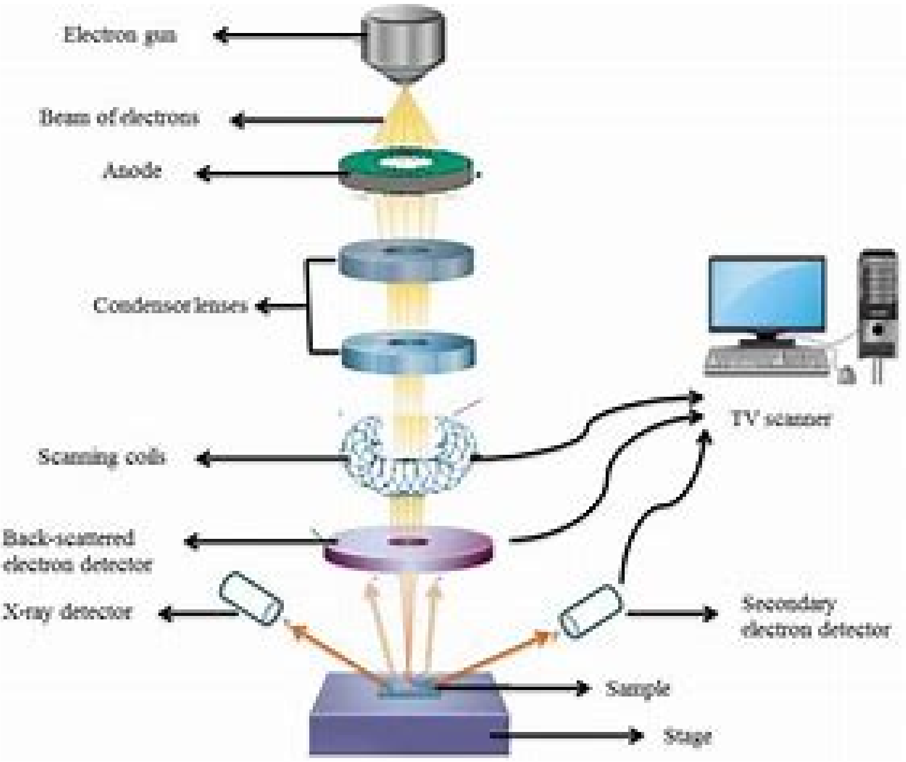

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Figure 4.12: Working Principle of SEM
PIC CREDIT: Working-principle-of-scanning-electron-microscopy

4.14 Applications of the Scanning Electron Microscope (SEM)

1]Used for spot chemical analysis in energy-Dispersive X-ray Spectroscopy.
2]Used in the analysis of cosmetic components which are very tiny in size.
3]Used to study the filament structures of microorganisms.
4]Used to study the topography of elements used in industries.

4.15 Advantages of the Scanning Electron Microscope (SEM)

1]They are easy to operate and have user-friendly interfaces.
2]They are used in a variety of industrial applications to analyze surfaces of solid objects.
3]Some modern SEMs are able to generate digital data that can be portable.
4]It is easy to acquire data from the SEM, within a short period of time of about 5 minutes.

4.16 Limitations of SEM

1]They are very expensive to purchase.
2]They are bulky to carry.
3]They must be used in rooms that are free of vibrations and free of electromagnetic elements.
4]They must be maintained with a consistent voltage.
5]They should be maintained with access to cooling systems.

Figure 4.13: SEM setup at Goa University

Chapter 5

Results and Discussions

5.0.1 PXRD Analysis

The PXRD data was collected on the prepared ground sample with 2θ varying from 10^o to 80^o with a step size of 0.02^o using Copper $K\alpha$ radiation of wavelength 1.5408 Å on the Rigaku SmartLab X-Ray Diffractometer. The collected Data was subjected to the Profile matching using FullProf software. The Profile matching was carried out on the PXRD data indicate that all 6 as-prepared samples have a cubic structure belonging to the Fm-3m space group as reported in[10].[8]

The graphs of all five compounds was plotted in Origin pro software.

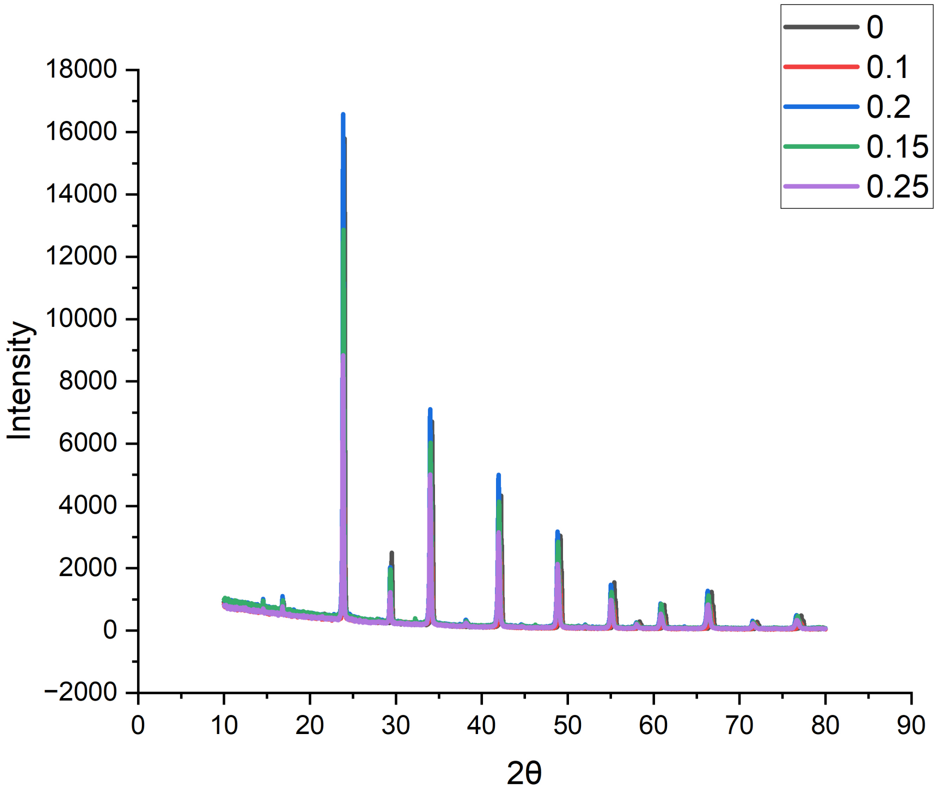

Figure 5.1: PXRD Of All Samples Plotted At same time

After plotting some part of the graph was zoomed to see the trend(whether it is shifting towwards right side or left

$Cs_2AgIn_{(1-x)}Bi_xCl_6$	X=0	X=0.1	X=0.15	X=0.2	X=0.25
Lattice parameter Å	10.4770	10.5031	10.5350	10.5444	10.5483
Unit Cell Volume $\AA^3$	1150.06	1158.65	1169.25	1172.40	1173.67

Table 5.1: Lattice parameters of $Cs_2AgIn_{(1-x)}Bi_xCl_6$

side)....

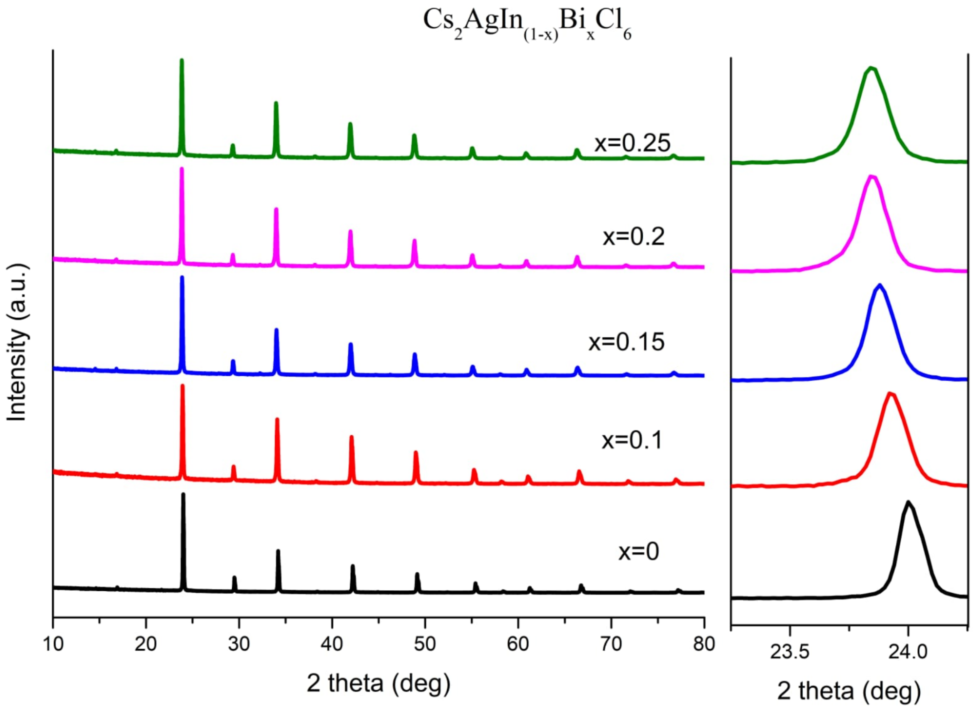

Figure 5.2: X ray Diffraction Patterns of as prepared $Cs_2AgIn_{(1-x)}Bi_xCl_6$

It was seen that as the concentration of doping was increasing the peaks were shifting to left side i.e the bond length was increasing.

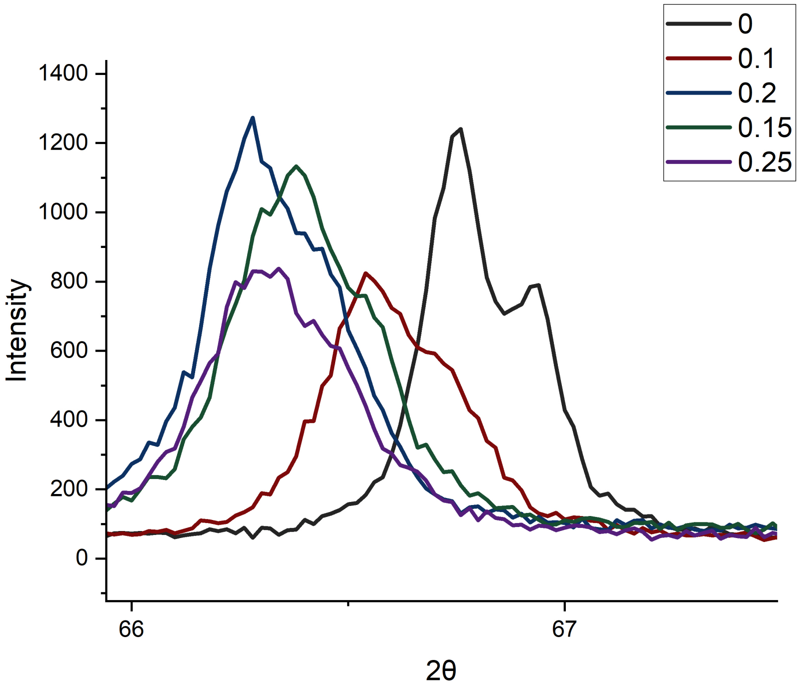

Figure 5.3: Zoomed view of part of graph

5.1 Profile Matching

Profile Matching is used as an alternative to the Rietveld method when the crystal structure of the material is not known. Parameters related to scale factor,peak shape,background are refined to match observed and calculated intensities but their atomic positions and chemical composition are not considered to minimize the difference between observed and calculated peaks.This method is known as profile matching.

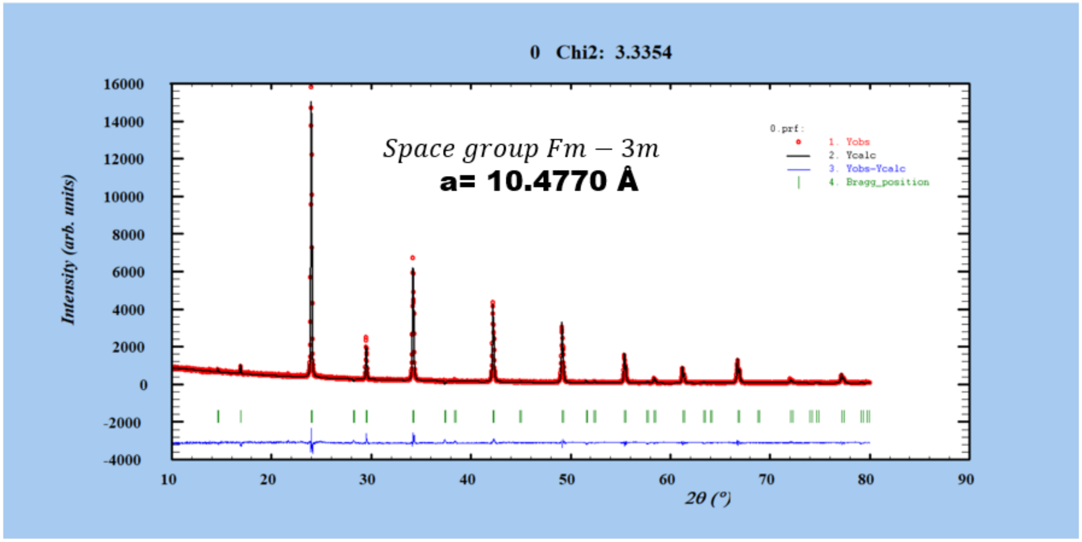

Figure 5.4: Profile Matching of X=0
Bragg R-Factor=1.316
RF-factor=1.910

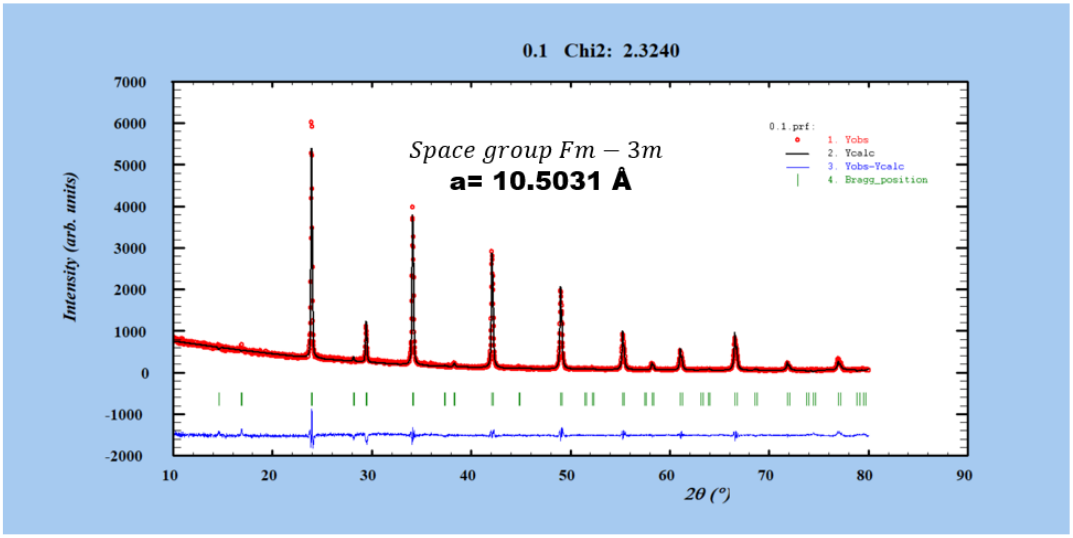

Figure 5.5: Profile Matching of X=0.1
Bragg R-Factor=1.090
RF-factor=1.910

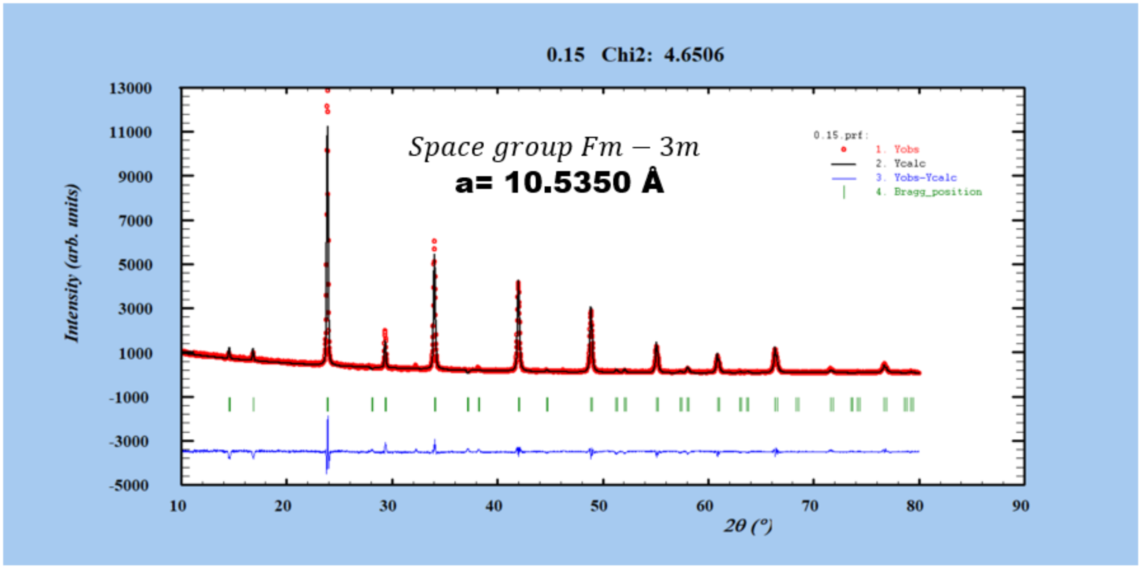

Figure 5.6: Profile Matching of X=0.15
Bragg R-Factor=0.9883
RF-factor=1.766

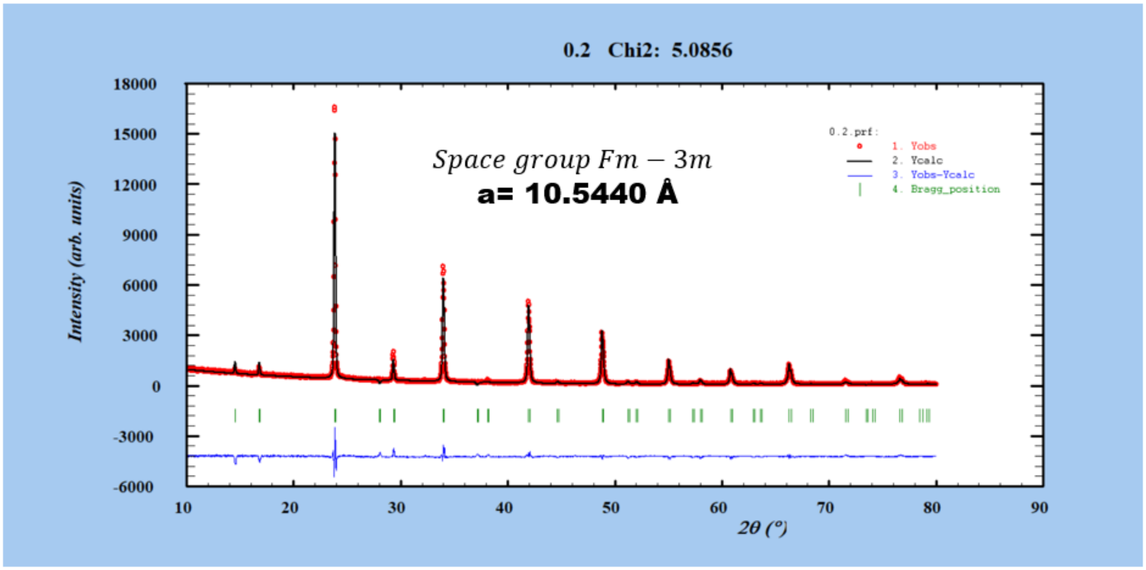

Figure 5.7: Profile Matching of X=0.2
Bragg R-Factor=1.147
RF-factor=1.856

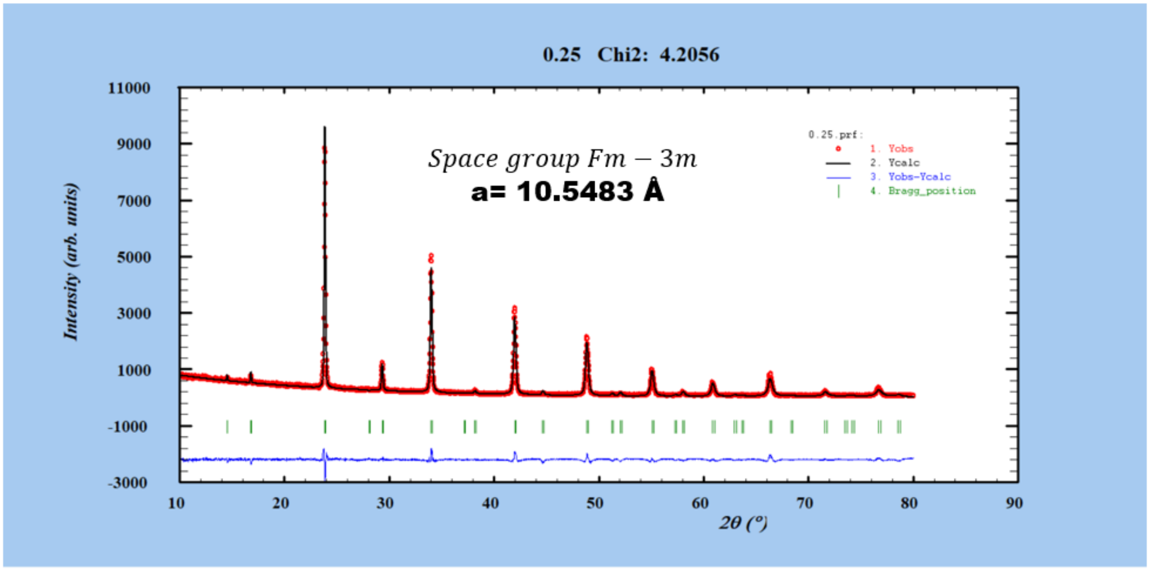

Figure 5.8: Profile Matching of X=0.25
Bragg R-Factor=0.9776
RF-factor=1.258

5.2 Morphology Study (Scanning Electron Microscopy)

SEM images of synthesized $Cs_2AgIn_{(1-x)}Bi_xCl_6$ were taken using Zeiss Scanning Electron Microscope. SEM was performed and we can see the particle formed with similar morphology and uniform size.

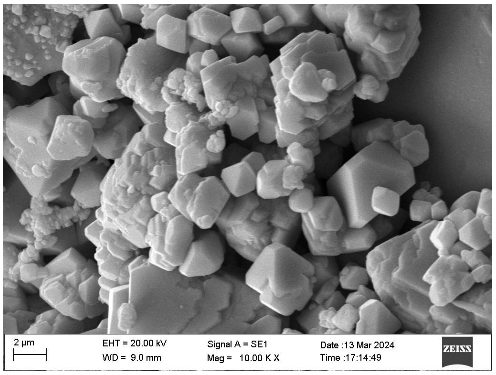

Figure 5.9: SEM image of $Cs_2AgIn_{(1-x)}Bi_xCl_6$ for X=0

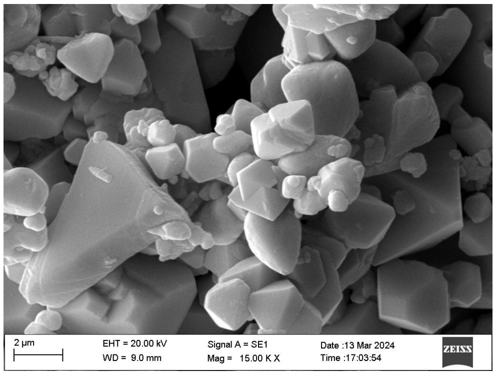

Figure 5.10: SEM image of $Cs_2AgIn_{(1-x)}Bi_xCl_6$ for X=0

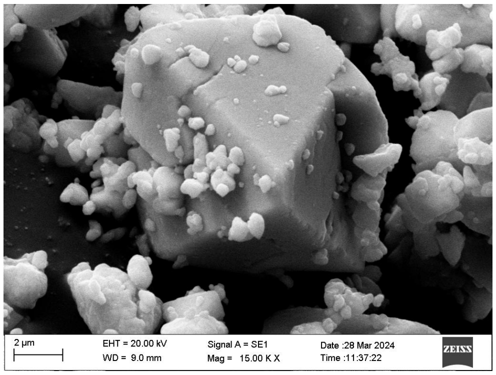

Figure 5.11: SEM image of $Cs_2AgIn_{(1-x)}Bi_xCl_6$ for X=0.15

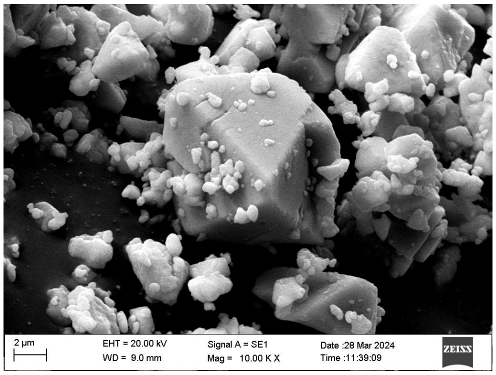

Figure 5.12: SEM image of $Cs_2AgIn_{(1-x)}Bi_xCl_6$ for X=0.15

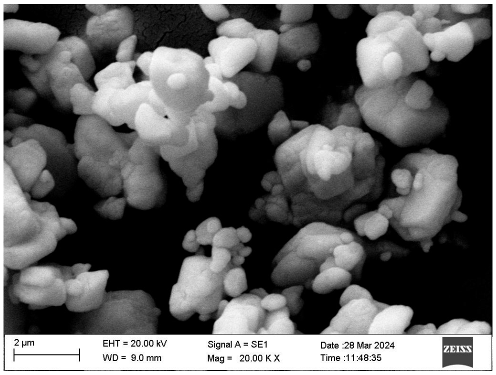

Figure 5.13: SEM image of $Cs_2AgIn_{(1-x)}Bi_xCl_6$ for X=0.2

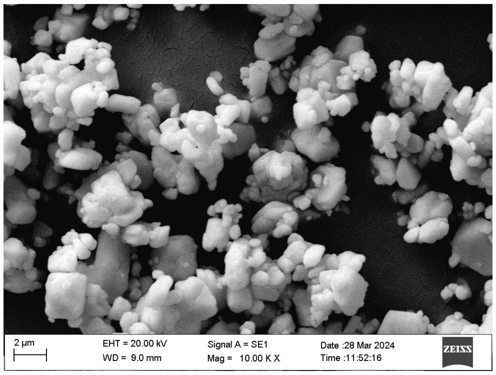

Figure 5.14: SEM image of $Cs_2AgIn_{(1-x)}Bi_xCl_6$ for X=0.2

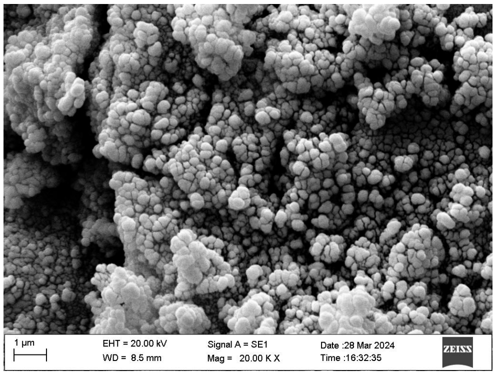

Figure 5.15: SEM image of $Cs_2AgIn_{(1-x)}Bi_xCl_6$ for X=0.25

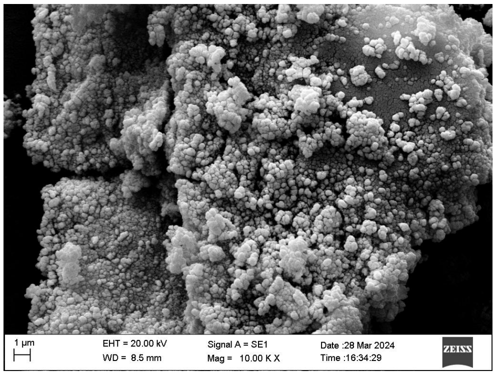

Figure 5.16: SEM image of $Cs_2AgIn_{(1-x)}Bi_xCl_6$ for X=0.25

5.3 Photocatalysis

The primary aim of the project was to test the prepared samples for photocatalytic applications. Methyl Orange was chosen for the photo-degradation experiment.The experiment was carried out in Lelesil UV-Vis Photochemical Reactor consisting of a 250W UV Lamp with a predominant wavelength of 280 nm. To prepare the dye solution 5mg of dye was dissolved in 50ml of solvent which was further diluted 10 times to get 10mg/L solution. The Methyl Orange solution was prepared in ethanol.5ml of dye solution was taken in 45 ml ethanol and 25 mg of compound was added in this solution and stirred for 1 hour in the dark to reach adsorption desorption equilibrium before turning on the UV Lamp. 3ml of this solution was taken out in a quartz cuvette using a syringe and absorbance spectra was recorded from 300nm to 600nm on Shimadzu UV-Vis Spectrophotometer.After turning UV lamp on the readings were taken in the interval of 10 min/20 min. This experiment was carried out for x=0,0.1,0.15,0.20,0.25 for $Cs_2AgIn_{(1-x)}Bi_xCl_6$.

Figure 5.17: Photocatalysis setup at Goa University

The characteristic absorption peak for methyl orange exists at 418 nm.

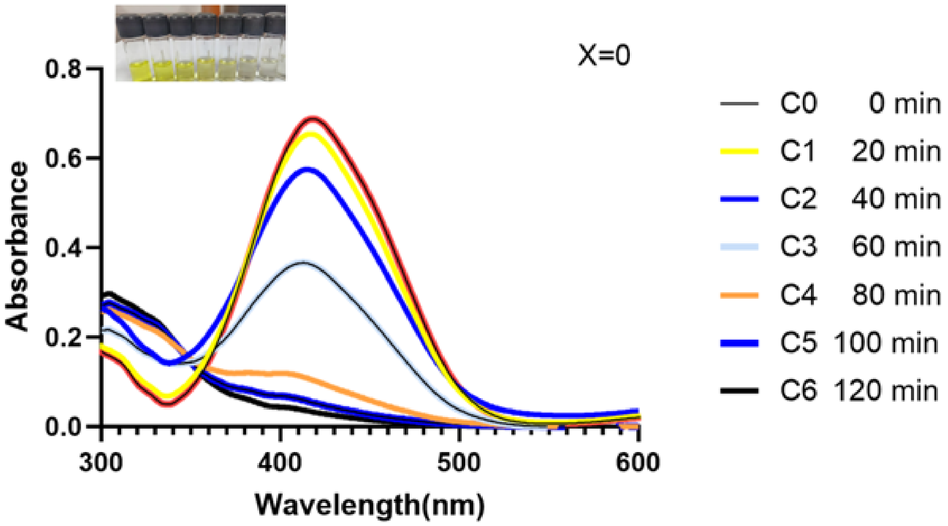

Figure 5.18: UV–Vis absorption spectra for Methyl Orange For X=0

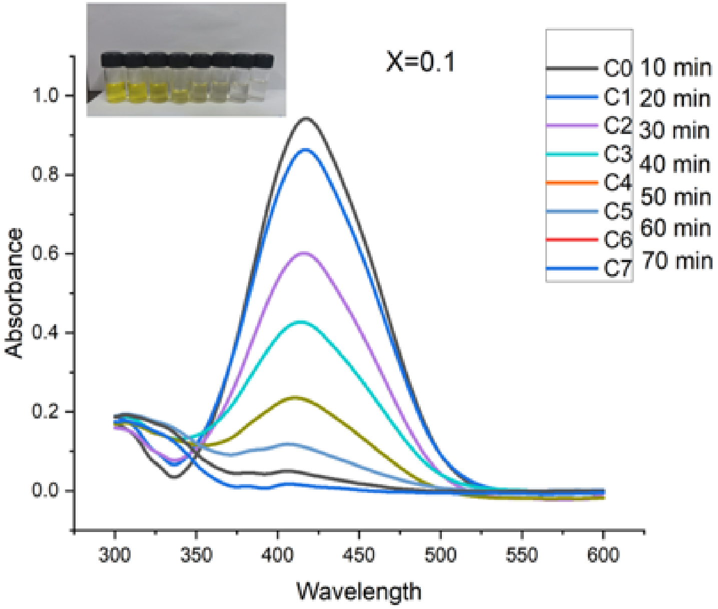

Figure 5.19: UV–Vis absorption spectra for Methyl Orange For X=0.1

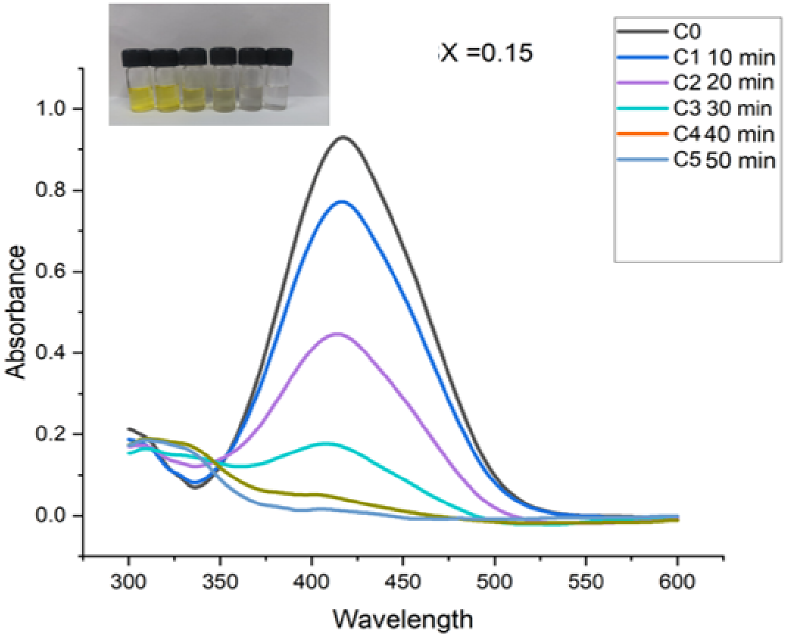

Figure 5.20: UV–Vis absorption spectra for Methyl Orange For X=0.15

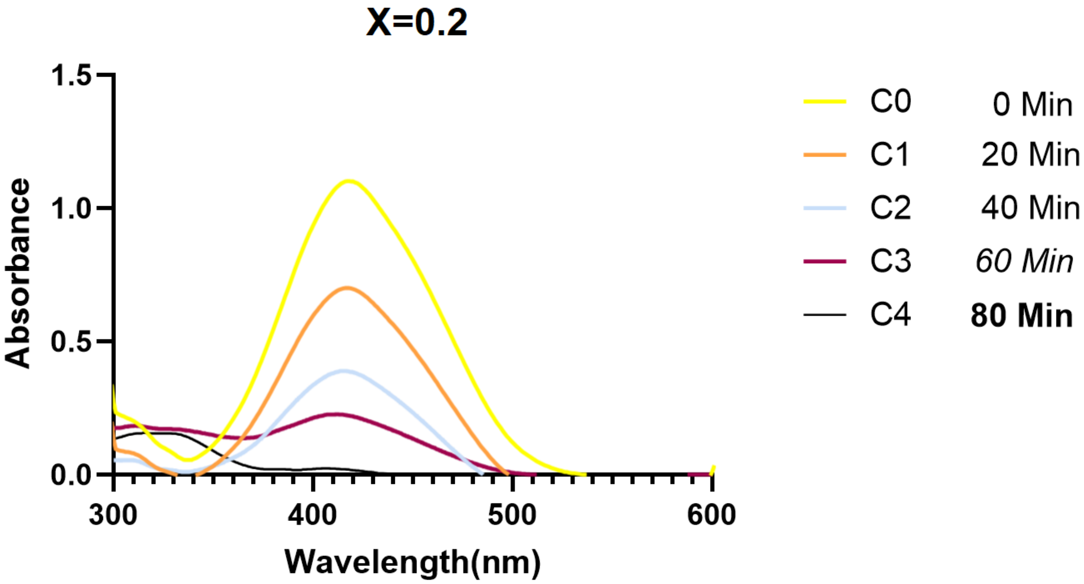

Figure 5.21: UV–Vis absorption spectra for Methyl Orange For X=0.2

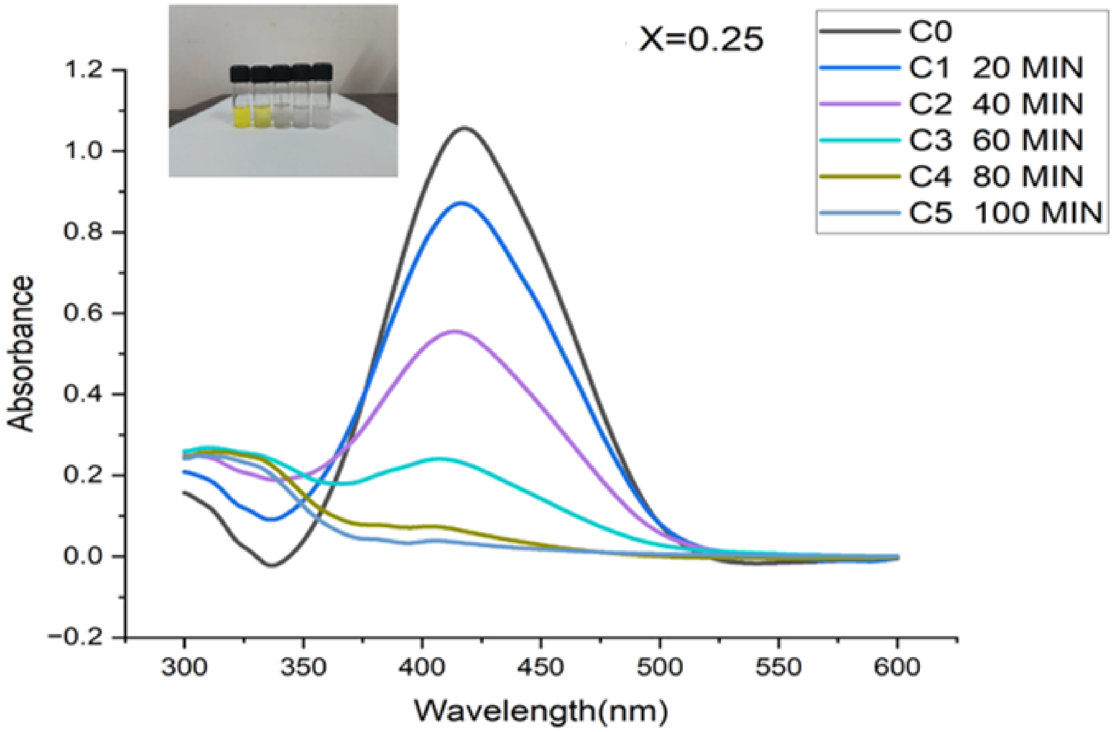

Figure 5.22: UV–Vis absorption spectra for Methyl Orange For X=0.25

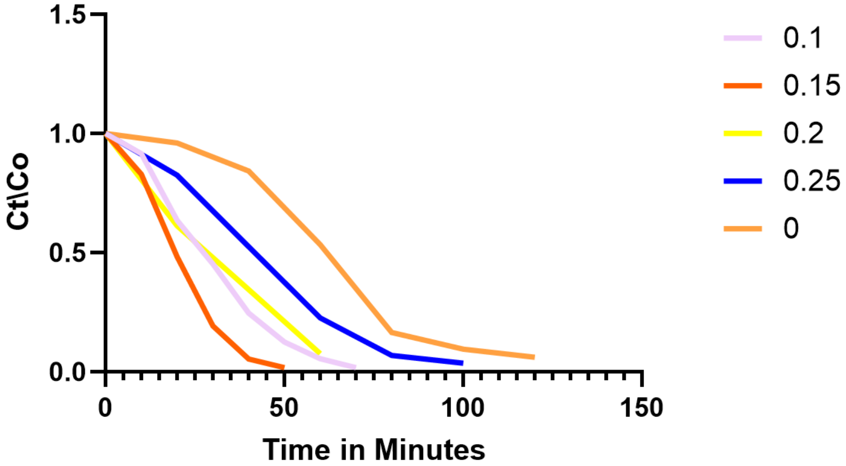

Figure 5.23: Plots of Ct/Co vs the irradiation time for photocatalytic degradation of Methyl Orange in the presence $Cs_2AgIn_{(1-x)}Bi_xCl_6$

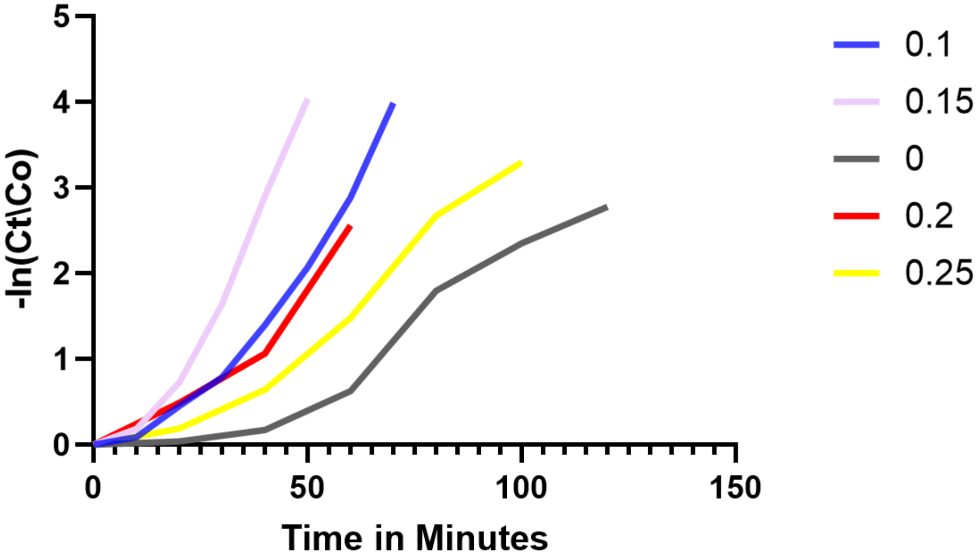

Figure 5.24: Kinetic Curves of photocatalytic degradation reaction of Methyl Orange in the presence $Cs_2AgIn_{(1-x)}Bi_xCl_6$

$Cs_2AgIn_{(1-x)}Bi_xCl_6$	X=0	X=0.1	X=0.15	X=0.2	X=0.25
Dye Degradation constant for Methyl orange	0.02604	0.05639	0.08359	0.04126	0.03539

Table 5.2: Dye Degradation value for different values of concentration

$Cs_2AgIn_{(1-x)}Bi_xCl_6$	X=0	X=0.1	X=0.15	X=0.2	X=0.25
Time taken to degrade methyl orange(in mins)	120	70	50	80	100

Table 5.3: Time taken to degrade methyl orange

It is observed that methyl orange degrades faster in the presence of $Cs_2AgIn_{(1-x)}Bi_xCl_6$ as the catalyst

From literature it is clear that $Cs_2AgBiBr_6$ takes 300 mins to degrade methyl orange , and $Cs_2AglnCl_6$ takes 60 mins to degrade...

And our compound $Cs_2AgIn_{(1-x)}Bi_xCl_6$ takes 100 min degrade methyl orange when x=0.25 and 120 min for x=0 and it takes 50 mins for x=0.1 and 0.15. So it shows good results for x=0.1 and x=0.15..

5.4 Summary

1.Powdered crystalline samples of $Cs_2AgIn_{(1-x)}Bi_xCl_6$ were prepared using time efficient and simple acid precipitation method.
2.The samples were subjected to Profile matchingusing Fullprof software.
3.The lattice parameter increases with increasing Bi concentration.
4.The samples exhibit good photocatalytic behavior and were able degrade Methyl orange efficiently in the presence of UV light.

5.5 Further Investigation

1.The photocatalytic experiments can be repeated and carried out for more dyes such as Methylene blue and Rhodamine B and for Sudan Red III .
2.Single crystals of the samples can be prepared to improve purity

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