



SEMICONDUCTING COPPER SULPHIDE GROWN CRYSTAL IN GEL AND ITS CHARACTERISATION.

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ABSTRACT

A crystal of copper sulphide have been grown by simple single diffusion gel technique A cubical bigger sized crystal were obtained for this alternative supernatants ,incorporating solutions its concentrations affects on growth of these crystals. Structural analysis optimum condition, infra radiations, gap,energy dispersive analysis were performed , spectrophotometer and diffract meter are used to obtain spectra for content determination and hkl calculation.

Key words: X-ray diffraction, FT-IR, UV-VIS spectrophotometer, Energy gap, gel technique, unit cell, EDAX.

I. INTRODUCTION:

In 1913 Liesgang was studying the growth of crystal in gel and he recorded he studied the formations of rings. Afterwards, mechanism of growth had been discussed extensively by many his coworkers, this work were accelerated by researchers still today. The growth of crystal in silica gel at an ambient temperature for the material, which is sparingly soluble in water, is an attractive alternative to the techniques involving high temperature. A variety of crystals required for the purpose of application can be grown in silica gel. During the last few years, a successful application of gel growth technique has been demonstrated by the preparation of crystals of alkaline earth metal sulphides. The gel growth technique appeared quite attractive for growing crystals of such compounds on account of its unique advantage in terms of crystals produced and the simplicity of the process. The crystals of sulphide exhibit non linear properties .A non linear optical phenomenon's are found to be a wide variety of applications in many areas of modern science engineering and technology. A variety of crystals for research and technology can be grown in silica gel. In this method almost complete suppression of large scale movement like convection is achieved which otherwise affects to the crystals perfection. The growing crystal are held in the gel in a strain free manner thus limiting effects due to impact of the bottom or the sides of the container which are used.

In gel method, the rate of diffusion of reactant can be controlled science, the gel are network of cavities of several tens to several thousand of angstroms in diameter, communicating through slightly smaller orifices .Gel technique is inexpensive and simple but quite attractive, The beauty and sparkle of many faced crystal found all over the earth's, the earth's crust have attracted mans interest in the history. Crystal has been treasured primarily because of their ornamental value. A new application for crystals has been discovered in solid state devices. The word of minerals provides many examples of crystals bounded by well developed plane faces which exhibit the point group symmetry of the crystal structure. According to Researchers similar faced on different crystal of the same mineral form identical angles. These angles are characteristics of each different kind of crystal. This law is the foundation of the science of crystallography.

It is also reported that sulphide are semiconductor in nature the synthesis of sulphide are complicated because of relative low vapour pressure of the sulphur ,neverth less successively more attention is being turns toward investigating sulphide of various materials .There is no need to explain the role of semiconductor in the development of present electronic industries and semiconductor device for

e.g. Zink sulphide (ZnS) used for lenses and other optical devices lead sulphide used in infra, red sensors ; cadmium sulphide [cds] which is used in photocell. Iodate, iodides and sulphide are taken it basic material copper, it is known that copper and its compounds has a wide spread use in a different range of application. It is used to make electrical products and electronics in electric generators and motors, electrical power and lighting fixture. Electrical wiring, chemical and pharmaceutical manufacturing, radio and television sets, computers air conditioning system and other electrical appliances in building construction .

In the present work, an attempt has been made to characterize gel grown crystals of copper Sulphide by X-ray diffractometry, infrared spectroscopy, Thermal analysis i.e.TGA and DSC, EDAX, Chemical Analysis, UV-VIS spectrophotometer. The results the observations have been described in this chapter.



II. EXPERIMENTAL PROCEDURE:

A copper sulphide crystal are grown using chemical reaction method. This method involves growing of copper sulphide crystals by allowing the reaction of two solutions of soluble salts by diffusion through a gel containing copper chloride and distilled water containing H_2S gas with subsequent nucleation and the crystal growth which continues due to the gradual precipitation of insoluble product.

Preparation of gel:

Initially different concentration solution of sodium Meta silicate taken for e.g. 10gm,12gm ,14 gm, 16 gm, 18 gm, 21gm, 22gm in distilled water to get 250cc solution. The solution is constantly stirred and then filtered by Dr Watts filter paper. It is then kept in to an airtight bottle free from dust and contamination. Density of the solution was measured using specific gravity bottle. A solution of different molarities prepared by adding proper amount of chemicals to the double distilled water for copper nitrate, copper chloride, Hydrogen sulphide gas, acetic acid and sodium meta silicate. A gel formation of mineral or organic acid takes place with a mixing of sodium meta silicate solution. It forms process of polymerization in the mixture of solution or resultant solution. In the present work, various concentration of acetic acid and those of sodium meta silicate were tried for optimum condition with different concentrations of Hydrogen Sulphide gas solution.

Single diffusion methods:

In the present research work, single diffusion method was used to obtain crystals of copper sulphide in gel medium. In actual procedure, 5cc of 2N acetic acid was taken in a small beaker, to which sodium Meta silicate solution of density 1.04 gm/cc was added drop wise from burette with constant stirring performed with the help of magnetic stirrer, till pH of the mixture reaches a value 4.4. A pH meter HANNA instrument of digital pocket sized is used for this purpose. A 5cc of copper chloride solution of concentration 0.4M was added with constant stirring in mixture of acetic acid and sodium meta silicate solution .A continuous stirring process required to avoids excessive ion concentration which otherwise causes premature local gelling and makes the final medium inhomogeneous and turbid .The pH of the mixture was maintained at 4.4 Number of attempts were tried for optimum condition for appropriate range of pH values and allowed gel to obtain crystals of copper sulphide.

The gel setting time required for the silica gel solution of pH greater than 4.5was short, it is observed that the mixture of solution with pH value less than 4.2 required quite greater number of days, however in the pH range 4.2 to 4.4 there is appropriate waiting in gelation time. Room temperature and atmospheric effect also plays an important role on gelation, aging that is evaporation of water molecules form on surface of gel. To perform these experiment borosil glass test tubes of diameter 2.5cm and height 25cm was used as crystallizing vessels. This mixture was then transferred to the test tube, a mouth of test tube closed using cotton plug. which is used to avoid contamination and dust affecting from atmosphere. The gel setting time was 12 to13days .This completely set gel was left for aging for 4days.i.e.96 hour's to120 hours .It is also observed that the aging of gel reduces the diameter of the capillaries in gel so that reaction can be controlled. H_2S gas dissolved in distilled water was used as supernatant. The chemical reaction inside the gel can be expressed as $XCl_2 + Y_2S \rightarrow XS + Y_2Cl_2$ developed crystals. However, very slow rate in one

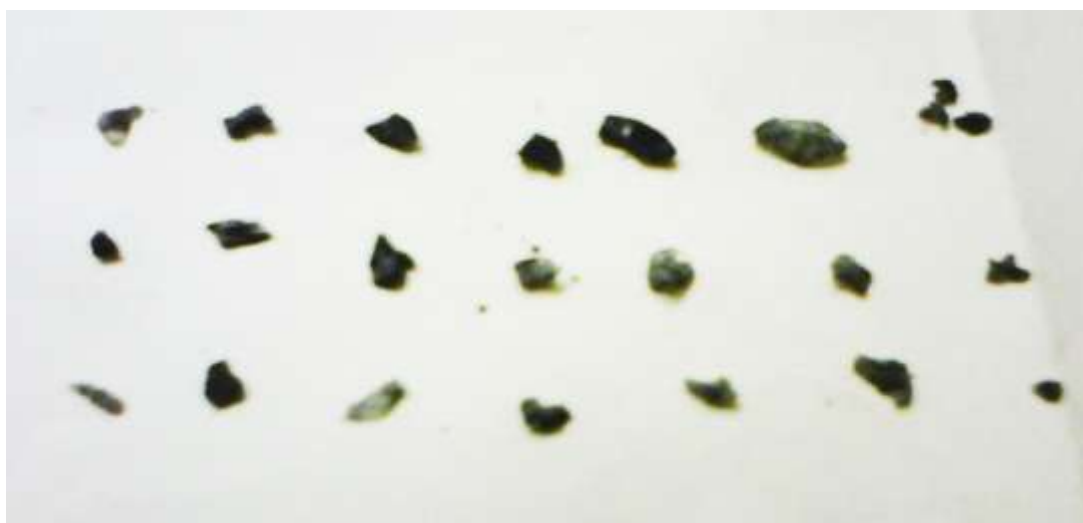


Figure 1.0 Number of grown crystals of copper sulphide



Nucleation:- A formation of nuclei depends on number of parameters such as pH of solution maintained, concentrations of reactants, aging of gel, density of gel .It was observed that initial nucleation of this gel takes place on the surface of the gel and rarely inside the gel.. Nucleation of copper nitrate or copper chloride gel takes place after 9 to 12 days. Generally this time varies few hours too few days depending upon the ambient temperature.

III. RESULT AND DISCUSSIONS:

The optimum growth conditions for the growth of copper sulphide crystals are represented in table 1.0. The different parameters such as gel density, gel setting time; concentrations of reactants pH of gel etc have the considerable effect on the growth rate. In the steady state of concentrations gradient, growth rate also becomes steady which favors well particular direction results in the different size of the crystals. Fast growth rate in one particular direction leads to the formation of elongated crystals like whiskers or dendrites.

In the present investigation, the growth of copper sulphide occurs in three different forms like whisker, dendritic and cubical. The whisker and dendrites growth occurs near the gel interface. It does mean that opaque whiskers and dendrites' are found to grow in the region of high concentration gradient respectively when the growth rate is very high. Just below the interface the concentration gradient is very high and hence the growth rate is also very high causing the whiskers of copper sulphide to grow in this region. As we go below away from the gel interface, the concentration gradient goes on decreasing. Hence below the whisker growth there is dendritic growth of copper sulphide. Near the bottom of the test tube far away from the gel interface, the rate of diffusion of the feed solution of hydrogen gas reduces and becomes steady causing well developed cubical crystals are obtained.

The rate of arrival of the solute at the crystal surface influences perfection of the crystal, Hence, growth of more perfect crystal also occurs due to slow and steady diffusion of feed solution. No gel inclusion is observed in these crystals grown inside the gel .it is due to the effect of pH and diffusion of hydrogen sulphide gas in distilled water used as supernatant repeatedly . In Table 1.0 the parameters such as concentrations of reactants, pH of gel impurities in solvent, gel setting time, gel aging time etc have the considerable effect on growth rate of copper sulphide crystals.

Table 1.0

Lattice parameter	Copper sulphide concentrations hy	4.4 bre
Density of sodium Meta silicate	1.04kg/m ³ the	
pH of mixture	4.4 par	
Amount of 2N acetic acid	5ml de	
Temperature	Room temperature gel pr	
Gel setting time	18 days	ha
Gel aging time	6 days rea	
Concentration of CuCl ₂	1M	
Concentration of Cu(NO ₃) ₂	1M	1.
Period of growth	4 weeks	

Optimum lattice parameters:

Increase in aging of gel reduces number of nucleation centers. Insufficient gel aging often leads to the fracturing of gel. At the time of addition of supernatant. Higher pH value gel sets early but crystals obtained are less transparent due to the inclusion of silica gel in them. Gel with pH less than takes longer time to set and there is possibility of aking of gel. Higher concentrations of reactants of drogen sulphide gas results on size of crystals



near gel interface. It is necessary to study the effect of various ameters on crystal growth which is mainly ends on gel cell size, and cell size is influenced by density etc. Hence, these parameters have ofound influence on nucleation density, growth rate bit and quality of crystals. Concentration of ctants is also important.

IV. OBSERVATIONS

The numbers of trials are performed to obtain optimum condition for growing copper sulphide crystals. Appreciable sizes of crystals are grown in gel medium. In some test tubes numbers of crystals are small and some are slightly big in size which are 6 Effect of gel density:

The gels of different densities were obtained by mixing sodium Meta silicate solutions of specific gravity 1.02 to 1.08 with 2N acetic acid, keeping pH value constant. It was observed that transparency of the gel decreased with increase of gel density gels with higher densities required less setting time of gel compared to the gels with lower densities. It may be noted that well defined and transparent crystals were obtained with sodium Meta silicate solution of density 1.04gm/cc. On the other hand, gels with densities below 1.04 gm/cc required longer time to set and still gels were not stable. Density of 1.02 gm/cc was the lower practical limit .The effect of gel densities on the quality of crystals and the variation of gelation time with gel density shown in figure1.1. It is observed that the gelation time decreases with increase in gel density. figures shows the effect of density on number of nuclei formed. A greater gel density implies smaller pore size and poor communication among the pores and thus decreasing the nucleation density. Bechhold et al showed that diffusion coefficient becomes distinctly smaller as gel densities increased. There is no evidence that the diffusion constant of small atoms was greatly influenced by the silica gel density as long as the density is low. Thus, the diffusion constant is not greatly influenced by the presence of dilute gel.

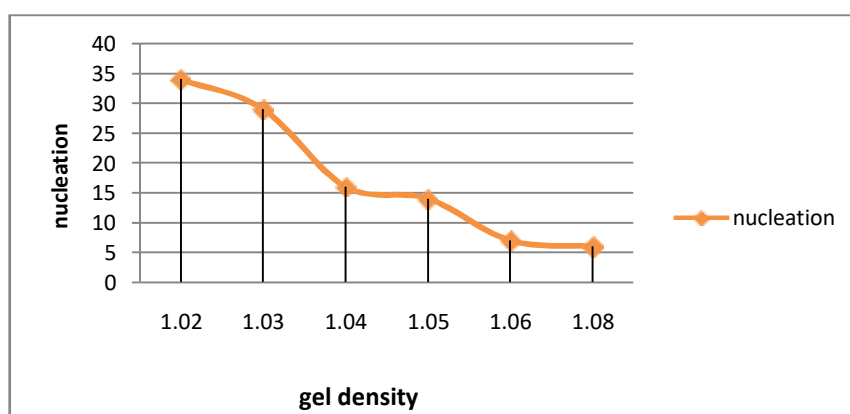


Figure 1.1 plot of gel density against nucleation density

V. EFFECT OF PH OF GEL

A value of pH directly affects on transparency of growing crystal and gelation of solution containing in test tube, by changing the pH of gel without changing gel composition and concentration of reactants, the effect of pH on growth was studied. The pH value of gel was varied from 2 to 7 .The crystal grown at higher values of pH were not transparent and well defined. This may be due to contamination of the crystals with silica gel. Gel takes longer time to set with smaller pH values, such gel can be easily fractured at the time of addition of supernatant. The pH observed is the composition of acetic acid and sodium Meta silicate solution, for the optimum condition different pH values were tried and gel setting time. The value of gel pH to get ideal gel is found to be 4.4 .At pH values less than 4.4, the time for gelation increased, and the resultant gel was unstable ,and for pH values greater than 4.4, the gelation occurred very soon and the resultant gel was not transparent . Figure1.2 shows the graph of pH against setting time in days.

In the present work, pH value of 4.4 is the optimum condition to grow good quality crystal. Gel aging plays an effective role on the growth of copper sulphide crystals .To investigate the effect of aging on gels, gel of same pH and density were allowed to age for various periods before adding the feed solution over a set gel containing copper chloride. Supernatant of constant molarity was then added as a feed solution over the set gel. It was found that number of copper sulphide crystal decreases with increase in aging of gel. Aging of gel decreases the pore size as well as diffusion and nucleation density. More aging causes more amount of water evaporation out of the gel. The effect of water evaporation should be considered before and after the formation of gel framework. Before the gel is set the evaporation of water causes an increase in gel density which in turn decreases the diffusivity of reactive sulphide ions in the gel, thereby decreasing the number of nucleation sites.



After the gel containing copper chloride is set, the evaporation of water causes not only the lack of ionic carriers in the channel of gel framework, but also discontinuities in the channel due to the shrinkage of gel. Both these effects would adversely affect the diffusion of Hydrogen sulphide gas used as supernatant. Hence, observed the decrease in the number of nucleation sites.

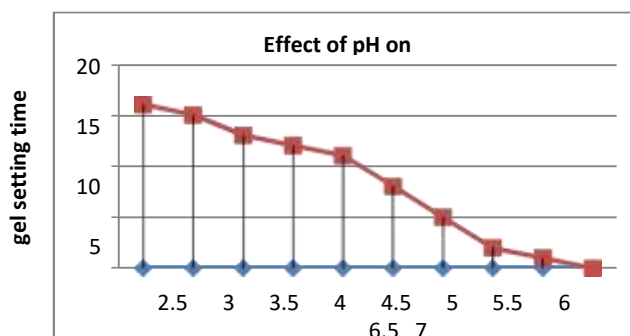


Figure. 1.2 Plot of pH against gel setting time in days

VI. EFFECT OF GEL AGING:

In present work, aging of 120 hours was found suitable because it makes gel neither dry or brittle nor fragile. The aim of reduction in nucleation centers can also be achieved. Hence aging period of 120 hours is the optimum condition for the growth of good quality crystals.

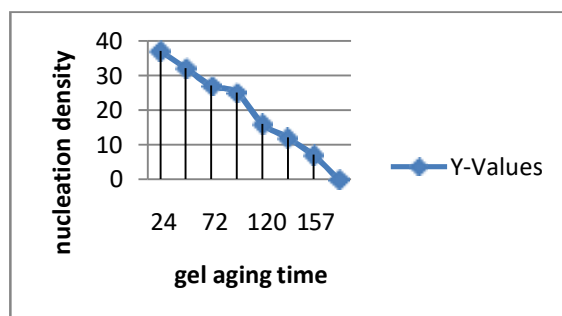


Figure 1.3 Plot of gel aging time against nucleation density for H₂S gas

Effect of copper chloride gel aging time pH=4.4 , feed solution H₂S containing distilled water

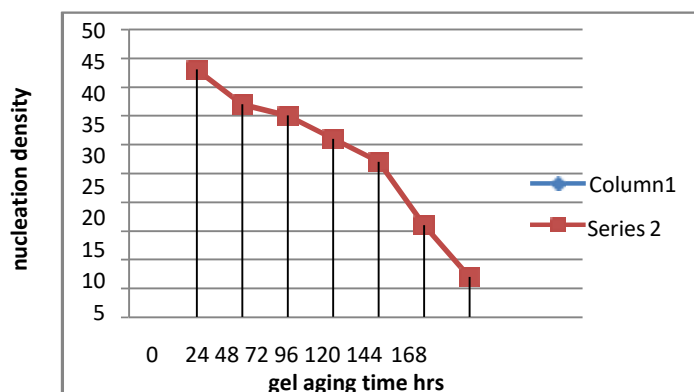


Figure 1.4 Plot of gel aging time against nucleation density

VII. EFFECT OF CONCENTRATION OF REACTANTS

In the present work different test tubes of copper chloride and copper nitrate solutions are used as reactant in silica gel medium. The grown crystals were found as shown in Figure after the diffusion of hydrogen sulphide gas solution in gel containing copper nitrate. The concentration of copper nitrate solution varied from 0.1M to 1.5M. A feed solution replaced with equal volume of 5ml in test tube repeatedly. The numbers of test tube were



arranged having copper chloride solution incorporated in gel, a concentration of solution changed from 0.1M, 0.5M and 1.5M,. Due to this reactant in gel, large numbers of crowded crystals were attached to themselves of tiny size. As concentration of reactant increased, transparent crystals of copper sulphide were grown. Increase in concentration of copper chloride used to obtained bigger size crystals.

VIII. EFFECT OF CONCENTRATION PROGRAMMING

Concentration programming is useful to improve the quality of crystal at the time of growing process, as shown in Table 5.7 many attempts were performed to grow good quality crystal of copper sulphide. A feed solution increases nuclei were formed. Further increase in concentration created very few nucleation centers and helps the previous nuclei to grow optimum size of copper sulphide crystal. Finally quality and transparency of copper sulphide crystal were increased due to the increase in concentration of feed solution or supernatant of hydrogen sulphide gas. In present work, solutions of hydrogen sulphide gas of same concentration were used as supernatant over a set gel containing of copper chloride. A feed solution was replaced by another dual volume in next 24 hour of the strength 0.4 M. This process was continued until the concentration of hydrogen gas reached for diffusion. It is observed that for lower concentration of feed solution, there will be no nucleation as observed.

IX. CHARACTERIZATIONS OF GEL GROWN CRYSTALS OF COPPER SULPHIDE

The growth of newer Engineering Semiconducting material in the form of crystal is widely useful in different technologies. Some grown crystals having optical, piezoelectric and NLO behavior. Copper sulphide crystals are insoluble in water which is decomposing before melting point. In the work reported have the determination of the optical band gap of the sulphide crystal, its structural behavior explained and calculated. Copper sulphide is a metallic conductor due to the incomplete occupancy of the sulfur, the determination of properties of copper sulfides is generally monovalent copper compounds. Today crystals of Sulphide is quiet interest due to wide variety of applications in many areas of engineering, modern science and technology, the nonlinear devices find large application in optical communication , image processing and wave guide coupling ,Research on thin film solar cells with copper sulphide doped in iron, indium, cadmium, bismuth is great interest today.

The present work describes the characterization of copper sulphide crystals by Following Techniques.

X-ray diffraction (XRD) :

X-ray diffractogram is useful in the analysis of crystal structure, d-values, cell parameters, unit cell volume and lattice system etc. can be evaluated using X-ray diffractogram. When the high frequency electromagnetic waves are selected to have wavelength comparable to the interplaner spacing of the crystals, they are diffracted according to the physical laws. The inter planer spacing (d) can be calculated to four digits and even more significant figures by measuring the diffraction angles. This, in turn, can be used to determine cell parameters and the system to which the sample under study belongs, etc. the reflecting planes in crystal h, k, l values can be calculated (5).

X-ray diffractogram of gel grown crystal of copper sulphide was recorded using Minislex model, Japan with $\text{CuK}\alpha$ radiation of wave length 1.5408°A and scanning speed of $10^\circ/\text{minute}$. A copper target and nickel filter were used From the powder diffractogram on data of copper sulphide which shows twenty different peaks and corresponding d values and (h k l) values were computed by using computer program POWD [An interactive powder diffraction data interpretation and indexing program] The recorded X-ray diffractogram is as shown in fig. 1.5The study was carried out at Department of Physical sciences, North Maharashtra University Jalgaon, Maharashtra.

These values are computed using computer programmed, POWD is as shown in the table 1.1. From POWD it found the lattice parameter of unit cell satisfy condition $a \neq b \neq c$ and $\alpha = \beta = 90$ and $\gamma \neq 90$.so unit cell structure is monoclinic. Calculated unit cell lattice parameter of the copper sulphide crystal are given in table 1.1 as follows

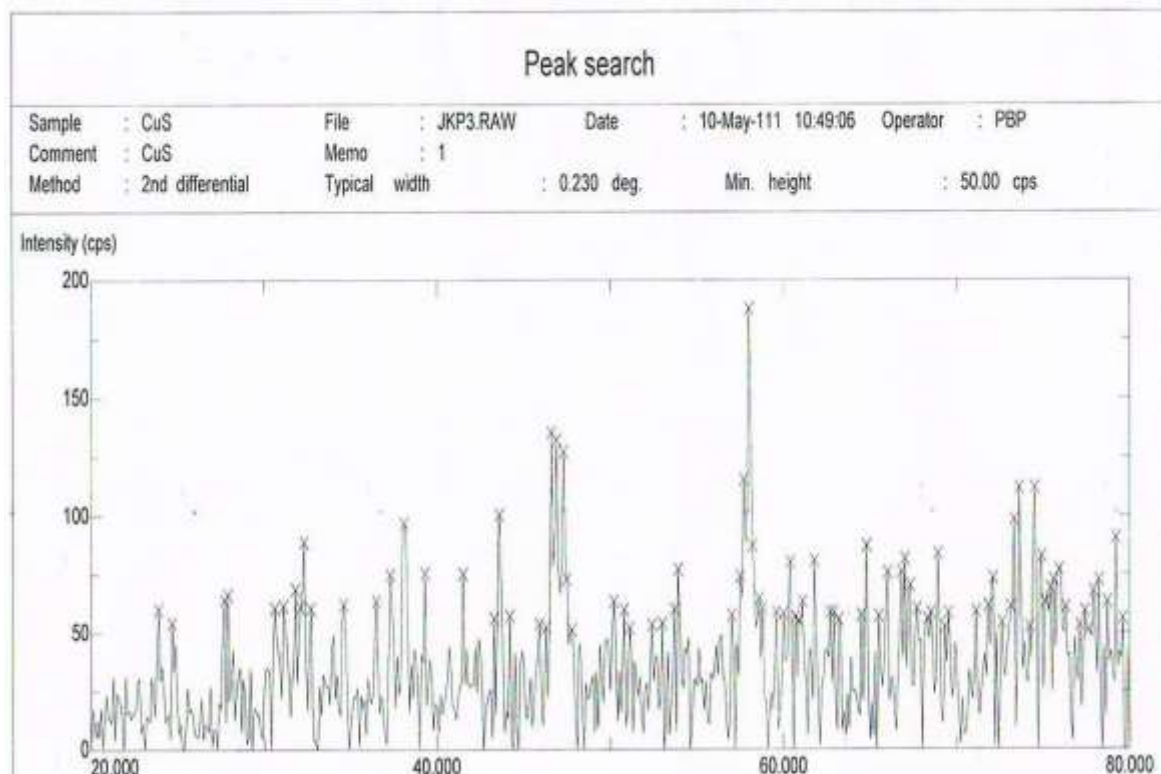


Figure 1.5 X-ray Diffractogram of copper sulphide

Table1.1 :Lattice Parameters:

Parameter	Copper sulphide
system	Monoclinic
a	8.617 Å
b	4.3443 Å
c	5.6428 Å
α	90°
γ	123.31 Å
β	90°
V	175.56 (Å) ³
	1.5405 Å

FT-IR of copper sulphide:

Studies of infrared radiation spectra provide important and valuable information about the basic characteristics of the molecule namely the nature of the atoms their special arrangements and their chemical linkage forces. The infra red spectrum results when a molecule, due to vibration and rotation of atoms within the molecule produces change in permanent electric dipole of the molecule.

Researchers have shown that an infra red spectrum is a useful technique for the optical study of crystals, which strongly absorb in the visible light region. The technique when coupled with intensity measurement may be used for quantitative analysis. One of the most advantageous of infrared spectroscopy over the usual method of structural analysis is structure of molecules quickly without tiresome valuations method. The number of problems in coordination chemistry and in organic chemistry solved using infrared spectroscopy.

IR absorption spectroscopy is one of the most powerful techniques used for chemical substance. As compared to other absorption spectroscopy technique the IR spectrum provides a wealth of structural information about molecules. IR spectroscopy involves two kind of fundamental vibration for molecules stretching and bending. IR spectroscopy is the measurement of wavelength and intensity of the absorption of



mid-infra light by a sample. Mid infrared light of $2.5\text{--}50\ \mu\text{m}$, $500\text{cm}^{-1}\text{--}4000\text{cm}^{-1}$ is energetic enough to excite molecular vibration to finds its greatest utility for identification of organic and metallic molecules.

In the present work, FT-IR absorption spectra were obtained with the help of SHIMADZU spectrophotometer at the University Department of Chemical technology; under North Maharashtra University Jalgaon. The spectrum was scanned by placing the sample pellet in the sample beam in the range $4000\text{--}500\text{cm}^{-1}$.

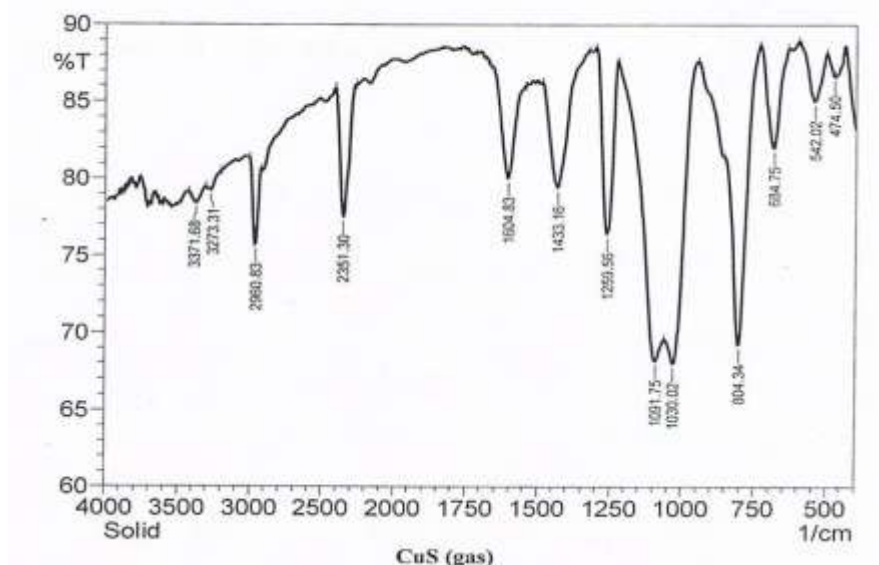


Figure 1.6 FT-IR spectrum of copper sulphide.

FT-IR is used for structural analysis In the present work IR spectrum of copper sulphide sample was recorded using SHIMADZU Spectrophotometer at North Maharashtra University Department of Chemical Technology Jalgaon . The IR spectra of these gel grown copper sulphide was recorded in the wave number range $500/\text{cm}$ to $4000/\text{cm}$ for KBr Line as shown in Figure 1.6

The bands at 3371.68cm^{-1} to 3273.31cm^{-1} are due to O-H stretching shows effect of C-H and N-H stretching in lower frequencies the fundamental frequencies of sulphoxide sulphides and sulphones are observed in all sulphide group compounds , which are also found in presents FT-IR analysis, which confirmed sulphide group of grown crystals. The bands at 1433.16cm^{-1} are due to SO_2 sulphate and 1259.56cm^{-1} due to sulphones are due to -N-H stretching bands.

A stretching frequency observed at 1091.75cm^{-1} and 1031.02cm^{-1} are due to S-O-C or Si -O - Si stretching exhibits sulphoxides by -C-O and S=O stretching vibration .A pair of strong nitrites band observed at 804.34cm^{-1} due N-O stretching nitrites .The organo halogen compound are detected due to carbon -halogen stretching of vibration bands at 684.75cm^{-1} to 542.02cm^{-1} .The C-H stretching are due to 2351.30cm^{-1} band A band of 1604.83cm^{-1} nitro group of CO^- stretching and final libration of compound occurs at 474.50cm^{-1} . The assignment of copper sulphide peaks as shown in Table. The optical property of copper sulphide crystal can be studied using UV-VIS spectrophotometer. A fine powdered form of copper sulphide crystal was used as sample . The reflection= 3.64 eV

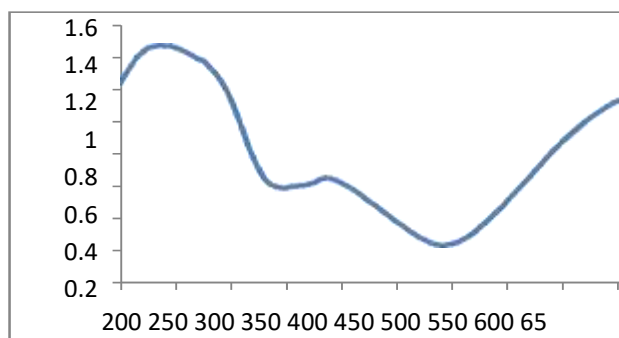


Figure 1.7 UV-VIS Spectra of copper Sulphide



Band gap of copper sulphide=1240/340

X. CONCLUSION

- The crystal of copper sulphide can be grown by using gel technique Single diffusion gel growth technique is suitable copper sulphide crystals.
- Different habits of copper sulphide crystals can be obtained by changing and absorption spectra of copper sulphide crystals have been recorded over the wavelength range 200 to 700 nm using a UV-2450 spectrophotometer of SHIMADZU scientist instruments at the room temperature. The experiment was carried out in the research laboratory of the physics department at Pratap College, Amalner Maharashtra.
- parameter like gel density, gel aging, pH of gel concentration of reactants etc.
- Chemical composition of the grown crystal by chemical analysis and EDAX match with the theoretical calculation from molecular formula.
- Unit cell parameter value and d values match very with the reported ones
- The structure of copper sulphide is monoclinic confirmed by X-ray diffraction.
- FT-IR analysis confirms the presence of fundamental infra-red frequencies, generally observed in all sulphide compounds.
- Water of crystallization is present in grown crystal confirmed by FT-IR analysis.

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