GROWTH OF COPPER SULPHIDE CRYSTAL IN GEL AND ITS THERMAL SPECTROSCOPIC SEMICONDUCTING CHARACTERISATIONS WITH KINETIC PARAMETERS

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ABSTRACT:

Copper sulphides crystals are grown using simple gel technique at ambient temperature. The various lattice parameters, gel aging time, gel setting time, Effect of pH observed, Different characterization like gel aging, pH of gel, setting of gel with their analysis and Thermal behavior of grown crystal like Thermo gravimetric Analysis TGA are Discussed. The chemical analysis confirmed contents in grown crystal of copper sulphides.

Keywords: Gel method, Monoclinic, TGA, Gel, Chemical Analysis, Color

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1. INTRODUCTION

Copper Sulphides crystals are of considerable interest, particularly for basic studies of some of their interesting physical properties. For the growth of copper sulphides crystals, it is simple but skilled to diffuse copper chloride solution into the gel of sodium meta silicate solution and hydrogen sulphides gas doped with gel which is already acidified by acetic acid. It has been reported that the size of copper sulphides crystals growing in the gel did not improve even after applying nucleation control techniques like concentration programming and neutral gel methods. But copper sulphides crystal respond for P^H 4.3. to 4.4 Most of the earlier works on pure copper iodate and sulphides crystals were done with an aim of increasing the size of the crystal by controlling parameters and defects of the grown crystals. With an aim of controlling nucleation and improving the size, in the recent doping gas technics, we have grown pure copper sulphides crystals using copper chloride mixed with

acetic acid and added sulphides gas as the supernatant for solution. The grown crystals have been characterized. In the present work, an attempt has been made to characterize gel grown crystals of copper Sulphides by Thermal analysis i.e. TGA , Chemical Analysis, effect of Gel aging on pH ,Gel Setting time, Nucleation, Gel Density on setting time ,effect of concentration on Reactant and Supernatants ,concentration programming using copper chloride and copper nitrate as Dopants etc.

It is also reported that sulphides are semiconductor in nature the synthesis of sulphides are complicated because of relative low vapor pressure of the Sulphur ,neverth less successively more attention is being turns toward investigating sulphides of various materials (1). There is no need to explain the role of semiconductor in the development of present electronic industries and semiconductor device for e.g. Zink sulphides (ZnS) used for lenses and other optical devices lead sulphides used in infra, red sensors; cadmium sulphides (cds) which is used in photocell. Iodate, iodides and sulphides are taken it basic material copper (2).

2. MATERIALS AND METHODS:

A copper sulphides crystal are grown using chemical reaction method. Using this method gel of copper chloride formed and water containing H_2S gas filled with subsequent nucleation and the crystal growth of copper sulphides takes place.

2.1 Preparation of gel:

Initially different concentration solution of sodium Meta silicate taken for e.g. 11gm,13gm,15 gm, 17 gm, 19 gm, 23gm, 25gm in distilled water to get 250 cc solution. The solution is constantly stirred and filtered. A solution of different molarities prepared by adding proper amount of copper nitrate, copper chloride, Hydrogen sulphides 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 (3). 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 Sulphides gas solution.

2.2 Single diffusion methods:

Copper sulphides crystals was synthesized from acetic acid and hydrogen sulphides gas, Acid taken in the molar ratio of 1:1, by slow gel technique. The reactants were thoroughly dissolved in double distilled water and stirred well using a temperature controlled magnetic stirrer to yield a homogeneous mixture of the solution. Then the solution was allowed to evaporate at room temperature up to 30⁰ c which is good for crystallization and aging of the gel reaction, which results in the yield of green crystalline salt by the nucleation. The seed crystals were harvested from the solution after 8 to 10 days and a suitable seed was selected. The selected seed was suspended in the freshly prepared solution. After a period of 14 days, optically transparent, defect-free crystals were obtained from the mother solution.

In actual procedure, 5cc of 2N acetic acid was taken, 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 5cc of copper chloride solution of concentration 0.4 M was added with constant stirring in mixture of acetic acid and sodium Meta silicate solution. 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 sulphides.

Table 1: Optimum lattice parameters:

Sr. No.	Condition Lattice parameter	Copper sulphides concentrations
1	Density of sodium Meta silicate	1.04kg/m ³
2	pH of mixture	4.4
3	Amount of 2N acetic acid	5ml
4	Temperature	Room temperature
5	Gel setting time	12-14 days
6	Gel aging time	5-6 days
7	Concentration of CuCl ₂	1M
8	Concentration of Cu(NO ₃) ₂	1M
9	Period of growth	24 days

2.3 Observations:

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 to 14days. 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. H₂S gas dissolved in distilled water was used as supernatant.

Table 2: Effect of gel density on setting time (pH=4.4, feed solution H₂S dissolved in distilled water)

Sr. No.	Acetic acid 2N (cc)	CuCl ₂ incorporate In gel 1M	Density of gel (gm/cc)	Gel Setting time (days)	Observations
1	5	5	1.02	15	Gel is not gel
2	5	5	1.03	13	Long time required to set gel
3	5	5	1.04	12	Few crowded crystals
4	5	5	1.05	10	Number of crystals decreases
5	5	5	1.06	08	Less transparent

The effect gel density and Gel setting time varies with constant acidification of 5 cc using acetic acid. The incorporated solution of copper chloride of 1m used for gelling mechanism.it is observed that as density of gel varies from1.02 to 1.04 quite number of crystal grown re decreases but at the stage of density of gel 1.04 gm/cc few crowded crystals of copper sulphides crystals are seen. The number of grown crystals of copper sulphides decreases with gel setting time of 10 days. The number of grown crystals increases from decreasing gel density 1.07 to 1.05 gm/cc. The crystals which were grown in test tube are transparent. The gel setting time from 7 days to 15 days which matters on crystal growth of copper hydrogen sulphides.

2.4 Effect of gel aging:

Gel aging plays an effective role on the growth of copper sulphides crystals. To investigate the effect of aging on gels(4-5), 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 sulphides 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 and decrease diffusivity of reactive sulphides ions in the gel, thereby decreasing the number of nucleation sites.

Table-3. Shows the effect of aging time on number and the quality of crystal. 1—shows graph of aging in hours against the number of crystals.

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.

1.1 Effect of gel aging time

Figure 1: Plot of gel aging time against nucleation density pH=4.4, feed solution H₂S gas dissolved in distilled water

Table: 3: Effect of gel density on number of nucleation pH =4.4 and 1M of CuCl₂ :

Test tube no.	Acetic acid 2N (cc)	CuCl ₂ incorporated In gel 1M	Density of gel (gm/cc)	Number of nuclei formed	Observations
1	5	5	1.02	34	Small but crowded crystals
2	5	5	1.03	29	Number of crystal decreases
3	5	5	1.04	16	Different Shaped number of crystals
4	5	5	1.05	14	translucent crystals
5	5	5	1.06	07	Low nucleation small transparent
6	5	5	1.07	06	Few crystals are not well defined

Table 4 : Effect of pH on gel Aging period =5 days, feed solution of H₂S dissolved in distilled water

Test Tube No.	Acetic acid (cc)	CuCl ₂ In gel 0.4 M, cc	Sodium meta silicate 1.04 gm/cc	pH	Gel setting time days	Observation
1	5	5	15	2.0		Gel is not set
2	5	5	16	2.5	16	Gel is not set
3	5	5	16.5	3.5	15	Whisker crystals of sulphides
4	5	5	17	4.0	13	Small growth of whisker crystals
5	5	5	18	4.2	12	Longer whisker crystals
6	5	5	19	4.4	11	Crowded large number crystals

It is observed that lower value of pH is quietly effect on setting of the gel as shown in table 4 . As pH value ranges from 2.0 to 2.5 then gel is not set and the number of days not only affect for growing crystal and setting of gel but also on the value of pH which acidified the solution in test tube. The time for gel setting is an important parameter for setting gel and growing crystals of copper sulphides. It is observed that the pH value from 3.5 pertains for growing crystals in test tube. No doubt at this stage atmospheric conditions up to higher temperature 32⁰c is suitable for growing crystals. A longer whisker crystals are seen at pH 4.2.but large number of crowded whisker crystals are obtained at pH 4.4.the figure of merit is large number of 23 copper sulphide crystals are obtained as shown in figure 2

Figure 2: Large number of Whisker crystals of copper sulphide

Table 5: Effect of concentration of reactant on habit, quality and size of copper sulphide crystals

Sr no.	Concentration of reactant in gel	Concentration of reactant above gel	Observation
1	CuCl ₂ , 0.5 M, 5ml	H ₂ S dissolved In distilled water	Large number of crowded micro crystal were produced, these crystal were attached to themselves form a thick layer of crystal at the interface. These crystals are tinny in size.

2	CuCl ₂ , 1 M, 5ml	H ₂ S dissolved in distilled water	Large numbers of crystal are produced. Transparent copper sulphide crystals are grown.
3	CuCl ₂ , 1.5 M, 5ml	H ₂ S dissolved in distilled water	Large number of cubical crystals and some different crystals of big in size grown compared to second stage.

2.5 Effect of Concentration Programming:

Crystal at the time of growing process, as shown in Table 3, many attempts were performed to grow good quality crystal of copper sulphides (6-8). 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. shown in Table 3. 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

Colour: The large number of copper sulphide crystals are transparent

2.6 Chemical analysis:

Copper is estimated gravimetrically using dilute HCl by homogeneous precipitation. Accurately weighed 0.1 gm of sample in powder form was dissolved in small quantity of double distilled water. Few drops of nitric acid were added while heating to dissolve the powder completely (9-11). Few ml of dilute sulphuric acid was slowly added with constant stirring until precipitation was obtained. It was allowed to stand for same time. Precipitate was filtered in fresh water. In a previously weighed porcelain crucible, the filter paper along with the precipitate was ignited. First it was slowly heated to dry the filter paper. The precaution should be taken that the filter paper should not catch the fire. When the filter paper was completely dried, the precipitate was strongly ignited to get ash of CuSO₄. The residue was cooled. The weight of residue obtained was 0.1984 gm.

Table 6.0 Chemical Analysis

Ob. no.	Content of sample	Weight
1	Weight of sample	0.1 gm
2	Weight of filter paper +sample	1.1472 gm
3	Weight of filter paper	1.05 gm
4	Weight of the residue	0.1984 gm

Table 7: Result of chemical analysis:

Element	Theoretical	Practical value (%)
Copper	66.51%	65.9%
Sulphur	32.56%	32.6%

2.7 Thermo gravimetric Analysis (TGA):

TGA curve of copper sulphide showed clearly two stage of decomposition. TGA curve did not show an appreciable weight change in the temperature range 0°C to 140°C Indicating that the crystals of copper sulphide are thermally stable in this range .The crystal becomes thermally unstable beyond 100°C The observed and calculated weight loss shown in Table 8.

Figure 3. TGA curve of copper sulphide crystal

Reaction:

The first stage of decomposition occurs in the temperature range 142°C to 180°C, in which weight loss of 11.5% agrees very well with the calculated weight loss of 11.54%. This weight loss is attributed to loss of $\text{H}_2\text{O} + 0.5 \text{SO}_2$ and continuous decomposition of crystal occurs. The second stage of decomposition occurs in the temperature range 220.03 °C to 310 °C In which observed weight loss of 47.15% agrees very well with the calculated weight loss of 47.23%. This weight is attributed to loss of 3.2SO_2 and continuous decomposition of crystal occurs. The observed trend above 600 °C suggest that the product formed is continuously getting decomposed. It may attribute to the formation of copper oxide of 40.48%.

Table 8: TGA data of copper sulphide.

Stage	Temperature range (°C)	Observed weight loss %	Calculated weight loss %	Probable loss of water Molecules
1	142°C to 180°C	11.5%	11.54 %	$\text{H}_2\text{O} + 0.5 \text{SO}_2$
2	220.03°C to 310°C	47.15%	47.23 %	$3.2 \text{SO}_2 \uparrow$
3	Residue CuO_7	41.5%	40.48 %	CuO_7

3. Conclusion:

- 1) The crystal of copper sulphide can be grown by using gel technique Single diffusion gel growth technique is suitable copper sulphide crystals.
- 2) Different habits of copper sulphide crystals can be obtained by changing different parameters in crystal growth.
- 3) Chemical composition of the grown crystal by chemical analysis and EDAX match with the theoretical calculation from molecular formula.
- 4) Unit cell parameter value and d values match very with the reported ones

- 5) The structure of copper sulphide is monoclinic confirmed by X-ray diffraction.
- 6) FT-IR analysis confirms the presence of fundamental infra-red frequencies, generally observed in all sulphide compounds.
- 7) TGA and DSC analysis confirms the presence of copper in the grown crystals.

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