

CHAPTER 3.

GROWTH OF  $\text{CuInS}_2$  SINGLE CRYSTALS BY CHEMICAL  
VAPOUR TRANSPORT (CVT) TECHNIQUE

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### 3.1. INTRODUCTION

The choice of a growth technique for a particular material depends on many factors: the chemical reactivity of the compound and constituent elements, the vapour pressures of the constituent elements and dissociation pressure of the compound and whether the compound melts (or freezes) congruently or incongruently, the extent over which the composition can deviate from stoichiometry and still be single phase, and the presence or absence of phase transformation. There are several methods for growing single crystals, the techniques being fully described in the text books and reviews [1-11]. Following are three major classification of crystal growth generally employed. The classification is based on the nature of the phase adjacent to the growth face.

- 1 Solution Growth.
- 2 Melt Growth.
- 3 Vapour Growth.

It is well established that compounds of I-III-VI<sub>2</sub> chalcopyrites family are insoluble in water, which naturally prevents their growth from aqueous solution i.e. solution growth. Single crystal growth from its own melt revealed to be very difficult or impossible as was also observed by Binsma et

al. [12]. It was discovered that  $\text{CuInS}_2$  undergoes two solid state phase transitions, at  $980^\circ\text{C}$  and  $1045^\circ\text{C}$  before melting at  $1090^\circ\text{C}$ . These transitions, when passed upon cooling, lead to cracking of the crystals. Such phase transitions are severe handicaps for single crystal growth from the melt and indeed several authors [13,14] reported difficulties in preparing single crystals of  $\text{CuInS}_2$ .

The importance of growing single crystals of  $\text{CuInS}_2$  by means of chemical vapour transport technique has already been discussed in chapter 1. The salient features of this technique are described in detail in this chapter. Because of the tendency of thermal decomposition and of the large affinity of the constituents for oxygen, chemical vapour transport is carried out in closed systems. In principle, open tube chemical vapour deposition techniques can be applied, but are not likely to produce large single crystals.

Thus the growth of single crystals of  $\text{CuInS}_2$  was carried out at a temperature below the phase transitions (about  $800^\circ\text{C}$ ) by means of chemical vapour transport (CVT) using iodine as the transporting agent.

## 3.2. EXPERIMENTAL SET UP

### 3.2.1. Two Zone Horizontal Furnace

In order to achieve the steady thermal gradient

required for obtaining large single crystals of high quality, horizontal two zone static furnace is used (Fig.3.1). This has been designed and fabricated indigenously. The furnace was constructed locally in our University Science and Instrumentation Centre (USIC), by using a special sillimanite threaded tube (grade KR80 GAHG), closed at one end having 54 cm length, 7 cm outer diameter and 6 cm inner diameter with threads of pitch 0.3 cm. These tubes were imported from Fabriken Feuerfester, Germany. Super Kanthal A-1 wire of 17SWG was wound directly on to the furnace tube in two different regions. Then the tube was enclosed in the hot face insulating brick slabs. The complete brick shell was fully enclosed in thick asbestos sheets and the entire assembly was supported in a steel frame work. This arrangement is shown in Fig. 3.2.

As sizable crystals require longer time to grow, the temperature in the furnace must be accurately controlled. The power supplied to the furnace windings was regulated by the control circuit shown in Fig. 3.3. The two regions of windings are provided with independent power supplies 'INDOTHERM-401' temperature controllers. Transformers with 70, 80 and 100V taps with 20A current capacity in secondary were used to supply sufficient power in order to achieve the required high temperature.

Inside the furnace two chromel-alumel thermocouples monitor the temperatures of the hot (reaction) zone and of the cooler (growth) zone. Furnace temperatures are stabilised to  $\pm 1^{\circ}\text{C}$ . The temperature gradient between reaction and growth zones is kept appreciably linear over the length of the ampoule.

### 3.2.2. Ampoule

High quality fused quartz tubes used in the growth experiments have a melting point of about  $1500^{\circ}\text{C}$ . Tubes of various diameters were used. Tubes with internal diameter 14 mm and length 140 mm were found to be more suitable for the present growth experiments. One end of the tube was sealed and the other was drawn into a neck and joined to a silica tube of 10 mm inner diameter to connect it to the vacuum system for evacuation after introducing the source material.

### 3.2.3. Cleaning of Ampoule

First the ampoule was washed with boiled water and then with boiling concentrated  $\text{HNO}_3$  and  $\text{HF}(49\%)$  taken in equal proportions. Afterwards it was washed with distilled water. A further washing was carried out with concentrated  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  in equal proportions followed by a final washing for

about nine to ten times with double distilled water. The ampoule was then kept in a SICO constant temperature oven at  $100^{\circ}\text{C}$  and left for over night heating to make it moisture free.

### 3.3. CRYSTAL GROWTH

#### 3.3.1. Charge Preparation

For preparation of starting material (charge), powders of copper, indium and sulphur were first weighed accurately on a microsensitive balance and then introduced into a transparent ampoule duly cleaned and dried by the process explained above in stoichiometric proportion. The materials used and their source of supply are listed in Table 3.1. The ampoule containing the source material is then connected to a vacuum system, precaution being taken to evacuate the ampoule so slowly that none of the materials from the ampoule entered the vacuum system. When the vacuum was being reached, the ampoule was tapped slowly so that the air between the particles of the materials was removed. When a vacuum of the order  $10^{-5}$  torr was reached, the ampoule was sealed off at the neck.

The sealed ampoule with the elemental powder was shaken thoroughly to ensure proper mixing of the contents. The mixture was then distributed uniformly all over the length of

the ampoule. The ampoule was thus ready for keeping it in the furnace.

After keeping the ampoule at an appropriate place in the horizontal furnace, the synthesis of the compound was carried out by heating the ampoule gradually upto 1100°C and holding for 6-12hrs. Due to the high vapour pressure of sulphur (2 atoms. at 493°C) and to avoid explosion, the samples were heated slowly. The powder was then identified to be single phase CuInS<sub>2</sub> by X-ray diffraction.

### 3.3.2. Single Crystals

The single phase CuInS<sub>2</sub> powder compound thus prepared was then transferred into another evacuated quartz growth ampoule containing 8-10 mg/c.c. iodine transporter. There after it was placed in the furnace whose temperature profile is shown in Fig.3.4. A vapour transport growth in a two-zone furnace with reaction zone at higher temperature and growth zone at lower temperature was carried out. In a CuInS<sub>2</sub>-I<sub>2</sub> closed system, when compared its equilibrium constants of the forward reaction with those of other reactions, only the following reaction was considered [15].

The details of the growth run are given in Table

3.2. The resulting single crystals were needle shaped and shining black in colour. The average dimensions of the large size crystals thus grown were about  $14 \times 2 \times 1 \text{ mm}^3$ . Fig. 3.5 shows a photograph of the crystals thus grown.

#### 3.4. MICROSTRUCTURES

Upto now only a few authors have examined the growth mechanisms of CVT grown crystals using detailed surface microtopography in order to verify whether growth takes place via spiral growth, nucleation or by another mechanisms [16,17]. A microtopographic investigation that particularly dealt with the growth mechanisms of the top faces of needles and the narrow side faces of plates was carried out by Nittono et al. [18]. They grew copper whiskers via hydrogen reduction of cuprous iodine vapour by making use of rather a chemical vapour deposition (CVD) than a CVT technique. It was concluded from their observations by means of scanning electron microscopy and X-ray microanalysis that growth of the needle tops and lateral expansion of the needles and platelets proceeded via a vapour-liquid-solid (VLS) mechanism with CuI as liquid agent.

Binsma et al. [19,20] have also carried out



detailed surface microtopographic studies on  $\text{CuInS}_2$  crystals by means of optical microscopy, scanning electron microscopy and X-ray microanalysis. Similar to Nittono et al. [18], they showed that vapour-liquid-solid (VLS) growth with CuI as liquid phase plays a main role during the growth of these crystals. Besides VLS growth patterns, growth by spirals with very low step heights were commonly observed in the needle side faces and the top and bottom surfaces of platelets.

The present work describes a detailed investigations of the microstructures on the as-grown faces of the crystal grown by the CVT technique as described earlier in this chapter.

Since the morphology of a crystal surface, according to Neumann principle, under near equilibrium condition reflects the inherent crystal symmetry, the as-grown crystal surfaces often exhibit some features which signify the mechanism by which the crystals grow.

The as-grown faces of single crystals of  $\text{CuInS}_2$  were examined under 'Epignost' optical microscope and since no crystal was found to contain any kind of spiral traces, we strongly believe that  $\text{CuInS}_2$  crystals grown in the present work do not grow by screw dislocation mechanism. Typical

surface features of the kind shown in Fig.3.6 were frequently observed on the as-grown faces of  $\text{CuInS}_2$  crystals. One can clearly see growth layers starting from the edges of the crystals. The irregular nature of growth layers predicts that the growth is rapid. Fig.3.7 shows that impurities present on the surface also serve as the initiation point for the growth layers. Sometimes as shown in Fig. 3.8 striations present on the surfaces lead to a modification of the growth layers.

In Fig. 3.9, one can clearly identify that the left half of the face appears to be flat and smooth with growth layers initiating from crystal edges and boundary on the right half of the face.

A flat face being the surest test of two dimensional layer theory, author is inclined to believe that  $\text{CuInS}_2$  crystals in the present work grow by mechanism of piling and spreading of layers.

In conclusion it can be said that crystal growth of  $\text{CuInS}_2$  has been found to occur by two dimensional layer propagation theory and the dislocation mechanisms is inapplicable.

The absence of growth spirals on the surfaces of

the crystals also lead to the conjecture that the crystals are nearly free from dislocations which might act as spiral centres.

### 3.5. CONCLUSIONS

1. It is concluded that in order to grow larger single crystals of  $\text{CuInS}_2$ , the crystal growth process should be performed below the lowest transition temperature ( $980^\circ\text{C}$ ).
2. Hence forth the growth of single crystals of  $\text{CuInS}_2$  was carried out at a temperature below the phase transition (about  $800^\circ\text{C}$ ) by means of chemical vapour transport (CVT) using iodine as transporting agent.
3. The presence of layers on the surfaces of the as-grown crystals suggests a layer growth mechanisms for their growth.

TABLE 3.1      Materials from which the crystals were  
grown with source of supply.

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Sr. No.	Material	Purity %	Supplier
1.	Copper (Cu)	99.999	Johnson-Mathey Chemicals Ltd., England
2.	Indium (In)	99.999	Chiti-Chem. Corp. Baroda, India
3.	Sulphur (S)	99.999	Chiti-Chem. Corp. Baroda, India.

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$\frac{5220}{210} = 24$   
 $\frac{120}{144} = \frac{5}{6}$  days  
 $\frac{144}{24} = 6$  days

Table 3.2 Growth parameters of CuInS<sub>2</sub> single crystals

Compound preparation		Single crystals growth	
Temperature distribution		Growth time	Ampoule dimensions
Hot zone	Cold zone	hrs	mm x mm
1100	820	144	140 x 14 (ID)

**CAPTIONS TO THE FIGURES.**

- Fig. 3.1. Schematic representation of the furnace.
- Fig. 3.2. Photograph of Two-zone horizontal tube muffle furnace.
- Fig. 3.3. Control circuit for regulating the power.
- Fig. 3.4. Temperature-distance profile in the furnace for synthesis of  $\text{CuInS}_2$  single crystals.
- Fig. 3.5. Maximum size of the as-grown  $\text{CuInS}_2$  single crystals.
- Fig. 3.6. Growth layers starting from the edges of the crystals. The irregular nature of growth layers predict that the growth is rapid.
- Fig. 3.7. Impurities serving as the initiation points for the growth layers.
- Fig. 3.8. Modification of growth layers by striations.
- Fig. 3.9. A flat portion along with irregular growth layers on the same face of the crystal.

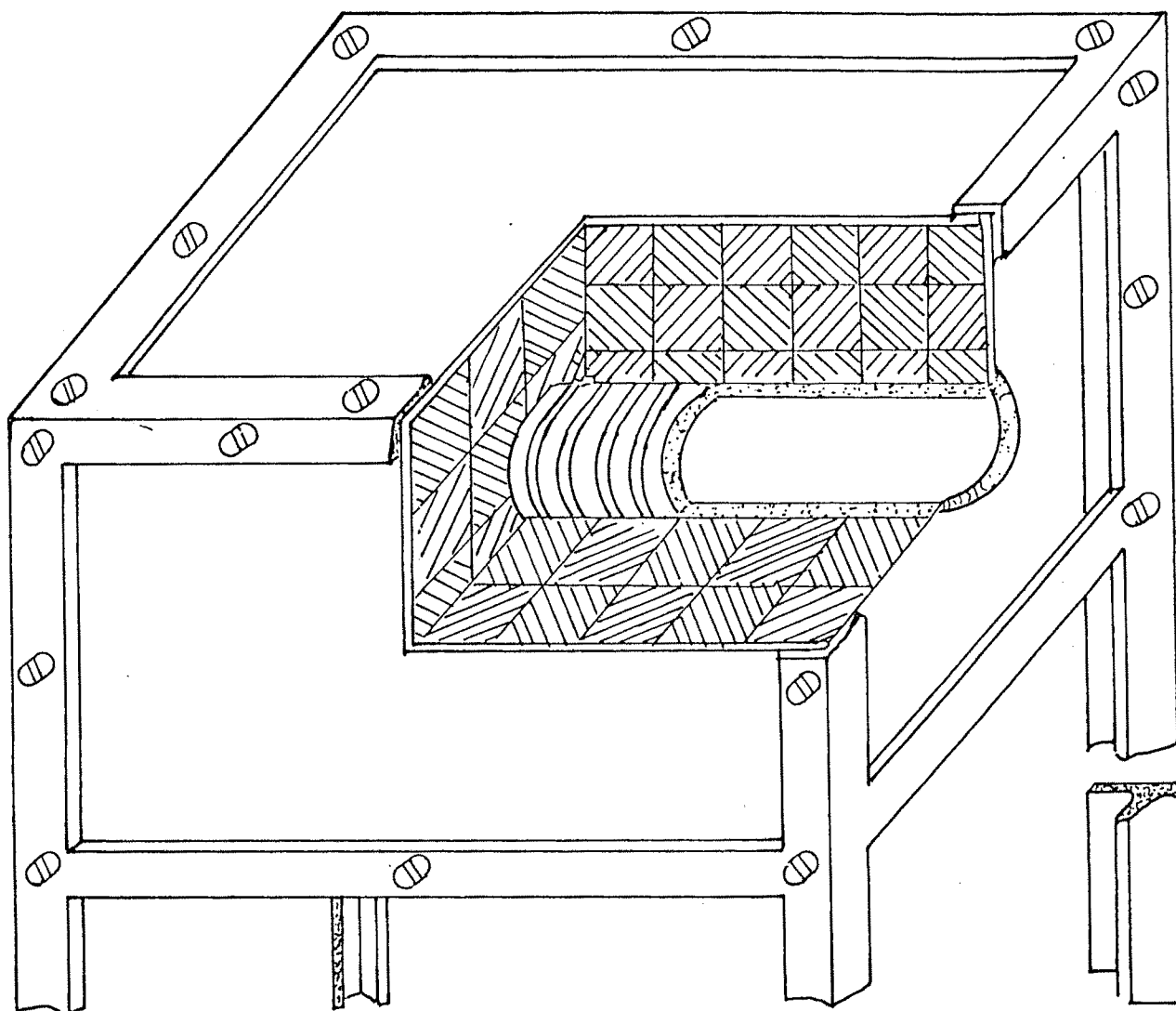


fig. 3·1

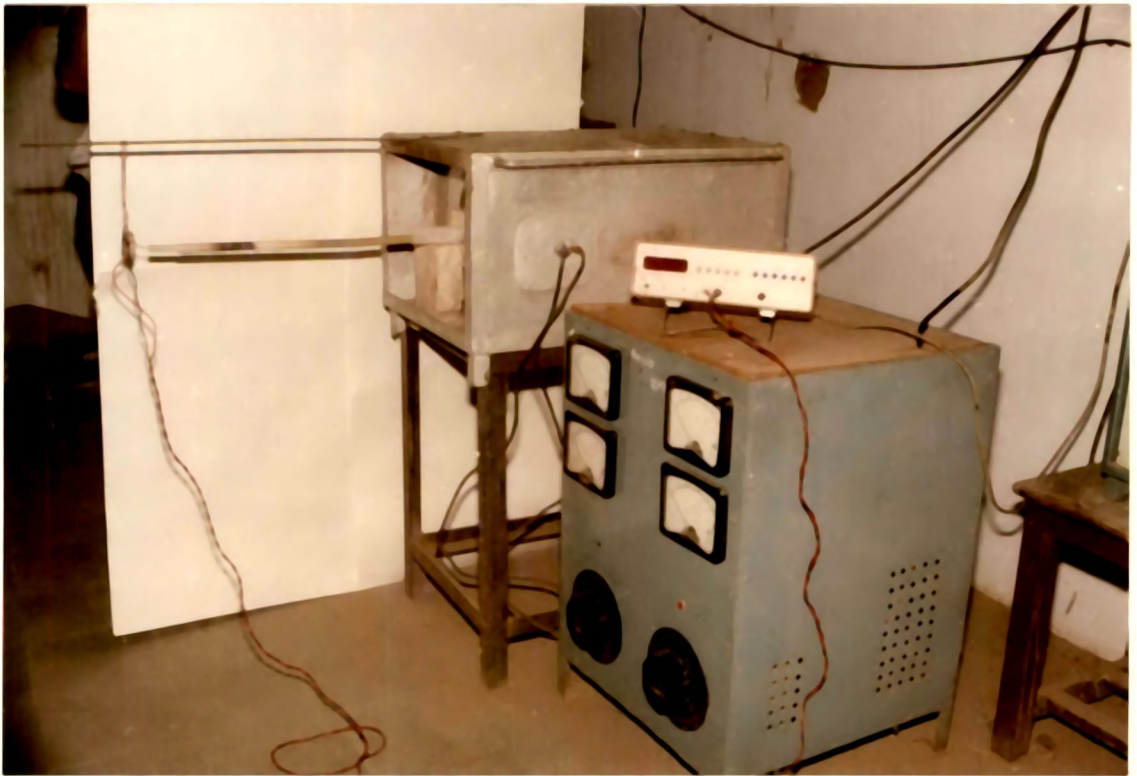


Fig. 3·2



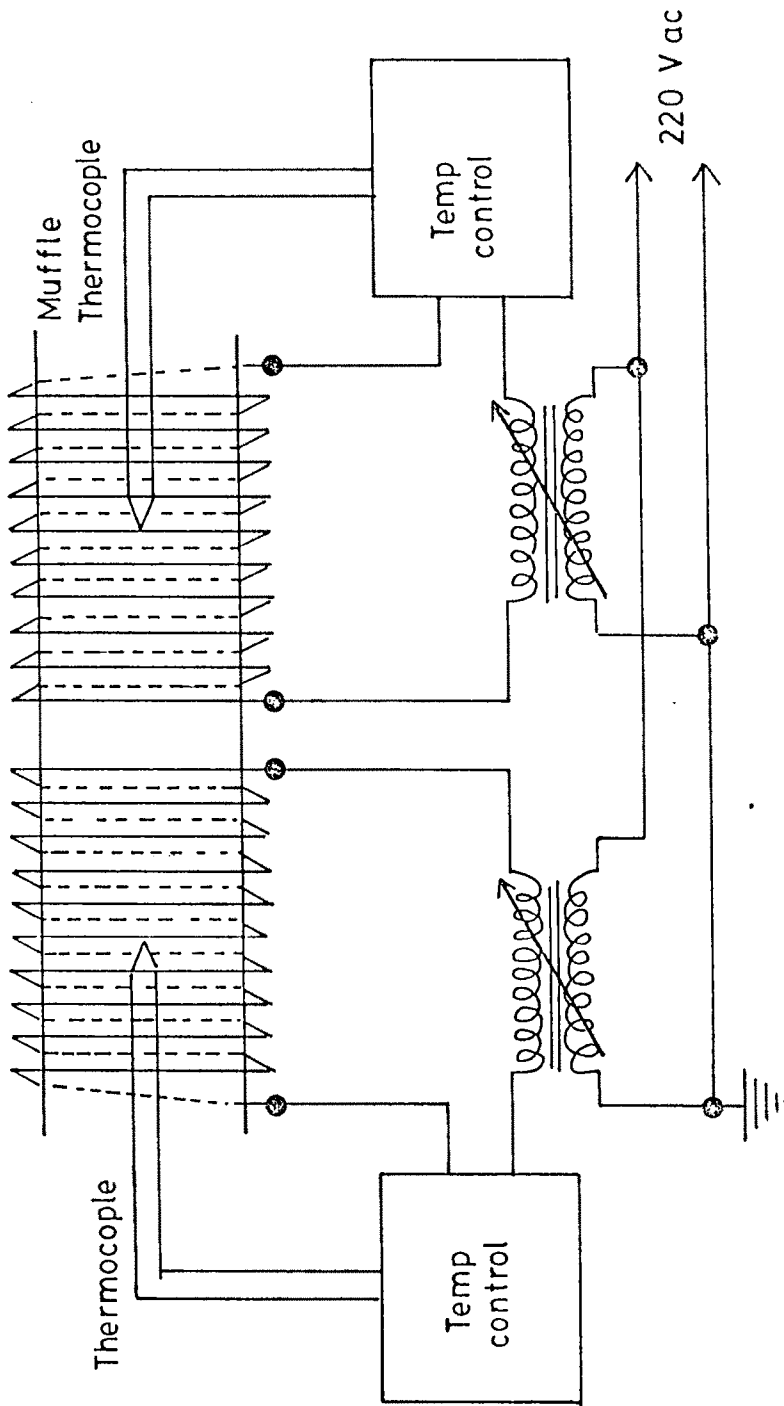


fig. 3-3

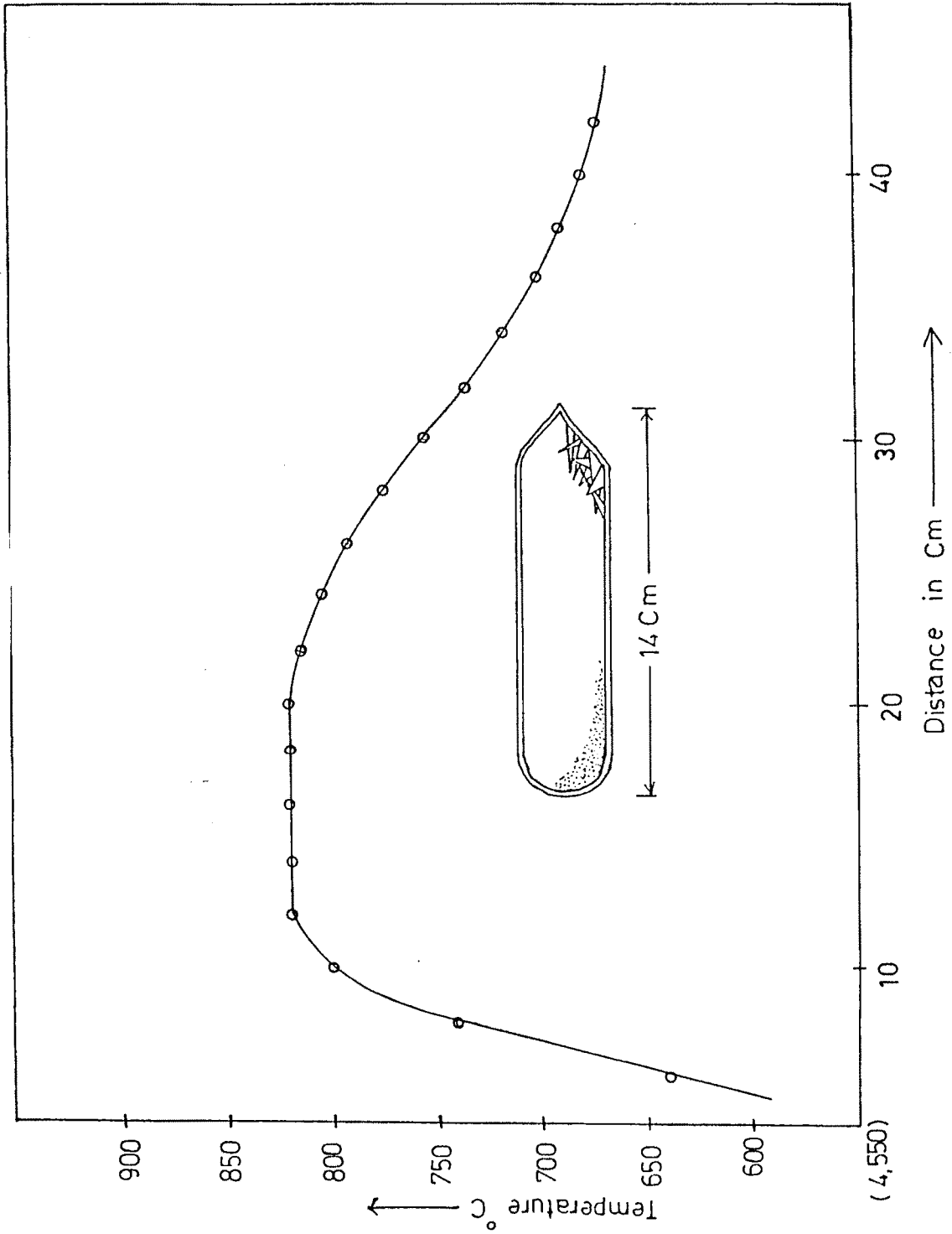


Fig. 3.4



Fig. 3·6

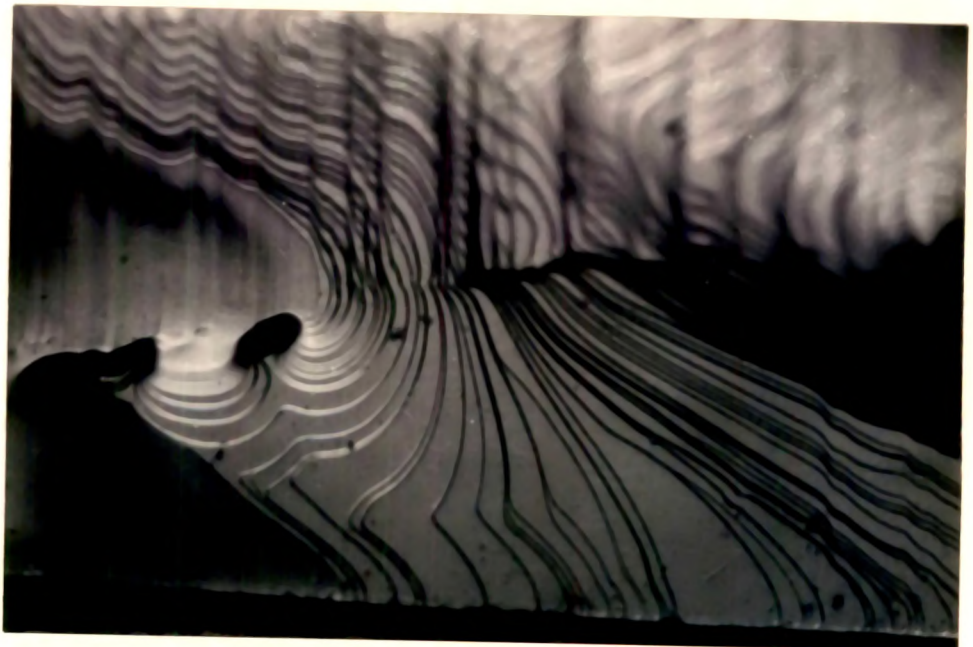


Fig. 3·7

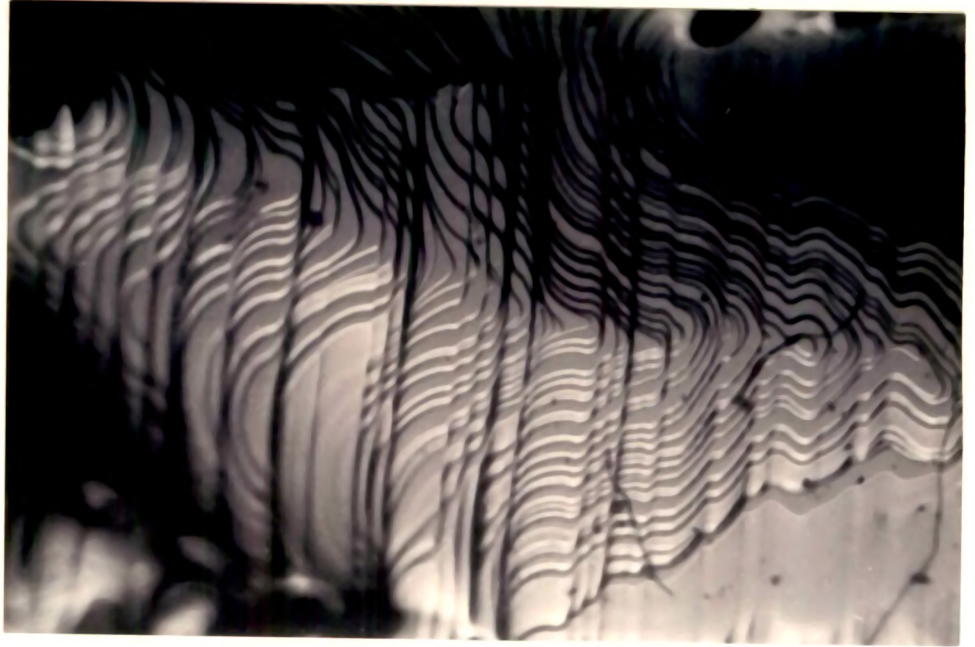


Fig. 3·8

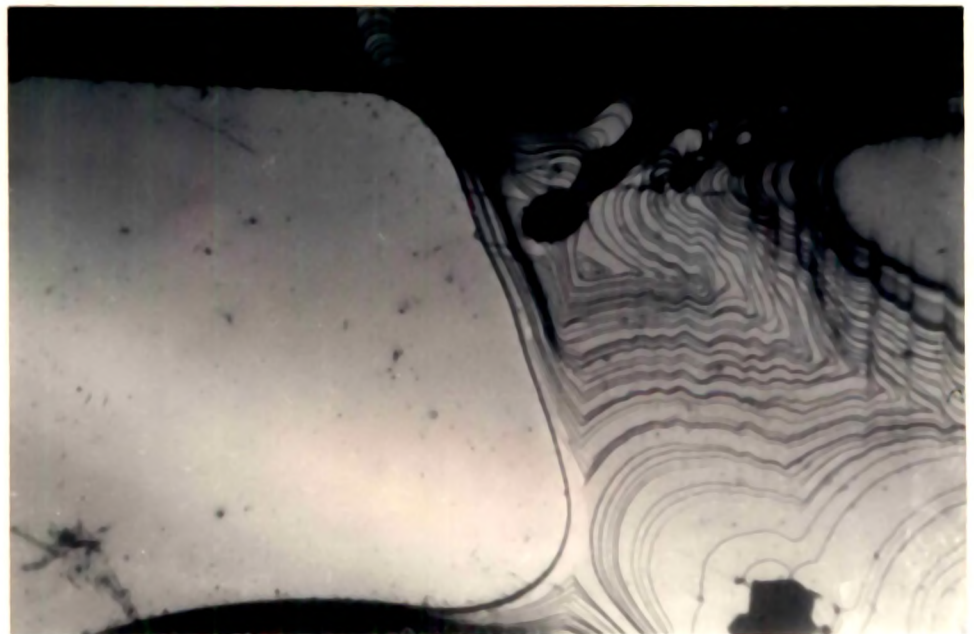


Fig. 3·9

## REFERENCES

1. "Crystal Growth" Disc Faraday Soc. 5 (1949).
2. Crystal Growth; H.E. Buckley [John Wiley & Sons, New York] (1951).
3. Preparation of Single Crystals; W.D. Lawson and S.Nielson [Butterworths Scientific Publ., London] (1958).
4. Einkristalle Wachstum; A.Smakula [Springer, Berlin, Germany] (1962).
5. The Art and Science of Growing Crystals; Ed. J.J.Gilman [John Wiley and Sons, New York] (1963).
6. E.A.D.White; Brit. J.Appl. Phys. 25,151 (1970).
7. The growth of single Crystals; R.A. Laudise [Prentice Hall Inc., New Jersey] (1970).
8. Crystal growth in Gels; H. K. Henisch [The Pennsylvania State University Press, University Park, London] (1970).
9. R.L. Parkar; Solid State Phys. 25,151 (1970).
10. Crystallization; J.W. Mullin [Butterworths Scientific Publ., London] (1972).
11. The Chemistry of imperfect Crystals; F.Kroger [North-Holland Publ., Amsterdam] (1973).

12. J. J. M. Binsma, L.J.Giling and J. Bloem; J.Cryst. Growth **50**, 4 429 (1980).
13. A. W. Verheijen, L.J. Giling and J.Bloem; Mater. Res. Bull. **14**, 237 (1979).
14. T. V. Tyagunova, F.F.Kharakhorin and E. N. Kholina; Neorg Mater. **13**, 46 (1977).
15. The Chemistry of Diamond-like Semiconductors; N. A. Goryunova [MIT, Cambridge, MA] (1965).
16. R.A.M. Lieth; Phys. Stat. Sol. (a)**12**,399 (1972).
17. E. Kaldis; J.Crystal Growth **5**,376 (1969).
18. O. Nittono, H. Hasegawa and S.Nagakura; J. Crystal Growth**42**, 175 (1977).
19. J. J. M. Binsma, W. J. P. Van Enckevort and G. W. M. Staarink; J. Cryst. Growth **61**, 138 (1983).
20. W. J. P. Van Enckevort, K. Tsukamoto and J. J. M. Binsma; J. Cryst. Growth **61**, 157 (1983).