

# GROWTH OF ZnS SINGLE CRYSTALS BY CVT TECHNIQUE UNDER DIFFERENT MASS TRANSPORT STABILITY CONDITIONS

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**Abstract:** A thermodynamic model was used to find out the optimum temperature for the growth of ZnS single crystals in closed ampoules by chemical vapor transport technique. Based on this model 1002 °C was found to be optimum temperature for 2 mg/cm<sup>3</sup> concentration of transporting agent (iodine). ZnS Crystals were grown in optimum (1002 °C) and non-optimum (902 °C and 1102 °C) temperatures. The composition structure and microstructure of the grown crystals were studied by Atomic absorption spectroscopy, X-ray diffraction and Scanning electron microscopy measurements. Properties of the grown crystals were correlated to the growth conditions especially a stability in mass transport along the closed tube length.

**Keywords:** Semiconductors, Crystal growth, Electron microscopy, X-ray diffraction, Microstructure.

## 1. INTRODUCTION

ZnS, a II-VI wide band gap material, has attracted considerable attention due to its many potential applications in the field of short-wavelength photoelectronic devices, especially for ultra-violet laser diodes and photo detectors [1,2]. The ZnS-based devices have been fabricated by using heteroepitaxial technique. However, both the heterovalency and the difference of the thermal expansion coefficient between the ZnS epilayer and the substrates have made it difficult to reduce the defect density. The natural way to avoid these problems would be to grow the ZnS-based structures on ZnS substrates. Therefore, the growth of large, high-quality ZnS bulk crystals is indispensable in order to achieve the fabrication of optoelectronic devices. These bulk crystals have been grown by different techniques [3-6].

By the conventional growth methods which are carried out at high temperatures, hexagonal crystals containing strained regions and stacking faults are obtained. Therefore, the CVT technique can be used as an advantageous method to grow II-VI compounds [7]. The advantages of CVT include: applicability to the growth of various materials, lower growth temperatures than the melting and sublimation points of materials, no loss of source materials or leak of toxic gas compared with chemical vapor deposition

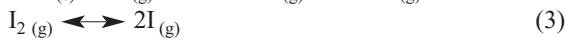
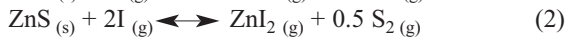
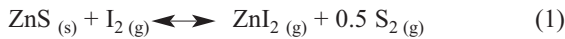
(CVD), technical simplicity in process control, especially in growing materials in space. However, CVT has some disadvantages such as the problem of establishing optimum growth condition. The exploratory work needed to achieve the desired results, when carried out in an empirical, trial and error fashion, will often be ineffective and time consuming. The slowness of the empirical approach arises from the many experimental variables which can affect the results, coupled with the time needed to set up and run an experiment before it can be evaluated [8,9]. In general, the perfection of the crystals grown by vapor methods depends on constancy of the flow of material which is carried out from the source zone to the deposition zone through different mechanisms such as diffusion, Stefan flow and convection. The flow of material is very much temperature dependent and control of temperature at the growth interface is always poor than the accuracy shown by temperature controllers in the furnace. It has been shown that the temperature profile inside a closed CVT ampoule can deviate greatly from that of its external heat source. Due to some factors such as optical and convective properties of the system, it is difficult to determine the temperature distribution inside a closed ampoule. The exact temperature distribution is different from that of the heating arrangement and temperature

oscillations of up to  $\pm 25$  °C under typical growth conditions have been measured [10]. This instability affects to a large extent on compositional and structural uniformity of a growing crystal. Proper change in other growth parameters such as concentration of the transporting agent makes it possible to reduce the effect of the temperature on flow of the material. In present work, a simple thermodynamic model has been introduced for the ZnS-I<sub>2</sub> system which enabled us to calculate the optimum conditions for the growth of ZnS single crystals by CVT technique. Experiments have been carried out to grow ZnS crystals at both optimum and non-optimum conditions. Structural and microstructural analyses have been carried out for all the grown crystals to find out the ability of theoretical model in prediction of optimum growth condition.

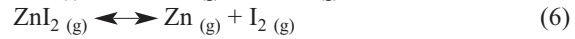
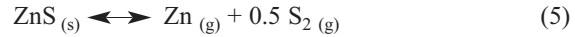
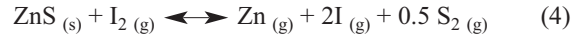
## 2. EXPERIMENTAL DETAILS

### 2. 1. Estimation of Optimum Growth Condition

The main reactions to describe the vapor phase chemical transport of ZnS with iodine are [11].



There are some possible reactions as below, which are neglected because of determinative role of (1) - (3).



By considering reactions (1) - (3), there are four components in the vapor phase which are I, I<sub>2</sub>, S<sub>2</sub> and ZnI<sub>2</sub>. Conservation of iodine inside the ZnS-I<sub>2</sub> system and assuming the exact stoichiometry of ZnS in source material give the following equations respectively.

$$n_{I_2}^o = n_{I_2} + 0.5n_I + n_{\text{ZnI}_2} \quad (7)$$

$$P_{\text{ZnI}_2} = 2P_{\text{S}_2} \quad (8)$$

Where  $n_{I_2}^o$  is the mole numbers of initial iodine and the other  $n$ 's are the mole numbers of the corresponding components. The equilibrium constants for reactions (1) and (3) are given as:

$$K_{(1)} = \frac{P_{\text{ZnI}_2} (P_{\text{S}_2})^{0.5}}{P_{I_2}} \quad (9)$$

$$K_{(3)} = \frac{P_I^2}{P_{I_2}} \quad (10)$$

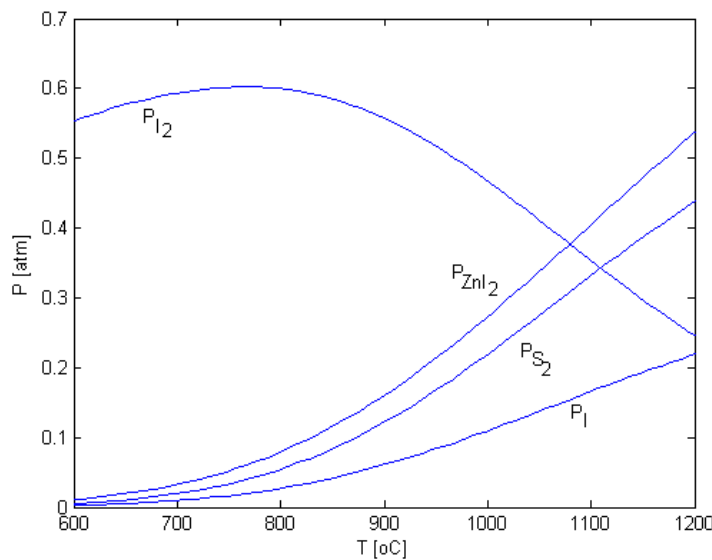


Fig. 1. Partial pressures  $P_I$ ,  $P_{I_2}$ ,  $P_{S_2}$  and  $P_{\text{ZnI}_2}$  as a function of temperature for 2mg/cm<sup>3</sup> iodine

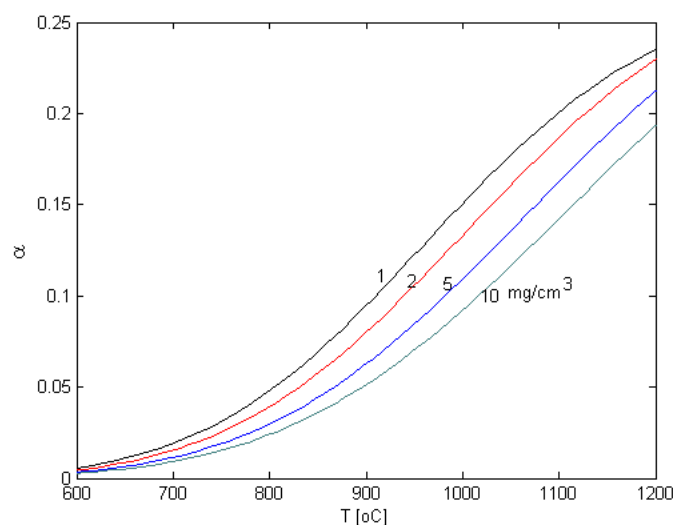


Fig. 2. Variation of  $\alpha$  with temperature for various concentrations of iodine.

The partial pressures of components inside the  $\text{ZnS-I}_2$  may be calculated as a function of temperature ( $T$ ) and the initial concentration of iodine ( $C$ ) by numerically solving the equations (7) to (10) in the temperature range 600-1200 °C in steps of 50 °C, with transporter concentrations of 1-10  $\text{mg/cm}^3$ . The solution method is similar to [8] using the thermodynamic data given in [12].

Fig.1 shows the calculated partial pressures of  $P_I$ ,  $P_{I_2}$ ,  $P_{S_2}$  and  $P_{ZnI_2}$  for  $C=2 \text{ mg/cm}^3$  as a function

of temperature. The value of  $\alpha = \frac{P_{ZnI_2}}{P_{I_2}^0}$  where

$$P_{I_2}^0 = P_{I_2} + 0.5P_I + P_{ZnI_2} \quad (11)$$

correlates the ratio between vapor pressure of the  $\text{ZnI}_2$  molecules and iodine molecules in the gaseous phase, inside the  $\text{ZnS-I}_2$  system. Fig.2 represents the variation of  $\alpha$  as a function of temperature for various concentrations of transporter for  $T_2-T_1=50 \text{ }^\circ\text{C}$ . Fig. 3 shows the  $\Delta\alpha = \alpha(T_2) - \alpha(T_1)$  where,  $T_2-T_1=50 \text{ }^\circ\text{C}$  as a function of deposition temperature ( $T_1$ ) for various concentrations of the transporter. Since there is not



Fig. 3. Variation of  $\Delta\alpha$  with deposition temperature ( $T_1$ ) for various concentration of iodine.

much difference between the values of  $P_{I_2}^0$  in source and deposition zones for  $\Delta T=50^\circ\text{C}$ ,  $\Delta \alpha$  can be approximated as  $\frac{\Delta P_{ZnI_2}}{P_{I_2}^0}$ .

In addition, it has been shown that the change in transport rate is proportional to the  $\Delta P_{ZnI_2}$ , i.e., the difference in partial pressures of  $ZnI_2$  in source and growth zones [13]. Without considering the type of migration along the tube, it can be assumed that the transport rate is proportional to  $\Delta \alpha$ , i.e.,  $n_{ZnS}$  is proportional to  $\Delta \alpha \Delta t$ , where  $n_{ZnS}$  is the mole numbers of ZnS transported in time  $t$ . It can be observed from Fig.3 that, as the concentration of transporting agent increases, the curves broaden and the position of the peaks are shifted to higher temperatures. For all the curves,  $\Delta \alpha$  changes slowly at the temperatures close to the peaks. This in fact, shows that for a particular amount of concentration of transporter, there is an optimum growth temperature. When crystal is growing at this temperature, the flow of material has more stability along the ampoule. For growth temperatures near each peak, the sensitivity of transport rate to the temperature fluctuations is less. The flow of material is very much temperature-dependent and our experimental works have shown that the control of temperature at the growth interface is always poor than the

accuracy shown by temperature controllers. Table 1 compares both the predicted optimum growth temperature calculated by present theory and growth temperatures experienced by different researchers to grow ZnS single crystals.

For ZnSe crystals [7] the similar table has been brought for more comparison. Comparing Tables 1 and 2 with each other, shows that the difference between theoretically predicted and experimentally applied growth temperatures for ZnS crystals is higher than for ZnSe crystals.

This discrepancy can be explained based on the following reasons;

1. ZnSe single crystals have been grown by different researchers in limited temperature range of  $700-850^\circ\text{C}$  whereas ZnS crystals have been grown in wider temperature range of  $700-1150^\circ\text{C}$ .
2. This theory shows that by increasing concentration of iodine the theoretically predicted optimum growth temperatures increase for both ZnSe and ZnS compounds. From Tables 1 and 2 it is observed that by increasing iodine concentration, the reported experimental growth temperatures increase for ZnSe in more regular manner compared to those of the ZnS crystals.

**Table 1.** Experimentally applied and theoretically predicted optimum conditions for the growth of ZnS single crystals.

Ref. No	Growth conditions (Experimental values)			Predicted growth temperatures ( $^\circ\text{C}$ )	$\Delta T = T_{\text{Predicted}} - T_{\text{Exp.}}$ ( $^\circ\text{C}$ )
	C $\text{mg}/\text{cm}^3$	$T_2$ ( $^\circ\text{C}$ )	$T_1$ ( $^\circ\text{C}$ )		
[11]	2	900	850	1002	152
[13]	2	950	940	1002	62
[14]	5	850	840	1062	222
[15]	5	1000	750	1062	312
		1300	1150	1062	-88
[16]	5	850	840	1062	222
[17]	1-5	874	854	962	108
				1062	208
[18]	2-5	1000	700	1002	302
		1200	1000	1062	62
[19]	1-7	800	765	962	197
			797	1087	290

**Table 2.** Experimentally applied and theoretically predicted optimum conditions for the growth of ZnSe single crystals.

Ref. No.	Growth conditions (Experimental values)			Predicted growth temperatures (°C)	$\Delta T = T_{\text{Exp.}} - T_{\text{Predicted}}$ (°C)
	C mg/cm <sup>3</sup>	T <sub>2</sub> (°C)	T <sub>1</sub> (°C)		
[13]	2	800	<del>780</del> -790		18
[20]	3.6	900	850	792	58
[9]	4-6	765-825	750-800	<del>802</del> -822	
[15]	5	1050	<del>880</del>		-12
[16]	5	850	840	812	+28
[14]	5	850	840	812	+28
[21]	5	810	790	812	-22
[22]	5	850-860	<del>840</del> -850		+33
[23]	5.4	850	840	812	+28
		900			
		1070			
[24]	0.3-10	800-900	700-850	687-842	+10.5

In general, the literature survey for the growth of both ZnS and ZnSe crystals by CVT technique shows no clear reason for selecting the optimum growth temperature and it seems that this growth parameter has been chosen empirically in most of the cases. But in our theoretical work we have introduced a model, based on which, there is no need to carry on different growth runs in wide temperature range (700-1150 °C). At least for each concentration of iodine there is a limited temperature range at which the transport of material is less affected by thermal fluctuation inside the tube.

Both Tables 1 and 2 show that experimental undercooling values for the growth of both ZnS and ZnSe have been reported in the wide temperature range starting from 10 °C and ending to almost 300 °C, Where as in our theoretical model we have considered only constant undercooling value of 50 °C for all the cases.

## 2. 2. Crystal Growth

Ampoule with the length of 150 mm and inner diameter of 12 mm was filled with 2 grams of heat-treated ZnS polycrystalline powder along with iodine at a concentration of 2 mg/cm<sup>3</sup> of the empty space of the ampoule. All compounds were purchased from Fluka with a purity of 99.999%. The ampoule was cooled by ice and evacuated to 2 10-6 torr and sealed off. The ampoule was placed

into a three-zone horizontal furnace controlled by Eurotherm controllers. A reverse temperature profile was developed across the ampoule with growth zone at a higher temperature for 12 hours to remove the sticking powders from deposition zone of the ampoule and to diminish the active sites. Different growth runs were carried out for the same amount of undercooling ( $\Delta T = 50$  °C), starting material and ampoule geometry but with various growth temperatures. The optimum growth temperature ( $T_1$ ) was selected at 1002 °C corresponding to 2 mg/cm<sup>3</sup> concentration of iodine. The non-optimum growth temperatures were selected 100 °C either higher or lower than the optimum value for the same concentration of iodine. Each growth run was repeated twice and carried out for 12 days. At the end of each growth process, the furnace was slowly cooled to room temperature at a cooling rate of 50 °C/h in order to prevent thermal strains. The compositions of grown crystals were determined with a Shimadzu 680 AA atomic absorption spectrometer equipped with a hollow cathode lamp and a deuterium background corrector, at respective wavelengths using an air-acetylene flame. The instrumental parameters were those recommended by the manufacturer. For most of the growth runs less than five percent deficiency of zinc atoms was observed for the grown crystals. The structure and morphology of the grown crystals were studied by using computer aided single crystal X-ray diffractometer (make: Enraf-Nonius CAD4-F)

attached with rotating goniometer. The results showed that the samples were well crystallized in cubic structure for most of the cases with  $a=5.40 \text{ \AA}$  and faulty structures for some of crystals grown at  $1102 \text{ }^\circ\text{C}$ . The microscopic observation of the as-grown crystals surfaces was carried out using scanning electron microscope (SEM), (Philips, XL-30/TMP), gold coating was made on all the samples before they were analyzed by SEM.

3. RESULTS AND DISCUSSION

The results of growth runs have been summarized in Table 3. ZnS crystals, depending on growth conditions, exhibit sphalerite, wurtzite

or intermediate structures which are crystals with stacking fault and polytypes. ZnS undergoes phase transition at  $1024 \text{ }^\circ\text{C}$  from low temperature stable phase sphalerite (cubic) to wurtzite (hexagonal). The production of ZnS crystals with a homogeneous structure is very difficult. Polytypes and one-dimensional disorder are due to the growth conditions, principally the temperature. Under stable temperature and constant material flow rate, growth of structurally homogeneous hexagonal or cubic ZnS has been reported [18]. The results of growth experiment are found to have a good agreement with the theoretical calculations. The crystals which have been grown at  $1002 \text{ }^\circ\text{C}$  showed smooth, flat and

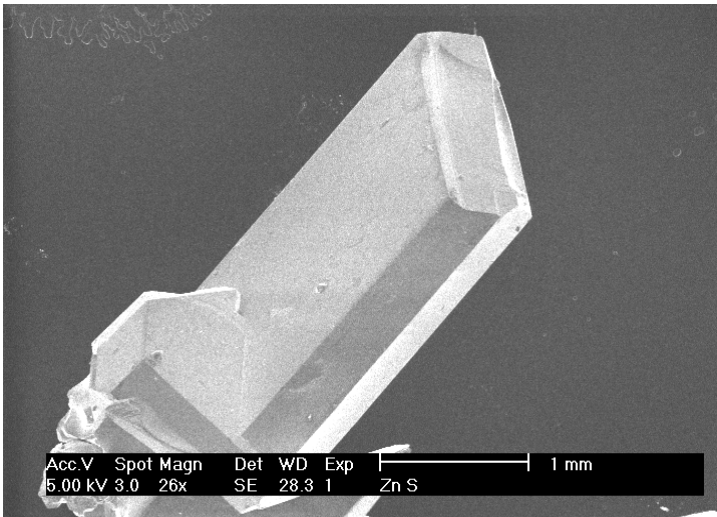


Fig. 4. ZnS single crystal in tablet form grown at  $1002 \text{ }^\circ\text{C}$ .

Table 3. The growth conditions and properties of ZnS crystals.

Growth parameters			Crystal habit, shape and dimensions (mm <sup>3</sup> ) (shown in)	Observed microstructures (shown in)
C mg/cm <sup>3</sup>	$\Delta T$ ( $^\circ\text{C}$ )	$T_1$ ( $^\circ\text{C}$ )		
2	50	1002	Cubic, Tablets ( $3 \times 1 \times 0.5$ ) and Platelets ( $0.5 \times 0.5 \times 0.2$ ) (Figs.4,5)	-
2	50	902	Cubic, Polyhedra $3 \times 2 \times 2$ and Tablets $3 \times 1.5 \times 0.5$ (Figs. 6,7)	Spirals (Fig.6)
2	50	1102	Polytypes, Polyhedra $2 \times 2 \times 2$ and Irregular habit crystallites (Figs. 8,9)	Strips+Kinks (Figs.8,10)



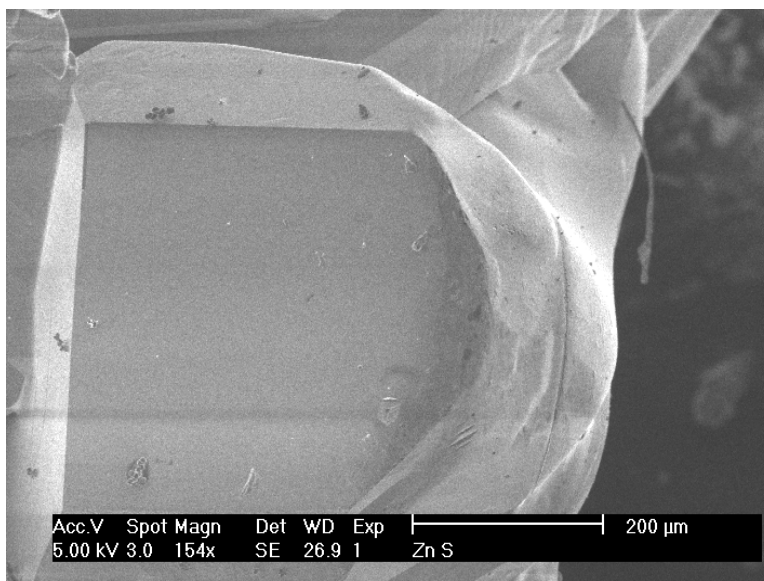


Fig. 5. ZnS single crystal in platelet form grown at 1002 °C.

complete faces without microstructures under a SEM magnification of 3000X. Figs 4 and 5 show these crystals in the form of tablet and platelet respectively with (111) as based face having cubic structure. These crystals were colorless to pale yellow – green in color and more transparent compared to the ZnS crystals grown at 902 °C and 1102 °C. This quality of crystal surface is due

to the stability in flow of the materials which are transported from source zone to the growth zone at theoretically predicted optimum growth temperature (i.e. 1002 °C for  $C=2 \text{ mg/cm}^3$ ). The crystals which have been grown at 902 °C (Figs. 6, 7) were found to have uncompleted faces. This deficiency in quality can be due to inconstancy of the transport rate caused by small thermal

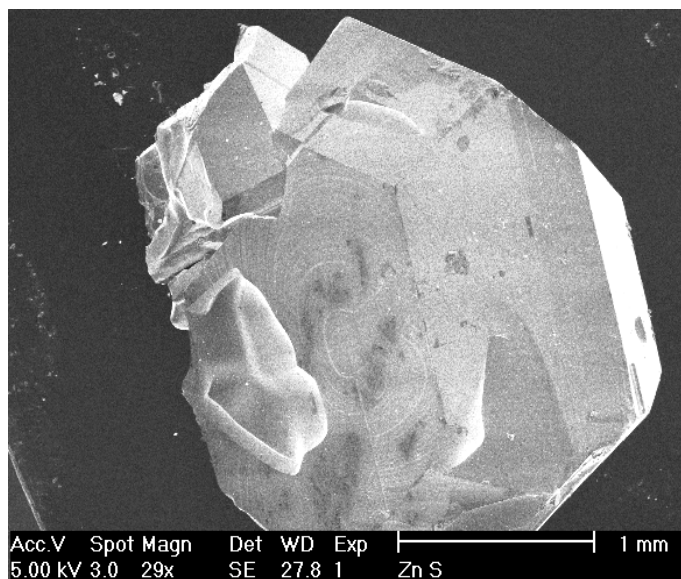


Fig. 6. ZnS single crystal in polyhedral form grown at 902 °C .

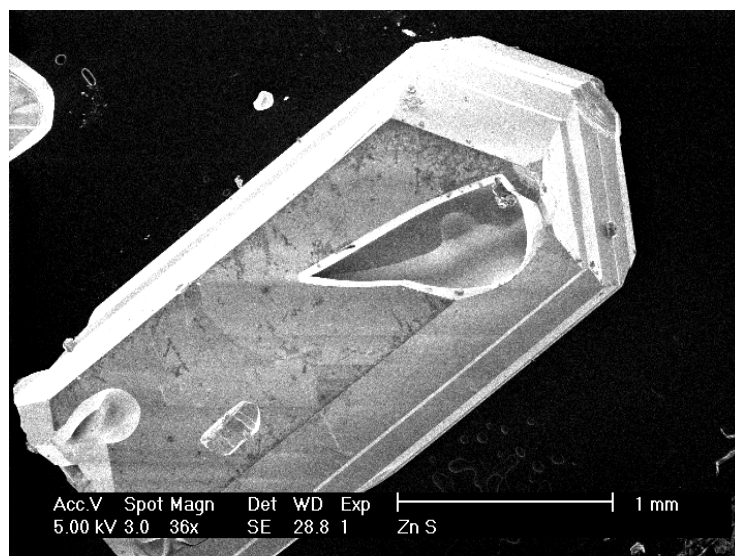


Fig. 7. ZnS single crystal in tablet form grown at 902 °C.

fluctuations in temperature of the deposition zone. This growth temperature (902 °C) lies in the range where ZnS crystals have stable cubic form [18]. Fig.6 shows a polyhedral form of ZnS crystal with (111) upper face on which steps in the form of spirals has been grown. The result of AAS measurements on these crystals showed that there was less than 5% deviation in stoichiometry of the grown crystals due to the deficiency of the

zinc atoms. It has been reported that deviation from stoichiometry causes well-developed (111) faces for ZnS and ZnSe crystals grown by CVT technique [13]. These grown steps on the surface indicate that screw dislocations have contributed to the growth process. Developing a big cavity on surface of ZnS grown crystal in Fig.7 is due to inconstancy in flow of material transported from source zone to deposition zone. ZnS crystals

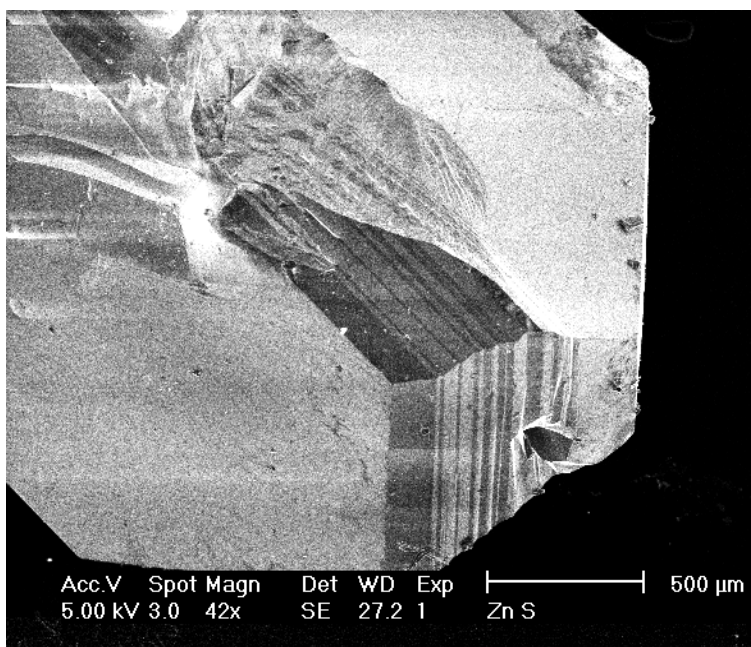
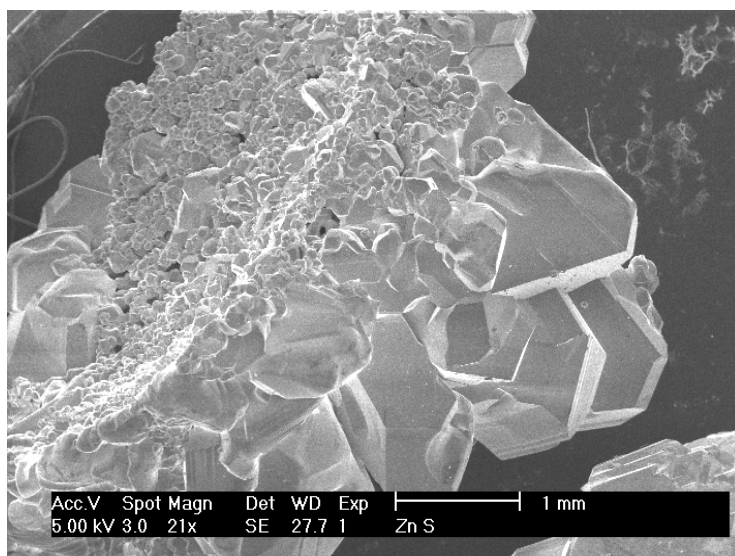


Fig. 8. ZnS single crystal in polyhedral form grown at 1102 °C





**Fig. 9.** Spurious nucleation of ZnS crystals at 1102 °C.

grown at 1102 °C (Fig.s 8, 9) showed the most imperfection and the lowest quality among all the grown crystals. For this growth temperature again has more slope compared to optimum value and transport of material will be more disturbed by small thermal fluctuations in growth zone. Fig 8 shows the ZnS crystal in polyhedral form in which the bright and dark stripes present the hexagonal and cubic structures respectively. These stripes may have the hexagonal wurtzite

structure, the cubic sphalerite structure or one of many possible polytypic structures. The above results were expected since 1102 °C lies in the temperature range where growth of these crystals with faulty structures was reported [18]. These stacking disorders consist of an intimate intergrowth of the cubic and hexagonal structures. The cubic (111) planes join the hexagonal (0001) plane and these junctures are observed as striations parallel to these planes



**Fig. 10.** Kinks formed on rough surface of ZnS crystals grown at 1102 °C

[25]. Fig. 9 shows the spurious nucleation which has been occurred due to sudden change in supersaturation at the growth zone caused by temperature oscillations [26]. The crystallites have different sizes and irregular habits. Series of kinks were also observed on the rough surface of the crystals grown at 1102 °C, which have been shown in Fig.10. This type of microstructure has also been observed on the surface of the ZnSe single crystals grown by CVT technique under high undercooling condition [27].

#### 4. CONCLUSIONS

A good agreement was observed between the prediction of a theoretical model and results of experiments in growth of ZnS crystals by CVT technique. For example for 2 mg/cm<sup>3</sup> concentration of iodine, the ZnS crystals grown at optimum temperature (1002 °C) showed better structural and microstructural qualities compared with the ZnS crystals grown at non-optimum temperatures (902 °C and 1102 °C). ZnS crystals grown at non-optimum temperatures showed more structural and microstructural imperfections due to instability in transport of materials inside the CVT tube.

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