SIMULTANEOUS CHEMICAL TRANSPORT REACTION OF ZINC- AND CADMIUM- CHALCOGENIDES

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SIMULTANEOUS CHEMICAL TRANSPORT REACTION OF ZINC- AND CADMIUM- CHALCOGENIDES

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To my parents, brothers and sisters

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ABSTRACT

Using thermodynamical data and a computer program a selection of source and deposit temperature at which 1:1 metallic atomic ratio of ternary single crystals of zinc cadmium chalcogenides can be synthesized from the binary Zinc- and cadmium- chalcogenides were determined. In the group of bromine, chlorine and iodine the best transporting agent was selected. At theoretically determined source and deposit temperature ternary single crystals of cadmium zinc sulfide and cadmium zinc selenide were synthesized by CTR. In this case, 2×10^{-6} mg/cm^3 of iodine were used as transporting agent in an ampoule of length 10 - 11cm with 14mm ID and 17mm OD. Finally the compositions of the synthesized ternary crystals were determined by AAS. The experimental results are in agreement with the theoretical predictions with very small error.

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1. INTRODUCTION

Single crystals of binary compounds of Zinc- and Cadmium-Chalcogenides are semiconducting material with a high potential for preparation of electronic devices such as green and blue light emitting diodes, Laser diodes and solar cells [1-6]. One of the methods by which such crystals can be produced is by chemical transport reaction (CTR) [7-16]. In chemical transport reaction one or more solids interact with volatile substances such as Cl_2, Br_2, I_2, HCl, and NH_4Cl at a higher temperature to one or two gaseous species in the source part of the reaction vessel and then they are transported as gases to another side of the reaction tube. At this end the chemical equilibrium shifts and the crystals will be deposited. Such technique is used for preparing more pure crystals and material of better crystal perfection than that obtained by the melt or solution growth process [17].

The growth of ternary II-VI single crystal semiconductors (e.g. $Cd_{1-x}Zn_xS$, $Cd_{1-x}Zn_xSe$ and $Cd_{1-x}Zn_xTe$) opens the possibility for the construction of novel optoelectronic devices [18-24]. The preparation of ternary and higher compounds of Cadmium - Zinc - Chalcogenides by means of chemical transport reaction is difficult, because it requires transport conditions which transports both binary chalcogenides in similar way from the source to the deposit site. By thermodynamical calculation, one can determine the pressure difference of the gaseous species between source and deposition range of the reaction tube for a given set of T_1 and T_2. By application of computer technique this calculation can be done for a lot of temperature combinations in short time. In a previous master thesis [25], the technique was applied to find optimal transport condition for binary systems. In this case the same technique is applied to

find transport conditions, which transports two binary systems to the same extent to get a ternary product of atomic ratios of 1:1 such as $Zn_{0.5}Cd_{0.5}S$, $Zn_{0.5}Cd_{0.5}Se$, $Zn_{0.5}Cd_{0.5}Te$.

In the second part of this work the calculated transport conditions are tested experimentally to show if it is possible to realise a simultaneous chemical transportation based on theoretical predictions.

For this purpose

- thermodynamical data for all the required substances were collected
- the computer program was modified
- theoretical calculations were performed for 18 transport systems
- binary powders of Zinc and Cadmium-Chalcogenides were synthesized
- an adequate two- zone transport furnace was constructed
- simultaneous CTR of Zinc- and Cadmium- Chalcogenides were conducted
- the binary powders and the ternary single crystals grown were characterized by Atomic Absorption Spectroscopy

2. LITERATURE SURVEY

2.1 Principles of Chemical Transport Reaction (CTR)

A chemical transport reaction is a reaction in which a solid source material reacts with a gaseous transport agent at a source temp. (T_s) to produce exclusively gaseous products, while at another location in the system at a deposit temp. (T_d) the reverse reaction occurs causing the deposition of the same solid (Fig. 1) [26]. In simple cases the reaction is demonstrated by the reaction scheme.

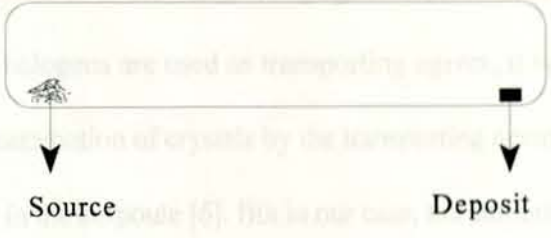
$$aA(s) + bB(g) \rightleftharpoons cC(g) + dD(g) \qquad 2.1$$

In this reaction , A denotes the substance to be transported

B denotes the transporting agent

C and D denotes the gaseous products obtained as the result of the interaction of the solid material with transporting agents at the source and a, b, c, and d are the stoichiometric coefficients.

Depending up on the thermodynamic properties of the transport reaction the deposition zone will be at lower or at higher temp. than the source temperature. Mainly, temperature, type and amount of transporting agent input can affect the transporting conditions [27].



$$aA(s) + bB(g) \rightarrow cC(g) + dD(g) \rightarrow aA(s) + bB(g)$$

Fig. 1 Growth by CTR

2.1.1 Temperature

The theoretically determined source and deposit temp. should be kept constant to get the required single crystal with the necessary stoichiometry. However, the higher temp. at the source will introduce a variation of transport rate of the adatoms, and the higher the temp. at the deposit zone may cause re-evaporation of the adatoms. As the result, the required crystals can not be produced. On the other hand, the lower temp. at the source may hinder the transport [28].

2.1.2 Concentration and type of the transporting agent

The concentrations of the transporting agent affect chemical transport by changing the transport rate. When halogens are used as transporting agents, it was observed that the rate of transport and the contamination of crystals by the transporting agent was increases with the concentration of halogens in the ampoule [6]. But in our case, the amount of transporting agent introduced into the reactor (ampoule) is very small and the contamination of our crystals may be negligible.

2.2 Binary systems with different transporting agents

The single crystals of ZnS, ZnSe, ZnTe, CdS, CdSe and CdTe have been grown successfully by many people and various methods.

2.2.1 Zinc sulfide

Growth of single crystals of ZnS by chemical transport has been achieved in Vycor capsule ranging from 0.40 to 2.20 cm inner diameter (ID) and 5.0 to 14 cm in length using iodine as transporting agent [10]. The iodine concentration which was employed ranged nearly from 0 to 7 mg/cm^3. The source temp. was maintained at 800 C, the growth region was at 800 C - ΔT, where ΔT ranged from 3^0C to 75^0C in various runs.

The synthesized crystals through CTR were transparent and color less to pale yellow- green in color. They frequently assumed the form of hexagonal plates. Crystals grown were subjected to

examination by powder and single - crystal diffraction techniques. At high concentration of iodine the product is entirely sphalerite while at low iodine concentration wurtzite structure was predominating. Intermediate iodine concentration produced crystals with severe stacking disorder.

The CTR of ZnS also conducted by using NH_4Cl and I_2 [29]. In this case different ampoule types and size were used. The amount of iodine or NH_4Cl was varied from 0.1 to 10.0mg/ml. The temp. of the source was varied from 840 - 1160^{0}C, and the temp of deposit was varied from 630 - 1070^{0}C (many experiments were conducted). The growth process was maintained for 40 - 60 hr then the crystals were either cooled rapidly by removing the whole ampoule from the furnace system, or cooled slowly over a period of 6 - 10 hr by pulling the ampoule through a slowly decreasing temperature range. Experimental results showed that crystals grown by NH_4Cl as transporting agent at the source and deposit temp. of 1160 and 1070^{0}C with 0.8 mg/cm^3 NH_4Cl produced perfect hexagonal crystals with max. size 4 - 5 mm and with a growth rate of 1.0mg/hr. On the other hand the crystals grown at 1060^{0}C (T_s) and 950^{0}C (T_d) with 0.5 mg/cm^3 produced perfect cubic crystals, max. size 5 - 10 mm with a transport rate of 17mg/hr. Using iodine generally resulted in the formation of heavily faulted blocks or boules. In the case of NH_4Cl no blocks or boules, only separated single crystals of up to 10 x 5 x 2 mm^3 were grown. The structure of the crystals obtained from various runs was also analyzed by X - ray Laue technique. The analysis results showed that crystals with the highest perfection are those grown by NH_4Cl.

2.2.2 Zinc Selenide

Growth of ZnSe crystal by CTR was studied by using I_2 (5 mg/cm^3) as transporting agent over the range of 750 - 900^{0}C in a quartz tube of 10cm long with 8mm ID and 15mm OD [7]. Under this condition single crystals of ZnSe up to 2cm in length have been grown with 3 to 5^{0}C thermal gradient. Growth continued for one to six months with the tubes stationary. About 12 hr were allowed for the crystals to cool from growth temperature of about 850^{0}C to 24^0 C with 5 C thermal gradient between the feed materials and the crystal grown region. In this study the best crystals were obtained in between 850 - 860^{0}C. Growth temp. less than ^{0}830 C gave polycrystalline growth while greater temperature than 890^{0}C gave no crystal growth. The Laue patterns and EPR measurements revealed that the ZnSe crystals grown by iodine through CTR were cubic with high crystal perfection.

2.2.3 Cadmium sulfide

The chemical transport kinetics of CdS was studied in a horizontal closed ampoule of 18cm long with 10cm ID using iodine as transporting agent at a source and growth temp. of 1173 and 1143^{0}K respectively [8]. In this case the overall pressure was varied in the range of 0.5 to 2.5 atm. When working at sufficiently high temperature there is no practical evidence of activation barriers at the gas - solid interfaces. By increasing the diameter and the pressure in the cylindrical ampoules the transport rate is increasing and it is controlled by thermal convective processes. Under this experimental condition the grown crystal's quality was not studied.

2.2.4 Cadmium Telluride

Growth of CdTe by CTR in a closed tube has been described in [30], where the transport agent is HCl obtained by thermal dissociation of NH_4Cl. A CTR has been carried out in quartz ampoules where geometry has been devised to reduce the thermal convection in the transport mechanism. The quartz ampoules were with diffusion parts of 2 - 3 mm ID separated into two parts (source and deposit) of the ampoule. Both sides are 10cm long and 1cm ID. In this case various source and deposit temperatures have been used for CdTe single crystal growth. A T_s of 800 - 700°C and T_d of 730 - 500 °C with NH_4Cl concentration varied between 0.22 - 0.3 mg/cm ^{3} were used. It was observed that when source temp. Was 800° C and deposit temp. was 660 - 730°C with NH_4Cl concentration 0.3 mg/cm^3 well-developed crystals in the shape of platelets were grown on the colder end of the tube. The transports were conducted for about 50 - 100 hr with the transport rate of 1.4 - 5.4 x 10^{-9} mole/sec. were observed. The transport rate increased as the difference between the temp. gradient increased (keeping the source temp. at 800°C). A Debye- Scherrer analysis showed that all the crystals have sphalerite structures, with a = 6.481Å.

2.3 Ternary Single Crystals

Ternary single crystals have been produced by various methods, but there is no report with respect to CTR for the synthesis of ternary single crystals of Zinc Cadmium Chalcogenides.

3. MATERIALS AND METHODS

3.1 Theoretical part

For the calculation of the transport conditions we used a model [31], which was constructed with the following simplifications:

1. The ampoule is divided into two equal parts as shown in Fig. 2

2. Half of the tube is at T_1 and half at T_2

3. The solid phase at T_1 and T_2 is in complete equilibrium with the vapour

The calculations were made for the following notations of the chemical transport reaction.

$$ZnS(s) + Cl_2(g) \rightleftharpoons ZnCl_2(g) + \tfrac{1}{2} S_2(g) \qquad 3.1$$

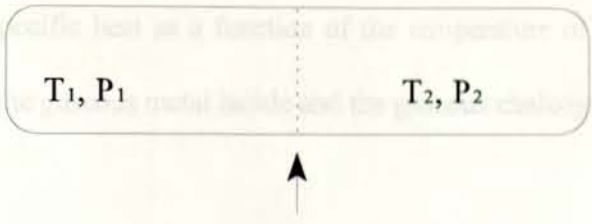
and the analogous formula for the following 17 transporting systems

ZnS with Br_2, and I_2 (2)

CdS with Cl_2, Br_2, and I_2 (3)

ZnSe, CdSe with Cl_2, Br_2, and I_2 (6)

ZnTe, CdTe with Cl_2, Br_2, and I_2 (6)



$$\Delta P = P_2 - P_1$$

Fig. 2 The ideal division of the ampoule according to the theoretical model

3.1.1 The Computer Program

The program for the calculation of the transport conditions was written in a previous master thesis in Turbo Pascal 6.0 (Borland International, Inc.). This program makes use of different thermodynamic data and the amount of transporting agents as inputs. For this purpose, the thermodynamical data were collected from reference [32], and the values are given in Table 1. The specific heat as a function of temp. is given in Ref. [32] in the form of

$$C_p = a + b \times 10^{-3} T + c \times 10^{6} T^{-2} \qquad 3.2$$

For simplification of the computer program, the constants $\Delta_r a$, $\Delta_r b$, and $\Delta_r c$ were calculated separately for the transport reactions according to:

$$\Delta_r a = a(ZnCl_2) + a(\tfrac{1}{2} S_2) - a(ZnS) - a(Cl_2) \qquad 3.3$$

and analogously for the other coefficients and transport reactions.

The values used for calculations are listed in Table 1 column 5 - 7 and the results in Table 2.

The program requires as input data the standard heat of formation (ΔH^0), the standard entropy (ΔS^0) and the specific heat as a function of the temperature of the solid chalcogenide, the gaseous halide, the gaseous metal halide and the gaseous chalcogenide.

Using the input data the computer program calculates the following for the transport reaction: The standard heat of reaction ($\Delta_r H^0_{298}$), the standard entropy ($\Delta_r S^0_{298}$), the heat of reaction for a given temperature ($\Delta_r H^0_T$), the entropy of reaction for a given temperature ($\Delta_r S^0_T$) and the free energy for a given temperature ($\Delta_r G^0_T$) according to the following equations:

$$\Delta_r H^0_{298} = \Delta_f H^0_{298}(ZnCl_2) + \Delta_f H^0_{298}(\tfrac{1}{2}S_2) - \Delta_f H^0_{298}(ZnS) - \Delta_f H^0_{298}(Cl_2) \qquad 3.4$$

$$\Delta_r S^0_{298} = \Delta_f S^0_{298}(ZnCl_2) + \Delta_f S^0_{298}(\tfrac{1}{2}S_2) - \Delta_f S^0_{298}(ZnS) - \Delta_f S^0_{298}(Cl_2) \qquad 3.5$$

$$\Delta_r H^0_T = \Delta_r H^0_{298} + \Delta_r a \times (T - 298) + \Delta_r b/2 \times 10^{-3}[T^2 - (298)^2] - \Delta_r c \times 10^6 [T^{-1} - (298)^{-1}] \qquad 3.6$$

$$\Delta_r S^0_T = \Delta_r S^0_{298} + \Delta_r a \times \ln(T/298) + \Delta_r b \times 10^{-3}[T - 298] - \Delta_r c/2 \times 10^6 [T^{-2} - (298)^{-2}] \qquad 3.7$$

In the same way the computer calculates $\Delta_r H^0_{298}$, $\Delta_r S^0_{298}$, $\Delta_r H^0_T$ and $\Delta_r S^0_T$ for rest of 17 transport reactions.

$$\Delta_r G^0_T = \Delta_r H^0_T - T\Delta_r S^0_T \qquad 3.8$$

In the rest step, the program calculates the chemical equilibrium constant K_p for a given temperature T according to equation

$$K_p(T) = \exp^{\frac{-\Delta G_T^0}{RT}} \qquad 3.9$$

The chemical equilibrium constant also related to partial pressures of the reactant and product species according to equation:

$$K_p = \frac{P(ZnCl_2)\sqrt{P(S_2)}}{P(Cl_2)} \qquad 3.10$$

and where $p(\frac{1}{2}S_2) = p(ZnCl_2) = X$, $P(Cl_2) = P^0(Cl_2) - P(ZnCl_2)$

Where p^0 is the initial pressure of halogen gases, X is the partial pressure of gaseous metal halide or gaseous chalcogenides ($\frac{1}{2}S_2$, $\frac{1}{2}Se_2$, $\frac{1}{2}Te_2$)

TABLE 1

Subs.	State	ΔH^0_{298} kJ/mol.	S^0_{298} J.mol/k	$C_p = a + b*10^{-3}T + c*10^6T^{-2}$ J/mol.k			T interval in ^0K
				a	b	c	
$ZnCl_2$	g	-267.3	277.1	61.71	-	- 0.43	298-2000
$ZnBr_2$	g	-185.8	303.8	58.16	-	-	298
ZnI_2	g	-63.4	328.2	58.16	-	-	298
$CdCl_2$	g	-205.2	294.7	63.3	-	-0.46	298 - 2000
$CdBr_2$	g	-144.9	315.5	65.4	-	-0.46	298 - 2000
CdI_2	g	-58.4	322.7	66.23	-	- 0.5	298 - 2000
ZnS	s	-205	57.7	49.25	5.27	-0.46	298 -1293
ZnSe	s	-170.3	77.7	50.17	5.77	-	298 - 1799
ZnTe	s	-119.2	77.8	44.1	18.74	-	298 - 1748
CdS	s	-154.6	74.4	44.56	13.81	-	298 - 1748
CdSe	s	-145.6	84.1	46.82	9.33	-	298 - 1512
CdTe	s	-97.9	93.2	52.51	19	-0.74	298 - 1372
Cl_2	g	0	223.1	36.61	1.08	-0.27	298 - 2000
Br_2	g	30.9	245.4	37.36	0.46	-1.3	298 - 2000
I_2	g	62.2	260.2	37.25	0.78	-0.05	298 - 2000
S_2	g	128.6	228.2	35.06	2.58	-0.29	298 - 2000
Se_2	g	136.7	243.6	44.6	-2.66	-0.25	298 - 2000
Te_2	g	160.4	262.2	34.64	6.62	-0.03	298 - 2000

TABLE 2

Reactions	$\Delta_r C_p = \Delta_r a + \Delta_r b * 10^{-3} T + \Delta_r c * 10^{6} T^{-2}$ J/mol.k		
	$\Delta_r a$	$\Delta_r b$	$\Delta_r c$
$ZnS(s) + I_2(g) \rightleftharpoons ZnI_2(g) + ½ S_2(g)$	-10.81	-4.76	0.365
$ZnS(s) + Br_2(g) \rightleftharpoons ZnBr_2(g) + ½ S_2(g)$	-10.92	-4.44	1.615
$ZnS(s) + Cl_2(g) \rightleftharpoons ZnCl_2(g) + ½ S_2(g)$	-6.62	-5.06	-0.335
$CdS(s) + I_2(g) \rightleftharpoons CdI_2(g) + ½ S_2(g)$	1.95	-13.3	-0.595
$CdS(s) + Br_2(g) \rightleftharpoons CdBr_2(g) + ½ S_2(g)$	1.01	-12.98	0.695
$CdS(s) + Cl_2(g) \rightleftharpoons CdCl_2(g) + ½ S_2(g)$	-0.34	-13.6	-0.335
$ZnSe(s) + I_2(g) \rightleftharpoons ZnI_2(g) + ½Se_2(g)$	-6.96	-7.88	-0.075
$ZnSe(s) + Br_2(g) \rightleftharpoons ZnBr_2(g) + ½Se_2(g)$	-9.07	-7.5	1.175
$ZnSe(s) + Cl_2(g) \rightleftharpoons ZnCl_2(g) + ½Se_2(g)$	-2.17	-11.74	-0315
$CdSe(s) + I_2(g) \rightleftharpoons CdI_2(g) + ½Se_2(g)$	4.46	-11.44	-0.575
$CdSe(s) + Br_2(g) \rightleftharpoons CdBr_2(g) + ½Se_2(g)$	3.54	-11.12	-0.285
$CdSe(s) + Cl_2(g) \rightleftharpoons CdCl_2(g) + ½Se_2(g)$	2.17	-11.74	-0.315
$ZnTe(s) + I_2(g) \rightleftharpoons ZnI_2(g) + ½ Te_2(g)$	-5.87	-16.21	0.035
$ZnTe(s) + Br_2(g) \rightleftharpoons ZnBr_2(g) + ½Te_2(g)$	-5.98	-15.89	1.285
$ZnTe(s) + Cl_2(g) \rightleftharpoons ZnCl_2(g) + ½ Te_2(g)$	-1.68	-16.51	-0.175
$CdTe(s) + I_2(g) \rightleftharpoons CdI_2(g) + ½ Te_2(g)$	-6.21	-16.47	0.275
$CdTe(s) + Br_2(g) \rightleftharpoons CdBr_2(g) + ½Te_2(g)$	-7.15	-16.15	2.565
$CdTe(s) + Cl_2(g) \rightleftharpoons CdCl_2(g) + ½Te_2(g)$	-8.5	-16.77	0.535

One can calculate the partial pressure of the metal halide (X) from the equilibrium constant. To do so one has to solve the following cubic equation:

$$\frac{X\sqrt{(0.5X)}}{(P^0-X)} = K_p(T) = \exp^{\frac{-\Delta_r G^0_T}{RT}} \qquad 3.11$$

The partial pressure differences were calculated on the assumption of diatomic sulfur, selenium and tellurium gases (for each reaction given in table 3) [10].

Halogen concentration: all calculations were performed by varying halogen concentration from 3×10^{-5} to 1×10^{-6} mol/c.c for each reaction given in table 3.

The program calculates for each pair of T_1 and T_2 between 300 - 1300°K in steps of 2.5°K and the corresponding Δp. The values of Δp were drawn in different colors. The advantage of this is that one can easily select the probable ranges in relatively short time.

Line drivers: Another program was formulated to draw the line of Δp that show the minimum and maximum value of the difference of the partial pressure ranges, and then by additional program all the colors were removed.

The printout: The graphical results printed out in each case of cadmium - chalcogenide was taken and overlapped with zinc- chalcogenide of those having the same concentration of halogen for determination of single T_s versus T_d sets for working condition.

3.1.2 Selection of T_s and T_d sets

For the simultaneous chemical transport reaction of zinc- and cadmium- chalcogenides, the point, in most cases at which the ΔP value 5×10^{-2} atm. and 10^{2} atm. lines intersected were selected, using this intersection point the source and deposit temperatures were determined in each case. At the intersection point the transport rates for both metal chalcogenide is approximately the same, and as a result the required 1:1 stoichiometric ratio will be obtained. Some of the calculated results are given in Table 3.

TABLE 3. T_s and T_d sets for different iodine concentration of simultaneous transport reaction

a) For ZnS and CdS

$[I_2]$ mol/cm^3	T_s (^{0}K)	T_d (^{0}K)	ΔT (^{0}K)	ΔP atm.	T_s (^{0}K)	T_d (^{0}K)	ΔT (^{0}K)	ΔP atm.
6×10^{-6}	1020	988	32	5×10^{-2}	-	-	-	-
4×10^{-6}	1037	962	75	5×10^{-2}	-	-	-	-
3 x 10-6	1044	950	94	5×10^{-2}	-	-	-	-
2×10^{-6}	**1050**	**925**	**125**	5×10^{-2}	970	940	30	10^{-2}
1×10^{-6}	-	-	-	-	960	900	60	10^{-2}

b)For ZnTe and CdTe

$[I_2]$ mol/cm^3	T_s (^{0}K)	T_d (^{0}K)	ΔT (^{0}K)	ΔP atm.
2.5×10^{-5}	506	500	6	5×10^{-2}
6×10^{-6}	538	506	32	5×10^{-2}
5×10^{-6}	538	494	44	5×10^{-2}
4×10^{-6}	540	490	50	5×10^{-2}
3×10^{-6}	550	488	62	5×10^{-2}
2×10^{-6}	**560**	**450**	**110**	5×10^{-2}

c)For ZnSe and CdSe

$[I_2]$ mol/cm^3	T_s (^{0}K)	T_d (^{0}K)	ΔT (^{0}K)	ΔP atm.	T_s (^{0}K)	T_d (^{0}K)	ΔT (^{0}K)	ΔP atm
1×10^{-5}	912	881	31	5×10^{-2}	-	-	-	-
9×10^{-6}	900	863	37	5×10^{-2}	-	-	-	-
2×10^{-6}	**915**	**800**	**85**	5×10^{-2}	850	825	25	10^{-2}
1×10^{-6}	-	-	-	5×10^{-2}	881	831	50	10^{-2}

3.1.3 Choice of the transporting agent

It was observed from the calculations, as the concentration of iodine for the transport reaction was increased, the T_s value was decreased and vice versa (see Table 3). Iodine is a better transporting agent than bromine and chlorine, while chlorine is the least. Generally seen bromine and chlorine cannot be used as transporting agent in simultaneous CTR of cadmium and zinc chalcogenide for the following reasons:

i) combinations of T_s and T_d where CTR is in relation 1:1 is possible were found only below 400 ^{0}K

ii) this combination at low chlorine and bromine concentrations

iii) the pressure difference (ΔP) between source and deposit parts of the ampoule were very low Therefore, we restricted the synthesis of ternary cadmium zinc chalcogenide crystals only by using iodine. The source and deposit temperature conditions for working determined from the graphical overlap of binary cadmium and zinc chalcogenide to conduct the experiment is given in Table 4.

TABLE 4

Sub.	T_s (^{0}K)	T_d (^{0}K)	ΔT (^{0}K)	$[I_2]$ mol/c.c	Δp atm
ZnS +CdS	1050	925	125	2×10^{-6}	5×10^{-2}
ZnSe + CdSe	915	800	85	2×10^{-6}	5×10^{-2}
ZnTe + CdTe	560	450	110	2×10^{-6}	5×10^{-2}

3.2 Experimental part

3.2.1 Preparation of quartz tube

The ampoule used in our experiments is made of quartz glass, cylindrical in shape with an inner diameter (ID) of 14 mm and an outer diameter (OD) of 17mm. The quartz ampoule was designed to the reactor by using oxy- acetylene flame with required length. The prepared ampoule was washed with nitric acid solution and distilled water several times then dried before the sample is introduced.

3.2.2 Preparation of cadmium and zinc chalcogenide binary powders

The synthesis of metal chalcogenides are possible in the range of 500 - 900^{0}C [6]. For the preparation of powders of ZnSe, ZnTe, CdS, CdSe, and CdTe powders of commercially available Zn, Se, S, Te and a metal strip of Cd were taken. The cadmium metal strip was grounded into fine powders.

3.2.2.1 Preparation of ZnSe and CdSe powder

1g of Zn with 1.2079g Se and 1g of Cd with 0.7025g Se in an atomic ratio of 1:1, were introduced in separates ampoules of 10 cm length. The ampoules were evacuated and flushed with nitrogen three times following evacuation Consequently. At the end, they were evacuated for about an hour and then sealed. The sealed ampoules were placed in the muffle furnace. The

temperature was slowly increased from room temperature to 500 ^{0}C in 12 hrs and maintained at this temperature for about 24 hrs. This slow heating is necessary to avoid any possibility of an explosion due to the strongly exothermic reaction between the elements [33]. After 24 hr heating they were cooled to room temperature. The substances were properly mixed and then placed in the furnace. The temperature was slowly increased to 600^{0}C in 2hrs time and maintained for about 6 hrs at this temperature. Finally, the power was turned off and the ampoules were removed from the muffle furnace.

3.2.2.2 Preparation of ZnTe, CdTe and CdS powder

The type and size of the ampoules used were similar with those of ZnSe and CdSe synthesis. In this case 0.512g Zn with 1g Te, 0.881g Cd with 1g Te and 1g Cd with 0.2853g S were introduced in three different ampoules respectively. The ampoules were evacuated and sealed with the same procedure as that of ZnSe and CdSe. The three ampoules were placed in the muffle furnace at room temperature, and the temperature was increased slowly to 600^{0}C in 5 hrs and kept at this temperature for about 26 hrs and then cooled to room temperature. The ampoules were taken from the furnace and the powders were mixed properly and then placed in the furnace in between 660 - 700^{0}C for 24hrs. Finally, they were cooled to room temperature.

3.2.3 Construction of transport furnace

The parts of our furnace are the heating metal wire support, metal wire wound on the support, heat- insulating paste fixing the metal wire, heat- insulating silicate fibers, metal jacket, closing metal plates and lids of the furnace tube. The metal wire which is the heating material is also called Kanthal wire.

The construction was done first by cleaning the cylindrical furnace tube in order to remove any impurities that may contaminate wire and the heat insulating pastes.

The furnace tube is 50 cm long with 2 cm ID and 2.4 cm OD. The wire was coiled up uniformly at two separate positions of the cylindrical furnace tube with a separation of 1cm space from each other at the center. The gap between each coiled wire is nearly 1.5mm. The wire was wound on a total of 26cm length, which means on 13cm from both sides.

After the winding of wire was completed, it was washed with distilled water three times properly and was allowed to dry. Then it was followed by cementing with heat-insulating paste almost on 30cm parts leaving 10cm from of the ends and we let to drying for one week by exposing to air at a room temp.

After drying, it was wrapped with cotton like silicate fibers and placed in a metal jacket. Finally, these silicate fibers were closed using metal plates.

This furnace is different from the previously prepared one [25], which was only designed to prepare binary single crystals. The wire winding is at two separate positions. Each wire winding (a and b of Fig. 3)is connected to each transformer as a result, almost, accurate regulation of the source and deposit temperature is possible. If one makes use of one transformer, in the preparation of ternary crystals, the temperature is not controlled properly and the expected 1:1

stoichiometric ratio is impossible. The parts of a constructed furnace is given in Fig.3.

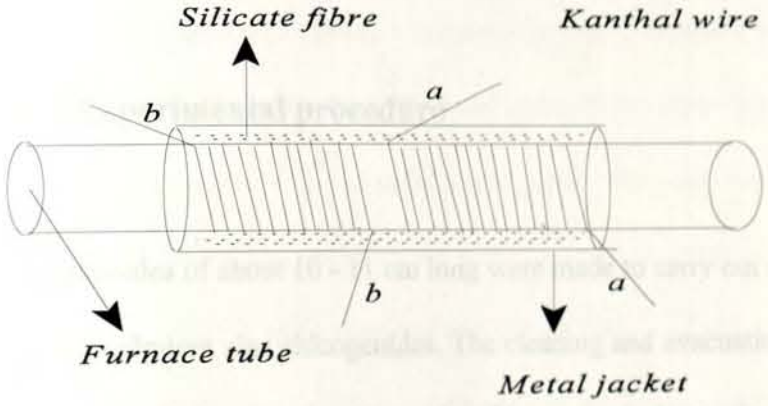


Fig. 3. Transport furnace

3.2.4 Measurement and Regulation of Temperature

Temperature is most conveniently measured with thermocouples made of two different metals or alloys. They occupy less space, have small heat capacities, follow changes of the temperature quite rapidly [34].In our case the furnace was regulated by type N thermocouple (Nickel-Chromium - Silicon alloy vs Nickel - Silicon - Magnesium alloy) which is connected to a digital voltmeter constructed for this purpose. The type N thermocouple temperature value and voltage output were taken from [35]. Since the thermoelectric power of a thermocouple may deteriorate during it is use due to oxidation, surface reaction and impurity contamination that may diffuse from the furnace tube [17], it was calibrated before use at 0^0C using ice and at boiling points of

water. Further adjustments were made to correlate the reading on the voltmeter with the value in the table at different temperature.

3.2.5 The transport experiment

3.2.5.1 Experimental procedure

Quartz ampoules of about 10 - 11 cm long were made to carry out synthesis of ternary single crystals of cadmium zinc chlcogenides. The cleaning and evacuation of the ampoules are the same as for the binary powder preparation. However, during sealing time the part of a quartz ampoule loaded with mixed powders of iodine, cadmium chalcogenide and zinc chalcogenide were inserted in a tube containing ice mixed with common salt. This prevents evaporation of our starting materials.

Before the ampoules were placed in the proper growth temperature range, the deposit zone was heated at a higher temperature to get a back transport. Such heat treatment is important mainly for cleaning the nucleation area by removing any volatile impurities.

At the end of transporting time the deposition zone must be kept at high temperature to prevent deposition of any volatile impurities and transport agent on the crystal surface. Moreover, the temperature must be cooled to room temperature before removing the ampoule from the furnace in order to prevent risk of an ampoule explosion [16].

3.2.5.2 Synthesis of Cadmium Zinc Sulfide Crystal

0.1g of ZnS (commercially available chemical), 0.1483g of CdS and 4mg iodine were introduced into cleaned and properly designed quartz ampoule of final length 10.5 cm of the same type of quartz ampoule used previously. The ampoule was evacuated, flushed with nitrogen gas consequently after evacuation three times and sealed by the same procedure given under 3.2.5.1. The sealed ampoule was slowly inserted in the furnace with end containing the started materials at low temp. By slowly increasing the tap position on the transformer on both sides, the material was subjected to 500^{0}C while the other end was at 700^{0}C for about 12 hrs. After this time the direction of temp. gradient was changed slowly and the source material was subjected to 775^{0}C while the deposit end at 652^{0}C for a transporting time of 56 hrs.

3.2.5.3 Synthesis of cadmium zinc selenide crystal

Following the above experimental procedure, 0.1g ZnSe, 0.1326g CdSe and 4mg of iodine (2 x 10^{-6} mol/c.c) were introduced into a cleaned ampoule. The ampoule was evacuated and flushed with nitrogen followed by evacuation consequently three times, and sealed as stated above.

The sealed ampoule was first placed in two zone furnace horizontally. The heating started with the deposit part at a temperature higher than the powder to perform a thermal cleaning of the nucleation site. By slowly increasing the tap position on both transformers until the temperature reading is 640^{0}C at the deposit site and 500^{0}C at the source. This temperature was maintained for about 10hr. Then for transporting purpose deposition temperature (T_d) was slowly decreased

to about 527^{0}C and the source temperature (T_S) was increased to about 642 C. After 42 hrs transporting time, a reverse temperature gradient heating was done for about 6 hrs and slowly cooled to room temperature. Finally, the ampoule was removed from the furnace.

3.2.5.4 Synthesis of Cadmium Zinc Telluride Crystal

0.1g ZnTe, 0.1244g CdTe and 4.3mg of iodine were introduced in a cleaned and dried 11 cm quartz ampoule. The ampoule was evacuated and sealed by the same procedure given under 3.2.5.1, and placed at the center of the two zone furnace. Heating started in a reverse direction keeping the powder portion at lower temperature of about 300^{0}C and the deposit part at 500^{0}C for 10hr. Then the deposition zone temperature was decreased to 177^{0}C slowly keeping the source zone at 287^{0}C. This temperature was maintained for about 40 hrs.

4. Characterization of the product by atomic absorption spectroscopy (AAS)

4.1 Use and principle of AAS

AAS is used primarily for quantitative elemental analysis of metals. It does not differentiate between a metal as a free atom, an aqueous metal ion, or a metal ion or atom in a compound. It instead measures how much of the element present regardless of the form or forms in which it is found in the sample [36, 37].

In AAS a flame is used to break compounds apart into their individual free atoms before absorbing electromagnetic radiation (light beam) by evaporating the solvent. The beam of light has the same frequency that the excited atoms would themselves emit. These free atoms absorb energy from the light beam and excited then the beam leaves the high - temp. region with a reduced intensity. This is the basis of AAS for quantitative analysis. The more atoms present of the type that can absorb the light radiation, the lower will be the intensity of the transmitted light. The absorbance of radiation is related to the concentration by Beer`s law [38], equation 4.1 below.

$$A = \epsilon bc \qquad 4.1$$

Where ϵ = absorption coefficient

b = path length and

c = concentration of the solution

4.2 Standard calibration curve

Calibration curves are determined experimentally by preparing a series of standard solutions, each with a known concentration of the absorbing solutions. The absorbance of unknown concentration of the same type of element in the sample will be measured. The concentration is determined from the calibration curve. However, in our case, all calculations and preparation of a series of standard solution were performed by a computer attached to AAS.

For analysis of Cd and Zn, 3 ppm Cd and 1.5 ppm Zn standard solutions were prepared. AAS has high sensitivity detection limit at and below 3 ppm Cd and 1.5 ppm Zn concentrations. Calibration curves for both were prepared by computer through dilution of standard solution.

4.3 The quality of data

All analytical results are subject to error, for a variety of reasons. For analytical data to be meaningful, it is essentially that the error involved in the procedure be measurable. The most commonly used method of presenting the quality (reliability) of results is in terms of standard deviation (δ). The probability of a measurement lying within a range of approximately $\pm 2\delta$ and $\pm 3\delta$ of the mean value would be 95% and 99.7% [39], respectively.

4.4 Determination of composition by AAS

To determine Zn and Cd content in our synthesized homogenized binary powder and ternary crystals of zinc- and cadmium- chalcogenide, a small sample was taken from each synthesized product and weighed, placed in cleaned and dried 25ml flask, dissolved in concentrated nitric acid then diluted to the volume.

When the surface of ternary crystals of zinc cadmium sulfide was observed, it had shown two different colors, red- brown at the outer (on very small parts) of red- orange surfaces at the inner deposit surface. Therefore, the sample was taken from both for analysis. The results are given in Table 5 with 99.7% confidence interval. The theoretically expected values are also given in the same Table, a and b denote sample taken from outer and inner parts of zinc cadmium sulfide crystal respectively.

TABLE 5. AAS analysis results for synthesized ternary crystals

Compoud (sample type)	AAS analysis of Zn and Cd in the sample in mg/L		Theoretical expected Zn and Cd in the sample in mg/L		Mole ratio from AAS analysis.	Total mass taken in mg for analy.
	Zn	Cd	Zn	Cd	Cd :Zn	
$Cd_xZ_{1-x}S^a$	1.565 ± 0.001	1.954 ± o.002	2.162	3.717	0.73 : 1.0	0.2
$Cd_xZ_{1-x}S^b$	17.809 ± 0.003	30.086 ± 0.004	18.375	31.598	0.98 : 1.00	1.7
$Cd_xZ_{1-x}Se$	14.726 ± 0.004	28.156 ± 0.007	14.799	25.449	1.0 : 0.9	1.9

Where $0 \leq x \leq 1$

5. RESULTS AND DISCUSSION

5.1 Theoretical results

The main purpose of the theoretical part is to find a combination of T_s and T_d at which a CTR with 1:1 atomic ratio of Zn and Cd is possible using halogen as transporting agent. From the theoretical calculation bromine and chlorine cannot be used for simultaneous CTR of zinc- and cadmium- chalcogenide for the reasons explained earlier.

For ZnS and CdS simultaneous transport with I_2 is possible at source temperature of 775^{0}C and at deposit temperature of 652^{0}C.

For ZnSe and CdSe simultaneous transport with I_2 is possible at source temperature of 642^{0}C and at deposit temperature of 527^{0}C.

For ZnTe and CdTe simultaneous transport with I_2 is possible at source temperature of 287^{0}C and at deposit temperature of 177^{0}C. .

5.2 Transport experiment

The theoretical results were verified by experimental using the source and deposit temp. theoretically determined. By simultaneous chemical transport of cadmium- and zinc- selenide a dark-grey crystal was produced with the growth rate of 5.2 mg/hr. In the case of zinc- and cadmium- sulfide a red - orange crystal in the inner part of the deposition and a red brown colored crystal at the outer part of the deposition was obtained with the growth rate of 4.3 mg/hr.

In the synthesis of cadmium- and zinc- telluride ternary crystals, no transport was occurred at the calculated conditions. The chemical transport reaction at this low temperature is hindered mainly for kinetic reasons. Due to low temperature:

i) the reaction of ZnTe with iodine at the surface of the source material is hindered.

ii) the diffusion of the gases is too low.

The experimental conditions and results are summarized in Table 6, while the temp. profile of the furnace employed for the transport experiments is given in Fig 4.

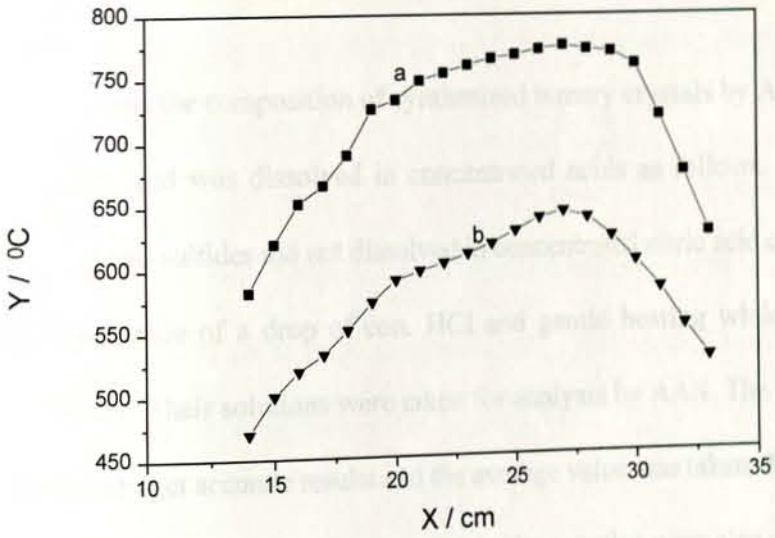


Fig. 4 Temperature profiles of the furnace in the experiment of ternary crystals of

a. Zinc cadmium sulfide (T_s at 27 cm and T_d at 16.5 cm)

b. Zinc cadmium selenide (T_s at 27 cm and T_d at 16.5 cm)

TABLE 6

Sub.	weight of source (g)	weight of product (g)	[Iodine] (mg/cm^3)	tube vol.(cm^3)	Temp. gradient (^0K)	Tran. Time (hrs)	Transport rate (mg/hr)
A	0.2483	0.2429	0.254	16.17	1048 - 925	56	4.3
B	0.2326	0.2176	0.254	16.17	915 - 800	42	5.2
C	0.2244	0	0.254	16.94	560 - 450	40	0

(where A= ZnS + CdS, B = ZnSe + CdSe, and C = ZnTe + CdTe ternary crystals)

5.3 Determination of composition

To determine the composition of synthesized ternary crystals by AAS small sample was taken from each and was dissolved in concentrated acids as follows. The ternary zinc cadmium selenides and sulfides did not dissolved in concentrated nitric acid even after gentle heating, but in the presence of a drop of con. HCl and gentle heating while shacking, they dissolved completely. Their solutions were taken for analysis by AAS. The measurements were done in triplicates to get accurate results and the average value was taken. The probable deviation of the result found by AAS from the true value in the samples were also given by $\pm 3\delta$ which is in the confidence interval of 97.7%. As one can see from Table 5, the deviation observed is very small. The chemical composition of each sample was determined based upon the AAS results and the following chemical formulas $Cd_{0.42}Zn_{0.58}S^a$, $Cd_{0.496}Zn_{0.504}S^b$, and $Cd_{0.53}Zn_{0.47}Se$ were calculated. As it can be seen from the chemical formulas, the outer part of cadmium zinc sulfide is rich in zinc while the bottom one is almost with the required atomic ratios of Zn and Cd, which is the same as the theoretically expected product. From this we can conclude that the material

transported in the first hours has exactly the stoichiometric composition as expected. At the end of the transport experiment, perhaps the CdS was finished and results in a change of stoichiometry.

Another possibility is that the long time Constance of the temperature profile of the furnace is not as good as expected.

The cadmium zinc selenide crystal is only a few more rich in cadmium than zinc as one can see from the chemical formula. This very good agreement with the expected results has different reasons:

i) the transport was performed in a temperature range which is quite easy to handle with our equipment

ii) the transport rate is high enough to get a result in quite short time, which minimizes the influence of the temperature fluctuation of the furnace.

The deviation of stoichiometric ratios of metals from 1:1 in the case of $CdZnS^{b}$ is lower than that of CdZnSe. Generally observed, both synthesized crystals of zinc cadmium sulfide and zinc cadmium selenide are in good agreement with theoretically determined one, in spite of many difficult and influencing factors that hinder CTR.

6. CONCLUSION

Thermodynamic calculations can give a useful information in selecting favorable transporting agents and also to determine the source and deposit temperatures at which the synthesis of 1:1 atomic ratio of Zn: Cd ternary single crystal is possible.

By thermodynamic calculation it was found that a simultaneous chemical transport of ZnS and CdS is possible at source temperature of 775^{0}C and at deposit temperature of 652^{0}C with I_2.

For ZnSe and CdSe simultaneous transport with I_2 is possible at source temperature of 642^{0}C and at deposit temperature of 527^{0}C.

For ZnTe and CdTe no simultaneous transport with I_2 is possible.

For experimental realization a two-zone furnace was used and ternary single crystals were synthesized. The synthesized crystals were analyzed by AAS. The results found were in good agreement for both cadmium zinc sulfide and cadmium zinc selenide. This new method of computer program had some success in intepreting a simultaneous CTR of two binary compounds.

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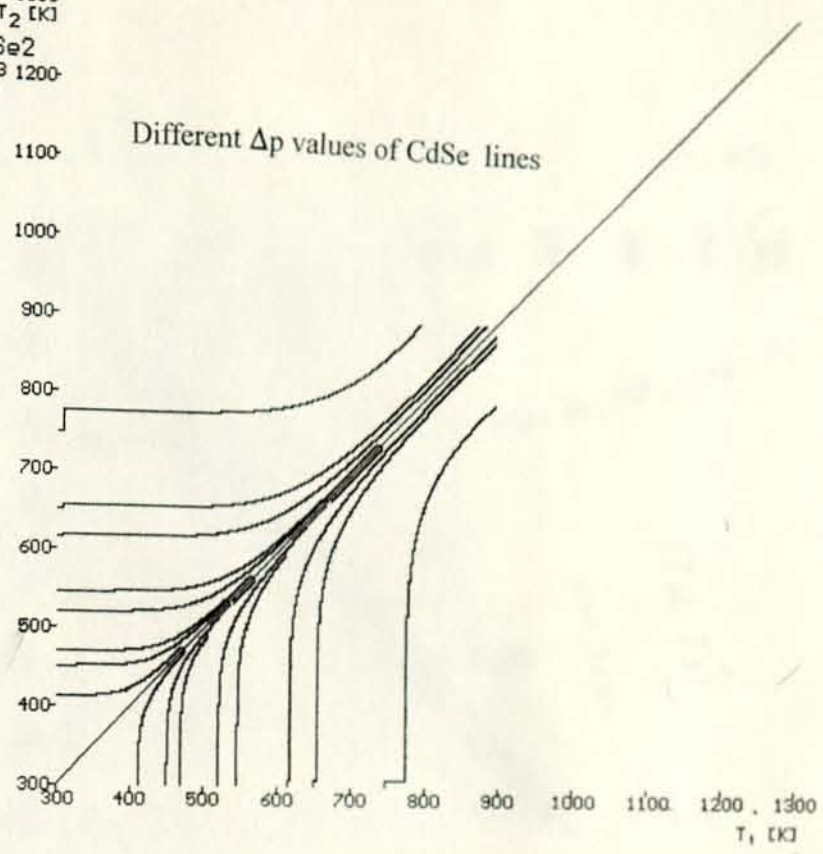
APPENDIX

CdSe + I2=CdI2 + 0.5Se2

Halogen 0.000002 mol/cm^3

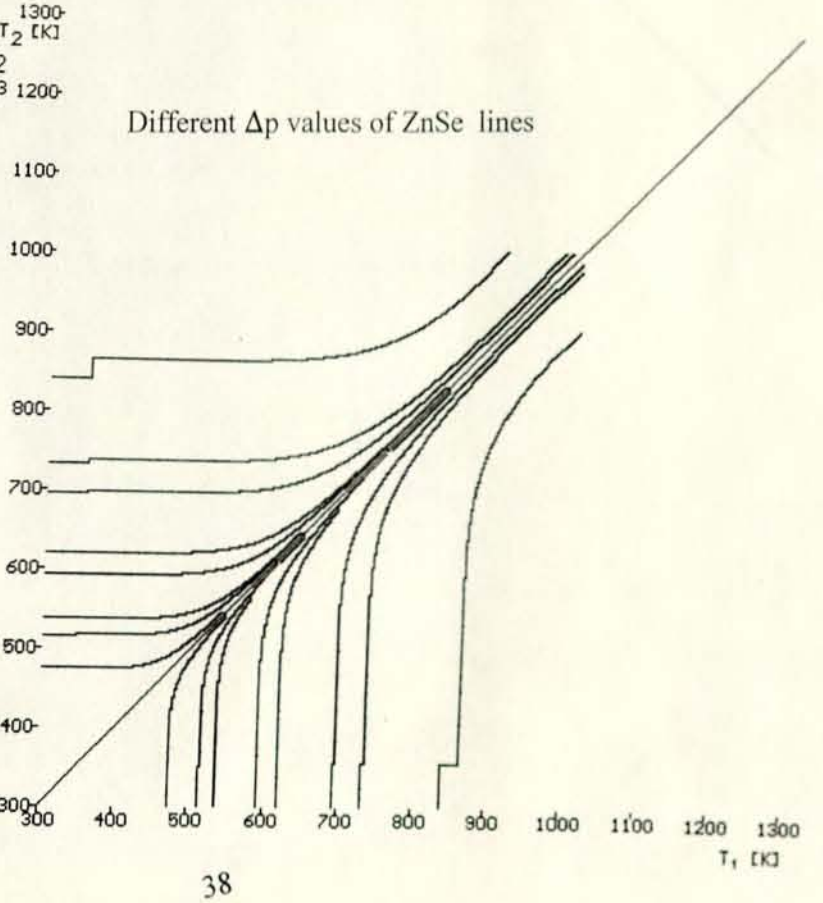
$d_f H_{298}$	MCh	-145.60	kJ/mol
	X_2	62.20	kJ/mol
	MX_2	-58.40	kJ/mol
	Ch_2	136.70	kJ/mol
$d\ S_{298}$	MCh	84.10	J/molK
	X_2	260.20	J/molK
	MX_2	322.70	J/molK
	Ch_2	243.60	J/molK
c_p	A	4.46000000	
	B	-11.44000000	
	C	-0.57500000	

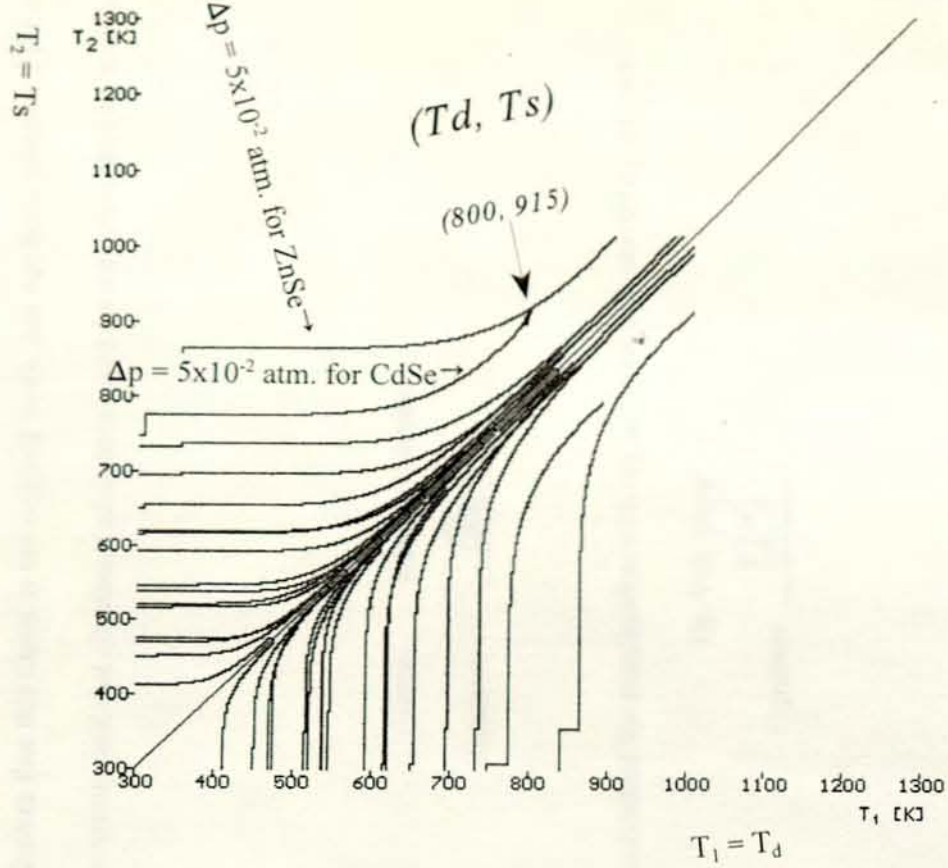


ZnSe +I2=ZnI2 +0.5Se2

Halogen 0.000002 mol/cm^3

$d_f H_{298}$	MCh	-170.30	kJ/mol
	X_2	62.20	kJ/mol
	MX_2	-63.40	kJ/mol
	Ch_2	136.70	kJ/mol
$d\ S_{298}$	MCh	77.70	J/molK
	X_2	260.20	J/molK
	MX_2	328.20	J/molK
	Ch_2	243.60	J/molK
c_p	A	-6.96000000	
	B	-7.88000000	
	C	-0.07500000	



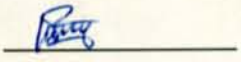


Different Δp values of ZnSe and CdSe overlapped lines

DECLARATION

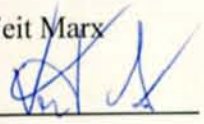
I, the undersigned, declare that this thesis is my original work, has not been presented for a degree in any other university, and that all sources of material used for the thesis have been duly acknowledged.

Name: Kebede Keterew

Signature 

This thesis has been submitted for examination with my approval as a university advisor

Dr. Veit Marx

Signature 

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