IARJSET

ISSN (Online) 2393-8021
ISSN (Print) 2394-1588

International Advanced Research Journal in Science, Engineering and Technology
Vol. 3, Issue 5, May 2016

The Processes and Enthalpies in Synthesis of Cu_2ZnSnS_4 in Molten CdI_2

Godswill Nkwusi[1], Inga Leinemann[1], Mare Altosaar[1]

Institute of Materials Science, Tallinn University of Technology, Estonia[1]

Abstract: Synthesis of Cu_2ZnSnS_4 (CZTS) in molten CdI_2 for solar cell absorber layer in monograin powder form is studied. The aim is to understand the chemical reactions and to describe the conditions for the synthesis of CZTS starting from binary compound precursors. It is found that the formation of Cu_2ZnSnS_4 proceeds mainly in the liquid phase of CdI_2 where CdS and $Zn_{1-x}Cd_xS$ form and initiate the formation of $Cu_2Zn_{1-x}Cd_xSnS_4$. The formed phases in the mixtures of CdI_2 with precursor compounds detected by XRD and Raman analyses are presented. The formation enthalpy for Cu_2SnS_3 and Cu_2ZnSnS_4 are13±2kJmol^{-1} and 8±2 kJmol^{-1} respectively.

Keyword: Cu_2ZnSnS_4, $Cu_2Zn_{1-x}Cd_xSnS_4$, Monograin powder, Enthalpies.

I.INTRODUCTION

CZTS monograin layer solar cells have shown power conversion efficiency of 9.4 % (measured from the active area of solar cell) [1]. Monograin technology (MGT) explores the use of suitable flux to aid the growth of single crystalline CZTS powder particles. As the monograin powder growth is carried out at high temperatures in a molten salt, the semiconductor compound crystals are doped with the constituent elements of the used salts (KI, NaI) at the level of their solubility at synthesis temperature. The solubility of precursor compounds in KI was determined as follows: 3.6 mole% CuSe, 0.27 mole% SnSe and 0.086 mole% ZnSe [2].

The solubility of $Cu_2ZnSnSe_4$ in KI was 0.61 mole% [2]. In addition, the doping of the synthesized monograin powder with Na and K, also with Cl, has a rather big influence on the monograin absorber material properties [3-4].

Using CdI_2 as a flux in monograin powder growth allows to produce a material without K/Na doping and to study the influence of intentional Na and/or K doping of CZTS. I. Leinemann (Klavina), studied the formation of CZTSe in NaI and KI and determined CZTSe formation reactions enthalpies [5-6]. It was also found that in the synthesis of $Cu_2ZnSnSe_4$ in CdI_2, Cd from CdI_2 incorporated into the crystals of CZTSe forming a solid solution of $Cu_2Zn_{1-x}Cd_xSnSe_4$, however, the formation of Cu_2ZnSnS_4 in CdI_2 and the reaction enthalpies have not been studied yet.

In this report, we present the reaction path of CZTS synthesis in CdI_2 starting from binary compound precursors. In this study, various mixtures of the individual precursors with CdI_2, as well as the precursor mixtures for the synthesis of CZTS in CdI_2 were used. We also report the chemical reactions and their enthalpies occurring in the growth process. All chemical reactions and enthalpy calculations are based on DTA-DSC analysis data and on phase changes determined by XRD and Raman analyses.

II.EXPERIMENTAL

Copper Zinc Tin Sulphide (CZTS) monograin powder was synthesized from a mixture of precursors (Cu_2S+SnS+ZnS+S) in the presence of molten phase of CdI_2. Separate quasi-binary mixtures (Cu_2S+CdI_2), ($ZnS+CdI_2$), ($SnS+CdI_2$) ($S+CdI_2$), also mixture for ternary Cu_2SnS_3 (CTS) compound ($Cu_2S+SnS+S+CdI_2$) were studied as described in [7]. An empty quartz ampoule was used as a reference for the DTA measurements. Pure CdI_2 was selected as the reference material for the DTA-DSC enthalpy calibrations for two reasons; firstly, the processes taking place in the synthesis occur in the same temperature region as the melting of CdI_2 and secondly, our experimentally determined melting point of CdI_2 coincide with the value found from literature (T_{melt}= 385°C) [8]. Our readings from DTA curves in µV.s. were converted to J/mol using the value of enthalpy of fusion of CdI_2 (15.31kJ/mol [9]) considering that our experimental heat value for melting of CdI_2 is 666 ± 2 µVs which corresponds to ≈5.23J (constant for our calculations). The DTA heating's and cooling's were carried out in two runs. The obtained energy values were used for the evaluation of the enthalpies of the occurring processes with error margin estimated as 5 %, given as the largest deviation of the individual process value from the average value. The applied heating and cooling rates from room temperature to 800°C were 5 and 10°C per minute, respectively. After recording the thermal effects by DTA, the changes in the phase composition of different precursor mixtures with CdI_2 were determined by Raman and XRD analyses. For the phase analyses, separate mixture samples with bigger amounts but in the same molar proportions as for DTA were prepared for each thermal effect observed in the DTA curves. The samples were heated in closed quartz ampoules for 4 hours at temperatures slightly higher than the observed thermal effects in DTA curves. After heating, the bigger samples were quenched from the heating temperature to room temperature in cold water. The heated and quenched powder samples were analyzed by SEM, EDX, Raman and XRD methods both before and after separation of CdI_2 (by washing with deionized water).

DOI 10.17148/IARJSET.2016.3524

Details of the used analytical set-ups are reported elsewhere [10,6].

III.RESULTS AND DISCUSSIONS

The melting temperatures of the studied mixtures (Cu_2S+CdI_2), ($ZnS+CdI_2$), ($SnS+CdI_2$), ($Cu_2S+SnS+S+CdI_2$) and ($Cu_2S+SnS+ZnS+S+CdI_2$), picked up from DTA curves, are presented in Figure 1. It can be seen that the melting of the precursor mixtures with CdI_2 takes place at lower temperatures than the melting temperature of pure CdI_2 (385 °C) [8]. The lowering of melting temperatures shows some solubility of the precursors in molten CdI_2 and/or the formation of new phases.

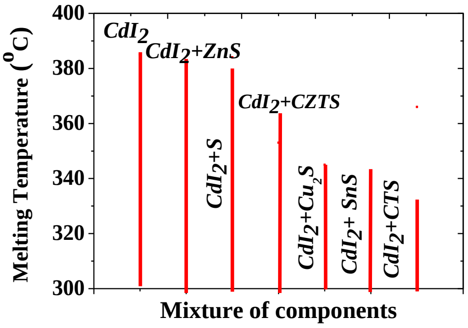

Fig 1. Melting temperatures of studied mixtures as determined from DTA curves

A. CdI_2

At temperatures above the melting point, CdI_2 exists in gaseous as monomeric $CdI_{2(g)}$ and dimeric $Cd_2I_{4(g)}$ forms [11-13]. According to Shushic et.al. and Corbett et.al. [14], molten CdI_2 has a brown colour, since a certain amount of free iodine is always in equilibrium with the melt [15]. Iodine is known as an oxidizing agent which may limit the reactions between CdI_2 and the precursors. The DTA probe of pure CdI_2 (see Figure 2) gave an endothermic effect at 385^{O}C in heating and an exothermic effect at 366^{O}C in cooling cycle which can be attributed to the melting and freezing of CdI_2 with enthalpy signal of 666.± 2 µV.s. This signal is equal to 5.23J, as calculated from the obtained peak area for correspondent 0.00034 mole of CdI_2 in the ampoule (molar mass of CdI_2=366.22 g/mol and the molar fusion enthalpy value for pure CdI_2 is 15.31kJ/mol) .

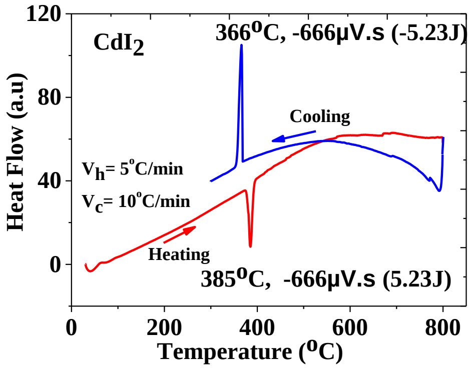

Fig 2. DTA curves of CdI_2

B. CdI_2 + Cu_2S

By phase analyses the sample of the mixture heated just above the melting temperature of CdI_2 revealed the formation of CuI, while Cu_2S had been transformed to $Cu_{1.96}S$ at 353^{o}C, correspondently to the Cu-S phase diagram [16]. In the DTA curves of the mixture of CdI_2 + Cu_2S (see Figure 3), there is seen an endothermic melting effect at 353 ^{O}C and an exothermic effect of freezing of CdI_2 at 338^{O}C. We can observe a decrease in the energy value of melting process from 5.23 J (666 µV.s.) for pure CdI_2 to 2.1 J (264 µV.s) in CdI_2+Cu_2S mixture. This decrease can be ascribed to the simultaneous exothermic reactions occurring alongside the melting of CdI_2. By XRD and Raman, different compounds - $Cu_{1.96}S$, CuI, $Cu_2Cd_3I_4S_2$, CdS and Cu_4Cd_3 - were found in CdI_2+Cu_2S mixtures heated for 4 hours at temperature a little bit above the melting point of the mixture (353 ^{O}C) (see Tabel 1). This confirms the chemical interaction between the flux material and Cu_2S. By XRD and Raman analyses, we found that some of these processes occurring during the melting and freezing of the mixture (CdI_2+Cu_2S) are reversible: Cu_2S, as observed by XRD, transformed to $Cu_{1.96}S$ and re-transformed to Cu_2S by cooling down - that is in accordance with the report [16-17]. In the heating process, in addition to the main fusion peak at 353^{O}C there is seen another endothermic DTA peak at 400^{o}C. The phase analysis of the bigger sample heated and quenched at 420^{o}C shows that this peak corresponds to the decomposition of $Cu_2Cd_3I_4S_2$ with formation of CdS, CuI_2 and Cu_4Cd_3 (see equation (5) in the Tabel 1) with summary thermal effect of 77 mVs (0.6J).

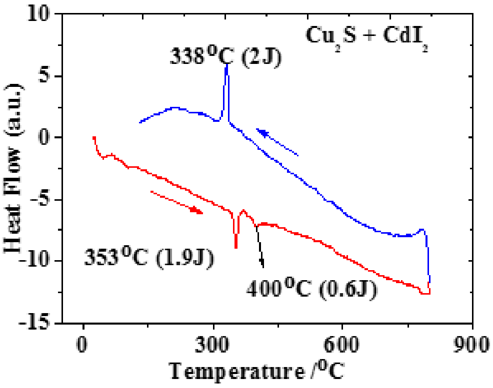

Fig 3: DTA curves of CdI2+Cu2S

C. CdI_2 +ZnS

The DTA heating and cooling curves of this mixture are presented in Figure 4. It shows an endothermic peak at 382^{o}C in the heating cycle, slightly lower than the melting temperature of pure CdI_2 (T_{melt}=385^{o}C) with the thermal effect of 2.7 J, that is much lower than in the melting of pure CdI_2 (5.23J). It means that some exothermic process compensates the endothermic melting effect. However, no new phases other than CdI_2 and ZnS were found by XRD and Raman in the sample heated and quenched at 385^{o}C, may be due to the low sensitivity of XRD. In the cooling curve two exothermic peaks at 354^{o}C and 338^{o}C are seen. This implies that CdI_2 in the mixture with ZnS melts close to the melting temperature of its pure form.

DOI 10.17148/IARJSET.2016.3524

Table 1: The annealing conditions, determined phases, reactions and calculated ΔG values for $CuS+CdI_2$ quasi-binary system

Annealing conditions	**Phases By Raman and XRD**	**Reactions**		**ΔG $kJmol^{-1}$**	
Heated to 353°C, annealed for 4 hours	CuS, $Cu_{1.96}S$, CuI, $Cu_2Cd_3I_4S_2$ CdS, Cu_4Cd_3	(1)	$Cu_2S+CdI_2 \leftarrow 2CuI+CdS$ [18-20]	-49 | T=300°C	-31.5 | T=400°C
		(2)	$CdS+Cu_2S+2CdI_2 \leftrightarrow Cu_2Cd_3I_4S_2$	Proposed	
Heated to 400oC, annealed for 4 hours		(3)	$Cu_2S + CdI_2(g) = 2CuI + CdS$ [18,20]	-43.6 | T=300°C	-1.8 | T= 600°C
Heated to 800°C and cooled down to 330°C	CdS, Cu_4Cd_3, CuS, $Cu_2Cd_3I_4S_2$, CuI	(4)	$CuS+CdI^+(g) \rightarrow CuI +CdS$ [18,21]	-152 | T=300°C	-84.7 | T=800°C
		(5)	$2Cu_2Cd_3I_4S2 \leftrightarrow Cu_4Cd_3 +2CdS+CdI_2 +I_2$	Proposed	

That can be an evidence about minimal interaction between each other, or some compensating process can interfere. The peak at 338^OC corresponds to an energy signal of about 1.8J (234 µV.s) much lower than that of freezing of pure CdI_2. Analyses by XRD and Raman showed that there had been formed a solid solution of $Zn_{1-x}Cd_xS$ in the mixture of $ZnS + CdI_2$ (see Table 2). As the formation of $Zn_{1-x}Cd_xS$ presupposes the formation of CdS that incorporates into ZnS, the overall enthalpy of the process was found as 3.42J.

In Figure 4, the slight lowering of melting temperature of CdI_2 in the DTA curve and lowered melting effect suggests that there has been some interaction between the molten CdI_2 and ZnS. In equation (8), there exist a thermo-dynamical possibility for a possible reaction between ZnS and CdI^+ for temperatures between 0 and 1000°C. In equation (6), the calculations of Gibbs energy change gave positive values for the reaction between solid CdI_2 and ZnS and therefore the CdS formation from solids is thermodynamically impossible. The probability of the reaction (6 and 11) should be therefore excluded. However, (see Table 2 and 5) we found $Zn_{1-x}Cd_xS$ and $Cu_2Zn_{1-x}Cd_xSnS_4$ formed in the studied samples. Explanation for the possibility to form $Zn_{1-x}Cd_xS$ in the mixture of liquid CdI_2 and solid ZnS could be therefore found by studying the properties of liquid and gaseous phases of CdI_2. It is well known that many salts in their molten phase are in the form of ionic liquids, but not CdI_2. MX_2 salts retain their solid phase structure even in liquid phase, in which the small $metal^{2+}$ ions occupy tetrahedrally coordinated sites in a closely packed anion structure, with strong intermediate range ordering [22-23]. Konigns et. al. in their work [13] studied the vapors over $CdI_2(l)$ and they found it to consist of monomeric and dimeric molecules.

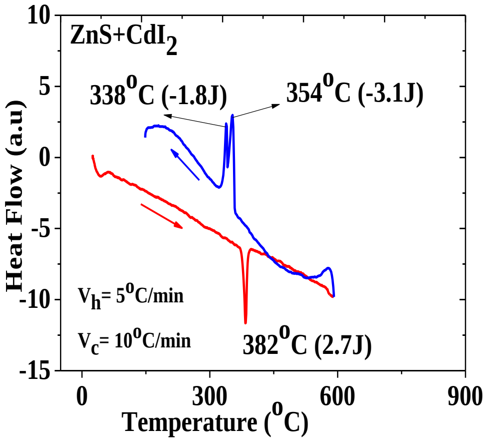

Fig 4: DTA curves of CdI_2+ZnS mixture

Also, measurements of the scattering of thermal neutrons in natural samples of molten $ZnCl_2$, $ZnBr_2$ and ZnI_2 confirmed a structural model in which the small Zn^{2+} ions occupy tetrahedrally coordinated sites in a closely packed anion structure, with strong intermediate range ordering [24-26]. Therefore, in the cooling process, some ZnS that had been dissolved in the molten phase and reacted with CdI^+ forming CdS and ZnI_2 (see reaction 8), precipitates from the melt as solid solution of $Zn_{1-x}Cd_xS$ at 354°C. Probably ZnI_2-CdI_2 liquid solution freezes at 338°C. According to Chikanov et.al, in ZnI_2-CdI_2 mixtures there form continuous row of solid solutions [27]. After opening the ampoule, ZnI_2 could not be detected by phase analyses due to its very high hygroscopicity. So, the possible explanation for the $Zn_xCd_{1-x}S$ formation can be given through the formation of CdI^+ in the equations (9) and (10).

D. CdI_2 + SnS

The melting was observed at 345°C (see Figure 5), at much lower temperature than for pure CdI_2. This fact suggests to a higher solubility/interaction of SnS in CdI_2. XRD and Raman studies of the bigger samples: (a) heated to 800 °C and cooled down to 350°C and then quenched to room temperature and (b) cooled down to 250°C from 800°C before quenching rapidly; revealed that SnI_4, Sn_2SI_2 and CdS had been formed (shown in Table 3). The final freezing of $SnS+CdI_2$ mixture can be detected in the cooling curve at 300°C (see Fig 5). The enthalpy observed in the cooling process is -6.23J. It can be attributed to the exothermic freezing of CdI_2 with cumulatively formed tin iodides and CdS as observed by phase analysi

DOI 10.17148/IARJSET.2016.3524

Table 2: The annealing conditions, determined phases, reactions and calculated ΔG values for ZnS+CdI_2 binary system

Annealing conditions	**Phases by Raman and XRD**		**Reactions**	**ΔG kJmol^{-1}**	
Annealed at 385°C and quenched to RT	ZnS, CdI_2	(6)	$ZnS_{(s)} + CdI_{2(s.l)} \rightarrow ZnI_2 + CdS$, [27]	44.1 | T=0°C	51.8 | T=800°C
		(7)	$ZnS + CdI_{2(g)} = ZnI_2 + CdS$. [27-29]	-8.3 | T=300°C	Positive above 300°C
Heated to 800°C, cooled down and quenched at 330°C to RT	$Zn_{0.94}Cd_{0.066}S$, $(Zn_{0.8}Cd_{0.2})S$, CdI_2, ZnS,	(8)	$ZnS + I^- + CdI^+_{(g)} \rightarrow CdS + ZnI_{2(g)} + I_{(g)}$ [29]	-59.5 | T=300°C	-86.2 | T=800°C
Heated to 800°C, cooled down to and quenched at 350°C RT		(9)	$ZnS + I^+ + CdI^+_{(g)} \rightarrow ZnS + CdI_2$ [27-29]	-186.7 | T=300°C	-113 | T=800°C
		(10)	$ZnS + I^+ + CdI^+(g) \rightarrow Zn_{1-x}C_xdS + 1-xCdI_2$	Proposed	
		(11)	$ZnS\ (s) + CdI_2\ (s) \rightarrow Zn_{1-x}C_xdS\ (s)$	Proposed	

Table 3: The annealing conditions, determined phases, reactions and calculated ΔG values for SnS+CdI_2 binary system

Annealing conditions	**Phases by Raman and XRD**		**Reactions**	**ΔG kJmol^{-1}**	
Heated to 350 °C and quenched	CdI_2, CdS, SnI_2 Sn_2SI_2	(12)	$SnS + CdI_2\ (g) = SnI_2 + CdS$ [17,30]	-79.5 | $T \geq 0$	-9.6 | $T \leq 500$
		(13)	$2SnS + I_2 \rightarrow Sn_2SI_2 + S$	proposed on phases observed	
		(14)	$2SnS + CdI_2 \rightarrow Sn_2SI_2 + CdS$	proposed on phases observed	
		(15)	$CdI_2(g) + S \rightarrow I_2 + CdS$,	-43.2 | T=0°C	9.7 | T=400°C
Heated to 800 °C and cooled down to 250°C	SnI_4 SnS, $SnSI_2$, CdS SnI_2	(16)	$SnS_{2(g)} = SnS + S$ [29-30]	-196.8 | T=100°C	-98.6 | T=800°C
		(17)	$SnI4 + 2CdS = SnS + 2CdI_2 + S$	-11.7 | T=100°C	-22.8 | T=800°C
		(18)	$I_2 + CdS = CdI_2(g) + S$	26.5 | T=100°C	-50 | T= 800°C
		(19)	$SnS_2 + 2CdI^+(g) \rightarrow 2CdS + SnI_2\ (SnSI_2)$ [27]	-379 | T=0°C	-162.4 | T=800°C
		(20)	$2CdI^+(g) + 2S = I_2 + 2CdS$	-368.9 | T=0°C	-132 | T=800°C

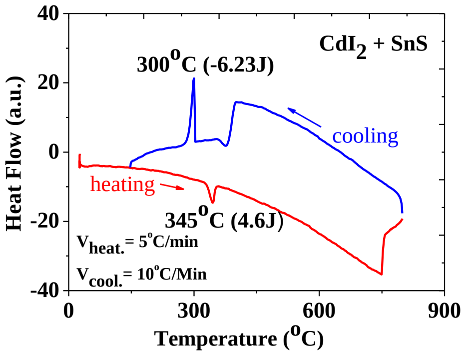

Fig 5: DTA curves of CdI2+SnS mixture

E. Mixture for synthesis of Cu_2SnS_3 (CdI_2 +SnS+Cu_2S+S)

In the mixture of (Cu_2S+SnS+S+CdI_2), we observed two endothermic peaks in the heating process with enthalpy signals of 0.7J (88µV.s) and 2.0J (265 µV.s) at 339°C and 360°C respectively. The former is attributed to the melting of CdI_2 while the latter can be attributed to the transformation of Cu_2S to $Cu_{1.96}S$ as it was observed already in (Cu_2S+CdI_2). In addition, SnS_2 was also found by XRD. XRD analysis of the mixture of (CdI_2 +SnS+Cu_2S+S) heated just above the melting of CdI_2, revealed the formation of ternary compound Cu_2SnS_3. The low enthalpy signal can be attributed to the net effect of the endothermic melting of CdI_2 and the exothermic formation of SnS_2 and Cu_2SnS_3 alongside the other concurrent processes. The enthalpy of the cumulative formation process in the heating process can be given as (666µV.s - 88µV.s = 578µV.s) - this corresponds to 13±2kJmol^{-1}. In the cooling process, the observed exothermic enthalpy signal of 2.7J (343 µV.s) at 343 °C is lower than freezing of pure CdI_2, probably due to some dissolved compound, for example SnI_2 or SnI_4, in it. XRD

DOI 10.17148/IARJSET.2016.3524

analysis of the sample mixture of CdI_2 +SnS+Cu_2S+S heated to 800°C and then cooled down to 300°C before quenching rapidly to room temperature showed the presence of Cu_2SnS_3. In the second heating/cooling process, we observed single endothermic /exothermic peaks for the melting and freezing of the mixture with close enthalpy signal values as observed in the first heating/cooling process. The reaction between Cu_2S+SnS+S leads to the formation of ternary compounds Cu_2SnS_3 [31] and Cu_4SnS_6 [32] (see table 4) and the formation of the ternaries takes place during the melting of the flux (CdI_2) see figure 6.

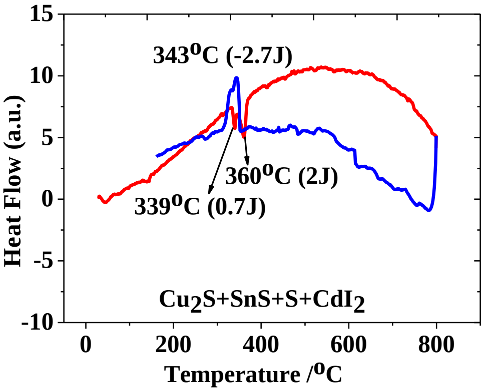

Fig 6: DTA curve of CdI_2 + SnS + Cu2S + S mixtures

Table 4: The annealing conditions, determined phases, reactions and calculated ΔG values for (CdI_2 + SnS + Cu2S + S) ternary system

Annealing conditions	**Phases by Raman and XRD**		**Reactions**	**ΔG $kJmol^{-1}$**	
Heated to 490 °C	CdI_2, CuS, SnS, Cu_2SnS_3	(21)	$2CuS \rightarrow Cu_2S + S_{(l)}$ [27][33]	-4.48 |T= 500°C	-39.88 |T= 1000
Heated to 560 °C		(22)	$2SnS + 2S \rightarrow 2SnS_2$	-28.6 | T=400°C	
		(23)	$2CuS + SnS \rightarrow Cu_2SnS_3$[31][34]	Proposed	
Heated to 800 °C and cooled down to 300°C	CdI_2, Cu_2S, SnS_2, Cu_2SnS_3 Cu_4SnS_6	(24)	$2CuS$+ SnS (melt) $\rightarrow Cu_2SnS_3$	Proposed	
Heated to 800 °C and cooled down to 470°C		(25)	$2Cu_2S + SnS_2 + 2S \rightarrow Cu_4SnS_6$[31]	Proposed	

F. Mixture for quaternary CZTS compound, (CdI_2 + SnS + Cu_2S + S + ZnS).

The mixture of CdI_2 with the binary precursors in the required stoichiometric composition for the formation of Cu_2ZnSnS_4 , melts/solidifies at 366°C/353°C respectively with thermal effects of 2.4J (308 µV.s) in the endothermic and exothermic processes as seen in DTA curves (see Figure 7) accompanied by other multiple processes proceeding at the same time, considering the reduced enthalpy signal. In order to study the formed phases present in the quaternary system, mixtures of CdI_2 + SnS + Cu_2S + S + ZnS were heated to 800°C and cooled down to 600°C and 350°C respectively before quenching rapidly to room temperature. We found by XRD and Raman the formation Cu_2SnS_3, $Cu_2ZnCdSnS_4$, Cu_2ZnSnS_4 and $Zn_{1-x}Cd_xS$, which confirms that the other (exo-endo) reactions also occur alongside in the molten phase of CdI_2. In another sample heated to 500°C and quenched to room temperature, CZTS was detected by Raman, which confirms that CZTS already begins to form starting from the formation of ternary Cu_2SnS_3 compound. Cu_2SnS_3 reacts with $Zn_xCd_{1-x}S$ (described for the mixture of (ZnS+CdI_2) to form $Cu_2ZnCdSnS_4$ as the final product. The formation of CZTS in molten CdI_2 proceeds via a complex exothermic process with enthalpy signal of (666µV.s -308 µV.s = 358µV.s.) that corresponds to enthalpy value of 8±2 $kJmol^{-1}$. $Cu_2Zn_{1-x}Cd_xSnS_4$ is the prevailing phase with its characteristic Raman peaks at 166, 250, 286, 336, 374cm^{-1} in the unwashed sample. CdI_2 with its Raman peak at 110 cm^{-1} and CuI at 145 cm^{-1} were detected only in unwashed samples but not in washed samples. CuI is soluble in KI or NaI solutions, as also reported in our previous report, allowing separation of single phase CZTS [35,7]. All phases detected by Raman and XRD and the proposed reaction path are summarized in Table 5. The formed solid solution of $Cu_2Zn_{1-x}Cd_xSnS_4$ was confirmed by EDX analysis and by the shift of Raman peak from 338cm^{-1} to 332cm^{-1} [36]. We propose that the formation of $Cu_2Zn_{1-x}Cd_xSnS_4$ solid solution proceeds via an intermediate reaction between $Zn_{1-x}Cd_xS$ and Cu_2SnS_3 equation (26) or directly by reaction (27) in the molten phase of CdI_2.

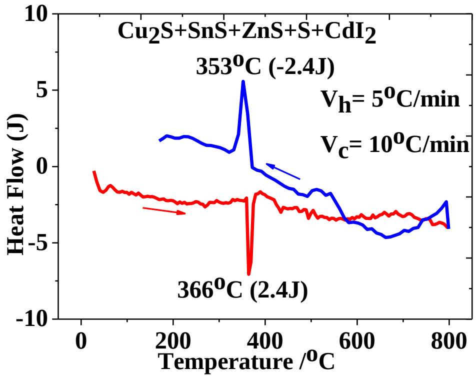

Fig 7. DTA curves of precursor mixtures CdI_2 + SnS + Cu_2S + S + ZnS

DOI 10.17148/IARJSET.2016.3524

Table 5: The annealing conditions, determined phases, reactions and calculated ΔG values for (CdI_2 + SnS + Cu_2S + S + ZnS) quaternary system

Annealing conditions	**Phases by Raman and XRD**		**Reactions**	**ΔG (kJ)**
Heated to 800°C	$Cu_2Zn_{1-x}Cd_xSnS_4$	26	$Cu_2SnS_3 + Zn_{1-x}Cd_xS \rightarrow Cu_2Zn_{1-x}CdxSnS_4$	
Heated to 800°C and cooled to 600°C	CdI_2, $Cu_{2-x}S$, Cu_2SnS_3, $Cu_2ZnCd_{1-x}SnS_4$, SnI_4,	27	$Cu_2S + SnS + Zn_{1-x}Cd_xS + S \rightarrow Cu_2Zn_{1-x}Cd_xSnS_4$	Proposed
Heated to 800°C and cooled to 350°C	CdI_2,CuI,SnI_4, $Cu_2ZnCd_{1-x}SnS_4$			

In figure 8, on the base of the ΔG calculations for different reactions, we show that the most probable route to the formation of $Cu_2(ZnCd)SnS_4$ through the intermediate formation of $Zn_{1-x}Cd_xS$ is by the formation of $CdI^+_{(g)}$. The chemical interaction between ZnS and solid CdI_2 at temperatures lower than 400°C is not favourable because the ΔG value is positive. Therefore this rules out the possibility of formation of quaternary $Cu_2Zn_{1-x}Cd_xSnS_4$. As mentioned earlier, there exist a thermo-dynamical possibility for a possible reaction between ZnS and CdI^+ to form ($Zn_{(1-x)}Cd_xS$) at temperatures between 0 and 1000°C which is the only favourable path for the formation of $Cu_2(ZnCd)SnS_4$.

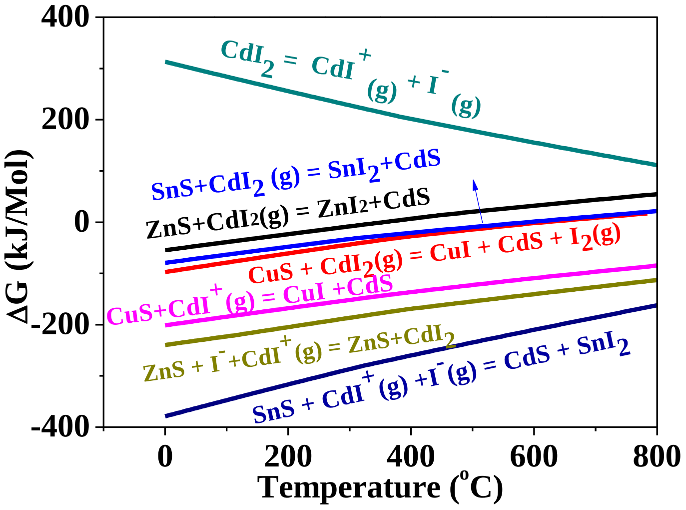

Fig 8: Calculated ΔG values for different reactions showing the possible reaction path for the synthesis of $Cu_2ZnCdSnS_4$ in molten CdI_2

IV. CONCLUSIONS

By studying mixtures of CdI_2 with individual precursors for synthesis of CZTS we found that CdI_2 mixed with S, ZnS, Cu_2S or SnS melts at temperatures lower than pure CdI_2 due to the freezing-point depression effect showing some solubility of the precursors in molten CdI_2. CdS and different iodine-containing compounds (SnI_4, Sn_2SI_2, CuI, and $Cu_2Cd_3I_4S_2$) form in CdI_2+Cu_2S and CdI_2+SnS. The overall enthalpy value of the processes in each case studied is formed via an exothermic process alongside the endothermic melting of the CdI_2 which gives rise to a lower melting temperature and enthalpy of fusion of the CdI_2 flux. CZTS formation in molten CdI_2 can be described as a two-stage process: first CdI^+ reacts with ZnS forming CdS, that after alloying with ZnS results in $Zn_{1-x}Cd_xS$. The amount of CdI^+ increases with temperature with the released Iodine acting as an oxidizing agent which reacts with Cu_2S and SnS resulting in different iodine containing compounds. Secondly, Cu_2S and SnS react to form ternary Cu_2SnS_3. The formation of Cu_2SnS_3 from Cu_2S+SnS+S in CdI_2 gave an enthalpy value of 13±2kJmol^{-1}. The $Zn_{1-x}Cd_xS$ and Cu_2SnS_3 combines to form a quaternary CZCdTS. The synthesis of CZTS monograin powders in CdI_2 results in the formation of solid solutions of $Cu_2Zn_xCd_{1-x}SnS_4$ with limited Cd content. The reaction of formation $Cu_2Zn_xCd_{1-x}SnS_4$ in the liquid phase of CdI_2 takes place with the experimentally determined enthalpy of 8±2 kJmol-1. The low enthalpy of formation of $Cu_2Zn_xCd_{1-x}SnS_4$ compared to high formation enthalpy of the ternary Cu_2SnS_3 could confirm that the solid $Cu_2Zn_xCd_{1-x}SnS_4$ solution is formed from the reaction between Cu_2SnS_3 and $Zn_{1-x}Cd_xS$. The formation of CdI^+ in the liquid phase is proposed to be a limiting

DOI 10.17148/IARJSET.2016.3524

factor in the CdS formation and due to this also the incorporation of Cd into CZTS crystals is limited

ACKNOWLEDGEMENT

This work was supported by institutional research funding IUT 19-28 of the Estonian Ministry of Education and Research and by the European Union through the European Regional Development Fund, Project TK141. Funding for facilities used in this research was provided by the core infrastructure support IUT-T4 of the Estonian Ministry of Education and Research.

REFFERENCES

[1] Kauk-Kuusik, M., Timmo, K., Danilson, M., Altosaar, M., Grossberg, M., & Ernits, K. (2015). p–n junction improvements of Cu2ZnSnS4/CdS monograin layer solar cells. Applied Surface Science, 357, 795-798.

[2] Klavina, I., Kaljuvee, T., Timmo, K., Raudoja, J., Traksmaa, R., Altosaar, M., & Meissner, D. (2011). Study of Cu2 ZnSnSe4 monograin formation in molten KI starting from binary chalcogenides. Thin Solid Films, 519(21), 7399-7402.

[3] Timmo, K., Altosaar, M., Raudoja, J., Mellikov, E., Varema, T., Danilson, M., & Grossberg, M. (2007). The effect of sodium doping to CuInSe2 monograin powder properties. Thin solid films, 515(15), 5887-5890.

[4] Kauk, M., Altosaar, M., Raudoja, J., Timmo, K., Varema, T., Danilson, M., ... & Mellikov, E. (2008, February). The influence of doping with donor type impurities on the properties of CuInSe2. In Physica Status Solidi C Conferences (Vol. 5, No. 2, p. 609). John Wiley & Sons, Ltd.

[5] I. Leinemann, J. Raudoja, M. Grossberg, M. Altosaar, D. Meissner, R. Traksmaa, and T. Kaljuvee, Comparison of Copper Zinc Tin Selenide Formation In Molten Potassium Iodide and Sodium Iodide As Flux Material. 2011.

[6] I. Klavina, J. Raudoja, M. Altosaar, E. Mellikov, D. Meissner. CZTS (Cu2ZnSnSe4) crystal growth for use in monograin membrane solar cells. CYSENI 2010, May 27–28, Kaunas, Lithuania. ISSN 1822-7554

[7] Nkwusi, G., Leinemann, I., Raudoja, J., Grossberg, M., Altosaar, M., Meissner, D., ... & Kaljuvee, T. (2012). Formation of copper zinc tin sulfide in cadmium iodide for monograin membrane solar cells. In Conf. of Young Scientists on Energy Issues, Kaunas (Vol. 2, pp. 24-25).. .

[8] Pfennig, B. W. (2015). Principles of Inorganic Chemistry. John Wiley & Sons.

[9] CRC PRESS LLC. Standard Thermodynamic Properties of Chemical Ssubstance (continued). CRC Handb Chem Phys. 2012;13(4):5.4 - 5.41, (http://www.update.uu.se/~jolkkonen/pdf/CRC_TD.pdf) retrived on 11/04/2016.

[10] Nkwusi, G., Leinemann, I., Raudoja, J., Mikli, V., Kauk-Kuusik, M., Altosaar, M., & Mellikov, E. (2014). Synthesis of Cu2(ZnCd)SnS4 Absorber Material for Monograin Membrane Applications. In MRS Proceedings (Vol. 1638, pp. mrsf13-1638). Cambridge Universi.

[11] Kaupp, M., & von Schnering, H. G. (1994). Ab Initio Comparison of the (MX2)2 Dimers (M= Zn, Cd, Hg; X= F, Cl, H) and Study of Relativistic Effects in Crystalline HgF2. Inorganic Chemistry, 33(21), 4718-4722.

[12] Topor, L., & Moldovea. I. (1974). Vapor-pressures of molten CdBr2, CdI2, MgBr2 and molecular association in gaseous phase. revue roumaine dE Chimie, 19(6), 985-990.

[13] Konings, R. J. M., Booij, A. S., & Cordfunke, E. H. P. (1991). High-temperature infrared study of the vaporization of CsI, CdI2 and Cs2CdI4. Vibrational spectroscopy, 2(4), 251-255.

[14] Corbett, J. D., von Winbush, S., & Albers, F. C. (1957). The Solubility of the Post-Transition Metals in their Molten Halides1. Journal of the American Chemical Society, 79(12), 3020-3024.

[15] M. V. Šušic, S. V.Mentus, Cyclic voltammetry of molten CdI2 and Cd-CdI2. Bulletin Tome LXVIII: Classe Des Sciences Naturelles Et Mathematiques, Academie Serbe des sciences et des arts, Nr 19 - 1979, Beograd.

[16] Dumon, A., Lichanot, A., & Gromb, S. (1974). Study of Cu-S Phase-Diagram in Compositional Area Cu2, 000S-Cu1, 960S. Journal De Chimie Physique et de Physico-Chimie Biologique, 71(3), 407-414.

[17] Buerger, N. W. (1939). The Polymorphism of Cu2S, and the Relations Between the Solid Phases in the System Cu2S–CuS. The Journal of Chemical Physics, 7(11), 1067-1068.

[18] Börnstein, L. (1999). Thermodynamic Properties of Inorganic Material, Scientific Group Thermodata Europe (SGTE).

[19] SGTE 94, Scientific Group Thermodata Europe, Grenoble Campus, 1001 Avenue Centrale, BP 66, F-38402 Saint Martin d'Héres, France, 1994 (HSE software).

[20] Donald, K. J., Hargittai, M., & Hoffmann, R. (2009). Group 12 dihalides: structural predilections from gases to solids. Chemistry–A European Journal, 15(1), 158-177.

[21] Barin I: Thermochemical Data of Pure Substances, Part II,VCH Verlags Gesellschaft, Weinheim, 1993 (HSC software).

[22] Russell, T. D. (1986). Vapor-phase composition above the cadmium iodide-sodium iodide and the thorium tetraio-dide-sodium iodide systems. The Journal of Physical Chemistry, 90(24), 6590-6594.

[23] Allen, D. A., Howe, R. A., Wood, N. D., & Howells, W. S. (1991). Tetrahedral coordination of Zn ions in molten zinc halides. The Journal of chemical physics, 94(7), 5071-5076.

[24] Zeidler, A., Chirawatkul, P., Salmon, P. S., Usuki, T., Kohara, S., Fischer, H. E., & Howells, W. S. (2015). Structure of the network glass-former ZnCl2: From the boiling point to the glass. Journal of Non-Crystalline Solids, 407, 235-245.

[25] Özen, A. S., Akdeniz, Z., Ruberto, R., Pastore, G., & Tosi, M. P. (2014). The origins of tetrahedral coordination in molten and glassy ZnCl2 and other group-2B metal dihalides. Physics Letters A, 378(4), 431-433.

[26] Glushko, V. P. (1994). Thermocenter of the Russian Academy of Sciences. IVTAN Association, Izhorskaya, 13(19), 127412.

[27] Glushko Thermocenter of the Russian Academy of Sciences, IVTAN Association, Izhorskaya 13/19, 127412 Mos-cow, Russia, 1996 .

[28] Landolt-Börnstein: Thermodynamic Properties of Inorganic Material,. Sci Gr Thermodata Eur (SGTE), Berlin-Heidelberg,Springer-Verlag,. 1999 (HSC 6.0 software).

29] http://zonvark.wustl.edu/geopig/index.html, Everett Shock, Department of Earth and Planetary Sciences, Washing-ton University, One Brookings Drive, St Louis MO, 63130-4899, http://www.earthsci.unibe.ch/t, http://www.nmt.edu.

[30] Gurvich, L.V., Veitz, I.V., et al. Thermodynamic Properties of Individual Substances. Fourth edition in 5 volumes, Hemisphere Pub Co. NY, L., Vol 1 in 2 parts, 1989, etc. (= TSIV 82).

[31] Olekseyuk, I. D., Dudchak, I. V., & Piskach, L. V. (2004). Phase equilibria in the Cu2S–ZnS–SnS2 system. Journal of alloys and compounds, 368(1), 135-143.

[32] Schurr, R., Hölzing, A., Jost, S., Hock, R., Voβ, T., Schulze, J., ... & Kötschau, I. (2009). The crystallisation of Cu2ZnSnS4 thin film solar cell absorbers from co-electroplated Cu–Zn–Sn precursors. Thin Solid Films, 517(7), 2465-2468.

[33] Knacke O., Kubaschewski O., Hesselman K., Thermochemical properties of inorganic substances, 2nd ed., Springer-Verlag, Berlin, pp.1114-2412, 1991.

[34] Fiechter, S., Martinez, M., Schmidt, G., Henrion, W., & Tomm, Y. (2003). Phase relations and optical properties of semiconducting ternary sulfides in the system Cu–Sn–S. Journal of Physics and Chemistry of Solids, 64(9), 1859-1862.

[35] Altosaar, M., Jagomägi, A., Kauk, M., Krunks, M., Krustok, J., Mellikov, E.,& Varema, T. (2003). Monograin layer solar cells. Thin Solid Films, 431, 466-469.

[36] Timmo, K., Kauk-Kuusik, M., Altosaar, M., Raudoja, J., Raadik, T., Grossberg, M., & Mellikov, E. (2013, Septem-ber). Novel Cu2CdSnS4 and Cu2ZnGeSe4 absorber materials for monograin layer solar cell application. In Proceed-ings of the 28th European Photovo.