

# The Processes and Enthalpies in Synthesis of $\text{Cu}_2\text{ZnSnS}_4$ in Molten $\text{CdI}_2$

Godswill Nkwusi<sup>1</sup>, Inga Leinemann<sup>1</sup>, Mare Altosaar<sup>1</sup>

Institute of Materials Science, Tallinn University of Technology, Estonia<sup>1</sup>

**Abstract:** Synthesis of  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS) in molten  $\text{CdI}_2$  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  $\text{Cu}_2\text{ZnSnS}_4$  proceeds mainly in the liquid phase of  $\text{CdI}_2$  where  $\text{CdS}$  and  $\text{Zn}_{1-x}\text{Cd}_x\text{S}$  form and initiate the formation of  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$ . The formed phases in the mixtures of  $\text{CdI}_2$  with precursor compounds detected by XRD and Raman analyses are presented. The formation enthalpy for  $\text{Cu}_2\text{SnS}_3$  and  $\text{Cu}_2\text{ZnSnS}_4$  are  $13 \pm 2 \text{ kJmol}^{-1}$  and  $8 \pm 2 \text{ kJmol}^{-1}$  respectively.

**Keyword:**  $\text{Cu}_2\text{ZnSnS}_4$ ,  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$ , 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  $\text{Cu}_2\text{ZnSnSe}_4$  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  $\text{CdI}_2$  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  $\text{Cu}_2\text{ZnSnSe}_4$  in  $\text{CdI}_2$ , Cd from  $\text{CdI}_2$  incorporated into the crystals of CZTSe forming a solid solution of  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnSe}_4$ , however, the formation of  $\text{Cu}_2\text{ZnSnS}_4$  in  $\text{CdI}_2$  and the reaction enthalpies have not been studied yet.

In this report, we present the reaction path of CZTS synthesis in  $\text{CdI}_2$  starting from binary compound precursors. In this study, various mixtures of the individual precursors with  $\text{CdI}_2$ , as well as the precursor mixtures for the synthesis of CZTS in  $\text{CdI}_2$  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 ( $\text{Cu}_2\text{S} + \text{SnS} + \text{ZnS} + \text{S}$ ) in the presence of molten phase of  $\text{CdI}_2$ . Separate quasi-binary mixtures ( $\text{Cu}_2\text{S} + \text{CdI}_2$ ), ( $\text{ZnS} + \text{CdI}_2$ ), ( $\text{SnS} + \text{CdI}_2$ ) ( $\text{S} + \text{CdI}_2$ ), also mixture for ternary  $\text{Cu}_2\text{SnS}_3$  (CTS) compound ( $\text{Cu}_2\text{S} + \text{SnS} + \text{S} + \text{CdI}_2$ ) were studied as described in [7]. An empty quartz ampoule was used as a reference for the DTA measurements. Pure  $\text{CdI}_2$  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  $\text{CdI}_2$  and secondly, our experimentally determined melting point of  $\text{CdI}_2$  coincide with the value found from literature ( $T_{\text{melt}} = 385^\circ\text{C}$ ) [8]. Our readings from DTA curves in  $\mu\text{V.s}$  were converted to J/mol using the value of enthalpy of fusion of  $\text{CdI}_2$  ( $15.31 \text{ kJ/mol}$  [9]) considering that our experimental heat value for melting of  $\text{CdI}_2$  is  $666 \pm 2 \mu\text{V}$ s which corresponds to  $\approx 5.23 \text{ J}$  (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  $800^\circ\text{C}$  were 5 and  $10^\circ\text{C}$  per minute, respectively. After recording the thermal effects by DTA, the changes in the phase composition of different precursor mixtures with  $\text{CdI}_2$  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  $\text{CdI}_2$  (by washing with deionized water).

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

### III.RESULTS AND DISCUSSIONS

The melting temperatures of the studied mixtures ( $\text{Cu}_2\text{S}+\text{CdI}_2$ ), ( $\text{ZnS}+\text{CdI}_2$ ), ( $\text{SnS}+\text{CdI}_2$ ), ( $\text{Cu}_2\text{S}+\text{SnS}+\text{S}+\text{CdI}_2$ ) and ( $\text{Cu}_2\text{S}+\text{SnS}+\text{ZnS}+\text{S}+\text{CdI}_2$ ), picked up from DTA curves, are presented in Figure 1. It can be seen that the melting of the precursor mixtures with  $\text{CdI}_2$  takes place at lower temperatures than the melting temperature of pure  $\text{CdI}_2$  ( $385^\circ\text{C}$ ) [8]. The lowering of melting temperatures shows some solubility of the precursors in molten  $\text{CdI}_2$  and/or the formation of new phases.

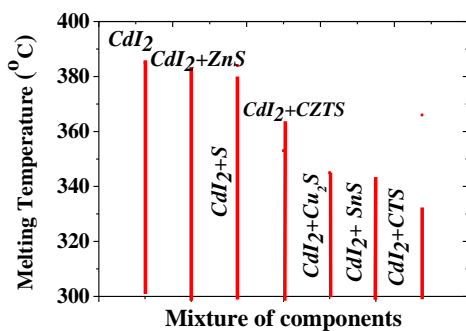


Fig 1. Melting temperatures of studied mixtures as determined from DTA curves

#### A. $\text{CdI}_2$

At temperatures above the melting point,  $\text{CdI}_2$  exists in gaseous as monomeric  $\text{CdI}_{2(g)}$  and dimeric  $\text{Cd}_2\text{I}_{4(g)}$  forms [11-13]. According to Shushic et.al. and Corbett et.al. [14], molten  $\text{CdI}_2$  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  $\text{CdI}_2$  and the precursors. The DTA probe of pure  $\text{CdI}_2$  (see Figure 2) gave an endothermic effect at  $385^\circ\text{C}$  in heating and an exothermic effect at  $366^\circ\text{C}$  in cooling cycle which can be attributed to the melting and freezing of  $\text{CdI}_2$  with enthalpy signal of  $666 \pm 2 \mu\text{V.s}$ . This signal is equal to 5.23J, as calculated from the obtained peak area for correspondent 0.00034 mole of  $\text{CdI}_2$  in the ampoule (molar mass of  $\text{CdI}_2=366.22 \text{ g/mol}$  and the molar fusion enthalpy value for pure  $\text{CdI}_2$  is  $15.31\text{kJ/mol}$ ).

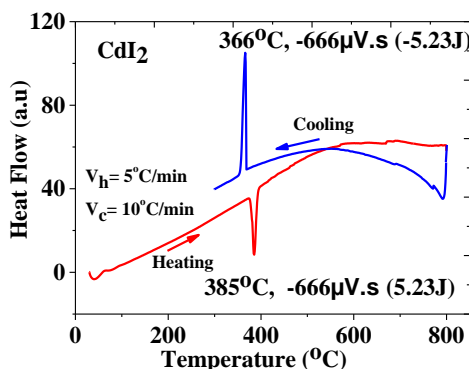


Fig 2. DTA curves of  $\text{CdI}_2$

#### B. $\text{CdI}_2 + \text{Cu}_2\text{S}$

By phase analyses the sample of the mixture heated just above the melting temperature of  $\text{CdI}_2$  revealed the formation of  $\text{CuI}$ , while  $\text{Cu}_2\text{S}$  had been transformed to  $\text{Cu}_{1.96}\text{S}$  at  $353^\circ\text{C}$ , correspondently to the  $\text{Cu-S}$  phase diagram [16]. In the DTA curves of the mixture of  $\text{CdI}_2 + \text{Cu}_2\text{S}$  (see Figure 3), there is seen an endothermic melting effect at  $353^\circ\text{C}$  and an exothermic effect of freezing of  $\text{CdI}_2$  at  $338^\circ\text{C}$ . We can observe a decrease in the energy value of melting process from 5.23 J ( $666 \mu\text{V.s}$ ) for pure  $\text{CdI}_2$  to 2.1 J ( $264 \mu\text{V.s}$ ) in  $\text{CdI}_2+\text{Cu}_2\text{S}$  mixture. This decrease can be ascribed to the simultaneous exothermic reactions occurring alongside the melting of  $\text{CdI}_2$ . By XRD and Raman, different compounds -  $\text{Cu}_{1.96}\text{S}$ ,  $\text{CuI}$ ,  $\text{Cu}_2\text{Cd}_3\text{I}_4\text{S}_2$ ,  $\text{CdS}$  and  $\text{Cu}_4\text{Cd}_3$  - were found in  $\text{CdI}_2+\text{Cu}_2\text{S}$  mixtures heated for 4 hours at temperature a little bit above the melting point of the mixture ( $353^\circ\text{C}$ ) (see Tabel 1). This confirms the chemical interaction between the flux material and  $\text{Cu}_2\text{S}$ . By XRD and Raman analyses, we found that some of these processes occurring during the melting and freezing of the mixture ( $\text{CdI}_2+\text{Cu}_2\text{S}$ ) are reversible:  $\text{Cu}_2\text{S}$ , as observed by XRD, transformed to  $\text{Cu}_{1.96}\text{S}$  and re-transformed to  $\text{Cu}_2\text{S}$  by cooling down - that is in accordance with the report [16-17]. In the heating process, in addition to the main fusion peak at  $353^\circ\text{C}$  there is seen another endothermic DTA peak at  $400^\circ\text{C}$ . The phase analysis of the bigger sample heated and quenched at  $420^\circ\text{C}$  shows that this peak corresponds to the decomposition of  $\text{Cu}_2\text{Cd}_3\text{I}_4\text{S}_2$  with formation of  $\text{CdS}$ ,  $\text{CuI}$  and  $\text{Cu}_4\text{Cd}_3$  (see equation (5) in the Tabel 1) with summary thermal effect of 77 mVs (0.6J).

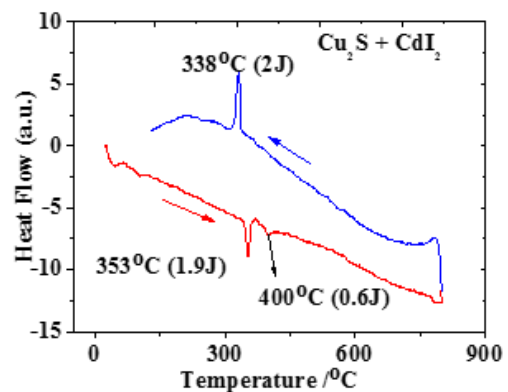


Fig 3: DTA curves of  $\text{CdI}_2+\text{Cu}_2\text{S}$

#### C. $\text{CdI}_2 + \text{ZnS}$

The DTA heating and cooling curves of this mixture are presented in Figure 4. It shows an endothermic peak at  $382^\circ\text{C}$  in the heating cycle, slightly lower than the melting temperature of pure  $\text{CdI}_2$  ( $T_{\text{melt}}=385^\circ\text{C}$ ) with the thermal effect of 2.7 J, that is much lower than in the melting of pure  $\text{CdI}_2$  (5.23J). It means that some exothermic process compensates the endothermic melting effect. However, no new phases other than  $\text{CdI}_2$  and  $\text{ZnS}$  were found by XRD and Raman in the sample heated and quenched at  $385^\circ\text{C}$ , may be due to the low sensitivity of XRD. In the cooling curve two exothermic peaks at  $354^\circ\text{C}$  and  $338^\circ\text{C}$  are seen. This implies that  $\text{CdI}_2$  in the mixture with  $\text{ZnS}$  melts close to the melting temperature of its pure form.

Table 1: The annealing conditions, determined phases, reactions and calculated  $\Delta G$  values for CuS+CdI<sub>2</sub> quasi-binary system

Annealing conditions	Phases By Raman and XRD	Reactions	$\Delta G$ kJmol <sup>-1</sup>
Heated to 353°C, annealed for 4 hours	CuS, Cu <sub>1.96</sub> S, CuI, Cu <sub>2</sub> Cd <sub>3</sub> I <sub>4</sub> S <sub>2</sub>	(1) Cu <sub>2</sub> S+CdI <sub>2</sub> ←→2CuI+CdS [18-20]	-49   T=300°C -31.5   T=400°C
		(2) CdS+Cu <sub>2</sub> S+2CdI <sub>2</sub> ↔Cu <sub>2</sub> Cd <sub>3</sub> I <sub>4</sub> S <sub>2</sub>	Proposed
Heated to 400°C, annealed for 4 hours	CdS, Cu <sub>4</sub> Cd <sub>3</sub>	(3) Cu <sub>2</sub> S + CdI <sub>2</sub> (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 <sub>4</sub> Cd <sub>3</sub> , CuS, Cu <sub>2</sub> Cd <sub>3</sub> I <sub>4</sub> S <sub>2</sub> , CuI	(4) CuS+CdI <sup>+</sup> (g)→ CuI +CdS [18,21]	-152   T=300°C -84.7   T=800°C
		(5) 2Cu <sub>2</sub> Cd <sub>3</sub> I <sub>4</sub> S <sub>2</sub> ↔Cu <sub>4</sub> Cd <sub>3</sub> +2CdS+CdI <sub>2</sub> +I <sub>2</sub>	Proposed

That can be an evidence about minimal interaction between each other, or some compensating process can interfere. The peak at 338°C corresponds to an energy signal of about 1.8J (234 μV.s) much lower than that of freezing of pure CdI<sub>2</sub>. Analyses by XRD and Raman showed that there had been formed a solid solution of Zn<sub>1-x</sub>Cd<sub>x</sub>S in the mixture of ZnS + CdI<sub>2</sub> (see Table 2). As the formation of Zn<sub>1-x</sub>Cd<sub>x</sub>S 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<sub>2</sub> in the DTA curve and lowered melting effect suggests that there has been some interaction between the molten CdI<sub>2</sub> and ZnS. In equation (8), there exist a thermodynamical possibility for a possible reaction between ZnS and CdI<sup>+</sup> 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<sub>2</sub> 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<sub>1-x</sub>Cd<sub>x</sub>S and Cu<sub>2</sub>Zn<sub>1-x</sub>Cd<sub>x</sub>Sn<sub>4</sub> formed in the studied samples. Explanation for the possibility to form Zn<sub>1-x</sub>Cd<sub>x</sub>S in the mixture of liquid CdI<sub>2</sub> and solid ZnS could be therefore found by studying the properties of liquid and gaseous

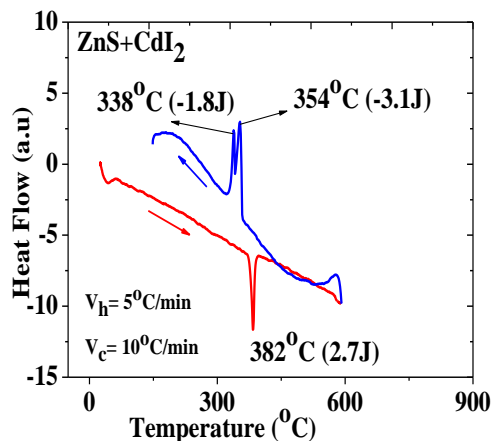


Fig 4: DTA curves of CdI<sub>2</sub>+ZnS mixture

phases of CdI<sub>2</sub>. It is well known that many salts in their molten phase are in the form of ionic liquids, but not CdI<sub>2</sub>. MX<sub>2</sub> salts retain their solid phase structure even in liquid phase, in which the small metal<sup>2+</sup> 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<sub>2</sub>(l) and they found it to consist of monomeric and dimeric molecules.

Also, measurements of the scattering of thermal neutrons in natural samples of molten ZnCl<sub>2</sub>, ZnBr<sub>2</sub> and ZnI<sub>2</sub> confirmed a structural model in which the small Zn<sup>2+</sup> 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<sup>+</sup> forming CdS and ZnI<sub>2</sub> (see reaction 8), precipitates from the melt as solid solution of Zn<sub>1-x</sub>Cd<sub>x</sub>S at 354°C. Probably ZnI<sub>2</sub>-CdI<sub>2</sub> liquid solution freezes at 338°C. According to Chikanov et.al, in ZnI<sub>2</sub>-CdI<sub>2</sub> mixtures there form continuous row of solid solutions [27]. After opening the ampoule, ZnI<sub>2</sub> could not be detected by phase analyses due to its very high hygroscopicity. So, the possible explanation for the Zn<sub>x</sub>Cd<sub>1-x</sub>S formation can be given through the formation of CdI<sup>+</sup> in the equations (9) and (10).

#### D. CdI<sub>2</sub> + SnS

The melting was observed at 345°C (see Figure 5), at much lower temperature than for pure CdI<sub>2</sub>. This fact suggests to a higher solubility/interaction of SnS in CdI<sub>2</sub>. 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<sub>4</sub>, Sn<sub>2</sub>SI<sub>2</sub> and CdS had been formed (shown in Table 3). The final freezing of SnS+CdI<sub>2</sub> 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<sub>2</sub> with cumulatively formed tin iodides and CdS as observed by phase analysi

Table 2: The annealing conditions, determined phases, reactions and calculated ΔG values for ZnS+CdI<sub>2</sub> binary system

Annealing conditions	Phases by Raman and XRD	Reactions	ΔG kJmol <sup>-1</sup>
Annealed at 385°C and quenched to RT	ZnS, CdI <sub>2</sub>	(6) ZnS <sub>(s)</sub> + CdI <sub>2(s,l)</sub> → ZnI <sub>2</sub> + CdS, [27]	44.1   T=0°C      51.8   T=800°C
		(7) ZnS + CdI <sub>2(g)</sub> = ZnI <sub>2</sub> + 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 <sub>0.94</sub> Cd <sub>0.06</sub> <sub>6</sub> S, (Zn <sub>0.8</sub> Cd <sub>0.2</sub> ) <sub>5</sub> , CdI <sub>2</sub> , ZnS,	(8) ZnS + I + CdI <sub>(g)</sub> <sup>+</sup> → CdS + ZnI <sub>2(g)</sub> + I <sub>(g)</sub> [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 <sup>+</sup> + CdI <sub>(g)</sub> <sup>+</sup> → ZnS + CdI <sub>2</sub> [27-29]	-186.7   T=300°C      -113   T=800°C
		(10) ZnS + I <sup>+</sup> + CdI <sub>(g)</sub> <sup>+</sup> → Zn <sub>1-x</sub> C <sub>x</sub> dS + 1-xCdI <sub>2</sub>	Proposed
		(11) ZnS (s) + CdI <sub>2</sub> (s) → Zn <sub>1-x</sub> C <sub>x</sub> dS (s)	Proposed

Table 3: The annealing conditions, determined phases, reactions and calculated ΔG values for SnS+CdI<sub>2</sub> binary system

Annealing conditions	Phases by Raman and XRD	Reactions	ΔG kJmol <sup>-1</sup>
Heated to 350 °C and quenched	CdI <sub>2</sub> , CdS, SnI <sub>2</sub> , Sn <sub>2</sub> SI <sub>2</sub>	(12) SnS + CdI <sub>2</sub> (g) = SnI <sub>2</sub> + CdS [17,30]	-79.5   T ≥ 0      -9.6   T ≤ 500
		(13) 2SnS + I <sub>2</sub> → Sn <sub>2</sub> SI <sub>2</sub> + S	proposed on phases observed
		(14) 2SnS + CdI <sub>2</sub> → Sn <sub>2</sub> SI <sub>2</sub> + CdS	proposed on phases observed
		(15) CdI <sub>2</sub> (g) + S → I <sub>2</sub> + CdS,	-43.2   T=0°C      9.7   T=400°C
Heated to 800 °C and cooled down to 250°C	SnI <sub>4</sub> , SnS, SnSI <sub>2</sub> , CdS, SnI <sub>2</sub>	(16) SnS <sub>2(g)</sub> = SnS + S [29-30]	-196.8   T=100°C      -98.6   T=800°C
		(17) SnI <sub>4</sub> + 2CdS = SnS + 2CdI <sub>2</sub> + S	-11.7   T=100°C      -22.8   T=800°C
		(18) I <sub>2</sub> + CdS = CdI <sub>2</sub> (g) + S	26.5   T=100°C      -50   T= 800°C
		(19) SnS <sub>2</sub> + 2CdI <sub>(g)</sub> <sup>+</sup> → 2CdS + SnI <sub>2</sub> (SnSI <sub>2</sub> ) [27]	-379   T=0°C      -162.4   T=800°C
		(20) 2CdI <sub>(g)</sub> <sup>+</sup> + 2S = I <sub>2</sub> + 2CdS	-368.9   T=0°C      -132   T=800°C

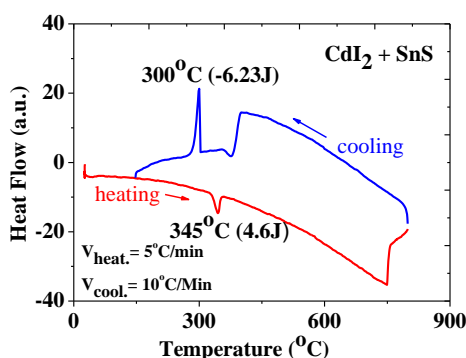


Fig 5: DTA curves of CdI<sub>2</sub>+SnS mixture

E. Mixture for synthesis of Cu<sub>2</sub>SnS<sub>3</sub> (CdI<sub>2</sub> + SnS + Cu<sub>2</sub>S + S)

In the mixture of (Cu<sub>2</sub>S + SnS + S + CdI<sub>2</sub>), 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<sub>2</sub> while the latter can be attributed to the transformation of Cu<sub>2</sub>S to Cu<sub>1.96</sub>S as it was observed already in (Cu<sub>2</sub>S + CdI<sub>2</sub>). In addition, SnS<sub>2</sub> was also found by XRD. XRD analysis of the mixture of (CdI<sub>2</sub> + SnS + Cu<sub>2</sub>S + S) heated just above the melting of CdI<sub>2</sub>, revealed the formation of ternary compound Cu<sub>2</sub>SnS<sub>3</sub>. The low enthalpy signal can be attributed to the net effect of the endothermic melting of CdI<sub>2</sub> and the exothermic formation of SnS<sub>2</sub> and Cu<sub>2</sub>SnS<sub>3</sub> 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<sup>-1</sup>. 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<sub>2</sub>, probably due to some dissolved compound, for example SnI<sub>2</sub> or SnI<sub>4</sub>, in it. XRD

analysis of the sample mixture of  $\text{CdI}_2 + \text{SnS} + \text{Cu}_2\text{S} + \text{S}$  heated to  $800^\circ\text{C}$  and then cooled down to  $300^\circ\text{C}$  before quenching rapidly to room temperature showed the presence of  $\text{Cu}_2\text{SnS}_3$ . 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  $\text{Cu}_2\text{S} + \text{SnS} + \text{S}$  leads to the formation of ternary compounds  $\text{Cu}_2\text{SnS}_3$  [31] and  $\text{Cu}_4\text{SnS}_6$  [32] (see table 4) and the formation of the ternaries takes place during the melting of the flux ( $\text{CdI}_2$ ) see figure 6.

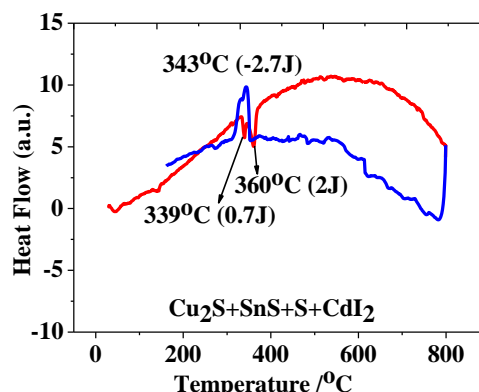


Fig 6: DTA curve of  $\text{CdI}_2 + \text{SnS} + \text{Cu}_2\text{S} + \text{S}$  mixtures

Table 4: The annealing conditions, determined phases, reactions and calculated  $\Delta G$  values for ( $\text{CdI}_2 + \text{SnS} + \text{Cu}_2\text{S} + \text{S}$ ) ternary system

Annealing conditions	Phases by Raman and XRD	Reactions	$\Delta G \text{ kJmol}^{-1}$
Heated to $490^\circ\text{C}$	$\text{CdI}_2$ , $\text{Cu}_2\text{S}$ ,	(21) $2\text{CuS} \rightarrow \text{Cu}_2\text{S} + \text{S}_{(l)}$ [27][33]	-4.48   $T=500^\circ\text{C}$ -39.88   $T=1000$
Heated to $560^\circ\text{C}$	$\text{SnS}$ , $\text{Cu}_2\text{SnS}_3$	(22) $2\text{SnS} + 2\text{S} \rightarrow 2\text{SnS}_2$ (23) $2\text{CuS} + \text{SnS} \rightarrow \text{Cu}_2\text{SnS}_3$ [31][34]	-28.6   $T=400^\circ\text{C}$ Proposed
Heated to $800^\circ\text{C}$ and cooled down to $300^\circ\text{C}$	$\text{CdI}_2$ , $\text{Cu}_2\text{S}$ ,	(24) $2\text{CuS} + \text{SnS} (\text{melt}) \rightarrow \text{Cu}_2\text{SnS}_3$	Proposed
Heated to $800^\circ\text{C}$ and cooled down to $470^\circ\text{C}$	$\text{SnS}_2$ , $\text{Cu}_2\text{SnS}_3$ $\text{Cu}_4\text{SnS}_6$	(25) $2\text{Cu}_2\text{S} + \text{SnS}_2 + 2\text{S} \rightarrow \text{Cu}_4\text{SnS}_6$ [31]	Proposed

F. Mixture for quaternary CZTS compound, ( $\text{CdI}_2 + \text{SnS} + \text{Cu}_2\text{S} + \text{S} + \text{ZnS}$ ).

The mixture of  $\text{CdI}_2$  with the binary precursors in the required stoichiometric composition for the formation of  $\text{Cu}_2\text{ZnSnS}_4$ , melts/solidifies at  $366^\circ\text{C}/353^\circ\text{C}$  respectively with thermal effects of  $2.4\text{J}$  ( $308 \mu\text{V.s}$ ) 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  $\text{CdI}_2 + \text{SnS} + \text{Cu}_2\text{S} + \text{S} + \text{ZnS}$  were heated to  $800^\circ\text{C}$  and cooled down to  $600^\circ\text{C}$  and  $350^\circ\text{C}$  respectively before quenching rapidly to room temperature. We found by XRD and Raman the formation  $\text{Cu}_2\text{SnS}_3$ ,  $\text{Cu}_2\text{ZnCdSnS}_4$ ,  $\text{Cu}_2\text{ZnSnS}_4$  and  $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ , which confirms that the other (exo-endo) reactions also occur alongside in the molten phase of  $\text{CdI}_2$ . In another sample heated to  $500^\circ\text{C}$  and quenched to room temperature, CZTS was detected by Raman, which confirms that CZTS already begins to form starting from the formation of ternary  $\text{Cu}_2\text{SnS}_3$  compound.  $\text{Cu}_2\text{SnS}_3$  reacts with  $\text{Zn}_x\text{Cd}_{1-x}\text{S}$  (described for the mixture of ( $\text{ZnS} + \text{CdI}_2$ )) to form  $\text{Cu}_2\text{ZnCdSnS}_4$  as the final product. The formation of CZTS in molten  $\text{CdI}_2$  proceeds via a complex exothermic process with enthalpy signal of ( $666 \mu\text{V.s}$  -  $308 \mu\text{V.s}$  =  $358 \mu\text{V.s}$ ) that corresponds to enthalpy value of  $8 \pm 2 \text{ kJmol}^{-1}$ .  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  is the prevailing phase with its characteristic Raman peaks at  $166, 250, 286, 336, 374 \text{ cm}^{-1}$  in the unwashed sample.

$\text{CdI}_2$  with its Raman peak at  $110 \text{ cm}^{-1}$  and  $\text{CuI}$  at  $145 \text{ cm}^{-1}$  were detected only in unwashed samples but not in washed samples.  $\text{CuI}$  is soluble in  $\text{KI}$  or  $\text{NaI}$  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  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  was confirmed by EDX analysis and by the shift of Raman peak from  $338 \text{ cm}^{-1}$  to  $332 \text{ cm}^{-1}$  [36]. We propose that the formation of  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  solid solution proceeds via an intermediate reaction between  $\text{Zn}_{1-x}\text{Cd}_x\text{S}$  and  $\text{Cu}_2\text{SnS}_3$  equation (26) or directly by reaction (27) in the molten phase of  $\text{CdI}_2$ .

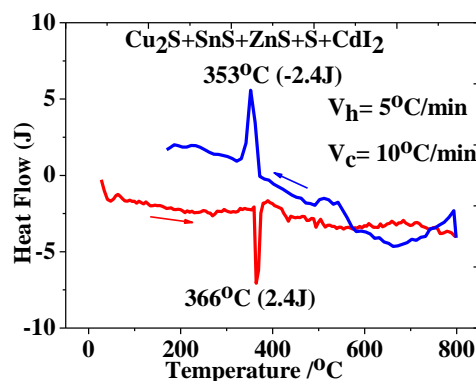


Fig 7. DTA curves of precursor mixtures  $\text{CdI}_2 + \text{SnS} + \text{Cu}_2\text{S} + \text{S} + \text{ZnS}$

Table 5: The annealing conditions, determined phases, reactions and calculated  $\Delta G$  values for  $(\text{CdI}_2 + \text{SnS} + \text{Cu}_2\text{S} + \text{S} + \text{ZnS})$  quaternary system

Annealing conditions	Phases by Raman and XRD	Reactions	$\Delta G$ (kJ)
Heated to 800°C	$\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$	26 $\text{Cu}_2\text{SnS}_3 + \text{Zn}_{1-x}\text{Cd}_x\text{S} \rightarrow \text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$	
Heated to 800°C and cooled to 600°C	$\text{CdI}_2$ , $\text{Cu}_{2-x}\text{S}$ , $\text{Cu}_2\text{SnS}_3$ , $\text{Cu}_2\text{ZnCd}_{1-x}\text{SnS}_4$ , $\text{SnI}_4$ ,	27 $\text{Cu}_2\text{S} + \text{SnS} + \text{Zn}_{1-x}\text{Cd}_x\text{S} + \text{S} \rightarrow \text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$	Proposed
Heated to 800°C and cooled to 350°C	$\text{CdI}_2$ , $\text{CuI}$ , $\text{SnI}_4$ , $\text{Cu}_2\text{ZnCd}_{1-x}\text{SnS}_4$		

In figure 8, on the base of the  $\Delta G$  calculations for different reactions, we show that the most probable route to the formation of  $\text{Cu}_2(\text{ZnCd})\text{SnS}_4$  through the intermediate formation of  $\text{Zn}_{1-x}\text{Cd}_x\text{S}$  is by the formation of  $\text{CdI}^+(\text{g})$ . The chemical interaction between  $\text{ZnS}$  and solid  $\text{CdI}_2$  at temperatures lower than 400°C is not favourable because the  $\Delta G$  value is positive.

Therefore this rules out the possibility of formation of quaternary  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$ . As mentioned earlier, there exist a thermo-dynamical possibility for a possible reaction between  $\text{ZnS}$  and  $\text{CdI}^+$  to form  $(\text{Zn}_{(1-x)}\text{Cd}_x\text{S})$  at temperatures between 0 and 1000°C which is the only favourable path for the formation of  $\text{Cu}_2(\text{ZnCd})\text{SnS}_4$ .

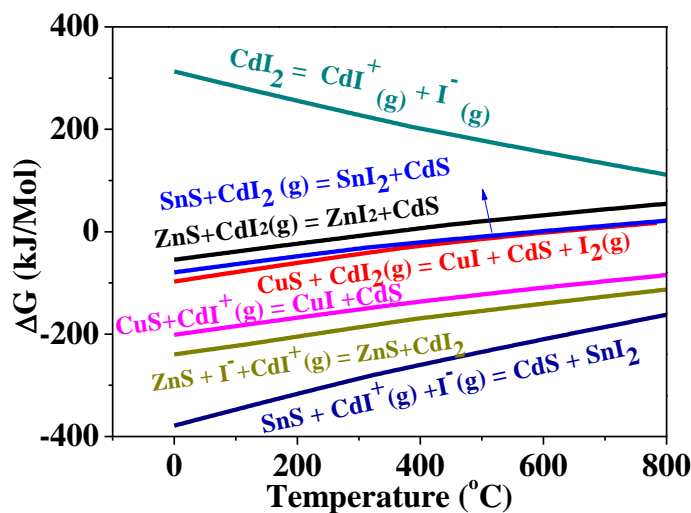


Fig 8: Calculated  $\Delta G$  values for different reactions showing the possible reaction path for the synthesis of  $\text{Cu}_2\text{ZnCdSnS}_4$  in molten  $\text{CdI}_2$

#### IV. CONCLUSIONS

By studying mixtures of  $\text{CdI}_2$  with individual precursors for synthesis of CZTS we found that  $\text{CdI}_2$  mixed with  $\text{S}$ ,  $\text{ZnS}$ ,  $\text{Cu}_2\text{S}$  or  $\text{SnS}$  melts at temperatures lower than pure  $\text{CdI}_2$  due to the freezing-point depression effect showing some solubility of the precursors in molten  $\text{CdI}_2$ .  $\text{CdS}$  and different iodine-containing compounds ( $\text{SnI}_4$ ,  $\text{Sn}_2\text{SI}_2$ ,  $\text{CuI}$ , and  $\text{Cu}_2\text{Cd}_3\text{I}_4\text{S}_2$ ) form in  $\text{CdI}_2 + \text{Cu}_2\text{S}$  and  $\text{CdI}_2 + \text{SnS}$ . The overall enthalpy value of the processes in each case studied is formed via an exothermic process alongside the endothermic melting of the  $\text{CdI}_2$  which gives rise to a lower melting temperature and enthalpy of fusion of the  $\text{CdI}_2$  flux. CZTS formation in molten  $\text{CdI}_2$  can be described as a two-stage process: first  $\text{CdI}^+$  reacts with  $\text{ZnS}$  forming  $\text{CdS}$ , that after alloying with  $\text{ZnS}$  results in  $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ . The amount of  $\text{CdI}^+$  increases with temperature

with the released Iodine acting as an oxidizing agent which reacts with  $\text{Cu}_2\text{S}$  and  $\text{SnS}$  resulting in different iodine containing compounds. Secondly,  $\text{Cu}_2\text{S}$  and  $\text{SnS}$  react to form ternary  $\text{Cu}_2\text{SnS}_3$ . The formation of  $\text{Cu}_2\text{SnS}_3$  from  $\text{Cu}_2\text{S} + \text{SnS} + \text{S}$  in  $\text{CdI}_2$  gave an enthalpy value of  $13 \pm 2 \text{ kJmol}^{-1}$ . The  $\text{Zn}_{1-x}\text{Cd}_x\text{S}$  and  $\text{Cu}_2\text{SnS}_3$  combines to form a quaternary CZCdTS. The synthesis of CZTS monograin powders in  $\text{CdI}_2$  results in the formation of solid solutions of  $\text{Cu}_2\text{Zn}_x\text{Cd}_{1-x}\text{SnS}_4$  with limited Cd content. The reaction of formation  $\text{Cu}_2\text{Zn}_x\text{Cd}_{1-x}\text{SnS}_4$  in the liquid phase of  $\text{CdI}_2$  takes place with the experimentally determined enthalpy of  $8 \pm 2 \text{ kJmol}^{-1}$ . The low enthalpy of formation of  $\text{Cu}_2\text{Zn}_x\text{Cd}_{1-x}\text{SnS}_4$  compared to high formation enthalpy of the ternary  $\text{Cu}_2\text{SnS}_3$  could confirm that the solid  $\text{Cu}_2\text{Zn}_x\text{Cd}_{1-x}\text{SnS}_4$  solution is formed from the reaction between  $\text{Cu}_2\text{SnS}_3$  and  $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ . The formation of  $\text{CdI}^+$  in the liquid phase is proposed to be a limiting

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.

### REFERENCES

- [1] Kauk-Kuusik, M., Timmo, K., Danilson, M., Altosaar, M., Grossberg, M., & Ernits, K. (2015). p-n junction improvements of Cu<sub>2</sub>ZnSnS<sub>4</sub>/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 Cu<sub>2</sub>ZnSnSe<sub>4</sub> 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 CuInSe<sub>2</sub> 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 CuInSe<sub>2</sub>. 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 (Cu<sub>2</sub>ZnSnSe<sub>4</sub>) 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 Substance ( continued ). *CRC Handb Chem Phys*. 2012;13(4):5.4 - 5.41, ([http://www.update.uu.se/~jolkkonen/pdf/CRC\\_TD.pdf](http://www.update.uu.se/~jolkkonen/pdf/CRC_TD.pdf)) retrieved on 11/04/2016.
- [10] Nkwusi, G., Leinemann, I., Raudoja, J., Mikli, V., Kauk-Kuusik, M., Altosaar, M., & Mellikov, E. (2014). Synthesis of Cu<sub>2</sub>(ZnCd)SnS<sub>4</sub> 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 (MX<sub>2</sub>)<sub>2</sub> Dimers (M= Zn, Cd, Hg; X= F, Cl, H) and Study of Relativistic Effects in Crystalline HgF<sub>2</sub>. *Inorganic Chemistry*, 33(21), 4718-4722.
- [12] Topor, L., & Moldovea. I. (1974). Vapor-pressures of molten CdBr<sub>2</sub>, CdI<sub>2</sub>, MgBr<sub>2</sub> 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, CdI<sub>2</sub> and Cs<sub>2</sub>CdI<sub>4</sub>. *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 Halides I. *Journal of the American Chemical Society*, 79(12), 3020-3024.
- [15] M. V. Šušić, S. V. Mentus, Cyclic voltammetry of molten CdI<sub>2</sub> and Cd-CdI<sub>2</sub>. *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 Cu<sub>2</sub>, 000S-Cu1, 960S. *Journal De Chimie Physique et de Physico-Chimie Biologique*, 71(3), 407-414.
- [17] Buerger, N. W. (1939). The Polymorphism of Cu<sub>2</sub>S, and the Relations Between the Solid Phases in the System Cu<sub>2</sub>S-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'Hères, 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 tetraiodide-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 ZnCl<sub>2</sub>: 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 ZnCl<sub>2</sub> 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, Washington 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] Oleksyuk, I. D., Dudchak, I. V., & Piskach, L. V. (2004). Phase equilibria in the Cu<sub>2</sub>S-ZnS-SnS<sub>2</sub> system. *Journal of alloys and compounds*, 368(1), 135-143.
- [32] Schurr, R., Hölzing, A., Jost, S., Hock, R., Voß, T., Schulze, J., ... & Kötschau, I. (2009). The crystallisation of Cu<sub>2</sub>ZnSnS<sub>4</sub> 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, September). Novel Cu<sub>2</sub>CdSnS<sub>4</sub> and Cu<sub>2</sub>ZnGeSe<sub>4</sub> absorber materials for monograin layer solar cell application. In *Proceedings of the 28th European Photovo.*