Formation and Growth of Cu_2ZnSnS_4 Monograin Powder in Molten CdI_2

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PRESS

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Declaration:
I hereby declare that this doctoral thesis, my original investigation and achievement, submitted to Tallinn University of Technology in partial fulfilment of my doctoral degree program, has not been submitted for any academic degree.

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LIST OF PUBLICATIONS

The thesis is based on the following papers, referred to in the text by Roman numerals

I.   **Nkwusi, G.**, Leinemann, I., Raudoja, J., Mikli, V., Kärber, E., Altosaar, M. Impact of growth-synthesis conditions on $Cu_2Zn_{1-x}Cd_xSnS_4$ monograin material properties. *Superlattices and Microstructures*, **98** (2016) 400-405;   (1.1)

II. **Nkwusi, G.**, Leinemann, I., Altosaar, M. The Processes and Enthalpies in Synthesis of Cu_2ZnSnS_4 in Molten CdI_2. *International Advanced Research Journal of Science, Engineering and Technology,* **3** (2016) 113-119;   (1.2)

III. **Nkwusi, G.,** Leinemann, I., Raudoja, J., Mikli, V., Kauk-Kuusik, M. Altosaar, M., Mellikov E. (2014). Synthesis of $Cu_2(ZnCd)SnS_4$ Absorber Material for Monograin Membrane Applications.– *[CD-ROM] MRS Proceedings 2014: 2013 MRS Fall Meeting. SCHOLARONE Manuscripts, (Symposium W – Next-Generation Inorganic Thin-Film Photovoltaics),* 1638.   (3.1)

AUTHOR'S OWN CONTRIBUTION

The contributions by the author in the papers I, II and III included in the thesis are as follows:

I   Raman and XRD sample preparation, quenching, sample washing and reporting of the results, major part of Raman measurement, plotting and analysis of the results, preliminary SEM-EDX measurements on a simple laboratory set-up, data analyses, and reporting/ interpretation of the results and major part of writing;

II   DTA, Raman and XRD data analyses, and reporting/ interpretation of the results, major part of thermodynamic calculations (ΔG) of the work with HSC program and major part of writing;

III Sample preparation, quenching, sample washing for Raman, and XRD, reporting of the results of preliminary simple laboratory SEM-EDX measurements, data analyses, and reporting/ interpretation of the results, major part of Raman measurements, plotting and analysis of the results, analysis of XRD results and reporting, major part of writing.

LIST OF ABBREVIATIONS AND SYMBOLS

ΔH_f	-	enthalpy of formation
ΔG	-	change in Gibbs free energy
ΔH	-	change in enthalpy
ΔH_{fus}		enthalpy of melting, heat of fusion
a-Si	-	amorphous silicon
at.	-	Atomic
cc	-	centered cubic
c-Si	-	crystalline silicon
CCdTS	-	copper cadmium tin sulfide, Cu_2CdSnS_4
CIGSe	-	copper indium-gallium diselenide, $Cu(InGa)Se_2$
CISe	-	copper indium diselenide, $CuInSe_2$
CTS		copper tin sulfide, Cu_2SnS_3
CZTS	-	copper zinc tin sulfide, Cu_2ZnSnS_4
CZTSe	-	copper zinc tin selenide, $Cu_2ZnSnSe_4$
CZTSSe	-	copper zinc tin sulpho-selenide, $Cu_2ZnSn(SSe)_4$
DTA	-	differential thermal analysis
EDX	-	energy dispersive X-ray spectroscopy
g	-	gaseous phase
hv		energy of photon
i	-	intrinsic
ICDD	-	International Centre for Diffraction Data
J	-	Joule
JCDPS	-	Joint Committee on Powder Diffraction Standards
KS	-	kesterite
L	-	liquid phase
MGL	-	monograin layer
MS	-	mass spectroscopy
NREL	-	National Renewable Energy Laboratory
p-n	-	hole-electron
PCE	-	power conversion efficiency
PV	-	photovoltaic
SEM	-	scanning electron microscopy
T_b	-	boiling temperature
TCO	-	transparent conductive oxide
TG	-	thermogravimetric
T_m	-	melting temperature
UV	-	ultraviolet
W_p		Watt peak
wt.	-	weight

INTRODUCTION

Recently, research in the field of low-cost solar cells has become popular in many countries. High-efficiency copper zinc tin sulphide (CZTS) based solar cell have received huge attention due to the need to develop a more environmentally friendly solar absorber material with relatively abundant and non-toxic elemental components[1]. Currently, one of the greatest limitations for large scale production of CZTS-based solar cells is the inability to reach efficiencies higher than the current record at 12.6% [2] made by the IBM company using the hydrazine-solution method. In 1988, *Ito et al.* reported first evidence of the PV effect of CZTS, using the thin film technology in which the active absorber material is a thin-film with a typical thickness of about 1 micrometer[3]. In 2007, an efficiency of 6.7% was reported. Till now, with more concerted efforts, the CZTS based solar cell has attained double efficiency, which is still far from the theoretical limit of 30%[4]. But unlike CZTS, other chalcogenides, such as $Cu(InGa)Se_2$ (CIGSe) and CdTe, have shown significant improvement in the device efficiencies (CIGSe 23.3% and CdTe 22.1% respectively[5] within the last 30 years and have currently reached mass production[6]. This has posed serious questions on how to improve the efficiency of CZTS-type solar cells to reach a mass production level.

From a scientific and technical point of view, the development of new technologies with higher conversion efficiencies and low production costs are a key requirement for enabling the deployment of solar energy at a large scale. The technology of monograin layer (MGL) solar cell is an alternative to the thin film technology. It allows the separation of materials formation from module fabrication. Large-area modules of monograin membranes are fabricated at room temperature in a continuous roll-to-roll process. Homogeneous composition of monograin powders gives an additional advantage, leading to up-scaling of homogeneous modules[7,8]. The best CZTS monograin layer solar cell has shown a conversion efficiency of 7.04% (active area 9.38%[9]). The monograin powder growth technology explores the use of suitable fluxes to aid the growth of single crystalline CZTS powders known as monograin powders[10]. In the monograin layer solar cell technology, a narrow size fraction of the powder grains, usually 30 to 100 μm, is embedded into a thin layer of the epoxy resin, forming a monolayer that serves as the light absorbing layer. As the synthesis of the monograin absorber material is carried out in molten flux, different fluxes (KI, NaI, CdI_2, and $SnCl_2$) have been used for the synthesis- growth[10–12]. The shape, size and properties of powder particles are influenced by different factors: time, temperature, nature and amount of used flux salt. Also, some other low melting intermediate components formed during the heating up period of synthesis and before the used flux salt melts can influence the shape and size of formed powder crystals through sintering of initial precursor particles. However, the impact of growth-synthesis conditions of CZTS in molten CdI_2 on the CZTS monograin material properties (morphology, yield, Cd incorporation from CdI_2) have not been studied yet. Knowledge about the formation process, understanding of the

chemical reaction pathway and the fundamental thermodynamic properties of the material may give additional information about the reasons for the poor crystal quality sometimes encountered and other limitations of the material. In addition, the constituent elements of the used salts (for example, K, Na and I) growing into the crystals dope the semiconductor compound at the level of their solubility at the growth temperature. CdI_2 contains only iodine as foreign dopant, Cd incorporates into crystal lattice as a substitutional component of compounds belonging to the group I_2-II-IV-VI_4. In this case, it is possible to study the impact of cationic substitution in the CZTS monograin powder.

In this thesis, we present the results of studies on chemical reactions and the enthalpies leading to the formation of CZTS in molten CdI_2[II]. Using different analytical methods – DTA, EDX, XRD, Raman, sieving and SEM – we have analyzed the reactions occurring in the separate mixtures of CdI_2 with individual binary precursor compounds (ZnS, SnS, and Cu_2S), and in the mixtures for synthesis of ternary Cu_2SnS_3 and quaternary Cu_2ZnSnS_4 compounds[II]. Focus was also on the impact of preparation conditions (temperature, time, amount of CdI_2 in synthesis) on the growth process and on the quality of Cu_2ZnSnS_4 monograin powder crystals[I].

The thesis is divided into three parts. The first part provides the literature overview; the second part describes the materials and methods used in this work. The third part describes and reports the experimental results obtained. It is subdivided into three main subparts: the first section presents the results of the formation and growth of CZTS in the molten CdI_2 as flux[III]. The second subsection presents the impact of preparation condition on the material properties[I]. The last part reports the thermo-analytical studies of mixtures of CdI_2 with different precursors and results in the enthalpies of the reactions occurring in different systems, starting from the individual binary precursors in the flux, followed by mixtures for the formation of ternary and quaternary compounds [III]. The results obtained and the conclusions of the work are summarized in the final part of the experimental section.

1. LITERATURE REVIEW

1.1 Solar cells

The history of solar technology is dated back to the 7th century Before Christ, where magnifying glass was used to concentrate the sun's rays to make fire and to burn ants[13,14]. The starting point of the research and development of solar cells was set by the discovery of the photovoltaic (PV) effect by the French experimental physicist Aléxandre Edmond Becquerel in 1839[15]. In 1883, an American inventor Charles Fritts described the first solar cells made from selenium wafers[6,17]. By 1905, Albert Einstein published his paper explaining the photoelectric effect on a quantum basis[18]. In the year 1954, Chapin *et al.*[19] at Bell Labs invented and developed silicon single-crystalline solar cell with 6% efficiency and improved the efficiency up to 15%. Today, silicon-based cells, also known as monocrystalline silicon, (classified as first generation solar cells) still dominate the solar cell industry. Photovoltaics is the most efficient method to produce electricity from the sun. The world's record with an efficiency of 25.6% was set in 2014 for Si (crystalline) laboratory solar cell[6] and 22.5% for commercially produced solar cells in 2010[6]. Other types of cells have been developed to add diversity in potential applications and also offer alternative options for low-cost PV cells. These alternative cells are based on different technologies, including the polycrystalline, the thin film and other emerging solar cell technologies, such as the monograin, quantum dot, and nanocrystals. For the thin film technology, the layers of semiconductor absorber materials are much thinner, only a few nanometers to tens of micrometers when compared to crystalline silicon, which is between 100- 500μm[20,21]. They are made by depositing one or more thin layers (thin films) of photovoltaic material on a substrate. They are cheaper and inexpensive to make, but efficiency is lower when compared to the monocrystalline silicon-based technology. They also consume a larger area per watt produced. The efficiency loss can be compensated by the low cost of production. Currently researched thin film solar cells include: amorphous silicon (a-Si) and other thin-film silicon (TF-Si), Cadmium Telluride (CdTe), Copper Indium Gallium Selenide (CIS or CIGSe), Dye-sensitized solar cell (DSC), and Copper Zinc Tin Sulphide (CZTS) solar cell. The other types of cells are organic dyes and organic polymers that are deposited on supporting substrates. However, recent results reported cover advancements in the efficiencies and performance of copper zinc tin sulfide (CZTS), copper zinc tin selenide (CZTSe) and solid solutions of them (CZTSSe) for both thin film and monograin technology. But so far, no commercial production has been reached for these materials[22–26].

1.2 Absorber materials in thin film solar cells

In the manufacture of solar absorber materials, despite the continued rapid cost reduction, concerns about material price and availability as well as toxicity have been raised. The high demand for indium used in copper indium gallium selenide (CIGSe) and the presence of cadmium as a major element in the case of CdTe have proved essential in the development of the current commercially available low-cost solar absorbers. $Cu_2ZnSn(SSe)_4$ (CZTSSe) enables us to alleviate the material bottlenecks present in CIGSe and CdTe. CZTS offers favorable optical and electronic properties similar to CIGSe (copper indium gallium selenide). But unlike CIGSe and CdTe, CZTS is composed only of abundant and non-toxic elements. The desire for clean solar technology has been a major motivation for alternative thin film solar cell materials. The first CZTS was shown to exhibit photovoltaic (PV) effect in 1988[3] and in 1997, a solar cell efficiency of 2.3% was recorded for CZTS with more progress every year[27–32]. Conventionally, a solar cell absorber should be a direct bandgap semiconductor material with a bandgap of 1–1.5 eV[33,34] and with a high optical absorption coefficient, i.e., greater than 10^4 cm^{-1}, long diffusion length, low recombination velocity, it should be able to form a good electronic *p-n* junction[35]. The chalcopyrites are similar to the kesterite in some regards and thus a comparison of both materials can provide vital information on how to improve the efficiency of CZTS. For instance, I_2-II-IV-VI$_4$ quaternary compound Cu_2ZnSnS_4 (and related compounds) can be presented as $CuInSe_2$ (compounds of group I–III–VI ternaries), where indium, which is very expensive, has been replaced by Zn and Sn, which are cheap and readily available[36,37]. In the Laboratory of Semiconductor Materials of Tallinn University of Technology, we use CZTS solar cell absorber material in the monograin layer (MGL) form where every grain functions (works) as a single solar cell. The problems of the grain boundaries appearing in the thin-film solar cell technologies do not exist in the MGL solar cell[38]. The aim of the studies of the group of Tallinn University of Technology researchers started in 2008 is to create and commercialize modules of powder-based $Cu_2ZnSn(S_xSe_{1-x})_4$ (CZTSSe) MGL solar cells. The studies have continued in collaboration with the Tallinn University of Technology spin-off company *Crystalsol OÜ*. A pilot production line was set up in the research and development facility of *Crystalsol GmbH* in Austria[38].
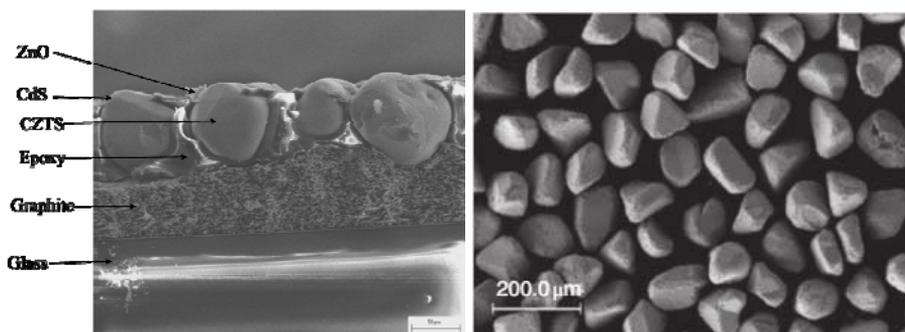
Figure 1. Cross-section of monograin layer solar cell structure (left) and SEM micrograph of an overview of Cu₂ZnSn(Se,S)₄ monograin powder synthesized in KI flux (size fraction 90-100 μm)[39].

1.3 The monograin growth technology and the use of flux in the synthesis of single crystalline powder materials

In the monograin technology, a solvent material is used to synthesize an absorber material usually referred to as flux material. The amount of the used flux material makes the main difference between monograin growth and sintering of the formed crystals in the thin film technology. In the thin film technology, a limited amount of the liquid phase (which allows the formation of contracting force between the crystals) (CuSe, Na₂S(Se)) formed in the thin film production process helps to grow the initial larger absorber crystallites and sinter them into compact and continuous thin films[38,40]. Meanwhile, in the monograin growth technology, it proceeds in the molten fluxes, which are present in an amount that fills all empty space between crystals and allows increasing the repulsive forces between crystals. In this case, initially formed crystals start to grow separate from each other and, as a result, single-crystalline powder forms. Since it is generally difficult to grow high-quality single crystals of the CZTS-type compounds from their melt due to the high melting temperature of the precursor materials, and because most of the compounds grow through a peritectic reaction or have a solid state phase transition during the cooling process[41], the monograin technology helps to achieve this goal. The powder growth technology explores the use of suitable salts as fluxes to aid the growth of single crystalline CZTS powders known as monograin powders[42,43] and by melting, the used salt creates a molten phase between the solid precursor particles. The molten phase between crystals helps to promote fast diffusion of constituent elements through the liquid phase and as compared to the thin film sintering process, a more homogeneous material can be produced. The driving force in the isothermal growth process of monograin materials is the difference in the surface energies of crystals of different sizes. The growth of single-crystalline powder grains takes place at temperatures higher than the melting point of the used flux material, but it could be much lower than the

melting point of the forming semiconductor compound. The role of the molten salts is to enhance the rate of solid state reactions due to much higher diffusion rates between reaction components in the molten media[38]; to lower the reaction temperature; to increase the degree of homogeneity (the distribution of constituent elements in the solid product); to control the particle size and shape; and to control their agglomeration state. This melt acts as a contracting or as a repulsion agent depending on the amount of it. If a suitable solvent material is present in an amount sufficient for the repulsion of initial crystallites, it allows growing separate powder grains. This leads to the formation and growth of single-crystalline powder materials with uniform composition and narrow-disperse granularity known as monograin powders. Some important requirements for a flux material include:

- Low melting point - lower than the melting point of Cu_2ZnSnS_4;
- It should be stable, readily available, inexpensive and soluble in water – easily removable[44];
- It should have a low vapor pressure at the heating temperature and it should not cause undesirable reactions with either the reactants or the product;
- It should allow the possibility to control the composition of Cu_2ZnSnS_4 (not contain constituent elements of the compound);
- It consists of components that could improve the properties of Cu_2ZnSnS_4 (as dopants)[38,39].

To improve the quality of the grains used in solar cells, different salts (KI, ZnI_2, CdI_2 and NaI) have been studied as fluxes[43]. Each of these flux materials has one advantage to be considered over the others. For instance, KI is not highly hygroscopic, with high melting temperature (686 °C)[45,46] NaI is more hygroscopic than KI[44], but with a lower melting temperature (651 °C)[47]. CdI_2 has a low melting temperature (387 °C)[48,49] and is much less hygroscopic compared[50] to NaI and KI but concerns may be raised with respect to the amount of Cd present after synthesis.

1.4 Monograin layer solar cells

The history of monograin membrane technology is dated back as far as the 1960s when Ties Siebold te Velde from the Philips Company filed the first patent in 1965 on monograin layers, mainly of II-VI group compounds, using already a *p-n* junction. During the next year, they filed the first patent on monograin membrane devices[51]. The first patent of researchers of TTÜ for using monograin powders as solar cell absorbers "Monocrystalline powder and monograin membrane production" was filed in 1998 (WO9967449, priority date June 25, 1998) by M. Altosaar, D. Meissner, and E. Mellikov[8]. In their work, monocrystalline absorber crystals were synthesized and the formed powder grains were grown in the molten phase of a suitable flux salt. The resultant monograin powder was used in PV solar cells as absorber material in the monograin layer (MGL) form. The MGL

solar cell combines the features of a monocrystalline solar cell and a thin film solar cell.

In the MGL design, each *p-type* single crystal of an absorber covered with a thin layer of *n-type* material (usually CdS, deposited by chemical solution deposition before making membrane) works as an individual solar cell. To make a monograin membrane, grains of known size are embedded into a thin layer of epoxy resin (or some other polymer) to avoid the coverage of the upper surfaces of crystals with a polymer to form a monolayer. Narrow size fractions of the powder grains separated by sieving from powder grains (usually with diameter between 30 to 100 µm) are used for a membrane. The polymer film thickness is adjusted to half of the grain size. This implies that for a perfect monograin layer, the shape of the grains is very important. Spherical grains give a higher possibility to form a perfect monolayer and prevent stacking of grains when compared to the grains with tetrahedral pyramidal structure, which could give higher packing density[8]. After polymerization of epoxy, the CdS layer is deposited onto the front side of the monograin layer, followed by a ZnO window layer by RF-sputtering and then glued onto the glass. After glueing the structures on glass, the back contact area of crystals is opened by etching epoxy with H_2SO_4, followed by an additional abrasive treatment. The back contact is made using graphite paste. The final solar cell structure is graphite/CZTS/CdS/ZnO (see Figure 2). Currently, CZTS monograin layer solar cells have shown power conversion efficiency of about 9.38% (calculated from the active area of the solar cell)[9,39].
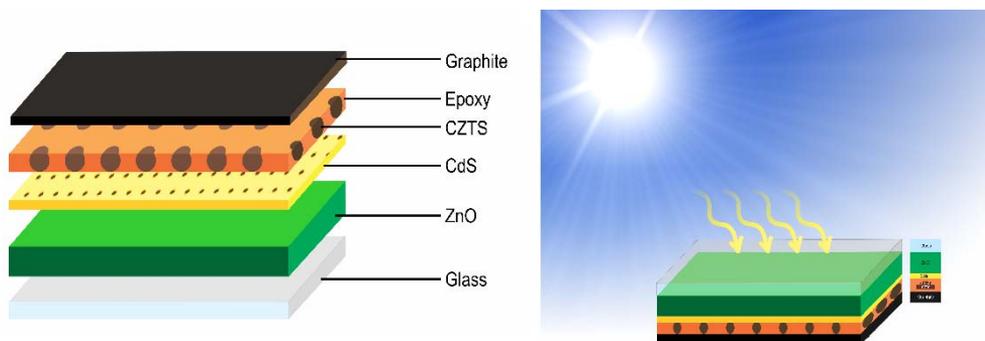
Figure 2. Scheme of monograin layer solar cell structure: graphite/CZTS/CdS/ZnO on glass (or a polymer encapsulation can be used).

1.5 Phase diagrams

The T-x phase diagrams provide information about the phases in the equilibrium state at certain temperatures depending on the composition of its component materials. In our system, CZTS is synthesized using three binary precursors (Cu$_x$S, SnS, and ZnS) and elemental sulphur in a molten flux to achieve the desired deviation from stoichiometry under experimentally clarified Cu-poor and Zn-rich growth conditions. Previous studies including those by the research group of Tallinn University of Technology have already demonstrated the complexity of the phase diagram of CZTS[52] but a good understanding of the currently available information will help to guide our work and provide a better understanding of the results obtained. According to previous work by Nagoya *et al.*, the first-principles studies of the phase stability and defect formation in Cu$_2$ZnSnS$_4$ showed that CZTS is thermodynamically stable for a small confined domain of chemical potentials. It means that a slight deviation in the optimal growth conditions will result in the formation of secondary phases[53]. This section gives a general overview of the phase diagrams of the used binary precursors, formed ternary CTS and quaternary CZTS compounds.

1.5.1 Phase diagrams of binary precursor compounds (Cu-S, Sn-S, and Zn-S)

In the synthesis of CZTS in CdI$_2$ starting from the binary precursors Cu$_2$S, SnS, ZnS and S, we studied the thermal behavior of each individual compound by using phase diagrams as comparable material. Cu$_2$S, ZnS and SnS$_2$ melt congruently at 1130 °C, 1700 °C and 860 °C, respectively, with very narrow homogeneity regions[54]. Figure 3 presents the phase diagram of Cu-S and Sn-S. The phase diagram of Cu-S shows that at low temperature, copper sulphide may occur in different phases, such as the monoclinic low α- chalcocite (αCh), hexagonal high temperature-chalcocite (βCh), and covellite (Cv) (CuS). The covellite goes through peritectic transformation to digenite with deliberation of S and is stable up to 507±2 °C[55]. The hexagonal high temperature-chalcocite (βCh) is stable from 103.5± 0.5 °C at the Cu-rich limit of stoichiometric Cu$_2$S, and also from 93±2 °C to 435 °C at 33.44 at.% S to 33.34 at.% S. There is cubic γ-modification at temperatures above 435 °C. ZnS is a well-known wide-gap semiconductor (3.6 eV) of *n- type* conductivity[56]. It exists both in the zinc-blende structure and in the wurtzite structure with the phase transition zinc blende⇔wurtzite occurring at 1020 °C[57]. For a SnS system, it is known that the S–Sn system contains four solid solution phases: (a) the four elemental solid phases (α-S, β-S, α-Sn and β-Sn) where α-, β- are low-temperature and high-temperature phases of the elements, respectively; (b) the liquid and the intermediate compounds of Sn-S that contain: (1) the low-temperature α-phase, (2) B16 spatial group Pbnm (α- SnS), (3) high-temperature β-phase with type II lattice B33 and (4) the spatial group Cmcm (β-SnS); (c) a gas phase of SnS, Sn$_2$S$_3$, and SnS$_2$[58] and (d) allomorphs[59]. The

elasticity of SnS vapor showed that the melting point of SnS in a neutral atmosphere is 880 °C, and the boiling point at normal air pressure is 1230 °C. The maximum melting point of 881 °C was found for SnS at sulfur pressure 3.34×10^3 Pa[58].

All the binaries melt at a very high temperature[59,60], as compared to the melting temperature of the flux material (CdI$_2$). The compounds existing in Cu-S, Zn-S and Sn-S binary systems and their thermal stability regions, crystal structures, XRD cards, and Raman data are presented in Table 1.
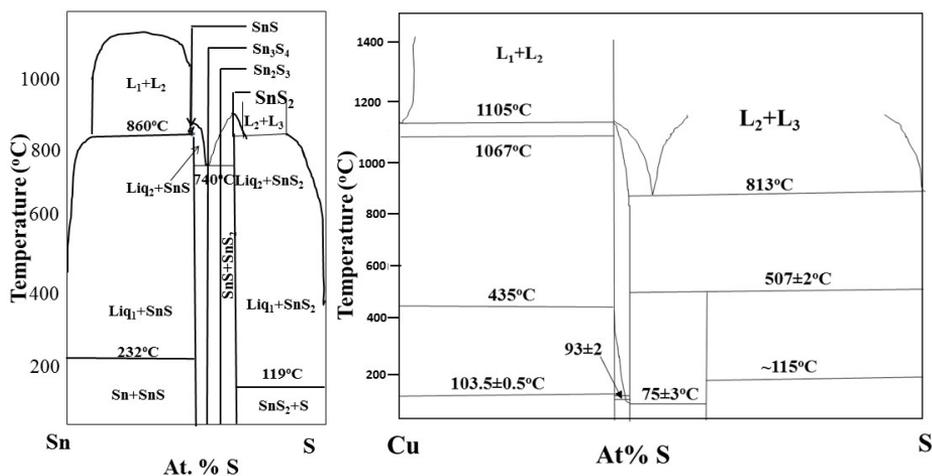
Figure 3. *Phase diagram of (a) Sn-S system, (b) phase diagram of Cu-S system adopted from*[55,58,59].

Table 1. Compounds in Cu-S, Zn-S and Sn-S binary systems

Compound Formula	Mineral name	Stability area (^{O}C)	Crystal structure/ space group	XRD ICDD file no	Raman peaks (cm^{-1})
CuS	Covellite	T < 507	hexagonal	06-0464 75-2233	474[63–65]
Cu_2S	Low-temp. Chalcocite	0 < T < 104	orthorhombic	23-0961 73-1138	257,478,465
	High-temp. Chalcocite	90 < T < 435	hexagonal	84-0206	264, 475[66–68]
Cu_xS	Digenite (Cu1.86-1.80S)	72 < T < 1130	rhombohedral	47-1748 84-1770	259,264,466,475[68,69]
	Djurleite (Cu1.95-1.91S)	T < 93	orthorhombic	42-0564 83-1463	
	Anilite (Cu1.75-1.65S)	T < 75	orthorhombic	72-0617	
ZnS	Wurtzite	T < 1020	hexagonal	79-2204	275,352[67]
	Sphalerite	T >1020	cubic	05-0566 71-5975	
SnS	Herzenbergite	*T*< 602	orthorhombic		96,163, 186,220,288[60, 69, 70]
		T> 602	*Pnma*		
Sn_2S_3	Ottemanite		*Pnma*	75-21830	52, 60, 307[61,72]
SnS_2	Berndtite		Hexagonal an extended R$\bar{3}$ polytype $P\bar{3}m1$	23-0677 83-1705	312[61,70,71]

1.5.2 Quasi-binary phase diagrams

The studies of the interaction between Cu_2S, SnS and ZnS in CdS showed that the solubility of Cu_2S in CdS at eutectic point (1011 ^{o}C) is 55 mol% CdS and decreases to 40 mol% CdS at 915 ^{o}C and 10 mol% at 555 ^{o}C[54]. In the case of a SnS-CdS system, the SnS_2-CdS system is also an eutectic type with eutectic point coordinates at 22 mol% CdS at 770 ^{o}C. Two different studies by Piskach *et al*. showed the formation of different compounds ($CdSn_2S_5$, $CdSnS_3$ and Cd_2SnS_4)[62]. The ZnS-CdS phase diagram was studied by Ballantyne and Ray *et al*.[73]. They

found the formation of solid solutions over the complete range of compositions in sphalerite (sph), wurtzite (wu) and greenockite (grn) structure (the melting point of CdS is 1750 °C). And there exist equilibria between the zinc blende and wurtzite $Cd_xZn_{1-x}S$ solid solutions formed[74–76]. In the Cu_2S–$Zn(Cd)S$ system, the maximum solubility of ZnS in Cu_2S was 42 mol% of ZnS at the peritectic temperature at 1185 °C with limited solubility in the solid state[54], but it decreases as the temperature falls to less than 1 mol% ZnS at 397°C[77,78]. In the phase diagram of Cu_2S–SnS_2 system (Figure 4), the liquidus line starts at the melting point of Cu_2S at approximately 810 °C and decreases down to the first eutectic point at T_{eut1}=800 °C and ends at the melting point of SnS_2 at 865 °C. At the first eutectic point, Cu_4SnS_4, Cu_2S, liquid and vapor phase in equilibrium. The eutectic composition denotes the lowest possible solidification and melting temperatures in the sub-system Cu_4SnS_4–Cu_2S[77].

According to Fiechter $et\ al.$ and Olekseyuk $et\ al.$, four stable ternary phases of CTS; $Cu_4Sn_3S_8$, Cu_4SnS_4, Cu_2SnS_3 and $Cu_2Sn_3S_7$ exist, three of these ternaries Cu_4SnS_4, Cu_2SnS_3 and $Cu_2Sn_3S_7$ form in the Cu_2S–SnS_2 section and their melting point was determined as 833, 860 and 803 °C, respectively[54,77]. $Cu_2Sn_3S_7$ is stable only at 685 °C, other ternaries are stable at room temperature. They were characterized by four eutectic points and a series of solid–solid phase transitions for $x > 50$ mol% SnS_2 with a wide homogeneity range of $Cu_2Sn_{3+x}S_{7+2x}$ at elevated temperatures and a polymorphic transformation of the ternary compound Cu_2SnS_3 found at 780 °C[77,79]. Cu_2SnS_3 can be formed from two eutectic sections L⇔Cu_2SnS_3+α and L⇔Cu_2SnS_3+γ at 820 and 788 °C, respectively. In addition, the quasi-ternary system Cu_4SnS_4 and $Cu_2Sn_4S_9$ were formed by α+Cu_2SnS_3 at 810 °C and Cu_2SnS_3+γ at 670 °C, respectively, where α and γ are Cu_2S and SnS_2, respectively (Figure 4). The solubility of (Cu_2S–SnS_2) is minor and does not exceed 5 mol% of either one. Cu_2S undergoes polymorphic transformations at 383 and 108 °C as Cu_2S: α⇔α′+Cu_4SnS_4 and α′⇔α″+Cu_4SnS_4, where α, α′ and α″and low, medium and high-temperature phases of Cu_2S. In the ZnS–SnS_2 system, the studies by Nekrasov $et\ al.$ and G.H. Moh $et\ al.$ reported in[80,81] showed that ZnS–SnS_2 is a quasi-binary section of a ternary system with no ternary phases formed in the system. The eutectic point coordinates were found to be 2.5 mol% ZnS at 800 °C and the solubility does not exceed 1 mol% of ZnS in SnS_2 and 5 mol% of SnS_2 in ZnS. In the formation of CZTS, ZnS–SnS_2 was observed as the limiting side of the reaction[54].
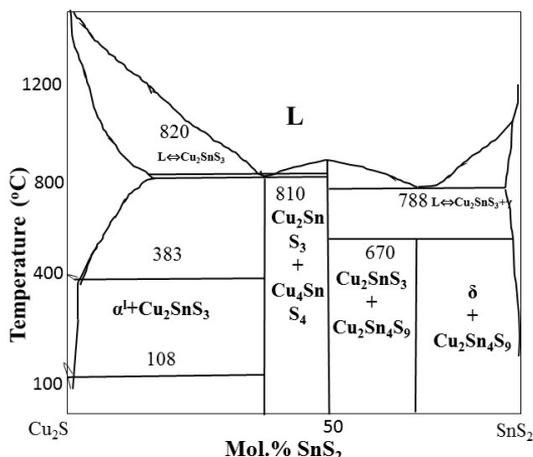
Figure 4. Summary of the phase diagram of the Cu₂S–SnS₂ system; α and γ are Cu₂S and SnS₂, respectively[82].

1.5.3 Quasi ternary and quaternary mixtures

The study of the phase diagram of Cu_4SnS_4-CdS by Olekseyuk and Piskach revealed the formation of the quaternary compound Cu_2CdSnS_4 that melts congruently at 905 °C[62]. A eutectic section is formed between Cu_2SnS_3 and Cu_2CdSnS_4 at 853 °C and 15 mol% CdS. The various transitions and phases formed were reported in[62]. At various compositions of mixtures of Cu_2S-SnS-CdS, different quaternary phases ($Cu_2CdSn_3S_8$, Cu_2CdSnS_4, $Cu_2CdSn_4S_9$) were formed with their character and temperatures reported in [62]. The quasi-ternary Cu_2S–CdS–SnS_2 system is separated into two quasi-ternary subsystems Cu_2S–Cu_2SnS_3–CdS and CdS–Cu_2SnS_3–SnS by the quasi-binary Cu_2SnS_3–CdS.

In the Cu_2SnS_3–ZnS system (Figure 5), a quaternary compound, Cu_2ZnSnS_4, forms in it at 980 °C by the peritectic reaction L+β⇔Cu_2ZnSnS_4 (where β is the solid solution range of the low-temperature modification of ZnS). According to[54], the study of an isothermal section of Cu_2S−ZnS−SnS_2 at 397 °C showed the formation $Cu_2ZnSn_3S_8$ quaternary compound. $Cu_2ZnSn_3S_8$ is formed by the reaction $SnS_2+Cu_2ZnSnS_4⇔Cu_2ZnSn_3S_8$ at 697 °C. At 670 °C, a ternary compound $Cu_2Sn_4S_9$ forms in the quasi-binary section of Cu_2S–SnS_2 by the peritectoid reaction $Cu_2SnS_3+SnS_2⇔Cu_2Sn_4S_9$. The formation of $Cu_2Sn_4S_9$ causes the existence of a plane at 660 °C in the quasi-ternary phase diagram of Cu_2S–SnS_2–ZnS system, which corresponds to the reaction $Cu_2SnS_3+SnS_2+Cu_2ZnSnS_4⇔Cu_2ZnSn_3S_8+Cu_2Sn_4S_9$.
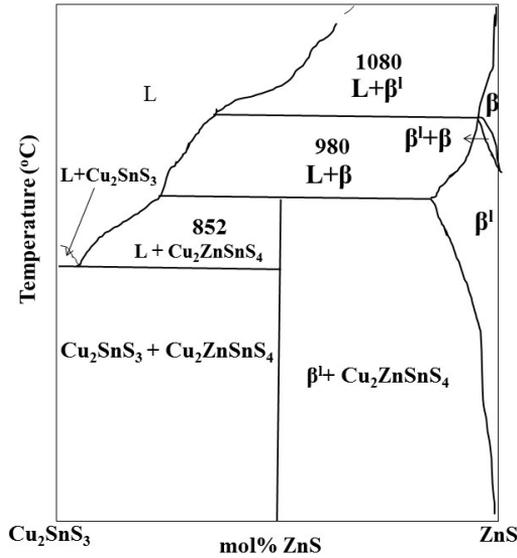
Figure 5. Phase diagram of various quasi ternary mixtures of CTS+ZnS where β and $β^l$ are high-temperature and low-temperature ZnS, respectively.

In Figure 6, considering the Cu_2S–A section (A=50 mol% ZnS and 50 mol% SnS_2)[54], the liquidus consists of three lines that limits the field of primary crystallization of the α-solid solution. The lines are 880 and 790 °C, which correspond to ternary peritectic reactions $L+β^l⇔α+δ$ and $L+β^l⇔δ+γ$, respectively and at 697 °C where $Cu_6Sn_3S_8$ is formed (given that α, β, $β^l$, γ and δ are Cu_2S, LT-ZnS, HT-ZnS, SnS_2 and Cu_2ZnSnS_4, respectively) and at 697 °C where $Cu_6Sn_3S_8$ is formed. The single phase region δ is limited by the three phase region $L+ β^l + δ$, and the line between them is two-phase $β^l+δ$ homogeneity region of the δ-solid solution, which has a tendency to increase slightly with temperature (see Figure 6). The SnS_2–B section (B-50 mol% ZnS, 50 mol% Cu_2S) also contains three horizontal lines that correspond to ternary peritectic reactions similar to Cu_2S–A section (A-50 mol% ZnS, 50 mol% SnS_2) at 697, 790 and 880 °C. The quaternary compound Cu_2ZnSnS_4 has a homogeneity region of 3 mol% of either initial component at 733 °C. Further away from this point and 733 °C, the field apart breaks into the two two-phase fields; $γ+Cu_2ZnSn_3S_8$ and $Cu_2ZnSn_3S_8+δ$, which is caused by the formation of $Cu_2ZnSn_3S_8$. In the Cu_4SnS_4–Cu_2ZnSnS_4 section, the crystallization of the alloys terminates in the ternary peritectic reaction $L+Cu_2SnS_3⇔Cu_4SnS_4+δ$ at 807 °C and the solubility based on Cu_2ZnSnS_4 is less than 5 mole% of Cu_4SnS_4. Considering the $Cu_2Sn_4S_9$–ZnS section, the liquidus of the $Cu_2Sn_4S_9$–ZnS section consists of lines that correspond to the fields of primary crystallization of the γ-, δ-, $β^l$- and β-solid solutions and the secondary crystallization that ends at 763 °C in a ternary eutectic reaction. In the sub-solidus region, the phase equilibria are caused by the formation of $Cu_2Sn_4S_9$ on the side

and of $Cu_2ZnSn_3S_8$ within the concentration triangle. Investigation of the Cu_2S-ZnS-SnS_2 pseudo-ternary system showed that the single-phase Cu_2ZnSnS_4 is present only within a rather narrow range of compositions[54,83]. Theoretically, even a 2-3% compositional variation could lead to phase separation. The CZTS compound exists under the line between Cu_2SnS_3 and ZnS[84]. Table 2 shows Raman and XRD data for our materials.
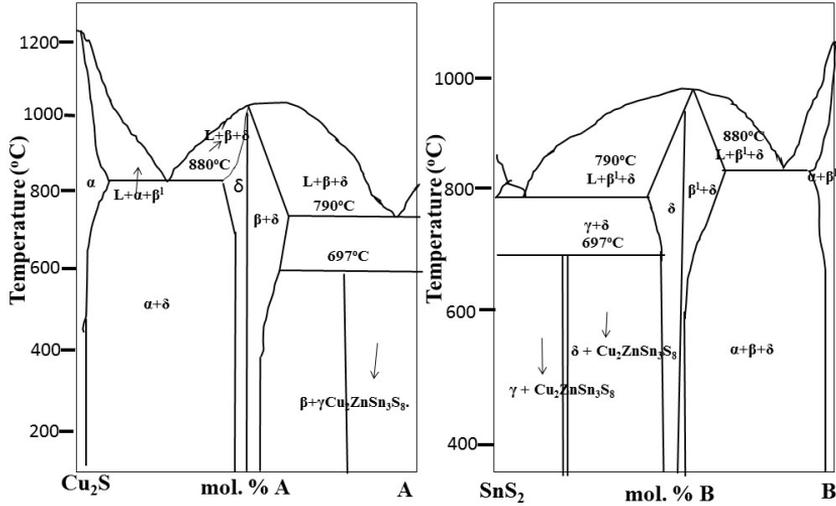
Figure 6. The phase diagram of Cu_2S-A (A-50 mol% ZnS, 50 mol% SnS₂) and SnS₂-B (B-50 mol% ZnS, 50 mol% Cu₂S) where α, β, βˡ, γ and δ are Cu₂S, LT- ZnS, HT- ZnS SnS₂ and Cu₂ZnSnS₄, respectively.

Tabel 2. Compounds existing in Cu-S, Zn-S and Sn-S binary systems

Compound formula	Mineral name	(°C)	Crystal structure/ space group	XRD	Raman peaks (cm⁻¹)
Cu_2SnS_3	Mohite	-	Monoclinic	04-010-5719	290, 352, 314, 374[71,85]
		T> 400	Cubic	89-2877	267, 303, 356[66,67]
		T< 400	Tetragonal	89-4714[86]	297, 337, 352[66,67]
CZTS	Kesterite	>500[87]	Tetragonal	26-0575	68, 82, 97, 140, 164, 255, 263, 271, 287, 302, 316, 338, 347, 353, 367, 374[88,89]

1.6 Theoretical background of molten salt synthesis and the CZTS formation process in molten fluxes

Kesterite structured Cu_2ZnSnS_4 (CZTS) (and other compounds of this group) as absorber for a solar cell is a promising semiconductor for low-cost and sustainable energy production[23,90]. As reported earlier, different molten salts (fluxes) have been used in ceramics as additives to enhance the rates of solid state reactions for a long time[91]. In this case, the amount of salt is small, typically a few percent of the total weight. The small amount of flux helps to sinter together and grow solid crystals (particles) in the thin film technology also[38]. In contrast, in the molten salt synthesis, a large amount of salt is used as the solvent to control powder characteristics (size, shape, etc.). In this sense, the molten salt synthesis is different from the flux method, which uses the salt as an additive to enhance the reaction rate. Salt with a low melting point is added to the reactants and heated above the melting point of the salt. The molten salt acts as the solvent. In many cases, the formation reaction occurs in the presence of solid reactant particles. In this sense, molten salt is somewhat different from ordinary solvents, which dissolve all reactant particles and the product particles precipitate from a homogeneous liquid phase[91].

The role of flux material makes the main difference between the monograin growth (solid precursor particles are surrounded with a large amount of molten flux that allows growth of individual crystals and no sintering together) and the thin film synthesis methods (limited amount of flux helps to sinter individual crystals together, forming a solid film). In the isothermal crystalline growth process of monograin materials, the driving force is the differences in the surface energies of crystals of different sizes. The growth of single-crystalline powder grains takes place at temperatures higher than the melting point of the used flux material, i.e., much lower than the melting point of the semiconductor compound. An optimal amount of the used flux material is observed if the volume of the liquid phase is about 0.7 of the volume of the solid phase[92]. 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 the synthesis temperature. On the other hand, the used precursor compounds and the formed CZTS dissolve in the molten flux to some extent. The solubility of precursor compounds in KI was determined by I. Klavina *et al.*[10] as follows: 3.6 mol% CuSe, 0.27 mol% SnSe and 0.086 mol% ZnSe at T=740 ºC. The solubility of $Cu_2ZnSnSe_4$ in KI was determined as 0.61 mol%. In addition, the doping of the synthesized monograin powder with Na and K, also with Cl, has a rather strong influence on the monograin absorber material properties[93,94]. On the contrary, use of CdI_2 as a flux in monograin powder growth allows us to produce a material without K (Na) doping and allows further possibilities to study the influence of intentional Na and/or K doping of CZTS. K. Timmo *et al.* showed that the solubility of the synthesized material in the flux affects the shape of growing grains[95].

In the monograph technology (MGT), the growth process is carried out in a closed ampoule and proceeds via isothermal conditions with the flux salt being saturated by precursors and the formed compound. The dissolution and crystal growth processes go on simultaneously; the smaller crystals dissolve in the flux and deposit onto surfaces of larger crystals through mass transport (diffusion) in the molten phase that surrounds every crystal. The dissolution is more intensive in places where the surface energy is higher (grain borders, tips) and deposition on plain surfaces (facets). Increasing the solubility of the formed compound in the flux (by increasing the temperature or by using a flux material that permits higher solubility), the dissolution process can prevail and the border of crystals takes more rounded shape. At equilibrium, the dissolution-deposition rates are equal to each other and crystals tend to attain equilibrium shape. The equilibrium can be related to the volume of the growth solution and the time of growth[96,97]. In the review paper of M. A. Lovette *et al.*[97], the formation of a solid polyhedron with volume V from a fluid phase was described by Gibbs-Thomson for the change of free Gibbs energy ΔG. Although Gibbs was the first to develop the criteria for equilibrium crystal shapes, he recognized that crystal shapes are usually determined by kinetics rather than by thermodynamics alone. In the synthesis-growth process, solid, powdery precursors are used[95]. They have different solubility in molten salts, which is comparatively low. When the mixtures are heated up and the molten phase starts to form but the dissolution of solids in the liquid flux has not reached the equilibrium state, the primary solid particles can sinter together. When the amount of liquid phase increases, it could penetrate into capillaries, repelling the weakly joined particles from each other.

1.7 Some limitations identified in the monograin growth process

Current information about the chemical reaction pathway leading to the formation of CZTS in molten salts is limited. According to Jackson *et al.*, CZTS is thermodynamically stable with respect to its component elements[52]. Studies have already demonstrated the complexity of its phase diagram and the possibility to form multiple secondary phases which may be due to incomplete reaction or partial decomposition of the material at certain reaction conditions, such as temperature, pressure and synthesis time. It was previously reported that in CZTS thin film growth by the vacuum evaporation method, CZTS began to decompose intensively at a temperature above 500 $^{\circ}$C under sulfur pressure of 10^{-2} Pa, also with some SnS evaporation at temperatures as low as 350 $^{\circ}$C[98] according to equations (1) and (2). This report showed that the partial pressure of sulphur is critical in the region 10^{-4} mbar (10^{-2} Pa) and sufficient SnS vapor can prevent irreversible evaporation[87].

$$Cu_2ZnSnS_4 \, (s) = Cu_2S \, (s) + ZnS \, (s) + SnS \, (s) + 1/2 \, S_2 \, (g) \qquad (1)$$

$$SnS \, (s) = SnS \, (g) \qquad (2)$$

Another significant finding by Scragg *et al.* was the gain in the configurational entropy caused by high-temperature annealing (≥500 ºC), which leads to significant cation disorder[99]. Furthermore, there is no adequate information about the route to the formation of CZTS in molten flux. Fundamental thermodynamic properties of the material are not well understood. The presence of secondary phases on the surface of grown absorber material crystals is still a major setback because it can lower the final output parameters of a solar cell and be detrimental to solar cell efficiency. For instance, zinc sulfide (ZnS) is a stable binary phase with a high negative enthalpy of formation of 205 kJmol^{-1} and has a much larger bandgap than CZTS. ZnS separate phase leads to the formation of internal barriers in thin films, which are expected to degrade the solar cell performance[100]. In their study[101], Qin Li *et al.* reduced experimentally the band gap of ZnS from 3.1 to 2.3 eV by the formation of $Zn_{1-x}Cd_xS$[101]. For CIGS solar cells, the band gap of 1.1~1.13 eV is considered to be optimum. In CZTS, the band gap is 1.3-1.5 eV [102–104]. Jie Fu *et al.*[104] suggested that the ideal way to reach the optimum band gap level would be to reduce the S content by introducing some selenium in the synthesis process or by the metal cation substitution process. In their work, they incorporated successfully about 5% of Cd into the host lattice of CZTSSe to form a homogeneous $Cu_2Zn_{1-x}Cd_xSn(SSe)_4$, which improved the crystal growth process, lowered the band gap (1.12 eV) and improved the solar cell efficiency from 5.41 to 8.11 %[104]. This result was also confirmed by Sun *et al.* [102] where the solar cell efficiency was increased from 5.3 to 9.8 %. The exchange of Zn with Cd helps to reduce the formation of Cu_{Zn} and Zn_{Cu} antisite defects which form due to the similar ion radii of Cu and Zn[104]. And finally, the substitution of Zn with Cd also helps to reduce the narrow single-phase region of CZTS [105]. As part of the efforts to improve CZTS solar cell efficiency, new strategies are needed to produce a more homogeneous material and minimize secondary phases. An understanding on how to resolve the aforementioned limitations could help to explain the formation process and to understand the properties of the as-grown monograin powder. This adds weight to the study of the reactions path and mechanism for the formation of CZTS.

1.8 Summary of literature review and aim of the current study

From the review of literature, the following main observations can be presented:
1. The direct band gap of 1.45-1.5 eV, large absorption coefficient 10^4 cm^{-1}, and abundant and nontoxic constituent elements make CZTS attractive as an absorber material for solar cell application. CZTS thin film technology has been overtaken and developed from the technology of CIGSe, but the non-vacuum methods developed lately are even more efficient, reaching the CZTSSe solar cell efficiency with tuned band gap material up to 12.6 %.
2. Monograin technology allows us to produce absorber materials in single crystalline powder form and to use monograin membrane layers made

from these powders in solar cell structures where each grain can work as a single crystalline solar cell. So far, 9.5 % of certified efficiency has been reached for $Cu_2ZnSn(SeS)_4$ monograin layer solar cells.

3. Previous reports have shown that quaternary selenide CZTSe in monograin powder form can be synthesized in different flux materials, such as KI (T_m=686 °C[106]), NaI (T_m=661 °C[107]), and CdI_2 (T_m=387 °C[108]). CdI_2 can be used as a low-temperature flux, allowing the formation of CZTSe at much lower temperatures than in KI and NaI.

4. According to I. Leinemann *et al.*, the formation process of $Cu_2ZnSnSe_4$ takes place in NaI and KI fluxes and the chemical interactions between the binary precursor compounds CuSe, SnSe, ZnSe in molten NaI and KI in vacuum ampoules but not for CdI_2. It was shown that monograin powders of $Cu_2ZnSnSe_4$ with tailored chemical composition could be synthesized and the powder crystals can be grown by isothermal heating of initial binary compound precursors in molten KI. In conclusion, they found that NaI as a flux material is preferable due to the possibility to reduce the synthesis temperature, but the issue of hygroscopicity of NaI is a drawback. KI is a good choice but it has a high melting temperature[11,12].

5. Recent studies have shown that the metal cationic substitution of Cd with Zn could help improve the efficiencies of CZTSSe solar cells[102,109,110]. In studies where Zn is partly replaced with Cd, the bandgap shifting to the lower energy side occurs[104,111,112], enabling better fitting of the solar cell absorber material with the solar spectrum.

However, the formation pathway of Cu_2ZnSnS_4 in molten CdI_2 is still unexplored and the chemical interactions of precursors with molten CdI_2 are unclear. Neither has the impact of growth-synthesis conditions of CZTS in CdI_2 on the CZTS monograin material properties been studied.

Therefore, the aim of the present thesis is:
- to study the formation of CZTS crystals in molten CdI_2 in closed vacuum ampoules starting from binary compound precursors (ZnS, SnS, Cu_2S, S) and to describe the chemical pathway;
- to find out and describe the physical and chemical processes occurring in the thermal heating of CdI_2 with individual precursor compounds, also in the mixture of CdI_2 with precursors for synthesis of ternary CTS and quaternary CZTS compounds in closed vacuum ampoules;
- to study the influence of growth process conditions on the CZTS monograin material properties by using prolonged heating durations and increased flux concentrations at different temperatures on the shape of the crystals, on the Cd content in product crystals and on the yield of useful size fractions of the grown monograin powders.

2.0 EXPERIMENTAL

This section presents the experimental procedures for this work in brief. Comprehensive details are reported in the publications given in Appendix A.

2.1 Methodology, materials and sample preparation

In this thesis, the chemical interactions between the used precursor compounds and CdI_2 as a flux material in the synthesis of CZTS were studied [II, III]. The investigations of mixtures of CdI_2 with individual binary compounds (Cu_2S, ZnS, and SnS) and S were followed by studies on more complicated mixtures for synthesis of Cu_2SnS_3 (CTS) and Cu_2ZnSnS_4 (CZTS). We started with the determination of temperatures and enthalpies of possible reactions or phase changes by the differential thermal analysis (DTA) in CdI_2/precursor mixtures of 0.25g, where the ratio of CdI_2/precursor was kept at the ratio 1:1. DTA studies were performed in vacuum-sealed quartz ampoules adopted for the used DTA set-up. For DTA calibrations, the same flux salt CdI_2 was used as reference material because the traditionally used reference materials were not stable in contact with quartz ampoules or gave a very weak signal. After that, to determine the processes accompanied with thermal effects, we prepared individual samples for every thermal effect detected by DTA and heated them for prolonged time (4 hours) at temperatures a little above the recorded effect and quenched. Then the phase composition of these larger samples was analyzed by Raman spectroscopy, by X-ray diffraction (XRD) and by energy dispersive X-ray spectroscopy (EDX) and the changes in the phase compositions were found by comparison. The scheme of the sequence of experimental work is given in Figure 7.

The probability of possible chemical reactions was evaluated by the calculations of Gibbs free energy change using "*Database of HSC Chemistry Ver. 6.0*". All used binary precursor materials (Cu_2S, SnS and ZnS) for CZTS were self-synthesized, starting from high purity (99.999%) elements (MERCK) in evacuated quartz ampoules. Before using the binary compounds for the experiments, their composition was controlled by XRD, Raman and EDX analysis methods. CdI_2 (>99%) was purchased from Sigma-Aldrich company. Composition of precursor material mixtures was taken into consideration to have the quaternary compound with the final composition $Cu_{1.85}ZnSnS_{3.85}$ that is characterized by molar ratios: Cu/(Zn+Sn)=0.92, Zn/Sn=1 and S/metals=1 to result in Cu-poor composition. Flux material and precursors (in mass ratio 1:1) were mixed by grinding in an agate mortar, sample mixtures were degassed and encapsulated into quartz ampoules. Separate mixtures of every individual precursor with flux: (Cu_2S+CdI_2), (CdI_2+S), ($ZnS+CdI_2$), ($SnS+CdI_2$), mixtures for ternary Cu_2SnS_3 (CTS) compound ($Cu_2S+SnS+S+CdI_2$) and for quaternary Cu_2ZnSnS_4 compound ($Cu_2S+SnS+ZnS+S+CdI_2$) were studied by the DTA method. A DTA setup

(Thermogravimetric Analyzer Labsys 1600, Setaram Instrumentation) was used to determine temperatures of phase changes and/or chemical interactions between the initial binaries and the flux material. An empty degassed and sealed quartz ampoule of equal mass was used as a reference for the DTA measurement.
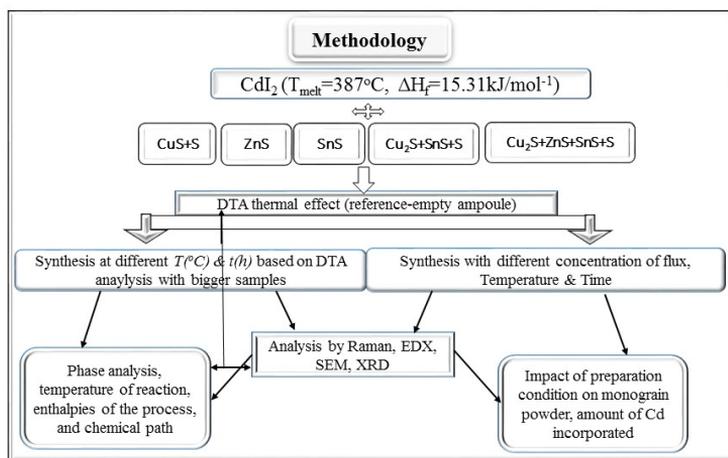
Figure 7. Scheme of the sequence of experimental work.

2.2 Determination of thermal processes and their enthalpies

We recorded the thermal effects in the studied samples by DTA and the changes in the phase composition of different mixtures by Raman and XRD analyses [II]. Pure flux material (CdI$_2$) was selected as the reference material for the DTA enthalpy calibrations for two reasons: firstly, the processes taking place in the synthesis occur in the same temperature region as the melting of flux material and secondly, our experimentally determined melting point of flux coincides with the value found from literature (T_m=387 °C)[108]. Our readings from DTA curves in µV s were converted to J/mol using the value of enthalpy of fusion of CdI$_2$ (15.31 kJ/mol [113]), considering that our experimental heat value for melting of CdI$_2$ is 666 ± 2 µV s, which corresponds to ≈5.23 J (constant for our calculations). The enthalpies of the individual processes occurring concurrently with the melting process of CdI$_2$ were determined by subtracting enthalpy of pure CdI$_2$ from the cumulative enthalpy values of processes in the mixtures. The DTA heating and cooling were carried out in two runs. The obtained energy values were used for the evaluation of the enthalpies of the occurring processes with an error margin estimated at 5 %, given

as the largest deviation of the individual process value of the average value. The applied heating and cooling rates from room temperature to 800 ºC were 5 ºC and 10 ºC 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 larger 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, larger 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).

2.3 Preparation of samples for growth process studies

To study the impact of preparation on the growth process, the concentration of flux salt in the synthesis mixtures was varied so that the ratio of the liquid flux (V_{CdI_2}) volumes to solid precursors for CZTS (V_{CZTS}), (V_{CdI_2}/V_{CZTS}) =5, 3, 1, 0.5 (if the ratio V_{CdI_2}/V_{CZTS}=1, it is marked as C_l). The volumes were determined by considering the density of the flux material and the density of the precursor, the solubility of CZTS in flux was not taken into account[l]. Table 3 presents the properties of precursor material and the flux material, as well as CZTS.

Table 3. Precursors used for the synthesis of CZTS and their densities

Compound (phase)	Density (g/cm^3)
Cu_2S (solid)	5.6[114]
ZnS (solid)	4.09[115]
SnS (solid)	5.22[116]
CdI_2 (liquid)	5.64[116]
CZTS (solid)	4.56[117]

We carried out the time-dependent experiments at 650 ºC for 24, 160 and 300 hours. Samples were quenched rapidly to the room temperature in cold water. The formed powder particles were separated from the flux material by washing several times with deionized water. Sample was dried and separated into various size fractions ranging from ≤38 micrometer to ≥125 micrometer by sieving using the Retsch AS200 sieving machine. The concentration of Cd incorporated into CZTS was studied as depending on the synthesis temperature and time and determined by EDX from polished powder crystals. Samples were heated for 15 hours at 280 ºC, 370 ºC, 500 ºC, 600 ºC, 700 ºC and 780 ºC and at 600 ºC for 6, 22, 32, and 60 hours. 280 and 370 ºC were considered based on the effect observed by DTA. The

element ratios in the mix of binary precursors for CZTS synthesis were chosen as [Cu]/([Zn]+[Sn])=0.92 and [Zn]/[Sn]=1.03, considering that single phase CZTS monograin powders can be grown in molten KI with precursor metal ratios [Cu]/([Zn]+[Sn])=0.92≤0.95 and [Zn]/[Sn]=1.0≤1.03[54,118,119,83]. The Cd incorporated into the crystals was determined by EDX from polished crystals.

2.4 Instrumentation

The morphology and chemical composition of the synthesized powders were analyzed using energy dispersive X-ray spectroscopy (SEM- AsB and by 20 keV EDX) on Zeiss HR-SEM ULTRA 55. The EDS analysis was made at least from 10 crystals of each analyzed sample. The phases formed in the annealed samples were determined by the Raman spectra recorded using a Horiba LabRam HR high-resolution spectrometer equipped with a multichannel CCD detection system in a backscattering configuration. Incident laser light of 532 nm was focused on different 1 μm^2 spots of the studied sample and an average of five readings were taken for every sample to obtain an objective phase composition of the sample. The XRD measurements were performed using a Bruker D5005 diffractometer. For the analysis, the ICDD-4 + 2009 database was used. The DTA analysis was carried out using a Thermogravimetric Analyzer Labsys 1600, Setaram Instrumentation.

3 RESULTS AND DISCUSSIONS

3.1 Synthesis and characterization of CZTS monograin powder in molten CdI_2

In our earlier studies[120], we applied the combination of different analytical methods - the experimental DTA results with the phase analysis by Raman and XRD. As a result, we found that the formation of CZTS in the mixture of CdI_2 flux with binary precursors in amounts needed for the formation of near-stoichiometric composition of Cu_2ZnSnS_4 ($Cu_2S+SnS+ZnS+S+CdI_2$) started already at temperatures lower than 400 ºC. At 280 ºC, much below the melting point of CdI_2, the formation of CZTS quaternary compound was not detected. As the temperature increased up to 370 ºC, just below the melting temperature of pure CdI_2, the formation of CZTS began. At this temperature, the Raman spectra confirmed the presence of different secondary phases co-existing with CZTS as it was shown in[120,III]. In order to study the formed phases present in the quaternary system, mixtures of $CdI_2+SnS+Cu_2S+S+ZnS$ were a) heated to 500 ºC and quenched and b) heated to 800 ºC and cooled down to 350 ºC before quenching to room temperature, respectively. The phase analysis showed that in sample mixtures ($Cu_2S+SnS+ZnS+S+CdI_2$) heated and quenched at 500 ºC, besides Cu_2SnS_3, ZnI_2 was also found. Samples quenched at 800 ºC showed that the ternary Cu_2SnS_3 compound had reacted with ZnS to form Cu_2SnS_3, $Cu_2Zn_{1-x}Cd_xSnS_4$, 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. Analyzing the DTA results, we recognized that the formation of CZTS proceeded in two stages. In the first step, Cu_2SnS_3 formed from Cu_2S, SnS, and S. After that, Cu_2SnS_3 reacted with ZnS to form CZCdTS. In Figure 8, Raman spectrum of the washed CZTS sample heated up to 800 ºC and cooled down to 350 ºC is presented. CZCdTS is the prevailing phase with its characteristic Raman peaks at 92, 166, 249, 285, 333, 372 cm^{-1} [121,122]. All Raman peaks were shifted slightly to lower wave numbers of pure CZTS. Raman peak at 110 cm^{-1} could belong to CdI_2[123] used as flux material and Raman peak of SnI_4 as a secondary phase can be detected at 145 cm^{-1}, as it was described also in the previous report[120] CuI, $Cu_{1.6}S$, SnI_4 phases were also detected by XRD in the unwashed samples but not in washed samples. CuI is soluble in KI or NaI solutions, as also described in our previous report, allowing separation of single phase CZCdTS[120,II]. The synthesis temperature of 800 ºC was chosen for experimental purpose to see if the lower melting temperature of CdI_2 could avoid sintering that occurs when KI (T_{mKI}=685 ºC) as flux was used. Also, syntheses at higher temperatures are possible (T_{Synt}=700≥x≤780 ºC) in a small range of temperatures above the melting temperature of KI as flux. Using CdI_2 (T_{mCdI2} = 387 ºC) synthesis is possible in a

large temperature region (T_{synt} =370≥x≤800 °C) that could increase or decrease the sintering effect which may not be favorable for monograin growth[124–126].
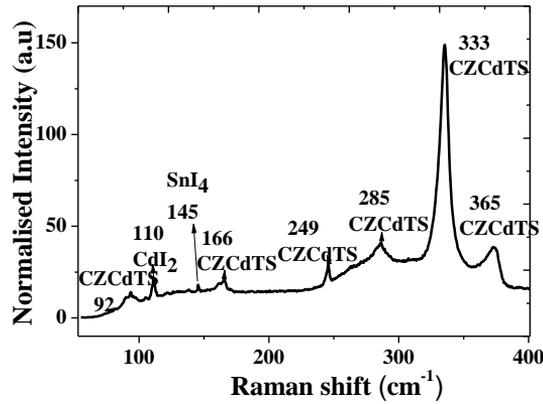
Figure 8.Raman spectrum of CZTS sample heated up to 800 °C and cooled down to 350 °C. CdI$_2$ is mainly washed out. The shift in Raman peak to a lower wave number value confirmed the formation of CZCdTS.
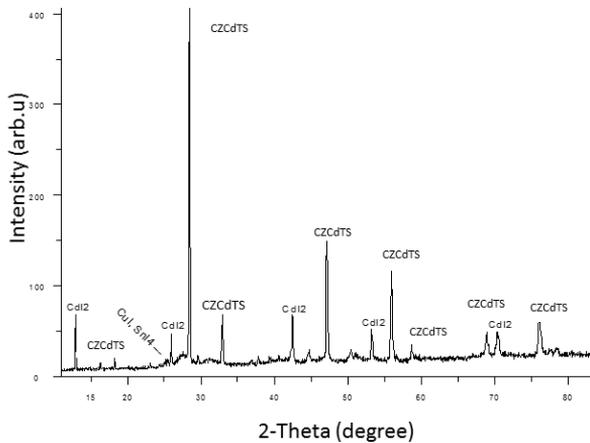
Figure 9. XRD pattern of the mixture of Cu$_2$S+SnS+ZnS+S+CdI$_2$ heated up to 800 °C, cooled to 350 °C and quenched to room temperature.

3.2 Impact of synthesis-growth conditions on the material properties

Focus in this part is on the impact of synthesis-growth conditions on the material properties. We considered the effects of temperature, synthesis time and amount of flux on the grain size and yield, composition of the synthesized CZTS and concentration of Cd in the as-grown CZTS monograin powder.

3.2.1 Impact of flux concentration and synthesis time on the grain size and yield of powders

By sieving the powders into different size fractions, the amount of fractions with grain size ≥ 45 µm (usable in monograin solar cells)[43] was determined. In Figure 10, the total quantity of synthesized powder material with size ≥ 45 µm without considering the different fractions and the yield of the total amount of CZTS monograins powder decreases as the volume ratio of the liquid flux (V_{CdI2}) to solid precursors for CZTS (V_{CZTS}), i.e., (V_{CdI2}/V_{CZTS}) increases from 0.5 to 5 at 650 °C and for 24, 160 and 300 hours, respectively. It is understandable if we consider that by increasing the amount of liquid phase, the diffusion between different crystals takes more time and the amount dissolved in the molten phase of flux increases. However, the lowest used amount of CdI_2 (0.5 C_l) (see Figure 10, left) results in grains with sizes over 45 µm in larger amounts than could be expected from the small linear decline when $C_l \geq 1$ (see Figure 10a, right). This phenomenon could be understandable under the consideration that the single grain growth limit is roughly determined as $V_{Liquid}/V_{Solid} \geq 0.5$[127]. Therefore, the amount of larger grains (formed due to a higher degree of sintering) is increased for $C = 0.5$ in comparison with used larger flux amounts ($C > 0.5$) where single grain growth prevails [I].

In addition, at $C < 0.5$, the amount of flux is insufficient to aid the growth process and sintering to prevail. As the density of CZTS is not determined for higher temperatures, the amounts for initial liquid to solid volume ratio < 0.5 could result in both the single grain growth and some sintering process occurring at the same time and at $C_l < 0.5$, even greater sintering may occur, which may affect the quality of the CZTS monograin powder[128]. In addition, the yield of the total amount of CZTS monograins decreases as the flux amount increases and vice versa - it increases as the growth time increases (see Figure 10b). It is also seen that the total yield of powder is larger than the total amount of initial precursor compounds ($Cu_2S+SnS+ZnS+S$) for the synthesis, particularly for heating times 160 and 300 hours. The increase in the total amount of yield over the summarized amount of precursor compounds can take place due to the replacement of Zn by Cd (with higher molar mass than Zn) in the crystal lattice of formed CZCdTS compound when CdI_2 is the only source of Cd. During the growth process, the concentration gradient drives the mass transfer of the crystal constituents from the fluid phase to the crystal phase. The mass flux at the

growth interface depends on the direction-dependent concentration gradient [128] and the larger the flux amount, the slower and less chance of higher agglomeration and vice versa, which leads to smaller grains that can be easily washed off during the separation of monograin powder from the flux. In summary, Figure 10a shows that the grain size and the total yield of synthesized powder increases by the synthesis time but decreases with the increasing flux amount.
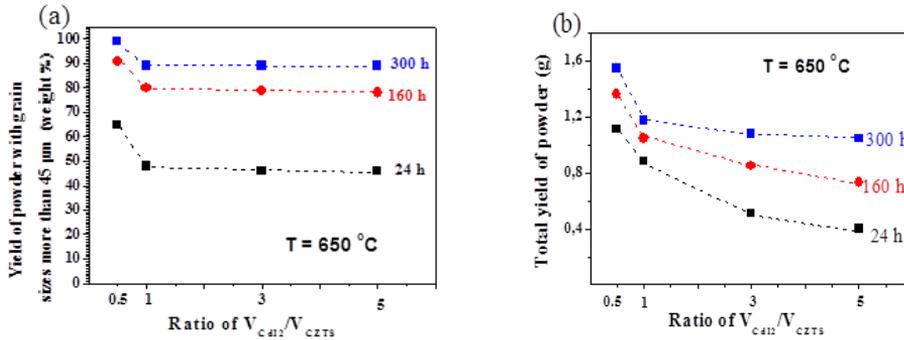
Figure 10. CZCdTS powder fractions with grain size larger than 45 μm (a) grain size distribution (b) total yield of synthesized powder. The synthesis temperature is 650 ºC with different heating time 24, 160 and 300 hours, the left side of Figure 10a emphasizes the effect of sintering due to small flux amount (0.5C₁) [1].

3.2.2 Impact of flux amount and synthesis-growth time on grain morphology

SEM images of individual CZCdTS crystals synthesized at 650 ºC are presented in Figure 11. It can be seen that the grains produced by using smaller flux amounts are less faceted and have a more rounded shape. With the time increasing as well as with the increasing flux amount, faceted crystals became more obvious. The most round shaped grains were formed in the samples with the lowest amount of CdI_2 heated for 160 hours. Longer time (300 hours) promotes the faceting. However, in the crystals heated for 300 hours, secondary agglomeration can also be observed – the crystals are formed from different blocks. The primary sintering effect at the lowest used flux amount (*0.5C₁*) seems to be helpful for getting rounder and compact grains after long crystallization time (160 and 300 hours). Comparison of all the syntheses at 650 ºC shows that the grains are less faceted and larger and the yield is higher as the flux concentration decreases. This can be attributed to the effect of sintering.
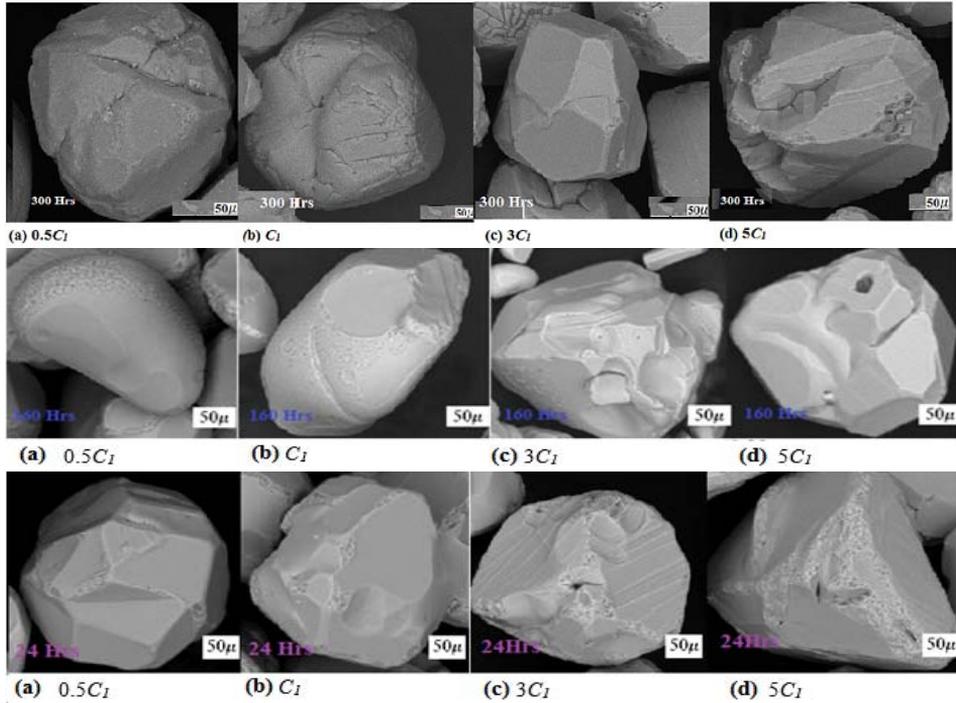
Figure 11. SEM images of individual CZCdTS powder grains synthesized at T= 650 °C for 300 (upper row), 160 (middle row) and 24 (lower row) hours with increasing (from left to right) amount of CdI₂. C₁ corresponds to $V_{CdI2}/V_{CZTS}=1$ [1].

3.2.3 Phase analysis by Raman

Raman spectra of powder crystals synthesized under different conditions (temperature, time, and flux amount) are presented in Figure 12. Raman spectrum of the sample held for 300 hours at 650 °C and synthesized with the lowest flux amount (*0.5C₁*) shows that the most intensive Raman peak is at 337cm⁻¹, which is close to the most intensive Raman peak position of pure CZTS (at 338 cm⁻¹) while the most intensive Raman peak of the sample with the highest amount of CdI₂ (*5C₁*) is at 332 cm⁻¹, at the same place as the most intensive Raman peak of pure Cu_2CdSnS_4 (332 cm⁻¹)[129] (see Figure 12a). In[119] it was found that with an increasing Cd content in the $Cu_{1.85}(Cd_xZn_{1-x})_{1.1}SnS_{4.1}$ monograin powders grown in KI, the peak position of A1 Raman mode decreased linearly from 338 to 332 cm⁻³ in the interval of x values from 0 to 0.4. Then, with higher Cd contents, the A1 peak position did not shift any more. In our study, Raman peak of CZTS, synthesized for 15 hours at different temperatures (500, 600, 700 and 780 °C) is shifted to 332 cm⁻¹, as the temperature increased to 780 °C (see Figure 12b). The shift of Raman peak confirms that solid solution of $Cu_2Zn_{1-x}Cd_xSnS_4$ is formed in our powder samples.
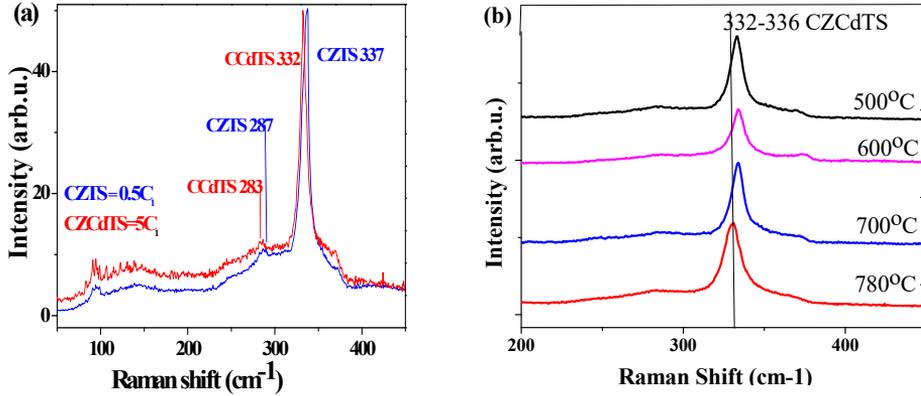
Figure 12. Normalized Raman spectra of powder crystals (a) synthesized with different ratios of CdI₂/CZTS (red=5 and blue CdI₂/CZTS=0.5) (b) synthesized at different temperatures for 15 hours and CdI₂/CZTS =1. The Raman peak shifts from 336 cm⁻¹ at 500 °C to 332 cm⁻¹ at 780 °C.

3.2.4 Compositional analyses by EDX

We determined the cadmium concentration in the as-grown CZTS powders synthesized at different temperatures for constant time and for different time at constant temperature. Our focus was also on the influence of different amounts of CdI$_2$ present in the synthesis of CZTS monograin powders on the final composition of powders.

3.2.4.1 Cd concentration in CZTS powder crystals by EDX

We determined the Cd concentration in CZTS crystals grown for 15 hours in CdI$_2$ of constant volume ratio V$_{CdI_2}$/V$_{CZTS}$=1 at different synthesis temperatures. It is seen that Cd concentration in the as-grown CZTS monograin powder heated at different temperatures for constant time increases with temperature (Figure 13a). In addition, with the increasing amount of used CdI$_2$, the Cd concentration in the formed compound also increases as the flux amount increases (see Figure 13b). However, from Figure 13c it is obvious that annealing for 6 hours leads to a large dispersion in the measurement data. This is attributable to the non-equilibrium status of the system. Furthermore, the Cd concentration in CZTS grown at constant temperature (600 °C) for different annealing times showed no increase, it stayed constant after heating for 22 hours. Due to the inconsistency in the obtained data we can conclude that 6 hours is not enough to reach the

equilibrium. This result is also confirmed by the Raman peak position in Figure 13d. It can be seen that the Raman peak shifts from 336 cm^{-1} (6 hours) to 333 cm^{-1} for 22 hours and remains constant (up to 60 hours). This confirms that the Cd incorporation into CZTS is not a time dependent process. The maximum amount of Cd incorporated into $Cu_2Z_{1-x}Cd_xSnS_2$ is at x=0.3 at 780 ^{o}C and increases to x=0.4 as the flux amount increases to $5C_1$.
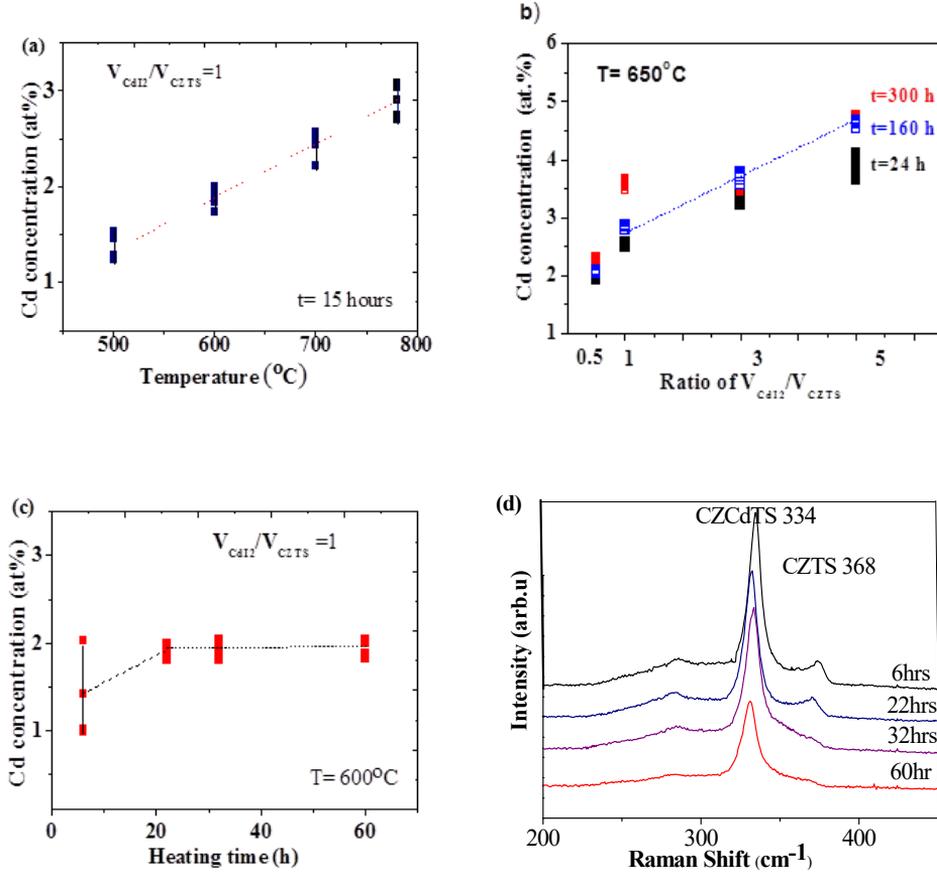
Figure 13. Cd content incorporated into CZTS (a) from constant amount of CdI$_2$ flux (V_{CdI2}/V_{CZTS} =1) as a function of heating temperature, (b) as a function of CdI$_2$/CZTS for different time (24, 160 and 300 hours) at T= 650 ^{o}C, (c) Cd content in powders heated in the constant amount of CdI$_2$ at 600 ^{o}C for different time, (d) Raman spectra of CZTS heated in the constant amount of CdI$_2$ at 600 ^{o}C for different time. Raman peak shifts from 334 cm^{-1} at 6 hours to 332cm^{-1} at 22 hours and remains constant until 60 hours.

3.2.4.2 Composition of synthesized powders by EDX

The common formula of the product powders is almost the same for all samples with a deviation in the range of limits for EDX and can be expressed as $Cu_{1.9\pm0.01}Zn_{1-x}Cd_xSnS_{3.97\pm0.04}$ with variable Cd content (x values). The values of x depending on the heating conditions are given in Table 4. As it can be seen, the Cd concentration in $Cu_2Zn_{1-x}Cd_xSnS_4$ increases with the increasing amount of CdI_2 in the synthesis. The incorporation of Cd into $Cu_2(ZnCd)SnS_4$ through the intermediate formation of $Zn_{1-x}Cd_xS$ is occurring by the replacement of Zn^{2+} by Cd^{2+}. All the used analytical methods confirm that during the synthesis of CZTS in CdI_2, as the flux Cd incorporates from CdI_2 into the crystal lattice of CZTS, the result is the formation of solid solutions with a common formula of $Cu_{1.9\pm0.01}Zn_{1-x}Cd_xSnS_{3.97\pm0.04}$. This is in contrast to the results of Pilvet et al. [119], where it was shown that by using CdS and ZnS as precursors, the whole row of solid solutions of $Cu_{1.85}(Cd_xZn_{1-x})_{1.1}SnS_{4.1}$ ($0 \leq x \leq 1$) can be synthesized. In our system, the Cd content is limited by the amount of CdI_2 in the synthesis-growth process.

Table 4. Composition of CZCdTS for different flux concentrations and heating time as determined by EDX (T=650 °C), deviation error of ± 0.02

	Heating time (h)		
	24	160	300
V_{CdI_2}/V_{CZTS}	Value of x in $Cu_{1.9\pm0.01}(Zn_{1-x}Cd_x)SnS_{3.97\pm0.04}$		
0.5	0.15	0.18	0.16
1	0.15	0.26	0.22
3	0.25	0.28	0.28
5	0.3	0.35	0.35

Figure 14 shows the changes in Zn concentration in powders grown at different temperatures. It can be seen that [Zn] in the CZTS powders is reduced as compared with the Zn content in precursors and it decreases with increasing temperature and also with the increasing Cd content. Such behavior can be attributed to the replacement of Zn by Cd. In addition, the sum of Zn and Cd contents also increases with increasing temperature. The ratio of [Zn]/[Sn] decreases while the ratio [Cu]/[Sn] increases due to the decrease in [Zn] in the final powder. It was suggested that the decrease in the Cu content in the precursors should lead to an increase in the substitution of Zn atoms by Cd atoms[119]; therefore, a decrease in [Zn] can be attributed to the substitution of Cd at Zn site from CdI_2. The single phase solid solution of $Cu_2Zn_{1-x}Cd_xSnS_4$ forms intensively, starting from 500 °C[120]. As the direct exchange reaction between solid ZnS and CdI_2 resulting in the formation of CdS and ZnI_2 is

thermodynamically not favored (based on available thermodynamic data), the formation of solid solution $Cu_2Zn_{1-x}Cd_xSnS_4$ (Cd incorporation at the Zn site) can take place due to the processes in liquid CdI_2 that may result in the formation of continuous row of solid solution between ZnS and CdS[101,130]. In the next step, $Zn_{1-x}Cd_xS$ reacting with Cu_2SnS_3 results in the formation of $Cu_2Zn_{1-x}Cd_xSnS_4$ [III], although we believe that the dissolution of ZnS in CdI_2 occurs in the liquid phase.
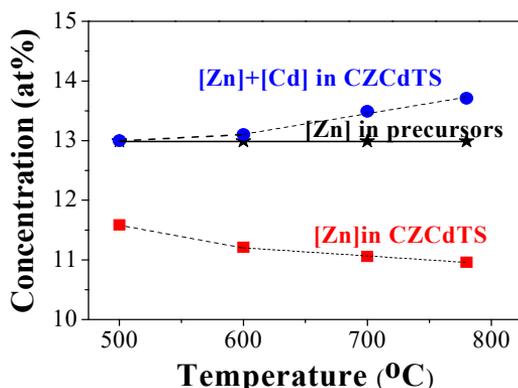
Figure 14. Variation of Zn concentration in the $Cu_2Zn_{1-x}Cd_xSnS_4$ powders synthesized in CdI_2 at different temperatures [1].

3.2.5 Activation energy of Cd incorporation to the CZTS crystals in the synthesis process

In Figure 15, the Arrhenius plot of Cd concentration in the formed $Cu_2Zn_{1-x}Cd_xSnS_4$ is shown. The Cd concentration in the formed CZCdTS increased with temperature and it could be expressed as $[Cd] \sim e^{-\Delta E/kT}$. The overall activation energy of the Cd incorporation process estimated from the Arrhenius plot is 17.5 ± 2 kJ mol^{-1}. The formation of $Zn_{1-x}Cd_xS$ seems to be a major step for the Cd incorporation from CdI_2 into the crystal lattice of the CZTS monograins[131]. The formation of solid solution of $Cu_2Zn_{1-x}Cd_xSnS_4$ was reported earlier in[120] and in[I]. By our first considerations, based on ΔG calculations of different reactions, the only possible route for Cd incorporation is through the CZTS formation reaction in participation of more electronegative CdI_2^+ ion. The latter was found in the gaseous phase of CdI_2 by the mass spectrometric investigations with modified Knudsen cell–mass spectrometer by W. Kuncewicz-Kupczyk *et al.*[132]. In their work, they confirmed the presence of CdI_2^+, Cd^+ and I^- formed as fragment ions in the gaseous phase of CdI_2 (g), consisting mainly of monomers CdI_2 (g) and dimers Cd_2I_4 (g) at 261 to 340 °C. But the formation of ZnI_2 and CdS by the participation of gas phase ions seems to be improbable. In the next part of the thesis, we present results of different chemical interactions occurring between CdI_2 and precursor compounds.
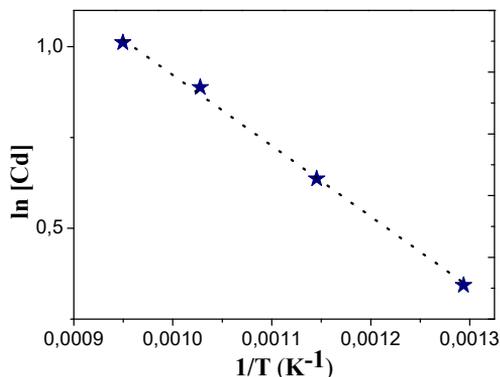
Figure 15. Arrhenius plot of [Cd] in Cu₂Zn₁₋ₓCdₓSnS₄ powders grown in the constant amount of CdI₂ flux (ratio of precursors to CdI₂=1:1) for constant time (32 hours) at different temperatures.

3.3 Studies of interactions of precursors with CdI₂

To understand the entire formation process of the CZTS in molten CdI_2, our studies of the interactions of CdI_2 with every individual precursor separately started by considering the enthalpies in the entire synthesis process. Our aim was to understand the individual chemical reactions that could occur between CdI_2 and the precursors in different combinations. All the possible chemical reactions and their thermodynamic probabilities (by ΔG calculations) will be reported.

3.3.1 Synthesis temperature of mixtures

The melting temperatures of CdI_2 and the studied mixtures (Cu_2S+CdI_2), ($ZnS+CdI_2$), ($SnS+CdI_2$), ($Cu_2S+SnS+S+CdI_2$) and ($Cu_2S+SnS+ZnS+S+CdI_2$) from the DTA curves are presented in Figure 16. It can be seen that the melting of the flux in the mixtures of the precursors with flux takes place at lower temperatures than the melting temperature of pure CdI_2 (387 °C)[108]. The lowering of melting temperatures shows some solubility of the precursors in molten CdI_2 and/or the formation of new phases. It is well known that the amount of dissolved solute is dependent on the amount of solvent and temperature. For the melting temperatures in Figure 16, the ratio of the precursor to flux material mixtures needed to synthesize a single phase $Cu_2Zn_{1-x}Cd_xSnS_4$ was considered and presented for all the mixtures.

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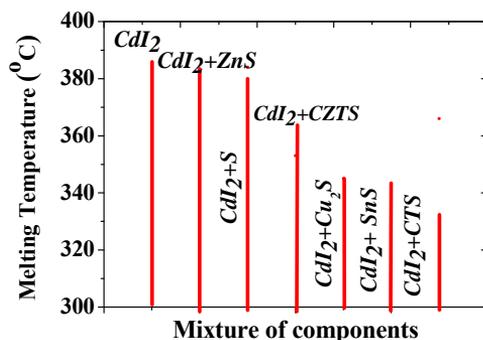
Figure 16. Melting temperatures of studied mixtures as determined from the DTA curves.

3.3.2 CdI$_2$

At temperatures above the melting point, CdI$_2$ could exist in gaseous form both in its monomeric (CdI$_2$(g)) and dimeric (Cd$_2$I$_4$(g)) form[133,134]. According to Corbett *et al.*[135,136], molten CdI$_2$ has brown color, which is due to the free iodine that is in equilibrium with the melt. Iodine is an oxidizing agent, which may limit the reactions between CdI$_2$ and the precursors. The DTA curves of pure CdI$_2$ (see Figure 17) gave an endothermic effect at 385 °C in heating and an exothermic effect at 366 °C in the cooling cycle, which can be attributed to the melting and freezing of CdI$_2$ with an enthalpy signal of 666 ± 2 µV s. This signal is equal to 5.23 J, as calculated from the obtained peak area for corresponding 0.125 g (0.00034 moles) of CdI$_2$ (the molar mass of CdI$_2$=366.22 g mol^{-1} and the molar fusion enthalpy value for pure CdI$_2$ is 15.31 kJ mol^{-1} [113]). Any deviation from this value in the mixtures studied may be attributed to the various interactions and processes occurring in the sample mixtures.
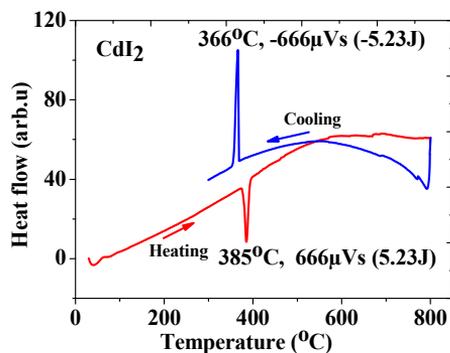
Figure 17. DTA curves of CdI$_2$.

3.3.3 CdI$_2$+Cu$_2$S

The DTA curve of the mixture of CdI$_2$+Cu$_2$S (Figure 18) shows an endothermic melting effect at 353 °C and an exothermic effect of freezing of CdI$_2$ at 338 °C. We can observe a decrease in the energy value of the melting process from 5.23 J (666 µV s) for pure CdI$_2$ to 2.1 J (264 µV s) in CdI$_2$+Cu$_2$S mixture. This decrease can be ascribed to the simultaneous exothermic reactions occurring alongside the melting of CdI$_2$. By XRD and Raman; we found different compounds - Cu$_{1.96}$S, CuI, Cu$_2$Cd$_3$I$_4$S$_2$, CdS and Cu$_4$Cd$_3$ in CdI$_2$+Cu$_2$S sample heated for 4 hours at temperatures slightly above the melting point of the mixture (353 °C) (see Table 5). This confirms the chemical interaction between the flux material and Cu$_2$S. By XRD and Raman analyses; we found that some of these processes occurring during the melting and freezing of the mixture CdI$_2$+Cu$_2$S are reversible: Cu$_2$S, as observed by XRD, transformed to Cu$_{1.96}$S and re-transformed to Cu$_2$S by cooling down, which is in accordance with the Cu-S phase diagram[55]. In the heating process, in addition to the main fusion peak at 353 °C, another endothermic DTA peak is observed at 400 °C. The phase analysis of the larger sample heated and quenched at 420 °C shows that this peak corresponds to the decomposition of Cu$_2$Cd$_3$I$_4$S$_2$ to CdS, CdI$_2$ and Cu$_4$Cd$_3$ and I$_2$ (see equation 5) with a summary thermal effect of 77 mV s (0.6 J). The phases detected by Raman are given in Figure 19 (XRD patterns can be found in Appendix B)
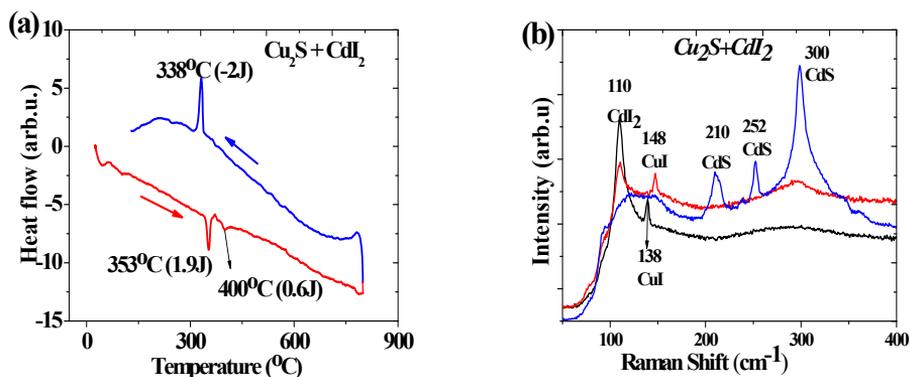
Figure 18. DTA curves (a) and Raman spectra (b) of Cu$_2$S+CdI$_2$: red - heated and quenched at 353 °C, blue - heated and quenched at 400 °C, black- heated to 800 °C and cooled down to 330 °C before quenching to room temperature.

Table 5. Annealing conditions, determined phases, reactions and their calculated ΔG values for the CuS+CdI₂ mixture

Annealing conditions (°C)	Phases by XRD	Phases by Raman/peak position (cm⁻¹)	Equation	Reactions	ΔG (kJ mol⁻¹)/Temperature (°C)	
Heated to 353, annealed for 4 hours	CuS, $Cu_{1.96}S$,	CdS/294[24] CdI$_2$/110[137] CuI/148[10,138]	1	$Cu_2S + CdI_2 = 2CuI + CdS$[139,140]	-49.1/T=300	-31.5/T=400
			2	$CdS + Cu_2S + 2CdI_2 = Cu_2Cd_3I_4S_2$	Proposed	
Heated to 400, annealed for 4 hours	CuI, $Cu_2Cd_3I_4S_2$, CdS, Cu_4Cd_3		3	$Cu_2S + CdI_2(g) = 2CuI + CdS$[139,140]	-43.6/T=300	-1.8/T= 600
Heated to 800 and cooled down to 330	CdS, Cu_4Cd_3, CuS, $Cu_2Cd_3I_4S_2$, CuI	CdS/294[24] CuS/474[63-65]	4	$CuS + CdI^+(g) = CuI + CdS$[139,141]	-151.9/T=300	-84.7/T=800
			5	$2Cu_2Cd_3I_4S_2 = Cu_4Cd_3 + 2CdS + CdI_2 + I_2$	Proposed	

3.3.4 CdI$_2$+SnS

The melting effect of this mixture was observed at 345 ^{o}C (see Figure 20), i.e., at much lower temperature than for pure CdI$_2$. This fact suggests a higher solubility/interaction of SnS in CdI$_2$. In the XRD and Raman studies, the larger samples (a) were heated to 800 ^{o}C and cooled down to 350 ^{o}C and then quenched to room temperature and (b) cooled down to 250 ^{o}C from 800 ^{o}C before quenching rapidly. It was revealed that SnI$_4$, Sn$_2$SI$_2$ and CdS had been formed (shown in Table 6). The final freezing of SnS+CdI$_2$ mixture can be detected in the cooling curve at 300 ^{o}C. The enthalpy observed in the cooling process is -6.23 J. It can be attributed to the exothermic freezing of CdI$_2$ with cumulatively formed tin iodides and CdS, as observed by phase analysis. The phases detected by Raman are given in Figure 21. XRD patterns are presented in Appendix B.
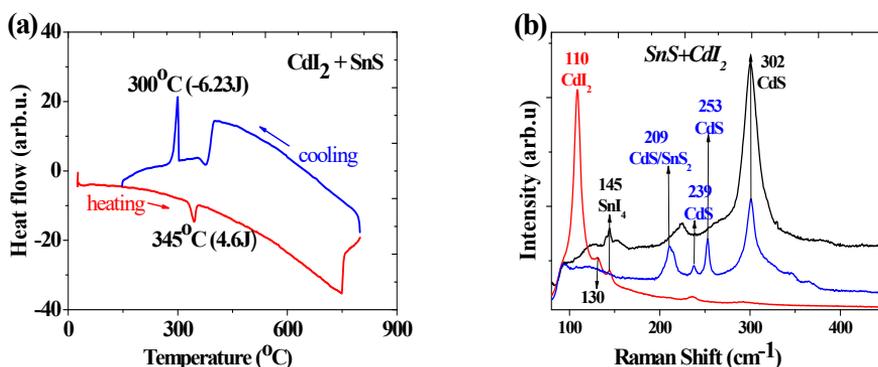
Figure 19. (a) DTA curves of CdI$_2$+SnS mixture (b) Raman spectra of SnS+CdI$_2$ heated and quenched at different temperatures :blue- heated and quenched at 353°C, red - heated to 800 ^{o}C and cooled down to 300 ^{o}C before quenching to room temperature, black - heated to 800 ^{o}C and cooled down to 250 ^{o}C before quenching to room temperature.

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Table 6. Annealing conditions, determined phases, reactions and their calculated ΔG values for SnS+CdI₂ mixture

Annealing conditions (°C)	Phases by XRD	Phases by Raman/peak position (cm⁻¹)	Equation	Reactions	ΔG (kJ mol⁻¹)/Temperature (°C)	
Heated to 350 and quenched	CdI_2, CdS, SnI_2, Sn_2SI_2	SnS CdS/301[24]	6	$SnS + CdI_2\,(g) = SnI_2 + CdS$[142,143]	-79.470/T≥0	-9.642/T≤500
			7	$2SnS + I_2 = Sn_2SI_2 + S$	proposed on phases observed	
			8	$2SnS + CdI_2 = Sn_2SI_2 + CdS$	proposed on phases observed	
			9	$CdI_2\,(g) + S = I_2 + CdS$	-43.220 T=0 °C	9.741/T=400
Heated to 800 and cooled down to 300 and 250	SnI_4, SnS, $SnSI_2$, CdS SnI_2	CdS SnI_4/145	10	$SnS_2(g) \leftrightarrow SnS + S$[72,143]	-196.792/T=100	-98.555/T=800
			11	$SnI_4 + 2CdS = SnS + 2CdI_2 + S$	-11.667/T=100	-22.807 T=800
			12	$I_2 + CdS = CdI_2\,(g) + S$	26.513/T=100	-50.033/T=800
			13	$SnS_2 + 2CdI^+(g) = 2CdS + SnI_2/(SnSI_2)$[144]	-378.909/T=0	-162.389/T=80
			14	$2CdI^+(g) + 2S = I_2 + 2CdS$	-368.913/T=0	-131.958/T=800

3.3.5. CdI$_2$+ZnS

The DTA heating and cooling curves of this mixture of CdI$_2$ +ZnS are presented in Figure 20a. It shows an endothermic peak at 382 °C in the heating cycle, slightly lower than the melting temperature of pure CdI$_2$ (T$_{melt}$=385 °C, see Figure 17) with the thermal effect of 2.7 J, which is lower than in the melting of pure CdI$_2$. 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 °C, which may be due to the low sensitivity of XRD; but the lowering of the enthalpy suggests that some interaction is occurring in the liquid phase. In the cooling curve, two exothermic peaks at 354 °C and 338 °C are seen. The peak at 354 °C, slightly lower than the freezing temperature of pure CdI$_2$ (T$_f$ =366 °C), confirms the solidification of CdI$_2$ with an enthalpy value of 3.1 J. The peak at 338 °C corresponds to an energy signal of about 1.8 J (234 µV s), which is much lower than that of the freezing of pure CdI$_2$. Analysis by XRD showed that a solid solution of Zn$_{1-x}$Cd$_x$S was formed in the mixture of ZnS+CdI$_2$ (see Figure 21). The XRD pattern for the samples cooled down to 330 °C, confirms the formation of Zn$_{1-x}$Cd$_x$S solid solution[101]. As the formation of Zn$_{1-x}$Cd$_x$S is only found in the cooling phase, we can conclude that Zn$_{1-x}$Cd$_x$S was formed in the molten phase by replacement of Zn by Cd. Solid solutions were formed by precipitation in cooling due to lowered solubility at 338 °C. The overall enthalpy of the process was found as 1.8 J.

In equation (17), a thermo-dynamical possibility of a reaction exists between ZnS and CdI$^+$ for temperatures between 0 and 1000 °C. In equation (15), the calculations of Gibbs energy change gave positive values for the reaction between solid CdI$_2$ and ZnS. Therefore, the CdS formation from solids is thermodynamically impossible, coupled with the fact that CdS was not found in the solid product. The probability of the reactions (15) and (20) should be therefore excluded. However, we found Zn$_{1-x}$Cd$_x$S and Cu$_2$Zn$_{1-x}$Cd$_x$SnS$_4$, respectively, (see Tables 7 and 9) in the studied samples. The phases detected by Raman are given in Figure 20b.
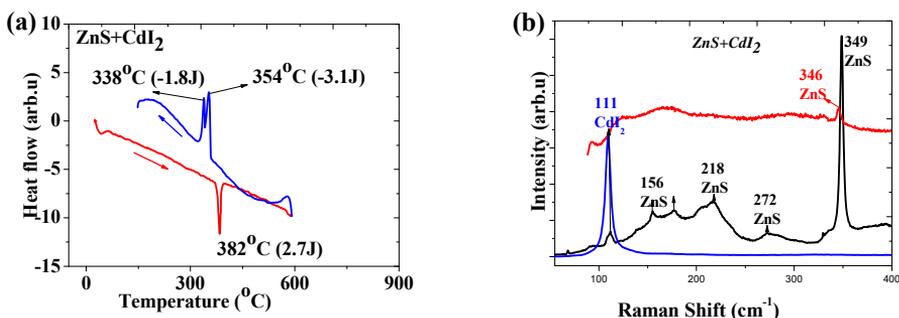
Figure 20. (a) DTA curves of the CdI$_2$+ZnS mixture, (b) Raman spectra of the ZnS+CdI$_2$: blue - heated and quenched at 385 ºC, red - heated to 800 ºC and cooled down to 330 ºC before quenching to room temperature, black - heated to 800 ºC and cooled down to 350 ºC before quenching to room temperature.
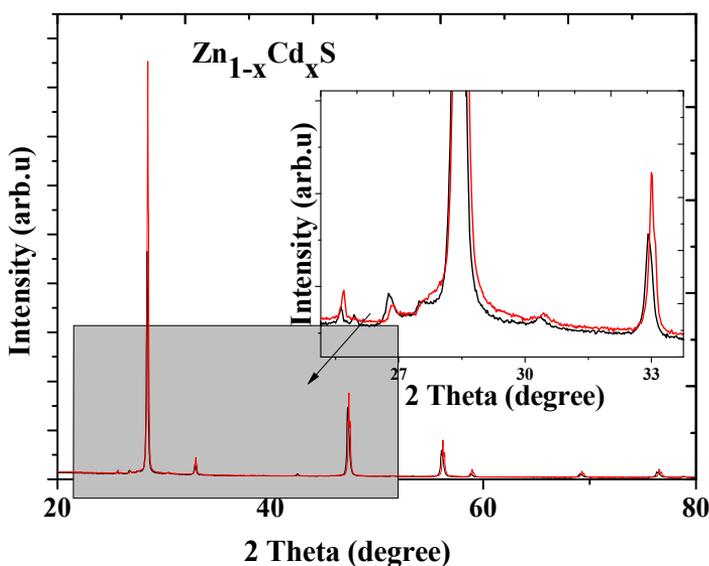
Figure 21. XRD pattern of Zn$_{1-x}$Cd$_x$S, (red-samples heated to 800 ºC and cooled down to 354 ºC before quenched to room temperature, black- samples heated to 800 ºC and cooled down to 330 ºC before quenching to room temperature.

Li Q. *et al.*[101] described similar formation of Zn$_{1-x}$Cd$_x$S solid solutions from solid powder of Zn- and Cd- thiourea (Tu) complexes under high-temperature heat-treatment (500 ºC for 30 min in N$_2$). Decomposition of Zn-Cd-Tu complexes provided active Cd^{2+}, Zn^{2+} and S^{2-} that reacted and formed Zn$_{1-x}$Cd$_x$S solid solutions. In our study, some amount of ZnS dissolves in liquid CdI$_2$ and in

cooling when solubility is decreasing, the solid solution crystallizes out on cooling to 338 °C. More information could be found by studying the properties of liquid (and/or gaseous) phase of CdI_2. Considering that the process under discussion takes place simultaneously with melting of CdI_2, the possible reactions involving CdI_2 (g) seem to be less probable and we should consider the processes in liquid phase. It is well known that many salts in their molten phase are in the form of ionic liquids, but not CdI_2. It was found that the melt of MX_2 (M=Zn, Cd, Hg and X=Cl, Br, I) has an extremely low ionic conductivity[145]. 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 a strong intermediate range ordering[146,147]. Also, measurements of the scattering of thermal neutrons from natural samples of molten $ZnCl_2$, $ZnBr_2$ and ZnI_2 confirmed a structural model of $[ZnI_4]^{2-}$, in which the small Zn^{2+} ions occupy tetrahedrally coordinated sites in a closely packed anion structure, with a strong intermediate range ordering[142]. Therefore, we suppose that a small amount of ZnS dissolves in liquid CdI_2 and the bonds of solid ZnS should be broken in the dissolution process. The dissolved Zn^{2+} can displace Cd^{2+} ions in the closely packed anion structure $[CdI_4]^{2-}$ in molten CdI_2. In the solidification, S^{2-} ions react with deliberated Cd^{2+} ions, forming CdS and ZnI_2 (see reaction 17), precipitating from the melt as solid solution of $Zn_{1-x}Cd_xS$ at 354 °C. We see also solidification at 338 °C, at much lower temperature than in the pure CdI_2. Probably ZnI_2-CdI_2 liquid solution freezes at 338 °C. According to Chikanov et $al.$[130], in ZnI_2-CdI_2 mixtures there forms a continuous row of solid solutions[144]. After opening the ampoule, ZnI_2 could not be detected by phase analyses due to its high hygroscopicity. The phases detected by Raman are shown in Figure 20b. (XRD patterns can be found in Appendix B).

Table 7. Annealing conditions, determined phases, reactions and calculated ΔG values for ZnS+CdI₂ mixture

Annealing conditions (°C)	Phases by XRD	Phases by Raman/peak position (cm^{-1})	Equation	Reactions	ΔG $(kJ\ mol^{-1})$/Temperature (°C)	
Annealed at 385 and quenched to RT	ZnS, CdI₂	ZnS/ 218, 272	15	$ZnS_{(s)} + CdI_2 (s, l) = ZnI_2 + CdS$[144]	44.1/T=0	51.8/ T=800
		CdI₂/ 110	16	$ZnS + CdI_2 (g) = ZnI_2 + CdS$ [148]	-8.28/ T=300	Positive T>300
Heated to 800, cooled down and quenched at 330 to RT	$Zn_{0.94}Cd_{0.06}S$ $(Zn_{0.8}Cd_{0.2})S$ CdI₂, ZnS	CdI₂, ZnS	17	$ZnS + I^+ + CdI^+ (g) = CdS + ZnI_2(g)$ [148]	-59.455/ T=300	-86.182/ T=800
Heated to 800, cooled down to and quenched at 350 to RT	CdI₂, ZnS	CdI₂, ZnS	18	$ZnS + I^+ + CdI^+ (g) = ZnS + CdI_2$[148]	-186.686/ T=300	-112.968/ T=800
			19	$ZnS + I^+ + CdI^+ (g) = Zn_{1-x}C_xdS + 1-xCdI_2$	Proposed	
			20	$ZnS + CdI_2 (l) = Zn_{1-x}Cd_xS (l) + ZnI_2 (l)$	Proposed	

3.3.6 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 (88µVs) and 2.0J (265 µVs) at 339 and 360 °C, respectively. The former is attributed to the melting of CdI_2 while the latter is attributed to the transformation of Cu_2S to $Cu_{1.96}S$ similar to Cu_2S+CdI_2 (Part 3.3.3). The low enthalpy signal in Figure 22a 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. This confirms a high solubility/interaction between the flux material and the precursor compounds. The enthalpy calculation for the cumulative formation process in the heating can be given as (666 µV s – 88 µV s = 578 µV s) - this corresponds to 13 ± 2 kJ mol^{-1}. In the cooling process, the enthalpy signal was observed as a single freezing exothermic process attributed to the freezing of CdI_2 with an enthalpy signal of 2.7 J (343 µV s). The XRD analysis of the sample mixture of $CdI_2+SnS+Cu_2S+S$ heated to 800 °C and then cooled down to 340 °C before quenching rapidly to room temperature showed the presence of Cu_2SnS_3 and another ternary CTS. 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 $Cu_2S+SnS+S$ in the flux leads to the formation of ternary compounds Cu_2SnS_3[54] and Cu_4SnS_6[149] (see Table 8), as detected by XRD and the formation of the ternaries takes place during the melting of the flux (CdI_2). Figure 22 shows the Raman spectra of the studied mixtures.
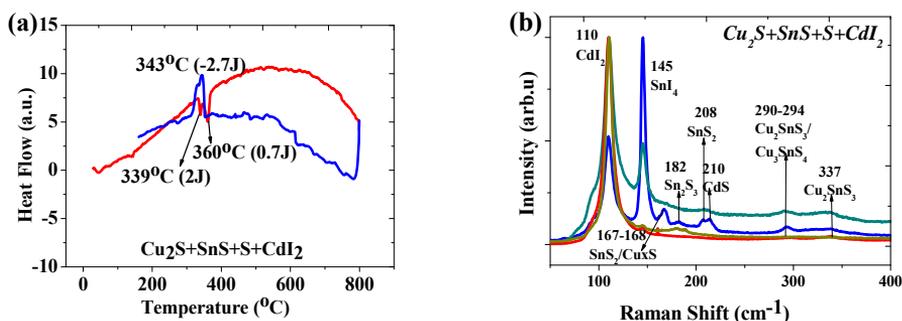
Figure 22. (a) DTA curves of $CdI_2+SnS+Cu_2S+S$ mixture (b) Raman spectra of $Cu_2S+SnS+S+CdI_2$ heated and quenched at different temperatures: blue - heated to 339 °C quenched to room temperature, red - heated to 360 °C and quenched to room temperature, pink- heated to 800 °C and cooled down to 340 °C before quenching to room temperature, black - heated to 800 °C and cooled down to 470 °C before quenching to room temperature.

Table 8. Annealing conditions, determined phases, reactions and calculated ΔG values for CdI₂+SnS+Cu₂S+S mixture

Annealing conditions (°C)	Phases by XRD	Phases by Raman/peak position (cm⁻¹)	Equa-tion	Reactions	ΔG (kJ mol⁻¹)/Temperature (°C)
Heated to 339	CdI₂, Cu₁.₉₆S,	Raman spectra are very difficult to analyze due to the overlapping of peaks of multi-component systems	23	$2CuS = Cu_2S + S(l)$[144,150]	-4.48/T=500 ; -39.88/ T=1000
Heated to 360	CuI, SnS, Sn₂SI₂, Cu₂SnS₃		24	$2SnS + 2S = 2SnS_2$	-28.6/T=400
			25	$2CuS + SnS (melt) = Cu_2SnS_3$[54,77]	Proposed
Heated to 800 and cooled down to 340	CdI₂, Cu₂S, SnS₂, CuI, Cu₂SnS₃, Cu₄SnS₆,	Raman spectra are very difficult to analyze due to the overlapping of peaks of multi-component systems	26	$2CuS+ SnS (melt) = Cu_2SnS_3$; $Cu_2S + SnS = Cu_2SnS_3$[54,77]	Proposed
			27	$2Cu_2S + SnS_2 + 2S = Cu_4SnS_6$[54]	Proposed

3.3.7 Mixture for synthesis of quaternary CZTS compound (CdI$_2$+SnS+Cu$_2$S+S+ZnS)

DTA curves show that the mixture of CdI$_2$ with the binary precursors in the required stoichiometric composition for the formation of Cu$_2$ZnSnS$_4$ melts and solidifies at 366 °C and at 353 °C, respectively, with thermal effects of 2.4 J (308 µV s) in the endothermic and exothermic processes (see Figure 23a). Considering the reduced enthalpy signals, the melting/solidification processes are accompanied by other multiple processes proceeding simultaneously, as described in the previous sections. By the DTA analysis, we found that the formation of CZTS in molten CdI$_2$ proceeds via an exothermic process with an enthalpy signal of (666 µV s - 308 µV s = 358 µV s), which corresponds to an enthalpy value of 8± 2 kJ mol^{-1}. Most of the secondary phases formed during the intermediate processes were consumed during the formation process giving rise to Cu$_2$Zn$_{1-x}$Cd$_x$SnS$_4$ as the prevailing phase. All phases detected by Raman and XRD and the proposed reaction path are summarized in Table 9. The formed solid solution of Cu$_2$Zn$_{1-x}$Cd$_x$SnS$_4$ was confirmed by the EDX analysis and by the shift of Raman peak from 338 cm^{-1} to 333 cm^{-1} [129]. We suggest that the formation of Cu$_2$Zn$_{1-x}$Cd$_x$SnS$_4$ solid solution proceeded via an intermediate reaction between Zn$_{1-x}$Cd$_x$S and Cu$_2$SnS$_3$ by equation (28) or directly by reaction (29) in the molten phase of CdI$_2$. Phases detected by Raman are given in Figure 23b, all details of the XRD patterns for the phases detected are presented in Appendix B.
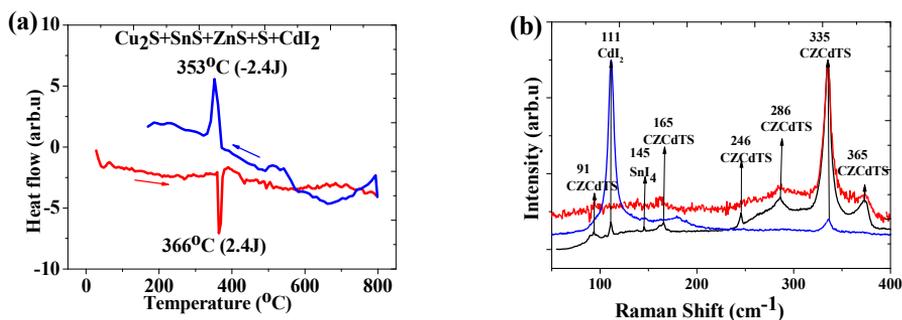
Figure 23. (a) DTA curves of precursor mixture CdI$_2$+SnS+Cu$_2$S+S+ZnS, (b) Raman spectra of Cu$_2$S+SnS+ZnS+S+CdI$_2$: blue - heated to 800 °C and quenched to room temperature, red - heated to 800 °C and cooled to 600 °C before quenching to room temperature, black - heated to 800 °C and cooled down to 350 °C abd quenched rapidly to room temperature.

Table 9. Annealing conditions, determined phases, reactions and calculated ΔG values for CdI$_2$+SnS+Cu$_2$S+ZnS+S mixture

Annealing conditions (°C)	Phases by XRD	Phases by Raman/Raman peak position (cm^{-1})	Equation	Reactions	ΔG (kJ mol^{-1}) Temperature (°C)
Heated to 800	Cu$_2$Zn$_{1-x}$Cd$_x$SnS$_4$	CdI$_2$/110[10] CuI/148[10,138] Cu$_2$Zn$_x$Cd$_{1-x}$SnS$_4$/ 333, 374[67]	28	Cu$_2$SnS$_3$ + Zn$_{1-x}$Cd$_x$S = Cu$_2$Zn$_{1-x}$Cd$_x$SnS$_4$	Proposed
Heated to 800 and cooled to 600	CdI$_2$, Cu$_{2-x}$S, Cu$_2$SnS$_3$, Cu$_2$Zn$_{1-x}$Cd$_x$SnS$_4$, SnI$_4$	CdI$_2$/110[10] CuI/148[10,138] CZTS Cu$_2$Zn$_x$Cd$_{1-x}$SnS$_4$/ 333, 374[67]	29	Cu$_2$S + SnS + Zn$_{1-x}$Cd$_x$S + S = Cu$_2$Zn$_{1-x}$Cd$_x$SnS$_4$	
Heated to 800 and cooled to 350	CdI$_2$, CuI, SnI$_4$, Cu$_2$Zn$_{1-x}$Cd$_x$SnS$_4$	CdI$_2$/110[10] CuI/148[10,138] Cu$_2$Zn$_x$Cd$_{1-x}$SnS$_4$/ 333, 374[67]			

The ΔG calculations presented in Figure 24 show that the most probable route to the $Cu_2Zn_{1-x}Cd_xSnS_4$ formation is possible by the intermediate formation of $CdI^+_{(g)}$. The interaction between solid binaries (ZnS, SnS, and CuS) and CdI_2 at a temperature lower than 400 °C is not favorable because ΔG is positive for $Zn_{1-x}Cd_xS$ formation; therefore, this rules out the possibility to form a quaternary $Cu_2Zn_{1-x}Cd_xSnS_4$. As mentioned earlier, there exists a thermo-dynamical possibility for a reaction between ZnS and CdI^+ to form $(Zn_{1-x}Cd_xS)$ for temperatures between 0 and 1000 °C, which is the only favorable path for the formation $Cu_2Zn_{1-x}Cd_xSnS_4$ by means of gas phase reaction. However, we have recognized that the formation of liquid phase of CdI_2 triggers all the observed exothermic processes that are accompanied by a sudden decrease in the fusion enthalpy and the melting temperature of CdI_2, suggesting that the formation of $Cu_2Zn_{1-x}Cd_xSnS_4$ proceeds in molten phase. However, we could not find data for thermodynamical calculations of processes in liquid CdI_2. Therefore, we may seek further understanding of the processes occurring in molten CdI_2.
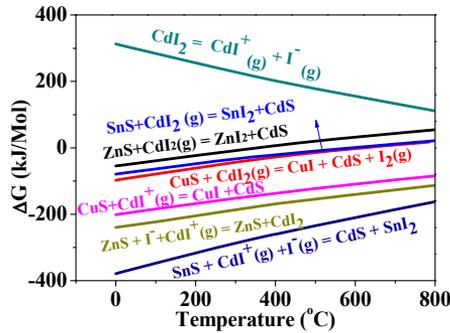
Figure 24. Calculated ΔG values for different reactions showing the possible reaction probability for the synthesis of $Cu_2ZnCdSnS_4$ in molten CdI_2.

In this work, we found that the Cd concentration in the formed CZCdTS increases with increasing amounts of CdI_2 in the synthesis. Cd incorporation is dependent on the temperature and on the amount of CdI_2, but not influenced by the heating time. The direct exchange reaction between solid ZnS and CdI_2, resulting in the formation of CdS and ZnI_2 is thermodynamically impossible because ΔG>0. By the DTA analysis, we obtained a much lower endothermal effect of melting of the precursor mixture of $ZnS+CdI_2$ in comparison with pure CdI_2. The reason can be in the occurrence of some simultaneous compensating exothermal process. We detected also some lowering of the melting temperature that may occur due to the dissolution of ZnS in molten CdI_2. Therefore, we believe that the formation of CdS and $Zn_{1-x}Cd_xS$ is enabled by the dissolution of some ZnS in molten CdI_2. It is well known that the amount of dissolved solute is dependent on the amount of solvent and temperature, as in the case of Cd content in $Zn_{1-x}Cd_xS$ and also Cd content in the formed CZCdTS monograins, which was found to be dependent on the temperature and on the amount of used CdI_2 as solvent in the present work.

CONCLUSIONS

Based on the results of my PhD research, the following conclusions were reached:

1) We found that solid solutions $Cu_2Zn_{1-x}Cd_xSnS_4$ with limited Cd content form in the synthesis of CZTS in molten CdI_2 from binary precursor compounds through an intermediate formation of $Zn_{1-x}Cd_xS$.
   - Based on our experimental findings, $Cu_2Zn_{1-x}Cd_xSnS_4$ formation can be described as a two-stage process: firstly, $Zn_{1-x}Cd_xS$ and Cu_2SnS_3 form in molten CdI_2; secondly, $Zn_{1-x}Cd_xS$ and Cu_2SnS_3 react to form $Cu_2Zn_{1-x}Cd_xSnS_4$.
   - The solubility of ZnS in the liquid phase of CdI_2 is suggested to be a limiting factor in the $Zn_{1-x}Cd_xS$ formation, which determines the amount of Cd incorporated into CZTS crystals.
   - The formation of liquid phase CdI_2 was accompanied by a sudden decrease in the enthalpy of fusion for CdI_2 in the mixtures with precursors. We therefore suggest that the formation process starts slightly below the melting temperature of pure CdI_2 and proceeds through the liquid phase at the melting of the flux.
2) From the study of the physical and chemical process occurring in the thermal heating of mixtures of CdI_2 with individual precursor compounds, we conclude the following:
   - The melting temperatures of CdI_2 in each studied mixture were found to be lower than the melting temperature of pure CdI_2, which is attributed to the interaction between the precursor compound and the flux.
   - The overall enthalpy values of the processes in each studied mixture are 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.
   - The formation of Cu_2SnS_3 from $Cu_2S+SnS+S$ in CdI_2 gave an enthalpy value of 13 ± 2 kJ mol^{-1} while the formation reaction of $Cu_2Zn_xCd_{1-x}SnS_4$ in the liquid phase of CdI_2 takes place with the experimentally determined enthalpy of 8 ± 2 kJ mol^{-1}.
   - The low enthalpy of $Cu_2Zn_xCd_{1-x}SnS_4$ formation compared to high enthalpy of the ternary Cu_2SnS_3 formation 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 activation energy of the Cd incorporation process into the CZCdTS crystals was estimated as 17.5 ± 2 kJ/mol.
3) From the study of the influence of growth process conditions on the CZTS monograin material properties, we found that the properties of the synthesized monograin powder can be modified by changing the synthesis conditions:

- Materials synthesized with smaller flux concentrations and at higher temperatures show less facet and have a more rounded shape. With increasing time as well as with increasing flux concentrations, faceted crystals became more obvious. The most round shaped grains were formed in the samples with the lowest used amount of CdI_2.
- The yield of usable powder grains with a size of 50-100 µm was higher as the flux concentration decreased. This may be due to the increased sintering effect.
- The amount of Cd incorporated into forming $Cu_2Zn_{1-x}Cd_xSnS_4$ from CdI_2 increases as the synthesis temperature rises and the amount of used CdI_2 grows.

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KOKKUVÕTE

Antud doktoritöö keskendub keemiliste protsesside uurimisele, mis toimuvad Cu_2ZnSnS_4 (CZTS) süntees-kasvatusel sulas CdI_2-s eesmärgiga selgitada välja võimalused ühefaasilise monoterapulbri sünteesiks, mis sobib kasutamiseks absorberkihina monoterakiht-päikesepatareides. Otsene keelutsoon 1,43-1,5 eV, suur valguse neeldumisvõime (absorptsioonikoefitsient üle 10^4 cm^{-1}) ja odavate koostiselementide laialdane esinemine maakoores teevad CZTS atraktiivseks päikesepatarei absorbermaterjaliks. $Cu_2ZnSn(SeS)_4$ baasil kilelise päikesepatarei rekordefektiivsus on 12.6 % .

Üheks odavaks absorbermaterjali sünteesi- ja saamismeetodiks on monoterapulbrite sünteeskasvatus, milles iga sünteesuv kristall võib moodustuda ja kasvada kui monokristall. Praegu on $Cu_2ZnSn(Se,S)_4$ monoterakiht-päikesepatarei (crystalsol OÜ) sertifitseeritud kasutegur 9.5 %, mis on monoterakiht päikesepatarei struktuuri tõttu väiksem kui aktiivmaterjali kasutegur selles (ligikaudu 13%). Töö eesmärgiks oli kirjeldada keemilisi vastasmõjusid CZTS pooljuhtühendi sünteesiprotsessis osalevate lähteühendite ja sulafaasilist keskkonda võimaldava CdI_2 vahel ja leida võimalused CZTS ühefaasilise monoterapulbrilise absorbermaterjali sünteesiks ja tootmiseks. Uuringud olid vajalikud, kuna ühefaasilise absorbermaterjali saamine sulades soolades on keerukas mitmete kõrvalühendite tekkevõimaluse tõttu ja kuna CZTS sünteeskasvatuse keemilist kulgu CdI_2-s polnud seni veel uuritud.

Doktoritöö keskendub CZTS keemilise moodustumise kirjeldamisele kasutades lähteühenditena Cu_2S, ZnS, SnS ja elementaarset väävlit. Käesolevas doktoritöös kasutati erinevaid analüüsimeetodeid: differentsiaal-termilist analüüsi (DTA) termiliste efektide toimumise avastamiseks uuritavates proovides ja nendes toimuvate protsesside soojusefektide määramiseks, skaneerivat elektronmikroskoopiat (SEM) moodustunud kristallide morfoloogia uurimiseks, energia-dispersiivset spektroskoopiat (EDX) elementkoostise ja Raman spektroskoopiat ning röntgendifraktsiooni (XRD) faasikoostise määramisel. Keemiliste protsesside toimumise tõenäosust hinnati-kontrolliti Gibbsi vaba energia muutuste arvutuste abil kasutades andmebaasi „*Database of HSC Chemistry Ver. 6.0*". DTA uuringud viidi läbi vastavale analüüsiseadmele kohandatud suletud kvartsampullides. DTA kalibratsiooniks kasutati võrdlusainena sama CdI_2, mis sünteeskasvatuselgi, kuna tavaliselt kasutatavad võrdlusained ei sobinud kalibreerimiseks kvartsampullides. Pärast DTA abil detekteeritud termiliste efektidega kaasnevate protsesside toimumistemperatuuride leidmist ja protsessientalpiate määramist valmistati identsed proovid suuremates kogustes iga avastatud protsessi jaoks ja kuumutati proove 4 tundi kinnistes vaakumampullides DTA abil leitud temperatuuridest veidi kõrgematel temperatuuridel, et leida toimunud faasimuutused. Sellisel teel leiti ühendid, mis tekkisid või lagunesid vastavatel temperatuuridel. Kasutades ülalkirjeldatud eksperimentaalset lähenemist ja analüütiliste võimaluste

kompleksi määrati antud töös eksperimentaalselt Cu_2SnS_3 ja $Cu_2Zn(Cd)SnS_4$ tekkeentalpiad.

Töö tulemusena leiti, et CZTS monoterapulbrite sünteeskasvatusel sula CdI_2 keskkonnas toimub Cd inkorporeerumine Cu_2ZnSnS_4 võresse ja .... $Cu_2Zn_{1-x}Cd_xSnS_4$ tahke lahuse tekkimine, milles Cd sisaldus on piiratud kasutatud CdI_2 hulga ja süntees-kasvatuse temperatuuriga. Cd inkorporeerumise protsessi aktivatsioonienergiaks hinnati 17.5 ± 2 kJ mol^{-1}. Leiti, et $Cu_2Zn_{1-x}Cd_xSnS_4$ moodustumist võib kirjeldada kahe-astmelise protsessina: esmalt tekivad $Zn_{1-x}Cd_xS$ ja Cu_2SnS_3, mis omavahel moodustavad $Cu_2Zn_{1-x}Cd_xSnS_4$. DTA kõverate võrdlemisel leiti, et kõikide uuritud kvaasi-binaarsete süsteemide (lähteühend-sulandaja) ühine joon on, et (a) segude (CdI_2 segus S, ZnS, Cu_2S või SnS) sulamistemperatuurid on madalamad kui puhtal soolal, mis on indikaatoriks mõningasele lähteühendi lahustumisele CdI_2-s; (b) kohe vahetult pärast endotermilist sulamisprotsessi algust ilmub eksotermiline efekt, mis alandab CdI_2 sulamisprotsessi entalpiat, näidates keemilist aktiivsust segudes olevate ühendite vahel vahetult pärast sula faasi teket; (c) CdI_2+Cu_2S ja CdI_2+SnS segudes avastati CdS ja erinevate joodi sisaldavate ühendite (SnI_4, Sn_2SI_2, CuI, ja $Cu_2Cd_3I_4S_2$) teke ja CdI_2+ZnS segus $Zn_{1-x}Cd_xS$ teke. Võttes arvesse eksperimentaalselt leitu ja kirjandusest teadaolevat fakti, et CdI_2 säilitab sulamisel oma $[CdI_4]^{2-}$ anioon-struktuuri, kus väikesed Cd^{2+} ioonid asetsevad tetraheedselt koordineeritud kohtades, pakutakse töös välja versioon, et erinevate jodiidide ja CdS teke on võimalik, kui Cd^{2+} ioonid asenduvad lahustunud Zn, Sn või Cu ioonidega. CdS teke on eelduseks $Zn_{1-x}Cd_xS$ tekkele ja Cd haaramisele nelikühendi võresse. ZnS lahustumine sulas CdI_2-s on limiteerivaks teguriks Cd inkorporeerumisele Cu_2ZnSnS_4 võresse ja $Cu_2Zn_{1-x}Cd_xSnS_4$ tekkele. Cu_2SnS_3 tekke-entalpia CdI_2-($Cu_2S+SnS+S$) segus oli 13 ± 2 kJ mol^{-1} ja $Cu_2Zn_xCd_{1-x}SnS_4$ tekkereaktsiooni entalpia sulas CdI_2-s leiti olevat 8 ± 2 kJ mol^{-1}. Tööst selgus, et moodustuvate $Cu_2Zn_{1-x}Cd_xSnS_4$ kristallide kuju ja suurust saab muuta varieerides sünteesiprotsessi tingimusi. Nii väiksemate CdI_2 koguste kasutamisel kui ka kõrgematel temperatuuridel moodustuvad ümarama kujuga kristallid. Monotera-membraanides kasutatavate kristallide (50-100 µm) saagis on suurem, kui kasutada väiksemaid koguseid CdI_2-sulandajat.

ABSTRACT

This thesis is focused on the studies of chemical processes in the synthesis-growth of Cu_2ZnSnS_4 (CZTS) in molten CdI_2 with the aim to produce single absorber materials for monograin layer solar cells. The direct band gap, high absorption coefficient and low cost and earth-abundant non-toxic constituent elements make CZTS attractive as absorber material for solar cells. Cu_2ZnSnS_4-type materials in thin film solar cells have shown record efficiency of 12.6 %.

Monograin powder growth is one of the cheapest synthesis methods, allowing production of materials where every grain can be formed and grown as a single crystalline particle. So far, 9.5 % of certified efficiency has been reached for $Cu_2ZnSn(Se, S)_4$ monograin layer solar cells by Crystalsol OÜ; due to the specific structure, the power conversion efficiency of the active material is around 13%. The chemical interactions between precursor compounds for CZTS synthesis and CdI_2 in molten phase have not been studied yet. Therefore, the thesis is centered on possible chemical reactions between molten CdI_2 and individual binary compounds - Cu_2S, ZnS, SnS - followed by studies on more complicated mixtures for synthesis of Cu_2SnS_3 (CTS) and CZTS in CdI_2 with the aim to fully understand the formation pathway of CZTS in molten CdI_2.

By variation of synthesis-growth conditions, the possibilities to change the properties of produced powders were studied. Different analytical methods were used: differential thermal analysis (DTA) for the detection of temperatures of processes accompanied with thermal effects and for the determination of enthalpies of these processes, scanning electron microscopy (SEM) was used for morphology studies, energy dispersive spectroscopy (EDX) for elemental composition, Raman spectroscopy and X-ray diffraction (XRD) for phase determination. The probability of possible chemical reactions was evaluated by calculations of Gibbs free energy change using "*Database of HSC Chemistry Ver. 6.0*". DTA studies were performed in vacuum-sealed quartz ampoules adopted for the used DTA set-up. For DTA calibrations, the same CdI_2 flux salt as reference material was used because the traditionally used reference materials were unstable or gave low signal in quartz ampoules. After the detection of temperatures of thermal effects by DTA, larger identical samples were prepared for each detected effect. These samples were heated for 4 hours at slightly higher temperatures than the occurrence of thermal effects for discovering possible phase changes. Using the experimental approach described above and the complex of analytical methods, the formation enthalpy values of Cu_2SnS_3 and Cu_2ZnSnS_4 were experimentally determined.

In the present thesis, different aspects that determine the path of synthesis of the CZTS compound and the shape of crystals were found. The synthesis of CZTS monograin powders in CdI_2 resulted in the formation of solid solutions of $Cu_2Zn_xCd_{1-x}SnS_4$ with limited Cd content. The amount of Cd incorporated from CdI_2 into forming $Cu_2Zn_{1-x}Cd_xSnS_4$ increased as the synthesis-growth process temperature was raised and the amount of CdI_2 grew. The activation energy of

the Cd incorporation process was estimated as 17.5 ± 2 kJ mol^{-1}. $Cu_2Zn_{1-x}Cd_xSnS_4$ formation in molten CdI_2 can be described as a two-stage process: firstly, $Zn_{1-x}Cd_xS$ and Cu_2SnS_3 form in molten CdI_2; secondly, $Zn_{1-x}Cd_xS$ and Cu_2SnS_3 react to form $Cu_2Zn_{1-x}Cd_xSnS_4$. By studies of mixtures of individual precursors with CdI_2 we found chemical possibilities for the intermediate formation of $Zn_{1-x}Cd_xS$ taking into account our experimental findings: (a) CdI_2 mixed with different precursors - S, ZnS, Cu_2S or SnS - melts at temperatures lower than pure CdI_2, showing some solubility of the precursors in molten CdI_2; (b) the formation of liquid phase of CdI_2 was accompanied with exothermic processes manifested by sudden decrease in the fusion enthalpy of CdI_2 mixtures with precursors; (c) CdS and different iodine-containing compounds - SnI_4, Sn_2SI_2, CuI, and $Cu_2Cd_3I_4S_2$ - were formed in CdI_2+Cu_2S and CdI_2+SnS and a solid solution of $Zn_{1-x}Cd_xS$ in CdI_2+ZnS.

Combining our experimental findings with the knowledge from literature that molten phase of CdI_2 retains its solid closely packed anion structure of $[CdI_4]^{2-}$ in which the small Cd^{2+} ions occupy tetrahedrally coordinated sites, we propose that the formation of different iodides and CdS can occur due to the displacement of Cd^{2+} ions by Zn^{2+} (or by Sn and Cu ions) dissolved in CdI_2. The formation of CdS is the presupposition for $Zn_{1-x}Cd_xS$ formation. The solubility of ZnS in the liquid phase of CdI_2 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. The formation of Cu_2SnS_3 from $Cu_2S+SnS+S$ in CdI_2 gave an enthalpy value of $13\pm2 kJmol^{-1}$ while 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 kJ mol^{-1}. The low formation enthalpy of $Cu_2Zn_xCd_{1-x}SnS_4$ compared to high formation enthalpy of the ternary Cu_2SnS_3 confirm that the solid solution $Cu_2Zn_xCd_{1-x}SnS_4$ is formed from the reaction between Cu_2SnS_3 and $Zn_{1-x}Cd_xS$. It was found that the shape and size of crystals can be modified by changing the synthesis conditions. Using smaller flux concentrations and higher temperatures less faceted and more rounded crystals can be grown. The yield of powder grains usable in monograin membranes with a size of 50-100 µm was higher as the flux concentration decreased

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Appendix A

Article I

Nkwusi, G., Leinemann, I., Raudoja, J., Mikli, V., Kärber, E., Altosaar, M. Impact of growth-synthesis conditions on $Cu_2Zn_{1-x}Cd_xSnS_4$ monograin material properties. *Superlattices and Microstructures*, **98** (2016) 400- 405.

Impact of growth-synthesis conditions on $Cu_2Zn_{1−x}Cd_xSnS_4$ monograin material properties

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A B S T R A C T

This paper presents the impact of growth conditions on the properties of copper zinc cadmium tin sulfide ($Cu_2Zn_{1−x}Cd_xSnS_4$) monograin powder synthesized in molten CdI_2. We studied the effects of synthesis time and flux amount on the properties of the monograin powder. Our results showed that we could control the phase composition, grain size and the morphology of the as grown $Cu_2Zn_{1−x}Cd_xSnS_4$ powder by changing the synthesis conditions. We found that in comparison with other used fluxes (KI, NaI), monograin powders synthesized in molten CdI_2 were less faceted and more round shaped. The average grain size increased as the flux amount decreased. The optimum synthesis time to obtain usable grain size with 50−100μ was found to be 160 h with CdI_2 flux amount, providing the ratio of the volumes of CdI_2/CZTS is 0.5.

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1. Introduction

It is generally difficult to grow high-quality single crystals of the CZTS-type compounds from their melt, because most of the compounds grow through a peritectic reaction or have a solid-state phase transition during the cooling process [1,2]. The monograin technology was developed as a possible alternative to thin film technology with its solar cell efficiency at about 9.4% based on CZTS powders synthesized in KI as flux [3−6]. In monograin technology (MGL), we explore the use of suitable flux to aid the growth of single crystalline CZTS powders known as monograin powders [7]. These powders are embedded into a thin layer of epoxy resin to form a monolayer [8]. A narrow size fraction of the powder grains, usually between 30 and 100 μm, is used. This implies that for a perfect monograin layer, the shape of the grains is very important. Spherical grains give higher possibility to form a perfect monolayer and prevent stacking of grains when compared to the grains with tetrahedral pyramidal structure with higher packing density [9]. *Timmo* et al. showed that the solubility of the synthesized material in the flux could affect the shape of growing grains [10]. In MGL, the synthesis-growth process is carried out in a closed ampoule and proceeds via isothermal conditions with the flux salt being saturated by dissolving precursors. Hence, the only driving force for crystal growth in this technology is the difference in surface energy of crystals of different sizes. The dissolution and crystal growth processes go on concurrently; the smaller crystals dissolve in flux and deposit onto surfaces of bigger crystals through mass transport (diffusion) in the molten phase that surrounds every crystal. The dissolution is more intensive in places where the surface energy is higher (grain borders, tips) and deposit onto plain surfaces (facets). If the solubility of compounds in the flux increases (by increasing temperature or by using flux material which permits high solubility of the precursors in a bigger

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amount), the dissolution process can prevail and crystals' borders take more rounded shape. At equilibrium, the dissolution-deposition rates are equal to each other and crystals tend to attain equilibrium shape. The equilibrium can be related to the volume of the growth solution and the time of growth [11,12]. In the review paper of M. A. Lovette et al. [12], the formation of a solid polyhedron with volume V from a fluid phase was described by the Gibbs-Thomson formula for the change of free Gibbs energy ΔG. Although Gibbs was the first to develop the criteria for equilibrium crystal shapes, he recognized that crystal shapes are usually determined by kinetics rather than by thermodynamics alone. In the synthesis-growth process, solid, powdery precursors are used. Their solubility in molten salts differs from each other, but is comparatively low [10]. When the mixtures are heated up and the molten phase starts to form but the dissolution of solids in the liquid flux has not reached the equilibrium state, the primary solid particles can sinter together. When the amount of liquid phase increases, it could penetrate into capillaries, repelling the weekly joined particles from each other. In our previous work [13], we confirmed the formation of solid solution of $Cu_2Zn_{1-x}Cd_xSnS_4$ (CZCdTS) when CZTS was synthesized in CdI_2 as a flux. Maris et al. studied (CuS, ZnS, CdS, SnS) in a molten KI [14], but the impact of growth-synthesis conditions on $Cu_2Zn_{1-x}Cd_xSnS_4$ monograin material properties was not reported. In this work, we investigated how the shape of the crystals of synthesized CZCdTS monograin powders can be controlled by the amount of low melting CdI_2 used as flux. We considered the use of CdI_2 as flux due to the future possibility to monitor KI doping when used as a flux among other reasons and to achieve a much lower synthesis temperature (below 750 °C in the case of KI and NaI). In addition, we study the influence of different preparation conditions such as synthesis time and the flux amount on the composition, material properties and morphology of the as grown CZTS monograin powders. We gave Special attention to the changes in the macrostructure of re-crystallized powder crystals and to the incorporation of Cd from CdI_2 into the crystals of CZTS.

2. Experimental

All samples were synthesized from binary precursor compounds of CuS, SnS and ZnS in molten CdI_2 as flux material. Flux material and precursors were mixed and ground in an agate mortar, mixtures were degassed and sealed into quartz ampoules as described in Ref. [4]. The concentration of flux salt in synthesis mixtures was varied so that the ratio of volumes of the liquid flux (V_{CdI2}) to solid precursors for CZTS (V_{CZTS}) V_{CdI2}/V_{CZTS} = 5, 3, 1, 0.5 (if the ratio V_{CdI2}/V_{CZTS} = 1, it is marked as C1) 0.5 was considered as the to avoid sintering at lower V_{CdI2}/V_{CZTS} ratio. We carried out the time dependent experiments at 650 °C only for 24, 160 and 300 h. Currently, CZTS is synthesis in our Laboratory at 750°C in molten KI, 650 °C was chosen for CdI_2 considering that it has a lower melting temperature compare to KI and based our previous report in Ref. [15]. After heating, the samples were quenched rapidly to room temperature in cold water. All synthesized powders were washed with de-ionized water to separate the monograins from the flux. We used sieving analysis to study the size distribution of grains and the yield of powders usable for making monograin layers. Low temperature (10 K) photoluminescence (PL) measurements were carried out to monitor the change in the band gap energy values of the formed monograins due to Cd incorporation. The 441 nm laser line with 100 mW intensity was used for the excitation and the PL spectra were detected using InGaAs detector. The morphology was studied with the scanning electron microscope (SEM) and chemical composition of the synthesized powders was analyzed using energy dispersive X-ray spectroscopy (EDX) (SEM-AsB and by 20 keV EDX) on Zeiss HR SEM ULTRA 55. The phases present in the powders was studied by room temperature (RT) micro-Raman spectroscopy using a Horiba LabRam HR800 high-resolution spectrometer with a multichannel CCD detection system in backscattering configuration with incident laser light of 532 nm focused on a 1-μm spot of the studied sample.

3. Results and discussions

3.1. Impact of flux concentration and synthesis time on the grain size and yield of powders

By sieving the powders into different size fractions, the amount of fractions with grain size $\geq$45 μm (usable in monograin solar cells, grain size lower than $\geq$45 μm may be too small to obtain a uniform unstacked layer) [8] was determined. In Fig. 1a, the synthesized powder with size $\geq$45 μm, decreases as the flux amount increases from 0.5C1–5C1 at 650°C and for 24, 160 and 300 h respectively. It is understandable if we consider that by increasing the amount of liquid phase, the diffusion between different crystals takes more time and the amount dissolved in the molten phase of flux increases. However, the lowest used amount of CdI_2 (0.5 C1) (see left side in Fig. 1), results in grains with sizes over 45 μm in bigger amount than could be expected from the small linear decrease when $C_1 \geq 1$ (right part in Fig. 1a). This phenomenon could be understandable if to take into account that the single grain growth limit is roughly determined as VLiquid/VSolid $\geq$0.5 [16] Therefore the amount of bigger grains increases for C = 0.5 in comparison with bigger used flux amounts (>0.5). In addition, at $C_1 < 0.5$, there is insufficient amount of flux to aid the growth process and sintering may begin to occur As the density of CZTS is not determined for higher temperatures, the amounts for initial liquid to solid volume ratio <0.5 could result in both the single grain growth and some sintering process occurring at the same time and at $C_1 < 0.5$, even greater sintering may occur which may affect the quality of the CZTS monograin powder. Fig. 1a also confirmed that the grain size increases as the temperature increases [17]. In addition, the yield of the total amount of CZTS monograins decreases as the flux amount increases and vice versa, it increases as the growth time increases (see Fig. 1b). From Fig. 1b, it is seen that the total yield of powder is bigger than the amount of input precursors for synthesis, particularly for heating times 160 and 300 h. The increase in the total amount of yield over the summarized amount of precursors can take place due to the replacement of Zn by Cd (with higher molar mass
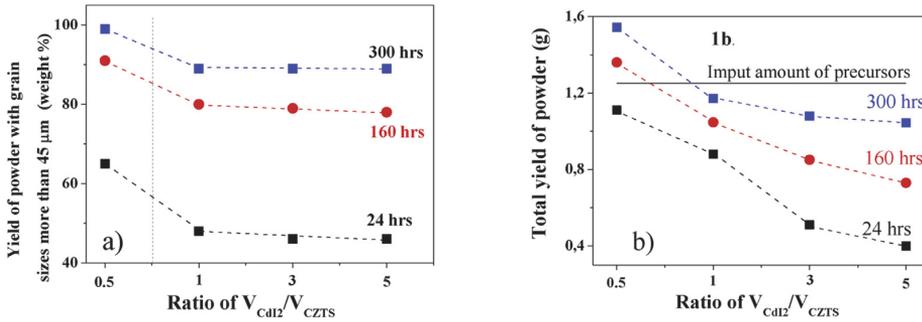
Fig. 1. Yield of powder fractions with grain size bigger than 45 μm (1a) and total yield of powders (1b) synthesized at 650 °C with different amounts of CdI₂. The input amount of precursors is constant and shown as a horizontal solid line in 1b). Heating time 24, 160 and 300 h.

than Zn) in the crystal lattice of formed CZCdTS compound while CdI$_2$ is the only source of Cd. During the growth process, the concentration gradient drives the mass transfer of the crystal constituents from the fluid phase to the crystal phase. The mass flux at the growth interface depends on the direction-dependent concentration gradient [17] and the larger the flux amount the slower and less chance of higher agglomeration and vice versa, this leads to smaller grains that can be easily washed off during separation of monograin powder from the flux. Summarizing, from Fig. 1, it can be recognized that the grain size increases by synthesis time, but decreases with the increasing flux amount.

3.2. Impact of flux amount and synthesis-growth time on grain morphology

SEM images of individual CZCdTS crystals are presented in Fig. 2 (synthesized at 650 °C). It can be seen that the grains produced by the smaller flux amount and are less faceted and have a more rounded shape. With increasing time as well as with the increasing flux amount, faceted crystals became more obvious. The most round shaped grains were formed in the samples with the lowest amount of CdI$_2$ heated for 160 h. Longer time (300 h) promotes the faceting. However, in crystals heated for 300 h, there can be observed also secondary agglomeration – the crystals are formed from different blocks. The
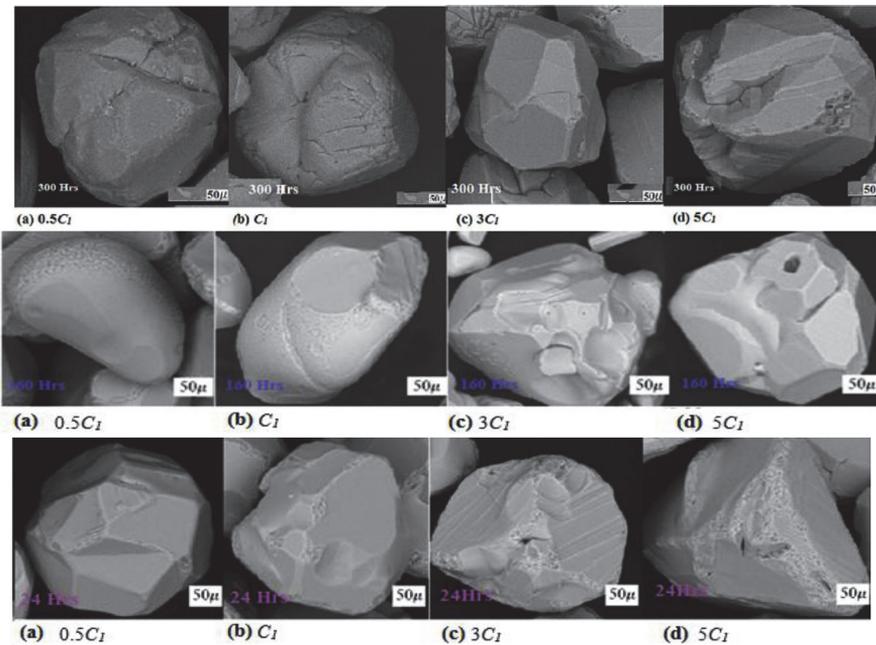
Fig. 2. SEM images of individual CZCdTS powder grains synthesized at T = 650 °C for 300 (upper row), 160 (middle row) and 24 (lower row) hours with increasing (from left to right) amount of CdI$_2$. C1 corresponds to V$_{CdI2}$/V$_{CZTS}$ = 1.
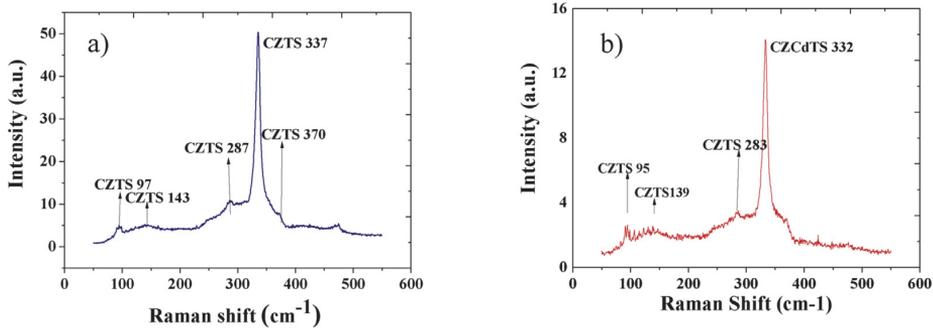
Fig. 3. Raman spectra of powder crystals synthesized at 650 °C for 300 h; a) with amount of CdI_2/CZTS = 0.5 and b) CdI_2/CZTS = 5. The Raman peaks at 337 cm^{-1} and 332 cm^{-1} are the expected peak positions respectively for pure CZTS and CCdTS as shown in the graphs.

primary sintering effect at the lowest used flux amounts ($0.5C_1$) seems to be helpful for getting rounder and compact grains after long time of crystallization (160 and 300 h). All the samples synthesized at 650 °C shows that the grains are less faceted and bigger and the yield is higher as the flux concentration decreases.

3.3. Composition of materials

3.3.1. Raman spectroscopy
Raman spectra of powder crystals synthesized at 650 °C for 300 h are presented in Fig. 3. Raman spectra of the sample held for 300 h at 650 °C with the lowest amount of CdI_2 reveal the most intensive Raman peak at 337 cm^{-1} which is close to the most intensive Raman peak position of pure CZTS at 338 cm^{-1} [15] while the most intensive Raman peak of the sample with the highest amount of CdI_2 is at 332 cm^{-1} where is also the most intensive Raman peak of pure Cu_2CdSnS_4 - 332 cm^{-1} [18]. Raman peaks of samples with intermediate amounts of CdI_2 C1 and $3C_1$ are at 333 cm^{-1} and 335 cm^{-1} respectively. In Ref. [20] there was shown that increasing Cd content in the $Cu_{1.85}$ (Cd_xZn_{1-x}) $_{1.1}SnS_{4.1}$ monograin powders grown in KI decreased linearly the peak position of A1 Raman mode from 338 to 332 cm^{-3} in the interval of x values from 0 to 0.4, then, with higher Cd content the A1 peak position did not shift.

3.3.2. EDX analysis
The composition of the synthesized CZTS monograin powders was determined by EDX method. The common formula of product powders is the same for all samples with deviation in the range of limits for EDX and can be expressed as $Cu_{1.9\pm0.01}Zn_{1-x}Cd_xSnS_{3.97\pm0.04}$ with variable Cd content (x values). The values of x depending on heating conditions are given in Table 1. Table 1 also gives the compositions of $Zn_{1-x}Cd_xS$ (found by XRD) in washed powder samples. As it can be seen, the Cd concentration in $Cu_2Zn_{1-x}Cd_xSnS_4$ and in $Zn_{1-x}Cd_xS$ increases with increasing amount of CdI_2 in synthesis. The incorporation of Cd into $Cu_2(ZnCd)SnS_4$ through the intermediate reaction of $Zn_{1-x}Cd_xS$ is by the formation of $CdI^+(g)$ which also increases with temperature [19]. In Fig. 4. It is seen that as the flux amount increases the, [Cd] also increases. However, from Table 1, we can conclude that 24 h is not enough long time to reach the equilibrium due to the inconsistency in the obtained data.

3.3.3. Photoluminescence
The PL spectra of CZTS monograin powder samples grown in CdI_2 for 160 h with ratios of V_{CdI2}/V_{CZTS} = 5 and 0.5 at T = 650 °C show PL band maxima at 1.05 eV and 1.07 eV respectively (see Fig. 5). Single broad and asymmetric PL bands have been reported for pure CZTS at 1.27 eV and 1.3 eV due to BI-recombination (Band-Impurity) and attributed to a deep acceptor defect [20], also PL bands at 1.39 eV (Band-to-tail) and 1.53 eV (Band –to band) have been observed for CZTS [21]. In

Table 1
Composition of CZCdTS and $Zn_{1-x}Cd_xS$ for different flux concentrations and heating time as determined by EDX (T = 650 °C).

V_{CDI2}/V_{CZTS}	Heating time (hours)					
	24	160	300	24	160	300
	Value of x in $Cu_{1.9\pm0.01}(Zn_{1-x}Cd_x)SnS_{3.97\pm0.04}$			Value of x in $Zn_{1-x}Cd_xS$		
0.5	0.15	0.18	0.16			
1	0.15	0.26	0.22	0.1	0.25	0.15
3	0.25	0.28	0.28		0.22	0.22
5	0.3	0.35	0.35		0.35	0.39
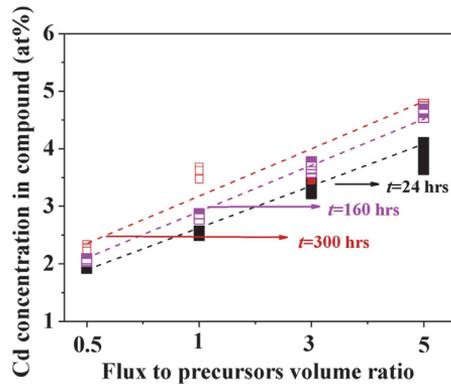
Fig. 4. Cd concentration in powders synthesized in different amounts of CdI$_2$ for different time at T = 650 °C as determined by EDX analysis.

our work, we found that the CZCdTS PL band position varied slightly from 1.05 eV for 5C1 to 1.07 eV for 0.5C$_1$. The PL band of pure Cu$_2$CdSnS$_4$ is measured at 1.1 eV [21]. In the paper of M. Pilvet et al. [14] a shift of the PL band of Cu$_{1.85}$(Cd$_x$Zn$_{1-x}$)$_{1.1}$SnS$_{4.1}$ ($0 \leq x \leq 1$) monograin powders (grown in KI) towards lower energies with increasing Cd content was observed in the region $0 \leq x < 0.4$. Therefore, we attribute the shift in PL band maximum to the Cd incorporation into the crystal lattice of CZTS. Fig. 5 presents the PL spectra of CZTS synthesized for 160 h at 650 °C with ratios of V$_{CdI2}$/V$_{CZTS}$ 0.5 and 5. The Cd content of each sample as determined by EDX is shown in Table 1.

All the used analytical methods confirm that during the synthesis of CZTS in CdI$_2$ as flux Cd incorporates from CdI$_2$ into the crystal lattice of CZTS resulting in the formation of solid solutions with a common formula of Cu$_{1.9\pm0.01}$Zn$_{1-x}$Cd$_x$SnS$_{3.97\pm0.04}$. In the work of Pilvet et al. [14] it was shown that by using CdS and ZnS as precursors the hole row of solid solutions of Cu$_{1.85}$(Cd$_x$Zn$_{1-x}$)$_{1.1}$SnS$_{4.1}$ ($0 \leq x \leq 1$) can be synthesized. In our system the Cd content is limited by the amount of CdI$_2$. In Ref. [15] we found that the Cd concentration in formed CZCdTS increased with temperature and it could be expressed as [Cd] $\sim e^{-\Delta E/kT}$, where the activation energy of the process $\Delta E = 17.5 \pm 2$ kJ/mol. In this work we found that the Cd concentration in formed CZCdTS and in Zn$_{1-y}$Cd$_y$S increases with increasing amounts of CdI$_2$ in synthesis. The formation of Zn$_{1-x}$Cd$_x$S seems to be the rate-determining step for the Cd incorporation into the crystal lattice of the CZTS monograins. Cd incorporation is dependent on temperature and on the amount of CdI$_2$, but not influenced by heating time. The direct exchange reaction between solid ZnS and CdI$_2$ resulting in the formation of CdS and ZnI$_2$ is thermodynamically impossible because $\Delta G > 0$ [22,23]. We detected by DTA analysis a much lower endothermal effect of melting of the precursor mixture of Zn + CdI$_2$ in comparison with pure CdI$_2$ [18]. That can be explained by the occurrence of some simultaneous compensating exothermal process. We detected also some lowering of melting temperature, that can may due to the dissolution of ZnS in molten CdI$_2$. Therefore, we believe that the formation of CdS and Zn$_{1-x}$Cd$_x$S is enabled by dissolution of some ZnS in molten CdI$_2$. It is well known that the amount of dissolved solute is dependent on the amount of solvent and temperature as seen in the case of Cd content in Zn$_{1-x}$Cd$_x$S and also Cd content in formed CZCdTS monograins which was found to be dependent on temperature and on the amount of used CdI$_2$ as solvent in the present work.
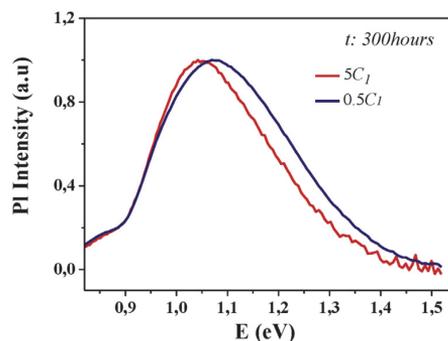
Fig. 5. Low temperature (T = 10 K) PL spectra of CZTS monograin powders grown at 650 °C for 160 h in CdI$_2$ with 5C1 and 0.5C1.

4. Conclusions

The impact of different technological conditions such as flux concentration, synthesis temperature and time on the properties of the synthesized CZTS monograins was studied. We found that the grains produced with smaller flux concentrations and at higher temperature are less faceted and have a more rounded shape. With increasing time as well as with increasing flux concentrations, faceted crystals became more obvious. The most round shaped grains were formed in the samples with the lowest amount of CdI_2. It was found that the yield of usable powder grains with a size of 50–100 μm was higher as the flux concentration decreased. Optimum synthesis conditions were found as time 160 h at 650 °C with CdI_2 flux concentration providing $V_{CdI2}/V_{CZTS} = 0.5$. EDX results showed the all the powders were $Cu_2Zn_{1-x}Cd_xSnS_4$ solid solutions. The Cd incorporation into the crystals of the monograin powders was found to be dependent on the flux concentration but not on time. Cd content in synthesized powders was in the range of 1.9–4.8 at % with the used V_{CdI2}/V_{CZTS} ratios in between 0.5 and 5 at 650 °C.

Acknowledgments

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Article II

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The Processes and Enthalpies in Synthesis of Cu$_2$ZnSnS$_4$ in Molten CdI$_2$

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Abstract: Synthesis of Cu$_2$ZnSnS$_4$ (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$_2$ZnSnS$_4$ proceeds mainly in the liquid phase of CdI$_2$ where CdS and Zn$_{1-x}$Cd$_x$S form and initiate the formation of Cu$_2$Zn$_{1-x}$Cd$_x$SnS$_4$. 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$_2$SnS$_3$ and Cu$_2$ZnSnS$_4$ are13±2kJmol^{-1} and 8±2 kJmol^{-1} respectively.

Keyword: Cu$_2$ZnSnS$_4$, Cu$_2$Zn$_{1-x}$Cd$_x$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 Cu$_2$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 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$_2$ZnSnSe$_4$ in CdI$_2$, Cd from CdI$_2$ incorporated into the crystals of CZTSe forming a solid solution of Cu$_2$Zn$_{1-x}$Cd$_x$SnSe$_4$, however, the formation of Cu$_2$ZnSnS$_4$ 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$_2$S+SnS+ZnS+S) in the presence of molten phase of CdI$_2$. Separate quasi-binary mixtures (Cu$_2$S+CdI$_2$), (ZnS+CdI$_2$), (SnS+CdI$_2$) (S+CdI$_2$), also mixture for ternary Cu$_2$SnS$_3$ (CTS) compound (Cu$_2$S+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$_{melt}$= 385ºC) [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 800ºC were 5 and 10ºC 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).

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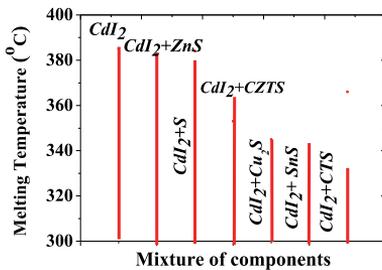
Fig 1. Melting temperatures of studied mixtures as determined from DTA curves

A. CdI₂

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^OC in heating and an exothermic effect at 366^OC in cooling cycle which can be attributed to the melting and freezing of CdI_2 with enthalpy signal of 666.$\pm$ 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) .
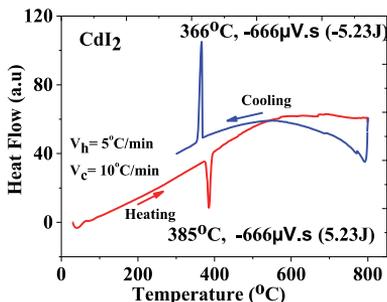
Fig 2. DTA curves of CdI_2

B. CdI₂ + Cu₂S

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^oC, 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 ^OC and an exothermic effect of freezing of CdI_2 at 338^OC. 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 ^OC) (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^OC there is seen another endothermic DTA peak at 400^oC. The phase analysis of the bigger sample heated and quenched at 420^oC shows that this peak corresponds to the decomposition of $Cu_2Cd_3I_4S_2$ with formation of CdS, CuI and Cu_4Cd_3 (see equation (5) in the Tabel 1) with summary thermal effect of 77 mVs (0.6J).
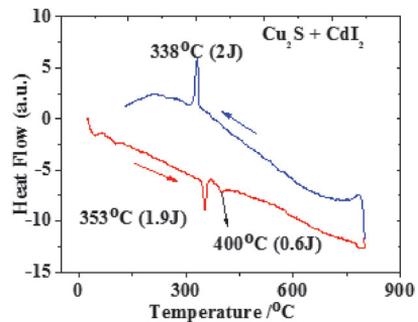
Fig 3: DTA curves of CdI2+Cu2S

C. CdI₂ +ZnS

The DTA heating and cooling curves of this mixture are presented in Figure 4. It shows an endothermic peak at 382^oC in the heating cycle, slightly lower than the melting temperature of pure CdI_2 (T_{melt}=385^oC) 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^oC, may be due to the low sensitivity of XRD. In the cooling curve two exothermic peaks at 354^oC and 338^oC are seen. This implies that CdI_2 in the mixture with ZnS melts close to the melting temperature of its pure form.

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$_2$Cd$_3$I$_4$S$_2$ CdS, Cu$_4$Cd$_3$	(1)	Cu$_2$S+CdI$_2$←2CuI+CdS [18-20]	-49 ǀ T=300°C	-31.5 ǀ T=400°C	
		(2)	CdS+Cu$_2$S+2CdI$_2$↔Cu$_2$Cd$_3$I$_4$S$_2$	Proposed		
Heated to 400oC, annealed for 4 hours		(3)	Cu$_2$S + CdI$_2$(g) = 2CuI + CdS [18,20]	-43.6 ǀ T=300°C	-1.8 ǀ T= 600°C	
Heated to 800°C and cooled down to 330°C	CdS, Cu$_4$Cd$_3$, CuS, Cu$_2$Cd$_3$I$_4$S$_2$, CuI	(4)	CuS+CdI$^+$(g)→ CuI +CdS [18,21]	-152 ǀ T=300°C	-84.7 ǀ T=800°C	
		(5)	2Cu$_2$Cd$_3$I$_4$S2↔Cu$_4$Cd$_3$ +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°C 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$_x$S in the mixture of ZnS + CdI$_2$ (see Table 2). As the formation of Zn$_{1-x}$Cd$_x$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$_2$ 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$_x$S and Cu$_2$Zn$_{1-x}$Cd$_x$SnS$_4$ formed in the studied samples. Explanation for the possibility to form Zn$_{1-x}$Cd$_x$S 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.

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$_x$S 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$_x$Cd$_{1-x}$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 ^{o}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$_2$SI$_2$ 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
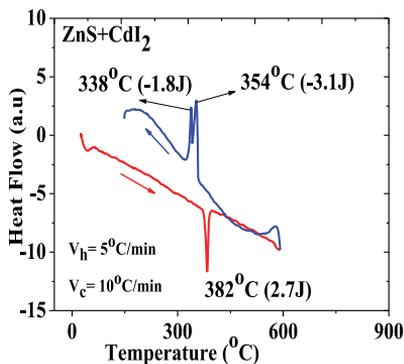
Fig 4: DTA curves of CdI$_2$+ZnS mixture

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$_{2(s.l)}$→ 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$_{0.06}$ $_6$S, (Zn$_{0.8}$Cd$_{0.2}$)S, CdI$_2$, ZnS,	(8)	ZnS + I$^-$+ CdI$^+_{(g)}$ → 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$^+_{(g)}$ → ZnS+CdI$_2$ [27-29]	-186.7 | T=300°C	-113 | T=800°C
		(10)	ZnS+I$^+$+CdI$^+$(g)→Zn$_{1-x}$C$_x$dS+1-xCdI$_2$	Proposed	
		(11)	ZnS (s)+CdI$_2$ (s) → Zn$_{1-x}$C$_x$dS (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 ^{o}C and quenched	CdI$_2$, CdS, SnI$_2$ Sn$_2$SI$_2$	(12)	SnS+CdI$_2$ (g) = SnI$_2$+CdS [17,30]	-79.5 | T ≥ 0	-9.6 | T≤ 500
		(13)	2SnS+I$_2$→Sn$_2$SI$_2$+S	proposed on phases observed	
		(14)	2SnS+CdI$_2$→Sn$_2$SI$_2$+CdS	proposed on phases observed	
		(15)	CdI$_2$(g) +S → I$_2$ + CdS,	-43.2 | T=0°C	9.7 | T=400°C
Heated to 800 ^{o}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) → 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
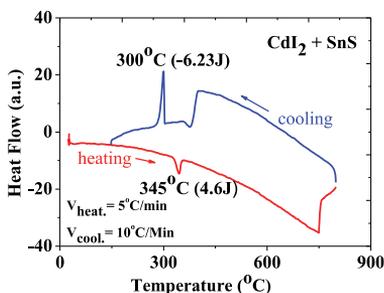
Fig 5: DTA curves of CdI2+SnS mixture

E. Mixture for synthesis of Cu$_2$SnS$_3$ (CdI$_2$ +SnS+Cu$_2$S+S)

In the mixture of (Cu$_2$S+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$_2$S to Cu$_{1.96}$S as it was observed already in (Cu$_2$S+CdI$_2$). In addition, SnS$_2$ was also found by XRD. XRD analysis of the mixture of (CdI$_2$ +SnS+Cu$_2$S+S) heated just above the melting of CdI$_2$, revealed the formation of ternary compound Cu$_2$SnS$_3$. 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$_2$SnS$_3$ 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 ^{o}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

analysis of the sample mixture of CdI_2 +SnS+Cu_2S+S heated to 800^oC and then cooled down to 300^oC 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.
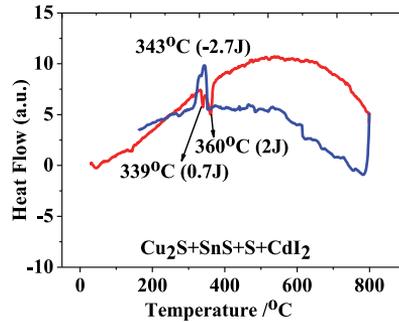
Fig 6: DTA curve of CdI_2 + SnS + Cu2S + S mixtures

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 ^oC	CdI_2, CuS,	(21)	$2CuS \rightarrow Cu_2S + S_{(l)}$ [27][33]	-4.48 ǀT= 500^oC	-39.88 ǀT= 1000
Heated to 560 ^oC	SnS, Cu_2SnS_3	(22)	$2SnS + 2S \rightarrow 2SnS_2$	-28.6 ǀ T=400^oC	
		(23)	$2CuS+SnS \rightarrow Cu_2SnS_3$[31][34]	Proposed	
Heated to 800 ^oC and cooled down to 300^oC	CdI_2, Cu_2S,	(24)	$2CuS+ SnS (melt) \rightarrow Cu_2SnS_3$	Proposed	
Heated to 800 ^oC and cooled down to 470^oC	SnS_2, Cu_2SnS_3 Cu_4SnS_6	(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 $366^oC/353^oC$ 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^oC and cooled down to 600^oC and 350^oC 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^oC 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.
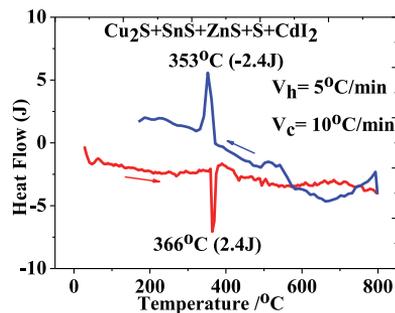
Fig 7. DTA curves of precursor mixtures CdI_2 + SnS + Cu_2S + S + ZnS

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 $Cu_2(ZnCd)SnS_4$.
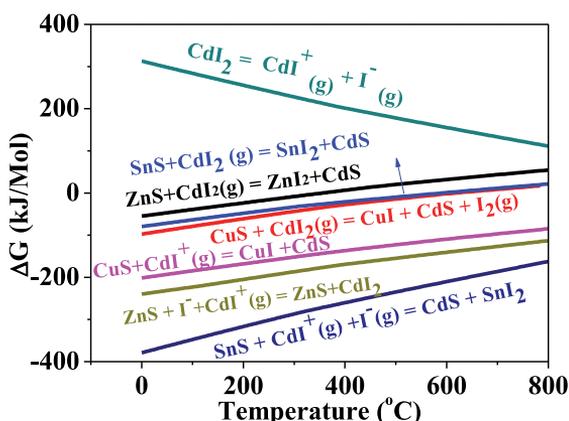
Fig 8: Calculated ΔG values for different reactions showing the possible reaction path for the synthesis of $Cu_2ZnCdSnS_4$ in molten CdI_2

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 $13\pm2kJmol^{-1}$. 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

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

ACKNOWLEDGEMENT

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Article III

Nkwusi, G., Leinemann, I., Raudoja, J., Mikli, V., Kauk-Kuusik, M. Altosaar, M., Mellikov E. (2014). Synthesis of $Cu_2(ZnCd)SnS_4$ Absorber Material for Monograin Membrane Applications.– *[CD-ROM] MRS Proceedings 2014: 2013 MRS Fall Meeting. SCHOLARONE Manuscripts, (Symposium W – Next-Generation Inorganic Thin-Film Photovoltaics),* 1638.

Synthesis of Cu2(ZnCd)SnS4 Absorber Material for Monograin Membrane Applications

Synthesis of $Cu_2(ZnCd)SnS_4$ Absorber Material for Monograin Membrane Applications

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ABSTRACT

CZTS monograin powder samples were synthesized in CdI_2 as flux material. The obtained materials were analysed by EDX, SEM, and Raman methods. It was found that Cd from flux was incorporated into the formed compound leading to the formation of solid solution $Cu_2Zn_{1-x}Cd_xSnS_4$. The content of Cd in the compound was studied in the dependence of synthesis temperature and time. It was found that Cd content in the formed $Cu_2Zn_{1-x}Cd_xSnS_4$ did not depend on synthesis duration at constant temperature and increased with temperature. The activation energy of the Cd incorporation process was estimated as 17.5 ± 2 kJ/mol.

Keyword: CZTS, monograin powder, CdI_2 flux, Cd incorporation

INTRODUCTION

Kesterite structured Cu_2ZnSnS_4 (CZTS) as an absorber material for solar cell is a promising semiconductor for low-cost and sustainable energy production [1-5]. Thin film technology of quaternary CZTS solar cell has been widely studied over the last decade with the contribution of different authors aimed at understanding the best preparation conditions and to improve the solar cell efficiency, that is currently 11.1 % for $Cu_2ZnSn(S, Se)_4$ synthesized in hydrazine [6]. Monograin technology has been developed as a possible alternative to thin film technology with current CZTS monograin layer (MGL) solar cell efficiency of over 8%. In the monograin technology, synthesis and isothermal recrystallization of polycrystalline powders in the presence of the liquid phase of a suitable solvent (flux) in sufficient amount, aids the formation of powders with single crystalline structure of powder grains [2].

CZTS in monograin form has been grown in different flux materials such as KI, NaI and CdI_2 [7-10] . Cadmium Iodide (CdI_2) had been used as a low temperature flux in our previous report [11]. It was confirmed that CZTS monograin powder can be grown in molten CdI_2 at lower temperatures relative to the melting temperature of KI [12]. According to *Klavina I, et al*, it is known that during the synthesis of CZTS in CdI_2 as flux , Cd incorporates into the crystals of CZTS forming a solid solution of $Cu_2(CdZn)SnS_4$. However, how to reach single phase absorber material in monograin powder form and how to avoid the formation of by-products was not discussed. Also, the incorporation of Cd from CdI_2 into CZTS crystals affects the properties of solar cell absorber materials. Therefore, the regularities and extent of Cd incorporation into CZTS have been studied in this report. The influence of synthesis temperature and time on the Cd incorporation into CZTS is reported. Finally, based on the obtained experimental data the activation energy of the Cd incorporation was determined.

EXPERIMENTAL DETAILS

Copper Zinc Tin Sulfide (CZTS) monograin powder was synthesised from precursors Cu_2S, SnS, ZnS and S in molten CdI_2 as flux material taken in mass ratio of $CZTS/CdI_2$ equal to 1:1 The precursor binaries and CdI_2 were mixed by grinding in an agate mortar, degassed and encapsulated into quartz ampoules. The formation reaction of CZTS from precursors in liquid flux at high temperature was described in [11]. Samples were quenched rapidly to the room temperature in cold water. The formed powder particles were separated from flux material by washing with deionized water. The amount of Cd incorporated into CZTS was studied as depending on synthesis temperature and time: samples were heated for 15 hours at 280ºC, 370ºC, 500ºC, 600ºC, 700ºC and 780ºC and at 600ºC for 6, 22, 32 and 60 hours. The ratios of metals in the mix of binary precursors was chosen as $[Cu]/([Zn]+[Sn]) = 0.92$ and $[Zn]/[Sn] = 1.03$, considering that the best solar cell efficiencies could be achieved with single phase CZTS without the presence of secondary phases in the range of compositions $[Cu]/([Zn]+[Sn])$ $0,82 \leq x \leq 0,93$ and $([Zn]/[Sn] \geq 1.03$ [13-15]. All compositional analyses were carried out using energy dispersive X-ray spectroscopy (EDS). Cd incorporated into the crystals was determined from polished crystals. The EDS analysis was made at least from 10 crystals of an analysed sample. The phases formed in the annealed samples were determined by the Raman spectra recorded using a Horiba LabRam HR high resolution spectrometer equipped with a multichannel CCD detection system in backscattering configuration. Incident laser light of 532 nm was focused on different 1 μm^2 spots of the studied sample and an average of five readings were taken for every sample to obtain an average result of the sample.

RESULTS AND DISCUSSION

Temperature dependence

At 280ºC, much below the melting point of CdI_2, the formation of quaternary compound was not detected. As the temperature increases up to 370ºC, just below the melting temperature of pure CdI_2, the formation of CZTS begins. At this temperature the Raman spectra confirm the presence of different secondary phases coexisting with CZTS as it was shown already in [11]. Cd concentration in CZTS crystals grown in CdI_2 at different temperatures is presented in Figure 1. With increasing annealing temperature, Cd content in formed CZTS increases reaching the maximum average value 2.75 at% at 780ºC.
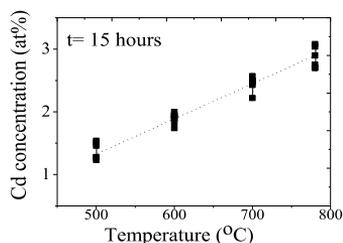
Figure 1. Cd content incorporated into CZTS from CdI_2 flux as a function of heating temperature.

Time dependence

Cd concentration in CZTS grown at 600 ^{o}C for different annealing times is presented in Figure 2. It is obvious that annealing for 6 hours leads to the large dispersion in measurement data attributable to the non-equilibrium status of the system. After heating for 22 hours the Cd concentration in grown CZTS crystals reaches the equilibrium concentration at 600 ^{o}C.
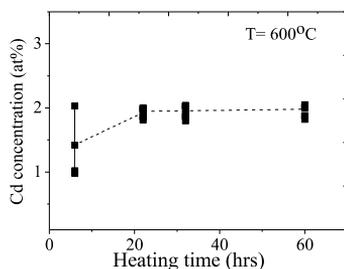
Figure 2: Time dependency of Cd incorporation into CZTS from CdI_2 flux.

Figure 3 shows the SEM images of samples synthesized at 600°C for different times starting from 6 hours up to 60 hours. It is obvious that as the synthesis time increases, the grain size increases. At the same time there is no remarkable changes in the morphology of crystals.
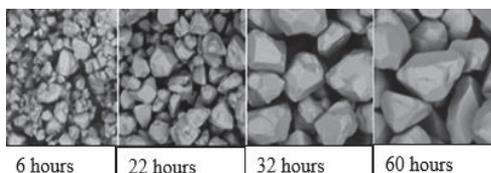
Figure 3: SEM images of powder samples synthesized at 600 ^{o}C for different synthesis time: 6 hours; 22 hours; 32 hours and 60 hours.

Phase Composition

In Figure 4a and 4b, Raman spectra of the various powder samples are presented. The spectra are very similar to each other and no other peaks than those belonging to CZTS can be recognized. The most intense Raman peak of pure CZTS is at 338 cm^{-1} [2, 11]. It is seen that this Raman peak in our samples is shifted to lower values. In the Raman spectrum of pure Cu_2CdSnS_4 the most intense Raman peak is at 332 cm^{-1} [17]. The shift in Raman spectra is the sign that solid solution of $Cu_2Zn_{1-x}Cd_xSnS_4$ is formed in our powder samples.
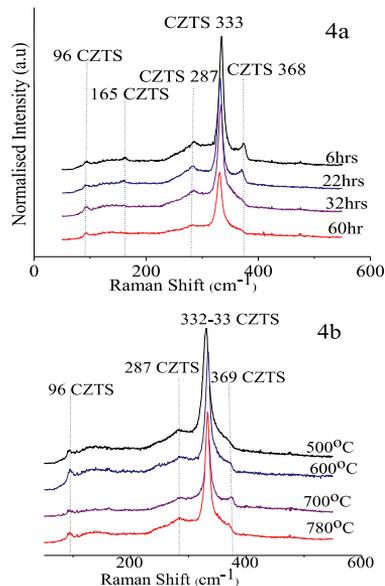
Figure 4: Raman spectra of samples with different preparation conditions; (4a) Raman spectra of samples synthesized at 600°C for different times (4b) Raman spectra of samples synthesized for 15 hours at different temperatures.
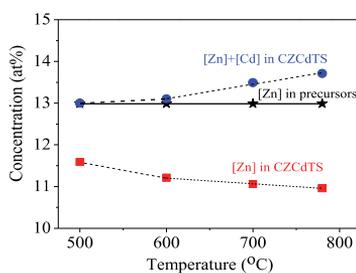
Figure 5: Variation of Zn concentration in the $Cu_2Zn_{1-x}Cd_xSnS_4$ powders synthesized in CdI_2 at different temperatures.

In Figure 5, the changes of Zn concentration in powders grown at different temperatures are presented. It can be seen that [Zn] in the CZTS powders is reduced if compared with the Zn content in precursors and it decreases with temperature and with increasing Cd content, which can be attributed to the replacement of Zn by Cd. In addition, the sum of Zn and Cd contents also increases with increasing temperature. The ratio of [Zn]/[Sn] decreases while the ratio [Cu]/[Sn] increases due to the decrease in [Zn] in the final powder. It was confirmed by our group that the

syntheses of $Cu_2Zn_{1-x}Cd_xSnS_4$ solid solutions in potassium iodide using CdS as Cd source could increase the level of incorporation of Cd into CZTS depends only on the initial [Cu]/[Sn] ratio and not on the [Zn]/[Sn] ratio [14]. It was also suggested that the decrease in Cu content in the precursors should lead to an increase in the substitution of Zn atoms by Cd atoms [14], therefore a decrease in [Zn] can be attributed to the atomic substitution of Cd at Zn site from CdI_2. The single phase solid solution of $Cu_2Zn_{1-x}Cd_xSnS_4$ forms starting from 500ºC. As the direct exchange reaction between ZnS and CdI_2 resulting in the formation of CdS and ZnI_2 is thermodynamically impossible, then the formation of solid solution $Cu_2Zn_{1-x}Cd_xSnS_4$, , (Cd incorporation at the Zn site) can take place due to some fragmentation of CdI_2 dimeric molecules (Cd_2I_4) in its liquid or gaseous phase resulting in the release of CdI_2^+ and $Cd_2I_3^+$ ions, as it was shown for CdI_2 gaseous phase in [16]. Now the reaction $xCdI_2^+ + xe^- + ZnS = Zn_{1-x}Cd_xS + ZnI_2$ is possible. In the next step $Zn_{1-x}Cd_xSe$ reacting with Cu_2SnS_3 results in the formation of $Cu_2Zn_{1-x}Cd_xSnS_4$ [11].

Activation energy of the process

In Figure 5 the Arrhenius plot of Cd concentration in formed $Cu_2Zn_{1-x}Cd_xSnS_4$ is shown. The formation of solid solution of $Cu_2Zn_{1-x}Cd_xSnS_4$ was reported earlier in [11] and confirmed in the present study. By our considerations the only possible route for Cd incorporation is through the CZTS formation reaction in participation of more electronegative CdI_2^+. The latter was found in the gaseous phase of CdI_2 by the mass spectrometric investigations with modified Knudsen cell–mass spectrometer by W. Kuncewicz-Kupczyk et al [16]. In their work, they confirmed the presence of CdI_2^+, Cd^+ and I^- formed as fragment ions in the gaseous phase of $CdI_2(g)$ consisting mainly of monomers $CdI_2(g)$ and dimers $Cd_2I_4(g)$ at 534 to 613 K.

The overall activation energy of the process estimated from the Arrhenius plot (see Figure 5) is 17.5 ± 2 kJ/mol.
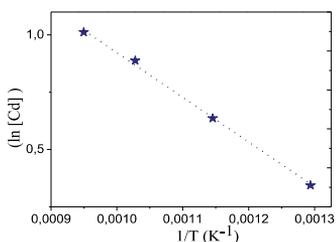
Figure 5: Arrhenius plot of [Cd] in $Cu_2Zn_{1-x}Cd_xSnS_4$ powders grown in CdI_2.

CONCLUSIONS

It was shown that in the synthesis process of CZTS in CdI_2 flux the amount of Cd, incorporated into CZTS from CdI_2 and resulting in the formation of solid solution of $Cu_2Zn_{1-x}Cd_xSnS_4$, changes from 1.3 at% at 500 ºC to 2.75 at % at 780 ºC. We found that Cd concentration in the formed $Cu_2Zn_{1-x}Cd_xSnS_4$ did not depend on synthesis time after reaching the equilibrium state at constant temperature and it increased with temperature. The activation energy of the Cd incorporation process was estimated as 17.5 ± 2 kJ/mol. Finally, it was found that the incorporation of Cd took place at the Zn site and depended on the Cu/Sn ratio and not on

the Zn/Sn ratio. Therefore a decrease of Cu content in the precursors would lead to an increase in the amount of Cd incorporated into $Cu_2Zn_{1-x}Cd_xS_4$ solid solution. The route of Cd incorporation into CZTS from CdI_2 was described as a CZTS formation process in partipicipation of CdI_2^+ formed in molten phase of cadmium iodide due to the fragmentation of cadmium iodide molecules.

ACKNOWLEDGMENTS

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Appendix B

XRD pattern of studied mixtures: $Cu_2S + CdI_2$, $SnS + CdI_2$, $ZnS + CdI_2$, $(Cu_2S + SnS + S + CdI_2)$, $(Cu_2S + SnS + ZnS + S + CdI_2)$.

Cu₂S+CdI₂ -330°C

2-Theta - Scale

d-3.73025Å, 2Theta-23.834°

Intensity (arb.u)

File: CuS+Cdl2 - 3.raw - Start: 15.000 ° - End: 84.000 ° - Step: 0.040 ° - Step time: 5. s - Creation: 30.01.2012 15:03:31 -
00-041-1049 (*) - Greenockite, syn - CdS - Hexagonal - a 4.14092 - b 4.14092 - c 6.71980 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P63mc (186) - 2 - 99.7885 - I/Ic PDF 1. - S-Q 19.7 % - F30=317(0.
00-033-0239 (*) - Cadmium Iodide - Cdl2 - Hexagonal - a 4.24810 - b 4.24810 - c 13.72650 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P63mc (186) - 2 - 214.526 - I/Ic PDF 1. - S-Q 50.8 % - F30= 25(0
00-006-0246 (*) - Marshite, syn - CuI - Cubic - a 6.05100 - b 6.05100 - c 6.05100 - alpha 90.000 - beta 90.000 - gamma 90.000 - Face-centered - F-43m (216) - 4 - 221.555 - I/Ic PDF 1. - S-Q 13.7 % - F20=124(0.0085,
00-018-0255 (I) - Cadmium Copper - Cu4Cd3 - Tetragonal - a 13.70100 - b 13.70100 - c 9.94400 - alpha 90.000 - beta 90.000 - gamma 90.000 - Primitive - P42/ncm (138) - 17 - 1866.66 - I/Ic PDF 1. - S-Q 15.8 % - F3

Cu₂S+CdI₂-353°C

Intensity (arb.u)

2-Theta - Scale

d-1.71657Å, 2Theta-53.325°

File: CuS+CdI2 - 5.raw - Start: 15.000 ° - End: 84.000 ° - Step: 0.040 ° - Step time: 5. s - Creation: 31.01.2012 14:53:58 -
00-033-0239 (*) - Cadmium Iodide - CdI2 - Hexagonal - a 4.24810 - b 4.24810 - c 13.72650 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P63mc (186) - 2 - 214.526 - I/Ic PDF 1. - S-Q 18.2 % - F30= 25(0
00-041-1049 (*) - Greenockite, syn - CdS - Hexagonal - a 4.14092 - b 4.14092 - c 6.71980 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P63mc (186) - 2 - 99.7885 - I/Ic PDF 1. - S-Q 10.9 % - F30=317(0.
00-040-0560 (N) - Copper Cadmium Iodide Sulfide-2 - Cu2Cd3I4S2 - Hexagonal - a 4.30914 - c 7.14123 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P63mc (186) - 114.838 - I/Ic PDF 1. - S-
00-026-1116 (C) - Copper Sulfide - Cu2S - Hexagonal - a 3.96100 - b 3.96100 - c 6.72200 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P63/mmc (194) - 2 - 91.3353 - I/Ic PDF 1. - S-Q 18.3 % - F20=305
00-033-0490 (I) - Chalcocite-M - Cu2S - Monoclinic - a 15.23500 - b 11.88500 - c 13.49600 - alpha 90.000 - beta 116.260 - gamma 90.000 - Primitive - P21/c (14) - 48 - 2191.49 - I/Ic PDF 1. - S-Q 17.8 % - F30= 17(0.0

ZnS+CdI$_2$ 370°C

Intensity (arb.u)

2-Theta - Scale

File: ZnS+CdI2 - Q370°C.raw - Start: 11.078 ° - End: 84.058 ° - Step: 0.040 ° - Step time: 5. s - Creation: 27.02.2012 17:14:01 -
00-033-0239 (*) - Cadmium Iodide - CdI2 - Hexagonal - a 4.23925 - b 4.23925 - c 13.68074 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P63mc (186) - 2 - 212.921 - I/Ic PDF 1. - S-Q 62.7 % - F30= 25(0.
00-005-0492 (A) - Wurtzite-2H, syn - ZnS - Hexagonal - a 3.82000 - b 3.82000 - c 6.26000 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P63mc (186) - 2 - 79.1101 - I/Ic PDF 1. - S-Q 37.3 % - F30= 28(0.

SnS+CdI$_2$ – 350°C

Intensity (arb.u)

2-Theta – Scale

SnS+CdI₂ – 300°C

Intensity (arb.u)

2-Theta - Scale

Cu$_2$S+SnS+S+ CdI$_2$ at 340°C

Intensity (arb.u)

2-Theta – Scale

File: Cu2S+SnS+S+CdI2 _ (Cooled down to 340°C).raw - Start: 15.110 ° - End: 84.082 ° - Step time: 5. s - Creation: 23.02.2012 14:27:52
00-041-1049 (*) - Greenockite, syn - CdS - Hexagonal - a 4.11849 - b 4.11849 - c 6.71980 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P63mc (186) - 2 - 98.7104 - I/Ic PDF 1. - S-Q 10.9 % - F30=317(0.
00-033-0239 (*) - Cadmium Iodide - CdI2 - Hexagonal - a 4.24810 - b 4.24810 - c 13.72650 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P63mc (186) - 2 - 214.526 - I/Ic PDF 1. - S-Q 21.8 % - F30=
00-029-0578 (I) - Chalcocite-Q, syn - Cu1.96S - Tetragonal - a 4.04002 - b 4.04002 - c 11.28700 - alpha 90.000 - beta 90.000 - gamma 90.000 - Primitive - P43212 (96) - 4 - 184.224 - I/Ic PDF 1. - S-Q 10.0 % - F24=
00-026-1116 (C) - Copper Sulfide - Cu2S - Hexagonal - a 3.95110 - b 3.95110 - c 6.71920 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P63/mmc (194) - 2 - 90.8415 - I/Ic PDF 1. - S-Q 9.2 % - F20=305(
00-027-0198 (I) - Mohite, syn - Cu2SnS3 - Triclinic - a 6.64000 - b 11.51000 - c 19.93000 - alpha 90.000 - beta 109.750 - gamma 90.000 - Primitive - P1 (1) - 12 - 1433.58 - I/Ic PDF 1. - S-Q 17.0 % - F27= 1(0.0616,4
00-036-0053 (I) - Copper Tin Sulfide - Cu4SnS6 - Rhombo. - a 3.74300 - b 3.74300 - c 32.99200 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P63/mmc (194) - 2 - 90.8415 - I/Ic PDF 1. - S-Q 9.2 % - F20=305(
00-006-0246 (*) - Marshite, syn - CuI - Cubic - a 6.01066 - b 6.01066 - c 6.01066 - alpha 90.000 - beta 90.000 - gamma 90.000 - Face-centered - F-43m (216) - 4 - 217.153 - I/Ic PDF 1. - S-Q 41.0 % - F20=124(0.0085,
00-027-0898 (I) - Tin Iodide Sulfide - Sn2I2S - Orthorhombic - a 17.42240 - b 25.34520 - c 4.34587 - alpha 90.000 - beta 90.000 - gamma 90.000 - Primitive - Pnam (62) - 12 - 1919.02 - I/Ic PDF 1. - S-Q 12.1 % - F21=

Cdl$_2$+SnS+Cu$_2$S+S, Q 339°C

Intensity (arb.u)

2-Theta - Scale
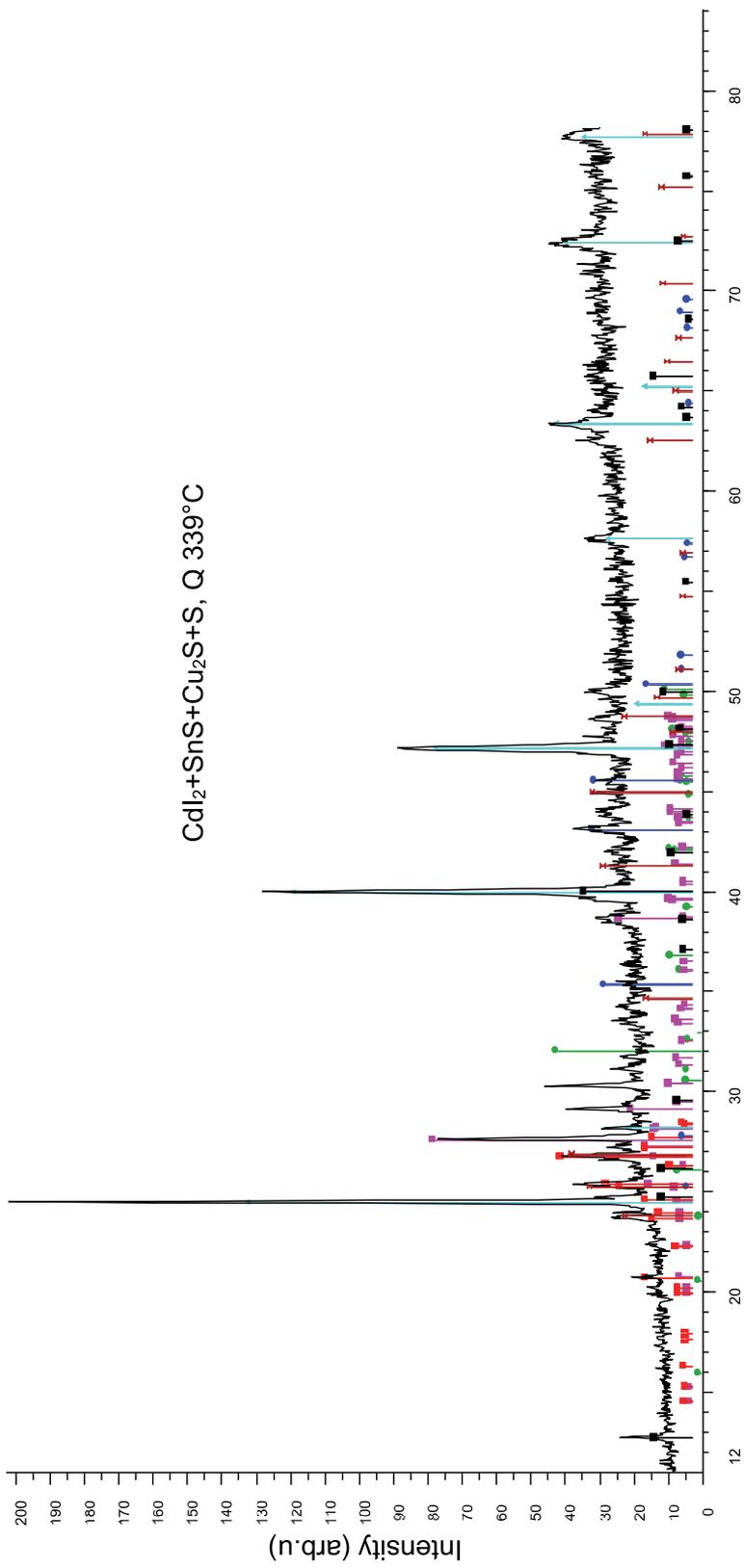
File: Cdl2+SnS+Cu2S+S - Q339°C.raw - Start: 11.045 ° - End: 84.034 ° - Step: 0.040 ° - Step time: 5. s - Creation: 23.02.2012 14:27:52 -

00-053-0526 (I) - Tin Sulfide - SnS - Orthorhombic - a 3.98030 - b 4.33120 - c 11.18020 - alpha 90.000 - beta 90.000 - gamma 90.000 - Primitive - Pcnm (53) - 4 - 192.741 - I/Ic PDF 1. - S-Q 13.3 % - F24= 40(0.0224,2

00-029-0578 (I) - Chalcocite-Q, syn - Cu1.96S - Tetragonal - a 4.04002 - b 4.04002 - c 11.28700 - alpha 90.000 - beta 90.000 - gamma 90.000 - Primitive - P43212 (96) - 4 - 184.224 - I/Ic PDF 1. - S-Q 10.0 % - F24=

00-027-0198 (i) - Mohite, syn - Cu2SnS3 - Triclinic - a 6.64000 - b 11.51000 - c 19.93000 - alpha 90.000 - beta 109.750 - gamma 90.000 - Primitive - F1 (1) - 12 - 1433.50 - I/Ic PDF 1. - S-Q 17.0 % - Γ27= 1(0.0616,4

00-006-0246 (*) - Marshite, syn - CuI - Cubic - a 6.01066 - b 6.01066 - c 6.01066 - alpha 90.000 - beta 90.000 - gamma 90.000 - Face-centered - F-43m (216) - 4 - 217.153 - I/Ic PDF 1. - S-Q 41.0 % - F20=124(0.0085,

00-026-1116 (C) - Copper Sulfide - Cu2S - Hexagonal - a 3.95110 - b 3.95110 - c 6.71920 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P63/mmc (194) - 2 - 90.8415 - I/Ic PDF 1. - S-Q 9.2 % - F20=305(

00-041-1049 (*) - Greenockite, syn - CdS - Hexagonal - a 4.11849 - b 4.11849 - c 6.71980 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P63mc (186) - 2 - 98.7104 - I/Ic PDF 1. - S-Q 10.9 % - F30=317(0.

00-033-0239 (*) - Cadmium Iodide - Cdl2 - Hexagonal - a 4.24810 - b 4.24810 - c 13.72650 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P63mc (186) - 2 - 214.526 - I/Ic PDF 1. - S-Q 10.0 % - F30= 25(0

Cu$_2$S+SnS+S+CdI$_2$, Q360°C

2-Theta - Scale

Intensity (arb.u)
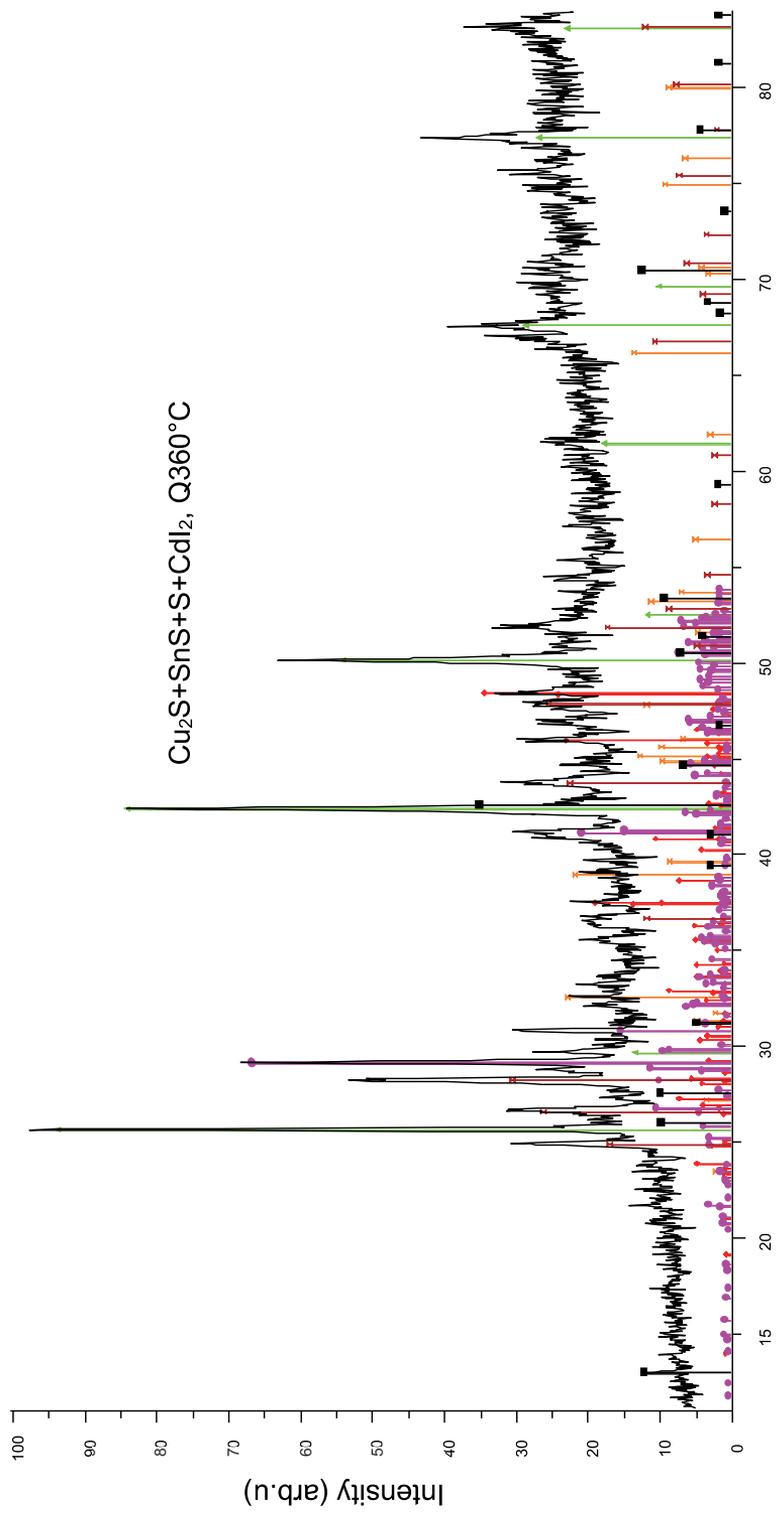
File: Cu2S+SnS+S+CdI2 – Q360°C.raw - Start: 11.063 ° - End: 84.047 ° - Step: 0.040 ° - Step time: 5. s - Creation: 21.02.2012 17:39:31 - 270°C - 1
00-033-0239 (*) - Cadmium Iodide - CdI2 - Hexagonal - a 4.24810 - b 4.24810 - c 13.72650 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P63mc (186) - 2 - 214.526 - I/Ic PDF 1. - S-Q 15.5 % - F30= 25(0
00-029-0578 (I) - Chalcocite-Q, syn - Cu1.96S - Tetragonal - a 4.04002 - b 4.04002 - c 11.28700 - alpha 90.000 - beta 90.000 - gamma 90.000 - Primitive - P43212 (96) - 4 - 184.224 - I/Ic PDF 1. - S-Q 10.0 % - F24=
00-033-0490 (I) - Chalcocite-M - Cu2S - Monoclinic - a 15.23500 - b 11.88500 - c 13.49600 - alpha 90.000 - beta 116.260 - gamma 90.000 - Primitive - P21/c (14) - 48 - 2191.49 - I/Ic PDF 1. - S-Q 15.2 % - F30= 17(0.0
00-006-0246 (*) - Marshite, syn - CuI - Cubic - a 6.05100 - b 6.05100 - c 6.05100 - alpha 90.000 - beta 90.000 - gamma 90.000 - Face-centered - F-43m (216) - 4 - 221.555 - I/Ic PDF 1. - S-Q 41.7 % - F20=124(0.0085,
04-012-7393 (A) - Tin Iodide Sulfide - Sn2SI2 - Orthorhombic - a 17.44700 - b 25.33400 - c 4.39100 - alpha 90.000 - beta 90.000 - gamma 90.000 - Primitive - Pnam (62) - 12 - 1940.83 - I/Ic PDF 7.2 - S-Q 4.2 % - F30
00-041-1049 (*) - Greenockite, syn - CdS - Hexagonal - a 4.14092 - b 4.14092 - c 6.71980 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P63mc (186) - 2 - 99.7885 - I/Ic PDF 1. - S-Q 13.4 % - F30=317(0.

Cu$_2$S+SnS +ZnS+S+CdI$_2$ – 350°C

Intensity (arb.u)

2-Theta - Scale
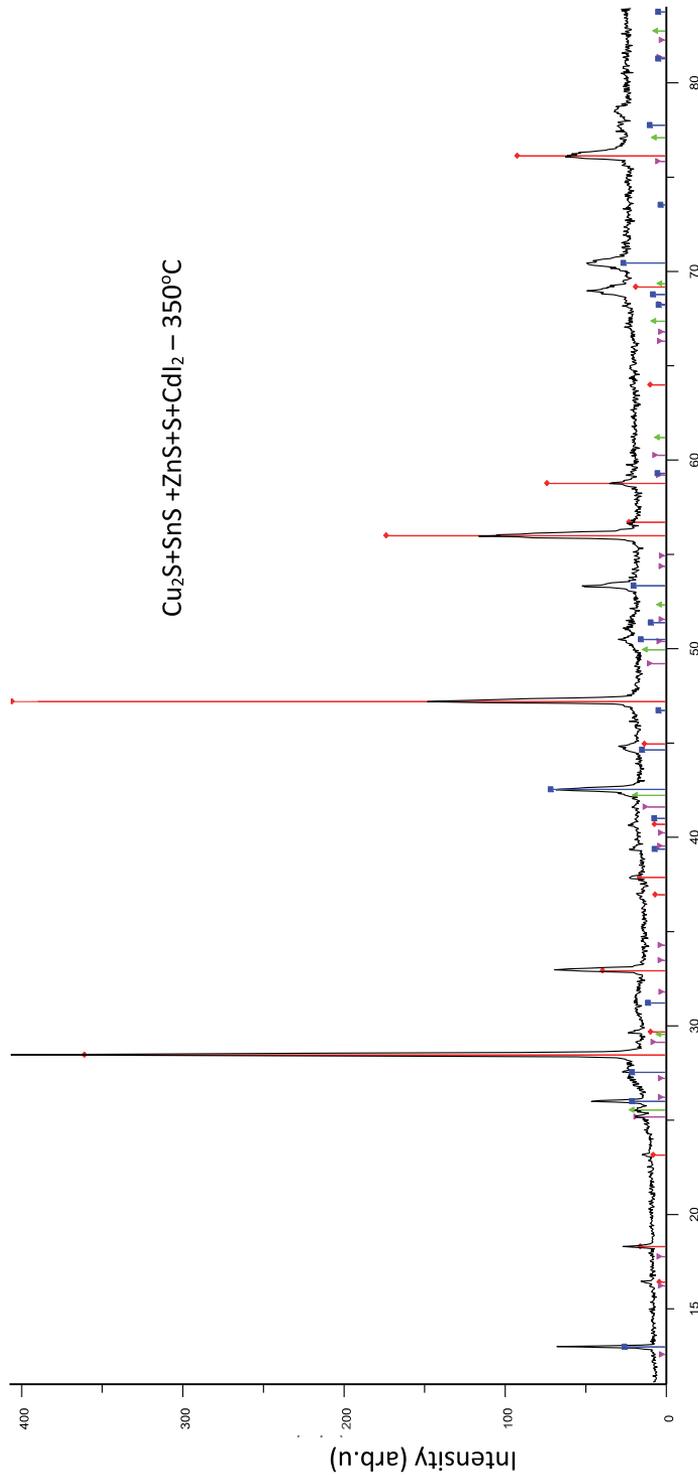
W File: Cu2S+SnS+ZnS+CdI2+S - Cooled 350°C.raw - Start: 11.031 ° - End: 84.023 ° - Step: 0.040 ° - Step time: 10. s - Creation: 29.02.2012 20:02:36 -
■ 00-033-0239 (*) - Cadmium Iodide - CdI2 - Hexagonal - a 4.24810 - b 4.24810 - c 13.72650 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P63mc (186) - 2 - 214.526 - I/Ic PDF 1. - S-Q 11.0 % - F30= 25(0
◆ 00-026-0575 (I) - Kesterite, syn - Cu2ZnSnS4 - Tetragonal - a 5.44283 - b 5.44283 - c 10.84800 - alpha 90.000 - beta 90.000 - gamma 90.000 - Body-centered - I-42m (121) - 2 - 321.365 - I/Ic PDF 1. - S-Q 83.4 % - F1
◄ 00-006-0246 (*) - Marshite, syn - CuI - Cubic - a 6.05100 - b 6.05100 - c 6.05100 - alpha 90.000 - beta 90.000 - gamma 90.000 - Face-centered - F-43m (216) - 4 - 221.555 - I/Ic PDF 1. - S-Q 3.0 % - F20=124(0.0085,2
▶ 00-006-0232 (*) - Tin Iodide - SnI4 - Cubic - a 12.27300 - b 12.27300 - c 12.27300 - alpha 90.000 - beta 90.000 - gamma 90.000 - Primitive - Pa-3 (205) - 8 - 1848.64 - I/Ic PDF 1. - S-Q 2.6 % - F27= 21(0.0116,113)

Appendix C

Curriculum Vitae

1. Personal data

   First name and Surname   God'swill Chimezie Nkwusi
   Date and place of birth   02.04.1982 Ilesha,
   Nationality   Nigerian
   Email   godswillnkwusi@yahoo.com

2. Education

Educational institution	Year	Education (field of studies/degree)
Tallinn University of Technology	2013-2017	Doctoral Study
Tallinn University of Technology/Tartu University	2011-2013	Masters Study/MSc. in Natural Science
University of California Berkeley	01.2013-06.2013	Visiting research student /Exchange program
Federal University of Agriculture Abeokuta	2001-2006	Bachelor Study/BSc. Chemistry
African Church Grammar School/Oyemekun Grammar School	1993-2000	Senior Secondary School Certificate
Arisoyin Primary School /IMG Ibadan	1987-1993	Primary School Leaving Certificate

3. Language competence/skills

Language	Level
English	Fluent
Igbo	Native
Yoruba,	Fluent
Hausa	Basic
Estonian	Basic

4. Special Course/Conferences/Scientific work

Period	Educational or Other Organisation
24.05.2012-25.05.2012	9th International Conference of Young Scientists on Energy Issues, Kaunas, May 24-25, 2012/Oral presentation
30.07.2012-17.08.2012	European Innovation Academy/Training
01.12.2013-06.12.2013	MRS Boston/Poster presentation
13.11.2014-14.11.2014	5th European Kesterite Workshop, Tallinn, 13-14 November 2014
15.09.2014-18.09.2014	E-MRS Fall Meeting/Oral presentation

5. Professional Employment

Period	Organisation	Position
09.2016-	Euro Academy, Tallinn, Estonia	Lecturer/Environmental Chemistry
09.2014- 2017	EBS, Estonian Busines School, Tallinn, Estonia	School Representative
08.2015-07.2017	Association of African Students Estonia-AASE	President
07.2013-12.2016	Tallinn University of Technology	Student Adviser/ Teaching Assistant
09.2011-12.2012	Arvato Bertelsmann/Microsoft, Tallinn, Estonia	Customer Support
07.2008-08.2011	CAP Plc/UAC/Akzo Nobel, Nigeria	Research and Development Chemist
02.2007-02.2008	UNAAD, University of ADO'EKITI, Nigeria	Teaching Assistant
04.2005-07.2005	GSK, Nigeria	Trainee Chemist

6. Defended thesis

Year	Topic	Supervisor
2013	Formation of Cu_2ZnSnS_4 in molten CdI_2 for monograin membrane solar cells/Masters' thesis	Ms Inga Leinemann
2006	Synthesis Characterization and Antibacterial Effect of Metal-antibiotic drug complexes/Bachelor thesis,	Dr Amolegbe

7. Main field of research and scientific work

Natural Sciences and Engineering; Process Technology and Materials Science; Material Technology; Materials Science and Technology.

List of publications

1. **Nkwusi, G.**, Leinemann, I., Raudoja, J., Mikli, V., Kärber, E., Altosaar, M. Impact of growth-synthesis conditions on $Cu_2Zn_{1-x}Cd_xSnS_4$ monograin material properties. *Superlattices and Microstructures,* **98** (2016) 400- 405.
2. **Nkwusi, G.**, Leinemann, I., Altosaar, M.. The Processes and Enthalpies in Synthesis of Cu_2ZnSnS_4 in Molten CdI_2. *International Advanced Research Journal of Science, Engineering and Technology* **3** (2016), 113- 119.
3. **Nkwusi, G.**, Adeaga, S.; Ayejuyo, S., Annuk, A.. Climate Change; Farmers' Awareness, Perceptions and Responses in Lagos State. *Journal Applied Ecology and Environmental Sciences,* **3** (2015) 95−99, 10.12691/aees-3-4-1.
4. **Nkwusi, G.**; Leinemann, I.; Raudoja, J.; Mikli, V.; Kauk-Kuusik, M.; Altosaar, M.; Mellikov, E. Synthesis of $Cu_2(ZnCd)SnS_4$ Absorber Material for Monograin Membrane Applications. *MRS Proceedings / Volume 1638 / 2014: 2013 MRS Fall Meeting.* Scholarone Manuscripts, 1638. (1638 - Symposium W – Next-Generation Inorganic Thin-Film Photovoltaics).
5. **Nkwusi, G.**, Leinemann, I.; Grossberg, M.; Kaljuvee, T.; Traksmaa, R.; Altosaar, M.; Meissner, D. Formation of Copper Zinc Tin Sulfide in Cadmium Iodide for Monograin Membrane Solar Cells. *Conference Proceedings of the 9th International Conference of Young Scientists on Energy Issues*, Kaunas, May 24-25, 2012. II 38−II 46.

ELULOOKIRJELDUS

1. Isikuandmed

Ees- ja perenimi	God'swill Chimezie Nkwusi
Sünniaeg, -koht	02.04.1982, Ilesha
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2. Haridus

Õppeasutus	Õppeaeg	Haridus
Tallinna Tehnikaülikool	2013-2017	Doktoriõpe
Tallinna Tehnikaülikool /Tartu Ülikool	2011-2013	Magistriõpe/loodusteaduste magister
California Berkeley Ülikool	01.2013-06.2013	Vahetusüliõpilane/vahetusprogramm
Abeokuta Põllumajandusülikool	2001-2006	Bakalaureuseõpe/keemia bakalaureusekraad
Aafrika Kiriklik Gümnaasium /Oyemekuni Gümnaasium	1993-2000	Keskharidus
Arisoyin algkool /IMG Ibadan	1987-1993	Algharidus

3. Keelteoskus/tase

Keel	Tase
Inglise keel	kõrgtase
Igbo keel	emakeel
Yoruba keel	kõrgtase
Hausa keel	algtase
Eesti keel	algtase

4. Täiendusõpe/konverentsid/teadustööd

Periood	Organisatsioon
24.05.2012-25.05.2012	9. rahvusvaheline noorteadlaste konverents Conference of Young Scientists on Energy Issues, Kaunas, 24.-25. mai 2012/suuline ettekanne
30.07.2012-17.08.2012	Euroopa Innovatsiooniakadeemia/Koolitus
01.12.2013-06.12.2013	MRS Boston/Poster ettekanne
13.11.2014-14.11.2014	5th European Kesterite Workshop, Tallinn, 13-14 November 2014, posterettekanne
15.09.2014-18.09.2014	E-MRS Fall Meeting/ suuline ettekanne

5. Teenistuskäik

Töötamise aeg	Tööandja	Ametikoht
09.2016-	Euroakadeemia, Tallinn, Eesti	Lektor/keskonnakeemia
09.2014- 2017	EBS, Tallinn, Eesti	Esindaja
08.2015-07.2017	Aafrika Üliõpilaste Ühing Eestis - AASE	President
07.2013-12.2016	Tallinna Tehnikaülikool	Üliõpilaste nõustaja/õppeassistent
09.2011-12.2012	Arvato Bertelsmann/Microsoft, Tallinn, Estonia	Klienditugi
07.2008-08.2011	CAP Plc/UAC/Akzo Nobel, Nigeria	Uurimis- ja arenduskeemik
02.2007-02.2008	UNAAD, ADO'EKITI Ülikool, Nigeria	Õppeassistent
04.2005-07.2005	GSK, Nigeria	Keemia praktikant

6. Kaitstud lõputööd

Aasta	Teema	Juhendaja
2013	Cu_2ZnSnS_4 moodustumine sula CdI_2 keskkonnas./ Magistritöö	Ms Inga Leinemann
2006	Metall-antibiootik ravim-komplekside süntees, karakteriseerimine ja antibakteriaalne toime/Bakalaureuse lõputöö	Dr Amolegbe

7. Uurimis- ja teadustöö alad

Loodusteadused ja inseneeria, protsessitehnoloogia ja materjaliteadus, materjalitehnoloogia, päikeseenergia materjalide süntees ja uurimine.

Teaduspublikatsioonide nimekiri

1. **Nkwusi, G.**, Leinemann, I., Raudoja, J., Mikli, V., Kärber, E., Altosaar, M. Impact of growth-synthesis conditions on $Cu_2Zn_{1-x}Cd_xSnS_4$ monograin material properties. *Superlattices and Microstructures,* **98** (2016) 400- 405.
2. **Nkwusi, G.**, Leinemann, I., Altosaar, M.. The Processes and Enthalpies in Synthesis of Cu_2ZnSnS_4 in Molten CdI_2. *International Advanced Research Journal of Science, Engineering and Technology* **3** (2016), 113- 119.
3. **Nkwusi, G.**, Adeaga, S.; Ayejuyo, S., Annuk, A.. Climate Change; Farmers' Awareness, Perceptions and Responses in Lagos State. *Journal Applied Ecology and Environmental Sciences,* **3** (2015) 95−99, 10.12691/aees-3-4-1.
4. **Nkwusi, G.**; Leinemann, I.; Raudoja, J.; Mikli, V.; Kauk-Kuusik, M.; Altosaar, M.; Mellikov, E. Synthesis of $Cu_2(ZnCd)SnS_4$ Absorber Material for Monograin Membrane Applications. *MRS Proceedings / Volume 1638 / 2014: 2013 MRS Fall Meeting.* Scholarone Manuscripts, 1638. (1638 - Symposium W – Next-Generation Inorganic Thin-Film Photovoltaics).
5. **Nkwusi, G.**; Leinemann, I.; Grossberg, M.; Kaljuvee, T.; Traksmaa, R.; Altosaar, M.; Meissner, D. Formation of Copper Zinc Tin Sulfide in Cadmium Iodide for Monograin Membrane Solar Cells. *Conference Proceedings of the 9th International Conference of Young Scientists on Energy Issues*, Kaunas, May 24-25, 2012. II 38−II 46.

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