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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$_2$Zn$_{1-x}$Cd$_x$SnS$_4$. 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$_2$Zn$_{1-x}$Cd$_x$SnS$_4$ 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$_2$ZnSnS$_4$ (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$_2$ZnSn(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$_2$S, SnS, ZnS and S
in molten CdI₂ as flux material taken in mass ratio of CZTS/CdI₂ equal to 1:1. The precursor binaries and CdI₂ 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 280°C, 370°C, 500°C, 600°C, 700°C and 780°C and at 600°C 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 ≤ x ≤ 0.93 and ([Zn]/[Sn] ≥ 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 μm² 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 280°C, much below the melting point of CdI₂, the formation of quaternary compound was not detected. As the temperature increases up to 370°C, just below the melting temperature of pure CdI₂, 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 CdI₂ 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 780°C.

![Figure 1](image1.png)

**Figure 1.** Cd content incorporated into CZTS from CdI₂ flux as a function of heating temperature.

Time dependence

Cd concentration in CZTS grown at 600 °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 °C.

![Figure 2](image)

**Figure 2**: Time dependency of Cd incorporation into CZTS from CdI₂ 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](image)

**Figure 3**: SEM images of powder samples synthesized at 600 °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 Cu₂CdSnS₄ the most intense Raman peak is at 332 cm⁻¹ [17]. The shift in Raman spectra is the sign that solid solution of Cu₂Zn₁₋ₓCdₓSnS₄ 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$_2$Zn$_{1-x}$Cd$_x$Sn$_4$ 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$_2$Zn$_{1-x}$Cd$_x$Sn$_4$ 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$_2$Zn$_{1-x}$Cd$_x$Sn$_4$ forms starting from 500°C. 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$_2$Zn$_{1-x}$Cd$_x$Sn$_4$, (Cd incorporation at the Zn site) can take place due to some fragmentation of CdI$_2$ dimeric molecules (Cd$_2$I$_4$) in its liquid or gaseous phase resulting in the release of CdI$_2^+$ and Cd$_2$I$_3^+$ ions, as it was
shown for CdI₂ gaseous phase in [16]. Now the reaction \( x\text{CdI}_2^+ + xe^- + \text{ZnS} = \text{Zn}_{1-x}\text{Cd}_x\text{S} + \text{ZnI}_2 \) is possible. In the next step \( \text{Zn}_{1-x}\text{Cd}_x\text{Se} \) reacting with \( \text{Cu}_2\text{SnS}_3 \) results in the formation of \( \text{Cu}_x\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4 \) [11].

**Activation energy of the process**

In Figure 5 the Arrhenius plot of Cd concentration in formed \( \text{Cu}_x\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4 \) is shown. The formation of solid solution of \( \text{Cu}_x\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4 \) 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 \( \text{CdI}_2^+ \). The latter was found in the gaseous phase of \( \text{CdI}_2 \) 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 \( \text{CdI}_2^+ \), \( \text{Cd}^+ \) and \( \Gamma^− \) formed as fragment ions in the gaseous phase of \( \text{CdI}_2(g) \) consisting mainly of monomers \( \text{CdI}_2(g) \) and dimers \( \text{Cd}_2\text{I}_4(g) \) at 534 to 613 K.

The overall activation energy of the process estimated from the Arrhenius plot (see Figure 5) is \( 17.5 \pm 2 \) kJ/mol.

![Figure 5: Arrhenius plot of [Cd] in \( \text{Cu}_x\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4 \) powders grown in CdI₂.](image)

**CONCLUSIONS**

It was shown that in the synthesis process of CZTS in CdI₂ flux the amount of Cd, incorporated into CZTS from CdI₂ and resulting in the formation of solid solution of \( \text{Cu}_x\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4 \), changes from 1.3 at% at 500 °C to 2.75 at % at 780 °C. We found that Cd concentration in the formed \( \text{Cu}_x\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4 \) 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 \( 17.5 \pm 2 \) 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 \( \text{Cu}_x\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4 \) solid solution. The route of Cd incorporation into CZTS from CdI₂ was described as a CZTS formation process in participation of \( \text{CdI}_2^+ \) formed in molten phase of cadmium iodide due to the fragmentation of cadmium iodide molecules.

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