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The effect of the sulfur on the purity and the crystallization of Cu_2ZnSnS_4 compound

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ABSTRACT

The effect of sulfur (S) content on the purity, stability and crystallization of Cu_2ZnSnS_4 material has been investigated. It was found that, for an excess sulfur starting concentration from 3 wt% to 12 wt%, high purity Cu_2ZnSnS_4 single phase compound could be obtained. In this sulfur range composition, Cu_2ZnSnS_4 alloy has been synthetized and vertically well textured along melt flow. Depending on the sulfur starting composition, binary SnS and ternary $Cu_4Sn_7S_{16}$ phases can be precipitated and their concentration is connected to the initial sulfur quantity in the starting charge.

1. Introduction

Actually, in the market of highly efficient solar cell materials, CdTe compound is powerful, but unfortunately, cadmium toxicity, tellurium scarcity and the cost are obstacles to continue to use this material. Others crystalline materials such Si and GaAs are also important, but the crystal growth technology is rather difficult and the growth equipment are so expensive, so it is very important to look for new alternative materials to reach low cost, light weight and the most important thing is to have clean materials without toxicity and not complex to synthetize as high purity single phase or single crystal with good crystallinity. In a recent study [1], Cu_2ZnSnS_4 was identified as material with low extraction cost. This compound belongs to Cu–Zn–Sn–S quaternary system and has recently attracted great attention as promised photovoltaic materials [2]. In the case of photovoltaic material, the band gap is the most important property and Cu_2ZnSnS_4 compound has a band-gap value of 1.5 eV [3] is considered as ideal for effective phonon absorption and photogeneration. In addition, this material possesses promising characteristic optical properties and large absorption coefficient in the order of $10^4\ cm^{-1}$ [4]. The performance of this material is connected to its crystallographic structure with a specific cations arrangement over the crystallographic organization. The Cu_2ZnSnS_4 is based on kesterite (A_2BCX_4) mineral structure, crystallizes in a tetragonal structure, space group QUOTE with unit cell parameters $a=5.43$ Å, $c=10.85$ Å [5,2]. The p-type behavior of Cu_2ZnSnS_4 phase is controlled by Cu_{Zn} and Cu_{Sn} antisite donor defects, in addition this can also result to the presence of copper vacancy and compensation of Zn_{Cu} antisite and the sulfur (S) vacancy [6]. This material is stoichiometric, but as it belongs to quaternary system [7], it is not easy to elaborate single phase or grow single crystal under stationary stable regime. Quite often, during the synthesis of this material, if the starting composition is

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not controlled and the preparation conditions are not well optimized, a parasite binary stable phases such ZnS, Cu_2S and SnS_2 can be precipitated as barrier for the Cu_2ZnSnS_4 formation. In addition other ternary phases such $Cu_2Sn_4S_9$, Cu_2SnS_3 and Cu_4SnS_4 can be also formed [7]. The sulfur is an important element in the stoichiometric and the performance of Cu_2ZnSnS_4 phase, any change in its composition will be accompanied by the apparition of impurities and the change of monophased field. Sulfur melts at low temperature (115 °C) and has a boiling point at 445 °C. The melting temperature of Cu_2ZnSnS_4 is around 990 °C and has a non-congruent behavior [8], as it is very important to elaborate this phase near melting temperature, it is very interested to look for the best way to have the good sulfur concentration in the phase and to use the appropriate method to surmount the losses of sulfur during elaboration process.

Following our knowledge and the available data, there aren't a lot of informations about the effect of sulfur on the kinetic formation of Cu_2ZnSnS_4 phase. In this paper, we will present the influence of sulfur on the purity and the single phase domain of Cu_2ZnSnS_4 compound.

2. Experimental procedure

Cu_2ZnSnS_4 bulky materials with different starting excess sulfur concentration were prepared. The starting materials were Cu (99.9995%) and Zn (99.999%) lanthanide metals plus Sn (99.9999%) and S (99.99%). For the synthesis of the Cu_2ZnSnS_4 phase, Cu, Zn, Sn and S were mixed in the atomic ratio 2:1:1:4 and excess of sulfur (3 wt%, 4 wt%, 6 wt%, 8 wt%, 9 wt%, 11 wt% and 12 wt%) was used. The mixture were pressed into rectangular pellets under 15 t and a heat treatment was performed in sealed quartz tube under a vacuum (Fig. 1). Fig. 2 shows the heat treatment cycles. Because of the volatility of sulfur and the possible decomposition of the phase during the reaction step, all the precautions have been taken in account to surmount the strong decomposition of the starting charge and the explosion of quartz tube. The first low heating rate (1 °C/min) and annealing stage at 400 °C allow the fixation of the sulfur and the initiation of Cu_2ZnSnS_4 phase reaction. The complete reaction was obtained at the second annealing stage at 1050 °C. At the end of the annealing, powder diffraction data were collected using CuKα radiation with $5 < 2\theta < 70$, 0:03° 2θ as step width and 10 s as step time. For each prepared sample, the chemical compositions were controlled by plasma emission spectroscopy (ICP), the morphology of samples was checked by Leica optical microscope. Raman spectroscopy study was performed using the 633 nm excitation wavelength of an He/Ne laser beam and confirmed the single phase composition.

3. Results

As a function of the starting sulfur excess concentration, the reactions formation of Cu_2ZnSnS_4 phase is shown in Fig. 3. It can be seen from the diffraction diagram the prepared samples with different sulfur excess include a similar main phase, the diffraction peaks of which indicated by black circles in Fig. 3. These peaks belongs to the diffraction kesterite (A_2BCX_4)-type structure with the strongest (1 1 2) intensity in good agreement with the JCPDS file (04-003-8920). Except for this main phase, depending on S excess concentration, each sample contains few secondary phases amount, mainly SnS (00-014-0620) and $Cu_4Sn_7S_{16}$ (04-009-7946) compounds. In the elaboration conditions, using Cu_2ZnSnS_4 stoichiometric composition without any excess of sulfur, 3 wt% was lost and the composition is shifted from sulfur 29 wt% (stoichiometric) to 26 wt%

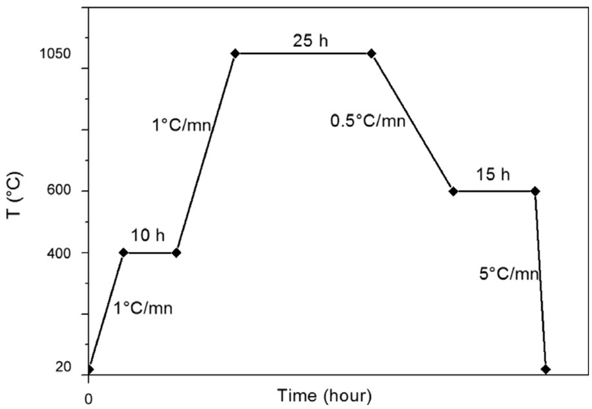

Fig. 2. Heating cycle for Cu_2ZnSnS_4 synthesis.

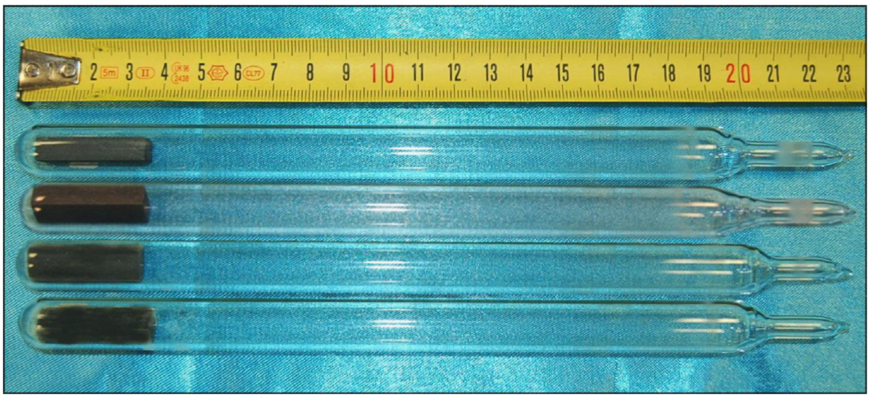

Fig. 1. Cu_2ZnSnS_4 samples sealed in quartz tubes for heating operation.