Optimum parameters for obtaining the CuGaS$_2$ compound for photovoltaic use

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In this paper, we were interested in the investigation of the optimum parameters for the elaboration of the CuGaS$_2$ compounds destined to the solar cells fabrication .These parameters that are constituted essentially of the temperature, the duration and the rate of the heating stage, the fusion, the crystallization and the cooling were optimised. The prepared sample presented a good morphology. Analysis by x ray diffraction has allowed the study of the crystalline structure of the obtained CuGaS$_2$ ingot and the determination of the different crystalline planes and the different present phases. These analysis have shown that the obtained ingot is polycrystalline and of chalcopyrite structure.

1. Introduction

The photovoltaic conversion is based on solar cells that transform the solar rays to electrical current. In this transformation, the silicon based solar cells have a preponderant portion for the earth energetic needs. However, the researches on solar cells based on chalcopyrite structure materials have shown a major interest in the photovoltaic conversion [1-3]. Theoretical efficiency exceeds 30 % for solar cells using Cu(In,Ga)S$_2$ as absorber [4]. This quaternary compound is obtained by introducing Indium into ternary CuGaS$_2$. These materials have an absorption capacity more important than that of silicon [5], therefore less quantity of matter, and significant reduction in fabrication cost. Before using the CuGaS$_2$ compound as thin films, it is prepared as ingot, for this, we are interested in investigating the optimum parameters for the elaboration of CuGaS$_2$ destined to solar cells fabrication. These parameters are essentially constituted of the heating stages, the fusion, the crystallization, and the cooling.

2. Experimental condition

For obtaining the CuGaS$_2$ compound we followed the next steps: we put the mixture of the three elements (Cu, Ga, S) in a sealed quartz tube under a secondary vacuum of 10^{-6} torr. A wire resistant to the temperature maintains the tube containing the mixture in the middle of the furnace (Fig. 1).

The elements of the mixture are pellets of high purity: 5 N for the copper and 6 N for the gallium and sulphur, in order to get a compound whose properties are not deteriorated by parasitic phases. After the sealing, the tube is put inside a furnace where it is subjected to many temperature cycles.

A scanning electron microscope (SEM), associated with an energy dispersion spectrometer (EDS) were used respectively to study the morphology of the ingot and to determine the chemical composition of their constituents. An X-ray diffractometer with a copper Kα radiation Before introducing the mixture, a test was made in order to insure that the furnace follows the desired cycle. At the end of the thermal cycle which lasted 5 days we got out the quartz tube from the furnace and recovered the formed compound.(λ=1,54051 Å) was used to analyze the crystalline structure of the obtained CuGaS$_2$ ingot and to determine the various plans of crystallization as well as the various involved phases.
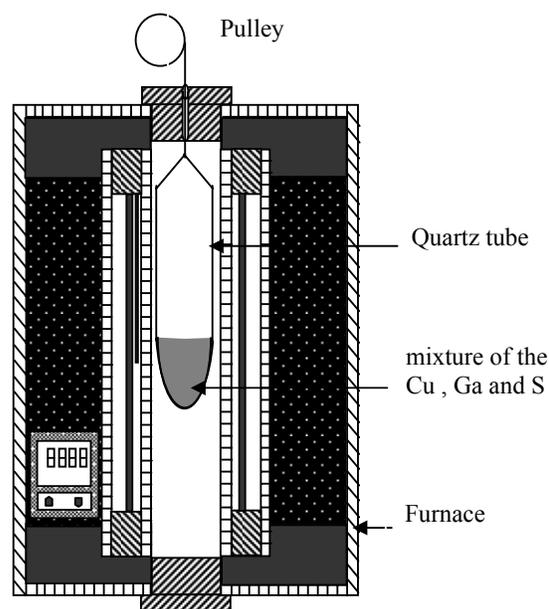

Fig. 1. Schematic representation of the furnace and the quartz tube containing the mixture of the three elements (Cu, Ga, S).

3. Results and discussion

3.1. Optimum parameters for obtaining the CuGaS$_2$

After introducing the tube inside the furnace, we heat this latter at a rate of 10 °C/mn until the fusion temperature of copper 1083 °C where we maintain this value for 10 hours to allow its fusion. After that comes the crystallization stage, where the temperature is reduced at a rate of 5 °C/mn down to 900 °C, where its maintained constant for 10 hours for allowing the formation of the chalcopyrite phase. We finish by the cooling stage where the temperature is reduced at a rate of 10 °C/mm down to room temperature. During the heating stage the quartz tube was broken this was probably due to the sulphur instability and to the influence of binaries formation reaction.

3.1.1. Heating rate

In order to reduce the sulphur instability and the influence of binaries formation reaction during the increase of the temperature, the heating rate was reduced to 1 °C/mm in addition of a flat stage at 300 °C for 5 hours. The quartz tube was not broken. However the obtained sample was not solidified, this is probably due to the fusion of binaries which did not happen [6, 7].

3.1.2. Fusion temperature

All the experimentation parameters were maintained, but the fusion temperature was increased to 1130 °C [6]. A partial solidification of the samples was obtained. We can deduce that 1130 °C is the right fusion temperature, and in order to get a complete homogenization of the solidification the duration of the fusion stage must be increased to allow the temperature to propagate inside the mixture.

3.1.3. Duration of the fusion stage

The heating rate was maintained at 1 °C/mn, the fusion temperature at 1130 °C, the crystallization rate at 5 °C/mn, the cooling rate at 10 °C/mn, and the duration of the fusion was varied. This was increased by 5 hours each time, until we get the right value. We obtained a complete homogenization of the solidification of the sought after compound for a fusion duration of 25 hours. However the obtained sample does not present a good morphology (Fig. 2), to avoid this, the crystallization rate must be reduced.

Fig. 2. Sample of CuGaS$_2$ Showing a poor morphology.

3.1.4. Crystallization rate

The heating rate was maintained at 1 °C/mn, the fusion temperature and duration were respectively 1130 °C and 25 hours, the cooling rate at 10 °C/mn and the crystallization rate was reduced to 1 °C/mn. The resulting samples had a good morphology. Their mechanical characterization shows that they were fragile; this is due to the rapidity of the cooling rate that would have created internal constraints inside the samples.

3.1.5. Cooling rate

The heating rate was maintained at 1 °C/mn, the fusion temperature and duration were respectively 1130 °C and 25 hours, the crystallization rate at 1 °C/mn, and the cooling rate was varied. In order to avoid the internal constraints in the sample, the cooling rate was reduced from 10 °C/mn to 1 °C/mn. Fig. 3 shows the CuGaS$_2$ sample obtained using the parameters values that were optimised wihin the framework of this report.

Fig. 3. Sample of CuGaS$_2$ showing a complete solidification and a good morphology.

Having obtained the optimum parameters of the CuGaS$_2$ compound preparation, a seven stages thermal cycle was established (Fig. 4).

Stage 1: progressive heating (1 °C/mn) from room temperature to 300 °C.

Stage 2: a flat level at 300 °C for 5 hours.

Stage 3: progressive heating (1°C/mn) up to 1130 °C.

Stage 4: fusion at 1130 °C during 25 hours.

Stage 5: crystallization from 1130 °C to 900 °C at 1 °C/mm.

Stage 6: crystallization at 900 °C for 10 hours.
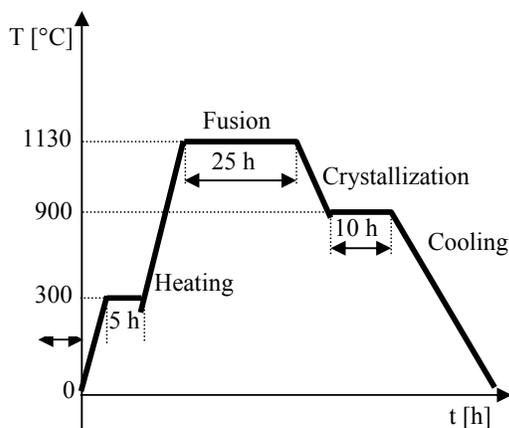
Stage 7: slow cooling (1 °C/mn) down to room temperature.

Fig. 4. Thermal cycle for the CuGaS$_2$.

The sample of CuGaS$_2$ prepared has been characterized by EDS. The chemical composition of the constituents is obtained after analysis of five different positions of the ingot. The results obtained (24,62 % for the copper, 25,74 % for the gallium, 49,64 % for the sulphur) show that our sample has a good stoechiometry.

The chalcopyrite structure lattice parameters were determined from the XRD patterns. The average lattice parameters calculated from the X-ray Analysis by X-ray diffraction has allowed the study of the crystalline structure of the obtained CuGaS$_2$ ingot and the determination of the different crystalline planes and the different present phases (Fig. 5).

These analysis have shown that the obtained ingot is polycrystalline and of chalcopyrite structure. The CuGaS$_2$ ingot deposited shows a preferential orientation according to the direction (112). Kanan et al. [8] indicated that the planes of orientation (112) are desirable for photovoltaic conversion. diffraction peaks were: a = 5,367 Å and c = 10,502 Å. These lattice constants are in good agreement with the reported values [4].
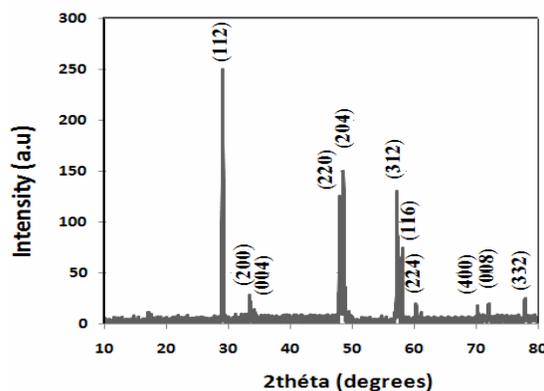

Fig. 5. X-ray diffraction patterns of CuGaS$_2$ sample.

4. Conclusion

In the framework of this report we have optimized the CuGaS$_2$ compound preparation parameters. The heating rates, the crystallization, and the cooling must be slow, around 1 °C/mn. The fusion has a duration of 25 hours. In addition of the fusion flat level at 1130 °C, a first flat level at 300 °C and a second at 900 °C must be established in order to reduce the sulphur instability du ring the heating and allow the formation of the chalcopyrite phase during the crystallization. After the optimisation of the preparation parameters the obtained ingot had a good morphology. The analysis by x ray diffraction have shown that the obtained ingot is polycrystalline and have a chalcopyrite structure, and hence can be used for the solar cells fabrication.

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