

Fabrication, Characterization and Optical Properties of CuIn₃Se₅ Bulk Compounds

Dayane Habib¹, Ouloum Aoudé², Slyman Karishy¹, Georges El Haj Moussa^{1,3}

¹Physics Department, Faculty of Sciences II, Lebanese University, Jdeidet, Lebanon ²Physics Department, Faculty of Sciences IV, Lebanese University, Zahleh, Lebanon ³Centre Electronique et Micro-optoélectronique de Montpellier (CEM2), Faculté Sciences et Techniques du Languedoc Université de Montpellier II, Montpellier, France Email: <u>dayane_habib@yahoo.fr</u>

Received 1 July 2015; accepted 16 August 2015; published 19 August 2015

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Abstract

The present work prepared the $CuIn_3Se_5$ ingots by using a horizontal Bridgman method and investigated the Energy Dispersive Spectrometry (EDS) and X-Ray Diffraction (XRD) to calculate the compositions of the ingots. Photoluminescence was used to check their optical properties. It was found that $CuIn_3Se_5$ had either a Stanite structure, an Ordered Defect Chalcopyrite (ODC) structure, or an Ordered Vacancy Chalcopyrite (OVC) structure. The gap energy obtained by Photoluminescence (PL) for the different samples is 1.23 eV. Studying the variation of the gap as a function of the temperature shows that the transition is a D-A type.

Keywords

Chalcopyrite, Photovoltaic, Photoluminescence, Optical Response, X-Ray Diffraction

1. Introduction

Cu(In,Ga)Se₂ is one of the most promising semiconductors for the absorber-layer of thin-film solar cells [1]. The conversion efficiency of such cells on glass substrates is approaching 20% [2]. Some studies have shown that higher efficiency is reached in samples where a Cu(In_{1-x}Ga_x)₃Se₅ phase is formed at the surface of the CuIn_{1-x}Ga_xSe₂ layer [3] [4]. Therefore, CuIn₃Se₅ has been of interest to many groups [4]-[6]. In this work crystals of CuIn₃Se₅ (when x = 0) were grown by the horizontal Bridgman methods using a direct combination of high purity 5N for Cu, 6N for Se and Ga. The elements were placed in a quartz tube sealed under a vacuum of 5×10^{-6} Torr. This tube was placed on a horizontal furnace, for 48 hours, at a temperature higher than the melting temperature of the compound and then left to slowly cool down. Energy Dispersive Spectrometry (EDS) and

How to cite this paper: Habib, D., Aoudé, O., Karishy, S. and El Haj Moussa, G. (2015) Fabrication, Characterization and Optical Properties of Culn₃Se₅ Bulk Compounds. *World Journal of Condensed Matter Physics*, **5**, 201-208. <u>http://dx.doi.org/10.4236/wjcmp.2015.53021</u> X-Ray Diffraction (XRD) were used to calculate the compositions of the ingots considered as very important parameters. The hot point probe method is used in order to determine the conduction types of these ingots. Photoluminescence allowed us to check their optical properties. The type of transition was determined by varying the gap energy as a function of the temperature and as a function of the excitation power.

2. Experiments

Crystals with different compositions were synthesized by direct combination of high purity 5N for Cu and In, 6N for Ga and Se in the desired proportions. The elements were placed in a quartz tube sealed under a vacuum of 5×10^{-6} Torr. This tube was placed ina horizontal heater that reached a temperature exceeding the melting point of the compound. It was left in the heater for 72 hours at which point it was allowed to slowly cool down [7].

To characterize the crystals, X-Ray Diffraction was carried out using a Seifert MZIV powder diffractometer (θ , 2θ geometry) with Cu (K α) radiation ($\lambda = 1.5406$ Å). The chemical composition of the obtained samples were given by EDS (Link type AN 1000 55/S) coupled to a scanning microscope (Cambridge type S360). The Photoluminescence (PL) measurements were performed at different temperatures (from 4.2 K to 85 K) by directly immersing the samples into liquid helium. Excitation was provided by a 632.8 nm He-He laser (20 mW). The illumination of the samples was realized using fiber optic light guides (UV-visible). A3 mm spot was focused on the sample with a power of 2 mW/cm². The emission spectrum, collected through another fiber (visible-IR), was analyzed using a grating monochromator (30 cm focal length, 600 lines/mm, blazed at 760 nm).

3. Results and Discussion

3.1. Characterization by EDS

In **Table 1** the characterization results of CuIn₃Se₅ materials by EDS are presented. The samples show a nearly perfect stochiometry since the magnitude of deviation from stochiometry, $\Delta y (\Delta y = (3 \times Cu)/In - 1)$, is very small [8]. The results of the chemical compositions of a CuIn₃Se₅ sample have a large value of Δy (0.3). A detailed analysis is done in order to study the secondary phases that appear in this sample which will be discussed later on. The CuIn₃Se₅ samples present n-type conductivity.

3.2. Characterization by X-Ray Diffraction

The spectra of different $CuIn_3Se_5$ samples obtained by X-Ray Diffraction are shown in **Figure 1**. These samples are well-crystallized and all existent peaks are similar to those found in previous publications [9]-[11]. Thus, our XR spectra show the presence of several preferential orientations according to planes (112), (220) and (312) for all samples. Since the characteristic peaks concerning the chalcopyrite structure were not observed, the conclusion was made that unlike the CuInSe₂ compounds, the CuIn₃Se₅ compounds do not have a chalcopyrite structure [4] [12]. They either have a Stanite structure [13], an Ordered Defect Chalcopyrite structure (ODC), oran Ordered Vacancy Chalcopyrite structure (OVC).

Sample (E) was studied using X-Ray Diffraction (Table 1) and was found to have bad steechiometry as the magnitude of deviation from steechiometry was high ($\Delta y = 0.3$). The spectrum presented in Figure 2 shows the characteristic peaks concerning CuIn₃Se₅ an dadditional peaks associated with other secondary phases [14]:

CuIn ₃ Se ₅					
samples	% Cu	% In	% Se	Δу	conductivity type
А	11.2	32.4	56.4	+0.037	n
В	11.3	32.9	55.8	+0.030	n
С	11.2	32.5	56.3	+0.034	n
D	11.3	33	55.7	+0.027	n
Е	14.8	31.5	53.3	+0.409	n

Table 1. Chemical compositions of CuIn₃Se₅ bulk samples obtained by EDS



Figure 1. Spectrum of CuIn₃Se₅ obtained by X-Ray Diffraction for one sample.



Figure 2. Spectrum of $CuIn_3Se_5$ obtained by X-Ray Diffraction for sample (E). The symbol (*) indicates the InSe phase and the symbol (?) indicates the $CuIn_2Se_{3.5}$ phase.

- Peaks located at $2\theta = 11.4^{\circ}$, 21.21° , 13.04° and 30.96° indicated by the symbol (*), represent the InSe phase.
- Peaks located at $2\theta = 15.28^{\circ}$ and 26° indicated by the symbol (?) can be associated with a CuIn₂Se_{3.5} phase [15].

The presence of these phases in the case of CuIn₃Se₅ is sometimes possible when CuIn₃Se₅ is equivalent to the CuInSe₂ compound with indium excess. The *a* and *c* lattice parameters of CuIn₃Se₅ presented in Table 2 have been calculated from the spectra where a = 5.76, c = 11.52. These values of *a* and *c* are in agreement with those reported in Marin *et al.* and Negami *et al.* [16] [17].

3.3. Photoluminescence

Figure 3 presents the photoluminescence spectrum of $CuIn_3Se_5$ obtained at 4.2 K. The spectrum shows the exciton position which is required to determine the gap value of 1.23 eV [14] [18]. The activation energy level implicated in the optical transition is found by subtracting the emission peak located at 1.09 eV from the gap value. In other words the activation energy is equal to 1.23 - 1.09 = 0.140 eV (140 meV). The same value has been





found by varying the temperature of the $CuIn_3Se_5$ samples. In the case of $CuIn_3Se_5$, the fiber optic presents absorption at 1 eV, because of this the corrected photoluminescence spectrum of the fiber absorption shows two peaks.

3.3.1. Influence of Temperature

Figure 4 presents the different photoluminescence spectra of $CuIn_3Se_5$, as a function of the temperature at constant excitation intensity (114 mW/cm²). By increasing the temperature, the intensity of the emission peak decreases and a deviation toward low energies is observed.

Figure 5 shows the intensity curve of the photoluminescence signal as a function of $10^3/T$, thus the slope of the line tangent to the curve gives the activation energy in the order of 145 meV.

The full width at half maximum (FWHM) of the peak is found to be in the order of 105 meV. This value shows that the transition is a D–A type. Since CuIn₃Se₅ is equivalent to CuInSe₂ with an indium excess, the defects that appear are probably In_{Cu}, V_{Cu} and In_{Se}. Defect In_{Cu} is more probable than V_{Cu} and In_{Se} given that it has a low formation energy ε [19]-[21] [(ε _{In_{Cu}} = 1.4 eV) < (ε _{V_{Cu}} = 2.6 eV) < (ε _{In_{Se}} = 5 eV)]. Figure 6 presents the variation of the gap energy as a function of the temperature with the condition that the

Figure 6 presents the variation of the gap energy as a function of the temperature with the condition that the activation energy remains constant. Between 4.2 K and 77 K, a decrease of the gap energy is approximately 60 meV. This variation can be expressed as the following linear equation:

$$E_g = 1.23 - 0.0008$$
 T

3.3.2. Influence of the Excitation Power

In order to distinguish a D-A transition from other types of transitions, a method of increasing the excitation power and observing a shift of the peak toward high energies was used (Figure 7). When this occurs the pairs number becomes increasingly important in this transition and the remote pairs will also begin to take place in the



Figure 4. Variation of $CuIn_3Se_5$ photoluminescence spectra with temperature at a constant excitation power (114 mW/cm²).



Figure 5. Photoluminescence signal intensity of $CuIn_3Se_5$ as a function of $10^3/T$.



Figure 6. Variation of the peak position (Δ) and the value of the gap (\Box) along with the temperature of the CuIn₃Se₅ sample.

transition. In a D-A type transition, it is known [22] that the signal intensity, I, depends on the power, P, according to a law given by $I = C.P^{\alpha}$, where C and α are constant. The variation of photoluminescence spectra as a function of the excitation intensity at a constant temperature of 4.2 K (Figure 7) permits the finding of the value of α .

The variation of the light intensity of CuIn₃Se₅ emission peak as a function of the excitation power at a constant temperature of 4.2 K is shown in **Figure 8**. The value of α found is in the order of 0.76, and thus I = C.P^{α} can be rewritten as I = 0.028P^{0.76}.

4. Conclusion

Firstly, samples of CuIn₃Se₅ have been prepared by the Bridgman method. The different samples have then been characterized by several techniques (EDS, XR, hot point probe and photoluminescence). All but one sample present good steechiometry and are well crystallized. Their lattice parameters *a* and *c* are similar to those in previous publications, specifically $c/a \approx 2$. The characterization by photoluminescence allowed the gap value of 1.23 eV to be determined for these compounds. Studying the variation of the gap as a function of the temperature showed that the variation coefficients of the gap along with the temperature of our CuIn₃Se₅ compounds had the same order of magnitude. These coefficients were found to be negative for our samples. The CuIn₃Se₅ sample differed from the rest as it was from good steechiometry. Further analysis of this sample showed the existence of other secondary phases (InSe and CuIn₂Se_{3.5}).



Figure 7. Variation of $CuIn_3Se_5$ photoluminescence spectra with excitation power at a constant temperature of 4.2 K.



Figure 8. Variation of light intensity of the $CuIn_3Se_5$ emission peak as a function of the excitation power at a constant temperature of 4.2 K.

Acknowledgements

The authors wish to express their sincere thanks to Marcelle Farhat for her helpful collaboration.

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