

Crystal Growth, Structural and Optical Studies of CuGa_3Se_5 Bulk Compounds

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Received 14 December 2015; accepted 30 January 2016; published 3 February 2016

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Abstract

Bulk materials were synthesized by the Bridgman technique using the elements Cu, Ga, Se. These samples were characterized by Energy Dispersive Spectrometry (EDS) to determine the elemental composition, as well as by X-ray diffraction for structure, hot point probe method for type of conductivity. Optical response (Photoconductivity) and Photoluminescence (PL) and PL-excitation (PLE) at temperatures from 4.2 to 77 K were also used to estimate the band-gap energy of CuGa_3Se_5 . They show a nearly perfect stoichiometry and present p-type conductivity. CuGa_3Se_5 either have an Ordered Defect Chalcopyrite structure (ODC), or an Ordered Vacancy Chalcopyrite structure (OVC). The gap energy obtained by Photoconductivity and Photoluminescence (PL) for the different samples is 1.85 eV. Studying the variation of the gap as a function of the temperature shows that the transition is a D-A type. The defects that appear are probably Ga_{Cu} .

Keywords

Chalcopyrite, Photovoltaic, Bulk Materials Photoluminescence, Optical Response, X-Ray Diffraction, Photoconductivity

1. Introduction

$\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ and the related I-III-VI₂ chalcopyrite compounds are of great interest due to their potential in photovoltaic and nonlinear optical applications [1]-[3]. Another attractive property is their tolerance to a large range of anion-to-cation off stoichiometry, manifested by the existence of an ordered defect compounds (ODC) with large variations in their Cu/In, Ga/Se ratio [4]. These ODCs, like $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)_3\text{Se}_5$, generally possess wider gap and the formation of ternary Cu-In-Ga-Se compounds with varying gaps enables the formation of hetero-

junctions used in the design of high-performance electronic and optoelectronic devices. Ternary semiconductor compound CuGa_3Se_5 (when $x = 1$) is a promising material for creation on its basis of a number of semiconductor devices, such as infra-red and visible radiation sources, high-efficient solar cells and other devices of semiconductor and quantum electronics [5]-[7]. The present work prepared the samples of CuGa_3Se_5 (when $x = 1$) by the horizontal Bridgman methods [8] [9] using a direct combination of high purity 5 N for Cu, 6 N for Se and Ga. The elements were placed in a quartz tube sealed under a vacuum of 5×10^{-6} Torr. Energy Dispersive Spectrometer (EDS) and 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. Photoconductivity and 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. These studies contribute in the future to improving the efficiency of solar cells formed by heterojunctions made of $\text{Cu}(\text{In}_x\text{Ga}_{1-x})_3\text{Se}_5$ which are promising materials.

2. Experiments

The several crystals used in this work, were synthesized by direct combination of high purity 5 N for Cu and Ga, 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. The latter was placed in a 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 [8] [9].

Our crystals were characterized by X-Ray Diffraction using a Seifert MZIV powder diffractometer (θ , 2θ geometry) with Cu ($K\alpha$) radiation ($\lambda = 1.5406 \text{ \AA}$).

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).

To determine the type of conductivity, the hot point probe method was used.

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). A 3 mm spot was focused on the sample with a power of 2 mW/cm^2 . 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).

To get the gap energy value at room temperature, we used the photoconductivity technique. The samples spectral response was measured at a constant light power over the wavelengths range 400 nm - 2000 nm.

3. Results and Discussion

3.1 Characterization by EDS

The chemical compositions of CuGa_3Se_5 materials by EDS are presented in **Table 1**. The samples show a nearly perfect stoichiometry since the magnitude of deviation from stoichiometry, Δy ($\Delta y = (3 \times \text{Cu}) / \text{Ga} - 1$), is very small [10]. The CuGa_3Se_5 samples present p-type conductivity.

3.2. Characterization by X-Ray Diffraction

The spectra of our samples, obtained by X-Ray Diffraction are identical. **Figure 1** presents one spectrum of a CuGa_3Se_5 sample. They are well-crystallized and all existent peaks are similar to those found in previous work

Table 1. Chemical compositions of CuGa_3Se_5 bulk samples obtained by EDS.

Samples	CuGa_3Se_5				Δy	Conductivity type
	% Cu	% Ga	% Se			
A	12	33	55	+0.09	<i>p</i>	
B	10.4	32.9	56.7	-0.04	<i>p</i>	
C	11.2	32.7	56.1	+0.027	<i>p</i>	
D	11.7	33.1	55.2	+0.06	<i>p</i>	

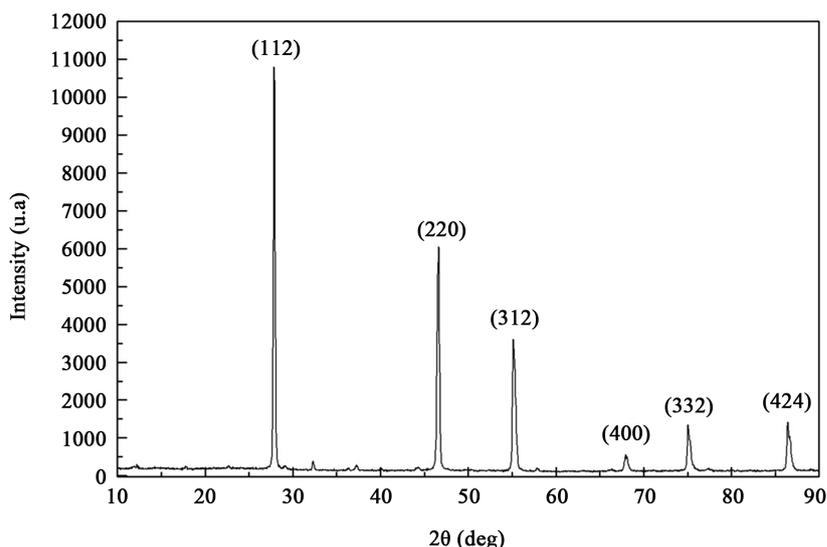


Figure 1. Spectrum of CuGa_3Se_5 obtained by X-Ray Diffraction for one sample.

[11]. Thus, our XR spectra show the presence of several preferential orientations according to planes (112), (220) and (312) for all samples. The CuGa_3Se_5 have a Stannite structure [12] [13], an Ordered Defect Chalcopyrite structure (ODC), or an Ordered Vacancy Chalcopyrite structure (OVC). **Table 2** gives the lattice parameters, $a = 5.49$ and $c = 10.93$ of CuGa_3Se_5 , calculated from the spectra. These values are in agreement with literature [14].

3.3. Characterization by Photoluminescence

The photoluminescence spectrum of CuGa_3Se_5 is formed of one single emission peak of full width at half maximum of the order of 156 meV peak (**Figure 2**). The gap energy of our samples at the temperature of liquid helium (4.2 K) is equal to 1.83 eV, these results are in good agreement with literature [14]-[17].

3.3.1. Influence of Temperature

Figure 3 shows the different photoluminescence spectra of CuGa_3Se_5 , as a function of the temperature at constant excitation intensity (114 mW/cm^2). By increasing the temperature, the intensity of the emission peak decreases and a deviation toward low energies is observed. The full width at half maximum increases and the peak intensity decreases, varying the temperature from 4.2 to 77 K.

The activation energy given by the slope of the tangent value to the curve “Intensity of photoluminescence signal as a function of $10^3/T$ ” shown in **Figure 4** was about 185 meV. This value shows that the transition is a D-A type. The defects that appear are probably Ga_{Cu} , V_{Cu} , Ga_{Se} [18] [19]. The presence of these types of defects is caused by an excess of Gallium in CuGa_3Se_5 .

Figure 5 shows the positions of emission peak for different values of temperature. The gap energy is determined by adding to the photoluminescence peak value, that of the activation energy, assuming that the latter remains constant. The temperature variation from 4.2 K to 60 K causes a gap energy decrease in the order of 35 meV. This variation can be written as follows:

$$E_g = 1.83 - 0.0005 T$$

The coefficients of the temperature gap variation for CuIn_3Se_5 [13] and CuGa_3Se_5 compounds are in the same order of magnitude. For these samples, the coefficient is negative and slightly higher for CuIn_3Se_5 [13] than for CuGa_3Se_5 .

3.3.2. Influence of the Excitation Power

Figure 6 shows the variation of CuGa_3Se_5 photoluminescence spectra as a function of the excitation power at a constant temperature of 4.2 K. In increasing the excitation power, a shift of the peak toward high energies was observed. This result permits us to distinguish the D-A transition from other types of transitions. When this oc-

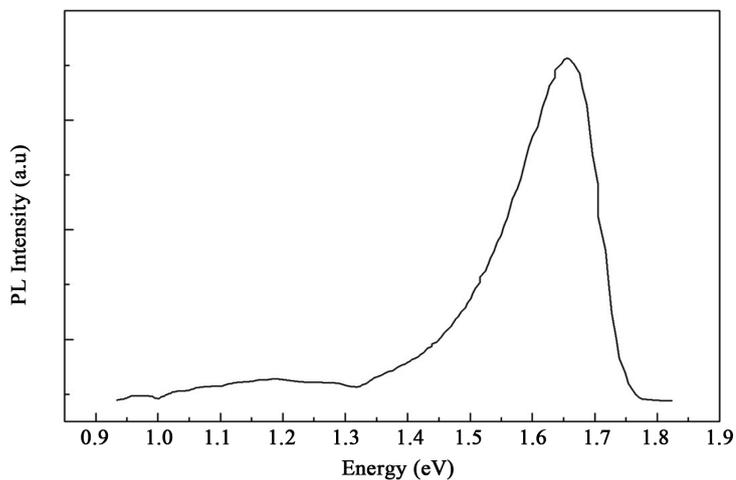


Figure 2. Photoluminescence spectrum of CuGa_3Se_5 at 4.2 K.

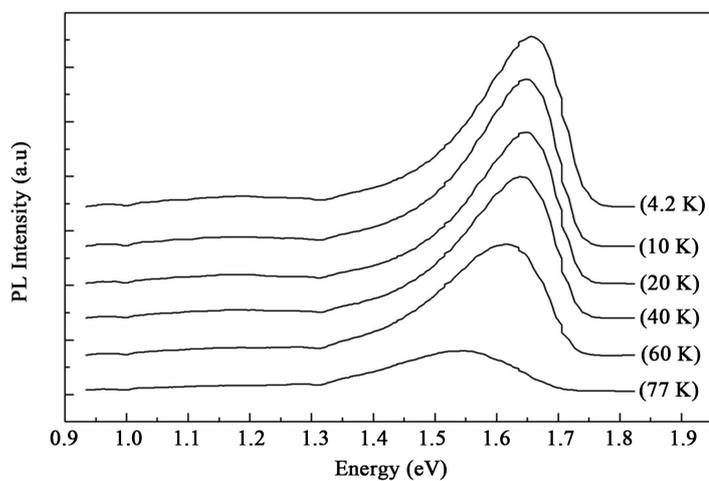


Figure 3. Variation of CuGa_3Se_5 photoluminescence spectra with temperature at a constant excitation power (114 mW/cm^2).

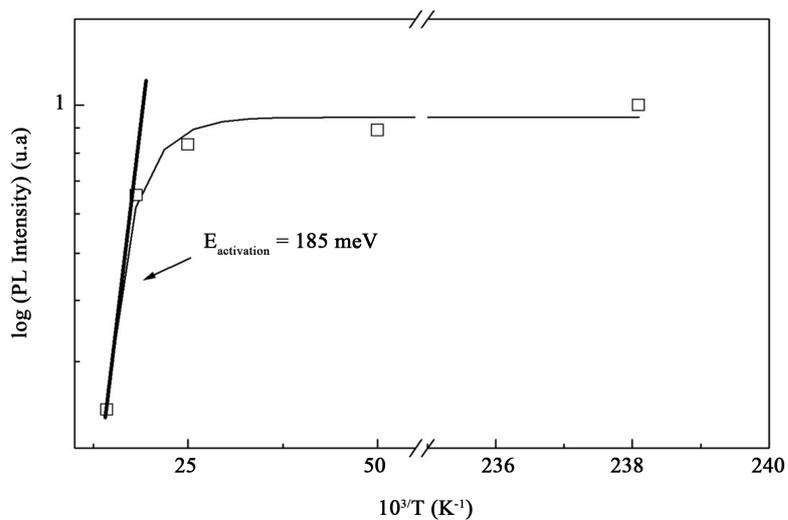


Figure 4. Photoluminescence signal intensity of CuGa_3Se_5 as a function of $10^3/T$.

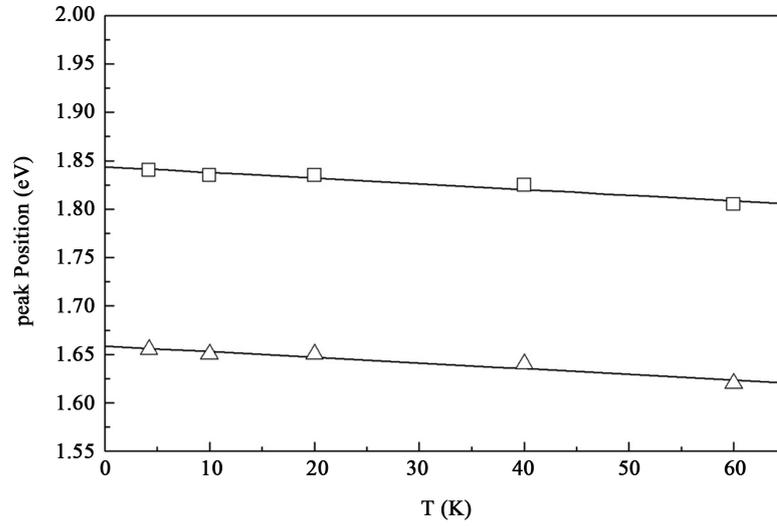


Figure 5. Variation of the peak position (Δ) and the value of the gap (\square) along with the temperature of the CuGa_3Se_5 sample.

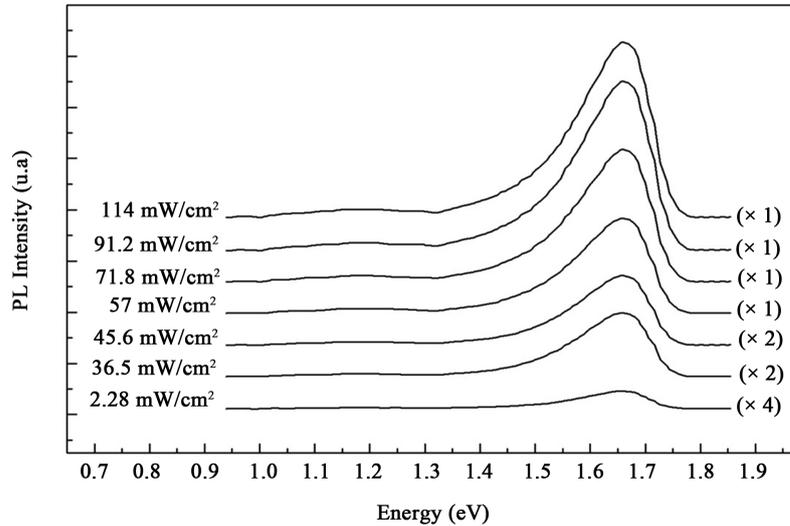


Figure 6. Variation of CuGa_3Se_5 photoluminescence spectra with excitation power at a constant temperature of 4.2 K.

Table 2. Values of a , c and c/a lattice parameters of the different CuGa_3Se_5 samples.

Samples	a	c	c/a	$\Delta(c/a)$
A	5.44	10.9	2.0037	+0.0037
B	5.57	11.1	1.9928	-0.0072
C	5.42	10.88	2.0074	+0.0074
D	5.49	10.93	1.9908	-0.0091

curs the pairs number becomes increasingly important in this transition and the remote pairs will also begin to take place in the transition. In a D-A type transition, it is known [20] that the signal intensity, I , depends on the power, P , according to a law given by $I = C \cdot P^\alpha$, where C and α are constant. From Figure 6, the α value can be calculated.

Figure 7 presents the variation of the light intensity of CuGa_3Se_5 emission peak as a function of the excitation power at a constant temperature of 4.2 K. The α value found is in the order of 0.925, and thus $I = C \cdot P^\alpha$ can be rewritten as $I = 0.0135P^{0.925}$.

3.4. Characterization by Photoconductivity

We have determined the band gap energy value by analyzing our samples using spectral Photoconductivity [21]. **Figure 8** illustrates the Photoconductivity spectrum ($(ah\nu)^2$ as a function of $h\nu$) of CuGa_3Se_5 . This spectrum denotes high speeds of surface recombination. A saturation level at high energy was not observed. In these cases, the gap value is given by an approximate value which was found by taking the abscissa of each curve at $\text{PC}_{\text{max}}/2$. The gap value at room temperature is 1.80 eV, which match those found by Photoluminescence and in literature [14]-[17].

4. Conclusion

The CuGa_3Se_5 samples have been prepared by the Bridgman method. The different samples have then been characterized by several techniques (EDS, XR, hot point probe, photoconductivity and photoluminescence). All samples present good stoichiometry and are well crystallized. Their lattice parameters a and c are similar to those in previous publications, specifically $c/a \approx 2$. The CuGa_3Se_5 samples present p-type conductivity. The characterization by photoluminescence allowed the gap value of 1.83 eV to be determined for these compounds.

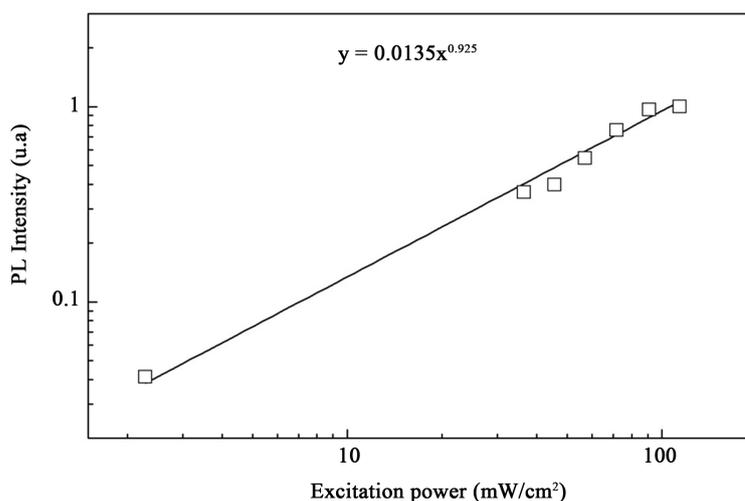


Figure 7. Variation of light intensity of the CuGa_3Se_5 emission peak as a function of the excitation power at a constant temperature of 4.2 K.

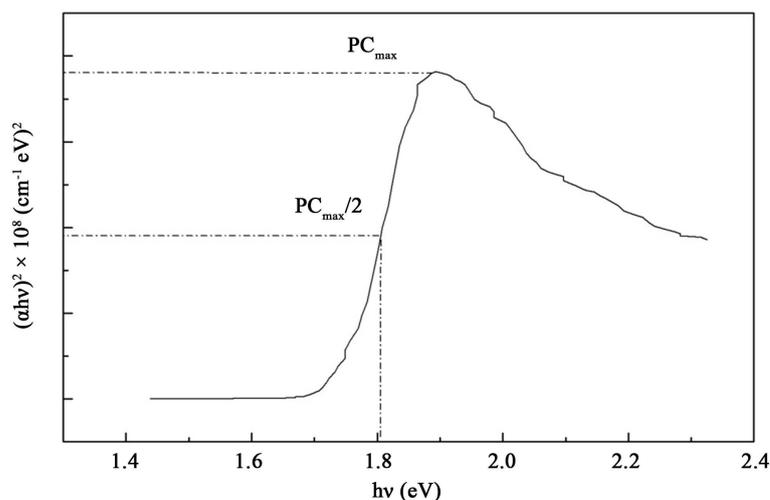


Figure 8. Photoconductivity spectrum ($(ah\nu)^2$ as a function of $h\nu$) of CuGa_3Se_5 at room temperature.

Studying the variation of the gap as a function of the temperature and of the excitation power showed that the transition is a D-A type and that the appeared defects are probably Ga_{Cu} , V_{Cu} , Ga_{Se} . The gap value at room temperature determined by Photoconductivity is equal to 1.8 eV. These results will allow the fabrication in the near future of solar cells formed by heterojunctions made of $\text{Cu}(\text{In}_x\text{Ga}_{1-x})_3\text{Se}_5$ to get a good efficiency at a low cost.

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