Le 4ème Séminaire International sur les Energies Nouvelles et Renouvelables
The 4th International Seminar on New and Renewable Energies

Unité de Recherche Appliquée en Energies Renouvelables,
Ghardaïa – Algeria 24 - 25 Octobre 2016

SIENR

Formation of defect chalcopyrite compound CuIn₃Se₅ by high-energy ball milling

S. Rahal*[1], M. Benabdeslem[1], M. Chaouche[1], K. Hamdani[1], N. Benslim1[1], L. Bechiri[1], T. Touam[2], A. Djekoun[3], X. Portier[4]

[1]Laboratoire LESIMS. Département de physique. Université d'Annaba. Algeria.
[2]Laboratoire LSC. Département de physique. Université d'Annaba. Algeria.
[3]Laboratoire LM2S. Département de physique. Université d'Annaba. Algeria.
[4]ENSICAEN, Université, 6-Boulevard du Maréchal Juin 14050, Caen. France
*E-mail: rahalsamia98@yahoo.fr

Abstract—— **Ordered vacancy compound (OVC) CuIn₃Se₅ has been investigated in this work. The material has been synthesized by mechanical milling process from elemental Cu, In and Se precursors. X-ray diffraction (XRD) has been used to identify the structure of the material, whereas morphology and composition have been characterized respectively by scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS). The diffraction powder data showed that the as grown sample is polycrystalline in nature and displays the main peaks (110) and (114) characteristic of the OVC structure. The lattice parameters a and c have been found to be a = 5.83 Å and c = 11.71 Å. From the EDS, the composition of the elements showed large excess of In. The optical band gap of the semiconductor has been found around 1.35 eV.**

Keywords— **Solar cells, CuIn₃Se₅, OVC, Milling, Nanoparticles**

I. INTRODUCTION

New promising materials for photovoltaic applications in replacement of the standard silicon appeared in the last decade. The semiconductors based copper and called chalcopyrite materials belonging to the I-III-VI₂ family are the subject of intense attention because of their high absorption of about 10^5 cm⁻¹ and of their band gap of 1 eV matching well with the solar spectrum [1-5]. Recent studies showed the existence of a defect chalcopyrite layer formed on the surface of In rich absorber CuInSe₂ and called ordered vacancy compound (OVC) [6-8]. The crystal structure of the (OVC) CuIn₃Se₅ derived from the ordered chalcopyrite structure of CuInSe₂ by substituting In at Cu sites and leaving Cu sites vacant. The desirable properties of this defect chalcopyrite compound are advantageous and can play an important role for achieving high-efficiency solar cells [9]. Indeed this compound adapts well with the other partner CIS for a heterojunction and this because perfect matching of the lattices between the two materials. In the present work, nanocrystalline powders of CuIn₃Se₅ prepared by mechanical milling considered as a simple and economical method for short reaction times. This non-vacuum method is a simple processing route for the synthesis of nanocrystalline materials. The main purpose of the reported work is to study for the first time the structural and optical properties of CuIn₃Se₅ obtained by mechanical milling reaction technique.

II. EXPERIMENTAL DETAILS

Nano powders of CuIn₃Se₅ were prepared by milling pure Cu, In and Se elements (99.99%) in a planetary ball mill (Fritsch Pulverisette 7) using hardened steel balls. In order to reduce the particle size of the alloy to the nanometer range, the milling process was carried out at 250 rpm speed and the ball weight to charge weight ratio has been1:15. The three elements once weighted were introduced into cylindrical steel vials. To prevent atmospheric contamination, the vials were filled in a glove box under high purity argon gas. After 60 min milling period, small amounts of the milled powders were consolidated in the form of circular compact pasts of 10 mm in diameter and 1 mm in thickness. The structure of the prepared powder was studied using a Philips X-ray diffractometer with Cu (Kα) radiation having wavelength λ = 0.15406 nm. The sample was scanned from 10° to 90° (2θ) with a step size of 0.02°. The morphology and composition were checked using scanning electron microscope (SEM) on a Jeol 6400 coupled with an energy dispersive spectroscopy (EDS) for the composition. The AFM experiments were carried out in contact mode by a Nanosurf easyScan 2 equipped with a 10 μm × 10 μm high resolution scanner with vertical range of 2 μm. AFM images have been recorded with a resolution of 256 × 256 pixels over scanning areas of 2.5 × 2.5 μm² and the SPIP™ software program. The Raman scattering measurements were performed at 300 K using a Dilor XY system with the 514.5 nm Ar⁺ ion laser as the excitation source. The spectrometer was calibrated using the Γ25 phonon of diamond Si (Fd-3m). At ambient conditions we estimate a resolution of 1 cm⁻¹ for the Raman peak position and 0.5 cm⁻¹ for the peak full width at half maximum. X-ray Photoelectron Spectra (XPS) was used to investigate the valence states of the elements in the CuIn₃Se₅ product. The XPS measurements were carried out on an ESCALAB 250 spectrometer using an Al (Kα) X-ray as the excitation source. The Cu2p3, In3d5, and Se3d core levels were examined, respectively and the binding energies obtained in the XPS analysis were corrected for specimen

Le 4ème Séminaire International sur les Energies Nouvelles et Renouvelables
The 4th International Seminar on New and Renewable Energies

Unité de Recherche Appliquée en Energies Renouvelables,
Ghardaïa – Algeria 24 - 25 Octobre 2016

charging by referencing the C1s to 285.07 eV. A Perkin-Elmer λ9 (UV-VIS-NIR) spectrophotometer was used for optical studies in the 400–2000 nm wavelength range at room temperature.

<center>III. RESULTS</center>

A. Structural properties

X-ray diffraction pattern represented in Fig. 1, showed that the synthesised material is polycrystalline in nature and the crystallographic structure is quite similar to that of CuInSe$_2$. It can be seen that the diffraction pattern involves the (110), (200), (202), and (114) reflection peaks typical of an imperfect chalcopyrite structure. The detected lines (110) and (114) indexed by ASTM files (JCPDS Card file No, 40-1487) are specific to the OVC structure (space group $I\bar{4}2m$). This kind of structure is attributed to the difference in atomic arrangement of the cation sub-lattice in the crystal structure.
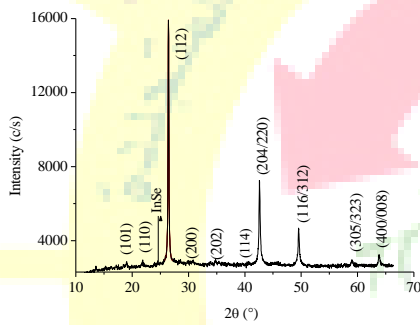

Fig. 1 X-Ray diffraction patterns of CuIn$_3$Se$_5$

It is to be noted that the XRD pattern contains extra reflection corresponding to the weak peak indexed to the InSe secondary phase. Taking into account the quadratic form for the tetragonal system, the lattice constants a and c of the unit cell were calculated by the least squares fit method. The obtained values a = 5.83 Å and c = 11.71 Å, with a distortion factor c/a = 2.008 have been found slight larger than those reported in literature [10]. This increase in lattice parameters can be caused by the increase in the defect density because of milling process. Assuming the particles spherical in shape, the size D was first estimated by Scherrer equation by fitting the most intense peak (112) in Lorentzian profile:

$$D = \frac{k\lambda}{\delta \cos\theta} \qquad (1)$$

k is a constant whose value is approximately 0.9, λ is the X-ray wavelength, δ is the full width at half maximum

(FWHM) of the diffraction peak and θ the Bragg diffraction angle.

Hall-Williamson was also applied to estimate qualitative information regarding size and micro strain present in the milled samples [11]. In this method, both size and strain broadening are assumed to be Lorentzian. The effects of the strain (ε) and crystallite sizes (D) on the FWHM (δ) can be expressed by the following equation:

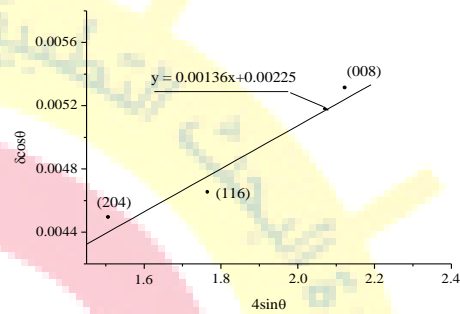$$\delta \cos\theta = \frac{0.9\lambda}{D} + 4\varepsilon \sin\theta \qquad (2)$$

Fig. 2 Hall–Williamson of CuIn$_3$Se$_5$

From the linear fit of the data reported in Fig. 2, we can estimate the grain size D from the intercept of the curve with y axis and ε from the slop of the fit. It is to be noted that the positive slope indicates the presence of tensile strain in the studied sample. The dislocation density is calculated using Williamson and Smallman's equation [12]:

$$\Delta = \frac{1}{D^2} \qquad (3)$$

Table I
Structural parameters of CuIn$_3$Se$_5$ calculated from XRD peak positions

	Crystallite size D (nm)		Strain ε	Dislocation Δ (Lines/m^2)
	Scherrer	H-W		
CuIn$_3$Se$_5$	52	60	13.6 x 10^{-4}	2.78x10^{14}

Dislocation density Δ, D and ε for the milled specimen are shown in Table I.

<center>2</center>

Le 4ème Séminaire International sur les Energies Nouvelles et Renouvelables
The 4th International Seminar on New and Renewable Energies

Unité de Recherche Appliquée en Energies Renouvelables,
Ghardaïa – Algeria 24 - 25 Octobre 2016

SIENR

B. Morphology

The morphology of the $CuIn_3Se_5$ sample was studied by plane-view study scanning electron microscopy (SEM) and AFM technique. The powder morphology appeared formed of small particles and due to the welding process, the crystallites agglomerate to form large grains as seen in Fig. 3a. The large difference in crystallite size values calculated from XRD data and SEM image may be due to that each grain observed under the SEM profile contains several individual nanocrystallites.
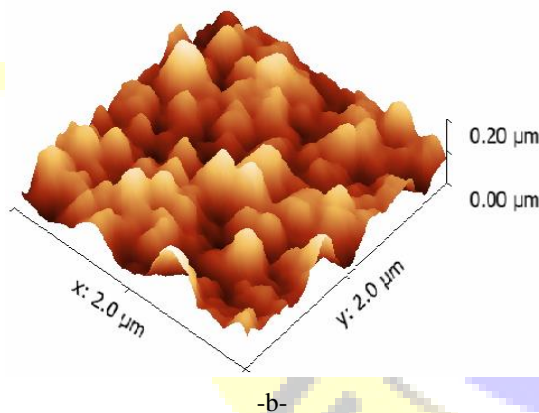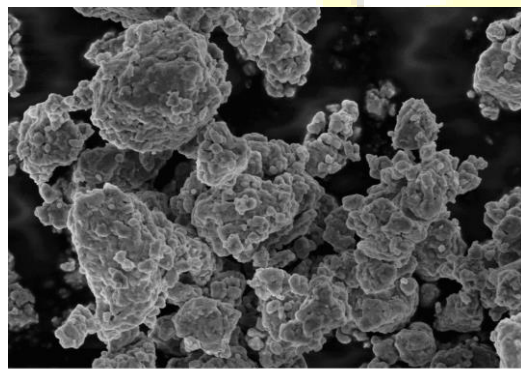
C. Composition

In the EDS spectrum as seen in Fig. 4, the starting elements copper, indium and selenium have been detected and elemental analysis performed on different points of the crystal revealed specimen with large excess of In. The global composition of the compound within an accuracy of ±0.1% is Cu (at %): 5.10, In (at %): 36.58 and Se (at %): 58.32. After 60 mn of milling, the final composition of the product corresponds to the chemical formula $Cu_{0.63}In_{3.29}Se_{5.06}$.
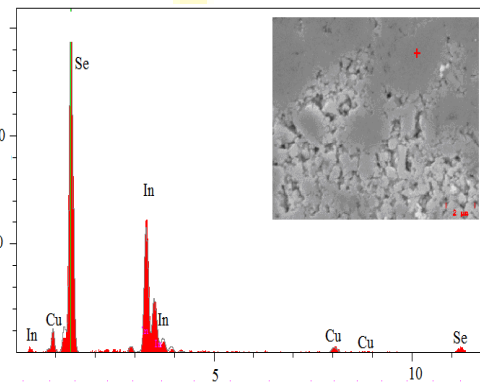

Fig. 4 Spectrum EDS of $CuIn_3Se_5$

-a-

-b-

Fig. 3 SEM (a) and AFM (b) images of $CuIn_3Se_5$

D. Photoelectron Spectroscopy (XPS)

The valence states of the elements in the $CuIn_3Se_5$ have been examined by XPS and reported in Fig. 5. The Cu2p core-level spectrum indicates the presence of two intense peaks. The first one is located at 932.16 eV corresponding to the binding energy for Cu $2p_{3/2}$ whereas the second around 952.2 eV is assigned to the binding energy for Cu $2p_{1/2}$. Both peaks were emitted from states of Cu element in $CuIn_3Se_5$. The peaks located at 444.76 eV and 452.30 eV are assigned to In $3d_{5/2}$. A depth profile showed binding energy peaks centred at 53.95 eV and coincided well with Se $3d_{5/2}$ electronic state. The oxidation of the surface related to the presence of O1s peak (not shown in Fig. 5) can be attributed to air contamination of the material. The XPS data indicate that the binding energies in $CuIn_3Se_5$ phase are higher than those present in chalcopyrite $CuInSe_2$.
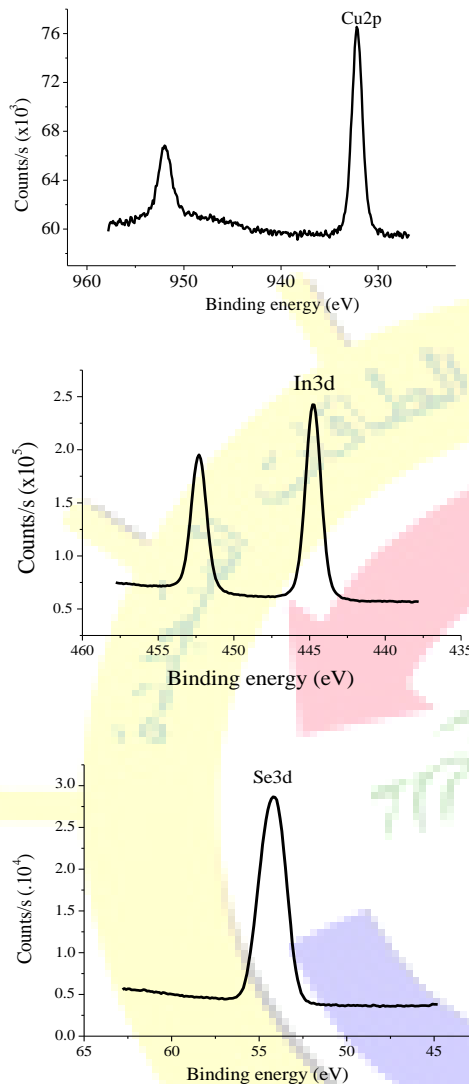
Complementary information about the structural and topographic surface of the $CuIn_3Se_5$ was provided by atomic force microscopy (AFM) as shown in Fig. 3b. The three- dimensional (3D) AFM image shows that the $CuIn_3Se_5$ material is well defined nanosized grains, having a root-mean-square roughness (RMS) value calculated from the number of scans at different areas of the sample and found to be 30 nm.

Le 4ème Séminaire International sur les Energies Nouvelles et Renouvelables
The 4th International Seminar on New and Renewable Energies
Unité de Recherche Appliquée en Energies Renouvelables,
Ghardaïa – Algeria 24 - 25 Octobre 2016

Fig. 5 XPS depth profiles of Cu2p, In3d, and Se3d core level spectra around the CuIn$_3$Se$_5$

To note that the weak peak localised at 117 cm^{-1} corresponds to the InSe binary.
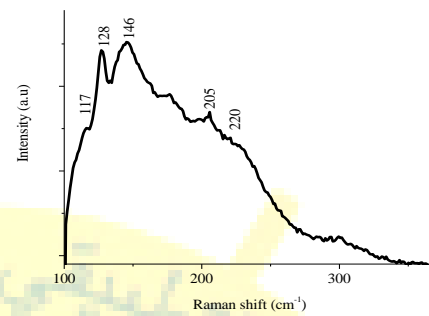

Fig. 6 Raman spectra of CuIn$_3$Se$_5$

It is important to note that the lines observed in the spectrum present a reduction in their frequencies as compared to the corresponding values in CuInSe$_2$. This is due to the presence in this compound of an array of vacancies occupying particular sites in the cation sublattice.

F. Optical properties

The absorption coefficient α of the OVC CuIn$_3$Se$_5$ has been calculated from optical transmission (T) and reflectance (R). As the compound has been reported to be direct in nature, the relation describing the absorption spectrum near the band gap is expressed with the following formula:

$$\alpha = \frac{1}{d}\left[2\ln(T) - \ln(R)\right] \qquad (4)$$

The variation of α with hν near the main absorption edge is expected to follow:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \qquad (5)$$

The bandgap E$_g$ of the CuIn$_3$Se$_5$ compound was estimated from the intersection of the straight line of $(\alpha h\nu)^2$ with the energy axis hν. As shown in Fig. 7, the direct optical band gap value was found around 1.35 eV close to the optimal value of 1.40 eV. Nevertheless the gap obtained is slightly larger than the reported data for this compound [13-15]. The increment of the direct bandgap occurs due to the finally resultant OVC phase of and also due to the nano-crysatlline nature of the synthesized material.

E Raman analysis

Fig. 6 shows the optical vibrational modes of the ordered vacancy compound CuIn$_3$Se$_5$ obtained by Raman spectra at room temperature. Two intense peaks appeared at 128 cm^{-1} and 146 cm^{-1} contributed to the B1 modes of CuIn$_3$Se$_5$. The two intensity peaks at 205 cm^{-1} and 220 cm^{-1} and can be attributed to the phonon modes (B2, E) for CuIn$_3$Se$_5$. Similar peak values have been reported in this OVC compound [12].

Le 4ème Séminaire International sur les Energies Nouvelles et Renouvelables
The 4th International Seminar on New and Renewable Energies
Unité de Recherche Appliquée en Energies Renouvelables, Ghardaïa – Algeria 24 - 25 Octobre 2016
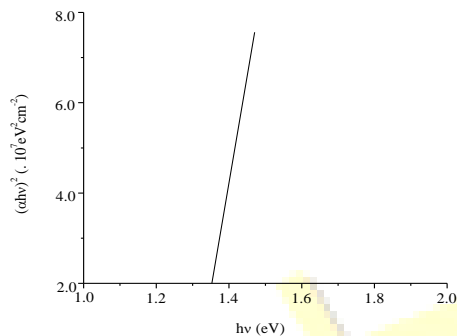
Fig. 7 Plot of $(\alpha h v)^2$ versus photon energy hv of $CuIn_3Se_5$

IV. CONCLUSION

Nanoparticles of the ordered defect compound $CuIn_3Se_5$ have been successfully prepared by mechanical milling and the properties of the material were characterized. XRD results showed that the $CuIn_3Se_5$ crystal has characteristic diffraction peaks of the ordered defect structure. Size and strain contributions to line broadening have been analyzed by the Williamson–Hall method. The binding energies of Cu, In and Se in the $CuIn_3Se_5$ phase were higher than those in the $CuInSe_2$ phase. The measured bandgap E_g showed that $CuIn_3Se_5$ prepared by milling can be potentially applied as an absorber in heterojunction.

REFERENCES

[1] C. Calderon, P. Bartolo-Perez, O. Rodriguez and G. Gordillo, "Phase identification and XPS studies of $Cu(In,Ga)Se_2$ thin films," Microelectronics Journal., vol. 39, pp. 1324- 1326, Nov. 2008.

[2] C. Chityuttakan, P. Chinvetkitvanich, K. Yoodee and S. Chatraphorn, "In situ monitoring of the growth of $Cu(In,Ga)Se_2$ thin film," Solar Energy Materials and Solar Cells., vol. 90, pp. 3124-3129, Nov. 2006.

[3] M. A. Contreras, M. J. Romero and R. Noufi, "Characterization of $Cu(In,Ga)Se_2$ materials used in record performance solar cells," Thin Solid Films., vol. 511-512, pp. 51-54, July. 2006.

[4] T. Delsol, M. C. Simmonds and I. M. Dharmadasa, "Chemical etching of $Cu(In,Ga)Se_2$ layers for fabrication of electronic devices," Solar Energy Materials and Solar Cells., vol. 77, pp. 331-339, June. 2003.

[5] P. Jackson, D. Hariskos, E. Lotter, S. Paetel, R. Wuerz, R. Menner, W. Wischmann and M. Powalla, "New world record efficiency for $Cu(In,Ga)Se_2$ thin-film solar cells beyond 20%," Progress in Photovoltaics., vol. 19, pp. 894-897, Nov. 2011.

[6] Y. Bharath Kumar Reddy and V. Sundara Raja, "Optical, structural and electrical properties of co-evaporated $CuIn_2Se_{3.5}$ thin films," Materials Letters., vol. 58, pp. 1839-1843, May. 2004.

[7] C. Rincon, S. M. Wasim, G. Marın, A. Rincon, P. Bocaranda, C. Torres, G. Bacquet and G. Sanchez Perez, "Optical characterization of bulk $CuIn_3Se_5$," Materials Letters., vol. 41, pp. 222-228, Dec. 1999.

[8] W Paszkowicz, R Lewandowska and R Bacewicz, "Rietveld refinement for $CuInSe_2$ and $CuIn_3Se_5$," Journal of Alloys and Compounds., vol. 362, pp. 241-247, Jan. 2004.

[9] D. Schmid, M. Ruckh, F. Granwald and H. W. Schock, " Chalcopyrite/defect chalcopyrite heterojunctions on the basis of $CuInSe_2$," J. Appl. Phys., vol. 73, pp. 2902–2909, Mar. 1993.

[10] Se Han Kwon, Byung Tae Ahn, Seok Ki Kim, K.yung Hoon Yoon and Jinsoo Song. "Growth of $CuIn_3Se_5$ layer on $CuInSe_2$ films and its effect on the photovoltaic properties of $In_2Se_3/CuInSe_2$ solar cells," Thin Solid Films., vol. 323, pp. 265-269, June. 1998.

[11] G. K. Williamson and W. H. Hall, "X-ray line broadening from filed aluminium and wolfram," Acta Metallurgica., vol. 1, 22-31, Jan. 1953.

[12] C. Rincon, S. M. Wasim. G. Marin, J. M. Delgado, J. R. Huntzinger, A. Zwick and J. Galibert, "Raman spectra of the ordered vacancy compounds $CuIn_3Se_5$ and $CuGa_3Se_5$," J. Appl. Phys. Lett., vol. 73, pp. 441-443, July.1998.

[13] D. Schmid, M. Ruckh, F. Grunwald and H. W. Schock, " Chalcopyrite/defect chalcopyrite heterojunctions on the basis of $CuInSe_2$," J. Appl. Phys., vol., 73, pp. 2902–2909, Mar.1993.

[14] G. Marin, S. M. Wasim, C. Rincon, G. Sanchez Perez, Ch. Power and A. E. Mora, "Temperature dependence of the fundamental absorption edge in $CuIn_3Se_5$," J. Appl. Phys., vol. 83, pp. 3364–3366, Mars.1998.

[15] C. Rincon, S.M. Wasim, G. Marin, A. Rincon, P. Bocaranda, C. Torres, G. Bacquet and G. Sanchez Perez, " Optical characterization of bulk $CuIn_3Se_5$," Mater. Lett., vol. 41, pp. 222–228, Dec. 1999.