The unit cell parameters and electrical conduction of some new solar cell materials

L. Essaleh [a *], G. Marín [b], S. M. Wasim [c], C. Rincón [c]

[a] *Laboratoire de Matière Condensée et Nanostructures (LMCN), Univertité Cadi-Ayyad. FSTG, Departement de Physique Appliquée, Marrakech, Maroc*

[b] *Laboratorio de Estructura e Ingeniería de Materiales Nanoestructurados (LEIMN), Centro de Ingeniería y Estructura de Materiales (CITeMa), Instituto Venezolano de Investigaciones Tecnológicas (IVIC), Maracaibo 4101, Venezuela*

[c] *Centro de Estudios de Semiconductores (CES), Facultad de Ciencias, Universidad de Los Andes, Mérida 5101, Venezuela.*

** Corresponding author: Pr. L. Essaleh*

Phone: (+212) 6 68 05 13 56, Fax: Fax: (+212) 5 24 43 31 70, E-mail: lessaleh@gmail.com, l.essaleh@uca.ma

Abstract

New materials are being investigated that could yield solar energy conversion efficiency comparable in device production cost to the standard electric power generators. Continuing with this effort, in recent years solar cells with efficiency close to 20 %, prepared with alloys of $CuIn_{1-x}Ga_xSe_2$ has been reported. It is shown that the normalized values of the unit cell parameters *a* and *c* of the ordered defect compounds with respect to their corresponding 1:1:2 phase, that are formed on the In(Ga)-rich side of the pseudo-binary phase diagram of $[Cu_2(Se,Te)]_X$–$[(In_2,Ga_2)(Se_3,Te_3)]_{1-X}$, vary linearly with the effective cation radius r_{eff} for the tellurides and selenides of Cu-In and Cu-Ga systems. This universal relationship has important significance. The unit cell dimensions of other chalcopyrite-related ordered defect compounds of these systems that have not been synthesized so far can be estimated. Because of the presence of shallow donor and acceptor levels due to the presence of cation-cation disorders in $Cu(In,Ga)Se_2$ and ordered defects in $Cu(In,Ga)_3(Se,Te)_5$, the impurity band in these compounds starts to form between liquid helium and nitrogen temperatures. This permits to study the variable range hopping (VRH) conduction in the impurity band over a much wider temperature range.

Keywords: Photovoltaic devices; Solar cells; Semiconductors; Ternary compounds; Ordered defect compounds; Variable range hopping conduction.

I. Introduction

Several ternary compounds, that have vacancy of one or two cations over the anions, are formed on the (In,Ga)-rich side of the pseudo-binary phase diagram of $[Cu_2(Se,Te)]_{1-x}$ $[(In_2,Ga_2)$ $(Se_3,Te_3)]_x$ [1]. These vacancies are considered to be atoms that contribute zero electrons. These were earlier called Ordered Vacancy Compounds (OVCs) [2]. Their existence can also be explained as a repeat of one unit of interacting donor-acceptor defect pair (DADP) $[(In,Ga)^{+2}_{Cu}, 2V^{-1}_{Cu}]$ in each n = 4, 5, 6, 7, 8 and 9 units respectively of the ternary compound Cu(In,Ga) (Se_2,Te_2) of the I-III-VI_2 family [3]. Based on this, the general formula of these compounds can be written as $n[Cu(In,Ga)$ $(Se_2,Te_2)]$ $+[(In,Ga)^{+2}_{Cu}, 2V^{-1}_{Cu}]$ = $Cu_{n-3}(In_{n+1},Ga_{n+1})$ (Se_{2n},Te_{2n}). Because of this, lately they are also called Ordered Defect Compounds (ODCs). The selenides belonging to the ODCs with n = 5 are considered to be useful absorber materials in the fabrication of heterojunction solar cells. $CuIn_3Se_5$ is reported to segregate as a secondary phase at the surface of polycrystalline thin films [3,4]. Recently, it is found that $CuGaSe_2$ thin films also show the formation of ODC-related phases [4]. On the other hand, solar cells based on $CuIn_{1-x}Ga_xSe_2$ have demonstrated efficiencies of up to 19.3% [4,5]. It is thus suggested that layers of the alloy system $Cu(In_{1-x}Ga_x)_3Se_5$ might play an important role in the optimization of the efficiency of solar cells based on $CuIn_{1-x}Ga_xSe_2$. The only exception is $CuIn_5Se_8$ that has hexagonal and $CuGa_5Te_8$ that has cubic structure [5]. The linear increase in the dimension of the unit cell is

explained in terms of the decrease of the parameters *m* and l. The former (*m*) represents the fraction of the cation vacancies to the total number of cation positions and the latter the fraction of DADP per unit, respectively, in the chemical formula. It can be observed from table 1 and 2 of reference [6] that *m* and l have the same value and are reciprocal of *n*. It is established recently that the decrease in the unit cell dimensions is related to the decrease in the effective cation radius r_{eff} which is defined by $[(n\text{-}3)r_{Cu}^{+1} + (n\text{+}1)r_{In(Ga)}^{+3}]/2n$. In this relation r_{Cu}^{+1} = 0.60 Å, r_{In}^{+3} = 0.76 Å and r_{Ga}^{+3} = 0.61 Å are the ionic radius reported by Shanon [7]. Here, we establish that the variation of the normalized values of the parameters *a*, *c* and V of the ODCs of tellurides and selenides of Cu-In and Cu-Ga systems, respectively with respect to their corresponding 1:1:2 phase fall on universal straight lines.

II. Experimental

The growth of single crystals and the technique used for the X-ray diffraction (XRD) analysis of the ODCs of these compounds has been reported earlier [7, 8]. The indexing of the registered peak positions of their X-ray powder diffraction patterns is carried out with the computer program DICVOL91. After the indexing procedure was completed, the diffraction pattern was evaluated by means of NBS*AIDS83 program. This evaluation produced the unit cell parameters of the ODCs that are for example a = 5.789 Å and c = 11,612 Å for $CuInSe_2$ and a = 5,7508 Å and c = 11,5769 Å for $CuIn_3Se_5$.

III. Results and discussion

1. The unit cell parameters

The values of the parameters *a*, *c* and V published by us earlier and by other authors on bulk crystals and thin films of the $Cu_{n-3}(In_{n+1},Ga_{n+1})(Se_{2n},Te_{2n})$ system are given in Table1. For a comparative study, the values of *a*, *c*, and V of the corresponding 1:1:2 phases are also included. As an illustration, the plot of unit lattice parameter *a* against the effective cation radius r_{eff} for the selenides and telllurides of these ODCs are given in Fig. 1. The data of Cu-In-Se, Cu-In-Te, Cu-Ga-Se and Cu-Ga-Te systems are fitted separately by straight lines.

Compound	***m*** **(l)**	r_{eff} **(Å)**	***a*** **(Å)**	***c*** **(Å)**
$CuInSe_2$	0	0.680	5.789	11.612
$CuIn_3Se_5$	1/5	0.576	5.7541(5)	11.538(3)
$CuGaTe_2$	0	0.605	6.021(2)	11.937(5)
$CuGa_3Te_5$	1/5	0.486	5.9321(8)	11.825(4)

Table1: The values of *m*, l, effective cation radius r_{eff}, unit cell lattice parameters *a* and *c* of the $Cu_{n-3}(In_{n+1},Ga_{n+1})(Se_{2n},Te_{2n})$ systems, that are given in Refs. [6,7], and their corresponding normalized values.

It can be concluded that, consistent with Vergard's law, the reduction of the unit cell parameters in the ODCs is due to the decrease of their effective cation radius caused by the decrease in *n* or increase in *m*(l) [6,7]. Similar is the case with *c* and V reported in reference [6,7].

This linear dependence permits us to interpolate the values of the unit cell parameters *a*, *c* and V of the chalcopyrite-related ODCs that already appear in the literature and others that have not yet been synthesized. However, these curves are not universal. The normalized values of the unit cell parameters of the ODCs with respect to their corresponding 1:1:2 phase, denoted by a_{ODC}/a_{112} and c_{ODC}/c_{112}, are also given in Table 1 and plotted in Figs. 1 and 2, respectively.

It is interesting to observe from these figures that the normalized values of the unit cell parameters of the ODCs of Cu-In and Cu-Ga systems can be fitted by straight lines. The corresponding standard deviations (SD) are indicated in.

This universal behavior is of significant importance because from the interpolation of the appropriate curve, one can predict the unit cell parameters of the ODCs of those systems that not yet been synthesized, if they have the same chalcopyrite-related structure.

Furthermore, one could even speculate on the possible unit cell parameters of the sulfides of Cu-In and Cu-Ga if they also have chalcopyrite-related structure and most probably like the tellurides and selenides fall on the same straight lines. In the parameter *c* larger dispersion of the experimental data can be noticed. This is due to the tetragonal distortion of the unit cell.

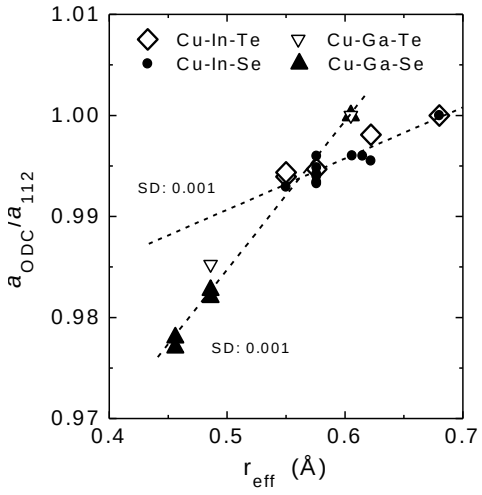

Fig. 1: Variation of the normalized unit cell parameter a_{ODC}/a_{112} with the effective cation radius r_{eff}. A linear dependence for Cu-In selenides and tellurides, represented by (●) and (◇) and, for Cu-Ga selenides and tellurides represented by (▲) and (∇), can be observed.

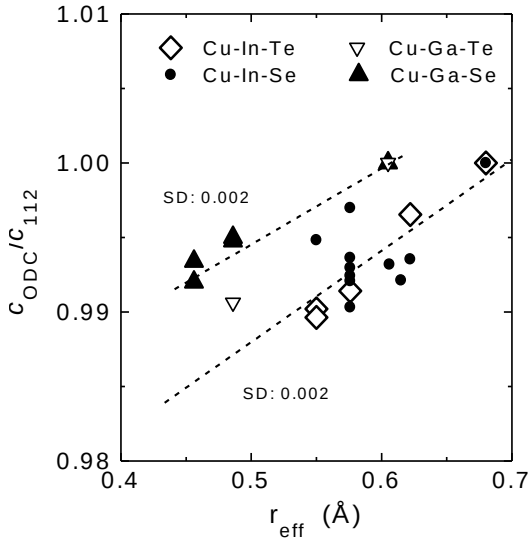

Fig. 2. Variation of the normalized unit cell parameter c_{ODC}/c_{112} with the effective cation radius r_{eff}. A linear dependence for Cu-In selenides and tellurides, represented by (●) and (◇) and, for Cu-Ga selenides and tellurides represented by (▲) and (∇), can be observed.

2. Electrical transport

The Electrical transport properties between 2 and 300 K were measured by standard technique which has been described earlier [9]. Hall effect measurements indicates that our samples falls on the insulator side of the metal-insulator transition. The variation of the electrical resistivity ρ and Hall coefficient R_H as a function of temperature up to 300 K is given in Figure 3 for one representative sample of $CuGaTe_2$ and another of $CuInSe_2$.The temperature dependent behavior of these parameters are indicative that the conductivity is metallic in nature in $CuGaTe_2$. In the case of $CuInSe_2$, the resistivity shows a weak minimum around 190 K and below this it increases with decreasing temperature. It is found to be very nearly exponential in two different temperature ranges. On the other hand, the temperature dependence of R_H shows a maximum around 70 K. This is a characteristic sign that at higher temperatures, above the maximum, the contribution to the electrical conduction is predominantly from electrons in the conduction band and at lower temperatures, below the maximum, from the impurity band formed by shallow intrinsic defects levels. The variation of electron mobility μ with temperature is given for $CuInSe_2$ in Fig 4. At 250 K, it is about 1250 cm^2/Vs. It increases with the decrease of temperature, reaches a maximum and then starts to decrease. The maximum mobility of 1549 cm^2/Vs observed at 138 K is the highest reported so far in n-type $CuInSe_2$ samples. In general, the temperature dependence of the electrical mobility originates from a combined effect of the contribution of scattering mechanism of electrons such as ionized and neutral impurities, acoustic phonons, polar and non - polar optical phonons and the space charge effect.

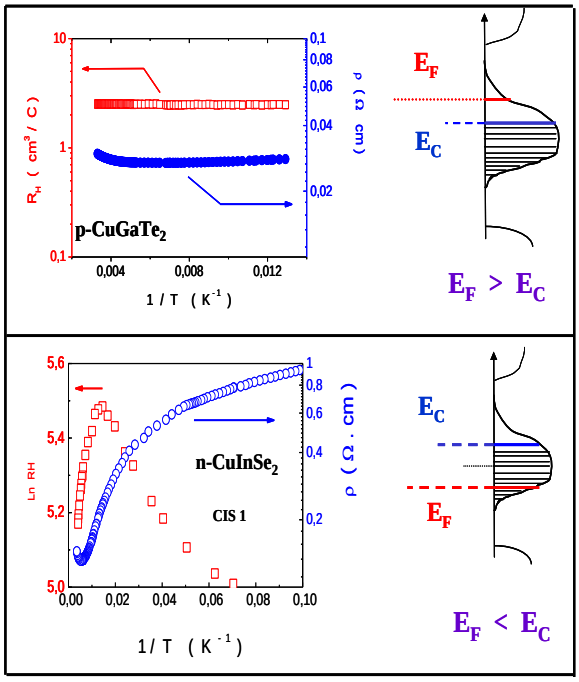

Fig. 3: Variation of the electrical resistivity ρ and Hall coefficient R_H as a function of temperature in p-$CuGaTe_2$ and n-$CuInSe_2$. The relative position of the Fermi level E_F and the mobility edge E_C in the impurity band are indicated.

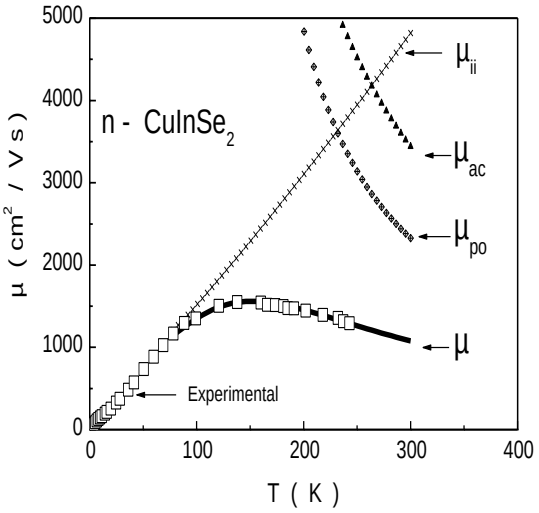

Fig. 4: Experimental and theoretical electrical mobility in $CuInSe_2$ as a function of temperature. The calculated curves μ_{ii}, μ_{ac}, μ_{po} represent the contribution due to the scattering mechanism of electrons by ionized impurities, acoustic phonons and polar optical phonons, respectively. The total mobility is obtained from $\mu^{-1} = \mu_{ii}^{-1} + \mu_{ac}^{-1} + \mu_{po}^{-1}$.

The temperature dependence of the electrical resistivity for other materials like $CuIn_3Te_5$ and $CuGa_3Te_5$, together with $CuInSe_2$, is represented in figure 5. The data show that in the low temperature region, the predominant conduction mechanism is the variable hopping of Mott type. This we can see in figure 6 where the Mott's law $\rho = \rho_o \exp(T_o / T)^{1/4}$ [10,11] is well verified in different temperature ranges. The existence of VRH in these materials in indicative of the strong localization of the impirity electron states in the impurity band formed by shallow intrinsic defects levels.

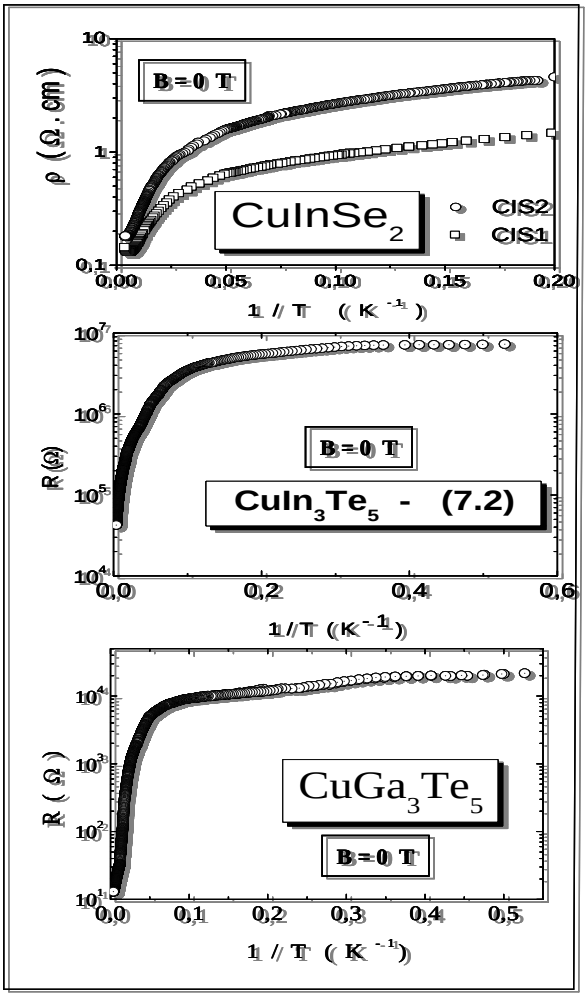

Fig. 5: Variation of electrical resistivity as a function of temperature in two n-type samples CIS1 and CIS2 of $CuInSe_2$ and electrical resistance of $CuIn_3Te_5$ and $CuGa_3Te_5$ in the absence of magnetic field is shown.

IV. Conclusion

In conclusion, it is established that the copper ternaries in addition to being SMART materials for their possible applications in opto-electronic devices such as solar cells are also of great academic interest. This is because they permit us to investigate physical phenomenon that can not be studied easily with elemental and binary compound semiconductors.

A comparative study of the unit cell parameters *a*, *c* and V of the chalcopyrite-related ODCs that can be derived from the formula $Cu_{n-3}(In_{n+1},Ga_{n+1})(Se_{2n},Te_{2n})$, where n = 4, 5, 6, 7, 8 and 9 with their corresponding 1:1:2 phase of Cu-III-VI_2 family, is made. It is established that the decrease in

r_{eff} reduces the dimension of the unit cells in these ODCs.

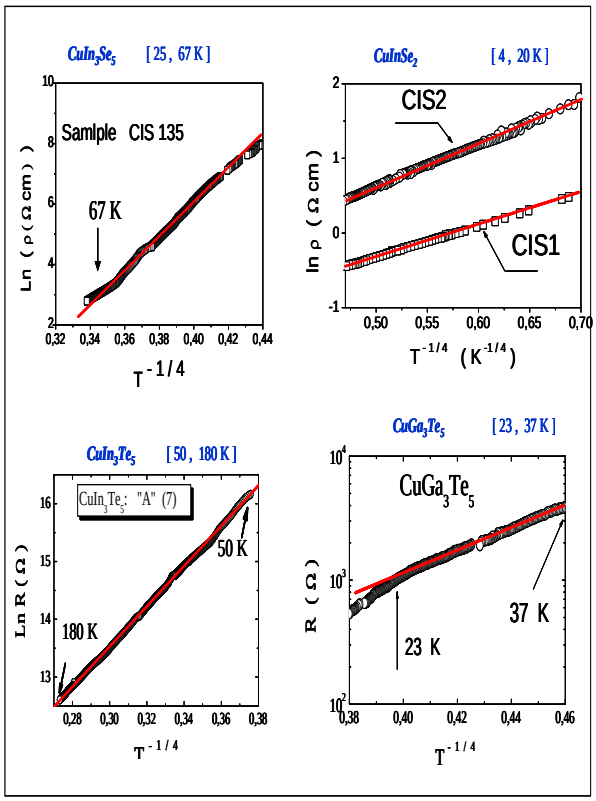

Fig. 6: Variation of electrical resistivity as a function of $T^{-1/4}$ in two n-type samples CIS1 and CIS2 of $CuInSe_2$ and $CuIn_3Se_5$ and electrical resistance of $CuIn_3Te_5$ and $CuGa_3Te_5$ in the absence of magnetic field. Some of the representative temperature ranges where Mott's law is observed, are indicated.

The normalized unit cell parameters (a_{ODC}/a_{112}) and (c_{ODC}/c_{112}) of the selenides and tellurides of Cu-In and Cu-Ga systems of these ODCs fall on universal straight lines. This has important significance and can be used to predict the unit cell parameters of other ODCs, in particular those of the sulphides, that may have chalcopyrite-related structure and have not been reported so far. From the analysis of the temperatura dependence of the electrical resistivity, it is shown that Mott - type variable range hopping is the predominant electrical conduction mechanism at low temperatures on insulator side of the metal insulator transition (MIT).

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