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RESEARCH ARTICLE

DETERMINATION OF THE EXCITONIC RYDBERG ENERGY, THE EXCITON BOHR RADIUS FOR FREE EXCITON ACCORDING TO THE RATIO $[Ga]/([Ga]+[In])$ AND BANDGAP ENERGY IN THE CHALCOPYRITE SOLAR CELL.

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Abstract

In the paper, we studied the evolution of the excitonic Rydberg Energy, the exciton Bohr radius of free electron in the $Cu(In_{1-x}Ga_x)Se_2$ chalcopyrite solar cells for values x= 0; 0.3 and 1**([Ga]/ ([Ga] + [In])**). The study shows that the excitonic Rydberg Energy ($\mathbf{R^*_y}$) and Bohr radius ($\mathbf{a_B}$) move inversely. Indeed R^*_yincrease which x while $\mathbf{a_B}$ decrease which x. Given the approach used, the effective mass of hole and electron of free excitons were also determined as the reduced masse. The evolution of the reduced mass may be related to the performance of the cell. Indeed the greatest reduced mass was obtained for x=0,3 corresponding to the rate where the efficiency is more higher and Cu-poor type.

Introduction:-

Solar cells with$Cu(In_{1-x},Ga_x)Se_2$absorber layers are the leading thin-film technology in terms of conversion efficiencies. Depending on the value of$x = \frac{[Ga]}{[Ga]+[In]}$, there may be different solar cells which the conversion efficiencies different. For the $CuInSe_2$, le $Cu(In,Ga)Se_2$ and $CuGaSe_2$, we obtained the conversion efficiencies between 20% and 22.3% [1].

With a theoretical efficiency of over 30%, these types of cells will be in the future leaders of PV technology. Despite the bright future and the many possible combinations and alloys, the major problem of these cell types is the lack of understanding of internal processes that impact on the final efficiency. [1]

The study of the quality of these cells can be done with different methods of characterization. Among these methods to characterize the photoluminescence can be identified and its variants, which allow to know the quality of each material in terms of defects. This method shows the different types existing transitions in the material. There are: transitions acceptors or donors (DA) and excitonic transitions (EX**) [2].** These excitonic transitionsshows the quality of material and are caused by excitons. The exciton can be defined as an excited state formed an electron-hole pair strongly linked and generated by optical excitation or a double injection of charge carriers. Excitons are often located on a molecule, or part of the chain of a polymer, then it is agreed to consider the exciton as a moving particle, neutral. Therefore, the exciton has a spin following the usual conservation rules.

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The exciton is characterized by its level of electronic energy Eex located in the forbidden band, Bex its binding energy and radius. Bex is inversely proportional to the permittivity of the material and thus the mobility of the charge carriers. There are two types of exciton: that described by Frenkel and described by Wannier. For Frenkel exciton is as strongly related electron-hole pair excitation but can jump from one atom to another. Said Wannier excitons are instead delocalized over several molecules or atoms (free exciton) [3].
Our work aims the determination of the excitonic Rydberg energy, the exciton Bohr radius for free exciton and this evolution according the stoichiometry and bandgap energy.

Model utilisize:-

We use the result of low-field perturbation approach and the hydrogenic model. To be able to determine the characteristics of the exciton, we initially will determine the hole and electron effective mass of the free exciton and then will determine the reduced mass of this one.

Effective mass of electron and hole:-

In solid state Physics, the effective mass is defined by the tensor of order 2 of the derivative second of energy E compared to the vector of wave k:

$$\frac{1}{m_{ij}} = \frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k_i\, \partial k_i} \quad (\mathbf{1})$$

According to the dynamics of Bloch, the effective mass of the electron and hole are given by [4]:

$$m_e^* = \hbar^2 \left(\frac{\partial^2 E_n}{\partial \vec{k}^2}\right)^{-1} \quad (\mathbf{2})$$

$$m_e^* = -m_t^* \mathbf{(3)}$$

In this paper we have another approach of calculation, resulting from results of other research.

Effective mass of electron:-

Given the working Clas Pearson **[5],** the relation binding the effective mass of Cu(In_{1-}xGax)Se2 to the free electron mass and to x is given by:

$$me\ [Cu(In_{1-x}Ga_x)Se_2 = me\ (CuInSe2) + (0.05x)m0 \mathbf{(4)}$$

$$wich \mathbf{me\ (CuInSe_2) = 0.09\ m0} \quad \mathbf{(5)}$$

$$me\ [Cu(In_{1-x}Ga_x)Se_2] = 0.09\ m0 + (0.05x)m0 = [0.09 + 0.05x]\ m0 \quad \mathbf{(6)}$$

m0: free electron mass, me: effective mass

Using the relation **(4)** and varying x to 0, 0.3 and 1, the values obtained of me are mentioned in the table **1**:

Table 1:-Values of effective mass according to x.

x	Cu(In_{1-x} Gax)Se2	me
0	$CuInSe_2$	$0.09 \times m_0$
0.3	Cu $In_{0.7}Ga_{0.3}$ Se_2	$0.105 \times m_0$
1	$CuGaSe_2$	$0.14 \times m_0$

Effective mass of hole:-

The effective mass of hole to CuGaSe2 was given in the ref **[6].** The value of effective mass hole is$m_h = 0.64\ m_0$.For the CuInSe2 the effective mass is $m_h = 0.71\ m_0$**[7].**
For the effective mass of hole in Cu $In_{0.7}Ga_{0.3}$ Se_2, we used the relation binding the density states in the valence band Nv and the effective masse of holem_h^*. It's given as follows:

$$N_V = 2\left(\frac{2\pi m_h^* k_B T}{h^2}\right)^{3/2} \quad (\mathbf{8})$$

$$m_h^* = \frac{(2N_V)^{2/3} \times h^2}{2\pi k_B T} \quad (\mathbf{9})$$

$\boldsymbol{N_V}$ ($CuIn_{0.7}Ga_{0.3}Se_2$) based in the literature is equal a 9.10^{18} cm^{-3}**[8].**
k_B: Boltzmann constant ($1{,}38.10^{-23}$ $J.K^{-1}$)

T: Temperature Kelvin (K^{-1}) ;h: Planck Constant (J.s).
The table 2 summarizes the different values of effective mass of hole (**mh)** to free exciton.

Table 2:-Mass effective of hole to free exciton for $CuInSe_2$, Cu $In_{0.7}Ga_{0.3}$ Se_2 and $CuGaSe_2$

x	$CuIn_{1-x}Ga_xSe_2$	mh
0	$CuInSe_2$	$0.71 \times m_0$
0.3	Cu $In_{0.7}Ga_{0.3}$ Se_2	$1.27 \times m_0$
1	$CuGaSe_2$	$0.64 \times m_0$

Reduced mass:-

The reduced mass is done by relation:

$$\mu = \frac{m_e m_h}{m_e + m_h} (\mathbf{10})$$

All results are mentioned in the table 3.
Table 3:-Reduced mass for free exciton for $CuInSe_2$, Cu $In_{0.7}Ga_{0.3}$ Se_2 and $CuGaSe_2$

x	$CuIn_{1-x}Ga_xSe_2$	μ
0	$CuInSe_2$	0.179 x m_0
0.3	Cu $In_{0.7}Ga_{0.3}$ Se_2	0.118 x m_0
1	$CuGaSe_2$	0.115 x m_0

ExcitonicRydberg energy, Bohr radius and band energy:-

Excitonic Rydberg energy:-

The model of reference often used is an alternative of the photoluminescence. It is the magnetoluminescence with magnetic field. The energy of a magnetic dipole in a magnetic field is proportional to B, involving a total quadratic dependence of excitonic energy compared to B in the area of the weak magnetic field in the following way[9]:

$$E_n(B) = E_n(0) + \sigma\left(\frac{5n^4 + n^2}{6}\right)B^2 (\mathbf{11})$$

If i considered the first-order perturbation approach used (n=1) to evaluate the dependence of diamagnetic energy shifts ΔEdwe obtained:

$$\Delta E_d = E(B) - E(0) = \sigma B^2 (\mathbf{12})$$

Where E(0) is the zero-field spectral position of the exciton peak and σ, the rate of the shift. Expression of σ is $\frac{\hbar^4 \varepsilon^2}{4C^2 \mu^3 e^2}$. The exciton energy decreases whichmagnetic field intensity [**6]**.The excitonic Rydberg energy is given by the next formula [**6]**

$$R_y^* = 13.6\ eV \times \frac{\mu}{m_0} \times \frac{1}{\varepsilon^2} (\mathbf{13})$$

Where μ **the reduced mass, m_0 free electron mass and ε the dielectric constant.**

The results of calculations using the relation is mentioned in table 4.
Table 4:-Excitonic Rydberg energy to free exciton forCuInSe2, Cu $In_{0.7}Ga_{0.3}$ Se_2 and CuGaSe2

x	$CuIn_{1-x}Ga_xSe_2$	ε	μ	R_y^***(meV)**
0	$CuInSe_2$	11.3	$0.079 \times m_0$	8.41
0.3	Cu $In_{0.7}Ga_{0.3}$ Se_2	13.6	$0.118 \times m_0$	8.67
1	$CuGaSe_2$	11	$0.115 \times m_0$	12.92

Exciton Bohr radius:-

Using the relation from in the paper [**7**] given the relation of Exciton bohr radius:

$$a_B = \frac{a_B^H \times m_0 \times \varepsilon}{\mu} (\mathbf{14})$$

Where a_B^H the bohr radius of Hydrogen and ε the dielectric constant. The results of a_B are given in the table 5.

Table 5: Exciton Bohr radius for the free exciton in $CuInSe_2$, Cu $In_{0.7}Ga_{0.3}$ Se_2 and $CuGaSe_2$

x	$CuIn_{1-x}Ga_xSe_2$	ε	μ	$a_B\ (nm)$
0	$CuInSe_2$	11.3	$0.079 \times m_0$	7.58
0.3	Cu $In_{0.7}Ga_{0.3}$ Se_2	13.6	$0.118 \times m_0$	6.1
1	$CuGaSe_2$	11	$0.115 \times m_0$	5.1

Energy band:-

Referring to the work of Tinoco and al. [10], the energy gap is given by the relation:

$$E_g(y) = (1.620 - 0.840\,y + 0.175\,y^2)(eV)(\mathbf{15})$$

Where y= 1-x. By varying x from 0, 0.3 to 1, we obtained the table 6:

Table 6:-Bandgap Eg according to x.

x	y	$CuIn_{1-x}Ga_xSe_2$	Eg (eV)
0	1	$CuInSe_2$	0.955
0.3	0.7	Cu $In_{0.7}Ga_{0.3}$ Se_2	1.118
1	0	$CuGaSe_2$	1.620

Results and Interpretation:-

The results of all calculations are mentioned in the table 7.

Table 7:-Recapitulative of all results.

x	$CuIn_{1-x}Ga_xSe_2$	me	mh	μ	ε	$a_B\ (nm)$	R^*_y(meV)	Eg (eV)
0	$CuInSe_2$	$0.09 \times m_0$	$0.71\times m_0$	$0.079 \times m_0$	11.3	7.58	8.41	0.955
0.3	Cu $In_{0.7}Ga_{0.3}$ Se_2	$0.105 \times m_0$	$1.27\times m_0$	$0.118 \times m_0$	13.6	6.1	8.67	1.118
1	$CuGaSe_2$	$0.14\times m_0$	$0.64\times m_0$	$0.115 \times m_0$	11	5.1	12.92	1.620

Effective and reduced mass:-

The effective mass of the electron to the free exciton increases a function of x. If x increases, increases like we shown in Figure 1.

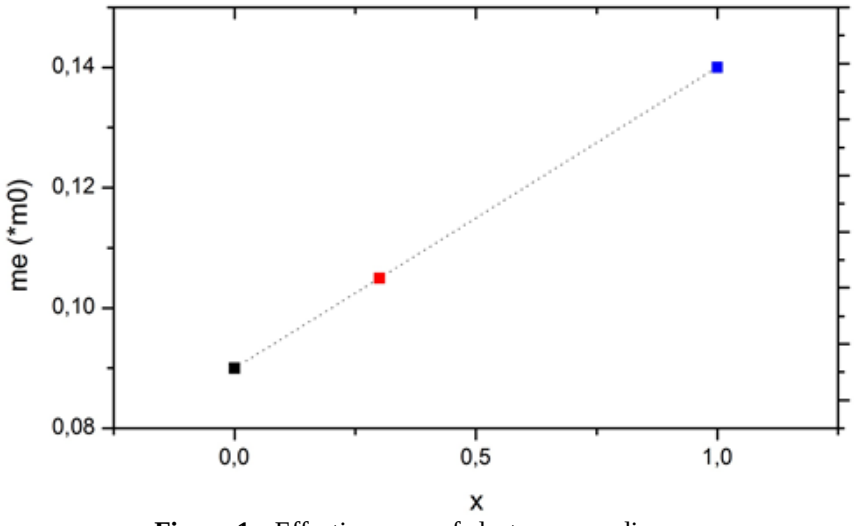

Figure 1:- Effective mass of electron according x.

The effective mass of the electron to the free exciton in CuInSe2 is less than that in $CuIn_{0.7}$ $Ga_{0.3}$ $Se_2$and $CuGaSe_2$. There is another variation curve for the effective mass of the free exciton hole (Figure 2). For this case, the maximum value is obtained for $CuIn_{0.7}Ga_{0.3}Se_2$, and a value for the $CuInSe_2$ greater than that of $CuGaSe_2$.

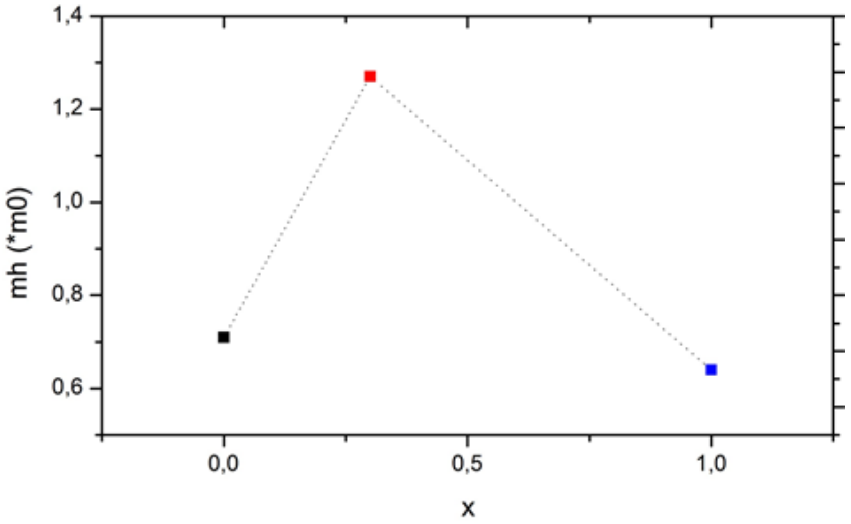

Figure 2:- Effective mass of holes according x.

The same type of evolution is observed for the reduced mass (Figure 3). Indeed the mass is again much higher for $CuIn_{0.7}Ga_{0.3}Se_2$.

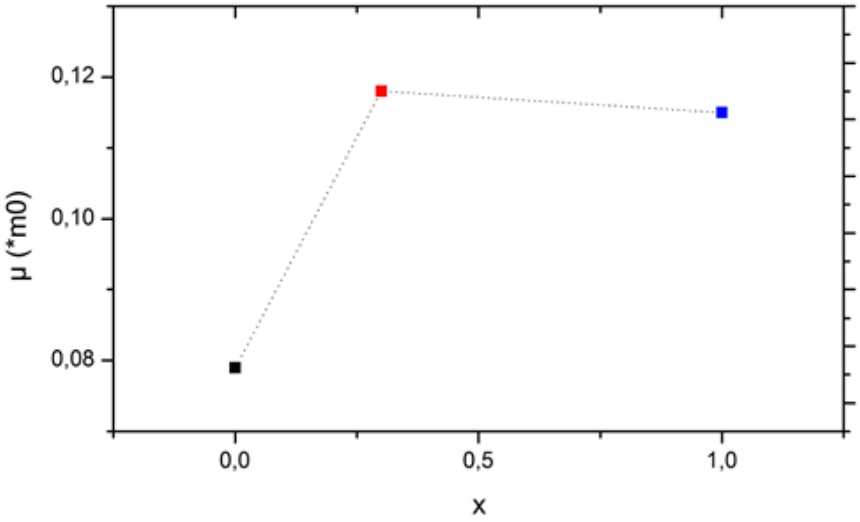

Figure 3:- Reduced mass of hole according to x

Can bind the evolution of the mass reduced to the performance of these cell types. The best performance is obtained for Cu $In_{0.7}Ga_{0.3}Se_2$ and which is a cell with Cu-poor absorber.

Bohr raduis and Exciton Rydberg Energy:-

By varying the value of x from 0,0.3 to 1, we see that the exciton Bohr radius of the exciton free decreases (Figure 4). The radius of the exciton in $CuInSe_2$ is much greater than that in the $CuIn_{0.7}Ga_{0.3}Se_2$ and $CuGaSe_2$.

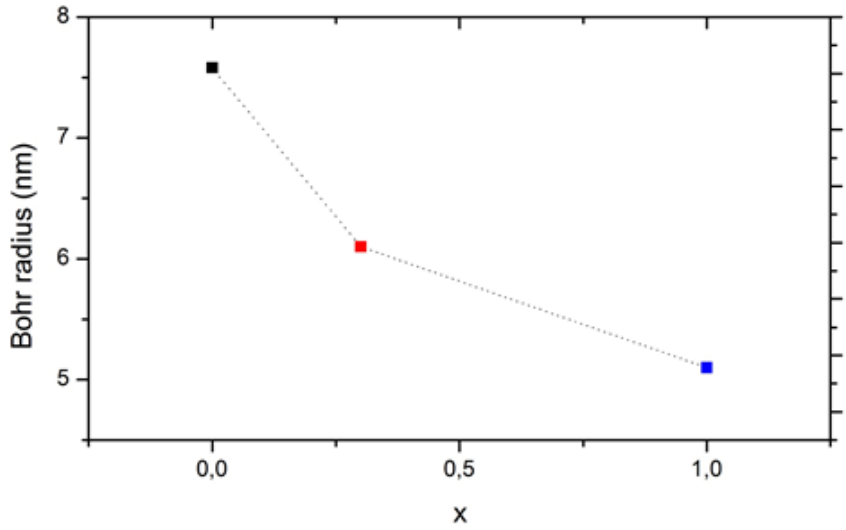

Figure 4:- Bohr raduisaccording x.

For the exciton Rydberg Energy, we note the oppose effect (**figure 3**). Indeed the exciton Rydberg Energy is much higher when x = 1 and corresponding a CuGaSe2. If increase, R^*_y increase too. X and R^*_y **varies together.** The value of x is related to the rate Ga. One can say that the addition of Ga decreases the radius of bohr and increases the excitonic Rydberg Energy of exciton.

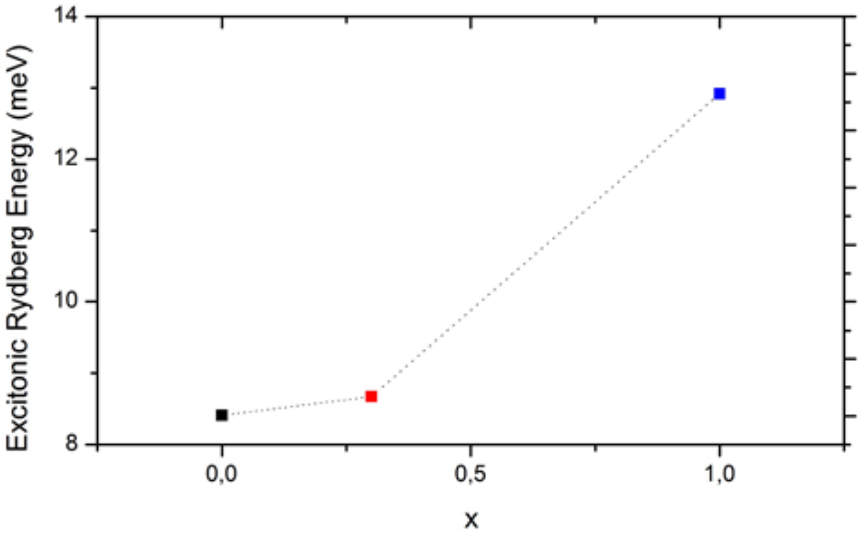

Figure 5:-Excitonic Rydberg Energy according the stoichiometry.

Bohr radius a_B and Excitonic Rydberg Energy R^*_y according to Bandgap Eg:-

The addition of Ga on CuInSe2 also affects the energy gap by increasing it. Eg increases with [Ga] / ([Ga] + [In]). The evolution of the parameters of the exciton with x being already studied, and given also that Eg increases with x, the relationship between Eg and the exciton parameters can be established easily.

Thus the evolution of Excitonic Rydberg Energy in function of Eg is given by Figure 6, and we note that it evolves with x.

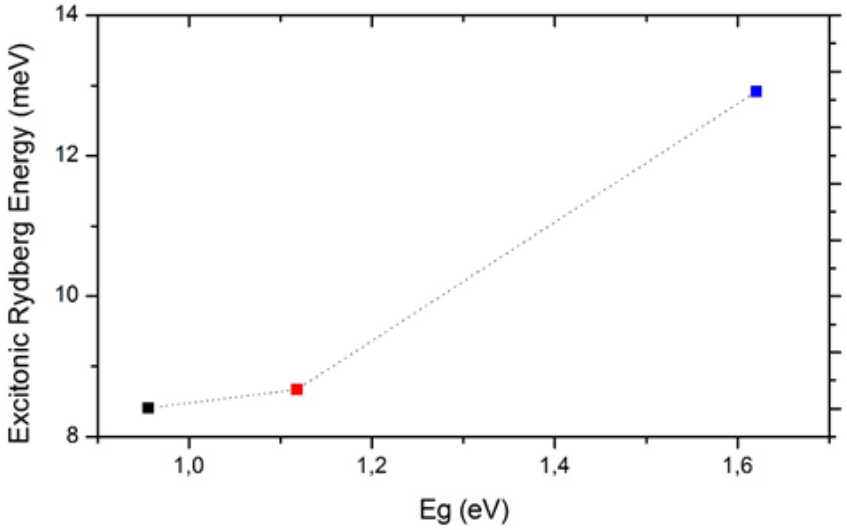

Figure 6:-Excitonic Rydberg Energy according the bandgap energy.

Excitonic Rydberg Energy is related to the bandgap. If the bandgap is high, this energy is high. This trend was deductible because the exciton is a state between the conduction band and valence band (gap of Energy), and these two bands are far more space for the formation of the exciton is great.

We note a Bohr radius of evolution according to Eg contrary to that of excitonic Rydberg Energy (Figure7). Indeed the Bohr radius decreases with increasing Eg.

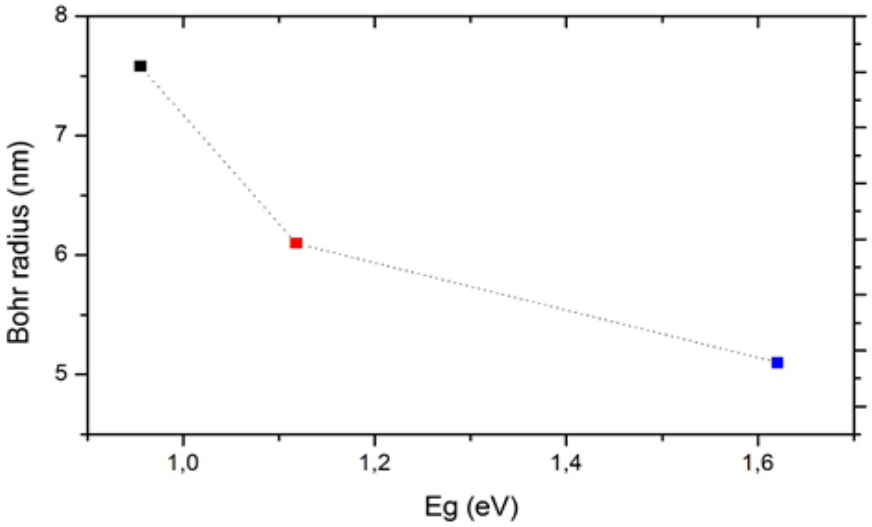

Figure 7:-Bohr radius according the bandgap energy.

Conclusion:-

Based on previous results, we can conclude that the performance of these types of cells depends on the reduced mass and the bigger it is the more the performance of the cell are large. The evolution to the performance cannot be directly related to the bohr radius of and exciton Rydberg energy. We found that for the best cell ($CuIn_{0.7}Ga_{0.3}Se_2$), the characteristics of the exciton (R^*_y and aB) are free intermediate to the other two respectively corresponding to x = 0 and x = 1. Compared to the gap, the exciton bohr radius a_B increases inversely with the energy gap and R^*_y increases with the energy gap.

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References:-

1. White paper for CIGS thin film solar cell technology 2015
2. S. Siebentritt, L. Gütay, D. Regesch, Y. Aida, V. Deprédurand.2013. Why do we make Cu(In,Ga)Se_2 solar cells non-stoichiometric? Journal Solar Energy Materials & Solar Cells 119 (2013) 18–25.DOI.org/10.1016/J.SOLMAT.2013.04.014
3. Excitons Excitons – Types, Energy Transfer Types, Energ.2003 –Hangout.Organic Optoelectronics - Lecture 7
4. Cours dynamique de bloch (Chapitre 4), Grenoble Inp
5. Clas Persson.2008.Anisotropic hole-mass tensor of $CuIn_{1-x}Ga_x(S,Se)_2$: Presence of free carriers narrows the energy gap.Appl. Phys. Lett. 93, 072106; DOI: 10.1063/1.2969467
6. F. Luckert,M. V. Yakushev,C. Faugeras, A. V. Karotki, A. V. Mudryi, R.W Martin.2010.Diamagnetic shift of the A free exciton in CuGaSe2 single crystals. APPLIED PHYSICS LETTERS **97**, 162101.DOI:10.1063/1.3502603.
7. F. Luckert,M. V. Yakushev,C. Faugeras, A. V. Karotki, A. V. Mudryi, R.W Martin.2010.Excited states of the free excitons in CuInSe2 single crystals.APPLIED PHYSICS LETTERS **97**, 152110.DOI:10.1063/1.3502603.
8. Roland Scheer, Hans-Werner Schock.2011.Chalcogenide Photovoltaics Physics, Technologies, and Thin Film Devices.WILEY-VCH Verlag& Co. KGaA.ISBN: 978-3-527-31459-1.
9. S. Taguthi, T. Goto, M. Takeda and G. Kido.1988.Magneto-optical effects of the wannier exciton in the biaxial ZnP2 Crystal.I. Journal of the physical Society of Japon. Vol 57 n°9,pp 3256-3261.
10. T. Tmoco, C. Rincon, M. Quintero and G. S Perez.1991. Phase Diagram and Optical Energy Gaps for $CuIn_yGa_{1-y}Se_2$alloys.Phys. stat. **sol.** (a) **124,** 427