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## Photoconductivity in the ordered vacancy compound $\text{CuIn}_7\text{Se}_{12}$

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### ABSTRACT

Photoconductivity measurements are done in the temperature range 10K to 300K on thin films of the off-tie line ordered vacancy compound  $\text{CuIn}_7\text{Se}_{12}$  which incorporates a single pair of the defect complex ( $2V_{\text{Cu}} + \text{In}_{\text{Cu}^{++}}$ ) and two neutral Cu vacancies in every 6 units of  $\text{CuInSe}_2$ . The rapid increase in photoconductivity on illumination and the rapid decay of conductivity on removal of illumination in the transient photoconductivity curves are explained as a consequence of the reduction in inter grain potential barrier on illumination and its restoration on removal of illumination. The non-exponential long-term decay observed is suggestive of a deep level trap-emptying process associated with the decay process. The temperature dependence of photosensitivity and the decay constants of the material are investigated. Analysis of dark conductivity and steady state photoconductivity measurements yielding the variation of barrier height from 0.09 eV to 0.0024 eV is found to corroborate the inferences from transient photoconductivity. Photoluminescence and spectral response measurements are done to obtain information regarding the defects present in the samples.

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### KEYWORDS

Ordered vacancy compound;  
Photoluminescence;  
Photoconductivity;  
Solar cell materials;  
Spectral response.

### INTRODUCTION

In recent years, the I-III-VI chalcopyrite compounds have attracted great attention not only due to the tremendous possibility of these compounds in photovoltaic applications but also due to the fact that their opto-electronic properties can be tailored by varying their stoichiometry<sup>[1-3]</sup>. The extreme limit of their off-stoichiometry is manifested by the existence of a series of non-stoichiometric stable compounds like  $\text{CuIn}_5\text{Se}_8$ ,  $\text{CuIn}_3\text{Se}_5$ ,  $\text{CuIn}_2\text{Se}_{3.5}$  etc whose formation can be explained as due to the presence of a single

pair of the defect complex ( $2V_{\text{Cu}} + \text{In}_{\text{Cu}^{++}}$ ) in definite number of units of  $\text{CuInSe}_2$ . With the success of exploiting the junction between p- $\text{CuInSe}_2$  (CIS) and the Ordered Vacancy Compound (OVC)  $\text{CuIn}_3\text{Se}_5$  as the active pn-junction for solar cell<sup>[4]</sup>, the investigations on the photoconducting properties of CIS related OVC's like  $\text{CuIn}_5\text{Se}_8$ ,  $\text{CuIn}_3\text{Se}_5$ ,  $\text{CuIn}_2\text{Se}_{3.5}$  etc. have gained significant interest<sup>[5-7]</sup>. But no reports are available to the best of our knowledge, on the photoconducting properties of the off-tie line compound  $\text{CuIn}_7\text{Se}_{12}$  which incorporates two neutral Cu vacancies in addition to a single pair of the defect com-

plex ( $2V_{Cu^{+}} + In_{Cu^{++}}$ ) in every 6 units of  $CuInSe_2$ <sup>[4]</sup>.

The present paper reports the studies on the photoconducting properties of the OVC  $CuIn_7Se_{12}$ , which can be considered as a better candidate for solar cell fabrication due to its enhanced optical band gap in comparison to that of  $CuIn_3Se_5$  which has been found to be a successful n-counterpart in solar cells<sup>[5,6]</sup>. Studies are done on transient photoconductivity, steady state photoconductivity and spectral response of the films at room temperature and temperatures down to 10K. The photoluminescence spectra at room temperature together with the spectral response curves have been used to study the possible defect transitions in the compound films.

## EXPERIMENTAL

Thin films of  $CuIn_7Se_{12}$  (thickness  $\sim 0.3$  to  $0.4 \mu m$ ) were deposited on optically flat soda lime glass substrates at a temperature of about 650 K by multisource co- evaporation technique, by a modified form of Gunther's three temperature method. The preparation and the preliminary characterization techniques of the films are reported elsewhere<sup>[3,6]</sup>.

Photoconductivity measurements were done loading the sample in a CIT cryostat and cooling down to 10K initially. Silver electrodes of uniform thickness applied at the ends of the samples with a spacing of 0.3 cm between them for illumination were ensured to be ohmic by taking I-V measurements. To check for any photoconductivity saturation effect, the photocurrents at different illumination intensities from  $50 mW/cm^2$  to  $110 mW/cm^2$  were measured using a Keithley 236 source measurement unit and a 100W Oriel quartz halogen source for illumination. The transient photoconductivity measurements at intensity of illumination  $100 mW/cm^2$  and at various fixed temperatures from 10 K upwards were done during the heating cycle. After ensuring a linear response in the voltage range 5V to 30V, the current measurements at a d.c voltage of 10V were taken for calculations. The steady state photoconductivity measurements were also performed in the heating cycle from 10K upwards, keeping the temperature steady at the required, pre-determined value using a Lakeshore programmable temperature controller. During the spectral response studies, the source was ad-

ditionally coupled with an Oriel 7240 grating monochromator for varying the incident energy in the required range. The dark current measurement for photosensitivity determination was also done using the same set up before illuminating the samples. PL measurements were carried out at room temperature with a Nd-Yag frequency doubled 532nm laser. The analysis and recording of the PL signal was done using NIR 512 spectrophotometer Ocean optics and OOI base 32 software respectively.

## RESULTS AND DISCUSSION

The X-ray diffraction (XRD) and the X-ray energy dispersive analysis (EDAX) of the films clearly revealed the formation of the OVC  $CuIn_7Se_{12}$ . The XRD pattern indicating characteristic reflection of the OVC from (110) plane and reflection from (103) plane characteristic of chalcopyrites is shown in Figure 1. EDAX spectrum of the compound showing a % composition Cu:In:Se = 5:36:59 is given in Figure 2.

The transient photoconductivity behaviour of a typical  $CuIn_7Se_{12}$  film at an illumination intensity of  $100 mW/cm^2$  at different temperatures between 10K and 300K is represented in Figure 3 The transient photoconductivity curve is observed to have a sharp rise in conductivity on illumination and a fast decay followed by a slow decay process on removal of illumination. In general, the manifestation of the photoeffect in a polycrystalline material will be reflected in the production of additional minority carriers in the

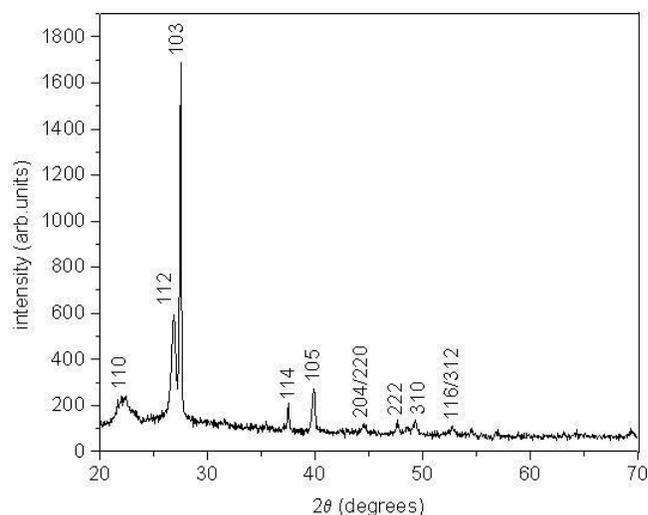
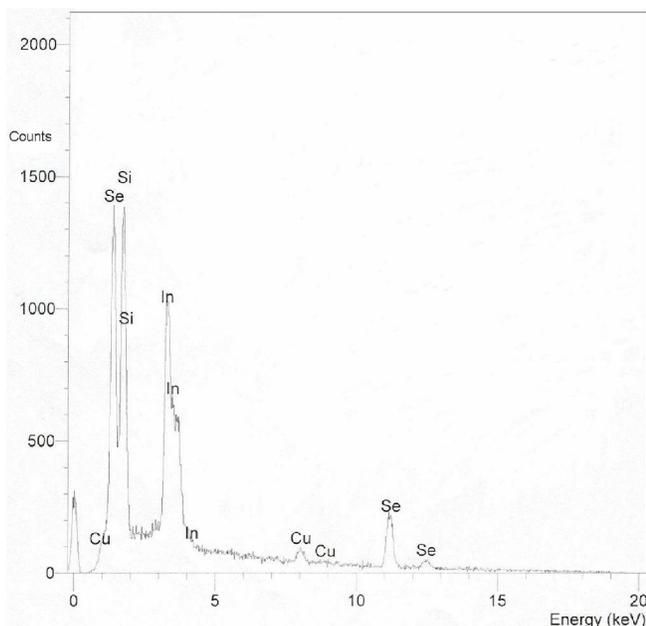
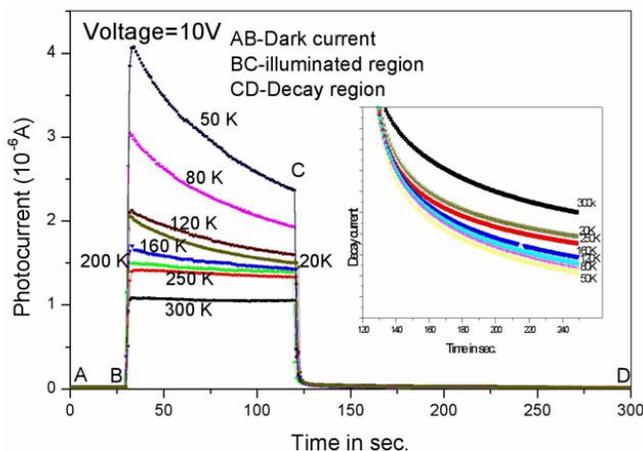


Figure 1 : X-ray diffraction pattern on a typical  $CuIn_7Se_{12}$  film.

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**Figure 2 :** Energy dispersive X ray analysis spectrum for composition determination of the films. K-ray for Cu and L-rays for In and Se are used in the analysis



**Figure 3 :** Transient photoconductivity on a  $\text{CuIn}_7\text{Se}_{12}$  film. Inset shows decay of the transient photoconductivity.

material along with a reduction ( $\Delta E_{b\phi}$ ) of the intercrystalline barrier height ( $E_b$ ) due to the exposure to the incident radiation of intensity  $\phi$ , so that the change in conductivity can be expressed as

$$\Delta\sigma = \sigma_{\phi} - \sigma_d = \Delta\sigma_n + \Delta\sigma_{Eb}$$

where  $\sigma_{\phi}$  is conductivity on illumination,  $\sigma_d$  is dark conductivity,  $\Delta\sigma_n$  represents the change in conductivity due to additional carriers created and  $\Delta\sigma_{Eb}$  corresponds to the change in conductivity due to change in the barrier potential  $\Delta E_{b\phi}$  [8,12].

Now the equation may be written as

$$\Delta\sigma = q\mu_0(n+\Delta n) \exp(-E_b/kT) \exp(\Delta E_{b\phi}/kT) - q\mu_0 n \exp(-E_b/kT)$$

$$\Delta\sigma = q\mu_0 \exp(-E_b/kT) [\exp(\Delta E_{b\phi}/kT)(n+\Delta n) - n]$$

so that

$$\Delta\sigma_n = q\mu_0 \Delta n \exp(-E_b/kT)$$

and

$$\Delta\sigma_{Eb} = q\mu_0 n [\exp(\Delta E_{b\phi}/kT) - 1] \exp(-E_b/kT)$$

$$\Delta\sigma_{Eb} = \sigma_d [\exp(\Delta E_{b\phi}/kT) - 1]$$

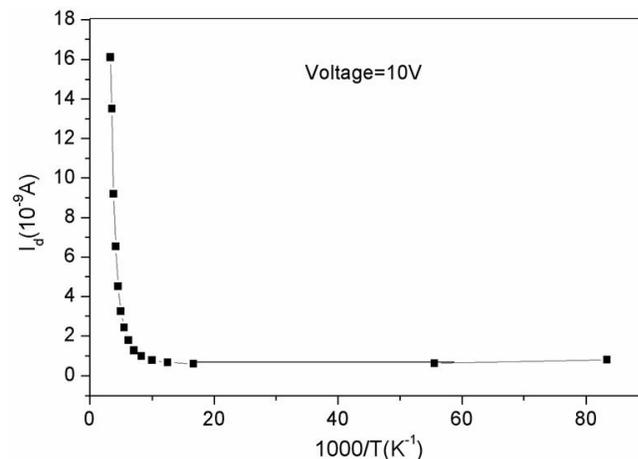
If the effect of change in majority carriers can be considered insignificant, the electrical conductivity on illumination is given by

$$\sigma_{\phi} = (q^2 n L) / (2\pi m e^* K T)^{1/2} \exp\{-E_{b\phi} / K T\}$$

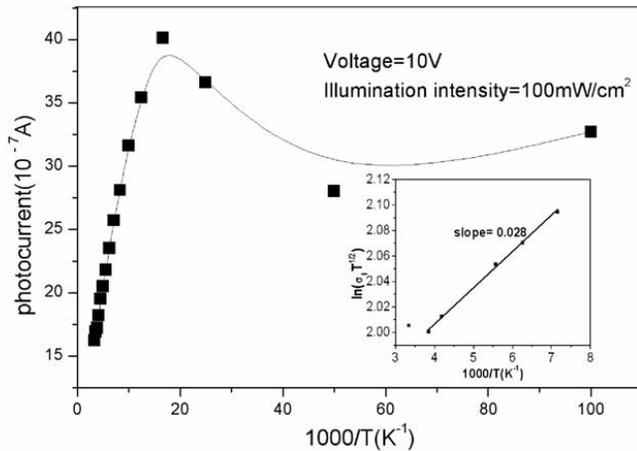
where  $E_{b\phi}$  is the potential barrier height on illumination,  $T$  is the absolute temperature,  $n$  is the carrier concentration and  $L$  is the grain width [8-12].

The comparison of inter grain barrier height (around 0.09 eV) from dark conductivity plots in Figure 4 with the barrier height (around 0.0024 eV) from steady state photoconductivity plots in Figure 5, which were evaluated by plotting  $\ln(\sigma_{\phi} T^{1/2})$  versus  $1000/T$  graphs (Figure 5 inset) indicated reduction in barrier height on illumination in these films. This could also be the reason for the fast rise in photocurrent on illumination in the transient curves since the potential barrier height reduction on illumination makes the conducting grains electrically "better connected" among them, due to the photo generated hole flux arriving to the inter-grain region, thus increasing the tunneling probability of electrons through the barrier [11]. The fast decay is determined by the fast inter-grain barrier recovery as the hole flux arriving at the intergrain region suddenly ceases on removal of illumination.

The slow decay region is analyzed with the pur-



**Figure 4 :** Dark current variation with temperature in  $\text{CuIn}_7\text{Se}_{12}$  film.



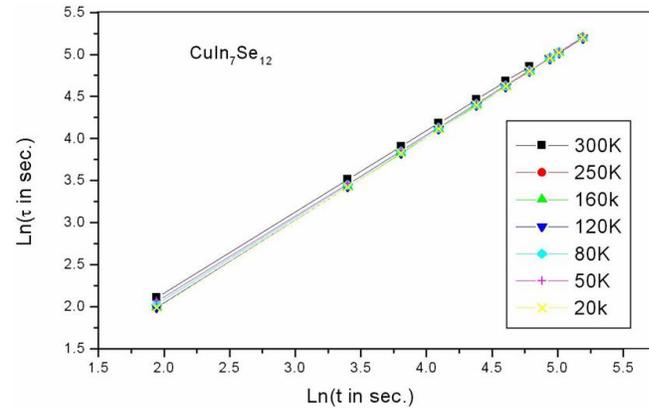
**Figure 5 :** Variation of steady state photocurrent with temperature in  $\text{CuIn}_7\text{Se}_{12}$  film. Inset shows  $\ln(\sigma_0 T^{1/2})$  versus  $1000/T$  graph for barrier height determination on illumination.

pose of obtaining the decay time constants and it is found that the curves could not be fitted with a simple exponential function but are time dependent, indicating the involvement of sustained trap emptying processes. A possible origin of such a trap in the OVC films is the donor defect  $\text{In}_{\text{Cu}}$  0.23 eV to 0.27 eV below the conduction band minimum, the occurrence of which is in conformity with the structural and compositional studies<sup>[6]</sup> and agrees very well with the presence of the complex  $(2V_{\text{Cu}} + \text{In}_{\text{Cu}++})$  in this defect compound..

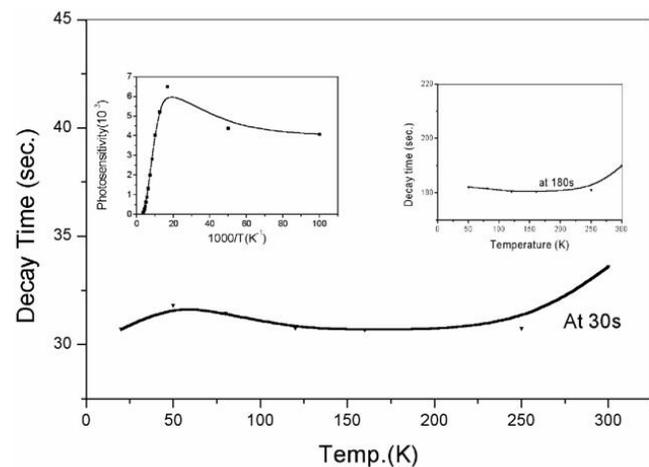
The non- exponential decay process is analyzed using the differential life- time concept suggested by Fuhs et al<sup>[12]</sup>. The life- time  $\tau_d$  is calculated using the equation  $\tau_d = -[I_{\text{ph}} \times (dI_{\text{ph}} / dt)]^{-1}$  where  $I_{\text{ph}}$  is the maximum photocurrent at  $t=0$  for a given applied voltage.

The life-time from the decay curve is found to vary with time for the OVC and the dependence of  $\tau_d$  on time (t) is represented in the  $\ln(\tau_d)$  versus  $\ln(t)$  plot in Figure 6. The variation of lifetime with temperature at 30s and 180s after cutting off the illumination is represented in Figure 7. The lifetime is found to decrease with decrease in temperature up to around 180K while below that the decay behaviour in the films does not show a particular dependence on temperature. It can be assumed that the temperature independent decay at low temperatures is due to localized- localized recombination process for which no thermal activation is necessary<sup>[13]</sup>. Further, the variation in photosensitivity  $((I_{\text{ph}} - I_d)/I_d)$  with change in temperature shown in Figure 7

inset2, indicates that  $\text{CuIn}_7\text{Se}_{12}$  is a photosensitive compound and the photoconductivity is found to be temperature dependent except at very low temperatures as indicated by the variation of decay constant with temperature.



**Figure 6 :** Variation of  $\ln(\tau_d)$  with  $\ln(t)$  at different temperatures on  $\text{CuIn}_7\text{Se}_{12}$  film.



**Figure 7 :** Variation in decay time with temperature at time 30s after cutting off illumination. Inset 1 shows variation in decay time with temperature at time 180s after cutting off illumination. Inset2 shows variation of photosensitivity with temperature in  $\text{CuIn}_7\text{Se}_{12}$ .

In the photoluminescence spectrum of  $\text{CuIn}_7\text{Se}_{12}$ , a peak of 5 meV FWHM at 1.113eV and another sharp peak of 3meV FWHM at 0.755 eV are seen as in Figure 8. Keeping in mind that the band gap estimated for the compound  $\text{CuIn}_7\text{Se}_{12}$  is 1.37eV<sup>[6]</sup>, the emission at 1.113eV with difference of 257meV from the band to band energy gap can be considered to have their origin from a radiative D-A pair recombination between the donor defect state  $\text{In}_{\text{Cu}+}$  which is assumed to have activation energy around 250meV and the acceptor state  $V_{\text{Cu}}$  verified by different investigators to have an acti-

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vation energy ranging from 10-50meV<sup>[14]</sup>. Selenium vacancies also have the donor levels at the same position but transition from  $\text{In}_{\text{Cu}}$  has more probability in the OVC samples where the ordered arrangement of defect  $\text{In}_{\text{Cu}}$  and  $\text{V}_{\text{Cu}}$  is always expected<sup>[15]</sup>. Further, according to the composition determination through energy dispersive analysis by X-rays, the samples are slightly In-rich which adds to the possibility of presence of the defect  $\text{In}_{\text{Cu}}$  having a lower formation energy  $\sim 1.4$  eV compared to the possibility of presence of  $\text{V}_{\text{Se}}$  with formation energy 2.4 eV in the OVC.<sup>[16]</sup> The result is in good agreement with the spectral photoconductivity studies where the photoactive transition peak around 1.1eV which is observed in  $\text{CuIn}_7\text{Se}_{12}$  films can be said to involve the same defect states  $\text{In}_{\text{Cu}}$  and  $\text{V}_{\text{Cu}}$ <sup>[6]</sup>. In spec-

tral response (PC) studies, especially at low temperatures (Figure 9) a broad photoactive band is observed in the energy range  $\sim 0.75\text{eV}$  to  $0.9\text{eV}$ , and a comparison of the PL and PC gives rise to the speculation that the defect states involved behind the PL peak observed near  $0.75\text{eV}$  at room temperature might be the same as that behind the broad band transition observed in the PC. There is a possibility that as the OVC is more In-rich and more deficient in Cu than in  $\text{CuInSe}_2$ , the donor level may be becoming more spread out in the former, where as the levels are usually observed at  $0.34$  eV and  $10\text{-}50\text{meV}$  in the latter, so that a D-A transition between the two levels in the OVC can give a PL peak at  $0.75\text{eV}$ .

The analysis of the PC measurements together with the observed optical band gap  $\sim 1.37\text{eV}$ <sup>[6]</sup> in the OVC compound establishes its potential to be a successful n-counterpart with P-CIS in the fabrication of highly efficient solar cells since the junction formed can have better lattice matching too.

## CONCLUSION

The steady state and transient photoconductivity experiments together throw light on some of the possible process that leads to the photoactive behaviour of the OVC  $\text{CuIn}_7\text{Se}_{12}$ . The photoluminescence and spectral response measurements are in support of the structural and compositional characterization of these films vindicating the defect complex formation in these compounds. The n-type compound is found to be highly photosensitive and thus useful as the wide band gap n-layer in solar cell fabrication.

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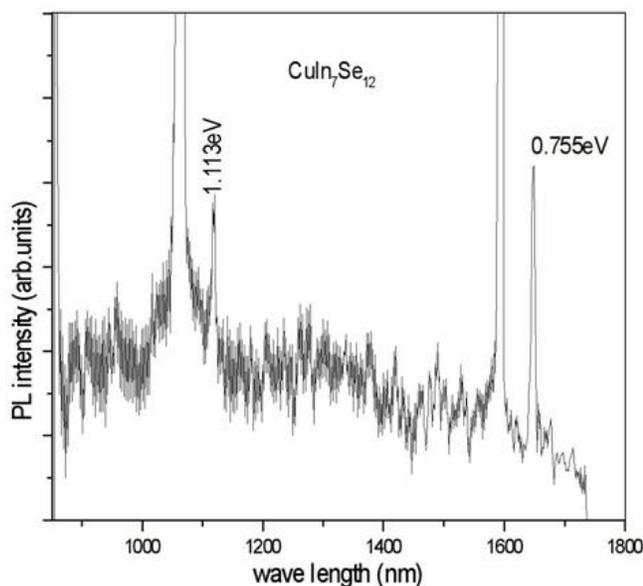


Figure 8 : PL spectrum on  $\text{CuIn}_7\text{Se}_{12}$  at room temperature.

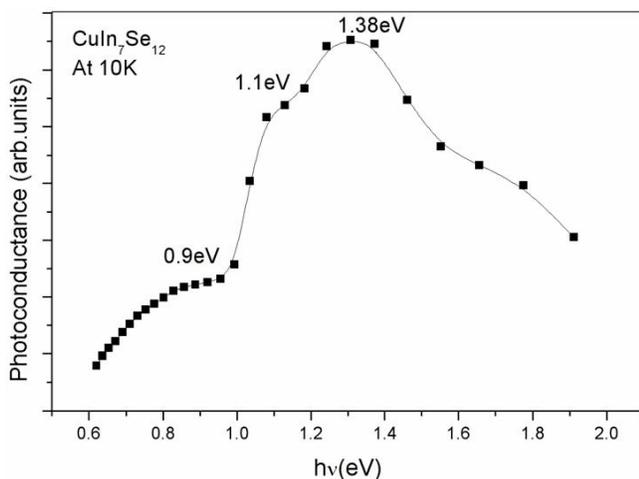


Figure 9 : Spectral response on  $\text{CuIn}_7\text{Se}_{12}$  at 10K.

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