Solvothermal Synthesis and Characterisation of Chalcopyrite Copper Indium Diselenide (CIS) Nanostructures.

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ABSTRACT *Crystalline chalcopyrite semiconductor CuInSe2 nanostructures were prepared using a solvothermal route. Cupric chloride, Indium chloride, and Selenium were used as precursors with Dimethyl Formamideor Benzene as a solvent. The process does not require a post-synthesis selenisation step. Structural, morphological and optical properties of the as-synthesized CuInSe2 nanocrystalswere characterized using powder X-ray diffraction analysis, scanning electron microscopy, UV–Vis absorption spectroscopyand dielectric studies. The results indicate that the as synthesized product is of ordered chalcopyrite tetragonal structure with a bandgapof 1.13eV. The shape obtained varies according to the changes in solvent.*

INTRODUCTION

Renewable energy is a widely discussed topic these days. In his plenary talk "Powering the Planet", held at the MRS 2007 Spring Meeting, Nathan S. Lewis discussed ideas concerning the energy supply for the future [1]. It was pointed out, that current reserves of oil, natural gas and coal are sufficient to satisfy the energy need for another century. However, the consumption of fossil energy sources dramatically increases the level of carbon dioxide in the atmosphere, which should enhance public interest in renewable energy.

Solar source may be used as a powerful photon delivering energy source for solar thermal and photovoltaic applications. The photovoltaic industry has grown by more than 40% per year over the last five years.[2] The current shortage of solar grade silicon increases the interest in thin-film solar cell technologies.[3] Amongst the commonly applied thin-film technologies, solar cells based on the compound semiconductor $CuInSe_2$ and its multinary alloys have shown the highest energy conversion efficiency.[4] Thin film solar cells based on the chalcopyrite $CuInSe_2$ and its alloys have reached efficiencies up to 19.5% on the laboratory scale [5] and 13.1% on large-area solar modules [6].

The ternary chalcopyritesemiconductor $CuInSe_2$(CIS)of nanostructure is an attractive alternative due to its relatively low toxicity and excellent optical and electrical properties. $CuInSe_2$ with a band gap of 1.04eV[7]is a promising candidate for photovoltaic application due to its radiation stability, high absorption coefficient and direct band gap, which matches well with the solar spectrum.

Great progress has been made in the synthesis of the $CuInSe_2$nanocrystals and their derivatives in recent years[8–11]. Forexample, Xie and his co-workers synthesized the nanoparticles of$CuInSe_2$, $CuInS_2$ and $CuInSe_xS(1−x)$ via solvothermal reactionusing CuCl, $InCl_3$ and Se powder as reagents.[12]Gedanken and his co-workers synthesized the $CuInSe_2$ and $CuInTe_2$ nanoparticles via microwave assisted polyol method [13].However, these reportedmaterial systems contain either binary products or additionalphases, thus it is difficult for ternary compounds to control theircomposition and structure. Recently, the Cu-GaSe$_2$, $CuInSe_2$, andCu(InGa)Se$_2$ nanoparticles were also

synthesized by the solvothermal route[14] and an efficiency of 3.2% of the simple solar cellbased on these hexagonal nanorings under AM 1.5 illumination was also reported [15].

This paper, reports a simple solvothermal method to synthesize CIS nanocrystals from CuCl InCl$_3$ and Se powder with Benzene or dimethyl formamide (DMF) as the solvent. In a solvothermal process, the solvent plays a key-role through the control of the chemical mechanisms leading to the target-material. The reaction mechanisms induced during the solvothermal reactions are dependent on the physico-chemical properties of the solvent. [16] Complexing properties of solvents can also play an important role in the reaction mechanisms. The complexing properties of the solvent can lead to the intermediate formation of stable complex systems (M(en) 2+). In some cases the formation of complex-cations is important as an intermediate step during the solvothermal reaction mechanisms. This is the case of the solvothermal preparation of the semiconductor material $CuInSe_2$.[18] The starting products were CuCl, $InCl_3$ and Se. This report is based on the changes observed in the size , morphology and conductivity of the formed $CuInSe_2$due to the change in the solvent .

1. EXPERIMENT

1.1 Materials

All chemicals used were of analytical grade. Selenium metal powder (99.9 %), copper (I) chloride (97%), and indium (III) chloride (>99.999%) were purchased from SISCO Research Laboratories, SIGMA – ALDRICH. DMF (N,N-Dimethyl Formamide) and Benzene was obtained from MERCK.

1.2 Procedure

In a typical experimental procedure, selenium metal powder (0.46 g, 6mmol) was dissolved in 80 mL of benzene with magnetic stirring for 2 hours. Then $CuCl_2$(0.3 g, 3mmol) and $InCl_3$ (0.66 g, 3mmol) were added in a ratio of 1:1:2 ratio. The earlier mixture was continuously stirred for 2 hours and then was loaded into a Teflon–lined stainless steel autoclave of 100ml capacity. The autoclave was sealed and maintained at 240 ^{0}C for 48 hours in Matri Hot Air Oven after which , the autoclave was allowed to cool naturally to room temperature. Nanoparticles in the form of a black coloured powder were collected by centrifuga-

tion. The synthesized product was then washed thoroughly with deionised water and absolute ethanol several times by means of suction method. This step removes the by-products. Finally, the pure product was obtained and stored. The procedure was repeated under the same experimental conditions with DMF as the solvent..

2. Characterisation study
• The phase and crystallinity of the as-prepared sample was characterised by X-ray diffraction (XRD) on a D8 ADVANCED MODEL BRUKER, equipped with Cu Kα (λ = 0.15406 nm) radiation in the 2 range from 20^0 to 80^0 while the voltage and electric current were maintained at 40 kV and 40 mA, respectively.

- Scanning electron microscopy (SEM) images were obtained using FEI QUANTA FEG 200 HIGH RESOLUTION SCANNING ELECTRON MICROSCOPE.
- The UV-Vis absorption spectrum of the obtained product was recorded using CARY 5E UV – VIS – NIR SPECTRO PHOTOMETER.
- The dielectric constant and dielectric loss of $CuInSe_2$ nanoparticles prepared at 240^0 C for 48 hours were measured using HIOKI 3532 LCR Hi TESTER in the frequency range from 50 Hz to 5 MHz. The relevant graphs were drawn.

3. Results and discussion
The as-synthesized product was analysed for its crystal structure through X- ray diffraction analysis. The obtained peaks were compared with the standard JCPDS card (40-1487).Fig.1 represents the X-ray diffraction pattern of the particles
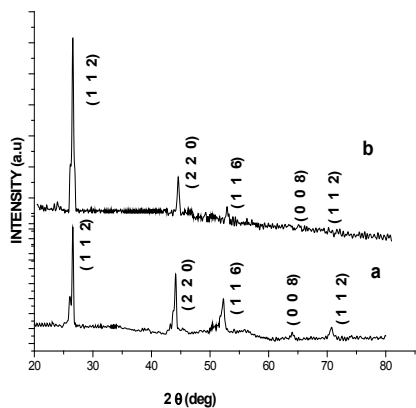

Fig.1 XRD pattern for CIS a) prepared with Benzene as the solvent

b)prepared with DMF as the solvent
The strongest diffraction peaks at 2θ=26.908 deg and 2θ=44.485 deg indicate the diffraction from (112) and (220) planes.

Two commonly encountered crystal structures found in synthesizing $CuInSe_2$nanocrystals are the ordered chalcopyrite [19],[20] (body-centered tetragonal) or disordered sphalerite[19], [20],[21] (face-centered cubic) structures. The difference between the crystal structures for $CuInSe_2$ can be seen in XRD patterns. For sphalerite the major peaks are observed at 26.3°

(111), 43.6° (220), and 51.7° (311) whereas for chalcopyrite the major peaks are observed at 26.6° (112), 44.2° (204/220) and 52.353(116/312). Therefore from the obtained XRD results , we infer that the CIS synthesized is of

chalcopyrite body-centered tetragonal structure.

The strongest peaks obtained for both the samples prepared with two different solvents indicate that the preferred growth direction as (112) . The calculated lattice constants a=5.78 A^0 and c= 11.61954 A^0 are in good agreement with the reported data (a=5.77 A^0 and c= 11.619 A^0, JCPDS card number (40-1487).

Using Scherrer formula(1), the average grain size was calculated 40 nm for the sample prepared with benzene as the solvent :

Scherrer formula D = kλ/β cos θ   (1)
Where , D is the grain size , k is the geometric factor , θ is the angle of diffraction, λ is the X-ray wavelength and β is the full width half maximum of diffraction peak. The average grain size calculated for CIS prepared with DMF as the solvent is 25 nm. It is observed that there is a decrease in the average grain size with the change of solvent. It is known that above a certain grain size limit (~20 nm) the strength of the material increases with the decreasing grain size[22,23].

The average strain of the prepared CIS with Benzene as the solvent was calculated to be 9.14 x 10 $^{-2}$ using Stokes-Wilson equation :

$$\varepsilon_{strain} = \beta /4 \tan \theta \qquad (2)$$

Where β is the full width half maximum of diffraction peak and θ is the angle of diffraction. The average strain increases to be 0.2219 when DMF was used as the solvent .

The dislocation density is the length of dislocation lines per unit volume of the crystal [24].Dislocation density for the two samples had been calculated to be 897 x 10 ^{16} lines / $m^2$and 2.6 x 10 ^{17} lines / m^2 respectively using the formula:

$$\eth = 15 \beta\cos \theta /4a D \qquad (3)$$

where ð is the dislocation density, β is the full width half maximum of diffraction peak, θ is the angle of diffraction , a is the lattice parameter and D is the average grain size. The dislocation density increases with the decrease in the grain size. The movement of the dislocation is impeded by other dislocations present in the sample. Therefore a larger dislocation density implies larger hardness [25]. It has also been shown that as the dislocation density increases the lattice average strain increases and the average grain size decreases[26].

The values of the average grain size, the dislocation density and the average strain are enumerated in Table 1. The average grain size decreases with the change of the solvent and increases the dislocation density and the average strain. We infer that CIS prepared with DMF as the solvent is of greater strength compared to CIS prepared with benzene as the solvent.

Table 1 The average grain size, average strain and dislocation density of CIS prepared with two different solvents

Sample	Average grain size(nm)	Average strain	Dislocation density lines /m^2
CIS the benzene	59	9.14 x 10 $^{-2}$	4.02721 x 10 ^{16}

With DMF	30	0.2219	1.922×10^{17}

Benzene is a non polar solvent and DMF is a polar (hydrophilic) aprotic solvent with a high boiling point. As a polarizing solvent DMF possesses more solubility. Probably the nature of DMF has reduced the average grain size of the sample and has considerably increased its strength.

Fig.2.shows the UV – Vis absorption spectrum of the $CuInSe_2$ nanoparticles prepared at 240^0 C for 48 hours with benzene (N,N-Dimethyl Formamide) as the solvent. The sample was dispersed in absolute ethanol under intense sonication for 20 mins. and ethanol was also subsequently used as a reference. The nature of the optical transition can be identified based on the dependence of absorption coefficient α on the photon energy hυ. The variation of $(\alpha h\upsilon)^2$ with hυ for the as – synthesized samples are shown in Figure 2a and 2b. The energy band gaps for the samples are calculated by extrapolating the graph. The band gap of the $CuInSe_2$ nanoparticles are calculated using the direct band gap method, and the value was determined to be 1.09eV for the sample prepared with benzene as the solvent which is consistent with the reported value of 1.04 eV for $CuInSe_2$ thin film. The sample obtained at 240^0C through the present method, is still too large to observe the blue-shift due to quantum confinement effect. The corresponding energy band gap for $CuInSe_2$ prepared with DMF as solvent is 1.13 eV. For the sample prepared with DMF as the solvent, there is a decrease in the grain size which in turn increases the energy bandgap.
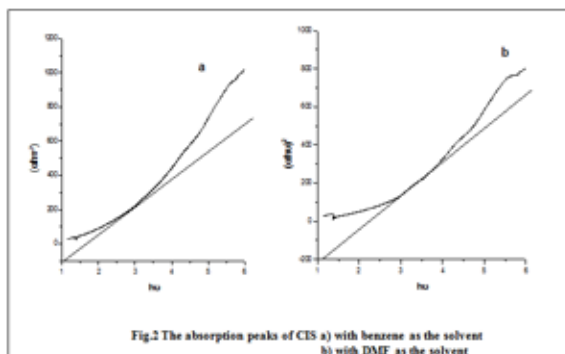

Fig.2 The absorption peaks of CIS a) with benzene as the solvent

b) with DMF as the solvent

The size and morphology of the $CuInSe_2$ synthesized at 240 ^0C for 48hours were investigated by scanning electron microscope (SEM) and shown in the Fig 3. The product is composed of a large amount of nanoparticles and these particles are of irregular shape. When the solvent benzene is replaced by DMF the shape of the particles changes from an irregular shape to a more flake like structure.

Compared to the non polar solvent benzene, DMF is a polar (hydrophilic) aprotic solvent with a high boiling point. In addition to its complexing properties, it has an effect in the reaction mechanisms. As a polarizing solvent, DMF possesses more solubility. The variation in the shape of the nanoparticles from an irregular shape to flake like structure when the solvent was replaced by DMF is probably due to the higher solubility of the solvent.
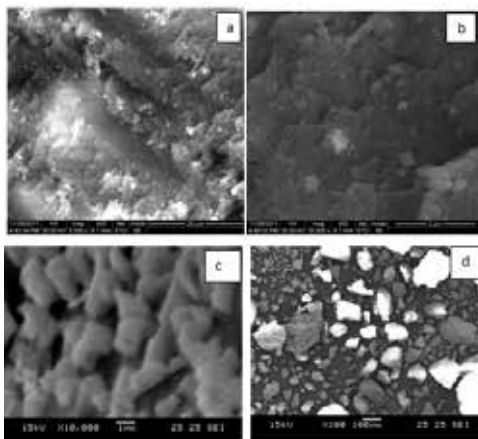

Fig.3 SEM images of CIS a and b. with Benzene as the solvent c and d. with DMF as the solvent

The dielectric constant and the dielectric loss of $CuInSe_2$ nanoparticles prepared at 240 ^0C for 48 hours were measured using HIOKI 3532 LCR Hi TESTER in the frequency range from 50 Hz to 5 MHz. The samples were coated with silver paint to ensure proper electrical contact between the pellet and the electrodes. They are mounted between the two electrodes. The capacitance of the parallel plate capacitor formed by the electrodes, with the sample as a dielectric medium was measured. The variation of capacitance was recorded in the frequency range 50 Hz to 5MHz at different temperatures. This was observed in the case of $CuInSe_2$ nanoparticles prepared at 240^0 C for 48 hours.

Conductivity for the prepared samples was calculated from the resistance values and geometrical dimension of the sample. Conductivity graphs are shown in Figure 4a,4b,4c. The conductivity increases with an increase in temperature indicating the semiconducting behavior of $CuInSe_2$.The conductivity of the sample prepared with DMF as the solvent is of an higher range compared to the one prepared with Benzene as the solvent as shown in Fig. 4c .
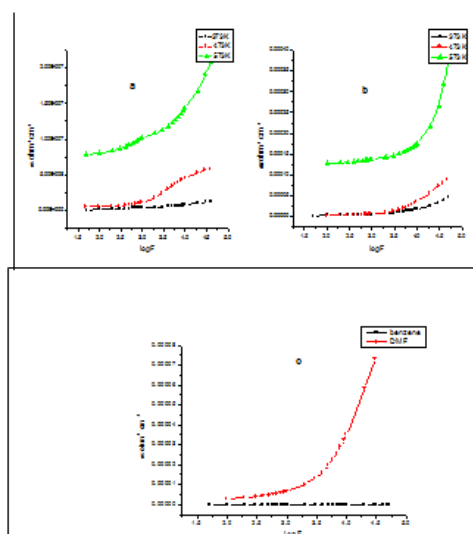

Fig. 4 Variation in Conductivity with respect to log frequency

a. CIS prepared with benzene
b. CIS prepared with DMF
c. **Comparison between the**

conductivity of CIS prepared with DMF and Benzene

The variations of dielectric loss with frequencies are shown in Fig.5For the given sample if there is a low dielectric loss with high frequency, it suggests that the sample possesses as good optical quality with lesser defects. Both the samples possess the same range of dielectric loss at higher frequency as shown in Fig.5.This indicates that both the samples prepared with two different solvents are of lesser defects.
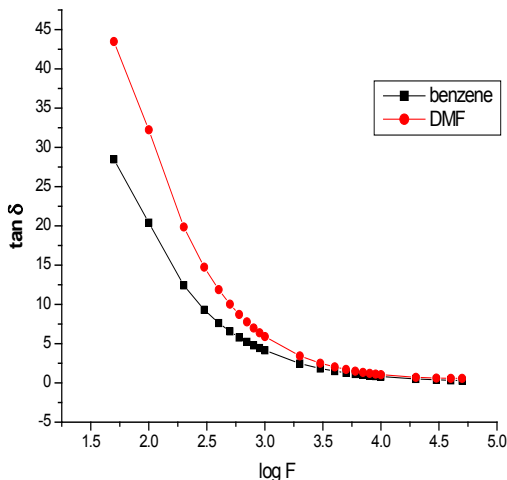

Fig.5log Frequency Vs dielectric loss curve for CIS nanoparticles prepared at 240 ⁰C for 48 hours with
a)DMF as the solvent
b)benzene as the solvent(measured at 573 K)

The dielectric constant (ε_r) of the material was calculated for different frequencies from the measured capacitance values. The plot of the dielectric constant versus applied frequency is shown in Fig.6. It is observed that the dielectric constant is high in the low frequency region and thereafter decreases with the applied frequency. The high value of (ε_r) at low frequencies may be due to the presence of all the four polarizations namely space charge, orientation, electronic and ionic polarization and the low values at higher frequencies may be due to the loss of significance of these polarizations gradually. The frequency response curve for CIS prepared with benzene is flat . Therefore we infer that the dielectric constant is independent of frequency.
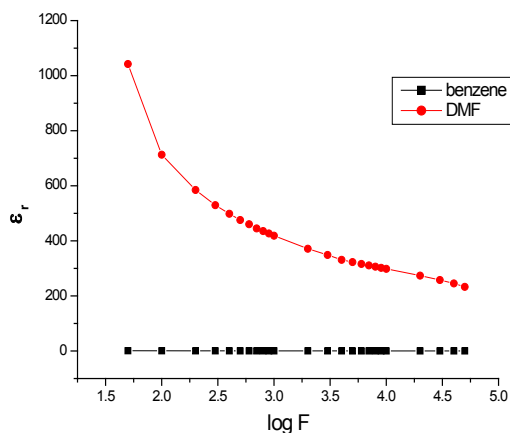

Fig. 6 log Frequency Vs Dielectric constant curve for CIS nanoparticles prepared at 240 ⁰C for 48 hours with
a) DMF as the solvent
b) benzene as the solvent (measured at 573 K)

4. CONCLUSIONS

Nanocrystals of CIS has been successfully synthesized by a simple solvothermal route.XRD, UV – Vis studies confirm the formation of pure chalcopyrite tetragonal $CuInSe_2$. CIS formed with DMF as the solvent is of reduced average grain size. Size and morphology of the synthesized product varies from an irregular shape to flake like structure when benzene the solvent is replaced by DMF. The conductivity of the prepared samples increases with the increase in temperature .

REFERENCE [1] S. Lewis: "Powering the Planet", plenary talk at the Mrs 2007 spring meeting, 9-13 April 2007, San Francisco, Ca, USA, a summary of the talk is printed in Mrs Bulletin 32 (7) (2007) 574 . | [2] Jäger-Waldau: "PV status report 2006, research, solar cell production and market implementation of photovoltaics", European Commission, DG Joint Research Centre, Institute for Environment and Sustainability, Renewable energies unit, Eru 22346 en (2006) | [3] M. Fawer: "Solarenergie 2006 – Licht Und SchattenseitenEinerboomendenindustrie", bank Sarasin, Basel, Switzerland (2006). | [4] M.A. Green, K. Emery, Y. Hisikawa, W. Warta: progress in photovoltaics: research and application 15 (2007) 425-430. | [5] M.A. Contreras, K. Ramanathan,J. Abushama, F. Hasoon, D.L. Young, B. Egaas,R.Noufi: progress in photovoltaics: Research and applications13 (2005-21) 2096 | [6] J. Palm, V. Probst, W. Stetter, R. Toelle, S. Visbeck, H. Calwer, T. Niesen, H. Vogt, O. Hernández, M. Wendl, J.H. Karg: Thin solid films451-452 (2004) 544–551. | [7] W.Paszkowicz, R. Lewandowska,R. Bacewicz: Journal of alloys and compounds362 (2004) 241-247 | [8] M.A. Malik, P. O'brien, N. Revaprasadu, Adv. mater. 11 (1999) 1441–1444. | [9] Y.H.Yang, Y.T. Chen, J. Phys. Chem. B 110 (2006)17370–17374. | [10] H. Zhong, Y. Li, M. Ye, Z. Zhu, Y. Zhou, C. Yang, Et Al.,nanotechnology18 (2007) 025602–025607. | [11] H.L. Yang, D.T. Schoen, S. Meister, X.F. Zhang, Y. Cui,J. Am. chem. soc. 129 (200734–35. | [12] B. Li, Y. Xie, J.X. Huang, Y.T. Gian, Adv. mater. 11 (1999)1456–1459. | [13] H. Grisaru, O. Palchik, A. Gedanken, V. Palchik, M.A. Slifkin, M.A. Weiss, Inorg. chem. 42 (2003) 7148–7155. | [14] J. Tang, S. Hinds, S.O. Kelley,E.H. Sargent, Chem. mater. 20 (2008) 6906–6910. | [15] Q. Guo, S.I. Kim, M. Kar, W.N. shafarman, R.W. Birkmire, E.A. Stach, et al., nanolett.8 (2008) 2982–2987. | [16] B. Li, Y. Xie, J.X. Huang, H.L. Su and Y.T. Qian, J. Solid State Chemistry146(1999) 47. | [17] D.J. Jia, Y. Zhang, J. Ai, Q.Y. Zhu and X.M. Gu , J. SolidState Chem. 177 (2004)2476. | [18] B. Li, Y. Xie, H. Huang and Y. Qian, Adv. mater. 11 (1999) 1456 | [19] Arici, E.; Hoppe, H.; Schaffler, F.; Meissner, D.; Malik, M. A.; Sariciftci, N. S. Applied Physics a-Materials Science & Processing 2004, 79, (1), 59-64. | [20] Guo, Q.; Kim, S. J.; Kar, M.; Shafarman, W. N.; Birkmire, R. W.; Stach, E. A.; Agrawal, R.; Hillhouse, H. W. Nano Letters2008, 8, (9), 2982-2987. | [21] Liu, H.; Jin, Z.; Wang, W.; Li, J.Crystengcomm2011, 13, (24), 7198-7201. | [22] Weertman J.R, Hall. ;Mater.Sci.Eng.A. 1993; 166 (1-2) : 161-167. | [23] Van Swygenhoven H, Science,2002; 296 (5565) | [24] Nehru L.C.Swaminathan V, Sanjeevaraja C., American.J. Mat. Sci. 2012 ; 2 (2) : 6-10 | [25] SirdeshmukhDB ,Sirdeshmuk I, Subadhra KG. Springer ,New York .2006 | [26] ChinhNQ ,Gubigza J , Langdon TG J. Mater.Sci.2007 ; 42 (5) : 1594-1605. |