



Preparation and characterization of CuInSe₂ Nano-particles

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Abstract

CuInSe₂ synthesized by a modified solvothermal route could be altered considerably by controlling the reaction temperature, reaction time and washing agents. Synthesized CuInSe₂ powders were characterized by X-ray diffraction. The thermal properties of lattice strain (ϵ), particle size (t), lattice parameters (a , c) and Debye-Waller factor (B) were determined from the half-widths and integrated intensities of the Bragg reflections. CuInSe₂ powder was strained by Temperature values 150 °C, 160 °C, 170 °C, 180 °C and 190 °C. From a study of X-ray diffractograms recorded at different stages of different temperature values, it is observed that it has systematic effect on the particle size. The particle shape was spherical when deionized water was used as washing agent and Particles with the size down to 26.6nm were obtained. When the washing agent changed to ethanol, nano-rods with the diameter ranged from 100 to 200nm and the length of several micrometer were observed in the TEM. The variation of energy of vacancy formation as a function of lattice strain has been studied.

Keywords: X-ray diffraction, particle size, lattice strain, Debye-Waller factor, vacancy formation energy

1. Introduction

Hybrid solar cells based on conjugated polymers and inorganic compounds such as CdSe and CuInSe₂ in the form of nano rod had been developed as next generation solar cells emphasizing the low cost production [1, 2] and with superior properties for photovoltaic applications [3]. The Debye-Waller factor is an important lattice dynamical property. But it is interesting to study the effect of particle size and lattice strains on the Debye-Waller factors of CuInSe₂. There is considerable X-ray work on the Debye-Waller factors of CuInSe₂ particles can be synthesized by a solvothermal route [4, 6]. The present work was carried out by same earlier chemical method and it was successfully modified for preparing the CuInSe₂ nano-rods. Crystalline phase and microstructure of CuInSe₂ nano-particles were characterized and reported in this paper.

2. Experimental

CuInSe₂ particles were synthesized by a modified solvothermal route using a mixture of Se powder (2.59 mmol, 99.9% purity), CuCl₂.2H₂O (1.26 mmol) and InCl₃.4H₂O (1.29 mmol). The reagents were loaded into a 60 ml Teflon beaker and filled with anhydrous ethylenediamine as chelating agent up to 80% of the total volume. Chemical solution was stirred by a magnetic bar for 2 hours. After mixing thoroughly, the Teflon beaker was then sealed in a stainless steel container and heated in an oven at a temperature ranged from 150 to 200 °C for at least 15 hours. It was subsequently cooled to room temperature, the precipitate was then filtered and washed with absolute ethanol and distilled water several times in order to remove by-products. Finally, CuInSe₂ powder in black colour was obtained after drying in an oven at 60 °C for 3 hours. We also used diethylamine as chelating agent in our experiments. Unfortunately, it caused the formation of second phases such as InSe and In₂Se₃ in the final product. Thus, we normally use anhydrous ethylenediamine due to its capability

to produce single-phase CuInSe₂ with higher purity and smaller particle size. X-ray diffractograms were obtained with a Philips CWU 3710 X-ray powder diffractometer in the 2θ range 20 -120° using filtered CuK _{α} at a goniometer speed of 0.5° per minute and a chart speed of 20 mm/min. All measurements were made at room temperature. The XRD patterns of CuInSe₂ powder is given in Figure 1 at temperature 150°C. The observed integrated intensities have been corrected for thermal diffuse scattering using the method of Chipman and Paskin [7].

3. Analysis of Data

The procedure for the determination of directional mean-square amplitudes of vibration $\langle u_{\parallel}^2 \rangle$ and $\langle u_{\perp}^2 \rangle$ from the intensity data and the estimation of associated errors is as discussed by Gopi Krishna *et al.* [8]. The average mean square amplitude $\langle u_{av}^2 \rangle$ can be obtained from the relation,

$$\langle u_{av}^2 \rangle = 1/3 (\langle u_{\parallel}^2 \rangle + 2 \langle u_{\perp}^2 \rangle) \quad (1)$$

and the directional Debye-Waller factors B_{\perp} and B_{\parallel} were obtained from the equations

$$\left. \begin{aligned} B_{\perp} &= 8\pi^2 \langle u_{\perp}^2 \rangle \\ B_{\parallel} &= 4\pi^2 \langle u_{\parallel}^2 \rangle \end{aligned} \right\} \quad (2)$$

The mean Debye-Waller factor B is given by

$$B = (2B_{\perp} + B_{\parallel}) / 3$$

The directional Debye temperatures θ_{\perp} , θ_{\parallel} and mean Debye temperature θ_M were obtained from B_{\perp} , B_{\parallel} and B , respectively using the Debye-Waller theory [9] relation,

$$\left. \begin{aligned} B &= (6h^2/M k_B \theta_M) W(X) \\ B_{\perp} &= (6h^2/M k_B \theta_{\perp}) W(X) \\ B_{\parallel} &= (6h^2/M k_B \theta_{\parallel}) W(X) \end{aligned} \right\} \quad (3)$$

Where h is the Planck's constant, k_B the Boltzmann constant, M the atomic weight. The function $W(X)$ is given by

$$W(X) = [\phi(X)/X + (1/4)] \quad (4)$$

where $X = \theta_M/T$, T is the temperature of the crystal and $\phi(X)$ is the Debye function. The values of $W(X)$ for a wide range of X can be obtained from standard tables^[10].

Lattice strain and Particle size determination

When the size of the individual crystals is less than about 100nm the term "particle size" is usually used. When the crystallites of a material are smaller than 100nm, they have too small a number of parallel diffraction planes and so they produce broadened diffraction peaks instead of a sharp peak. Lattice strain present in the sample is another cause of broadening of Bragg diffraction peaks. In addition to this, there are instrumental factors such as unresolved a_1 and a_2 peaks, imperfect focusing which lead to the line broadening. There are various methods in practice to estimate the particle size. X-ray diffraction is a simpler and easier approach for the determination of precise particle size and the lattice strain in powder samples. The principle involved in the X-ray diffraction approach is precise quantification of the broadening of the Bragg diffraction peaks. Scherrer equation, Hall-Williamson method and Warren-Averbach method are some of the techniques based on this principle. Of the above methods, Scherrer equation method for the estimation of particle size does not take into account the broadening due to lattice strain present in the sample. As such in the present investigation, the lattice strains have been estimated using Hall-Williamson method. Recently, Bharati *et al.*^[16] have used this method to estimate the lattice strain and particle sizes of silver nano particles and composite silver nano particles. In this method the integral breadth of the diffraction peak is determined. The integral breadth is given by the integrated intensity divided by the maximum intensity. Thus, the observed peak broadening B_o may be represented as

$$B_o = B_i + B_r \quad (5)$$

where B_o is the observed peak broadening in radians, B_i is the instrumental broadening in radians and B_r is the broadening due to the small particle size and lattice strain. The instrumental broadening has been estimated using a pure strain-free fine sodium chloride powder sample subjected to XRD under identical conditions as those for the strained metallic powders. Eq. (5) holds good if the diffraction peaks exhibit purely Cauchy profile. However, when the diffraction peaks are partly Cauchy and partly Gaussian for profiles, the following relation between B_o , B_i and B_r holds good, Bharati *et al.*^[11]

$$B_r = [(B_o - B_i) (B_o^2 - B_i^2)^{1/2}]^{1/2} \quad (6)$$

Now, according to Scherrer equation, the broadening due to small particle size may be expressed as

$$B_c = \frac{k\lambda}{t} \cos\theta \quad (7)$$

where B_c is the broadening solely due to small crystallite size, K a constant whose value depends on particle shape and usually taken as unity, t the crystallite size in nanometers, θ the Bragg angle and λ is the wavelength of incident X-ray beam in nanometers.

Similarly, According to Wilson^[12], the broadening due to lattice strain may be expressed by the relation,

$$B_s = \varepsilon \tan\theta \quad (8)$$

where B_s is the peak broadening due to lattice strain and ε the strain distribution within the material and θ is the Bragg angle. Based on Eqs. (7) and (8) the total peak broadening B_r may be expressed as,

$$B_r = \frac{k\lambda}{t \cos\theta} + \varepsilon \tan\theta \quad (9)$$

which can be written as

$$B_r \cos\theta = \frac{k\lambda}{t} + \varepsilon \sin\theta \quad (10)$$

Figure 2: The plot of $B_r \cos\theta/\lambda$ versus $\sin\theta/\lambda$ is a straight line with slope equal to ε and hence the particle size 't' can be estimated from the intercept. Typical Hall-Williamson plot between $B_r \cos\theta/\lambda$ and $\sin\theta/\lambda$ is shown in Figure (2).

The lattice strains were determined from the plot of $B_r \cos\theta/\lambda$ against $\sin\theta/\lambda$ following standard procedures^[13]. The measured half-widths were corrected for instrumental broadening with reference to a pure strain-free silicon powder. The variation of particle size with milling time is within the limits of experimental errors. This shows that while the milling is enough to create strains, it affect the particle size to a measurable extent. A typical Hall-Williamson plot is shown in Figure 2 for CuInSe_2 at the temperature 180°C .

4. Results and discussion

Table-1: The values of the particle size, lattice strain, root mean square amplitude of vibrations, Debye-Waller factor and Debye temperature of CuInSe_2 powders, ground for different durations, obtained in the present study are given in Table-1. Although, values of Debye-Waller factor, amplitude of vibration and Debye temperature in the 'a' and 'c' directions have been determined separately, the average values of these quantities are given in Table-1. as the objective of the present work is to investigate the strain dependence of Debye-Waller factors. Debye-Waller factor Mg powder sample carries an effect due to lattice strain. While comparing the Debye-Waller factors calculated from the lattice dynamical models with experimental results Vetelino *et al* [14] have attributed the difference to inaccuracies in the experimental values caused by neglecting the TDS corrections. The repeated milling of the

powder sample leads to lattice distortion which gives rise to microstrains in the lattice. These microstrains increase the contribution of static component of Debye-Waller factor. Thus both lattice strain and the observed Debye-Waller factor, which is the sum of static and thermal components, increase with grinding time. Thus, whenever Debye-Waller factors are determined from X-ray intensities on powder samples, it is desirable, to make an estimate of the lattice strain and if the strain is large, a suitable correction is to be made as in the present study.

Glyde^[15] derived the following relation between the energy of vacancy formation (E_f) and the Debye temperature (θ) of a solid. The relation is

$$E_f = A(k/h)^2 M\theta^2 a^2 \quad (11)$$

where a is the interatomic spacing, A a constant shown to be equal to 1.17×10^{-2} , M the molecular weight and h and k are the Planck's and the Boltzmann's constants, respectively. Glyde recommended the use of X-ray based values in eq. (11). The validity of eq. (11) was verified for a number of fcc, bcc and hcp metals^[16]. Therefore, the X-ray Debye temperatures obtained in the present work have been used to study the variation of vacancy formation energy as a function of lattice strain in CuInSe₂. The values of vacancy formation energies are also included in Table-1.

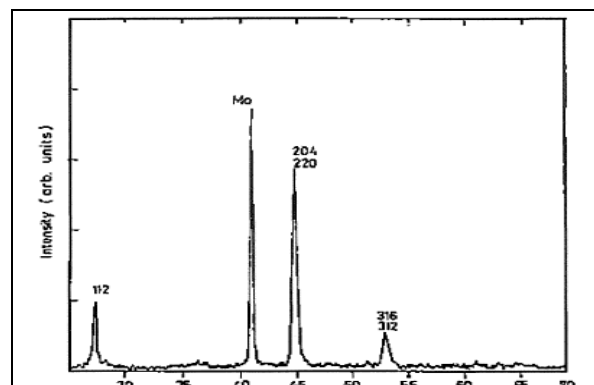


Fig 1: XRD Pattern of CuInSe₂

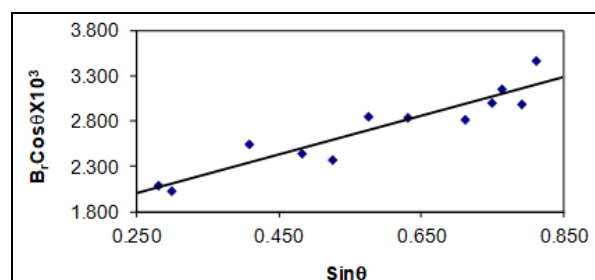


Fig 1: Plot of $B_1 \cos \theta / \lambda$ Vs $\sin \theta / \lambda$ for CuInSe₂ at the temperature 180 °C.

Table 1: Values of particle size (t), lattice strain (ϵ), mean Debye-Waller factor (B), amplitudes of vibration $\langle u \rangle$, Debye temperature (θ_M) and energy of vacancy formation (E_f) of CuInSe₂ nano powder.

Material	Temperature (°C)	$\epsilon \times 10^3$	t	a	c	U	B	θ_M	E_f
			(nm)	(nm)	(nm)	(Å)	(Å ²)	(K)	(eV)
CuInSe ₂	150	1.12	49.8	0.5843	1.1583	0.00175	0.1382	275	1.42
	160	1.18	38.4	0.5892	1.1526	0.00177	0.1396	273	1.66
	170	1.2	36.2	0.5885	1.1532	0.00179	0.1415	271	1.87
	180	1.26	39.4	0.5884	1.1515	0.00186	0.1468	266	2.20
	190	1.31	28.3	0.5894	1.1521	0.00194	0.1532	260	2.42
	200	1.38	26.6	0.5895	1.1521	0.00205	0.1621	253	2.83

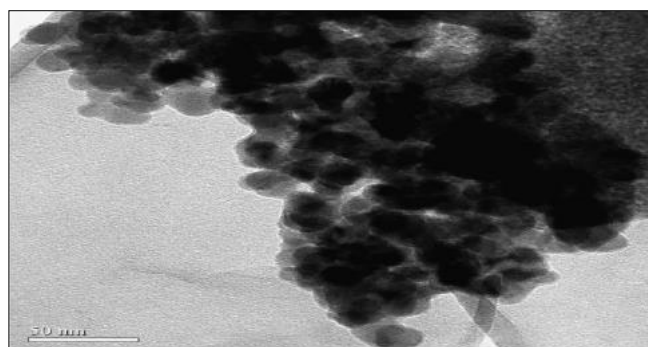


Fig 3: A TEM micrograph of spherical CuInSe₂ particles prepared by using deionized water as washing agent CuInSe₂ at the temperature 150 °C.

5. Conclusion

CuInSe₂ powder was strained by Temperature values 150 °C, 160 °C, 170 °C, 180 °C and 190 °C. From a study of X-ray diffractograms recorded at different stages of different temperature values, it is observed that it has systematic effect on the particle size. However, the increasing temperature produces lattice strain and also enhances the effective Debye-Waller factor. The variation of energy of vacancy formation as a function of lattice strain has been studied.

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