

Influence of Microwave Power on Structural and Optical Properties of CuSe Nanoparticles Synthesized via Microwave Assisted Technique

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Abstract: In the present paper, different particle size and phase of CuSe nanoparticles with hexagonal (Klockmannite) and cubic (Berzelianite) structure were successfully synthesized via microwave assisted method from $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, Na_2SeO_3 and hydrazine hydride ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) as copper, selenium and reducing agent respectively. The influence of microwave power on structural and optical properties of CuSe NPs were investigated. The resulting nanoparticles in different sizes were characterized by X-ray diffraction (XRD). The crystallite size was calculated based on the full width at half maximum of the most intense peak in the XRD spectra using the prominent Scherer's equation. The crystallite size was found to increase between 43.30nm to 118.70nm with the increase in microwave power. The optical properties of the as-synthesized CuSe nanoparticles were determined with the help of Photoluminescence spectroscopy (PL). The optical band gap obtained from the PL result was found to be equal to 2.03eV. Therefore, this research provides a facile synthesis method that is environmentally friendly, low cost and time saving approach to synthesized semiconductor nanomaterials that could be used for optoelectronics and solar cell applications.

Keywords: Copper selenide, microwave power, band gap, Klockmannite, Berzelianite.

Due to their interesting properties and potential applications, extensive attention has been paid to the preparation and characterisation of metal selenides [1]. Copper selenides are semiconductors with p-type conductivity, and their possible applications in solar cells, optical filters and super ionic materials optoelectronic applications, optical fibres, etc. have been extensively studied [2]. Copper selenides have more stoichiometries and phases relative to other promising metallic selenides. Specific stoichiometric compositions (Cu_2Se , Cu_3Se_2 , CuSe and CuSe_2 , Cu_7Se_4 etc.) and non-stoichiometric compositions (Cu_{2-x}Se) and structural types are well known [3]. It has been stated that depending on their stoichiometries or phases, the thermal stability and bandgap of copper selenides differ [4].

A variety of methods have been investigated for the synthesis of copper selenides, such as mechanical alloy [5], gamma-irradiation [6], microwave [7], ultra-sonic synthesis [8], hydrothermal [9], sol-gel [10], solid-state [11] and chemical reaction solution-phase [12]. Bulk copper selenide can traditionally be prepared in flowing Argon by heating Cu and Se powders at high temperature. The final products' composition and crystal structure are usually dependent on the methods of preparation [3]. Moreover, copper selenides' preparation methods and size or shape control are less versatile than other metal selenides like CdSe, and studies

related to their optical properties are minimal. Therefore, new methods to prepare and monitor the size and shape of copper selenide nanostructures need to be developed.

Here in, copper selenide nanoparticles were successfully synthesized via microwave assisted method by varying the microwave power condition. The structural and optical properties of the as-synthesized CuSe NPs were characterized by means of X-ray diffraction (XRD) and photoluminescence spectroscopy (PL). Copper selenide in mixed phases comprising of hexagonal (CuSe) and cubic (Cu₂Se) were observed from the XRD results. The crystallite size was found to increase between 43.30nm to 118.70nm with an increase in microwave power. The band gap obtained from the PL result was found to be 2.07eV which is consistent with that of the previous works.

In the present work, the raw materials used for synthesizing CuSe were; sodium selenide (Na₂SeO₃ > purity 99% Sigmah Aldrich), copper (II) chloride 2-hydrate. (CuCl₂ .2H₂O> purity 99% HmBG Chemicals) L-(+) -tartaric acid (C₄H₆O₆, > purity 99.5% HmbG Chemicals), hydrazine hydride (N₂H₄.H₂O>purity80% Sigmah Aldrich) and deionized water as a solvent. All the chemicals were of analytical grade and used as received without further purification or treatment, because they are of standard research grade.

Copper selenide nanoparticles (NP) were synthesized using a microwave-assisted synthesis technique. In a typical synthesis procedure, 2mmol of CuCl₂.2H₂O (0.3459 ±0. 0002g) was dissolved in 50 ml of deionized water. In a separate beaker, 2mmol of Na₂SeO₃ (0.3457± 0.0002g) and 8ml of hydrazine hydride were fully dissolved in 50 ml of deionized water. Both solutions were stirred at room temperature at 500 rpm for 5 minutes. The two solutions were then blended together and the mixture became brownish in colour immediately. To achieve a homogeneous solution, the mixture was subjected to a steady 20 minute stirring at 500 rpm. The beaker was then moved to a microwave oven (Electrolux Microwave Oven ELE-EMM 2001S, 700W) for 10 minutes of irradiation at 230W microwave power. The solution was then allowed to cool down at room temperature, and the sediments were sonicated for 5 minutes and centrifuged for 10 minutes at 300 rpm several times with deionized water and ethanol respectively. The precipitates were then dried overnight in an oven at 600C and the precipitates produced were then grinded with mortar and pestle. In order to study the influence microwave power on the structural and optical properties of CuSe nanoparticles, the microwave power conditions were varied from low (230W), medium (380W), medium high (520) and high (700). Table 1 give the summary of the experimental conditions.

Table 1: A Summary of the experimental condition

Sample designation	CuCl ₂ .2H ₂ O (mM)	Na ₂ SeO ₃ (mM)	N ₂ H ₄ . H ₂ O (mL)	Irradiation Time (min.)	Microwave Power (watt)
CuSe-230W	2	2	3	10	230
CuSe-380W	2	2	3	10	380
CuSe-520W	2	2	3	10	520
CuSe-700W	2	2	3	10	700

Powder X-ray diffraction (PXRD) patterns of copper selenide nanoparticle synthesized via microwave assisted synthesis method was recorded using X-ray diffractometer (X'pert Pro, PANalytical, The Netherlands) with CuK_α radiation (λ=0.154187nm) at 40 kV and 40mA in the range of 20° to 80°. The optical properties of the sample was deduced from the

Photoluminescence spectra over a wavelength ranging from 500nm to 700nm by fluoromax3 spectrophotometer at excitation wavelength of 400nm.

Figure 1 depicts the powdered X-ray diffraction (PXRD) spectra of the as-synthesized CuSe nanoparticle synthesized via microwave assisted synthesis technique at various microwave irradiation power. All the diffraction peaks from the XRD spectra confirms the crystalline nature of the as-synthesized sample. For all the various microwave power condition, the XRD peaks confirms the formation of two phases. The peaks of the dominant phase were observed at 2θ value of 28.22° , 31.32° , 41.10° , 46.23° , 50.20° , 53.50° , 56.83° and 70.53° , which correspond to the hkl plane of reflection (012), (006), (112), (018), (010), (116), and (028) respectively. These observed diffraction peaks match well with the Klockmannite phase (hexagonal structure) and suits well with the ICSD card No. 98-004-8769. Two other peaks were also observed at 2θ value of 26.78° and 45.62° which correspond to (011) and (110) reflection plane which match well with Berzelianite phase (cubic structure, ICSD No. 98-002-3551). It can be observed from the XRD spectra that the full width at half maximum (FWHM) decreases as we increase the microwave irradiation power, which correspond to the increase in crystallite size. The intensity of the diffraction peaks increase with respect to the increase in microwave power, signifying an increase in crystallinity of the as-synthesized sample. The average crystallite size was obtained base on the (012) peak broadening which is the most intense peak in the XRD spectra. The prominent Scherer's formula was used to calculate the average crystallite size of the as-synthesized CuSe nanoparticle as given in the equation (1).

$$D = \frac{0.94\lambda}{\beta \cos \theta} \quad (1)$$

Where λ refers to the wavelength of the X-ray used, β is the full width at half maximum (FWHM) and θ is the Bragg's angle of reflection. The average crystallite size calculated using equation (1) shows the crystallite size increases with increase in the microwave irradiation power. (see table 1). The crystallite size was found to increase between 43.30nm to 118.70nm with increase in microwave power. Therefore, it can be deduced that higher microwave irradiation power favours the formation of CuSe nanoparticles with larger size.

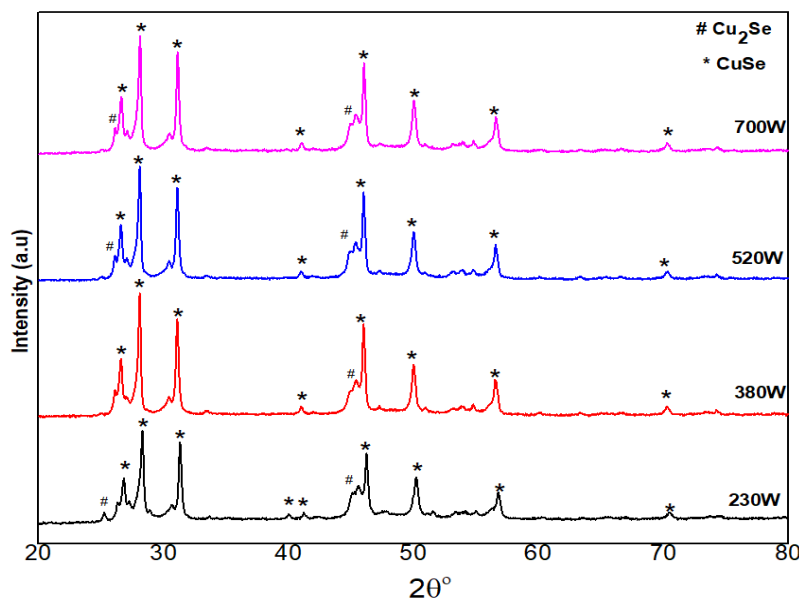


Figure 1: X-ray diffraction spectra of CuSe nanoparticle at different microwave power (a) 230W (b) 380W (c) 520W and (d) 700W.

The micro strain (ε) was obtained by using equation (2) below:

$$\varepsilon = \frac{\beta \cos \theta}{4} \quad (2)$$

Where, β is the full width at half maximum (FWHM) of the diffraction peaks and θ is the Bragg's angle. The dislocation density for all the samples were also calculated with help of the following equation (3):

$$\delta = \frac{1}{D^2}$$

Where D is the crystallite size of the as-synthesised CuSe nanoparticle for various microwave power conditions.

The micro strain and the dislocation density for the as-synthesized CuSe nanoparticle at various microwave irradiation power condition were seen to decrease with the increase in microwave power. This may be attributed to the increase crystallinity of the as-synthesized product observed with the increase in microwave power condition. Table 2 summarise the result of the structural properties of the as-synthesized CuSe NPs.

Table 2: Summary of the structural results

Sample designation	2 θ Value (Degree)	FWHM 2 θ ICSD	Crystallite Size D _{XRD} (nm)	Strain (ε) $\varepsilon \times 10^{-4}$	$\delta \times 10^{-4}$ (nm ⁻²)
CuSe-230W	25.22	0.2376	43.30	4.54	5.33
CuSe-380W	28.06	0.1980	55.30	3.35	3.27
CuSe-520W	28.07	0.1584	75.80	2.62	1.74
CuSe-700W	28.10	0.1188	118.70	1.88	0.71

Figure 2 shows the room temperature PL spectra of the as-synthesized CuSe nanoparticles at different microwave power condition under 400nm excitation in the wavelength range of 500nm to 700nm. It can be seen clearly that two peaks are overserved, a shallow peak at 530nm and an intense peak at 610nm. The first peak is related to the defects associated with the sample. This defect might be due to presence of copper vacancies, interstitials and antisite related defects of the as-synthesised sample [13]. The second peak is related to the sample emission when an electron is been excited from the balance band to the conduction band. The optical band gap obtained from the PL spectra for the as-synthesized CuSe nanoparticle at various microwave power condition was found to be 2.03eV. The optical band gap obtained is consistent with that of previous works [9].

In conclusion, Copper selenide nanoparticles were successfully synthesized via microwave assisted synthesis technique. The influence of microwave power condition on structural and optical properties were fully investigated. The method involves the use of CuCl₂.2H₂O, Na₂SeO₃ and hydrazine hydride as copper, selenium and reducing agent respectively. The XRD result reveal that a crystalline material of mixed phase comprising of hexagonal (Klockmannite) and Cubic (Berzelianite) structure were obtained. The crystallite size was found to increase between 43.30nm to 118.70nm with the increase in microwave power condition. The energy band gap obtained from the PL spectra was found to be 2.03eV.

Therefore, this research provides a facile synthesis method that is environmentally friendly, low cost and time saving approach to synthesized semiconductor nanomaterials that could be used for optoelectronics and solar cell applications

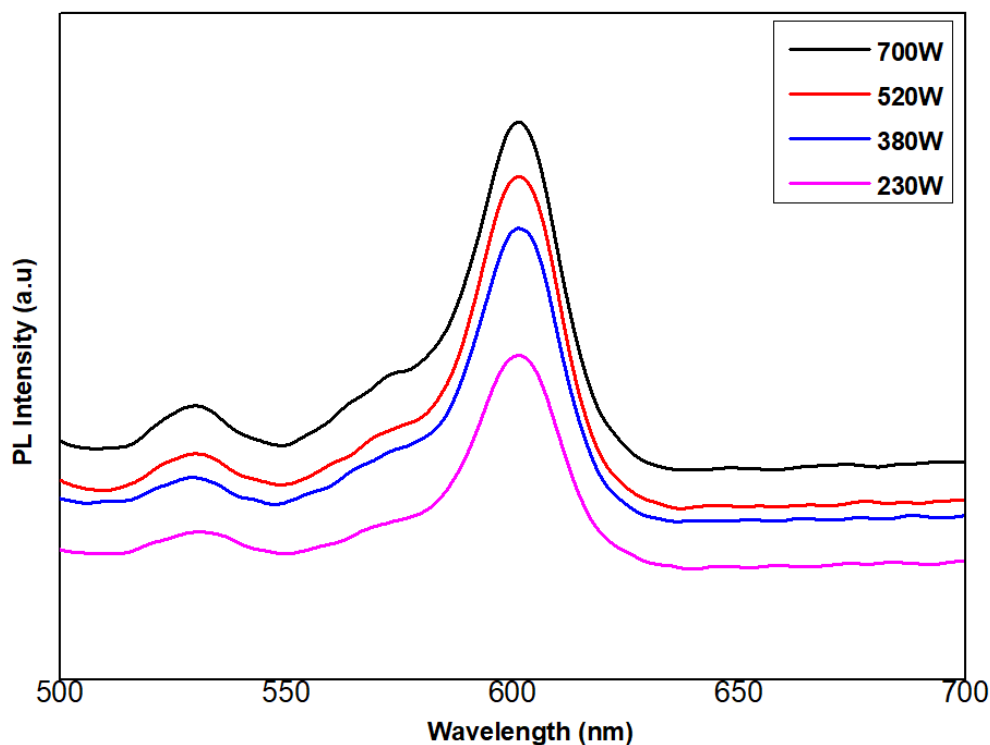


Figure 2: PL spectra of the as-synthesized CuSe nanoparticles

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