Published by :
http://www.ijert.org

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 9 Issue 10, October-2020

Structural, Optical and Thermal Characterization of Non-Stoichiometric $Cu_{2-x}Se$ Nanoparticles

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Abstract— **Fluorescent $Cu_{2-x}Se$ nanoparticles were prepared by a fast, versatile, microwave-assisted solvothermal method using microwave oven. Copper ions were from copper acetate dihydrate, selenite ions were from sodium selenite and reaction medium consisted of ethylene glycol and distilled water. The XRD patterns indicate that all the peaks are matching the peaks of non-stoichiometric $Cu_{1.78}Se$ and the average size of the nanoparticle is found to be 15nm. XRD, SEM, EDX and FTIR studies confirm the morphology and composition of $Cu_{2-x}Se$ nanoparticles. The optical band gap energy of the material was estimated using Tauc relation from UV-Visible spectrum. In the PL spectrum a sharp, intense blue emission peak is observed at 439.6nm. TGA shows that the prepared $Cu_{2-x}Se$ nanoparticles are very stable up to 486^{0}C.**

Keywords—Chalcogenide, Copper selenide, non-stoichiometric, microwave, solvothermal.

I. INTRODUCTION

It is amazing that metallic copper becomes a semiconductor nanoparticle when its dimensions are reduced to the nanoscale. Significant attention was given to semiconductor metal chalcogenides due to its diverse physical and chemical properties [1]. The unique properties of these materials depend on, their size, shape and method of preparation etc. [2]. The Copper selenide belongs to the semiconductor group received considerable attention in the past two decades for its application in solar cells, optical filters, superionic conductors, thermoelectric converters, nano switches, thermoelectric and photoelectric transformers, optoelectronic devices, photocatalysis, photothermal treatment of cancer cells etc. [3-11] because of its excellent thermoelectric, photocatalytic/photochemical, and optical properties [12]. They exist in several crystallographic forms like monoclinic, cubic, tetragonal, hexagonal, etc. [4-12]. Due to their metal-like behavior, copper selenide nanocrystals have strong localized surface plasmon resonance (LSPR) absorption tunable by their size, shape, and chemical composition. Strong and widely tunable LSPRs in near and mid-infrared spectral regions make copper selenide an ideal candidate for solar energy harvesting, photodetector and plasmonic sensing applications [13]. Copper selenide is also a potential candidate for heterojunction solar cells [10,14].

Non-stoichiometric copper selenide ($Cu_{2-x}Se$) is one among the copper chalcogenide family that has different stoichiometric phases such as CuSe, Cu_2Se, $CuSe_2$, Cu_3Se_2, Cu_5Se_4, Cu_7Se_4, etc. and non-stoichiometric phases ($Cu_{2-x}Se$) [4-10]. The thermal stability and energy bandgap of copper selenides vary with their stoichiometric composition or phases, which depend on the method of preparation [7]. Copper-deficient $Cu_{2-x}Se$ is an intrinsic p-type semiconductor [3,4,9-13] which exhibit both direct and indirect bandgap [8,10,14]. Non-stoichiometry in $Cu_{2-x}Se$ nanoparticles affects their electronic properties and significantly alters their crystalline structure [14]

Based on the literature survey carried out, a variety of techniques have been developed to synthesize metal nanoparticles. The objective of this work is to use a simple and rapid method that combines both advantages of the solvothermal synthesis and the rapid and efficient microwave heating for the fast preparation of nanomaterials. Therefore, a conventional microwave-assisted solvothermal method [15]is chosen for the synthesis of nanometals of controlled size and shape. In order to obtain small and uniform particles, organic solvents are often used to stabilize the particles in solution and control particle growth that are useful in the fields of photovoltaic devices, light-emitting diodes, biological imaging, and bio diagnostics. Ethylene glycol has been used as the solvent which act as a reducing agent for the preparation of metal particles at higher temperatures. Interaction of the dipole moment of the molecules with the high-frequency microwave radiation produces heating [16].

In this work, semiconductor, non-stoichiometric copper selenide nanoparticles were prepared by a simple microwave driven solvothermal process with simple precursors.

II. MATERIALS AND METHODS

A. *Synthesis of $Cu_{2-x}Se$ nanoparticles*

Fluorescent $Cu_{2-x}Se$ nanoparticles were prepared by a simple microwave-assisted solvothermal method using a microwave oven. Copper ions were from copper acetate dihydrate, selenide ions were from sodium selenite, and reaction medium consisted of ethylene glycol (EG) and distilled water. All the chemicals were pure and used as received without further purification. Copper acetate dihydrate and sodium selenite were dissolved in ethylene glycol and eventually with the addition of distilled water, followed by vigorous stirring using a magnetic stirrer. Subsequently, this mixture was loaded into the microwave oven with a frequency of 2.45 GHz until the solvent gets evaporated. The colloidal precipitate was collected, and washed several times with distilled water and then with acetone to remove the organic impurities and, filtered-off. Finally, the resulting product was naturally dried. The sample thus prepared was annealed at 100°C for 1 hour to improve ordering. [15]

RESULTS AND DISCUSSION

Greenish black non-stoichiometric $Cu_{2-x}Se$ nanoparticles were successfully prepared by microwave driven solvothermal method.

B. Powder X-Ray Diffraction (XRD) Analysis

The powder XRD analysis for the as-prepared sample was done using Bruker AXS D8 Advance diffractometer with Copper target and Cu-Kα (λ=1.5406 Å) radiation. The reflections were indexed and lattice parameters were determined. Fig.1. shows the X-ray diffractogram of the as-prepared $Cu_{2-x}Se$ nanoparticles. The XRD pattern shows sharp and broad peaks, which are characteristics of Nano-sized crystalline particles. XRD patterns of the synthesized powder indicated single-phase $Cu_{2-x}Se$ nanoparticle formation. The peak positions and intensities were matching well with the standard ICSD data for cubic crystals of $Cu_{1.78}Se$ (PDF 01-082-1208), with the space group Fm-3m (225) having unit cell parameters a= 5.74640A°, Z=4, mol weight =192.07, volume [CD]= 189.75$(A^{o})^{3}$, Dx= 6.71. The diffracted peaks corresponding to the face-centered cubic crystal structure of $Cu_{1.78}Se$ can be indexed to the planes (111), (200), (220), (311), (400), (420) located at 2ϴ angles 26.9, 44.6, 52.8, 61.9, and 73.6. The average crystallite size was calculated by the Debye-Scherer formula [17-20] was 17 nm. The size of the particles ranges from 13 nm to 20 nm.

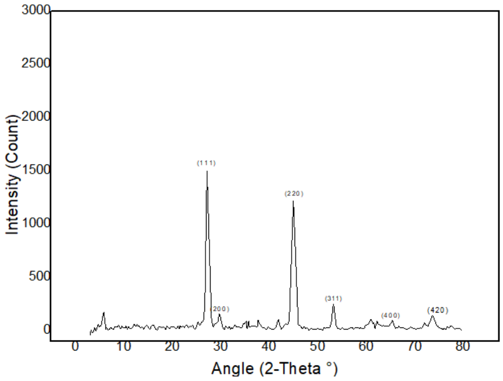

Fig.1: XRD pattern of as prepared $Cu_{2-x}Se$ nanoparticles

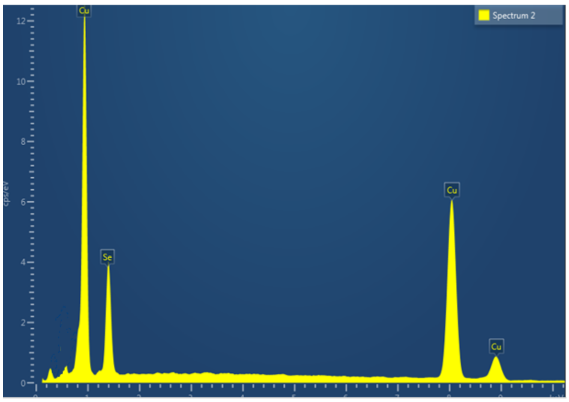

Fig.2: EDX spectrum of as prepared $Cu_{2-x}Se$ nanoparticles

C. *Energy Dispersive X-Ray Spectroscopy (EDX) Analysis*

EDX is an important technique to analyze the composition of elements quantitatively and to find the chemical identity of metals. EDX analysis was done using the Oxford XMX N EDX analyzer. Fig.2. shows the EDX spectrum of as-prepared $Cu_{2-x}Se$ nanoparticles. The EDX studies on the as-prepared nanoparticles confirm the presence of Cu and Se. No trace of other elements is observed. From the EDX analysis, it is clear that the obtained products are pure copper selenide nanoparticles. The EDX results are consistent with the XRD results and confirm that the prepared sample is copper selenide.

D. *Scanning Electron Microscope (SEM) Analysis*

Scanning electron microscopy (SEM) was carried out to analyze the morphology and the growth features of the aggregates of the as-prepared nanoparticles. SEM was carried out using a Hitachi S-3400 N scanning electron microscope operated at 3 kV. SEM images of as-prepared copper selenide nanoparticles are shown in fig.3. which shows that the particles are well agglomerated. The pictures confirm the formation of uniform spherical luminescent copper selenide nanoparticles. In the higher resolution, image formation of many small particles are seen which are possibly formed by the nucleation process. It is evident from the figure that the particles are luminescent quantum dots.

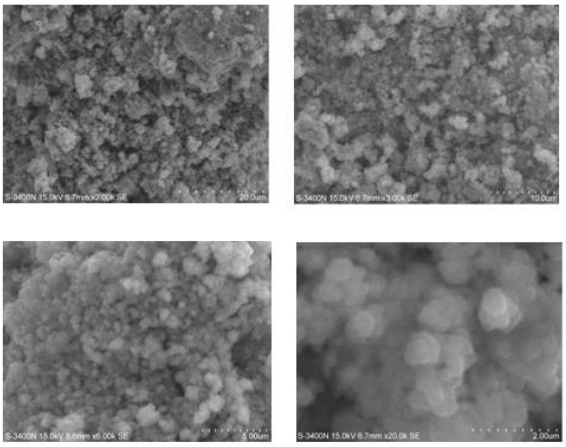

Fig.3: SEM micrograph of as prepared $Cu_{2-x}Se$ nanoparticles

E. FTIR Spectroscopy Analysis

The surface morphology of the as-synthesized $Cu_{2-x}Se$ nanocomposite was investigated and recorded by means of a Thermo Nicolet**,** Model; 6700 Fourier Transform Infrared Spectrometer. The infrared molecular spectrum of as-prepared Cu_2-xSe nanoparticles is shown in fig.4. The very weak peak observed at 442.35cm^{-1}may be due to the presence of Se, and the weak peak at 512.5 cm-^{1}is attributed to Cu-O band [21]. The bending vibration of Cu-Se is seen at 630.6 cm^{-1}. The peak at 740 cm^{-1} is attributed to the anti-symmetric stretching vibration of Se-O-Se [22]. The very weak peak at 966.3cm^{-1}assigned to Cu-O-Se stretching.

F. UV-Vis absorption spectroscopy Analysis

The optical absorption spectrum of the as-prepared non-stoichiometric $Cu_{2-x}Se$ nanoparticles was analyzed using VARIAN 5000 UV-Vis-NIR Spectrophotometer in the wavelength range of 200-900 nm and is shown in fig.5(a). An absorption edge is observed around 460 nm in the absorption spectrum. The increase in absorbance at the lower energy around 800 nm region originates from the indirect bandgap of the semiconductors [3]. The peak in the visible region is due to the recombination of holes resulted from photon emission with charge ionization in inherent deficiencies. Maximum absorption is observed in the ultraviolet and infra-red regions. The diffused reflectance spectrum is shown in fig.5(b). which shows a sharp reflectance around 583 nm.

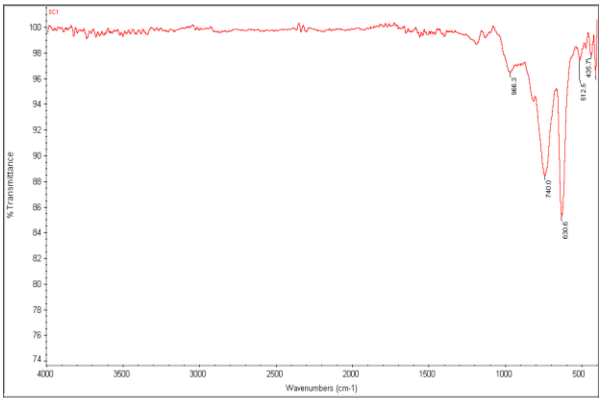

Fig.4: FTIR spectrum of non-stoichiometric as prepared $Cu_{2-x}Se$ nanoparticles.

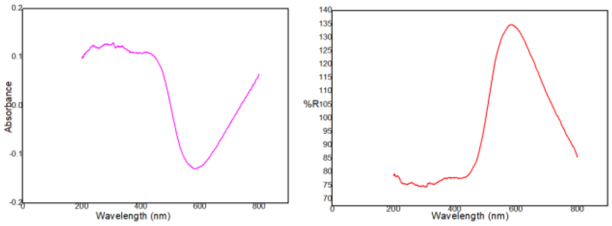

Fig.5(a): V-VIS-IR Absorption spectrum and (b) Diffused reflectance spectrum of as prepared $Cu_{2-x}Se$ nanoparticles.

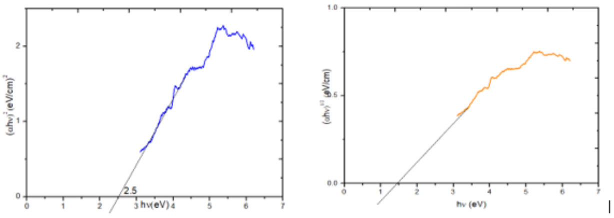

Fig.6(a): Taucplot for direct transition and b) indirect transition of as prepared $Cu_{2-x}Se$ nanoparticles.

UV-Vis absorption spectrum is very useful to calculate the optical band gap (Eg). From the relationship of near-edge optical absorption of semiconductors[7,24,25]. The plot of $(\alpha h\nu)^2$ versus hv (Tauc plot) is shown in Fig.6(a)&(b), from which the optical energy bandgap Eg= 2.5 eV for direct allowed transition and Eg=1.5 eV for indirect allowed transition is estimated by extrapolating the linear part up to zero on the energy axis. This is in good agreement with the reported values.

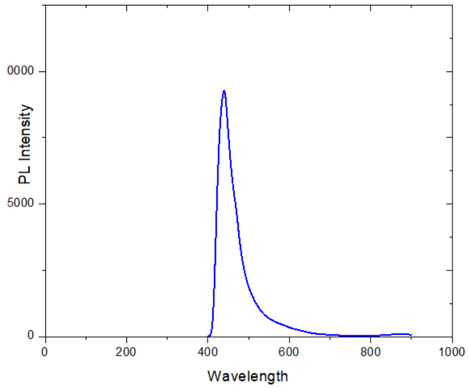

Fig.7: Photoluminescence spectrum of as prepared $Cu_{2-x}Se$ nanoparticles

G. Photoluminescence (PL) Analysis

The photoluminescence spectrum of the sample was recorded with a VARIAN ECLIPSE Fluorescence

Spectrophotometer. The photoluminescence spectrum of non-stoichiometric $Cu_{2-x}Se$ nanoparticles prepared by microwave-assisted solvothermal process excited at wavelength 380 nm is shown in fig.8. The spectrum exhibits a sharp, intense peak at 439 nm. Blue emission can be considered as direct recombination of conducting electron in conduction band and hole in valence band [23].

G. Thermal Analysis

Thermogravimetric (TG) and Differential thermogravimetric analysis (DTG) for the as-prepared Cu_2-xSe nanoparticles was performed on a Q600 SDT Thermal analyzer at a heating rate of 20 °C /min. Fig.4.9. shows the results of the thermal analysis of the greenish-black powder at a heating rate of 20°C/min in the nitrogen atmosphere. There is no weight loss in the range 0–486.38°C in the TG trace, which indicates the absence of coordinated or uncoordinated water molecules. This thermogram shows a two-step weight loss in the temperature range 486.38°C to 521.4°C and 870.19°C to 894.35°C. The first weight loss of 17.62% in the TG trace could be recognized in accordance with the endothermal reaction in the DTA trace (Fig.8). In the endothermal reaction, the thermal absorption could be due to the transformation to another phase of copper selenide. The second weight loss of 6.222% in the TG trace could also be recognized in accordance with the endothermal reaction. The prepared Cu_2-xSe nanoparticles are thermally stable up to 486^{o}C.

IV CONCLUSION

The nanostructured cubic Cu_2-xSe nanoparticles were prepared by a simple solvothermal method using a microwave oven. The prepared material was characterized and confirmed that the material was in nanoscale by XRD analysis. EDX analysis results confirm the presence of Cu and Se in the prepared samples. The direct and indirect bandgap energy of the material was estimated to be 2.5 eV and 1.5eV from the UV-Visible spectrum. The PL spectrum of the sample exhibits a sharp, intense peak at 439 nm. From the thermogram it is observed that the material is stable up to 486°C. From the results obtained it is evident that this material has good optical qualities and is well suited for optoelectronic devices and is a potential candidate for solar cells. As this is a non-toxic luminous, magnetic particle, this could be an interesting material for biological imaging and labeling as well.

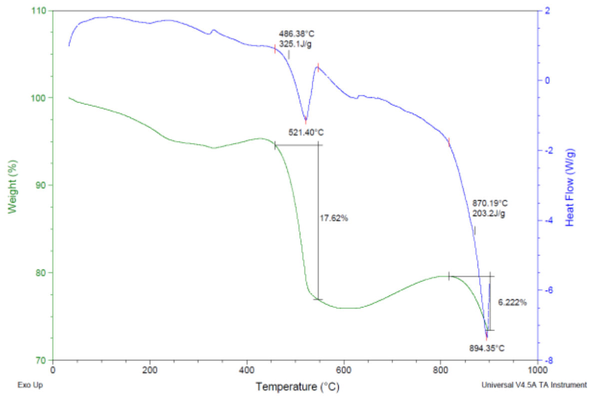

Fig.8: TGA curve of as prepared $Cu_{2-x}Se$ nanoparticles.

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