https://doi.org/10.30799/jnst.sp204.18040202 J. Nanosci. Tech. - Volume 4 Issue 2 (2018) 345–347

Share Your Innovations through JACS Directory

Journal of Nanoscience and Technology

Visit Journal at http://www.jacsdirectory.com/jnst

ISSN: 2455-0191

Special Issue on "International Conference on Nanomaterials - 2018" – Alagappa University *Issue Editor:* Dr. G. Ramalingam

Structural and Optical Characterization of Copper Selenide ($Cu_{2-X}Se$) Nanoparticles

Namith Nava Krishnan[1], S. Vijayakumar[1,2,*], P. Gnanadurai[3], R. Shabu[4], K.C. Preetha[5]

[1]*Department of Physics, Christian College, Chengannur – 689 121, Kerala, India.*
[2]*Department of Physics, NSS College, Pandalam – 689 501, Kerala, India.*
[3]*Department of Physics and Research Centre, NMSSVN College, Nagamalai, Madurai – 625 019, Tamilnadu, India.*
[4]*Department of Physics and Research Centre, Scott Christian College (Autonomous), Nagercoil – 629 003, Tamilnadu, India.*
[5]*Department of Physics, Sree Narayana College, Kannur – 670 007, Kerala, India.*

ARTICLE DETAILS

Article history:
Received 21 March 2018
Accepted 28 March 2018
Available online 06 April 2018

Keywords:
Copper Selinide
Nanoparticle
Spectral Studies

ABSTRACT

The stoichiometric Cu_2Se and non-stoichiometric $Cu_{1.98}Se$ nanoparticles were prepared by a simple chemical method at room temperature The X-ray diffraction patterns revealed the formation of single phase nanostructured Cu_2Se and $Cu_{1.98}Se$ particles with cubic lattice for different deposition conditions and the particle size is 17.45 nm, 26.85 nm respectively for Cu_2Se and $Cu_{2-x}Se$. Fourier transform infrared spectroscopy (FTIR) confirmed the formation of single phase Cu_2Se and $Cu_{1.98}Se$ nanoparticles, with characteristic vibrational modes of Cu and Se ions. Scanning electron microscopy (SEM) studies revealed that the Cu_2Se particle surface is found to be textured with grains of irregular shapes while for $Cu_{1.98}Se$, a mesh like structure which is loosely packed than Cu_2Se is observed. This distinction may be due to variations in Cu content as seen from EDAX analysis. UV-Vis Studies specify blue shift from the bulk copper selenide as observed from the absorption shoulders occurs at 281 nm for Cu_2Se and 276 nm for $Cu_{1.98}Se$ samples. The Optical band gap obtained for Cu_2Se and $Cu_{2-x}Se$ nanoparticles are 4.41 eV and 4.52 eV respectively.

1. Introduction

Nano crystalline copper chalcogenides have attracted an extensive attention due to their interesting properties and their great potential applications in many different fields. Copper selenide (Cu_2Se) belongs to II-VI group, which has received considerable attention in the past two decades because of its application in solar cell, optical filter, super ionic conductors, thermo electric converters, etc., [1]. Copper selenides are well known as a p-type semiconductor possessing a direct band gap, as well as an indirect band gap [2]. However, their band gap value (E_g) varies with the change of their stoichiometries or phases. Hong-Liang Li *et al.* [3] have employed a sonochemical-assisted approach to prepare α-CuSe crystals and the size and the shape of the products can be affected by changing the reaction time. Copper selenide can exist in a wide range of stoichiometric compositions (CuSe, Cu_2Se, $CuSe_2$, Cu_3Se_2, Cu_5Se_4, Cu $_7Se_4$, etc.) and non-stoichiometric compositions ($Cu_{2-x}Se$) and can be constructed into several crystallographic forms (monoclinic, cubic, tetragonal, hexagonal, etc. The special constitutions and properties of these compositions make copper selenide an ideal candidate for scientific research [1]. Pushpendra Kumar and Kedar Singh [4] have reported on successful synthesis of luminescent and crystalline copper selenide QDs in aqueous solution of hydrazine hydrate and ethylene glycol. They have found that from the absorption and photoluminescence studies display large blue shift and due to the quantum confinement effect copper selenide QDs could be potential building blocks to construct functional devices and solar cell. Pengfei Hu and Yali Cao [5] have reported a precipitation reaction route for the tuned preparation of different copper selenides ($Cu_{2-x}Se$ and CuSe) nanocrystals at room temperature. Yan Zhang [6] have synthesized via a modified composite hydroxide mediated method to prepare single crystalline $Cu_{2-x}Se$ nanowires with lengths up to 50 μm and from the UV-visible-near-infrared reflection spectrum demonstrates the absorption edges of the $Cu_{2-x}Se$ nano wires in the ultraviolet and near-infrared region, which could be interpreted in terms of direct transitions and indirect transitions respectively. Arokiya Mary and Joe Jesudurai [7] have synthesized Cu_2Se particles by the hydrothermal method at a temperature of 200 °C. Peranantham et al. [8] were prepared copper selenide and indium telluride thin films at different substrate temperatures by a vacuum evaporation technique and the optical transmittance measurements indicated the existence of direct and indirect transitions in copper selenide films. Chrissafis et al. [9] have studied the thermal effect accompanying the transition of $Cu_{2-x}Se$ into a superionic conduction state was studied by non-isothermal measurements at different heating and cooling rates and the phase transformation occurs at a peak temperature 136.8 °C for Cu_2Se and 133.3 °C for $Cu_{1.99}Se$. Arellano tanori et al. [10] have prepared the copper-selenide (CuSe)) copper-telluride (CuTe) and studied their optical properties. Fengxia Rong et al [11] have studied cuprous selenide (Cu_2Se) nanoparicles at room temperature. Ying Chyl Liew et al. [12] have prepared thin films of copper selenide and the structural, electrical properties are discussed. Gosavi et al. [13] have reported the physical, optical and electrical properties of CuSe thin films deposited by solution growth technique at room temperature. Hamzic et al. [14] have studied the magnetic transitions in $Cu_{2-x}Se$ below room temperature and found that on heating above 170 K it becomes completely diamagnetic. X-ray diffraction and Raman studies on $Cu_{2-x}Se$ prepared in non-vacuum process are carried out by Ara Cho et al. [15].

2. Experimental Methods

The $Cu_{2-x}Se$ nanoparticles were prepared at room temperature synthesis reported in the literature [16]. Copper nanocrystalline chlcogenides $Cu_{2-x}Se$ has been successfully synthesized in a mixture of ethlenediamine and hydrazine hydrate as a solvent at room temperature. All reagents were of analytical grade or better and used without further purification. A suitable proportion of powered copper oxide and Se were put into a conical flask with a capacity of 100 mL, and then mixed with solvent consisting of ethylenediamine and hydrazine hydrate.

$$4CuO+2N_2H_4.H_2O+3Se \longrightarrow 2Cu_2Se+4NH_4+3H_2O+2OH^-+Se^{2-}{}_3+2N_2.$$

The flask was maintained at room temperature with a constant electromagnetic stirring for 24 hours. The mixture initially changed to a dark greenish black color and finally to dark green with a black precipitate.

*Corresponding Author:jevijay@gmail.com(S. Vijayakumar)

https://doi.org/10.30799/jnst.sp204.18040202

Cite this Article as: Namith Nava Krishnan, S. Vijayakumar, P. Gnanadurai, R. Shabu, K.C. Preetha, Structural and optical characterization of copper selenide ($Cu_{2-X}Se$) nanoparticles, J. Nanosci. Tech. 4(2) (2018) 345–347.

The precipitate was collected by centrifuge and washed several times with hot distilled water (80 °C) and absolute ethanol. Then the washed precipitate is dried at 70 °C for 4 hours. The molar concentration of the solution is calculated as given below.

Mol. Wegt = Molecular Weight * Mole%* Vol. solvent /1000

In this paper we report a novel method for preparing nano copper selenide at room temperature. The copper selenide nanoparticles were characterized by X-ray diffraction (XRD), SEM with EDAX, UV, and FTIR.

3. Results and Discussion

The XRD patterns of as-prepared nano Cu_2Se and $Cu_{2-x}Se$ are shown in Fig. 1 within the 2θ range 10° to 70°. The characteristic peaks appearing at angles 26.9628°, 44.7188°, 53.0743° can be attributed to (111), (220) and (311), lattice planes of nanocrystaline Cu_2Se,and that appearing at angles 27.01°, 44.84°, 53.13° can be attributed to (111) , (220) and (311), lattice planes of nanocrystaline $Cu_{2-x}Se$. All peaks shown in Fig. 1 can be indexed to cubic phase copper selenide, the calculated cell constant is close to the value of JCPDS 88-2043, no impurity phase could be detected [17]. The XRD peaks are fairly broad suggesting nanostructure of Cu_2Se and $Cu_{2-x}Se$.

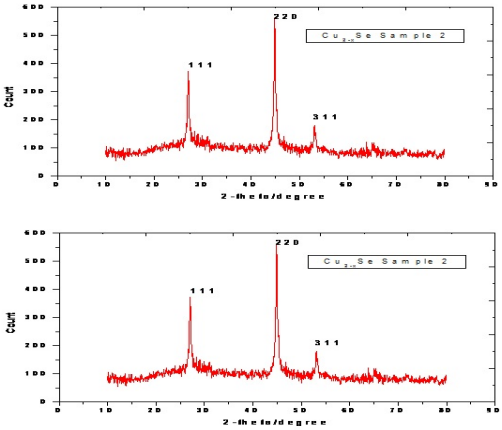

Fig. 1 XRD patterns of the (a) Cu_2 Se and (b) $Cu_{1.98}Se$

Tables 1 and 2 show the XRD data of copper Cu_2Se, $Cu_{2-x}Se$ nanocrystaline particles respectively. The XRD pattern matches well with reported cubic phase of Cu_2Se [17]. A simple method is used to calculate the grain size is based on the assignment of FWHM of XRD peaks.

The grain size was calculated scherrer's formula [18]

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

where λ is the wavelength of the X-ray, β is the full width at half maximum (radian); θ is the Bragg diffraction angle (Degree) of copper selenide peak.

Table 1 X-ray diffraction data of Cu_2Se nano particles

2θ (Deg)	FWHM (Deg)	hkl	d-spacing (Å)	Grain size calculated (nm)	d-spacing JCPDS (Å)
26.96	0.3936	111	3.30691	20.7475	3.2874
44.71	0.4920	220	2.02657	17.4530	2.0131
53.07	0.5904	311	1.72555	15.0343	1.7168

The particle size which was determined from the FWHM using Scherrer's formula was 17.45 nm, 26.85 nm respectively for Cu_2Se and $Cu_{2-x}Se$. From the diffraction peak, the cubic berzelianite Copper Selenide having lattice parameter 5.7320 Å, 5.7126 Å respectively for Cu_2Se and $Cu_{2-x}Se$. The lattice parameter of $Cu_{2-x}Se$ decreases from 5.7320 Å to 5.7126 Å due to the decrease of concentration of Cu vacancies.

Table 2 X-ray diffraction data of $Cu_{1.98}Se$ nano particles

2θ (Deg)	FWHM (Deg)	hkl	d-spacing (Å)	Grain size Calculated (nm)	d-spacing JCPDS (Å)
27.01	0.39	111	3.29845	20.9410	3.2874
44.84	0.32	220	2.01972	26.8545	2.0131
53.13	0.4	311	1.72244	22.201	1.7168

Fig. 2 shows the SEM micrograph and EDAX of the copper selenide nano particles. Microstructures of Cu_2Se exhibit remarkable difference as that of second one, $Cu_{2-x}Se$, and these changes can be attributed to change in. The micrograph reveals that the particle surface is found to be regularly textured with grains of irregular shapes. For $Cu_{2-x}Se$, morphology indicates a mesh like structure which is not densely packed as previous one. This variation may be due to variations in Cu content as seen from EDAX analysis. EDAX analysis results confirm the presence of Cu and Se in samples. The composition of Cu_2Se and $Cu_{2-x}Se$ was studied by EDAX technique. The elemental analysis result showed that the atomic ratio of Cu/Se is 2.30. The C atom signal (23.73%) and N atom signal (8.66%) and O atom signal (3.74%) are due to the organic matrix used before loading in to the machine. The elemental analysis result showed that the atomic ratio of Cu/Se is 1.97.

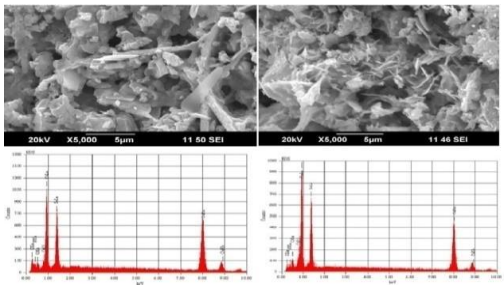

Fig. 2 SEM and EDAX of Cu_2Se and $Cu_{1.98}Se$

UV-Vis spectra of Cu_2Se and $Cu_{2-x}Se$ copper selenide nano particles are shown in Fig. 3. For Cu_2Se nano particles, an absorption shoulder was at 276 nm, indicating a band-gap energy of 4.41 eV, and for $Cu_{2-x}Se$ nano particles, an absorption shoulder was at 276 nm, indicating a band-gap energy of 4.52 eV, respectively. The optical band gap obtained for nano Cu_2Se and $Cu_{2-x}Se$ are 4.41 eV and 4.52 eV respectively. And the optical band gap of bulk crystal about 3.0 eV [1]. The optical band gap nano copper selenide is larger than that of bulk crystal. The blue shift of Cu_2Se and $Cu_{2-x}Se$ nano particles is 1.41 eV and 1.52 eV respectively. Optical band gaps were calculated using square and quadratic laws for indirect and direct transition via relation, $\alpha(h\nu)=A(h\nu-E_g)^{1/2}$, where α is the absorption coefficient, A is the constant, s=1/2 is for direct transitions, and s=2 is for indirect transitions[19].

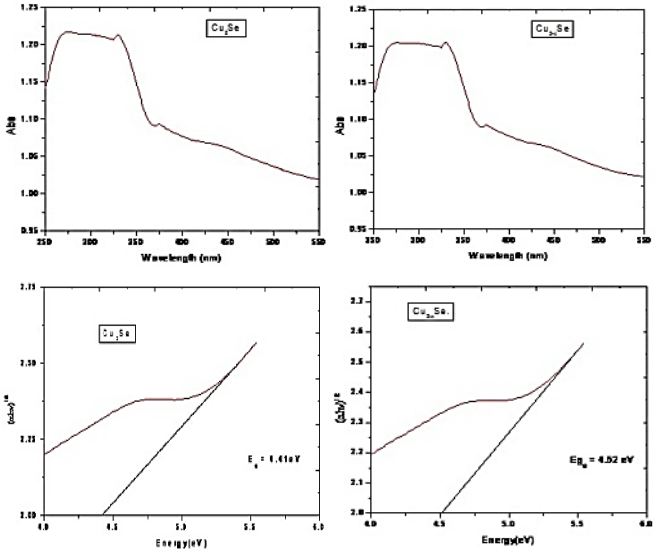

Fig. 3 Absorbance spectrum and Tauc's Plot of Cu_2Se and $Cu_{1.98}Se$

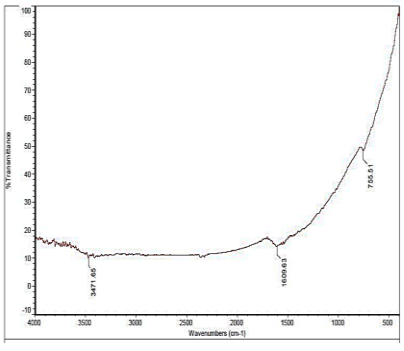

Fig. 4 FTIR spectrum of $Cu_{2-x}Se$ nanoparticles

https://doi.org/10.30799/jnst.sp204.18040202

Cite this Article as: Namith Nava Krishnan, S. Vijayakumar, P. Gnanadurai, R. Shabu, K.C. Preetha, Structural and optical characterization of copper selenide ($Cu_{2-x}Se$) nanoparticles, J. Nanosci. Tech. 4(2) (2018) 345–347.

Fourier transform infrared spectrum of the $Cu_{2-x}Se$ nanoparticles in the range of 500 – 4000 cm^{-1} is shown in Fig. 4. Two major peaks were observed at 1609.63 cm^{-1} and 3471.65 cm^{-1}. The peak at 1609.63 cm^{-1} may be attributed to the presence of Cu^{2+} ion in the present system. The peak at around 3471.65 cm^{-1} may corresponds to N-H stretching vibration band which can be attributed to the interaction of N_2H_4 with copper ions [20, 21].

4. Conclusion

The nano structured $Cu_{2-x}Se$ was prepared in chemical reaction method at room temperature and their particle size less than 30 nm. The prepared materials were characterized and confirmed that the size was in nanometers range by XRD analysis. The band gap energy of the nano $Cu_{2-x}Se$ estimated from UV-Visible spectrum. The SEM studies were carried out in nano Copper Selenide. EDAX analysis results confirm the presence of Cu and Se in $Cu_{2-x}Se$ samples. The FTIR studies were also carried out.

Acknowledgements

The authors wish to acknowledge CSIR-CECRI, Karaikudi for recording Laser Raman Spectrum; and STIC, Cochin University P.O., Cochin, for recording SEM With EDX, UV-VIS spectrum, DSC, FTIR spectrum.

References

[1] S.Y. Zhang, C.X. Fang, Y.P. Tian, K.R. Zhu, B.K. Jin, Y.H. Shen, J.X. Yang, Synthesis and characterization of hexagonal CuSe Nanotubes by templating against trigonal Se nanotubes, Cryst. Growth Des. 6 (2006) 2809-2813.

[2] A.M. Hermann, L. Fabick, Research on polycrystalline thin-film photovoltaic devices, J. Cryst. Growth 61 (1983) 658-664.

[3] H.L. Li, Y.C. Zhu, S. Avivi, O. Palchik, J. Xiong, Y. Koltypin, V.P. Aharon Gedanken, Sonocheical process for the preparation of α-CuSe nanocrystals and flakes, J. Mater. Chem, 12 (2002) 3723-3727.

[4] P. Kumar, Kedar Singh, Synthesis, characterizations, and optical properties of copper selenide quantum dots, Struct. Chem. 22 (2011) 103-110.

[5] P. Hu, Y. Cao, Synthesis of rod and lath-shaped CuSe and tremella-shaped $Cu_{2-x}Se$ nanostructures at room temperature, and their optical properties, J. Nanopart. Res. 14 (2012) 703-711.

[6] Y. Zhang, C. Hu, C. Zheng, Y. Xi, B.Wan, Synthesis and thermoelectric property of $Cu_{2-x}Se$ nanowires, J. Phys. Chem. C 114 (2010) 14849-14853.

[7] T. Arokiya Mary, Joe Jesudurai, A simple hydrothermal route for synthesizing copper selenide nano-flakes, Elixir Nanocomp. Mater. 50 (2012) 10499-10500.

[8] P. Peranantham, Y.L. Jeyachandran, C. Viswanathan, N.N. Praveena, P.C. Chitra, D. Mangalaraj, K. Narayandass, The effect of annealing on vacuum-evaporated copper selenide and indium telluride thin films, Mater. Charact. 58 (2007) 756-764.

[9] K. Chrissafis, K.M. Paraskevopoulos, C. Manolikas, Studying $Cu_{2-x}Se$ phase transformation through DSC examination, J. Therm. Anal. Calorim. 84 (2006) 195-199.

[10] O.A. Tanori, M.C. Acosta-Enriuez, R. Ochoa Landin, R. Iniguez-Palomares, T. Mendivil-Reynnoso, M. Flores-Acosta, Soso. J. Castillo, Copper-selenide and copper-telluride compostes powders synthesised by ionic exchange, Chalcogenide Lett. 11 (2014) 13-19.

[11] F. Rong, Y. Bai, T. Chen, W. Zheng, Chemical synthesis of Cu_2Se nanoparticles at room temperature, Mater. Res. Bull. 47 (2012) 92-95.

[12] J.Y. Chyi Liew, Z.A. Talib, W. Mahmood, M. Yunus, Z. Zainal Shaari, A. Halim, M.M. MoksinWan Mohd Yusoff, K. Pah Lim, Structural, morphology and electrical properties of layered copper selenide thin film, Cent. Eur. J. Phy. 7 (2009) 379-384.

[13] S.R. Gosavi, N.G. Deshpande, G. Gudage ramphal, Physical, Optical and electrical properties of copper selenide (CuSe) thin films deposited by solution growth technique at room temperature, J. Alloys Compd. 448 (2008) 344-348.

[14] Hamzić, Z. Ogorelec, K. Zadro, M. Basletić, Magnetic transitions in $Cu_{2-x}Se$ below room temperature, J. Magn. Magn. Mater. 233 (2001) 181-186.

[15] A. Cho, S. Ahn, J. Ho Yun, J. Gwak, S. Kyu Ahn, K.Shin, J. Yoo, H.n Song , K. Yoon, The growth of $Cu_{2-x}Se$ thin films using nanoparticles, Thin Solid Films 546 (2013) 299 -307.

[16] Y. Yan, K.M. Jones, J. Abu Shama, M.M. Al-Jassim, R. Noufi, A TEM study of the microstructure evolution of $Cu(In,Ga)Se_2$ films from Cu-Rich to In-Rich compound semiconductor, Photovolt. Mater. 668 (2011) 1-6.

[17] Y. Jiang, B. Xie, J. Wu, S. Yuan, Y. Wu, H. Huang, Y. Qian, Room-temperature synthesis of copper and silver, nanocrystalline chalcogenides in mixed solvents, J. Solid State Chem. 167 (2002) 28-33.

[18] S. Sonia, P. Suresh Kumar, D. Mangalaraj, N. Ponpandian, C. Viswanathan, Influence of growth and photocatalytic properties of copper selenide (CuSe) nanoparticles using reflux condensation method, Appl. Surf. Sci. 283 (2013) 802-807.

[19] M.L. Liu, L.B. Wu, F.Q. Huan, L.D. Chen, Promising p-type transparent conducting material: layered oxysulfide $[Cu_2S_2][Sr_3Sc_2O_5]$, Jour. Appl. Phy. 102 (2007) 116108-1-3.

[20] K.L. Krishnakumar, Mathew Paul, Metal complexes of heterocyclic unsaturated 1, 3 – diketones, Int. J. Pharm. Sci. Res. 4 (2013) 1154-1158.

[21] A.N. Parikh, S.D. Gillmor, J.D. Beers, K.M. Beardmore, R.W. Cutts, B.I. Swanson, Characterization of chain molecular assemblies in long-chain, layered silver thiolates: a joint infrared spectroscopy and X-ray diffraction study, J. Phys. Chem. B 103 (1999) 2850-2861.

About the Conference: "International Conference on Nanomaterials (ICAN) - 2018" has been organized by Dr. G. Ramalingam, ICAN-2018 Organizing Secretary, Assistant Professor, Department of Nanoscience and Technology, Alagappa University, Karaikudi, TN, India at his designated venue on 26th & 27th February 2018.

https://doi.org/10.30799/jnst.sp204.18040202

Cite this Article as: Namith Nava Krishnan, S. Vijayakumar, P. Gnanadurai, R. Shabu, K.C. Preetha, Structural and optical characterization of copper selenide ($Cu_{2-x}Se$) nanoparticles, J. Nanosci. Tech. 4(2) (2018) 345–347.