# SYNTHESIS AND CHARACTERIZATION OF FUNCTIONAL MATERIALS FOR ENERGY APPLICATIONS

***Summary of the Thesis***

**Submitted for the Award of the Degree**
**of**

**Doctor of Philosophy**

**In**
**Applied Physics**


**Submitted By**

**Krishan Pal**

**Enrollment No. 054/12**

**Under the supervision of**

**Dr. Khem Bahadur Thapa**

**Department of Applied Physics**
**School for Physical Sciences**
**Babasaheb Bhimrao Ambedkar University**
**(A Central University)**
**Lucknow -226025, U.P. (India)**


**2021**

# SUMMARY

## *SYNTHESIS AND CHARACTERISATION OF FUNCTIONAL MATERIALS FOR ENERGY APPLICATIONS*

Modern civilization is fully dependent on materials. Materials influence our daily life of every segment of transportation, housing, clothing, telecommunication, food production, etc. Earlier civilizations have been designated by the level of the development of their materials such as the Stone Age, Bronze Age, and Iron Age**.** The twenty first century is an era of technological development of functional and smart materials for sustainable energy applications. Researchers in materials science and engineering under *Science, Technology, Engineering and Mathematics* are looking at functional materials of metals and alloys, polymers, ceramics and composites as energy materials. The energy materials based on nanostructured functional materials are developing and considering the best materials for the manufacture of sustainable energy devices. To meet the demand for low cost and eco-friendly sustainable energy, energy materials and their new technologies are needed to be developed. Today, researchers around the world are focusing on the development of efficient and cost effective energy devices to meet the challenge of increasing energy demand. In addition to this, the energy devices must be fabricated in such a way that such devices are to be for environmental friendly. In this direction, new methods are being explored to convert solar energy into electrical energy by photovoltaic (PV) solar cells, which is the best way to obtain plentiful sustainable energy. The design and manufacture of PV solar cells are being used as the low cost and eco-sustainable devices. To develop innovative approaches, researchers are striving to engineer the low-cost, bearable and highly efficient equipment using abundant materials. Therefore, we have also attempted to study how functionalized ZnO, SnS, CZTS materials using abundant

materials are synthesized by low-cost synthesis processes. Based on the literature survey of functional materials for energy devices, we focused our study on the selection of functional materials (FMs) containing environmentally friendly, non-toxic, and low-cost constituent elements as well as environmentally friendly synthesis methods.

After selection of the constituents for compositions and synthesis methods, various characterization techniques were used to characterize as-synthesized functional materials and studied the electronic and optical properties of the FMs for energy applications. The ceramics, metals, polymers, and composite functional materials (FMs) have specific or native properties of the materials and used in ferroelectricity, piezoelectricity, magnetism, electron-transport property, and energy storage functions. Semiconductors have the intermediate characteristics property between the conductors and insulators. Semiconductor has lower energy band gap than insulator, but higher energy band gap than conductor. Furthermore, if we increase the concentration of impurity in the semiconductor or extrinsic semiconductor, the electrical and optical properties of the semiconductors become more sensitive than the intrinsic semiconductor. The Si, Ge, GaAs, Al, $BaTiO_3$, CdS, $Cu_2InS_3$, and $Cu_2ZnSnS/Se$ are the popular semiconductor materials and the functional elements like In, Se, Cd, etc. are frequently doped in pure materials. Generally these functional elements are rare-earth elements. In extrinsic semiconductors, the use of rare-earth elements makes them costlier than the abundant earth elements. This is the main drawback of such energy efficient materials to use in the solar cells. Besides this, some rare-earth elements are toxic in nature, which are hazardous for the environment.

Nowadays, the inorganic transition metal chalcogenides have generated a great interest among researchers to investigate due to their low-cost, efficient and eco-friendly materials. Using these chalcogenide materials, the cost-effective energy devices can be fabricated in electronic chips, energy conversions, and energy storage devices. The transition metal chalcogenides are emerging chalcogenide nanocomposites, which mainly include binary, ternary, quaternary metal chalcogenides, etc. Ternary and quaternary compounds have Perovskite-type structures, which are significant materials for both fundamental and scientific research. Besides this, SnS (binary chalcogenide) is also quite interesting owing to its excellent properties of hydrophobic and absorption that ensures its applicability in photodetector application.

In PhD research work, we have discussed the present issues of photovoltaic devices. We came to know that the efficiency and toxicity as well as cost of photovoltaic cells are the main issues, which are to be solved. The study shows that the inorganic functional materials at nanometer scale can resolve all these issues. CZTS, ZnO, SnS etc. are some inorganic materials that can be used as the energy materials. For instant, CZTS materials have a high absorption coefficient, suitable bandgap, low cost and eco-friendly photovoltaic properties and can be used to fabricate photovoltaic devices. Therefore, the researchers have already strived towards the synthesis of such materials from different methods to achieve various photovoltaic applications i.e. solar cells. We have also studied the synthesis methods and characterization techniques of such inorganic materials for their potential applications and found the inorganic chalcogenide materials may be excellent materials for energy conversion devices.

In the **chapter first**, we have studied the brief introduction of the functional materials for synthesis and characterization for potential applications. Here, we have given the study of the historical background of functional materials especially energy materials, and also their technical development in the field of Materials science and Engineering. This chapter mainly has focused on the inorganic chalcogenide materials, CZTS, SnS, ZnO, as the functional materials for photovoltaic cell applications and has also described the CZTS phases, electronic band structures, and important parameters to enhance the photovoltaic efficiency. CZTS is an $I_2$-II-IV-$VI_4$ group functional material and it can be used in solar cell due to have high absorption coefficient, suitable bandgap, low cost and eco-friendly material. In photovoltaic cell, the various types of effective parameters are considered and discussed how to resolve the hurdles of efficiency, toxicity and cost of solar cells. Besides this, we have also tried to find out the issues of the Kesterite materials based on the structure, band structure, electronic structure and studied how to get more than 20% efficiency of solar cells using the defects and different buffer layers **[1, 2]**.

**Second chapter** concludes the synthesis methods and characterization techniques for functional materials or energy materials for their potential applications in photovoltaic solar cells. The synthesis methods especially Co-precipitation, Spray

Pyrolysis and Hydrothermal/Solvothermal are described and explained that how these methods are suitable to synthesis the inorganic functional nanomaterials for photovoltaic purposes. Beside this, we have also discussed the characterization tools like XRD, EDS, SEM & FESEM, UV-Visible, Raman spectroscopy, XPS, I-V characteristics measurement Keithley that are useful tools to study the crystal structure, element composition surface morphology, energy band gap, phase identification, etc.

**Chapter three** deals with the synthesis of II-VI group functional nanomaterial, ZnO nanomatrial by Co-precipitation method and has characterized the as-synthesized material **[3]**. The results have found that the II-VI group functional nanomaterial may be used as the window layer in solar cell applications. The functional material ZnO was synthesized by Co-precipitation method without any surfactants and vacuum/noble gases and this method is an economically low-cost method for synthesis of ZnO nanomatrial in comparison to the other synthesis methods. This work suggests that the synthesis of ZnO without any surfactant is beneficial for commercial productions of the ZnO nanomaterial as well.

**Chapter four** deals with the synthesis of CZTS nanocrystals with S variation in the CZTS composition by Co-precipitation method without any types of annealing. In the synthesis of nanocrystals, no surfactant has been used in the precursor solutions. XRD, EDS, SEM, Raman, UV-Visible techniques are used to characterize the synthesized of CZTS with 18mmol quantity of sulphur in precursor solution (sample-B) and it is found in the investigation that CZTS is stoichiometric form and polycrystalline nature. The observed polycrystalline results are similar to the results found by vacuum annealing/sulphurization method. The surface electron microscope (SEM) reveals that the polycrystalline CZTS phase has good morphology and good morphology of CZTS, which is good for electronic and optical characteristic properties. The obtained results are very exciting and demonstrated that the synthesized nanocrystals by proper route may fulfill the promise of low-cost thin film for photovoltaic cell applications. The novelty of this work is the synthesis of CZTS nanocrystals with suitable quantity of sulphur in precursor solution by Co-precipitation method without any sulphurization and selenisation processes **[4]**. This route of synthesis offers for low cost, less time-consuming and nontoxic CZTS nanocrystals and suitables to use as the absorber layer in Kesterite photovoltaic applications**.**

**Chapter five** discusses the synthesis and characterization of IV-VI group functional material SnS for energy applications. The SnS nano flakes thin-film is fabricated with help of the self-made low cost spray pyrolysis method (SPM). The spray pyrolysis is a cheap, less time consuming, non-toxic and ecofriendly method. First time, we have grown SnS thin films by SPM method and SnS nano flakes are found hydrophobic and scratchproof nature. The SnS thin film by the SPM route is found low response/recovery time in comparison to the CVD route and useful for photodetector applications **[5]**. The stability of the SnS photodetector is also found to be much stable i.e. for around one year. The SnS nanoflakes trap the light and increase the absorption as shown in optoelectronic and I-V characteristics.

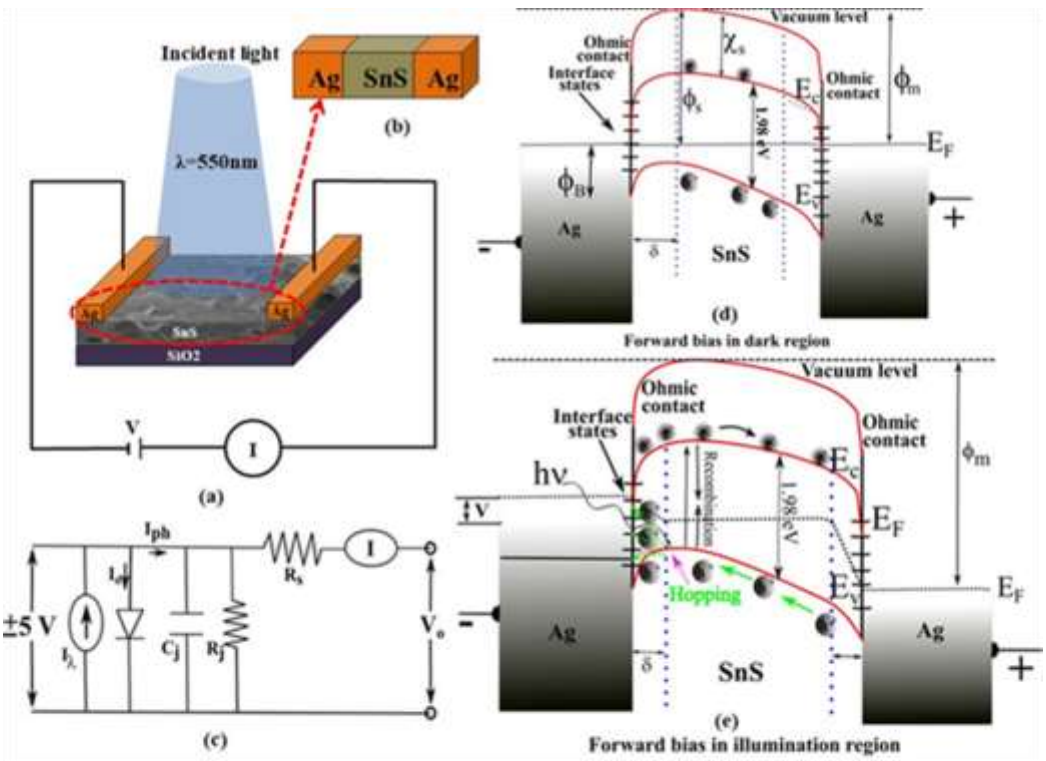


**Figure 1:** Schematic diagram representation: (a) Photodetector device with average wavelength 550nm light source for photo response measurement, (b) Photodetector contacts with metal (Ag)/Semiconductor (SnS)/metal (Ag) bricks, (c) Equivalent circuit diagram of photodetector (Input voltage= ± 5V, illumination current =$I_\lambda$, dark current = $I_d$, Junction capacitance =$C_j$, Junction resistance =$R_j$, Series resistance =$R_s$,

photo current $=I_{ph}$) (d) The electronic band structure for forward bias in dark region, (e) Electronic band structure for forward bias in illumination region at -5V to +5V.

The high absorption of light may be helpful in the photovoltaic industry. The photo parameter of the SnS nano-flakes layer has been analyzed and investigated the photo response, photosensitivity, photocurrent and photo resistance and shown in Fig. 1. These photo parameters justify the application of low cost photo-detector. The thin-film SnS photodetector is feasible for commercial application devices because it is grown by nontoxic, eco-friendly, less time consuming and low cost SPM method with abundant precursors. The SnS layer has one advanced feature of hydrophobicity, which provides to the automated dust-free devices. This research work is suitable for commercial application with money saving and eco-friendly.

A layer of SnS nano flake may also be suitable for the JABS layer or interfacial layer into the Kesterite hetero-junction photovoltaic devices because it has a positive band offset, which removes the thermionic loss and diffusion loss of charge carriers at the interface. In the JABS mechanism, the efficiency of Kesterite type photovoltaic (PV) device of structure, *Ag/ARC/Al-ZnO/i-ZnO/CdS/**SnS**/CZTS/ITO*, is helpful to enhance the conversion efficiency. Such an arrangement may be capable to achieve the highest record efficiency of CZTS solar cell. The SnS thin film may also resolve the usual problem of thermionic and diffusion losses, as well as recombination of electrons-holes in the CZTS solar cell. Hence, the SnS thin film may be used as a JABS layer in the hetero-junction device with structure *Ag/ARC/Al-ZnO/i-ZnO/CdS/**SnS**/CZTS/ITO* for the record efficiency of CZTS solar cell **[6]**.

**Chapter six** concludes the conclusion and future prospects of this research work. In this chapter, we suggest that the functional materials can be used to resolve the issues of stoichiometry phase, toxic environment and high cost of materials. The inorganic functional materials are easily synthesized with spray pyrolysis method, which is a less time taking process in comparison to the complicated synthesis method like CVD. We also conclude that the thermionic and diffusion losses, and recombination of electrons-holes, are also resolved by selecting suitable functional materials and synthesis techniques. The low cost synthesis methods like precipitation and spray pyrolysis method are suitable for functional nanomaterials. The characterization techniques for the as-synthesized functional materials are also revealed that the inorganic functional materials are useful to fabricating the energy devices for commercial use. The whole conclusion of the research work is tabulated in Tab. 1.

**Table 1:** The chapter wise conclusion of this thesis:

| **Chapter No.** | **Photovoltaic Materials** | **Size (nm)** | **Energy Band-gap (eV)** | **Applications** | **Recovery Time (s)** | **Response Time (s)** | **Toxicity Nature** | **References** |
|---|---|---|---|---|---|---|---|---|
| Ch. 1 | Introduction | | | | | | | **[1, 2]** |
| Ch. 2 | Synthesis Methods and Characterization Techniques | | | | | | | |
| Ch. 3 | ZnO without surfactant | 22-28 | 3.2 | Window layer | | | Non-toxic | **[3]** |
| Ch. 4 | $Cu_2ZnSnS_4$ | 15-17 | 1.33 | Absorber layer | | | Non-toxic | **[4]** |
| Ch. 5 | SnS flakes | 27.68 | 1.98 | Photodetector | 1.56 | 1.69 | Non-toxic | **[5]** |
| | | | | JABS layer in Photovoltaic Cells | | | | **[6]** |
| Ch. 6 | Conclusion and Future Prospects | | | | | | | |

The low cost, non-toxic and eco-friendly functional nanomaterials are synthesized with the feasible synthesis methods at room temperature. For this, we have synthesized ZnO, CZTS and SnS functional materials by Coprecipitation method (CPM) and spray pyrolysis method (SPM). The Zn, Cu, Sn, Zn and S are abundant earth elements and CPT/SPT are cost-effective and eco-friendly synthesis methods. Using CPT, we have synthesized the II-IV group (ZnO) functional material without any surfactants. The characterizations of ZnO nanomaterials have been justified that

ZnO nanomaterials may be used as window layer of the hetero-junction Kesterite solar cell. By taking balanced stoichiometric ratio of the precursor of Zn, Cu, Sn and S elements, the stable quaternary compound of CZTS can be synthesized in the open environment. The characterizations of CZTS nanomaterials have been validated that CZTS compound may be suitable for absorber layer in photovoltaic solar cells. Using SPM, a thin film of SnS functional nanomaterials has synthesized and the SnS thin film has hydrophobic characteristic property that may be used as the hydrophobic photodetectors. The I-V characterizations of SnS functional nanomaterials have been justified for hydrophobic photodetector with better photo response and recovery time in comparison to the traditional photodetector. Our studies reveal that the CPT and SPT are the best synthesis methods for the low-cost, high efficient and eco-friend functional nanomaterials (ZnO, CZTS and SnS) for optical and electronic devices. The photovoltaic solar cells and hydrophobic photodetectors may be fabricated with low cost, non-toxic and eco-friendly elements of the compounds as well as the synthesis methods.

By adopting the abundant earth elements (Zn, Cu, Sn, Zn and S) and cost-effective and eco-friendly synthesis methods (CPT/SPT), the photovoltaic solar cells and hydrophobic photodetectors may be fabricated in future. Such devices may be the low-cost, high efficient and eco-friendly for photovoltaic cells and hydrophobic photodetectors that may be adopted to industry for mass production. As we know that the ratio of the performance to the cost of the functional material should be high for commercial use of any functional materials in the field of Materials Science and Engineering. This ratio may be achieved high by choosing the low cost, non-toxic and eco-friendly elements for compositions, and low cost and ecofriendly fabrication for synthesis and processing.

# References:

[1] K. Pal, K. B. Thapa, and A. Bhaduri, A Review on the Current and Future Possibilities of Copper-Zinc Tin Sulfur Thin Film Solar Cell to Increase More Than 20% Efficiency, ***Adv. Sci. Eng. Med***., 10, 1-7, 2018.

[2] K. Pal, P. Singh, A. Bhaduri and K. B. Thapa, Current challenges and future prospects for a highly efficient (> 20%) kesterite CZTS solar cell: A review, ***Sol. Energy Mater. & Sol. Cells.,*** 196, 138–156, 2019.

[3] Shweta, K. Pal and K. B. Thapa, Synthesis and characterization of ZnO nano-particles for solar cell application by the cost effective co-precipitation method without any surfactants, ***AIP Conf. Proc.,*** 2142, 030008-1–030008-4, 2019.

[4] K. Pal, D. K. Maurya, P. Chaudhary, K. B. Thapa, and B. C. Yadav, Co-precipitation Synthesis with a Variation of the Sulphur Composition of Kesterite Phase $Cu_2ZnSnS_4$ (CZSS) without Annealing, ***Process, J. Phys. Sci.,*** 32(2), 27–39, 2021.

[5] K. Pal, P. Chaudhary, R. K. Tripathi, S. Tiwari, and K. B. Thapa, B. C. Yadav, Non-toxic, low cost, stable, and auto-cleaned visible photodetector of Tin (II) Sulphide (SnS) nanoflakes for commercial application, ***Mater. Chem. & Phys***., August 2021(*Communicated-JESTCH-S-21-05227*).

[6] K. Pal, R. K. Tripathi, K. B. Thapa, Non-peel-off and recombination reducing JABS layer into the hetero-junction $Cu_2ZnSnS_4$ solar cell: A new approach, ***Asia-Pacific Journal of Science and Technology***, August 2021(*Communicated-APST-S-21-01397*).

# LIST OF PUBLICATIONS

I. **Krishan Pal**, Pawan Singh, Abhishikta Bhaduri and Khem B. Thapa, Current challenges and future prospects for a highly efficient (> 20%) kesterite CZTS solar cell: A review, ***Sol. Energy Mater. & Sol. Cells.,*** 196, 138–156, 2019.

II. **Krishan Pal**, Khem B. Thapa, and Abhisikta Bhaduri, A Review on the Current and Future Possibilities of Copper-Zinc Tin Sulfur Thin Film Solar Cell to Increase More Than 20% Efficiency, ***Adv. Sci. Eng. Med***., 10, 1-7, 2018.

III. **Krishan Pal**, Pawan Singh, Abhishikta Bhaduri and Khem B. Thapa, Current challenges and future prospects for a highly efficient (> 20%) kesterite CZTS solar cell: A review, ***Sol. Energy Mater. & Sol. Cells.,*** 196, 138–156, 2019.

IV. **Krishan Pal,** Dheeraj Kumar Maurya, Priyanka Chaudhary, Khem Bahadur Thapa, and Bal Chandra Yadav, Co-precipitation Synthesis with a Variation of the Sulphur Composition of Kesterite Phase $Cu_2ZnSnS_4$ (CZSS) without Annealing, ***Process, J. Phys. Sci.,*** 32(2), 27–39, 2021.

V. Shweta, **Krishan Pal** and Khem B. Thapa, Synthesis and characterization of ZnO nano-particles for solar cell application by the cost effective co-precipitation method without any surfactants, ***AIP Conf. Proc.,*** 2142, 030008-1–030008-4, 2019.

VI. Pawan Singh, **Krishan Pal**, Khem B. Thapa, Narinder Kumar, Devesh Kumar,
First edition, Advances in Photonic Crystals and Devices: Embedded Liquid Crystal Defect with Graphene Layers in Asymmetric One-Dimensional Photonic Crystal as Sensor Application, ISBN:9781351029421, ***CRC Press,*** Boca Raton Florida 2019.

VII. Pawan Singh, Khem B Thapa , Narinder Kumar, **Krishan Pal** and Devesh Kumar, Graphene layers on semi-finite 1D asymmetric periodic structure of Si/Glass materials with defect of nematic liquid crystal for a sensor device, ***Mater. Res. Exp.***, 6, 066209, 2019.

VIII. Varsha Gautam, **Krishan Pal**, Narendra Kumar, DR G N Pandey, Bhuvneshwer Suthar, Khem B. Thapa, Sant P. Ojha, Low cost synthesis of ZnO nano-particles, and characterization study for the device of water disinfection, ***AIP Conf. Proc.,*** 2220(1), 020170, 2020.

IX. Roshni Maurya, Pawan Singh, Prabal P. Singh, **Krishan Pal**, Girijesh N. Pandey, and Khem B. Thapa, Absorption and bandwidth properties of graphene based 1D-photonic crystal for THz devices, ***AIP Conf. Proc.,*** 2220, 020084, 2020.

X. Asish Kumar, Pawan Singh, **Krishan Pal**, Narendra Kumar, Khem B. Thapa, Broadband reflector of 1D photonic crystal containing $TiO_2/SiO_2$ material at visible region, ***AIP Conf. Proc.,*** 2220(1), 020068, 2020.

## COMMUNICATED MANUSCRIPTS

I. **Krishan Pal**, Priyanka Chaudhary, Ravi Kant Tripathi, Sumit Tiwari, and Khem B. Thapa, B. C. Yadav, Non-toxic, low cost, stable, and auto-cleaned visible photodetector of Tin (II) Sulphide (SnS) nanoflakes for commercial application, ***Mater. Chem. & Phys***., August 2021(*Communicated-JESTCH-S-21-05227*).

II. **Krishan Pal**, Ravi K. Tripathi, Khem B. Thapa, Non-peel-off and recombination reducing JABS layer into the hetero-junction $Cu_2ZnSnS_4$ solar cell: A new approach, ***Asia-Pacific Journal of Science and Technology***, August 2021(*Communicated-APST-S-21-01397*).

III. Priyanka Chaudhary, Arpit Verma, Akash Mishra, **Krishan Pal**, E. Ranjith Kumar, B. C. Yadav, Khem B. Thapa, Surbhi Mishra, D. K. Diwedi, Preparation of carbon quantum dot using bike pollutant: Evalution of structural, optical and moister sensing properties, ***Mater. Sci. & Eng.,*** July 2021.