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Influence of PVP on the properties of solvothermally synthesized famatinite nanoparticles: Structural, morphological and optical insights

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ABSTRACT

Famatinite (Cu_3SbS_4) nanoparticles were synthesized through a solvothermal approach using various polyvinylpyrrolidone (PVP) ratios as a capping agent with a binary solvent of ethylene glycol and water in equal parts. Incremental additions of PVP, ranging from 0 to 1.5 g, exerted significant influence on the material's characteristics. Through comprehensive analysis involving X-ray diffraction, Raman spectroscopy, Scanning electron microscopy (SEM) with Energy dispersive spectrometer (EDS), and UV diffuse reflectance spectroscopy, critical insights were obtained. XRD analysis confirmed the tetragonal crystal structure and revealed reduced crystallite sizes due to the incorporation of PVP. Raman spectroscopy validated the presence of pure famatinite phase with 0.5 g and 1.0 g PVP. SEM analysis uniformly depicted a spherical morphology in all samples, emphasizing PVP's role in mitigating nanoparticle agglomeration. UV diffuse reflectance spectroscopy disclosed direct bandgaps falling within the 0.88 – 0.97 eV range. The collective findings highlighted the substantial impact of PVP in the binary solvent on the structural, morphological, and optical properties of Cu_3SbS_4 nanoparticles. These results underscore the potential application of these tailored nanoparticles as promising candidates for advanced photovoltaic absorber materials.

1. Introduction

In the quest for more efficient, versatile, and cost-effective solar energy, thin-film photovoltaics have emerged as a prime example. Thin-film photovoltaics represent a transformative leap in solar energy technology, offering a lightweight, flexible, abundant and cost-effective alternative to traditional silicon-based cells [1–3]. Cu-Sb-S based materials are still in the early phases of study, but their non-toxic composition and tunable features make them a possible sustainable substitute for hazardous absorber materials based on Cd, Te, Pb, and Se as well as for the scarce In and Ga based absorber materials [4]. The challenge lies in optimizing their performance to match or surpass the efficiency levels of CdTe (20.6 %), CIGS (20.8 %) [5], DSSC (13 %) [6], CZTS (11 %) [7] and perovskite (15.4 %) [8] based photovoltaic materials.

Tenary copper antimony sulphide compound has four phases: CuSbS_2 (Chalcostibite) [8,9,10], Cu_3SbS_4 (Famatinite) [11,12], Cu_3SbS_3 (Skinnerite) [13], and $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ (Tetrahedrite) [14,15]. Their diverse range of optical and electrical properties, high absorption coefficient of

around 10^5 cm^{-1} and p-type conductivity make them ideal candidates for use as p-type absorber materials in photovoltaics. These phases offer a spectrum of bandgap values, typically ranging from around 0.5–2 eV, making them well-suited for absorbing a broad range of solar spectrum [16]. Scientists and engineers can experiment with these materials' tunable qualities to optimise the efficiency of solar cells. Tailoring the bandgap and optimizing the electronic structure could lead to enhanced efficiency and stability, making Cu-Sb-S group materials stand out in the crowded field of photovoltaics [17]. Famatinite (Cu_3SbS_4) has been gaining attention as a promising absorber layer in solar cells since it exhibits excellent light absorption characteristics, especially in the visible and near-infrared regions of the solar spectrum [18]. Famatinite nanoparticles can be synthesized over a variety of methods [19–22], and these methods typically involve mixing precursor solutions or reactants under controlled conditions, enabling the gradual formation and growth of nanoparticles with desired properties. The adjustment of parameters such as temperature, pressure, precursor concentrations, and reaction times allows precise control over the synthesis process, providing

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opportunities for customized applications in fields like solar energy, thermoelectric energy [23] and optoelectronics [24].

Changhua An et al. used a mild hydrothermal process to synthesize Cu_3SbS_4 nanofibers, and the reaction temperature and medium greatly influenced the phases and the morphology of the final product [21]. Qun Wang et al. produced hierarchical flower-like microspheres composed of Cu_3SbS_4 nanoflakes doped with chlorine (Cl-) through a one-pot solvothermal ion exchange process. This synthesis method utilized a solvent mixture consisting of 3:1 ethylene glycol to acetylacetone. [25]. M. Bella et al. synthesised pure Cu_3SbS_4 nanocrystals by varying the surfactant to solvent volumetric ratio and sulfur to copper molar ratio [11]. Sulawan Kaowphong et al. prepared CuInS_2 nanoparticles by using a mixed solvent of water and ethylene glycol (1:1) as a liquid medium, expecting that altering the reaction medium could tailor the characteristics of the synthesized CuInS_2 particles, such as purity, crystallinity, shape, particle size, and particle size distribution [22]. In order to prevent the formation of a well-crystalline metal ion-En complex, Mou Pal et al. reported the synthesis of phase pure chalcocite CuSbS_2 nanocrystals by employing ethylenediamine and deionized water with varied ratios as solvent by solvothermal technique [26].

Polymers have been widely used in various applications due to outstanding properties such as their low cost, stability, easy fabrication, etc. [27]. Furthermore, their favorable mechanical, thermal, and electrical characteristics have rendered them highly intriguing for both research and industrial applications [28]. Polymer blends have recently emerged as highly promising materials for many applications including solar cells, sensors, energy storage, as well as water desalination [29]. One such polymer is PVP, which has been found to exhibit chemical inertness, non-toxic, and readily soluble in water [30]. PVP is a significant polymer due to its capacity to improve physical qualities [31]. In their solvothermal synthesis of Cu-Sb-S nanoparticles, Bincy John et al. utilized PVP as a size-reducing agent and to stabilize the growth and formation of well-defined structure [32]. In their recent study Kallum et al. reported that PVP can serve as an excellent stabilizer and shape-directing agent in the synthesis of metal chalcogenide (MC) nanoparticles, preventing their aggregation and passivating surface states. They also noted that the utilization of PVP can improve optical properties under specific circumstances [33].

B. John et al. reported on the effects of PVP on the structural, morphological, optical, and electrical properties of the synthesised CuSbS_2 nanoparticles by the solvothermal method using ethylene glycol as solvent [34]. The influence of varying PVP ratios on the phase composition and morphology of CuSbS_2 nanoparticles that were synthesised by microwave radiation was investigated by Wei Wang et al. [35]. The above-mentioned research articles employed varied solvent compositions and adjusted capping agent concentrations. This deliberate manipulation enables us to customize the chemical and physical properties of Cu_3SbS_4 nanoparticles within the solvothermal system.

The present research utilized a novel mixed binary solvent composed of distilled water and ethylene glycol to initiate the synthesis of tetragonal famatinite nanocrystals. The quantity of the capping agent (polyvinylpyrrolidone, PVP) was varied to modify the structural, morphological, and optical characteristics of the material. During the synthesis process, PVP is essential for stabilising nanoparticles and regulating their growth by preventing them from agglomerating or getting too big. The size, shape, crystal structure and morphology of the synthesized Cu_3SbS_4 nanoparticles were influenced by the concentration of PVP used. The findings of this work will make a captivating subject in the ongoing quest for more efficient, earth abundant, less toxic, affordable and promising photovoltaic absorber material.

2. Experimental procedure

2.1. Chemicals

Copper (II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) and antimony

trichloride (SbCl_3) were purchased from Sigma Aldrich. Thiourea ($\text{CH}_4\text{N}_2\text{S}$) was purchased from Loba Chemie Pvt. Ltd. Polyvinylpyrrolidone (PVP) with a molecular weight of 40000 was purchased from Sisco Research Laboratories Pvt. Ltd (SRL). Ethylene glycol was purchased from Merck. All the chemicals purchased were in analytical grade and used without further purification.

2.2. Synthesis of Cu_3SbS_4 nanoparticles

The synthesis of famatinite nanoparticles employed a simple solvothermal approach utilizing a binary solvent. This solvent was prepared by mixing 75 ml of ethylene glycol with 75 ml of distilled water, resulting in a total volume of 150 ml. To this solvent mixture, 25 mM of copper (II) chloride dihydrate, 25 mM of antimony trichloride, and 75 mM of thiourea were added and stirred for 30 min. This solution was labelled as PVP_0 because polyvinylpyrrolidone (PVP) was not added during the synthesis process. Subsequent solutions, designated as $\text{PVP}_{0.5}$, $\text{PVP}_{1.0}$, and $\text{PVP}_{1.5}$, were prepared by adding varying amounts of PVP (0.5 g, 1.0 g, and 1.5 g, respectively) during the stirring process. Following preparation, each solution was transferred straight into a 200 ml teflon-lined autoclave and subjected to a temperature of 180°C for 24 h in a hot air oven. Once the desired time elapsed, the hot air oven was allowed to cool down to room temperature. Then, the autoclave was removed from the oven, and the resulting nanoparticles were recovered by repeated centrifugation using distilled water and ethanol at 3000 rpm for 10 min, aiming to remove excess capping agent, reaction byproducts, and unreacted salts. The synthesized nanoparticles were black in color and were subsequently dried overnight at 150°C . This process ensured the production of famatinite nanoparticles with the desired properties for further characterization.

2.3. Characterization

The synthesized Cu_3SbS_4 nanoparticles were characterized by Powder X-ray diffraction (BRUKER-binary V4) equipped with Cu-K alpha1 ($\lambda=1.54060 \text{ \AA}$, 40 kV, 30 mA and step width 0.04). The phase of the synthesized nanoparticles was confirmed by Raman analysis technique (Invia reflex raman microscope with spectrometer) with an excitation of 785 nm near IR laser light. The morphology, particle size and chemical composition were determined by Scanning electron microscopy and Energy dispersive spectrometer (SEM with EDS, ZEISS at accelerating voltage of 10 KV). The optical properties of the nanoparticles were determined by UV Diffuse reflectance spectroscopy, (SHIMADZU UV 2600) in the range of 220 – 1400 nm.

3. Results and discussion

3.1. Structural analysis

The structure, crystallite size and phase of the synthesized nanoparticles with different PVP ratios of PVP_0 , $\text{PVP}_{0.5}$, $\text{PVP}_{1.0}$ and $\text{PVP}_{1.5}$ were analysed using XRD technique. Fig. 1 represents the XRD patterns of all the above samples and their comparison with JCPDS (PDF: 01-085-1344) card. The XRD patterns of all these samples confirmed the famatinite (Cu_3SbS_4) phase of nanoparticles and they have tetragonal crystal structure.

PVP_0 displays the famatinite (Cu_3SbS_4) phase at specific angles $2\theta = 28.81^\circ$, 29.98° , 33.28° , 47.88° and 56.75° , corresponding to planes (112), (103), (200), (204) and (312) respectively [36]. Additionally, it shows the presence of chalcocite (CuSbS_2) phase at $2\theta = 49.88^\circ$, identified with the (521) plane [32]. Meanwhile, $\text{PVP}_{1.5}$ reveals the famatinite phase at $2\theta = 28.67^\circ$, 29.89° , 33.13° , 47.92° and 56.57° , associated with planes (112), (103), (200), (204) and (312) [36] along with chalcocite peaks at $2\theta = 49.81^\circ$ and 54.28° , linked to planes (521) and (621) respectively (PDF: 00-044-1417) [32]. However, both $\text{PVP}_{0.5}$ and $\text{PVP}_{1.0}$ exclusively exhibit the famatinite phase at $2\theta = 28.69^\circ$, 29.85° ,

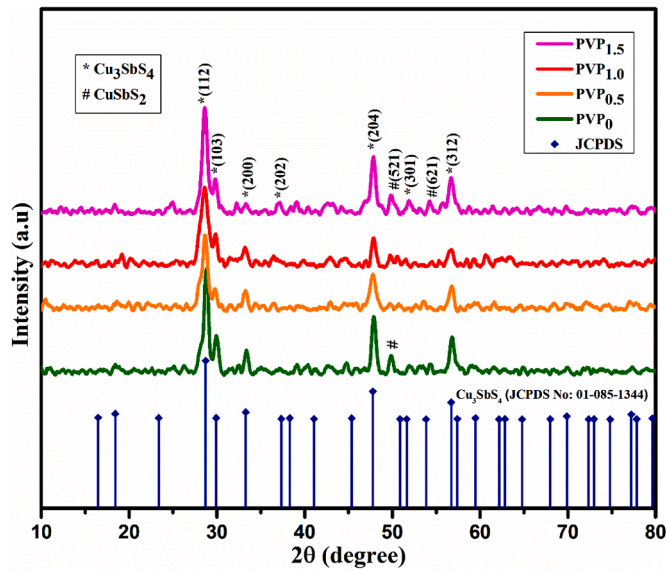


Fig. 1. XRD pattern of Cu_3SbS_4 nanoparticles prepared with different PVP ratios.

33.20°, 47.75° and 56.69°, corresponding to planes (112), (103), (200), (204) and (312), and at $2\theta = 28.61^\circ$, 29.90°, 33.30°, 47.73°, and 56.62°, attributed to planes (112), (103), (200), (204), and (312) respectively. Shigeru Ikeda et al. synthesized Cu_3SbS_4 nanoparticles which shows sharp peaks in XRD analysis at angles $2\theta = 28.5^\circ$, 32.5° , 47.5° and 56.5° attributed to planes (112), (200), (204) and (312) respectively (30). These findings align well with the values in the JCPDS card (PDF: 01–085–1344) for Cu_3SbS_4 nanoparticles and (PDF: 00–044–1417) for CuSbS_2 nanoparticles.

The crystallite size of the nanoparticles was calculated using Debye Scherrer's formula

$$D = \frac{K\lambda}{(\beta \cos \theta)}$$

Where K – Scherrer's constant ($K = 0.89$)

λ – wavelength of the radiation used Cu-K alpha 1 ($\lambda = 1.54060 \text{ \AA}$)

β – full width at half maximum of the diffraction peaks

θ – bragg's angle

Table 1 demonstrates the average crystallite sizes of the synthesized Cu_3SbS_4 nanoparticles (PVP₀, PVP_{0.5}, PVP_{1.0}, PVP_{1.5}). The addition of PVP played a crucial role in diminishing the crystallite size of the nanoparticles. As seen in Table 1, PVP_{0.5} demonstrates a smaller crystallite size of 20.405 nm, while PVP₀ displays a larger crystallite size of 30.664 nm. Meanwhile, PVP_{1.0} and PVP_{1.5} exhibit crystallite sizes of 23.916 nm and 25.183 nm respectively. Incrementally adding more PVP, in 0.5 g steps, results in an expansion of the crystallite size. Nevertheless, these crystallite sizes consistently remain smaller than those observed in nanoparticles prepared without PVP, i.e., PVP₀.

Table 1

The average crystallite size and observed lattice values of Cu_3SbS_4 nanoparticles synthesized with different PVP ratios.

Name of the sample	Average crystallite size (D) nm	Lattice values - Observed			Lattice values – JCPDS (PDF: 01–085–1344)		
		a(Å)	b(Å)	c(Å)	a(Å)	b(Å)	c(Å)
PVP ₀ (180°C)	30.664	5.379	5.379	10.659	5.380	5.380	10.760
PVP _{0.5} (180°C)	20.405	5.392	5.392	10.740	5.380	5.380	10.760
PVP _{1.0} (180°C)	23.916	5.376	5.376	10.885	5.380	5.380	10.760
PVP _{1.5} (180°C)	25.183	5.402	5.402	10.715	5.380	5.380	10.760

Theoretical values of lattice parameters from JCPDS card (PDF: 01–085–1344) and observed values are also listed in table 1. It is observed that the lattice parameter values of the four synthesised nanoparticles (PVP₀, PVP_{0.5}, PVP_{1.0}, and PVP_{1.5}) nearly match with the values found in the JCPDS dataset (PDF: 01–085–1344) as well as in the reported values. Erika Dutkova et al. synthesized Cu_3SbS_4 nano powders with lattice parameters $a = b = 5.3911 \text{ \AA}$ and $c = 10.7633 \text{ \AA}$ [37]. However, compared to the other nanoparticles, the lattice parameter values of PVP_{0.5} has more consistency with JCPDS readings. Table 2

Raman analysis has been carried out to all the four samples (PVP₀, PVP_{0.5}, PVP_{1.0} and PVP_{1.5}) in order to confirm the phases present in the process of synthesizing phase pure Cu_3SbS_4 . The spectrum ranging from 200 cm^{-1} to 800 cm^{-1} is depicted in the graph in Fig. 2. This analysis utilized near-infrared laser light, specifically at 785 nm for excitation. The Raman spectrum (Fig. 2) indicates that all four samples exhibit a mode at 314 cm^{-1} , corresponding to the Cu_3SbS_4 phase which is further validated by RRUFF data (RRUFF ID: R110022). The spectrum seen in PVP₀ and PVP_{1.5} revealed an additional mode at 328 cm^{-1} , corresponding to the CuSbS_2 phase, signifying the presence of this secondary phase in these two samples. This observation is supported by RRUFF data (RRUFF ID: R060262). The identified findings unveiled that PVP_{0.5} and PVP_{1.0} exhibited phase-pure famatinite nanoparticles, aligning well with the outcomes derived from XRD analysis.

3.2. Morphological and compositional analysis

The morphology and compositional analysis of the synthesized nanoparticles (PVP₀, PVP_{0.5}, PVP_{1.0} and PVP_{1.5}) are investigated using Scanning electron microscopy with Energy dispersive spectroscopy. Fig. 3. (a–d) represents the SEM images of the synthesized nanoparticles with different PVP ratios. In Fig. 3(a), the morphology of PVP₀ is depicted, featuring nanoparticles displaying a spherical shape. Notably, this image emphasizes the agglomeration of the nanoparticles, indicating the absence of PVP during synthesis. Fig. 3(b) presents the morphology of PVP_{0.5}, showcasing nanoparticles with a clearly defined spherical structure. This image highlights the absence of agglomeration,

Table 2

Compositional analysis of the synthesized Cu_3SbS_4 nanoparticles with different PVP ratios.

Sample	Element/Series	Weight%	Atomic%	{[Cu]+[Sb]}/[S]
PVP ₀	Cu L	25	38	1.43
	Sb L	25	21	
	S K	50	41	
PVP _{0.5}	Cu L	30	42	1.36
	Sb L	42	15	
	S K	28	42	
PVP _{1.0}	Cu L	27	37	1.41
	Sb L	22	21	
	S K	51	41	
PVP _{1.5}	Cu L	21	32	1.13
	Sb L	27	21	
	S K	52	47	

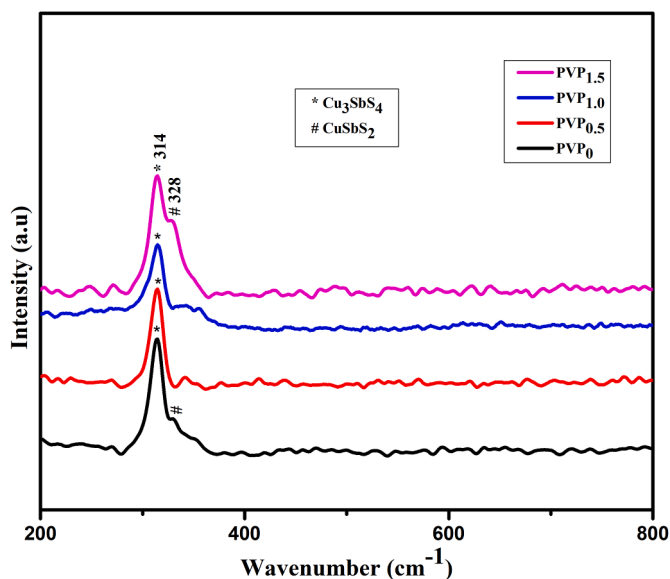


Fig. 2. Raman spectra of Cu_3SbS_4 nanoparticles synthesized with different PVP ratios.

a result of the incorporation of 0.5 g of PVP during synthesis. Fig. 3(c) displays the spherical morphology of $\text{PVP}_{1.0}$, revealing a lesser degree of agglomeration compared to PVP_0 . In Fig. 3(d), the morphology of $\text{PVP}_{1.5}$ is shown, exhibiting a spherical structure with reduced agglomeration compared to $\text{PVP}_{1.0}$. Evidently, increasing the amount of PVP in the synthesis process diminishes agglomeration and leads to a reduction in the size of the spherical particles. Among these, nanoparticles synthesized with 0.5 g of PVP ($\text{PVP}_{0.5}$) demonstrate the most desirable characteristics: a well-defined spherical morphology without any agglomeration. Similar morphology was observed in the Cu_3SbS_4

nanoparticles synthesized by Bella et al. via surfactant assisted solvothermal synthesis [11].

Fig. 4 (a-d) represents the EDX patterns of the synthesized Cu_3SbS_4 nanoparticles with different PVP ratios (PVP_0 , $\text{PVP}_{0.5}$, $\text{PVP}_{1.0}$ and $\text{PVP}_{1.5}$). The quantities of sulphur, antimony, and copper in the synthesised nanoparticles are determined by analysing their elemental composition using the Cu L, Sb L, and S K series in EDX analysis. The Cu: Sb:S ratios of the synthesized nanoparticles $\text{PVP}_{0.5}$ almost corresponds to Cu_3SbS_4 whereas, for $\text{PVP}_{1.5}$ the ratio is close to 1. Fig. 5 depicts the elemental mapping of Cu, Sb, S nanoparticles of $\text{PVP}_{0.5}$. From the images it can be concluded that the dispersion of the resulting Cu_3SbS_4 nanoparticles is homogenous and uniform.

3.3. Optical properties of Cu_3SbS_4 nanoparticles

Fig. 6 (a & b) represents the optical absorption and reflectance spectrum of the synthesized Cu_3SbS_4 nanoparticles (PVP_0 , $\text{PVP}_{0.5}$, $\text{PVP}_{1.0}$ and $\text{PVP}_{1.5}$). In the absorption spectrum it is seen that $\text{PVP}_{0.5}$ and $\text{PVP}_{1.0}$ shows continuous absorption in the entire visible region and the near IR region. Both samples exhibit a drop in absorption around 1350 nm [23,38], which corresponds to the reported absorption edge of Cu_3SbS_4 nanoparticles. A dip in the curve near 800 nm [39,40] corresponds to the CuSbS_2 phase observed in PVP_0 and $\text{PVP}_{1.5}$. Bincy John et al. performed UV – Diffused Reflectance Spectroscopy for their synthesized nanoparticles with absorption over entire visible region and the absorption sharply descended around 800 nm indicating CuSbS_2 phase (37). The additional phase of CuSbS_2 is confirmed in XRD and Raman analysis. Following the decline at 800 nm, there's a consistent absorption observed up to 1350 nm in both PVP_0 and $\text{PVP}_{1.5}$ corresponding to Cu_3SbS_4 phase. From Fig. 6(b) it is clear that the diffuse reflectance of PVP_0 and $\text{PVP}_{1.5}$ descends around 800 nm to the lower wavelength region which corresponds to CuSbS_2 phase. The absorption of all the four samples covered entire visible region and for $\text{PVP}_{0.5}$ and $\text{PVP}_{1.0}$ it is upto near IR region. This is very ideal for materials intended for photovoltaic application since the absorbance covered the entire visible region as well

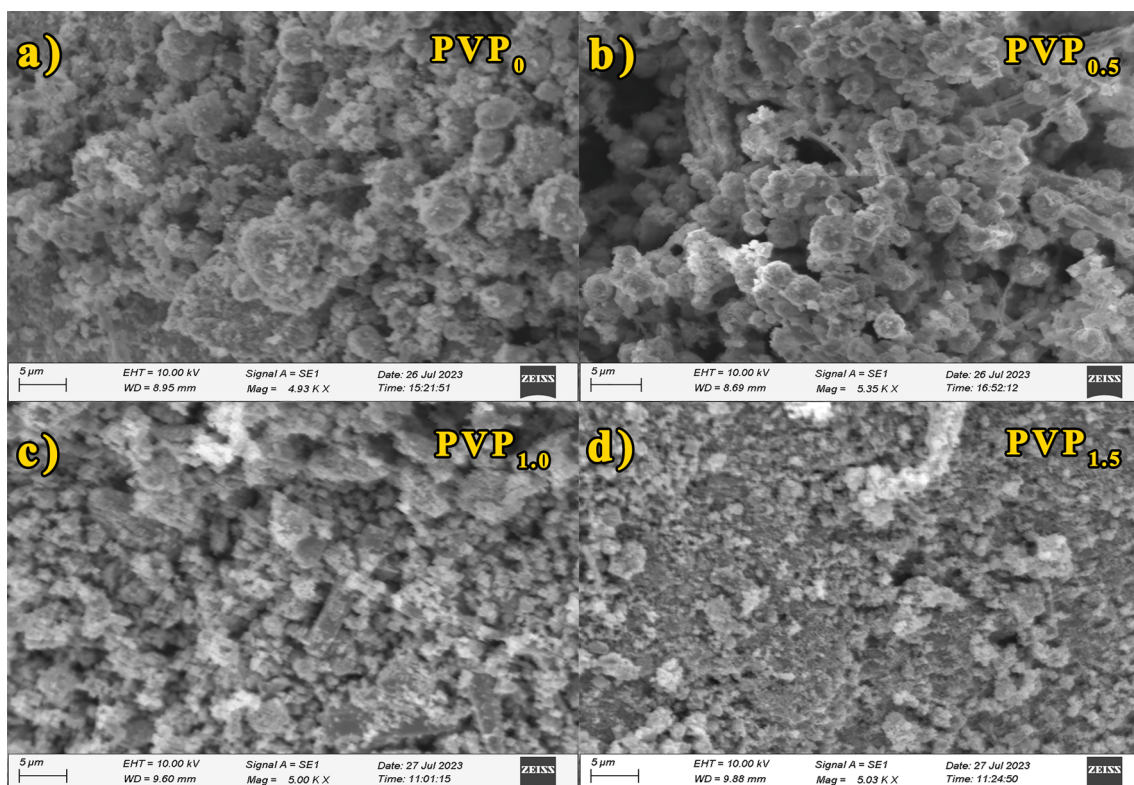


Fig. 3. SEM images of the synthesized Cu_3SbS_4 nanoparticles with different PVP ratios (a) PVP_0 , (b) $\text{PVP}_{0.5}$, (c) $\text{PVP}_{1.0}$, (d) $\text{PVP}_{1.5}$.

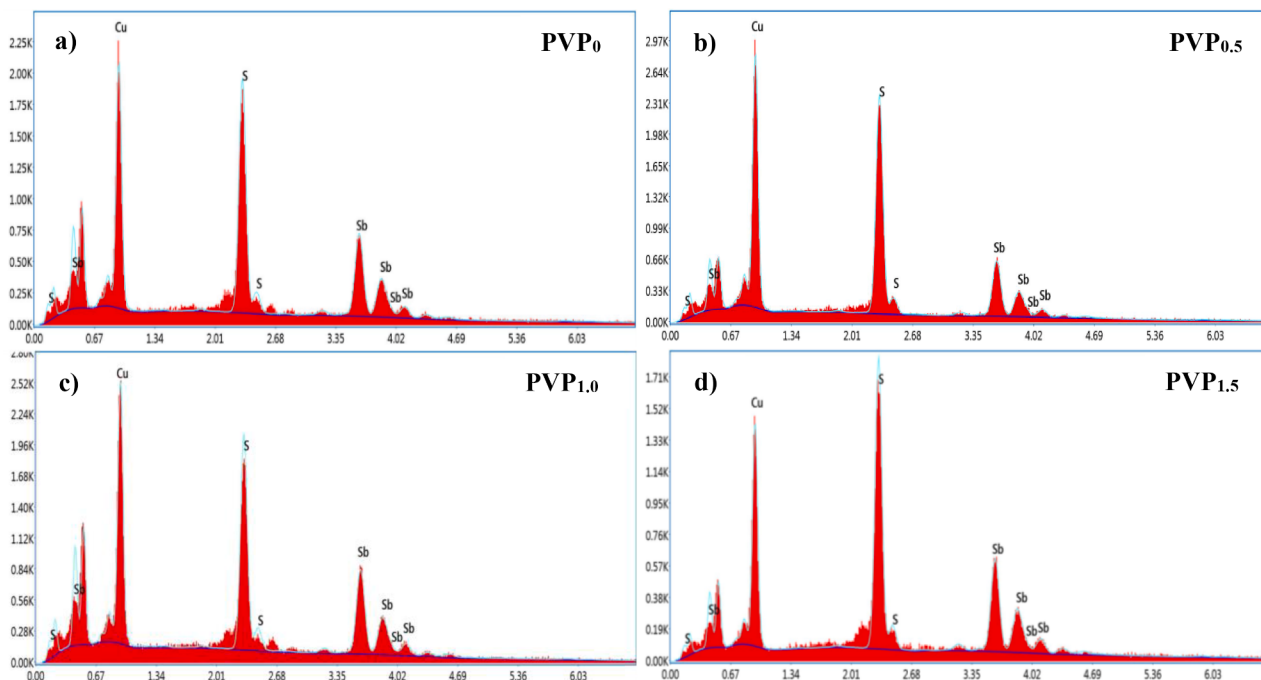


Fig. 4. EDX patterns of the synthesized Cu_3SbS_4 nanoparticles with different PVP ratios (a) PVP_0 , (b) $\text{PVP}_{0.5}$, (c) $\text{PVP}_{1.0}$, (d) $\text{PVP}_{1.5}$.

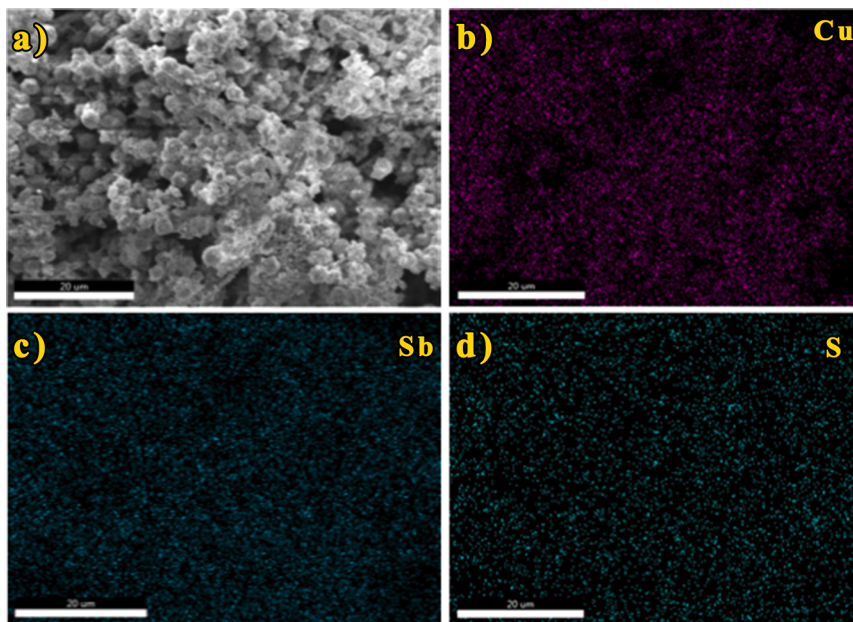


Fig. 5. (a) SEM image and (b), (c), (d) the elemental mapping of Cu, Sb and S of synthesized Cu_3SbS_4 nanoparticles ($\text{PVP}_{0.5}$).

as the near infrared region.

Optical bandgap values of the samples were determined using Kubelka-Munk transformations. The relation for Kubelka-Munk transformations is

$$F(R) = \frac{(1 - R)^2}{2R}$$

Where,

$F(R)$ – Kubelka-Munk function

R - Reflectance (%)

Fig. 6(c) represents the bandgap diagram of the synthesized Cu_3SbS_4 nanoparticles with different PVP ratios (PVP_0 , $\text{PVP}_{0.5}$, $\text{PVP}_{1.0}$ and

$\text{PVP}_{1.5}$). The direct bandgap energies of the synthesized nanoparticles were determined by extrapolating the linear portion of the graph correlating the modified Kubelka-Munk function $(F(R)h\nu)^2$ and photon energy ($h\nu$), where h represents Planck's constant and ν stands for frequency. The synthesised Cu_3SbS_4 nanoparticles PVP_0 , $\text{PVP}_{0.5}$, $\text{PVP}_{1.0}$ and $\text{PVP}_{1.5}$ possess the estimated bandgap energies of 0.97 eV, 0.88 eV, 0.92 eV and 0.94 eV respectively. This is the ideal value for a material intended for photovoltaic absorber layer and the above results were perfectly matched with the reported values. G. H. Albuquerque et al. reported a bandgap value of 0.9 eV for Cu_3SbS_4 films for the application of solar cell absorber material [41]. Qiang Zeng et al. conducted UV-Vis spectrophotometry on the Cu_3SbS_4 nanocrystals they synthesized,

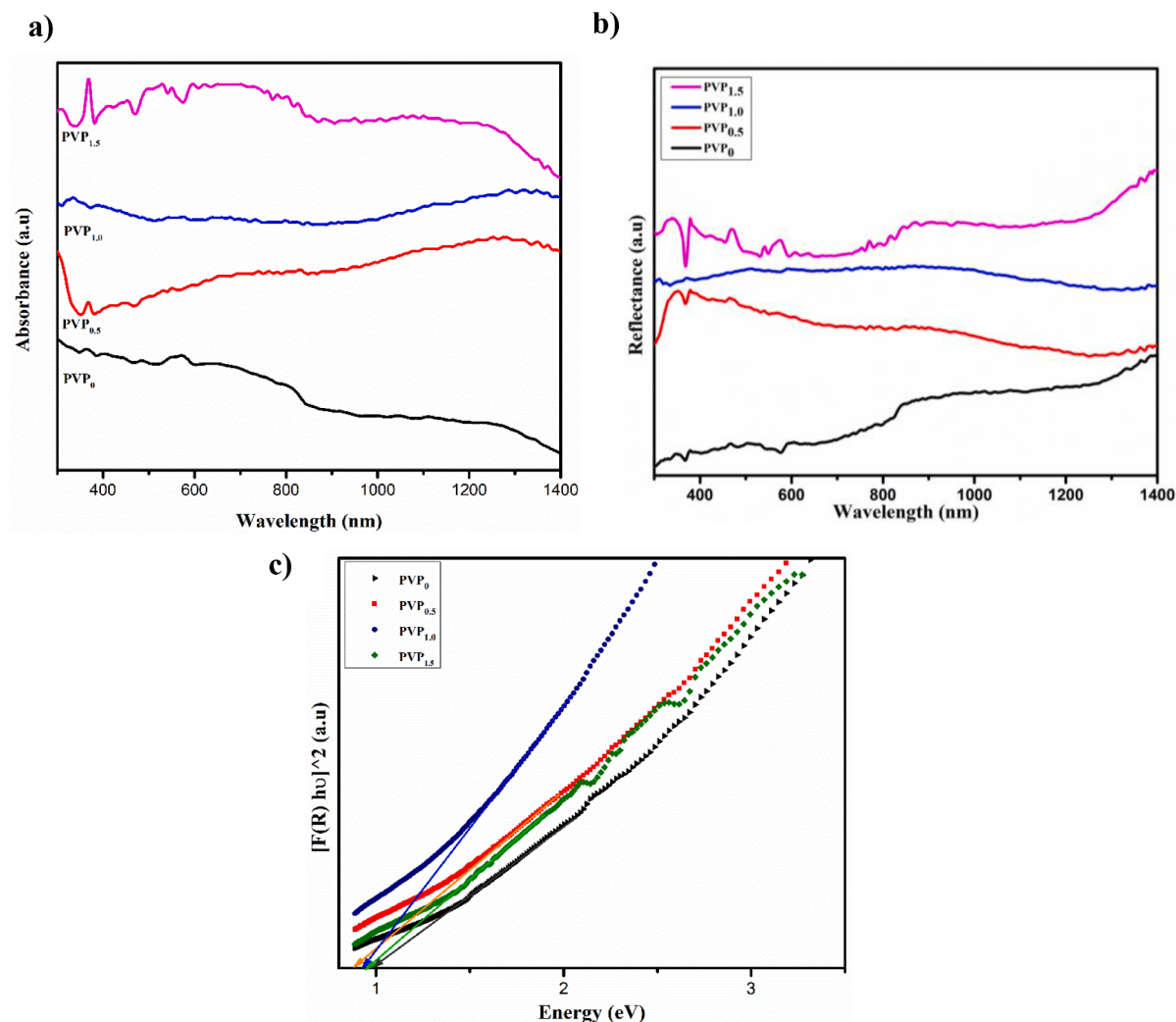


Fig. 6. a) Absorption spectra and b) Reflectance spectra and c) Band gap calculation of synthesized Cu_3SbS_4 nanoparticles with different PVP ratios.

revealing a strong absorption edge at approximately below 1300 nm. They further determined the optical band gap of the Cu_3SbS_4 nanocrystals as 0.89 eV [38]. It is clearly seen that PVP plays a major role in defining the bandgap values of the synthesized Cu_3SbS_4 nanoparticles. The Cu_3SbS_4 nanoparticles synthesized with 0.5 g PVP ($\text{PVP}_{0.5}$) exhibits the optimum bandgap value of 0.88 eV for photovoltaic application.

4. Conclusion

Cu_3SbS_4 nanoparticles were synthesized using different ratios of polyvinylpyrrolidone (PVP) via a solvothermal method employing a binary solvent. All four samples exhibited the famatinite phase and tetragonal crystal structure, matching the data from the JCPDS card. $\text{PVP}_{0.5}$ and $\text{PVP}_{1.0}$ demonstrated a phase-pure famatinite phase, whereas PVP_0 and $\text{PVP}_{1.5}$ exhibited an additional chalcocite phase. The crystallite size of the nanoparticles ranged from 20.405 nm to 30.664 nm, with $\text{PVP}_{0.5}$ exhibiting the smallest crystallite size of 20.405 nm. Raman analysis highlighted the significant influence of PVP on phase formation, resulting in the production of phase-pure Cu_3SbS_4 with $\text{PVP}_{0.5}$ and $\text{PVP}_{1.0}$, while PVP_0 and $\text{PVP}_{1.5}$ exhibited an additional CuSbS_2 phase. These results were consistent with RRUFF data. Despite all four samples having a sphere-like morphology, $\text{PVP}_{0.5}$ showed less agglomeration compared to the others. Optical studies indicated absorption across the entire visible and near-infrared regions for all samples and absorption edge falling around 1350 nm, confirming the Cu_3SbS_4 phase. However,

PVP_0 and $\text{PVP}_{1.5}$ exhibited a drop around 800 nm, indicating the presence of the CuSbS_2 phase. The estimated bandgap values for PVP_0 , $\text{PVP}_{0.5}$, $\text{PVP}_{1.0}$, and $\text{PVP}_{1.5}$ were 0.97 eV, 0.88 eV, 0.92 eV, and 0.94 eV, respectively. These comprehensive findings suggest Cu_3SbS_4 as a promising candidate for a photovoltaic absorber material in the photovoltaic sector.

CRediT authorship contribution statement

Prakash Iruthayanathan: Writing – original draft, Validation, Methodology, Investigation, Data curation. **Anne Sarah Christinal:** Visualization, Formal analysis. **Amutha Soosairaj:** Writing – review & editing, Resources. **Leo Rajesh Asirvatham:** Validation, Supervision, Resources, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data are included in the manuscript in the form of figures and tables.

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