Advances in low-cost and nontoxic materials based solar cell devices

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Abstract. Photovoltaics (PV) have become increasingly popular and reached as the third-largest renewable energy source. Thin-film solar cells made from earth-abundant, inexpensive and environmentally friendly materials are needed to replace the current PV technologies whose large-scale applications are limited by material and/or resource constraints. Near optimum direct optical bandgap of 1.3 eV, high absorption coefficient (>10^4 cm^-1), less toxic, and abundant raw resources along with considerable scalability have made tin sulfide (SnS) as a strategic choice for next-generation PVs. In this review, limitations of leading commercial PV technologies and the status of a few alternate low-cost PV materials are outlined. Recent literature on crucial physical properties of SnS thin-films and the present status of SnS thin-film-based solar cells are discussed. Deficiency and adequacy of some of the key properties of SnS including carrier mobility (µ), minority carrier lifetime (τ), and absorption coefficient (α) are discussed in comparison of existing commercial solar cell materials. Future research trends on SnS based solar cells to enhance their conversion efficiencies towards the theoretical maximum of 24% from present ~5% and its prospectus as next-generation solar cell is also discussed.

Keywords: Tin sulfide (SnS), Photovoltaics, Optical absorption, Conduction band offset (CBO).

1. Introduction
Meeting the increasing energy demand and climate change along with depletion of non-renewable fossil fuels and global warming are the major challenges today. Renewable energy sources are one of the alternative solutions to mitigate all the above. The most abundant and clean renewable energy source available on earth is solar energy. The earth receives about 1.8 × 1011 MW power from the sun which is many-fold times larger than the present consumption rate of all commercial energy sources [1]. A variety of technologies convert sunlight into usable energy which includes solar photovoltaics (PV), concentrated solar power (CSP), and solar thermal. Solar cell, a device directly converts sunlight into electricity using the principle of photovoltaic effect. Power generation from PV has become increasingly popular and it becomes now a third-largest renewable energy technology, as shown in figure 1[3], as per the International Renewable Energy Agency’s (IRENA) 2019 data. Renewable energy roadmap (REmap) anticipated the PV share of global power generation would reach 13% by 2030 and 25% by 2050 (from 3% in 2019) [2].
The leading commercial semiconductor PV materials include single crystalline silicon (c-Si), polycrystalline silicon, multicrystalline silicon (mc-Si), amorphous silicon (a-Si:H), cadmium telluride (CdTe) and copper indium gallium selenide (CIGS). Solar cells and PV modules based on these materials have been produced with high power conversion efficiency. Green et al. [4] consolidated the highest confirmed efficiencies of few leading PV materials measured under the global AM1.5 spectrum (1000 W/m2) and are mentioned in table 1 along with the abundance of constituent elements [5] and environmental concerns.

| PV material       | Efficiency (%) | Abundance of elements in earth’s crust | Environmental Concerns/remark                                      |
|-------------------|----------------|----------------------------------------|------------------------------------------------------------------|
| c-Si (crystalline)| 26.7           | 28.15%                                 | High processing cost of solar grade silicon. Low efficiency and degradation of a-Si:H |
| a-Si (thin film)  | 10.2           |                                        |                                                                  |
| CdTe (thin film)  | 21.0           | Cd (0.2 ppm)Te (0.001 ppm)             | Toxic Cd, scarce Te                                              |
| CIGS (thin film)  | 23.3           | In (0.1 ppm) Ga (15 ppm) S (260 ppm)   | Scarcity In, expensive Ga, complexity of quaternary alloy        |
| CZTSSe (thin film)| 11.3           | Sn (2ppm) Cu (55 ppm) Zn (70 ppm) Se (0.05 ppm) | Toxic Se                                                          |
| GaAs (thin film)  | 29.1           | As (1.8 ppm)                           | Toxic As, withstands high temperature, space applications        |

The majority of the commercially produced solar cell (about 90%) is the Czochralski-grown silicon in monocrystalline (c-Si) and block-cast material in multicrystalline form (mc-Si). However, the Czochralski process of growing silicon ingot involves a high production cost because of the need for high temperature process of solar grade silicon (purity, 99.9999%). Because of grain boundaries and defects, polycrystalline silicon solar cells are less efficient than c-Si wafers-based cells. Gallium arsenide (GaAs) cells offers advantage of bandgap tailoring and also fabricate multi-junctions with the highest efficiency of 38% [4]. Today, the availability of critical materials and their toxicity along with manufacturing complexity are the major concerns of PV technologies (see table 1). For example...
scarcity of indium, gallium, tellurium and toxicity of cadmium, selenium, arsenic likely limit their future use in large-scale applications. On the other hand, the hydrogenated amorphous silicon (a-Si:H) based solar cells have major roadblock of poor efficiency and outdoor reliability due to the degradation in their efficiencies within a few months of exposure to sunlight, losing about 10 to 15% [6]. As a result, the production of solar cells with cheaper and nontoxic materials remains a crucial and challenging issue.

### Table 2. Optical bandgap and typical efficiency value of low-cost PV materials

| PV Material | Band gap (eV) | Efficiency (%) | Reference                      |
|-------------|--------------|----------------|--------------------------------|
| FeS₂        | 0.95         | 1.98           | Prabukanthan et al., 2017 [9] |
| Cu₂S        | 1.25         | 10             | R. B. Hall et al., 1981 [10]  |
| SnS         | 1.3          | 4.36           | Prasert et al., 2014 [11]    |
| Cu₂SnS₃     | 1.16         | 6              | Mitsutaro et al., 2013 [12]  |
| Sb₂S₃       | 1.7          | 5.4            | Hui Deng, et al., 2019 [13]   |
| Cu₂O        | 2.2          | 8.1            | Tadatsugu Minami, 2016 [14]   |

A low-cost PV technology to produce current at a cheap price requires both low-cost raw materials and economical production processes. In this context, chalcogenides of relatively abundant and less toxic elements like copper (Cu), tin (Sn), iron (Fe), antimony (Sb), emerged as promising alternative PV materials. Some of the inexpensive materials investigated for PV applications with their optical bandgap and typical conversion efficiencies are listed in table 2. Few of the low-cost materials, mentioned in table 2, are also used in dye-sensitized solar cells (DSSCs), which are showing good performance. For example, FeS₂ based DSSC showed a power conversion efficiency of 7.38% [7]. SnS-reduced graphene oxide (RGO) composite used as a counter electrode in DSSC exhibited a power conversion efficiency of 8.21% [8]. For high conversion efficiency, the band gap of the semiconductor absorber has to be matched with the solar spectrum. An ideal solar cell material has a direct band gap of 1.5 eV to absorb the maximum number of light photons from the sun's radiation. The energy band gap of CdTe (1.45 eV) is a good match to the solar spectrum and thus it can enable the conversion of more energy from the solar spectrum than the low energy bandgap silicon (1.1 eV).

In recent times, much attention has been focused on tin sulfide (SnS) as an alternative material for PV applications due to its desirable properties such as direct optical band gap of 1.3 eV, high absorption coefficient (>104 cm⁻¹), and abundant, cheap, less toxic constituent elements Sn and S [15-19]. Although SnS based solar cells have been studied for a decade, they still suffer from acceptable efficiency required for commercial production and further investigations are necessary to push the efficiency of these solar cells toward their theoretical limit of 24%. The recently discovered SnS with the cubic crystal structure, having an optical bandgap of 1.7 eV is recognized as a polymorph of naturally occurring orthorhombic SnS, and its photovoltaic properties are less reported in the literature [20-24]. There are a few reviews on synthesis methods and physical properties of SnS thin films and single crystals [25,26] and efficiencies of SnS solar cell fabricated by various deposition techniques [27]. However, there are no reviews on the key PV properties of SnS in comparison with leading PV materials to identify the impediments in achieving commercially viable efficiency. PV properties of recently identified SnS with a cubic crystal structure are missing in any of the reviews on SnS. This review summarizes recent literature on crucial physical properties of SnS relevant to PV application and the present status of SnS thin-film solar cell. The deficiency and adequacy of some of the key properties of SnS are discussed with respect to existing commercial solar cell materials. Future
2. Properties of SnS

In this section, we discuss some important findings on physical properties (structure, optical, electrical) of both orthorhombic and cubic phase SnS (SnS-CUB) and relevance of these properties in fabricating efficient solar cell devices.

2.1. Crystal structure of SnS

Tin sulfide (SnS) is a binary compound that belongs to the IV-VI group and occurs naturally as herzenbergite, a rare mineral. It is a dark-gray inorganic solid with a melting point of 882 °C, boiling point of 1230 °C, and density of 5.22 g/cm³. It has a layered structure like the other family members of layered group IV mono-chalcogenides (SnSe, GeS, and GeSe). The crystals consist of double layers perpendicular to the c-axis in which ‘Sn’ and ‘S’ atoms are tightly bound. The bonding between the layers is weak and van der Waals type. The original structure assignment of SnS was made by Hoffmann [28], who described the unit cell as orthorhombic with space group symmetry \( D_{2h}^{16} (P_{bmn}) \) and lattice parameters \( a = 0.433 \) nm, \( b = 1.118 \) nm and \( c = 0.398 \) nm. Properties of orthorhombic SnS are highly anisotropic along the different crystallographic axis. The electrical conductivity along the c-axis is about six times smaller than in the direction perpendicular to the c-axis [29].

It is found recently that SnS also has a cubic crystal structure (SnS-CUB) which is less stable than orthorhombic SnS [30]. Cubic tin sulfide with a comparatively large unit has been recognized as a polymorph of naturally occurring orthorhombic SnS [12,13]. The cubic phase of SnS is of immense practical interest as a symmetric phase of SnS since physical properties are dependent on crystallographic direction. The SnS-CUB has 64 atoms in the unit cell with a lattice constant \( a = 11.6 \) Å which is “large” compared to orthorhombic [31]. Intrinsically SnS is a p-type semiconductor with hole densities of the order of 1015–1018 cm⁻³ and ionized tin vacancies (VSn) are known to be responsible for its p-type conductivity. Its electrical conductivity is controlled using extrinsic dopants such as In, Al, Ag, Fe, Cl, and Cu [32-34]. Doped SnS films with antimony, a potential n-type dopant, found to increase the electrical resistance of the SnS [35]. Patel et al. [36] obtained enhanced photocurrent density of 3.2 mA cm⁻² in the photo-electrochemical cell of Cu doped SnS and high open-circuit voltage of 462 mV in the developed Cu:SnS/In2S3 heterojunction solar cell.
2.2. Optical absorption and bandgap
Tin The energy distribution within the solar spectrum is approximately 9% UV, 49% visible, and 42% in infra-red region [37]. The ideal absorber material in a solar cell effectively uses the entire visible, UV, and NIR region of the solar spectrum for energy conversion. Figure 3 shows the absorption and diffuse reflectance spectra of SnS single crystal in the wavelength range 200–2500 nm [38]. The absorption spectrum reveals the presence of a broad absorption band for the wavelengths in the range 400 to 1100 nm, which closely matches with a significant part of the solar radiation spectrum. Tin sulfide, as a PV material can effectively use the entire visible spectrum and some part of NIR spectrum for energy conversion. The single crystal of SnS has an indirect band gap of 1.06 eV and direct band gap of 1.21 eV, with an absorption coefficient >10$^3$ cm$^{-1}$ above the fundamental absorption edge [38].

The reported direct and indirect optical band gap energies for SnS thin films varied in the range of 1.2–2 eV and 0.8–1.2 eV, respectively [39-42]. This wide variation in the reported band gap depends on the degree of crystallinity, grain size, and the stoichiometry of the thin film [43].

![Figure 3](image1.png)

Figure 3. Optical absorption spectra of the as-prepared and annealed cubic SnS nanoparticles at different temperatures. (© Elsevier, Reprinted with permission from Elsevier)

To date SnS thin films have been synthesized using a range of methods including sputtering, spray pyrolysis, thermal evaporation, chemical bath deposition, electrodeposition, atomic layer deposition, etc. [44-48]. Figure 4 shows transmittance vs. wavelength spectra of SnS film deposited at an optimum substrate temperature of 300 °C by thermal evaporation technique and subsequently annealed. Transmission falls sharply at different wavelengths near the visible region due to the onset of fundamental absorption. For the films deposited at 300°C a sharp fall is seen around 1250 nm. The films deposited at 300 °C is stoichiometric, highly crystalline, free from other impurity phases, and have a direct optical band gap of 1.33 eV with a high absorption coefficient (>10$^4$ cm$^{-1}$) above the fundamental absorption edge.

The optical bandgap and absorption coefficient ($\alpha$) of the light absorber material is of vital importance in photovoltaic applications. The amount of light absorbed by the absorber film depends on the optical path length and the absorption coefficient. The absorption depth $L_a$ ($L_a = 1/\alpha$) describes how deeply light penetrates into a semiconductor before being absorbed. Absorption depth affects aspects of solar cell design, such as the thickness of the semiconductor material required. For maximum efficiency, the thickness of the active layer ($d$) should be more than absorption depth $L_a$ to get complete light absorption and electron-hole pair generation. At the same time, the thickness should be less than diffusion length, $L$, for minimum recombination and highest charge collection. These factors limit the
thickness of the absorber layer of a solar cell. It is not possible always to get $L_a < d < L$, except in some material having a high minority carrier lifetime. In the material with a low carrier lifetime, the thickness of the active layer needs to be optimized.

The absorption coefficient of an indirect gap material is typically 100 times smaller than that of direct band gap material for the same value of photon energy [49]. For example, in the case of silicon with indirect bandgap, the absorption coefficient is about 103 cm$^{-1}$ at a wavelength of 800 nm and hence requires a thick layer for complete absorption of solar energy. The typical thickness of a commercially available silicon solar cell is 200–300 μm, as compared to the solar cell made from GaAs, CdTe(1–3 μm thickness) and so on [50]. CIGS shows a high absorption coefficient (3–6 × 105 cm$^{-1}$), rendering it absorbs more than 90% light with only about 1 μm thick absorber. The absorption coefficient ($\alpha$) reported for SnS thin film is of the order of $10^4$ to $10^6$ cm$^{-1}$ for the visible range of the solar spectrum indicating ~ 1 μm film can absorb solar radiation completely. Nanocrystalline thin films of SnS (t < 100 nm) exhibited a very high absorption coefficient of $10^6$ cm$^{-1}$ [51]. The cubic SnS has a characteristic high optical bandgap of 1.72 eV reported for thin film of 500 nm thickness. Hegde et al. [30,52] reported thermal stability, optical properties and photocatalytic application of cubic SnS nanoparticles. It is found that the cubic phase remained structurally stable up to 400 °C and nearly at 450 °C cubic structure transformed into orthorhombic. Figure 5 shows the optical absorbance vs. wavelength plot of as-prepared and annealed cubic SnS-nanoparticles. The as-prepared cubic SnS nanoparticles with a direct optical band gap of ~1.68 eV, which is strongly absorbing in the visible wavelength range of ~400 nm -700 nm. Nanoparticles annealed at 450 °C exhibited a direct bandgap of 1.32 eV and an indirect bandgap of 1.05 eV.

2.3. Conductivity, mobility, and carrier lifetime

The decisive semiconductor parameters that determine the design and performance of a solar cell are mobility ($\mu$), minority carrier lifetime ($\tau$), and diffusion length (L). The minority carrier lifetime and diffusion length also determine the I-V characteristics of any solar cell. At a given carrier concentration, a longer minority carrier lifetime causes increased short circuit current ($J_{sc}$) and open-circuit voltage ($V_{oc}$) of a solar cell. This straightforwardly based on the fact that the longer a minority carrier lifetime, the greater is its chances of being collected by the electric field at the junction and of contributing to the photocurrent. Carrier lifetime ($\tau$) is extremely sensitive to the smallest amounts of impurities or intrinsic defects of the absorber layer and hence an ideal parameter for characterization of material quality for device application. Typical minority carrier lifetime, diffusion length, and mobility of charge carriers of the leading solar cell materials along with SnS are listed in Table 3.

| Material          | Minority carrier lifetime (τ) | Minority carrier diffusion length (L) | Mobility of electrons ($\mu_e$) and holes ($\mu_h$) (cm$^2$/Vs) |
|-------------------|-------------------------------|--------------------------------------|---------------------------------------------------------------|
| c-Si wafer        | 1 ms                          | 100-300 μm                           | $\mu_e$=1350, $\mu_h$=475                                   |
| CdTe              | 10-30 ns                      | 0.4-2 μm                             | $\mu_e$=1050, $\mu_h$=80 (single crystal), $\mu_e$=300, $\mu_h$=5 (thin films) |
| CIGS              | 200 ns                        | 10 μm                                | $\mu_e$=50, $\mu_h$=20                                      |
| SnS (thin film)   | 41 ps                         | 54 nm                                | $\mu_h$=90                                                |

The length traversed by photogenerated charge carriers in time $\tau$ would depend on the charge carrier velocity/mobility. The higher the mobility, the less time a charge carrier will spend in a device, and the less likely it will be lost due to recombination. For example, the source of the low efficiency of amorphous silicon photovoltaics (a-Si) is largely due to the low hole mobility of the material caused
by the dangling bond. The Hall mobility for SnS crystal grown by the PVD technique is reported in the range 12 to 48 cm²/Vs [53-55,38]. Reddy et al. [56] reported mobility of 180 cm²/Vs for SnS thin films grown by spray pyrolysis method. Chemically deposited thin film of cubic SnS shows hole mobility of 75.1 cm² V⁻¹ s⁻¹ [57]. It is evident from table 3 that the charge carrier mobility of SnS is inferior to some of the leading PV material but still comparable to CIGS. The low mobility value of SnS single crystal and the thin film is due to the presence of a high concentration of various defects. Thin films of SnS with large grains and fewer grain boundaries and defects are needed to minimize the scattering of charge carriers at the grain boundaries to enhance mobility.

The excellent photovoltaic performance of any p-n junction solar cell is ascribed to its optoelectronic characteristics, such as high absorption coefficient, long carrier diffusion length, high carrier mobility and long recombination lifetime. The carrier lifetime of PV material (τ) can be as low as nano-seconds to high as milli-seconds. Silicon with a carrier lifetime more than several micro-seconds is considered a good material for solar cell. Comparison of carrier lifetime (τ) of PV material (see table 3) makes it clear that τ of SnS thin films must increase by 1000-fold for SnS solar cells to join CdTe and CIGS as a high-performing thin-film solar cell technology. Grain boundaries and their associated defects are mainly responsible for low carrier lifetime in any thin films. Materials research with a focus on enhancing the minority-carrier lifetime of the light absorber layer is key to advancing PV technology for both novel and established material.

![AFM pictures of SnS thin films deposited at substrate temperatures 50 and 300 °C.](©Lattice Science Publication, Reprinted with permission Lattice Science Publication)

Jaramillo et al. [58] observed an increase in the minority carrier lifetime of SnS thin films annealed in H₂S gas due to passivation of defects. However, reported results to date have only demonstrated lifetimes at or below 100 ps. Alex Polizzotti et al. [59] used defect modelling to identify recombination-active defects and methods to improve lifetimes to >3 ns through high-purity thin-film and mitigating harmful defects. Chakraborty et al. [60] used SnS grown on graphene substrate as a means to reduce the density of lifetime-limiting defects. SiO₂/graphene/SnS structure showed an increase in the effective lifetime (41 ps) relative to the SiO₂/SnS sample (21 ps). Minority carrier lifetime (τ) is related to the recombination rate (R) and the excess minority carrier concentration (Δn) by the relation, τ=Δn/R. Different recombination mechanisms associated with the lifetime include radiative, Auger, Shockley-Read-Hall (SRH), and surface recombination. Detailed knowledge of defects and recombination process is required to enhance carrier lifetime and facilitate the design of high-efficiency SnS solar cell. Typically, the efficiency of a solar cell device will improve with an increase in grain size of the polycrystalline absorber film, which in turn depends on the technique used for deposition and deposition conditions. Figure 6 shows AFM pictures of SnS thin films deposited at substrate temperature 50 °C and 300 °C depicting the increase in grain size. In order to prevent
significant grain boundary recombination of the minority carrier, it is also desirable that the lateral grain size in the material be larger than the minority carrier diffusion length.

3. Progress of SnS photovoltaics

Near optimum optical bandgap of 1.3 eV, high absorption coefficient (>10^4 cm^{-1}), p-type electrical conductivity, and less toxic, abundant raw material made tin sulfide (SnS) a strategic choice for next-generation PVs. Despite several reports on the fabrication of SnS solar cells, their efficiency is still very low at ~5%, which is far less than the theoretical conversion efficiency of 24% as predicted by Loferski [61] based on the bandgap-efficiency diagram. Table 4 depicts the solar cell performance parameters reported for SnS solar cells with the combination of various buffer/window layers.

Table 4. Solar cell parameters of SnS with various absorber/buffer or window layer combination

| Absorber/buffer or window layer | J_{sc} (mA/cm^2) | V_{oc} (mV) | FF (%) | η (%) | Reference |
|--------------------------------|-----------------|-------------|--------|-------|-----------|
| SnS/TiO_2                     | 24.7            | 330         | 58.5   | 4.8   | [62]      |
| SnS/Zn(O,S)                   | 20.2            | 370         | 58     | 4.36  | [11]      |
| SnS/Zn (O,S)                  | 20.6            | 334         | 56.3   | 3.88  | [63]      |
| SnS/MgSnO                     | 21              | 313         | 33     | 2.1   | [64]      |
| SnS/ZnMgO                     | 12.1            | 270         | 64     | 2.1   | [65]      |
| SnS/CdS                       | 20.7            | 346         | 58.7   | 4.225 | [66]      |
| Cubic SnS/CdS                 | 6.2             | 470         | 44     | 1.28  | [67]      |

The difference in efficiency among the reported SnS solar cells is primarily due to the quality of absorber film, conduction band offset (CBO), and lattice mismatch between the p-type absorber and n-type buffer layer. The prevalent low efficiencies in SnS solar cells are attributed to unfavourable heterojunction band alignment apart from various other reasons, such as bulk material impurities and defects, interface trap states. A thin buffer layer is usually introduced to improve interface between ‘window’ and ‘absorber’ layer and also to optimize conduction-band offset. The CBO between the absorber and buffer layer (see figure7) plays a significant role in reducing recombination of holes and electrons and enhance the performance of the heterojunction solar cells. A large negative CBO (cliff) gives rise to the increase in the interface recombination, while a large positive CBO (spike) creates a barrier that impedes the collection of photocurrent. So, a small positive CBO in the range of 0 eV to +0.4 eV is optimal band alignment, to minimize the interface recombination in SnS solar cell with high recombination velocity [68].
A few theoretical as well as experimental studies are available in the literature on optimization of band offset between SnS absorber and buffer layers to achieve high conversion efficiencies. Mangan et al. [69] performed device simulation and presented a framework for SnS/Zn(O,S) solar cell which supports efficiencies above 20% at a buffer-layer carrier concentration >10^{18} \text{cm}^{-3} and a broad range of conduction band offsets (-0.2 eV cliff to +0.2 eV spike). Sun et al. [70] optimized S/Zn ratios in Zn(O,S) buffer layer of SnS/Zn(O,S) heterojunctions to have desirable small positive CBO. Optimization of CBO was carried out by Takashi et al. [65] for SnS/ZnMgO heterojunction by varying the Mg content (x) of the Zn_{1-x}Mg_xO buffer layer. Solar cells with a CBO value of -0.1 to 0 eV exhibited a conversion efficiency of 2.1%. Recently, a considerable efficiency of 4.36% was achieved by tuning the CBO between Zn(O,S) buffer and SnS absorber to an optimum spike value (< +0.4 eV) by Prasert et al. [11]. To achieve this efficiency, several modifications are done in the fabrication process, which includes annealing the SnS films in H_2S to form larger grains with fewer grain boundaries to reduce recombination at grain boundaries; inserting a few monolayers of SnO_2 between p-SnS/n-Zn(O,S) to minimize recombination near the junction. Recently Sung Yun et al. [62] reported photoconversion efficiency of 4.8% for Au/SnS/TiO_2/FTO solar cell. The thin film of SnS deposited onto nanocrystalline TiO_2 layer using SnCl_2-thiourea complex solution was highly crystalline with (040) orientation and post-treatment of SnS with SnCl_2 enhanced the photoconversion efficiency (PCE) of the cell.

4. Impediment and future trends

Research on SnS is mainly focused on the synthesis and improving the physical properties of the SnS absorber film rather than investigations on hindering factors that limit the efficiency of the fabricated solar cell. Intense investigation on bulk and interface recombination, grain boundary and surface passivation improving minority carrier lifetime (τ), CBO study of SnS/buffer interface is required in line with established PV technology. Studies on defect states at SnS/buffer junction, defects especially voids present in absorber/back contact interface and their effect on solar cell performance have not been effectively probed. Efficiency can be enhanced substantially by optimizing Mo/SnS back contact, improving bulk minority carrier diffusion length, enhancing the quality of bulk SnS, and suppressing the recombination at the junction and grain boundaries. Such studies could help to clarify underperformance of SnS based solar cells and pave a way to improve their solar energy conversion. A thin intermediate layer of Ag between Mo back contact and SnS absorber is a possible solution to inhibit the formation of SnS_2, MoS_2, and other defects especially voids [71]. This also reduces the series resistance and recombination leading to substantially higher short circuit current density (J_{SC}) and fill factor. In polycrystalline materials, grain boundaries (GB) are active recombination centers of photo-generated electrons and holes as well as scattering centers of free carriers. Hence GB passivation is a key step in making high-efficiency cells. Surface passivation is another technique used to reduce interface recombination in established thin-film solar cell technology like CIGS and CdTe. Research on high-efficiency SnO_x/CdS/CdTe solar cell confirmed the presence of O in the CdS layer significantly suppresses the interdiffusion at the CdS/CdTe junction and thereby reduces the defects states [72]. A very thin passivation layer of SnO_2 or Sn(S,O)_2 between SnS absorber and the buffer layer is proposed to suppress the interface recombination.

The optical loss (reflection) in the solar cell is minimized by using anti-reflection coating (ARC) and increasing optical path length by a combination of surface texturing and light trapping. Minbashi et al. [73] simulated the J-V characteristics of the solar cell prepared by glancing angle deposition (GLAD)technique and recorded 7.68% efficiency. It is concluded that the increase in efficiency is a result of trapping of incident light on the cell’s surface and reduction in reflectance loss facilitated by GLAD deposited SnS thin film. Quantum well (QW) structures are found to increase the efficiency of absorption of the wide solar spectrum and inhibit the recombination of charge carriers thereby leading to an increase in power conversion efficiency. A thin layer (thickness, L ~ \lambda\text{de-Brogle}) of lower band gap orthorhombic SnS (1.3 eV) between wide band gap cubic SnS (1.7 eV) possibly creates a quantum
well of discrete energy states. The fabricated QW structure is expected to absorb photons over a wide wavelength range (300-1100nm) and also inhibit the recombination of photogenerated charge carriers and enhance the charge collection efficiency due to tunnelling and thermal escape process.

5. Summary
In this review, we discussed material availability, environmental concerns of the present commercially available PV technologies such as c-Si, a-Si:H, CdTe, CIGS based solar cells, which have become a roadblock in making solar energy cheaper and widespread. Relatively abundant and less toxic chalcogenide materials like SnS, FeS₂, Cu₂S, Sb₂S₃, etc., emerged as promising alternative PV materials. Tin sulfide (SnS) with a direct optical band gap of 1.3 eV, high absorption coefficient (>10⁴ cm⁻¹) and abundant, cheap, less toxic constituent elements Sn and S has an edge over other low-cost PV material. The cubic phase of SnS with an optical bandgap of 1.7 eV is of immense practical interest as a symmetric phase of SnS. It is found that cubic SnS remains structurally stable up to 400 °C and nearly at 450 °C cubic structure transformed into orthorhombic. Deficiency and adequacy of some of the key PV properties of SnS in comparison with leading PV technologies are discussed in this review and future research trends on SnS to meet the theoretical maximum conversion efficiency of 24% from present ~5% are highlighted. The absorption and diffuse reflectance spectra of the SnS single-crystal reveals the presence of a broad absorption band for the wavelengths in the range 400 to 1100 nm, which closely matches with a significant part of the solar radiation spectrum. The absorption coefficient (α) reported for SnS thin film is of the order of 10⁴ to 10⁵ cm⁻¹ for the visible range of the solar spectrum indicating ~ 1 µm of SnS film can absorb solar irradiation completely. The thickness of the absorber required in the SnS solar cell is comparable to a commercial solar cell made from GaAs, CdTe (1−3 μm thickness). Nanocrystalline thin films of SnS (t < 100 nm) exhibited a very high absorption coefficient of 10⁶ cm⁻¹. Charge carrier mobility (µ), minority carrier lifetime (τ), and diffusion length (L) are decisive semiconductor parameters that determine the I-V characteristics of any solar cell. The typical mobility value of 75.1 cm² V⁻¹ s⁻¹ reported for SnS thin film is inferior to some of the leading PV materials but still comparable to CIGS. The carrier lifetime of PV material (τ) can be as low as nano-seconds to high as milli-seconds. Silicon with a carrier lifetime of several microseconds to 1 ms is considered as a good material for solar cell. Carrier lifetime (τ) must increase by 1000-fold for SnS solar cells to join CdTe and CIGS as a high-performing thin-film solar cell technology. Intense investigations on bulk and interface recombination, grain boundary and surface passivation, improving minority carrier lifetime (τ), CBO study of SnS/buffer interface is required to make low-cost, commercial SnS solar cell a reality.

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