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# Influence of Lithium-Ion Concentration on the Optical Properties of Spray-Made ZnS Thin Films

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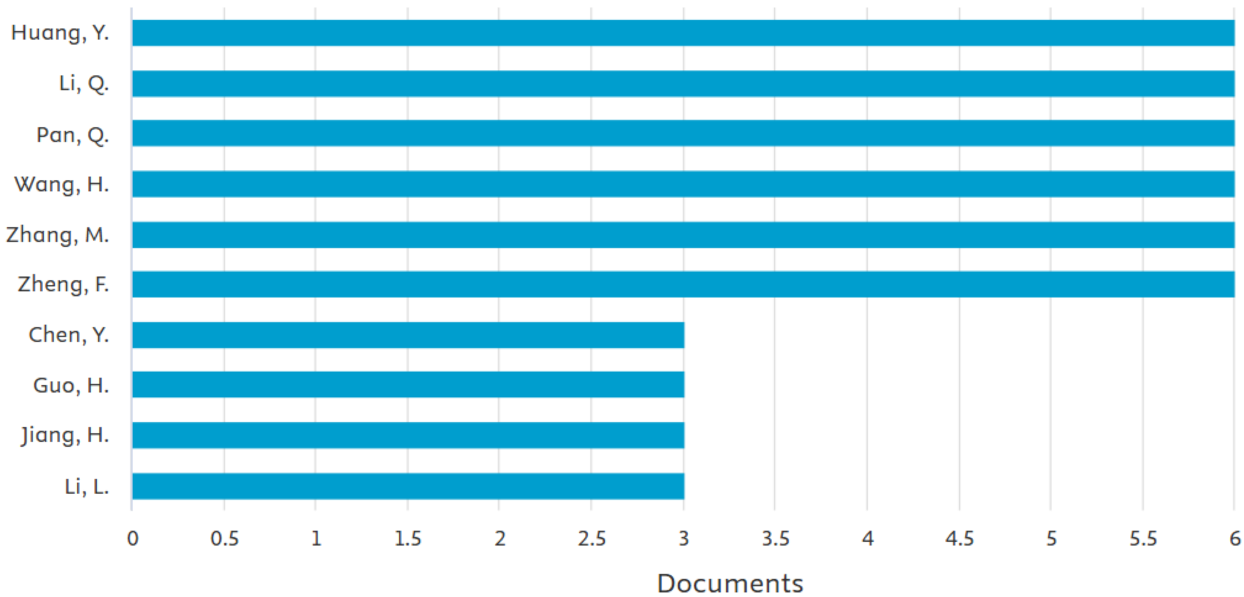
**Abstract:** ZnS doped with varying concentrations of lithium ion solutions were grown on cleaned glass micro slides (substrates) at a constant substrate temperature of 200°C employing the relatively simple technique of spray pyrolysis. The final spray solution for the growth of the films contained aqueous solutions of zinc sulphate heptahydrate, thiourea, and lithium perchlorate. The source of the zinc ion, sulphur ion and lithium ion were zinc sulphate heptahydrate, thiourea and lithium perchlorate respectively. The optical absorbance spectra of the spray-made films were recorded in the wavelength range (400-1100) nm using a HINOTEK 756S UV-VIS-NIR Spectrophotometer. From the analysis of the absorbance's data, other optical parameters such as transmittance, reflectance, absorption coefficient, band gap and optical density were determined. Generally, the films exhibited strong absorption in the ultra-violet regions and high transmission in the entire regions whereas reflection was generally low in all the regions of electromagnetic spectrum. The coefficients of absorption values were found to be high in the order of $10^9$ $m^{-1}$. The film indicated direct band gap energy range of 2.33 - 2.81eV. The optical density indicated range of 0.4 - 9.6. Based on the strong absorption of the films in the ultra-violet regions, the films are suitable materials for solar thermal applications. The high transmittance of the films across the entire electromagnetic spectrum, make the films suitable materials for solar control coatings inside buildings. The relatively low reflectance of the films in all the regions of electromagnetic spectrum indicate they are right materials for anti-dazzling coating applications in automotive industries. The high absorption coefficients of the films showed they can be utilized as an ideal absorber in photovoltaic conversions in energy industries. The fairly high direct band gap exhibited by the films make them appropriate materials for photovoltaic applications. The optical density values indicated by the films are good for anti-reflection coatings in optics.

## 1. Introduction

In recent times, attention of researchers has been drawn towards the deposition and characterization of thin films of metal chalcogenides such as Zinc Sulphide (ZnS) due its excellent optical properties and possible applications in modern optoelectronic devices, especially in solar cells, light emitting diodes, optical window layers of photovoltaic cells, photodetectors, photoresistors etc. Also, it is a binary semiconductor compound suitable for use as anti-dazzling coatings and thermal coatings in automotive and architectural industries respectively (Igweoko *et al.,* 2025). It is characterized by high refractive index, wide direct energy gap and high transmittance in the visible spectra (Luque *et al.,* 2015), non-poisonous and ecofriendly (Derbali *et al.,* 2018). Its wide band gap lets high energy incident photons to arrive to the window-absorber junction of solar cells which greatly appreciates the blue response of photovoltaic cells (Chelvanathan *et al.,* 2015)

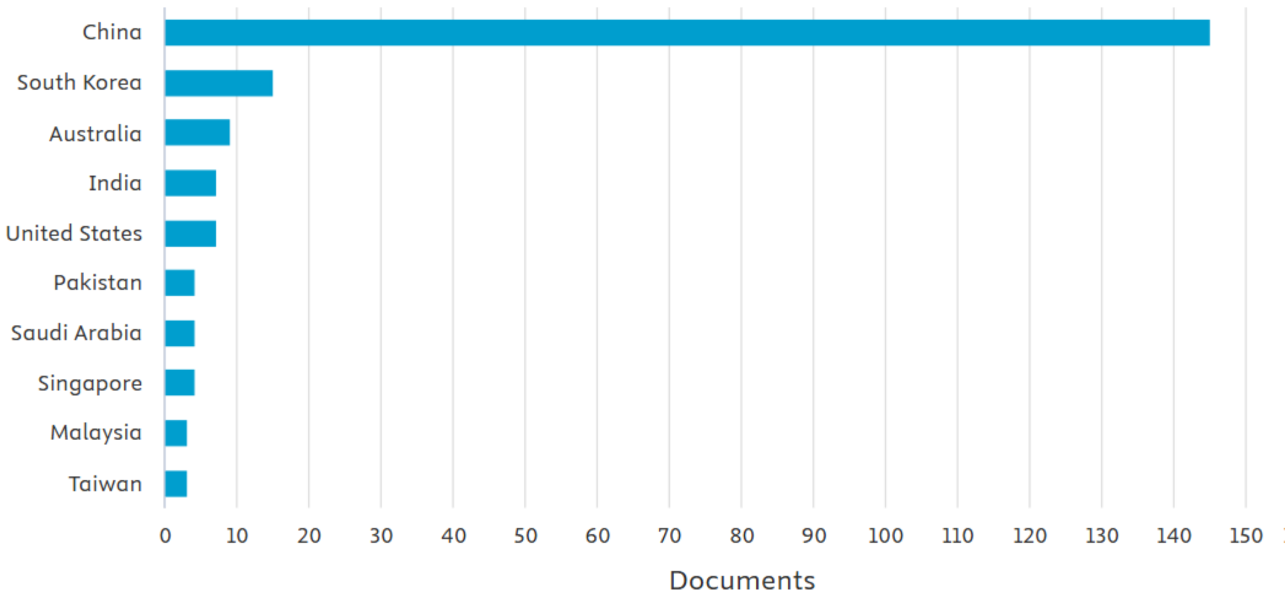
Current reports in the literature indicate that ZnS films can be grown using various thin film deposition methods and these include; Chemical Spray Pyrolysis (CSP) (Meshram and Thombre, 2021; Essan *et al.,* 2023; Offor *et al.,* 2023; Ajayi *et al.,* 2023; Ali *et al.,* 2023; Igweoko *et al.,* 2025), Chemical Bath Deposition (CBD) (Onochie et al., 2021; Jiji *et al.,* 2021), Dip Coating Technique (DT) (Garrido-Hernandez *et al.,* 2021), Pulsed-Laser Deposition (PLD)(Ahmed *et al.,* 2022), Successive Layer Adsorption and Reaction (Sundhar, 2022), Electrodeposition method (Madhuwanthi et al., 2022).

Bibliometric analysis is recently used to give a quantitative visibility on the profiler authors, affiliations, countries and collaborations (Ellegaard & Wallin, 2015; Ahmed *et al.,* 2022; N'diyae *et al.,* 2022; Pham-Duc & Nguyen, 2022; Aichouch *et al.,* 2025; Hammouti *et al.,* 2025). Bibliometric analysis based on Scopus data showed that only 179 articles are published using the two keywords "Lithium-Ion and ZnS" from 2008 to present. **Scheme 1** indicated that the six most published authors belonged to Guangxi Normal University, Guilin, China. In other words, China is the most interested country in the domain of ZnS thin films doped of lithium-ion to optical and photovoltaic applications (**Scheme 2**).




**Scheme 1.** The ten most published authors in the field "Lithium-Ion and ZnS"

In this present investigation, chemical spray pyrolysis method was used because of the ease and versatility of the method in growing high quality thin films (Kurniawan *et al.,* 2024; Falcony *et al.,* 2018; Naciri *et al.,* 2009; Patil *et al.,* 1999). Chemical Spray Pyrolysis (CSP) is a versatile technique for depositing thin films onto substrates. In this process, a precursor solution is sprayed onto a heated substrate, where it undergoes thermal decomposition, resulting in the formation of a uniform, dense, and adherent film. The simplicity and low cost of CSP make it an attractive method for various applications, including solar cells, fuel cells, sensors, and coatings (Raphael *et al.,* 2022; Idu *et al.,* 2023; Islam, *et al.,* 2025). By controlling process parameters such as precursor solution, substrate temperature, spray rate, and carrier gas, researchers can tailor the film's composition, structure, and properties to suit specific requirements. CSP's ability to deposit a wide range of materials at atmospheric pressure has made it a valuable tool in materials science and engineering (Aziz *et al.,* 2012; & Ikhioya, *et al.,* 2022).




**Scheme 2** the visible Countries in the field "Lithium-Ion and ZnS"

The aim of this study is to grow thin films of ZnS doped with varying volumes of lithium-ion solutions, and to characterize the films using optical spectroscopy to investigate the optical properties. The obtained results are discussed and compared with other research results reported. This work is a fundamental step toward exploring new pathways for utilization of ZnS-based thin films in different device designs.

## 2. Methodology

### *2.1 Substrate cleaning and reagents*

Substrate cleaning plays a vital role in thin film deposition. The soda-lime substrates (glass slides) of area 75mm by 25mm, thickness 1.0mm were procured from local suppliers. Before the spray, the soda-lime substrates were dipped in concentrated hydrochloric acid for 60minutes, removed and washed with sponge in a kiln detergent solution and rinsed with sachet water. Thereafter, the glass slides were rinsed in distilled water. Lastly, they were properly dried inside a sterilizing oven.

### *2.2 deposition of ZnS thin films doped with varying volumes of lithium-ion solutions*

20 ml of 0.02 M $ZnSO_4.7H_2O$, 20 ml of 0.02 M $SC(NH_2)_2$ and 5 ml of lithium ions solution were measured into 50 ml glass beaker. The mixture was stirred vigorously under high speed for about 15 minutes using magnetic stirrer to obtain a homogeneous solution. Immediately after the stirring, 10 ml of the solution was measured out using pump syringe into spray-pyrolysis sample bottle which was fastened on the nozzle valve rod of the air brush. The precursor was sprayed for 30seconds on the

heated substrates (glass slides) at a constant temperature of 200 $^{o}$C using electrical hot plate. The above procedures were repeated when the volumes of lithium-ion solutions were varied to 10ml, 15ml, and 20 ml and keeping the volumes of zinc and sulphur ion solutions constant for other depositions. The idea was to investigate the influence of volumes of lithium ions solutions on growth of ZnS thin films. The volumes of the lithium ions solutions were measured with a beaker and recorded as shown in Table 1. Table 1 shows the spray constituents for the growth of ZnS thin films doped with varying volumes of lithium ions solutions.

**Table 1** Variation of Volume of lithium ions solutions on the spray deposited ZnS Thin Films

| **Sample** | **$ZnSO_4.7H_2O$ (ml)** | **$SC(NH_2)_2$ (ml)** | **LiClO4 (ml)** |
|---|---|---|---|
| ZnS: 5 ml Lithium ion | 20.0 | 20.0 | 5.0 |
| ZnS: 10 ml Lithium ion | 20.0 | 20.0 | 10.0 |
| ZnS: 15 ml Lithium ion | 20.0 | 20.0 | 15.0 |
| ZnS: 20 ml Lithium ion | 20.0 | 20.0 | 20.0 |

### *2.3 Characterisation and computation of optical properties*

Optical characterization of the films was carried out using HINOTEK 756S UV-VIS spectrophotometer at wavelength interval of 400 nm to 1100 nm. Absorbance values of the films were obtained using the spectrophotometer and other optical properties such as transmittance, reflectance, absorption coefficient, energy band gap and optical density were calculated using the following equations as obtained from literatures. Transmittance of the films were calculated using **Eqn. 1** given by (Onochie *et al.,* 2012; Igweoko *et al..,* 2025)

$$T = 10^{-A} \quad \textbf{Eqn. 1}$$

Reflectance of the films were obtained using the expression in **Eqn. 2** as given by (Obot *et al*., 2023)

$$R = 1 - (A + T) \quad \textbf{Eqn. 2}$$

The absorption coefficient $(\alpha)$ of the films were calculated from the transmittance values using the **Eqn. 3** as given by (Najim *et al.* 2022; Offor *et al.* 2023; Igweoko *et al*. 2025)

$$\alpha = \frac{2.303A}{t} \quad \textbf{Eqn. 3}$$

Where (t) is the thickness of the deposited thin films.
The energy band gaps were calculated using Tauc's model given in **Eqn. 4** as (Meshram and Thombre, 2021; Celik and Temiz, 2023, Igweoko *et al.* 2025)

$$(\alpha h v)^n = \left(h v - E_g\right) \quad \textbf{Eqn. 4}$$

Where β is a constant, n = 2 for direct band gap. The energy band gaps of the films were obtained by extrapolating the straight portion of the plot of $(\alpha hv)^2$ against the photon energy (hv) at $(\alpha h v)^2 = 0$
Optical densities were estimated using **Eqn. 5** (Nwofe, 2017)

$$\rho = \sigma t \quad \textbf{Eqn. 5}$$

Where t is the film thickness

## 3. Results and Discussion

### *3.1 Absorbance spectra*

**Figure 1** shows the plots for absorbance against wavelength for ZnS doped with varying volumes of lithium ion solutions. It was observed that the absorbance generally decreased with increase in wavelength from the region of higher photon energies (lower wavelengths) to the region of lower photon energies (longer wavelengths). Also, it was observed that the films exhibited maximum absorption at the UV region when compared with other regions of the electromagnetic spectrum. Such behaviors are commonly noticed in the graphs of absorbance versus wavelength for various chalcogenide thin films (Nwofe, 2017; Ozutok *et al.,* 2012; Offor *et al.,* 2020; Onochie *et al.,* 2021; Igweoko *et al.,*2025). For ZnS thin films doped with 20ml volume of lithium-ion solution, absorbance decreased from 0.97 at 397.61nm to 0.41 at 1100.75nm. For ZnS thin films doped with 15ml volume of lithium-ion solution, absorbance decreased from 0.43 at 397.61nm to 0.20 at 1100.75nm. For ZnS thin films doped with 10ml volume of lithium-ion solution, absorbance decreased from 0.38 at 397.61nm to 0.19 at 1100.75nm. For ZnS thin films doped with 5ml volume of lithium-ion solution, absorbance decreased from 0.51 at 397.61nm to 0.20 at 1100.75nm. It was also observed that the change in volume of lithium-ion solution that was introduced to spray solution modified the absorption spectra. There was no clear trend in relation between absorbance and volume of $Li^+$ solution as can be seen in the plots. Furthermore, it was also noticed that the overall absorbance of the films was within the limit stipulated by the Lambert-Beer's law. Strong absorptions were observed at wavelength of 400nm. Hence the films have potential application in fabrication of solar cells.

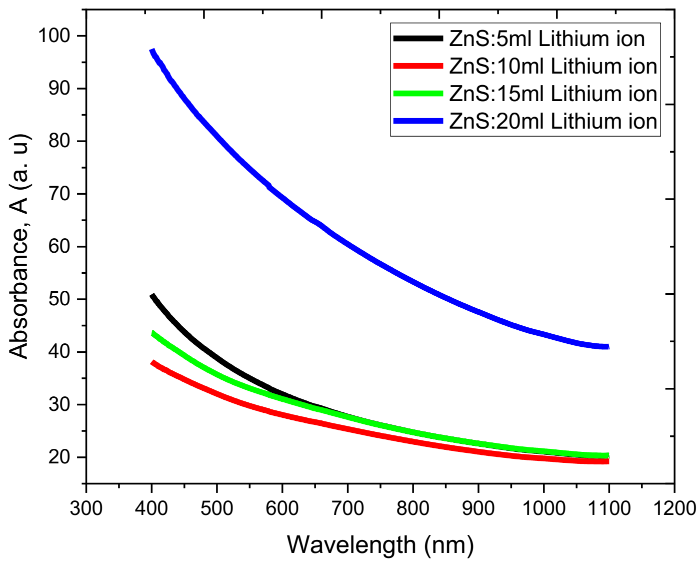



**Figure 1.** Plots of absorbance against wavelength for ZnS doped with varying volumes of lithium-ion solutions

### *3.2 Transmittance spectral*

**Figure 2** shows the plots for transmittance against wavelength for ZnS doped with varying volumes of lithium-ion solutions. It was observed that the transmittance generally increased with increase in wavelength and has relatively high values in the IR region of the solar radiation. For ZnS thin films doped with 20ml volume of lithium-ion solution, transmittance increased from 10.56 % at 401.09 nm to 39.04% at 1100nm. For ZnS thin films doped with 15 ml volume of lithium-ion solution, transmittance increased from 36.36 % at 401.09 nm to 62.49 % at 1100 nm. For ZnS thin films doped with 10 ml volume of lithium-ion solution, transmittance increased from 41.37 % at 401.09 nm to 64.22 % at 1100 nm. For ZnS thin films doped with 5ml volume of lithium-ion solution, transmittance increased from 30.74 % at 401.09 nm to 62.49 % at 1100 nm. The overall transmittance is high in the infrared region for all the films. Again, all the plots of transmittance versus wavelength showed that transmittance varied directly with wavelength. The findings concur with the report of other researchers, from the following references in the literature (Derbali *et al.,* 2018; Wanjala *et al.,* 2016; Nwofe, 2017; Offor *et al.,* 2020; Igweoko *et al.,*2025). The change in optical transmittance with the variation of lithium ion volume solution may be attributed to the variation in the film thickness. Tatar and Duzgun (2012) noted that an increase in the concentration of grains lead to high surface roughness which can decrease optical transmittance. The relationship between the optical transmission and thickness is given by Beer-Lambert equation (Reddy *et al.,*2006). The equation shows that the optical transmission is inversely proportional to the thickness of the film. With respect to the decrease in transmittance of the ZnS film doped with 20ml, it can also be explained on the basis of the thickness vis-à-vis concentration of the reagents used. Decrease in transmittance implies increase in film thickness in accordance with Lambert-Beer's law. At higher concentration, the constituent atoms increase as well as the light-particle collisions with atoms and the more difficult light can pass through. (Kamran, 2012; Nagayasami *et al.,* 2013).

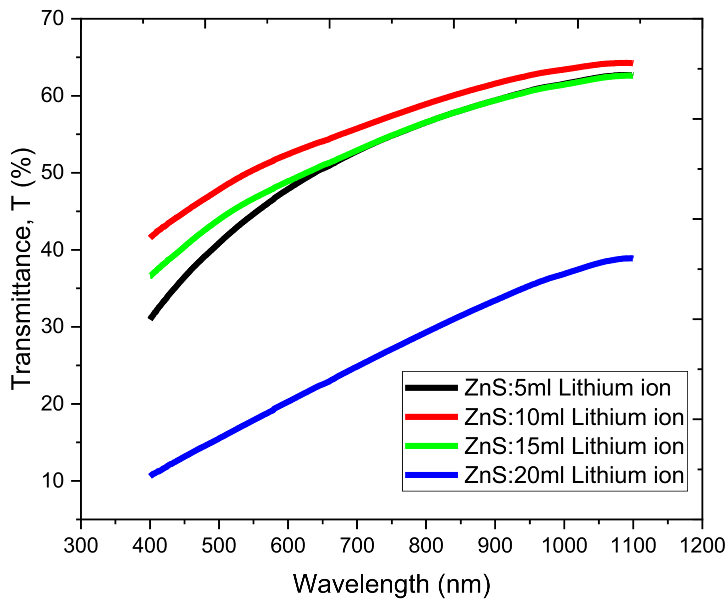



**Figure 2.** Plots of transmittance against wavelength for ZnS doped with varying volumes of lithium-ion solutions

The transmittance of ZnS thin films can be greatly altered by addition of different dopants or deposition variables. In the literature, several researchers have reported widely on the doping of ZnS with different impurities: ZnS thin films doped with manganese (Ozutok *et at.,* 2012), ZnS thin films doped with Copper (Suhail and Ahmed, 2014), ZnS thin films doped with lead (Suhail and Ahmed, 2014), ZnS thin films doped with tin (Wanjala, 2016), ZnS thin films doped with manganese (Ghazai *et al.,* 2020), ZnS thin films doped with silver (Essa *et al.,* 2023), ZnS doped with magnesium (Ali *et al.,* 2023) ZnS doped with lithium (Offor *et al.,* 2023) and ZnS doped with *H. Sabbdariffa* extracts (Igweoko *et al.,* 2025). Also in the literature, several researchers have reported on variation of transmittance of ZnS thin films caused by deposition variables;such as annealing (Kumar et al., 2013; Rahman et al., 2013) Substrate temperature (Whyte *et al.,* 2020; Temiz and Celik, 2024). Change in transmittance caused by deposition conditions such as studies involving deposition time, temperature, concentration etc have also been reported in the literature (Derbali et al., 2018 and Celik and Temiz, 2023). The characteristic of high transmittance in the infrared region demonstrated by the films in this work make them proper materials for thermal control coatings inside buildings.Thus, the films can be coated on the roofs and walls of poultry houses to facilitate transmission of infrared radiation (thermal portion of electromagnetic spectrum) into the building to generate heat for the purpose of warming young chicks. Those engaged in poultry farms spend a lot of fortune on charcoal to produce energy required to warm young birds. The cost incurred in purchasing charcoal to warm young birds can be minimized by the application of the sprayed films in poultry houses. Theses findings are corroborated by the report of other authors (Onochie *et al.,* 2012; Igweoko *et al.,* 2025).

### *3.3 Reflectance spectral*

From the spectra, it was observed that the overall reflectance is ≤ 20%. The peak reflectance value compared favourably with the value reported elsewhere for various thin film materials (Ukpai, 2021). However, it is above the value reported by Ozutok et al. (2012) for spray-deposited ZnS thin films doped with manganese and lower than the value reported by Okpara (2018) for spray-deposited ZnS thin films doped with manganese. In addition, the reflectance curves observed in this work are similar to those of other authors (Asogwa *et al.,* 2009). Films that exhibit low value of reflectance are reported to be suitable materials for anti-reflection coating such as coating of windscreens and driving mirrors to reduce effect of dazzling light from vehicles following behind at night (Aniefuna *et al.,* 2014). Again, this low reflectance property is imperative since, being the window layer part of solar cell, its reflectivity is supposed to be as low as possible (Wanjala *et al.,* 2016). Therefore, the reflectance properties exhibited by all the films in this research work make them suitable materials for the window layer part of solar cells in the solar industry.

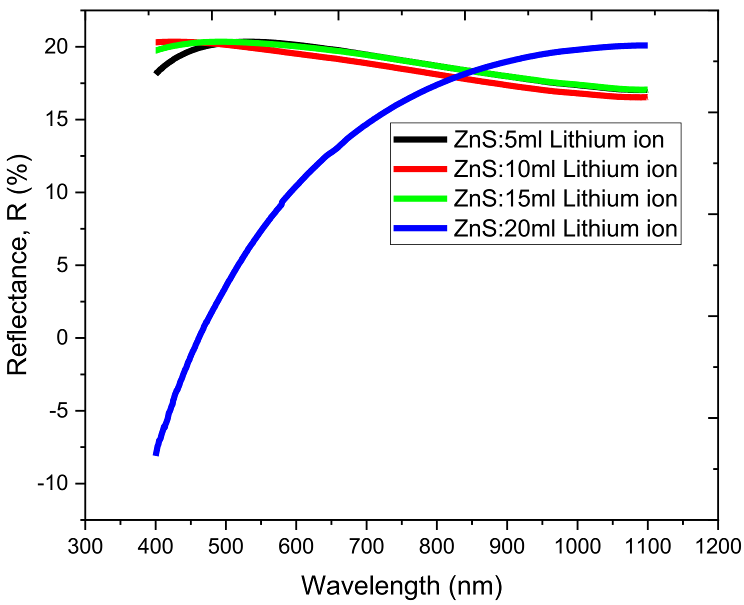



**Figure 3.** Plots of reflectance against wavelength for ZnS doped with varying volumes of lithium-ion solution

### *3.4 Absorption coefficient*

**Figure 4** shows plots of absorption coefficient as a function of photon energy for ZnS thin films doped with varying volumes of lithium-ion solutions. It was observed that coefficient of absorptions increases as photon energy increases. For ZnS thin films doped with 20 ml volume of lithium-ion solution, absorption coefficient increased from 0.011 at 1.11eV to 0.026 at 3.11eV. For ZnS thin films doped with 15ml volume of lithium-ion solution, absorption coefficient increased from 0.007 at 1.11eV to 0.015 at 3.11eV. For ZnS thin films doped with 10ml volume of lithium-ion solution, absorption coefficient increased from 0.0068 at 1.11eV to 0.014 at 3.11eV. For ZnS thin films doped with 5ml volume of lithium-ion solution, absorption coefficient increased from 0.0068 at 1.11eV to 0.017 at 3.11eV. This increase in absorption coefficient with photon energy concurs with the reports of Ali *et al.* (2023) for Mg-doped ZnS thin films deposited by spray pyrolysis method, Offor *et al.* (2023) for Li-doped ZnS thin films prepared by spray pyrolysis method, Igweoko *et al.* (20225) for *H.Sabbdariffa* dye-doped ZnS thin films grown by spray pyrolysis method, Suhail and Ahmed (2014) for spray-deposited ZnS doped with lead thin films and Suhail and Ahmed (2014) for spray-deposited ZnS doped with copper thin films. The absorption coefficient values indicated by the films suggest that they could be used in photovoltaic applications.

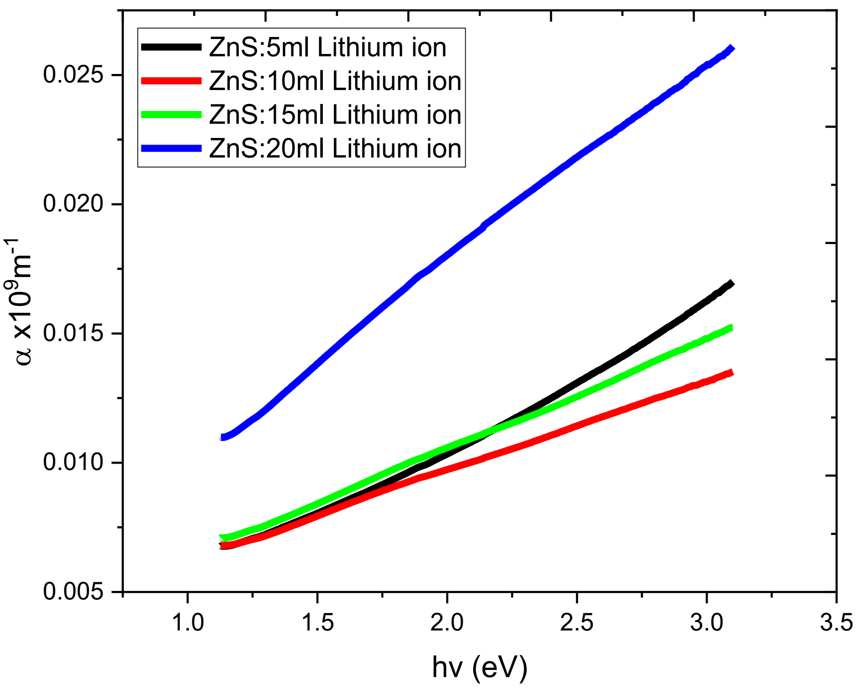



**Figure 4.** Plots of α as a function of hv for ZnS thin films doped with varying volumes of lithium-ion solutions

### *3.5 Band gap*

**Figure 5** shows plots of $(\alpha hv)^2$ as a function of photon energy (hv) for ZnS thin films doped with varying volumes of lithium ion solutions. The energy band gap, $E_g$,, of the films were determined from extrapolation of the straight portion to the energy axis at $(\alpha hv)^2 = 0$. Optical energy gap was typically in the range 2.25-2.67eV. The obtained range of optical energy gaps were above the range reported by Thiruvenkadam and Rajesh (2014). However, they were below the range reported by Suhail and Ahmed (2014) for copper doped ZnS thin films deposited by spray pyrolysis method, Suhail and

Ahmed (2014) for lead doped ZnS thin films deposited by spray pyrolysis method, Okpara (2018) for manganese doped ZnS thin films deposited by spray pyrolysis method and Wanjala (2016) for tin doped ZnS thin films deposited by spray-pyrolysis method. Asogwa *et al.* (2009) opined that thin film with band gap energy lower than 1.90eV are employed as absorber materials in solar cell architecture while those with higher band gap energy can be used as window layers. Since the obtained values in this research are above this value 1.90eV, therefore, high efficiency solid state solar cell (SSSC) window material for the photovoltaic conversion of solar energy, is plausible.

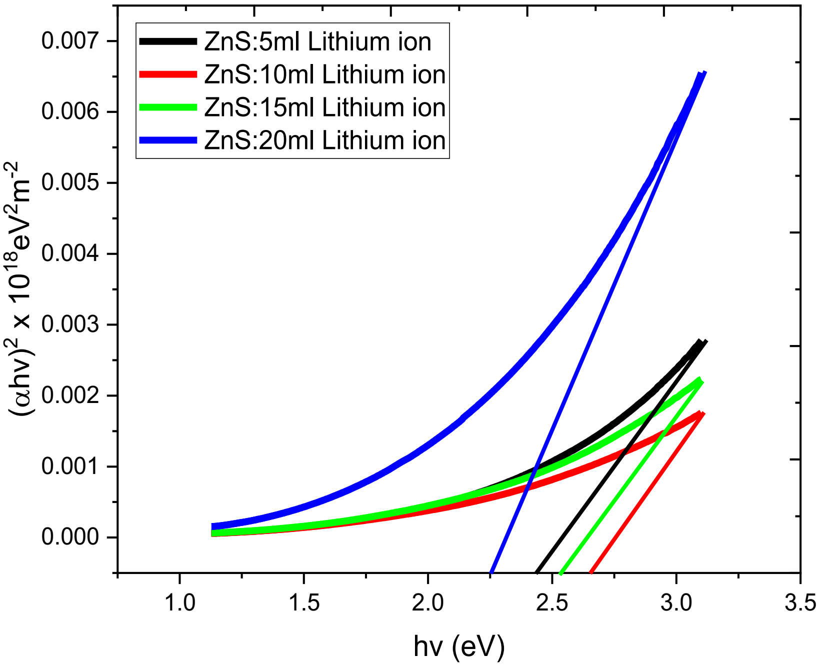



**Figure 5.** Plots of $(\alpha h\nu)^2$ as a function of hv for ZnS thin films doped with varying volumes of lithium-ion solution

### *3.6 Optical density*

**Figure 6** shows plots of optical density ($\rho$) as a function of photon energy (hv) for ZnS thin films doped with varying volumes of lithium-ion solutions. It was observed that the optical density increased as the photon energy increased. For ZnS thin films doped with 20ml volume of lithium-ion solution, optical density increased from 0.94 at 1.13eV to 2.25 at 3.11eV. For ZnS thin films doped with 15ml of lithium-ion solution, optical density increased from 0.47 at 1.13eV to 0.99 at 3.11eV. For ZnS thin films doped with 10ml volume of lithium ions solution, optical density increased from 0.47 at 1.13eV to 0.88 at 3.11eV.

For ZnS thin films doped with 5ml volume of lithium-ion solutions, optical density increased from 0.44 at 1.13eV to 1.17 at 3.11eV. This variation in optical density as photon energy is increased concurs with the report of other authors (Nwofe, 2017). In addition, the range of values are lower in magnitude when compared with the values reported by Nwofe (2017) for ZnS thin films dye doped with *Naulcea latifolia* extracts deposited by chemical bath method. The types of organic dye, deposition conditions and methods used in depositing the films could be responsible for the difference in the range of values of optical densities. The optical densities indicated by films suggest that the films are good materials for anti-reflection coatings in optics.

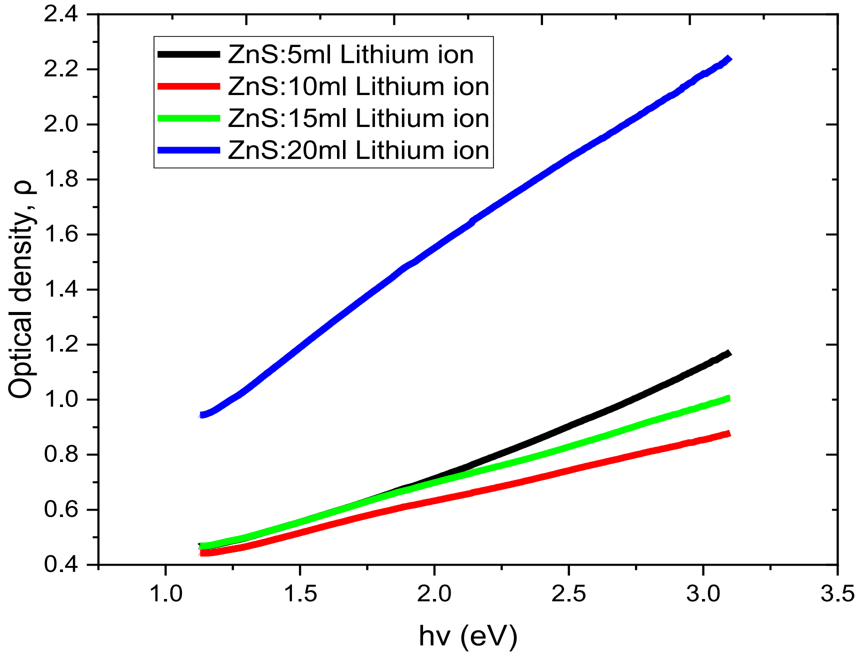



**Figure 6.** Plots of $\rho$ as a function of hv for ZnS thin films doped with varying volumes of lithium ion solution

## Conclusion

Lithium-doped zinc sulphide thin films were successfully grown on microslides (substrates) using the chemical spray pyrolysis method and optical spectroscopy was used for the characterization. The variation of lithium-ion solutions in zinc sulphide greatly modified the optical properties of the spray-made thin films. The films indicated strong absorption in the ultraviolet region and relatively high transmission in the visible and near infrared regions, whereas the reflectance was generally low in all the regions of electromagnetic spectrum (EMS). The coefficients of absorption values were found to be high in the order of $10^9$ $m^{-1}$. Te film indicated direct band gap energy range of 2.33 - 2.81eV. The optical density indicated range of 0.4 - 9.6. Based on these excellent optical properties exhibited by the films, it can be concluded that they are suitable for various industrial applications such as in the design of solar cells, optical window layers of photovoltaic cells, photodetectors, photoresistors, etc.

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**Disclosure statement:** *Conflict of Interest:* The authors declare that there are no conflicts of interest.

*Compliance with Ethical Standards:* This article does not contain any studies involving human or animal subjects.

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