

Effect of tin on bandgap narrowing and optical properties of ZnO–Zn₂SnO₄ electrospun nanofibre composite

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ABSTRACT

The quest for improved visible light absorption in ZnO-based photocatalysts and photodetectors is a prevailing research problem. One method of solving this problem is by narrowing the band gap of this material well into the range of visible light energy. In this work, we have demonstrated considerable band narrowing into the visible region in our electrospun ternary ZnO–Zn₂SnO₄ nanofibres. We also showed that band narrowing is highly dependent on the amount of Sn in the synthesized composite which could be attributed to the creation of localized states in the ZnO band and the attendant structural changes. However, beyond 15%wt doping there were observed changes in the trend of the bandgap reduction, crystallite sizes, and width of the localized states in the ternary ZnO–Zn₂SnO₄ band. The details of experimental procedures and discussion of results have been included in this paper.

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1. Introduction

ZnO is one of the most explored materials for photocatalysis and photodegradation applications [1–5]. However, the bandgap energy of pure zinc oxide makes it only favourable for ultraviolet-assisted photocatalytic and photodegradation despite its versatility. Hence, further research and enhancement have given way to a better-developed ternary like Zn₂SnO₄ which has emerged as a new compound belonging to II₂–IV–VI₄ semiconductor family [6]. ZnO and Zn₂SnO₄ are non-toxic transparent wide bandgap direct semiconductor materials with excellent functional properties such as high photocatalytic activity and electron mobility [7]. These properties have made these materials to be extensively used in diverse applications such as a dye-sensitised solar cell [8,9], gas sensor [10], photovoltaic [11] and optoelectronics [12]. Zn₂SnO₄ has been synthesized by several methods; mechanochemical [13], thermal evaporation [14] hydrothermal [15] and sputtering [16]. Few researchers have attempted to investigate different compositions and ratio of Zn and Sn in the ZnO–Zn₂SnO₄ composite; Bai et al. [17] used molar ratio 2: 1 of Zn to Sn, Wang and Wang [18] have also tried weight per cent ratio of 9: 1, Chen et al. [19] also used a molar per cent of 75% Zn to 25% Sn, while Iglesias et al. [20] have also used molar concentration of 0.1, 1 and 10 mol per cent of Sn in the ZnO–Zn₂SnO₄ composite.

The compositions of semiconductor material along with its morphology play an essential role in its properties [11,21,22]. Aside the well-studied binary semiconductor oxides such as ZnO, TiO₂, SnO₂, ternary oxides such as Zn₂SnO₄ semiconductor-semiconductor heterojunction or coupling of metal oxides are well fascinating due to their modified optical and electronic properties [23–25]. For instance, the suitability of binary-based ternary oxide as inorganic-organic pollutant removal had been reported by Yiang et al. and Qian et al. [26,27]. The use of core-shell nanostructure of Au–ZnO–Pd ternary had been utilized to synergistically improve the electron co-trapping catalyst and plasmonic effect for the enhancement of photocatalytic performance [28].

Since it had been established that semiconductor material composition in ternary semiconductors plays a vital role in their final structural and optical properties; hence this work sought to investigate the effect of tin (Sn) concentration on the structural and optical properties of the ternary structure of ZnO–Zn₂SnO₄. The choice of Sn⁴⁺ as dopant is due to the formation of inverse spinel structure of Zn₂SnO₄ (whereby Zn²⁺ and Sn⁴⁺ share the octahedral site) which is known to be responsible for the Zn₂SnO₄ extended conduction band and its high electronic conductivity. However, to the best of our knowledge, very few works have been done to investigate how the Sn⁴⁺ concentration affect the energy band properties.

2. Materials and method

Poly(vinyl acetate) (PVAc) ($M_w = 500,000$ g by GPC), tin (ii) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) salt $\geq 98\%$ assay and zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) salt $\geq 99\%$ assay from Sigma-Aldrich and anhydrous N-N-dimethylformamide $\geq 99.8\%$ assay from Scharlau were used as purchased as precursor material. The coupled oxide of $\text{ZnO-Zn}_2\text{SnO}_4$ was synthesized from $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. Two (2) gram mixture of zinc and tin salts were prepared using weight percentage of 95% to 5%, 90% to 10%, 85% to 15%, 80% to 20% and 75% to 25%, respectively. The mixed salt was then dissolved in the polymer solution containing 1.6 g of PVAc dissolved in 10 ml of N, N, dimethylformamide (DMF) and was stirred until it was homogeneous. The glass substrates used were pre-cleaned

using dilute ethanol, hydrochloric (HCl) acid and distilled water. The solution was electrospun for about 3 h to have a thick fibre formation using a DC voltage of capable of reaching 25 kV developed at the Centre for Energy Research & Development, Obafemi Awolowo University, Ile-Ife. The spinneret to substrate distance was maintained at 20 cm with the fibres electrospun at 12 kV. The deposited fibres were calcined at 700°C in a tubular furnace in air. The as-spun and calcined fibre were later analysed for their chemical, structural, optical and electrical properties.

TESCAN scanning electron microscope equipped with Oxford Instrument X-Max (EDS) was used for the surface morphology and elemental composition studies of the as-spun and calcined fibres. 1.7 MeV Ion Beam Accelerator was used for the Rutherford backscattering analysis to determine the elemental concentration

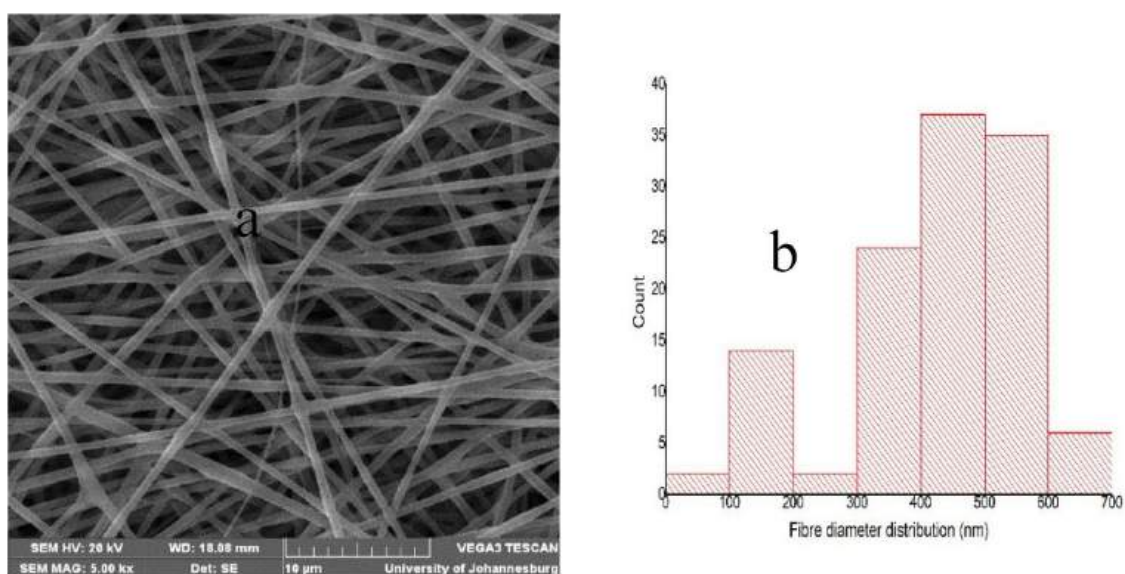


Figure 1. SEM image of as-spun $\text{ZnO-Zn}_2\text{SnO}_4$ and the fibre diameter distribution plot.

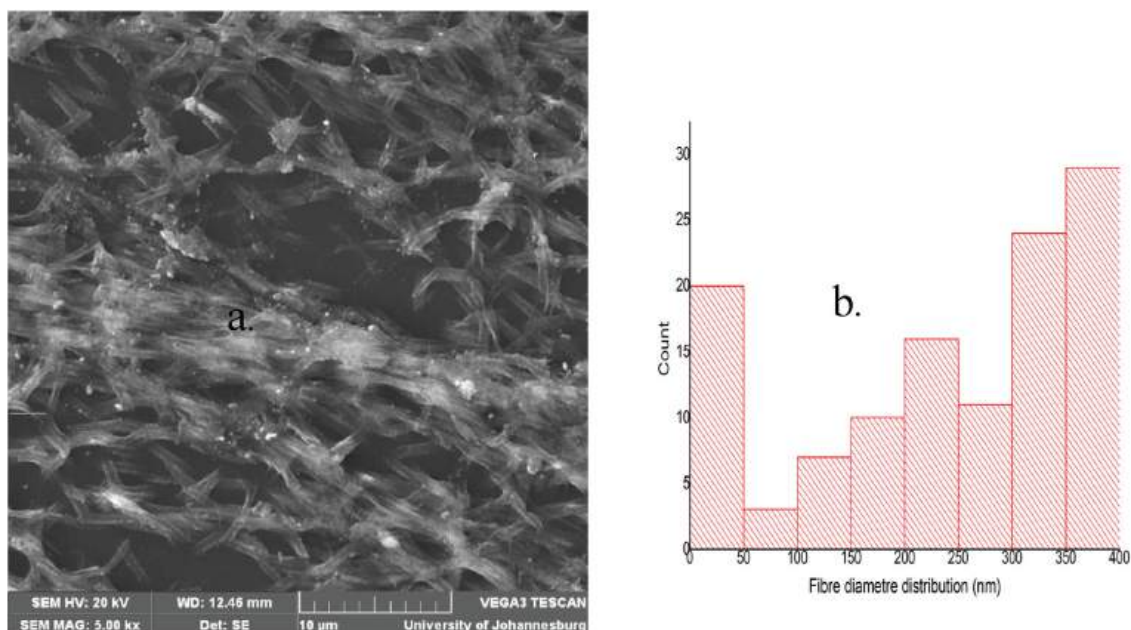


Figure 2. SEM image of calcined electrospun $\text{ZnO-Zn}_2\text{SnO}_4$ at 700°C and the corresponding fibre diameter distribution plot.

Table 1. Fibre diameter distribution of the as-spun and calcined ZnO–Zn₂SnO₄ nanofibre.

ZnO–Zn ₂ SnO ₄ nanofibre	Mean	Standard deviation	Minimum	Maximum
As-spun (nm)	484.25	117.85	156	697
Calcined (nm)	280.72	86.71	72	396

and the thickness of the deposited fibre. The Fourier transform infrared (FTIR) analyses were carried out using NICOLET S5 from Thermo Scientific. Stellanet Ultraviolet Spectrometer EP2000 (UV-VIS-NIR) was used for the optical characterization of the electrospun fibres. Fibre diameters were determined using ImageJ software. The crystal structure analyses were carried out using Bruker D8 high-resolution X-ray diffractometer.

3. Results and discussion

3.1. Morphology

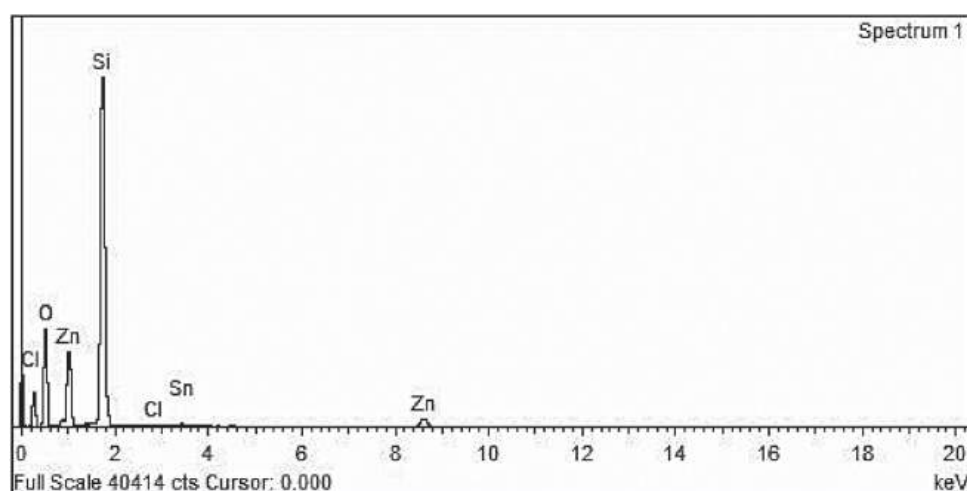
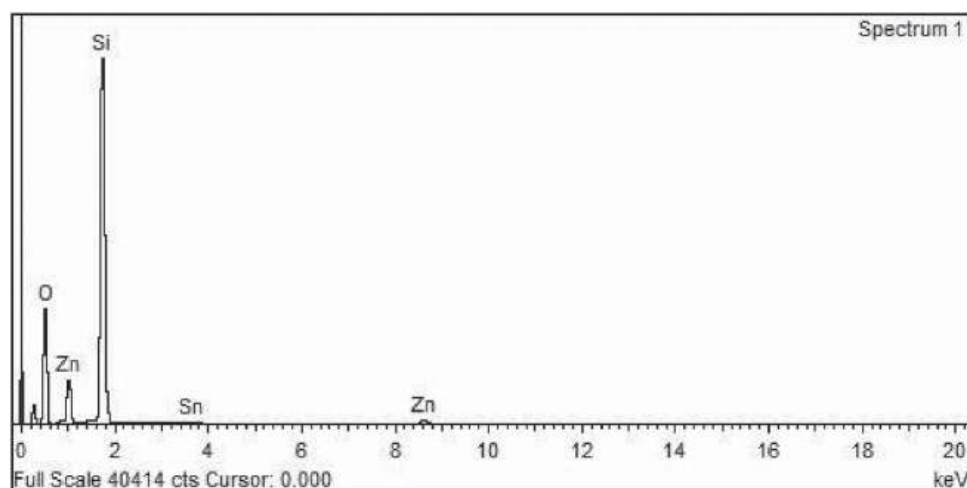
Figures 1 and 2 show the samples of the SEM images of the as-spun and calcined ZnO–Zn₂SnO₄ nanofibre respectively. The mean diameter of the bead

free non-woven nanofibre was found to reduce from 484.25–280.72 nm after calcination. This is given in Table 1. The reduction in the fibre diameter after calcination is attributed to the decomposition of the PVAc polymer that serves as a carrier for the metal salt.

3.2. Chemical and elemental analysis

The energy dispersive X-ray (EDX) analysis was carried out on some of the calcined samples to confirm the presence of the deposited metal such as Zn and Sn and also to determine the possible impurities that may be present in the samples. Figures 3–5 show the EDX spectra of the calcined samples and Tables 2–4 show the elementary compositions in the sample. It is evident from the spectra that the selected fibres contained the desired elements.

A little amount of chlorine observed in Figure 3 could be because the chlorine atom has not entirely evaporated for the sample calcined at 600°C while total evaporation of the chlorine was observed for the samples calcined at 700°C. Asokan et al. [29] observed that for annealing at the temperature range of 200–575°C,

**Figure 3.** EDX of calcine 5% Sn in ZnO–Zn₂SnO₄ nanofibre at 600°C.**Figure 4.** EDX of calcine 15% Sn in ZnO–Zn₂SnO₄ nanofibre at 700°C.

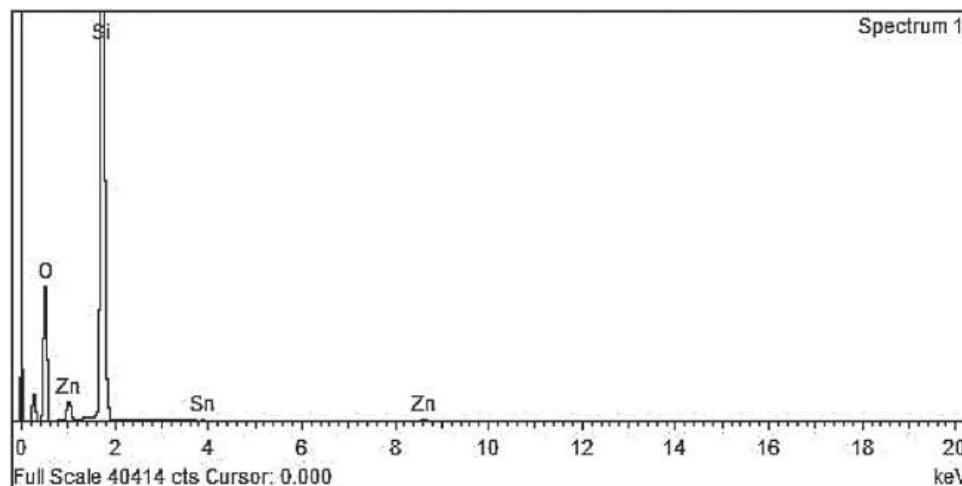


Figure 5. EDX of calcine 25% Sn in ZnO–Zn₂SnO₄ nanofibre at 700°C.

Table 2. EDX result of the composition determination and the corresponding compound formula for the elements in the calcine electrospun 5% Sn in ZnO–Zn₂SnO₄ nanofibre at 600°C.

Elements	Weight%	Atomic%	Compound %
Si K	39.51	30.61	84.53
Cl K	0.17	0.11	0.00
Zn K	11.42	3.80	14.22
Sn L	0.85	0.16	1.08
O	48.04	65.33	

Table 3. EDX result of the composition determination and the corresponding the compound formula for the elements in the calcine electrospun 15% Sn in ZnO–Zn₂SnO₄ nanofibre at 700°C.

Elements	Weight%	Atomic%	Compound %
Si K	41.99	31.61	89.83
Zn K	7.30	2.36	9.09
Sn L	0.85	0.15	1.08
O	49.86	65.88	

Table 4. EDX result of the composition determination and the corresponding compound formula for the elements in the calcine electrospun 20% Sn in ZnO–Zn₂SnO₄ nanofibre at 700°C.

Elements	Weight%	Atomic%	Compound %
Si K	44.94	32.71	96.13
Zn K	2.61	0.82	3.25
Sn L	0.48	0.08	0.61
O	51.97	66.39	

the acetate group in the zinc acetate and chloride in SnCl₂ · 2H₂O could not evaporate below this temperature. They observed that organic molecule and solvent can still pose as obstacles to charging carrier concentration and accumulation in the conduction band. For complete transformation from the amorphous state (as-spun) to the crystalline state they propose a calcination temperature higher than 575°C. It is expected that above 575°C the precursor salt should have been totally decomposed. Song and Dong [30] observed an exothermic peak at 734°C, but no other peak was experienced beyond 750°C. The observed curve by Song and Dong

[30] in the range of 530–750°C was attributed to the decomposition of the chloride and acetate from the tin and zinc salts respectively. The absence of peak beyond 750°C signifies no further decomposition of the organic components or other unwanted constituents. From the above findings, it shows that the required temperature for total decomposition of the unwanted constituents varies, depending on so many parameters, which may include among others the starting precursor, electro-spinning process and optimization of the calcination process. In this work traces of chlorine was still observed in the samples calcined at 600°C but were not presents in the samples calcined at 700°C. With this, it shows that the required temperature for the total decomposition of the organic constituents and the chlorine and acetate from the tin and zinc salt precursor occurred between 600°C and 700°C. The presence of silicon in all the calcined samples of Figures 3–5 can be attributed to the substrate.

The Rutherford backscattered (RBS) result for selected calcined samples at 700°C is shown in Figures 6 and 7. The result is to complement the EDX studies. The distinct nature of the peaks from the spectra suggests that the electrospun nanofibre adheres firmly to the substrate. The RBS spectra suggest the decomposition of the starting precursor material to form the oxides of the metals present in the salt used. The spectra also show little or no trace of impurities from the organic constituent like chlorine or acetate from the precursor salt used indicating that the peaks are mainly for the metal oxide deposited. It could also be observed from the spectra that the peaks corresponding to each element of Zn, Sn is well separated, this can be attributed mainly to the mass difference of the element that made up of the nuclei of the targeted atoms such as zinc and tin [31].

3.3. Fourier transform infrared

The FTIR analysis of the studied ZnO–Zn₂SnO₄ electrospun nanofibre for the as-spun and calcined fibres

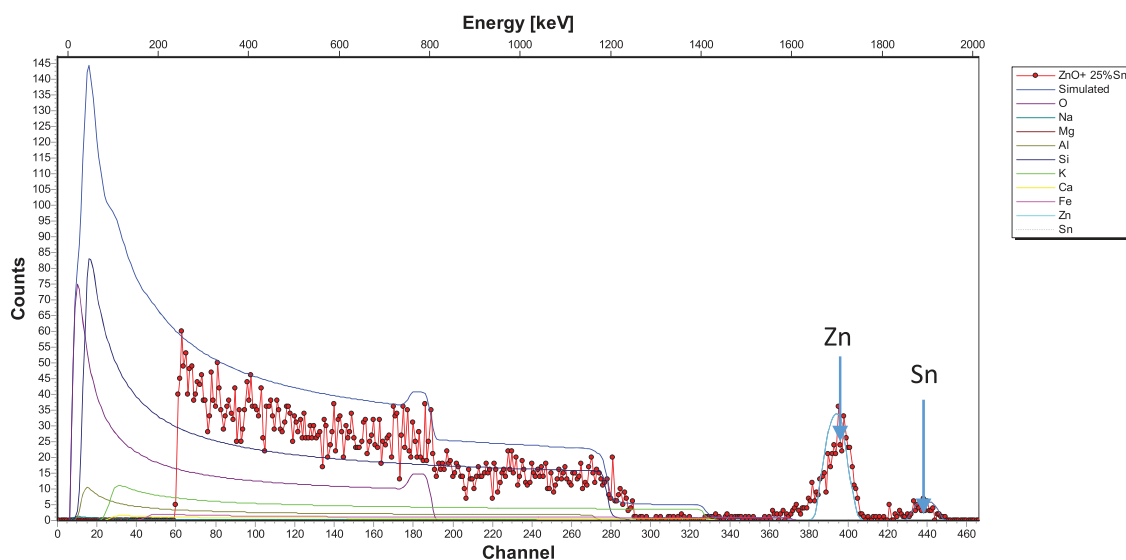


Figure 6. RBS spectrum of the calcined 15% Sn in ZnO–Zn₂SnO₄ nanofibre.

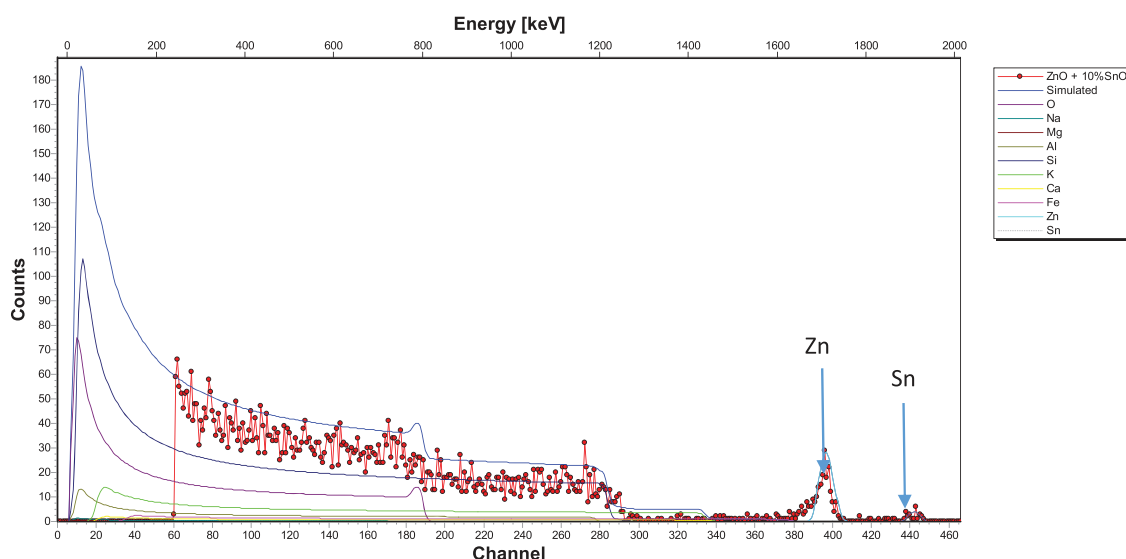


Figure 7. RBS spectrum of the calcined 25% Sn in ZnO–Zn₂SnO₄ nanofibre.

are given in Figure 8(a,b), respectively. The broad peak observed at 3499 cm^{-1} in Figure 8(a) signifies the bonded O–H stretching frequencies of the alcohol for the as-spun nanofibre samples. These O–H stretching could arise from the polyvinyl acetate, or from the water molecule of the metal salt used. The strong O–H stretching peaks observed for the calcined samples at 3658 cm^{-1} Figure 8(b) probably account for the non-bonded free O–H stretching frequencies in the calcined samples. The associated hypochromic shift (blueshift) observed for the calcined samples compared with the as-spun samples might be due to the effect of calcination on the samples. The double bond of CH, CH₂ or CH₃ observed at 2920 cm^{-1} in the as-spun fibre is attributed to the long chain of the PVAc polymer used. The absence of this bond in the calcined sample showed that the PVAc polymer had been removed from the sample as a result of the calcination.

3.4. Structural characterisation

The X-ray diffraction patterns of the calcined samples were studied to confirm the crystallinity of the samples and investigate their crystal structure. The ZnO–Zn₂SnO₄ composite electrospun nanofibre is presented in Figure 9 showing polycrystalline nature consisting of several diffraction peaks.

The main characteristic diffraction plane for the ZnO is at [101], [002] and [101] with the most pronounced peak indicating a preferred growth along the [002] direction. The major matching characteristics diffraction plane for Zn₂SnO₄ is at [131] and [222] with the preferred growth plane at [131]. These entries correspond to the database COD-Inorg REV140301 2015.07.06 with the entry 96-101-0111 [32,33]. The ZnO has a hexagonal wurtzite structure, while the Zn₂SnO₄ is a cubic structure. Rietveld refinement converges for the samples with the chi-square ranging from 6.2–9.3 and the

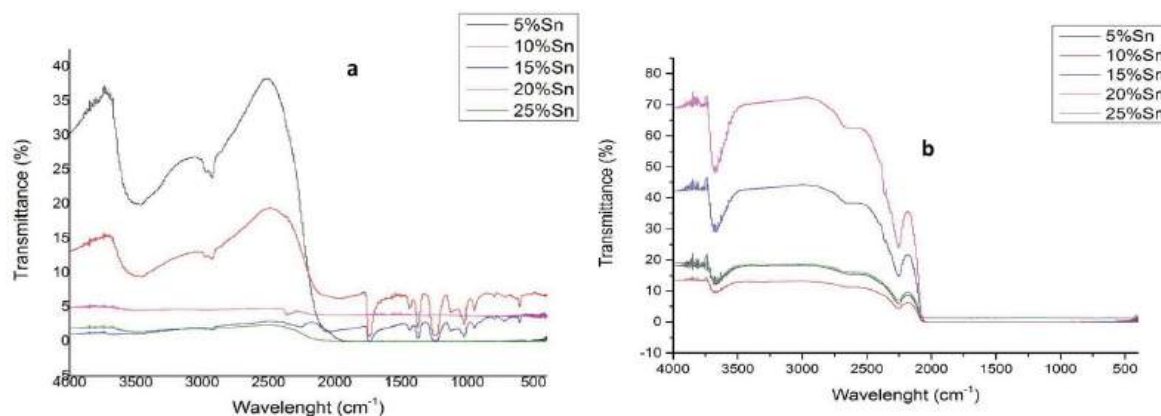


Figure 8. FTIR spectra ZnO-Zn₂SnO₄ nanofibre composite different percentage composition of added Sn content (a) as-spun (b) calcined samples at 700°C.

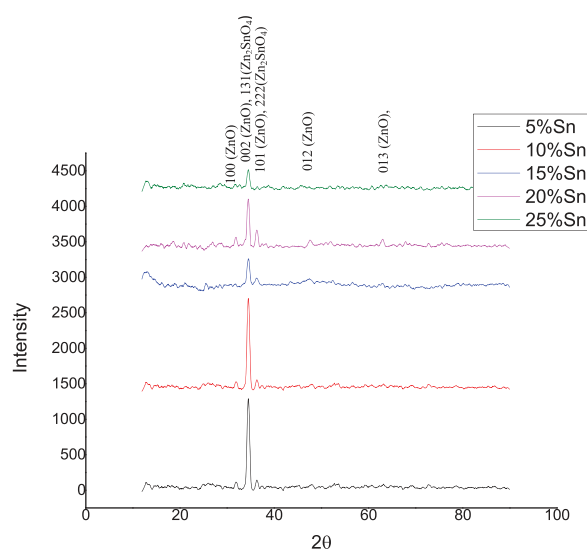


Figure 9. The XRD spectra of the calcined ZnO-Zn₂SnO₄ nanofibre composite.

Bragg's weighted average ranging from 98 to 99. The concentration of the phases as given by the match3 software for Rietveld refinement shows that the amount of the Zn₂SnO₄ increases from 51.5% to 61.2% and the ZnO decreases from 48.5% to 38.8% as the concentration of the zinc decreases and tin increases in the sample. In our earlier work [34], we reported the preferred growth direction for ZnO at [100], the shift in the 2θ position for the ZnO in the ZnO-Zn₂SnO₄ is attributed to the interaction between the ZnO and the Zn₂SnO₄. The calculated crystallite size for the diffraction peaks using Scherrer relationship given Equation (1) is 14.78, 13.29, 12.31, 13.57 and 12.69 nm for 5% Sn, 10% Sn, 15% Sn, 20% Sn and 25% Sn respectively. This show that the crystallite size decreases as the Sn contents increase up to 15% Sn before it dropped and then increases.

$$D = \frac{0.9\lambda}{B\cos\theta} \quad (1)$$

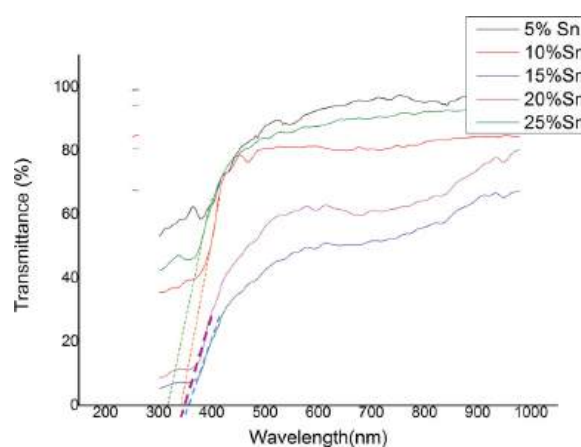


Figure 10. Transmission spectra of the calcined ZnO-Zn₂SnO₄ electrospun nanofibre.

3.5. Optical properties – UV-Visible spectrometric

The transmittance and absorption plot for the ZnO-Zn₂SnO₄ nanofibre presented in Figure 10 shows an increase in the percentage transmittance between 0.8% and 18% to between 66% and 98% for the as-spun and calcine fibres, respectively. A decrease in the percentage transmittance was observed for 5% Sn to 15% Sn, which later slightly increases from 20% Sn up to 25% Sn. Rakshit et al. [22] while studying the effect of SnO₂ on the properties of ZnO-SnO₂ observed that the Sn is majorly doped into the lattice of ZnO up to 15% concentration of SnO₂ in the composite using X-ray photoelectron spectroscopy. They further observed that the phases are segregated for concentration above 15% Sn. Similarly, Jooyoung et al. [35] also observed that increasing the concentration of SnO₂ in the SnO₂/ZnO composite changes the composite from its crystalline state to an amorphous state. It could be established from these findings that increasing the Sn concentration in the SnO₂-ZnO composite leads to changes in the phase of SnO₂-ZnO composite, which will also lead to changes in the other properties of the material such as the optical

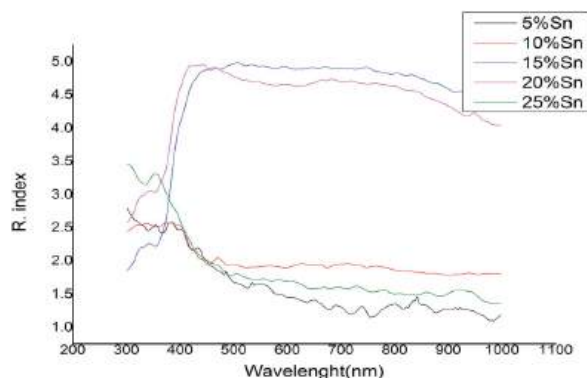


Figure 11. Refractive index spectra of ZnO–Zn₂SnO₄ electrospun nanofibre.

and electrical properties. The observed changes in the transmittance pattern above 15% Sn in ZnO–Zn₂SnO₄ phase could be attributed to some structural changes and variations in the degree of the crystallinity of the ZnO–Zn₂SnO₄ composite material.

3.5.1. Refractive index and extinction coefficient

The refractive index of semiconducting materials plays an essential role in their electrical and optical properties [36]. The refractive index of the material was determined using Equations (2) and (3) and the plot is given in Figure 11.

$$R = 1 - (T_{exp}(A))^2 \quad (2)$$

$$n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}} \quad (3)$$

where R is the reflectance, T is the transmittance, A is the absorbance and n is the refractive index.

The range of the refractive index is in agreement with those observed for the studied metal oxides by various researchers, such as in [37–39]. It can be seen that anomalous behaviour was observed in some of the refractive index spectra of 15%Sn and 20%Sn which could be attributed to change in phase of the material [22,35].

Extinction coefficient k , given by Equation (4) is a parameter that defines how strongly a material absorbs light at any given wavelength. The extinction coefficient is also related to the refractive index of the material. This relation is given by Gadallah and Nahass [40] in Equation (5). The extinction coefficient of the material was determined using Equation (5).

$$k = \frac{\alpha \lambda}{4\pi} \quad (4)$$

where k is the extinction coefficient, α is the absorption coefficient and λ is the wavelength.

$$n = \left(\frac{1 + R}{1 - R} \right) \sqrt{\frac{4R}{(1 - R)^2} - k^2} \quad (5)$$

The plot of the extinction values obtained using Equation (5) is given in Figure 12. It could be observed

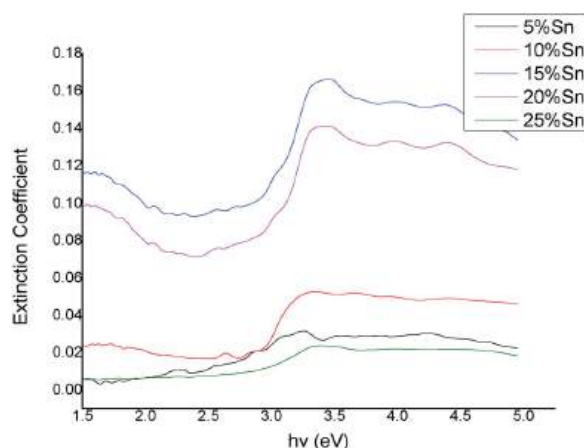


Figure 12. Graph of the extinction coefficient against the photon energy for ZnO–Zn₂SnO₄ electrospun nanofibre.

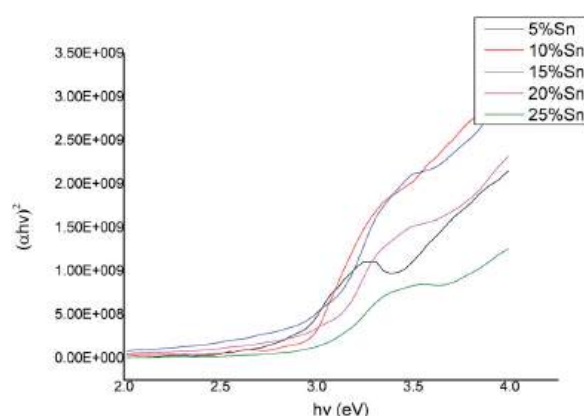


Figure 13. The plot of photon energy for allowed direct bandgap ZnO–Zn₂SnO₄ electrospun nanofibre.

that the values of the extinction coefficient of the material increases as the Sn concentration increases up to 15%Sn before it starts suddenly decreases. This result is consistent with the transmittance pattern and the value obtained for the bandgap (Figure 13).

3.5.2. Optical band gap determination

The optical bandgap of materials is known as the minimum energy required by semiconductor material to excite a photon. To determine the optical bandgap of the materials deposited, we used the Tauc plot given in Equation (6).

$$\alpha = A \frac{(hv - E_g)^n}{hv} \quad (6)$$

A plot of $(\alpha hv)^n$ against hv gives the Tauc plot for the determination of the bandgap. The intersection of the linear fit with the hv axis at $(\alpha hv)^n = 0$ gives the optical bandgap, E_g . Since both ZnO and Zn₂SnO₄ are direct bandgap semiconductor material, the value of n is given to be 2. A plot of this is shown in Figure 14; the two possible band gap values obtained suggested that the composite of ZnO–Zn₂SnO₄ had transited to an indirect bandgap material. The result is further confirmed by the plot of $(\alpha hv)^{1/2}$ against hv in Figure 14 given only one

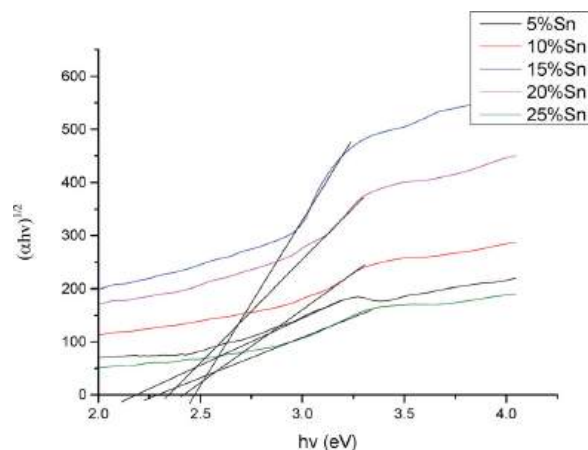


Figure 14. The plot of photon energy for allowed indirect bandgap ZnO–Zn₂SnO₄.

Table 5. Obtained values for the indirect bandgap.

Sample	Indirect bandgap value
5%Sn	2.16
10%Sn	2.32
15%Sn	2.47
20%Sn	2.35
25%Sn	2.27

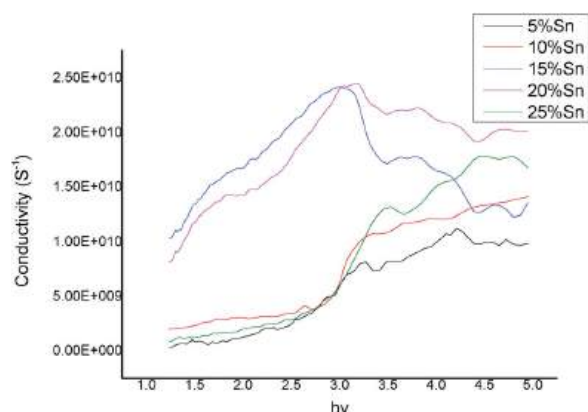


Figure 15. Plot showing the variation of optical conductivity against the photon energy for ZnO–Zn₂SnO₄ electrospun nanofibre.

energy bandgap. The obtained optical bandgap values of between 2.95 and 2.50 eV for ZnO and the Zn₂SnO₄ phases in all the compositions are lower compared to the 3.1–3.3 eV and 3.2–3.9 eV reported in the literature [41,42]. This result indicates that the wide bandgap of the semiconductor ZnO and Zn₂SnO₄ has transformed to a narrow bandgap material.

The extrapolated results from the indirect bandgap plot presented in Table 5 further shows the bending of the optical bandgap of the composite ZnO–Zn₂SnO₄ from the ultraviolet to a visible region. It could be observed that the bandgap values were increasing up to 15%Sn content before a reversal in the phase.

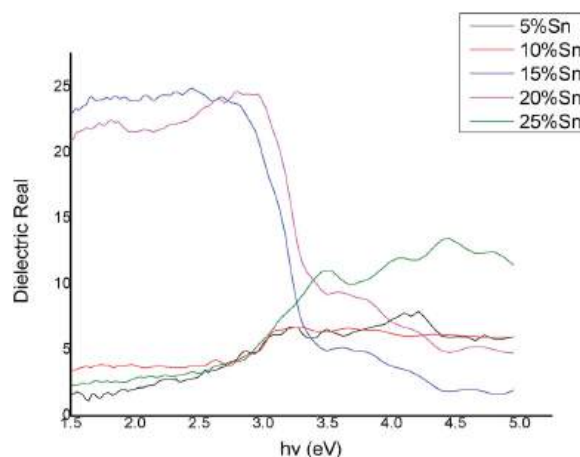


Figure 16. Plot showing variation of the real dielectric as a function of Photon energy for ZnO–Zn₂SnO₄ electrospun nanofibre.

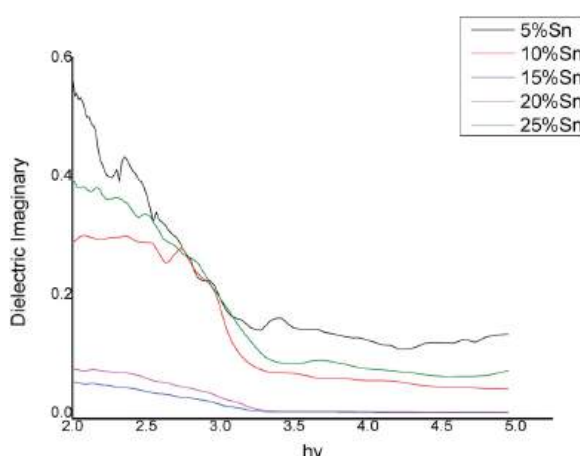


Figure 17. Plot showing variation of the imaginary dielectric as a function of Photon energy for ZnO–Zn₂SnO₄ electrospun nanofibre.

3.5.3. Dielectric properties

The real and imaginary part of the dielectric constant, and the optical conductivity of the nanofibre materials were calculated from the values of the extinction coefficient, and the refractive index using Equations (7)–(9), respectively, are presented in Figure 15–17.

$$\epsilon_r = n^2 - k^2 \quad (7)$$

$$\epsilon_i = 2nk \quad (8)$$

$$\text{Conductivity} = \frac{\alpha nc}{4\pi} \quad (9)$$

where ϵ_i , ϵ_r , k , n , α and c are the imaginary dielectric constant, real dielectric constant, extinction coefficient, refractive index, absorption coefficient and speed of light, respectively.

Figure 13 shows that the conductivity increases towards the high photon energy and increases sharply around the value of the bandgap energy. We also observed that the conductivity increases with the increase in the Sn concentration up to 15%W of Sn in the region of the lower photon energy. The graph of

the real dielectric shows the same trend as that of the conductivity. The observation in the real dielectric plot is inverse to that obtained for the imaginary part. The sharp increase in the conductivity around the bandgap can be attributed to the strong interaction between the photon and electron. The results obtained are similar to that obtained by [43,40], for the dielectric property of ZnO.

3.5.4. Tail width of localized states

According to [44] "The exponential tail appears because disordered and amorphous materials produced localized states extended in the bandgap." The spectral dependence of the absorption edge in the low photon energy is assumed to obey the Urbach rule given in Equation (10)

$$\alpha(\nu) = \alpha_0 \exp\left(\frac{h\nu}{\Delta E}\right) \quad (10)$$

where α_0 is a constant, $h\nu$ is the photon energy and ΔE denotes "the width of the tail of localized states in the bandgap" (Urbach energy).

By plotting $\ln(\alpha)$ against $h\nu$, the inverse of the slope from the linear fit of the linear portions of the curves gives the Urbach tail width energy of the localized state of the bandgap. The results obtained are presented in Figure 18 and Table 6. It is evident from table 4.18 that the degree of the disorderliness increases in the ZnO–Zn₂SnO₄ from 5% wt of Sn up to 15% wt of Sn before it starts to decrease again. Since the disorderliness in materials decreases their crystallinity, it could be

said that the crystallinity of the materials reduces with the addition of Sn up to 15% wt of Sn before it starts to increase again. This observation is an agreement with the observation of [35].

The result confirms that the observed sudden increase in the transmittance pattern in Figure 10 after 15% wt of Sn is as a result of a change in the degree of crystallinity.

4. Conclusion

The variation of Sn in the nanofibre composite has been observed to affect the optical and structural properties of the ternary ZnO–Zn₂SnO₄. It was also observed that there is a turning effect in the properties of the composite material around the 15% Sn. The narrowing of the optical bandgap from the ultraviolet to visible region suggests its usage as a narrow bandgap material in applications such as visible light photocatalysis, photodetection and other light-harvesting applications.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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Table 6. Urbach tail width for the calcine electrospun nanofibre.

Samples	ΔE (meV)
ZnO–Zn ₂ SnO ₄ (95%Zn, 5%Sn)	428
ZnO–Zn ₂ SnO ₄ (90%Zn, 10%Sn)	615
ZnO–Zn ₂ SnO ₄ (85%Zn, 15%Sn)	725
ZnO–Zn ₂ SnO ₄ (80%Zn, 20%Sn)	680
ZnO–Zn ₂ SnO ₄ (70%Zn, 25%Sn)	424

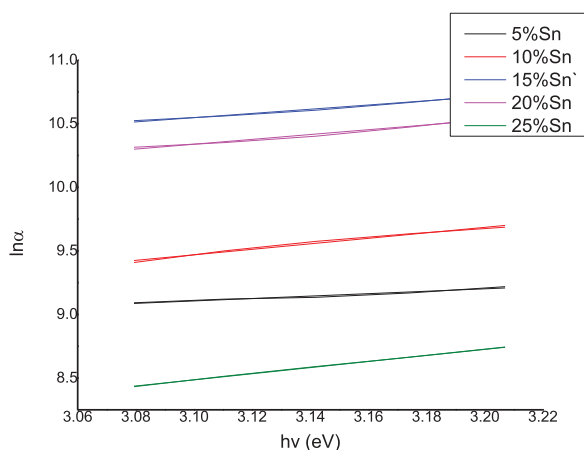


Figure 18. The Urbach tail plot for the ZnO–Zn₂SnO₄ nanofibre Urbach tail.

References

- [1] Al-Marzouqi F, Al-Adawi H, Qi K, et al. A green approach to the microwave-assisted synthesis of flower-like ZnO nanostructures for reduction of Cr (VI). *Toxicol Environ Chem.* 2019;101(1-2):1–12.
- [2] McLaren A, Valdes-Solis T, Li G, et al. Shape and size effects of ZnO nanocrystals on photocatalytic activity. *J Am Chem Soc.* 2009;131(35):12540–12541.
- [3] Wan Q, Wang TH, Zhao JC. Enhanced photocatalytic activity of ZnO nanotetrapods. *Appl Phys Lett.* 2005;87(8):083105.
- [4] Jang ES, Won JH, Hwang SJ, et al. Fine tuning of the face orientation of ZnO crystals to optimize their photocatalytic activity. *Adv Mater.* 2006;18(24):3309–3312.
- [5] Al-Abri R, Al-Marzouqi F, Kuvarega AT, et al. Nanostructured cerium-doped ZnO for photocatalytic degradation of pharmaceuticals in aqueous solution. *J Photochem Photobiol A.* 2019;384:112065.
- [6] Dridi R, Saafi I, Mhamdi A, et al. Structural, optical and AC conductivity studies on alloy ZnO–Zn₂SnO₄ (ZnO–ZTO) thin films. *J Alloys Compd.* 2015;634:179–186.
- [7] Zhou R-L, Kong X-Y. Photoluminescence and characterization of ZnO/Zn₂SnO₄ nanocables. *J Inorg Mater.* 2011;26(6):597–601. DOI: 10.3724/SP.J.1077.2011.00597.
- [8] Choi S-H, Hwang D, Kim D-Y, et al. Amorphous zinc stannate (Zn₂SnO₄) nanofibers networks as photoelectrodes for organic dye-sensitized solar cells. *Adv Funct Mater.* 2013;23(25):3143–3155.

- [9] Mali SS, Shim CS, Hong CK. Highly porous zinc stannate (Zn₂SnO₄) nanofibers scaffold photoelectrodes for efficient methyl ammonium halide perovskite solar cells. *Sci Rep*. 2015;5:1–10. | DOI: 10.1038/srep11424.
- [10] Ganbavle VV, Patil MA, Deshmukh HP, et al. Development of Zn₂SnO₄ thin films deposited by spray pyrolysis method and their utility for NO₂ gas sensors at moderate operating temperature. *J Anal Appl Pyrol*. 2014;107:233–241. DOI:10.1016/j.jaap.2014.03.006.
- [11] Das PP, Roy A, Tathavadekar M, et al. Photovoltaic and photocatalytic performance of electrospun Zn₂SnO₄ hollow fibers. *Appl Catal B*. 2016;203:692–703. DOI: 10.1016/j.apcatb.2016.10.035.
- [12] Jaculine MM, Ra CJ, Das SJ. Hydrothermal synthesis of highly crystalline Zn₂SnO₄ nanoflowers and their optical properties. *J Alloys Compd*. 2014;577:131–137. DOI:10.1016/J.JALLCOM.2013.04.158.
- [13] Nikolic N, Marinkovic Z, Sreckovic T. The influence of grinding conditions on the mechanochemical synthesis of zinc stannate. *J Mater Sci*. 2004;39:5239–5242.
- [14] Tharsika T, Haseeb AS, Akbar MA, et al. Gas sensing properties of zinc stannate (Zn₂SnO₄) nanowires prepared by carbon assisted thermal evaporation process. *J Alloys Compd*. 2015;618:455–462.
- [15] Jaculine MM, Raj CJ, Das SJ. Hydrothermal synthesis of highly crystalline Zn₂SnO₄ nanoflowers and their optical properties. *J Alloys Compd*. 2013;577:131–137.
- [16] Tang TY, Ren SQ, Jing YL, et al. Characterization of Zn₂SnO₄ thin films prepared by RF magnetron sputtering. *Russ J Phys Chem B Nanomater*. 2018;12:503–509.
- [17] Bai X-L, Pan N, Wang X-P, et al. Synthesis and photocatalytic activity of one-dimensional ZnO-Zn₂. *Chin J Chem Phys*. 2008;21(1):81–86.
- [18] Wang R-C, Hung J-S. ZnO–sn:ZnO core–shell Nanowires and ZnO–Zn₂SnO₄ comb-like nanocomposites. *J Nanosci Nanotechnol*. 2010;10(9):5634–5640.
- [19] Chen Y-C, You H-M, Shen Y-R. Microstructures and dielectric properties of Zn₂SnO₄ thin films by sputtering from a ZnO doped ceramic target. *Integr Ferroelectr*. 2016;176(1):228–235.
- [20] Iglesias Y, Peiteado M, de Frutos J, et al. Current–voltage characteristic behaviour of dense Zn₂SnO₄-ZnO ceramics. *J Eur Ceram Soc*. 2007;27(13-15):3931–3933.
- [21] Hu Z, Huang D, Qin Y, et al. Preparation and photoelectric properties of Zn₂SnO₄/TiO₂ composite film electrodes for dye-sensitized solar cells, IEEE, 2011.
- [22] Rakshit T, Manna I, Ray SK. Effect of SnO₂ concentration on the tuning optical and electrical properties of ZnO-SnO₂ composite thin film. *J Appl Phys*. 2015;117(2):025704–025704-8. DOI: 10.1063/1.4905835.
- [23] Zhang Z, Shao C, Li X, et al. Electrospun nanofibers of p-type NiO/n-type ZnO heterojunctions with enhanced photocatalytic activity. *ACS Appl Mater Interfaces*. 2010;2(10):2915–2923.
- [24] Zhang Z, Shao C, Li X, et al. Electrospun nanofibers of ZnO–SnO₂ heterojunction with high photocatalytic activity. *J Phys Chem C*. 2010;114(17):7920–7925. DOI: 10.1021/jp100262q.
- [25] Liu H, Zhang G, Sun W, et al. ZnO hierarchical nanostructure photoanode in a CdS quantum dot-sensitized solar cell. *PLoS One*. 2015;10(9):0138298–0138298-17. DOI: 10.1371/journal.pone.0138298.
- [26] Liang Y, Lin S, Liu L, et al. Oil-in-water self-assembled Ag@AgCl QDs sensitized Bi₂WO₆: Enhanced photocatalytic degradation under visible light irradiation. *Appl Catal B*. 2015;164:192–203. DOI: 10.1016/j.apcatb.2014.08.048.
- [27] Qian X, Yue D, Tian Z, et al. Carbon quantum dots decorated Bi₂WO₆ nanocomposite with enhanced photocatalytic oxidation activity for VOCs. *Appl Catal B*. 2016;193:16–21.
- [28] Li B, Wang R, Shao X, et al. Synergistically enhanced photocatalysis from plasmonics and a co-catalyst in Au@ZnO–Pd ternary core–shell nanostructures. *Inorg Chem Front*. 2017;4(12):2088–2096. DOI:10.1039/C7QI00586E.
- [29] Asokan K, Park JY, Choi S, et al. Nanocomposite ZnO-SnO₂ nanofibre synthesised by electrospinning method. *Nanoscale Res Lett*. 2010;5:747–752.
- [30] Song C, Dong X. Synthesis and formation mechanism of TiO₂/SnO₂ composite nanobelts by electrospinning. *Optoelectron Adv Mater Rapid Commun*. December 2011;5(12):1296–1300.
- [31] Adeoye AE, Ajenifuja E, Taleatu BA, et al. Rutherford backscattering spectrometry analysis and structure properties of Zn_xPb_{1-x}S thin film deposited by chemical spray pyrolysis. *J Mater*. 2015;2015:215210–215210-8. DOI: 10.1155/2015/215210.
- [32] Martin S, Liangfeng G, Satyan T, et al. Simultaneous determination of several crystal structures from powder mixtures: the combination of powder X-ray diffraction, band-target entropy minimization and Rietveld methods. *J Appl Crystallogr*. 2014;47(2):659–667.
- [33] Barth TF, Posnjak E. Spinel structures: with and without variate atom equipoints. *Z Krist Krist Krist Krist*. 1932;82:325–341.
- [34] Bolarinwa HS, Onuu MU, Fasasi AY, et al. Determination of optical parameters of zinc oxide nanofibre deposited by electrospinning technique. *J Taibah Univ Sci*. 2017;11:1245–1258.
- [35] Jooyoung P, Ikjae L, Jaeyong K. Physical and optical properties of SnO₂/ZnO film prepared by an RF magnetron sputtering. *J Nanosci Nanotechnol*. 2016;16(3):2983–2986.
- [36] Baydogan N, Ozdurmusoglu T, Cimenoglu H, et al. Refractive index and extinction coefficient of ZnO:Al thin films derived by sol-gel dip coating technique. *Defect Diffus Forum*. 2013;334-335:290–293.
- [37] Sonmezoglu S, Erdogan B, Askeroglu I. Investigation of optical, structural and morphological properties of nanostructure boron doped TiO₂ thin film. *Bull Mater Sci*. 2013;36(7):1239–1245.
- [38] Zamiri R, Tobaldi DM, Ahangar HA, et al. Study of far infrared optical properties and photocatalytic activity of ZnO/ZnS heteronanocomposite structure. *RSC Adv*. 2014;4:35383–35389.
- [39] Akimov VV, Tyukhai EA, Tauson VL, et al. Characteristics of morphology, structure and composition of titanium surface under its modification by electrochemical polarization in phosphate-alkaline solutions. *Surf Interface Anal*. 2015;47(12):1081–1097. DOI: 10.1002/sia.5848.
- [40] Gadallah A-S, El-Nahass MM. Structural, optical constants and photoluminescence of ZnO thin films grown by sol-Gel spin coating. *Adv Condens Matter Phys*. 2013;2013:1–11. DOI: 10.1155/2013/234546.
- [41] Zhao Y, Hu L, Liu H, et al. Band gap tunable Zn₂SnO₄ nanocubes through thermal effect and their outstanding ultraviolet light photoresponse. *Sci Rep*. 2014;4:6847–6847-8. DOI: 10.1038/srep06847.
- [42] Ramelan AH, Wahyuningsih S, Munawaroh H, et al. ZnO wide bandgap semiconductor preparation for optoelectronic device. *IOP Conference Series: Material Science and Engineering*, p. 176, 2017.

- [43] Yakuphanoglus F, Ilican S, Caglarb M, et al. The determination of the optical band and optical constants of non-crystalline and crystalline ZnO thin films deposited by spray pyrolysis. *J Optoelectron Adv Mater.* July 2007;9(7):2180–2185.
- [44] Ikhmayies SJ, Ahmad-Bitar RN. A study of the optical bandgap energy and Urbach tail of spray-deposited CdS:In thin films. *J Mater Res Technol.* 2013;2(3):221–227. DOI: [10.1016/j.jmrt.2013.02.012](https://doi.org/10.1016/j.jmrt.2013.02.012).