Effect of Calcination Temperature on the Sol-Gel Synthesis of Aluminum-Doped ZnO Nanoparticles for Photovoltaic Applications

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Research Article

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Abstract

This study investigates the synthesis and characterization of zinc oxide (ZnO) nanoparticles doped with 3% aluminum (Al) for photovoltaic applications. The ZnO nanoparticles were synthesized using the sol-gel technique and subsequently calcined at 400°C, 500°C, and 600°C. X-ray diffraction (XRD) analysis confirmed the formation of ZnO nanoparticles with a hexagonal wurtzite crystal structure. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images revealed that the nanoparticle size increased with higher calcination temperatures. Energy-dispersive X-ray spectroscopy (EDX) confirmed the presence and homogeneous distribution of Zn, O, and Al within the samples. Fourier-transform infrared (FTIR) spectroscopy identified the presence of ZnO across all samples. Furthermore, the optical properties of the doped ZnO nanoparticles exhibited temperature dependent variations in absorbance, reflectance, and transmittance within the UV and Visible-IR spectra. The observed optical gap energies correlated with the calcination temperatures, suggesting a relationship between temperature, gap energy, and nanoparticle size. Overall, this study provides valuable insights into the synthesis and characterization of 3% Al-doped ZnO nanoparticles, emphasizing the significant influence of calcination temperature on their structural, morphological, and optical properties, which can be tailored for enhanced photovoltaic applications.

I. Introduction

In recent years, nanomaterials, particularly zinc oxide (ZnO) nanoparticles, have garnered significant attention for their diverse applications in fields such as sensors, solar cells, photocatalysis, and optoelectronic devices [1] [2] [3]. ZnO possesses unique properties, including a wide bandgap, high electron mobility, biocompatibility, and environmental friendliness, rendering it highly promising [4] [5]. To further enhance the performance of ZnO nanoparticles, researchers have explored doping with various elements. Among these dopants, aluminum (Al) stands out for its ability to modify the structural, optical, and electronic properties of ZnO [6] .

In this study, we focus on synthesizing and characterizing ZnO nanopowders doped with 3% aluminum. Employing the sol-gel technique, we synthesized the nanoparticles, followed by calcination at different temperatures to investigate the effects of thermal treatment on their properties. Through a comprehensive characterization process, including X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), Fourier-transform infrared (FTIR) spectroscopy, and UV-visible spectroscopy, we aimed to elucidate the structural, morphological, and optical properties of the doped ZnO nanoparticles. Our study also delves into the influence of calcination temperature on these properties. Understanding the relationship between synthesis parameters and nanoparticle properties is essential for optimizing ZnO-based nanomaterials for various application.

II. Materials and Methods

1. Elaboration of Al-doped ZnO Nanoparticles

Zinc oxide (ZnO) nanoparticles doped with aluminum (Al) were synthesized via the sol-gel technique. Initially, a sol-gel solution was prepared by dissolving 0.71g of zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$), acetic acid (CH_3COOH) with a concentration of 0.1 mol/l, and 3% aluminum nitrate nonahydrate (Al(NO3)3.9H2O) in 50ml of pure methanol. The solution was then subjected to reflux stirring at 130°C for two hours. Following a 24-hour aging period to facilitate gel formation, the solution exhibited complete dissolution and clarity. Subsequently, microwave drying was employed to eliminate the solvent, resulting in the production of fine, white, and shiny nanopowders. Finally, the nanopowders underwent calcination in an oven to achieve the desired crystallinity.

2. Thermal Treatment

A subsequent thermal treatment was conducted through calcination at varied temperatures (400°C, 500°C, 600°C) with the objective of optimizing the interaction between two key operating parameters: the concentration of the dopant (Al) and the calcination temperature. This step aimed to determine the most favorable conditions for the desired material properties. The heat treatment process was performed in an oven, utilizing a single-stage thermal cycle lasting 4 hours. The temperature ramping and cooling rates were maintained at 60°C/min to ensure controlled and uniform heating throughout the process. This systematic approach allowed for the exploration of the synergistic effects between dopant concentration and calcination temperature on the final characteristics of the synthesized nanoparticles.

III. Results and Discussion

1. Structural Analysis of Zinc Oxide Doped with 3% Al Nanoparticles by XRD

The XRD diffraction peaks of 3% Al-doped ZnO nanoparticles are illustrated in Figure (1), revealing a crystal structure consistent with hexagonal wurtzite. No additional diffraction peaks corresponding to other phases were detected, indicating the formation of ZnO nanoparticles doped with 3% Al in the wurtzite phase. Furthermore, Figure (2) demonstrates the broadening of the XRD diffraction peaks of the nanoparticles doped at different calcination temperatures. Interestingly, an increase in the calcination temperature from 400°C to 600°C resulted in a reduction in peak width and an enhancement in peak intensity. This observation suggests a potential enhancement in crystallinity and structural ordering of the doped nanoparticles with increasing calcination temperature.

To calculate the size of nanoparticles using the Debye-Scherrer relationship, We used the following formula [7]:

G=$O,9\lambda/\beta cos\theta$

G is grain size

Θ is peak position

λ is wave length

β is width at half height

The size of ZnO nanoparticles doped with 3% Al exhibits a discernible dependence on the diffraction direction (hkl), as evident from the findings summarized in Table 1. Across the investigated range of calcination temperatures, spanning from 400°C to 600°C, a clear trend emerges: higher calcination temperatures correlate with larger nanoparticle sizes. Specifically, nanoparticles subjected to calcination at 400°C demonstrated the smallest average size at 37.54 nm, while those calcined at 600°C exhibited the largest average size at 66.05 nm. This pronounced correlation underscores the notable influence of calcination temperature on nanoparticle dimensions, with elevated temperatures resulting in augmented particle sizes. Noteworthy is the observation that calcination at 400°C yielded the smallest nanoparticle size among all examined temperatures. These reported sizes, representing averages of 37.54 nm and 66.05 nm for 400°C and 600°C respectively, encapsulate the overall nanoparticle size distribution across diverse diffraction directions (hkl) for each corresponding calcination temperature, providing a comprehensive insight into the relationship between processing conditions and nanoparticle morphology.

Table 1
Variation of 3% Al-doped ZnO nanoparticle size with calcination temperature

Position du pic (hkl)	**(100)**	**(002)**	**(101)**	**G average (nm)**	
G (nm)	**400°C**	35.86	29.55	32.67	37.54
	500°C	40.34	36.10	36.28	42.32
	600°C	46.10	46.10	40.81	66.05

The lattice parameters a and c of the synthesized 3% Al-doped ZnO nanoparticles were determined using the Bragg law, with the equations [8]:

$$a = \lambda / (\sqrt{3} \sin\theta_{(100)}) \text{and} c = \lambda / \sin\theta_{(002)}$$

Where λ is the X-ray wavelength and θ (100) and θ (002) are the Bragg angles corresponding to the (100) and (002) diffraction peaks, respectively. Table (2) presents the evolution of these lattice parameters for ZnO nanoparticles doped with 3% Al across varying calcination temperatures. It is observed that both parameters, a and c, increase with rising calcination temperature, a trend attributed to the enlargement of nanoparticle sizes resulting from higher temperatures. The increasing lattice parameters suggest the localization of aluminum (Al) atoms in the interstitial sites within the ZnO lattice structure, reflecting the incorporation of dopant species into the nanoparticle matrix.

Table 2
Lattice parameters "a" and "c" for ZnO nanoparticles doped with 3% Al at different calcination temperatures

Tc (°C)	400	500	600
a (Å)	3.2584	3.2622	3.2715
c (Å)	5.2204	5.2241	5.2389

The substitutional elements of Zn in ZnO nanoparticles typically include elements from group III, such as In, Ga, and Al, while the substitutional elements of O are typically elements from group VII, such as Cl and I [9]. In our study, ZnO was doped with 3% Al, leading to the introduction of a small amount of impurities and defects into the crystal lattice. The dislocation density, a measure of these defects, was calculated using the formula [10] :

$$\delta = 1/\mathrm{G}^2$$

Where G represents the nanoparticle size determined by XRD analysis. Interestingly, we observed that increasing the calcination temperature and consequently the size of ZnO nanoparticles doped with 3% Al resulted in a decrease in defect density. This observation suggests a correlation between nanoparticle size and defect density, with larger nanoparticles exhibiting lower defect densities. The presence of structural defects in the crystal lattice can lead to shifts in the positions of diffraction peaks, which explains the observed changes in peak positions in doped ZnO samples.

Table 3
Dislocation density values of ZnO doped with 3% Al

Tc (°C)	400	500	600
δ (nm^{-2})	0.0007	0.0006	0.0002

2. Morphological Study of Al-doped ZnO by TEM

The microstructure of ZnO nanoparticles doped with 3% Al was investigated using Transmission Electron Microscopy (TEM). The images captured in Figure (3) reveal variations in nanoparticle diameter corresponding to different calcination temperatures. Specifically, nanopowders subjected to calcination at 400°C, 500°C, and 600°C exhibited average sizes of 17.72 nm, 21.68 nm, and 26.03 nm, respectively. This observation indicates that increasing the calcination temperature leads to a progressive enlargement in nanoparticle diameter. Notably, the nanoparticles synthesized at 400°C demonstrated the smallest average size among all investigated temperatures. These findings underscore the significance of calcination temperature in controlling the morphology and size of 3% Al-doped ZnO nanoparticles, with calcination at 400°C yielding nanoparticles with the minimum size.

Comparing our results with previous studies, we observed differences in the effects of calcination temperature on nanoparticle properties. For instance, while other studies noted a slight increase in crystallite size with higher Al doping percentages, we found that 400°C produced nanoparticles with minimal size and improved structural integrity, ideal for applications like photovoltaics [11].

3. **High Resolution SEM**

High-resolution scanning electron microscopy (SEM) observations, as depicted in Figure (4), provide insights into the distribution of Zn, O, and Al within the ZnO nanopowders doped with 3% Al. On the surface, zinc and oxygen dominate, while small aluminum grains are dispersed uniformly throughout, indicating a homogeneous distribution. This even distribution can be attributed to the well-executed sol-gel synthesis method, which yielded a transparent and highly homogeneous solution. The Energy Dispersive X-ray (EDX) analysis of the ZnO nanoparticle samples doped with 3% Al, also illustrated in Figure (4), reveals the chemical composition of the synthesized nanoparticles, with the main constituents being Zn, O, and Al. Importantly, the EDX results confirm the absence of impurities, validating the purity of the synthesized nanoparticles.

4. Phonon Properties

Fourier Transform Infrared (FTIR) spectroscopy provides a comprehensive analysis of the chemical composition of synthesized 3% Al-doped ZnO nanoparticles. The results presented in Figure (5) indicate the presence of ZnO in all samples calcined at various temperatures. Additionally, a peak observed at 2350 cm^{-1} corresponds to CO_2, likely associated with synthesis conditions. This FTIR analysis offers valuable insights into the chemical structure and composition of the synthesized nanoparticles, confirming the formation of ZnO and providing information about potential impurities or environmental influences during synthesis.

5. **Optical Properties**

The investigation into the optical properties of ZnO nanoparticles doped with 3% aluminum, subjected to varying calcination temperatures figure (6), has unveiled intriguing insights into their behavior across the UV and Visible-IR spectra. Notably, while the nanoparticles exhibit consistent absorbance levels in the UV range regardless of calcination temperature, there is a temperature-dependent effect on absorbance in the Visible-IR range, with nanoparticles calcined at 500°C demonstrating higher absorbance compared to other temperatures. Moreover, uniform UV reflectance across all calcination temperatures underscores the robustness of the material's reflective characteristics in this spectral region. Importantly, nanoparticles calcined at 400°C exhibit superior UV transmittance, emphasizing the significant role of calcination temperature in tailoring optical transparency. The observed optical gap energies reveal a nuanced relationship with calcination temperature, with nanoparticles calcined at 400°C and 500°C (3.17 eV) sharing higher energy levels compared to those calcined at 600°C (3.15 eV). This correlation suggests a link between calcination temperature, gap energy, and nanoparticle size, with higher temperatures leading to reduced gap energies and potentially larger nanoparticle sizes.

Our results indicate a bandgap energy of 3.15 eV to 3.17 eV, for ZnO doped with 3% Al. Other studies have found that Al ion can agglomerate and reduce the size of the crystallites according to the percentage used [12]. Additionally, there is an inverse relationship between the grain size and the gap energy, leading to a decrease in the gap energy when the size increases.

These findings highlight the strong influence of calcination temperature on the optical properties of ZnO nanoparticles doped with 3% aluminum, presenting opportunities for tailored optical characteristics in diverse applications such as sensors, photovoltaics, and optoelectronic devices. Further research into the underlying mechanisms driving these temperature-dependent effects will deepen our understanding and enable precise control over the optical behavior of these materials for future technological advancements.

IV. Conclusion

In this study, ZnO nanoparticles doped with 3% Al underwent calcination at various temperatures (400°C, 500°C and 600°C) using the sol-gel method, with a primary focus on determining the optimal calcination temperature for Al-doped ZnO. The investigation led to the selection of a calcination temperature of 400°C as it yielded ZnO nanoparticles doped with 3% Al with minimal size, along with desirable structural, chemical, morphological, and optical properties suitable for photovoltaic applications. Moving forward, future research will explore the impact of doping with different percentages of Al at the optimal calcination temperature of 400°C, aiming to further enhance the performance and characteristics of the synthesized nanoparticles.

Declarations

Author Contribution

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Figures

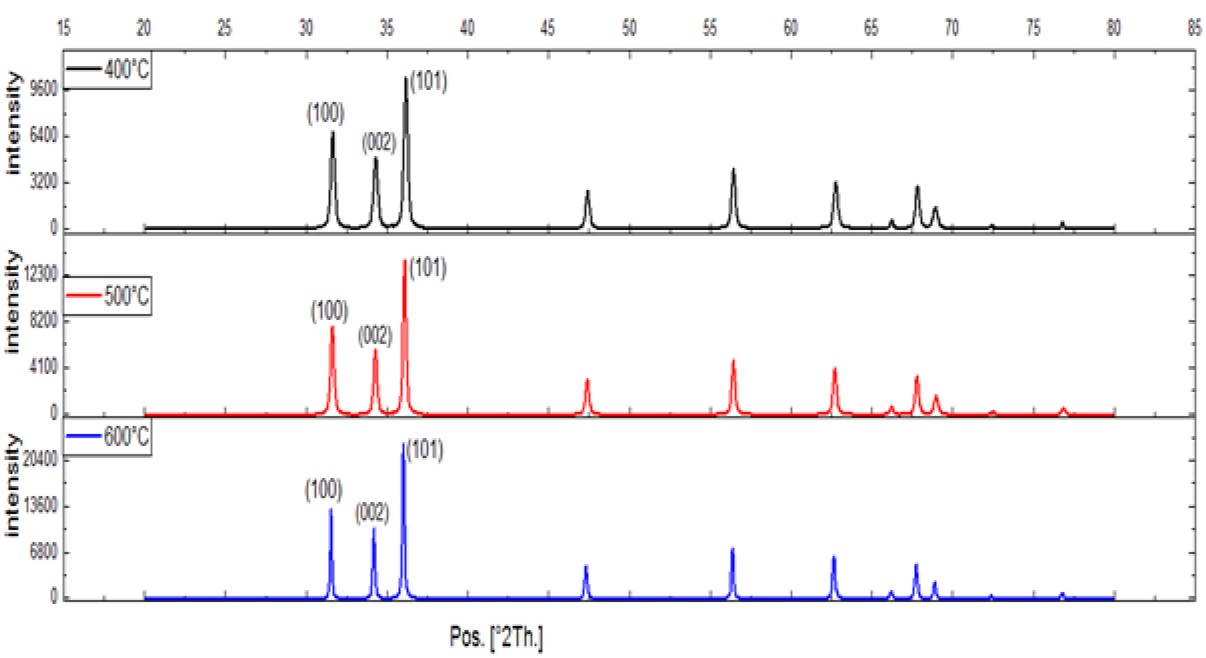


Figure 1

XRD spectrum of 3% Al doped ZnO nanoparticles at different calcination temperatures (400°C, 500°C and 600°C)

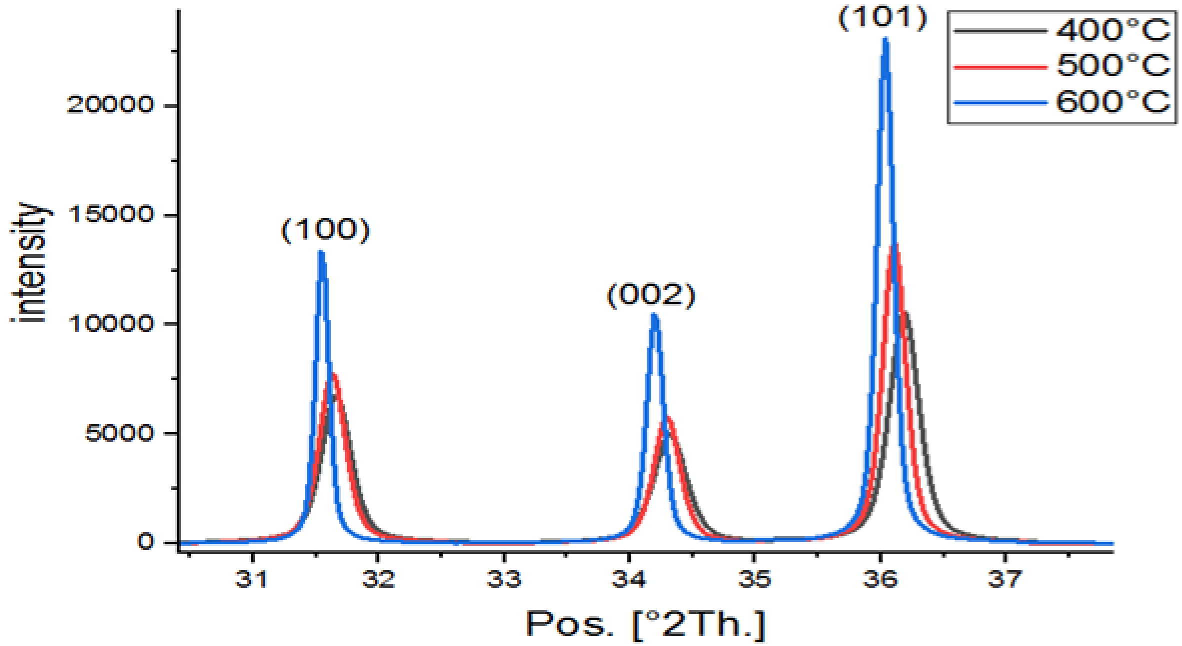


Figure 2

XRD spectra of 3% Al-doped ZnO nanoparticles at different calcination temperatures of (100), (002) and (101) peak positions

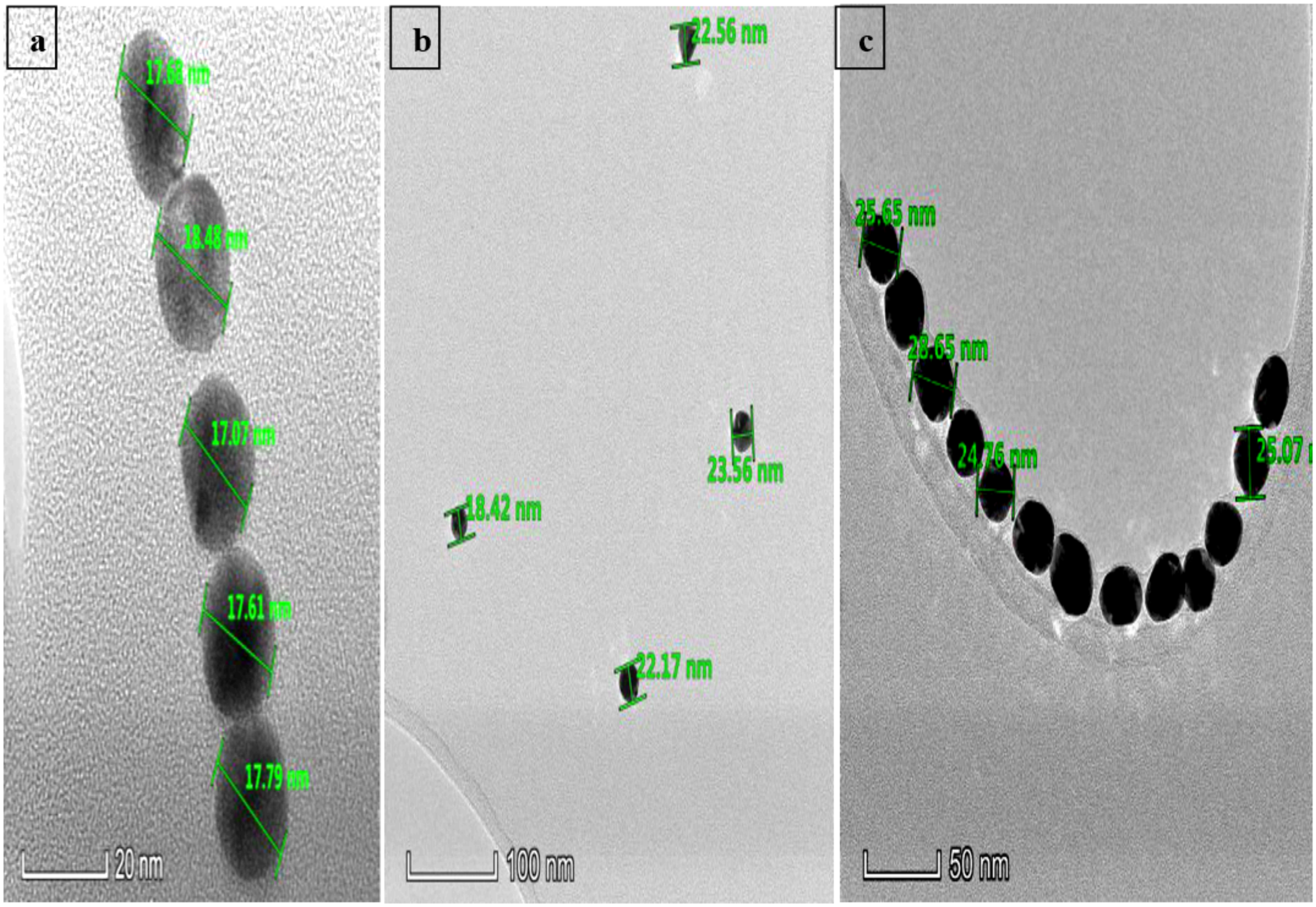
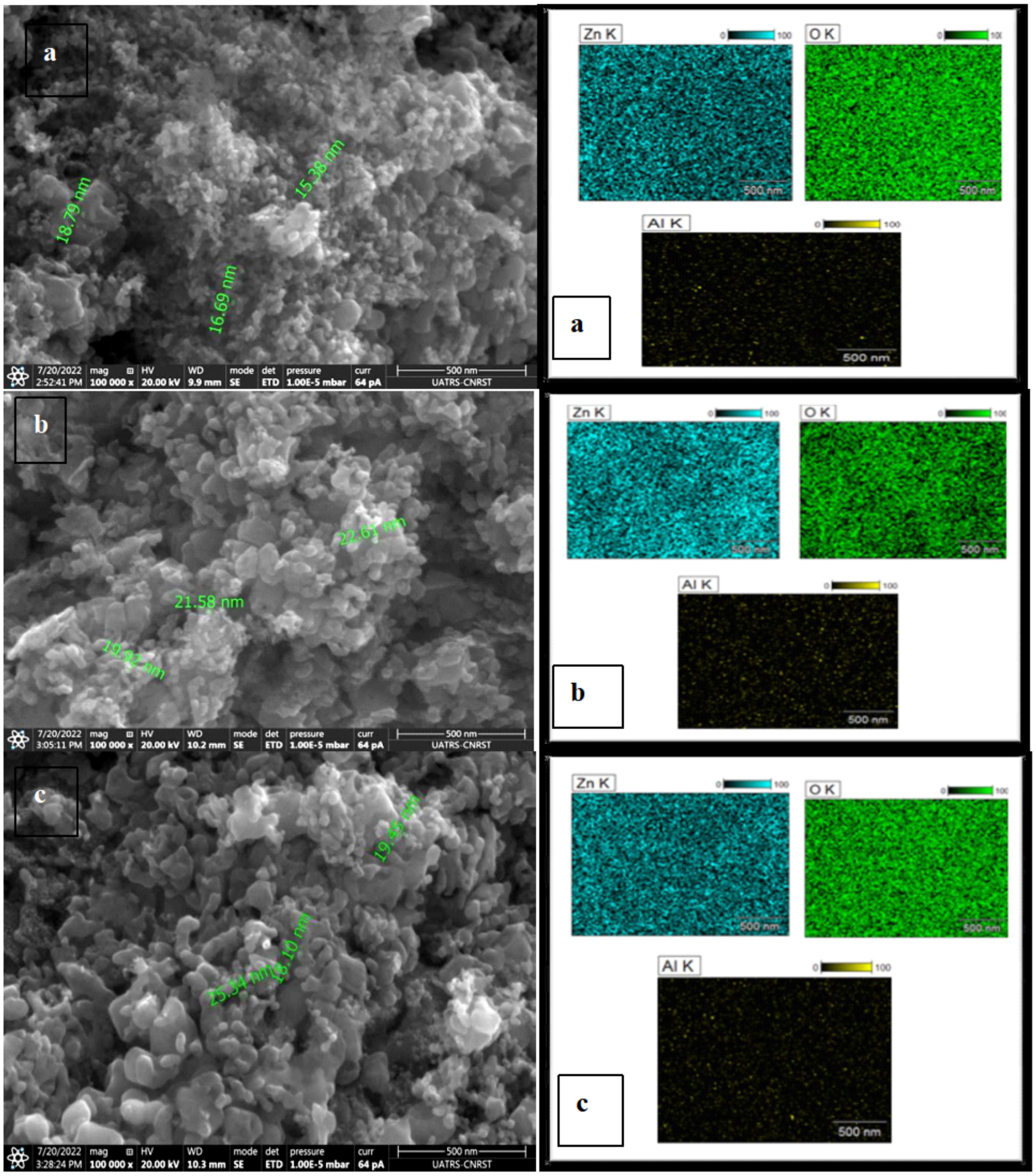
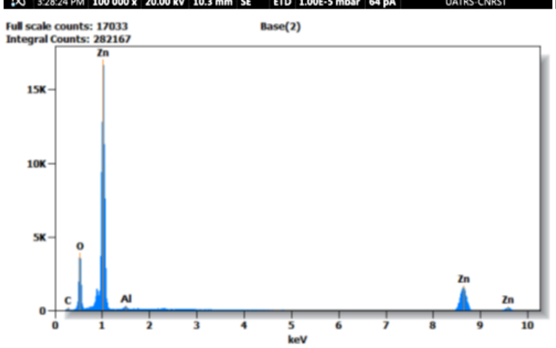


Figure 3

TEM images of ZnO doped with 3% Al synthesized at different calcination temperatures, a (400°C), b (500°C), c (600°C)





Samples	% atom ZN	% atom O	% atom Al
400°C	39.0	59.8	1.2
500°C	52.1	45.8	2.1
600°C	42.5	56.0	1.4

Figure 4

High resolution SEM image of ZnO doped with 3% Al at different calcination temperatures, a (400°C), b (500°C), c (600°C)

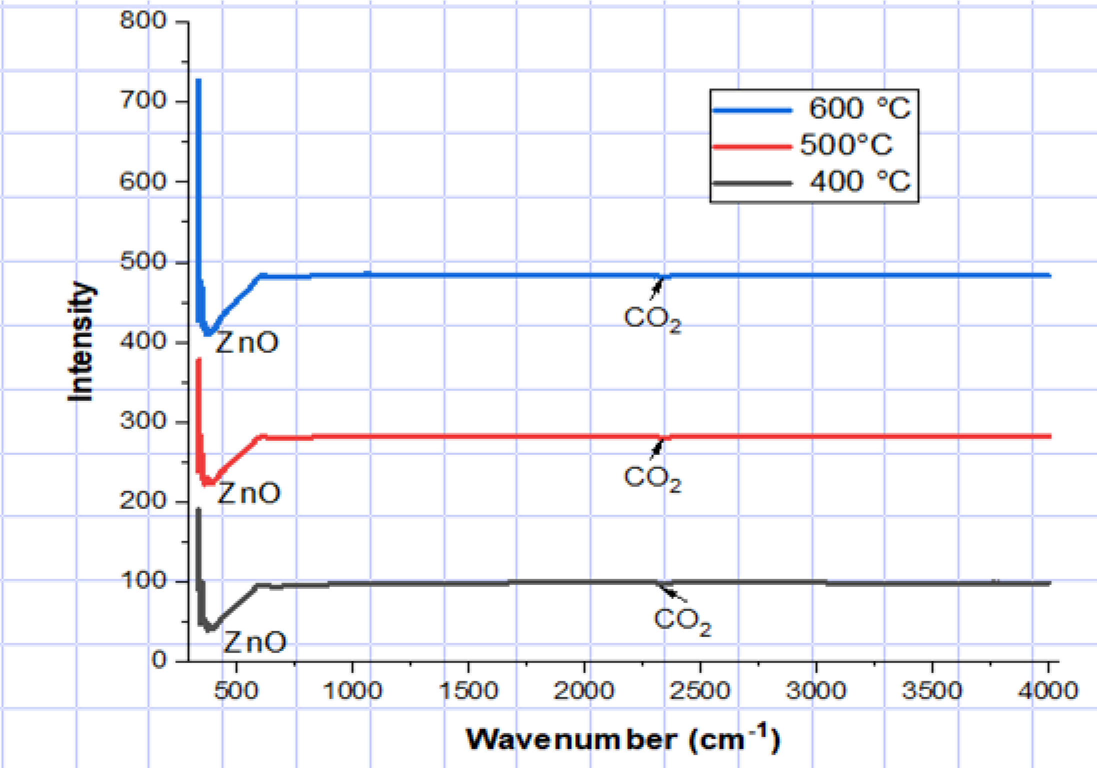


Figure 5

FTIR spectrum of 3% Al doped ZnO nanoparticles at different calcination temperatures

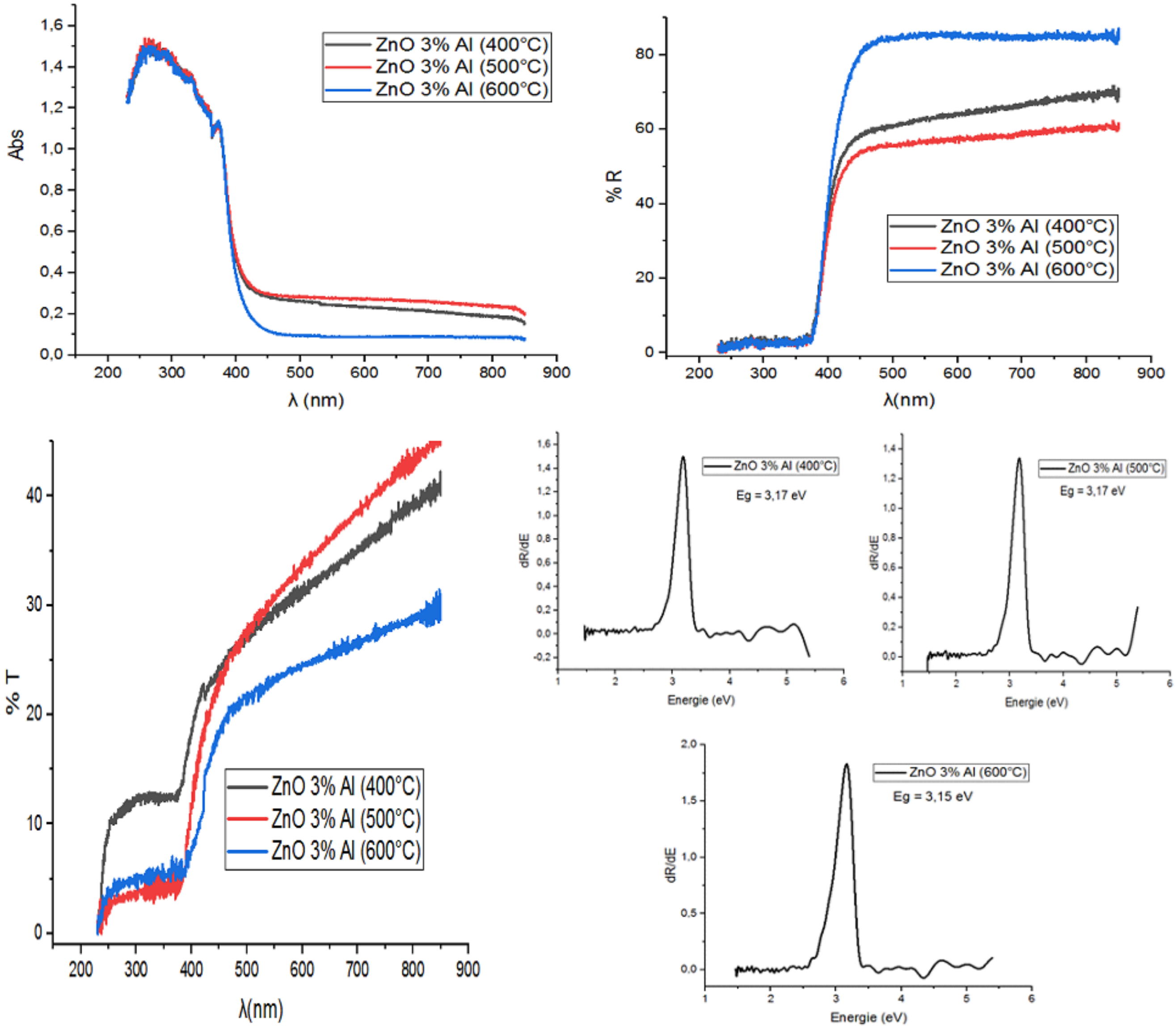


Figure 6

Optical properties of ZnO doped with 3% Al at different calcination temperatures