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EFFECT OF CU CONCENTRATION AND ANNEALING TEMPERATURE ON STRUCTURAL AND OPTICAL PROPERTIES OF FE/CU CO-DOPED ZNO NANOPARTICLES

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Abstract

Fe/Cu co-doped ZnO nanoparticles were successfully synthesized via the sol–gel method and subsequently annealed at different temperatures (400 °C and 600 °C) to investigate the effect of Cu concentration and annealing on their structural and optical properties. The prepared samples were characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), UV–visible spectroscopy, and scanning electron microscopy (SEM). XRD analysis confirmed the formation of a hexagonal wurtzite structure with no significant impurity phases, while variations in peak positions and intensities indicated successful incorporation of dopant ions and changes in crystallite size. An increase in annealing temperature resulted in improved crystallinity and increased crystallite size, whereas increasing Cu concentration led to a reduction in crystallite size and induced lattice distortion. FTIR spectra verified the presence of Zn–O bonding along with slight shifts due to doping effects. UV–visible analysis revealed a noticeable shift in the absorption edge and variation in the optical band gap, attributed to defect states and dopant-induced modifications in the electronic structure. SEM analysis showed agglomerated nanoparticles with morphology influenced by both annealing temperature and dopant concentration. The combined results demonstrate that tuning Cu concentration and annealing conditions significantly influences the structural and optical behavior of ZnO nanoparticles, making them suitable for potential applications in optoelectronic devices.

1. INTRODUCTION:

Zinc oxide (ZnO) is a wide band gap semiconductor material that has attracted significant attention due to its unique structural, optical, and electronic properties [1,2]. With a direct band gap of approximately 3.3 eV and high exciton binding energy, ZnO is widely used in optoelectronic devices, sensors, solar cells, and photocatalytic applications [3,4]. Its stability, non-toxicity, and low cost further enhance its importance in modern material science research.

In recent years, the properties of ZnO have been effectively tuned through doping with transition metal ions. Doping introduces defects and modifies the electronic structure, which can significantly influence the structural, optical, and morphological characteristics of the material [5,6]. Among various dopants, iron (Fe) and copper (Cu) have gained considerable interest due to their ability to alter the band structure and defect states of ZnO [7,8]. Fe doping is known to influence crystallinity and defect formation, while Cu doping plays an important role in modifying optical absorption and band gap behavior.

Co-doping of ZnO with two different elements has been found to produce enhanced and more controlled properties compared to single doping [9]. In particular, Fe/Cu co-doping can lead to improved structural stability, modified crystallite size, and enhanced optical response. Additionally, synthesis conditions such as annealing temperature play a crucial role in determining the final properties of the material. Higher annealing temperatures generally improve crystallinity, reduce defects, and influence particle growth, which directly affects the optical performance of nanoparticles.

Various synthesis techniques have been employed for the preparation of doped ZnO nanoparticles; however, the sol–gel method is widely preferred due to its simplicity, cost-effectiveness, and ability to produce uniform and high-purity nanostructures [10]. This method allows better control over composition and particle size, making it suitable for doping and co-doping processes.

In this study, Fe/Cu co-doped ZnO nanoparticles were synthesized using the sol–gel method, followed by annealing at different temperatures (400 °C and 600 °C). The main objective is to investigate the effect of Cu concentration and annealing temperature on the structural and optical properties of ZnO nanoparticles. The prepared samples were characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), UV–visible spectroscopy, and scanning electron microscopy (SEM). The findings of this work provide a better understanding of how doping and thermal treatment influence ZnO nanoparticles, which is important for their potential applications in optoelectronic and energy-related devices.

2. EXPERIMENTAL DETAILS

Fe/Cu co-doped ZnO nanoparticles were synthesized using the sol–gel method due to its simplicity, cost-effectiveness, and ability to produce homogeneous nanostructures [11]. Analytical grade precursors including zinc nitrate [Equation]$Zn(NO_3)_2 \cdot 6H_2O$, iron nitrate [Equation]$Fe(NO_3)_3 \cdot 9H_2O$, and copper nitrate [Equation]$Cu(NO_3)_2 \cdot 3H_2O$ were used without further purification. Distilled water was used as the solvent throughout the synthesis process.

Initially, an appropriate amount of zinc nitrate was dissolved in distilled water under continuous magnetic stirring to form a clear solution. Subsequently, calculated amounts of iron nitrate and copper nitrate were added to the solution to achieve the desired co-doping concentrations. The mixture was stirred continuously to ensure uniform distribution of dopant ions. A suitable complexing agent (such as citric acid) was then added to the solution to promote gel formation and improve homogeneity [12].

The resulting solution was heated at a moderate temperature under constant stirring until a viscous gel was formed. The gel was further dried to obtain a precursor powder. The dried samples were then subjected to annealing at two different temperatures, 400 °C and 600 °C, for a fixed duration to study the effect of thermal treatment on structural and optical properties [13]. After annealing, the samples were allowed to cool naturally to room temperature and were ground into fine powder for characterization.

The structural properties of the synthesized nanoparticles were analyzed using X-ray diffraction (XRD) with Cu-Kα radiation to determine phase formation, crystallinity, and crystallite size [14]. Fourier transform infrared spectroscopy (FTIR) was employed to identify functional groups and confirm Zn–O bonding. The optical properties were investigated using UV–visible spectroscopy in the wavelength range of 200–800 nm to determine absorption characteristics and optical band gap. Surface morphology and particle distribution were examined using scanning electron microscopy (SEM) [15].

3. RESULTS AND DISCUSSION

3.1. XRD Analysis: The structural properties of Fe/Cu co-doped ZnO nanoparticles were analyzed using X-ray diffraction (XRD). The diffraction patterns confirmed the formation of a hexagonal wurtzite structure of ZnO, indicating that the synthesized samples possess good crystallinity without the presence of significant impurity phases [16]. The observed peaks correspond to the standard crystallographic planes of ZnO such as (100), (002), and (101), which verify the successful formation of the ZnO phase.

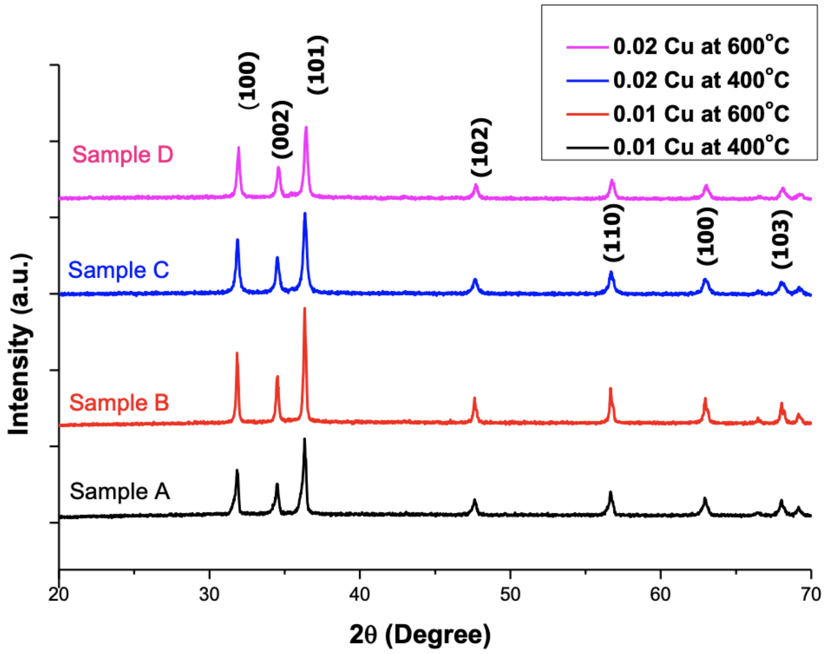

Figure 1. XRD peaks for Zn0.96Fe0.03Cu0.01, Zn0.95Fe0.03Cu0.02 Nanoparticles After annealing at 400oC and 600oC prepared by Sol-Gel method.

A clear change in peak intensity and sharpness was observed with variation in annealing temperature. The samples annealed at 600 °C exhibited sharper and more intense peaks compared to those annealed at 400 °C, indicating improved crystallinity and increased grain size [17]. This enhancement is attributed to better atomic arrangement and reduction of structural defects at higher annealing temperatures.

In addition, a slight shift in peak positions was observed with increasing Cu concentration. This shift confirms the successful incorporation of Fe and Cu ions into the ZnO lattice. The substitution of Zn^{2+} ions by Fe^{3+} and Cu^{2+} ions cause lattice distortion due to differences in ionic radii, resulting in internal strain within the crystal structure [19].

The crystallite size of the nanoparticles was calculated using the Scherrer equation from the full width at half maximum (FWHM) of the dominant diffraction peak. It was observed that the crystallite size increased with increasing annealing temperature, which is consistent with enhanced particle growth at higher temperatures [20]. However, with increasing Cu concentration, a decrease in crystallite size was observed, which can be attributed to the hindrance of crystal growth caused by dopant ions and the introduction of lattice defects.

Table 1. Crystallite Size Calculation of Zn0.96Fe0.03Cu0.01, Zn0.95Fe0.03Cu0.02 Nanoparticles After annealing at 400oC and 600oC prepared by Sol-Gel method.

Sample	Peak Position (Intense Peak)	d-spacing (Å)	FWHM (°)	Crystallite Size (D) (nm)	Lattice parameters		(c/a) ratio
					a=b (Å)	c (Å)	

Zn0.96Fe0.03Cu0.01 At 400°C	37.1	2.43	0.31716	27.61	3.23	5.17	1.60
Zn0.96Fe0.03Cu0.01 At 600°C	37.1	2.43	0.22514	38.89	3.23	5.19	1.60
Zn0.95Fe0.03Cu0.02 At 400°C	37.1	2.43	0.32768	26.72	3.23	5.17	1.60
Zn0.95Fe0.03Cu0.02 At 600°C	37.1	2.43	0.29922	29.26	3.23	5.20	1.60

Furthermore, peak broadening in doped samples indicates the presence of microstrain within the lattice [18]. Overall, the results demonstrate that both Cu concentration and annealing temperature significantly influence the crystallinity, lattice structure, and crystallite size of ZnO nanoparticles.

3.2. FTIR Analysis: Fourier transform infrared (FTIR) spectroscopy was used to examine the chemical bonding and functional groups present in the Fe/Cu co-doped ZnO nanoparticles. The FTIR spectra confirmed the formation of ZnO and provided information about the effect of Cu concentration and annealing temperature on bonding characteristics [21].

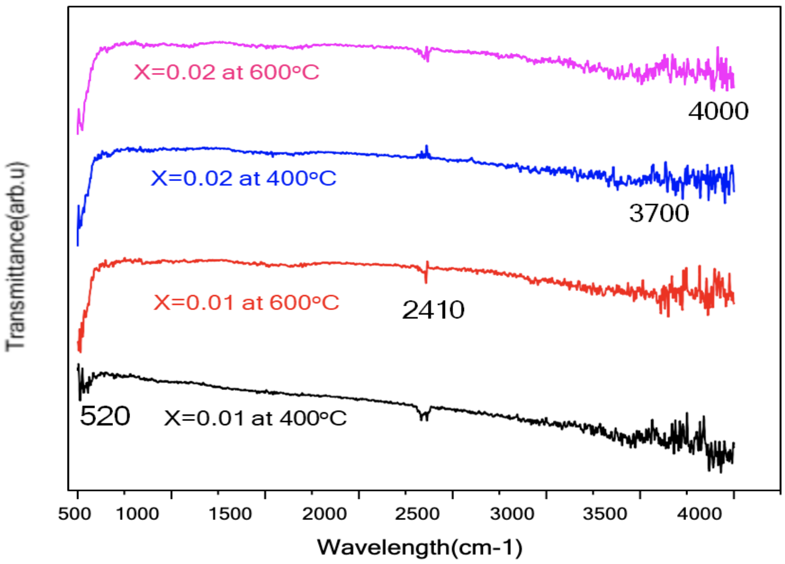

Figure .2 FTIR graph of different vibrational modes for Zn0.96Fe0.03Cu0.01, Zn0.95Fe0.03Cu0.02 Nanoparticles After annealing at 400oC and 600oC prepared by Sol-Gel method.

The main absorption band observed in the lower wavenumber region is assigned to the Zn–O stretching vibration, confirming the formation of ZnO nanoparticles [22]. This characteristic band verifies the successful synthesis of the ZnO structure. Other weak absorption bands appearing in the higher wavenumber region may be related to residual organic groups, adsorbed moisture, or hydroxyl species remaining from the synthesis process. Bands in the region of about 1400–1700 cm^{-1} can be associated with C–O or C=O vibrations, while the broad band around 3000–3500 cm^{-1} is attributed to O–H stretching vibrations.

A slight shift in the Zn–O absorption band with increasing Cu concentration indicates the successful incorporation of dopant ions into the ZnO lattice. This shift may be attributed to changes in bond strength and local lattice distortion caused by Fe/Cu co-doping. Moreover, samples annealed at higher temperatures show reduced intensity of impurity-related bands, indicating improved structural purity and removal of residual organic contents.

Table 2. Shows the different functional groups present in samples Zn0.96Fe0.03Cu0.01, Zn0.95Fe0.03Cu0.02 Nanoparticles After annealing at 400oC and 600oC.

Zn0.96Fe0.03Cu0.01 at 400°C	Zn0.96Fe0.03Cu0.01 at 600°C	Zn0.95Fe0.03Cu0.02 at 400°C	Zn0.95Fe0.03Cu0.02 at 600°C	Modes
520	520	520	520	ZnO lattice Vibration
2410	2410	2410	2410	C=C bond
3680	3680	3680	3680	O-H stretching
4000	4000	4000	4000	N-H stretching

Overall, the FTIR results support the successful formation of Fe/Cu co-doped ZnO nanoparticles and show that both Cu concentration and annealing temperature influence the bonding environment and structural quality of the samples [23].

3.3. UV-Visible Analysis: UV–visible spectroscopy was used to investigate the optical properties of Fe/Cu co-doped ZnO nanoparticles. The absorption spectra provide information about the optical behaviour and band gap variation with Cu concentration and annealing temperature [24].

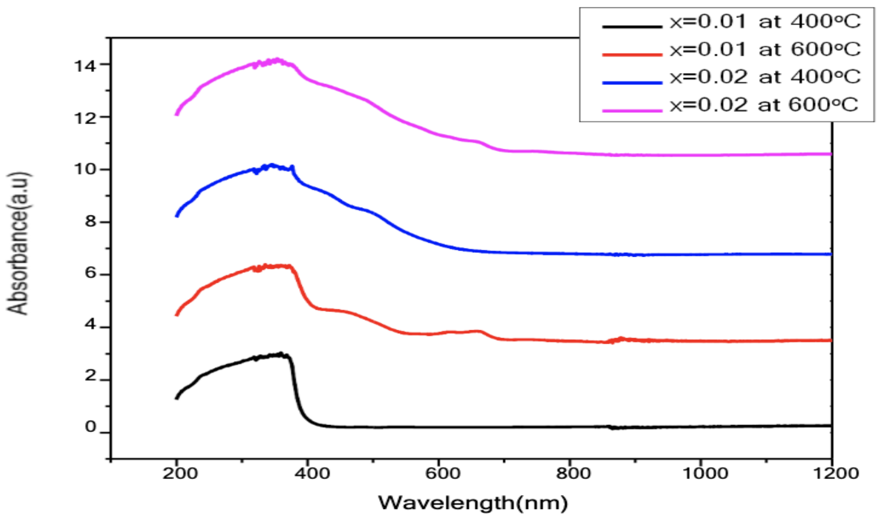

Figure 3 UV-Visible peaks for Zn0.96Fe0.03Cu0.01, Zn0.95Fe0.03Cu0.02 Nanoparticles After annealing at 400oC and 600oC prepared by Sol-Gel method.

The absorption spectra show a strong absorption edge in the ultraviolet region, which is a characteristic feature of ZnO nanoparticles [25]. A noticeable shift in the absorption edge is observed with increasing Cu concentration, indicating changes in the optical properties due to doping. This shift is attributed to the introduction of defect states and modification of the electronic structure caused by Fe and Cu ions.

The optical band gap of the synthesized nanoparticles was calculated using the Tauc relation by plotting (αhν)2 versus photon energy (hν), assuming a direct allowed transition. The linear portion of the plot was extrapolated to determine the band gap energy.

It is observed that the band gap varies with Cu concentration and annealing temperature. The shift in band gap values can be attributed to the presence of defect levels, lattice distortion, and interaction between dopant ions and the ZnO matrix. In general, annealing at higher temperature results in improved crystallinity, which influences the optical behavior, while doping introduces localized states that modify the band structure

Table 3. shows the wavelength and energy band gap for Zn0.96Fe0.03Cu0.01 At 400o c, Zn0.96Fe0.03Cu0.01 At 600o c, Zn0.95Fe0.03Cu0.02 At 400o c, Zn0.95Fe0.03Cu0.02 At 600o c.

SAMPLE	WAVELENGTH	ENERGY BAND GAP
	λ(nm)	E_g (eV)
Zn0.96Fe0.03Cu0.01 At 400o c	368	3.365
Zn0.96Fe0.03Cu0.01 At 600o c	374	3.313
Zn0.95Fe0.03Cu0.02 At 400o c	379	3.269
Zn0.95Fe0.03Cu0.02 At 600o c	386	3.204

The variation in band gap is mainly associated with dopant-induced defect states and changes in particle size. The reduction in crystallite size and lattice distortion can lead to band gap modification, while improved crystallinity at higher annealing temperature tends to stabilize the optical properties. Overall, the UV–visible analysis demonstrates that both Cu concentration and annealing temperature play a significant role in tuning the optical properties of ZnO nanoparticles, making them suitable for applications in optoelectronic devices [26].

3.4. SEM Analysis: Scanning electron microscopy (SEM) was used to examine the surface morphology of Fe/Cu co-doped ZnO nanoparticles and to evaluate the effect of Cu concentration and annealing temperature on particle distribution and surface features [27].

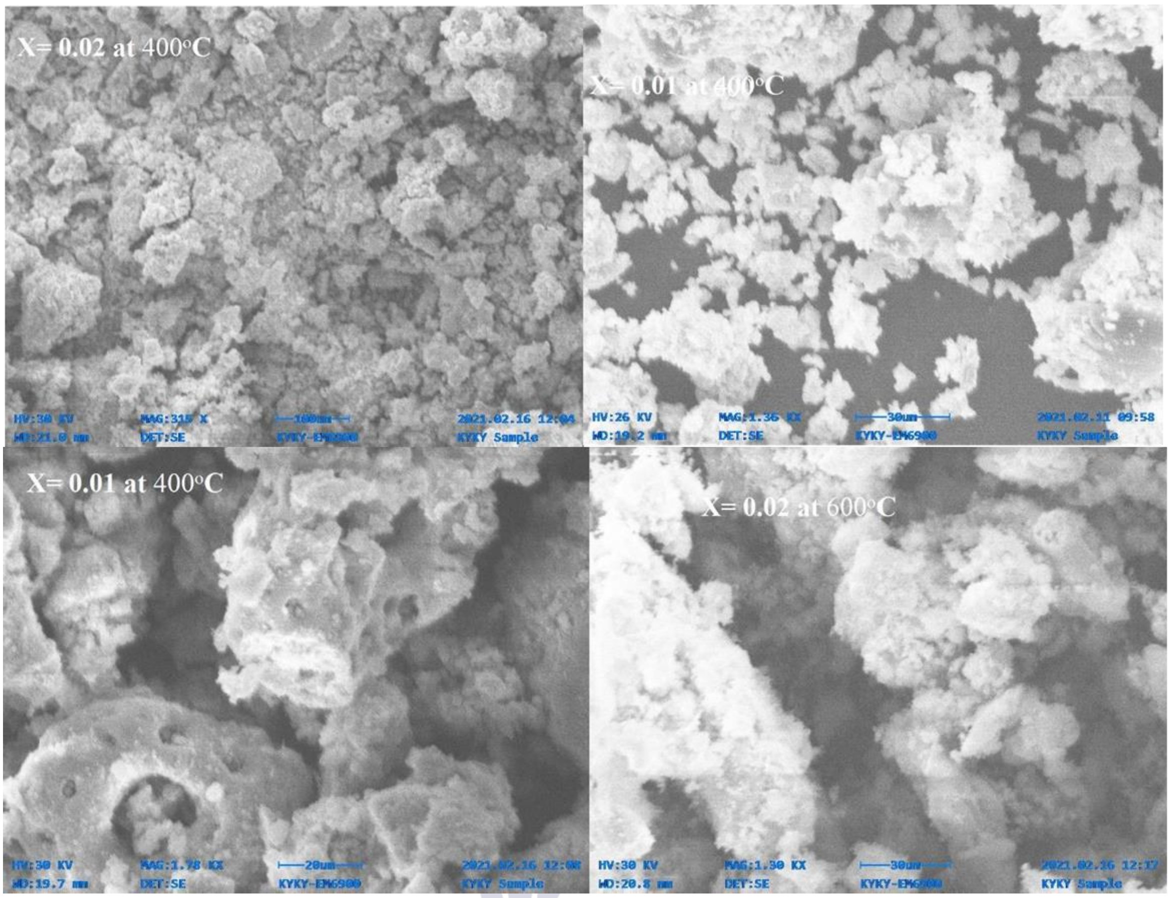

Fig 4 showing SEM results of Zn0.96Fe0.03Cu0.01 At 400o c, Zn0.96Fe0.03Cu0.01 At 600o c, Zn0.95Fe0.03Cu0.02 At 400o c, Zn0.95Fe0.03Cu0.02 At 600o c.

The SEM micrographs show that the prepared nanoparticles are agglomerated and irregularly distributed. This agglomeration is commonly observed in ZnO-based nanoparticles due to their high surface energy and strong interparticle attraction [28]. Despite this agglomeration, the formation of nanosized particles is clearly evident.

A visible change in morphology is observed with increasing annealing temperature. The samples annealed at 600 °C show relatively larger and more compact particles than those annealed at 400 °C, indicating grain growth and particle coalescence at higher temperature. This behavior is consistent with the XRD results, where improved crystallinity and increased crystallite size were observed after annealing at higher temperature.

The variation in Cu concentration also affects the surface morphology of the samples. The incorporation of Cu into Fe-doped ZnO influences the nucleation and growth process, which leads to changes in particle arrangement, agglomeration, and surface texture. These morphological changes confirm that both Cu concentration and annealing temperature play an important role in determining the final microstructure of Fe/Cu co-doped ZnO nanoparticles.

Overall, the SEM results support the successful synthesis of Fe/Cu co-doped ZnO nanoparticles and show that thermal treatment and dopant concentration significantly influence the morphology of the prepared samples [29].

4. Conclusion

Fe/Cu co-doped ZnO nanoparticles were successfully synthesized using the sol–gel method and annealed at two different temperatures (400 °C and 600 °C) to investigate the effect of Cu concentration and thermal treatment on their structural and optical properties [30]. XRD analysis confirmed the formation of a hexagonal wurtzite structure, with improved crystallinity and increased crystallite size at higher annealing temperature.

The incorporation of Fe and Cu ions into the ZnO lattice resulted in peak shifting and lattice distortion, indicating successful doping.

FTIR analysis verified the presence of Zn–O bonding and showed that annealing reduced impurity-related bands, leading to improved structural purity. UV–visible analysis revealed a shift in the absorption edge and variation in the optical band gap with changing Cu concentration and annealing temperature, which is attributed to dopant-induced defect states and modification of the electronic structure [31]. SEM analysis showed agglomerated nanoparticles with noticeable changes in morphology and particle growth at higher annealing temperature.
Overall, the results demonstrate that both Cu concentration and annealing temperature significantly influence the structural, optical, and morphological properties of ZnO nanoparticles. The ability to tune these properties makes Fe/Cu co-doped ZnO nanoparticles a promising candidate for potential applications in optoelectronic and energy-related devices [32].

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