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FULL PAPER

Effect of magnetic field on the preparation of Cu doped zinc oxide nanostructures in different temperatures

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We tried to overcome some industrial defects of crystals (Cu doped ZnO) while improving some of its features through the use of three important factors: Doping (5% Cu), temperature, and magnetic field effect. We have identified some of its properties and dimensions through UV, XRD and FE-SEM measurements. We have succeeded in preparing Cu doped ZnO Nanostructure with different lengths and diameters, more uniform crystals, as well as multiple energy gap values. This allows it to be used in a wide range of technology applications. Energy gap values are clearly affected by the increase in temperature and the presence of the magnetic field. The size of the crystals increases with the increase in temperature and the presence of the magnetic field. The crystals become more uniform and the artificial defects decrease. The change in the dimensions of the crystals with increasing temperature depends on the nature of doping and the nature of semiconductor metallurgy. Lengths and diameters of the Nanostructure increase with increasing temperature and with the presence of the magnetic field, which means more attractive and useful features. Enhanced catalytic efficiency of Cu-doped ZnO is attributed to intrinsic oxygen vacancies mainly due to high surface to volume ratio in nanorods and as well as extrinsic defect due to Cu doping. While the method (Cu doped ZnO) demonstrates the half-metallic ground state as well and the high ferromagnetic stability for all the measured Cu concentrations mostly within the generalized gradient approximation.

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KEYWORDS

Nanoscience; nanoparticles; magnetic field; hydrothermal; Cu doped ZnO; semiconductor; doping.

Introduction

Nanoscience is one of the modern sciences that have achieved wide popularity and attracted a large number of scientists and researchers, as well as applications in various fields of technology, which are connected with the study of materials on the Nanoscale level since these materials have unique features that fulfill many human desires. Also, it has become easy to control their dimensions and shapes [1,2] and its properties thanks to the different techniques in preparing these materials, including the hydrothermal technology [3]. Hydrothermal technology is an important and easy-to-use technology that mainly depends on water or other solvents such as alcohol, through which it is possible to control the shapes, sizes and properties of nanomaterials by manipulating solvents, temperature or time, all of which are important factors that are reflected in the photoelectric and optical properties of these materials [3-5]. Semiconductors occupied an important place in the field of technology for a long time, and their importance increased when prepared in Nanoscale dimensions[6]. Among the most important of these materials is ZnO nanoparticle (Solid powder, white in color, odorless). ZnO has a wide band of 3.37 eV and a large exciton binding energy of 60 meV., which was used in the fields of solar cells, medical, agricultural and industrial applications, as well as electronics and sensors [7-9]. Doping plays an important role in improving semiconductor features as well as controlling them. Zinc oxide Nanostructure are doped with copper to reach more important features and are suitable for some uses in technology, in addition to improving some photoelectric and optical properties of zinc oxide [3-7]. The presence of the magnetic field plays an important role in overcoming some of the industrial defects of nanoparticles, as well as arranging the crystals in a more tight and smaller size, which gives them unique features [10]. That is why we worked to prepare Nanoscale semiconductors (zinc oxide) under magnetic field effect (UMFE) in a hydrothermal method to have unique features and also in an easy, inexpensive, economic and environmentally friendly way.

Experimental

Methodology

Cu doped ZnO Nanostructure was prepared at a range of temperatures of 70-190 °C using 1 M zinc acetate ($Zn(CH_3COO)_2.2H_2O$, M.W=219.49, THOMAS BAKER), 5M sodium hydroxide (NaOH, MW=40, 99.98%, ALPHA) and 5%wt copper acetate ($(CH_3COO)_2Cu\, H_2O$, M.W =199.65,98%, THOMAS BAKER). All solutions were prepared using 96% methanol (CH_3OH, MW= 32.04, CDH) as a solvent. Hydrothermal technique was used by Teflon-lined stainless steel autoclave system (type PPL) to maintain high temperature and high pressure. The autoclave was embraced with curled heater reactor to maintain equal and consistent heat distribution throughout the reaction. We used two pieces of 325 Tesla magnets plates on both sides of the reactor, which were submerged into two water basins in order not to be affected by high Temperatures, to expose the reactor to a strong magnetic field, as shown in Figure 1. 10 mL of Zn ($CH_3COO)_2.2H_2O$ was mixed inside the reactor with 40 mL of NaOH, then sealed and left at the above temperatures for at least 10 hours. The solution was then decanted in a 100 mL beaker and washed several times with distilled water until reached a pH of 7. Then, it was washed at least three times with ethanol as a final wash. The powder of the nanostructures was then isolated and dried for 2 hrs under100 °C.

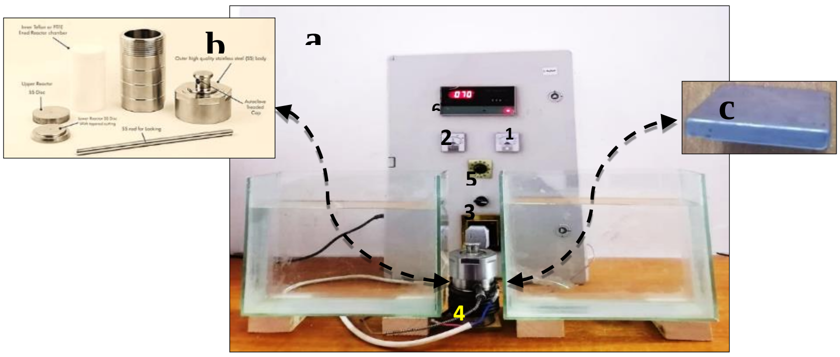


FIGURE 1 Hydrothermal system consists of three main parts: (a) Temperature controller unit which include: 1-Voltage gauge 2-Amperage gauge 3-power key 4-sensor 5-power control and 6-Temprature screen, (b) Reaction unit which consists of Teflon lined stainless steel autoclaves (the reactor) shielded with a curled heater to maintain equal and continuous heat distribution during operating time, (C) Two magnet plates with a force of 325 Tesla mounted on two side glasses (facing autoclave unit) of two 25 °C water baths

Characterizations

Virtual properties

The color gradation of a single group with an increase in temperature from 70 – 190 °C gives an initial idea of a change in the size of the crystals and thus a change in the optical properties. It is known that nanomaterials change the absorbance of their wavelengths with the change of the sizes of their crystals. Also, a slight change in the colors of the samples of the same material was observed at the same temperature when exposed to the influence of a magnetic field. This gave us an initial idea of the extent of the magnetic field effect on the formation of crystals as well as the change in their optical properties.

UV-Vis spectroscopy: Cu doped ZnO nanostructured with and without magnetic field effect

UV measurements show that at 70 °C, the absorbance increases with the presence of the magnetic field, also at 100 °C, the absorbance values increase with the presence of the magnetic field, while at 130 °C, the absorbance decreases with the presence of the magnetic field. Then at 160 °C absorbance increases with the presence of the magnetic field while at 190 °C, absorbance values are equal at the presence of the magnetic field. This generally means that the effect of the magnetic field increases with increasing the temperature of Cu doped ZnO (Figures 2 and 3). As such a clear increase for λmax was recorded in the presence of the magnetic field for most of temperatures, thus there is a decrease in the energy gap values in general as shown in Table 1. Hence, we conclude that the effect of the magnetic field and the increase in temperature depends on the type of the doping. Energy gap was calculated by Einstein's equation $E = hV = \frac{hc}{\lambda}$ where E=band gap energy, V=frequency of photon/Electromagnetic radiation, c=Speed of light in a vacuum =3x10^{8} m/s, h=Planck constant =6.63x10^{-34} Js, 1eV=1.6X10^{-19} J (Conversion factor), λ= Wavelength of photon/Electromagnetic radiation.

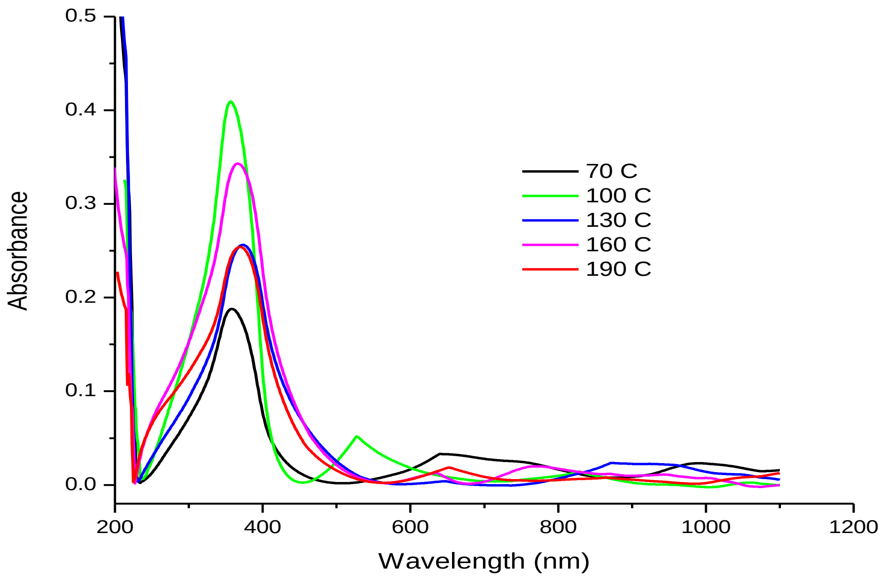


FIGURE 2 UV spectra for Cu doped ZnO at the region of (200- 1200) nm with absorption peaks at the range of temperatures of (70-190) °C

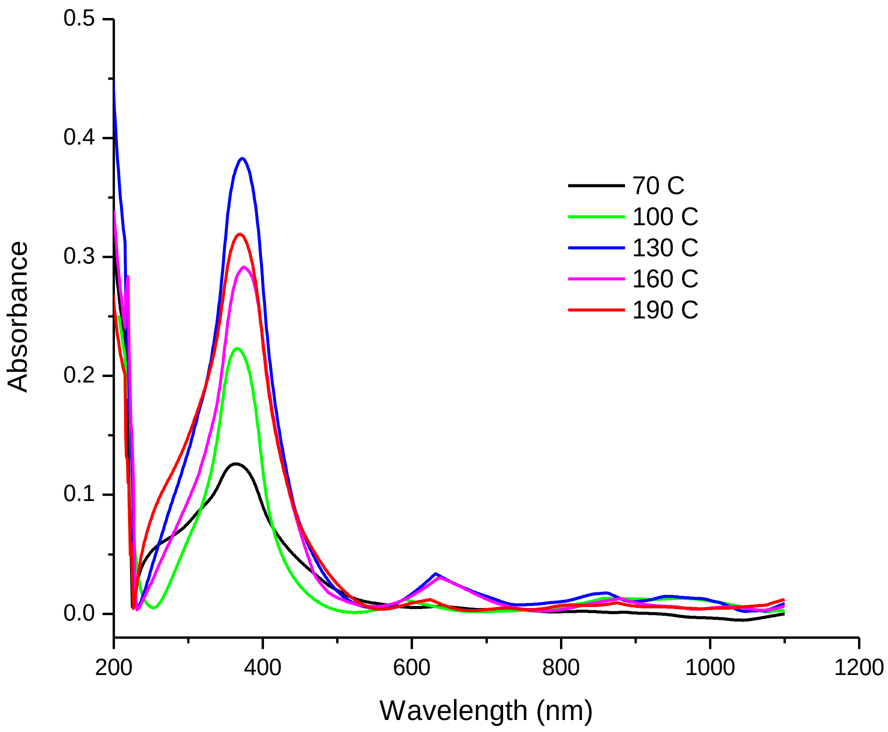


FIGURE 3 UV spectra for Cu doped ZnO under magnetic field effect at the region of (200- 1200) nm with absorption peaks at the range of temperatures of (70-190) °C

TABLE 1 Energy gab values for Cu doped ZnO nanostructures with and without magnetic field effect prepared at 70, 100, 130, 160 and 190 °C calculated via Einstein's equation

Temperature(°C)	Cu doped ZnO		Cu doped ZnO $_{UMFE}$	
	λ_{max}(nm)	Energy gap(eV)	λ_{max}(nm)	Energy gap(eV)
70	358	3.46	363	3.41
100	356	3.48	365	3.39
130	373	3.32	372	3.33
160	366	3.38	374	3.31
190	369	3.36	369	3.36

FE-SEM microscopy

An apparent temperature and magnetic field effect on the growth and morphology of Cu doped ZnO Nanostructure was shown by FE-SEM microscopy. This is consistent with previous work of our group in which it was assumed that it is due to a natural phenomenon called Ostwald ripening [11-13]; the growth and change of particle sizes and shapes should be anticipated as temperature or incubation period, or perhaps both, increase. Figures 4, 5 and 6 display images of FE-SEM for Cu doped ZnO Nanostructure with and without magnetic field effect that were synthesized at three different temperatures of 70, 130 and 190 °C respectively and at three different bars of 200 nm and 500 nm, respectively (Table 2). The average size of nanostructure with polygonal dots like shapes was found in Figure 4 to be equal to (20-50) nm. In Figures 5 and 6, the average size of nanostructure was found to be equal to (200-300) nm with a variation from trigonal to hexagonal rods like shapes.

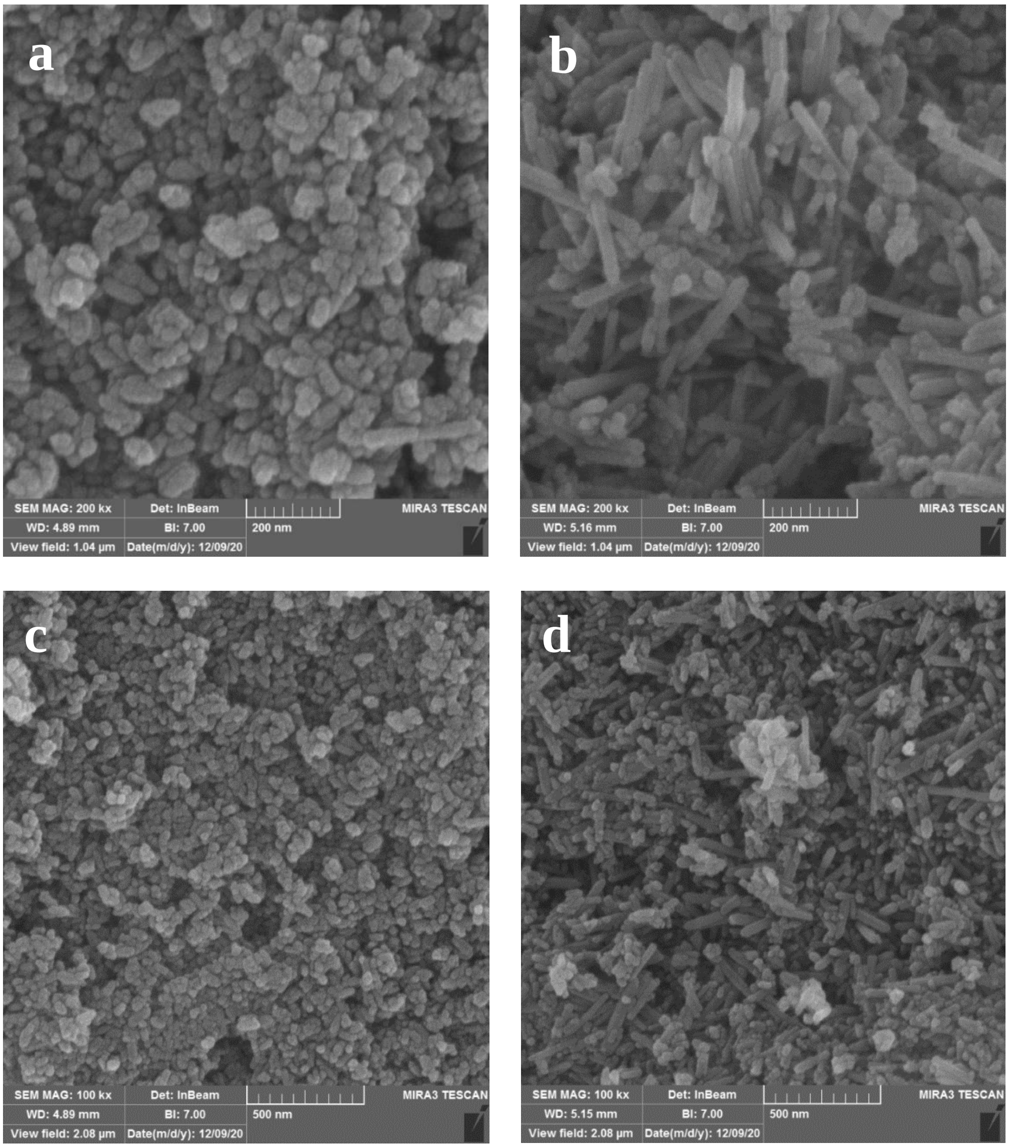
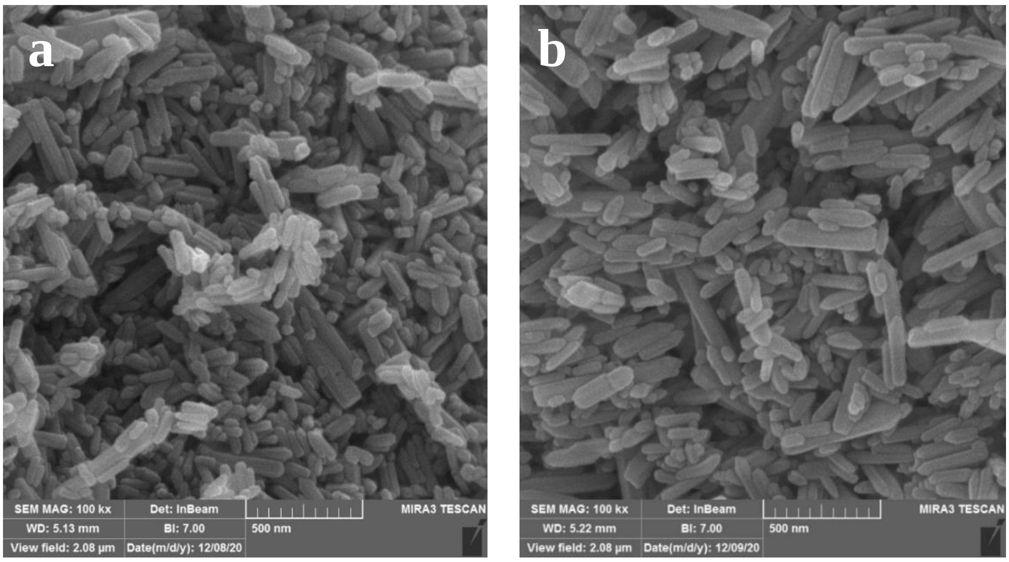


FIGURE 4 FE-SEM images. a, c for Cu doped ZnO Nanostructure and b, d for Cu dopet ZnO Nanostructure under magnetic field effect. Both at 70 °C



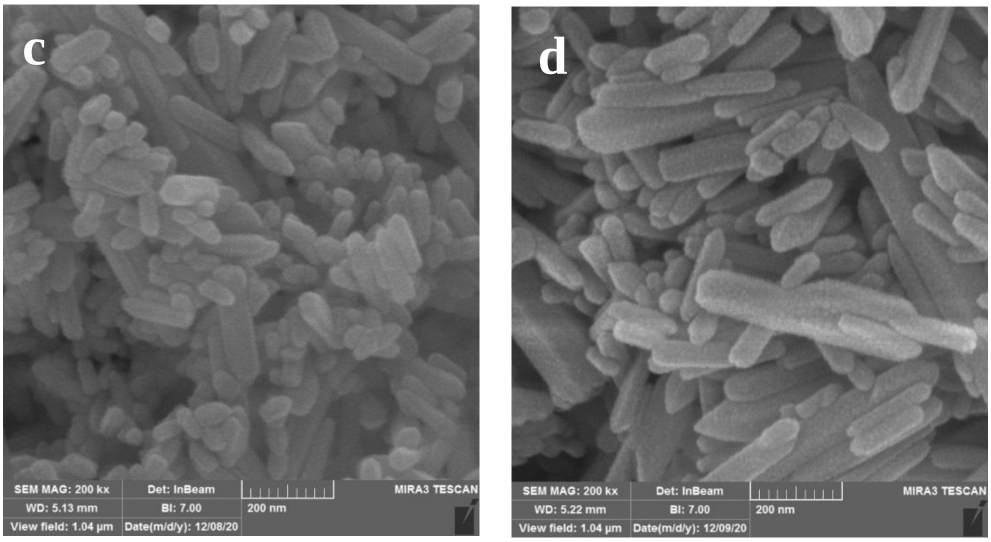


FIGURE 5 FE-SEM images. a, c for Cu doped ZnO Nanostructure and b, d for Cu dopet ZnO Nanostructure under magnetic field effect. Both at 130 °C

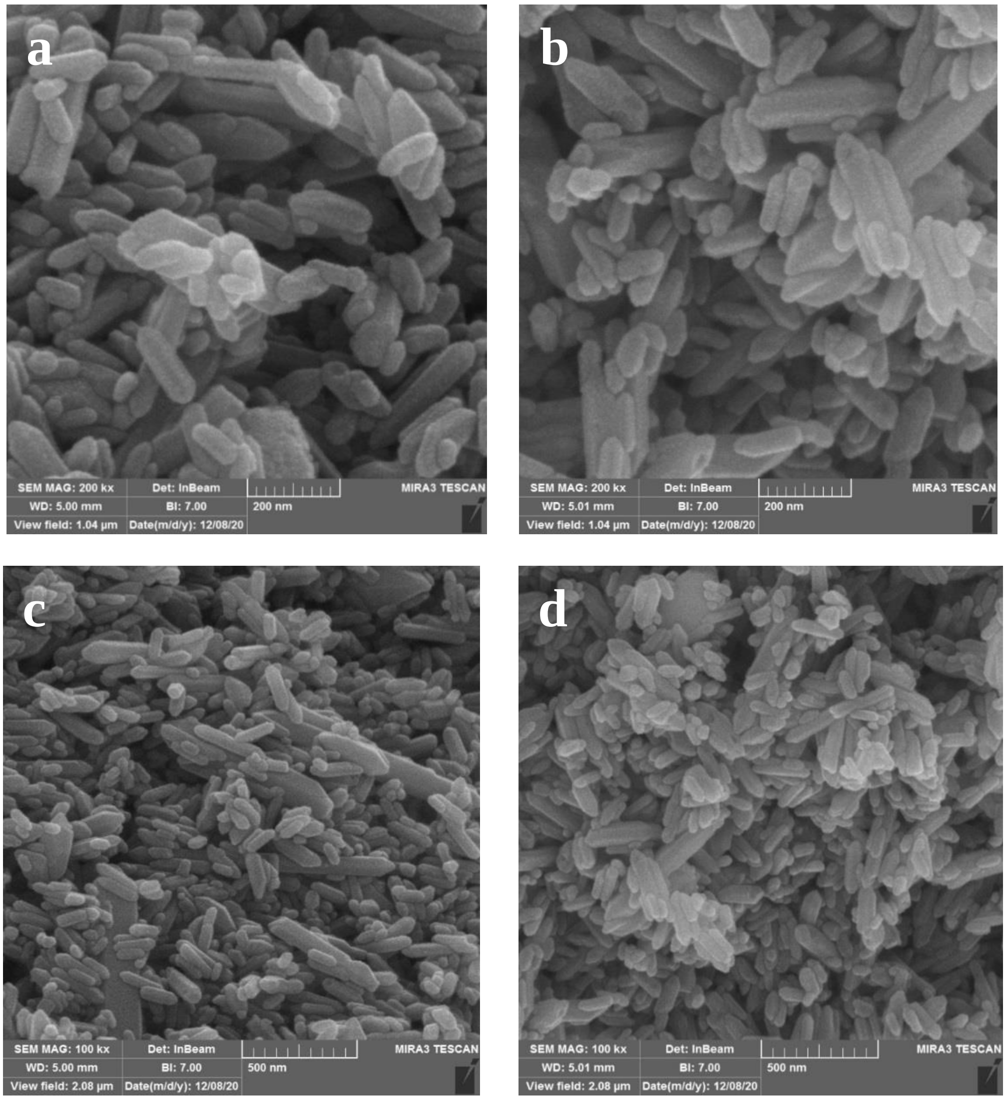


FIGURE 6 FE-SEM images. a, c for Cu doped ZnO Nanostructure and b, d for Cu dopet ZnO Nanostructure under magnetic field effect. Both at 190 °C

TABLE 2 The change in dimensions as temperatures increase for Cu doped ZnO Nanostructure with and without magnate filed effect

Sample	Temperatures (℃)	Width of Particles	Length of Particles
Cu doped ZnO	70	28.64 nm	64.41 nm
Cu doped ZnO	130	53.61 nm	130.83 nm
Cu doped ZnO	190	50.16 nm	176.10 nm
Cu doped ZnO UMFE	70	33.83 nm	137.52 nm
Cu doped ZnO UMFE	130	53.03nm	192.16 nm
Cu doped ZnO UMFE	190	43.16 nm	168.16 nm

It was observed that with the effect of the magnetic field, the width and length of the Nanostructure increased up to 130 °C and then decreased at 190 °C. This is very logical and completely consistent with the results of XRD crystallography.

XRD crystallography for Cu doped ZnO and Cu doped ZnO under magnetic field effect at 70, 130 *and* 190 °C

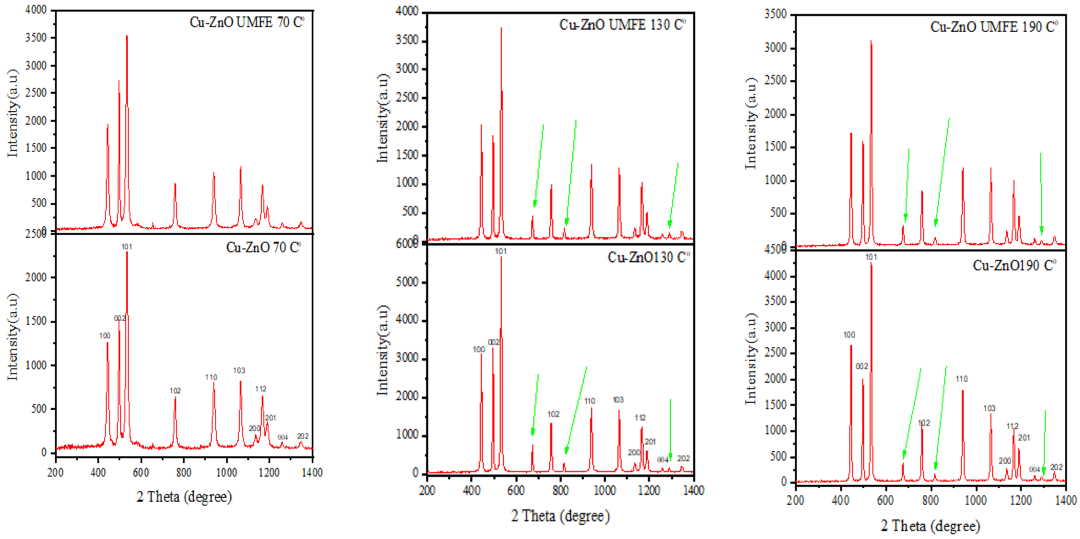


FIGURE 7 XRD crystallography for Cu doped ZnO and Cu doped ZnO nanoparticles under magnetic field effect at 70, 130 and 190 °C. The patterns indicated Wurtzite hexagonal configuration which perfectly match pattern given by Reference code: 01-079-0205

XRD crystallography measurements showed a clear increase in absorbance by increasing the temperature from70 to 130 °C, as the value increased from 2450 to 5800 a.u., while it decreased at 190 °C to stabilize at 4400 a.u. Also, with an increase in temperature, the position of peaks and angles change a little, as shown in Figure 7. The presence of a magnetic field of 325 Tesla led to a clear decrease in the absorbance for all temperatures, as shown in Figure 7. These changes in position, angles, and absorption of peaks are necessarily leading to changing the dimensions of crystals [14-17]. Important factors, temperature and magnetic field, play an important role in increasing the uniformity of crystal shapes and reducing industrial defects, which makes them possess unique photoelectric and optical features. It is also found that three new peaks at 130 and 190 °C (indicated by blue arrows) were not present in pure ZnO, which means that they belong to copper and were first recorded by previous work of our group [3]. As shown in Table 3, the size of crystals increases with increase in temperature to 130 °C, while it decreases at

190 °C, and this is due to the metallurgical nature of the semiconductor (Cu doped ZnO), as well as the presence of the magnetic field that increases their size and conjunction in general.

TABLE 3 Cristal size (nm) from XRD measurement for Cu dopet ZnO and Cu dopet ZnO under magnetic field effect at 70, 130 and 190 °C

Substances	Temperature (°C)	Cristal size (nm)
Cu doped ZnO	70	22.10
Cu doped ZnO UMFE	70	32.01
Cu doped ZnO	130	32.62
Cu doped ZnO UMFE	130	33.41
Cu doped ZnO	190	31.13
Cu doped ZnO UMFE	190	31.86

Conclusion

Energy gap values are clearly affected by the increase in temperature and the presence of the magnetic field. Size of the crystals increases with the increase in temperature and the presence of the magnetic field. The crystals become more uniform and the artificial defects decrease. The change in the dimensions of the crystals with increasing temperature depends on the nature of doping and the nature of semiconductor metallurgy. Lengths and diameters of the Nanostructure increase with increasing temperature and with the presence of the magnetic field, which means more attractive and useful features.

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