

REPUBLIC OF TURKEY
FIRAT UNIVERSITY
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES



**PRODUCTION AND CHARACTERIZATION OF THE
METAL OXIDE - ORGANO METALIC COMPOSITES
BY HYDROTHERMAL METHOD**

MASTER THESIS
Rekawt Khdir HAMAD
151114106

Department: Physics
Program: Solid State Physics
Supervisor: Assoc. Prof. Dr. Canan Aksu CANBAY

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Thesis submission date: 10 - May - 2017

Thesis presentation date: 26 - May - 2017

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ACKNOWLEDGEMENTS

I would like to express my deep gratitude to my master thesis advisor, Assoc. Prof. Dr. Canan AKSU CANBAY. I have learned many things since I became Prof. Dr. Canan AKSU CANBAY'S student. She spends very much time instructing me how to search literature and how to collect data.

I would like to express my appreciation to Prof. Dr. Fahrettin YAKUPHANOĞLU, for giving permission to use his laboratory instruments during this process and his grateful advices.

Thanks to each and every person who gives in any ways to complete this thesis, during the period of two years, many friends are helpful to color my life.

Last but not the least important, I owe more than thanks to my family members which includes my parents, sisters and brothers, for their financial support and encouragement throughout my life. Without their support, it is impossible for me to finish my college and graduate education seamlessly.

I would like to acknowledge and thanks **FÜBAP** (Firat University Scientific Research Projects Unit) for financial support for this research work under project number FF. 16. 33.

Rekawt khdir HAMAD

ELAZIG - 2017

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SUMMARY

PRODUCTION AND CHARACTERIZATION OF THE METAL OXIDE - ORGANO METALIC COMPOSITES BY HYDROTHERMAL METHOD

In this master thesis, our aim is to produce composite material in different composition based on ZnO by hydrothermal method which is the new production method. Structural, morphological, optical and electrical properties of the obtained composite materials were investigated. For these examinations, respectively; (XRD), scanning electron microscopy (SEM), Fourier transform infrared (FTIR), UV-VIS-NIR spectrophotometer and two probe method measurements. Chemical compositions of the compounds were determined by using energy dispersive X-ray (EDX). X-ray analysis revealed diffraction pattern in the structure, grain structure was determined by SEM analysis and structural bonds by FTIR analysis. Forbidden band gap was calculated by optical measurements and electrical conductivity were calculated by electrical conductivity measurements.

Keywords: Hydrothermal method, composite material, structural analysis, semi-conductors.

ÖZET

HİDROTHERMAL METOD İLE METAL OKSİT-ORGANO METALİK KOMPOZİTLERİN ÜRETİLMESİ VE KARAKTERİZASYONU

Yapılan bu yüksek lisans tez çalışmasında amacımız yeni bir üretim yöntemi olan hidrotermal metod ile farklı kompozisyonlarda ZnO esaslı kompozit malzeme üretilmesidir. Elde edilen kompozit malzemelerin yapısal, morfolojik, optik ve elektriksel özellikleri araştırıldı. Bu incelemeler için sırasıyla; X-ışını kırınımı (XRD), taramalı elektron mikroskobu (SEM), Fourier transform infrared (FTIR), UV-VIS-NIR spektrofotometre ve iki prob yöntemi ölçümleri kullanıldı. Bileşimlerin analizleri enerji dispersive X-ray (EDX) analizi ile yapıldı. X-ışını analizleri ile yapıda difraksiyon veren düzlemler belirlendi, SEM analizleri ile tane yapısı belirlendi, FTIR analizleri ile yapısal bağlar incelendi. Optik ölçümler ile yasak bant aralığı hesaplandı ve elektriksel iletkenlik ölçümleri ile elektriksel iletkenlik değerleri hesaplandı.

Anahtar Kelimeler: Hidrotermal metod, kompozit malzeme, yapısal analiz, yarıiletken.

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ABBREVIATIONS

ZnO	: Zinc Oxide
PMC	: Polymer Matrix Composite
MMC	: Metal Matrix Composite
CuPc	: Copper Phthalocyanine
FTIR	: Fourier Transform Infrared
SEM	: Scanning Electron Microscope
XRD	: X-ray Diffraction
EDX	: Energy Dispersive X-ray
HOMO	: Highest Occupied Molecular Orbital
LUMO	: Lowest Unoccupied Molecular Orbital

1. INTRODUCTION

Metal oxides play a very important role in many areas of chemistry, physics and materials science. The metal elements are able to form a large diversity of oxide compounds. These can adopt a vast number of structural geometries with an electronic structure that can exhibit metallic, semiconductor or insulator character. In technological applications, oxides are used in the fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, coatings for the passivation of surfaces against corrosion, and as catalysts. In the emerging field of nanotechnology, a goal is to make nanostructures or Nano arrays with special properties with respect to those of bulk or single particle species [1-12].

Oxide nanoparticles can exhibit unique physical and chemical properties due to their limited size and a high density of corner or edge surface sites. Particle size is expected to influence three important groups of basic properties in any material. The first one comprises the structural characteristics, namely the lattice symmetry and cell parameters. Bulk oxides are usually robust and stable systems with well-defined crystallographic structures. However, the growing importance of surface free energy and stress with decreasing particle size must be considered: changes in thermodynamic stability associate with size can induce modification of cell parameters and structural transformations and in extreme cases the nanoparticle can disappear due to interactions with its surrounding environment and a high surface free energy. In order to display mechanical or structural stability, a nanoparticle must have a low surface free energy. As a consequence of this requirement, phases that have a low stability in bulk materials can become very stable in nanostructures. This structural phenomenon has been detected in TiO_2 , VO_x , Al_2O_3 or MoO_x oxides [13-18].

Size-induced structural distortions associated with changes in cell parameters have been observed, for example, in nanoparticles of Al_2O_3 , NiO , Fe_2O_3 , ZrO_2 , MoO_3 , CeO_2 , and Y_2O_3 . As the particle size decreases, the increasing number of surface and interface atoms generates stress/strain and concomitant structural perturbations. Beyond this “intrinsic” strain, there may be also “extrinsic” strain associated with a particular synthesis method which may be partially relieved by annealing or calcination. Also, non-stoichiometry is a common phenomenon. On the other hand, interactions with the substrate on which the nanoparticles are supported can

complicate the situation and induce structural perturbations or phases not seen for the bulk state of the oxide [19-25].

The word 'Phthalocyanine' is derived from the Greek terms 'naphtha' (rock oil) and 'cyanine' (dark blue). Phthalocyanines are organic semiconductors receiving considerable attention because of their suitability as an active layer for organic electronic devices. One of the significant properties of Phthalocyanine is their high chemical and thermal stability. Phthalocyanines are a class of highly stable organic semiconductors and have attracted much attention because of their low cost and little toxicity. The phthalocyanine (Pc) polymers have become one of the most studied of all organic functional materials and have recently attracted considerable interest due to their high thermal and chemical stability [26-32].

Metal Phthalocyanine is one of the promising organic semiconductors due to the possibility of applications in electro-optic devices; photo conducting agents, photovoltaic cell elements, nonlinear optics, electro catalysis, and other photo electronic devices. The versatility, architectural flexibility and ease of processing make them eligible candidates for use not only in electronic industry but also in photonic technology. These compounds have a longer storage life and high read out times for use in optical storage systems. The potential uses of Phthalocyanines include sensing elements in chemical sensors, electro-chromic display devices, photodynamic reagents, electro-catalysts for fuel cells, photovoltaic cell elements, dyes, color photocopying, conducting polymers solar cells and cardiac pacemakers. There are several studies devoted to the fabrication of copper phthalocyanine (CuPc) based devices [33-38].

The purpose of the work is to product composite organic semiconductor materials using various polymers and organic compounds to obtain new organic semiconductors.

2. ORGANIC SEMICONDUCTORS

Semiconductors can be broadly classified into two main groups as inorganic and organic semiconductors. Though inorganic semiconductors like germanium and silicon are used extensively in electronic industry, now it is expected that organic semiconductors will replace inorganic semiconductors in the near future. Forrest reported that organic semiconductors have attracted much attention due to their successful application in optical and electronic devices with encouraging performances [39].

Aromatic hydrocarbons such as anthracene and phthalocyanine are found to possess semiconducting properties. The basic property of semiconductors is its electrical conductivity, which depends on the mobility and concentration of charge carriers. The electrical conductivity, carrier concentrations and mobility of organic semiconductors are low in comparison with those of inorganic semiconductors. A comparison of the organic semiconductor (Copper phthalocyanine) with those of a conventional semiconductor (Germanium) is given in Table 2.1 [40, 41].

Table 2.1. Comparison of the electrical properties of the inorganic semiconductor germanium and organic semiconductor CuPc [40, 41].

Properties	Inorganic	Organic
Mobility ($\text{cm}^2/\text{V} \cdot \text{Sec}$)	3900	0.02
Carrier concentration (cm^{-3})	2.5×10^{13}	8×10^7
Trap density (cm^{-3})	-	$10^{12} - 10^{14}$
Resistivity ($\text{ohm} \cdot \text{cm}$)	43	10^{14}
Band gap (eV)	0.67	3.02

Altindal et al. have observed that phthalocyanine thin films have good sensitivity and selectivity. In organic semiconductors, the electrical properties are sensitive to the impurity content and doping. In organic solids, the molecules interact by relatively weak Van der Waals or London type forces so that the intermolecular separations are larger compared with

separations between atoms or ions of inorganic lattice. Consequently, there is only a weak overlap of molecular orbitals and the intermolecular electron exchange is small. Inorganic semiconductors are characterized by covalent bonding between ions of the crystal. Electrons can be excited optically, thermally or any other way, promoting free electrons into the conduction band and leaving holes in the valence band. Under an applied electric field, the free charge carriers are transported causing conduction. Electronic charge transport in organic semiconductors does not require perfect single crystals. A regular arrangement of atoms, ions or molecules over a distance of only a few lattice spacing of the structural units is the only necessary and sufficient condition for conductivity in organic semiconductors [42, 43].

The electrons within a molecule are tightly bound, if there is an intermolecular overlap of electron wave. Their electrical and electronic behavior is of considerable significance in biological processes. Phthalocyanines are thermally stable and can be sublimed to form thin films without decomposition. Therefore, in contrast to many other organic materials, the preparation of phthalocyanine thin films by vacuum sublimation is feasible [44].

2.1. Optical Properties of Organic Semiconductors

Organic semiconductors commonly have a π -conjugated electron system forming by the p_z -orbitals of sp^2 hybridization in C atoms. (Fig. 2.1) shows σ - and π -bondings taking ethane as the simplest example. The π -bonding is significantly weaker than the σ -bonding. The energy levels of bonding orbitals (σ - and π - orbitals) as well as antibonding orbitals (σ^* - and π^* - orbitals) are presented on the right in (Fig. 2.1) The lowest electronic transition occurs between the π - and π^* - orbitals. Here the π -orbital is the highest occupied molecular orbital (HOMO) and the π^* -orbital corresponds to the lowest unoccupied molecular orbital (LUMO). The transition energy lies generally between 1.5 and 3 eV, resulting in absorption or emission in the visible light range. This stimulates photoelectronic devices based on organic semiconductors [45].

Optical properties of organic solids are rather different from that of inorganic ones due to the fact that organic solids are bonded via van der Waals force between molecules, which is much weaker than that of covalent bonds in molecules. In addition, the optical excitation of

organic solids tends to be localized near individual molecules. Thus the properties of organic solids are quite similar to those of single molecule [45].

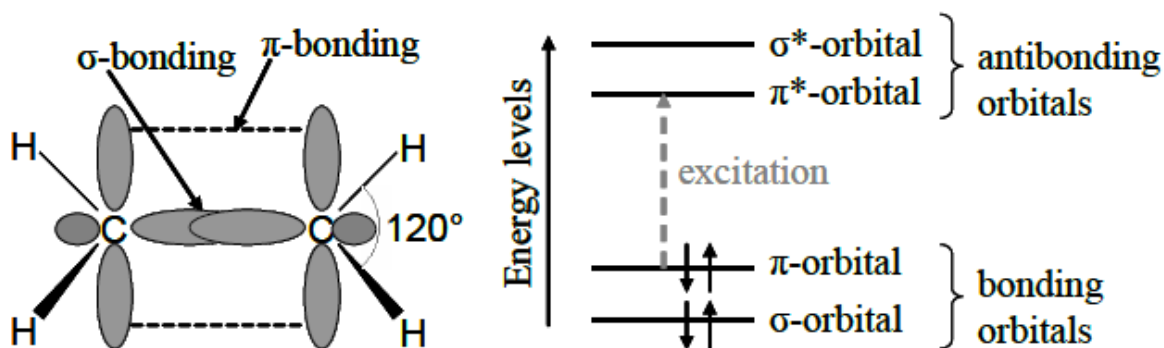


Figure 2.1. Left: σ - and π -bondings in ethane. Right: energy levels of a π -conjugated [45].

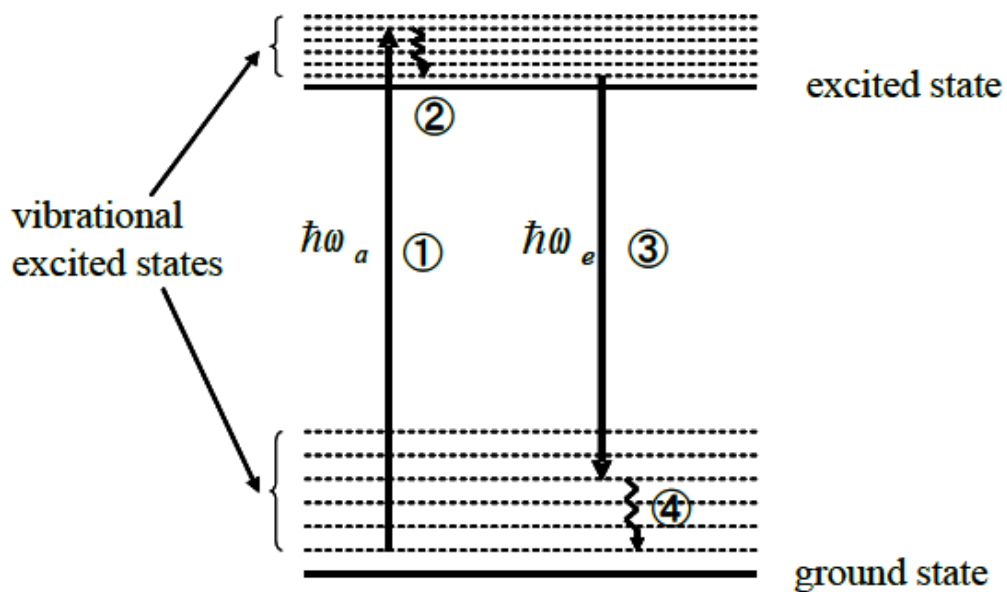


Figure 2.2. Sketch of the vibrational-electronic transitions in a molecule. The numbered four processes are respectively: (1) absorption; (2) non-radiative relaxation; (3) emission; (4) non-radiative relaxation [45].

The optical transitions of molecules are vibronic, implying that the transition changes the electronic and vibrational states of a molecule simultaneously. This is also true for organic solids. The basic of vibronic transitions of molecules is illustrated in (Fig. 2.2). The diagram shows absorption and emission between two electronic states: ground and excited states. The non-radiative relaxation in process (2) and (4) is a transition between vibrational states. It is obvious that the absorption occurs at a higher energy than the emission. This is very often found in organic solids. The energy difference between the maximum absorption and the maximum emission is called Stokes shift [45].



3. METAL-OXIDE SEMICONDUCTORS

Metal-Oxide semiconductors for example TiO_2 , ZnO , SnO_2 and In_2O_3 have encouraged incredible interest in the past period. They are fascinating for many applications containing gas sensors, clear conducting films, catalysis, energy storage and conversion, and optoelectronics. Their nanostructures, particularly, have been broadly examined as gas sensors because of their lesser dimensions, low cost, and high compatibility with microelectronic processing. Because of their large surface-to-volume ratio and a debye length equivalent to the small size, they show high sensitivity to surface chemical processes. Yamazoe demonstrate that the sensor performance is highly developed when the volume of the nanocrystals is lesser than twice the Debye length (~ 3 nm for SnO_2). The catalysis effect is another fascinating field where high surface area and size-dependent properties play important roles. These essential features have guided scholars to examine nanostructured materials with a vast variety of experimental probes. Size effect (quantum confinement), for instance, is well studied using Raman scattering [46-50].

The subsequent sections will recap the general properties and practical applications of several wide-band-gap oxide semiconductors. I will then give a more detailed discussion on ZnO nanostructures, the subject of this research [51].

3.1. Titania (TiO_2)

Titania (TiO_2) is a broad band gap semiconductor that has been energetically examined because of its range of applications. It shows two main crystalline phases, anatase (suitable for catalysis and supports) and rutile (used for optoelectronic purposes). New interest in TiO_2 nanocrystals is powered by its main role in the injection process in a photochemical solar cell with high conversion efficiency. By utilizing semiconductor films containing of nanometer-sized TiO_2 particles, O'Regan and Grätzel developed the efficiency and strength of the solar cell. Studying the adsorption of carboxylic acids, in order that TiO_2 -based dye-sensitized electrochemical procedures, is also essential. Fourier transform infrared spectroscopy (FTIR)

is generally utilized for studying the adsorption properties of organic types such as formic acid, where formate signatures can easily be discovered by IR [52-56].

3.2. Tin Oxide (SnO₂)

Tin oxide (SnO₂) is another fascinating semiconducting oxide material. Its large band gap (3.6 eV at room temperature), great transparency in the visible region and high conductivity cause the material ideal for transparent conductive electrode on devices for example solar cells. SnO₂ nanoparticles have also been broadly used as a sensor material, because of its high sensitivity to low gas concentrations. Using photoluminescence (PL) experiments, Faglia *et al.* Reported that the visible emission of SnO₂ nanobelts is slaked reversibly after exposing to NO₂ at ppm levels, showing the strong sensitivity of SnO₂. Furthermore, Lu *et al.* revealed that the sensitivity of nano-sized SnO₂ powder, developed by sol-gel method, improved with the decrease of particle size. They indicated that the reply to 500 ppm CO increases severely for particles with diameter smaller than 10 nm. This size effect benefit of sensing is anticipated to be the identical in other oxide nanostructured materials [57-60].

3.3. Zinc Oxide (ZnO)

Zinc oxide (ZnO) is one of the most noticeable and broadly studied semiconductors in the metal oxide types. Its wide band gap (3.37 eV) and great exciton binding energy (60 meV) make sure efficient exciton ultraviolet (UV) emission at room temperatures. ZnO has been utilized as a buffer layer for growth of GaN-based devices, as a clear conductive oxide in solar cells, and as a transducer for micro electrical-mechanical methods. ZnO nanostructures propose promising applications in nanotechnologies and procedures. Ferromagnetic quantum dots can also be utilized in high density storing devices [61-66].

ZnO exist in the hexagonal wurtzite crystal structure (Fig. 3.1) with $c = 0.52069$ nm and lattice parameters $a = 0.32495$ nm. The ratio of $c/a = 1.602$ is near to the model hexagonal

structure, 1.633. The Zn atoms form a tetrahedral coordination with four O atoms, where the Zn d -orbitals hybridize with the p -orbitals of O atoms [67].

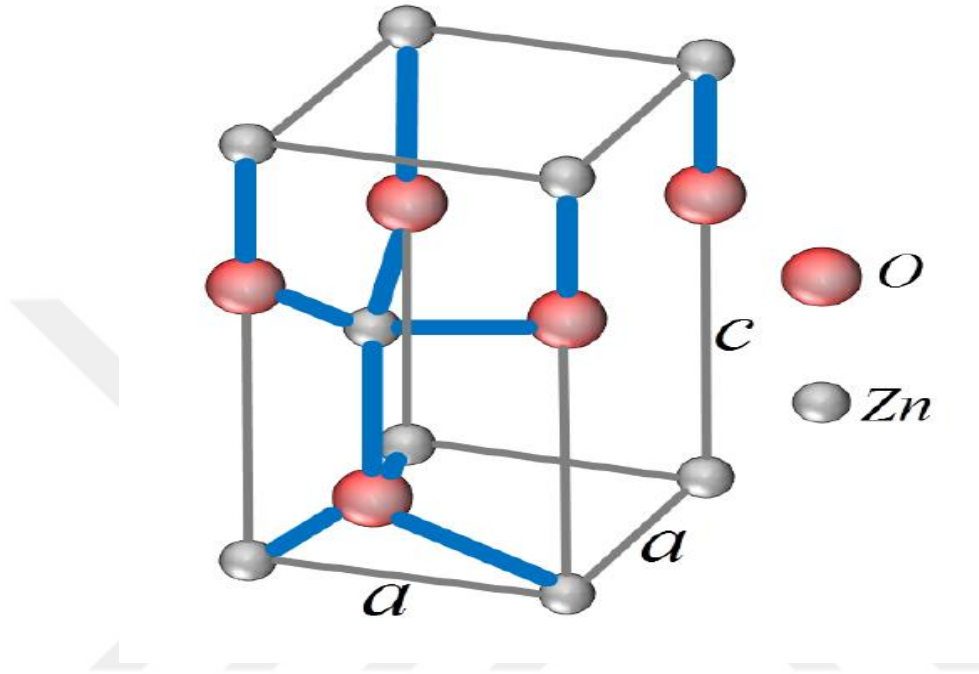


Figure 3.1. Hexagonal wurtzite ZnO [67].

3.3.1. Electrical Properties

As-developed, ZnO is normally n -type in bulk and thin films, that has long been consider to indigenous defects like O vacancies or Zn interstitials [68-72]. Though, theoretical calculations display that the O vacancy is a profound donor and does not participate to n -type conductivity. Electron paramagnetic resonance (EPR) consequences as well as displayed that O vacancy signals might be noticed only after high-energy electron irradiation [73-77].

Zn interstitials are thin donors but are unstable at room temperature as pointed out by theory and experiment. Even that indigenous defects spell out n -type conductivity, contaminations are probably show the major role. Lately it was displayed that H and the group-III elements are showed in bulk ZnO Crystals and work as donors First-principles calculations

have revealed that H is a thin donor in ZnO, drawing attention to examine its role in the electronic properties of ZnO. The thin donor nature of H in ZnO was admitted experimentally utilizing muon spin rotation (μ SR) and electron nuclear double resonance (ENDOR) techniques. Dependable p-type ZnO leftovers controversial in spite of many reports in the literature. Suggested acceptor dopants comprise substitution of N on O sites, and group-I elements for example Li and group-IB elements like Cu replacing on Zn sites. On the other hand, new studies have presented that Li and Cu are deep acceptors. Calculations have proposed that N, once believed to be a hydrogenic acceptor, is truly a deep acceptor with important lattice relaxation. New experimental consequences are consistent with this deep-acceptor model [78-87].

3.3.2. Optical Properties

The optical properties of ZnO rely on both intrinsic and extrinsic effects. In the center of zone, the conduction band is chiefly s like and the valence band is p like, deviding into three levels (A, B, and C) due to spin-orbit and crystal-field splitting. PL measurements showed that the A free exciton has a binding energy of 60 meV, causing in efficient excitonic emission that persists at room temperature. Room-temperature UV lasing has been showed in ZnO nanowires. Using PL experiments, Huang et al. observed the lasing action in nanowires through the development of the emission spectra with increasing pump power. ZnO has also strong non-linear optical applications, exhibiting second-order nonlinear optical behavior [88-90].

The green luminescence band centered on 2.4 eV is the widely seen defect emission in ZnO. Its attribution stays extremely debatable. Primary studies displayed that Cu impurities, common trace impurities in ZnO, cause green emission. The following, native defects like O vacancies and Zn vacancies were suggested as a key source. Theoretical calculations revealed that the movement between the conduction band and thle Zn vacancy acceptor level can provide rise to a PL around 2.5 eV. The main focus of this work is to examine the defect properties of ZnO nanocrystals, with accentuating on acceptor type defects [91-93].

4. COMPOSITE MATERIALS

4.1. Definition Composite Materials

A composite material is created by combining two or more materials – frequently ones that have so much different properties. The two materials work together to provide the composite unique properties. However, inside the composite you could easily tell the different materials a part as they do not dissolve or mix into each other [94].

4.2. Early Composites

Mankind has been creating composites for thousands years. One early example is sludge bricks. Sludge could be dried into a block shape to provide a building material. It is strong if you try to press it (it has a very good compressive strength) but it breaks quite easily if you try to curve it (it has bad tensile strength). Hay looks very strong if you want to stretch it, but you will crush it up easily. By combining mud and straw with each other it is suitable to create clays that are resilient to both squeezing and destroying and built excellent building bricks.

Another old composite is concrete, concrete is a mix of mortar (small stones or gravel), sand and cement. It has got an excellent compressive strength (it resists squashing). Recently it has been discovered that adding metal rods or wires to the concrete increases its bending strength. Concrete containing such wires or rods is known as reinforced concrete [94].

4.3. Classification of Composite Materials

There are many methods to divide composite materials. For instance, in agreement with the reinforcing principle, there are diffusion-enhanced composite materials, particle-enhanced composite materials and fiber-reinforced composite materials. Grounded on diverse application requirement, there are structural and functional composite materials. Functional composite materials, in harmony with its function, in addition should be divided into electrical functional composite materials, thermal functional composite materials, optical functional composite materials, and so on [95].

According to the naming principles of composite materials and classification of composite materials are following.

(1) Classification in accordance with the type of matrix material.

- Metal matrix composites (MMC's).
- . Polymer matrix composites (PMC's).
- Inorganic non-metallic matrix composite materials [95].

The most significant inorganic non-metallic matrix composite materials are ceramic matrix composites (CMC's) and carbon-based composite materials like C/C composite materials. In the polymer matrix composite materials, there are thermosetting resin-based composite materials and thermoplastic resin-based composite materials, also one part polymer matrix composite materials and polymer blends matrix composite materials [95].

(2) Classification in accordance with the form of dispersed phase.

- Continuous fiber-reinforced composite materials.
- Fibrous fabric, braid reinforced composite materials.
- Sheet reinforced composite materials.
- Short fiber or whisker reinforced composite materials.
- Nanometer particle reinforced composite materials.
- Particle reinforced composite [95].

(3) Classification in accordance with the type of reinforcing fibers.

- Carbon Fiber composite material.
- Glass fiber composite materials.
- Organic fiber composite materials [95].

5. EXPERIMENTAL DETAILS

5.1. Synthesis of Composites

Firstly we have got two different solutions Zinc acetate $\text{Zn}(\text{CH}_3\text{COO})_2$ and sodium hydroxide NaOH. Zinc acetate 0.035 gm was dissolved in 20 ml distilled water. Separately sodium hydroxide 0.85 gm was dissolved in 20 ml distilled water. We put magnetic fish in two both of solution and stirring during 1h on magnetic stirrer. After this we take the two solution into 1 cup then we put this cup into hydrothermal equipment at 160 °C and stayed for 12 h. Then we open the hydrothermal system and final solution was transferred to autoclave and heated material dried at 100°C for 24h. In this thesis we produced four different samples.

Sample 1: $\text{ZnO}_{0.01}$ Mix with 2ml $\text{C}_6\text{H}_5\text{Cl}$ inside cup.

Sample 2: $\text{ZnO}_{0.01}$ Mix with $\text{CuPc}_{0.001}$ and 2ml $\text{C}_6\text{H}_5\text{Cl}$ inside cup.

Sample 3: $\text{ZnO}_{0.01}$ Mix with $\text{CuPc}_{0.002}$ and 2ml $\text{C}_6\text{H}_5\text{Cl}$ inside cup.

Sample 4: $\text{ZnO}_{0.01}$ Mix with $\text{CuPc}_{0.003}$ and 2ml $\text{C}_6\text{H}_5\text{Cl}$ inside cup.

For each sample we bring four glass and washing by water, after this coating glass by each sample, then we waited for drying of the samples. Then we take SEM, EDX, FTIR, XRD, I-V Characteristic and optical measurement analysis.

5.2. X-ray Diffraction (XRD)

Normally X-ray is an electromagnetic radiation possesses a wave length of $1\text{\AA}$ in between gamma-rays and ultraviolet. In material science X-rays diffraction is called a characterization technique which examine the crystalline structures of the developed nanostructures. This non-destructive analytical technique is fairly valuable in order to study chemical composition, crystal structures and size, symmetry of the unit cell, their phases, and lattice constants of nanoparticles and physical properties of developed materials. It is significant to indicate that more than 90% solid materials are crystalline in nature and each crystalline has a unique X-ray diffraction pattern that could be utilized as a ‘fingerprint’ so as

to recognize the material. The interaction of X-ray beam with crystal led to a diffraction pattern that recognizes the material and corresponding phase. When an X-ray beam possesses wave length λ strikes the solid crystal with an angle θ , the outcome of scattered radiation is defined by virtue of Bragg's law [96-98].

$$n\lambda = 2d \sin \theta \quad (5.1)$$

Where d is the vertical spacing between planes of atoms, θ is the angle of the incident radiation, n is an integer and λ is the wavelength of the source [99].

Come into mind which the group of d -planes is unique for all material. It is significant to indicate that by controlling various parameters such as the geometry of incident rays and the face of the detector and crystal, someone can get completely the probable diffraction directions of the lattice [97, 99]. The X-ray diffraction pattern of pure CuPc is given in Fig. (5.1) [100].

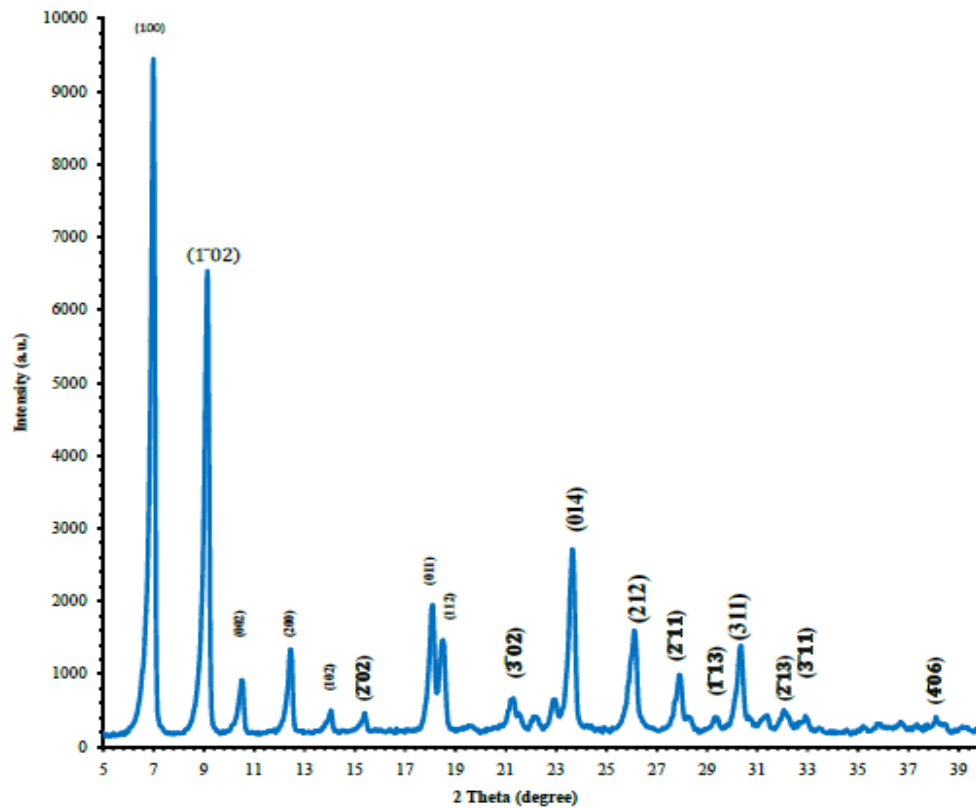


Figure 5.1. The XRD spectrum for CuPc powder [100].

5.3. Fourier Transform Infrared (FTIR) Spectroscopy

The main experimental technique employed in this work was Fourier transform infrared (FTIR) spectroscopy. It is based on the interaction of electromagnetic radiation with a molecular system, chiefly through the absorption of energy from the incident beam. The heart of a FTIR spectrometer is a Michelson interferometer, containing of a fixed mirror, a movable mirror and a beam splitter (Fig. 5.2). A beam emitted by a source is divided into two parts and then recombines at a semitransparent beam splitter. The recombined beam travels through the sample and finally hits the detector [101-103].

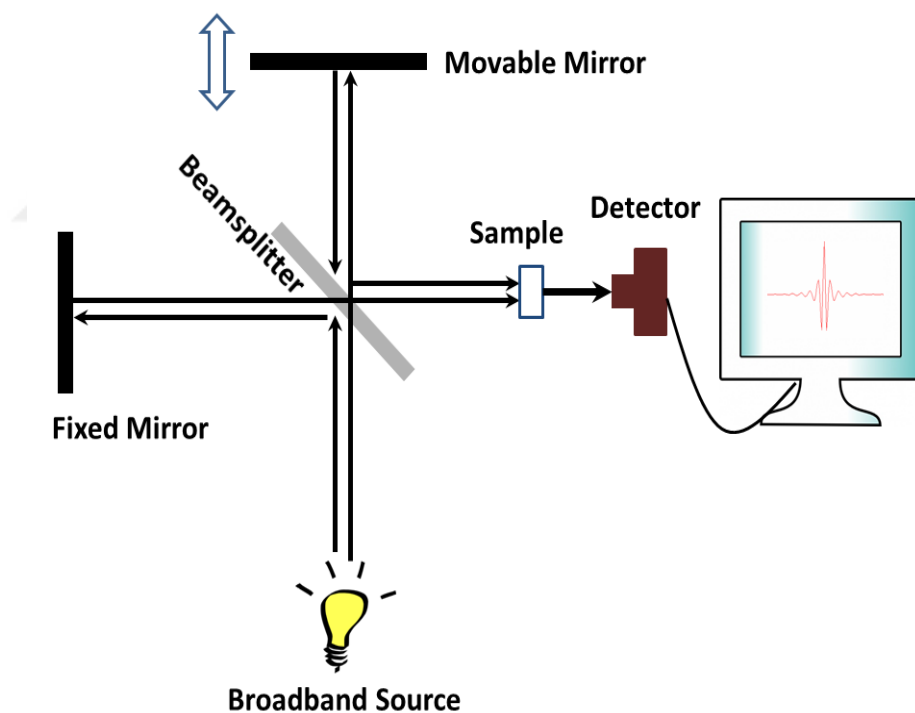


Figure 5.2. Schematic diagram of a FTIR spectrometer [103].

5.4. Scanning Electron Microscope

The scanning electron microscope (SEM) is a type of electron microscope (SEM) that aids in shaping an image of the sample surface by scanning. The electrons in the beam interact with the atoms in the surface to produce signals that hit beneficial light properties like electrical conductivity, composition and topography. The by the name „signals“ made by an SEM contain secondary and back-scattered electrons, specimen current, characteristic x-rays and light. All SEMs typically have the ability to detect secondary electrons but it's highly unprovable that a single SEM will have the ability to detect all the signals stated above. SEM aids in 4 gaining high resolution images of specimens ranging in size from those visible to the bared eye to those that are just a few nanometers in size [104-106].

In maximum of the applications, the data gathered is over a preselected area of the sample surface and succeeding this, a 2D image is produced which demonstrates the different spatial variations. Conventional SEMs with an enlargement range of 20X-30000X with a spatial resolution of 50-100 nm is able to scan areas that differ from 1 cm to 5 μm in width. SEMs similarly have the capability to analyze particular points as is able to be perceived at the time EDX operations which aid in defining the chemical composition of the sample concerned [105]. SEM analysis is supposed to be a nondestructive analysis as the bombardment of electrons do not make any destruction to the samples in any way at all [106]. In Fig. (5.3) a schematic drown of SEM is shown [107].

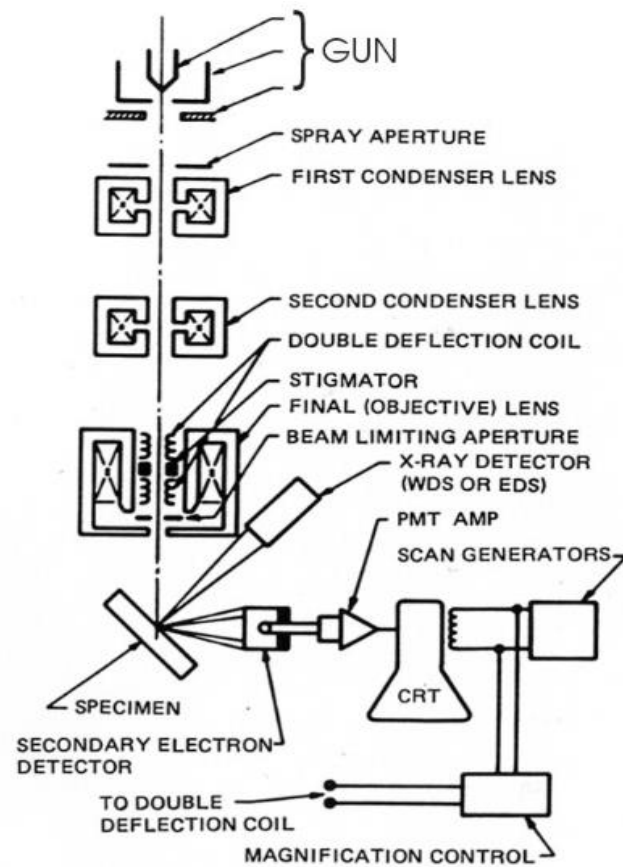


Figure 5.3. Schematic drawing of the electron and x-ray optics of combined SEM –EPMA [107]

Essential components of all SEMs include the following:

- Electron Source ("Gun")
- Sample Stage
- Electron Lenses
- Display / Data output devices
- Detectors for all signals of interest
- Infrastructure Requirements:
 - Cooling system
 - Vacuum System

- Power Supply
- Room free of ambient magnetic and electric fields
- Vibration-free floor [107].

Sample preparation is not actually a difficulty in case of SEM analysis as the merely necessity for a sample to undertake SEM analysis is that it can be conductive. It similarly lets a large quantity of the sample to be emphasized simultaneously as it possesses a huge depth of field. The high resolution images got also aid in analyzing the spatial features carefully. A mixture of all these features has created the SEM one of the most widespread devices in the world on materials science [108].

5.5. Energy Dispersive X-Ray Spectroscopy

Energy dispersive X-ray analysis, similarly is called EDX or EDAX, EDS, is a technique recognized the elemental composition of a sample. At the time of EDS, a sample is exposed to an electron beam inside a (SEM). These electrons hit with the electrons within the sample, producing some of them to be passed of their orbits. The emptied positions are packed by higher energy electrons which emit X-rays in the process. By analyzing the emitted X-rays, the elemental composition of the sample is able to be defined. EDS is an extremely useful instrument for doing the constitutional analysis of any sort of material [109].

5.6. UV-Visible Spectroscopy

A device utilized in the ultraviolet-visible spectroscopy is called UV/Vis spectrophotometer. The wavelength of UV is shorter than the visible light. It ranges from 100 to 400 nm. In a standard UV-V is spectrophotometer, a beam of light is split; a half of the beam (the sample beam) is directed via a transparent cell including a solution of the compound being analyzed, and a half (the reference beam) is directed through an identical cell that does not comprise the compound but comprise the solvent. The device is made in order that it is able to create a comparison of the strengths of the two beams when it scans over the wanted region of the wavelengths. If the mixture of absorbs light at a particular wavelength, the intensity of the

sample beam (IS) is going to be less than that of the resource beam [110]. Absorption of radiation by a sample is measured at various wavelengths and plotted by a recorder to lend the spectrum that is a plot of the wavelength of the entire region versus the absorption (A) of light at each wavelength. Ultraviolet and visible spectrometry is nearly completely utilized for quantifiable analysis; that is, the approximation of the amount of a compound recognized to be showed in the sample. The sample is typically in solution [111].

5.7. I-V Characterization

It comprise simply on applying a voltage between two investigations in the sample and computing the current that flows through the sample. The equipment utilized was the D-A output channel of a Lock-in Amplifier to supply the bias voltage and a Keithley picoammeter that measures the current (Fig. 5.4). There is a resistance before the Keithley to protect it from high currents. To do the characterization we utilized a computer program which scans voltage at constant rate up to high desired voltage [112].

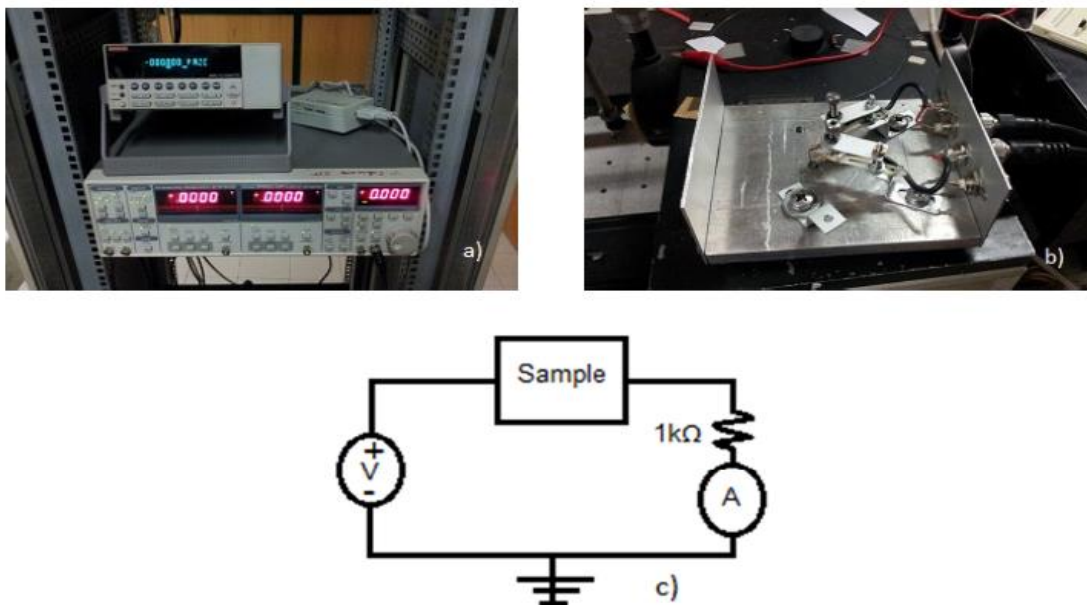
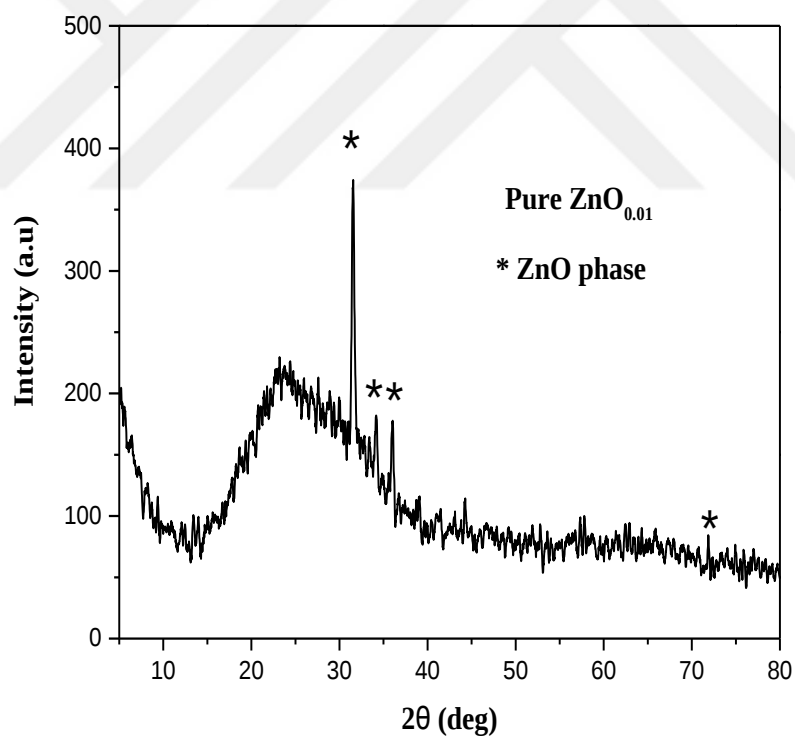


Figure 5.4. a) Keithley picoammeter and Lock-In amplifier, b) our probe station measuring an I-V characteristic c) circuit schematic of I-V measurement [112].

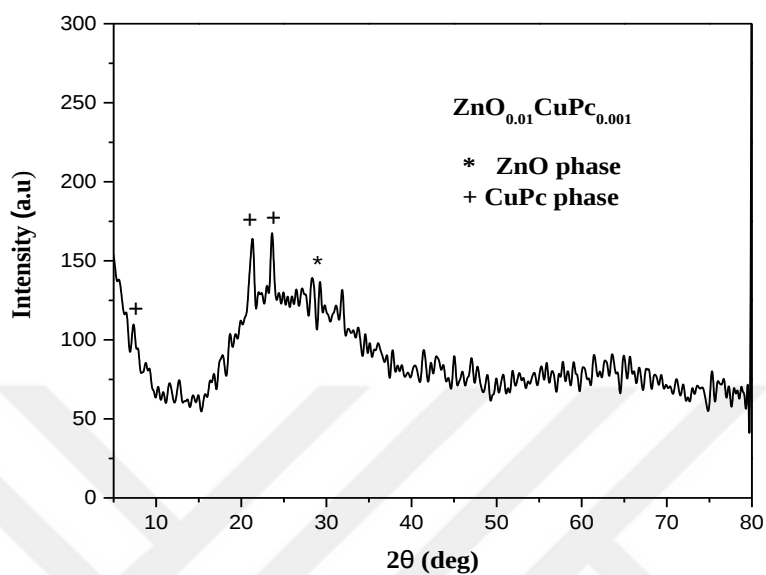
6. RESULTS AND DISCUSION

6.1. X-ray Diffraction Analysis

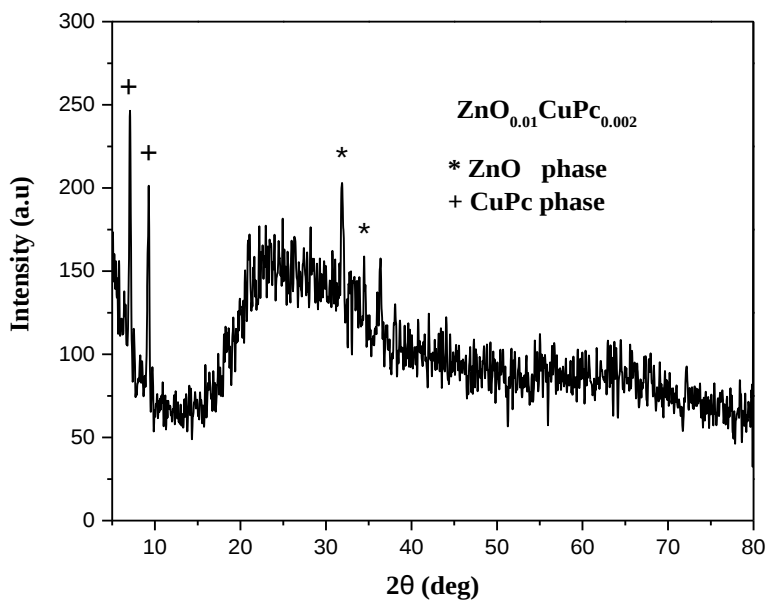
Fig.6.1 shows the X-ray diffraction patterns for ZnO-CuPc composite thin films deposited on a glass substrate. The prepared ZnO-CuPc nanocomposite diffraction pattern display the phase hexagonal ZnO and for Cu-Pc have different crystal phases: α -, β - and χ -phases. All the peaks of the ZnO thin films correspond to the peaks ZnO (JCPDS # 0.36- 1451). Peaks ZnO was signed by (*) and peaks CuPc was signed by (+).



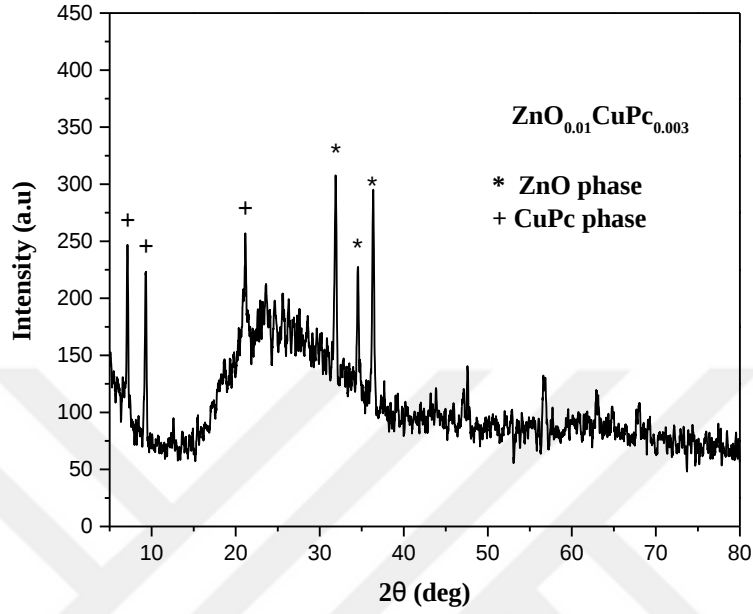
(a)



(b)



(c)



(d)

Figure 6.1. Diffraction pattern for (a) Pure ZnO (b) $\text{ZnO}_{0.01}\text{CuPc}_{0.001}$ (c) $\text{ZnO}_{0.01}\text{CuPc}_{0.002}$ (d) $\text{ZnO}_{0.01}\text{CuPc}_{0.003}$

The value of d-spacing, relative intensity and FWHM corresponding to xray diffraction for all four sample have been tabulated in Table 6.2. we found the value d-spacing by this equation [113].

$$n\lambda = 2d \sin\theta \quad (6.1)$$

The crystallites sizes (D) of the films are estimated using the Scherrer formula [113].

$$D = \frac{K\lambda}{\beta \cos(\theta)} \quad (6.2)$$

Where λ is the wavelength of X-Ray used ($\lambda = 1.54 \text{ \AA}$), k is shape factor a constant taken to be 0.94, θ is diffracting angle and β is the full width at half maximum of peaks XRD pattern. We found the value of crystallite size in Table 6.1. there is slight increase the CuPc for my sample the value crystal size increase.

The dislocation density (δ), defined as the length of dislocation lines per unit volume, are estimated using the equation [114].

$$\delta = \frac{1}{D^2} \quad (6.3)$$

We found the dislocation density (δ) showed in Table 6.1.

The value of lattice Strain (ϵ) of the thin films is estimated using the equation [113].

$$\epsilon = \frac{\beta \cos(\theta)}{4} \quad (6.4)$$

We found value of lattice Strain (ϵ) showed in Table 6.1.

Table 6.1. (2θ), d-spacing, FWHM, Crystallite size, strain and dislocation for ZnO-CuPc nanocomposite samples.

Sample	(2θ)($^\circ$)	d ($\text{\AA}$)	FWHM ($^\circ$)	FWHM (rad)	Crystallite size (nm)	Strain (* 10^{-3})	Dislocation (* 10^3)(nm) $^{-2}$
Pure ZnO _{0.01}	31.69	2.82	0.44	0.0076	19.45	1.86	2.64
ZnO _{0.01} CuPc _{0.001}	7.42	12.03	0.36	0.0062	23.6	1.54	1.79
ZnO _{0.01} CuPc _{0.002}	9.26	9.62	0.39	0.0068	21.49	1.69	2.16
ZnO _{0.01} CuPc _{0.003}	7.13	1.24	0.31	0.0054	26.76	1.34	1.39

Table 6.2. (2 θ), d-spacing, FWHM and percentage intensity for ZnO-CuPc nanocomposite samples.

Smple	(hkl)	(2 θ) (°)	d (Å)	FWHM (°)	Intensity (%)
Pure ZnO _{0.01}	100	31.69	2.82	0.44	100
	002	34.56	2.59	0.41	21.04
	004	72.50	1.3	0.35	9.81
ZnO _{0.01} CuPc _{0.001}	100	7.42	12.03	0.36	36.93
	211	21.24	4.1	0.35	92.03
	100	31.69	2.82	0.31	45.18
ZnO _{0.01} CuPc _{0.002}	100	7.09	12.62	0.38	100
	102	9.26	9.62	0.39	76.99
	100	31.74	2.82	0.41	34.4
ZnO _{0.01} CuPc _{0.003}	100	7.13	1.24	0.31	100
	102	9.26	9.62	0.33	78.2
	002	31.69	2.82	0.34	50.8

6.2. FTIR Analysis

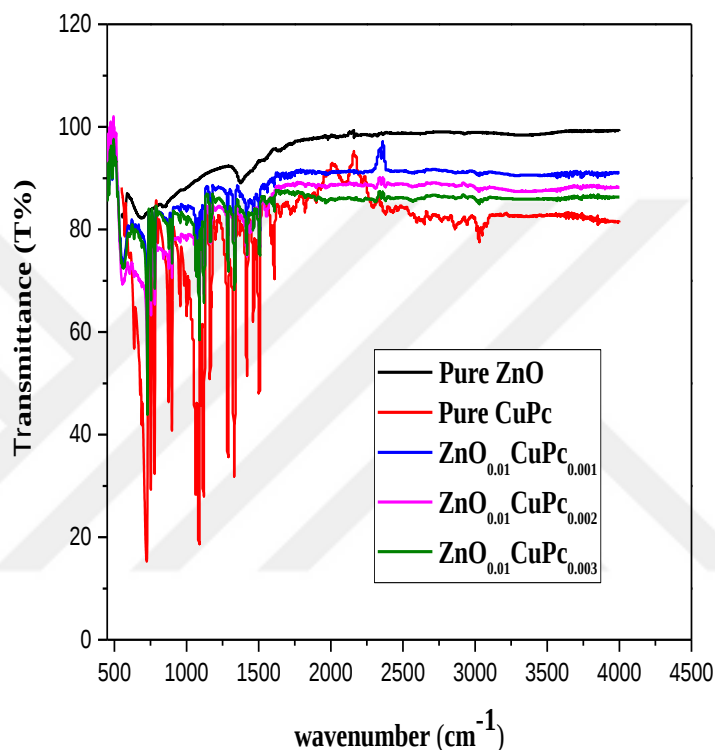


Figure 6.2. FTIR spectra for ZnO nanoparticles doped CuPc.

The FTIR spectra for ZnO-CuPc Nano composite has been recorded to study the various functional groups of Nano composite displayed in Fig. 6.2. FTIR spectra for ZnO nanoparticles, Infrared studies were carried out in order to ascertain the purity and nature of the metal nanoparticles, metal oxides generally give absorption bands in fingerprint region i.e. below 1000 cm^{-1} arising from inter-atomic vibrations. The peak observed at 1119.15 cm^{-1} are may be due to O-H stretching and deformation, respectively assigned to the water adsorption on the metal surface. The characteristic wurtzite lattice vibrations (Zn-O) are corresponding to the broadband in rang $400\text{-}600\text{ cm}^{-1}$ [115, 116]. The FTIR spectrum for CuPc, It has characteristic

peaks at 3040 cm^{-1} and 2930 cm^{-1} for aromatic C–H stretching, 1609 cm^{-1} for C=C macro cycle ring deformation, 1504 cm^{-1} for C=N stretching, 1331 cm^{-1} for C–C stretching in isoindole, 1090 cm^{-1} for C–H in plane deformation, and 728 cm^{-1} for C–H out of plane deformation. The other peaks at 1290 cm^{-1} , 1161 cm^{-1} and 1119 cm^{-1} correspond to C–N stretching in isoindole, C–N in plane bending, C–H in plane bending, respectively [117].

6.3. Morphological Analysis

In adding to automated SEM techniques, SEM morphological analysis to fully characterize materials. Though automated SEM analysis offers measured information about size, amount of phases and particles present and chemistry, morphological analysis offers information about the physical relationships of the phases present, crystallinity and size [118].

The surface morphology of ZnO-CuPc nanocomposite was studied using FESEM at various magnification and shown in Fig (6.3-6.6) the Fig 6.3 (a,b,c,d) we have pure ZnO, clearly shows at (x2500, x5000, x10000, x15000) magnification the formation of typical rod and clusters. In Fig. (6.4-6.6) (a,b,c,d) for ZnO-CuPc clearly shows at (x2500, x5000, x10000, x15000) magnification the formation of typical rod and clusters. In Fig. 6.3. (e) Shows EDX spectrum measurements of pure ZnO showing peaks i.e. zinc, oxygen. Fig. 6.4. (e) Shows EDX spectrum measurements of $\text{ZnO}_{0.01}\text{CuPc}_{0.001}$ showing peaks i.e. zinc, oxygen, nitrogen, carbon and copper. Fig. 6.5. (e) Shows EDX spectrum measurements of $\text{ZnO}_{0.01}\text{CuPc}_{0.002}$ showing peaks i.e. zinc, oxygen, nitrogen, silicon, carbon and copper. Fig. 6.6. (e) Shows EDX spectrum measurements of $\text{ZnO}_{0.01}\text{CuPc}_{0.003}$ showing peaks i.e. zinc, oxygen, nitrogen, silicon, carbon and copper.

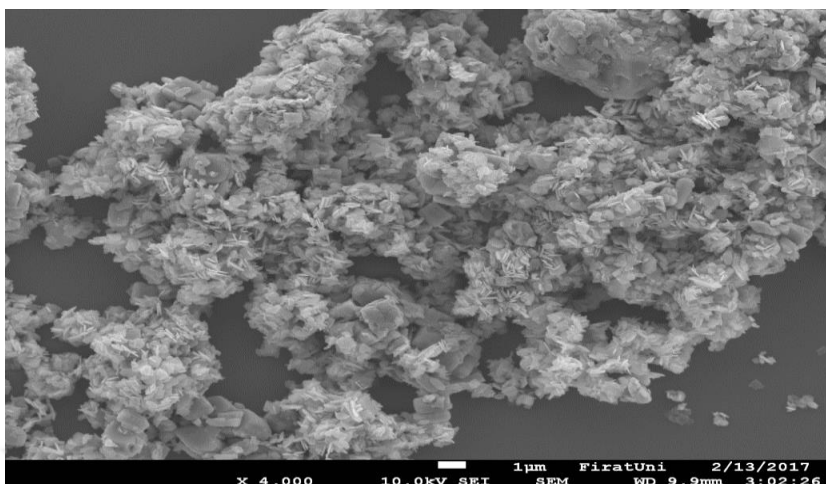


Figure 6.3 (a). SEM micrograph for pure ZnO_{0.01} at 4000x magnification.

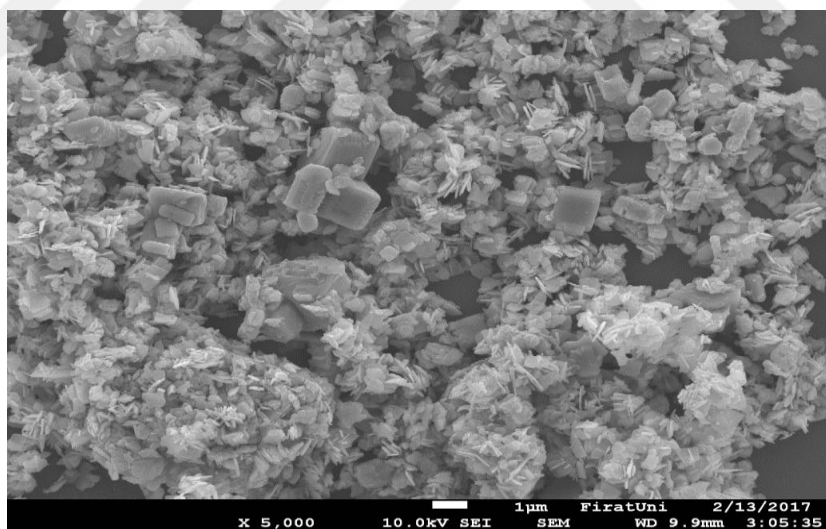


Figure 6.3 (b). SEM micrograph for pure ZnO_{0.01} at 5000x magnification.

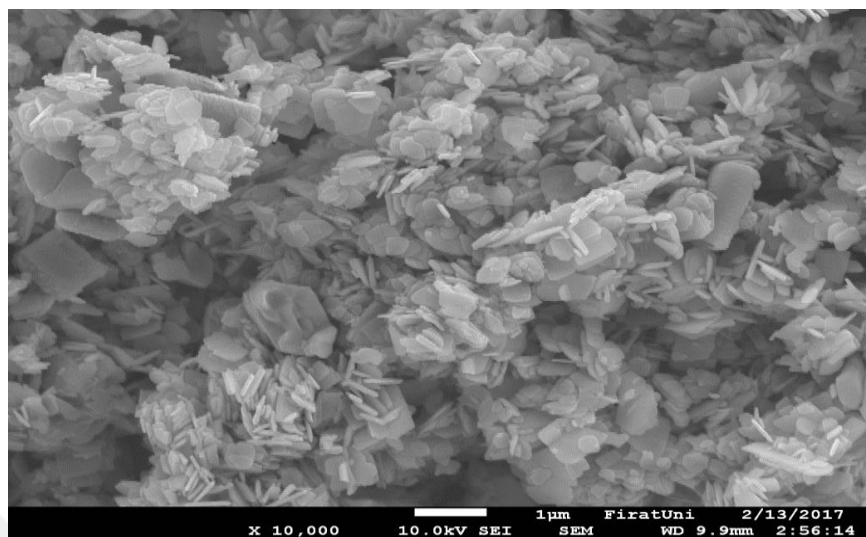


Figure 6.3 (c). SEM micrograph for pure ZnO_{0.01} at 10000x magnification.

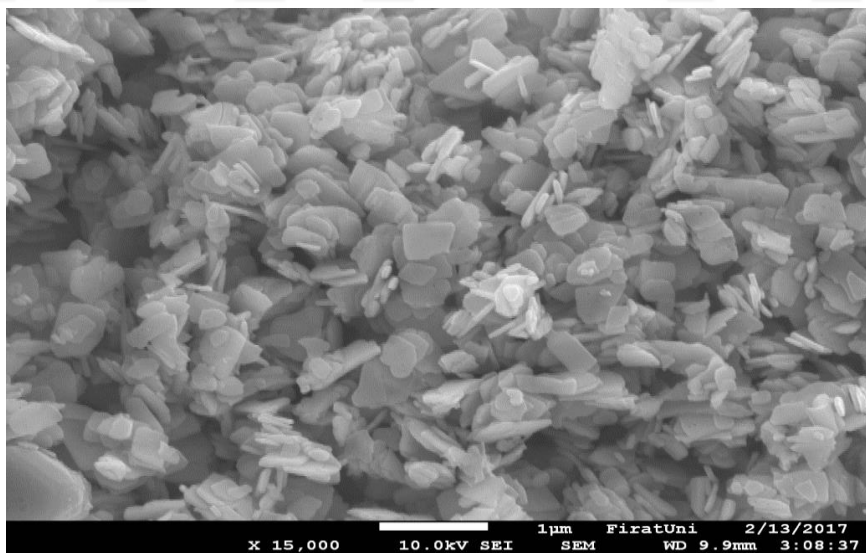
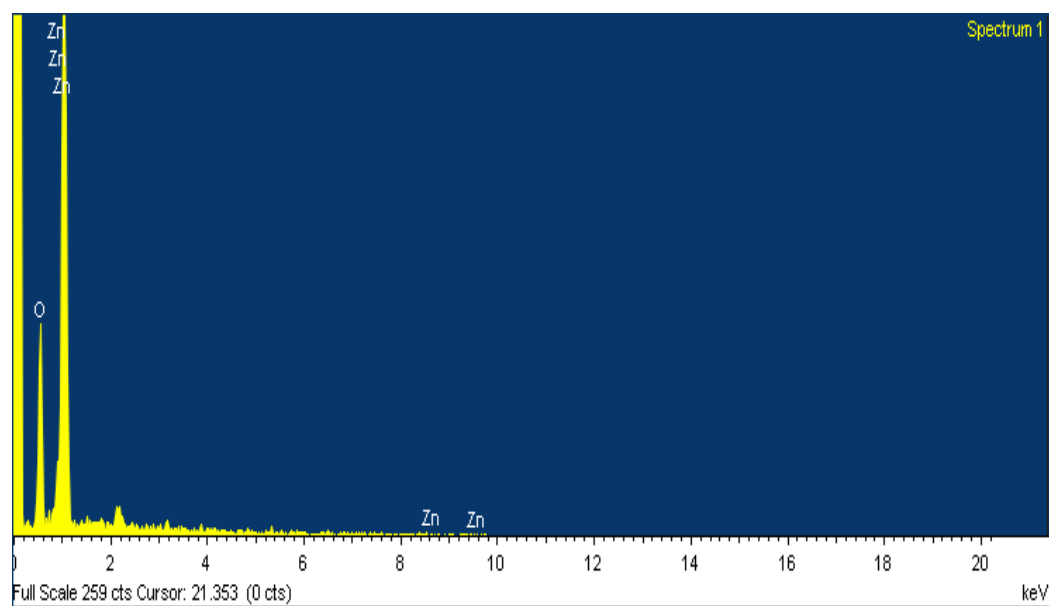


Figure 6.3 (d). SEM micrograph for pure ZnO_{0.01} at 15000x magnification.



Element	Weight%	Atomic%
O K	21.33	52.56
Zn L	78.67	47.44
Totals	100.00	

Figure 6.3 (e). EDXanalysis for pure ZnO_{0.01} sample.

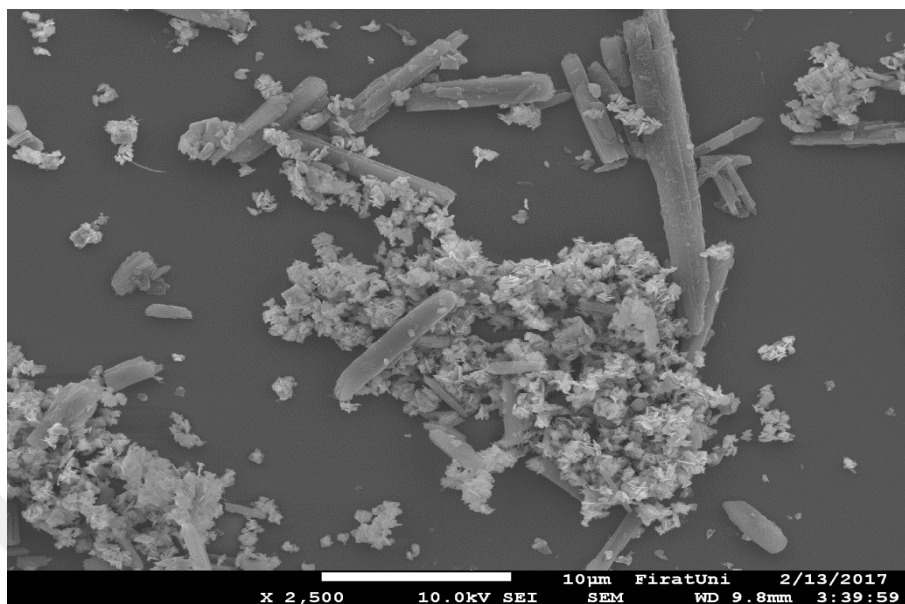


Figure 6.4 (a). SEM micrograph for ZnO_{0.01} CuPc_{0.001} at 2500x magnification.

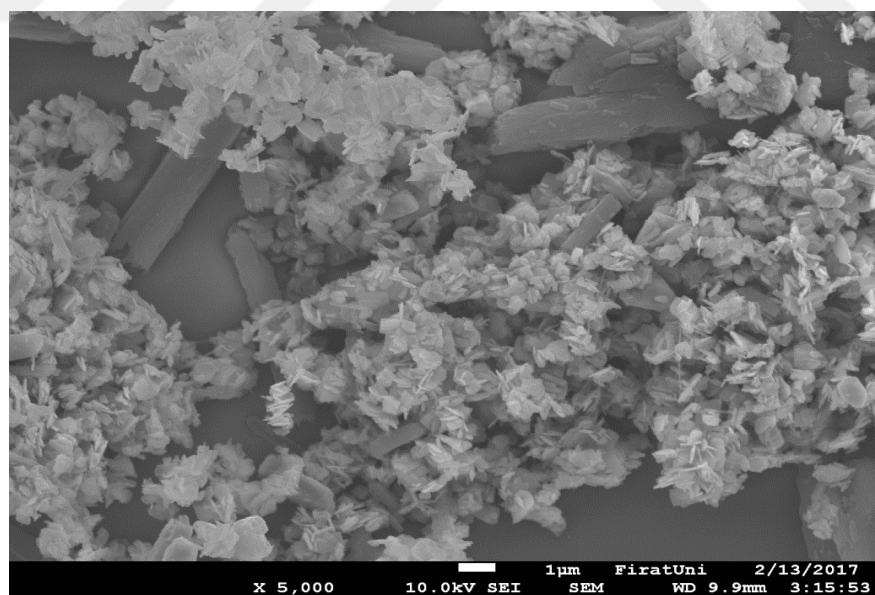


Figure 6.4 (b). SEM micrograph for ZnO_{0.01} CuPc_{0.001} at 5000x magnification.

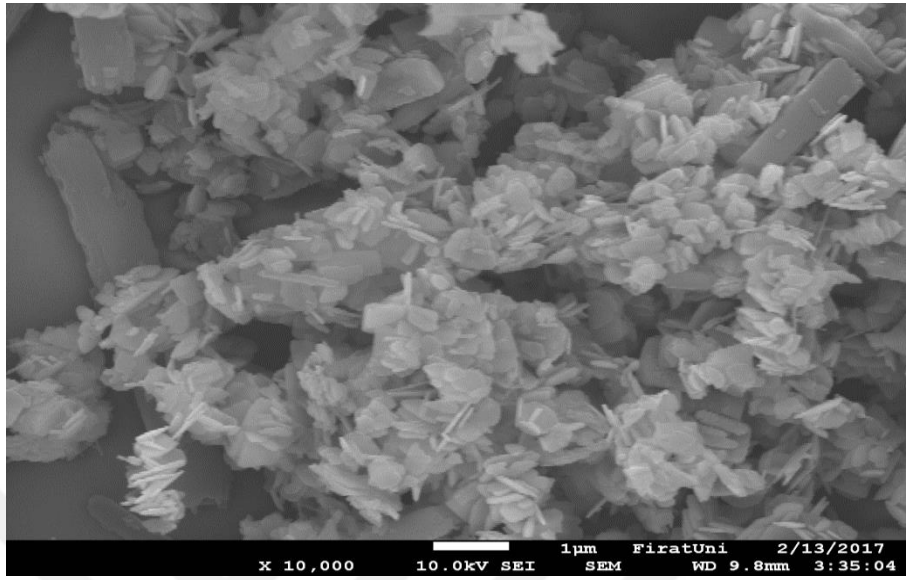


Figure 6.4 (c). SEM micrograph for $\text{ZnO}_{0.01} \text{CuPc}_{0.001}$ at 1000x magnification.

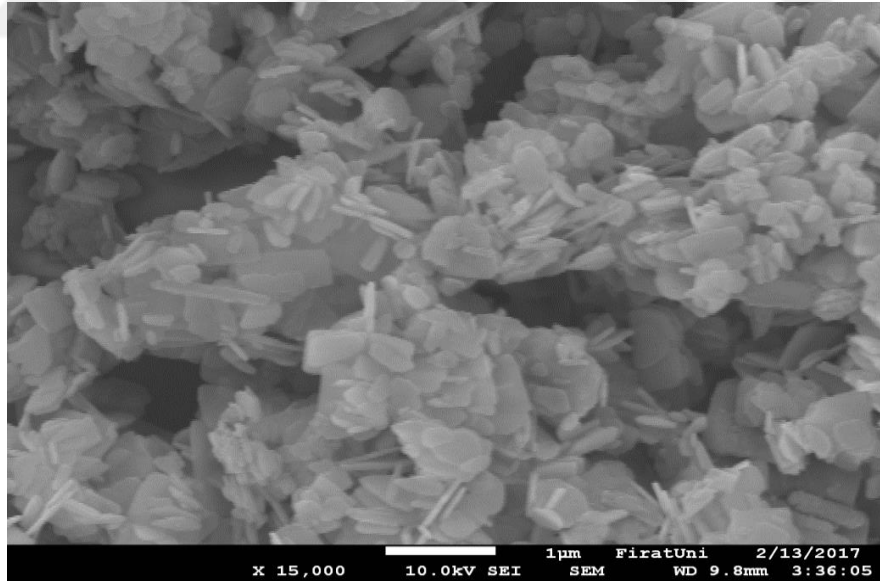
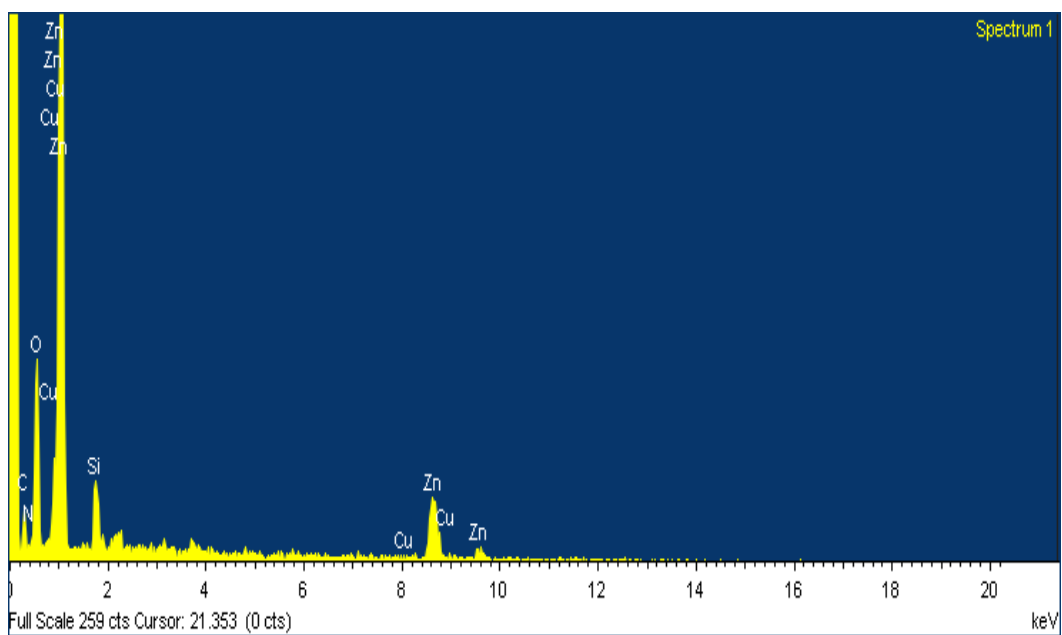


Figure 6.4 (d). SEM micrograph for $\text{ZnO}_{0.01} \text{CuPc}_{0.001}$ at 15000x magnification.



Element	Weight%	Atomic%
C K	32.87	52.08
N K	8.05	11.89
O K	17.78	22.97
Cu L	1.43	0.46
Zn L	39.87	12.61
Totals	100.00	

Figure 6.4 (e). EDX analysis for ZnO_{0.01} CuPc_{0.001} sample.

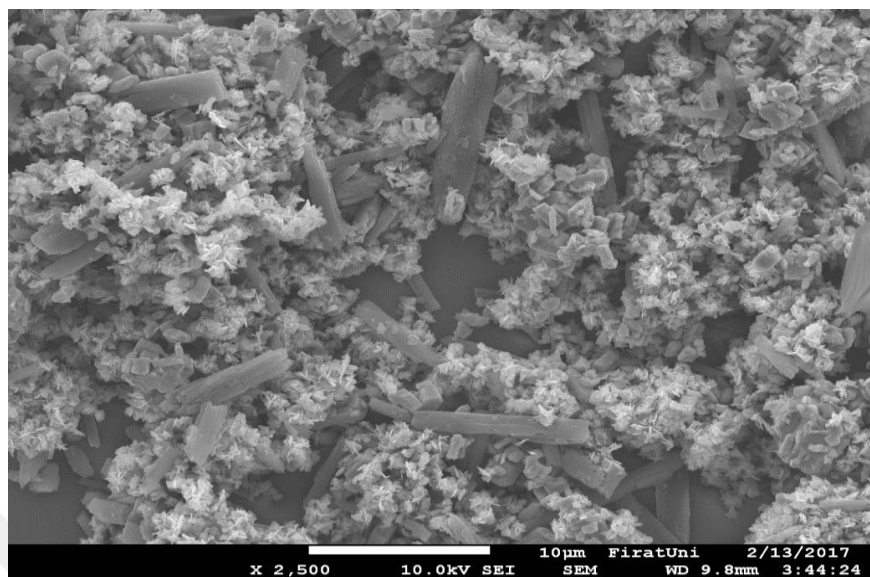


Figure 6.5 (a). SEM micrograph for $\text{ZnO}_{0.01} \text{CuPc}_{0.002}$ at 2500x magnification.

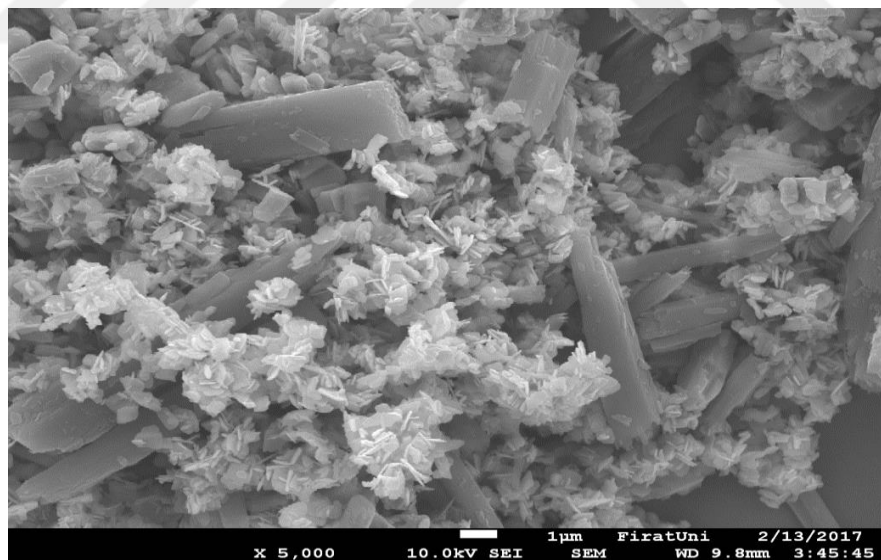


Figure 6.5 (b). SEM micrograph for $\text{ZnO}_{0.01} \text{CuPc}_{0.002}$ at 5000x magnification.

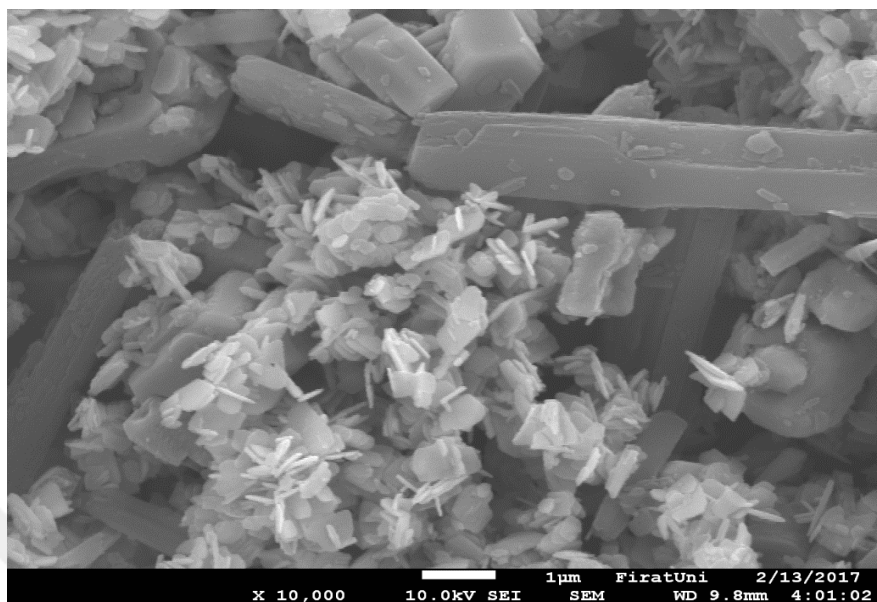


Figure 6.5 (c). SEM micrograph for $\text{ZnO}_{0.01} \text{CuPc}_{0.002}$ at 10000x magnification.

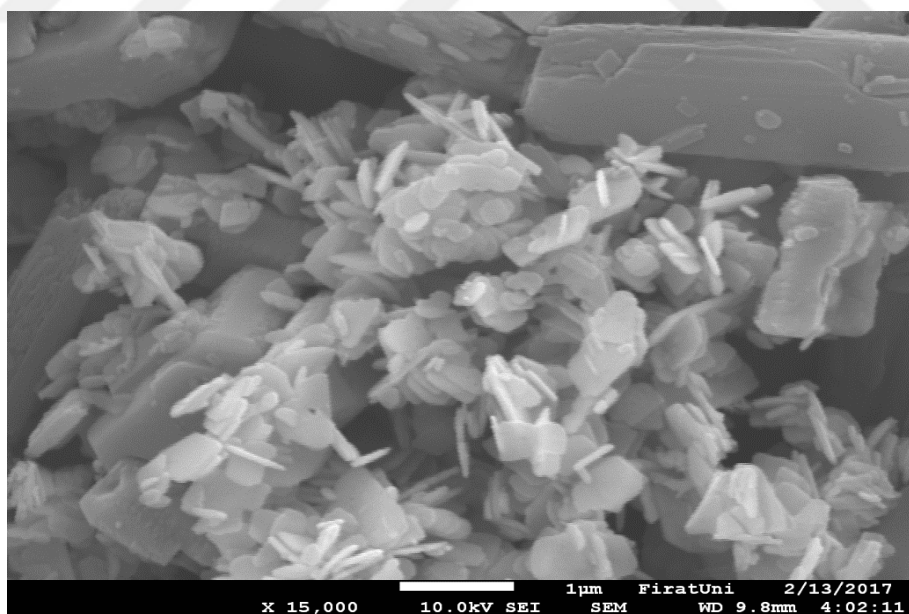
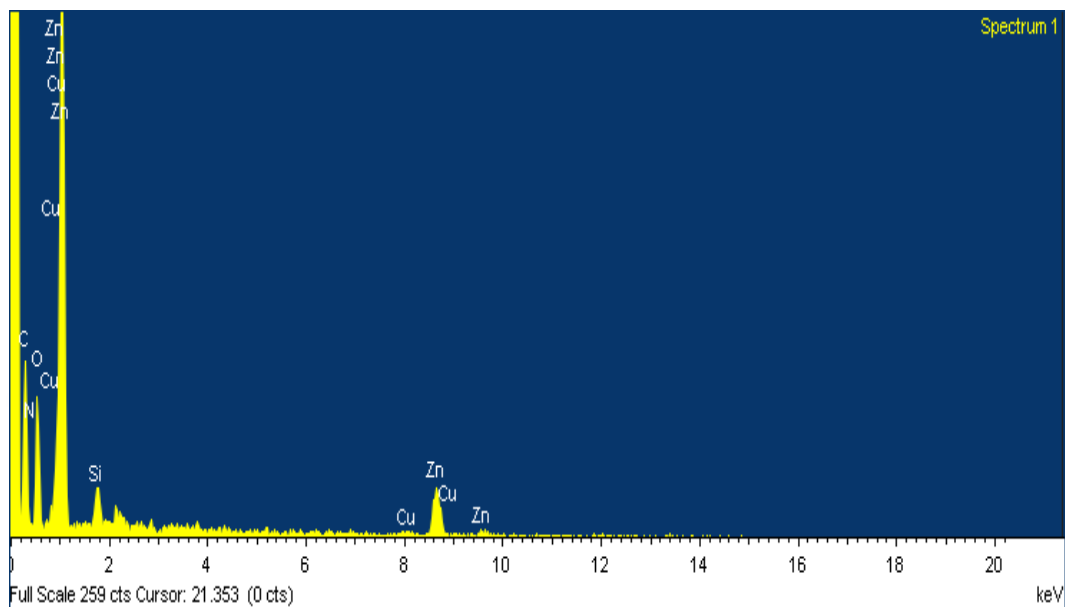


Figure 6.5 (d). SEM micrograph for $\text{ZnO}_{0.001} \text{CuPc}_{0.002}$ at 15000x magnification.



Element	Weight%	Atomic%
C K	59.83	75.30
N K	13.45	14.51
O K	5.55	5.24
Cu L	8.27	1.97
Zn L	12.91	2.99
Totals	100.00	

Figure 6.5 (e). EDX analysis for $\text{ZnO}_{0.01} \text{CuPc}_{0.002}$ sample.

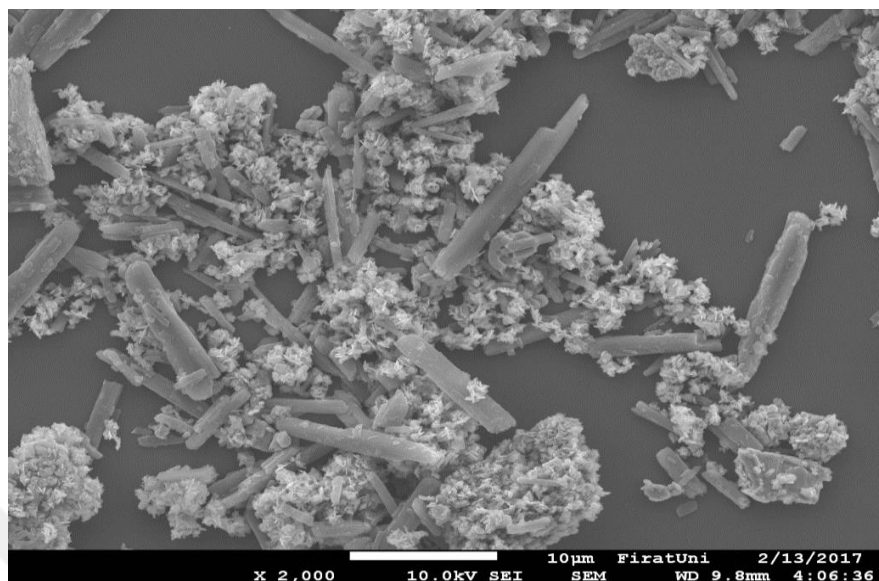


Figure 6.6 (a). SEM micrograph for $\text{ZnO}_{0.01} \text{CuPc}_{0.003}$ at 2000x magnification.

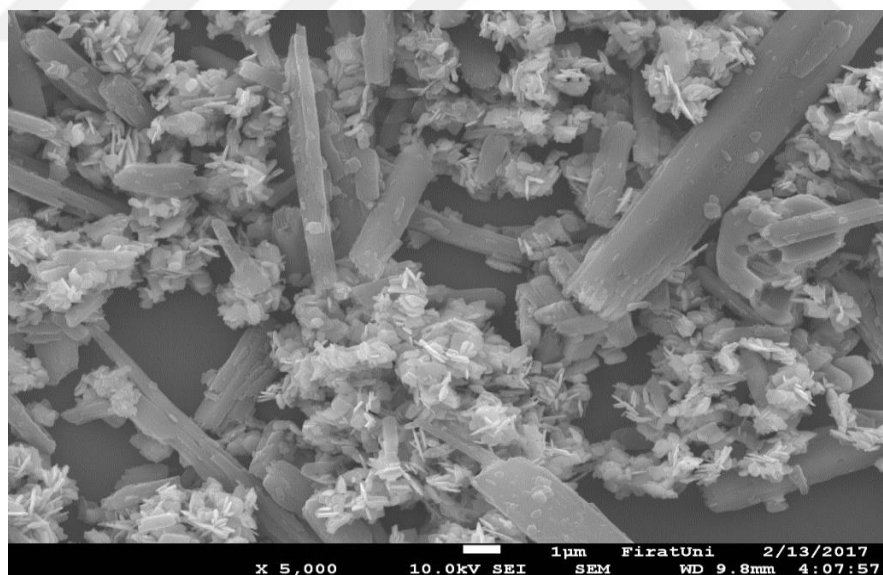


Figure 6.6 (b). SEM micrograph for $\text{ZnO}_{0.01} \text{CuPc}_{0.003}$ at 5000x magnification.

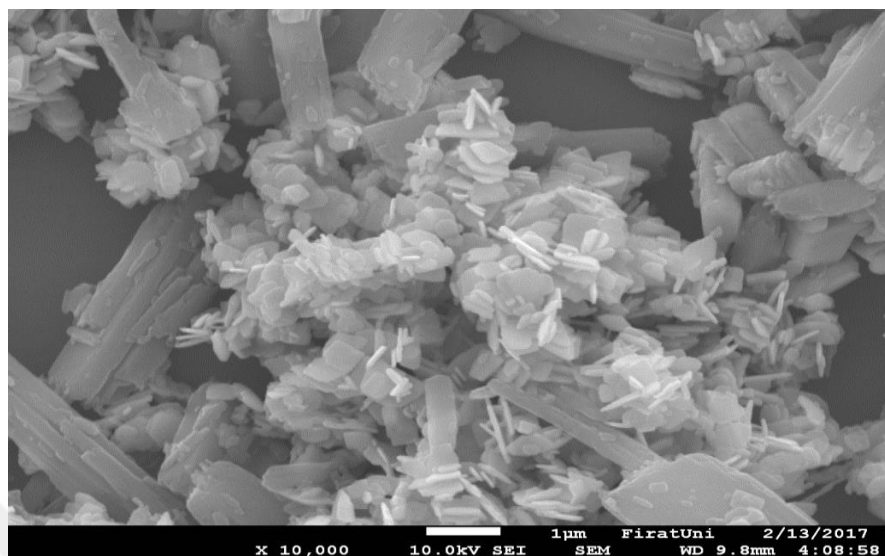


Figure 6.6 (e). SEM micrograph for $\text{ZnO}_{0.01} \text{CuPc}_{0.003}$ at 10000x magnification.

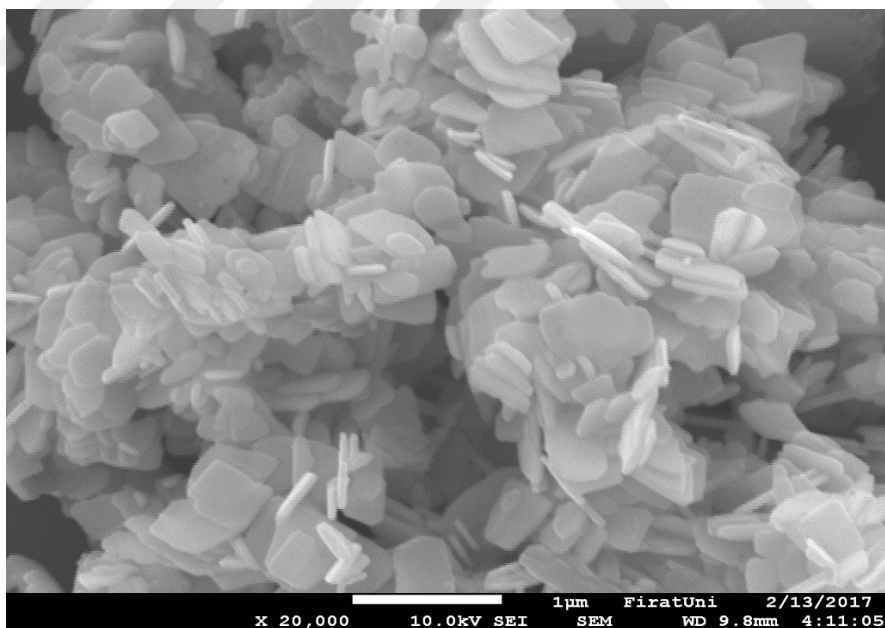
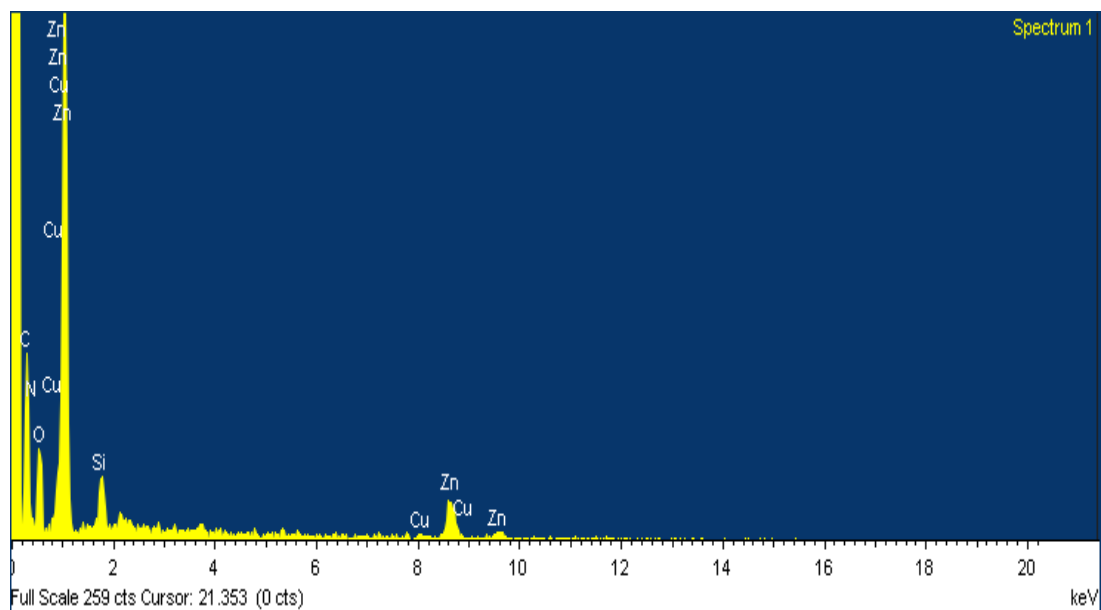


Figure 6.6 (d). SEM micrograph for $\text{ZnO}_{0.01} \text{CuPc}_{0.003}$ at 20000x magnification.



Element	Weight %	Atomic%
C K	43.14	64.27
N K	9.15	11.69
O K	12.98	14.52
Cu L	1.45	0.41
Zn L	33.28	9.11
Totals	100.00	

Figure 6.6 (e). EDX analysis for $\text{ZnO}_{0.01} \text{CuPc}_{0.003}$ sample.

6.4. Optical Analysis

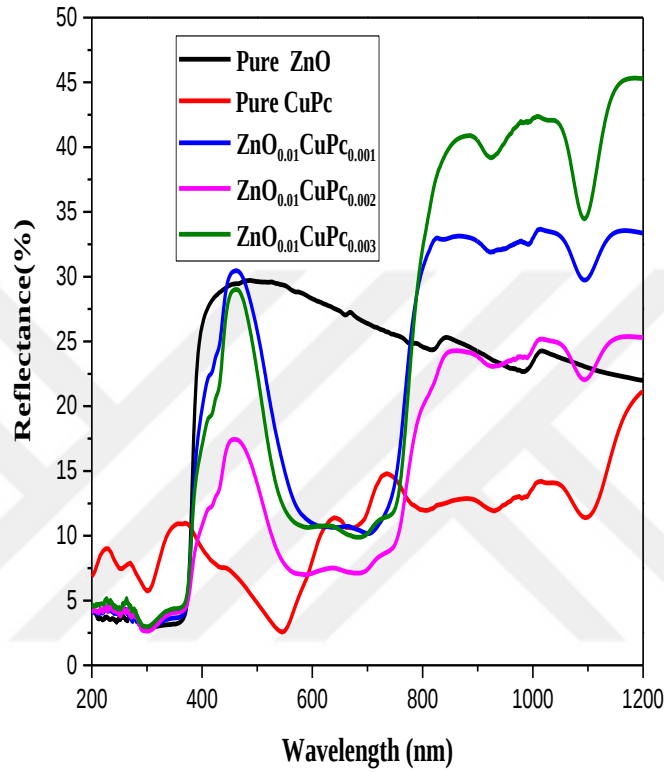


Figure 6.7. Reflectance spectra for pure ZnO, pure CuPc and doping ZnO with CuPc composites.

The spectral distribution of reflectance $R(\lambda)$ at ordinary incident for all the sample is displayed in Fig. 6.7. The light penetrate inside the sample and undergoes combination of scattering and absorption inside the sample. Some of the radiation is reflected back towards the surface. This reflected radiation contains useful information due to higher order of interaction. The reflected radiation is known as Kubelka-Munk (KM) reflectance and is defined by a function. The KM function $F(R)$, could be utilized to near the optical absorbance of the sample from is reflectance and is given by [119].

$$F(R) = \frac{(1-R)^2}{2R} \quad (6.5)$$

So by replacing the absorption coefficient α in the Tauc's equation we get

$$(\alpha \cdot h\nu) = A (h\nu - E_g)^n \quad (6.6)$$

From equation (6.6) we get

$$\alpha = \frac{A (h\nu - E_g)^n}{h\nu} \quad (6.7)$$

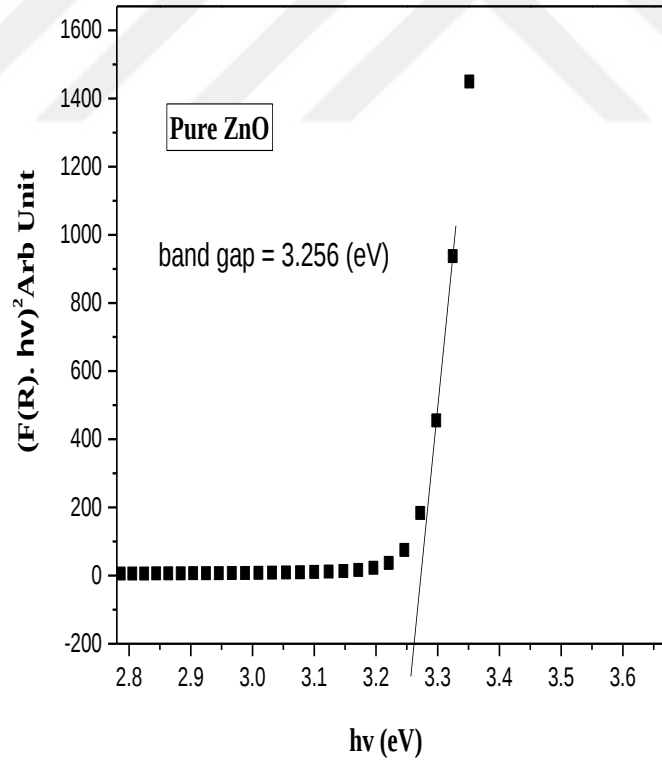


Figure 6.8 Band gap energy for pure ZnO Nano composite.

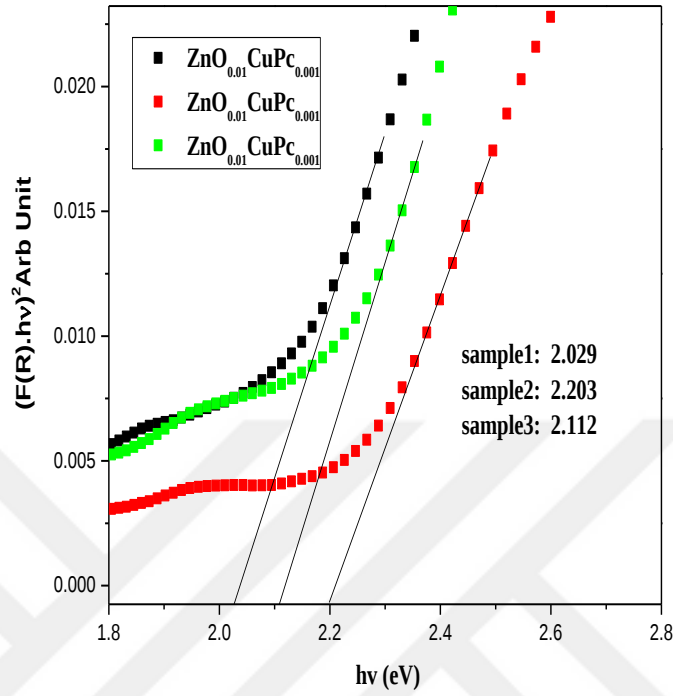


Figure 6.9. Band gap energy for doping ZnO and CuPc Nano composite.

In equation (6.7) Where, α is the absorption coefficient, A is a constant, $h\nu$ is the energy of incident photons and exponents n whose value depends upon the type the transition which may have values $1/2$, 2 , $3/2$ and 3 corresponding to the allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions [120]. For the direct band gap, the draw between $(F(R).h\nu)^2$ and photon energy ($h\nu$) has been shown in Fig. (6.8, 6.9) with n values of $1/2$. The band gap energy value could be determine by extrapolating the graph of the linear region of the plot to energy axis at $(F(R).h\nu)^2 = 0$, We found the ban gap energy for pure ZnO is equal to 3.256 (eV), but the standard value band gap energy for pure ZnO is equal to 3.37 (eV) and the standard value band gap energy for pure CuPc is equal to 3.02 (eV), then if the mass of ZnO stay constant, small increase the mass CuPc, we see the value band gap decrease because the value band gap for ZnO bigger then CuPc, then the band gap for sample $\text{ZnO}_{0.01}\text{CuPc}_{0.001}$ is equal to be 2.029(eV), for sample $\text{ZnO}_{0.01}\text{CuPc}_{0.002}$ band gap energy is equal to 2.203(eV), and for sample $\text{ZnO}_{0.01}\text{CuPu}_{0.003}$ the value band gap energy is equal to 2.112(eV).

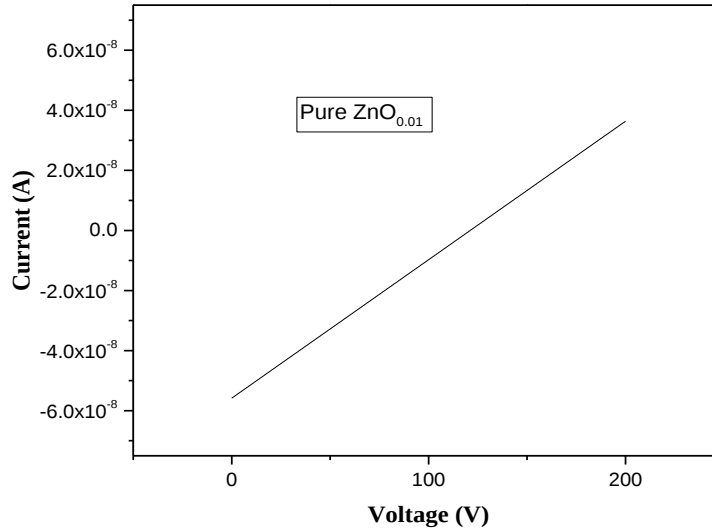
6.5. Electrical Conductivity

Electrical conductivity is the measure of the amount of electrical current a material could carry or its ability to carry a current. Electrical conductivity is also known as specific conductance. Conductivity is an intrinsic property of a material [121].

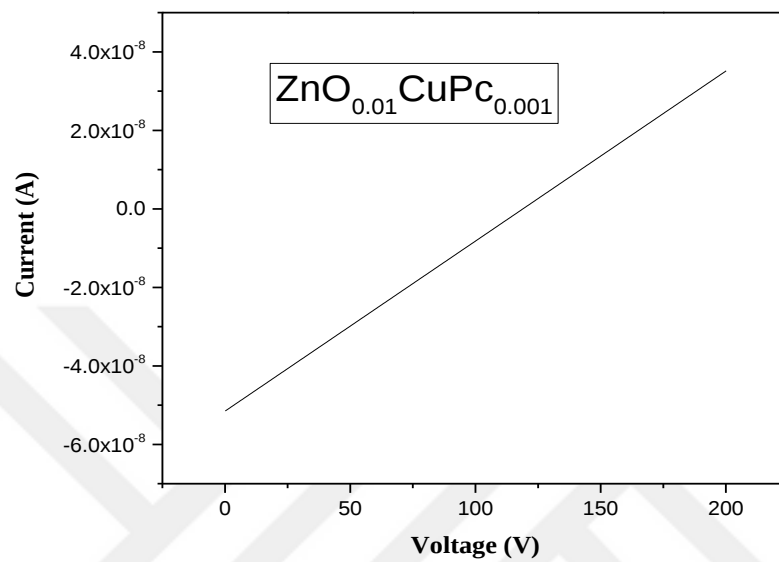
In order to investigate the electrical properties of the samples the dc conductivity of the sample was measured by I-V graph. The (I-V) graph for four sample has been displayed in Fig. 6.10. (a-d). We were found electrical conductivity for four sample by this equation.

$$\sigma = \frac{I}{V} \times \frac{l}{A} \quad (6.8)$$

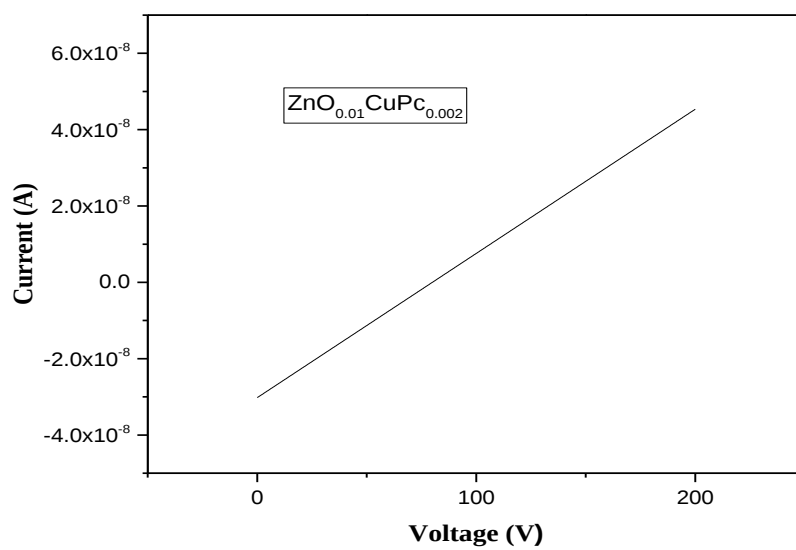
In this equation σ the electrical conductivity and $\frac{I}{V}$ is equal slope, (l) is contact distance and (A) the surface area, and we have slope, distance and area we can find electrical conductivity. The electrical conductivity for sample Pure ZnO_{0.01} was found is equal to 0.586×10^{-8} S/cm, For ZnO_{0.01}CuPc_{0.001} is equal to 0.55×10^{-8} S/cm, for ZnO_{0.01}CuPc_{0.002} is equal to 0.47×10^{-8} S/cm, for ZnO_{0.01}CuPc_{0.003} is equal to 0.58×10^{-8} S/cm. We can clearly see from the graphs below that the conductivity is decreasing with increase CuPc.



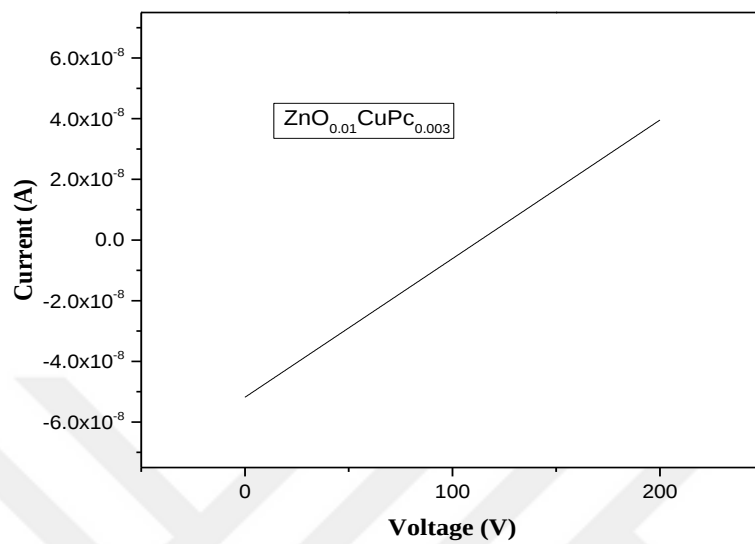
(a)



(b)



(c)



(d)

Figure 6.10. DC conductivity for pure ZnO and doped with CuPc **(a)** pure ZnO **(b)** $\text{ZnO}_{0.01}\text{CuPc}_{0.001}$ **(c)** $\text{ZnO}_{0.01}\text{CuPc}_{0.002}$ **(d)** $\text{ZnO}_{0.01}\text{CuPc}_{0.003}$.

7. CONCLUSION

ZnO were synthesized by using the hydrothermal technique then doped with CuPc to make a composite. Characterization study was carried out using XRD and SEM. The XRD patterns are used for phase identification and they showed amount of impurities and structure depending on the peaks present in the structure. Diffraction pattern display the phase hexagonal ZnO and for Cu-Pc have different crystal phases: α -, β - and χ - phases. XRD Scherer's formula is used to find particle size of ZnO and doped with CuPc ($0.9\lambda / (B * \cos \theta)$). Size was found to be 19.4 nm for pure ZnO, Size was found to be 23.6 nm, Size was found for ZnO_{0.01}CuPc_{0.001}, Size was found to be 21.49 nm for ZnO_{0.01}CuPc_{0.002} and Size was found to be 26.76 nm for ZnO_{0.01}CuPc_{0.003}. SEM micrograph used to determine the thin films micro structure, the SEM detect films are formation typically rod and clusters. FTIR spectra have been recorded to several functional groups. The optical properties of thin films investigated by using Tauc's equation The estimated optical band gap for pure ZnO was (3.256 eV) and for doped CuPc were decreased to (2.029(eV), 2.203(eV), 2.112(eV)) respectively. The electrical conductivity was measured for pure ZnO was equal to $0.586 \times 10^{-8} \text{ S/cm}$, for ZnO_{0.01}CuPc_{0.001} was equal to $0.55 \times 10^{-8} \text{ S/cm}$, for ZnO_{0.01}CuPc_{0.002} was equal to $0.47 \times 10^{-8} \text{ S/cm}$ and for ZnO_{0.01}CuPc_{0.003} was equal to $0.58 \times 10^{-8} \text{ S/cm}$).

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