

ABANT İZZET BAYSAL UNIVERSITY
THE GRADUATE SCHOOL OF NATURAL AND APPLIED
SCIENCES



CHARACTERIZATION OF ZnO BASED DILUTED MAGNETIC
SEMICONDUCTOR THIN FILMS AND NANO PARTICLES PRODUCED
BY SOL-GEL METHOD

DOCTOR OF PHILOSOPHY

ELİF AŞIKUZUN

BOLU, JANUARY 2016

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APPROVAL OF THE THESIS

“CHARACTERIZATION OF ZnO BASED DILUTED MAGNETIC SEMICONDUCTOR THIN FILMS AND NANO PARTICLES PRODUCED BY SOL-GEL METHOD” submitted by **Elif AŞIKUZUN** in partial fulfillment of the requirements for the degree of Doctor of Philosophy in **Department of Physics,** **Abant Izzet Baysal University** by,

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DECLARATION

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Elif AŞIKUZUN

ABSTRACT

CHARACTERIZATION OF ZnO BASED DILUTED MAGNETIC SEMICONDUCTOR THIN FILMS AND NANO PARTICLES PRODUCED BY SOL-GEL METHOD

PHD THESIS

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ABANT İZZET BAYSAL UNIVERSITY GRADUATE SCHOOL OF
NATURAL AND APPLIED SCIENCES
DEPARTMENT OF PHYSICS

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BOLU, JANUARY 2016

In recent years, ZnO-based diluted magnetic semiconductor materials are a field of great interest because of their using in technological applications. Applications of the produced ZnO-based nano-particle and nano thin film are the thermal glass, piezoelectric devices, solar cells, solid-state gas sensors, surface acoustic wave devices, laser devices, microelectromechanical systems (MEMS), organic light-emitting diodes and spintronic (reader head in magnetic hard disks and giant magnetoresistance (GMR)). Spintronic is replacing by semiconductor technology-based memory production. For this reason, researches are increasing gradually both the fundamental scientific and technological. Therefore, in this thesis, transition metal and rare earth element doped nano thin films and bulk samples of diluted magnetic semiconductors (DMSs) which have dual structure of $(\text{Zn}_{1-x}\text{B}_x)\text{O}$ ($\text{B}=\text{Co}, \text{Er}$) and ternary structure of $(\text{Zn}_{1-x}\text{B}_x\text{CO})$ ($\text{C}=\text{Cu}, \text{Cd}$) are prepared by using sol-gel method. The microstructure, electrical, optic, magnetic and micromechanic properties of prepared nano thin films and nano bulk materials are investigated. Firstly, the materials which have the greatest doping rate to determination of optimum annealing temperature of nano bulk materials are subjected to last heat treatment at 400°C , 450°C , 500°C , 550°C and 600°C for 30 min after first heat treatment. After this process, all of doped nano thin film and nano bulk materials are annealed under determined annealing temperature. The systems, $(\text{Zn}_{1-x}\text{B}_x)\text{O}$ dual and $(\text{Zn}_{1-x}\text{B}_x\text{CO})$ ternary structures, are prepared as polycrystalline nanoparticle powders by applying the sol-gel method. Nano thin films are coated on the glass substrate by using the dip coating method. The X-ray diffractometer (XRD), scanning electron microscopy (SEM), energy dispersive spectrometer (EDS) and atomic force microscopy (AFM) are used to determination of structural properties such as crystal structures, grain sizes, percent of elements, surface morphology; hall effect measurements system is used to determination of electrical properties of materials; UV-VIS spectrophotometer is used to determination of optic properties; vibrating sample magnetometer (VSM) system is used to determination of magnetic properties and Vickers microhardness device is used to determination of micromechanic properties of produced nano thin film and nano bulk materials.

KEYWORDS: Diluted Magnetic Semiconductor (DMS), Sol-Gel Method, ZnO, Nano Thin Film, Nanoparticle

ÖZET

SOL-GEL YÖNTEMİYLE ÜRETİLEN ZnO TABANLI SEYRELTİK MANYETİK YARIİLETKEN İNCE FİLMLEİN VE NANO PARÇACIKLARIN KARAKTERİZASYONU

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Son yıllarda ZnO tabanlı seyreltik manyetik yarıiletken malzemeler teknolojik uygulamalarda kullanılması nedeniyle oldukça büyük bir ilgi odağı olmuştur. ZnO tabanlı nano tanecikler ve nano kalınlıkta ince filmlerin uygulama alanları; ısıtıcı camlar, piezoelektrik aygıtlar, güneş pilleri, katıhal gaz algılayıcıları, yüzey akustik dalga cihazları, lazer aygıtlar, mikro elektromekaniksel sistemler (MEMS), organik ışık yutan diyotlar ve en önemlisi spintroniktir (manyetik hard disklerde okuyucu kafası ve büyük manyetik direnç (GMR)). Spintronik yarı iletken teknoloji tabanlı hafıza üretimin yerini almaktadır. Bu sebeple araştırmalar gerek temel bilimsel gerek teknolojik bağlamda her geçen gün artarak devam etmektedir. Bu nedenle bu tez çalışmasında geçiş metali ve nadir toprak elementi katkılı $(Zn_{1-x}B_x)O$ ($B=Co, Er$) ikili ve $(Zn_{1-x}B_xCO)$ ($C=Cu, Cd$) üçlü yapıya sahip seyreltik manyetik yarıiletken nano ince filmler ve bulk (yığın) malzemeler sol-gel metodu kullanılarak üretilmiştir. Hazırlanan film ve bulk malzemelerin mikroyapısal, elektriksel, optik, manyetik ve mikromekaniksel özellikleri incelenmiştir. Malzeme üretimi esnasında ilk olarak bulk (yığın) malzemelerin optimum tavlama sıcaklığının tespiti için en yüksek katkı oranındaki malzemeler ön ısıtım işleminden sonra sırasıyla 400°C, 450°C, 500°C, 550°C ve 600°C' de 30 dk son ısıtım işlemine tabi tutulmuştur. Bu işlemin ardından tüm katkılı nano ince film ve bulk malzemeler belirlenen optimum tavlama sıcaklıklarında tavlınmıştır. $(Zn_{1-x}B_x)O$ ikili ve $(Zn_{1-x}B_xCO)$ üçlü yapıya sahip DMS yapılar polikristal nanotozlar olarak sol-gel metodu kullanılarak hazırlanmıştır. İnce filmler cam altlık üzerine daldırarak kaplama yöntemi kullanılarak kaplanmıştır. Tez kapsamında üretilen nano ince film ve bulk malzemelerin mikroyapısal özelliklerinin belirlenebilmesi için X-ışınları kırınım difraktometresi (XRD), taramalı elektron mikroskobu (SEM), enerji dağılım spektrometresi (EDS), atomik kuvvet mikroskobu (AFM), elektriksel özelliklerinin tespiti için hall effect ölçüm sistemi, optik özelliklerinin tespiti için UV-VIS spektrofotometresi, manyetik analizleri için VSM sistemi ve mikromekanik analizleri için ise Vickers mikrosertlik cihazı kullanılmıştır.

ANAHTAR KELİMELEER: Seyreltik Manyetik Yarıiletkenler (DMS), Sol-Gel Method, ZnO, Nano İnce Film, Nanoparçacık

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CHAPTER 1

INTRODUCTION

Transition metals and rare earth elements doped ZnO's are called diluted magnetic semiconductors (DMS). DMS's are ferromagnetic semiconductor materials that have the formula of $Zn_{1-x}B_xO$ (B ; transition metal=Co, Mn, Cr, Fe, Cu, Ni, Al, Mg etc.) or $Zn_{1-x}R_xO$ (R ; rare earth element= La, Y, Er, Cd, Yb, Ce etc.) and wurtzite structure. Due to their different electrical, magnetic, and optical properties, ZnO and ZnO doped semiconductors have a potential to use on many different areas (Heiba and Arda, 2009; Zhao et al., 2012; Vidyasagar et al., 2011; Muthukumaran and Gopalakrishnan, 2012). DMS 's are used giant magnetic resistance (GMR), tunnel magnetic resistance (TMR), spin-based light-emitting diodes, sensors and transistors devices that are promising especially in spintronic. These magnetic materials are widely used on spintronic devices because of the electron spin are controlled with magnetic field.

The development of new materials which have nano size, low cost and ferromagnetic properties above room temperature will be provided by sol-gel process. In our country, the development of these materials, the spintronic applications and usage of these materials in the electronics industry will be extremely important in terms of technological applications. There are many studies on the structural and electrical properties of DMS in the literature but there are still continued problems. In addition, determination of mechanical properties of these materials will be worth to examination (Tosun et al., 2014; Arda et al., 2013). A large blank is available related to this subject in the literature.

In the proposed thesis, characterizations of produced rare earth element and transition metal doped ZnO -based diluted magnetic semiconductor nano thin film and nano bulk material are carried out in detail. The X-ray Diffractometer (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive Spectrometer (EDS) and Atomic Force Microscopy (AFM) are used to determination of structural properties

such as crystal structures, grain sizes, percent of elements, surface morphology; Hall effect measurements system is used to determination of electrical properties; UV-Vis spectrophotometer is used to determination of optic properties; Vibrating sample magnetometer (VSM) system is used to determination of magnetic properties and Vickers microhardness device is used to determination of micromechanic properties of produced nano thin film and nano bulk materials. These measurements and obtained results are given in the Chapter 6. The introduction of thesis is given in the Chapter 1; the aim and scope of the study is given in the Chapter 2; the general information about the DMSs and semiconductors are given in the Chapter 3; the devices used in the measurements and properties of their are given in the Chapter 4; the production method of nano thin film and nano bulk materials are given in the Chapter 5; experiments, results and discussion are given in the Chapter 6 and finally conclusions are given in the Chapter 7.

CHAPTER 2

AIM AND SCOPE OF THE STUDY

In the proposed thesis, firstly, transition metal (Co, Cu, Cd) and rare earth element (Er) doped diluted magnetic semiconductor nano thin films and nanoparticles which have in the ZnO based dual structure of $\text{Zn}_{1-x}\text{B}_x\text{O}$ and ternary structure of $\text{Zn}_{1-x-y}\text{B}_x\text{C}_y\text{O}$ are prepared by using sol-gel method. Microstructure, electric, optic, magnetic and micromechanic properties of diluted magnetic semiconductors that are produced with doping ratios are analyzed as detail. The band gap of $\text{Zn}_{1-x}\text{B}_x\text{O}$ and $\text{Zn}_{1-x-y}\text{B}_x\text{C}_y\text{O}$ nano thin films are changed and effect of band gap on structures is investigated. Besides, variation of mechanical properties of DMS's with doping ratios are investigated, thus role of double and ternary doping on mechanic properties are investigated so production of DMS materials which are cheap, long life and suitable in terms of technological applications are aimed.

The synthesis and characterizations of these materials that have so many applications are increased the importance of the thesis. New researches will be started for electronic and spintronic devices based magnetic nano particles and nano film semiconductors which have $(\text{Zn}_{1-x}\text{B}_x)\text{O}$ dual and $(\text{Zn}_{1-x-y}\text{B}_x\text{C}_y\text{O})$ ternary structure with the implementation of the thesis.

To achieve this aim;

- Transition metal element (Co, Cu, Cd) doped oxide nano bulk materials which have dual structure of $(\text{Zn}_{1-x}\text{B}_x)\text{O}$ and ternary structure of $(\text{Zn}_{1-x-y}\text{B}_x\text{C}_y\text{O})$ are synthesized by sol-gel method.
- Rare earth element (Er) doped oxide nano bulk materials which have dual structure of $(\text{Zn}_{1-x}\text{B}_x)\text{O}$ and ternary structure of $(\text{Zn}_{1-x-y}\text{B}_x\text{C}_y\text{O})$ are synthesized by sol-gel method.
- Transition metal element (Co, Cu, Cd) doped oxide nano thin films which have dual structure of $(\text{Zn}_{1-x}\text{B}_x)\text{O}$ and ternary structure of $(\text{Zn}_{1-x-y}\text{B}_x\text{C}_y\text{O})$ are

synthesized by sol-gel method.

- Rare earth element (Er) doped oxide nano thin films which have dual structure of $(\text{Zn}_{1-x}\text{B}_x)\text{O}$ and ternary structure of $(\text{Zn}_{1-x-y}\text{B}_x\text{C}_y\text{O})$ are synthesized by sol-gel method.

- Microstructure, electric, optic, magnetic and mechanic characterizations of produced nano powder and nano thin films are performed. Vickers microhardness of the material with the models that are used to microhardness analyses in the literature is examined in detail.



CHAPTER 3

THE PROPERTIES OF DILUTED MAGNETIC SEMICONDUCTORS (DMSs)

3.1 Introduction

The production and control of the spin-polarized currents in semiconductor materials are very attractive in recent years. Ferromagnetic semiconductors enable easier integration of spintronic into existing semiconductor devices. For example, while only a few percent of the spin polarization is possible between the ferromagnetic metal and semiconductor interfaces due to the conductivity mismatch, highly efficient spin injection is possible between the semiconductor and semiconductor interfaces (Schmidt et al., 2010). Ferromagnetic semiconductors allow production of devices which will be used in conventional semiconductor technology. Thus, a material class known as dilute magnetic semiconductors (DMS) has been developed. DMSs are the semiconductors which are doped by a few percent of magnetic atoms. Magnetic atoms hold a lattice points and these atoms lead to ferromagnetism in the non-magnetic host semiconductor. DMSs typically exist at much lower temperatures than room temperature. There are some successful studies that have reached to ferromagnetism at room temperature but the results are not repeated by the other study groups and the results have conflicted with some theoretical predictions.

DMS attract attention as a spin polarized source for next-generation semiconductor devices which can be used charge and spin of carriers at the same time. Due to possible room temperature (RT) ferromagnetism, transition metal doped ZnO is very important compared with GaMnAs and InMnAs. Theoretically, Dietl et al. (2000) first found that p-type Mn doped ZnO indicates ferromagnetic properties with T_c well above room temperature. In contrast, Co-doped ZnO is theoretically

showed to become ferromagnetic with n-type doping (Sato and Katayama-Yoshida, 2002).

In some cases, the ferromagnetism has been attributed to uncontrollable ferromagnetic clusters or secondary phases (Wang et al., 2000; Heald et al., 2009). These behaviors are not present in single-phase samples (Pei et al., 2009). The high-temperature ferromagnetism might have been caused by defects, such as oxygen valences, H contaminations, which are present in transition metal doped ZnO , as described by the bound magnetic polaron (BMP) model (Liu et al., 2009).

In addition, several groups observed that distinct ferromagnetic signals in ZnO nano thin films and nanoparticles without transition metal doping. But all of these cases are not true for DMSs. In a true DMS, the spins of the magnetic dopant preserve permanent alignment under the influence of spin polarized free carriers (Pearson et al., 2003).

Behan et. al. (2008) observed robust carrier-induced ferromagnetism and strong magneto-optical signals in metallic Al doped ZnCoO film with high carrier density alleging a real magnetic semiconductor. However, Kapsar et. al. (2008) expressed that lack of ferromagnetism is observed in the ZnO: CoAl films with a very high carrier concentration (10^{20} cm^{-3}). The reasons of significant distinct between these works are not clear until now. In fact, most of these films are typically polycrystalline and the reproducibility of them is poor. Therefore more careful studies of the structural and magnetic characteristics of high-quality single crystal films with good reproducibility are required to clarify the mechanism of ferromagnetism in Co-doped ZnO films.

Recently, ZnO attracts much attention because of its cheapness, abundance and being compatible with the environment. Also, ZnO has wide band gap energy of 3.3 eV and large exciton binding energy of 60 meV. Therefore, it is one of the most promising materials for the optoelectronic materials. In the $III - V$ semiconductor based DMS, the low solubility of the transition metal atoms is inadequate to form large magnetization. Recently, Fukumura et al. (1999), Jin et. al. (2000) experimentally indicated that 3d transition metal atoms have are a resolution of a few % in ZnO . For this reason, ZnO is very promising in this point. $II - VI$ semiconductors are not suitable for production of functional DMS. As previously indicated, this difficulty has been exceeded by co-doping method. Therefore,

investigation of the carrier-induced ferromagnetism is more important in *ZnO* based DMS.

Finally, it can be summarized that:

- DMSs are semiconductors where a fraction of the cations in the lattice are replaced substitution by magnetic ions.
- The atomic spin on these magnetic dopants is expected to interact with the carriers in the lattice.
- They have unusual magnetic characteristics due to the presence of isolated magnetic ions in semiconducting lattice.
- DMSs have been of great interest as they combine the two large branches in condensed matter physics; semiconductor and magnetism.
- DMSs have been of much interest and have been studied actively for the purpose of the use of both charge and spin of electrons in semiconductors.
- ZnO-based semiconductors are important for industrial products.
- Additional investments and efforts increase massively day by day to improve the technology behind the film and nanoparticles production.
- Therefore ZnO-based semiconductor bulk and film materials have been prepared by many different groups using various methods such as magnetron sputtering, sol–gel process, pulsed laser deposition, spray pyrolysis, laser molecular beam epitaxy and metal organic chemical vapor deposition.
- Among these methods, the sol–gel method has some advantages such as continuous processing at room temperature, better homogeneity, low cost and simplicity.
- There is a great interest in the physical properties of DMSs for their potential technological applications to optoelectronics, magnetoelectronics, and microwave devices.
- Applications of the *ZnO*-based nano-particle and nano thin film produced are the thermal glass, piezoelectric devices, solar cells, solid-state gas sensors, surface acoustic wave devices, laser devices, organic light-emitting diodes and spintronic. Spintronic is replacing by semiconductor technology-based memory production. For this reason, both scientific and technological researches continue to increase gradually.

- Recently, ZnO alloying with the 3d TM has attracted much attention as a DMS, with room temperature ferromagnetism.

3.2 What Is Spintronic?

The using of two fundamental characteristics of the electron (spin + charge) to create of the new instrument design is called spin electronic or spintronic (Prinz, 1995; Prinz, 1998; Wolf et al., 2006). Spintronics may lead to the production of devices such as spin-polarized LEDs, spin-FETs and spin-based qubits for quantum computers. The increasing functions such as magnetic/electronic processes that are integrated on the same chip are expected. At present, a small number of spintronic devices have been produced and these devices have an amazing impact on technology. For example, metallic-multilayered structures that display large amounts of magnetoresistance (so-called Giant Magnetoresistance) have replaced by conventional hard-disk read heads leading to huge increases in hard-disk storage (Prinz, 1995).

The integration of magnetic materials and impurities into nanoelectronic devices enables the use of the electron spin addition to its charge for carrying information. This new paradigm in information processing devices has been called “spintronics”. The discovery of functional spintronic devices provides development and integration of diverse materials with atomic-level control.

Magnetic Tunnel Junctions (MTJ) are the prototypical spintronic devices. They have three layers: a ferromagnetic metal, an insulator, and another ferromagnetic metal. The insulator layer is only a few nanometers thick, which is thin enough to allow tunneling of electrons from one metallic electrode to the other. When the magnetizations of the ferromagnetic layers are aligned, the tunneling current is large and the resistance of device is low. When the magnetizations of the ferromagnetic layers are anti-aligned, the tunneling current is small and the resistance of device is large. If the magnetization of one electrode is fixed, for example by exchange coupling to a neighboring antiferromagnet, and the other layer can switch depending on an applied magnetic field, the MTJ exhibit magnetoresistance, where the resistance state of the device depends on the sign of

the applied field. MTJs are already used as sensors in the read heads of magnetic hard disk drives. These sensors have become an important form of solid state magnetic detection technology. GMR technology has become an industry and the advent of this technology which has created revolution of read heads used in hard drive technology.

3.3 Ferromagnetic Materials

Recently ferromagnetic semiconductors form by replacement of a small number of non-magnetic host semiconductor atoms with magnetic ions has attracted attention because of their potential as spin-polarized carrier source. These materials are potential candidates for technological applications such as optoelectronic, magnetoelectronic and microwave devices. Ferromagnetism of the host material is an important necessity to produce practical devices at room temperature or above.

After the discovery of the theory of room temperature ferromagnetism by Dietl and groups in 2000 (Dietl et al., 2000), ZnO-based ferromagnetic semiconductors become more important. They used the mean field theory to show the Curie temperature of a ferromagnetic semiconductor and predicted that room temperature ferromagnetism can be formed with substitution of Mn ions into the wide-band-gap semiconductors such as ZnO or GaN.

3.4 What's Piezoelectric Materials?

The electric production property of materials with amount of applied external pressure is called piezoelectric. The piezoelectric effect is the electric polarization produced by mechanical stress. When pressure is applied from both ends of structure, the potential difference (V) between the two ends can be measured. This feature was discovered by Pierre Curie in 1880 (Curie, 1880). The reverse is also true. So when external voltage is given, the shape of the crystal structure slightly varies. When these materials are under the influence of a force, electric current produces and form of materials changes about 4% under the electric effect. This feature is used in the

pressure measuring instruments, sound recording and production devices, optical focusing devices. Devices can operate at high frequencies such as 400 kHz.

Piezoelectric materials are crystals that are converted electrical effect to mechanical size and mechanical effect to electrical size and don't have symmetry center. If a pressure is applied on the asymmetric ionic crystal that has a constant polarization, distance between the poles decreases. Therefore, a voltage difference between the two ends arises and if it is combined with a conductor current increases.

Thus, mechanical effect converts to electrical size. On the other hand, if a voltage is applied between the two edges of the same crystalline, (-) and (+) charges are pulled toward (+) and (-) electrodes, respectively. The distance between (+) and (-) charge centers increases and as a result crystal size increases. If the direction of the field is changed, the same sign charges repel each other and the crystal size decreases. Thus, electrical effect converts to mechanical size. This behavior is called piezoelectric properties.

3.5 The Conductors, Insulators and Semiconductors

3.5.1 Semiconductors and Some Properties of Semiconductors

The semiconductors are substances that do not allow the flow until a value of electric current and show an infinite small resistance after this value. Semiconductors are 3rd and 5th group in the periodic table. This means that donor or acceptor of electron in the last orbital is more than conductor, is less than the insulator.

Conductors: Pt, Ni, Au, Cu, Al, Fe etc.

Insulation: Ebonite, Glass, Wood, Water etc.

Semiconductors: S, D, B, Al, In etc.

- Conductivity values are $10^{10} (\Omega\text{cm})^{-1}$ and $10^{-22} (\Omega\text{cm})^{-1}$ for metals and insulating, respectively. Conductivity of semiconductors varies between these values.
- In some cases, semiconductors act as a semiconductor, but they sometimes act as a conductor.

- Semiconductors may be in elemental or compound form.
- Semiconductors cannot conduct electricity at low temperatures and act as an insulator. Because the energy of electron above full band (valance band) is smaller than E_g .
- While holes contribute to current from the valence band, electrons contribute to current from the conduction band.
- If the conductivity band interferences with the semi full band, materials become conductive.

3.5.2 Energy Levels and Band Structures of Semiconductors

As it is known, electrons continuously revolve around the nucleus of atoms in specific orbits. Moving electrons remain in orbit by the effect of two forces.

- 1- The pulling force of nucleus
- 2- The centrifugal force generated by rotation motion

3.5.2.1 Energy Levels

Electrons have certain energy due to the motion on the each orbit. If the energy is applied over the energy of electron, intermediate electrons transfer to a higher orbit. The electron leaves from atom with energy that is applied to valence electron. Free of valence electron means that material gains conductivity.

The factors that gives energy to the valence electrons:

- Electrical effect
- Thermal effect
- Light effect
- Bombardment effect carried out by electrons
- Magnetic effect

But the energy levels in which the valence electrons free vary according to the structure of material as follows:

- A low level of energy is enough for conductors.
- A quite a lot energy is required in the semiconductor.
- A very great must be given energy for isolators.

3.5.2.2 Band Structures

Degree of conductivity of substances is defined by band energies.

Valence band energy level:

Each of valence electrons has a specific energy level. It is called the valence band energy (Fig.3.1).

Conductivity band energy level:

There is an energy that is required to separate the valence electrons from the atoms. This energy is defined as conduction band energy.

The energy that should be given for conduction in the conductors:

As can be seen from Figure 3.1, the energy level of valence band and the energy level of conduction band of the conductors are adjacent. Therefore, many valence electrons become free with a small energy applied.

The energy that should be given for conduction in the semiconductors:

As can be seen from Figure 3.1, there is a certain gap band between the valence band and the conduction band of the semiconductors. If an additional energy is applied to valance electron as the band gap energy, the semiconductor becomes conductor.

The energy that should be given for conduction in the isolators:

As can be seen from Figure 3.1, there is a wide band gap in the insulators. So a quite great energy must be applied to the electrons for transition to the conduction band from the valence band.

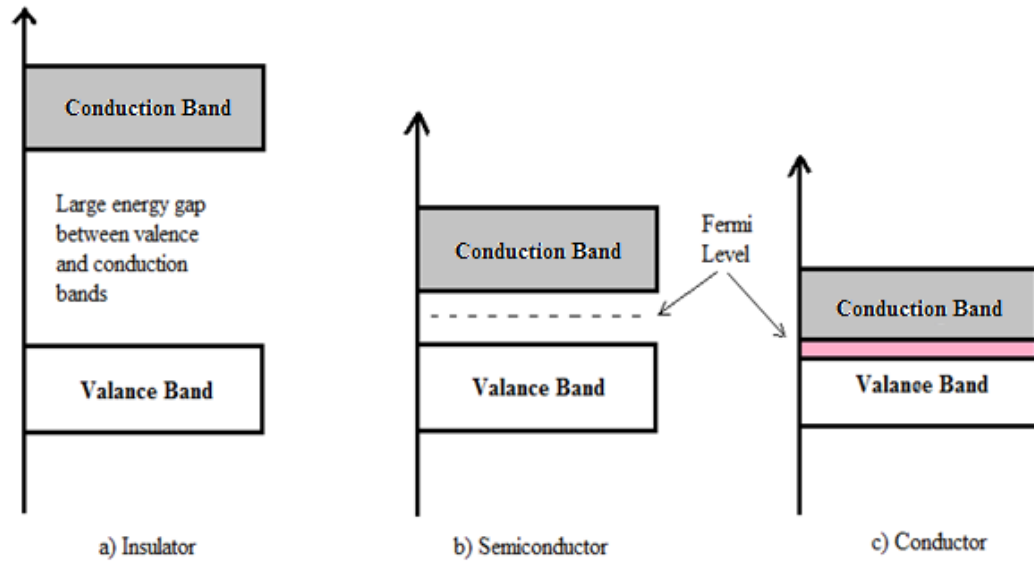


Figure 3.1. The varying band energies according to the conductivity band a) Conductor, b) Semiconductor, c) Isolator

The all materials are composed of atoms on Earth. The atom consists of a nucleus and electrons that move in different orbits around the nucleus. Electrons have a negative electrical charge. The movement of electrons separated from atom creates an electric current with an interaction within a circuit. The movement of electrons is not the same in each substance. According to the electron movement substances are divided into three:

- Conductors
- Isolators
- Semiconductors

3.5.3 Conductors and Some Properties of Conductors

- Conductors are good transmit the electric current.
- Electrons which are in the outer orbit of the atom weakly connect to atom. They are easily separated from atom by the heat, light and electrical effects.
- Electrons that is in the outer orbit is called valance electron.
- Metals, some liquids and gases are used as conductor. It is well known that metals are better conductors than liquids and gases.

- Metals are divided into groups as good conductors and bad conductors.
- The metals that have 1 valence-electron are good conductors. As an example; gold, silver, copper.
- When compared to gold and silver, because copper can not obtained full pure, Although it is a bit worse conductor, it is cheap and abundant, it is the most widely used metal.

3.5.4 Insulators

- They are substances that can not transmit the electric current. For example glass, mica, paper, rubber and plastic materials.
- Electrons are tightly connected to atoms.
- Due to the number of electrons in the outer orbit is 8 and close to 8, The detracting of electrons from the atoms is difficult.

Table 3.1. Some insulator and place of use

NAME	PLACE OF USE
Germanium (Ge) (basic element)	Diode, transistor, integrated circuit
Silicon (Si) (basic element)	Diode, transistor, integrated circuit
Selenium (Se) (basic element)	Diode
Copper oxide (CuO) (Compound element)	Diode
Gallium Arsenide (Ga As) (Compound element)	Tunnel diode, laser, photodiode, LED
Indium phosphide (In P) (Compound element)	Diode, transistor
Lead Sulfur (Pb S) (Compound element)	Solar battery (photocell)

3.6 ZnO Based Semiconductors

The last 10 years, the interest has been increased rapidly in the one-dimensional (1D) material. Due to the reduction of material size and orientation, many new electrical, mechanical, chemical and optical properties are obtained. Zinc oxide (ZnO) is an unique material that have semiconductor, piezoelectric and pyroelectric properties. Therefore, especially nano-sized ZnO structures have a wide interest in photonic, optical and electronic applications.

3.6.1 Crystal Structure of ZnO

- ZnO semiconductors are used as DMS in nowadays and it is the most advantageous semiconductors. Zinc oxide (ZnO) is a degenerate semiconductor and has a wide band gap (3.3 eV), a large binding exciton energy (60 MeV) and transparent feature in the visible region. Because of these properties, they are widely used in solar cells, flat panel displays and other optoelectronic applications.

- Zinc oxide is an inorganic compound and its formula is ZnO. ZnO is usually called as II – VI group semiconductors in materials science because zinc and oxygen belongs to II. and VI. group of the periodic table, respectively,

- ZnO arises in the form of three different crystals. These are hexagonal (Wurtzite), cubic zinc blende and rarely cubic rock salt (Fig.3.2).

- Wurtzite structure is the most stable at ambient conditions and hence is the most common.

- Lattice constants are $a = 3.25\text{\AA}$ ve $c = 5.20\text{\AA}$. $c/a \sim 1.60$ value is close to the ideal value of hexagonal cell ($c/a = 1.633$).

- ZnO has usually n-type character.

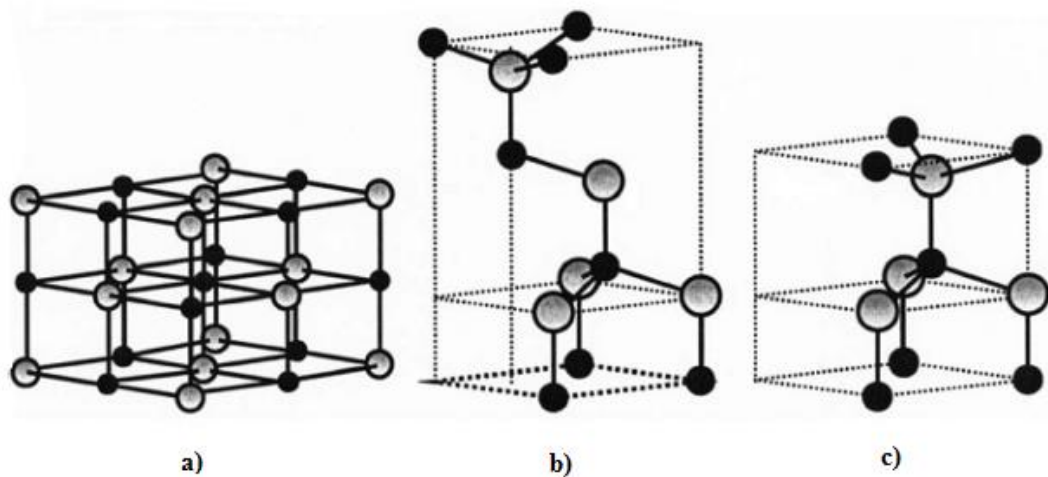


Figure 3.2 Crystal structures of ZnO a) rock salt, b) wurtzite and c) zinc blende (Ozgur et al., 2005)

3.7 Semiconductor Nano Thin Films

Centuries before, the use of nano thin films as decoration on glass and ceramic has attracted the attention on semiconductor technology until today from 1940's. Especially in recent years, the science of semiconductor nano thin film that has an important place in scientific and technological researches has developed as the basic research topic all over the world. Nano thin films are formed as a thin layer by coating of atoms or molecules of required material on the substrate using the different production techniques and a thickness is typically about 1 μm . The importance of coating and the synthesis of new materials for the industry have led to a large and significant increase in nano thin film processing technology. Just now, these developments advance at scientific and technological areas in the microelectronics, optics and nanotechnology. Films are important for the production in many areas. These are areas such as heat-resistant material coating processes and protected clothing, the increasing of material lifetime, the protection of materials against to atmosphere pressure and heat, solar cells, optical and electronic circuits, the memory portions of computers (Eckertova, 1986).

Nowadays the rapid change in the thin-film materials creates new opportunities for the development of new processes, materials and technologies. Therefore many experiments are carried out to improve of the progression in this area and model systems are developed.

In the recent years the production of semiconductor nano thin film materials that are nanometer size has a significant point of interest. Nano-crystal semiconductor materials that are nano thin film format allow to improving of characteristic properties of materials. A gradual transition is observed to molecular structure from rigid structure due to the increasing the number of particle that forms the material in this type materials.

Semiconductor nano thin films are divided into three main groups depending on reduction of structural perfection degrees. These are; i) single crystal films that are called as single layer (homo epitaxial) and are precipitated upon the single crystal of same material, ii) single crystal films that are called as multilayer (hetero epitaxial) and are grown upon the single crystal of different material, iii)

polycrystalline films that are precipitated upon the amorphous substrates such as glass, quartz. Polycrystalline films are semiconductor materials that are grown on substrates such as metal, glass, ceramic, granite which have a large surface, have many applications such as solar cell, semiconductor photodetectors, and diodes and are obtained by simple and various methods (Sze, 1981). In this study, ZnO based diluted magnetic semiconductors that are in the third group are produced by the sol-gel method.

3.7.1 Piezoelectric Properties

Piezoelectric effect is one of the important features of ZnO is inclusively studied in different application areas such as pressure sensing, acoustic wave production, acoustic-optic modulators. The origin of piezoelectric behavior is hidden in the crystal structure of zinc and oxygen atoms that are connected to the tetrahedral structure. Positive and negative charge centers can be changed with lattice deformation originates from an external pressure in the crystal structure that does not have central symmetry. Deformation leads to both formation of the regional poles and macroscopic dipole moment in the all crystal structure.

ZnO that is among the semiconductors forms by tetrahedral structure has a high piezoelectric tensor which enables the electro-mechanical polarization. The investigation of piezoelectric behavior of different ZnO structures is important for the development of potential nano-electromechanical systems in future.

3.7.2 Electrical Properties

ZnO is a material that exhibits electrically very different properties to conductivity from insulator. Although ZnO that has defects such as oxygen vacancy and interstitial zinc atoms in the crystal structure are evaluated in n-type semiconductors groups, it shows p-type conductivity under certain conditions (Fan and Lu, 2005). In 1930, Wagner et al. investigated the variation of electrical conductivity of ZnO (Wagner and Schottky, 1930). Although the conductivity of the material slightly increased under air atmosphere at 900°C, it was observed that value

of conductivity showed a significantly increase at the same temperature under reductor atmosphere. The greatest reason is that oxygen vacancies form in the structure becomes carrier with increasing temperature under reductor atmosphere.

The non-linear current-voltage (I-V) characteristic of ZnO is first discovered in 1968 by Matsuoka. This feature is the change of current value that occurs corresponds to the changing voltage value. In other words, it is the change of resistance of the material.

Today, electronic circuits are preserved against voltage changes by ZnO varistor with the discovery of this feature that is called varistor effect (Steele, 1991). The electrical properties of ZnO that depends on the direction show change because it has an anisotropic crystal structure.

3.7.3 Magnetic Properties

One of the factors which plays role in achievement to the present level of television technology is zinc oxide that significantly improves to the magnetic properties of nickel-iron alloys. In 1946, Snoek showed that if ZnO substitutes with certain proportion of NiO, the magnetic properties of ferrite-based materials increase (Snoek, 1946). For example, addition of ZnO at the molar weight percentages of 35% is seen that the magnetic permeability of the ferrite increases by 3000%. In 1948, Neel from the Philips Company explained to basics of this effect (Neel, 1948). Thus, Zn^{+2} atoms added in the structure push Fe^{+3} atoms from the tetrahedral position.

Octahedral units that contain more magnetic atom than tetrahedrals are the most important reason of a sharp increase in the magnetic properties. In addition to improving the magnetic properties, zinc oxide addition reduces the Curie temperature of structure and decreases electrical losses.

Recently, it is determined that ZnO is not only doping material but also a material that exhibits ferromagnetic properties with some additions. It is observed that Mn, Co and Fe atoms added to the structure allow having ferromagnetic property of material in ZnO nano thin film applications (Fan and Lu, 2005).

3.7.4 Optical Properties

In 1947 Destria found a new method for the production of light using zinc oxide. Destria observed that when changing voltage values is applied to zinc oxide distributed in the oil that is placed between two conducting plates, continuous spectrum is observed (Destriau, 1947). This feature shows up as a result of having high activation energy of 60 meV and band gap of 3.4 eV of ZnO compared with GaN (25 MeV). Other optical property of ZnO is a high diffraction index (~ 2.0). Because of the diffraction index is immediately after from the diamond, it has an effective usage within whitening pigments and UV protectors (Wang, 2004).

3.8 Magnetic Properties of Solids

Materials may be classified by their response to externally applied magnetic fields as diamagnetic, paramagnetic, ferromagnetic, ferrimagnetic or antiferromagnetic. These materials exhibit different responses to the applied magnetic field.

3.8.1 Diamagnetism

Diamagnetism is a property of all materials and opposes applied magnetic fields. The orbital motion of electrons creates small atomic current loops, which produce magnetic fields. When an external magnetic field is applied to a material, these current loops will tend to align in such a way as to oppose the applied field. This may be viewed as an atomic version of Lenz's law: induced magnetic fields tend to oppose the change which created them. Materials in which this effect is the only magnetic response are called diamagnetic. All materials are naturally diamagnetic, but if the atoms have some net magnetic moment as in paramagnetic materials, or if there is long-range ordering of atomic magnetic moments as in ferromagnetic materials, these stronger effects are always dominant. Diamagnetism is the residual magnetic behavior when materials are neither paramagnetic nor ferromagnetic.

Any conductor will show a strong diamagnetic effect in the presence of changing magnetic fields because circulating currents will be generated in the conductor to oppose the magnetic field changes. A superconductor will be a perfect diamagnet since there is no resistance to the forming of the current loops.

3.8.2 Paramagnetism

Paramagnetism is stronger than diamagnetism and produces magnetization in the direction of the applied field, and proportional to the applied field. This class of materials, some of the atoms or ions in the material have a net magnetic moment due to unpaired electrons in partially filled orbitals. One of the most important atoms with unpaired electrons is iron. However, the individual magnetic moments do not interact magnetically, and like diamagnetism, the magnetization is zero when the field is removed. In the presence of a field, there is now a partial alignment of the atomic magnetic moments in the direction of the field, resulting in a net positive magnetization and positive susceptibility.

3.8.3 Ferromagnetism

Ferromagnetic effects are very large, producing magnetizations sometimes orders of magnitude greater than the applied field and as such are much larger than either diamagnetic or paramagnetic effects.

When you think of magnetic materials, you probably think of iron, nickel or magnetite. Unlike paramagnetic materials, the atomic moments in these materials exhibit very strong interactions. These interactions are produced by electronic exchange forces and result in a parallel or antiparallel alignment of atomic moments. Exchange forces are very large, equivalent to a field on the order of 1000 Tesla, or approximately a 100 million times the strength of the earth's field. Ferromagnetic materials exhibit parallel alignment of moments resulting in large net magnetization even in the absence of a magnetic field. The elements Fe, Ni, and Co and many of their alloys are typical ferromagnetic materials.

CHAPTER 4

CHARACTERIZATION OF ZnO BASED MATERIALS

4.1 Structural Analyses of Materials

4.1.1 X-Rays Diffraction

The periodicity of atoms or atomic groups is called crystal structure in a certain symmetry arrangement in the three-dimensional space. The information about the structure of crystalline solids is obtained from the examining as macroscopic or microscopic of external appearance of the sample. However we can not obtain information about the structure using visible light. Because the wavelength of visible light is quite large compared with the gap between atom and molecule of crystal. Wavelength of X-ray is same size with the gap in the crystal. So obtaining information about the crystal is easy using X-rays.

The viewing of atomic structure of a material is possible using various electron microscopes that have high resolution. But the diffraction spectra must be used to determine unknown structures or structural parameters. The most commonly diffraction technique used to examine the crystal structure of the solid is X-ray diffraction. X-ray diffraction is used to study on the crystal structures of materials. The energy of X-ray is inversely proportional with the wavelength of X-ray and energy is $E = hc/\lambda$. Wavelength of X-ray varies between 0.1 Å and 100 Å. X-rays that varies between 0.2 Å and 2.5 Å are used for crystal studies.

A simple chemical analysis that performed for a material can only provide information elements in the material. However the qualitative analysis can be performed by determining the type of chemical components and the phases of these components in the material using the X-ray diffraction.

The same time quantitative analysis is possible, because the peak intensity of component depends on the proportion of these components in material. In this way, an unknown material can be determined using diffraction spectrum and JCPD (Joint Committee on Powder Diffraction Standards) cards. The unknown material used in chemical analysis is not damaged by XRD and also a small part of the material is enough for this analysis.

The information about the crystallization of the material can be obtained by the intensity of the peaks in the spectrum, the half peak width and intensity of background. XRD spectra of the material that has a good crystallization has a minimum background intensity, a high peak intensity and peak that has narrow half peak width. If the intensity of background is high, half peak width is large, intensity of the peak is low, it can be said that level of the crystallization is bad.

4.1.1.2 Properties of X-Rays

- X-rays are invisible.
- X-rays have no mass.
- X-rays travel at the speed of light in a vacuum.
- X-rays cannot be optically focused.
- The X-ray beam used in diagnostic radiography comprises many photons that have much different energy.
- X-rays travel in straight lines.
- X-rays can cause some substances to fluoresce.
- X-rays cause chemical changes to occur in radiographic and photographic film.
- X-rays can be absorbed or scattered by tissues in the human body.
- X-rays can produce secondary radiation.
- X-rays can cause chemical and biologic damage to living tissue.

In this thesis, XRD measurements are performed by Bruker D8 Advance X-ray powder diffractometer (Figure 4.1) using Cu – K_{α} radiation in the range of $30 \leq 2\theta \leq 90^{\circ}$ at a scan speed of $2^{\circ}/\text{min}$. The phase structures and lattice

parameters of samples are determined by Bruker-EVA 10.0.1.0 analysis program and ICDD PDF2-2002 data cards.



Figure 4.1. X-Ray Diffractometer

4.1.2 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is one of the most versatile instruments available for the examination and analysis of the microstructure morphology and chemical composition characterizations. It is necessary to know the basic principles of light optics in order to understand the fundamentals of electron microscopy. The unaided eye can discriminate objects subtending about $1/60^\circ$ visual angle, corresponding to a resolution of ~ 0.1 mm (at the optimum viewing distance of 25 cm). Optical microscopy has the limit of resolution of ~ 2.000 Å by enlarging the visual angle through optical lens. Light microscopy has been, and continuous to be, of great importance to scientific research. Since the discovery that electrons can be deflected by the magnetic field in numerous experiments in the 1980s (Wells, 1974), electron microscopy has been developed by replacing the light source with high-energy electron beam (Zhou et al., 2006).

- Accelerating voltage 100 V – 30000 V.
- Resolution 0.7 nm – 5 nm (depends on the kind of electron gun)
- Samples should be electrically conductive and also be mounted electrically conductive on the holder
- Size of sample is limited by the specimen chamber (Su, 2010)

4.1.2.1 Sample Preparation

- Remove all water, solvents, or other materials that could vaporize while in the vacuum.
- Firmly mount all the samples.
- Non-metallic samples, such as plants, fingernails, and ceramics, should be coated so they are electrically conductive.

4.1.2.2 Magnification

In a SEM, magnification results from the ratio of the dimensions of the raster on the specimen and the raster on the display device. Assuming that the display screen has a fixed size, higher magnification results from reducing the size of the raster on the specimen, and vice versa. Magnification is therefore controlled by the current supplied to the x, y scanning coils, and not by objective lens power.

In this thesis, surface morphology and elemental analyses of samples are performed by Quanta FEG 250 scanning electron microscopy (Figure 4.2).

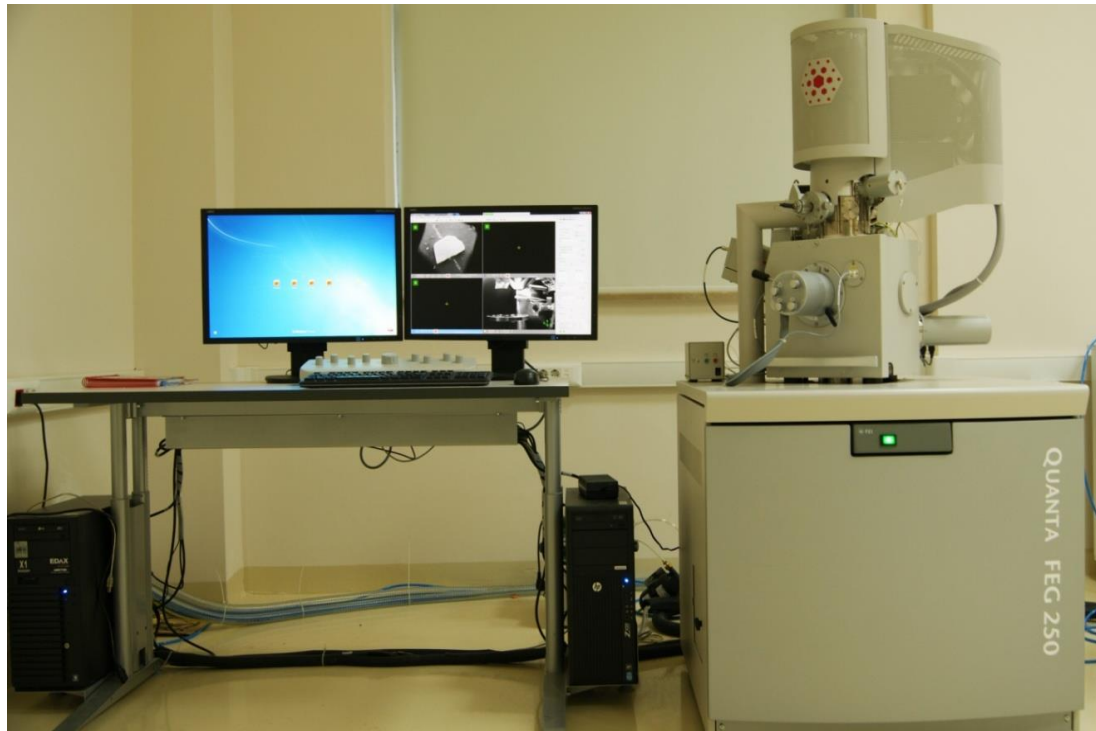


Figure 4.2. Scanning Electron Microscopy (Quanta FEG 250)

4.1.3 Atomic Force Microscopy (AFM)

The surface of the many conductor material is investigated successfully at the atomic scale using Scanning Tunneling Microscopy (STM). The success of STM has led to the development of new scanning tip (probe) microscopes. Atomic Force Microscopy that is one of them is a technique that can measure the surface topography up to 100 – 150 microns from angstrom level. AFM is invented by Binnig, Quate and Gerberat at 1986 (Binnig et al.,1986). Technical is based on inter-atomic interactions between technical tip-surface. Working principle of a typical AFM is very simple. As seen from the Figure 4.3, surface of sample is scanned by a tip that is placed in the end of cantilever, length of few microns and atomic size. Inter-atomic forces (10^{-11} - 10^{-6} N) between the tip-surface cause to deviation of the elastic holder cantilever during scanning. The surface topography of the area scanned on the surface of sample is obtained by measuring of this deviation. The information about surface mode of growth, roughness of the sample, type and density of defects on the sample surface can obtained from the surface topography of sample by Atomic Force Microscopy (AFM). Unlike the STM, the major advantage of the technique is not need to be electrically conductive of material. AFM does not require

vacuum as other techniques (SEM, TEM, STM) used for similar purposes and it can operate in air and liquid. Also it does not damage the surface because it does not require sample preparation such as coating. Therefore it is a versatile, fast and low cost technique. The resolution of the AFM is better than Scanning Electron Microscope (SEM). When the appropriate conditions are provided, it is comparable to STM and Tunneling Electron Microscopy (TEM). An important disadvantage of AFM techniques are that it is affected from piezoelectric material, the image quality is limited by the curvature radius of tip.

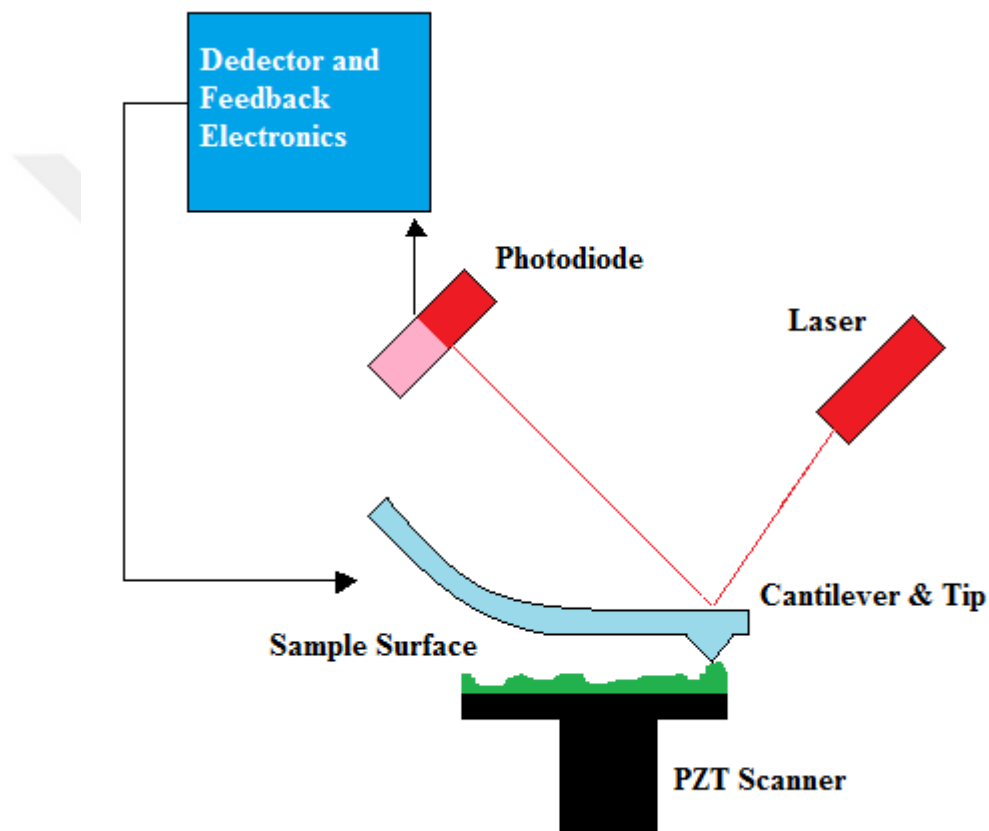


Figure 4.3. Surface of sample is scanned by tip

AFM measurements are carried out in three different modes including contact, semicontact or tapping and non-contact. The process mode is determined by the tip-sample distance. The variation of forces between tip and surface of sample with distance is given in Figure 4.4. Firstly the tip is approximated to sample and tip is pulled weakly by surface of sample (left side of the curve). This attraction increases until distance where electron clouds of atoms on surface of sample and tip start to repulsion electrostatically each other with reduction of the tip-surface distance. When the distance is slightly reduced, repulsive force increases and net

force is zero at a distance that is in the range of chemical bond length (several Å). At this point, physical contact starts between the tip and surface of sample. The repulsive force is dominant in the next closer distance (right side of the curve). The distance of tip-sample is a several Å range in the contact mode. Therefore tip slightly keeps in physical touch with the surface of sample. In this mode, surface topography can be obtained in two different ways. i) from deviation of cantilever by the scanning result at a constant height and ii) from the variation of height of surface with a constant deviation of cantilever. In non-contact mode, the distance of tip-sample is about 50–150 Å range. In this case, tip is exposed to weak attractive forces. This attractive force is weaker than force of the contact mode and as can be seen from the force-distance curve, surface is less sensitive to change in height. Therefore, a different mechanism than the contact mode is used to obtain the surface topography in this mode. Cantilever is vibrated at a frequency near to the resonance frequency. When the tip is pulled to the surface, changes of frequency or amplitude are detected. Non-contact measurements are quite affected from external vibrations, the quality of tip and cantilever. Semi-contact mode is a slightly different form of non-contact mode. In this mode, the cantilever is vibrated in its resonance frequency. Tip provides physical contact with surface of the sample at each oscillation. When the tip is pulled to the surface, change that occurs with the oscillation intensity is taken as a basis. However in this mode, the forces are higher than non-contact mode, measurement is insensitive to quality of tip or external vibrations (Binnig et al., 1986).

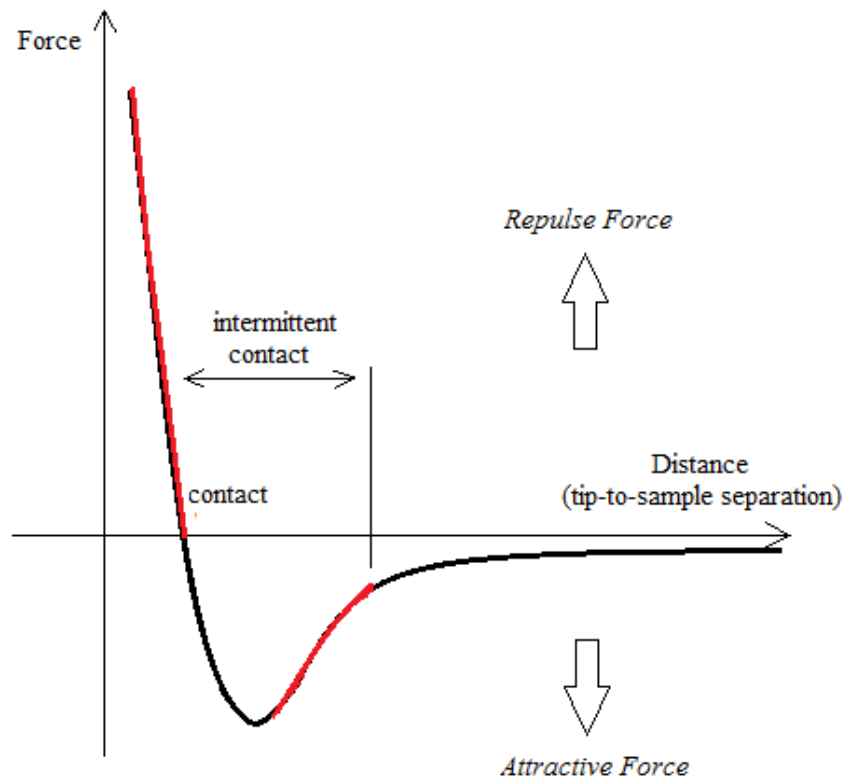


Figure 4.4. The variation of the Van der Waals forces between the tip-sample with the distance

In this thesis, AFM measurements are performed by Bruker model atomic force microscopy (Figure 4.5). The surface roughness of the material is determined using this analysis.

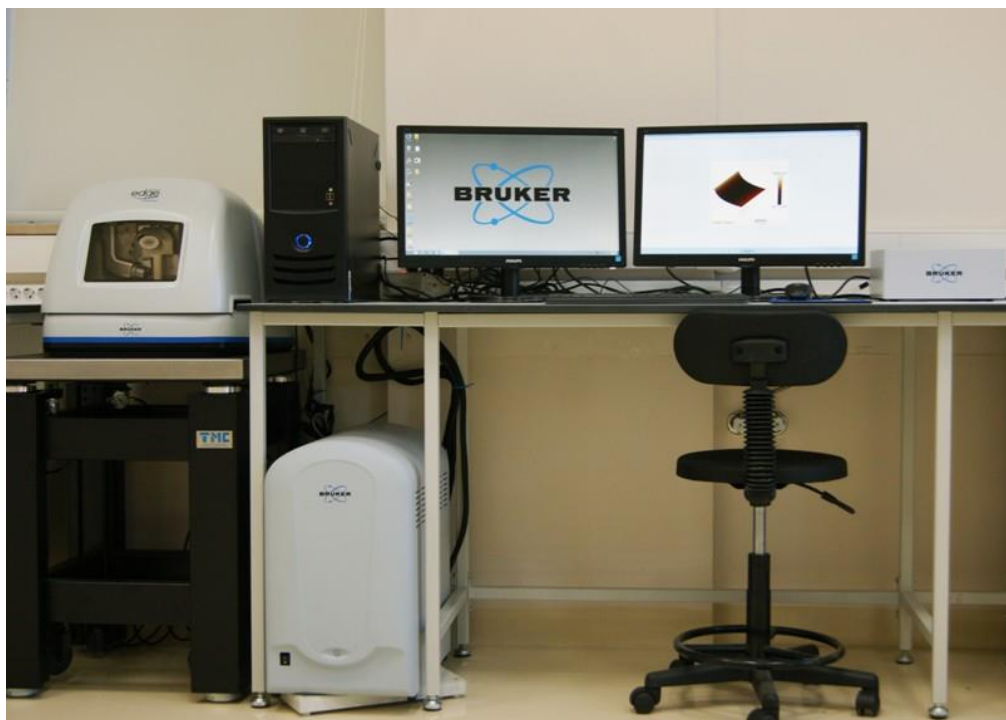


Figure 4.5. Atomic Force Microscopy (BRUKER)

4.2 Mechanical Characterization of Materials

4.2.1 Introduction

Nowadays it seems that technological device, equipment, vehicles, machine and constructions which are manufactured and used for various industrial purposes are manufactured from materials such as metal, ceramic, glass, plastic, paper, composites that have different properties. The selection of the most qualified, the most durable and the most economic materials is very important due to the service conditions, the applied load type and value and the place of use of each product by design engineers. The mechanic, electrical, optical, thermal, corrosion properties of materials must be known very well for selection of material.

Behavior of materials under a specific load is called mechanical properties of the materials (Şahin et al., 2007; Sangwall et al., 2002; Graaf et al., 2004). The mechanical properties of materials vary according to the type of applied load.

Generally it is seen that two different load types as static or dynamic effect to materials. The various mechanical properties of materials are determined depending on these applied load type. For example, the fatigue toughness is one of important properties of the materials is identified by the behavior of the material under the applied dynamic load. On the other hand, the properties of materials such as the tensile strength, yield strength, fracture toughness, toughness, ductility, elastic modulus and hardness are determined by the behavior of the material under applied static load.

The different test methods are used to determine the mechanical properties of materials. The most common test methods are (1) tensile test, (2) compression test, (3) torsion test, (4) bending test (5), hardness test and (6) creep test using static load. Using dynamic load, the most common test methods are (1) fatigue test and (2) notch impact test.

4.2.2 Vickers Microhardness Tester

In this thesis, the mechanical characterizations of nano bulk materials are performed using Shimadzu brand HMV-2 model digital microhardness tester (Figure 4.6). Vickers microhardness test is used for measurements. In the Vickers hardness test, indentation tip that is the pyramid-shaped is used. The apex angle of pyramid made from diamond is $\alpha = 136^\circ$.

In the Vickers hardness test, tip is immersed on the surface of the material under a load selected according to the material (such as 10, 25, 50, 100, 200, 300, 400, 500 g and 1 kg) with a certain period (such as 10, 15 s) and diagonal length of indentation is measured. Vickers microhardness value is calculated by Eqn. (4.1).

$$H_v = 1854.4 \left(\frac{F}{d^2} \right) \quad (GPa) \quad (4.1)$$

where, H_v is the Vickers microhardness in GPa, F is the applied load in N and d is the diagonal length of the indentation in μm .

In order to investigate the effect of doping rate on the mechanical properties, Vickers microhardness measurements are performed on the sample surfaces at the room temperature. The applied load is changed in the range 0.245 – 2.940 N for 10 s. Microhardness values are determined with an average of 7 readings at different parts of the sample surfaces making sure that the indentations do not overlap.

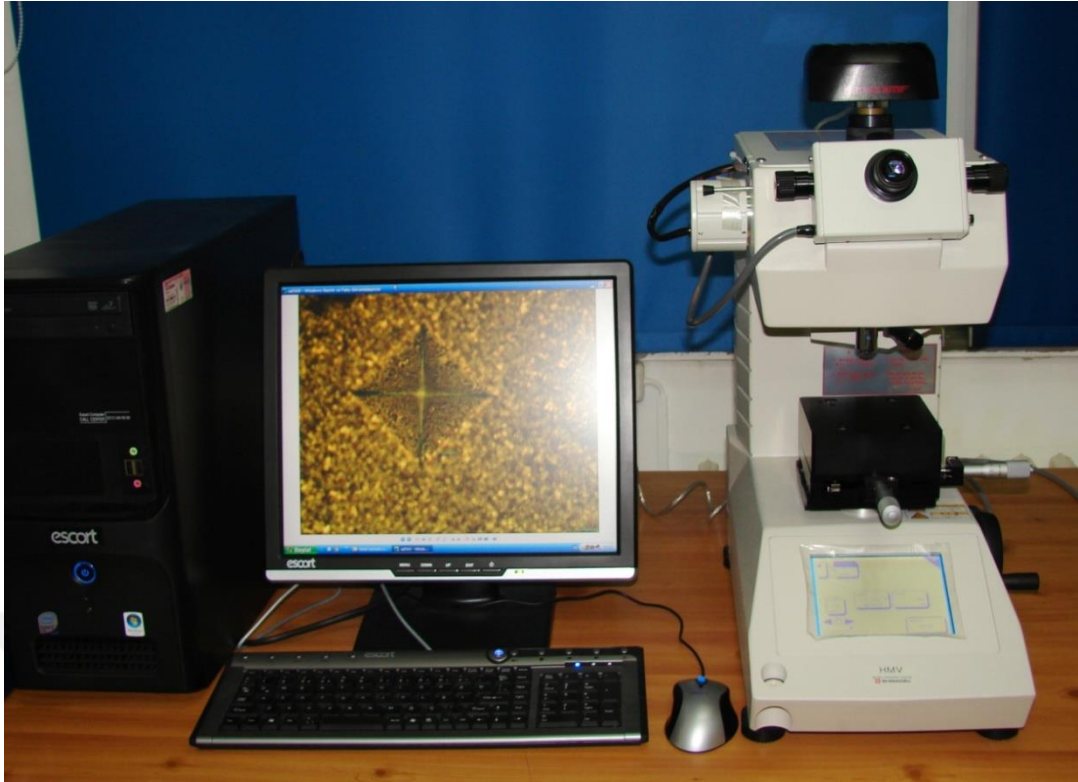


Figure 4.6. HMV Microhardness Device (SHIMADZU)

4.2.3 Benefits and Losses of Vickers Hardness Method

Benefits:

- It is quite accurate and sensitive method.
- Hardness of the material is not limiter.
The thickness of control part or surface size of control part does not affect the result.
- A very few deterioration occurs on the control surface.
- Successful results obtain with very little control force.
- It is the most used effective methods.

Losses:

- The evaluation of the results takes more time compared to other methods.
- It is sensitive to dash and rocking.

- It is expensive as optical because the very sensitive process is performed.

4.3 Optical Characterization of Materials

The spectrophotometer which is the SHIMADZU brand and can measure in the UV–Vis region is used for determining the optical properties of ZnO based nano thin films (Figure 4.7). The optical transmission and reflection properties of nano thin films are examined by spectrophotometer. Measurements are performed in the range of 190 – 1100 nm wavelength. The optical band gap of nano thin film is calculated from the data obtained from results of measurement.



Figure 4.7. UV-VIS Spectrophotometer

4.4 Electrical Characterizations of Materials

The electrical properties of nano thin films (resistance, conductivity type, carrier concentration and mobility) are determined using the four-probe Van der Pauw technique by HMS-5000 Hall effect measurement system (Figure 4.8). Van der Pauw method is used to measure the resistivity of the thin layer where the four contacts are placed around the sample (Kaufmann, 2003; Valdes, 1954; Hall, 1967).



Figure 4.8. HMS5000 system full set view

The four point probe method as shown in Figure 4.9 consists probes that have four equally distance positioned on the same plane. Probe tips must be quite small compared with a that is distance between probes. It is assumed that there is an ohmic contact between probe and sample. Generally, current (I) passes through two external probes. Voltage (V) is measured through two internal probes.

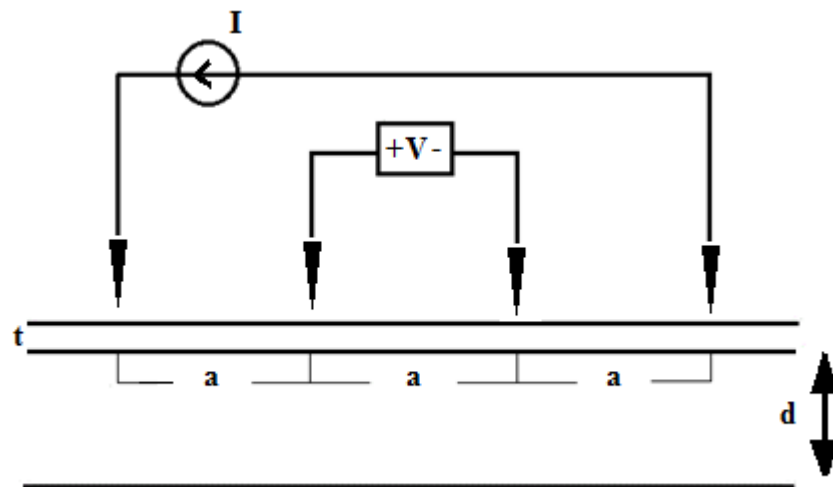


Figure 4.9. The schematic diagram of 4PP the method

HMS5000 system mainly consists of “Main body System”, “Magnet Kit and temperature controlling system” and “software program”.

4.5 Magnetic Characterizations of Materials

The magnetic measurements are carried out by vibrating sample magnetometer (VSM). The schematic diagram of VSM system is given below (Figure 4.10)

- VSM is a device used to measure magnetic moment and hysteresis
- It uses the electromagnetic induction and lock-in principle of measurement
- Commercially available VSM magnetometers have sensitivity below 10^{-9} Am⁻² (depending on acquisition time).

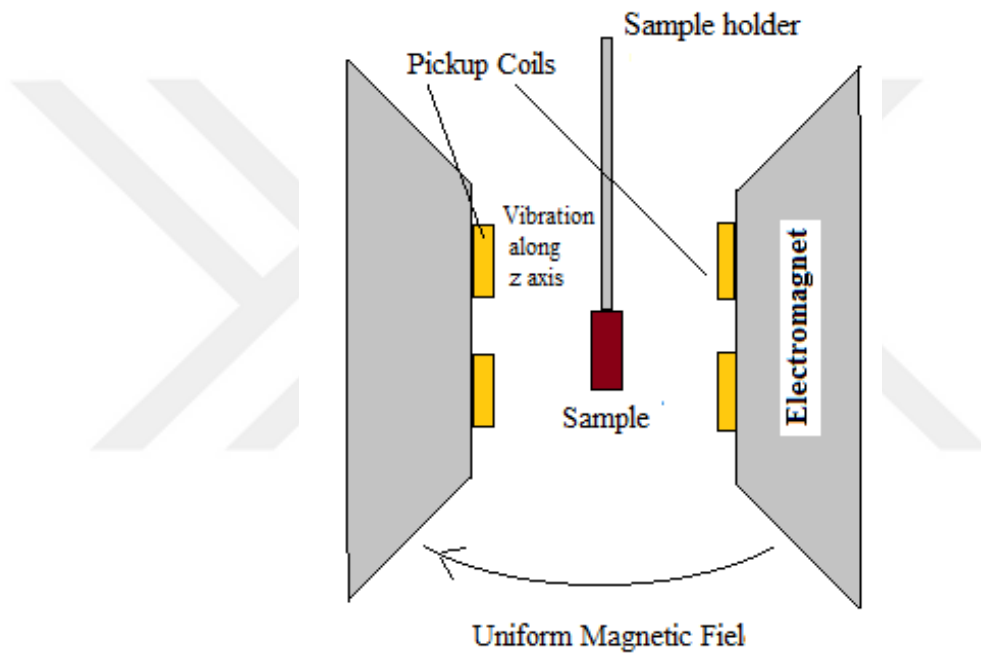


Figure 4.10. The schematic diagram of VSM system

CHAPTER 5

PRODUCTION METHOD OF NANO THIN FILM AND NANO BULK MATERIALS

In this study, all nano thin films and nano bulk materials are produced by sol-gel method. Information about the sol-gel method is described below.

5.1 Sol-Gel Process

Sol-gel technology is common name that is given to the technique of the production such as ceramic, glass and composite materials.

- A solution is formed by combining of inorganic compounds such as metal alkoxide solution or metal powders, nitrates, hydroxides and oxides with acid and water in certain amounts.
- As a result of mixing of the solution at certain temperatures, a consecutive series of chemical reactions occur in solution and a gelation occurs by electro-chemical interactions of surface charge of particles, this gelation grows gradually and reaches all points in the system and a gel form
 - **Sol**; is a stable suspension of colloidal solid particles in the liquid.
 - **Colloid**; are particles have 500 nm ($1\text{ nm} = 10^{-9}\text{ m}$) and below sizes. These particles are invisible using normal optical microscope. Because the maximum sizes are equal to the wavelength of light.
 - **Gel**; is called precipitate that is obtained by precipitation of colloidal particles and contains large amount of water. The gel is an interface phases between solid and liquid.

5.1.1 Advantages of Sol-Gel Method

- Chemical features of method can be controlled.
- Better homogeneity is provided compared with raw material.
- Size of powder is obtained under micron.
- The low temperatures are adequate for the production.
- Obtaining of new materials and properties is possible.
- It does not cause air pollution.

5.1.2 Disadvantages of Sol-Gel Method

- Costs of the powders produced by this method are high.
- During the process, the amount of shrinkage is large.
- Structure may include small pores.
- Residues of hydroxyl and carbon can take place in structure.
- Organic solvents are harmful to health.
- The processing time is long.

5.2 Production of Nano Bulk Materials

In this thesis, firstly transition metal and rare earth element doped DMS nano bulk materials which have in the ZnO based dual and ternary structure are produced. These materials are produced as 4 groups. Each series are prepared for different doping rates among these. These series of materials are as follows.

5.2.1 Transition metal doped DMS materials which have in the ZnO based dual structure of $\text{Zn}_{1-x}\text{B}_x\text{O}$ (B=Co)

$\text{Zn}_{1-x}\text{Co}_x\text{O}$ system is prepared as polycrystalline nanoparticles with various compositions ($0.0 < x < 0.10$) using sol-gel techniques. Zinc acetate dihydrate and cobalt acetate tetrahydrate are used as precursors. Methanol and acetyl acetone are

used as a solvent to preparing a homogenous solution. After weighing at appropriate rates, the cover of beakers are closed and the precursors and solvents are stirred using the heater magnetic stirrer at 60°C for 8 h until a transparent solution is obtained (Figure 5.1.a and b). Then the cover of beakers is opened and solutions are evaporated using the heater magnetic stirrer at 60°C until a gelation is observed. Finally, gelations are preheated at 200°C for 5 min in air using the muffle furnace (Figure 5.1.c). After this process, powders are obtained. Powder nanoparticles are pressed under 4 tons for 5 min into disk shaped compacts with a thickness of 2 mm and a diameter of 10 mm (Figure 5.1.d).



a)



b)



c)



d)

Figure 5.1. The production processes of nano bulk material

Before from production of doped nano bulk materials:

Firstly $\text{Zn}_{1-x}\text{Co}_x\text{O}$ (for $x = 0.05$) powders are prepared as described above using sol-gel techniques. Pressed samples are annealed at 400°C, 450°C, 500°C,

550°C and 600°C for 30 min under 5B argon for determining the optimum annealing temperature (Figure 5.2) and then XRD analysis is performed and the optimum temperature is determined as **500°C**. Finally samples are prepared at different doping rates ($x=0.1, 0.2, 0.3, 0.4, 0.5$ and 0.10) are annealed at 500°C for 30 min under 5B Ar pressure. The samples are named as $\text{Zn}_{0.99}\text{Co}_{0.01}\text{O}$, $\text{Zn}_{0.98}\text{Co}_{0.02}\text{O}$, $\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$, $\text{Zn}_{0.96}\text{Co}_{0.04}\text{O}$, $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ and $\text{Zn}_{0.90}\text{Co}_{0.10}\text{O}$.

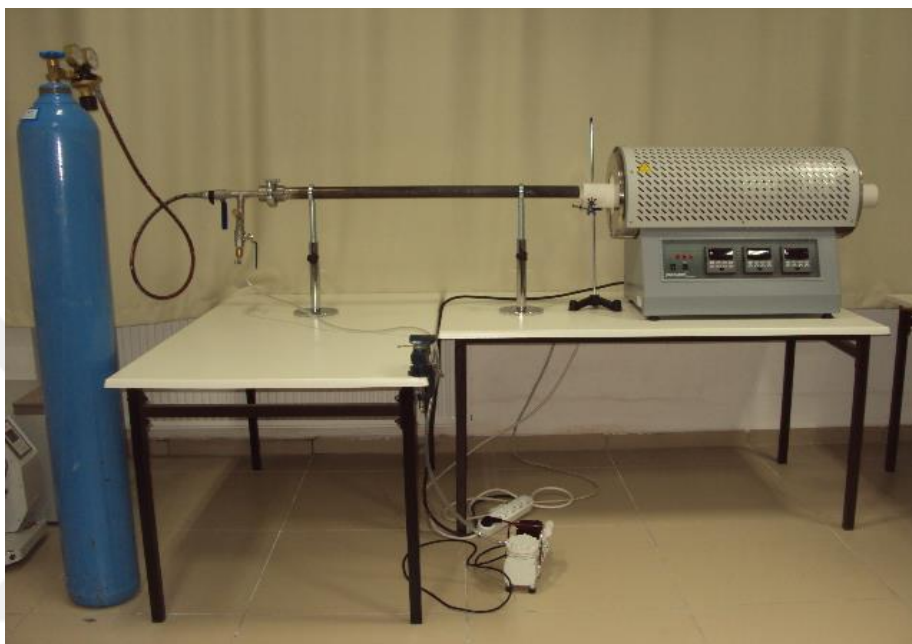


Figure 5.2. High temperature tube furnace and production system of materials under Argon pressure

5.2.2 Transition metal doped DMS materials which have in the ZnO based ternary structure of $\text{Zn}_{1-x-y}\text{B}_x\text{C}_y\text{O}$ ($\text{B}=\text{Cu}$, $\text{C}=\text{Co}$)

$\text{Zn}_{1-x-y}\text{Cu}_{0.01}\text{Co}_y\text{O}$ system is prepared as polycrystalline nanoparticles with various compositions ($x = 0.01$ and $0.0 < x < 0.05$) using sol–gel techniques. Zinc acetate dihydrate, cobalt acetate tetrahydrate and copper acetate tetrahydrate are used as precursors. Methanol and acetyl acetone are used as a solvent to preparing a homogenous solution. After weighing at appropriate rates, the precursors and solvents are stirred using the heater magnetic stirrer at 60°C for 8 h until a transparent solution is obtained.

Before from production of doped nano bulk materials:

Firstly $\text{Zn}_{1-x-y}\text{Cu}_{0.01}\text{Co}_y\text{O}$ (for $x = y = 0.05$) powders are prepared using sol-gel techniques. Then $\text{Zn}_{0.90}\text{Cu}_{0.05}\text{Co}_{0.05}\text{O}$ powders are preheated at 250°C for 5 min in air and grounded. Grounded nanoparticles are pressed under 4 tons for 5 min into disk shaped compacts with a thickness of 2 mm and a diameter of 10 mm. Pressed samples are annealed at 400°C , 450°C , 500°C , 550°C and 600°C for 30 min under 5B argon for determining the optimum annealing temperature and then XRD analysis is performed and the optimum temperature is determined as **600°C** . Finally samples are prepared at different doping rates ($x = 0.01, 0.02, 0.03, 0.04$ and 0.05) are annealed at 600°C for 30 min under 5B Ar pressure.

When $\text{Zn}_{1-x-y}\text{Cu}_x\text{Co}_y\text{O}$ ($x = 0.01, 0.02, 0.03, 0.04$ and 0.05) samples are annealed under different temperature in 5B Argon pressure, it is found that there is a peak about at 43° . This peak is not observed in $\text{Zn}_{1-x-y}\text{Co}_x\text{O}$ samples annealed in the same conditions. There is a dominant peak of Cu at this angle. This peak is not observed in the samples annealed under oxygen atmosphere. $\text{Zn}_{1-x-y}\text{Co}_x\text{Cu}_y\text{O}$ samples are prepared after from $\text{Zn}_{1-x-y}\text{Cu}_x\text{Co}_y\text{O}$ samples. Here, we aimed to determination of optimum Cu doping rate where there is no peak at 43° . According to XRD analyses of produced samples, $x = 0.01$ is determined as optimum doping rate for Cu. As can be seen from the XRD analyses, there is peak about at 43° after from this value. As a result $\text{Zn}_{1-x-y}\text{Cu}_x\text{Co}_y\text{O}$ ($x=0.01$ and $y = 0.0, 0.01, 0.02, 0.03, 0.04$ and 0.05) samples are prepared under the same conditions.

The samples are named as $\text{Zn}_{0.99}\text{Cu}_{0.01}\text{O}$, $\text{Zn}_{0.98}\text{Cu}_{0.01}\text{Co}_{0.01}\text{O}$, $\text{Zn}_{0.97}\text{Cu}_{0.01}\text{Co}_{0.02}\text{O}$, $\text{Zn}_{0.96}\text{Cu}_{0.01}\text{Co}_{0.03}\text{O}$, $\text{Zn}_{0.95}\text{Cu}_{0.01}\text{Co}_{0.04}\text{O}$ and $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$.

5.2.3 Transition metal doped DMS materials which have in the ZnO based ternary structure of $\text{Zn}_{1-x-y}\text{B}_x\text{C}_y\text{O}$ (B=Mg, C=Co)

The mixed oxides $\text{Zn}_{0.95-x}\text{Mg}_x\text{Co}_{0.05}\text{O}$ are prepared as polycrystalline nanoparticle powders with various compositions ($x = 0.01, 0.03, 0.04$ and 0.05) using the sol-gel technique. Zinc acetate dihydrate ($\text{C}_4\text{H}_6\text{O}_4\text{Zn} \cdot 2\text{H}_2\text{O}$, ZnAc), Mg 2,4

pentanedionate ($[\text{CH}_3\text{COCHC}(\text{O})\text{CH}_3]_2\text{Mg} \cdot 2\text{H}_2\text{O}$, MgAcAc) and cobalt acetate tetrahydrate ($\text{CoC}_4\text{H}_6\text{O}_4 \cdot 4\text{H}_2\text{O}$, CoAc) are used as precursor materials and methanol (CH_3OH), glacial acetic acid (GAA) and acetylacetone ($\text{C}_5\text{H}_8\text{O}_2$, AcAc) are used as solvents and chelating agent. The appropriate weighing amount of the ZnAc, MgAcAc and CoAc are put all together in a Pyrex container and dissolved in methanol. Following this, GAA and AcAc are added to container. They are mixed with a magnetic stirrer at room temperature until a transparent solution is obtained. Powder samples are prepared by gelling and drying of sol-gel derived precursors solutions in a beaker. The powders are preheated individually at 400°C for 10 min in air. The obtained powders are pressed under 4 tons of pressure. The pressed samples are annealed in air at temperature 900°C using tube furnace.

5.2.4 Rare earth element doped DMS materials which have in the ZnO based dual structure of $\text{Zn}_{1-x}\text{B}_x\text{O}$ (B=Er)

$\text{Zn}_{1-x}\text{Er}_x\text{O}$ system is prepared as polycrystalline nanoparticles with various compositions ($0.0 < x < 0.10$) using sol-gel techniques. Zinc acetate dihydrate and Erbium 2-4 pentanedionate are used as precursors. Methanol and acetyl acetone are used as a solvent to preparing a homogenous solution. After weighing at appropriate rates, the precursors and solvents are stirred using the heater magnetic stirrer at 60°C for 8 h until a transparent solution is obtained.

Before from production of doped nano bulk materials:

Firstly $\text{Zn}_{1-x}\text{Er}_x\text{O}$ (for $x = 0.05$) powders are prepared using sol-gel techniques. Then $\text{Zn}_{0.95}\text{Er}_{0.05}\text{O}$ powders are preheated at 200°C for 5 min in air and grounded. Grounded nanoparticles are pressed under 4 tons for 5 min into disk shaped compacts with a thickness of 2 mm and a diameter of 10 mm. Pressed samples are annealed at 400°C , 450°C , 500°C , 550°C and 600°C for 30 min for determining the optimum annealing temperature and then XRD analysis is performed and the optimum temperature is determined as **400°C** . Finally samples are prepared at different doping rates ($x = 0.01, 0.02, 0.03, 0.04, 0.05$ and 0.10) are annealed at

400°C for 30 min. The samples are named as $\text{Zn}_{0.99}\text{Er}_{0.01}\text{O}$, $\text{Zn}_{0.98}\text{Er}_{0.02}\text{O}$, $\text{Zn}_{0.97}\text{Er}_{0.03}\text{O}$, $\text{Zn}_{0.96}\text{Er}_{0.04}\text{O}$, $\text{Zn}_{0.95}\text{Er}_{0.05}\text{O}$ and $\text{Zn}_{0.90}\text{Er}_{0.10}\text{O}$.

5.2.5 Rare earth doped DMS materials which have in the ZnO based ternary structure of $\text{Zn}_{1-x-y}\text{B}_x\text{C}_y\text{O}$ (B=Er, C=Cd)

$\text{Zn}_{1-x-y}\text{Er}_x\text{Cd}_y\text{O}$ system is prepared as polycrystalline nanoparticles with various compositions ($x = 0.05$ and $0.0 < y < 0.10$) using sol-gel techniques. Zinc acetate dehydrate, Erbium 2-4 pentanedionate and Cadmium nitrate tetrahydrate are used as precursors. Methanol and acetyl acetone are used as a solvent to preparing a homogenous solution. After weighing at appropriate rates, the precursors and solvents are stirred using the heater magnetic stirrer at 60°C for 8 h until a transparent solution is obtained.

Before from production of doped nano bulk materials:

Firstly $\text{Zn}_{1-x-y}\text{Er}_x\text{Cd}_y\text{O}$ (for $x = 0.03$ and $y = 0.02$) powders are prepared using sol-gel techniques. Then $\text{Zn}_{0.95}\text{Er}_{0.03}\text{Cd}_{0.02}\text{O}$ powders are preheated at 350°C for 10 min in air and grounded. Grounded nanoparticles are pressed under 4 tons for 5 min into disk shaped compacts with a thickness of 2 mm and a diameter of 10 mm. Pressed samples are annealed at 400°C, 450°C, 500°C, 550°C and 600°C for 30 min for determining the optimum annealing temperature and then XRD analysis is performed and the optimum temperature is determined as **400°C**. Finally samples are prepared at different doping rates ($x = 0.05$ and $0.0 < y < 0.10$) are annealed at 400°C for 30 min. The samples are named as $\text{Zn}_{0.94}\text{Er}_{0.05}\text{Cd}_{0.01}\text{O}$, $\text{Zn}_{0.93}\text{Er}_{0.05}\text{Cd}_{0.02}\text{O}$, $\text{Zn}_{0.92}\text{Er}_{0.05}\text{Cd}_{0.03}\text{O}$, $\text{Zn}_{0.91}\text{Er}_{0.05}\text{Cd}_{0.04}\text{O}$, $\text{Zn}_{0.90}\text{Er}_{0.05}\text{Cd}_{0.05}\text{O}$ and $\text{Zn}_{0.85}\text{Er}_{0.05}\text{Cd}_{0.10}\text{O}$.

In addition, undoped ZnO samples are prepared using sol-gel techniques. Zinc acetate dehydrate is used as precursors. Methanol and acetyl acetone are used as a solvent to preparing a homogenous solution. After weighing at appropriate rates, the precursors and solvents are stirred using the heater magnetic stirrer at 60°C for 8 h

until a transparent solution is obtained. ZnO powders are preheated at 300°C for 5 min in air. And then undoped ZnO powders are annealed at 600°C for 30 min.

5.3 Production of Nano Thin Film Materials

In this thesis, after producing of ZnO based nano bulk materials, 4 group nano thin film materials that are transition metal and rare earth element doped DMS materials and have in the ZnO based dual and ternary structure are produced. Each series are prepared for different doping rates among these. These series of nano thin film materials are as follows.

5.3.1 Transition metal doped DMS nano thin film materials which have in the ZnO based dual structure of $\text{Zn}_{1-x}\text{B}_x\text{O}$ (B=Co)

$\text{Zn}_{1-x}\text{Co}_x\text{O}$ DMS system is prepared at different range ($x = 0.00, 0.01, 0.02, 0.03, 0.04$ and 0.05) using the sol-gel method. While solutions are prepared, Zinc acetate dihydrate and cobalt acetate tetrahydrate are used as starting material and methanol and monoethanolamine (MEA) in order to improve the adhesion on the glass substrate are used as solvent. The solution is stirred until a clear solution is obtained using a temperature controlled magnetic stirrer at 60°C for 8 h (Figure 5.3.a). Zinc acetate is first soluble in the solution.



a)



b)

Figure 5.3. The production processes of nano thin film material

The glass substrates are cleaned for 5 min by using an ultrasonic bath in sulfuric acid solution before coating. Then the glasses are washed with pure water and dried by hot air flow. The glass substrates are covered with solutions at 400°C in the vertical furnace using the dip-coating method. Coated nano thin films are annealed for 2 min in the furnace and cooled for 3 min before other dip (Figure 5.3.b). This process is repeated 10 times in order to achieve a homogeneous and denser coating. After the coating process, films are subjected to last heat treatment at 600°C that is determined annealing temperature for nano bulk materials for 30 min using the muffle furnace (Figure 5.4). The nano thin film samples are named as $\text{Zn}_{0.99}\text{Co}_{0.01}\text{O}$, $\text{Zn}_{0.98}\text{Co}_{0.02}\text{O}$, $\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$, $\text{Zn}_{0.96}\text{Co}_{0.04}\text{O}$ and $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$.



Figure 5.4. The high temperature muffle furnace

5.3.2 Transition metal doped DMS nano thin film materials which have in the ZnO based ternary structure of $\text{Zn}_{1-x-y}\text{B}_x\text{C}_y\text{O}$ ($\text{B}=\text{Cu}$, $\text{C}=\text{Co}$)

$\text{Zn}_{1-x-y}\text{Cu}_x\text{Co}_y\text{O}$ system is prepared at different range ($x = 0.00, 0.01, 0.02, 0.03, 0.04$ and 0.05) using the sol-gel method. Zinc acetate dihydrate, cobalt acetate tetrahydrate and copper acetate tetrahydrate are used as precursors. Methanol and acetyl acetone are used as a solvent to preparing a homogenous solution and in order

to improve the adhesion on the glass substrate are used as solvent. The experimental procedure is the same as described above for the all of nano thin films. The nano thin film samples are named as $\text{Zn}_{0.97}\text{Cu}_{0.02}\text{Co}_{0.01}\text{O}$, $\text{Zn}_{0.96}\text{Cu}_{0.02}\text{Co}_{0.02}\text{O}$, $\text{Zn}_{0.95}\text{Cu}_{0.02}\text{Co}_{0.03}\text{O}$, $\text{Zn}_{0.94}\text{Cu}_{0.02}\text{Co}_{0.04}\text{O}$ and $\text{Zn}_{0.93}\text{Cu}_{0.02}\text{Co}_{0.05}\text{O}$.

5.3.3 Rare earth element doped DMS nano thin film materials which have in the ZnO based dual structure of $\text{Zn}_{1-x}\text{B}_x\text{O}$ (B=Er)

$\text{Zn}_{1-x}\text{Er}_x\text{O}$ (ZnErO) DMS system is prepared at different range ($x = 0.00, 0.01, 0.02, 0.03, 0.04$ and 0.05) using the sol-gel method. While solutions are prepared, Zinc acetate dihydrate and Erbium 2-4 pentanedionate are used as starting material and methanol and monoethanolamine (MEA) in order to improve the adhesion on the glass substrate are used as solvent. The experimental procedure is the same with other nano thin films. The nano thin film samples are named as $\text{Zn}_{0.99}\text{Er}_{0.01}\text{O}$, $\text{Zn}_{0.98}\text{Er}_{0.02}\text{O}$, $\text{Zn}_{0.97}\text{Er}_{0.03}\text{O}$, $\text{Zn}_{0.96}\text{Er}_{0.04}\text{O}$, $\text{Zn}_{0.95}\text{Er}_{0.05}\text{O}$ and $\text{Zn}_{0.90}\text{Er}_{0.10}\text{O}$.

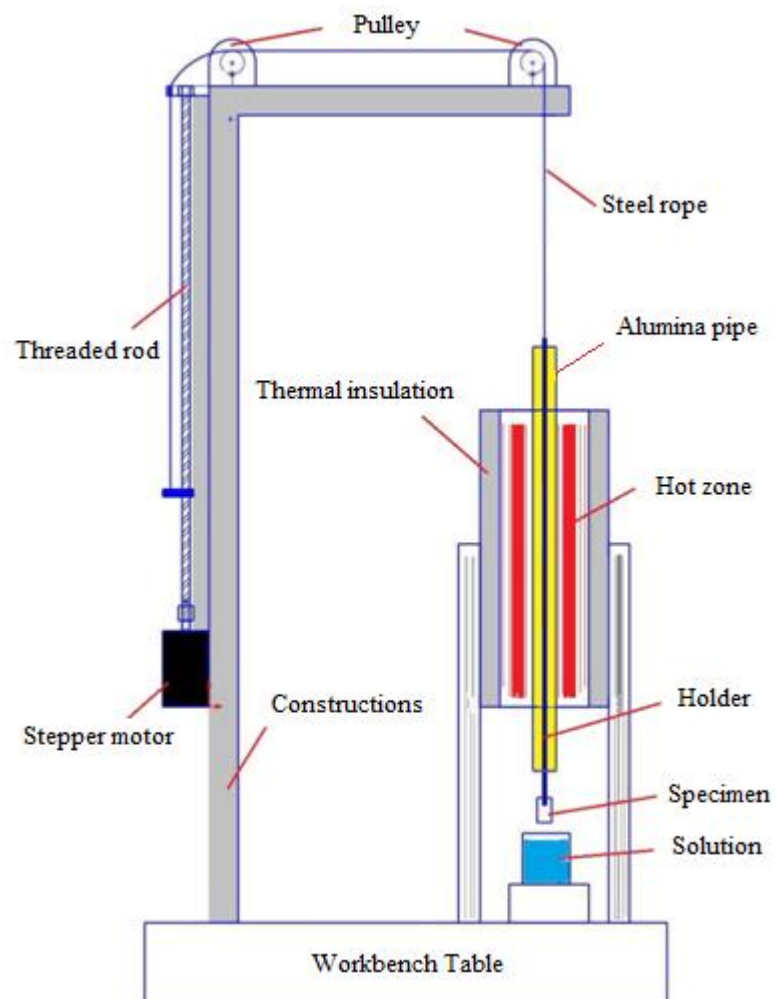
5.3.4 Rare earth doped DMS nano thin film materials which have in the ZnO based ternary structure of $\text{Zn}_{1-x-y}\text{B}_x\text{C}_y\text{O}$ (B=Cd, C=Er)

$\text{Zn}_{1-x-y}\text{Cd}_x\text{Er}_y\text{O}$ DMS system is prepared at different range ($x = y = 0.00, 0.01, 0.02, 0.03, 0.04$ and 0.05) using the sol-gel method. Zinc acetate dehydrate, Erbium 2-4 pentanedionate and Cadmium nitrate tetrahydrate are used as precursors. Methanol and acetyl acetone are used as a solvent. The experimental procedure is the same with other nano thin films. The nano thin film samples are named as $\text{Zn}_{0.95}\text{Cd}_{0.01}\text{Er}_{0.04}\text{O}$, $\text{Zn}_{0.95}\text{Cd}_{0.02}\text{Er}_{0.03}\text{O}$, $\text{Zn}_{0.95}\text{Cd}_{0.03}\text{Er}_{0.02}\text{O}$, $\text{Zn}_{0.95}\text{Cd}_{0.04}\text{Er}_{0.01}\text{O}$ and $\text{Zn}_{0.95}\text{Cd}_{0.05}\text{O}$.

All of the nano thin film samples are coated using dip-coating method on glass substrate. Dip coating method and used coating system (Figure 5.5 and Figure 5.6) are described below. In addition, the technical characteristic of coating cycle system is given Table 5.1.



Figure 5.5. Dip coating measurement system for nano thin film



a)

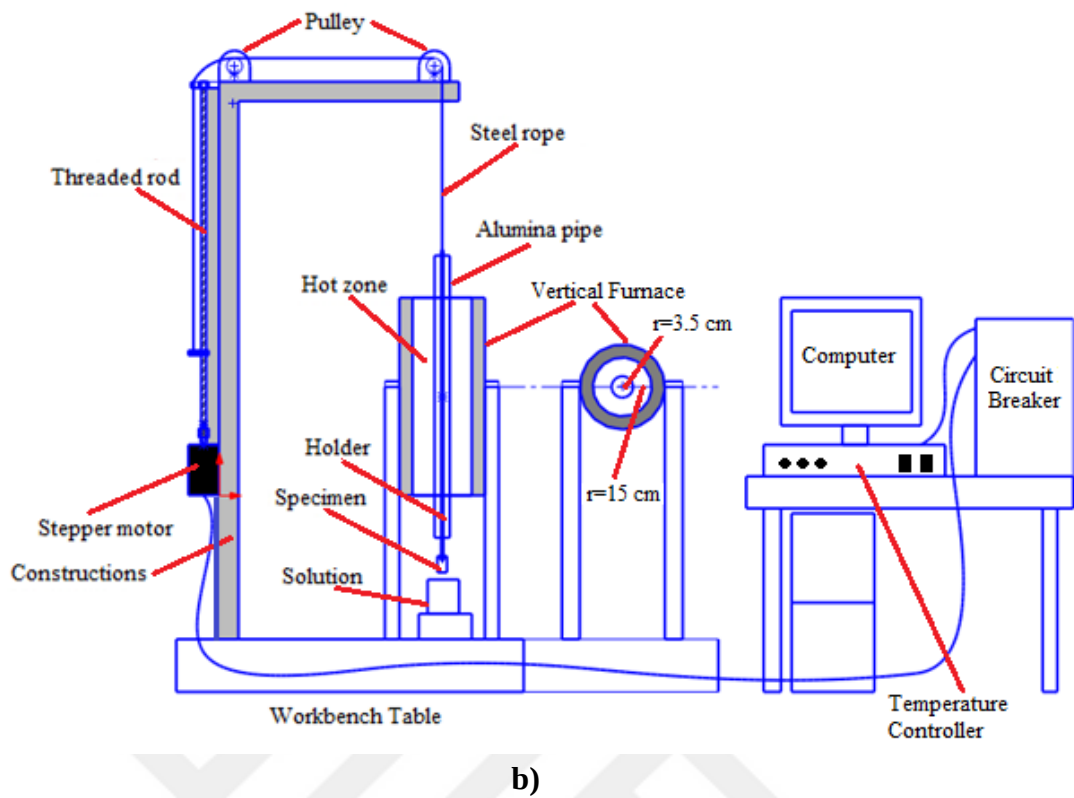


Figure 5.6. The schematic diagram of dip coating system for nano thin films

Table 5.1. Technical characteristic of coating cycle system

Properties	Values
Maximum stroke	0-750 mm
Number of cycle	10,000
Maximum speed	200 mm/min
Acceleration	200 mm/s
Stepper motor angle	1/8° full steps
Working temperature	-10°C to 600°C

5.4 Dip Coating Method

This method is often used to produce transparent layers. Dip coating method is based on the dip and withdraws of used substrate material with a certain speed into the solution. Dip coating method is performed in five steps (Figure 5.7). These steps are shown in the figure below. Film is formed as a result of this process.

The dip coating method is dipping substrate into a solution for coating and it is a withdrawal process

- at a constant speed
- controlled temperature and
- in atmospheric conditions

Coating thickness depends on the

- withdrawal speed of substrate
- surface tension of substrate
- the density and viscosity of the solution

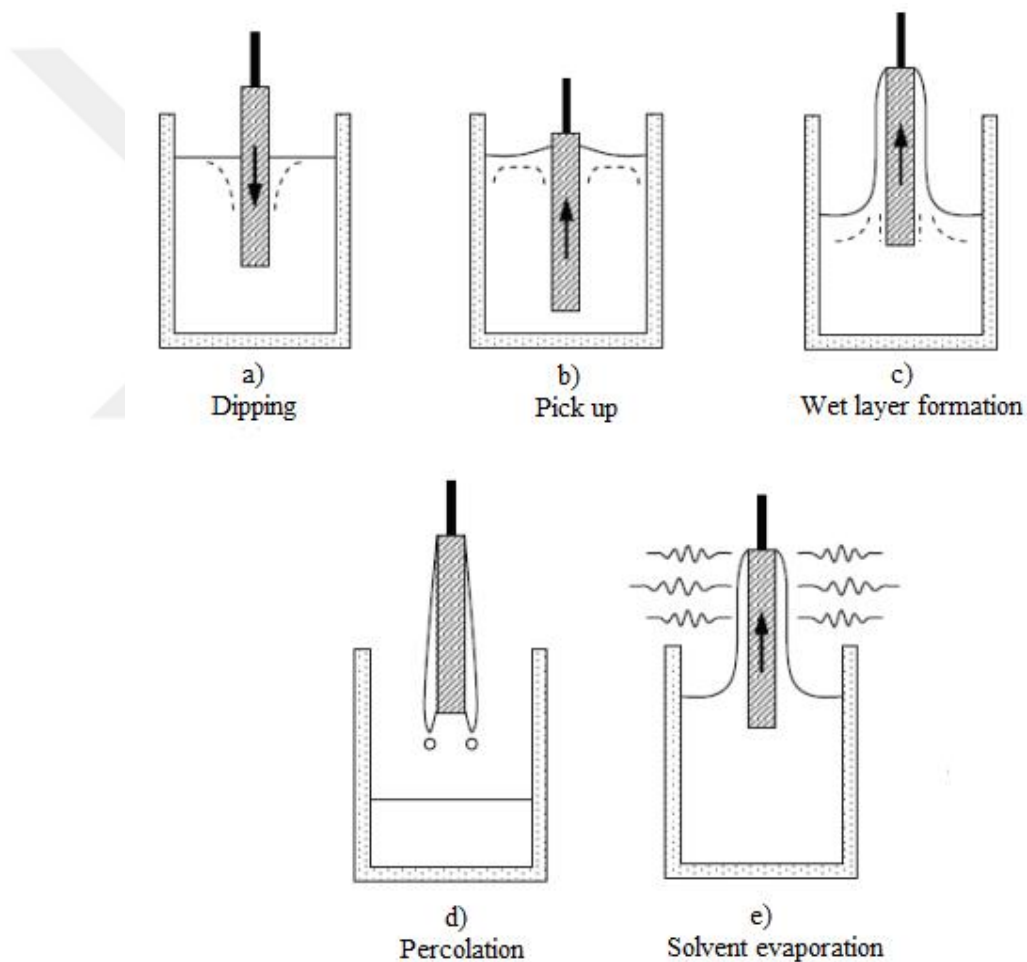


Figure 5.7. Schematic diagram of the dip coating method

Stages of dip coating method

- The dipping of substrate into solution
- The removing of substrate from the solution
- The evaporation of the solvent from the solution on the surface of substrate

There is no need to percolation phase for coatings that are performed in solvent such as alcohol. After the substrate dipped into the solvent, a boundary layer is formed on the coating surface that contains the solution boundary layer is divided into the inner layer and outer layer in coating and percolation stage. While the inner layer is moving with substrate, the outer layer moves in the opposite direction and returns to the sole. Film thickness depends on the intensity of the main streamline. These are;

- Tensile force of moving substrate due to the viscosity.
- Gravitational force
- The resultant force of liquid surface tension
- The inertia force of boundary layer of the liquid
- Gradient of surface tension
- Separating and joining pressure (important for films that have thickness less than 1 micron)

CHAPTER 6

RESULT AND DISCUSSION

6.1 Introduction

Recently, an intense research has been done on developing new materials with superior properties which are not observed in conventional materials in technological applications. Among these materials ZnO based ceramic composite is a leading study area because of its exceptional properties like 3.3 eV wide band gap, 60 meV exciton binding energy, a large conductivity range from 10^4 to 10^{-12} Ω .cm, and low optical absorbance. The ZnO is known to exist in three structural modifications which are hexagonal wurtzite, zinc blende and rock salt. Among these structures hexagonal wurtzite structure is thermodynamically stable under ambient conditions. Therefore, it is attracted considerable attention due to its various applications in many areas such as: solar cells, flat panel displays, transparent electrode and various optoelectronic applications. Moreover, ZnO is a non-toxic, chemically stable, abundant and cheap material. It is observed that physical and chemical properties and applications of ZnO can be dramatically changed by doping with different types of ions (Ozgur et al., 2005; Kilinc et al., 2012; Heiba et al., 2015; Kilinc et al., 2010; Heiba and Arda, 2009).

Transition-metals (Cr, Ni, Co, Fe, V etc.) and rare earth elements (RE) (Er, Yb, Y, Ge) have been determined as the most suitable dopants for the DMS and displayed ferromagnetism with a Curie temperature above the room temperature (Heiba et al., 2013; Dogan et al., 2015; Arda et al., 2012; Cakiroglu et al., 2015). The transparent conducting films are formed by doping with a small amount of Al, Ga, In, Cu, Mg etc. into the ZnO to increase electrical conductivity and transmittance in the visible range and stability against heat. Rare earth elements (RE) (Er, Yb, Y, Ge), which are a hot topic to study for their optical emission due to their intra 4f- 4f shell

transitions, doping into the ZnO can achieve photoluminescence properties of ZnO (Jang et al., 2011; Vettumpperumal et al., 2015).

The goals of the thesis are as follows; to investigate processing, characterization and some sol-gel parameters (solution properties, withdrawal rate, drying, heat treatment), to growth crack free, pinhole-free, uniform and highly oriented nano thin films and to investigate the effect of doping concentration and annealing temperature on the structural, electric, magnetic, optic and mechanic properties of ZnO based nano thin films and nano particles.

The mechanical properties are mainly due to interatomic bonding forces. In addition to this, the internal structure of the material and mechanical properties may be significantly improved with the internal structural modifications. As it is known, important parameters such as hardness, yield strength, elastic modulus, fracture toughness and brittleness for the mechanical characterization of the materials change extremely with different doping (Siddheswaran et al., 2012; Rajkovic et al., 2012; Shun et al., 2012; Arda et al., 2013). The determination of mechanical properties of nano bulk materials is important in the applications including window materials for display, solar cells, liquid crystal displays and heat mirrors.

In the proposed thesis, characterizations of produced rare earth element and transition metal doped ZnO -based DMS nano thin film and nano bulk materials are carried out in detail. XRD, SEM, EDS and AFM are used to determination of structural properties such as crystal structures, grain sizes, percent of elements, surface morphology; Hall effect measurements system is used to determination of electrical properties; UV-Vis spectrophotometer is used to determine the optic properties; Vibrating sample magnetometer (VSM) system is used to determine the magnetic properties and Vickers microhardness device is used to determine the micromechanic properties of produced nano thin film and nano bulk materials.

6.2 X-Ray Diffraction (XRD) Measurements of Nano Bulk and Nano Thin Film Materials

6.2.1 Transition Metal Doped $\text{Zn}_{1-x}\text{B}_x\text{O}$ ($\text{B}=\text{Co}$) DMS Nano Bulk Materials

Firstly $\text{Zn}_{1-x}\text{Co}_x\text{O}$ (for $x = 0.05$) samples are annealed at 400°C , 450°C , 500°C , 550°C and 600°C for 30 min under 5B argon for determining the optimum annealing temperature. And then XRD analysis is performed and the optimum temperature is determined as 500°C (Fig. 6.1). Finally samples are prepared at different doping rates ($x = 0.01, 0.02, 0.03, 0.04, 0.05$ and 0.10) are annealed at 500°C for 30 min under 5B Ar pressure. The analyses are shown below.

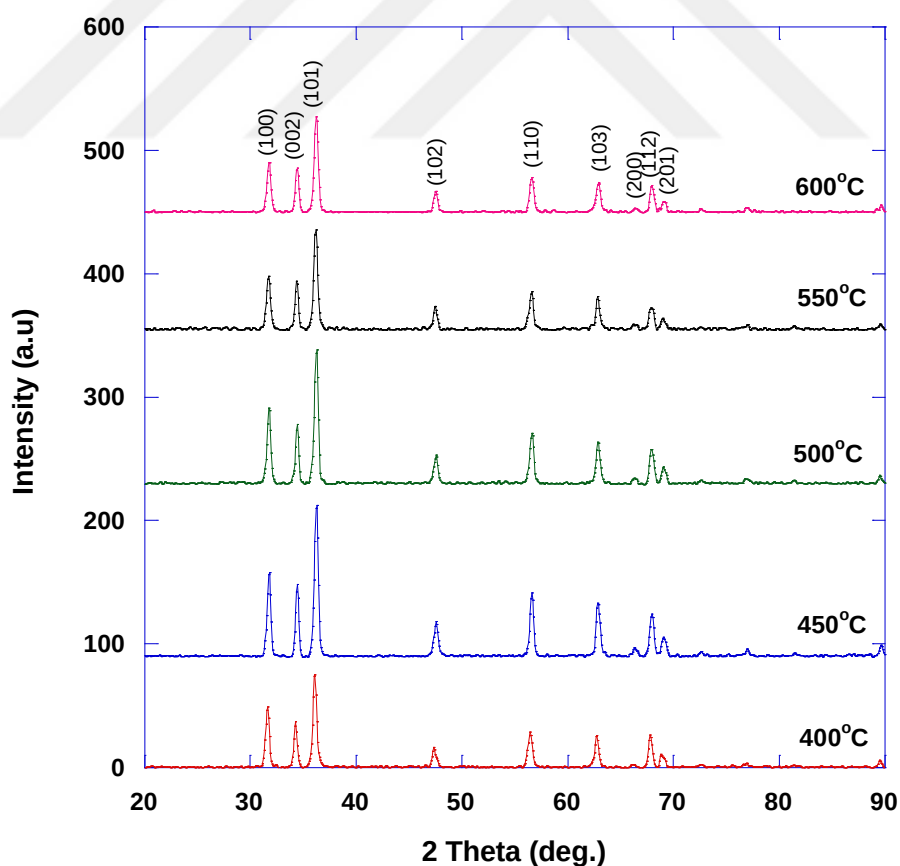


Figure 6.1. XRD patterns of Co doped ZnO nano bulk materials under different temperature

Table 6.1. Some structural values **Co** doped **ZnO** nano bulk materials

<i>Samples</i>	<i>a (Å)</i>	<i>c (Å)</i>	<i>Grain Size (nm)</i>	<i>c/a</i>
400°C	3.75	5.21	25.32	1.38
450°C	3.73	5.20	26.00	1.39
*500°C	3.73	5.20	25.79	1.39
550°C	3.75	5.16	25.57	1.37
600°C	3.73	5.19	23.00	1.39

*Optimum annealing temperature for Zn_{1-x}Co_xO nano bulk materials

The XRD analyzes are carried out in order to the structural quality of undoped and Co doped ZnO based nano bulk materials. X-ray diffraction peak of the samples shows that there is no phase of the Co ions. This means that the presence of Co⁺² ions in the ZnO lattice affects crystal structure. The reason of that is the small amount of Co enters into the structure in grain boundary of the lattice. All of the samples have hexagonal wurtzite crystal structure that is specific structure of ZnO (ICDD data card no: 01-080-0075 and 01-070-8070 for undoped ZnO and Co doped ZnO, respectively). It can be said from the X-ray diffraction peaks that the intensity of peak decreases with increasing the Co doping (Fig. 6.2a). Increasing concentrations of Co leads to distortion of the crystal structure of ZnO (Liu et al., 2012). In addition, the grain size decreases with increasing the Co doping. This value is 36.95 Å and 30.99 Å for $x = 0.01$ and $x = 0.10$ doping rate, respectively. In other words, the position of the peak shifts to the smaller 2 theta angle (Fig. 6.2b) with Co concentration. This is an indication that the hexagonal structure deteriorates with doping.

a and c lattice constant of hexagonal structure are determined by the following formula;

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (6.1)$$

Lattice parameters a and c are slightly reduced with Co doping. This reduction shows that Zn⁺² ions substitute with Co⁺² ions.

The lattice parameters of a -axis are reduced about 30% faster than the lattice parameters of c -axis. The reason is that Zn – O bonds which are along the c axis is stronger than Zn – Zn bonds which are along a axis. Strong ZnO bonds may be an indication of changing of crystal structure.

Grain size value, determined from the X-Ray diffraction patterns, is one of the most important characteristics for the engineering, industrial and technological applications of the superconducting materials. The value can be calculated with the well-known approach, Warren-Scherrer method as given below (Ozturk et al., 2014; Ozturk et al., 2013; Yildirim et al., 2012)

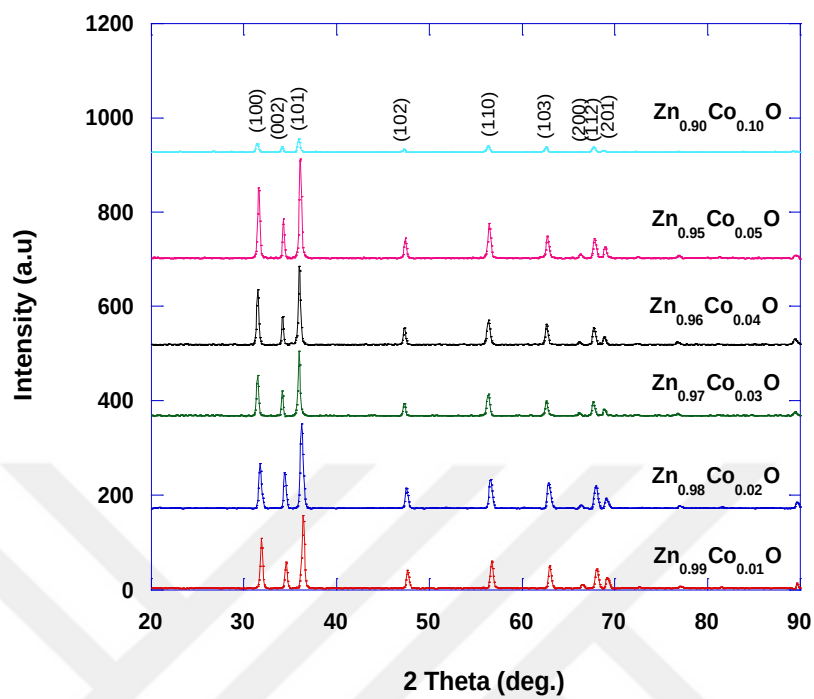
$$D = 0,941\lambda/B\cos\theta \quad (6.2)$$

$$B^2 = B_s^2 - B_m^2 \quad (6.3)$$

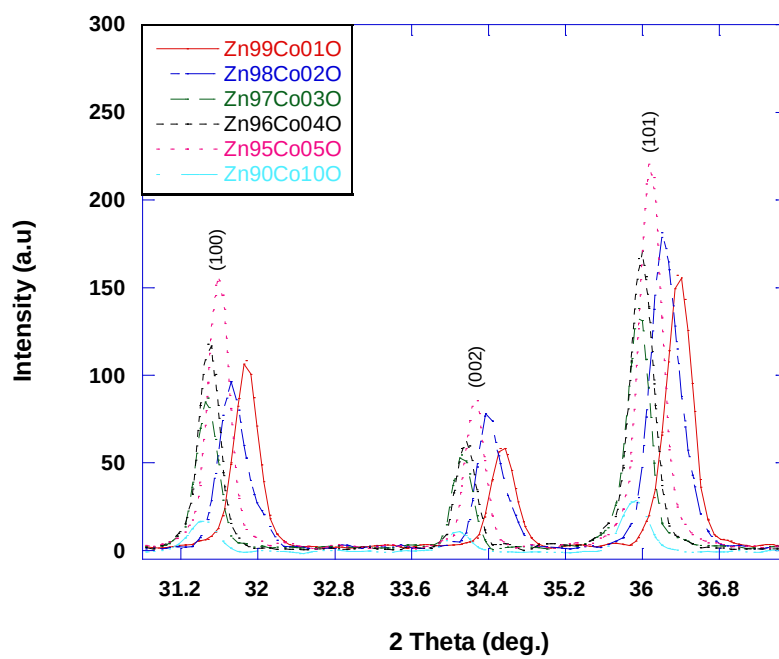
Here, D denotes the grain size, λ presents the wavelength of the X-ray used and B depicts the full width half of the maximum peak intensity in the radian unit. Also, B_m is a constant value when θ is an angle belonging to this peak. The results of the grain size calculations are shown in Table 6.2 in detail. It is obvious from the table that the grain size value tends to increase with the enhancement of the Co inclusions inserted in the ZnO based material. The largest value of 36.95 nm is calculated for the Co0.01 sample whereas the value reduces to 23.00 nm for the undoped sample. This result is even supported by the SEM images.

Table 6.2. Some structural values Co doped ZnO nano bulk materials

<i>Samples</i>	<i>a (Å)</i>	<i>c (Å)</i>	<i>Grain Size (nm)</i>	<i>c/a</i>
Undoped ZnO	3.74	5.22	26.71	1.40
Zn_{0.99}Co_{0.01}O	3.73	5.18	36.95	1.38
Zn_{0.98}Co_{0.02}O	3.73	5.18	36.85	1.38
Zn_{0.97}Co_{0.03}O	3.73	5.19	36.29	1.39
Zn_{0.96}Co_{0.04}O	3.73	5.19	36.14	1.39
Zn_{0.95}Co_{0.05}O	3.74	5.12	35.95	1.37
Zn_{0.90}Co_{0.10}O	3.73	5.19	23.99	1.39



a)



b)

Figure 6.2. XRD patterns of undoped ZnO and Co doped ZnO (with $x=0.0$ - 0.10) nano bulk materials

6.2.2 Transition Metal Doped $\text{Zn}_{1-x-y}\text{B}_x\text{C}_y\text{O}$ (B=Cu, C=Co) DMS Nano Bulk Materials

$\text{Zn}_{1-x-y}\text{Cu}_x\text{Co}_y\text{O}$ (for $x = y = 0.05$) samples are annealed at 400°C, 450°C, 500°C, 550°C and 600°C for 30 min under 5B Ar for determining the optimum annealing temperature. And then XRD analysis is performed and the optimum temperature is determined as 600°C (Fig.6.3). Finally samples are prepared at different doping rates ($x = 0.05$; $y = 0.01, 0.02, 0.03, 0.04$ and 0.05) are annealed at 600°C for 30 min under 5B Ar pressure. The analyses are shown below (Table 6.3).

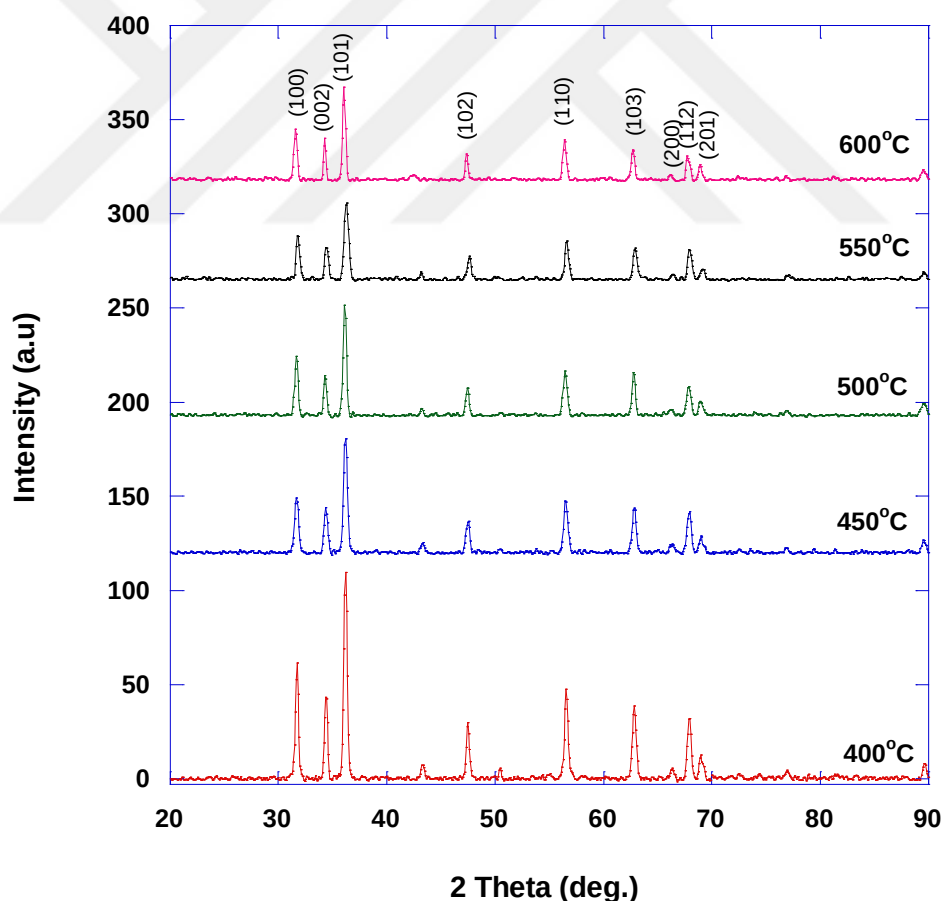


Figure 6.3. XRD patterns of $\text{Zn}_{1-x-y}\text{Cu}_x\text{Co}_y\text{O}$ (for $x=y=0.05$) nano bulk materials under different temperature

Table 6.3. Some structural values Cu/Co doped ZnO nano bulk materials

Samples	a (Å)	c (Å)	Grain Size (nm)	c/a
400°C	3.73	5.19	29.67	1.39
450°C	3.74	5.18	24.15	1.38
500°C	3.74	5.20	29.67	1.39
550°C	3.74	5.17	24.02	1.38
600°C	3.75	5.21	32.52	1.38

*Optimum annealing temperature for $\text{Zn}_{1-x-y}\text{Cu}_x\text{Co}_y\text{O}$ nano bulk materials

When $\text{Zn}_{1-x-y}\text{Cu}_x\text{Co}_y\text{O}$ samples are annealed under different temperature in 5B Argon pressure, it has found that there is a peak about at 43° (Fig.6.3). This peak is not observed in $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples annealed in the same conditions. There is a dominant peak of Cu at this angle. This peak is not observed in the samples annealed under oxygen atmosphere.

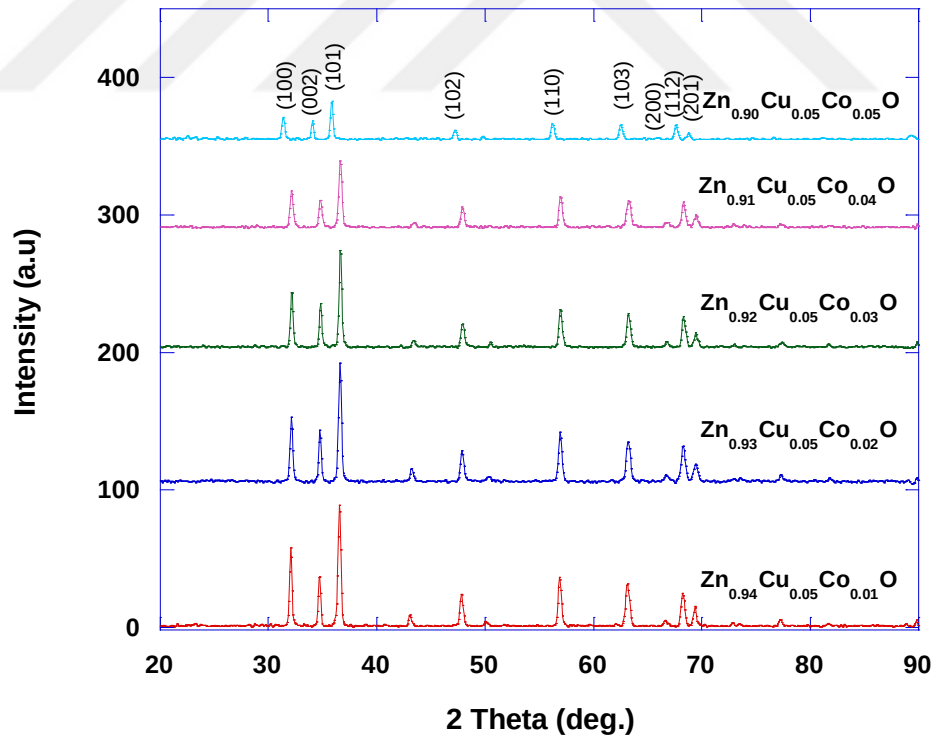
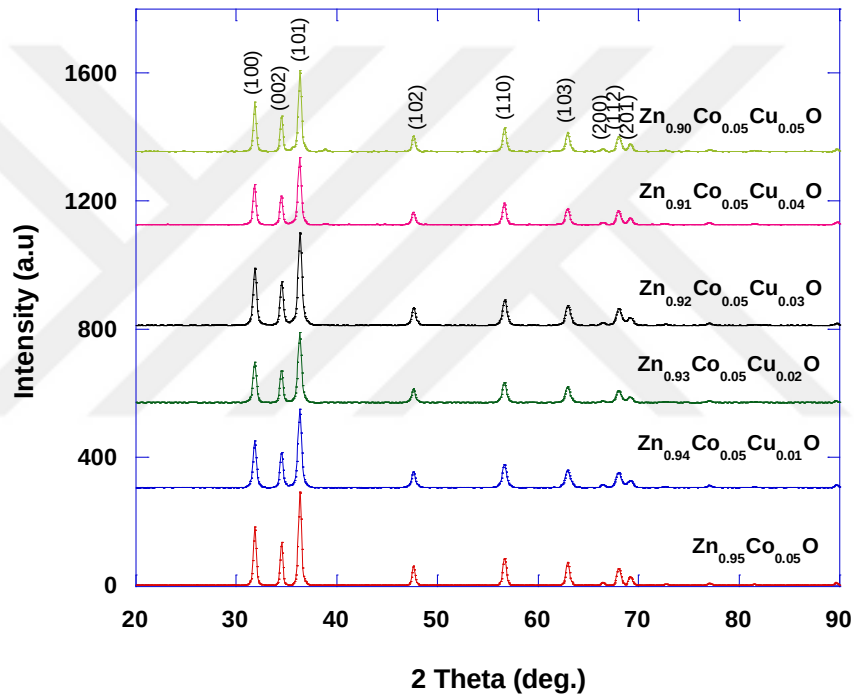
**Figure 6.4.** XRD patterns of Cu/Co doped ZnO nano bulk materials

Table 6.4. Some structural values Cu/Co doped ZnO nano bulk materials

Samples	a (Å)	c (Å)	Grain Size (nm)	c/a
Undoped ZnO	3.74	5.22	26.71	1.40
$\text{Zn}_{0.90}\text{Cu}_{0.05}\text{Co}_{0.05}\text{O}$	3.75	5.21	32.50	1.38
$\text{Zn}_{0.91}\text{Cu}_{0.05}\text{Co}_{0.04}\text{O}$	3.69	5.19	26.82	1.40
$\text{Zn}_{0.92}\text{Cu}_{0.05}\text{Co}_{0.03}\text{O}$	3.69	5.19	34.11	1.40
$\text{Zn}_{0.93}\text{Cu}_{0.05}\text{Co}_{0.02}\text{O}$	3.69	5.19	31.07	1.40
$\text{Zn}_{0.94}\text{Cu}_{0.05}\text{Co}_{0.01}\text{O}$	3.70	5.20	33.06	1.40

**Figure 6.5.** XRD pattern of the $\text{Zn}_{0.95-x}\text{Co}_{0.05}\text{Cu}_x$ materials annealed under oxygen atmosphere**Table 6.5.** Some structural values $\text{Zn}_{0.95-x}\text{Co}_{0.05}\text{Cu}_x$ nano bulk materials under oxygen atmosphere

Samples	a (Å)	c (Å)	Grain Size (nm)
$\text{Zn}_{0.90}\text{Co}_{0.05}\text{Cu}_{0.05}\text{O}$	3.69	5.24	29.92
$\text{Zn}_{0.91}\text{Co}_{0.05}\text{Cu}_{0.04}\text{O}$	3.52	5.55	28.93
$\text{Zn}_{0.92}\text{Co}_{0.05}\text{Cu}_{0.03}\text{O}$	3.53	5.62	21.97
$\text{Zn}_{0.93}\text{Co}_{0.05}\text{Cu}_{0.02}\text{O}$	3.48	5.75	21.79
$\text{Zn}_{0.94}\text{Co}_{0.05}\text{Cu}_{0.01}\text{O}$	3.48	5.75	21.62
$\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$	3.48	5.75	21.42

$\text{Zn}_{1-x-y}\text{Co}_x\text{Cu}_y\text{O}$ samples are prepared after from $\text{Zn}_{1-x-y}\text{Co}_x\text{Co}_y\text{O}$ samples. Here, we aimed to determination of optimum Cu doping rate.

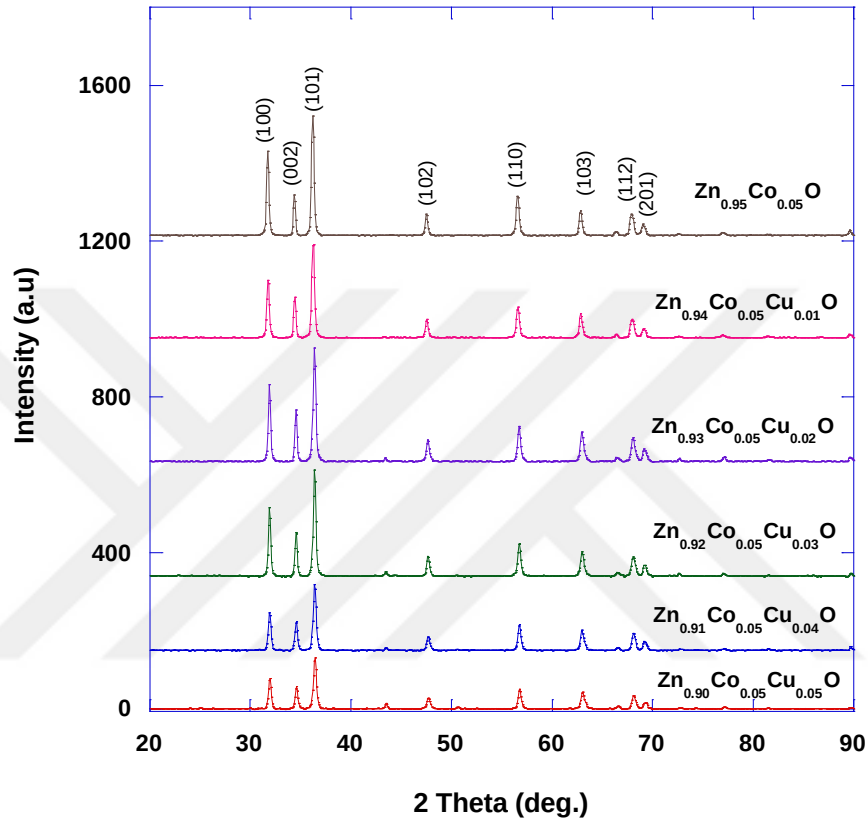


Figure 6.6. XRD pattern of the $\text{Zn}_{1-x-y}\text{Co}_x\text{Cu}_y\text{O}$ materials

As a result;

- $x = 0.01$ is determined as optimum doping rate for Cu. As can be seen from the XRD analyses, there is peak about at 43° after from this value (Figure 6.6).
- It is found that this peak observed in the all of XRD analyses of ZnCuCo and ZnCoCu bulk samples is related with Cu.
- As can be said for this peak that is not observed in the oxygen atmosphere that oxygen is blocked to the Cu cluster. The XRD peak intensities of samples annealed in the oxygen atmosphere are lower than the XRD peak intensities of samples annealed under argon pressure. This means that oxygen suppresses structure. It can be said for studies carried out under argon pressure, when oxygen in the

environment is removed by vacuum just before the argon flow, Cu clusters are not suppressed in the structure and the intensity of peak increases.

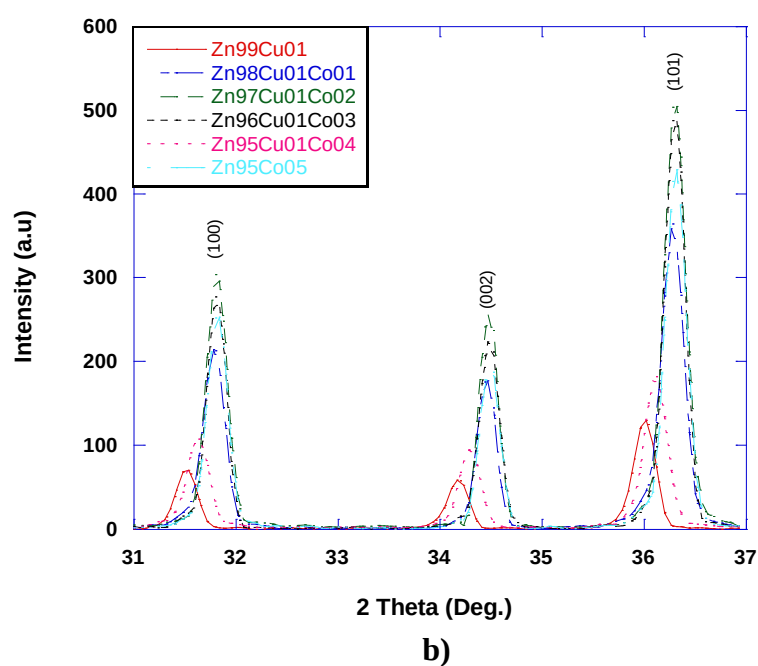
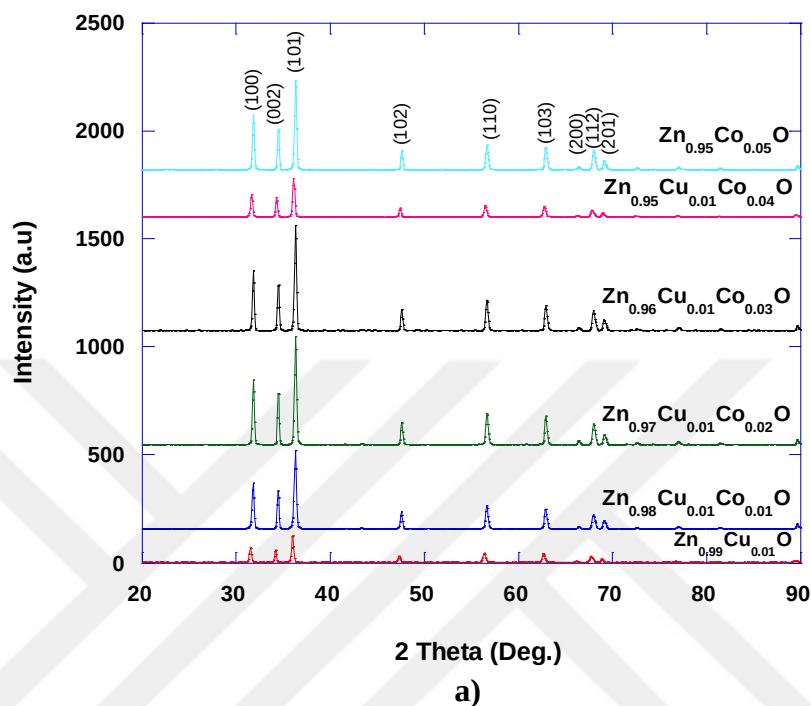


Figure 6.7. XRD patterns of undoped ZnO and Co doped ZnO (with $x=0.0-0.10$) nano bulk materials

Table 6.6. Some structural values $\text{Zn}_{0.99-x}\text{Cu}_{0.01}\text{Co}_x$ nano bulk materials under oxygen atmosphere

<i>Samples</i>	<i>a (Å)</i>	<i>c (Å)</i>	<i>Grain Size (nm)</i>	<i>c/a</i>
Undoped ZnO	3.74	5.22	26.71	1.40
$\text{Zn}_{0.99}\text{Cu}_{0.01}\text{O}$	3.76	5.20	40.69	1.38
$\text{Zn}_{0.98}\text{Cu}_{0.01}\text{Co}_{0.01}\text{O}$	3.73	5.17	42.56	1.38
$\text{Zn}_{0.97}\text{Cu}_{0.01}\text{Co}_{0.02}\text{O}$	3.73	5.17	44.59	1.38
$\text{Zn}_{0.96}\text{Cu}_{0.01}\text{Co}_{0.03}\text{O}$	3.73	5.17	44.40	1.38
$\text{Zn}_{0.95}\text{Cu}_{0.01}\text{Co}_{0.04}\text{O}$	3.75	5.21	44.93	1.38
$\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$	3.74	5.12	35.95	1.37

When the XRD analyses of ZnO based DMS nano bulk materials which have ternary structure of $(\text{Zn}_{1-x-y}\text{Cu}_{0.01}\text{Co}_y)\text{O}$ is investigated, the same peaks are observed at almost the same angle for all samples (Figure 6.7). The different of Co doping ratio does not lead to the formation of additional phases or compounds. Hexagonal crystal structure is observed in all samples (ICDD data card no: 01-080-0075 and 01-089-7102 for undoped ZnO and Co doped ZnO, respectively). The grain size increases with increasing Co doping (Table 6.7).

6.2.3 Transition Metal Doped $\text{Zn}_{1-x-y}\text{B}_x\text{C}_y\text{O}$ (B=Mg, C=Co) DMS Nano Bulk Materials

Figure 6.8 illustrates X-Ray Diffraction of the Mg/Co doped ZnO samples. As shown in Fig. 6.8, all prepared samples are single phase with ZnO wurtzite hexagonal structure. This means that Mg and Co ions incorporated substitutionally in the ZnO lattice replacing the Zn ions. The grain sizes of all samples have been measured using XRD analysis and Warren–Scherer relation (Eqn. 6.2). The calculations are examined using the highest three XRD intensities of samples XRD peaks.

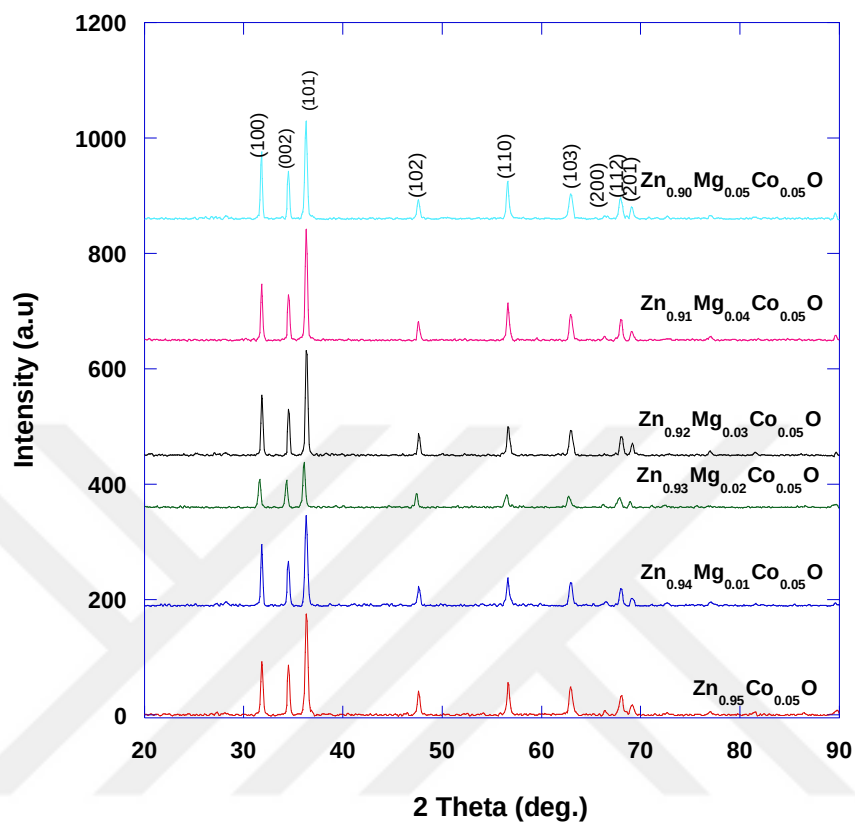


Figure 6.8. XRD patterns of Mg/Co doped ZnO nano bulk materials

Table 6.7. Some structural values $\text{Zn}_{1-x-y}\text{Mg}_x\text{Co}_y\text{O}$ nano bulk materials

<i>Samples</i>	<i>a</i> (Å)	<i>c</i> (Å)	<i>Grain Size (nm)</i>
$\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$	3.74	5.12	42.20
$\text{Zn}_{0.94}\text{Mg}_{0.01}\text{Co}_{0.05}\text{O}$	3.76	5.20	43.10
$\text{Zn}_{0.93}\text{Mg}_{0.02}\text{Co}_{0.05}\text{O}$	3.76	5.20	41.28
$\text{Zn}_{0.92}\text{Mg}_{0.03}\text{Co}_{0.05}\text{O}$	3.76	5.20	43.31
$\text{Zn}_{0.91}\text{Mg}_{0.04}\text{Co}_{0.05}\text{O}$	3.75	5.21	44.15
$\text{Zn}_{0.90}\text{Mg}_{0.05}\text{Co}_{0.05}\text{O}$	3.75	5.21	44.85

6.2.4 Rare Earth Doped $\text{Zn}_{1-x}\text{B}_x\text{O}$ (B=Er) DMS Nano Bulk Materials

$\text{Zn}_{1-x}\text{Er}_x\text{O}$ (for $x = 0.05$) samples are annealed at 400°C, 450°C, 500°C, 550°C and 600°C for 30 min for determining the optimum annealing temperature. And then XRD analysis is performed and the optimum temperature is determined as 400°C (Fig.6.9). Finally, samples are prepared at different doping rates ($x = 0.01, 0.02, 0.03, 0.04, 0.05$ and 0.10) are annealed at 400°C for 30 min. These analyzes are shown below (Table 6.8).

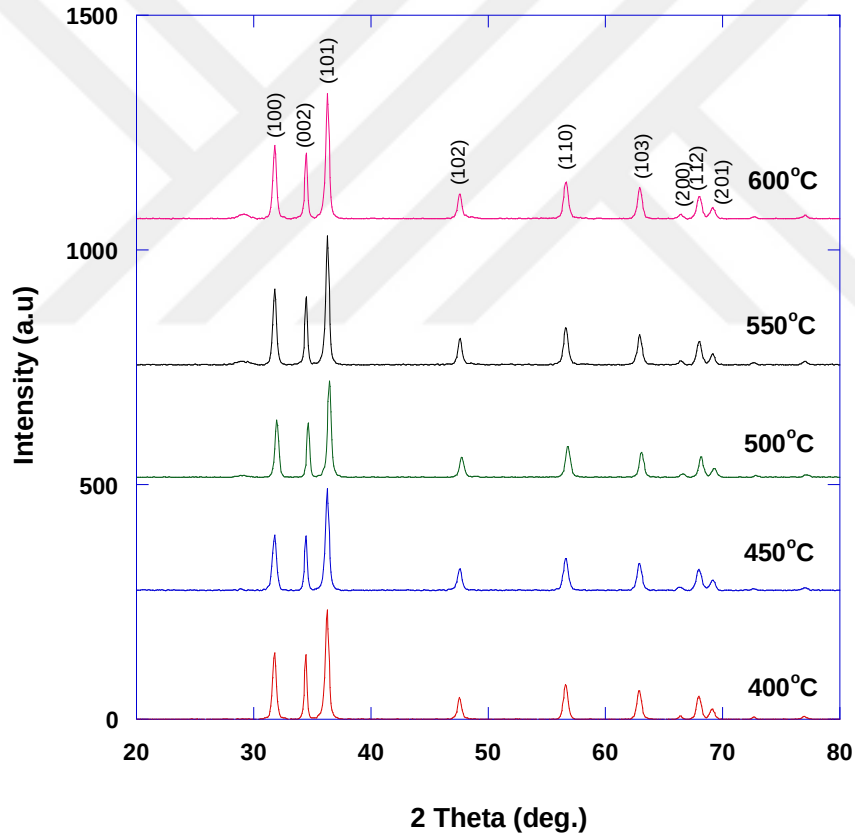


Figure 6.9. XRD patterns of $\text{Zn}_{1-x}\text{Er}_x\text{O}$ (with $x=0.05$) nano bulk materials under different temperature

Table 6.8. Some structural values $\text{Zn}_{1-x}\text{Er}_x\text{O}$ nano bulk materials

Samples	a (Å)	c (Å)	Grain Size (nm)	c/a
*400°C	3.39	5.96	28.69	1.75
450°C	3.39	5.95	26.34	1.75
500°C	3.38	5.95	28.70	1.76
550°C	3.39	5.95	28.82	1.75
600°C	3.38	5.97	30.00	1.76

*Optimum annealing temperature for $\text{Zn}_{1-x}\text{Er}_x\text{O}$ samples

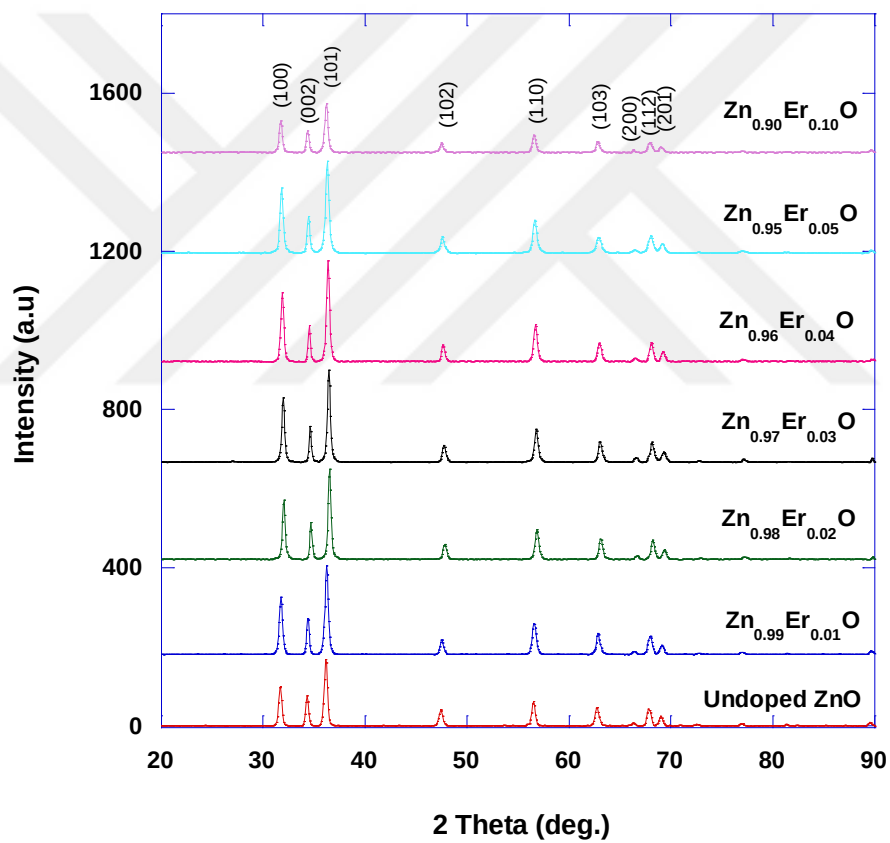


Figure 6.10. XRD patterns of $\text{Zn}_{1-x}\text{Er}_x\text{O}$ nano bulk materials

Table 6.9. Some structural values $\text{Zn}_{1-x}\text{Er}_x\text{O}$ nano bulk materials

<i>Samples</i>	<i>a (Å)</i>	<i>c (Å)</i>	<i>Grain Size (nm)</i>	<i>c/a</i>	<i>Grain Size (nm) (using SEM)</i>
$\text{Zn}_{0.99}\text{Er}_{0.01}\text{O}$	3.39	5.89	27.55	1.73	27.03
$\text{Zn}_{0.98}\text{Er}_{0.02}\text{O}$	3.36	5.88	31.68	1.75	28.67
$\text{Zn}_{0.97}\text{Er}_{0.03}\text{O}$	3.38	5.88	30.51	1.73	30.48
$\text{Zn}_{0.96}\text{Er}_{0.04}\text{O}$	3.38	5.89	29.17	1.74	30.18
$\text{Zn}_{0.95}\text{Er}_{0.05}\text{O}$	3.39	5.96	31.69	1.65	30.62
$\text{Zn}_{0.90}\text{Er}_{0.10}\text{O}$	3.41	5.91	32.83	1.73	39.59

The XRD analyses of Er doped ZnO based bulk samples are shown in Figure 6.10. As can be seen in the figure, Er doped all samples have a hexagonal wurtzite type structure and the same peak at the same angle as undoped ZnO (ICDD data card no: 01-080-0075 and 01-089-7102 for undoped ZnO and Er doped ZnO, respectively). There is no phase of the Er ions. This means that Er^{+2} ions are replaced with Zn^{+2} ions in the ZnO lattice.

In addition, the position of the peak shifts to the greater 2 theta angle (Fig.6.11) until $x = 0.02$ from $x = 0.01$ of Er doping rate (Asikuzun et al., 2012). And then the position of the peak shifts to the smaller angle. However, the lattice parameters a and c firstly decreases and then slightly increases with Er doping. This is an expected result. Because the ionic radius of Zn^{+2} (0.74Å) is smaller than the ionic radius of Er^{+2} (0.88Å). Grain size of all samples is calculated using the Warren-Scherer Formula (Eqn.6.2). As shown in Table 6.9. Er doped bulk samples exhibit greater grain size than the undoped ZnO samples. Difference of size may be caused from ionic radius difference between zinc and doping element.

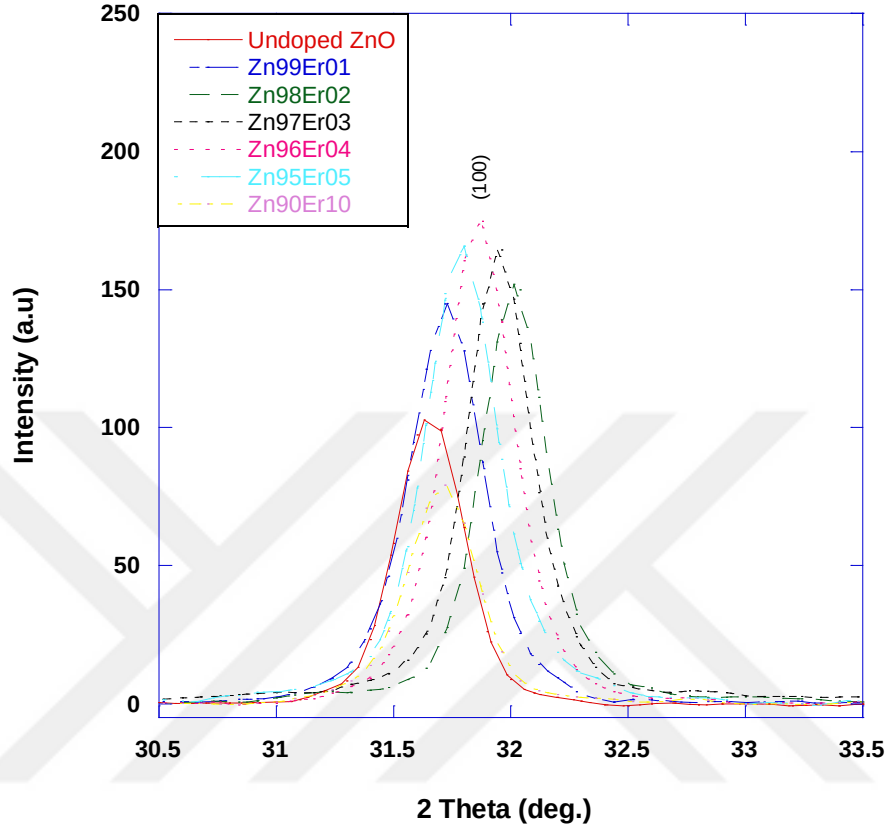


Figure 6.11. XRD patterns of $\text{Zn}_{1-x}\text{Er}_x\text{O}$ nano bulk materials

6.2.5 Rare Earth Doped $\text{Zn}_{1-x-y}\text{B}_x\text{C}_y\text{O}$ (B=Er, C=Cd) DMS Nano Bulk Materials

$\text{Zn}_{1-x-y}\text{Er}_x\text{Cd}_y\text{O}$ (for $x = y = 0.05$) samples are annealed at 400°C, 450°C, 500°C, 550°C and 600°C for 30 min for determining the optimum annealing temperature. And then XRD analysis is performed and the optimum temperature is determined as 400°C (Fig.6.12). Finally samples are prepared at different doping rates ($x = 0.05$; $y = 0.01, 0.02, 0.03, 0.04, 0.05$ and 0.10) are annealed at 400°C for 30 min (Table 6.10). The analyses are shown below.

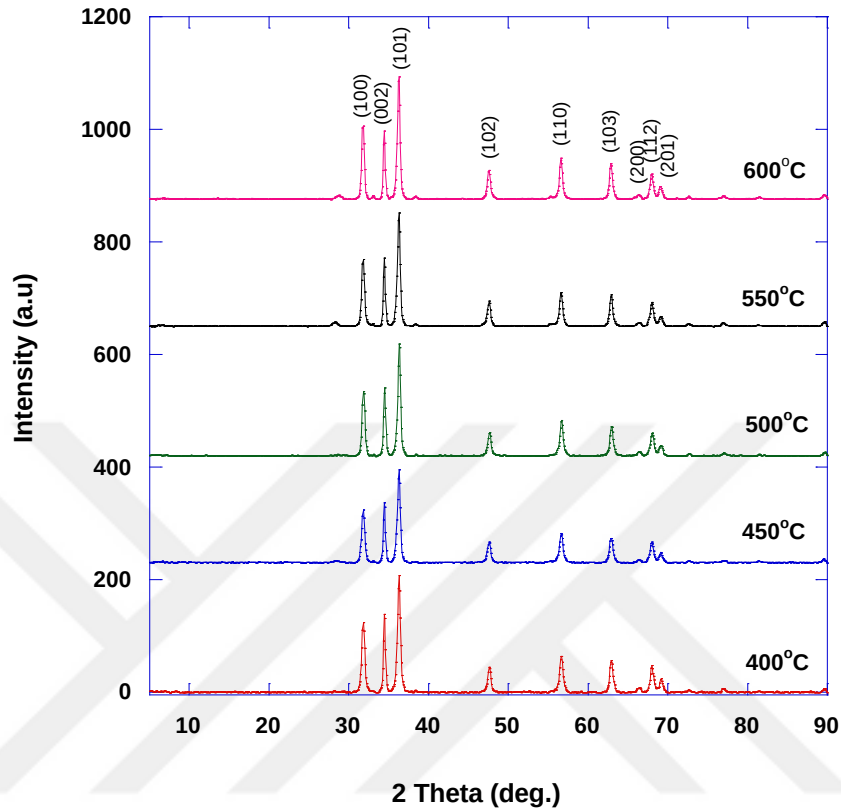


Figure 6.12. XRD patterns of $\text{Zn}_{1-x-y}\text{Er}_x\text{Cd}_y\text{O}$ nano bulk materials

Table 6.10. Some structural values $\text{Zn}_{1-x-y}\text{Er}_x\text{Cd}_y\text{O}$ nano bulk materials

Samples	a (Å)	c (Å)	Grain Size (nm)
*400C	3.39	5.96	26.20
450C	3.39	5.97	24.97
500C	3.38	5.96	27.58
550C	3.39	5.96	25.15
600C	3.38	5.98	28.21

*Optimum annealing temperature for $\text{Zn}_{1-x-y}\text{Er}_x\text{Cd}_y\text{O}$ samples

The XRD analyses of Cd doped ZnO based bulk samples are shown in Figure 6.13. As can be seen in the figure, Cd doped all samples have a hexagonal wurtzite type structure and the same peak at the same angle as undoped ZnO. There is no phase of the Cd ions until $x = 0.04$ Cd doping rate. This means that Cd^{+2} ions replacement with Zn^{+2} ions in the ZnO lattice. After from this doping value there are two peaks of CdO phase. The hexagonal wurtzite type structure is deteriorated with

increasing *Cd* doping (ICDD data card no: 01-080-0075 and 01-075-1526 for undoped ZnO and *Cd* doped ZnO, respectively).

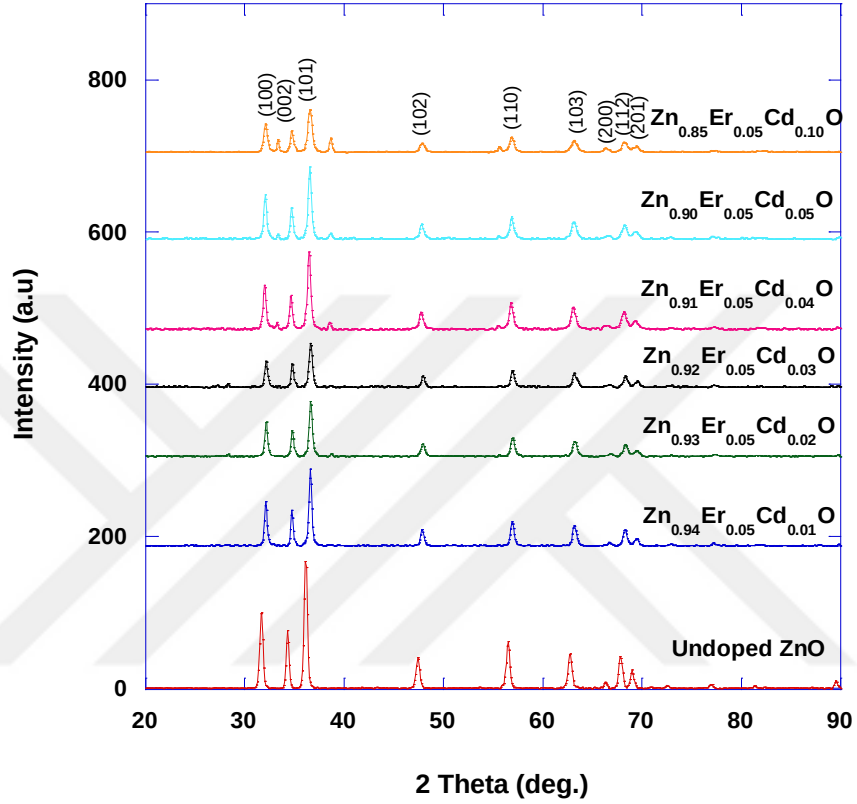


Figure 6.13. XRD patterns of $\text{Zn}_{1-x-y}\text{Er}_x\text{Cd}_y\text{O}$ nano bulk materials

Table 6.11. Some structural values $\text{Zn}_{1-x-y}\text{Er}_x\text{Cd}_y\text{O}$ nano bulk materials

<i>Samples</i>	<i>a</i> (Å)	<i>c</i> (Å)	<i>Grain Size</i> (nm)
$\text{Zn}_{0.94}\text{Er}_{0.05}\text{Cd}_{0.01}\text{O}$	3.70	5.21	29.57
$\text{Zn}_{0.93}\text{Er}_{0.05}\text{Cd}_{0.02}\text{O}$	3.70	5.19	27.00
$\text{Zn}_{0.92}\text{Er}_{0.05}\text{Cd}_{0.03}\text{O}$	3.70	5.18	26.72
$\text{Zn}_{0.91}\text{Er}_{0.05}\text{Cd}_{0.04}\text{O}$	3.72	5.18	26.21
$\text{Zn}_{0.90}\text{Er}_{0.05}\text{Cd}_{0.05}\text{O}$	3.71	5.18	25.93
$\text{Zn}_{0.85}\text{Er}_{0.05}\text{Cd}_{0.10}\text{O}$	3.70	5.20	20.88

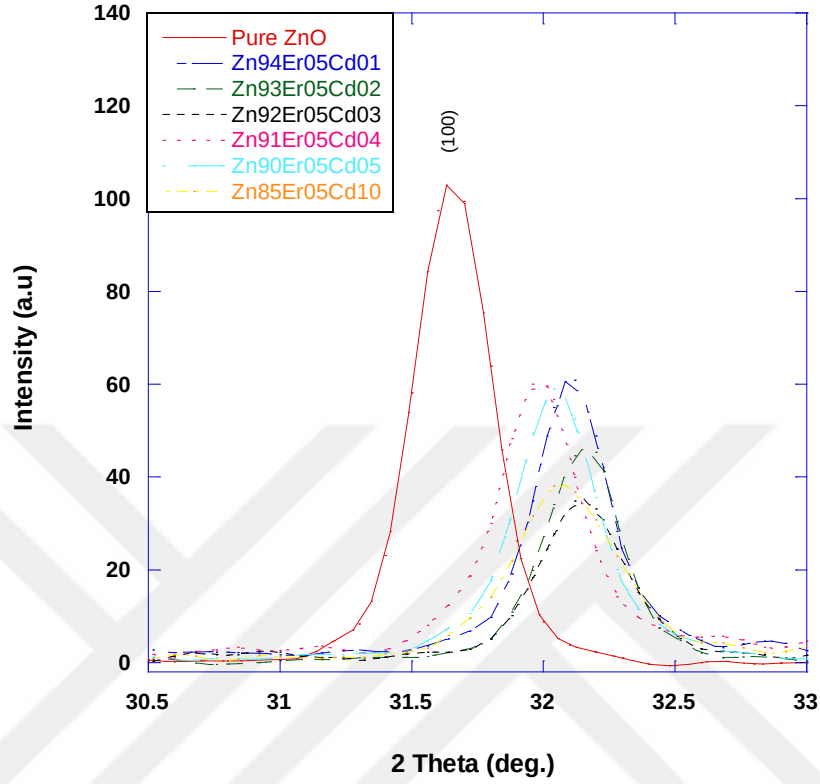


Figure 6.14. XRD patterns of $\text{Zn}_{1-x-y}\text{Er}_x\text{Cd}_y\text{O}$ nano bulk materials

The position of the peak shifts to the greater 2 theta angle (Fig.6.14). And then the position of the peak shifts to the smaller angle (Takci et al., 2014). However, the lattice parameter c firstly decreases and then slightly increases with Cd doping. This is an expected result. Because the ionic radius of Zn^{+2} ($0.74\text{\AA}$) is smaller than the ionic radius of Cd^{+2} ($0.97\text{\AA}$). As shown in Table 6.11. Er doped bulk samples exhibit greater grain size than the undoped ZnO samples. Difference of size may be caused from ionic radius difference between zinc and doping element.

6.2.6 Transition Metal Doped DMS $\text{Zn}_{1-x}\text{B}_x\text{O}$ (B=Co) Nano Thin Film Materials

XRD analysis of the Co doped ZnO nano thin films are given in Figure 6.15a. As seen from the figure, all of undoped and Co doped ZnO films are oriented along the (002) plane as the dominant and have a hexagonal wurtzite type structure. No extra diffraction peak from Co -related second phase is observed. This can be explained as; Co^{+2} ions substituted for Zn^{+2} ions of ZnO host semiconductor without changing the wurtzite structure. (002) peak position shifts to lower angle compared to the undoped ZnO film (34.46°) (Fig.6.15b). This means that the lattice parameter increases with Co doping compared with undoped ZnO. This is an expected result. Because the ionic radius of Zn^{+2} (0.74 Å) is smaller than the ionic radius of Co^{+2} (0.79 Å). The larger lattice constant denotes that Co^{+2} ions incorporate into the ZnO lattice and substitutes the Zn^{+2} sites. Also the (002) peak intensity decreases with increasing the Co doping. The increasing of Co concentration leads to deterioration of the ZnO crystal structure. This is associated with the formation of the amorphous structure.

According to the XRD peaks, it can be said Co doped ZnO films are partially oriented to the (101) plane after from Co0.02 doping rate. But the orientation of (002) plane is dominant. These results are supported with calculation of the degree of orientation (Table 6.12). The change of orientation is lead to changes of the bond angles α and β . Values of α which is 90 for hexagonal wurtzite ZnO structure are 108, 108, 109, and 109 for Co0.02, Co0.03, Co0.04 and Co0.05, respectively. Values of β which is 120 for hexagonal wurtzite ZnO structure are 111, 111, 110 and 110, respectively.

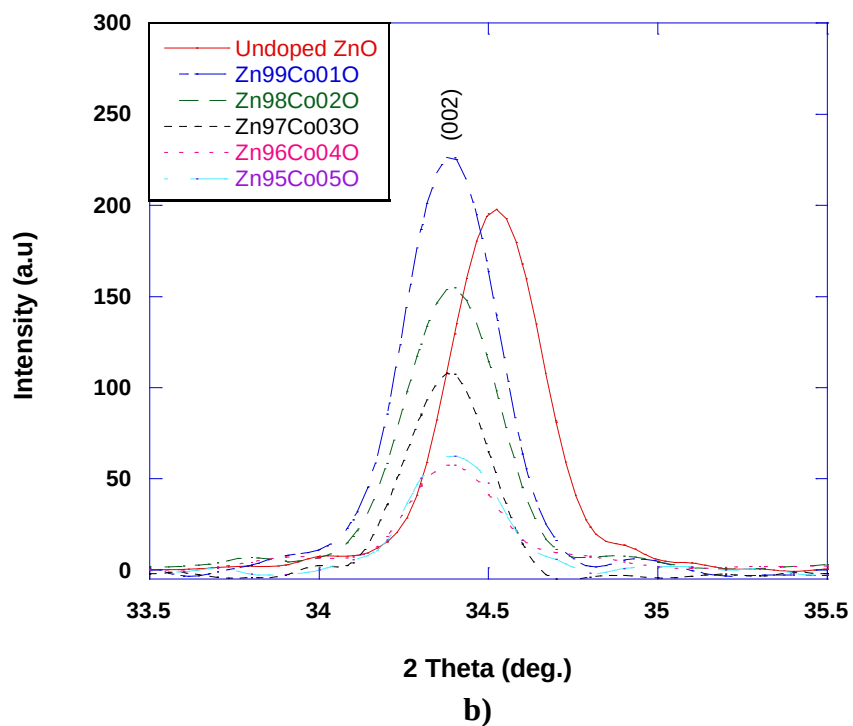
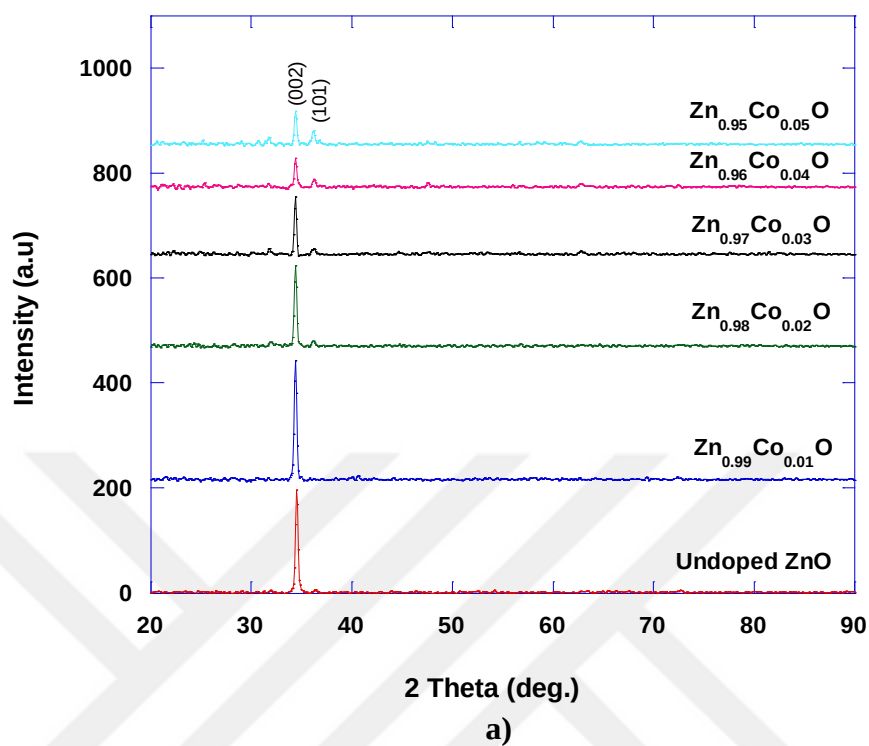


Figure 6.15. XRD patterns of Zn_{1-x}Co_xO nano thin film materials

The FWHM value of the (002) peak is larger in doped films than undoped ZnO film. These results show that the Co doped ZnO films have better crystal size than undoped ZnO nano thin film. ZnO nano thin films that are produced by sol-gel are oriented along the (002) plane in the most of previous studies. M. Ohyama et.al reported that ZnO nano thin films produced by sol-gel show a high degree of orientation along the (002) plane with MEA (Monoethanolamine) doping and this orientation decreases with DEA (Diethanolamine) doping (Ohyama et al., 1997). Also, this case is proved by the orientation of degree calculation (Tsay et al., 2010) (Eqn. 6.4).

$$f(hkl) = \frac{P(hkl) - P_0(hkl)}{1 - P_0(hkl)} \quad (6.4)$$

$$P(hkl) = I(hkl) / \sum I(hkl) \quad (6.5)$$

$$P_0(hkl) = I_0(hkl) / \sum I_0(hkl) \quad (6.6)$$

where $f(hkl)$, $P(hkl)$ and $P_0(hkl)$ are defined as the degree of (hkl) orientation, $P(hkl) = I(hkl) / \sum I(hkl)$ and $P_0(hkl) = I_0(hkl) / \sum I_0(hkl)$ respectively. Here, $I(hkl)$ is the (hkl) peak intensity and $\sum I(hkl)$ is the total intensity of all peaks in the ZnO films. Besides, $I_0(hkl)$ and $\sum I_0(hkl)$ are (hkl) intensity and total intensities of all peaks belonging to ZnO data which is taken from JCPDS card no:01-080-0074. The degree of orientation is related to lattice match between substrate and film. Although the glass substrate has an amorphous property, ZnO crystallization along the (002) plane maybe easier than as Al_2O_3 and Si substrate (Gao et al., 2005; Chakrabarti et al., 2004). In this study, degree of orientation of (002) plane increases with increasing Co doping. It can be clearly said that the degree of orientation is influenced by the Co doping.

The crystal orientation of the ZnO nano thin films produced by sol-gel is related to the solvent, the MEA/Zn ratio, the sol concentration, the coating parameters (film thickness), the heat treatment conditions and the substrate. ZnO nano thin films have (002) orientations. The highest concentration of ZnO is found along (002) plane. Plane has higher particle clusters.

The results obtained are very close to the value read from the JCPDS (ICDD) data card. Furthermore, When Zn^{+2} ions substitute with Co^{+2} ions ZnO band length

changes. ZnO bond length is calculated by the following equation (Srivastava et al., 2013);

$$L = \sqrt{\left(\frac{a^2}{3}\right) + \{(0.5) - u\}^2 c^2} \quad (6.7)$$

Here, a and c are lattice constants of ZnO, u is given for wurtzite structure as follows

$$u = \left(\frac{a^2}{3c^2}\right) + 1/4 \quad (6.8)$$

u is associated with a/c ratio. In addition, the bond angles α and β are calculated;

$$\alpha = \frac{\pi}{2} + \cos^{-1} \left[\sqrt{\left(1 + 3\left(\frac{c}{a}\right)^2 \left(-u + \frac{1}{2}\right)^2\right)} \right]^{-1} \quad (6.9)$$

$$\beta = 2\sin^{-1} \left[\sqrt{\left(\frac{4}{3} + 4\left(\frac{c}{a}\right)^2 \left(-u + \frac{1}{2}\right)^2\right)} \right]^{-1} \quad (6.10)$$

We can say that the covalent bond length formed between Zn and O ions varies as an inversely proportional with Co doping. The fluctuations are observed in the c-axis with increasing the Co doping. The reason for this is stress. The following formula is used for biaxial stress along the c axis.

$$\sigma = -453.6 \times 10^9 [(c - c_0)/c_0] \quad (6.11)$$

c and c_0 are parameters that are obtained from the XRD data and JCPDS data card, respectively. The negative sign in the Eqn. (6.11) refers to the compressive stress. The positive stress shows biaxial stress explained as a tensile (Table 6.12). Especially, the total stress consists from two contents. The first one is internal stress that includes defects and impurities. The order one is external stress which is caused by the lattice mismatch between substrate and film. Lattice parameter a is calculated because orientation of nano thin films toward to (101) plane. A significant change is not observed in the lattice parameter a .

The particle size of undoped and Co doped ZnO nano thin films is calculated by using Scherer formula. As can be seen from Table 6.12, grain size of nano thin films increases to with Co doping compared with undoped ZnO. But grain size decreases with increasing Co doping from 0.01 to 0.05. Transition metal element

doped ZnO nano thin films exhibit greater particle size than the undoped ZnO nano thin film. This size difference may be due to differences between ionic radius of doping element and zinc. Additionally, the entering of doping elements into the ZnO structure can cause the formation of more nucleation center. These results are supported with SEM analyses.

Table 6.12. Some structural values ZnO and Co doped ZnO nano thin films

<i>Samples</i>	<i>c (002)</i>	<i>a (101)</i>	<i>FWHM (deg.)</i>	<i>Grain Size (nm)</i>
<i>Undoped ZnO</i>	5.18	-	0.256	31.73
<i>Zn_{0.99}Co_{0.01}O</i>	5.20	-	0.300	34.37
<i>Zn_{0.98}Co_{0.02}O</i>	5.20	3.24	0.294	35.36
<i>Zn_{0.97}Co_{0.03}O</i>	5.22	3.25	0.296	35.02
<i>Zn_{0.96}Co_{0.04}O</i>	5.20	3.24	0.319	31.62
<i>Zn_{0.95}Co_{0.05}O</i>	5.20	3.24	0.320	31.48

Table 6.13. Some structural values ZnO and Co doped ZnO nano thin films

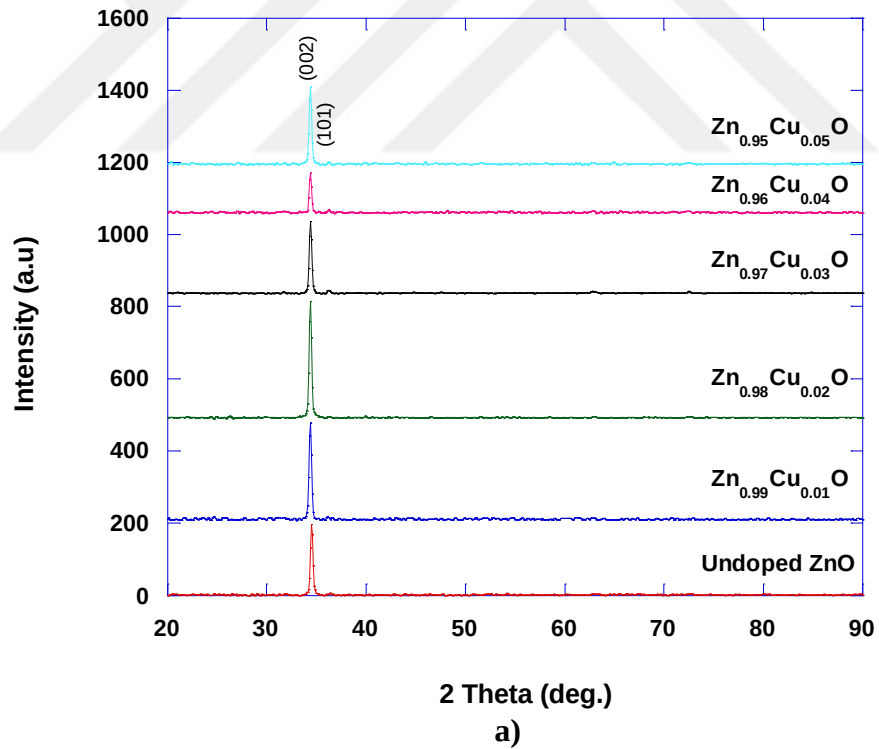
<i>Samples</i>	<i>f (degree of orientation)</i>	<i>L (nm)</i>	<i>α (°)</i>	<i>β (°)</i>	<i>σ*10⁹ (N/m²)</i>
<i>Undoped ZnO</i>	1.000	1.29	90	120	-1.75
<i>Zn_{0.99}Co_{0.01}O</i>	0.973	1.30	90	120	-0.872
<i>Zn_{0.98}Co_{0.02}O</i>	1.036	0.61	108	111	-0.872
<i>Zn_{0.97}Co_{0.03}O</i>	1.073	0.62	108	111	0.869
<i>Zn_{0.96}Co_{0.04}O</i>	1.119	0.63	109	110	-0.872
<i>Zn_{0.95}Co_{0.05}O</i>	1.159	0.63	109	110	-0.872

6.2.7 Transition Metal Doped DMS Zn_{1-x}B_xO (B=Cu) Nano Thin Film Materials

XRD analysis of the Cu doped ZnO nano thin films is given in Figure 6.16. As seen from the figure, all of undoped and Cu doped ZnO films are oriented along the (002) plane as the dominant and have a hexagonal wurtzite type structure. No extra diffraction peak from Cu-related second phase is observed. This can be explained as; Cu⁺² ions substituted for Zn⁺² ions of ZnO host semiconductor without changing the wurtzite structure. (002) peak position shifts to lower angle compared

to the undoped ZnO film (34.46°) (Fig.6.16b). This means that the lattice parameter increases with Cu doping compared with undoped ZnO. Also the (002) peak intensity generally decreases with increasing the Cu doping. The increasing of Cu concentration leads to deterioration of the ZnO crystal structure. This is associated with the formation of the amorphous structure.

According to the XRD peaks, it can be said Cu doped ZnO films are partially oriented to the (101) plane after from Cu0.03 doping rate. But the orientation of (002) plane is dominant. These results are supported with calculation of the degree of orientation (Table 6.14). The change of orientation is lead to changes of the bond angles α and β . Values of α which is 90 for hexagonal wurtzite ZnO structure are 108, 109 and 109 for Cu0.03, Cu0.04 and Cu0.05, respectively. Values of β which is 120 for hexagonal wurtzite ZnO structure are 111, 110 and 110, respectively.



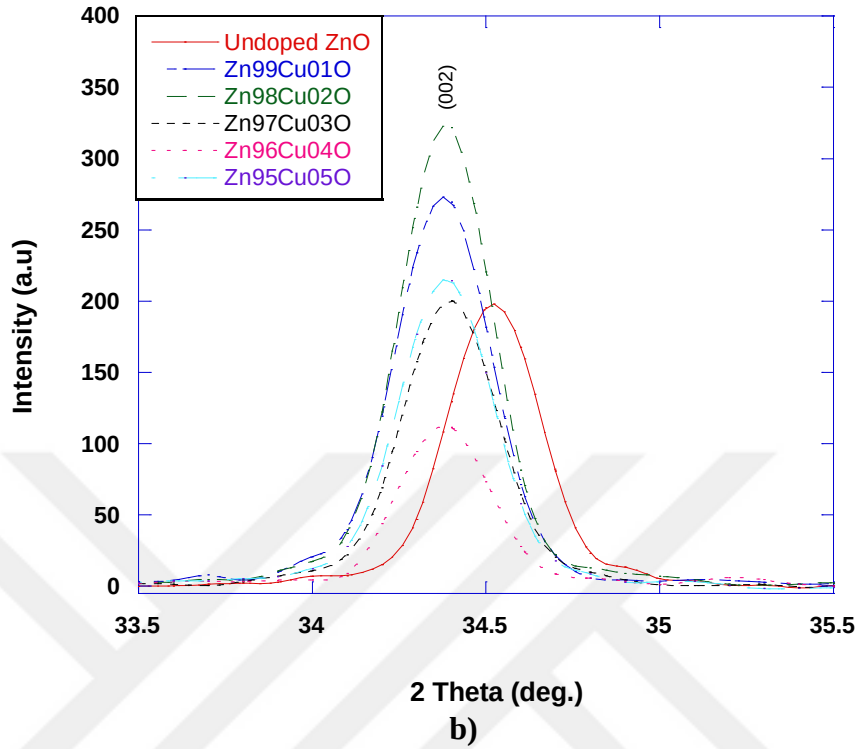


Figure 6.16. XRD patterns of $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ nano thin film materials

The FWHM value of the (002) peak is larger in doped films than undoped ZnO film. These results show that the Cu doped ZnO films have better crystal size than undoped ZnO nano thin film. This case is proved by the orientation of degree calculation (Eqn. 6.4). Degree of orientation of (002) plane increases with increasing Cu doping. It can be clearly said that the degree of orientation is influenced by the Cu doping. In addition, values of bond length given in the Table 6.14 decreased with increasing the Cu doping.

Lattice parameter c increases with doping compared with undoped ZnO. The fluctuations are observed in the c -axis with increasing the Cu doping. The reason for this is stress (Table 6.14). The positive stress shows biaxial stress explained as a tensile. Lattice parameter a is calculated because orientation of nano thin films toward to (101) plane. Lattice parameter a decreases with Cu doping.

Table 6.14. Some structural values ZnO and Cu doped ZnO nano thin films

<i>Samples</i>	<i>c</i> (002)	<i>a</i> (101)	<i>FWHM</i> (deg.)	<i>Grain</i> <i>Size</i> (nm)	<i>f</i>	<i>L</i> (nm)	<i>α</i> (°)	<i>β</i> (°)	<i>σ*10⁸</i> (N/m ²)
<i>Undoped ZnO</i>	5.18	-	0.256	31.73	1.000	1.29	90	120	-17.5
<i>Zn_{0.99}Cu_{0.01}O</i>	5.22	-	0.325	26.93	0.940	1.30	90	120	19.0
<i>Zn_{0.98}Cu_{0.02}O</i>	5.21	-	0.314	27.88	0.847	1.30	90	120	13.9
<i>Zn_{0.97}Cu_{0.03}O</i>	5.21	3.25	0.324	27.92	0.997	0.62	108	111	11.0
<i>Zn_{0.96}Cu_{0.04}O</i>	5.21	3.23	0.307	28.52	1.072	0.63	109	110	5.51
<i>Zn_{0.95}Cu_{0.05}O</i>	5.21	3.23	0.319	28.74	0.984	0.63	109	110	6.75

6.2.8 Transition Metal Doped Zn_{1-x-y}B_xC_yO (B=Cu, C=Co) DMS Nano Thin Film Materials

XRD analysis of the Cu and Co doped ZnO nano thin films are given in Figure 6.17. As seen from the figure, all of undoped and doped ZnO films are oriented along the (002) plane as the dominant and have a hexagonal wurtzite type structure. No extra diffraction peak from Cu or Co related second phase is observed. This can be explained as; Co⁺² and Cu⁺² ions substituted for Zn⁺² ions of ZnO host semiconductor without changing the wurtzite structure. (002) peak position shifts to lower angle compared to the undoped ZnO film (34.46°) (Fig.6.17b). This means that the lattice parameter increases with doping compared with undoped ZnO. The larger lattice constant denotes that ions of doping elements incorporate into the ZnO lattice and substitutes the Zn⁺² sites.

According to the XRD peaks, it can be said Cu/Co doped ZnO films are partially oriented to the (101) plane after from Cu0.03 doping rate. But the orientation of (002) plane is dominant. These results are supported with calculation of the degree of orientation (Table 6.15). The change of orientation is lead to changes of the bond angles α and β . Values of α which is 90 for hexagonal wurtzite ZnO structure are 108 for Co0.03, Co0.04, and Co0.05, respectively. Values of β which is 120 for hexagonal wurtzite ZnO structure are 110.

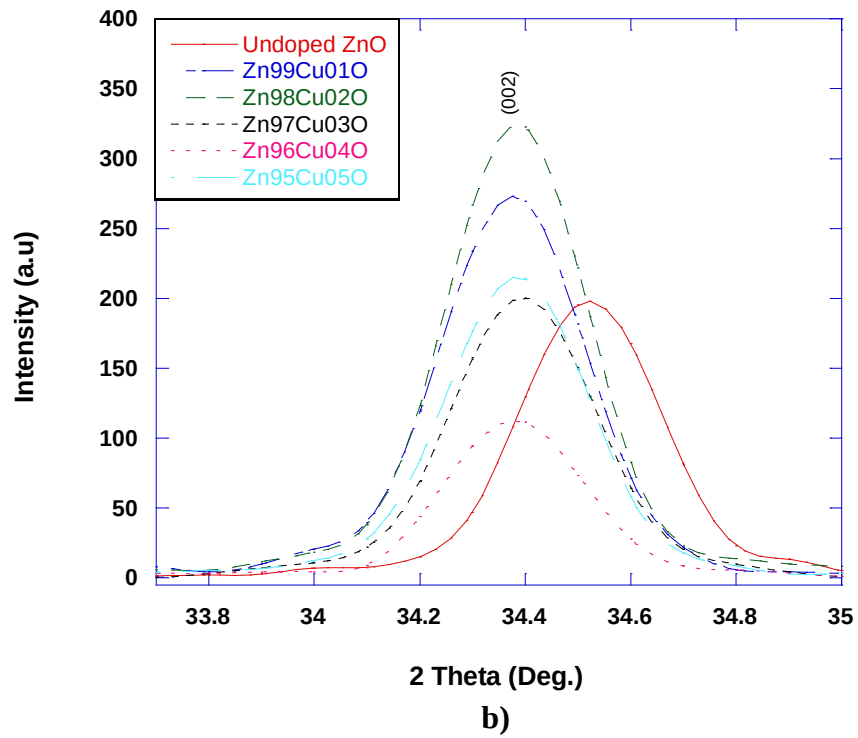
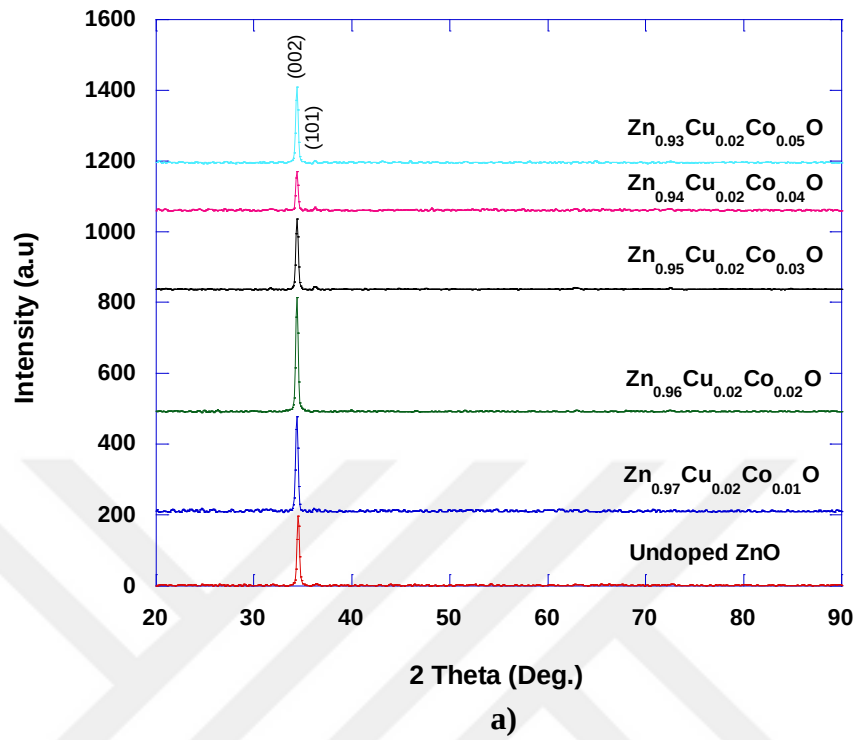


Figure 6.17. XRD patterns of Zn_{1-x-y}Cu_xCo_yO nano thin film materials

Table 6.15. Some structural values ZnO and Cu/Co doped ZnO nano thin films

Samples	<i>c</i> (002)	<i>a</i> (101)	FWHM (deg.)	Grain Size (nm)	<i>f</i>	<i>L</i> (nm)	α (°)	β (°)	$\sigma \cdot 10^8$ (N/m ²)
Undoped ZnO	5.18	-	0.256	31.73	1.000	1.29	90	120	-17.5
Zn _{0.97} Cu _{0.02} Co _{0.01} O	5.19	-	0.245	33.13	0.982	1.29	90	120	-9.63
Zn _{0.96} Cu _{0.02} Co _{0.02} O	5.20	-	0.258	32.51	1.014	1.30	90	120	-7.26
Zn _{0.95} Cu _{0.02} Co _{0.03} O	5.21	3.24	0.269	30.19	1.042	0.62	108	110	1.67
Zn _{0.94} Cu _{0.02} Co _{0.04} O	5.20	3.24	0.292	27.85	1.055	0.62	108	110	-1.04
Zn _{0.93} Cu _{0.02} Co _{0.05} O	5.20	3.25	0.372	21.86	1.082	0.62	108	110	-7.34

The FWHM value of the (002) peak is larger in doped films than undoped ZnO film. These results show that the Cu/Co doped ZnO films have better crystal size than undoped ZnO nano thin film. This case is proved by the orientation of degree calculation. Degree of orientation of (002) plane increases with increasing Cu/Co doping. It can be clearly said that the degree of orientation is influenced by the Cu/Co doping. In addition, values of bond length (*L*) given in the Table 6.15 decreased with increasing the Cu/Co doping.

Lattice parameter *c* increases with doping compared with undoped ZnO. Lattice parameter *a* increases with Cu/Co doping.

6.2.9 Rare Earth Element Doped Zn_{1-x}B_xO (B=Er) DMS Nano Thin Film Materials

XRD analysis of the Er doped ZnO nano thin films are given in Figure 6.18. As seen from the figure, all of undoped and Er doped ZnO films are oriented along the (002) plane and have a hexagonal wurtzite type structure. No extra diffraction peak from Er-related second phase is observed. This can be explained as; Er⁺³ ions substituted for Zn⁺² ions of ZnO host semiconductor without changing the wurtzite structure. (002) peak position shifts to lower angle compared to the undoped ZnO film (34.46°) (Fig.6.18b). This means that the lattice parameter increases with Er doping. This is an expected result. Because the ionic radius of Zn⁺² (0.74Å) is smaller than the ionic radius of Er⁺³ (0.88Å).

The larger lattice constant denotes that Er^{+3} ions incorporates into the ZnO lattice and substitutes the Zn^{+2} sites. Also the (002) peak intensity decreases with increasing the Er doping. The increasing of Er concentration leads to deterioration of the ZnO crystal structure. This is associated with the formation of the amorphous structure.

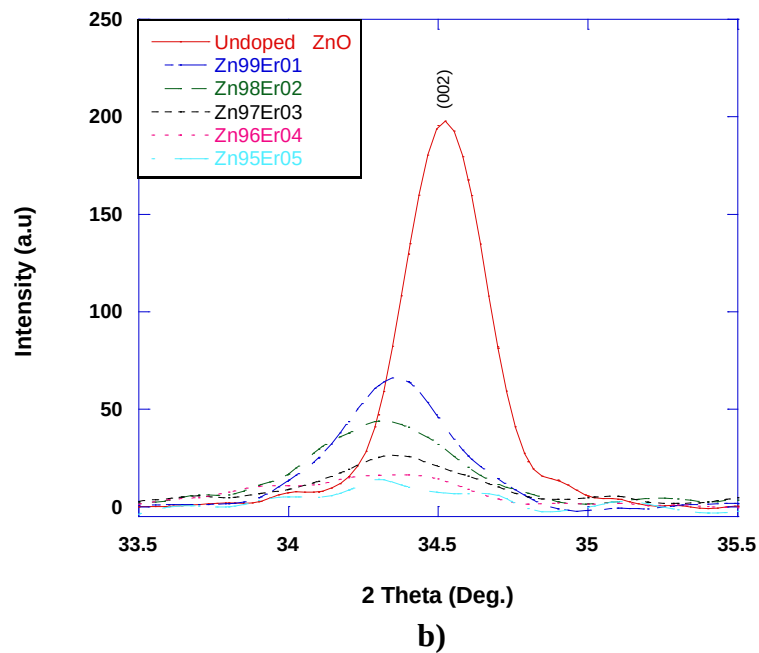
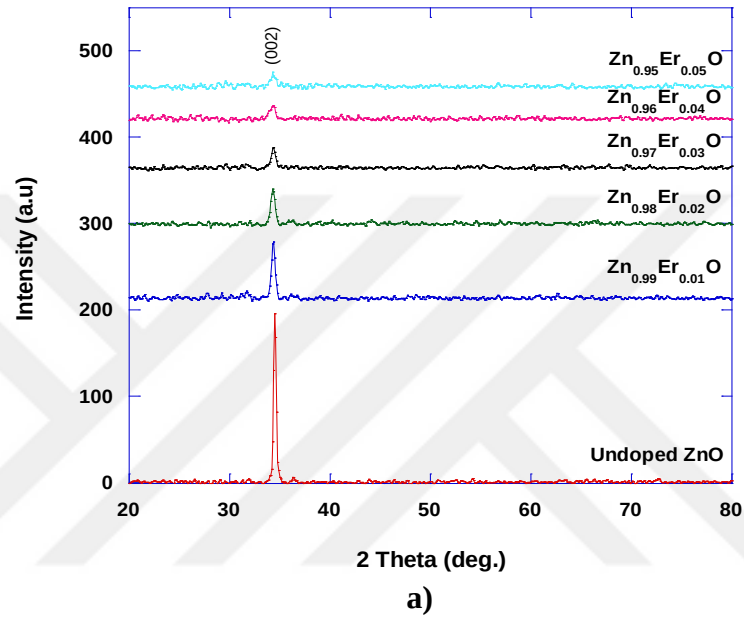


Figure 6.18. XRD patterns of Zn_{1-x}Er_xO nano thin film materials

The FWHM value of the (002) peak is larger in doped films than undoped ZnO film. These results show that the Er doped ZnO films have better crystal size than undoped ZnO nano thin film. ZnO nano thin films that are produced by sol-gel are oriented along the (002) plane in the most of previous studies. Also, this case is proved by the orientation of degree calculation.

In this study, degree of orientation of (002) plane increases with increasing Er doping. It can be clearly said that the degree of orientation is influenced by the *Er* doping (Table 6.16).

c lattice constant of hexagonal structure is determined. The results obtained are very close to the value read from the JCPDS data card. Furthermore, When Zn^{+2} ions substitute with Er^{+3} ions, ZnO band length changes. ZnO bond length is calculated (Table 6.16). We may say that the covalent bond length formed between *Zn* and *O* ions varies as an inversely proportional with *Er* doping. The fluctuations are observed in the *c*-axis with increasing the *Er* doping. The reason for this is stress. The biaxial stress along the *c* axis is calculated. The positive stress shows biaxial stress explained as a tensile (Table 6.16). Especially, the total stress consists from two contents. The first one is internal stress that includes defects and impurities. The order one is external stress which is caused by the lattice mismatch between substrate and film.

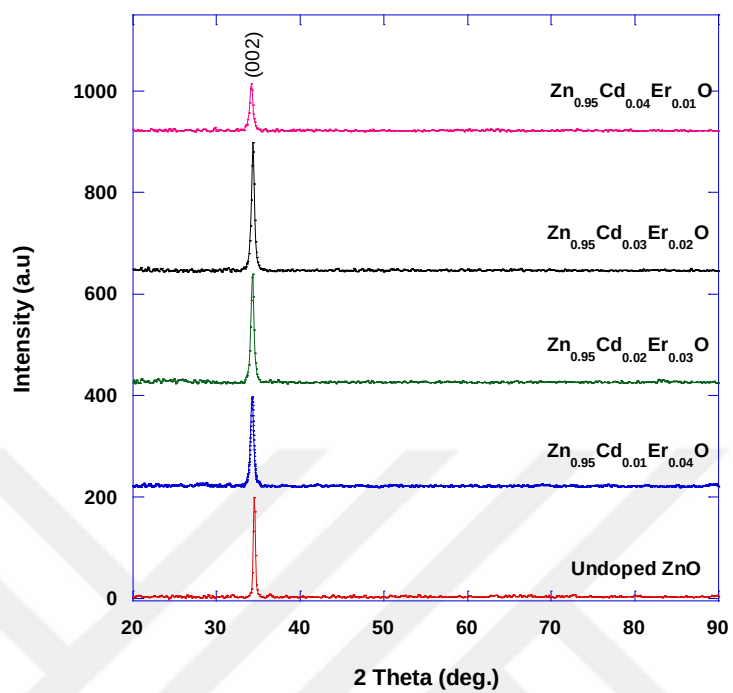
The particle size of undoped and Er doped ZnO nano thin films are calculated by using Scherer formula (Asikuzun et al., 2015). As can be seen from Table 6.16, particle size of nano thin films decreases to 16.32 nm from 31.73 nm with Er doping. Rare earth metal doped ZnO nano thin films exhibit smaller particle size than the undoped ZnO nano thin film. This size difference may be due to differences between ionic radius of doping element and zinc. Additionally, the entering of doping elements into the ZnO structure can cause the formation of more nucleation center. These results are supported with SEM analyses.

Table 6.16. Some structural values ZnO and Er doped ZnO nano thin films

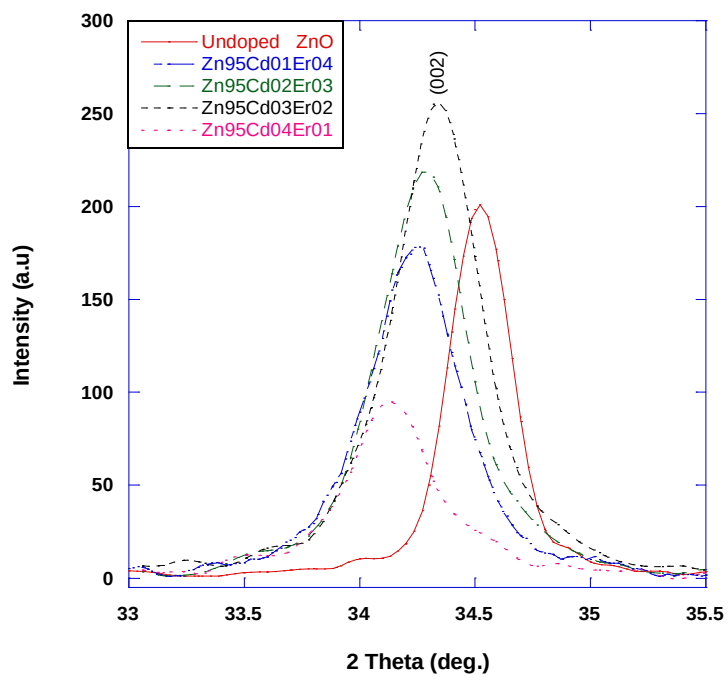
<i>Samples</i>	<i>c</i> (002)	<i>FWHM</i> (deg.)	<i>Grain</i> <i>Size</i> (nm)	<i>f</i>	<i>L</i> (nm)	<i>α</i> (°)	<i>β</i> (°)	<i>σ*10⁹</i> (N/m ²)
Undoped ZnO	5.18	0.256	31.73	1.000	1.29	90	120	-1.75
Zn_{0.99}Er_{0.01}O	5.21	0.444	18.32	1.110	1.30	90	120	1.02
Zn_{0.98}Er_{0.02}O	5.22	0.477	17.05	1.131	1.30	90	120	1.87
Zn_{0.97}Er_{0.03}O	5.22	0.506	16.07	1.136	1.30	90	120	1.93
Zn_{0.96}Er_{0.04}O	5.23	0.466	17.47	1.150	1.30	90	120	3.10
Zn_{0.95}Er_{0.05}O	5.23	0.498	16.32	1.168	1.30	90	120	3.20

6.2.10 Rare Earth Element Doped Zn_{1-x-y}B_xC_yO (B=Er, C=Cd) DMS Nano Thin Film Materials

XRD analysis of the Cd/Er doped ZnO nano thin films are given in Figure 6.19. As seen from the figure, all of undoped and doped ZnO films are oriented along the (002) plane and have a hexagonal wurtzite type structure. No extra diffraction peak from Cd and Er related second phase is observed. This can be explained as; Cd⁺² and Er⁺³ ions substituted for Zn⁺² ions of ZnO host semiconductor without changing the wurtzite structure. (002) peak position shifts to lower angle compared to the undoped ZnO film (34.46°) (Fig.6.19b). This means that the lattice parameter increases with Cd/Er doping compared with undoped ZnO nano thin film. This is an expected result. Because the ionic radius of Zn⁺² (0.74Å) is smaller than the ionic radius of Er⁺³ (0.88Å) and Cd⁺² (0.97Å). The larger lattice constant denotes that Er⁺³ and Cd⁺² ions incorporate into the ZnO lattice and substitutes the Zn⁺² sites.



a)



b)

Figure 6.19. XRD patterns of Zn_{1-x-y}Cd_xEr_yO nano thin film materials

The FWHM value of the (002) peak is larger in doped films than undoped ZnO film. These results show that the Cd/Er doped ZnO films have better crystal size than undoped ZnO nano thin film. ZnO nano thin films that are produced by sol-gel are oriented along the (002) plane in the most of previous studies. Also, this case is proved by the orientation of degree calculation.

c lattice constant of hexagonal structure is determined. The results obtained are very close to the value read from the JCPDS data card. Furthermore, When Zn^{+2} ions substitute with Cd^{+2} and Er^{+3} ions, ZnO band length changes. ZnO bond length is calculated (Table 6.17). The fluctuations are observed in the c -axis with increasing the Cd/Er doping. The reason for this is stress. The biaxial stress along the c axis is calculated. The positive stress shows biaxial stress explained as a tensile (Table 6.17).

The particle sizes of undoped and Cd/Er doped ZnO nano thin films are calculated by using Scherer formula. As can be seen from Table 6.17, particle size of nano thin films decreases from 31.73 nm to 21.90 nm with doping. Rare earth metal doped ZnO nano thin films exhibit smaller particle size than the undoped ZnO nano thin film. This size difference may be due to differences between ionic radius of doping element and zinc. Additionally, the entering of doping elements into the ZnO structure can cause the formation of more nucleation center. These results are supported with SEM analyses.

Table 6.17. Some structural values ZnO and Cd/Er doped ZnO nano thin films

<i>Samples</i>	<i>c (Å)</i>	<i>Grain Size (nm)</i>	<i>FWHM</i>	<i>f</i>	<i>L (nm)</i>	<i>α (°)</i>	<i>β (°)</i>	<i>σ*10⁸ (N/m²)</i>
Undoped ZnO	5.18	31.73	0.256	1.000	1.30	90	120	-0.90
Zn_{0.95}Cd_{0.01}Er_{0.04}O	5.22	21.90	0.465	1.015	1.30	90	120	-7.26
Zn_{0.95}Cd_{0.02}Er_{0.03}O	5.22	21.75	0.452	0.987	1.30	90	120	1.67
Zn_{0.95}Cd_{0.03}Er_{0.02}O	5.20	22.76	0.435	0.954	1.31	90	120	8.60
Zn_{0.95}Cd_{0.04}Er_{0.01}O	5.24	24.21	0.413	1.123	1.30	90	120	-0.90

6.3 Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) Measurements of ZnO Based Nano Bulk and Nano Thin Film Materials

6.3.1 Transition Metal Doped $\text{Zn}_{1-x}\text{B}_x\text{O}$ (B=Co) DMS Nano Bulk Materials

SEM images and EDS analysis of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ bulk series in 200000 and 25000 magnification that are annealed at 5 bar Argon ambient pressure are given in the Figure 6.20-6.26. When the images are analyzed, it is observed that the grain size decreases with increasing Co doping. The grain sizes are scaled during SEM measurements, but they do not very clear. It is observed by using this scale that the grain sizes decrease with Co doping. In addition, Warren- Scherer values are calculated using the XRD data shown that the grain sizes decrease with increasing the Co doping. But the compared with undoped ZnO, the grain size increases with Co doping. The size difference may be due to the difference between ionic radius of doping element ($\text{Co}^{+2} = 0.79\text{\AA}$) and host element ($\text{Zn}^{+2} = 0.74\text{\AA}$). The entering of doping element into the structure of ZnO can cause to the formation of more nucleation centers (Tsay et al., 2013).

The change in Zn content with Co doping is investigated by using the EDS analysis (Figure 6.20-6.26). It is observed that the atomic percentage of Zn decreases with Co doping (Table 6.18-6.24). This is an expected result. As interpreted from the XRD analysis, the Co^{+2} ions replacement with Zn^{+2} ions in the ZnO lattice due to the ionic radius of Co ($0.79\text{\AA}$) is greater than the ionic radius of Zn ($0.74\text{\AA}$). Therefore there is no peak of the Co atoms. In addition, this result is observed using EDS measurement. According the EDS analyses the amount of Zn decreases with Co doping.

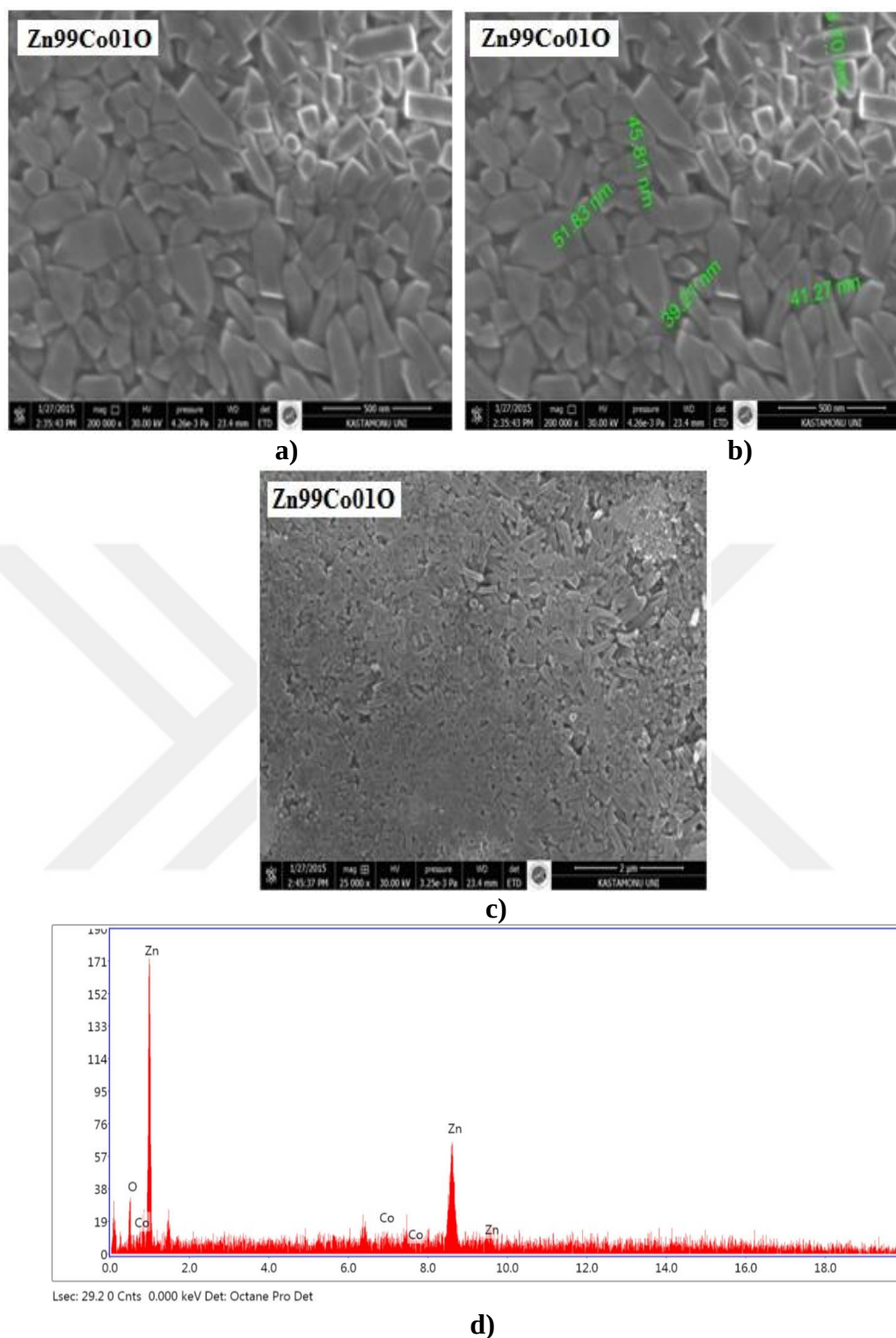


Figure 6.20. SEM images a) and b) at 200000 magnification, c) at 25000 magnification and d) EDS of Zn_{0.99}Co_{0.01}O nano bulk materials

Table 6.18. EDS results of Zn_{0.99}Co_{0.01}O nano bulk materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	35.12	68.81	7.92
Co	1.51	0.81	1.61
Zn	63.37	30.39	31.63

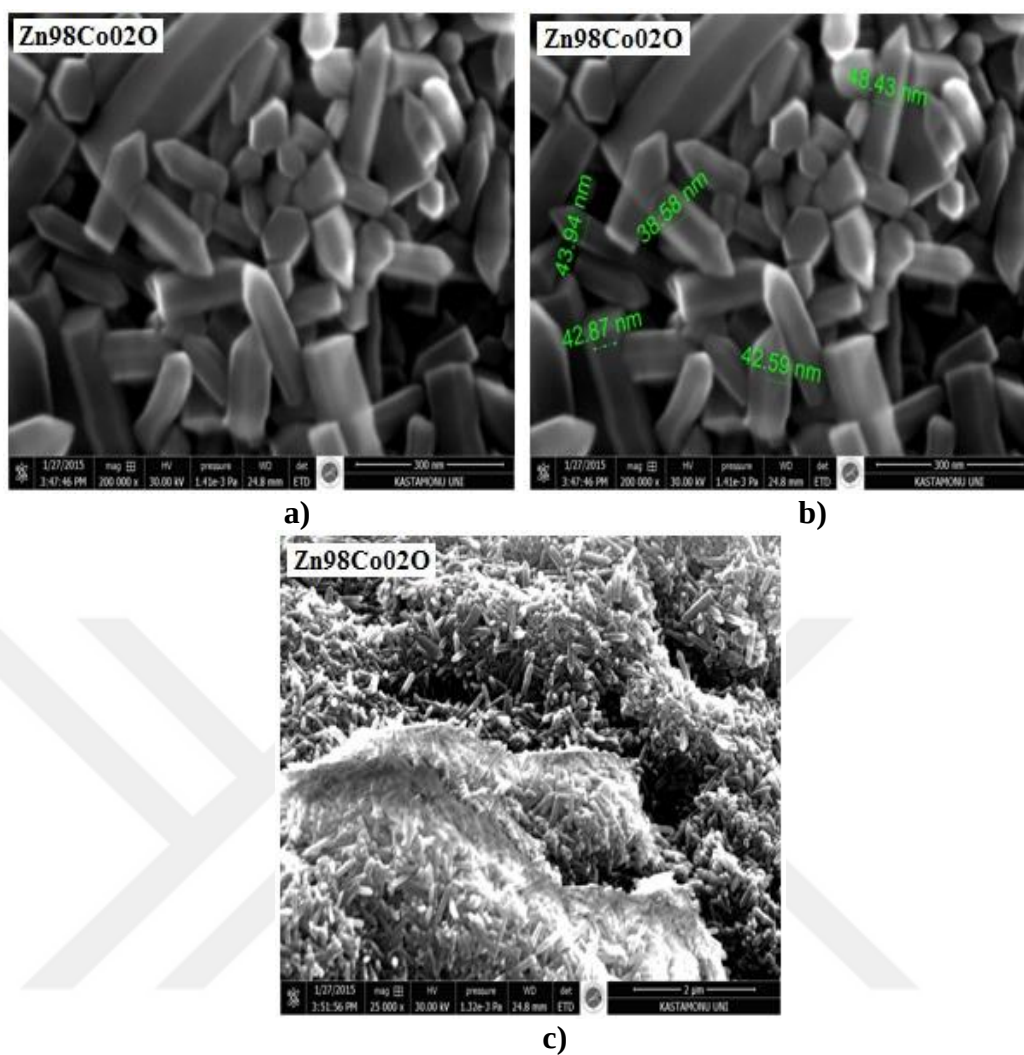


Figure 6.21. SEM images a) and b) at 200000 magnification, c) at 25000 magnification and d) EDS of Zn_{0.98}Co_{0.02}O nano bulk material

Table 6.19. EDS results of Zn_{0.98}Co_{0.02}O nano bulk materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	37.88	56.66	1.64
Co	1.61	1.25	1.12
Zn	60.51	28.09	27.02

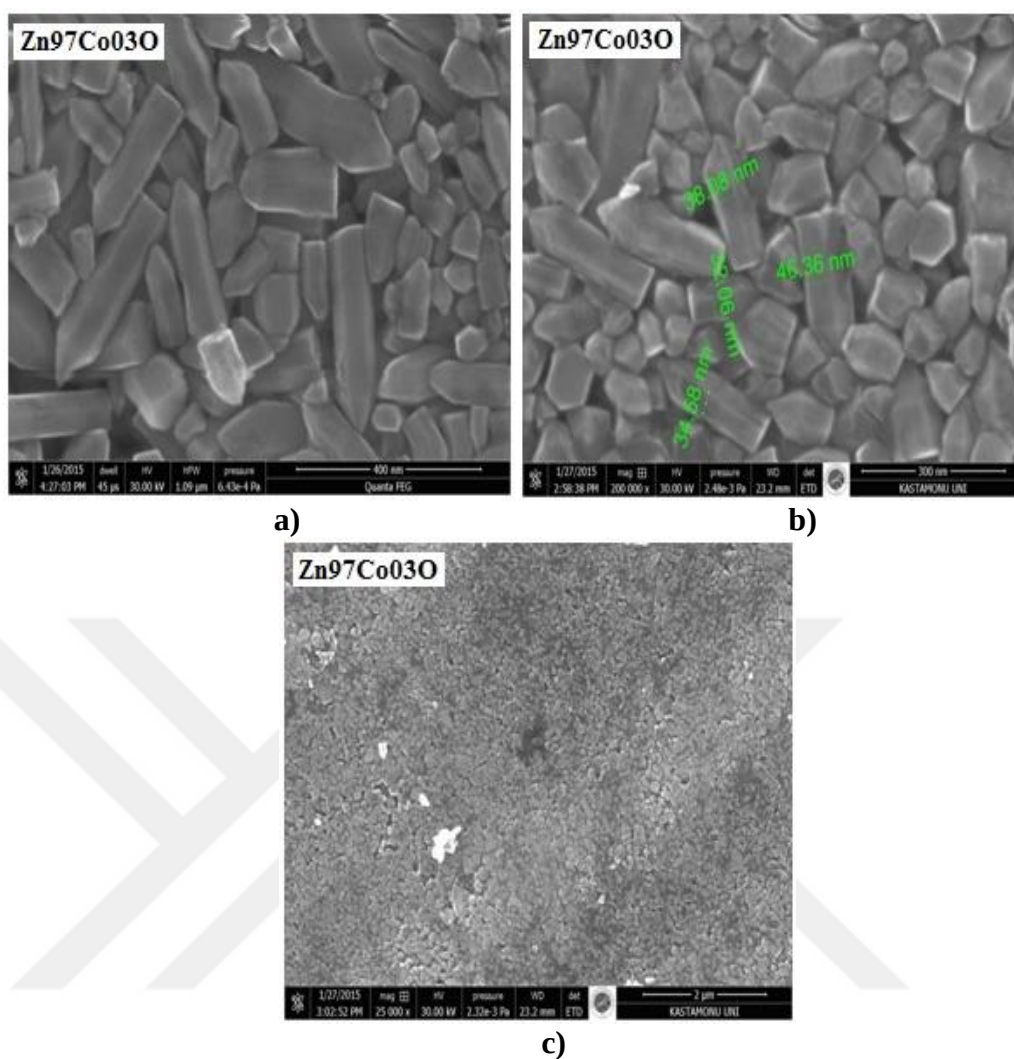


Figure 6.22. SEM images a) and b) at 200000 magnification, c) at 25000 magnification and d) EDS of $\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$ nano bulk material

Table 6.20. EDS results of $\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$ nano bulk materials

Element	Weight %	Atomic %	Net Int.
O	37.95	57.14	3.73
Co	3.74	2.38	2.92
Zn	58.31	40.48	27.44

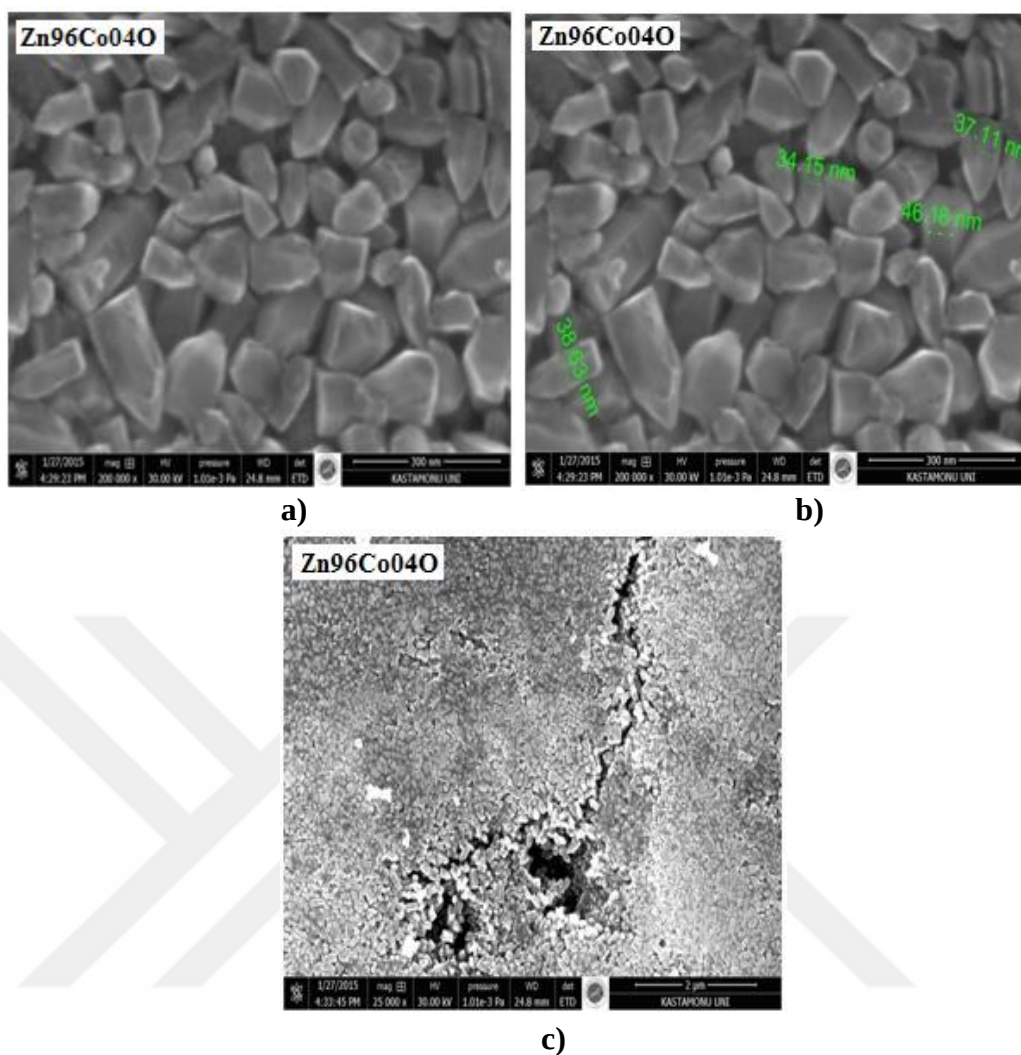


Figure 6.23 SEM images a) and b) at 200000 magnification, c) at 25000 magnification and d) EDS of Zn_{0.96}Co_{0.04}O nano bulk material

Table 6.21. EDS results of Zn_{0.96}Co_{0.04}O nano bulk materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	36.19	57.62	8.81
Co	5.68	3.72	10.97
Zn	58.13	40.65	70.02

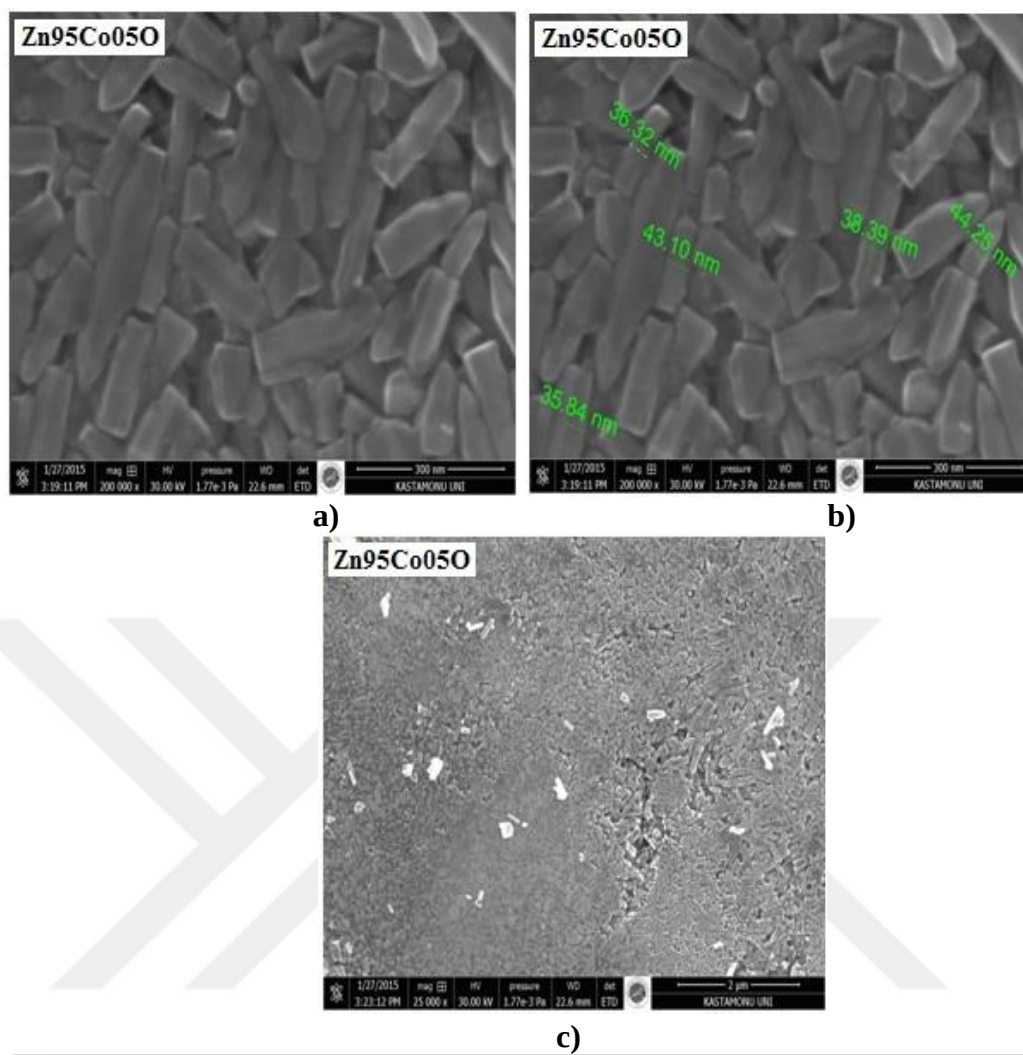


Figure 6.24. SEM images a) and b) at 200000 magnification, c) at 25000 magnification and d) EDS of Zn_{0.95}Co_{0.05}O nano bulk material

Table 6.22. EDS results of Zn_{0.95}Co_{0.05}O nano bulk materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	32.72	56.23	9.61
Co	10.11	6.21	16.11
Zn	57.17	38.56	54.83

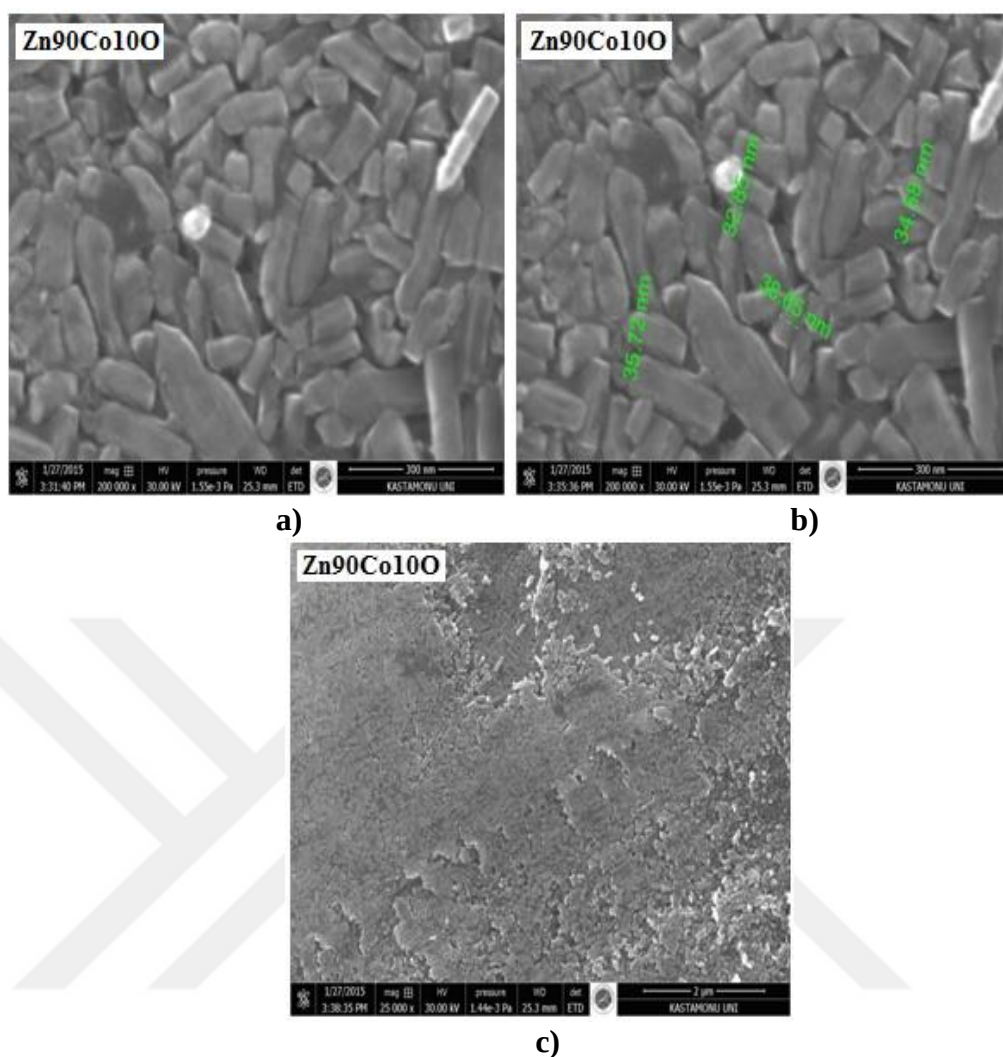


Figure 6.25. SEM images a) and b) at 200000 magnification, c) at 25000 magnification and d) EDS of Zn_{0.90}Co_{0.10}O nano bulk material

Table 6.23. EDS results of Zn_{0.90}Co_{0.10}O nano bulk materials

Element	Weight %	Atomic %	Net Int.
O	25.84	58.14	4.74
Co	16.95	10.35	11.82
Zn	57.21	31.5	22.76

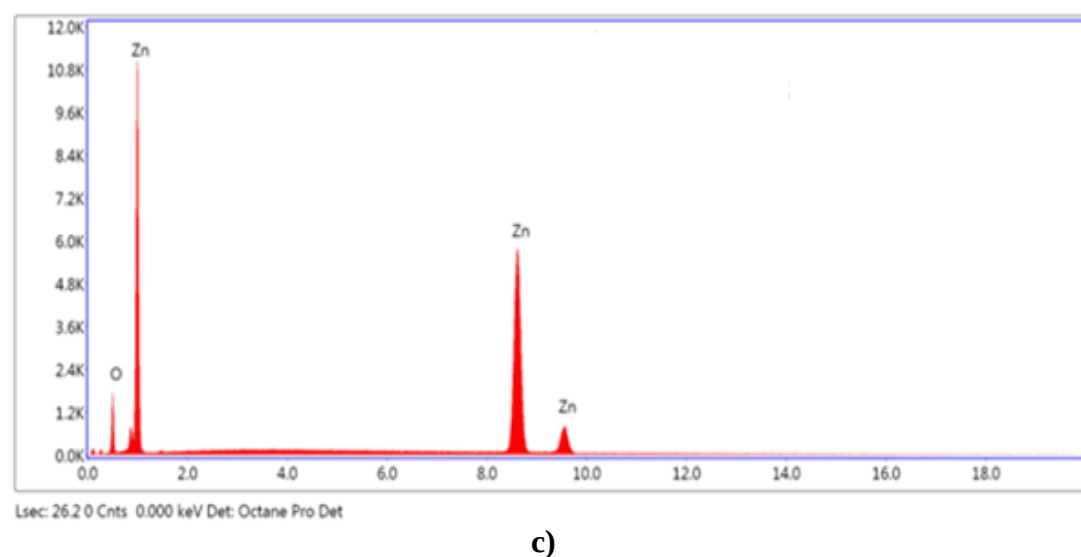
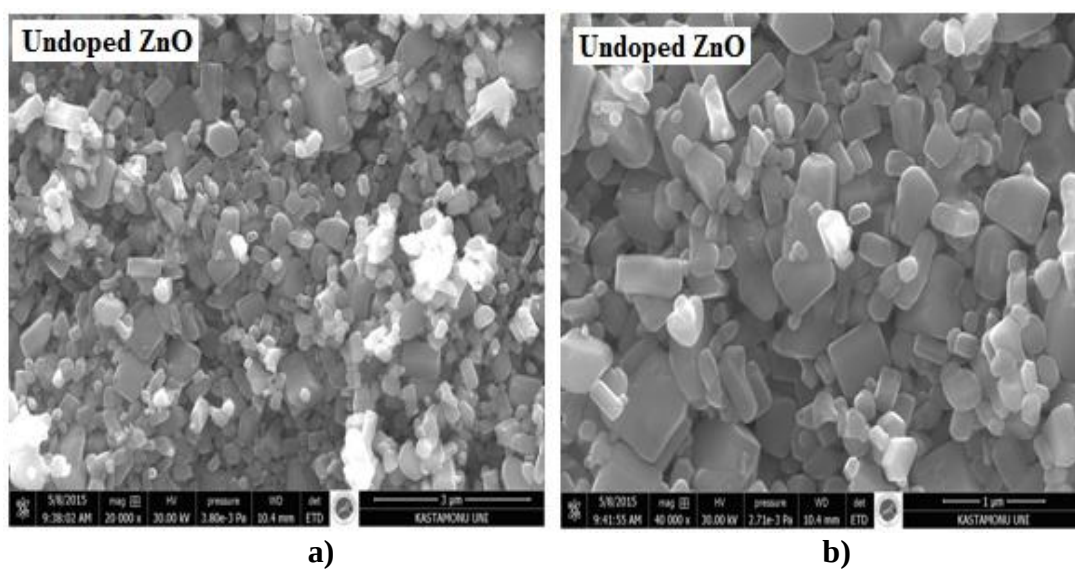


Figure 6.26. SEM images a) at 20000 magnification, b) at 40000 magnification and c) EDS of undoped ZnO nano bulk material

Table 6.24. EDS results of undoped ZnO nano bulk materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
<i>O</i>	17.73	46.83	292.81
<i>Zn</i>	82.27	53.17	3602.95

6.3.2 Transition Metal Doped $\text{Zn}_{1-x-y}\text{B}_x\text{C}_y\text{O}$ (B=Cu, C=Co) DMS Nano Bulk Materials

SEM images and EDS analysis of $\text{Zn}_{1-x}\text{Cu}_{0.01}\text{Co}_x\text{O}$ bulk series in 80000 and 40000 magnification that are annealed at 5 bar Argon ambient pressure are given in the Figure 6.27-6.31. When the images are analyzed, it is observed that the grain size increases with increasing Cu/Co co-doping. The grain size values are calculated using the XRD data shown that the grain sizes increase with increasing the Cu/Co doping and the compared with undoped ZnO.

The change in Zn content with Co and Cu doping is investigated by using the EDS analysis. It is observed that the atomic percentage of Zn decreases with Co doping (Table 6.25-6.29). This is an expected result. As interpreted from the XRD analysis, the Co^{+2} ions replacement with Zn^{+2} ions in the ZnO lattice due to the ionic radius of Co^{+2} (0.79Å) and Cu^{+2} (0.87Å) is greater than the ionic radius of Zn (0.74Å). Therefore there is no peak of the Co and Cu atoms.

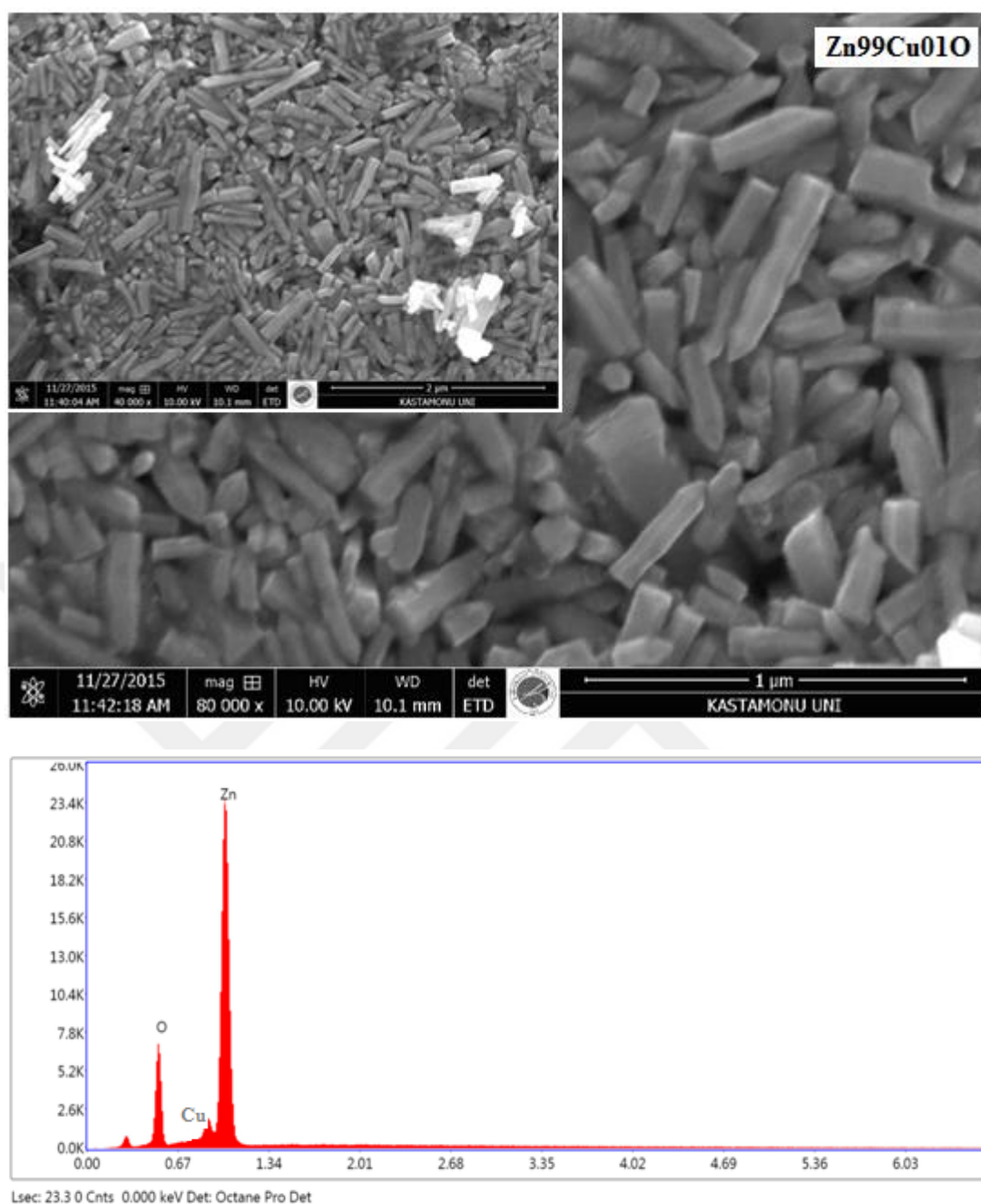


Figure 6.27. SEM and EDS images of $Zn_{0.99}Cu_{0.01}O$ nano bulk material

Table 6.25. EDS results of $Zn_{0.99}Cu_{0.01}O$ nano bulk materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
<i>O</i>	14.87	40.61	1419.25
<i>Cu</i>	1.32	1.4	104.44
<i>Zn</i>	83.81	57.99	5673.37

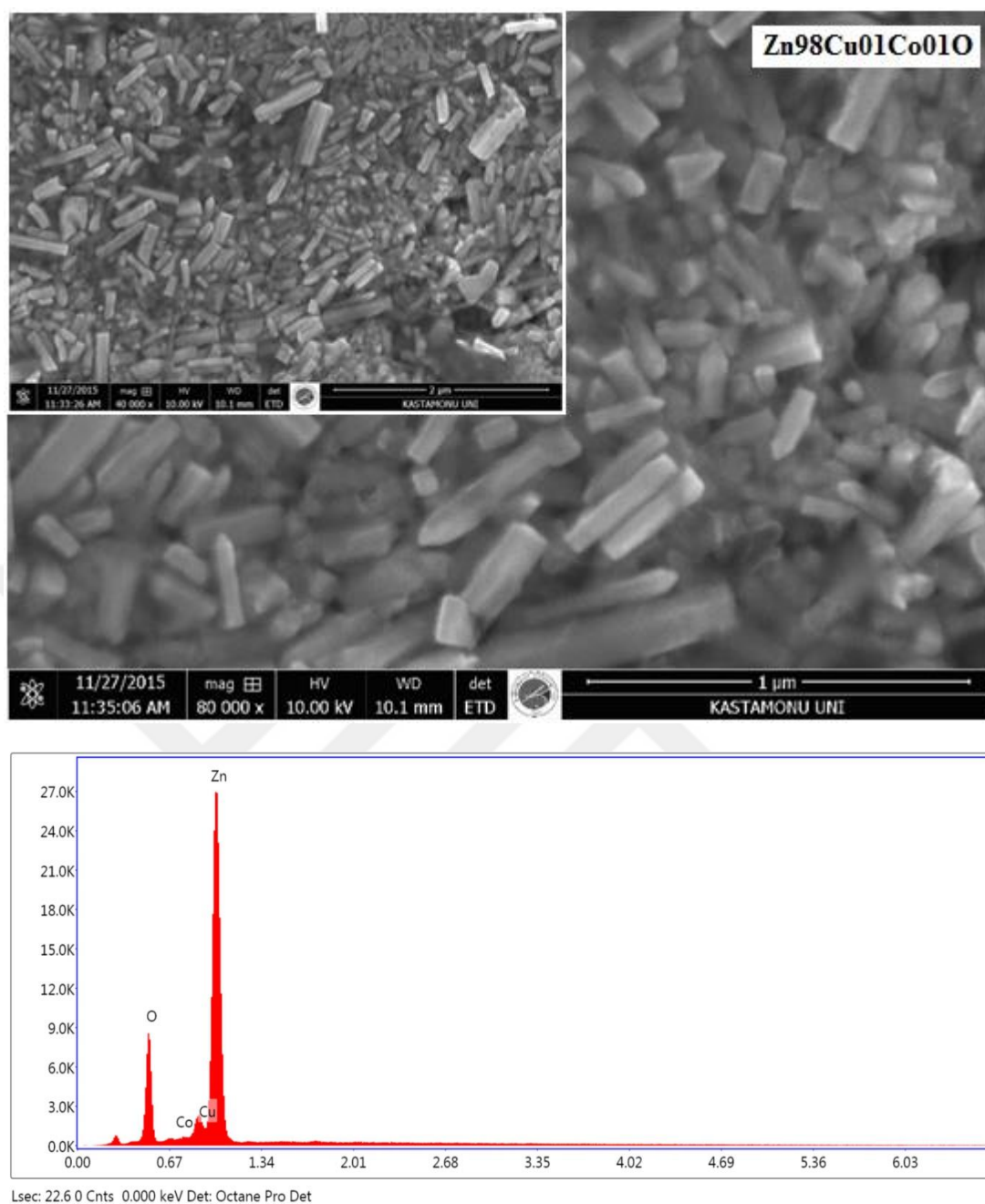


Figure 6.28. SEM and EDS images of $\text{Zn}_{0.98}\text{Cu}_{0.01}\text{Co}_{0.01}\text{O}$ nano bulk material

Table 6.26. EDS results of $\text{Zn}_{0.98}\text{Cu}_{0.01}\text{Co}_{0.01}\text{O}$ nano bulk materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	15.2	42.25	1789.94
Co	0.58	0.44	39.52
Cu	1.26	0.88	115.06
Zn	82.95	56.42	6643.65

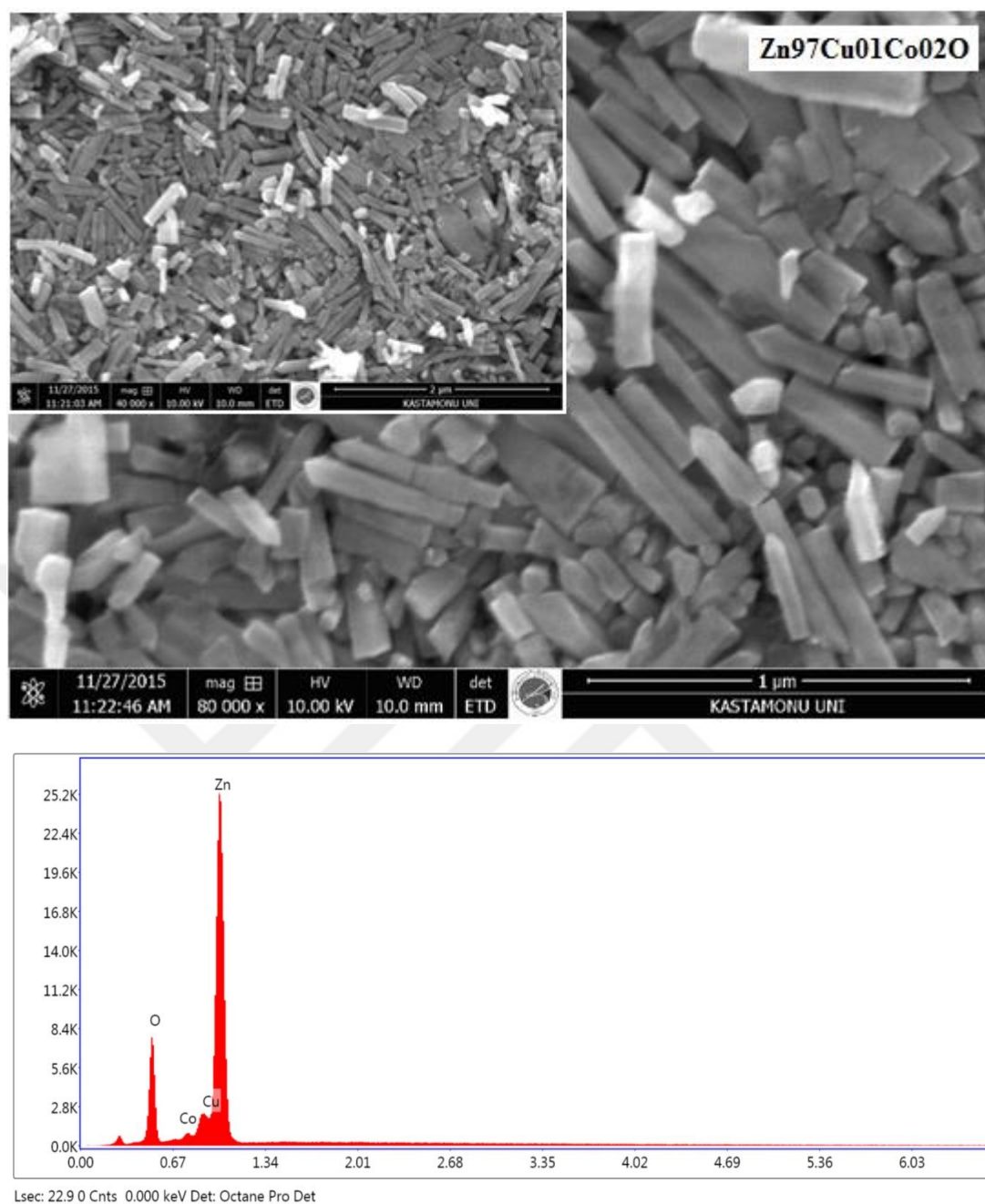


Figure 6.29. SEM and EDS images of $\text{Zn}_{0.97}\text{Cu}_{0.01}\text{Co}_{0.02}\text{O}$ nano bulk material

Table 6.27. EDS results of $\text{Zn}_{0.97}\text{Cu}_{0.01}\text{Co}_{0.02}\text{O}$ nano bulk materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	14.37	40.61	1595.39
Co	1.25	0.96	80.36
Cu	2.98	2.12	254.29
Zn	81.41	56.31	6013.62

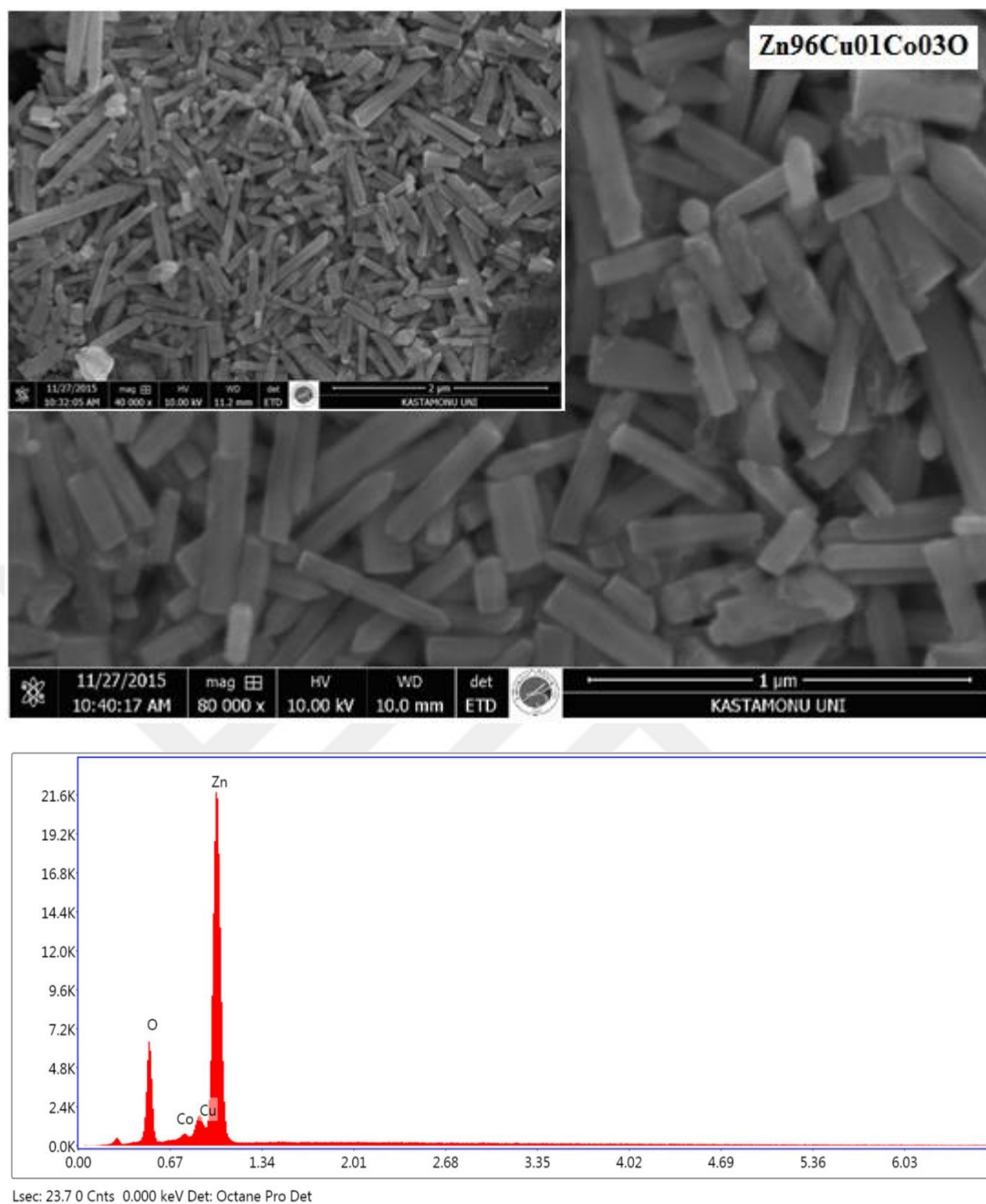


Figure 6.30. SEM and EDS images of $\text{Zn}_{0.96}\text{Cu}_{0.01}\text{Co}_{0.03}\text{O}$ nano bulk material

Table 6.28. EDS results of $\text{Zn}_{0.96}\text{Cu}_{0.01}\text{Co}_{0.03}\text{O}$ nano bulk materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	16.17	40.23	1263.65
Co	1.33	1.03	69.23
Cu	1.58	1.13	108.86
Zn	80.92	57.62	5010.65

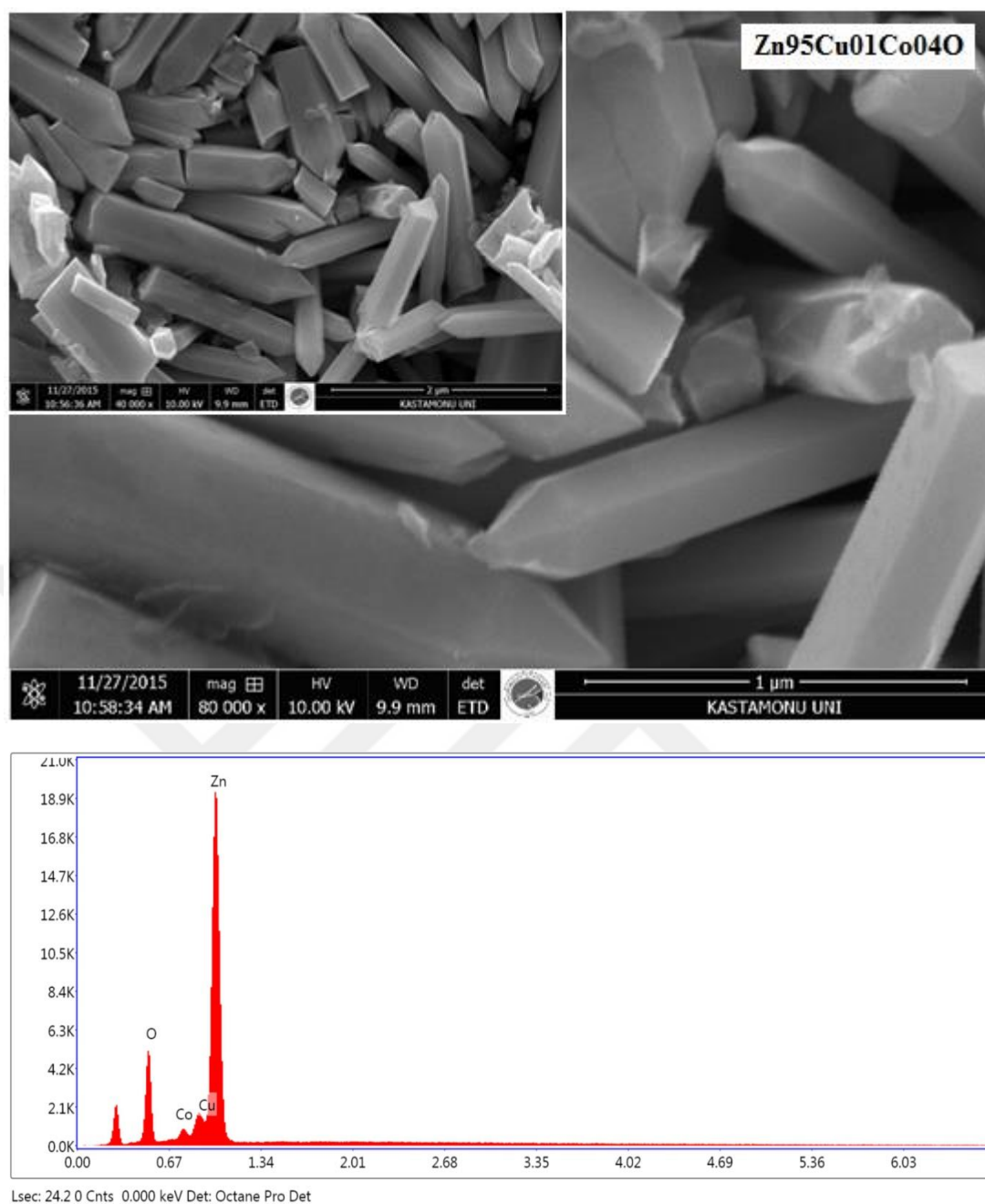


Figure 6.31. SEM and EDS images of $\text{Zn}_{0.95}\text{Cu}_{0.01}\text{Co}_{0.04}\text{O}$ nano bulk material

Table 6.29. EDS results of $\text{Zn}_{0.95}\text{Cu}_{0.01}\text{Co}_{0.04}\text{O}$ nano bulk materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	15.74	37.31	975.65
Co	1.52	1.21	69.06
Cu	2.3	1.7	137.96
Zn	80.44	59.79	4337.46

6.3.3 Transition Metal Doped $\text{Zn}_{1-x-y}\text{B}_x\text{C}_y\text{O}$ (B=Mg, C=Co) DMS Nano Bulk Materials

SEM images of $\text{Zn}_{1-x-y}\text{Mg}_x\text{Co}_y\text{O}$ bulk series in 100000 and 50000 magnification are given in the Figure 6.32-6.37. When the images are analyzed, it is observed that the grain size increases with increasing Mg doping. The grain size values calculated using the XRD data are supported this results.

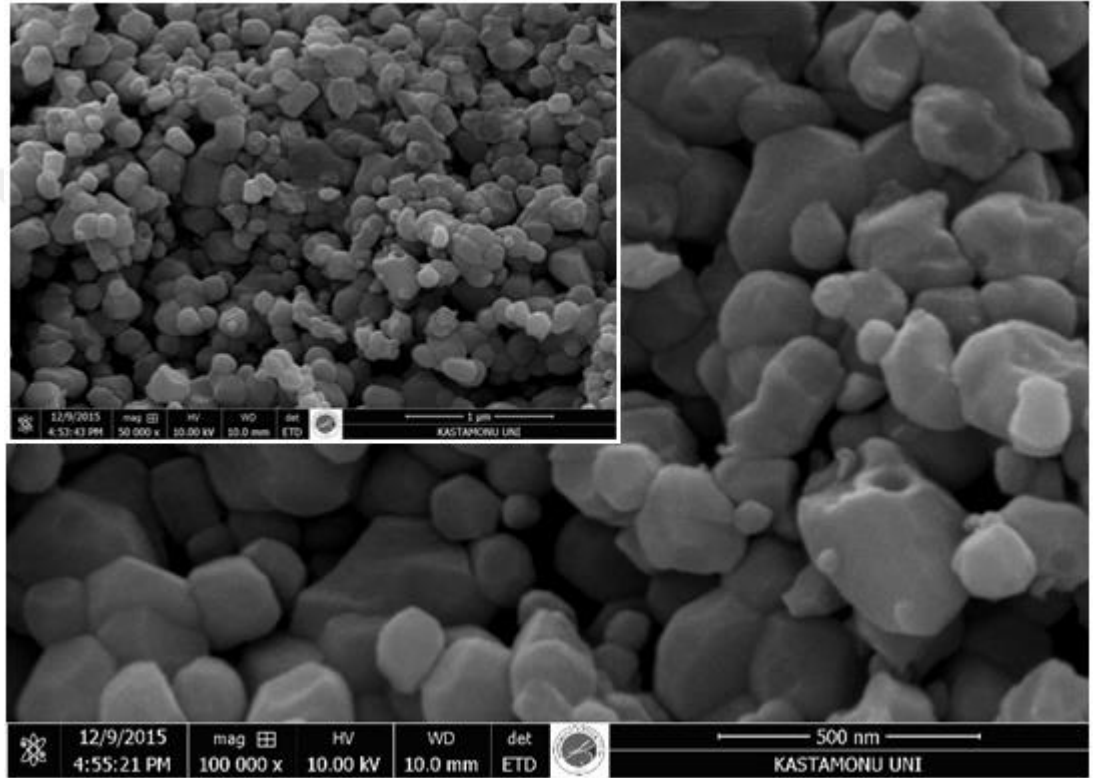


Figure 6.32. SEM images of $\text{Zn}_{0.90}\text{Mg}_{0.05}\text{Co}_{0.05}\text{O}$ nano bulk material

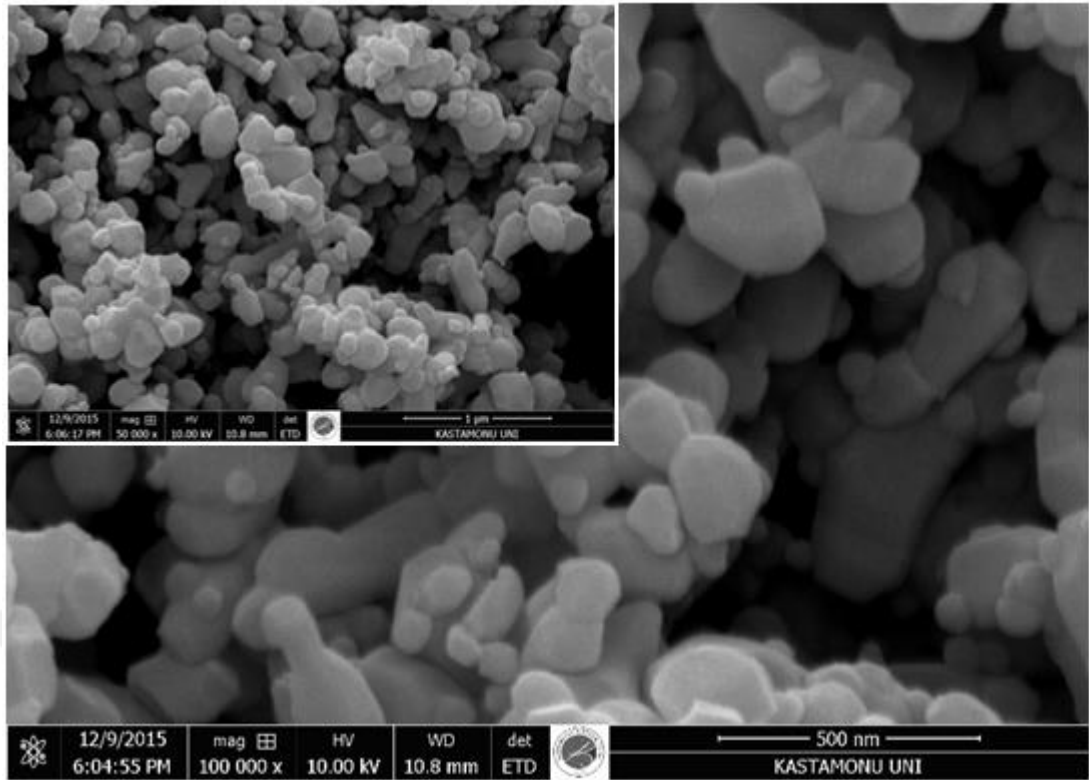


Figure 6.33. SEM images of $\text{Zn}_{0.91}\text{Mg}_{0.04}\text{Co}_{0.05}\text{O}$ nano bulk material

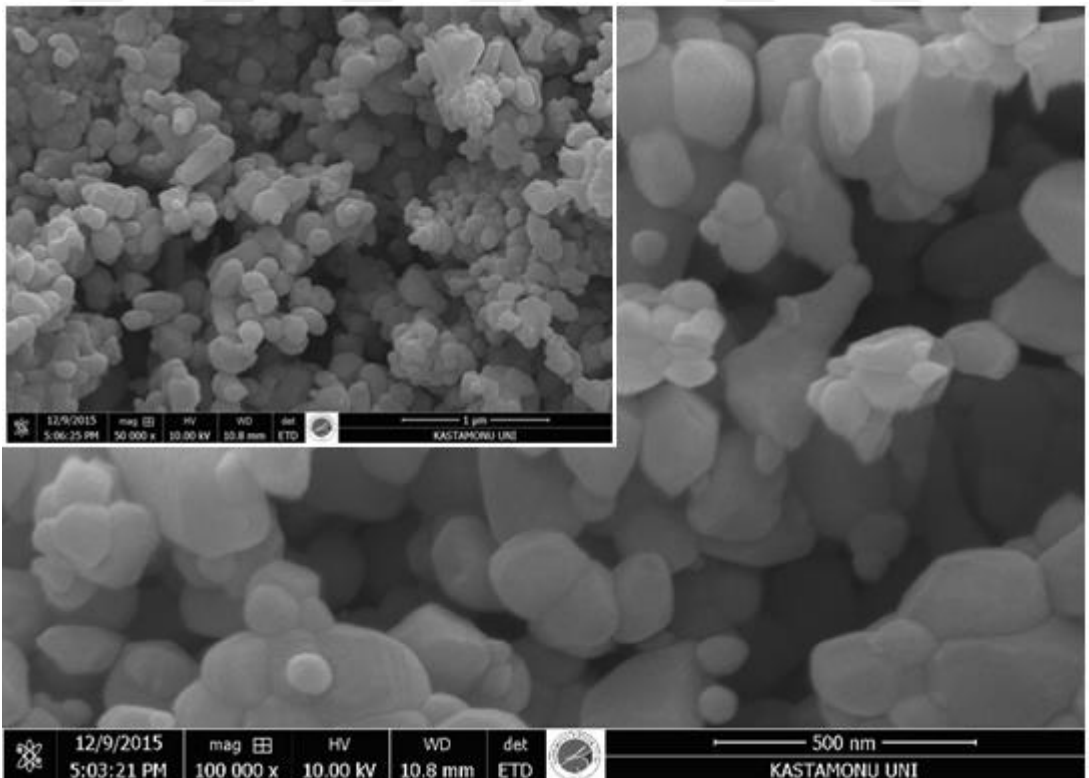


Figure 6.34. SEM images of $\text{Zn}_{0.92}\text{Mg}_{0.03}\text{Co}_{0.05}\text{O}$ nano bulk material

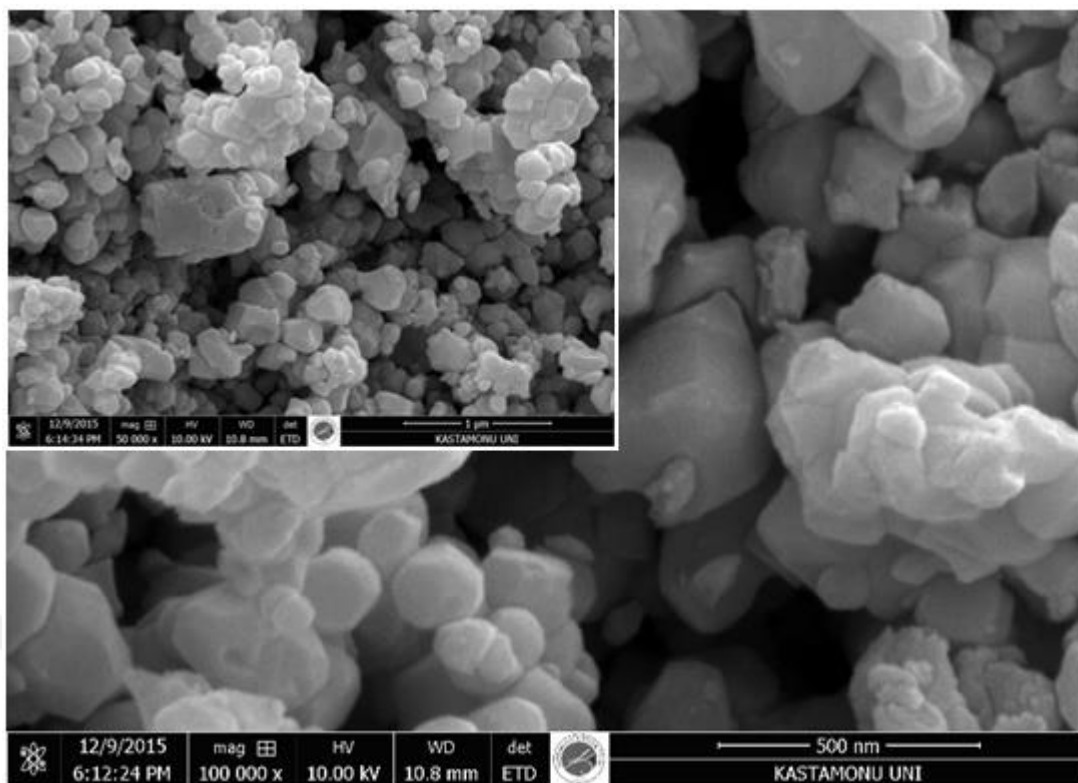


Figure 6.35. SEM images of $\text{Zn}_{0.93}\text{Mg}_{0.02}\text{Co}_{0.05}\text{O}$ nano bulk material

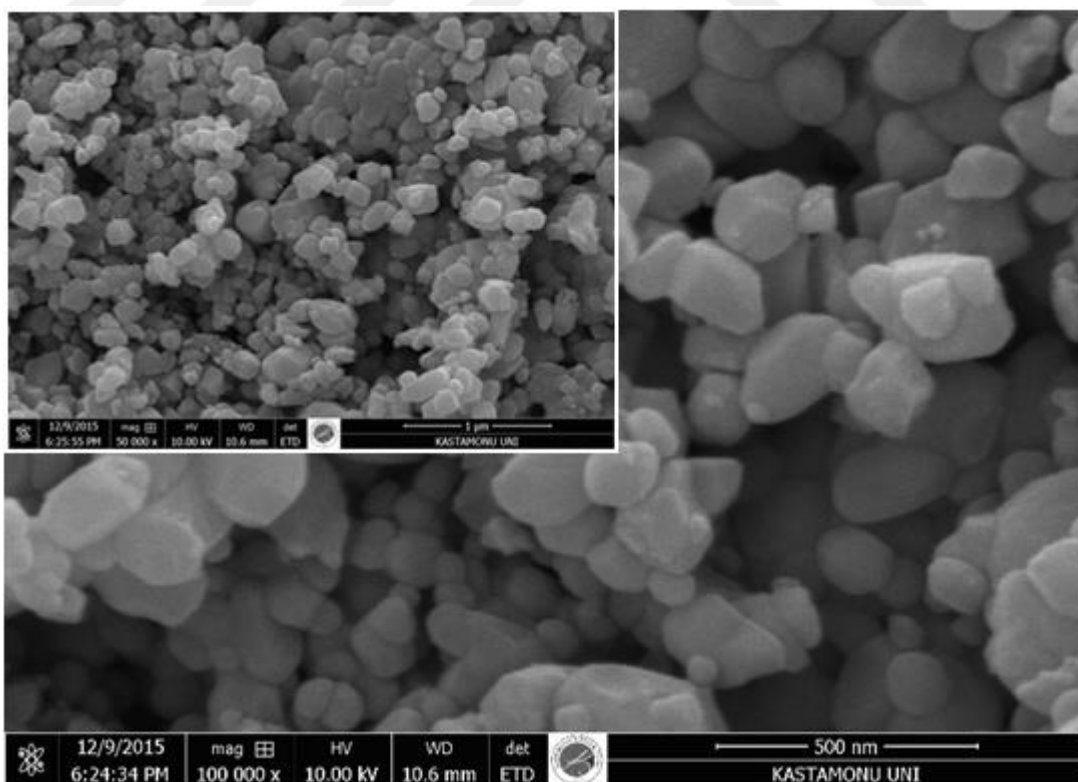


Figure 6.36. SEM images of $\text{Zn}_{0.94}\text{Mg}_{0.01}\text{Co}_{0.05}\text{O}$ nano bulk material

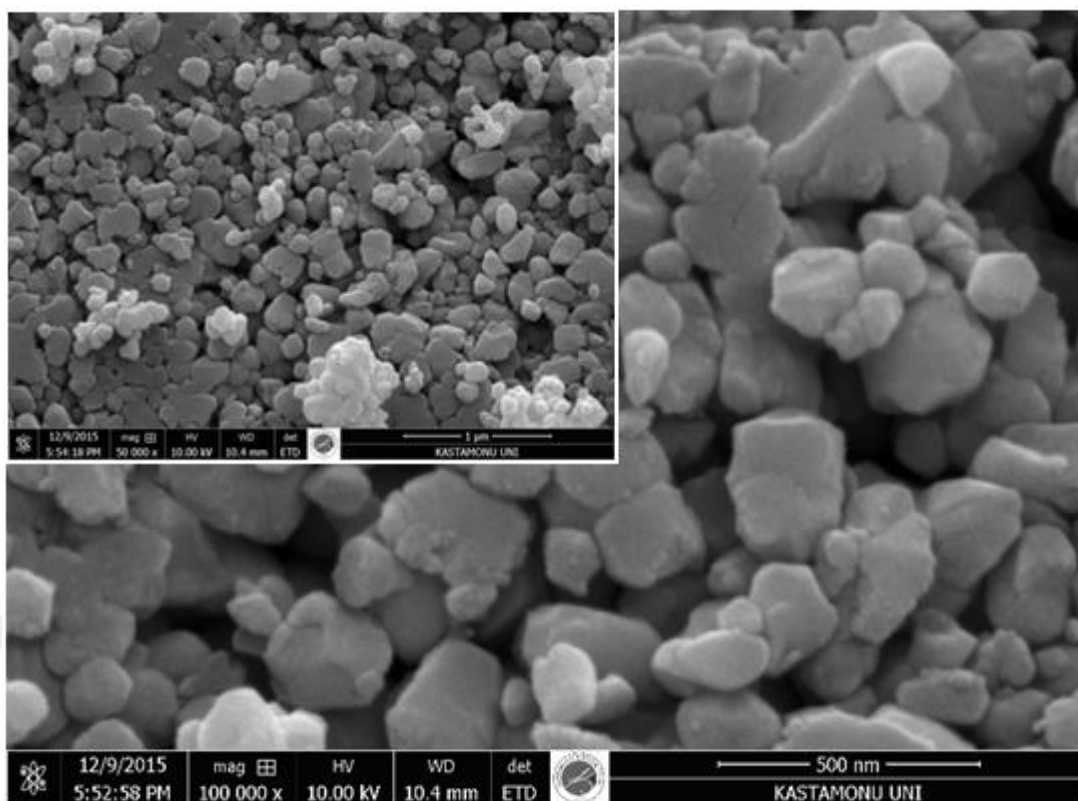


Figure 6.37. SEM images of $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ nano bulk material

6.3.4 Rare Earth Doped $\text{Zn}_{1-x}\text{B}_x\text{O}$ (B=Er) DMS Nano Bulk Materials

SEM images and EDS analysis of $\text{Zn}_{1-x}\text{Er}_x\text{O}$ bulk series in 200000 and 80000 magnification are given in the Figure 6.38-6.43. When the images are analyzed, it is observed that the grain size increases with increasing Er doping. The grain sizes are scaled during SEM analysis. It is observed by using this scale that the grain sizes increase with Er doping. The grain size values calculated using the XRD data are supported this results. But the compared with undoped ZnO , the grain size increases with Er doping. The size difference may be due to the difference between ionic radius of doping element ($\text{Er}^{+2} = 0.88\text{\AA}$) and host element ($\text{Zn}^{+2} = 0.74\text{\AA}$).

The change in Zn content with Er doping is investigated by using the EDS analysis. It is observed that the atomic percentage of Zn decreases with Er doping (Table 6.30-6.35). This is an expected result due to the Er^{+2} ions replacement with Zn^{+2} ions in the ZnO lattice.

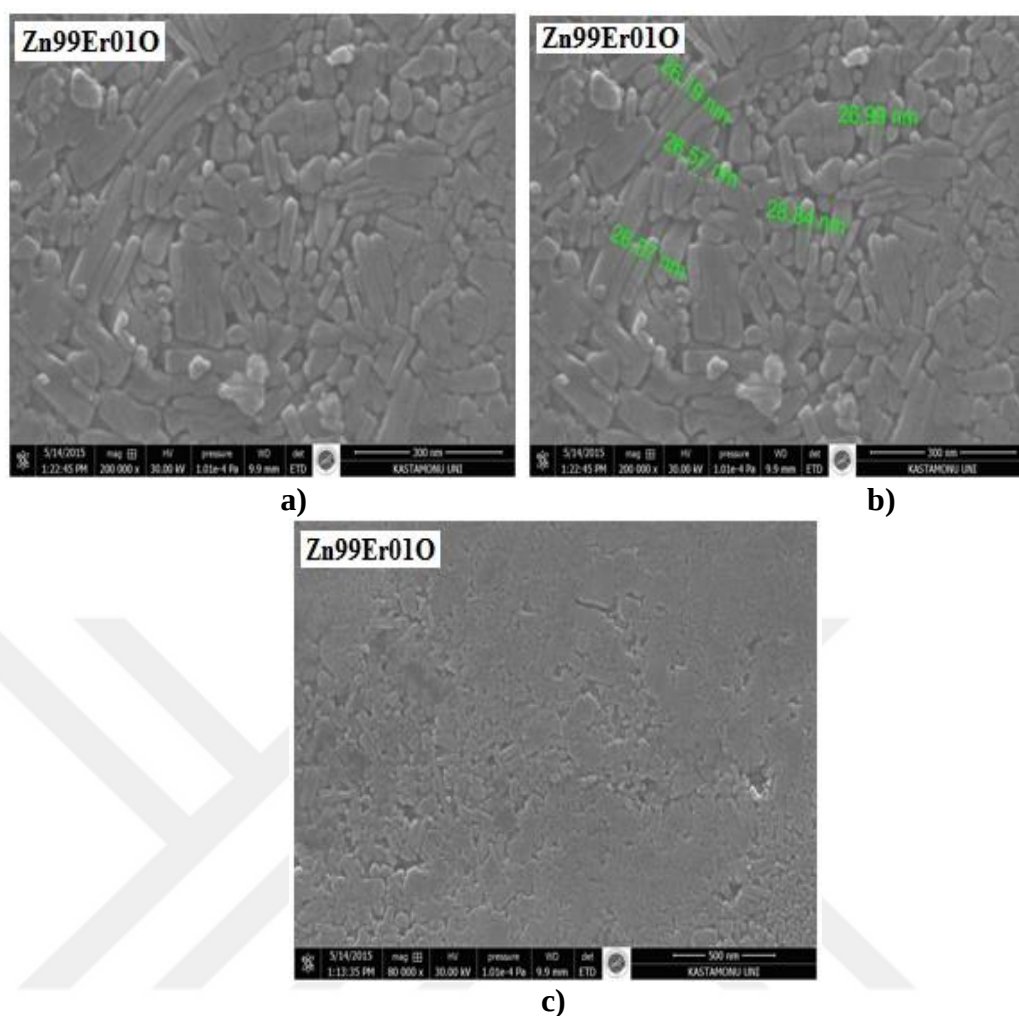


Figure 6.38. SEM images a) and b) at 200000 magnification, c) at 80000 magnification and d) EDS of Zn_{0.99}Er_{0.01}O nano bulk material

Table 6.30. EDS results of Zn_{0.99}Er_{0.01}O nano bulk materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	18.64	48.6	377.94
Er	1.31	0.33	69.96
Zn	80.05	51.07	4276.86

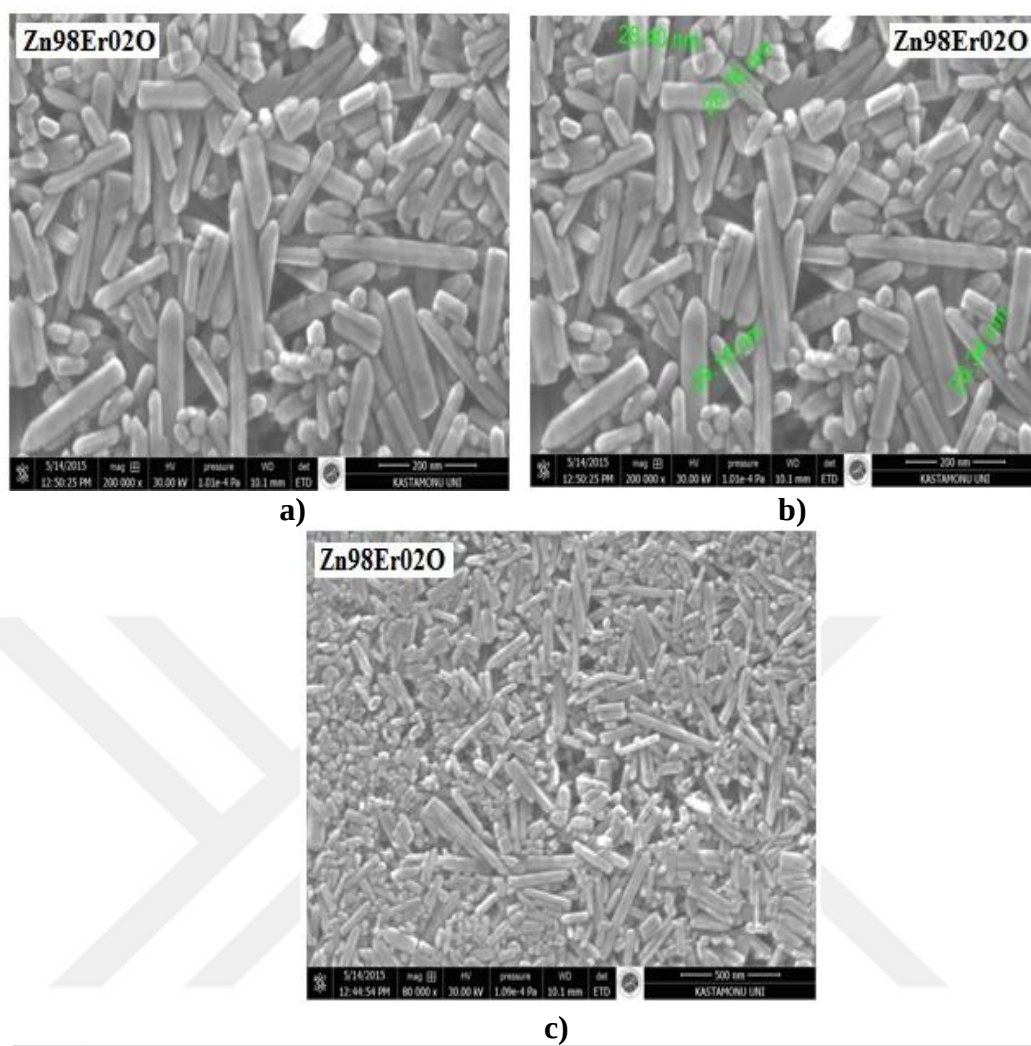


Figure 6.39. SEM images a) and b) at 200000 magnification, c) at 80000 magnification and d) EDS of $\text{Zn}_{0.98}\text{Er}_{0.02}\text{O}$ nano bulk material

Table 6.31. EDS results of $\text{Zn}_{0.98}\text{Er}_{0.02}\text{O}$ nano bulk materials

Element	Weight %	Atomic %	Net Int.
O	17.44	46.79	349.33
Er	2.47	0.63	127.1
Zn	80.08	52.58	4279.88

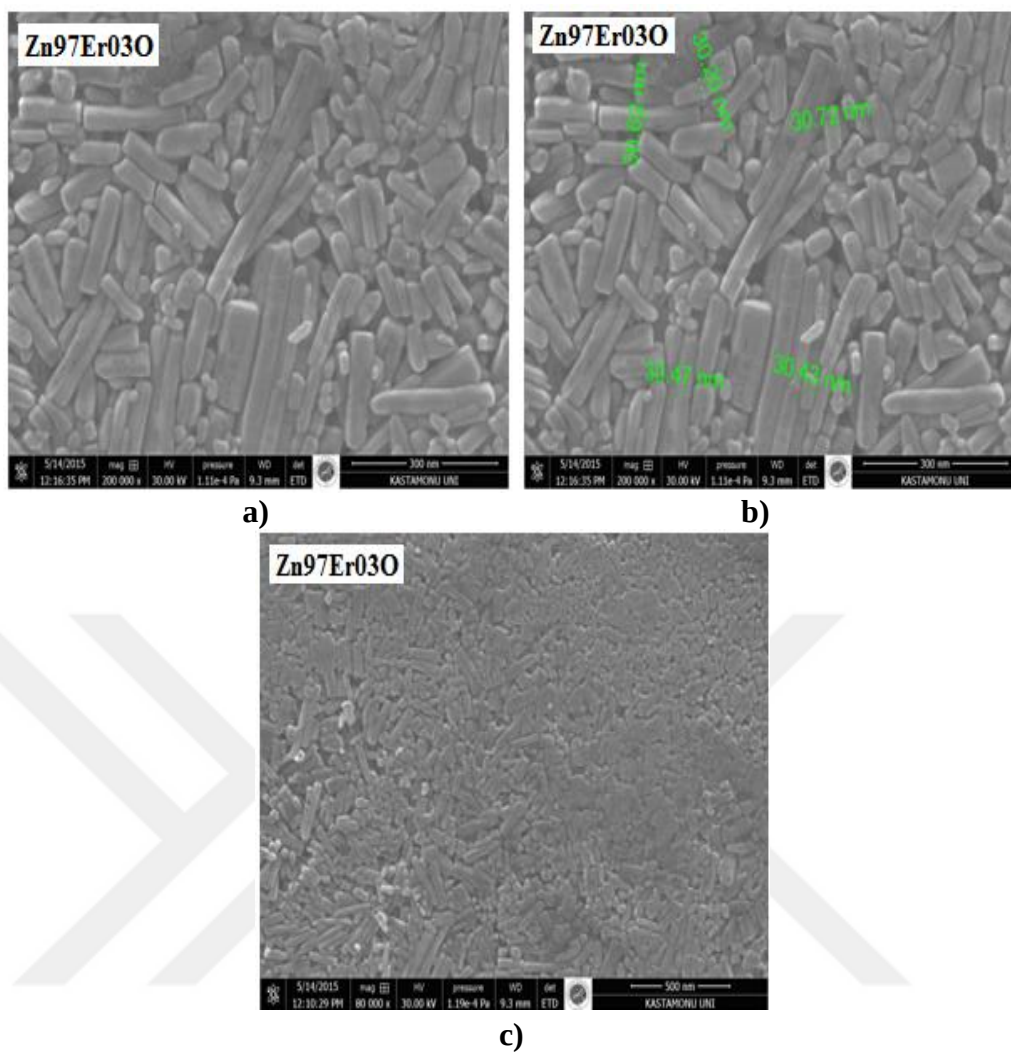


Figure 6.40. SEM images a) and b) at 200000 magnification, c) at 80000 magnification and d) EDS of $\text{Zn}_{0.97}\text{Er}_{0.03}\text{O}$ nano bulk material

Table 6.32. EDS results of $\text{Zn}_{0.97}\text{Er}_{0.03}\text{O}$ nano bulk materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	18.28	48.6	335.74
Er	4.47	1.14	198.65
Zn	77.25	50.27	3770.15

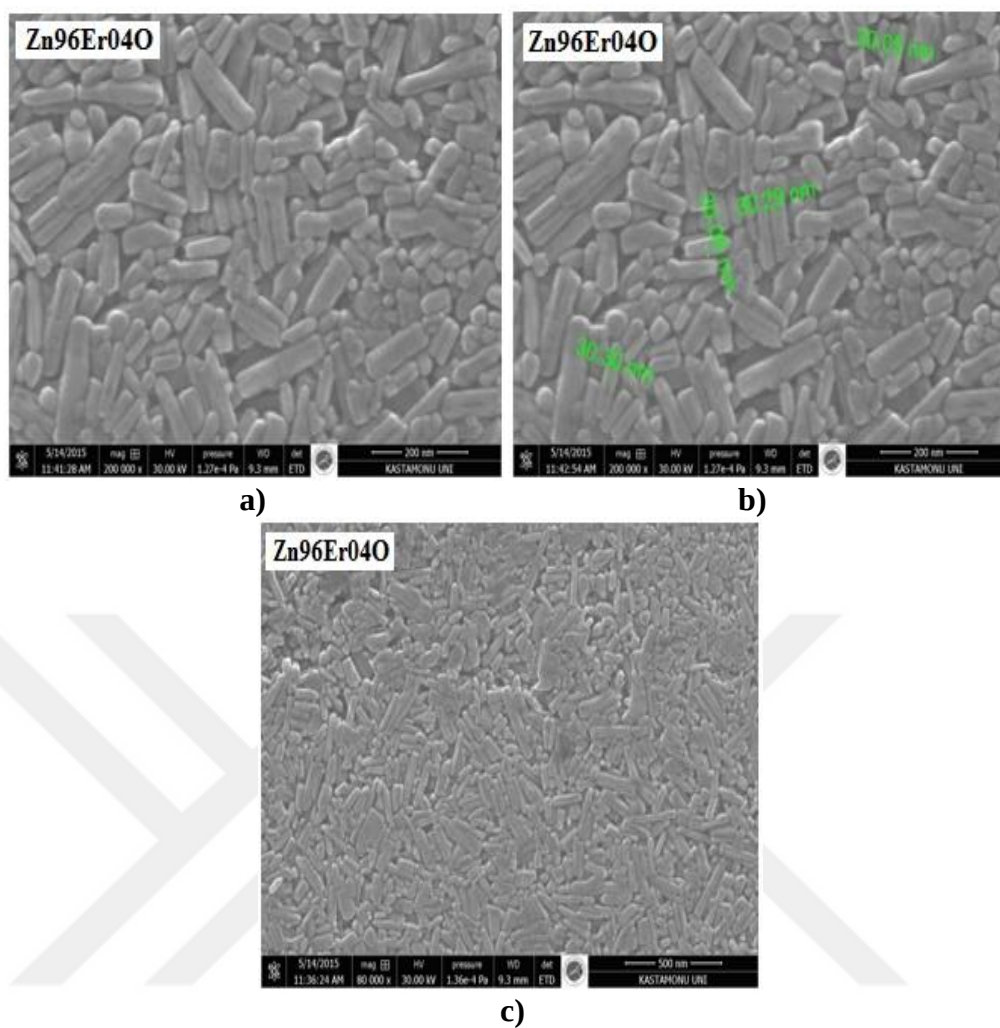


Figure 6.41. SEM images a) and b) at 200000 magnification, c) at 80000 magnification and d) EDS of Zn_{0.96}Er_{0.04}O nano bulk material

Table 6.33. EDS results of Zn_{0.96}Er_{0.04}O nano bulk materials

Element	Weight %	Atomic %	Net Int.
O	18.73	49.68	371.57
Er	6.17	1.57	286.08
Zn	75.10	48.75	3953.28

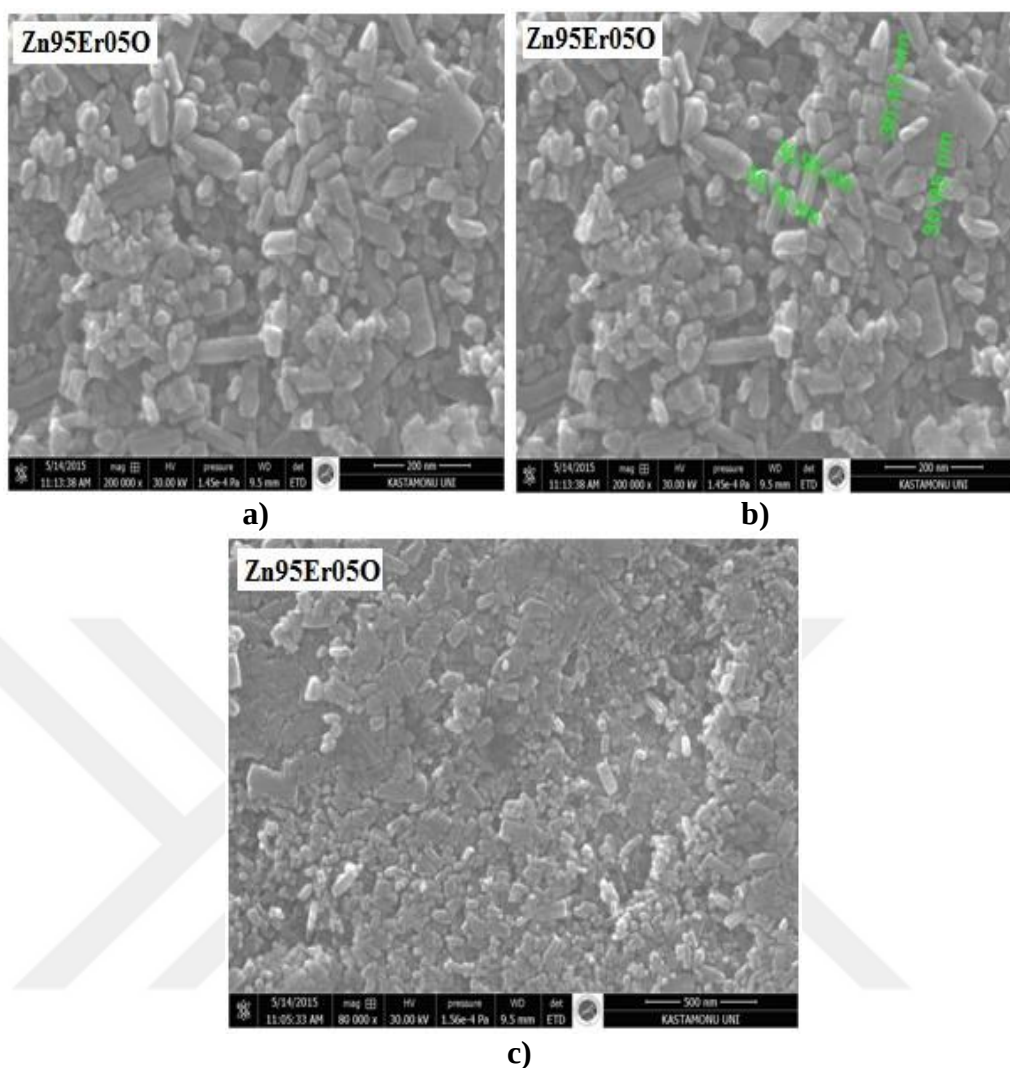


Figure 6.42. SEM images a) and b) at 200000 magnification, c) at 80000 magnification and d) EDS of $\text{Zn}_{0.95}\text{Er}_{0.05}\text{O}$ nano bulk material

Table 6.34. EDS results of $\text{Zn}_{0.95}\text{Er}_{0.05}\text{O}$ nano bulk materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	18.33	49.08	343.28
Er	6.47	1.66	282.67
Zn	75.20	49.27	3750.31

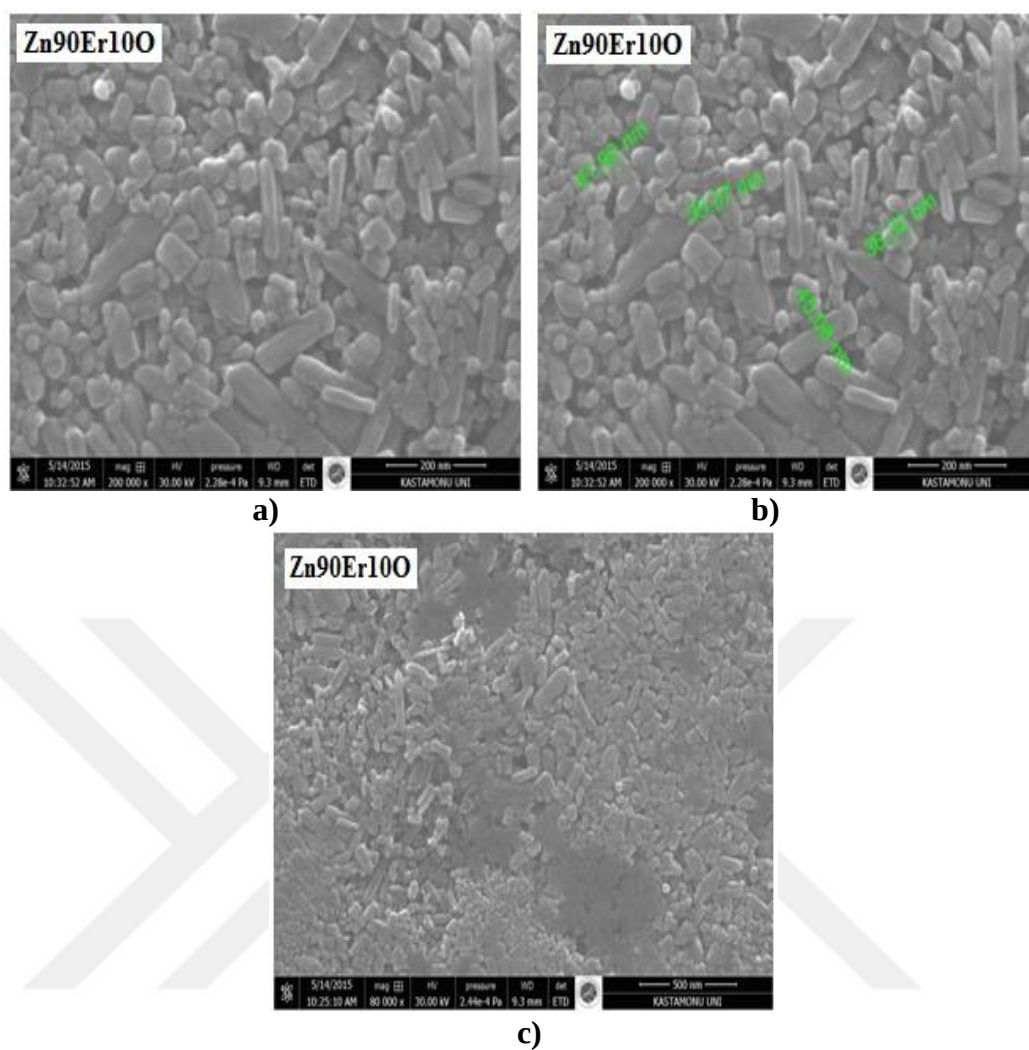


Figure 6.43. SEM images a) and b) at 200000 magnification, c) at 80000 magnification and d) EDS of Zn_{0.90}Er_{0.10}O nano bulk material

Table 6.35. EDS results of Zn_{0.90}Er_{0.10}O nano bulk materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	19.95	53.26	358.79
Er	13.95	3.56	539.76
Zn	66.10	43.18	3157.26

6.3.5 Rare Earth Doped $\text{Zn}_{1-x-y}\text{B}_x\text{C}_y\text{O}$ (B=Er, C=Cd) DMS Nano Bulk Materials

SEM images and EDS analysis of Er and Cd doped DMS materials which have in the ZnO based ternary structure of $\text{Zn}_{1-x-y}\text{B}_x\text{C}_y\text{O}$ in 40000, 80000 and 160000 magnification are given in the Figure 6.44-6.49. According the SEM measurements, it is observed that the grain size decreases with increasing Cd doping. The size difference may be due to the difference between ionic radius of doping element ($\text{Cd}^{+2} = 0.97\text{\AA}$) and host element ($\text{Zn}^{+2} = 0.74\text{\AA}$).

When the EDS measurements are analyzed, it can be said that the atomic percentage of Zn decreases with Cd doping (Table 6.36-6.41). This is an expected result due to the Cd^{+2} ions replacement with Zn^{+2} ions in the ZnO lattice.

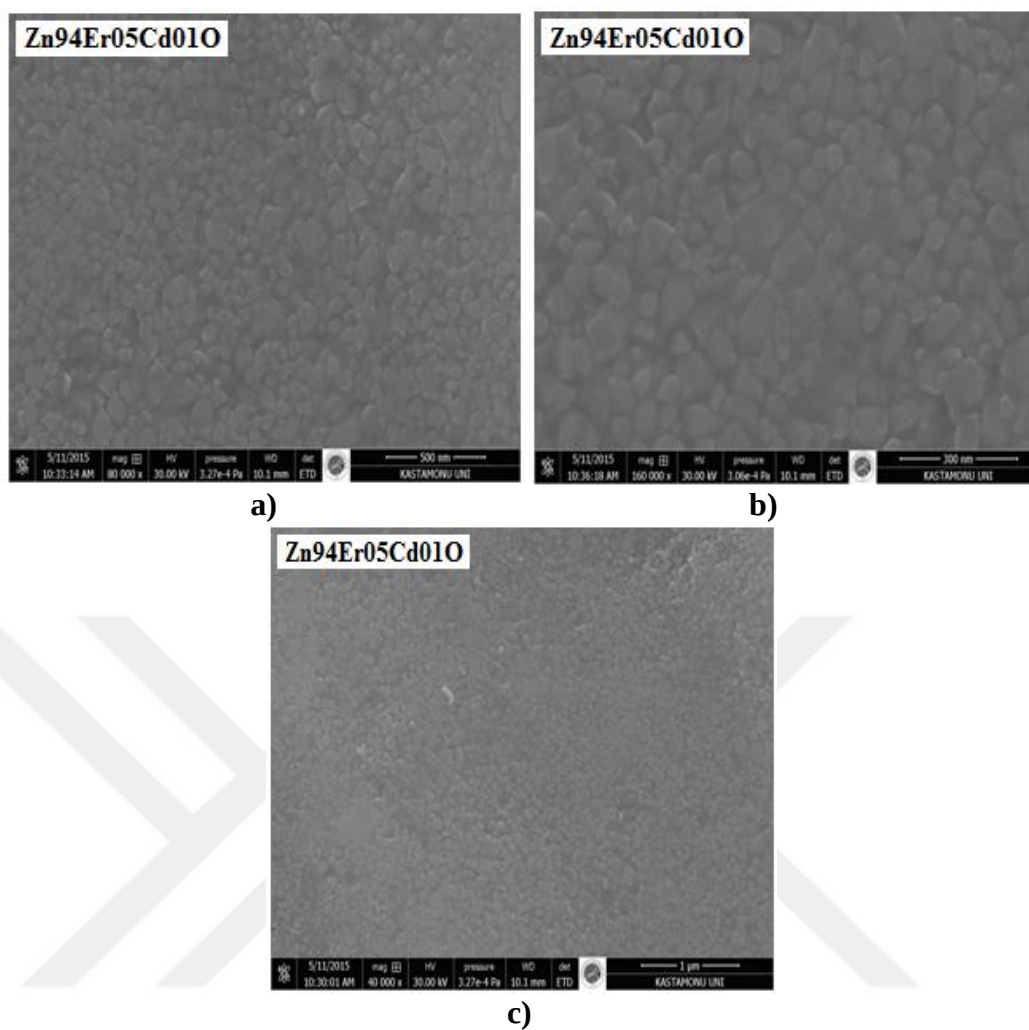


Figure 6.44. SEM images a) at 40000 and b) at 80000 magnification, c) at 160000 magnification and d) EDS of Zn_{0.94}Er_{0.05}Cd_{0.01}O nano bulk material

Table 6.36. EDS results of Zn_{0.94}Er_{0.05}Cd_{0.01}O nano bulk materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	18.22	49.12	239.46
Cd	0.86	0.33	32.92
Er	7.12	1.84	219.32
Zn	73.8	48.71	2634.01

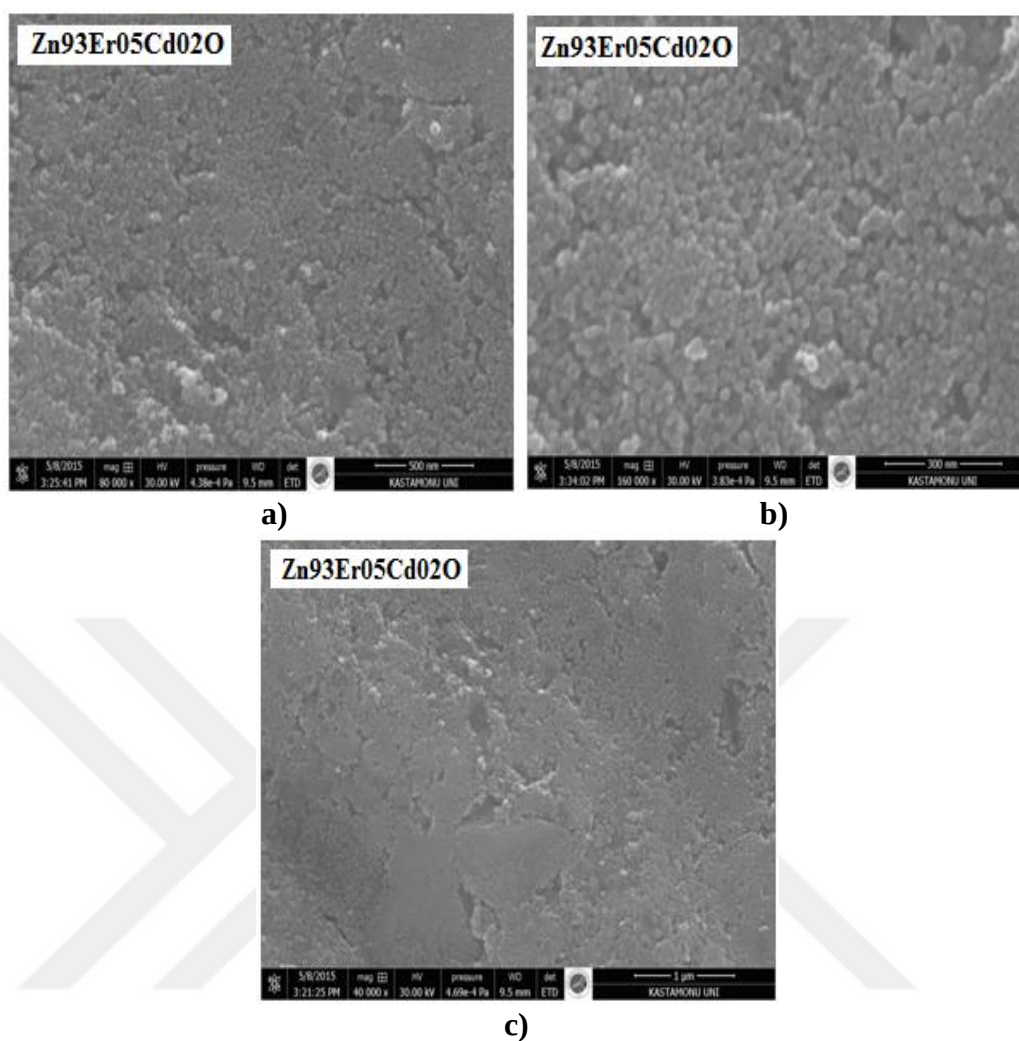


Figure 6.45. SEM images a) at 40000 and b) at 80000 magnification, c) at 160000 magnification and d) EDS of Zn_{0.93}Er_{0.05}Cd_{0.02}O nano bulk material

Table 6.37. EDS results of Zn_{0.93}Er_{0.05}Cd_{0.02}O nano bulk materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	18.61	49.94	256.07
Cd	2.21	0.84	90.86
Er	6.99	1.79	228.91
Zn	72.19	47.42	2759.9

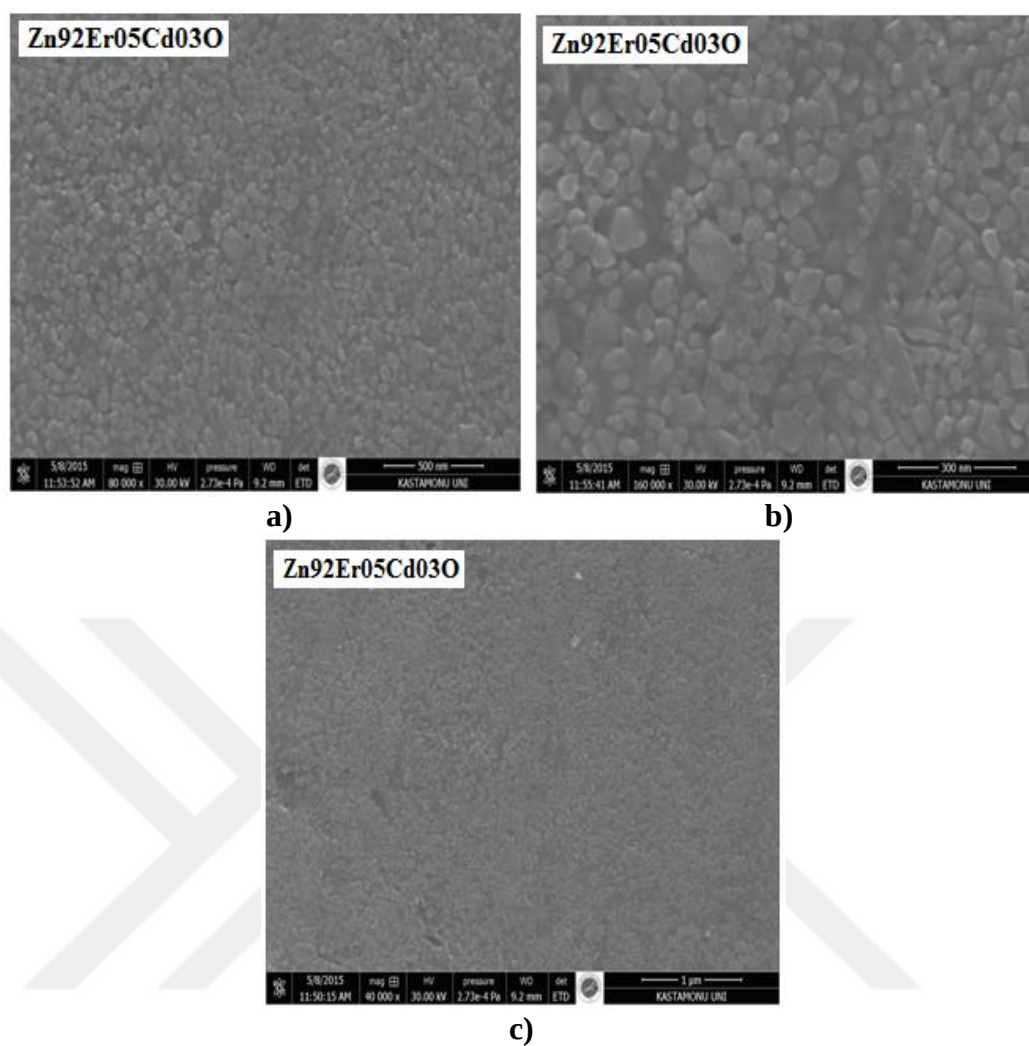


Figure 6.46. SEM images a) at 40000 and b) at 80000 magnification, c) at 160000 magnification and d) EDS of $\text{Zn}_{0.92}\text{Er}_{0.05}\text{Cd}_{0.03}\text{O}$ nano bulk material

Table 6.38. EDS results of $\text{Zn}_{0.92}\text{Er}_{0.05}\text{Cd}_{0.03}\text{O}$ nano bulk materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	14.9	43.36	178.69
Cd	2.26	0.94	82.54
Er	7.56	2.10	221.88
Zn	75.27	53.59	2587.78

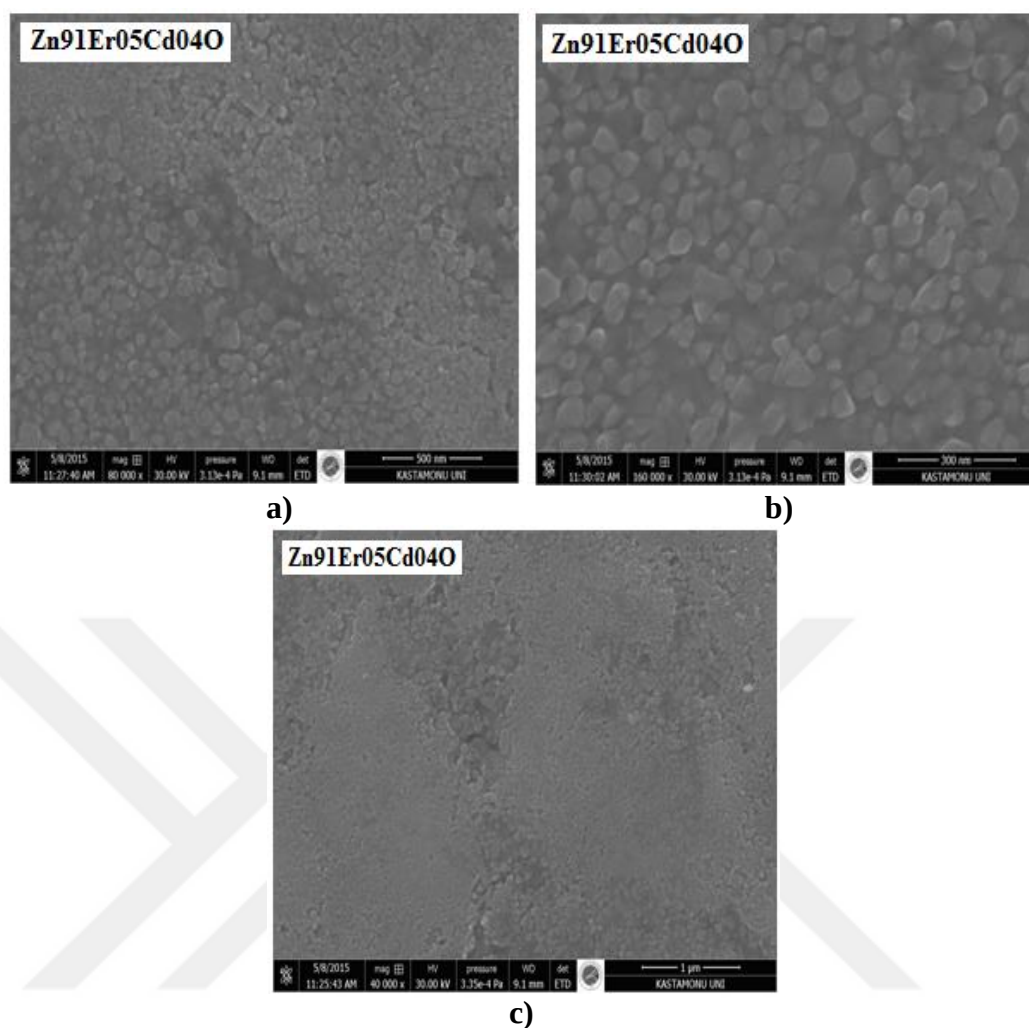


Figure 6.47. SEM images a) at 40000 and b) at 80000 magnification, c) at 160000 magnification and d) EDS of Zn_{0.91}Er_{0.05}Cd_{0.04}O nano bulk material

Table 6.39. EDS results of Zn_{0.91}Er_{0.05}Cd_{0.04}O nano bulk materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	15.77	45.16	199.71
Cd	3.44	1.40	135.15
Er	7.45	2.04	232.98
Zn	73.33	51.40	2703.08

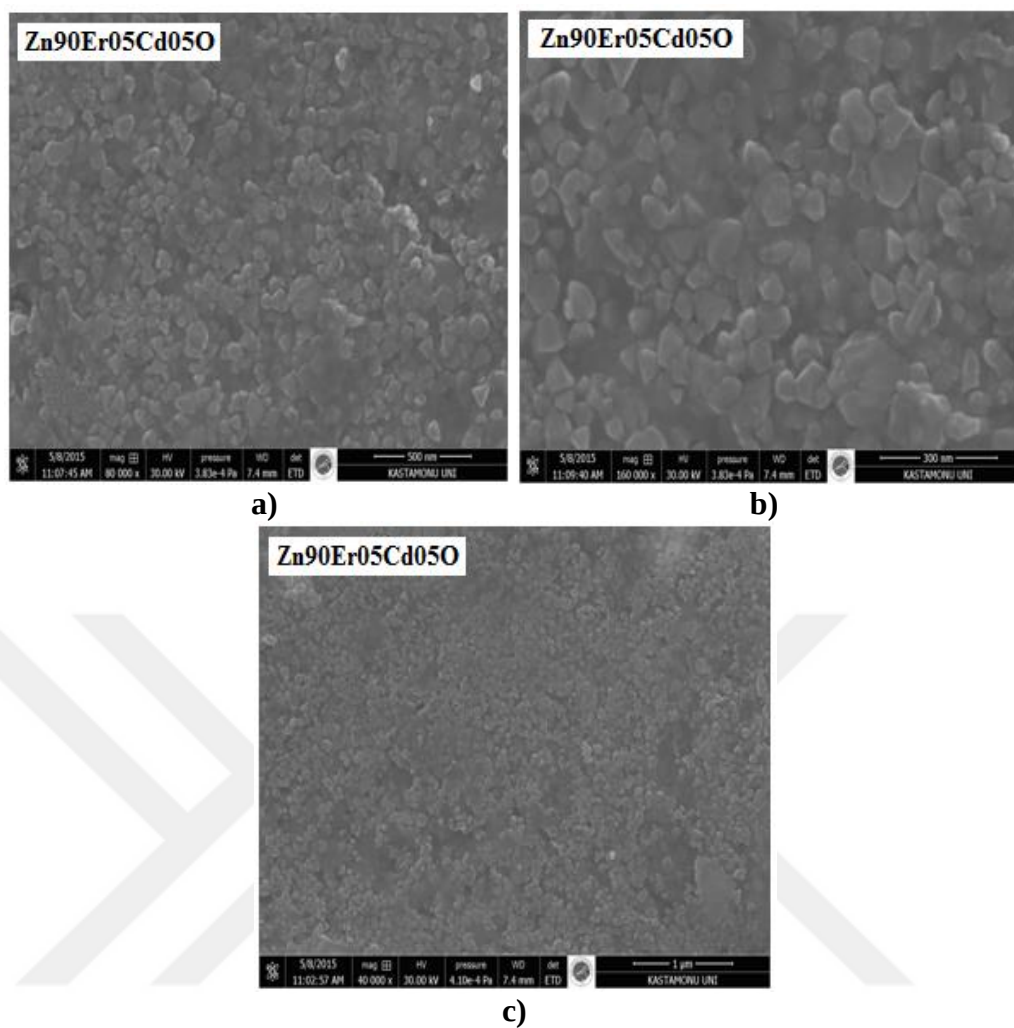


Figure 6.48. SEM images a) at 40000 and b) at 80000 magnification, c) at 160000 magnification and d) EDS of Zn_{0.90}Er_{0.05}Cd_{0.05}O nano bulk material

Table 6.40. EDS results of Zn_{0.90}Er_{0.05}Cd_{0.05}O nano bulk materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
<i>O</i>	17.15	47.91	245.42
<i>Cd</i>	4.52	1.80	202.95
<i>Er</i>	7.83	2.09	275.64
<i>Zn</i>	70.51	48.20	2963.71

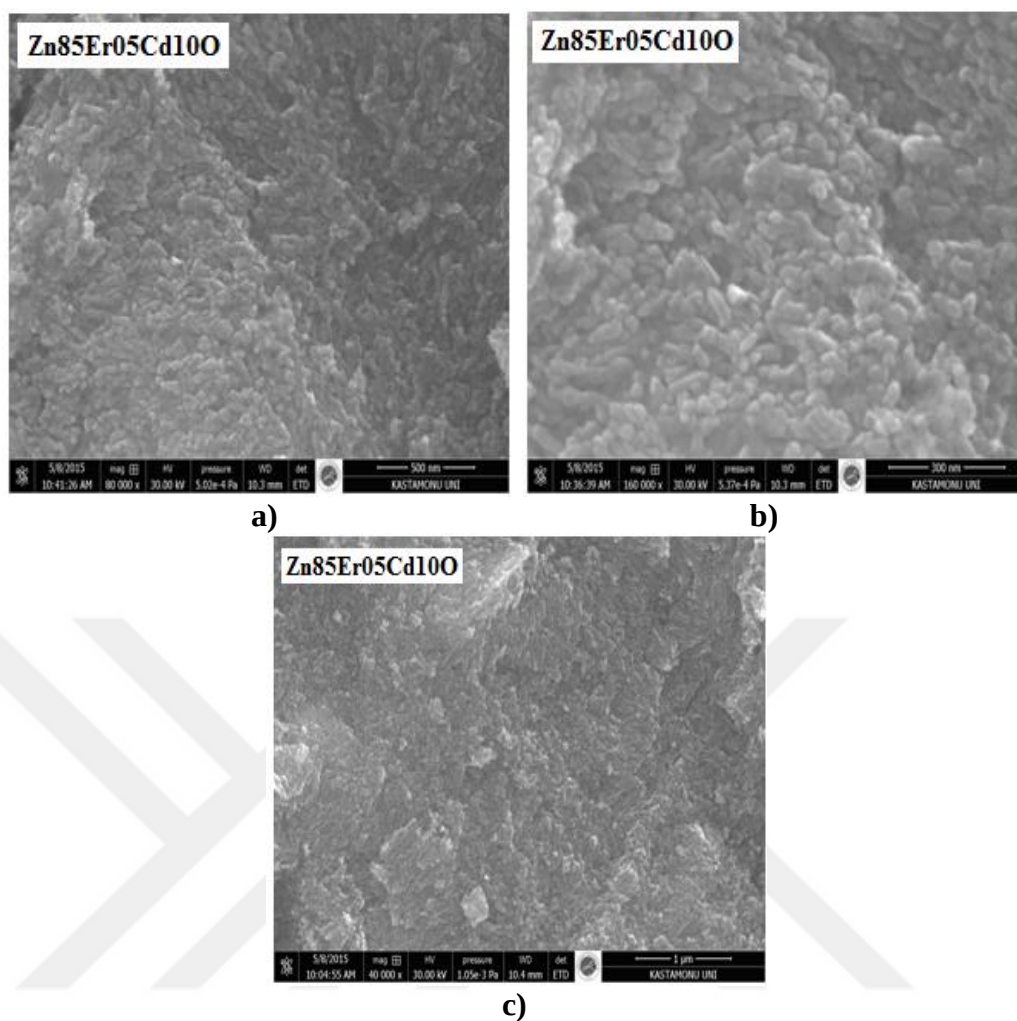


Figure 6.49. SEM images a) at 40000 and b) at 80000 magnification, c) at 160000 magnification and d) EDS of Zn_{0.85}Er_{0.05}Cd_{0.10}O nano bulk material

Table 6.41. EDS results of Zn_{0.85}Er_{0.05}Cd_{0.10}O nano bulk materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	19.25	50.91	283.52
Cd	9.83	3.70	505.08
Er	7.31	0.33	54.47
Zn	63.62	45.06	3237.22

6.3.6 Transition Metal Doped $\text{Zn}_{1-x}\text{B}_x\text{O}$ (B=Co) DMS Nano Thin Film Materials

SEM images and EDS analysis of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ nano thin film series in 40000 and 80000 magnification are given in the Figure 6.50-6.55. When the images are analyzed, it is observed that the grain size decreases with increasing Co doping. In addition, Warren-Sheerer values are calculated using the XRD data shown that the grain sizes decrease with increasing the Co doping. But the compared with undoped ZnO, the grain size increases with Co doping. The size difference may be due to the difference between ionic radius of doping element ($\text{Co}^{+2} = 0.79\text{\AA}$) and host element ($\text{Zn}^{+2} = 0.74\text{\AA}$).

The change in Zn content with Co doping is investigated by using the EDS analysis. It is observed that the atomic percentage of Zn decreases with Co doping (Table 6.42-6.47). This is an expected result. As interpreted from the XRD analysis, the Co^{+2} ions replacement with Zn^{+2} ions in the ZnO lattice due to the ionic radius of Co ($0.79\text{\AA}$) is greater than the ionic radius of Zn ($0.74\text{\AA}$). Therefore there is no peak of the Co atoms. In addition, this result is observed using EDS measurement. According the EDS analyses the amount of Zn decreases with Co doping.

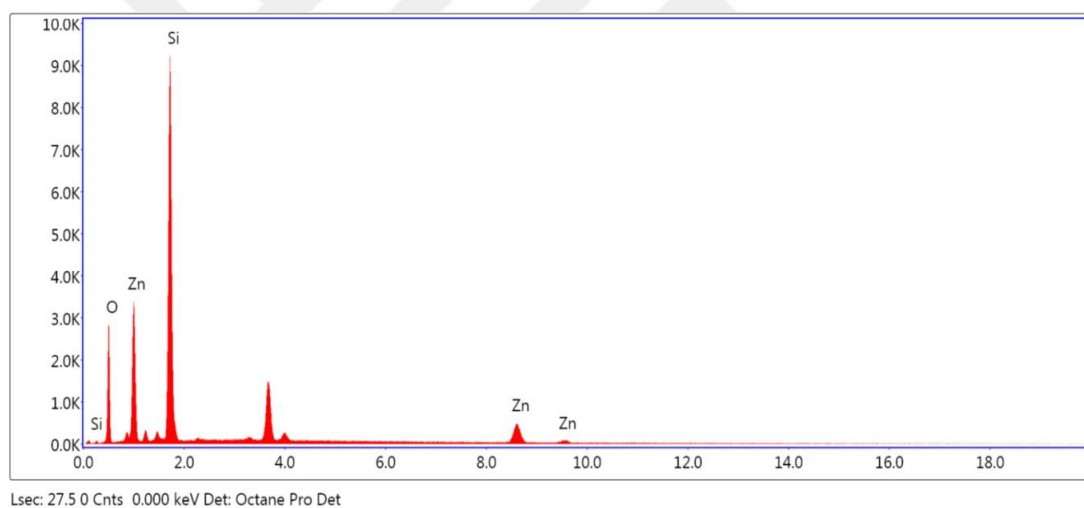
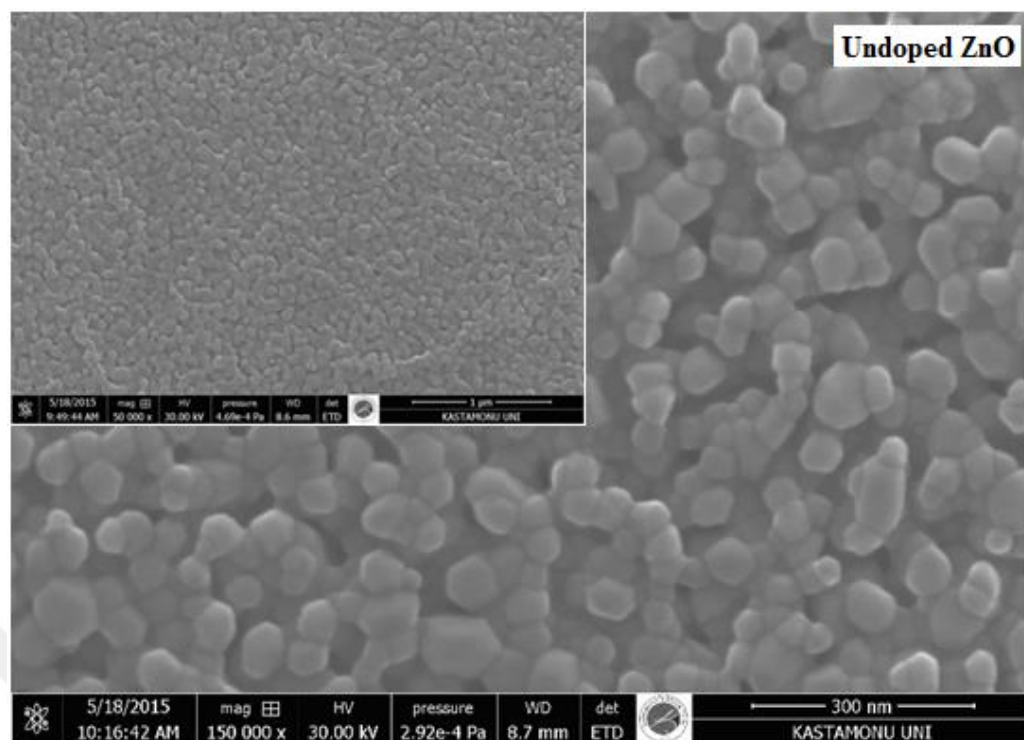


Figure 6.50. SEM and EDS images of undoped ZnO nano thin film material

Table 6.42. EDS results of undoped ZnO nano thin film materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	47.98	64.50	501.16
Si	42.09	32.23	2482.8
Zn	9.92	3.26	264.95

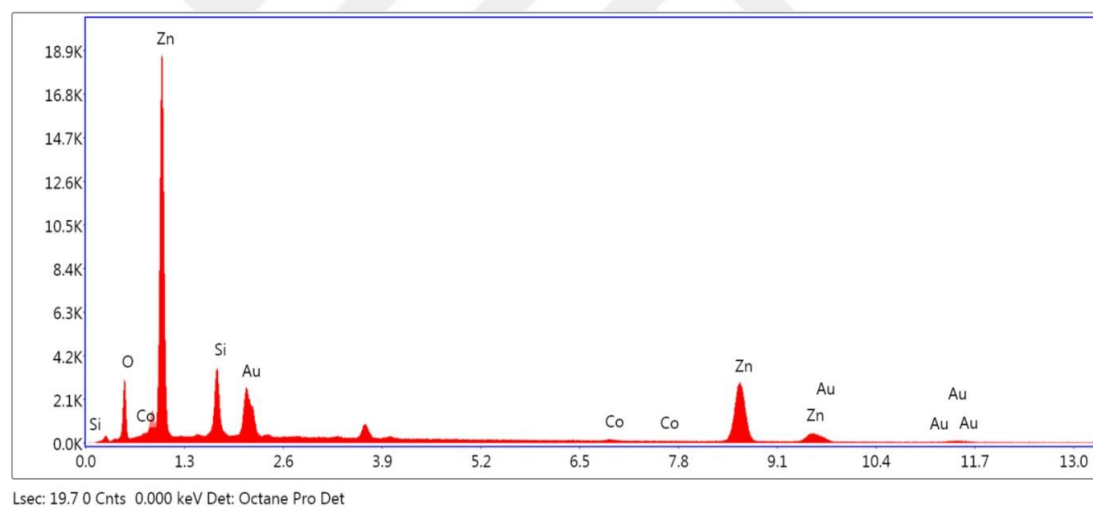
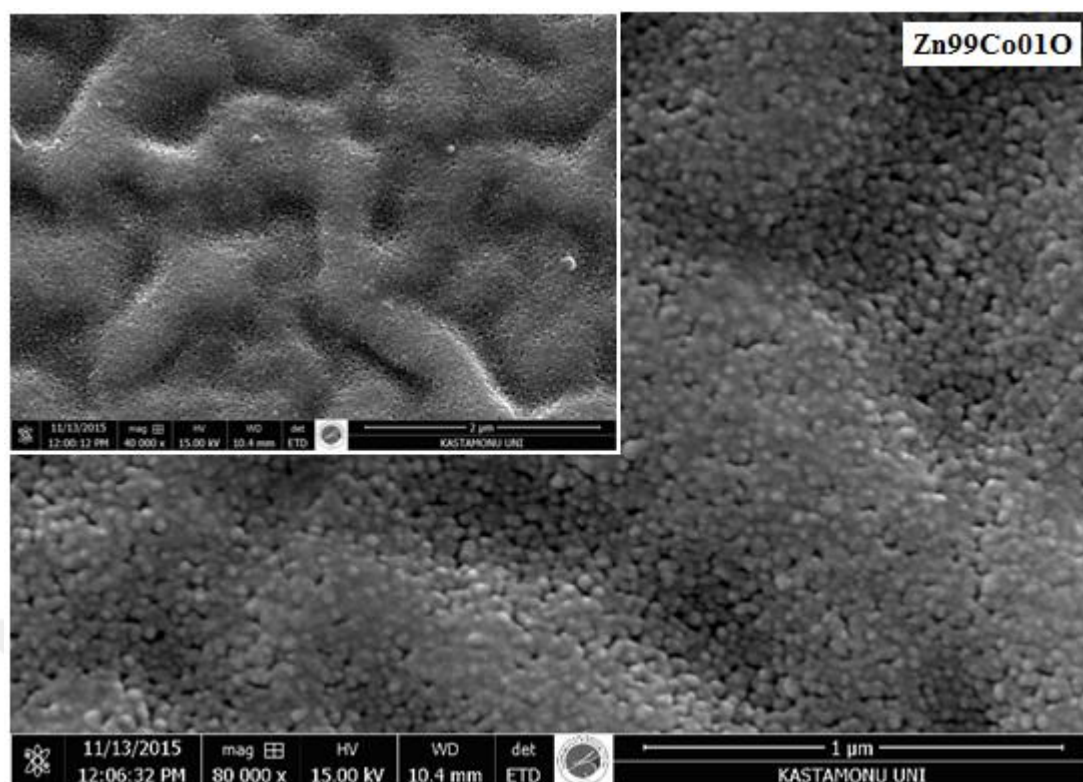
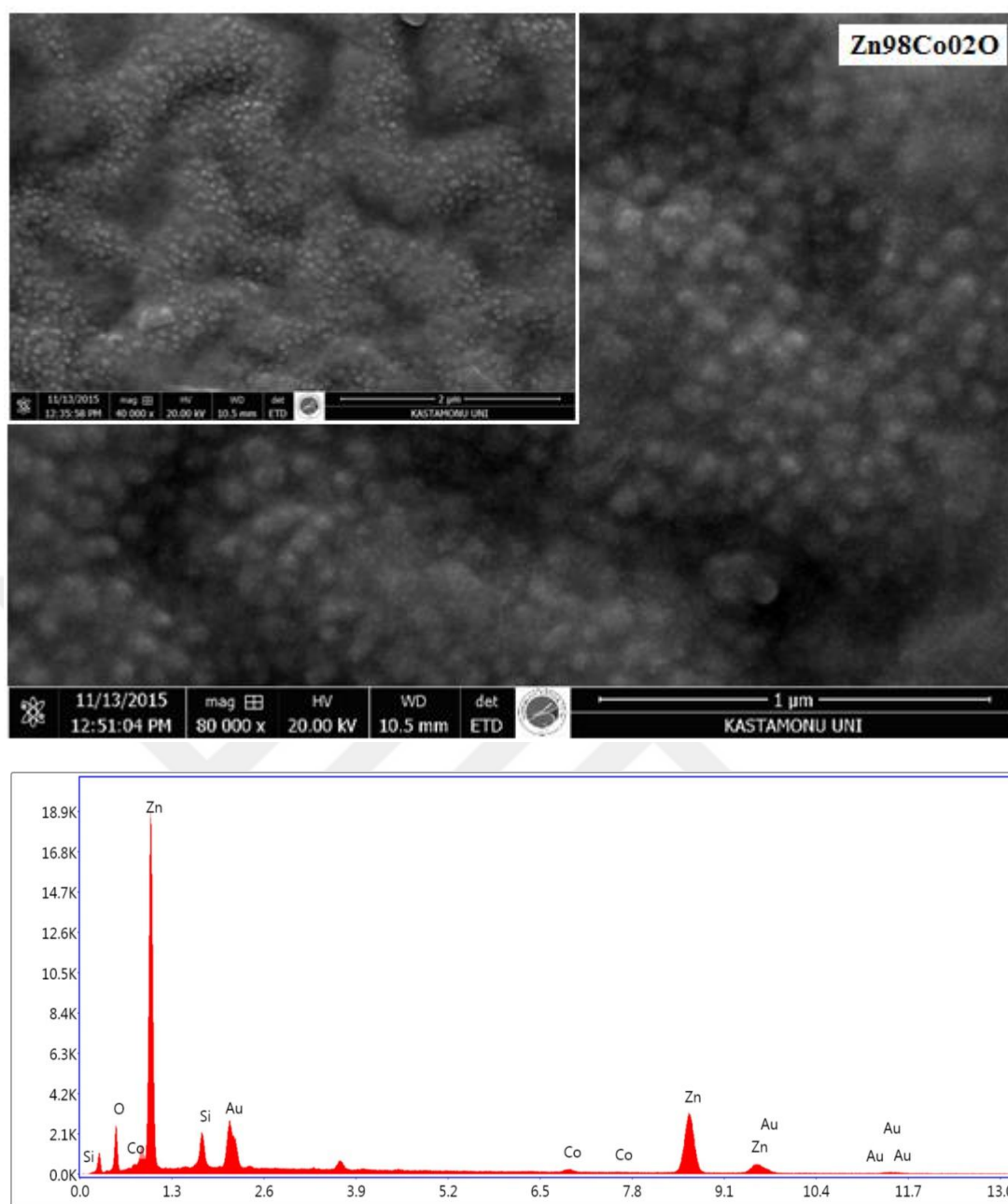


Figure 6.51. SEM and EDS images of $\text{Zn}_{0.99}\text{Co}_{0.01}\text{O}$ nano thin film material

Table 6.43. EDS results of $\text{Zn}_{0.99}\text{Co}_{0.01}\text{O}$ nano thin film materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	13.66	38.44	698.09
Si	9.70	15.54	1289.39
Co	0.43	0.33	36.32
Zn	61.46	42.32	2375.63
Au	14.74	3.37	153.04



Lsec: 19.7 0 Cnts 0.000 keV Det: Octane Pro Det

Figure 6.52. SEM and EDS images of Zn_{0.98}Co_{0.02}O nano thin film material

Table 6.44. EDS results of Zn_{0.98}Co_{0.02}O nano thin film materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	11.31	34.77	567.45
Si	5.98	10.47	748.09
Co	1.23	1.03	102.51
Zn	66.47	49.99	2534.34
Au	15.00	3.75	153.72

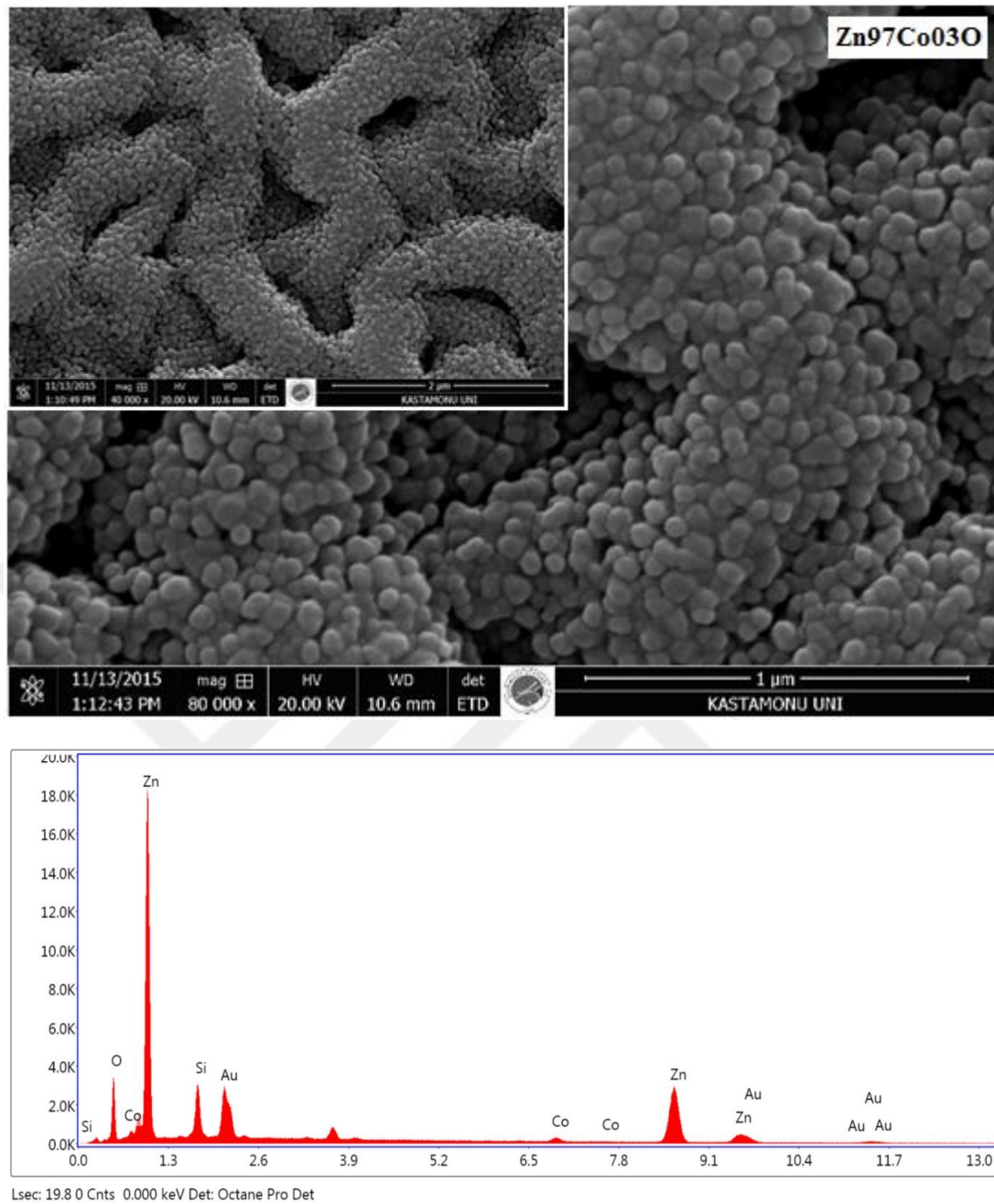


Figure 6.53. SEM and EDS images of $\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$ nano thin film material

Table 6.45. EDS results of $\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$ nano thin film materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	15.22	42.09	785.82
Si	8.09	12.74	1065.68
Co	1.53	1.15	125.6
Zn	60.02	40.62	2297.59
Au	15.13	3.40	155.5

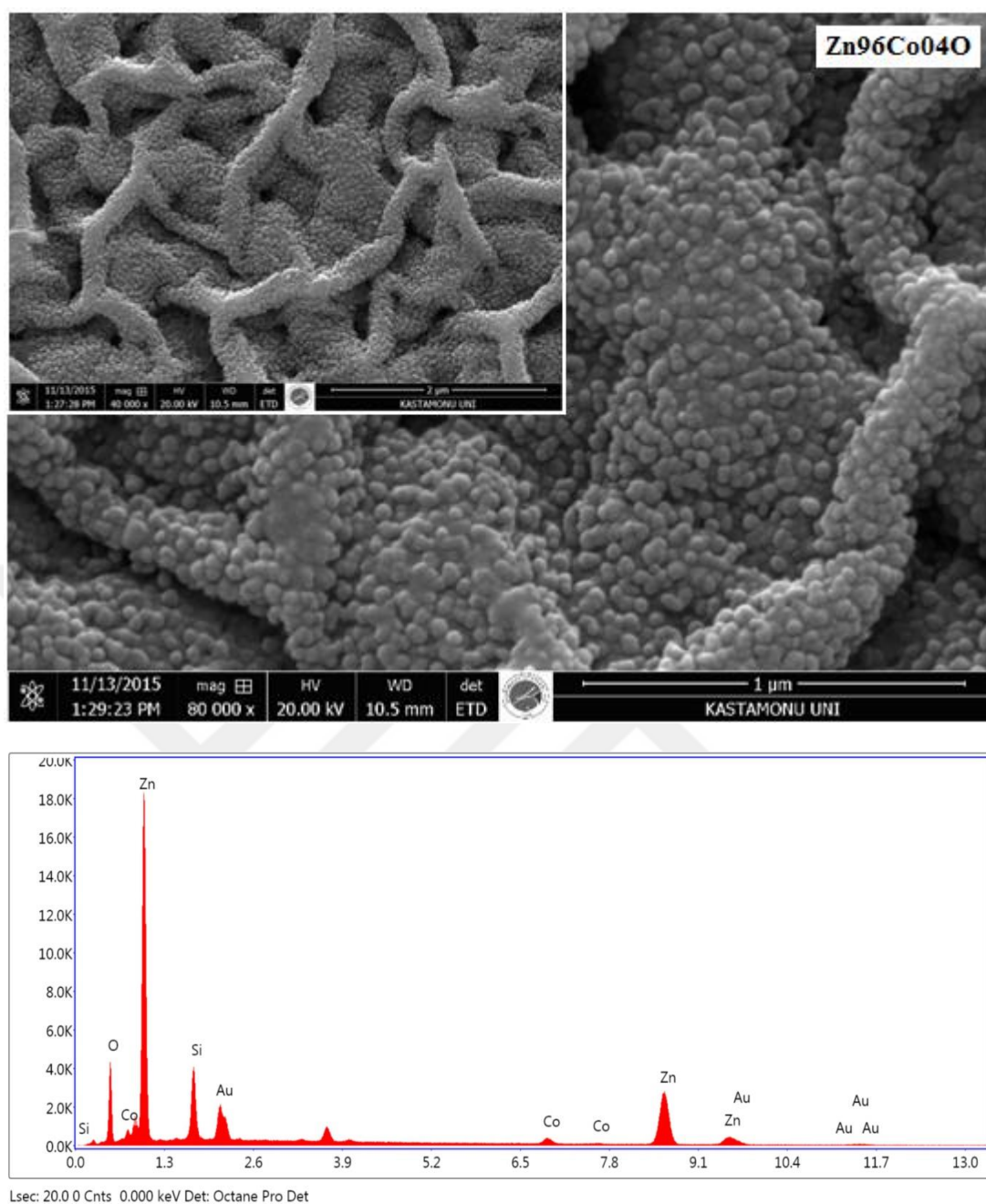


Figure 6.54. SEM and EDS images of Zn_{0.96}Co_{0.04}O nano thin film material

Table 6.46. EDS results of Zn_{0.96}Co_{0.04}O nano thin film materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	18.35	45.75	995.51
Si	10.71	15.22	1451.97
Co	2.42	1.64	198.40
Zn	57.70	35.21	2194.73
Au	10.82	2.19	111.55

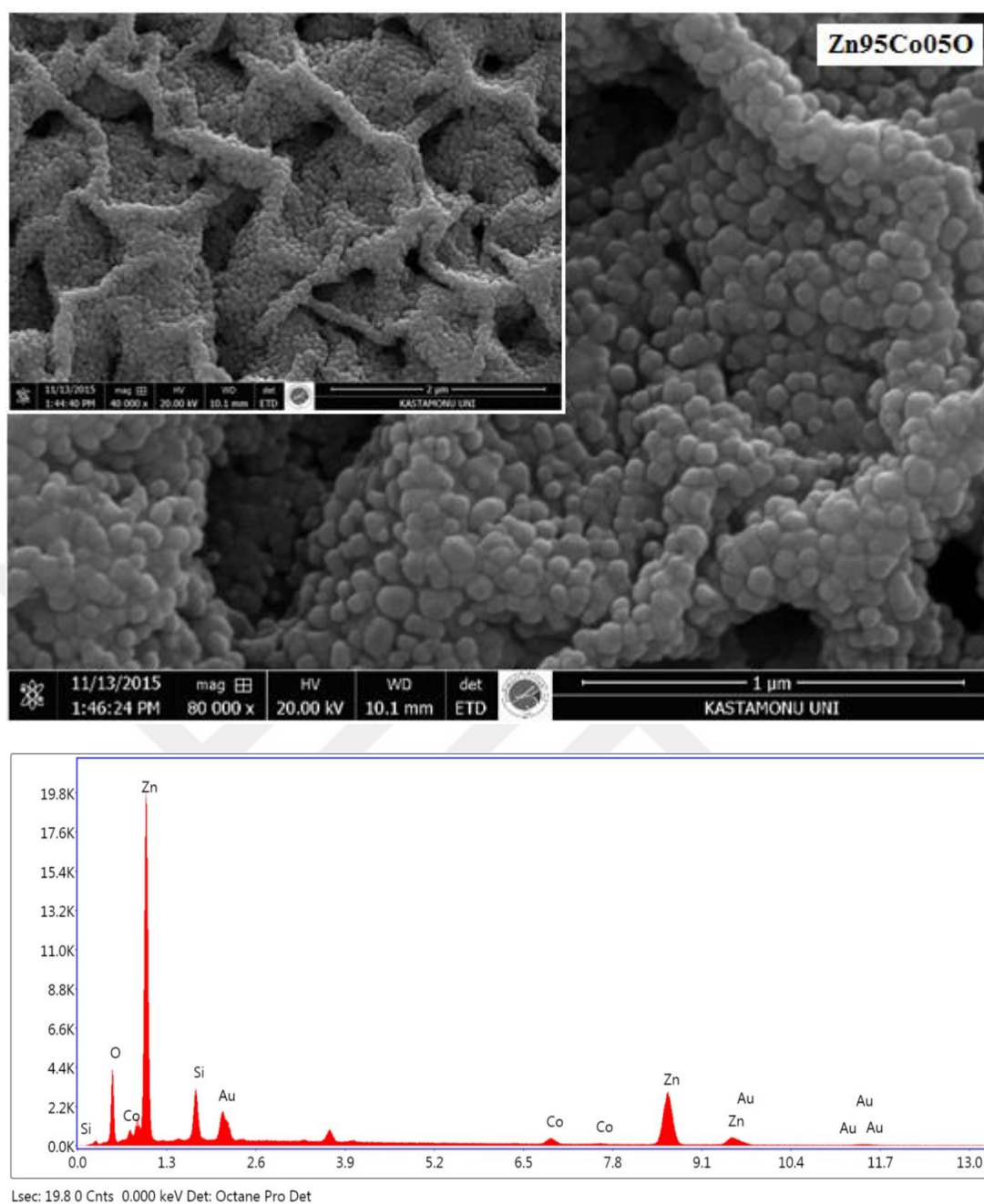


Figure 6.55. SEM and EDS images of $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ nano thin film material

Table 6.47. EDS results of $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ nano thin film materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
<i>O</i>	17.72	45.36	977.84
<i>Si</i>	8.42	12.28	1113.78
<i>Co</i>	2.72	1.89	227.25
<i>Zn</i>	61.35	38.43	2342.89
<i>Au</i>	9.78	2.03	101.4

6.3.7 Transition Metal Doped $\text{Zn}_{1-x}\text{B}_x\text{O}$ (B=Cu) DMS Nano Thin Film Materials

The surface morphology of Cu-doped ZnO nano thin films using different doping rate (0.0, 0.1, 0.2, 0.3, 0.4 and 0.5) with different magnifications (5000 and 10000) are shown in the Figure 6.56-6.61. Grain size of $\text{Zn}_{0.95}\text{Cu}_{0.05}\text{O}$ nano thin film (28.74 nm) is greater than other materials that are produced with different doping rate. This means that grain size of Cu doped ZnO nano thin films increase with increasing the Cu doping. In addition, ZnO films show a wrinkle network with spherical nano-sized crystallites.

The results are supported by particle size calculations calculated by XRD data. Besides SEM results are compatible with SEM analyses of ZnO -based nano thin films prepared by sol-gel method using MEA (monoethanolamine) in the literature (Tsay et al., 2010; Caglar et al., 2010).

Chemical purity and stoichiometries of the nano thin film samples are analyzed by EDS measurement. The EDS analyses of Cu doped ZnO nano thin films covered by dip coating are shown in Figure 6.56-6.61. Weight, atomic percentage and intensity of compositional elements such as Zn, Cu and O are given in the Table 6.48-6.53. The EDS data shows the presence of Cu in ZnO nano thin film. The atomic percentage of zinc is the highest value (at. %0.10) in $\text{Zn}_{0.95}\text{Cu}_{0.05}\text{O}$ nano thin film. In addition, the presence oxygen is low in $\text{Zn}_{0.95}\text{Cu}_{0.05}\text{O}$ nano thin film than other doped nano thin films. This behavior observed that existence of defects is lower in this film.

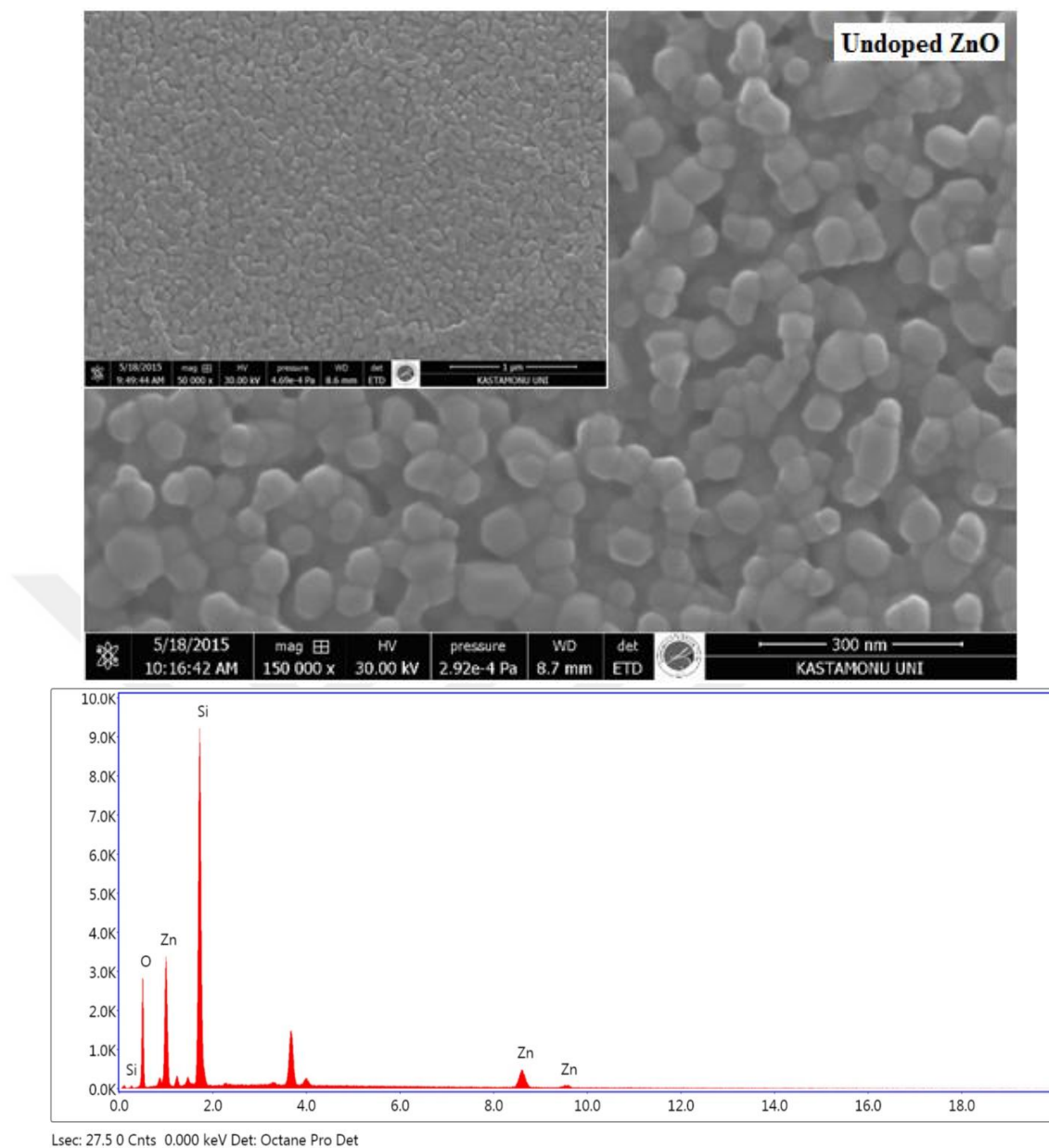


Figure 6.56. SEM and EDS images of undoped ZnO nano thin film material

Table 6.48. EDS results of undoped ZnO nano thin film materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	47.98	64.50	501.16
Si	42.09	32.23	2482.8
Zn	9.92	3.26	264.95

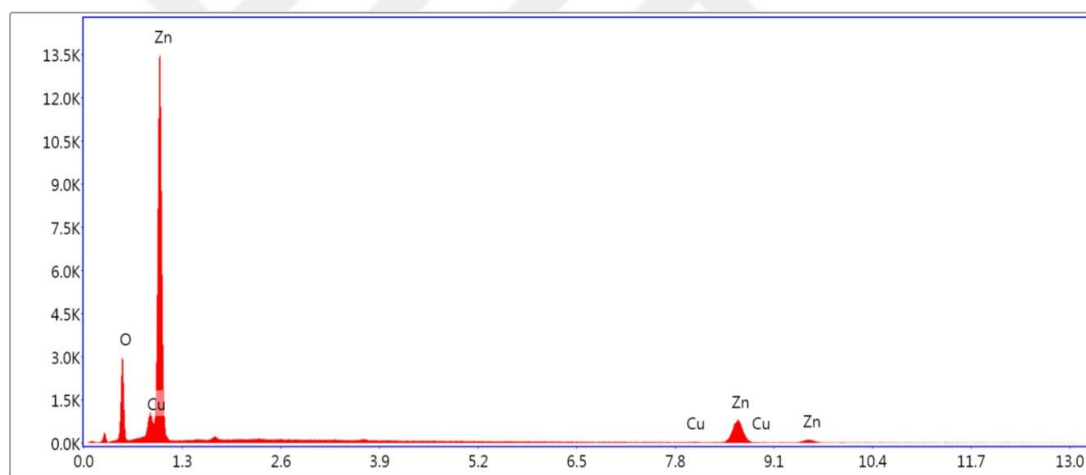
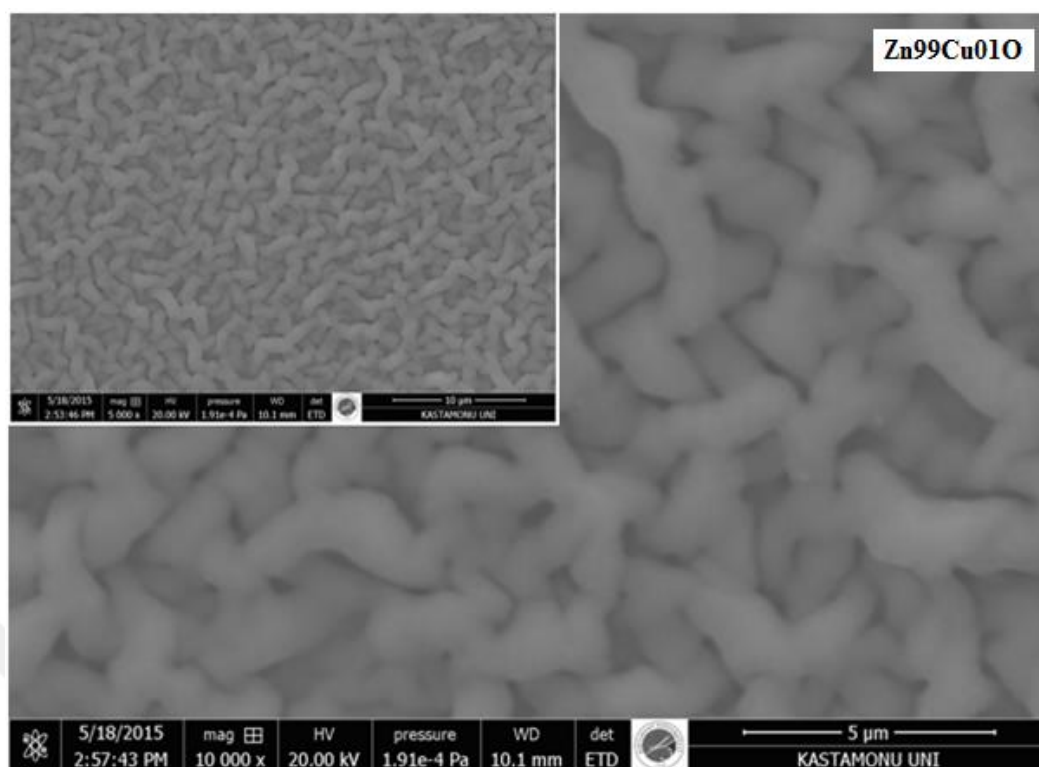
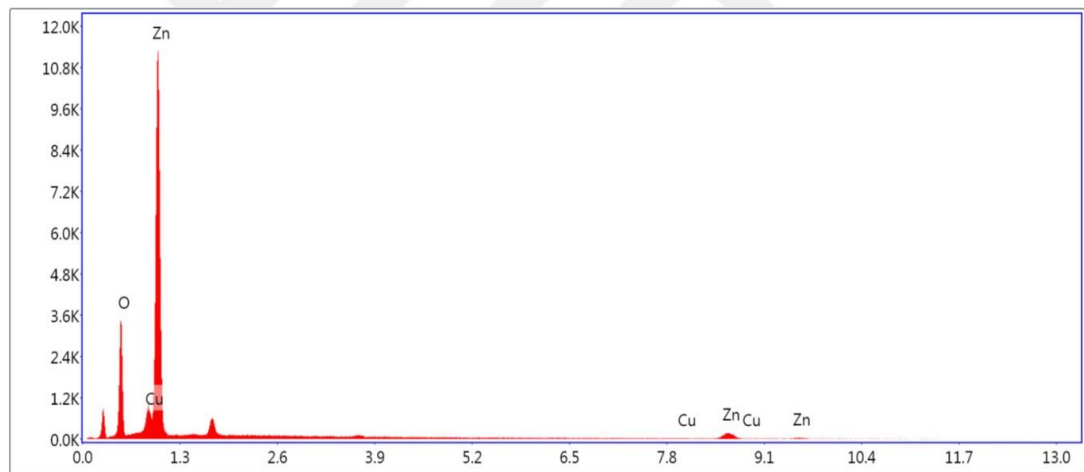
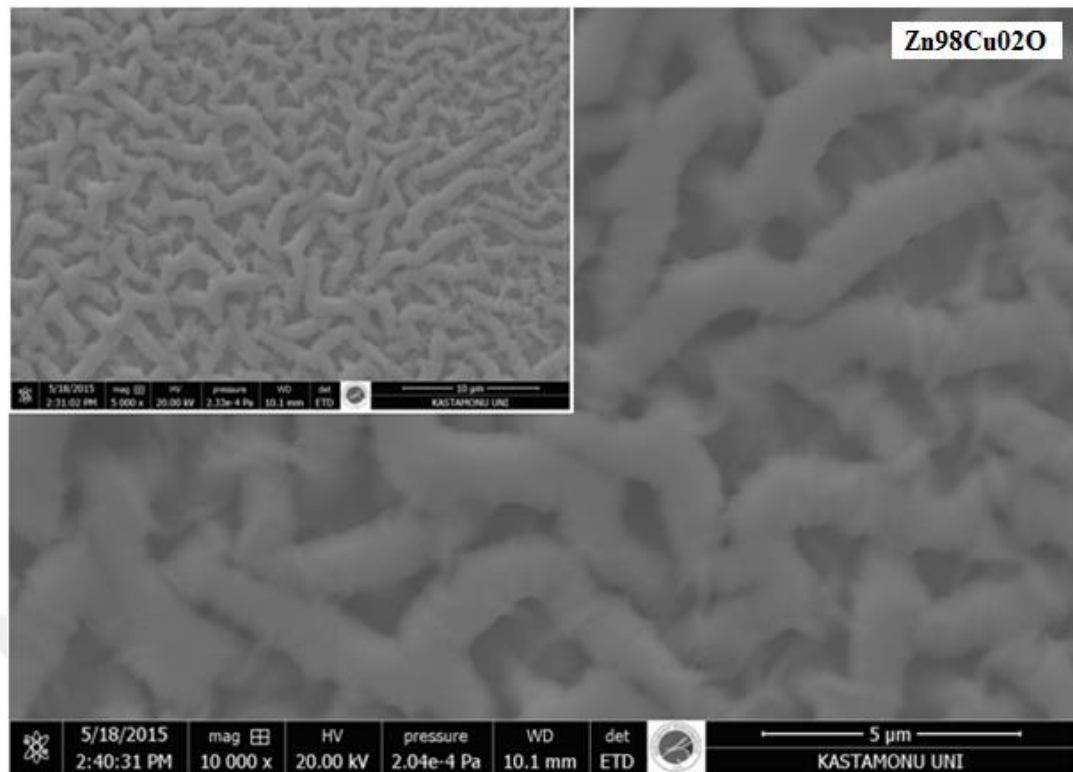


Figure 6.57. SEM and EDS images of $\text{Zn}_{0.99}\text{Cu}_{0.01}\text{O}$ nano thin film material

Table 6.49. EDS results of $\text{Zn}_{0.99}\text{Cu}_{0.01}\text{O}$ nano thin film materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	37.30	70.85	536.73
Cu	0.56	0.27	6.35
Zn	62.14	28.88	463.24



Lsec: 27.6 0 Cnts 0.000 keV Det: Octane Pro Det

Figure 6.58. SEM and EDS images of $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ nano thin film material

Table 6.50. EDS results of $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ nano thin film materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
<i>O</i>	71.13	90.96	660.29
<i>Cu</i>	0.05	0.02	0.26
<i>Zn</i>	28.81	9.02	90.57

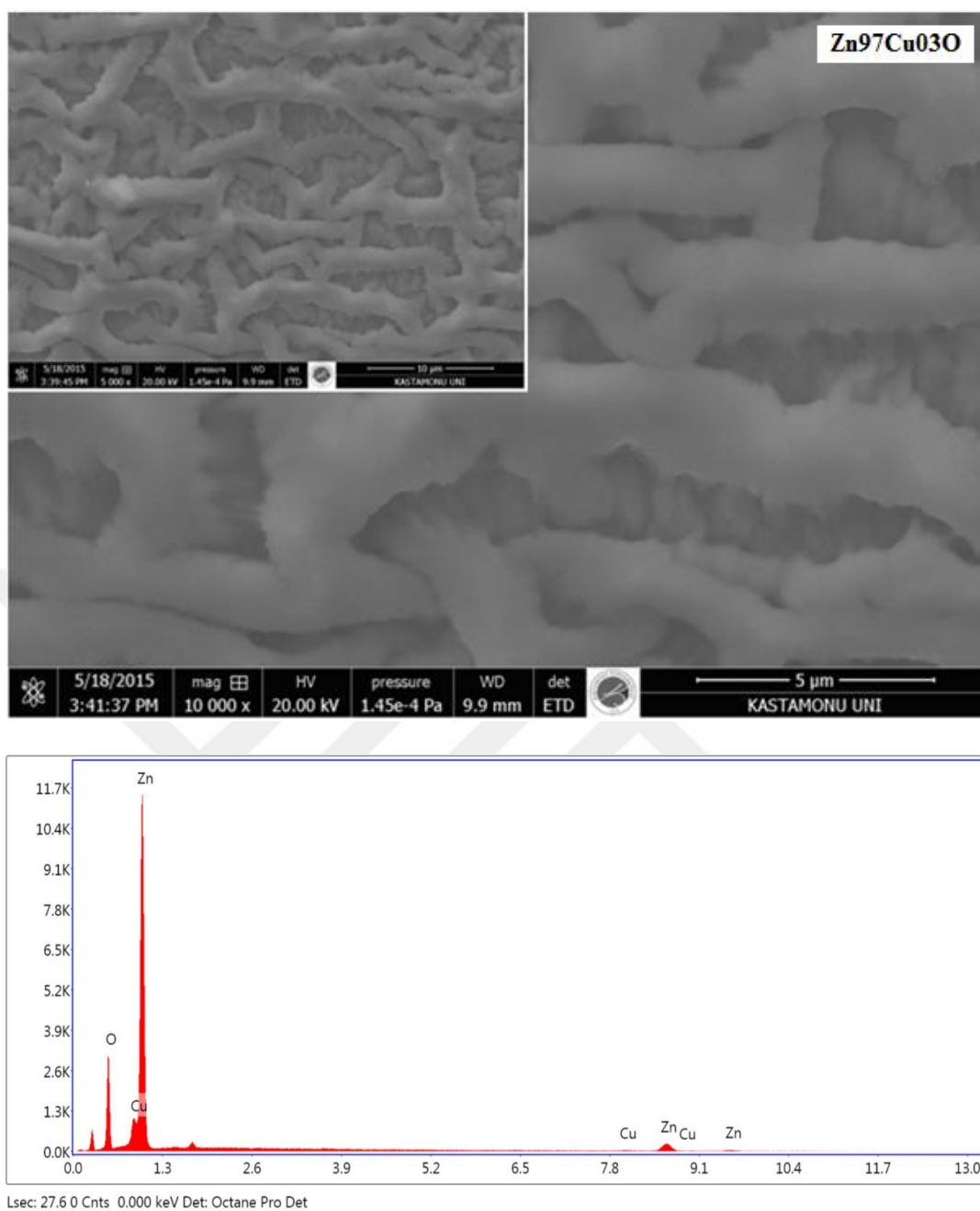
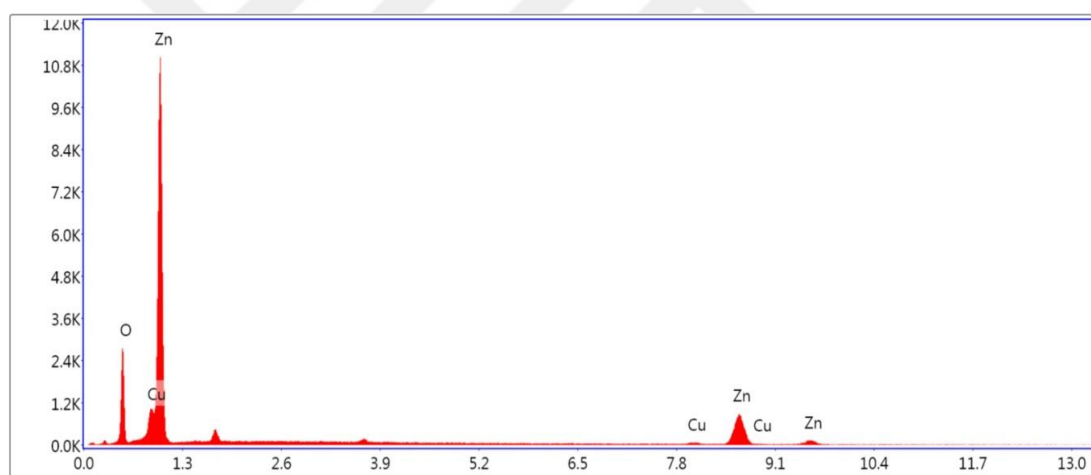
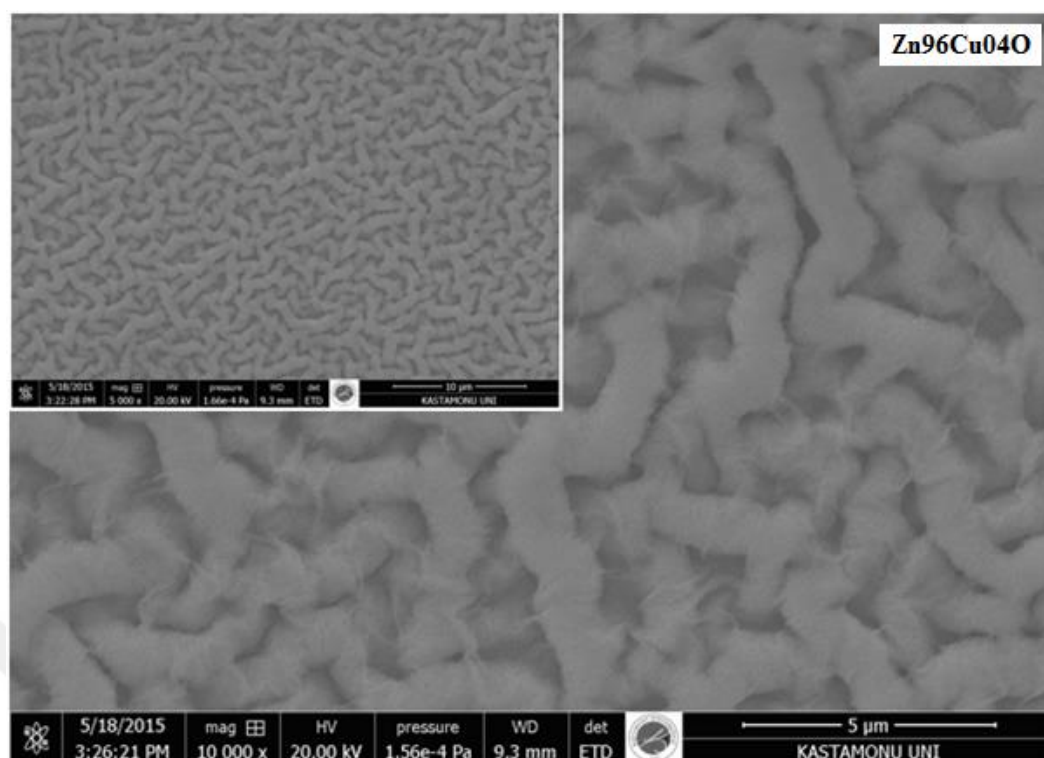


Figure 6.59. SEM and EDS images of $\text{Zn}_{0.97}\text{Cu}_{0.03}\text{O}$ nano thin film material

Table 6.51. EDS results of $\text{Zn}_{0.97}\text{Cu}_{0.03}\text{O}$ nano thin film materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	62.53	87.20	583.77
Cu	1.25	0.44	6.62
Zn	36.22	12.36	128.7



Lsec: 27.6 0 Cnts 0.000 keV Det: Octane Pro Det

Figure 6.60. SEM and EDS images of $\text{Zn}_{0.96}\text{Cu}_{0.04}\text{O}$ nano thin film material

Table 6.52. EDS results of $\text{Zn}_{0.96}\text{Cu}_{0.04}\text{O}$ nano thin film materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	33.98	67.75	488.46
Cu	2.41	1.21	27.01
Zn	63.62	31.05	488.18

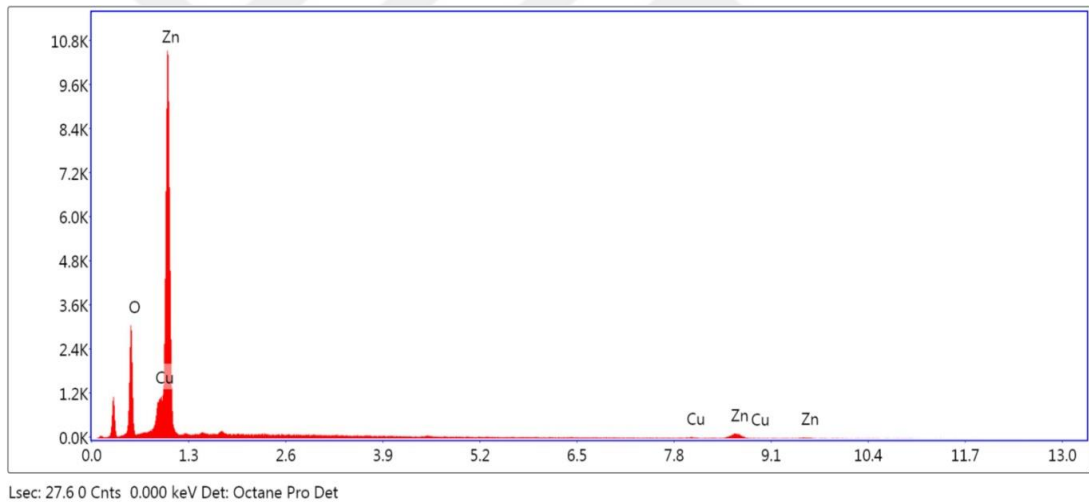
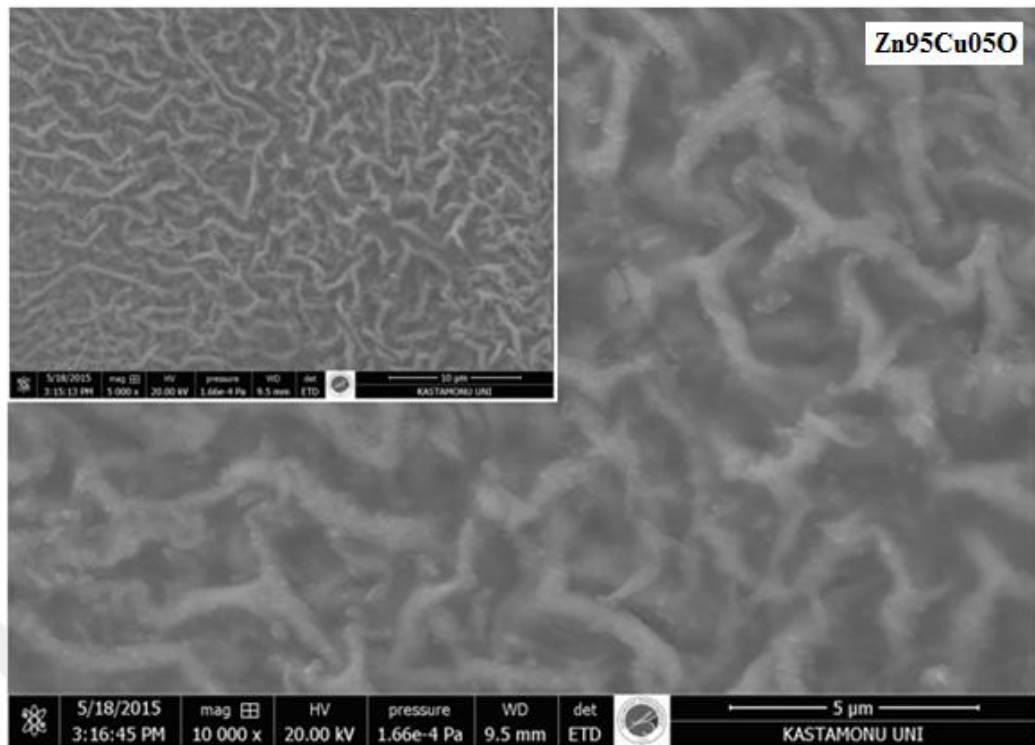


Figure 6.61. SEM and EDS images of $\text{Zn}_{0.95}\text{Cu}_{0.05}\text{O}$ nano thin film material

Table 6.53. EDS results of $\text{Zn}_{0.95}\text{Cu}_{0.05}\text{O}$ nano thin film materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	18.25	47.71	528.29
Cu	81.60	52.20	2557.28
Zn	0.15	0.10	3.84

6.3.8 Transition Metal Doped $\text{Zn}_{1-x-y}\text{B}_x\text{C}_y\text{O}$ (B=Cu, C=Co) DMS Nano Thin Film Materials

Scanning electron microscopy (SEM) images of undoped and Co doped ZnO films are shown in Figure 6.62-6.67. According to the SEM results, films exhibit wrinkle network structure with nano-sized crystals. The results indicate that the surface morphology changes with Co doping. Wrinkle structure does not change with increasing the Co doping, but grain size changes. More dense structure forms. The average grain size of the films is 29.108 nm. Each of Co atoms that enter into the ZnO lattice leads to smaller particles. This reduction occurs in the particle size with increasing the Co doping shows that Co^{+2} ions plays a role as particle growth inhibitor in the ZnO lattice.

The gradually reduction of particle size due to the Co content can be explained in two ways: The pinning effect is induced by $\text{Zn}_{1-x-y}\text{Cu}_x\text{Co}_y\text{O}$ particles at the grain boundaries and the dragging effect is between grain boundaries and Co ions. A reduction is observed on the mobility of the grain boundaries due to these two effects.

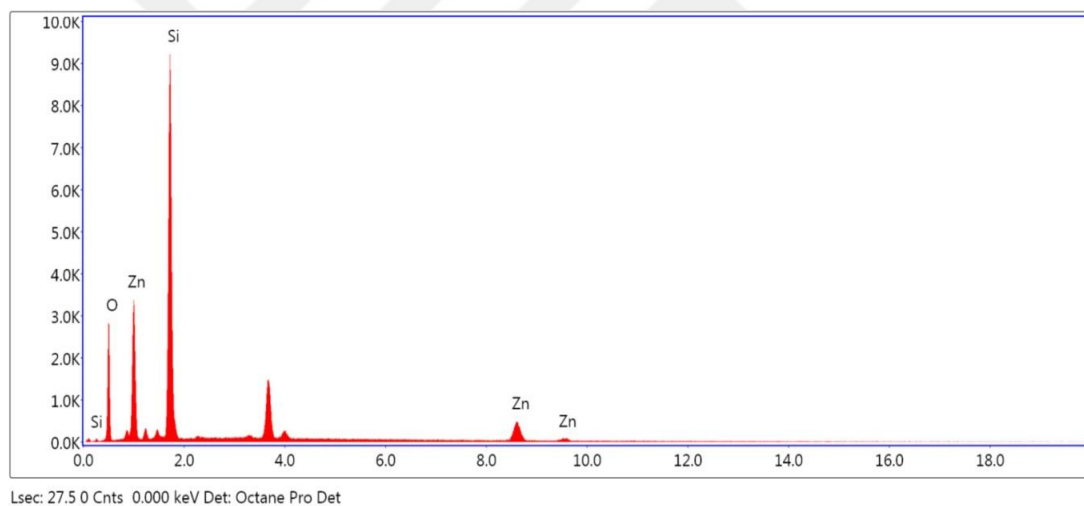
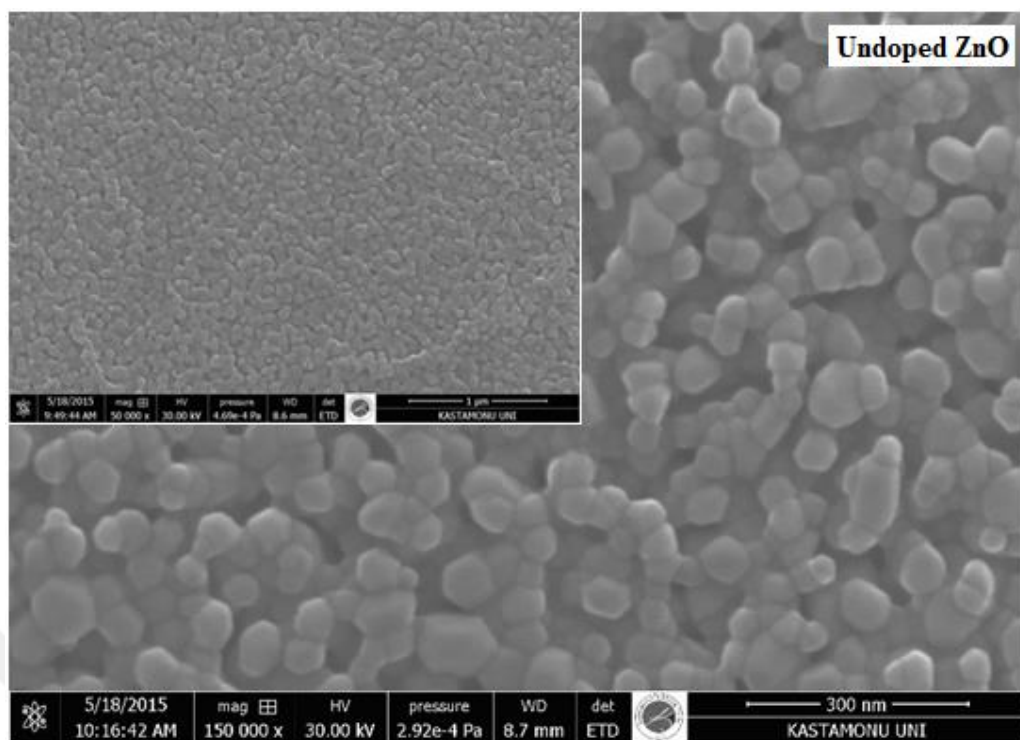


Figure 6.62. SEM and EDS images of undoped ZnO nano thin film material

Table 6.54. EDS results of undoped ZnO nano thin film materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	47.98	64.50	501.16
Si	42.09	32.23	2482.8
Zn	9.92	3.26	264.95

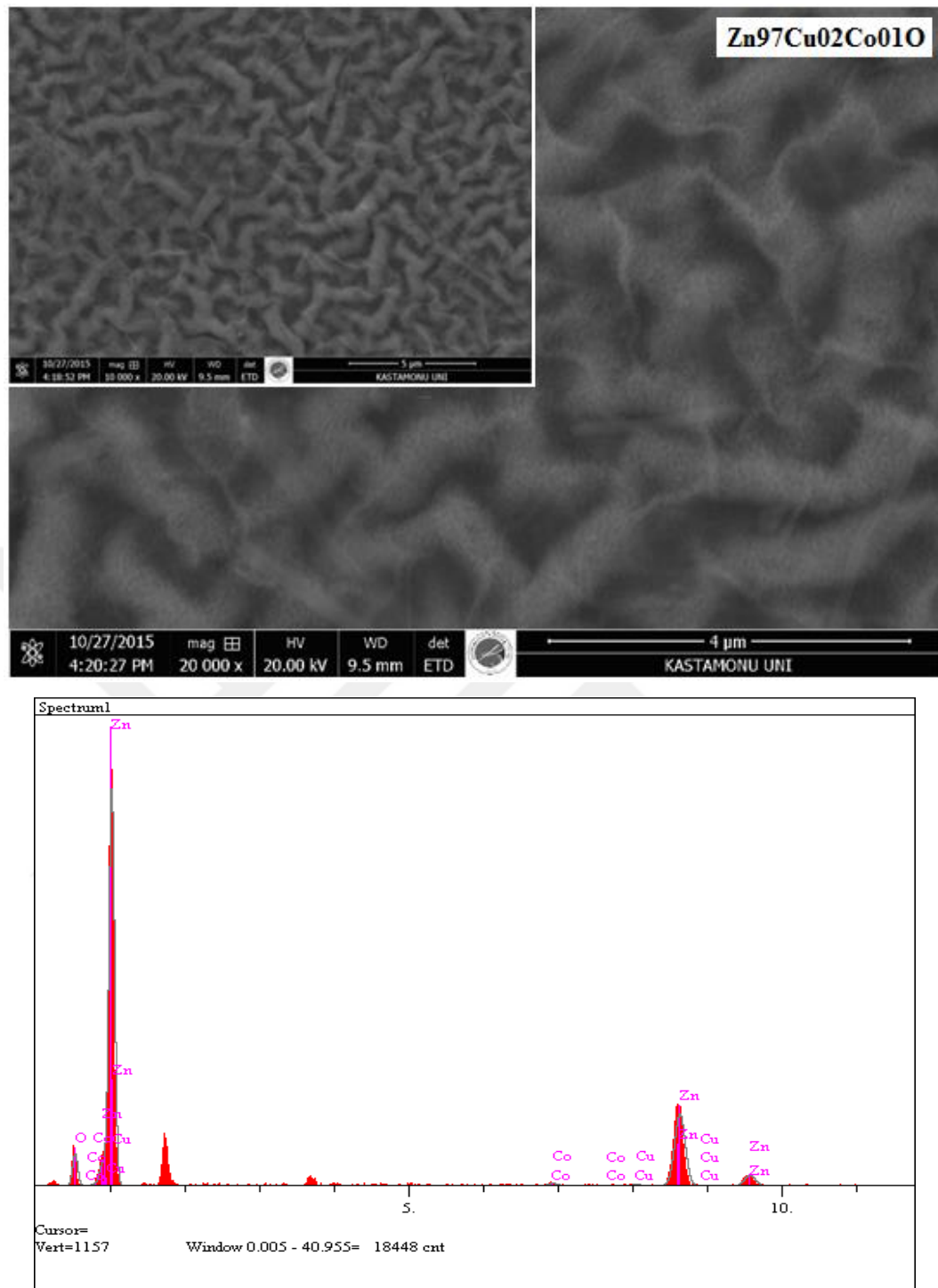


Figure 6.63. SEM and EDS images of $\text{Zn}_{0.97}\text{Cu}_{0.02}\text{Co}_{0.01}\text{O}$ nano thin film material

Table 6.55. EDS results of $\text{Zn}_{0.97}\text{Cu}_{0.02}\text{Co}_{0.01}\text{O}$ nano thin film materials

<i>Element</i>	<i>Weight %</i>	<i>Net Int.</i>
O	21.628	22.76
Co	0.861	3.28
Cu	0.959	1.80
Zn	76.552	104.58

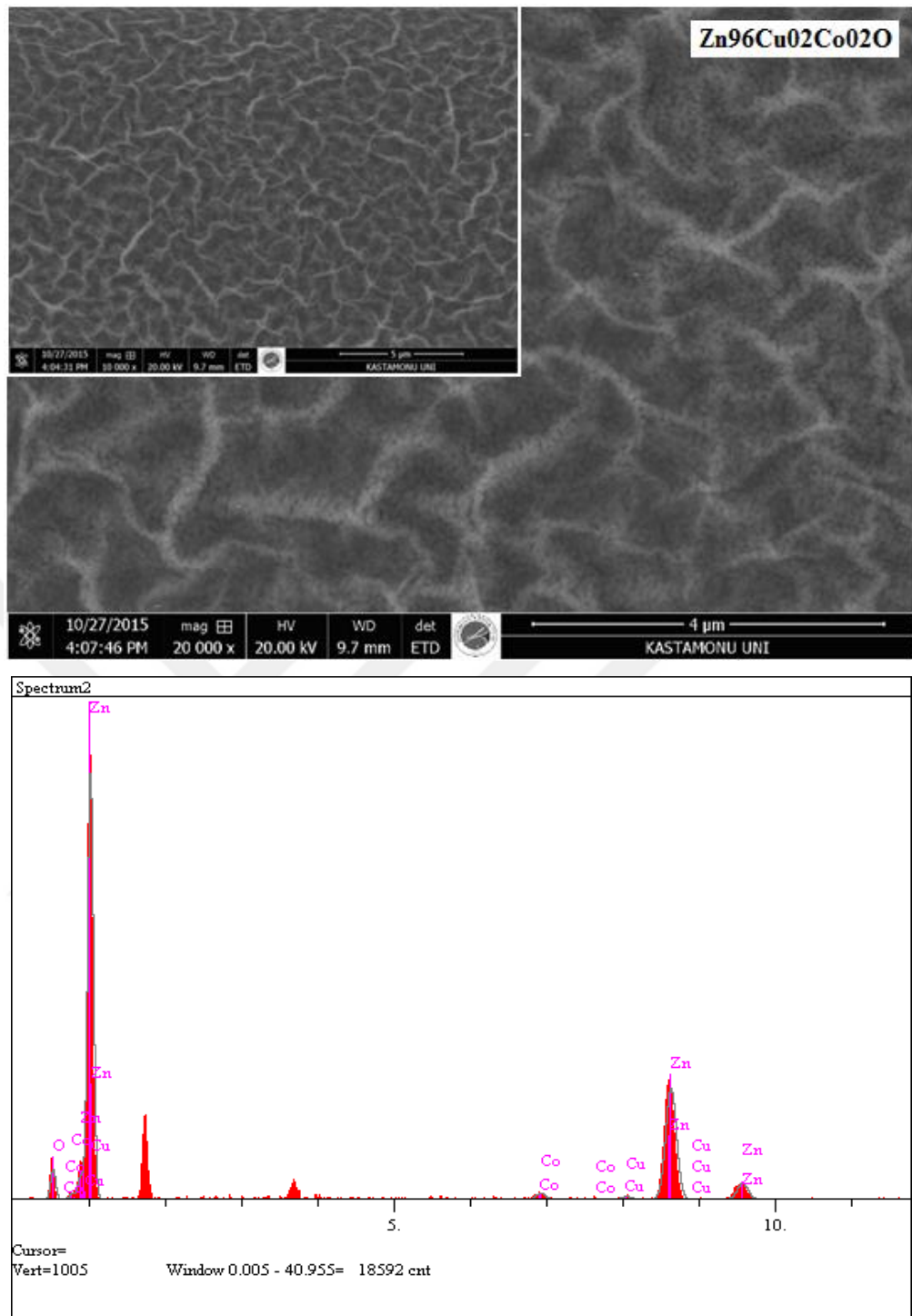


Figure 6.64. SEM and EDS images of $\text{Zn}_{0.96}\text{Cu}_{0.02}\text{Co}_{0.02}\text{O}$ nano thin film material

Table 6.56. EDS results of $\text{Zn}_{0.96}\text{Cu}_{0.02}\text{Co}_{0.02}\text{O}$ nano thin film materials

<i>Element</i>	<i>Weight %</i>	<i>Net Int.</i>
O	14.569	17.02
Co	1.519	6.56
Cu	1.672	3.63
Zn	82.240	131.51

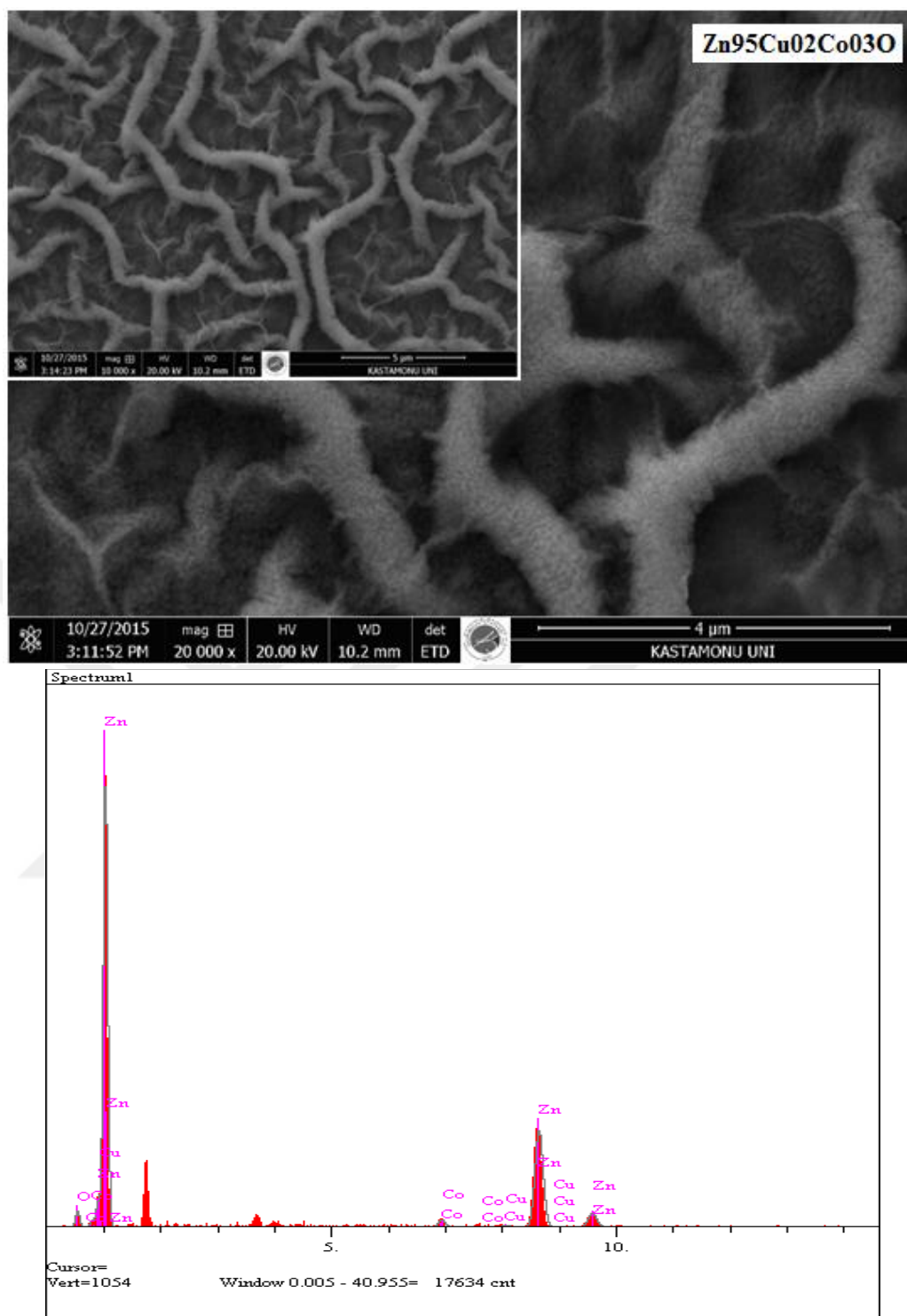


Figure 6.65. SEM and EDS images of $\text{Zn}_{0.95}\text{Cu}_{0.02}\text{Co}_{0.03}\text{O}$ nano thin film material

Table 6.57. EDS results of $\text{Zn}_{0.95}\text{Cu}_{0.02}\text{Co}_{0.03}\text{O}$ nano thin film materials

<i>Element</i>	<i>Weight %</i>	<i>Net Int.</i>
<i>O</i>	10.068	9.23
<i>Co</i>	2.114	7.41
<i>Cu</i>	1.293	2.27
<i>Zn</i>	86.526	112.13

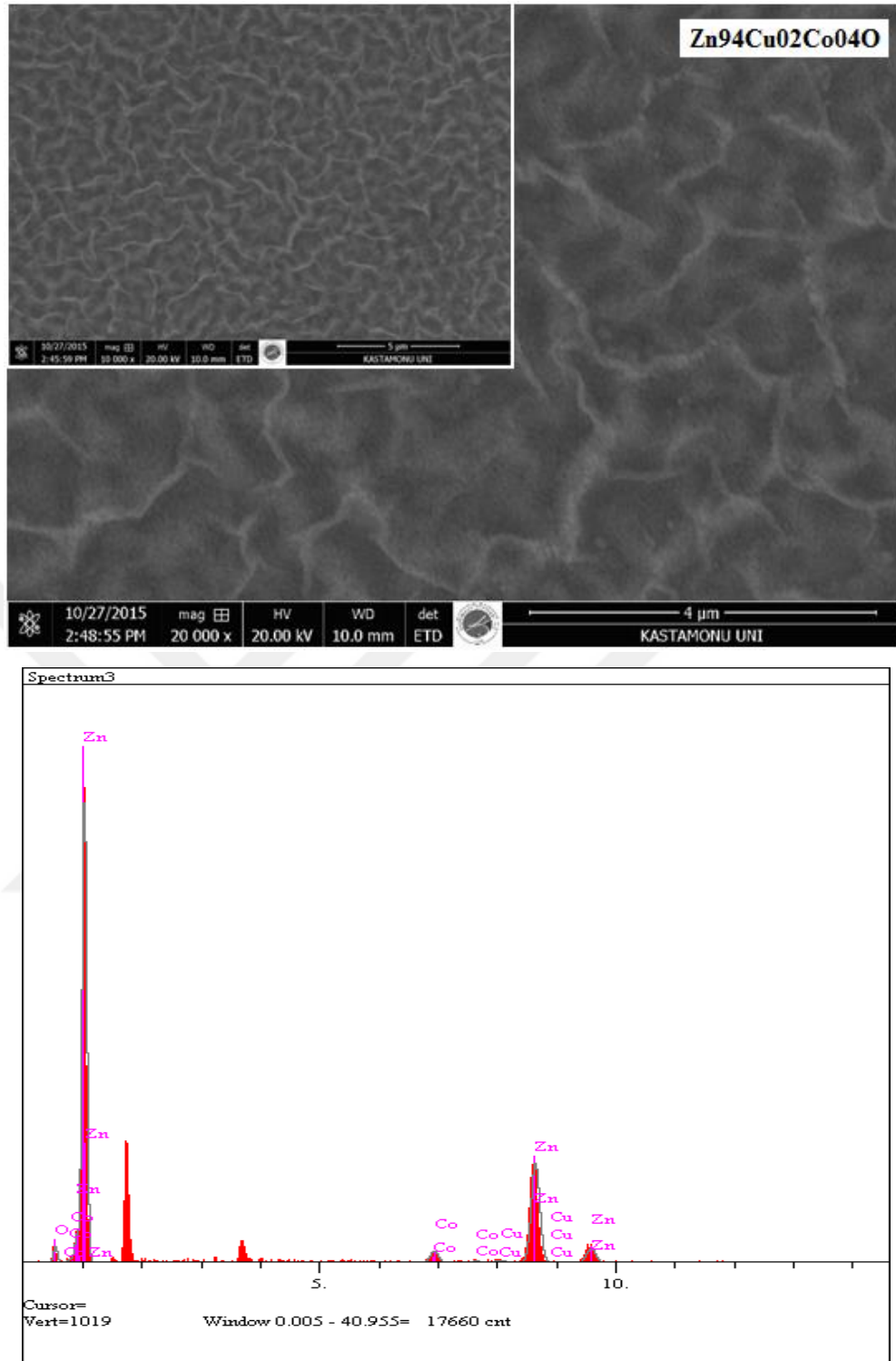


Figure 6.66. SEM and EDS images of Zn_{0.94}Cu_{0.02}Co_{0.04}O nano thin film material

Table 6.58. EDS results of Zn_{0.94}Cu_{0.02}Co_{0.04}O nano thin film materials

Element	Weight %	Net Int.
O	9.344	8.02
Co	3.536	11.07
Cu	1.457	2.35
Zn	85.662	103.93

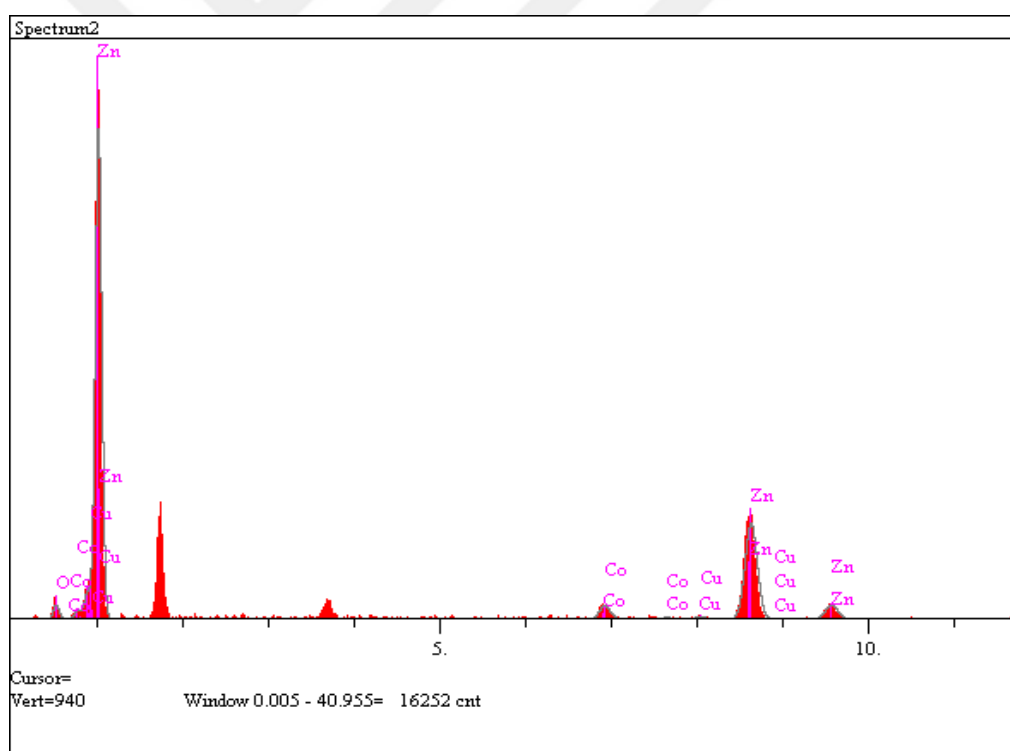
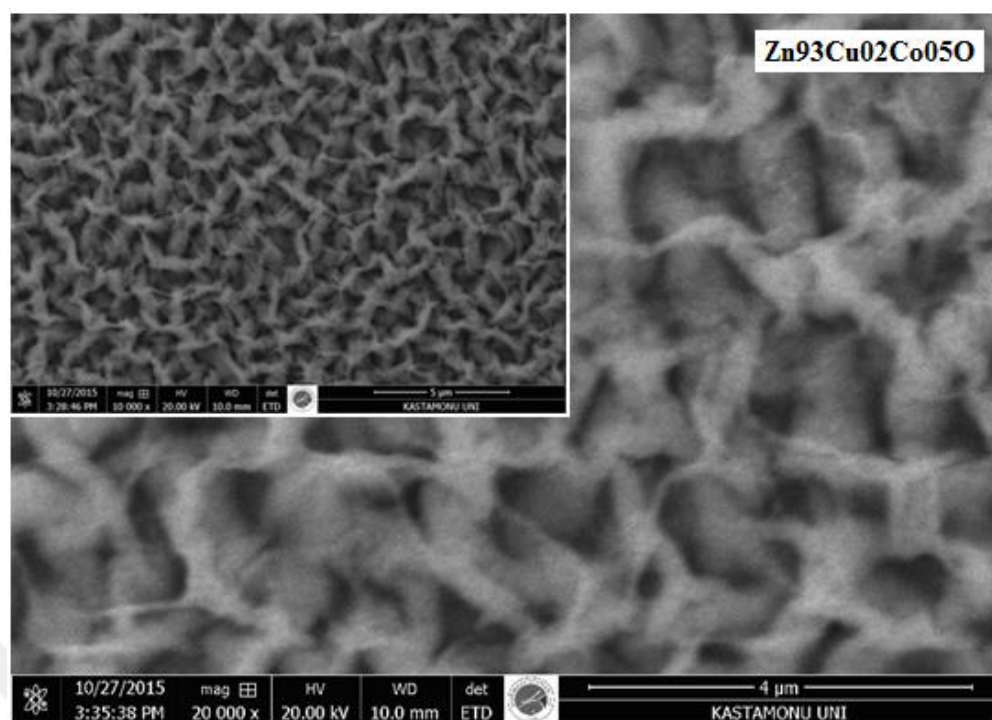


Figure 6.67. SEM and EDS images of $\text{Zn}_{0.93}\text{Cu}_{0.02}\text{Co}_{0.05}\text{O}$ nano thin film material

Table 6.59. EDS results of $\text{Zn}_{0.93}\text{Cu}_{0.02}\text{Co}_{0.05}\text{O}$ nano thin film materials

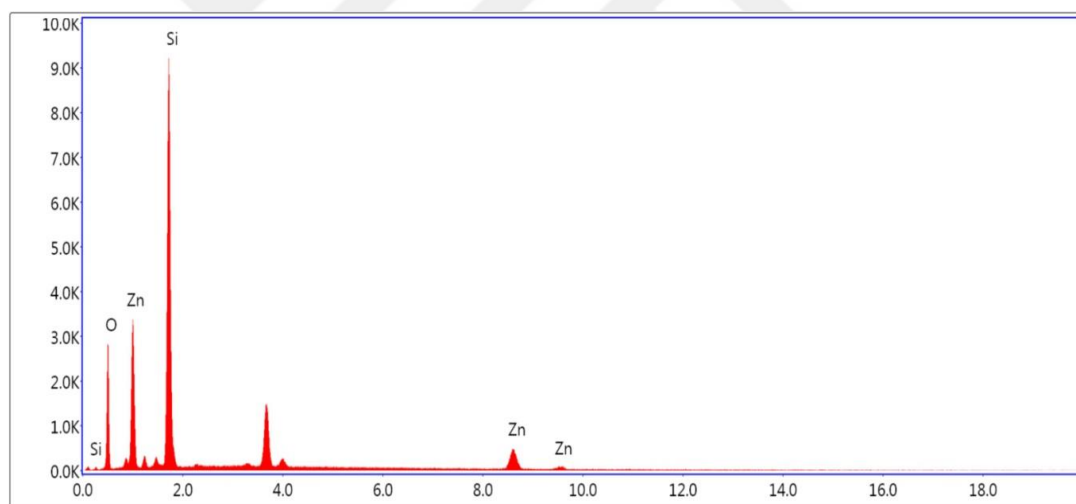
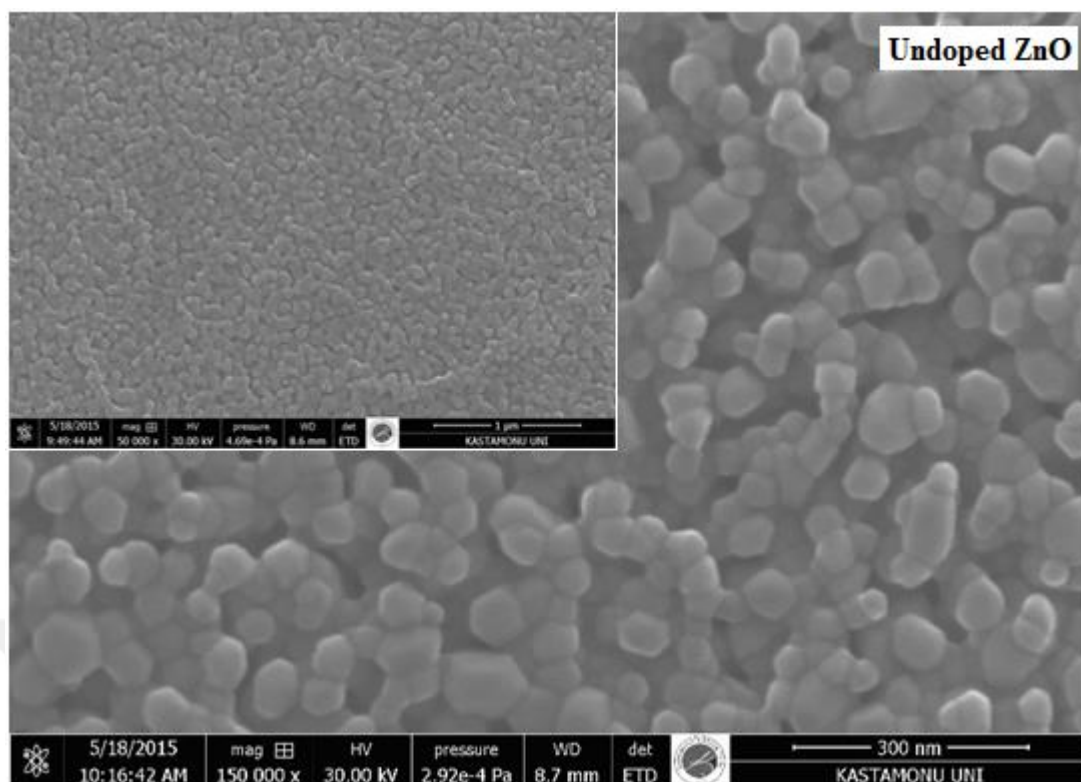
<i>Element</i>	<i>Weight %</i>	<i>Net Int.</i>
<i>O</i>	8.714	6.62
<i>Co</i>	4.381	11.92
<i>Cu</i>	1.481	2.10
<i>Zn</i>	85.423	91.87

6.3.9 Rare Earth Element Doped $\text{Zn}_{1-x}\text{B}_x\text{O}$ (B=Er) DMS Nano Thin Film Materials

Scanning electron microscopy (SEM) images of undoped and Er doped ZnO films are shown in Figure 6.68-6.73. The average grain size of the films is 17.046 nm. Er atoms affect the size of ZnO particles. Particle size decreased with increasing the Er doping. It is shows that Er^{+3} ions play a role as particle growth inhibitor in the ZnO lattice.

The gradually decreasing of particle size due to the Er content can be explained in two ways: First way the pinning effect is induced by $\text{Zn}_{1-x}\text{Er}_x\text{O}$ particles at the grain boundaries. Second way the dragging effect is between grain boundaries and Er ions. A reduction is observed on the mobility of the grain boundaries due to these two effects.

The compositions of all nano thin films which are detected by EDS are shown in Figure 6.67-6.72. The Zn and Er peaks are clearly seen from figures. Zn and Er contents of the nano thin films are the same as those in the preparation of samples.



Lsec: 27.5 0 Cnts 0.000 keV Det: Octane Pro Det

Figure 6.68. SEM and EDS images of undoped ZnO nano thin film material

Table 6.60. EDS results of undoped ZnO nano thin film materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	47.98	64.50	501.16
Si	42.09	32.23	2482.8
Zn	9.92	3.26	264.95

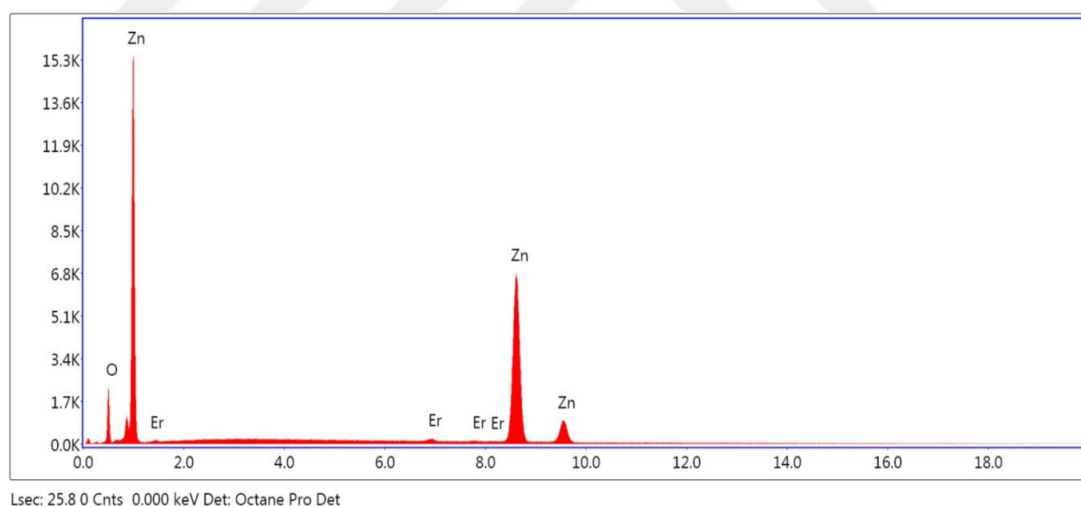
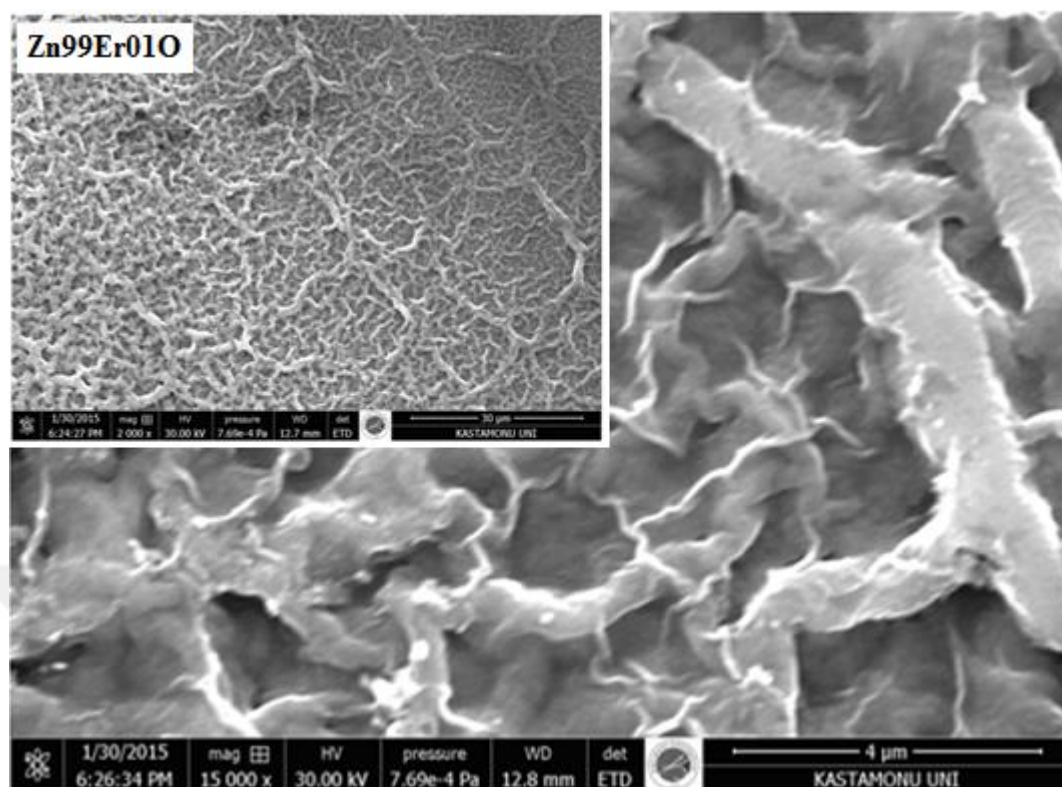


Figure 6.69. SEM and EDS images of Zn_{0.99}Er_{0.01}O nano thin film material

Table 6.61. EDS results of Zn_{0.99}Er_{0.01}O nano thin film materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
<i>O</i>	18.64	48.60	377.94
<i>Er</i>	1.31	0.33	69.96
<i>Zn</i>	80.05	51.07	4276.86

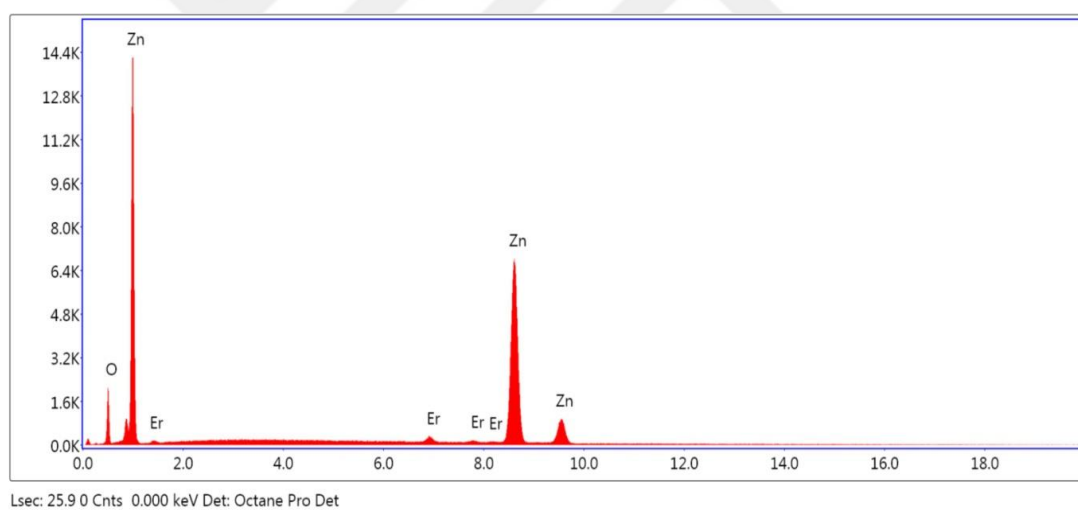
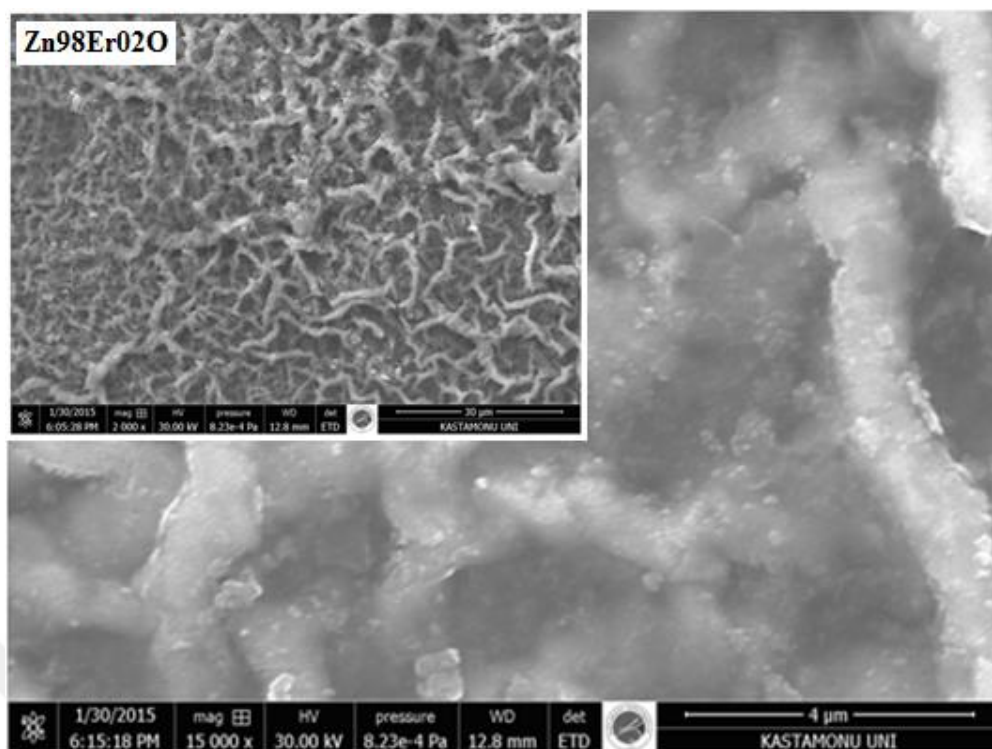


Figure 6.70. SEM and EDS images of $\text{Zn}_{0.98}\text{Er}_{0.02}\text{O}$ nano thin film material

Table 6.62. EDS results of $\text{Zn}_{0.98}\text{Er}_{0.02}\text{O}$ nano thin film materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	17.44	46.79	349.33
Er	2.47	0.63	127.1
Zn	80.08	52.58	4279.88

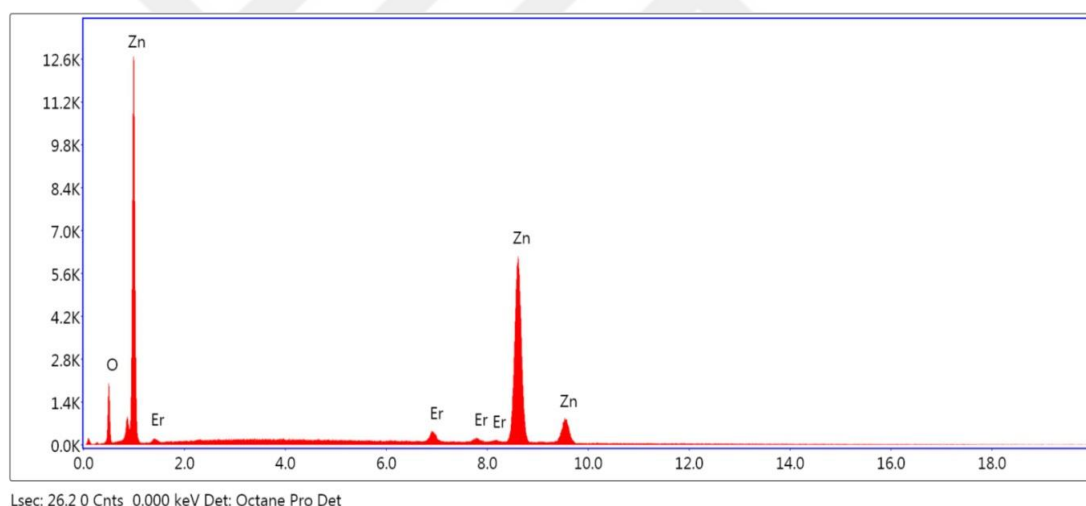
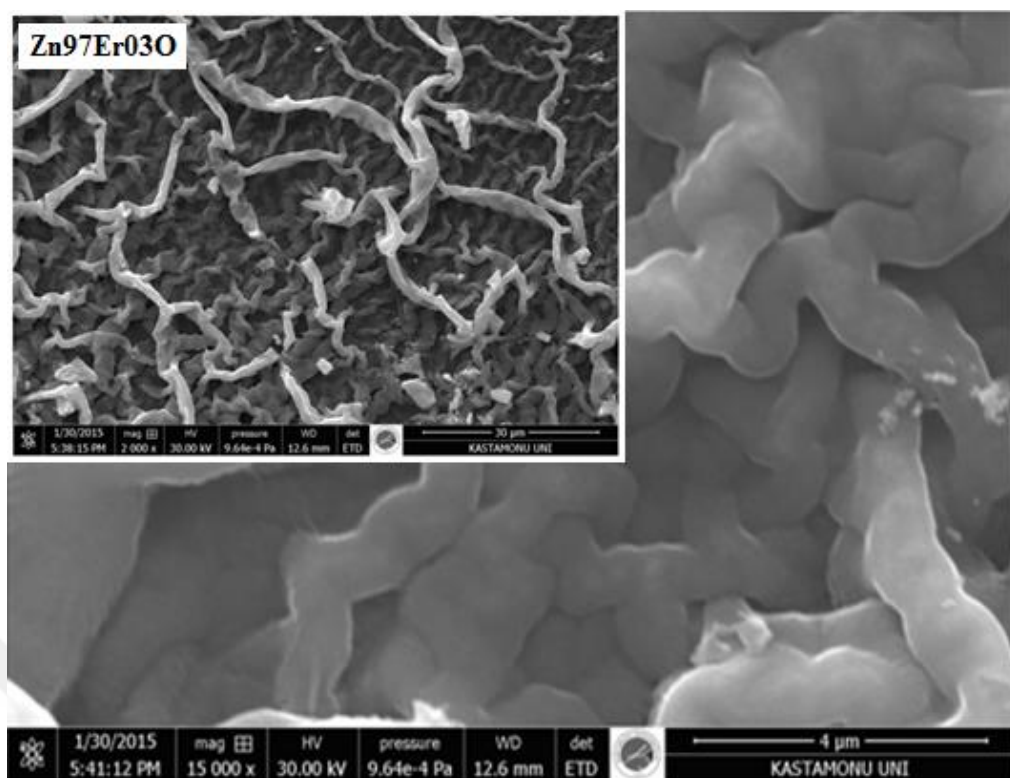


Figure 6.71. SEM and EDS images of $\text{Zn}_{0.97}\text{Er}_{0.03}\text{O}$ nano thin film material

Table 6.63. EDS results of $\text{Zn}_{0.97}\text{Er}_{0.03}\text{O}$ nano thin film materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
<i>O</i>	18.28	48.60	335.74
<i>Er</i>	4.47	1.14	198.65
<i>Zn</i>	77.25	50.27	3770.15

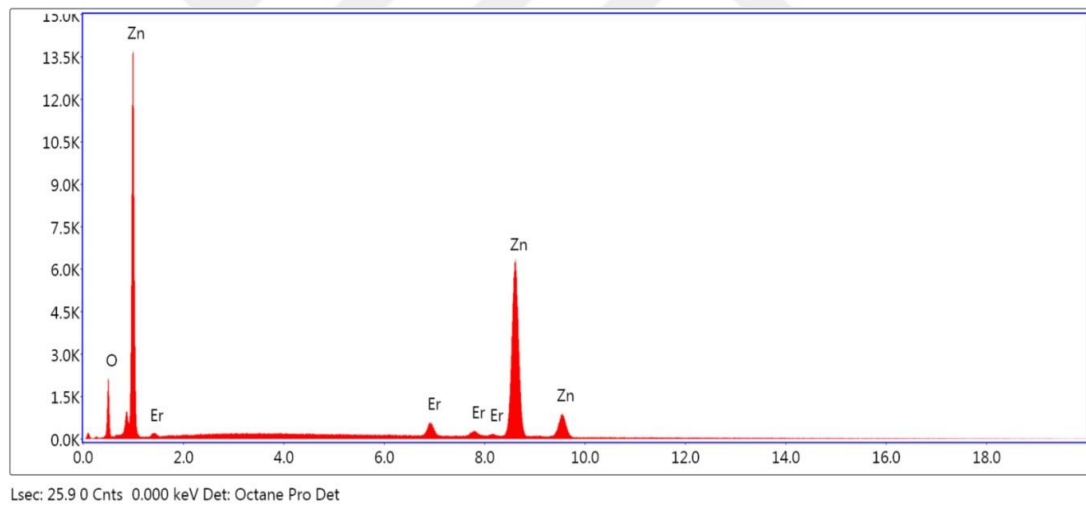
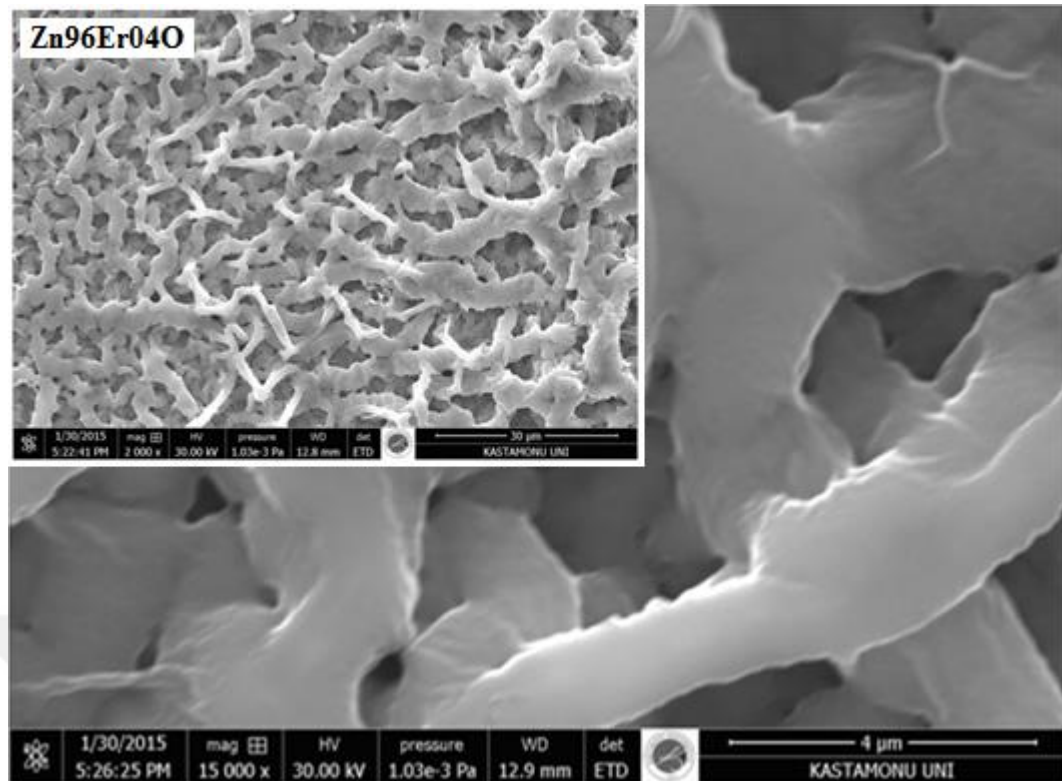


Figure 6.72. SEM and EDS images of $\text{Zn}_{0.96}\text{Er}_{0.04}\text{O}$ nano thin film material

Table 6.64. EDS results of $\text{Zn}_{0.96}\text{Er}_{0.04}\text{O}$ nano thin film materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
<i>O</i>	18.73	49.68	371.57
<i>Er</i>	6.17	1.57	286.08
<i>Zn</i>	75.10	48.75	3953.28

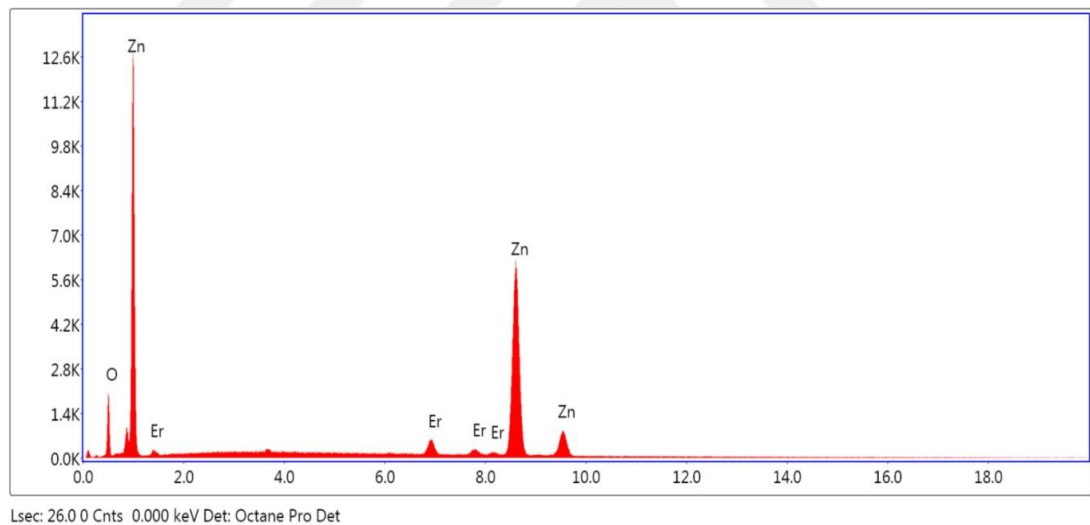
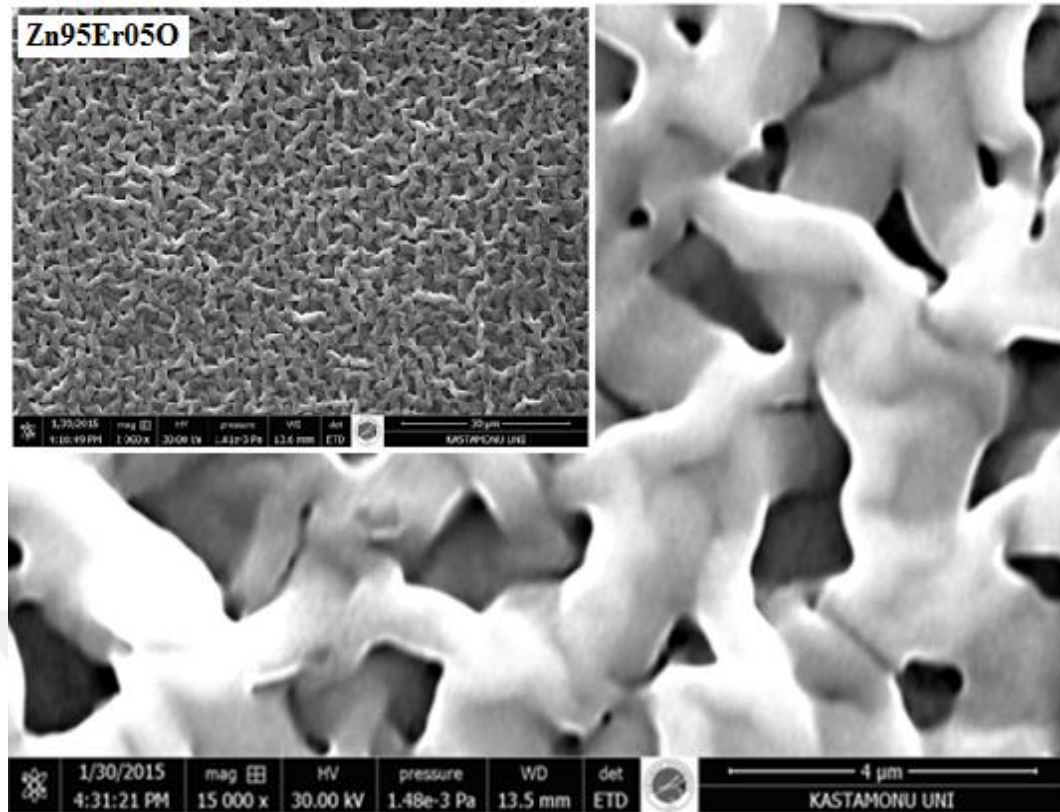


Figure 6.73. SEM and EDS images of Zn_{0.95}Er_{0.05}O nano thin film material

Table 6.65. EDS results of Zn_{0.95}Er_{0.05}O nano thin film materials

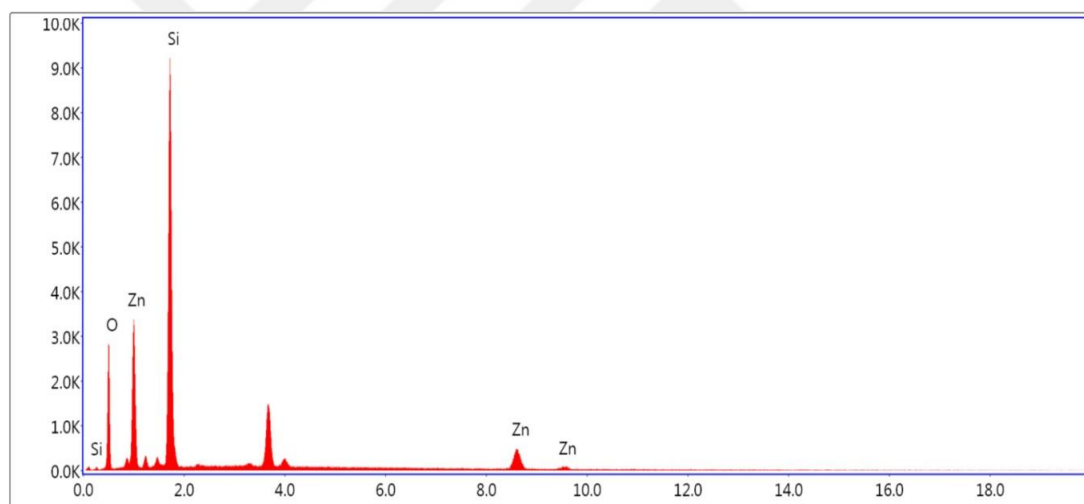
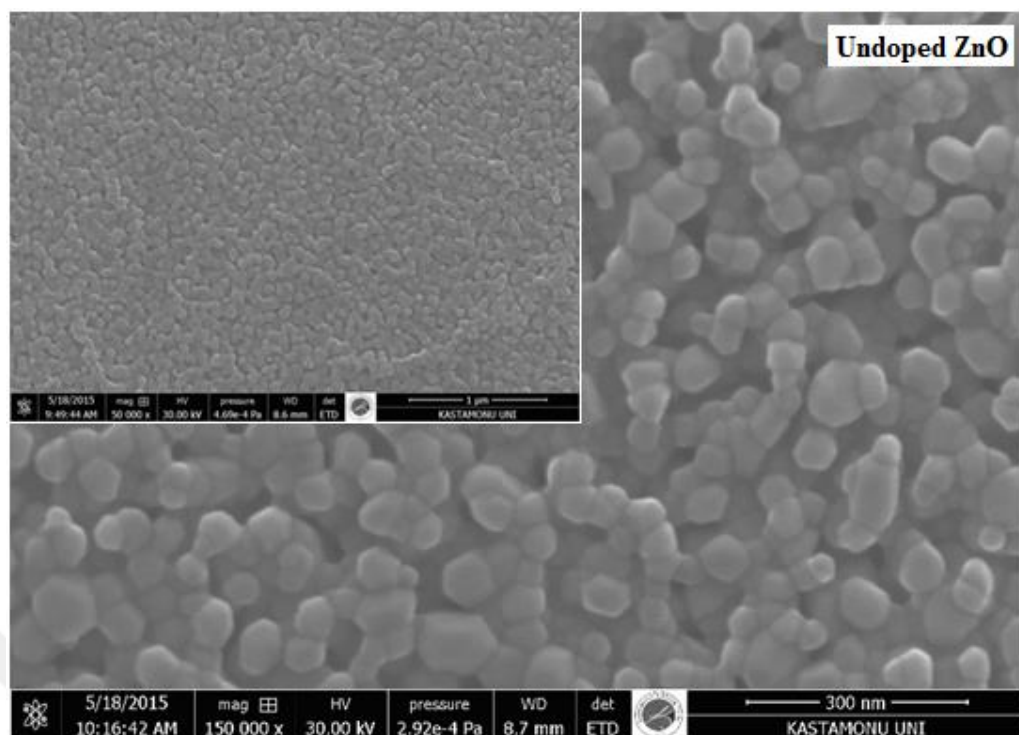
<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	18.33	49.08	343.28
Er	6.47	1.66	282.67
Zn	75.20	49.27	3750.31

6.3.10 Rare Earth Element Doped $\text{Zn}_{1-x}\text{B}_x\text{C}_y\text{O}$ (B=Er, C=Cd) DMS Nano Thin Film Materials

Scanning electron microscopy (SEM) images of undoped and Cd doped ZnO nano thin films are shown in Figure 6.74-6.78. The average grain size of the films is 22.655 nm. Particle size increased with increasing the Cd doping.

The compositions of all nano thin films which are detected by EDS are shown in Figure 6.74-6.78. Zn, Cd and Er peaks are clearly seen from figures. Zn, Cd and Er contents of the nano thin films are the same as those in the preparation of samples.





Lsec: 27.50 Cnts 0.000 keV Det: Octane Pro Det

Figure 6.74. SEM and EDS images of undoped ZnO nano thin film material

Table 6.66. EDS results of undoped ZnO nano thin film materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	47.98	64.50	501.16
Si	42.09	32.23	2482.8
Zn	9.92	3.26	264.95

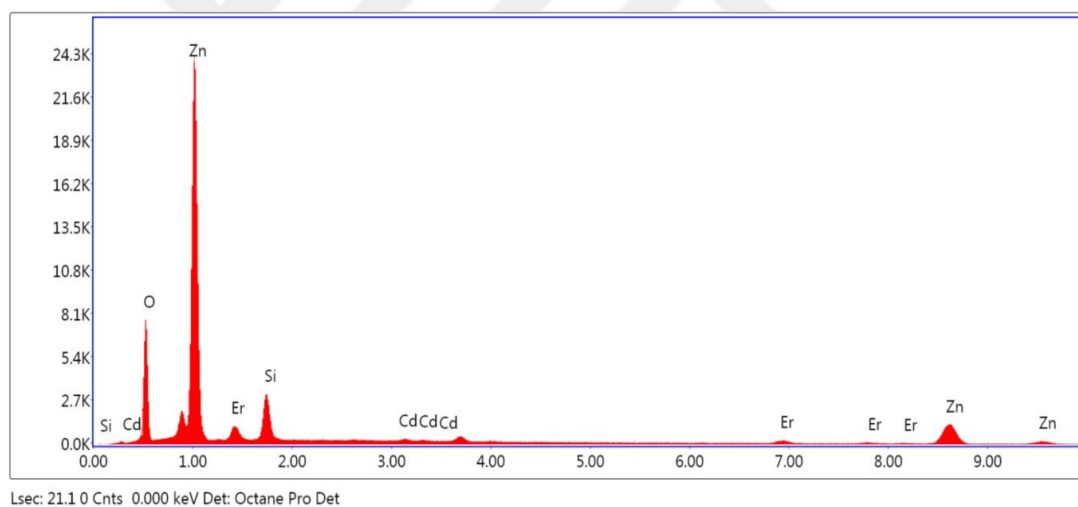
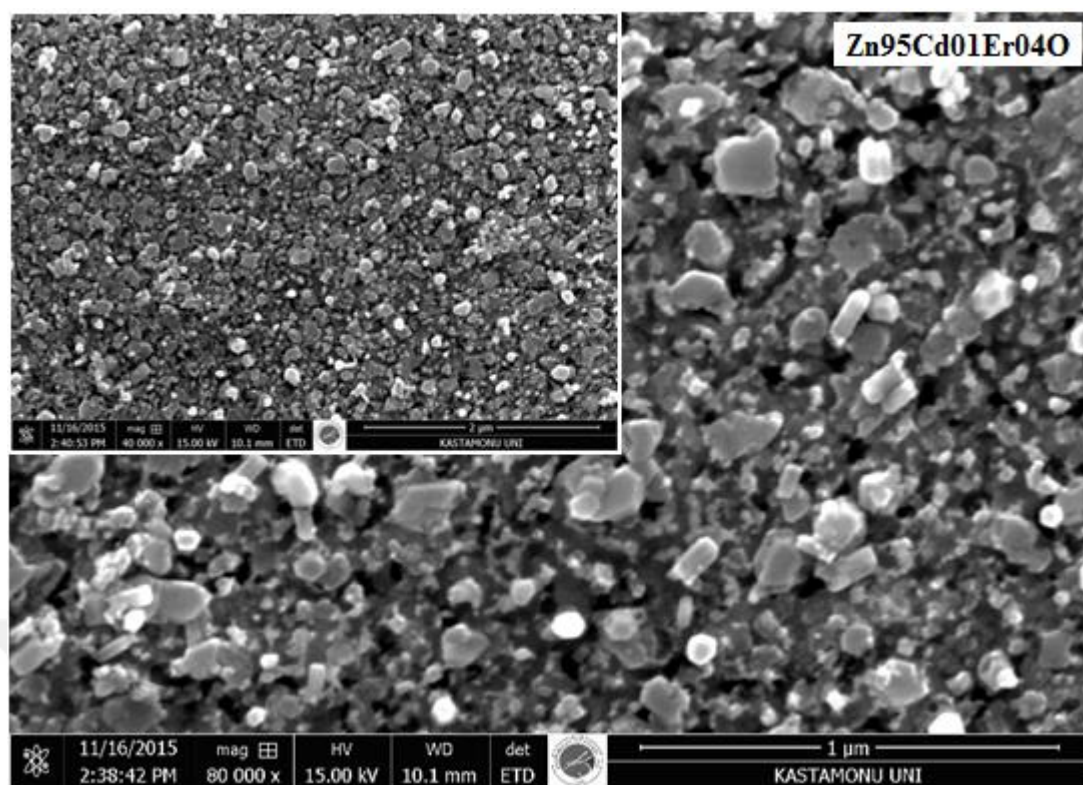


Figure 6.75. SEM and EDS images of $\text{Zn}_{0.95}\text{Cd}_{0.01}\text{Er}_{0.04}\text{O}$ nano thin film material

Table 6.67. EDS results of $\text{Zn}_{0.95}\text{Cd}_{0.01}\text{Er}_{0.04}\text{O}$ nano thin film materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	20.61	50.09	1744.99
Si	6.95	9.62	1002.38
Cd	0.68	0.23	44.54
Er	7.28	1.69	124.42
Zn	64.49	38.36	951.3

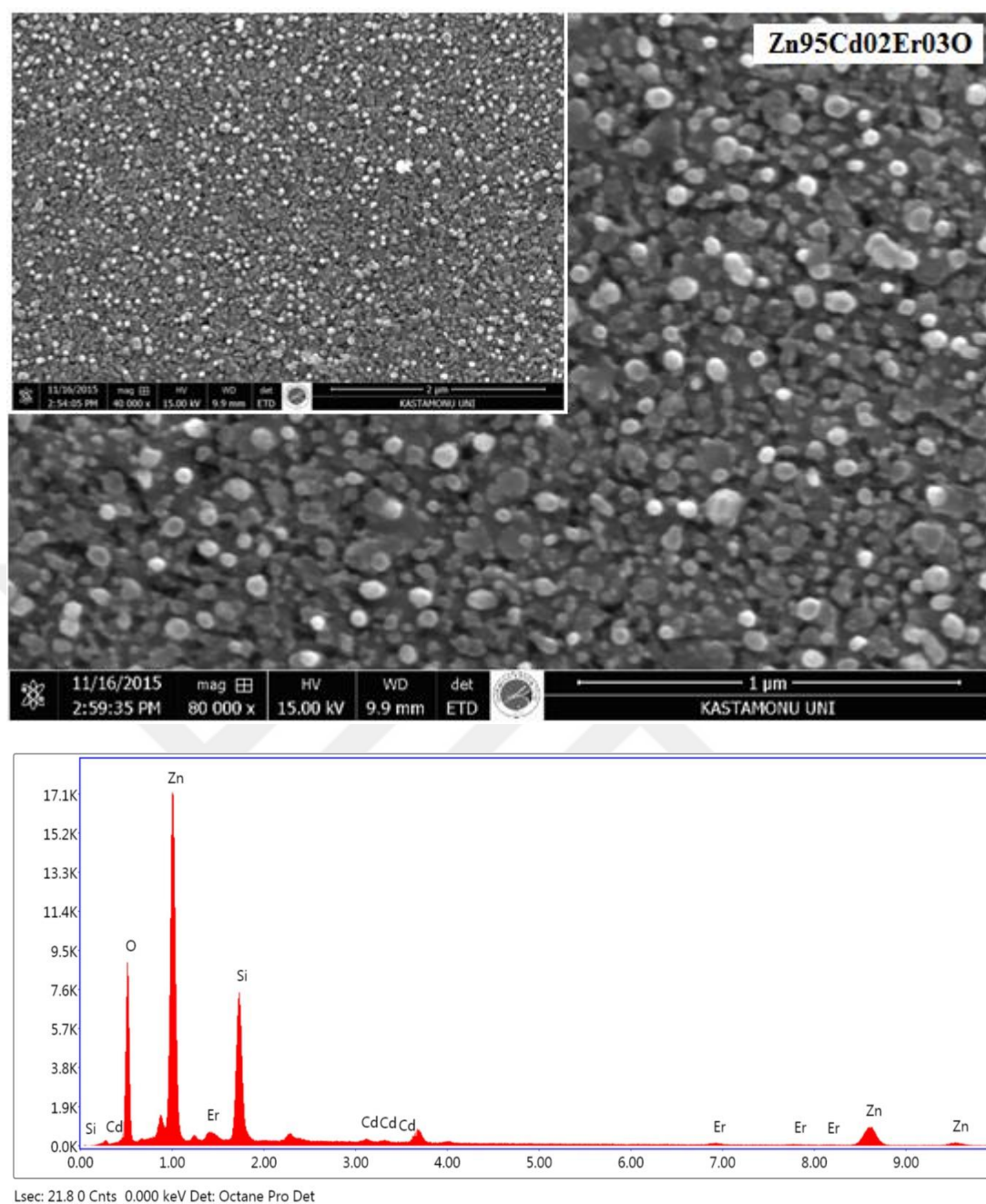


Figure 6.76. SEM and EDS images of Zn_{0.95}Cd_{0.02}Er_{0.03}O nano thin film material

Table 6.68. EDS results of Zn_{0.95}Cd_{0.02}Er_{0.03}O nano thin film materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	25.87	52.63	1939.14
Si	17.59	20.39	2475.1
Cd	1.17	0.34	67.58
Er	3.01	0.59	46.44
Zn	52.35	26.06	665.83

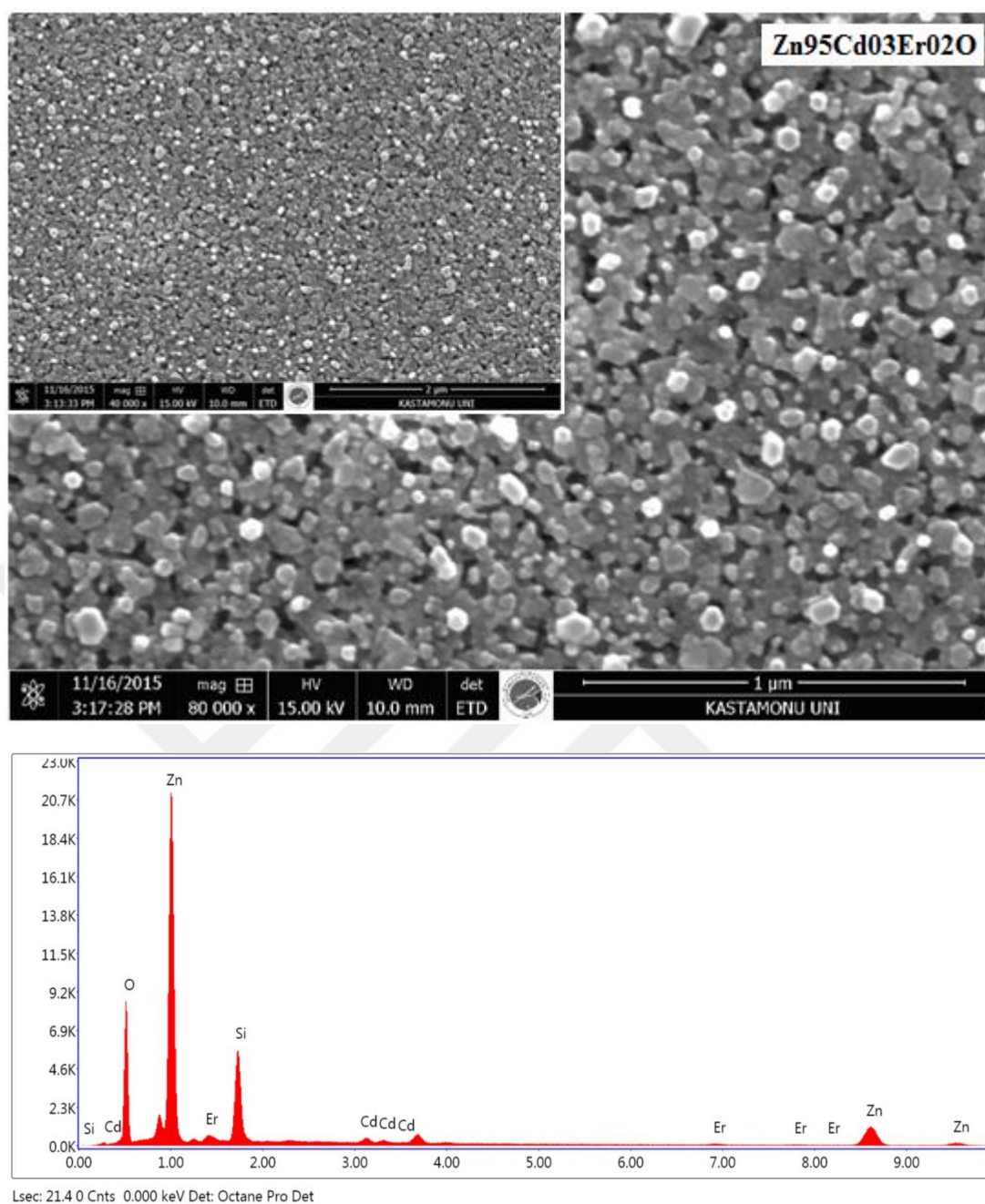


Figure 6.77. SEM and EDS images of $\text{Zn}_{0.95}\text{Cd}_{0.03}\text{Er}_{0.02}\text{O}$ nano thin film material

Table 6.69. EDS results of $\text{Zn}_{0.95}\text{Cd}_{0.03}\text{Er}_{0.02}\text{O}$ nano thin film materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
<i>O</i>	23.64	51.38	1926
<i>Si</i>	12.89	15.95	1914.8
<i>Cd</i>	1.85	0.57	117.31
<i>Er</i>	2.10	0.44	36.91
<i>Zn</i>	59.53	31.66	836.24

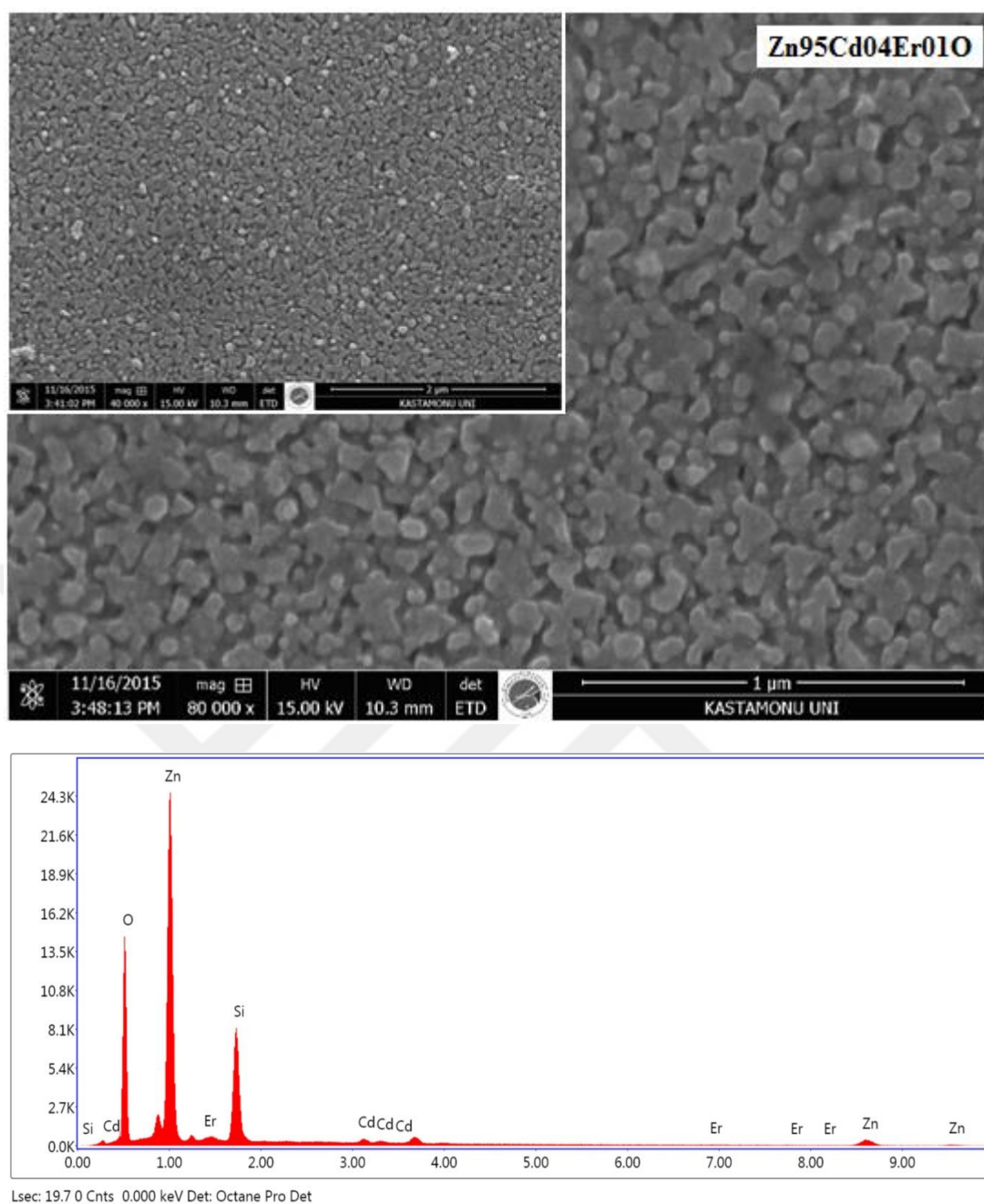


Figure 6.78. SEM and EDS images of Zn_{0.95}Cd_{0.04}Er_{0.01}O nano thin film material

Table 6.70. EDS results of Zn_{0.95}Cd_{0.04}Er_{0.01}O nano thin film materials

<i>Element</i>	<i>Weight %</i>	<i>Atomic %</i>	<i>Net Int.</i>
O	46.94	71.00	3615.01
Si	20.65	17.79	3003.63
Cd	2.68	0.58	140.12
Er	1.70	0.25	22.5
Zn	28.04	10.38	316.18

6.4 Vickers Microhardness Measurements of ZnO Based Nano Bulk Materials

Vickers hardness test is developed to measure the hardness of materials as an alternative to Brinell method by Robert L. Smith and George E. Sandland in 1921 (Smith and Sandland, 1921). The basic principle, as with all the general principles of hardness, shows the response of material resist to plastic deformation formed with a load applied from a source standard in the material. Vickers test can be used for all materials and has one of the widest scales among hardness tests. Hardness unit is converted to unit of Pascal but should not be confused with the pressure has a Pascal unit. Hardness is determined with the force is applied by indenter on the surface area. In our study, hardness unit is taken as GPa.

H_v hardness is determined by F/A ratio. F is applied load on the surface of material. A is surface area in terms of micrometers square. A can be calculated by the following formula:

$$A = \frac{d^2}{2 \sin(136^\circ/2)} \quad (6.12)$$

$$A \approx \frac{d^2}{1854.4} \quad (6.13)$$

The Vickers microhardness values (H_v) of different applied loadings in the range of 0.245– 2.940 N for 10 s can be calculated using the Eqn.6.14. This process is repeated 7 times and average value of hardness is found.

$$H_v = F/A \approx \frac{1854.4 F}{d^2} \quad GPa \quad (6.14)$$

Description of mechanical parameters

The modulus of elasticity (E) is a measure of elastic deformation of the material under force. In some sources, it is also referred to as Young's modulus and calculated as described below. Materials become more rigid with increasing the E . In order words, material shows less deformation with strain. When elasticity modulu is small, the material acts more flexible/elastic.

$$E = 81.9635 H_V \quad (6.15)$$

Brittleness (B_i) is the tendency of a material has undergone very little fracture or has not no deformation that is pre-determined to fracture in technical using. It means that material doesn't have the ability to plastic deformation. B_i is the opposite ductility (D). Ductility is the ability of a material to permanent deformation.

$$B_i = H_v/K_{IC} \quad (6.16)$$

$$D = 1/B_i \quad (6.17)$$

Toughness of the material is a maximum amount of energy is absorbed before fracture. At the same time, it is described as plastic deformation capability of the material. Because elastic and plastic deformation allow for absorption of a majority of energy by the material, toughness can be small in brittle materials. In materials science, fracture toughness is a property that defines the ability of the material which contains cracks formed by fracture and is one of the important features of any material in many design applications. Linear elastic fracture toughness of a material is determined by the formation of a crack that begins to grow in the material. It is shown as fracture toughness (K_{IC}) and its unit is $\text{Pa}\sqrt{\text{m}}$ or $\text{psi}\sqrt{\text{in}}$.

$$K_{IC} = \sqrt{2E\gamma} \quad (6.18)$$

Yield strength (Y) represents transition point from elastic deformation to plastic deformation.

$$Y \approx H_V/3 \quad (6.19)$$

6.4.1 Transition Metal Doped $\text{Zn}_{1-x}\text{B}_x\text{O}$ ($\text{B}=\text{Co}$) DMS Nano Bulk Materials

It is known that hardness is a mechanical parameter which is related to the content and structure of the solids. Therefore, importance of the microhardness tests is increasing more and more to characterize a substance (Asikuzun et al., 2012; Khalil, 2001; Aydın et al., 2009; Quinn et al., 1997; Ozturk et al., 2015). In this study, microhardness values are measured using a Vickers micro- hardness tester for its common usage and non-destructive measuring conditions regarding to the sample

surfaces. Force is applied from 25 N to 300 N on the material's surface; diagonals of the trace left by the indenter are read using the microscope and load/trace area. Vickers hardness is calculated using the relation given in Eqn.6.14.

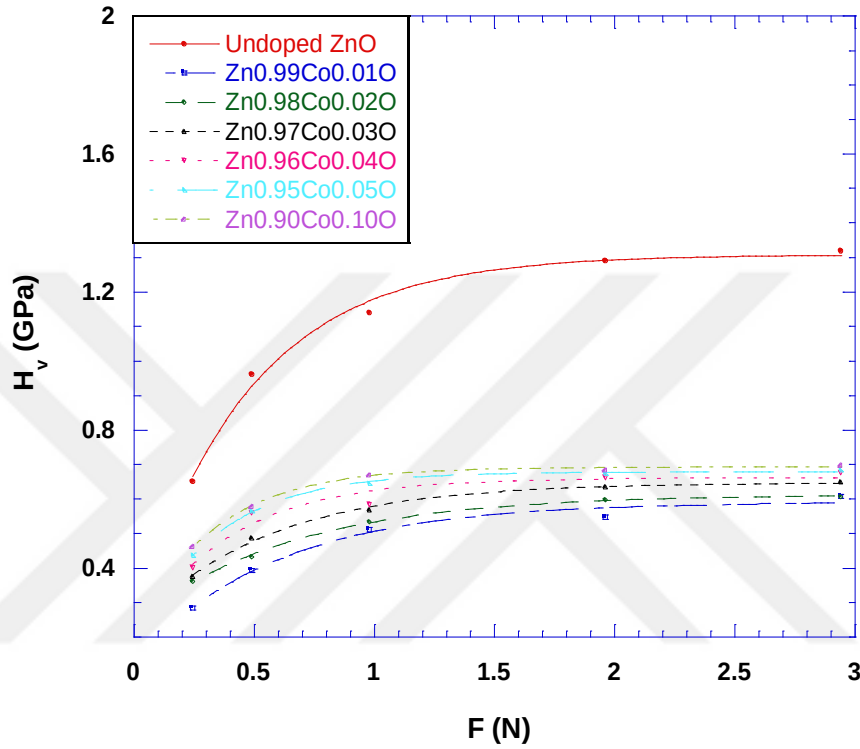


Figure 6.79. The variations of microhardness with load for the samples

It can be seen from Figure 6.79 that the microhardness values decrease with increasing the *Co* doping level and these values increase with applied load. Microhardness values have reached the plateau (saturation region) around about 1 *N* for the samples.

The hardness value of the sample observed Reverse Indentation Size Effect (RISE) behavior depends on the applied load. It shows that the indenter size is associated with applied load. This nonlinear case is named as RISE in the literature (Gong et al., 1999; Elmustafa et al., 2003). Smaller indentation load shows a smaller hardness value.

Parameters such as *E*, *B_i*, *K_{IC}*, *Y* and *D* that are as important as hardness to mechanical characterizations of materials are also calculated and values of these

parameters are given in Table 6.71. We can say from table that E , B_i , K_{IC} , Y and D values increased because these parameters are relation to the hardness.

Increase of the K_{IC} value is an expected result due to dependency E . The optical trace photos of the indentations for each sample under 2.940 N load are shown in Figure 6.80.

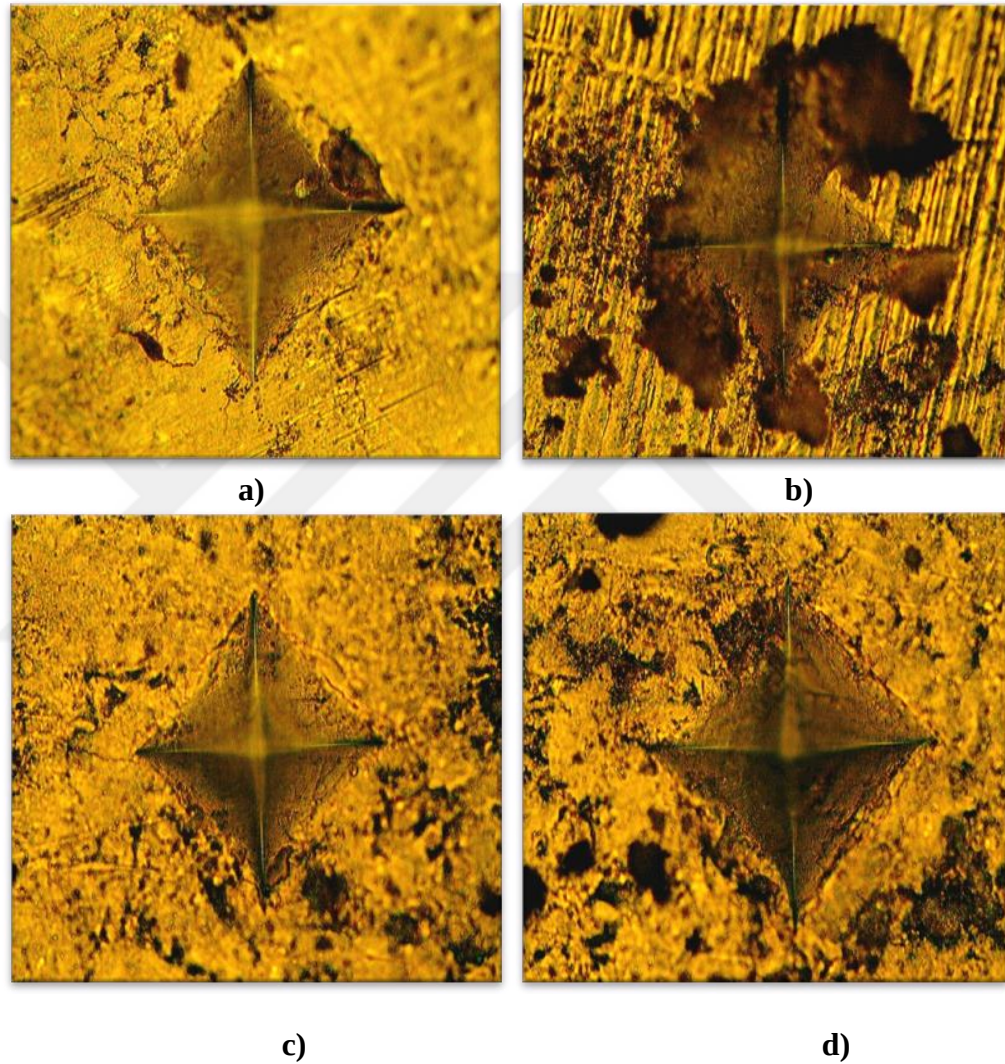


Figure 6.80. The optical trace photos under 2.940 N load for the samples: a) $Zn_{0.99}Co_{0.01}O$, b) $Zn_{0.98}Co_{0.02}O$, c) $Zn_{0.97}Co_{0.03}O$, d) $Zn_{0.96}Co_{0.04}O$, e) $Zn_{0.95}Co_{0.05}O$, f) $Zn_{0.90}Co_{0.10}O$ and g) Undoped ZnO

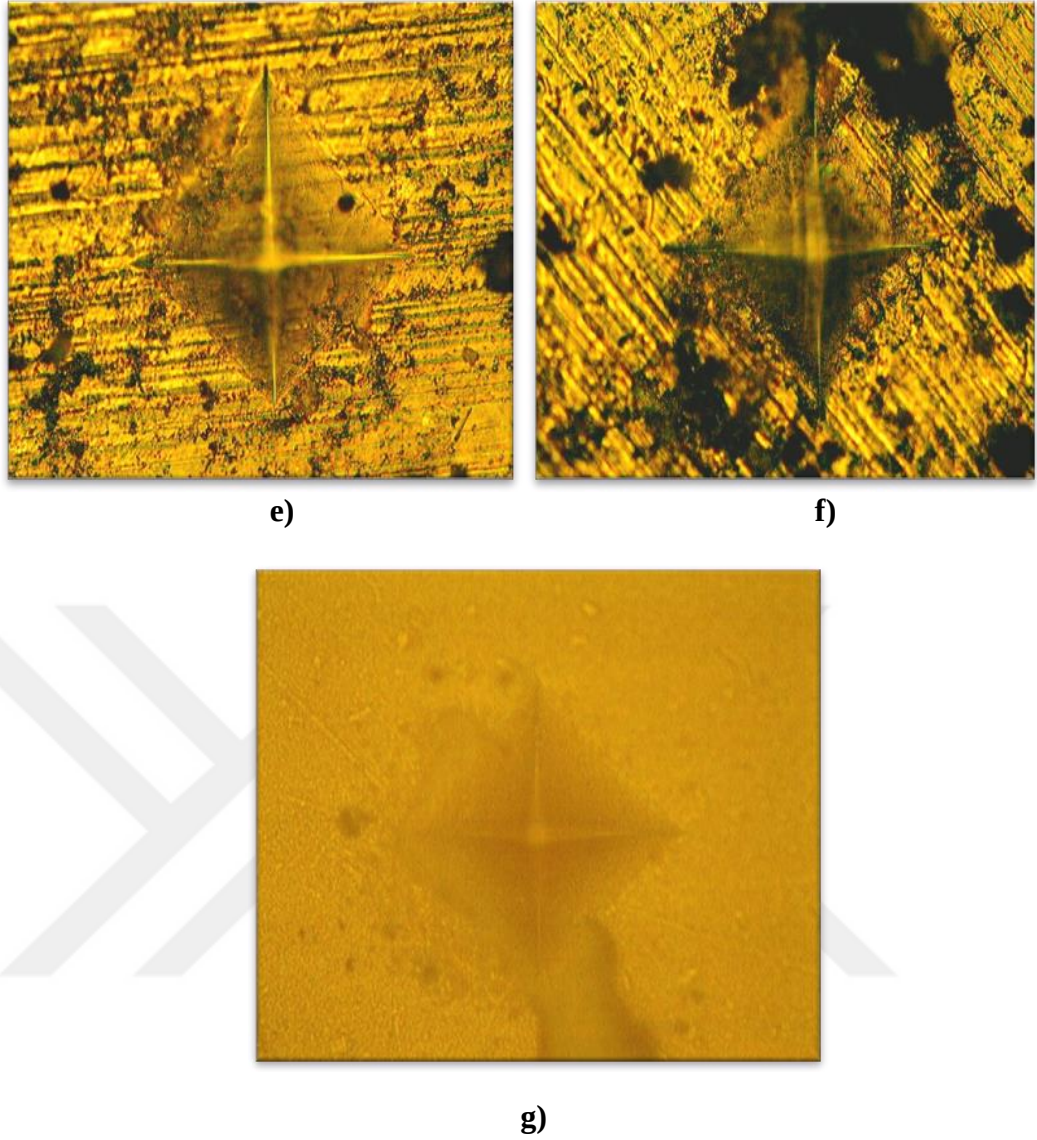


Figure 6.81. (Continued)

More detailed analysis is made using data obtained from all results regarding microhardness of materials that have RISE behavior. Therefore, the different models are presented in order to explain the ISE/RISE behavior in the literature (Arda et al., 2013; Kölemen et al., 2006; Sahin et al., 2008, Koralay et al., 2014). In this section, the comparisons are relevant to hardness are made using the Meyer Law, the proportional sample resistance (PSR), the modified proportional sample resistance (MPSR), the elastic/plastic deformation (EPD) and Indentation Induced Cracking (IIC) model and the HK approach. Analyses on these models are given below.

Table 6.71. The calculated load dependent H_V , E , Y , K_{IC} , B_i and D for the samples

Samples	F (N)	H_V (GPa)	d (μm)	Plateau Region (GPa)	E (GPa)	Y (GPa)	$K_{IC} \times 10^3$ ($Pa \cdot m^{1/2}$)	$B_i \times 10^3$ ($m^{1/2}$)	D ($m^{1/2}$)
Undoped ZnO	0.245	0.651	26.40	1.140 - 1.320	53.35	0.217	-1225	-531	-1.881
	0.490	0.962	30.72		78.84	0.320	-1490	-645	-1.548
	0.980	1.140	39.92		93.43	0.380	-1622	-702	-1.422
	1.960	1.290	53.08		105.73	0.430	-1725	-747	-1.337
	2.940	1.320	64.26		108.19	0.440	-1745	-756	-1.322
Zn_{0.99}Co_{0.01}O	0.245	0.284	39.98	0.511 - 0.608	23.27	0.094	-716	-396	-2.521
	0.490	0.393	48.05		32.21	0.131	-843	-466	-2.145
	0.980	0.511	59.63		41.88	0.170	-961	-531	-1.880
	1.960	0.547	81.44		44.83	0.182	-994	-550	-1.817
	2.940	0.608	94.68		49.83	0.202	-1048	-580	-1.723
Zn_{0.98}Co_{0.02}O	0.245	0.361	35.45	0.534 - 0.606	29.58	0.120	-679	-531	-1.880
	0.490	0.433	45.80		35.49	0.144	-743	-582	-1.715
	0.980	0.534	58.28		43.76	0.178	-825	-647	-1.545
	1.960	0.597	77.99		48.93	0.199	-873	-683	-1.462
	2.940	0.606	94.78		49.66	0.202	-879	-689	-1.450
Zn_{0.97}Co_{0.03}O	0.245	0.375	34.79	0.568 - 0.649	30.73	0.125	-695	-539	-1.853
	0.490	0.487	43.18		39.91	0.162	-792	-614	-1.626
	0.980	0.568	56.54		46.55	0.189	-855	-664	-1.505
	1.960	0.634	75.67		51.96	0.211	-904	-701	-1.425
	2.940	0.649	91.60		53.19	0.216	-914	-710	-1.408
Zn_{0.96}Co_{0.04}O	0.245	0.400	33.67	0.584 - 0.675	32.78	0.133	-666	-600	-1.665
	0.490	0.559	40.28		45.81	0.186	-787	-710	-1.407
	0.980	0.584	55.77		47.86	0.194	-804	-726	-1.376
	1.960	0.662	74.08		54.25	0.220	-857	-772	-1.294
	2.940	0.675	89.85		55.32	0.225	-865	-780	-1.281
Zn_{0.95}Co_{0.05}O	0.245	0.436	32.25	0.645 - 0.684	35.73	0.145	-635	-686	-1.456
	0.490	0.565	40.06		46.30	0.188	-723	-781	-1.279
	0.980	0.645	53.04		52.86	0.215	-773	-834	-1.198
	1.960	0.674	73.42		55.24	0.224	-790	-853	-1.172
	2.940	0.684	89.21		56.06	0.228	-796	-859	-1.163
Zn_{0.90}Co_{0.10}O	0.245	0.463	31.32	0.670 - 0.698	37.94	0.154	-626	-739	-1.352
	0.490	0.579	39.60		47.45	0.193	-700	-827	-1.209
	0.980	0.670	52.06		54.91	0.223	-753	-889	-1.123
	1.960	0.685	72.81		56.14	0.228	-761	-900	-1.111
	2.940	0.698	88.37		57.21	0.232	-768	-908	-1.100

6.4.1.1 Meyer's Law

Meyer's law which is an expression of simple experimental is developed to explain of ISE (Indentation Size Effect) or RISE (Reverse Indentation Size Effect) behavior of materials (Tosun et al., 2014).

$$F = Kd^n \quad (6.20)$$

Meyer number n is a measure of ISE or RISE. If the n value is greater than 2, RISE behavior is obtained. If the n value is less than 2, ISE behavior is obtained (Quinn et al., 1997; Ozturk et al., 2011; Cetinkara et al., 2009, Turkoz et al., 2013). Obtained results are shown in Table 6.72. As shown in table, n values of the all samples are greater than 2. As a result, according to results of Meyer's Law, all samples show RISE behavior.

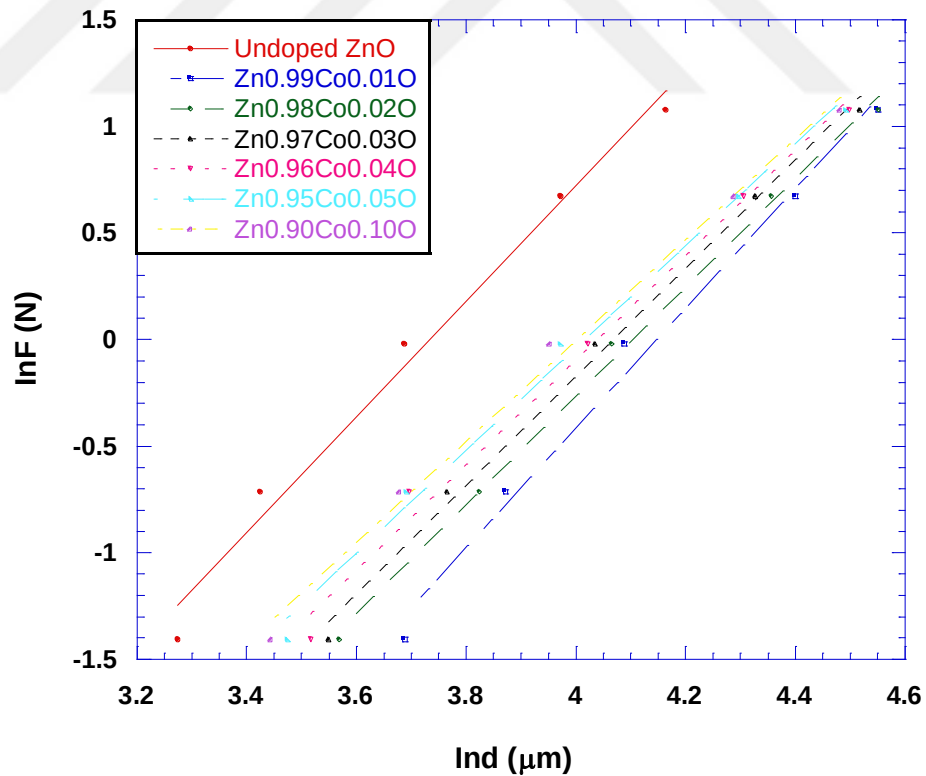


Figure 6.82. Variation of applied load $\ln F$ with diagonal $\ln d$ for the samples

Table 6.72. Best-fit results of experimental data according to Meyer's law

<i>Samples</i>	<i>Meyer number</i> n_k	<i>InK (GPa)</i>	<i>R</i>
Undoped ZnO	2.71	-10.12	0.9926
Zn_{0.99}Co_{0.01}O	2.80	-11.53	0.9947
Zn_{0.98}Co_{0.02}O	2.54	-10.45	0.9984
Zn_{0.97}Co_{0.03}O	2.54	-10.35	0.9976
Zn_{0.96}Co_{0.04}O	2.45	-9.93	0.9956
Zn_{0.95}Co_{0.05}O	2.40	-9.64	0.9966
Zn_{0.90}Co_{0.10}O	2.36	-9.46	0.9972

6.4.1.2 Proportional Sample Resistance (PSR) Model

In this model, it is expressed that sample resistance is not constant and increases with indentation depth like in Hays Kendall approach (Eqn. 6.21).

$$F/d = \alpha + \beta d \quad (6.21)$$

where α and β values are obtained from $(F/d) - d$ graph in Figure 6.83. α is the value where $(F/d) - d$ axis intersected and β is the slope of the line. Obtained results are shown in Table 6.73. In this model, load-independent hardness values are calculated with the Eqn. (6.22).

$$H_{PSR} = 1854.4\beta \quad (6.22)$$

From Table 6.73 it is seen that the value of α is negative for all samples. Negative α values in the Co doped ZnO diluted magnetic semiconductor bulk samples confirm that the character of the displacement of these materials is in the form of the *RISE* behavior. This situation confirms that the plastic deformations occur in these samples which show the *RISE* behavior.

Quinn and Quinn (1997) show that there is a transition region to plateau where hardness remains unchanged after from a certain of load value in hardness-load change curves. They denote that the hardness value corresponds to hardness in this region is called as the plateau region is true hardness. When H_v values of produced ZnCoO semiconductors are analyzed (Table 6.71), it is observed that hardness reached to plateau region after 1N. If H_{PSR} hardness values are compared

with value that corresponds to the plateau region, it can be seen clearly that these microhardness values are quite far from the plateau region. Therefore, it is apparent that the *PSR* model is inadequate to determine the real hardness values of the materials.

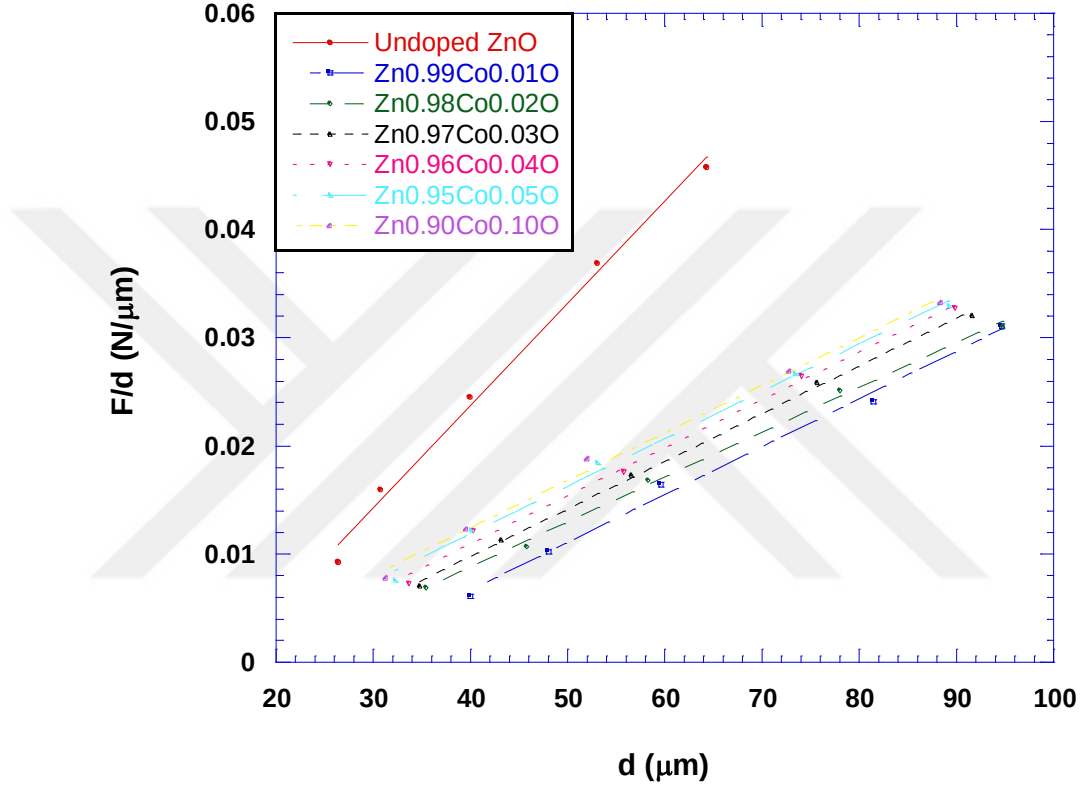


Figure 6.83. Plots of F/d versus d for the samples

Table 6.73. Best-fit results of experimental data according to *PSR* model

Samples	$\alpha \times 10^{-3}$ (N)	$\beta \times 10^{-5}$ (N/ μm)	R	Load independent hardness H_{PRS} (GPa)	Load dependent hardness (in plateau region) H_V (GPa)
Undoped ZnO	-14.07	94.58	0.9967	1.753	1.140-1.320
$\text{Zn}_{0.99}\text{Co}_{0.01}\text{O}$	-11.02	44.15	0.9971	0.818	0.511-0.608
$\text{Zn}_{0.98}\text{Co}_{0.02}\text{O}$	-7.78	41.46	0.9987	0.768	0.534-0.606
$\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$	-7.86	44.08	0.9992	0.817	0.568-0.649
$\text{Zn}_{0.96}\text{Co}_{0.04}\text{O}$	-6.76	44.26	0.9972	0.820	0.584-0.675
$\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$	-5.65	43.82	0.9977	0.812	0.645-0.684
$\text{Zn}_{0.90}\text{Co}_{0.10}\text{O}$	-5.16	43.98	0.9976	0.815	0.670-0.698

In addition, load independent values of E , Y and K_{IC} are also calculated and given in Table 6.74 using H_{PSR} value which is independent of the load. Load independent values of increase when compared to the load dependent values. According to all these results, it can be said that the obtained results are consistent with the literature (Veerender et al., 1994; Khalil, 2005).

Table 6.74. The calculated load independent H_o , E_o , Y_o and K_{IC} for the samples

<i>Samples</i>	<i>H_o (GPa)</i>	<i>E_o (GPa)</i>	<i>Y_o (GPa)</i>	<i>K_{ic} (Pa.m^{1/2})</i>	<i>H_v (Gpa)</i>
Undoped ZnO	1.753	143.68	0.584	2010.77	1.140-1.320
Zn_{0.99}Co_{0.01}O	0.818	67.04	0.272	1373.56	0.511-0.608
Zn_{0.98}Co_{0.02}O	0.768	62.94	0.256	1330.92	0.534-0.606
Zn_{0.97}Co_{0.03}O	0.817	66.96	0.272	1372.72	0.568-0.649
Zn_{0.96}Co_{0.04}O	0.820	67.21	0.273	1375.24	0.584-0.675
Zn_{0.95}Co_{0.05}O	0.812	66.55	0.270	1368.51	0.645-0.684
Zn_{0.90}Co_{0.10}O	0.815	66.80	0.271	1371.04	0.670-0.698

6.4.1.3 Modified Proportional Sample Resistance (MPSR) Model

In order to investigate of material behavior, Gong et al. (1999) suggested the modified PSR model as the following (Turkoz et al., 2013).

$$F = W + a_1 d + a_2 d^2 \quad (6.23)$$

According to this model, the physical meaning of a_1 and a_2 parameters are the same as the ones in PSR model (Ozturk et al., 2014). The load independent microhardness value due to MPSR model can be calculated using;

$$H_{MPSR} = 1854.4 a_2 \quad (6.24)$$

The values of W , a_1 , a_2 and related load independent microhardness values are depicted in Table 6.75. As seen from the table, the values of load independent microhardness values calculated by MPSR model are far from the values of the plateau region. As a result, the MPSR model is not suitable for the description of the mechanical properties of the materials prepared.

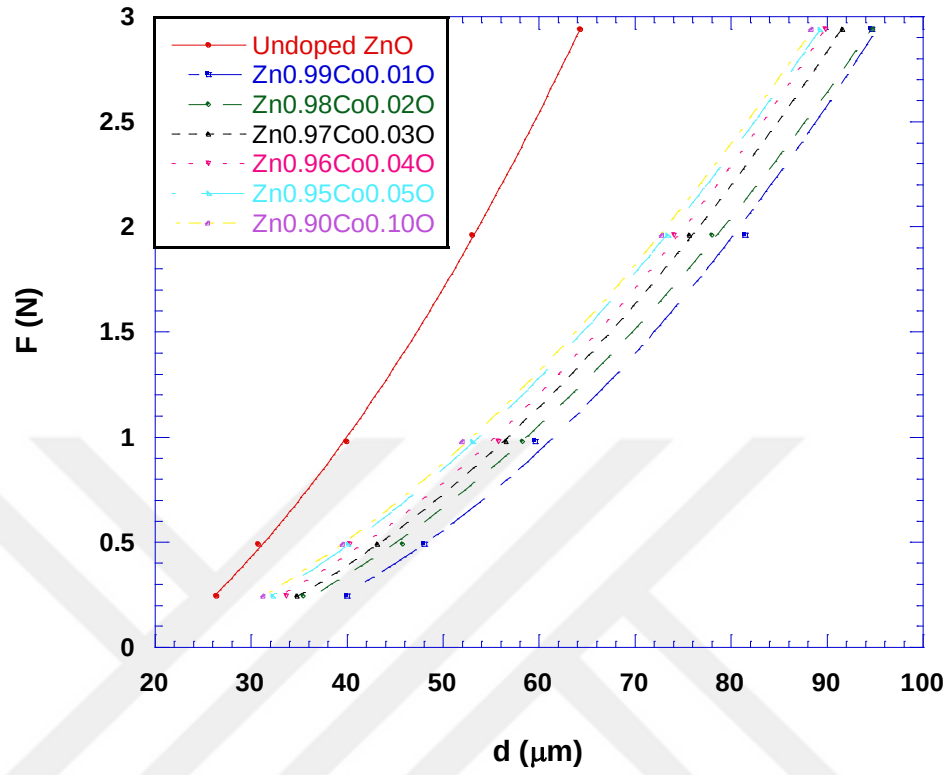


Figure 6.84. Variation of applied load with the indentation diagonal length for the samples

Table 6.75. Best-fit results of experimental data according to MPSR model

<i>Samples</i>	W_{MPSR} (N)	$a_1 \times 10^{-4}$ (N/ μm)	$a_2 \times 10^{-4}$ (N/ μm^2)	<i>R</i>	H_{MPSR} (GPa)	H_V (GPa)
Undoped ZnO	-0.49	-110.03	6.61	0.9998	1.225	1.140-1.320
Zn_{0.99}Co_{0.01}O	-0.06	-88.65	4.24	0.9989	0.786	0.511-0.608
Zn_{0.98}Co_{0.02}O	-0.23	-7.15	3.47	0.9997	0.643	0.534-0.606
Zn_{0.97}Co_{0.03}O	-0.22	-4.97	3.72	0.9999	0.689	0.568-0.649
Zn_{0.96}Co_{0.04}O	-0.12	-20.10	4.02	0.9996	0.745	0.584-0.675
Zn_{0.95}Co_{0.05}O	-0.29	-57.17	3.41	0.9999	0.632	0.645-0.684
Zn_{0.90}Co_{0.10}O	-0.26	-56.17	3.46	0.9999	0.641	0.670-0.698

6.4.1.4 Elastic/Plastic Deformation (EPD) Model

In the most of the indentation tests, the size of indentation is measured after indenter is removed from sample surface. Elastic recovery is observed around of indentation trace forms after indenter is removed. So that, the indentation size decreases until a certain value. Taking into account this condition, the addition of a new term to measured indentation size is deemed appropriate for calculation the load independent hardness (Tarkanian et al., 1973; Upit and Varchenya, 1966; Bull et al., 1989; Ozturk et al., 2015). According to this result, hardness in the *EDP* model,

$$F^{1/2} = A_1^{1/2} d_p + A_2^{1/2} d_e \quad (6.25)$$

is given by Eqn. 6.25.

Where A_2 is a constant, d_e is related to the plastic deformation (d_p), A_2 and d_e values can be calculated from graph of $F^{1/2}-dp$ (Fig.6.85). In this model, hardness value independent of the load is given below.

$$H_{EPD} = 1854.4A_2 \quad (6.26)$$

When this model is applied, as seen in Table 6.76, d_e value found from the point where the graph intersects the y axis is negative for all samples. In other words, no elastic deformation is observed for the applied loads. The microhardness values are quite far from the plateau region. As a result, this model is not sufficient for determination of true hardness.

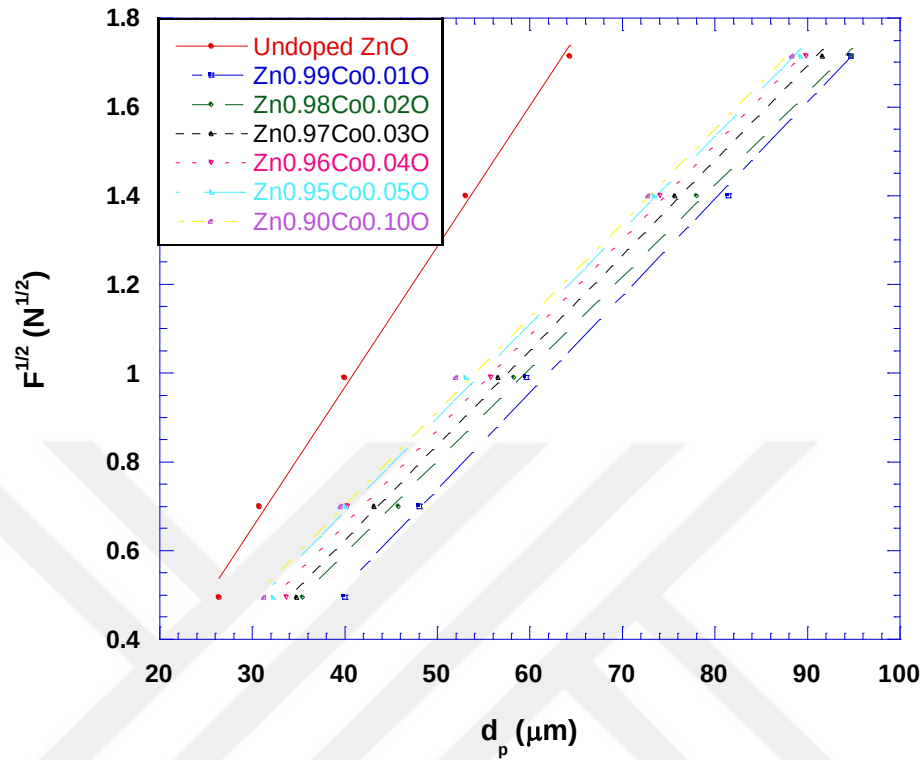


Figure 6.85. Plots of diagonal length versus square root of applied loads for the samples

Table 6.76. Best-fit results of experimental data according to EDP model

Samples	Load independent hardness constant $A_2^{1/2}$ (GPa)	d_e (μm)	R	H_{EDP} (GPa)	H_V (GPa)
Undoped ZnO	0.0317	-0.29	0.9980	1.863	1.140-1.320
Zn _{0.99} Co _{0.01} O	0.0218	-0.35	0.9985	0.881	0.511-0.608
Zn _{0.98} Co _{0.02} O	0.0207	-0.23	0.9994	0.794	0.534-0.606
Zn _{0.97} Co _{0.03} O	0.0214	-0.23	0.9995	0.849	0.568-0.649
Zn _{0.96} Co _{0.04} O	0.0213	-0.19	0.9988	0.841	0.584-0.675
Zn _{0.95} Co _{0.05} O	0.0211	-0.16	0.9990	0.825	0.645-0.684
Zn _{0.90} Co _{0.10} O	0.0211	-0.14	0.9991	0.825	0.670-0.698

6.4.1.5 Hays-Kendall Approach

Hays and Kendall suggested that minimum load value (W) can create permanent deformation in a sample (Hays and Kendall, 1973). If the applied load

does not exceed this resistance, permanent deformation does not occur and only elastic deformation occurs. So, a test load may be generated only elastic deformation under a certain limit value and both elastic and plastic deformation above this critical value (Gane and Bowden, 1968). According to *HK* approach, effective load $F_{eff} = F - W_{HK}$ is used instead of applied load F .

$$F - W_{HK} = A_{HK}d^2 \quad (6.27)$$

where A_{HK} is a constant with independent from the applied load. W_{HK} and A_{HK} values are calculated from $F - d^2$ graph (Fig.6.86). In this model, independent of the load, the hardness value is calculated as

$$H_{HK} = 1854.4A_{HK} \quad (6.28)$$

As can be seen from F vs. d^2 graph, the curves are linear for all samples. Therefore, the slope of the graph in Figure 6.86 gives A_{HK} value. In Table 6.77, the values of W_{HK} , A_{HK} and the H_{HK} values are tabulated. The values of W_{HK} are negative for all samples. The load applied being sufficient to generate a plastic deformation, but insufficient to produce an elastic deformation may be an interpretation of W_{HK} being negative (Awad et al., 2011). According to this result, only plastic deformation is observed on all bulk samples. In addition, the hardness value obtained with *HK* model is so far the hardness value in the plateau region. So this model is not sufficient for determination of true hardness.

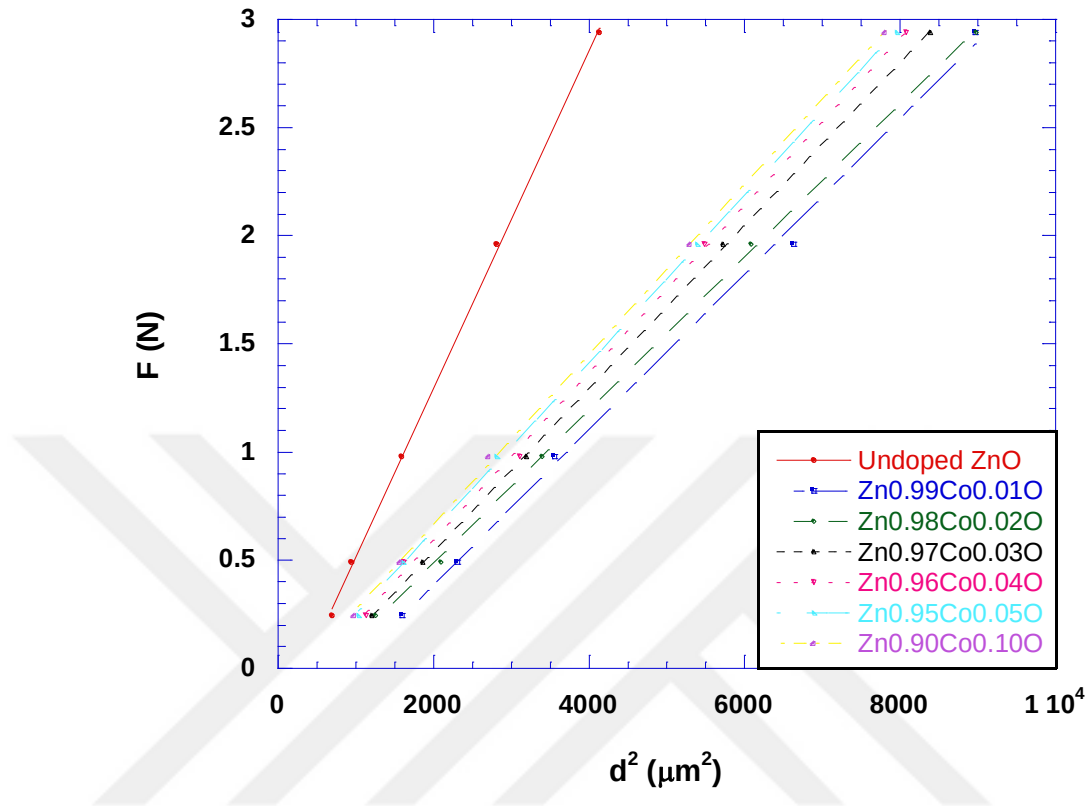


Figure 6.86. Graph of the applied load against the square of the diagonal length for the samples

Table 6.77. Best-fit results of experimental data according to HK model

<i>Samples</i>	<i>Load independent hardness constant $A_{HK} \times 10^{-5} \text{ (GPa)}$</i>	W_{HK} (N)	R	H_{HK} (GPa)	H_V (GPa)
Undoped ZnO	78.13	-0.26	0.9997	1.448	1.140-1.320
Zn_{0.99}Co_{0.01}O	35.95	-0.33	0.9987	0.666	0.511-0.608
Zn_{0.98}Co_{0.02}O	35.32	-0.21	0.9997	0.654	0.534-0.606
Zn_{0.97}Co_{0.03}O	37.65	-0.21	0.9999	0.698	0.568-0.649
Zn_{0.96}Co_{0.04}O	38.65	-0.17	0.9995	0.716	0.584-0.675
Zn_{0.95}Co_{0.05}O	38.76	-0.13	0.9998	0.718	0.645-0.684
Zn_{0.90}Co_{0.10}O	39.27	-0.12	0.9998	0.728	0.670-0.698

6.4.1.6 Indentation-Induced Cracking (IIC) Model

IIC model is developed to explain the *RISE* behavior in the samples (Li and Bradt, 1996). In *RISE* behavior, hardness of the samples increases with applied loads. Although observing this behavior in various samples, the reason still not fully explained. There are different approaches in the literature. It is expressed that metallic samples can be hardener during the loading and there may occur some cracks in fragile samples during the loading of the indenter. According to Feltham and Banerjee; this behavior is related to energy loss due to some comminutions occurred around the indenter (Feltham and Banerjee, 1992). Because the slit in the sample causes the formation of a smaller size and thus higher microhardness values can be obtained with applying load during the indentation process.

The formation of cracks occurred in the sample during indentation causes the release of the elastic deformation energy. This reduces the resistance to indenter of the sample. Maximum depth of the applied test load is offset by the total sample resistance. This resistance can be expressed as

$$F = R_e + R_f + R_p + R_c \quad (6.29)$$

F , is the applied test load, R_e is the resistance due to elastic deformation, R_f is the resistance due to slip of the interface of the sample, R_p is the resistance due to plastic deformation and R_c resistance due to cracks occurred in the sample. The hardness value in this model can be expressed as

$$H_v = \lambda_1 K_1 \left(\frac{P}{d^2} \right) + K_2 \left(\frac{P^{5/3}}{d^3} \right) \quad (6.30)$$

Here, d is the diameter of the trace, λ_1 ; K_1 and K_2 are constants. While K_2 is depend on the applied load, K_1 is a constant depending on the indenter geometry. For ideal plastic material, $H_v = K_1 (P/d^2)$ $\lambda_1 = 1$ ve $K_2 (P^{5/3}/d^3) = 0$ and for perfect brittle solids $H_v = K_2 (P^{5/3}/d^3)$ ve $\lambda_1 = 0$ can be write. For equation(6.30), $d = 7h$ can be written. This equation relates the angle 148° between opposite sides, h is the depth of the indentation trace. If the sample being tested is fragile, only a second portion of the equation is used. In this study, in all the samples the plastic deformation is

observed. It means that the fragility is high. Therefore, by using the equation (6.31) derived from equation (6.30), the hardness values of the samples are calculated.

$$H_v = K \left(\frac{P^{5/3}}{d^3} \right)^m \quad (6.31)$$

K and m values are independent of load and can be calculated from $\ln(H_v)$ - $\ln(P^{5/3}/d^3)$ graph (Figure 6.87). m index is used for explaining *ISE* and *RISE* behavior. While $m > 0,6$, the sample shows normal *ISE* behavior, when it is $m < 0,6$, it shows *RISE* behavior (Bull et al., 1989; Sangwal, 2000).

m index calculated from the slope of graph is 0.48, 0.48, 0.44, 0.44, 0.43 and 0.41, respectively, for undoped and *Co* doped ZnO series; For all samples $m < 0,6$ confirms that *RISE* behavior is observed in the samples (Table 6.78).

Analyzing data in Table 6.78, it can be seen that IIC model hardness values are close to hardness values of the sample that shows *RISE*. This result confirms that only plastic deformation is observed in the samples. All the hardness values of the samples are given in Table 6.78 in order to analyze comparatively. As can be seen from the table, IIC model is the most appropriate model for all other samples that show *RISE* behavior (Table 6.79).

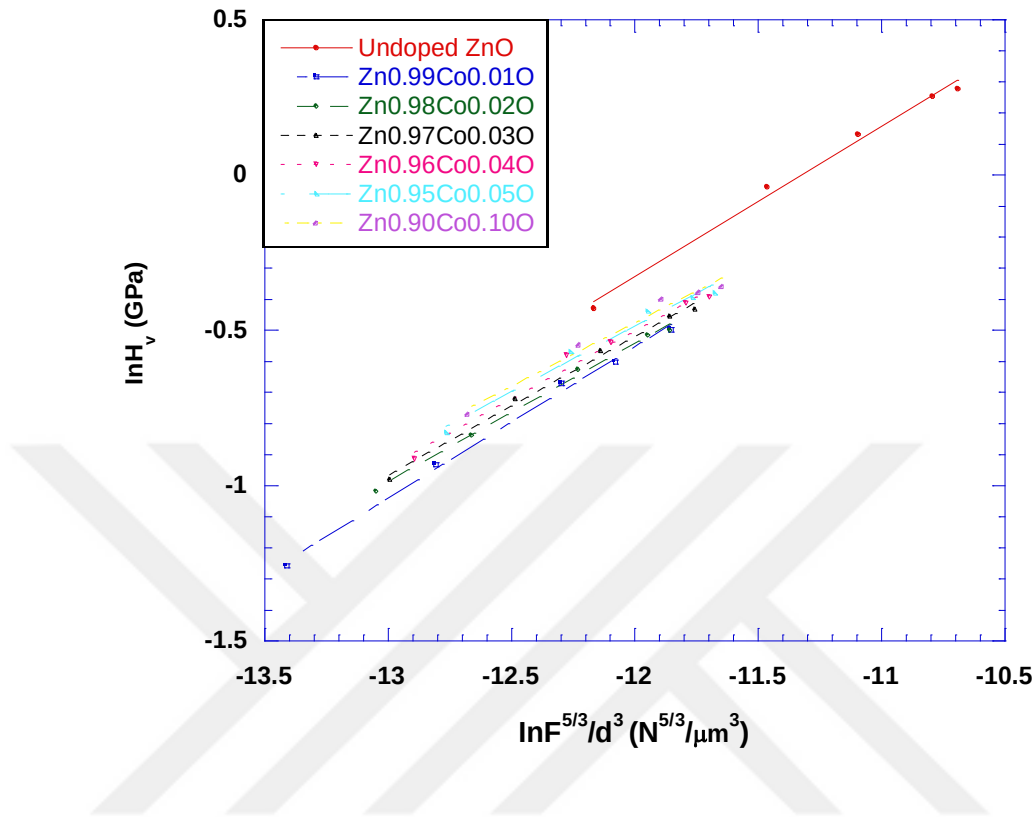


Figure 6.87. Variation of from $\ln(H\nu)$ with $\ln(F^{5/3}/d^3)$ according to IIC model

Table 6.78. Best-fit results of experimental data according to IIC model

<i>Samples</i>	<i>m</i>	$\ln K$ ($N^{(3-5m)/3}/\mu m^{(2-3m)}$)	<i>R</i>	H_{IIC} (GPa)	H_V (GPa)
<i>Undoped ZnO</i>	0.48	5.48	0.9962	1.125	1.140-1.320
<i>Zn_{0.99}Co_{0.01}O</i>	0.48	5.32	0.9979	0.526	0.511-0.608
<i>Zn_{0.98}Co_{0.02}O</i>	0.44	4.79	0.9978	0.535	0.534-0.606
<i>Zn_{0.97}Co_{0.03}O</i>	0.44	4.84	0.9967	0.588	0.568-0.649
<i>Zn_{0.96}Co_{0.04}O</i>	0.43	4.75	0.9917	0.691	0.584-0.675
<i>Zn_{0.95}Co_{0.05}O</i>	0.41	4.54	0.9903	0.669	0.645-0.684
<i>Zn_{0.90}Co_{0.10}O</i>	0.40	4.40	0.9890	0.667	0.670-0.698

Table 6.79. The results of load dependent Vickers microhardness at the plateau region and load independent hardness values calculated using *PSR*, *MPSR*, *EPD*, *HK* and *IIC* models

<i>Samples</i>	H_{PSR} (GPa)	H_{MPSR} (GPa)	H_{EPD} (GPa)	H_{HK} (GPa)	H_{IIC} (GPa)	H_V (GPa)
Undoped ZnO	1.753	1.225	1.863	1.448	1.125	1.140-1.320
Zn_{0.99}Co_{0.01}O	0.818	0.786	0.881	0.666	0.526	0.511-0.608
Zn_{0.98}Co_{0.02}O	0.768	0.643	0.794	0.654	0.535	0.534-0.606
Zn_{0.97}Co_{0.03}O	0.817	0.689	0.849	0.698	0.588	0.568-0.649
Zn_{0.96}Co_{0.04}O	0.820	0.745	0.841	0.716	0.691	0.584-0.675
Zn_{0.95}Co_{0.05}O	0.812	0.632	0.825	0.718	0.669	0.645-0.684
Zn_{0.90}Co_{0.10}O	0.815	0.641	0.825	0.728	0.667	0.670-0.698

6.4.1.7 Conclusions of Vickers Microhardness Analyses

In this section, microhardness measurements are performed to investigate the effect of *Co* doping on the mechanical properties of *ZnO* based DMS materials. The increase in the microhardness values of the all sample depends on the increase of applied load, which shows *RISE* behavior. Behavior of the materials is not changed with *Co* doping. Only the values of microhardness changed with doping.

- H_v decrease with *Co* doping when compared with undoped ZnO sample. But these values increase with increasing the *Co* doping.
- If a plastic material is requested for industrial applications, *Co*0.01 doped ZnO nano bulk material is the most appropriate material among all samples (microhardness value is between 0.511-0.608 GPa).
- The load-dependent elastic modulus, yield strength, fracture toughness, brittleness and ductility are calculated. As a result it found that these values load dependent increased with doping.
- Also the Vickers microhardness values computed are noted to increase with increasing the applied load. The dependence of the load shows that *RISE* has an influence on the samples. The results of the microhardness measurements are analyzed by employing Meyer's law, *PSR*, *MPSR*, *EDP*, *IIC* models and *HK* approach.

- As a result, Indentation-Induced Cracking (IIC) model is more suitable to determine the micromechanical properties and RISE behavior of Co doped ZnO semiconductors.

6.4.2 Transition Metal Doped $\text{Zn}_{1-x-y}\text{B}_x\text{C}_y\text{O}$ (B=Cu, C=Co) DMS Nano Bulk Materials

The change of the load dependent microhardness values as a function of the test loads are shown in Figure 6.88 in detail. It can be seen that the microhardness values decrease with increasing the Co doping in the ZnCuO structure. In addition, microhardness values have reached the plateau (saturation region) around about 1.5 N for the samples. The hardness value of the sample observed RISE behavior depends on the applied load. The variation of the parameters against the applied indentation test loads are numerically tabulated in Table 6.80. It is visible from the table that the load dependent values of E , Y , K_{IC} , B_i and D decrease with the increment in the Co content and increase with the increment in the applied test load.

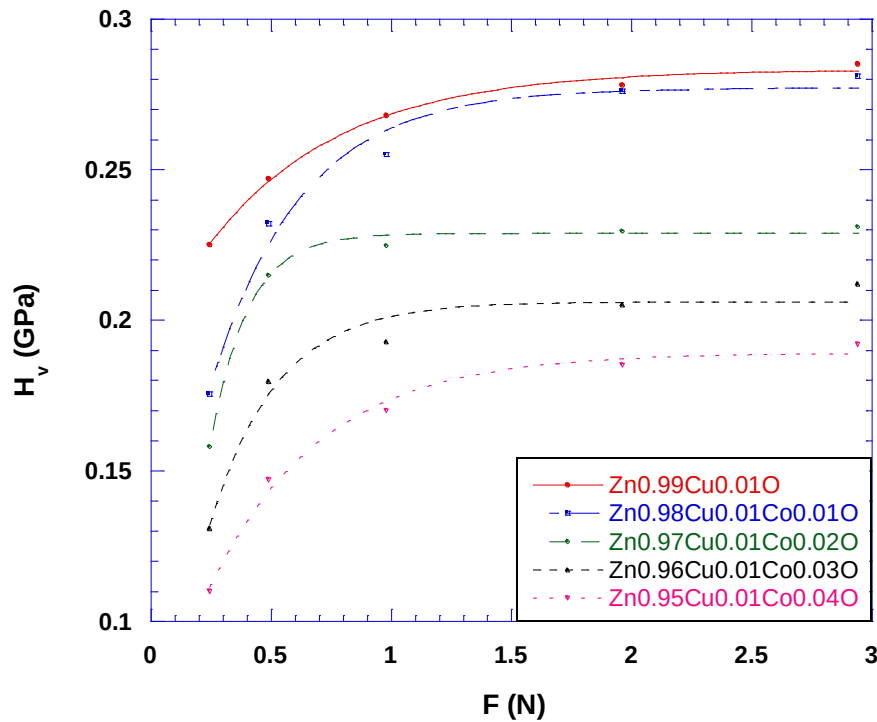


Figure 6.88. The variations of microhardness with load for the samples

Table 6.80. The calculated load dependent H_v , E , Y , K_{IC} , B_i and D for the samples

Samples	F (N)	H_v (GPa)	d (μm)	Plateau Region (GPa)	E (GPa)	Y (GPa)	$K_{IC} \times 10^3$ ($Pa.m^{1/2}$)	$B_i \times 10^{-3}$ ($m^{1/2}$)	D ($m^{-1/2}$)
Undoped ZnO	0.245	0.651	26.40	1.140 - 1.320	53.35	0.217	-1225	-531.42	-1.881
	0.490	0.962	30.72		78.84	0.320	-1490	-645.63	-1.548
	0.980	1.140	39.92		93.43	0.380	-1622	-702.83	-1.422
	1.960	1.290	53.08		105.73	0.430	-1725	-747.82	-1.337
	2.940	1.320	64.26		108.19	0.440	-1745	-756.44	-1.322
Zn_{0.99}Cu_{0.01}O	0.245	0.225	44.93	0.278 - 0.285	18.44	0.075	-279	-804.63	-1.242
	0.490	0.247	60.65		20.24	0.082	-292	-843.06	-1.186
	0.980	0.268	82.34		21.96	0.089	-305	-878.17	-1.138
	1.960	0.278	114.3		22.78	0.092	-310	-894.38	-1.118
	2.940	0.285	138.3		23.36	0.095	-314	-905.57	-1.104
Zn_{0.98}Cu_{0.01}Co_{0.01}O	0.245	0.175	50.87	0.276 - 0.281	14.34	0.058	-334	-523.18	-1.911
	0.490	0.232	62.58		19.01	0.077	-385	-602.39	-1.660
	0.980	0.255	84.41		20.90	0.085	-403	-631.55	-1.583
	1.960	0.276	114.75		22.62	0.092	-420	-657.05	-1.522
	2.940	0.281	139.29		23.03	0.093	-423	-662.97	-1.508
Zn_{0.97}Cu_{0.01}Co_{0.02}O	0.245	0.158	53.60	0.229 - 0.231	12.95	0.052	-236	-668.02	-1.497
	0.490	0.215	65.00		17.62	0.071	-275	-779.24	-1.283
	0.980	0.224	89.93		18.36	0.074	-281	-795.37	-1.257
	1.960	0.229	125.81		18.77	0.076	-284	-804.19	-1.243
	2.940	0.231	153.57		18.93	0.077	-286	-807.69	-1.238
Zn_{0.96}Cu_{0.01}Co_{0.03}O	0.245	0.130	58.893	0.205 - 0.212	10.65	0.043	-262	-495.5	-2.018
	0.490	0.179	71.109		14.67	0.059	-307	-581.45	-1.719
	0.980	0.192	97.071		15.73	0.064	-318	-602.18	-1.660
	1.960	0.205	133.13		16.80	0.068	-329	-622.21	-1.607
	2.940	0.212	160.34		17.37	0.070	-335	-632.76	-1.580
Zn_{0.95}Cu_{0.01}Co_{0.04}O	0.245	0.110	64.26	0.185 - 0.192	9.016	0.036 7	-271	-404.56	-2.471
	0.490	0.147	78.62		12.04	0.049	-314	-467.66	-2.138
	0.980	0.170	103.39		13.93	0.056	-338	-502.93	-1.988
	1.960	0.185	140.16		15.16	0.061	-352	-524.66	-1.906
	2.940	0.192	168.50		15.73	0.064	-359	-534.48	-1.871

The optical trace photos of the indentations for each sample under 2.940 N load are shown in Figure 6.89.

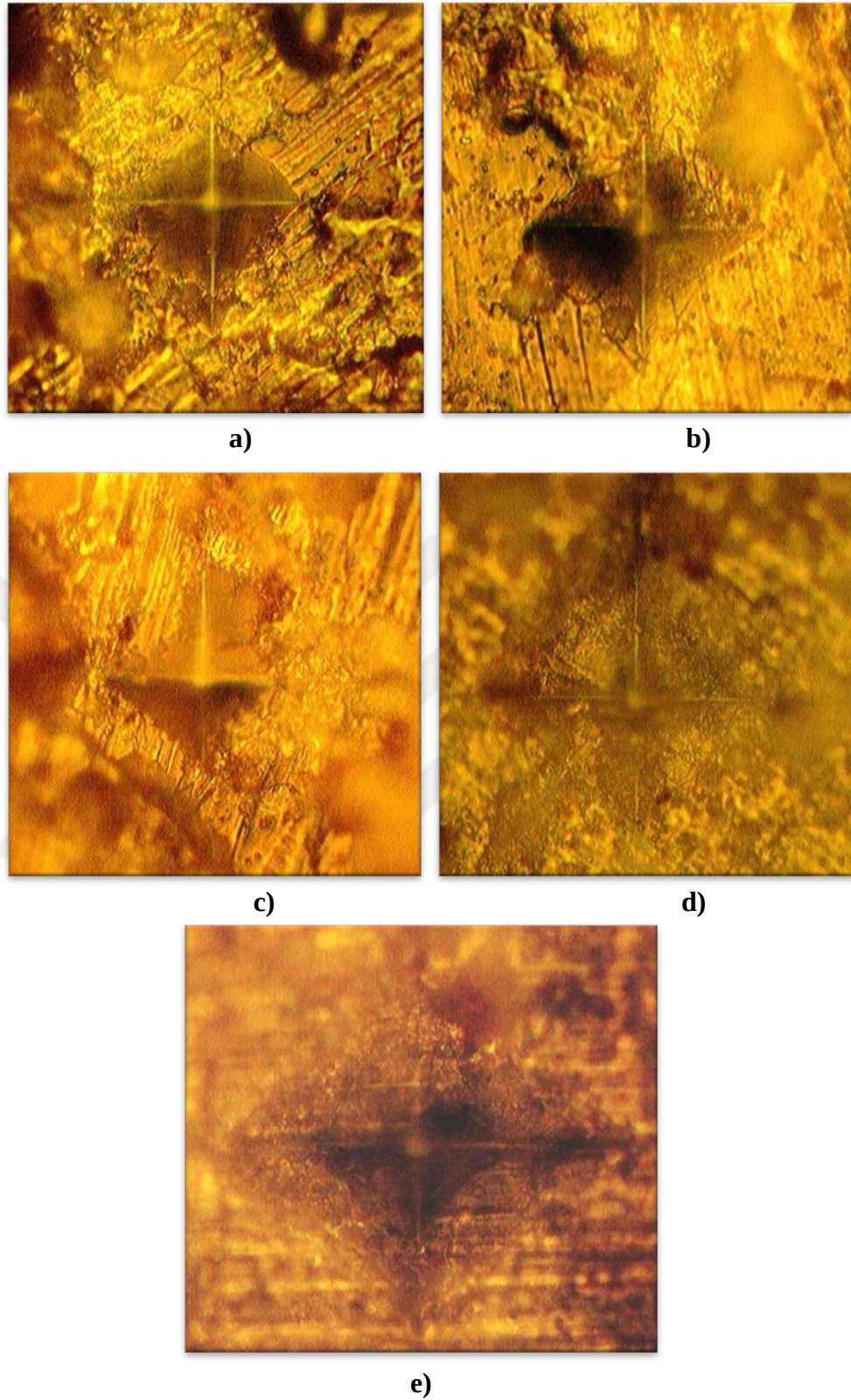


Figure 6.89. The optical trace photos under 0.980 N load for the samples: a) $\text{Zn}_{0.99}\text{Cu}_{0.01}\text{O}$, b) $\text{Zn}_{0.98}\text{Cu}_{0.01}\text{Co}_{0.01}\text{O}$, c) $\text{Zn}_{0.97}\text{Cu}_{0.01}\text{Co}_{0.02}\text{O}$, d) $\text{Zn}_{0.96}\text{Cu}_{0.01}\text{Co}_{0.03}\text{O}$ and e) $\text{Zn}_{0.95}\text{Cu}_{0.01}\text{Co}_{0.04}\text{O}$

The microhardness behaviors of samples are investigated according to the Meyer's law, *PSR*, *MPSR*, *EPD*, *IIC* models and *HK* approach.

6.4.2.1 Meyer's Law

The $\ln F - \ln d$ graphs of the undoped and Co doped ZnCuO samples are given in Figure 6.90. n values are found to be greater than 2 ($n > 2$) for each sample. According to results of Meyer's Law, all samples show RISE behavior (Table 6.81).

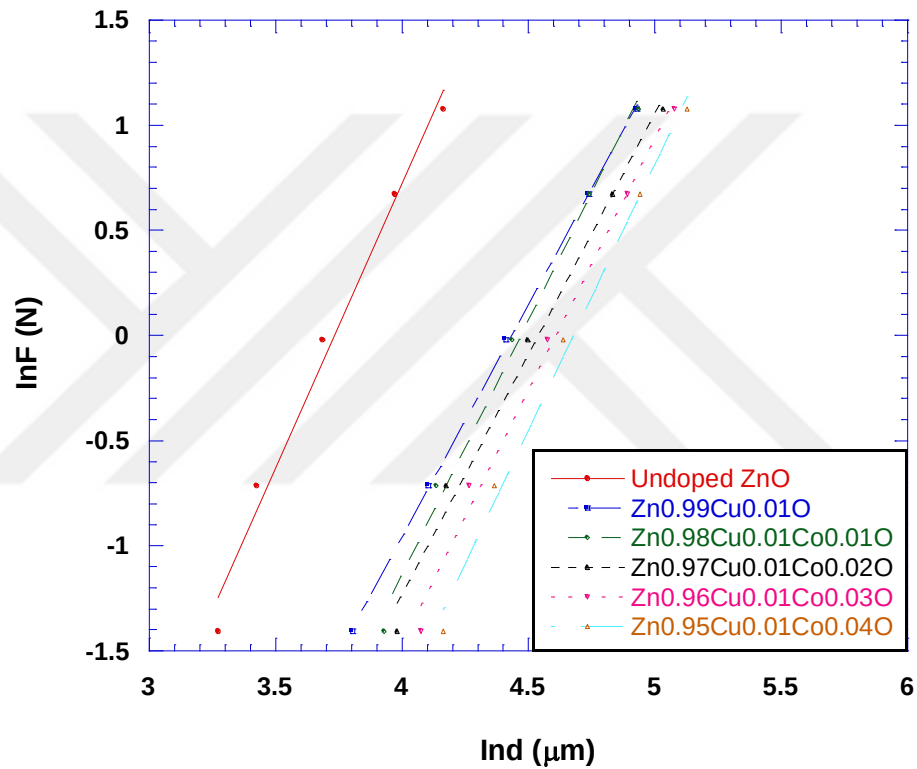


Figure 6.90. Variation of applied load $\ln F$ with diagonal $\ln d$ for the samples

Table 6.81. Best-fit results of experimental data according to Meyer's law

Samples	Meyer number n_k	$\ln K$ (GPa)	R
Undoped ZnO	2.71	-10.12	0.9926
$\text{Zn}_{0.99}\text{Cu}_{0.01}\text{O}$	2.20	-9.48	0.9998
$\text{Zn}_{0.98}\text{Cu}_{0.01}\text{Co}_{0.01}\text{O}$	2.42	-10.81	0.9969
$\text{Zn}_{0.97}\text{Cu}_{0.01}\text{Co}_{0.02}\text{O}$	2.28	-10.37	0.9951
$\text{Zn}_{0.96}\text{Cu}_{0.01}\text{Co}_{0.03}\text{O}$	2.40	-11.08	0.9957
$\text{Zn}_{0.95}\text{Cu}_{0.01}\text{Co}_{0.04}\text{O}$	2.53	-11.83	0.9967

6.4.2.2 Proportional Sample Resistance (PSR) Model

According to this approach, α constant of all the samples is obtained to be only the negative values. This result confirms that the only plastic deformation is shown in the samples presenting the RISE behavior.

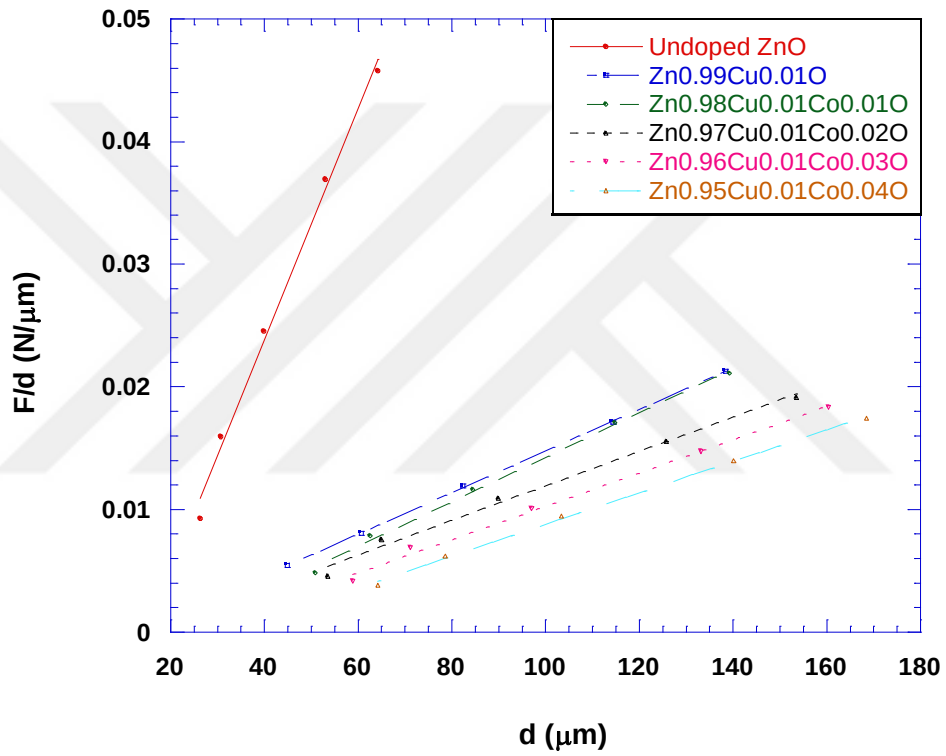


Figure 6.91. Plots of F/d versus d for the samples

Table 6.82. Best-fit results of experimental data according to PSR model

Samples	$\alpha \times 10^{-3}$ (N)	$\beta \times 10^{-5}$ (N/ μm)	R	H_{PRS} (GPa)	H_v (GPa)
Undoped ZnO	-14.07	94.58	0.9967	1.753	1.140-1.320
$\text{Zn}_{0.99}\text{Cu}_{0.01}\text{O}$	-2.12	16.90	0.9999	0.313	0.278-0.285
$\text{Zn}_{0.98}\text{Cu}_{0.01}\text{Co}_{0.01}\text{O}$	-3.90	18.13	0.9984	0.336	0.276-0.281
$\text{Zn}_{0.97}\text{Cu}_{0.01}\text{Co}_{0.02}\text{O}$	-2.16	14.05	0.9956	0.260	0.229-0.231
$\text{Zn}_{0.96}\text{Cu}_{0.01}\text{Co}_{0.03}\text{O}$	-3.23	13.52	0.9975	0.250	0.205-0.212
$\text{Zn}_{0.95}\text{Cu}_{0.01}\text{Co}_{0.04}\text{O}$	-4.10	12.88	0.9989	0.238	0.185-0.192

The load-independent microhardness values calculated in accordance with the *PSR* model are given in Table 6.82. It is obvious from the table that the transition values of the samples to the plateau are quite far from the microhardness values calculated using the *PSR* model

Additionally, load independent E , Y and K_{IC} values are calculated using load independent H_{PSR} value and the findings obtained are numerically listed in Table 6.83. According to the results, the sharper increase in the load independent values is observed as compared to load dependent values.

Table 6.83. The calculated load independent H_o , E_o , Y_o and K_{IC} for the samples

<i>Samples</i>	H_o (GPa)	E_o (GPa)	Y_o (GPa)	K_{IC} (Pa.m ^{1/2})	H_v (GPa)
Undoped ZnO	1.753	143.68	0.584	-2.010	1.140-1.320
Zn_{0.99}Cu_{0.01}O	0.313	25.65	0.104	0.329	0.278-0.285
Zn_{0.98}Cu_{0.01}Co_{0.01}O	0.336	27.54	0.112	0.327	0.276-0.281
Zn_{0.97}Cu_{0.01}Co_{0.02}O	0.260	21.31	0.086	0.303	0.229-0.231
Zn_{0.96}Cu_{0.01}Co_{0.03}O	0.250	20.49	0.083	0.363	0.205-0.212
Zn_{0.95}Cu_{0.01}Co_{0.04}O	0.238	19.50	0.079	0.399	0.185-0.192

6.4.2.3 Modified Proportional Sample Resistance (MPSR) Model

The values of W , a_1 and a_2 associated load independent hardness values are given in Table 6.84. As seen in the table, the values of load independent hardness calculated using *MPSR* model are also far from the values of the plateau region.

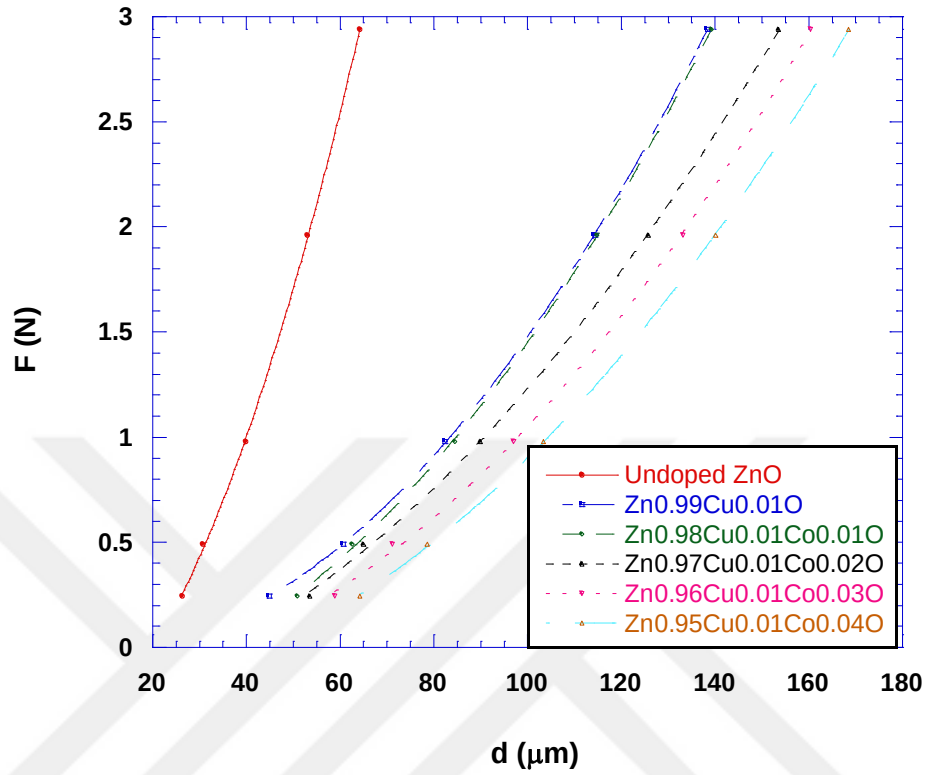


Figure 6.92. Variation of applied load with the indentation diagonal length for the samples

Table 6.84. Best-fit results of experimental data according to MPSR model

Samples	W_{MPSR} (N)	$a_1 \times 10^{-4}$ (N/ μm)	$a_2 \times 10^{-4}$ (N/ μm^2)	R	H_{MPSR} (GPa)	H_V (GPa)
Undoped ZnO	-0.49	-110.3	6.61	0.9998	1.225	1.140-1.320
Zn _{0.99} Cu _{0.01} O	-0.008	-19.0	1.67	0.9999	0.309	0.278-0.285
Zn _{0.98} Cu _{0.01} Co _{0.01} O	-0.21	13.5	1.52	0.9999	0.281	0.276-0.281
Zn _{0.97} Cu _{0.01} Co _{0.02} O	-0.25	39.2	1.09	0.9998	0.202	0.229-0.231
Zn _{0.96} Cu _{0.01} Co _{0.03} O	-0.14	0.15	1.19	0.9998	0.220	0.205-0.212
Zn _{0.95} Cu _{0.01} Co _{0.04} O	-0.20	0.084	1.10	0.9999	0.203	0.185-0.192

6.4.2.4 Elastic/Plastic Deformation (EPD) Model

When the microhardness is analyzed by this model (Fig.6.93), d_e value is negative for all samples as seen in Table 6.85. In other words, no elastic deformation

is observed for the applied loads. Only plastic deformation is observed in the all samples. The microhardness values are quite far from the plateau region. As a result, this model is not sufficient for determination of true hardness.

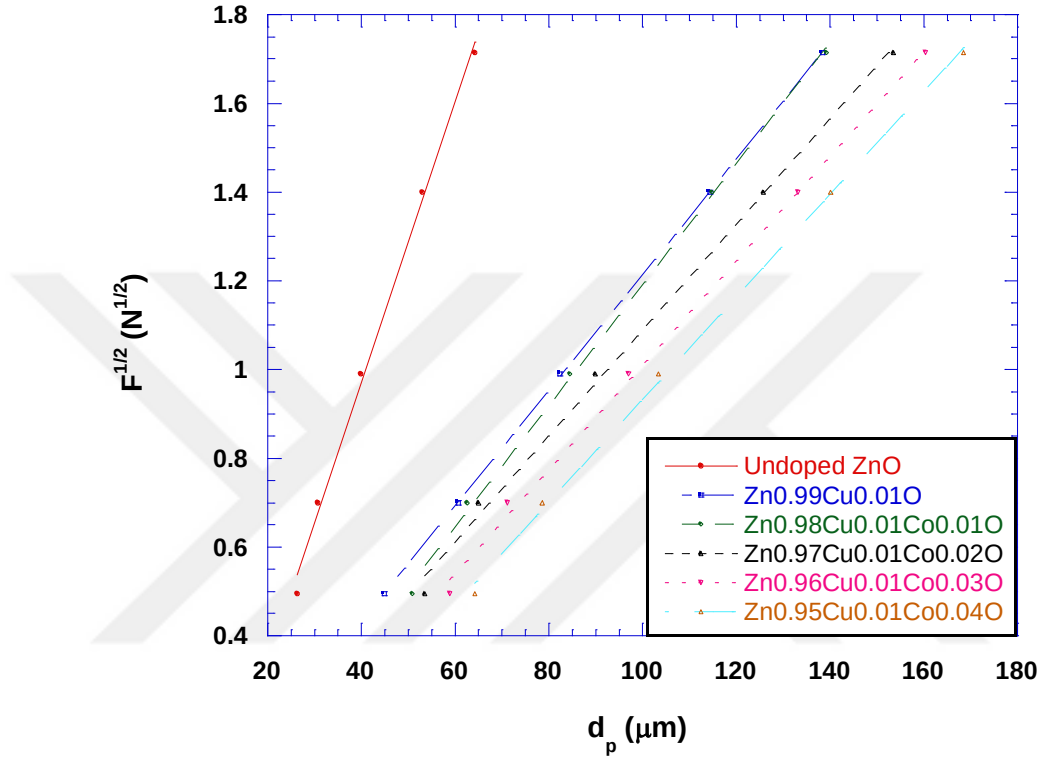


Figure 6.93. Plots of diagonal length versus square root of applied loads for the samples

Table 6.85. Best-fit results of experimental data according to EDP model

Samples	$A_2^{1/2}$ (GPa)	d_e (μm)	R	H_{EDP} (GPa)	H_V (GPa)
Undoped ZnO	0.0317	-0.29	0.9980	1.863	1.140-1.320
$\text{Zn}_{0.99}\text{Cu}_{0.01}\text{O}$	0.0130	-0.09	0.9999	0.313	0.278-0.285
$\text{Zn}_{0.98}\text{Cu}_{0.01}\text{Co}_{0.01}\text{O}$	0.0136	-0.17	0.9993	0.342	0.276-0.281
$\text{Zn}_{0.97}\text{Cu}_{0.01}\text{Co}_{0.02}\text{O}$	0.0119	-0.10	0.9984	0.262	0.229-0.231
$\text{Zn}_{0.96}\text{Cu}_{0.01}\text{Co}_{0.03}\text{O}$	0.0117	-0.16	0.9989	0.253	0.205-0.212
$\text{Zn}_{0.95}\text{Cu}_{0.01}\text{Co}_{0.04}\text{O}$	0.0115	-0.22	0.9993	0.245	0.185-0.192

6.4.2.5 Hays-Kendall Approach

W_{HK} , A_{HK} and the H_{HK} values calculated according to this approach are tabulated in the Table 6.86. The values of W_{HK} are negative for all samples. According to this result, only plastic deformation is observed on all bulk samples. In addition, the hardness value obtained with HK model is so far the hardness value in the plateau region. So this model is not sufficient for determination of true hardness.

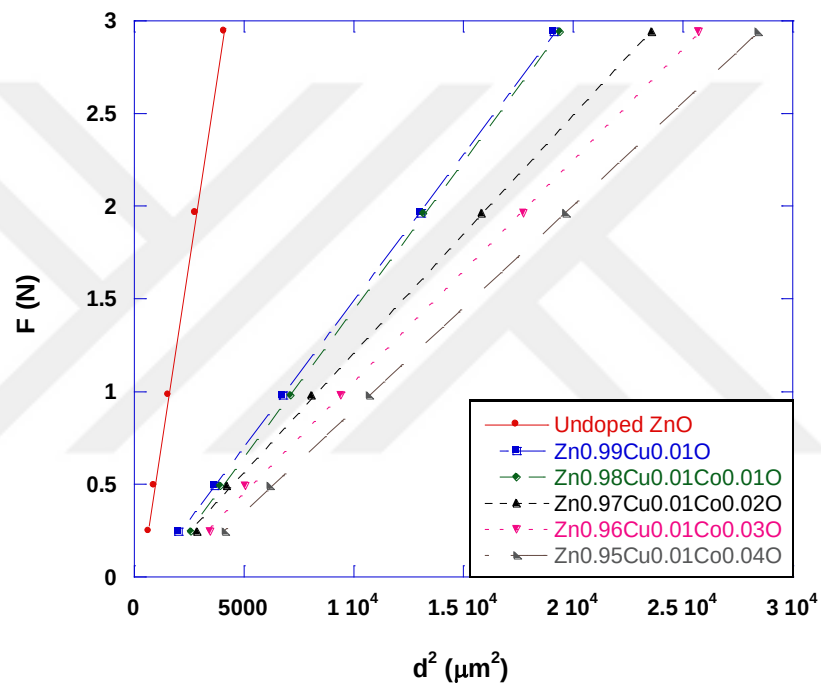


Figure 6.94. Graph of the applied load against the square of the diagonal length for the samples

Table 6.86. Best-fit results of experimental data according to HK model

Samples	$A_{HK} \times 10^{-5}$ (GPa)	W_{HK} (N)	R	H_{HK} (GPa)	H_V (GPa)
Undoped ZnO	78.13	-0.26	0.9997	1.448	1.140-1.320
$Zn_{0.99}Cu_{0.01}O$	15.75	-0.08	0.9999	0.292	0.278-0.285
$Zn_{0.98}Cu_{0.01}Co_{0.01}O$	15.97	-0.15	0.9999	0.296	0.276-0.281
$Zn_{0.97}Cu_{0.01}Co_{0.02}O$	12.85	-0.08	0.9996	0.238	0.229-0.231
$Zn_{0.96}Cu_{0.01}Co_{0.03}O$	11.97	-0.14	0.9998	0.221	0.205-0.212
$Zn_{0.95}Cu_{0.01}Co_{0.04}O$	11.05	-0.20	0.9999	0.204	0.185-0.192

6.4.2.6 Indentation-Induced Cracking (IIC) Model

According to this model, m index calculated from the slope of graph is 0.48, 0.49, 0.49, 0.52, 0.55, 0.56 and 0.55, respectively, for undoped and Co doped ZnCuO series; for all samples $m < 0,6$ confirms that RISE behavior is observed in the samples (Table 6.87).

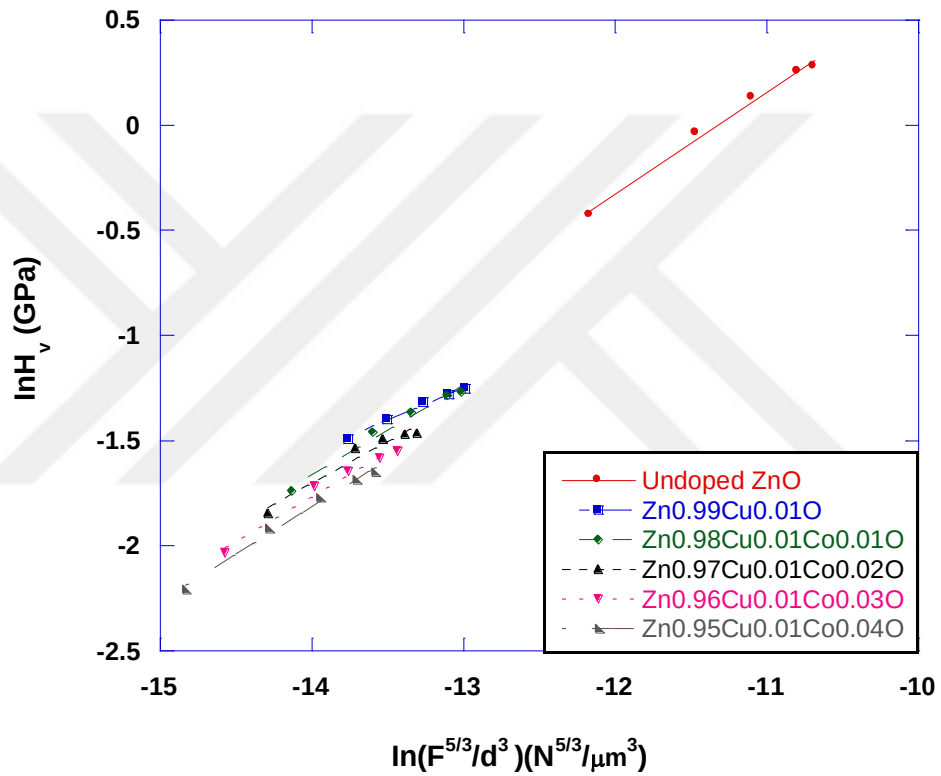


Figure 6.95. Variation of from $\ln(H_v)$ with $\ln(F^{5/3}/d^3)$ according to IIC model

It can be seen that IIC model hardness values are close to hardness values of the sample that shows RISE (Table 6.87). This result confirms that only plastic deformation is observed in the samples. All the hardness values of the samples are given in Table 6.88 in order to analyze comparatively. As can be seen from the Table 6.89, IIC model is the most appropriate model for all other samples that show RISE behavior.

Table 6.87. Best-fit results of experimental data according to IIC model

Samples	m	$\frac{InK}{(N^{(3-5m)/3}/\mu m^{(2-3m)})}$	R	H_{IIC} (GPa)	H_V (GPa)
Undoped ZnO	0.48	5.48	0.9962	1.125	1.140-1.320
$Zn_{0.99}Cu_{0.01}O$	0.30	2.76	0.9946	0.291	0.278-0.285
$Zn_{0.98}Cu_{0.01}Co_{0.01}O$	0.42	4.26	0.9918	0.253	0.276-0.281
$Zn_{0.97}Cu_{0.01}Co_{0.02}O$	0.39	3.85	0.9927	0.231	0.229-0.231
$Zn_{0.96}Cu_{0.01}Co_{0.03}O$	0.42	4.18	0.9887	0.196	0.205-0.212
$Zn_{0.95}Cu_{0.01}Co_{0.04}O$	0.44	4.45	0.9954	0.178	0.185-0.192

Table 6.88. The results of load dependent Vickers microhardness at the plateau region and load independent hardness values calculated using PSR, MPSR, EPD, HK and IIC models

Samples	H_{PSR} (GPa)	H_{MPSR} (GPa)	H_{EPD} (GPa)	H_{HK} (GPa)	H_{IIC} (GPa)	H_V (GPa)
Undoped ZnO	1.753	1.225	1.863	1.448	1.125	1.140-1.320
$Zn_{0.99}Cu_{0.01}O$	0.313	0.309	0.313	0.292	0.291	0.278-0.285
$Zn_{0.98}Cu_{0.01}Co_{0.01}O$	0.336	0.281	0.342	0.296	0.253	0.276-0.281
$Zn_{0.97}Cu_{0.01}Co_{0.02}O$	0.260	0.202	0.262	0.238	0.231	0.229-0.231
$Zn_{0.96}Cu_{0.01}Co_{0.03}O$	0.250	0.220	0.253	0.221	0.196	0.205-0.212
$Zn_{0.95}Cu_{0.01}Co_{0.04}O$	0.238	0.203	0.245	0.204	0.178	0.185-0.192

6.4.2.7 Conclusions of Vickers Microhardness Analyses

In this section, the results of microhardness measurements performed to investigate the effect of Co doping on the mechanical properties of ZnCuO materials are reported. The increase in the microhardness values of the all sample depends on the increase of applied load, which shows RISE behavior.

- H_V decrease with Co doping when compared with undoped ZnO sample while microhardness values increase with applied load.
- The load-dependent E , Y , K_{IC} , B_i and D are calculated. As a result it found that these values load dependent decreased with Co doping in the ZnCuO nano bulk material series.
- Also the Vickers microhardness values computed are noted to increase with increasing the applied load. The dependence of the load showed that *RISE* has an influence on the samples. The results of the microhardness measurements are

analyzed by employing Meyer's law, *PSR*, *MPSR*, *EDP*, *IIC* models and *HK* approach.

- As a result, *IIC* model is more suitable to determine the micromechanical properties and RISE behavior of Co doped semiconductors.

6.4.3 Rare Earth Element Doped $\text{Zn}_{1-x}\text{B}_x\text{O}$ ($\text{B}=\text{Er}$) DMS Nano Bulk Materials

The change of the load dependent microhardness values as a function of the test loads are shown in Figure 6.96 in detail. It can be seen from figure that the microhardness values decrease with increasing the Er doping in the ZnO structure. In addition, microhardness values have reached the plateau (saturation region) around about 2 N for the samples. The hardness value of the sample observed RISE behavior depends on the applied load.

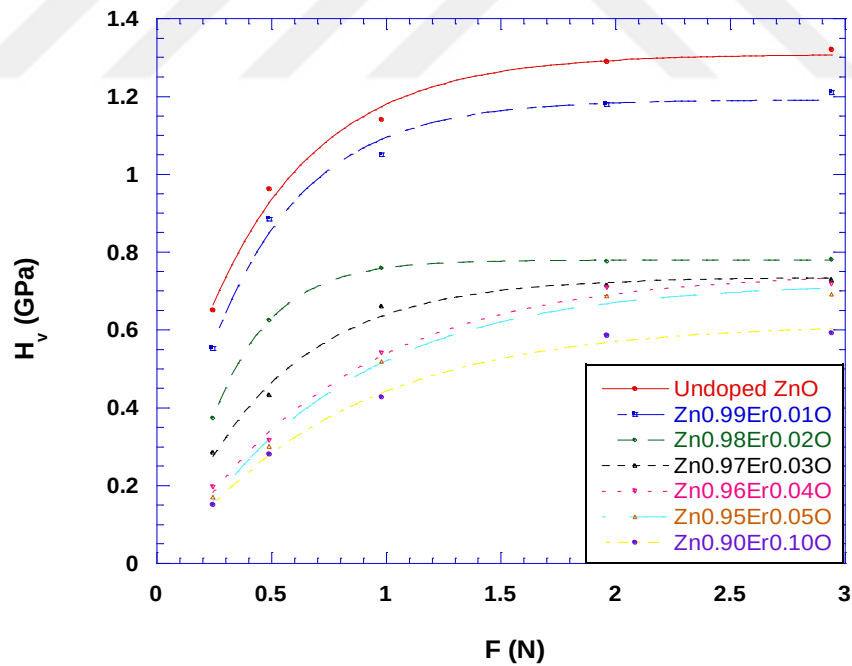


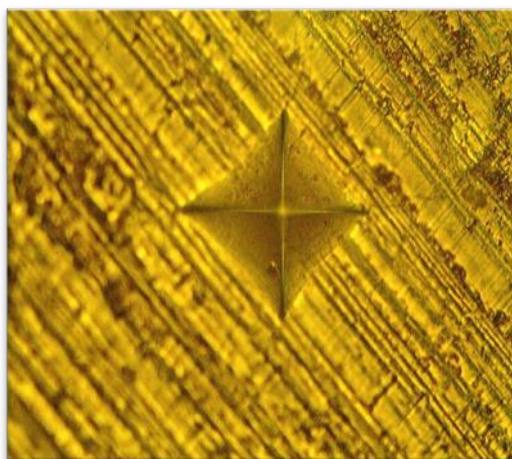
Figure 6.96. The variations of microhardness with load for the samples

The variation of the parameters against the applied indentation test loads are numerically tabulated in Table 6.89. It is visible from the table that the load dependent values of E , Y , K_{IC} , B_i and D decrease with the increment in the Er content and increase with the increment in the applied test load.

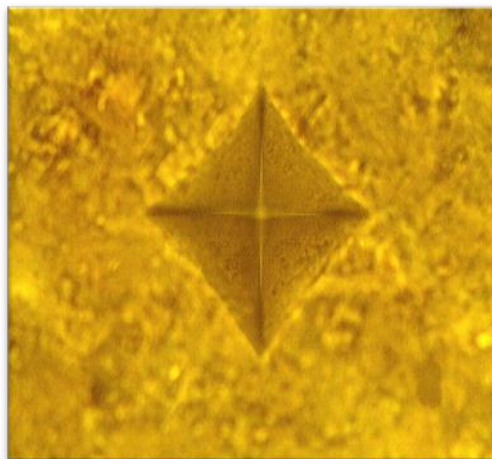
Table 6.89. The calculated load dependent H_v , E , Y , K_{IC} , B_i and D for the samples

Samples	F (N)	H_v (GPa)	d (μm)	Plateau Region (GPa)	E (GPa)	Y (GPa)	$K_{IC} \times 10^3$ ($Pa.m^{1/2}$)	$B_i \times 10^{-3}$ ($m^{1/2}$)	D ($m^{-1/2}$)
Undoped ZnO	0.245	0.651	26.40	1.140 - 1.320	53.35	0.217	-1225	-531.42	-1.881
	0.490	0.962	30.72		78.84	0.320	-1490	-645.63	-1.548
	0.980	1.140	39.92		93.43	0.380	-1622	-702.83	-1.422
	1.960	1.290	53.08		105.73	0.430	-1725	-747.82	-1.337
	2.940	1.320	64.26		108.19	0.440	-1745	-756.44	-1.322
Zn_{0.99}Er_{0.01}O	0.245	0.552	28.68	1.180 - 1.210	45.24	0.184	-1143	-482.94	-2.070
	0.490	0.885	32.04		72.53	0.295	-1447	-611.61	-1.635
	0.980	1.050	41.60		86.06	0.350	-1576	-666.24	-1.501
	1.960	1.180	55.49		96.71	0.393	-1671	-706.16	-1.416
	2.940	1.210	67.12		99.17	0.403	-1692	-715.13	-1.398
Zn_{0.98}Er_{0.02}O	0.245	0.373	34.88	0.777 - 0.781	30.57	0.124	-740	-504.05	-1.983
	0.490	0.624	38.14		51.14	0.208	-957	-652.04	-1.533
	0.980	0.758	48.94		62.12	0.252	-1055	-718.48	-1.391
	1.960	0.777	68.38		63.68	0.259	-1068	-727.53	-1.374
	2.940	0.781	83.51		64.01	0.260	-1071	-729.23	-1.371
Zn_{0.97}Er_{0.03}O	0.245	0.284	39.93	0.715 - 0.730	23.27	0.094	-846	-335.70	-2.978
	0.490	0.433	45.77		35.49	0.144	-1045	-414.35	-2.413
	0.980	0.661	52.42		54.17	0.220	-1291	-512.01	-1.953
	1.960	0.715	71.27		58.60	0.238	-1343	-532.39	-1.878
	2.940	0.730	86.40		59.83	0.243	-1357	-537.95	-1.858
Zn_{0.96}Er_{0.04}O	0.245	0.195	48.18	0.708 - 0.717	15.98	0.065	-966	-201.86	-4.953
	0.490	0.315	53.65		25.81	0.105	-1228	-256.51	-3.898
	0.980	0.540	58.00		44.26	0.180	-1608	-335.82	-2.977
	1.960	0.708	71.60		58.03	0.236	-1841	-384.57	-2.600
	2.940	0.717	87.18		58.76	0.239	-1853	-386.94	-2.584
Zn_{0.95}Er_{0.05}O	0.245	0.170	51.59	0.688 - 0.692	13.93	0.056	-932	-182.40	-5.482
	0.490	0.300	55.00		24.58	0.100	-1238	-242.33	-4.126
	0.980	0.519	59.13		42.53	0.173	-1628	-318.80	-3.136
	1.960	0.688	72.68		56.39	0.229	-1875	-366.93	-2.725
	2.940	0.692	88.76		56.71	0.230	-1880	-368.09	-2.716
Zn_{0.90}Er_{0.10}O	0.245	0.152	54.63	0.586 - 0.592	12.45	0.050	-820	-185.37	-5.394
	0.490	0.280	56.92		22.95	0.093	-1114	-251.35	-3.978
	0.980	0.427	65.19		34.99	0.142	-1375	-310.55	-3.220
	1.960	0.586	78.71		48.03	0.195	-1611	-363.75	-2.749
	2.940	0.592	95.96		48.52	0.197	-1619	-365.66	-2.734

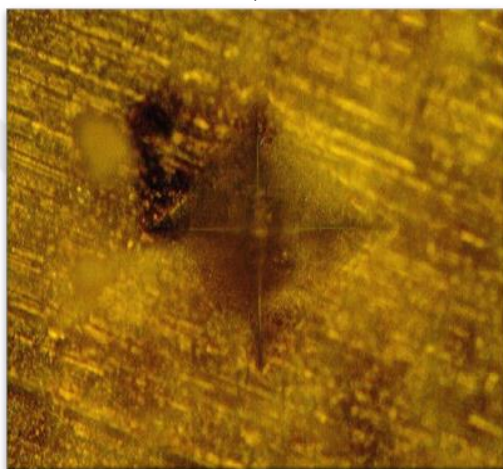
In addition, the optical trace photos of the indentations for each sample under 2.940 N load are shown in Figure 6.97.



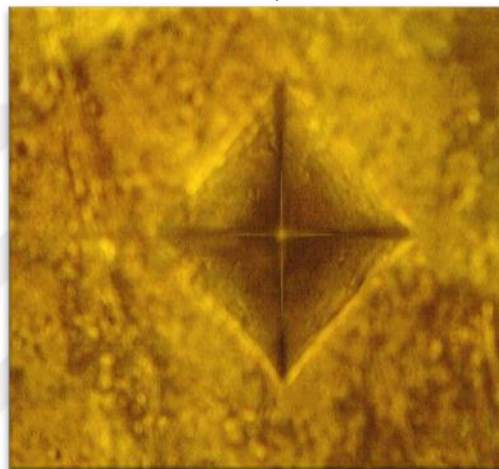
a)



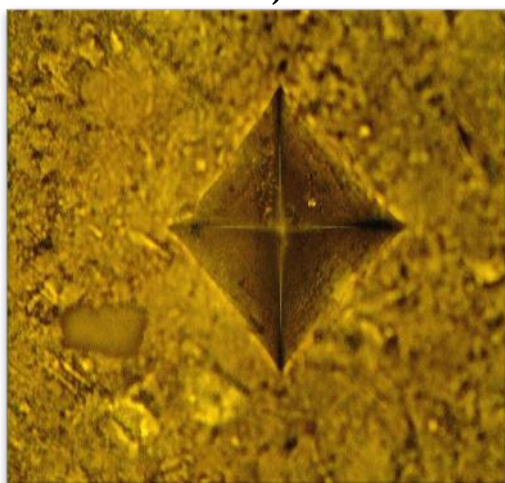
b)



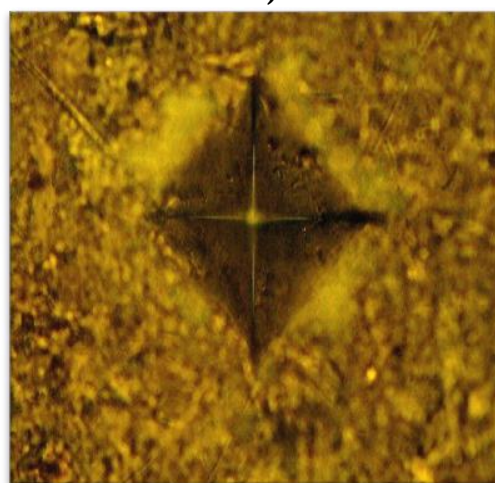
c)



d)



e)



f)

Figure 6.97. The optical trace photos under 2.940 N load for the samples: a) $\text{Zn}_{0.99}\text{Er}_{0.01}\text{O}$, b) $\text{Zn}_{0.98}\text{Er}_{0.02}\text{O}$, c) $\text{Zn}_{0.97}\text{Er}_{0.03}\text{O}$, d) $\text{Zn}_{0.96}\text{Er}_{0.04}\text{O}$, e) $\text{Zn}_{0.95}\text{Er}_{0.05}\text{O}$ and f) $\text{Zn}_{0.90}\text{Er}_{0.10}\text{O}$

After this section, the microhardness behaviors belonging to the undoped and *Er* doped ZnO diluted magnetic semiconducting samples are investigated according to the Meyer's law, *PSR*, *MPSR*, *EPD*, *IIC* models and *HK* approach.

6.4.3.1 Meyer's Law

The $\ln F - \ln d$ graphs of the undoped and *Er* doped ZnO samples are given in Figure 6.98. One can see from the figure that n values are found to be greater than 2 ($n > 2$) for each sample. As a result, according to results of Meyer's Law, all samples show *RISE* behavior (Table 6.90).

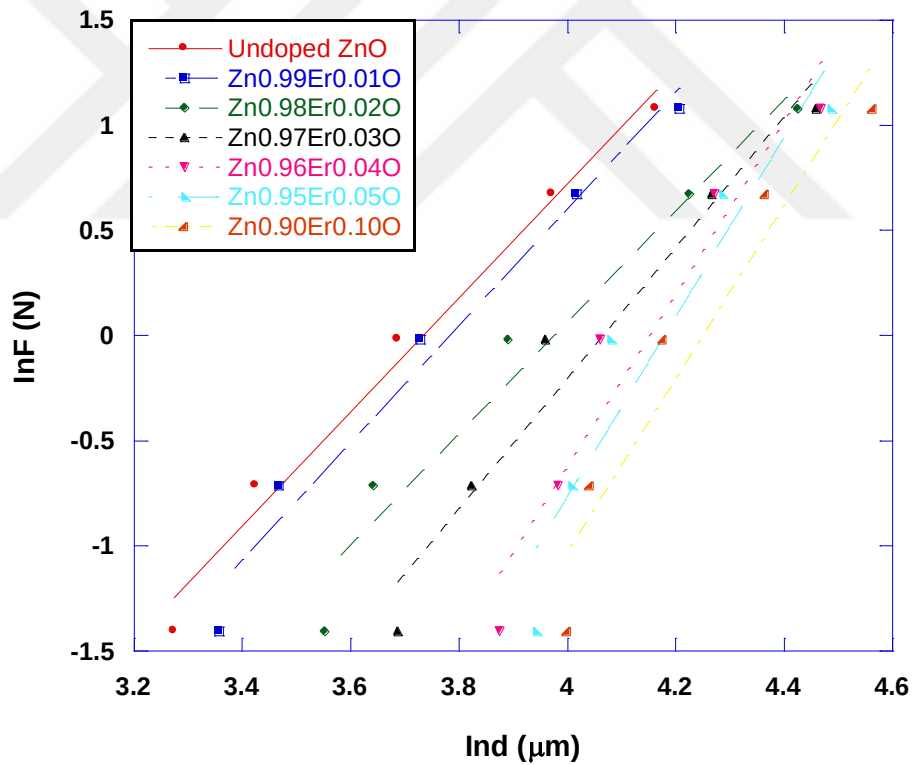


Figure 6.98. Variation of applied load $\ln F$ with diagonal $\ln d$ for the samples

In fact, the decrement in the n values guarantees that the *Er* additives lead to exhibit more and more *RISE* nature of the samples. Moreover, it is necessary to underline that n values vary between 1 and 1.6 for only the hard materials whereas

higher values ($n > 1.6$) are attributed to the soft materials. Based on the results obtained from the samples prepared, each material is regarded as the soft materials (Table 6.90).

Table 6.90. Best-fit results of experimental data according to Meyer's law

<i>Samples</i>	<i>Meyer number n_k</i>	<i>lnK (GPa)</i>	<i>R</i>
Undoped ZnO	2.71	-10.12	0.9926
Zn_{0.99}Er_{0.01}O	2.77	-10.50	0.9871
Zn_{0.98}Er_{0.02}O	2.64	-10.51	0.9795
Zn_{0.97}Er_{0.03}O	3.10	-12.61	0.9784
Zn_{0.96}Er_{0.04}O	4.09	-17.01	0.9649
Zn_{0.95}Er_{0.05}O	4.28	-17.90	0.9465
Zn_{0.90}Er_{0.10}O	4.11	-17.50	0.9589

6.4.3.2 Proportional Sample Resistance (PSR) Model

According to this approach, the $F/d - d$ graphs of the undoped and Er doped ZnO samples are given in Figure 6.99. It can be seen from Table 6.91 that α constant of all the samples is obtained to be only the negative values. This result confirms that the only plastic deformation is shown in the samples presenting the RISE behavior.

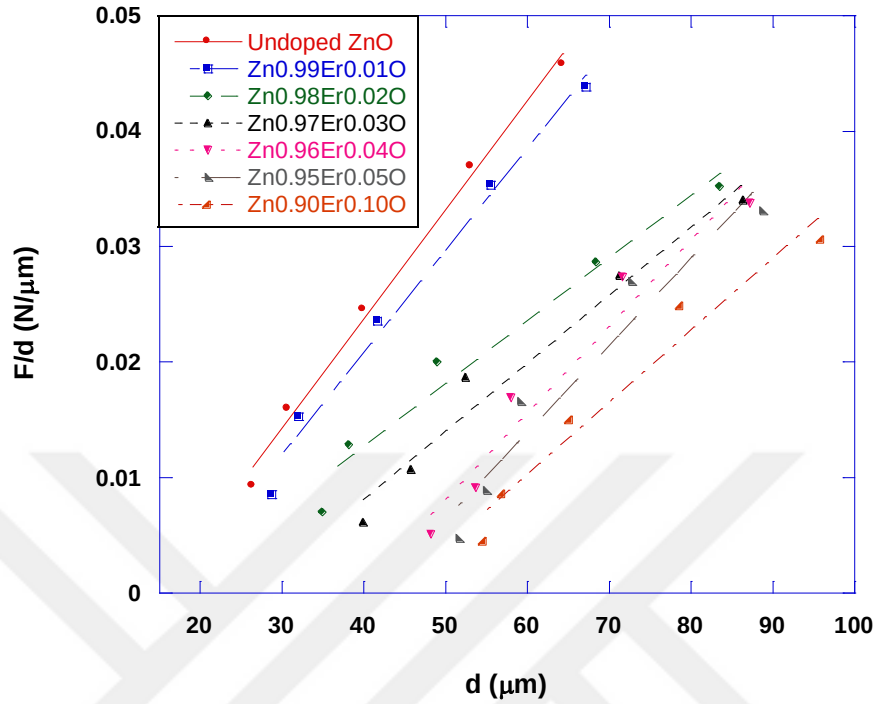


Figure 6.99. Plots of F/d versus d for the samples

The load-independent microhardness values calculated in accordance with the *PSR* model are given in Table 6.91. It is obvious from the table that the transition values of the samples to the plateau are quite far from the microhardness values calculated using the *PSR* model. Therefore, it is obvious that the *PSR* model is not adequate for the determination of true microhardness values of both the undoped and *Er* doped DMS materials.

The load independent E , Y and K_{IC} values are calculated using load independent H_{PSR} value and the findings obtained are numerically listed in Table 6.92. According to the results, the sharper increase in the load independent values is observed as compared to load dependent values.

Table 6.91. Best-fit results of experimental data according to PSR model

<i>Samples</i>	$\alpha \times 10^{-3}$ (N)	$\beta \times 10^{-5}$ (N/ μm)	<i>R</i>	H_{PRS} (GPa)	H_v (GPa)
Undoped ZnO	-14.07	94.58	0.9967	1.753	1.140-1.320
Zn_{0.99}Er_{0.01}O	-14.44	88.34	0.9934	1.638	1.180-1.210
Zn_{0.98}Er_{0.02}O	-8.96	54.25	0.9832	1.006	0.777-0.781
Zn_{0.97}Er_{0.03}O	-15.40	58.84	0.9829	1.091	0.715-0.730
Zn_{0.96}Er_{0.04}O	-29.23	74.80	0.9756	1.387	0.708-0.717
Zn_{0.95}Er_{0.05}O	-31.18	75.26	0.9653	1.395	0.688-0.692
Zn_{0.90}Er_{0.10}O	-27.04	62.28	0.9774	1.154	0.586-0.592

Table 6.92. The calculated load independent H_o , E_o , Y_o and K_{IC} for the samples

<i>Samples</i>	H_o (GPa)	E_o (GPa)	Y_o (GPa)	K_{IC} (Pa.m ^{1/2})	H_v (GPa)
Undoped ZnO	1.753	143.68	0.584	-2.010	1.140-1.320
Zn_{0.99}Er_{0.01}O	1.638	134.26	0.546	-1.969	1.180-1.210
Zn_{0.98}Er_{0.02}O	1.006	82.455	0.335	-1.215	0.777-0.781
Zn_{0.97}Er_{0.03}O	1.091	89.422	0.363	-1.659	0.715-0.730
Zn_{0.96}Er_{0.04}O	1.387	113.68	0.462	-2.577	0.708-0.717
Zn_{0.95}Er_{0.05}O	1.395	114.33	0.465	-1.888	0.688-0.692
Zn_{0.90}Er_{0.10}O	1.154	94.58	0.384	-2.261	0.586-0.592

6.4.3.3 Modified Proportional Sample Resistance (MPSR) Model

The values of W , a_1 and a_2 associated load independent hardness values are given in Table 6.93. As seen in the table, the values of load independent hardness calculated using MPSR model are also far from the values of the plateau region.

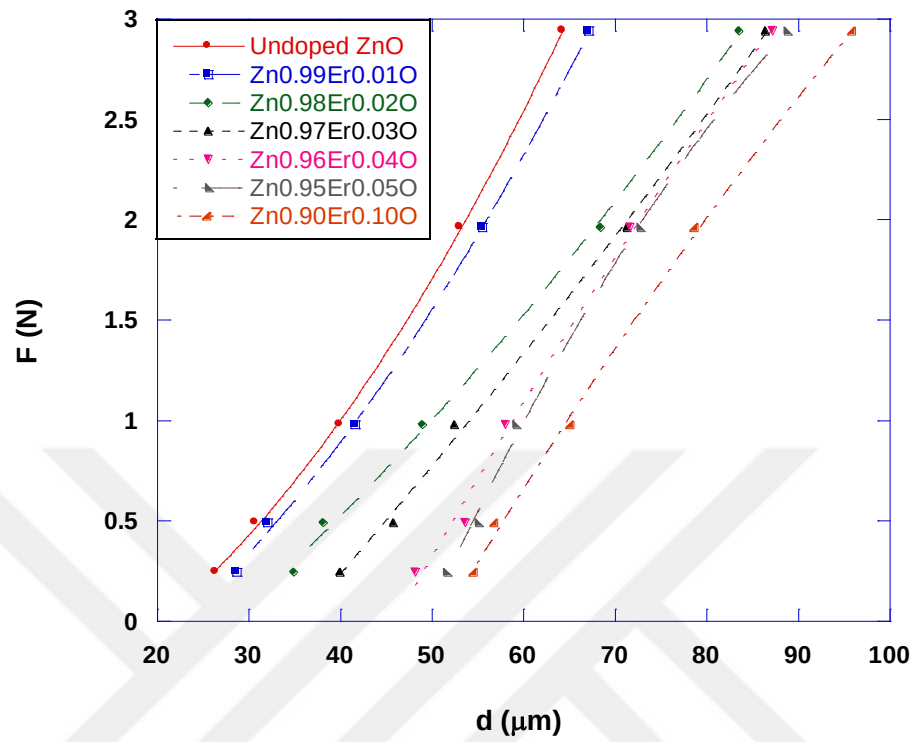


Figure 6.100. Variation of applied load with the indentation diagonal length for the samples

Table 6.93. Best-fit results of experimental data according to MPSR model

Samples	W_{MPSR} (N)	$a_1 \times 10^{-3}$ (N/ μ m)	$a_2 \times 10^{-4}$ (N/ μ m ²)	R	H_{MPSR} (GPa)	H_V (GPa)
Undoped ZnO	-0.49	-11.03	6.61	0.9998	1.225	1.140-1.320
Zn _{0.99} Er _{0.01} O	-0.66	17.43	5.40	0.9996	1.001	1.180-1.210
Zn _{0.98} Er _{0.02} O	-0.97	28.99	2.11	0.9992	0.391	0.777-0.781
Zn _{0.97} Er _{0.03} O	-1.66	42.93	1.18	0.9990	0.218	0.715-0.730
Zn _{0.96} Er _{0.04} O	-4.19	101.63	2.25	0.9978	0.417	0.708-0.717
Zn _{0.95} Er _{0.05} O	-6.41	161.29	6.30	0.9992	1.168	0.688-0.692
Zn _{0.90} Er _{0.10} O	-4.56	101.90	2.46	0.9993	0.456	0.586-0.592

6.4.3.4 Elastic/Plastic Deformation (EPD) Model

When the microhardness is analyzed by this model (Figure 6.101), d_e value is negative for all samples as seen in Table 6.94. In other words, no elastic deformation is observed for the applied loads. Only plastic deformation is observed in the all samples. The microhardness values are quite far from the plateau region. As a result, this model is not sufficient for determination of true hardness.

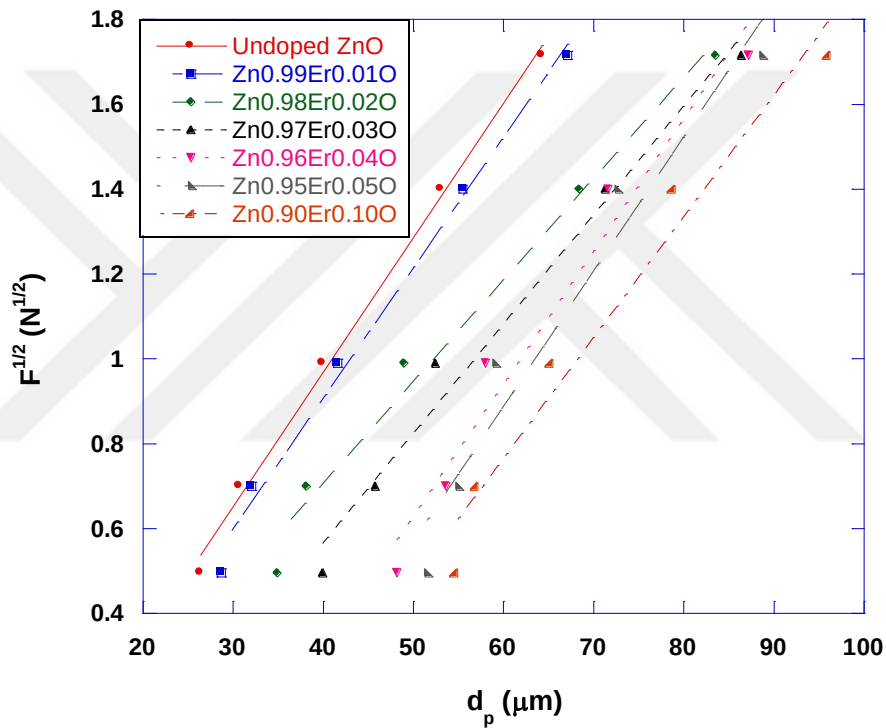


Figure 6.101. Plots of diagonal length versus square root of applied loads for the samples

Table 6.94. Best-fit results of experimental data according to EDP model

Samples	$A_2^{1/2}$ (GPa)	d_e (μm)	R	H_{EDP} (GPa)	H_V (GPa)
Undoped ZnO	0.0317	-0.29	0.9980	1.863	1.140-1.320
Zn _{0.99} Er _{0.01} O	0.0307	-0.32	0.9961	1.747	1.180-1.210
Zn _{0.98} Er _{0.02} O	0.0239	-0.25	0.9922	1.059	0.777-0.781
Zn _{0.97} Er _{0.03} O	0.0256	-0.46	0.9905	1.215	0.715-0.730
Zn _{0.96} Er _{0.04} O	0.0312	-0.92	0.9822	1.805	0.708-0.717
Zn _{0.95} Er _{0.05} O	0.0317	-1.01	0.9731	1.863	0.688-0.692
Zn _{0.90} Er _{0.10} O	0.0285	-0.94	0.9817	1.506	0.586-0.592

6.4.3.5 Hays-Kendall Approach

W_{HK} , A_{HK} and the H_{HK} values calculated according to this approach are tabulated in the Table 6.95. The values of W_{HK} are negative for all samples. The load applied being sufficient to generate a plastic deformation, but insufficient to produce an elastic deformation may be an interpretation of W_{HK} being negative. According to this result, only plastic deformation is observed on all bulk samples. In addition, the hardness value obtained with HK model is so far the hardness value in the plateau region. So this model is not sufficient for determination of true hardness.

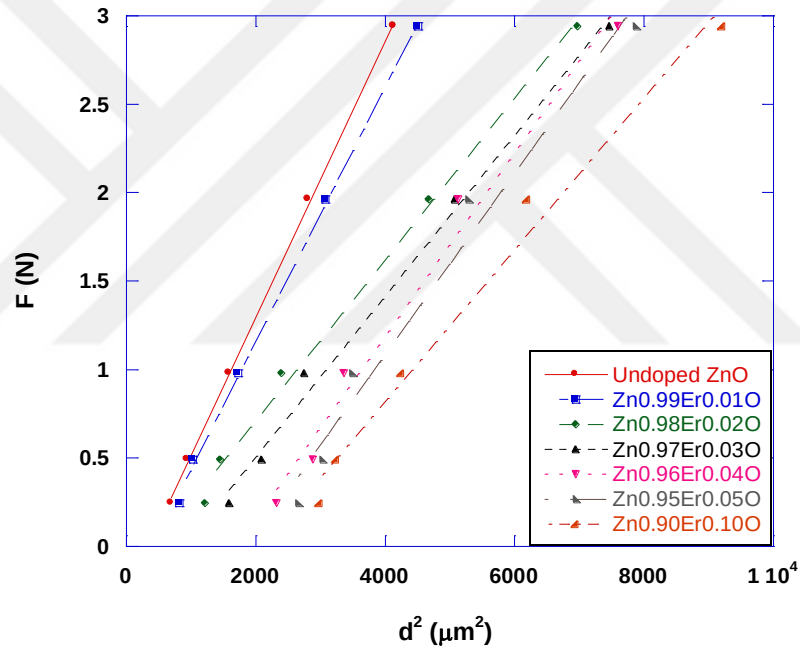


Figure 6.102. Graph of the applied load against the square of the diagonal length for the samples

Table 6.95. Best-fit results of experimental data according to HK model

Samples	$A_{HK} \times 10^{-5}$ (GPa)	W_{HK} (N)	R	H_{HK} (GPa)	H_V (GPa)
Undoped ZnO	78.13	-0.26	0.9997	1.448	1.140-1.320
$Zn_{0.99}Er_{0.01}O$	72.16	-0.28	0.9993	1.338	1.180-1.210
$Zn_{0.98}Er_{0.02}O$	45.56	-0.20	0.9977	0.844	0.777-0.781
$Zn_{0.97}Er_{0.03}O$	45.51	-0.40	0.9967	0.843	0.715-0.730
$Zn_{0.96}Er_{0.04}O$	51.70	-0.87	0.9917	0.958	0.708-0.717
$Zn_{0.95}Er_{0.05}O$	51.21	-0.96	0.9877	0.949	0.688-0.692
$Zn_{0.90}Er_{0.10}O$	42.92	-0.89	0.9925	0.795	0.586-0.592

6.4.3.6 Indentation-Induced Cracking (IIC) Model

According to this model, m index calculated from the slope of graph is 0.48, 0.49, 0.49, 0.52, 0.55, 0.56 and 0.55, respectively, for undoped and *Er* doped ZnO series; for all samples $m < 0,6$ confirms that *RISE* behavior is observed in the samples (Table 6.96).

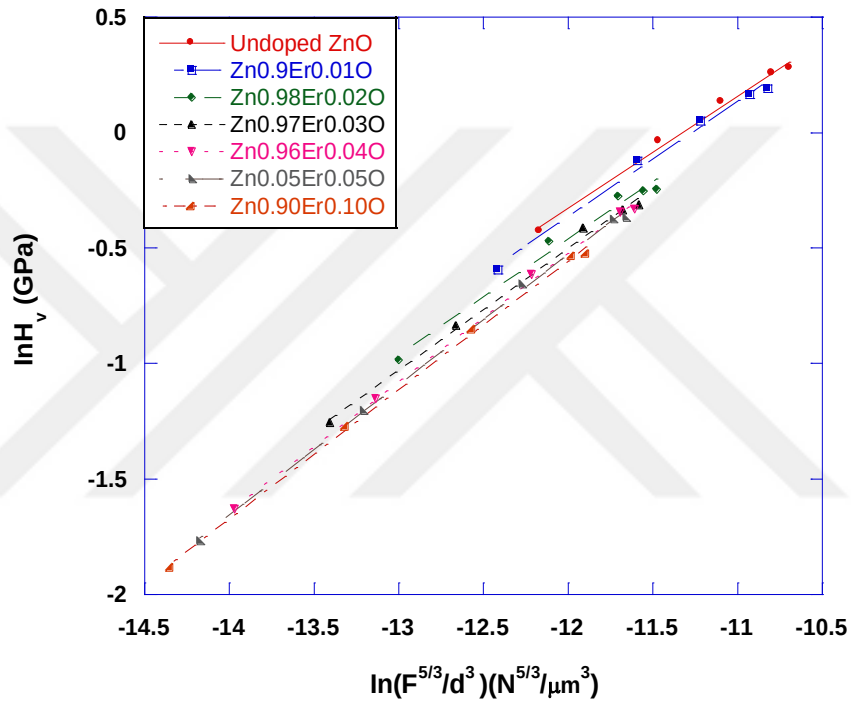


Figure 6.103. Variation of from $\ln(Hv)$ with $\ln(F^{5/3}/d^3)$ according to IIC model

Analyzing data in Table 6.96, it can be seen that *IIC* model hardness values are close to hardness values of the sample. This result confirms that only plastic deformation is observed in the samples. All the hardness values of the samples are given in Table 6.97 in order to analyze comparatively. As can be seen from the table, *IIC* model is the most appropriate model for all other samples that show *RISE* behavior (Asikuzun et al., 2015).

Table 6.96. Best-fit results of experimental data according to IIC model

Samples	<i>m</i>	$\frac{InK}{(N^{(3-5m)/3}/\mu m^{(2-3m)})}$	<i>R</i>	<i>H_{IIC}</i> (GPa)	<i>H_V</i> (GPa)
Undoped ZnO	0.48	5.48	0.9962	1.125	1.140-1.320
Zn _{0.99} Er _{0.01} O	0.49	5.61	0.9956	1.065	1.180-1.210
Zn _{0.98} Er _{0.02} O	0.49	5.53	0.9917	0.739	0.777-0.781
Zn _{0.97} Er _{0.03} O	0.52	5.81	0.9975	0.606	0.715-0.730
Zn _{0.96} Er _{0.04} O	0.55	6.16	0.9993	0.539	0.708-0.717
Zn _{0.95} Er _{0.05} O	0.56	6.24	0.9993	0.498	0.688-0.692
Zn _{0.90} Er _{0.10} O	0.55	6.15	0.9992	0.401	0.586-0.592

Table 6.97. The results of load dependent Vickers microhardness at the plateau region and load independent hardness values calculated using *PSR*, *MPSR*, *EPD*, *HK* and *IIC* models

Samples	<i>H_{PSR}</i> (GPa)	<i>H_{MPSR}</i> (GPa)	<i>H_{EPD}</i> (GPa)	<i>H_{HK}</i> (GPa)	<i>H_{IIC}</i> (GPa)	<i>H_V</i> (GPa)
Undoped ZnO	1.753	1.225	1.863	1.448	1.125	1.140-1.320
Zn _{0.99} Er _{0.01} O	1.753	1.001	1.863	1.338	1.065	1.180-1.210
Zn _{0.98} Er _{0.02} O	1.638	0.391	1.747	0.844	0.739	0.777-0.781
Zn _{0.97} Er _{0.03} O	1.006	0.218	1.059	0.843	0.606	0.715-0.730
Zn _{0.96} Er _{0.04} O	1.091	0.417	1.215	0.958	0.539	0.708-0.717
Zn _{0.95} Er _{0.05} O	1.387	1.168	1.805	0.949	0.498	0.688-0.692
Zn _{0.90} Er _{0.10} O	1.395	0.456	1.863	0.795	0.401	0.586-0.592

6.4.3.7 Conclusions of Vickers Microhardness Analyses

In this section, the results of microhardness measurements performed to investigate the effect of *Er* doping on the mechanical properties of *ZnO* based DMS materials are reported. The increase in the microhardness values of the all sample depends on the increase of applied load, which shows *RISE* behavior.

- *H_V* decreases with *Er* doping when compared with undoped ZnO sample while microhardness values increase with *F*.
- If a plastic material is requested for industrial applications, Er0.10 doped ZnO nano bulk material is the most appropriate material among all samples (microhardness value is between 0.586 – 0.592 GPa).
- The load-dependent *E*, *Y*, *K_{IC}*, *B_i* and *D* are calculated. As a result it found that these values load dependent decreased with *Er* doping.

- Also the Vickers microhardness values computed are noted to increase with increasing the applied load. The dependence of the load showed that *RISE* has an influence on the samples. The results of the microhardness measurements are analyzed by employing Meyer's law, *PSR*, *MPSR*, *EDP*, *IIC* models and *HK* approach.
- As a result, Indentation-Induced Cracking (IIC) model is more suitable to determine the micromechanical properties and *RISE* behavior of Er doped-ZnO semiconductors.

6.4.4 Rare Earth Element Doped $Zn_{1-x}B_xC_yO$ (B=Er, C=Cd) DMS Nano Bulk Materials

One can see the change of the load dependent microhardness values as a function of the test loads in Figure 6.104 in detail. It can be seen from figure that the microhardness values decrease with increasing the Cd doping in the ZnErO structure. In addition, microhardness values have reached the plateau (saturation region) around about 1N for the samples. The hardness value of the sample observed *RISE* behavior depends on the applied load.

It is to be mentioned here that the mechanical values given above vary from a material to another material. The variation of the parameters against the applied indentation test loads are numerically tabulated in Table 6.98. It is visible from the table that the load dependent values of E , Y , K_{IC} , B_i and D decrease with the increment in the Cd content and increase with the increment in the applied test load. As well known from the literature, these parameters are strongly dependence upon the applied load for the all samples exhibiting the *RISE* feature.

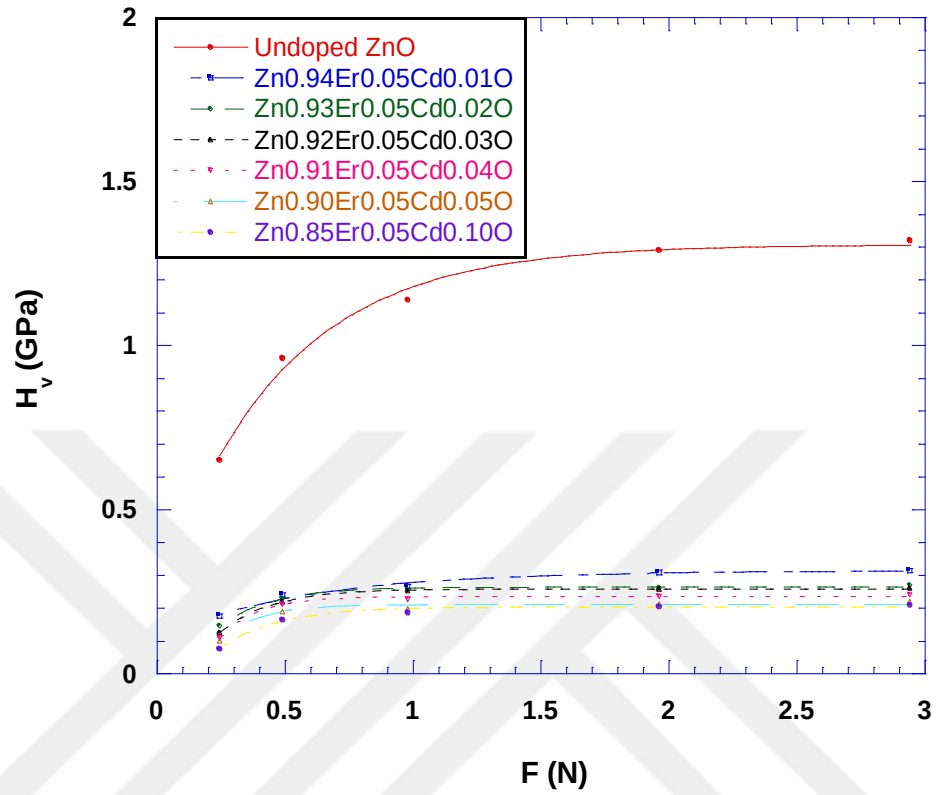


Figure 6.104. The variations of microhardness with load for the samples

Additionally, there are several models describing the microhardness characteristics and behavior (ISE or RISE) of the samples in the literature (Awad et al., 2011; Awad et al., 2000; Zalaoglu et al., 2013). In this section, Meyer's law, HK, PSR, MPSR, EPD, IIC models and HK approach allow us to examine the corresponding microhardness behaviors belonging to the undoped and Cd doped ZnO diluted magnetic semiconducting samples.

Table 6.98. The calculated load dependent H_v , E , Y , K_{IC} , B_i and D for the samples

Samples	F (N)	H_v (GPa)	d (μm)	Plateau Region (GPa)	E (GPa)	Y (Gpa)	$K_{IC} \times 10^3$ (Pa.m ^{1/2})	$B_i \times 10^{-3}$ (m ^{1/2})	D (m ^{-1/2})
Undoped ZnO	0.245	0.651	26.40	1.140 - 1.320	53.35	0.217	-1225	-531.42	-1.881
	0.490	0.962	30.72		78.84	0.320	-1490	-645.63	-1.548
	0.980	1.140	39.92		93.43	0.380	-1622	-702.83	-1.422
	1.960	1.290	53.08		105.73	0.430	-1725	-747.82	-1.337
	2.940	1.320	64.26		108.19	0.440	-1745	-756.44	-1.322
Zn_{0.94}Er_{0.05}Cd_{0.01}O	0.245	0.176	50.80	0.265 - 0.314	14.42	0.058	-637	-276.30	-3.619
	0.490	0.240	61.53		19.67	0.080	-743	-323.01	-3.095
	0.980	0.265	82.71		21.72	0.088	-781	-339.31	-2.947
	1.960	0.308	108.47		25.24	0.102	-842	-365.80	-2.733
	2.940	0.314	131.74		25.73	0.104	-850	-369.41	-2.707
Zn_{0.93}Er_{0.05}Cd_{0.02}O	0.245	0.145	55.82	0.257 - 0.271	11.88	0.048	-368	-394.02	-2.537
	0.490	0.230	62.85		18.85	0.076	-463	-496.76	-2.013
	0.980	0.257	84.06		21.06	0.085	-490	-524.49	-1.906
	1.960	0.262	117.60		21.47	0.087	-495	-529.29	-1.889
	2.940	0.271	141.83		22.21	0.090	-503	-538.77	-1.856
Zn_{0.92}Er_{0.05}Cd_{0.03}O	0.245	0.126	59.87	0.253 - 0.261	10.32	0.042	-312	-403.85	-2.476
	0.490	0.220	64.25		18.03	0.073	-412	-533.98	-1.872
	0.980	0.253	84.66		20.73	0.084	-442	-572.40	-1.747
	1.960	0.258	118.61		21.14	0.086	-446	-578.48	-1.728
	2.940	0.261	144.29		21.39	0.087	-449	-581.29	-1.720
Zn_{0.91}Er_{0.05}Cd_{0.04}O	0.245	0.110	64.24	0.226 - 0.240	9.016	0.036	-287	383.28	-2.609
	0.490	0.211	65.53		17.29	0.070	-397	-531.49	-1.881
	0.980	0.226	89.57		18.52	0.075	-411	-549.88	-1.818
	1.960	0.235	124.16		19.26	0.078	-419	-560.86	-1.783
	2.940	0.240	150.53		19.67	0.080	-424	-566.04	-1.766
Zn_{0.90}Er_{0.05}Cd_{0.05}O	0.245	0.100	67.10	0.198 - 0.220	8.196	0.033	-276	-362.32	-2.760
	0.490	0.190	68.99		15.57	0.063	-380	-500.00	-2.000
	0.980	0.198	95.69		16.22	0.066	-388	-510.31	-1.959
	1.960	0.214	130.29		17.54	0.071	-404	-529.70	-1.887
	2.940	0.220	157.32		18.03	0.073	-409	-537.90	-1.859
Zn_{0.85}Er_{0.05}Co_{0.10}O	0.245	0.076	77.32	0.187 - 0.211	6.229	0.025	-286	-265.73	-3.763
	0.490	0.165	74.21		13.52	0.055	-421	-391.92	-2.551
	0.980	0.187	98.58		15.32	0.062	-448	-417.41	-2.395
	1.960	0.205	133.15		16.80	0.068	-469	-437.10	-2.287
	2.940	0.211	160.74		17.29	0.070	-476	-443.28	-2.255

In addition, the optical trace photos of the indentations for each sample under 2.940 N load are shown in Figure 6.105.

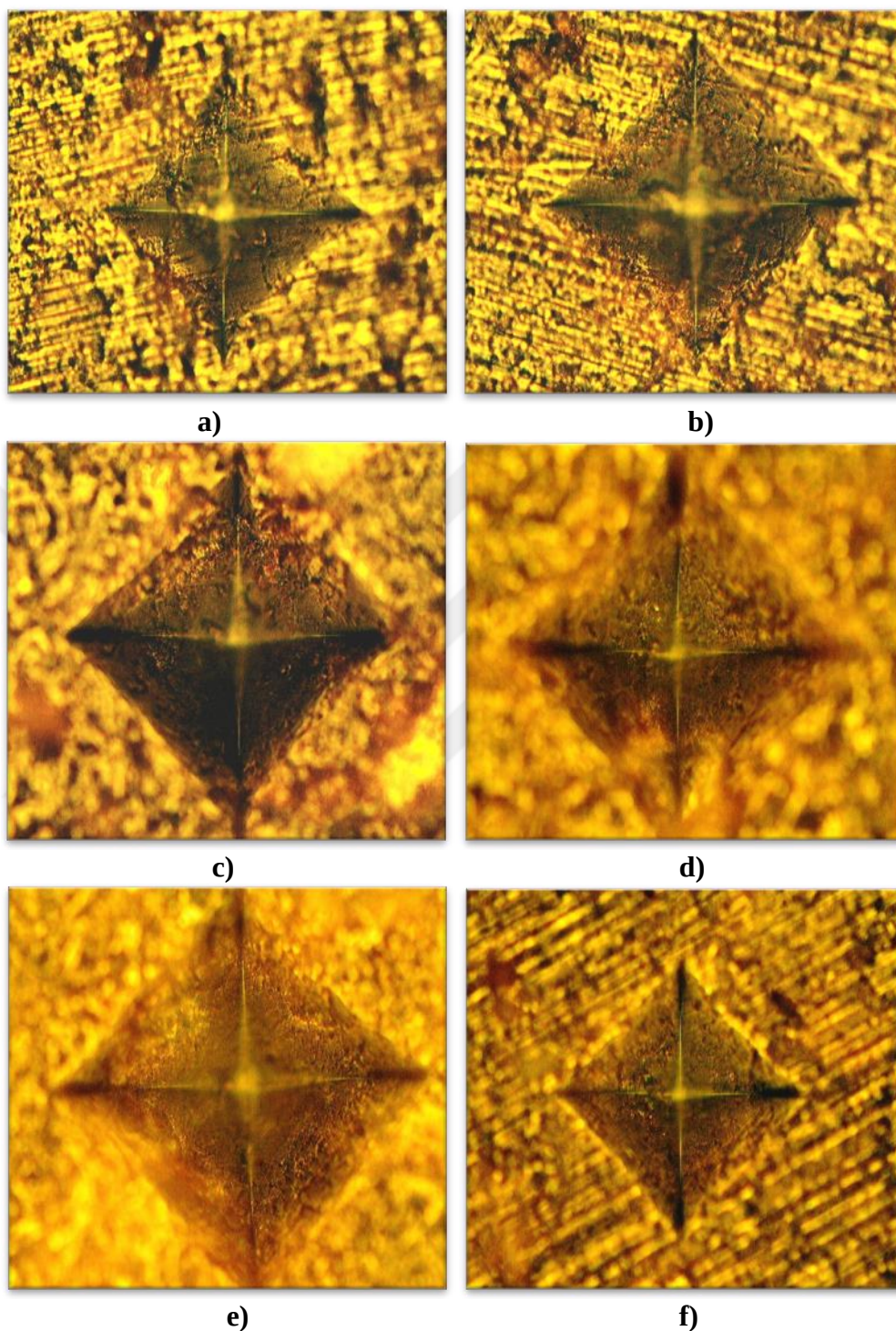


Figure 6.105. The optical trace photos under 2.940 N load for the samples: a) $\text{Zn}_{0.94}\text{Er}_{0.05}\text{Cd}_{0.01}\text{O}$, b) $\text{Zn}_{0.93}\text{Er}_{0.05}\text{Cd}_{0.02}\text{O}$, c) $\text{Zn}_{0.92}\text{Er}_{0.05}\text{Cd}_{0.03}\text{O}$, d) $\text{Zn}_{0.91}\text{Er}_{0.05}\text{Cd}_{0.04}\text{O}$, e) $\text{Zn}_{0.85}\text{Er}_{0.05}\text{Cd}_{0.10}\text{O}$

6.4.4.1 Meyer's Law

According to this approach, the $\ln F - \ln d$ graphs of the undoped and Cd doped ZnO samples are given in Figure 6.106. One can see from the figure that n values are found to be greater than 2 ($n > 2$) for each sample. This is in association with the fact that all the samples obey the *RISE* behavior as a consequence of the displacement character with the applied test load. As a result, according to results of Meyer's Law, all samples show *RISE* behavior (Table 6.99).

In fact, the decrement in the n values guarantees that the Cd additives lead to exhibit more and more *RISE* nature of the samples. Moreover, it is necessary to underline that n values vary between 1 and 1.6 for only the hard materials whereas higher values ($n > 1.6$) are attributed to the soft materials (Sahin et al., 2005). Based on the results obtained from the samples prepared, each material is regarded as the soft materials (Table 6.99).

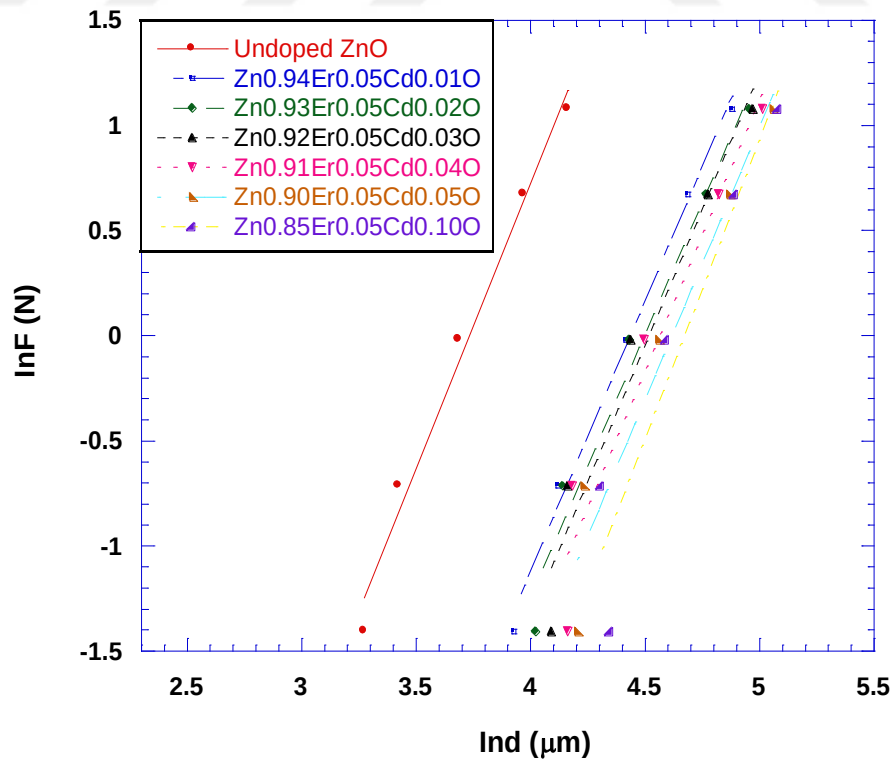


Figure 6.106. Variation of applied load $\ln F$ with diagonal $\ln d$ for the samples

Table 6.99. Best-fit results of experimental data according to Meyer's law

<i>Samples</i>	<i>Meyer number n_k</i>	<i>InK (GPa)</i>	<i>R</i>
<i>Undoped ZnO</i>	2.71	-10.12	0.9926
<i>Zn_{0.94}Er_{0.05}Cd_{0.01}O</i>	2.56	-11.38	0.9967
<i>Zn_{0.93}Er_{0.05}Cd_{0.02}O</i>	2.50	-11.25	0.9871
<i>Zn_{0.92}Er_{0.05}Cd_{0.03}O</i>	2.58	-11.69	0.9778
<i>Zn_{0.91}Er_{0.05}Cd_{0.04}O</i>	2.57	-11.77	0.9697
<i>Zn_{0.90}Er_{0.05}Cd_{0.05}O</i>	2.59	-11.98	0.9732
<i>Zn_{0.985}Er_{0.05}Cd_{0.10}O</i>	2.84	-13.27	0.9504

6.4.4.2 Proportional Sample Resistance (PSR) Model

According to this approach, the $F/d - d$ graphs of the undoped and Cd doped ZnO samples are given in Figure 6.107. It can be seen from Table 6.100 that α constant of all the samples is obtained to be only the negative values. This result confirms that the only plastic deformation is shown in the samples presenting the RISE behavior.

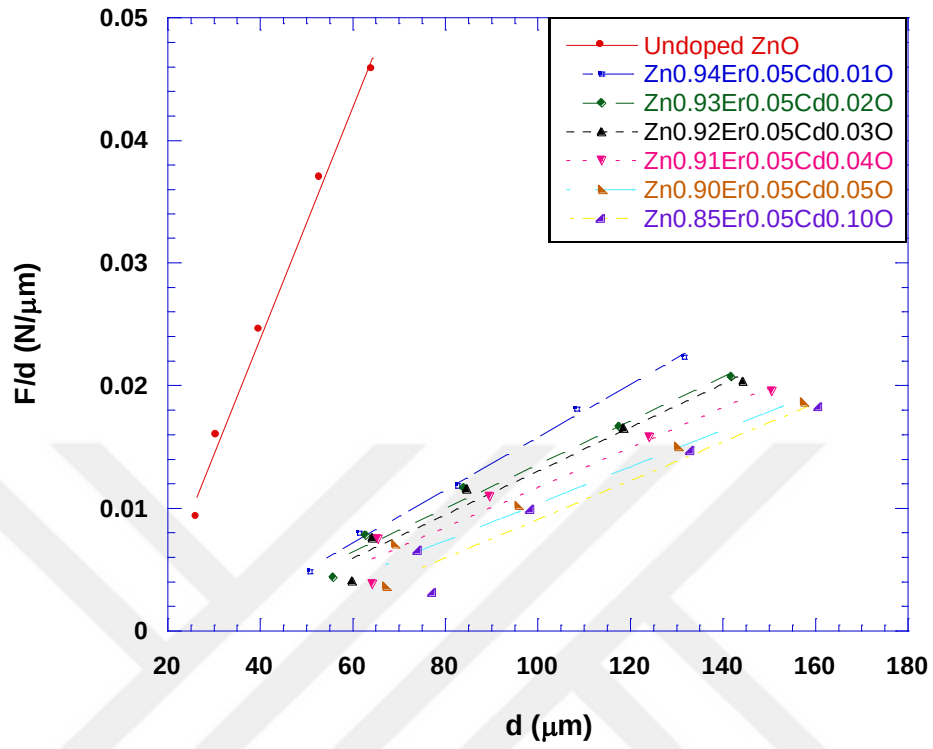


Figure 6.107. Plots of F/d versus d for the samples

Table 6.100. Best-fit results of experimental data according to PSR model

Samples	$\alpha \times 10^{-3}$ (N)	$\beta \times 10^{-5}$ (N/ μm)	R	H_{PRS} (GPa)	H_V (GPa)
Undoped ZnO	-14.07	94.58	0.9967	1.753	1.140-1.320
$\text{Zn}_{0.94}\text{Er}_{0.05}\text{Cd}_{0.01}\text{O}$	-5.71	21.50	0.9983	0.398	0.265-0.314
$\text{Zn}_{0.93}\text{Er}_{0.05}\text{Cd}_{0.02}\text{O}$	-4.21	17.81	0.9902	0.330	0.257-0.271
$\text{Zn}_{0.92}\text{Er}_{0.05}\text{Cd}_{0.03}\text{O}$	-4.72	17.76	0.9821	0.329	0.253-0.261
$\text{Zn}_{0.91}\text{Er}_{0.05}\text{Cd}_{0.04}\text{O}$	-4.57	16.28	0.9768	0.301	0.226-0.240
$\text{Zn}_{0.90}\text{Er}_{0.05}\text{Cd}_{0.05}\text{O}$	-4.66	15.02	0.9810	0.278	0.198-0.220
$\text{Zn}_{0.985}\text{Er}_{0.05}\text{Cd}_{0.10}\text{O}$	-6.57	15.73	0.9675	0.291	0.187-0.211

Table 6.101. The calculated load independent H_o , E_o , Y_o and K_{IC} for the samples

<i>Samples</i>	<i>H_o (GPa)</i>	<i>E_o (GPa)</i>	<i>Y_o (GPa)</i>	<i>K_{IC} (Pa/m^{1/2})</i>	<i>H_v (GPa)</i>
Undoped ZnO	1.753	143.68	0.584	-2.010	1.140-1.320
Zn_{0.94}Er_{0.05}Cd_{0.01}O	0.398	32.621	0.132	-0.610	0.265-0.314
Zn_{0.93}Er_{0.05}Cd_{0.02}O	0.330	27.048	0.110	-0.227	0.257-0.271
Zn_{0.92}Er_{0.05}Cd_{0.03}O	0.329	26.966	0.109	-0.504	0.253-0.261
Zn_{0.91}Er_{0.05}Cd_{0.04}O	0.301	24.671	0.100	-0.474	0.226-0.240
Zn_{0.90}Er_{0.05}Cd_{0.05}O	0.278	22.786	0.092	-0.460	0.198-0.220
Zn_{0.985}Er_{0.05}Cd_{0.10}O	0.291	23.851	0.097	-0.559	0.187-0.211

The load-independent microhardness values calculated in accordance with the PSR model are given in Table 6.100. It is obvious from the table that the transition values of the samples to the plateau are quite far from the microhardness values calculated using the PSR model (Quinn and Quinn, 1997). Therefore, it is obvious that the PSR model is not adequate for the determination of true microhardness values of both the undoped and Cd doped DMS materials.

Additionally, load independent E, Y and K_{IC} values are calculated using load independent H_{PSR} value and the findings obtained are numerically listed in Table 6.101. According to the results, the sharper increase in the load independent values is observed as compared to load dependent values.

6.4.4.3 Modified Proportional Sample Resistance (MPSR) Model

According to PSR model, when $d = 0$ the resistance of the sample (W) becomes zero (Kölemen et al., 2006; Gong et al., 1999). That means the minimum amount of applied load needed permanent deformation is zero. Gong et. al. proposed that the sample subject to mechanical treatments like surface polishing can be considered as a compressed spring rather than a relaxed one (Gong et al, 1999).

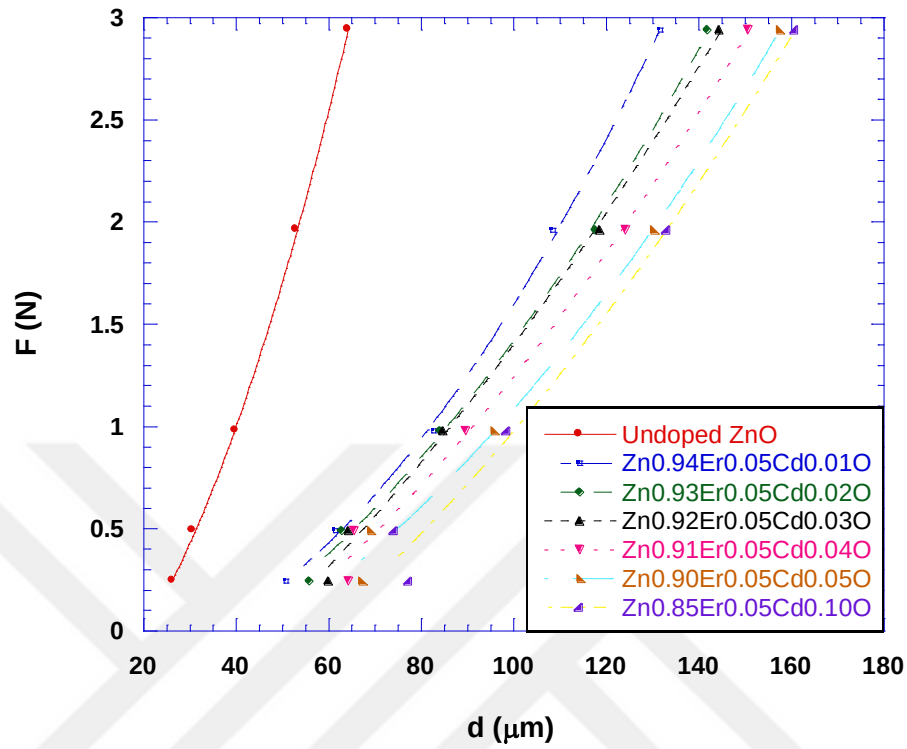


Figure 6.108. Variation of applied load with the indentation diagonal length for the samples

The values W_{MPSR} , a_1 and a_2 parameters calculated from fitting of the curve in Figure 6.108 and the associated load independent microhardness values are given in Table 6.102. From the table it can be seen that the microhardness values calculated using the model are far from the values of the plateau region.

Table 6.102. Best-fit results of experimental data according to MPSR model

Samples	W_{MPSR} (N)	$a_1 \times 10^{-4}$ (N/ μm)	$a_2 \times 10^{-4}$ (N/ μm^2)	R	H_{MPSR} (GPa)	H_V (GPa)
Undoped ZnO	-0.49	-110.03	6.61	0.9998	1.225	1.140-1.320
$Zn_{0.94}Er_{0.05}Cd_{0.01}O$	-0.19	-8.10	1.87	0.9996	0.222	0.265-0.314
$Zn_{0.93}Er_{0.05}Cd_{0.02}O$	-0.46	67.87	1.20	0.9992	0.157	0.257-0.271
$Zn_{0.92}Er_{0.05}Cd_{0.03}O$	-0.79	134.25	0.85	0.9987	0.181	0.253-0.261
$Zn_{0.91}Er_{0.05}Cd_{0.04}O$	-0.61	87.34	0.98	0.9975	0.200	0.226-0.240
$Zn_{0.90}Er_{0.05}Cd_{0.05}O$	-0.43	44.06	1.08	0.9977	0.165	0.198-0.220
$Zn_{0.985}Er_{0.05}Cd_{0.10}O$	-0.80	89.24	0.89	0.9948	0.222	0.187-0.211

6.4.4.4 Elastic/Plastic Deformation (EPD) Model

In indentation tests used, the indentation size is measured after indenter is removed. Hence, the indentation size contracts due to the elastic recovery and Tarkanian et al. (1973) suggested a new term to add into the measured indentation size to find the load independent microhardness values.

As seen from Table 6.103, the value of d_e is negative for all samples. That means for this range of applied loads elastic deformation is not observed along with plastic deformation. For all samples only plastic relaxation is present. Absence of elastic deformation along with plastic deformation is the reason of *RISE* behavior for our samples.

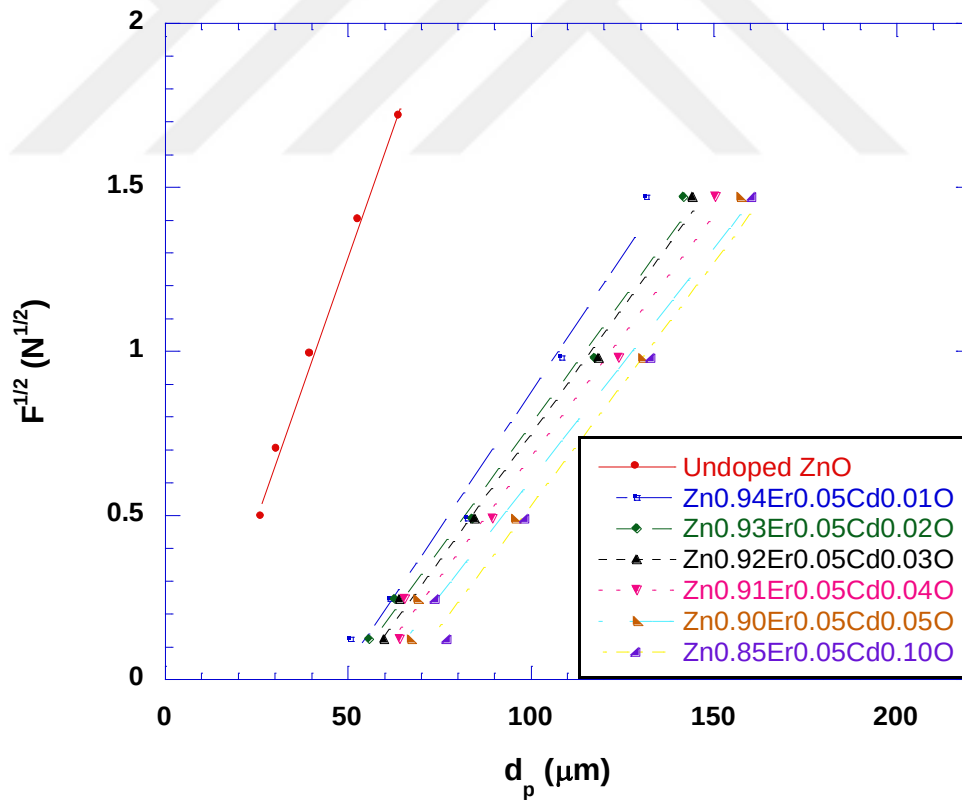


Figure 6.109. Plots of diagonal length versus square root of applied loads for the samples

Table 6.103. Best-fit results of experimental data according to EDP model

<i>Samples</i>	$A_2^{1/2}$ (GPa)	d_e (μm)	<i>R</i>	H_{EDP} (GPa)	H_V (GPa)
Undoped ZnO	0.031	-0.29	0.9980	1.863	1.140-1.320
Zn_{0.94}Er_{0.05}Cd_{0.01}O	0.016	-0.78	0.9920	0.474	0.265-0.314
Zn_{0.93}Er_{0.05}Cd_{0.02}O	0.015	-0.74	0.9956	0.417	0.257-0.271
Zn_{0.92}Er_{0.05}Cd_{0.03}O	0.015	-0.78	0.9970	0.417	0.253-0.261
Zn_{0.91}Er_{0.05}Cd_{0.04}O	0.014	-0.79	0.9948	0.363	0.226-0.240
Zn_{0.90}Er_{0.05}Cd_{0.05}O	0.014	-0.80	0.9939	0.363	0.198-0.220
Zn_{0.985}Er_{0.05}Cd_{0.10}O	0.014	-0.95	0.9926	0.363	0.187-0.211

6.4.4.5 Hays-Kendall Approach

The load independent W and A_{HK} values determined are displayed in Table 6.104. The negative values of W may be attributed to the fact that the applied load is not sufficient to produce the elastic deformation as well as the plastic deformation in the specimen (Ma et al., 1995; Yilmazlar et al., 2007; Sangwal, 2000; Awad et al., 2011). According to the results observed, the plastic deformation is observed in undoped and Cd-doped ZnO based DMS materials. As a result, the microhardness values calculated using HK approach are quite far to those of the plateau (saturation) region like other model results for all the samples exhibiting the *RISE* behavior.

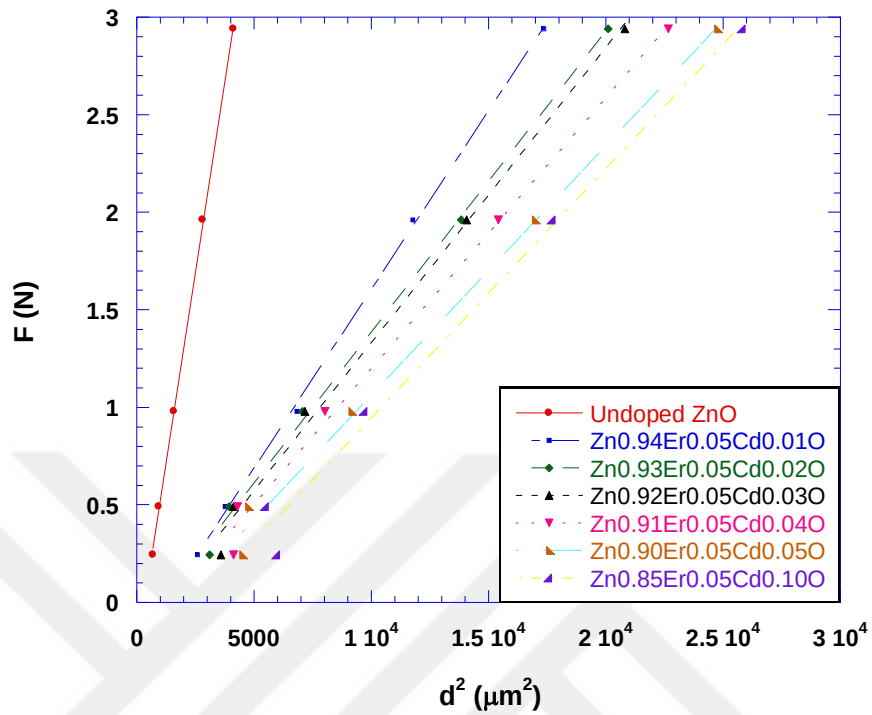


Figure 6.110. Graph of the applied load against the square of the diagonal length for the samples

Table 6.104. Best-fit results of experimental data according to *HK* model

Samples	$A_{HK} \times 10^{-5}$ (GPa)	W_{HK} (N)	R	H_{HK} (GPa)	H_V (GPa)
Undoped ZnO	78.13	-0.26	0.9997	1.448	1.140-1.320
$Zn_{0.94}Er_{0.05}Cd_{0.01}O$	18.29	-0.22	0.9996	0.339	0.265-0.314
$Zn_{0.93}Er_{0.05}Cd_{0.02}O$	15.44	-0.16	0.9989	0.286	0.257-0.271
$Zn_{0.92}Er_{0.05}Cd_{0.03}O$	15.12	-0.18	0.9977	0.280	0.253-0.261
$Zn_{0.91}Er_{0.05}Cd_{0.04}O$	13.91	-0.19	0.9970	0.257	0.226-0.240
$Zn_{0.90}Er_{0.05}Cd_{0.05}O$	12.78	-0.21	0.9976	0.236	0.198-0.220
$Zn_{0.985}Er_{0.05}Cd_{0.10}O$	12.75	-0.32	0.9944	0.236	0.187-0.211

6.4.4.6 Indentation-Induced Cracking (IIC) Model

According to this model, load independent parameters (K and m) calculated from $\ln(H_V) - \ln(F^{5/3}/d^3)$ graph (Figure 6.111) are given in the Table 6.105.

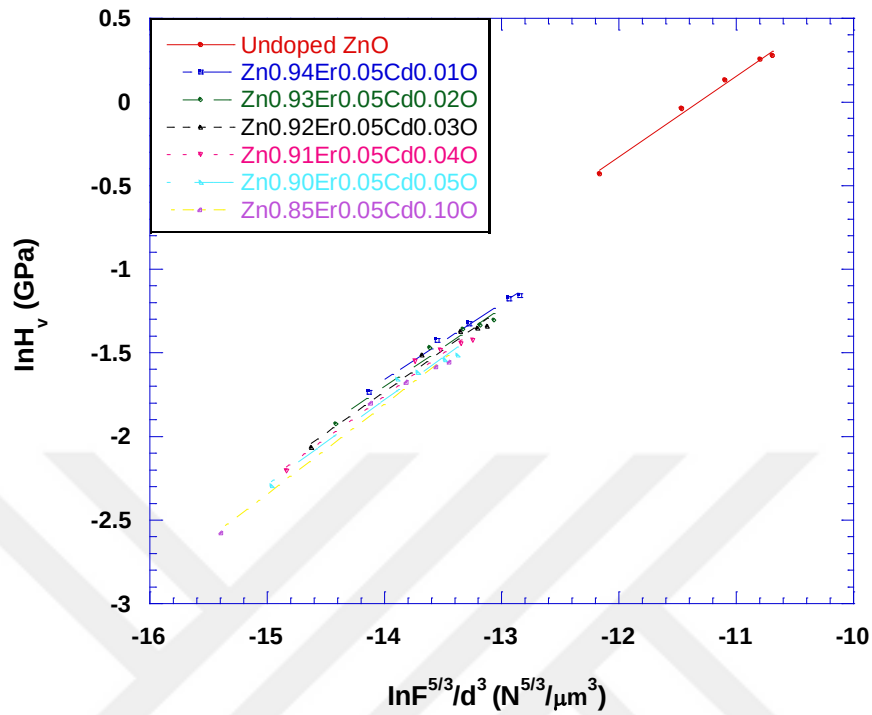


Figure 6.111. Variation of $\ln(H_v)$ with $\ln(F^{5/3}/d^3)$ according to IIC model

m index calculated from the slope of graph is 0.45, 0.47, 0.49, 0.50, 0.50 and 0.53, respectively, for undoped and *Cd* doped ZnO series; For all samples $m < 0,6$ confirms that *RISE* behavior is observed in the samples (Table 6.105). m index is used for explaining material behavior. While $m > 0,6$, the sample shows normal *ISE* behavior, when it is $m < 0,6$, it shows *RISE* behavior.

Analyzing data in Table 6.106, it can be seen that *IIC* model hardness values are close to hardness values of the sample that shows *RISE*. This result confirms that only plastic deformation is observed in the samples. All the hardness values of the samples are given in Table 6.106 in order to analyze comparatively. As can be seen from the table, *IIC* model is the most appropriate model for all other samples that show *RISE* behavior.

Table 6.105. Best-fit results of experimental data according to IIC model

Samples	m	InK ($N^{(3-5m)/3}/\mu m^{(2-3m)}$)	R	H_{IIC} (GPa)	H_V (GPa)
Undoped ZnO	0.48	5.48	0.9962	1.125	1.140-1.320
$Zn_{0.94}Er_{0.05}Cd_{0.01}O$	0.45	4.69	0.9962	0.273	0.265-0.314
$Zn_{0.93}Er_{0.05}Cd_{0.02}O$	0.47	4.90	0.9879	0.239	0.257-0.271
$Zn_{0.92}Er_{0.05}Cd_{0.03}O$	0.49	5.24	0.9897	0.249	0.253-0.261
$Zn_{0.91}Er_{0.05}Cd_{0.04}O$	0.50	5.36	0.9890	0.229	0.226-0.240
$Zn_{0.90}Er_{0.05}Cd_{0.05}O$	0.50	5.29	0.9897	0.198	0.198-0.220
$Zn_{0.985}Er_{0.05}Cd_{0.10}O$	0.53	5.69	0.9943	0.182	0.187-0.211

Table 6.106. The results of load dependent Vickers microhardness at the plateau region and load independent hardness values calculated using *PSR*, *MPSR*, *EPD*, *HK* and *IIC* models

Samples	H_{PSR} (GPa)	H_{MPSR} (GPa)	H_{EPD} (GPa)	H_{HK} (GPa)	H_{IIC} (GPa)	H_V (GPa)
Undoped ZnO	1.753	1.225	1.863	1.448	1.125	1.140-1.320
$Zn_{0.94}Er_{0.05}Cd_{0.01}O$	0.398	0.222	0.474	0.339	0.273	0.265-0.314
$Zn_{0.93}Er_{0.05}Cd_{0.02}O$	0.330	0.157	0.417	0.286	0.239	0.257-0.271
$Zn_{0.92}Er_{0.05}Cd_{0.03}O$	0.329	0.181	0.417	0.280	0.249	0.253-0.261
$Zn_{0.91}Er_{0.05}Cd_{0.04}O$	0.301	0.200	0.363	0.257	0.229	0.226-0.240
$Zn_{0.90}Er_{0.05}Cd_{0.05}O$	0.278	0.165	0.363	0.236	0.198	0.198-0.220
$Zn_{0.985}Er_{0.05}Cd_{0.10}O$	0.291	0.222	0.363	0.236	0.182	0.187-0.211

6.4.4.7 Conclusions of Vickers Conclusions of Vickers Microhardness Analyses

In this section, microhardness measurements are performed to investigate the effect of *Cd* doping on the mechanical properties of ZnO based DMS materials. The increase in the microhardness values of the all sample depends on the increase of applied load, which shows *RISE* behavior. Behavior of the materials is not changed with *Cd* doping. Only the values of microhardness changed with doping.

- H_v decrease with increasing the *Cd* doping when compared with undoped ZnO sample.
- If a plastic material is requested for industrial applications, *Cd*0.10 doped ZnO nano bulk material is the most appropriate material among all samples (microhardness value is between 0.187 – 0.211 GPa).

- The load-dependent E , Y , K_{IC} , B_i and D are calculated. As a result it found that these values load dependent decreased with doping.
- Also the Vickers microhardness values computed are noted to increase with increasing the applied load. The dependence of the load showed that *RISE* has an influence on the samples. The results of the microhardness measurements are analyzed by employing Meyer's law, *PSR*, *MPSR*, *EDP*, *IIC* models and *HK* approach.
- As a result, *IIC* model is more suitable to determine the micromechanical properties and *RISE* behavior of *Cd* doped-ZnO semiconductors.

6.5 Optical Measurements of ZnO Based Thin Materials

6.5.1 Transition Metal Doped $\text{Zn}_{1-x}\text{B}_x\text{O}$ (B=Cu) DMS Nano Thin Film Materials

The typical room temperature transmittance spectra of all nano thin films prepared by sol-gel technique are given in Figure 6.112. $\text{Zn}_{0.99}\text{Cu}_{0.01}\text{O}$ nano thin film has broad transmittance band in UV region and stronger transmittance in the visible region. The transmittance values decrease with increasing Cu doping. The high transmittance is very convenient for industrial applications as transparent electrode. In addition, the observed weak transmittance shows large defect in the material. More defect increases the absorption in visible region and so the transmittance decreases.

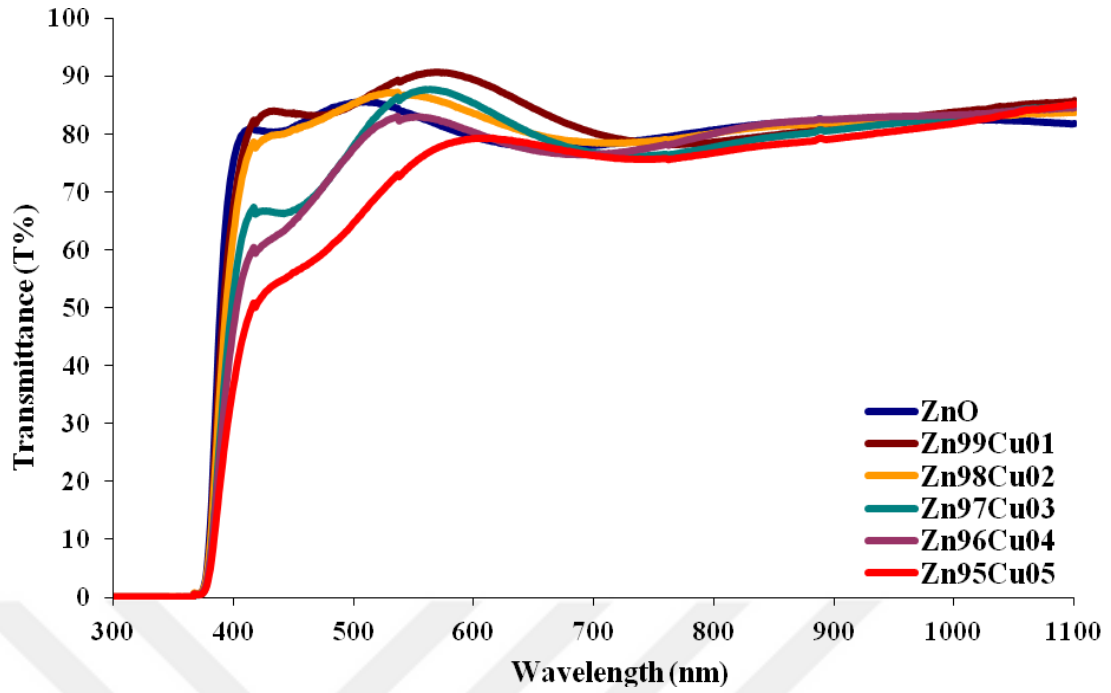


Figure 6.112. Optical transmittance spectra of all ZnO nano thin films

The decrease in the optical band gap can be attributed to the better crystallinity with increasing grain size. When Cu ions are located at substitution sites, the carrier concentration increases and as a result the band gap energy decreases. In the present work, the grain size of nano thin films increases with Cu doping. Consequently the band gap decreases with the increase of average grain size. The change in energy gap is due to grain size. The crystallinity of $\text{Zn}_{0.95}\text{Cu}_{0.05}\text{O}$ nano thin film is better compared to the other nano thin films.

The transmittance of ZnO based nano thin films can be affected by defects such as film thickness, surface roughness, grain size and nano pores (Chien-Yie and Wen-Che, 2013). The absorption coefficient α is calculated using the formula

$$\alpha = \frac{1}{t} \ln \left(\frac{1}{T} \right) \quad (6.32)$$

where t is thickness and T is transmittance of the film. In order to determine the energy gap of the films produce, the plots of the square of Kubelka-Munk function $((\alpha h\nu)^2)$ versus to energy $(h\nu)$ for ZnO and ZnCuO nano thin films are given in Figure 6.113. The optical band gap energy (E_g) values for undoped and Cu doped ZnO nano thin films are calculated using the formula

$$\alpha h\nu = A(h\nu - E_g)^n \quad (6.33)$$

where A is constant, α is the absorption coefficient, $h\nu$ is the discrete photon energy, E_g is the band gap energy, and n depends on the type of optical transmission in the band gap. $n = 1/2$ is for direct band gap crystalline semiconductors. The Tauc plot which is extrapolating the linear portion to zero absorption coefficient gives the optical band gap energy of the films.

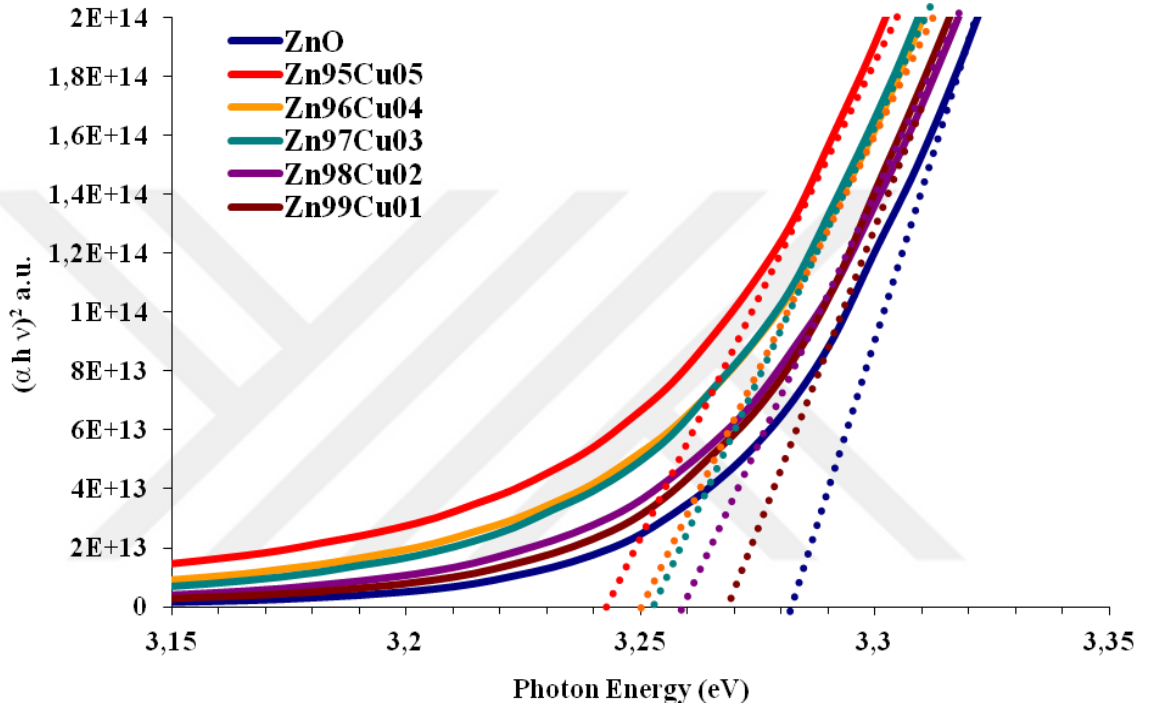


Figure 6.113. The plots of $(\alpha h\nu)^2$ vs $(h\nu)$ for ZnO and ZnCuO nano thin films

While the optical band gap energy is about 3.28 eV for undoped ZnO film, it is in the range of 3.24 – 3.27 eV for Cu doped nano thin films as shown in Figure 6.113 and Table 6.107. Bandgap energy of the doped films is smaller than the undoped film. Narrowing of this band gap is due to the increase in the band tail width. Semiconductor materials coupled with a dopant cause the formation of the band tail in band gap.

The exponential relationship between photon energy and absorption coefficient is known as the Urbach rule. It is associated with the electronic transitions to the conduction band from valence band in irregular materials (Rai, 2013). Urbach

tail of the films are calculated by the following equation (Caglar et al., 2012; Ilican et al., 2010)

$$\alpha = \alpha_0 + \exp\left(\frac{h\nu}{E_u}\right) \quad (6.34)$$

where α_0 is a constant and E_u is Urbach energy that is related to the width of the band tail. It is calculated by the inverse of the slope of $\ln(\alpha)$ – Photon energy graph (Fig 6.114). Urbach energy (E_u) tends to increase with increasing Cu doping (Fig.6.115). Urbach energy is given by

$$E_u = k_B T / \beta \quad (6.35)$$

where k_B and T are Boltzmann constant and temperature (300K), respectively. β is value of steepness parameter. It decreases with the increment of the Urbach energy. In addition, steepness parameter decreases as a function of Cu doping concentration.

Table 6.107. Average transmittance, Energy Gap (E_g), Urbach energy (E_u) and steepness parameter and values for ZnO and Cu doped ZnO nano thin films

<i>Samples</i>	<i>Average transmittance (%)^a</i>	<i>Energy Gap (eV)</i>	<i>^bE_U (meV)</i>	<i>Steepness Parameter $\beta \cdot 10^{-1}$</i>
Undoped ZnO	81.12	3.28	98.10	2.63
Zn_{0.99}Cu_{0.01}O	82.72	3.27	100.70	2.56
Zn_{0.98}Cu_{0.02}O	77.75	3.26	107.99	2.39
Zn_{0.97}Cu_{0.03}O	66.13	3.25	123.76	2.08
Zn_{0.96}Cu_{0.04}O	57.66	3.25	140.25	1.84
Zn_{0.95}Cu_{0.05}O	51.34	3.24	160.00	1.61

^aThe average transmittance values are calculated from the transmittance data of wavelength from 400-700 nm.

^b $K_b = 8.617 \times 10^{-2}$ MeV/K and $T = 300$ K.

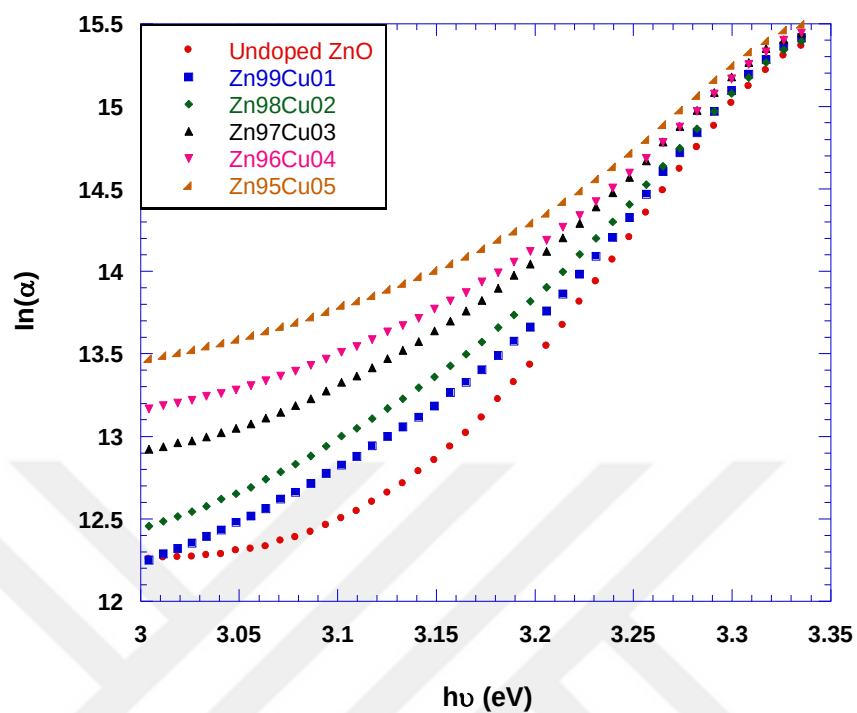


Figure 6.114. The Urbach plots of the ZnO:Cu nano thin films

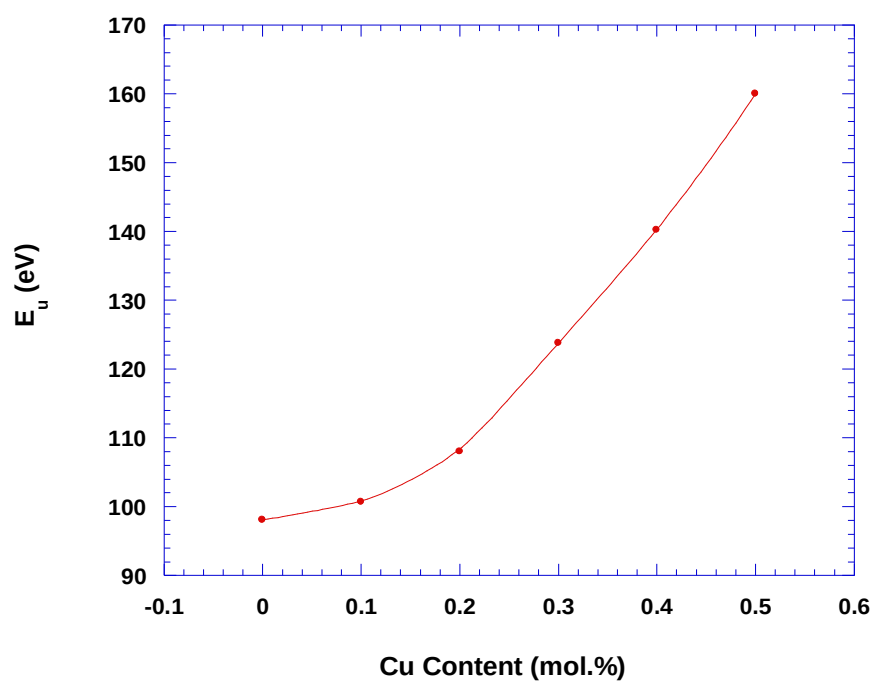


Figure 6.115. Variations of Urbach energies and steepness parameter as a function of Cu content

6.5.2 Transition Metal Doped $\text{Zn}_{1-x}\text{B}_x\text{O}$ (B=Co) DMS Nano Thin Film Materials

The transmittance-wavelength graph of the *Co* doped ZnO nano thin films is shown in Figure 6.116. $\text{Zn}_{0.99}\text{Co}_{0.01}\text{O}$ nano thin film has broad transmittance band in UV region and stronger transmittance in the visible region. The transmittance values significantly decrease with increasing Co doping. The high transmittance is very convenient for industrial applications as transparent electrode. In addition, the observed weak transmittance shows large defect in the material. More defect increases the absorption in visible region and so the transmittance decreases.

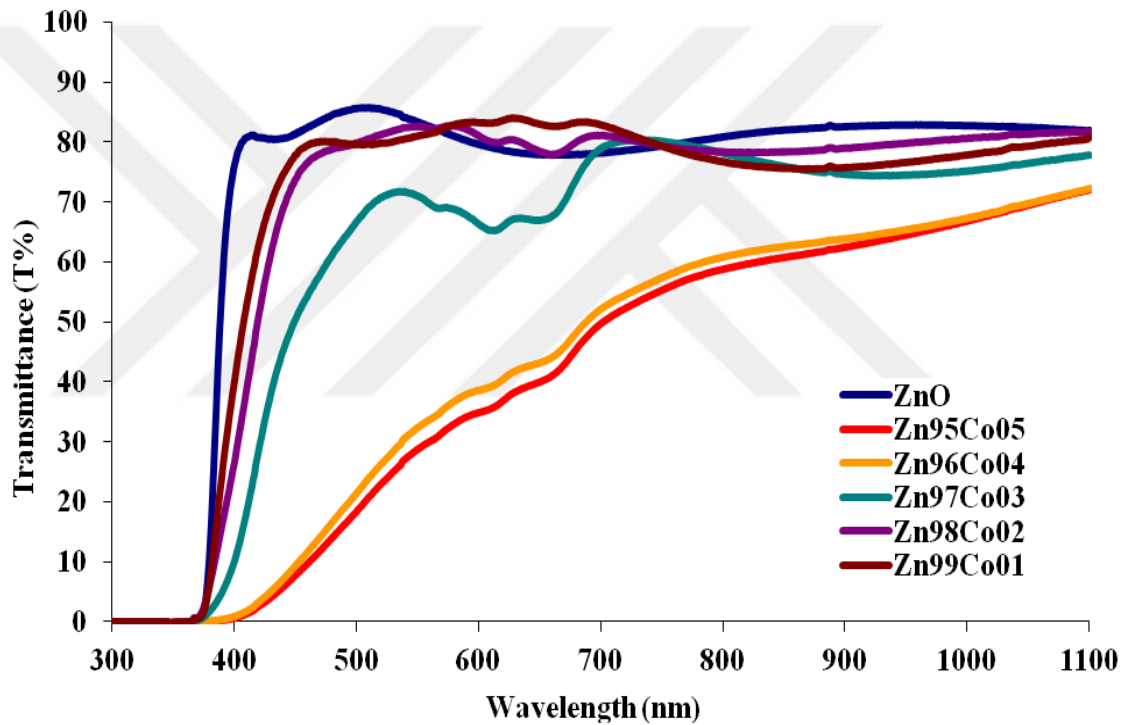


Figure 6.116. Optical transmittance spectra of all ZnO nano thin films

The decrease in the optical band gap can be attributed to the better crystallinity with increasing grain size. The crystallinity of $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ nano thin film is better compared to the other nano thin films. When *Co* ions are located at substitution sites, the carrier concentration is increased and as a result the band gap energy decreased.

While the optical band gap energy is about 3.28 eV for undoped ZnO film, it is in the range of 2.88 – 3.27 eV for Co doped nano thin films as shown in Figure

6.117 and Table 6.108. Band gap energy of the doped films is smaller than the undoped film.

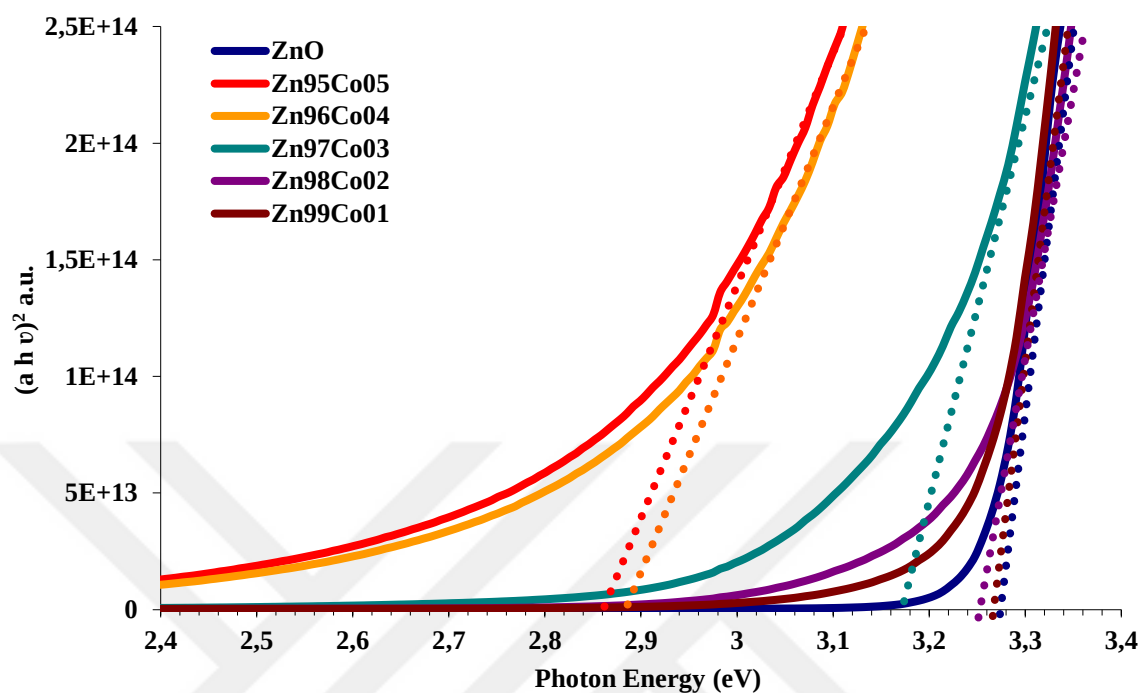


Figure 6.117. The plots of $(\alpha h\nu)^2$ vs $(h\nu)$ for ZnO and ZnCoO nano thin films

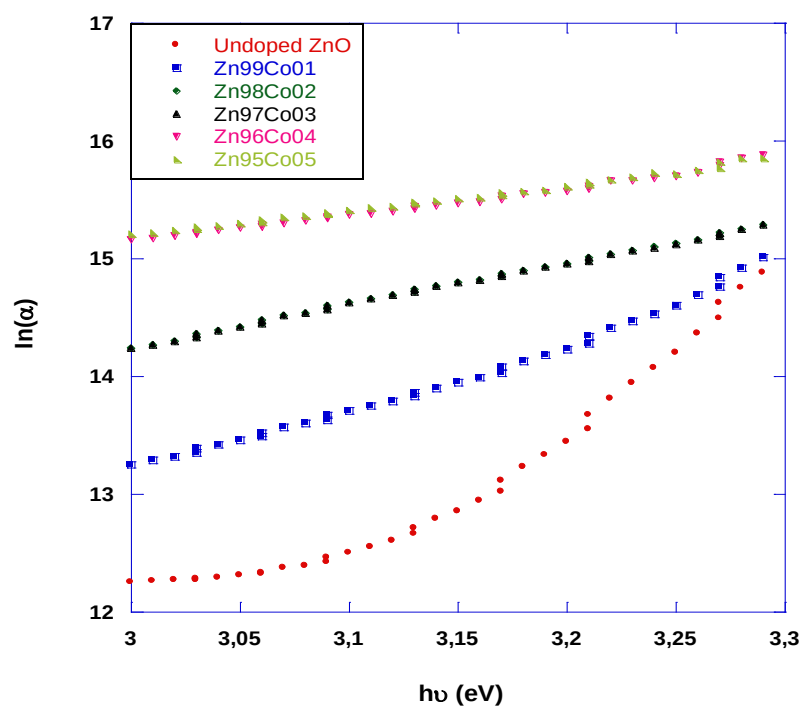


Figure 6.118. The Urbach plots of the ZnO:Co nano thin films

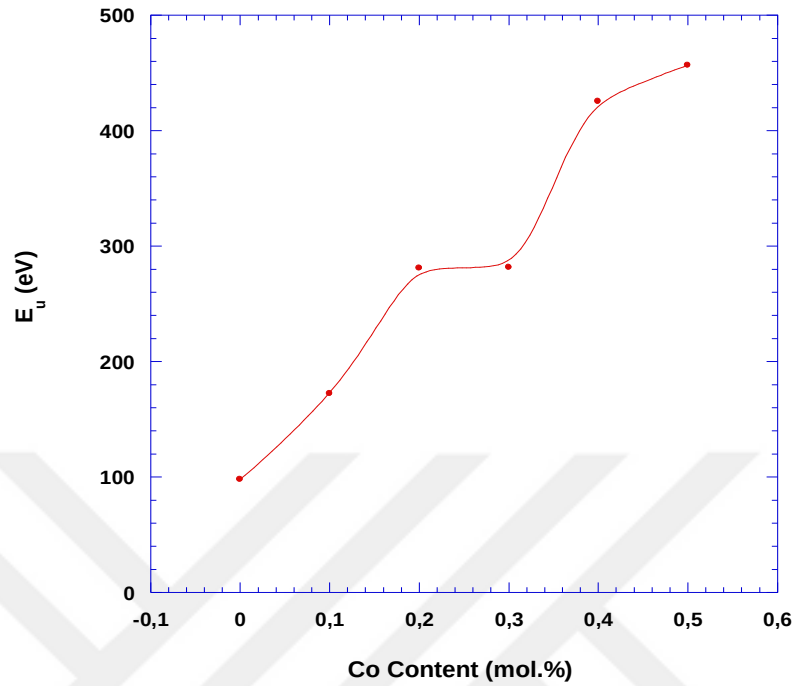


Figure 6.119. Variations of Urbach energies and steepness parameter as a function of Co content

Table 6.108. Average transmittance, Energy Gap (E_g), Urbach energy (E_u) and steepness parameter and values for ZnO and Co doped ZnO nano thin films.

Samples	Average transmittance (%) ^a	Energy Gap (eV)	^b E_u (meV)	Steepness Parameter $\beta \cdot 10^{-1}$
Undoped ZnO	81.12	3.28	98.10	2.63
Zn _{0.99} Co _{0.01} O	79.83	3.27	172.41	1.49
Zn _{0.98} Co _{0.02} O	78.00	3.26	280.89	0.92
Zn _{0.97} Co _{0.03} O	70.88	3.16	281.69	0.91
Zn _{0.96} Co _{0.04} O	40.50	2.90	425.53	0.60
Zn _{0.95} Co _{0.05} O	37.59	2.88	456.62	0.56

^aThe average transmittance values are calculated from the transmittance data of wavelength from 400-700 nm.

^b $K_b = 8.617 \times 10^{-2}$ MeV/K and $T = 300$ K.

As can be seen from Table 6.108 Urbach energy (E_u) tends to increase with increasing Co doping. The steepness parameter decreases with increasing the Urbach energy Steepness parameter decreases as a function of Co doping concentration.

6.5.3 Transition Metal Doped $\text{Zn}_{1-x-y}\text{B}_x\text{C}_y\text{O}$ (B=Cu, C=Co) DMS Nano Thin Film Materials

The transmittance-wavelength graph of the Cu/Co doped ZnO nano thin films is shown in Figure 6.120. According to the optical transmission spectrum, absorption is observed in the wavelength range between 360 – 450 nm. When Cu and Co ions are incorporated into the ZnO structure, a significantly shift is observed in the absorption edge.

The optical transmittance of undoped ZnO film is about 81% in the visible region at wavelength of about 405 nm for, it exhibits an absorption edge (Table 6.109). The average transmittance values of all doped ZnO films are under 80% and their transmittances are smaller than undoped ZnO sample.

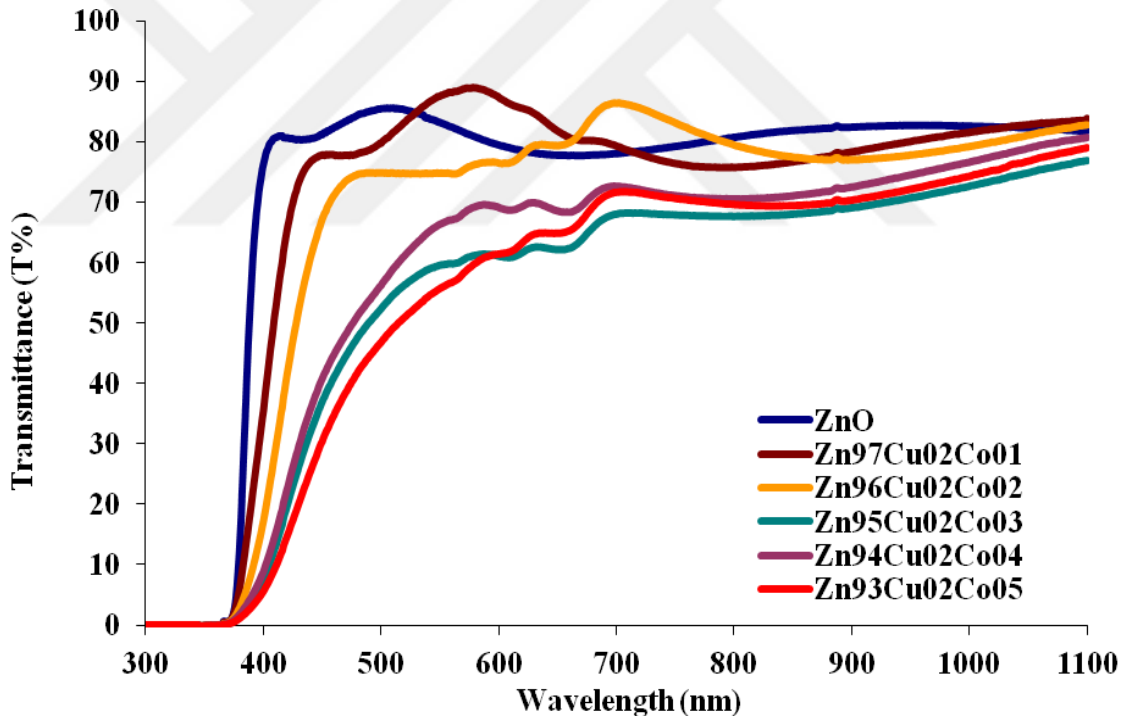


Figure 6.120. Optical transmittance spectra of all ZnO nano thin films

While the optical band gap energy is about 3.28 eV for undoped ZnO film, it is in the range of 3.22 – 3.27 eV for Cu/Co doped nano thin films as shown in Figure 6.120 and Table 6.109. Band gap energy of the doped films is smaller than the undoped film. Narrowing of this band gap is due to the increase in the band tail width.

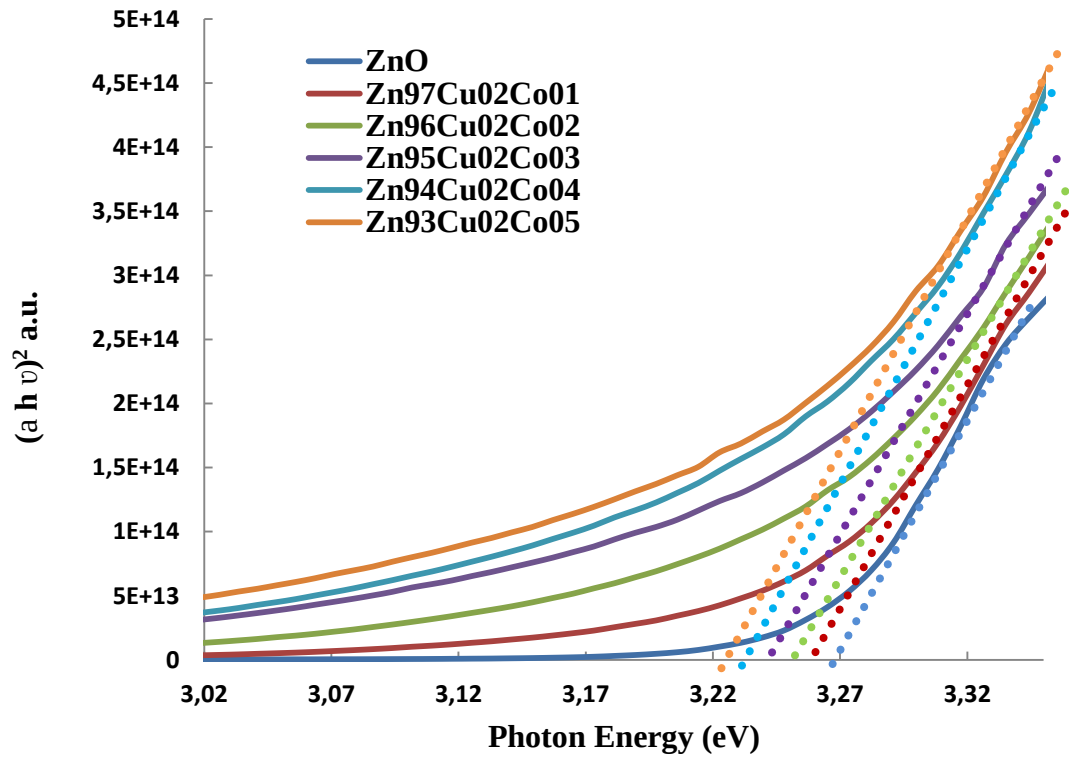


Figure 6.121. The plots of $(\alpha h\nu)^2$ vs $(h\nu)$ for ZnO and ZnCuCoO nano thin films

As can be seen from Table 6.110, E_u tends to increase with increasing Cu/Co doping (Fig.6.123). The steepness parameter decreases with increasing the Urbach energy.

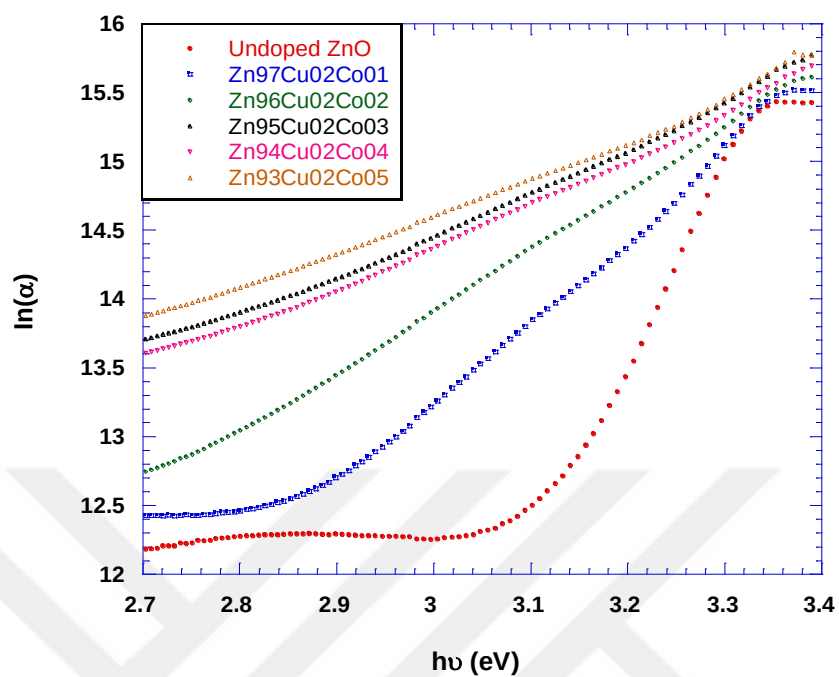


Figure 6.122. The Urbach plots of the ZnCuO:Co nano thin films

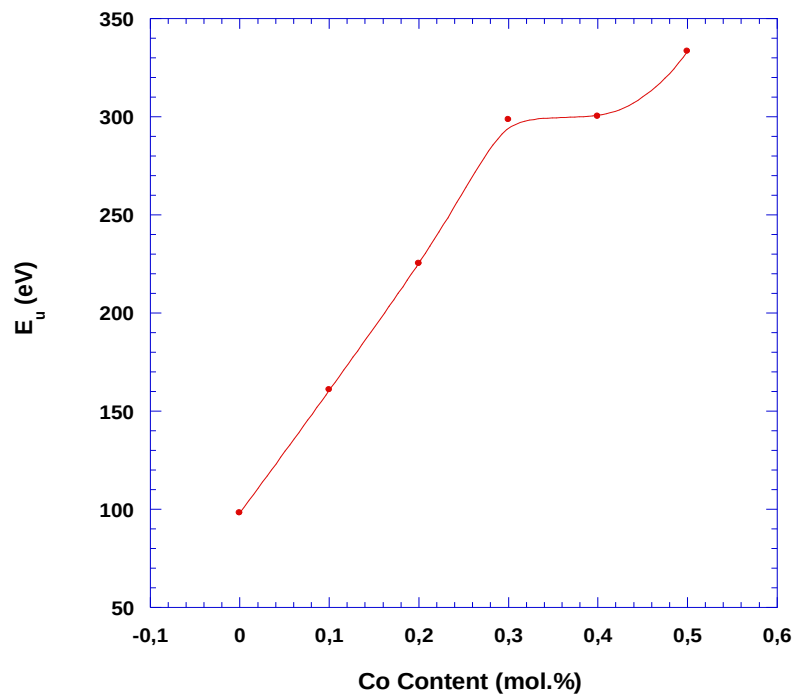


Figure 6.123. Variations of Urbach energies and steepness parameter as a function of Co content

Table 6.109. Average transmittance, Energy Gap (E_g), Urbach energy (E_u) and steepness parameter and values for ZnO and Cu/Co doped ZnO nano thin films.

<i>Samples</i>	<i>Average transmittance (%)^a</i>	<i>Energy Gap (eV)</i>	<i>^bE_U (meV)</i>	<i>Steepness Parameter $\beta \times 10^{-1}$</i>
Undoped ZnO	81.12	3.28	98.10	2.63
Zn_{0.97}Cu_{0.02}Co_{0.01}O	77.79	3.27	160.77	1.62
Zn_{0.96}Cu_{0.02}Co_{0.02}O	73.57	3.25	225.22	1.14
Zn_{0.95}Cu_{0.02}Co_{0.03}O	67.22	3.24	298.50	0.86
Zn_{0.94}Cu_{0.02}Co_{0.04}O	59.82	3.23	300.30	0.86
Zn_{0.93}Cu_{0.02}Co_{0.05}O	57.26	3.22	333.33	0.77

^aThe average transmittance values are calculated from the transmittance data of wavelength from 400-700 nm.

^b $K_b = 8.617 \times 10^{-2}$ MeV/K and $T = 300$ K .

6.5.4 Rare Earth Element Doped Zn_{1-x}B_xO (B=Er) DMS Nano Thin Film Materials

The transmittance-wavelength graph of the *Er* doped ZnO nano thin films is shown in Figure 6.124. According to the optical transmission spectrum, a sharp absorption is observed in the wavelength range between 360-400 nm. When Er ions are incorporated into the ZnO structure, a significantly shift is not observed in the absorption edge.

It is observed that the average optical transmittance is about 81% in the visible region, it exhibits an absorption edge at wavelength of about 405 nm for undoped ZnO film (Table 6.110). The average transmittance values of all doped ZnO films are above 85% and their transmittances are higher than undoped ZnO sample.

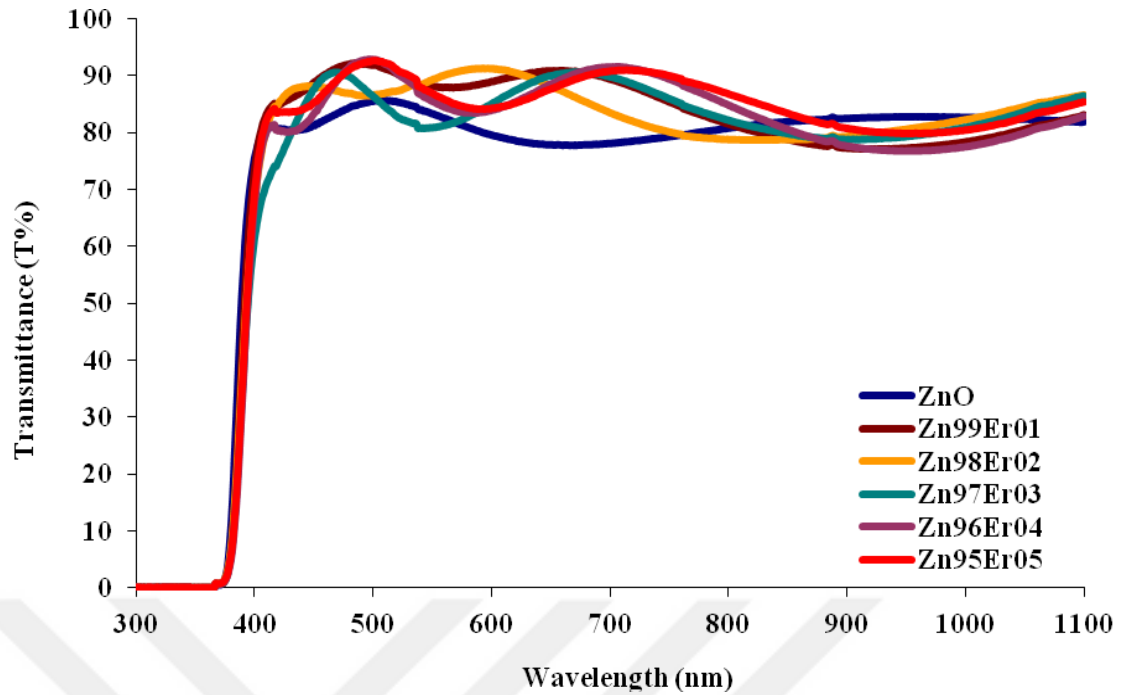


Figure 6.124. Optical transmittance spectra of all ZnO nano thin films

While the optical band gap energy is about 3.28 eV for undoped ZnO film, it is in the range of $3.24 - 3.26\text{ eV}$ for *Er* doped nano thin films as shown in Figure 6.125 and Table 6.110. Bandgap energy of the doped films is smaller than the undoped film. Narrowing of this band gap is due to the increase in the band tail width. Semiconductor materials coupled with a dopant cause the formation of the band tail in band gap.

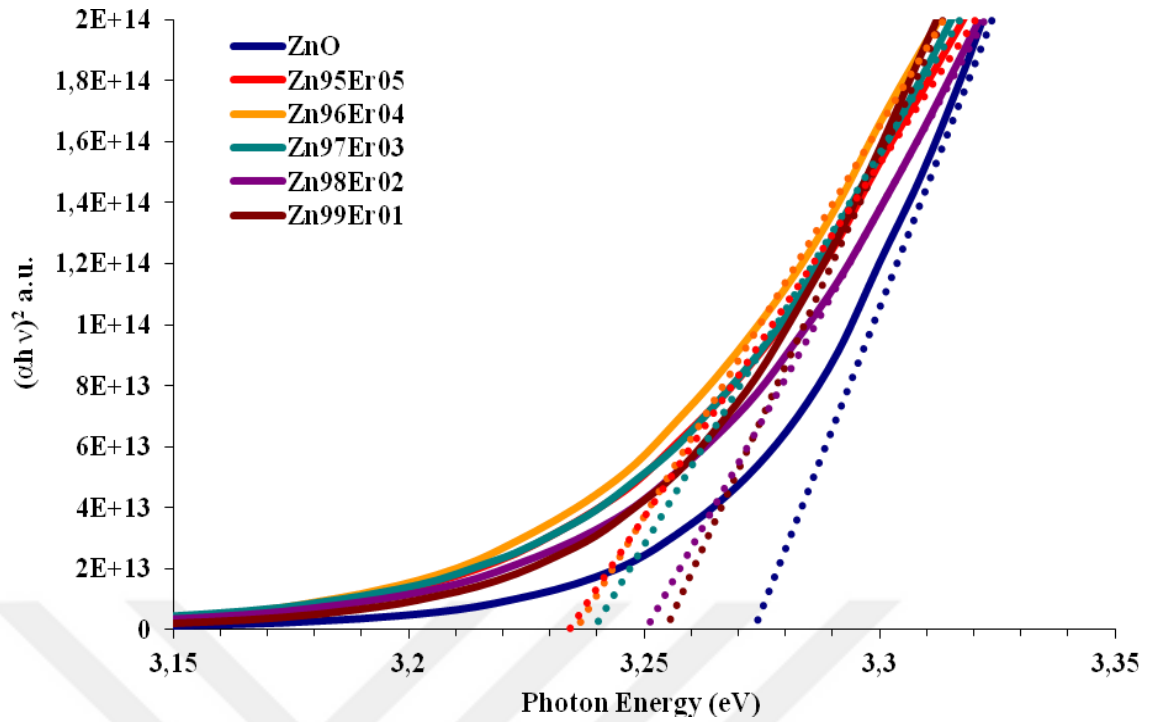


Figure 6.125. The plots of $(\alpha h\nu)^2$ vs $(h\nu)$ for ZnO and ZnErO nano thin films

As can be seen from Table 6.110, E_u tends to decrease with increasing Er doping. This is explained by defects resulted with doping. The change in the value of E_u is affected from all possible defects such as structural disorder and carrier-impurity interactions (Dimova-Malinovska et al., 2008). The steepness parameter increases with the reduction of the Urbach energy. Urbach energy decreases as a function of Er doping concentration (Fig.6.127).

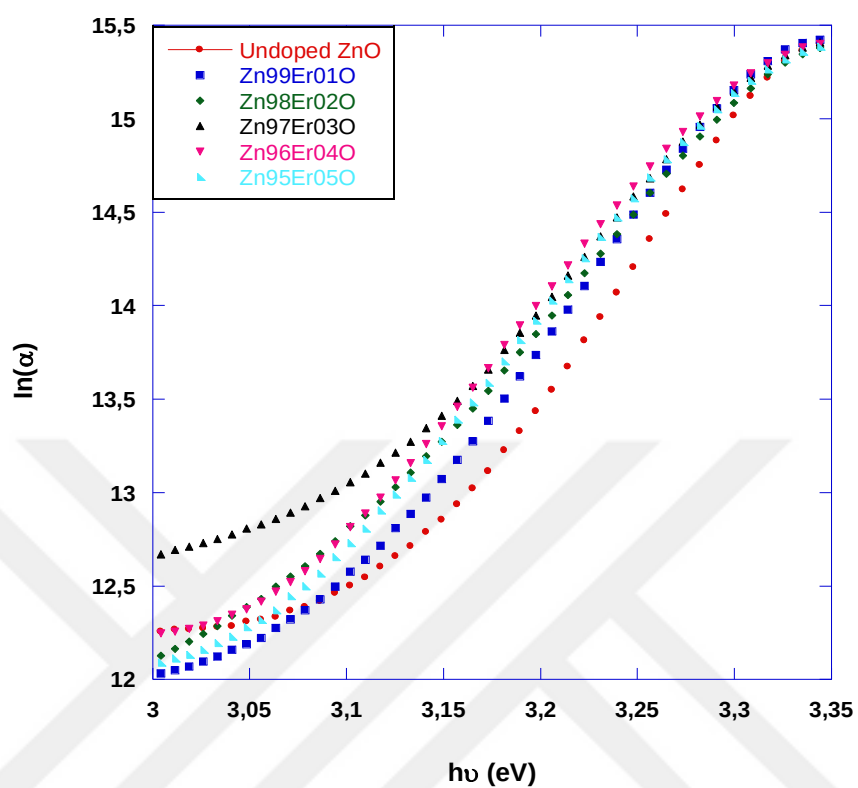


Figure 6.126. The Urbach plots of the ZnO:Er nano thin films

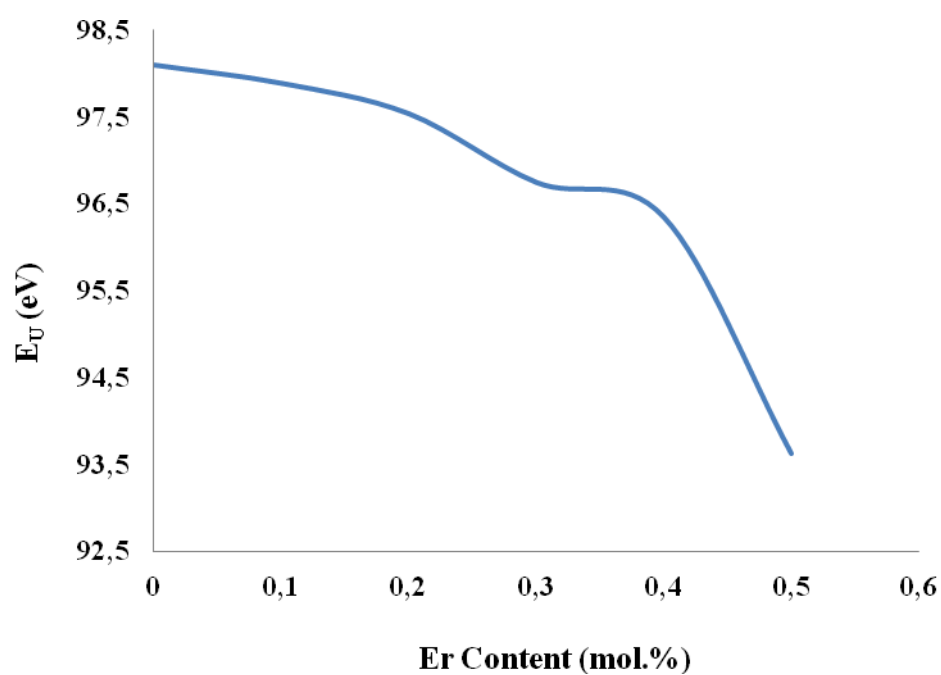


Figure 6.127. Variations of Urbach energies and steepness parameter as a function of Er content

Table 6.110. Average transmittance, Energy Gap (E_g), Urbach energy (E_u) and steepness parameter and values for ZnO and Er doped ZnO nano thin films.

<i>Samples</i>	<i>Average transmittance (%)^a</i>	<i>Energy Gap (eV)</i>	<i>^bE_U (meV)</i>	<i>Steepness Parameter $\beta \cdot 10^{-1}$</i>
Undoped ZnO	81.12	3.28	98.10	2.63
Zn_{0.99}Er_{0.01}O	89.15	3.26	97.89	2.64
Zn_{0.98}Er_{0.02}O	87.56	3.26	97.54	2.65
Zn_{0.97}Er_{0.03}O	84.93	3.24	96.75	2.67
Zn_{0.96}Er_{0.04}O	86.62	3.24	96.35	2.68
Zn_{0.95}Er_{0.05}O	87.14	3.24	93.63	2.76

^aThe average transmittance values are calculated from the transmittance data of wavelength from 400-700 nm.

^b $K_b = 8.617 \times 10^{-2}$ meV/K and $T = 300$ K .

6.5.5 Rare Earth Element Doped Zn_{1-x-y}B_xC_yO (B=Er, C=Cd) DMS Nano Thin Film Materials

The transmittance-wavelength graph of the Er/Cd doped ZnO nano thin films is shown in Figure 6.128. According to the optical transmission spectrum, a sharp absorption is observed in the wavelength range between 350-400 nm. When Cd ions are incorporated into the ZnO structure, a significantly shift is not observed in the absorption edge.

It is observed that the average optical transmittance is about 81% in the visible region, it exhibits an absorption edge at wavelength of about 405 nm for undoped ZnO film (Table 6.111). The average transmittance values of all doped ZnO films are above 71% and their transmittances are smaller than undoped ZnO sample.

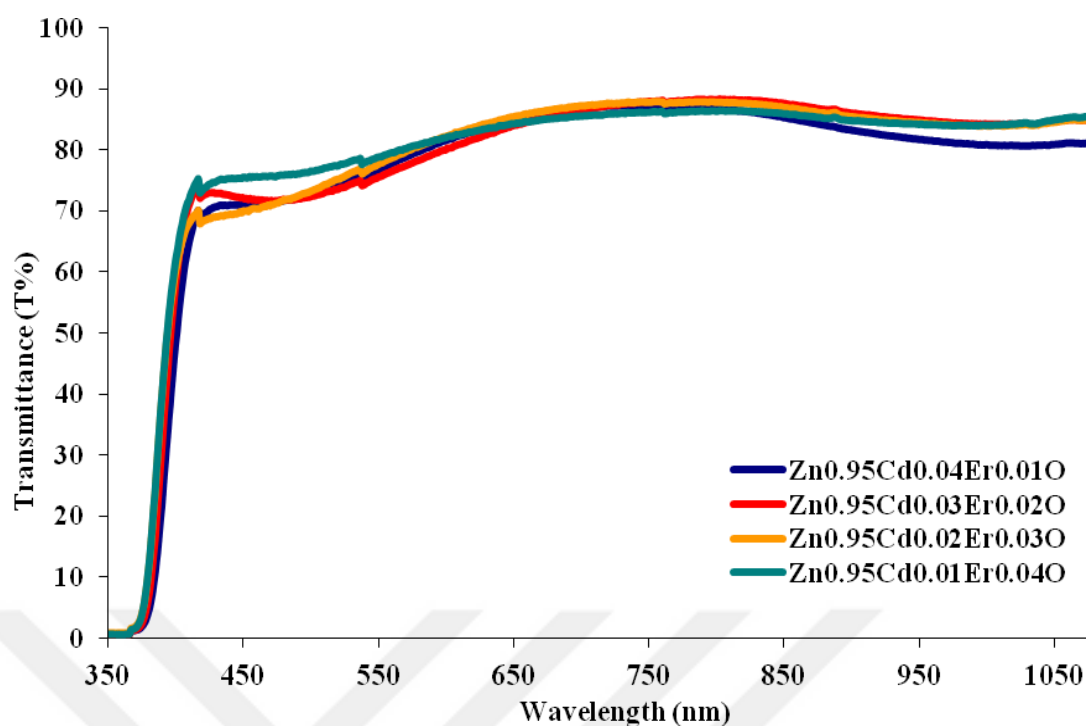


Figure 6.128. Optical transmittance spectra of all ZnO nano thin films

While the optical band gap energy is about 3.28 eV for undoped ZnO film, it is in the range of 3.21 – 3.26 eV for *Er/Cd* doped nano thin films as shown in Figure 6.129 and Table 6.111. Bandgap energy of the doped films is smaller than the undoped film. Narrowing of this band gap is due to the increase in the band tail width.

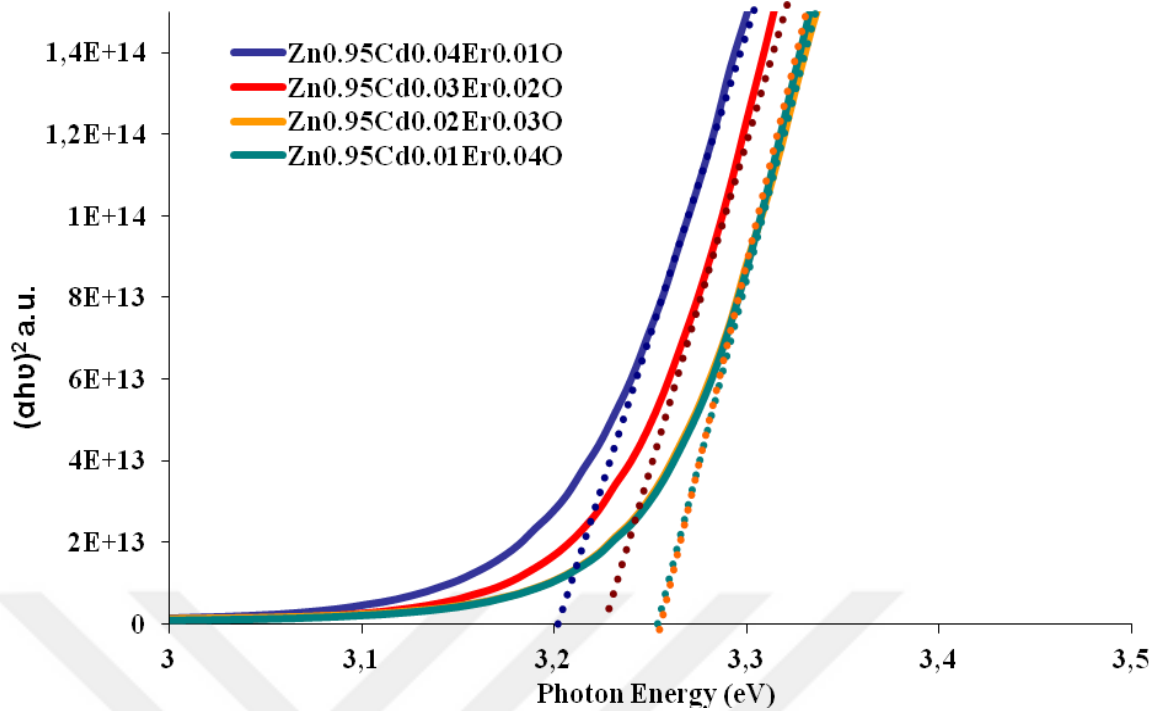


Figure 6.129. The plots of $(\alpha h\nu)^2$ vs $(h\nu)$ for ZnO and ZnErO nano thin films

As can be seen from Table 6.111, E_u tends to increase with increasing Cd doping compared with undoped ZnO. The steepness parameter decreases with increasing of the Urbach energy. In addition, Urbach energy increases as a function of Cd doping concentration (Figure 6.131).

Table 6.111. Average transmittance, Energy Gap (E_g), Urbach energy (E_u) and steepness parameter and values for ZnO and Cd/Er doped ZnO nano thin films.

<i>Samples</i>	<i>Average transmittance (%)^a</i>	<i>Energy Gap (eV)</i>	<i>^bE_U (meV)</i>	<i>Steepness Parameter $\beta \cdot 10^{-1}$</i>
Undoped ZnO	81.12	3.28	98.10	2.63
Zn_{0.95}Cd_{0.01}Er_{0.04}O	75.28	3.26	126.10	2.05
Zn_{0.95}Cd_{0.02}Er_{0.03}O	69.59	3.25	130.27	1.98
Zn_{0.95}Cd_{0.03}Er_{0.02}O	69.28	3.24	132.37	1.95
Zn_{0.95}Cd_{0.04}Er_{0.01}O	69.04	3.21	135.85	1.90

^aThe average transmittance values are calculated from the transmittance data of wavelength from 400-700 nm.

^b $K_b = 8.617 \times 10^{-2}$ meV/K and $T = 300$ K.

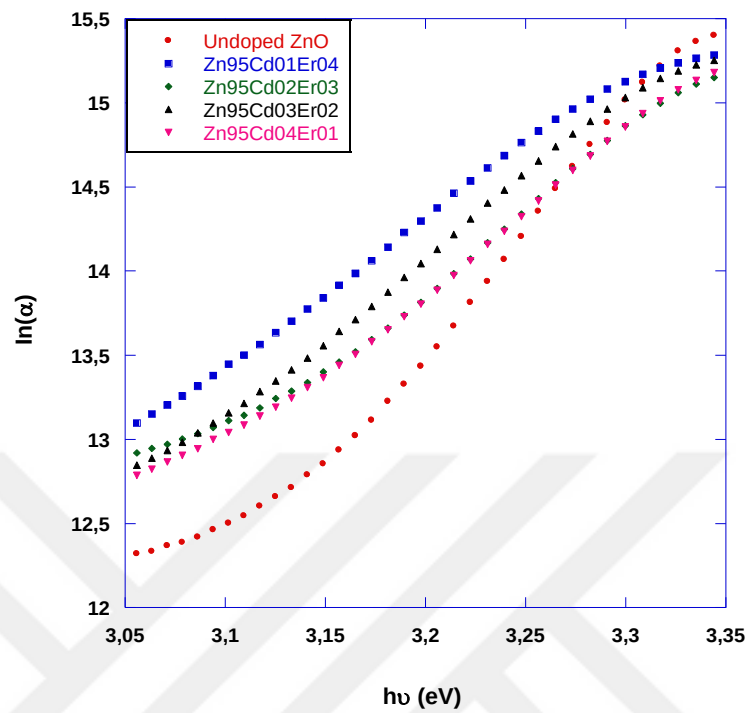


Figure 6.130. The Urbach plots of the ZnO:Cd/Er nano thin films

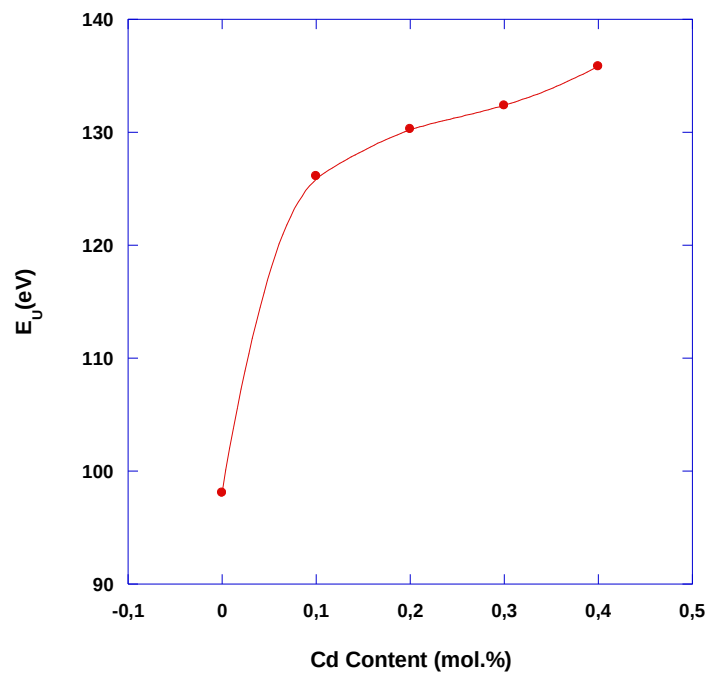
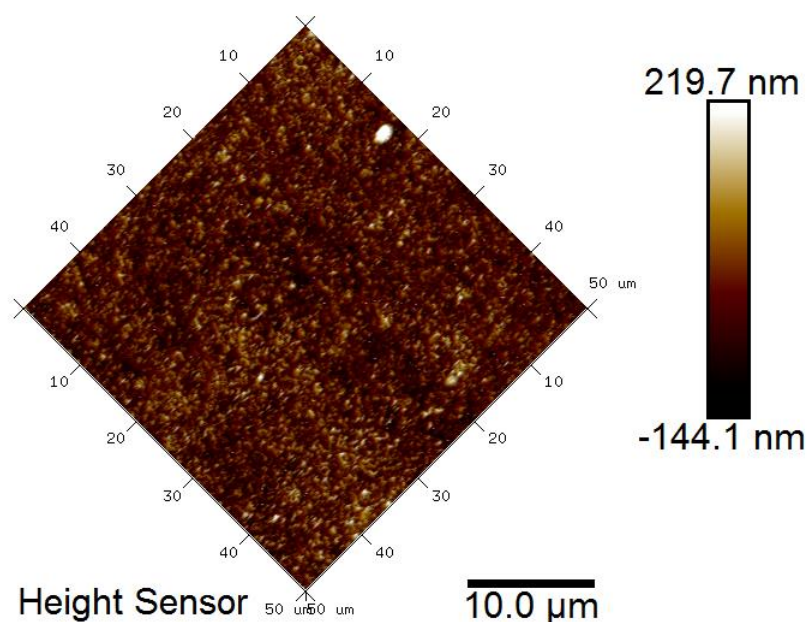


Figure 6.131. Variations of Urbach energies and steepness parameter as a function of Cd content

6.6 Atomic Force Microscopy (AFM) Measurements of ZnO Based Thin Film Materials

6.6.1 Transition Metal Doped $\text{Zn}_{1-x}\text{B}_x\text{O}$ (B=Cu) DMS Nano Thin Film Materials

2D and 3D views of the surface morphology of *Cu*-doped ZnO -based diluted magnetic semiconductor nano thin films are given in Figure 6.132-6.137 (20x20 μm). As seen from AFM images, surface morphology of nano thin films changes with increasing *Cu* doping. While the film surface of *Cu*0.01 sample that has the lowest doping amount is smoother, the film surface of *Cu*0.05 that has maximum doping amount is rougher. Surface flatness significantly affects to the transmittance of films in the ZnO based nano thin films (Tsay et al., 2010). The most fundamental reason for the weak transmittance of the films may be light scattered and reflected from the rough surface of film. Thus increasing surface roughness is reduced transmittance values (Fig. 6.112).



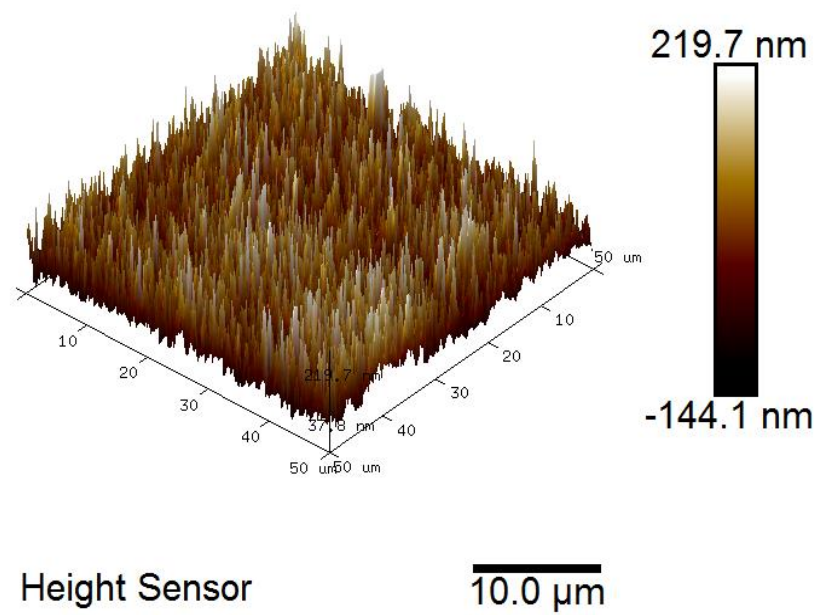
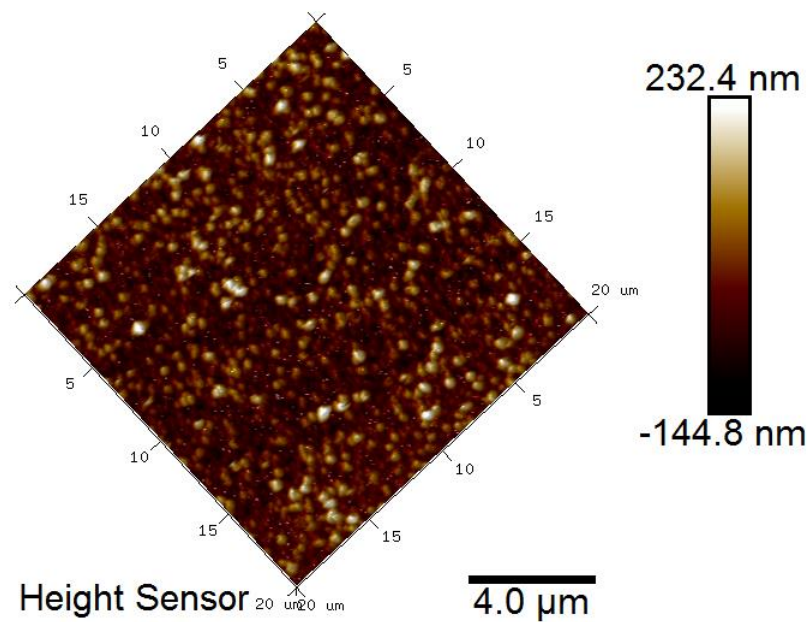


Figure 6.132. AFM analyses of undoped ZnO nano thin film materials



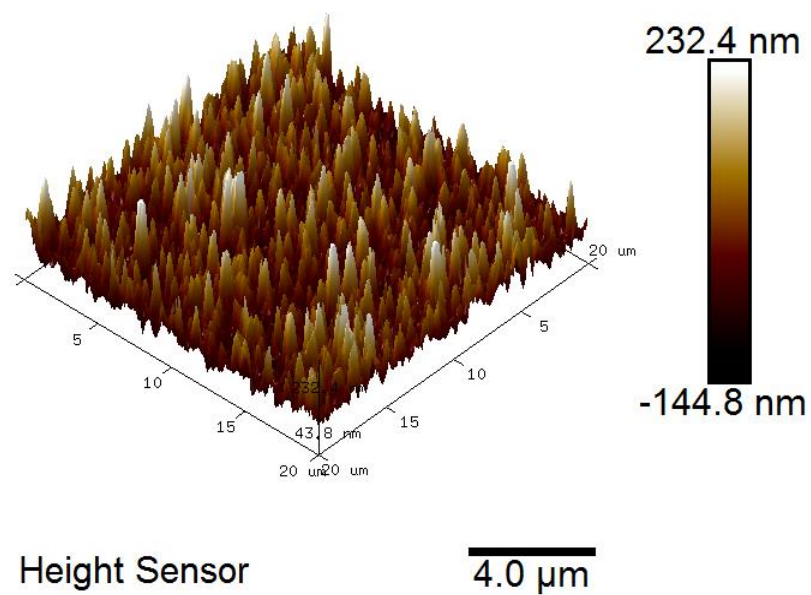
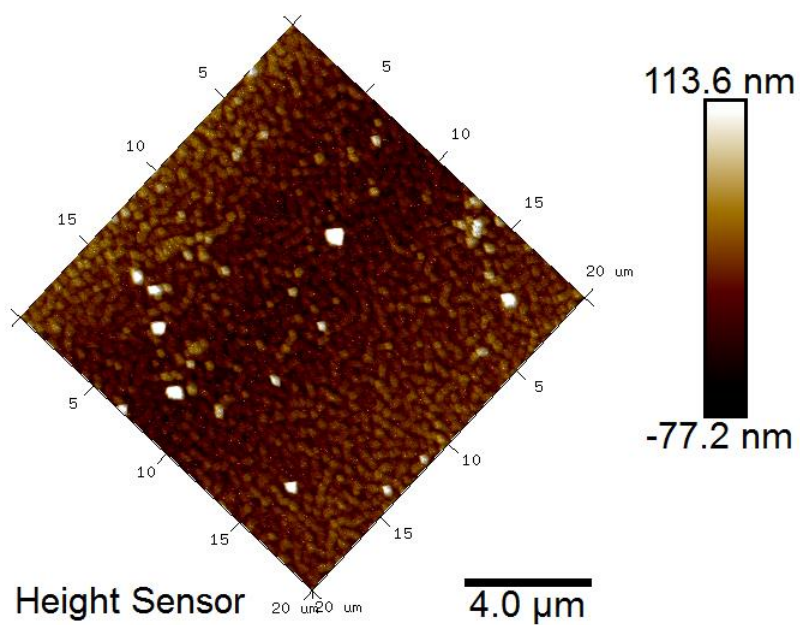
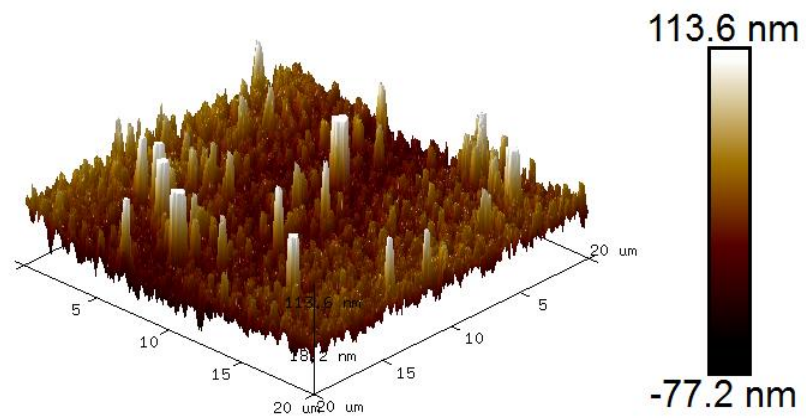


Figure 6.133. AFM analyses of $\text{Zn}_{0.95}\text{Cu}_{0.05}\text{O}$ nano thin film materials

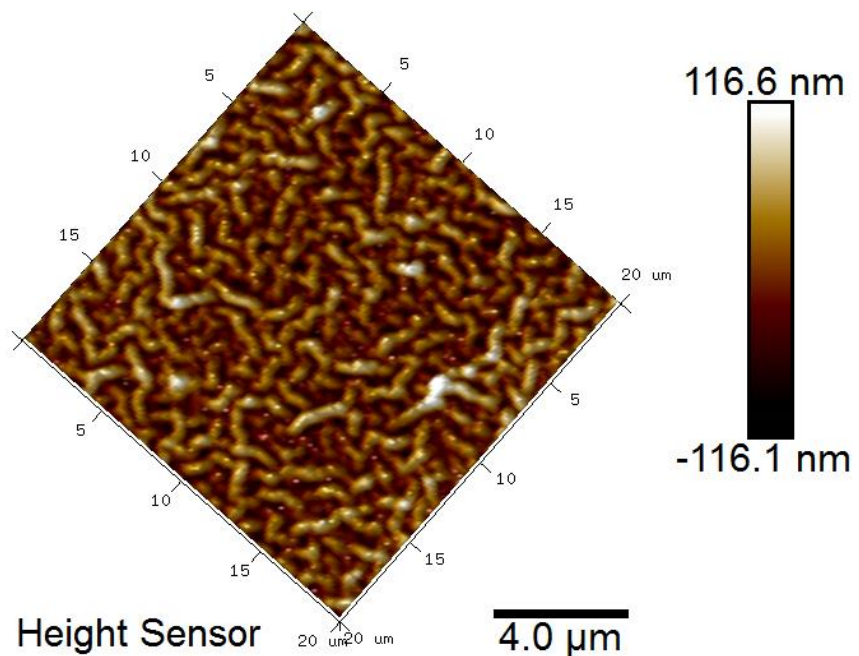




Height Sensor

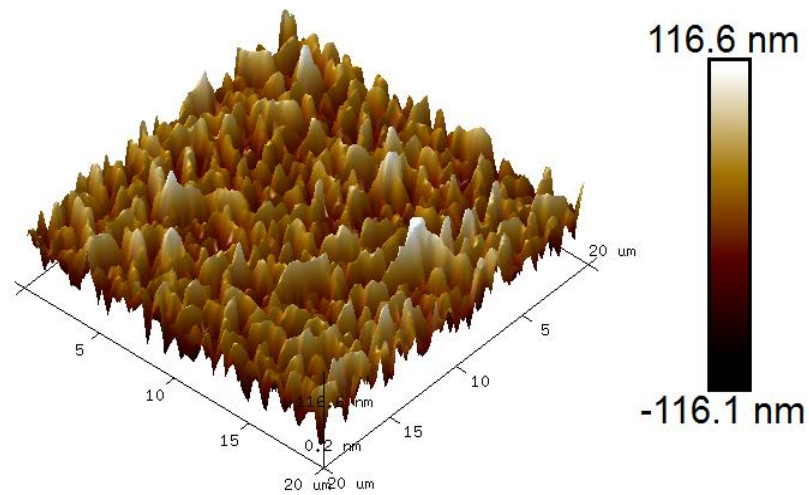
4.0 μm

Figure 6.134. AFM analyses of $\text{Zn}_{0.96}\text{Cu}_{0.04}\text{O}$ nano thin film materials



Height Sensor

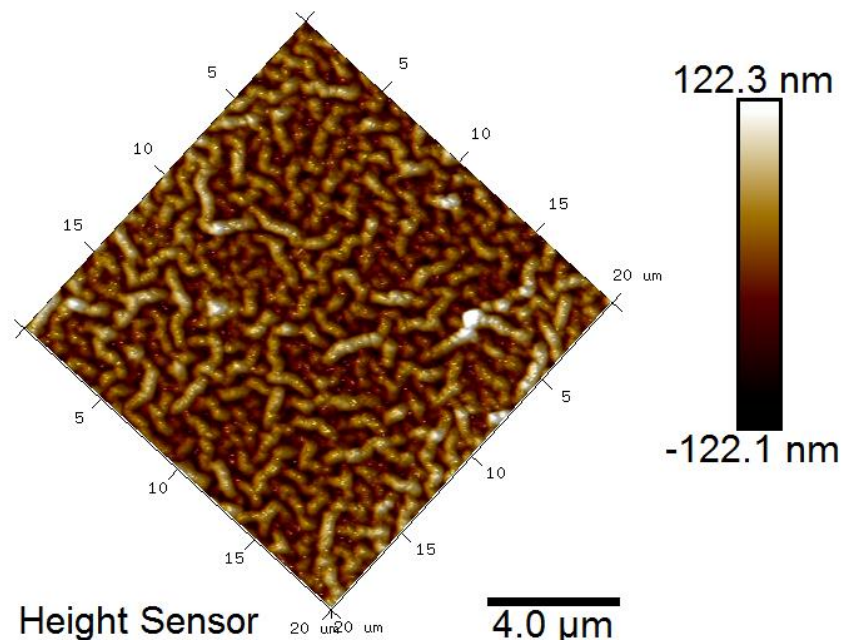
4.0 μm



Height Sensor

4.0 μm

Figure 6.135. AFM analyses of $\text{Zn}_{0.97}\text{Cu}_{0.03}\text{O}$ nano thin film materials



Height Sensor

4.0 μm

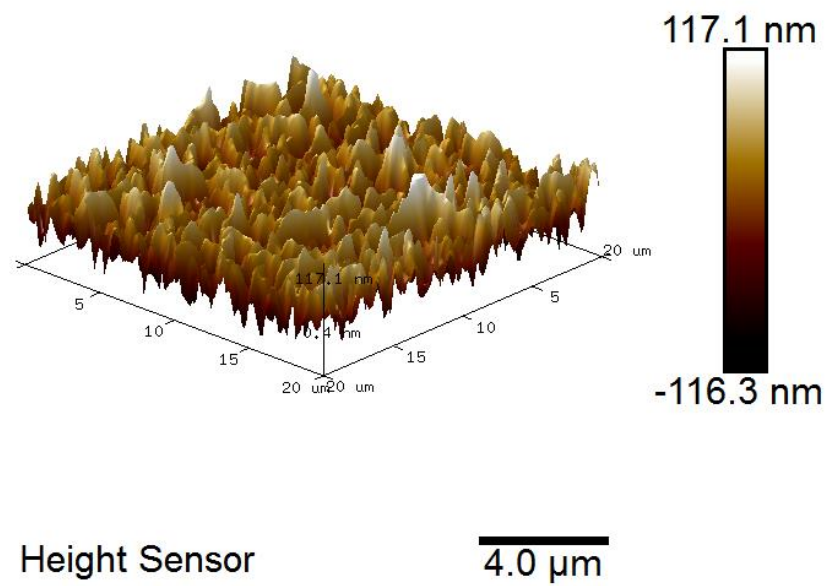
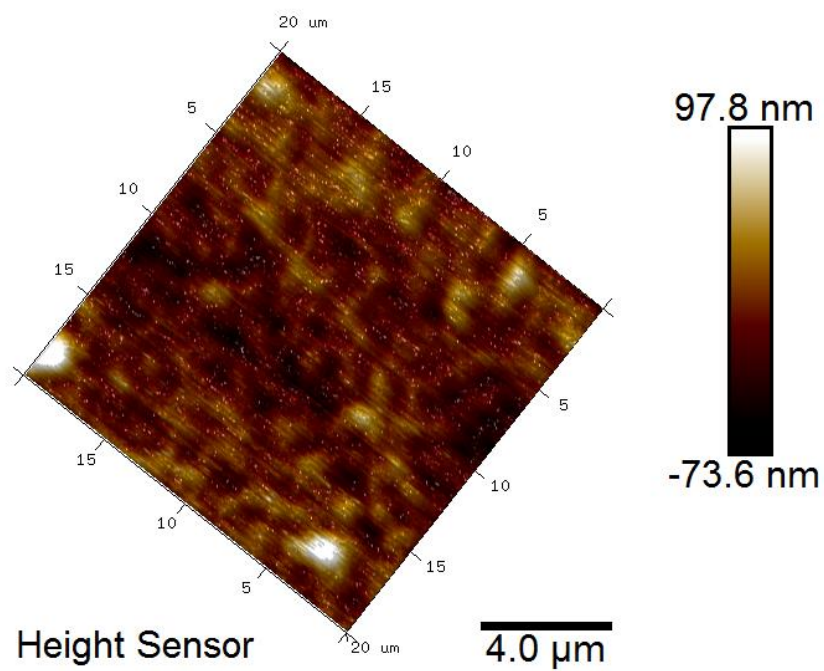


Figure 6.136. AFM analyses of $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ nano thin film materials



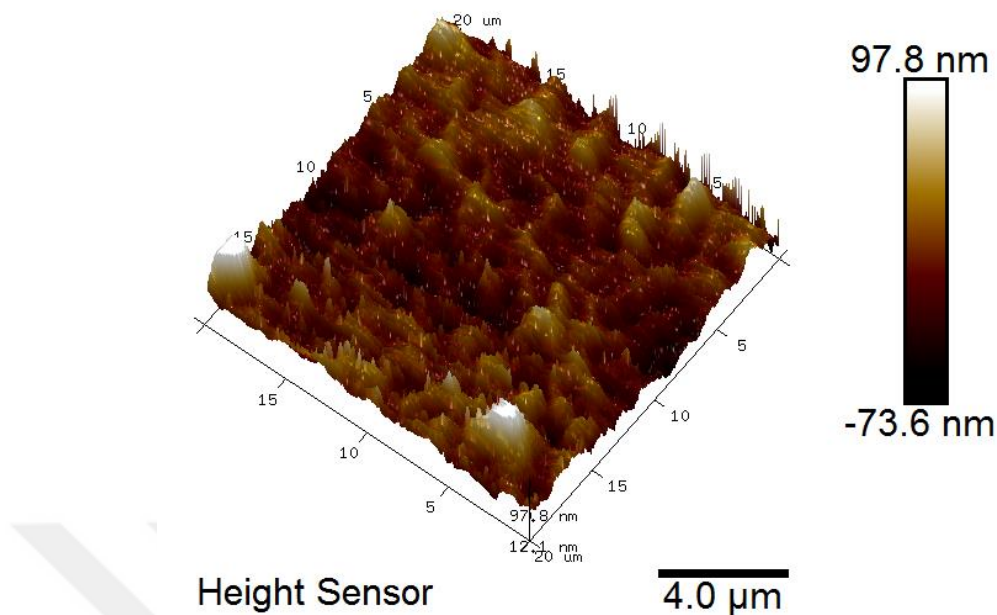


Figure 6.137. AFM analyses of $\text{Zn}_{0.99}\text{Cu}_{0.01}\text{O}$ nano thin film materials

6.6.2 Transition Metal Doped $\text{Zn}_{1-x}\text{B}_x\text{O}$ (B=Co) DMS Nano Thin Film Materials

2D and 3D views of the surface morphology of *Co*-doped ZnO -based diluted magnetic semiconductor nano thin films are given in Figure 6.138-6.142 (20x20 μm). As seen from AFM images, surface morphology of nano thin films changes with increasing *Co* doping. While the film surface of Co0.01 sample that has the lowest doping amount is smoother, the film surface of Co0.05 that has maximum doping amount is rougher. Surface flatness significantly affects to the transmittance of films in the ZnO based nano thin films. The most fundamental reason for the weak transmittance of the films may be light scattered and reflected from the rough surface of film. Thus increasing surface roughness is reduced transmittance values (Fig. 6.116).

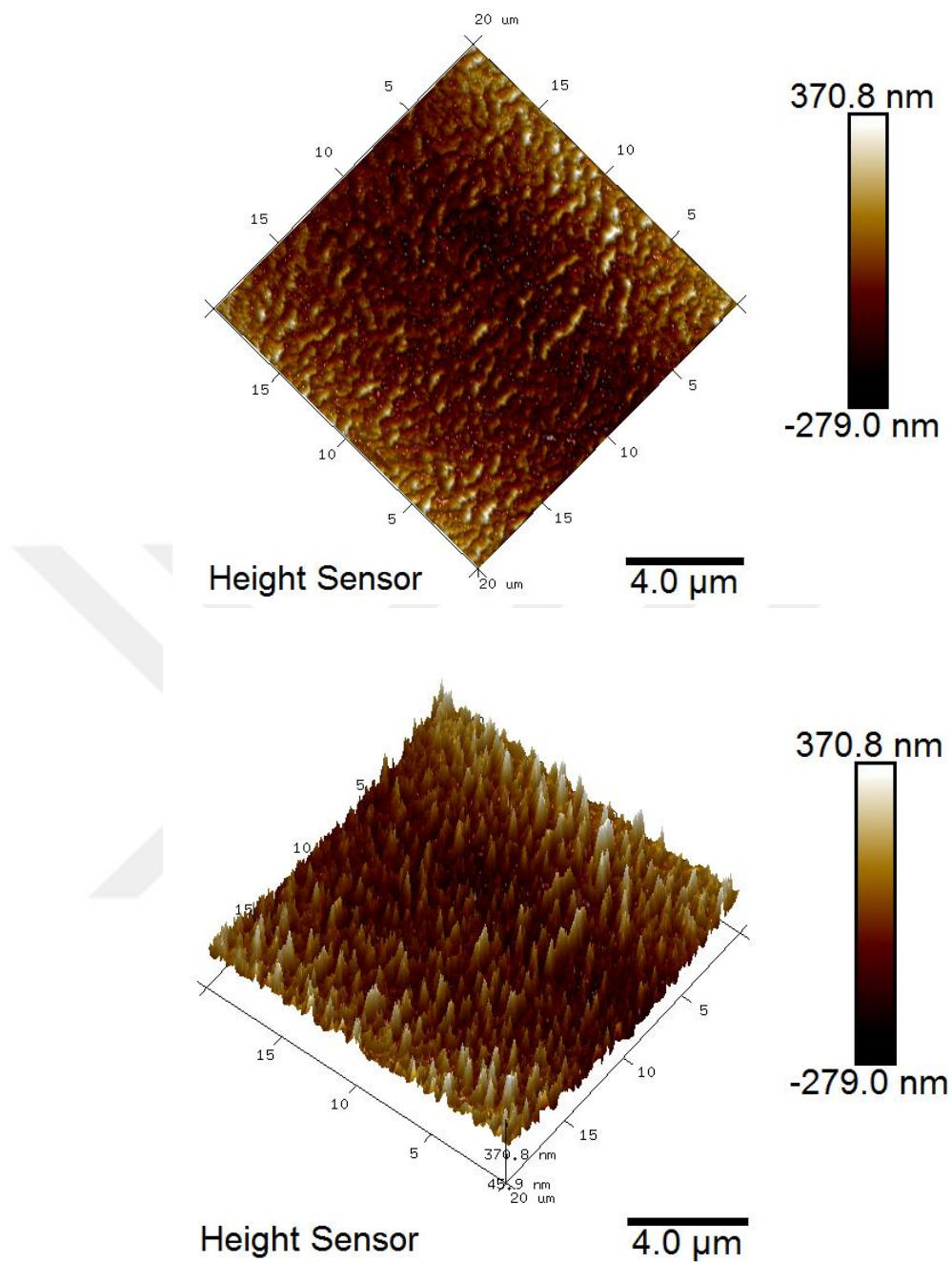


Figure 6.138. AFM analyses of $\text{Zn}_{0.99}\text{Co}_{0.01}\text{O}$ nano thin film materials

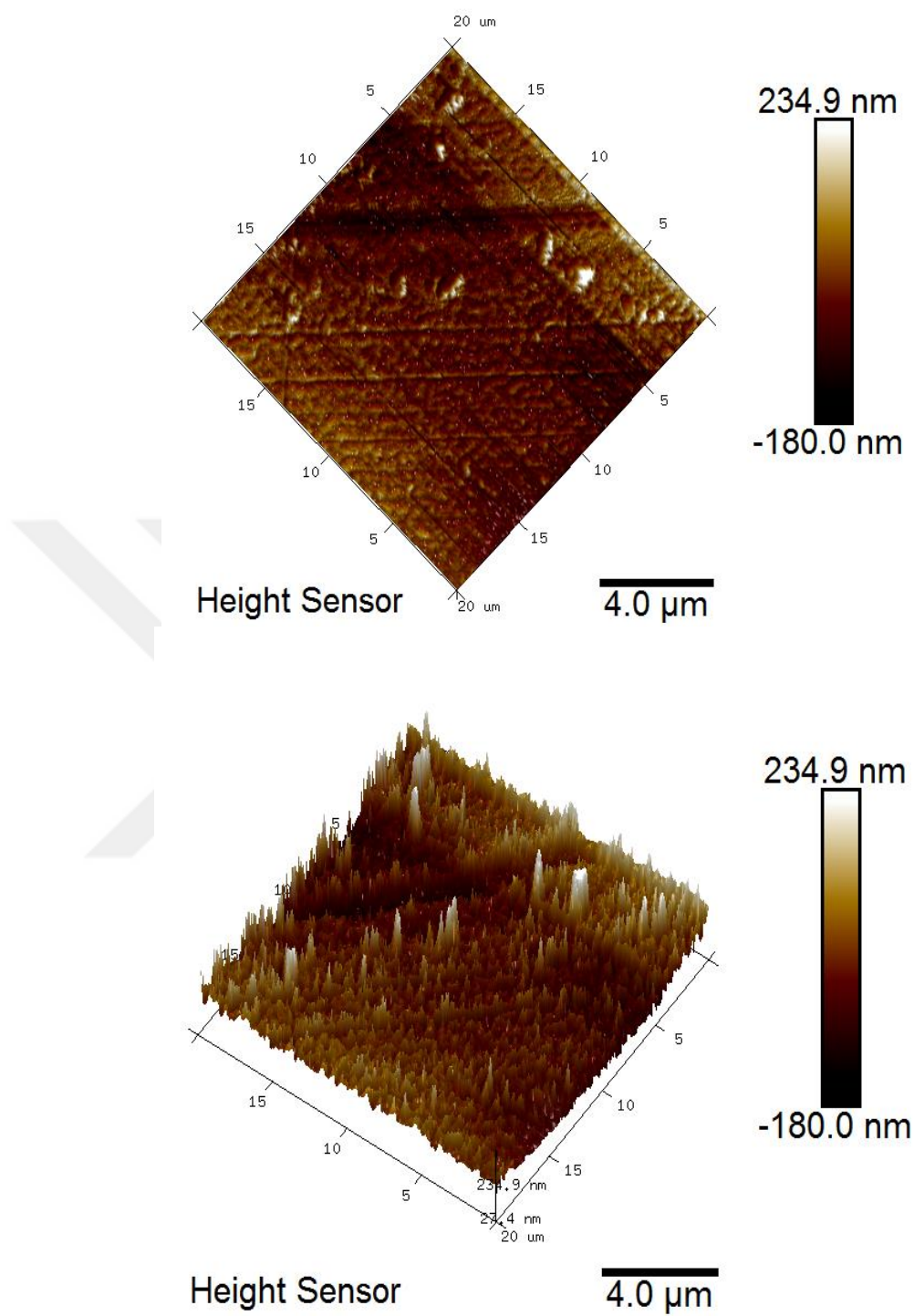


Figure 6.139. AFM analyses of $\text{Zn}_{0.98}\text{Co}_{0.02}\text{O}$ nano thin film materials

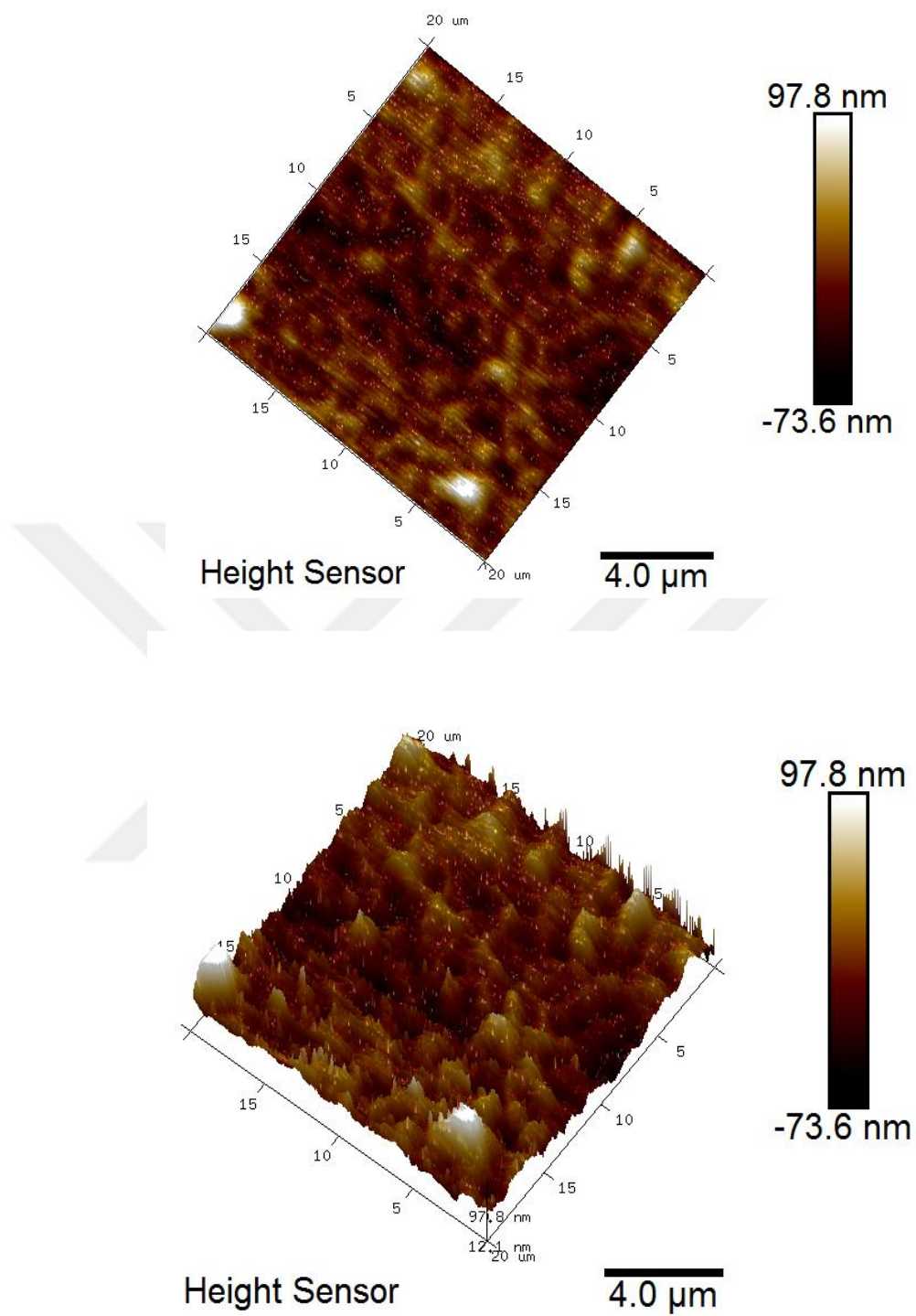


Figure 6.140. AFM analyses of $\text{Zn}_{0.97}\text{Co}_{0.03}\text{O}$ nano thin film materials

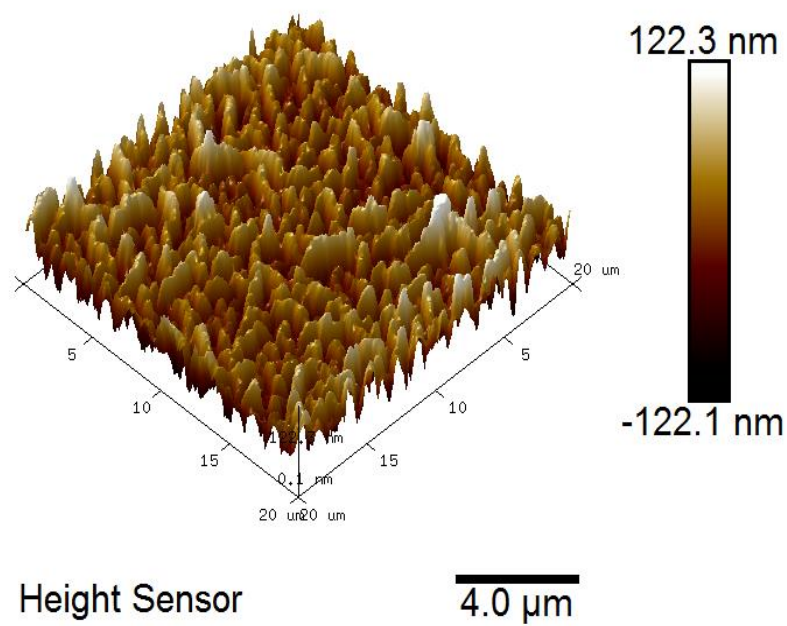
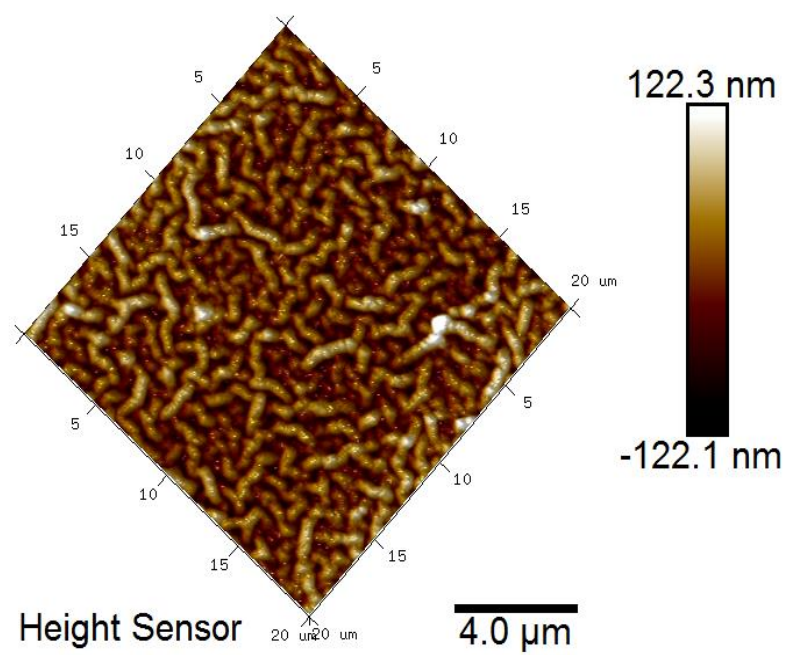


Figure 6.141. AFM analyses of $\text{Zn}_{0.96}\text{Co}_{0.04}\text{O}$ nano thin film materials

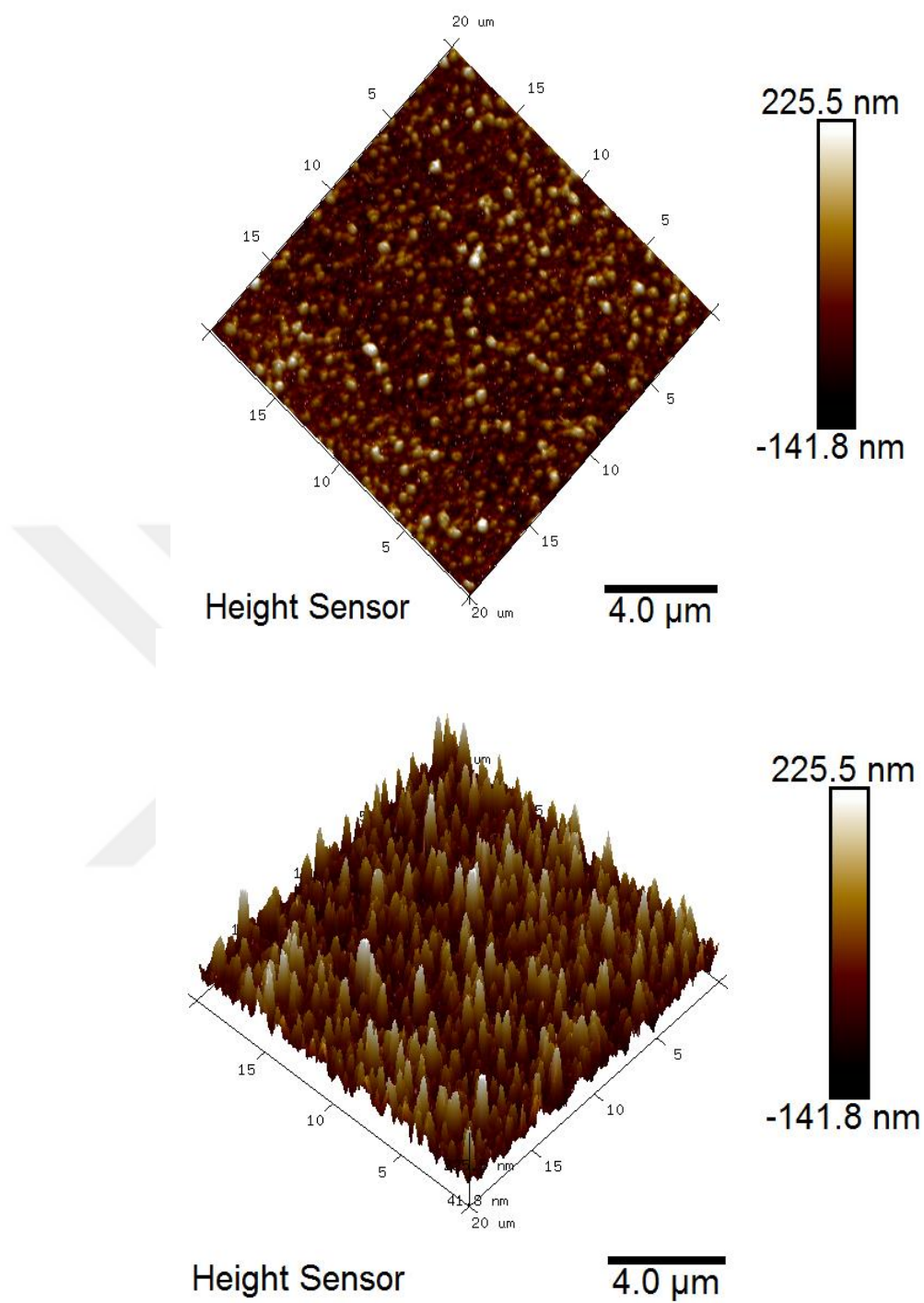


Figure 6.142. AFM analyses of $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ nano thin film materials

6.6.3 Transition Metal Doped $\text{Zn}_{1-x-y}\text{B}_x\text{C}_y\text{O}$ (B=Cu, C=Co) DMS Nano Thin Film Materials

2D and 3D views of the surface morphology of Cu/Co doped ZnO -based diluted magnetic semiconductor nano thin films are given in Figure 6.143-6.147 (20x20 μm). As seen from AFM images, surface morphology of nano thin films changes with increasing Cu/Co doping. While the film surface of Co0.01 sample that has the minimum doping amount is smoother, the film surface of Co0.05 that has maximum doping amount is rougher. Surface flatness significantly affects to the transmittance of films in the ZnO based nano thin films. The most fundamental reason for the weak transmittance of the films may be light scattered and reflected from the rough surface of film. Thus increasing surface roughness is reduced transmittance values (Fig. 6.120)

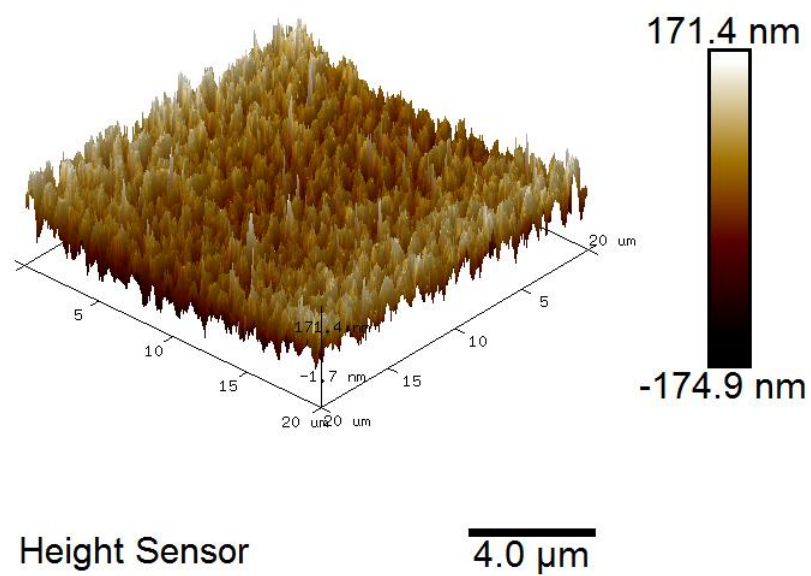
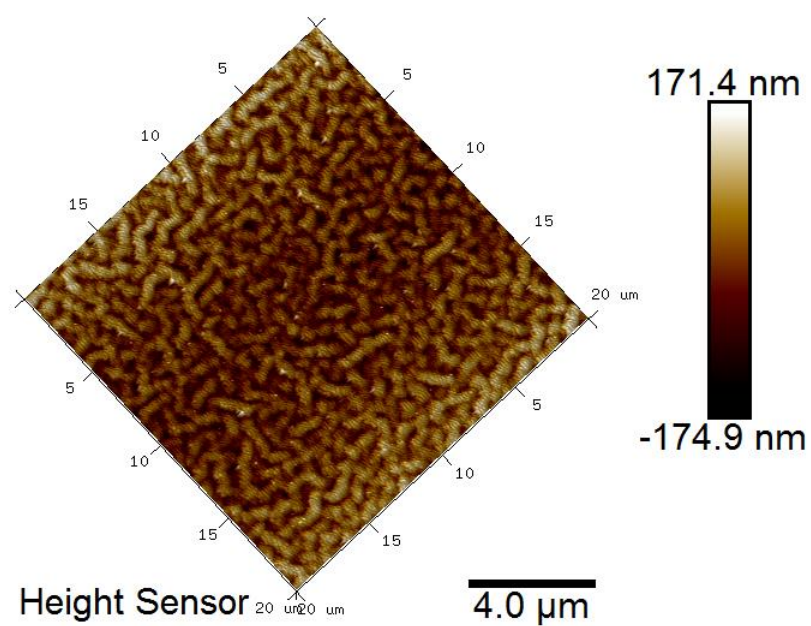


Figure 6.143. AFM analyses of $\text{Zn}_{0.93}\text{Cu}_{0.02}\text{Co}_{0.05}\text{O}$ nano thin film materials

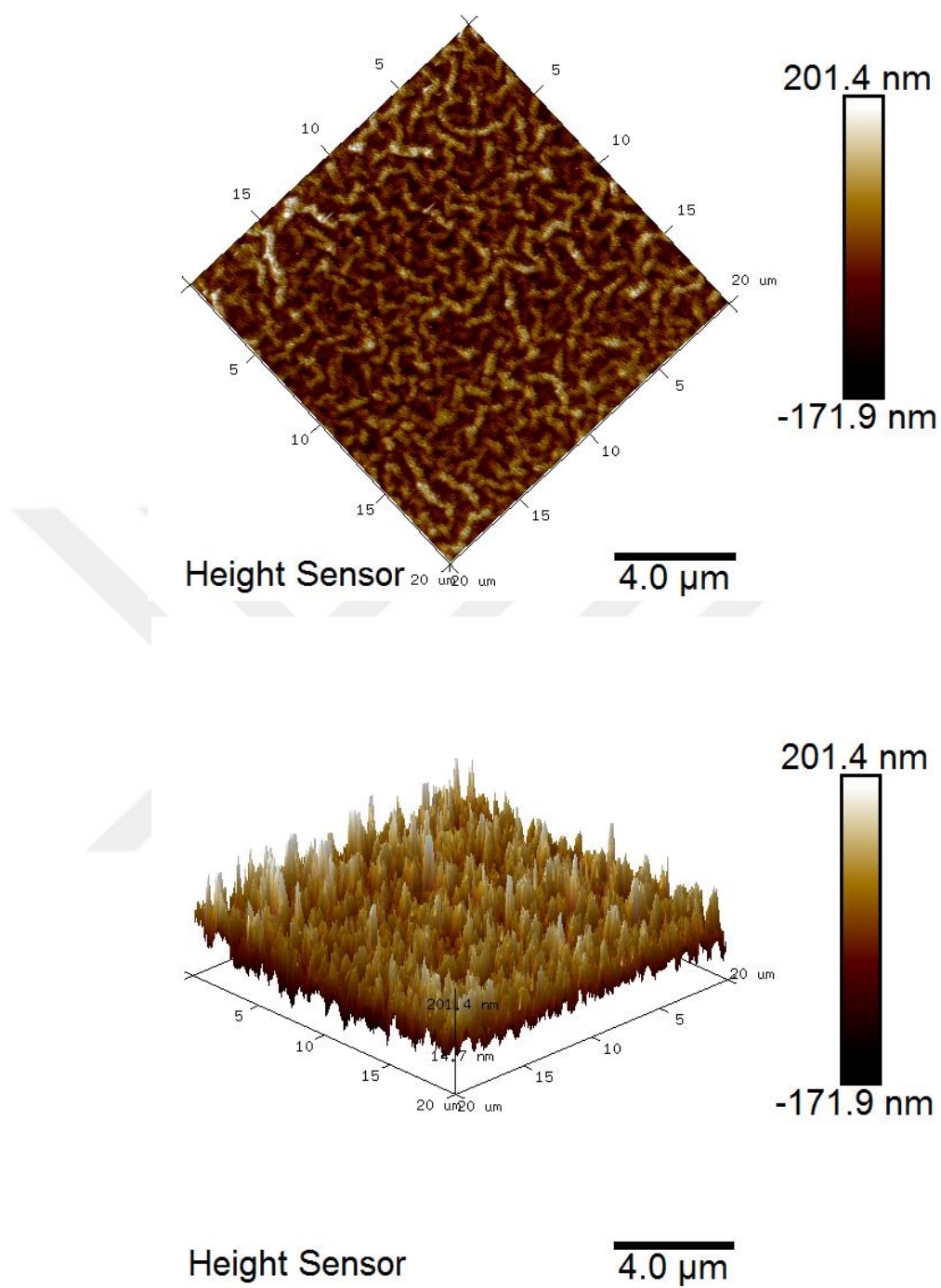


Figure 6.144. AFM analyses of $\text{Zn}_{0.94}\text{Cu}_{0.02}\text{Co}_{0.04}\text{O}$ nano thin film materials

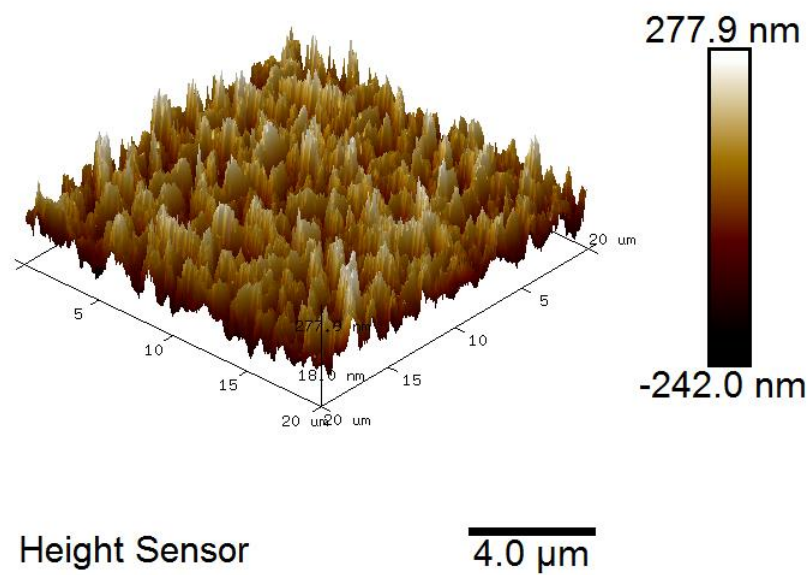
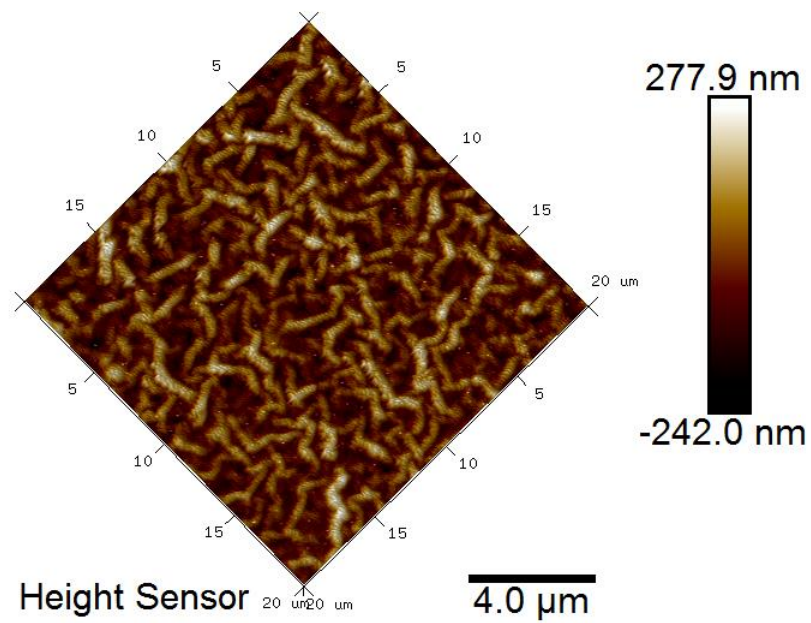


Figure 6.145. AFM analyses of $\text{Zn}_{0.95}\text{Cu}_{0.02}\text{Co}_{0.03}\text{O}$ nano thin film materials

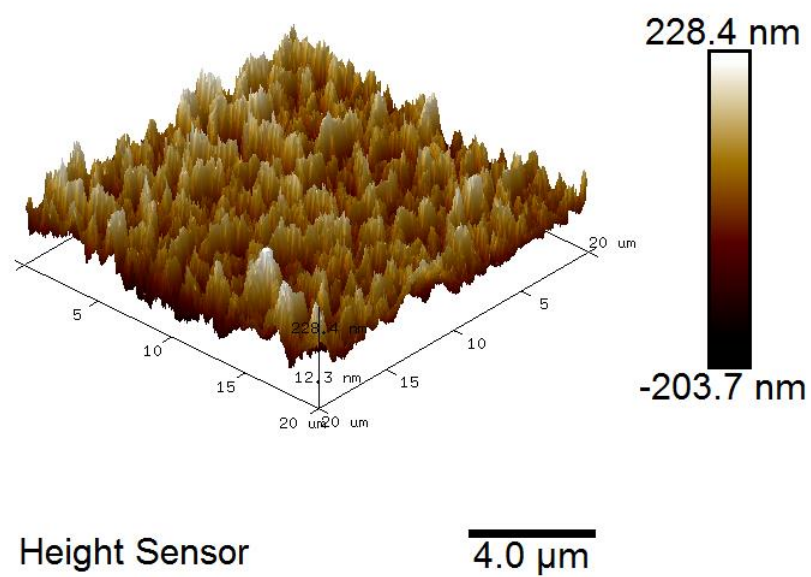
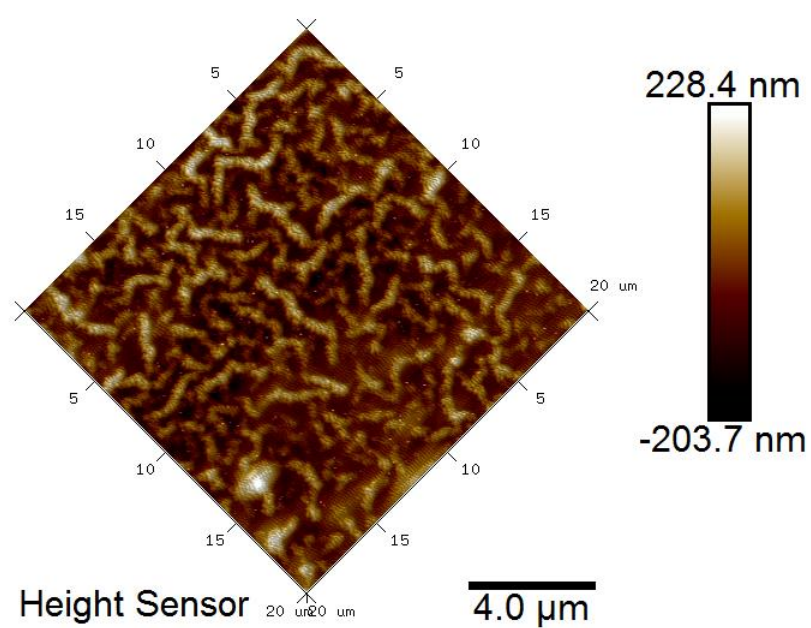


Figure 6.146. AFM analyses of $\text{Zn}_{0.96}\text{Cu}_{0.02}\text{Co}_{0.02}\text{O}$ nano thin film materials

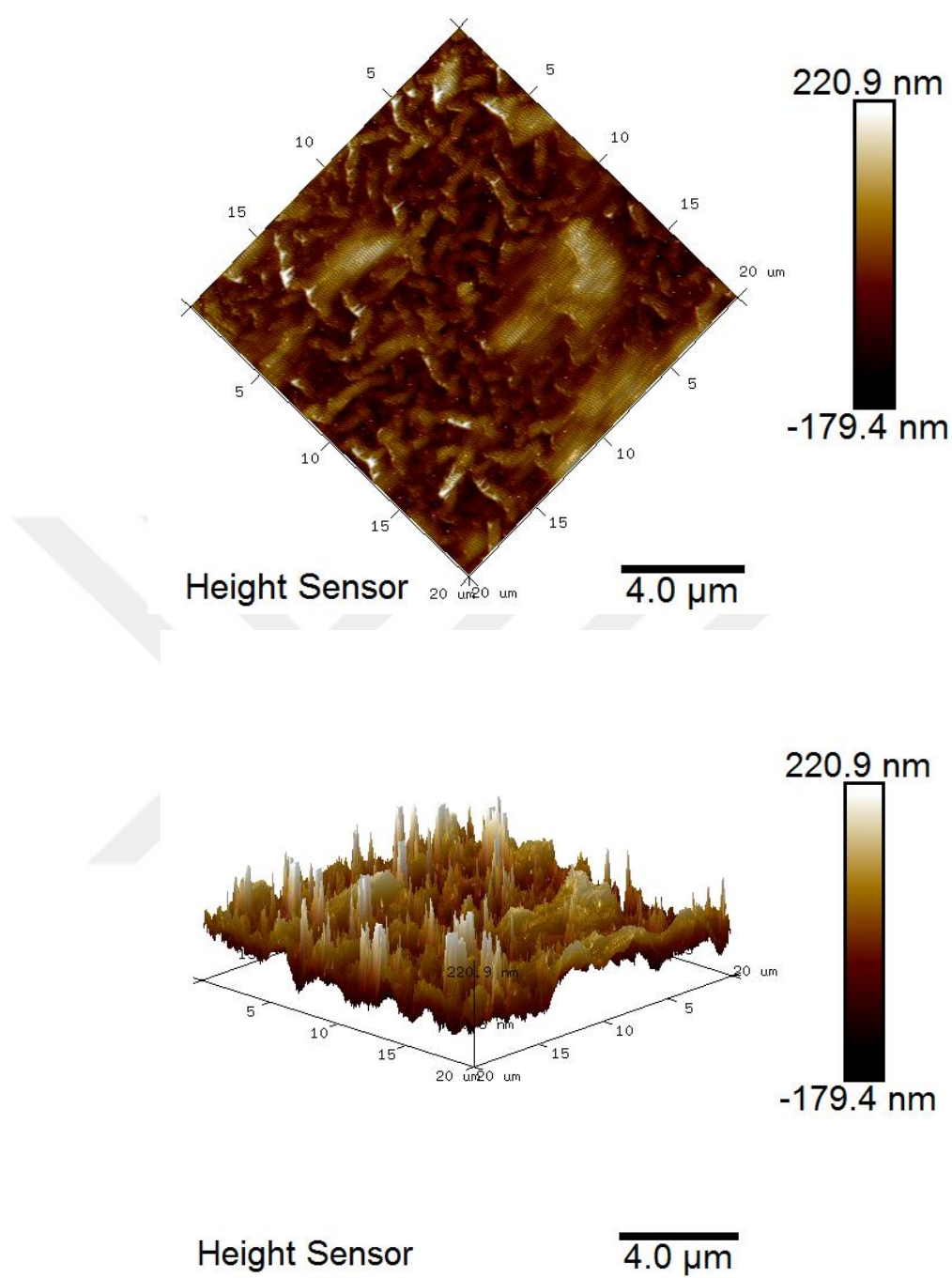


Figure 6.147. AFM analyses of $\text{Zn}_{0.97}\text{Cu}_{0.02}\text{Co}_{0.01}\text{O}$ nano thin film materials

6.6.4. Rare Earth Element Doped $\text{Zn}_{1-x}\text{B}_x\text{O}$ ($\text{B}=\text{Er}$) DMS Thin Film Materials

2D and 3D views of the surface morphology of *Er* doped ZnO-based diluted magnetic semiconductor thin films are given in Figure 6.148-6.152 ($20 \times 20 \mu\text{m}$). As seen from AFM images, surface morphology of thin films changes with increasing *Er* doping. Thus decreasing surface roughness is increased transmittance values compared with undoped ZnO (Fig. 6.124).

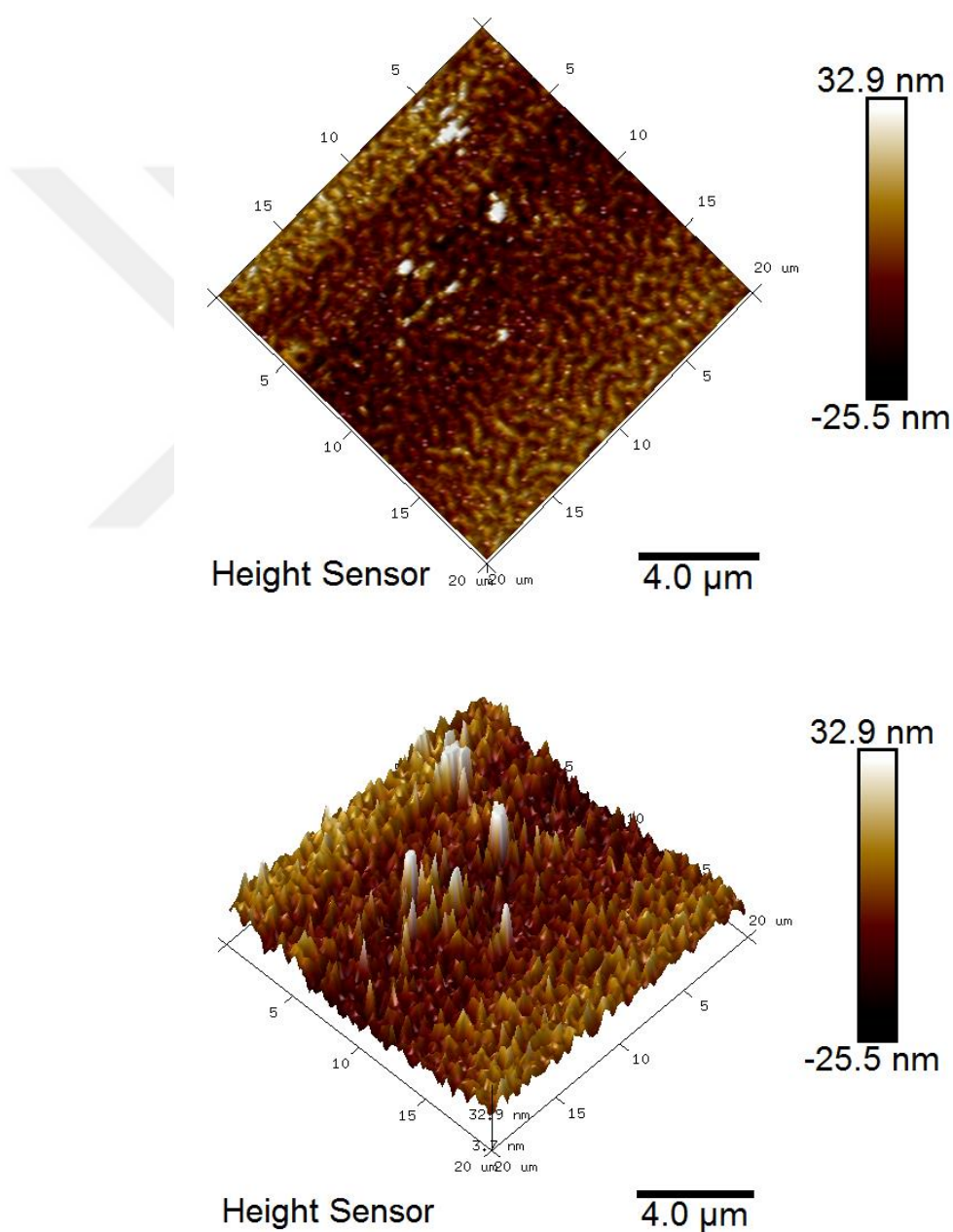


Figure 6.148. AFM analyses of $\text{Zn}_{0.99}\text{Er}_{0.01}\text{O}$ thin film materials

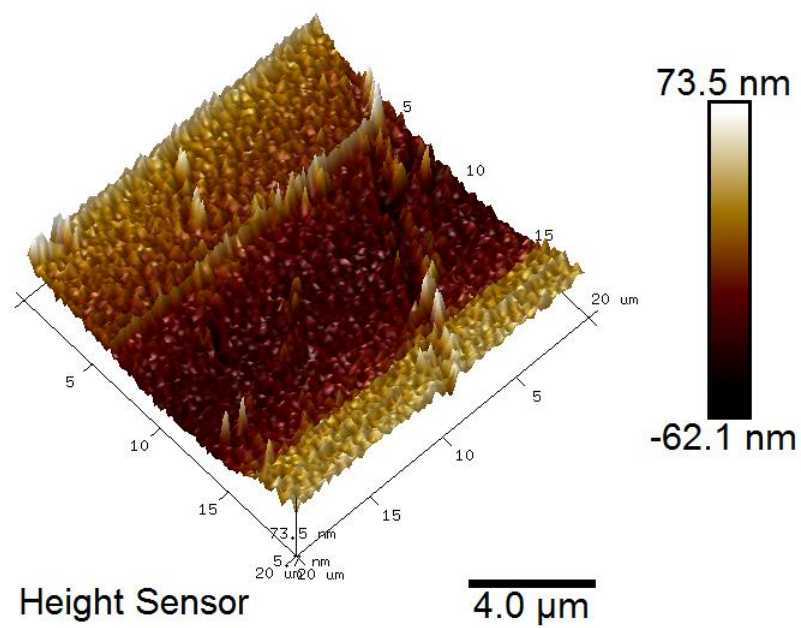
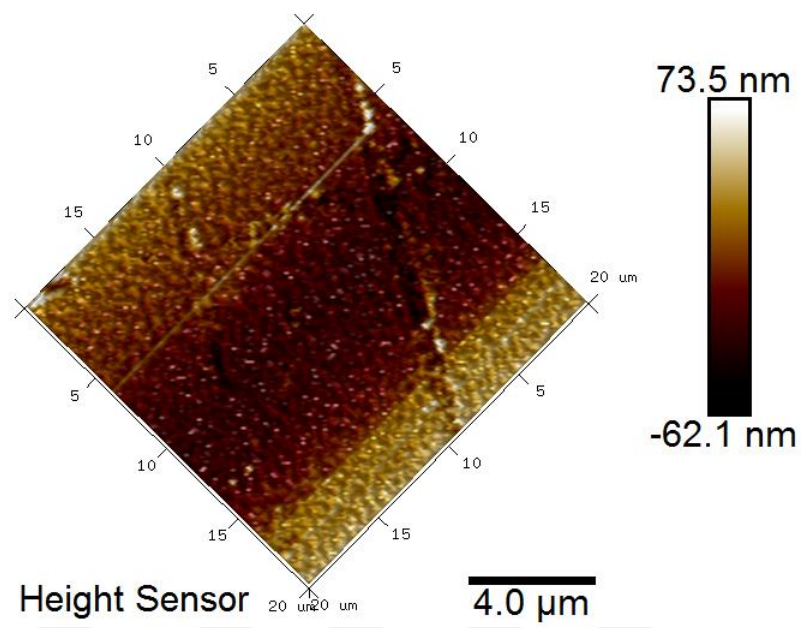


Figure 6.149. AFM analyses of $\text{Zn}_{0.98}\text{Er}_{0.02}\text{O}$ thin film materials

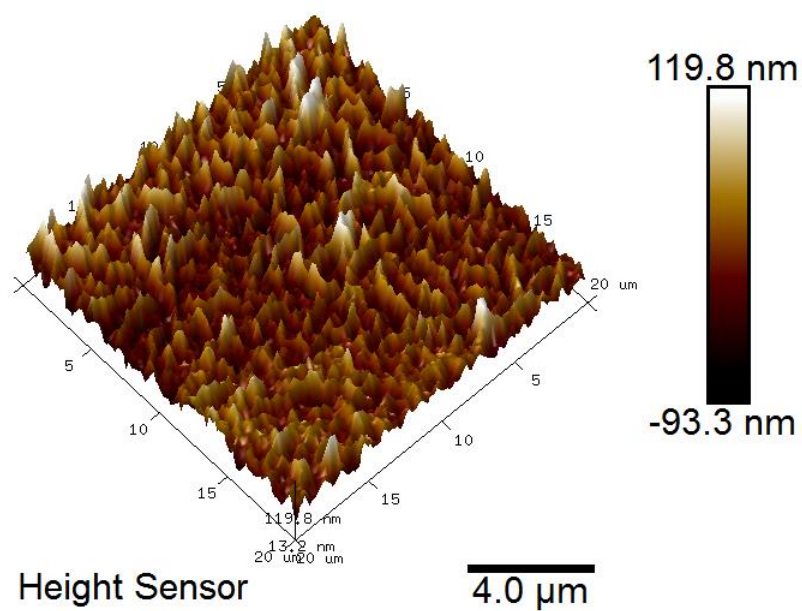
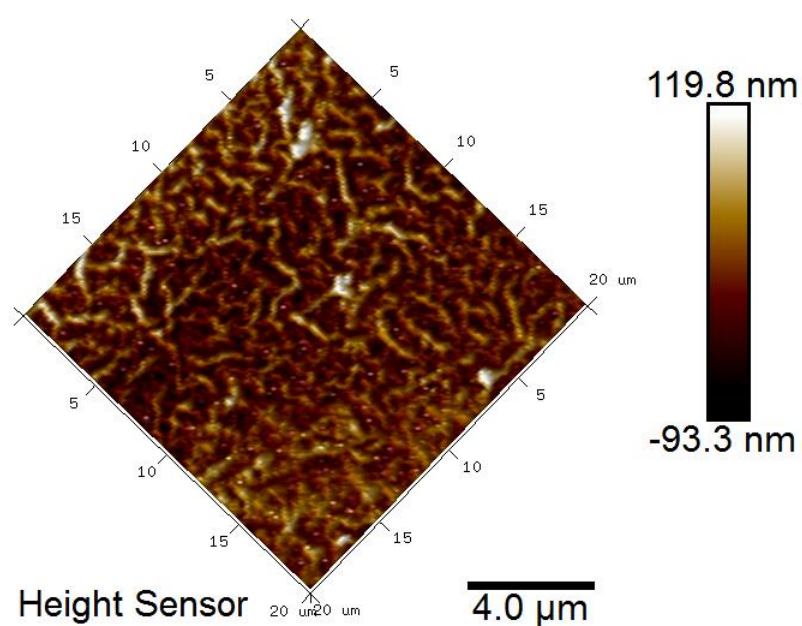


Figure 6.150. AFM analyses of $\text{Zn}_{0.97}\text{Er}_{0.03}\text{O}$ thin film materials

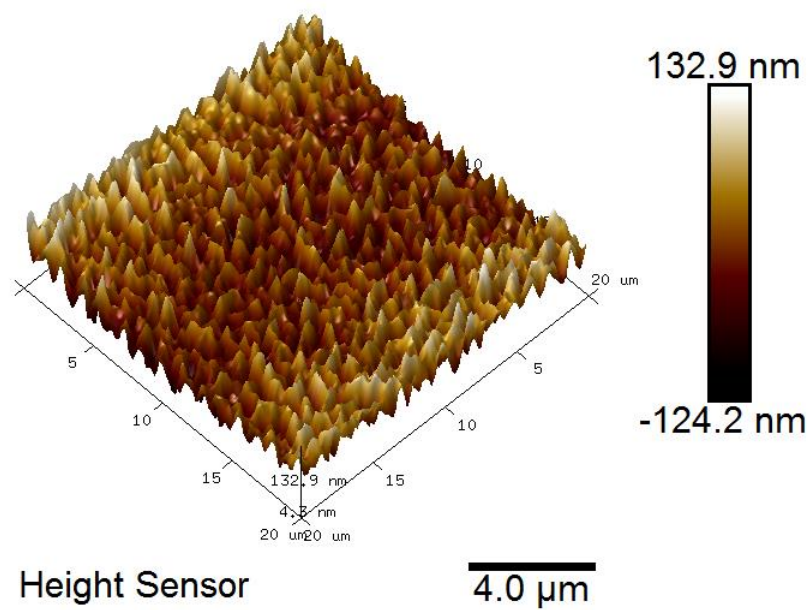
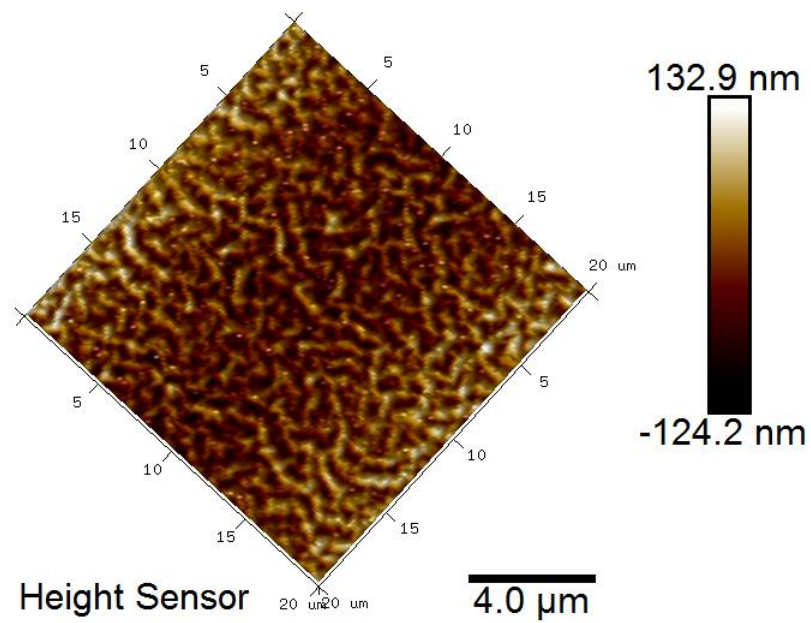


Figure 6.151. AFM analyses of $\text{Zn}_{0.96}\text{Er}_{0.04}\text{O}$ thin film materials

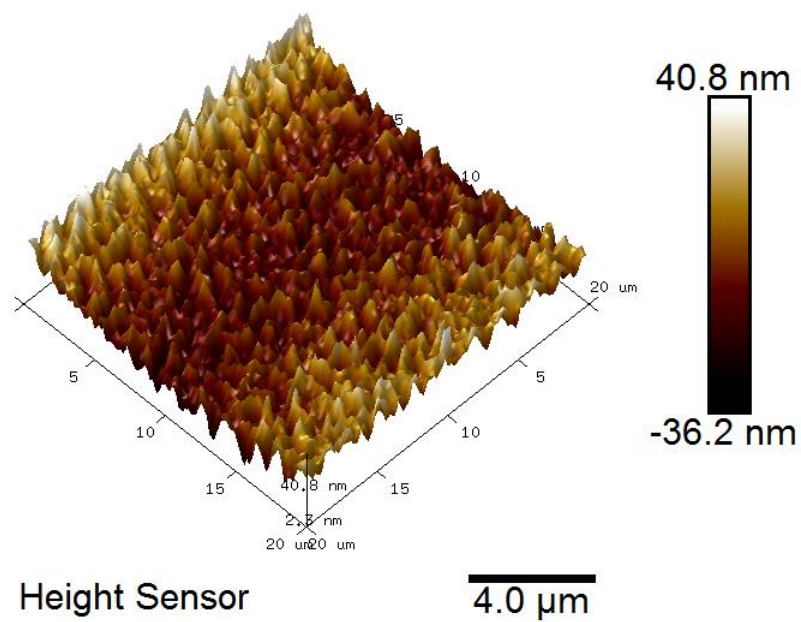
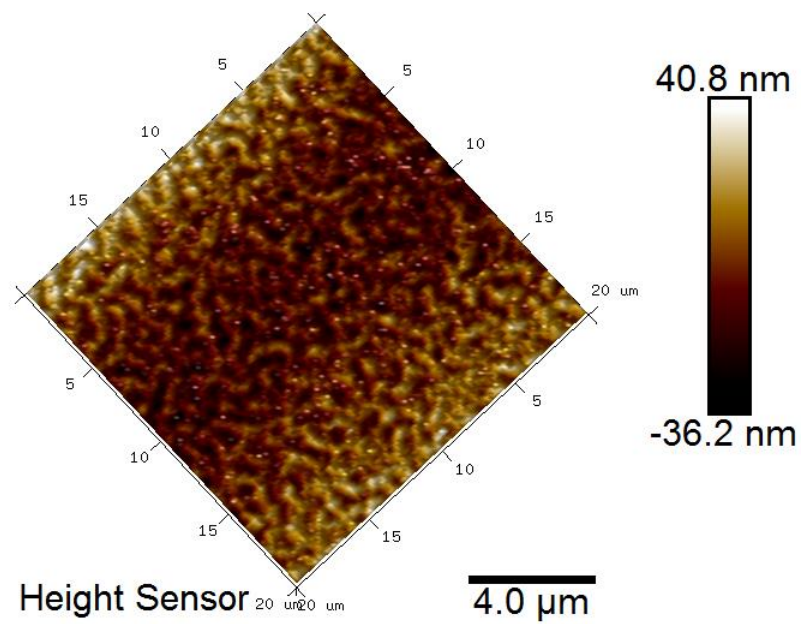


Figure 6.152. AFM analyses of $\text{Zn}_{0.95}\text{Er}_{0.05}\text{O}$ thin film materials

6.6.5. Rare Earth Element Doped $\text{Zn}_{1-x-y}\text{B}_x\text{C}_y\text{O}$ (B=Er, C=Cd) DMS Thin Film Materials

2D and 3D views of the surface morphology of Er/Cd doped ZnO -based diluted magnetic semiconductor nano thin films are given in Figure 6.153-6.157 (20x20 μm). As seen from AFM images, surface morphology of nano thin films changes with increasing Er/Cd doping.

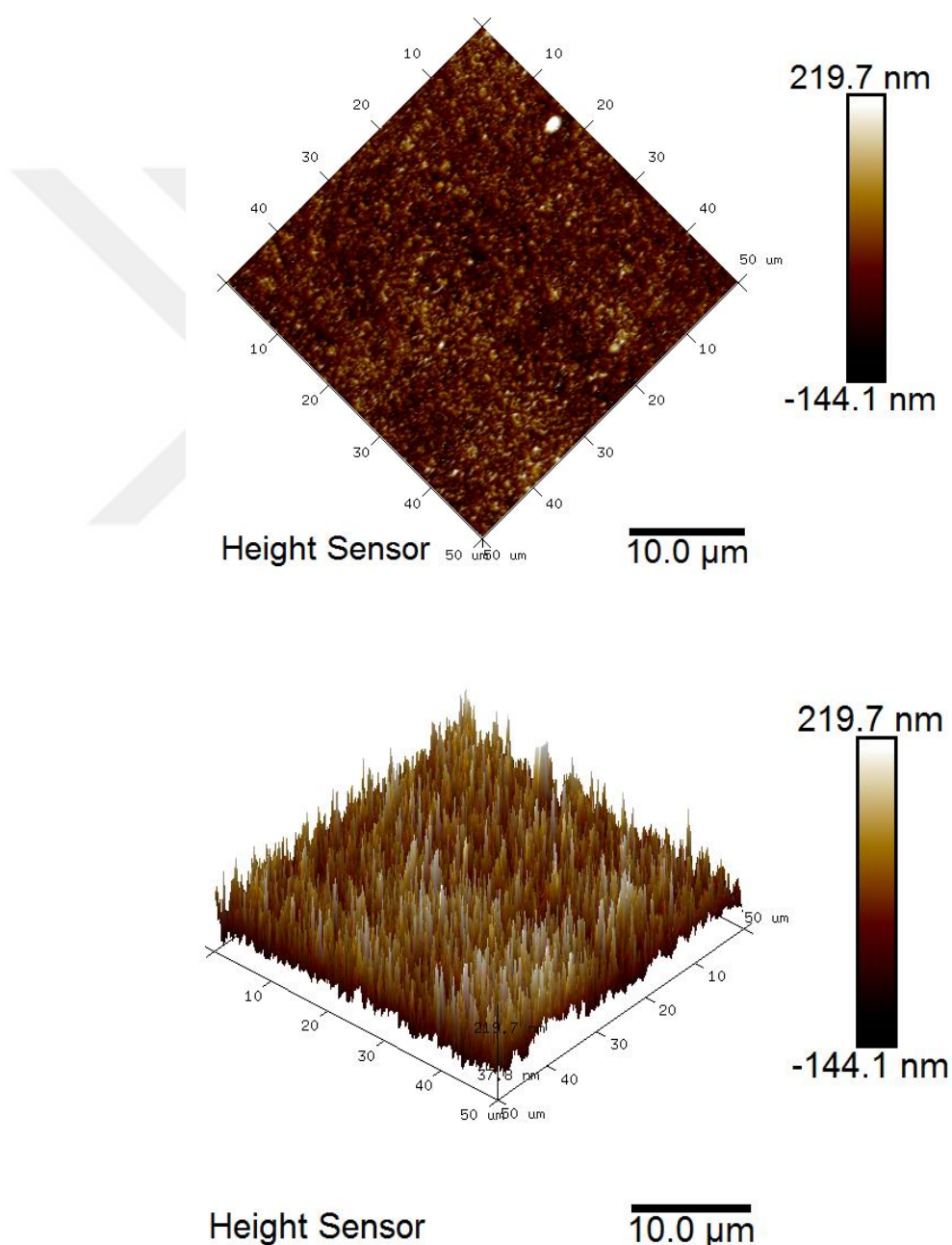


Figure 6.153. AFM analyses of undoped ZnO nano thin film materials

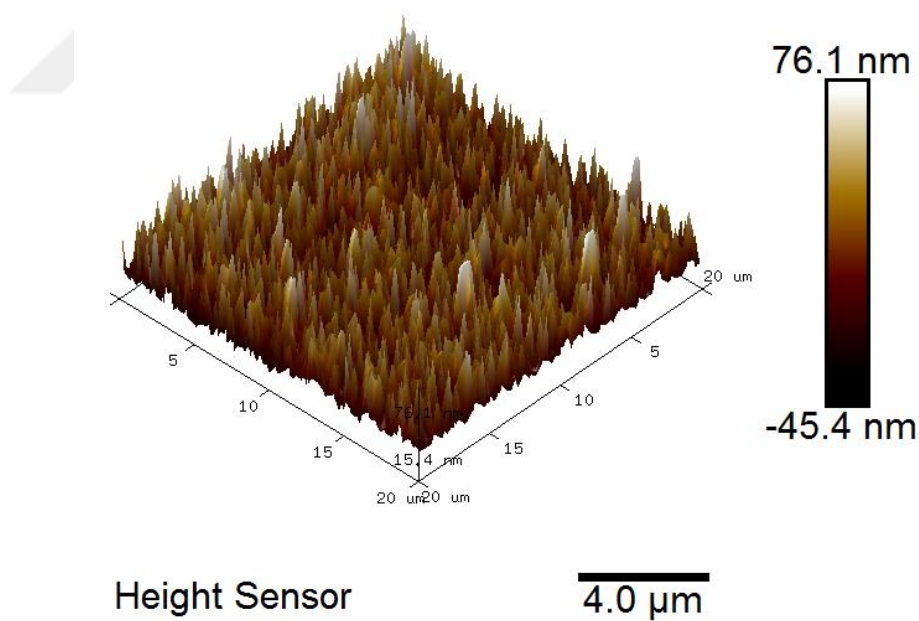
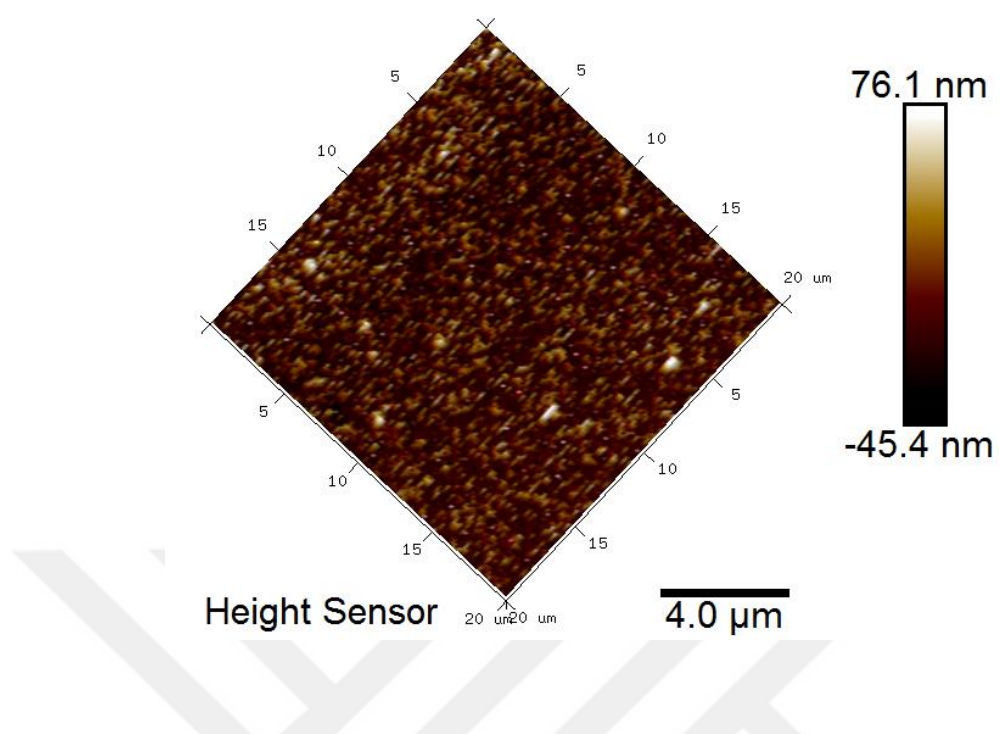


Figure 6.154. AFM analyses of $\text{Zn}_{0.95}\text{Cd}_{0.01}\text{Er}_{0.04}\text{O}$ nano thin film materials

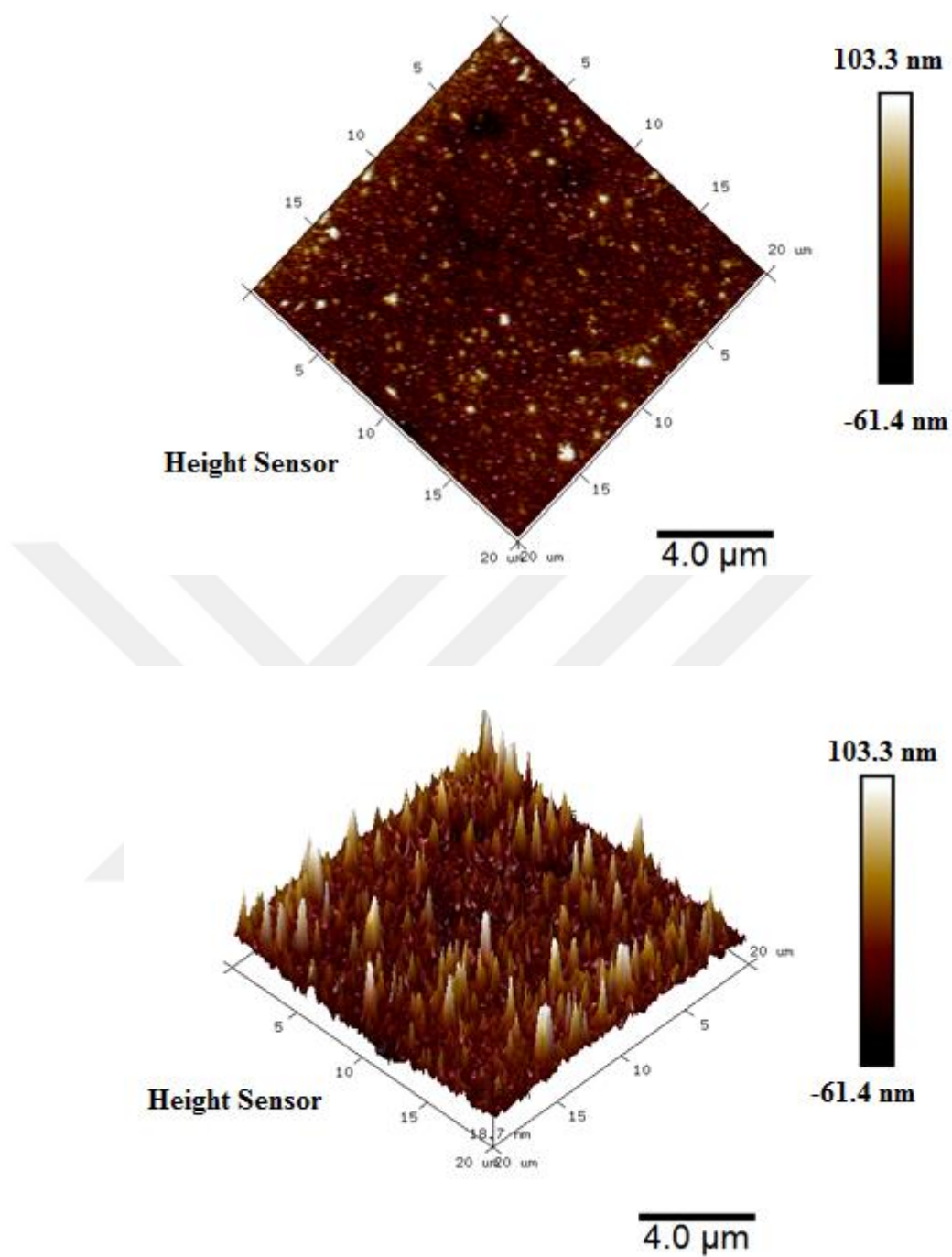


Figure 6.155. AFM analyses of $\text{Zn}_{0.95}\text{Cd}_{0.02}\text{Er}_{0.03}\text{O}$ nano thin film materials

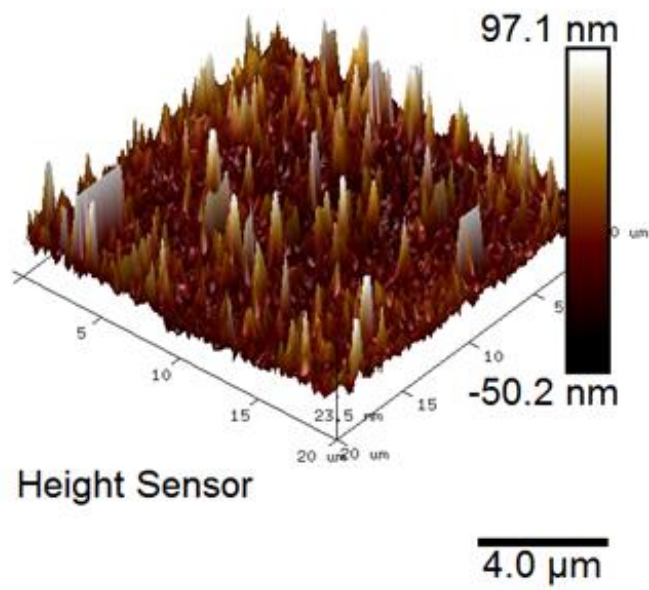
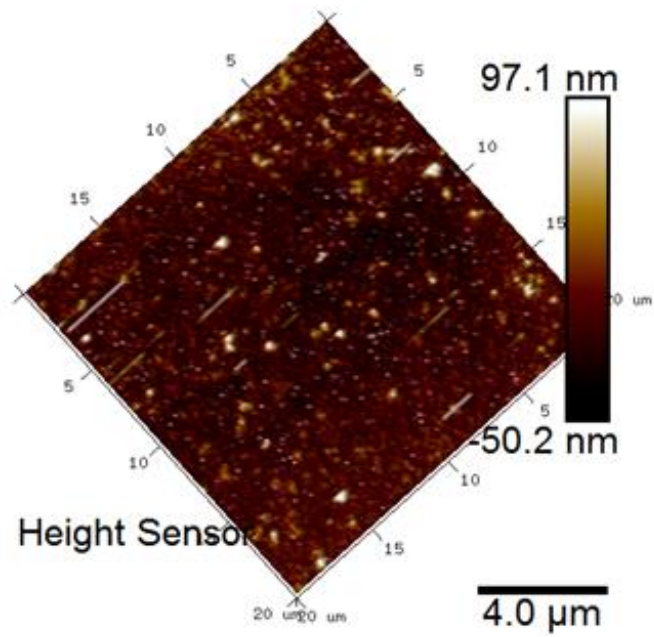


Figure 6.156. AFM analyses of $\text{Zn}_{0.95}\text{Cd}_{0.03}\text{Er}_{0.02}\text{O}$ nano thin film materials

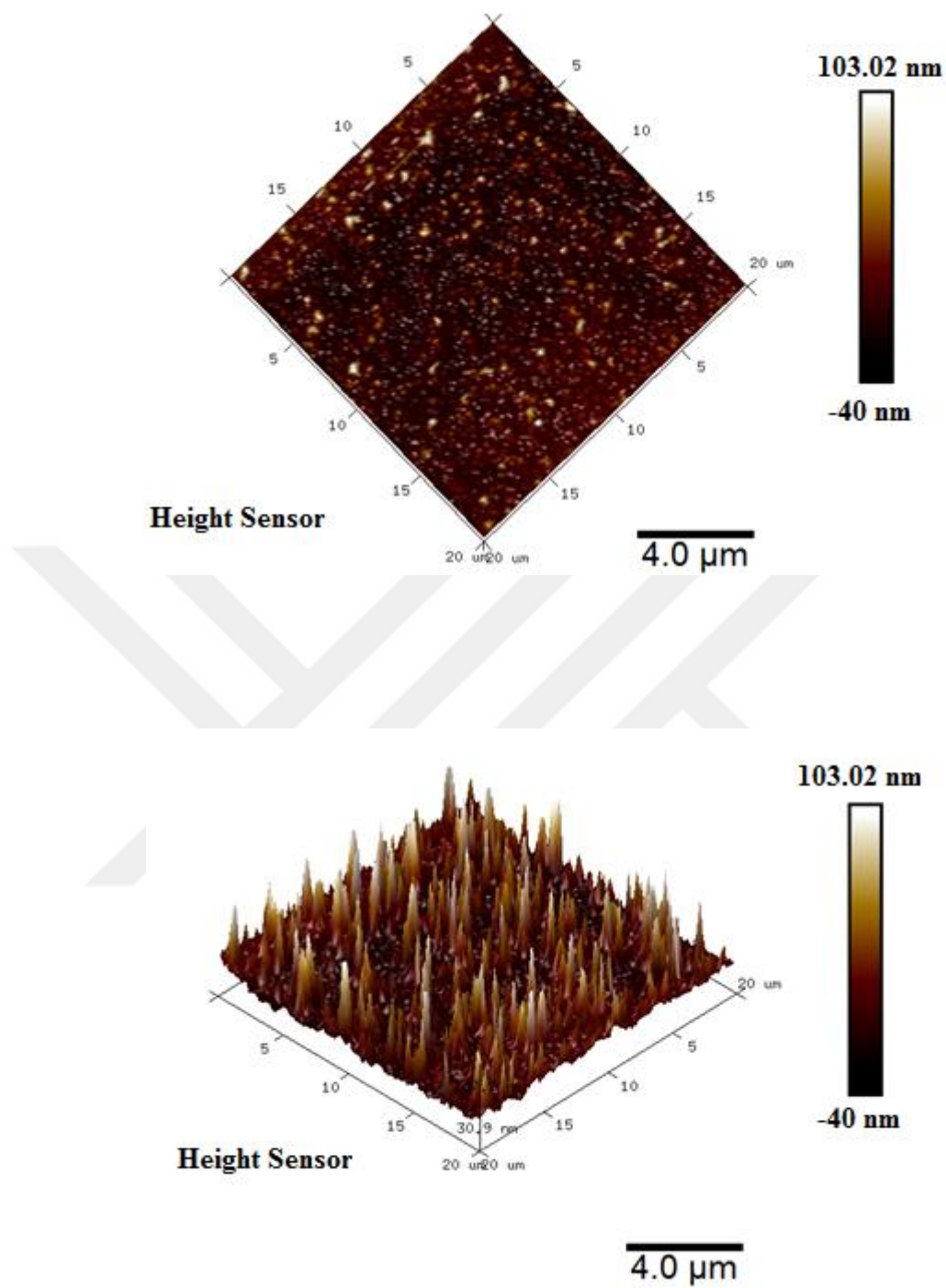


Figure 6.157. AFM analyses of $\text{Zn}_{0.95}\text{Cd}_{0.04}\text{Er}_{0.01}\text{O}$ nano thin film materials

6.7 Magnetic Measurements of $\text{Zn}_{0.95-x}\text{Mg}_x\text{Co}_{0.05}\text{O}$ Nano Bulk Materials

Furthermore, magnetization hysteresis loops are measured at various temperatures (10, 50, 100, 200, and 300 K) so as to characterize the samples. We can see a virtually linear shape in the field range used, $H < 30 \text{ kOe}$ and at all temperatures between 10 and 300 K.

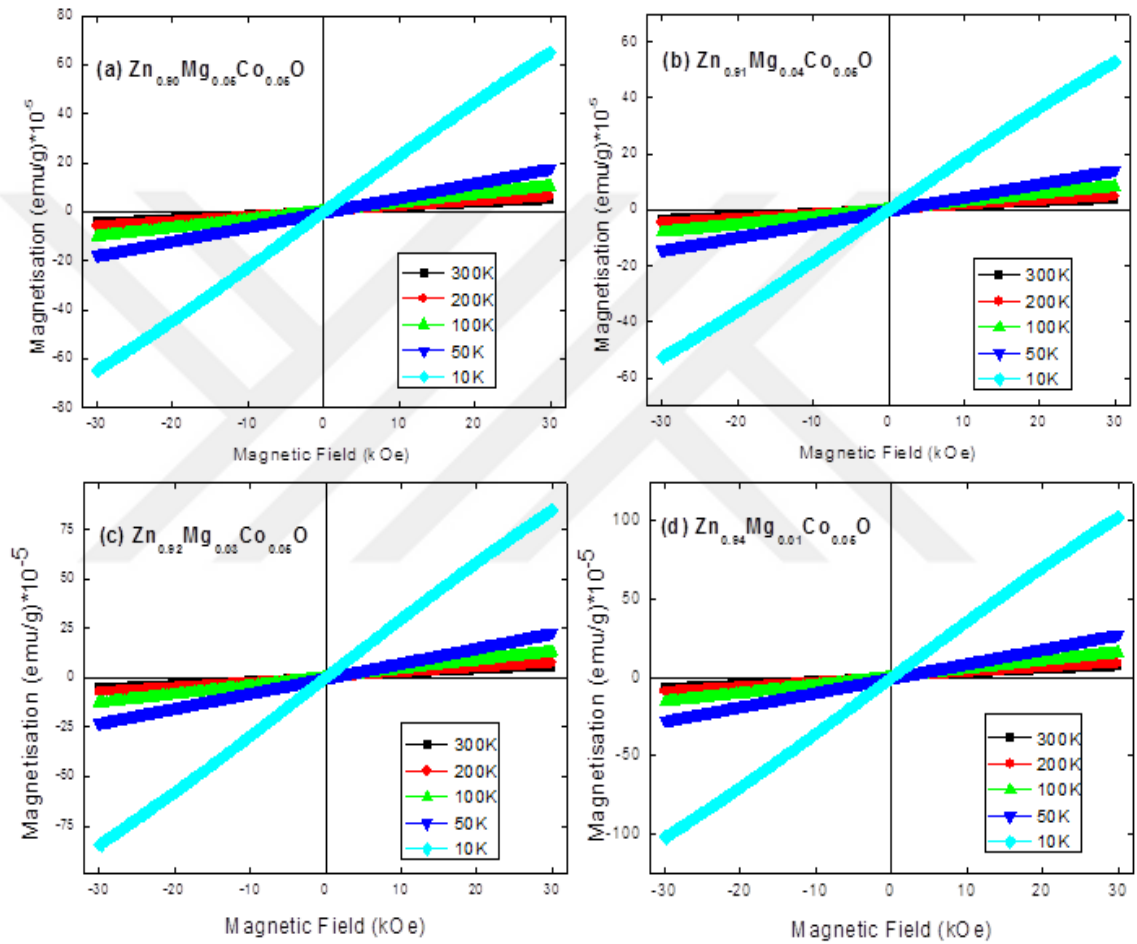


Figure 6.158. Magnetic hysteresis loops of $\text{Zn}_{0.95-x}\text{Mg}_x\text{Co}_{0.05}$ nanoparticles at various temperature

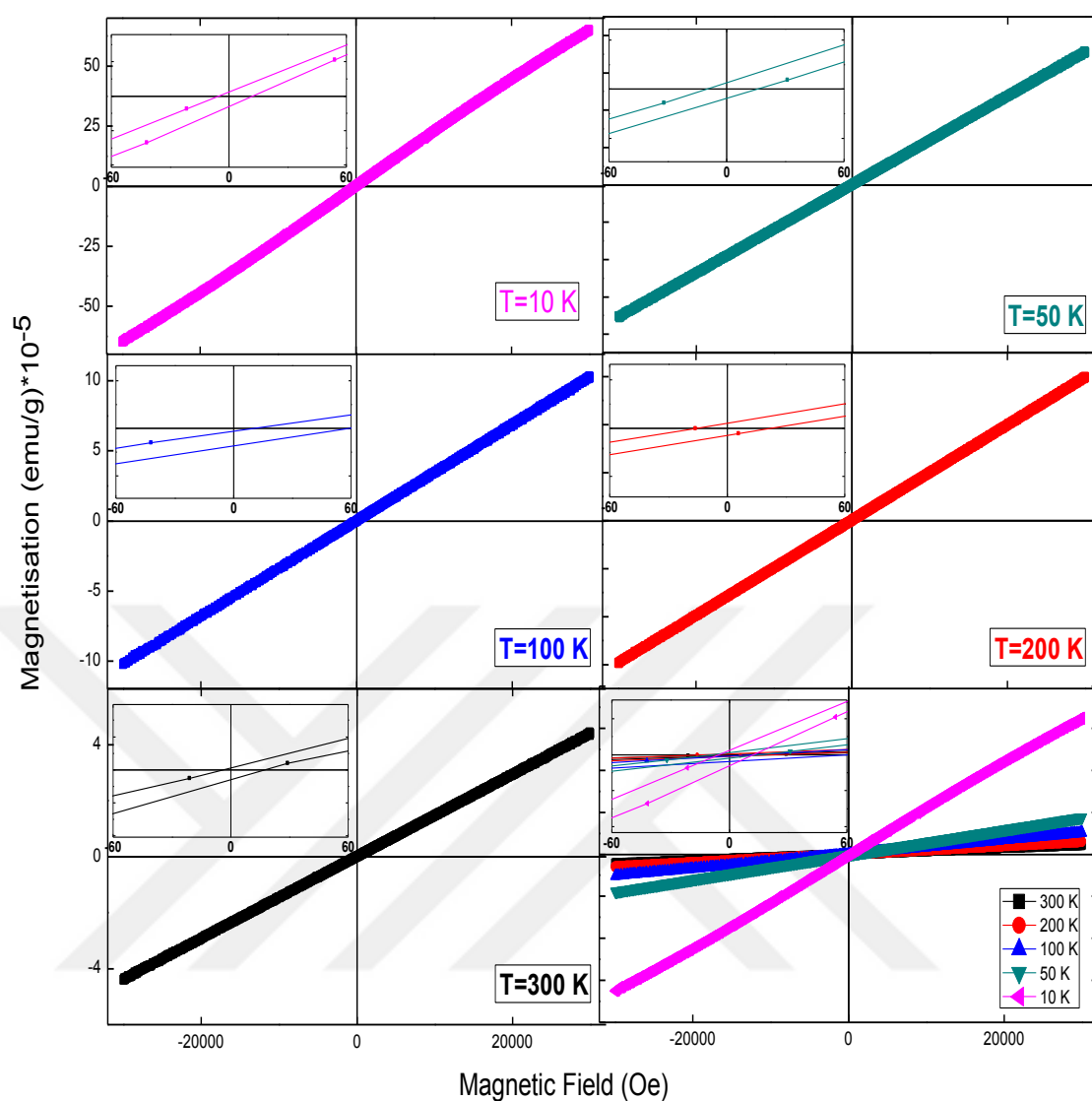


Figure 6.159. M-H loops of $\text{Zn}_{0.90}\text{Mg}_{0.05}\text{Co}_{0.05}$ 800°C 30 minute are drawn at some selected temperature. Innermost small graphics, which are built into the great graphics, show the zoomed part of M-H curves for corresponding temperature with a magnetic field scale of ± 60 Oe.

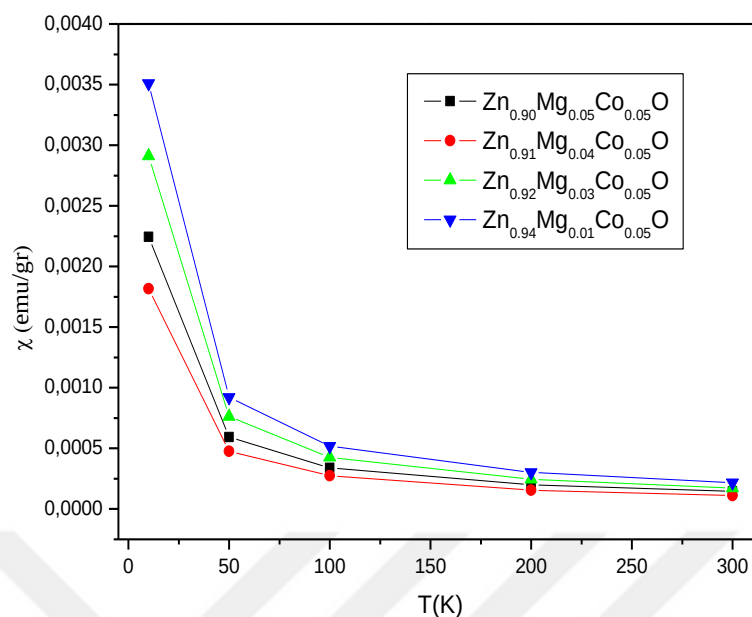


Figure 6.160. Temperature dependence of the susceptibility of the samples

6.7.1 ZFC-FC Measurements of Zn_{0.95-x}Mg_xCo_{0.05} Nano Bulk Materials

It should be noticed that the difference in the magnetic moment measured in ZFC and FC sequences is insignificant.

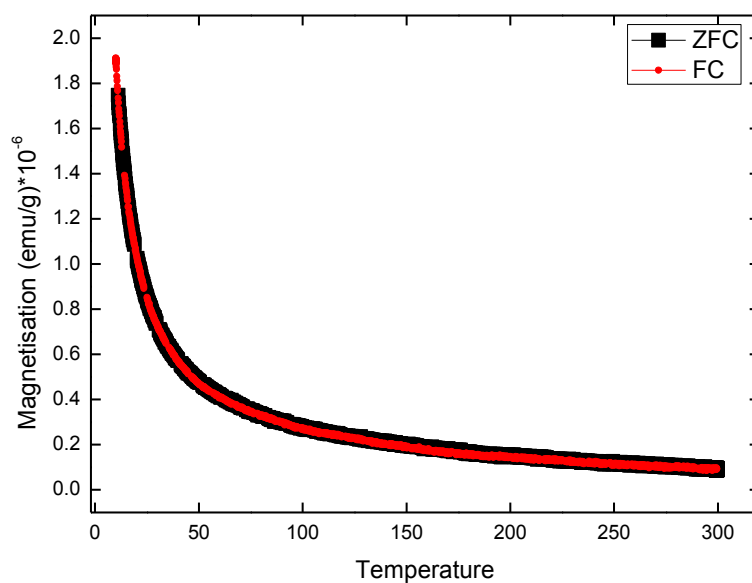


Figure 6.161. Temperature variation of magnetization of Zn_{0.90}Mg_{0.05}Co_{0.05} 800°C 30 minute under 100 Oe applied magnetic field

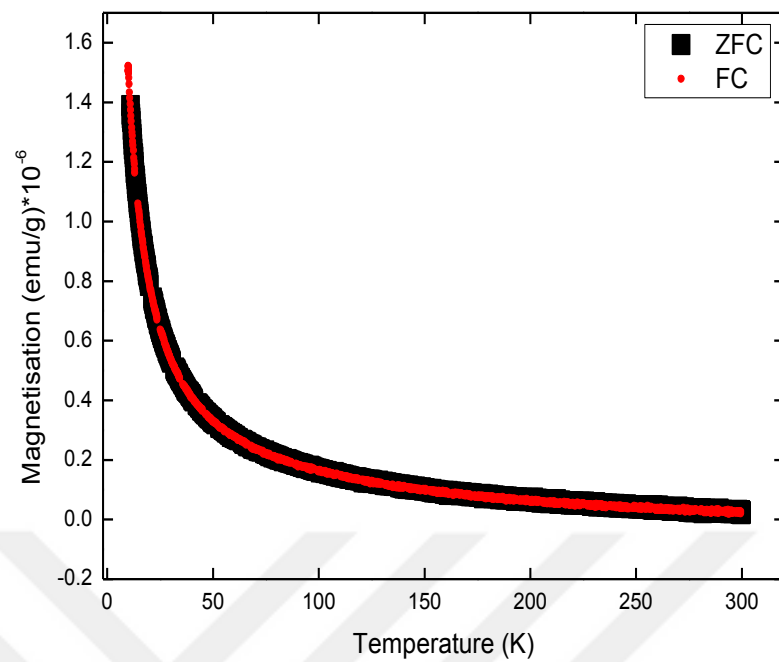


Figure 6.162. Temperature variation of magnetization of $\text{Zn}_{0.91}\text{Mg}_{0.04}\text{Co}_{0.05}$ 800⁰C 30 minute under 100 Oe applied magnetic field

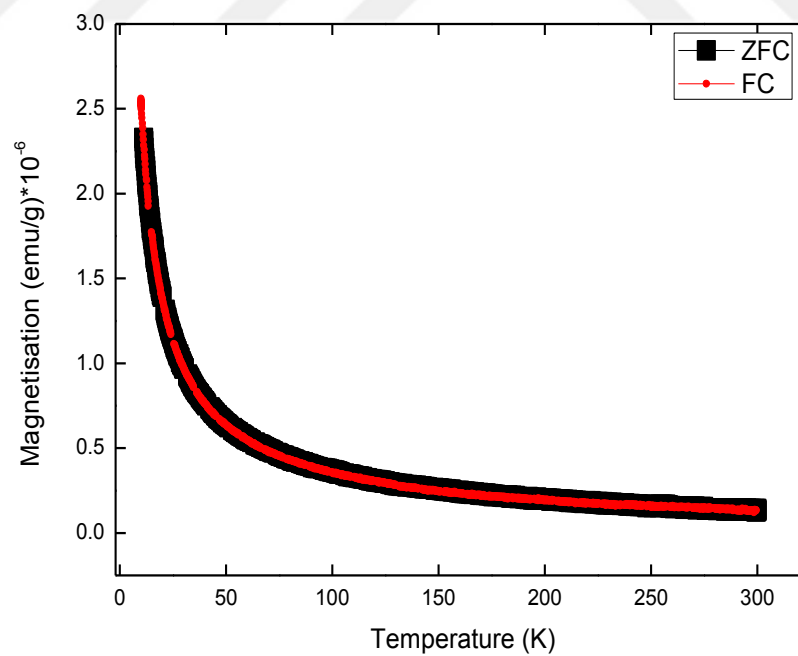


Figure 6.163. Temperature variation of magnetization of $\text{Zn}_{0.92}\text{Mg}_{0.03}\text{Co}_{0.05}$ 800⁰C 30 minute under 100 Oe applied magnetic field

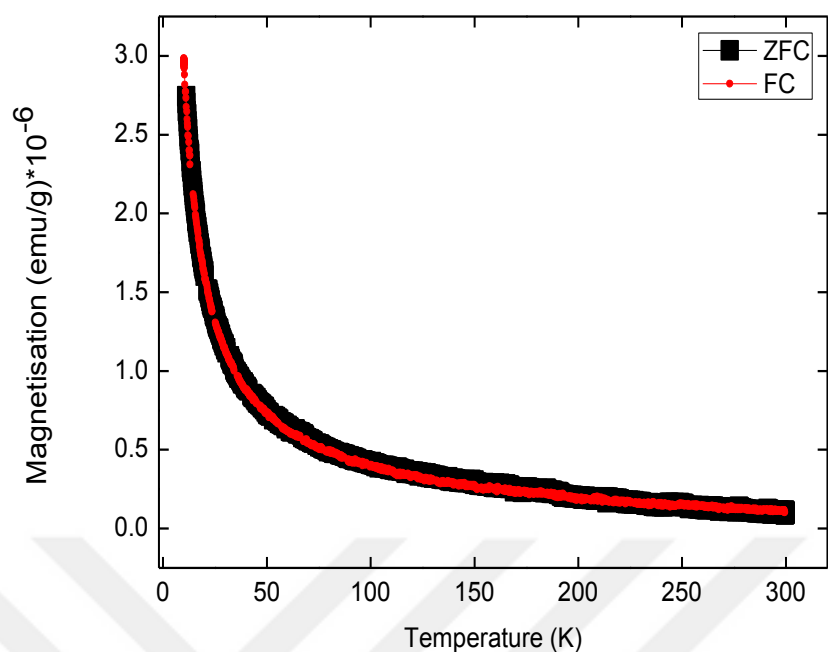


Figure 6.164. Temperature variation of magnetization of $\text{Zn}_{0.94}\text{Mg}_{0.01}\text{Co}_{0.05}$ 800^oC 30 minute under 100 Oe applied magnetic field

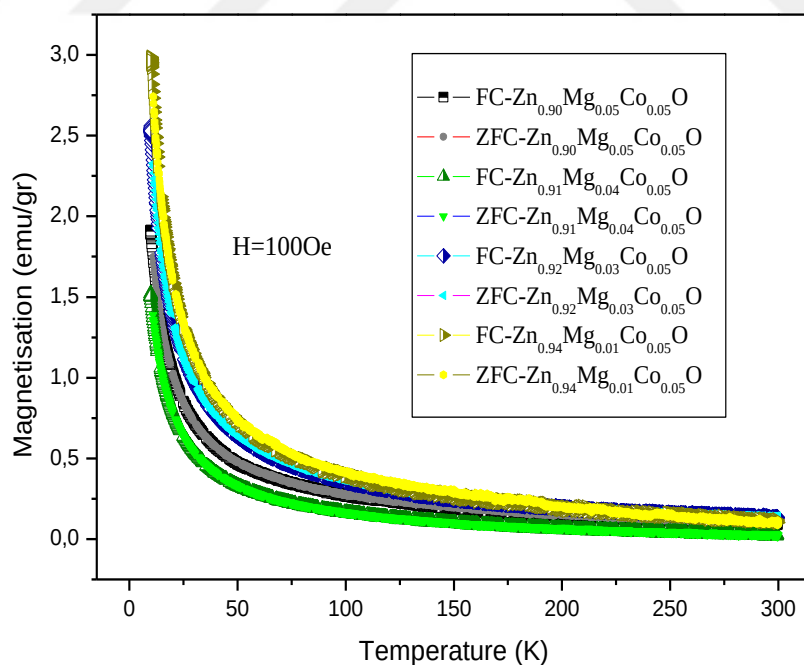


Figure 6.165. Temperature variation of magnetization of $\text{Zn}_{0.95-x}\text{Mg}_x\text{Co}_{0.05}$ samples under 100 Oe applied magnetic field

To give more evidence to our claims, we studied the relationship between magnetization (M) and applied magnetic field (H) at both 300 K and 20 K on these doped samples. As shown in Figure 6.166, a linear increase of the magnetization with the magnetic field is observed. It confirms that the magnetic field can partially remove spin degeneracy even at room temperature. Basically, a considerable number of free spins is aligned with the strong field thus partially removing their degeneracy and hence the spin entropy is reduced remarkably, resulting in the observed large magnetothermo power.

The $M - H$ curves also evidence that the spin entropy is markedly suppressed by raising the magnetic field from 4 to 8 T. $M - H$ curves at 20 K are shown in the inset of Fig. 6.166. We find that they do not exhibit a hysteresis at this temperature. The $M - H$ curves deviate from a linear behavior for all doped samples due to the onset of magnetic coupling at low temperatures. Comparing with $M - H$ curves at 300 K, they all exhibit larger magnetization values due to the enhanced magnetic coupling at low temperatures.

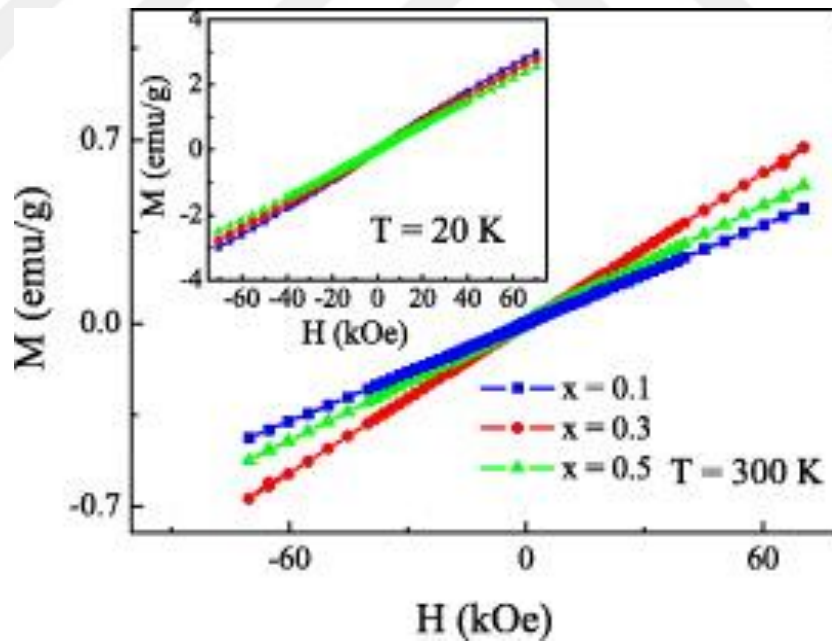


Figure 6.166. The relationship between magnetization (M) and magnetic field (H) for $\text{Ca}_{3-x}\text{Ce}_x\text{Co}_4\text{O}_{9+\delta}$ ($x=0, 0.1, 0.3$ and 0.5) at 300 K. The inset shows the relationship at 20 K

To further characterize the samples, magnetization hysteresis loops after ZFC and FC are measured at 5 K for all wire sizes. Figure 6.167 depicts M vs. H curves

for $d_w = 6, 7, 8$ and 9 nm. For $d_w = 6$ nm, representatively, one observes a small coercivity of 230 Oe in the ZFC curve and a virtually linear shape in the field range used, $H < 40$ kOe. The hysteresis curve measured after FC in 40 kOe displays an enhancement of the coercive field to 570 Oe and a vertical shift to larger $M(H)$ values. The vertical shift also causes a horizontal shift (see inset), which should not be mistaken as an indication for exchange bias. Rather, this behavior of the $M(H)$ curve is in complete agreement with hysteresis curves observed on DAFF systems. A Qualitatively similar behavior is observed for all samples with different sizes (Figs. 6.167 (a)–(d)).

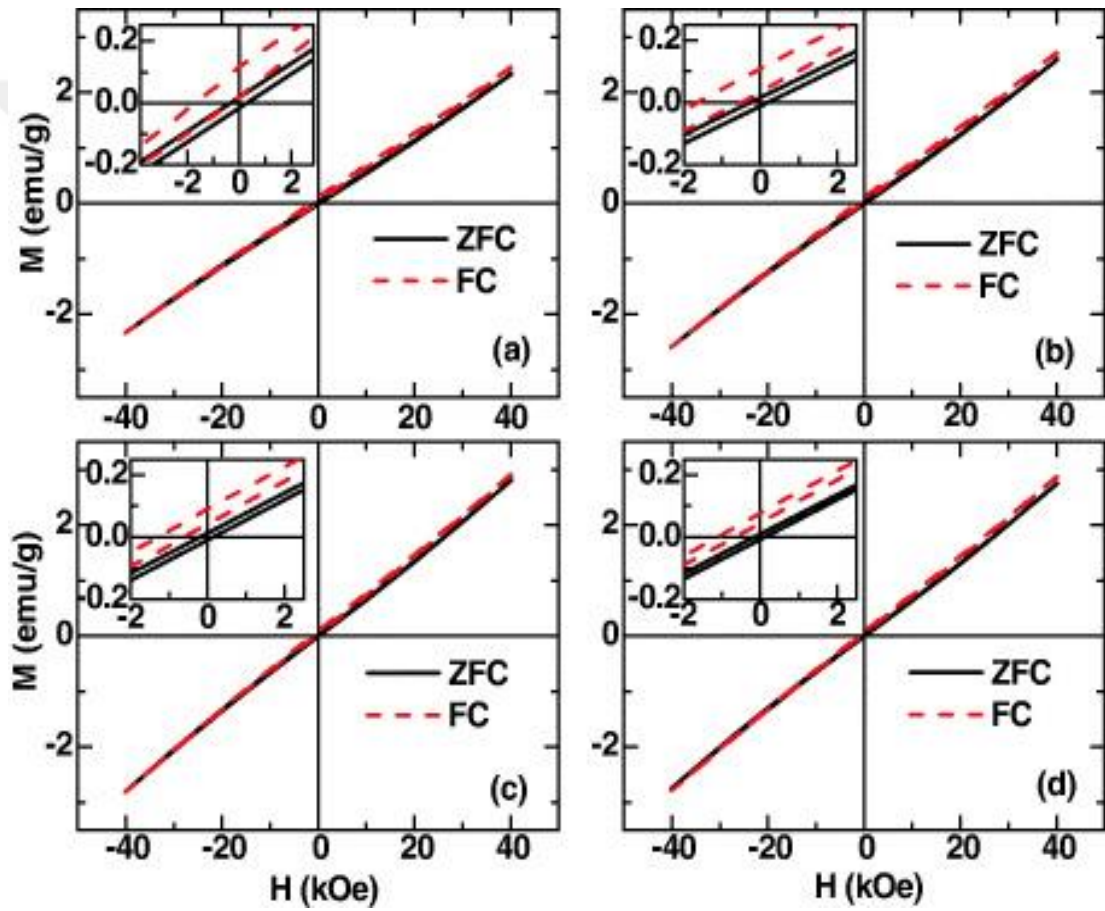


Figure 6.167. M vs. H hysteresis curves at 5 K after ZFC and after FC in 40 kOe for $d_w = 5$ (a), 6 (b) and 7 (c) and 9 nm (d). The insets show an enlarged view of the central part

6.8 Electrical properties of $\text{Zn}_{0.99-x}\text{Er}_x\text{O}$ Nano Thin Film Materials

The effects of doping rate on electrical properties of the films were performed by Van der Pauw Hall measurements. Figure 6.168 shows variation of the carrier concentration, mobility and resistivity of *Er* doped ZnO films with Er content in the range of 0% – 5% at room temperature.

Hall mobility are calculated as a function of carrier concentration by the following relation (Lu et al., 2006);

$$l = \frac{h}{2e} \left(\frac{3n_e}{\pi} \right)^{1/3} \mu_H \quad (6.36)$$

The carrier mobility in the polycrystalline semiconductors can be expressed as (Senol et al., 2015)

$$\frac{1}{\mu_H} = \frac{1}{\mu_i} + \frac{1}{\mu_n} + \frac{1}{\mu_g} + \frac{1}{\mu_l} + \frac{1}{\mu_c} \quad (6.37)$$

where μ_i , μ_n , μ_g , μ_l , and μ_c are mobilities cause to ionized impurity scattering, neutralism purity scattering, grain boundary scattering, lattice vibration scattering and intragrain cluster scattering, respectively.

The sheet resistance of the samples was calculated by using the Van der Pauw equation (Van der Pauw, 1958a; 1958b; Senol et al., 2014);

$$R_S = \frac{\pi R_A}{\ln 2} \quad (6.38)$$

$$R_A = \frac{V_{43}}{I_{12}} \quad (6.39)$$

where I_{12} is caused to flow along one edge of the sample and V_{43} is the voltage across the opposite edge.

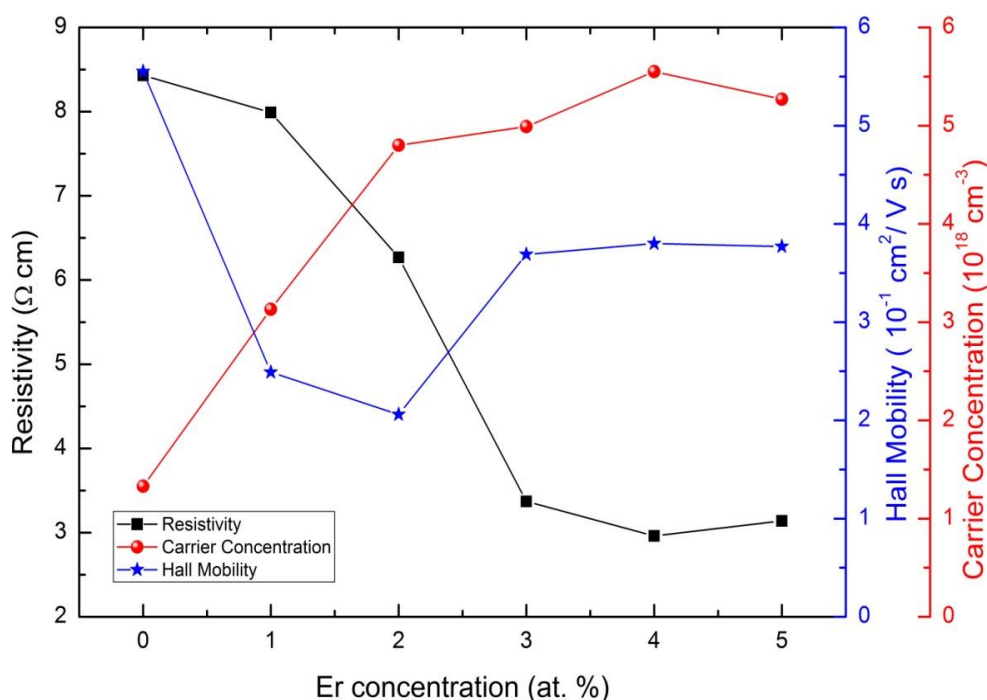


Figure 6.168. Dependence of electrical resistivity, carrier concentration and Hall mobility on the Er content

As can be seen from Figure 6.168, with increasing *Er* concentration from 0% to 4%, the resistivity of the films decreased, from 8.43 $\Omega.cm$ to 2.96 $\Omega.cm$, and then slightly increased to 3.14 at 5% *Er*. The point and surface defects, different scattering centers (impurity scattering and lattice scattering) and free carrier concentration play a crucial role in the resistivity of the films. The carrier concentration initially increases rapidly up to 4% *Er* concentration, thereafter decreases slowly for 5% *Er*. The increase in carrier concentration may be due to the incorporation of *Er* ions in interstitial positions or replacement of Er^{+3} ions at Zn^{+2} cation sites. The decrease of the carrier concentration at 5% *Er* is because of the increase in grain boundary defects that act as traps for free carriers. It is further seen from Fig. 6.168 that the Hall mobility of the films decreases rapidly from $5.55 \times 10^{-1} cm^2 V^{-1} s^{-1}$ for undoped ZnO to $2.06 \times 10^{-1} cm^2 V^{-1} s^{-1}$ for 2% *Er* content, and then increases to 3.69×10^{-1} for 3% *Er*. For higher *Er* concentrations, the Hall mobility reaches to a saturation. The first decrease in Hall mobility can be explained by ionized impurity scattering of the conduction electrons due to *Er* addition. Because the carrier mobility is governed mainly by the scattering of the charge

carriers, the ionized impurity scattering is an important mechanism for degenerate semiconductors in the low temperature region. The variation of Hall mobility with Er doping is in sync with the variation in grain size given in Table 6.16. The decrease in grain sizes results in an increase of the number of grain boundaries and vice versa. For 3% and higher doping ratios, the increase in carrier concentration and the scattering centers compensate each other resulting in a stable region of resistivity and mobility.



CHAPTER 7

CONCLUSION

In this thesis, transition metal and rare earth element doped nano thin films and bulk samples of diluted magnetic semiconductors which have dual structure of $(\text{Zn}_{1-x}\text{B}_x)\text{O}$ ($\text{B} = \text{Co}, \text{Er}$) and ternary structure of $(\text{Zn}_{1-x}\text{B}_x\text{CO})$ ($\text{C} = \text{Cu}, \text{Cd}$) are prepared by using sol-gel method. The microstructure, electrical, optic, magnetic and micromechanic properties of prepared nano thin films and nano bulk materials are investigated. Firstly, the materials which have the greatest doping rate to determination of optimum annealing temperature of nano bulk materials are subjected to last heat treatment at 400°C , 450°C , 500°C , 550°C and 600°C for 30 min after from first heat treatment. After from this process, all of doped nano thin film and nano bulk materials are annealed under determined annealing temperature. The systems, $(\text{Zn}_{1-x}\text{B}_x)\text{O}$ dual and $(\text{Zn}_{1-x}\text{B}_x\text{CO})$ ternary structures, are prepared as polycrystalline nanoparticle powders by applying the sol-gel method. Nano thin films are coated on the glass substrate by using the dip coating method. The X-ray diffractometer (XRD), scanning electron microscopy (SEM), energy dispersive spectrometer (EDS) and atomic force microscopy (AFM) are used to determination of structural properties such as crystal structures, grain sizes, percent of elements, surface morphology; hall effect measurements system is used to determination of electrical properties of materials; UV-VIS spectrophotometer is used to determination of optic properties; vibrating sample magnetometer (VSM) system is used to determination of magnetic properties and Vickers microhardness device is used to determination of micromechanic properties of produced nano thin film and nano bulk materials.

Obtained results are given below:

XRD Results of Co and Co/Cu doped nano bulk materials:

- X-ray diffraction peak of the samples shows that there is no phase of the Co and Cu ions. This means that the presence of Co^{+2} and Cu^{+2} ions in the ZnO lattice affect crystal structure.
- The grain size decreases with increasing Co doping for $\text{Zn}_{1-x}\text{Co}_x\text{O}$ materials. But these values increase with Co doping for $\text{Zn}_{1-x-y}\text{Cu}_{0.01}\text{Co}_y\text{O}$ materials. These results are even supported by the SEM images.
- Lattice parameters a and c are slightly reduced with Co doping. This reduction shows that Zn^{+2} ions substitute with Co^{+2} ions.

XRD Results of Er and Er/Cd doped nano bulk materials:

- Er doped all samples have a hexagonal wurtzite type structure and the same peak at the same angle as undoped ZnO. There is no phase of the Er ions. This means that Er^{+2} ions replacement with Zn^{+2} ions in the ZnO lattice.
- Cd doped all samples have a hexagonal wurtzite type structure and the same peak at the same angle as undoped ZnO. There is no phase of the Cd ions until $x = 0.04$ Cd doping rate. This means that Cd^{+2} ions replacement with Zn^{+2} ions in the ZnO lattice. After from this doping value there are two peaks of CdO phase. The hexagonal wurtzite type structure is deteriorated with increasing Cd doping.
- The lattice parameters a and c firstly decrease and then slightly increase with Er doping. This is an expected result. Because the ionic radius of Zn^{+2} ($0.74\text{\AA}$) is smaller than the ionic radius of Er^{+2} ($0.88\text{\AA}$).
- The lattice parameter c firstly decreases and then slightly increases with Cd doping.
- Er doped bulk samples exhibit greater grain size than the undoped ZnO samples. Difference of size may be caused from ionic radius difference between zinc and doping element. These results are even supported by the SEM images.
- Particle size of nano thin films decreases from 31.73 nm to 21.90 nm with Cd/Er doping. Rare earth metal doped ZnO nano thin films exhibit smaller particle size than the undoped ZnO nano thin film.

Vickers Microhardness Results of Co and Cu/Co doped nano bulk materials:

- The increase in the microhardness values of the all sample depends on the increase of applied load, which shows RISE behavior. Behavior of the materials is not changed with Co doping. Only the values of microhardness changed with doping.
- H_v decreases with Co doping when compared with undoped ZnO sample. But these values increase with increasing the Co doping.
- If a plastic material is requested for industrial applications, Co0.01 doped ZnO nano bulk material is the most appropriate material among all samples (microhardness value is between 0.511 – 0.608 GPa).
- The results of the microhardness measurements are analyzed by employing Meyer's law, PSR, MPSR, EDP, IIC models and HK approach. As a result, IIC model is more suitable to determine the micromechanical properties and *RISE* behavior of Co doped ZnO semiconductors.
- H_v decrease with Cu/Co doping when compared with undoped ZnO sample while microhardness values increase with F.
- IIC model is more suitable to determine the micromechanical properties and RISE behavior of Cu/Co doped semiconductors.

Vickers Microhardness Results of Er and Er/Cd doped nano bulk materials:

- H_v decreases with Er doping when compared with undoped ZnO sample while microhardness values increase with F.
- If a plastic material is requested for industrial applications, Er0.10 doped ZnO nano bulk material is the most appropriate material among all samples (microhardness value is between 0.586 – 0.592 GPa).
- IIC model is more suitable to determine the micromechanical properties and RISE behavior of Er doped-ZnO semiconductors.
- H_v decreases with increasing the Cd doping when compared with undoped ZnO sample.
- If a plastic material is requested for industrial applications, Cd0.10 doped ZnO nano bulk material is the most appropriate material among all samples (microhardness value is between 0.187 – 0.211 GPa).

- *IIC* model is more suitable to determine the micromechanical properties and *RISE* behavior of *Er* doped-ZnO semiconductors.

Optical Results of Co, Cu and Cu/Co doped nano thin film materials:

- $\text{Zn}_{0.99}\text{Cu}_{0.01}\text{O}$ nano thin film has broad transmittance band in UV region and stronger transmittance in the visible region. The transmittance values decrease with increasing *Cu* doping.

• The decrease in the optical band gap can be attributed to the better crystallinity with increasing grain size. When *Cu* ions are located at substitution sites, the carrier concentration increases and as a result the band gap energy decreases. While the optical band gap energy is about 3.28 eV for undoped ZnO film, it is in the range of 3.24 – 3.27 eV for *Cu* doped nano thin films

- The crystallinity of $\text{Zn}_{0.95}\text{Cu}_{0.05}\text{O}$ nano thin film is better compared to the other nano thin films.

• $\text{Zn}_{0.99}\text{Cu}_{0.01}\text{O}$ nano thin film has broad transmittance band in UV region and stronger transmittance in the visible region. The transmittance values significantly decrease with increasing Co doping.

• While the optical band gap energy is about 3.28 eV for undoped ZnO film, it is in the range of 2.88 – 3.27 eV for Co doped nano thin films. Band gap energy of the doped films is smaller than the undoped film.

- The crystallinity of $\text{Zn}_{0.95}\text{Cu}_{0.05}\text{O}$ nano thin film is better compared to the other nano thin films.

• According to the optical transmission spectrum of $\text{Zn}_{1-x-y}\text{Cu}_x\text{Co}_y\text{O}$, absorption is observed in the wavelength range between 360 – 450 nm. When Cu and Co ions are incorporated into the ZnO structure, a significantly shift is observed in the absorption edge.

- The average transmittance values of all doped ZnO films are under 80% and their transmittances are smaller than undoped ZnO sample.

• The optical band gap energy is in the range of 3.22 – 3.27 eV for Cu/Co doped nano thin films. Band gap energy of the doped films is smaller than the undoped film.

-

Optical Results of Er and Er/Cd doped nano thin film materials:

- According to the optical transmission spectrum, a sharp absorption is observed in the wavelength range between 360 – 400 nm.
- The average optical transmittance is about 81% in the visible region, it exhibits an absorption edge at wavelength of about 405 nm for undoped ZnO film.
- The average transmittance values of all doped ZnO films are above 85% and their transmittances are higher than undoped ZnO sample.
- While the optical band gap energy is about 3.28 eV for undoped ZnO film, it is in the range of 3.24 – 3.26 eV for Er doped nano thin films.
- According to the optical transmission spectrum of $\text{Zn}_{1-x-y}\text{Er}_x\text{Cd}_y\text{O}$, a sharp absorption is observed in the wavelength range between 350 – 400 nm.
- The average transmittance values of all Er/Cd doped ZnO nano thin films.
- The optical band gap energy is the optical band gap energy is in the range of 3.21 – 3.26 eV for Er/Cd doped nano thin films.

APPENDICES

APPENDIX A: DETERMINATION OF THE TEMPERATURE ZONE IN THE VERTICAL FURNACE

APPENDIX B: COMPARING OF TRANSITION METAL AND RARE EARTH ELEMENT DOPED ZnO MATERIALS WITH UNDOPED ZnO AS STRUCTURAL BY XRD DATA USING EVA PROGRAMME



APPENDIX A:

DETERMINATION OF THE TEMPERATURE ZONE IN THE VERTICAL FURNACE

In order to prepare high quality material, the calibration of the furnace used during the annealing is very important. For this purpose, the furnace is calibrated using a thermocouple and the regions of stable temperature are determined. The data for different temperatures are drawn in the graph shown below. Generally deviations of 3 – 5 °C from the set temperature are obtained.

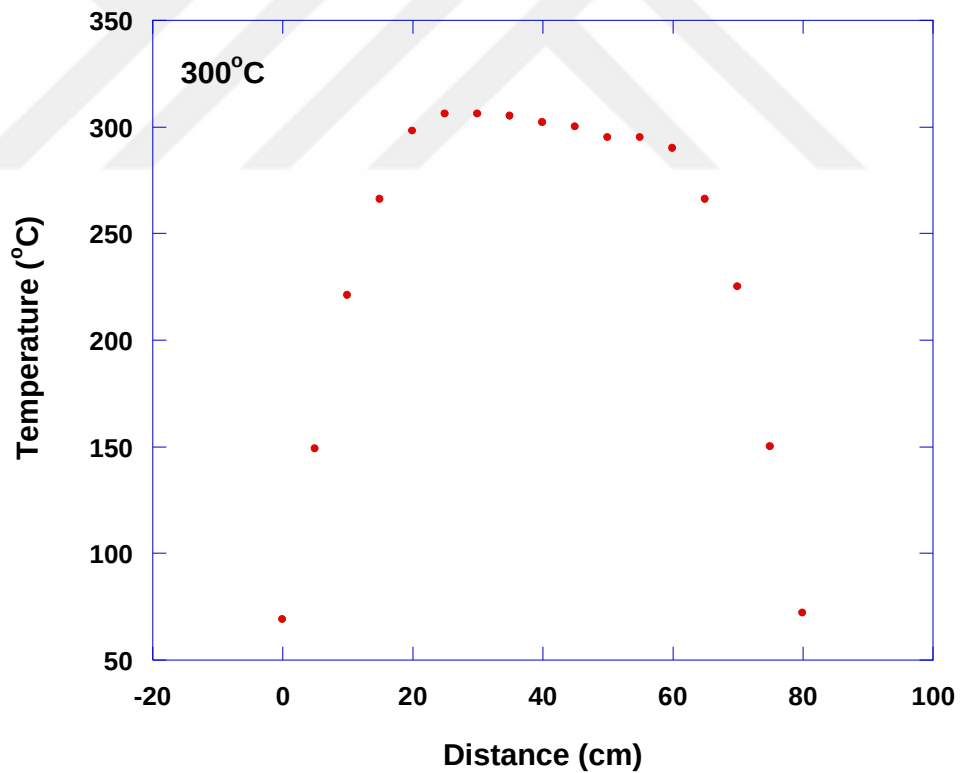


Figure A. 1. Calibration curve of the furnace (PROTHERM) at the set temperature 300°C

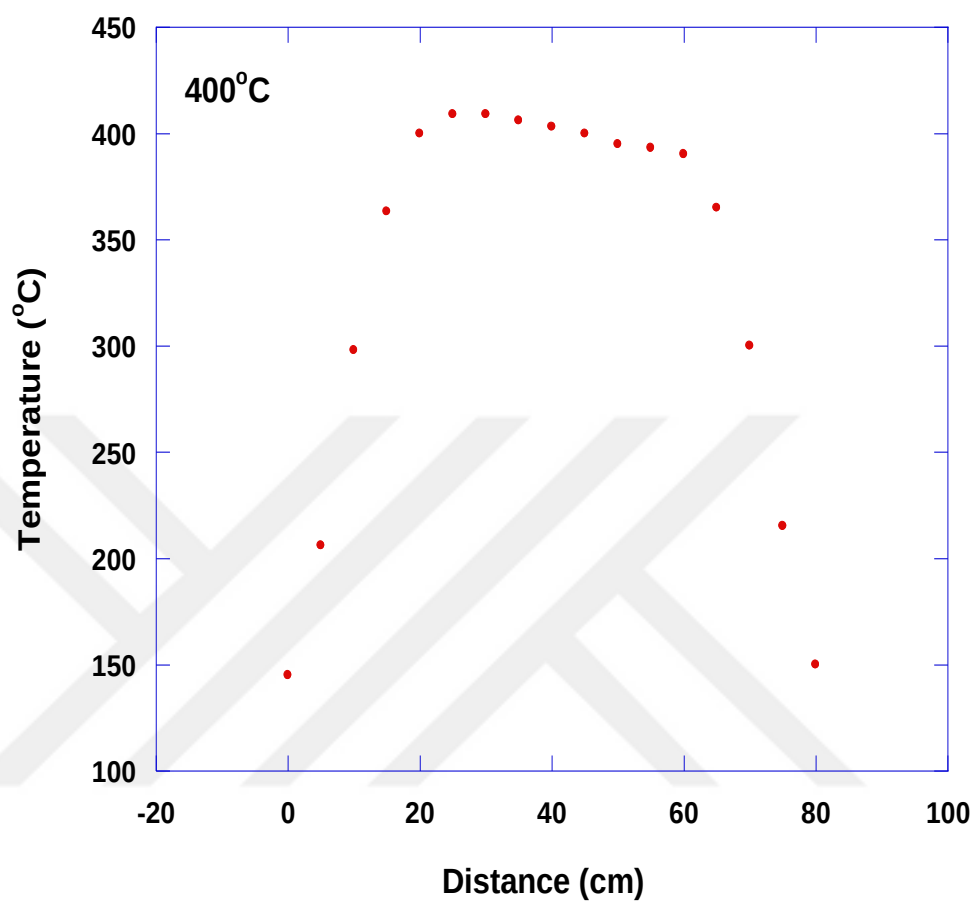


Figure A. 2. Calibration curve of the furnace (PROTHERM) at the set temperature 400°C

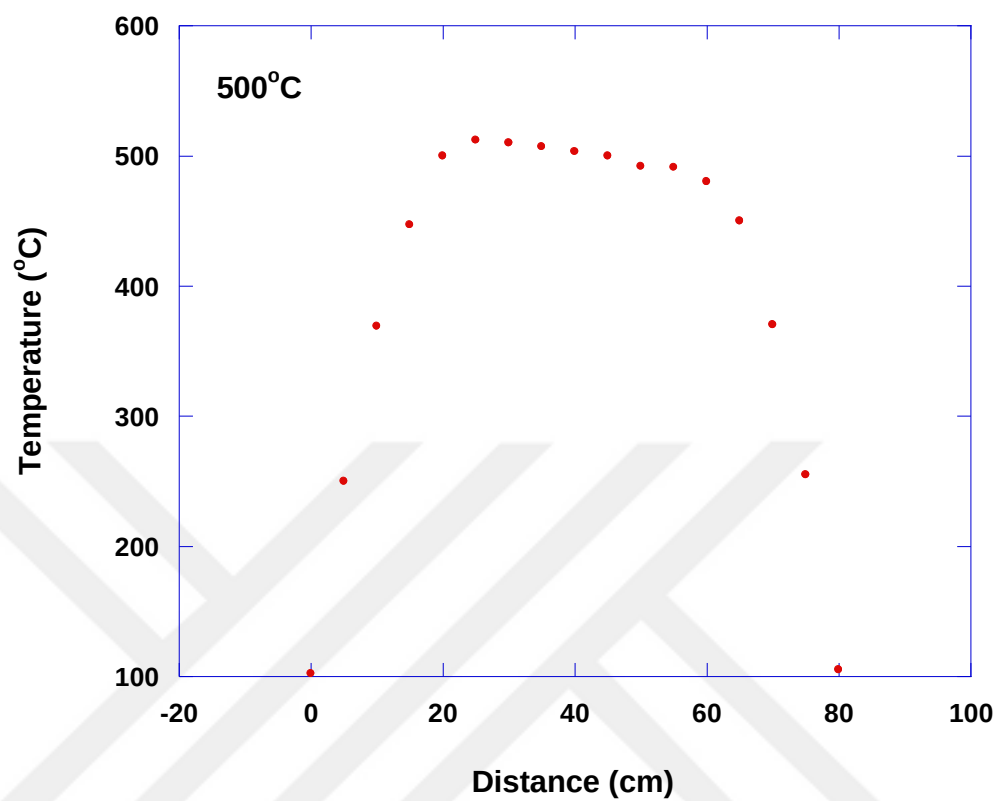


Figure A. 3. Calibration curve of the furnace (PROTHERM) at the set temperature 500°C

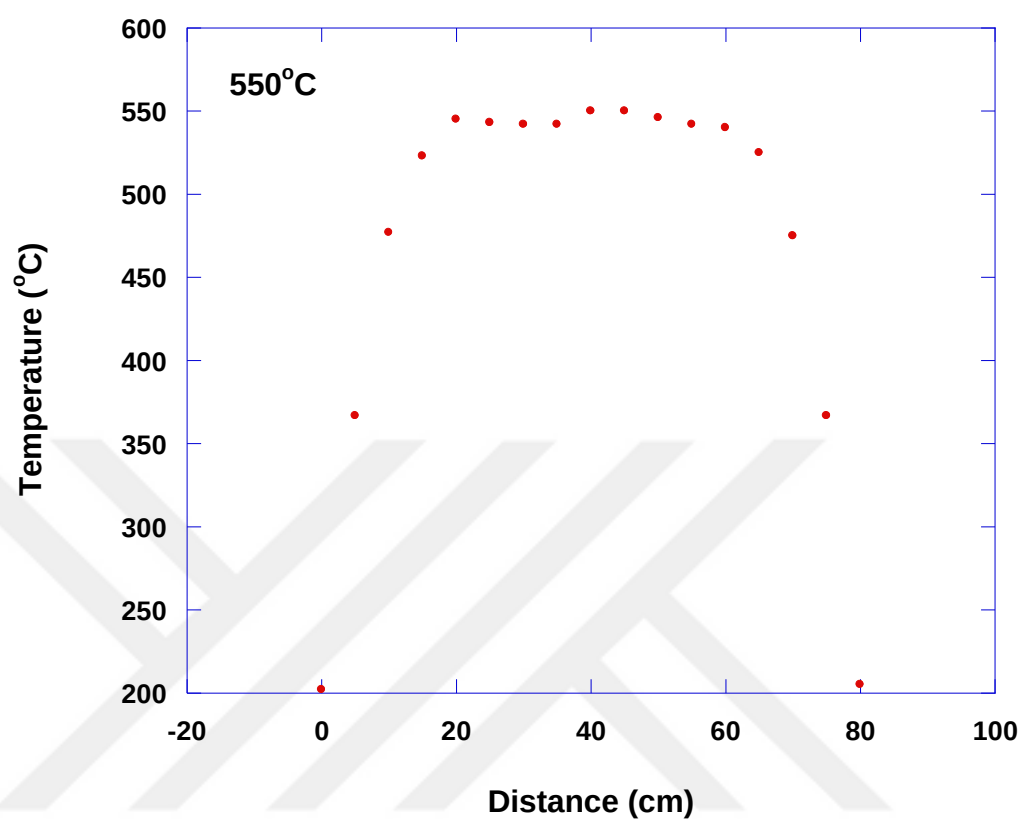


Figure A. 4. Calibration curve of the furnace (PROTHERM) at the set temperature 550°C

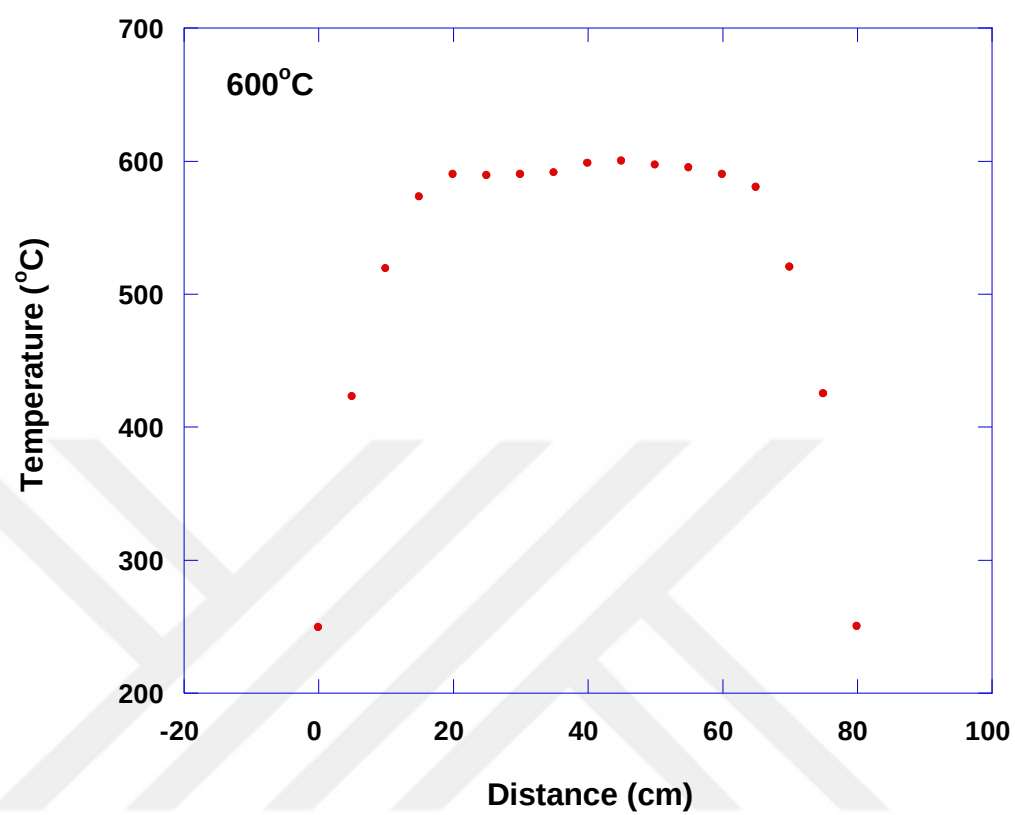


Figure A. 5. Calibration curve of the furnace (PROTHERM) at the set temperature 600°C

APPENDIX B:

COMPARING OF TRANSITION METAL AND RARE EARTH ELEMENT DOPED ZnO MATERIALS WITH UNDOPED ZnO AS STRUCTURAL BY XRD DATA USING EVA PROGRAMME

The transition metal and rare earth element doped ZnO based nano thin films and nano particles prepared using sol-gel method exhibit the similar structural properties compared with undoped ZnO material. Original XRD patterns and ICDD data cards of undoped and doped ZnO materials (for $x = 0.01$ doping rate) are given below.

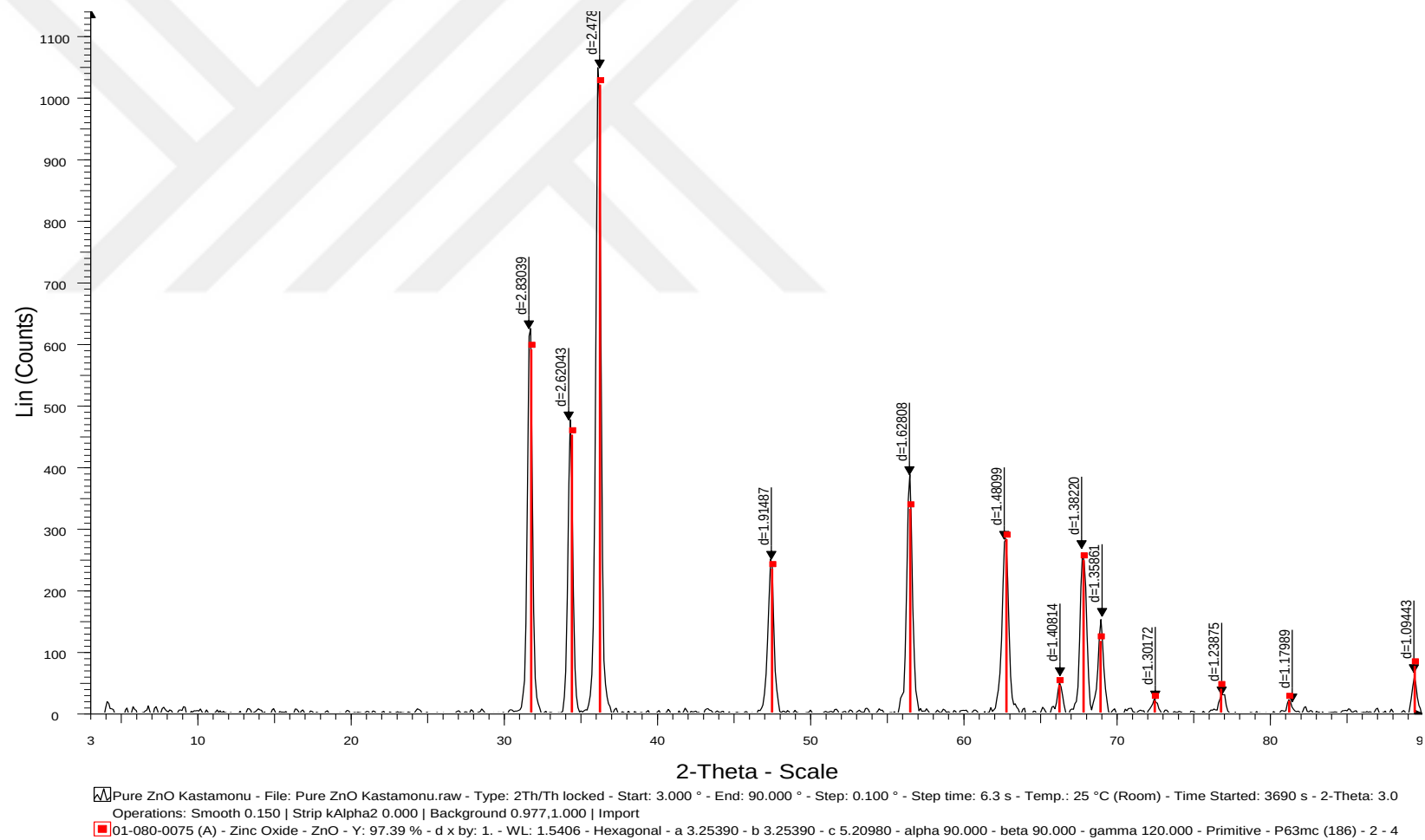


Figure B. 1. The XRD patterns of undoped ZnO nano bulk material

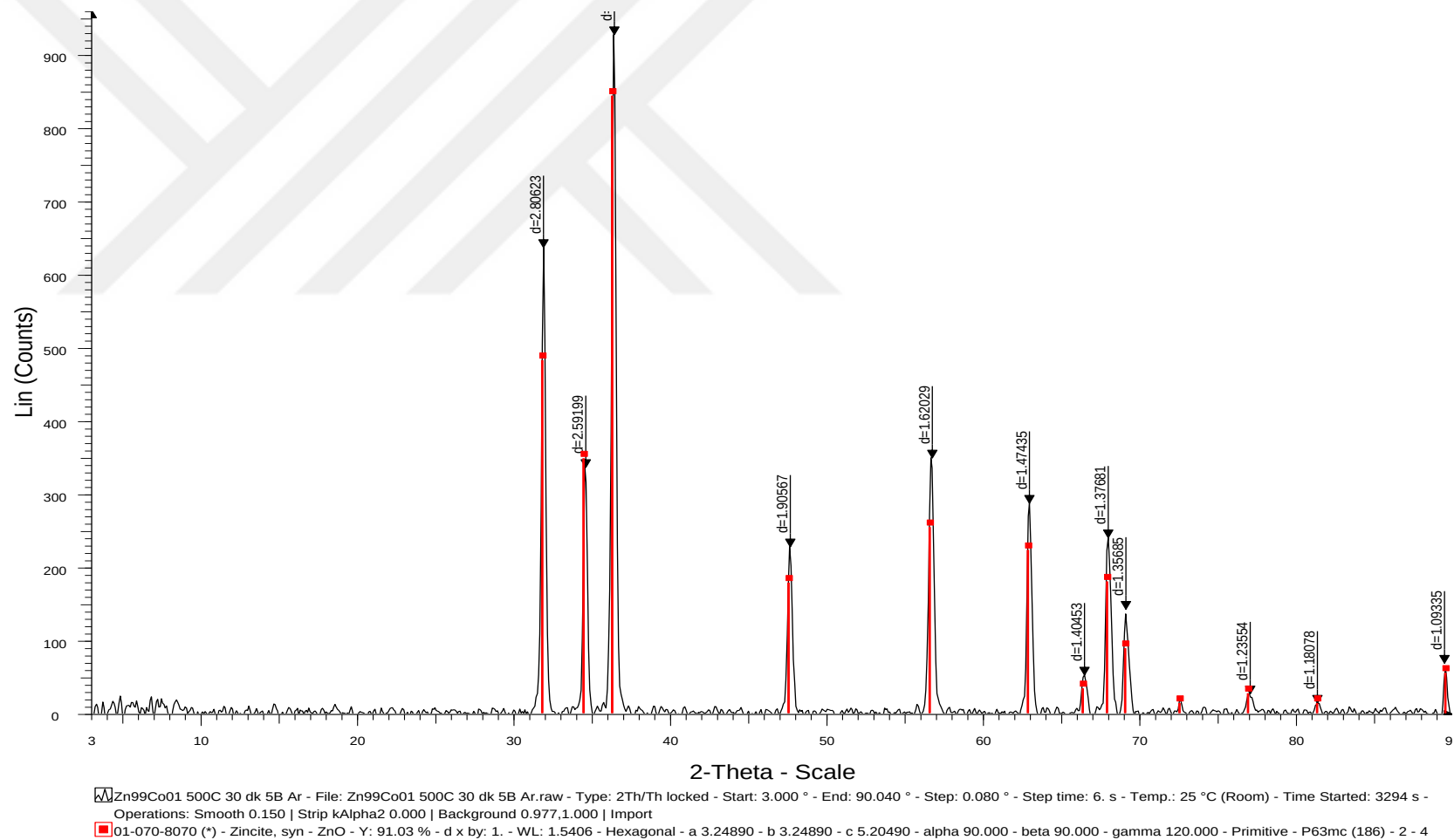


Figure B. 2. The XRD patterns of $\text{Zn}_{0.99}\text{Co}_{0.01}\text{O}$ nano bulk material

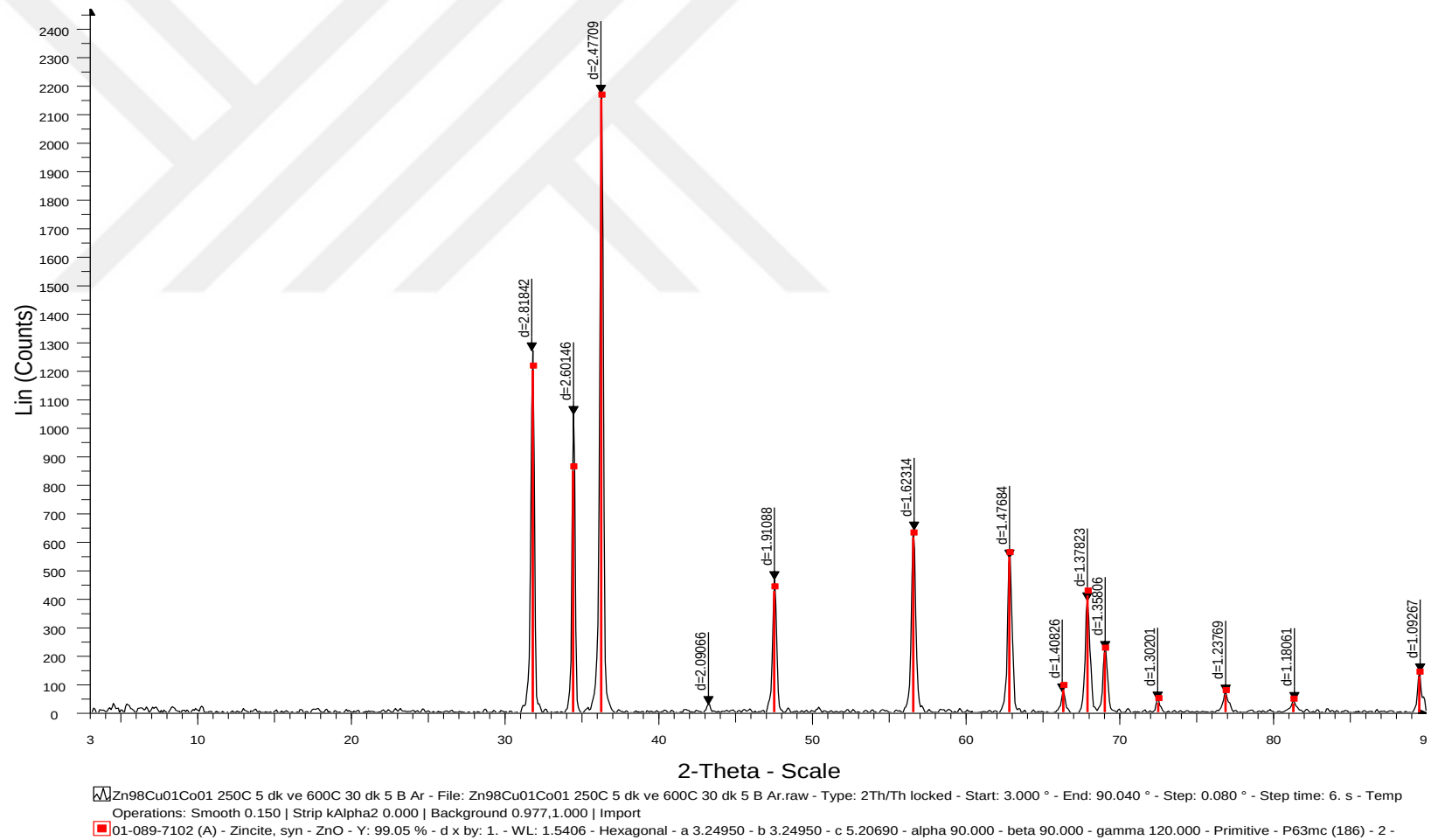


Figure B.3. The XRD patterns of $\text{Zn}_{0.98}\text{Cu}_{0.01}\text{Co}_{0.01}\text{O}$ nano bulk material

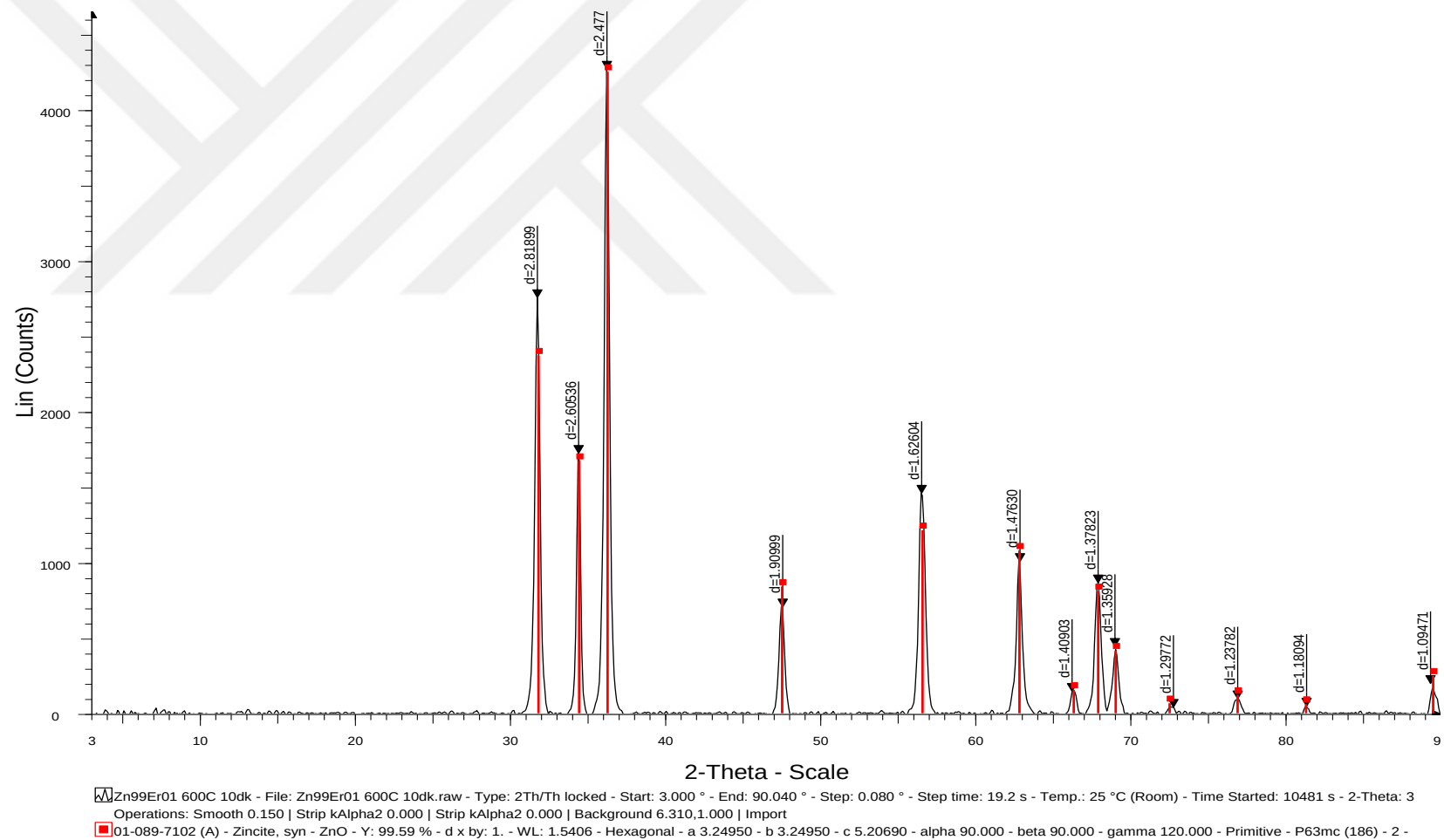


Figure B. 4. The XRD patterns of $\text{Zn}_{0.99}\text{Er}_{0.01}$ nano bulk material

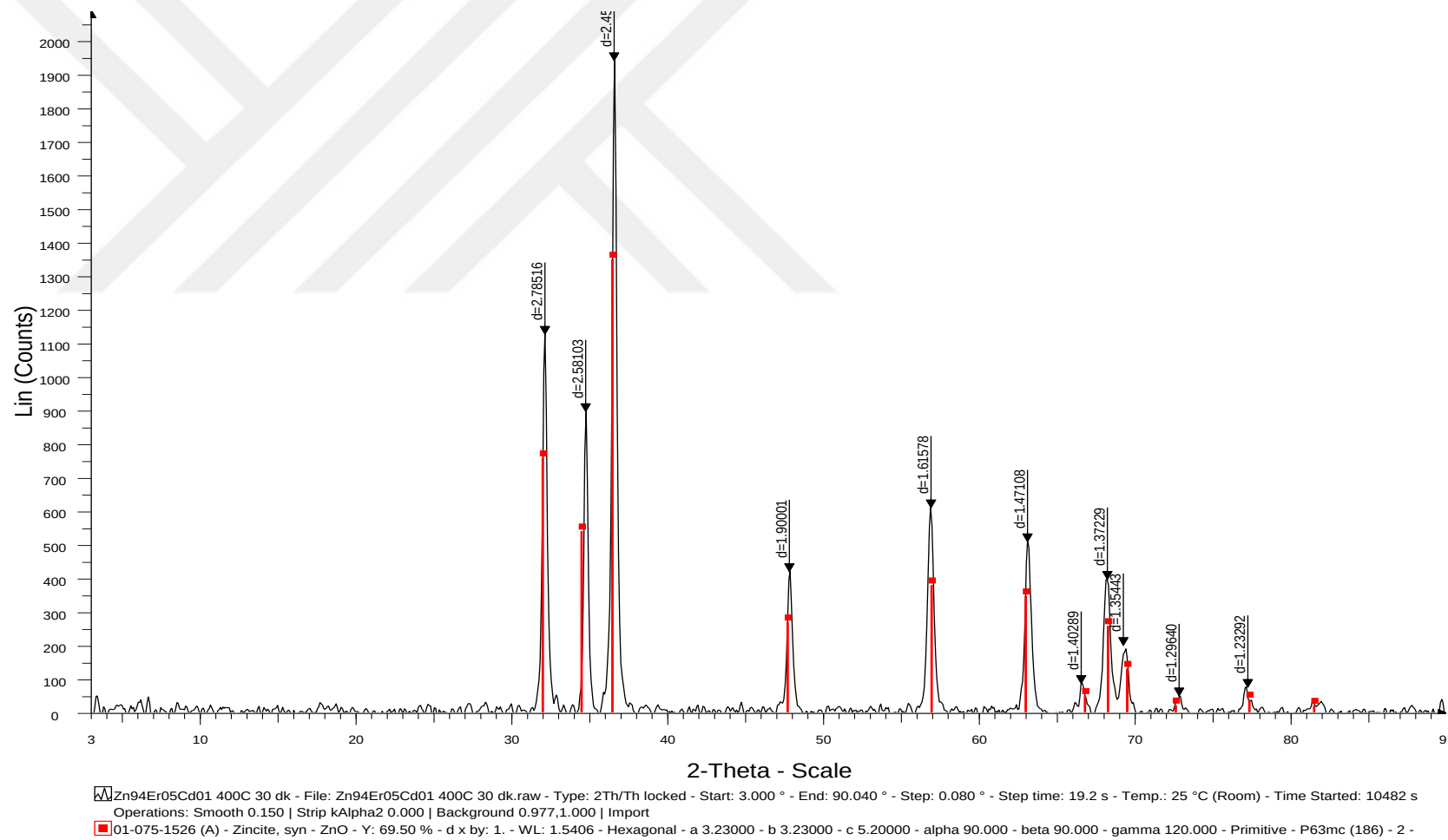


Figure B. 5. The XRD patterns of $\text{Zn}_{0.94}\text{Er}_{0.05}\text{Cd}_{0.01}\text{O}$ nano bulk material

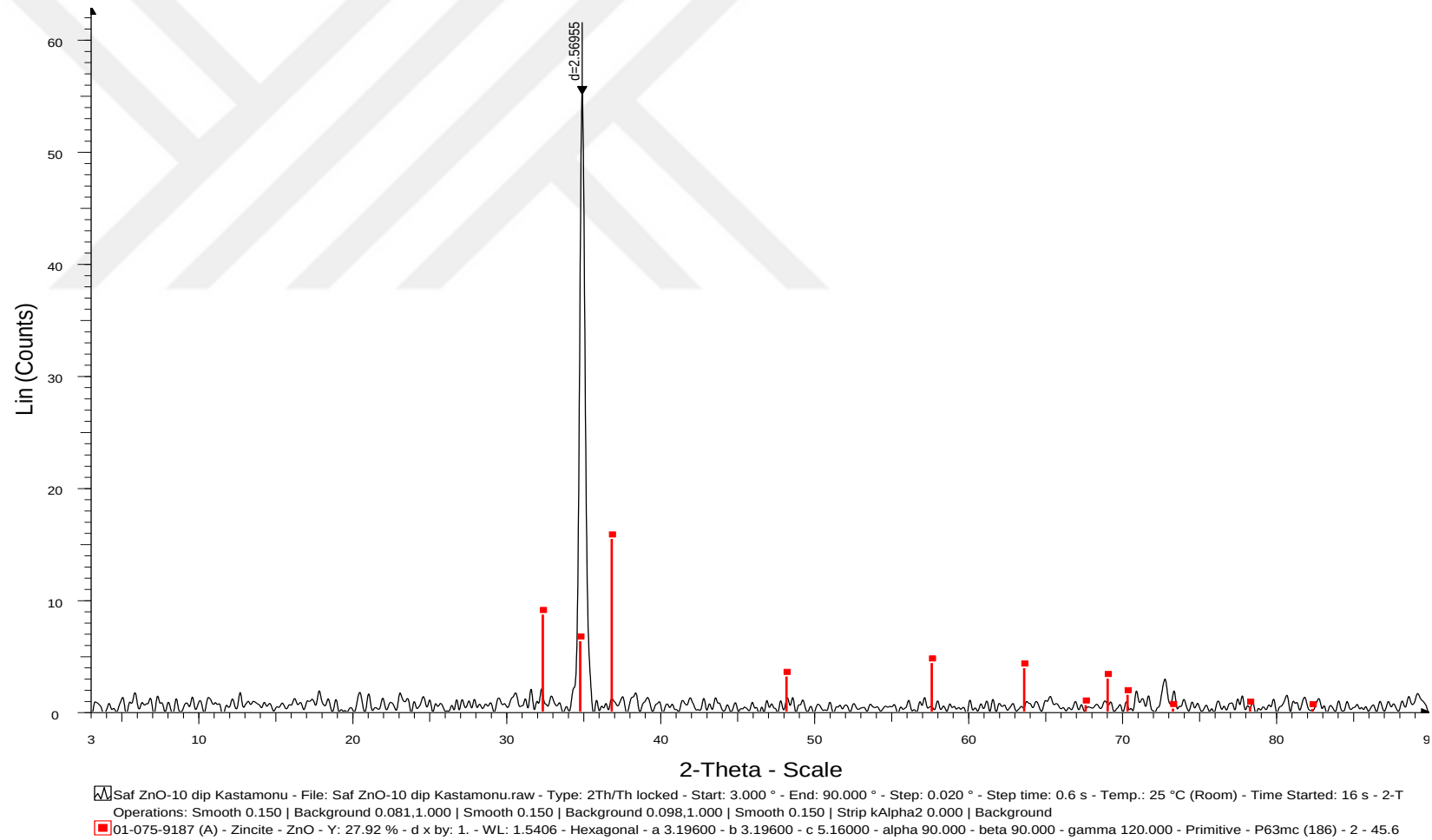


Figure B. 6. The XRD patterns of undoped ZnO nano thin film material

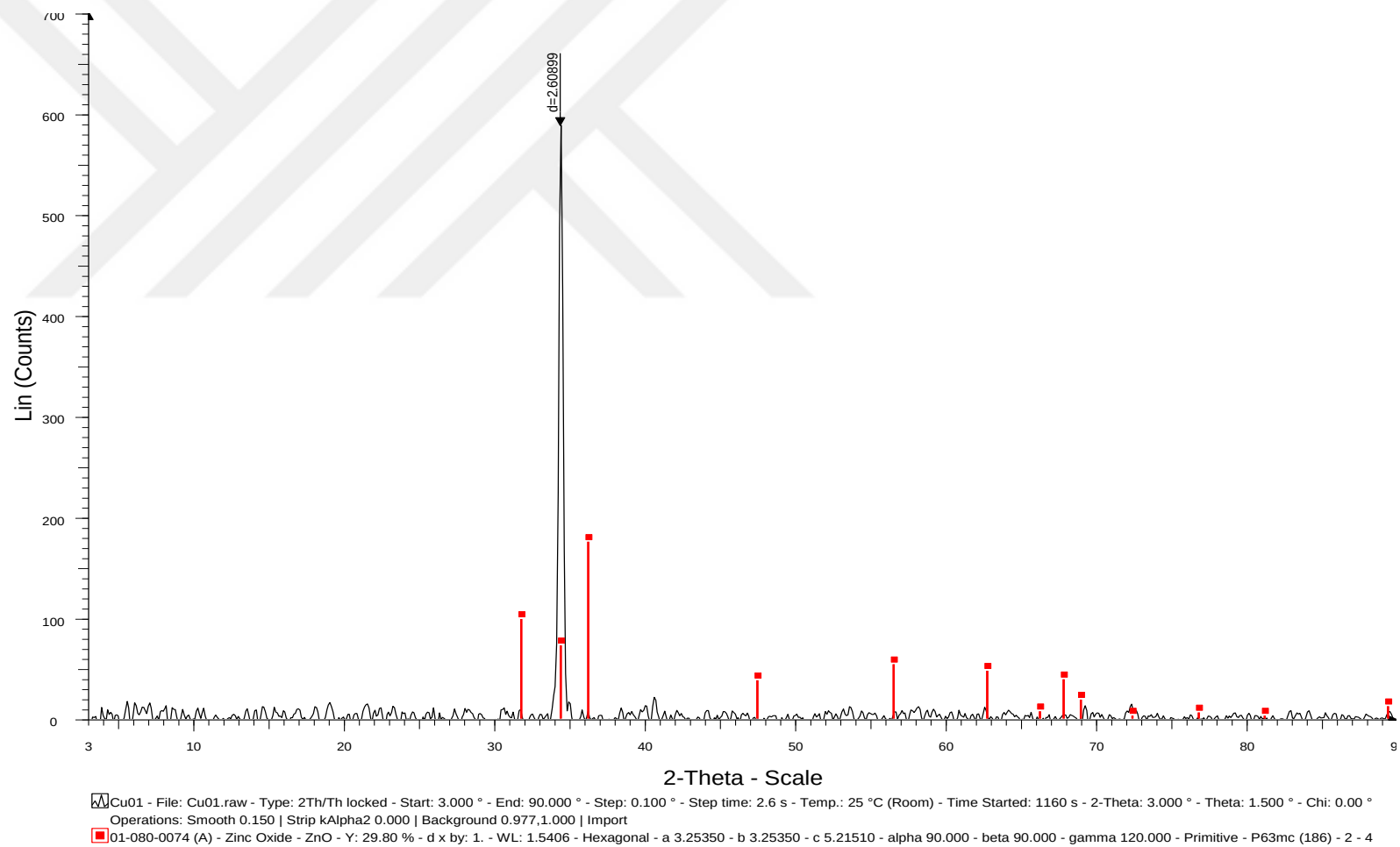


Figure B. 7. The XRD patterns of $\text{Zn}_{0.99}\text{Co}_{0.01}\text{O}$ nano thin film material

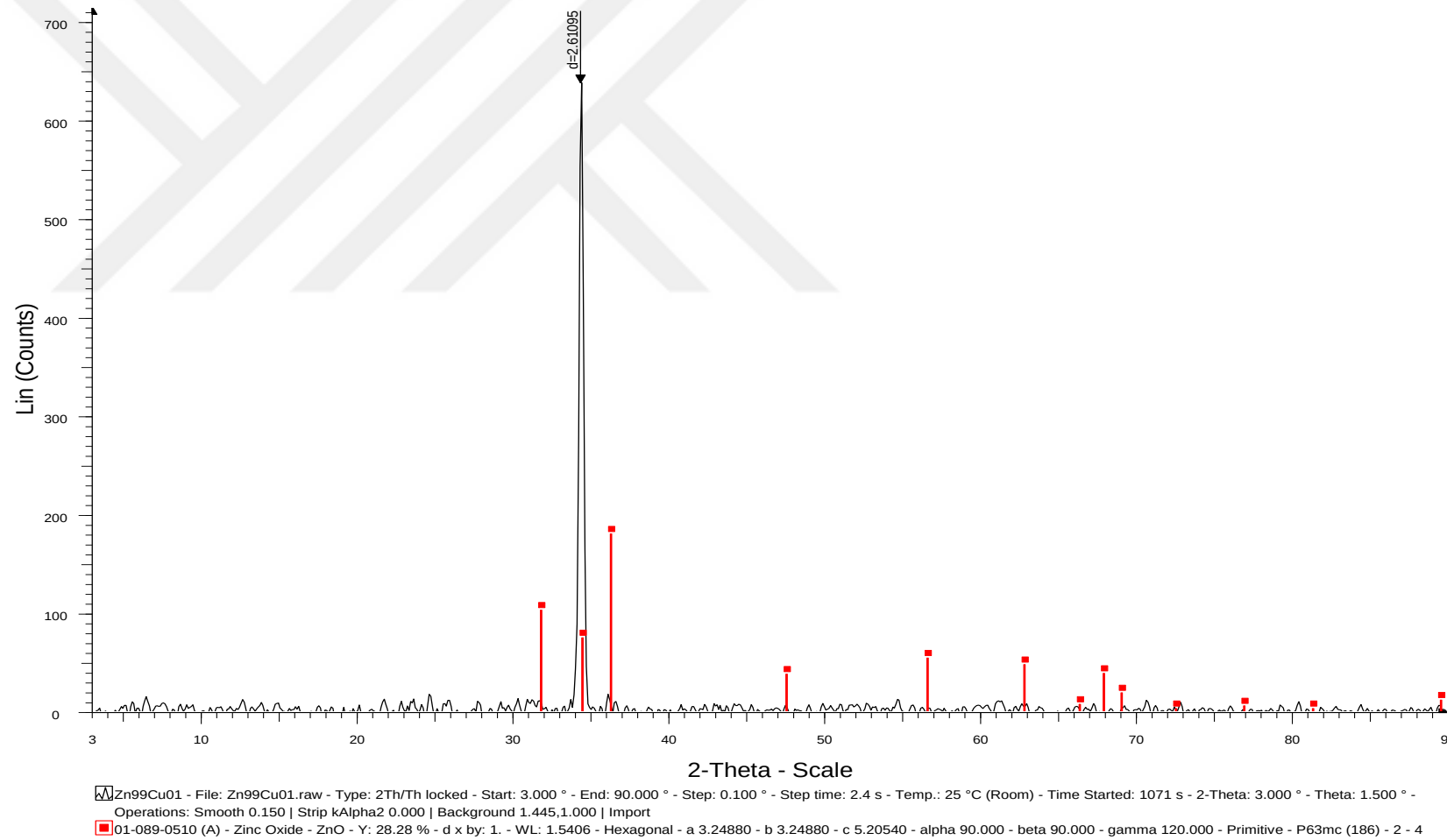


Figure B. 8. The XRD patterns of $\text{Zn}_{0.99}\text{Cu}_{0.01}\text{O}$ nano thin film material

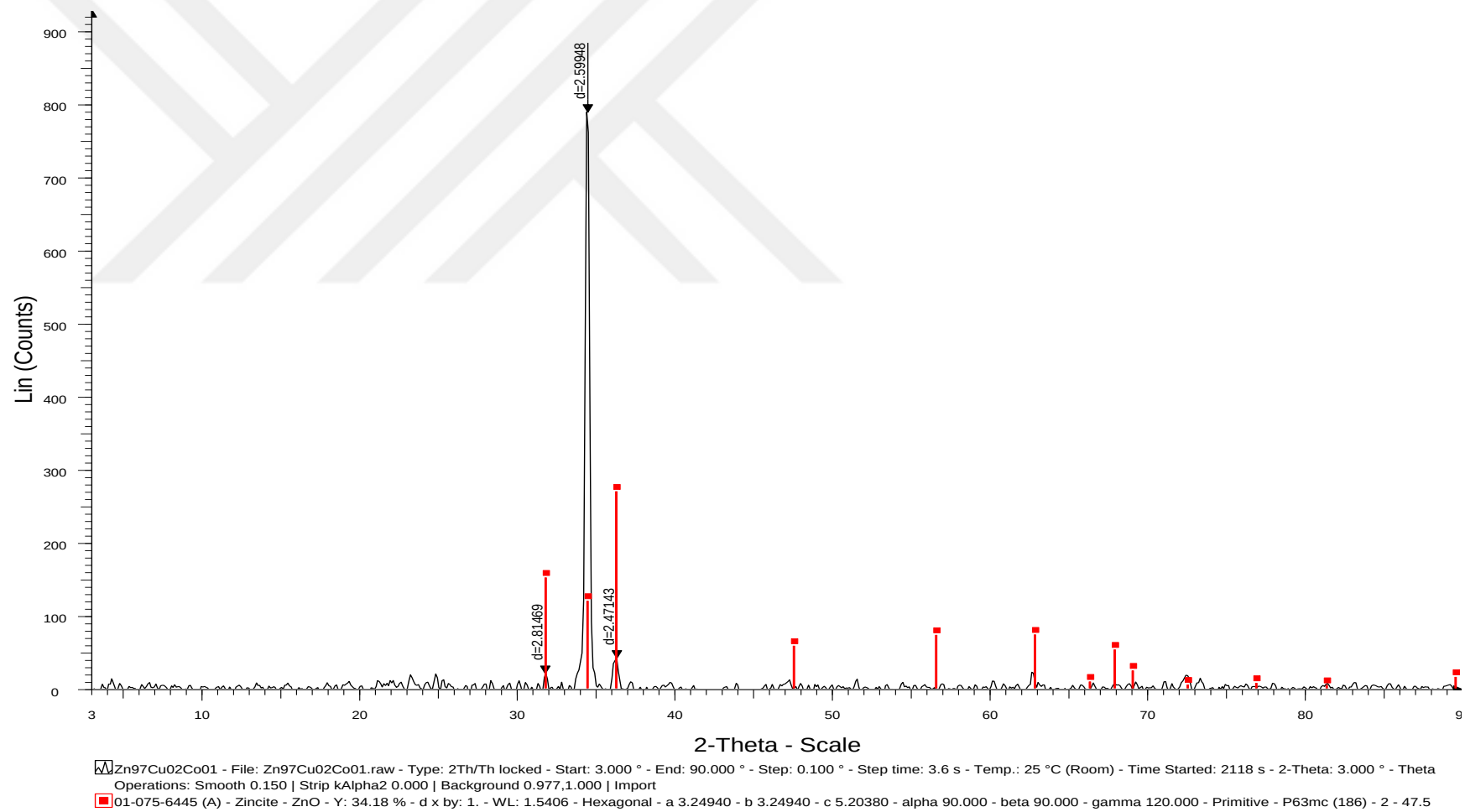


Figure B. 9. The XRD patterns of Zn_{0.97}Cu_{0.02}Co_{0.01}O nano thin film material

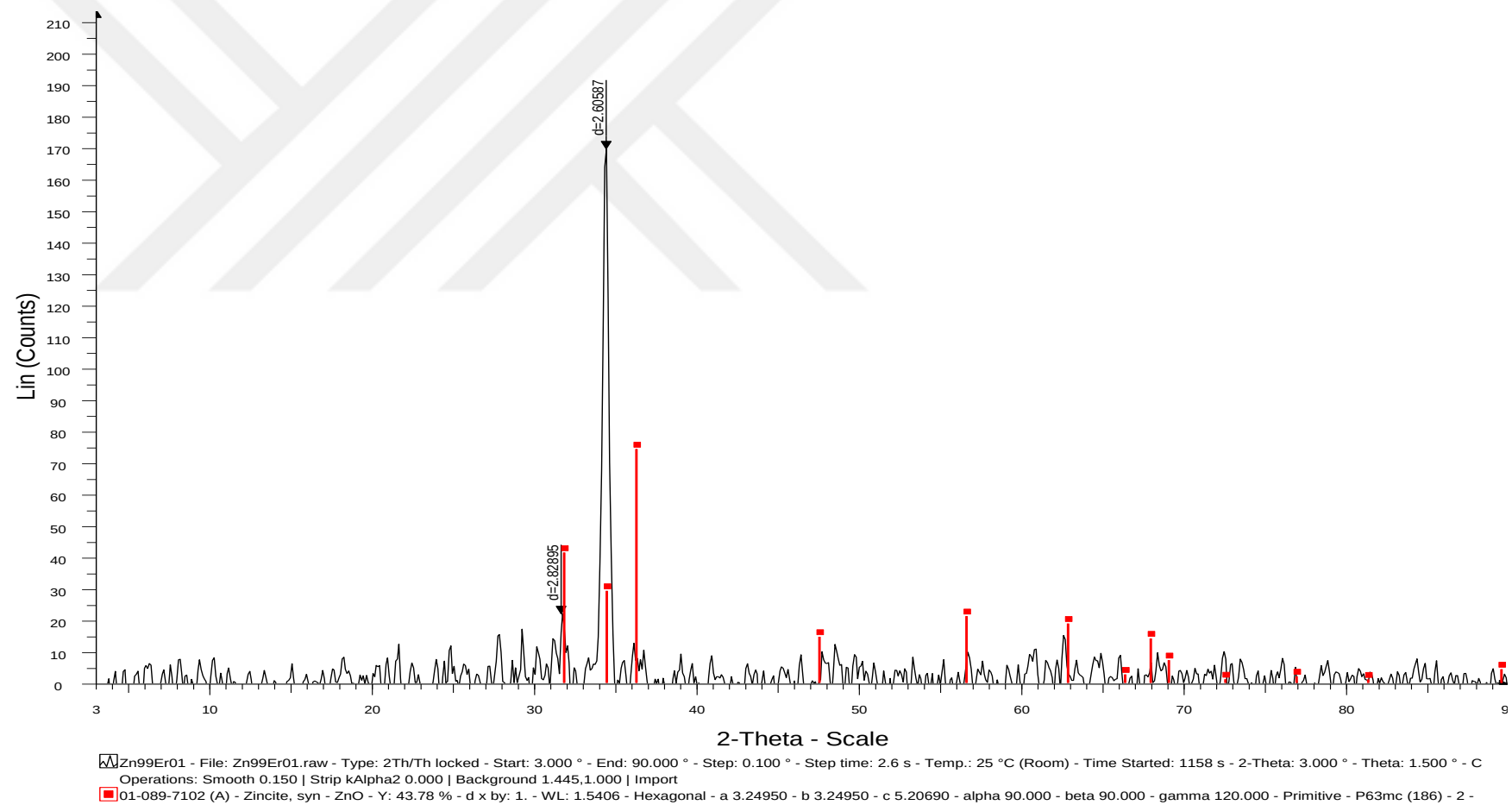


Figure B. 10. The XRD patterns of $\text{Zn}_{0.99}\text{Er}_{0.01}$ nano thin film material

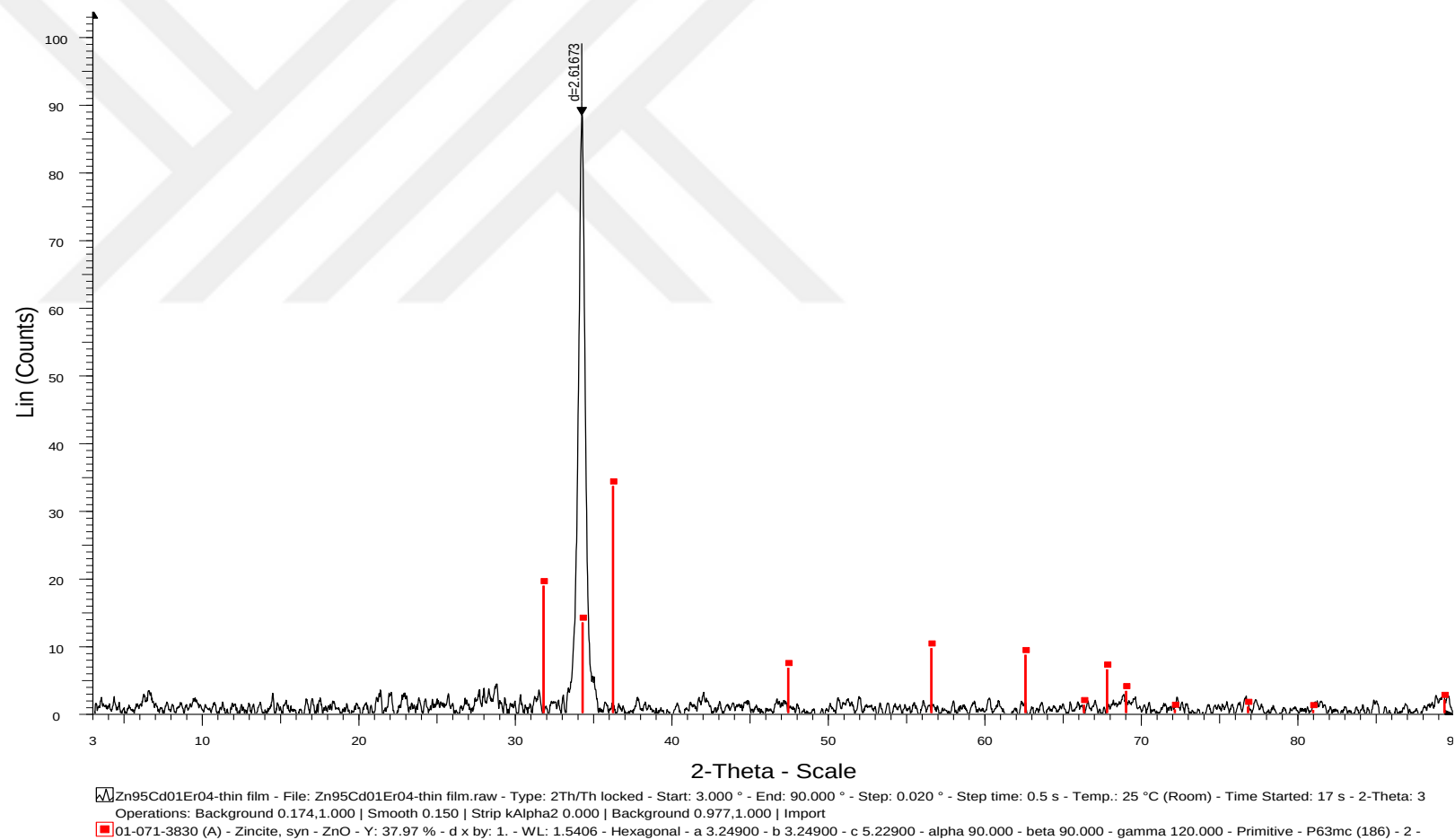


Figure B. 11. The XRD patterns of $\text{Zn}_{0.95}\text{Cd}_{0.01}\text{Er}_{0.04}\text{O}$ nano thin film material

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- Investigating of structural, electric and magnetic properties of rare earth and transition metal element doped ZnO-based diluted magnetic semiconductor material produced by sol-gel and solid state reaction method. Abant İzzet Baysal University Scientific Research Projects Coordination Department. Proje No: 2014.03.03.723, 2014-2016. **Assistant Researcher.**
- Determination of Micro-Structural, Electrical, Optical and Micro-Mechanical Properties of Rare Earth Element and Transition Metal Doped Diluted Magnetic Semiconductor Nano Particle and Film Samples Fabricated by Sol-Gel Process. The Scientific and Technological Research Council of Turkey (TÜBİTAK), Project Number: 114F259, 2014-2016. **Researcher.**
- Investigation of Optical and Structural Properties of ZnO based Diluted Magnetic Semiconductor Nano thin films Produced by Sol-Gel Method. The Kastamonu University Scientific Research Projects Coordination Department. Project No: KUBAP-01/2014-13. 2015-2016. **Assistant Researcher.**
- The production of ZnO based diluted magnetic semiconductor nano thin films which will be prepared to different solvent and thickness by using sol-gel method and structural, electrical and optic characterization. Kastamonu University Scientific Research Projects Coordination Department. Project No: KUBAP-05/2015-12. 2015-2016. **Assistant Researcher.**

PUBLICATIONS

A. ARTICLES PUBLISHED IN INTERNATIONAL REFEREED JOURNALS (SCI & SSCI & Arts and Humanities)

A1. O. Ozturk, H. A. Cetinkara, **E. Asikuzun**, M. Akdogan, M. Yilmazlar and C. Terzioglu, Investigation of Mechanical and Superconducting Properties of Iron Diffusion-Doped Bi-2223 Superconductors, Journal of Materials Science: Materials in Electronics, 22, 9, 1501-1508 (2011).

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A9. M. B. Turkoz, S. Nezir, O. Ozturk, **E. Asikuzun**, G. Yildirim, C. Terzioglu and A. Varilci, Experimental and Theoretical Approaches on Mechanical Evaluation of

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- A19.** **E. Asikuzun**, A. Donmez, L. Arda, D. Akcan, O. Ozturk, O. Cakiroglu, M. Tosun, S. Ataoglu and C. Terzioglu, Structural and mechanical properties of (Co/Mg) Co-doped nano ZnO, *Ceramics International*, 41, 6326-6334 (2015).
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- A23.** S. Safran, E. Kilicarslan, H. Ozturk, M. Alp, M. Akdogan, **E. Asikuzun**, O. Ozturk and A. Kilic, Superconducting and mechanical properties of the bulk Bi(Pb)SCCO system prepared via solid state and ammonium nitrate precipitation methods, *Physica B* 472, (2015) 34–40.
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B2. O. Ozturk, G. Yildirim, **E. Asikuzun**, A. Varilci, C. Terzioglu, Mechanical and structural characterization of Mn added $\text{Bi}_{1.8}\text{Pb}_{0.4}\text{Sr}_2\text{Mn}_x\text{Ca}_{2.2}\text{Cu}_{3.0}\text{O}_y$ ceramics, International Conference on Superconductivity and Magnetism ICSM-2012, İstanbul–Turkey, 29 April-4 May (2012).

B3. O. Ozturk, S. Kaya, **E. Asikuzun**, M. Coskunyurek, G. Yildirim, C. Terzioglu, Physical properties and diffusion coefficient calculation of Iron doped $\text{Bi}_{1.8}\text{Pb}_{0.35}\text{Sr}_{1.9}\text{Ca}_{2.1}\text{Cu}_3\text{O}_y$ system, International Conference on Superconductivity and Magnetism (ICSM-2012), Istanbul-Turkey, 29 April-4 May (2012).

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B5. E. Asikuzun, O. Ozturk, M. Coskunyurek, S. Kaya and G. Yildirim, Determination of Optimum Annealing Temperature and Time of Bi-2212 Superconductor by Structural Analysis and Mechanical Characterization, Turkish Physical Society 29th International Physics Congress, Bodrum-Turkey, 5-8 September (2012).

B6. M. Coskunyurek, O. Ozturk, **E. Asikuzun**, S. Kaya and N. Soylu, The Investigation of Structural and Mechanical Properties of Nd_2O_3 Doped Bi-2212 Superconductor, Turkish Physical Society 29th International Physics Congress, Bodrum-Turkey, 5-8 September (2012).

B7. E. Asikuzun, O. Ozturk, S. Kaya, M. Coskunyurek, N. Soylu, A. Varilci, C. Terzioglu, Investigation of Indentation Size Effect (ISE) of $\text{Bi}_2\text{Sr}_2\text{CaNd}_x\text{Cu}_2\text{O}_y$ Superconducting System Using Vickers Microhardness Test Method, APS March Meeting, Baltimore-Maryland, USA, 18-22 March (2013).

B8. S. Celik, O. Ozturk, E. Coşkun, **E. Asikuzun**, K. Ozturk, C. Terzioglu, Analysis of Indentation Size Effect (ISE) Behavior in Low-Load Vickers Microhardness Testing of $(\text{Sm}_{123})_{1-x}(\text{Nd}_{123})_x$ Superconductor System, APS March Meeting, Baltimore-Maryland, USA, 18-22 March (2013).

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B11. **E. Asikuzun**, S. Kaya, O. Ozturk, N. Soylu, A. Varilci and C. Terzioglu, The Effect of Different Argon Ambient Pressure and Different Annealing Time on Microstructural and Micromechanical Properties of Bulk MgB_2 Superconductor, 7th Asian Conference on Applied Superconductivity and Cryogenics (ACASC2013), Cappadocia, Turkey 23-25 October (2013).

B12. O. Ozturk, O. Cakiroglu, **E. Asikuzun**, D. Akcan, L. Arda and C. Terzioglu. Structural and Micro-Mechanical Properties of Al-Doped ZnMgO Nanoparticles Prepared by Sol-Gel Technique. International Conference on Superconductivity and Magnetism (ICSM 2014), Antalya-Turkey, 27 April-2 May (2014).

B13. O. Ozturk, T. Gokcen, S. Cavdar, H. Koralay, **E. Asikuzun**, Effect of Ru substitution on the mechanical properties of $\text{Bi}_{1-x}\text{Ru}_x\text{Pb}_{0.2}\text{Sr}_2\text{CaCu}_2\text{O}_{10+\delta}$ glass-ceramic, International Conference on Superconductivity and Magnetism (ICSM 2014), Antalya-Turkey, 27 April-2 May (2014).

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B15. O. Ozturk, **E. Asikuzun**, D. Akcan, L. Arda, A. T. Tasci, A. Senol, S. D. Senol, C. Terzioglu, Structural and Mechanical Properties of (Co/Cu) Co-doped Nano ZnO, APS March Meeting, San Antonio-Texas, USA, 2-6 March (2015).

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B17. O. Ozturk, **E. Asikuzun**, A. T. Tasci, L. Arda, S. Celik and C. Terzioglu, Microstructural and Optical properties of transition metal (Cu) doped ZnO diluted magnetic semiconductor nano thin films produced by sol gel method, APS March Meeting, Baltimore-Maryland, USA, March (2016).

B18. A. T. Tasci, **E. Asikuzun**, O. Ozturk, L. Arda, S. Celik and C. Terzioglu, Structural and Optical properties of Er doped ZnO diluted magnetic semiconductor nano thin films produced by sol gel method, APS March Meeting, Baltimore-Maryland, USA, March (2016).

C. Presentations in National Refereed Conventions and Symposiums:

C1. O. Ozturk, **E. Asikuzun**, M. Akdogan, D. Yegen, M. Erdem, I. Belenli, C. Terzioglu, Investigation of Mechanical Properties of Iron Diffusion-Doped Bi-2223 Superconductors, 4th. National Superconductivity Symposium, Trabzon, 10-13 August (2009).

C2. **E. Aşıkuzun**, O. Oztürk, C. Terzioglu, The effect of diffusion-annealing times on mechanical properties of Fe doped Bi-2223 superconductors by diffusion. 16th Intense Material Physics Ankara Meeting, Ankara, 6 December (2009).

C3. **E. Asikuzun**, O. Oztürk, O.Yildiz, G. Yildirim, C. Terzioglu, The investigation of mechanical properties of Pr (Praseodymium) doped Bi-2212 superconductors 17th Intense Material Physics Ankara Meeting, Ankara, 5 December (2010).

C4. E. Budak, C. Bozkurt, O. Oztürk, **E. Asikuzun**, Synthesis of nano crystal hexagonal boron nitride and measurements of microhardness, 25th National Chemistry Congress, Erzurum, 27 June-2 July (2011).

C5. **E. Asikuzun**, O. Ozturk, O. Yildiz, M. Coskunyürek, M. Erdem, C. Terzioglu, Micromechanical characterization of Pr doped Bi-2212 superconductor, 5th National Superconductivity Symposium, İzmir, 3-6 July (2011).

C6. O.Yıldız, O. Ozturk, **E. Asikuzun**, M. Coskunyürek, G. Yildirim, M. Yilmazlar, Vickers microhardness measurements and investigation of some physical properties of Lutetium (Lu) doped Bi-2212 superconductor, 5th National Superconductivity Symposium, İzmir, 3-6 July (2011).

C7. **E. Asikuzun**, O. Yildiz, M. Coskunyürek, S. Kaya, S.P. Altintas ve O. Ozturk, The effect of Lu (Lutesyum) doping on mechanical properties of Bi-2212 Superconductors. 18th Intense Material Physics Ankara Meeting, Ankara, 25 December (2011).

CONFERENCES AND SCHOOLS ATTENDED

1- 16th Intense Material Physics - Ankara Meeting, Gazi Univ., December (2009).

2- 17th Intense Material Physics - Ankara Meeting, Ankara Univ., December (2010).

3- 18th Intense Material Physics - Ankara Meeting, ODTU, December (2011).

4- Turkish Physical Society, 28th International Physics Congress,, TPS-28, Bodrum-Turkey (2011).

5- 5th National Superconductivity Symposium, IYTE, July (2011).

6- Turkish Physical Society, 29th International Physics Congress, TPS-29, Bodrum-Turkey (2012).

7- International Conference on Superconductivity and Magnetism ICSM-2012, İstanbul-Turkey, 29 April-4 May (2012).

8- 7th Asian Conference on Applied Superconductivity and Cryogenics (ACASC-2013). Kapodokya, Turkiye 23-25 October (2013)

9- American Physical Society (APS) March Meeting, Baltimore-Maryland, ABD, 18-22 March (2013).

10- International Conference on Superconductivity and Magnetism (ICSM 2014), Antalya-Turkey, 27 April-2 May (2014).

11- International Advanced Research School in Physics (IARS), Physics of Fundamental Effects in Condensed Matter Physics: Theory & Experiment, Institute of Theoretical and Applied Physics Turunç/Marmaris, Turkey 14-21 July 2010.

12- Cumhuriyet University 19 May Summer Schools, Physics and Technology of Solar Cells, Cumhuriyet University, Sivas/Turkey, 17-21 May 2010.

13- International Spring School and Education Courses-SSEC, Superconductivity and Magnetism, Kumburgaz/Istanbul, April 2012.

14- Autumn School and Education Courses (ASEC2013), Applied Superconductivity and Cryogenics Systems, Cappadocia-Turkey 2013.

COURSES

1- FIZ305 Quantum Physics Laboratory

2- FIZ103 Mechanics Laboratory

3- FIZ207 Electronic Laboratory-I

4- FIZ252 Electronic Laboratory-II

5- FIZ253 Waves and Optics Laboratory