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Structural, Optical Properties and Synthesis of Al and Co Doped ZnO Thin Films

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Abstract: ***The aluminum and cobalt-doped zinc oxide, (Al and Co-doped ZnO) structural and optical properties were analyzed and investigated. The composite was synthesized by combustion procedure that grants multiple financial benefits over other techniques. X-ray diffraction analysis, a Scanning Electron Microscope (SEM), vibrating sample magnetometer (VSM), and UV Vis spectroscopy analyses were produced to provide a better understanding of the physical characteristics of aluminum and cobalt Doped ZnO. The structure of crystal in the Quartz phase is demonstrated by X-ray diffraction. High-resolution scanning electron microscopy (SEM) image shows the morphology of the composite which is hetrogenous mixture. VSM reveals the magnetic property of the material. The material was found to be paramagnetic in nature since the magnetization is greater than 1.Furthermore, UV - vis absorption spectroscopy has examined the optical properties of Al and Co-doped ZnO.The expected outcome is to study and analyse the results of the material.***

Keywords: Al and Co doped ZnO, optical, Structural, Magnetic, Synthesized, Combustion, Morphology, Quartz, Diffraction

I. INTRODUCTION

Lately, due to its physical and chemical properties in comparison with other bulk materials, there has been an enormous interest in semiconductors for greater efficiency. Hence, semiconductor materials are therefore viewed as a solid candidate for many essential potential applications in technology. [7] Zinc oxide is one of the most multipurpose semiconductor materials for the production and use of optoelectronic tools, sensors, or unipolar (FET) sensors, gas, gas and solution sensors, as well as biosensors, in multiple areas. Due to its wide band gap of 3.37 eV, large bond intensity, and large exciting binding energy (60 meV) at room temperature, ZnO is also an attractive material. Because of reasonable cost and exceptional characteristics compared to ITO, zinc oxide can substitute for ITO. [4] We have added some extra amounts of Co to thin films in this study in order to enhance the electrical and optical properties of AZO thin-films. Different synthesis technologies have been widely used, including sound gel, laser deposition, chemical vapor deposition, pulse laser deposition and sputtering. In many finest film systems such as photovoltaic devices and flat panel displays, however, transparent conductive oxide (TCO) films have been intensively investigated.

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TCOs along with In_2O_3, SnO_2, and ZnO generally display 10^{-2}-10 cm of resistivity depending on the processes of synthesis and system parameters. [9] In view of the relatively low carrier concentrations of these undoped TCOs between 10^{18} and 10^{20} cm-3, extrinsic doping has been embraced to improve the performance and conductance of TCOs by enhancing their carrier concentrations. For the purpose of maintaining ZnO thin film's electrical conductivity and optical transmission, group III elements of the periodic table such as boron, aluminum, gallium, and indium are generally incorporated to ZnO.Therefore, these elements generally have higher valencies and smaller ionic sizes than the host cations, it is commonly accepted that extrinsic dopants substitute host cation sites and provide an extra electron. The synthesis of the composite was prepared using the combustion method. Typically, this technique is used because it is simple, progressively reproducible, and cost-efficient. Combustion method is a methodology that involves no expensive equipment. Thus, especially in comparison to alternative methods, the invention provides a very simple and cheap technique. For a better understanding of its physical properties, the structural, electrical and optical characterization of ZnO films was investigated. [14]

II. LITERATURE SURVEY

In [1] Hammad TM and Salem Jk discussed synthesizing and characterization of Mg- doped ZnO and observed ferromagnetic properties at room temperature, using metals like Cu, Zn, Ag, Mn and Cd called as transition metals, doped ZnO thin films (DMS) which showed interest in further experimentation. Though, in these compounds, the origin of ferromagnetic behavior is not usual. The inclusion of nanoscale oxides of the transition metals may result in ferromagnetism in these materials. In [2] Bhattacharya and Gedanken found that ZnO nanocrystals varied in size with cobalt concentration variation. Ferromagnetism was noted to be intrinsic in nature which is not caused by any formation of cobalt oxide phase or metallic separation of cobalt oxide and the composite size found to be around 5 nm. Their findings show that cobalt ions are well incorporated into interchangeable zinc sites in ZnO. In [3] the impact of aluminum and gallium dopants on zinc oxide was examined by M. Chul Jun, Snag Park, and Hyunk-Jung Koh. Sol-gel spin coating method for TCO applications was used to deposition of the composite.

The films have a crystal structure of hexagonal wurtziteAl and Ga were found to be acting as electrical dopants at the starting doping concentration and in the visible region, the transmission of AZO and GZO thin films was found to be above 85 %. Moreover, AZO and GZO's structural, morphological, optical, and electrical characteristics were observed, and gallium doping was figured more efficient than Al doping. In [4] A way was suggested by Rongliang He, B. Tang, and Tsuzuki to research the physical location and Co ions' valence states in the Co-doped ZnO. The conclusions showed that the ZnO lattice as 2+ valence state took in most cobalt ions. The cathodoluminescence (CL) reported that a new emission band at 1.85 eV, produced by the integration of Co^{2+} which was hardly reported in the past. At 1.85 eV, the existence of a CL reaches its heights and its red-shift with increasing dopant levels can be used as a strong confirmation for the Co^{2+} ions in ZnO crystal doping. In [5] Nickel and Aluminum co-doped ZnO nanostructured powders are successfully synthesized by Amor Savari and Lassaad El Mir by the sol-gel method at low temperature. High crystallinity in the hexagonal lattice of the composite can be seen by the XRD patterns. For the Nano powder samples involving 1.5 at. % of Al, the shortest lattice parameters and unit cell volume are acquired. In addition, it shows that aluminum is better incorporated with this Al content in the ZnO lattice. The synthesized materials can be used for photocatalytic, optoelectronic and magnetic devices. In [6] Synthesization of Co-doped ZnO nanoparticles done by Talaat M. Hammad and Jamil K. Salem by a schematic chemical process at low temperature. It is observed that with the increase in Co concentration with respect to ZnO, the relative magnitude or strength of the XRD peaks varied. 12-5 nm was the common particle size of the Co-doped ZnO calculated using TEM and XRD. In the XRD, SEM, and HRTEM, the creation of the superstructure was established and the ZnO Host Structure of Zn2+ successfully replaced with Co2+. The current doping method can therefore be viewed as an additional powerful way of modulating ZnO's optical properties. In [7] Mingpeng Yu, H. Qiu, and Xiobai Chen studied the sputter deposits of Al and Ni co-doped ZnO films, magnetized with a vacuum of 673 K for 2h, on glass substrates. In the visible wavelength range, the films showed an average transmission of 75 %.A c-axis position wurztile structure in the direction of film growth and consisting of lean columnar grains that are orthogonal to the substratum is discovered using SEM. Low resistance and high transparency have been achieved successfully. Furthermore, it is found that in optoelectronics and magneto electronic devices the material has feasible applications. In [8] Transparent conducting Al-doped ZnO thin films made by atomic layer deposition (ALD) was explored by Waeng, Jae-won Lee, and Bum-Kwun Chung. At an Al doping concentration of approximately 2.5 percent at 250 °C, best resistivity and transmission (4.2 m in cm and ~85 %) was noted. The carrier concentration increased with an increased doping concentration and deposition temperature. By contrasting the electric and structural characteristics, the difference between the carrier concentration was found to be very influential in varying the mobility as opposed to grain-boundary dispersion because of the desiring concentration. In [9], the undoped, Al-(AZO) and In-doped (IZO), zinc oxide thin films deposited in the glass spray pyrolyze clogged with fluorine-doped tin oxide (FT) were studied in M benhaliliba, F Yakuphanoglu, and C E Benouis. The results of the SEM show that the nanofiber structure of the AZO and IZO films has a diameter of 260 and 400 nm and XRD outcomes show that doping magnifies crystallinity, although transmittance decreases thickness. It concludes that many parameters like structural, textural, optic and electrical properties have been changed by doping.

III. EXPERIMENTAL PROCEDURE

In preparation of Al and Co-doped ZnO thin films, which provide several advantages such as simple apparatus, the combustion method (synthesis technique) has been used inexpensively in relation to other alternative techniques.Combustion method is one of the traditional methods and has been used in the production of a powdered form of the element for a variety of advanced applications and to make it suitable or compatible for the characterization process. [4]The synthesis of Al and Co-doped ZnO thin films is processed in the nanotechnology lab using a muffle furnace in Saveetha School of Engineering. The relationship between the combustion parameters and product microstructures are highlighted. These results area unit crucial not solely from the applying stand, however, more significantly lead to method benefits. Zinc oxide (9.1 g), Cobalt (0.38 g), and Aluminum (0.09 g) are blended and kept in the Plaster of Paris (POP). Urea is included as fuel which helps in the ignition and after that, the mixture is kept in a beaker. Prior to keeping the blend in a beaker, preheat it and we get the element in the solid state. The colour of the mixture outcomes in pink colour. Keep the mixture close for 1 to 2 hours. The following day put in inside the muffle furnace, a machine in which the samples can be tested at high-temperature. The corners or sides of the device heat the substance which is set inside the temperature radiantly so that material does not come in direct contact with the fire. Muffle furnace is an instrument which is broadly utilized in test research facilities with a compact means to create a high-temperature state up to 1200 degree Celsius to test the distinctive sorts of characteristics of the material for exceptionally precise test outcomes. Preheat the muffle furnace to 500 degrees Celsius and put the substance inside. After this let it cool, the next day take it out and we get the component in powder structure which is suitable to go for the different characterization. In order to study the very smaller scale structure of the material, X-ray diffraction and Scanning Electron microscope (SEM) were investigated.

Examining the transmission properties and the magnetic properties were discovered using ultraviolet-visible spectroscopy (UV-vis) and Vibrating Sample Magnetometer. (VSM)

IV. RESULTS AND DISCUSSIONS

A. X-ray diffraction

X-ray diffraction is a method that permits the deduction of crystallographic density and the structure of the crystal of an unknown crystalline solid is determined. Ensure your sample is dry and start by grinding it in a pestle and mortar to a fine powder of evenly sized particles then spread it uniformly across the frosted well on the glass plate. Take care while spreading the sample to ensure that the delicate glass is not damaged. Unlock the door of the instrument and

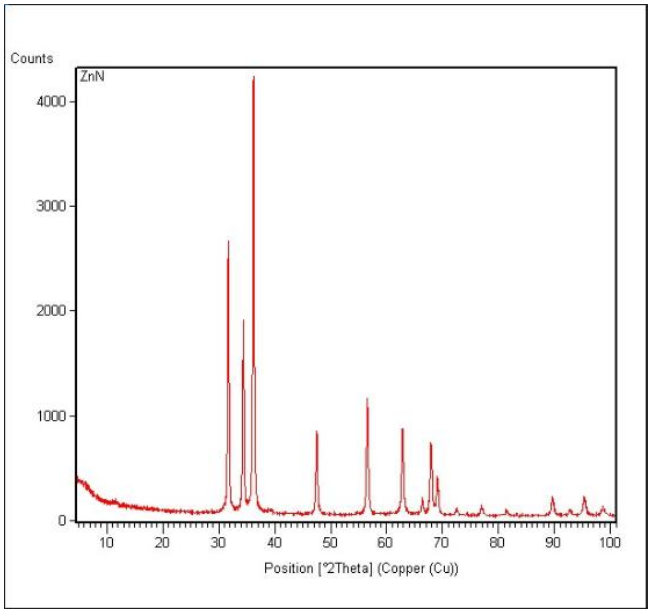

Fig. 1. XRD patterns of Al and Co doped ZnO

to unlock the door press the door lock button, an alarm will sound until the door is locked again. [11] The powder x-ray diffractometer contains three main components and they are x-ray generator, sample holder and the sample detector. The detector is similar to a typical digital camera except that it detects x-rays instead of visible wavelengths and inside the x-ray, generator electrons are accelerated across a potential difference towards a metal target, as the electron hit the target some will collide and eject the core-shell electron from the metal leaving the vacant site. [15]An electron is sent into a vacant orbital from a higher energy orbit and an x-ray photon will be discharged. Most of the x-ray produced pass straight through the sample through a small proportion is diffracted through the sample and calculated via the detector. This is the mechanism that happens inside the instrument. The diffraction peak position is noted as the detector angle, 2θ. [6] They make the electronic cloud move, right at the moment when rays are incident on an atom, as executes an electromagnetic wave. Due to a variety of effects, the movement of these charges re-radiates waves of a similar frequency fuzzy a bit, this phenomenon is known as Rayleigh scattering (or elastic scattering). [13] The Dispersed waves can be dispersed on their own, but the secondary dispersion is presumed to be insignificant. Onceyour sample is prepared, open the door and slide the sample into clips to hold it in place. Lock the door once the sample is in place and beeping will stop. After keeping the sample inside the instrument, open the mini flex software ensuring the diffractometer is on. [12] To collect the pattern, click the yellow general measurement button which brings up a new window in which the name and directory of your data are to be saved. After choosing the name and directory select the stop x-ray option and press set measurement conditions. Press and run and then start the experiment. After you run and start the experiment the analysis of powder is shown in the monitor screen. [10] Figure 1 shows XRD patterns for Al and Co-doped ZnO thin films where some major peaks occur. The figure above shows the peak position in the graph which describes the translational symmetry, in particular, the cell size and shape, while the peak intensities provide details of the electron density within the unit cell. [2] Nanoparticles synthesized are naturally crystalline. Using the Scherrer equation, the average crystal size was estimated on the basis of diffraction peak associated with the crystal plane.

$$d=K\lambda/(\beta \cos \theta) \quad (1)$$

Where d is the mean crystallite size (nm), K is the shape factor of the crystalline form with a good approximation to 0.9, lamda is the X-ray wavelength, β is the full width of the X-ray diffraction peak, and theta is the angle of the Bragg's. [5] It is noticed that the Films are growing with a hexagonal wurtzite type structure and

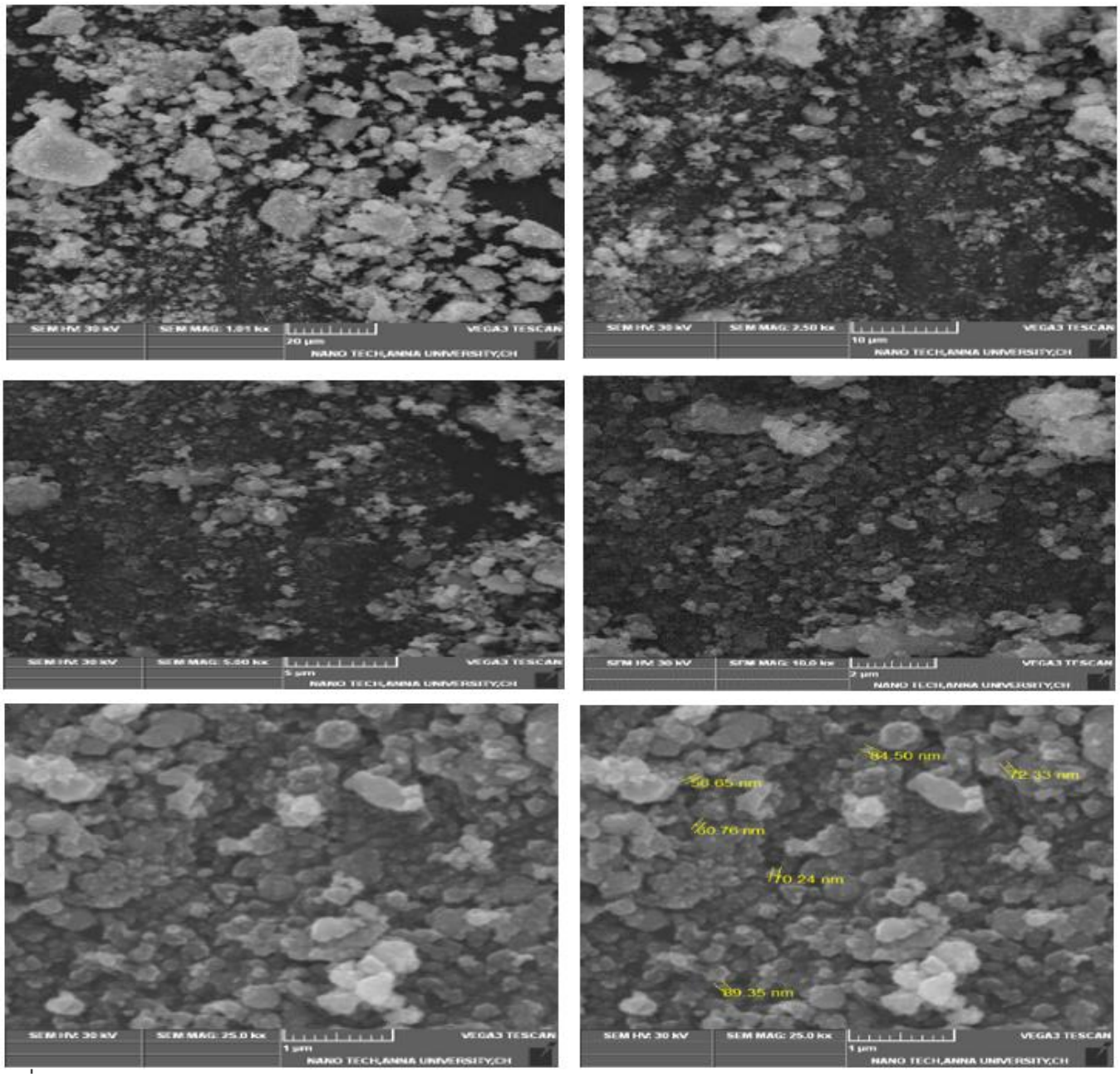

Fig. 2. SEM micrographs of the Al and Co doped ZnO thin films showing morphology at different magnifications

doping changes, the film structure.

B. Scanning Electron Microscopy

The Scanning Electron Microscopy is a microscope that makes use of electrons as a substitute of sunshine to type animage. Over traditional microscopes, the scanning electron microscope has several advantages. The SEM has an enormous area depth that allows more specimens to be at one time in the focal point. Moreover, the SEM has so much greater decision; closely spaced apart specimens can be magnified at considerable larger phases as well. Due to the point that the SEM makes use of electromagnets instead than lenses, the researcher has far more control in the degree of magnification. [10] The SEM is instrument that produces a generally magnified picture by making use of electrons alternatively.On top of the microscope, a beam of electrons is generated through an electron gun beam that chases a vertical course through the microscope held in a vacuum. The beam travels down towards the pattern with the help of electromagnetic fields and lenses. [8] Electrons andx-rays are released from the sample after the beam strikes the sample. These X-rays, backscattered electrons, and secondary electrons are accumulated by detectors and translated into a signal that's sent to be disclosed, much like a TV monitor. [16] This produces the finalsnapshot. SEM imaging can provide more detailed surface information. Detection of the X-rays generated by the interaction of electron matter is also commonly used in many microscopes to carry out elemental sample analysis. Each material generates

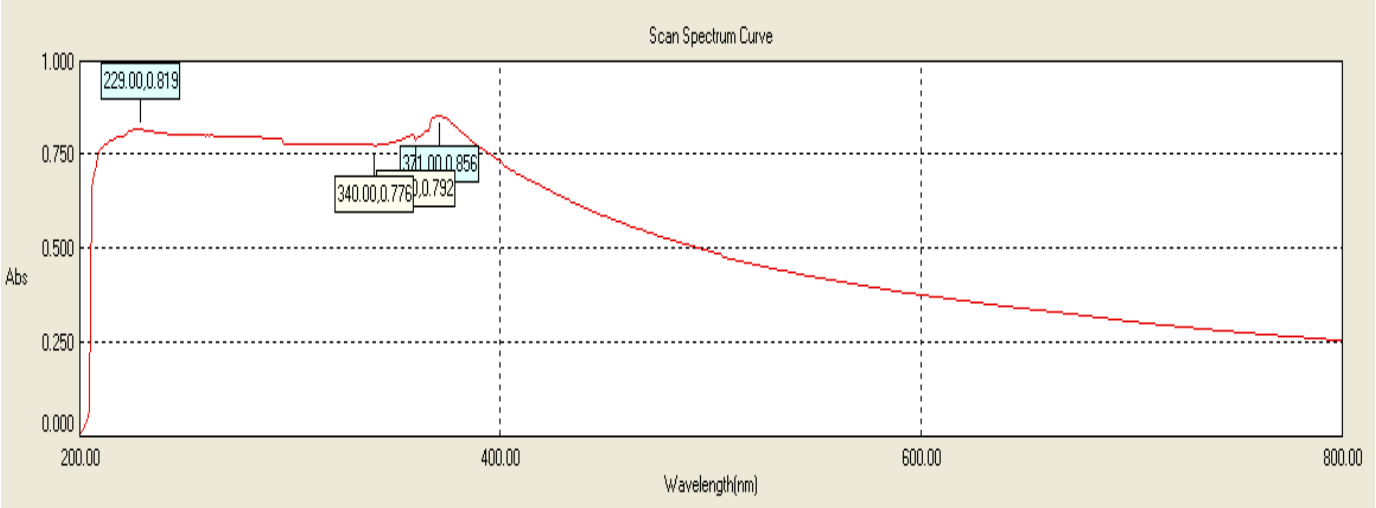

Figure 3. UV-vis spectra of Al and Co doped ZnO nanoparticle

X-rays with particular energy; X-rays are the fingerprint of the material. Hence, it is possible to identify all the elements that it consists of, by monitoring the energies of X-rays that appear from a sample with unknown composition. [15]
Figure 4 shows SEM images of Al and Co-doped ZnO thin films with various magnifications (20, 10, 5, 2 and 1μm) of morphology. Non-uniform particle diffusion is found out from SEM micrographs. The crystallite shape was quite different. Al and Co-doped ZnO's average inter-fringe distance was calculated around 56.65 nm, with a heterogeneous microstructure. We observe that the Co and Al atoms have been incorporated into ZnO's crystal lattice, based on the outcomes of XRD pattern and SEM images. [3]

C. UV- vis spectroscopy

UV- vis spectroscopy is a method that estimates the absorbability of a solution across the ultraviolet and visible regions of the light spectrum, hence the name is UV-vis. The Alignment 8453 spectrophotometer and the chemstation software is used. The spectrophotometer has two lamps, deuterium lamp which generates light in the UV region which is between 190 and 400 nm and a tungsten lamp which generates light in the visible and near IR- region of 400 and 1100 nm in wavelength. Switch ON the instrument and let it warm for 45 minutes to make sure that the lamps are nice and hot and the measurement is of a good quality. We used different types of cuvettes, some of them are like quartz one and has a frosted side and the others are plastic types that is regularly used and are disposable. [17] Blank the cuvette and add an ml of water and wait till we get ablack which is nice and flat and put the cuvette in the sample holder. The optical properties of the Al and Co doped ZnO were studied and observed by UV-vis absorption spectroscopy. UV-vis absorption spectroscopy has examinedand observed the optical characteristics of the Al and Codoped ZnO.
Figure 3 shows the pure and Al and Co-doped ZnO spectrum typically absorbed particles within the 200 to 800 nm wavelength range. Four highest peaks were noted and located at 229, 340,360 and 371 nm. All films display a transmittance with a sharp fundamental edge of absorption within the Ultra violet region.

D. Vibrating Sample Magnetometer

Vibrating sample magnetometer is used to determine the magnetic properties of the material. Magnetic materials can be classified by their response to external magnetic field into categories such as diamagnetism, Para magnetism, ferromagnetism, antiferromagnetic, and ferrimagnetism. It has electromagnets which provide a uniform magnetic field. Figure 4 shows Al and Co-doped ZnO thin films' magnetic properties. A VSM initially places the sample in a constant magnetic field to be examined. This constant magnetic field magnetizes the sample, if the sample is magnetic, through systematizing the field of the magnetic domains or the individual magnetic spins. The stronger the constant field, the greater the magnetization. The magnetic dipole moment of the sample generates a magnetic field, called the magnetic stray field on both sides of the sample. With the passage of the sample, this magnetic stray field is changed according to time and can be observed with pick-up coils. According to Faraday's Law of Induction, the alternating magnetic field will result in an electrical field in the pick - up coils. The current will be proportional to the sample's magnetization. The greater the magnetization, the greater the current induced. A trans-impedance amplifier and lock-in amplifier amplify the induction current.A computer interface is associated with the different components. The system can report, to what extent the sample is magnetized and how its magnetization relies on the strength of the constant magnetic field utilizing control and monitoring software. [16] A typical sample measurement shall be taken as follows. The constant magnetic field strength is initially set and the sample immediately begins to tremble. The signal from the probe provided or received is described as a value for the sample's magnetic moment.

The strength of the constant magnetic field will modify to a new value and no data will be taken during the whole transition. A new value is obtained from the strength of the continuous magnetic field and once more the signal from the probe becomes a new value for the sample's magnetization. [13]

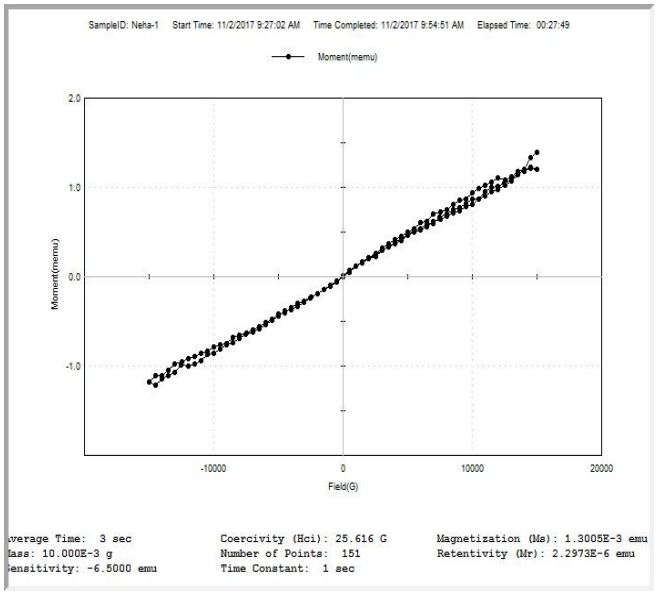

Figure 4: Magnetic properties of Al and Co doped ZnO

Lastly, the magnetic field constantly differs over a given range, and there is a magnetization plot (M) against the magnetic field strength (H) often referred to as the hysteresis loop. This instrument displays the magnetic moment in e.m.u units. Itis observed that the particle is a paramagnetic material since the magnetization is found to be 1.3005E-3 emu. In addition, the Coercivity and Retentivity was observed as 25.616 G and 2.2973e-6 emu. [14]

V. CONCLUSION

We have synthesized Al and Co doped ZnO thin films nanoparticles by a method called combustion method which is also called as top down approach to convert the element into the powder form. The pinnacle position in the XRD diagram shows the translational symmetry of the unit cell size and form, while the pinnacles give information about the electron density within the unit cell. The SEM confirmed that the microstructures of thin films are heterogeneous at different magnifications. The films exhibit a transmittance within Ultra violet region with a sharp fundamental absorption edge which was discovered using UV-vis spectroscopy. The VSM results revealed that the particle is paramagnetic in nature and other properties like retentivity and coercivity were disclosed. The current doping method can, therefore, be termed as an additional effective approach for modulating nanoparticles' optical and other physical characteristics.

VI. FUTURE ENHANCEMENT

Semiconducting materials in nanostructures form remain an extensively investigated nanotechnology, subject materials in science current and solid Physics state (nanoscience, physics) and Chemistry. Most of the promising technological applications deals with size dependent properties. The ability to manipulate matter at the atomic scale bears promise to produce devices of unprecedented speed and efficiency. The emerging area called nanoscience and nanotechnology which has seen phenomenal growth in the past decade and is likely to be the frontal area of research for the next few decades. The outcome of this research is likely to revolutionize technology. Nanotechnology is driven by the fact that some structures that are generally smaller than 100 nm have new properties and tendencies that are not represented in the same composition by the bulk matter. Particles that are versatile with the particular phenomena are often shown to display new physics and new chemistry, leading to new properties,reliant upon size. One of the most intuitive effects may be due to the surface to volume ratio change. When the structure's size is reduced, the ratio significantly increments and surface phenomena prevail over bulk chemistry and physics. Hence in manufacturing devices, sensors, LED's, and LASER's it is important to design and control better because nanoscience deals in new phenomena and new sensor devices can be manufactured that benefit from such problems.

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