OPICAL AND THERMAL MEASURMENT OF MIXED CuO-ZnO NANOPARTICLES

S.G.Rejith[a*]
[a]Department of physics, St.Xavier's College, Palayamkottai – 627 002, Tamilnadu, India

***Abstract*:** Nanocrystalline materials may be considered as the challenge of this age. CuO-ZnO as a narrow band gap P-type semiconductor has been recognized industrially important material for a variety of application such as catalysis, batteries, solar energy conversion, sensors etc, In this work I have successfully prepared mixed CuO-ZnO by microwave assisted solvothermal method using copper acetate and zinc acetate as the starting material. And also I have evaluated structural, optical and thermal properties of prepared sample. The synthesized pure CuO-ZnO nanoparticles have been characterized by using XRD, SEM, UV-visible and TG/DTA techniques. The optical property of copper oxide and zinc oxide nanoparticles are measured by UV-visible spectroscopy. Thermo gravimetric analysis (TGA) is used to determine a materials thermal stability and the fraction of volatile components.

***IndexTerms-* Nanostructures, metal oxides, solvothermal method, X-ray diffraction, optical and thermal properties.**

I. INTRODUCTION

Nanotechnology (sometimes shortened to "nanotech") is the study of manipulating matter on an atomic and molecular scale. Intensive investigation was stimulated for several applications for these new classes of materials. Generally, nanotechnology deals with developing materials, devices, or other structure possessing at least one dimension sized from 1-100 nm. Quantum mechanical effects are important at this Quantum-realm scale [1]. The oxides of transition metals are an important class of semiconductor, which have applications in magnetic storage media, solar energy transformation, electronics and catalysis [2]. Transition metal oxide nanomaterials have gained much attention due to their small size effect, high surface to volume ratio which lead to many advantages in applications like gas sensors, catalysts, battery electrodes, photo electronic devices, magnetic materials, electrochemical devices[3-7]. In past decade, there has been an increasing interest in the synthesis of nanosized crystalline metal oxides because of their large surface areas to volume ratio, high chemical reaction rate, unusual absorptive, properties, surface defects, and fast diffusivities [8]. In many of them, the main objective is to reduce the costs of synthesis and to produce high phase purity materials for technological applications [9].

Among the oxides of transition metals copper oxides nanoparticles are of special interest because of the efficiency as nano fluids in heat transfer applications. CuO is semiconducting compound with narrow band gap and used for photo conductive and photothermal applications. ZnO is frequently used in several areas of technology, it is worthy to investigate high quality self – structure ZnO film synthesized on different kinds of structure [10]. ZnO has great advantages for LED's and laser diodes over the currently used semiconductors. ZnO as II-VI semiconductor is promising for various technological application especially for opto electronics short wavelength light emitting devices due to its wide direct band [11].

Nanotechnology may be able to create many new materials and devices with a vast range of applications such as medicine, electronics, biomaterials, and energy protection on the other hand nanotechnology raises many of the same issuse as any two technology. Nanoparticle research is gaining increasing interest due to their unique properties such as increased electrical conductivity toughness and ductility, increased hardness and strength of metals and alloys luminescent efficiency of semiconductors formability of ceramic. Copper is a Block-D period 4 element while oxygen is a Block-P period 2 element.

Copper oxide nanoparticle appears a brownish black powder. They can be reduced to metallic copper when exposed to hydrogen or carbon monoxide under high temperature. They are graded harmful to humans and as dangerous for the environment with adverse effect on aquatic life.

Zinc oxide is an organic compound with the formula ZnO. ZnO is a white powder that is insoluble in water, which is widely used as an additive in numerous material and products including plastics, ceramics glass, cement, lubricants, paints, ointments, adhesives, sealants, pigments, foods, batteries, ferrites, fire retardants, and first aid taps. It occurs naturally as the mineral zincite but most zinc oxide is produced synthetically. In material science ZnO is a wide band gap semiconductor of the II-VI semiconductor graph(since oxygen was classed as element of VI A group (the 6^{th} main group ,now reffered to as 16^{th})of the periodic table and Zinc a transition metal as a member of the II B now 12^{th} group. The native doping of the semiconductor in n-type .

II . EXPERIMENTAL

2.1 GENERAL

X-ray diffraction is an ideal technique for the determination of crystallite size of the powder samples. The basic principle for such a determination involves precise quantification of the broadening of the diffraction peaks. The average crystallite size (D) has been calculated from the line broadening using Scherrer's relation $D = K\lambda /\beta\cos\theta$, where the constant K is taken to be 0.94, λ is the wavelength of X-ray used which is CuKα radiation (λ= 1.5406 Å) and β is the full width at half maximum of the diffraction peak corresponding to 2θ.The powder XRD pattern of the prepared nanoparticles is recorded with automated X-ray diffractometer (X-PERT PRO Philips System) operating CuK_{α} at wavelength 1.54056 Å. The morphology of the powder samples was characterized by scanning electron microscope (SEM) JEOL/EO JSM-6390. The UV spectrum was obtained using LAMBDA-35 UV visible spectro photometer. UV-Visible absorption spectrum of synthesized nanoparticles shows the band edge-absorption peak is found to be at 350 nm. Perkin Elmer, Diamond TG/DTA is used for thermo gravimetric analysis.

2.2. Procedure

The mixed CuO-ZnO nanoparticles were synthesized using microwave assisted solvo thermal process. copper acetate, zinc acetate, urea were taken as solute in the molecular ratio 1:3 and dissolved in 50ml ethylene glycol as individually with the help of magnetic stirrer around 15 minutes. Then the three solutions were mixed together stirrered again for 10 minutes. The colour was noted as light green, the solution was kept in microwave oven operated with 2.45GHz and power 800W. Microwave irradiation was carried out for about 10 minutes till the solvent was evaporated completely. The colloidal precipitate obtained was dark green coloured, then this precipitate was washed three times with distilled water and then washed with acetone two times to remove the organic compounds present, if any. Then the sample was dried in atmospheric air and collected as the yield. The synthesized NPs have been characterized by using X-ray Diffraction (XRD), Scanning Electron Microscopy with EDAX (SEM-EDAX), UV-visible spectroscopy (UV-Vis) and Thermal analysis (TG/DTA).

III. Results and Discussion

The PXRD patterns obtained in the present study for copper oxide mixed zinc oxide nanoparticles are presented in figures. X-ray diffraction is a powerful tool to study the crystal structure of semiconductors. XRD gives information about crystalline phase, quality, orientation, composition, lattice parameters, defects stress and strain of samples. Even crystalline solid has its unique “finger print” crystals are regular arrays of atoms and they are arranged in a way that a series of planes separated from one another by a distance d. A typical X-ray diffractometer (XRD) pattern of nanocrystalline CuO shows Monoclinic structure and ZnO shows Hexagonal wurtzite structure. Zinc oxide crystallizes in three forms: hexagonal wurtzite, cubic zincblende, and the rarely observed cubic rocksalt. The wurtzite structure is most common at ambient conditions.

The particle size were estimated using the scherer’s formula by taking the average of three main line widths obtained from the PXRD patterns. The peak position of the sample exhibited the monoclinic structure for CuO and hexagonal wurtzite structure for ZnO. Further no other impurity peak was observed in the X ray spectra showing the formation of CuO-ZnO nanoparticles. The lattice parameters for unit cell of CuO are found to be a=4.691 Å, b=3.472 Å, c=5.138 Å and ZnO are found to be a=4.691 Å, b=3.253 Å, c=5.209 Å.

It is clear from the figure that the intensity of peak could increase with temperature indicate the intense of sample crystallinity. Simultaneously the peak because narrower as the temperature increases resulting increase of crystalline size. So we could get the correct order with annealing. The increase in crystal-size with temperature attribute the atomic diffusion.The prepared nanoparticles are compared well with the available JCPDS data, numbered 3614150 and 770196 indicates the a, b, c values of my sample is 4.725, 2.590 and h k l planes corresponds to 2θ values are 33.50^0, 59.68^0, 66^0 which confirm the formation of CuO-ZnO nanoparticles.

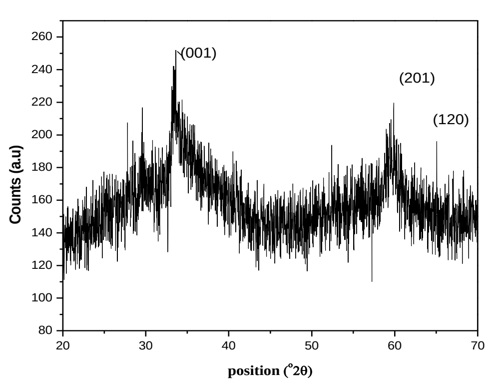

Figure : PXRD spectrum for CuO-ZnO Nanoparticles

The UV-Vis spectrum of the sample is shown in fig. The sample absorbs the radiation in the UV range up to 240 nm and almost all the visible spectrum radiation are transmitted by the CuO-ZnO nanoparticles. The band of the particles was calculated by extrapolating the curve drawn between hγ and **(αhυ)**^{2}. Where υ in the frequency and α is the optical absorption coefficients. The band gap energy obtained by extrapolating tauc plot a found to be approximately 3.7 eV.

The oxide have distinctive colour in colloidal solution due to its tiny dimensions. The electron cloud on the surface of nanoparticles oscillates and absorbs electromagnetic radiation at particular energy The particular type of resonance arises is called Plasmon resonance .The shifting of absorption spectra towards red and or blue end depends upon the particle size, shape, surrounding medium and state of aggregation.

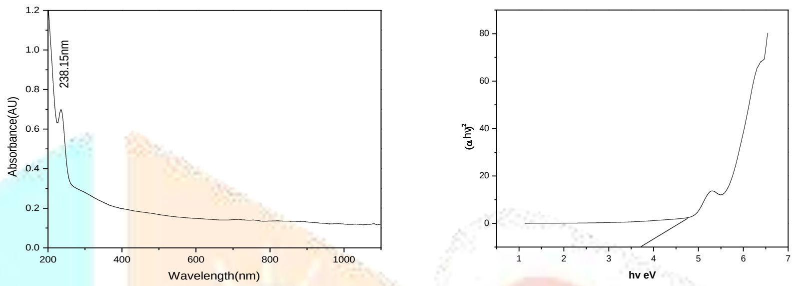

Fig : UV-Vis and bandgap Spectrum For CuO Mixed Zno

SEM image of the as prepared sample is shown in fig , reveals that the particles are spherical and having granular nature. In the higher resolution SEM image the agglomeration of particle is observed. The micrographs are shown in the figure reveal that a report that a network formation at ZnO – CuO has taken place. It clearly indicates that the agglomeration has taken place. It is not possible to protect the exact size of the individual particle, which can be done through TEM analysis. The agglomeration of my as prepared nanoparticles micrograph indicates the amorphous phase of nanoparticles. Which can improve further annealing process. Though SEM image we can infer that CuO-ZnO nanoparticles is successfully formed. From SEM image we can find dimension as a group or cluster of nanoparticles based on the magnification ranges.

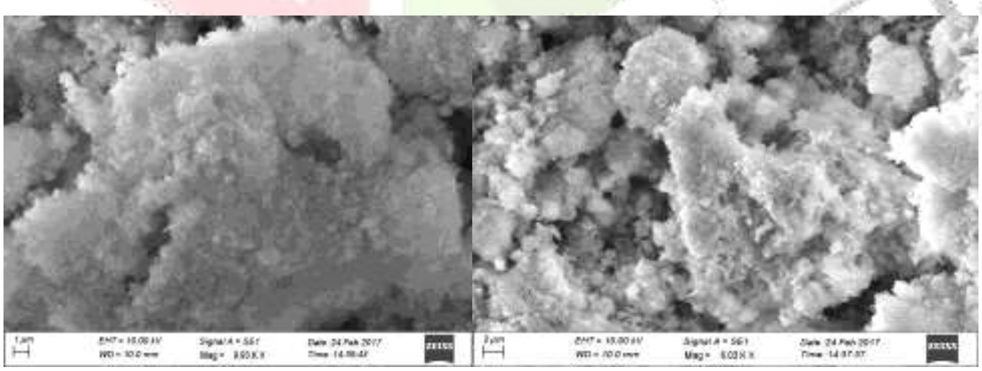

Fig : SEM image for CuO-ZnO Nanoparticle

Thermo gravimetric analyses were carried out using Perkin-Elmer, Diamond TG/DTA thermal analyzer. Thermo Gravimetric analysis(TGA) is an analytical technique used to determine a material's thermal stability and the fraction of volatile components by monitoring the weight change that occurs as the specimen is heated. Te measurement is normally carried out in air or in an inert atmosphere, like helium or argon, and the weight is recorded as a function of temperature. Fig shows the simultaneous thermo gravimetric (TG) and Differential thermal analysis (DTA) curves for the prepared CuO-ZnO samples. In order to obtain we used copper acetate, zinc acetate and urea as the precursors. The decomposition behavior of the acetate precursors can be identified from the respective weight losses in the thermogram and from the endothermic or exothermic peaks in the DTA plot.

Thermo gravimetric Analysis or TGA is a type of testing that is performed on samples to determine changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three instruments: weight, temperature and temperature change. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative weight loss curve can be used to tell the point at which weight loss is most apparent. Thermal gravimetric analysis measures the mass change of the sample with a thermo-balance. A variation on this is DTG, or derivative thermo gravimetric, which measures the slope or derivative of the mass change with temperature, dm/ dt.

Thermal analysis is carried out by raising the temperature gradually and plotting weight against temperature. The temperature in many testing methods routinely reaches 750^0 C or greater, but the oven is so greatly insulated that an operator would 160 not be aware of any change in temperature even if standing directly in front of the device. After the data is obtained, curve smoothing and other operations may be done such as to find the exact points of inflection. Fig shows that continuous weight loss happened up to 500^0C, after that no significant loss of heat was absorbed. And also indicates that a sharpen exothermic peak obtained in the temperature range around 250^0C, which means particles release energy by heat.

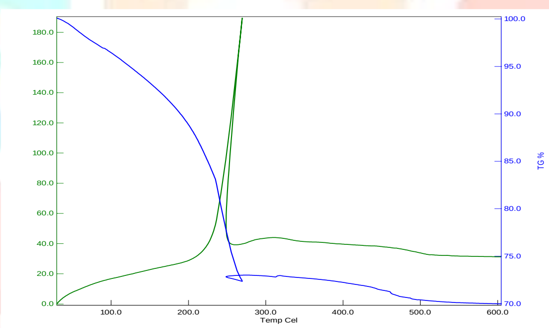

FIG : TGA-DTA FOR CUO-ZNO NANOPARTICLES

Summary and conclusion:

copper oxide mixed zinc oxide nanoparticles were prepared by using the simple solvothermal methods are characterized by PXRD, UV-vis, SEM, TG/DTA. From the studies we observed that prepared nanoparticlesin nanometer dimension. UV-visible absorption spectrum of synthesize nanoparticles show the band edge absorption peak and is found to be at 240nm. The obtained bandgap values are 3.7eV for the sample. The agglomeration of my as prepared nanoparticles micrograph indicates the amorphous phase of nanoparticles. Which can improve further annealing process. Though SEM image we can infer that CuO-ZnO nanoparticles is successfully formed. TG/DTA graph shows that continuous weight loss happened up to 500^0C, after that no significant loss of heat was absorbed. And also indicates that a sharpen exothermic peak obtained in the temperature range around 250^0C.

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