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# ELECTRICAL AND MAGNETIC PROPERTIES OF THE SOLVOTHRMALLY SYNTHESIZED Mn-DOPED CuO NANOPARTICLES

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## ABSTRACT

Pure and manganese-doped copper oxide nanoparticles were successfully prepared by microwave assisted solvothermal method. The samples were characterized by X-ray diffraction (XRD), Energy dispersive X-ray spectroscopy (EDS), Vibrating Sample Magnetometer (VSM) and Dielectric (AC) studies. The average crystallite sizes of pure and Mn-doped CuO nanoparticles calculated from XRD pattern was 10-14 nm and 9-34 nm. Energy dispersive X-ray spectra show that doped impurity has entered in the crystal matrix of CuO. It is expected that the doped ions will be replacing the $O^{2-}$ ions instead of occupying the interstitials.VSM analysis shows antiferromagnetic nature of pure CuO and Ferromagnetic nature of Mn-doped CuO nanoparticles. The dielectric parameters increase with increase in temperature for prepared samples.

Keywords: Nanostructures, oxides, solvothermal method, X-ray diffraction, properties.

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## 1.1. INTRODUCTION

Nanotechnological products called often as a technology of the future used in various fields such as electronics, computer technology, cosmetics industry and drug delivery or medical diagnostics. These practical applications explain why nano material's are arousing great interest in the scientific and economic sphere. Metal oxides represent the most diverse class of materials with properties covering almost all aspects of materials science and physics. Copper oxide is an important p-type semiconductor with the band gap in the range of 1.8-2.5 eV [12]. In recent years, great efforts have been made to develop nanostructured metal oxides with p-type semiconductivity. Metal oxide nanoparticles have attracted their great attention due to its tunable optical, electronic, magnetic and catalytic properties [2, 16].

The crystalline $Cu_2O$ with nanoscale dimensions could be anticipated to have spatially confined excitons and thereby increase their concentration. The large excitonic binding energy offers the possibilities to observe excitonic features in the absorption and luminescence spectrum [4, 8]. Such unique electronic structures of $Cu_2O$ spur a growing amount of interest in its crystalline nanostructures. Cubic crystalline structure and the electronic properties of $Cu_2O$ stimulated many researchers to study optical and electronic properties in different shapes and sizes [6-3]. CuO nanoparticles are found to be monoclinic structured AFM semiconductors [15]. The study of semiconductor nanoparticles or quantum dots is a major field of research in condensed matter physics. Particularly interesting are the quantum size effects on the optical properties of the semiconductor nanoparticles [19, 5]. Moreover the doping of the semiconductor nanoparticles with transition metal ions has been the subject of research in recent years to find out the potential applications in photonic field [11, 17]. The engineering of band gap and influencing physical, chemical, and electronic properties of the semiconductors are possible by the use of the right dopants. Norman et al [13] showed the tuning of the emission energy of Mn doped MnSe nanoparticles.

Ferromagnetism and superparamagetism were observed in the CuO powders and nanoparticles, which were ascribed to the existence of uncompensated spins at the surface of the particles. The ab initio calculations predicted that Mn-doped is ferromagnetic following a metal insulator transition due to the double exchange coupling. Mn-induced donor levels enable conduction through ferromagnetically aligned Mn centers and ferromagnetic CuO planes via double exchange. In the paramagnetic insulating phase, a polaron hopping mechanism consistent with the experiments is envisaged. Our results suggest the intriguing possibility of designing double-exchange driven ferromagnetic cuprates [1].

There are several methods reported to synthesize copper oxide NPs like sol-gel, hydrothermal route, electrochemical [10-18] etc. Here in, we report a microwave assisted solvothermal synthetic method and characterization of pure CuO and Mn-doped CuO nanoparticles with spherical like shape, Manganese (Mn) is a metal with important industrial metal alloy uses, particularly in stainless steel. The most stable oxidation state of Mn is+2. Manganese metal and its common ions are paramagnetic. Moreover, these types of CuO nanostructures show an excellent electrochemical behavior and good cycle stability.

1.2. Experimental

1.2.1. General

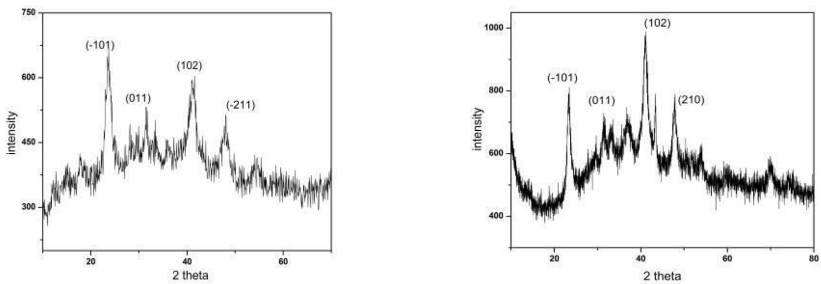
X-ray diffraction is an ideal technique for the determination of crystallite size of the powder samples. The basic principle for such a determination involves precise quantification of the broadening of the diffraction peaks. The average crystallite size (D) has been calculated from the line broadening using Scherrer's relation $D = K\lambda / \beta\cos\theta$, where the constant K is taken to be 0.94, $\lambda$ is the wavelength of X-ray used which is CuKα radiation ($\lambda$= 1.5406 Å) and $\beta$ is the full width at half maximum of the diffraction peak corresponding to $2\theta$.The powder XRD pattern of the prepared nanoparticles is recorded with automated X-ray diffractometer (X-PERT PRO Philips System) operating $CuK_\alpha$ 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. The antiferromagnetic (AFM) nature of CuO nanoparticles are studied using Lake Shore: Model: 7404 vibrating sample magnetometer (VSM). Perkin Elmer, Diamond TG/DTA is used for thermo gravimetric analysis. Thermo Nicolet, Avatar 370 FTIR spectrometer is used for IR absorption studies in the spectral range of 4000- 400 $cm^{-1}$. Dielectric parameters of the prepared samples were measured using (Agilent 4284 A) LCR meter.

1.2.2. Procedure

Copper oxide nanoparticles have been prepared by several methods ranging from thermal reduction, sonochemical method, sol-gel reaction, to gas phase process. Compared to the wet-phase sol-gel based method and the thermal reduction, both of which require inherent multistep processes, gas-phase methods are capable of continuous production of nanoparticles with a single step. Therefore microwave synthesis has been developed for large-scale industrial production of nanoparticles. Among those, solvothermal process has been shown to be a powerful technique for generating novel materials with interesting properties. Particularly, the solvothermal technique provides the alternative approach that allows the economical synthesis of fundamentally important well-defined nanometer-sized materials at mild conditions. To our knowledge, this new synthetic technique has not been applied in the synthesis of transition metal oxides such as copper oxide. The present work is focused on the synthesis and characterization of nanometer-sized

CuO particles (pure and 2wt% Mn-doped) by a simple microwave assisted solvothermal method. Analytical reagent (AR) grade copper acetate, manganese acetate, urea, ethylene glycol (as solvent) are used as precursors. Copper acetate and urea are taken as solute in the molecular ratio 1:3 and dissolved in 100 ml ethylene glycol as individually. For manganese doping, manganese acetate (2 wt %) are added. Microwave irradiation is carried out for about 20 minutes till the solvent is evaporated completely. The obtained colloidal precipitate is black in colour. In the end, the precipitate is washed several times with distilled water and acetone to remove the organic impurities. The synthesized NPs have been characterized by using X-ray Diffraction (XRD), EDAX , Vibrating Sample Magnetometer (VSM) and Dielectric (AC) studies.

**1.3. Results and Discussion**



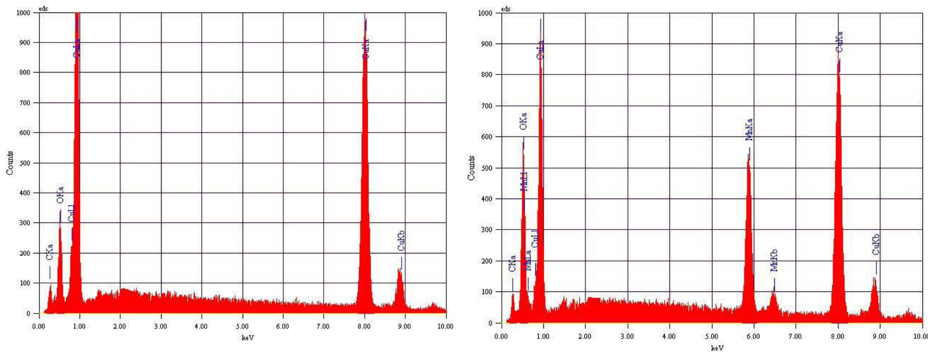

(a) (b)

Fig. A: PXRD pattern for (a) pure CuO (b) Mn-doped CuO

The XRD pattern which is obtained in the present study for pure and 2wt% of manganese -doped copper oxide nanoparticles are presented in Fig. A. All diffraction peaks can be indexed in the CuO monoclinic phase. The lattice parameters are calculated using the least square refinement from the UNITCELL-97 program. The copper oxide nanoparticles retained its monoclinic structure with lattice parameters a= 4.682 Å, b= 3.424 Å, C=5.127 Å with volume cell of 81.52 $Å^3$. These values are consistent with the reported literatures and with the respective "JCPDS" (Joint Committee on Powder Diffraction Standards) card No.89-5895. In the XRD spectrum, the diffraction peaks are considerably broadened that is attributed to the small crystallite sizes. Small crystallites have relatively few lattice planes that contribute to the diffraction lines. Broadening the peak may also occur due to micro straining of the crystal structure arising from defects like dislocation and twinning etc. In Mn-doped copper oxide nanoparticles spectrum the diffraction pattern peaks are considerably narrowed that are attributed to the change in crystallite sizes. The grain sizes which obtained are small enough to have the quantum confinement. Using Scherer's equation, the crystallite sizes find to be in the range of nanometer.

XRD pattern of pure CuO nanoparticles reveals intense diffraction peaks at 2Θ = 23.594°, 41.577°, 31.550° and 47.916°,corresponding to d-spacing values 3.767, 2.170, 2.833 and 1.896 reveals lattice planes (-101), (011), (102)and (-211). The average grain sizes for this peaks are measured as 10-14 nm. XRD patterns of 2wt% of Mn-doped CuO nanoparticles reveals intense and narrow diffraction peaks at 41.1392°, 23.4447°, 43.3919°, and 47.7935°, corresponding to d-spacing values 2.19424, 3.79456, 2.08541, and 1.90313 reveals lattice planes (101), (201), (012)and (210). The average grain sizes for these peaks are measured as 9-34 nm.

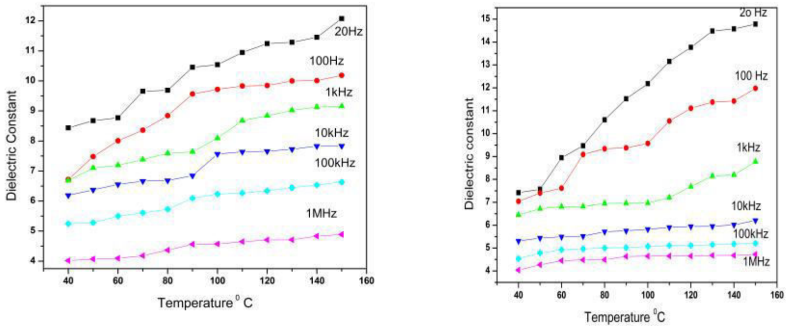
Energy dispersive X-ray spectroscopy (EDS) was used for the elemental analysis or chemical characterization of all the samples considered. EDAX spectra for pure and 2wt% of Mn-doped CuO nanoparticles are shown in Fig. b. An EDS spectrum displays peak corresponding to the energy level for which the most X-rays had been received. Each of these peaks is unique to an atom and therefore corresponds to single elements Cu, Mn and O.




(a) (b)

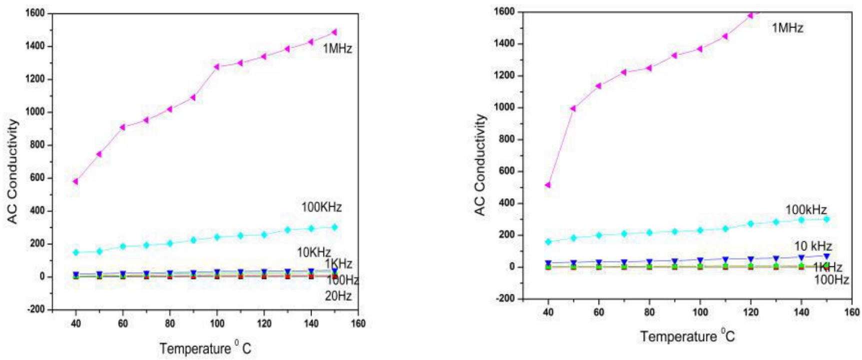
Fig. B: EDAX spectra for (a) pure CuO (b) Mn-doped CuO

This shows that doped impurity has entered in the crystal matrix of CuO. It is expected that the doped ions will be replacing the $O^{2-}$ ions instead of occupying the interstitials.




(a) (b)

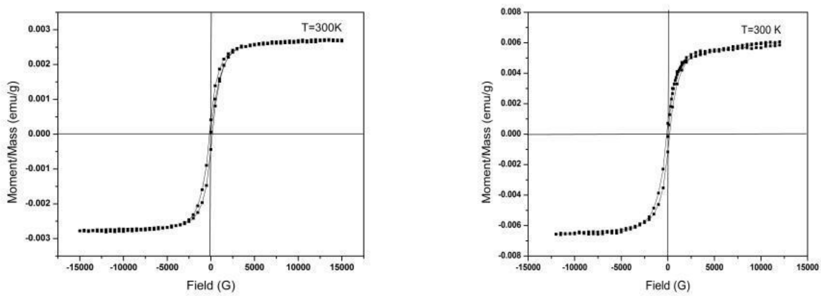
Fig. C: Dielectric constant for (a) pure CuO (b) Mn-doped CuO




(a) (b)

Fig. D: AC conductivity for (a) pure CuO (b) Mn-doped CuO

The dielectric parameters such as dielectric constant ($\varepsilon_r$) and AC electrical conductivity ($\sigma_{ac}$) observed in the present study are provided in FigC and Fig. D. The dielectric constant ($\varepsilon_r$) is attributed to four types of polarization which are space charge, dipolar, ionic and electronic. At lower frequencies, all four types of polarizations contribute. The rapid increase in dielectric constant is mainly due to space charge and dipolar polarizations which are strongly temperature dependent. The ($\sigma_{ac}$) values observed in the present study are very small which increases with increasing temperature. Thus the space charge contribution plays an important role in the charge transport process and polarizability in the present study. From the dielectric studies it is seen that the dielectric constant increases with decreasing frequency and increase in temperature. Nano crystalline materials posses' enormous number of interfaces and the large number of defects present at these interfaces can cause a change off positive and negative space charge distribution. When an electric field is applied these space charges move and trapped by these defects, resulting in the formation of dipole moments. This is called space charge polarization. From the AC Conductivity graph, it is seen that as frequency increases the conductivity remains more or less constant at low frequencies, but at higher frequencies, as the frequency increases the conductivity also increases. The variations are similar for other temperatures, but the values are shifted upwards as the temperature rises.




(a) (b)

Figure E: VSM spectrum for (a) pure CuO (b) Mn-doped CuO

The magnetizations versus magnetic field (M-H) curves for the prepared CuO nanoparticles recorded at 300 K are shown in Fig. E. The measured coercivities, saturated magnetizations (Ms) mass and Retentivity (Mr) values of the pure CuO nanoparticles are are 166.43 G, 2.7610E-3 emu/g, 57.570E-3 g and 424.04E-6 emu/g respectively. And of 2wt% Mn-doped CuO nanoparticles are 157.82 G, 6.3284E-3 emu/g, 20.430E-3 g and 937.69E-6 emu/g respectively. Ferromagnetism and superparamagetism were observed in the CuO powders and nanoparticles, which were ascribed to the existence of uncompensated spins at the surface of the particles. The abs initio calculations predicted that Mn-doped is ferromagnetic following a metal insulator transition due to the double exchange coupling. Mn-induced donor levels enable conduction through ferromagnetic ally aligned Mn centers and ferromagnetic CuO planes via double exchange. In the paramagnetic insulating phase, a polaron hopping mechanism consistent with the experiments is envisaged. Our results suggest the intriguing possibility of designing double-exchange driven ferromagnetic cuprites. Ferromagnetic semiconductors (FS) are key materials for spin injection in electronic and optoelectronic semiconductor devices that can be controlled by weak magnetic field, such as spin transistors, polarizing light-emitting diodes, and nonvolatile storage devices. As the efficiency of spin injection depends on the interface quality and impedance matching, all-semiconductor structures benefit the performance of spintronic devices [14].

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The magnetizations of the samples increase with increasing magnetic field strength. It is also observed that at smaller magnetic fields the magnetizations increase with magnetic field nonlinearly whereas at relatively higher magnetic fields the magnetizations increase with magnetic field almost linearly. These are characteristics of antiferromagnetic materials. There is no sign of saturation of magnetizations for these samples because antiferromagnetic materials usually require very high magnetic field to saturate. The surface of nanostructured magnetic material known to exhibit lower magnetic properties compared to the bulk due to the lack of structural periodicity that leads to the formation of noncollinear spin configuration at the surface. With the decrease in nanoparticle size, the reduced coordination and hence broken superexchange bonds between surface spins result in an alteration of the orientation of each magnetic moment and consequently to a disordered spin configuration and a reduction of the average net moment.

## 1.4. Conclusion

Manganese-doped CuO nanoparticles with monoclinic structure have been synthesized successfully by microwave assisted solvothermal method. Nanoparticles in the size range of 10-14 nm and 9-34 nm are core materials for implementing many nanotechnology initiatives.The electrical and magnetic properties of the nanoparticles strongly depend on their size. For example, the color of semiconductor nanoparticle based display is strongly dependent on the size of the nanoparticles. Thus, many studies on nanoparticles have focused on size controlled synthesis of uniform spherical Nanocrystalline Mn doped- CuO are found to be ferromagnetic at room temperature. The dielectric parameters increase with increase in temperature.

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