STRUCTURAL, MICROSTRUCTURAL AND RAMAN STUDY OF CO-DOPED ZNO NANOCRYSTALS SYNTHESIZED BY SOLUTION COMBUSTION METHOD

Mast Ram[1], G. S. Arya[1], Kusum Parmar[1], R. K. Kotnala[2] and N. S. Negi[1]
[1]Department of Physics, Himachal Pradesh University Shimla-171005, India
[2]National Physical Laboratory, New Delhi, India

ABSTRACT
Zn1-xCoxO (ZC) [x=0.00(ZC0), 0.01(ZC1), 0.03(ZC3) and 0.05(ZC5) mol%] nanocrystalline samples were successfully synthesized by solution Combustion method. All the samples were annealed at 600 0C. The prepared nanoparticles were characterized by using X-ray diffraction (XRD), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy. XRD patterns of the prepared nanoparticles of different Co2+ concentrations reveal some shifting in the peak positions toward the higher angle as compared to that of the pure ZnO, which is attributed to the structural deformation in the presence of Co2+. XRD results show the mean grain size in the range of ~20-40 nm. Furthermore, TEM studies have been performed for studying their morphology and confirmation of particle size. TEM study clearly shows the formation of spherical and quasi spherical shaped nanoparticles. FTIR spectroscopy also confirmed the standard ZnO profiles at lower doping ratios but additional phases at higher doping and some organic impurities. From the Raman Spectroscopy all the peaks observed in undoped and Co-doped samples matched with the Raman active modes of ZnO Wurtzite hexagonal crystal structure. The main characteristic peak at 439 cm-1 which is the finger print of ZnO wurtzite structure is observed. However in case of Co (5 mol %) doped ZnO sample, additional modes were observed that can be related to the defect states.

KEYWORDS- *ZnO, nanoparticles, Co2+ doping, XRD, Raman Spectroscopy, Magnetic properties*

I. INTRODUCTION

In the last few decades, considerable interest has been focused on transition metal(TM) oxides nanoparticles due to their potential use in new spin based devices (spintronics). In spintronics devices there is a possibility to utilize both charge and spin degree of freedom, which results in the design and fabrication of new generation of microelectronic devices [1-3]. The properties of these nanomaterials extraordinarily changed due to quantum confinement and enhanced surface to volume ratio [4]. Among the most studied transition metal oxides nanoparticles, ZnO is extensively investigated due to its many potential applications, low cost of synthesis, environmentally friendly and highly versatile device fabrication. Besides this ZnO has large band gap (3.37eV) at 300K and large excitonic binding energy of nearly 60 meV [5-6] and diversified applications in the spin based devices, bmiosensors, gas sensors, micro and optoelectronic devices. The noteworthy feature of investigation of TM doped ZnO nanoparticles are that its physical and chemical properties can be easily tailored as per the demand of device fabrication. Presently, a significant attention has been recently committed to investigate the effect of doping elements (such as V, Cr, Fe, Co, Ni) on its electrical, optical and magnetic properties. Furthermore, many theoretical and experimental evidences suggested that ZnO doped with transition metals is a promising host semiconductor material exhibiting ferromagnetism when doped with TM [7]. However, the source of ferromagnetic behaviour is not very well clear in these ZnO nanocrystals. In theory there are two main explanations of origin of room temperature

ferromagnetism in diluted magnetic semiconductors (DMS). First theory was proposed by Dietl et al. [8] which were based on carrier–mediated mechanism and second one is proposed by Coey et al. [9] which was based on bound magnetic polarons (BMP) model. The main basis of this model is the presence of charge defect concentration which holds the electrons to cause the super exchange interaction between two metal ions. Furthermore, it was a spin-split band theory in which shallow donors controlled the magnetic moment of dopants in n-type wide band gap DMSs. It is worthy to mention that in case of DMSs, the kind of carriers, their mobility and density provide an opportunity to manipulate the ferromagnetic properties. In recent research papers, it had been revealed that the ferromagnetism in these materials can be induced by incorporation of nanoscale oxides of transition metals [10] and nanoparticles containing a large concentration of magnetic ions [11 -15]. Therefore, not only on nanosized magnetic ions, the magnetic properties observed in transition metal doped ions in ZnO nanostructures are also depend upon individual magnetic spins of these dopants and Bound Magnetic Polaron Model (BMP). Now in this context, the preliminary identification of these charged active centers/defects was analysed through Raman study. This concept formed the central idea of present work where Raman studies of different composition of Co substituted ZnO were investigated for these defect states. There are a wide variety of synthesis methods for the preparation of ultrafine oxide nanoparticles such as sol-gel, hydrothermal, microwave, solid state techniques and a spray pyrolysis methods etc. [16-22]. Out of these methods, we prepared Co doped Zinc Oxide (ZnO) nanostructures by using solution combustion method which is robust and reliable to control the shape and size of particles without requiring the expensive and complex equipments.

II. EXPERIMENTAL DETAILS

The $Zn_{1-x}Co_xO$ (ZC) nanoparticles samples were prepared by solution combustion method for 0, 1, 3 and 5 mol% of Co concentration by using $Zn(NO_3)_2.6H_2O$, $Co(NO_3)_2.6H_2O$ as oxidizers and urea as fuel were taken as the starting materials. All the precursor salts were taken in appropriate amount dissolved in distilled water and stirred at room temperature. These precursor solutions were heated at 70-80 °C for 2h with stirring, after that a 5 drops of poly vinyl alcohol (PVA) was added which acts as surfactant and the temperature was increased to 100 °C, when water was completely evaporated, the solution finally converted into a gel form. The gel was subsequently swelling into foam like and undergoes a strong self-propagating extensive exothermic reaction and a large amount of gas is released during the reaction. After that a fine powder is obtained. This fine powder was grinded for 20 min and annealed at 600 ^oC for 3h in the furnace in ambient conditions. The crystalline structure of ZC samples was analyzed by X-ray diffraction (XRD) using X'Pert PRO PANalytical system and microstructure by using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Raman spectra of the samples was recorded on Renishaw UK system using Ar excitation laser source of 514.5 nm wavelength. In this work we present systematic investigation of structural, microstructural, FTIR and Raman study of Zn1-xCoxO nanocrystalline samples.

III. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the all the samples ZC0, ZC1, ZC3 and ZC5 which are annealed at 600^0C for 3h. Intense diffraction peaks of the ZnO were indexed to (100), (002),(101), (102),(110),(103), (200), (112) and (201) planes after comparing them with the data in the JCPDF file # 06-2151. It is revealed by the XRD patterns all the samples have wurtzite type structure. It is worth to mention that no obvious significant changes were observed in the XRD patterns of Co doped ZnO nanoparticles but the overall intensity of the XRD peaks decreased with increase in Co concentration, which indicates decrease in crystallinity of ZnO nanoparticles. To further explore the effect of the Co doping on the structure of ZnO nanoparticles, lattice parameters (*a* and *c*) and average crystallite size, FWHM and Volume of unit cell from XRD with Co doping in ZnO were calculated and are tabulated in table 1. The resulting value of distortion c/a ratios are 1.597, 1.594, 1.589 and 1.587. The average grain size from XRD peaks using Scherer relation ($x = \frac{0.9\lambda}{\beta \cos\theta}$) is 29, 25, 24 and 20 nm, respectively, for ZC0, ZC1, ZC3 and ZC5 samples. This indicates that the Co doped ZnO has smaller lattice parameters and reduction in average crystallite size, which might originates from the smaller

ion radius of Co^{2+} (0.058 nm) compared to Zn^{2+} (0.060 nm). This further confirms the incorporation of Co and the Wurtzite structure is not influenced with Co-doping as no secondary phases such as CoO, Co_2O_3, $ZnCo_2O_4$ detected in the samples. Fig. 2 shows SEM images of ZC nanostructures which reveal the surface morphologies of all the samples. The micrographs have clearly showed random shaped particles of the samples with wide size distributions. It is clear from SEM images that the average crystallite size of ZnO nanostructures decreases as the doping concentration of Co increases. This further, supports the XRD results that the grain size decreases as the doping concentration of Co increases. Fig. 3(a-d) shows TEM micrographs of ZC5 sample. The morphology of the sample has been found to be spherical with irregular particle size distribution. The Crystallite has wide size distribution ranging from 20 to 40 nm which is consistent with XRD results. The crystalline characteristics of the nanocrystals are demonstrated by the HRTEM image Fig. 3(c). Lattice fringes clearly reveal the crystalline nature of sample and crystallinity of the sample is further supported by SAED (Selected area electron diffraction) pattern of the sample. Furthermore, bright sports can be indexed as crystalline wurtzite type hexagonal structure of ZnO. No traces of transition metal cluster of any secondary phase are observed in the sample. Therefore, it is important to mention that XRD, HRTEM as well as SAED analysis reveals that most of the Co ions go in the lattice as substitutional ions replacing the Zn ions instead of getting into void spaces.

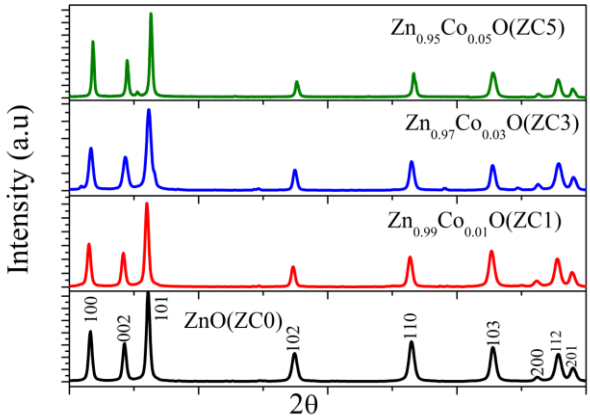

Fig. 1 XRD patterns of undoped and Co doped ZnO nanoparticles synthesized with different concentrations of Co

Table 1: Values of lattice parameters (a and c), volume of unit cell, FWHM and average particles size from XRD (x) of ZC nanocrystalline samples.

Sample	a(Å)=b(Å)	c(Å)	V(Å^3)	FWHM	x (nm)
ZC0	3.446	5.201	47.277	0.26614	31
ZC1	3.227	5.175	47.148	0.30552	27
ZC3	3.211	5.153	47.126	0.38835	21
ZC5	3.205	5.133	46.175	0.41587	20

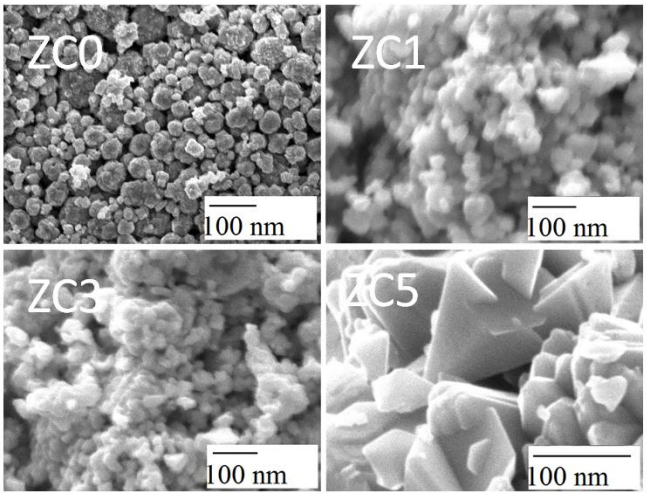

Fig. 2 SEM images of ZC0, ZC1, ZC3 and ZC5 nanoparticles

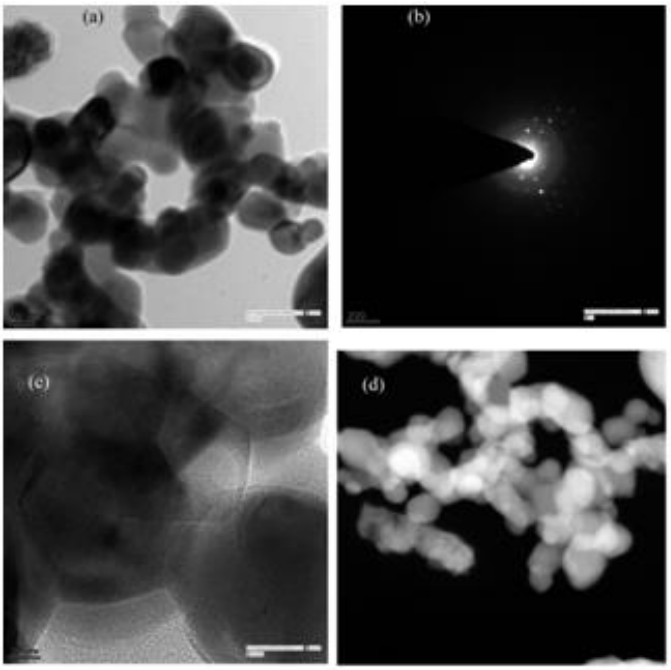

Fig. 3 (a) TEM micrographs of ZC5 nanoparticles (b) SAED patterns of ZC5 (c) HRTEM image of an individual ZC5 nanoparticle (d) A HAADF STEM image of Co doped nanoparticles.

Fig. 4 shows the FTIR spectroscopy of ZnO nanocrystalline samples recorded in the range of 480-4500 cm^{-1}, For the FTIR measurement, a certain amount of synthesized pure and Co doped nanocrystalline sample was mixed with potassium bromide (KBr), and the subsequent mixture was then compressed in the form of pellet under high pressure. The obtained pellets, composed of pure and Co doped nanocrystals and KBr, was then used for the FTIR measurement. The observed FTIR spectrum shows a well-defined band at 515 cm^{-1} which was originated due to formation of metal-oxygen (Zn-O) bond. In addition of Zn-O bond, absorption bands near 1600 cm^{-1} and 3411cm^{-1} represent O-H stretching and bending mode of vibrations respectively, while bands at 2911cm^{-1} and 1409-1605 cm^{-1} are stretching modes of C-H and C=O respectively. As the temperature increases, the organic band at 1409-1605 cm^{-1} is removed. But the bands arising from the absorption of atmospheric CO_2 on the metallic cations are at 2303 cm^{-1}.

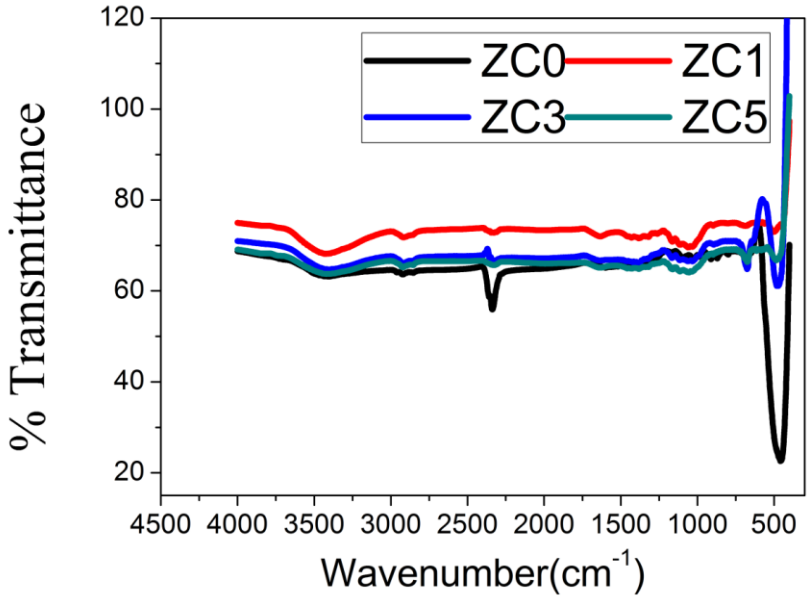

Fig. 4 FTIR spectra of the Co doped ZnO nanoparticles at various doping concentrations.

Fig. 5 shows the Room temperature Raman spectra of pure and Co doped ZnO nanocrystals recorded in the range of wave numbers 200-800 cm^{-1}. It is important to mention that Raman scattering is a versatile technique for detecting the substitution of dopants and the resulted defects and lattice disorder in the host lattice. Further, it could also reveal the existence of secondary phases due to the substitution of dopants by revealing the additional vibrational modes, as these secondary phases could not be detected by XRD because of the detection limit. ZnO is a II-VI group semiconductor which belongs to the wurtzite type hexagonal structure with space group of $P^6{}_3mc$. In this case optical phonon branches could be represented by an equation $T_{opt} = A_1 + 2B_1 + E_1 + 2E_2$ where A_1 and E_1 modes are polar and split into the transverse optical (TO) and longitudinal optical (LO) phonons, while the B_1 modes are Raman inactive [2-7]. Thus, it comes out that all the expected phonon modes at 328, 383, 437 and 581 cm^{-1} have been observed in the spectra of undoped ZnO. The sharpest and the strongest peak at 439 cm^{-1} can be assigned $E_2^{(high)}$ due to the high frequency branch of E_2 mode of ZnO, which is the strongest and characteristic mode of wurtzite crystal structure. Which is the finger print of wurtzite type hexagonal structure and owes its presence due to oxygen atoms [21-26]. All the prominent peaks belonging to ZnO Raman spectra are also confirmed for Co doped ZnO. But small shifting of peaks along with decrease of intensity and splitting of peak at higher concentration indicates the incorporation of the Co^{2+} ions at the Zn^{2+} lattice site in the wurtzite hexagonal crystal structure. These changes may be related to the different size of Co^{2+} and Zn^{2+} ionic radii. Thus, it clearly reveals the formation of structural defects and creation of intrinsic defects.

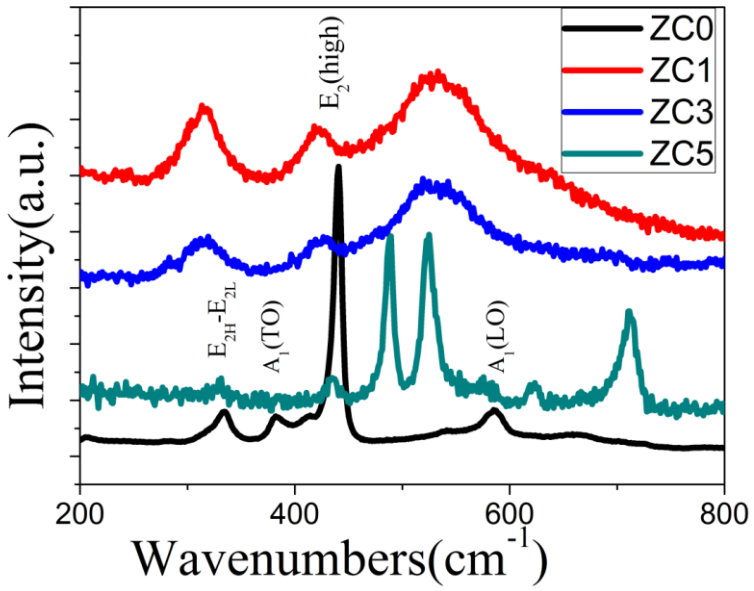

Fig. 5 Raman spectra of the nanocrystalline Co doped ZnO with different Co contents.

Furthermore, peak intensity change due to doping of Co in ZnO confirms the formation of charged defect states in the ZnO lattice. For higher composition of Co (5% mol), peak splitting is observed at 500 cm^{-1} which might be resulted from the formation of excessive defect states. Therefore the Co doping in ZnO increases the net defect concentration which can be used to explain its magnetic properties.

IV. CONCLUSION

In summary, the Co-doped ZnO nanocrystals were successfully synthesized by Solution Combustion method following by annealing at 600 ^{o}C for different doping concentrations. The XRD and SEM measurement confirms the formation of single phase nanoparticles. TEM studies confirm the growth of ZnO nanoparticles with some agglomeration. HRTEM images clearly demonstrate that all the nanoparticles are single crystalline and free from any lattice defects. It has also been found that the average particles size of the prepared ZnO nanoparticles decreases with Co doping. One can surely say on the basis of XRD results that with Co doping Wurtzite type structure is retained by the ZnO samples as well as the doping of Co cation took place at the Zn site. Further, some organic impurities are observed in Co doped ZnO nanoparticle FTIR spectra which indicate that they are probably near surface impurities. Raman studies reveal wurtzite type hexagonal structure as all the prominent modes are present including its finger print mode at 439 cm^{-1}. It also indicates the formation of excessive surface defects with increase of Co doping which can be applied to explain the magnetic properties of these samples. Finally, it is concluded that structural defects as well as stoichiometry defects might be present which can be manipulated for ferromagnetic properties of ZnO nanoparticles.

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AUTHORS BIOGRAPHY

Mast Ram is pursuing Ph.D. from Himachal Pradesh University, Summer hill, Shimla. He Joined as faculty member at Department of Physics, Govt. College Arki, Himachal Pradesh, India in 1999. He has attended four international and four national conferences/workshops and presented papers. His area of research focused on Diluted Magnetic Semiconductors.

Ghanshyam Arya did his M.Sc., M.Phil and Ph.D. from Himachal Pradesh University. His area of research is multiferroic materials. Presently he is Asstt. Prof. in Department of physics, Maharaja Agrasen University Baddi, Himachal Pradesh, India.

Kusum Parmar has obtained her M.Sc. degree in 2007 and M. Phil degree in 2009 in Physics from Himachal Pradesh University, Shimla and has joined Ph.D from the same University. She has attended six national conferences and workshops. Her area of research interest is ferrite/ferroelectric composite materials and thin film.

R. K. Kotnala obtained Ph.D. degree from Indian Institute of Technology, Delhi in 1982. At present working as a chief scientist at National Physical Laboratory, New Delhi, India and he is Fellow IGU. His current field of interest is multiferroics, magnetic materials, magnetic standards and sensor materials inclusive of nanomagnetism of materials.

N. S. Negi joined the Himachal Pradesh University, Shimla in October 1997 after two years as a faculty member at Department of Physics, Govt. Degree College Seema, India. He received his PhD degree from Himachal Pradesh University Shimla. He has wide experience in multiferroic thin films, high K materials, diluted magnetic semiconductors & pyrophoric materials. He has published over 50 papers in international journals. Currently he is a Professor in Department of Physics, H.P. University, Shimla