DOPING INFLUENCE OF Mn^{+2} IONS ON ZINC OXIDE NANOPARTICLES SYNTHESIZED BY CHEMICAL CO-PRECIPITATION METHOD

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Abstract: Pristine and manganese doped Zinc Oxide (ZnO) nanoparticles are synthesized through chemical co-precipitation method beneficially at room temperature without any capping agent. After the finishing point of synthesis the powders are cautiously subjected to various characterizations such as X-ray Diffraction (XRD), Scanning electron microscopy (SEM) with Energy-Dispersive X-ray spectroscopy (EDS), Transmission electron microscopy (TEM), and observed the influence of Mn^{+2} ions on structural and morphological properties of Zinc Oxide nanostructures. XRD information shows that both samples obtain hexagonal wurtzite crystal structure, also found nonappearance of secondary phase, which indicates the complete dissolution of dopant into ZnO host lattice. The accurate size of crystallites is evaluated through TEM descriptions which are just about corroborated through the XRD data. The morphology of the samples is found through Scanning electron microscopy (SEM) illustrations and Energy dispersive X-ray spectroscopy (EDS) spectrum reveals that no impurities are in existence other than manganese.

Key words: Crystallite, secondary phase, XRD, SEM/EDS

1. Introduction

Zinc oxide [ZnO] exhibits numerous interesting properties [1-7]. It is an intrinsic n-type II-VI semiconductor by a broad band gap of 3.37 eV at room temperature and a huge excitation binding energy of 60 meV. Because of these properties, ZnO demonstrate a strong excitonic UV light emission at room temperature [2-6]. It also shows a high photoconductivity and extensive piezoelectric and pyroelectric properties [1]. Because of these properties, ZnO has attracted a lot attention for prospective applications in diverse electronic and optoelectronic devices. In particular, the interest in ZnO has considerably been increased in the last few years [7-21] while the theoretical forecast of above room temperature ferromagnetism [RTFM] in manganese doped ZnO diluted magnetic semiconductors [8]. Dilute magnetic semiconductors are materials that concurrently demonstrate ferromagnetic and semiconducting properties. In DMS materials, magnetic transition ions substitute a small percentage of cation sites of the host semiconductor and are coupled with free carriers to give ferromagnetism by indirect interaction [9-12]. DMSs are considered to be very important materials in future semiconductor spintronic applications owing to the simultaneous control of 'electron' charge and spin [9-12]. Among all the magnetic transition metal doped ZnO systems, manganese doping is by and large the single most concerned mostly because of the fact that the thermal solubility of metallic manganese is larger than 10 mol% in ZnO, and the 'electron effective mass' is as huge as approximately 0.3 me, where 'me' is the free-electron mass [13].Consequently, injected spins and carriers in the nanostructures can be big, therefore making manganese doped ZnO perfect for the manufacture of spintronic nanodevices. For practical applications, a high-performance DMS through a high Curie temperature and saturation magnetic moments is necessary. Nevertheless, until now, the mechanism

concerned in ferromagnetism is complicated and the reproducibility of ferromagnetic performance is still a difficult problem. Because numerous groups have obtained diverse properties such as paramagnetism, anti-ferromagnetism, and ferromagnetism in manganese doped Zinc Oxide [12,13,19-21], these magnetic properties are robustly dependent on the sample preparation conditions. Hence, the progress of a more convenient and repeatable synthetic route for room temperature ferromagnetism manganese doped ZnO nano/microstructures is vital to their practical applications.

2. Experimental section

2.1. Synthesis

For the synthesis of pure and manganese doped Zinc Oxide nanoparticles, Zinc acetate de hydrate ($Zn(CH_3COO)_2\ 2H_2O$), Potassium hydroxide (KOH), are taken as preliminary materials and All the chemicals are analytical grade and used devoid of additional purification. To synthesize pure and manganese doped ZnO nanostructures of 0.1M solution, Zinc acetate de hydrate ($Zn(CH3COO)_2\ 2H_2O$), is dissolved in de-ionized water, potassium hydroxide (KOH) solution is then added drop wise in constant stirring of 9 hrs to form white precipitate. Manganese acetate tetra hydrate ($Mn(CH_3COO)_2\ .4H_2O$) is added drop wise to synthesize manganese doped Zinc Oxide nanostructures. Via filtering the formed Precipitate and washed several times with de-ionized water unnecessary chemicals formed during the process of synthesis are removed. Following that all the samples are dried at 70 $^{\circ}$C for 10 hrs and grind the samples finely with the help of agate mortar. Eventually all the samples are annealed in the furnace at 400 $^{\circ}$C for 2hours.

2.2. Characterizations

The prepared nanopowders are carefully subjected to the following characterizations. Powder X-ray diffraction (XRD) pattern is recorded on Bruker diffracto meter within 2θ range of 20° to 80° via CuKα as X-ray source (λ = 1.53906 Å). The morphological and elemental analysis of pure and manganese doped Zinc Oxide nanopowders are calculated by scanning electron microscopy (SEM) through energy dispersive spectroscopy (EDS) (model CARL-ZEISS EVOMA 15). The properties obtained by XRD are coincided with transmission electron microscopy (TEM) (Model: philips CM200)

3. Results and Discussions

3.1. Structural Properties

XRD Analysis

The XRD images of Pristine and manganese doped nanostructures are shown in the figure 1. The diffraction peaks are similar to the planes (100), (002), (101), (102), (110), (103) (200), (112), (201), (202) and known as hexagonal wurtzite crystalline structure. The diffraction peaks of pure and manganese doped ZnO connect to hexagonal wurtzite crystal phase of Zinc Oxide (ZnO) and the positions of diffracted peaks are consistent by the standard pattern of (JCPDS card number: 36-1451). Nonappearance of secondary phases indicates no impurity phases linking to manganese within the detection frontier of the instrument. The size of nanoparticle is evaluated by the Debye-Scherer formula $d=0.91\lambda/\beta\cos\theta$, where'd' is the nanoparticle size, 'λ' is the wavelength of the X-rays and 'θ' is the Bragg's angle of diffraction. The calculated crystallite size of pure and manganese doped Zinc Oxide (ZnO) is 21 and 20 nm respectively. From the calculations of diffraction peaks, observed that the crystallite size decreases by the adding of manganese into ZnO. Here it is illustrious that as of XRD pattern shown that doped Zinc Oxide nanoparticles include huge crystalline nature compared to pristine ZnO nanoparticles.

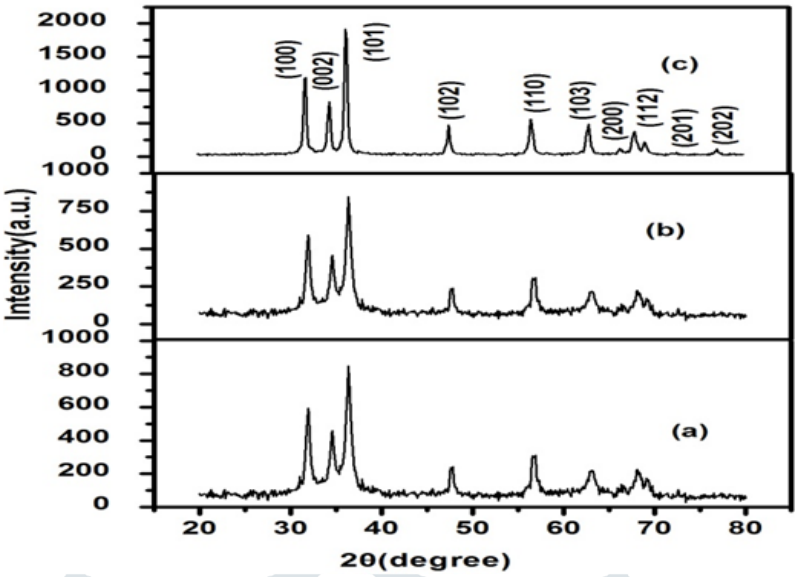

Figure 1. XRD pattern of (a) pure ZnO, (b) 1 mol% and(c) 2 mol% of manganese doped ZnO nanoparticles.

3.2 Morphological and elemental Analysis

3.2.1 SEM and EDS studies

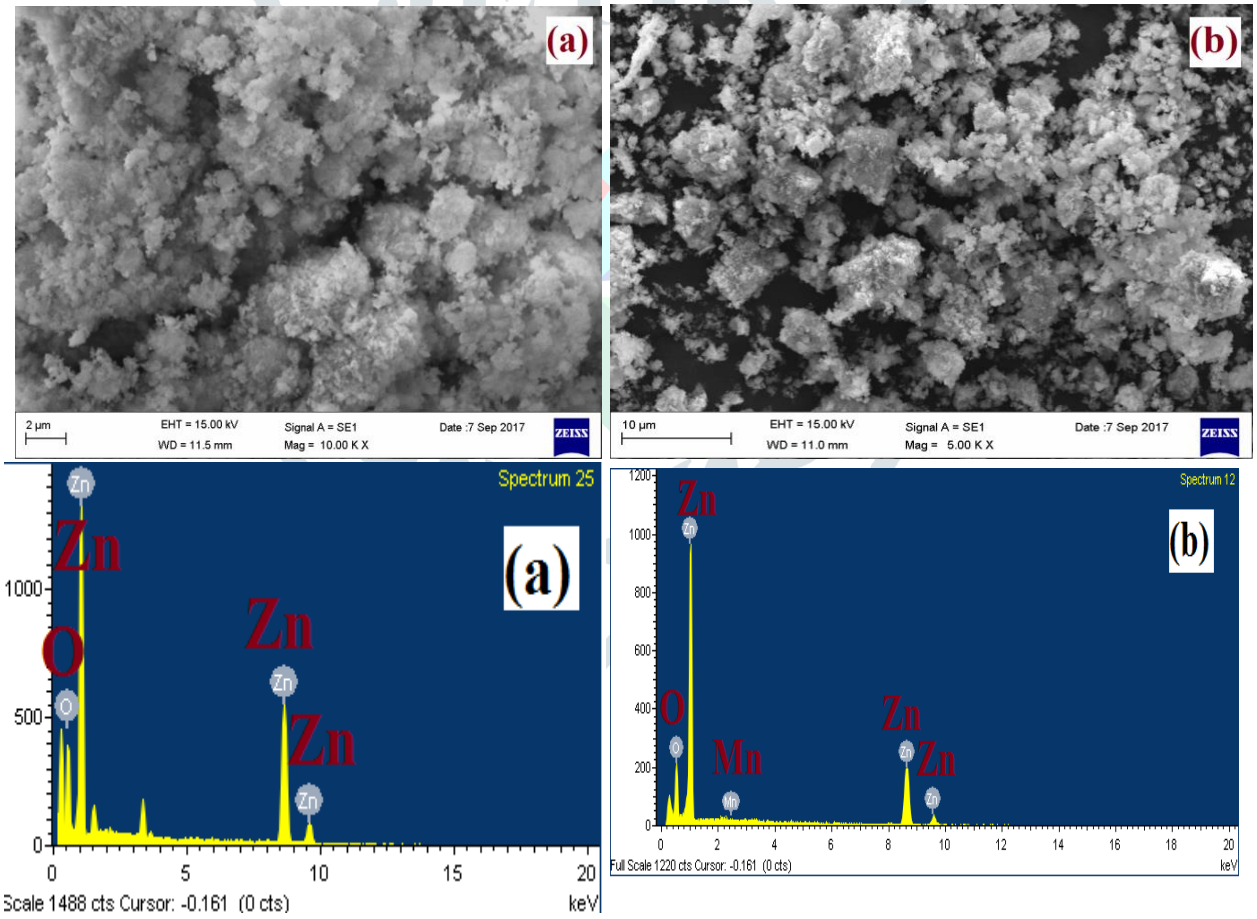

Figure 2. SEM and EDS images of (a) Pure ZnO (b) 1 mol% manganese doped Zinc Oxide nanoparticles.

Scanning electron microscopy (SEM) is taken to approximate the morphology of Pristine and (Mn^{+2}) co-doped ZnO nanoparticles. The image of the Pristine ZnO nano particles shows large agglomeration where as co-doped samples shows low agglomeration by increasing the iron concentration. All the images

are clearly demonstrating the non uniform spherical and irregular shape of the nanoparticles. EDS spectrum shows the incorporation of dopant elements into Zinc Oxide host lattice, it obviously shows the existence of impurities such as iron and aluminium and nonexistence of other impurities in ZnO host lattice. The EDS spectrum of Pristine ZnO reveals only Zinc and oxygen elements.

3.2.2 TEM Observations

Transmission electron microscopy (TEM) is taken to estimate the correct size of the pure and manganese doped Zinc Oxide nanoparticles. Figure 3 shows the images of pure and manganese doped Zinc Oxide nanoparticles. The crystallite sizes estimated through TEM descriptions are 50 nm and 20 nm respectively which are approximately confirmed by the XRD data.

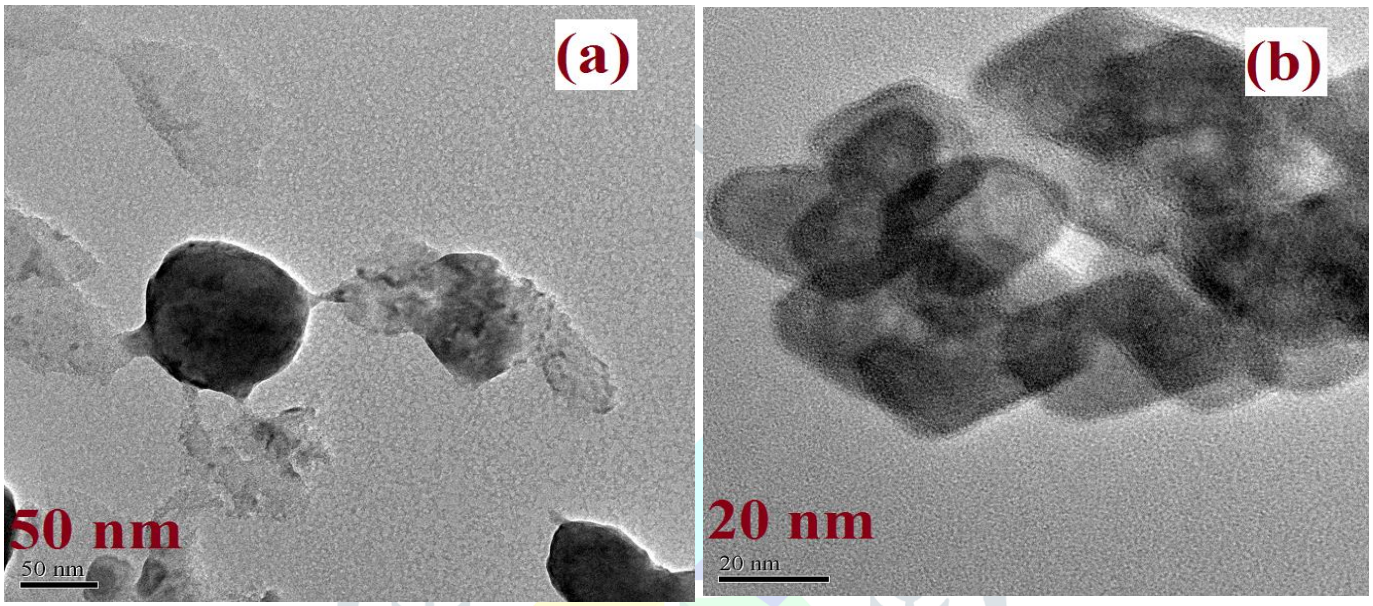

Figure 3. TEM images of (a) Undoped ZnO (b) 1 mol% manganese doped ZnO nanoparticles.

4. Conclusions

Undoped and manganese doped Zinc Oxide (ZnO) nanoparticles are prepared by chemical co-precipitation technique constructively at room temperature devoid of any capping agent. The prepared samples are characterized by XRD, SEM/EDS, and TEM. XRD results show that all the samples have hexagonal wurtzite crystal structure. SEM observations reveal that the morphology of the particles is approximately spherical; EDS study reveals the chemical composition and confirms the dopant incorporation.TEM analysis shows that the particle sizes are approximately co-incided with XRD data.

5. References

[1] Wang Z, Song J: Piezoelectric nanogenerators based on zinc oxide nanowire arrays. Science 2006, 312:242-246.
[2] Tang Z, Wong G, Yu P, Kawasaki Y: Room- temperature ultraviolet laser emission from self-assembled ZnO microcrystallite thin films. Appl Phys Lett 1998, 72:3270-3272.
[3] Bilecka I, Elser P, Niederberger M: Kinetic and thermodynamic aspects in the microwave- assisted synthesis of ZnO nanoparticles in benzyl alcohol. ACS nano 2009, 3:467-477.
[4] Qurashi A, Tabet N, Faiz M, Yamzaki T: Ultra-fast microwave synthesis of ZnO nanowires and their dynamic response toward hydrogen gas. Nanoscale Res Lett 2009, 4:948-954.
[5] Chen H, Wu X, Gong L, Ye C, Qu F, Shen G: Hydrothermally grown ZnO micro/nanotube arrays and their properties. Nanoscale Res Lett 2010, 5:570-575.
[6] Dhara1 S, Giri P: Enhanced UV photosensitivity from rapid thermal annealed vertically aligned ZnO nanowires. Nanoscale Res Lett 2011, 6:504.

[7] Balti I, Mezni A, Dakhlaoui-Omrani A, Leone P, Viana B, Brinza O, Smiri L, Jouini N: Comparative study of Ni- and Co-substituted ZnO nanoparticles: synthesis, optical, and magnetic properties. J Phys Chem C2011, 115:15758-15766.
[8] Dietl T, Ohno H, Matsukura F, Cibert J, Ferrand D: Zener model description of ferromagnetism in zinc-blende magnetic semiconductors. Science 2000, 287:1019-1022.
[9] Zhou S, Liu L, Yuan H, Chen X, Lou S, Hao Y, Yuan R, Li N: Magnetic properties of Ni-doped ZnO nanocombs by CVD approach. Nanoscale Res Lett 2010, 5:1284-1288.
[10] Shi H, Duan Y: First-principles study of magnetic properties of 3d transition metals doped in ZnO nanowires. Nanoscale Res Lett 2009, 4:480-484.
[11] Zhou S, Yuan H, Liu L, Chen X, Lou S, Hao Y, Yuan R, Li N: Roomtemperature ferromagnetism of diamagnetically-doped ZnO aligned nanorods fabricated by vapor reaction. Appl Phys A 2011, 102:367-371.
[12] Yang H, Yu S, Lau S, Herng T, Tanemura M: Ultraviolet laser action in ferromagnetic. Zn1xFexO nanoneedles. Nanoscale Res Lett 2010, 5:247-251.
[13] Fukumura T, Jin Z, Ohtomo A, Koinuma H, Kawasaki M: An oxide-diluted magnetic semiconductor:Mn-doped ZnO. Appl Phys Lett 1999, 75:3366-3368.
[14] Zeng X, Yuan J, Zhang L: Synthesis and photoluminescent properties of rare earth doped ZnO hierarchical microspheres. J Phys Chem C 2008, 112:3503-3508.
[15] Barick K, Aslam M, Dravid V, Bahadur D: Self-aggregation and assembly of size-tunable transition metal doped ZnO nanocrystals. J Phys Chem C2008, 112:15163-15170.
[16] Liu Z, Zhang Q, Shi G, Li Y, Wang H: Solvothermal synthesis and magneto-optical properties of Zn-Ni-O hierarchical microspheres. J Magn Magn Mater 2011, 323:1022-1026.
[17] Duan L, Zhao X, Liu J, Geng W, Xie H, Chen S: Structural, thermal and magnetic investigations of heavily Mn-doped ZnO nanoparticles. J Magn Magn Mater 2011, 323:2374-2379.
[18] Mi W, Bai H, Liu H, Sun C: Microstructure, magnetic, and optical properties of sputtered Mn-doped ZnO films with high-temperature ferromagnetism. J Appl Phys 2007, 101:023904-023908.
[19] Liu J, Wang K, Yu M, Zhou W: Room-temperature ferromagnetism of Mn doped ZnO aligned nanowire arrays with temperature dependent growth. J Appl Phys 2007, 102:024301-024306.
[20] Cheng X, Chien C: Magnetic properties of epitaxial Mn-doped ZnO thin films. J Appl Phys 2003, 93:7876-7878.
[21] Yoon S, Cho S, We S, Yoon S, Suh B, Song H, Shin Y: Magnetic properties of ZnO-based diluted magnetic semiconductors. J Appl Phys 2003, 93:7879-7881.