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Research Paper

Analysis of XRD Patterns of ZnO and Mn Doped ZnO Nanoparticles

Chemistry

KEYWORDS : XRD pattern, doped, nanoparticles, crystallite.

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ABSTRACT

The study is based on the analysis of XRD patterns of ZnO and Mn doped ZnO nanoparticles. In this paper, different author's papers are summarized for the analysis of XRD patterns of the above metal oxide nanoparticles. This study is very helpful to synthesize ZnO and Mn doped ZnO nanoparticles. It would also results helpful in predicting the type of ZnO crystallite structure formed and what changes takes place in its crystallite structure after doping it with manganese .

1. Introduction:

Over the past few years, ZnO nano-materials with various interesting structures and properties have been synthesized, such as nanoparticles, nano-rods, nano-belts, nano-combs, nano--wires etc. ZnO materials are believed to be non-toxic, bio-safe and biocompatible and have been used in many applications of daily life, such as drug carriers, photocatalysis, etc. ZnO materials have received broad attention due to their well-known performance in electronics, optics and photonics. The device application of micro and nanostructure of ZnO is one of the major focuses among researchers to diminish the size of the device in order to achieve higher speeds in its electrical transport and also to study the effect of confinement on optical properties. It is well known that doping a selective element into ZnO is the primary method for controlling its properties. Recently, many studies have focused on the doping of transition metals such as Mn, Ni, Fe, Co and Cr. Out of the above transition metals, doping with Mn results very useful.

But in the present study, crystallite structure of ZnO and Mn doped ZnO nanoparticles and effect of doping on ZnO structure is determined by analysing various XRD patterns.

2. Review of Past Work:

Riyadh M. Alwan, Quraish A. Kadhim, Kassim M. Sahan, Rawaa A. Ali, Roaa J. Mahdi, Noor A. Kassim and Alwan N. Jassim: In this work, zinc oxide nanoparticles were readily synthesized through sol-gel method using zinc acetate as a precursor. The crystalline structure of synthesized ZnO nanoparticles were observed using powder X-ray diffraction (XRD). The phase purity and composition of the particles obtained by a sol - gel process examined by XRD. Figure (1) shows a typical XRD pattern of ZnO nanoparticles, prepared in this work. A number of Bragg reflections with 2θ values of 31.74°, 36.83° and 47.62° are observed corresponding to (100), (101) and (102) planes, shows a typical XRD pattern of ZnO nanoparticles in the range of 5° -50° at a scanning step of 0.01 (ICPDS card No.89.1397). Average size of the zinc oxide nanoparticles was determined as 58.3 nm from the width of dominate peaks (100) and (101) reflections according to the Debye - Scherer equation. All diffraction peaks are indexed according to the hexagonal phase of ZnO. No characteristic peaks of impurity phases except ZnO are found which revealed that good crystalline in nature of the samples.

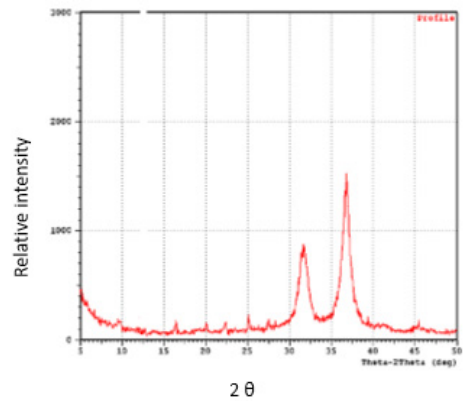

Fig.1 Shows Typical XRD pattern of ZnO nanoparticles

R. K. Sharma, Sandeep Patel and K. C. Pargaien: The study involved the synthesis of undoped and Mn doped ZnO nanocrystals (NCs) in aqueous solutions by using zinc acetate, manganese acetate and potassium hydroxide as the starting materials. 1.975g of $Zn(CH_3COO)_2{\cdot}2H_2O$ and 0.079g of $Mn(CH_3COO)_2{\cdot}2H_2O$ were dissolved in 100 ml of ultra-pure water from a millipore water purification system in a flask. 0.28g of KOH was dissolved in 10ml of ultra-pure water. Aqueous solution of zinc acetate and manganese acetate at room temperature was stirred for about 30min using a magnetic stirrer. Then the KOH solution was added slowly drop wise up to aqueous solution of zinc acetate and manganese acetate at 80–85°C under constant stirring. After 3hrs of reaction, the white precipitate deposited in the bottom of the flask was collected and washed with ethanol and de-ionized water. Finally, the precipitate was centrifuged with spinning speed of 3000rpm and dried over 50°C for 6hrs in order to remove water molecules to obtain ZnO nanocrystal in powder form. Prepared samples have been characterized by a powder X-ray diffractometer with CuKα X-ray radiation (λ=0.15496nm). The crystalline nature of ZnO samples is confirmed by sharp intense peaks. The sharp intense peaks of ZnO confirmed the good crystalline nature of ZnO and the diffraction peaks can be indexed to a hexagonal wurtzite structured ZnO, whereas the centres of all diffraction peaks have a slight shift compared with undoped NC samples (the spectra of undoped ZnO NCs are shown with red lines in fig. 2). As for Mn-doped NCs, the lattice parameter c calculated from the (002) peaks of the samples is 5.186Å, and that for the undoped ones is 5.210Å. The decrease of the lattice parameter (about 0.024Å) indicates that Mn is introduced into the ZnO crystal lattice and substitutes for the Zn^{2+} site. Furthermore, compared with the undoped ZnO, introduced manganese ions shift the diffraction peaks to higher angles by 0.17°. Such changes are indeed to be expected if Mn ions replace Zn ions in the lattice, as the Mn ions have smaller ionic radii (0.66Å) than Zn ions (0.74Å). The shift degrees indicate decrease

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of lattice parameters. The XRD result confirms the synthesis of Mn-doped ZnO nanocrystals without any phase-segregation.

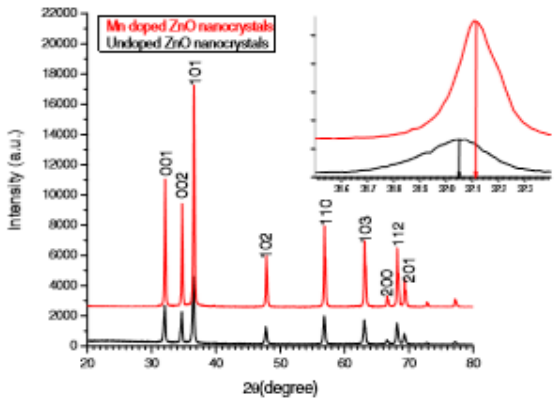

Fig.2. XRD pattern of the prepared (red) Mn-doped ZnO nanocrystals and (black) undoped ZnO nanocrystals. The inset plots the (001) peaks in magnified scale.

N. Srinivasa Rao and Mandava V. Basaveswara Rao: In this experiment 0.4 M aqueous ethanol solution of zinc chloride was kept under constant stirring using magnetic stirrer to completely dissolve the zinc chloride for 1hr and 0.8M aqueous ethanol solution of Potassium hydroxide was also prepared in the same way with stirring of 1hr. After complete dissolution of zinc chloride, 0.8 M KOH aqueous solutions were added under high speed constant stirring drop by drop (slowly for 45 min) touching the walls of the vessel. The reaction was allowed to proceed for 2 hrs after complete addition of KOH. The beaker was sealed at this condition and the solution was allowed to settle for overnight. Further, the supernatant solution was separated carefully. The remaining solution was centrifuged for 10 min and the precipitate was removed. Thus, precipitated ZnO nanoparticles were cleaned three times with deionised water and ethanol to remove the by products which were bound with the nanoparticles and then dried in air atmosphere at about 60°C. During drying, $Zn(OH)_2$ is completely converted in to ZnO and in a similar manner ZnO nanoparticles were synthesized from zinc nitrate.\

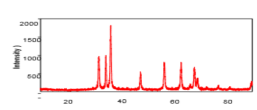

Fig.3.1. XRD pattern of ZnO Nanoparticles synthesized from Zinc Chloride

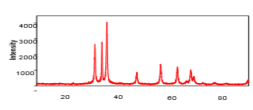

Fig.3.2. XRD pattern of ZnO Nanoparticles synthesized from Zinc Nitrate

ZnO nanoparticles with different grain sizes can be obtained from different precursors. Fig 2.1 & Fig 2.2 represent the XRD patterns of ZnO nanoparticles synthesized from Zinc Chloride and Zinc Nitrate respectively. The XRD data was recorded using CuKβ radiation. The intensity data was collected over a 2θ range of 20-80°. These XRD patterns show much sharper peaks. In the Fig3.1, the distinctive ZnO peaks at 31.51, 34.658, 36.453, 47.74, 56.78, 62.99, 66.38, 68.06, 69.16 and 79.96 respectively. In the Fig 3.2, the distinctive ZnO peaks at 31.946, 34.631, 36.448, 47.755, 56.769, 62.928, 66.45, 68.09, 69.19, 77.17 and 88.56 respectively.

These patterns represent the wurtzite phase of ZnO. A definite line broadening of the diffraction peaks also resembles that the synthesized particles are in nm range and no characteristic peaks were observed other than ZnO peaks. The average crystalline size calculated using Debye- Scherer equation of the diffraction peak was found to be 21.59 nm and 19.6nm for ZnO particles synthesized from Zinc chloride and Zinc nitrate respectively. A significant decrease in crystallite size was observed with the change of precursor. These XRD results reveal that the molar ratio of OH^- to Zn^{2+} is a dominant factor for the formation of the ZnO nanoparticles.

K. Rajendrana, S. Banerjeeb, S. Senthilkumaarc, T.K. Chinib and V. Sengodand : Undoped and Mn doped ZnO samples with different percentage of Mn content (1 mol%, 2 mol% and 3mol%) were synthesized by a simple solvo-thermal method. Powder X-ray diffraction patterns of undoped ZnO and Mn doped ZnO are shown in Fig.3. The characteristic peaks with high intensities corresponding to the planes (100), (002), (101) and lower intensities at (102), (110), (103), (200), (112) and (201) indicate the annealed product is of high-purity hexagonal ZnO wurtzite structure. It's evident from the XRD data that there are no extra peaks due to manganese metal, other oxides or any zinc manganese phase, indicating that the as-synthesized samples are single phase. The Mn ion was understood to have substituted the Zn site without changing the wurtzite structure at 500°C. The peaks of the diffraction patterns of doped samples are slightly shifted to left as compared to the undoped ZnO. This shows that small variation in the lattice parameters occur as Mn concentration in the sample increases..

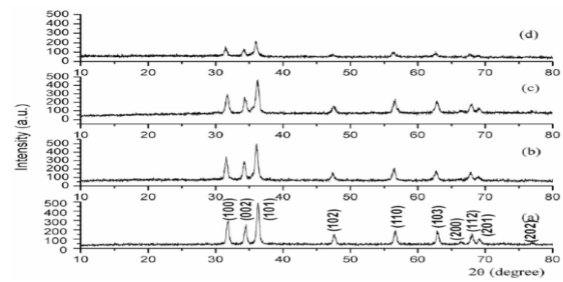

Fig.4. XRD patterns of samples annealed in ambient air at 500°C for 1hr. (a) undoped ZnO; (b) 1mol% Mn doped ZnO; (c) 2 mol% Mn doped ZnO and (d) 3 mol% Mn doped ZnO.

Katya Milenova, Boris Kunev, Vladimir Blasko , Sasho Vassile and Irina Stambolova: Zinc oxide photocatalysts doped with manganese (0.04–1 at.%) were synthesized via precipitation technique and the final samples doped with 0.04, 0.20, 0.36 and 1 at.% Mn were named with codes ZM1, ZM2, ZM3 and ZM4 respectively. Their characteristics were studied by X-ray diffraction (XRD). The calculated mean size of the crystallites was in the range of 31–45 nm. Manganese doping of ZnO samples results in slight decrease in crystalline size. The X-ray diffraction analysis of the oxide samples (Fig.5) illustrates the formation of wurtzite ZnO phase. It can be seen from the figure that the increase of manganese concentration results in lower crystallinity of the ZnO samples.

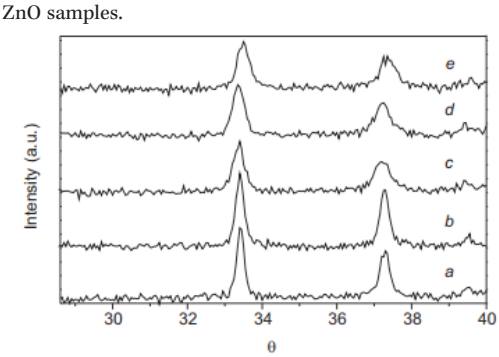

Fig.5. XRD spectra of samples: (a) ZnO; (b) ZM1; (c) ZM2; (d) ZM3; (e)

3. Analysis and Conclusions: From the analysis of above research papers, it can be concluded that ZnO and Mn doped ZnO

nanoparticles can be prepared by using different methods like solvo-gel method, precipitation method, etc with different precursors. And also the present study was mainly focused on the analysis of XRD pattern of ZnO and Mn doped ZnO nanoparticles which leads to a conclusion that ZnO nanoparticles that were formed, are of high purity hexagonal Wurtzite type crystal structures and Mn doping simply substituted the Zn ions without disturbing the Wurtzite type crystal structure of ZnO nanoparticles. In the starting Mn doping results in the crystal size decrease but later it increased the size of the crystal or lower the crystallinity of ZnO samples.

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