



Solubility of Mn in ZnO Nanocrystallites using Wet Chemical Synthesis

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ABSTRACT

There is a substantial amount of literature dealing with many aspects of synthesis and characterization of pure and doped binary compounds including Mn-doped ZnO which has been widely studied due to its superb properties as a dilute magnetic semiconductor (DMS). Aspects concerning doping limits for these compounds is an important stage in the search for new materials. Samples of $Zn_{1-x}Mn_xO$ nanocrystal were synthesized at temperatures of 180 °C and 200 °C using wet or liquid phase synthesis method. Dopant concentrations $x=0.5, 1, 1.5, 2, 2.5, 5, 10, 20, 30, 40$ and 50 per cent were studied. Powder x-ray diffraction (PXRD) patterns of the samples were analyzed with a view to determining the onset of secondary phases and hence the solubility limit of the dopant. The solubility limit for Mn in ZnO samples synthesized at temperature of 200 °C is realized at $x < 20\%$. For samples synthesized at temperature of 180 °C, the solubility limit is $x < 0.5\%$.

Keywords: Doping Concentration, Liquid Phase, Nanoparticles, Solubility Limit, Temperature, ZnO

1 Introduction

Given the wide range of useful and applicable properties displayed by metallic oxides and the increasing ability to modify these properties via various techniques, Mn-doped ZnO has been widely studied, especially, the magnetic, semiconducting and optical properties [1], [2]. Additionally, Mn-doped ZnO is a good candidate for the realization of superb properties of dilute magnetic semiconductors (DMS) in which, in addition to the charge state, electron spin is exploited as a further degree of freedom with implications for the efficacy of data storage and transfer. There is a substantial amount of literature dealing with many aspects of synthesis and characterization of pure and doped binary compounds. Among the many transition metal oxides used as dopants in these binary compounds, manganese is especially important because it exhibits a variety of oxidation states (2+, 3+, 4+, 5+, 6+ and 7+) resulting in different chemical and structural forms [3], [4]. The properties of doped ZnO depend largely on the extent to which dopant such as Mn can be taken up by ZnO. Aspects concerning doping limits for these compounds are not much considered. Therefore, determination of the solubility limits for these dopants is an important stage in the search for new materials.

A widely used synthesis route for ZnO (un-doped and doped) crystallites involves the liquid phase (precipitation). Here the crystallites are grown at very low temperatures (~50 °C). However, these temperatures need to be maintained for a very long time in some instances, 12 hours and above. In some few cases the samples are annealed or calcined at temperatures above 300 °C. Also, because the sample precipitates, a large volume of solvent is used. In all cases, centrifuging, washing, rewashing several times and discarding of the by-product solution are necessary. There have been numerous publications on the synthesis of pure and Mn-doped ZnO nanoparticles for the past decade, with quite a lot of possible routes for the preparation of these nanoparticles. However, most of these methods are restricted to research purposes because of either the use of toxic precursors and reagents, high temperature, high pressure,



expensive equipment or long reaction period. For instance, in synthesizing Mn doped ZnO nanostructures by wet chemical technique, Sundar and John [5] use 0.2, 0.4, 0.6, 0.8, 1.0 and 5.0 weight percentage of manganese chloride as dopant and zinc acetate dehydrate as precursor. The dried material obtained after heating at 160 °C overnight was grinded to obtained powder which was washed several times using ethanol and deionized water and calcinated at 500 °C for four hours. The XRD results are indented to a hexagonal wurtzite structured of zinc oxide and show no evidence of any secondary phase. Iqbal et al [6] prepared pure ZnO and Mn doped ZnO nanoparticles at doping concentrations of 1%, 2%, 3% and 4% by mixing citric acid and zinc nitrate hexa-hydrate in de-ionized water for 3 hours at ~80 °C. Gel obtained was further heated at 250 °C into ash, grinded and again calcinated at 300 °C for 6 hours. The diffraction peaks of the XRD show hexagonal wurtzite structure for all the samples

In the work of Kumbhar et al [7], Zinc oxide nanoparticles were prepared by sol-gel method using zinc acetate dihydrate in distilled water with addition of ammonium hydroxide and dried at 80 °C for 6 h to get gel. The gel so obtained was calcinated at 400 °C for 3 h to obtain the pure zinc oxide nanoparticles. Same procedure was adopted for doping ZnO with Mn acetate at 1, 3 and 5%. From the XRD results, all the peaks were attributed to ZnO without any secondary phases observed. Vijayakumar and Bhoopathi [8] synthesized un-doped and Mn doped ZnO nanoparticles at 2.0, 2.5 and 3.0% by chemical precipitation method using zinc and manganese acetate dihydrate dissolved in ethanol adding a solution of sodium hydroxide. The precipitates formed were filtered, washed several times with distilled water and ethanol and finally dried in hot air oven at 200 °C. According to the XRD results, all the peaks correspond to wurtzite structure ZnO with no characteristic peaks of impurities detected. Boumezoued et al [9] synthesized pure and Mn-doped ZnO nanopowders at 1, 3, 5 and 7% by sol-gel technique using zinc acetate dehydrate, citric acid monohydrate, monoethanolamine, ethylene glycol as a as starting material, stabilizer and solvent, respectively with manganese chloride as the dopant. The obtained solution is stirred at 130 °C for 2h to obtain a homogeneous and transparent solution and finally calcined at 500 °C for 4h in a furnace. The XRD spectra exhibit peaks of the wurtzite structure. However, the 5% doping shows peaks corresponding to Mn₃O₄ phase. In synthesizing Mn-doped ZnO nanoparticles (1, 2 and 3%) by coprecipitation method, Yuwita et al [10] uses dehydrate zinc acetate and manganese powders and HCl and NH₄OH solvents as precursors. The solution, stirred for 4h at 80 °C was heated at 100 °C for 24 hrs. The precipitate was filtered, washed using distilled water, dried at temperature of 100 °C and calcined at 400 °C for 3 hours. XRD results show that there is an additional peak corresponding to ZnMnO₃ phase with respect to the 3% doping with Mn ion.

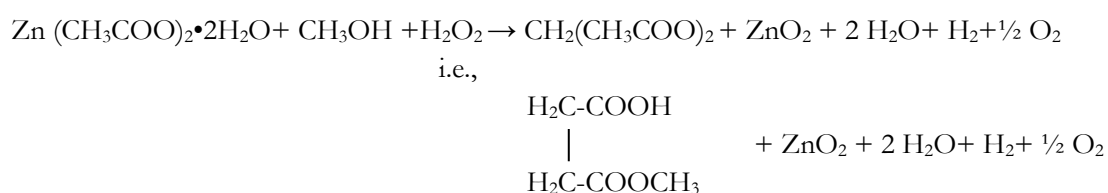
Mn-doped ZnO nanoparticles without post heat treatment or annealing has rarely been investigated. It is against this background that we seek to develop a very simple, inexpensive and environmentally friendly synthesis technique to produce both pure and Mn-doped ZnO nanoparticles within the minimum possible reaction period without washing of sample. The method used for the synthesis of the un-doped and Mn-doped ZnO nanoparticles in this work involves the hydrolysis of zinc and manganese acetates in alcohol. The method is very simple, eco-friendly and does not involve the release of toxic gases into the environment.

2 Experimental Procedures

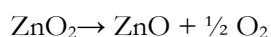
2.1 Synthesis of Pure Un Doped ZnO Nanocrystals

ZnO nanoparticles were prepared by grinding an amount of 3.292g zinc acetate in an agate mortar with pestle and poured into a beaker containing 40 ml of methanol to dissolve. This was placed in a sonicator and sonicated for about 20 minutes till all the solute was dispersed. During the sonicating process drops of hydrogen peroxide (2 ml) were injected into the solution using a disposable syringe. The reaction mixture was transferred to a hot plate and heated slowly to temperature range between 55 °C and 64 °C for complete dissolution of precursors and until all fluid was evaporated. The temperature was then raised and held at 120 °C until the gel dehydrated and solidified into crystals. The white crystals were then cooled and ground.

They were then returned to the hot plate at temperatures starting from 120 °C and gradually increasing to 140 °C (or 160 °C, 180 °C and 200 °C) within 10 minutes and maintained at this temperature for about one and half hours till the colour changed from white to yellowish white. This was done in order to complete thermal decomposition of the initial precursors. During drying, complete conversion of ZnO₂ into ZnO occurred and was observed as a colour change. The use of zinc acetate is due to the fact that, metal acetate precursors generate fine-grained, sky-scraping specific surface area and powders free of aggregate and environmentally friendly. Methanol is used because of its dihydrating property and also zinc acetate dihydrate has also been found to be more soluble in methanol and the reflux time necessary for the formation of ZnO is faster [11]. Also, interaction of alcohols with Zn metal was found to be a simple reaction [12], [13]. The hydrogen peroxide as used in this work, supplies the oxide oxygen while the acetate acts as base. The mechanisms of thermal decomposition of zinc and manganese acetates play an essential role in the preparation of ZnO nanoparticles from the wet or liquid phase. Oxides are formed during hydrolysis and condensation of the dissolved species. The mechanism of thermal decomposition of zinc acetates in methanol is according to the following reaction:



During calcinating, complete conversion of ZnO₂ into ZnO occurred and was observed as a colour change. The decomposition of ZnO₂ is according to the equation:



2.2 Synthesis of Mn Doped ZnO Nanocrystals

In the doping process, the appropriate amount of zinc acetate and manganese acetate were ground in an agate mortar with pestle and poured into a beaker containing methanol. The procedure used for the synthesis of the ZnO as already outlined above was followed thereafter. The solution became brownish due to the introduction of the dopant and consequently produced brownish crystal. The temperature used for the doping process was at 180 °C and 200 °C. The colour of the crystals became deeper as the dopant concentration increased. The entire process was repeated for all the dopant concentrations, x= 0.5, 1, 1.5, 2, 2.5, 5, 10, 20, 30, 40 and 50 per cent.

2.3 Characterization

XRD analysis of the un-doped and Mn-doped ZnO nanocrystal samples was carried out using an X-ray powder diffractometer (PANalytical) using the CuK α line at $\lambda = 1.54056 \times 10^{-10}$ m. This system uses a Cu source with K α_1 radiation ($\lambda=0.154060$ nm). A 2θ scanning range from 20° to 70° was examined using a step size of 0.0060 and scan step time of 0.7 s and measuring temp of 25 °C.

3 Results and Discussion

With reference to the sample synthesized at 120 °C during the first stage of the synthesis of ZnO, the peaks are observed at approximately 31.54°, 36.63°, 52.86°, and 62.83° corresponding to reflections from the planes (111), (200), (220) and (311) as shown in figure 1.

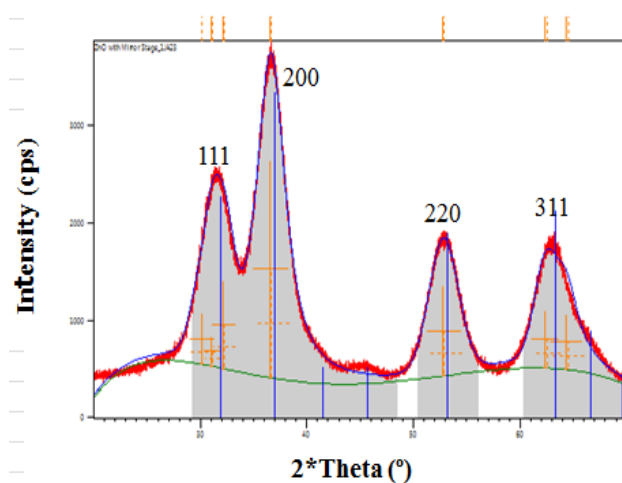


Figure 1: Diffraction pattern of pure ZnO at T = 120 °C

The XRD diffraction pattern corresponds to that of the zinc peroxide (ZnO_2) cubic structure according to ICSD card number 00-013-0311. All the observed diffraction peaks of this work match the reported results for cubic zinc peroxide with JCPDS card No. 13-0311 using the same zinc acetate dehydrate and hydrogen peroxide (30%) for synthesis [14], [15]. The XRD pattern of nanoparticles synthesized at temperatures of 140 °C and 160 °C shown in figure 2(a) and (b) confirms the ZnO hexagonal wurtzite structure according to ICSD card numbers 01-078-3315 and 01-071-6424 respectively.

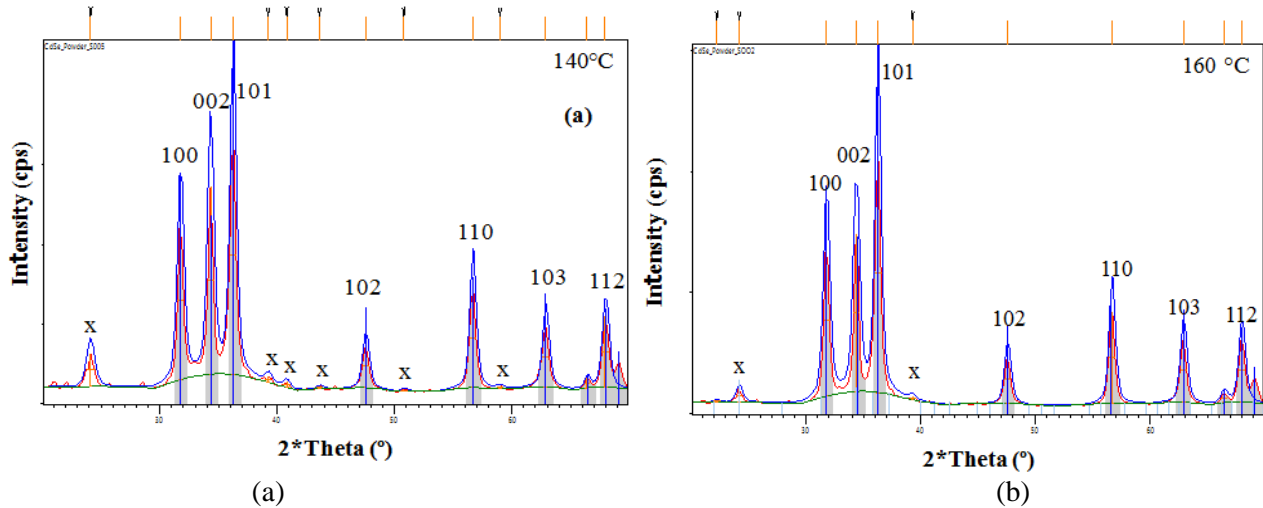


Figure 2: Diffractograms of (a) pure ZnO at $T = 140\text{ }^\circ\text{C}$ and (b) pure ZnO nanoparticles at $T = 160\text{ }^\circ\text{C}$

After peak indexing, the diffractogram produced the following planes: (100), (002), (101), (102), (110), (103) and (112) at peak positions (2θ values) of approximately 31.76° , 34.31° , 36.22° , 47.52° , 56.63° , 62.83° and 67.92° , respectively. It could be observed that, in addition to the reflections from planes indexed to ZnO, there are additional peaks with low intensity at approximately indexed as 'x'. All the secondary peaks indexed as 'x' could be traced to the diffractogram of the zinc acetate. They could be attributed to undissolved zinc acetate and its associate by-product which is a colloid complex of water and methyl succinate. It is interesting to note that, these additional peaks have also been observed by [16]. As the temperature was raised to 180 °C and then to 200 °C, all the additional 'x' peaks disappeared as can be seen in figures 3(a) and 3(b) respectively using scanning range from 20° to 70° .

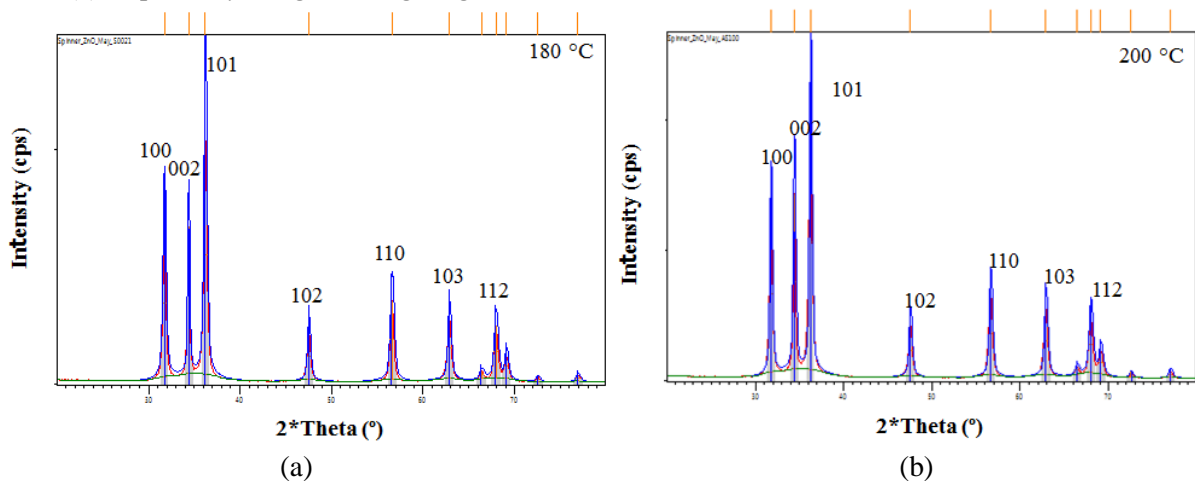


Figure 3: Diffractograms of pure ZnO nanoparticles obtained at (a) $T = 180\text{ }^\circ\text{C}$ and (b) $T = 200\text{ }^\circ\text{C}$

The powder XRD pattern for $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ crystallites samples grown at $T = 180\text{ }^\circ\text{C}$ and $T = 200\text{ }^\circ\text{C}$ are presented in figures 4-8. Figure 4 shows powder XRD pattern for $x = 0.5\%$. The appearance of additional peaks at $T = 180\text{ }^\circ\text{C}$ (figure. 4a) indicate existence of secondary phases. On the basis of the XRD, the additional peaks could be attributed to un-dissolved zinc acetate, although, one of the phases was identified

as Mn_3O_4 . These features indicate that the Mn (Zn) ions substitute Zn (Mn) in ZnO wurtzite structure. However, the XRD pattern at $T = 200^\circ C$ (figure 4b) for $x = 0.5\%$ does not show any additional peaks.

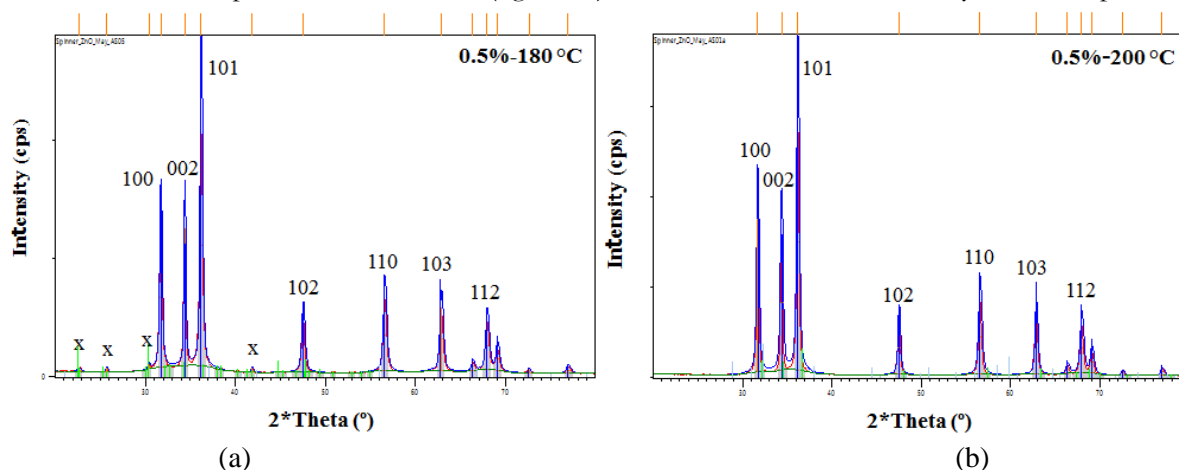


Figure 4: XRD pattern for $Zn_{1-x}Mn_xO$ ($x = 0.5\%$) at (a) $T = 180^\circ C$ and (b) $T = 200^\circ C$

For 1% doping concentration at $T = 180^\circ C$ as shown in figure 5(a), seven (7) additional peaks with higher intensities were observed. These peaks are absent at $T = 200^\circ C$ (figure 5b).

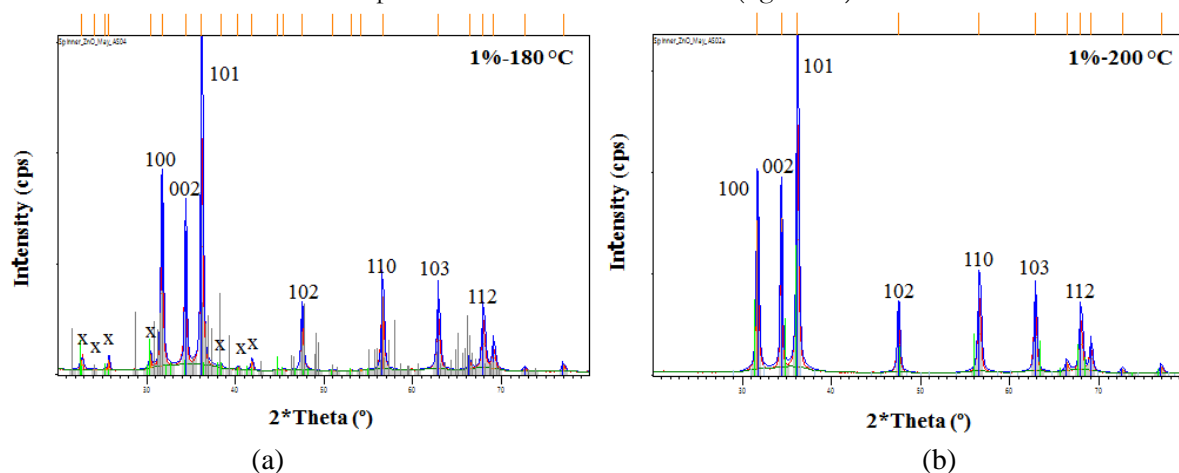


Figure 5: XRD pattern for $Zn_{1-x}Mn_xO$ ($x = 1.0\%$) at (a) $T = 180^\circ C$ and (b) $T = 200^\circ C$

Between $x = 1\%$ and $x = 10\%$ at $T = 180^\circ C$, the number of additional peaks and their intensities increases as dopant concentration is increased (figure 6a). Again, these peaks are absent at $T = 200^\circ C$ (figure 6b).

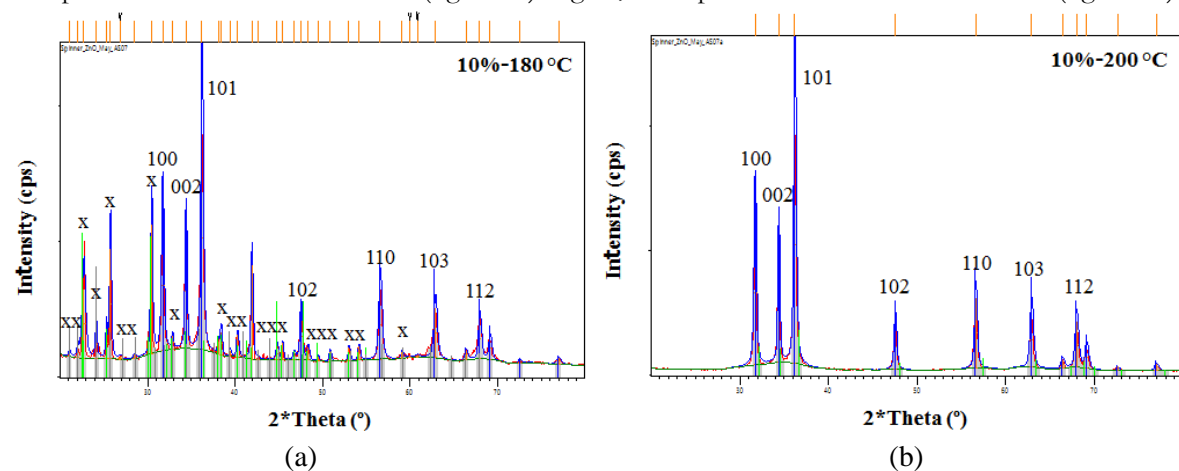


Figure 6: XRD pattern for $Zn_{1-x}Mn_xO$ ($x = 10\%$) at (a) $T = 180^\circ C$ and (b) $T = 200^\circ C$

However, at $T = 200\text{ }^{\circ}\text{C}$, these secondary peaks are observed when $x = 20\%$ (figure 7).

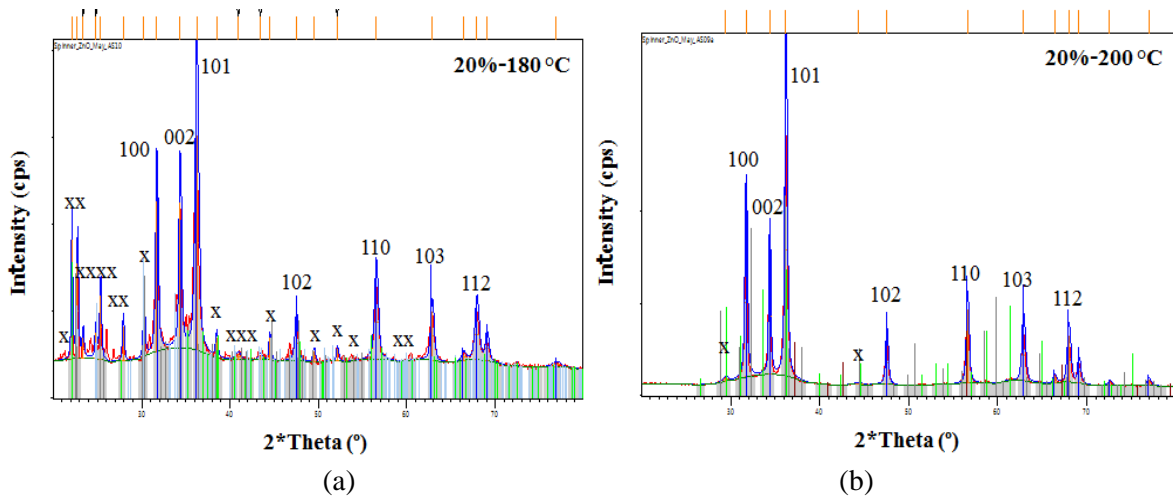


Figure 7: XRD pattern for $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($x = 20\%$) at (a) $T = 180\text{ }^{\circ}\text{C}$ and (b) $T = 200\text{ }^{\circ}\text{C}$

For $x > 20\%$, it was observed that, as the dopant concentration is increased, the number of additional peaks labeled 'x' as well as their intensities increased significantly at both temperatures up to $x = 50\%$ (figure 8).

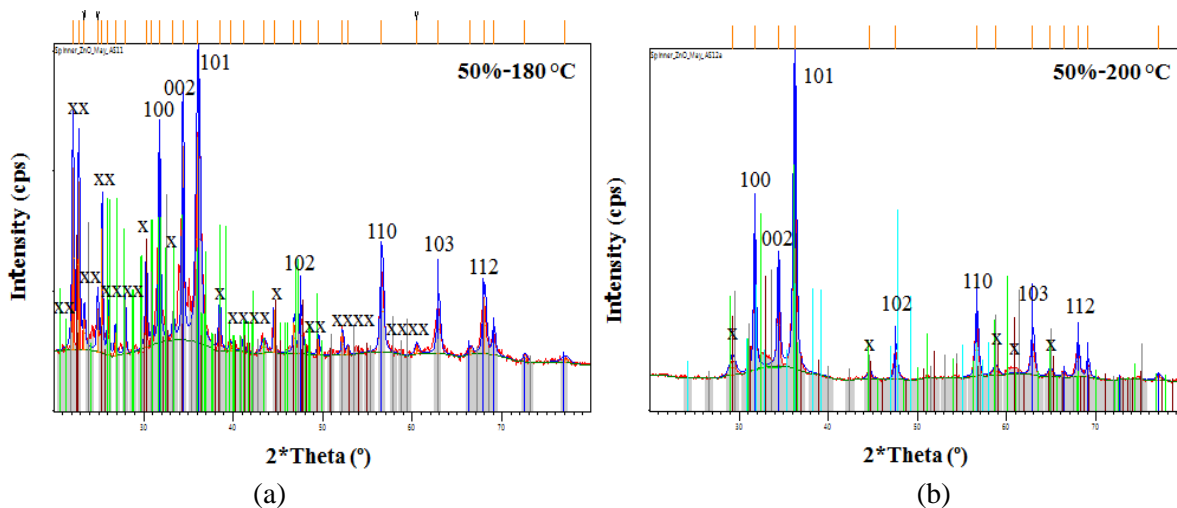


Figure 8: XRD pattern for $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($x = 50\%$) at (a) $T = 180\text{ }^{\circ}\text{C}$ and (b) $T = 200\text{ }^{\circ}\text{C}$

Based on the XRD results, the intermediary compounds corresponding to the unwanted peaks indexed as 'x' which were attributed to the incomplete decomposition of the metal-organic source of the zinc and manganese acetate by-products which are expected to be removed by evaporation were zinc hydroxide, zinc stearate, zinc oxalate hydrate, zinc formate hydrate, zinc carbonate hydroxide, manganese formate, manganese oxides and manganese oxalate. Manganese organic compounds resulting from the dissociation of manganese acetate are expected to be melting or melted within the temperature range $180\text{ }^{\circ}\text{C} - 200\text{ }^{\circ}\text{C}$ and therefore n species will become available for incorporation into the ZnO lattice. At this temperature, oxides of Mn will begin to form instead. Similarly, in the synthesis of Mn_3O_4 structures by [17], two stages decomposition of manganese formate occur. The weight loss associated with the decomposition occurs between $180\text{ }^{\circ}\text{C}$ and $268\text{ }^{\circ}\text{C}$. However, the Mn_3O_4 structures were observed to occur at $200\text{ }^{\circ}\text{C}$. Clearly, therefore a slight change in temperature of $20\text{ }^{\circ}\text{C}$ could cause a change in solubility.

In comparing the relative intensity of XRD peaks at different doping concentrations, the two prominent peaks indexed by the XRD at (100) and (002) planes which are observed at peak positions (2θ values) of approximately 31.7° and 34.3° respectively are used with reference to the most prominent peak at 36.2° of

(101) plane. Mn doped ZnO nanoparticles synthesized at temperatures of 200 °C is considered, the changes in relative intensity with different doping concentrations are therefore tabulated below (Table 1).

Table 1: Relative intensity of Mn doped ZnO nanoparticles synthesized at temperatures of 200 °C

Mn Doping (%)	Relative Intensity (%) at 200 °C	
	(1 0 0) Plane	(0 0 2) Plane
0.0	61.68	68.58
0.5	60.07	53.25
1.0	58.74	58.80
1.5	57.77	57.09
2.0	60.96	50.09
2.5	58.87	54.33
5.0	57.77	58.57
10.0	60.36	48.80
20.0	58.95	46.08
30.0	55.23	45.65
40.0	51.74	44.57
50.0	47.11	36.60

All the peaks observed in this work matched directly the literature data for Mn-doped ZnO wurtzite structure [18], [19] with the (101) peak being the most prominent. The appearance of additional unidentified ('x') peaks implies the existence of secondary phases or impurities. It can therefore be assumed that the absence of these 'impurity' peaks implies that the doping percentage is well within the solubility limit of Mn in ZnO. Clearly, this is a function of the temperature of doping, as pointed out earlier. In this work, this limit is found to be $x < 20\%$ for 200 °C and $x < 0.5\%$ for the 180 °C samples. Above these limits the dopants degrades the structure of the sample owing to the formation of secondary phases for Mn clusters that do not settle at the Zn^{2+} site of ZnO [9], [20], [21].

Substitution of Mn for Zn^{2+} requires local expansion or contraction of the lattice to accommodate the manganese ion due to ionic radii differences. Since Mn can exist as Mn^{2+} , Mn^{3+} and Mn^{4+} (respective ionic radii are 0.83Å, 0.65Å and 0.53Å), one cannot be certain of the actual distribution of Mn in the lattice [22], [23]. If Mn^{2+} ion of greater ionic radius substitutes Zn^{2+} (0.74 Å), the peaks will shift towards the lower angles because of increase in d -spacing due to substitution of lattice site by ion of higher radius. For smaller ionic radii like Mn^{3+} and Mn^{4+} , settlement in interstices of ZnO become dominant instead of substitution of Zn^{2+} . However, when Mn^{3+} and Mn^{4+} go into interstitial sites, they impel the surrounding atoms because their size is greater than interstitial sites. Consequently, the lattice is stretched and interplanar distances increase. This again results in increase in d -spacing and the peaks shift towards lower angles [24].

4 Conclusion

A very simple, inexpensive and environmentally friendly synthesis technique is adopted to produce Mn-doped ZnO nanoparticles without post heat treatment or annealing within the minimum possible reaction period and temperature. The solubility limit for Mn in ZnO for synthesized at 200 °C is realized at $x < 20\%$ and for the lower temperature of 180 °C, the corresponding figure is $x < 0.5\%$ respectively. Beyond these dopant concentrations, several secondary peaks are observed in the XRD patterns indicating the presence of phase other than $Zn_{1-x}Mn_xO$. The result of this study has set a doping limit for Mn in ZnO based on the synthesis conditions used.

5 Declarations

5.1 Acknowledgments

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5.2 Competing Interests

The authors declared that they do not have any conflict of interest in this publication.

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