Mn-Doped ZnO Nanoparticles Prepared by Solution Combustion Method

Murugesan Silambarasan†
Centre for Photonics and Nanotechnology, Sona College of Technology, Salem 636 005, Tamil Nadu, India

Shanmugam Saravanan
Department of Physics, Sona College of Technology, Salem 636 005, Tamil Nadu, India

Tetsuo Soga
Department of Frontier Materials, Nagoya Institute of Technology, Nagoya 466-8555, Japan

In this paper, we have reported the structural, morphological and optical studies of pure and Mn-doped ZnO nanoparticles synthesized by the simple solution combustion method. The structural, morphological and optical studies are carried out by powder XRD, FE-SEM, HR-TEM, Raman, UV-vis absorption and PL spectra. The XRD pattern indicates that the prepared particles are in hexagonal wurtzite structure with the crystalline size of around 30-60 nm. The FE-SEM and HR-TM images are coincide with each other for aggregation of particles nature. The elemental analyses of pure and doped samples are evaluated by EDX. Raman spectra of the samples show remarkable result in the polar and non-polar branches. Room temperature PL shows the near band edge related emission and the results are related several intrinsic defects in the Mn-doped ZnO nanoparticles. Blue shift of the UV emission has occurred in all the doped samples attributable to Burstein-Moss shift. [DOI: 10.1380/ejssnt.2014.283]

Keywords: Zinc oxide; X-ray diffraction; SEM; Raman scattering spectroscopy; Photoluminescence; Combustion synthesis

I. INTRODUCTION

Zinc Oxide (ZnO) nanostructures are the topic of great interest due to their unique physical, chemical and biological properties with wide bandgap (3.37 eV) and large exciton binding energy (60 meV). The ZnO is a very promising II-VI compound semiconducting material for a wide range of application in optoelectronics and solar cells. Among the II-VI semiconductors, although Cadmium Selenide and Cadmium Telluride have shown to be promising in solar cell applications, they are toxic and harmful to the environment. With an increasing awareness of green and clean energy, ZnO based nanostructures are more suitable candidates for cost-effective and environmentally friendly energy conversion devices [1–7]. The ZnO nanoparticles (NP) can be synthesized by various approaches including chemical precipitation, ball milling, sol-gel processing, microwave-assisted synthesis, organometallic synthesis, spray pyrolysis, hydrothermal method and mechanochemical synthesis [8–14]. Physical properties of ZnO NP can be tailored by controlling the dopants and doping concentration [15]. Doping of transition metal (TM) ions in the ZnO has lead to enhancement of bandgap, optical, electrical and magnetic properties. The TM ions have several advantages as a dopant for ZnO that makes easy to incorporate into ZnO crystal structures and induced the magnetic as well as optical properties [16, 17]. Especially, the study of the effect of dopants on optical properties of ZnO based nanomaterials is very important for photonic applications. The optical properties of ZnO can be improved by incorporating various ions in the crystal lattice.

In this work, we reported the structural, morphological and optical studies of pure and Mn-doped ZnO NP synthesized by the simple solution combustion method. In this method, a mixer of ethanol and ethylene glycol (EG) are used as the solvent, zinc acetate dihydrate as the zinc source, oxygen gas in the atmosphere as the oxygen source and manganese(II) chloride as the doping agent as well as manganese source. The combustion reaction was carried out in air under ambient pressure and ZnO NP (both pure and doped) was obtained in one step. Therefore, the synthetic approaches provide a simple, cost-effective, easy, and convenient route to obtain large quantities of ZnO NP.

II. EXPERIMENTAL

The synthesis method is similar to our previous report [18], 0.05 M and 0.1 M of zinc acetate dihydrate is dissolved in 100 ml of mixed solvent of ethanol and EG with the volume ratio of 60/40 ml, respectively. Then, different millimole of (1, 2, 5 and 10) manganese(II) chloride is introduced into the above solution under constant magnetic stirring. The solution is transferred into a spirit lamp with an absorbent cotton lamp wick and then the spirit lamp is fired. After the lamp wick is extinguished, the samples are repeatedly dispersed into distilled water to wash and remove the impurity by ultrasonic process. Finally, the sample is dried in hot air oven.

Powder X-ray diffraction (XRD) of the samples are carried out by a Rigaku-rint 2100 with Cu-Kα radiation (λ = 0.1540598 nm) at the scanning rate of 0.02°/sec from 20° to 70°. The field emission-scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectrometry (EDX) images are analyzed through Quanta-200F SEM with AMETEK EDX. High resolution-
**TABLE I:** Crystalline size of pure and Mn-doped ZnO NP.

| S No. | Unit of doping agent | Crystalline size of Mn-doped ZnO NP |
|-------|---------------------|-----------------------------------|
|       | 0.05 M of precursor | 0.1 M of precursor                |
| 1     | Pure ZnO            | 46 nm                            |
| 2     | 1 mM                | 52 nm                            |
| 3     | 2 mM                | 52 nm                            |
| 4     | 5 mM                | 50 nm                            |
| 5     | 10 mM               | 45 nm                            |

transmission electron microscopy (HR-TEM) images are obtained by a FEI-Tecnai F20 TEM. Raman spectra are measured with an Ar⁺ laser line (λ = 513.4 nm) as the excitation source. The ultraviolet-visible (UV-vis) absorbance spectrum is carried out by UV-2600 Shimadzu with the spectral resolution of 1 nm. Room temperature Photoluminescence (PL) spectra are recorded to study the optical characterization of the ZnO NP using a Horiba Jobin Spectrofluorimeter with (Source: Xenon lamp 450 W) excitation wavelength of 325 nm.

**III. RESULTS AND DISCUSSION**

Figure 1(a) and 1(b) show the powder XRD pattern of pure and Mn-doped ZnO NP for 0.05 and 0.1 M of zinc precursor with different millimole of (1, 2, 5 and 10 mM) Mn doping, respectively. All the diffraction lines are assigned well to the hexagonal phase of wurtzite structure of ZnO with a reference pattern as mentioned in the JCPDS.No:05-0664 with space group $P6_3mc$. The strong and narrow diffraction peaks represent the good crystalline nature of ZnO NP. All the peaks in the XRD patterns of Mn-doped ZnO sample could be fitted with the hexagonal wurtzite structure and there are no extra peaks due to manganese metal, other oxides or any zinc manganese phase. This observation suggests that the doped samples are single phase and Mn ion might have substituted Zn site without changing the hexagonal structure. The XRD peak broadening is produced by both size and strain which are compared from the bulk ZnO. Hence the full-width at half-maximum (FWHM) of XRD peaks have been deconvoluted by pseudo Voigt curve fitting. The Lorentzian part of the peak is used to estimate crystalline size and the Gaussian part of the peak is used to find the strain in the nanocrystals [18]. The crystalline sizes have been calculated by Scherrer equation and listed in Table I. The crystalline size varied from 35-55 nm. Figures 2(a) and 2(b) show the Williamson-Hall plot of the prepared samples in order to find the lattice strain. The
obtained results indicate the same trend of tensile strain due to positive slope. Hence, the prominent surface and strain resulting from decompression of the prepared ZnO lattice can be expected which would have important effects on the optical properties of the pure and Mn-doped ZnO NP.

The morphological information about pure and metal doped ZnO NP are obtained from the FE-SEM. Figure 3(a) and 3(b) show the FE-SEM images of the pure and Mn-doped ZnO NP for 0.05 M of zinc precursor and 10 mM of Mn-doping, respectively. The agglomerated particles neck with their neighbors, they form hexagonal shapes intermitted with voids, ensuring high surface area. The presence of some bigger particles might be attributed to the aggregation of smaller particles. The particle morphology changes significantly with respect to the incorporation of doping agent.

Figure 4(a) shows the TEM images of pure ZnO NP for 0.1 M of zinc precursor. It clearly indicates that the particles are aggregating or overlapping of smaller particle to each other. The selected area electron diffraction (SAED) of pure ZnO NP is shown in Fig. 4(b). The diffraction rings indicates that the prepared samples are polycrystalline nature of ZnO. Figure 4(c) and 4(d) show the bright and dark field TEM images of 2 mM Mn-doped ZnO NP, respectively. Figure 4(e) shows the TEM images of 10 mM Mn-doped ZnO NP. The aggregations of particles are increased for 10 mM of Mn-doped ZnO than the pure ZnO whereas the particles aggregations have been reduced for the 2 mM of Mn-doped ZnO samples. The FE-SEM and HR-TEM images are coincide with each other for aggregation of particles nature. The HR-TEM images of 2 mM Mn-doped ZnO NP sample are presented in Fig. 4(f). The ZnO NP is structurally uniform and well-oriented lattice fringe of d-spacing around 0.25 nm. The d-spacing value is well matched with the standard value of (101) plane.

Figure 5(a) and 5(b) show the EDX analysis of pure and Mn-doped ZnO NP for 0.05 M zinc precursor with 10 mM of Mn-doping, respectively. The atomic percentages of all the elements are listed in Table II. The EDX spectra of pure ZnO NP have Zn and O elements. Also, we found week amount of Carbon element due to the environment and experimental setup. The atomic concentration of Mn ions in 10 mM of Mn-doped ZnO NP (0.05 M) sample was 9.6% whereas the Mn ions has been reduced as 4.9% when increase the precursor concentration as 0.1 M for the same amount of doping concentration. The stoichiometric ratio is comparatively good in the Mn-doped samples. Also, it clearly indicates that the Mn ions incorporated into Zn lattice. The XRD and EDX are in good agreement with each other.

The Raman spectra are more sensitive to crystallization, structural disorder and defects in micro and nanostructures. The vibration properties of the hexagonal shaped ZnO NP were investigated by Raman scattering.
According to the group theory, the following optical modes should exist in first-order Raman scattering. According to Kieffer et al. [22], the A\(_{\text{1}}\) and E\(_{\text{2L}}\) modes are two polar branches, which split into longitudinal optical (LO) and transverse optical (TO) components with different frequencies due to macroscopic electric fields associated with the LO phonons. The E\(_{\text{2}}\) mode consists of two nonpolar modes of low and high frequency phonons (E\(_{\text{2L}}\) and E\(_{\text{2H}}\)), which is associated with vibration of heavy Zn sublattice and oxygen atoms, respectively. The A\(_{\text{1}}\), E\(_{\text{1}}\) and E\(_{\text{2}}\) modes are first order Raman-active modes according to the Raman selection rule. The B\(_{\text{1}}\) modes are generally inactive in Raman spectra and are called silent modes [19, 20].

The Raman spectra of pure and Mn-doped ZnO NP are presented in Fig. 6 for 0.05 M of zinc precursor with and without 10 mM of Mn-doping. In the pure ZnO NP the absorption peak at about 369 nm can be noted.

On the other hand Mn-doped sample has peaks at 310 nm. The PL spectra of the pure and Mn-doped ZnO NP are studied by UV-vis absorption and PL spectroscopies. The UV-vis absorption spectra of the pure and Mn-doped ZnO NP are presented in Fig. 7 for 0.05 M of zinc precursor with and without 10 mM of Mn-doping. In the pure ZnO NP the absorption peak at about 369 nm can be noted.

The PL spectra of the pure and Mn-doped ZnO NP are

![FIG. 5: EDX spectra of (a) pure ZnO and (b) 10 mM of Mn-doped ZnO NP for 0.05 M of zinc precursor.](image)

**TABLE II: EDX Results of pure and Mn-doped ZnO NP.**

| Element | Pure ZnO 0.05 M | Pure ZnO 0.1 M | Atomic percentage (%) | Mn-doped ZnO 0.05 M | Mn-doped ZnO 0.1 M |
|---------|----------------|----------------|----------------------|---------------------|-------------------|
| C       | 3.79           | —              | 4.04                 | 3.27                |
| O       | 37.57          | 41.14          | 38.77                | 38.92               |
| Zn      | 58.64          | 58.86          | 53.40                | 48.22               |
| Mn      | 58.64          | —              | 53.40                | 48.22               |
| Total   | 100.00         | 100.00         | 100.00               | 100.00              |

The doping of Mn ions in ZnO matrix has a remarkable effect on the polar and nonpolar branches. The high frequency branch of E\(_{\text{2H}}\) mode involves oxygen motion as well as sensitive to internal stress and is characteristic of wurtzite structure of ZnO nanostructures [23–25]. The mode has a drastic reduction in the intensity of all doped samples. It might be due to the breakdown of translational crystal symmetry by the incorporated defects and impurity. The A\(_{\text{1}}\)(TO) and A\(_{\text{1}}\)(LO)/E\(_{\text{1}}\)(LO) polar branches are appeared at about 380 and 570 cm\(^{-1}\), respectively for the doped samples. On the incorporation of Mn ions in ZnO, the A\(_{\text{1}}\)(LO)/E\(_{\text{1}}\)(LO) peak has been broadened and shifted towards lower energy. Such a shift and broadening in the A\(_{\text{1}}\)(LO)/E\(_{\text{1}}\)(LO) phonon mode can be attributed to scattering contribution of the A\(_{\text{1}}\)(LO)/E\(_{\text{1}}\)(LO) branch outside the BZ center [26] and this phonon mode is commonly assigned to the defect complexes containing oxygen vacancy (V\(_{\text{O}}\)) and zinc interstitial (Z\(_{\text{i}}\)) in ZnO. A characteristic broad peak at about 665 cm\(^{-1}\) was obtained for Mn-doped ZnO samples. It might be exhibiting the Hausmannite complex oxide of Manganese (Mn\(_{2}\)O\(_{3}\)) [27] to the incorporation of ZnO matrix or it might be related to intrinsic host lattice defects, which become activated as vibrating complexes [28]. These host lattice defects in ZnO are activated and amplified, which will soften the related phonon modes by reducing the force constant of atom vibration. The broad Raman peak between 1050 and 1180 cm\(^{-1}\) has been presented in all the doped samples and it shifts to the lower frequency side compared with the pure ZnO NP.

The optical properties of the prepared samples were studied by UV-vis absorption and PL spectroscopies. The UV-vis absorption spectra of the pure and Mn-doped ZnO NP are presented in Fig. 7 for 0.05 M of zinc precursor with and without 10 mM of Mn-doping. In the pure ZnO NP the absorption peak at about 369 nm can be noted. On the other hand Mn-doped sample has peaks at 310 nm. The PL spectra of the pure and Mn-doped ZnO NP are.
FIG. 6: Raman spectra of (a) pure ZnO and (b) Mn-doped ZnO NP for 0.05 M of zinc precursor with different millimole of Mn-doping.

FIG. 7: UV-vis absorption spectra of pure and 10 mM of Mn-doped ZnO NP for 0.05 M of zinc precursor.

shown in Fig. 8(a) and (b) for 0.05 and 0.1 M of zinc precursor with different millimoles (1, 2, 5 and 10) of Mn-doping, respectively. The pure ZnO NP shows the PL emission maximum at 416 nm (2.98 eV). The strong blue emission corresponds to the exciton recombination related near-band edge (NBE) emission of ZnO. It is also interesting to note that several shoulder peaks of blue and green emission are presented on the broad PL spectrum. Generally, the visible emissions are related to several intrinsic defects in ZnO NP, which include Zn vacancies (V\text{Zn}), oxygen vacancy (V\text{O}), zinc interstitial (Zn\text{i}), interstitial O(O\text{i}) and substitution of O at Zn position (O\text{Zn}).

The Mn-doped ZnO NP shows the blue shift of the NBE (obtained in UV region) for all the samples due to Burstein-Moss effect. According to the Burstein-Moss shift at metal doped ZnO, the Fermi level shifts into the conduction band (CB). It exhibits the absorption band transition from the valence band (VB) to the Fermi level in the CB instead of from the VB to the bottom of the CB [29]. Hence, the changes of transition levels lead to the energy gap broadening and result in the blue shift of UV emission. Also, we expect the blue shift of Mn-doped ZnO samples due to band gap of MnO (4.2 eV) [30].

The blue (430, 460 and 487 nm) and green (511, 535, 567 and 595 nm) emission are presented on the broad PL spectrum. The strong blue emission in the ZnO NP is usually attributed by two defects levels, either transition from Zn\text{i} to VB or transition from the bottom of the CB to O\text{i} level [31]. The other week blue emission which is around 460 nm (2.69 eV) can be assigned to the energy of transition of electron from Zn\text{i} to V\text{Zn} [32]. The blue-green emission of 487 nm (2.55 eV) is possible due to surface defects in the ZnO Nanocrystals. It can be attributed to the transition between V\text{O} to O\text{i} [33]. The green emission also represents the transition of photogenerated electron from the CB edge to a trap level [34]. The V\text{O} on the surface has been assumed to be the most likely candidate for the recombination centers. The 535 nm (2.32 eV) emission peak corresponds to the singly ionized V\text{O} in ZnO. The green emission peaks 567 nm is originated mainly from O\text{Zn} defects [35, 36]. The weak green band (595 nm) emission corresponds to the singly ionized oxygen vacancy and this emission results from the recombination of a photogenerated hole with the single ionized charge state of specific defects.

IV. CONCLUSIONS

In summary, we have studied the structural, morphological and optical properties of pure and various amounts Mn-doped ZnO NP synthesized by simple solution combustion method. The XRD pattern indicates that the prepared particles are in hexagonal wurtzite structure with the average particles size of around 30-60 nm. Raman scattering of ZnO NP has first and second orders optical modes which are the characteristic bonds of the wurtzite ZnO. The XRD, EDX and Raman results are correlating to each other for both pure and Mn-doped ZnO NP. The PL results are related to several intrinsic defects such as V\text{O}, V\text{Zn}, O\text{i} and etc. in the Mn-doped ZnO NP. The blue shift of the UV emission has been occurred in all the doped samples due to Burstein-Moss effect.

Acknowledgments

Dr. S. Saravanan (JSPS Invitation Fellow) would like to thank Japan Society for the Promotion of Science (JSPS), Japan. The authors would like to thank Ms. I. Sankeeda, Annamalai University, India for extending the PL characterization facility.
FIG. 8: Room Temperature PL spectra of pure and Mn-doped ZnO NP for (a) 0.05 M and (b) 0.1 M with different millimole of Mn-doping.

[1] Z. R. Tian, J. A. Voigt, J. Liu, B. Mckenzie, M. J. Menderott, M. A. Rodriguez, H. Konishi, and H. Xu, Nat. Mater. 2, 821 (2003).
[2] U. Ozgur, Y. I. Alivov, C. Liu, A. Teke, M. A. Reslchkov, S. Dogan, V. Avrutin, S. J. Cho, and H. Morkoc, J. Appl. Phys. 98, 041301 (2005).
[3] S. Chu, G. Wang, W. Zhou, Y. Lin, L. Chernyak, J. Zhao, J. Kong, L. Li, J. Ren, and J. Liu, Nat. Nanotechnol. 6, 506 (2011).
[4] H. Chen, L. Zhu, H. Liu, and W. Li, Nanotechnology 23, 075402 (2012).
[5] J. J. Cole, X. Wang, R. J. Knuesel, and H. O. Jacobs, Nano Lett. 8, 1477 (2008).
[6] H. M. Xiong, Adv. Mater. 25, 5329 (2013).
[7] Q. Yang, M. Tanaka, T. Yasuda, and H. Tatsuoka, e-J. Surf. Sci. Nanotech. 7, 25 (2009).
[8] E. A. Meulenkamp, J. Phys. Chem. B 102, 5566 (1998).
[9] S. Amirkhanlou, M. Ketabchi, and N. Parvin, Mater. Lett. 86, 122 (2012).
[10] I. Bilecka, P. Elser, and M. Niederberger, ACS Nano 3, 467 (2009).
[11] M. L. Kahn, M. Monge, V. Colliere, F. Senocq, A. Maisonnet, and B. Chaudret, Adv. Funct. Mater. 15, 458 (2005).
[12] C. Panatarani, I. W. Lenggoro, and K. Okuyama, J. Nanopart. Res. 5, 47 (2003).
[13] B. Baruwati, D. K. Kumar, and S. V. Manorama, Sens. Actuators B 119, 676 (2006).
[14] M. Vafaei and M. S. Ghamsari, Mater. Lett. 61, 3265 (2007).
[15] K. Jayanthi, S. Chawla, K. N. Sood, M. Chhibara, and S. Singh, Appl. Surf. Sci. 255, 5869 (2009).
[16] B. Pal and P. K. Giri, J. Appl. Phys. 108, 084322 (2010).
[17] I. Akyuz, S. Kose, F. Atay, and V. Bilgin, Semicond. Sci. Technol. 21, 1620 (2006).
[18] M. Silambarasan, S. Saravananan, N. Ohtani, and T. Soga, Jpn. J. Appl. Phys. 53, 05FB16 (2014).
[19] J. Zhao, X. Yan, Y. Yang, Y. Huang, and Y. Zhang, Mater. Lett. 64, 569 (2010).
[20] C. X. Xu, X. W. Sun, X. H. Zhang, L. Ke, and S. J. Chua, Nanotechnology 15, 856 (2004).
[21] R. P. Wang, G. Xu, and P. Jin, Phys. Rev. B 69, 113303 (2004).
[22] J. M. Calleja and M. Cardona, Phys. Rev. B 16, 3753 (1977).
[23] L. B. Duan, G. H. Rao, Y. C. Wang, J. Yu, and T. Wang, J. Appl. Phys. 104, 013909 (2008).
[24] N. Tripathi, K. Vijayarangamuthu, and S. Rath, Mater. Chem. Phys. 126, 568 (2011).
[25] B. Cao, W. Cai, H. Zeng, and G. Duan, J. Appl. Phys. 99, 073516 (2006).
[26] R. S. Zeferino, M. B. Flores, and U. Pal, J. Appl. Phys. 109, 014308 (2011).
[27] F. Buciuman, F. Patcas, R. Craciun, and D. R. T. Zahn, Phys. Chem. Chem. Phys. 1, 185 (1999).
[28] K. Samanta, S. Dussan, R. S. Katiyar, and P. Bhat-tacharya, Appl. Phys. Lett. 90, 261903 (2007).
[29] Z. B. Bahn and A. Y. Oral, Opt. Mater. 29, 672 (2007).
[30] S. V. Bhat and F. L. Deepak, Solid State Commun. 135, 345 (2005).
[31] X. M. Fan, J. S. Lian, Z. X. GuO, and H. J. Lu, Appl. Surf. Sci. 239, 176 (2005).
[32] S. Mahamuni, K. Borghain, and B. S. Bendre, J. Appl. Phys. 85, 2861 (1999).
[33] P. Jiang, J. J. Zhou, H. F. Fang, C. Y. Wang, Z. L. Wang, and S. S. Xie, Adv. Funct. Mater. 17, 1303 (2007).
[34] R. D. Yang, S. Tripathy, Y. Li, and H. J. Sue, Chem. Phys. Lett. 411, 150 (2005).
[35] K. Vanheusden, C. H. Seager, W. L. Warren, D. R. Tal- tant, and J. A. Voigt, Appl. Phys. Lett. 68, 403 (1996).
[36] Y. Yang, X. W. Sun, B. K. Tay, Peter H. T. Cao, J. X. Wang, and X. H. Zhang, J. Appl. Phys. 103, 064307 (2008).