

GSJ: Volume 8, Issue 8, August 2020, Online: ISSN 2320-9186 www.globalscientificjournal.com

Room Temperature Non-overlapping Small Polaron Tunneling (NSPT) conduction mechanism in Mn doped ZnO powder

by

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Abstract:

In the present work synthesis of undoped and Mn- doped ZnO nanoparticles by simple co precipitation method is reported. X-ray diffraction data revealed the formation of hexagonal wurtzite phase for both undoped and Mn-doped nanoparticles.

The ac conductivity and the dielectric constant of Mn-doped ZnO were investigated at temperatures from 320 to 515K in the frequency range from 10^2 to 10^6 Hz.

The temperature dependence of frequency exponent s is investigated to understand the conduction mechanism in the Mn doped ZnO samples of different concentrations .The non-overlapping small polaron tunneling model can explain the temperature dependence of the frequency exponent in the temperature range (320-410K), while the correlated barrier hopping model is the predominant conduction mechanism in the temperature range (410-515K).

Key words:

Diluted magnetic semiconductors, Mn-doped ZnO, AC conductivity

Introduction:

Zinc oxide (ZnO) is one of the most important II-VI semiconductors. This importance is arising from its high chemical stability, wide band gap (3.37 eV), high exciton enrgy (E= 60 meV) and high dielectric permittivity. Therefore, ZnO enters in many applications in industry such as, optical devices in UV region [1,2], in polymerization reactions as photo initiator [3], photo catalysis [4], water purification [5,6], solar cell windows [7,8], Sun screen [9], electric capacitors [10,11]. Furthermore, due to the good biocompatibility of

ZnO with the human body, ZnO nanoparticles is reported as antibacterial and antifungal material [12, 13]

Recently, Mn-doped ZnO is considered as one of the most important diluted magnetic semiconductors (DMS). The main advantage of this compound is its high blocking temperature (T_B) which means the presence of ferromagnetism at room temperature. A theoretical prediction, which reveals that hole mediated Mn doped ZnO can achieve Curie temperature above room temperature. Another theoretical study reported that, P-type Mn-doped ZnO is ferromagnetic while the n-type is antiferromagnetic. On the other hand, For Mn-doped ZnO nanoparticles many researchers have reported different magnetic behavior such as ferromagnetism [14], spin glass behavior [15] and paramagnetism [16].

On the other hand, the electrical conduction mechanism of Mn-doped ZnO is also affected by the preparation condition [17].The violation between the theoretical prediction and experimental observations is mainly related to two main factors: (i) the presence of oxygen vacancies. (ii) The presence of Mn ions with different valances during the preparation. Therefore, the elimination of the presence of oxygen vacancies and different valances on Mn ions may give clearer image about the physical properties of Mn-doped ZnO

In this study, the transport properties are investigated for Mn-doped ZnO samples which are prepared by simple method but in the presence of Ar gas atmosphere and at low temperature to eliminate the above two factors.

Synthesis and experimental techniques

The stoichiometric ratios of Zinc acetate dehydrate $[Zn(CH_3COO)_2, 2H_2O]$, and Manganese acetate tetra hydrate $[Mn(CH_3COO)_2, 4H_2O]$ were dissolved in 100 ml of distilled water according to the chemical formula $Zn_xMn_{1-x}O$, where X= 0.00, 0.01, 0.03, 0.05, 0.07, 0.09, 0.10 by a constant stirring (500 rpm) at 100°C for 30 minutes with the help of a magnetic stirrer to achieve a good homogeneity with subsequent addition of the drops of sodium hydroxide [NaOH] which was dissolved in 100 ml of distilled water according to the chemical reaction:

 $(1-X)Zn(CH_3COO)_2 + (X)Mn(CH_3COO)_2 + 2 NaOH \longrightarrow 2NaCH_3COO + Zn_{1-x}Mn_xO$

The precipitates which get formed were separated from the solution by filtration, washed several times with distilled water and then dried in an oven at 100°C overnight to obtain

Mn doped ZnO nanoparticles, then these materials were sintered at 700° C for 4 hours in argon gas atmosphere. Thereafter, the material was taken and grinded using a mortar, then pressed into pellets using a hydraulic piston with pressure of 5 tons/cm² for 10 minutes.

Characterization

X-ray diffraction (XRD) patterns were obtained using adiffractometer of type (X^{Pert} Graphics, Germany) withCuK α radiation (λ =1.54056Å).The data recorded from (2 θ =20° to 2 θ =80°) were used to identify the crystal structure of the samples while their particle sizes and morphology were investigated by Transmission Electron Microscope (TEM,) with accelerating voltage of 100 KV. Fourier transform infra-red spectroscopy (FTIR) was performed by (NICOLET 380 FT-IR) in range 400-4000 cm⁻¹ at room temperature in transmission mode which indicates absorption of electromagnetic waves at certain wave numbers. The position of absorption peaks indicates the bond strength and structural geometry in the molecule. The dielectric constant and the AC conductivity are measured using EUCOL U2826 LCR meter for a frequency range from 20 Hz 5 MHz at various temperatures ranging from 300- 520K.

Results and discussion:

XRD patterns of pure and Mn doped ZnO nanoparticles are shown in figure (1). All diffraction peaks could be indexed as wurtzite hexagonal ZnO phase. Furthermore, no other impurity peak was observed in the XRD pattern showing the single phase sample formation of ZnO nanoparticles up to x=0.05, beyond which an impurity phase of MnO was detected in higher dopant concentration (x=0.07, 0,09, and 0.10). The effect of Mn concentration on lattice parameters (a &c) is shown in figure (2). The obtained values of the lattice parameter of our samples are in good agreement with that reported before [18]. Also, it is clear that, the lattice parameters slightly increase with the increase of Mn concentration up to x=0.05 after which they decrease for higher doping concentration. For more understanding the effect of Mn doping on the micro strain and the grain size is shown in figure (3). It is obvious that, the grain size has the same behavior of the lattice parameters, on contradictory, the strain curve has sudden increase for x \geq 0.05. The above results could be explained as follows:

For Mn concentration up to x = 0.05, the crystal structure of ZnO in the form of Mn⁺² replacing Zn⁺². Since ionic radii of Mn⁺² (0.83 Å) is greater than that of Zn²⁺ (0.74Å), the lattice parameter and the crystallite size slightly increase.

On the other side, for x > 0.05, the formation of MnO phase comes into the picture and this phase resides at the grain boundaries. This phase makes compression stresses on the unit cell causing the lattice parameter and the crystallite size to decrease. The sudden increase of the micro strain for x > 0.05 confirms the presence of MnO phase at the grain boundaries which is in good agreement with the experimental results.

FTIR spectra of ZnO with Mn content have been measured in the range 1300-400 cm⁻¹ is shown in Figure 4. It is clear that, for pure ZnO sample, there is an absorption band at 437 cm⁻¹which is corresponding the stretching vibration of Zn-O bond [19]. It is relevant to observe that, this band has a blue shift with increasing Mn content. The shift of this band indicates a successful doping of Mn²⁺ ion into ZnO crystal structure where, the band position could be related to the change in the bond length that takes place upon substitution of Mn at Zn site [20]. Moreover, a new band is appeared at 650 cm⁻¹ for samples with $x \ge 0.07$. This band is corresponding to the vibrational modes of Mn-O bond. This observation proves the presence of MnO at the grain boundaries as was discussed in X-ray diffraction results.

Dielectric and conductivity measurements:

The dielectric constant (\mathcal{E}) and the conductivity (σ) were measured for $Mn_xZn_{1-x}O$ (x= 0.0,0.01, 0.03, 0.05, 0.07, 0.09, and 0.1). The measurements were carried out in temperature range from 300K to 520K and frequency range from 1000 Hz to 5 MHz.

The dependence of the dielectric constant \mathcal{E} with the frequency at various temperatures for Mn doped ZnO at different concentrations are shown in figure (5). It is obvious that, the magnitude of dielectric constant \mathcal{E} decrease with increasing frequency. The presence of oxygen vacancies, and grain boundaries defects are the reasons of the large value of the dielectric at low frequency while, the decrease in dielectric constant with frequency is attributed to the lagging between induced electric dipoles and the applied field at high i.e., the electron exchange between the charge carriers cannot follow the applied alternating field frequencies [21-22].

The frequency dependence of the conductivity σ at different selected temperatures is shown in figure (6). It is noticed that the electrical conductivity increases with increasing frequency. This could be attributed to the increase of hopping between the ch arge carriers with increasing the frequency which results an increase in conductivity value of all samples. Furthermore, the conductivity is found to decrease with the increase in Mn concentration. The incorporation of substitution Mn suppresses the formation of native defect such as oxygen vacancies [23]. Thus hopping between the charge carriers is not so ease at higher concentration of Mn. In other words Mn doping ceases hopping mechanism and hence results in a decrease in the electrical conductivity.

For studying the conduction mechanism of the prepared samples, it is well known that the Ac conductivity could be written as $\sigma = A \omega^{S}$ [24] where, A is a constant depending on temperature, ω is the angular frequency and s is the frequency exponent. Then the variation of exponent s with temperature is very important to study the conduction mechanism of the investigated samples in the present temperature range.

Figure (7) shows the variation of the exponent s with temperature. It is obvious that, this figure could be divided into two regions:

In region I, the exponent s increases with increasing temperature while in region II, The frequency exponent s decreases with increasing temperature.

In fact, the change of the exponent s with temperature depends on the conduction mechanism of the charge carriers where, according to Quantum mechanical tunneling (QMT), it is suggested that the exponent is independent of temperature which is not applicable for the experimental results.

In Overlapping large polaron tunneling (OLPT) [26] also is not applicable for the present system, since this model predicts that, s exhibits a minimum at a certain temperature and subsequently increases again.

In Non-overlapping small polaron tunneling (NSPT) model [27], the value of s decreases with increase of temperature where,

 $S = 1 - \frac{4}{\ln(\frac{1}{\omega\tau_O}) - W_H/KT}$, where, ω is the angular frequency, τ_O is the relaxation time, W_H is

the polaron hopping energy, K is Boltzmann's constant, and T is the temperature.

Hence, it is the most suitable mechanism for explaining the behavior of investigated data of Mn- doped ZnO in the frist region. On the other hand, according to Correlated barrier hopping (CBH) [28], the frequency exponent s is given by,

 $S = 1 - \frac{6KT}{W_M - KT \ln(\frac{1}{\omega \tau_O})}$, where, W_M is the maximum barrier height.

It is clear that CBH model predicts an increase of s with increasing temperature. Therefore, CBH model is the most suitable mechanism for explaining the conduction mechanism in the second region. This means that, there is a change in the conduction mechanism from NSPT to CBH at certain temperature. The arrows on figure (7) shows the transition temperature from NSPT mechanism to CBH. It is clear that, this transition temperature increases with increasing Mn-content. The above results could be explained as follows:

1- The preparation of Mn-doped ZnO samples in argon atmosphere eliminates the presence of Mn^{+4} and Mn^{+6} valances which causes the hopping mechanism of conduction needs more energy which in turn affect the temperature at which the hopping takes place.

2- The increase of the transition temperature from NSPT to CBH with increasing Mn content could be attributed to the increase of sp-d overlapping which increases the barrier height energy and reduces the oxygen deficiency.

According to the NSPT and CBH models the electrical conductivity is given by,

$$\sigma_{\text{NSPT}} = \frac{\pi^2}{24} e^2 KT \alpha^{-1} [N(E_F)]^2 \omega R_{\omega}^4 \text{ and}$$

$$\sigma_{\text{CBH}} = \frac{n\pi^3}{24} N^2 \varepsilon \varepsilon_0 \omega R_{\omega}^6 \text{ respectively}$$

Where, e is the electronic charge, α is the decay parameter for the localized wave function, N(E_F) is the density of states at the Fermi level, R_{ω} is the hopping distance, E and E_O are the dielectric constants of material and free space, respectively, and n is the number of electrons involved in the hopping process, n=1 for single polaron hopping, and n=2 for bipolaron hopping.

By making a fitting of the experimental data in the two regions, according to the above two models, the polaron radius (R_p) and the hopping distance (R_W) in both mechanisms could be calculated and tabulated in table (1). It is obvious that, the values R_p in NSPT model in the range of the lattice parameter of the samples while R_W in CBH model is larger than that of R_p with many order of magnitude of lattice parameter. Furthermore, the values of R_w decreases with increasing Mn-content which supports the decrease of the electrical conductivity with Mn- content. Moreover, the variation of the hopping energy W_H and the localized density of states N with Mn-content are also shown in table (1). One can see that, there is an increase in both of W_H and N with increasing Mn-content. This result support the increase of sp-d interaction with increasing Mn ratio in the samples.

Conclusion:

1-A series of nano crystalline Mn-doped ZnO particles were synthesized by coprecipitation method. The XRD patterns suggest that all of our nano crystalline Mndoped ZnO particles are constituted in a hexagonal wurzite structure, With the increase in Mn concentrations the lattice parameter, the average crystallite size increased up to 5%, then decreased, while the strain has showed the opposite behavior.

2- AC electrical conductivity measurements were carried out in the frequency range from 10^2 to 10^6 Hz and at different temperatures from 320 to 515K. From these measurements we can conclude that;

- The AC conductivity increases with the increase in temperature, and the frequency of the applied field, also it decreases with the increase in Mn concentration.
- The NSPT conduction mechanism is the predominant conduction mechanism in the temperature range 320-410K ,while the CBH conduction mechanism is the predominant one in the temperature range 410-515K in these materials.

3-The density of states N, the hopping distance R_w , the polaron hopping energy W_H , and the maximum barrier height W_M were obtained by fitting the experimental data to each model in the temperature range.

References:

- [1]C. F. Lin, W. Y. Su, and J. S. Huang, —Improving the property of ZnOnanorods using hydrogen peroxide solution, *Journal of Crystal Growth*, vol. 310, no. 11, pp. 2806–2809, 2008.
- [2] S. H. Yu and H. Cölfen, —Bio-inspired crystal morphogenesis by hydrophilic polymers, *Journal of Materials Chemistry*, vol. 14, no. 14, pp. 2124–2147, 2004.
- [3] Ali, A. M.; Emanuelsson, E. A. C.; Patterson, D. A. Appl. Catal. B, 97, 168–181.
 doi: 10.1016/j.apcatb.2010.03.037 (2010).
- [4] M. Yamaoto, G. Oster, J. Polym. Sci. Part A: Polym. Chem. 1966, 4, 1683.
- [5] M. R. Hoffmann, S. T. Martin, W. Y. Choi, D. W. Bahnemann, Chem. Rev. 1995, 95, 69–96.
- [6] L. Schmidt-Mende, J. L. MacManus-Driscoll, Mater. Today 2007, 10, 40–48.
- [7] R. Viswanatha, S. Sapra, B. Satpati, P. V. Satyam, B. N. Dev, and D. D. Sarma. J. Mater. Chem., 14, 661 (2004).
- [8]Zhong Chen, XiaoXiaLi, GuopingDu, NanChen and Andy Y.M.Suen., A sol-gel method for preparing ZnO quantum dots with strong blue emission, Journal of Luminescence., 2011, 131 2072–2077.
- [9] The Scientific Committee on Consumer Products, Intended for Consumer Opinion concerning Zinc oxide, Available from: ec.europa.eu/health/ph_risk/committees/sccp/documents/out222_en.pdf, June 24-25, 2003.
- [10] Y. Yen, W. Chen, C. Hsu, H. Chou, J. Lin, M. Yeh, "Arylamine-Based Dyes for p-Type Dye-Sensitized Solar Cells". Org. Lett., vol. 13, pp. 4930, 2011.
- [11] N. Padmavathy and R. Vijayaraghavan, —Enhanced bioactivity of ZnO nanoparticles—an antimicrobial study, *Science and Technology of Advanced Materials*, vol. 9, no. 3, Article ID 035004, 2008.

- [12] L. He, Y. Liu, A. Mustapha, and M. Lin, —Antifungal activity of zinc oxide nanoparticles against *Botrytis cinerea* and *Penicilliumexpansum*, *Microbiological Research*, vol. 166, no. 3, pp. 207–215, 2011.
- [13] S. A. Ansari, Q. Husain, S. Qayyum, and A. Azam, —Designing and surface modication of zinc oxide nanoparticles for biomedical applications, *Food and Chemical Toxicology*, vol. 49, no. 9, pp. 2107–2115, 2011.
- [14] S.-J. An, W. I. Park, G.-C.Yi, and S. Cho, Appl. Phys. A: Mater. Sci. Process. 74, 509 ~2002!.
- [15] T. Fukumura, Zhengwu Jin, A. Ohtomo, H. Koinuma, and M. Kawasaki, Appl. Phys. Lett. 75, 3366 (1999).
- [16] A. Tiwari, C. Jin, A. Kvit, D. Kumar, J. F. Muth, and J. Narayan, Solid State Commun. 121, 371 (2002).
- [17] N. Kılınc, L. Arda, S. O[°] ztu[°]rk, Z.Z. O[°] ztu[°]rk, Cryst. Res. Technol. 45(5), 29 (2010).
- [18] S. Chattopadhyay, S. Dutta, A. Banergee, D. Jana, S. Bandyopadhyay, S. Chattopadhyay, A Sarkar, "Synthesis and characterization of Single phase Mn-doped ZnO" vol 404, issue 8-11, pp1509-1514, 2009.
- [19] Gutul Tatyana, Rusu Emil, Condur Nadejda, Ursaki Veaceslav, Goncearenco Evgenii and Vlazan Paulina, Beilstein J. Nanotechnol 5 (2014) 402– 406.
- [20] M. Ebrahimizadeh Abrishami, S. M. Hosseini, E. AttaranKakhki, A. Kompany, and M. Ghasemifard, Int. J. Nanosci. (2009).
- [21] M. L. Dinesha, G. D. Prasanna, C. S. Naveen, and H. S.Jayanna, Indian J. Phys. 87(2), 147-153 (2013)
- [22] Abo El Ata A M and Attia S M 2003 J. Magn. Magn. Mater. 257 165
- [23] U. Philipose, S. V. Nair, S. Trudel, C. F. de Souza, S. Aouba, R. H. Hill, and H. E. Ruda, Appl. Phys. Lett. 88, 263101 _2006_.
- [24] Elliott S R 1987 Adv. Phys. **36** 135
- [25] Pollak M and Geballe T H, Low frequency conductivity due to hopping process in silicon. Phys. Rev. 122 (1961)1742.
- [26] A. R. Long, Frequency-dependent loss in amorphous semiconductors, Adv. Phys. 31 (1982) 553.
- [27] S.R.Elliott, AC conduction in amorphous chalcogenide and pnictide semiconductors, Adv. Phys. 36 (1987) 135.
- [28] S. R. Elliott, A theory of ac conduction in chalcogenide glasses, Philos. Mag. 36 (1977) 1291.



Figure (2)



Figure (4)



Figure (5)



Figure (6)





	NSPT at $T = 320$			CBH at T = 470 K		
	K					
Mn	R _w	W _H	α^{-1}	R _w	W _M	$N (m^{-3}. eV^{-1})$
(x)	(Å)	(eV)	(Å)	(Å)	(eV)	
0.00	4.4	0.21	1.1	86	0.19	2.5E+24
0.01	6.0	0.39	4.1	80	0.27	8.2E+24
0.03	4.9	0.31	0.7	60	0.28	1.9E+25
0.05	5.0	0.34	0.9	49	0.35	2.9E+25
0.07	4.8	0.40	0.8	39	0.53	2.9E+25
0.09	5.8	0.62	1.2	35	0.63	1.0E+26
0.10	5.0	0.69	0.8	30	0.74	1.3E+26

Table (1): The change of the polaron radius, activation energy and the density of states with Mn content

Figure captions:

Figure (1): XRD chart for $Mn_xZn_{(1-x)}O$ (x = 0.00, 0.01, 0.03, 0.05, 0.07, 0.08 and 0.10).

Figure (2): Effect of Mn content (x) on the lattice parameter of $Mn_xZn_{(1-x)}O$ samples.

Figure (3): Effect of Mn content (x) on the lattice strain and grain size of $Mn_xZn_{(1-x)}O$ samples.

Figure (4): FTIR spectrum of Mn_xZn_(1-x)O samples.

Figure (5): Frequency dependence of the dielectric constant of $Mn_xZn_{(1-x)}O$ samples at different temperatures.

Figure (6): Frequency dependence of the electrical conductivity of $Mn_xZn_{(1-x)}O$ samples at different temperatures.

Figure (7): Dependence of the s exponent on temperature.

