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Effect of NiO Doping on Structural Properties of ZnO

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Abstract: ***The functional material was formulated by adding the solutions of AR grade Zinc acetate ($Zn(O_2CCH_3)_2(H_2O)_2$) and Nickel chloride ($NiCl_2$) with different molar concentration and heated at 100°C . After heating it for 4h a resin like solid product was formed. The solid product was sintered for 4 h at temperature 1000°C; a light green colour solid product was obtained. Then it was milled for 2 h. The structural properties of the prepared powder materials were studied by X-ray analysis. The observed powder materials show the polycrystalline nature and the crystallite size found to be in the range of 22 to 35 nm. Thermogravimetric (TGA) and differential thermal analyses (DTA) of pure ZnO and NiO- doped ZnO samples were carried out. . The TGA analysis shows that t there is no significant % wt. loss in both samples. Hence the doped sample is observed to be stable. The DTA showed the endothermic nature of reactions for both pure and doped ZnO films.***

Keywords: ZnO, NiO, XRD, Crystallite size, TGA, DTA

1. Introduction

NiO is the most exhaustively investigated transition metal oxide. NiO is an antiferromagnetic, p- type semiconductor with a wide band gap of (3.8 eV) oxide. NiO finds wide range of applications due to its good chemical stability as well as electrical properties. NiO is often non stioichometric. wide-band-gap semiconductor, is used in magnetic, batteries, chemical sensing, mass flow/temperature sensing, electroluminescent, catalysis, fuel cells and smart windows applications. Nickel addition in tin oxide gas sensor has been investigated by various researchers [1-12].

ZnO is a II–VI group compound semiconductor with a hexagonal wurtzite crystal structure. It has a wide and direct band gap of 3.37 eV at 300 K and a large free exciton binding energy of 60 meV. It has unique physical and chemical properties, low-dimensional volume, high aspect ratio, light-matter interaction, cost-effectiveness and can be synthesized by various chemical and physical methods. ZnO has become one of the most popular materials for electrical and optical applications over the time. It is promising material for many optoelectronic applications such as ultraviolet lasers, light-emitting diodes, p–n junction devices, thinfilm transistor, solar cells, acoustic devices, chemical and biological sensors [13-20].

In the present work I investigated the effect of NiO doping on structural and morphological properties of ZnO. Doping of the base martial was carried out by adding the additives ($NiCl_2$) in the base material ZnO.

2. Experimental Procedure

2.1 Preparation of Functional Material

The pure AR grade powder of Zinc acetate ($Zn(O_2CCH_3)_2(H_2O)_2$) and Nickel chloride ($NiCl_2$) solution of different molar concentration were mixed and stirred for 10 min and heated at 100°C gives viscous solution. After heating it for 4h a resin like solid product was formed. The solid product was sintered for 4 h at temperature 1000°C; a light green colored solid product was obtained. Then it was milled for 2 h to obtain fine powder**.** The preparation condition for the formulation of functional materials is as shown in Table 1.

Table 1: Composition of functional material

Sample No.	*Composition*
S1(Pure ZnO)	Zn $(O_2CCH_3)_2(H_2O)_2$
S2(NiO doped ZnO)	0.9M Zn $(O_2CCH_3)_2(H_2O)_2$ +0.1M $NiCl_2$
S3(NiO doped ZnO)	0.5M Zn $(O_2CCH_3)_2(H_2O)_2$ + 0.5M $NiCl_2$

3. Physical Characterization

3.1 Structural Analysis

In order to understand the structural properties of pure ZnO and NiO doped ZnO powder materials at different molar concentration, X-ray diffraction analysis of these sintered powders were carried out using Cuk_α radiation.

Fig.1 (a-d) shows XRD pattern of ZnO obtained from Zinc acetate (Zn $(O_2CCH_3)_2(H_2O)_2$), NiO from Nickel chloride $NiCl_2$ and NiO- loaded ZnO materials at different molar concentration.

Fig.1 (a) shows that the observed diffraction peaks of ZnO are correspond to the hexagonal wurtzite structure of ZnO. The observed peaks are well matched with the JDPS (76-0704) reported data of ZnO. The sharp peaks of XRD are corresponds to ZnO material and are observed to be polycrystalline in nature. The higher peak intensities of an XRD pattern is due to the better crystallinity with preferred orientation along the (101) direction. Fig.1 (b) shows the diffraction peaks of NiO material was observed to be polycrystalline in nature corresponds to cubic structure and are well matched with the JDPS (75-0269) reported data of NiO. The observed peaks shows that the NiO material is not very crystalline but it having some preferred orientation along the (200) direction.

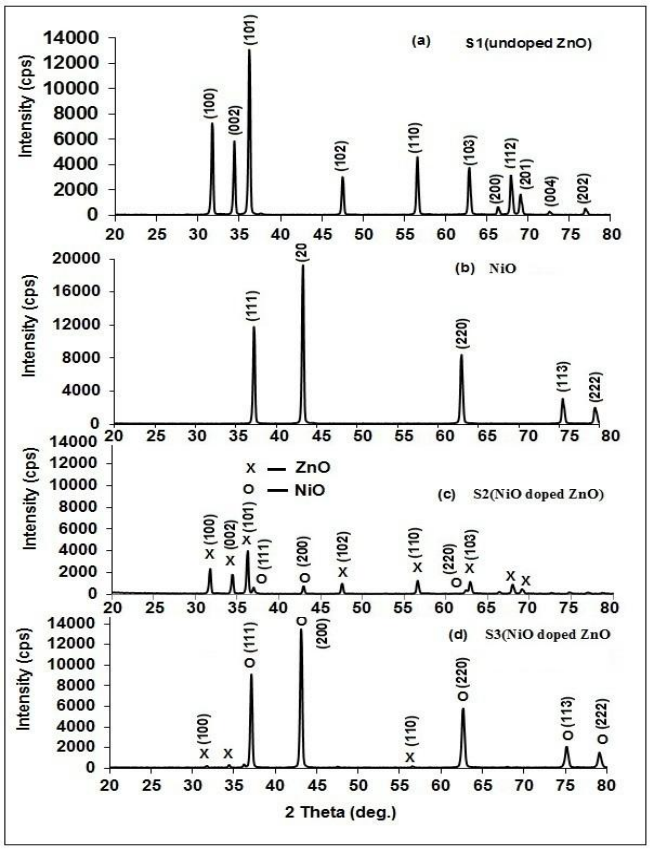


Figure 1: XRD Patterns of pure ZnO, NiO and NiO-ZnO composite materials.

Fig.1(c) shows the XRD pattern of sample S2. The observed peaks shows that the final compositions consists of two phases namely ZnO and NiO where ZnO peaks are dominant with some traces of NiO are also present. Fig 1 (d) shows the XRD pattern of sample S3. The observed peaks shows that the final compositions consists of two phases namely ZnO and NiO where NiO peaks are dominant with some traces of ZnO are also observed. It was confirmed by referring to JCPDF data for ZnO and NiO. The presence of both peaks in the final material composition would give the possibility of formation of p (NiO) - n (ZnO) heterojunction junction at grain boundaries of ZnO.

Detailed knowledge of crystallite size and shape in a finely divided powder often helps to correlate many physical properties of a system undergoing transformation in a solid state reaction. The average crystallite size from X-ray line broadening has been calculated using the Scherrer eq.(1)[21,22]. The d-spacing of the planes corresponding to the different observed peaks, FWHM, crystallite size and hkl-planes of the pure and NiO- loaded functional materials are listed in Table 2.

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

Where D- is average crystallite size, β - is the broadening of the diffraction line measured at half maximum intensity(FWHM), λ -is wavelength of the x- ray radiation and (0.1542 nm). θ - is the Bragg angle,λ -Wavelength of the x- ray radiation and θ -Bragg's angle.

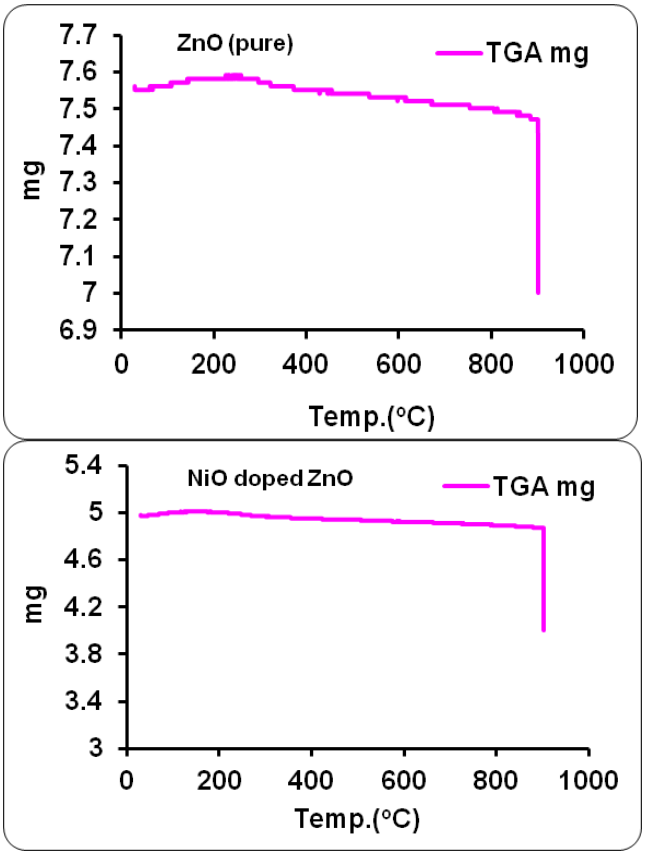
Table 2: XRD data of Sample- S1, S2, S3.

Sample No.	*2θ (deg.)*	*d-Spacing(Å)*	*FWHM*	*Crystallite Size (D nm)*	*(hkl)*
S1	31.70	2.82	0.265	35	Z-100
S2	31.80	2.81	0.275	33	Z-100
S3	31.70	2.82	0.393	23	Z-100
S1	77.00	1.22	0.422	27	Z-202
S2	77.00	1.24	0.660	22	Z-202
S3	77.00	1.24	0.660	22	Z-202

Table 2 shows the variation in the d- spacing and crystallite size of all samples corresponding to the different crystal planes. It shows that the doping would changes the d-spacing and crystallite size. The XRD pattern of doped samples shows that the intensity of observed peaks were decreased with increase in dopant concentration. The slightly broadening of diffraction lines may be attributed to small crystalline effects or chemical heterogeneity of the samples.

3.2 Thermal analysis

Thermogravimetric (TGA) and differential thermal analyses (DTA) of pure ZnO and NiO- doped ZnO samples were carried out under same condition in static air, and their profiles are given in Figs. 2[23, 24].



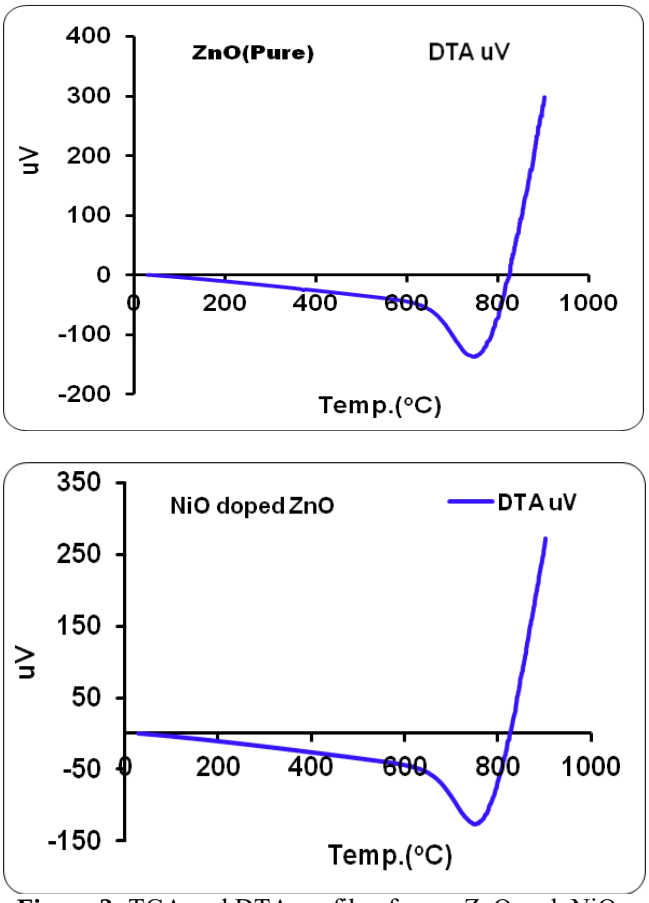


Figure 2: TGA and DTA profile of pure ZnO and NiO – ZnO composite.

Table 3: Weight loss of pure ZnO and NiO doped ZnO.

Temperature Range in °C	*Weight. Loss of pure ZnO*	*Temperature Range in °C*	*Weight. Loss of NiO – ZnO*
256-663	-0.068 mg -0.900 %	143 - 515	-0.079 mg -1.588 %

Table 3 shows that the loss in weight of pure ZnO and NiO-doped ZnO samples in the different ranges of temperature observed from TGA. It can be concluded from the profiles that there is no significant % wt. loss in both samples. Hence the doped sample is observed to be stable. The variation in weight with temperature was presented by TGA at a high resolution.

The DTA showed the endothermic nature of reactions for both pure and doped ZnO films. The heat absorbed by the samples may be due to the non-stoichiometry and oxygen deficiency of the film.

4. Conclusions

1) The NiO-ZnO composite materials were synthesized by adding Zinc acetate ($Zn(O_2CCH_3)_2(H_2O)_2$) and Nickel chloride ($NiCl_2$) with different molar concentration
2) The XRD pattern of doped samples shows that the intensity of observed peaks was decreased with increase in dopant concentration.
3) The observed X-ray data shows that the doping would changes the d-spacing and crystallite size.
4) The observed powder materials show the polycrystalline nature and the crystallite size found to be in the range of 22 to 35 nm.
5) Thermogravimetric (TGA) analysis shows that there is no significant % wt. loss in both pure and doped samples. Hence the doped sample is observed to be stable.
6) The differential thermal analyses (DTA) showed the endothermic nature of reactions for both pure and doped ZnO films

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References

[1] C. Kittel, Introduction to Solid State Physics. New York: Wiley, 1986.
[2] R. J. Powell and W. E. Spicer, “Optical properties of NiO and CoO,” Phys. Review B, vol. 2, no. 6, pp. 2182–2193, Sep. 15, 1970.
[3] T. Satoh, N. P. Duong, and M. Fiebig, “Coherent control of antiferromagnetism in NiO”, Physical Review B 74 (1), 012-404, 2006.
[4] L. Yuan, Z. P. Guo, K.Konstantinov, P. Munroe, and H. K. Liu, “Spherical clusters of NiO nanoshafts for lithium-ion battery anodes”, Electrochemical and solid-state letters 9 (11), A524-A528,2006
I. Hotovy, H. J. Huran, L. Spiess, R. Capkovic, and S. Hascik, “Preparation and characterization of nio thin films for gas sensor applications,” Vacuum, vol. 58, pp. 300–307, 2000
[5] J. A. Dirksen, K. Duval, and T. Ring, “NiO thin film formaldahyde gas sensor,” Sens. Actuators B, vol. 80, pp. 106–115, 2001
I. Hotovy, V. Rehacek, P. Siciliano, S. Capone, and L. Spiess, “Sensing characteristics of NiO thin films as NO2 gas sensor”, Thin Solid Films 418(1), 9-15,2002.
[6] C. R. Makkus, K. Hemmes, and J. H. W. Dewit, "A comparative-study of NiO(LI), $LiFeO_2$, and LiCOO2 porous cathodes for molten-carbonate fuel-cells", Journal of the Electrochemical Society, 141(12), , pp. 3429-34381994, 1994.
[7] M. N. Rumyantseva, L. I. Ryabova, T. A. Kuznetsova, M. Labeau, G.Delabouglise, A. M. Gas’Kov,"Sensor properties of polycrystalline SnO_2 films doped with Ni", Inorg Mater, 35(1), , pp. 54-59, 1999.
[8] Tian F, Liu Y, “Synthesis of p-type NiO/n-type ZnO heterostructure and its enhanced photocatalytic activity”, Scripta Mater., 2013, 69, 417–419
[9] Namseok Park, Ke Sun, Zhelin Sun, Yi Jing[a] and Deli Wang, “High efficiency NiO/ZnO heterojunction UV photodiode by sol–gel processing”,J. Mater. Chem. C, **1**,pp. 7333-7338, 2013.
[10] Xiaoyan Cai, Yun Cai, Yongjun Liu, He Li ,Fei Zhang,Yude Wang, “High efficiency NiO/ZnO heterojunction UV photodiode by sol–gel processing,

Structural and photocatalytic properties of nickel-doped zinc oxide powders with variable dopant contents", Journal of Physics and Chemistry of Solids,Volume 74, Issue 9, pp. 1196–1203, September 2013.
[11] D. C. Look, "Recent advances in ZnO materials and devices," Mater. Sci. Eng. B 80(1-3), pp.383–387 2001.
[12] Anderson Janotti and Chris G Van de Walle, "Fundamentals of zinc oxide as a semiconductor", IOP Publishing, reports on progress in Physics, 72, pp.126-501, 2009.
[13] M. S. Wu, A. Azuma, T. Shiosaki, A. Kawabata, "Low-loss ZnO optical waveguides for SAW-AO applications, IEEE Trans". Ultrasonics Ferroelec.Freq. Control (36),PP. 442–445, 1989.
[14] M. K. Jayaraj, A. Antony, M. Ramachandran, "Transparent conducting zinc oxide thin film prepared by off-axis RF magnetron sputtering", Bull. Mater. Sci.(25),PP. 227–230, 2002.
[15] K. Keis, C. Bauer, G. Boschloo, A. Hagfeldt, K. Westermark, H. Rensmo, H. Siegbahn, "Nanostructured ZnO electrodes for dye-sensitized solar cell applications", J. Photochem. Photobiol. A: Chem. (148),PP. 57–64, 2002.
[16] P. Yang, H. Yan, S. Mao, R. Russo, J. Johnson, R. Saykally, N. Morris, J. Pham, R. He, H. Choi, "Controlled growth of ZnO nanowires and their optical properties", Adv. Funct. Mater. (12),PP. 323–331, 2002.
[17] S. Roy, S. Basu, "Improved zinc oxide film for gas sensor applications", Bull. Mater. Sci. (25),PP. 513–515, 2002.
[18] A.R. Raju, C.N.R. Rao, "Gas sensing characteristics of ZnO and copper impregnated ZnO', Sens. Actuators B (3),PP. 305–310, 1991.
[19] B. D. Cullity, Elements of X-ray Diffractions, Addison-Wesley, Reading, MA,1978.
[20] H.P. Klug, L.E. Alexander, X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials, Wiley, New York, 1974.
[21] Yiwei Zhang, Ailin Xia, Weihua Chen, Renjun Ma," Structural and Magnetic Properties of Hydrothermal Spinel Ni0.4Zn0.6Fe2 O4 Ferrites" Materials Research, 18(6),pp.1251-1255, 2015.
[22] Munusamy Thirumavalavan, Kai-Lin Huang and Jiunn-Fwu Lee, "Preparation and Morphology Studies of Nano Zinc Oxide Obtained Using Native and Modified Chitosans", Materials, 6, pp.4198-4212, 2013.

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