Studies on Microstructure and Thermoelectric Properties of ZnO Doped with Sb_2O_3

N. Lalitha Kumari[a], B. Rajesh Kumar[b], C. Pullaiah[c]
[a]Department of Physics, Silver Jubilee Govt. College (Autonomous), Kurnool – 518 002, A.P, India
[b]Department of Physics, GITAM Institute of Technology, GITAM University,
Visakhapatnam – 530045, A.P, India

***Abstract*—**
In the present work ZnO doped with 2 wt% to 10 wt% of Sb_2O_3 is prepared by conventional solid state reaction method. From XRD patterns, the observed reflections were (100), (002) and (101) which were similar to the observed reflections in ZnO bulk. From XRD results, lattice parameters were calculated using the formula for hexagonal system. It was also observed that the particle size and lattice parameter increases with the increase of doping concentration of Sb_2O_3. The crystallite size estimated from Scherrer formula is found to be in the range of 32 to 56 nm. Scanning Electron Microscope (SEM) supplemented with EDS is carried out to study the surface morphology as well as to find the chemical composition of the ceramic material. Seebeck coefficient was measured as a function of temperature in the range 300–573 K. The sign of the thermoelectric power is found to be negative over entire temperature range showing that majority charge carriers are electrons and hence the compound is n-type semiconductor.

***Index Terms*— Ceramics, Solid-state reaction method, Seebeck coefficient, X-ray diffraction**

I. INTRODUCTION

ZnO has attracted much attention in the last few decades due to its wide variety of applications in optoelectronic devices. ZnO is a semiconductor with a wide bandgap of about 3·4 eV, which is tuned over a large energy range i.e. it is transparent in the visible region with high luminous transmittance. The stable structure of ZnO is wurtzite, in which four atoms of oxygen in tetrahedral coordination surround each atom of zinc. Combined with the high conductivity that can be achieved by doping, this leads to applications in surface acoustic wave devices and transparent conducting electrodes as reported by Raju and Rao [1]. It is strong piezoelectric and piezoelectric properties can change the characteristics of potential energy barriers at interfaces. The resulting piezoresistance is exploited in metal oxide varistors which can dissipate large amounts of power in short response times and are commonly found in electrical surge protectors as reported by Wang [2]. Semiconductor nanostructures are promising candidates for future electronic and photonic devices. Lee [3] suggested that nanostructures based on wide bandgap semiconductors such as GaN and ZnO are of particular interest because of their applications in short wavelength light emitting devices and field emission devices. ZnO is characterized by a large exciton binding energy (~ 60 meV) and the thermal energy at room temperature (~ 25 meV) and therefore, allows stable existence of excitons at room temperature as reported by Chia et al [4]. Various methods have been used for the deposition of ZnO like sol–gel by Kim et al [5], spray pyrolysis by Studenikin et al [6], metal organic chemical vapour deposition by Ohya et al [7] and so on. In this paper we report the microstructural and thermoelectric properties of ZnO doped with different concentrations of Sb_2O_3 synthesized by solid-state reaction route.

***Dr. N. Lalitha Kumari,** Department of Physics, Silver Jubilee Govt. College (Autonomous), Kurnool-518 002, Andhra Pradesh, India, Phone/ Mobile No.+91- 9490882626*

***Dr. B. Rajesh Kumar**, Department of Physics, GITAM University, Visakhapatnam – 530 045, Andhra Pradesh, India, Mobile No.+91-7396514545*

***Dr. C. Pullaiah**, Department of Physics, Silver Jubilee Govt. College (Autonomous), Kurnool-518 002, Andhra Pradesh, India, Mobile No.+91-9885352172*

II. EXPERIMENTAL DETAILS

In the present investigation the samples with composition of 2 % , 4%, 6%, 8% and 10% Sb_2O_3 doped in ZnO were synthesized by conventional solid-state reaction method. The appropriate ratio of the constituent oxides i.e. ZnO (as synthesized) and Sb_2O_3 (99.99% Aldrich Chemical USA) were thoroughly mixed and ground for several hours (2 to 4 hrs) with the help of mortar and pestle. This mixed powder was calcined at the temperature 1100 ^oC for 10 hours and then pressed into cylindrical pellets of 2 mm thickness and 10 mm in diameter using PVA (polyvinyl alcohol) as a binder at a pressure of 400 Kg Cm^2. Finally the Sb_2O_3 doped ZnO oxide pellets were sintered in a programmable SiC furnace at 1300 ^oC for 16 hrs. The X-ray diffraction patterns of the compounds were recorded at room temperature using Philips: PW 1830 with CuKα radiation (λ = 1.5418 Å) in a wide range of Bragg angles 2θ ($20^o < 2\theta < 70^o$) with scanning rate of $2^o\ min^{-1}$. The surface morphology of as synthesized materials has been carried out by a Carl Zeiss, EVO MA15 Instrument operated at 20 kV with a resolution of 3.5 nm. The compositional analysis of ZnO doped with Sb_2O_3 was carried out using energy-dispersive X-ray spectroscopy (EDS) in combination with SEM. The Seebeck coefficients were measured by a differential method from room temperature to 573K. The temperature gradient across the sample was measured using two pairs of copper constantan thermocouples. The sample was mounted on top of two well-separated copper blocks with silver paint. The temperature difference between two ends of the sample was kept at 10°C throughout the measured temperature range. A low value of constant voltage was applied across the sample and the current through the sample was measured as a function of temperature in the range 300–573 K.

III. RESULTS AND DISCUSSION

A. X-ray diffraction studies

To study the effect of doping on the crystallinity of the ZnO, the intensity of the (100), (002) and (101) diffraction peaks was monitored. The intensity of the diffraction peaks (100) and (101) decreased, and their full width at half-maximum (FWHM) increased for Sb_2O_3 doped samples (see Fig. 1). Such changes in crystallinity might be the result of changes in the atomic environment due to impurity doping on ZnO samples. From the

XRD data, we observed a change which indicates the lattice deformation of doped ZnO. In Fig. 1, there was a small shift (~0.12°) to a lower 2θ angle value of the XRD diffraction peaks for Sb_2O_3 doped ZnO as compared with those of pure ZnO. No change of the crystalline structure was detected, which suggests that the most Sb atoms were in the ZnO wurtzite lattice. Previously, a Sb dopant in ZnO was predicted to substitute a Zn atom and simultaneously connect two Zn vacancies to form a Sb_{Zn}-$2V_{Zn}$ complex, which is a shallow acceptor [8]. According to Xiu et al. [9] the complex Sb_{Zn}-$2V_{Zn}$ could be the explanation of strong p-type conductivity in Sb-doped ZnO films. This result is attributed to a small lattice mismatch between radii of Zn^{2+} (0.074 nm) and Sb^{3+} (0.076 nm), and it indicates that Sb ions systematically substituted Zn ions in the films without deteriorating its crystal structure. The crystallite size estimated from scherrer formula is found to be in the range of 32 to 56 nm.

The lattice constants a and c of wurtzite structure ZnO were calculated, according to Bragg's law [10]

$$2d\,Sin\theta = n\lambda \qquad (1)$$

where n is the order of diffraction (usually n = 1); λ is the X-ray wavelength; and d is the spacing between planes of given Miller indices h, k, and l. In the hexagonal structure of ZnO, the plane spacing is related to the lattice constant a and the Miller indices by the following relation

$$\frac{1}{d^2_{(hkl)}} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right)+\frac{l^2}{c^2} \qquad (2)$$

with the first-order approximation, n =1

$$Sin^2\theta = \frac{\lambda^2}{4a^2}\left[\frac{4}{3}(h^2+k^2+hk)+\left(\frac{a}{c}\right)^2 l^2\right] \qquad (3)$$

for the (1 0 0) orientation at 2θ , the lattice constant a was calculated by

$$a = \frac{\lambda}{\sqrt{3}Sin\theta} \qquad (4)$$

and for the (0 0 2) orientation at 2θ = , the lattice constant c was calculated by

$$c = \frac{\lambda}{Sin\theta} \qquad (5)$$

For Sb_2O_3 doped ZnO, an increase in the lattice parameters a and c would be expected when Zn^{2+} ions are replaced by Sb^{3+} ions due to mismatch in ionic radii. Another possibility for the increase in the lattice parameters could be the formation of electrically in active Sb_{Zn}-Sb_i pairs described by Wardle et al. [11]. Table I shows the structural parameters of ZnO doped with different concentrations of Sb_2O_3

Table : I Structural parameters of ZnO doped with different concentrations of Sb_2O_3

S. No	Compound name	Lattice parameters	
		a (nm)	c (nm)
1	ZnO + 2 wt% of Sb_2O_3	0.3261	0.5226
2	ZnO + 4 wt% of Sb_2O_3	0.3361	0.5272
3	ZnO + 6 wt% of Sb_2O_3	0.3414	0.5312
4	ZnO + 8 wt% of Sb_2O_3	0.3452	0.5386
5	ZnO + 10 wt% of Sb_2O_3	0.3486	0.5412

Fig. 2 shows the SEM images of ZnO doped with different concentrations of Sb_2O_3. From SEM images, the fine particles were observed when wt % of Sb became 10% with distinguished separate dark and light areas or, in other words, heterogeneous morphology, indicating excess Sb. Higher concentrations of Sb_2O_3 resulted in a fine grained microstructure, while at lower additions of the dopant, coarse-grained ceramics were obtained. The relative compositions obtained from EDS for 2%, 4%, 6%, 8% and 10% Sb_2O_3 doped with ZnO are in an atomic ratio of Zn/O/Sb are 59.81/38.42/1.77, 58.72/37.32/3.96,57.64/36.52/5.84,56.05/36.13/7.82 and 54.12/36.02 /9.86.

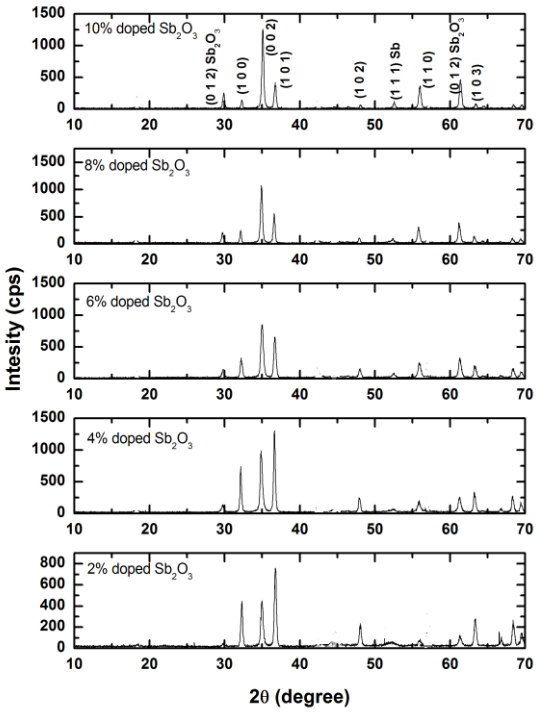

Fig. 1 XRD patterns of ZnO doped with different concentrations of Sb_2O_3

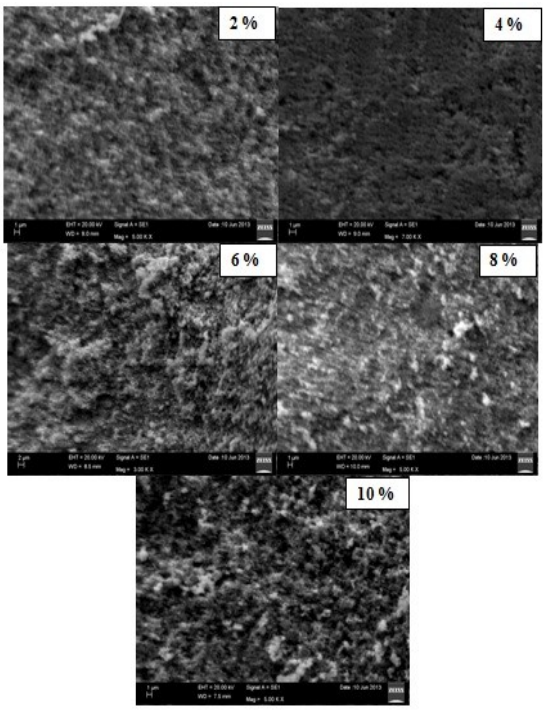

Fig. 2 SEM images of ZnO doped with different concentrations of Sb_2O_3

ISSN: 2278 – 7798

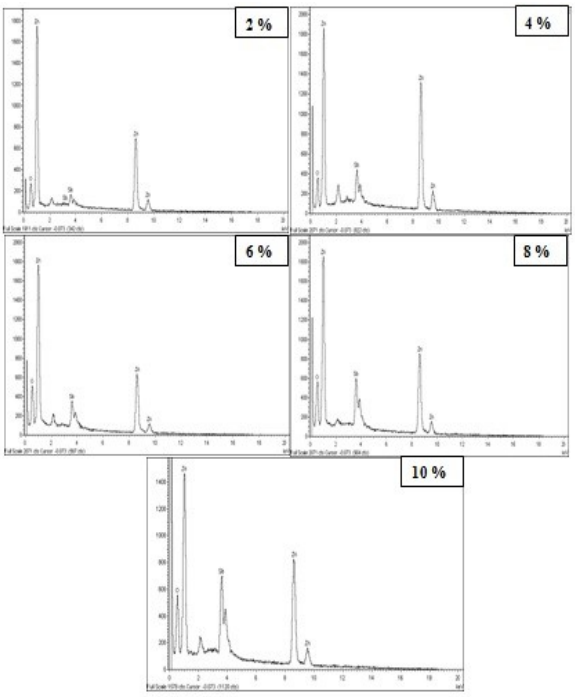

Fig. 3 EDS patterns of ZnO doped with different concentrations of Sb_2O_3

B. *Thermoelectric properties*

Fig. 4 shows the variation of Seebeck coefficient with temperature for ZnO doped with different concentrations of Sb_2O_3. The Seebeck coefficient (α) is evaluated from the relation

$$\alpha = \Delta V / \Delta T \qquad (6)$$

where ΔV is voltage measured across the sample, ΔT the temperature difference across the pellet. The sign of the thermoelectric power is found to be negative over entire temperature range studied; showing that majority charge carriers are electrons and hence compound is n-type semiconductor. These results qualitatively agreed with the increase of electrical conductivity. The similar phenomenon was also found in In-doped ZnO ceramics [12].

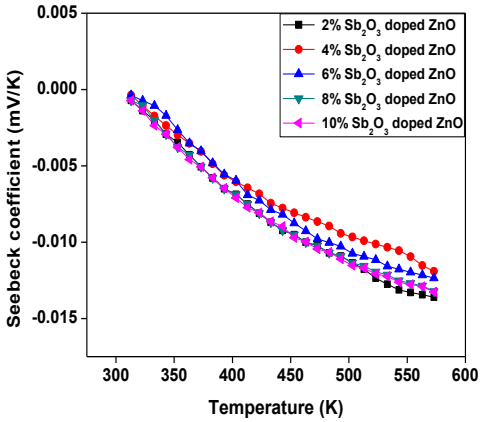

Fig. 4 Variation of thermoelectric power with temperature

IV. CONCLUSIONS

ZnO doped with different concentrations of Sb_2O_3 were prepared by solid state reaction method. From XRD measurements, the crystallite size estimated from Scherrer formula is found to be in the range of 26 to 36 nm. SEM images show heterogeneous morphology, indicating excess Sb with increase of Sb concentration. The sign of the seebeck coefficient is found to be negative over entire temperature range studied; showing that majority charge carriers are electrons and hence the compound is n-type semiconductor.

V. ACKNOWLEDGEMENTS

One of the authors Dr. N. Lalithakumari is thankful to UGC, New Delhi, India for financial support under the minor research project). (Letter No. F.MRP – 3807/2011 (MRP/UGC-SERO) (Link No: 3807).

REFERENCES

[1] A. R. Raju and C.N.R. Rao, "Gas-sensing characteristics of ZnO and copper-impregnated ZnO," *Sens. Actuators B* Vol. 3, pp. 305-310, April 1991.

[2] Z.L. Wang, "Zinc oxide nanostructures: growth, properties and applications," *J. Phys. Condens. Matter*, Vol. 16, pp. R829 -R858, June 2004.

[3] C.J. Lee, T. J. Lee , S.C. Lyu , Y. Zhang , H. Ruh and H. Lee, "Field emission from well-aligned zinc oxide nanowires grown at low temperature" *Appl. Phys. Lett.* Vol. 81, pp. 3648-3650, October 2002.

[4] C.H. Chia, T. Makino , K. Tamura , Y. Segawa , M. Kawasaki, A. Ohtomo and H. Koinuma, Confinement-enhanced biexciton binding energy in ZnO/ZnMgO multiple quantum wells, *Appl. Phys. Lett.* Vol. 82, pp. 1848-1850, March 2003.

[5] Y.M. Kim, M. Yoon , I. W. Park , Y.J. Park and J.H. Lyou, "Synthesis and magnetic properties of $Zn_{1-x}Mn_xO$ films prepared by the sol–gel method", *Solid state Comm*. Vol. 129, pp. 175-176, January 2004.

[6] S.A. Studenikin , N. Golego and M. Cocivera, "Fabrication of green and orange photoluminescent, undoped ZnO films using spray pyrolysis," *J. Appl. Phys.* Vol. 84, pp. 2287-2294, May 1998

[7] Y. Ohya, T. Niwa, T. Ban and Y. Takahashi, "Thin Film Transistor of ZnO Fabricated by Chemical Solution Deposition," *Jpn. J. Appl. Phys.* Vol. 40 pp. 297-298, January 2001

[8] S. Limpijumnong, S.B. Zhang, S.H. Wei, C. H. Park, "Doping by Large-Size-Mismatched Impurities: The Microscopic Origin of Arsenic- or Antimony-Doped p -Type Zinc Oxide ," *Phys. Rev. Lett.* Vol. 92, pp. 155504, April 2004

[9] F.X. Xiu, Z. Yang, L. J. Mandalapu, D. T. Zhao, J.L. Liu, "Photoluminescence study of Sb-doped -type ZnO films by molecular-beam epitaxy," *Appl. Phys. Lett.* Vol. 87, pp.252102 , December 2005.

[10] B.D. Cullity,S.R. Stock, Elements of X-Ray Diffraction, 2nd ed.; Prentice Hall: NJ, 2001.

[11] M.G. Wardle, J.P. Goss, P.R. Briddon, "Theory of Li in ZnO: A limitation for Li-based p -type doping," *Phys. Rev. B* Vol. 71, 155205, April 2005

[12] H. Ohta, W.S. Seo, K. Koumoto, "Thermoelectric Properties of Homologous Compounds in the ZnO–In_2O_3System," *J. Am. Ceram. Soc.* Vol. 79 pp. 2193-2196, September 1996.

Dr. N. Lalitha Kumari is a Lecturer in Physics, Silver Jubilee Govt. College (Autonomous), Kurnool,A.P .She obtained her M.Phil degree in Physics with Specialization Spectroscopy from S.V.University, Tirupathi, A.P. She obtained her Ph.D degree in Physics with specialization Spectroscopy from S.K. University, Anantapur, A.P. She has published 5 research papers in reputed International journals and attended many national and International conferences.

Dr. B. Rajesh Kumar is an Assistant Professor in Physics, GIT, GITAM University, Visakhapatnam. He obtained his Ph.D degree in Physics with specialization Materials Science-Thin Film Physics from Sri Venkateswara University, Tirupati, A.P. He has published several research papers in reputed international journals and attended many national and international conferences. He is a life member of Materials Research Society of India (MRSI), Indian Vacuum Society (IVS), Electron Microscope Society of India (EMSI).

Dr. C. Pullaiah is Vice-Principal and Lecturer in Physics in Silver Jubilee Govt. College (Autonomous), Kurnool, A.P. He obtained his Ph.D degree in Physics with specialization Polymers from Sri Krishnadevaraya University, Anantapur, A.P. He has published several research papers in reputed international journals and attended many national and international conferences.

ISSN: 2278 – 7798