



Synthesis, structural and optical properties of Cr doped ZnO nanoparticles†

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Nanosized Cr-doped ZnO particles were synthesized by facile sol-gel method. The structural and optical properties of the particles have been investigated by XRD and FTIR spectroscopy at room temperature for 0, 1 and 5 % concentration of Cr doping. X-ray diffraction analysis reveals that the Cr-doped ZnO crystallizes in a single phase polycrystalline nature with wurtzite lattice. The average crystallite size decreases with increase in Cr concentration (*i.e.* 33.5 nm for 0 % & 29.7 nm for 1 % and 24.7 for 5 %). FTIR results also indicate the correlation between structural and optical properties of the nanoparticles.

Key Words: Nanoparticles, Zinc oxide nanomaterials.

INTRODUCTION

In recent years, great interest in spintronic devices has stimulated extensive investigations on diluted magnetic semiconductors (DMS), which exploit the spin in magnetic materials along with the charge of electrons in semiconductors. The main challenge for practical applications of the diluted magnetic semiconductors materials is the attainment of curie temperatures around or preferably above room temperature (RT) to be compatible with junction temperatures. One of the promising materials is the wide-band gap (3.36 eV) and wurtzite-phase semiconductor ZnO, which is formed by tetrahedral (sp^3) bonding. Following the prediction of Dietl *et al.*¹ many systems of ZnO : TM (TM = Mn, Co, Ni, V, Cr, *etc.*) have been synthesized by different methods and extensively studied, but controversial results are reported for both thin films and bulk samples²⁻⁷. One of the fundamental and key questions is whether the fabricated material is indeed a solid solution of $Zn_{1-x}TM_xO$ or whether it remains as ZnO with embedded transition metal clusters, precipitates, or second phases that are responsible for the observed magnetic properties. Among dopant elements, Cr dopant is particularly interesting and it has attracted lots of attention^{8,9}. One of the reasons is that radius parameter of Cr^{3+} is closer to that of Zn^{2+} , which means that Cr^{3+} can easily penetrate into the ZnO crystal lattice or substitute for the position of Zn^{2+} in crystal ZnO¹⁰. In particular, unlike many other metals, Cr itself is antiferromagnetic

and it will not induce an extrinsic ferromagnetism even if Cr clustering occurs.

In this present work, the undoped and the Cr-doped ZnO nanoparticles were synthesized by sol-gel method and characterized by XRD and FTIR spectroscopy.

EXPERIMENTAL

All the chemical reagents in present experiment were of analytical grade purity. The initial materials included zinc acetate [$(CH_3COO)_2Zn \cdot 2H_2O$], chromium nitrate [$Cr(NO_3)_3 \cdot 9H_2O$] and ethanol. Zinc acetate and the appropriate amounts of chromium acetate ($x = 0, 0.01$ and 0.05) were dissolved into the ethanol to form the sol with stirring. Then, the mixture was polymerized to form the gel at 80 °C. When the swelled gel was dried at 150 °C, the amorphous composite precursor was obtained. The precursor was further ground into powder in an agate mortar. Finally, the powder of the precursor was annealed at 400 °C for 5 h in the furnace in the air atmosphere.

The structure characterization of Cr-doped ZnO nanoparticles was performed by XRD on copper rotating-anode X-ray diffractometer with CuK_{α} (1.54 Å) radiation (30 kV, 15 mA). The band gap energy calculated by using Perkin Elmer Spectrophotometer absorption data in the range of 270-800 nm. FTIR spectroscopy (Model PerkinElmer) was studied in the frequency range of 4000-400 cm^{-1} to characterize functional groups of the Cr doped ZnO nanoparticles.

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RESULTS AND DISCUSSION

XRD analysis: Fig. 1 shows the XRD patterns of the undoped ZnO and the Cr-doped ZnO samples. The diffraction peaks were indexed to the wurtzite hexagonal ZnO (space group P63mc) without any other impurity phases.

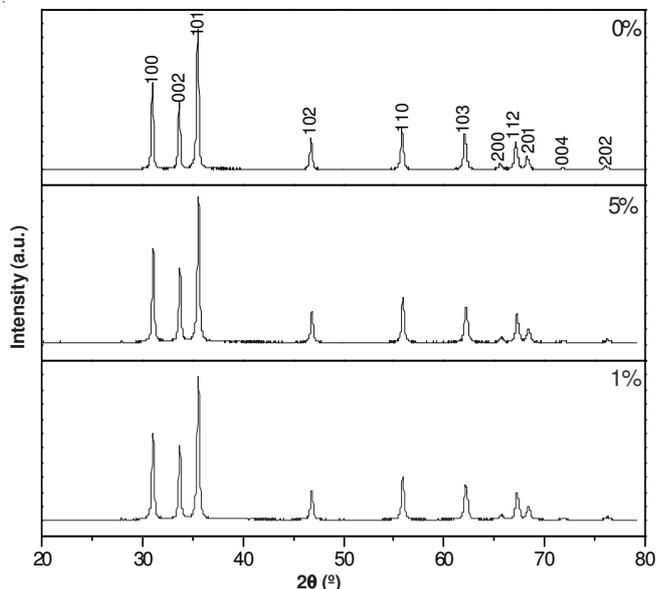


Fig. 1. XRD spectra of 0, 1 and 5 % Cr doped ZnO nanoparticles

The crystallite size was calculated using Scherrer's formula¹¹:

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

where, λ is the wavelength of X-ray radiation, β is the full width at half maximum (FWHM) of the peaks at the diffracting angle θ . The calculated crystallite size of each sample is depicted in Table-1. It can be observed from Table-1 that the crystallite size of ZnO decreased from 33.5 to 24.7 nm when Cr content increased from 0 to 5 %. This may be due to difference in ionic radii.

TABLE-1

VARIATION OF PARTICLE SIZE, LATTICE PARAMETERS AND CELL VOLUME WITH DOPING

Dopant concentration (%)	Crystal size (nm)	Lattice parameter a (Å)	Lattice parameter c (Å)	Cell volume (Å ³)
0	33.5	3.295	5.239	49.259
1	29.7	3.292	5.237	49.151
5	24.7	3.289	5.233	49.024

Band gap calculation: The optical band gap of the $Zn_{1-x}Cr_xO$ ($x = 0.0, 0.01$ and 0.05) samples were calculated using UV-visible spectrophotometer absorption data. The Tauc plot¹² for all the samples and the band gap is calculated by extrapolating the best linear fit as shown in Figs 2-4. For undoped ZnO the band gap comes out to be 3.27 eV and is in accordance with the reported value¹². For Cr-doped ZnO, i.e. $Zn_{1-x}Cr_xO$, where $x = 0.00, 0.01$ and 0.05 the optical band gap was obtained as 3.34, 3.40 and 3.43 eV, respectively.

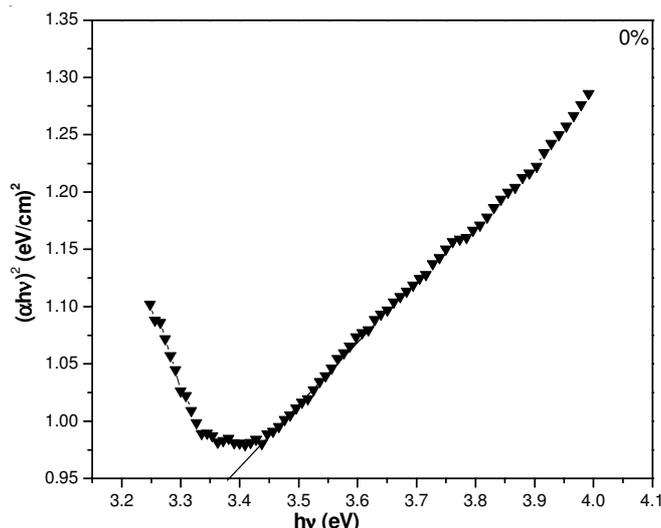


Fig. 2. Plot of $(\alpha hv)^2$ vs $h\nu$ for the 0 % Cr doping

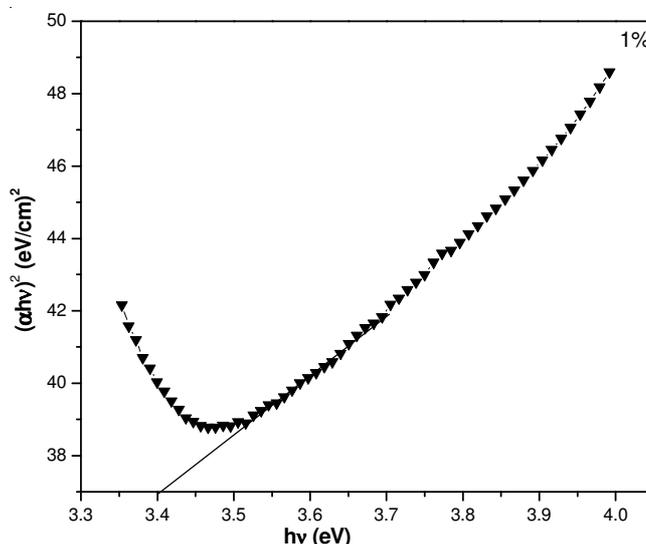


Fig. 3. Plot of $(\alpha hv)^2$ vs $h\nu$ for the 1 % Cr doping

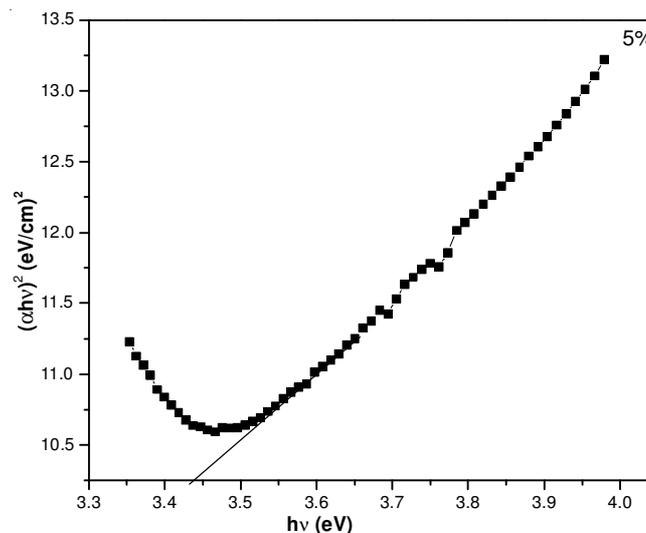


Fig. 4. Plot of $(\alpha hv)^2$ vs $h\nu$ for the 5 % Cr doping

FTIR analysis: The formation of the wurtzite ZnO structure in undoped and doped nanocrystalline powders is further confirmed by FTIR recorded in KBr matrix in 4000-400 cm^{-1}

in solid phase spectra (Fig. 5). In the infrared region ZnO usually shows distinct absorption band around wave number of 464 cm^{-1} . The position and number of this band not only depend on crystal structure and chemical composition but also on particle morphology^{13,14}. Studies concerned with this morphology dependency have shown that in case of spherical ZnO particles, calculated as well as measured spectra show one distinct absorption maximum at around 464 cm^{-1} ¹⁵. Reference spectra of ZnO powders often show two absorption maxima at around 512 and 406 cm^{-1} ¹⁶. The broad absorption peak centered 3418 cm^{-1} correspond to -OH group of H_2O , indicating of existence of water absorbed on the surface of nanocrystals, while the peaks at 449 cm^{-1} are attributed to the stretching mode which is typical for the ZnO wurtzite structure.

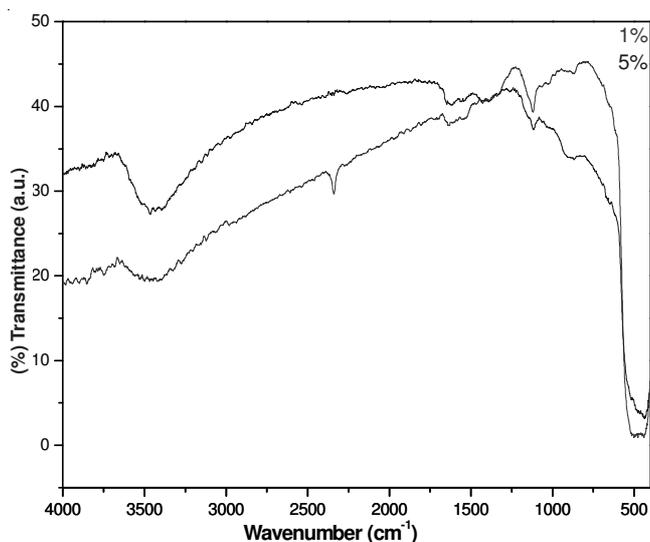


Fig. 5. FTIR spectra of 0, 1 and 5 % Cr doped ZnO nanoparticles

Conclusion

In summary, high-quality single crystals of pure and Cr-doped ZnO nanoparticles have been synthesized by a facile, low-cost, Sol-gel approach. It is found that the structural and

optical properties are sensitively dependent on the incorporation of Cr ions in the Zn^{2+} lattice site. Band gap to the higher-energy side relative to that of undoped ZnO. An FTIR spectrum also shows the stretching frequency of ZnO nanoparticles.

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REFERENCES

1. T. Dietl, H. Ohno, F. Matsukura, J. Cibert and D. Ferrand, *Science*, **287**, 1019 (2000).
2. J. Alaria, P. Turek, M. Bernard, M. Bouloudine, A. Berbadj, N. Brihi, G. Schmerber, S. Colis and A. Dinia, *Chem. Phys. Lett.*, **415**, 337 (2005).
3. T. Zhu, W.S. Zhan, W.G. Wang and J.Q. Xiao, *Appl. Phys. Lett.*, **89**, 022508 (2006).
4. S. Deka and P.A. Joy, *Chem. Mater.*, **17**, 6507 (2005).
5. N.H. Hong, J. Sakai and A. Hassini, *J. Appl. Phys.*, **97**, 10D312 (2005).
6. B.K. Roberts, A.B. Pakhomov, V.S. Shutthanandan and K.M. Krishnan, *J. Appl. Phys.*, **97**, 10D310 (2005).
7. C. Liu, F. Yun and H. Morkoç, *J. Mater. Sci.: Mater. Electron.*, **16**, 555 (2005).
8. L.J. Zhuge, X.M. Wu, Z.F. Wu, X.M. Chen and Y.D. Meng, *Scripta Mater.*, **60**, 214 (2009).
9. L. Schneider, S.V. Zaitsev, W. Jin, A. Kompch, M. Winterer, M. Acet and G. Bacher, *Nanotechnology*, **20**, 135604 (2009).
10. B.Q. Wang, J. Iqbal, X.D. Shan, G.W. Huang, H.G. Fu, R.H. Yu and D.P. Yu, *Mater. Chem. Phys.*, **113**, 103 (2009).
11. A.L. Patterson, *Phys. Rev. Online Archive (Prola)*, **56**, 978 (1939).
12. F.A. Sigoli, M.R. Davolos and M.J. Jafelicci, *J. Alloys Comp.*, **292**, 262 (1997).
13. S. Hayashi, N. Nakamori and H. Kanamori, *J. Phys. Soc. Jap.*, **46**, 176 (1979).
14. M. Andrés Verges, A. Mifsud and C.J. Serna, *J. Chem. Soc. Faraday Trans.*, **86**, 959 (1990).
15. The Infrared Spectra Handbook of Inorganic Compounds. Sadtler Research Laboratories, ed., Heyden & Son Ltd., London (1984).
16. H. Kleinwechter, C. Janzen, J. Knipping, H. Wiggers and P. Roth, *J. Mater. Sci.*, **7**, 4349 (2002).