

XRD, SEM and Raman Spectral Studies on ZnO Nanoparticles Prepared by a Simple Solvothermal Process

G.JanitaChristobel¹ and C.K.Mahadevan²Postdoctoral Fellow (UGC), Physics Research Centre, Dept. of Physics, S. T. Hindu College, Nagercoil, Tamil Nadu, India¹Professor, Dept. of Physics, Center for Scientific and Applied Research, PSN College of Engineering and Technology (Autonomous), Melathediyoor, Tirunelveli, Tamil Nadu, India²

ABSTRACT: ZnO nanoparticles have been successfully prepared by microwave irradiation using a domestic microwave oven and $Zn(CH_3COO)_2 \cdot 2H_2O$ only as the starting material (inorganic precursor). X-ray diffraction measurement indicated the formation of ZnO nanocrystals with hexagonal wurtzite structure. The SEM image recorded indicates the nearly uniform and spherical morphology. The Raman spectrum recorded clearly indicates that there is a strong quenching of the phonons due to confinement for the small particles, and the only clearly observed vibration is one at 436 cm^{-1} .

KEYWORDS: ZnO nanoparticles, XRD, SEM, Raman spectroscopy

I INTRODUCTION

ZnO is a II-VI semiconductor compound with a large, direct band gap of 3.4 eV. Its large exciton binding energy of 60 meV makes it very attractive for use in optoelectronic devices such as light-emitting diodes or laser diodes emitting in the blue and ultraviolet spectral range. In particular, nanosized ZnO finds wide applications in solar cells, capacitors, varistors, gas sensors, transparent UV resistance coating, photoprinting, electrophotography, electrochemical and electro mechanical nanodevices, sun screen lotion-cream-cosmetic and medicated creams, etc[1-4]. Some of the future applications include catalysts for organic reactions [5] and delivering drugs to infected areas of body[6].

ZnO nanoparticles have been prepared earlier by using several simple and involved methods [7]. The simplest earlier method used both zinc acetate dehydrate and urea as the precursors as the suppliers of Zn^{2+} and O^{2-} ions respectively. It is reported [8] recently that Co_3O_4 could be prepared successfully from cobalt acetate tetrahydrate only (without using any precursor to supply O^{2-} ion). The acetate itself was found to supply the required oxygen ions also. We have attempted, in the present study, to prepare ZnO nanoparticles in a similar way without using any additional precursor to supply the required oxygen ions. X-ray powder diffraction (XRD), scanning electron microscopic (SEM) and Raman spectral analyses were done to assess the quality of the sample prepared. The results obtained are reported herein.

II MATERIAL AND METHOD

Even though there are many methods adopted in the synthesis of ZnO, simple solvothermal method is followed here in the synthesis of ZnO. Zinc acetate dihydrate and urea of AR grade are bought from CDH and used without further purification. De-ionised water and acetone from NICE are used for washing. The whole of the experiment is done in a domestic microwave oven (solo) operating at a frequency 2.45 GHz and power 800 W. Zinc acetate and urea are mixed in the ratio 1:3 in 100 ml of ethylene glycol. The mixture is stirred well using magnetic stirrer for about 15 minutes. Then the mixture is kept in a domestic microwave oven for microwave irradiation until the whole of ethylene

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 9, September 2015

glycol is evaporated and a white precipitate is formed. Then the precipitate is washed with de-ionised water for several time and then with acetone. The sample then collected is dried in atmosphere and used for analyses.

III. EXPERIMENTAL

ZnO nanoparticles were prepared by adopting Mahadevan's method [7,8] from zinc acetate dihydrate(used as the precursor) dissolved in 100 ml of ethylene glycol and irradiated with microwave for 30 minutes using a domestic microwave oven (Frequency 2.45 GHz and power 800 W). The resulting white precipitate was first washed with de-ionised water several times and then with acetone and dried in atmosphere. X-ray powder diffraction, scanning electron microscopic and Raman spectral analyses have been carried out (using the required sophisticated instruments) on the as-prepared sample.

IV. RESULTS AND DISCUSSION

The XRD pattern observed are shown in Figure 1(a). All the diffraction peaks can be indexed to zinc oxide with hexagonal würtzite structure [JCPDS file number 36-1451]. The lattice constants could be estimated as $a=3.2478$ and $c=5.2035$ Å. The Scherrer formula [9] applied to the peaks gives the average crystallite size of the prepared ZnO nanoparticles to be less than 39 nm. The SEM image indicates nearly homogeneous and spherical morphology.

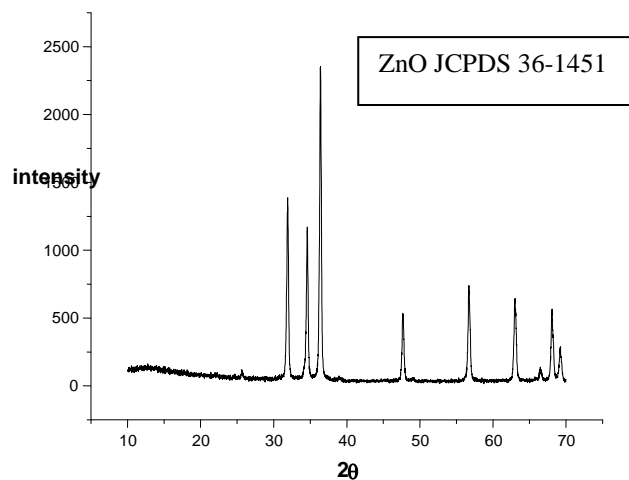


Fig.1: (a) The observed X-ray powder diffraction pattern peaks with (1010), (0002), (1011), (1012), (1120), (1013), (2020)

The SEM image of the synthesised ZnO sample is shown in the figure 1 (b). The image shows that the ZnO nanoparticles formed is spherical in shape with uniform morphology.

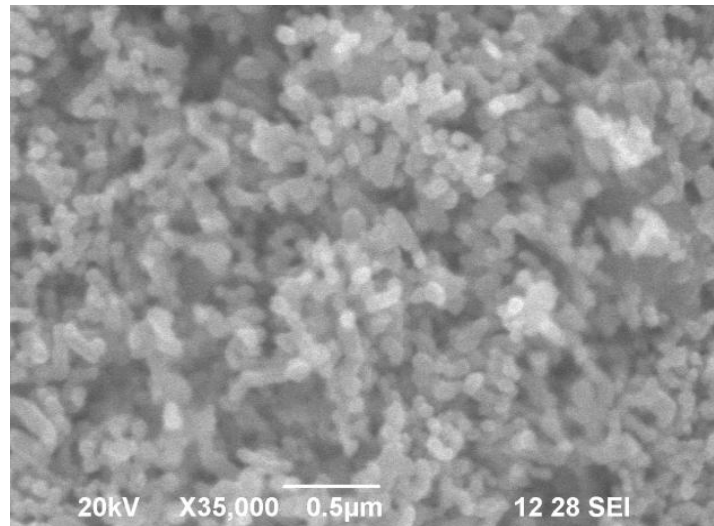


Fig: 1 (b) SEM image of ZnO nanoparticles indicates a spherical and uniform morphology

The observed Raman Spectra of the ZnO nanoparticles is shown in the Figure:2. ZnO has a wurtzite structure which belongs to the space group $C6v4$ with two formula units per primitive cell where all atoms occupy $C3v$. Zone center optical phonons predicted by group theory are $A_1+2E_2+E_1$. Here, A_1 and E_1 modes are polar and split into the transverse optical (TO) and longitudinal optical (LO) phonons. In addition, E_2 mode consists of two modes: $E_2(\text{high})$ is associated with the vibration of oxygen atoms and $E_2(\text{low})$ is associated with the Zn sublattice[10].

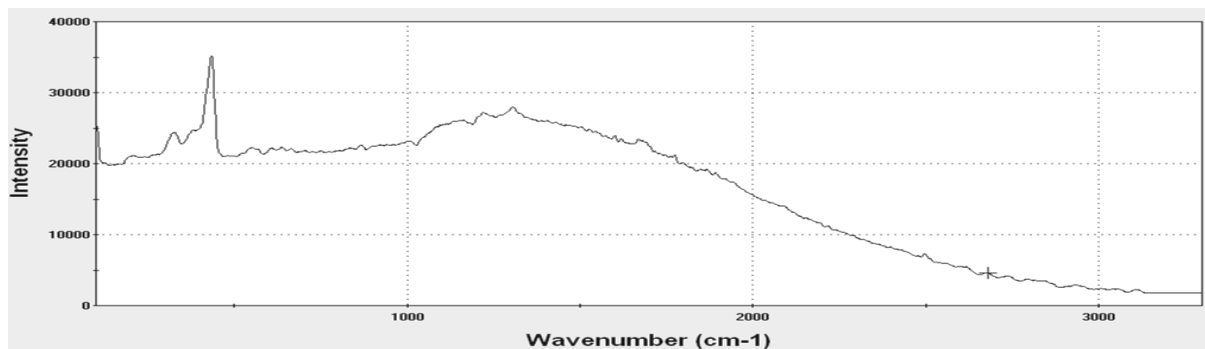


Fig. 2: The observed Raman spectrum of ZnO nanoparticles.

The observed Raman modes with high intensity include the $E_2(\text{high})$ - $E_2(\text{low})$ at about 330 cm^{-1} , the $A_1(\text{TO})$ at about 378 cm^{-1} , the $E_1(\text{TO})$ at about 410 cm^{-1} , and the $E_2(\text{high})$ at about 436 cm^{-1}

The observed Raman spectrum is shown in Figure 2. The observed Raman modes with high intensity include the $E_2(\text{high})$ - $E_2(\text{low})$ at about 330 cm^{-1} , the $A_1(\text{TO})$ at about 378 cm^{-1} , the $E_1(\text{TO})$ at about 410 cm^{-1} , and the $E_2(\text{high})$ at about 436 cm^{-1} . A mode with small intensity occurs in the LO phonon region at about 581 cm^{-1} . This frequency is between the above observed bulk values of the $A_1(\text{LO})$ mode at about 577 cm^{-1} and the $E_1(\text{LO})$ mode at about 588 cm^{-1} . The feature can be attributed to a quasi-LO mode, which is a mixed symmetry mode due to phonons propagating between the a-axis and the c-axis [11, 12]. The vibrational frequency of the quasi-LO mode corresponds to a random orientation of the nanoparticles [11]. The intensity of the quasi-LO mode is intensified by resonance effects as the

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 9, September 2015

spectrum was recorded with the blue 457.9 nm line of the Ar ion laser. The positions of the $E_2(\text{high})$ mode and the $E_2(\text{high})$ - $E_2(\text{low})$ mode agree well with the values of bulk ZnO. No peak shifting due to size effects is observed. In addition to the ZnO phonon modes, molecular vibrations of the organic ligands occur between about 750 cm^{-1} and 3100 cm^{-1} . Important organic vibrations are C-C stretching and C-H bending modes with frequencies between about 1400 cm^{-1} and 1500 cm^{-1} , and C-H stretching modes between about 2800 cm^{-1} and 3100 cm^{-1} . By comparison of the observed molecular vibrations with the vibrations of the pure ligand molecules, not all vibrations can be attributed to the acetate ligand, but a mixture of different molecules is required to account for the observed Raman features.

The presence of organic impurities observed through Raman spectral analysis is possible as the sample considered is the as-prepared one without any annealing done. Organic impurities present can be removed by annealing the as-prepared sample. Previous reports ([7] for example) indicate the requirement of annealing the as-prepared sample to attain high phase purity. Thus, the Raman spectral analysis indicates the requirement of annealing to be done at $100\text{ }^\circ\text{C}$ (at least) for about 1 hr to obtain highly phase pure sample. Finally, the present study indicates the possibility of preparing high quality nanoparticles of transition metal oxides from a single precursor using the simple method adopted in the present study.

V. CONCLUSION

We have synthesized ZnO nanoparticles by the rapid and inexpensive microwave irradiation method using a domestic microwave oven and easily available and low-cost single precursor. Structural, morphological and Raman spectral characterizations show that the synthesised nanoparticles are crystalline and of reasonably good quality ZnO phase. Results indicate the requirement of annealing at $100\text{ }^\circ\text{C}$ (at least) for about 1 hr to obtain highly phase pure sample.

ACKNOWLEDGEMENT

One of the authors, G. JanitaChristobel acknowledges gratefully for the Grant provided by UGC under the scheme Post Doctoral Fellowship for Women.

The Department of Nanotechnology of the Noorul Islam Centre For Higher Education, Kumarakoil is acknowledged for providing the Raman Spectrometer facility.

REFERENCES

1. H. T. Wang, B. S. Kang, F. Ren, L. C. Tien, P. W. Sadik, D. P. Norton, S.J. Pearton, and J. Lin, *Appl. Phys. Lett.* **86**, 243503 (2005).
2. J.-J. Wu, G.-R. Chen, H.-H. Yang, C.-H. Ku, and J.-Y. Lai, *Appl. Phys. Lett.* **90**, 213109 (2007).
3. S. F. Yu, C. Yuen, S. P. Lau, W. I. Park, and G.-C. Yi, *Appl. Phys. Lett.* **84**, 3241 (2004).
4. N. Serpone, D. Dondi, and A. Albini, *Inorg. Chim. Acta* **360**, 794 (2007).
5. W. J. Huang, G. C. Fang, and C. C. Wang, *Colloids Surf. A* **260**, 45 (2005).
6. C. Dai, B. Wang, and H. Zhao, *Colloids Surf. B* **41**, 117 (2005).
7. G. JanitaChristobel, M. Vimalan and C.K. Mahadevan, *Int. J. Mater. Sci.* **4**, 613 (2009).
8. S. Goma, and C.K. Mahadevan, *Proc. Natl. Sem. Rec. Adv. Mater. Res.* Scott Christian College, Nagercoil, pp.74 (2011).
9. B. D. Cullity, *The Elements of X-Ray Diffraction*, Addison-Wesley, pp. 120 (1978).
10. N. Ashkenov, B. N. Mbenkum, C. Bundesmann, V. Riede, M. Lorenz, D. Spemann, E. M. Kaidashev, A. Kasic, M. Schubert, M. Grundmann, G. Wagner, H. Neumann, V. Darakchieva, H. Arwin, and B. Monemar, *J. Appl. Phys.* **93**, 126 (2003).
11. L. Bergman, X.-B. Chen, J. Huso, J. L. Morrison, and H. Hoock, *J. Appl. Phys.* **98**, 093507 (2005).
12. R. Loudon, *Adv. in Phys.* **13**, 423 (1964).