STRUCTURAL AND OPTICAL PROPERTIES OF ZnS NANOPARTICLES SYNTHESIZED BY SOLID STATE REACTION METHOD

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The ZnS semiconducting nano particles were synthesized by solid state reaction method using Zinc acetate dehydrate and sodium sulfide as precursors at room temperature. The as-prepared ZnS nanoparticles have average particle size of 11 nm. Strain and the dislocation density were estimated by Stokes-Wilson formula. The structural features, chemical composition and optical properties of the nanoparticles were investigated by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier Transform Infra Red Spectroscopy (FTIR), Ultra Violet spectroscopy (UV) and Photoluminescence (PL) studies. The optical properties of the ZnS nanoparticles are also discussed.

1. Introduction

The formation of nanostructures with controlled size and morphologies has been the focus of intensive research in the past decade [1, 2]. In recent years, much effort has been devoted to the research of chalgogenide nanostructured materials. Many methods such as laser ablation [3], thermal evaporation [4], chemical vapor deposition [5], metal-organic chemical vapor deposition [6], molecular beam epitaxy [7] and template-based methods [8] have been developed to the synthesis of nanostructured materials with various shapes such as rod-like, flower-like, ribben-like and belt-like [9,10]. As one of the promising optoelectronic semiconductors, Zinc Sulfide (ZnS) has a wide energy gap of 3.7 eV at room temperature and is being used frequently in light emitting diodes, piezo-elctric devices and photodetectors [11,12]. It has become one of the benchmark materials to test several theoretical models in condensed matter physics [13,14]. On the other hand, infinite possibilities exist for innovative tuning of the materials according to technological need. This is reflected in the increasing interests and publications on ZnS related research [15]. In this paper, the solid state reaction method has been employed for the preparation of ZnS nanoparticles and the structural and optical results are discussed.

2. Experimental details

For synthesizing ZnS nanoparticles, zinc acetate dehydrate and sodium sulfide pellets were used without further purification. The precursors were mixed (molar ratio 1:1) and ground together in an agate mortar for 1 hour at room temperature. The reaction started immediately during the mixing process accompanied by the release of heat. The mixture was washed with distilled water in an centrifugator at 2000 rpm for 15 minutes and the product was dried for 2 hours in a muffle furnace to obtain ZnS nanopowders.

The as synthesized product was characterized using X-ray Diffraction (XRD) by means of an atomized diffractometer with Cu-Kα radiation to identify the crystalline phase of the material.

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The structural and optical properties of the ZnS nanoparticles were also studied by SEM, FTIR, UV and Photoluminescence studies.

3. Results and discussion

The XRD pattern of nanostructured ZnS is shown in Fig. 1. The figure shows three diffraction peaks at 2θ values of 28.68^0, 48.06^0 and 57.44^0 corresponding to d values of 3.112, 1.892 and 1.602 A ˚ respectively. The peaks are identified to originate from (111), (220) and (311) planes of the cubic (zinc blend) phase of ZnS [16]. None of the three most intense peaks of hexagonal phase corresponding to (100), (101) and (002) reflections is found in the diffraction pattern of the prepared ZnS sample excluding any possibility for the presence of wurtzite phase of ZnS in the sample. The broadening of the diffraction peaks in Fig. 1 indicates the nanocrystalline nature of the sample.
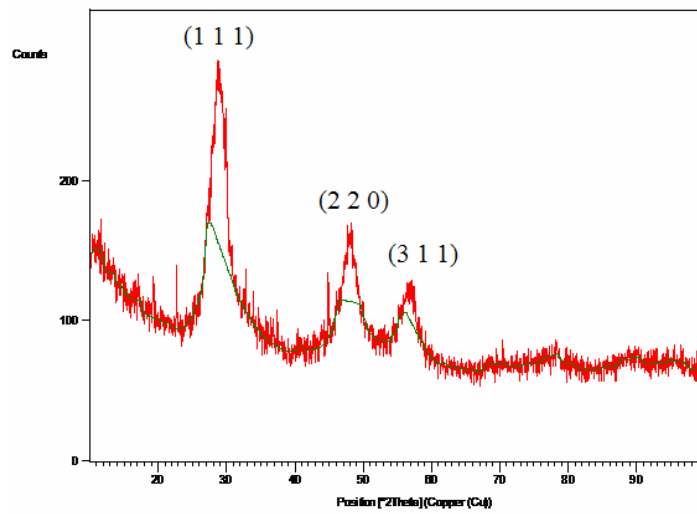

Fig. 1 XRD pattern of ZnS nanoparticles

The average crystallite size is calculated from the full width at half maximum (FWHM) of the diffraction peaks using the Debye–Scherrer formula [17] $D = k\lambda/\beta\cos\theta$ where D is the mean grain size, k is a geometric factor (=0.89), λ is the X-ray wavelength, β is the FWHM of diffraction peak and θ is the diffraction angle. The average grain size of the ZnS particles calculated from the most intense peaks is approximately 11 nm. The size of nanocrystals of our sample is thus in the strong charge confinement regime. The FWHM of the XRD peaks may also contain contributions from lattice strain. The average strain of the ZnS nanoparticles was calculated by Stokes – Wilson equation

$$\varepsilon_{str} = \beta / 4 \tan\theta \tag{2}$$

Lattice parameters 'a' and 'c' were calculated by the relation

$$1/d^2 = 1/a^2 (h^2 + k^2 + l^2) \tag{3}$$

The dislocation density was also calculated from the relation [18]

$$\delta = 15\varepsilon / aD \tag{4}$$

The average lattice strain and the dislocation density were estimated to be 2.65×10^{-3} and 4.35×10^{-15} lines/m.

The surface morphology of the prepared sample can be studied by SEM and the picture is shown in Fig. 2. The grain sizes of the samples estimated from the SEM picture is much larger than that obtained from XRD data. This means that, the SEM picture indicates the size of polycrystalline particles.
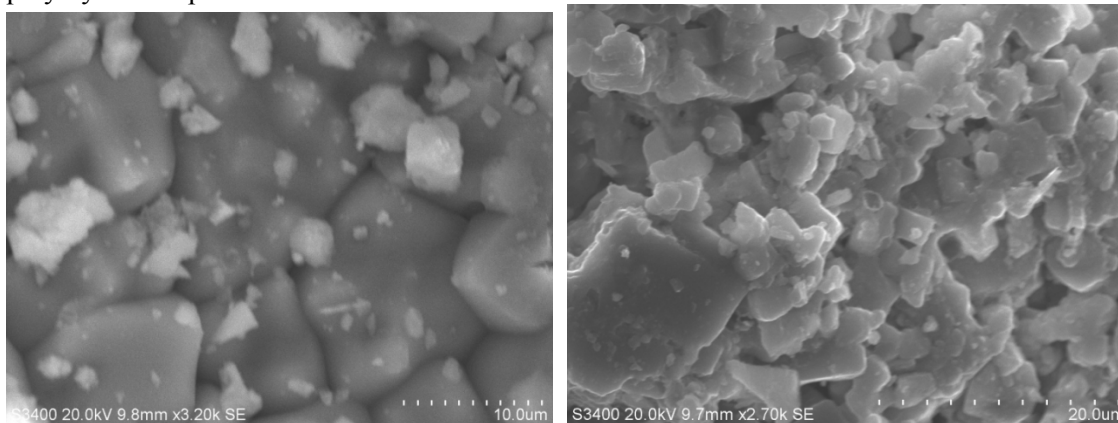

Fig. 2. SEM images of ZnS nanoparticles

The microscopic details of the process that induces the various vibration modes were studied using the FT-IR spectroscopy. The FT-IR spectrum of ZnS is shown in Fig.3. The spectrum of ZnS nanoparticles in the range 300-4000 cm^{-1} was showing IR absorption due to the various vibrations involved. The major peaks are at $526cm^{-1}$, $624.4cm^{-1}$, $1001.8cm^{-1}$, $1126.8cm^{-1}$, $1412cm^{-1}$, $1639.6cm^{-1}$ and $3342.4cm^{-1}$.

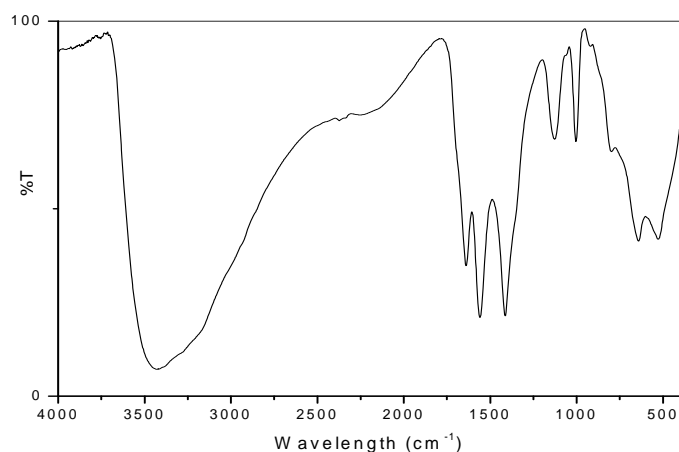*Fig. 3 FTIR spectrum of ZnS nanoparticles*

Strong interaction of water with the surface of ZnS could be the reason for the peaks at $\approx$ 3426.4 cm^{-1} and 1639.6 cm^{-1} due to O-H stretching and O-H bending modes respectively [18,19]. Peaks at 526.3 cm^{-1} and 642.4 cm^{-1} could be due to O-H stretch mode.

The UV spectrum (Perkin Elmer) is shown in the Fig. 4. The ZnS nanoparticles have an optical absorption edge at around 400nm. The calculated band gap is 3.62eV.
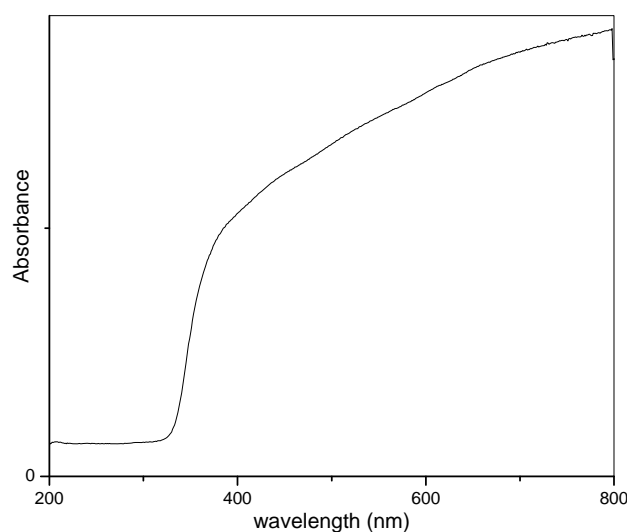
Fig. 4. UV Spectra of ZnS.

By UV excitation at the band gap, photoluminescence spectra of ZnS nanoparticles can be obtained as shown in Fig. 5. From the spectra blue emission band centered at 440 nm is observed, which arises from the recombination of vacancies. As the energies corresponding to these peaks are less than the band gap of ZnS, the probability of even the higher energy band to be due to band edge emission can be ruled out and band may be ascribed to transitions between discrete energy levels in the forbidden gap [19]. Tang et al.[20] in their study on nanoparticles of ZnS reported that both zinc and sulfur vacancies could create trap levels in the band gap. Lu et al. [21] in the case of cubic ZnS nanoparticles has reported a peak at 422 nm which they attributed to sulfur vacancies.
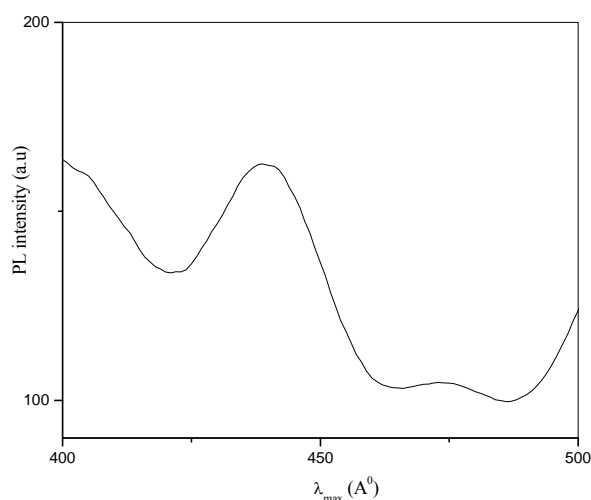

Fig. 5 Photoluminescence Spectra of ZnS.

Borse et al. [22] also attributed an emission peak at 425 nm observed in the case of nanoparticles of cubic ZnS to sulfur vacancies. Based on these reports, the peak at 438 nm observed in the present study can be assigned to sulfur vacancies, i.e, to the recombination of electrons at the sulfur vacancy with holes at the valance band [23].

4. Conclusion

The nanoparticles of Zinc Sulfide have been successfully synthesized by a simple solid state reaction method. The particle size calculated using FWHM of the XRD pattern by the Debye-Scherrer formula. Lattice strain and the dislocation density were also calculated. The morphology of the ZnS nanoparticles was studied using SEM. FTIR spectra showed the possible stretching and bending modes of the ZnS nanoparticles. The Photoluminescence investigations revealed the recombination mechanism in ZnS nanoparticles.

References

[1] B.Gates, B.Mayers, A.Grossman, Y.N.Xia, Adv.Matter, **14**, 1749 (2002).

[2] J. Y. Shen, Z. J. Chen, N.L.Wang, H.L.Yan, G.Q.Shi, A.Z.Jin, C.Z.Gu, Appl.Phys.Lett. **88**, 253106 (2006).

[3] M.H. Huang, S.Mao, H.Feick, H. Q. Yan, Y.Y.Wu, H.Kind, E. Weber R.Russo, P.D.Yang, Science. **292**, 1897 (2001).

[4] Z.W.Pan, Z.R.Dai, Z.L.Wang, Science. **291**,1947 (2001).

[5] J.J.Wu, S.C.Liu, Adv.Matter.**14**, 215 (2002).

[6] B.P.Zhang, N.T.Binh, Y.segawa, K.Wakatsuhi, N.Usami, Appl.Phys.Lett.**83**, 1635 (2003).

[7] Y.W.Heo, V.Varatharajan, M.kaufman, K.Kim, D.P.Norton, F.Ren, P.H.Fleming, Appl.Phys. Lett. **81**, 3046 (2002).

[8] Y.Li. G.W.Meng, L.D.Zhang, F.Phillipp, Appl.Phys.Lett, **76**, 2011 (2000).

[9] Y.S. Zhang, L.S. Wang, X.H. Liu, Y.J. Yan, C.Q. Chen, J. Zhu, J. Phys. Chem. B **109**, 13091 (2005).

[10] X.Wen, Y. Fang, Q. Pang, C. Yang, J.Wang,W. Ge, K.S.Wong, S. Yang, J. Phys. Chem. B **109,** 15303 (2005).

[11] X.Wang, Y. Ding, C.J. Summers, Z.L.Wang, J. Phys. Chem. B **108** (2004) 8773.

[12] A. Narayanaswamy, H.F. Xu, N. Pradhan, M. Kim, X. Peng, J. Am. Chem. Soc. **128**, 10310 (2006).

[13] W.Q. Peng, S.C. Qu, G.W. Cong, Z.G.Wang, Cryst. Growth Des. **6**, 1518 (2006).

[14] Z.P. Sun, L. Liu, L. Zhang, D.Z. Jia, Nanotechnology. **17**, 2266 (2006).

[15] C.R. Gorla, N.W. Emanetoglu, S. Liang,W.E. Mayo, Y. Lu, M.Wraback, H. Shen, J.Appl. Phys. **85**, 2595 (1999).

[16] JCPDS Card No. **36**-1450.

[17] B.D. Cullity, Elements of X-ray Diffraction, second ed., Addison-Wesley Company, USA, p. **102**.

[18] K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley, New York.

[19] Navendu Goswami, P. Sen, Solid State Comm. **132**, 791 (2004).

[20] S. Venkatachalam, R.T. Rajendrakumar, D. Mangalaraj, Sa.K. Narayandass, K. Kim, J. Yi, Solid State Electron, **48**, 2219 (2004).

[21] N. Chestnoy, T.D. Harris, R. Hull, L.E. Brus, J. Phys. Chem. **90,** 3393 (1986).

[22] H. Tang, G. Xu, L. Weng, L. Pan, L. Wang, Acta Mater. **52**, 1489 (2004).

[23] H.-Y. Lu, S.-Y. Chu, S.-S. Tan, J. Cryst. Growth. **269**, 385 (2004).

[24] P.H. Borse, N. Deshmukh, R.F. Shinde, S.K. Date, S.K. Kulkarni, J.Mater. Sci. **34**, 6087 (1999).

[25] S. Saravana Kumar, M. Abdul Khadar, S.K.Dhara, T.R. Ravindran,K.G.M.Nair. Nucl. Instr. and Meth. in Phys. Res. B. **251**, 435 (2006).