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Preparation of Nano-crystalline ZnS and Its Microstructure Characterization Employing Rietveld Method

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Abstract

In the present article, synthesis of zinc sulfide nanoparticles is reported. A top down approach is adopted here to synthesize nanocrystalline ZnS by using a high energy ball milling. Starting from pure ZnS powder, ZnS is milled up to 4.5 hours to reduce it to the nanometric dimension. At different stages of ball milling, structure and microstructure of ball milled samples have been critically analyzed from X-ray powder diffraction data employing Rietveld's powder structure refinement method. The detailed analysis reveals formation of nano-crystalline ZnS within 5min and also it confirms the stability of the cubic Sphalerite phase.

Keywords: *ZnS nano-particles, Ball mill, Rietveld method, X-ray microstructure*

1. Introduction

"There's Plenty of Room at the Bottom: Invitation to Enter a New Field of Physics" – a talk delivered by the renowned physicist Richard Feynman, in an American Physical Society meeting held at the California Institute of Technology in 1959 is often referred as the pioneering idea of manipulating solids in various particle size and different scale that leads to nanotechnology. Nanomaterial shows distinctive physical properties compared to its bulk counterpart. The size dependent properties at this scale make nano-materials capable of enhancing the performance and shelf life of number of products in the industrial sector. Nanostructured materials are a class of materials, having dimensions in the 1–100 nm range, which provide one of the greatest potentials for improving performance and extended capabilities of products in a number of industrial sectors (Xia et. al. 2003). Nanostructures can be divided into zero-dimensional (0D when they are uniform), one-dimensional (1D when they are elongated), and two-dimensional (2D when they are planar) based on their shapes. The recent emphasis in the nanomaterials research is put on 1D nano-structure at the expense of 0D and 2D ones, perhaps due to the intriguing possibility of using them in a majority of short-term future applications. There is a large number of new opportunities that could be realized by down-sizing currently existing structures into the nanometer scale (<100 nm), or by making new types of nanostructures. The most successful examples are seen in the microelectronics, where ''smaller'' has always meant a greater performance ever since the invention of transistors: e.g. higher density of integration, faster response, lower cost, and less power consumption (Fang et. al. 2008).

Group II–VI nanostructures, as typical wide band gap functional materials, are of great scientific and technical interest for their unique properties exhibited in luminescence (Borys et. al. 2010), (Chen et. al. 2008), field emission (Tabbakh et. al. 2010) (Fang et. al. 2007), electronic transportation (Gu et. al. 2010), (Shen et. el. 2008) and energy conversion (Huang et. al. 2010) (Lu et. al. 2009) (Krebs et. al.

2009). To date, various nanomaterials from ZnO (Wang et. al. 2003) (Wang et. al. 2007), CdSe (Choi et. al. 2009) to CdS (Govan et. al. 2010) have been synthesized with different morphologies. Specially, ZnS nanostructures have been systematically studied not only for its abundance and nontoxicity, but also for the flexible structures and attractive properties (Liu et. al. 2011) (Yan et. al. 2008) (Fang et. al. 2011) (Pons et. al. 2010) (Mattoussi et. al. 2000) (Fang et. al. 2010). Their hybrid counterparts also serve as versatile building blocks in nanoscale devices with tunable optoelectronic properties (Liu et. al. 2010) (Sain et. al. 2011) (Fang et. al. 2010). Doped ZnS nano-particles are also being synthesized and studied for their attractive optical and electrical properties (Chandrakar et. al. 2015) (Sharma et. al. 2017).

ZnS can exist in either zinc blende (ZB) or wurtzite (WZ) structure, or in combination of them. Different crystal structures yield different morphologies and present particular properties. To obtain ZnS nanostructures of desired morphology and dimension, the phase growth behavior should be controlled. Various methods, including the catalyzed chemical vapour deposition and template directed growth, have been adapted to grow versatile nanostructures. However, the complex synthesis steps and high energy consumption block their scale-up preparation and hence practical applications. In this article, a top down approach is adopted here to synthesize nanocrystalline ZnS by using a high energy ball milling. Starting from pure ZnS powder, ZnS is milled up to 4.5 hours to reduce to the nanometric dimension. And also the structure and detailed microstructure of these samples are critically analysed from X-ray powder diffraction data using Rietveld method.

2. Experimental

In a planetary ball mill, a rotating disk carries vials that rotate in opposite direction. The rotation speed of the disk was 300 rpm and that of the vials around 450 rpm. High energy ball milling of ZnS powder was conducted in a planetary ball mill (Model P5, M/S Fritsch, GmbH, Germany). Milling was done at room temperature in hardened chrome steel vial (volume 80ml) using 30 balls of 10mm diameter made of same material, keeping balls to powder mass ratio (BPMR) at 35:1 throughout the experiment. The powder mixture was milled for different periods varying from 5min to 4.5h.

The X-ray powder diffraction profiles of the unmilled (pure), ball milled samples were recorded using Ni-filtered Cu-K_α radiation from a highly stabilized and automated Philips X-ray generator (PW 1830) operated at 35kV and 25 mA. The generator is coupled with a Philips X-ray powder diffractometer consisting of a PW 3710 mpd controller, PW 1050/51 goniometer, and a proportional counter. For this experiment, 1^0 divergence slit, 0.2 mm receiving slit, 1^0 scatter slit and 5^0 soller slit system were used. The step-scan data (of step size 0.02^0 2θ and counting time 15-20s depending on the peak intensity) were recorded for the entire angular range 20-100^0 2θ.

3. Characterization by X-ray powder diffraction

In the present study, we have adopted the Rietveld's powder structure refinement analysis (Patra & Pradhan 2011) (Sain & Pradhan, 2011) (Bhaskar et.al. 2011) (Patra et. al. 2011) (Sain et. al. 2011) of X-ray powder diffraction step scan data of unmilled and ball milled samples to obtain the refined structural parameters, such as atomic coordinates, occupancies, lattice parameters, thermal parameters etc. and microstructural parameters, such as particle / crystallite size and r.m.s. lattice strain etc. The Rietveld software MAUD 1.85 (Lutterotti, 2002) is specially designed to refine simultaneously both the structural and microstructural parameters through a least-square method. The peak shape was assumed to be a pseudo-Voigt (*pV*) function with asymmetry. The background of each pattern was fitted by a polynomial function of degree 5. In the present study, refinements were conducted without refining the isotropic atomic thermal parameters.

From the X-Ray data, it reveals that ZnS has cubic Sphalerite structure. To simulate the theoretical X-ray powder pattern containing cubic Sphalerite phase in a single pattern the space group **F-43m** was taken with Zn and S atoms are in Atomic Positions, Zn: 0, 0, 0 S: 0.25, 0.25, 0.25. Initially, the

positions of the peaks were corrected by successive refinements of systematic errors taking into account the zero-shift error and sample displacement error. Considering the integrated intensity of the peaks as a function of structural parameters only, the Marquardt least squares procedures were adopted for minimization the difference between the observed and simulated powder diffraction patterns and the minimization was carried out by using the reliability index parameter, R_{wp} (weighted residual error), R_B (Bragg factor) and $R_{\exp}$ (expected error) (Lutterotti, 2002) (H.M. Rietveld, 1967) (H.M. Rietveld, 1969) (Young & Wiles, 1982) (Rietveld Method, Oxford University Press) (Wiles & Young, 1981). This leads to the value of goodness of fit: GoF = R_{wp}/R_{exp}
Refinement continues till convergence is reached with the value of the quality factor, GoF approaching 1, which confirms the goodness of refinement.

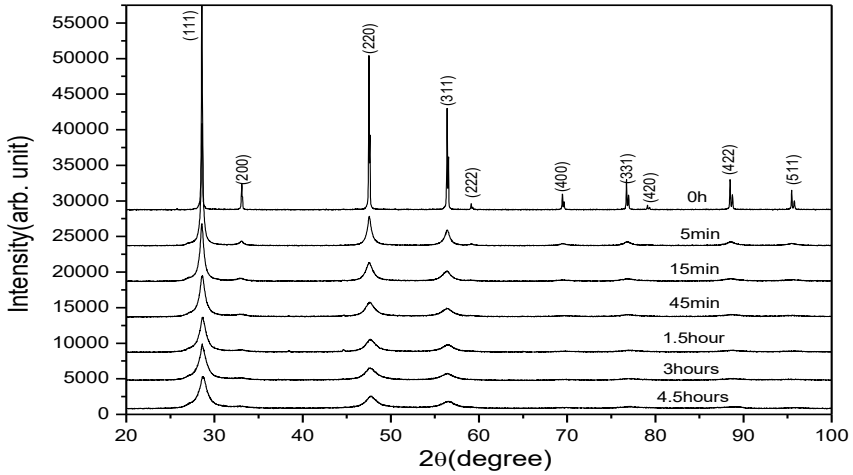
3.1. Size-strain analysis

The basic consideration of this method is the modeling of the diffraction profiles by an analytical function, which is a combination of Cauchyian, Gaussian, and an additional asymmetry function. It has been well established that the observed peak broadenings of the sample profiles are mainly due to the presence of small crystallite size and r.m.s. strain. The Cauchy and Gaussian type functions can better model the crystallite size and strain broadening respectively (Lutterotti, 2002) (Rietveld H.M., 1967) (Rietveld H. M., 1969) (Young & Wiles, 1982) (Rietveld Method, Oxford University Press) (Wiles & Young, 1981). Being a linear combination of a Cauchyian and Gaussian functions, the *pV* function is the most reliable peak-shape function and is being widely used in the Rietveld structure refinement softwares [LS1, GSAS, DBWS, and BGMN etc.].

4. Results and discussion

X-ray powder diffraction of the unmilled and ball milled samples are shown in the Fig. 1. As the milling time increases the intensities as well as sharpness of the peaks gradually decreases which shows clear indication of reduction of particle size. During milling time there is no transformation or growth of additional phase is observed. A detailed microstructure study of these X-ray diffraction patterns using Maud software reveals reduction of particle size and increase of r.m.s strain which are furnished in the table 1.

Fig 1: X-Ray diffraction data of pure and ball milled ZnS powder at different milling hour.



Variation of Lattice parameter of cubic sphalerite, Crystallite size (coherently diffracting domain) and r.m.s. lattice strain depending on different milling time, as obtained from Rietveld analysis are furnished in the table 1 below. Analysis shows that nanocrystalline ZnS powder formed within 5min and then with the progress of milling time the particle size gradually decreases to 7.84nm. Lattice parameter gradually decreases which increases r.m.s. strain. With the progress of milling time no growth of extra peaks confirms the stability of the cubic Sphalerite phase.

Table 1. Variation of lattice parameter, crystallite size and r.m.s. strain with milling time

Milling Time	Lattice parameter*a*(Angstrom)	Particle Size (nm)	R.m.s strain
5min	5.4068	27.58	29.68E-4
15min	5.4094	15.72	31.70E-3
45min	5.4014	11.06	29.72E-3
1.5h	5.3936	9.43	22.47E-3
3h	5.3968	8.63	3.330E-3
4.5h	5.3873	7.84	4.229E-3

5. Conclusion

X-Ray microstructure as revealed from Rietveld analysis of unmilled and ball milled samples confirms formation of nanocrystalline ZnS within 5 min, which reduces to 7.8nm within 4.5h of milling. During milling process no intermediate phase has developed which confirms the stability of the cubic Sphalerite phase. The particle size is reported here from the analysis of X-ray data.

Future plan of work

In future, photoluminescence and electrical properties of these samples would be studied and also electron microscopic image would be studied to compare the size of the particles as obtained from X-ray diffraction data analysis. And finally structure property co-relation would be made.

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References

Al-Tabbakh A. A., More M. A., Joag D. S., Mulla I. S., & Pillai V. K., (2010). The Fowler-Nordheim plot behavior and mechanism of field electron emission from ZnO tetrapod structures, *American Chemical Society Nano*, 4 (10) 5585-5590

Bhaskar U. K., Bid S., & S. K. Pradhan, (2011). Microstructure evaluation of nanostructured Ti0.9Al0.1N prepared by reactive ball milling, *Journal of Alloys & Compounds*, 509, 620-626.

Borys N. J., Walter M. J., Huang J., Talapin D.V. & Lupton J. M., (2010). The role of particle morphology in interfacial energy transfer in CdSe/ CdS heterostructure nanocrystals, *Science*, 330 (6009)1371-1374

Chandrakar R. K., Banghel R. N., Chandra V. K., and Chandra B. P. (2015). Synthesis, characterization and photoluminescence studies of Mn doped ZnS nanoparticles, *Superlattices and Microstructures*, 86, 256-269

Chen Z. G., Zou J., Liu G., Yao X. D., Li F., Yuan X.L., Sekiguchi T., Lu G. Q., & Cheng H. M., (2008). Growth, cathodoluminescence and field emission of ZnS tetrapod tree-like heterostructures, *Advanced Functional Materials*, 18 (19) 3063-3069

Choi C. L., Koski K. J., Sivasankar S., & Alivisatos A.P., (2009). Strain-dependent photoluminescence behavior of CdSe / CdS nanocrystals with spherical, linear, and branched topologies, *Nano Letters*, 9 (10) 3544-3549

Fang X. S., Bando Y., Gautam U. K., Ye C. H.& Golberg D. (2008). Inorganic semiconductor nanostructures and their field-emission applications, *Journal of Material Chemistry*; 18: 509–522.

Fang X. S., Bando Y., Liao M. Y., Zhai T. Y., Gautam U. K., Li L., Koide Y., & Golberg D., (2010). An Efficient Way to Assemble ZnS Nanobelts as Ultraviolet-Light Sensors with Enhanced Photocurrent and Stability, *Advanced Functional Materials*, 20 (3) 500-508

Fang X. S., Bando Y., Shen G. Z., Ye C. H., Gautam U. K., Costa P., Zhi C.Y., Tang C. C., & Golberg D., (2007). Ultrafine ZnS nanobelts as field emitters, *Advanced Materials*, 19 (18) 2593-2596

Fang X. S., Wu L. M., &Hu L. F., (2011). ZnS nanostructure arrays: a developing material star, *Advanced Materials*, 23 (5) 585-598.

Govan J. E., Jan E., Querejeta A., Kotov N. A., & Gun'ko Y. K., (2010). Chiral luminescent CdS nano-tetrapods, *Chemical Communication*, 4 (6/33) 6072-6074

Gu Y. D., Zhou J., Mai W., Dai Y., Bao G., & Wang Z. L., (2010). Measuring the transport property of ZnO tetrapod using in-situ nano probes, *Chemical Physics Letters*, 484 (4–6) 96-99

Huang C. Y., Wang D. Y., Wang C. H., Chen Y. T., Wang Y. T., Jiang Y. T., Yang Y. J., Chen C. C., & Chen Y. F., (2010). Efficient light harvesting by photon down conversion and light trapping in hybrid ZnS nanoparticles /Si nanotips solar cells, *American Chemical Society Nano*, 4 (10) 5849-5854.

Kong X. Y., Ding Y., Yang R., &Wang Z. L., (2004). Single-crystal nanorings formed by epitaxial self-coiling of polar nanobelts, Science, 303 (5662) 1348.

Krebs F. C., Gevorgyan S. A., & Alstrup J., (2009). A roll-to-roll process to flexible polymer solar cells: model studies, manufacture and operational stability studies, *Journal of Material Chemistry*, 19 (30) 5442-5451.

Liu W., Wang N., Wang R. M., Kumar S., Duesberg G. S., Zhang H. Z., & Sun K., (2011). Atom-Resolved Evidence of Anisotropic Growth in ZnS Nano tetrapods, *Nano Letters*, 11 (7) 2983-2988

Liu W., Wang R. M., & Wang N., (2010). From ZnS nanobelts to ZnO/ ZnS heterostructures: Microscopy analysis and their tunable optical property, *Applied Physics Letters*, 97 (4) 041916-041918.

Lu M.Y., Song J. H., Lu M. P., Lee C. Y., Chen L. J., & Wang Z. L., (2009). ZnO-ZnS Heterojunction and ZnS Nanowire Arrays for Electricity Generation, *American Chemical Society Nano*, 3 (2) 357-362.

Lutterotti L., Maud version 1.85. (2002) http://www.ing.unitn.it/~luttero/maud

Mattoussi H., Mauro J. M., Goldman E. R., Anderson G. P., Sundar V. C., Mikulec F. V., & Bawendi M. G., (2000). Self-Assembly of CdSe-ZnS Quantum Dot Bio conjugates Using an Engineered Recombinant Protein, *Journal of AmericanChemical Society*, 122 (49) 12142-12150.

Patra S., & Pradhan S. K., (2011). Quickest single-step one pot mechanosynthesis and characterization of ZnTe Quantum Dots, *Journal of Alloys and Compounds*, 509, 5567-5570

Patra S., Satpati B., & Pradhan S. K., (2011). Quickest single-step mechanosynthesis of CdS quantum dots and their microstructure characterization, *Journal of Nanoscience and Nanotechonology*, 11, 4771-4780

Pons T., Pic E., Lequeux N., Cassette E., Bezdetnaya L., Guillemin F., Marchal F., & Dubertret B., (2010). Cadmium-free CuInS2/ ZnS quantum dots for sentinel lymph node imaging with reduced toxicity, American Chemical Society Nano 4 (5) 2531-2538

Rietveld H. M., (1967). Line profiles of neutron powder-diffraction peaks for structure refinement, Acta Crystallographica. 22, 151-152.

Rietveld H. M., (1969). A profile refinement method for nuclear and magnetic structures, Journal of Applied Crystallography, 2, 65-71

Sain S., & Pradhan S. K. (2011). Mechanochemical solid state synthesis of (Cd0.8Zn0.2)S quantum dots: microstructure and optical characterizations, *Journal of Alloys and Compounds*, 509, 4176-4184.

Sain S., Patra S., & Pradhan S. K., (2011). Microstructure and optical band-gap of mechanosynthesized CdxZn1-xS quantum dots, Journal of Physics D: *Applied Physics*, 44, 075101 (8pp)

Sharma S., Singh I., Chitkara N., Kapoor A. (2017). Synthesis and characterization of aluminium doped zinc sulfide nanoparticles. Materials Research Express, Volume 4, Issue 7, article id. 075046.

Shen G. Z., Chen P. C., Bando Y., Golberg D., & Zhu C. W., (2008). Pearl-like ZnS-decorated InP nanowire heterostructures and their electric behaviors, *Chemistry of Materials*, 20 (21) 6779-6783.

Wang R. M., Xing Y. J., Xu J., & Yu D. P., (2003). Fabrication and microstructure analysis on zinc oxide nanotubes, *New Journal of Physics*, 5, 115-117

Wang X. D., Song J. H., Liu J., & Wang Z. L., (2007). Direct-current nanogenerator driven by ultrasonic waves, *Science*, 316 (5821) 102

Wiles D. B. &Young R. A., (1981). A new computer program for Rietveld analysis of X-ray powder diffraction patterns, Journal of Applied Crystallography, 14, 149-151

Xia Y. N., Yang P. D., Sun Y. G., Wu Y. Y., Mayers B., Gates B., Yin Y. D., Kim F. & Yan H. Q.(2003). One-dimensional nanostructures: synthesis, characterization, and applications. *Advanced Materials*; 15: 353–389.

Yan J., Fang X. S., Zhang L. D., Bando Y., Gautam U. K., Dierre B., Sekiguchi T., & Golberg D., (2008). Structure and cathodo luminescence of individual ZnS / ZnO biaxial nanobelts heterostructures, *Nano Letters*, 8 (9) 2794-2799

Young R. A. &Wiles D. B., (1982). Profile Shape Functions in. Rietveld Refinements, Journal of Applied Crystallography, 15, 430-438.

Young R. A., The Rietveld Method, edited by Young R. A., pp.1-38. Oxford University Press/ IUCr