# Structural analysis of PbS synthesized by different technique

**M.D. Chaudhary[1#], J.C. Patel[1], J.M. Chaudhari[1], M.D. Parmar[1]**
[1]Physics Department, M.N. College Visnagar, Visnagar, Gujarat, India-384315
[#]Email – maheshdchaudhary@yahoo.com

**Abstract:** The PbS in the form of nanoparticles (Nps) and thin films synthesized by chemical bath deposition at room temperature were characterized by powder X-ray diffraction (XRD) used to analyze the structural properties of PbS. The influence of the synthesis process on the formation of the PbS and the variation in the structural parameter were deliberate in details.

**Key Words:** Nanoparticles, Thin films, PbS, XRD.

## INTRODUCTION:

Semiconductor Nps and thin films have recently attracted much attention due to their applications in optoelectronics, photocatalysis, microelectronics, energy conversion industries and nonlinear optics [1-3]. These materials have been a new generation of advanced materials due to their novel structural, morphological, optical and electrical properties originating from size quantization [4]. PbS is an important IV-VI semiconductor material because of its direct bandgap of 0.41 eV and its exciton Bohr radius of 18nm at room temperature. Therefore when crystal sizes are smaller than the Bohr radius, such a small bandgap and a large exciton Bohr radius make it as an interesting system for studying the effect of size confinement. PbS Nps may also be useful in electroluminescent devices such as light emitting diodes and optical switch devices. Many physical and chemical properties such as melting point, color, bandgap, optical and electronic properties of materials strongly depend on the particle sizes [5-8]. Different morphologies can play roles in the properties. They include nanocrystals [9], nanorods [10-11], nanotubes [10], nanocubes [12], star shapes [13], dendrites [12, 14], and flower-like crystals [15]. All can be prepared by different methods, such as hydrothermal and solvothermal [16, 12], vacuum deposition [17], electrochemical deposition [18], pulsed laser deposition [19], microwave radiation [10], sonochemical [9], photochemical [20], chemical bath deposition (CBD) [21], γ-ray irradiation [22], successive ionic layer adsorption reaction (SILAR) [23], and spray pyrrolysis [24].

This work introduces comparative studies of structural parameters variation in PbS Nps and thin films synthesized by different technique.

## EXPERIMENTAL DETAILS:

The nanocrystalline PbS thin films (S1) deposited on glass substrates (72 × 25 × 1mm) using chemical bath deposition (CBD) technique at room temperature by R. Kumar [25]. In the typical synthesis a mixture of 0.06 M lead nitrate, 0.24 M thiourea, 0.6 M sodium hydroxide and a reducing agent 0.1 M hydroxylamine hydrochloride (All AR grade 99.9% pure) solution was prepared in appropriate ratio in a beaker. The pre-cleaned glass substrates were dipped vertically in the beaker for deposition of the films. The pH of the solution was maintained at 12.56. The prepared solution was continuously stirred 10min using magnetic stirrer. The final solution was transparent up to first 5 min of reaction time and then its turn into dark brown which indicating the formation of the PbS. The shiny dark black coating appears on the inner surface of the beaker after 30 min indicating the formation of the thin films on the substrate. After 30 min of deposition time, the films were removed from the solution, washed repeatedly in distilled water for removing possible contaminants from solid phases and then were dried in air at a room temperature and then it annealed at 400 $^{o}$C in air for an hour.

Lead sulphide (PbS) thin films (S2) synthesized using chemical bath deposition at room temperature by S.V. Bhatt et al [26]. In the typical synthesis clear solution of Lead Acetate (0.052mol/l) and thiourea (0.24mol/l) was prepared in 20ml distilled water separately. Both solutions were mixed together and continuously stirred for 30 minutes. Then, the pH of the solution was adjusted to 10 by drop-wise addition of ammonium hydroxide. pH of the final solution play significant role in the reaction rate. After mixing of the two precursors solution the pH of the solution is 6.62 and it increase up to 10 by adding ammonium hydroxide for doing fast nucleation on the glass

substrate. The mixture was then kept at room temperature and thoroughly cleaned glass slides were vertically placed in the beaker for deposition of the thin film of PbS. After 6 hours the films removed from the solution and washed with distilled water several times. The films were shiny dark black colour. Here the Lead acetate was used as $Pb^{2+}$and thiourea as $S^{2-}$ source in an aqueous medium.

The PbS Nps (S3) prepare using MA/octene-1 copolymer matrix at 80 $^{o}$C temperature by Z.Q. Mamiyev et al. [27]. PbS/copolymer N/C material was prepared as following procedure: After optimization of synthesis conditions, the PbS precursors were prepared by dissolving of 0.69 g of lead acetate and 1 g white color powder copolymer in 100ml DMF in the three mouth flask and the pH of the solution was maintained at 10 with KOH. The process was carried out by mixing at 80 C, after 4 h 0.16 g of thiourea was added rapidly to the flask with syringe and then the reaction was continued for another hour. At the end of reaction strong white clear solution turns to brownish black color which indicated the formation of PbS Nps. H. Karami et al. synthesized PbS Nps (S4) by chemical precipitation [28]. PbS Nps were synthesized through rate control by adding lead acetate solution into the sodium sulfide solution to precipitate lead sulfide. The pH of the solutions was adjusted by adding $HNO_3$ or NaOH solutions. The final solution was filter and washes several times with methanol.

**CHARACTERIZATION:**

The structural properties of the prepared films by R. Kumar were examined using a D8 Advance X-ray diffractometerwith Cu Kα irradiation (λ = 1.54060 Å) and operated at 40 kV and 100 mA (Fig. 1(a)). The XRD pattern of PbS thin films prepared films by S.V. Bhatt were collected on a Philips Xpert MPD, X-ray diffractometer with $CuK_{\alpha}$ radiation (λ=1.54060 Å). The scan rate of 0.20°/s was applied to record the pattern in the range of 3°- 99.97° (Fig. 1(b)). Bruker D8 Advance X-ray diffractometer was used to measure the size and shape of Z.Q. Mamiyev and H. Karami synthesized PbS Nps accurately (Fig. 1(c) & Fig. 1(d) respectively).

**RESULT AND DISCUSSION:**

The X-ray diffraction profiles of as-deposited PbS thin films are shown in Fig. 1(a). All the peaks of diffractions were indexed with face centered cubic structure of PbS only that confirmed by JCPDS-PbS; 78-1901. The narrow peaks show good crystallinity of the films.

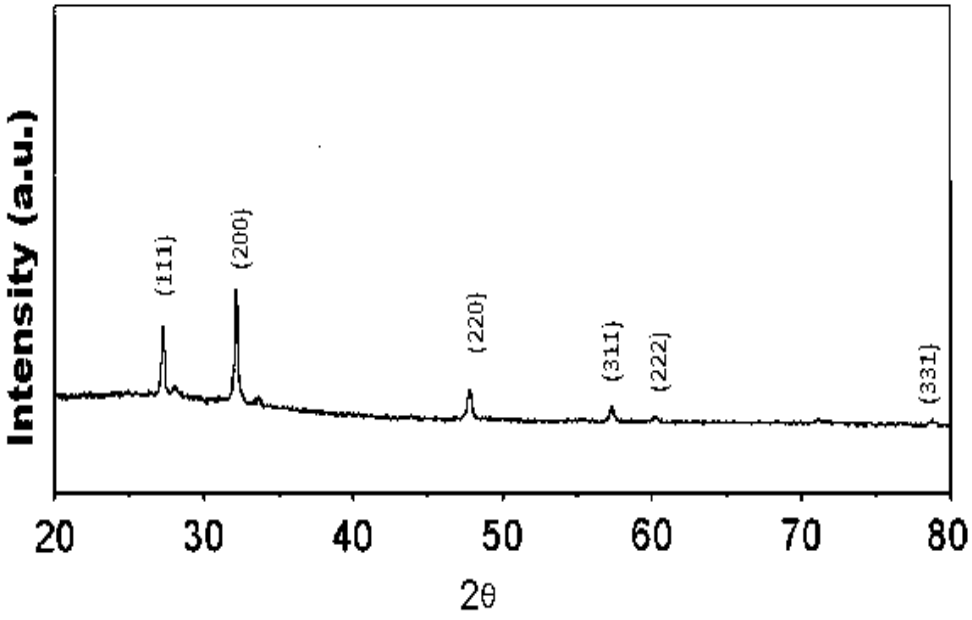


**Fig. 1(a)** X-ray diffraction pattern of as-deposited PbS thin films.

X-ray diffractogram of PbS thin films is shown in Fig. 1(b) and is indexed based on cubic system with the help of powder-X software. The value of the lattice parameter determined from the X-ray diffractogram is 5.93Å which is matching with the reported value of lattice parameter of bulk PbS (JCPDS 05-0592). The remain peaks may be corresponding to amorphous glass substrat. The different diffrection peaks appears in diffractrogram indicating the pollycrystalline nature of the synthesized thin films.

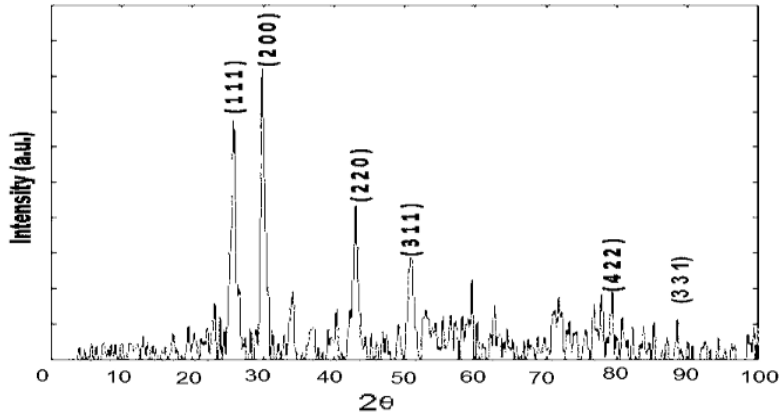


**Fig. 1(b)** X-ray powder diffractogram pattern of as deposited PbS thin films.

Structural identification of powder PbS Nps was carried out with X-ray diffraction in the range of angle 2θ between 20° and 65°. Fig. 1(c) shows the XRD pattern for obtained Nps, which were nanocrystalline in nature. Diffraction peaks at 2θ values 26°, 29°, 43°, 53° and 60° are observed. All diffraction peaks can be corresponding to the pure cubic phase of PbS (JCPDS card No. 05-0592) and the peaks are originating from (111), (200), (220), (222), (400) planes respectively. The highest intensity of the peak shows that the grains are preferentially oriented along (111) direction. Broad diffraction peaks (FWHM full with half maxima) indicating the nano size formation.

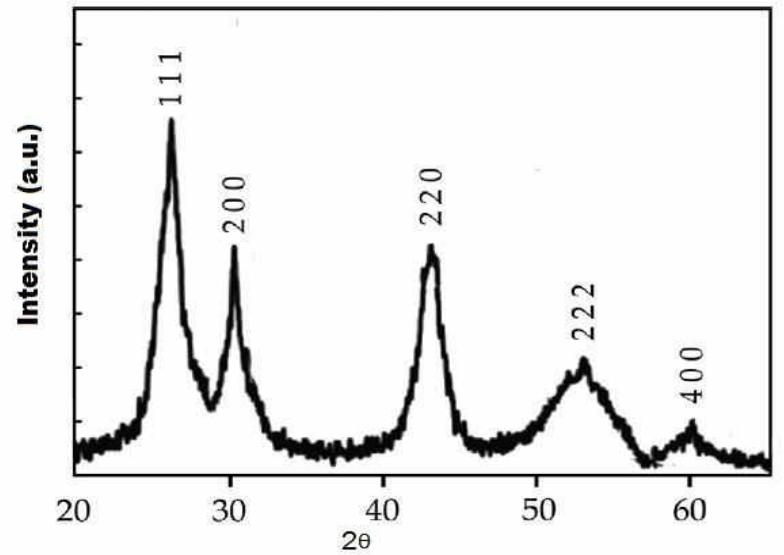


**Fig. 1(c)** Powder XRD pattern for PbS Nps embedded in MA/octene-1 copolymer matrix.

The X-ray diffraction pattern of the as-synthesized Nps were indexed with cubic structure of PbS. The sharp intense diffraction peaks indicating the good crystallinity and broadning of peak indicating the formation of nano.

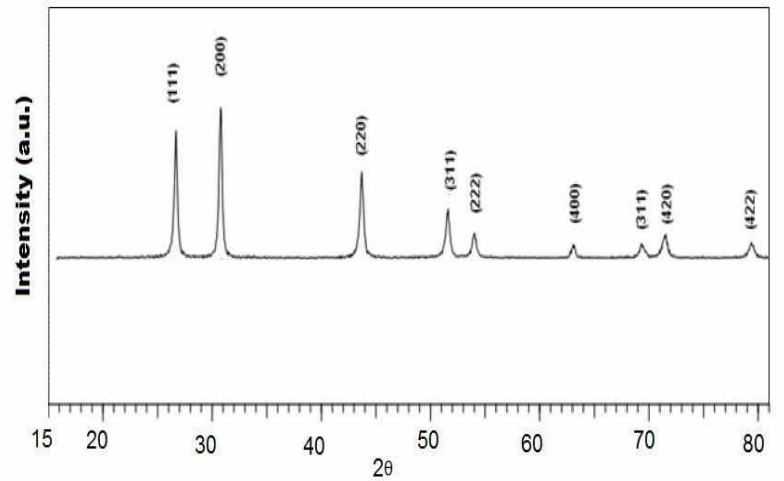


**Fig. 1(d)** XRD patterns of the PbS Nps.

**Table 1.** Structural parameters of the as-synthesized PbS.

| Sample | XRD | | | |
|---|---|---|---|---|
| | Preferred plane orientation | Structure | Lattice parameter a (Å) | Crystallite size (nm) |
| S1 | (200) | Cubic | 5.9362 | 40.7 |
| S2 | (200) | Cubic | 5.9300 | 18 |
| S3 | (111) | Cubic | 5.896 | 10–15 |
| S4 | (200) | Cubic | - | 32 |

The high crystallinity and the preferred plane orientation (111) for solar radiation absorption shown for the PbS Nps synthesized by MA/octene-1 copolymer matrix at 80 $^{o}$C temperature compared to Nps synthesized by chemical precipitation indicating the synthesis temperature play significant role for Nps growth. Crystallite size of the thin films increases with increase the pH of the final solution. S2 shows 18nm crystallite size while S1 having 40.7nm indicating the growth of PbS on the substrate for S1 is rapid compare to S2 due to pH of S1 is 12.56 and for S2 is 10 that enhance the reaction speed.

## CONCLUSION:

As-synthesized PbS thin films and Nps were used to study the structural parameters variation due to synthesis process. The plane orientation and lattice parameters are not affected by only changing the pH of the solution. The crystallite size only increased as the pH of the final solution increase. Nps synthesized in copolymer matrix shows distinguished properties that preferred plane orientation and nano crystallite size. Nps generally shows that as the synthesis temperature increase the crystallite size increase but with used of copolymer matrix the crystallite size decrease and the high temperature make the (111) plane orientation. As the crystallite size decrease the bandgap of the material increase. (111) plane oriented and wide bandgap PbS Nps widely applicable in optoelectronic devices.

## REFERENCES:


1. M. Salavati-Niasari, D. Ghanbari and F. Davar, Synthesis of different morphologies of bismuth sulphide nanostructures via hydrothermal process in the presence of thioglycolic acid, Journal of Alloys and Compounds, 488, 2009, 442–447.
2. M. Salavati-Niasari, D.Ghanbari and F. Davar, Shape selective hydrothermal synthesis of tin sulphide nanoflowers based on nanosheets in the presence of thioglycolic acid, Journal of Alloys and Compounds, 492, 2010, 570–575.
3. D. Ghanbari and M. Salavati-Niasari, The effect of CdS/organic nanostructure as additive on the thermal stability of ABS polymer, High Temperature Materials and Process, 31, 2012, 133-138.
4. A.N. Banerjee, The design, fabrication and photocatalytic utility of nanostructured semiconductors: focus on $TiO_2$-based nanostructures, Nanotechnology, Science and Applications, 4, 2011, 35–65.
5. Y. Ji, X. Ma, H. Zhang, J. Xu and D. Yang, Star-shaped PbS crystals fabricated by a novel hydrothermal method, Journal of Physics: Condensed Matter, 15, 2003, 7611–7615.
6. Y. Ni, X.Wei1, J. Hong and X. Ma, PbS microcrystals with a magic-square-like structure prepared by a simple hydrothermal method, Crystal Research Technology, 41, 2006, 885–888.
7. M. Salavati-Niasari, A. Sobhani and F. Davar, Synthesis of star-shaped PbS nanocrystals using single-source precursor, Journal of Alloys and Compounds, 507, 2010, 77–83.
8. M. Yousefi, F. Gholamian, D. Ghanbari and M. Salavati- Niasari, Polymeric nanocomposite materials: Preparation and characterization of star-shaped PbS nanocrystals and their influence on the thermal stability of acrylonitrile-butadience-styrene (ABS) copolymer, Polyhedron, 30, 2011, 1055–1060.
9. G. Ujjal and K.S. Ram, Preparation of PbS and PbSe nanocrystals by a new solvothermal route, Materials Research Bulletin, 39, 2004, 669-676.
10. S.F. Wang, F. Gu, M.K. Lu, G.J. Zhou and A.Y. Zhang, Sonochemical synthesis of PbS nanocubes, nanorods and nanotubes, Journals of Crystals Growth, 289, 2006, 621-625.
11. T. Saraidarov, R. Reisfeld, A. Sashchiuk and E. Lifshitz, Synthesis and characterization of PbS nanorods, Physica E, 37, 2007, 173-177.
12. Z. Wanqun, **Y**. Qing, X. Liqiang, Y. Weichao and Q. Yitai, Growth of Pbs crystals from nanocubes to eight-horn-shaped dendrites through a complex synthetic route, Materials Letters, 59, 2005, 3383-3388.
13. G. Zhou, M. Lu, Z. Xiu, S. Wang, H. Zhang, Y. Zhou, and S. Wang, Controlled synthesis of high quality PbS star-shaped dendrites, multipods, truncated nanocubes and nanocubes and their shape evolution process, Journal of Physics Chemistry B, 110, 2006, 6543-6548.

14. Z. Zhang, S.H. Lee, J.J. Vittal and W.S. Chin, A simple way to prepare PbS nanocrystals with morphology tuning at room temperature, Journal Physics Chemistry B, 110, 2006, 6649-6654.
15. N. Yonghong, F. Wang, L. Hongjiang, Y. Gui, H. Jianming, M. Xiang and X. Zheng, A novel aqueous-phase route to prepare flower-shaped PbS micron crystals, Journals of Crystals Growth, 262, 2004, 399-402.
16. W. Shiquan, P. Anlian, Y. Haoyong, H. Yuping, L. Yun, X. Zhude and Z. Bingsuo, Synthesis of PbS microcrystals via hydrothermal process, Materials Letters, 60, 2006, 1242-1246.
17. N.I. Fainer, M.L. Kosinova, Y.M. Rumyantsev, E.G. Salman and F.A. Kuznetsovh, Growth of PbS and CdS thinfilms by loe-pressure chemical vapour deposition using dithiocarbamates, Thin Solid Films, 280, 1996, 16-19.
18. A. Mondal and N. Mukherjee, Cubic PbS thin films on TCO glass substrate by galvanic technique, Materials Letters, 60, 2006, 2672-2674.
19. J. Vaitkus, V. Kazlauskiene, J. Miskinis and J. Sinius, PbS thin films formation on terrace-step surface by pulsed laser deposition, Materials Research Bulletin, 33, 1998, 711-716.
20. M. Ichemiura, T. Narita and K. Masui, Synthesis of PbS in aqueous solutions by photochemical reactions, Materials Science and Engineering: B, 96, 2002, 296-299.
21. A.P. Gaiduk, P.I. Gaiduk and A.N. Larsen, Chemical bath deposition of PbS nanocrystals: Effect of substrate, Thin Solid Films, 516, 2008, 3791-3795.
22. X. Changqi, Zh. Zhicheng, W. Hailong and Y. Qiang, A novel way to synthesize lead sulphide QDs via γ-ray irradiation, Materials Science and Engineering: B, 104, 2003, 5-8.
23. R. Resch, G. Friedbacher, M. Grasserbaner, T. Kanniainen, S. Lindoors, M. Leskela and L. Nijnisto, Lateral force microscopy and force modulation microscopy on SILAR grown lead sulphide samples, Applied Surface Science, 120, 1997, 51-57.
24. B.Thangaraju and P. Kaliannan, Spray pyrolytically deposited PbS thin films, Semiconductor Science and Technology, 15, 2000, 849-853.
25. R. Kumar, R. Das, M. Gupta and V. Ganesan, Preparation of nanocrystalline Sb doped PbS thin films and their structural, optical, and electrical characterization, Superlattices and Microstructures, 75, 2014, 601–612.
26. S.V. Bhatt, M.P. Deshpande, B.H. Soni, N. Garg and S. Chaki, Chemical bath deposition of lead sulphide (PbS) thin film and their characterization, Solid State Phenomena, 209, 2014, 111-115.
27. Z.Q. Mamiyev and N.O. Balayeva, Preparation and optical studies of PbS nanoparticles, Optical Materials, 46, 2015, 522-525.
28. H. Karami, M. Ghasemi and S. Matini, Synthesis, characterization and application of lead sulphide nanostructures as ammonia gas sensing agent, International Journal of Electrochemical Science, 8, 2013, 11661 – 11679.