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Growth and Characterization of PbS Nanoparticles Using THF

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ABSTRACT

PbS nano particles are grown by chemical method by using $PbCl_2$, S and $NaBH_4$. Three different ratio of 1:1:1, 1:1:3 and 1:1:5 of Sodium Borohydride among these reagents are used to grow nanoparticles in the medium THF. In each case the reagents are stirred for 4 hours by means of a magnetic stirrer at room temperature. The grown nanoparticles are characterised by electron diffraction, XRD and optical absorption. It is found that in case of higher ratio of sodium borohydride band gap decreases. This agrees with TEM images that crystal size also increases in case of higher ratio of sodium borohydride as a reducing reagent. Thus we see that nanoparticles show more quantum confinement for sample grown with lower ratio of $NaBH_4$.

Keywords: PbS nanoparticles; structural properties; EDX analysis; NIR absorption properties

1. Introduction

Now the research shows attraction in the synthesis of semiconducting nanomaterials due to their wide application in many devices. Semiconducting nanomaterials PbS is challenging materials in technology with tunable optical properties [1-3]. Greater optical nonlinearity and a strong confinement of the electron hole pair is seen in low band gap materials [4-7]. Such materials, PbS is quit important IV–VI group semiconductors having 0.41eV narrow band gap with an effective Bohr radius of 18 nm . The absorption across the visible to near infrared (NIR) regions (700–1600 nm) tuned the band gap [8-11]. Now infrared detectors, biomedical, communication and electroluminescent devices can be made from materials which exhibiting NIR absorption and emission. Their bulk properties like biological, optical, electrical and mechanical properties quit different in case of nanoparticles [12-16].

Various dimensional particles with various shape and size is obtained by Colloidal synthesis of nanoparticles [17-18]. Such PbS nanoparticles are synthesized under various process including gas phase, vapour deposition method, solution phase, solvothermal process, hot injection methods and polymer film routes [19-20]. These higher temperature complex methods need templates. The materials properties will be affected by the complexity and impurities due to Templates and surfactants. Material properties and application are also influenced by inorganic organic interface due to capping in chemical synthesis. In case of electronic and optical devices electron mobility must be affected by organic molecules of capping. Therefore we design a chemical reduction route to produce PbS nanoparticles to ensure compatibility without organic capping molecules nearby nano particles. So we report a simple room temperature synthesis method for PbS nano particles.

2. Experimental

2.1. Materials

We purchased the all chemicals from Sigma Aldrich. Lead Chloride {$PbCl_2 \bullet 3H_2O$}, sulphur (S) powder and Sodium Borohydride ($NaBH_4$), reagents are used without any further purification. The reaction process is continued in Standard air and dust free conditions.

2.2. Synthesis of PbS nanoparticles

In this process, 2.78g of Lead Chloride was dispersed into 50 ml of tetra hydrofuran (THF) in a beaker and stirring upto 30 min then 0.32g sulphur powder is added and then $NaBH_4$were added. At room temperature the reaction mixture was stirred under dry and dust free atmosphere for 4 hours. Initially the color of the solution was yellow, but after completion of the reaction it turned black. Volatile side products and solvents were removed by high vacuum. Finally the residue was dried for 2 weeks in filter paper setting in funnel under vacuum to obtain pure black PbS nanoparticles.

2.3. Chemical reaction

$PbCl_2 = \quad Pb^{+2} + 2Cl^-$

$NaBH_4 + 2Cl^- = NaCl + B_2H_6 + 2H^+ + 2e$

$2H+ + S^{-2} = H_2S$

$H_2S + Pb^{+2} + 2e = PbS + H_2$

2.4. Characterization

The as prepared PbS samples are Structurally characterized by TEM and XRD. For TEM sample preparation, small amounts of grown samples are dispersed in ethanol. Then few drops of dispersed samples are placed on carbon coated copper grid and dried. Jeol Jem-2100 TEM is used to acquire TEM images. SAED pattern are also taken from these samples. FESEM images of PbS nano powder were taken from Jeol Jsm 5800.

EDX analysis of the grown samples is also carried out.

XRD pattern of powder samples is acquired using high resolution Rigaku Mini Flex X-ray Diffractometer. Cu Kα is used as x ray source. Optical characterization of the grown samples is carried out using Shimadzu UV-Vis-NIR spectrophotometer (model-3600). The samples are dispersed in ethanol to observe absorption spectra.

3. Results and discussion

The TEM images of as grown nano PbS materials with different ratio of reducing agent are shown in figure 1a, 1b, 1c. It is observed that those sizes of the nanoparticles are small for sample grown in lower ratio of sodium borohydride. With increase of sodium borohydride ratio the particles agglomerate to larger nanoparticles. As reducing agent ratio increase, more sulphur is reduced. Thus reaction with lead is frequent. This in turn increases the possibility of particle agglomeration and crystal size is increased.

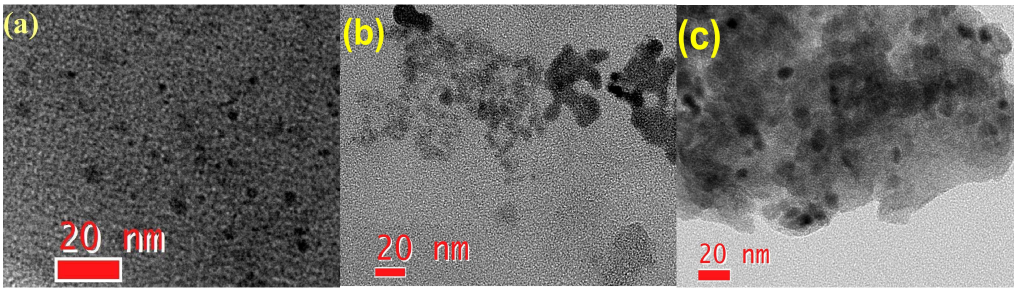

Figure 1: TEM images of PbS nanoparticles (a) 1:1:1 (b) 1:1:3 (c) 1:1:5

SAED pattern are also taken for these samples. Figure 2 shows the SAED pattern of grown PbS nanoparticles. The diffraction rings are indexed. The crystal plane values are well matched with standard results. The grown particles show cubic phase. Diffraction pattern indicates that polycrystalinity increase with increase of reducing agent.

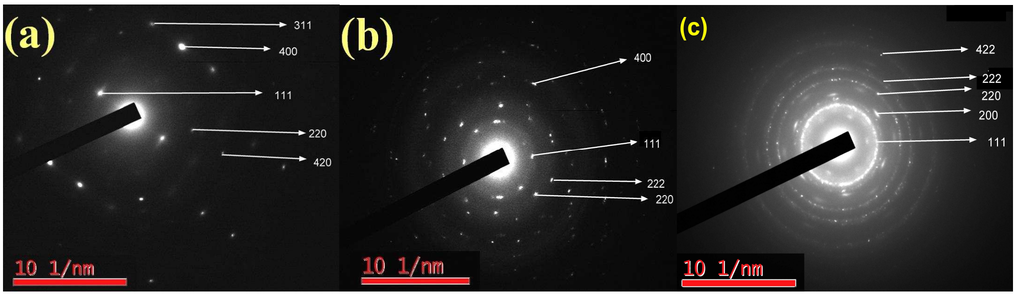

Figure 2: SAED pattern of PbS nanoparticles (a) 1:1:1 (b) 1:1:3 (c) 1:1:5

The EDX spectra of grown samples are shown in figure 3. EDX analyses of the grown samples are also carried out. The atomic percentages of Pb and S from EDX analysis are given in Table 1. The grown samples are free from any impurities. EDX analysis shows that with increase of NaBH4 ratio the lead content decreases but sulphur content increases.

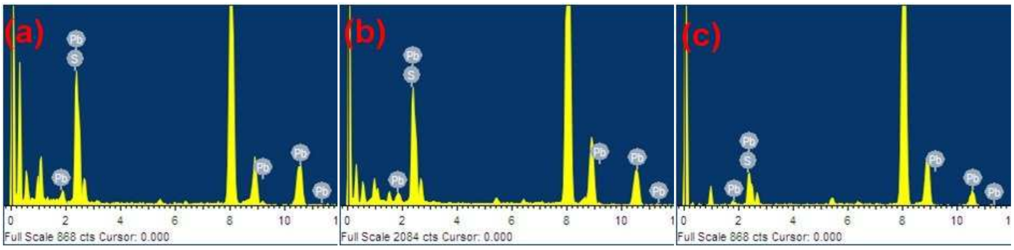

Figure 3: EDX pattern of PbS nanoparticles (a) 1:1:1 (b) 1:1:3 (c) 1:1:5

XRD pattern of grown samples is shown in figure 4. The diffraction peaks in 2θ plot is indexed with planes. The samples show cubic phase. The particle size of the grown samples is measured using Scherer's formula D = 0.9λ/ βcosθ where D= crystallite diameter (nm),λ= x-ray wavelength (0.154 nm for Cu Kα),β = Full-width at half max at Bragg angle of interest ,θ= Bragg Angle (angle of interest). The measured sizes are given in the table 1. XRD data shows peaks which agrees well with TEM data.

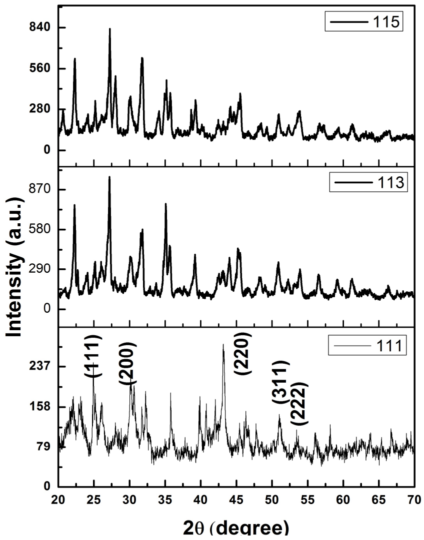

Figure 4: XRD pattern of PbS nanoparticles (a) 1:1:1 (b) 1:1:3 (c) 1:1:5

The FESEM micrographs of grown samples are displayed in figure 5. FESEM images show that particles are scattered at lower ratio. At higher reducing agent ratio nanoparticles form sheets which assemble.

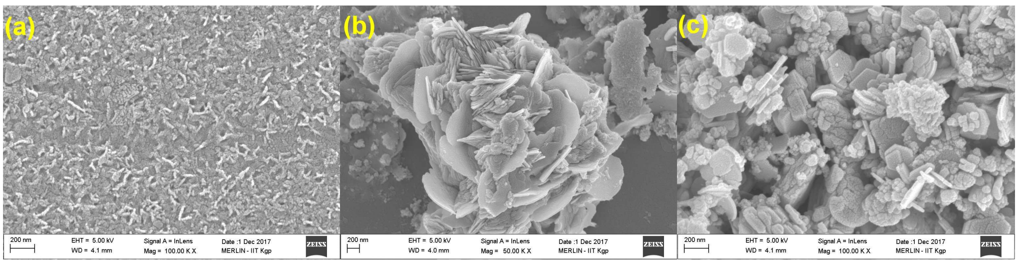

Figure 5: FESEM images of PbS nanoparticles (a) 1:1:1 (b) 1:1:3 (c) 1:1:5

Figure 6 shows vis-NIR absorption spectra of grown nanoparticles. The absorption edge is quite shifted to lower wavelength compared to bulk form of PbS. The band gap of the samples are calculated using Tauc relation $(\alpha h\nu)^2 = C(h\nu - E_g)$, where α is absorption coefficient, h is Plank constant, ν is frequency and E_g is band gap. It is observed that band gap increases with decrease of $NaBH_4$ ratio. Thus quantum confinement is greater for lower ratio $NaBH_4$ samples.

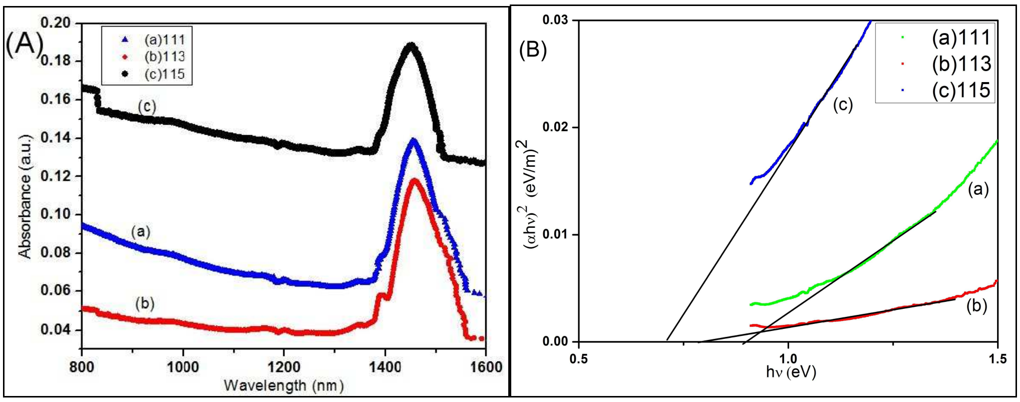

Figure 6:(A) Absorption spectra of PbS nanoparticles (a) 1:1:1 (b)1:1:3 (c)1:1:5 and **(B)** Band gap determination plot of grown samples (a) 1:1:1 (b)1:1:3 (c)1:1:5

Table 1 shows the characteristics of grown PbS nanoparticles.

Samples	Size (nm) from TEM	Size (nm)from XRD	Band Gap (eV)	Atomic% of (Pb and S) from EDX
PbS(1:1:1)	7	10	0.90	63:37
PbS(1:1:3)	8	13	0.82	61:39
PbS(1:1:5)	10	16	0.71	58:42

Table1: Summarization table

4. Conclusion

PbS nanoparticles are cost effectively prepared by chemical reduction method. Here reducing agent ratio affects the nanoparticle formation. In consequence band gap of the samples also decrease as particle size increases. The quantum confinement effect is confirmed from TEM as well as NIR absorption.

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