



# NON CONVENTIONAL SOLVOTHERMAL-ASSISTED SYNTHESIS OF NANO LEAD(II) SULFIDE FROM DITHIOCARBAMATE PRECURSOR BIS (N-PHENYL-1- NAPHTHYLDITHIOCARBAMATE) - CHARACTERIZATION

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**Abstract** - A non conventional solvothermal formation of PbS nano particles is reported with nickel dithiocarbamate as single source precursor. Morphology and composition of the nano product have been characterized by PXRD, SEM and EDX analysis. The precursor complex  $[Pb(pndtc)_2]$  (where  $pndtc = n$ -phenyl-1-naphthyl dithiocarbamate) are synthesized and characterized by elemental analysis, electronic, IR spectral,  $^1H$  and  $^{13}C$  NMR spectroscopy. Electronic spectral band of compound show bands at 435 nm due to charge transfer. For complex the  $\nu_{C-N}$  band are observed at  $1499\text{ cm}^{-1}$  in IR. In the  $^{13}C$  NMR spectra of the complexes the thioureide ( $N^{13}CS_2$ ) carbons resonate at 206.6 ppm.  $^1H$  NMR showed the observed deshielding of the  $-CH_2$  protons in the compounds attributed to the shift of electron density on the sulfur (or the metal) through the thioureide  $\pi$  system.

**Keywords:** dithiocarbamate, thioureide, solvothermal formation, scanning electron micrograph, powder diffraction.

## I. INTRODUCTION

Metal dithiolates are used as single source precursors for metal sulphides. Various iron, cobalt and nickel 1,1 dithiolates have been investigated as precursors in metal organic chemical vapour deposition [1-3]. The variety of dithiocarbamates bis (N-alkyl dithiocarbamate) nickel(II) complexes,  $[Ni(S_2CNH(n-pr)_2)]$ ,

$[Ni(S_2CNH(ipr')_2)]$  [4],  $[Zn(S_2CN(C_2H_5)_2)_2]$  [5,6],  $M[(S_2CN(C_2H_5)_2)_2]$  ( $M=Pb, Cd$ ) [7],  $Pb[(S_2CN(Bu_2'')_2)]$  [8],  $Cr[(S_2CN(C_2H_5)_2)_3]$  [9] and  $Cu[(S_2CN(Pr_2)_2)]$  [10] have been used as single source precursors for the production of thin layers of metal sulphides, viz., NiS, ZnS, PbS, CdS,  $Cr_2S_3$  and  $Cu_2S$  respectively by chemical vapour deposition method. Solvothermal synthesis has been used to produce nano structured products titanium dioxide [11], graphene [12], carbon sphere [13], chalcogenide [14] and other products. Synthesis of high quality CdS nano rods by solvothermal process and their photoluminescence has been reported [15]. The obtained product was investigated by PXRD, HRTEM, FE-SEM, UV-Vis spectrum and photoluminescence. Shape controlled synthesis of PbS microcrystals in large yields via a solvothermal synthesis [16]. A simple and facile solvothermal synthesis of Hierarchical PbS microstars with multidentric arms and their optical properties was investigated by PXRD, HRTEM, FT-IR, and photoluminescence. A conventional synthetic approach to prepare PbS nano particles via solvothermal method [17]. Synthesis of isotropic PbS nano particles from the single source precursor highly coordinate dithiocarbamate has been reported [18]. From these attempts, we have been focused to syntheses of PbS. Hence in this article we report the large scale PbS nano particles with high quality were successively synthesized by solvothermal process from lead(II) dithiocarbamates  $[Pb(pndtc)_2]$  and its subsequent use as single source precursor. From

this work material morphology and nature of PbS nanoparticles has been explored. The obtained nano lead(II)sulfide was investigated by PXRD, HRSEM, EDAX and IR analysis.

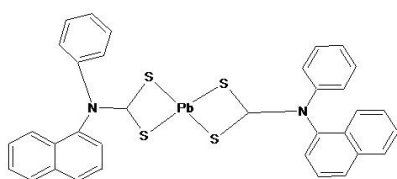
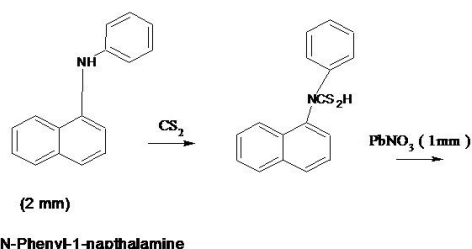
## II. EXPERIMENTAL

All the reagents and solvents employed were commercially available analytical grade materials and were used as supplied without further purification. N-Phenyl-1-Naphthylamine are supplied by Sigma Alrich. IR spectra were recorded on an Avatar Nicolet FT-IR spectrophotometer [Range 4000 - 400  $\text{cm}^{-1}$ ] as KBr pellets. Electronic spectra were recorded in  $\text{CH}_2\text{Cl}_2$  on a Hitachi U-2001 double beam spectrometer.  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AMX-400 spectrometer at room temperature using  $\text{CDCl}_3$  as solvent. Scanning electron micrographs of the sample are recorded with JOEL JSM-5610 v microscopes.

### II.1 Preparation of Bis (n-phenyl-1-naphthyl dithiocarbamate)

#### lead(II); $[\text{Pb}(\text{pndtc})_2]$

The compound  $[\text{Pb}(\text{pndtc})_2]$  was prepared by mixing N-phenyl-1-naphthylamine (4 mmol, 0.60 mL) and carbon disulphide (4 mmol, 0.24 mL) in ethanol under ice cold condition ( $5^\circ\text{C}$ ). To the yellow dithiocarbamic acid solution, aqueous solution of  $\text{Pb}(\text{NO}_3)_2$  (2 mmol, 0.660 g) was added with constant stirring. A white solid separated from the solution, which was filtered, washed with alcohol and was then dried in air. (Yield: 70%, dec.  $186^\circ\text{C}$ , anal. calc. for  $\text{C}_{34}\text{H}_{24}\text{N}_2\text{PbS}_4$  (796.0): Pb, 26.0; C, 51.3; H, 3.0; N 3.5%; found: Pb, 26.1; C, 51.9 H 3.6 N 3.9



### II.2 Synthesis of PbS nanoparticles by solvothermal decomposition method using $[\text{Pb}(\text{pndtc})_2]$ as a single source precursor;

A mixture of N-phenyl-1-naphthylamine dithiocarbamate (1 g) as a clear solution in chloroform (100 mL) was heated with diethylenetriamine (2 mL) at  $80^\circ\text{C}$ . The black nano PbS was obtained as a suspension. The precipitate was filtered and washed with ether, chloroform and the nanoparticles were collected and dried.

## III. RESULTS AND DISCUSSION

### III.1 Spectral studies

#### III.1.1 Infrared spectrum

Infrared spectra of the complex is shown in Fig.1 Some important spectral bands are presented in Table 1. The spectrum show two characteristic absorptions due to  $\nu_{\text{C-N}}$  and  $\nu_{\text{C-S}}$  vibrational modes. The  $\nu_{\text{C-N}}$  has been used as a measure of the contribution of the thioureide form to the structure of dithiocarbamate. A strong band around  $1499 \text{ cm}^{-1}$  is observed in all the complexes due to  $\nu_{\text{C-N}}$  stretching and the band around  $1000 \text{ cm}^{-1}$  is due to  $\nu_{\text{C-S}}$  stretching in the complexes. The phenyl ring C-H out of plane vibrations appear in the region:  $600-736 \text{ cm}^{-1}$ . The  $\nu_{\text{C-H}}$  aliphatic stretching appears around  $2950 \text{ cm}^{-1}$  in the complex [19]

Table 1 Infrared spectral data ( $\text{cm}^{-1}$ )

Complex	$\nu_{\text{C-N}}$ (thioureide)	$\nu_{\text{C-S}}$	Aromatic $\nu_{\text{C-H}}$	Aliphatic
$[\text{Pb}(\text{pndtc})_2]$	1499	1097	3013-3074	2852-2914

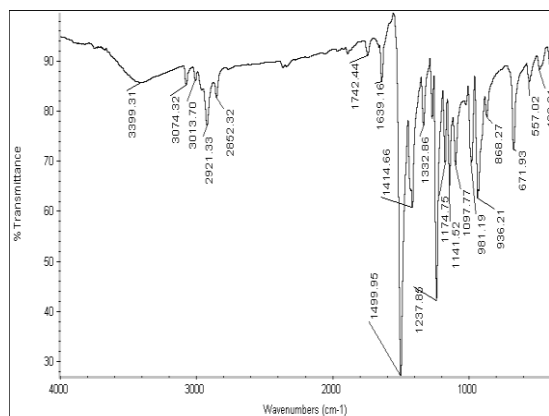


Fig 1 IR spectrum of [Pb(pndtc)<sub>2</sub>]

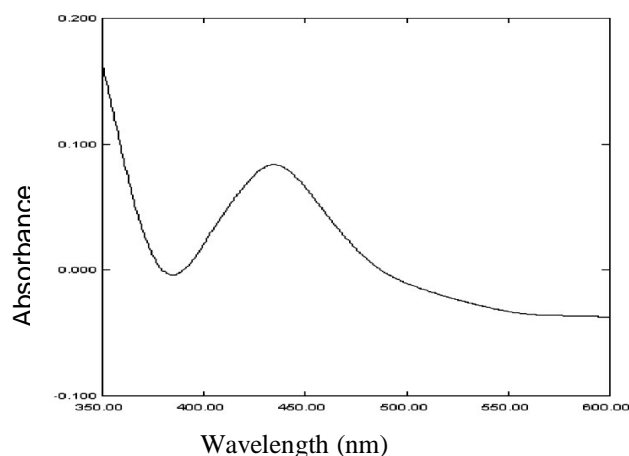


Fig 2 Electronic spectrum of [Pb(pndtc)<sub>2</sub>]

### III.1.2 Electronic spectrum

Electronic spectrum of the complex is shown in **Fig 2** and the corresponding  $\lambda_{\max}$  values are presented in **Table 2**. The parent lead dithiocarbamate complexes are colourless, The electronic spectra of the parent complex show charge transfer only. The ligand transitions of the dithiocarbamates are observed below 350 nm. The charge transfer transition in [Pb(pndtc)<sub>2</sub>] are observed at 435 nm[20]

Table 2 Electronic spectral data

Complex	$\lambda_{\max}$ (nm)
[Pb(pndtc) <sub>2</sub> ]	435

### III 1.3 NMR SPECTRUM.

NMR spectral data of the synthesized compound is given along with the splitting patterns.

#### III.1.3.1 <sup>1</sup>H NMR spectrum

<sup>1</sup>H NMR spectra of the complex is shown in **Fig 3** and the chemical shifts is given in **Table.3** <sup>1</sup>H NMR spectra of compound show the phenyl CH<sub>2</sub> proton signals at, 5.20 ppm, For the complex the aromatic protons resonate in the region 7.28-7.34 ppm... The equatorial proton attached to  $\beta$  and  $\gamma$ -carbons appear in the region of 1.71-2.03 ppm. The signals around 1.57 ppm are assigned to the  $\delta$ -protons[21].

Complex	Phenyl ring protons	$\alpha$ -CH	$\beta$ -CH	$\gamma$ -CH <sub>2</sub>	$\delta$ -CH <sub>2</sub>
[Pb(pndtc) <sub>2</sub> ]	7.28-7.34	5.04	1.71-2.03	-	1.57

Table 3 <sup>1</sup>H NMR spectral data (ppm)

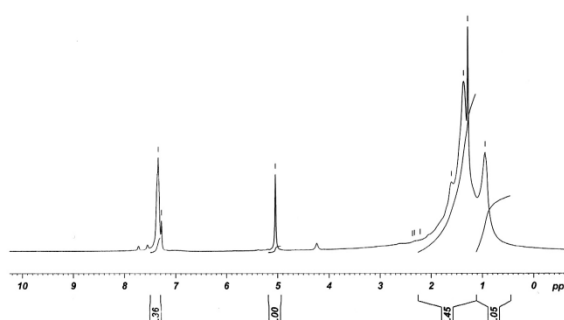


Fig 3 <sup>1</sup>H NMR spectrum of [Pb(pndtc)<sub>2</sub>]

#### III.1.3.2 <sup>13</sup>C NMR spectrum

<sup>13</sup>C NMR spectrum is shown in **Fig. 4** and the chemical shifts is given in **Table.4**. The most important chemical shifts of thioureide carbons (S<sub>2</sub><sup>13</sup>CN) are observed at 206.6, The mesomeric shift of electron density from dithiocarbamate moiety towards the metal



626,1047,1384  $\text{cm}^{-1}$  is assigned to hetero polar diatomic molecules of PbS.

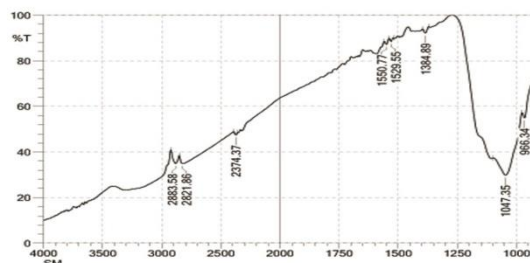


Fig.6 FT-IR spectrum of nano PbS

### III 1.3.5 SEM-EDX analysis

Fig 7 is a scanning electron micrograph of nano PbS and Fig 8 shows a typical EDX pattern of PbS nano particles

The elemental composition of PbS nano particles determined using SEM – energy dispersive (SEM) spectroscopy by performing the spot measurement on particles. The major peaks are due to the presence of Pb along with sulphur. The elemental ratio of Pb to S in PbS nano particles is 58.6 : 41.4

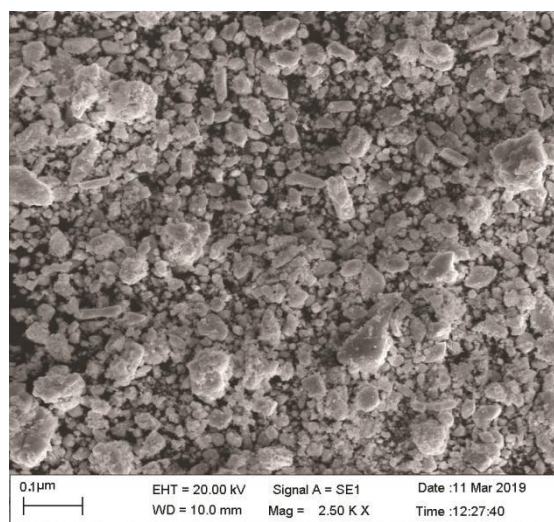


Fig.7 SEM IMAGE OF PbS

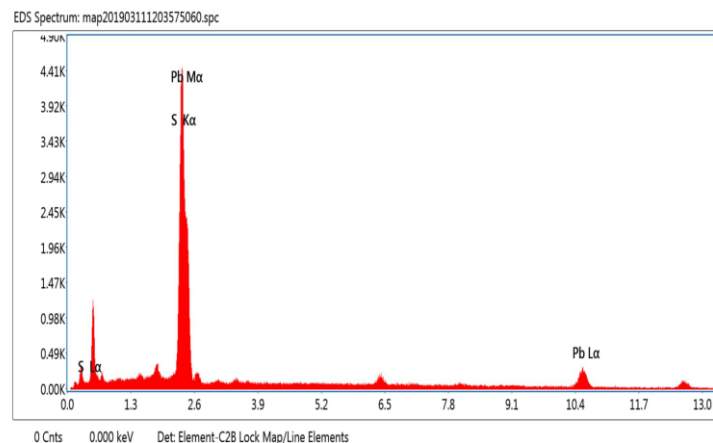


Fig 8 EDX pattern of PbS nano particles

## IV. CONCLUSION

I demonstrated that solvothermal method can be used to prepare a good quality nano PbS from dithiocarbamate as precursor. This paper presents production of PbS nano particles via solvothermal decomposition of  $[\text{Pb}(\text{pndtc})_2]$  at  $80^\circ\text{C}$ . The nano particles have regular shape and high purity showed by PXRD of the sample. EDAX pattern of nano PbS showed major peaks due to the presence of Pb along with sulphur in the ratio of 58.6 : 41.4

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