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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)$_2$](wherepndtc=n-phenyl-1-napht hyldithiocarbamate) are synthesized and characterisized by elemental analysis, electronic, IR spectral, ^{1}H and ^{13}C NMR spectroscopy. Electronic spectral band of compound show bands at 435 nm due to charge transfer. For complex the υ_{C-N} band are observed at 1499 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.^{1}H NMR showed the observed deshielding of the – CH$_2$ protons in the compoundis attributed to the shift of electron density on the sulfur (or the metal) through the thioureide π system.

Keywords: **dithiocarbamate, thioureide, solvothermalformation, scanning electron micrograph, powderdiffraction.**

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 dithiocarbamatesbis(N-alkyldithiocarbamato) 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 CdSnano rods by solvothermalprocess 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 PbSmicrocrystalsin large yields via a solvothermalsynthesis[16]. A simple and facile solvothermal synthesis of HieraricalPbSmicrostars with multidentric arms and their optical propertieswas investigated by PXRD, HRTEM, FT-IR, and photoluminescence. A conventional synthetic approach to prepare PbSnano particles via solvothermalmethod[17]. Synthesis of isotropic PbSnano particles from the single source precursor highly coordinate dithiocarbamatehas been reported[18]. From these attempts,we have been focused to syntheses of PbS. Hence in this article we report the large scale PbSnano particles with high quality were successively synthesed by solvothermalprocess from lead(II)dithiocarbamates [Pb(pndtc)$_2$] and its subsequent use as single source precursor.From

International Journal of Engineering Applied Sciences and Technology, 2019
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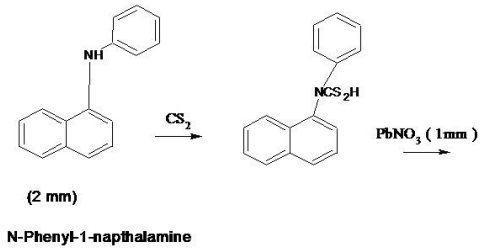
this work material morphology and nature of PbSnano particles has been explored. The obtained *nano*lead(II)sulfide was investigated by PXRD, HRSEM,EDAX and IR analysis.

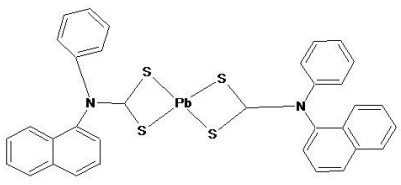
II. EXPERIMENTAL

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 cm^{-1}] as KBr pellets. Electronic spectra were recorded in CH_2Cl_2 on a Hitachi U-2001 double beam spectrometer. ^1H, ^{13}CNMR spectra were recorded on a Bruker AMX-400 spectrometer at room temperature using $CDCl_3$ as solvent. Scanning electron microgrphs of the sample are recorded with JOEL JSM-5610 v microscopes.

II.1 Preparation of Bis (n-phenyl-1-naphthyldithiocarabamato) lead(II); [Pb(pndtc)$_2$]

The compound [Pb(pndtc)$_2$] was prepared by mixingN-phenyl-1-naphthylamine (4 mmol, 0.60 mL) and carbon disulphide (4 mmol, 0.24 mL) in ethanol under ice cold condition (5°C). To the yellow dithiocarbamic acid solution, aqueous solution of $Pb(NO_3)_2$ (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°C, anal. calc. for $C_{34}H_{24}N_2PbS_4$ (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 [Pb(pndtc)$_2$] as a single source precursor;

A mixture of N-phenyl1-naphthalaminedithiocarbamate (1 g) as a clear solution in chloroform (100 mL) was heated with diethylenetriamine (2mL) at 80°C. The black nanoPbS 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 Table1. The spectrum show two characteristic absorptions due to ν_{C-N} and ν_{C-S} vibrational modes. The ν_{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 cm^{-1} is observed in all the complexes due to ν_{C-N} stretching and the band around 1000 cm^{-1} is due to ν_{C-S} stretching in the complexes. The phenyl ring C–H out of plane vibrations appear in the region: 600-736 cm^{-1}. The ν_{C-H} aliphatic stretching appears around 2950 cm^{-1} in the complex[19]

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

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

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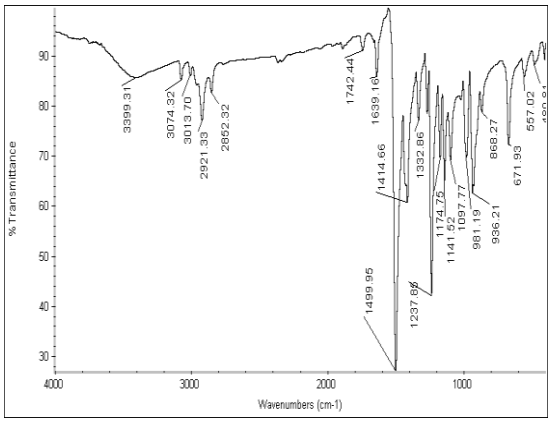

Fig 1 IR spectrum of $[Pb(pndtc)_2]$

III.1.2 Electronic spctrum

Electronic spectrum of the complex is shown in **Fig 2** and the corresponding λ_{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 $[Pb(pndtc)_2]$ are observed at 435 nm[20]

Table 2 Electronic spectral data

Complex	**λ_{max} (nm)**
$[Pb(pndtc)_2]$	435

Complex	**Phenyl ring protons**	**α–CH**	**β–CH-**	**γ–CH_2**	**δ–CH_2**
$[Pb(pndtc)_2]$	7.28-7.34	5.04	1.71-2.03	–	1.57

Table 3 ^{1}H NMR spectral data (ppm)

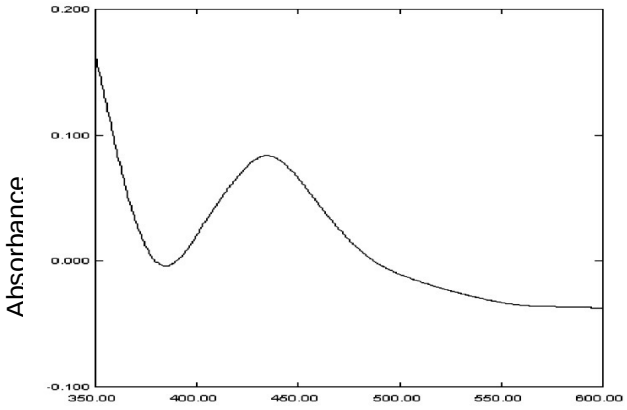

Fig 2 Electronic spectrum of $[Pb(pndtc)_2]$

III 1.3 NMR SPECTRUM.

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

III.1.3.1 ^{1}H NMR spectrum

^{1}H NMR spectra of the complex is shown in **Fig 3** and the chemical shifts is given in **Table.3** ^{1}H NMR spectra of compound show the phenyl CH_2 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 β and γ-carbons appear in the region of 1.71-2.03 ppm. The signals around 1.57 ppm are assigned to the δ-protons[21].

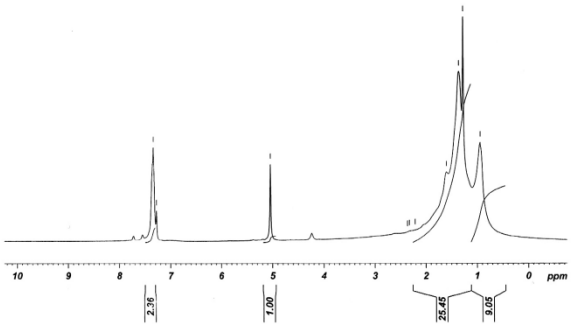

Fig 3 ^{1}H NMR spectrum of $[Pb(pndtc)_2]$

III.1.3.2 ^{13}C NMR spectrum

^{13}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 ($S_2{}^{13}CN$) are observed at 206.6, The mesomeric shift of electron density from dithiocarbamate moiety towards the metal

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centre contributes to the upfield shift from the normal chemical shift of $[Ni(dtc)_2]$ complexes (206-210 ppm) [22]. The observation is supported by the higher $\nu_{(N-C)}$ values observed (in IR) for complexes (2) and (3) in the present study. The common spin-lattice relaxation mechanism for ^{13}C results from dipole – dipole interaction with directly attached protons. Thus, non-protonated carbon atoms have longer T_1 relaxation times, which results in less intense signals, and this phenonmenon is clearly observed for thioureide ($N^{13}CS_2$) and NCS^- carbon signals, which are of very low in intensity. From the ^{13}C NMR spectra of the complex the chemical shift of the carbon atom of the NCS_2 moiety can be correlated to the extent of π-bonding in NCS_2 fragment [22]. In the IR spectra, ν_{C-N} (thioureide) vibration is usually observed at 1500 cm^{-1} for dialkyldithio-carbamates and 1450 cm^{-1} for phenyl substituted dithorcarbamates. The normal valence state transition metal dithiocarbmates have NCS_2 (thioureide) signal above 202 ppm and the main group metal dithiocarbamates have the NCS_2 signals below 202 ppm. Generally, higher ν_{C-N} (thioureide) correlates with lower NCS_2 chemical shifts δ ($N - {}^{13}CS_2$). Deprotonation of secondary amine by the addition of CS_2 is the first step in the preparation of dithiocarbamate complexes and this deprotonation leads to high C=N bond order which results in a higher value ν_{C-N} and a low δ ($N^{13}CS_2$) values. Complex shows ν_{C-N} band at 1499 cm^{-1} and the NCS_2 signal is observed at 206.6 ppm. In compound naphthalene ring carbons appears at the range of 127.9 -135.1 ppm[23].

Complex	Phenyl ring	$N^{13}CS_2$
$[Pb(pndtc)_2]$	127.9-135.1	206.6

Table 4 ^{13}C NMR spectral data (ppm)

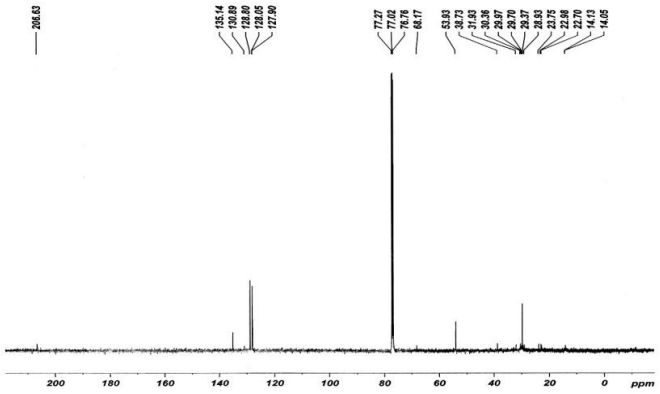

Fig.4 ^{13}C NMR spectra of $[Pb(pndtc)_2]$

III.1.3.3 Powder XRD measurement

Powder XRD pattern at room temperature is shown in **Fig. 5.** All the diffraction peaks in the XRD can be indexed to the pure PbS. The peaks correspond to (111), (200), (220), (311), (222), (400), (331) (420) and (422) which are in good agreement with the JCPDS-pattern (JCPDS File No.: 05-0592) for PbS [24]. All the diffraction peaks showed pure cubic phase of PbS The highest peak intensity indicate the grains are preferentially oriented along (111) direction. Broadened signals indicate diminished dimensions of the particles. Average crystal diameter of the nano PbS are estimated to be 21 nm by Debye-Scherrer formula from the XRD pattern [25].

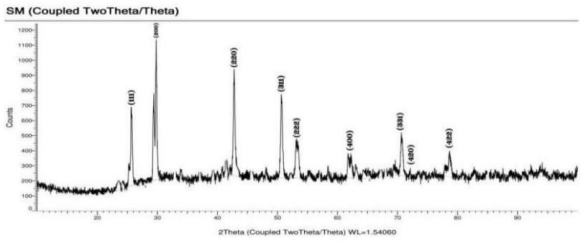

Fig.5 PXRD of $[Pb(pndtc)_2]$

III 1.3.4 IR SPECTRUM

The infrared spectrum of nano lead(II) sulphide is shown in **Fig 6** In the spectrum the broad band was appeared in the range 2883-2821 cm-I is assigned to O-H bending vibration in Pbs. It indicates Pbs absorbs moisture. The peaks observed at

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626,1047,1384 cm^{-1} is assigned to hetero polar diatomic molecules of Pbs.

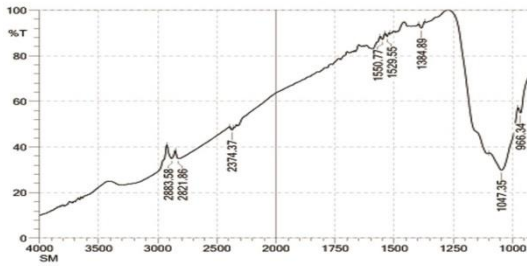

Fig.6 FT-IR spectrum of nano PbS

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

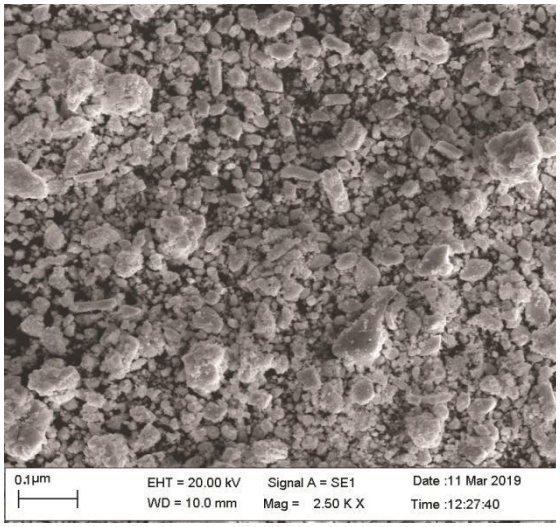

Fig.7 SEM IMAGE OF PbS

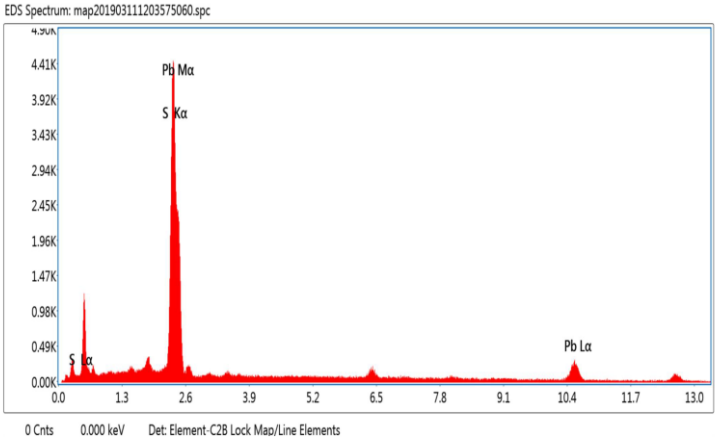

Fig 8 EDX pattern of PbS nano particles

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 $[Pb(pndtc)_2]$ at 80°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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