Synthesis and characterization

Of

Nickel Sulphide

A Dissertation report

Submitted in partial fulfilmen

Of

The Degree of M.Sc. (Physical Chem

By

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To the

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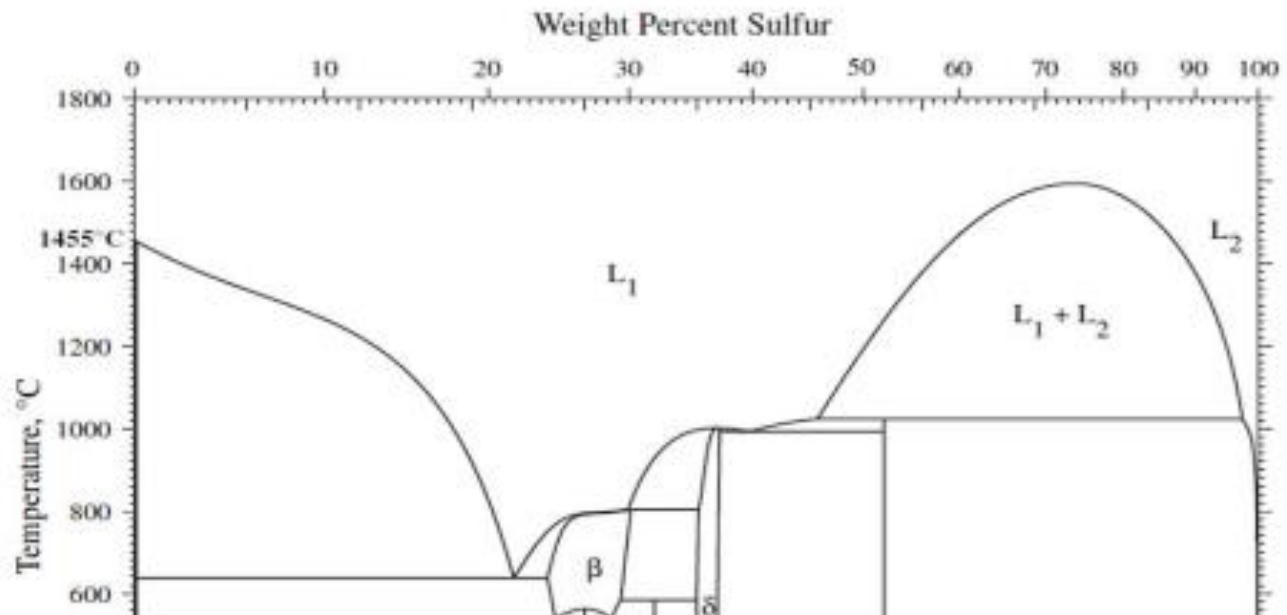
INTRODUCTION

Nickel sulphide as one of the transition metal sulphide has got a lot of attention due to it's distinctive electro first order phase transition from low temperature antiferromagnetic to a high temperature paramagnetic, cat sulphurisation and exhibit various application such as for solar cells devices, common cathode for recharg on[1].

Figure 1 nickel sulphide.

Nickel sulphide display various compositional structure and magnetic phase behaviour depending on its stoi Ni3S2,Ni3+xS2,Ni4S3+x,Ni6S5, Ni7S6, Ni9S8, Ni3S4, NiS2,NiS as shown in figure 2. [22] The phases that r phase which is low temperature rhombohedral (β-NiS) crystal structure. The high temperature is (α-NiS) cry (α-NiS) is antiferromagnetic which show a metal insulator transition with a change in magnetic susceptibili Below a Neel temperature α-NiS magnetic moment is around 1.7μB,but above Neel temperature magnetic suggested that antiferromagnetic particles during uncompensated number of spins of two sub –lattice shoul paramagnetic and weak ferromagnetic . Formation of nickel vacancies are related to the structure of NiAs N catalyst which shows good catalyst properties.



shows linkage of ions in unit cell. The metal ions and anions are located on interpenetrating simple hexago lattice.[4] The transition metal atoms take position i the octahedral holes in close packed hexagonal array of a transition metal atom I the trigonal prism geometry . The octahedral share faces which result with formati NiAs has the ability to accommodate addition transition metal atom in the trangonal bipyramidal holes an randomly or on the C axis perpendicularly

In millerite rhombohedral structure metal distance is 2.25A distance which are too small indicating intermet rhombohedral along C axis shows triangle of sulphur atom arranged at lattice point. The nickel atom are co- form two side of the corner to give trigonal prismatic column atom C sulphur is in five fold shown in figur

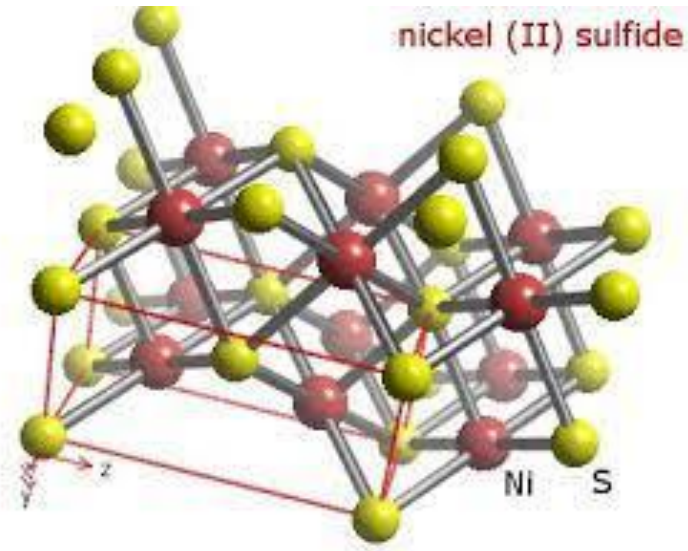


Figure 3 Solid state structure of nickel sulphide.

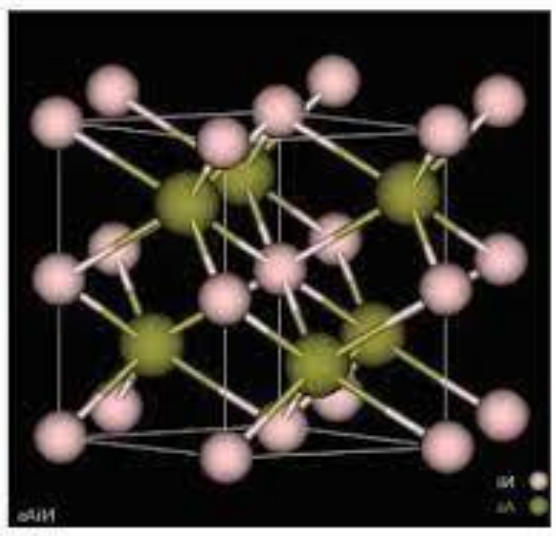


Figure 4 **NiAs type structure of nickel sulphide**

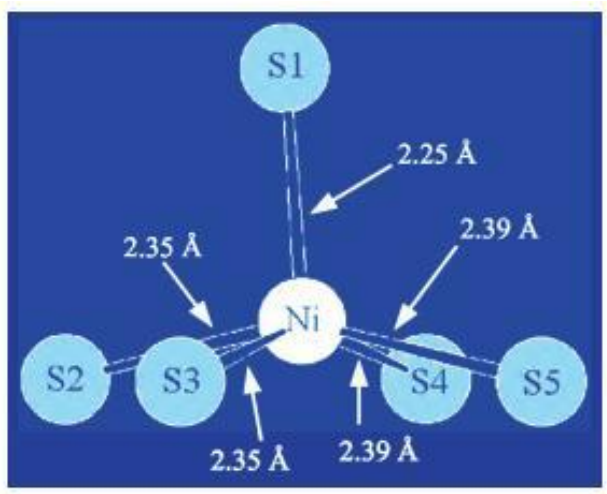


Figure 7 T**he local structural environment of the Ni atom which is penta coordinated with S**

Ni atom have five nearest neighbourhood S atom occupy the corner with a geometry of square pyramidal. L
atom which is penta co-ordinated with Satom millerite NiS .In this pyramidal geometry.[5]

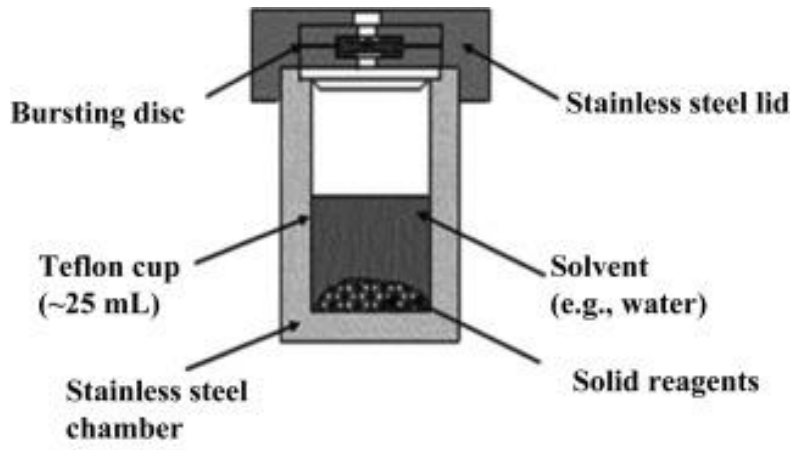
2) Synthesis methods

2.1) Hydrothermal method

Rekha Bhardwaj, Ranjanajha medha Bushan and Ajay kumar had used this method to synthesised nickel sul
below:

0.3 M nickel acetate tetra hydrate and sulphur powder was dissolved in deionised water. Stirred for 5 hour a
autoclave 140 degree Celsius for 14 hour. Black colour precipitate formed washed the precipitate with ethan
was produced with structure geometry rhombohedral. Sheet and cuboid nanostructure with size of grain wa

Niasari –Ghaleh Banaiean , Fatemeh davar Hamid emadi, they had studied nickel sulphide by hydrotherma
and thio glycolic acid 200 mL distilled water autoclave taflon in electric oven. black ppt formed with rho
with 30nm in size[7]. Another scientists Yuan Gao,Ka Wang and Shancheng Yan had studied by nickel sulph
and they followed the procedure as follows: 1mM Ni(NO3)2.6H2Oadded intaflon autoclave and 25 mLdeio
heated 180 degree Celsius ppt formed rhombohedral in structure with polyhedral block structure and 25 n



10 mL nickel acetate and 2ml 0.1 mL triethanolamine(TEA) was added to that 10mL 1M Na2S dropwise sti
washed with and ethanol. The black colour ppt was formed. NiS produced polycrystalline with orthorombic
shaped nanoparticle was formed with particle size was 20 nm.[8]

2.3)Sonochemical method

Matjaz krishi,Brina Dojer,Saso Gujergyeti,Janja krishti had studied nickel sulphide catalyst by sonochemica
followed is described below: 2.49g of Ni (CH3COO)2 · 4H2O and 0.75g C2H5NS was added in 50 mL wa
ambient atmosphere for 1 hour using a sonicator of vcx600 at a different amplitude 30%,50%,70% and 90%
after the some minute of sonication and amplitude. Ppt obtained was centrifused and washed with ethanol a
30% and 50%, shows incomplete reaction with green colour solution but 70% and 90%. Shows complete r
Further 70% used for synthesis. The nickel sulphide produce is crystalline in nature with rhohoderal phase
shaped with 13 -14 nm.[9]

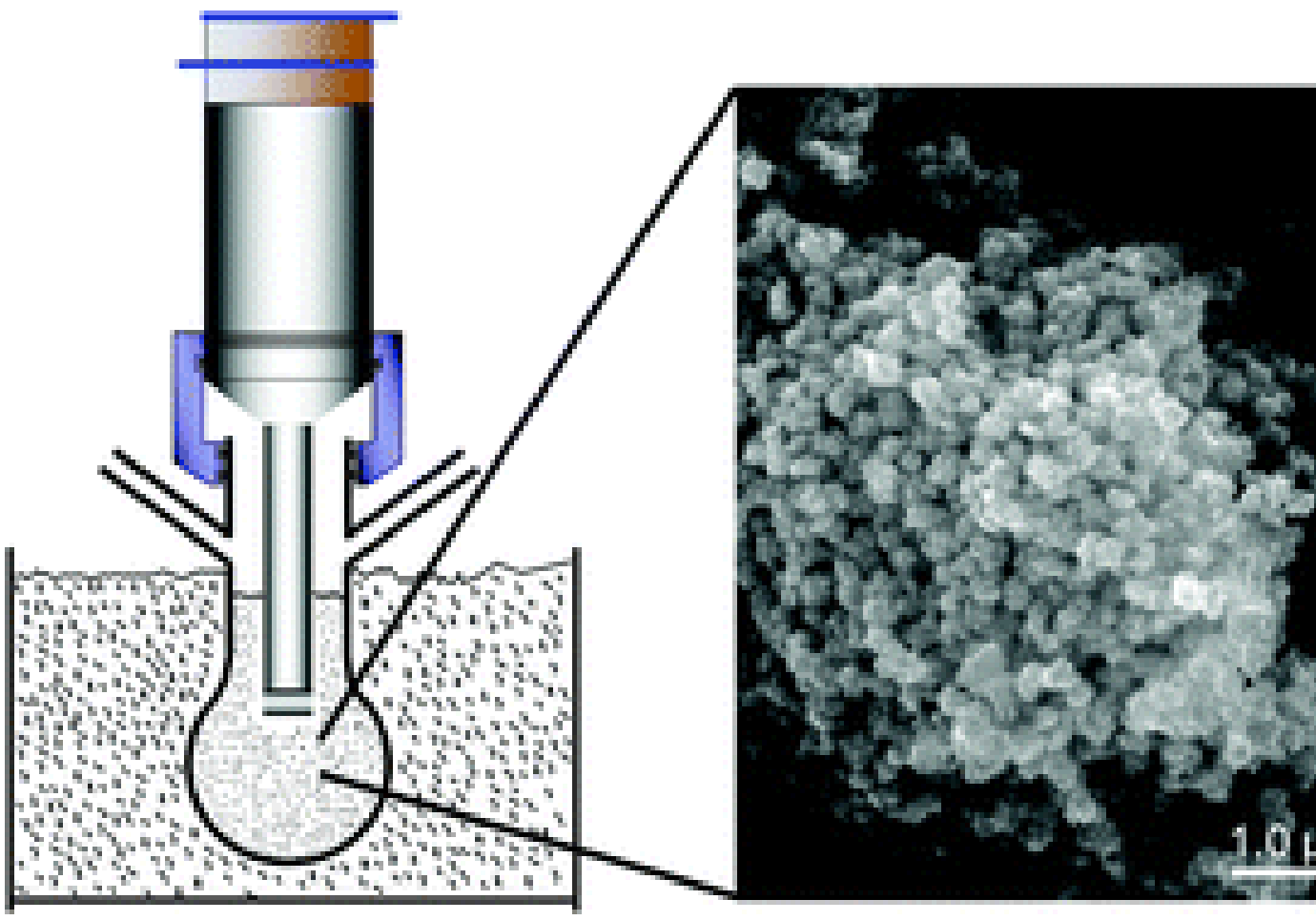


Figure 9 shows diagram of sonochemical method

2.4) Cyclic microwave radiation

Masoud salvati- niasari –Ghaleh Banaiean ,Mona fared Hamid emadi morkza Enhessari had studied nickel s
sulphide cyclic microwave radition method and the procedure they follows is given below .

This synthesis were performed in two step.

First step prepartation of Ni(HAP)2 as a precursor

6g of Ni(OAC)2 was dissolved in 50 ml of ethanol in a beaker .Then 8.2 mL of 2- hydroxyl acetaphenon
the solution of 2- hydroxy acetaphenone added dropwise to the solution of Ni(OAC)2 and stir
as a Ni ions source.

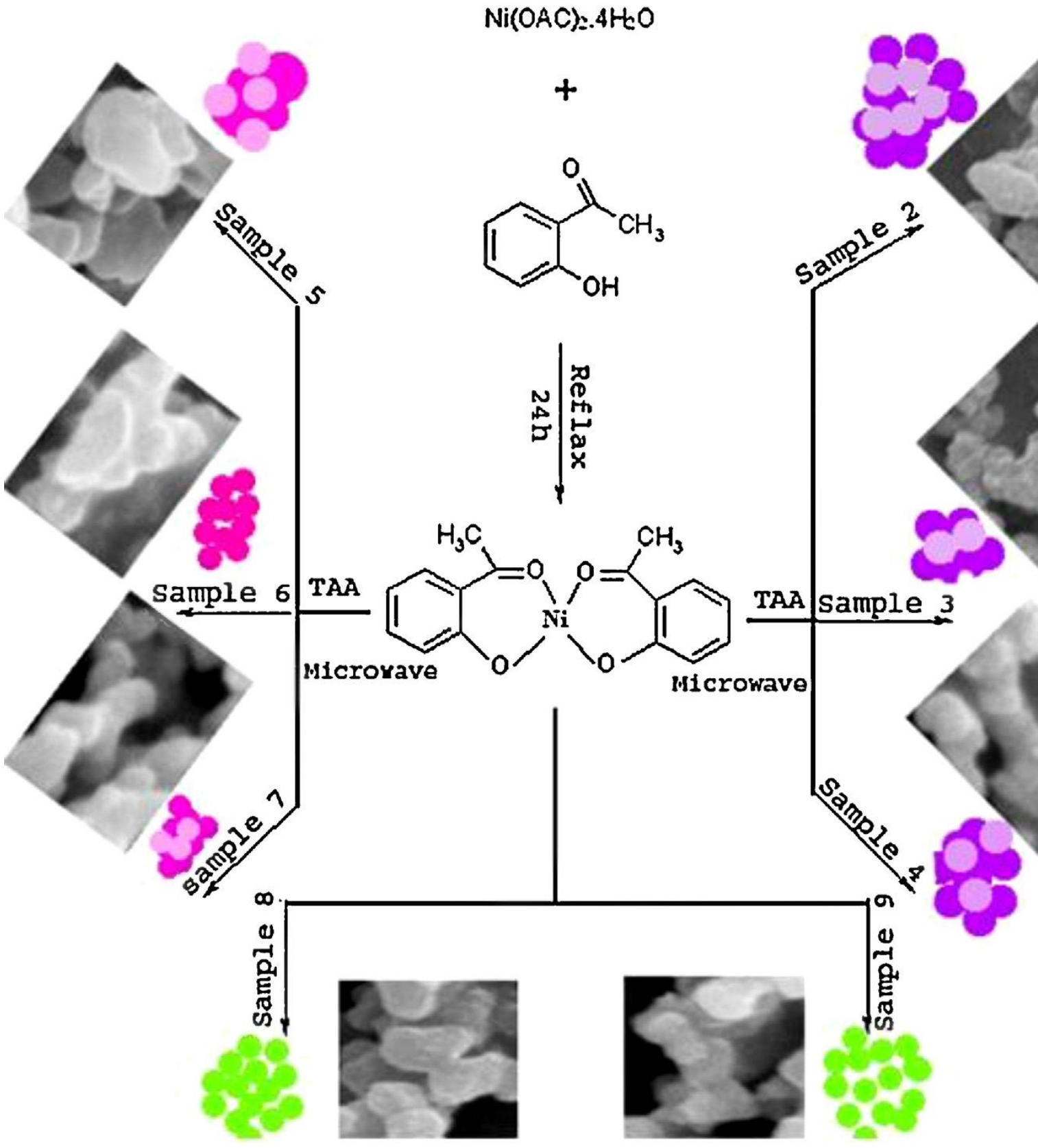


Figure 10

2.5)Synthesis by using imidazole dithio carbonate complexes

P.A. Ajabade ,A.NQOMBOLO had studied nickel sulphide catalyst by imidazole dithio carbonate complexe given below

Synthesis is done by two step

First step synthesis of nickel(II) imidazole dithiocarbonate complexes

it was prepared by 2.5mmol Nicl2 dissolve in 10 mL methanol added 10 ml of imidazole dithiocarbonate so with distilled water recrystallise with solvent.

Second step preparation of nickel sulphide nanoparticle

0.40 g metal precursor dissolved in 4mL TOP and than injected 3 g hot hexadecylamine at 220degree Cel

.

Step 2. Synthesis of Ni(II) Dithiocarbamate Complexes. 5mmol

(0.45g) of potassium salts of anisidine dithiocarbamate, dibenzyl dithiocarbamate (0.57 g), and butyl d
dissolved in 10mL of methanol in a beaker. 2.5mmol (0.59 g) of NiCl2 was dissolved in methanol in a se
mixed and stirred

for 1–3 hours. Product filtered and washed with water followed by diethyl ether and dried.The co
dithiocarbamate from dibenzyl dithiocarbamate, and [Ni(L3)2] from butyl dithiocarbamate ligand.

.

Step 3 Synthesis of NiS Nanoparticles.

The nickel complexes (0.2 g) were dissolved in 2mL tri-n-octylphosphine (TOP) and injected into 2
220∘C.The temperature was maintained for 1 hour at 220∘C. After this, the mixture was allowed to cool to
precipitate the NiS nanoparticles. The HDA-capped NiS nanoparticles were separated by centrifugatio
methanol and dried. The nanoparticles are labelled as NiS1 from nickel(II) anisidine dithiocarbamate comp
dibenzyl dithiocarbamate complex ([Ni(L2)2]), and NiS3 from nickel(II) butyl dithiocarbamate complex ([N
colour with square planar spherical in shaped with 12-38 nm particle size[12].

2.7) Synthesis by benzimidazole dithiocabomate Ni(II) Complex

C. S. THANGWANE, T. XABA*, M. J. MOLOTO had used this method to synthesise nickel sulphide proc

Step1 sodium hydroxide (0.78 g, 0.02 mol) dissolve distilled water and cold benzimidazole (2.36 g, 0.02 m
to that carbon disulphide (1.52 ml, 0.02 mol) drop-wise stirred for further 12 hrs at 25 °C. A 40 ml solutio
mol) added drop-wise into the corres dithiocarbamate ligand. The mixture was refluxed for 4hours at 60 °C

Step 2 2-methylbenzimidazole dithiocarbamate nickel(II) complex was prepared by the sausing 2-methylbe

Step 3 The complex (0.3 g) dissolved in 5.0 ml of tri-octylphosphine (TOP). The solution was Injected into
(HDA) (6.0 g) in a three-necked flask + excess methanol ppt formed

The ppt formed was black in colour rhomboheral spherical or rod shaped structure with 10-15 nm in size.[13

2.8) Solid phase method

Ni(acac)2 and alkyl sulfylhydrylinto that vaccenic acid solvent was added the ppt formed black in colour rh
70nm.(*98960B.Pdf*, n.d.)

2.9) Hot injection method

Rajan Karthikeyan,† Dheivasigamani Thangaraju,‡Natarajan Prakash,† and Yasuhiro
Hayakawa had done this method of synthesise of nickel sulphide and procedure of synthesise as follows

1mmol Ni(N03)2.6H2O was added to oleylamine (10mL) in three necked flask heated 100degree Celsius f

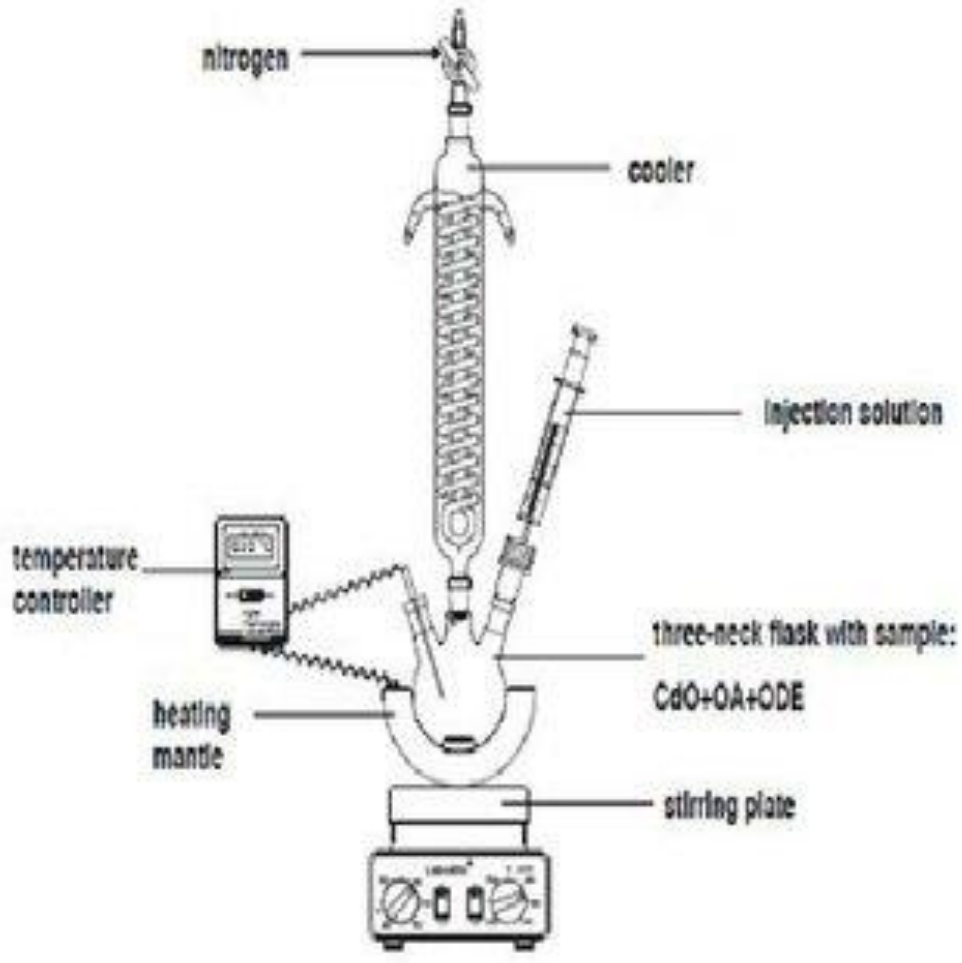


Figure11 shows schematic diagram of hot injection method

2.10)In situ sulphurisation and electrospinning method

Ibrahim M. Maafa had synthesised nickel sulphide by above method and procedure he had followed is give

In Polyvinylpyrroliden ethanol was added into that nickel acetate tetrahydrate and HH4S dropwise
electrospinning equipment the black ppt formed nanofibre or nanorod type structure wit

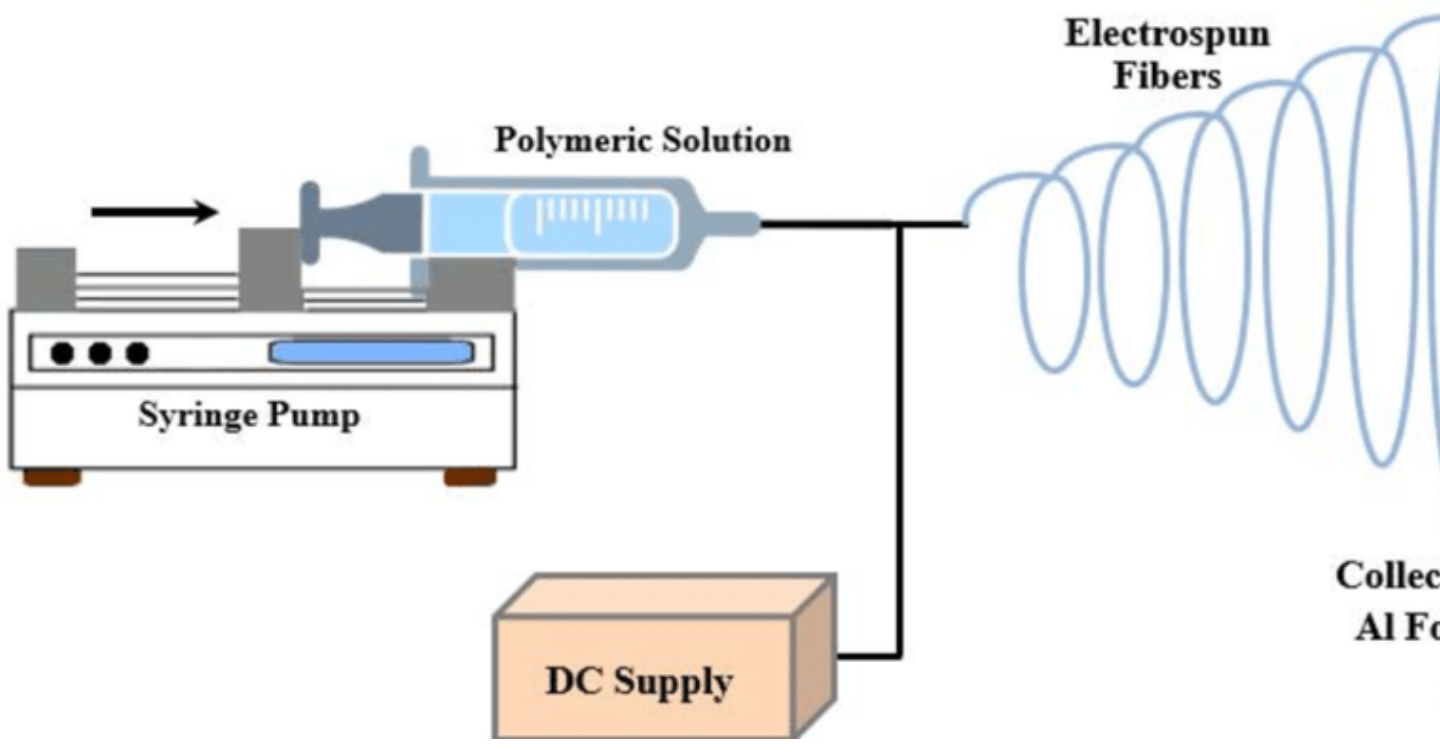


Figure 12 show schematic diagram of electrospinning method

nm and in nanopowder form.[16]

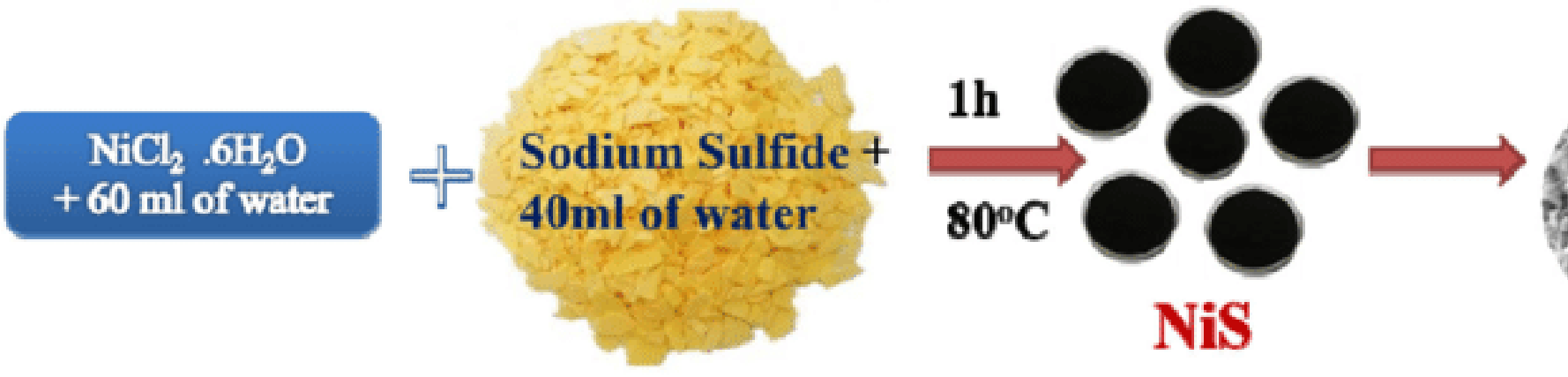


Figure 13 shows schematic diagram of coprecipitation method

2.12) Laser irradation method

Tai-Feng Hunga,b,*, Zu-Wei Yina,c, Sophia B. Betzlera, Wenjing Zhenga,d, Jiwoong Yanga, Haimei Zheng

Yina,c, Sophia B. Betzlera, Wenjing Zhenga,d, Jiwoong Yanga, Haimei Zheng had used the above mentione

catalyst and the procedure they follows is given below

10 mmol CH_3CSNH_2 was dissolved in DI water under magnetic stirrer and to that 3mL (HOCH2CH2)3N a

added. irradiated the mixture with laser the pulse energy of 700 mJ, frequency of 10 Hz, and pulse width of

C_2H_5OH drying in air. NiS nanostructure synthesized in 2h, 4h, and 6h were hereafter abbreviated as NiS-2h

The nanopowder with size 20-30nm.[17]

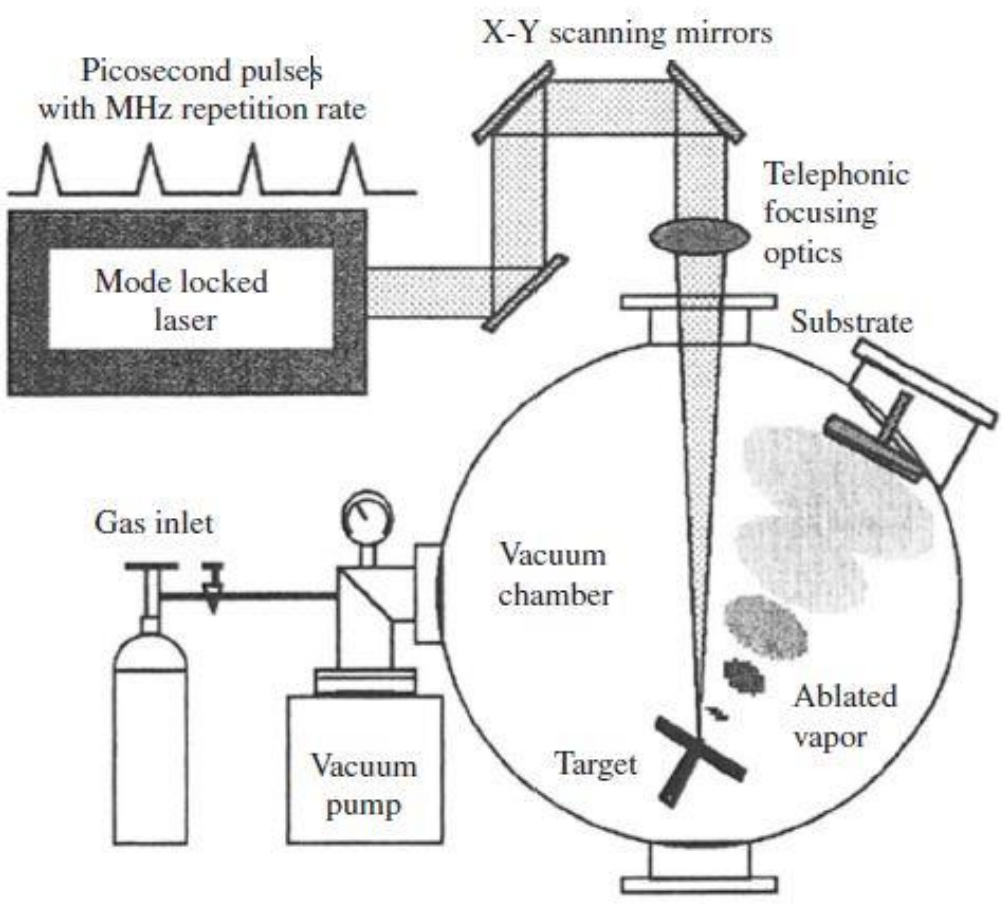


Figure14 shows schematic diagram of laser ablation method

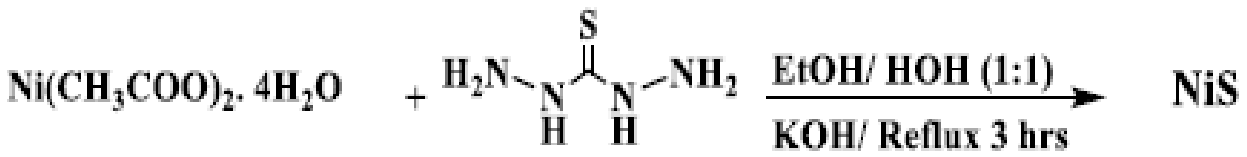


Fig 15reaction formation of NiS

Ni9S8 orthorhombic phase with particle size 15.76nm.

2.14) Non hydrolytic method of Nickel Sulphide

Mitchell G. S. da Silva, Celisnolia M. Leite, Marco A. L. Cordeiro, Valmor R. Mastelaro, and Edson R. Leit

hydrolytic method in this method N-methyl-2-pyrrolidone (NMP)

Was used as solvent, nickel(II) acetylacetonate [$Ni(acac)_2$] as Ni precursor, and 1-dodecanethiol (DDT) and

reaction was taken palce in MW reactor under irradiation power 1000 w for 1 hour the ppt formed was w

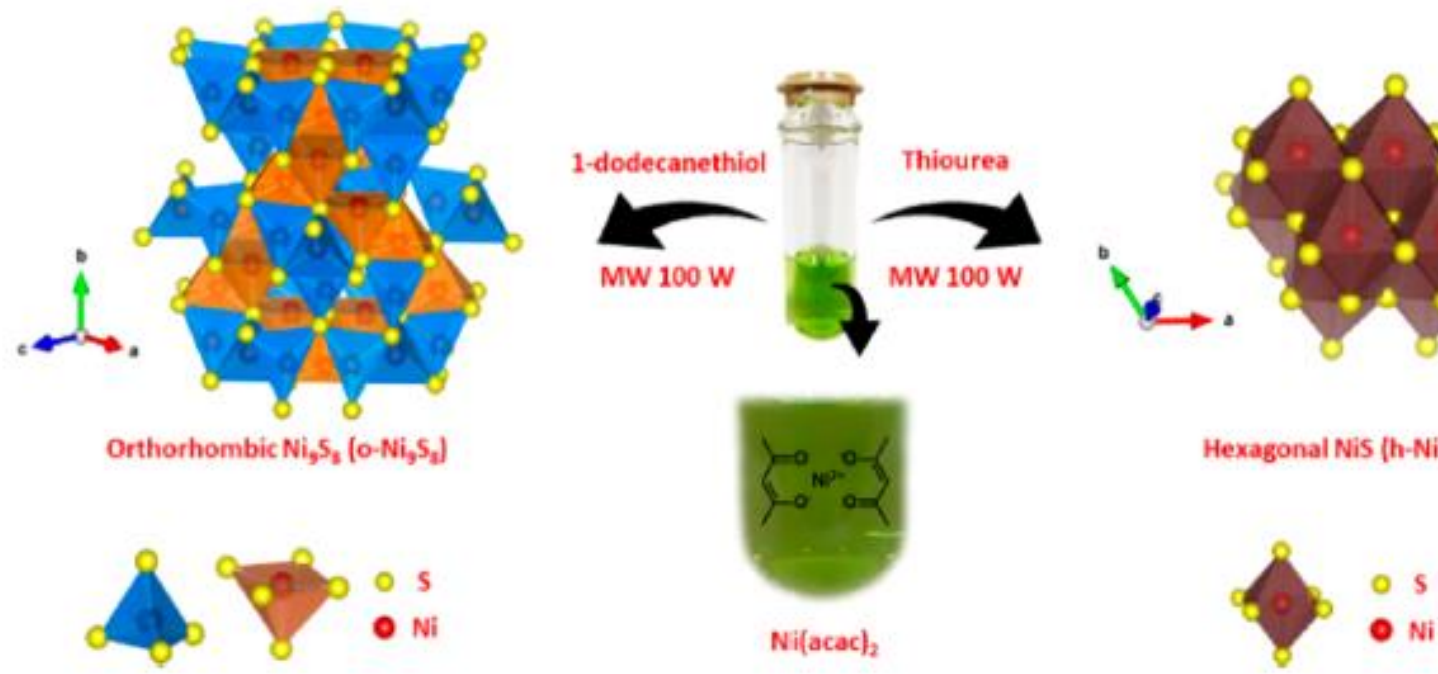


Figure 16 Synthesis of h-NiS and o-Ni9S8

When DDT was used as sulphur source orthorhombic nickel sulphide ($o\text{-}Ni_9S_8$) and thiourea used as sulph

nickel sulphide .[19]

2.15) Solvothermal process

Binxia Yuan had used this technique to synthesise nickel sulphide and there procedure are explain in below

that sulphur powder and 10mL oleylamine solvent was added and than heated oven for 260 degree Celsius

ethanol. The structure is hexagonal or orthorhombic with particle size is 6-10nm.[20]

temperature	NiS molar ratio	Residence time	Product
260	1:10	1	NiS2

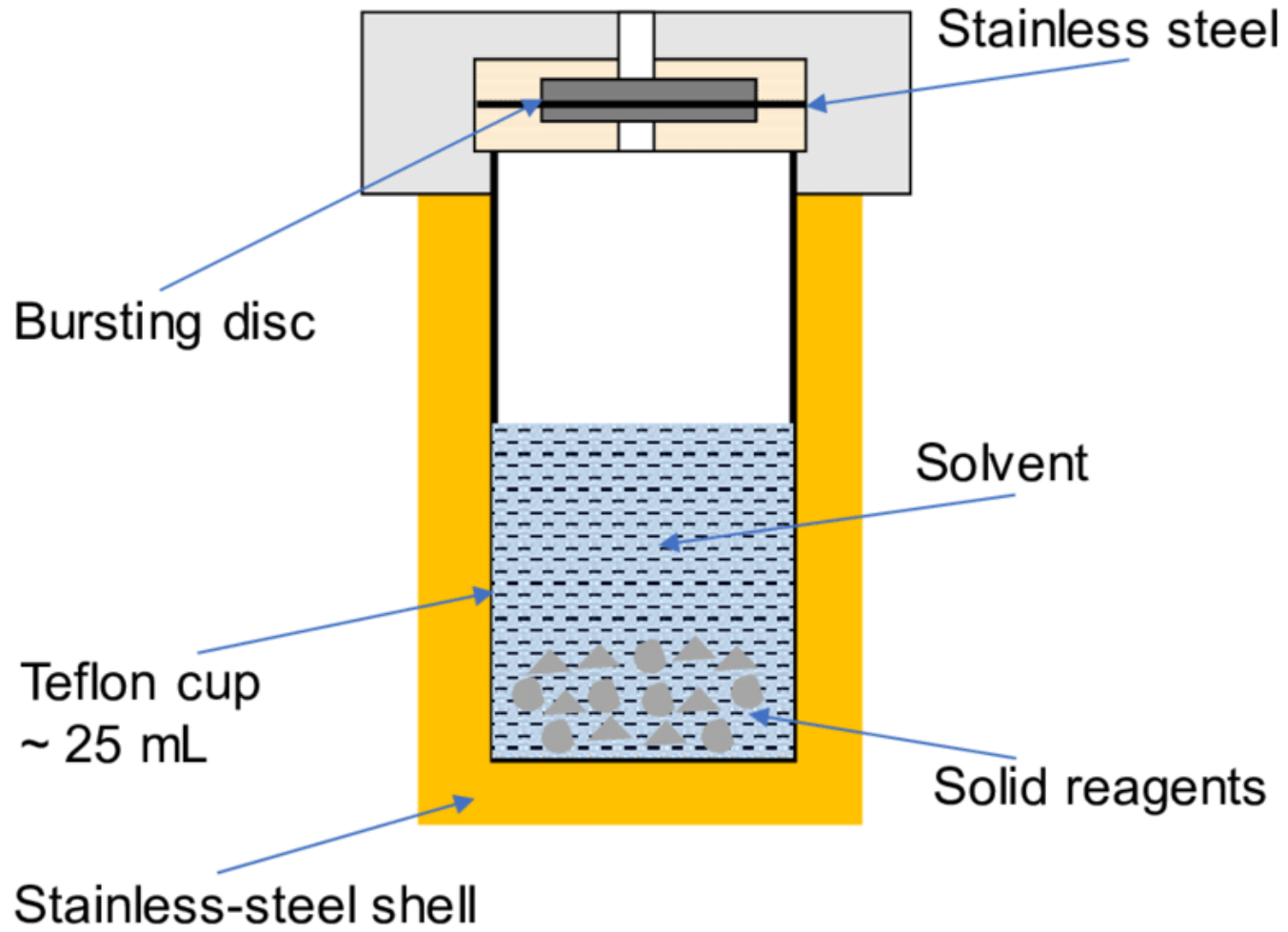


Figure 17 shows schematic digram of solvothermal process

2.16) Phase controlled synthesis method

Gozde Barim, Sara R. Smock, Priscilla D. Antunez, Daniela Glaser and Richard L. Brutchey had studied nic phase and procedure othis synthesises sre given below

N,*N*'-disubstituted thiourea into that hot solution of NiI_2 in oleylamine and 1-dodecanethiol was added blac ethanol and dried . the rhombohedral heazlewoodite structure and spherical shaped 10-45 nm in particle siz

This table shows various synthesise method of nickel sulphide

Sr. no	Method	Procedure	Precipitate colour	Structure	Nanostructure type	Part size Nm
1	Hydrothermal method	0.3 M nickel acetate tetra hydrate + sulphur powder dissolved in deionised water +stir 5 hour+transfer 250 ml taflon lined autoclave 140 degree Celsius for 14 hour.ppt formed washed with ethanol.	Black	Rhomboh edral	sheet and cuboid	34
		Ni(NO3)2.6H20 and thio glycolic acid	black	Rhomboh	Nanorod	30

	method	0.75g C2H5NS in 50 mL water.mixture sonicated 1 hour .ppt obtained washed with ethanol and dried 24 hour.				
4	Cyclic microwave radiation	6g of Ni(OAC)2 in a 50 ml of ethanol dissolved it 8.2 mL of 2-hydroxy acetaphenone added the solution stirred for 24 hours Ni(HAP)2 0.2g of Ni(HAP)2 in 30 mL ethylene glycol separately added in Ni(HAP)2 solution stir 1hour carried out 5 cycle in microwave each cycle 30 s and 60soff Ppt formed washed withwater and ethanol	Black		Quasi spherical shaped	13-
5	Synthesis by using imidazole dithiocarbomate complexes	2.5mmol Nicl2 dissolve in 10 mL methanol +imidazole dithiocarbonate solid ppt formed stir for 3 hour washed with distilled water recrysatllise with solvent. 0.40 g metal precursor+ 4mL TOP dissolved +injected 3 g hot hexadecylamine 220degree Celsius.kept in Constant temperature unde nitrogen flow . ppt formed will washed with methanol.	black	Rhomboh edral	Spherically shaped	5.1 11.6
6	Synthesis by Ni(II) dithiocarbomate complex	Step 15mmol of anisidine (6.16 g), dibenzylamine (10 mL),+ butylamine (5 mL) + 5mmol of potassium hydroxide (2.18 g) ice water and stirred, 5mmol (3 mL) of cold carbon disulphide dropwise 5mmol	black	Square planar	Spherical	12-

		(0.2 g) were dissolved in 2mL tri-n-octylphosphine (TOP) and injected into 2 g of hot hexadecylamine (HDA) at 220∘C. The temperature was maintained for 1 hour Ppt formrd centrifused				
7	Synthesis by benzimidazole dithiocabomate Ni(II) Complex	Step1 sodium hydroxide (0.78 g, 0.02 mol) dissolve distilled water + cold benzimidazole (2.36 g, 0.02 mol) in an ice bath. stirred 1 hour + carbon disulphide (1.52 ml, 0.02 mol) drop-wise stirred for further 12 hrs at 25 °C. A 40 ml solution of nickel chloride (2.37 g, 0.01 mol) added drop-wise into the corres dithiocarbamate ligand. The mixture was refluxed for 4 hours at 60 °C in a water bath. The ppt formed Step 2 2-methylbenzimidazole dithiocarbamate nickel(II) complex was prepared by the sausing 2-methylbenzimidazole (2.64 g, 0.02mol) Step 3 The complex (0.3 g) dissolved in 5.0 ml of tri-octylphosphine (TOP). The solution was Inject hot solution of hexadecylamine (HDA) (6.0 g) in a three-necked flask + excess methanol ppt formed	Black ppt	Rhobohedral	Spherical/rod shaped	10-
8	Solid phase method	Ni(acac)2+alkyl sulfylhydryl+ vaccenic acid solvent	balck	Rhomboh edral	nanorod	25-
9	Temperature controlled injection method	1mmol Ni(N03)2.6H2O +oleylamine (10mL) in three necked flask heated 100degree Celsius form nickel oleyamine	black	Ortorhombic	spherical	8-2

		oven 100 degree Celsius for 24 hours The method is repeated at pH 14 by adding sodium hydroxide and temperature 500 dgree Celsius				
12	Laser ablation method	10 mmol CH3CSNH2 dissolved in DI water +3mL(HOCH2CH2)3N and 4mmol (NICH3C00)2.4H20 added. irradiated the mixture with laser the ppt formed rinsed wih C2H5OH drying in air.	Black		Nanopowder	20-
13	Synthesis by using thiocarbohydrazide as a sulphur source	Aqueous hydrazine hydrate+ carbon disulphide according to taguchi method Ni (CH3COO)2.4H2O (0.005 M) in warm ethanol added to thiocarbohydrazide (0.005 M)+10 mL potassium hydroxide +heat	Black			
14	Non Hydrolytic method	N-methyl-2-pyrrolidone (NMP) + nickel(II) acetylacetonate [Ni(acac)2] as Ni precursor, + 1-dodecanethiol (DDT) and thiourea as S precursors.iradited sample in microwave wash ppt with ethnol	black	Hexagonal	Platelet shaped	30-
15	Solvothermal method	1mmol NiCl2.6H20+ sulphur powder+10mL oleylamine solvent + heated oven+ppt formed washed ethanol	Black	Hexagonal Orthorombic	Rice like structure	6-1

3.Characterisation

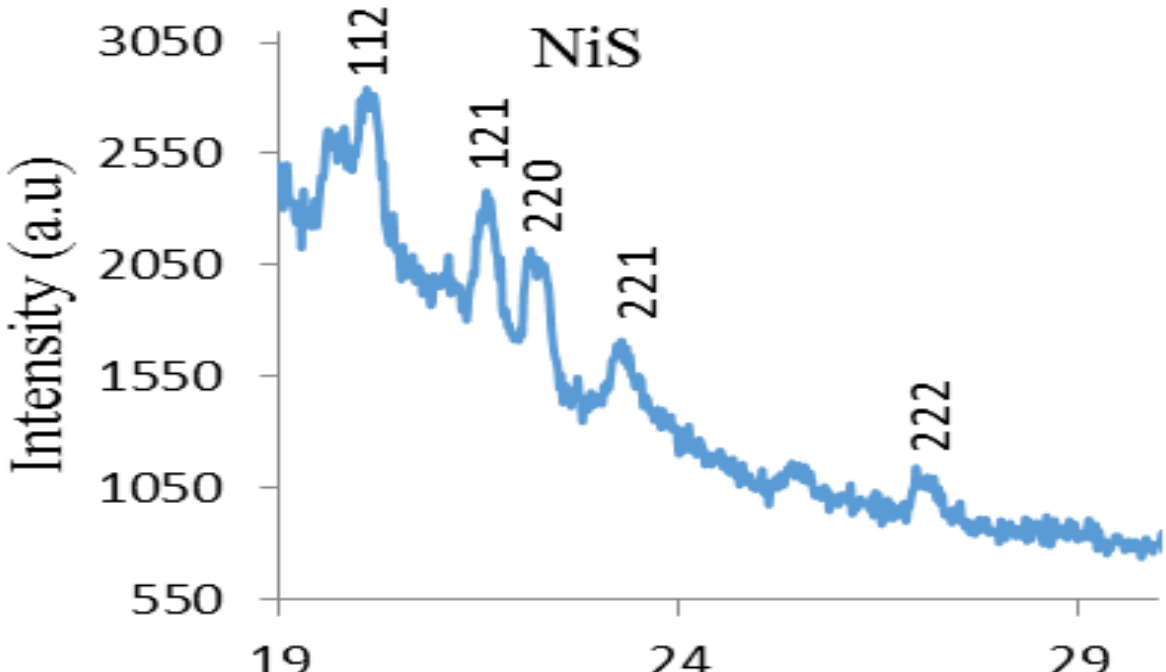
3.1XRD

The crystal structure was characterised by powder X-ray diffraction with a scan rate of 0.04 degree S inverse degree using Rigaku (Japan) X- ray diffractometer as shown

Ina figure

Figure 18 shows the image of XRD instrument

The structure and lattice parameter of NiS were determined by Nickel sulphide . Nickel sulphide prepared b found to be black in colour .The XRD results indicated that all the peaks are indexed mostly to rhombohedr and the cell parameter is 9.924 A and c=3.150 A . The crystalline nature phase was observed at 2 deta value correspond to (211) (121) (220) and (222) indices respectively[6]

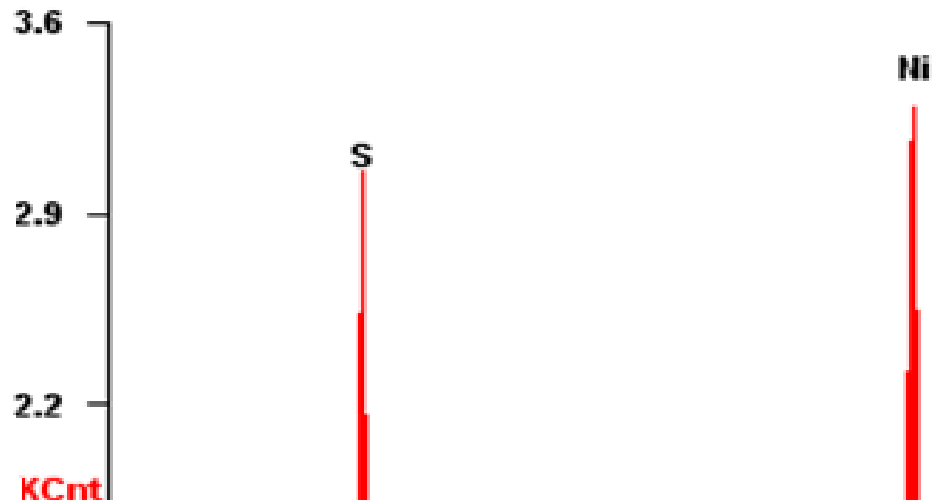


3.2 EDS

Energy dispersive spectra were processed using energy dispersive X-ray spectroscopy (EDS) attached to a J
system Six software

Figure 20 shows image of EDS instrument

The EDS analysis (Fig.21) was employed to determine the chemical composition of the products and to d
calculation of the peak areas the atomic ratio can be found out , the above synthesis method shows that the
products is 49:51, which further confirms that the products are nickel sulph



3.3 Micro Raman studies

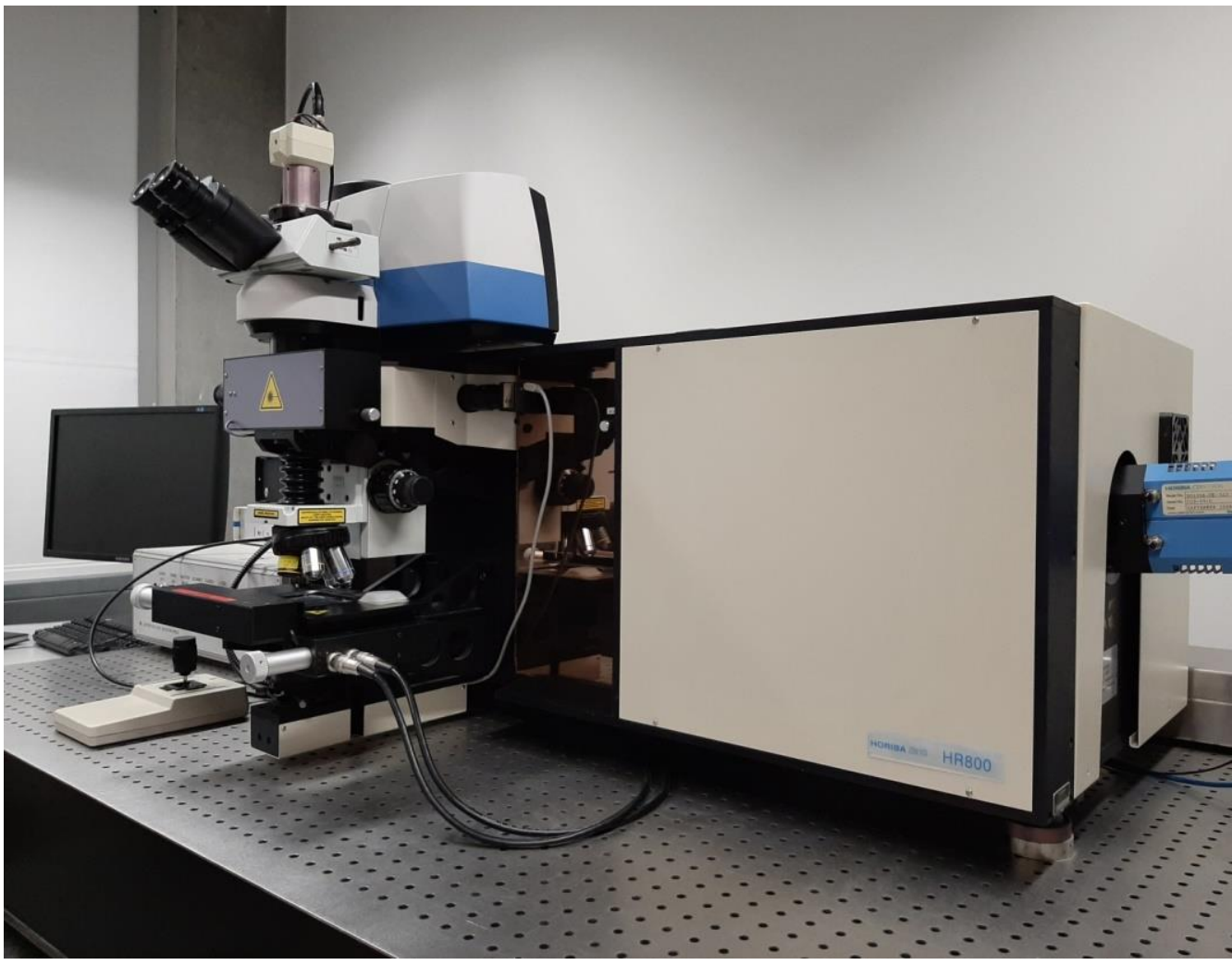


Figure 22 shows image of Micro Raman instrument

The Raman spectrum of nanoparticles of nickel sulphide synthesisd by above mentionded method was sho
shows peaks around 205, 465, 608, 984 and 1087 cm-1. These peaks positions were observed to be red shift
effect. [6]

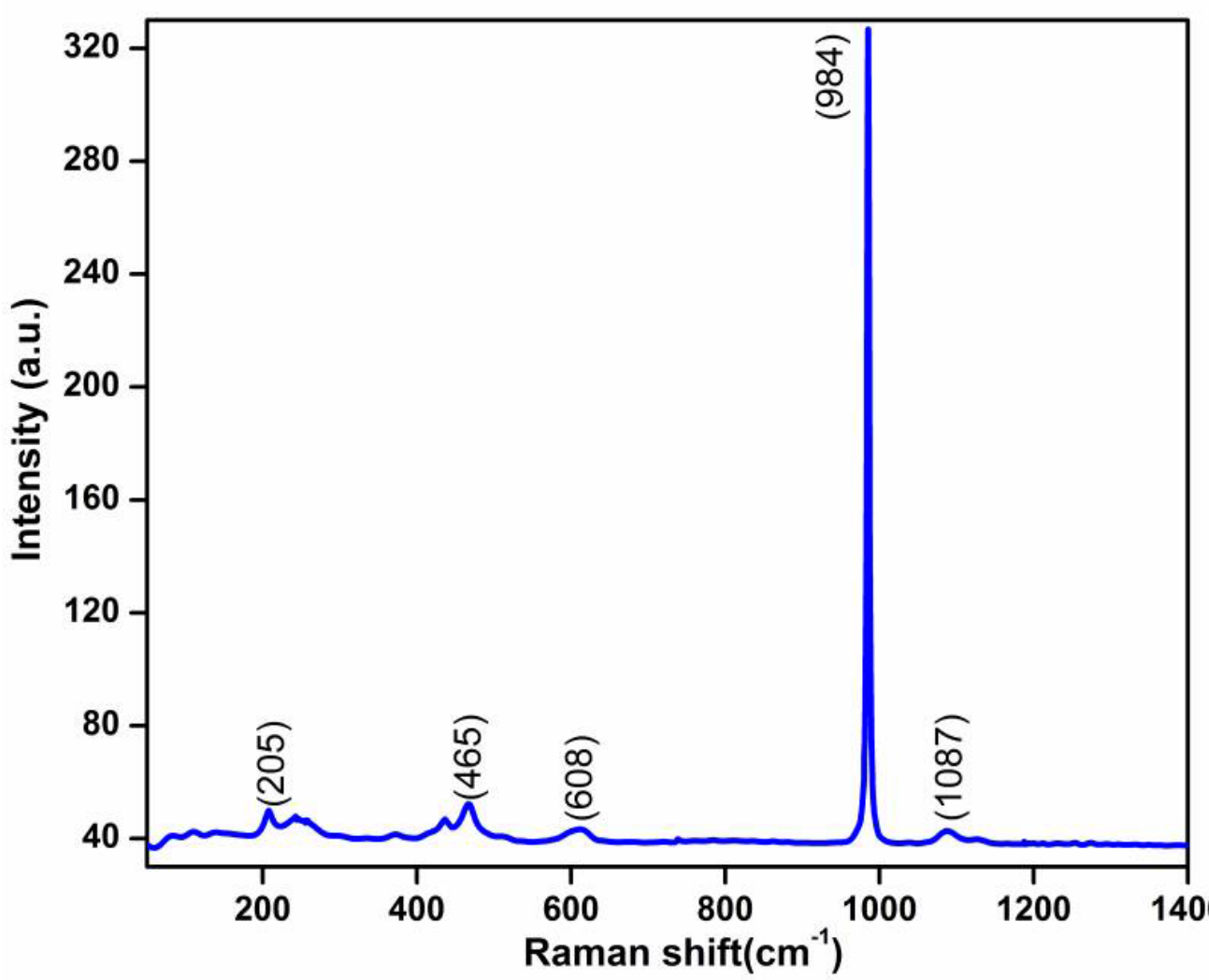


Figure 23 shows Micro Raman instrument

3.4 TEM

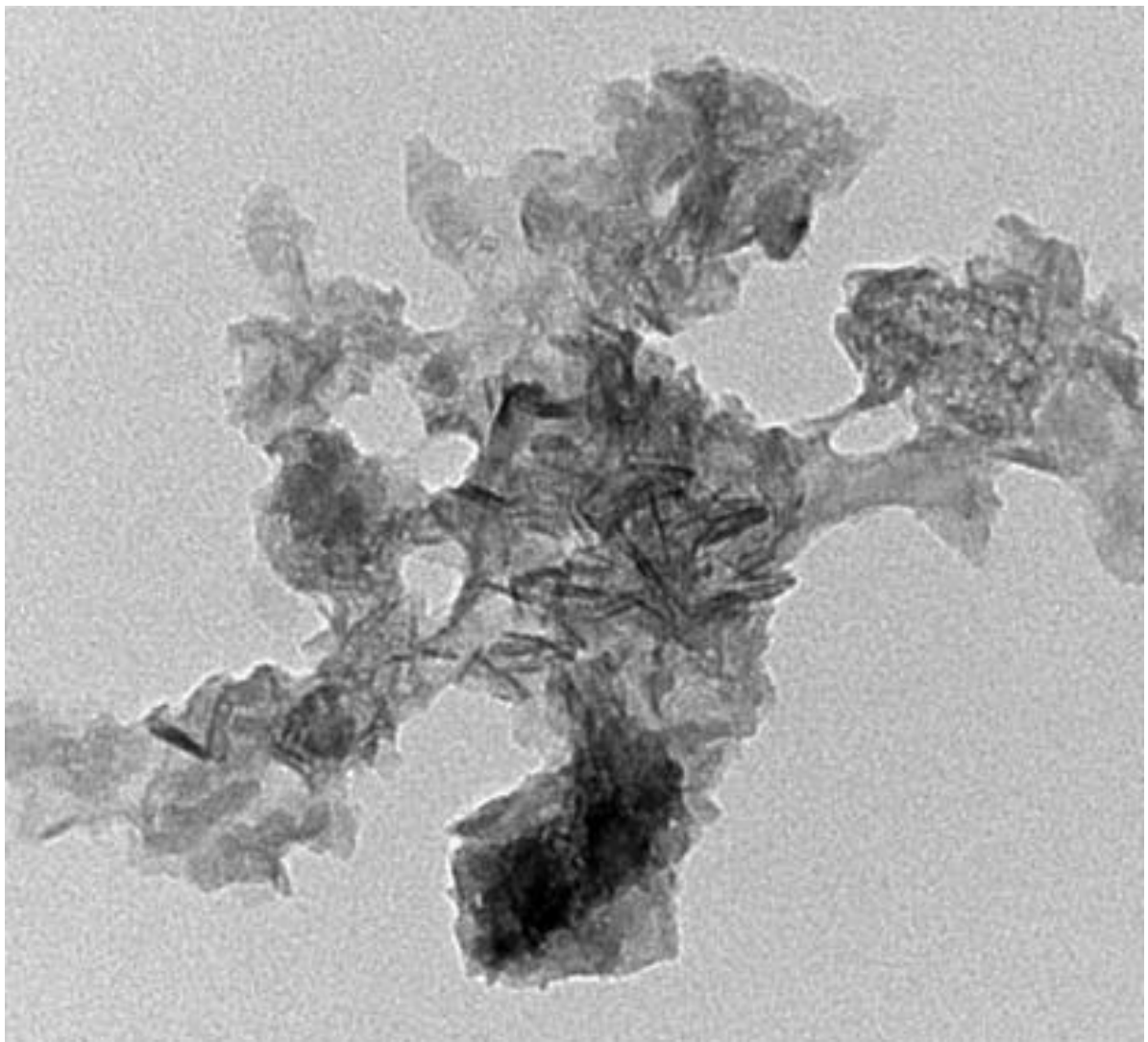
High resolution transmission electron microscopy (HRTEM) images recorded using JEOL JEM 2100 micro

200 kV as shown in figure

Figure 24 of high resolution electron microscope

The morphology and micro structure of NiS were characterised by TEM and SEM. The TEM image of NiS

nanoparticle with size ranges from 5.11-80 nm and some of particle aggregate to layer particle. [6]



3.5 SEM

The scanning electron microscopy (SEM) images were obtained on a Joel, JSM-6390 LV apparatus, using a
kV at different magnifications. [6]

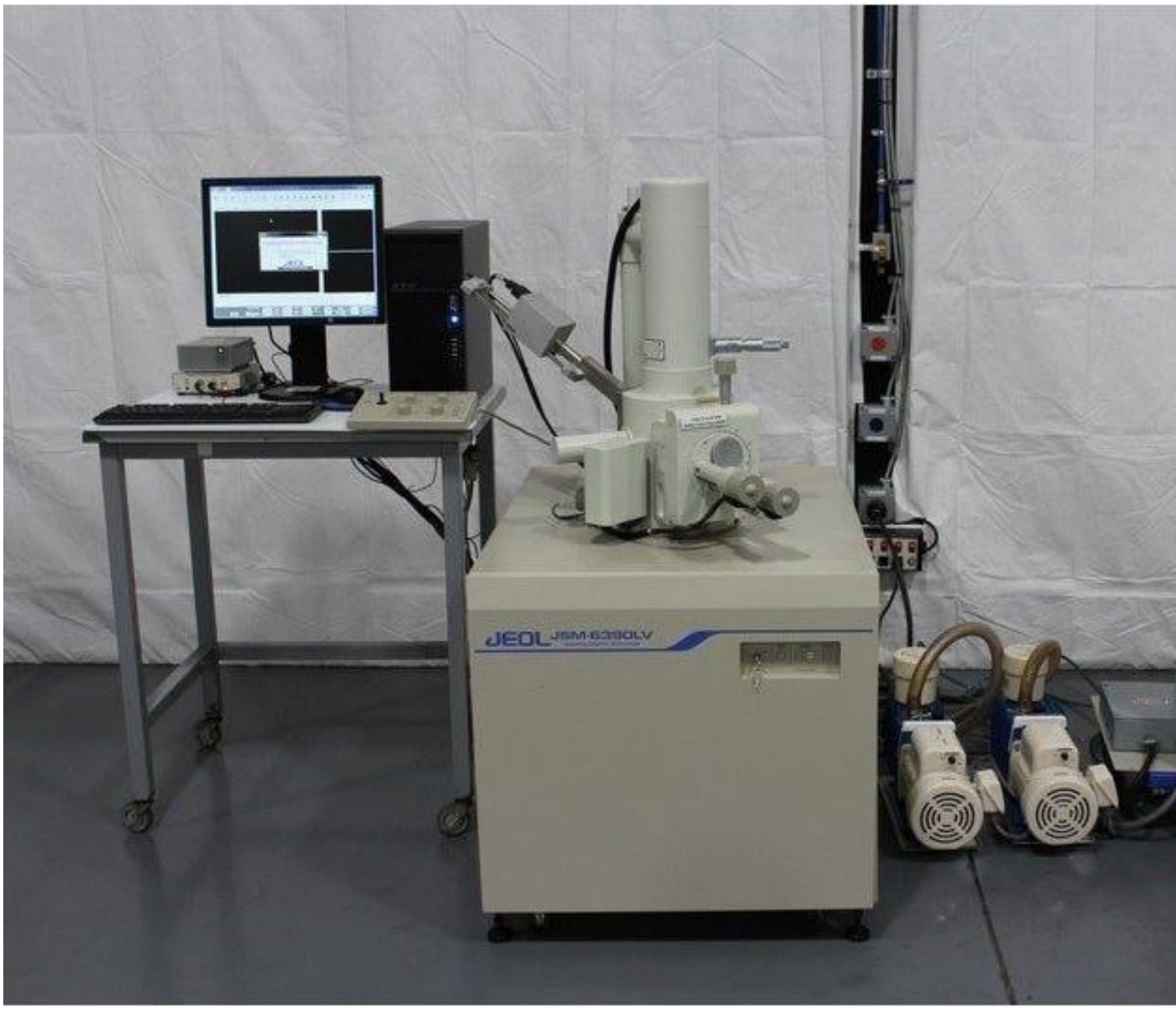
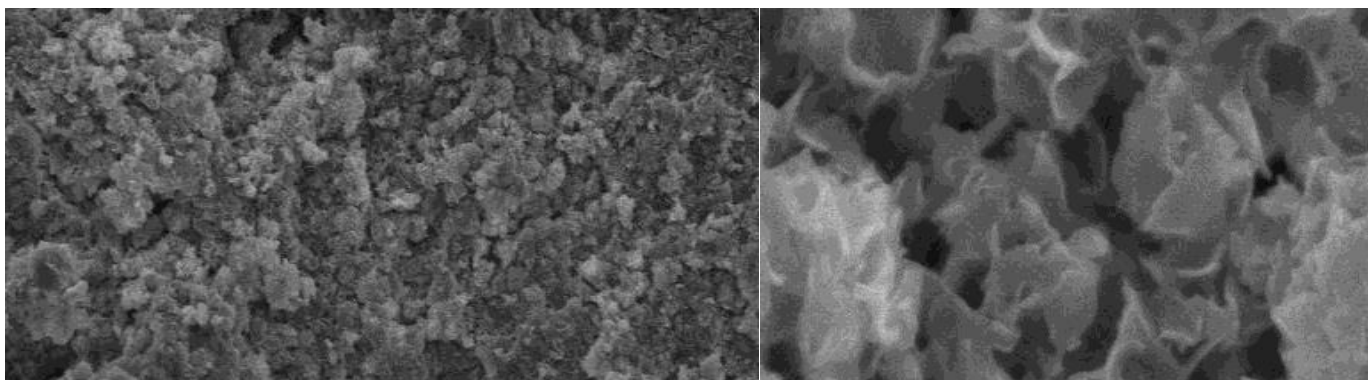


Figure: 26 Shows SEM instrument image

Surface morphology of the NiS were analysed scanning electron microscopy (SEM). The SEM images of N
magnification, the morphology of the particles consist of small spherically shaped particles with some small
magnification, the morphology are fine and smooth with fine structure that are closely packed together but t
pronounced.



Conclusion

Nickel sulphide have been prepared by various method such as sonochemical method, coprecipitation metho method of synthesis of nickel sulphide various morphology of nickel sulphide have been studied i.e NiS,Ni2 good crystalline nature and SEM and TEM reveal the morphology sometimes NiS in rod shaped, spherical wih various geometry such as rhombohedral, hexagonal , etc.

Reference

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