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Synthesis and Characterization of Zn doped NiS Capped Glycine Nanoparticles

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***Abstract*— — In this paper Synthesis and charactization of NiS nanoparticles doped with Zn dust and capped with Glycine is presented. The NiS: Zn-Glycine have been successfully prepared by chemical route method. The synthesized nanopaticles have been characterized by FTIR spectroscopy; UV-Visible Spectroscopy and Powder XRD study, SEM. The second Harmonic Generation was confirmed by Perry and Kurtz method. FTIR study has been performed which confirm the co-ordinations of the compound. XRD analyses revealed with that the morphology of the NIS:Zn-Gly nanoparticles has Hexagonal structure. NiS: Zn-Gly nanoparticles thus prepared wee of 4 nm to 2.45nm size. Morphology was determined by Scanning Electron Microscope (SEM). Thermal analysis has been also performed on synthesized materials.**

***Index Terms*— NiS, Nanoparticles, Synthesis, XRD**

I. INTRODUCTION

Semiconducting nanocrystals have received significant interest in the last decade.[1,2] These nano-sized and quantum confined materials have found many applications in non-linear optics and electronic devices and, more recently, in advanced biotechnology due to their unique physical, chemical and optical properties.[3,4] NiS is a transition metal compound and an interesting material showing metal insulator transition by doping or as a function of temperature. NiS compound shows anti-ferromagnetic semiconductor and paramagnetic properties in low and high temperature phases respectively. The Metal & nonmetal phase transition in NiS have long been studied but the transition mechanisms have not yet been absolutely understood [5, 6]. The optical spectra of NiS have been observed in IR and it was determined that at low temperature below 260K they are p-type and narrow band gap semiconductors with an energy gap of 0.15 eV. [1]. NiS materials thin films have been used as catalysis and coatings in photovoltaic cells. [7]. NiS used as a holder in hyder-process catalysis. In pure nickel sulphide production NiS and Ni3 S2 form as co-phases. [8]. Today glass coating are frequently put on the surfaces of glasses panels used in modern buildings. In most cases, these glass panels are thermally hardened for security and durability. If there are Nis phases in the glass thes hardened glasses may more easily crack under stretch as caused by the phases transition of the NiS from hexagonal structure to rhombhohedral [9]. Thus work on NiS is increasing day by day due to its involvement in the cracking process of glass panels. [10]. NiS heat analysis has been used with plasma mass spectroscopy to determine the platinum group elements in geological materials. This determination process is rather fast and sensitive [11, 12, 13]. There are a few works on the synthesis and growth and especially electrical properties (NLO) of NiS films in the literature. Our purpose in this work is to synthesis NiS:Zn-Gly using chemical precipitation method investigate their NLO Optical structure and other properties.

II. SYNTHESIS

Nicel acetate (17.678 gm) was dissolved in 250ml of water with constant stirring Thiourea (7.612 gm) was dissolved (5 wt %) was dissolved in 10 ml of deionized water. First $Ni(ac)_2$ solution and thiourea solutions were mixed together slowly with constant stirring. Faint green colour of Nickel acetate solution turned deep green by the addition of thiourea solution. Then NaOH solution was of the original solution. The colour of the solution tuned golden brown as the first drop of NaoH solution was more of addition. The colour deepened with dark green. The solution was stirred for four hours at 80° C. The solution of Na_2S was then added by drop with vigorous stirring to get NiS nanoparticles doped with molar% of Zn dust and capped with Glycine amino acid. This solution of NiS: Zn was kept in three different beakers and 2, 4,6 mole% Glycine was add to the respective beakers of NiS:Zn solution. Samples of NiS:Zn-Gly indicated like First NZG2 = (1:0.1:0.02); NZG3 = (1:0.1:0.04); NZG4 = (1:0.1:0.06).

III. CHARACTERIZATION

The Synthesis samples gas been subjected to powder X-ray diffraction analysis, NLO test, FTIR, TGA UV- spectra, SEM Characterization.

IV. RESULT AND DISCUSSION

A. NLO Test

The Second harmonic generation behavior was tested by Kurtz powder technique using ND: YAG laser as a source. The sample was prepared by sandwiching the graded crystalline powder between two glass slides. The powder sample of NZG was illuminated by the laser source (Wavelength= 1064nm) having pulse energy 2.35mJ, pulse duration 8 ns and repetition rate 10Hz has been used. The output has been measured at 532nm wavelength. The Second harmonic signal generated in the sample was collected by the lens and detected by the monochromator, which is coupled with the photomultiplier tube. The bright green emission was observed from the output

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of the powder form of the NZG. KDP sample was used for the reference material and output power intensity of NZG was comparable with the output power of KDP and it agrees well with the reported [18, 19]. The grown crystals have been subjected to the nonlinear optical study to measure the SHG efficiency with respect to the Pure KDP. To characterize the crystals, Kurtz and Perry method has been employed [20]. In this experiment Q-switched, mode locked Nd:YAG laser of wavelength 1064nm having pulse energy 3mJ/Pulse, pulse duration 10ns and repetition rate 15Hz has been used. The output has been measured at 532nm wavelength. The increase in the SHG efficiencies are due to the weakening of the bond between O–H and C=O due to hydrogen bonding [26, 27, 28]. Table 1.

NLO Sample	Input	SHG output Signal in mV	SHG efficiency
KDPM1	2.50mJ/pulse	78mV	1.41
KDPM2	2.50mJ/pulse	85mV	1.54
KPN1	2.50mJ/pulse	102mV	1.85
KPN2	2.50mJ/pulse	95mV	1.72
KDP	2.50mJ/pulse/ 3 mJ/pulse	55mV / 65 mV	1
NZG2	3 mJ/pulse	67.5 mV	1.03
NZG3	3 mJ/pulse	69.2 mV	1.06
NZG4	3 mJ/pulse	73.5 mV	1.13
L-Alanine acetate [21]	2 mJ/pulse	16.5 mV	0.30
Ammonium borodilactate [22]	2 mJ/pulse	30.36 mV	0.552
L-Histidine bromide [23]	2 mJ/pulse	66 mV	1.20
L-Arginine diphosphate [23]	2 mJ/pulse	53.9 mV	0.98
Lithium para-nitrophenolate trihydrate [23]	2 mJ/pulse	93.5 mV	1.70
Glycine potassium Sulphate [24]	2mJ/pulse	1.43	1.43
Benzoyl Glycine (25)	2mJ/pulse	1.41	1.41

B. X Ray Diffraction

The grown crystals have been characterized by X-ray powder technique using Rich-Seifert X-ray powder diffractometer with Cu Kα radiations of Wavelength (1.5406Å. The 2ɵ range analyzed was from 10 ° to 70 ° employing reflection mode for scanning. The detector used was a scintillation counter in Figure 1 to 4 represents the X-ray powder pattern for the grown- NiS: Zn-Gly metal nanoparticle. The X-ray diffract gram is shown in fig. The lattice parameters were calculated by using values of the high intensity peaks corresponding to the d-spacing and (hkl) Phases by computer programme POWD (Integrative powder diffraction and indexing programme). The XRD patterns are well matched to Hexagonal structure of NiS (JCPDS No-75-0613). Some differences such as the broadening of the diffraction peaks increasing or decreasing of some peaks intensity as well as the shift of the peaks position to slightly lower angles can be observed in spectra. In fact the intensities of the peaks in the host guest (Capped doped) Composite materials are increased with respect to those of Pure NiS: Zn. This increase of the peaks intensities can be related to the presence or incorporation of semiconductor inside the matrix structure. The X-ray diffraction patterns of NiS: Zn-Gly, NZG2, NZG3, NZG4 nanoparticles are presented in Fig**.** The XRD data was analyzed by using PowderX software.

The particle size of the synthesized nanoparticles was determined by using Debye-Scherer's equation:

$$D = \frac{k\lambda}{\beta \cos\theta}$$

Where, λ is the X-ray wavelength(1.54Å), k, the shape factor (0.94) , D, the average diameter of the crystals in Angstrom, θ, the Bragg angle in degree, and β is the line broadening measured by half-height (Full width at half maxima) in radians. The diffraction peaks for NiS at 2θ =22.313, 32.433, 38.64, 51.414, 58.55 degrees, for NiS: Zn-Gly2 at 2θ=32.126, 46.516,54 .757. 58.982, for NiS: Zn-Gly3 at 2θ=33.903, 47.223, 53.958, 56.592 NiS: Zn-Gly4 at 2θ=33.835, 45.013, 52.795, 67.605 were chosen to calculate the size of the nanoparticles. [17]

Table 2: Size of NiS nanoparticles calculated from XRD data.

Sample	Particle size (nm)
NiS	4.05nm
NiS:Zn-Gly2	3.65nm
NiS:Zn-Gly3	2.85nm
NiS:Zn-Gly4	2.45nm

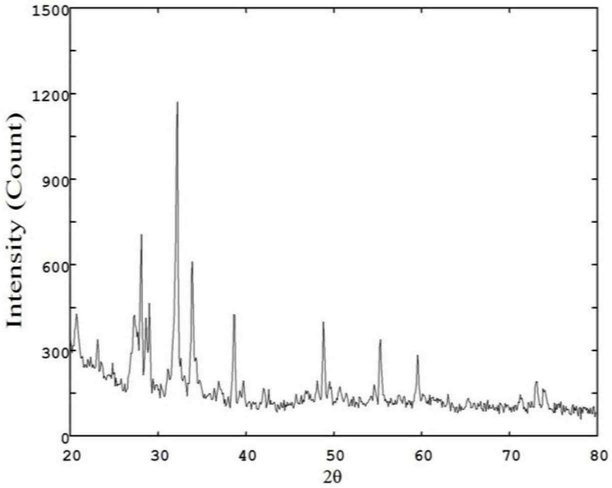

Figure 1 : - Pure NiS Pattern

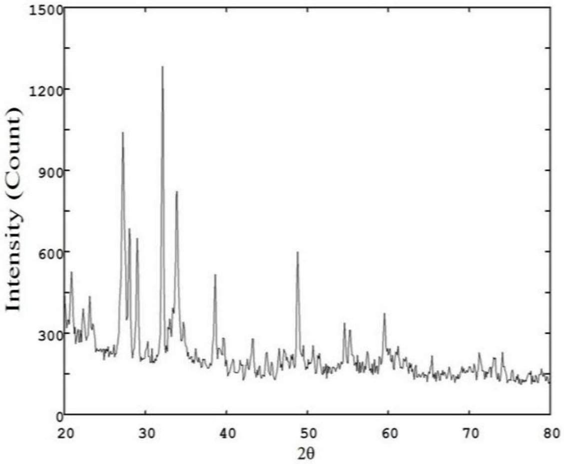

Figure 2:- NiS:Zn–Gly-2 (NZG2)

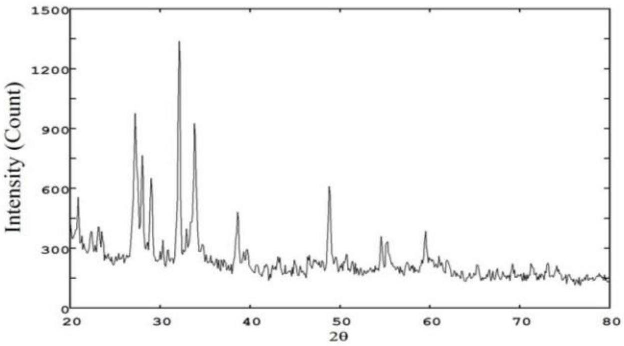

Figure 3 :- NiS:Zn-Gly-3 (NZG3)

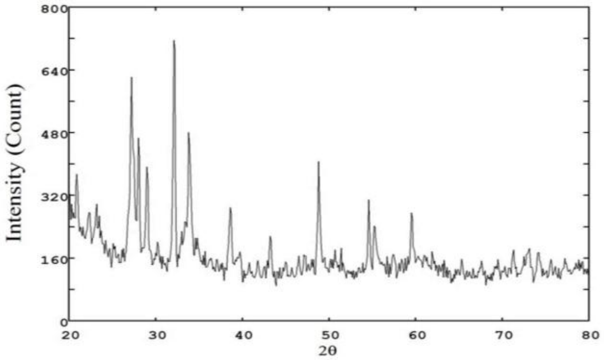

Figure 4: - NiS:Zn-Gly-4 (NZG4)

Tables 2

Samples	a	b	c
NiS	3.41705nm	5.2891nm	5.2891nm
NZG2	3.41840nm	5.2780nm	5.2781nm
NZG 3	3.35473nm	5.0334nm	5.0334nm
NZG4	3.31450nm	5.1204nm	5.1204nm

C. *SEM Analysis*

The particle size was confirmed by SEM image of the particles, which was recorded on the instrument JEOL - JSM-6380 Scanning Electron Microscope (Japan).The surface morphological features of synthesized nanoparticles were studied by scanning electron microscope. Figure 5 to 8 shows the SEM image of NiS and NiS:Zn-Gly sample 2,3,4, nanoparticles with magnification of 3000 and 6000. The instrumental parameters, accelerating voltage, spot size, and magnification and working distances are indicated on SEM image. The results indicate that mono-dispersive and highly crystalline NiS, NZG2,, NG3,NZG4 nanoparticles are obtained.

The appearance of samples NiS, NZG2, NZ3, NZG4 particles is aggregated with bad size dispersion. We can observe that the particles are highly agglomerated and they are essentially cluster of nanoparticles. The Sample NZG 2,3,4 paritcles shows in the resulted in very aggregated particles despite the small crystallite size. We can observe that the use of sample NiS resuted in less aggregated and much better dispersed particles.

The SEM picture indicates the size of polycrystalline particles. The observation of some larger nanoparticles may be attributed to the fact that NiS and other sample NZG nanoparticles have the tendency to agglomerate due to their high surface energy and high surface tension of the ultrafine nanoparticles. The fine particle size results in a large surface area that in turn, enhances the nanoparticles catalytic activity. So we can conclude that the prepared NiS and NZG particles are in nanometer range. The average diameter of the particle observed from SEM analysis is 40nm to 25nm, which is larger than the diameter predicted from X-Ray broadening. From the micrograph, it was observed that the nanoparticles are almost uniform in size. The particle morphology observed was either hexagonal or cubic like shape.

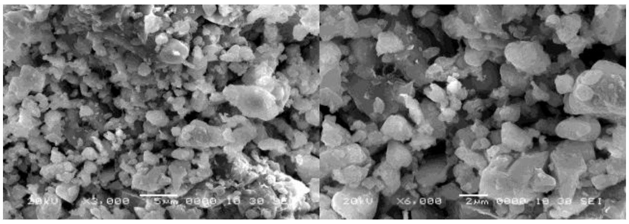

Figure 5: SEM of NiS

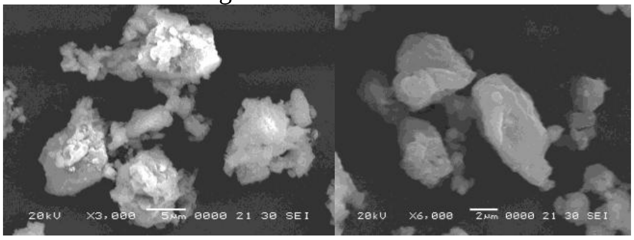

Figure 6: SEM of NiS: Zn-Gly 2

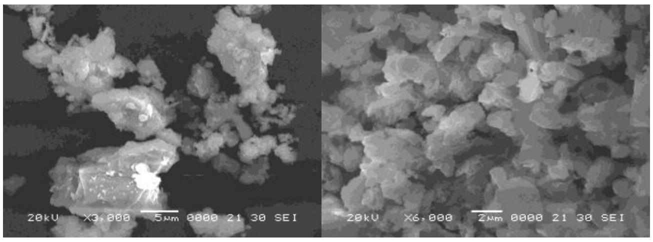

Figure 7: SEM of NiS: Zn-Gly 3

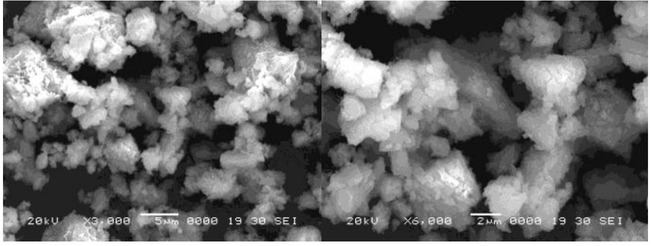

Figure 8: SEM of NiS: Zn-Gly 3

D. *FTIR Spectra*

The FT-IR spectrum of pure NiS and NZG2,NZG3,NZG4 have been recorded on Perkin Elmer FT-IR spectrophotometer within the wavenumber range 600cm^{-1} to 4000 cm^{-1} Pellets of the mixture of each sample with KBr have been prepared and used in the experiment Figure 9 & 10. According to Nakamoto and Ferraro νOH in free water molecules appears around 3600 to 3500 cm-1, but in the present case the broad and strong band appeared at 2923 cm-1, which is slightly lower than the expected. This may be possibly due to strong interaction between free water molecules .Another band, appearing at 1456cm-1 may be assigned to δOH and also supports presence of free water molecules in crystal lattice as suggested [29]. IR also shows a strong band at 1152 cm-1 indicating the presence of SO4- - ion in the crystal structure as predicted [30].

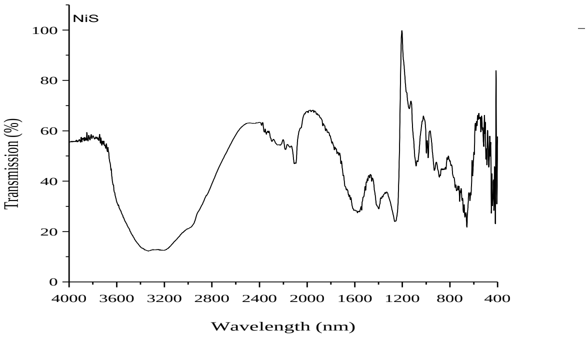

Figure 9: - FT-IR Spectrum Pure NiS

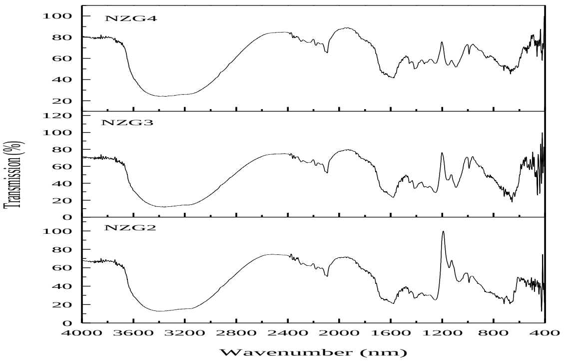

Figure 10: - FT-IR Spectrum NZG2, NZG3, NZG4

E. *UV Spectra*

The UV-Vis Spectral studies were carried out by using JASCO UV-Vis-NIR spectrometer, model name V-670 in the range 200nm – 800nm and Band width (UV/Vis) 200nm and Bandwidth (NIR) 20nm and it shown in Figure 11 to 12. The NZG has a good transmittance and the lower cut off wavelength is 200nm. The reflectance % show that the decay trends 250nm to 800nm range good visible region. The large transmission in the entire region enables it to be a good candidate for optoelectronic application. Reflectance peak corresponding to the fundamental reflection appears at 232nm for pure NiS , 219.5 for NZG2, 217.5 for NZG3, 214nm for NZG4. The shifting of peaks shows the good transparency. After that between the range of 438nm to 800nm (NiS); 442 to 800nm (NZG2); 439 to 800nm (NZG3); 439nm to 800nm (NZG4) the material is observed to be transparent and the reflectance is less and insignificant. The less reflectance in these regions is important for the material possessing NLO properties. The steep increase in reflectance below 219 nm is due to the colour of the synthesis materials in and beyond the visible region. From the spectra with the increase in the dopant concentration there is decrease in the reflectance, this might be due to the absorption energy level introduced by dopant. NiS is known as photoluminescence quencher hence there is increase in the reflectance. With further increase in the doping concentration but NZG4 there is decrease in the reflectance because NiS introduce new energy level in the band structure [15]. It acts as electron trapping center which results into nonradiative recombination [16]. Therefore, reflectance decrease as the molar concentration of dopant increases.

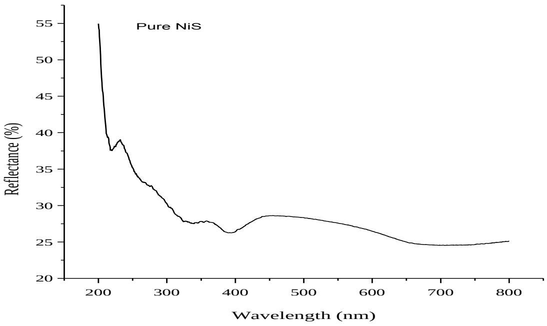

Figure 11: - UV Spectrum Pure NiS

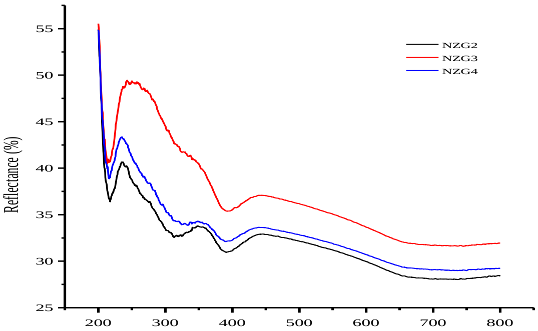

Figure 12: - UV Spectrum NZG2, NZG3, NZG4

F. *Thermal Analysis*

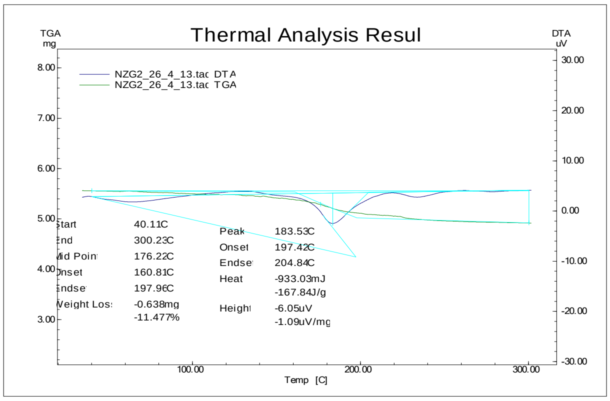

Figure 13 :- TGA Spectra

Thermogravimetric and differential thermal analysis give information regarding phase transition water of compounds materials and different stages of decomposition of the material system. The thermo gravimetric analysis of NZG2 sample is carried out between 40˚C to 300 ˚C in the air atmosphere at a heating rate of 12˚C/min using Perkin-Elmer thermal analyzer. The TGA spectrum obtained is shown in Fig. The TGA curve shows that there s a weight loss of about 11.477% in the temperature range 160.81 ˚C to 197.96 ˚C and it is assigned to loss of water and due to the liberation of volatile substances probably sulphur oxide in the compound. The DTA curve that NZG2 at 183.53 ˚C and it undergoes endothermic transition around 197.42˚C followed by another endothermic peak at 240˚C. The DTA curve indicates that the decomposition process is not a single stage and hence a complex character. The decomposition is accompanied by absorption of heat. The thermal Stability of the materials in working temperature range 40˚C to 300˚C. From the TGA curve it is obvious that the materials are very stable and there is no phase transition up to 197.96 ˚C after loss of weight NZG material thermally stable up to 300˚C.

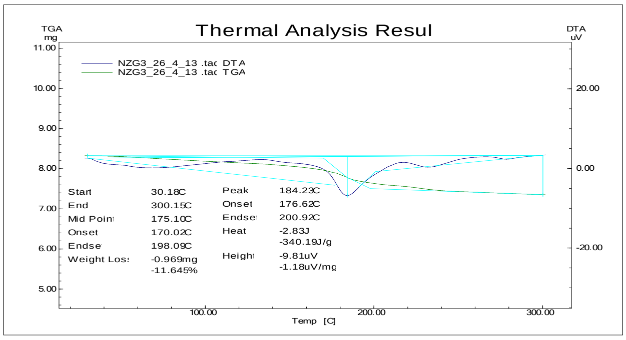

Figure 14: TGA Spectra NZG

The thermo gravimetric analysis of NZG3 sample is carried out between 30˚C to 300.15˚C in the air atmosphere at a heating rate of 12˚C/min using Perkin-Elmer thermal analyzer. The TGA spectrum obtained is shown in Fig 13 to 14. The TGA curve shows that there is a weight loss of about 11.645% in the temperature range 170˚C to 198.09˚C and it is assigned to loss of water and due to the liberation of volatile substances probably sulphur oxide in the compound. The DTA curve that NZG3 at 184.23 ˚C and it undergoes endothermic transition around 176.62˚C followed by another endothermic peak at 235˚C. The DTA curve indicates that the decomposition process is not a single stage and hence a complex character. The decomposition is accompanied by absorption of heat. The thermal Stability of the materials in working temperature range 40˚C to 300˚C. From the TGA curve it is obvious that the materials are very stable and there is no phase transition up to 198.09˚C after loss of weight NZG3 material thermally stable up to 300˚C.

V. CONCLUSION

NiS nanoparticles doped wth Zn and capped with Glycine have been successfully prepared by chemical route method. The method of preparation is inexpensive easy and environmental friendly. The NLO test confirms the nanocrystal may be used for optoelectronics. X ray diffraction analyses revealed that the morphology of the NiS:Zn-Gly nanoparticles has hexagonal structure with an average particle size 3nm. FT-IR spectroscope confirms the formation of the expected compound. UV-Visible spectroscopic study confirms the increase in band gap. TGA study confirms the thermal stability of the synthesis.

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